Supporting Information

Insight into highly selective photocatalytic oxidation of alcohols by a new trinuclear ruthenium complex with visible light

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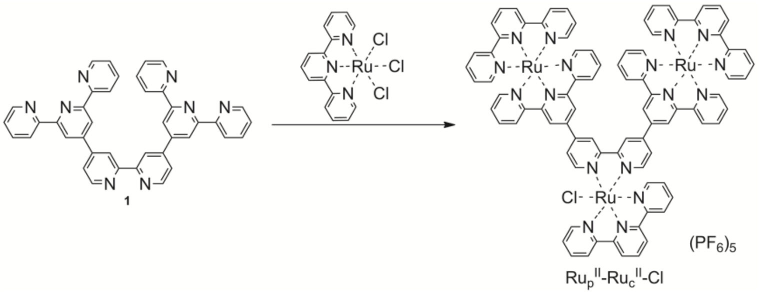
Experimental details

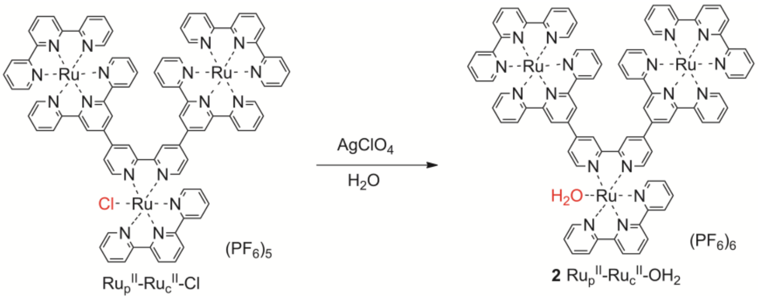
Materials: The compounds 2,2′-bipyridine-4,4′-dicarbaldehyde[1] and Ru(tpy)Cl_3[2] were synthesized according to the reported procedures. All solvents and other chemicals were obtained commercially and used without further purification.

Ligand 1 (tpy−bpy−tpy): A mixture of 4,4′-diformyl-2,2′-bipyridine (420 mg, 2.0 mmol), NaOH (480 mg, 12 mmol), aqueous NH_3 (20 mL, 24 mmol) and 2-acetylpyridine (1.5 g, 12 mmol) was heated at reflux in 100 mL of C_2H_5OH for 2 days under argon. The amount of 2-acetylpyridine more than 12 mmol could be needed for modest yield. After cooling to room temperature, the solution was stirred for additional 4 h. Then the solution was kept in a refrigerator overnight and the residue was collected by filtration and washed with 50 mL of water followed by 50 mL cold C_2H_5OH. Recrystallization from C_2H_5OH afforded white solid 1 (556 mg, 45%). MALDI-TOF-MS: 619.3 $[M+H]^+$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.01 (s, 2H), 8.89 (m, 6H), 8.75 (d, 4H, J = 4.4 Hz), 8.70 (d, 4H, J = 8 Hz), 7.91 (td, 4H, J = 8, 1.6 Hz), 7.86 (dd, 2H, J = 4.8, 1.6 Hz), 7.39 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.9, 154.5, 154.0, 148.0, 147.4, 146.1, 145.4, 135.1, 122.1, 120.2, 119.5, 117.6, 117.2. Elemental analysis: Calcd. for $C_{40}H_{26}N_8$: C, 77.65; H, 4.24; N, 18.11. Found: C, 77.43; H, 4.31; N, 18.01.

Chloro complex (Ru_p^{II}−Ru_c^{II}−Cl): A mixture of ligand **1** (62 mg, 0.1 mmol), Ru(tpy)Cl_3 (137 mg, 0.3 mmol) and N-ethylmorpholine (2 mL) was heated at reflux in 150 mL of C_2H_5OH for 16 h under argon. After the solution was cooled to room temperature, filtered and excess NH_4PF_6 was added into the filtrate to form a purple solid. The solid was collected and washed with water and C_2H_5OH and dried. The crude product was purified by column chromatography using silica gel and a mixture of acetonitrile/saturate KNO_3 aqueous solution (v/v, 3:1) as the eluent. The received band was treated with NH_4PF_6 and acetonitrile was evaporated. The precipitate was collected, washed with water, C_2H_5OH, diethyl ether and dried in vacuo. Yield: 214 mg (90%). ESI-MS: 331.6381 $[M\text{-}5(PF_6)]^{5+}$, 450.5413 $[M\text{-}4(PF_6)]^{4+}$. ^{1}H NMR (400 MHz, CD_3CN): δ 10.64 (d, 1H, J = 6 Hz), 10.20 (s, 1H), 9.92 (s, 1H), 9.80 (s, 2H), 9.42 (s, 2H), 9.11 (d, 2H, J = 8 Hz), 8.90 (d, 2H, J = 8.4 Hz), 8.85 (dd, 1H, J= 5.6, 1.2 Hz), 8.80 (d,2H, J = 8.4 Hz), 8.75 (d, 2H, J = 8.4 Hz), 8.66 (d, 2H, J = 8.4 Hz), 8.54 (d, 3H, J = 8 Hz), 8.49 (dd, 3H, J = 8, 2.8 Hz), 8.43 (t, 2H, J = 8 Hz), 8.28 (t, 1H, J = 8 Hz), 7.96 (m, 13H), 7.82 (d, 1H, J = 6 Hz), 7.57 (d, 2H, J = 5.2 Hz), 7.44 (m, 6H), 7.34 (d, 2H, J = 5.2 Hz), 7.23 (dd, 4H, J = 12.4, 5.2 Hz), 7.15 (m, 4H). Elemental analysis: Calcd. for $C_{85}H_{59}F_{30}N_{17}P_5ClRu_3$: C, 42.86; H, 2.50; N, 10.00. Found: C, 42.45; H, 2.74; N, 10.32.



Complex 4 (Ru_p^{II}–Ru_c^{II}–OH_2): A mixture of the chloro complex (50 mg, 0.02 mmol) and $AgClO_4$ (41 mg, 0.2 mmol) was heated at reflux in 30 mL water/acetone (v/v = 4:1) overnight in the dark under argon. After the solution was cooled to room temperature, filtered and excess NH_4PF_6 was added into the filtrate. Acetone was evaporated out in vacuo. The precipitate was collected, and then dissolved in a minimum of acetone. Diethyl was added into acetone solution, and filtrated. The resulting solid was dried in vacuo. Yield: 43 mg (86%). ESI-MS: 446.0505 $[M\text{-}5(PF_6)\text{-}H]^{4+}$, 643.0593 $[M\text{-}4(PF_6)\text{-}H]^{3+}$. ^{1}H NMR (400 MHz, CD_3CN): δ 9.99 (d, 1H, J = 4 Hz), 9.74 (s, 1H), 9.49 (s, 1H), 9.45 (s, 2H), 9.08 (s, 2H), 8.86 (d, 2H, J = 8 Hz), 8.79 (d, 2H, J = 8 Hz), 8.77 (d, 1H, J = 1.6 Hz), 8.74 (m, 4 H), 8.66 (d, 2H, J = 8 Hz), 8.57 (d, 2H, J = 8 Hz), 8.52 (d, 2H, J = 8 Hz), 8.46 (d, 3H, J = 8Hz), 8.42 (t, 2H, J = 8 Hz), 8.14 (t, 2H, J = 8 Hz), 7.98 (m, 5H), 7.88 (m, 6H), 7.74 (d, 1H, J = 4 Hz), 7.49 (m, 4H), 7.42 (d, 2H, J = 4 Hz), 7.33 (t, 4H, J = 4 Hz), 7.17 (m, 6H), 7.09 (t, 2H, J = 8 Hz). Elemental analysis: Calcd. for $C_{85}H_{61}F_{36}N_{17}P_6ORu_3$: C, 40.68; H, 2.45; N, 9.49. Found: C, 40.35; H, 2.68; N, 9.36.



Ru_p^{II}-Ru_c^{II}-Cl

2 Ru_p^{II}-Ru_c^{II}-OH_2

Measurements: The NMR spectra were carried out on a Bruker Avance 400 spectrometer. Electrospray ionization (ESI) mass spectra were run on a Finnigan LCQ quadrupole ion trap mass spectrometer. Matrix-Assisted Laser Desorption/Ionization Time of Flight (MALDI-TOF) mass spectra were recorded on a Bruker BIFLEX III mass spectrometer. UV-vis absorption spectra were run on a Hitachi U-3010 spectrophotometer. Cyclic voltammetry (CV) experiments were carried out on an EG&G model 283 potentiostat/galvanostat in a one-compartment cell equipped with a glassy carbon working electrode, a Ag/Ag^+ (10 mM $AgNO_3$ in CH_3CN) reference electrode for chloro complex or a SCE (saturated KCl aqueous Solution) reference electrode for **4**, and a platinum plate counter electrode at a scan rate of 100 mV s^{-1}. Differential pulse voltammogram (DPV) was performed on a computer-controlled CHI660C electrochemical workstation.

