catalysts

Supplementary Materials: Tetracopper(II) Cores Driven by an Unexplored Trifunctional Aminoalcohol Sulfonic Acid for Mild Catalytic C–H Functionalization of Alkanes

Inês F. M. Costa [1], Marina V. Kirillova [1,*], Vânia André [1], Tiago A. Fernandes [1] and Alexander M. Kirillov [1,2,*]

[1] Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal; inesfmcosta@outlook.com (I.F.M.C.); vaniandre@tecnico.ulisboa.pt (V.A.); tiago.a.fernandes@tecnico.ulisboa.pt (T.A.F.)

[2] Research Institute of Chemistry, Peoples' Friendship University of Russia (RUDN University), 6 Miklukho-Maklaya st., 117198 Moscow, Russia

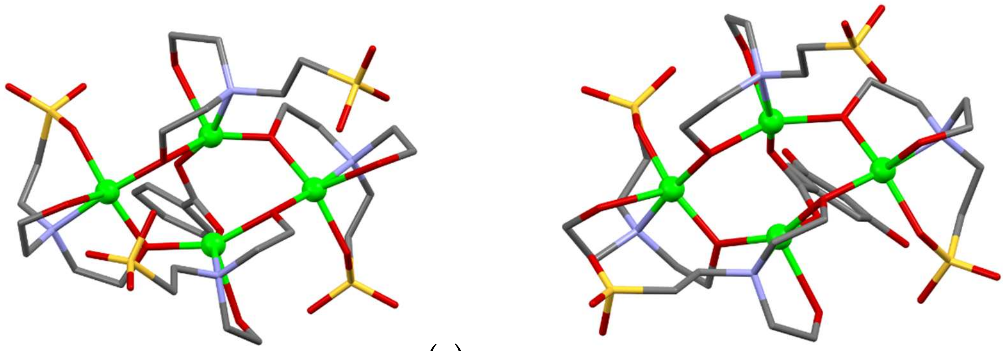
* Correspondence: kirillova@tecnico.ulisboa.pt (M.V.K.); kirillov@tecnico.ulisboa.pt (A.M.K.); Tel: +351-218417178 (M.V.K.)

S1. Crystal Data and Structure Refinement Details

Table S1. Crystal data and structure refinement details for **1**–**3**.

	1	**2**	**3**
formula	$C_{31}H_{58}Cu_4N_4O_{23}S_4$	$C_{31}H_{63}Cu_4N_4O_{25}S_4$	$C_{31}H_{58}Cu_4N_4O_{26}S_4$
fw	1237.21	1274.25	1285.25
Crystal form, color	Block, blue	Block, blue	Block, blue
Crystal size, mm	0.08 × 0.04 × 0.02	0.05 × 0.04 × 0.03	0.06 × 0.04 × 0.03
Crystal system	Monoclinic	Triclinic	Monoclinic
space group	*C*2/*c*	*P*-1	*C*2/*c*
a, Å	18.017(3)	13.9678(16)	18.866(2)
b, Å	21.288(3)	13.9777(18)	20.892(2)
c, Å	13.912(2)	14.1069(15)	14.0473(16)
α, deg	90.00	100.496(5)	90.00
β, deg	116.317(8)	107.510(4)	117.147(3)
γ, deg	90.00	108.292(4)	90.00
Z	4	2	4
V, Å^3	4782.9(14)	2374.7(5)	4926.8(9)
T, K	293(2)	293(2)	293(2)
D_c, g cm^{-3}	1.718	1.782	1.733
μ(Mo Kα), mm^{-1}	2.013	2.033	1.962
θ range (°)	1.583–26.934	1.590–26.398	2.221–26.521
refl. collected	18136	15835	38945
independent refl.	4965	7847	5087
R_{int}	0.1822	0.1003	0.1358
R_1 [a], wR_2 [b] [$I \geq 2\sigma(I)$]	0.1263, 0.3232	0.0605, 0.1391	0.1303, 0.3086
GOF on F^2	1.029	0.795	1.351

