Electronic Supplementary Information (ESI)

From α-Pinene Feedstock to Value-Added Products: Scalable and Recyclable Copper(II) Catalysts for Allylic Oxidation

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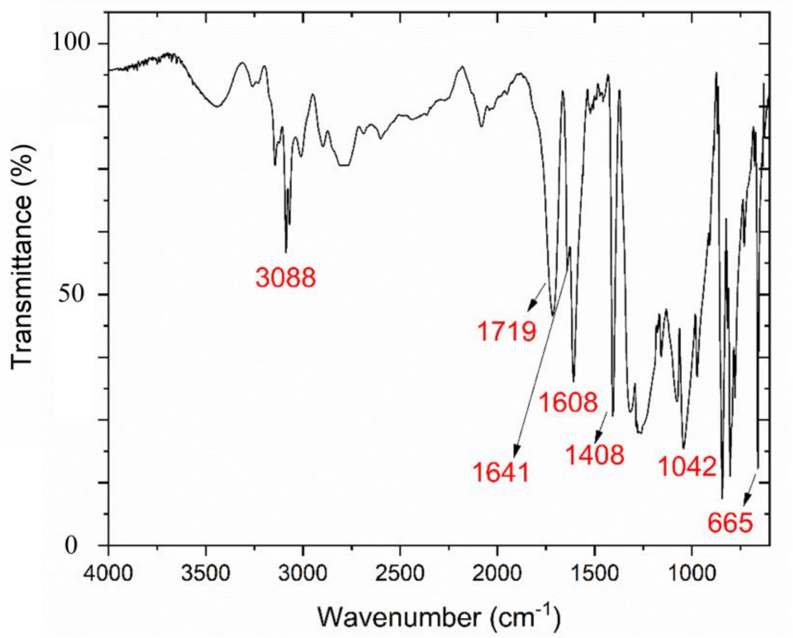


Figure S1. FTIR spectrum of 3,4-pyridinedicarboxylic acid.

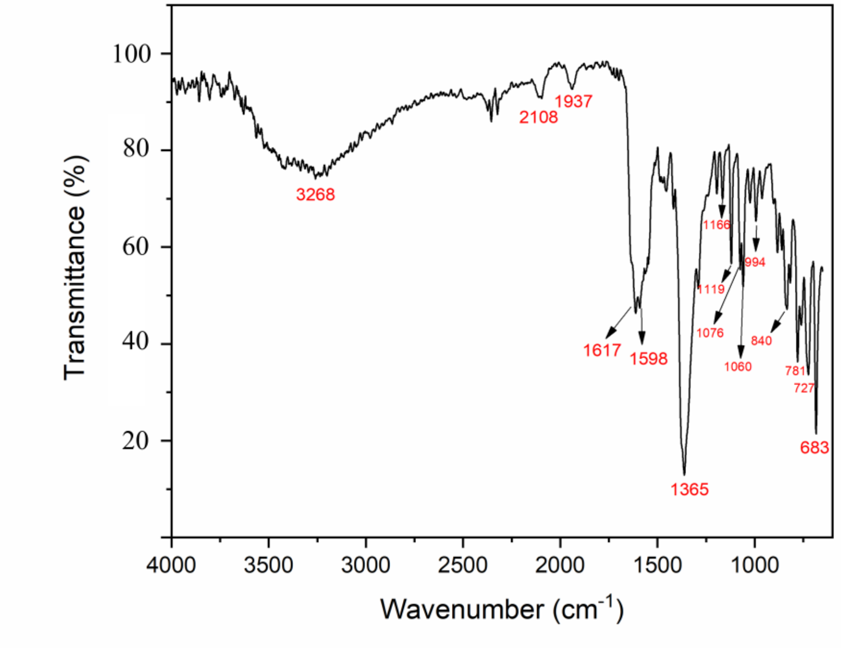
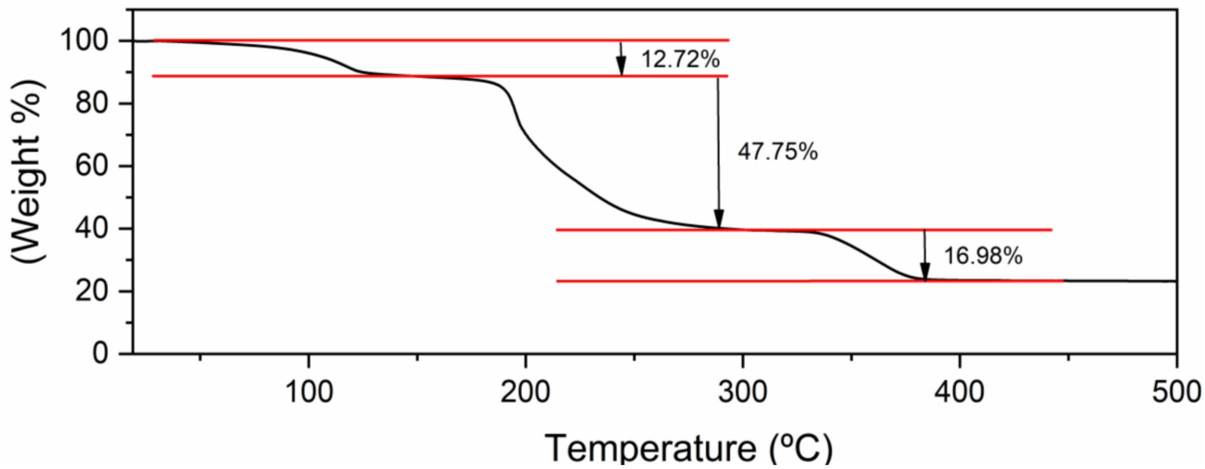


