Electronic Supplementary Material (ESI) for Dalton Transactions
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Electronic Supplementary Information

Hexanuclear and Undecanuclear Iron(III) Carboxylates as Catalyst Precursors for Cyclohexane Oxidation

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Table S1 Crystal data and details of data collection for **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{114.5}H_{150.5}Fe_6O_{65}$	$C_{175.25}H_{220.85}ClFe_{11}N_{3.75}O_{97.05}$
Fw	2901.95	4582.51
Space group	P–1	P–1
a [Å]	15.3674(7)	19.4468(13)
b [Å]	16.1325(7)	23.6865(16)
c [Å]	16.2835(7)	25.9226(17)
α[°]	73.631(2)	78.197(4)
β[°]	80.246(3)	87.186(4)
γ[°]	65.635(2)	71.921(4)
V [Å^3]	3521.8(3)	11109.8(13)
Z	1	2
λ [Å]	0.71073	0.71073
ρ_{calcd} [g cm^{-3}]	1.368	1.370
crystal size [mm^3]	0.50 × 0.50 × 0.17	0.40 × 0.35 × 0.35
T [K]	100(2)	100(2)
μ [mm^{-1}]	0.695	0.800
R_1[a]	0.0798	0.0824
wR_2[b]	0.2795	0.272
GOF[c]	1.046	1.067

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. [c] GOF $= \{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where n is the number of reflections and p is the total number of parameters refined.

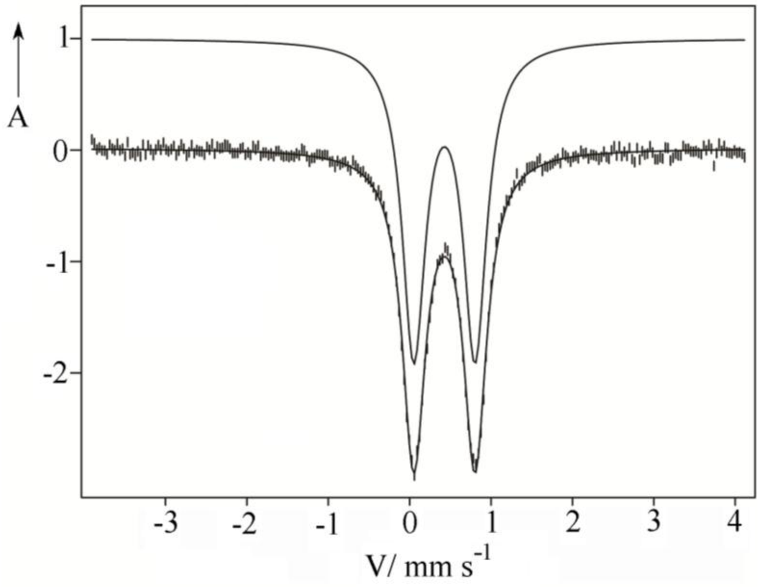

Fig. S1 Mössbauer spectrum of **1** at 300 K (δ = 0.43 mm s^{-1}, ΔE_Q = 0.75 mm s^{-1}).

