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Electronic Supporting Information

Water and catalytic isomerization of linear allylic alcohols by $[RuCp(H_2O\text{-}\kappa O)(PTA)_2]^+$ (PTA = 1,3,5-triaza-7-phosphaadamantane)

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1. Materials and methods

All chemicals were of reagent grade and, unless otherwise stated, were used as received from commercial suppliers. Likewise all reactions were carried out in a pure argon atmosphere by using standard Schlenk-tube techniques. Water was deoxygenated prior to use and organic solvents have been dried through standard methods. The complex [RuClCp($PTA)_2$] was prepared as described in the literature.[1] ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker DRX300 spectrometer operating at 300.13 MHz (^1H) and 75.47 (^{13}C), respectively. Peak positions are relative to tetramethylsilane and were calibrated against the residual solvent resonance (^1H) or the deuterated solvent multiplet (^{13}C). $^{31}P\{^1H\}$ and $^{19}F\{^1H\}$ NMR spectra were recorder on the same instrument operating at 121.49 and 282.40 MHz, respectively. Chemical shifts for $^{31}P\{^1H\}$ NMR were measured relative to external 85% H_3PO_4 and for $^{19}F\{^1H\}$ NMR to $CFCl_3$ with downfield values taken as positive in both cases. All NMR spectra were obtained at 25 °C. Infrared spectra were recorded as KBr disks using a Bruker Vertex 70 FT-IR spectrometer. Elemental analyses (C, H, N, S) were performed on a Fisons Instrument EA1108 elemental analyser. Gas chromatographic measurements were made on a Shimadzu GC-2010 Plus using a Supelco SP-2330 30 m, 0.25 mm, 0.2 μm column and flame ionization detector.

1.1 Synthesis of [RuCp(H_2O-κ*O*)($PTA)_2$](CF_3SO_3)·$3.5H_2O$ (1(CF_3SO_3)·$3.5H_2O$).

Into a solution containing complex [RuClCp (PTA)$_2$] (1.0 g, 1.94 mmol) dissolved in 50 mL of water was added a solution of AgCF$_3$SO$_3$ (493.5 mg, 1.92 mmol) in 20 mL of water. The resulting mixture was sonicated for 2 h at room temperature and then the precipitated AgCl was filtered through celite. The solvent was removed to dryness giving rise to an orange powder, which was washed with Et$_2$O (3 x 30 mL) and dried under vacuum. Brown-orange crystals of the complex suitable for single crystal X-ray diffraction grew from an aqueous 1.3 M solution after three days. Crystals yield: 1.17 g, 85%. $S_{25,H2O}$ (g/mL): 2. Elemental analysis for powder sample $C_{18}H_{38}F_3N_6O_{7.5}P_2RuS$ (710.6 g·mol^{-1}): Found C: 30.21; H 5.43; N 11.50; calcd. C 30.42; H 5.39; N 11.82. IR (KBr, cm^{-1}): 3082 (m); 2925 (m), 2896 (m); 1446 (m); 1412 (m), 1036 (s), 1014 (s), 972 (s); 1281 – 1260 (s), 1171 (s), 1098 (m); 948 (m), 893 (m), 803 (m), 644 (m); 575 (s). ^{1}H NMR (300.13 MHz, 22 °C, D$_2$O): δ 4.06 (m, NCH$_2$P, 12H), 4.53 (m, NCH$_2$N, 12 H), 4.71(s, Cp, 5H). ^{13}C{^{1}H} RMN (75.467 MHz, 22 °C, D$_2$O): δ 53.70 (t, $^1J_{CP}$ = 8.4 Hz, NCH$_2$P), 70.61 (s, NCH$_2$N), 75.45 (s, Cp). ^{31}P{^{1}H} NMR (121.49 MHz, 22 °C, D$_2$O): δ -24.75 (s). ^{19}F{^{1}H} NMR (282.40 MHz, 22 °C, D$_2$O): δ -78.908 (s).

1.2 Synthesis of [RuCp(H$_2$O-κ*O*)(PTA)$_2$](CF$_3$SO$_3$) (1(CF$_3$SO$_3$)).

The complex **1(CF$_3$SO$_3$)·3.5H$_2$O** (100 mg, 0.14 mmol) was dissolved in 10 mL of dry EtOH and then the solvent fully eliminated. The dissolution and evaporation process was repeated with the obtained powder for 3 more times. The final resulting yellow powder was stored under N$_2$.

