Supporting Information

for

Molecular Ruthenium Water Oxidation Catalysts Carrying Non-Innocent Ligands: Mechanistic Insight through Structure-Activity Relationships and Quantum Chemical Calculations

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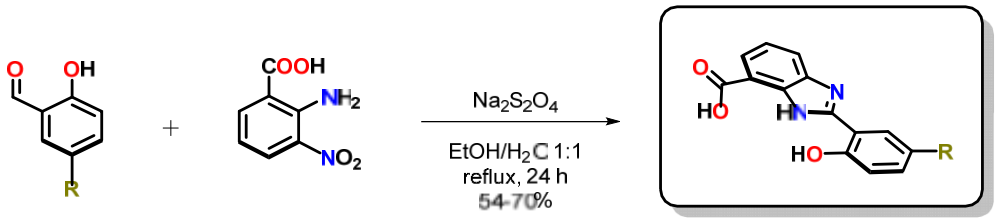
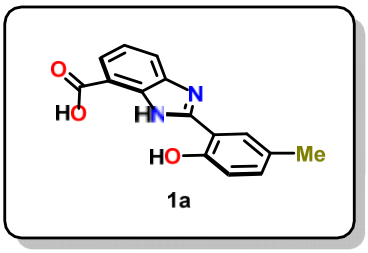
Experimental Section

General. Ligand **1b**,[S1] Ru-complex **2b**,[S1] $Ru(DMSO)_4Cl_2$,[S2] and $[Ru(bpy)_3](PF_6)_3$[S3] were prepared according to previously reported procedures. All other reagents including solvents were obtained from commercial suppliers and used directly without further purification. All solvents were dried by standard methods when needed. ^1H and ^{13}C NMR spectra were recorded at 400 MHz and at 100 MHz, respectively. Chemical shifts (δ) are reported in ppm, using the residual solvent peak [[D_6]DMSO (δ(H) = 2.50 and δ(C) = 39.52); [D_4]methanol (δ(H) = 3.31)] as internal standard. For ^{19}F NMR, the chemical shifts are reported with respect to trifluoroacetic acid as internal reference (δ(F) = –76.55). Splitting patterns are denoted as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad). High resolution mass spectra measurements were recorded on a Bruker Daltonics microTOF spectrometer with an electrospray ionizer. Elemental analyses were carried out at MEDAC Ltd, Chobham, Surrey, United Kingdom. IR spectra were recorded on a Perkin-Elmer Spectrum One spectrometer, using samples prepared as KBr discs. The UV/Vis absorption spectra were measured on a CARY 300 Bio UV-Visible spectrophotometer.

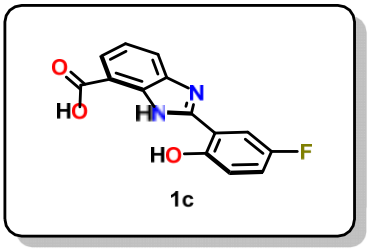
General procedure for the synthesis of ligands 1a, 1c and 1d



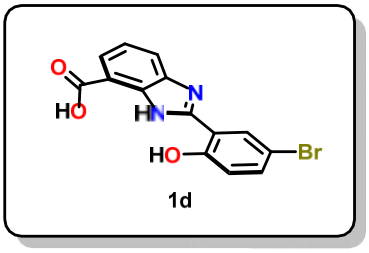
2-amino-3-nitrobenzoic acid (1.00 g, 5.49 mmol) and aldehyde (5.49 mmol) were dissolved in ethanol (30.0 mL). To this solution was added an aqueous solution (30.0 mL) of $Na_2S_2O_4$ (85 %, 3.37 g, 16.5 mmol). The mixture was then heated at 70 ºC for 24 h. After cooling to room temperature, the yellow precipitate was filtered off, washed with water (3x), ethanol (2x), Et_2O (2x) and dried under vacuum, affording the title compound as a solid.



Synthesis of 2-(2-hydroxy-5-methylphenyl)-1*H*-benzo[*d*]imidazole-7-carboxylic acid (1a). (0.80 g, 54.3% yield). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 13.23 (br, 1H), 12.23 (br, 1H), 8.19 (br, 1H), 7.92 (d, *J* = 7.90 Hz, 1H), 7.83 (dd, *J* = 7.70, 0.89 Hz, 1H), 7.35 (t, *J* = 7.80 Hz, 1H), 7.20 (dd, *J* = 8.39, 2.04 Hz, 1H), 6.95 (d, *J* = 8.40 Hz, 1H); ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 167.0, 154.9 (br), 152.4, 142.7 (br), 133.6 (br), 132.7, 128.3 (br), 128.1, 124.6, 123.1 (br), 122.0, 116.9, 114.9 (br), 113.1 (br); HRMS (ESI) Calcd. for $C_{15}H_{13}N_2O_3$ [M + H$^+$]$^+$: 269.0921; found: 269.0932; IR (KBr): ν_{max} = 3313, 3134, 2923, 2565, 1632, 1595, 1567, 1509, 1469, 1384, 1298, 1267, 757 cm^{-1}.

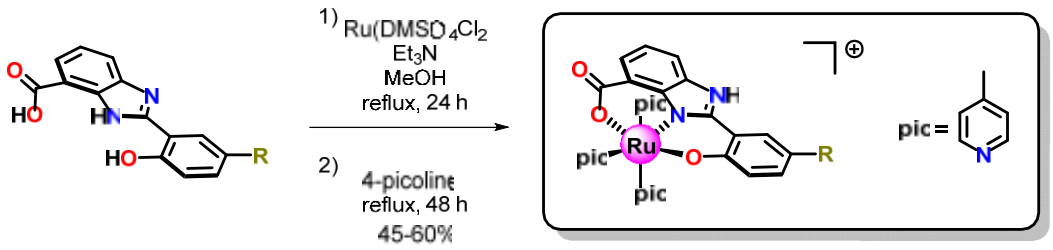


Synthesis of 2-(5-fluoro-2-hydroxyphenyl)-1*H*-benzo[*d*]-imidazole-7-carboxylic acid (1c). Dark-yellow solid (1.05 g, 70.3% yield). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 12.48 (br, 2H), 8.22 (br, 1H), 7.96 (d, *J* = 8.00 Hz, 1H), 7.86 (dd, *J* = 7.60, 0.92 Hz, 1H), 7.38 (t, *J* = 7.80 Hz, 1H), 7.25 (m, 1H), 7.07 (dd, *J* = 9.02, 4.80 Hz, 1H); ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 166.7, 155.2 ($^{1}J_{CF}$ = 235 Hz), 153.5 (br), 151.2, 141.3, 133.9, 124.9, 122.1, 118.6 (d, $^{2}J_{CF}$ = 23.4 Hz), 118.2 (d, $^{3}J_{CF}$ = 8.0 Hz), 115.8 (br), 114.0-113.1; ^{19}F NMR (400 MHz, [D$_6$]DMSO); δ = -123; HRMS (ESI) Calcd. for $C_{14}H_{10}FN_2O_3$ [M + H$^+$]$^+$: 273.0670; found: 273.0663; IR (KBr): ν_{max} = 3327, 3080, 2508, 1633, 1574, 1509, 1379, 1266, 1214, 762 cm^{-1}.

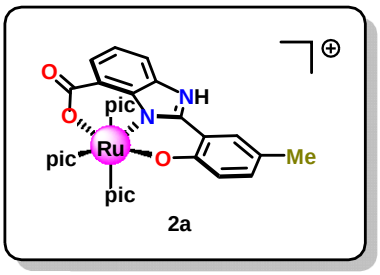


Synthesis of 2-(5-bromo-2-hydroxyphenyl)-1*H*-benzo[*d*]imidazole-7-carboxylic acid (1d). (1.14 g, 62.3% yield). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 13.02 (br, 2H), 12.60 (br, 1H), 8.61 (br, 1H), 7.96 (d, *J* = 8.01 Hz, 1H), 7.87 (dd, *J* = 7.63, 0.85 Hz, 1H), 7.52 (dd, *J* = 8.80, 2.52 Hz, 1H), 7.38 (t, *J* = 7.82 Hz, 1H), 7.02 (d, *J* = 8.80 Hz, 1H); ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 166.8, 156.6 (br), 151.0, 134.3, 129.9 (br), 125.2, 122.4, 119.3, 115.2 (br), 110.5; HRMS (ESI) Calcd. for $C_{14}H_{10}BrN_2O_3$ [M + H$^+$]$^+$: 332.9869; found: 332.9858; IR (KBr): ν_{max} = 3291, 3066, 2545, 1632, 1558, 1385, 1299, 1260, 758 cm^{-1}.

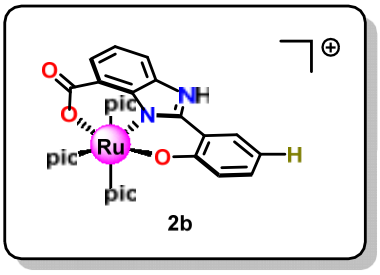
General procedure for the synthesis of complexes 2a, 2c and 2d



Ligand (0.31 mmol) and Et_3N (0.43 mL, 3.1 mmol) were dissolved in MeOH (3 mL). To this solution was added $Ru(DMSO)_4Cl_2$ (150 mg, 0.31 mmol) and the mixture was refluxed for 24 h. Then 4-methylpyridine (0.90 mL, 9.3 mmol) was added, and the mixture was further refluxed for 48 h. After addition of H_2O (6.0 mL), the complex precipitated as a solid. The precipitate was isolated by centrifugation, washed with water (4 x 10 mL) and Et_2O (2 x 10 mL), and dried under vacuum to afford the complex.

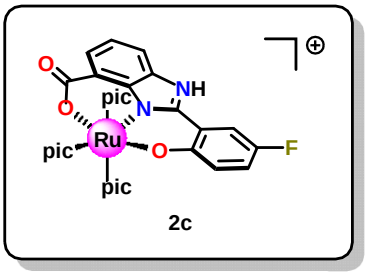


Synthesis of Ru complex 2a. Dark-brown solid (100 mg, 45% yield). ^{1}H NMR (400 MHz, [D_4]methanol + ascorbic acid): δ = 8.44-8.39 (m, 3H), 8.29 (d, *J* = 5.40 Hz, 4H), 7.94 (d, *J* = 7.60 Hz, 1H), 7.38-7.29 (m, 5H), 7.04-7.00 (m, 5H), 3.01 (s, 3H), 2.38 (s, 3H), 1.99 (s, 6 H); HRMS (ESI) Calcd. for $C_{33}H_{31}N_5O_3Ru$ [**2a**]$^+$: 647.1465; found: 647.1454; IR (KBr): ν_{max} = 3438, 2918, 1618, 1563, 1495, 1427, 1315, 1275, 1209, 814 cm^{-1}; Anal. Calcd. (%) for $C_{34}H_{34}ClN_5O_{3.5}RuS_{0.5}$ ([**2a**]Cl · 0.5DMSO): C 56.62, H 4.75, Cl 4.92, N 9.71 %; found: C 56.65, H 4.60, Cl 4.81, N 9.76 %.

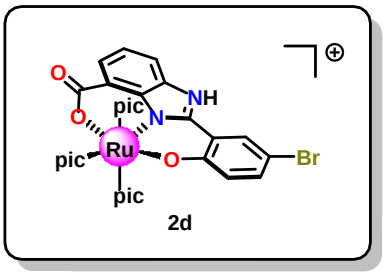


Synthesis of Ru complex 2b. Dark-green solid (48%). ^{1}H NMR (400 MHz, [D_4]methanol + ascorbic acid): δ = 10.19 (bs, 1H), 7.77 (d, *J* = 5.86 Hz, 2H), 7.41 (bs, 8H), 7.06 (d, *J* = 5.86 Hz, 2H), 6.60 (bs, 4H), 6.35 (bs, 2H), 3.01 (s, 3H), 1.95 (bs, 6H); HRMS (ESI)

Calcd. for $C_{32}H_{29}N_5O_3Ru$ [**2b**]$^+$: 633.1308; found: 633.1320; IR (KBr): ν_{max} = 3407, 2921, 1922, 1707, 1616, 1453, 1305, 1208, 1034, 813, 756 cm^{-1}; Anal. Calcd. (%) for $C_{33}H_{33}ClN_5O_4RuS_{0.5}$ ([**2b**]Cl · 0.5H_2O · 0.5DMSO): C 55.34, H 4.64, Cl 4.95, N 9.78 %; found: C 55.09, H 4.55, Cl 4.78, N 9.51 %.



Synthesis of Ru complex 2c. Dark-green solid (108 mg, 49% yield). ^{1}H NMR (400 MHz, [D_4]methanol + ascorbic acid): δ = 8.29 (dd, *J* = 5.42, 1.39 Hz, 2H), 7.83-7.75 (m, 3H), 7.40-7.27 (m, 7H), 7.01 (dd, *J* = 5.42, 1.39 Hz, 2H), 6.76-6.64 (m, 4H), 2.43 (s, 3H), 2.04 (s, 6H); HRMS (ESI) Calcd. for $C_{32}H_{28}FN_5O_3Ru$ [**2c**]$^+$: 651.1214; found: 651.1216; IR (KBr): ν_{max} = 3440, 2922, 1618, 1563, 1495, 1474, 1425, 1385, 1208, 813, 504 cm^{-1}; Anal. Calcd. (%) for $C_{32.5}H_{30.5}ClFN_5O_{3.75}RuS_{0.25}$ ([**2c**]Cl · 0.5H_2O · 0.25DMSO): C 54.62, H 4.30, Cl 4.96, N 9.80 %; found: C 54.65, H 4.14, Cl 4.82, N 10.04 %.



Synthesis of Ru complex 2d. Dark-green solid (140 mg, 60% yield). ^{1}H NMR (400 MHz, [D_4]methanol + ascorbic acid): δ = 8.42 (bs, 2H), 7.92 (d, *J* = 7.38 Hz, 2H), 7.63-7.45 (m, 6H), 7.35 (bs, 2H), 7.14-7.08 (m, 2H), 6.90-6.83 (m, 4H), 2.43 (s, 3H), 2.28 (s, 6H); HRMS (ESI) Calcd. for $C_{32}H_{28}BrN_5O_3Ru$ [**2d**]$^+$: 711.0414; found: 711.0442; IR (KBr): ν_{max} = 3396, 3072, 2919, 1928, 1725, 1618, 1496, 1470, 1453, 1209, 815, 504 cm^{-1}; Anal. Calcd. (%) for $C_{33.33}H_{31.5}BrClN_{5.17}O_{3.17}RuS_{0.17}$ ([**2d**]Cl · 1/6DMSO · 1/6Et_3N): C 51.53, H 4.09, Cl 4.56, N 9.31 %; found: C 51.65, H 3.97, Cl 4.68, N 9.37 %.

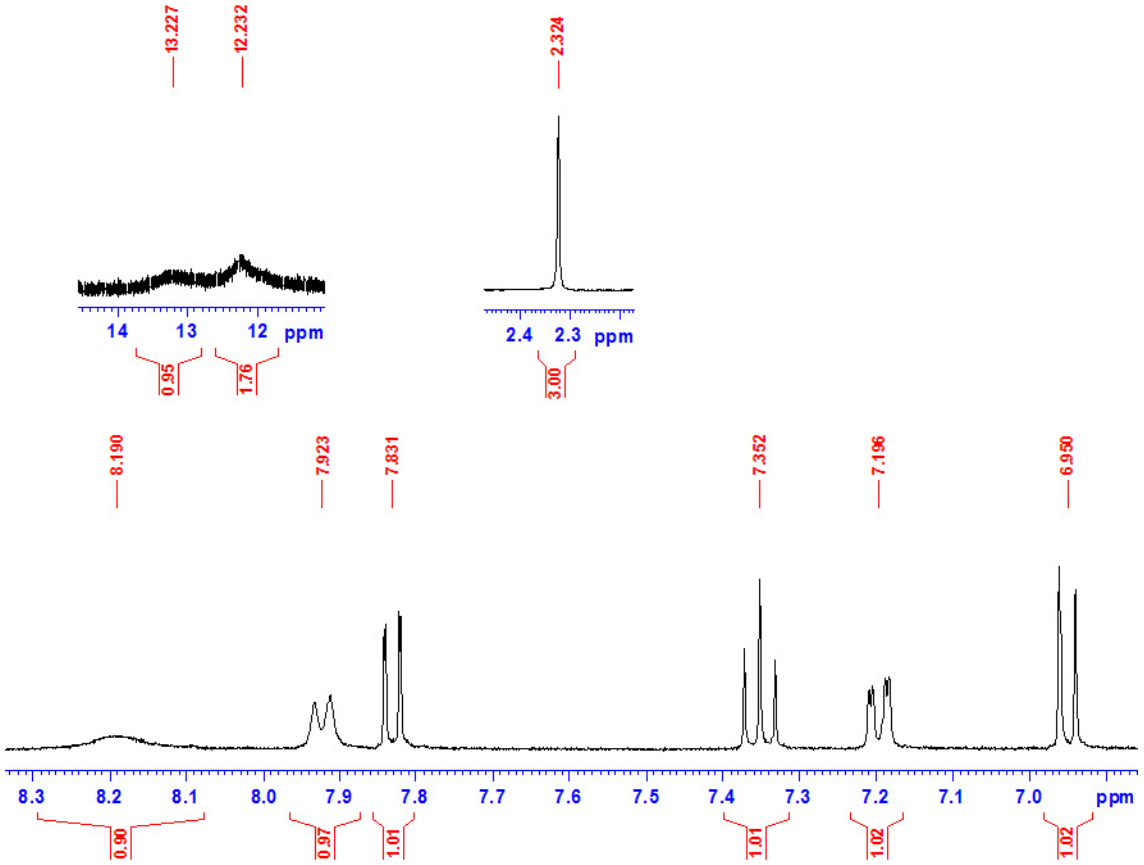


Figure S1. ^{1}H NMR spectrum of ligand **1a** in [D_6]DMSO.

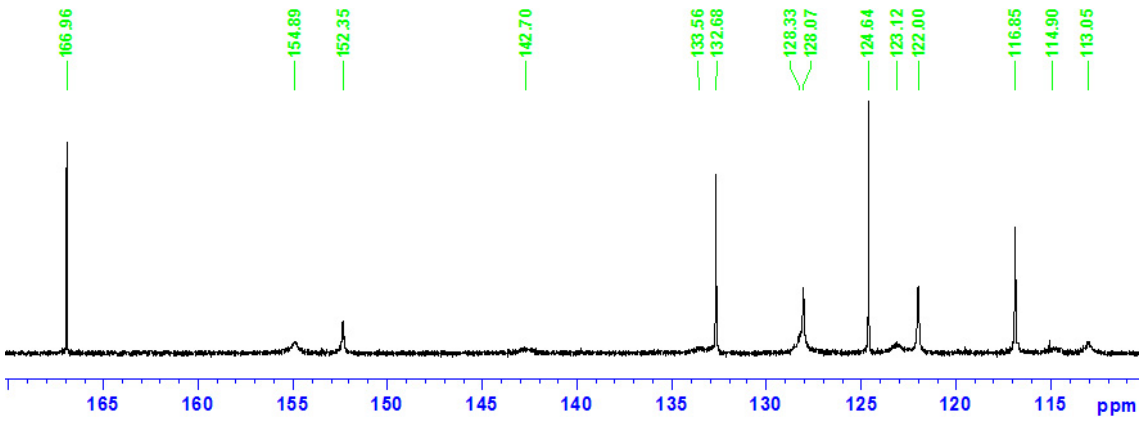


Figure S2. ^{13}C NMR spectrum of ligand **1a** in [D_6]DMSO.

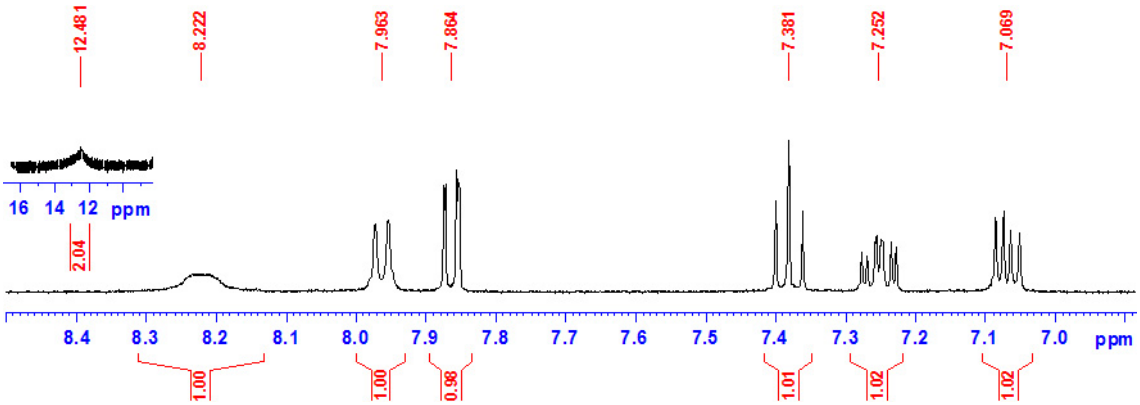


Figure S3. [1]H NMR spectrum of ligand **1c** in [D_6]DMSO.

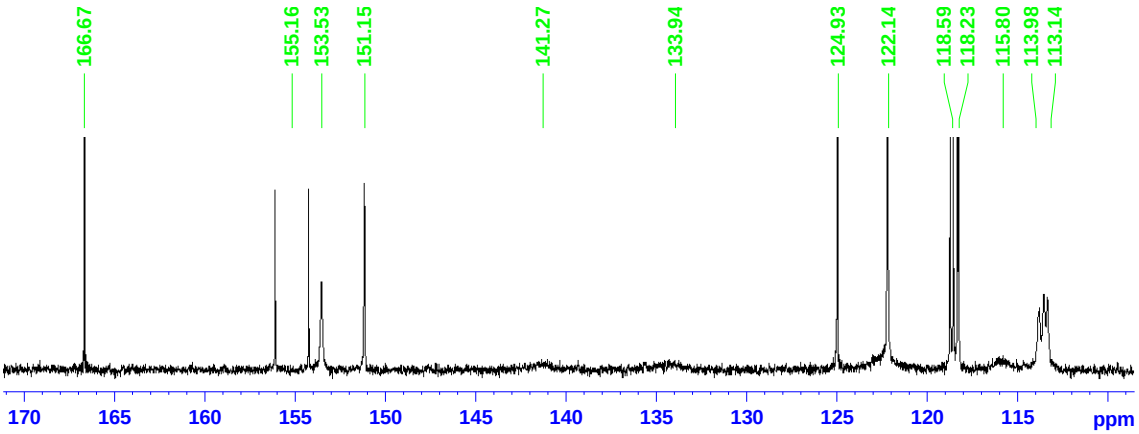


Figure S4. [13]C NMR spectrum of ligand **1c** in [D_6]DMSO.

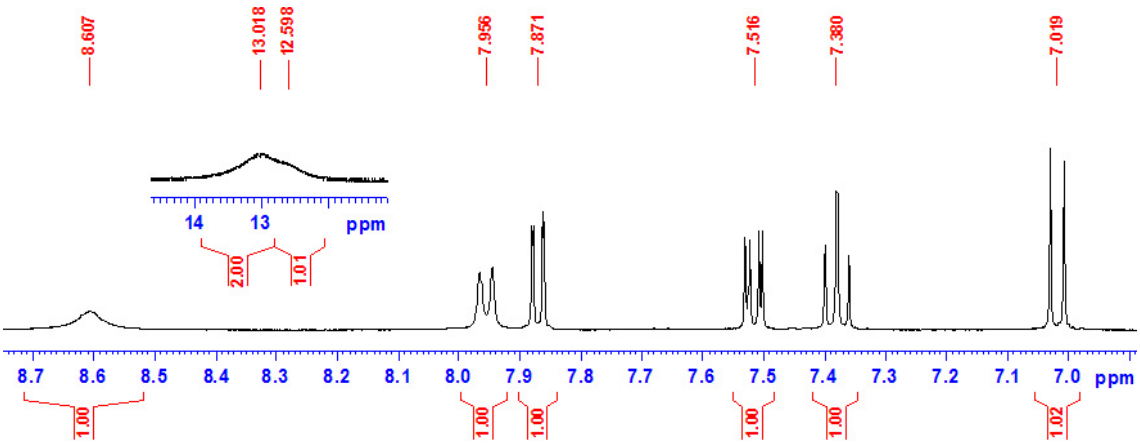


Figure S5. [1]H NMR spectrum of ligand **1d** in [D_6]DMSO.

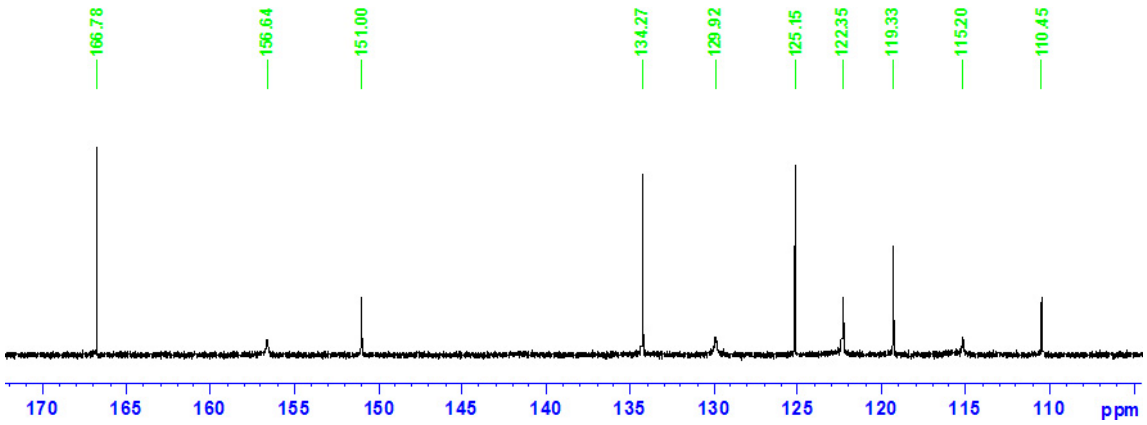


Figure S6. ^{13}C NMR spectrum of ligand **1d** in [D_6]DMSO.

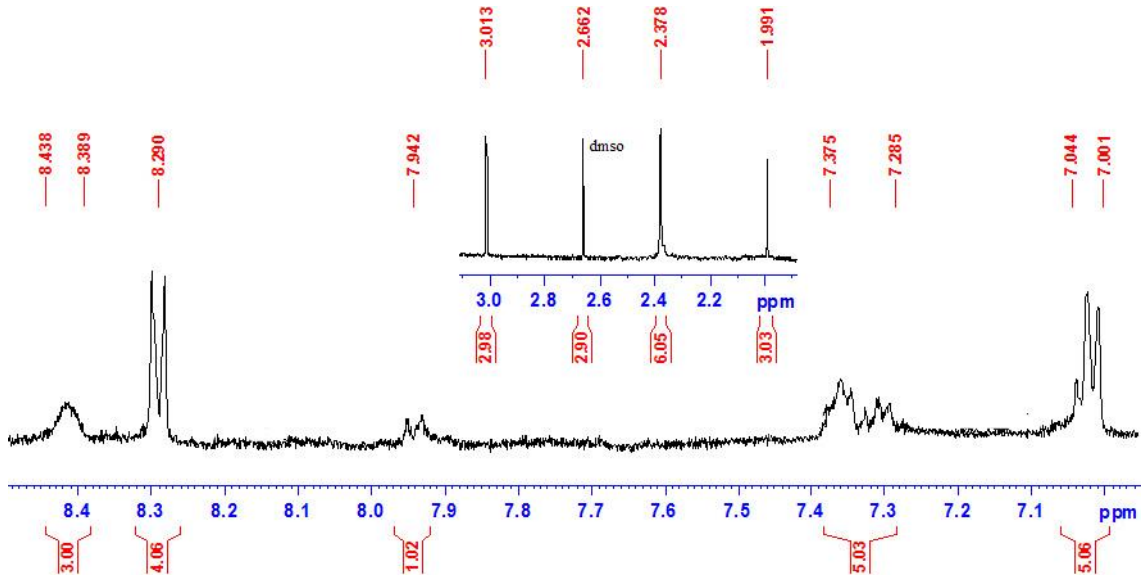


Figure S7. ^{1}H NMR spectrum of ruthenium complex **2a** in [D_4]methanol, in the presence of ascorbic acid.

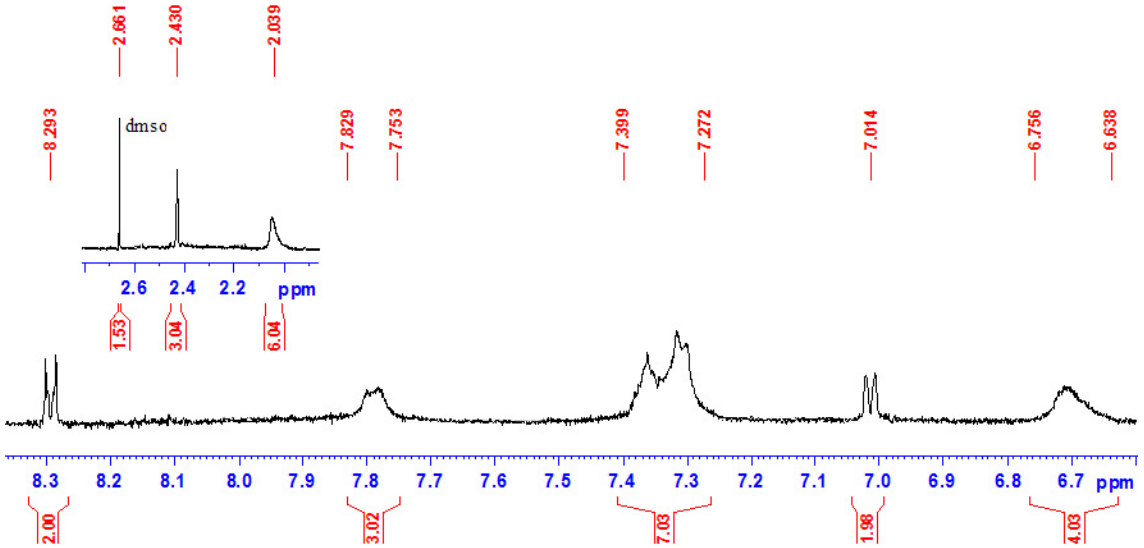


Figure S8. ^{1}H NMR spectrum of ruthenium complex **2c** in [D_4]methanol, in the presence of ascorbic acid.