Figure S2. FTIR spectrum of **Cu-mdea**.



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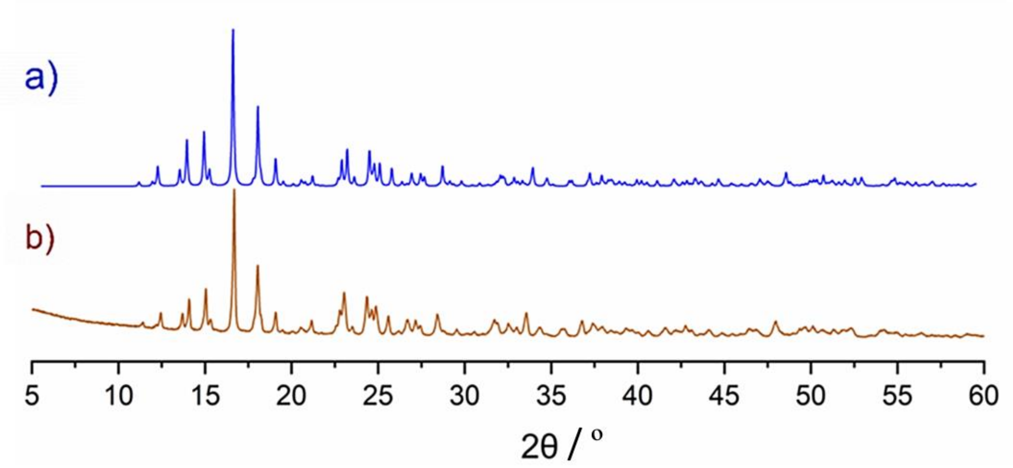


Figure S4. PXRD patterns of **Cu-mdea**: (a) simulated and (b) experimental.

