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Electronic Supplementary Information

Selective oxygenation of unactivated C-H bonds by dioxygen via an autocatalytic formation of iron(V)-oxo species

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Experimental Section

Materials.

All reagents were obtained commercially and used without further purification unless otherwise noted. $[Et_4N]_2[(bTAML)Fe^{III}\text{-}Cl]$ (**1a**), $[PPh_4][(bTAML)Fe^{III}\text{-}OH_2]$ (**1b**) and $[Et_4N]_2[(NO_2\text{-}bTAML)Fe^{III}\text{-}Cl]$ (**1c**) (bTAML = biuret-modified tetraamidomacrocyclic ligands) was synthesized by our previously reported method.[1,2] Acetone (HPLC grade, Aldrich) was rigorously purified as mention in literature.[3] All the substrates were purchased from Aldrich and TCI and were passed through activated neutral alumina, silica and $MgSO_4$ and distilled prior to use.

General Instrumentation.

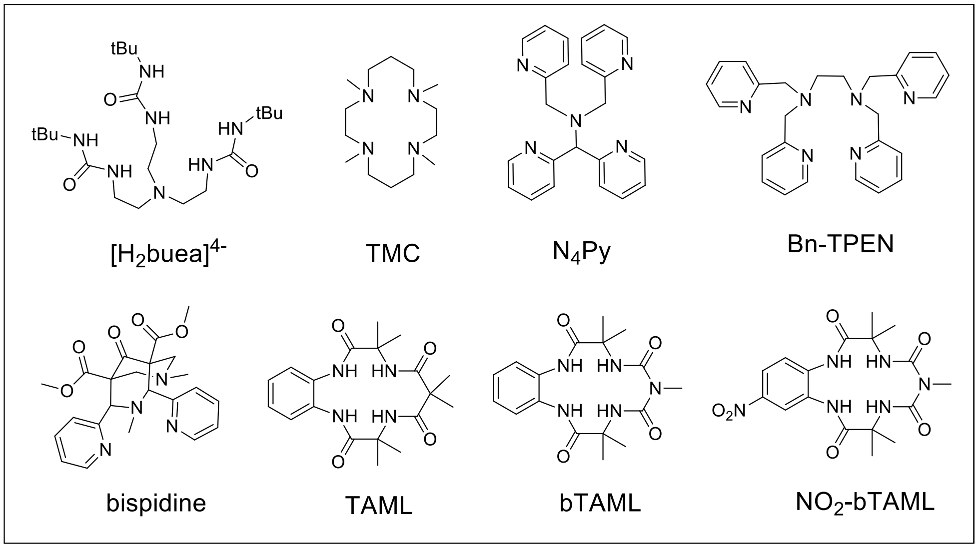
UV-vis spectral studies were carried out using Agilent diode array Cary 8454 spectrophotometer attached with an electrically controlled thermostat. GC-MS was performed on a Thermo Scientific ISQ QD Mass Spectrometer attached with Thermo Scientific TRACE 1300 gas chromatograph using an HP-5ms capillary column (30 m × 0.25 mm × 0.25 µm, J&W Scientific) with helium as the carrier gas. ESI-Mass was performed in a Thermo Scientific QExactive Orbitrap analyzer using an electrospray ionization source connected with a C18 column (150 m × 4.6 mm × 8.0 µm).

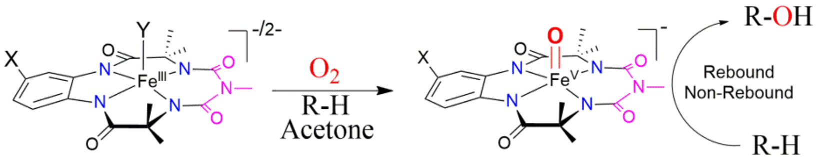
Catalytic reaction of 1a and 1c with substrates in air saturated acetone at room temperature.

All the catalytic reactions were performed in an optimized reaction condition where the iron complexe, $[(bTAML)Fe^{III}\text{-}Cl]^{2-}/[(NO_2\text{-}bTAML)Fe^{III}\text{-}Cl]^{2-}$ (**1a/1c)** (0.1 mM) was dissolved in aerated acetone solvent and 0.10 M of alkane substrate was added to the solution. The reaction mixture was kept for 20h at ambient pressure and temperature. After the reaction, the solution was passed through an alumina plug and diluted to 20 times before injection to GCMS. Bromobenzene was used as internal standard for all these reactions. The products were identified and quantified using GCMS.

Table S1. Iron complexes of different ligands employed for substrate oxygenation via O_2 activation vs autocatalytic oxidation

Catalysts	Oxidant	Active species	Proposed Mechanism	Substrates	Ref.
$[Fe^{II}(H_2buea)]^{2-}$	O_2	$Fe^{III}(O)$	O_2 activation	No report	4
$[Fe^{II}(TMC)]^{2+}$	O_2	$Fe^{IV}(O)$	O_2 activation	Ph_3P, Benzyl alcohol, cyclohexene	5
$[Fe^{II}(Bn\text{-}TPEN)]^{2+}$	O_2	$Fe^{IV}(O)$	O_2 activation	No report	6
$[Fe^{II}(N_4Py)]^{2+}$	O_2	$Fe^{IV}(O)$	O_2 activation	No report	6
$[Fe^{II}(bispidine)]$	O_2	$Fe^{IV}(O)$	Autocatalyzed	cis-dimethylcyclohexane	7
$[Ph_4P][Fe^{III}(OH_2)(TAML)]$	O_2	$Fe_2{}^{IV}O$	O_2 activation	Ph_3P, Benzyl alcohol	8
$Na[Fe^{III}(TAML)]$	O_2	$Fe^{V}(O)$	Autocatalyzed	cyclohexene	9
$[Ph_4P][Fe^{III}(OH_2)(bTAML)]$	O_2	$Fe_2{}^{IV}O$	O_2 activation	Alkenes (epoxidation)	10
$[Et_4N]_2[Fe^{III}(Cl)(bTAML)]$ and $[Et_4N]_2[Fe^{III}(Cl)(NO_2\text{-}bTAML)]$	O_2	$Fe^{V}(O)$	Autocatalyzed	Unactivated C-H bonds of alkanes	this work