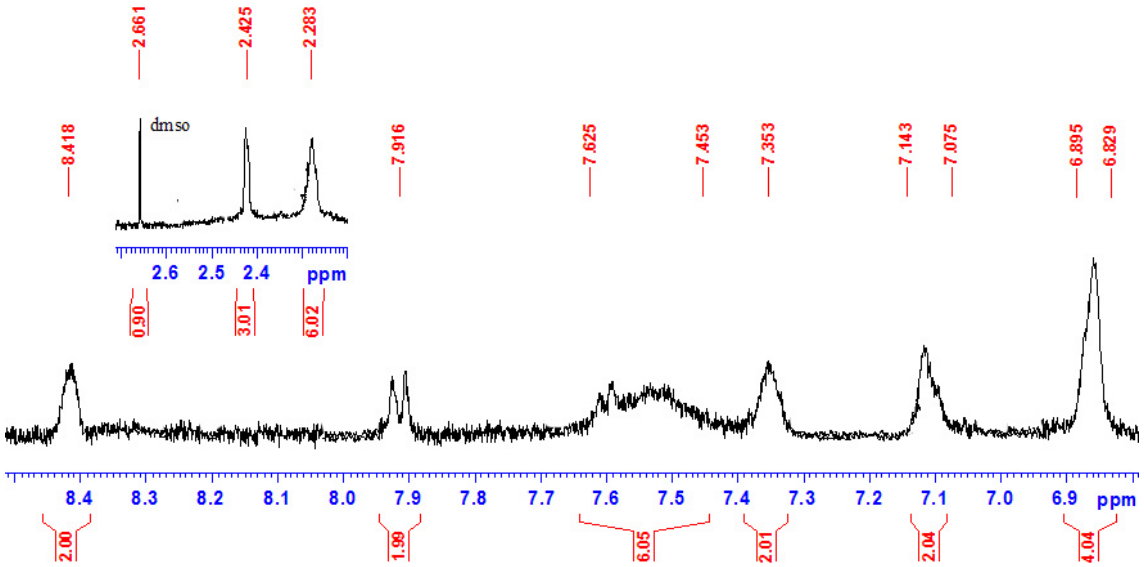


Figure S9. ^{1}H NMR spectrum of ruthenium complex **2d** in [D_4]methanol, in the presence of ascorbic acid.

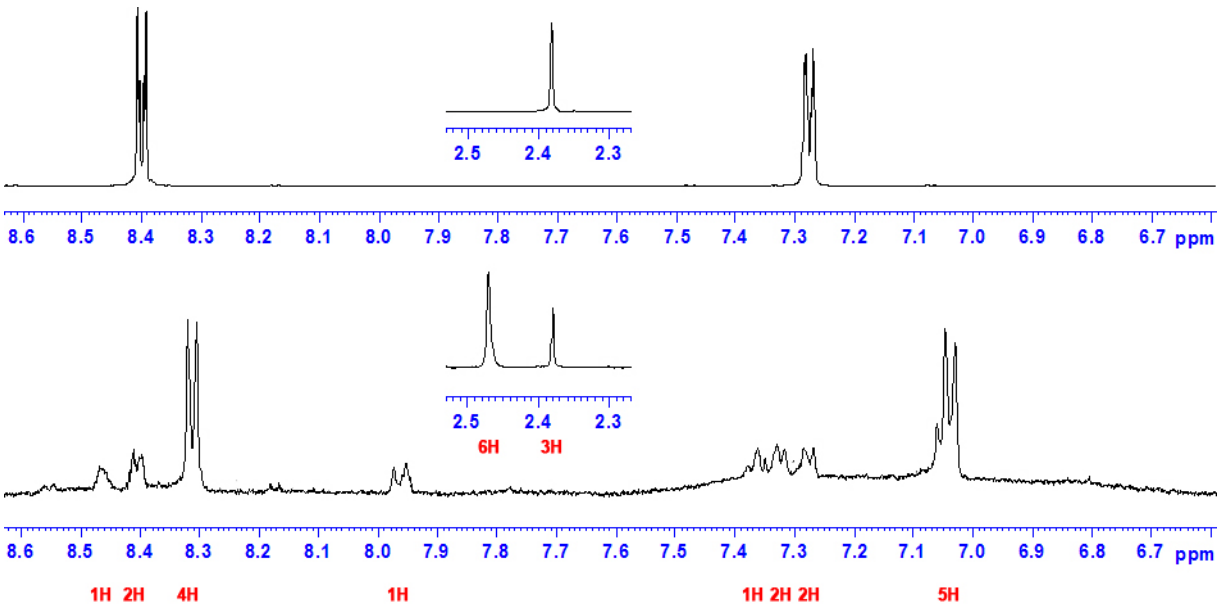


Figure S10. ^{1}H NMR spectrum of (top) free 4-picoline and (bottom) the ruthenium aqua complex **3a** in D_2O after reduction by $Na_2S_2O_3$.

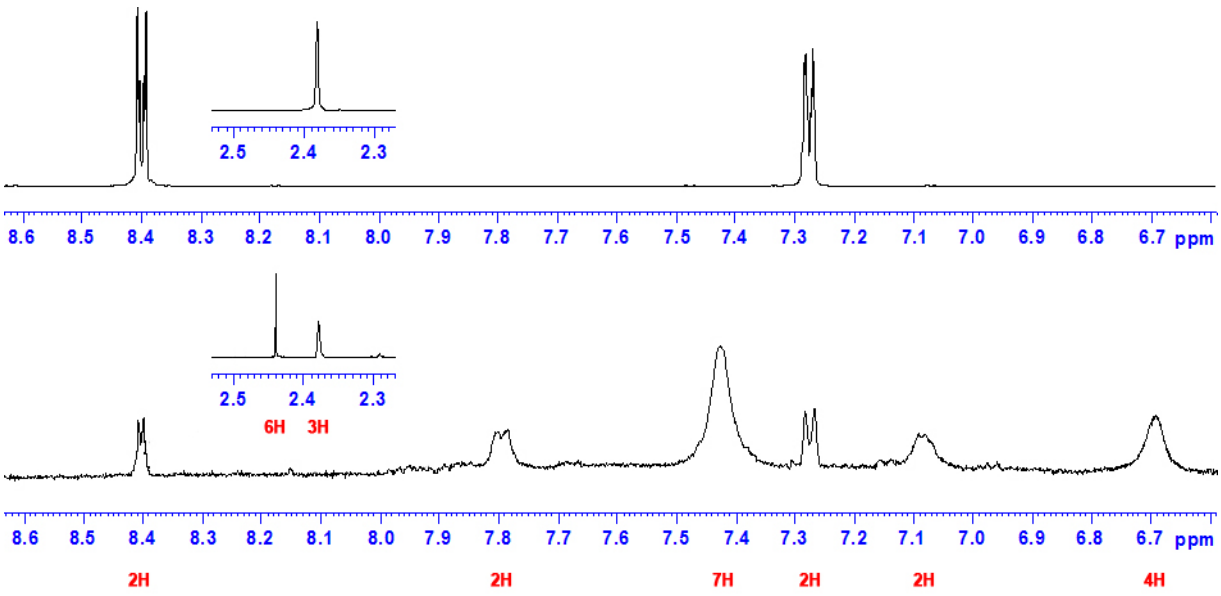


Figure S11. ^{1}H NMR spectrum of (top) free 4-picoline and (bottom) the ruthenium aqua complex **3b** in D_2O after reduction by $Na_2S_2O_3$.

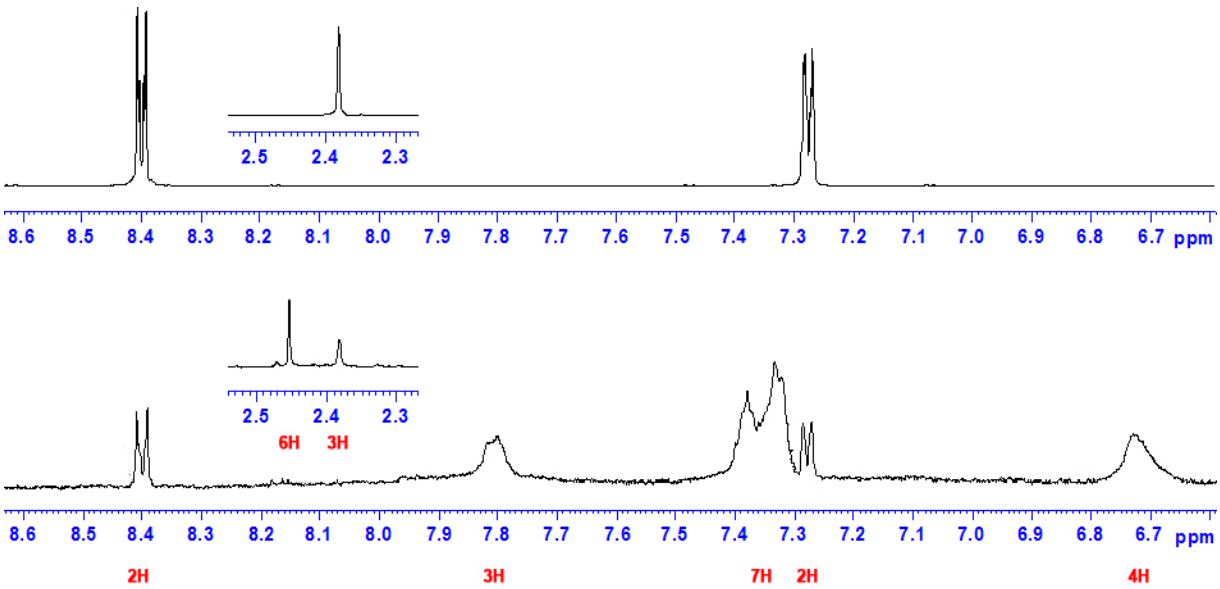


Figure S12. ^{1}H NMR spectrum of (top) free 4-picoline and (bottom) the ruthenium aqua complex **3c** in D_2O after reduction by $Na_2S_2O_3$.

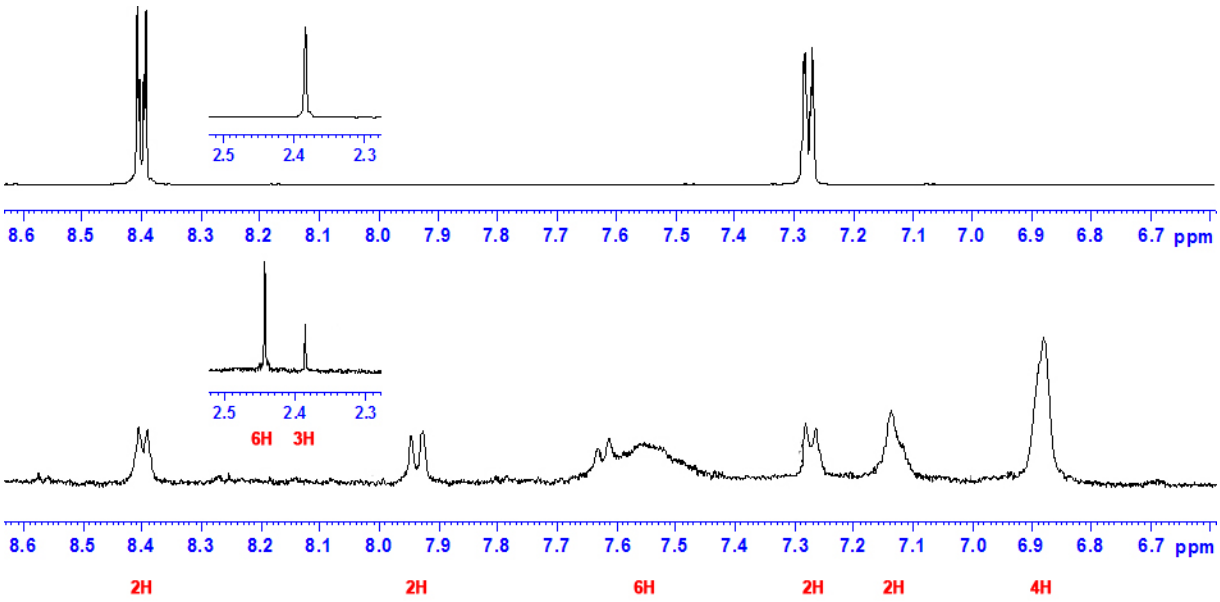


Figure S13. ^{1}H NMR spectrum of (top) free 4-picoline and (bottom) the ruthenium aqua complex **3d** in D_2O after reduction by $Na_2S_2O_3$.

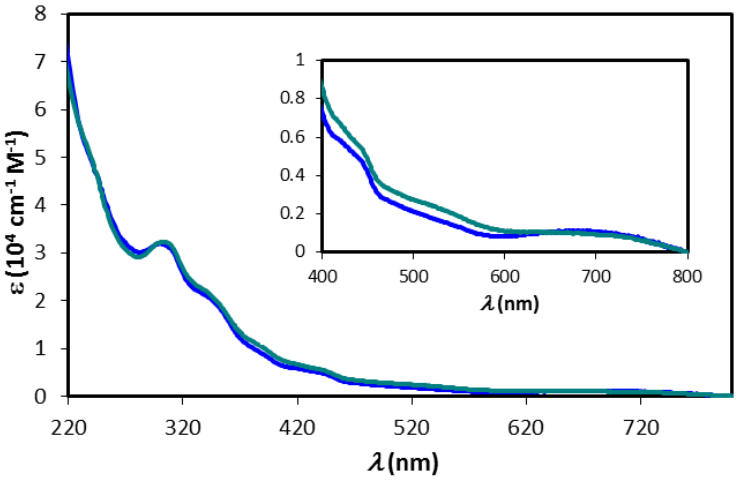


Figure S14. UV-vis spectra of ruthenium complex **2a** in (—) an aqueous phosphate buffer solution (0.1 M, pH 7.2) and (—) in an aqueous H_3PO_4 solution (0.1 M, pH 1).

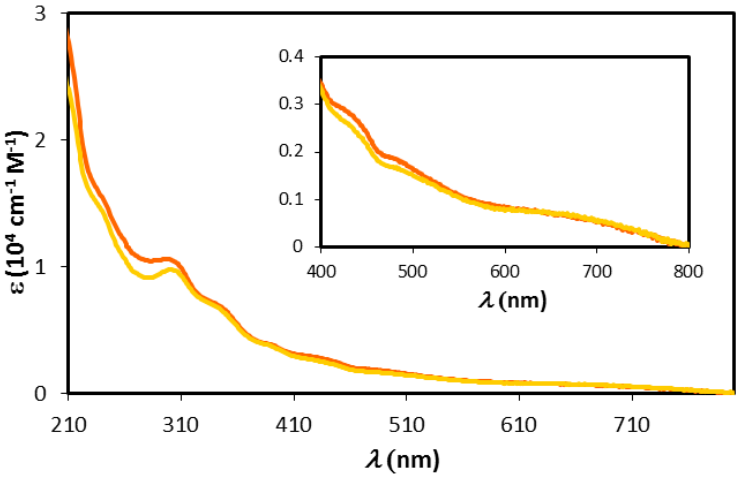


Figure S15. UV-vis spectra of ruthenium complex **2c** in (—) an aqueous phosphate buffer solution (0.1 M, pH 7.2) and (—) in an aqueous H_3PO_4 solution (0.1 M, pH 1).

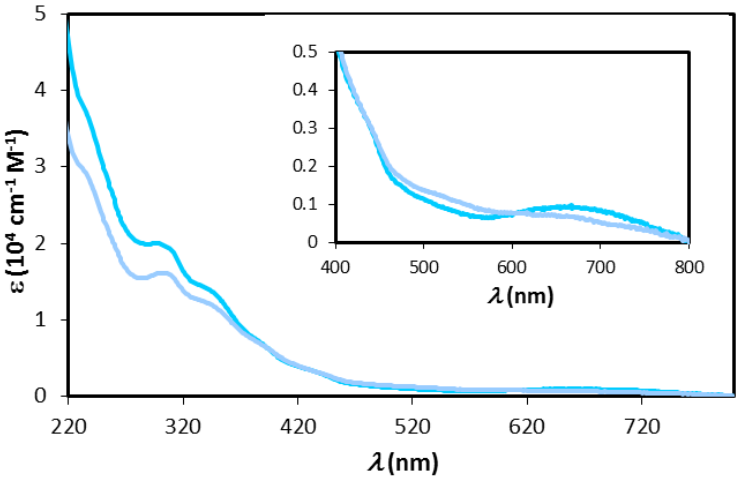


Figure S16. UV-vis spectra of ruthenium complex **2d** in (—) an aqueous phosphate buffer solution (0.1 M, pH 7.2) and (—) in an aqueous H_3PO_4 solution (0.1 M, pH 1).

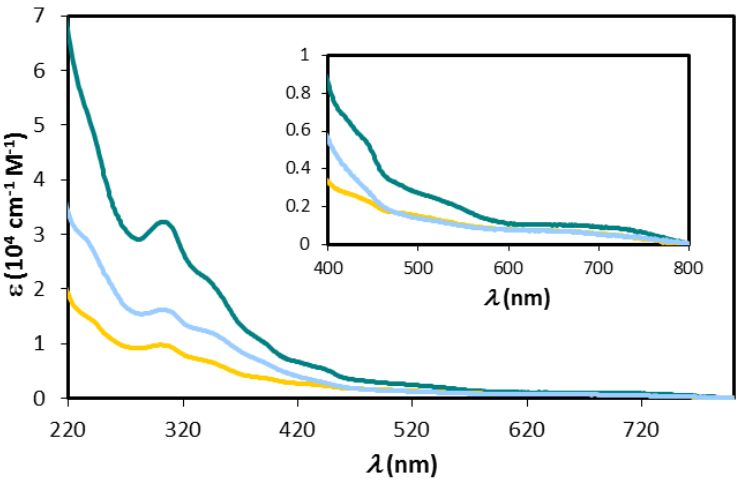


Figure S17. UV-vis spectra of ruthenium complexes **2a**, **2c** and **2d** in an aqueous phosphate buffer solution (0.1 M, pH 7.2). Complex **2a** (—), complex **2c** (—), complex **2d** (—).

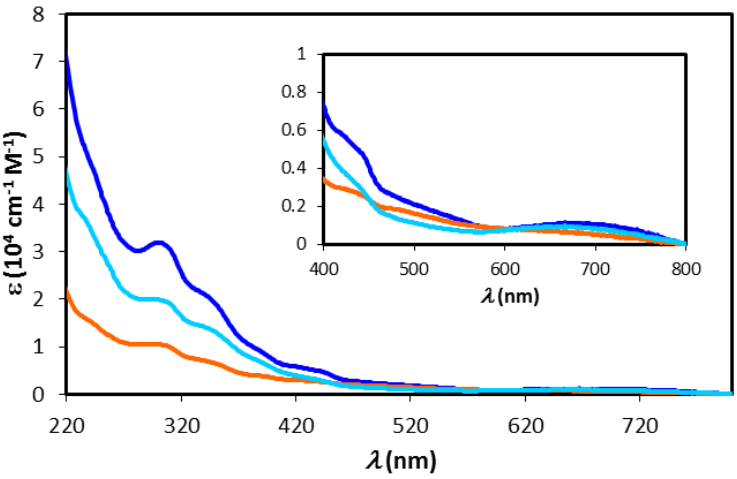


Figure S18. UV-vis spectra of ruthenium complexes **2a**, **2c** and **2d** in an aqueous H_3PO_4 solution (0.1 M, pH 1). Complex **2a** (—), complex **2c** (—), complex **2d** (—).

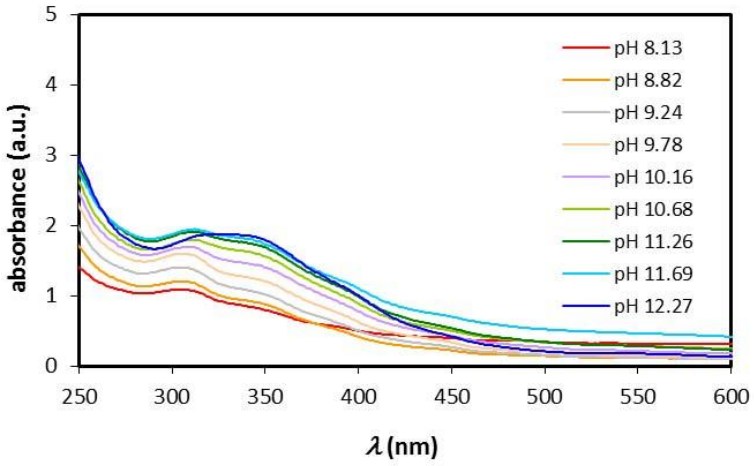


Figure S19. Spectrophotometric titration of complex **2a** in an aqueous phosphate buffer solution. The pH value was adjusted with aliquots of 1 M NaOH.

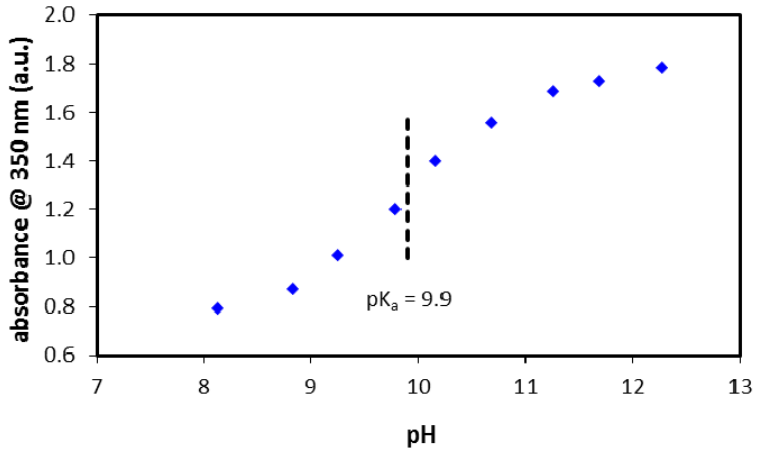


Figure S20. Spectrophotometric determination of pK_a value for complex **2a**.

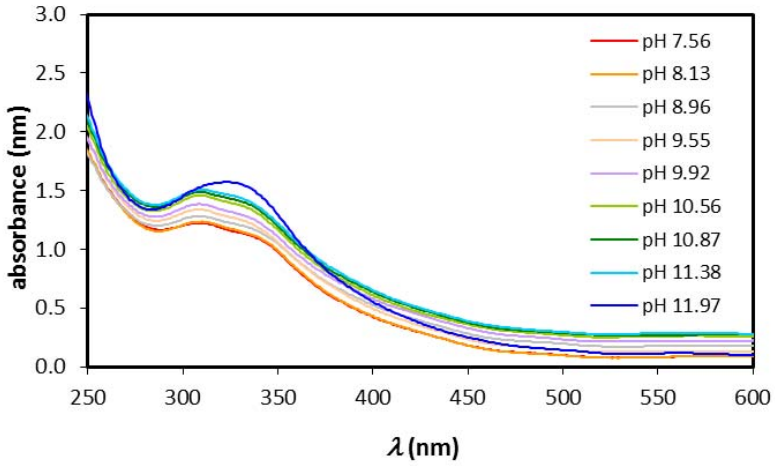


Figure S21. Spectrophotometric titration of complex **2b** in an aqueous phosphate buffer solution. The pH value was adjusted with aliquots of 1 M NaOH.

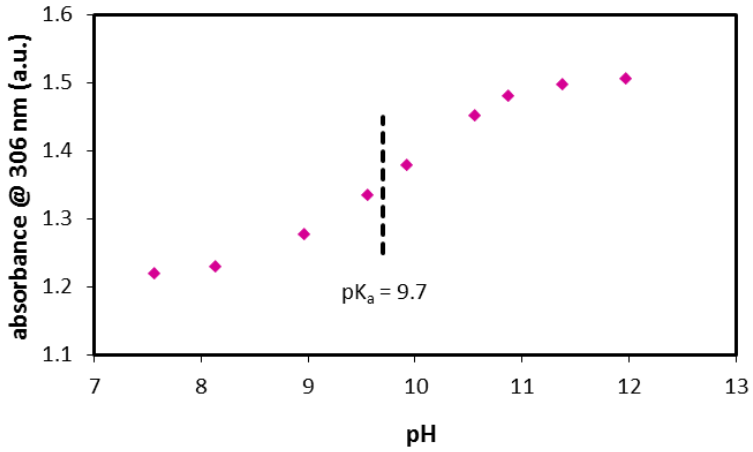


Figure S22. Spectrophotometric determination of pK_a value for complex **2b**.

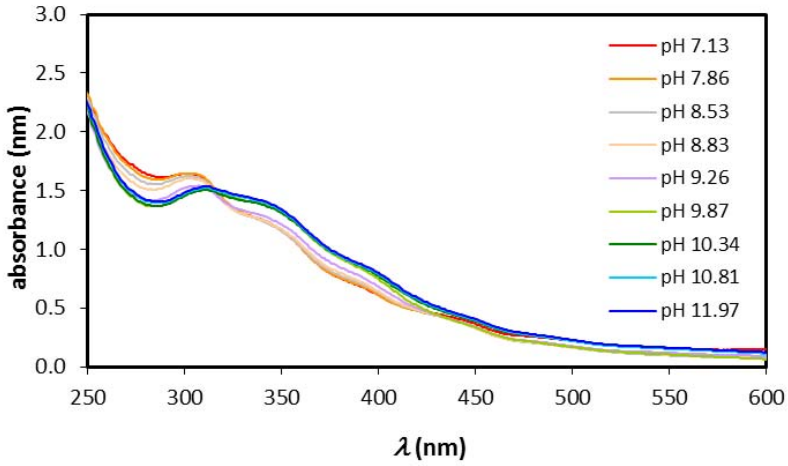


Figure S23. Spectrophotometric titration of complex **2c** in an aqueous phosphate buffer solution. The pH value was adjusted with aliquots of 1 M NaOH.

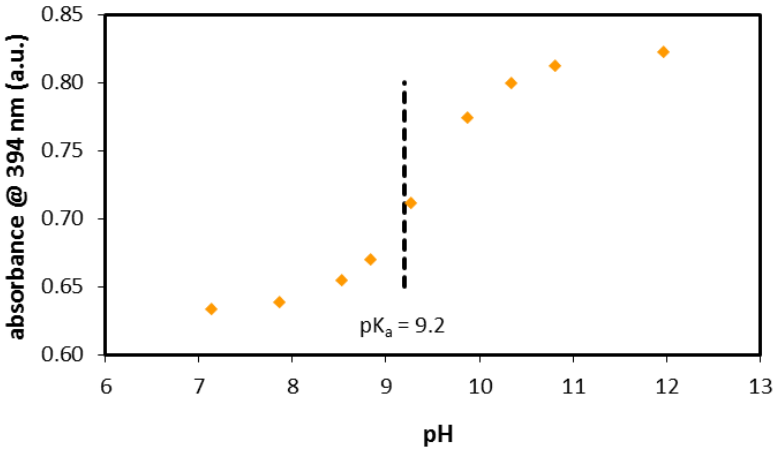


Figure S24. Spectrophotometric determination of pK_a value for complex **2c**.

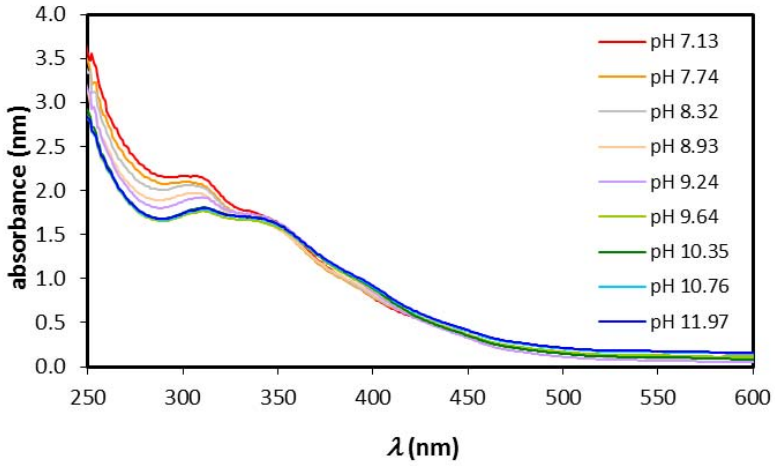


Figure S25. Spectrophotometric titration of complex **2d** in an aqueous phosphate buffer solution. The pH value was adjusted with aliquots of 1 M NaOH.

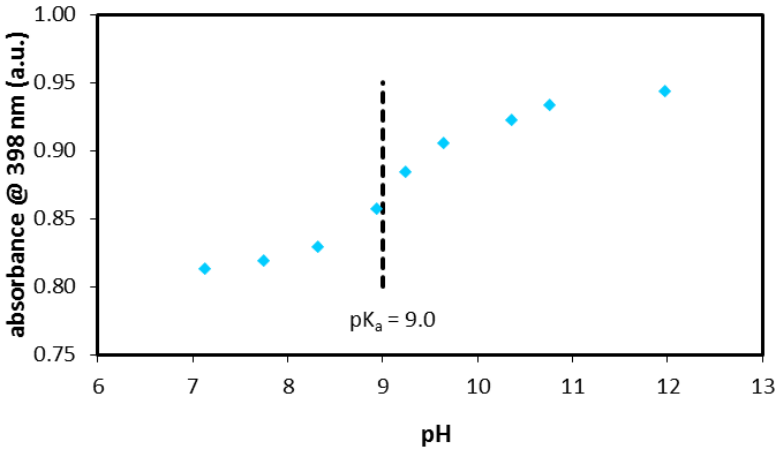


Figure S26. Spectrophotometric determination of pK$_a$ value for complex **2d**.

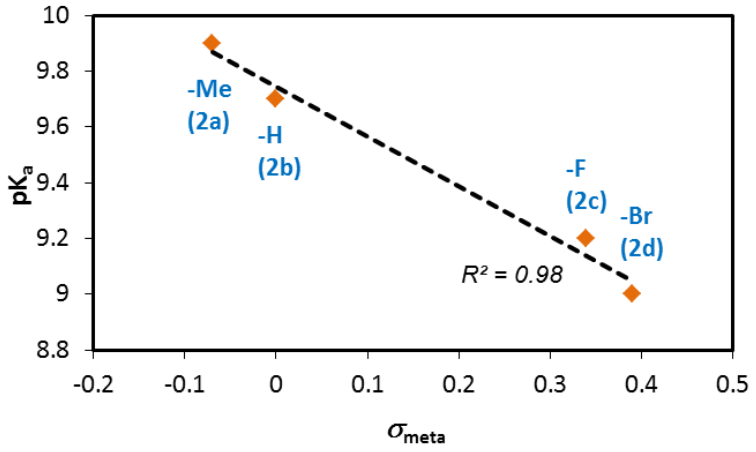


Figure S27. Hammett plot for the pK$_a$ values for complexes **2a-d**.

