

Supporting Information

Selective Photocatalytic Hydroxylation and Epoxidation Reaction by an Iron Complex Using Water as the Oxygen Source

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Experimental Section

Materials

All reagents were obtained commercially and used without further purification unless otherwise noted. [(bTAML)Fe-OH₂]⁻ (**1**) (bTAML = biuret-modified tetraamidomacrocyclic ligands) was synthesized by our previously reported method.¹ Tris(2,2'-bipyridine) ruthenium(II) chloride hexahydrate [Ru^{II}(bpy)₃]Cl₂·6H₂O was purchased from Sigma-Aldrich and used as received. [Co^{III}(NH₃)₅Cl]Cl₂ was purchased from Alfa Aesar and used as received. Acetonitrile (HPLC grade, Aldrich) was used after passing through an activated neutral alumina column. Purification of water (18.2 MΩ cm) was performed with a Milli-Q system. ¹⁸O-enriched water (98%) was procured from the Shanghai Research Institute of Chemical Industry (China). All the substrates were purchased from Aldrich and TCI and were passed through activated neutral alumina and distilled prior to use.

General Instrumentations

UV-vis spectral studies were carried out using an Agilent diode array 8453 spectrophotometer with an attached electrically controlled thermostat. Gas chromatography (GC) was performed on a Perkin Elmer Arnel Clarus 500 instrument equipped with a hydrogen flame ionization detector; BP20 columns (polar) (12 m × 0.32 mm × 1.0 μm) were used with helium as the carrier gas at a flow rate of 1 mL min⁻¹. GC-MS was performed on a Thermo Scientific ISQ QD Mass Spectrometer attached with Thermo Scientific TRACE 1300 gas chromatograph using an HP-5ms capillary column (30 m × 0.25 mm × 0.25 μm, J&W Scientific) with helium as the carrier gas. HR-MS was performed in a Thermo Scientific Q-Exactive Orbitrap analyzer using an electrospray ionization source connected with a C18 column (150 m × 4.6 mm × 8.0 μm). A homemade apparatus of light source which contains an array of six blue LEDs (λ_{max} = 440 nm, 3 watt) with a metallic water circulator having six holes to hold the reaction vials exactly over the lights used for photochemical oxidations.

Quantum yield determination:

The quantum yield of the photochemical reactions were determined by using a standard actinometer (potassium ferrioxalate).^{3,4} The reaction solution (1.0 mL) containing catalyst **1** (1.0×10^{-4} M), [Ru(bpy)₃]Cl₂.6H₂O (2.0×10^{-3} M), [Co(NH₃)₅Cl]Cl₂ (2.0×10^{-2} M) and substrate (3.0×10^{-3} M for alkanes and 5.0×10^{-3} M for alkenes) was irradiated with a blue LED light source ($\lambda_{\text{max}} = 440$ nm, 3 W) for 40 min. The product formed after the photochemical reaction was quantified using GC-MS. The photon flux was calculated to be 1.95×10^8 einstein s⁻¹. The quantum yields after the photochemical reaction of alkanes and alkenes were calculated using the following equation:

$$\Phi = \frac{\text{number of product molecules} \times 2}{\text{number of incident photons}} \times 100 \%$$

Table S1. Quantum yields of alkanes

| Entry | Substrate (Alkanes) | Quantum Yield (%) |
|-------|-------------------------------------|----------------------|
| 1. | Adamantane | 8.6 |
| 2. | Cumene | 4.3 |
| 3. | <i>cis</i> -1,2-Dimethylcyclohexane | 7.0 |
| 4. | <i>cis</i> -decalin | 12.2 |
| 5. | <i>trans</i> -decalin | 3.8 |
| 6. | Cedryl acetate | 4.6 |
| 7. | Ambroxide | 7.0 |
| 8. | Diphenyl methane | 7.2 |

Table S2. Quantum yields of alkenes

| Entry | Substrate (Alkenes) | Quantum Yield (%) |
|--------------|--------------------------------|------------------------------|
| 1. | Styrene | 13.9 |
| 2. | 4-chlorostyrene | 9.0 |
| 3. | 4-methoxystyrene | 18.7 |
| 4. | <i>cis</i> -stilbene | 9.8 |
| 5. | <i>cis</i> -cyclooctene | 10.2 |
| 6. | Norbornene | 12.6 |