1.3 Stability of 1(CF$_3$SO$_3$)·3.5H$_2$O and 1(CF$_3$SO$_3$) under air in solid state and water solution.

Crystalline **1(CF_3SO_3)·3.5H_2O** (7 mg) and **1(CF_3SO_3)** were kept under air at room temperature, the $^{31}P\{^1H\}$ NMR (D_2O) showed that the compound decomposes slowly under this conditions, achieving the total decomposition after 10 days. The stability in water solution was evaluated by dissolution of crystals of **1(CF_3SO_3)·3.5H_2O (**7 mg) and powder **1(CF_3SO_3)** (7 mg) in 0.5 mL of D_2O, the obtained solution cooled over ice and then air was bubbled during 2 min. The complete decomposition of the complex was observed before 3 days at room temperature and 2 h at 80 ºC. For both experiments the unique final compound observed by $^{31}P\{^1H\}$ NMR was O=PTA.

1.4 Stability of 1(CF_3SO_3)·3.5H_2O and 1(CF_3SO_3) under N_2 and air atmosphere.

In 5 mm NMR tubes the complex **1(CF_3SO_3)3.5H_2O** (14 mg, 0.02 mmol) and **1(CF_3SO_3)** (13 mg, 0.02 mmol) were dissolved in 0.5 mL of D_2O under N_2. The NMR tubes were cooled at 5 ºC and air bubbled for 5 minutes. The solutions were checked by $^{31}P\{^1H\}$ NMR at room temperature showing that complex **1** is stable in water solution under N_2 for one month but under air was decomposed in 1 hour, being the main signal observed by $^{31}P\{^1H\}$ NMR due to PTA=O.

1.5 Reactivity of 1(CF_3SO_3)·3.5H_2O with NaCl

Crystals of **1(CF_3SO_3)·3.5H_2O** (14 mg, 0.02 mmol) were dissolved in 0.5 mL of D_2O into a 5 mm NMR tube and then NaCl (1.2 mg, 0.02 mmol) was added. After 5 min the $^{31}P\{^1H\}$ NMR showed a singlet that only could be ascribable to [RuClCp(PTA)$_2$], which was the unique remaining signal after 2 h.

1.6 General procedure for catalytic isomerisation of allylic alcohols

In a typical reaction a variable volume of the studied substrate (or a mixture of substrates) was introduced into a solution of **1(CF$_3$SO$_3$)·3.5H$_2$O** (9.7 mg, 0.15 mmol) in 6 mL of water and/or MeOH. Experiments were also preformed using the substrate as solvent without and with variable amounts of water. In this case the water/allylic alcohol mixtures were composed using calibrated micropipettes. The preparation was made under air and under N_2, in this last case the used solvent was previously bubbled with N_2. The mixture was kept at desired reaction temperature in a sealed tube and stirred regularly (1000 rpm). At the chosen time the reaction was cooled at room temperature and extracted with $CHCl_3$ (5 x 1.5 mL for 1 mol% catalyst; 5 x 3 mL for 0.1 mol% catalyst). The collected organic phases were passed through a column (5 x 50 mm) packed with 60 mesh silica gel. The conversion of allylic alcohol into ketone was determined by gas chromatography. The identity of the ketones was assessed by comparison with commercially available pure samples. Reactions were checked by $^{31}P\{^1H\}$ NMR by extracting some aliquots at regular reaction time.

1.7 Catalytic isomerisation of allylic alcohols with 1(CF$_3$SO$_3$) in presence of NaCl.

Using the general procedure indicated previously the substrates were catalysed in water with **1(CF$_3$SO$_3$)** in presence of 5 eq. of NaCl. The observed isomerization conversions were similar to that produced by the complex [RuClCp(PTA)$_2$] in presence of NaCl.[2]

1.8 X-ray structure Determination.

Data of compound **1(CF$_3$SO$_3$)·3.5H$_2$O** was collected on an Oxford Diffraction Xcalibur diffractometer (Rutherford Appleton Laboratory. Oxfordshire, U.K.), using monochromated Mo

Kα radiation (λ = 0.7107 Å) at 100 K. The crystal parameters and other experimental details of the data collections are summarized in Table 1. The structures were solved by direct methods SHEL97[3] and refined by full-matrix least squares methods with SHEL-XTL[3] and refined by least-squares procedures on F^2 and final geometrical calculations and graphical manipulations were carried out with the SHELXS-XTL package.[3] All the non-hydrogen non-disordered atoms were refined with anisotropic atomic displacement parameters. Three 0.5 disordered (refined isotropically) water molecules were found. All hydrogen atoms, except for disordered water molecules, were included in calculated positions and refined using a riding model. Crystallographic data for the structure in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication. CCDC 1511862.