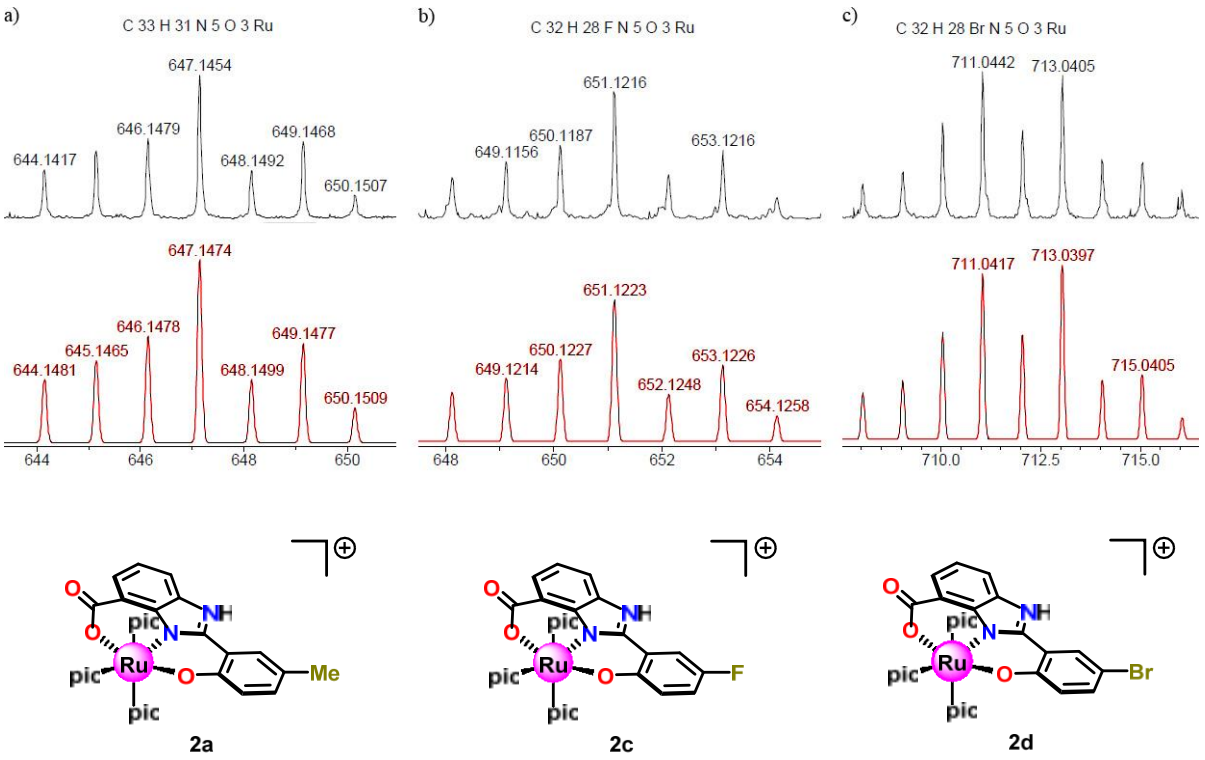


Figure S28. ESI-HRMS of Ru complexes **2a**, **2c** and **2d** in positive mode (pic = 4-picoline).

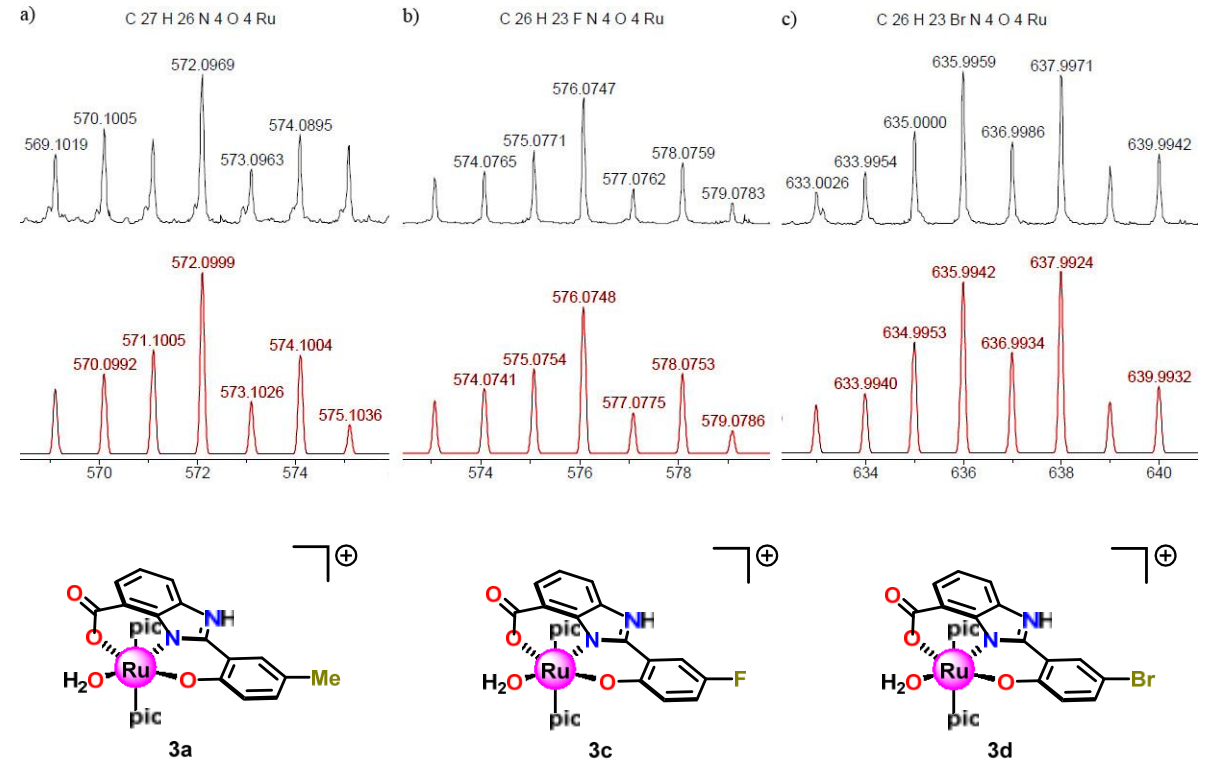
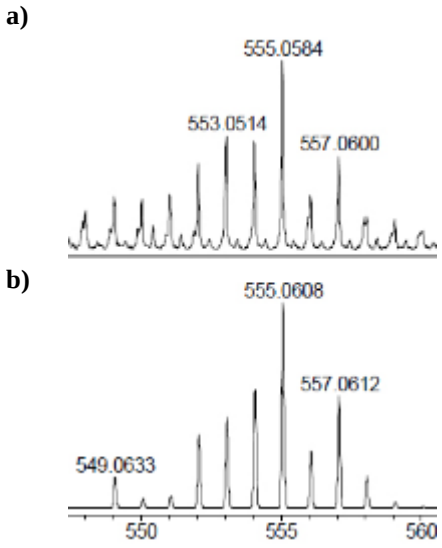
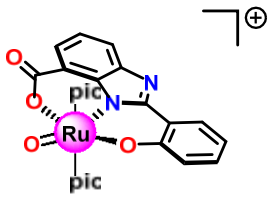


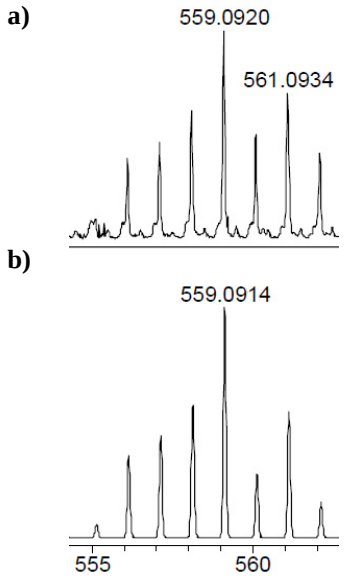
Figure S29. ESI-HRMS of the corresponding Ru^{III}-aqua complexes of **2a**, **2c** and **2d** in positive mode (pic = 4-picoline).





6b

Figure S30. (a) ESI-HRMS of the corresponding Ru^{VI}-oxo complex of **2b** (**6b**) in positive mode obtained after the addition of 15 equivalents of the oxidant $[Ru(bpy)_3](PF_6)_3$ to an aqueous solution containing complex **2b** and (b) the simulated spectrum (pic = 4-picoline).



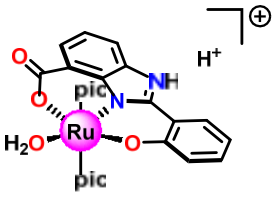


Figure S31. (a) ESI-HRMS of the corresponding Ru^{II}-aqua complex of **2b** in positive mode obtained after the addition of ascorbic acid to an aqueous solution containing complex **2b** and (b) the simulated spectrum (pic = 4-picoline).

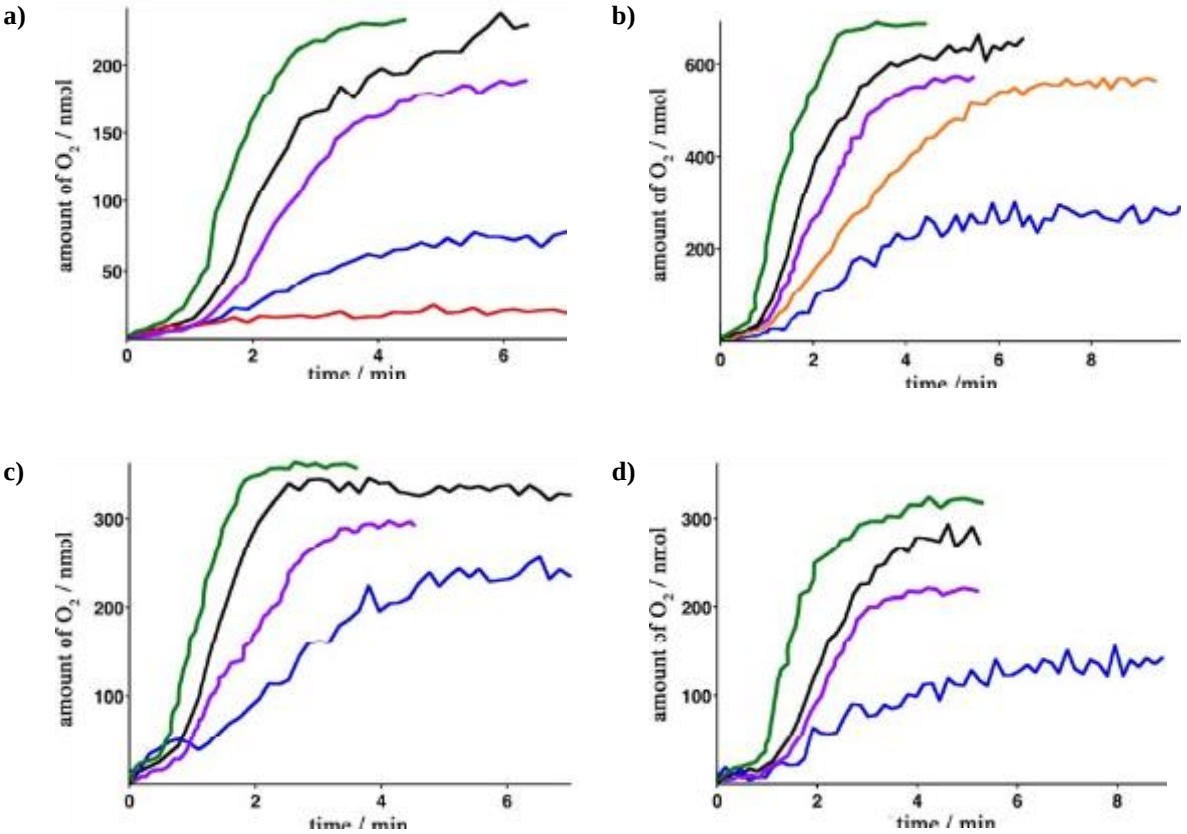


Figure S32. Kinetic curves of O_2 evolution by catalysts (a) **2a**, (b) **2b**, (c) **2c** and (d) **2d**. Reaction conditions: An aqueous phosphate buffer solution (0.1 M, pH 7.2, 0.5 mL) containing the catalyst was added to the oxidant $[Ru(bpy)_3](PF_6)_3$ (3.0 mg, 3.0 μmol). 4.0 μM (—), 3.3 μM (—), 2.0 μM (—), 0.73 μM (—), 0.33 μM (—), 0.066 μM (—).

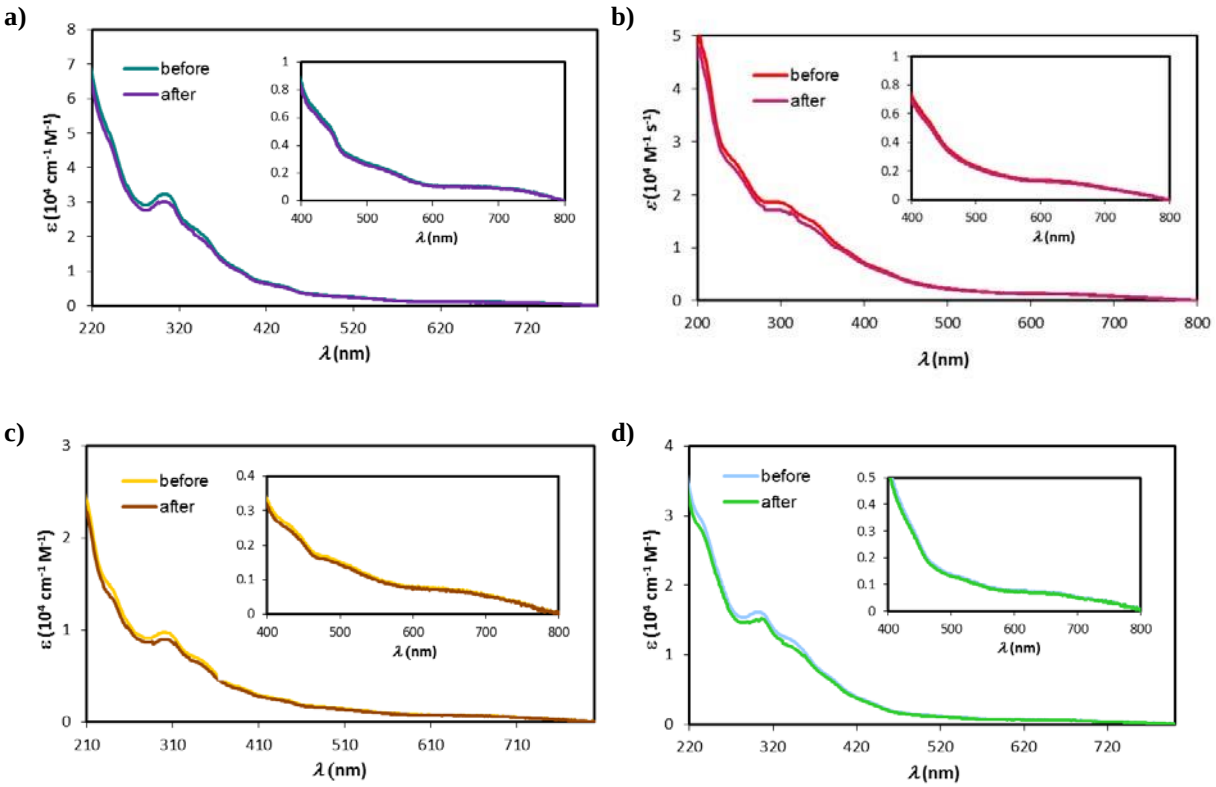
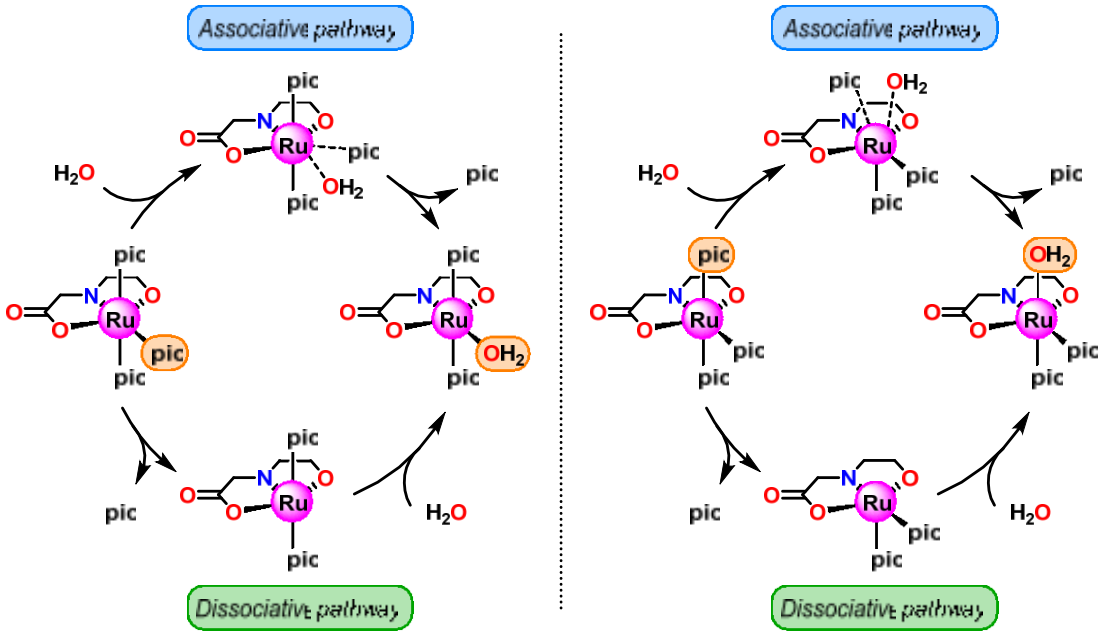
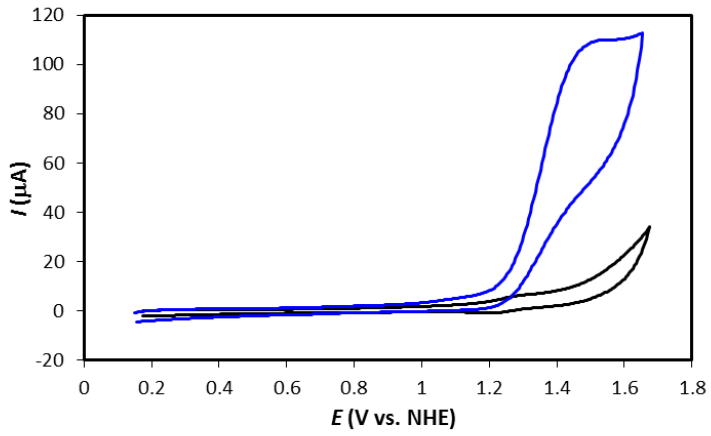


Figure S33. UV-vis spectra of Ru complexes (a) **2a**, (b) **2b**, (c) **2c** and (d) **2d** in aqueous phosphate buffer solutions (0.1 M, pH 7.2) before and after the addition of 25 equivalents of the oxidant $[Ru(bpy)_3](PF_6)_3$.

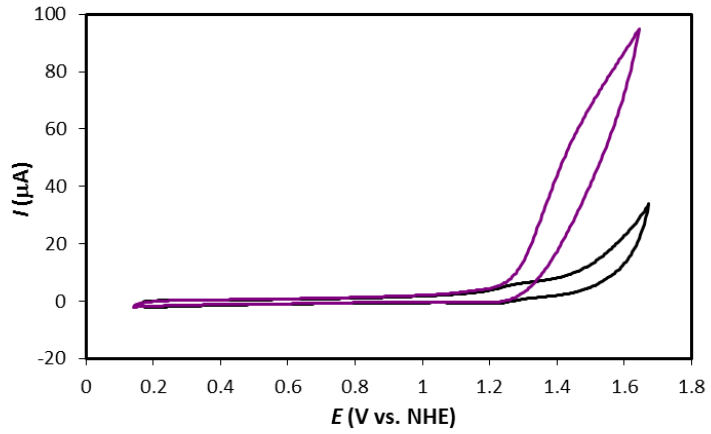


Scheme S1. Simplified depiction of the associative and dissociative pathways for equatorial (left) and axial (right) picoline-H_2O ligand exchange.

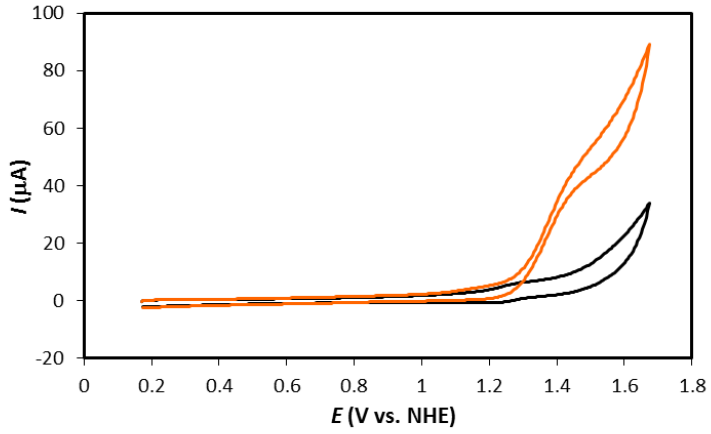
a)



b)



c)



d)

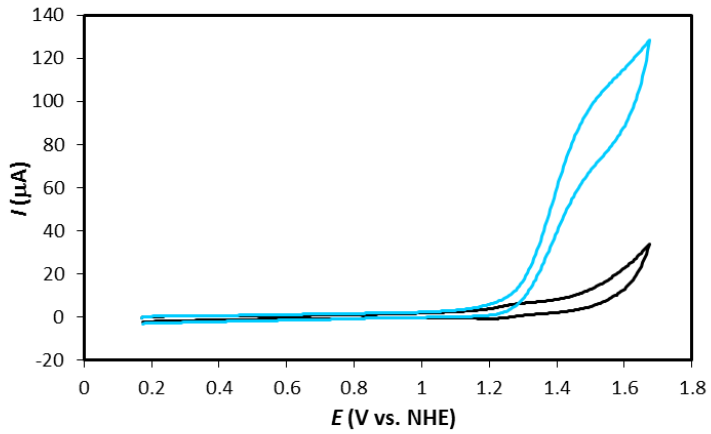
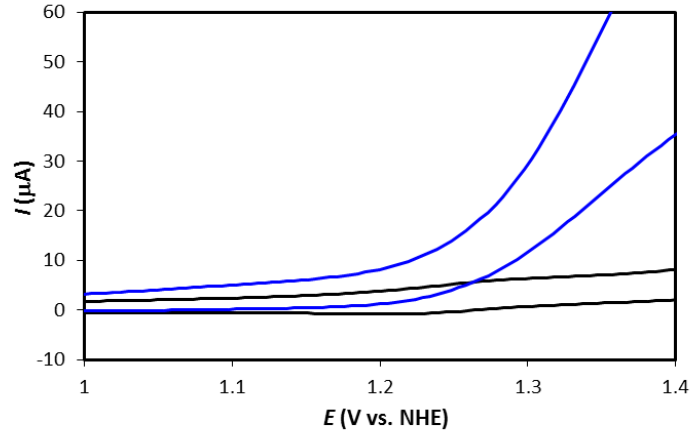


Figure S34. Cyclic voltammograms of (a) complex **2a** (b) **2b**, (c) **2c** and (d) **2d** in a pH 7.2 solution. Conditions: Voltammograms were recorded in an aqueous phosphate buffer solution (0.1 M, pH 7.2) containing complex **2a-d** (26 µM) with a scan rate of 0.1 V s^{-1}, using the $[Ru(bpy)_3]^{3+}/[Ru(bpy)_3]^{2+}$ couple as a standard ($E_{1/2}$ = 1.26 V vs. NHE). **2a** (—), **2b** (—),**2c** (—), **2d** (—), $[Ru(bpy)_3]Cl_2$ (—).

a)



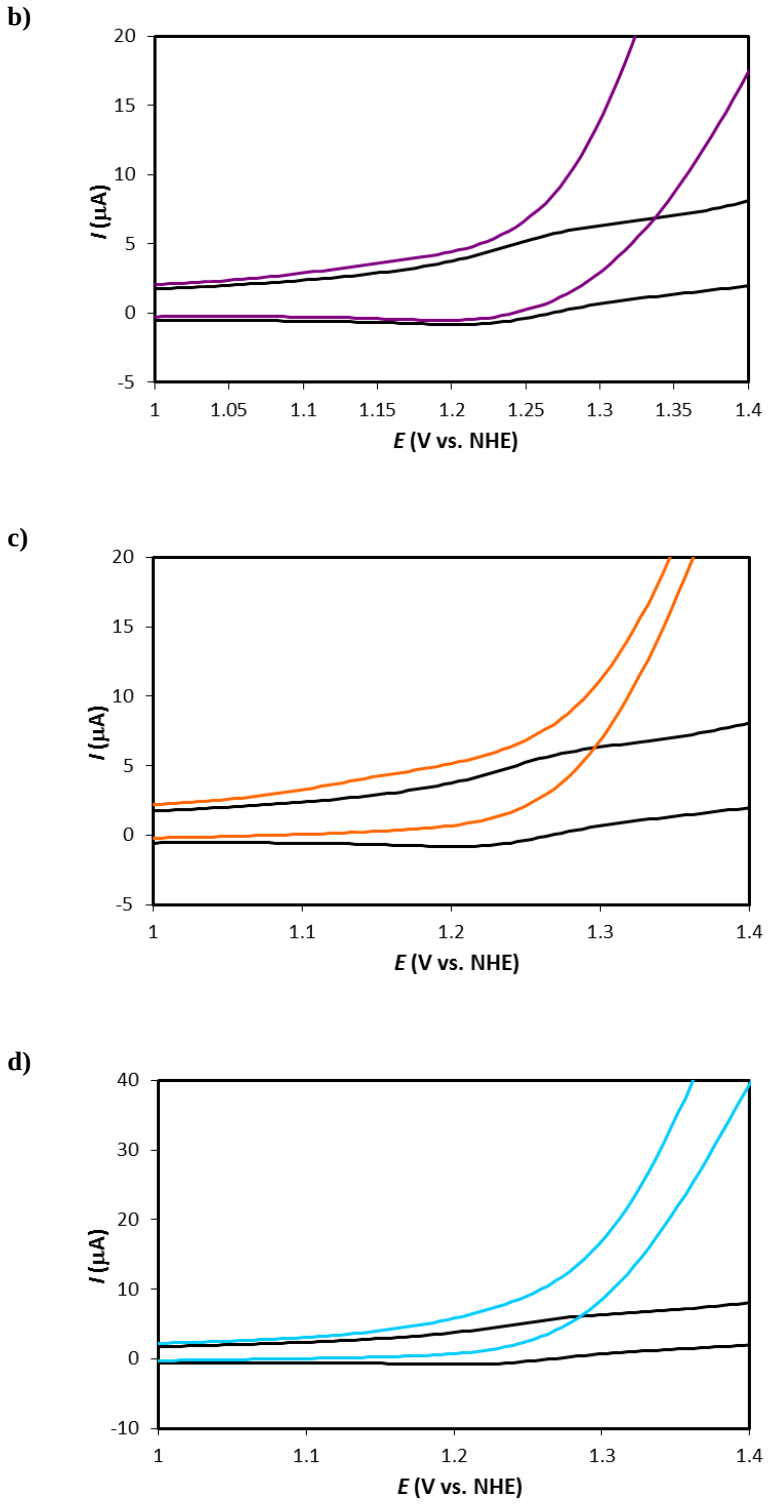
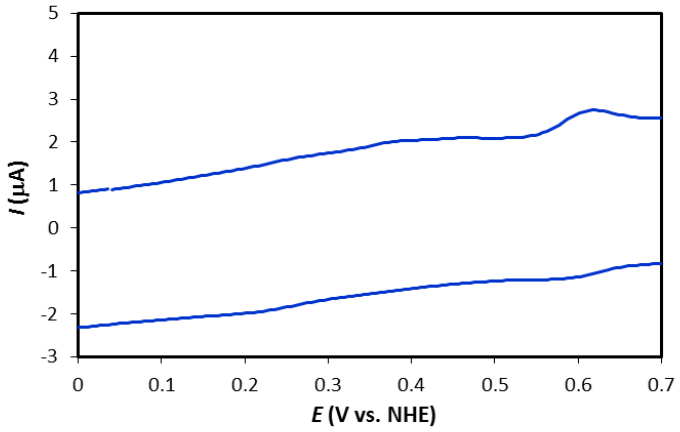


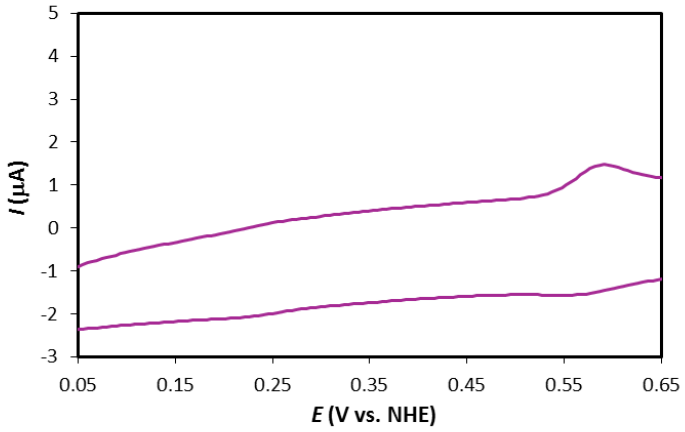
Figure S35. Magnification of catalytic curves (1.0 < *E* < 1.4 V) of (a) complex **2a**, (b) **2b**, (c) **2c** and (d) **2d** in a pH 7.2 solution. Conditions: Voltammograms were recorded in an aqueous phosphate buffer solution (0.1 M, pH 7.2) containing complex **2a-d** (26 µM) with a scan rate of 0.1 V s^{-1}, using

the $[Ru(bpy)_3]^{3+}/[Ru(bpy)_3]^{2+}$ couple as a standard ($E_{1/2}$ = 1.26 V vs. NHE). **2a** (—), **2b** (—),**2c** (—), **2d** (—), $[Ru(bpy)_3]Cl_2$ (—).

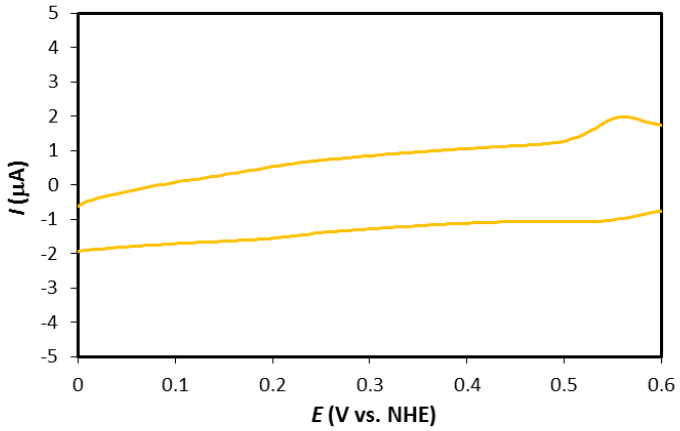
a)



b)



c)



d)

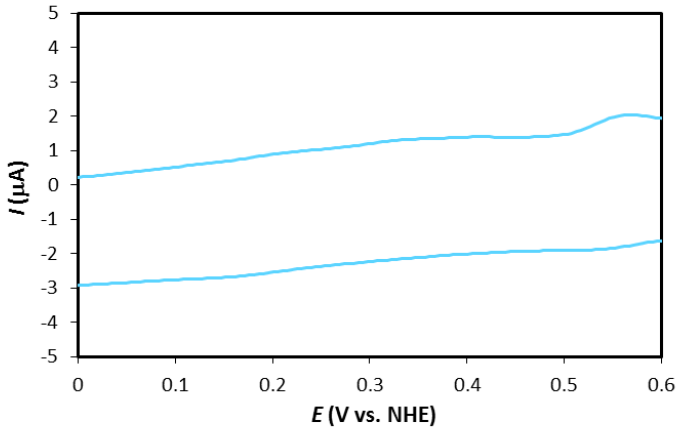


Figure S36. Magnification of catalytic curves (0.3 < *E* < 0.7 V) of (a) complex **2a**, (b) **2b**, (c) **2c** and (d) **2d** in a pH 7.2 solution. Conditions: Voltammograms were recorded in an aqueous phosphate buffer solution (0.1 M, pH 7.2) containing complex **2a**-**d** (26 µM) with a scan rate of 0.1 V s^{-1}, using the $[Ru(bpy)_3]^{3+}/[Ru(bpy)_3]^{2+}$ couple as a standard ($E_{1/2}$ = 1.26 V vs. NHE). **2a** (—), **2b** (—),**2c** (—), **2d** (—).