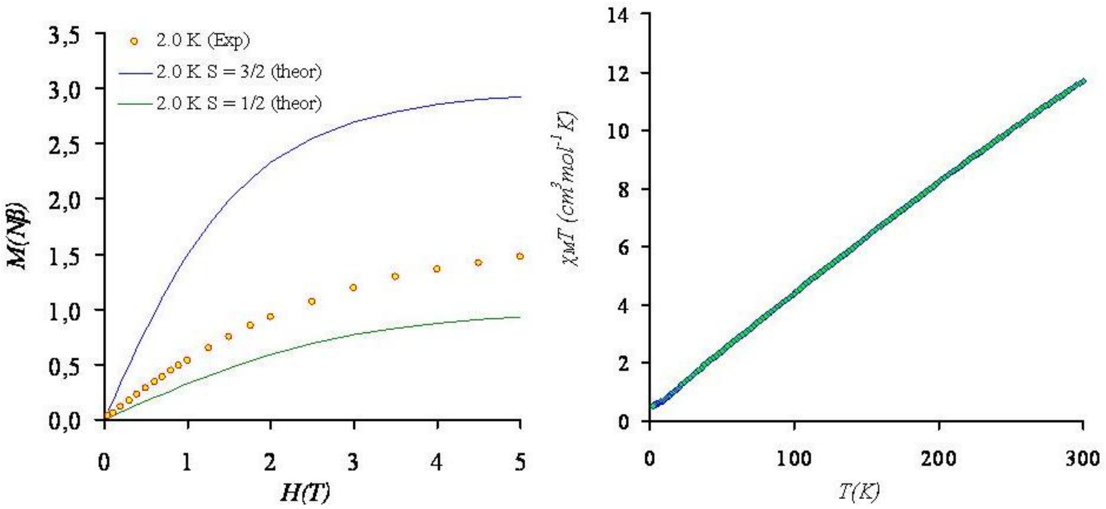

Fig. S2 Magnetization data for **2** at 2 K (left). Solid lines represent simulated according Brillouin function for S=1/2 (green line) and S=3/2 (blue line). Magnetic susceptibility (right) in a temperature range of 2 – 300 K under a field of 0.1 T.

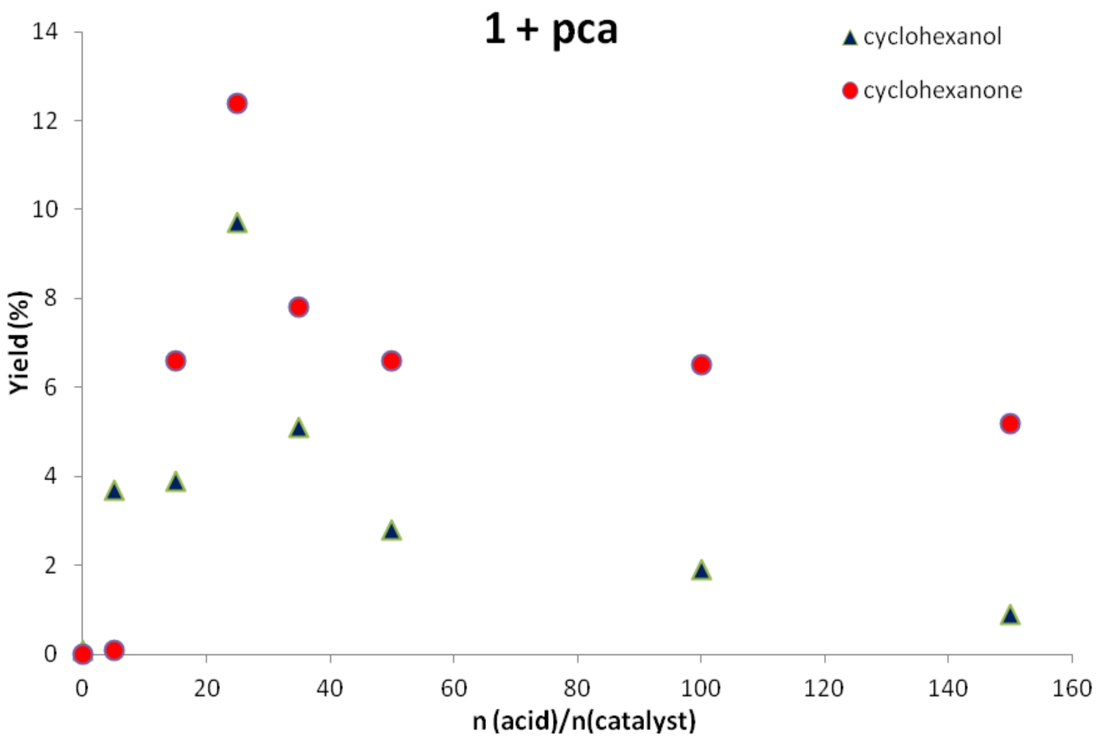

Fig. S3 Effects of the Hpca amount (molar ratios relatively to **1**) on the cyclohexanol (▲) or cyclohexanone (●) yield (mol%, based on substrate). Reaction conditions: $n(H_2O_2)/n(\mathbf{1})$ (2×10^4), MeCN (3.0 mL), cyclohexane (5.0 mmol), Hpca (0 – 150 mmol), 45 min, r.t.