R-H = Alkane substrates having C-H bonds

X = -H (**1a**/**1b**), -NO_2 (**1c**) and Y = Cl (**1a**/**1c**) or H_2O (**1b**)

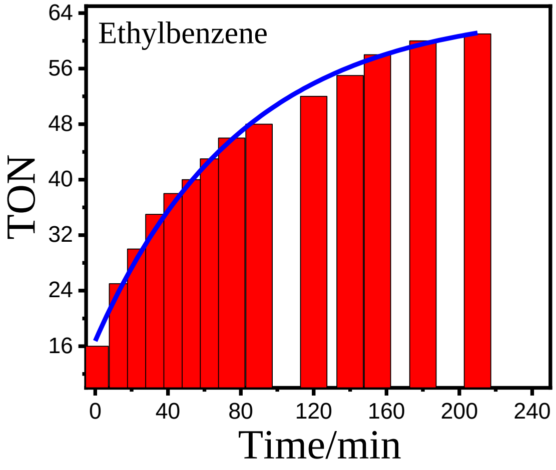


Fig. S1. TON vs time plot for the oxygenation of ethylbenzene (0.1 M) with **1a** (0.1 mM) in aerated acetone solvent for initial 4 h.

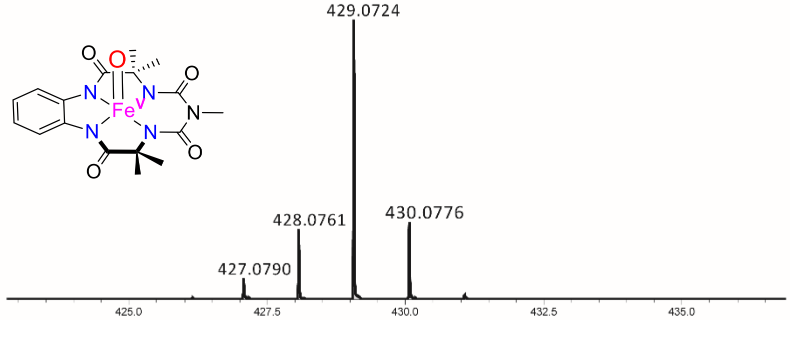


Fig. S2. HRMS spectrum of [Fe^{V}(O)(bTAML)]$^{-}$ generated from **1a** in aerated acetone in presence of diphenylmethane (0.1 M) at RT. The peak at *m/z* = 429.0724 corresponds to [Fe^{V}(O)(bTAML)]$^{-}$ (calculated *m/z* = 429.0730).

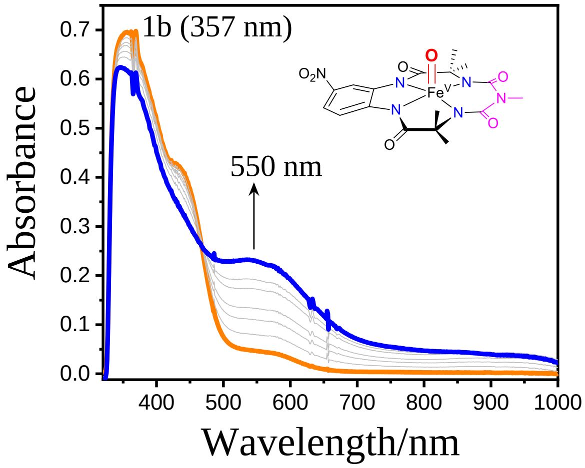


Fig. S3. UV-visible spectral changes observed for the formation of Fe^{V}(O) in the reaction of [Et$_4$N][(NO$_2$-bTAML)Fe^{III}-Cl] (0.10 mM) with adamantane (0.1 M) in aerated acetone solvent at room temperature.

