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Reductive activation of O_2 by a bioinspired Fe complex for catalytic epoxidation reactions

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Experimental Section

Materials. An axially ligated aqua complex [PPh_4][(bTAML)Fe^{III}-OH_2] (**1**) was synthesized by metathesis reaction of [Li][(bTAML)Fe^{III}-OH_2] with excess amount of PPh_4Cl in water.[1] Dichloromethane (DCM) and 1, 2-dichlorobenzene (DCB) were purified and dried according to the published procedure.[2] Styrene, 4-chlororstyrene, 4-methoxystyrene, 4-nitrostyrene were purchased from Aldrich and distilled before use. *cis*-stilbene, *trans*-stilbene, norbornene and methyl *trans*-cinnamate were purchased from Aldrich and used as received. All other solvents and reagents were purchased from Aldrich or other commercial sources and were used as received, unless otherwise noted. 98% ^{18}O enriched water ($H_2{}^{18}O$) was procured from Shanghai Research Institute of Chemical Industry, China. $^{18}O_2$ was received from Icon (Isotopes) Services Inc.

General Instrumentation. UV-vis spectral studies were carried out using Agilent diode array 8453 spectrophotometer attached with an electrically controlled thermostat. 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).

Catalytic reaction of 1 with alkenes under oxygen pressure. Complex **1** (0.25 mM) was dissolved in 5 mL dry DCM in a 20 ml reactor and 40 mM of substrates was added to the solution. Reactor was tightly closed and O_2 gas pressure {5 bar or as per need of experiment (10 bar, 20 bar)} was inserted through inlet of the reactor. Inlet was closed and reaction solution was stirred for 20 h under oxygen pressure. After end of the reaction, the product was identified and quantified by GC-MS. Calibration curve for all epoxides were obtained from corresponding authentic epoxides for product quantification. Similar reaction conditions were used for all the substrates.

Catalytic reaction of 1 with alkenes at different temperature in air (atmospheric pressure). The reaction condition used were similar for all the alkenes that are described below. Compound **1** (0.25 mM) was dissolved in 1,2-dichlorobenzene (5 ml) and 40 mM of styrene was added to the solution. The reaction mixture was stirred for 12-20 h. To observe the effect of temperature, reaction rates were estimated by monitoring the amount of product formed with time at temperatures of 25 ^oC, 50 ^oC and 70 ^oC. Due to insolubility of catalyst **1** in 1, 2-dichlorobenzene at 25 ^oC, a minimum amount of dichloromethane (300 μL) was added to solubilize it.

Reaction of 1 with thioanisole and styrene in presence of $^{18}O_2$. To a solution of complex **1** (0.25 mM) in dry and oxygen free dichloromethane (DCM) was added thioanisole (40 mM), and subsequently the solution was purged with $^{18}O_2$. After 10 minute of the reaction, product was analyzed with GC-MS. Similar procedure was adopted for the reaction with styrene (reaction time 60 minute).

Reaction of $[PPh_4][Fe^{III}(H_2O)bTAML]$ with styrene in presence of $H_2{}^{18}O$. To a solution of complex **1** (0.25 mM) in dichloromethane (DCM) was added styrene (40 mM) and 50 µL $H_2{}^{18}O$. After 60 minute of reaction, the product was analyzed with GC-MS