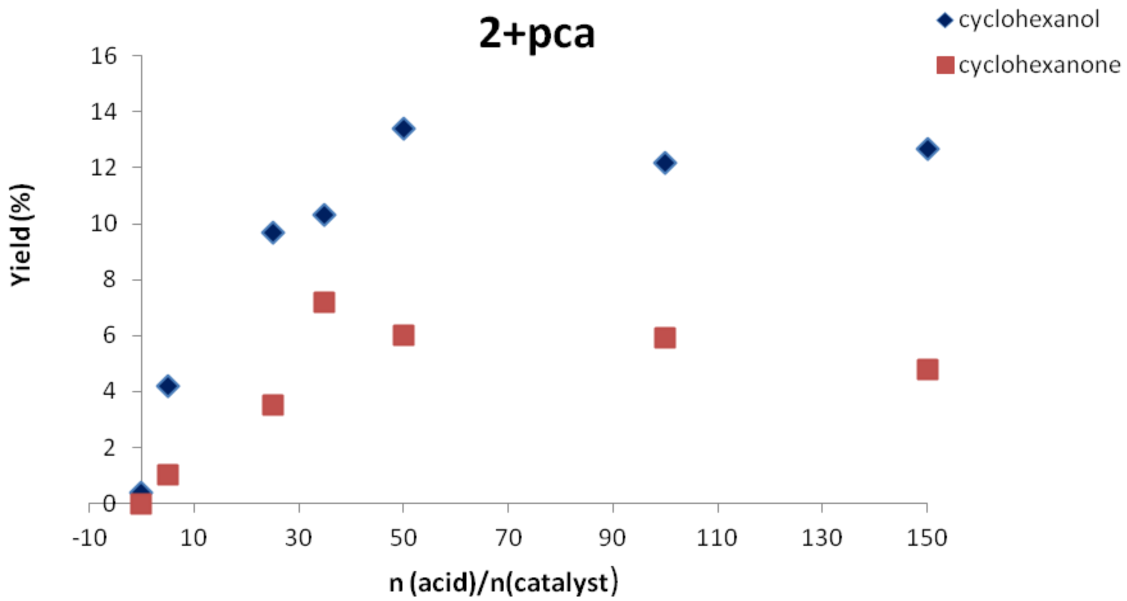

Fig. S4 Effects of the Hpca amount (molar ratios relatively to **2**) on the cyclohexanol (◆) or cyclohexanone (■) yield (mol%, based on substrate). Reaction conditions: $n(H_2O_2)/n(\mathbf{2})$ (2×10^4), MeCN (3.0 mL), cyclohexane (5.0 mmol), Hpca (0 – 150 mmol), 6 h, r.t.

