Supporting information

for

Strategic design of a ruthenium catalyst for both CO_2 reduction and H_2O oxidation: the electronic influence of the co-ligands

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Experimental Section

Commercially available reagents were used as received from Sigma Aldrich and Fisher chemicals. Solvents were taken from an Innovative Technology Pure Solvent Dispenser immediately prior to use. Anhydrous acetonitrile from the dispenser was kept over 3 Å molecular sieves overnight under high purity argon before use in cyclic voltammetry. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded using Bruker DPX 300, Bruker Avance III 500 or Bruker Avance III 600 spectrometers. High-resolution positive-mode ESI mass spectra were acquired on a Thermo-Fisher Orbitrap LTQ XL ion trap mass spectrometer using a nanospray ionisation source. Cyclic voltammograms were measured using a Pine AFCBP1 bipotentiostat. Potentials given in the text are relative to a non-leaking Ag/AgCl reference electrode. A freshly polished 1 mm diameter glassy carbon working electrode and a platinum-coated titanium bullet counter electrode were employed in all measurements. The UV-Vis-NIR spectra were recorded with a Varian Cary 50 UV/Vis spectrometer. Full details of the methods for the electrochemical experiments can be found in our previous reports.[1,2]

The precursors [(^{Bu}tpy)RuCl$_2$],[3] [Ru(Cl$_2$)(DMSO)$_4$],[4] phenCO$_2$H,[5] ^{NO2}tpy [6] and [(^{NO2}tpy)RuCl$_2$] [7] were prepared by using literature procedures.

Synthesis of [(^{Bu}tpy)Ru(phenCO$_2$)][PF$_6$] (**1**)

Complex **1** was prepared by heating [(^{Bu}tpy)RuCl$_2$ (0.1 g, 0.174 mmol) with phenCO$_2$H (0.043 g, 0.191 mmol, 1.1 equivalent) and triethylamine (0.25 mL, 1.8 mmol) at reflux in 30 mL ethanol-water (4:1) solvent mixture. The reaction was monitored by TLC. After 6 h, saturated aqueous K[PF$_6$] (0.5 mL) was added. Upon cooling, a maroon precipitate formed, which was collected by filtration and washed with 5 mL of ice-cold water. The resulting powder was recrystallised by slow diffusion of diethylether in to a concentrated acetonitrile solution of it, and afforded glinting maroon crystals of **1** (0.093 g, 61%): ^{1}H-NMR (400 MHz, methanol-d_4) shows the presence of **1** and solvato species with 5:1 ratio: δ 8.99 (s, 0.4H), 8.96 (s, 2H), 8.86 (d, 1H), 8.75 (d, 0.8H), 8.73 (d, 2.3H), 8.69 (d, 1H), 8.56 (d, 0.8H), 8.48 (d, 1H), 8.43 (s, 0.8H), 8.37 (d, 1H), 8.28 (d, 1H), 7.54 (m, 1.8H), 7.41 (m, 1H), 7.23 (m, 3H), 7.15 (d, 2H), 1.78 (s, 1.8H), 1.77 (s, 9H), 1.36 (s, 18H), 1.35 (s, 3.6H); (+)-ESI-MS (in MeOH): calcd. for *m/z* 726.23

([(^{Bu}tpy)Ru(PhenCO$_2$)]$^+$), found 726.42; HRMS (in MeOH): calcd. *m/z* 726.2377 ([(^{Bu}tpy)Ru(PhenCO$_2$)]$^+$), found 726.2371; Elemental anal. calcd. for $C_{40}H_{42}F_6N_5O_2PRu$ ([(^{Bu}tpy)Ru(PhenCO$_2$)](PF6)) : C, 55.17; H, 4.86; N, 8.04%; Found: C, 54.91; H, 5.30; N, 7.81%.

Synthesis of [(^{NO2}tpy)Ru(Cl)(PhenCO$_2$H)][PF$_6$] (**2**)

Complex **2** was prepared by refluxing a 25mL ethanol-water (4:1) solution of [(^{NO2}tpy)RuCl$_2$] (0.075 g, 0.139 mmol), phenCO$_2$H (0.032 g, 0.141 mmol) and triethylamine (0.3 mL, 2.15 mmol) for 5 h. The reaction was monitored by TLC. Addition of saturated aqueous K[PF$_6$] (1 mL), followed by cooling to room temperature did not cause any immediate precipitation. The solvent was evaporated to afford a tacky blue violet compound, which was washed with ice-cold water (2 x 5 mL). After drying under vacuum, the compound was dissolved in minimum amount of DCM-methanol (2:1). The solution was passed through a 50 cm neutral silica column using 20:1:1 DCM: MeOH: Et$_3$N as eluent. The pure compound (**2**) was collected from the column as the last compound, and dried overnight under vacuum to get a blue violet product (0.022 g, 18%). Upon attempted re-crystallization, **2** was observed to slowly decompose as evidenced by growth of new peaks in NMR spectra. A satisfactory partial elementary analysis (for C, H, N) therefore could not be obtained, but the complex was fully characterized by ^{1}H NMR, ^{13}C NMR, (+)-ESI-MS (with proper isotope pattern) and HRMS techniques. The ^{1}H NMR spectrum reveals **2** exists as the mixture of two isomers (7:3 ratio), which possibly makes the complex further difficult to crystallize. Inseparable peaks (due to overlap) of the isomers in NMR spectra were integrated together. ^{1}H-NMR (400 MHz, methanol d_4): δ 10.40 (dd, 0.39 H), 10.39 (dd, 1H), 9.51 (d, 1H), 9.40 (m, 0.1H), 9.35 (s, 0.75H), 9.34 (d, 1H), 8.95 (dd, 1H), 8.92 (m, 0.22H), 8.88 (m, 0.76H), 8.37 (m, 2.76H), 8.31 (m, 2.32H), 8.18 (m, 1.39H), 7.89 (m, 1.5H), 7.32 (m, 0.8H), 7.28 (d, 0.45H), 7.27 (d, 0.4H), 7.22 (m, 1.4H), 7.01 (d, 1H), 6.78 (dd, 1H); ^{13}C NMR(400 MHz, CD$_3$OD): δ = 171.5, 167.7, 165.5, 165.2, 164.8, 164.4, 163.9, 160.5, 160.2, 159.9, 159.7, 159.2, 155.3, 154.0, 152.7, 151.8, 150.2, 149.1, 139.6, 138.3, 133.5, 131.9, 130.4, 129.4, 127.8, 127.0, 126.3, 125.7, 123.3, 122.1 ppm. ESI-MS (in MeOH run after 5 min.): calcd. for *m/z* = 728.98 ([(^{NO2}tpy)Ru(Cl)(PhenCO$_2$H)]$^+$) and 750.96 ([(^{NO2}tpy)Ru(Cl)(phenCO$_2$)(Na)]$^+$), found 728.75 and 750.67; HRMS (in MeOH, service spectrum run after standing 24 h in solution): calcd. *m/z* 728.01839 ([(^{NO2}tpy)Ru(OH)(phenCO$_2$)(H$_2$O)]$^+$), found 728.02234.

X-ray crystallography

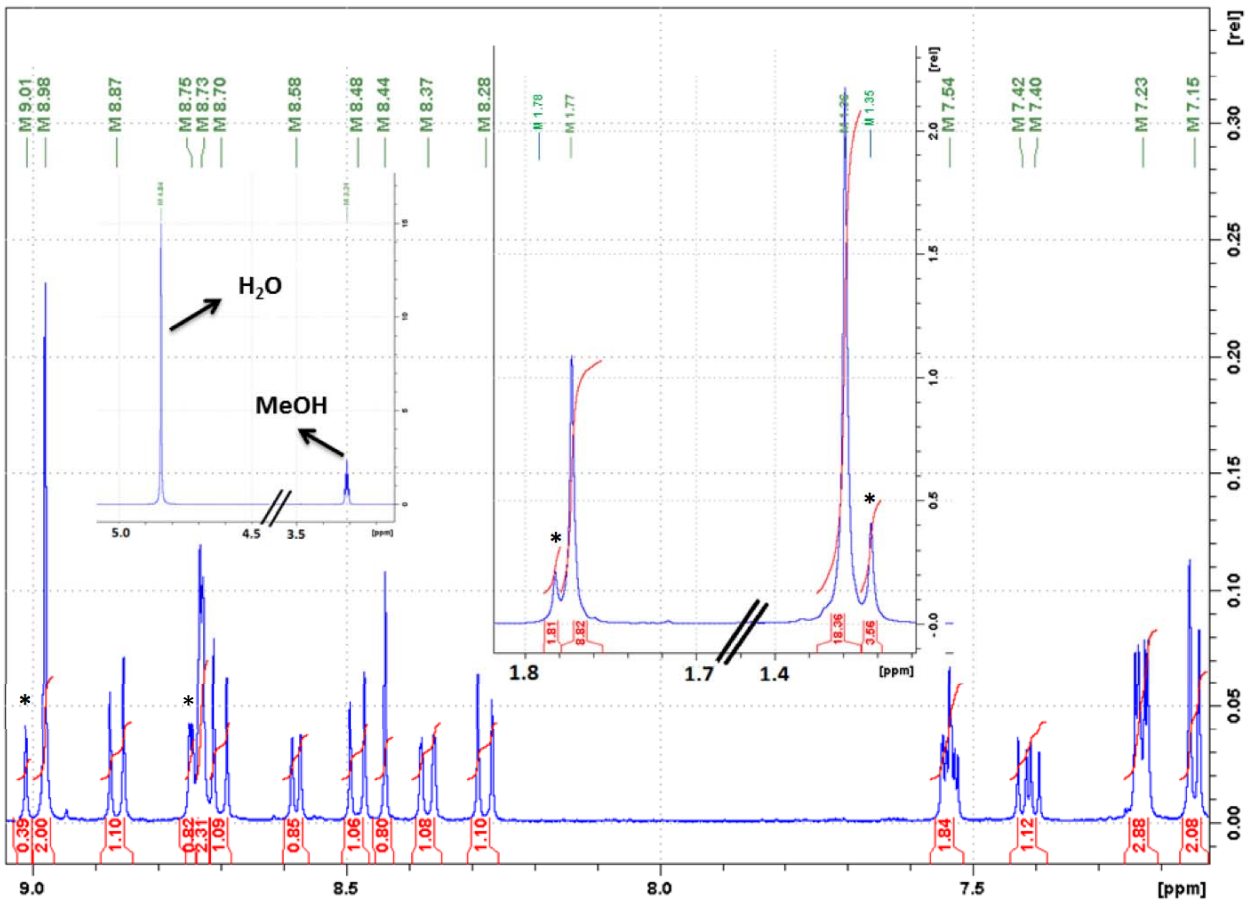
A dark red crystal of **1** was mounted on a Bruker Kappa-II CCD diffractometer at 150 K using a IμS Incoatec Microfocus Source with Mo-Kα radiation (λ = 0.710723 Å). Symmetry related absorption corrections using the program SADABS[1] were applied and the data were corrected for Lorentz and polarisation effects using Bruker APEX3 software.[8] The structure was solved by program SHELXT[9] (with intrinsic phasing) and the full-matrix least-square refinements were carried out using SHELXL-2014[10] through Olex2[11] suite of software.

Crystal data for **1**: $C_{40}H_{42}N_5O_3RuF_6P$, monoclinic , $P2_1/n$, a = 20.1625(9), b = 9.8756(5), c = 20.9277(11) Å, β = 109.407(2) °, V = 3930.3(3) $Å^3$, z = 4, D_c = 1.499 g cm^{-3}, $\mu(mm^{-1})$ = 0.513, F_{000} = 1816.0, Theta(max)= 26.98°, Final results (586 parameters, number of restraints 248): $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S: 0.048, 0.140, 1.07; CCDC No. 1557957.