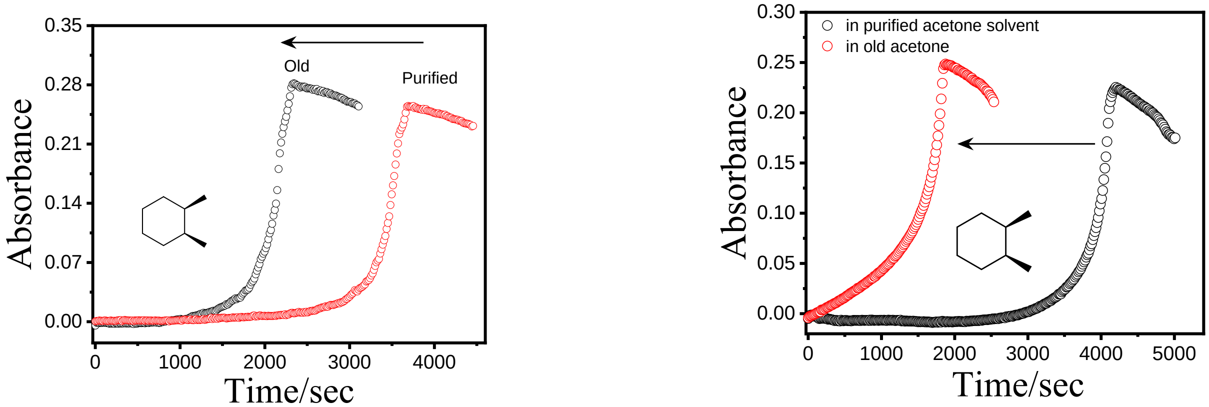


Fig. S4. UV-Vis time profiles at 613 nm for the formation of Fe^{V}(O) in the reaction of **(a) 1a** (0.1 mM) with cis-dimethycyclohexane (0.1 M) ((bottle grade and purified) and **(b) 1a** (0.1 mM) and cis-dimethycyclohexane (0.1 M) in aerated acetone (bottle grade and purified) at RT. The substrate and solvent are rigorously purified by passing through alumina, silica, MgSO$_4$ and distillation process.

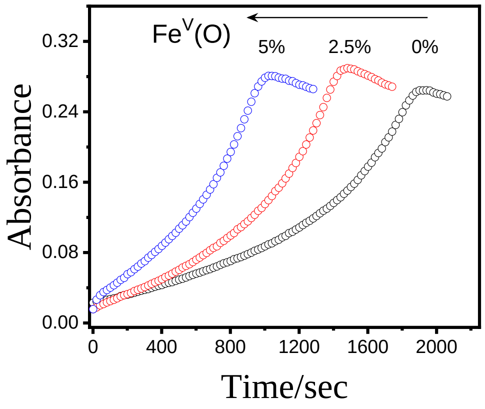


Fig. S5. UV-Vis time profiles at 613 nm for the formation of Fe^V(O) in the reaction of **1a** (0.1 mM) with ethylbenzene (0.1 M) in presence of Fe^V(O) (0-5%). This results in reduction of induction period.

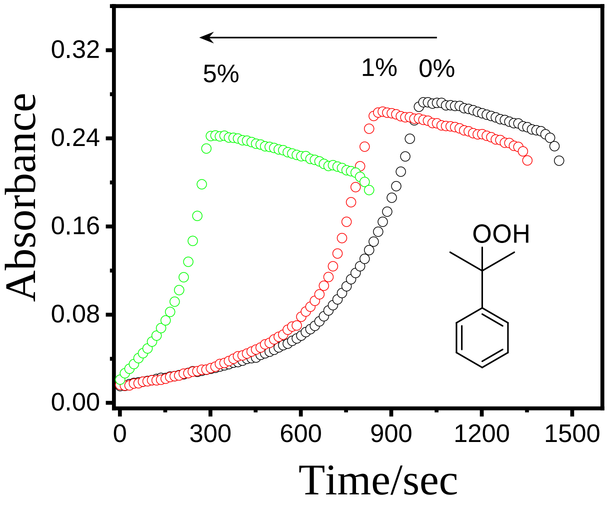


Fig. S6. UV-Vis time profiles at 613 nm for the formation of Fe^V(O) in the reaction of **1a** (0.1 mM) and diphenylmethane as substrate (0.1 M) in the presence of cumylhydroperoxide (0 to

5%) in aerated acetone at RT. This results in reduction of induction period with increasing cumylhydroperoxide.

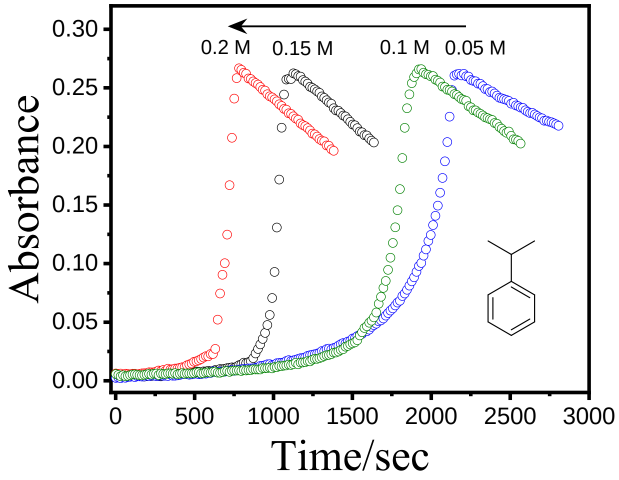
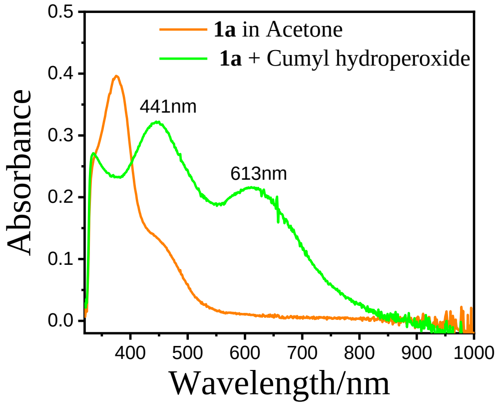


Fig. S7. UV-Vis time profiles at 613 nm for the formation of Fe^{V}(O) in the reaction of **1a** (0.1 mM) with increasing amount of substrate (cumene) (0.05M - 0.2 M) in aerated acetone at RT. This also results in reduction of induction period with increasing substrate concentration.



