Electronic Supplementary Information

for

Syntheses and crystal structures of benzene-sulfonate and -carboxylate copper polymers and their application to oxidation of cyclohexane in ionic liquid under mild conditions

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Table S1. Selected bond lengths (Å) and angles (°) for $[CuL(H_2tma)]_n$ (**1**) and $[\{Cu_2L_2(H_2pma)\}\cdot 8H_2O]_n$ (**2**). [a]

1			
Cu1–N1	2.0230(18)	N1–Cu1–O21	177.08(7)
Cu1–N2	1.9928(18)	N2–Cu1–O11	167.31(7)
Cu1–O11	1.9571(15)	O13^{i}–Cu1–N1	89.77(6)
Cu1–O21	1.9560(14)	O13^{i}–Cu1–N2	98.15(7)
Cu1–O13^{i}	2.3432(16)	O13^{i}–Cu1–O11	93.05(6)
		O13^{i}–Cu1–O21	90.31(6)
		N1–Cu1–N2	81.91(7)
		N1–Cu1–O11	92.22(7)
		N2–Cu1–O21	95.20(7)
		O11–Cu1–O21	90.69(6)
2			
Cu1–N1	1.9743(16)	N1–Cu1–O1	166.53(7)
Cu1–N2	2.0126(15)	N2–Cu1–O4	177.18(6)
Cu1–O1	1.9518(14)	O4^{ii}–Cu1–N1	98.87(6)
Cu1–O4	1.9603(12)	O4^{ii}–Cu1–N2	105.37(6)
Cu1–O4^{ii}	2.2480(12)	O4^{ii}–Cu1–O1	94.50(6)
		O4^{ii}–Cu1–O4	77.44(5)
		N1–Cu1–N2	82.18(7)
		N1–Cu1–O4	97.25(6)
		N2–Cu1–O1	92.69(6)
		O1–Cu1–O4	87.26(6)

[a] Symmetry codes as in Figures 1 (for **1**) and 2 (for **2**).

Table S2. Hydrogen bond interactions [distances in Å and angles in °] in $[CuL(H_2tma)]_n$ (**1**) and $[\{Cu_2L_2(H_2pma)\}\cdot 8H_2O]_n$ (**2**).

Compound	D–H···A	D···A	H···A	D–H···A	Symmetry codes
1	O23–H23O···O26’	2.676(2)	1.745(18)	176(3)	x, 3/2–y, -1/2+z
	O25–H25O···O22’	2.615(2)	1.705(18)	164(3)	–x, 1/2+y, 1/2–z
2	O6–H60···O10’	2.542(3)	1.79(3)	173(3)	–x, 1–y, –z
	O8–H8A···O5’	2.836(2)	2.03(4)	162(4)	1–x, 1–y, 1–z
	O8–H8B···O5’	2.805(3)	2.04(5)	150(4)	–1+x, y, z
	O9–H9A···O11	2.780(4)	1.90(5)	170(4)	
	O9–H9B···O7’	3.112(3)	2.38(6)	142(5)	1+x, y, –1+z
	O10–H10A···O2’	2.754(3)	1.90(5)	174(4)	–x, 1–y, –z
	O10–H10B···O9’	2.757(4)	1.98(4)	165(4)	–1+x, y, z
	O11–H11B···O3’	2.914(4)	2.15(6)	164(6)	1+x, y, z
	O11–H11B···O8’	2.985(5)	2.08(5)	169(4)	1–x, 1–y, 1–z

Table S3. Effect of catalysts recycling for the peroxidative oxidation of cyclohexane in the ionic liquid [bmim][PF_6].[a]

Entry	Products Yields (%) [b]			Total TON[c]	[CyOH] / [CyO] [d]	Original level of activity (%)
	CyOH	CyO	Total			
Catalyst 1						
1	29.3	6.7	36.0	83	4.4	100
2	28.7	6.3	35.0	81	4.6	97.2
3	28.9	6.4	35.3	81	4.5	98.1
Catalyst 2						
4	26.0	3.0	29.0	67	8.7	100
5	26.1	2.8	28.9	66	9.3	99.7
6	25.9	2.9	28.8	66	8.9	99.3

[a] Reaction conditions, unless stated otherwise: [catalyst] = 3×10^{-3} $molL^{-1}$, $[cyclohexane]_0$ = 0.46 $molL^{-1}$, $[total\ H_2O_2]_0$ = 2.2 $molL^{-1}$ (50% aqueous), [bmim][PF_6] up to 5 mL total volume, 30 ºC, reaction time = 120 min. [b] Based on GC analysis, after treatment with PPh_3. [c] Total (cyclohexanol+cyclohexanone) turnover number (moles of product per mol of catalyst). [d] Ratio between the concentrations of cyclohexanol (CyOH), and cyclohexanone (CyO).