Computational details

The standalone functional B97D3 (as implemented in the Gaussian09 package) was used throughout to optimize the geometries and for calculation of frequencies.[12] For geometry optimizations, the SDD pseudo-potential was used for the ruthenium atom and the 6-31G(d,p) basis set for all other atoms. Solvation effects were evaluated using the SMD model on the optimized geometries at the same level of theory as the geometry optimizations using the IEFPCM calculation with acetonitrile as the surrounding solvent. The views of the HOMO levels were drawn using GaussView software at appropriate isovalues (0.026 and 0.018, see Fig. 5).[13]

a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M 7.15
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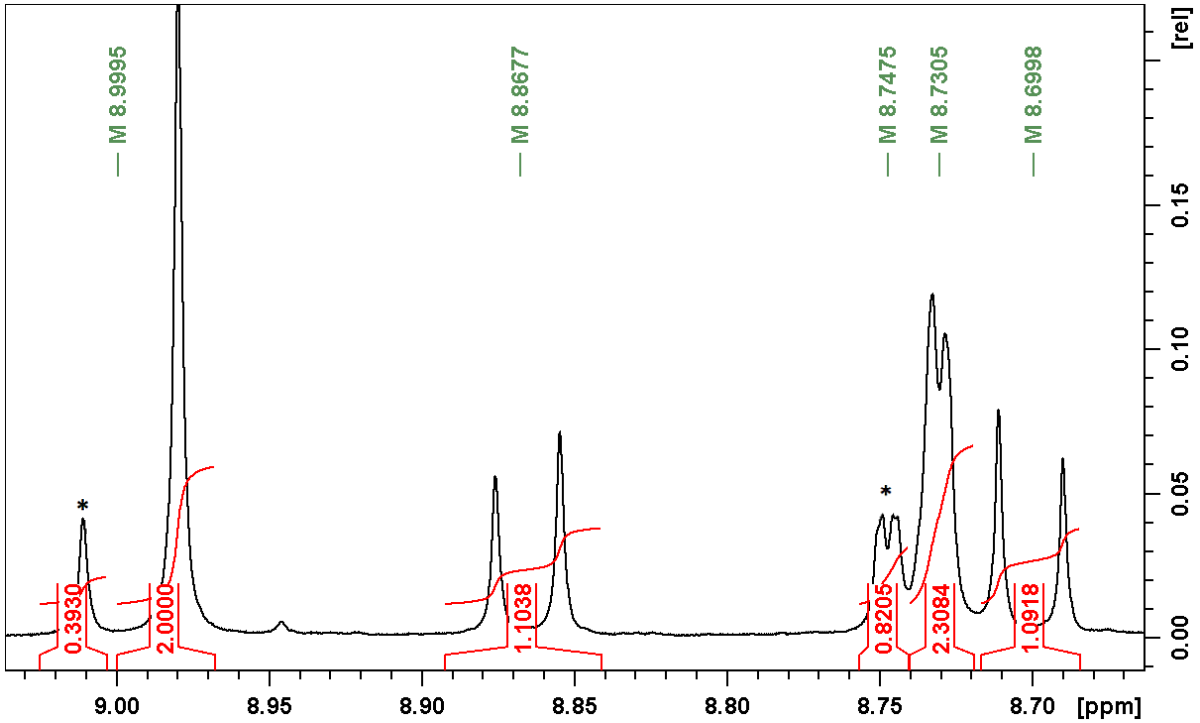
[ppm]

b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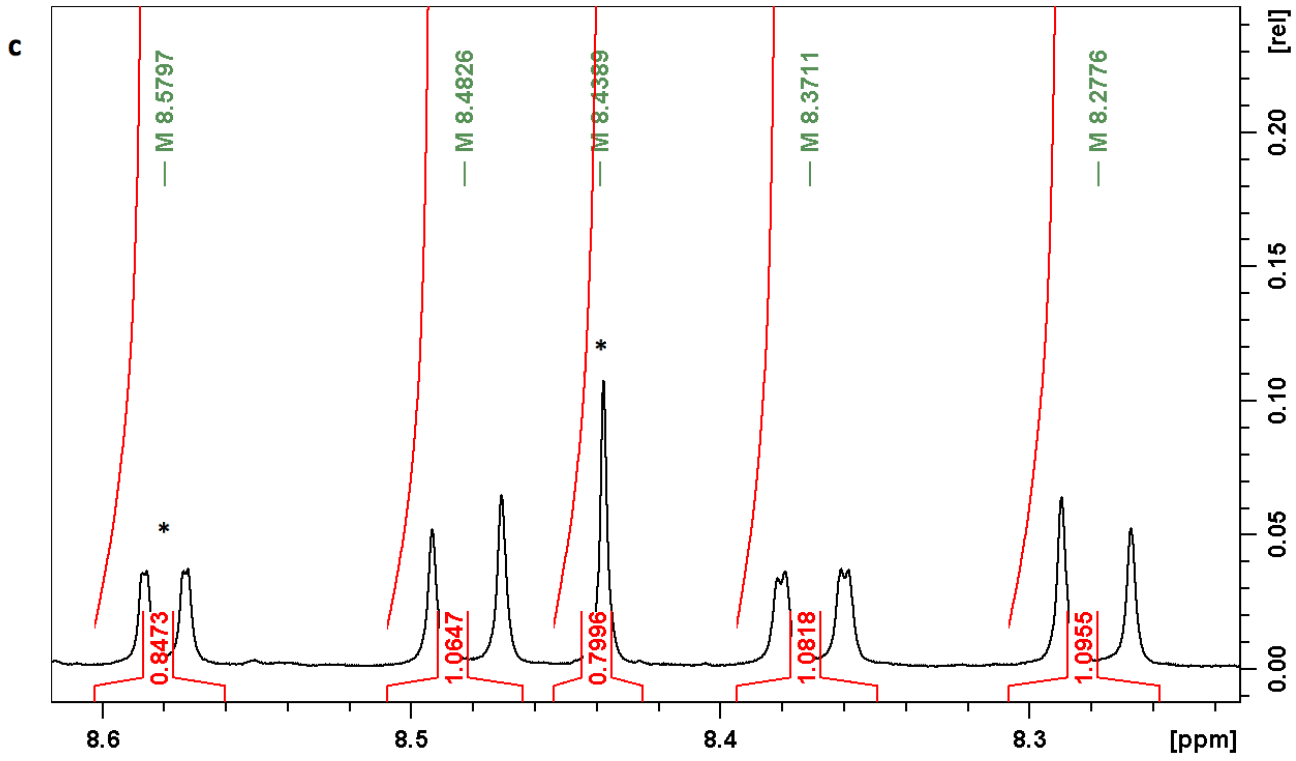
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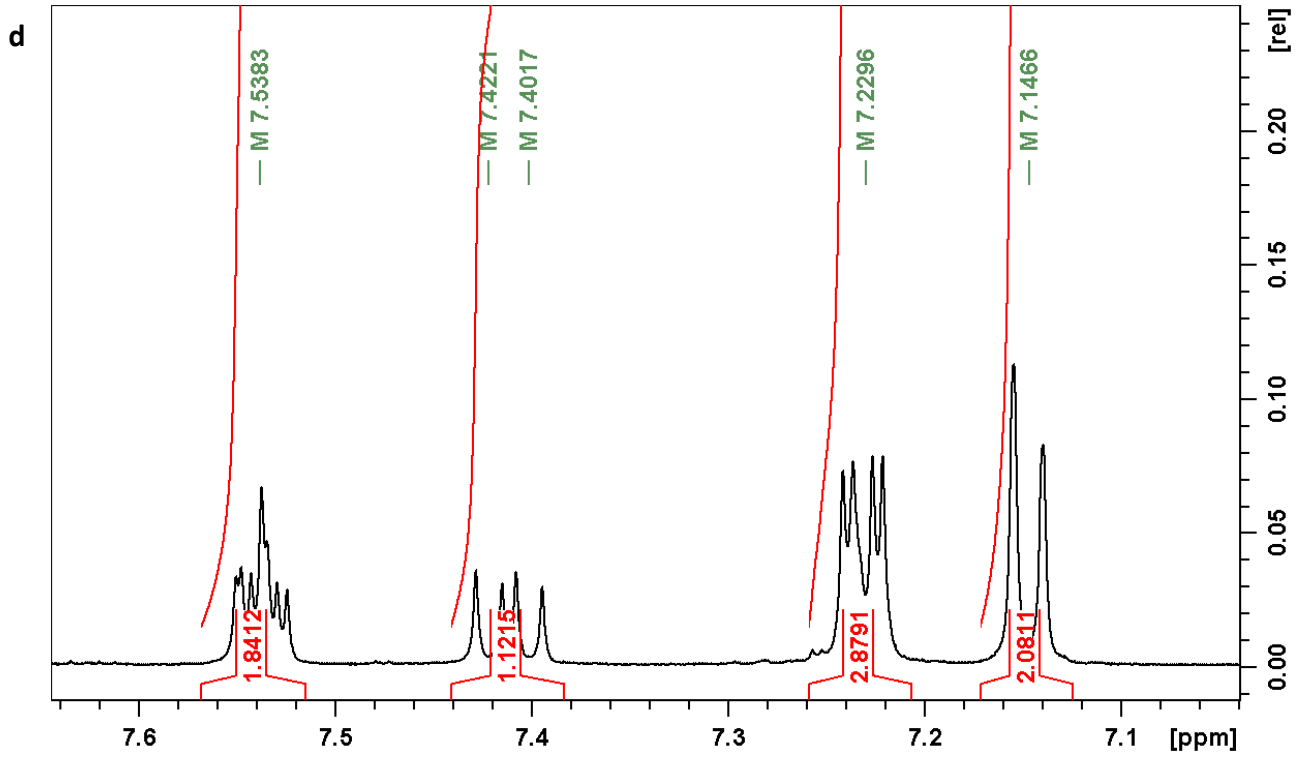
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7.2
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[ppm]
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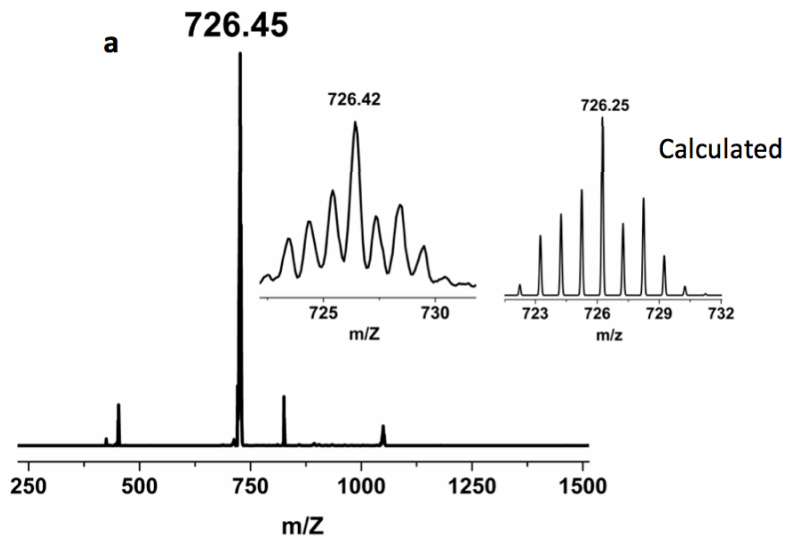
0.20
[rel]

Figure S1. (a) 400 MHz ^{1}H NMR spectrum of **1** (crystalline) dissolved in CD_3OD. The inset shows the signal for the *t*-butyl protons, water and methanol. Spectra (b) to (d) are expansions over the aromatic region. Some solvolysis of complex **1** to give the corresponding solvato species is apparent, and easily discerned peaks for the solvato species are marked with an asterisk in the above spectra (*).



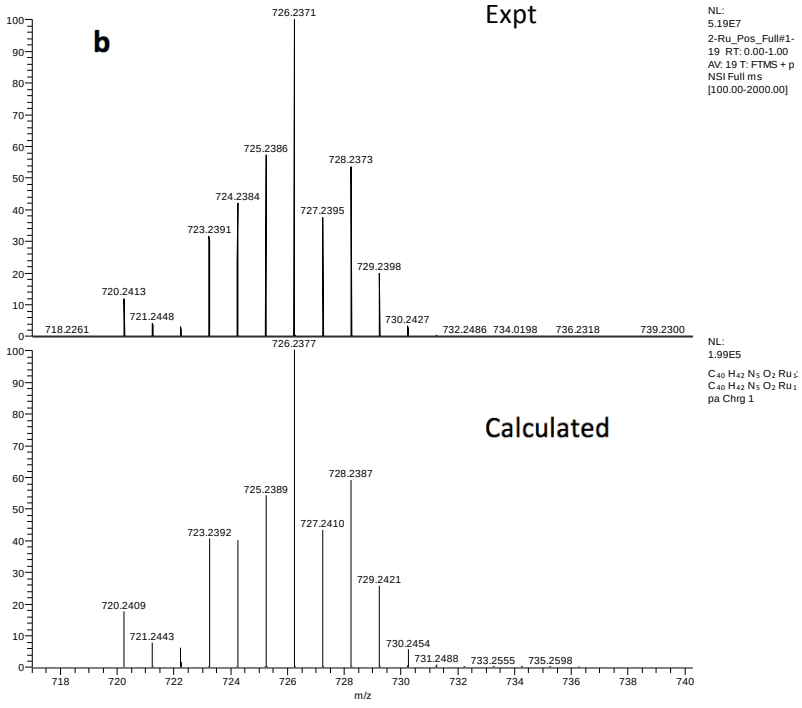


Figure S2. (a) (+)-ESI-MS spectrum of **1** in MeOH; the inset shows the isotope pattern [experimental (left) and calculated (right)] of the major peak ([(^{tBu}tpy)Ru^{II}(phenCO$_2$)]$^+$). (b) the (+)-HRMS spectrum of **1** [(experimental (top) and calculated (bottom)].