Scheme 1. Synthesis scheme of complex $[(bTAML)Fe^{IV}(Cl)]^-$

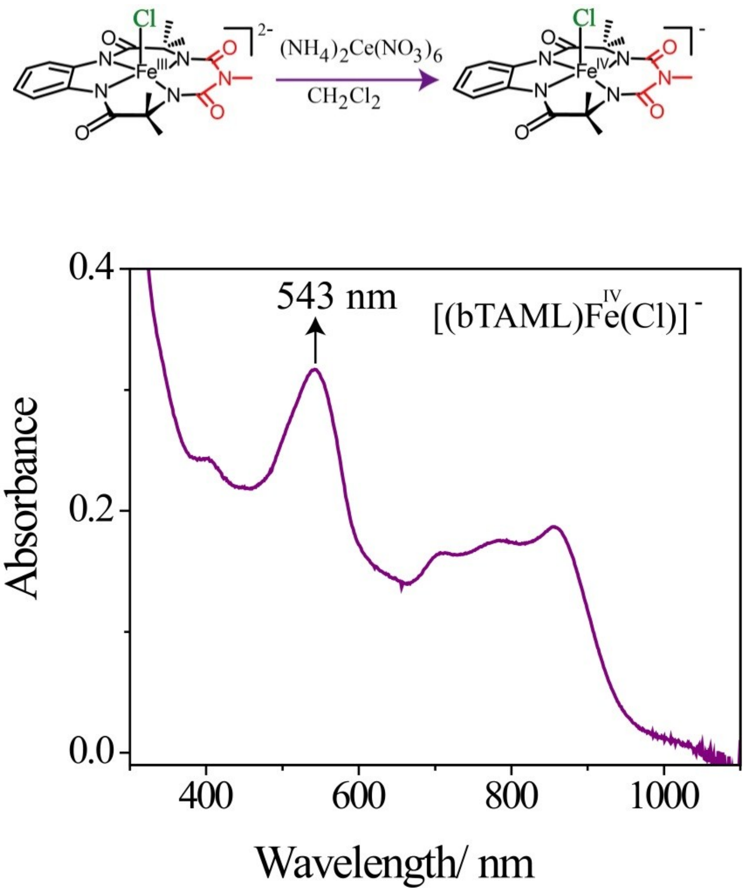

Figure S1. UV-vis spectrum of complex [(bTAML)Fe^{IV}(Cl)]$^-$ in dichloromethane formed by the the reaction of [(bTAML)Fe^{III}(Cl)]$^{2-}$ with $(NH_4)_2Ce(NO_3)_6$ at RT.

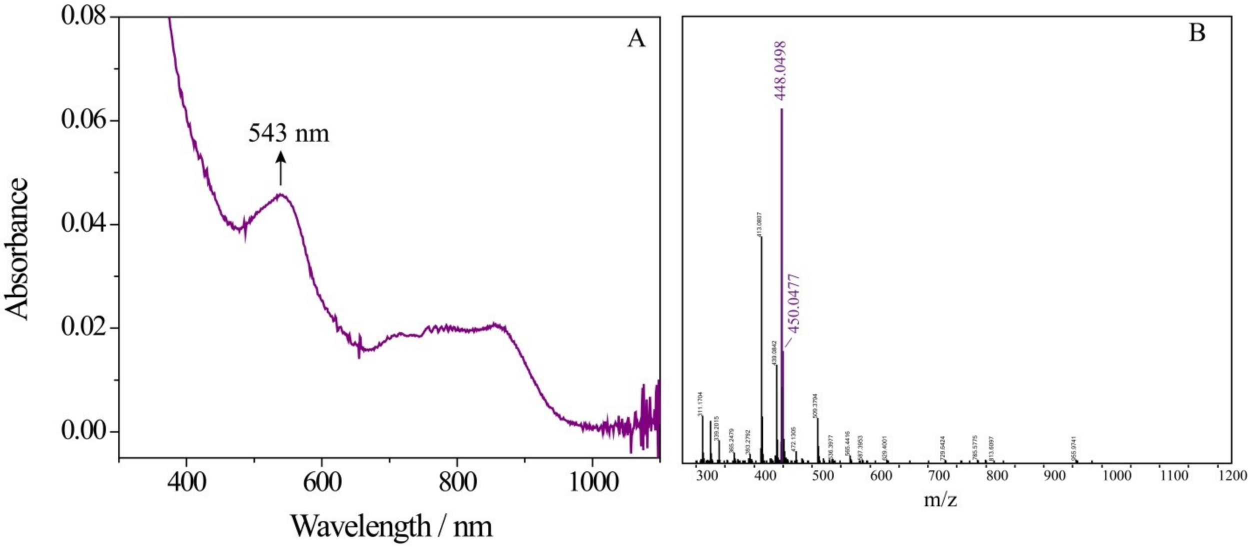

Figure S2. (A) UV-vis spectrum of reaction mixure after completion of reaction with complex **1** and styrene at 5 bar O_2 pressure. The UV-vis obsereved is similar to the $[(bTAML)Fe^{IV}(Cl)]^-$ complex. (B) HR-MS of reaction mixture after completion of reaction with complex **1** and styrene at 5 bar O_2 pressure. Calculated m/z of $[(bTAML)Fe^{IV}(Cl)]^-$ is 448.0475. Observed m/z 448.0498.