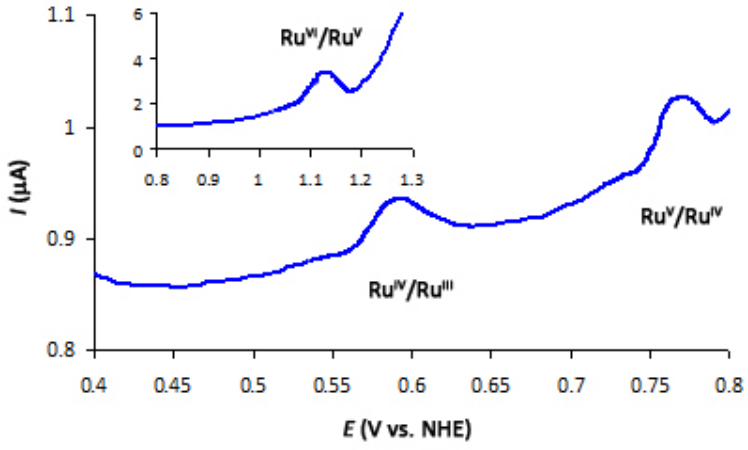


Figure S37. Differential pulse voltammogram of complex **2a** at pH 7.2. Conditions: Voltammogram was recorded in an aqueous phosphate buffer solution (0.1 M, pH 7.2) containing complex **2a** (26 µM) with a scan rate of 0.1 V s^{-1}, using the $[Ru(bpy)_3]^{3+}/[Ru(bpy)_3]^{2+}$ couple as a standard ($E_{1/2}$ = 1.26 V vs. NHE).

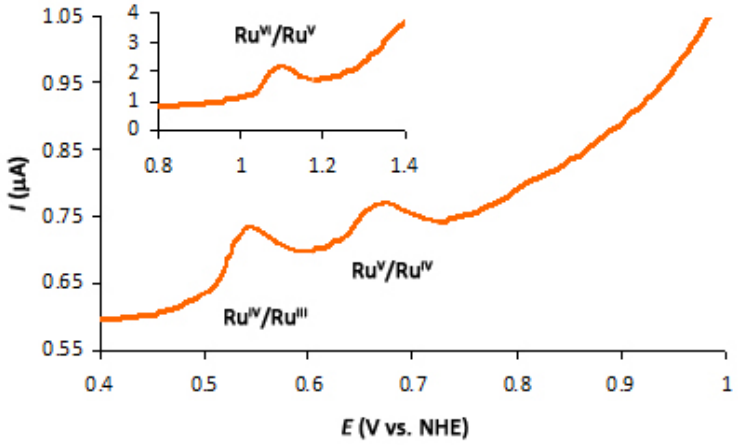


Figure S38. Differential pulse voltammogram of complex **2c** at pH 7.2. Conditions: Voltammogram was recorded in an aqueous phosphate buffer solution (0.1 M, pH 7.2) containing complex **2c** (26 µM) with a scan rate of 0.1 V s^{-1}, using the $[Ru(bpy)_3]^{3+}/[Ru(bpy)_3]^{2+}$ couple as a standard ($E_{1/2}$ = 1.26 V vs. NHE).

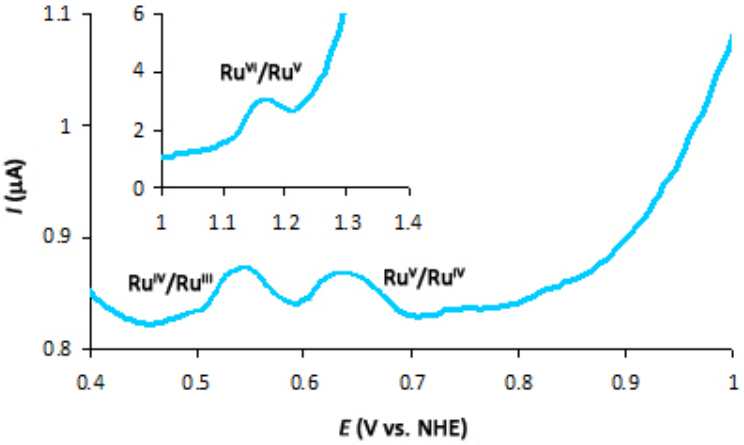


Figure S39. Differential pulse voltammogram of complex **2d** at pH 7.2. Conditions: Voltammogram was recorded in an aqueous phosphate buffer solution (0.1 M, pH 7.2) containing complex **2d** (26 µM) with a scan rate of 0.1 V s^{-1}, using the $[Ru(bpy)_3]^{3+}/[Ru(bpy)_3]^{2+}$ couple as a standard ($E_{1/2}$ = 1.26 V vs. NHE).

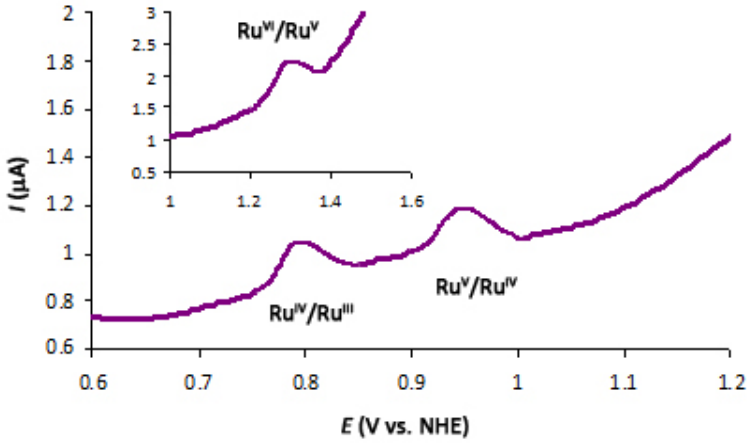


Figure S40. Differential pulse voltammogram of complex **2b** at pH 3.67. Conditions: Voltammogram was recorded in a Britton-Robinson buffer solution (0.1 M) containing complex **2b** (26 µM) with a scan rate of 0.1 V s^{-1}, using the $[Ru(bpy)_3]^{3+}/[Ru(bpy)_3]^{2+}$ couple as a standard ($E_{1/2}$ = 1.26 V vs. NHE).

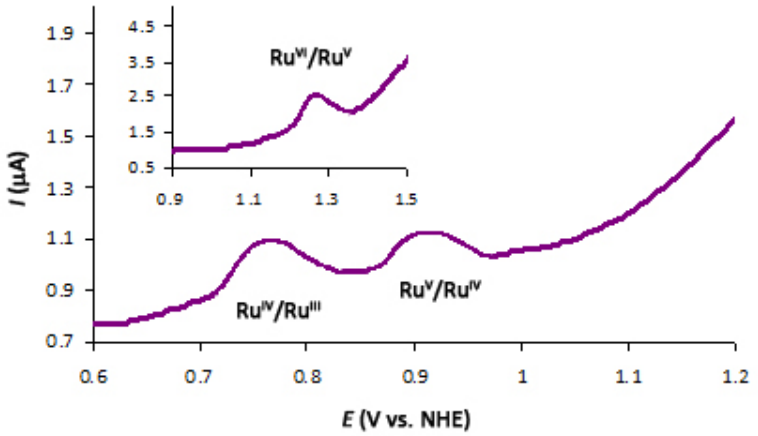


Figure S41. Differential pulse voltammogram of complex **2b** at pH 4.07. Conditions: Voltammogram was recorded in a Britton-Robinson buffer solution (0.1 M) containing complex **2b** (26 µM) with a scan rate of 0.1 V s^{-1}, using the $[Ru(bpy)_3]^{3+}/[Ru(bpy)_3]^{2+}$ couple as a standard ($E_{1/2}$ = 1.26 V vs. NHE).

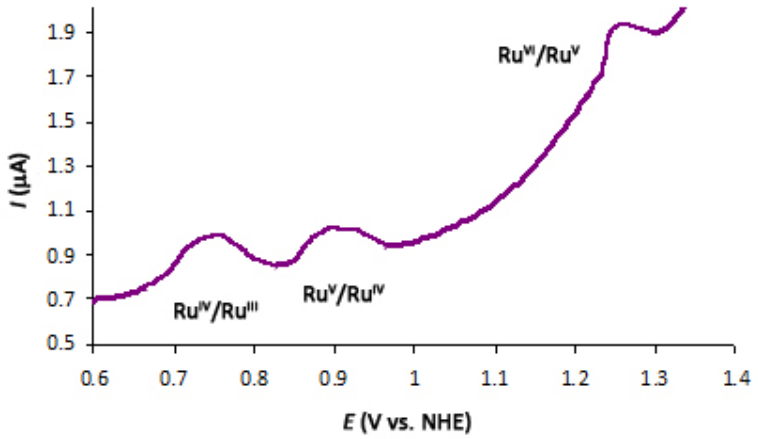


Figure S42. Differential pulse voltammogram of complex **2b** at pH 4.49. Conditions: Voltammogram was recorded in a Britton-Robinson buffer solution (0.1 M) containing complex **2b** (26 μM) with a scan rate of 0.1 V s^{-1}, using the $[Ru(bpy)_3]^{3+}/[Ru(bpy)_3]^{2+}$ couple as a standard ($E_{1/2}$ = 1.26 V vs. NHE).

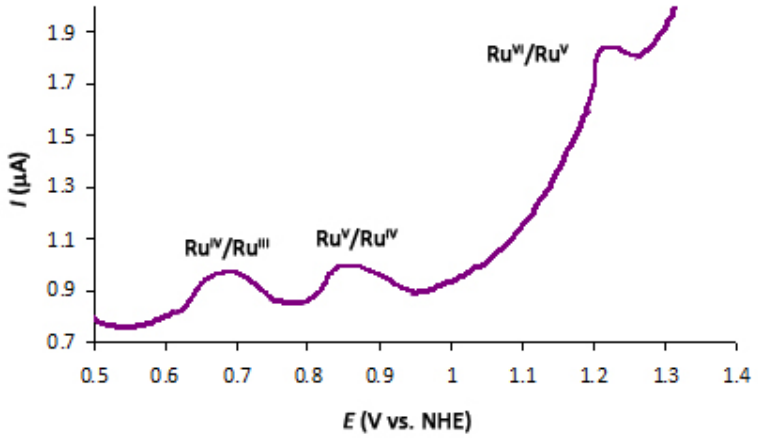


Figure S43. Differential pulse voltammogram of complex **2b** at pH 5.11. Conditions: Voltammogram was recorded in a Britton-Robinson buffer solution (0.1 M) containing complex **2b** (26 μM) with a scan rate of 0.1 V s^{-1}, using the $[Ru(bpy)_3]^{3+}/[Ru(bpy)_3]^{2+}$ couple as a standard ($E_{1/2}$ = 1.26 V vs. NHE).

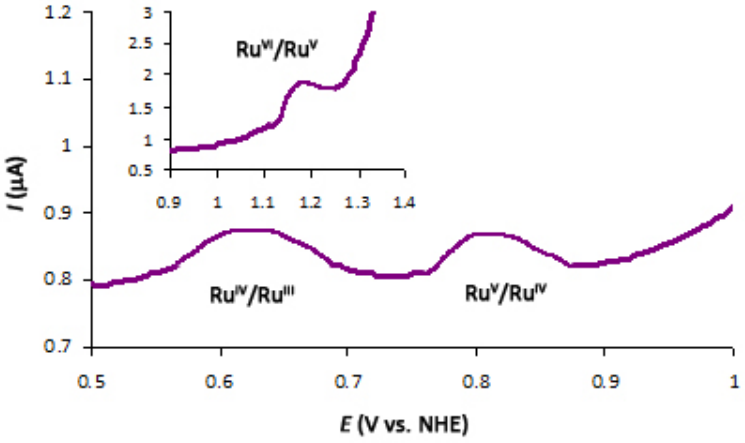


Figure S44. Differential pulse voltammogram of complex **2b** at pH 5.85. Conditions: Voltammogram was recorded in a Britton-Robinson buffer solution (0.1 M) containing complex **2b** (26 μM) with a scan rate of 0.1 V s^{-1}, using the $[Ru(bpy)_3]^{3+}/[Ru(bpy)_3]^{2+}$ couple as a standard ($E_{1/2}$ = 1.26 V vs. NHE).

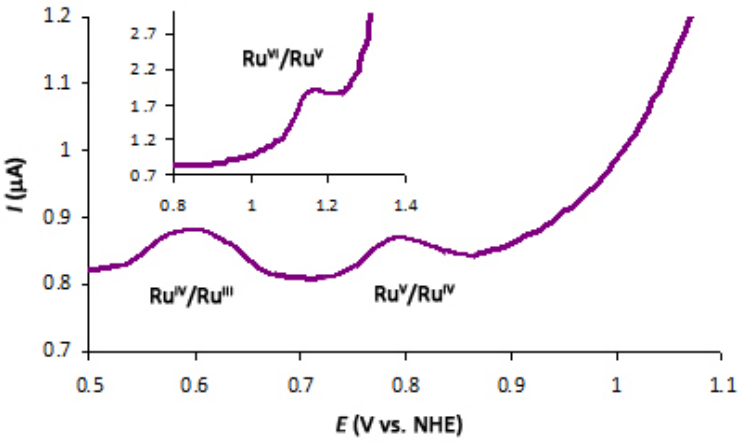


Figure S45. Differential pulse voltammogram of complex **2b** at pH 6.15. Conditions: Voltammogram was recorded in a Britton-Robinson buffer solution (0.1 M) containing complex **2b** (26 μM) with a scan rate of 0.1 V s^{-1}, using the $[Ru(bpy)_3]^{3+}/[Ru(bpy)_3]^{2+}$ couple as a standard ($E_{1/2}$ = 1.26 V vs. NHE).

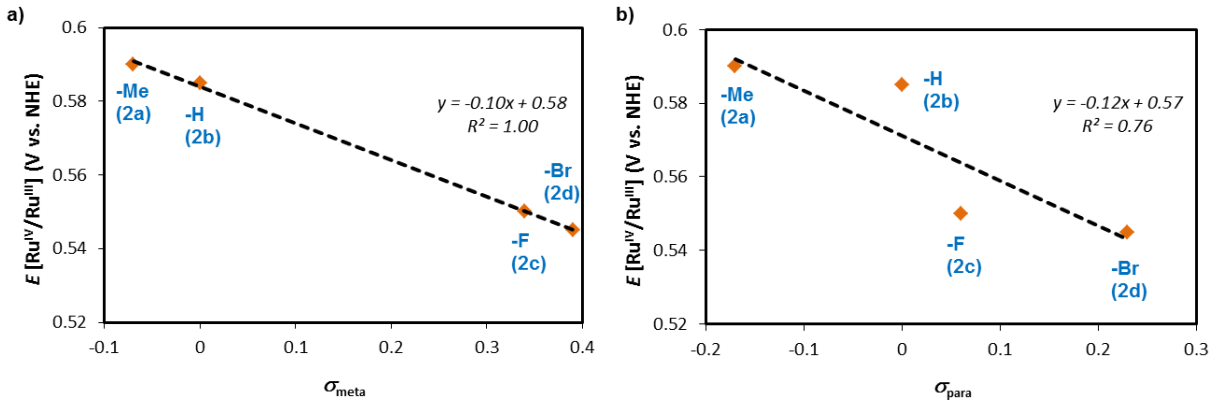


Figure S46. Hammett plots for the Ru^{IV}/Ru^{III} redox potentials for complexes **2a-d**.

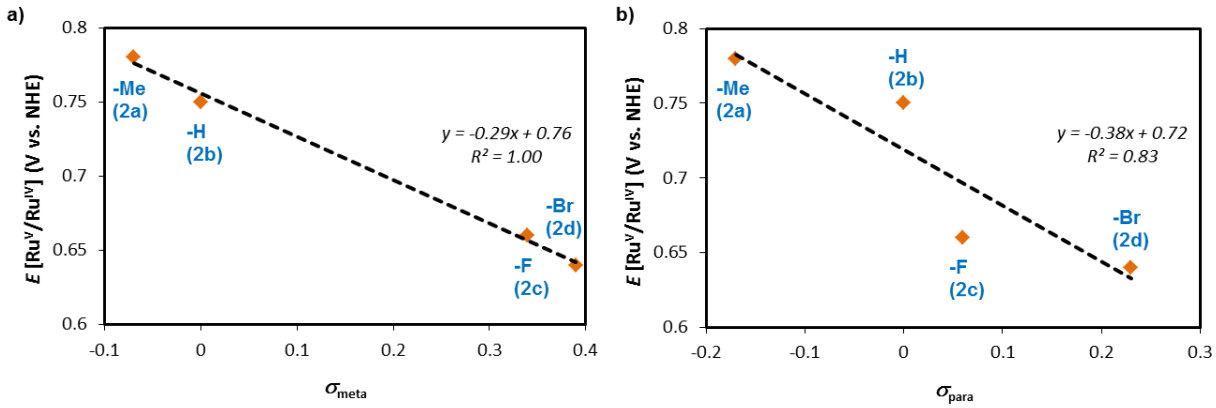


Figure S47. Hammett plots for the Ru^{V}/Ru^{IV} redox potentials for complexes **2a-d**.

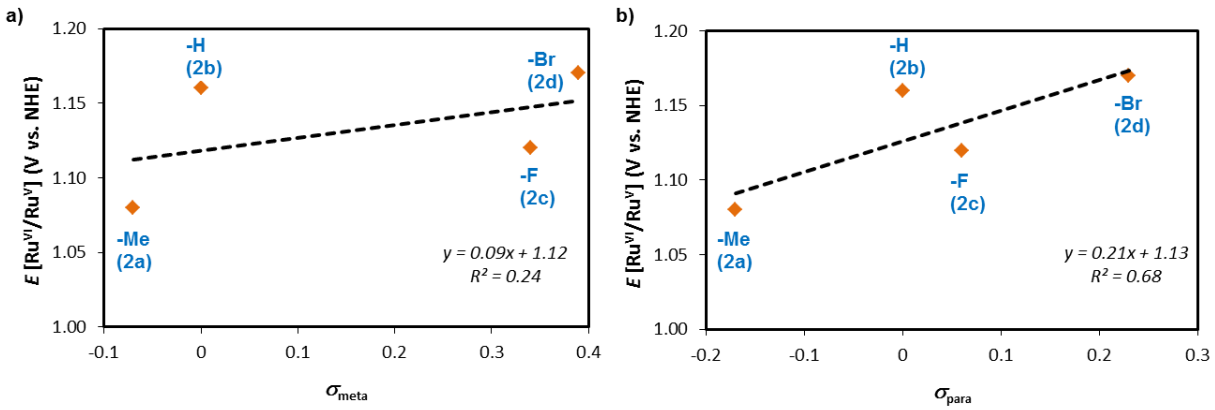


Figure S48. Hammett plots for the Ru^{VI}/Ru^{V} redox potentials for complexes **2a-d**.

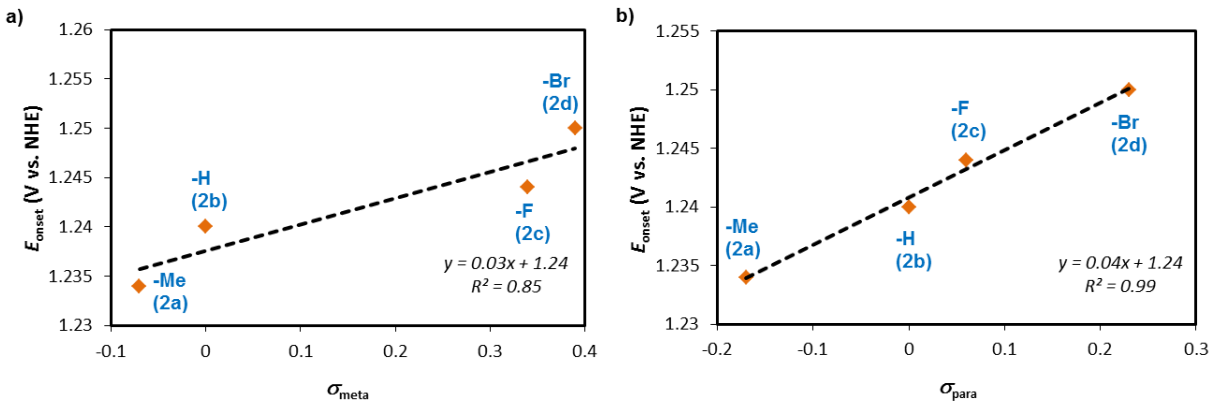


Figure S49. Hammett plots for the onset potentials for complexes **2a-d**.

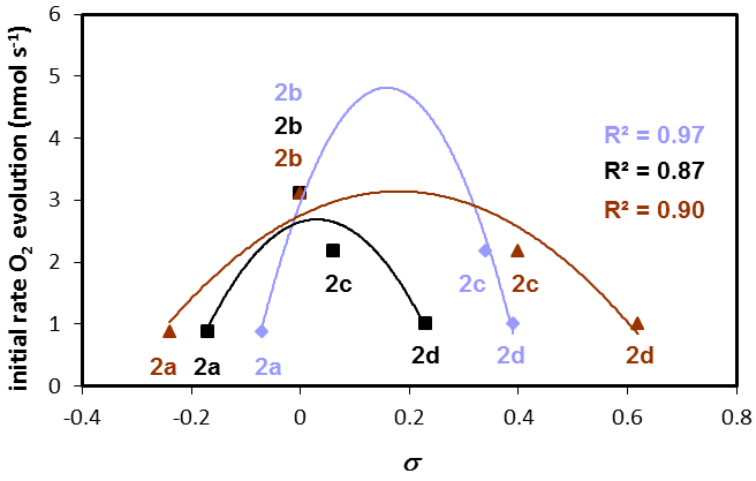


Figure S50. Plots of the initial rates as a function of the σ-parameters and fitting by a second-order polynomial function. σ_{meta} (◴), σ_{para} (■), σ_{sum} (▲).

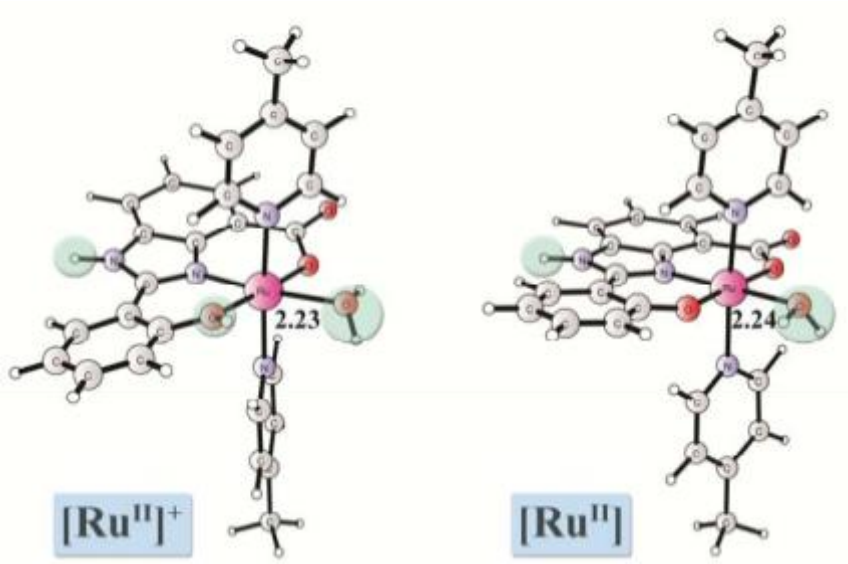


Figure S51. Optimized structures of the corresponding Ru^{II}-aqua complexes of Ru complex **2b** (left: total charge of +1, pK_a = –0.6; right: total charge of 0). Distances are given in Angstroms. The neutral Ru^{II}-aqua complex was found to be a closed-shell singlet in which the metal is coordinated to ligand **1b**, two 4-picoline molecules, and an aqua molecule. In the Ru^{II}-aqua complex, the ligand is dianionic (with a protonated imidazole), making the whole complex neutral. Under neutral conditions, a one-electron oxidation of the Ru^{II}-aqua complex occurs to generate the corresponding Ru^{III}-aqua complex **3b**.

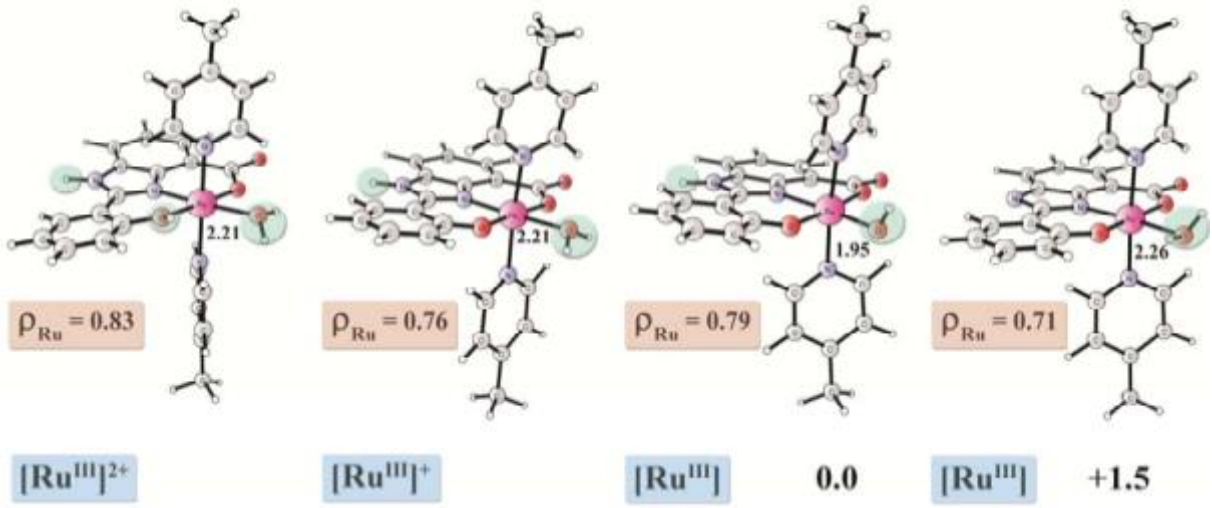


Figure S52. Optimized structures of the corresponding Ru^{III}-aqua/hydroxo complexes of Ru complex **2b** (left: total charge of +2, pK_a = –8.1; middle left: total charge of +1; middle right and right: total

charge of 0). Distances are given in Angstroms and spin densities are indicated for Ru. Relative energies are shown in kcal mol^{-1} for the neutral complexes (middle and right).

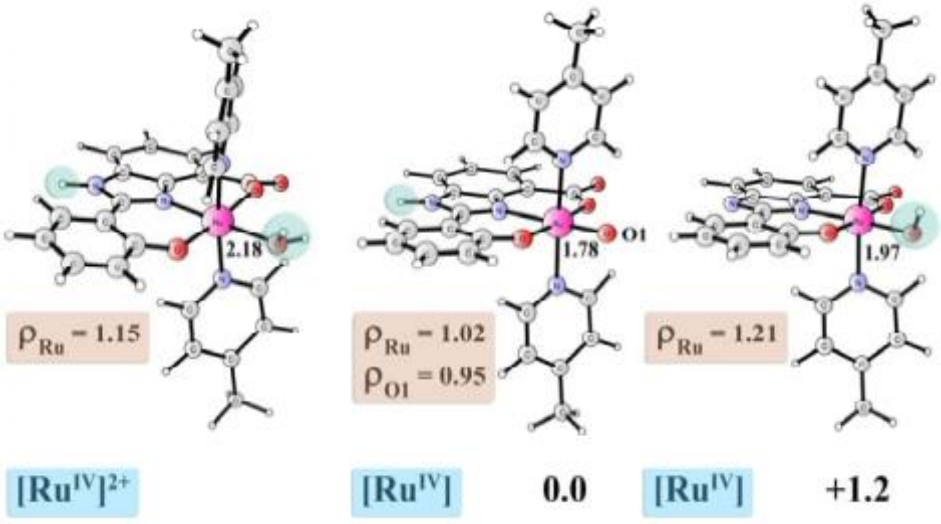


Figure S53. Optimized structures of the corresponding Ru^{IV}-aqua/hydroxo/oxo complexes of Ru complex **2b** (left: total charge of +2, pK_a = 1.1; middle and right: total charge of 0). Distances are given in Angstroms and spin densities are indicated for selected atoms. Relative energies are shown in kcal mol^{-1} for the neutral complexes (middle and right). It should be noted that isomer **4b'** houses an aqua ligand and the lowest triplet state lies at 5.2 kcal mol^{-1} relative to **4b**. In isomer **4b'**, the ligand can be considered as a radical cation, which ferromagnetically interacts with the low-spin Ru^{III} (S_{Ru} = 1/2) to form a triplet state, and the broken-symmetry singlet state was found to be 4.7 kcal mol^{-1} higher in energy.

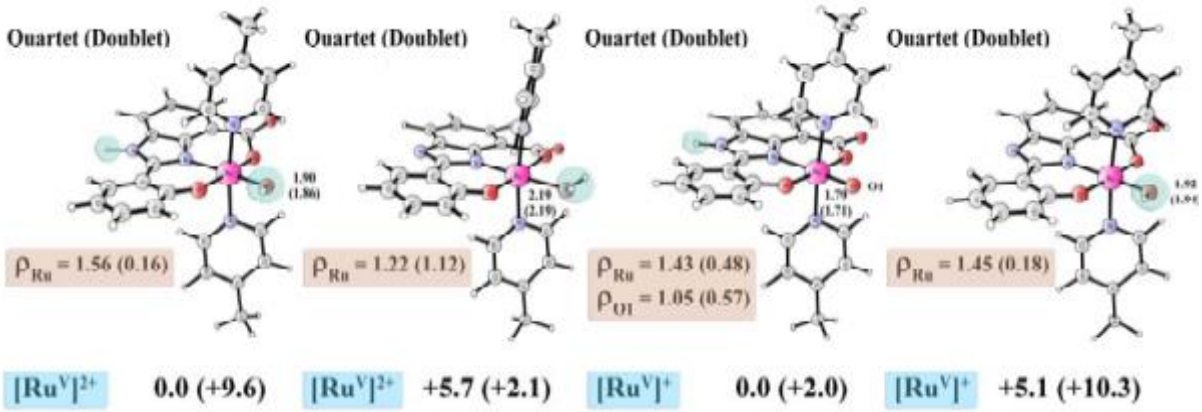


Figure S54. Optimized structures of the corresponding Ru^{V}-aqua/hydroxo/oxo complexes of Ru complex **2b** (left and middle left: total charge of +2, pK_a = –2.4; middle right and right: total charge of +1, pK_a = 6.3). Distances are given in Angstroms and spin densities are indicated for selected atoms. Relative energies are shown in kcal mol^{-1}.