Photocatalytic oxidation of alcohols: In a typical catalytic reaction, a quartz tube (15 mL) containing an aqueous solution (5 mL, pH 7.0) of 0.01 mM **4**, 10 mM alcohols, 20 mM $[Co(NH_3)_5Cl]Cl_2$, 0.1 M phosphate buffe was irradiated ($\lambda > 420$ nm) for 8 h at room temperature under argon or air atmosphere. Light illumination was supplied by 30 white LEDs (3 W). The resulting solution was extracted with CH_2Cl_2 (30 mL) for three times. The organic layer was dried with Na_2SO_4 overnight, and the solvent was evaporated in vacuo. Then proper $CDCl_3$ was added into the residue. The results were obtained through ^1H NMR spectroscopy with quantitative analyses by the ratio of integrated peak intensities of products to that of corresponding substrates. Control experiments showed that there was no product in the absence of any of the following components: light, **4**, $[Co(NH_3)_5Cl]Cl_2$ or alcohols.

References

[1] L. D. Ciana, W. J. Dressick and A. Von Zelewsky, *J. Heterocycl. Chem*. 1990, **27**, 163–165.

[2] B. P. Sullivan, J. M. Calvert, T. J. Meyer, *Inorg. Chem*. 1980, **19**, 1404–1407.

^{1}H NMR and Mass spectra for ligand and complexes

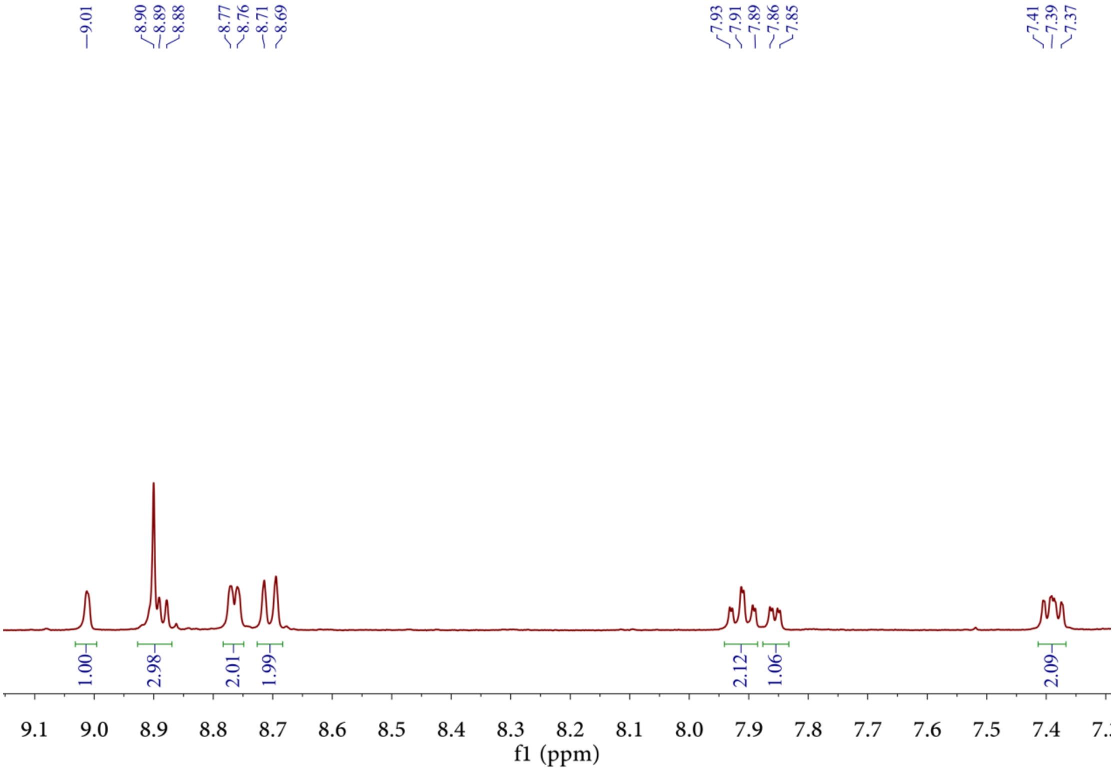


Fig. S1 ^{1}H NMR spectrum of ligand **1** in $CDCl_3$**.**

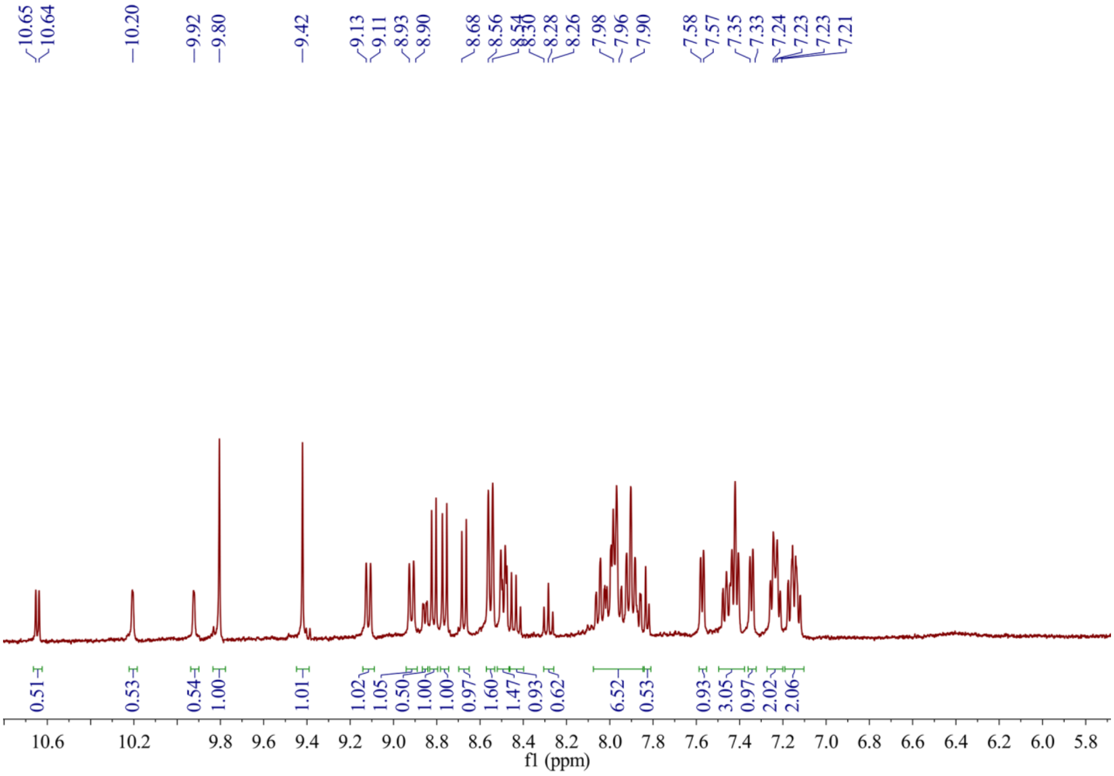


Fig. S2 ^{1}H NMR spectrum of chloro complex (Ru_p^{II}—Ru_c^{II}—Cl) in CD_3CN**.**

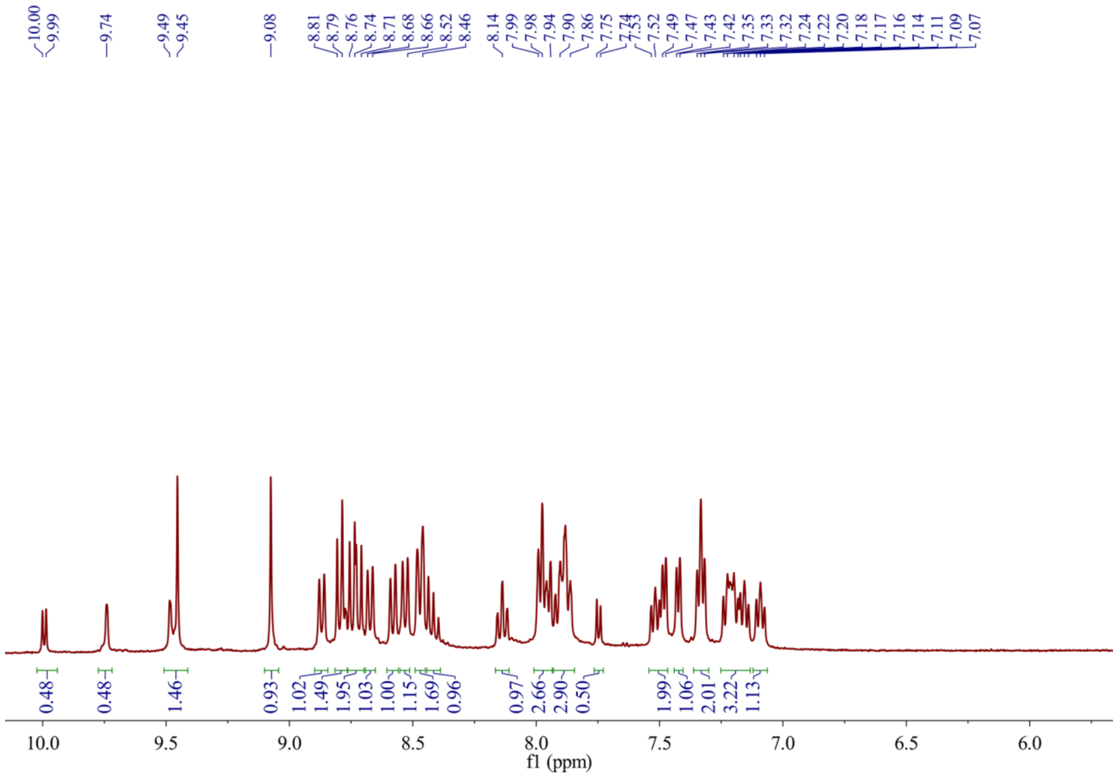


Fig. S3 ^{1}H NMR spectrum of **4** (Ru_p^{II}—Ru_c^{II}—OH_2) in CD_3CN. The signal of protons from H_2O group in the complex disappeared because of the displacement of H_2O for CD_3CN.

