

Electronic Supplementary Material

Copper(II) complexes with a new carboxylic-functionalized arylhydrazone of β -diketone as effective catalysts for acid-free oxidations

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X-ray structure determination

Table S1. Crystal data and structure refinement details for **2** and **3**.

	2	3
Formula unit	C ₃₀ H ₃₈ Cu ₂ N ₆ O ₁₄	C ₂₆ H ₂₈ Cu ₂ N ₄ O ₁₂
Formula weight	833.74	715.60
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> -1(No2)	<i>P</i> -1
<i>a</i> (Å)	8.6358(2)	9.1371(14)
<i>b</i> (Å)	10.3215(2)	9.2116(15)
<i>c</i> (Å)	10.8552(3)	10.2632(17)
α (°)	85.894(10)	63.521(8)
β (°)	71.985(2)	68.961(7)
γ (°)	66.5280(10)	72.657(7)
<i>Z</i>	1	1
Volume (Å ³)	842.52(4)	711.7(2)
<i>D</i> _c (g cm ⁻³)	1.643	1.670
μ (mm ⁻¹)	1.341	1.566
<i>F</i> (000)	430	366
Rfl collected/unique/obs	15771/3088/2867	8859/ 2876/ 1902
R _{int}	0.0291	0.0513
R ₁ ^a , wR ₂ ^b [<i>I</i> > 2σ(<i>I</i>)]	0.0250, 0.0689	0.0442, 0.1041
R ₁ , wR ₂ (all data)	0.0280, 0.0716	0.0896, 0.1243
GOF on <i>F</i> ²	0.973	0.976
Min. and Max. resd. dens. [e/ Å ³]	-0.347, 0.394	-0.621, 0.472

^a R1 = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^b wR2 = $[\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$

Cyclohexane Oxidation

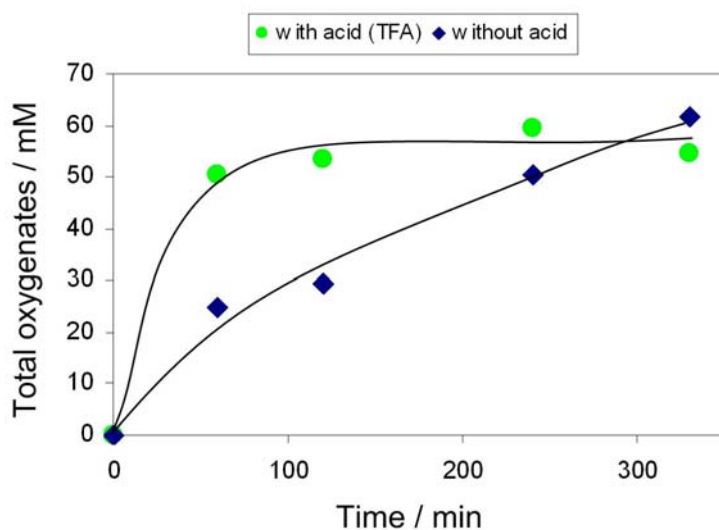


Figure S1. Accumulation of oxygenates [total concentration, mM ($\text{mmol} \cdot \text{L}^{-1}$), of cyclohexanol and cyclohexanone, after treatment with PPh_3] along the time in the oxidation of cyclohexane by H_2O_2 , catalyzed by complex **2** in the presence and in the absence of acid (TFA) additive. Reaction conditions: $[\mathbf{2}]_0 = 30 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, $[\text{TFA}]_0 = 0.01 \text{ mol} \cdot \text{L}^{-1}$, $[\text{Total H}_2\text{O}]_0 = 4.2 \text{ mol} \cdot \text{L}^{-1}$, $[\text{H}_2\text{O}_2]_0 = 2.2 \text{ mol} \cdot \text{L}^{-1}$ (50 % aqueous), $[\text{cyclohexane}]_0 = 0.46 \text{ mol} \cdot \text{L}^{-1}$, MeCN up to 5 mL total volume, 50 °C.