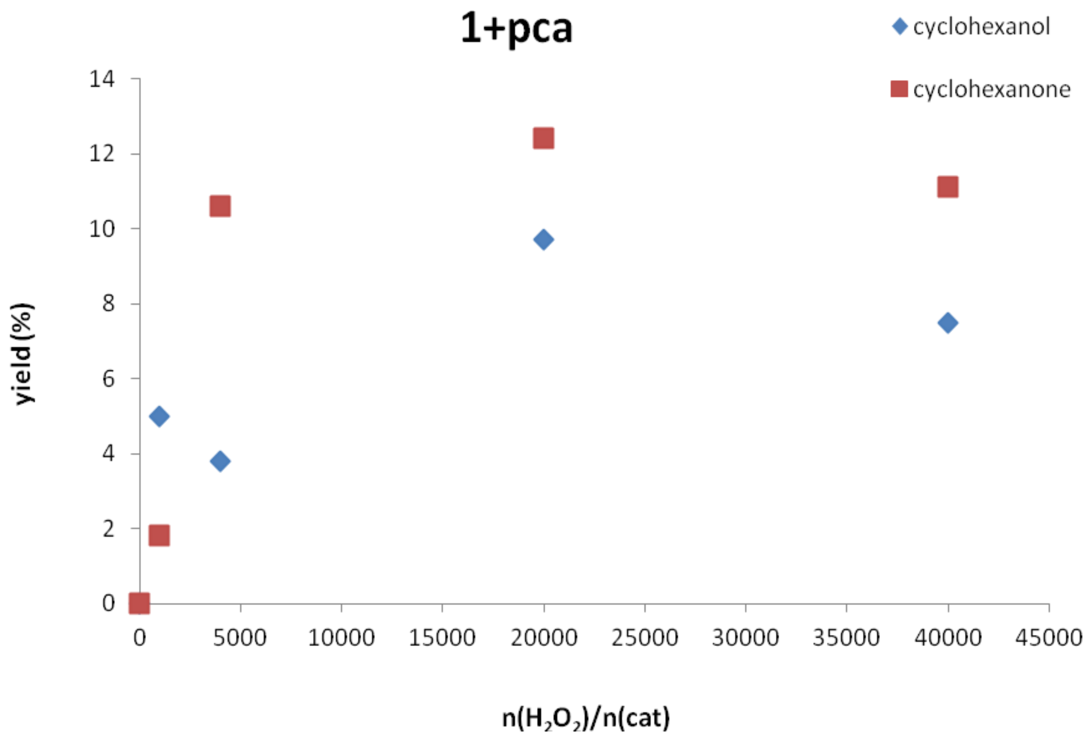

Fig. S5 Dependence of the cyclohexanol (◆) or cyclohexanone (■) yield (mol%, based on substrate) on the amount of oxidant (H_2O_2, molar ratio relatively to **1**) in the oxidation of cyclohexane. Reaction conditions: $n(H_2O_2)/n(\mathbf{1})$ (0 – 4 × 10^4), MeCN (3.0 mL), cyclohexane (5.0 mmol), *n*(Hpca)/*n*(**1**) (25.0), 45 min., r.t.

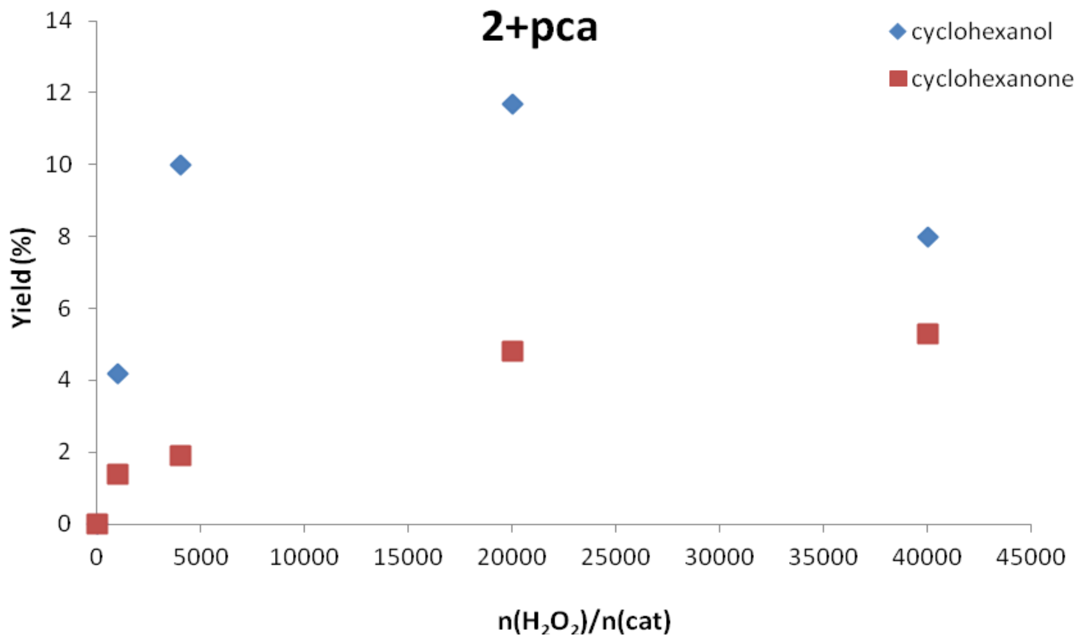

Fig. S6 Dependence of the cyclohexanol (◆) or cyclohexanone (■) yield (mol%, based on substrate) on the amount of oxidant (H_2O_2, molar ratio relatively to **2**) in the oxidation of cyclohexane. Reaction conditions: $n(H_2O_2)/n(\mathbf{2})$ ($0 - 4 \times 10^4$), MeCN (3.0 mL), cyclohexane (5.0 mmol), *n*(Hpca)/*n*(**2**) (50.0), 6 h, r.t.