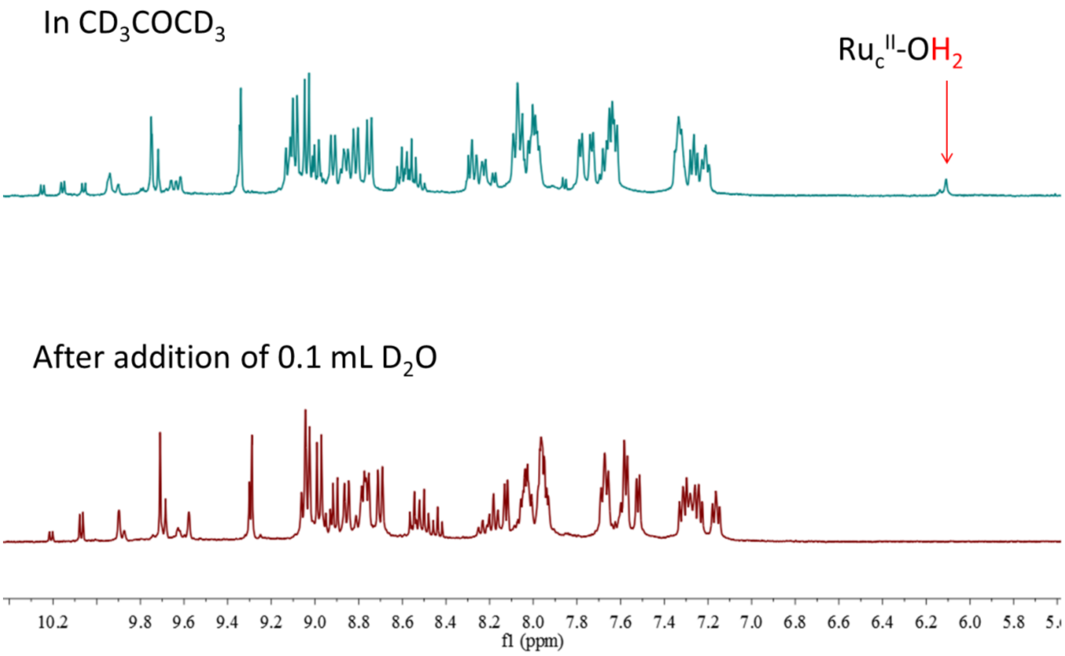


Fig. S4 Proton exchange experiment in CD_3COCD_3. The signal at 6.1 ppm (top) assigned to H_2O group of **4** disappeared after addition of 0.1 mL D_2O (down).

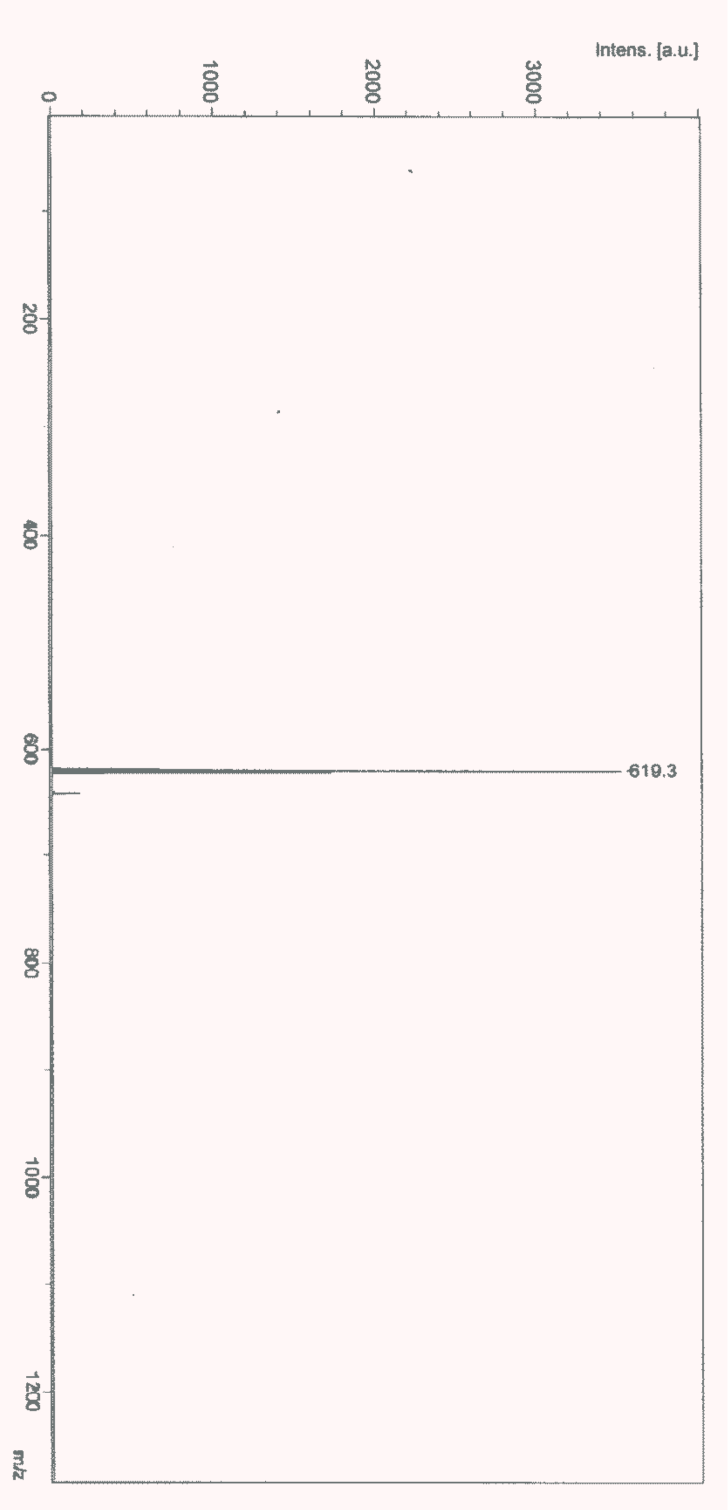


Fig. S5 MALDI-TOF mass spectrum of ligand **1**, the signal at m/z = 619.3 is ascribed to $[M\text{+H}]^+$.

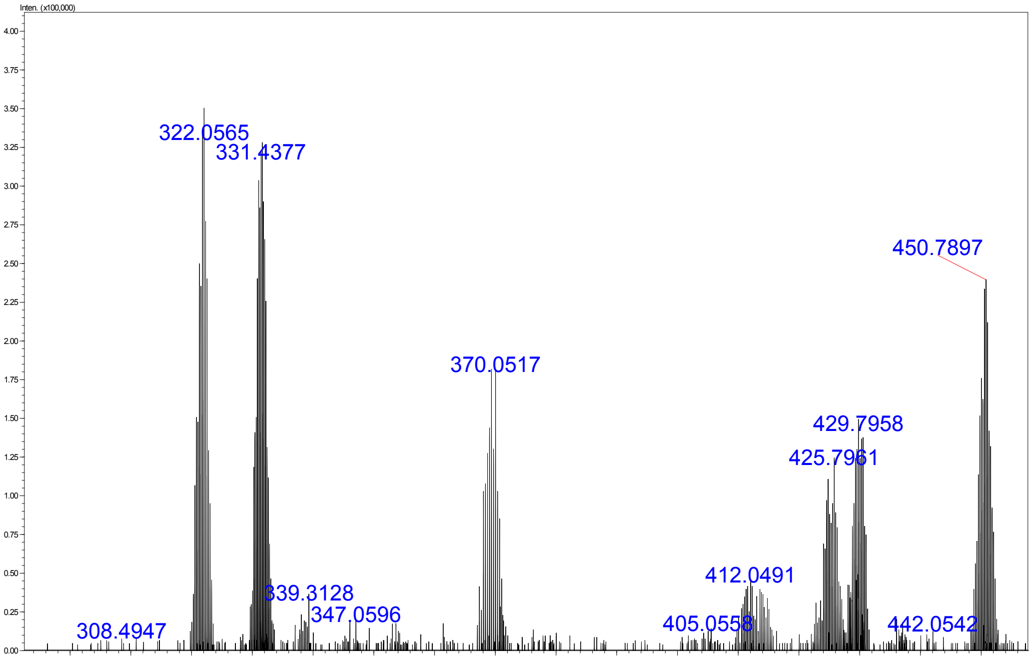


Fig. S6 ESI/MS spectrum of the chloro complex (Ru_p^{II}–Ru_c^{II}–Cl), signals at *m/z* =322.0565, *m/z* = 331.4377, *m/z* = 370.0517, *m/z* = 450.7987 are ascribed to [*M*-5(PF_6)-tpy-Ru-Cl]$^{4+}$, [*M*-5(PF_6)]$^{5+}$, [*M*-4(PF_6)-Cl+CH_3CN]$^{5+}$ and [*M*-4(PF_6)]$^{4+}$, respectively.

