

Electronic Supplementary Information

Chemical and photochemical oxidation of organic substrates by ruthenium aqua complexes with water as an oxygen source

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Materials

All synthetic reactions were carried out under N₂ atmosphere with standard Schlenk techniques. Solvents were dried and distilled prior to use according to the standard methods. Compounds [Ru(dmp)₂(H₂O)₂](PF₆)₂ (**1**),^[1] [Ru(bpy)₃]Cl₂^[2], Ru(tpy)Cl₃^[3] and [Ru(tpy)(bpy)Cl]Cl^[4] were prepared according to known procedures and stored in fridge under N₂ atmosphere. All other chemicals are commercially available. [Co(NH₃)₅Cl]Cl₂ and Ce(NH₄)₂(NO₃)₆ (Ce^{IV}) were purchased from Aldrich and Tianjin chemical company, respectively. H₂¹⁸O (97 atom%) was purchased from Aladdin chemical company.

Instruments

¹H NMR Spectra were collected at 298 K using a Bruker DRX-400 instrument. Electrospray ionization mass spectra were recorded on a Q-ToF Micromass spectrometer (Manchester, England). EI-MS analyses were carried out on a gas chromatograph fitted with a mass spectrometer (GC-MS 6890/5973, Agilent, USA). UV-Vis absorption measurements were carried out on a HP 8450 spectrophotometer.

Synthesis of [Ru(tpy)(bpy)(H₂O)](ClO₄)₂ (**2**)

[Ru(tpy)(bpy)(H₂O)](ClO₄)₂ was synthesized by a modified procedure reported by Berlinguette.^[4] To a 5 mL MeOH/H₂O (1:1 v:v) solution of [Ru(tpy)(bpy)Cl]Cl (168 mg, 0.3 mmol), was added AgNO₃ (102 mg, 0.6 mmol), the resulting mixture was heated at reflux for 3h and filtrated through Celite. Excess of NaClO₄ was added to the filtrate, slow evaporation of MeOH resulted in the formation of red crystals, which was collected and dried under vacuum (159 mg, 75 %). The structure of this complex was characterized by ¹H NMR, which is identical to that reported in literature.^[4]

General procedure for catalytic oxidation with Ce^{IV} as oxidant

To a N₂-degassed D₂O solution (1 mL) of alkene (0.1 mmol) and catalyst (0.001 mmol) was added Ce^{IV} (0.4 mmol), the mixture was stirred at room temperature for 3 h. The final solution was directly analyzed by ¹H NMR spectroscopy by adding fixed amount of DMF as an internal standard. Control experiment was carried out in a similar manner described above but without catalyst.

General procedure for photocatalytic oxidation

A N₂-degassed aqueous phosphate buffer solution (5 mL, pH 6.8) containing catalyst (2 × 10⁻⁵ M), [Ru(bpy)₃]Cl₂ (2 × 10⁻⁴ M), organic substrate (alcohol or sulfide 2 × 10⁻² M) and [Co(NH₃)₅Cl]Cl₂ (2 × 10⁻² M) was exposed to irradiation of an Xe lamp light source (500 W) with a cut-off filter ($\lambda > 400$ nm) and stirred for 5 h at room temperature. The resulted solution was extracted with CH₂Cl₂ for three times and dried with anhydrous Na₂SO₄. After removal of solvent, the products were characterized and quantified by ¹H NMR spectroscopy. Control experiment was carried out in a similar manner described above but without catalyst.

