

Supplementary material for the paper

Bio-inspired amino acid oxidation by a non-heme iron catalyst modeling the action of 1-aminocyclopropane-1-carboxylic acid oxidase

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Experimental

Materials

All manipulations were performed under pure dinitrogen or argon atmosphere unless otherwise stated, using standard Schlenck-type inert-gas techniques. Solvents used for the reactions were purified by literature methods and stored under argon. $[\text{Fe}^{\text{III}}(\text{Salen})\text{Cl}]$ and $[\text{Fe}^{\text{II}}(\text{N4Py})(\text{CH}_3\text{CN})](\text{ClO}_4)_2$ were prepared according to the literature [1, 2]. All other chemicals were commercial products and were used as received without further purification.

Analytical and physical measurements

Infrared spectra were recorded on an Avatar 330 FT-IR Thermo Nicolet instrument using samples mullied in Nujol between KBr plates or in KBr pellets. UV-Vis spectra were recorded on an Agilent 8453 spectrophotometer using quartz cells. GC analyses were performed on a Hewlett Packard 5890 gas chromatograph equipped with a flame ionization detector and a 30 m Super Cowax 10 column. Microanalyses were done by the Microanalytical Service of the University.

Determination of acetone, acetaldehyde and ethylene

Reactivity assays were performed as follows: respective amino acid (ACCH, AIBH, ALA) (3.6×10^{-4} mol) was dissolved in 10 cm^3 of DMF/ H_2O compound (3/1) in a sealable tube of 20 mL. To the mixture were then added MeCN (10 μL) as inner standard and the catalyst (7.2×10^{-8} mol). Hydrogen peroxide was then added through the septum with a syringe and the evolved acetone, acetaldehyde or ethylene were measured by removing 0.5 mL of the headspace (in every 5 minutes) with a gastight syringe and injecting the sample into a gas chromatograph. The concentration of acetone and acetaldehyde in the head space are linearly proportional to the concentration of acetone and acetaldehyde in the reaction mixture.

To get a direct evidence for the fact that only the high-valent oxoiron species are responsible for the catalytic reaction and to proof that hydroxyl radicals are not responsible, reactions were carried out in the presence of radical scavenger such as DMSO (hydroxyl radicals are very efficiently trapped by DMSO). The observed yields and TOF values for the DMSO-containing systems are identical within experimental error, excluding the formation of the hydroxyl radical (Fig. S5).

- 1 E. G. Samsel, K. Srinivasan, J. K. Kochi, *J. Am. Chem. Soc.*, 1985, **107**, 7606.
- 2 M. Lubben, A. Meetsma, E. C. Wilkinson, B. Feringa, L. Que, Jr., *Angew. Chem. Int. Ed. Engl.* 1995, **34**, 1512.

Table S1 Kinetic data for the Fe(Salen)Cl-catalysed amino acid oxidation reactions in DMF/water (3:1) at 25°C.