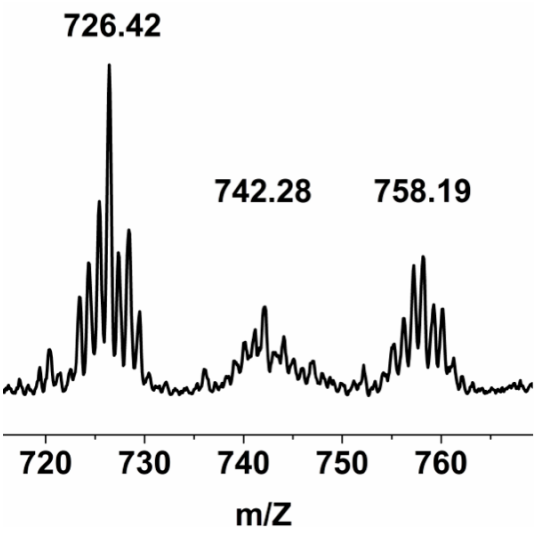


Figure S3. Expansion of the (+)-ESI-MS spectrum of **1** in acetonitrile approx. 1 min. after addition of 15 equiv. of *m*CPBA.

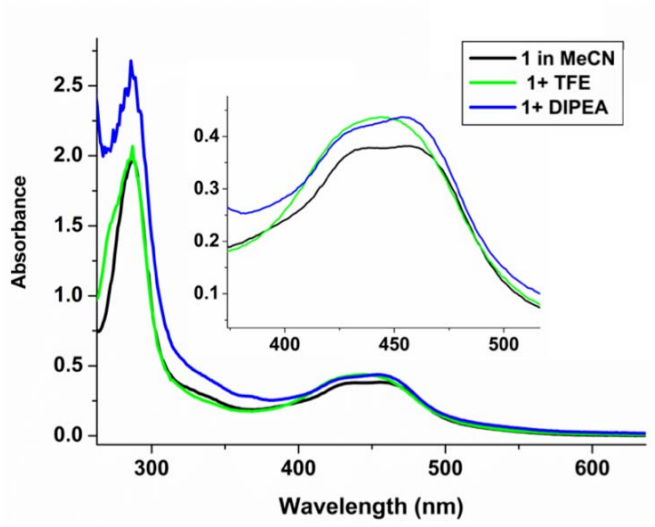


Figure S4. UV-Vis spectra of **1** in MeCN (black trace), in MeCN + TFE (0.32 M) (green trace), in MeCN + DIPEA (0.15 M) (blue trace).

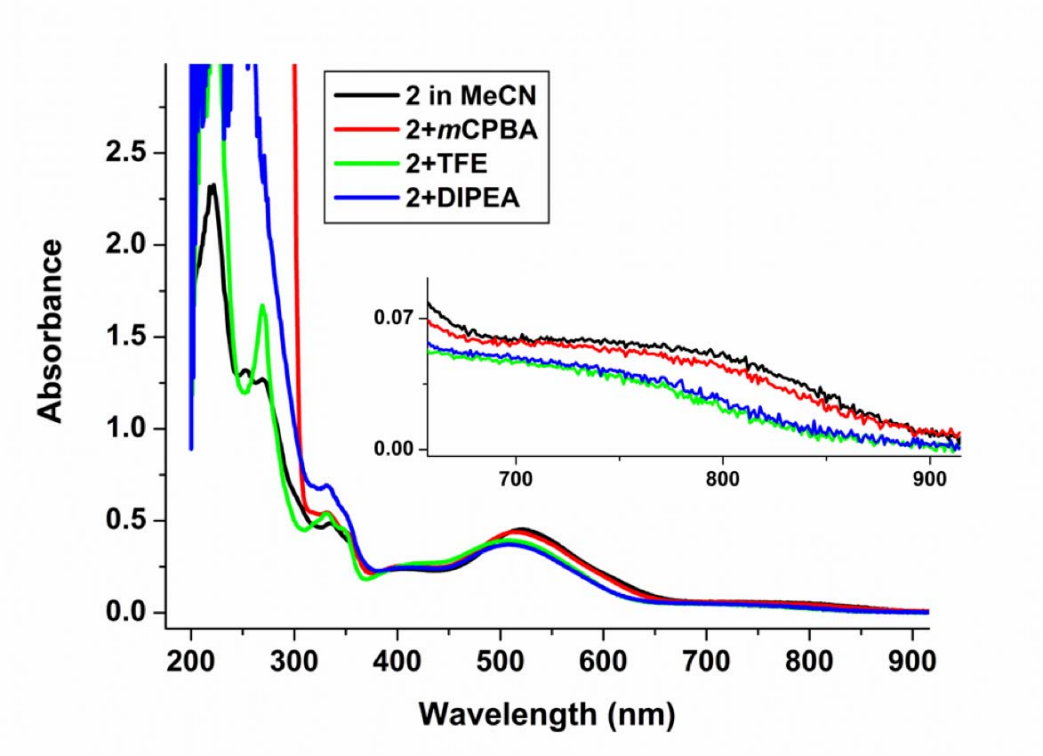
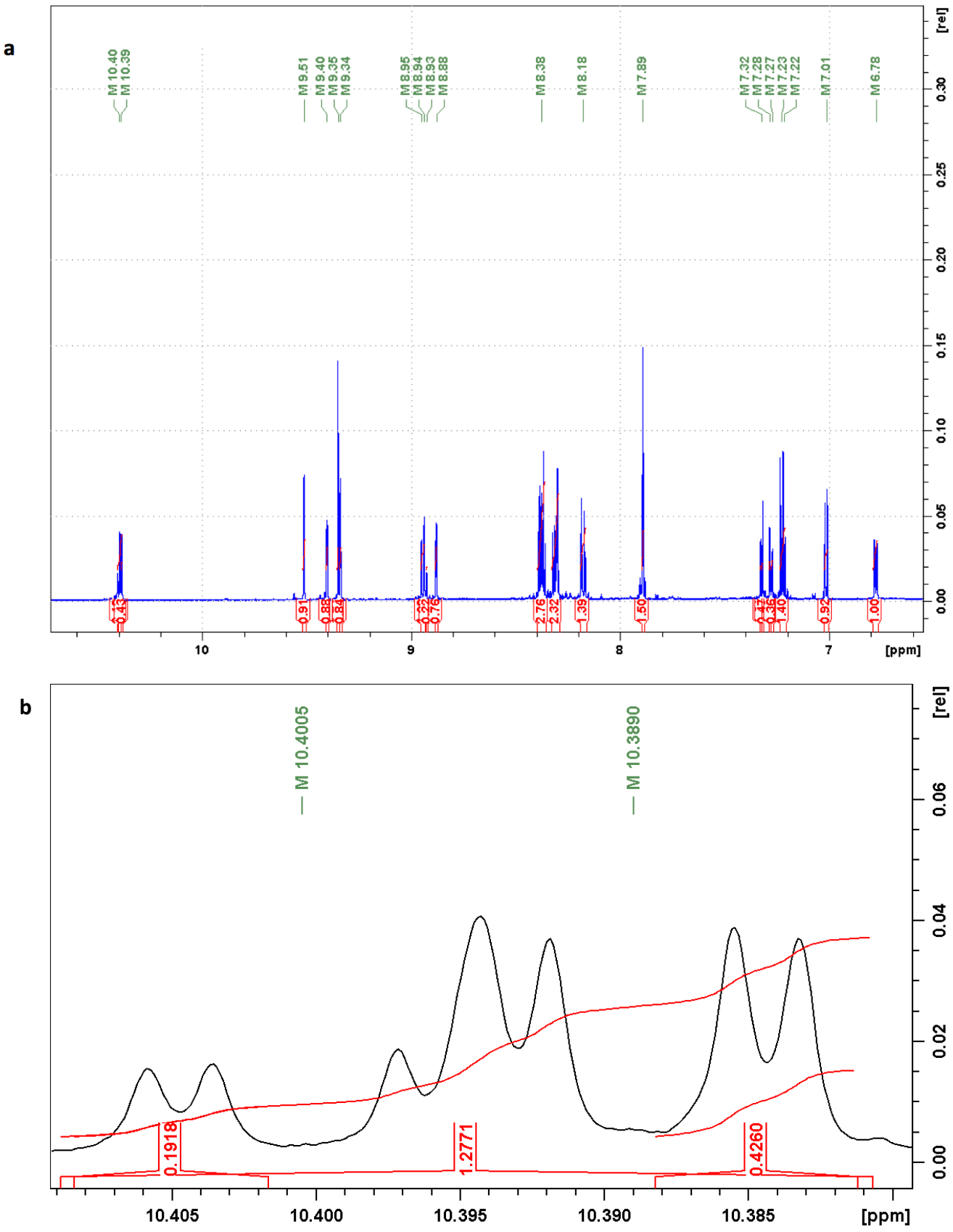


Figure S5. UV-Vis-NIR spectra of **2** (0.2 mM) in acetonitrile (black trace), and after adding 15 eq. of *m*-CPBA (red trace), after adding TFE (0.32 M, green trace) and after adding DIPEA (0.30 M, blue trace). Inset shows magnified Vis-NIR spectra.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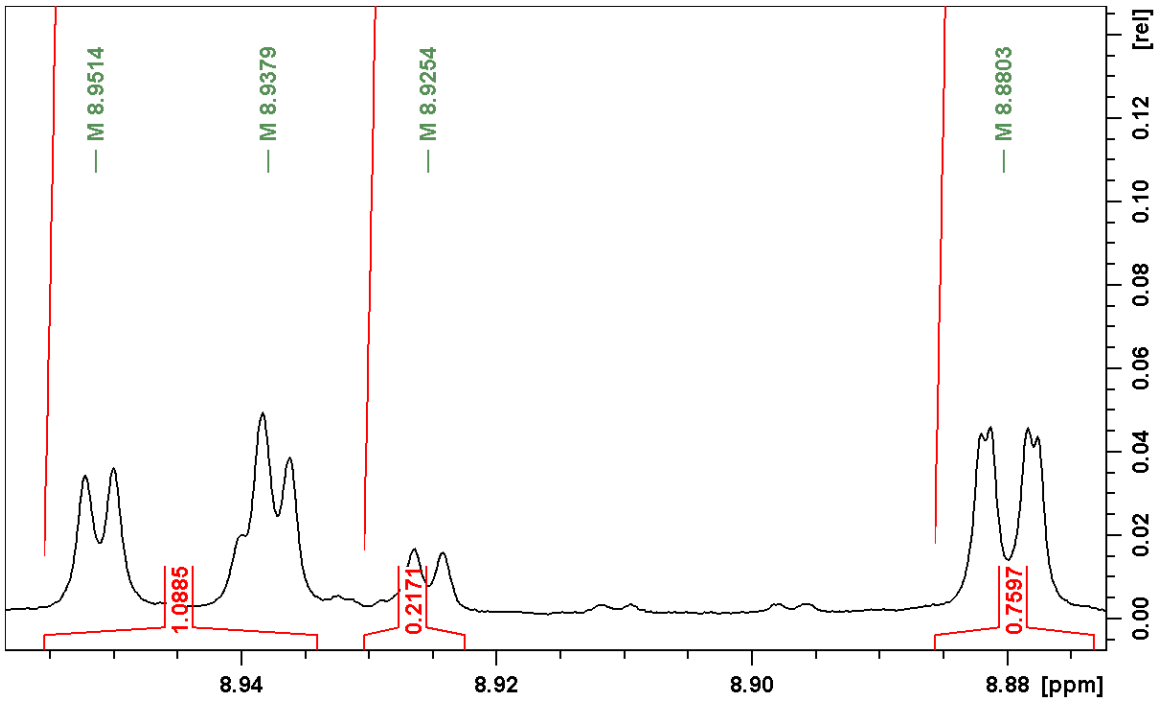
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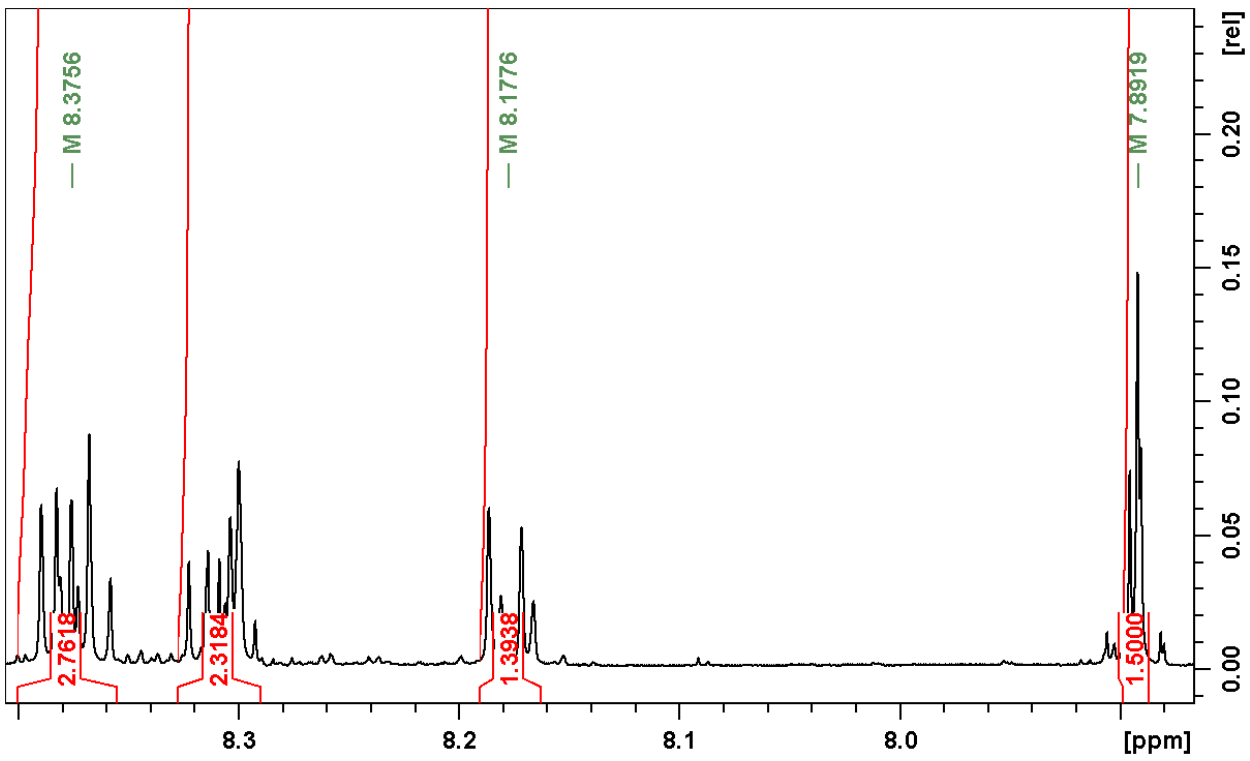
[ppm]