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

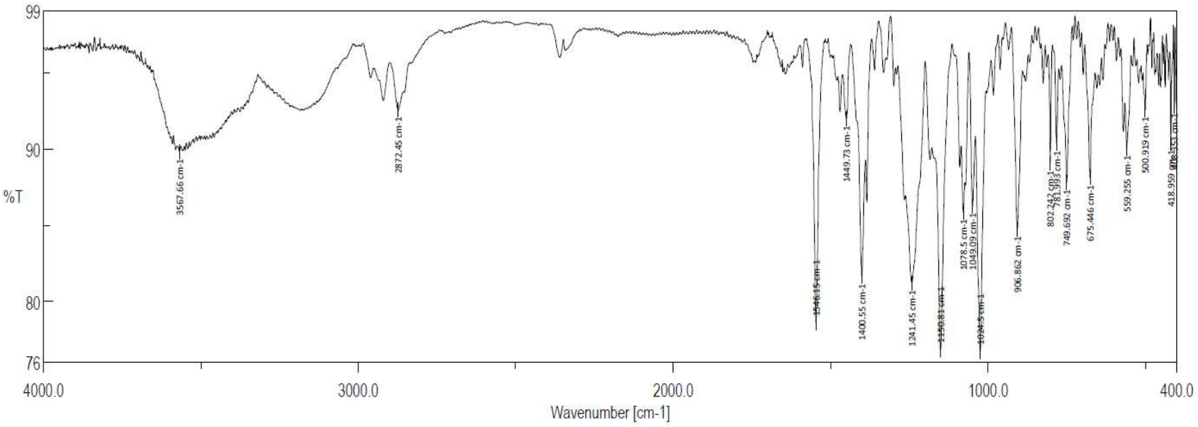


(a) (b)

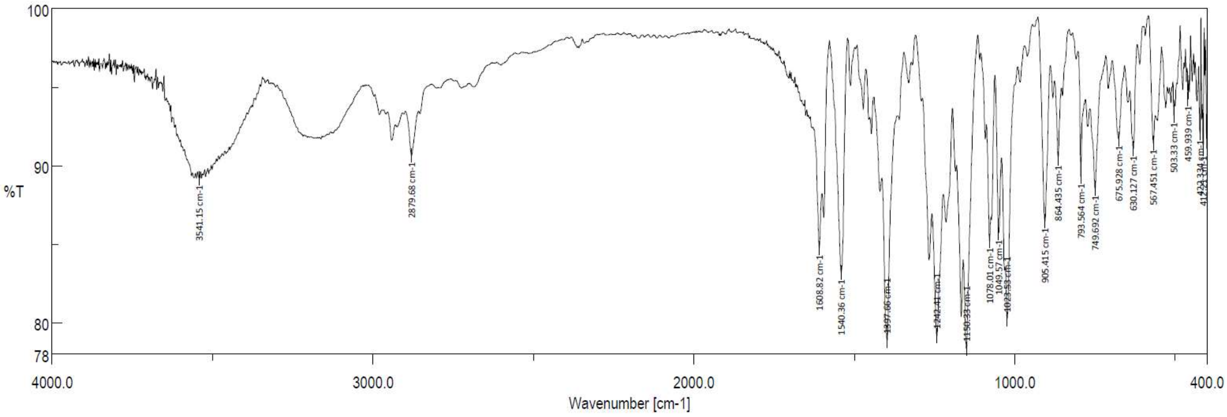
Figure S1. Crystal structures of compounds **1** (a) and **3** (b). H atoms are omitted for clarity; Cu (green balls), O (red), N (blue), S (yellow), C (gray).

S2. IR Data

(a)



(b)



(c)

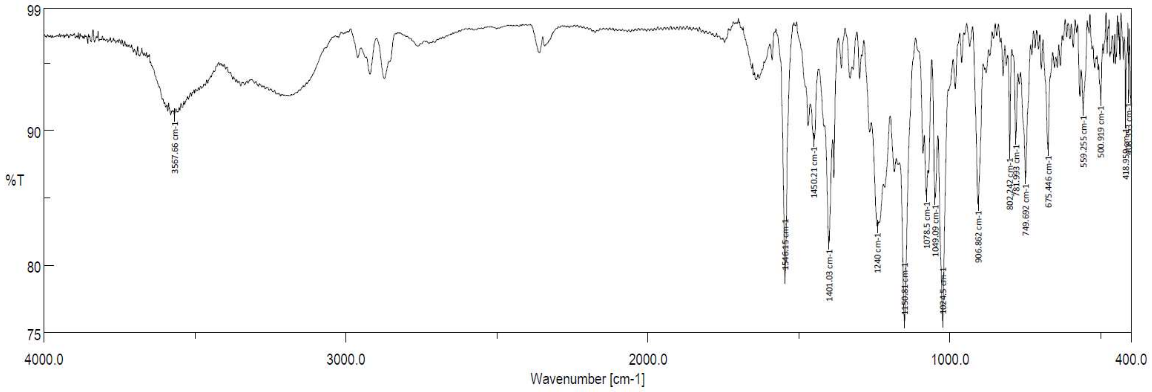


Figure S2. IR spectra of **1** (**a**), **2** (**b**), and **3** (**c**).

IR spectra of **1**–**3** feature common aspects due to the presence of similar types of Cu(II) cores (Cu_4(μ-Hbes)$_3$(μ-H_2bes)(μ-carboxylate)) and water molecules of crystallization. Characteristic vibrations include the ν(H_2O)/ν(OH) bands with maxima in the 3629–3324 cm^{-1} range due to OH/H_2O moieties. In the 3000–2700 cm^{-1} range, the weak ν_{as} and ν_s(CH) bands are observed due to asymmetric and symmetric CH vibrations. The IR spectra of **1**–**3** also reveal two groups of intense ν_{as}(COO) and ν_s(COO) vibrations in the range of 1600–1500 cm^{-1} and 1400–1300 cm^{-1}, respectively; these correspond to the carboxylate linkers. Furthermore, there are strong bands in the 1300–1000 cm^{-1} range, associated to the Hbes/H_2bes vibrations of ν(C–X) bands (X = C, N, S).