Table S4. Crystallographic data for $[CuL(H_2tma)]_n$ (**1**) and $[\{Cu_2L_2(H_2pma)\}\cdot 8H_2O]_n$ (**2**).

	1	**2**
Formula	$C_{21}H_{14}CuN_2O_9S$	$C_{17}H_{19}CuN_2O_{11}S$
Formula weight	533.94	522.94
Crystal colour	Green	Green
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P1$
a/Å	14.8737(5)	9.4867(3)
b/Å	8.9886(2)	10.6290(4)
c/Å	15.5407(5)	11.8068(5)
α/°	90.00	98.625(2)
β/°	98.3790(10)	92.974(2)
γ/°	90.00	116.1420(10)
V/Å^3	2055.52(12)	1047.28(7)
Z	4	2
2θ/°	5.25–52.80	4.81–57.18
μ (Mo Kα)/mm^{-1}	1.225	1.206
ρ_{calcd}/g cm^{-3}	1.725	1.658
F(000)	1084	536
Index ranges	$-18<h<18$	$-12<h<12$
	$-11<k<11$	$-14<k<14$
	$-19<l<19$	$-15<l<15$
Reflections collected	21481	34577
Independent reflections	4215	5345
R_{int}	0.0281	0.0325
R_1[a]/ wR_2[b] [I > 2σ(I)]	0.0337/0.0838	0.0361/0.0874
R_1[a]/ wR_2[b] [for all F_o^2]	0.0409/0.0884	0.0469/0.0929
GOF on F^2	1.094	1.094

