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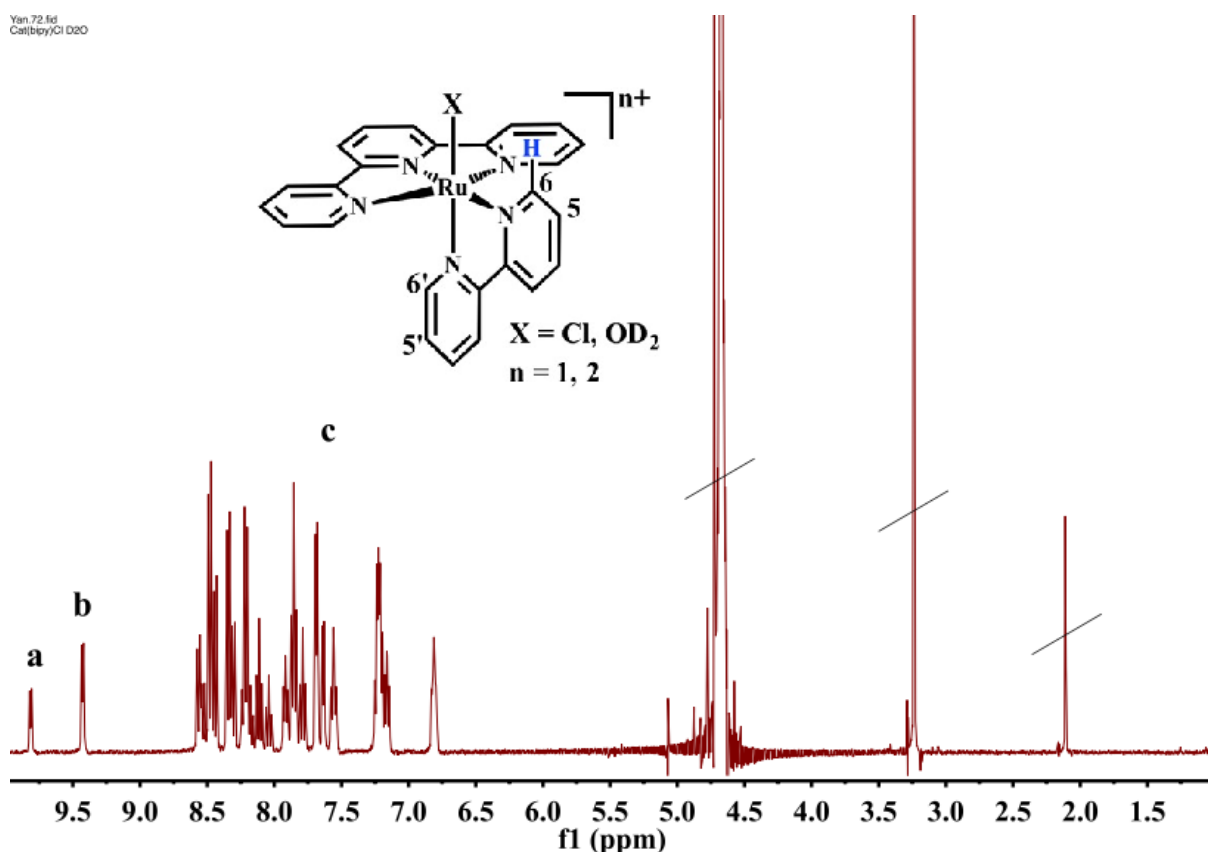
## Cooperative effects in homogenous water oxidation catalysis by mononuclear ruthenium complexes

Yanyan Mulyana,<sup>a</sup> F. Richard Keene<sup>b,c</sup> and Leone Spiccia<sup>\*a</sup>

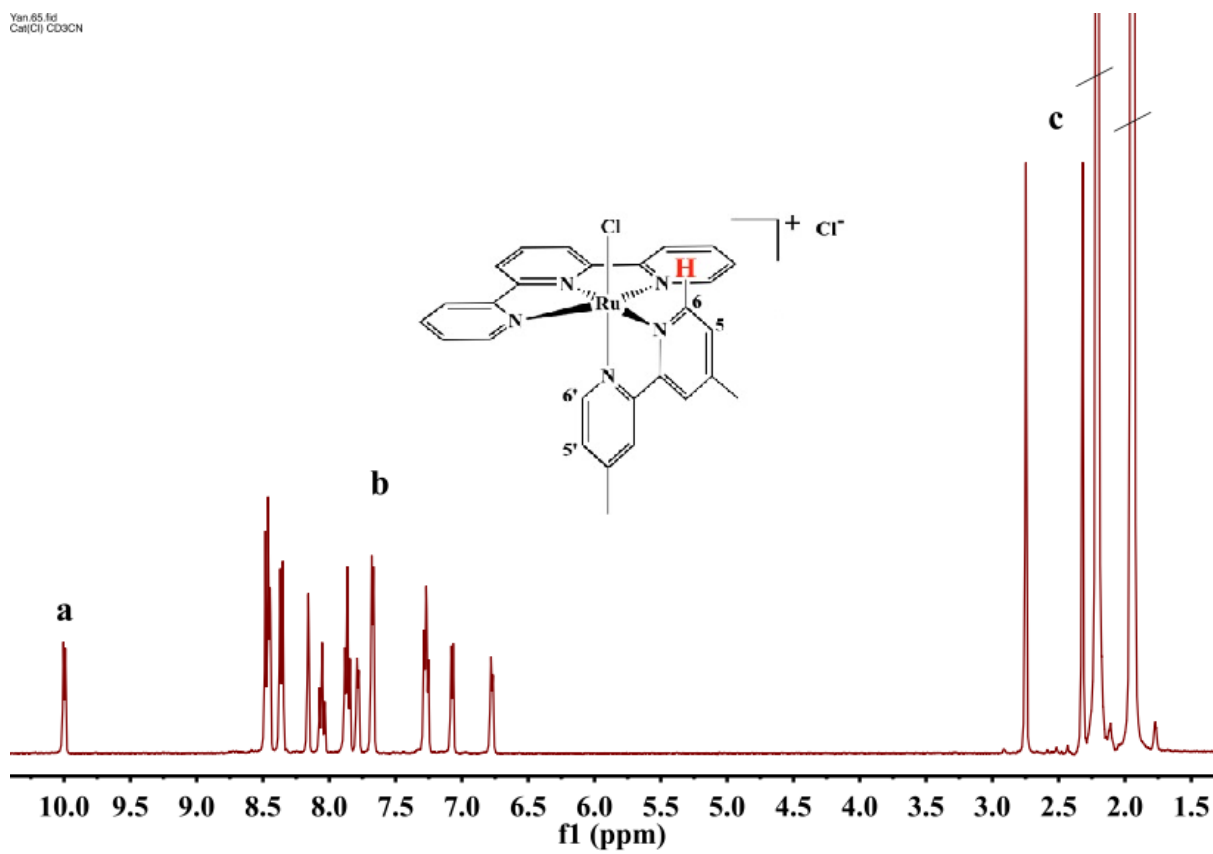
<sup>a</sup> School of Chemistry and Australian Centre of Excellence for Electromaterials Science, Monash University, Victoria 3800, Australia, email: [leone.spiccia@monash.edu](mailto:leone.spiccia@monash.edu)