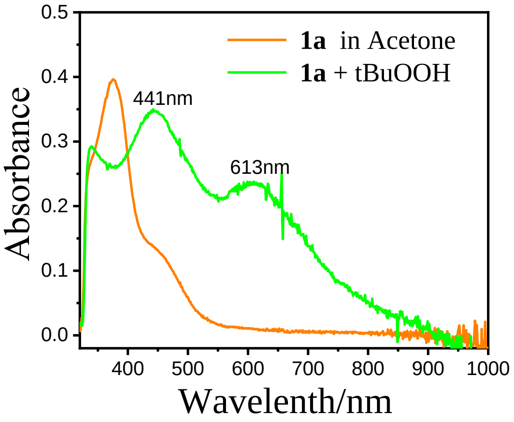


Fig. S8. UV-visible spectra for the formation of $Fe^{V}(O)$ in the reaction of $[Et_4N]_2[(bTAML)Fe^{III}-Cl]$ (**1a**) (0.10 mM) with cumyl hydroperoxide and t-butylhydroperoxide (0.15 mM) in aerated acetone solvent at room temperature.

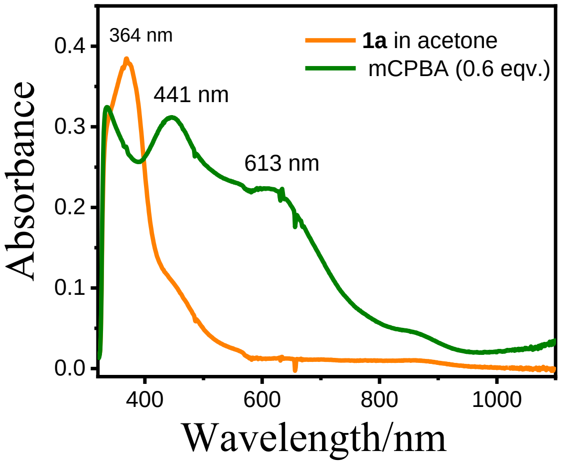


Fig. S9. UV-visible spectra for the formation of $Fe^{V}(O)$ from **1a** and mCPBA (0.6 eqv.) in aerated acetone solvent (regular HPLC grade) at room temperature. Interestingly, in regular HPLC grade acetone, $Fe^{V}(O)$ forms quickly without the formation of dimer species (**2**)

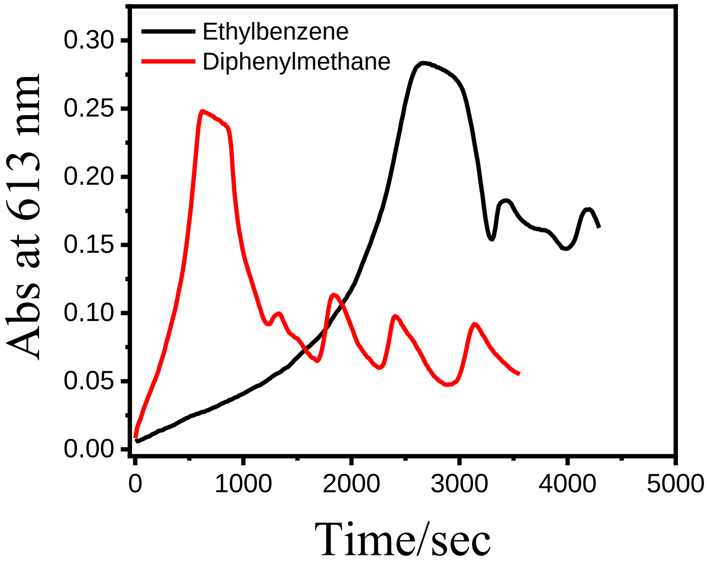


Fig. S10. UV-Vis time profiles at 613 nm for the formation of Fe^{V}(O) in the reaction of **1a** (0.1 mM) with diphenylmethane and ethylbenzene (0.1 M) in aerated acetone at RT.