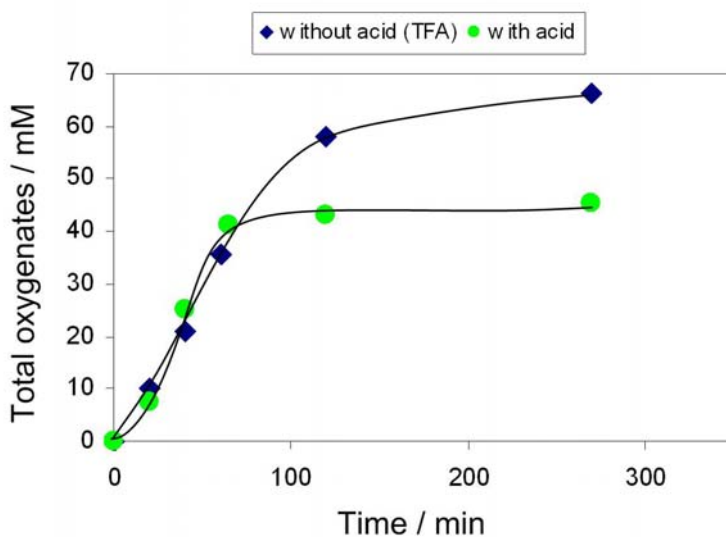


Figure S2. Accumulation of oxygenates [total concentration, mM ($\text{mmol} \cdot \text{L}^{-1}$), of cyclohexanol and cyclohexanone, after treatment with PPh_3] along the time in the oxidation of cyclohexane by H_2O_2 , catalyzed by complex **3** in the presence and in the absence of acid (TFA) additive. Reaction conditions: $[\mathbf{3}]_0 = 5 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, $[\text{Total H}_2\text{O}]_0 = 4.2 \text{ mol} \cdot \text{L}^{-1}$, $[\text{H}_2\text{O}_2]_0 = 2.2 \text{ mol} \cdot \text{L}^{-1}$ (50 % aqueous), $[\text{cyclohexane}]_0 = 0.46 \text{ mol} \cdot \text{L}^{-1}$, MeCN up to 5 mL total volume, 50 °C.