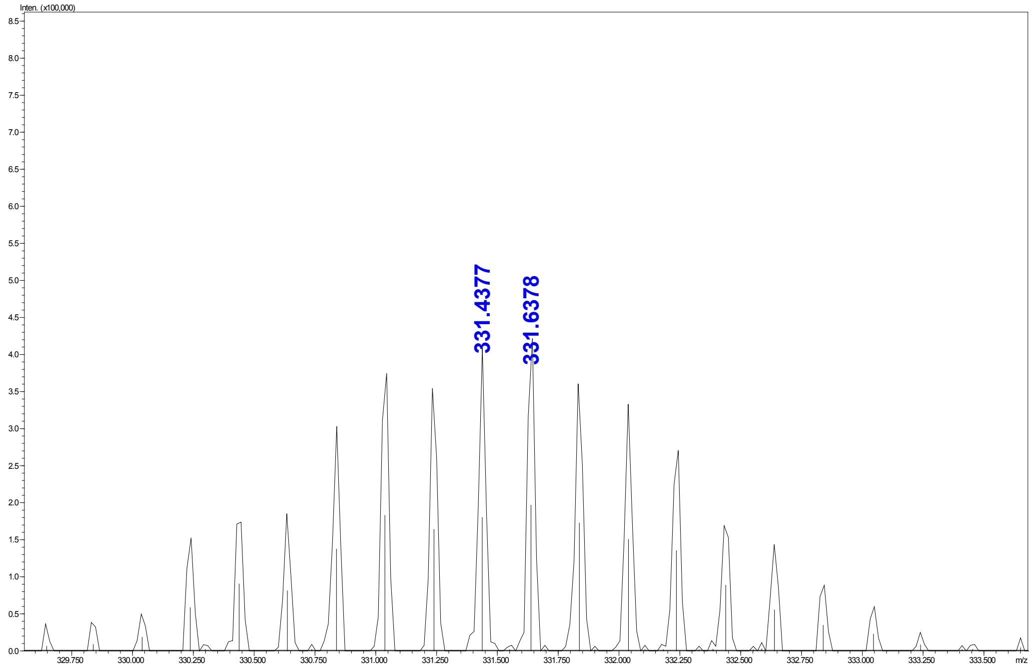


Fig. S7 Isotopic peaks of signals at *m/z* = 331.4377 ascribed to [*M*-5(PF_6)]$^{5+}$.

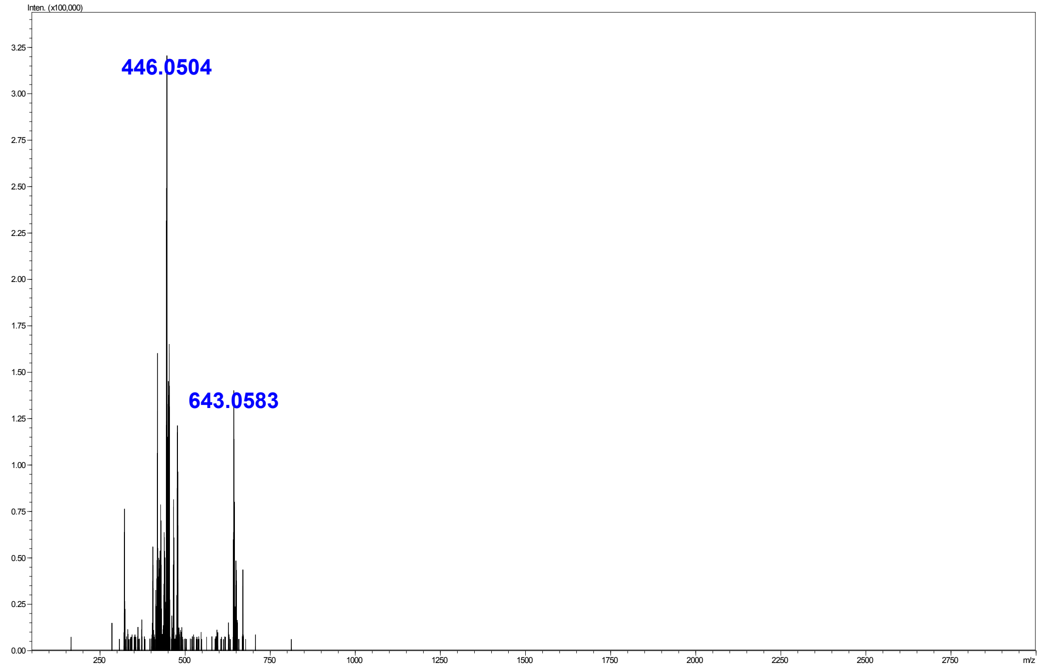


Fig. S8 ESI/MS spectrum of the **4** (Ru_p^{II}–Ru_c^{II}–OH_2), signals at *m/z* = 446.0504 and *m/z* = 643.0583 are ascribed to [M-5(PF_6)-H]$^{4+}$ and [M-4(PF_6)-H]$^{3+}$.

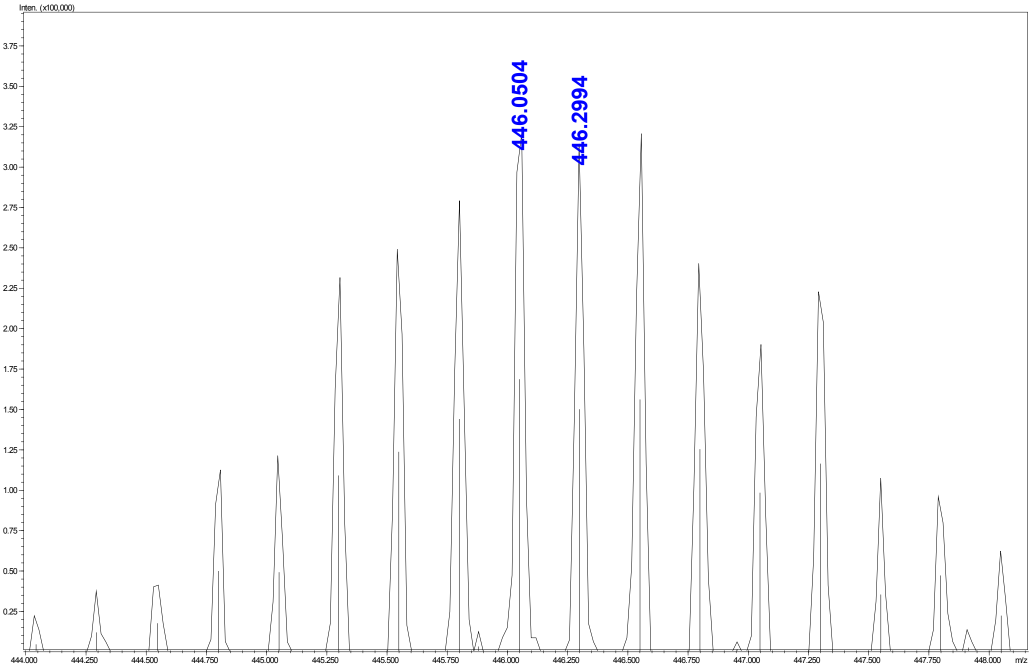


Fig. S9 Isotopic peaks of signals at *m/z* = 446.0504.

CV, DPV and UV-Vis spectra

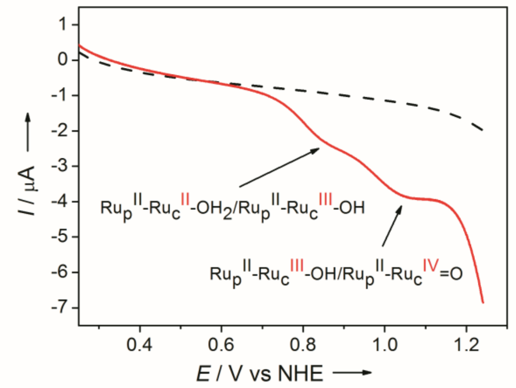


Fig. S10 Differential pulse voltammogram (DPV) of **4** was carried out in the phosphate buffer solution (0.1 M, pH 7.0) under air with a glassy carbon working electrode, a SCE (saturated KCl aqueous solution) reference electrode and a platinum plate counter electrode. The data were recorded with a step potential of 5 mV and an amplitude of 50 mV under an air atmosphere.