¹⁸O labeling experiment with cyclohexene as substrate

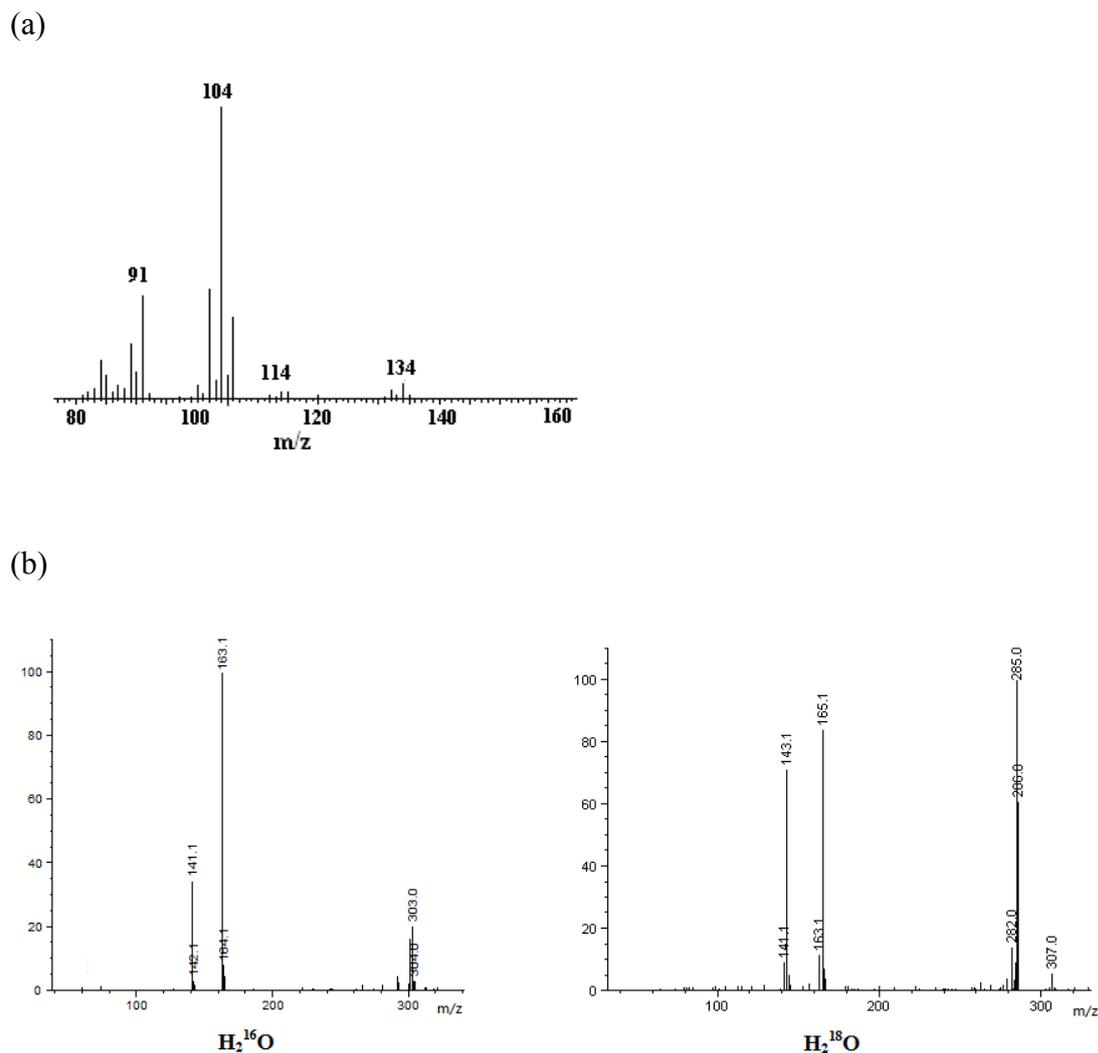
To a N₂-degassed H₂¹⁸O solution (0.5 mL) of cyclohexene (0.1 mmol) and catalyst (0.001 mmol) was added Ce^{IV} (0.4 mmol), the mixture was stirred at room temperature for 3 h. The final solution was extracted by diethyl ether and analyzed by GC-MS.

¹⁸O labeling experiment with thioanisole as substrate

A N₂-degassed H₂¹⁸O phosphate buffer solution (1 mL, pH 6.8) containing catalyst (2×10^{-5} M), [Ru(bpy)₃]Cl₂ (2×10^{-4} M), organic substrate (alcohol or sulfide 2×10^{-2} M) and [Co(NH₃)₅Cl]Cl₂ (2×10^{-2} M) was exposed to irradiation of an Xe lamp light source (500 W) with a cut-off filter ($\lambda > 400$ nm) and stirred for 5 h at room temperature. The resulted solution was extracted with CH₂Cl₂ and purified by a shot column. The product was finally analyzed by ESI-MS.