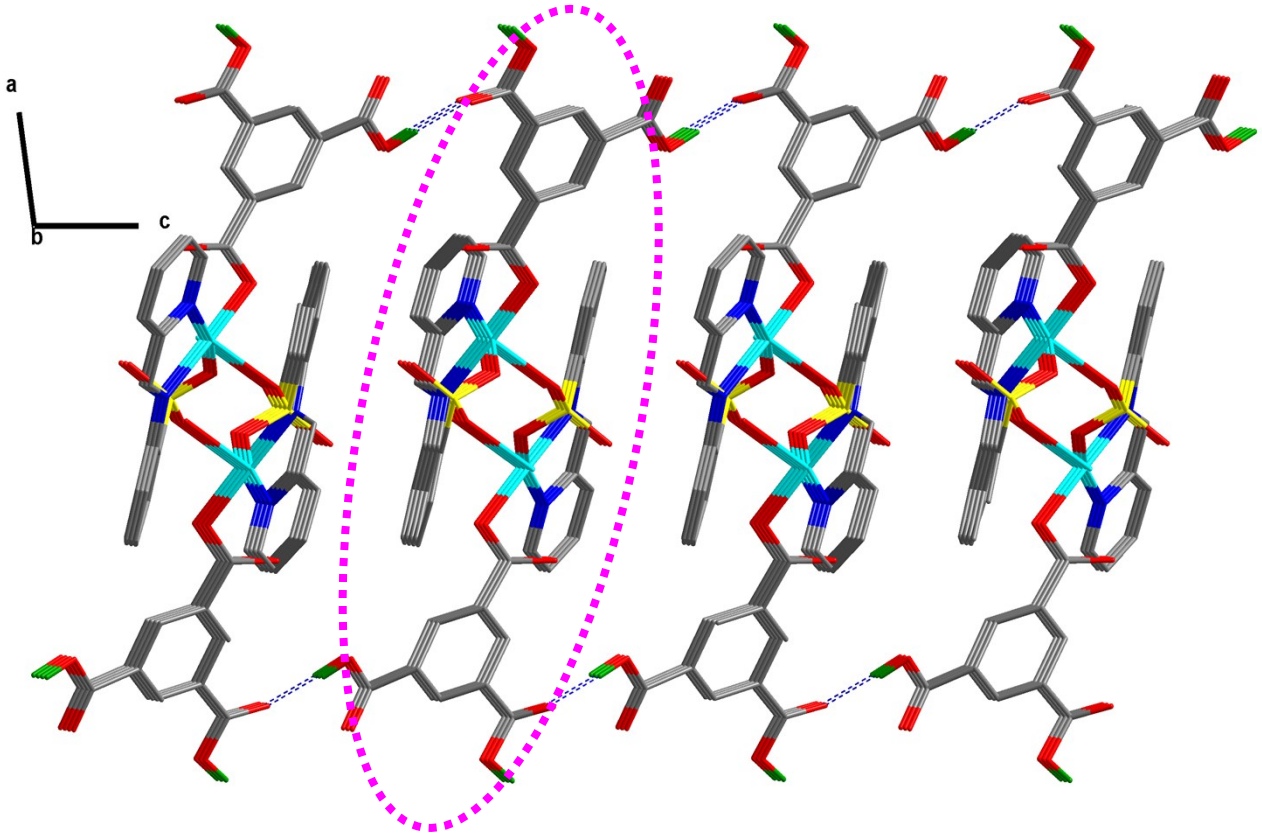


Fig. S1. Arbitrary view of the 3D motif in **1** resulting from the H-bond interactions depicted in Table S2.