Table S1. Selected Crystallographic Data for $\mathbf{1(CF_3SO_3)\cdot 3.5H_2O}$

	$\mathbf{1(CF_3SO_3)\cdot 3.5H_2O}$

Empirical formula	$C_{18}H_{38}F_3N_6O_{7.50}P_2RuS$
Formula weight	710.61
Crystal system	Triclinic
Space group	P-1
a [Å]	9.100(5)
b [Å]	10.706(5)
c [Å]	15.027(5)
α [^{0}]	76.368(5)
β [^{0}]	80.526(5)
γ [^{0}]	78.260(5)
Volume [$Å^3$]	1382.5(11)
Z	2
Goodness of fit on F^2	1.195
$\rho_{calcd.}$ [$mg \cdot m^{-3}$]	1.707
μ [mm^{-1}]	0.830
Data/Parameters	6954/362
R1 [I>2σ(I)] (all)	0.0224 (0.0257)
wR2 [I>2σ(I)] (all)	0.0531 (0.0549)
$\Delta\rho$ [$e \cdot Å^3$]	0.066; -0.456

2. Characterization of [RuCp(H_2O-κ*O*)(PTA)$_2$](CF_3SO_3)·3H_2O

2.1 NMR spectra of [RuCp(H_2O-κ*O*)(PTA)$_2$](CF_3SO_3)·3H_2O

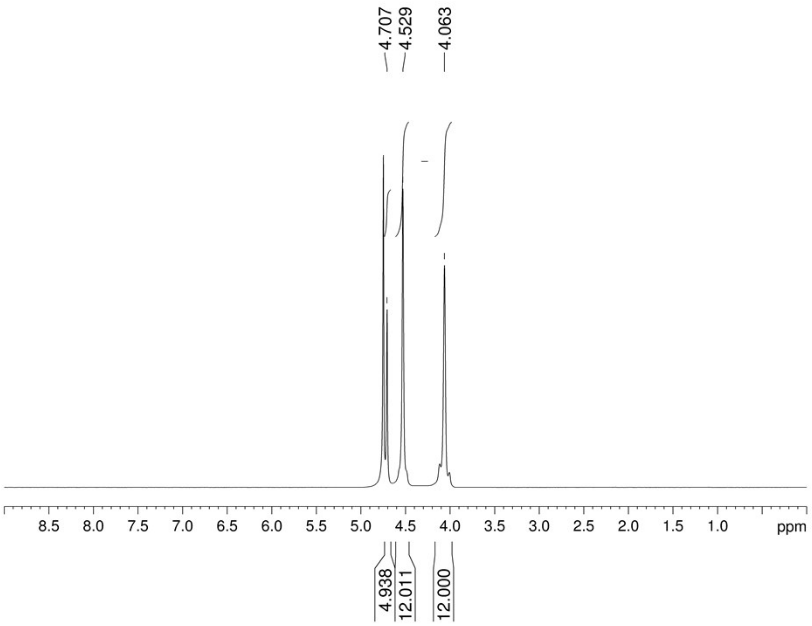

Figure S1: ^{1}H NMR (300.13 MHz, 22 °C, D_2O) of [RuCp(H_2O-κ*O*)(PTA)$_2$](CF_3SO_3)·3H_2O