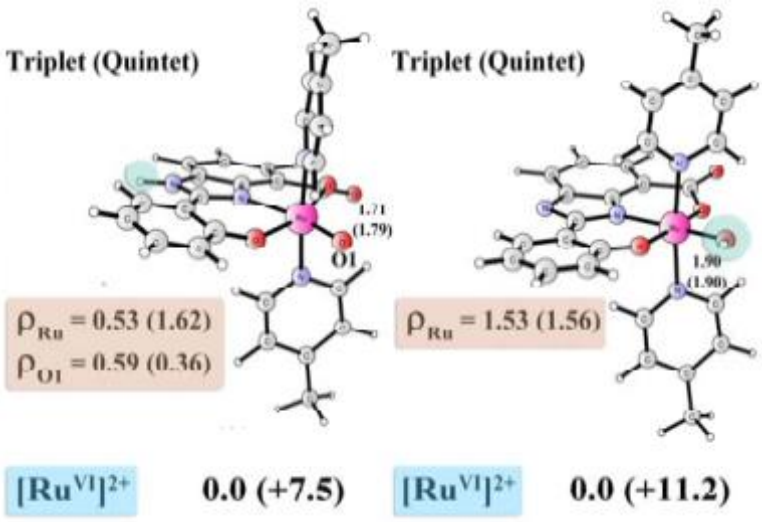


Figure S55. Optimized structures of the corresponding Ru^{VI}-hydroxo/oxo complexes of Ru complex **2b** (total charge of +2, pK_a = 1.3). Distances are given in Angstroms and spin densities are indicated for selected atoms. Relative energies are shown in kcal mol^{-1}.

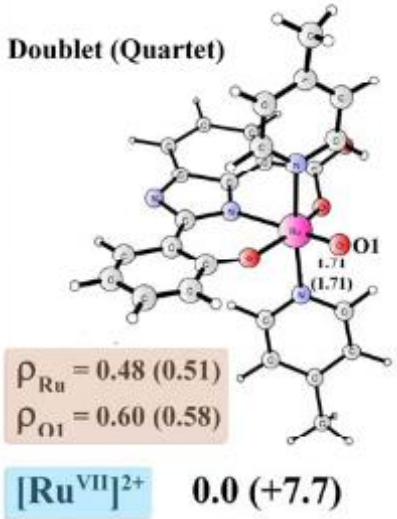


Figure S56. Optimized structure of the corresponding Ru^{VII}-oxo complex of Ru complex **2b** (total charge of +2). Distances are given in Angstroms and spin densities are indicated for selected atoms. Relative energies are shown in kcal mol^{-1}.

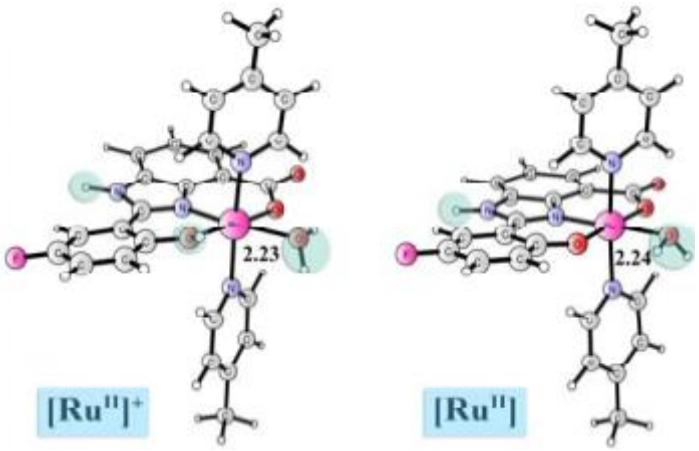


Figure S57. Optimized structures of the corresponding Ru^{II}-aqua complexes of Ru complex **2c** (left: total charge of +1, pK_a = 0.5; right: total charge of 0). Distances are given in Angstroms.

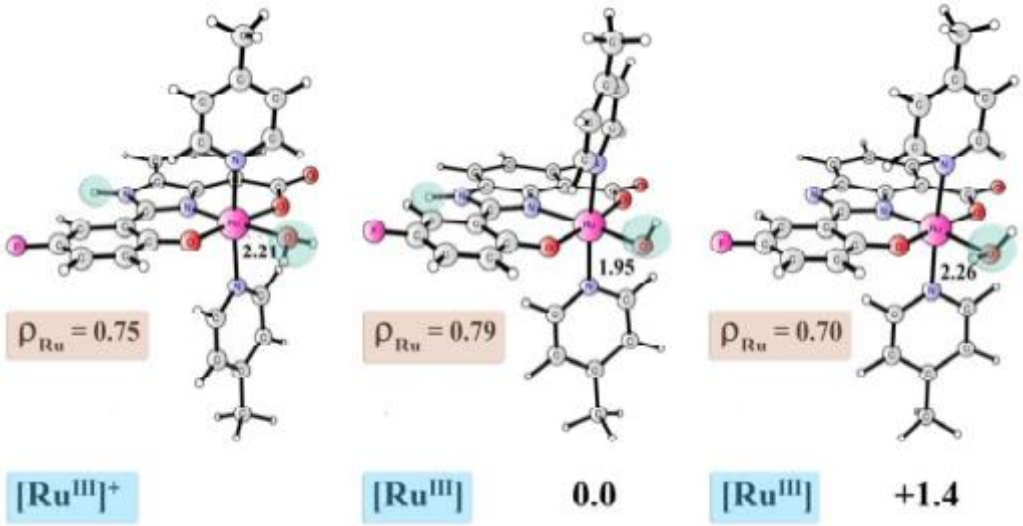


Figure S58. Optimized structures of the corresponding Ru^{III}-aqua/hydroxo complexes of Ru complex **2c** (left: total charge of +1, pK_a = 9.6; middle and right: total charge of 0). Distances are given in Angstroms and spin densities are indicated for Ru. Relative energies are shown in kcal mol^{-1} for the neutral complexes (middle and right).

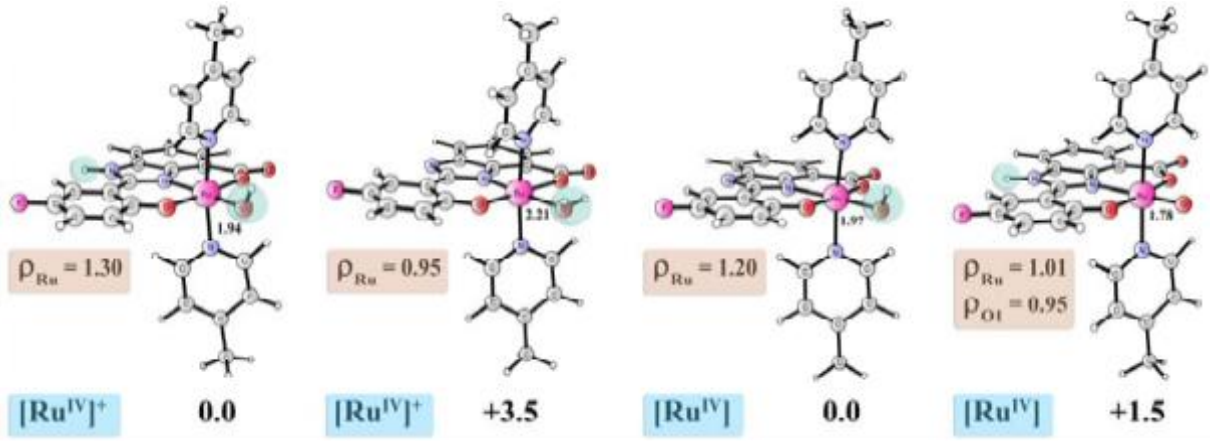


Figure S59. Optimized structures of the corresponding Ru^{IV}-aqua/hydroxo/oxo complexes of Ru complex **2c** (left (**4c**) and middle left (**4c'**): total charge of +1, pK_a = 6.0; middle right and right: total charge of 0). Distances are given in Angstroms and spin densities are indicated for selected atoms. Relative energies are shown in kcal mol^{-1}.

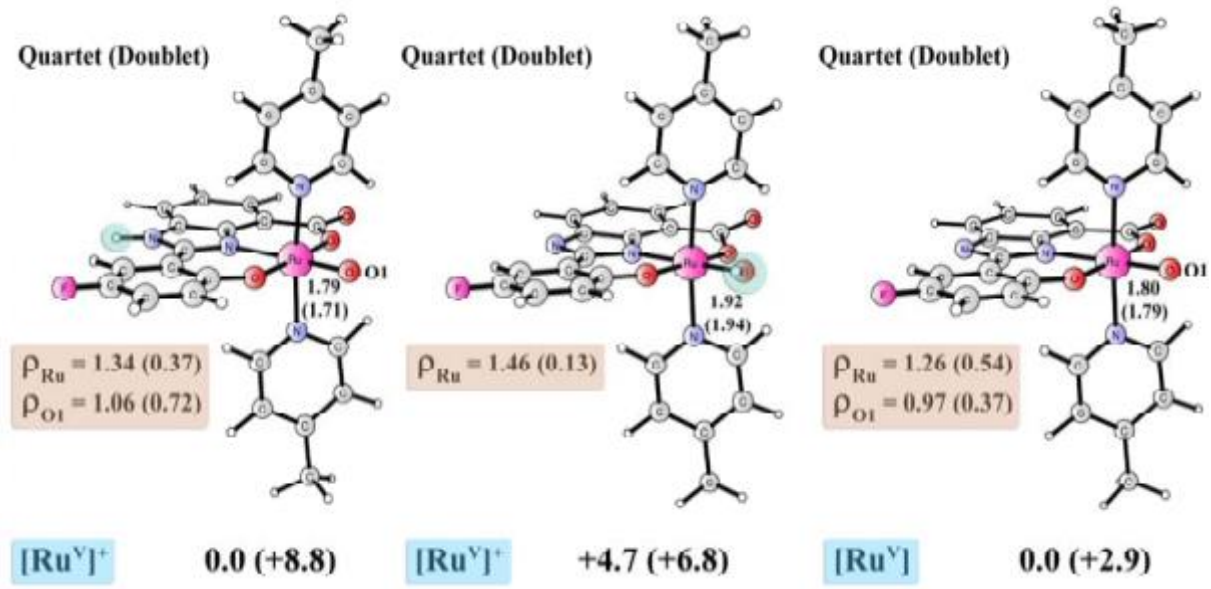


Figure S60. Optimized structures of the corresponding Ru^{V}-hydroxo/oxo complexes of Ru complex **2c** (left and middle: total charge of +1, pK_a = 6.0; right: total charge of 0). Distances are given in Angstroms and spin densities are indicated for selected atoms. Relative energies are shown in kcal mol^{-1}.

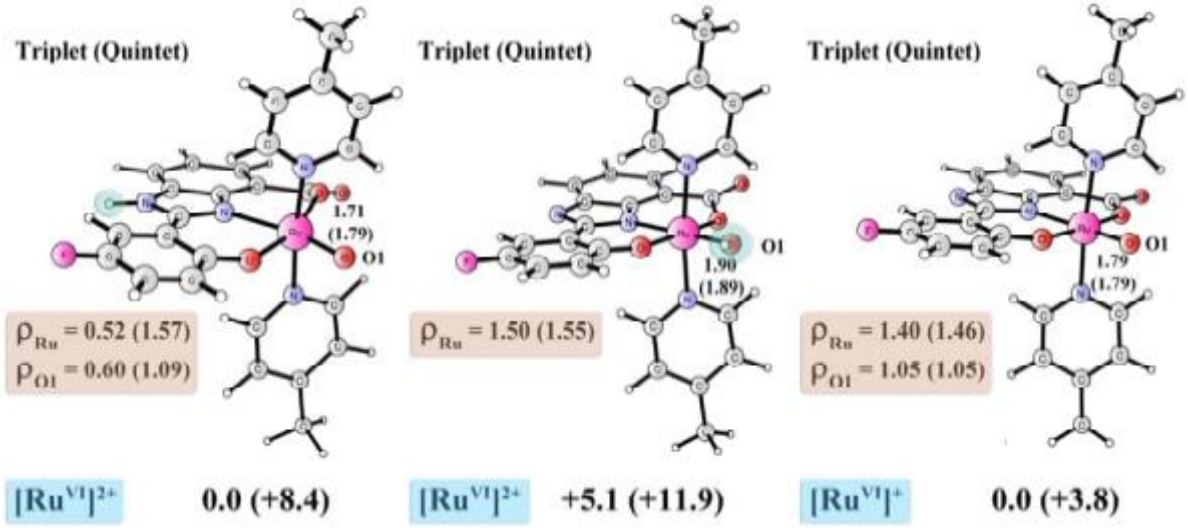


Figure S61. Optimized structures of the corresponding Ru^{VI}-hydroxo/oxo complexes of Ru complex **2c** (left and middle: total charge of +2, pK_a = 0.7; right: total charge of +1). Distances are given in Angstroms and spin densities are indicated for selected atoms. Relative energies are shown in kcal mol^{-1}.

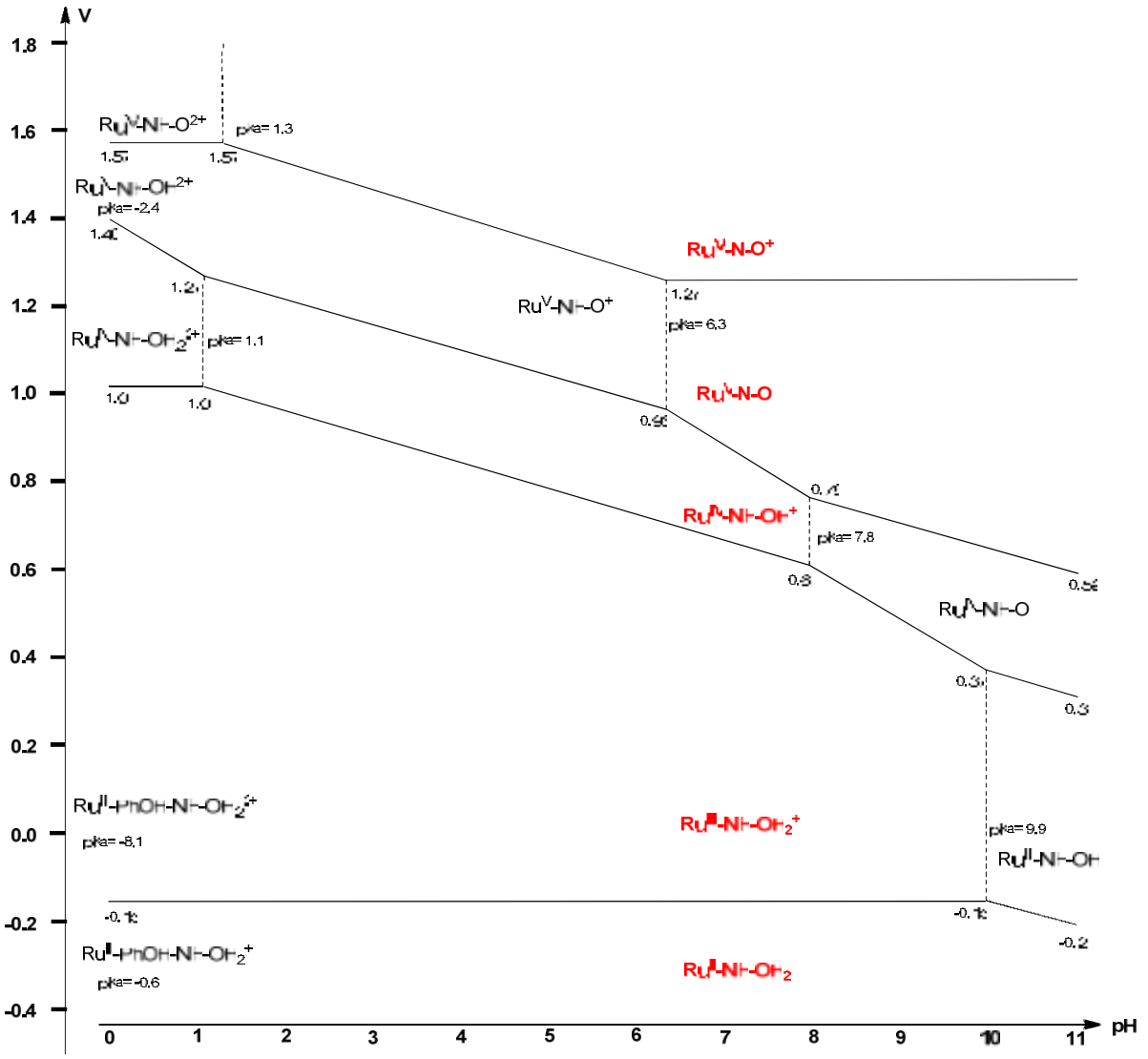


Figure S62. Calculated Pourbaix diagram (B3LYP*-D2 free energy) for Ru complex **2b** in the range 0 < pH < 11 (pK_a values are denoted by the vertical dashed lines). The relevant species at the working pH (7.2) are highlighted in red.

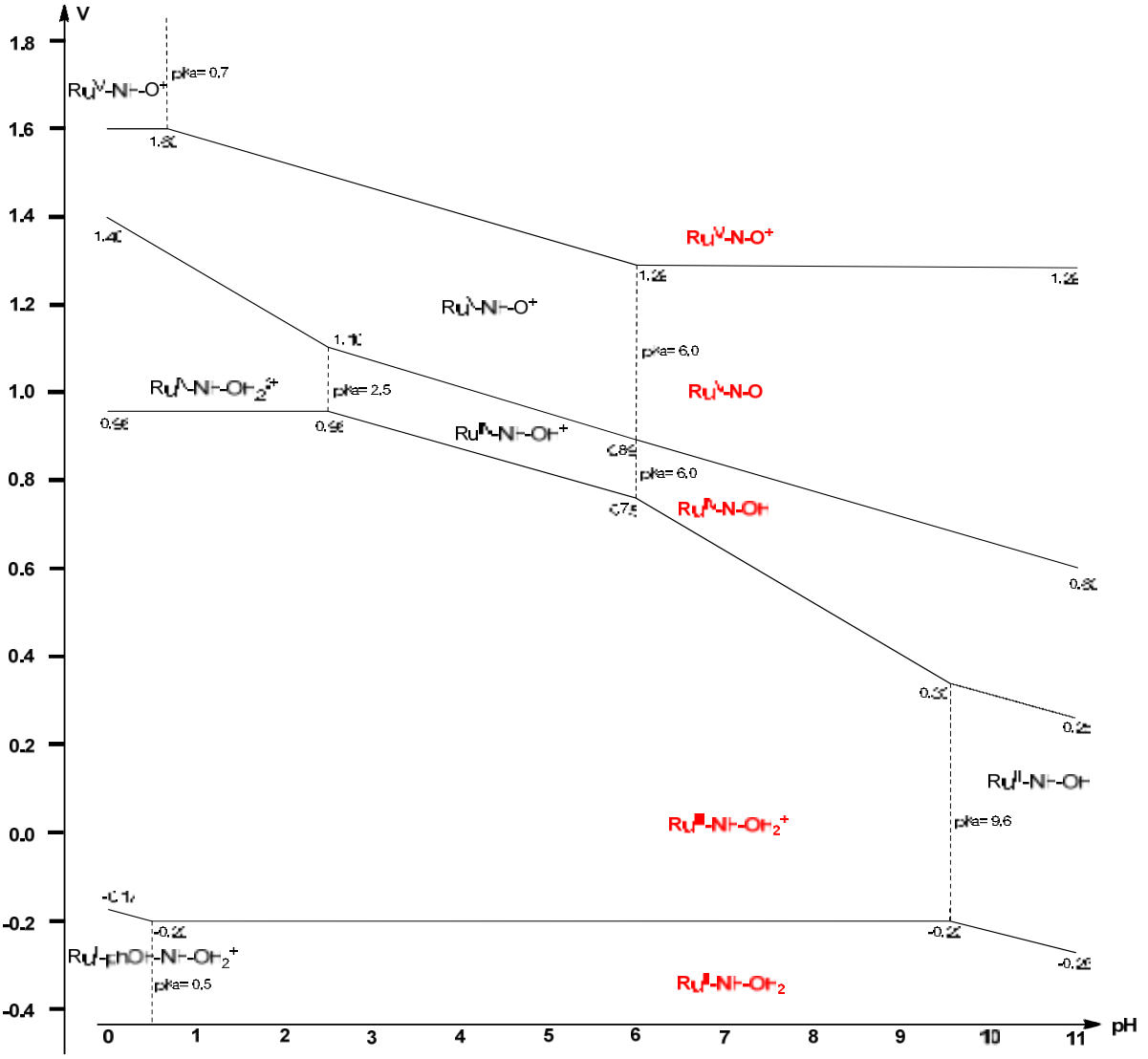


Figure S63. Calculated Pourbaix diagram (B3LYP*-D2 free energy) for Ru complex **2c** in the range 0 < pH < 11 (pK_a values are denoted by the vertical dashed lines). The relevant species at the working pH (7.2) are labeled in red.

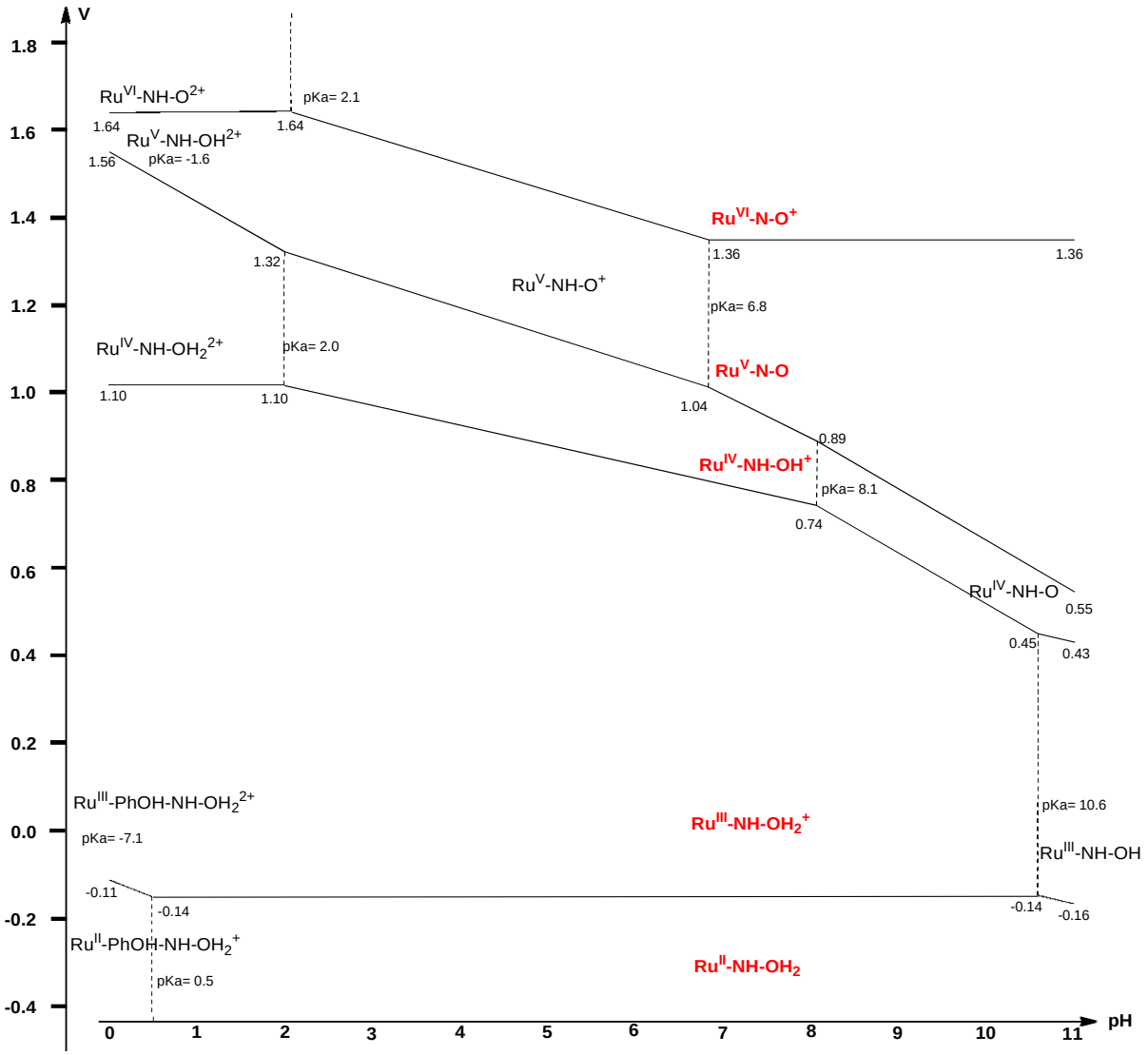


Figure S64. Calculated Pourbaix diagram (B3LYP-D2 free energy) for Ru complex **2b** in the range 0 < pH < 11 (pK_a values are denoted by the vertical dashed lines). The relevant species at the working pH (7.2) are labeled in red.

Table S1. Comparison of calculated (B3LYP*-D2 and B3LYP-D2) and experimental redox potentials at pH 7.2.

Redox couple	Complex **2b** **Potential (V vs. NHE)**			Complex **2c** **Potential (V vs. NHE)**		
	Calculated		**Experimental**[a]	**Calculated**		**Experimental**[a]
	B3LYP*-D2	B3LYP-D2		B3LYP*-D2	B3LYP-D2	

	D2	D2		D2	D2	
Ru^{IV}/Ru^{III}	0.65	0.79	0.585	0.61	0.79	0.55
Ru^{V}/Ru^{IV}	0.85	0.99	0.75	0.82	0.91	0.66
Ru^{VI}/Ru^{V}	1.27	1.36	1.16	1.29	1.34	1.12

[a] Electrochemical potentials were obtained from DPV in an aqueous phosphate buffer solution (0.1 M, pH 7.2). Conditions: Scan rate 0.1 V s^{-1}, glassy carbon disk as working electrode, a platinum spiral as counter electrode and a Ag/AgCl electrode as reference electrode. Potentials were converted to NHE by using the $[Ru(bpy)_3]^{3+}/[Ru(bpy)_3]^{2+}$ couple as a standard ($E_{1/2}$ = 1.26 V vs. NHE).

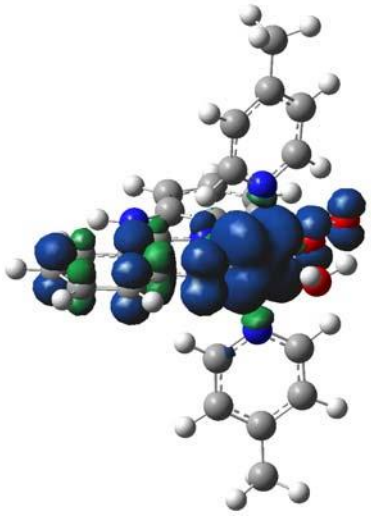


Figure S65. Spin isodensity of the doublet Ru^{III} state of complex **3b**.

Table S2. Calculated TDDFT doublet-doublet excitation wavelengths (λ), oscillator strengths (f) for Ru^{III} complexes **3a**, **3b** and **3c**. The nature of main transitions for complex **3b** is also shown.

	Complex 4a (CH3)		**Complex 4b (H)**			**Complex 4c (F)**	
	λ / nm	oscillator strength	λ / nm	oscillator strength	Nature of transition	λ / nm	oscillator strength
Excitation 1	3878.6	0	4023.0	0	126β→128β	3897.4	0
Excitation 2	2794.9	0.0002	2887.5	0.0001	127β→128β	2781.6	0.0002
Excitation 3	721.1	0.0548	679.8	0.0402	125β→128β	706.5	0.0481
Excitation 4	512.9	0.0460	505.1	0.0459	124β→128β	498.8	0.0370
Excitation 5	469.2	0.0045	469.5	0.0042	123β→128β	471.3	0.0045
Excitation 6	459.1	0.0001	459.0	0.0001	127β→135β	458.0	0.0001
Excitation 7	453.5	0	455.2	0	126β→135β	452.2	0
Excitation 8	435.9	0.0161	427.8	0.0114	128α→129α	440.9	0.0204
Excitation 9	411.1	0	410.1	0	126β→138β	411.8	0
Excitation 10	399.7	0.0223	394.6	0.0014	120β→128β	406.4	0.0169

Excitation 11	393.4	0.0003	394.3	0.0289	128α→129α	394.3	0.0004
Excitation 12	383.7	0.0005	383.7	0.0005	127β→135β	383.8	0.0023
Excitation 13	376.6	0.0060	376.0	0.0021	126β→129β	381.2	0.0031
Excitation 14	372.9	0.0050	372.3	0.0040	127β→138β	372.7	0.0041
Excitation 15	367.2	0.0086	368.7	0.0043	122β→128β	371.0	0.0025
Excitation 16	368.0	0.0019	367.6	0.0018	121β→128β	370.6	0.0007
Excitation 17	367.1	0.0025	366.7	0.0064	122β→128β	368.6	0.0004
Excitation 18	366.1	0.0011	366.0	0.0048	128α→133α	367.2	0.0048
Excitation 19	360.8	0.1164	358.1	0.0864	127β→129β	364.4	0.1202
Excitation 20	355.0	0.0058	353.2	0.0168	127β→130β	354.3	0.0152
Excitation 21	353.7	0.0186	351.0	0.0086	119β→128β	352.8	0.0448
Excitation 22	349.5	0.0247	348.3	0.0004	126α→129α	351.8	0.0251
Excitation 23	348.7	0.0144	345.8	0.0049	127β→131β	345.1	0.0022
Excitation 24	346.5	0.0034	344.8	0.0051	127β→131β	344.8	0.0010
Excitation 25	344.5	0.0156	341.7	0.0244	125β→129β	343.9	0.0080
Excitation 26	336.6	0.0462	335.2	0.0780	125β→129β	337.6	0.0610
Excitation 27	334.9	0.0134	331.9	0.0269	115β→128β	332.0	0.0211
Excitation 28	332.3	0.0109	329.5	0.0261	115β→128β	331.0	0.0068
Excitation 29	330.2	0.0200	328.1	0.0144	128α→130α	330.0	0.0112
Excitation 30	327.6	0.0116	326.5	0.0087	126β→130β	328.1	0.0035

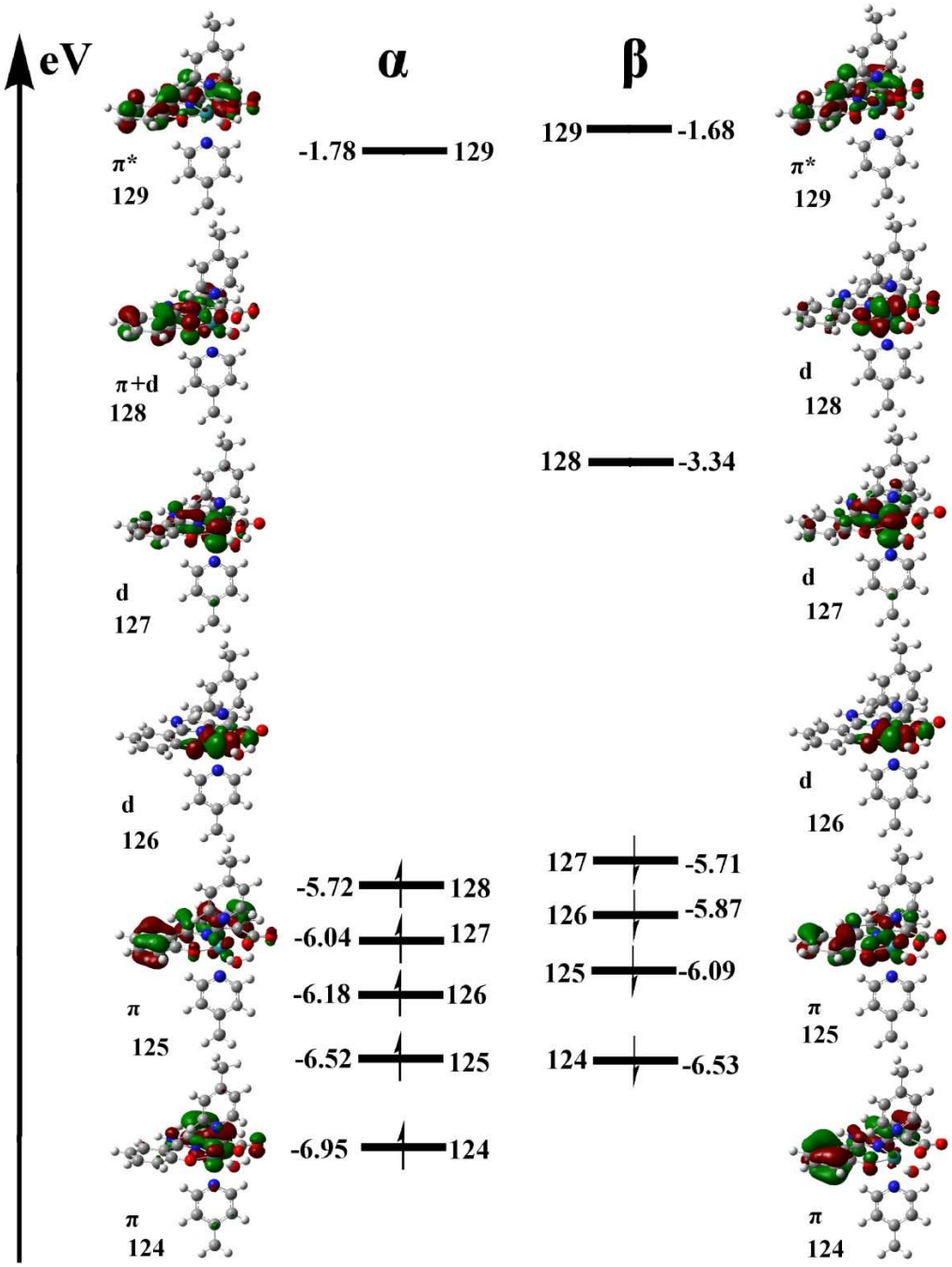


Figure S66. Schematic representation and isodensity surface plots of selected molecular orbitals for the doublet Ru^{III} complex **3b**. Energy levels of both α and β orbitals are given in eV.