Reaction condition: photochemical reaction yields were calculated using **1** (1.0×10^{-4} M) [Ru(bpy)₃]Cl₂·6H₂O (2.0×10^{-3} M), [Co(NH₃)₅Cl]Cl₂ (2.0×10^{-2} M) and substrate (3.0×10^{-3} M for alkanes and 5.0×10^{-3} M for alkenes) was irradiated with a blue LED light source ($\lambda_{\text{max}} = 440$ nm, 3 W) for 40 min. The quantum yields were calculated using the above mentioned equation.

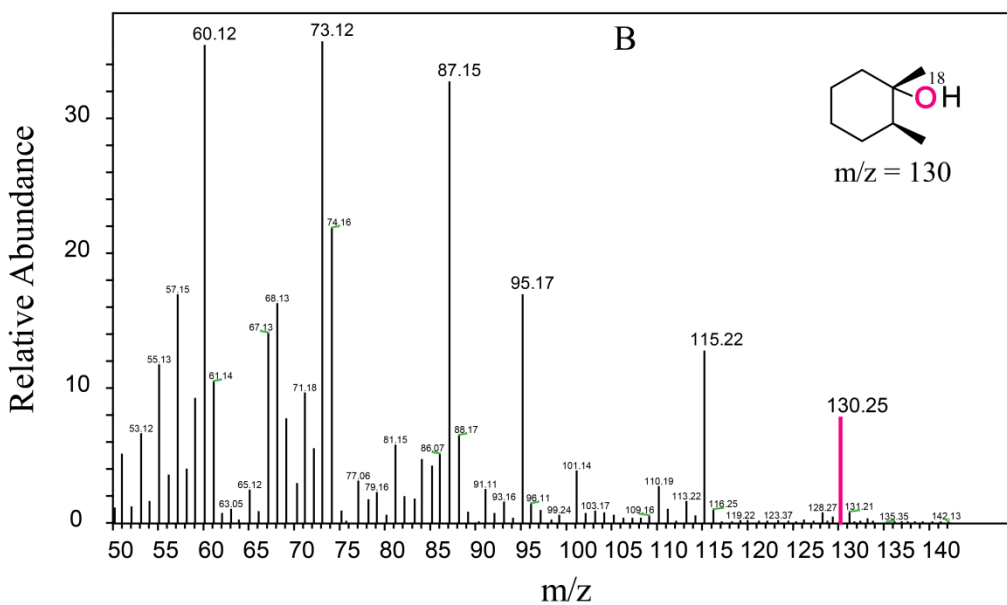
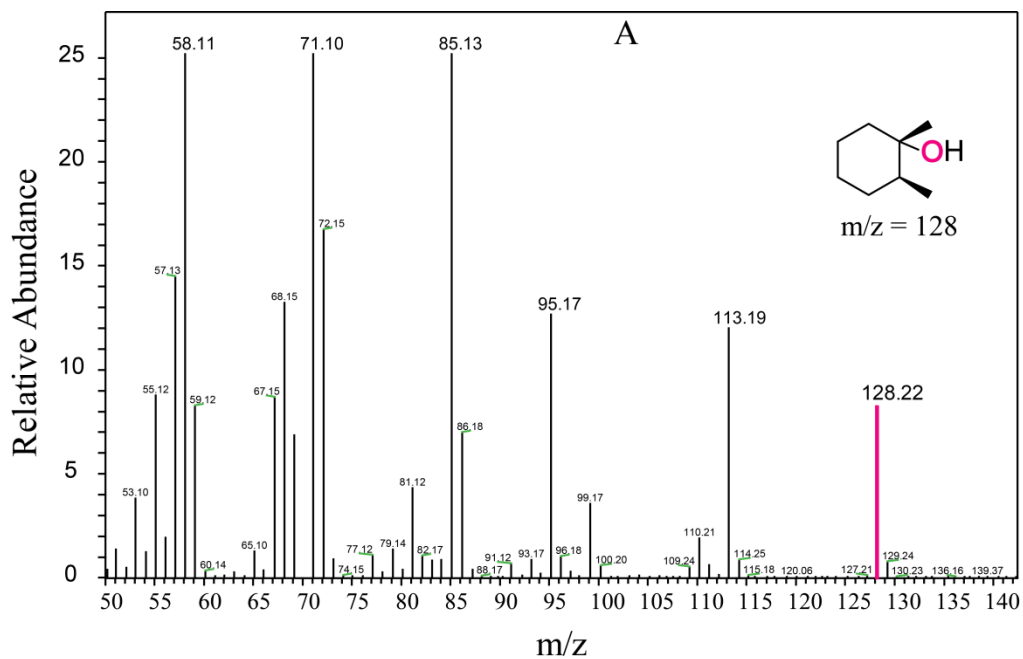