Run	Subs.	[Fe] ₀ ×10 ⁻⁵ M	[H ₂ O ₂] ₀ ×10 ⁻² M	[S] ₀ ×10 ⁻² M	[NH ₄ OH] ×10 ⁻² M	-d[S]/dt ×10 ⁻⁵ Ms ⁻¹	TOF 1/h	<i>t</i> (min)	Yield %
1.	AIBH	0.72	3.60	3.60	-----	1.41	4437	50	79.8
2.	AIBH	0.94	3.60	3.60	-----	2.01	6211	40	82.8
3.	AIBH	1.15	3.60	3.60	-----	2.26	6021	40	80.3
4.	AIBH	1.44	3.60	3.60	-----	2.73	7853	30	78.5
5.	AIBH	0.72	3.60	0.34	-----	0.56	-	30	100
6.	AIBH	0.72	3.60	0.66	-----	0.92	-	30	100
7.	AIBH	0.72	3.60	1.08	-----	1.17	-	30	100
8.	AIBH	0.72	3.60	2.16	-----	1.42	7327	40	97.7
9.	AIBH	0.72	3.60	2.88	-----	1.43	7500	40	100
10.	AIBH	0.72	1.13	3.60	-----	0.50	1344	50	22.4
11.	AIBH	0.72	2.25	3.60	-----	0.96	3112	40	41.5
12.	AIBH	0.72	1.13	3.60	0.28	0.56	2160	30	21.6
13.	AIBH	0.72	1.13	3.60	1.80	0.85	2300	30	23
14.	AIBH	0.72	1.13	3.60	3.60	0.95	2460	30	24.6
15.	AIBH	0.72	2.25	3.60	3.60	1.15	3637	40	48.5
16.	AIBH	0.72	3.60	3.60	3.60	1.79	4800	40	64
17.	AIB-D	0.72	1.13	3.60	-----	0.42	1200	90	36
18.	AIB-D	0.72	2.25	3.60	-----	0.74	1760	90	52.8
19.	AIB-D	0.72	3.60	3.60	-----	1.15	2560	90	76.8
20.	ALAH	0.72	3.60	3.60	-----	-----	-----	-----	-----
21.	ALAH	0.72	1.13	3.60	3.60	0.14	373	210	26.1
22.	ALAH	0.72	2.25	3.60	3.60	0.25	606	210	42.4
23.	ALAH	0.72	3.60	3.60	3.60	0.35	1226	210	85.8
24.	ALA-D	0.72	3.60	3.60	3.60	0.14	558	360	67
25.	ACCH	0.72	3.60	3.60	-----	-----	-----	-----	-----
26.	ACCH	0.72	3.60	3.60	3.60	0.10	361	340	40.9
27.	ACCH	0.72	12.60	3.60	3.60	0.51	1361	140	63.5
38.	ACCH	0.72	18.00	3.60	3.60	0.85	2739	100	91.3
29.	ACC-D	0.72	18.00	3.60	3.60	0.22	733	180	44

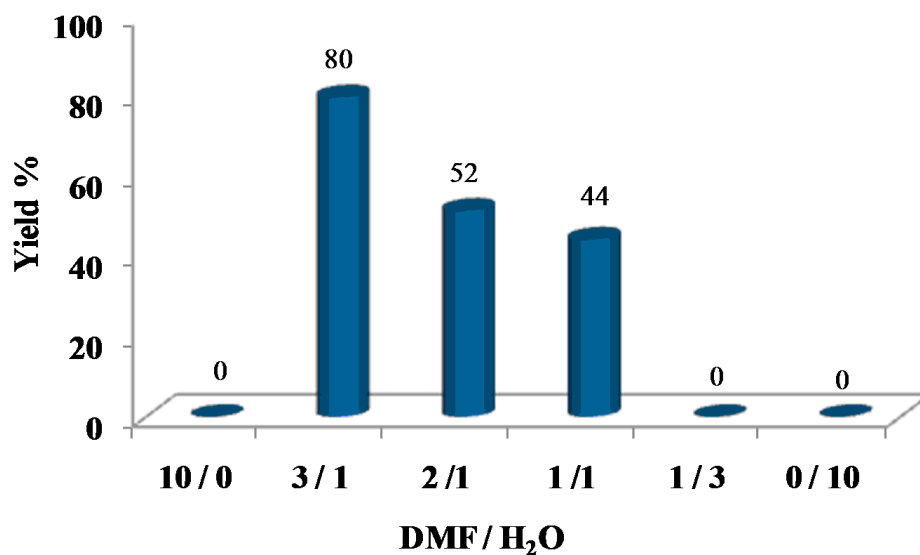


Fig. S1 Effect of the DMF/H₂O ratio to the yield in the amino acid oxidation reactions [AIBH] = 3.6×10^{-2} M, [Fe(Salen)Cl] = 7.2×10^{-6} M, [H₂O₂] = 3.6×10^{-2} M at 25°C.