Electrochemistry

The electrochemical measurements were recorded on a BAS-100W electrochemical potentiostat in a three-electrode cell under argon atmosphere. The working electrode was a glassy carbon disk (diameter, 3 mm) successively polished with 3 and 1 μm diamond pastes and sonicated in ion-free water before use. The counter electrode was a platinum wire. The reference electrode was an aqueous Ag/AgCl electrode. Potential versus NHE was calibrated by using Ru(bpy)₃Cl₂ as a reference with $E(\text{Ru}^{\text{II/III}}) = 1.26$ V.



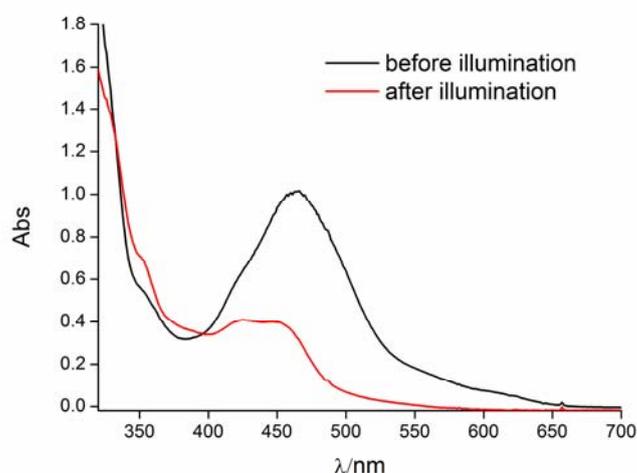


Figure S2 The adsorption of phosphate buffer solution consisting of complex **2** (6×10^{-5} M), $[\text{Ru}(\text{bpy})_3]^{2+}$ (3×10^{-5} M) and $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ (3×10^{-4} M) before and after visible light illumination. The band with maximum at 460 nm arising from MLCT transitions of **2** disappears as $\text{Ru}^{\text{II}}=\text{O}$ oxidized to $\text{Ru}^{\text{IV}}=\text{O}$ upon illumination,^[6] while the adsorption of photosensitizer at 420 and 450 nm remains.

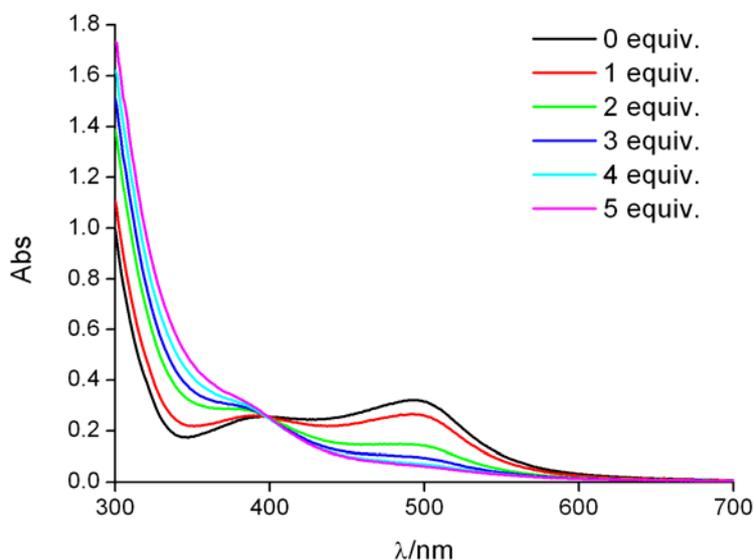


Fig. S3 UV/Vis spectral changes upon addition of 1 to 5 equiv. of Ce^{IV} into a deaerated aqueous solution of complex **1** (5×10^{-5} M), which reflects the species variation from Ru^{II} to Ru^{VI} .