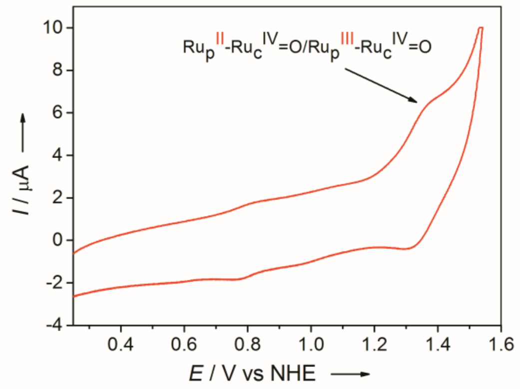


Fig. S11 Cyclic voltammogram (CV) of the complex **4** (Ru_p^{II}–Ru_c^{II}─OH_2) in a large potential range was carried out in the phosphate buffer solution (0.1 M, pH 7.0) with a glassy carbon working electrode, a SCE (saturated KCl aqueous solution) reference electrode and a platinum plate counter electrode. The data were recorded at a scan rate of 100 mV s^{-1} under an air atmosphere. The redox potential at 1.33 V was ascribed to Ru_p^{II}/Ru_p^{III}.

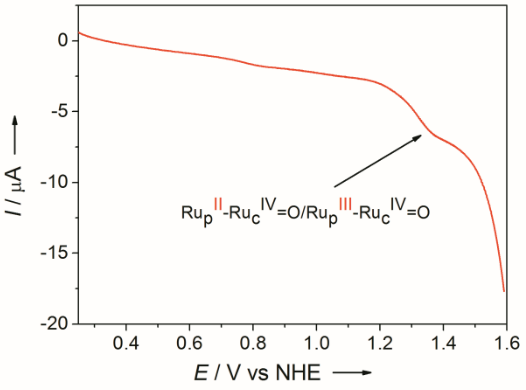


Fig. S12 Differential pulse voltammogram (DPV) of **4** in a large potential range was carried out in the phosphate buffer solution (0.1 M, pH 7.0) under air with a glassy carbon working electrode, a SCE (saturated KCl aqueous solution) reference electrode and a platinum plate counter electrode.

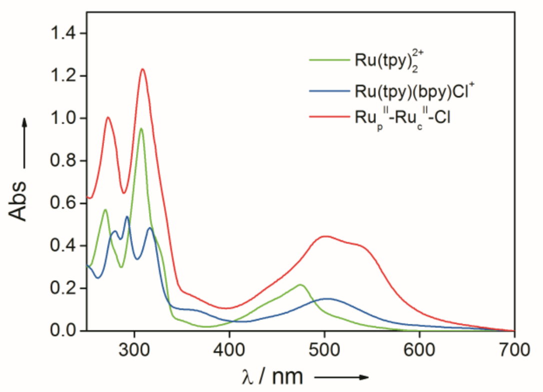


Fig. S13 UV-Vis absorption spectra of the chloro complex Ru_p^{II}—Ru_c^{II}—Cl (10 μM), $[Ru(tpy)_2]^{2+}$ (10 μM), $[Ru(tpy)(bpy)Cl]^+$ (10 μM) in acetonitrile.

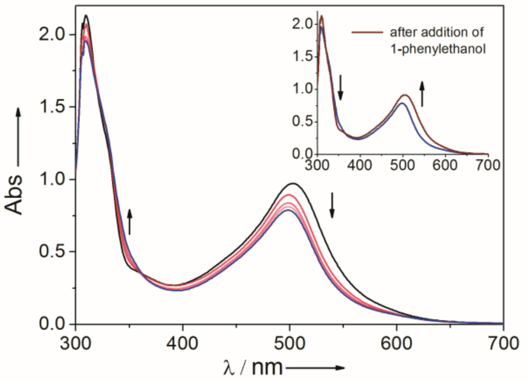


Fig. S14 Spectral changes were recorded at room temperature under an argon atmosphere for the phosphate buffer solution (3.0 mL, 0.1 M, pH 7.0) containing **4** (0.01 mM) and $[Co(NH_3)_5Cl]Cl_2$ (20 mM) without substrate alcohols upon light irradiation for 150 seconds; spectra were corrected for $[Co(NH_3)_5Cl]Cl_2$ absorption. Inset: the spectrum (blue line) mostly recovered (brown line) after addition of 1-phenylehanol into the irradiated solution in 5 minutes.

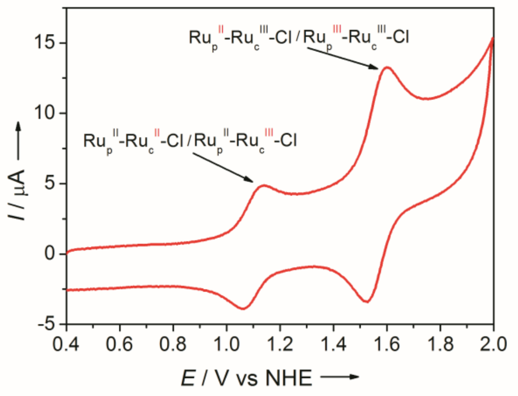


Fig. S15 Cyclic voltammogram (CV) of the chloro complex (Ru_p^{II}—Ru_c^{II}—Cl) was carried out in CH_3CN with a glassy carbon working electrode, a Ag/Ag^+ (10 mM $AgNO_3$ in CH_3CN) reference electrode and a platinum plate counter electrode containing $(Bu^n)_4N(PF_6)$. The data were recorded at a scan rate of 100 mV s^{-1} under argon atmosphere. The CV exhibited two redox potential at 1.09 V and 1.56 V ascirbed to Ru_c^{II}—Cl/Ru_c^{III}—Cl and Ru_p^{II}/Ru_p^{III}, respectively.

Photocatalytic oxidation of alcohols

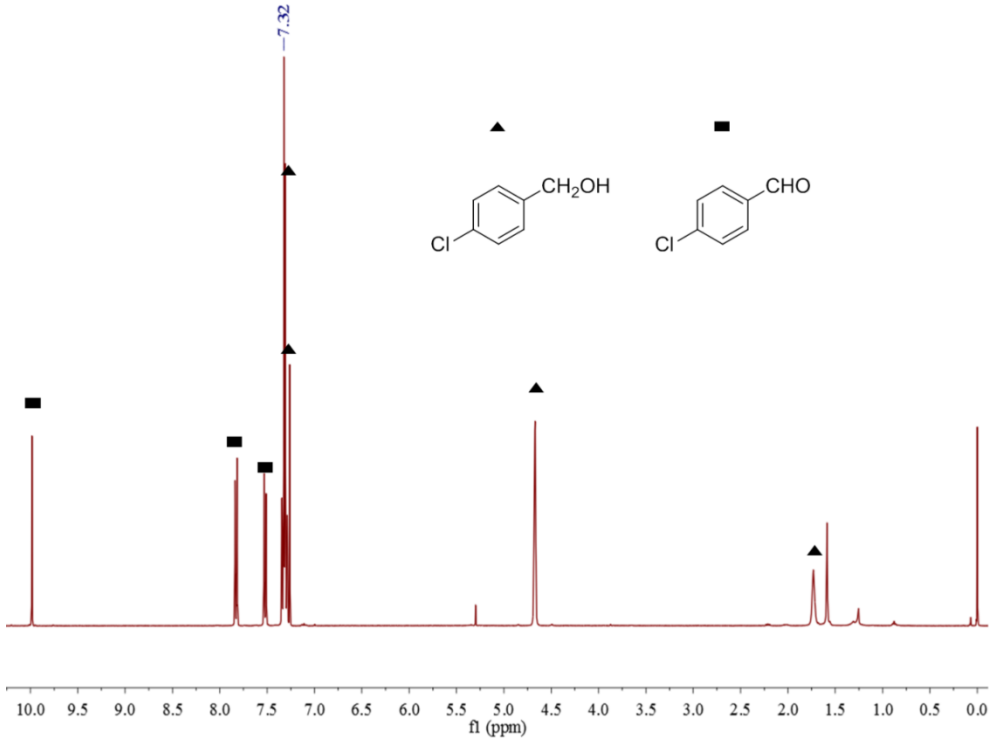


Fig. S16 ^{1}H NMR spectra ($CDCl_3$) of the product (4-chlorobenzyl alcohol) and substrate (4-chlorobenzaldehyde) using **4** in the photooxidation reaction under an argon atmosphere.