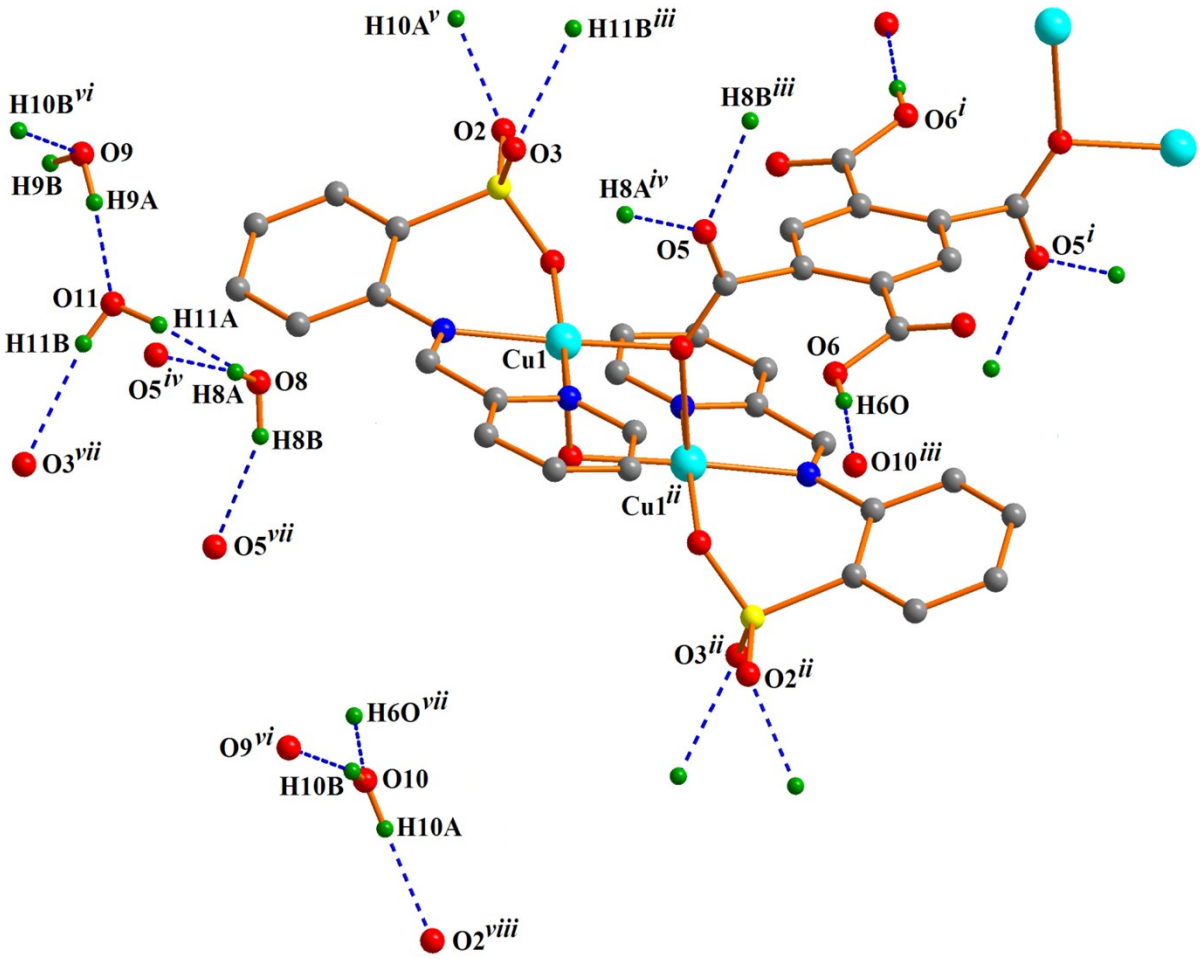


Fig. S2. H-bonding interactions in compound **2**. Symmetry codes to generate equivalent atoms: Symmetry: *i*) 3–x, 2–y, 1–z; *ii*) 2–x, 2–y, 1–z; *iii*) 1+x, y, z, *iv*) 1–x, 1–y, 1–z; *v*) 1+x, y, 1+z; *vi*) –x, 1–y, 1–z; *vii*) –1+x, y, z; *viii*) –1+x, y, –1+z.

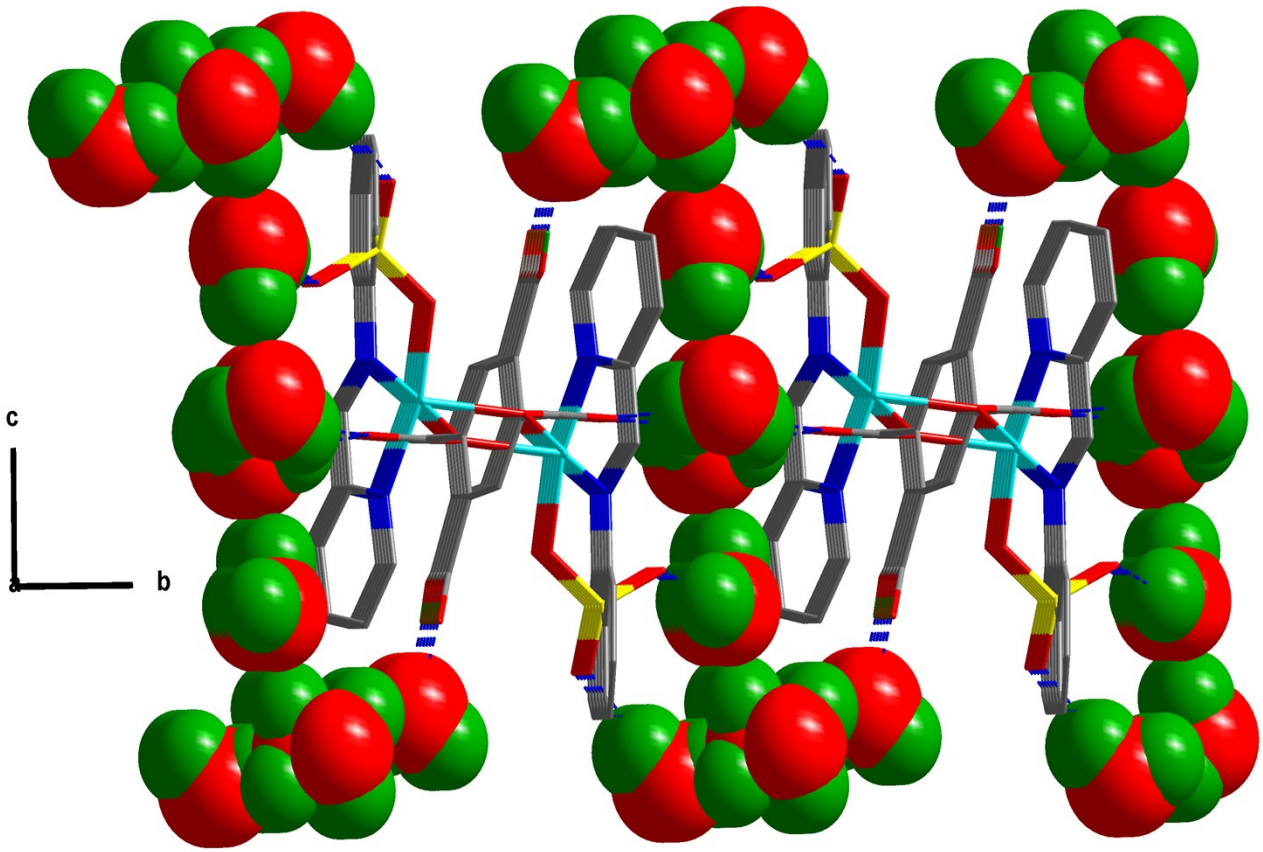


Fig. S3. Arbitrary view of the 3D motif in **2** resulting from the H-bond interactions depicted in Table S2.