S3. ESI-MS studies

To get further insight into the nature of catalytically active species, we investigated by ESI-MS(±) the catalysts **1**–**3** (Figures S3–S5), including the MS/MS studies of the parent fragments. In aqueous medium, the ESI-MS(+) plot of **3** presents the [{Cu_4(μ-Hbes)$_3$(μ-H_2bes)}{μ-Hthba}$_2$ + H]$^+$ (*m*/*z* = 1376) fragment related to molecular ion. In positive mode, the most intense signals are due subsequent fragmentation and adducts without 3-hydroxybenzoate moiety: [{Cu_4(μ-Hbes)$_4$} + H]$^+$ (*m*/*z* = 1099), [{Cu_3(μ-Hbes)$_2$(μ-H_2bes)$_2$} + H]$^+$ (*m*/*z* = 1038), [{Cu_2(μ-H_2bes)$_4$} + H]$^+$ (*m*/*z* = 977), [{Cu_3(μ-Hbes)$_3$} + H]$^+$ (*m*/*z* = 825), [{Cu_2(μ-Hbes)(μ-H_2bes)$_2$} + H]$^+$ (*m*/*z* = 764), [{Cu(μ-H_2bes)$_2$(μ-H_3bes)} + H]$^+$ (*m*/*z* = 701), [{Cu_2(μ-Hbes)$_2$} + H]$^+$ (*m*/*z* = 551), [{Cu(μ-H_2bes)$_2$} + H]$^+$, (*m*/*z* = 488), [{Cu(μ-Hbes)} + H]$^+$ (*m*/*z* = 275).

The ESI-MS(−) plots of compounds **1**–**3** present great similarities; the differences are due to auxiliary ligand, [ba]$^-$ (*m*/*z* = 121) for **1**, [fba]$^-$ (*m*/*z* = 137) for **2**, and [thba]$^-$ (*m*/*z* = 137) for **3**. Main differences concern a less abundant [Cu_2(μ-Hbes)(μ-bes)]$^-$ (*m*/*z* = 547) fragment and a new peak [Cu_3(μ-H_2bes)$_2$(μ-Hbes)]$^-$ (*m*/*z* = 823) in the spectrum of **2**. In general, the MS(−) mode fragmentation is poor and less informative for all samples **1**–**3**. Abundant adducts with importance for the characterization are [Cu_2(μ-H_2bes)$_2$(μ-Hbes)]$^-$, (*m*/*z* = 760), [Cu(μ-H_2bes)$_3$]$^-$ (*m*/*z* = 699), [Cu_2(μ-Hbes)(μ-bes)]$^-$ (*m*/*z* = 547), and [Cu(μ-Hbes)]$^-$ (*m*/*z* = 274).

To demonstrate that the copper compounds are robust in the catalytic reaction medium, we also recorded the ESI-MS(±) plots of the solutions of **2** (representative example) after addition of an acid promoter and hydrogen peroxide (Figures S6 and S7). The obtained spectra show essentially the same profile with slight differences in the relative abundance of some adducts (Figures S6 and S7). Hence, these experiments may confirm the preservation of the tetracopper cores in the catalytic reaction medium. Partial fragmentation of tetracopper cores (primarily induced by ESI) or their rearrangement due to partial decoordination of ligands might also occur to some extent, which can be induced by ESI, acid promoter, and/or oxidant.