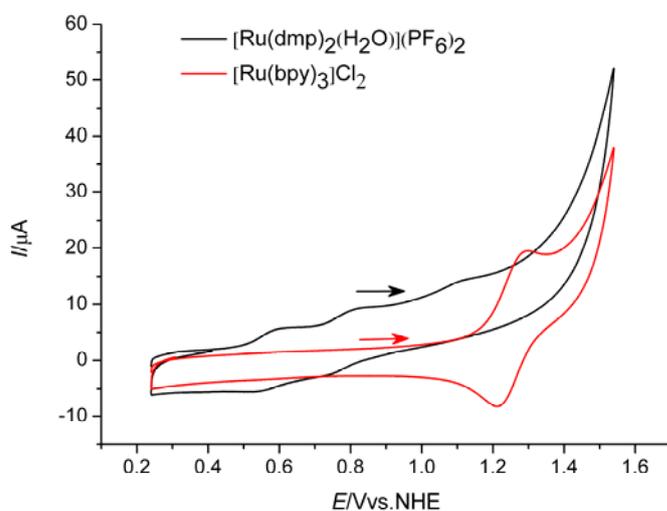


Fig. S4 Cyclic voltammograms of complex **1** (1 mM, black curve) and $[Ru(bpy)_3]^{2+}$ (1 mM, red curve) in phosphate buffer (pH 6.8, 50 mM) solutions, which indicates the oxidation of **1** by photogenerated $[Ru(bpy)_3]^{3+}$ is thermodynamically favorable. Electrode: GC, scan rate: 100 mV/s.

Control experiments in the absence of catalysts

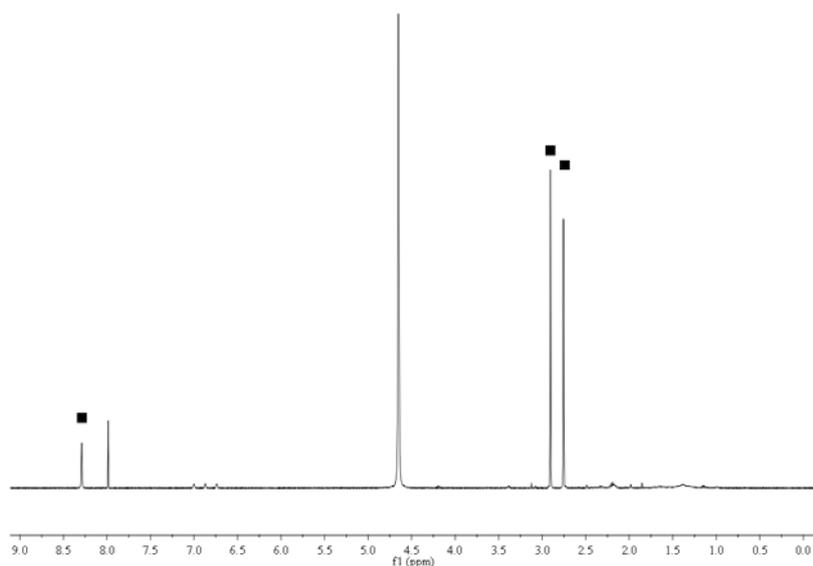


Fig. S5 1H NMR spectrum of the resulted solution from chemical oxidation of cyclohexene (internal standard DMF (■)). Reaction conditions: cyclohexene (0.1 mmol) and Ce^{IV} (0.4 mmol) in D_2O solution (1 mL) stirred for 3 h.