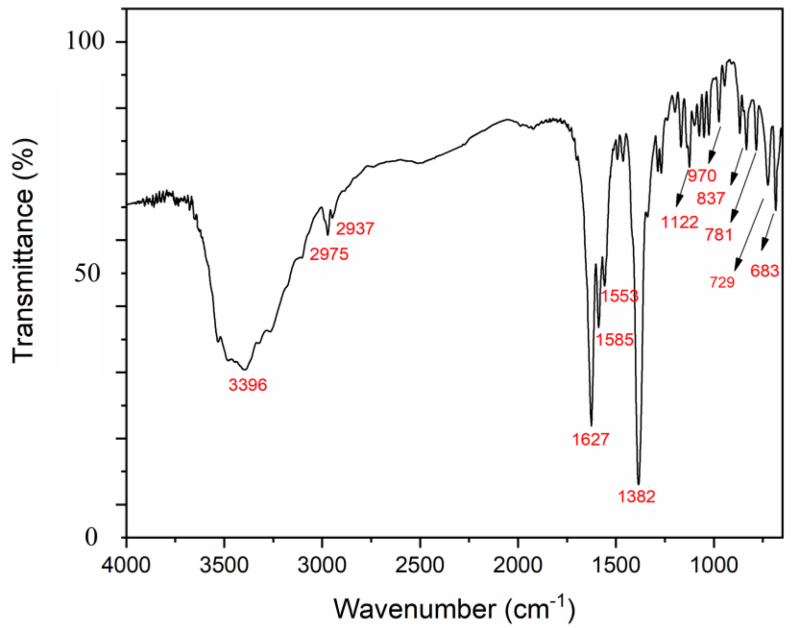
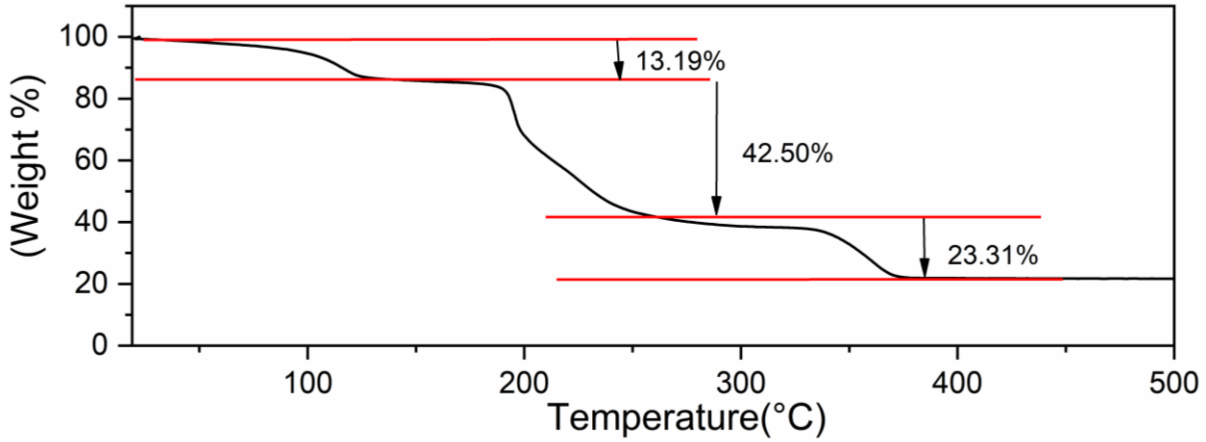


Figure S5. FTIR spectrum of **Cu-tipa**.



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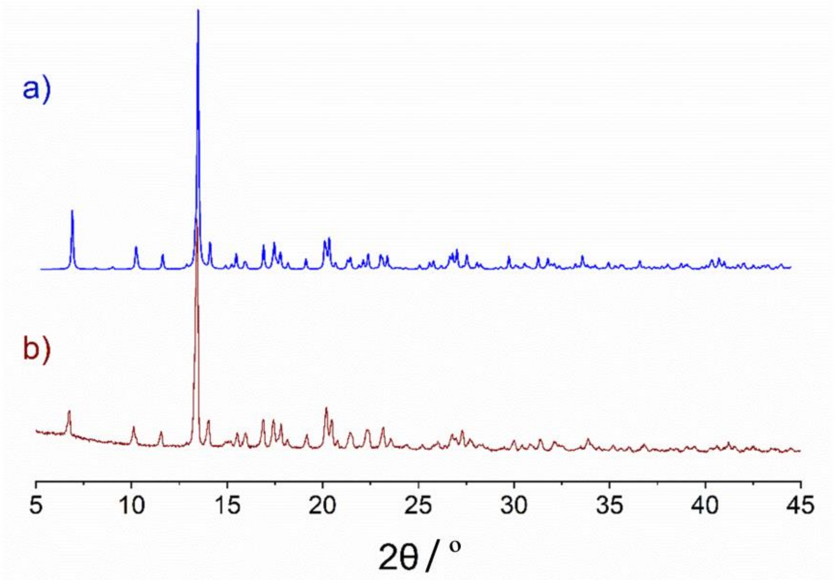


Figure S7. PXRD patterns for **Cu-tipa**: (a) simulated and (b) experimental.