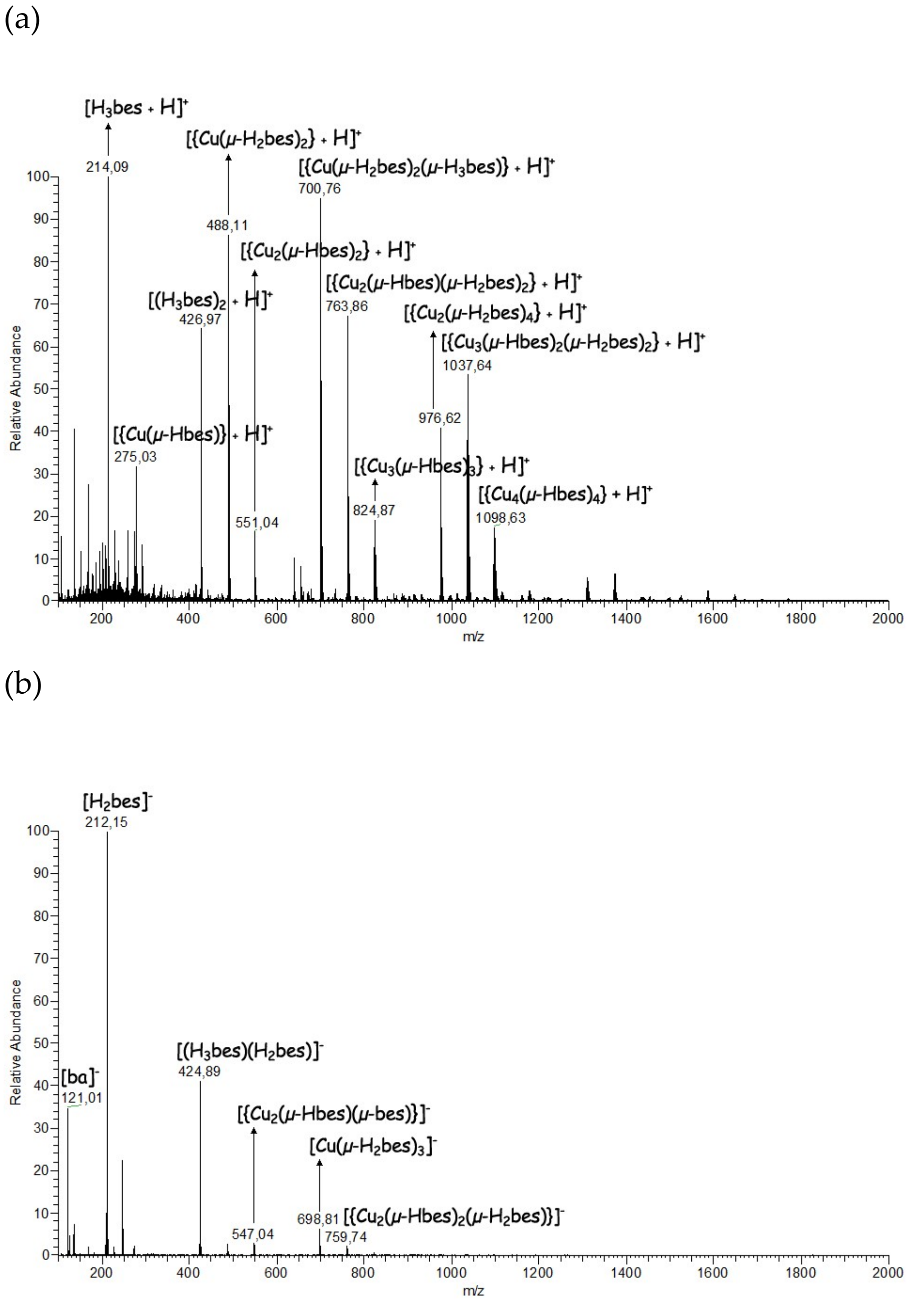


Figure S3. ESI-MS(+) and ESI-MS(−) spectra of **1**.