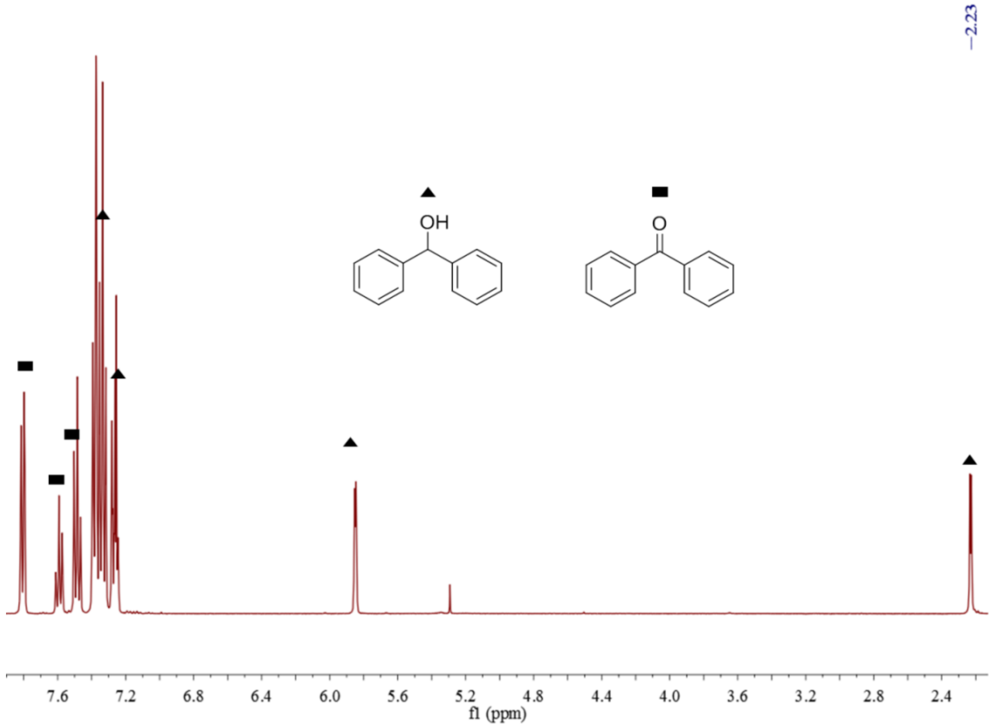


Fig. S17 ^{1}H NMR spectra ($CDCl_3$) of the product (diphenylmethanol) and substrate (benzophenone) using **4** in the photooxidation reaction under an air atmosphere.

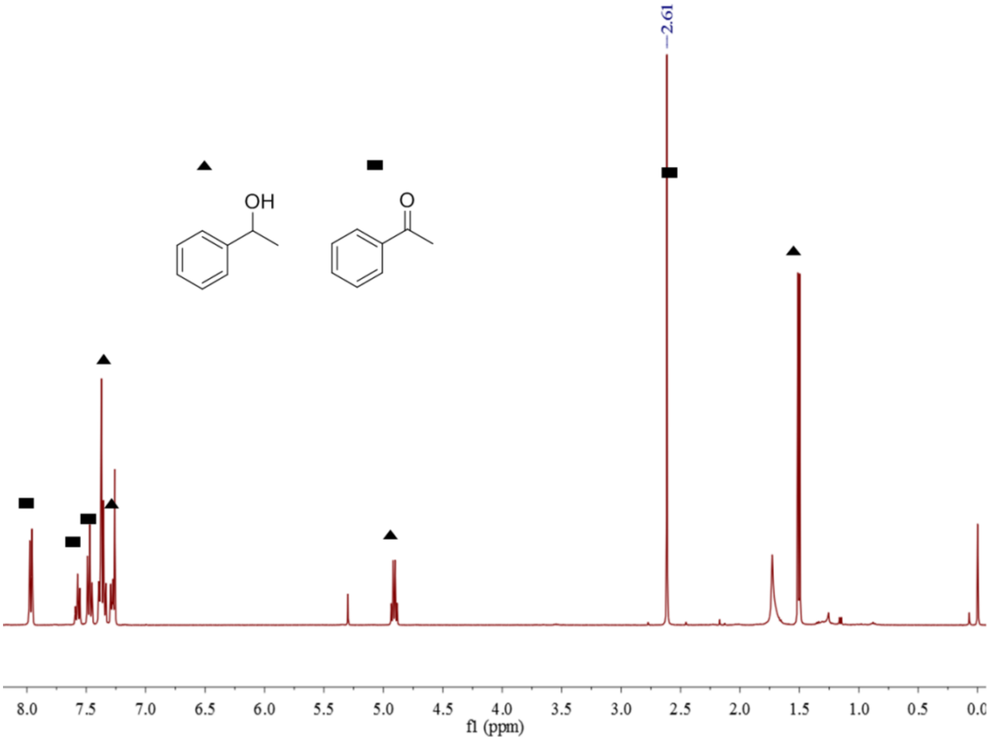


Fig. S18 ^{1}H NMR spectra ($CDCl_3$) of the product (acetophenone) and substrate (1-phenylethanol) using **4** in the photooxidation reaction by adding 3 mg $[Co(NH_3)_5Cl]Cl_2$ into the reaction solution containing $[Co(NH_3)_5Cl]Cl_2$ (20 mM) every hour for 8 h under an air atmosphere.

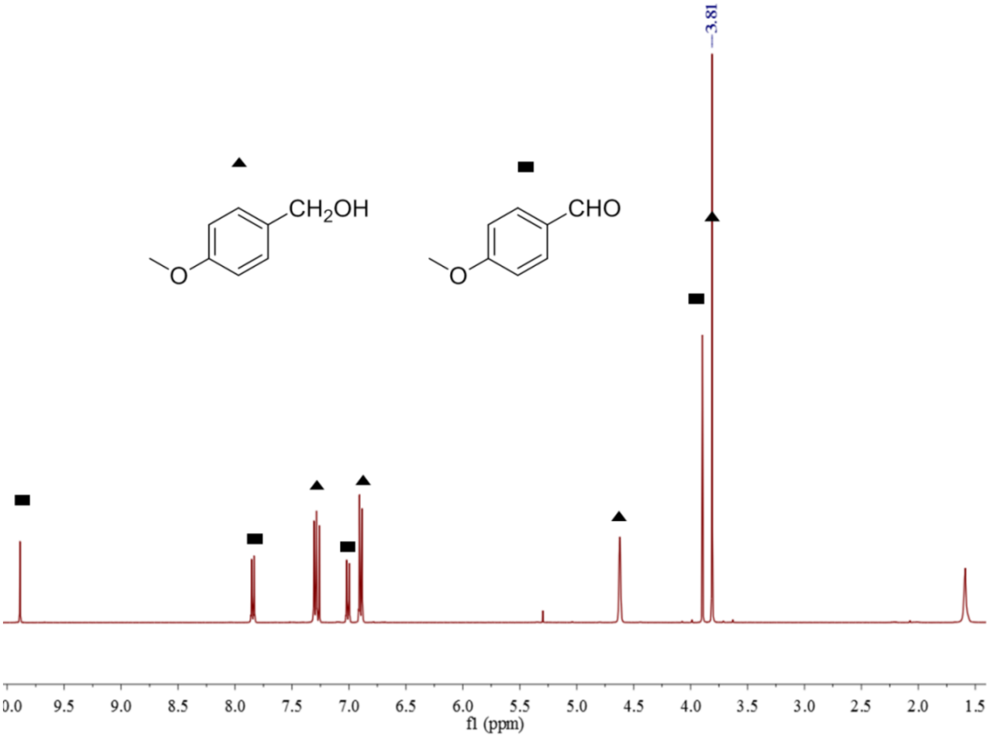


Fig. S19 ^{1}H NMR spectra ($CDCl_3$) of the product (4-methoxybenzyl alcohol) and substrate (4-methoxybenzaldehyde) using **4** in the photooxidation reaction under an air atmosphere.