d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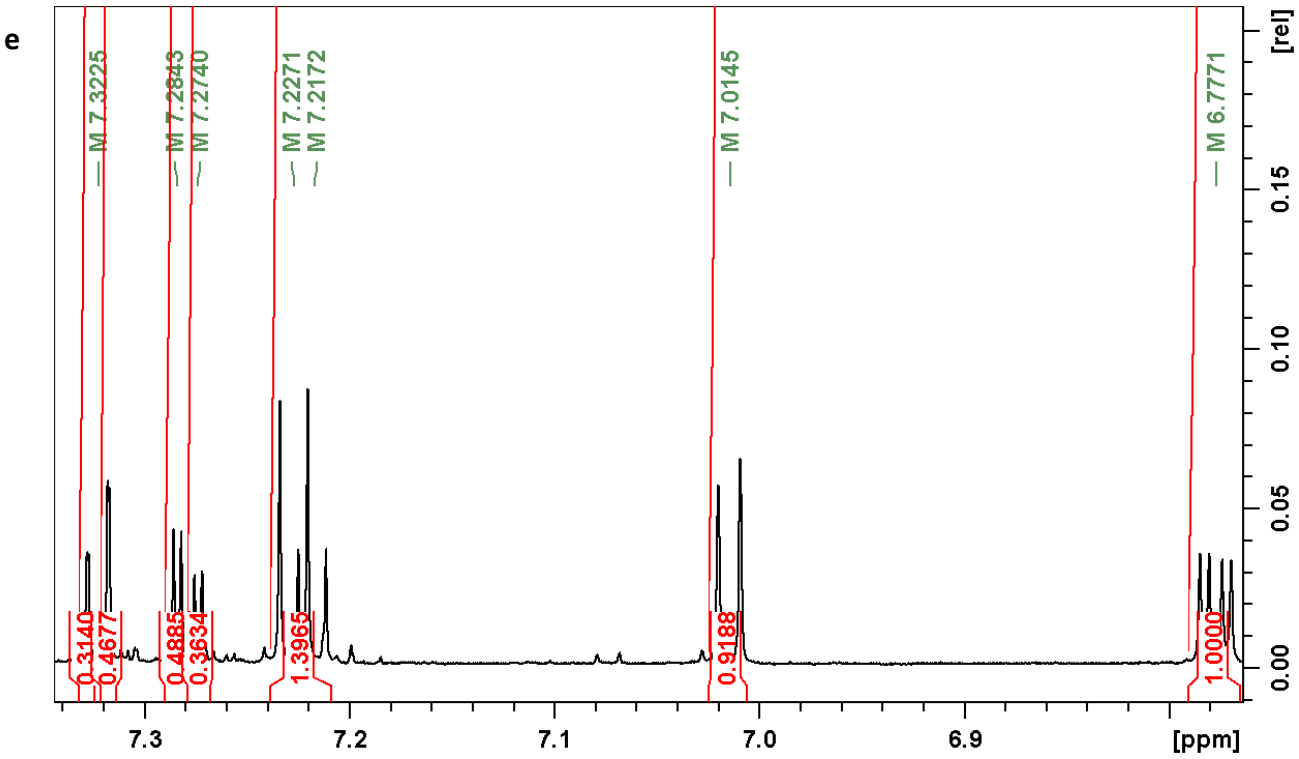


Figure S6. (a) - (e) Plots for the aromatic protons (including expansions) from the 600 MHz ^{1}H NMR spectrum of **2** in CD_3OD.

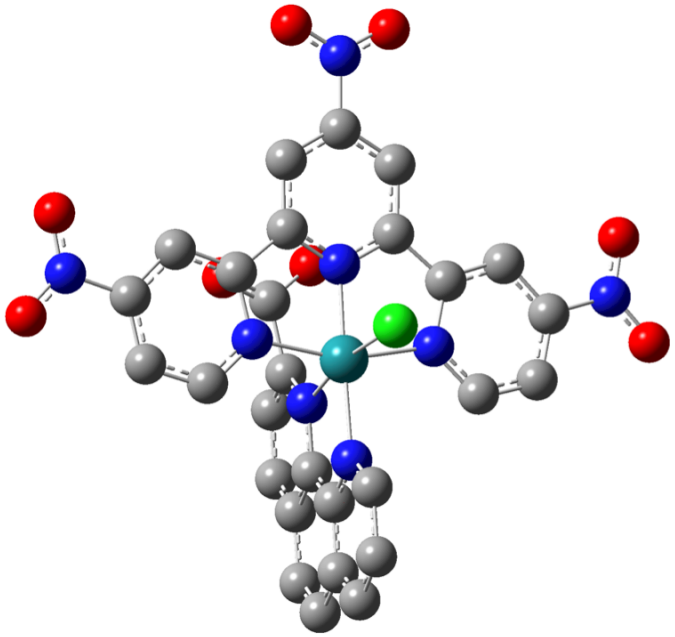


Figure S7. DFT optimized model for *anti*-[(^{NO2}tpy)Ru(Cl)(phenCO_2H)] (**2**).

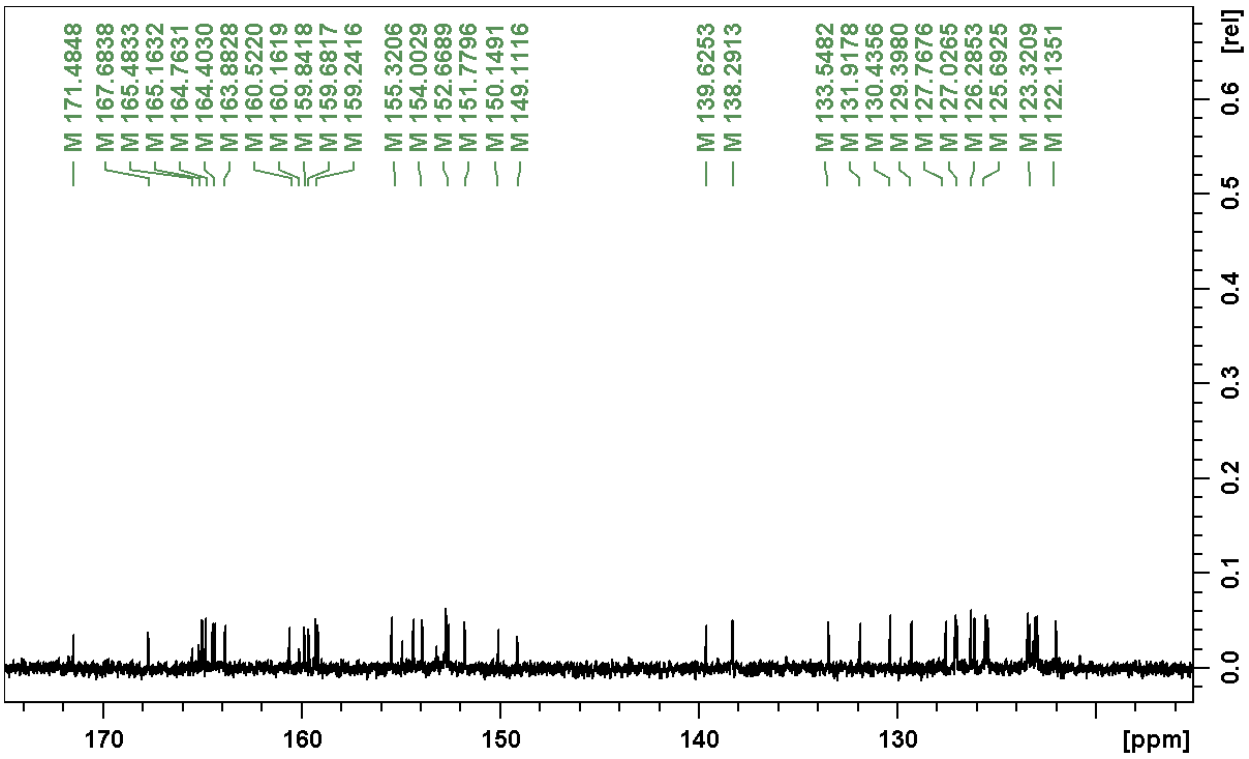


Figure S8. 400 MHz $^{13}C\{^{1}H\}$ NMR spectrum of **2** in CD_3OD over the aromatic region revealing aromatic C atoms consistent of having both the isomers present.

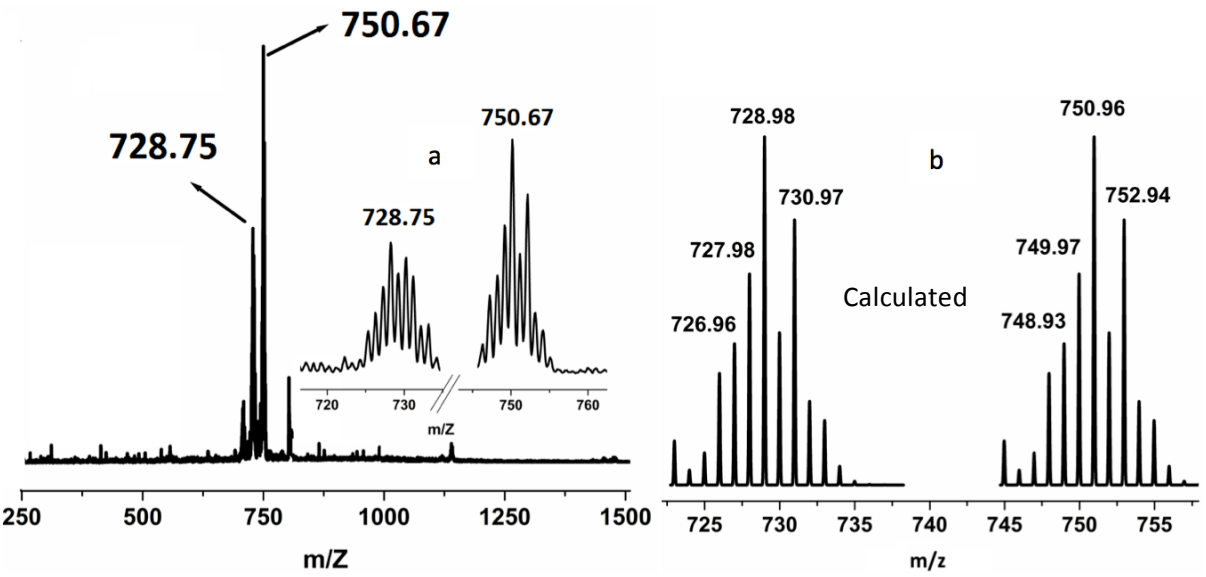


Figure S9. (+)-ESI-MS spectrum of freshly prepared complex **2** in MeOH. Inset: (a) the major peak envelopes at *m/z* 728.75 and 750.67 correspond to $[(^{NO2}tpy)Ru(phenCO_2H)(Cl)]^+$ and $[(^{NO2}tpy)Ru(phenCO_2)(Cl)+Na]^+$, respectively (see text). (b) Calculated isotope patterns for $[(^{NO2}tpy)Ru(phenCO_2H)(Cl)]^+$ (left) and $[(^{NO2}tpy)Ru(phenCO2)(Cl)+Na]^+$ (right).