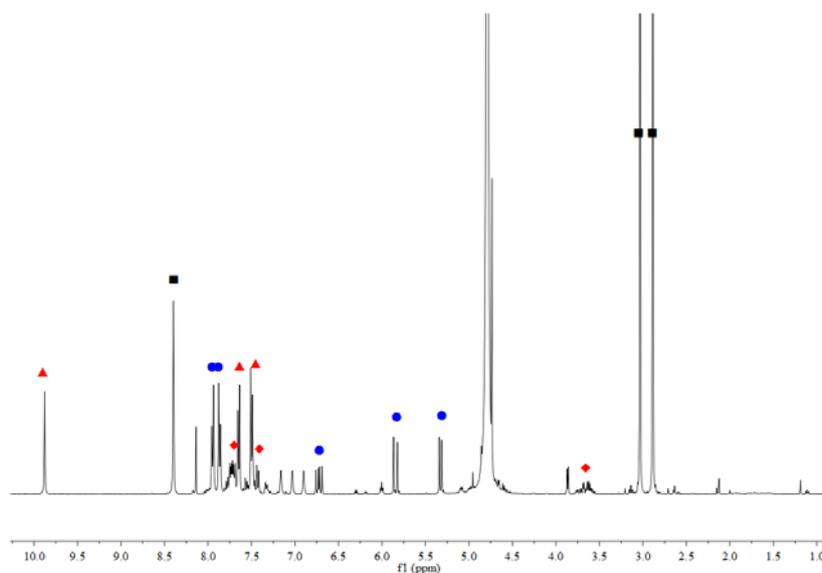


Fig. S6 ¹H NMR spectrum of the resulted solution from chemical oxidation of sodium *p*-styrene sulfate (sodium *p*-styrene sulfate (●), sodium 4-formylbenzenesulfonate (▲), sodium 4-(1,2-dihydroxyethyl)benzenesulfonate (◆), internal standard DMF (■)). Reaction conditions: sodium *p*-styrene sulfate (0.1 mmol) and Ce^{IV} (0.4 mmol) in D₂O solution (1 mL) stirred for 3 h.

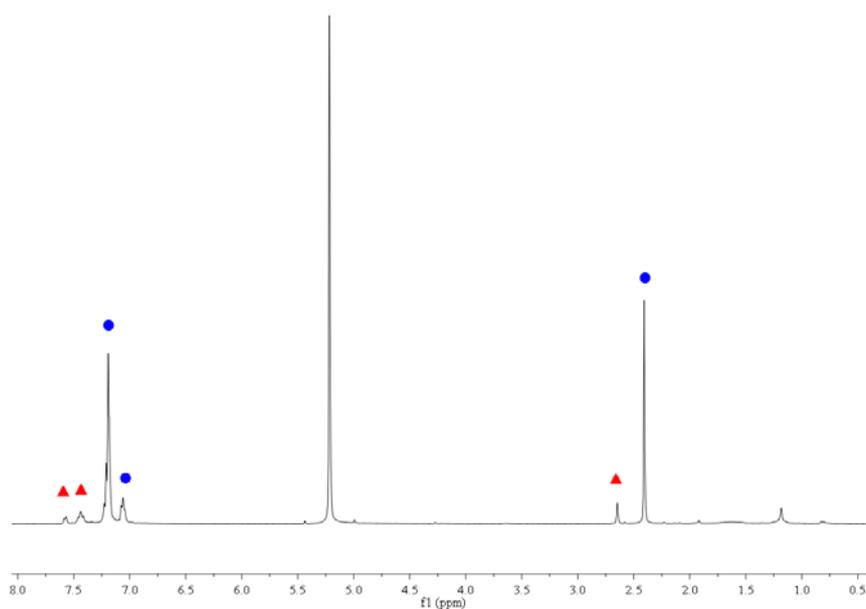


Fig. S7 ¹H NMR spectrum of the residue extracted by DCM from resulted solution of photocatalytic oxidation of thioanisole (solvent CDCl₃, thioanisole (●), methyl phenyl sulfoxide (▲)). Reaction conditions: [Ru(bpy)₃]Cl₂ (2 × 10⁻⁴ M), sulfide (2 × 10⁻² M),

and $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ (2×10^{-2} M) in 5 mL neutral phosphate buffer solution stirred for 5h under visible light illumination.