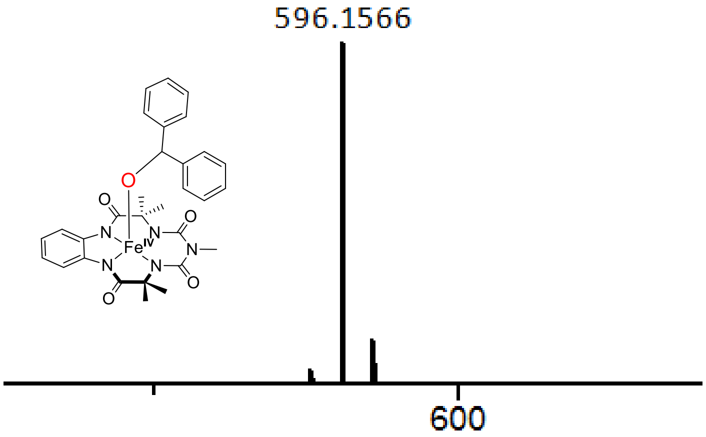
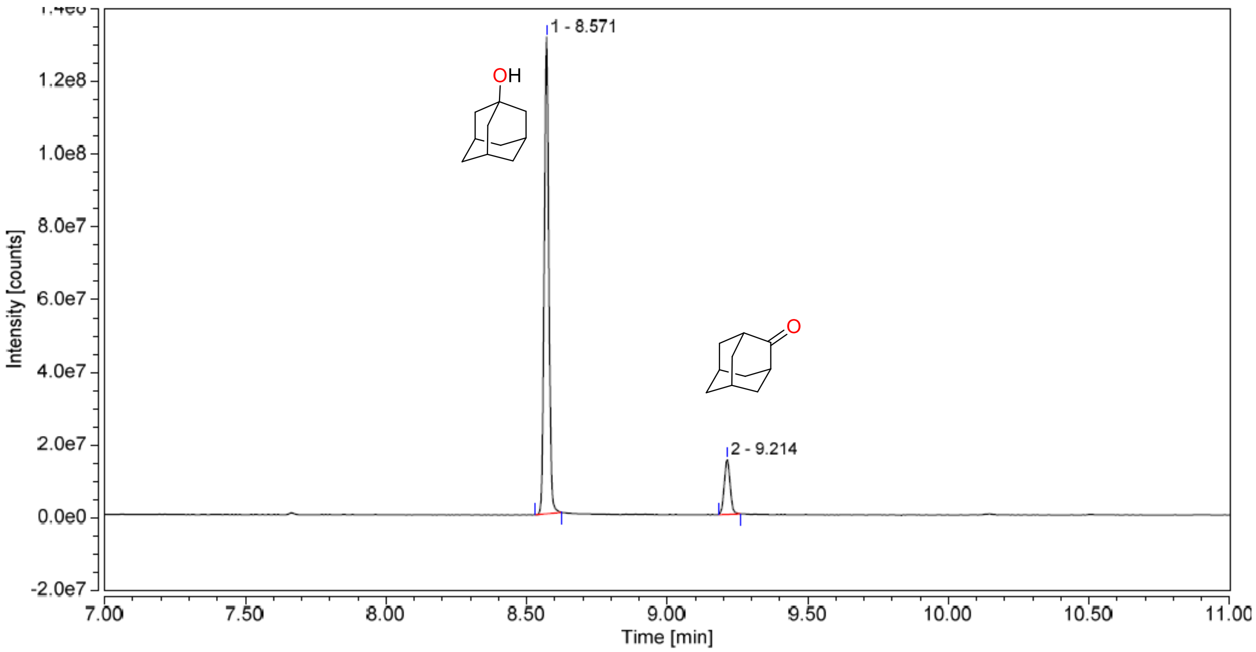
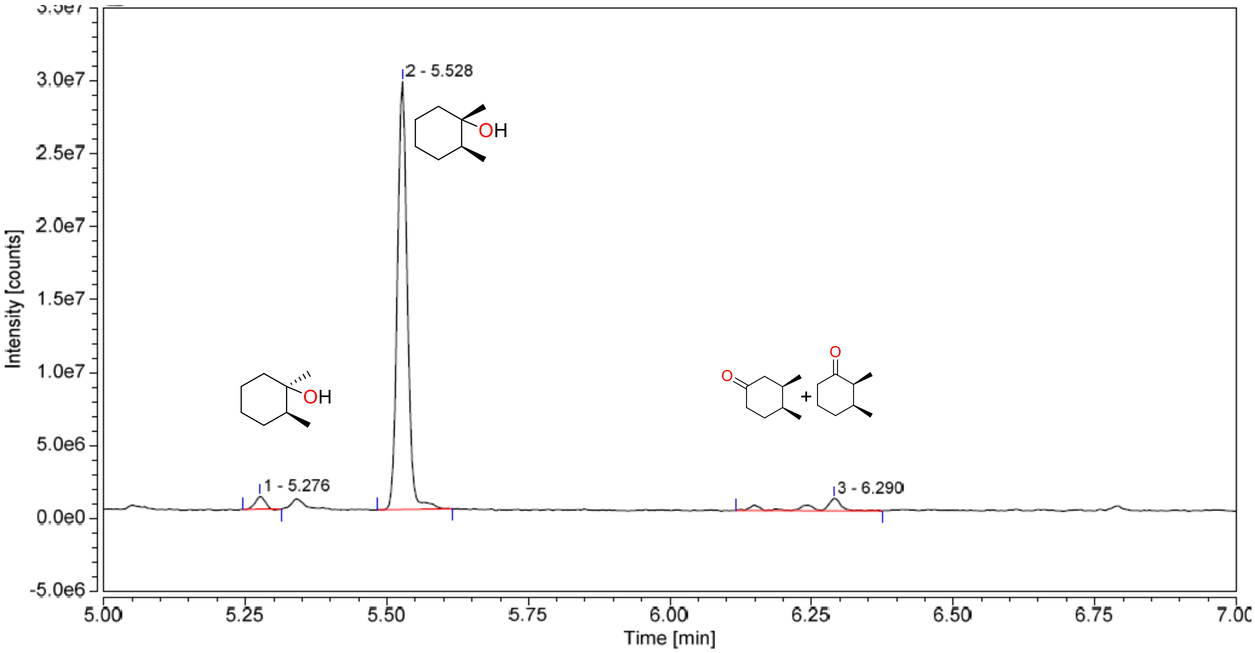


Fig. S11. ESI-MS spectrum of [(bTAML)Fe^{IV}-OR]$^{-}$ in the reaction of **1a** (0.1 mM) with diphenylmethane (RH) (0.1 M) in aerated acetone at RT. For [(bTAML)Fe^{IV}-OR]$^{-}$, the peak at m/z 596.1566 (the calculated peak at m/z 596.1596) obtained.