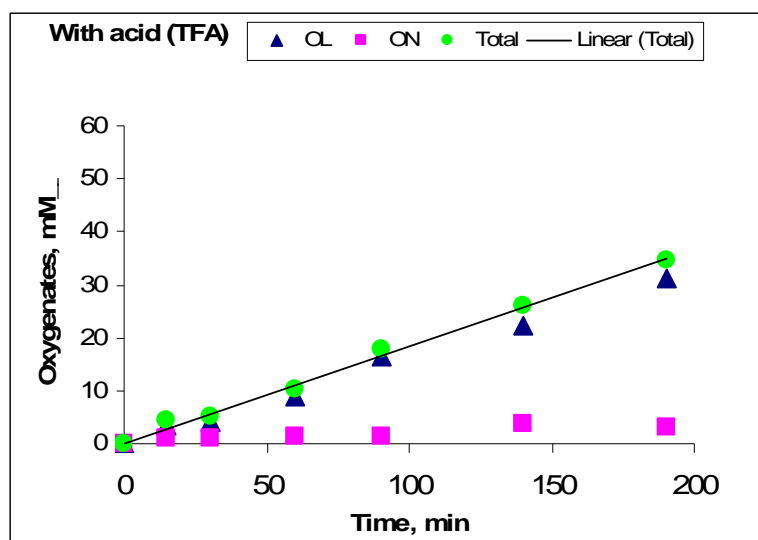


Figure S3. Accumulation of oxygenates [concentrations, mM ($\text{mmol} \cdot \text{L}^{-1}$), of cyclohexanol (OL) and cyclohexanone (ON), after treatment with PPh_3] along the time in the oxidation of cyclohexane by H_2O_2 , catalyzed by complex **2** in the presence of acid (TFA) additive. Reaction conditions: $[\mathbf{2}]_0 = 30 \times 10^{-5} \text{ M}$, $[\text{TFA}]_0 = 0.0035 \text{ mol} \cdot \text{L}^{-1}$, $[\text{Total H}_2\text{O}]_0 = 6.4 \text{ mol} \cdot \text{L}^{-1}$, $[\text{H}_2\text{O}_2]_0 = 2.2 \text{ mol} \cdot \text{L}^{-1}$ (50 % aqueous), $[\text{cyclohexane}]_0 = 0.46 \text{ mol} \cdot \text{L}^{-1}$, MeCN up to 5 mL total volume, 50 °C.

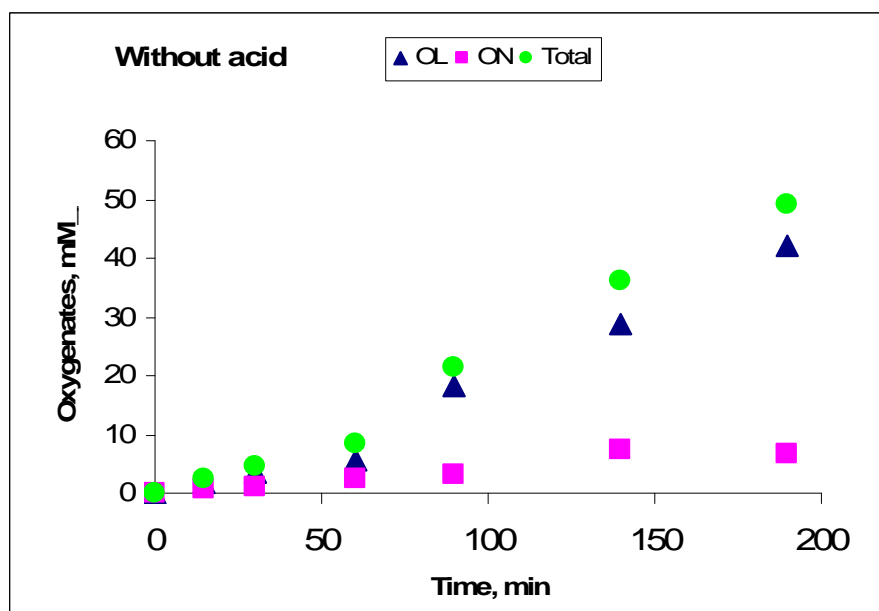


Figure S4. Accumulation of oxygenates [concentrations, mM ($\text{mmol} \cdot \text{L}^{-1}$), of cyclohexanol (OL) and cyclohexanone (ON), after treatment with PPh_3] along the time in the oxidation of cyclohexane by H_2O_2 , catalyzed by complex **2** in the absence of acid additive. Reaction conditions: $[\mathbf{2}]_0 = 30 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$, $[\text{Total H}_2\text{O}]_0 = 6.4 \text{ mol} \cdot \text{L}^{-1}$, $[\text{H}_2\text{O}_2]_0 = 2.2 \text{ mol} \cdot \text{L}^{-1}$ (50 % aqueous), $[\text{cyclohexane}]_0 = 0.46 \text{ mol} \cdot \text{L}^{-1}$, MeCN up to 5 mL total volume, 50 °C.