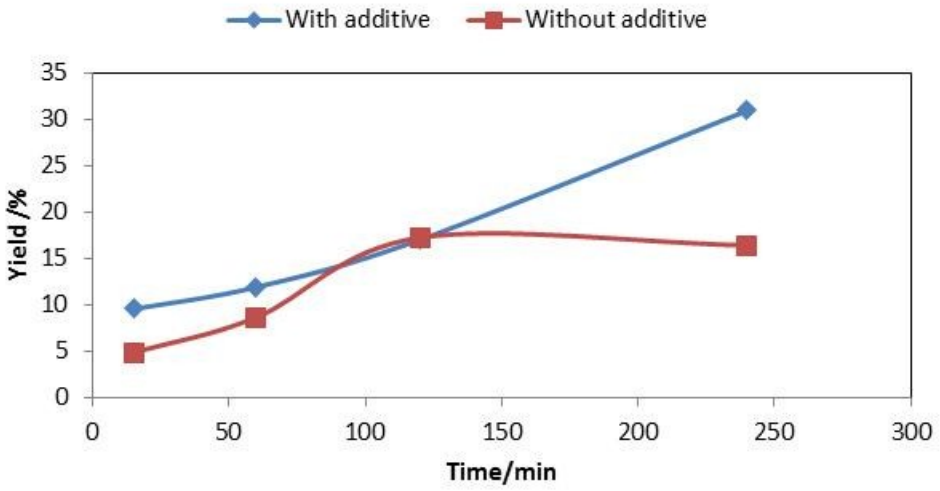


Fig. S4. Accumulation of oxygenates [total concentration (mmol L^{-1}) of cyclohexanol and cyclohexanone, after treatment with PPh_3] along the time in the oxidation of cyclohexane by H_2O_2, catalysed by complex **1** in the presence and in the absence of pyridine as additive. Reaction conditions: $[\mathbf{1}]_0 = 2 \times 10^{-3}$ mol L^{-1}, $[py]_0 = 0.005$ mol L^{-1}, [total $H_2O]_0 = 4.2$ mol L^{-1}, $[H_2O_2]_0 = 2.2$ mol L^{-1} (50 % aqueous), $[cyclohexane]_0 = 0.46$ mol L^{-1}, CH_3CN up to 5 mL total volume, 40 °C.