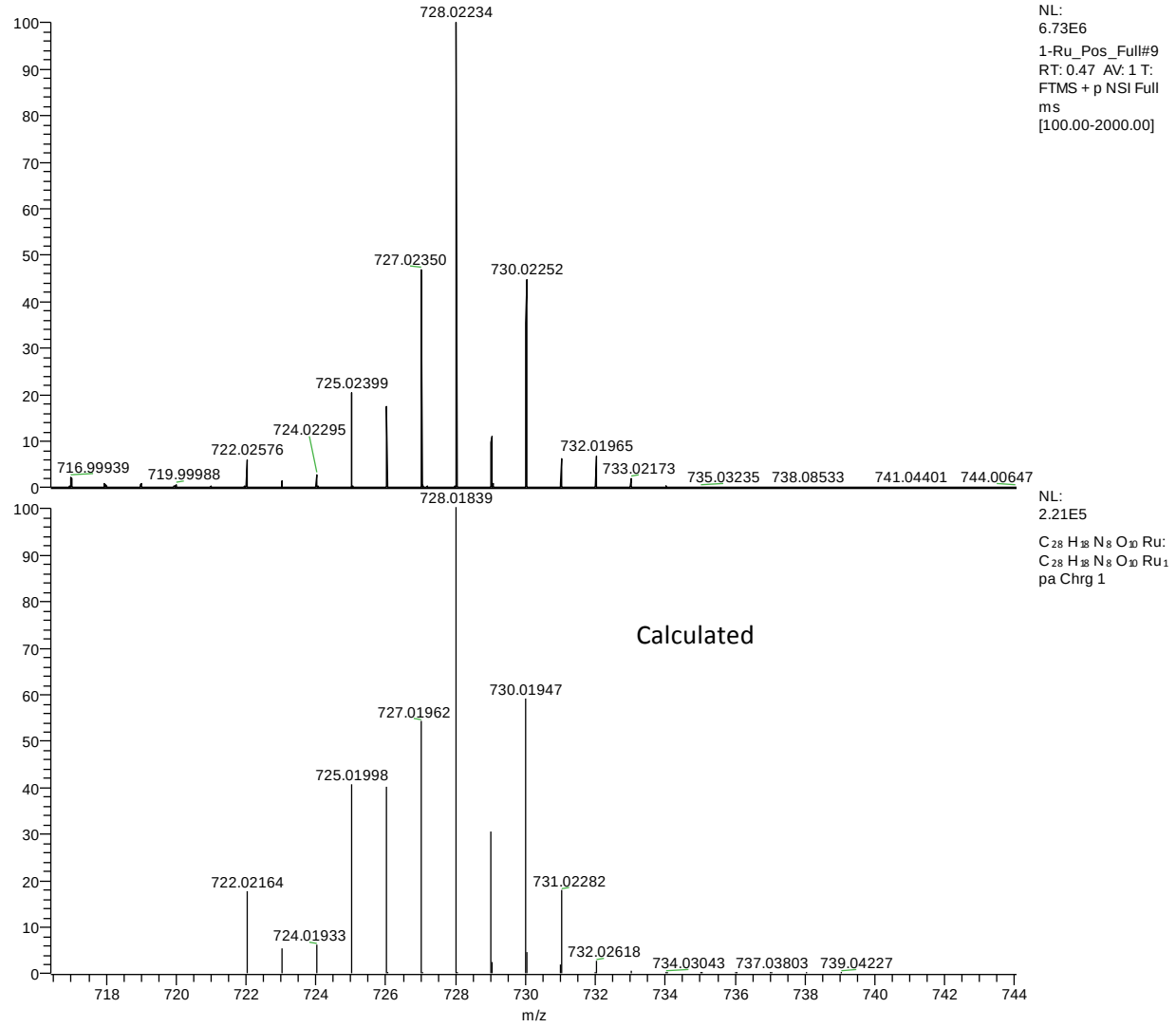


Figure S10. (+)-HRMS spectrum of of **2** in methanol solution kept overnight shows a peak envelop that corresponds to $[(^{NO2}tpy)Ru(OH)(phenCO_2)(H_2O)]^+$)

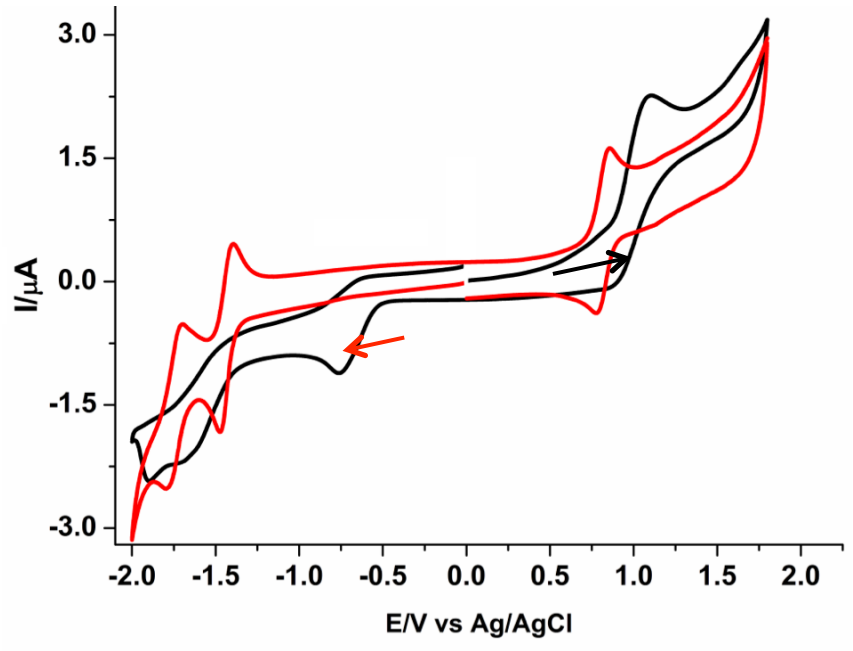


Figure S11. Cyclic voltammograms of **1** (1 mM, red trace) and **2** (1 mM, black trace) recorded in acetonitrile–0.1M $TBAPF_6$ at 100 mV/s scan rate and 295 K using a glassy carbon minidisk working electrode against a Ag/AgCl reference electrode.

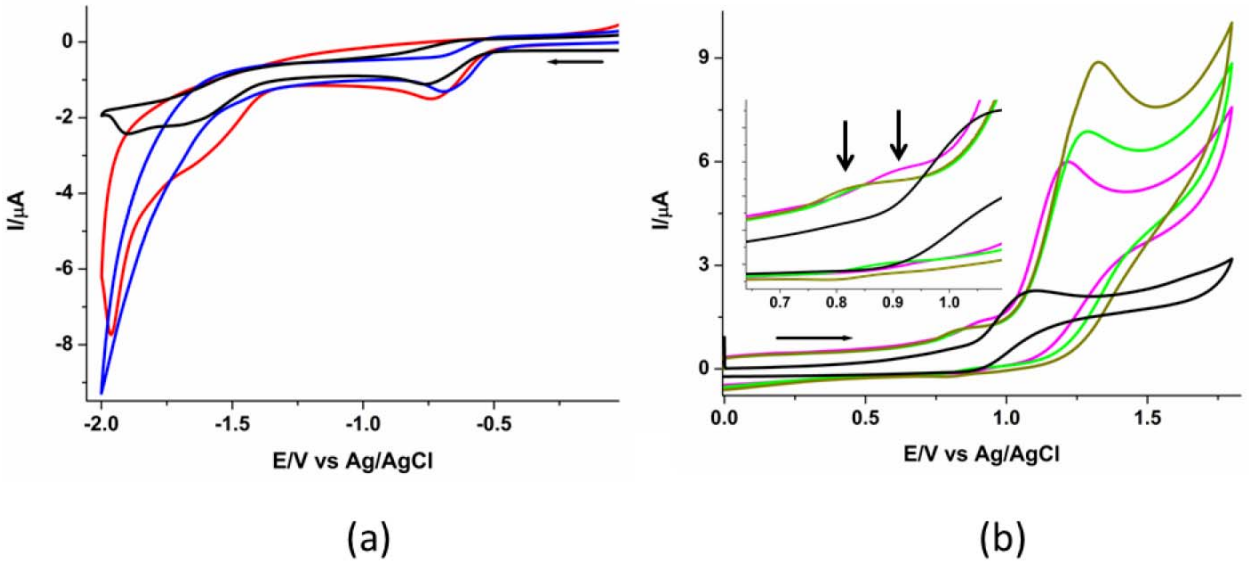


Figure S12. Electrocatalytic responses for complex **2**. (a) CO_2 reduction: CVs of **2** in MeCN–$TBAPF_6$ (0.1 M) under N_2 (black trace), under saturated CO_2 (red trace), and with 1.8 M water under saturated CO_2 (blue trace). (b) Water oxidation. CVs of **2** in in MeCN–$TBAPF_6$ (0.1 M) with different concentrations of water under N_2: no water (black trace), 1.5 M (pink trace), 2.1 M (green trace) and 3.0 M (dark yellow trace) water. The inset to (b) reveals growth of an anodic wave for oxidation of a new species as water is added, which is suggested to be an aqua complex that is oxidized at the new peak.

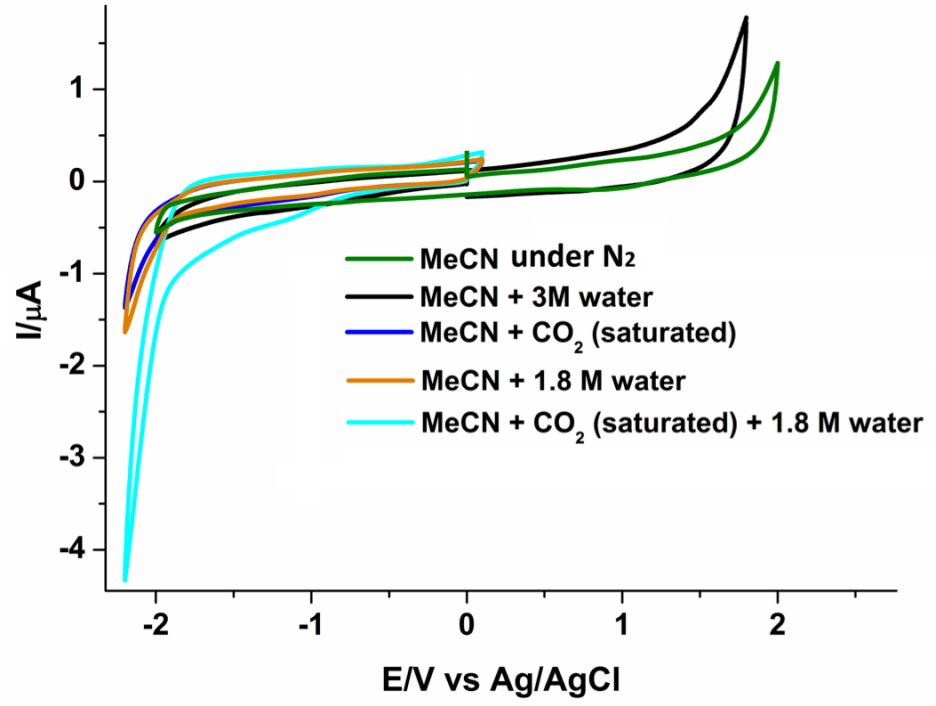


Figure S13. CVs of MeCN–$TBAPF_6$ (0.1 M) in absence of any metal catalyst. Under N_2 (olive trace), under N_2 in presence of 3 M water (conditions for water oxidation) (black trace), under CO_2 (blue trace), under N_2 in presence of 1.8 M water (conditions for proton reduction) (orange), and under CO_2 and in presence of 1.8 M water (cyan trace)— sharp increase in current after *ca*. –1.95 V arises due to the increase in acidity because of dissolved CO_2.