Fig. S1 GC-MS spectra of product after photochemical oxidation reaction with *cis*-1,2-dimethylcyclohexane as the substrate A) in $H_2^{16}O$; B) in $H_2^{18}O$.

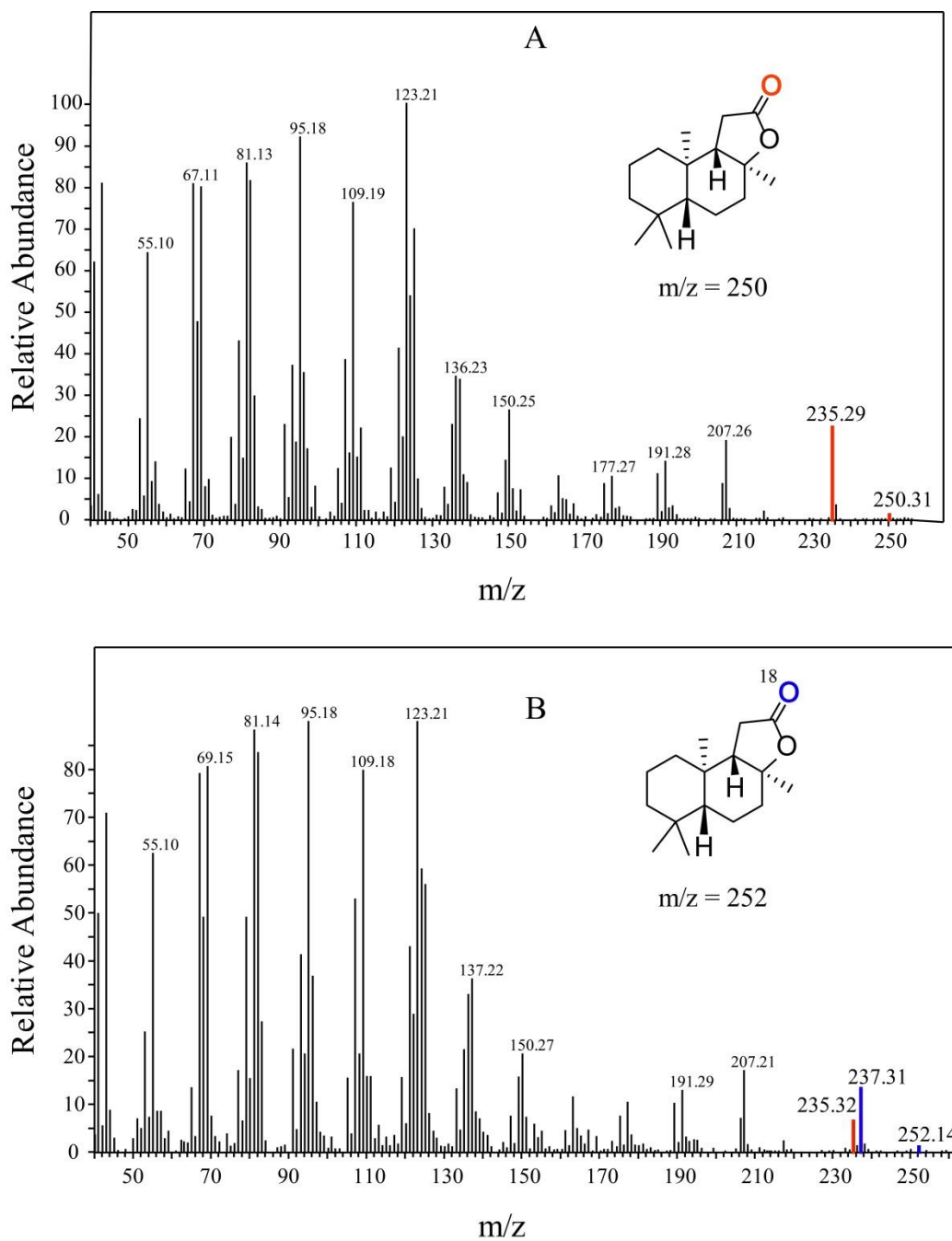


Fig. S2 GC-MS spectra of product after photochemical oxidation reaction ambroxide (30 mM) as the substrate with catalyst **1** (0.1 mM) A) in $H_2^{16}O$; B) in $H_2^{18}O$

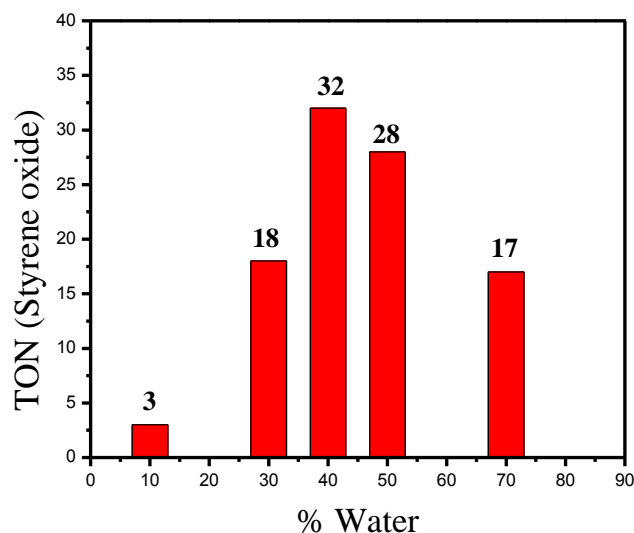


Fig. S3. Turnover number (TON) of styrene oxide vs. percentage of water in aqueous phosphate buffer-acetonitrile solvent mixture for the photochemical oxidation reaction of styrene with complex **1**. Using catalyst **1**, photosensitizer $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ and sacrificial electron acceptor $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ under blue LED light irradiation, we optimized the concentration of water in acetonitrile-water (phosphate buffer) mixture for the epoxidation of styrene. A very low product yield (TON 3) in 1:9 water- CH_3CN mixtures was attributed to the poor solubility of $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ and $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ in organic solvent (acetonitrile). When concentration of water was increased to 40%, the TON for styrene oxide increased to 32. Upon further increment of water concentration (70% water), epoxide product formation decreased to give TON of 17 which was most likely due to the insolubility of substrate as well as an enhanced competitive reaction of reactive intermediate with water.^{1b,2}