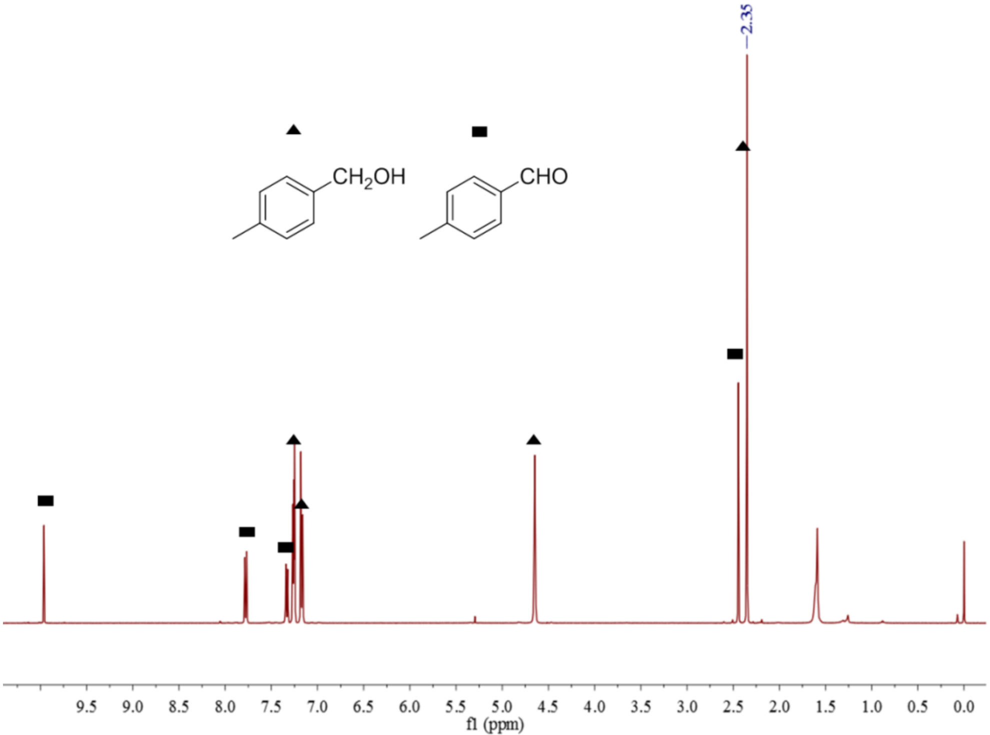


Fig. S20 ^{1}H NMR spectra ($CDCl_3$) of the product (4-methylbenzyl alcohol) and substrate (4-methylbenzaldehyde) using **4** in the photooxidation reaction under an argon atmosphere.

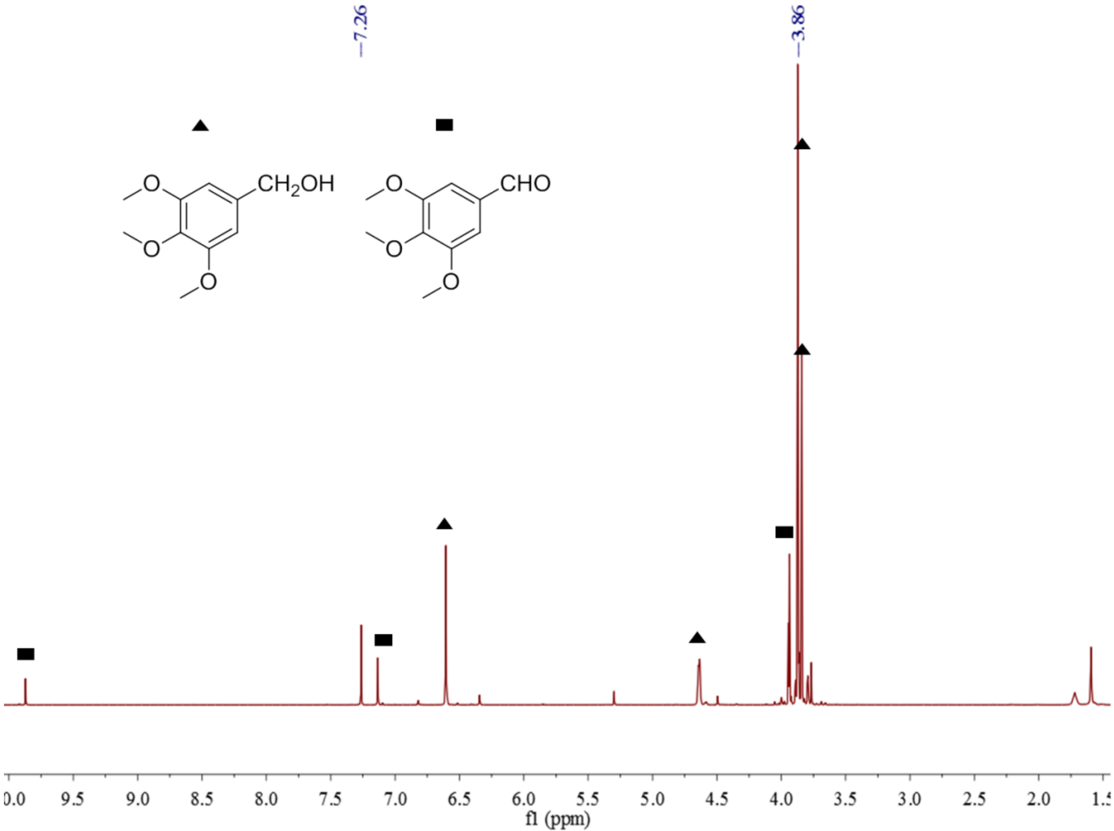


Fig. S21 ^{1}H NMR spectra ($CDCl_3$) of the product (3,4,5-trimethoxybenzaldehyde) and substrate (3,4,5-trimethoxyphenyl alcohol) using **4** in the photooxidation reaction under argon.

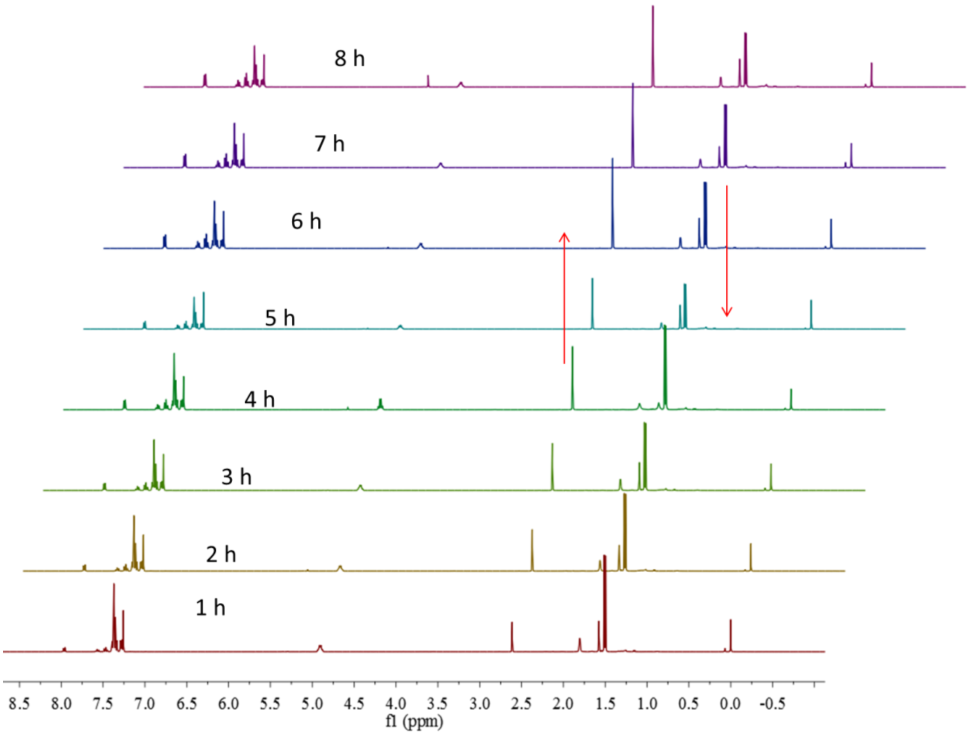


Fig. S22 ^{1}H NMR spectra ($CDCl_3$) of the product (acetophenone) and substrate (1-phenylethanol) using **4** in the photooxidation reaction in course of time under an argon atmosphere.

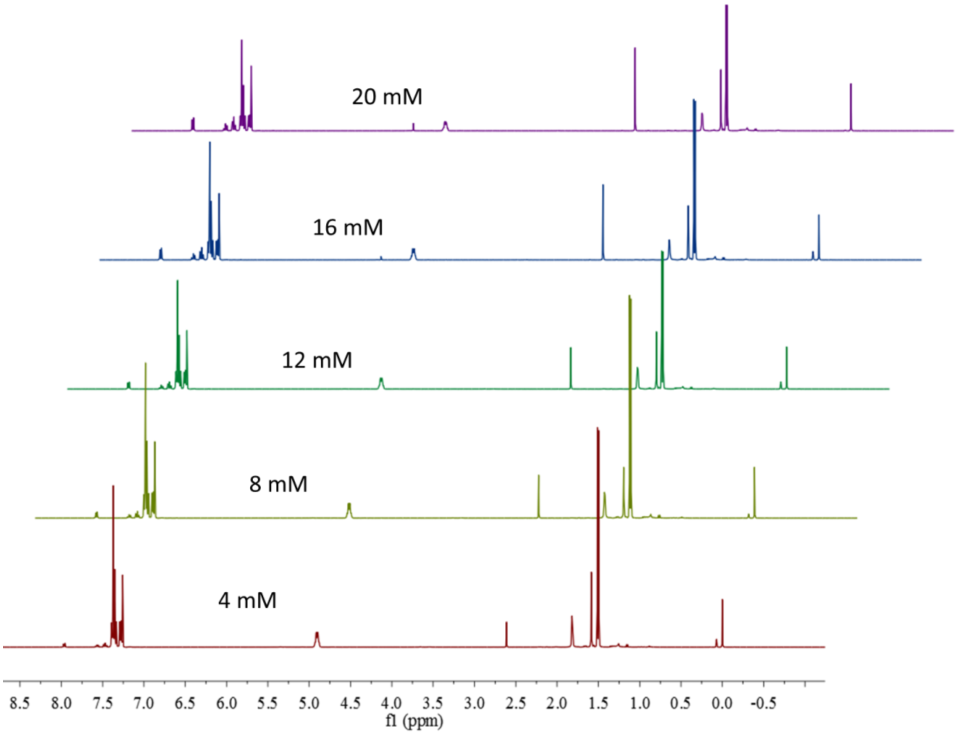


Fig. S23 ^{1}H NMR spectra ($CDCl_3$) of the product (acetophenone) and substrate (1-phenylethanol) using **4** in the photooxidation reaction for 2 h with different concentration of $[Co(NH_3)_5Cl]Cl_2$ under an air atmosphere.