Catalytic oxidation

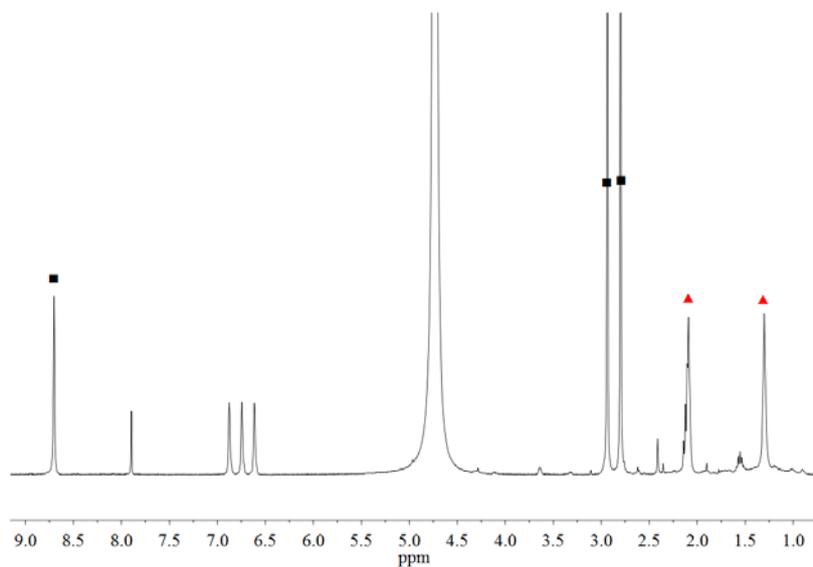


Fig. S8 ^1H NMR spectrum of the resulted solution from chemical oxidation of cyclohexene (adipic acid (▲), internal standard DMF (■)). Reaction conditions: complex **1** (0.001 mmol), cyclohexene (0.1 mmol) and Ce^{IV} (0.4 mmol) in D_2O solution (1 mL) stirred for 3 h.

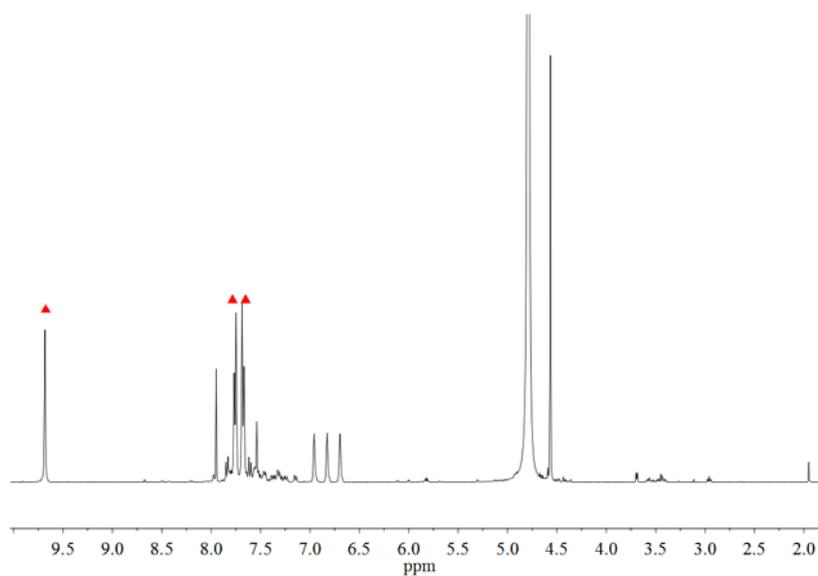


Fig. S9 ^1H NMR spectrum of the resulted solution from chemical oxidation of sodium *p*-styrene sulfate (sodium 4-formylbenzenesulfonate (▲)). Reaction conditions:

complex **1** (0.001 mmol), sodium *p*-styrene sulfate (0.1 mmol) and Ce^{IV} (0.4 mmol) in D₂O solution (1 mL) stirred for 3 h.