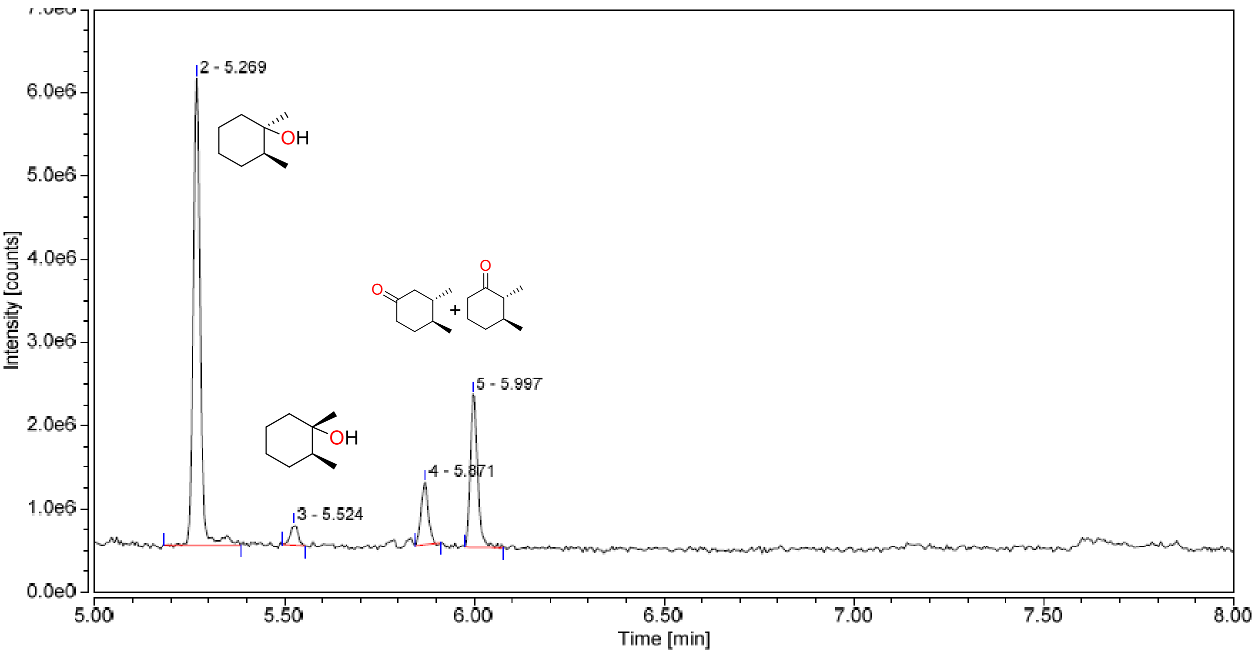
(S12) GC-MS trace for the oxygenation reaction of adamantane by O_2



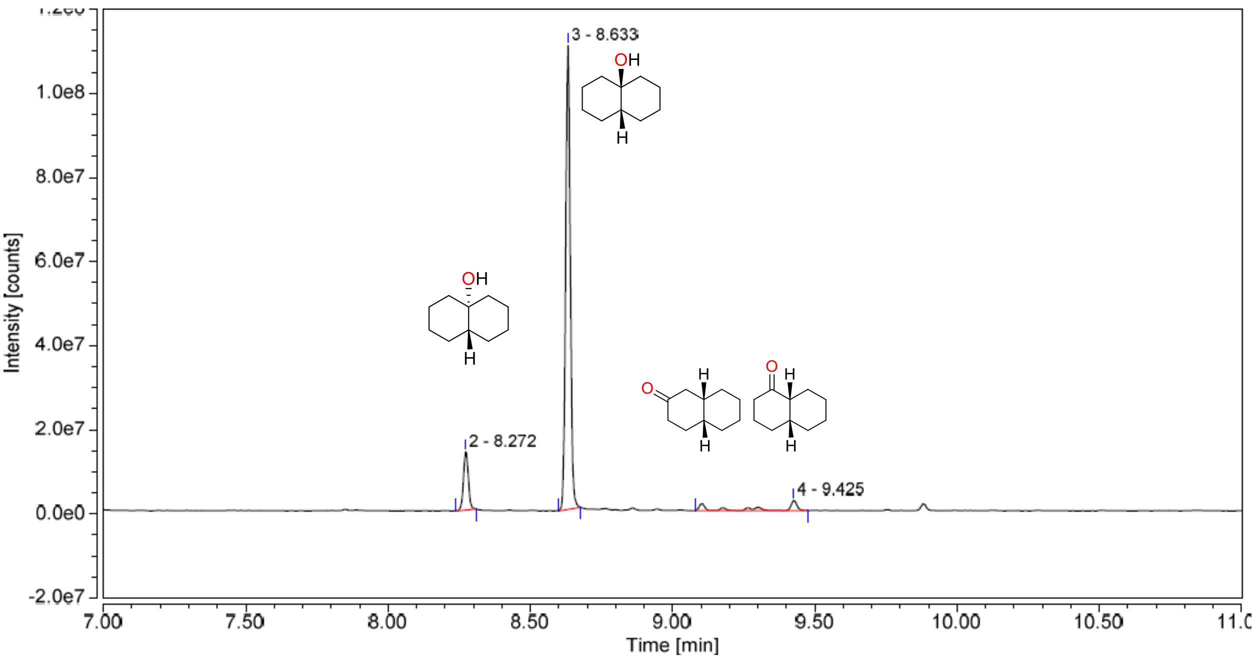
(S13) GC-MS trace for the oxygenation reaction of cis-1,2-dimethylcyclohexane by O_2