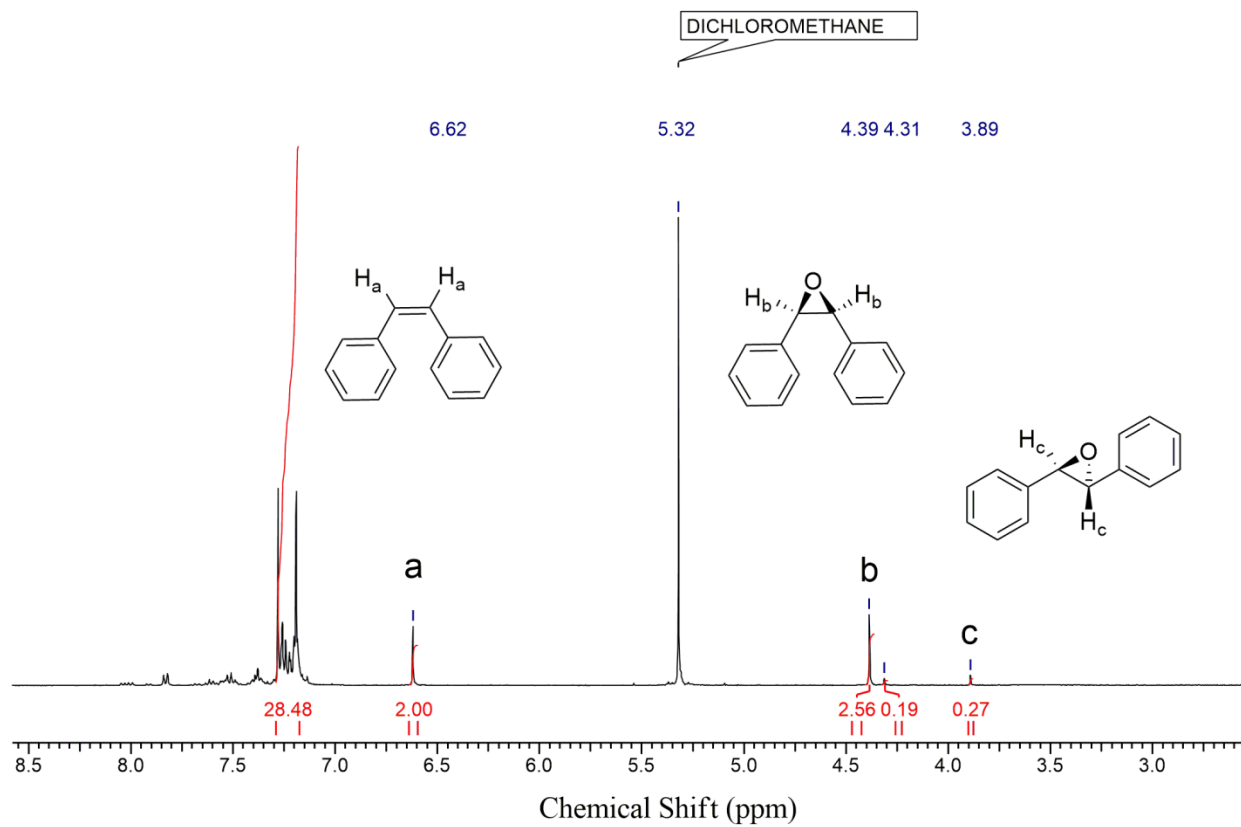


Fig. S4 $^1\text{H-NMR}$ spectra of *cis*-stilbene oxide (major) and *trans*-stilbene oxide (minor) formed in photochemical reaction of *cis*-stilbene. The ratio of *cis* to *trans* product was estimated to be 19:2.

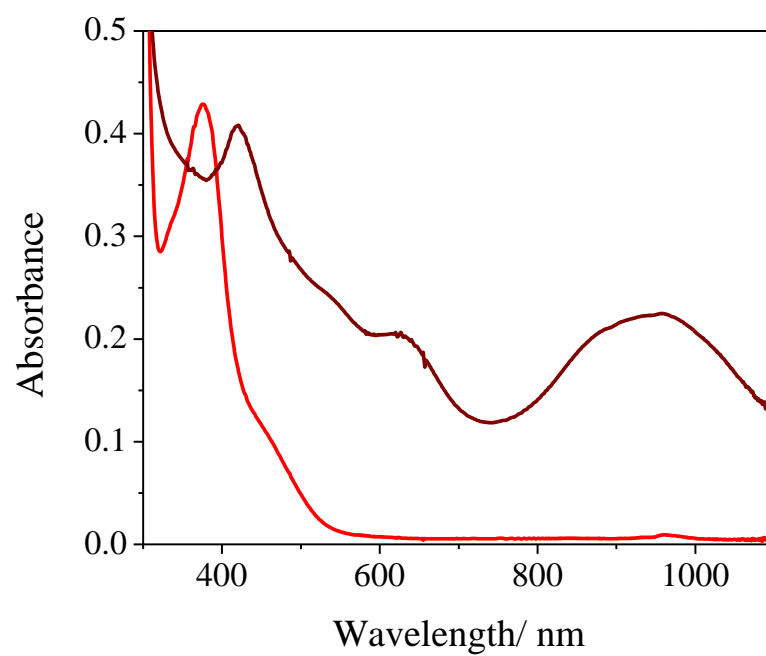


Fig. S5 UV-vis spectra of complex 2 (brown) formed with NaOCl and complex 1 (red).