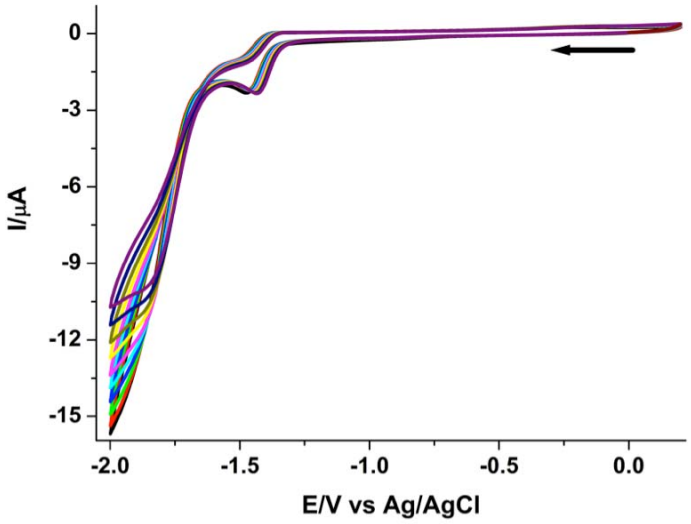


Figure S14. Multiple scan (10 scans at 100 mVs^{-1}) cyclic voltammetric responses of **1** in MeCN–$TBAPF_6$ (0.1 M) under CO_2.

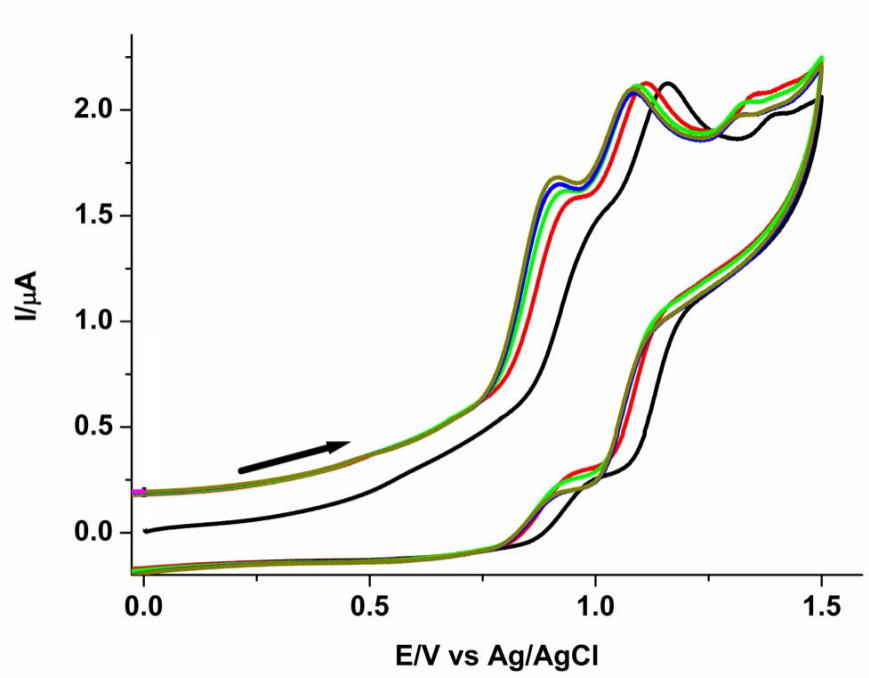


Figure S15. Multiple scan (5 scans at 100 mVs^{-1}) cyclic voltammetric responses of **1** in MeCN–$TBAPF_6$ (0.1 M) under N_2 in presence of 1 M water.

Controlled potential electrolysis

a) Under CO_2 in anhydrous MeCN.

The products of the reduction of CO_2 catalysed by [(^{Bu}tpy)Ru(phenCO_2)][PF_6] were determined by controlled electrolysis at − 1.88 V vs. Ag/AgCl using a three-electrode configuration. The experiments were carried out in a carefully sealed 100 mL BASi bulk electrolysis cell. The setup included a reticulated vitreous carbon (RVC) working electrode, a Pt wire counter electrode separated from the bulk solution by porous frit, and a silver wire pseudo-reference electrode separated from solution by a Vycor tip. A Gamry 600^{TM} Reference Potentiostat was used to apply the electrolysis potential and record current. The experiments were carried out in 25 ml of 1 mM solution of catalyst in MeCN containing 0.1 M $TBAPF_6$. The bulk electrolysis solutions were purged with dry CO_2 for 20 min prior to electrolysis. Solutions were constantly stirred throughout bulk electrolysis experiments. A gas-tight Hamilton syringe was used to sample 500 µL of the headspace gas for analysis by GC-MS.

b) Under N_2 in MeCN after addition of 2.1 M water (1:1 H_2O:H_2O^{18}).

The products of the water oxidation, catalysed by [(^{Bu}tpy)Ru(phenCO_2)][PF_6] were assessed by bulk electrolysis experiments using the same electrode set up as for CO_2 reduction, see above. The solution of 0.1 M Bu_4NPF_6 in MeCN (24.05 mL) – water (0.95 mL) containing 1 mM of catalyst was sparged with

dry N_2 for 20 minutes prior to applying a constant potential of + 1.1 V *vs*. Ag/AgCl. A gas-tight Hamilton syringe was used to sample 100 µL (to avoid the saturation) of the headspace gas for analysis by GC-MS.

GC-MS measurements:

Gas samples were analysed using a Thermo DSQ GC-MS equipped with a Restek RT-Msieve 5A 30 m x 0.32 mm PLOT column for separation of CO, N_2, O_2, CH_4 and H_2 but with CO_2 almost permanently retained (until bake-off). Ions at *m/z* 2, 28 and 32–36 were monitored in selected ion monitoring mode to determine the H_2, CO, $^{16}O_2$, ^{16}O-^{18}O and $^{18}O_2$ content, respectively. The system response to these gases was calibrated using Scotty Analyzed Gases (containing 1.0% each of H_2, O_2, CH_4, CO and CO_2 and balanced by N_2).

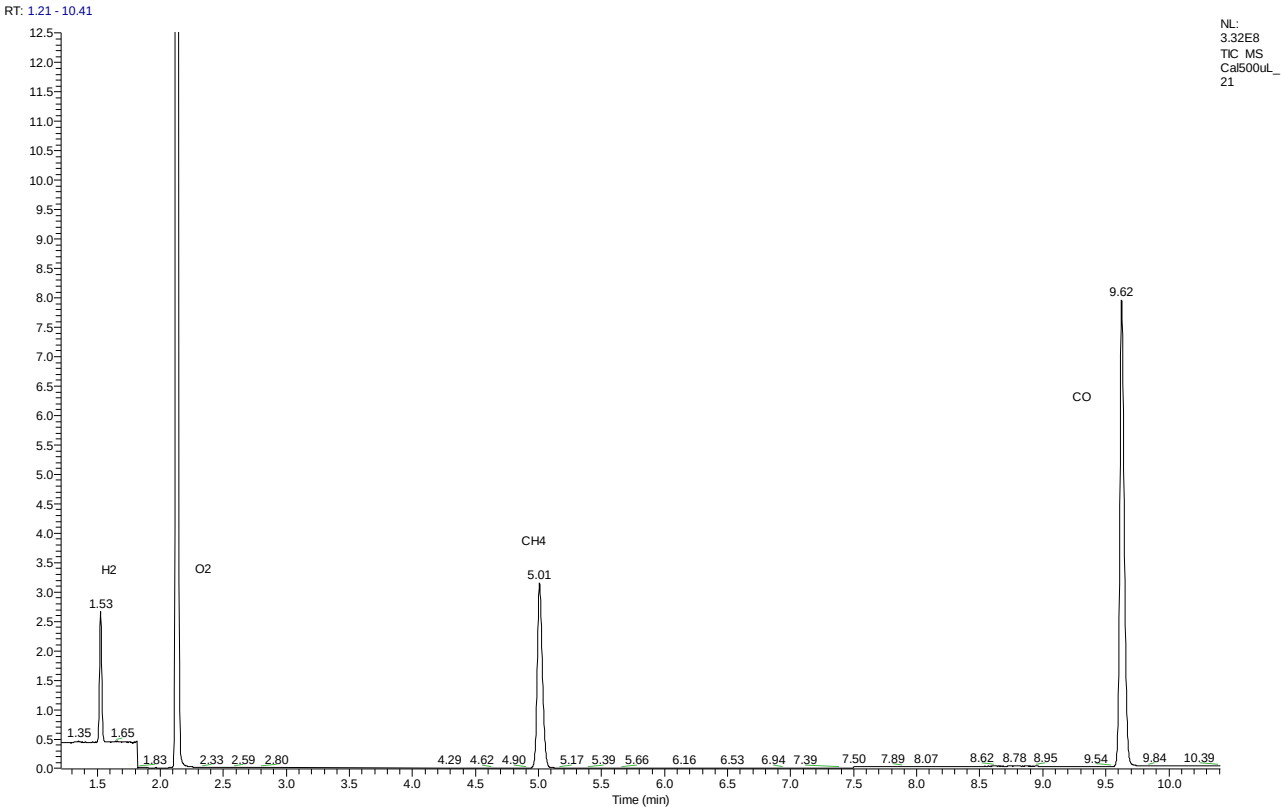


Figure 16. Gas chromatogram of 500 µL of calibration gas (Scotty Analyzed Gases). The H_2, O_2, CH_4 and CO retention times are 1.53, 2.11, 5.01 and 9.62, respectively.

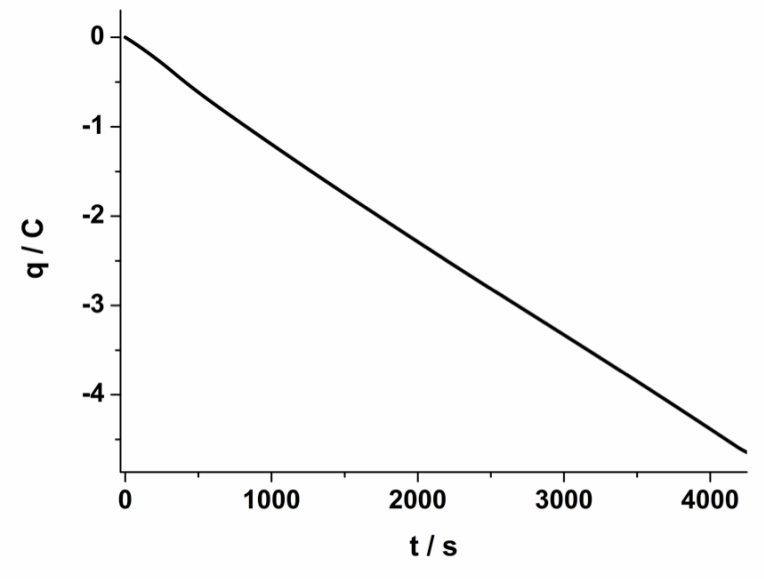


Figure 17. Controlled potential electrolysis of 1 mM [(^{Bu}tpy)Ru(phenCO$_2$)][PF$_6$] in a CO_2 saturated CH_3CN solution using 0.1 M Bu_4NPF_6 as a supporting electrolyte at a reticulated vitreous carbon (RVC) working electrode showing the charge consumed during the experiment. The potential was held at −1.88 V *vs*. Ag/AgCl, and the solution was stirred continuously during the experiment. A total of 4.57 C passed during the electrolysis period of 70 min.