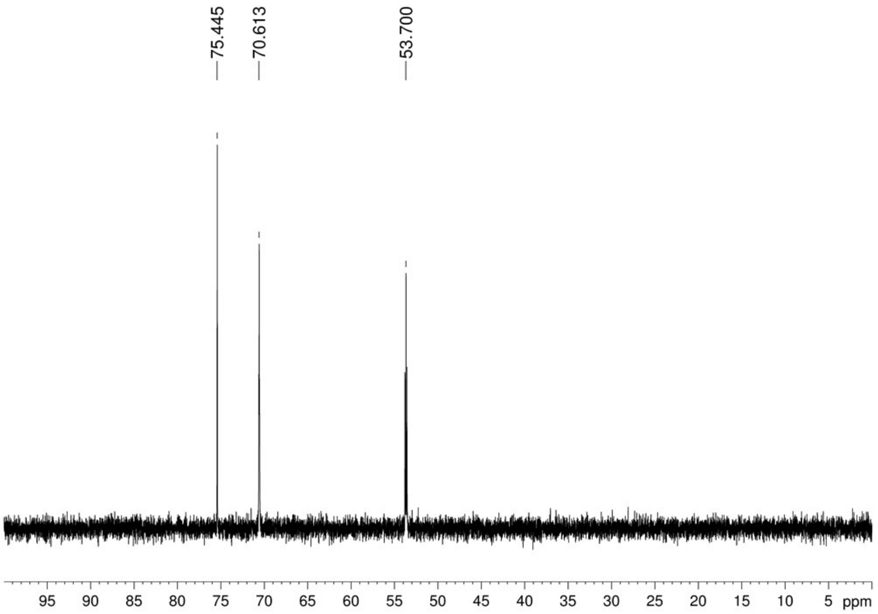

Figure S2: $^{13}C\{^1H\}$ NMR (75.47 MHz, 22 °C, D_2O) of [RuCp(H_2O-κ*O*)(PTA)$_2$](CF_3SO_3)·3H_2O

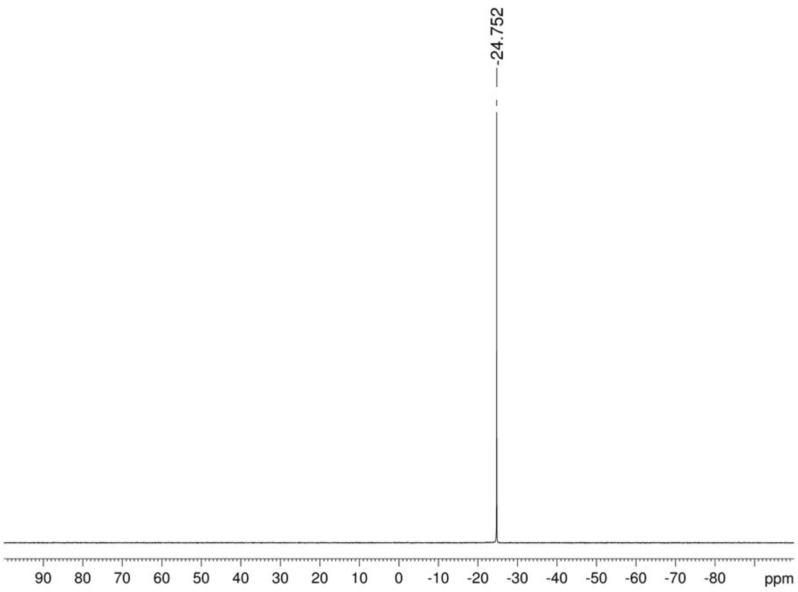

Figure S3: $^{31}P\{^1H\}$ NMR (121.49 MHz, 22 °C, D_2O) of [RuCp(H_2O-κ*O*)$(PTA)_2$](CF_3SO_3)·$3H_2O$

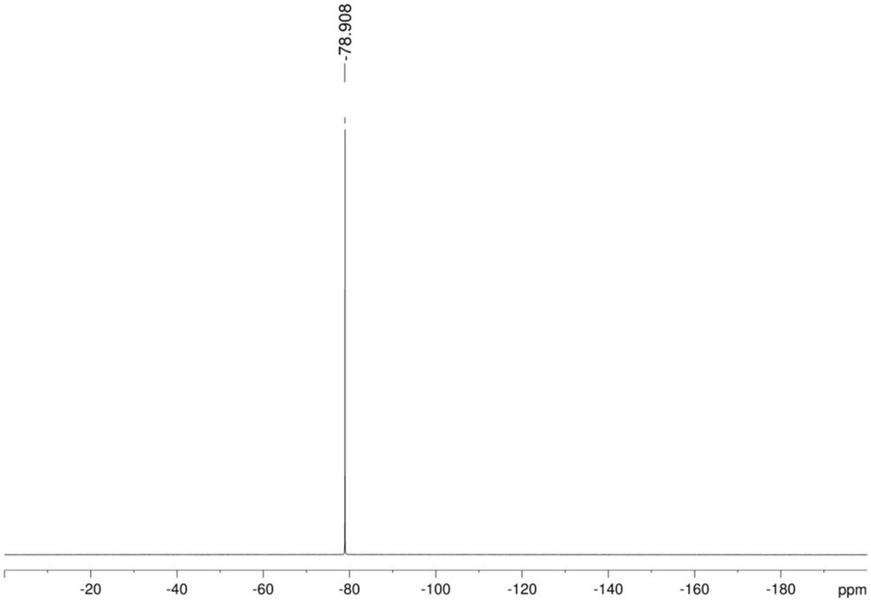

Figure S4: $^{19}F\{^1H\}$ NMR (282.40 MHz, 22 °C, D_2O) of [RuCp(H_2O-κ*O*)$(PTA)_2$](CF_3SO_3)·$3H_2O$

