

Supporting Information

Selective Activation of Secondary C-H Bonds by an Iron Catalyst: Insight into Possibilities Created by the Use of a Carboxyl-Containing Bipyridine Ligand

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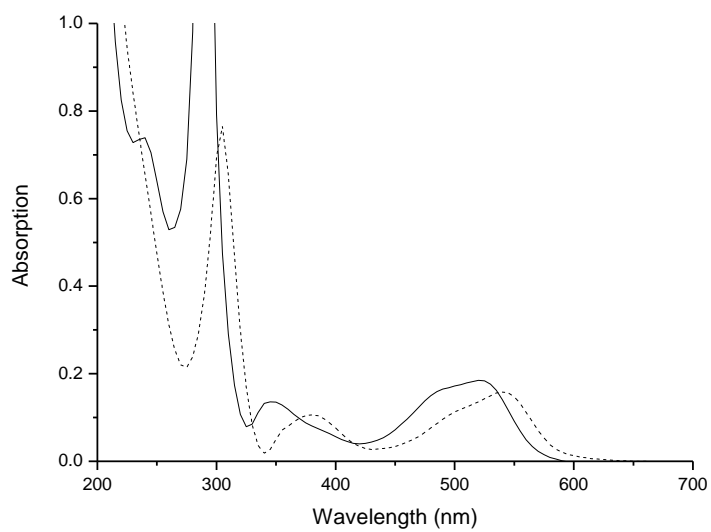
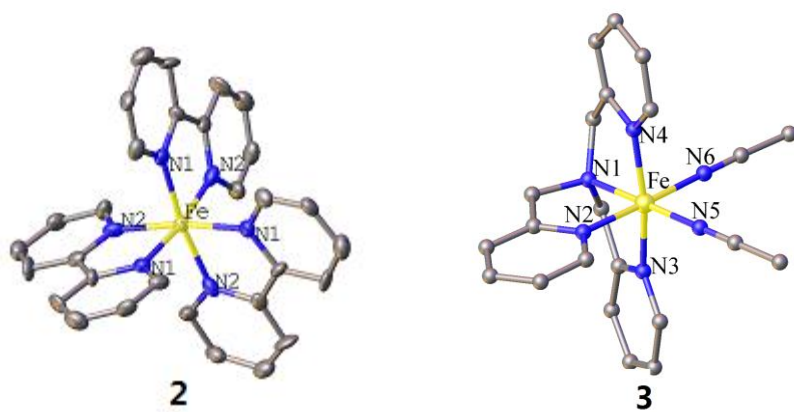


Figure S1. UV-VIS spectrum of **1** and **2**. Dash line, **1**. Real line, **2**.



Scheme S1. The crystal structure of **2** and **3**. Hydrogen atoms are omitted for clarity. [From Ref. S1 and S2]

Table S1. Oxidation of cyclohexane under other stoichiometric ratios and mixed solvent ratios^[a].

Entry	Promoter	I	TN	A/K
1	Fe ^{II}	+	0.4	0.60
2	Fe ^{II}	-	0.4	0.60
3	2	+	0.6	0.58
4	2	-	0.3	0.65
5	3	+	0.1	0.33
6	3	-	0.1	0.33
8	1	+	4.5	0.73
9	1	-	1.3	0.52

[a] Reaction conditions: 1.5 mM iron promoter, 150 mM alkane substrate and 150 mM H₂O₂ in 2.5 mL CH₃CN/H₂O solution (CH₃CN/H₂O (v/v) = 40/60), 20 h reaction time.

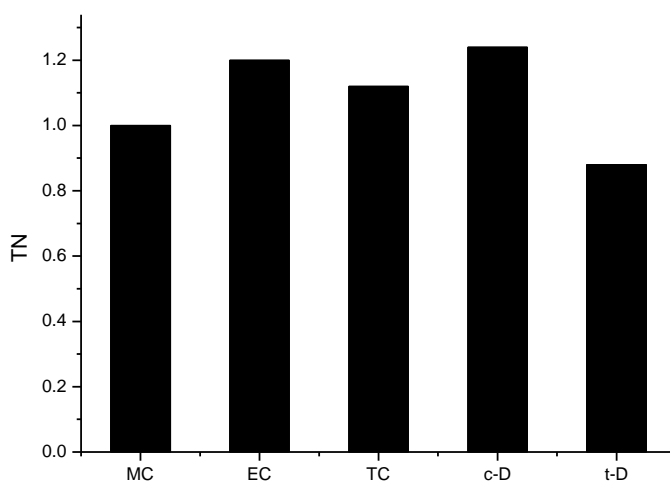


Figure S2. Oxidation of different substrates under other stoichiometric ratios and mixed solvent ratios with **1** as a promoter. Reaction conditions: 1.5 mM iron promoter, 6 mM alkane substrate and 205 mM H₂O₂ (CH₃CN/H₂O (v/v) = 40/60), 20 h reaction time. MC=methylcyclohexane, EC=ethylcyclohexane, TC=tert-butylcyclohexane, c-D=*cis*-decalin, t-D=*trans*-decalin.