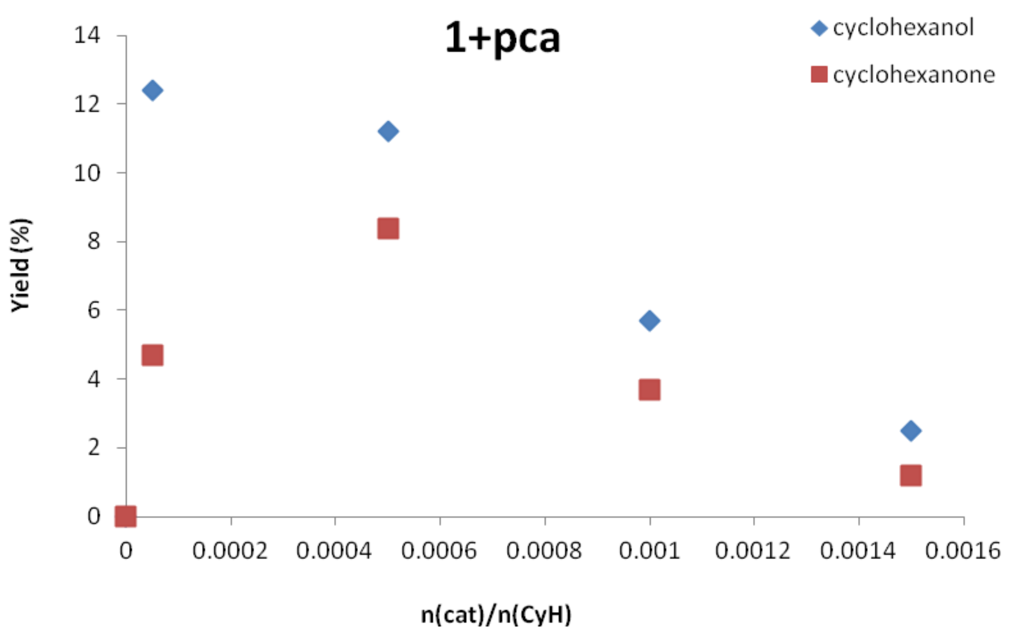

Fig. S7 Dependence of the cyclohexanol (◆) or cyclohexanone (■) yield (mol%, based on substrate) on the amount of catalyst **1** in the oxidation of cyclohexane. Reaction conditions: $n(H_2O_2)/n(\mathbf{1})$ (2×10^4), MeCN (3.0 mL), cyclohexane (5.0 mmol), *n*(Hpca)/*n*(**1**) (25.0), 45 min., r.t.