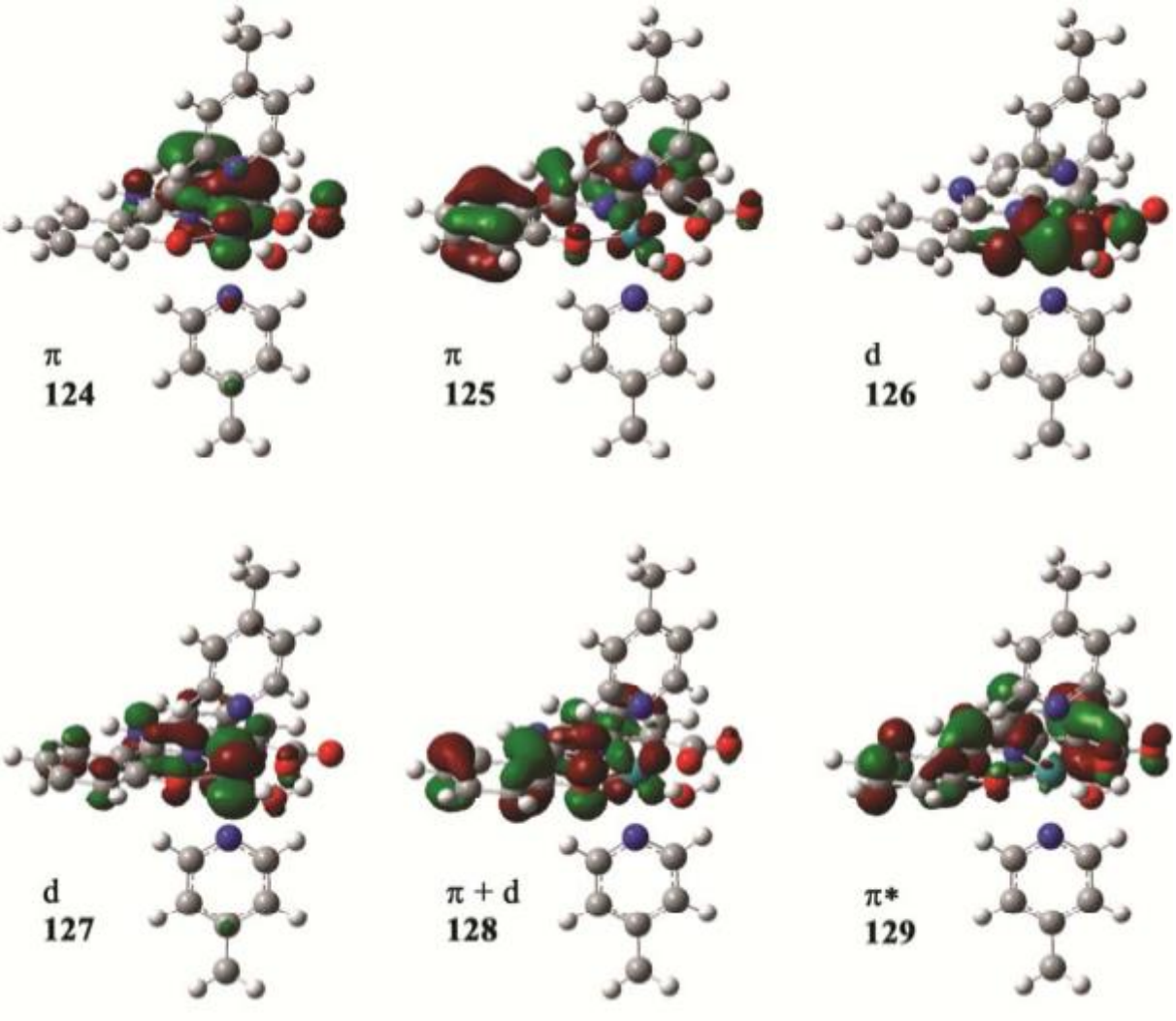


Figure S67. Schematic representation of selected α orbitals for Ru^{III} complex **3b**.

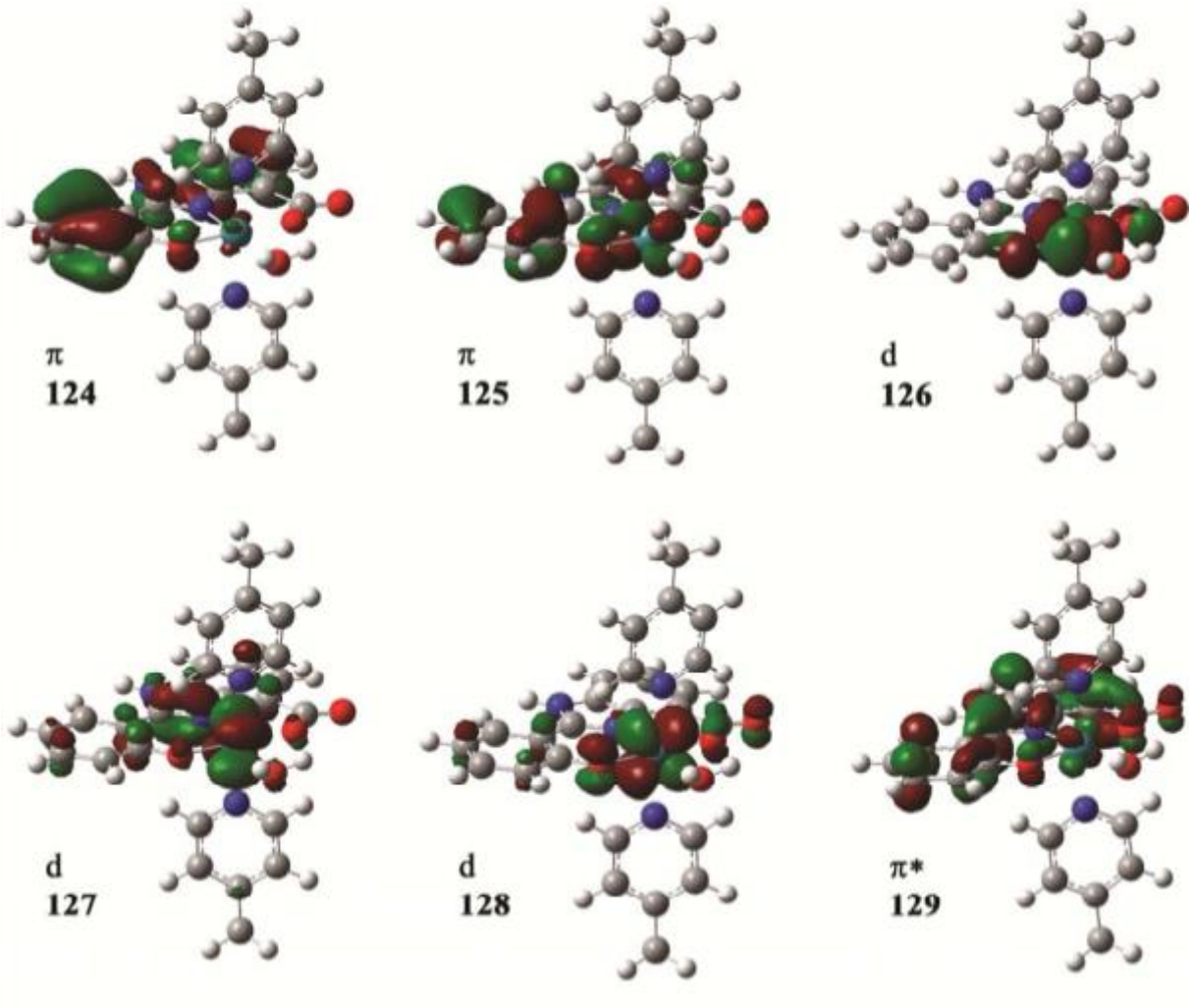


Figure S68. Schematic representation of selected β orbitals for Ru^{III} complex **3b**.

Table S3. Cartesian coordinates for the corresponding protonated Ru^{II}-aqua complex of Ru complex **2b** ($[Ru^{II}]^{+}$, singlet).

Center number	Atomic number	Atomic type	Coordinates (Angstroms)		
			X	Y	Z
1	44	0	-0.015831	-0.27247	-0.949551
2	8	0	-0.560124	-2.217192	-0.674718
3	8	0	-1.716322	-3.85076	0.305542
4	8	0	0.514484	1.874262	-1.183979
5	7	0	-0.049147	0.164595	1.005318
6	7	0	0.046296	1.082277	3.016207
7	6	0	-1.168727	-2.759739	0.365927
8	6	0	-1.130628	-2.020362	1.691252
9	6	0	-1.633628	-2.663489	2.823733
10	6	0	-1.601878	-2.074592	4.10145
11	6	0	-1.058892	-0.809898	4.315464
12	6	0	-0.555058	-0.155101	3.190969

13	6	0	-0.596387	-0.735099	1.907053
14	6	0	0.337433	1.245863	1.681229
15	6	0	1.001143	2.429858	1.135779
16	6	0	1.61377	3.348465	2.015266
17	6	0	2.224687	4.51279	1.568877
18	6	0	2.251991	4.797992	0.202732
19	6	0	1.679958	3.902727	-0.696856
20	6	0	1.067187	2.736051	-0.242979
21	6	0	2.412734	-1.973381	-0.230987
22	6	0	3.72981	-2.410603	-0.18776
23	6	0	4.740579	-1.685548	-0.832413
24	6	0	4.339708	-0.524548	-1.506473
25	6	0	3.004166	-0.144251	-1.504473
26	7	0	2.034338	-0.847147	-0.878324
27	8	0	-0.119588	-1.134876	-3.007007
28	6	0	-2.95876	-0.633163	-1.642023
29	6	0	-4.309495	-0.347858	-1.783294
30	6	0	-4.82195	0.885288	-1.360535
31	6	0	-3.90341	1.777702	-0.79394
32	6	0	-2.564662	1.425784	-0.683817
33	7	0	-2.074567	0.239481	-1.105564
34	1	0	-2.051586	-3.654373	2.684603
35	1	0	-2.006358	-2.62484	4.944794
36	1	0	-1.030534	-0.36322	5.303897
37	1	0	1.631631	3.132488	3.078423
38	1	0	2.724633	5.702461	-0.165078
39	1	0	1.710423	4.108132	-1.7647
40	1	0	2.682651	5.189735	2.281649
41	1	0	1.61522	-2.53668	0.234744
42	1	0	3.960182	-3.327418	0.346029
43	1	0	5.063716	0.086698	-2.036183
44	1	0	2.683866	0.756699	-2.016147
45	1	0	-2.560096	-1.593782	-1.940931
46	1	0	-4.960291	-1.099988	-2.218108
47	1	0	-4.226213	2.748745	-0.431509
48	1	0	-1.849914	2.108583	-0.239979
49	1	0	0.145456	1.789577	3.726733
50	1	0	0.731896	-1.230087	-3.45637
51	1	0	-0.336252	-2.024711	-2.656208
52	6	0	-6.277615	1.231946	-1.519816
53	1	0	-6.558747	2.085525	-0.898494
54	1	0	-6.498515	1.49051	-2.562271
55	1	0	-6.917048	0.384759	-1.255205
56	6	0	6.179746	-2.123079	-0.786746
57	1	0	6.64054	-1.823759	0.162321
58	1	0	6.266506	-3.210823	-0.85943
59	1	0	6.763013	-1.673663	-1.594
60	1	0	0.415392	2.319661	-2.0362

Table S4. Cartesian coordinates for the corresponding Ru^{II}-aqua complex of Ru

complex **2b** (Ru^{II}, singlet).

Center number	Atomic number	Atomic type	Coordinates (Angstroms)		
			X	Y	Z
1	44	0	0.001478	-0.126447	-0.948476
2	8	0	-0.046285	-2.225216	-0.919034
3	8	0	-0.130802	-4.282789	-0.05456
4	8	0	0.055289	1.95501	-1.074573
5	7	0	0.000988	-0.032159	1.03493
6	7	0	0.000026	0.674305	3.126918
7	6	0	-0.098041	-3.058683	0.0856
8	6	0	-0.100674	-2.506669	1.505062
9	6	0	-0.148826	-3.400354	2.581372
10	6	0	-0.14738	-2.96837	3.916731
11	6	0	-0.097702	-1.612257	4.253001
12	6	0	-0.049771	-0.711691	3.192247
13	6	0	-0.049521	-1.145987	1.849657
14	6	0	0.025058	1.06196	1.798955
15	6	0	0.053291	2.439112	1.335615
16	6	0	0.069445	3.481306	2.296089
17	6	0	0.087809	4.819146	1.952072
18	6	0	0.089498	5.165959	0.588365
19	6	0	0.074227	4.184286	-0.380943
20	6	0	0.057537	2.79162	-0.069309
21	6	0	2.764334	-1.382326	-1.216099
22	6	0	4.148243	-1.493567	-1.268954
23	6	0	4.957012	-0.362847	-1.102783
24	6	0	4.292813	0.852934	-0.90147
25	6	0	2.904461	0.895753	-0.863108
26	7	0	2.130937	-0.202771	-1.011785
27	8	0	-0.053808	-0.084496	-3.187306
28	6	0	-2.73046	-1.148387	-1.612017
29	6	0	-4.113533	-1.216139	-1.715487
30	6	0	-4.914473	-0.206962	-1.167187
31	6	0	-4.245881	0.84034	-0.52326
32	6	0	-2.857731	0.850113	-0.459193
33	7	0	-2.094613	-0.126314	-0.99486
34	1	0	-0.187579	-4.456452	2.338181
35	1	0	-0.186558	-3.706836	4.712168
36	1	0	-0.098222	-1.283731	5.287983
37	1	0	0.068332	3.230862	3.354281
38	1	0	0.101749	6.212251	0.293593
39	1	0	0.072864	4.440106	-1.436468
40	1	0	0.100252	5.584067	2.721519
41	1	0	2.112074	-2.241707	-1.328383
42	1	0	4.589677	-2.471618	-1.436997
43	1	0	4.851857	1.775562	-0.774648
44	1	0	2.370517	1.827171	-0.725596
45	1	0	-2.084664	-1.927581	-1.999294
46	1	0	-4.561496	-2.067831	-2.218852
47	1	0	-4.800594	1.655671	-0.068162
48	1	0	-2.326855	1.65822	0.028163
49	1	0	0.007621	1.299035	3.914738
50	1	0	0.684128	-0.59353	-3.550351

51	1	0	0.146414	0.851797	-3.342473
52	6	0	-6.41664	-0.237833	-1.283617
53	1	0	-6.892293	0.332355	-0.480713
54	1	0	-6.741964	0.200729	-2.235286
55	1	0	-6.797795	-1.262713	-1.251099
56	6	0	6.460826	-0.454155	-1.115448
57	1	0	6.843834	-0.659544	-0.108098
58	1	0	6.806979	-1.262728	-1.765635
59	1	0	6.916641	0.480811	-1.453617

Table S5. Cartesian coordinates for protonated **3b** ($[Ru^{III}]^{2+}$, doublet).

Center number	Atomic number	Atomic type	Coordinates (Angstroms)		
			X	Y	Z
1	44	0	-0.033946	-0.228236	-0.953266
2	8	0	-0.447309	-2.110933	-0.885015
3	8	0	-1.248831	-4.007535	-0.071297
4	8	0	0.350026	1.899936	-1.031374
5	7	0	-0.044773	0.026077	1.043196
6	7	0	0.051709	0.760454	3.115924
7	6	0	-0.874567	-2.881649	0.161802
8	6	0	-0.843902	-2.315563	1.545573
9	6	0	-1.207032	-3.128866	2.622574
10	6	0	-1.170398	-2.663338	3.951208
11	6	0	-0.764103	-1.369318	4.269515
12	6	0	-0.399935	-0.550505	3.197848
13	6	0	-0.447567	-1.0059	1.868836
14	6	0	0.264641	1.081892	1.803987
15	6	0	0.765857	2.374906	1.339353
16	6	0	1.252709	3.312129	2.276792
17	6	0	1.710487	4.567327	1.899419
18	6	0	1.704815	4.93097	0.551429
19	6	0	1.251963	4.024523	-0.405107
20	6	0	0.793514	2.771258	-0.015122
21	6	0	2.600762	-1.548147	-0.129753
22	6	0	3.946724	-1.878062	-0.159638
23	6	0	4.820358	-1.224841	-1.043163
24	6	0	4.253734	-0.241762	-1.870523
25	6	0	2.897867	0.034653	-1.794808
26	7	0	2.066448	-0.603921	-0.938927
27	8	0	-0.093765	-0.775051	-3.096652
28	6	0	-2.934637	-0.546793	-1.823703
29	6	0	-4.294311	-0.304743	-1.934431
30	6	0	-4.885477	0.762992	-1.241644
31	6	0	-4.030289	1.537604	-0.442213
32	6	0	-2.679629	1.237156	-0.36705
33	7	0	-2.119974	0.212736	-1.052397
34	1	0	-1.517954	-4.146068	2.41019
35	1	0	-1.462271	-3.336015	4.750414
36	1	0	-0.73315	-1.023854	5.297366
37	1	0	1.290757	3.048544	3.328293

38	1	0	2.058744	5.907976	0.240501
39	1	0	1.259259	4.296289	-1.458245
40	1	0	2.074594	5.257339	2.65242
41	1	0	1.918871	-2.054281	0.541568
42	1	0	4.310646	-2.655083	0.50484
43	1	0	4.866142	0.304491	-2.580488
44	1	0	2.453936	0.795343	-2.42872
45	1	0	-2.47669	-1.377322	-2.343546
46	1	0	-4.892031	-0.958653	-2.56107
47	1	0	-4.416497	2.373828	0.131437
48	1	0	-2.018153	1.825031	0.25677
49	1	0	0.157708	1.390035	3.897881
50	1	0	0.64825	-0.603623	-3.694847
51	1	0	-0.182884	-1.745354	-3.041327
52	6	0	-6.350373	1.067124	-1.363114
53	1	0	-6.714787	1.647271	-0.512667
54	1	0	-6.536015	1.655323	-2.27052
55	1	0	-6.941254	0.151258	-1.445634
56	6	0	6.285349	-1.549697	-1.086738
57	1	0	6.809595	-1.026224	-0.277511
58	1	0	6.458954	-2.619617	-0.944947
59	1	0	6.740182	-1.24067	-2.030157
60	1	0	0.183453	2.397565	-1.84614

Table S6. Cartesian coordinates for **3b** ($[Ru^{III}]^{+}$, doublet).

Center number	Atomic number	Atomic type	Coordinates (Angstroms) X	Y	Z
1	44	0	-0.004719	-0.124015	-0.933177
2	8	0	0.060303	-2.137015	-0.93042
3	8	0	0.273832	-4.190625	-0.108174
4	8	0	-0.099709	1.864438	-1.062358
5	7	0	0.005842	0.00516	1.051823
6	7	0	-0.004786	0.708609	3.13698
7	6	0	0.178481	-2.991266	0.091294
8	6	0	0.169131	-2.46451	1.506604
9	6	0	0.247301	-3.364016	2.573403
10	6	0	0.238225	-2.934119	3.91264
11	6	0	0.153473	-1.584562	4.256827
12	6	0	0.077376	-0.677768	3.200048
13	6	0	0.082801	-1.108774	1.860132
14	6	0	-0.042552	1.095731	1.819318
15	6	0	-0.103664	2.46159	1.330705
16	6	0	-0.142539	3.533916	2.249895
17	6	0	-0.187779	4.854526	1.836913
18	6	0	-0.194087	5.144407	0.464078
19	6	0	-0.159012	4.118204	-0.465028
20	6	0	-0.115409	2.760008	-0.073194
21	6	0	2.776677	-1.139847	-1.577123
22	6	0	4.159258	-1.166538	-1.688438
23	6	0	4.9317	-0.11588	-1.1768

24	6	0	4.233888	0.933717	-0.565066
25	6	0	2.84915	0.899916	-0.483759
26	7	0	2.119188	-0.120239	-0.981842
27	8	0	0.051996	-0.336681	-3.129218
28	6	0	-2.792027	-1.453746	-1.069159
29	6	0	-4.174337	-1.571272	-1.110157
30	6	0	-4.985905	-0.430354	-1.068046
31	6	0	-4.32301	0.80188	-1.000195
32	6	0	-2.936468	0.852226	-0.964224
33	7	0	-2.164755	-0.2575	-0.990694
34	1	0	0.316469	-4.419752	2.336044
35	1	0	0.30034	-3.675126	4.702771
36	1	0	0.14977	-1.264604	5.293578
37	1	0	-0.137835	3.329301	3.316704
38	1	0	-0.226726	6.175453	0.125629
39	1	0	-0.162102	4.324031	-1.530448
40	1	0	-0.217062	5.653168	2.570002
41	1	0	2.161269	-1.948346	-1.951472
42	1	0	4.628731	-2.014023	-2.177413
43	1	0	4.763945	1.785766	-0.151662
44	1	0	2.29996	1.709904	-0.021863
45	1	0	-2.149633	-2.324214	-1.109327
46	1	0	-4.612142	-2.562247	-1.176874
47	1	0	-4.88203	1.732047	-0.97892
48	1	0	-2.410248	1.796458	-0.927263
49	1	0	-0.44428	0.337174	-3.614876
50	1	0	-0.293766	-1.203877	-3.391081
51	6	0	-6.48692	-0.525551	-1.076397
52	1	0	-6.864215	-0.638931	-0.052771
53	1	0	-6.944087	0.373467	-1.497054
54	1	0	-6.829121	-1.392486	-1.647393
55	6	0	6.433695	-0.126586	-1.258743
56	1	0	6.856795	-0.649047	-0.392139
57	1	0	6.7806	-0.647657	-2.154734
58	1	0	6.842219	0.88697	-1.263489
59	1	0	-0.023687	1.332065	3.928173

Table S7. Cartesian coordinates for neutral **3b** ([Ru^{III}], doublet).

Center number	Atomic number	Atomic type	Coordinates (Angstroms) X	Y	Z
1	44	0	-0.057714	-0.195952	-0.968383
2	8	0	0.28162	-2.200065	-0.690545
3	8	0	1.060416	-4.10924	0.156642
4	8	0	-0.398433	1.835441	-1.008513
5	7	0	0.052306	0.028548	1.119271
6	7	0	0.111815	0.838117	3.179123
7	6	0	0.727849	-2.935825	0.299774
8	6	0	0.776897	-2.324092	1.680931
9	6	0	1.15622	-3.115983	2.769902
10	6	0	1.197693	-2.613571	4.078988

11	6	0	0.861896	-1.287934	4.366206
12	6	0	0.488078	-0.492549	3.286394
13	6	0	0.442758	-0.992846	1.967835
14	6	0	-0.133619	1.126734	1.853219
15	6	0	-0.501333	2.437422	1.360471
16	6	0	-0.760637	3.486322	2.275894
17	6	0	-1.068371	4.768058	1.863492
18	6	0	-1.122505	5.04046	0.483092
19	6	0	-0.886294	4.042258	-0.439992
20	6	0	-0.580855	2.704963	-0.049964
21	6	0	2.704263	-0.794104	-1.902616
22	6	0	4.067092	-0.660281	-2.135786
23	6	0	4.771669	0.42393	-1.600773
24	6	0	4.037944	1.336038	-0.833104
25	6	0	2.676302	1.143152	-0.637503
26	7	0	2.01286	0.093817	-1.158562
27	8	0	-0.032505	-0.364429	-2.915132
28	6	0	-2.644064	-1.818684	-0.857743
29	6	0	-4.003318	-2.105546	-0.887712
30	6	0	-4.939284	-1.0767	-1.042825
31	6	0	-4.42898	0.220481	-1.17087
32	6	0	-3.057546	0.43919	-1.13232
33	7	0	-2.166094	-0.560033	-0.964202
34	1	0	1.417332	-4.147378	2.560189
35	1	0	1.497441	-3.269881	4.890413
36	1	0	0.895715	-0.901233	5.380105
37	1	0	-0.738841	3.280956	3.343675
38	1	0	-1.356656	6.044284	0.138225
39	1	0	-0.927147	4.237518	-1.507017
40	1	0	-1.267711	5.546998	2.591865
41	1	0	2.124963	-1.615891	-2.304416
42	1	0	4.57334	-1.409121	-2.737134
43	1	0	4.520152	2.200617	-0.38722
44	1	0	2.086593	1.841889	-0.057113
45	1	0	-1.891616	-2.592529	-0.758854
46	1	0	-4.324675	-3.138272	-0.791945
47	1	0	-5.094546	1.068272	-1.303158
48	1	0	-2.631145	1.428317	-1.244471
49	1	0	0.110913	1.512817	3.925619
50	1	0	-0.92241	-0.535164	-3.255699
51	6	0	6.243912	0.613086	-1.86212
52	1	0	6.402911	1.099315	-2.832312
53	1	0	6.70948	1.241383	-1.098037
54	1	0	6.76939	-0.345921	-1.888953
55	6	0	-6.419192	-1.354101	-1.104838
56	1	0	-6.998829	-0.521006	-0.697296
57	1	0	-6.740736	-1.499568	-2.143387
58	1	0	-6.678937	-2.260582	-0.551468

Table S8. Cartesian coordinates for **3b'** ([Ru^{III}], doublet).

			Coordinates (Angstroms)		
Center	**Atomic**	**Atomic**	**X**	**Y**	**Z**

number	number	type			
1	44	0	-0.000402	-0.126642	-0.963281
2	8	0	-0.011979	-2.154349	-0.90564
3	8	0	0.013613	-4.194708	-0.027923
4	8	0	-0.024812	1.856704	-1.157858
5	7	0	-0.002771	0.029674	0.999439
6	7	0	-0.005767	0.869555	3.103062
7	6	0	0.007439	-2.981444	0.148589
8	6	0	0.002936	-2.413102	1.540568
9	6	0	0.00542	-3.264838	2.64937
10	6	0	-0.001234	-2.764183	3.967876
11	6	0	-0.008414	-1.397049	4.243645
12	6	0	-0.00951	-0.505777	3.158795
13	6	0	-0.006771	-1.03847	1.837234
14	6	0	-0.001662	1.146893	1.791467
15	6	0	0.024771	2.497622	1.225612
16	6	0	0.060272	3.58517	2.122633
17	6	0	0.095801	4.901026	1.685657
18	6	0	0.096313	5.172965	0.309686
19	6	0	0.059655	4.127774	-0.600343
20	6	0	0.023733	2.778271	-0.179813
21	6	0	2.721067	-1.201611	-1.654746
22	6	0	4.101887	-1.331575	-1.688667
23	6	0	4.912648	-0.427124	-0.990813
24	6	0	4.259439	0.587476	-0.282484
25	6	0	2.872132	0.660955	-0.285086
26	7	0	2.10754	-0.216546	-0.964865
27	8	0	0.058408	-0.086004	-3.222669
28	6	0	-2.776205	-1.348019	-1.340796
29	6	0	-4.160726	-1.454173	-1.342303
30	6	0	-4.953552	-0.366521	-0.956035
31	6	0	-4.277337	0.802382	-0.587896
32	6	0	-2.88945	0.846301	-0.611438
33	7	0	-2.137991	-0.210497	-0.985987
34	1	0	0.0126	-4.334085	2.466174
35	1	0	0.00023	-3.471026	4.793142
36	1	0	-0.011478	-1.026936	5.264767
37	1	0	0.059821	3.345262	3.18071
38	1	0	0.12534	6.198693	-0.047834
39	1	0	0.058533	4.31396	-1.670404
40	1	0	0.123658	5.712757	2.406372
41	1	0	2.065756	-1.899395	-2.161611
42	1	0	4.53959	-2.146495	-2.256799
43	1	0	4.82355	1.322866	0.282411
44	1	0	2.349699	1.430952	0.268245
45	1	0	-2.132319	-2.182937	-1.596645
46	1	0	-4.614359	-2.395706	-1.636225
47	1	0	-4.825017	1.685807	-0.274668
48	1	0	-2.351546	1.741401	-0.327923
49	1	0	-0.070243	0.8687	-3.347075
50	1	0	-0.706907	-0.524296	-3.61953
51	6	0	-6.455694	-0.460849	-0.90549
52	1	0	-6.782804	-0.805041	0.083197
53	1	0	-6.924369	0.510566	-1.085336
54	1	0	-6.837099	-1.173214	-1.642136

55	6	0	6.412651	-0.562164	-0.978413
56	1	0	6.725025	-1.279388	-0.209671
57	1	0	6.788194	-0.929491	-1.937811
58	1	0	6.899257	0.391227	-0.756674

Table S9. Cartesian coordinates for diprotonated **4b** ($[Ru^{IV}]^{2+}$, triplet).