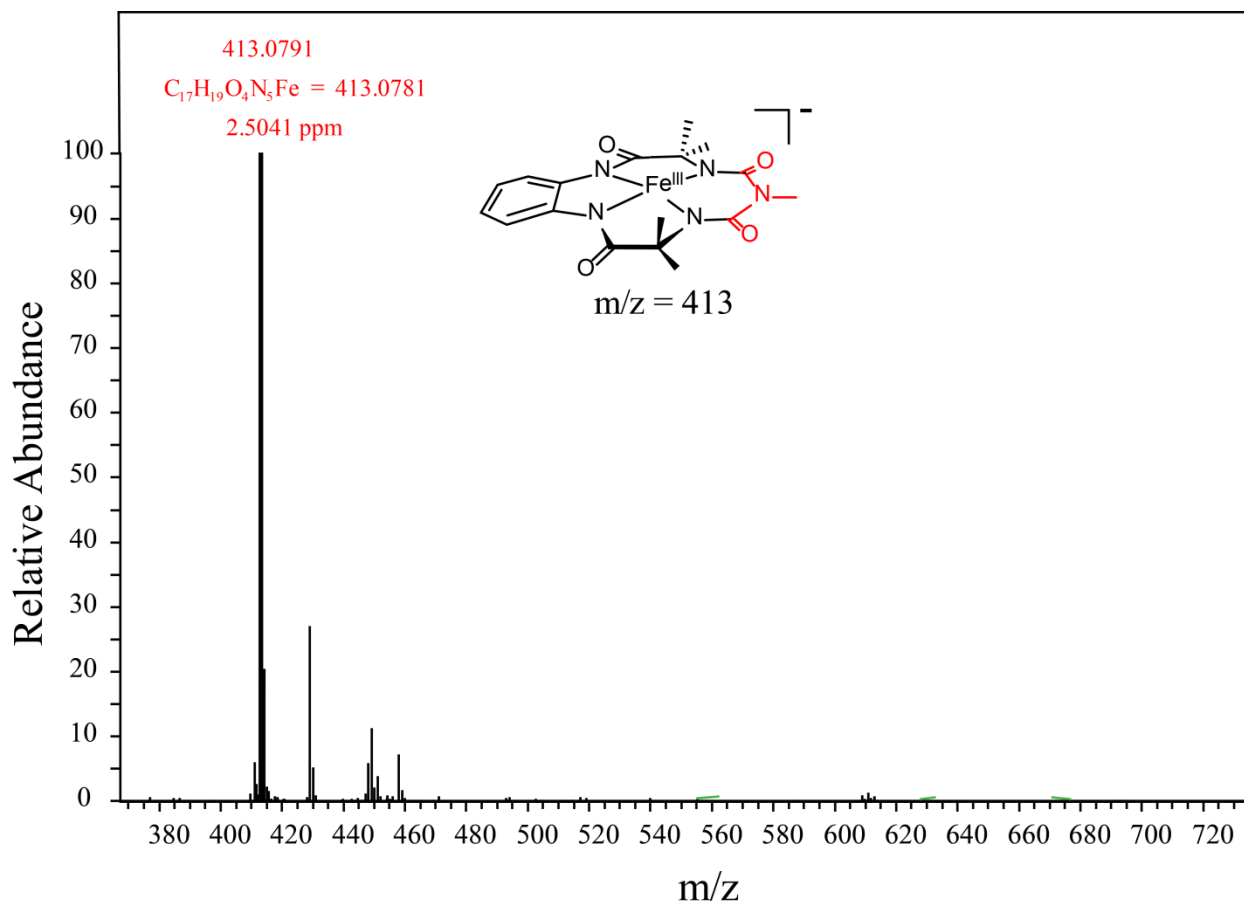


Fig. S6 HR-MS of catalyst **1** after 40 minutes of photochemical oxidation reaction with styrene using **1** (1.0×10^{-4} M), $[Ru^{II}(bpy)_3]^{2+}$ (2.0×10^{-5} M) and $[Co^{III}(NH_3)_5Cl]^{2+}$ (6.0×10^{-4} M) in acetonitrile-aqueous phosphate buffer (3:2 v/v) solvent.

References

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