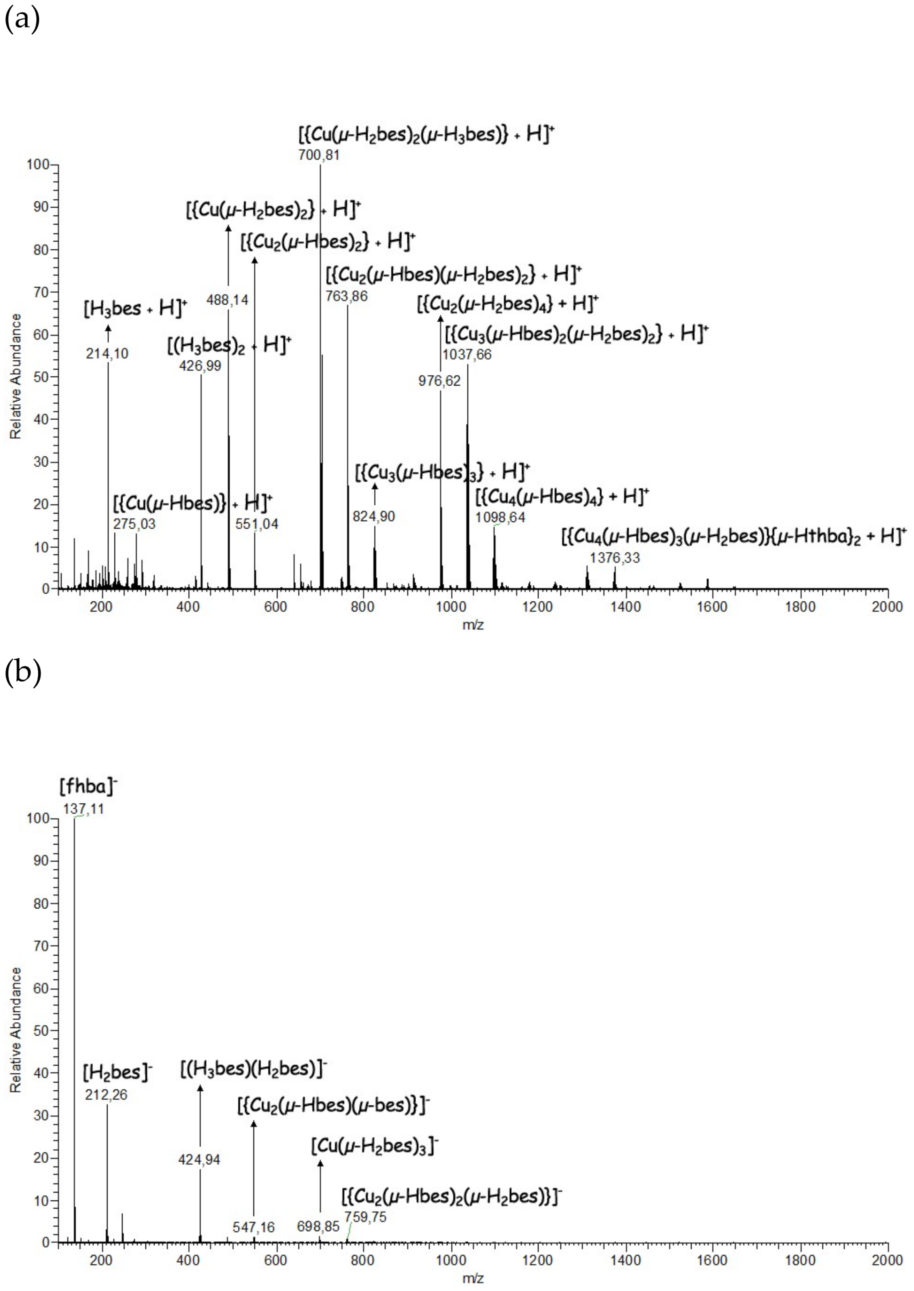


Figure S4. ESI-MS(+) and ESI-MS(−) spectra of **2**.

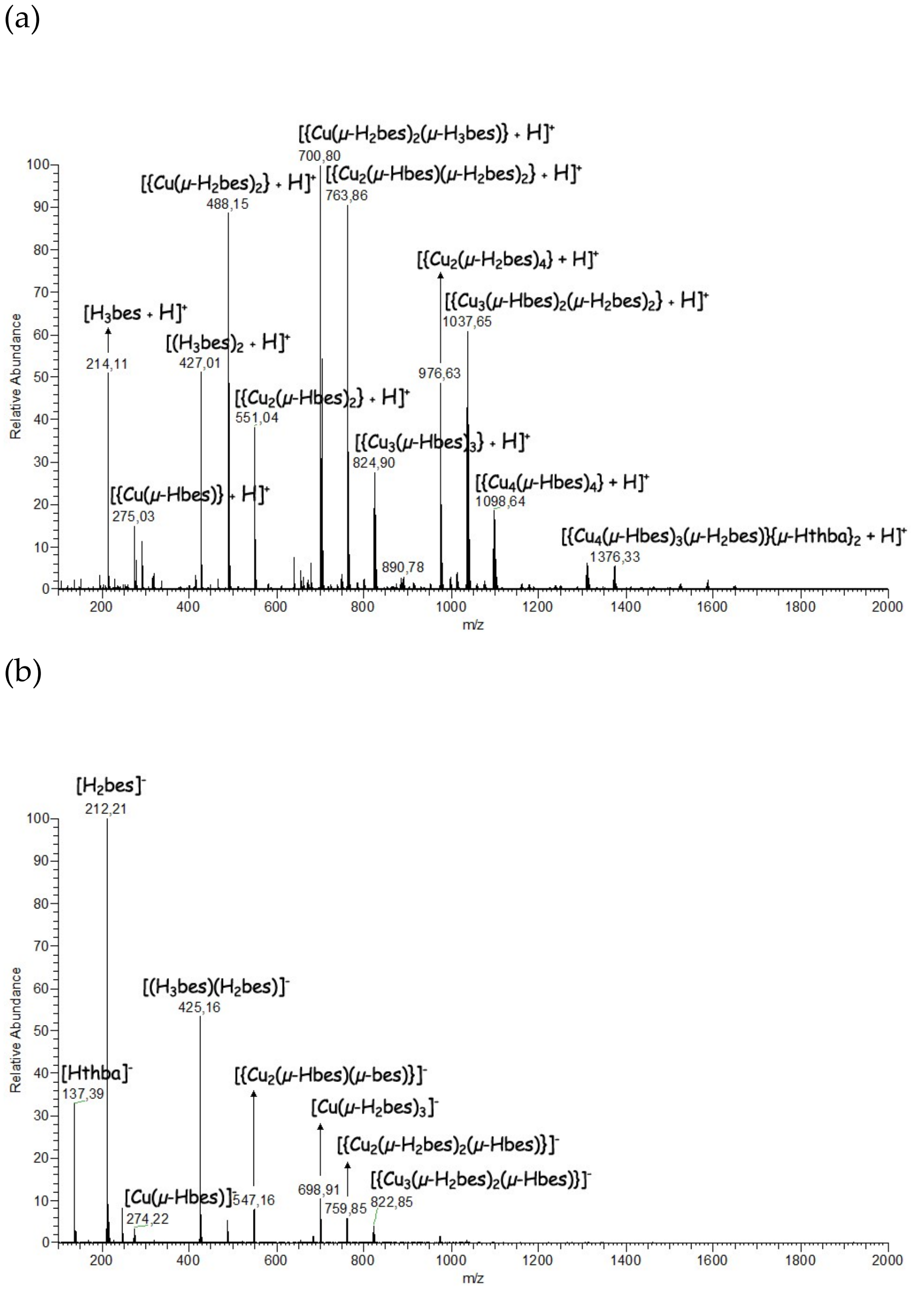


Figure S5. ESI-MS(+) and ESI-MS(−) spectra of **3**.