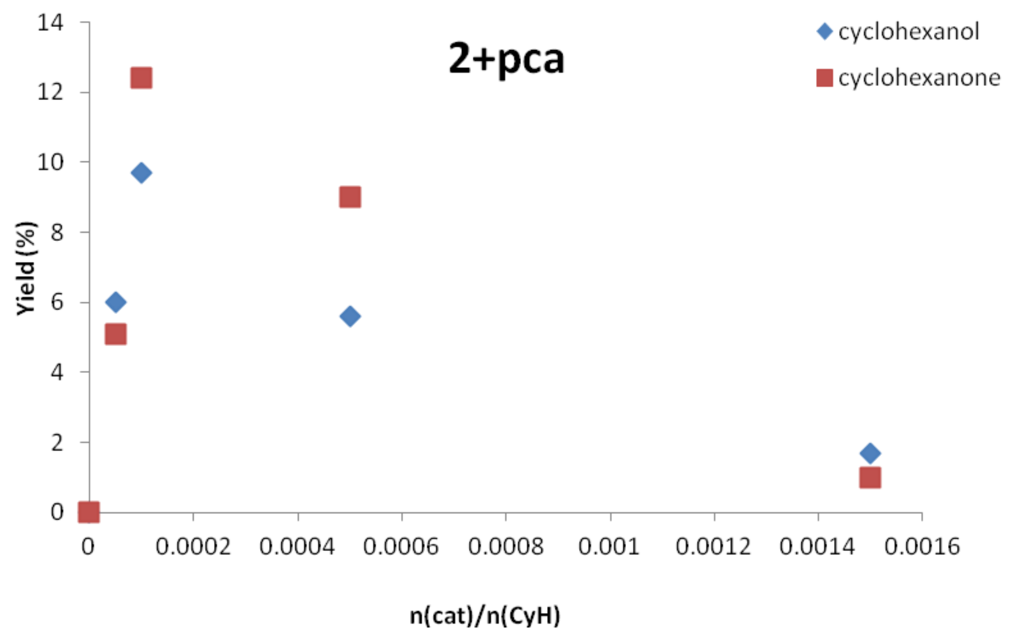

Fig. S8 Dependence of the cyclohexanol (◆) or cyclohexanone (■) yield (mol%, based on substrate) on the amount of catalyst **2** in the oxidation of cyclohexane. Reaction conditions: $n(H_2O_2)/n(\mathbf{2})$ (2×10^4), MeCN (3.0 mL), cyclohexane (5.0 mmol), *n*(Hpca)/*n*(**2**) (50.0), 6 h, r.t.

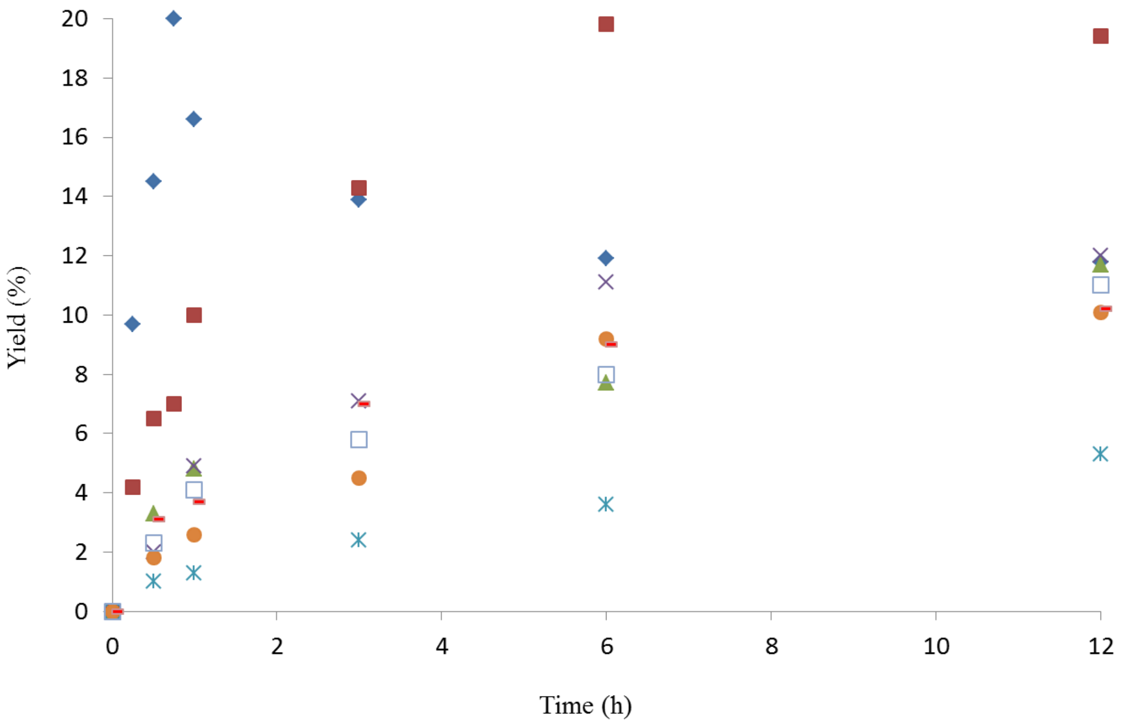

Fig. S9 Dependence of the overall yield (mol%, based on substrate) of the products on the reaction time in the presence of different iron species: **1**, **2**, $FeSO_4 \cdot 7H_2O$, $Fe(CF_3SO_3)_3$ or $[Fe_3OL_6(H_2O_3)_3]NO_3 \cdot HL$ (HL = 3,4,5-trimethoxybenzoic acid). Reaction conditions: MeCN (3.0 mL), cyclohexane (5.0 mmol), 0.5 μmol of catalyst percursor, $n(H_2O_2)/n$(catalyst precursor) (2×10^4), *n*(Hpca)/*n*(**1**) (25.0, ◆), *n*(Hpca)/*n*(**2**) (50.0, ■), $n(Hpca)/n(FeSO_4 \cdot 7H_2O)$ (25.0, ▲ or 50.0, X), $n(Hpca)/n(Fe(CF_3SO_3)_3)$ (25.0, ✳ or 50.0, ●), $n(Hpca)/n([Fe_3OL_6(H_2O_3)_3]NO_3 \cdot HL)$ (25.0, □ or 50.0, -), r.t.