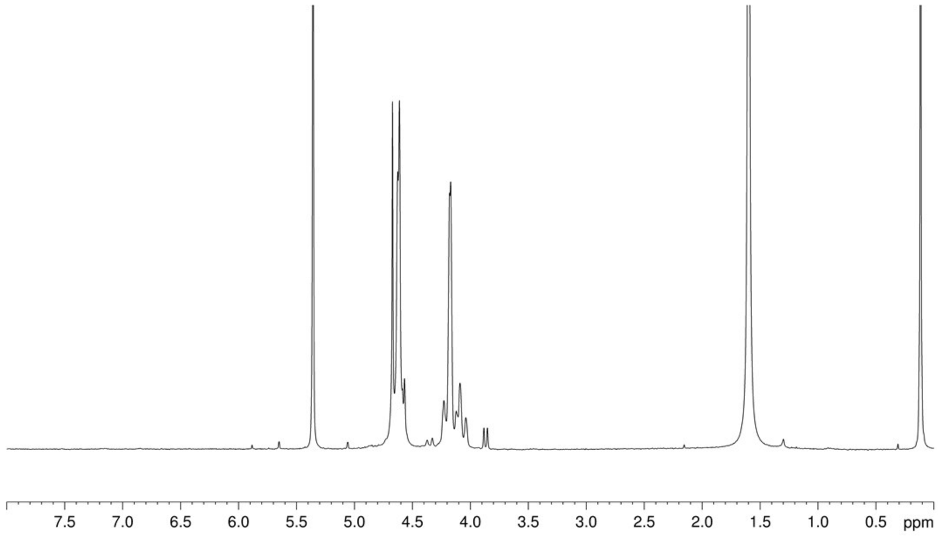

Figure S5: ^{1}H NMR (300.13 MHz, 22 °C, CD_2Cl_2) of [RuCp(H_2O-κ*O*)($PTA)_2$](CF_3SO_3)·3.5H_2O

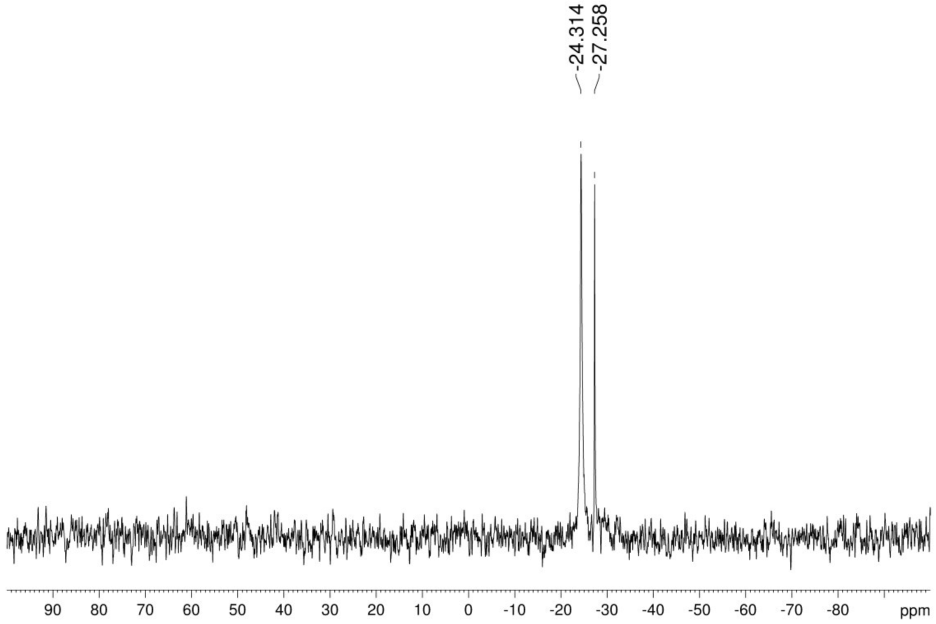

Figure S6: ^{31}P NMR (121.49 MHz, 22 °C, CD_2Cl_2) of $[RuCp(H_2O\text{-}\kappa O)(PTA)_2](CF_3SO_3)\cdot 3H_2O$