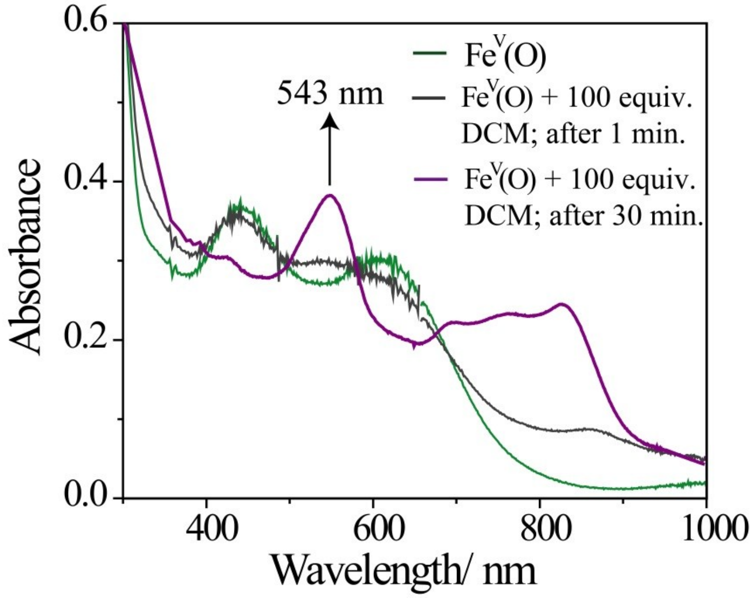

Figure S3. UV-vis spectral change for the reaction of [(bTAML)Fe^V(O)]$^-$ (1 × 10^{-4} M) with 100 equiv of CH_2Cl_2 in acetonitrile. Monomeric [(bTAML)Fe^{IV}(Cl)]$^-$ was formed at the end of the reaction.

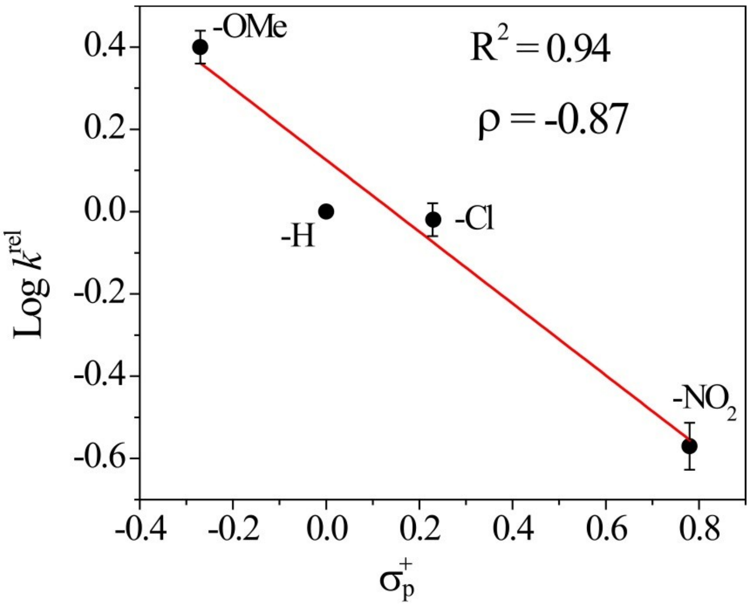

Figure S4. Hammett plots of logk^{rel} against *para*- σ^+ for the epoxidation of styrene and its *para*-substituted derivatives obtained from the reaction of complex **1** in DCB at 50 °C. Hammett value ρ is -0.87; $k^{rel} = k^X/k^H$, where k^X and k^H are concentration of epoxide product for *para*- substituted styrene and concentration of epoxide product for styrene respectively.