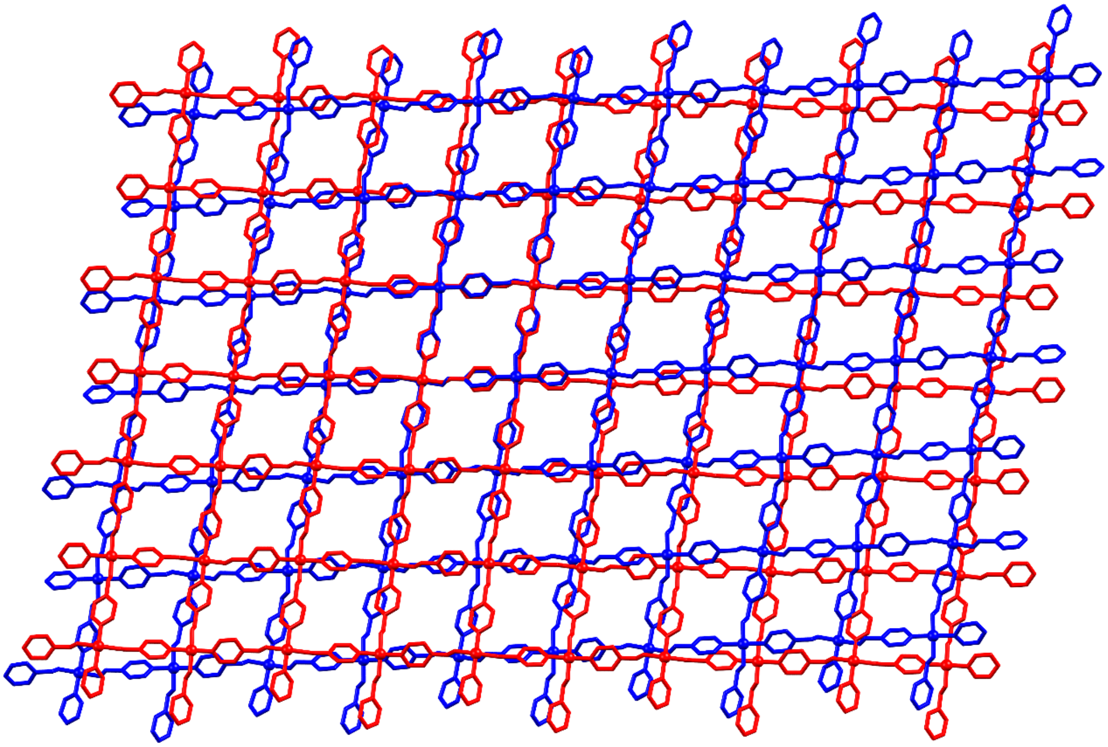


Figure S8. Representation of the intercalated 2D layers in **Cu-mdea** (red) and **Cu-tipa** (blue).

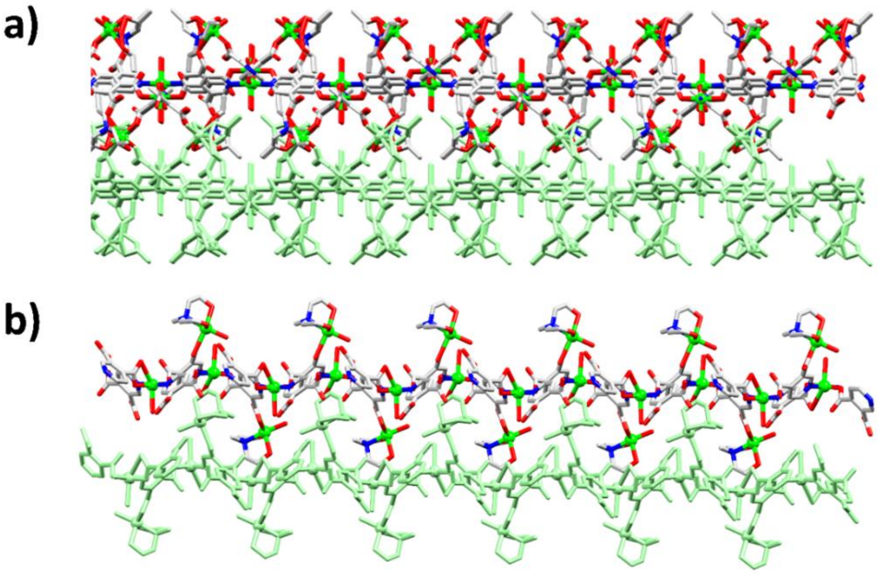


Figure S9. Crystal packing of the intercalated 2D layers in **Cu-mdea** (a) and **Cu-tipa** (b), blocking the potential voids.