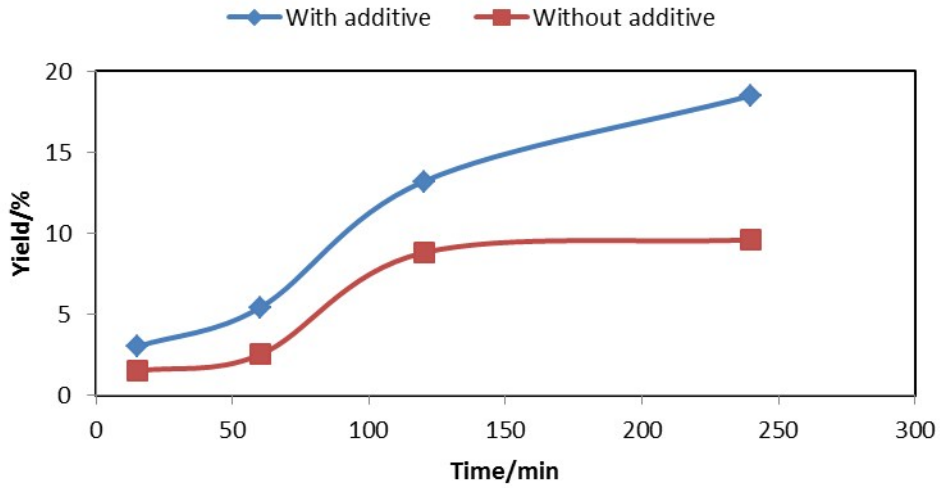
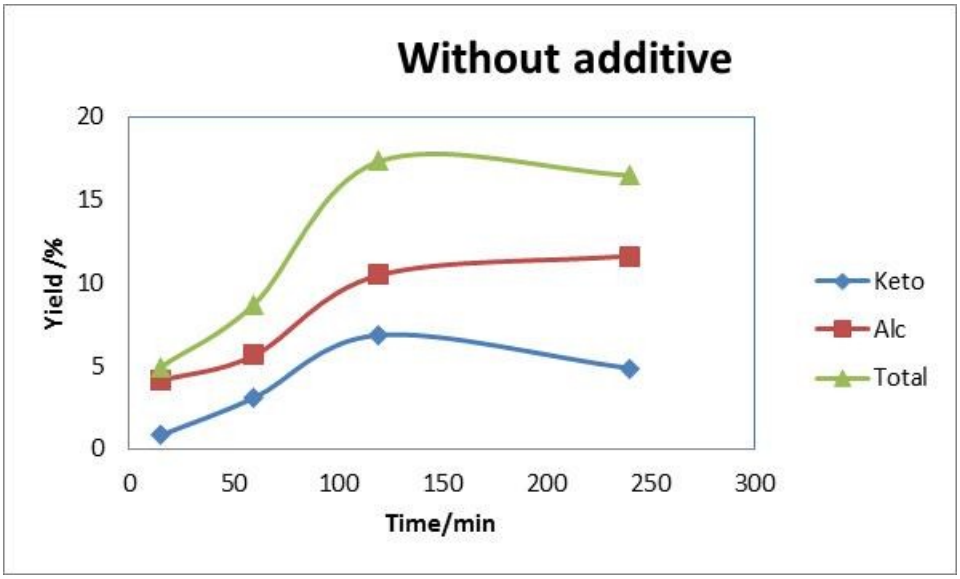
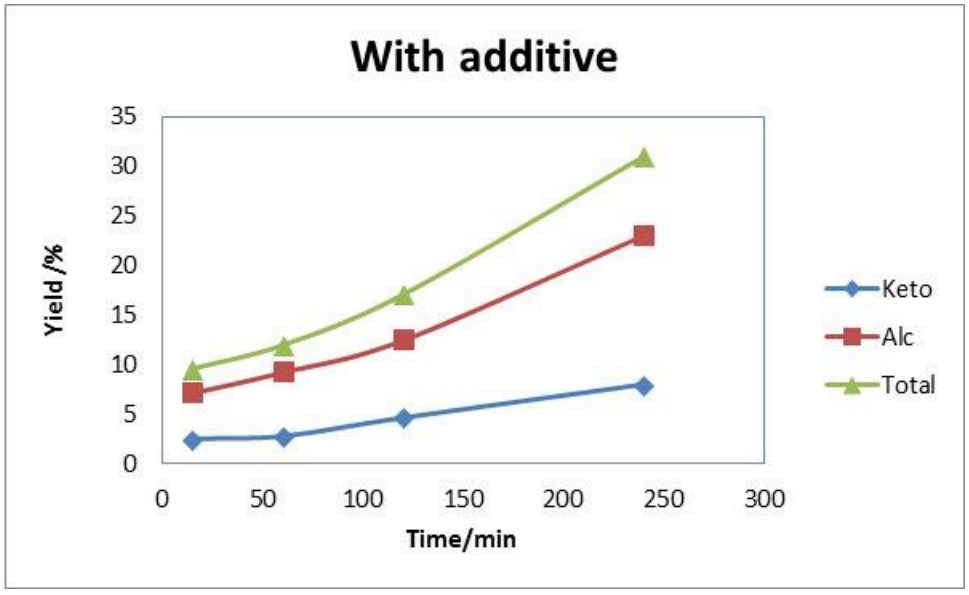


Fig. S5. Accumulation of oxygenates [total concentration (mmol L^{-1}) of cyclohexanol and cyclohexanone, after treatment with PPh_3] along the time in the oxidation of cyclohexane by H_2O_2, catalysed by complex **2** in the presence and in the absence of pyridine as additive. Reaction conditions: $[\mathbf{2}]_0 = 2 \times 10^{-4}$ mol L^{-1}, $[PY]_0 = 0.005$ mol L^{-1}, [total $H_2O]_0 = 4.2$ mol L^{-1}, $[H_2O_2]_0 = 2.2$ mol L^{-1} (50 % aqueous), $[cyclohexane]_0 = 0.46$ mol L^{-1}, CH_3CN up to 5 mL total volume, 40 °C.