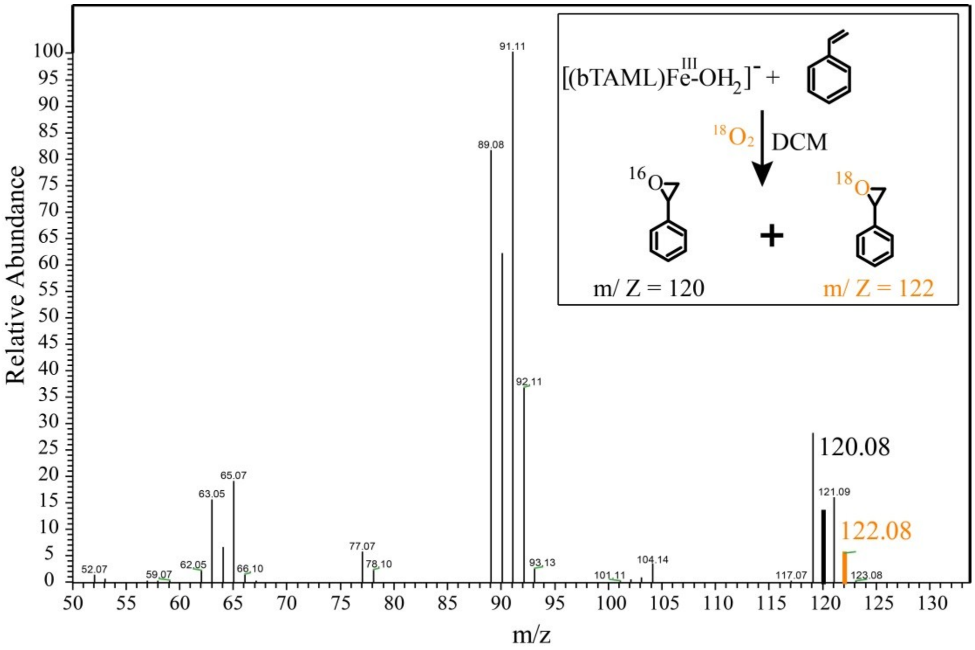

Figure S5. GC-MS spectra of product after 60 min of reaction with complex **1** and styrene in presence of $^{18}O_2$.

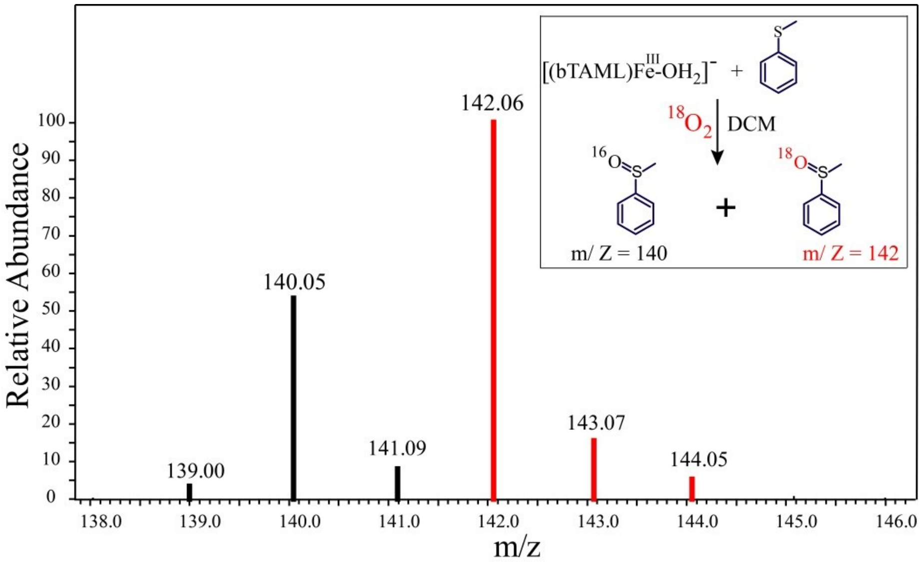

Figure S6. GC-MS spectra of product after 10 min of reaction with complex **1** and thioanisole in presence of $^{18}O_2$.