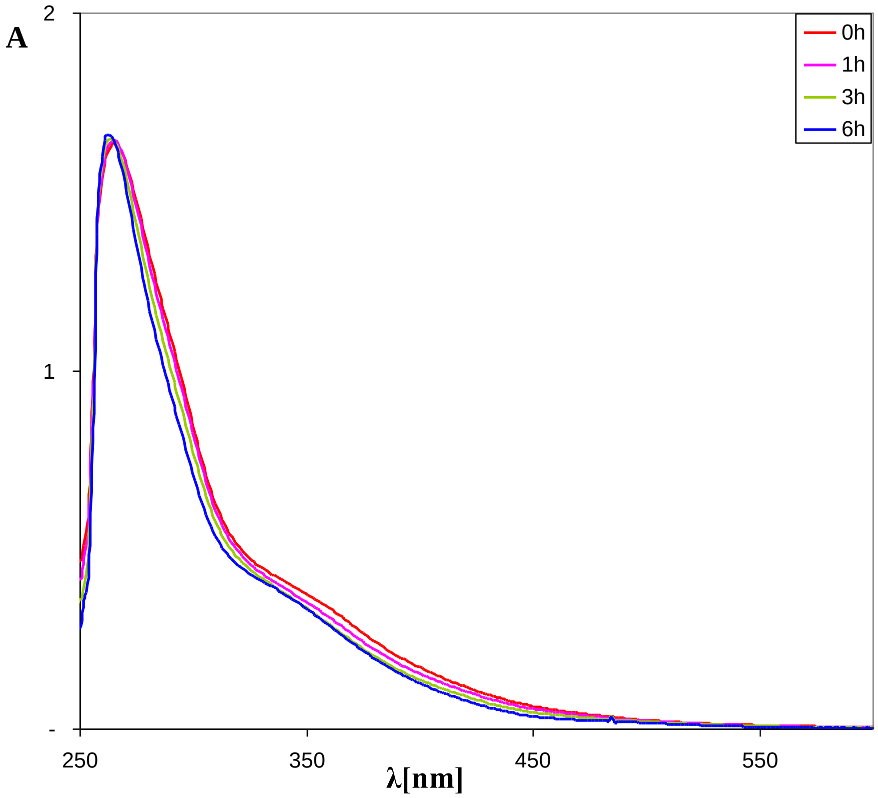

Fig. S10. UV–vis spectra of **2** in MeCN/dmf = 10:1 for 0, 1, 3 and 6 h.

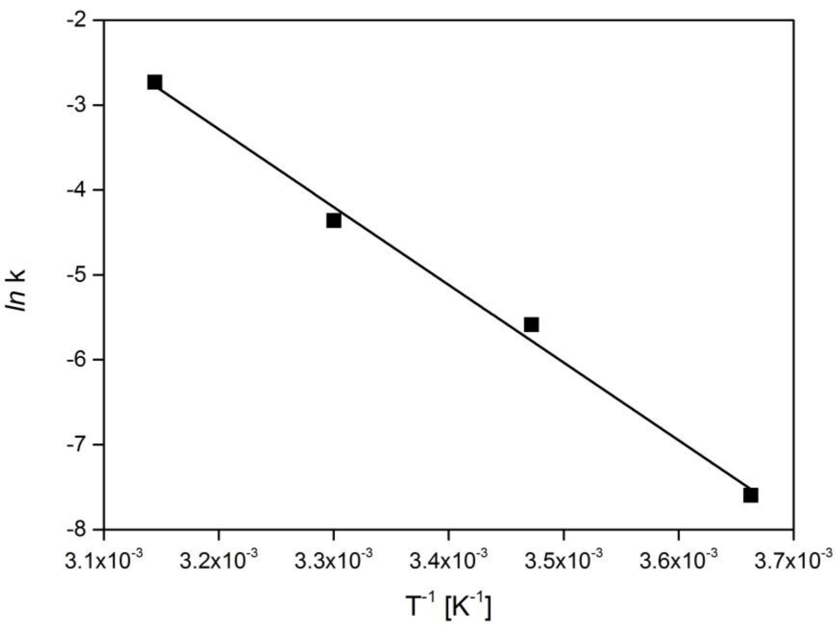

Fig. S11 Arrhenius plot for the **2**–H_2O_2 system. {c_2 = 1.25 × 10^{-4} M; **2**:H_2O_2 = 1:2000; in MeCN/dmf = 10:1; *k (rate constant)* at 0, 15, 30, 45 °C}