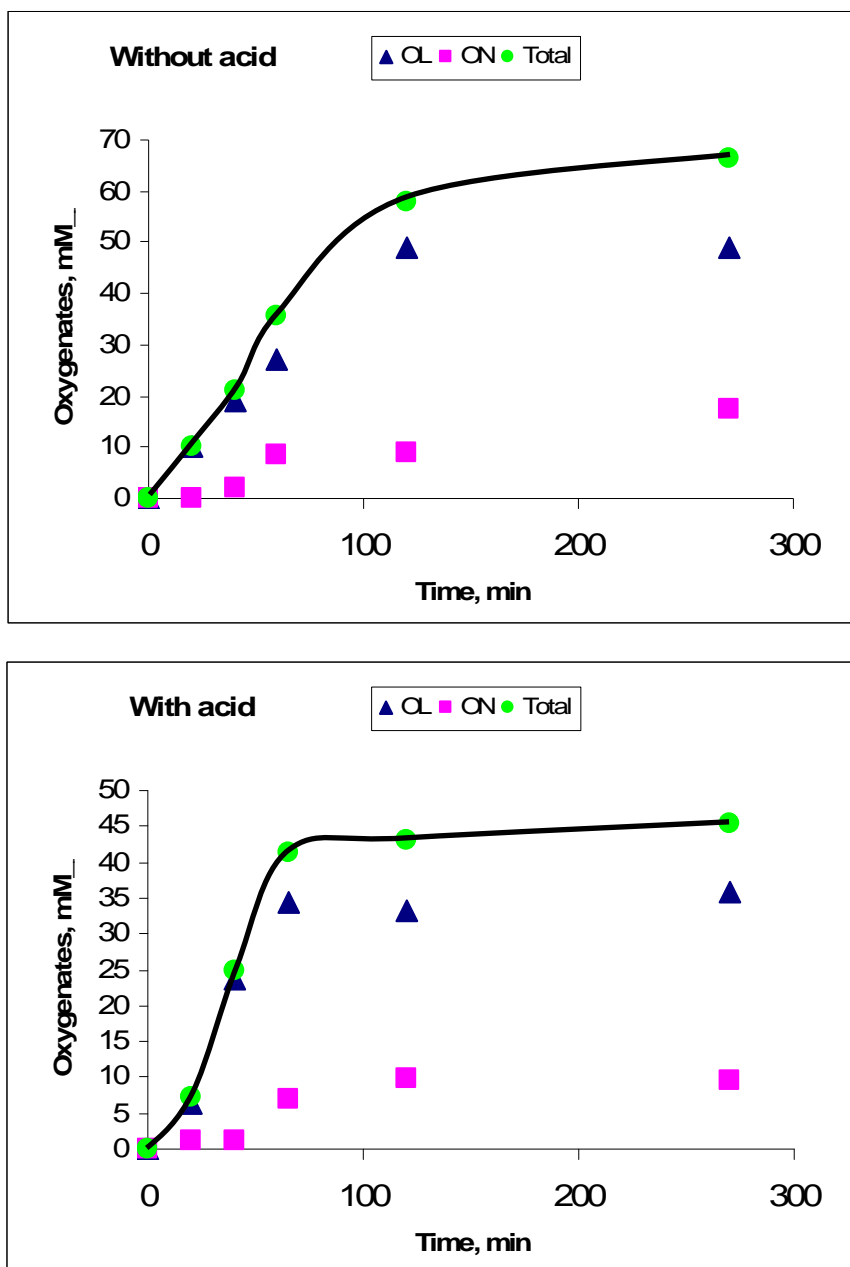


Figure S5. Accumulation of oxygenates [concentrations, mM ($\text{mmol} \cdot \text{L}^{-1}$), of cyclohexanol (OL) and cyclohexanone (ON), after treatment with PPh_3] along the time in the oxidation of cyclohexane by H_2O_2 , catalyzed by complex **3** in the absence (top) or in the presence (down) of TFA additive. Reaction conditions: $[\mathbf{3}]_0 = 5 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, $[\text{Total H}_2\text{O}]_0 = 4.2 \text{ mol} \cdot \text{L}^{-1}$, $[\text{H}_2\text{O}_2]_0 = 2.2 \text{ mol} \cdot \text{L}^{-1}$ (50 % aqueous), $[\text{cyclohexane}]_0 = 0.46 \text{ mol} \cdot \text{L}^{-1}$, MeCN up to 5 mL total volume, 50 °C.