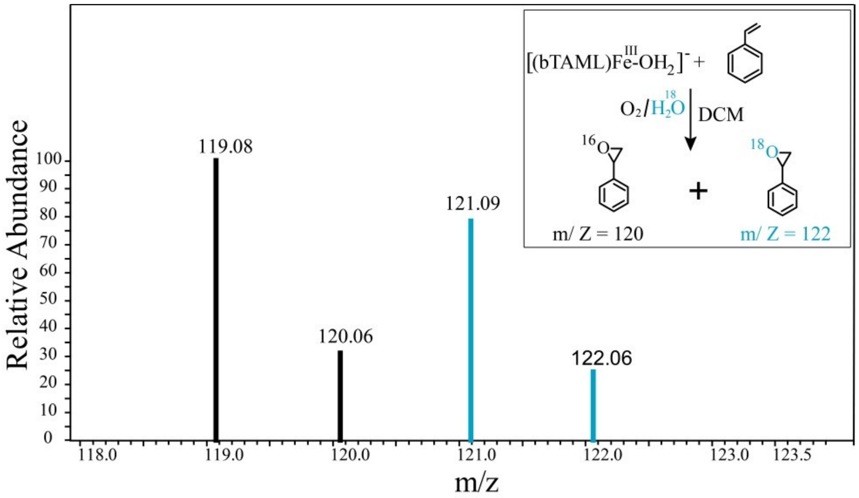

Figure S7. GC-MS spectra of product after 60 min of reaction with complex **1** and styrene in presence of $H_2{}^{18}O$ and air ($^{16}O_2$).

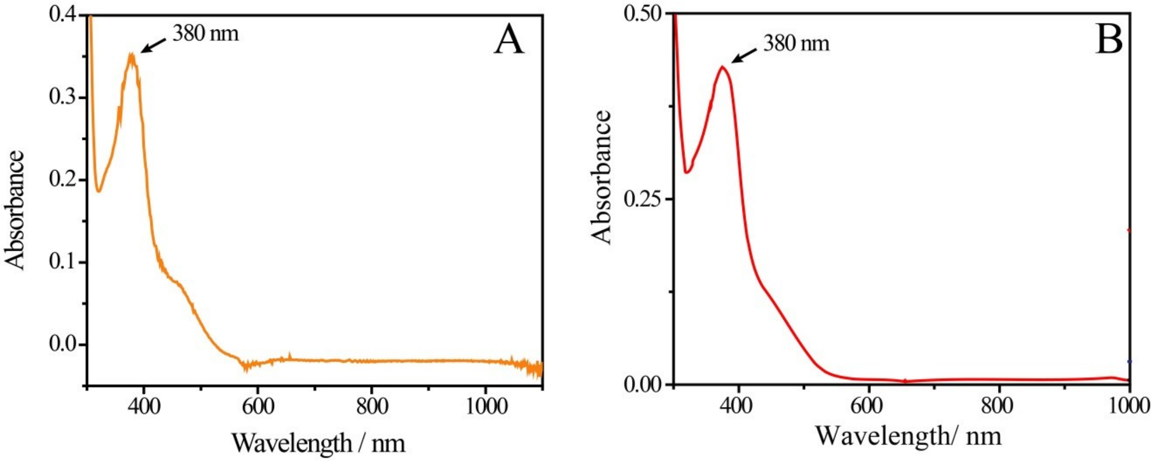

Figure S8. (A) The UV-vis spectra of the acetonitrile solution of precipitate formed after reaction of complex **1** (1 mM) with styrene in DCB; the spectral features are identical to the solution of (bTAML)Fe^{III} complex in acetonitrile. (B) UV-vis spectra of (bTAML)Fe^{III} complex in acetonitrile.