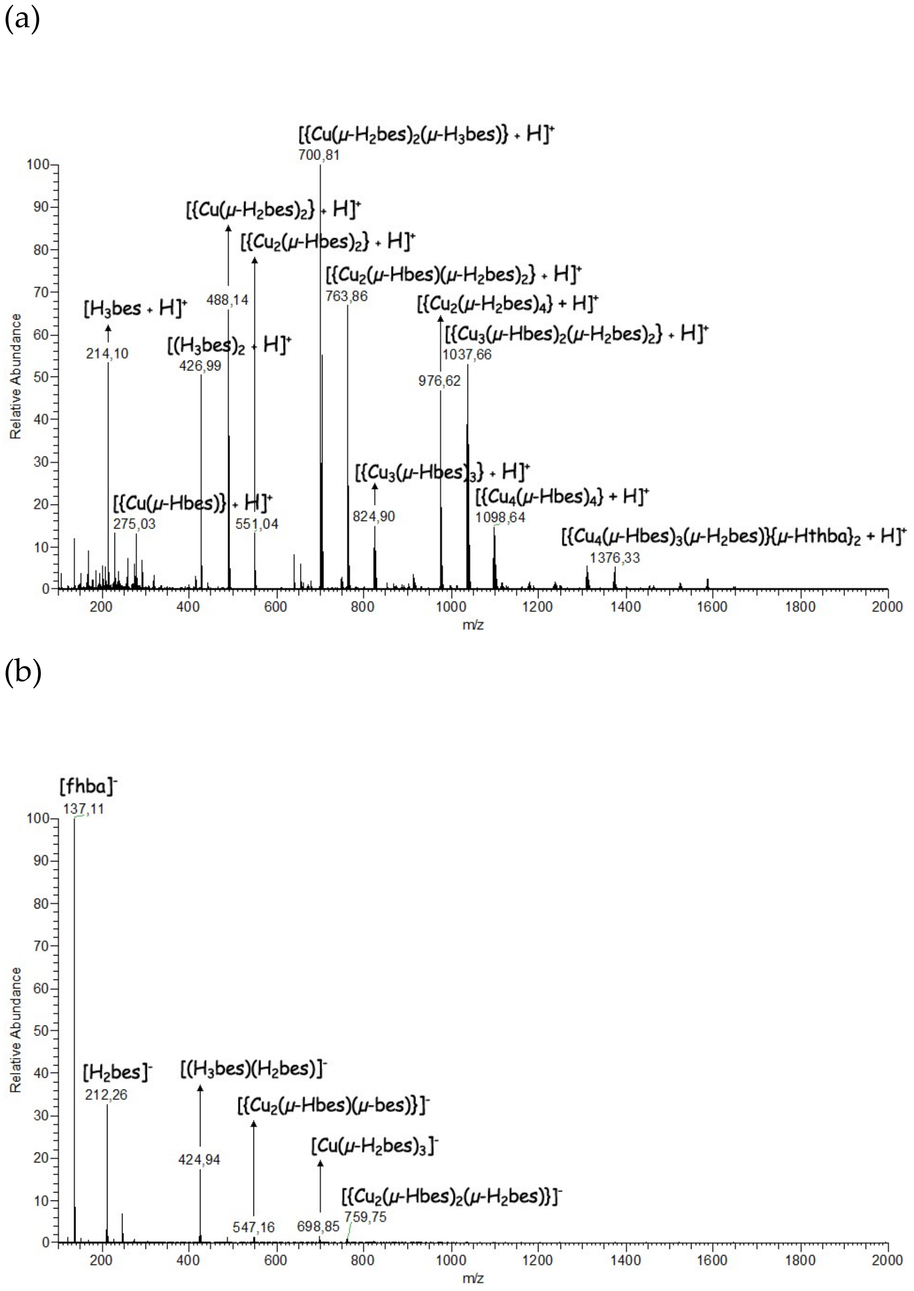


Figure S6. ESI-MS(+) and ESI-MS(−) spectra of **2/HNO$_3$**.