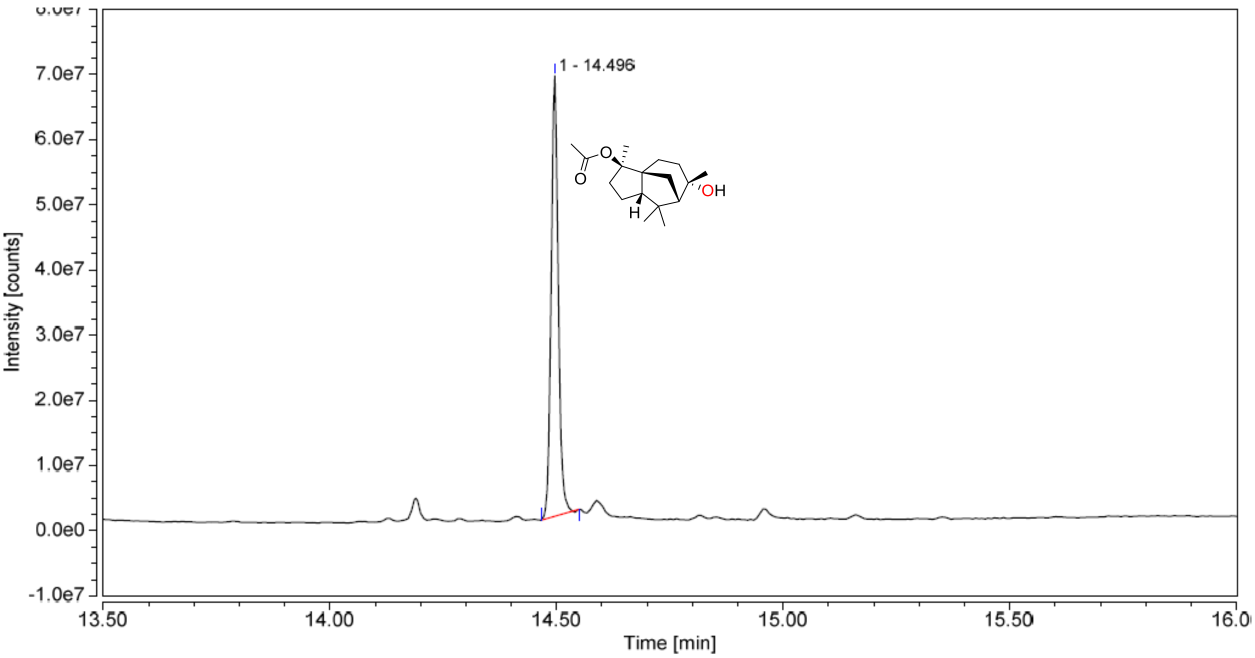
(S14) GC-MS trace for the oxygenation reaction of trans-1,2-dimethylcyclohexane by O_2



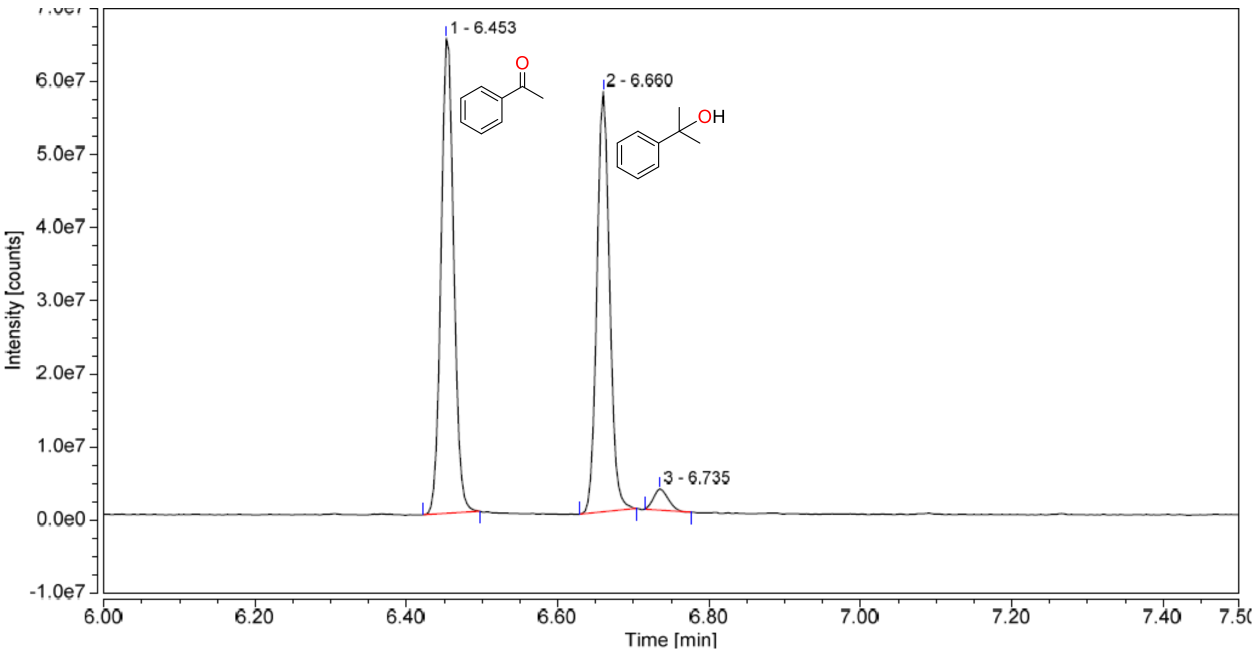
(S15) GC-MS trace for the oxygenation reaction of cis-decalin by O_2