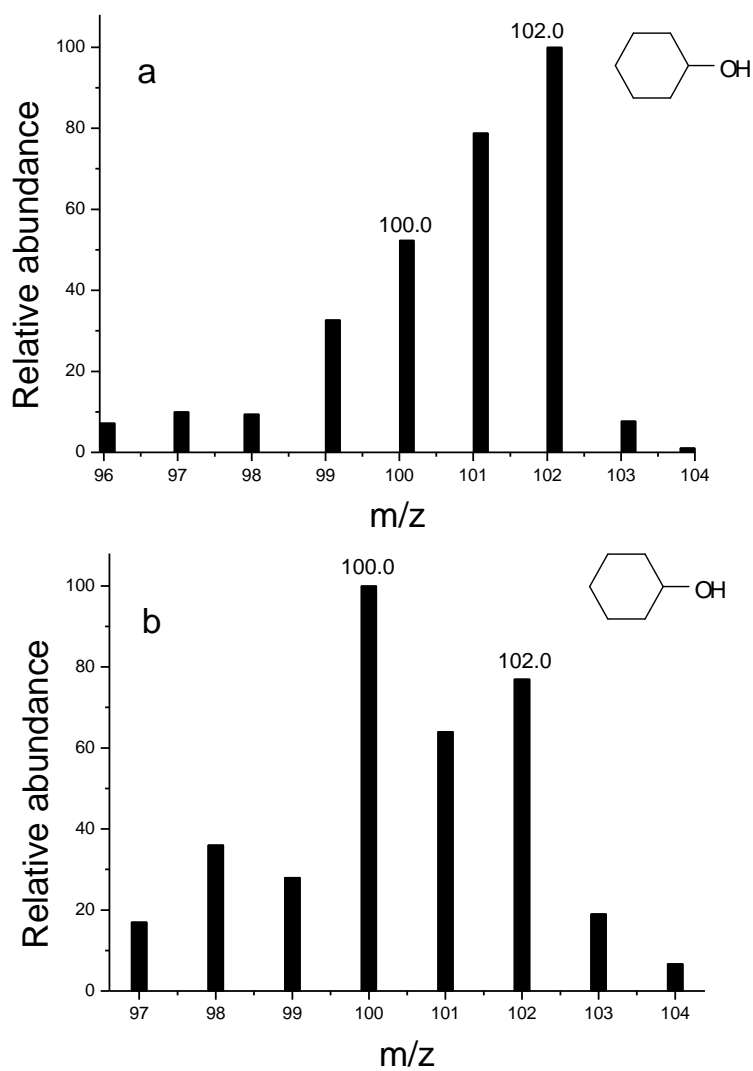


Figure S3. Isotope distribution of cyclohexanol in an ^{18}O labelled O_2 environment with **1** as the catalyst performed with irradiation (a) and without irradiation (b).

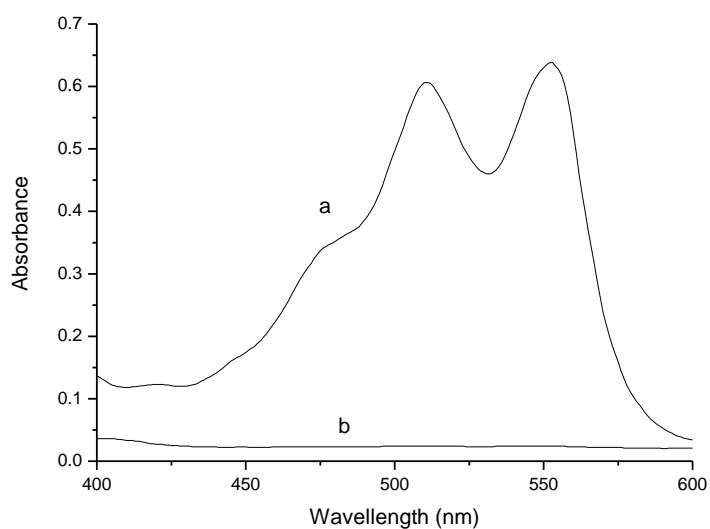
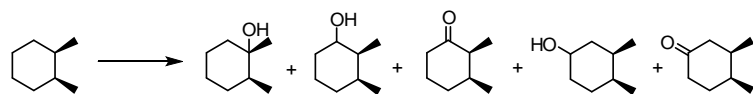