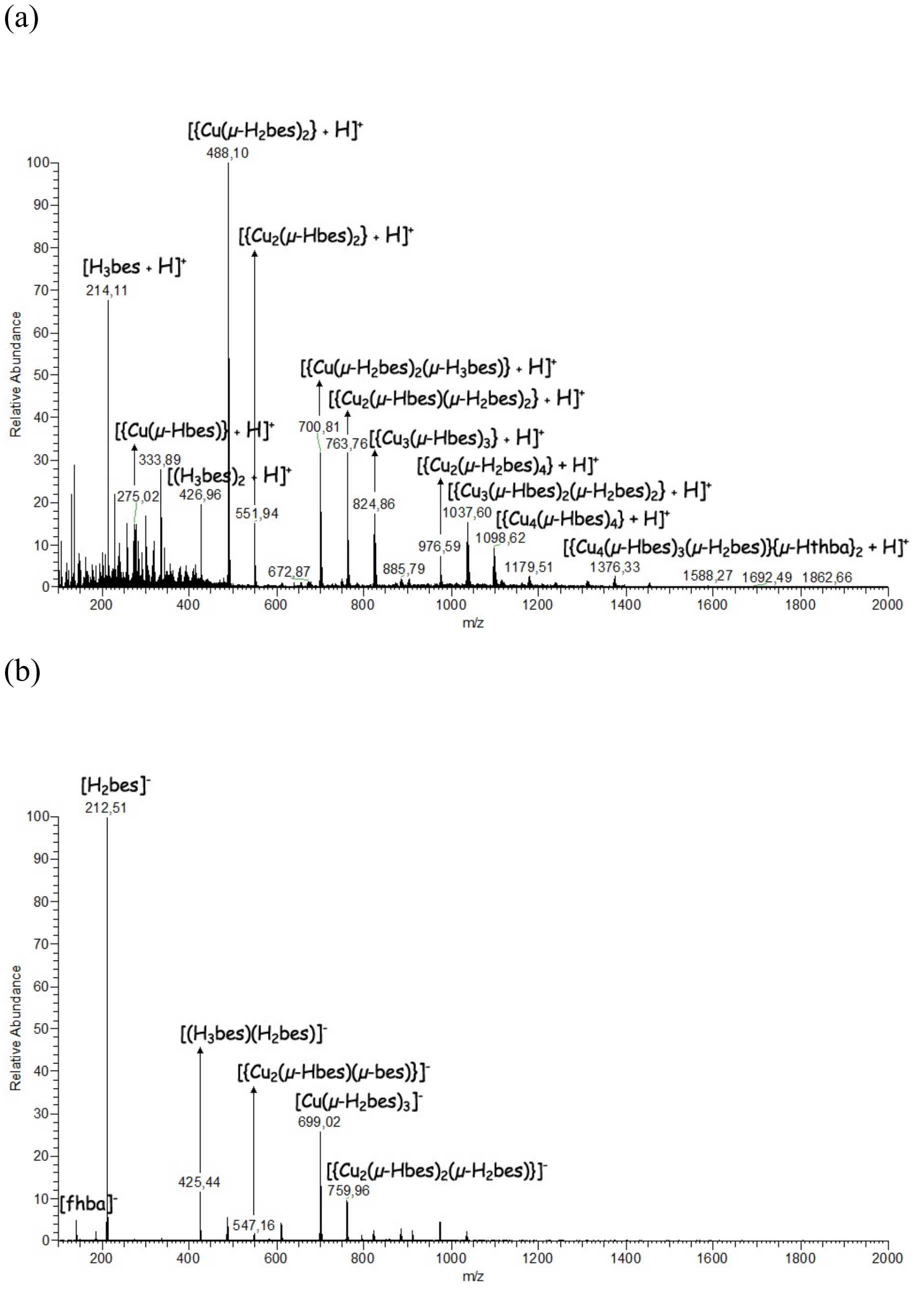


Figure S7. ESI-MS(+) and ESI-MS(−) spectra of **2**/HNO_3/H_2O_2.