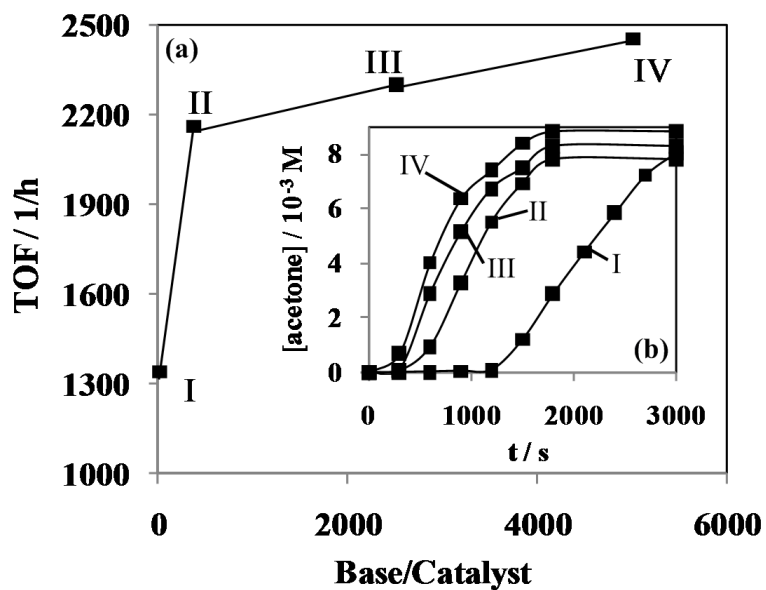


Fig. S2 (a) Change of TOF in the oxidation of AIBH in the presence of base in DMF/water (3:1) at 25°C. $[AIBH] = 3.6 \times 10^{-2}$ M, $[Fe(Salen)Cl] = 7.2 \times 10^{-6}$ M, $[H_2O_2] = 1.13 \times 10^{-2}$ M. (b) Time curves of acetone evaluation in the oxidation of AIBH in the presence of base in DMF/water at 25°C. $[AIBH] = 3.6 \times 10^{-2}$ M, $[Fe(Salen)Cl] = 7.2 \times 10^{-6}$ M, $[H_2O_2] = 1.13 \times 10^{-2}$ M.

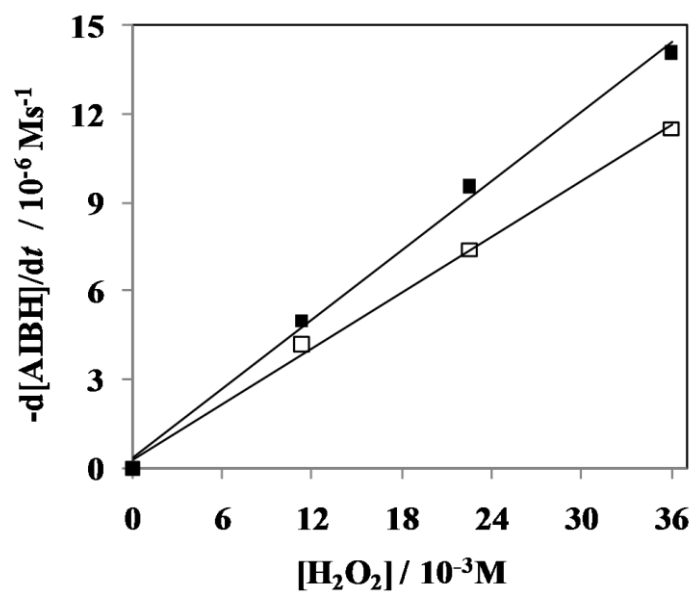


Fig. S3 Hydrogen peroxide dependence in the oxidation of AIBH (■) in DMF/water (3:1) at 25°C. (●) in DMF/deutero-water at 25°C. [AIBH] = 3.6×10^{-2} M, [Fe(Salen)Cl] = 7.2×10^{-6} M, at 25°C.