Table S1. Bond lengths in **Cu-mdea**.

Atom	***Atom***	***Length/Å***	***Atom***	***Atom***	***Length/Å***
Cu1	O4	1.983(3)	O7	C14	1.224(7)
Cu1	O5	1.989(4)	N3	C16	1.452(11)
Cu1	N2^1	2.016(4)	N3	C19	1.468(11)
Cu1	N1^2	2.009(4)	N3	C18	1.433(11)
Cu1	O9	2.395(4)	C7	C6	1.513(6)
Cu2	O1	1.979(4)	O11	C15	1.422(9)
Cu2	O12	1.984(4)	C3	C2	1.391(7)
Cu2	O10	1.969(5)	C2	C1	1.501(7)
Cu2	N3	2.032(7)	C2	C6	1.395(7)
Cu2	O11	2.221(5)	C13	C12	1.382(7)
O4	C7	1.282(6)	C13	C9	1.389(7)
O5	C8	1.261(7)	C13	C14	1.518(7)
O1	C1	1.276(7)	O8	C14	1.251(8)
O3	C7	1.224(6)	C6	C5	1.385(7)
N2	C12	1.348(6)	C11	C10	1.386(7)
N2	C11	1.333(7)	C8	C9	1.525(7)
N1	C3	1.328(7)	C9	C10	1.395(7)
N1	C4	1.347(7)	C4	C5	1.380(7)
O2	C1	1.229(6)	C15	C16	1.479(12)
O6	C8	1.232(7)	C17	C18	1.530(12)
O12	C17	1.429(10)			

*Symmetry code: **(1)** 1-X,1/2+Y,1/2-Z;**(2)** -X,-1/2+Y,1/2-Z*

Table S2. Bond angles in **Cu-mdea**.

Atom	*Atom*	*Atom*	*Angle/°*	*Atom*	*Atom*	*Atom*	*Angle/°*
O4	Cu1	O5	178.47(15)	O4	C7	C6	115.5(4)
O4	Cu1	N2^{1}	90.55(15)	O3	C7	O4	125.7(4)
O4	Cu1	N1^{2}	88.98(15)	O3	C7	C6	118.7(4)
O4	Cu1	O9	92.38(16)	C15	O11	Cu2	109.1(4)
O5	Cu1	N2^{1}	90.16(16)	N1	C3	C2	123.2(5)
O5	Cu1	N1^{2}	90.22(16)	C3	C2	C1	119.6(4)
O5	Cu1	O9	88.97(16)	C3	C2	C6	118.2(4)
N2^{1}	Cu1	O9	90.50(16)	C6	C2	C1	122.1(4)
N1^{2}	Cu1	N2^{1}	176.29(17)	O1	C1	C2	116.0(4)
N1^{2}	Cu1	O9	93.20(16)	O2	C1	O1	124.5(5)
O1	Cu2	O12	157.2(2)	O2	C1	C2	119.5(5)
O1	Cu2	N3	96.3(3)	C12	C13	C9	118.3(5)
O1	Cu2	O11	95.7(2)	C12	C13	C14	117.5(5)
O12	Cu2	N3	82.6(3)	C9	C13	C14	124.1(4)
O12	Cu2	O11	106.6(2)	N2	C12	C13	124.1(5)
O10	Cu2	O1	90.4(2)	C2	C6	C7	120.7(4)
O10	Cu2	O12	91.6(2)	C5	C6	C7	121.0(4)
O10	Cu2	N3	173.2(3)	C5	C6	C2	118.1(4)
O10	Cu2	O11	96.9(2)	N2	C11	C10	122.4(5)
N3	Cu2	O11	81.4(2)	O5	C8	C9	115.8(5)
C7	O4	Cu1	116.8(3)	O6	C8	O5	124.9(5)
C8	O5	Cu1	109.8(3)	O6	C8	C9	119.1(5)
C1	O1	Cu2	105.0(3)	C13	C9	C8	122.8(4)
C12	N2	Cu1^{3}	117.1(3)	C13	C9	C10	117.8(5)
C11	N2	Cu1^{3}	125.4(3)	C10	C9	C8	119.2(5)
C11	N2	C12	117.4(4)	N1	C4	C5	121.5(5)
C3	N1	Cu1^{4}	118.7(3)	C4	C5	C6	120.2(5)
C3	N1	C4	118.7(4)	C11	C10	C9	120.0(5)
C4	N1	Cu1^{4}	122.5(3)	O7	C14	C13	118.8(5)
C17	O12	Cu2	113.2(5)	O7	C14	O8	125.9(5)
C16	N3	Cu2	106.8(5)	O8	C14	C13	115.3(5)
C16	N3	C19	110.5(7)	O11	C15	C16	109.5(7)
C19	N3	Cu2	116.5(5)	O12	C17	C18	110.1(7)
C18	N3	Cu2	104.6(5)	N3	C16	C15	115.2(8)
C18	N3	C16	113.6(7)	N3	C18	C17	110.9(7)
C18	N3	C19	104.9(7)				