S4. Additional Catalysis Data

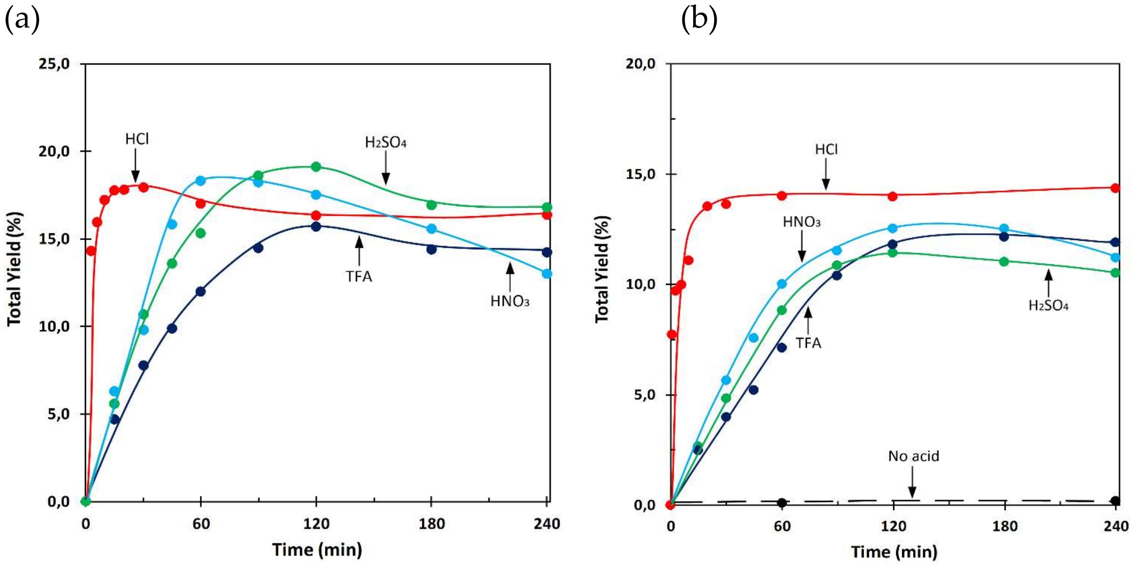


Figure S8. Effect of the type of acid promoter on the total yield of products (cyclohexanol and cyclohexanone) in the oxidation of C_6H_{12} with H_2O_2 catalyzed by **1** (a) or **3** (b). Conditions: Cu catalyst (2.5 µmol), C_6H_{12} (1 mmol), acid (50 µmol), H_2O_2 (5 mmol), CH_3CN (up to 2.5 mL of total volume), 50 °C.

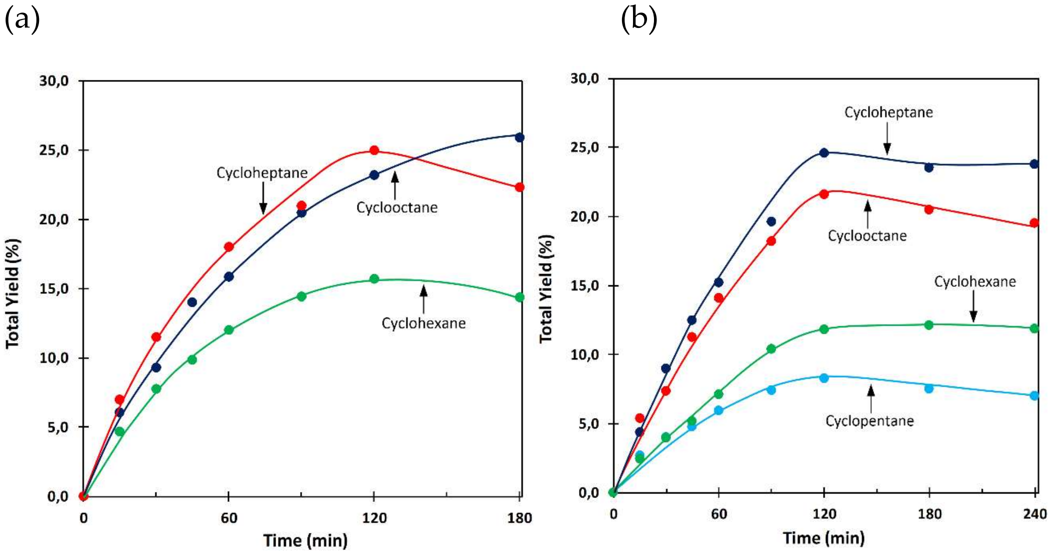


Figure S9. Oxidation of C_5–C_8 cycloalkanes to the corresponding alcohols and ketones (total product yield vs. time) with H_2O_2 catalyzed by **1** (a) or **3** (b). Conditions: Cu catalyst (2.5 µmol), cycloalkane (1 mmol), TFA (50 µmol), H_2O_2 (5 mmol), CH_3CN (up to 2.5 mL of the total volume), 50 °C.

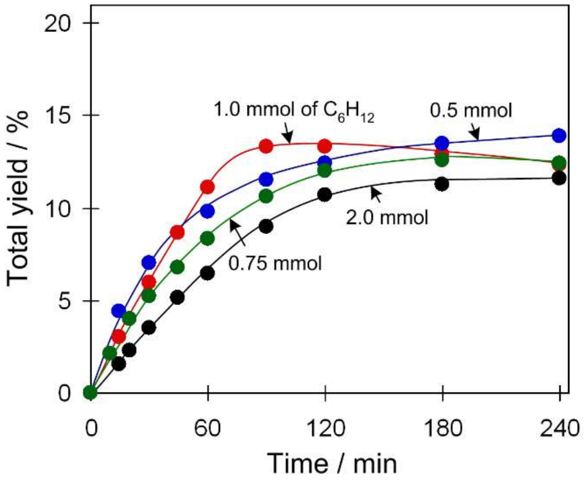


Figure S10. Effect of the cyclohexane amount on the total yield of the products (cyclohexanol and cyclohexanone) in the oxidation of C_6H_{12} with H_2O_2 catalyzed by **2**/TFA. Reaction conditions: catalyst **2** (2.5 µmol), C_6H_{12} (0.25–2 mmol), TFA (50 µmol), H_2O_2 (5 mmol), CH_3CN (up to 2.5 mL of the total volume), 50 °C.