Figure S4. Detection of H_2O_2 and organoperoxides with 1.5 M cyclohexane and 60 mM H_2O_2 in a 2.5 mL $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (60/40) solution with 1.5 mM **1** as the iron catalyst after 5 h of visible irradiation. Curve a was obtained via the addition of phosphate buffer (pH 6.8), DPD (N,N'-dialkyl-p-phenylenediamine), and POD (Horseradish peroxidase) to the solution. Curve b was obtained through the same procedure except that catalase (0.1 mL, 0.5%; activity greater than 2.0 U mg^{-1}) was added prior to the other reagents (DPD, POD).

Table S2. Comparison of regioselectivity during the oxidation of *cis*-1,2-dimethylcyclohexane by different catalytic systems.



entry	system	[2°]/[3°]	[<i>cis</i>]/[<i>trans</i>]	Ref.
1	1/H₂O₂ (this work)	78/22	55/45	
2	s-MMO ^[a]	80/20	70/30	S3
3	[ⁿ Bu ₄ N][Os(N)(O) ₃]/FeCl ₃ /Cl ₂ PyO ^[b]	40/60	>99/1	S4
4	Fe(TPFPP)(ClO ₄)/m-CPBA ^[c]	27/73	>99/1	S5
5	[Fe(II)(TPA)(CH ₃ CN) ₂](ClO ₄) ₂ /H ₂ O ₂ ^[d]	25/75	>99/1	S6
6	[Mn ₂ (Me ₃ TACN) ₂ O ₃](PF ₆) ₂ /peracetic acid ^[e]	25/75	95/5	S7
7	[Mn ₂ (Me ₃ TACN) ₂ O ₃](PF ₆) ₂ /H ₂ O ₂	17/83	86/14	S8
8	[Fe(II)(N ₄ Py)(CH ₃ CN)](ClO ₄) ₂ /H ₂ O ₂ ^[f]	<1/99	60/40	S9
9	HO·	<1/99	55/45	S10, S11
10	CH ₃ ReO ₃ /H ₂ O ₂	<1/99	>99/1	S12
11	Methyl(trifluoromethyl)dioxirane	<1/99	>99/1	S13

[a] s-MMO = soluble methane monooxygenases, *cis*-1,3-dimethylcyclohexane was used rather than *cis*-1,2-dimethylcyclohexane.

[b] Cl₂PyO = 2,6-dichloropyridine N-oxide.

[c] TPFPP = meso-tetrakis(pentafluorophenyl)porphinato dianion.

[d] TPA = *tris*-(2-pyridylmethyl)amine.

[e] Me₃TACN = 1,4,7-trimethyl-1,4,7-triazacyclononane.

[f] N₄Py = N,N-bis(2-pyridylmethyl)-N-bis(2-pyridyl)methylamine.

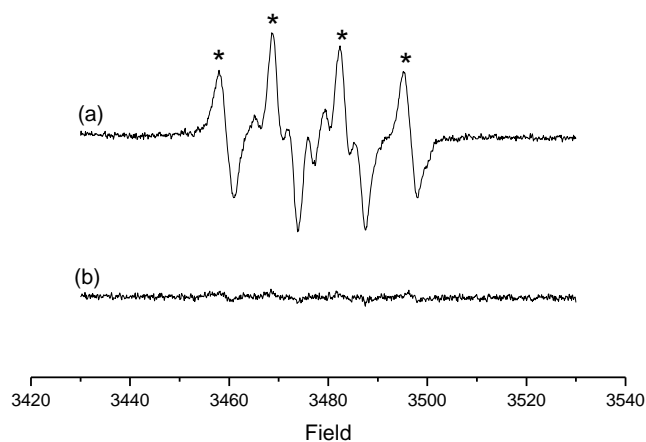


Figure S5. DMPO spin-trapping ESR spectra of different iron catalytic reactions under visible irradiation. 1.5 M cyclohexane, 60 mM H₂O₂ in a 2.5 mL CH₃CN/H₂O (60/40) solution with (a) 1.5 mM Fe(ClO₄)₂, (b) 1.5 mM **1**, respectively. Irradiation time: 5 min. (four-fold peaks with intensity of 1: 2: 2: 1 labelled by “*” are attributed to DMPO-OH, those peaks unlabeled are attributed to carbon centred or oxygen centred alkyl radical captured by DMPO)

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