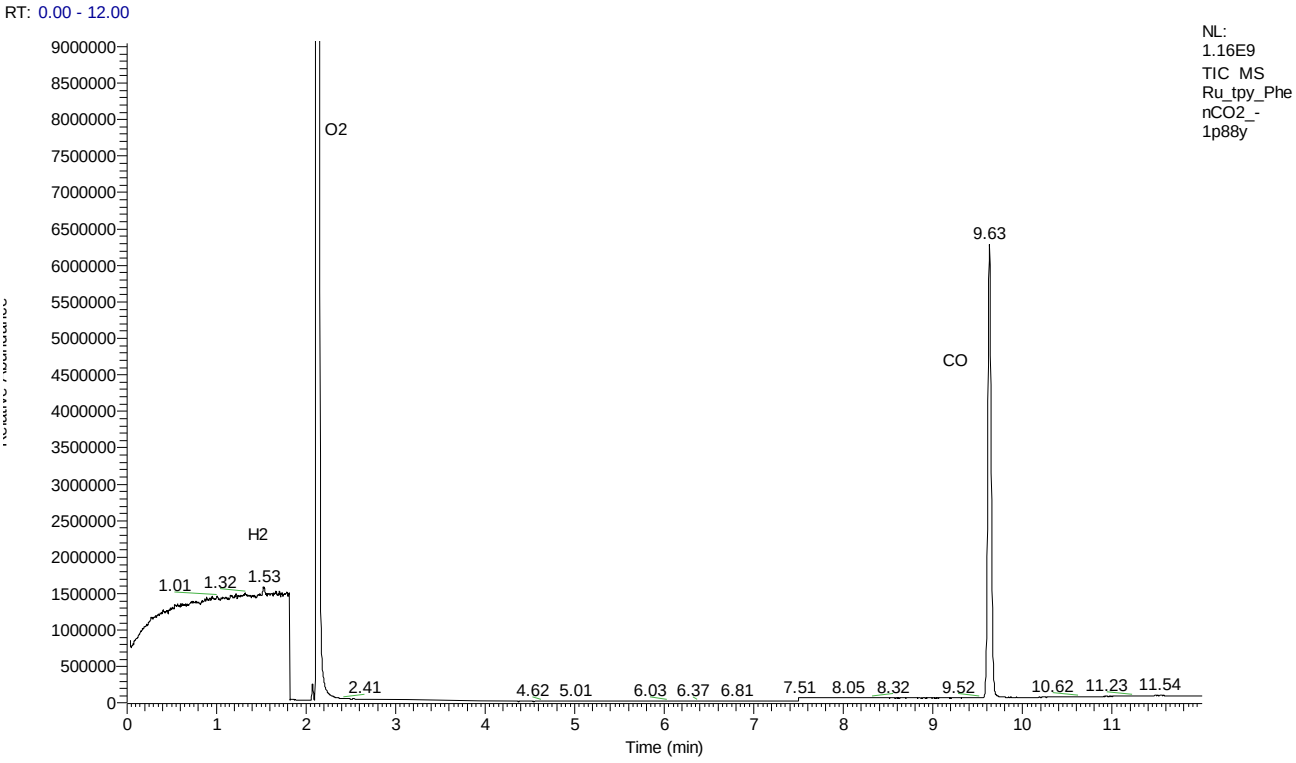


Figure 18. Gas chromatogram of 500 µL of headspace gas collected after (70 min) controlled potential electrolysis at –1.88V (Ag/AgCl) of a CO_2 saturated MeCN (25 mL) having 0.1 M Bu_4NPF_6 and 1 mM of [(^{Bu}tpy)Ru(phenCO$_2$)][PF$_6$]. CO (at retention time 9.63) was found to be the major product of the CO_2 reduction with an infinitesimally small amount of H_2 (at retention time 1.53, measured at 10x gain).

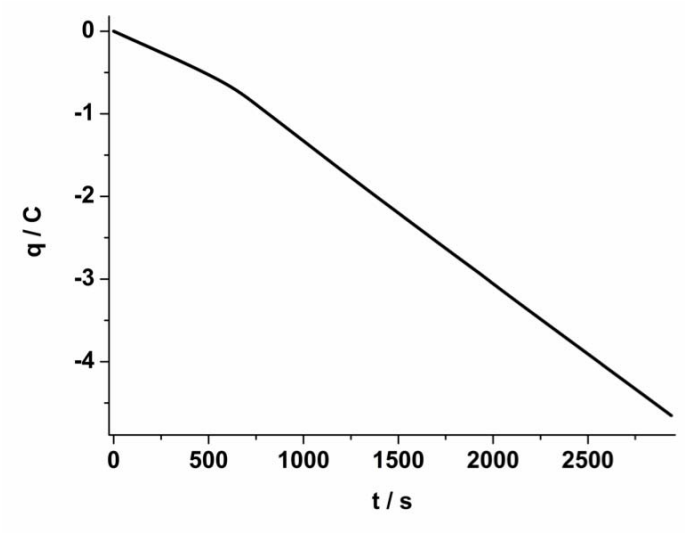


Figure 19. Controlled potential electrolysis of 1 mM [(^{Bu}tpy)Ru(phenCO_2)][PF_6] in a CO_2 saturated MeCN (24.35 mL) – water (0.65mL) solution with 0.1 M Bu_4NPF_6 as a supporting electrolyte at a reticulated vitreous carbon (RVC) working electrode showing the charge consumed during the experiment. The potential was held at −1.88 V *vs*. Ag/AgCl, and the solution was stirred during the experiment. A total of 4.68 C passed during the electrolysis period of 50 min.

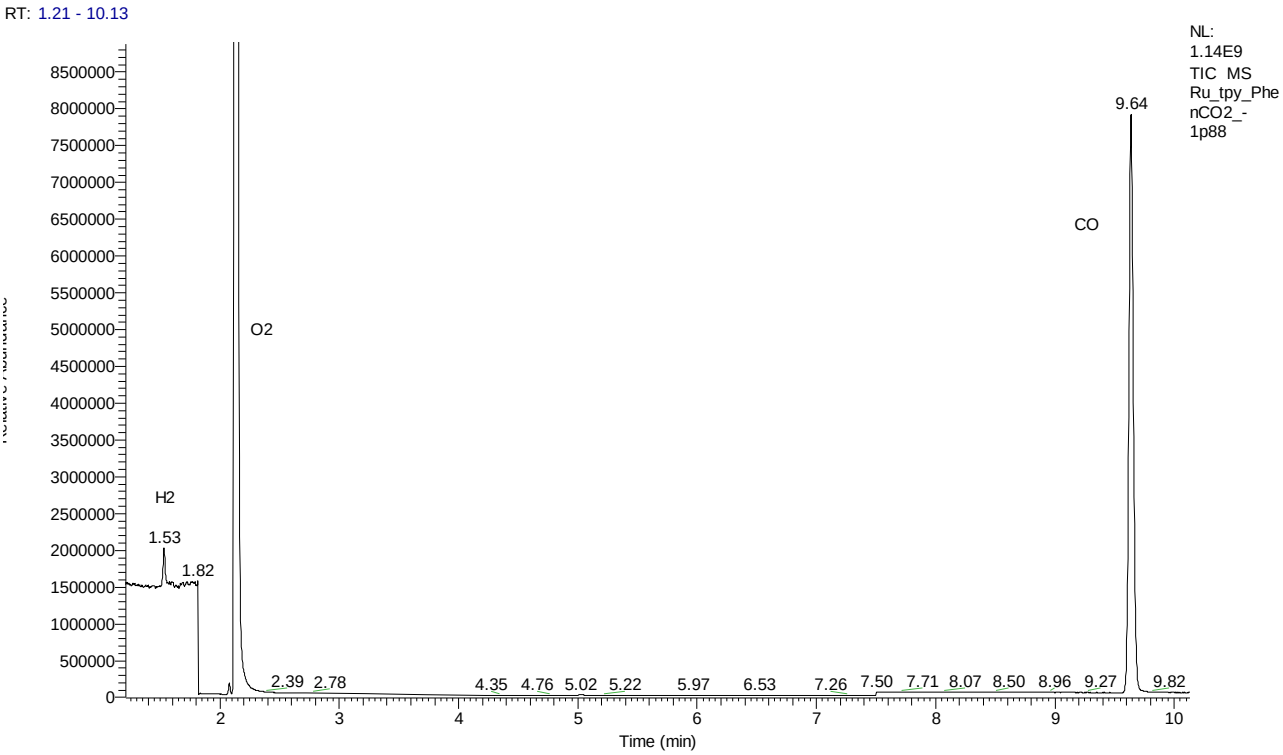


Figure 20. Gas chromatogram of 500 µL of headspace gas collected after (50 min) controlled potential electrolysis at –1.88 V (Ag/AgCl) of a CO_2 saturated MeCN (24.35 mL) + water (0.65 mL) solution having 0.1 M Bu_4NPF_6 and 1 mM of [(^{Bu}tpy)Ru(phenCO_2)][PF_6]. In this case, CO (at retention time 9.64) was again found to be the major product of the CO_2 reduction along with a small amount of H_2 (at retention time 1.53, measured at 10x gain) produced.

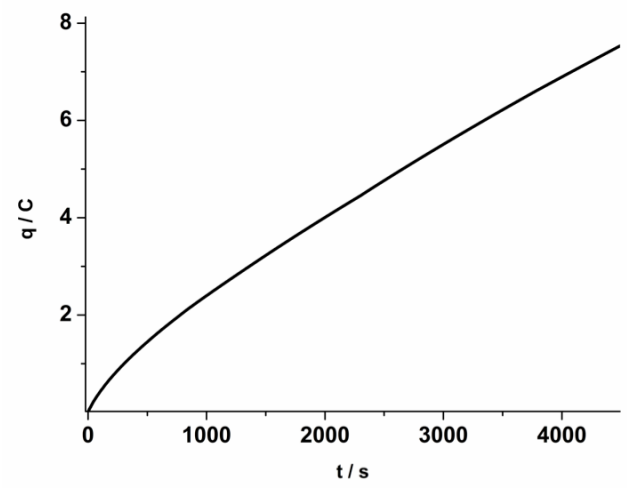


Figure 21. Controlled potential electrolysis of 1 mM [(^{Bu}tpy)Ru(phenCO_2)][PF_6] in a N_2 saturated MeCN(24.05 mL) + water (0.95 mL, 1:1 H_2O^{16}:H_2O^{18}) solution having 0.1 M Bu_4PF_6 as a supporting electrolyte at a reticulated vitreous carbon (RVC) working electrode showing the charge consumed during the experiment. The potential was held at +1.1 V vs. Ag/AgCl, and the solution was stirred during the experiment. A total of 7.52 C passed during the electrolysis period of 75 min.

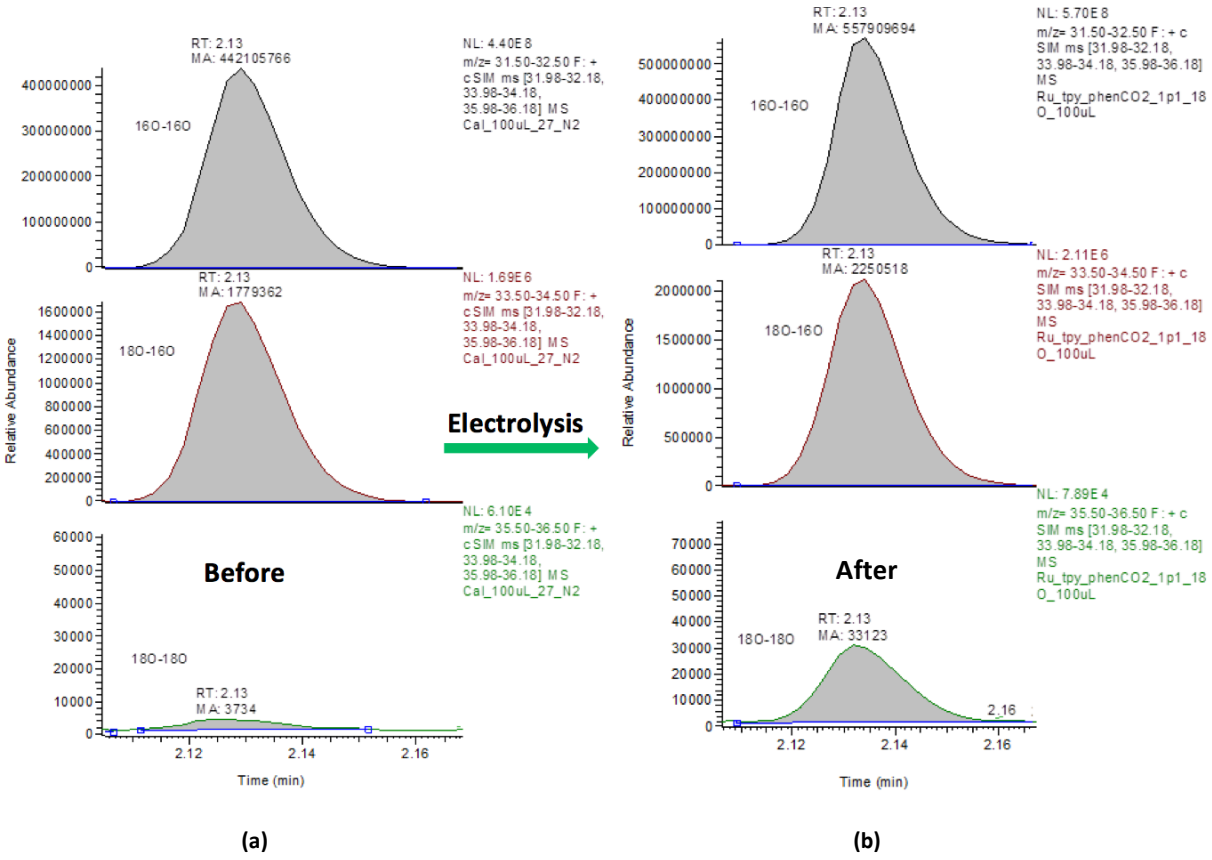
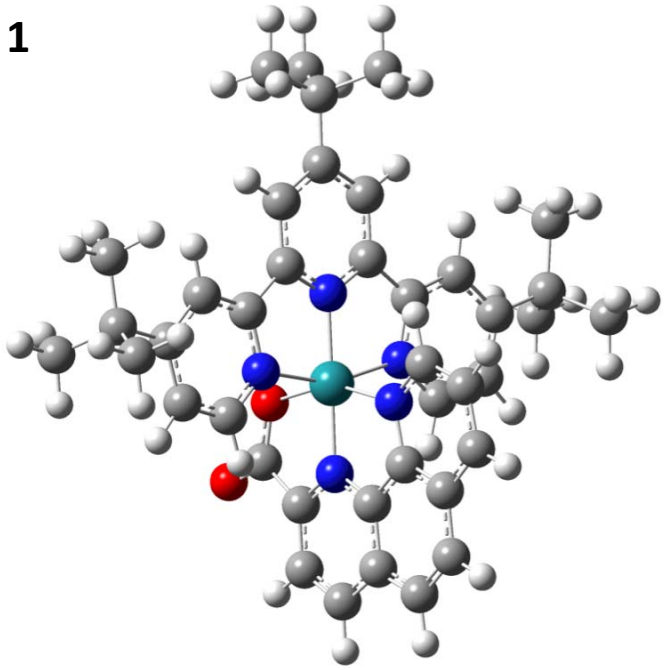