Mass spectra for complex

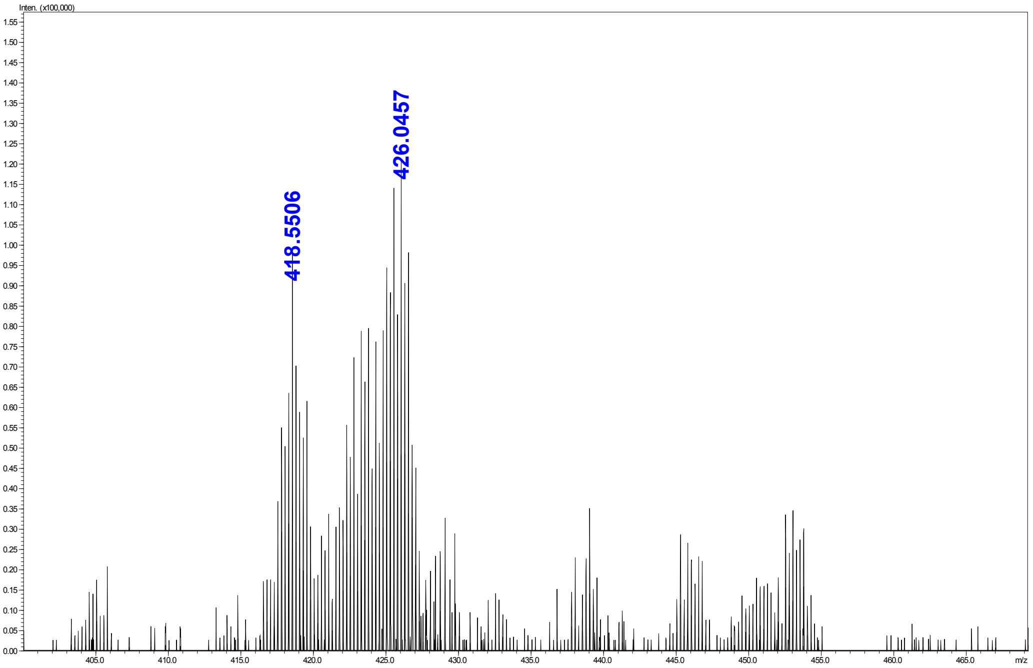


Fig. S24 ESI/MS spectrum of the irradiated solution containing **4** (0.01 mM) and $[Co(NH_3)_5Cl]Cl_2$ (20 mM).

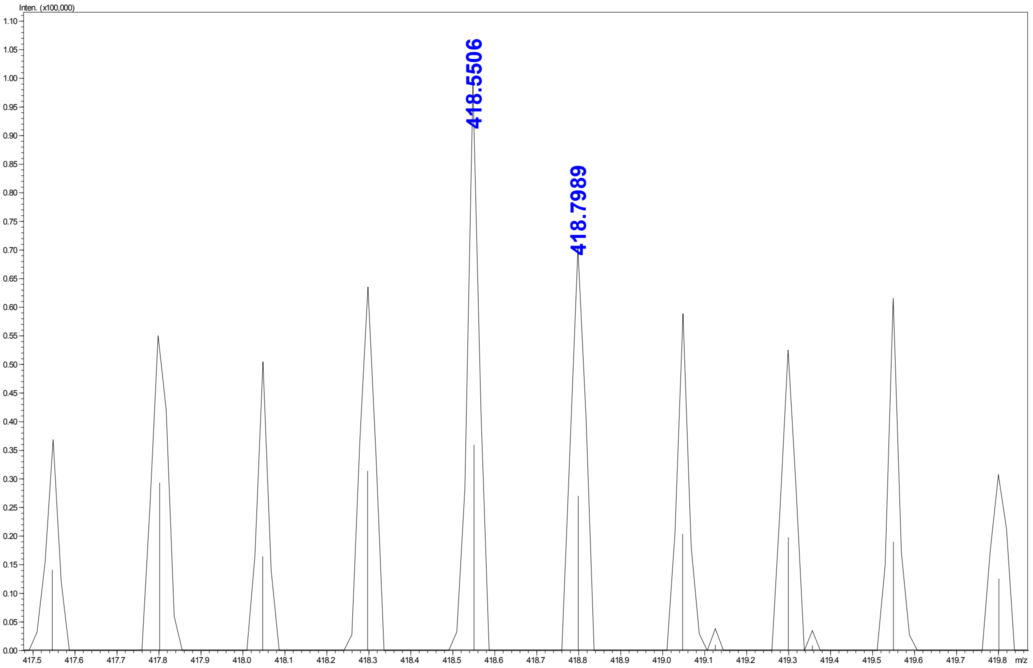


Fig. S25 Isotopic peaks of signals at *m/z* = 418.5506.

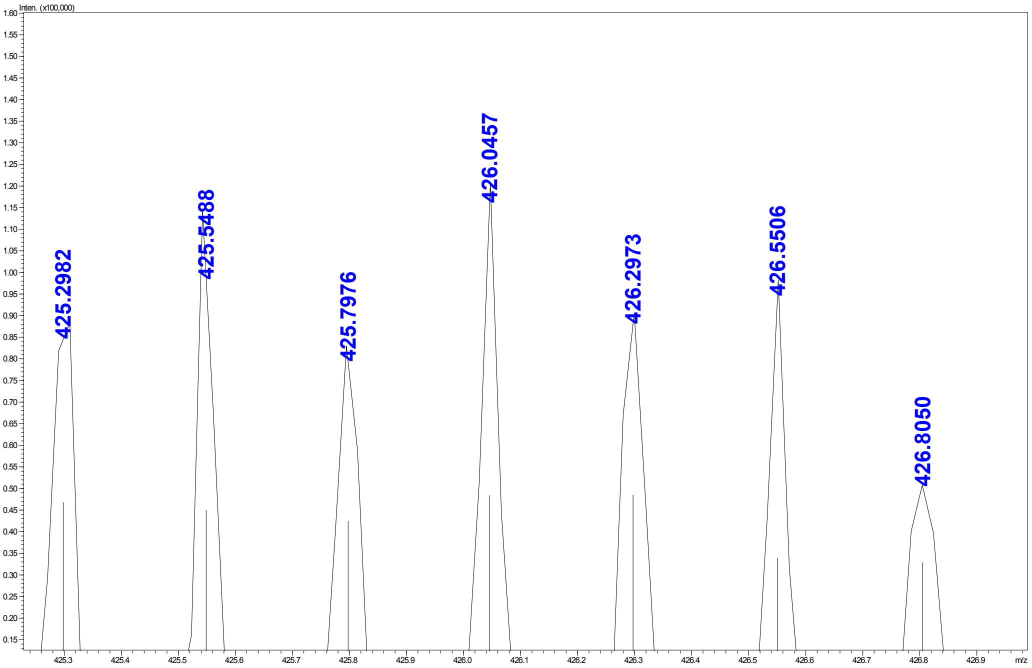


Fig. S26 Isotopic peaks of signals at *m/z* = 426.0457.

Photocatalytic oxidation of alcohols

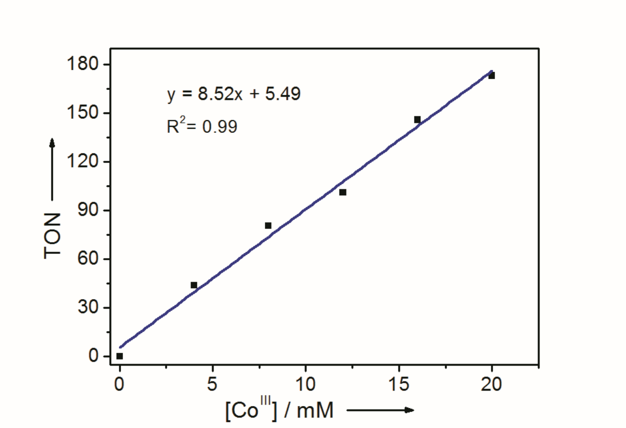


Fig. S27 The turnover number (TON) for the photocatlytic oxidation of 1-phenylethanol by **4** under argon as a function of the sacrificial oxidant $[Co(NH_3)_5Cl]Cl_2$ concentration upon light illumination for 2 h. The linear relationship was similar to that under air, indicating the catalytic system could also work well under an air atmosphere.