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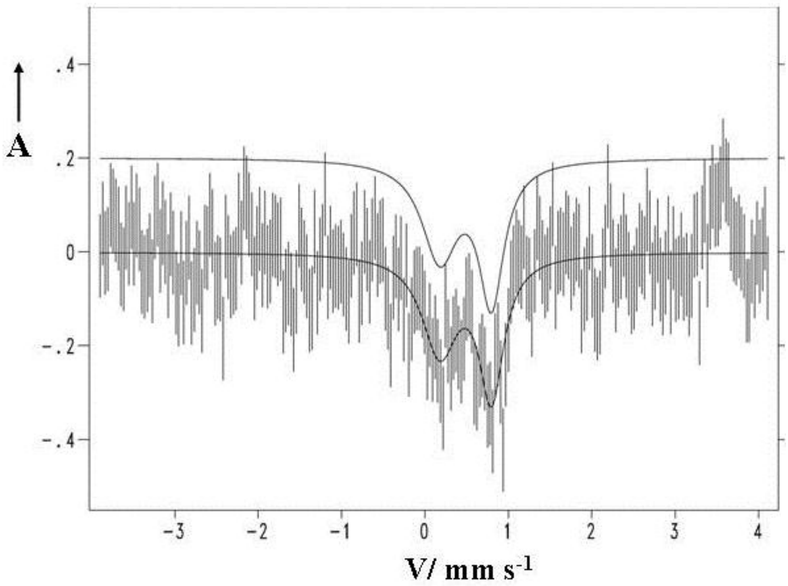

Fig. S12 Mössbauer spectrum of **2**-$^{57}Fe/H_2O_2$/Hpca system in MeCN measured immediately after its preparation at 80 K (δ = 0.49 mm s^{-1}, ΔE_Q = 0.62 mm s^{-1}, Γ_{left} = 0.52 mm s^{-1}, Γ_{right} = 0.36 mm s^{-1}).

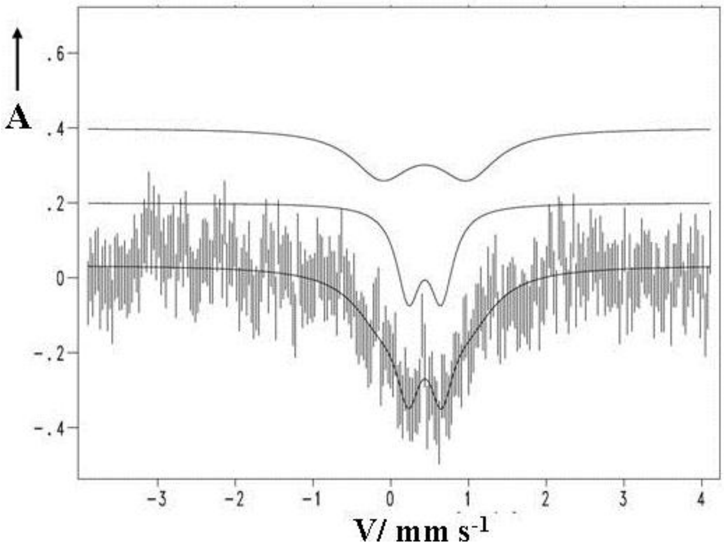

Fig. S13 Mössbauer spectrum of **2**-$^{57}Fe/H_2O_2$/Hpca system in MeCN at 80 K measured 30 min after its preparation (first lower doublet: δ = 0.44 mm s^{-1}, ΔE_Q = 0.42 mm s^{-1}, Γ_{left} = Γ_{right} = 0.37 mm s^{-1}; second upper doublet: δ = 0.43 mm s^{-1}, ΔE_Q = 1.10 mm s^{-1}, Γ_{left} = Γ_{right} = 0.90 mm s^{-1}; relative area 0.85:1.03).