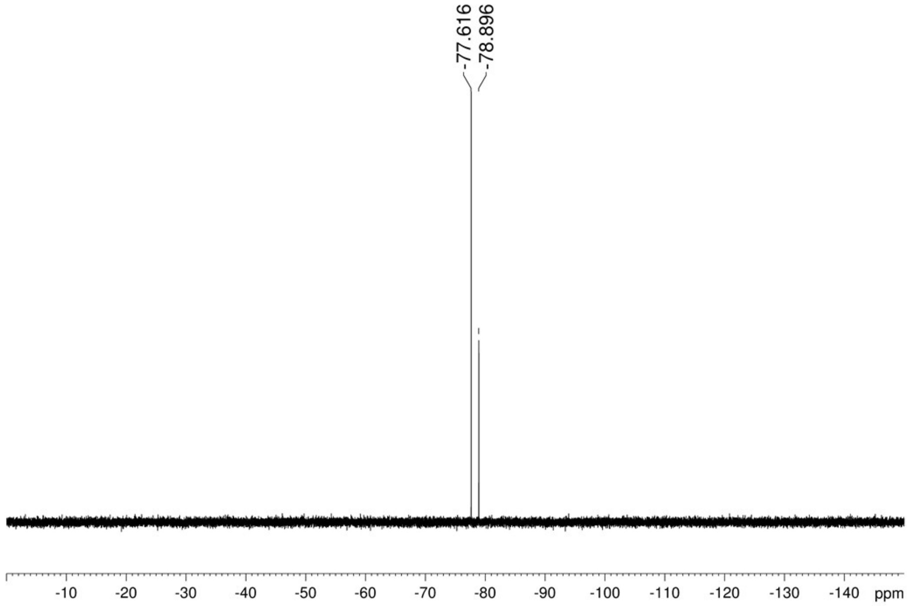

Figure S7: ^{19}F{^{1}H} NMR (282.40 MHz, 22 °C, CD_2Cl_2) of $[RuCp(H_2O\text{-}\kappa O)(PTA)_2](CF_3SO_3)\cdot 3H_2O$

2.2 IR spectrum of $[RuCp(H_2O\text{-}\kappa O)(PTA)_2](CF_3SO_3)\cdot 3H_2O$

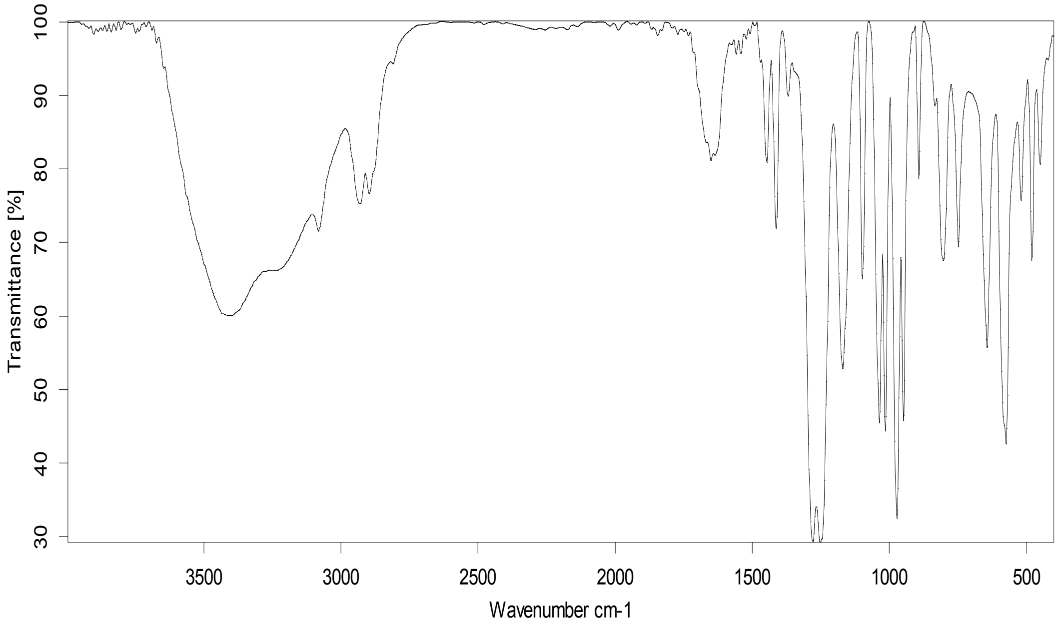

Figure S8: IR (KBr) of $[RuCp(H_2O\text{-}\kappa O)(PTA)_2](CF_3SO_3)\cdot 3H_2O$

3. References

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