Center number	Atomic number	Atomic type	Coordinates (Angstroms) X	Y	Z
1	44	0	0.026222	-0.115827	-0.920033
2	8	0	-0.422151	-1.9962	-0.824041
3	8	0	-1.943973	-3.583002	-0.400025
4	8	0	0.571422	1.761281	-0.864584
5	7	0	-0.048314	-0.039092	1.084554
6	7	0	0.100268	0.568111	3.195589
7	6	0	-1.269285	-2.671635	0.010866
8	6	0	-1.216955	-2.244874	1.439746
9	6	0	-1.73965	-3.048931	2.452342
10	6	0	-1.659011	-2.667533	3.80816
11	6	0	-1.057436	-1.475889	4.2094
12	6	0	-0.542684	-0.663027	3.196104
13	6	0	-0.624256	-1.038317	1.843351
14	6	0	0.387311	0.929003	1.910102
15	6	0	0.993635	2.17458	1.493149
16	6	0	1.510237	3.084777	2.432447
17	6	0	2.013246	4.320225	2.041241
18	6	0	1.999178	4.691748	0.684287
19	6	0	1.501101	3.822527	-0.269177
20	6	0	1.011361	2.547857	0.104853
21	6	0	2.494234	-1.888877	-0.411244
22	6	0	3.815345	-2.307484	-0.458044
23	6	0	4.797186	-1.502187	-1.054854
24	6	0	4.362261	-0.276705	-1.585039
25	6	0	3.027542	0.087758	-1.502726
26	7	0	2.091252	-0.70415	-0.926033
27	8	0	0.040022	-0.17835	-3.098655
28	6	0	-2.858245	-0.43399	-1.805175
29	6	0	-4.207776	-0.16112	-1.966729
30	6	0	-4.782662	0.969721	-1.366688
31	6	0	-3.923659	1.781426	-0.608511
32	6	0	-2.582479	1.456408	-0.482429
33	7	0	-2.044066	0.363305	-1.070469
34	1	0	-2.209587	-3.986857	2.176
35	1	0	-0.997606	-1.199974	5.256725
36	1	0	1.536404	2.825842	3.486328
37	1	0	2.383474	5.660965	0.383939
38	1	0	1.482655	4.084572	-1.321646
39	1	0	1.723008	-2.513911	0.018434
40	1	0	4.072858	-3.273498	-0.035947
41	1	0	5.062715	0.398064	-2.066553
42	1	0	2.68106	1.035525	-1.897795

43	1	0	-2.406411	-1.311502	-2.251947
44	1	0	-4.809744	-0.842101	-2.55958
45	1	0	-4.297511	2.671784	-0.113482
46	1	0	-1.910822	2.081042	0.093523
47	1	0	0.2738	1.138424	4.011074
48	1	0	0.76058	-0.632175	-3.561042
49	1	0	-0.21649	0.600504	-3.614555
50	6	0	-6.235142	1.304642	-1.545462
51	1	0	-6.613802	1.911673	-0.720172
52	1	0	-6.374482	1.879796	-2.469417
53	1	0	-6.845368	0.402097	-1.630185
54	6	0	6.238149	-1.920345	-1.106779
55	1	0	6.754005	-1.598285	-0.193506
56	1	0	6.337281	-3.006599	-1.170552
57	1	0	6.758405	-1.467754	-1.95397
58	1	0	-2.077385	-3.325222	4.562451
59	1	0	2.413367	4.998393	2.787114

Table S10. Cartesian coordinates for protonated **4b** ($[Ru^{IV}]^+$, triplet).

			Coordinates (Angstroms)		
Center number	**Atomic number**	**Atomic type**	**X**	**Y**	**Z**
1	44	0	-0.012512	-0.205812	-0.944165
2	8	0	-0.014184	-2.146729	-0.579736
3	8	0	0.065746	-4.124825	0.419141
4	8	0	-0.023725	1.748158	-1.126728
5	7	0	0.012077	0.157933	1.120677
6	7	0	0.006122	1.081758	3.127588
7	6	0	0.043856	-2.91266	0.517769
8	6	0	0.057112	-2.249398	1.863909
9	6	0	0.0806	-3.030742	3.020452
10	6	0	0.077581	-2.455782	4.304697
11	6	0	0.050272	-1.074888	4.493979
12	6	0	0.028861	-0.289627	3.3409
13	6	0	0.032304	-0.860405	2.053699
14	6	0	-0.001762	1.320664	1.7777
15	6	0	0.006391	2.630806	1.15571
16	6	0	0.02809	3.803504	1.938185
17	6	0	0.054564	5.063862	1.360405
18	6	0	0.062717	5.187189	-0.03797
19	6	0	0.040837	4.056814	-0.837139
20	6	0	0.009706	2.762047	-0.269378
21	6	0	2.641974	-1.239376	-1.858989
22	6	0	4.014747	-1.372922	-2.007748
23	6	0	4.88884	-0.522092	-1.31884
24	6	0	4.305062	0.442019	-0.485154
25	6	0	2.925091	0.519306	-0.371392
26	7	0	2.101405	-0.3068	-1.046235
27	8	0	0.054482	-0.479329	-2.862938
28	6	0	-2.745766	-1.478822	-1.358599
29	6	0	-4.123116	-1.607137	-1.468935

30	6	0	-4.959781	-0.510867	-1.220924
31	6	0	-4.331244	0.689294	-0.86161
32	6	0	-2.948497	0.754901	-0.77131
33	7	0	-2.157146	-0.311819	-1.010831
34	1	0	0.099554	-4.108256	2.900341
35	1	0	0.096389	-3.106591	5.172523
36	1	0	0.04725	-0.639981	5.487883
37	1	0	0.02586	3.733048	3.021955
38	1	0	0.086783	6.170529	-0.496724
39	1	0	0.047232	4.12427	-1.919714
40	1	0	0.070917	5.947101	1.989591
41	1	0	1.941929	-1.871485	-2.389802
42	1	0	4.396614	-2.145551	-2.667116
43	1	0	4.921575	1.133961	0.07928
44	1	0	2.457049	1.257115	0.26844
45	1	0	-2.077517	-2.314317	-1.531967
46	1	0	-4.53765	-2.570502	-1.748023
47	1	0	-4.914846	1.580385	-0.654003
48	1	0	-2.449108	1.678866	-0.510233
49	1	0	-0.000851	1.788592	3.846126
50	1	0	-0.820784	-0.400789	-3.272948
51	6	0	6.380067	-0.624978	-1.486077
52	1	0	6.693339	-0.114621	-2.404818
53	1	0	6.912365	-0.162485	-0.651665
54	1	0	6.698725	-1.667564	-1.569536
55	6	0	-6.453834	-0.611996	-1.359415
56	1	0	-6.965624	0.141513	-0.756067
57	1	0	-6.747466	-0.454485	-2.404375
58	1	0	-6.815004	-1.601016	-1.065748

Table S11. Cartesian coordinates for protonated **4b'** ($[Ru^{IV}]^+$, triplet).

Center number	Atomic number	Atomic type	Coordinates (Angstroms)		
			X	Y	Z
1	44	0	-0.00876	-0.117327	-0.884859
2	8	0	0.281319	-2.122411	-0.946056
3	8	0	1.061841	-4.082524	-0.230782
4	8	0	-0.348235	1.858819	-0.948762
5	7	0	0.029119	-0.053161	1.029486
6	7	0	-0.065529	0.658111	3.182227
7	6	0	0.691662	-2.949729	0.025424
8	6	0	0.642667	-2.454872	1.445069
9	6	0	0.905478	-3.3307	2.50782
10	6	0	0.847288	-2.903708	3.845796
11	6	0	0.524244	-1.585225	4.194263
12	6	0	0.263007	-0.690655	3.155917
13	6	0	0.32844	-1.13875	1.812388
14	6	0	-0.200474	1.009544	1.914367
15	6	0	-0.500067	2.350593	1.446685
16	6	0	-0.7367	3.357532	2.402162
17	6	0	-1.000737	4.66514	2.023985

18	6	0	-1.03213	5.014058	0.658645
19	6	0	-0.805766	4.053334	-0.306216
20	6	0	-0.540214	2.703469	0.051968
21	6	0	2.865718	-0.796105	-1.594969
22	6	0	4.237503	-0.648246	-1.735906
23	6	0	4.877263	0.506394	-1.266318
24	6	0	4.061604	1.478402	-0.668653
25	6	0	2.695285	1.273846	-0.561803
26	7	0	2.094351	0.15248	-1.017549
27	8	0	0.019461	-0.443445	-3.068925
28	6	0	-2.657761	-1.655206	-0.672734
29	6	0	-4.022403	-1.90037	-0.713534
30	6	0	-4.915904	-0.881068	-1.069818
31	6	0	-4.352933	0.364674	-1.381496
32	6	0	-2.980072	0.549059	-1.315093
33	7	0	-2.131132	-0.443871	-0.963575
34	1	0	1.156523	-4.357938	2.266773
35	1	0	1.058746	-3.621055	4.632261
36	1	0	0.478536	-1.267287	5.230353
37	1	0	-0.702468	3.07601	3.448806
38	1	0	-1.234409	6.039176	0.364558
39	1	0	-0.820225	4.2948	-1.364085
40	1	0	-1.180592	5.420416	2.781924
41	1	0	2.355064	-1.690402	-1.928754
42	1	0	4.803745	-1.443806	-2.208991
43	1	0	4.486639	2.400072	-0.28467
44	1	0	2.053653	2.017029	-0.10737
45	1	0	-1.949467	-2.433581	-0.424053
46	1	0	-4.382686	-2.894748	-0.470307
47	1	0	-4.981521	1.199316	-1.674848
48	1	0	-2.525	1.505052	-1.541835
49	1	0	-0.637224	-0.031351	-3.64713
50	1	0	-0.052802	-1.408831	-3.165082
51	6	0	-6.401814	-1.10726	-1.095659
52	1	0	-6.823771	-0.944675	-0.096353
53	1	0	-6.90183	-0.417774	-1.78002
54	1	0	-6.64464	-2.131804	-1.388901
55	6	0	6.36635	0.683085	-1.370811
56	1	0	6.853381	0.310412	-0.461306
57	1	0	6.777873	0.125255	-2.215336
58	1	0	6.637962	1.736259	-1.478644

Table S12. Cartesian coordinates for **4b** ([Ru^{IV}], triplet).

Center number	Atomic number	Atomic type	Coordinates (Angstroms)		
			X	Y	Z
1	44	0	-0.000178	-0.207366	-1.049076
2	8	0	0.000478	-2.247642	-0.690158
3	8	0	0.000668	-4.214733	0.345621
4	8	0	-0.000667	1.866978	-1.173327
5	7	0	0.000174	0.106396	1.066427

6	7	0	0.000992	0.98105	3.097452
7	6	0	0.000778	-2.986837	0.392124
8	6	0	0.001383	-2.320738	1.754409
9	6	0	0.002255	-3.123779	2.900653
10	6	0	0.002818	-2.582545	4.194917
11	6	0	0.002488	-1.202349	4.413696
12	6	0	0.001584	-0.39618	3.279061
13	6	0	0.001062	-0.935647	1.975417
14	6	0	0.0001	1.254011	1.747331
15	6	0	-0.000818	2.584707	1.175933
16	6	0	-0.001406	3.713321	2.033948
17	6	0	-0.002256	5.007787	1.55633
18	6	0	-0.002559	5.215087	0.162481
19	6	0	-0.002039	4.145055	-0.706541
20	6	0	-0.00116	2.790544	-0.252037
21	6	0	2.727856	-1.381959	-1.522861
22	6	0	4.109025	-1.498967	-1.608274
23	6	0	4.93258	-0.440218	-1.207431
24	6	0	4.294549	0.7085	-0.725202
25	6	0	2.907389	0.762617	-0.669534
26	7	0	2.131549	-0.265535	-1.057616
27	8	0	-0.000426	-0.458536	-2.813971
28	6	0	-2.72766	-1.383548	-1.52194
29	6	0	-4.108813	-1.501361	-1.606944
30	6	0	-4.932848	-0.443118	-1.205859
31	6	0	-4.295333	0.705982	-0.723771
32	6	0	-2.908215	0.760906	-0.668519
33	7	0	-2.131876	-0.266802	-1.056873
34	1	0	0.002463	-4.197157	2.747018
35	1	0	0.003509	-3.252346	5.049562
36	1	0	0.002902	-0.786348	5.416493
37	1	0	-0.001272	3.56651	3.111458
38	1	0	-0.003234	6.227122	-0.233994
39	1	0	-0.00228	4.289764	-1.782148
40	1	0	-0.002713	5.847537	2.243231
41	1	0	2.058258	-2.183989	-1.810525
42	1	0	4.536167	-2.42227	-1.987206
43	1	0	4.871083	1.567505	-0.395987
44	1	0	2.392475	1.646646	-0.315603
45	1	0	-2.05769	-2.185199	-1.8098
46	1	0	-4.535531	-2.424909	-1.985744
47	1	0	-4.872268	1.564637	-0.394336
48	1	0	-2.393716	1.645212	-0.314677
49	1	0	0.001175	1.670703	3.830134
50	6	0	6.432792	-0.525254	-1.316061
51	1	0	6.760358	-0.245383	-2.324753
52	1	0	6.925195	0.149757	-0.610929
53	1	0	6.788408	-1.54245	-1.128861
54	6	0	-6.433052	-0.528811	-1.31411
55	1	0	-6.925568	0.141591	-0.604647
56	1	0	-6.76145	-0.24299	-2.320867
57	1	0	-6.787749	-1.547374	-1.132829

Table S13. Cartesian coordinates for **4b'** ([Ru^{IV}], triplet).

Center number	Atomic number	Atomic type	Coordinates (Angstroms)		
			X	Y	Z
1	44	0	-0.021694	-0.214882	-0.967221
2	8	0	0.050369	-2.172293	-0.582039
3	8	0	0.313029	-4.116414	0.454581
4	8	0	-0.13259	1.748154	-1.189075
5	7	0	0.015428	0.170839	1.053931
6	7	0	0.01401	1.203122	3.088021
7	6	0	0.211888	-2.899744	0.528718
8	6	0	0.233974	-2.197041	1.851298
9	6	0	0.339692	-2.929361	3.033591
10	6	0	0.339511	-2.301797	4.300134
11	6	0	0.231586	-0.922578	4.437706
12	6	0	0.125126	-0.148867	3.267286
13	6	0	0.129622	-0.802072	1.996662
14	6	0	-0.05009	1.352385	1.755811
15	6	0	-0.137857	2.637476	1.087516
16	6	0	-0.187373	3.813411	1.86504
17	6	0	-0.254676	5.06726	1.280744
18	6	0	-0.272638	5.190314	-0.122629
19	6	0	-0.22607	4.06093	-0.916318
20	6	0	-0.159978	2.76426	-0.340376
21	6	0	2.678132	-1.075827	-1.914808
22	6	0	4.059342	-1.16587	-2.026278
23	6	0	4.885694	-0.35735	-1.237065
24	6	0	4.251369	0.528714	-0.357723
25	6	0	2.865692	0.566087	-0.28795
26	7	0	2.088293	-0.223639	-1.053071
27	8	0	0.03833	-0.509689	-2.914383
28	6	0	-2.687192	-1.574518	-1.384183
29	6	0	-4.061072	-1.772686	-1.42897
30	6	0	-4.935111	-0.751824	-1.037276
31	6	0	-4.352183	0.449376	-0.615005
32	6	0	-2.970787	0.585683	-0.595701
33	7	0	-2.14383	-0.408331	-0.975022
34	1	0	0.41936	-4.008349	2.953749
35	1	0	0.42436	-2.921274	5.188394
36	1	0	0.228756	-0.447774	5.414091
37	1	0	-0.168649	3.693656	2.942851
38	1	0	-0.322835	6.172798	-0.583118
39	1	0	-0.237628	4.121781	-1.999775
40	1	0	-0.291944	5.954619	1.905346
41	1	0	2.005689	-1.671839	-2.519006
42	1	0	4.484676	-1.870846	-2.733556
43	1	0	4.82969	1.190216	0.279479
44	1	0	2.352809	1.234186	0.392283
45	1	0	-1.980817	-2.352215	-1.651043
46	1	0	-4.442206	-2.731018	-1.767526
47	1	0	-4.968219	1.284905	-0.297753
48	1	0	-2.502488	1.506318	-0.27233
49	1	0	-0.819519	-0.319614	-3.320886

50	6	0	6.386901	-0.454413	-1.310624
51	1	0	6.86338	0.487709	-1.026502
52	1	0	6.753113	-1.228551	-0.625322
53	1	0	6.720899	-0.723884	-2.316355
54	6	0	-6.428457	-0.94603	-1.040165
55	1	0	-6.760627	-1.360058	-0.080368
56	1	0	-6.95493	0.000552	-1.188872
57	1	0	-6.738999	-1.644021	-1.822351

Table S14. Cartesian coordinates for diprotonated **5b** ($[Ru^{V}]^{2+}$, quartet).

Center number	Atomic number	Atomic type	Coordinates (Angstroms)		
			X	Y	Z
1	44	0	0.064751	-0.267392	-0.938912
2	8	0	-0.141301	-2.126886	-0.423779
3	8	0	-1.174735	-3.881903	0.481514
4	8	0	0.371334	1.687109	-1.236593
5	7	0	-0.024079	0.225405	1.070145
6	7	0	-0.041586	1.286132	3.007239
7	6	0	-0.728388	-2.769921	0.621048
8	6	0	-0.713947	-2.044249	1.926438
9	6	0	-1.053147	-2.704079	3.106022
10	6	0	-1.053059	-2.039005	4.352487
11	6	0	-0.726008	-0.690543	4.472316
12	6	0	-0.394381	-0.026209	3.288968
13	6	0	-0.378677	-0.686259	2.044236
14	6	0	0.168659	1.421716	1.66718
15	6	0	0.515895	2.652005	0.991241
16	6	0	0.772165	3.83158	1.709204
17	6	0	1.06293	5.028854	1.060489
18	6	0	1.100644	5.088915	-0.349422
19	6	0	0.858032	3.955555	-1.094394
20	6	0	0.572789	2.711814	-0.456906
21	6	0	2.587131	-1.786645	-1.50595
22	6	0	3.924357	-2.145259	-1.533526
23	6	0	4.88661	-1.360139	-0.877493
24	6	0	4.41694	-0.21942	-0.207275
25	6	0	3.066095	0.088718	-0.217265
26	7	0	2.157759	-0.679478	-0.855899
27	8	0	0.140092	-0.570814	-2.810025
28	6	0	-2.731554	-1.132083	-1.653927
29	6	0	-4.102519	-1.092255	-1.844954
30	6	0	-4.844266	0.034439	-1.453123
31	6	0	-4.125264	1.088134	-0.86472
32	6	0	-2.753637	0.990607	-0.699407
33	7	0	-2.057667	-0.102667	-1.084482
34	1	0	-1.321986	-3.753596	3.04833
35	1	0	-1.321488	-2.597426	5.242881
36	1	0	-0.734189	-0.190144	5.434587
37	1	0	0.756821	3.829055	2.794286
38	1	0	1.32519	6.02769	-0.844951

39	1	0	0.886662	3.965161	-2.178601
40	1	0	1.261178	5.920127	1.646347
41	1	0	1.831959	-2.379587	-2.006088
42	1	0	4.213057	-3.042935	-2.070533
43	1	0	5.102646	0.431767	0.324577
44	1	0	2.695148	0.96552	0.298557
45	1	0	-2.143981	-1.991557	-1.953324
46	1	0	-4.590186	-1.946383	-2.303407
47	1	0	-4.633187	1.989351	-0.537515
48	1	0	-2.188083	1.800247	-0.255058
49	1	0	0.017509	2.030869	3.687925
50	1	0	0.077999	0.221658	-3.372527
51	6	0	6.343723	-1.717843	-0.910864
52	1	0	6.773969	-1.441613	-1.881486
53	1	0	6.908332	-1.197159	-0.134987
54	1	0	6.488593	-2.795124	-0.791034
55	6	0	-6.325898	0.113719	-1.675693
56	1	0	-6.792168	0.870785	-1.042024
57	1	0	-6.531117	0.380099	-2.720189
58	1	0	-6.807188	-0.850223	-1.489884

Table S15. Cartesian coordinates for diprotonated **5b'** ($[Ru^{V}]^{2+}$, doublet).

Center number	Atomic number	Atomic type	Coordinates (Angstroms)		
			X	Y	Z
1	44	0	-0.019273	-0.174578	-0.858374
2	8	0	0.276925	-2.128003	-0.775198
3	8	0	1.406822	-3.913079	-0.056975
4	8	0	-0.440948	1.793028	-0.942228
5	7	0	0.051094	0.00159	1.07756
6	7	0	-0.079988	0.798132	3.227661
7	6	0	0.886023	-2.850544	0.196929
8	6	0	0.830634	-2.306659	1.594925
9	6	0	1.166095	-3.094698	2.691763
10	6	0	1.095588	-2.603456	4.038348
11	6	0	0.686093	-1.320096	4.340748
12	6	0	0.341511	-0.478311	3.251841
13	6	0	0.429493	-0.994879	1.900563
14	6	0	-0.25536	1.093465	1.916621
15	6	0	-0.629998	2.362533	1.429382
16	6	0	-0.925621	3.401303	2.358243
17	6	0	-1.243189	4.662439	1.919644
18	6	0	-1.273719	4.958164	0.521499
19	6	0	-0.99765	3.99232	-0.415184
20	6	0	-0.679176	2.663964	-0.010038
21	6	0	2.83345	-0.785946	-1.686415
22	6	0	4.187833	-0.598892	-1.906281
23	6	0	4.825709	0.572831	-1.46864
24	6	0	4.020004	1.516524	-0.809467
25	6	0	2.670638	1.273067	-0.619945
26	7	0	2.070043	0.138037	-1.051454

27	8	0	-0.02516	-0.522018	-3.01569
28	6	0	-2.641817	-1.73704	-0.470086
29	6	0	-3.992648	-2.036463	-0.551765
30	6	0	-4.892397	-1.122139	-1.120703
31	6	0	-4.343935	0.08361	-1.588175
32	6	0	-2.985826	0.329367	-1.4701
33	7	0	-2.129767	-0.565538	-0.91755
34	1	0	1.488719	-4.115623	2.510809
35	1	0	1.375109	-3.278489	4.840561
36	1	0	0.626493	-0.958205	5.3612
37	1	0	-0.889118	3.16223	3.414782
38	1	0	-1.521421	5.964715	0.198587
39	1	0	-1.01563	4.204598	-1.478535
40	1	0	-1.470106	5.446021	2.634725
41	1	0	2.335034	-1.692285	-2.005634
42	1	0	4.745155	-1.374969	-2.420552
43	1	0	4.442293	2.447585	-0.445772
44	1	0	2.042084	1.998296	-0.119974
45	1	0	-1.935163	-2.448084	-0.064775
46	1	0	-4.338251	-2.995006	-0.178493
47	1	0	-4.975267	0.836821	-2.048473
48	1	0	-2.554136	1.258968	-1.820379
49	1	0	-0.59314	-0.030299	-3.626933
50	6	0	6.29546	0.794071	-1.671404
51	1	0	6.534561	1.856873	-1.754579
52	1	0	6.852663	0.398844	-0.81238
53	1	0	6.659812	0.276912	-2.56197
54	6	0	-6.362527	-1.410091	-1.208442
55	1	0	-6.860721	-1.088746	-0.28496
56	1	0	-6.829843	-0.872926	-2.036855
57	1	0	-6.554615	-2.479282	-1.326006
58	1	0	-0.10527	-1.468169	-3.221913

Table S16. Cartesian coordinates for protonated **5b** ($[Ru^{V}]^{+}$, quartet).

Center number	Atomic number	Atomic type	Coordinates (Angstroms)		
			X	Y	Z
1	44	0	-0.000059	-0.218241	-1.000824
2	8	0	0.000094	-2.177356	-0.615708
3	8	0	0.000082	-4.113837	0.455025
4	8	0	-0.000197	1.758325	-1.216408
5	7	0	0.00004	0.189476	1.084419
6	7	0	0.000299	1.142685	3.075686
7	6	0	0.000165	-2.897449	0.511553
8	6	0	0.000343	-2.206362	1.849599
9	6	0	0.000574	-2.971658	3.01752
10	6	0	0.000747	-2.381614	4.295643
11	6	0	0.000686	-0.998582	4.471807
12	6	0	0.000445	-0.227782	3.309067
13	6	0	0.000278	-0.815287	2.028876
14	6	0	0.00006	1.361321	1.723005

15	6	0	-0.000167	2.658483	1.071455
16	6	0	-0.00029	3.843125	1.834388
17	6	0	-0.000509	5.096764	1.23949
18	6	0	-0.000618	5.202434	-0.160736
19	6	0	-0.000509	4.061585	-0.94303
20	6	0	-0.000284	2.768115	-0.362088
21	6	0	2.702351	-1.3959	-1.636893
22	6	0	4.078217	-1.534703	-1.740057
23	6	0	4.930975	-0.562017	-1.200267
24	6	0	4.321967	0.526427	-0.560365
25	6	0	2.939219	0.607727	-0.48936
26	7	0	2.137377	-0.337688	-1.016922
27	8	0	-0.000118	-0.488022	-2.767533
28	6	0	-2.702351	-1.396263	-1.636626
29	6	0	-4.078227	-1.535274	-1.739645
30	6	0	-4.93106	-0.562725	-1.199788
31	6	0	-4.322138	0.525823	-0.559928
32	6	0	-2.939415	0.607324	-0.489064
33	7	0	-2.137476	-0.337983	-1.016725
34	1	0	0.000618	-4.050811	2.911643
35	1	0	0.000928	-3.023759	5.170141
36	1	0	0.000815	-0.553791	5.461288
37	1	0	-0.000236	3.788823	2.919071
38	1	0	-0.000791	6.17995	-0.632271
39	1	0	-0.000591	4.113124	-2.02647
40	1	0	-0.000603	5.98803	1.857537
41	1	0	2.019756	-2.13411	-2.039679
42	1	0	4.479765	-2.406901	-2.245399
43	1	0	4.920446	1.315944	-0.117663
44	1	0	2.453041	1.446136	-0.006476
45	1	0	-2.019697	-2.134384	-2.039477
46	1	0	-4.479698	-2.407537	-2.24493
47	1	0	-4.920685	1.315244	-0.117139
48	1	0	-2.453305	1.44579	-0.006212
49	1	0	0.000397	1.858244	3.786022
50	6	0	6.425587	-0.669706	-1.325584
51	1	0	6.752372	-0.261948	-2.289903
52	1	0	6.936999	-0.108802	-0.539723
53	1	0	6.754615	-1.711258	-1.284351
54	6	0	-6.425679	-0.670454	-1.324978
55	1	0	-6.936932	-0.113735	-0.53602
56	1	0	-6.753068	-0.257739	-2.286988
57	1	0	-6.754319	-1.712296	-1.288932

Table S17. Cartesian coordinates for protonated **5b'** ($[Ru^{V}]^{+}$, quartet).

Center number	Atomic number	Atomic type	Coordinates (Angstroms)		
			X	Y	Z
1	44	0	0.078795	-0.261454	-0.944154
2	8	0	-0.042873	-2.173599	-0.47851
3	8	0	-0.794378	-4.033314	0.498235

4	8	0	0.293965	1.734433	-1.237509
5	7	0	-0.02465	0.181986	1.016635
6	7	0	-0.115239	1.284163	3.014471
7	6	0	-0.48513	-2.863066	0.58728
8	6	0	-0.513052	-2.120803	1.88665
9	6	0	-0.779601	-2.788795	3.086486
10	6	0	-0.818008	-2.110582	4.329735
11	6	0	-0.603882	-0.743381	4.425458
12	6	0	-0.341665	-0.038468	3.230902
13	6	0	-0.291631	-0.745302	1.988262
14	6	0	0.059329	1.395824	1.681207
15	6	0	0.284429	2.64706	1.017824
16	6	0	0.388588	3.830284	1.7895
17	6	0	0.584095	5.055558	1.19013
18	6	0	0.680355	5.155302	-0.224746
19	6	0	0.58097	4.036518	-1.013905
20	6	0	0.383241	2.74954	-0.427877
21	6	0	2.693432	-1.599855	-1.538925
22	6	0	4.052801	-1.873236	-1.559962
23	6	0	4.952592	-1.044836	-0.875306
24	6	0	4.407141	0.051297	-0.192006
25	6	0	3.03837	0.272578	-0.211112
26	7	0	2.190067	-0.537993	-0.874344
27	8	0	0.148442	-0.541569	-2.84259
28	6	0	-2.679338	-1.205865	-1.684883
29	6	0	-4.056345	-1.229022	-1.846217
30	6	0	-4.84165	-0.164556	-1.381698
31	6	0	-4.165067	0.897808	-0.765139
32	6	0	-2.785127	0.862696	-0.634427
33	7	0	-2.047844	-0.172521	-1.085277
34	1	0	-0.960805	-3.857661	3.040249
35	1	0	-1.026821	-2.683818	5.226903
36	1	0	-0.639348	-0.222597	5.376171
37	1	0	0.308803	3.73604	2.866372
38	1	0	0.834628	6.126753	-0.684059
39	1	0	0.651702	4.087516	-2.094883
40	1	0	0.665148	5.950166	1.798415
41	1	0	1.977353	-2.224915	-2.057244
42	1	0	4.404851	-2.737326	-2.113819
43	1	0	5.044312	0.736786	0.357088
44	1	0	2.602279	1.111144	0.316819
45	1	0	-2.049786	-2.015833	-2.032721
46	1	0	-4.511811	-2.082982	-2.336769
47	1	0	-4.708759	1.75721	-0.386759
48	1	0	-2.247675	1.674792	-0.161274
49	1	0	0.086092	0.274747	-3.364799
50	6	0	6.427925	-1.333944	-0.853219
51	1	0	7.013582	-0.424271	-0.700405
52	1	0	6.664093	-2.020933	-0.031389
53	1	0	6.754851	-1.810619	-1.780752
54	6	0	-6.338857	-0.174319	-1.517776
55	1	0	-6.78884	-0.725388	-0.682963
56	1	0	-6.750541	0.837553	-1.505784
57	1	0	-6.651347	-0.670045	-2.440477

Table S18. Cartesian coordinates for **5b** ([Ru^{V}], quartet).