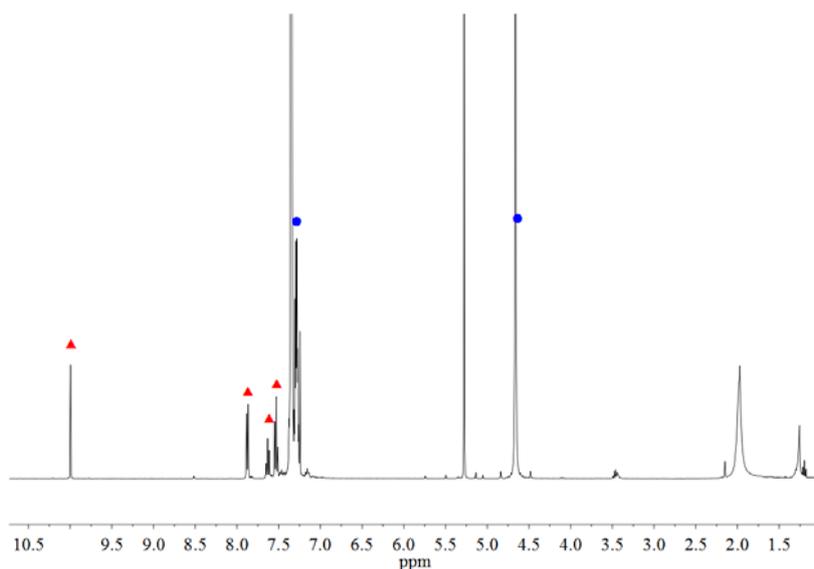


Fig. S10 ¹H NMR spectrum of the residue extracted by DCM from resulted solution of photocatalytic dehydrogenation of benzyl alcohol (solvent CDCl₃, benzyl alcohol (●), benzaldehyde (▲)). Reaction conditions: complex **1** (4×10^{-5} M), [Ru(bpy)₃]Cl₂ (4×10^{-4} M), alcohol (2×10^{-2} M), and [Co(NH₃)₅Cl]Cl₂ (2×10^{-2} M) in 5 mL neutral phosphate buffer solution stirred for 5h under visible light illumination.

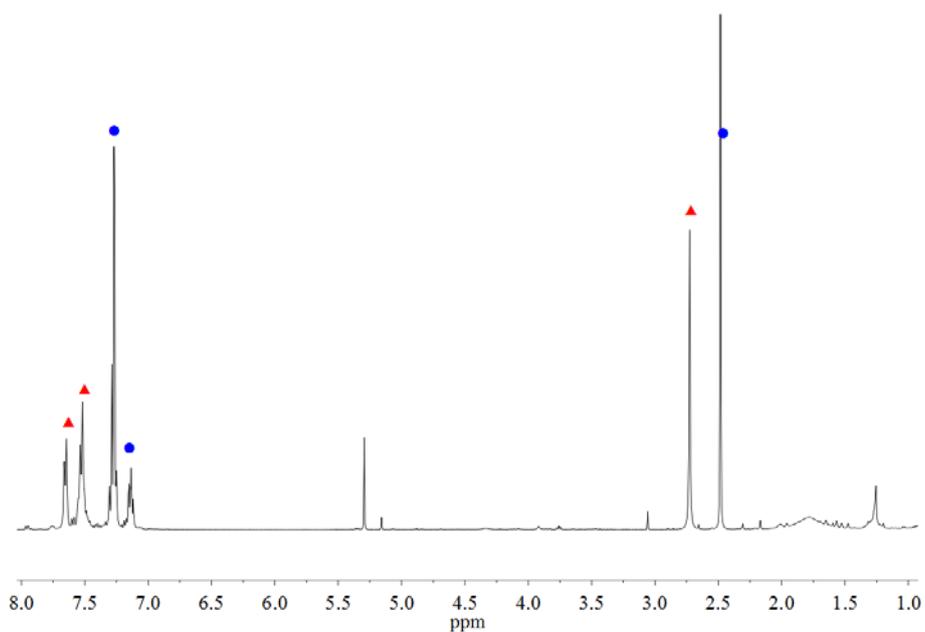


Fig. S11 ¹H NMR spectrum of the residue extracted by DCM from resulted solution

of photocatalytic oxidation of thioanisole (solvent CDCl_3 , thioanisole (●), methyl phenyl sulfoxide (▲)). Reaction conditions: complex **1** (4×10^{-5} M), $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ (4×10^{-4} M), sulfide (2×10^{-2} M), and $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ (2×10^{-2} M) in 5 mL neutral phosphate buffer solution stirred for 5h under visible light illumination.

References

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