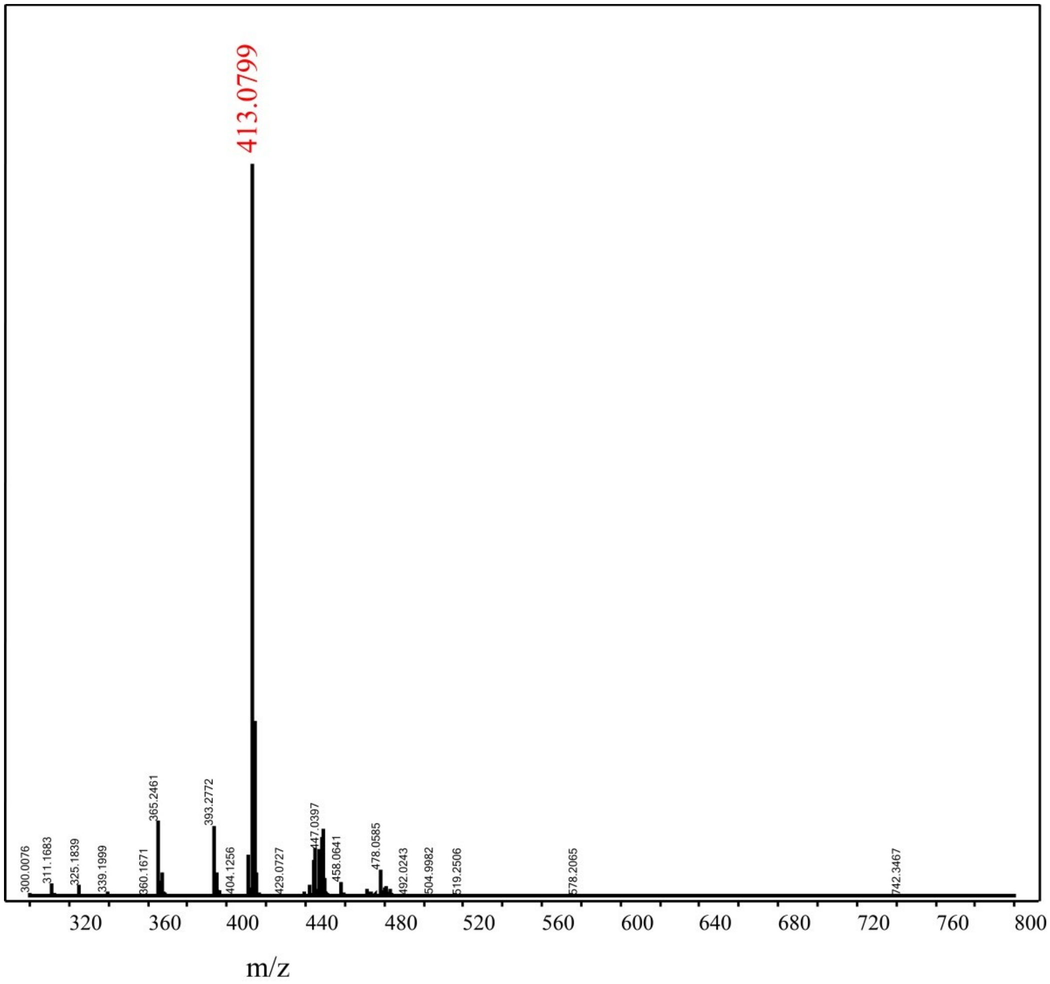

Figure S9. HR-MS of acetonitrile solution of precipitate formed after reaction of complex **1** (1 mM) with styrene in DCB. Calculated m/z of $[(bTAML)Fe^{III}]^-$ is 413.0786.