Symmetry code: ***(1)*** *1-X,1/2+Y,1/2-Z;* ***(2)*** *-X,-1/2+Y,1/2-Z;* ***(3)*** *1-X,-1/2+Y,1/2-Z;* ***(4)*** *-X,1/2+Y,1/2-Z*

Table S3. Bond lengths in **Cu-tipa**.

Atom	*Atom*	*Length/Å*	*Atom*	*Atom*	*Length/Å*
Cu1	O3	1.975(4)	N2	C8	1.335(7)
Cu1	O3^{1}	1.975(4)	N2	C12	1.326(7)
Cu1	N2	2.003(4)	O7	C14	1.225(7)
Cu1	N2^{1}	2.003(4)	C7	C6	1.508(7)
Cu1	O15	2.410(7)	C6	C2	1.392(7)
Cu2	O2	1.968(4)	C6	C5	1.393(7)
Cu2	O9	2.299(5)	C2	C1	1.506(7)
Cu2	N3	2.036(5)	C2	C3	1.383(7)
Cu2	O11A	1.961(8)	O9	C19	1.443(9)
Cu2	O12	1.978(5)	C19	C18	1.509(10)
Cu2	O11B	1.602(10)	C19	C20	1.496(12)
Cu3	N1^{2}	2.026(4)	C18	N3	1.505(8)
Cu3	N1^{3}	2.026(4)	N3	C15	1.475(9)
Cu3	O5^{4}	1.968(4)	N3	C21	1.511(8)
Cu3	O5	1.968(4)	C15	C16	1.509(10)
Cu3	O14	2.334(6)	C16	C17	1.527(11)

O3	C7	1.262(7)	C21	C22	1.503(11)
O2	C1	1.263(7)	C22	C23	1.488(11)
O10	C16	1.458(8)	C22	O11A	1.362(12)
O10	O11B	1.776(11)	O11A	O11B	1.493(15)
N1	C3	1.341(6)	C4	C5	1.383(7)
N1	C4	1.336(7)	C8	C9	1.379(7)
O4	C7	1.235(7)	C9	C10	1.408(7)
O6	C13	1.215(7)	C9	C14	1.507(7)
O5	C13	1.261(7)	C10	C13	1.510(7)
O8	C14	1.269(8)	C10	C11	1.396(7)
O1	C1	1.232(7)	C11	C12	1.380(7)

*Symmetry code: **(1)** 1-X,+Y,1/2-Z; **(2)** -1/2+X,1/2-Y,-1/2+Z; **(3)** 1/2-X,1/2-Y,1-Z; **(4)** -X,+Y,1/2-Z*

Table S4. Bond angles in **Cu-tipa**.