<sup>b</sup> School of Pharmacy & Molecular Sciences, James Cook University, Townsville, Queensland 4811, Australia

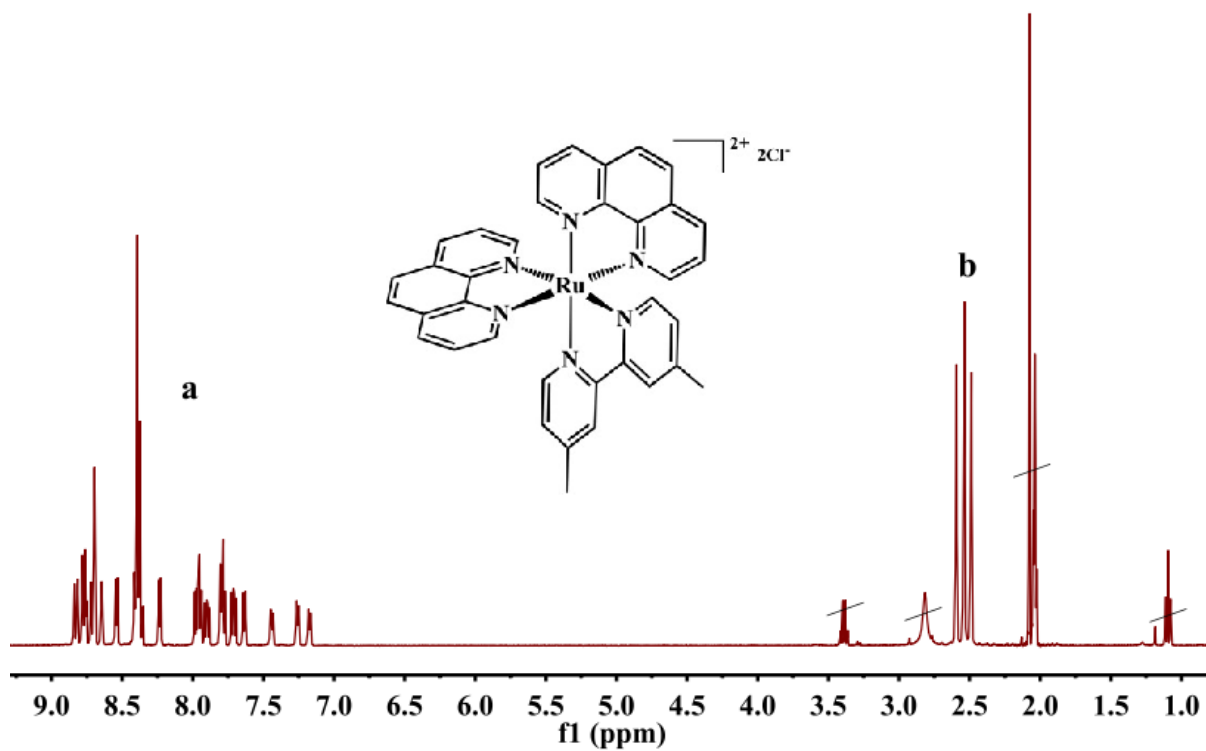
<sup>c</sup> School of Chemistry and Physics, University of Adelaide, Adelaide, South Australia 5007, Australia



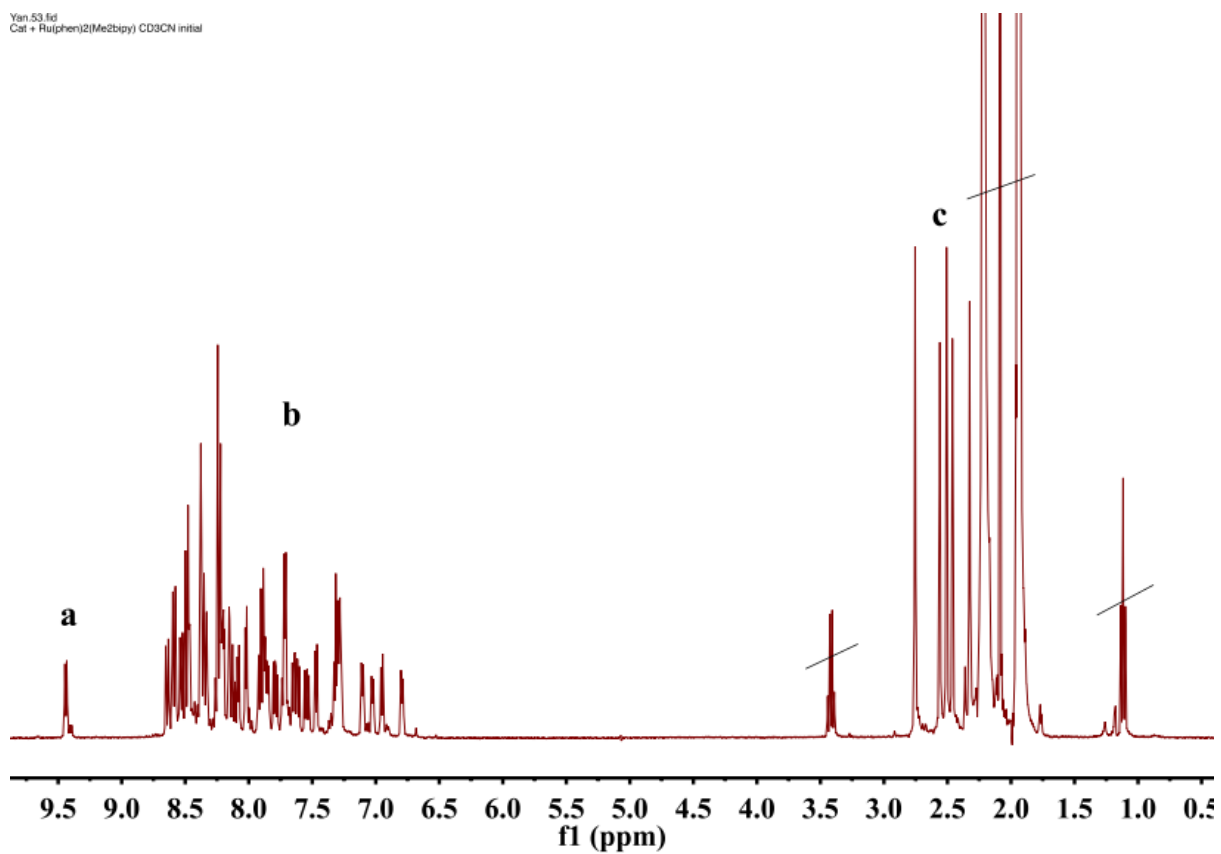
**Figure S1.** <sup>1</sup>H NMR spectrum of [Ru(terpy)(bipy)Cl]Cl (**1**) in D<sub>2</sub>O, showing the aquation of the complex to form [Ru(terpy)(bipy)(OD<sub>2</sub>)Cl]<sub>2</sub>; a = C6 proton of bipy in [Ru(terpy)(bipy)Cl]Cl (**1**); b = C6 proton of bipy in [Ru(terpy)(bipy)(OD<sub>2</sub>)Cl]<sub>2</sub>; c = other aromatic protons. Integration of the two C6 proton peaks indicates that the [Ru(terpy)(bipy)Cl]<sup>+</sup>/[Ru(terpy)(bipy)(OD<sub>2</sub>)]<sup>2+</sup> ratio was 2:1.



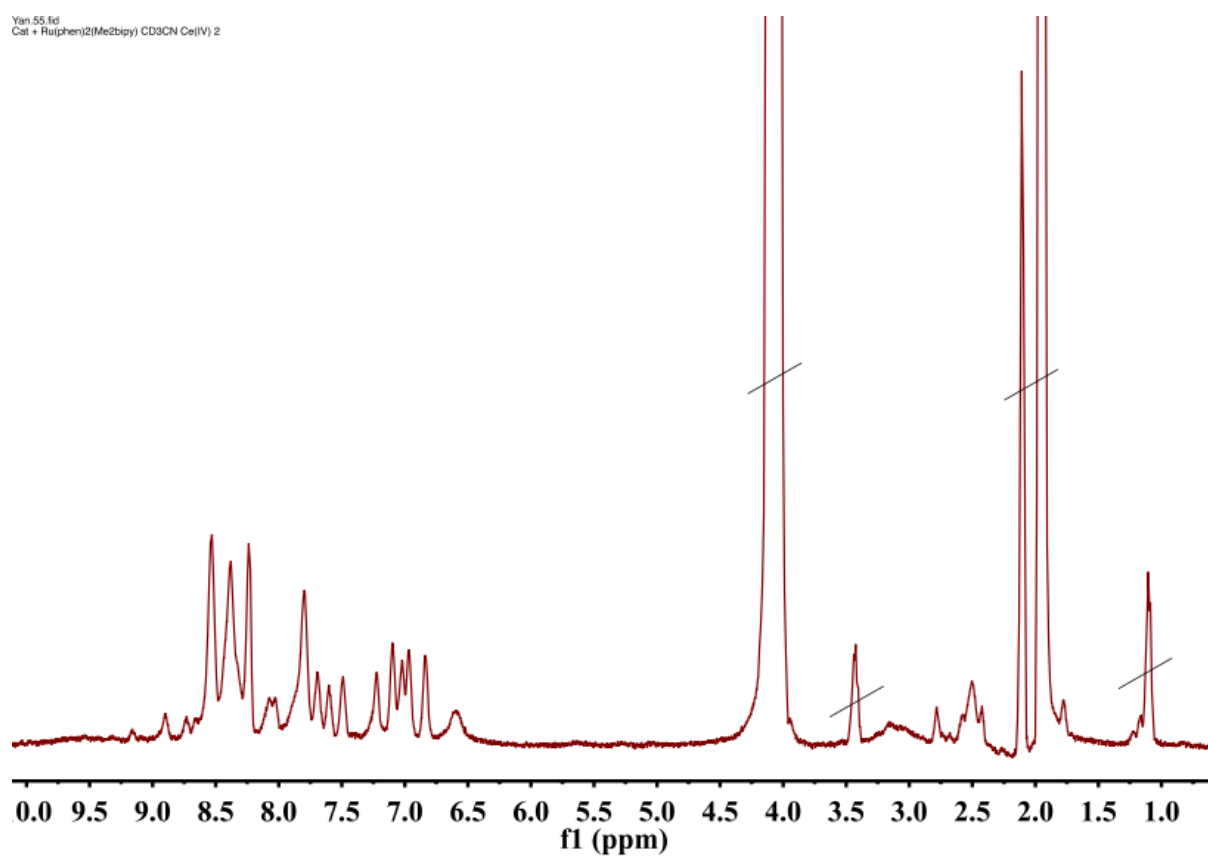
**Figure S2.**  $^1\text{H}$  NMR spectrum of  $[\text{Ru}(\text{terpy})(\text{Me}_2\text{bipy})\text{Cl}]\text{Cl}$  (2) in  $\text{CD}_3\text{CN}$ ; a = C6 proton of  $\text{Me}_2\text{bipy}$ ; b = other aromatic protons; c = methyl protons.



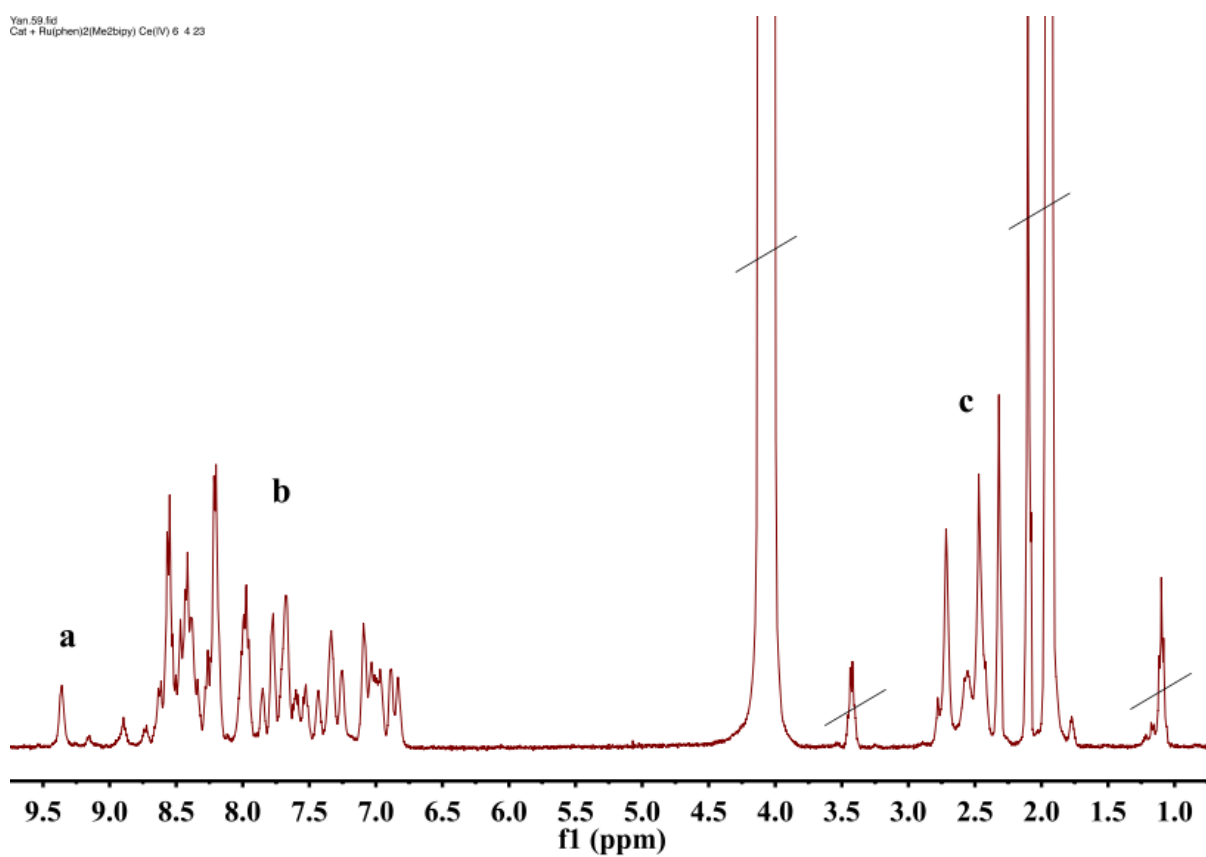
**Figure S3.** <sup>1</sup>H NMR spectrum of [Ru(phen)<sub>2</sub>(Me<sub>2</sub>bipy)]Cl<sub>2</sub> (**4**) in CD<sub>3</sub>CN; a = aromatic protons; b = methyl protons.



**Figure S4.**  $^1\text{H}$  NMR spectrum of **2/4** mixture in  $\text{CD}_3\text{CN}:\text{HClO}_4$  0.1 M in  $\text{D}_2\text{O}$  (1:4); a = C6 proton of  $\text{Me}_2\text{bipy}$  in  $[\text{Ru}(\text{terpy})(\text{Me}_2\text{bipy})\text{Cl}]^+$  with an apparent shoulder at 9.4 ppm due to the C6 proton of  $\text{Me}_2\text{bipy}$  of the aquation product  $[\text{Ru}(\text{terpy})(\text{Me}_2\text{bipy})(\text{OD}_2)]^{2+}$ ; b = other aromatic protons; c = methyl protons.



**Figure S5.**  $^1\text{H}$  NMR spectrum of **2/4** mixture in  $\text{CD}_3\text{CN}:\text{HClO}_4$  0.1 M in  $\text{D}_2\text{O}$  (1:4) measured 10 minutes after four equivalent  $\text{Ce}^{4+}$  was added showing the disappearance of the C6 proton.



**Figure S6.**  $^1\text{H}$  NMR spectrum of 2/4 mixture in  $\text{CD}_3\text{CN}:\text{HClO}_4$  0.1 M in  $\text{D}_2\text{O}$  (1:4) measured 180 minutes after four equivalent  $\text{Ce}^{4+}$  was added; a = C6 proton of  $\text{Me}_2\text{bipy}$  in the regenerated  $[\text{Ru}(\text{terpy})(\text{Me}_2\text{bipy})(\text{OD}_2)]^{2+}$ ; b = other aromatic protons; c = methyl protons.