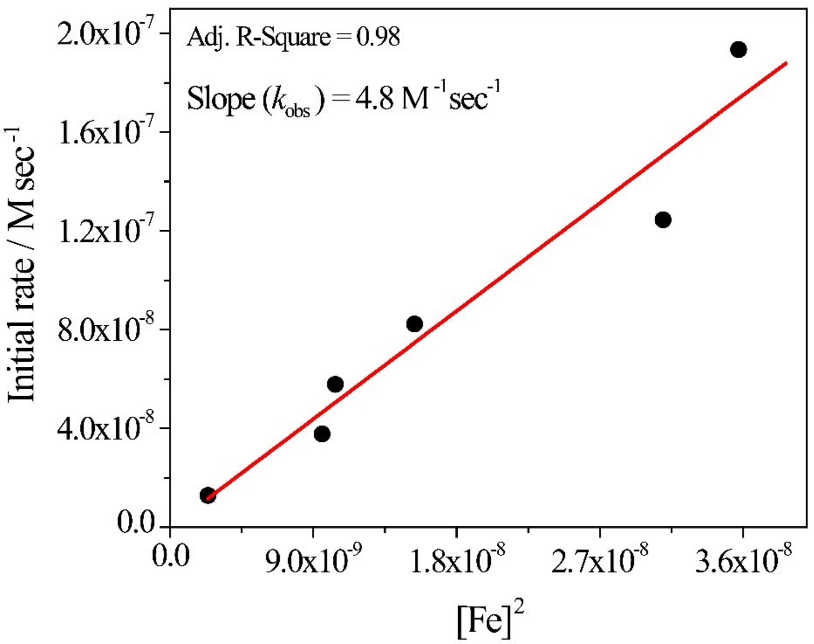

Figure S10. Plot of initial rate *vs* square of concentration of complex **1**. k_{obs} was obtained by linear fit according to the equation: rate = $k_{obs}[\text{catalyst}]^2$. Reaction was performed under air in dichloromethane at 25 °C.

Note: To obtain kinetic data for the formation of complex **2** ($Fe^{IV}OFe^{IV}$) from the proposed Fe-O_2 adduct, complex **1** was dissolved in DCM solvent (under air) and the change in absorbance at 950 nm (characteristic peak for $Fe^{IV}OFe^{IV}$) was monitored with time. As formation of $Fe^{IV}OFe^{IV}$ is a consequence of multistep reactions (currently unidentified) from Fe-O_2, we adopted an initial rate law approach to obtain order of reaction with respect to catalyst. Initial rate was obtained for different catalyst concentration with constant O_2 pressure (atmospheric air). Plot of initial rate *vs* square of catalyst concentration gives linear fit according to the equation: rate = $k_{obs}[\text{catalyst}]^2$; so, the reaction is indeed second order in [Fe], (Figure S10).