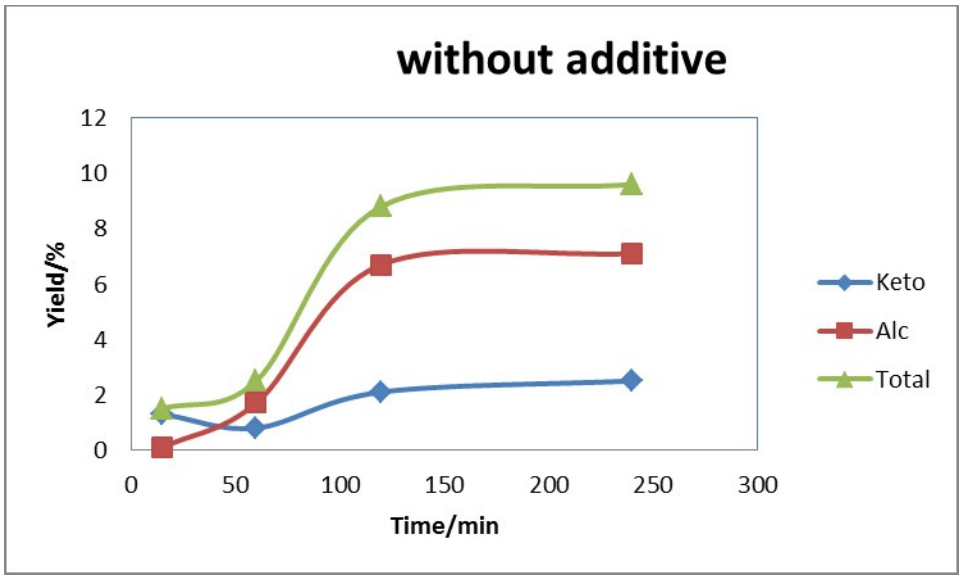


A

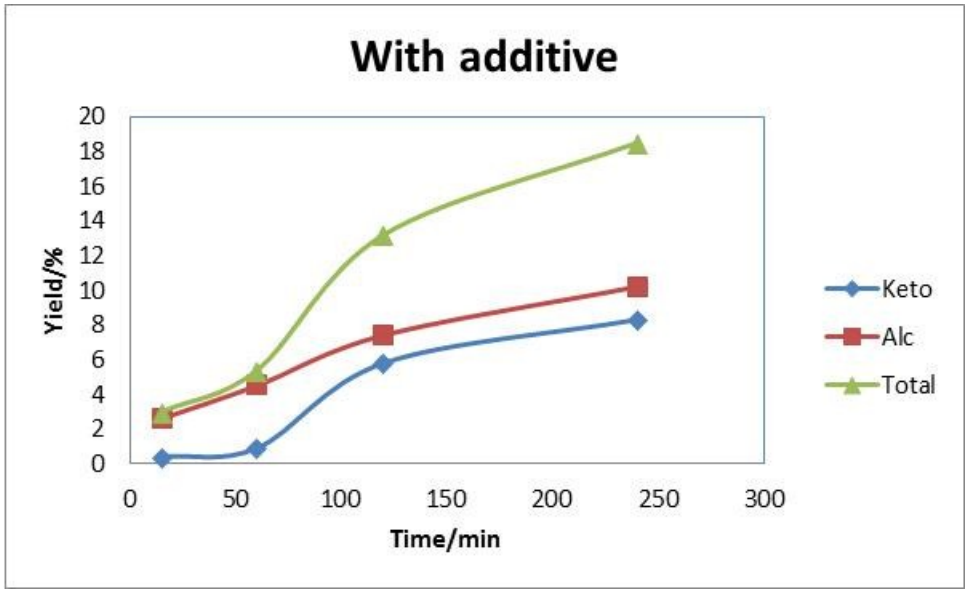


B

Fig. S6. Accumulation of oxygenates [total concentration (mmol L^{-1}) of cyclohexanol (CyOH, Alc) and cyclohexanone (CyO, Keto), after treatment with PPh_3] along the time in the oxidation of cyclohexane by H_2O_2, catalysed by complex **1** in the absence (plot **A**) or in the presence (plot **B**) of pyridine additive. Reaction conditions: $[\mathbf{1}]_0 = 2 \times 10^{-3}$ mol L^{-1}, $[Py]_0 = 0.005$ mol L^{-1}, [total $H_2O]_0 = 4.2$ mol L^{-1}, $[H_2O_2]_0 = 2.2$ mol L^{-1} (50 % aqueous), $[cyclohexane]_0 = 0.46$ mol L^{-1}, CH_3CN up to 5 mL total volume, 40 °C.