Center number	Atomic number	Atomic type	Coordinates (Angstroms) X	Y	Z
1	44	0	-0.000147	-0.229527	-1.028669
2	8	0	0.000219	-2.213152	-0.598043
3	8	0	0.001271	-4.114972	0.540159
4	8	0	-0.000562	1.776349	-1.289745
5	7	0	0.000045	0.211435	1.010948
6	7	0	0.000339	1.282418	3.028459
7	6	0	0.000822	-2.889748	0.546261
8	6	0	0.000921	-2.145639	1.855986
9	6	0	0.001431	-2.853311	3.058284
10	6	0	0.001578	-2.202413	4.316254
11	6	0	0.001243	-0.819119	4.428464
12	6	0	0.00073	-0.065818	3.237002
13	6	0	0.000558	-0.745504	1.976536
14	6	0	-0.000048	1.405955	1.684296
15	6	0	-0.000513	2.676535	0.992103
16	6	0	-0.000728	3.867388	1.75235
17	6	0	-0.001175	5.112673	1.151864
18	6	0	-0.001427	5.21923	-0.257387
19	6	0	-0.001218	4.083933	-1.035882
20	6	0	-0.000751	2.781649	-0.449666
21	6	0	2.705297	-1.342821	-1.707853
22	6	0	4.082933	-1.506554	-1.751241
23	6	0	4.92063	-0.616375	-1.06841
24	6	0	4.300502	0.42229	-0.36324
25	6	0	2.916198	0.529158	-0.357858
26	7	0	2.12866	-0.33747	-1.020066
27	8	0	-0.000304	-0.544687	-2.797301
28	6	0	-2.705321	-1.343946	-1.707017
29	6	0	-4.082909	-1.508135	-1.750176
30	6	0	-4.9208	-0.618075	-1.067424
31	6	0	-4.300909	0.420928	-0.362549
32	6	0	-2.916637	0.528249	-0.357389
33	7	0	-2.128914	-0.338253	-1.019534
34	1	0	0.001722	-3.936731	3.001174
35	1	0	0.001973	-2.811199	5.215795
36	1	0	0.001371	-0.32483	5.394919
37	1	0	-0.000531	3.763081	2.831833
38	1	0	-0.001785	6.198329	-0.727715
39	1	0	-0.001393	4.130819	-2.119912
40	1	0	-0.001338	6.009406	1.763956
41	1	0	2.026356	-2.014224	-2.218799
42	1	0	4.496568	-2.333055	-2.320262
43	1	0	4.888421	1.151036	0.185674
44	1	0	2.414569	1.318692	0.187365
45	1	0	-2.026234	-2.01525	-2.217898
46	1	0	-4.496356	-2.33489	-2.318964
47	1	0	-4.888986	1.149594	0.186301

48	1	0	-2.415198	1.318065	0.187601
49	6	0	6.417086	-0.785503	-1.069375
50	1	0	6.928577	0.171378	-0.935235
51	1	0	6.72672	-1.442785	-0.247715
52	1	0	6.766402	-1.239627	-2.000624
53	6	0	-6.417203	-0.787678	-1.068174
54	1	0	-6.726505	-1.445144	-0.246537
55	1	0	-6.928978	0.169027	-0.933868
56	1	0	-6.766513	-1.241823	-1.999416

Table S19. Cartesian coordinates for protonated **6b** ($[Ru^{VI}]^{2+}$, triplet).

Center number	Atomic number	Atomic type	Coordinates (Angstroms)		
			X	Y	Z
1	44	0	-0.102615	-0.449614	-0.942693
2	8	0	0.320515	-2.09286	-0.077396
3	8	0	2.077731	-3.379112	0.471773
4	8	0	-0.744102	1.468491	-1.20283
5	7	0	0.103773	0.323854	1.10591
6	7	0	0.147273	1.547291	2.956496
7	6	0	1.385793	-2.43073	0.731799
8	6	0	1.471329	-1.606694	1.964771
9	6	0	2.173057	-2.036175	3.087091
10	6	0	2.210692	-1.261931	4.271858
11	6	0	1.560989	-0.035827	4.377588
12	6	0	0.869172	0.402952	3.243427
13	6	0	0.821191	-0.363172	2.058062
14	6	0	-0.293323	1.479819	1.66254
15	6	0	-1.024523	2.512823	0.97356
16	6	0	-1.555779	3.623528	1.63791
17	6	0	-2.18355	4.654425	0.937242
18	6	0	-2.290582	4.610031	-0.47523
19	6	0	-1.793069	3.535	-1.169283
20	6	0	-1.166345	2.443892	-0.475891
21	6	0	2.7389	-0.976214	-1.843192
22	6	0	4.06524	-0.751726	-2.174158
23	6	0	4.663852	0.49012	-1.910099
24	6	0	3.8547	1.461496	-1.298136
25	6	0	2.534166	1.177456	-0.990346
26	7	0	1.977021	-0.025246	-1.251335
27	8	0	-0.221998	-0.754207	-2.616724
28	6	0	-2.561013	-1.804633	0.334509
29	6	0	-3.870533	-2.247076	0.441879
30	6	0	-4.821224	-1.895092	-0.528227
31	6	0	-4.375221	-1.075251	-1.577649
32	6	0	-3.054812	-0.659616	-1.629001
33	7	0	-2.154554	-1.015782	-0.683529
34	1	0	2.688847	-2.989955	3.045285
35	1	0	2.763781	-1.64055	5.124774
36	1	0	1.597323	0.544295	5.293358
37	1	0	-1.500817	3.694548	2.719528

38	1	0	-2.774429	5.42453	-1.004247
39	1	0	-1.863334	3.460698	-2.249097
40	1	0	-2.59219	5.498932	1.482396
41	1	0	2.265795	-1.929822	-2.045655
42	1	0	4.628191	-1.552065	-2.643121
43	1	0	4.250222	2.444941	-1.06638
44	1	0	1.895284	1.92174	-0.531219
45	1	0	-1.808014	-2.09523	1.055336
46	1	0	-4.142462	-2.880507	1.279816
47	1	0	-5.052424	-0.768771	-2.368197
48	1	0	-2.688217	-0.046283	-2.443663
49	1	0	0.020047	2.331146	3.58203
50	6	0	6.088665	0.771024	-2.289202
51	1	0	6.143578	1.042835	-3.350778
52	1	0	6.505875	1.599636	-1.713221
53	1	0	6.718843	-0.111096	-2.149293
54	6	0	-6.234078	-2.398988	-0.468588
55	1	0	-6.933101	-1.691111	-0.920339
56	1	0	-6.314661	-3.339553	-1.027866
57	1	0	-6.547021	-2.601278	0.558264

Table S20. Cartesian coordinates for protonated **6b'** ($[Ru^{VI}]^{2+}$, triplet).

Center number	Atomic number	Atomic type	Coordinates (Angstroms) X	Y	Z
1	44	0	0.05785	-0.298515	-0.935081
2	8	0	-0.053241	-2.15628	-0.3536
3	8	0	-0.77624	-3.961811	0.742444
4	8	0	0.253309	1.676677	-1.288026
5	7	0	-0.017692	0.256158	1.034298
6	7	0	-0.043247	1.463186	2.997464
7	6	0	-0.46502	-2.796221	0.765006
8	6	0	-0.452383	-1.986746	2.026725
9	6	0	-0.66741	-2.579557	3.267926
10	6	0	-0.669652	-1.83046	4.500649
11	6	0	-0.470221	-0.473371	4.532982
12	6	0	-0.254513	0.181236	3.280391
13	6	0	-0.242668	-0.603955	2.048362
14	6	0	0.086879	1.508885	1.631258
15	6	0	0.283062	2.709264	0.917123
16	6	0	0.392212	3.938254	1.620336
17	6	0	0.565655	5.122618	0.938826
18	6	0	0.632951	5.142941	-0.489987
19	6	0	0.526558	3.986056	-1.220264
20	6	0	0.351828	2.731528	-0.557786
21	6	0	2.653244	-1.683823	-1.514119
22	6	0	4.007621	-1.968445	-1.553725
23	6	0	4.933211	-1.121732	-0.9211
24	6	0	4.409247	0.00058	-0.26022
25	6	0	3.043363	0.233669	-0.257093
26	7	0	2.170826	-0.591676	-0.874604

27	8	0	0.116955	-0.648095	-2.799619
28	6	0	-2.683203	-1.322423	-1.634931
29	6	0	-4.057378	-1.378854	-1.797094
30	6	0	-4.871268	-0.321849	-1.35689
31	6	0	-4.218638	0.765518	-0.752531
32	6	0	-2.840063	0.765266	-0.618895
33	7	0	-2.07402	-0.261451	-1.051091
34	1	0	-0.841231	-3.65173	3.296304
35	1	0	-0.841427	-2.374606	5.423338
36	1	0	-0.475308	0.094655	5.456633
37	1	0	0.336111	3.913653	2.70254
38	1	0	0.770101	6.091305	-1.000249
39	1	0	0.574957	3.981258	-2.303571
40	1	0	0.652751	6.054503	1.487739
41	1	0	1.926296	-2.324913	-1.996586
42	1	0	4.338954	-2.85669	-2.08183
43	1	0	5.063741	0.695766	0.255
44	1	0	2.631324	1.094371	0.254888
45	1	0	-2.040178	-2.127656	-1.968929
46	1	0	-4.491527	-2.253927	-2.269644
47	1	0	-4.783627	1.615991	-0.385419
48	1	0	-2.327839	1.599285	-0.155153
49	1	0	0.006736	0.10998	-3.400045
50	6	0	6.406853	-1.400899	-0.968024
51	1	0	6.959421	-0.796028	-0.246785
52	1	0	6.613199	-2.457613	-0.774324
53	1	0	6.798505	-1.176368	-1.967711
54	6	0	-6.359641	-0.3477	-1.544273
55	1	0	-6.760561	-1.353775	-1.395383
56	1	0	-6.866817	0.340481	-0.865012
57	1	0	-6.610071	-0.049392	-2.570192

Table S21. Cartesian coordinates for **6b** ($[Ru^{VI}]^{+}$, triplet).

Center number	Atomic number	Atomic type	Coordinates (Angstroms)		
			X	Y	Z
1	44	0	0.1694	-0.453085	-0.962694
2	8	0	-0.059332	-2.162261	-0.086165
3	8	0	-1.403388	-3.722294	0.777878
4	8	0	0.585301	1.499647	-1.338084
5	7	0	-0.079861	0.33368	1.009278
6	7	0	-0.289931	1.697129	2.847992
7	6	0	-0.900252	-2.625324	0.876261
8	6	0	-1.031148	-1.736592	2.056916
9	6	0	-1.57341	-2.19494	3.259775
10	6	0	-1.68277	-1.356452	4.401967
11	6	0	-1.270187	-0.036799	4.379602
12	6	0	-0.732818	0.465865	3.168249
13	6	0	-0.611381	-0.401227	2.026428
14	6	0	0.076619	1.596134	1.539961
15	6	0	0.523061	2.711663	0.7744

16	6	0	0.713496	3.97233	1.399453
17	6	0	1.101404	5.070208	0.668721
18	6	0	1.309743	4.95578	-0.734411
19	6	0	1.132459	3.757419	-1.382603
20	6	0	0.739187	2.596362	-0.654104
21	6	0	2.745225	-1.985284	-1.229246
22	6	0	4.084415	-2.325996	-1.120161
23	6	0	4.979414	-1.472429	-0.459449
24	6	0	4.448854	-0.286072	0.064618
25	6	0	3.099003	-0.000903	-0.080945
26	7	0	2.256357	-0.834785	-0.719947
27	8	0	0.26074	-0.843866	-2.634723
28	6	0	-2.648066	-1.286407	-1.677488
29	6	0	-4.013208	-1.216816	-1.90887
30	6	0	-4.712488	-0.02773	-1.658424
31	6	0	-3.965896	1.052053	-1.166537
32	6	0	-2.60169	0.918933	-0.954706
33	7	0	-1.947601	-0.232935	-1.203765
34	1	0	-1.911644	-3.225088	3.307899
35	1	0	-2.10533	-1.772461	5.310408
36	1	0	-1.355197	0.605676	5.249324
37	1	0	0.540037	4.033642	2.467586
38	1	0	1.615326	5.82986	-1.301539
39	1	0	1.286272	3.651615	-2.450656
40	1	0	1.248596	6.027286	1.15746
41	1	0	2.036585	-2.632889	-1.730592
42	1	0	4.425139	-3.259932	-1.554957
43	1	0	5.082822	0.422594	0.587222
44	1	0	2.674705	0.908511	0.323489
45	1	0	-2.090623	-2.197059	-1.861918
46	1	0	-4.526486	-2.096265	-2.283548
47	1	0	-4.44233	2.001783	-0.946745
48	1	0	-2.010789	1.742842	-0.576159
49	6	0	-6.187057	0.087525	-1.927538
50	1	0	-6.641371	0.891339	-1.343821
51	1	0	-6.359079	0.308664	-2.987939
52	1	0	-6.70667	-0.847482	-1.702165
53	6	0	6.431726	-1.827744	-0.301349
54	1	0	7.046629	-0.941323	-0.129844
55	1	0	6.564602	-2.495907	0.558196
56	1	0	6.810482	-2.352445	-1.182429

Table S22. Cartesian coordinates for **7b** ($[Ru^{VII}]^{2+}$, doublet).

Center number	Atomic number	Atomic type	Coordinates (Angstroms)		
			X	Y	Z
1	44	0	0.156933	-0.555718	-0.882852
2	8	0	-0.039906	-2.116979	0.20584
3	8	0	-1.479362	-3.519881	1.203095
4	8	0	0.591276	1.366084	-1.444974
5	7	0	-0.085926	0.486799	1.007599

6	7	0	-0.264617	2.069473	2.699336
7	6	0	-0.926197	-2.451549	1.193318
8	6	0	-1.02368	-1.434867	2.27913
9	6	0	-1.544069	-1.732962	3.525629
10	6	0	-1.634171	-0.755856	4.592163
11	6	0	-1.229241	0.541603	4.433087
12	6	0	-0.703445	0.908386	3.151235
13	6	0	-0.597272	-0.105241	2.090238
14	6	0	0.087616	1.819412	1.384653
15	6	0	0.524025	2.817172	0.514888
16	6	0	0.712167	4.155036	0.976509
17	6	0	1.119782	5.132277	0.109899
18	6	0	1.358404	4.837429	-1.28226
19	6	0	1.188133	3.580132	-1.787374
20	6	0	0.76393	2.513965	-0.925251
21	6	0	2.752308	-2.044481	-1.242557
22	6	0	4.087151	-2.396381	-1.130654
23	6	0	4.971932	-1.605256	-0.380351
24	6	0	4.428994	-0.464426	0.23047
25	6	0	3.083956	-0.164399	0.080158
26	7	0	2.251017	-0.93664	-0.648109
27	8	0	0.232456	-1.073922	-2.507807
28	6	0	-2.641063	-1.52076	-1.507109
29	6	0	-3.995173	-1.503257	-1.799569
30	6	0	-4.722545	-0.304636	-1.728773
31	6	0	-4.009124	0.841728	-1.342313
32	6	0	-2.654846	0.760484	-1.061722
33	7	0	-1.971889	-0.402693	-1.136498
34	1	0	-1.896309	-2.74471	3.708171
35	1	0	-2.045473	-1.083246	5.541209
36	1	0	-1.299892	1.276158	5.227624
37	1	0	0.527416	4.362752	2.024002
38	1	0	1.68148	5.640286	-1.938268
39	1	0	1.360127	3.342294	-2.831135
40	1	0	1.269789	6.146514	0.465061
41	1	0	2.061853	-2.645206	-1.821989
42	1	0	4.434784	-3.291086	-1.636905
43	1	0	5.052029	0.194708	0.825917
44	1	0	2.655022	0.707828	0.557436
45	1	0	-2.069104	-2.43948	-1.564729
46	1	0	-4.47854	-2.430882	-2.088186
47	1	0	-4.506131	1.803203	-1.265586
48	1	0	-2.094087	1.641013	-0.773998
49	6	0	-6.181543	-0.24925	-2.075927
50	1	0	-6.671506	0.619362	-1.631087
51	1	0	-6.300992	-0.177	-3.164253
52	1	0	-6.702509	-1.154572	-1.753849
53	6	0	6.418345	-1.976607	-0.228409
54	1	0	7.013942	-1.144307	0.151255
55	1	0	6.518939	-2.811719	0.475519
56	1	0	6.842033	-2.307481	-1.18089

Table S23. Cartesian coordinates for $\mathbf{TS_{axial}}$.

Center number	Atomic number	Atomic type	Coordinates (Angstroms)		
			X	Y	Z
1	44	0	0.518586	0.099182	0.1571
2	8	0	-0.10461	1.156532	-1.44054
3	8	0	-1.42389	1.936384	-3.04924
4	8	0	1.20422	-1.12515	1.593347
5	7	0	-1.05643	-1.18029	-0.05212
6	7	0	-2.48175	-2.84934	0.168491
7	6	0	-1.17045	1.066736	-2.23051
8	6	0	-2.0556	-0.14755	-2.11953
9	6	0	-3.09857	-0.33255	-3.03097
10	6	0	-3.98739	-1.41714	-2.93272
11	6	0	-3.89547	-2.35618	-1.90395
12	6	0	-2.86247	-2.17288	-0.98578
13	6	0	-1.9486	-1.10865	-1.10438
14	6	0	-1.3892	-2.22216	0.713187
15	6	0	-0.72095	-2.60548	1.942138
16	6	0	-1.30142	-3.57484	2.790264
17	6	0	-0.6932	-3.97329	3.968076
18	6	0	0.537618	-3.40337	4.328153
19	6	0	1.135371	-2.45289	3.516508
20	6	0	0.530887	-2.01801	2.314072
21	6	0	2.199382	-0.2977	-2.26456
22	6	0	3.015019	-0.94292	-3.18239
23	6	0	3.373528	-2.28409	-2.99824
24	6	0	2.870147	-2.91158	-1.85146
25	6	0	2.060621	-2.21674	-0.96518
26	7	0	1.724549	-0.9224	-1.16294
27	6	0	-3.003	1.185827	1.348762
28	6	0	-4.2336	1.772654	1.073785
29	6	0	-4.2803	3.033032	0.464619
30	6	0	-3.051	3.640927	0.174298
31	6	0	-1.86651	2.985476	0.485138
32	7	0	-1.82641	1.76871	1.060382
33	1	0	-3.21006	0.400503	-3.82225
34	1	0	-4.7755	-1.52143	-3.6713
35	1	0	-4.59817	-3.17921	-1.82518
36	1	0	-2.26375	-4.00802	2.530995
37	1	0	1.027439	-3.70644	5.248623
38	1	0	2.091101	-2.01177	3.780213
39	1	0	-1.1669	-4.71282	4.604213
40	1	0	1.887259	0.728033	-2.4014
41	1	0	3.366505	-0.38664	-4.04542
42	1	0	3.10857	-3.94803	-1.63531
43	1	0	1.683052	-2.68023	-0.06559
44	1	0	-2.9514	0.209486	1.824192
45	1	0	-5.14898	1.251154	1.335984
46	1	0	-3.01367	4.619528	-0.29396
47	1	0	-0.90753	3.443639	0.265131
48	6	0	-5.58423	3.703082	0.122824
49	1	0	-5.57745	4.755392	0.422695

50	1	0	-5.75437	3.6773	-0.95981
51	1	0	-6.43045	3.210832	0.607663
52	6	0	4.232565	-3.01735	-3.99142
53	1	0	3.609411	-3.45598	-4.78027
54	1	0	4.945637	-2.34501	-4.47527
55	1	0	4.785916	-3.83231	-3.5183
56	6	0	3.103985	1.233942	1.297368
57	6	0	2.160126	2.665007	-0.25816
58	6	0	4.138592	2.125894	1.540586
59	1	0	3.027025	0.287808	1.819263
60	6	0	3.162399	3.604477	-0.05447
61	1	0	1.359148	2.826695	-0.97154
62	6	0	4.187233	3.353148	0.866238
63	1	0	4.902784	1.862044	2.264893
64	1	0	3.138338	4.531103	-0.61931
65	6	0	5.271845	4.360489	1.137846
66	1	0	4.991013	5.000724	1.982912
67	1	0	6.215032	3.872741	1.398036
68	1	0	5.441298	5.010505	0.275786
69	7	0	2.124686	1.492204	0.407512
70	1	0	-2.89931	-3.69572	0.522126
71	8	0	0.3497	1.439062	2.801378
72	1	0	-0.51279	1.605179	2.372586
73	1	0	0.192944	0.758258	3.467384

Table S24. Cartesian coordinates for $\mathbf{TS_{equatorial}}$.

Center number	Atomic number	Atomic type	Coordinates (Angstroms)		
			X	Y	Z
1	44	0	0.012114	-0.06657	-0.3886
2	8	0	-0.40179	1.00331	-2.11384
3	8	0	-1.196	2.579796	-3.47301
4	8	0	0.435423	-0.96659	1.355806
5	7	0	-1.60171	0.732167	0.446692
6	7	0	-3.20214	1.235108	1.877063
7	6	0	-1.22416	2.000906	-2.39786
8	6	0	-2.22058	2.407367	-1.34457
9	6	0	-3.1414	3.424558	-1.60859
10	6	0	-4.13304	3.786362	-0.68152
11	6	0	-4.26743	3.132377	0.544132
12	6	0	-3.35425	2.113764	0.811401
13	6	0	-2.33608	1.775181	-0.09897
14	6	0	-2.14107	0.403553	1.631043
15	6	0	-1.69212	-0.64987	2.511042
16	6	0	-2.49813	-1.04861	3.603722
17	6	0	-2.08175	-2.01594	4.498615
18	6	0	-0.8206	-2.61238	4.326219
19	6	0	-0.00998	-2.24673	3.266719
20	6	0	-0.4195	-1.27518	2.321612
21	6	0	-2.35561	-1.56723	-1.59279
22	6	0	-3.11859	-2.64274	-2.02818

23	6	0	-2.69457	-3.95325	-1.77816
24	6	0	-1.48387	-4.10141	-1.08653
25	6	0	-0.77056	-2.98306	-0.68382
26	7	0	-1.19693	-1.72679	-0.92402
27	6	0	1.617487	2.561697	-0.70914
28	6	0	2.392101	3.656676	-0.34821
29	6	0	2.798078	3.830083	0.980636
30	6	0	2.386389	2.848107	1.890622
31	6	0	1.61732	1.774385	1.463115
32	7	0	1.225197	1.624369	0.180405
33	1	0	-3.07219	3.923431	-2.56897
34	1	0	-4.82291	4.585988	-0.93044
35	1	0	-5.04902	3.401624	1.246868
36	1	0	-3.48357	-0.6093	3.733056
37	1	0	-0.47951	-3.36913	5.026311
38	1	0	0.967603	-2.69716	3.129366
39	1	0	-2.66165	-0.54823	-1.79354
40	1	0	-4.03827	-2.45092	-2.57126
41	1	0	-1.08754	-5.08784	-0.8678
42	1	0	0.174288	-3.07133	-0.16254
43	1	0	1.287184	2.417653	-1.72982
44	1	0	2.668833	4.37624	-1.11241
45	1	0	2.663167	2.912343	2.938287
46	1	0	1.310756	0.992692	2.14596
47	6	0	3.65265	4.994676	1.4024
48	1	0	3.497781	5.244875	2.454932
49	1	0	4.714943	4.753428	1.274672
50	1	0	3.444826	5.881851	0.798601
51	6	0	-3.50093	-5.14539	-2.21664
52	1	0	-4.07613	-5.54756	-1.37397
53	1	0	-4.20835	-4.88297	-3.00657
54	1	0	-2.85481	-5.94896	-2.58108
55	6	0	3.796777	-0.25268	-1.16214
56	6	0	3.203985	-1.92546	0.281701
57	6	0	5.122744	-0.67218	-1.18638
58	1	0	3.489616	0.620717	-1.73415
59	6	0	4.508763	-2.41558	0.318462
60	1	0	2.417442	-2.3873	0.870726
61	6	0	5.509868	-1.78911	-0.43155
62	1	0	5.846956	-0.13206	-1.78944
63	1	0	4.739818	-3.28271	0.930041
64	6	0	6.934651	-2.27781	-0.42929
65	1	0	7.276185	-2.49305	-1.44726
66	1	0	7.607088	-1.51633	-0.01897
67	1	0	7.047742	-3.18578	0.167308
68	7	0	2.834458	-0.864	-0.44829
69	8	0	0.924443	-1.15285	-2.59646
70	1	0	1.883619	-1.07695	-2.67104
71	1	0	0.544778	-0.3614	-3.02265
72	1	0	-3.72618	1.253748	2.737712
73	1	0	-2.72394	-2.31224	5.320674

Table S25. Cartesian coordinates for **Int_{axial}**.

Center number	Atomic number	Atomic type	Coordinates (Angstroms)		
			X	Y	Z
1	44	0	0.396658	0.025851	-0.58173
2	8	0	0.405688	-1.87871	-1.17401
3	8	0	-0.18279	-4.02083	-1.03011
4	8	0	0.293617	1.99586	-0.66281
5	7	0	-1.64538	0.013495	-0.63256
6	7	0	-3.77424	0.594624	-0.6501
7	6	0	-0.51498	-2.85047	-1.06961
8	6	0	-1.95957	-2.44802	-1.05506
9	6	0	-2.96225	-3.40304	-1.23822
10	6	0	-4.32338	-3.0501	-1.25417
11	6	0	-4.7482	-1.73251	-1.07641
12	6	0	-3.75137	-0.77771	-0.87659
13	6	0	-2.38949	-1.12765	-0.86635
14	6	0	-2.48739	1.044331	-0.51061
15	6	0	-2.09142	2.417978	-0.2683
16	6	0	-3.06365	3.395697	0.038702
17	6	0	-2.72386	4.724372	0.228626
18	6	0	-1.3817	5.115043	0.108447
19	6	0	-0.4038	4.178615	-0.18711
20	6	0	-0.72312	2.817113	-0.37157
21	6	0	1.024717	-1.56105	1.826038
22	6	0	1.062024	-1.89924	3.169138
23	6	0	0.47405	-1.06571	4.131703
24	6	0	-0.13774	0.103101	3.659994
25	6	0	-0.15423	0.390937	2.302944
26	7	0	0.420595	-0.42728	1.39394
27	1	0	-2.65985	-4.43479	-1.37984
28	1	0	-5.06609	-3.8248	-1.41319
29	1	0	-5.80127	-1.47207	-1.09301
30	1	0	-4.10461	3.104137	0.146479
31	1	0	-1.10415	6.155213	0.248064
32	1	0	0.63685	4.46722	-0.29036
33	1	0	-3.49046	5.453274	0.467669
34	1	0	1.459426	-2.19422	1.063173
35	1	0	1.55406	-2.82225	3.458211
36	1	0	-0.60861	0.799208	4.346372
37	1	0	-0.62509	1.288815	1.921352
38	6	0	0.48142	-1.42454	5.59179
39	1	0	-0.30757	-2.1558	5.80518
40	1	0	1.431799	-1.87957	5.883919
41	1	0	0.303787	-0.55058	6.222446
42	6	0	3.222851	1.176314	-0.39441
43	6	0	3.205224	-0.95347	-1.31123
44	6	0	4.597121	1.272685	-0.55412
45	1	0	2.639823	1.99024	0.02012
46	6	0	4.579993	-0.91734	-1.50022
47	1	0	2.607406	-1.81389	-1.59176
48	6	0	5.317471	0.212241	-1.12228
49	1	0	5.103357	2.178694	-0.2364

50	1	0	5.071101	-1.77663	-1.9456
51	6	0	6.803517	0.296111	-1.33983
52	1	0	7.01753	0.749465	-2.3154
53	1	0	7.285195	0.915931	-0.57914
54	1	0	7.266703	-0.69361	-1.33021
55	7	0	2.525519	0.079707	-0.76442
56	1	0	-4.5934	1.181869	-0.67255

Table S26. Cartesian coordinates for **$Int_{equatorial}$**.

Center number	Atomic number	Atomic type	Coordinates (Angstroms) X	Y	Z
1	44	0	-0.00123	-0.15283	-0.96643
2	8	0	0.003389	-2.154	-0.93349
3	8	0	0.011845	-4.20184	-0.06179
4	8	0	-0.00599	1.819251	-1.17698
5	7	0	0.001507	0.032624	0.98086
6	7	0	0.002272	0.79975	3.037032
7	6	0	0.007936	-2.99553	0.105382
8	6	0	0.007885	-2.43012	1.506955
9	6	0	0.011104	-3.29834	2.601322
10	6	0	0.011344	-2.826	3.926698
11	6	0	0.008542	-1.4639	4.228255
12	6	0	0.005364	-0.58762	3.143108
13	6	0	0.004966	-1.06288	1.819193
14	6	0	-0.00013	1.153602	1.711726
15	6	0	-0.0036	2.504515	1.183535
16	6	0	-0.00436	3.607316	2.067229
17	6	0	-0.00766	4.912468	1.606182
18	6	0	-0.01032	5.15496	0.223118
19	6	0	-0.00963	4.098648	-0.67185
20	6	0	-0.00625	2.755358	-0.23024
21	6	0	2.722847	-1.31016	-1.63751
22	6	0	4.096851	-1.39079	-1.80696
23	6	0	4.926592	-0.34457	-1.38117
24	6	0	4.293088	0.758815	-0.79416
25	6	0	2.912918	0.782021	-0.65631
26	7	0	2.12662	-0.23474	-1.07092
27	6	0	-2.72356	-1.32403	-1.62293
28	6	0	-4.0986	-1.41304	-1.78199
29	6	0	-4.93052	-0.36793	-1.35886
30	6	0	-4.29912	0.739644	-0.77667
31	6	0	-2.91847	0.770933	-0.64874
32	7	0	-2.12927	-0.24314	-1.06544
33	1	0	0.013433	-4.36329	2.397172
34	1	0	0.013805	-3.54406	4.740016
35	1	0	0.008822	-1.11147	5.254334
36	1	0	-0.00223	3.440085	3.140564
37	1	0	-0.01292	6.174685	-0.14922
38	1	0	-0.01164	4.265758	-1.7438
39	1	0	-0.00815	5.737369	2.31016

40	1	0	2.062716	-2.1146	-1.94057
41	1	0	4.515038	-2.27742	-2.27254
42	1	0	4.870612	1.608954	-0.44578
43	1	0	2.4121	1.635054	-0.21684
44	1	0	-2.06177	-2.12831	-1.92281
45	1	0	-4.51575	-2.30718	-2.23383
46	1	0	-4.87941	1.584842	-0.42074
47	1	0	-2.41964	1.625861	-0.21075
48	6	0	-6.42215	-0.42368	-1.54157
49	1	0	-6.94037	0.197721	-0.80723
50	1	0	-6.69428	-0.0541	-2.53776
51	1	0	-6.79562	-1.44771	-1.46054
52	6	0	6.421528	-0.41634	-1.52796
53	1	0	6.854398	-1.00571	-0.71057
54	1	0	6.705278	-0.90407	-2.46447
55	1	0	6.877286	0.576033	-1.49873
56	1	0	0.000993	1.447254	3.809375

Full reference 69 (Gaussian). Gaussian 09, Revision A.1: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2009**.

Supporting References

S1 M. D. Kärkäs, T. Åkermark, E. V. Johnston, S. R. Karim, T. M. Laine, B.-L. Lee, T. Åkermark, T. Privalov and B. Åkermark, *Angew. Chem. Int. Ed*., 2012, **51**, 11589–11593.

S2 E. Dulière, M. Devillers and J. Marchand-Brynaert, *Organometallics*, 2003, **22**, 804–811.

S3 R. E. DeSimone and R. S. Drago, *J. Am. Chem. Soc*., 1970, **92**, 2343–2352.