Figure S22. Gas chromatograms of 100 µL of headspace gas collected from a N_2 saturated MeCN (24.05 mL) + water (0.95 mL of 1:1 H_2O^{16}:H_2O^{18}) solution having 0.1 M Bu_4NPF_6 and 1 mM of [(^{Bu}tpy)Ru(phenCO_2)][PF_6] (a) before and (b) after 75 min. bulk electrolysis at +1.1 V (vs Ag/AgCl). The GC-MS traces show unequivocal evidence for an increased ^{18}O-^{18}O in the headspace gas after the electrolysis.

Cartesian coordinates of the DFT optimised geometries in MeCN

1



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C	0.03871300	4.05300900	0.16092000
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C	-0.04379900	-3.41568700	0.37122200
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H	6.87351500	-0.65675100	-1.56346000
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H	8.00460400	0.69103700	-1.32502500
C	6.82703100	0.09687700	1.11201000

H	6.32200400	0.37675300	2.04690300
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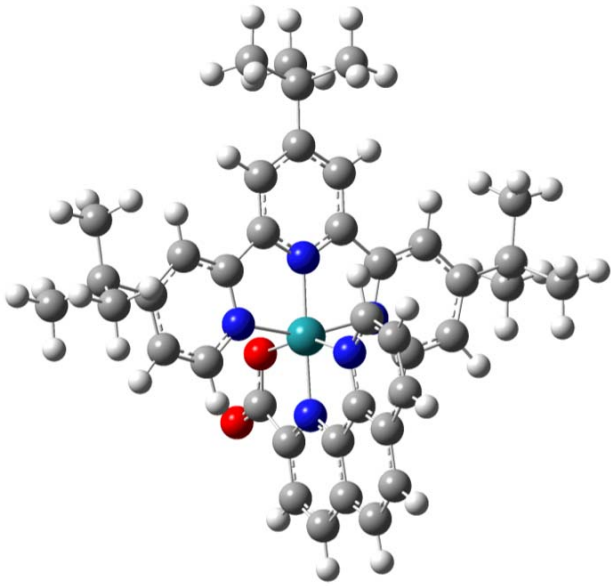
H	7.89141800	0.35330500	1.20577700

1 + e



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C	0.11074300	-3.41477300	0.36385500
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C	-6.95666400	0.34648400	-1.48712300
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C	0.66406000	5.93292200	1.63341100
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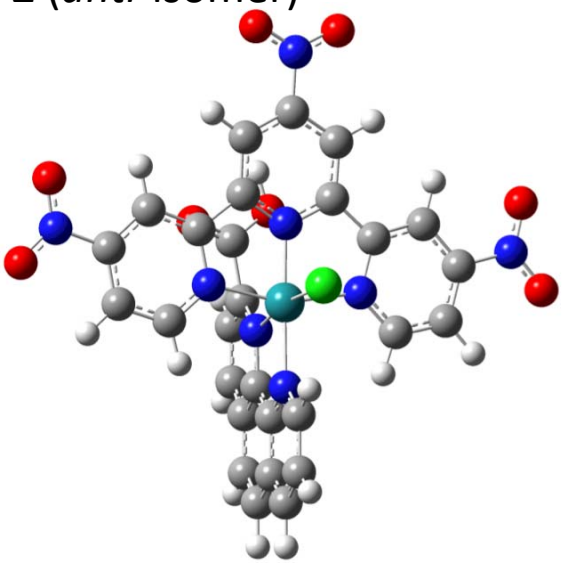
2 (*anti*-isomer)



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N	-1.93089300	0.32579900	-0.60290900
N	1.97305100	-0.67847300	-0.46862500
N	-0.43583200	-1.34552100	1.23084500
C	2.61835700	0.53052700	-0.28122900
C	-1.92921500	1.68804400	-0.36473100
O	-0.56378700	1.54041800	2.98225300
C	-0.92994200	-3.24493800	-0.13485400
C	1.72802200	1.69577300	-0.19707600
C	4.72539000	-0.59806100	-0.18901700
C	-0.59492600	2.28387600	-0.21060200
C	1.07007100	3.98487200	0.00445500
C	4.00562300	0.59495900	-0.14409400
H	4.51320100	1.54213300	0.00592700
C	-0.41307700	-0.76019900	2.44574100
C	-0.90524200	-2.63849400	1.15487900
C	-0.28329100	3.63723800	-0.07452200
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C	4.08428500	-1.82766000	-0.36447300
H	4.64044400	-2.75894100	-0.39875900

C	-3.12215700	2.40799800	-0.27508600
H	-3.12142900	3.47664300	-0.08557300
C	2.69867600	-1.82001600	-0.50312000
H	2.13986800	-2.73930700	-0.65178500
C	2.09541000	3.03526500	-0.07211400
H	3.13500800	3.34311000	-0.03717700
C	-0.52198300	-3.00633700	-2.41784200
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C	-1.35109700	-4.59366700	-0.28839200
C	-4.32054800	1.71204400	-0.42714200
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H	-3.05428100	-1.38705500	-0.94211800
C	-4.33680800	0.33554900	-0.66586700
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H	-0.87632200	-4.72243000	-3.66842600
C	-1.77693700	-5.32065300	0.87604300
H	-2.09996700	-6.35298800	0.75020300
C	-0.89596100	-1.39884700	3.60719500
H	-0.86967300	-0.86020100	4.55152400
C	-1.32958800	-5.13848600	-1.59513500
H	-1.64118200	-6.16937600	-1.75546200
C	0.28494100	0.56220700	2.61266000
C	-1.78606600	-4.72876600	2.11411000
H	-2.11993200	-5.27790500	2.99304300
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H	-1.71509100	-3.21985900	4.42815100
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N	-5.59679600	2.44988200	-0.32888500
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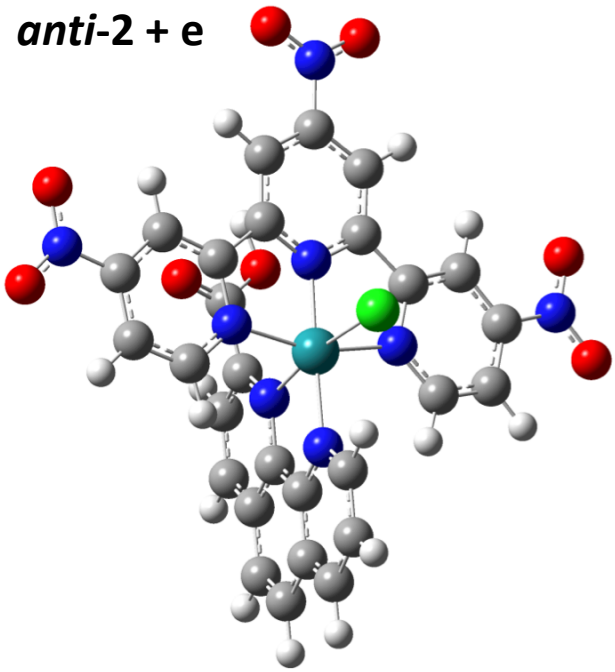
O	6.79996500	-1.63424200	-0.05433800
O	6.72640600	0.55446000	0.08096500
O	-6.64156400	1.80278200	-0.46859400
O	-5.54049000	3.66670700	-0.11228500
Cl	0.20619200	0.17701100	-2.98413100
H	-0.03225600	2.35149500	3.13983400

***anti*-2 + e**



0 2

Ru	-0.07703900	-0.52183500	-0.64154900
N	0.53347100	1.29211900	-0.22886600
O	1.63898200	0.47245300	2.54033200
N	-0.74485300	-2.42610600	-1.15562000
N	-1.87414000	0.46454200	-0.64357200
N	1.92337500	-0.86687400	-0.47098600
N	-0.55381700	-1.27551100	1.23260100
C	2.67111800	0.29041800	-0.27983900
C	-1.76021200	1.82900200	-0.39478900
O	-0.28258000	1.63412200	2.91804100
C	-1.27246900	-3.12680200	-0.09786900
C	1.88434500	1.52355700	-0.19335200
C	4.69324400	-1.00388900	-0.18514200
C	-0.38533200	2.30940600	-0.22854500
C	1.42209500	3.86735600	0.00157200
C	4.05714400	0.24027600	-0.14282800
H	4.63793200	1.14465900	0.00652900
C	-0.45997500	-0.67907700	2.44020700
C	-1.19631900	-2.49595000	1.17770800
C	0.03935300	3.62942400	-0.09564700
H	-0.65896400	4.45967100	-0.08411700
C	3.94083900	-2.18300300	-0.35955800
H	4.42138400	-3.15531200	-0.39078800
C	-2.88720400	2.64369200	-0.30090900
H	-2.79508300	3.70598600	-0.09906700
C	2.56638900	-2.06384100	-0.49885400
H	1.93478900	-2.93618400	-0.64566800
C	2.36326400	2.82410500	-0.06404800
H	3.42505800	3.04275700	-0.02379700
C	-0.76609000	-3.00657100	-2.37048300
H	-0.33949400	-2.42052000	-3.18046000
C	-1.87435800	-4.40718300	-0.23597800

C	-4.15209600	2.06759700	-0.46035000
C	-3.11539600	-0.06746600	-0.79862600
H	-3.15266500	-1.13386200	-1.00365600
C	-4.27589300	0.68639200	-0.71521700
H	-5.24959700	0.22592900	-0.84708600
C	-1.76985900	-3.12714600	2.31674500
C	-1.32255100	-4.28103200	-2.58554600
H	-1.30939100	-4.69408500	-3.59211000
C	-2.43849900	-5.03074100	0.93004700
H	-2.90765100	-6.00724400	0.81757000
C	-1.04279900	-1.22116400	3.60511600
H	-0.94565700	-0.67566500	4.54107800
C	-1.88723500	-4.98562900	-1.52825200
H	-2.33632800	-5.96636600	-1.67739300
C	0.42193500	0.52991500	2.59807400
C	-2.39548100	-4.41127400	2.15418500
H	-2.83189900	-4.88311500	3.03331000
C	-1.69617300	-2.44373400	3.55220500
H	-2.14037800	-2.88109500	4.44455300
N	1.89341700	5.23551800	0.14583600
N	6.13444100	-1.07453400	-0.04018600
N	-5.33351000	2.89772800	-0.35699200
O	1.04231200	6.14745200	0.18760400
O	3.12425500	5.42707100	0.22213900
O	6.66727700	-2.20495200	-0.06275100
O	6.76791200	-0.00578700	0.09966600
O	-6.44788100	2.34586900	-0.49587900
O	-5.18171500	4.11974000	-0.13284300
Cl	0.27239000	0.12462500	-3.00994900
H	0.35914400	2.36078200	3.07225900

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