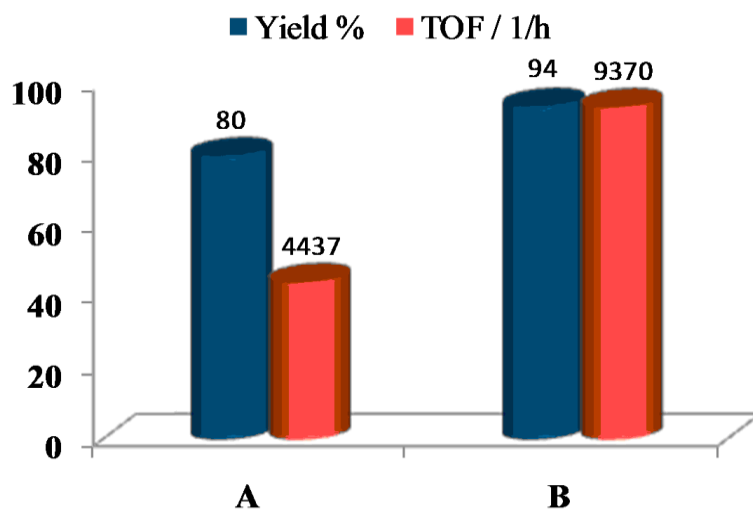


Fig. S4 Yields and TOF values in the oxidation of AIBH in DMF/water (3:1) at 25°C. A : $[\text{Fe}(\text{Salen})\text{Cl}] = 7.2 \times 10^{-6} \text{ M}$, B : $[\text{Fe}^{\text{II}}(\text{N4Py})(\text{CH}_3\text{CN})](\text{ClO}_4)_2 = 7.2 \times 10^{-6} \text{ M}$, $[\text{AIBH}] = 3.6 \times 10^{-2} \text{ M}$, $[\text{H}_2\text{O}_2] = 3.6 \times 10^{-2} \text{ M}$.

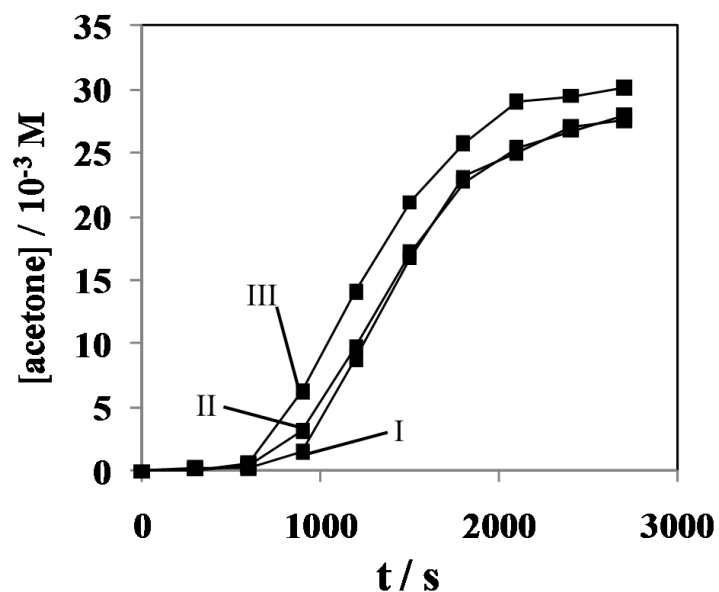


Fig. S5 (a) Change of acetone formation in the oxidation of AIBH in the presence of DMSO in DMF/water at 35°C. I: without DMSO; II: 0,5 mL DMSO was added; III: 1 mL DMSO was added. $[AIBH] = 3.6 \times 10^{-2}$ M, $[Fe(Salen)Cl] = 7.2 \times 10^{-6}$ M, $[H_2O_2] = 1.13 \times 10^{-2}$ M.