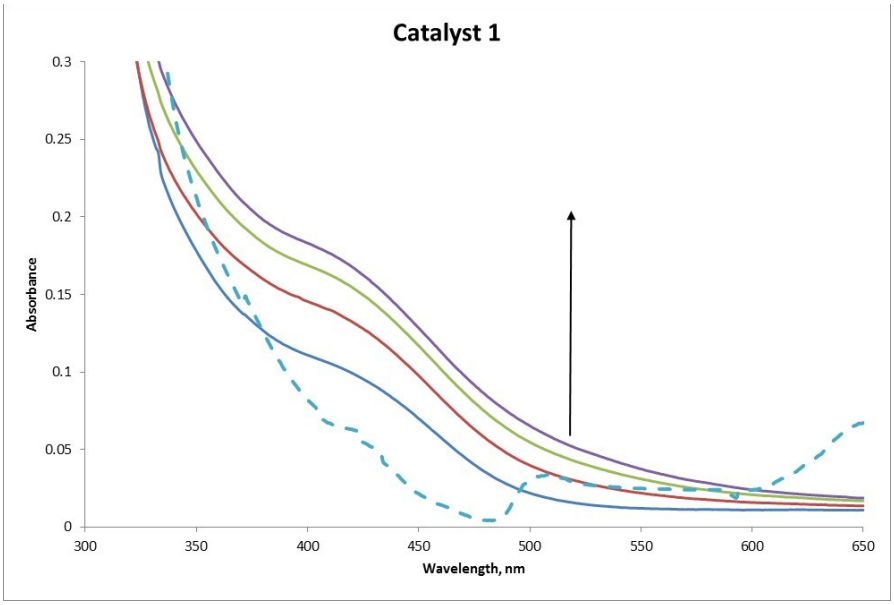


A

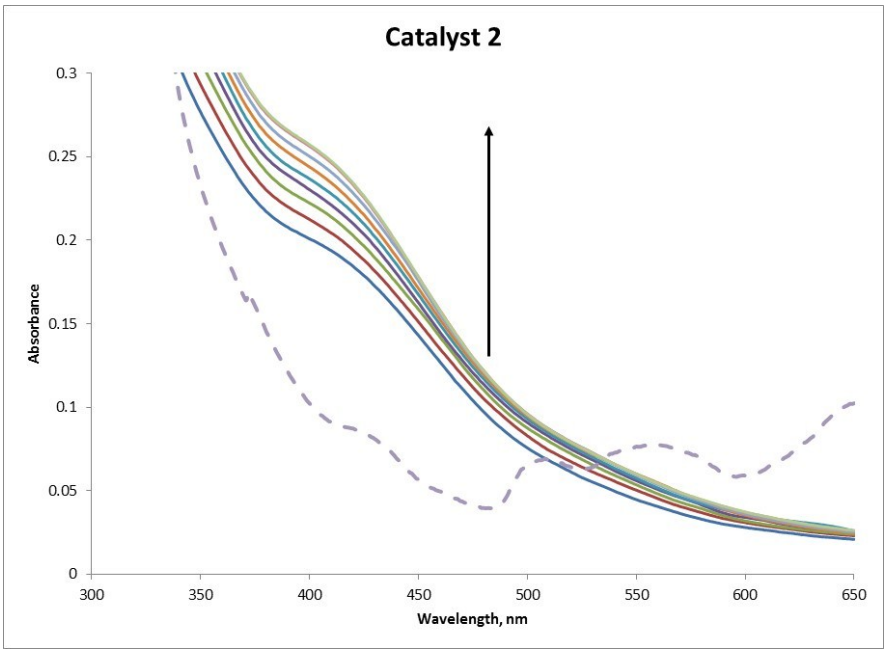


B

Fig. S7. Accumulation of oxygenates [total concentration (mmol L^{-1}) of cyclohexanol (CyOH, Alc) and cyclohexanone (CyO, Keto), after treatment with PPh_3] along the time in the oxidation of cyclohexane by H_2O_2, catalysed by complex **2** in the absence (plot **A**) or in the presence (plot **B**) of pyridine additive. Reaction conditions: $[\mathbf{2}]_0 = 2 \times 10^{-4}$ mol L^{-1}, $[Py]_0 = 0.005$ mol L^{-1}, [total $H_2O]_0 = 4.2$ mol L^{-1}, $[H_2O_2]_0 = 2.2$ mol L^{-1} (50 % aqueous), [cyclohexane]$_0 = 0.46$ mol L^{-1}, CH_3CN up to 5 mL total volume, 40 °C.



A



B

Fig. S8. UV-Vis spectra of catalyst **1** (**A**) and catalyst **2** (**B**), during 1h reaction, at room temperature. The dash line represents the catalyst and the full line is the addition of H_2O_2 to the catalyst, as a function of time.