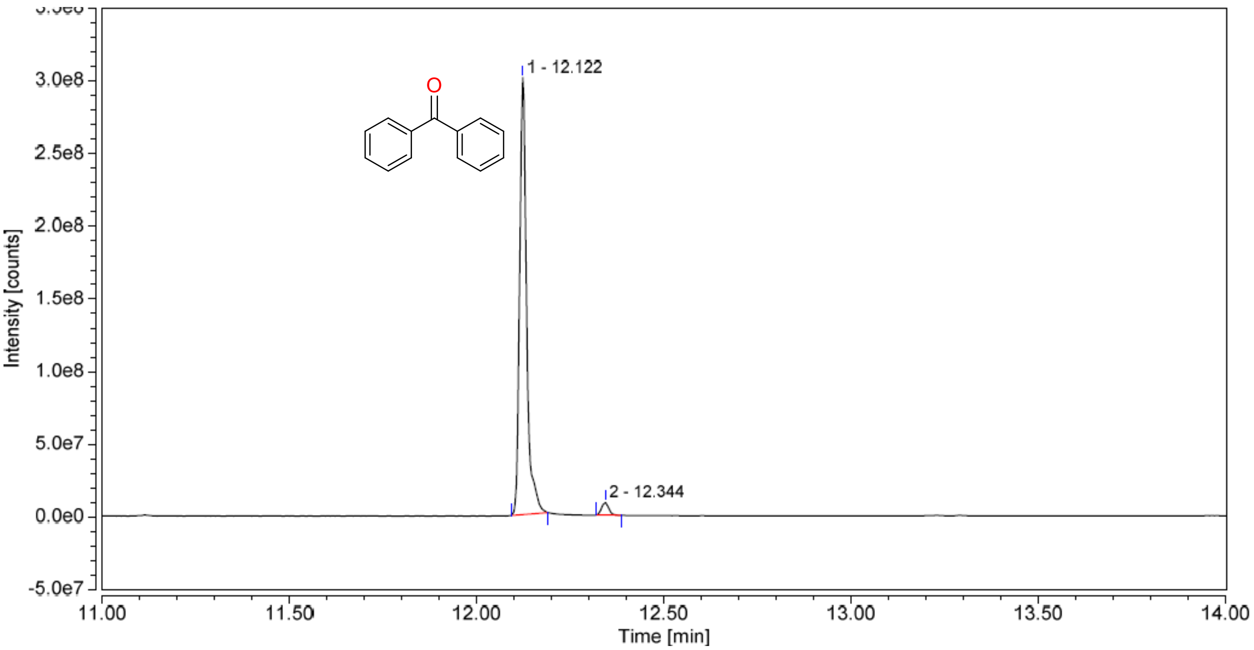
(S16) GC-MS trace for the oxygenation reaction of cedryl acetate by O_2



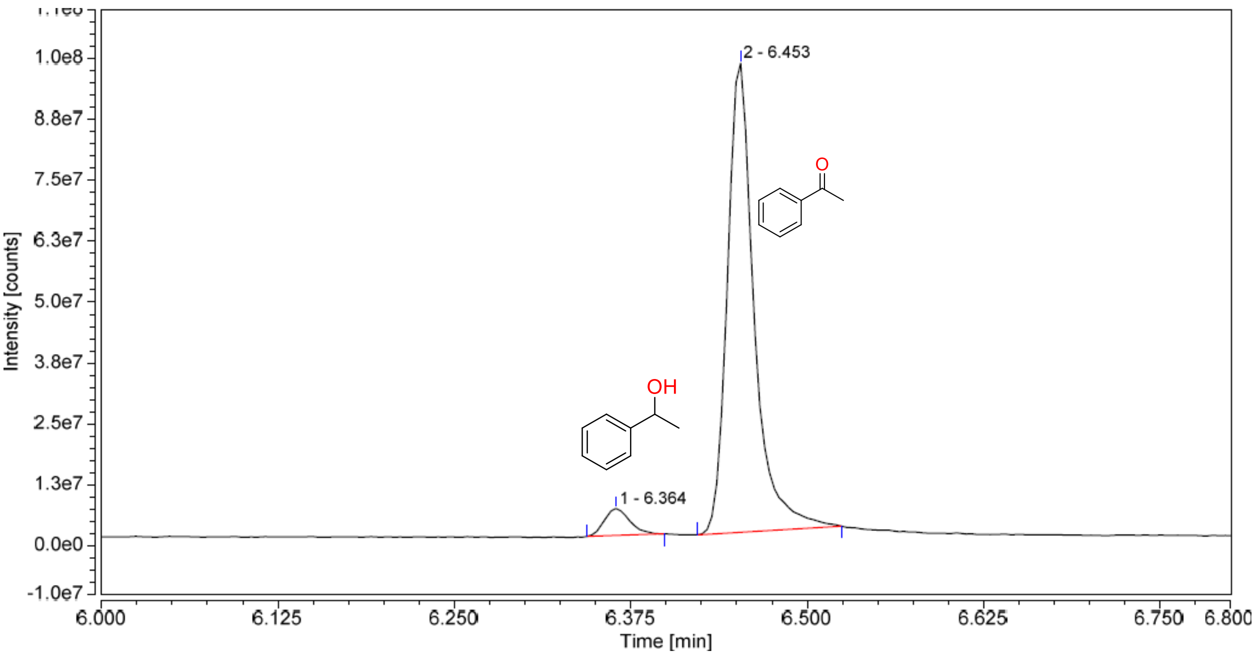
(S17) GC-MS trace for the oxygenation reaction of cumene by O_2



(S18) GC-MS trace for the oxygenation reaction of diphenylmethane by O_2



(S19) GC-MS trace for the oxygenation reaction of ethylbenzene by O_2



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