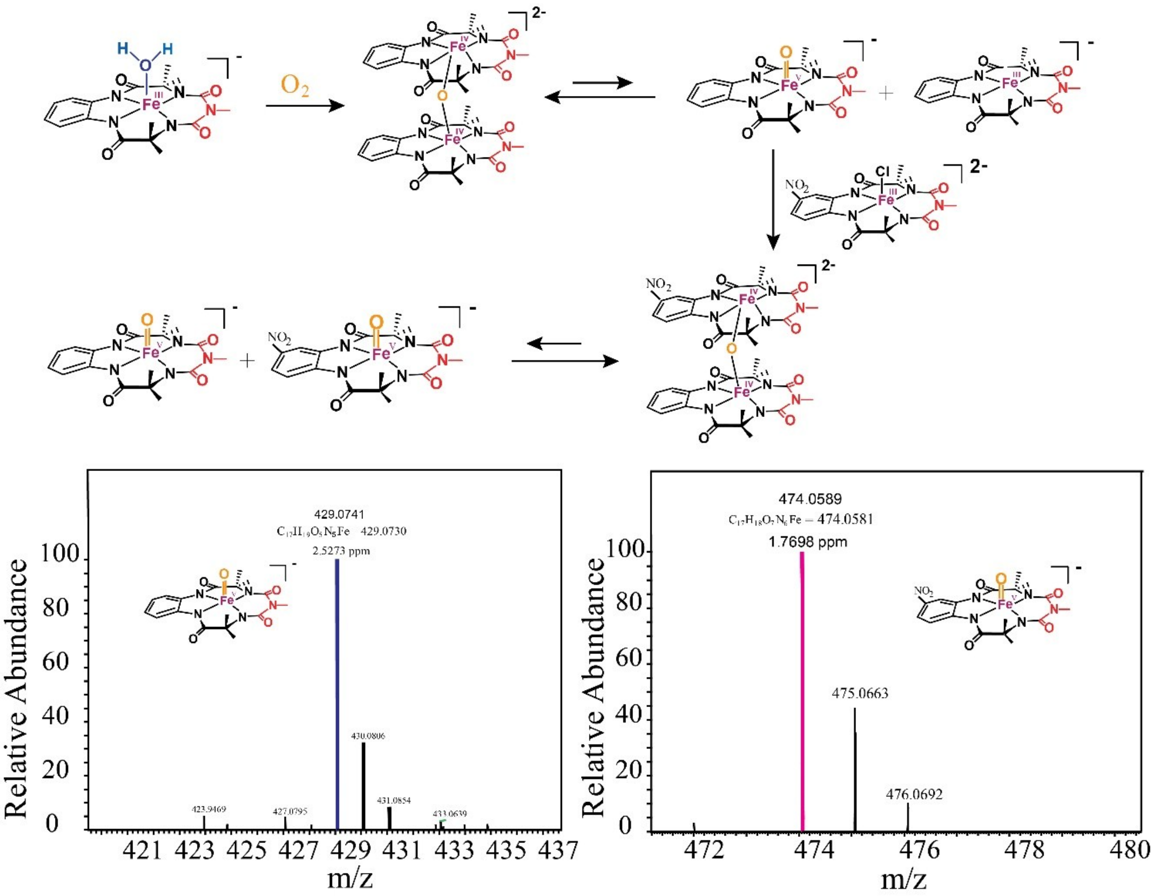

Figure S11. HR-MS of $[(\text{bTAML})\text{Fe}^{V}(\text{O})]^{-}$ and $[(\text{NO}_2\text{-bTAML})\text{Fe}^{V}(\text{O})]^{-}$ complexes which are formed after incubation of $[\{(\text{bTAML})\text{Fe}^{IV}\}_2\text{-}\mu\text{-Oxo}]^{2-}$ dimer (**2**) solution with a nitro substituted complex, $[(\text{NO}_2\text{-bTAML})\text{Fe}^{III}(\text{Cl})]^{2-}$. Calculated m/z of $[(\text{bTAML})\text{Fe}^{V}(\text{O})]^{-}$ and $[(\text{NO}_2\text{-bTAML})\text{Fe}^{V}(\text{O})]^{-}$ is 429.0730 and 474.0581 respectively.

Note: The mass spectrum of $[\{(\text{bTAML})\text{Fe}^{IV}\}_2\text{-}\mu\text{-Oxo}]^{2-}$ displayed two peaks corresponding to the mass of $[(\text{bTAML})\text{Fe}^{III}]^{-}$ and $[(\text{bTAML})\text{Fe}^{V}(\text{O})]^{-}$. Hence, the presence of mass corrsponding to $[(\text{NO}_2\text{-bTAML})\text{Fe}^{V}(\text{O})]^{-}$ after incubation of $[\{(\text{bTAML})\text{Fe}^{IV}\}_2\text{-}\mu\text{-Oxo}]^{2-}$ dimer (**2**) solution with a nitro substituted $[(\text{NO}_2\text{-bTAML})\text{Fe}^{III}(\text{Cl})]^{2-}$ complex is probably indicative of the presence of scrambled dimer.

Table S1. The effect of O_2 pressure on styrene epoxide formation (TON) for reaction of styrene (40 mM) with complex **1**(0.25 mM) in dichloromethane at RT.

O_2 pressure	**TON (after 20 h)**
1 bar	8
5 bar	40
10 bar	34
20 bar	26

References

S1. C. Panda, M. Ghosh, T. Panda, R. Banerjee and S. Sen Gupta, *Chem. Commun.*, 2011, **47**, 8016.

S2. K. M. Kadish and J. E. Anderson, *Pure &Appl. Chem*., 1887, **59**, 703.