Atom	*Atom*	*Atom*	*Angle/°*	*Atom*	*Atom*	*Atom*	*Angle/°*
O3	Cu1	O3^1	173.0(2)	C5	C6	C7	118.5(5)
O3^1	Cu1	N2	90.90(16)	C6	C2	C1	123.7(4)
O3	Cu1	N2^1	90.90(16)	C3	C2	C6	118.8(4)
O3	Cu1	N2	89.29(16)	C3	C2	C1	117.3(4)
O3^1	Cu1	N2^1	89.29(16)	O2	C1	C2	115.0(4)
O3^1	Cu1	O15	93.48(11)	O1	C1	O2	126.0(5)
O3	Cu1	O15	93.48(11)	O1	C1	C2	118.9(5)
N2	Cu1	N2^1	176.9(2)	C19	O9	Cu2	108.9(4)
N2^1	Cu1	O15	88.46(11)	O9	C19	C18	108.6(5)
N2	Cu1	O15	88.46(11)	O9	C19	C20	110.0(7)
O2	Cu2	O9	85.07(18)	C20	C19	C18	110.5(6)
O2	Cu2	N3	93.93(18)	N3	C18	C19	113.7(5)
O2	Cu2	O12	91.40(19)	C18	N3	Cu2	106.4(4)
N3	Cu2	O9	80.8(2)	C18	N3	C21	110.4(5)
O11A	Cu2	O2	177.0(3)	C15	N3	Cu2	111.7(4)
O11A	Cu2	O9	96.3(4)	C15	N3	C18	108.7(5)
O11A	Cu2	N3	83.7(3)	C15	N3	C21	111.6(5)
O11A	Cu2	O12	91.0(3)	C21	N3	Cu2	108.0(4)
O12	Cu2	O9	97.1(2)	N3	C15	C16	114.4(5)
O12	Cu2	N3	174.1(2)	O10	C16	C15	110.9(5)
O11B	Cu2	O2	130.1(4)	O10	C16	C17	109.8(6)
O11B	Cu2	O9	144.3(4)	C15	C16	C17	111.2(6)
O11B	Cu2	N3	89.5(4)	C22	C21	N3	111.5(6)
O11B	Cu2	O11A	48.3(5)	C23	C22	C21	112.1(8)
O11B	Cu2	O12	89.1(4)	O11A	C22	C21	110.2(8)
N1^2	Cu3	N1^3	177.8(2)	O11A	C22	C23	116.7(8)
N1^2	Cu3	O14	91.10(12)	C22	O11A	Cu2	115.4(6)
N1^3	Cu3	O14	91.10(12)	C22	O11A	O11B	97.0(9)
O5^4	Cu3	N1^3	88.96(16)	O11B	O11A	Cu2	53.2(4)
O5	Cu3	N1^3	90.99(16)	N1	C3	C2	123.7(5)
O5^4	Cu3	N1^2	90.99(16)	N1	C4	C5	122.6(5)
O5	Cu3	N1^2	88.96(16)	C4	C5	C6	120.0(5)
O5^4	Cu3	O5	177.0(2)	N2	C8	C9	124.1(5)
O5^4	Cu3	O14	91.49(12)	C8	C9	C10	118.2(5)
O5	Cu3	O14	91.48(12)	C8	C9	C14	116.2(5)
C7	O3	Cu1	116.3(3)	C10	C9	C14	125.3(4)
C1	O2	Cu2	125.4(3)	C9	C10	C13	124.2(5)
C16	O10	O11B	114.3(5)	C11	C10	C9	116.9(5)
C3	N1	Cu3^3	118.3(3)	C11	C10	C13	118.9(5)
C4	N1	Cu3^3	124.1(3)	O6	C13	O5	125.2(5)
C4	N1	C3	117.6(4)	O6	C13	C10	119.0(5)
C13	O5	Cu3	116.2(3)	O5	C13	C10	115.8(5)
C8	N2	Cu1	117.8(3)	C12	C11	C10	120.4(5)

C12	N2	Cu1	124.0(3)	N2	C12	C11	122.2(5)
C12	N2	C8	118.2(4)	O8	C14	C9	115.8(5)
O3	C7	C6	114.8(5)	O7	C14	O8	125.5(5)
O4	C7	O3	125.5(5)	O7	C14	C9	118.5(5)
O4	C7	C6	119.7(5)	Cu2	O11B	O10	103.7(4)
C2	C6	C7	124.0(4)	O11A	O11B	Cu2	78.5(6)
C2	C6	C5	117.5(5)	O11A	O11B	O10	149.3(7)

*Symmetry code: **(1)** 1-X,+Y,1/2-Z; **(2)** -1/2+X,1/2-Y,-1/2+Z; **(3)** 1/2-X,1/2-Y,1-Z; **(4)** -X,+Y,1/2-Z*

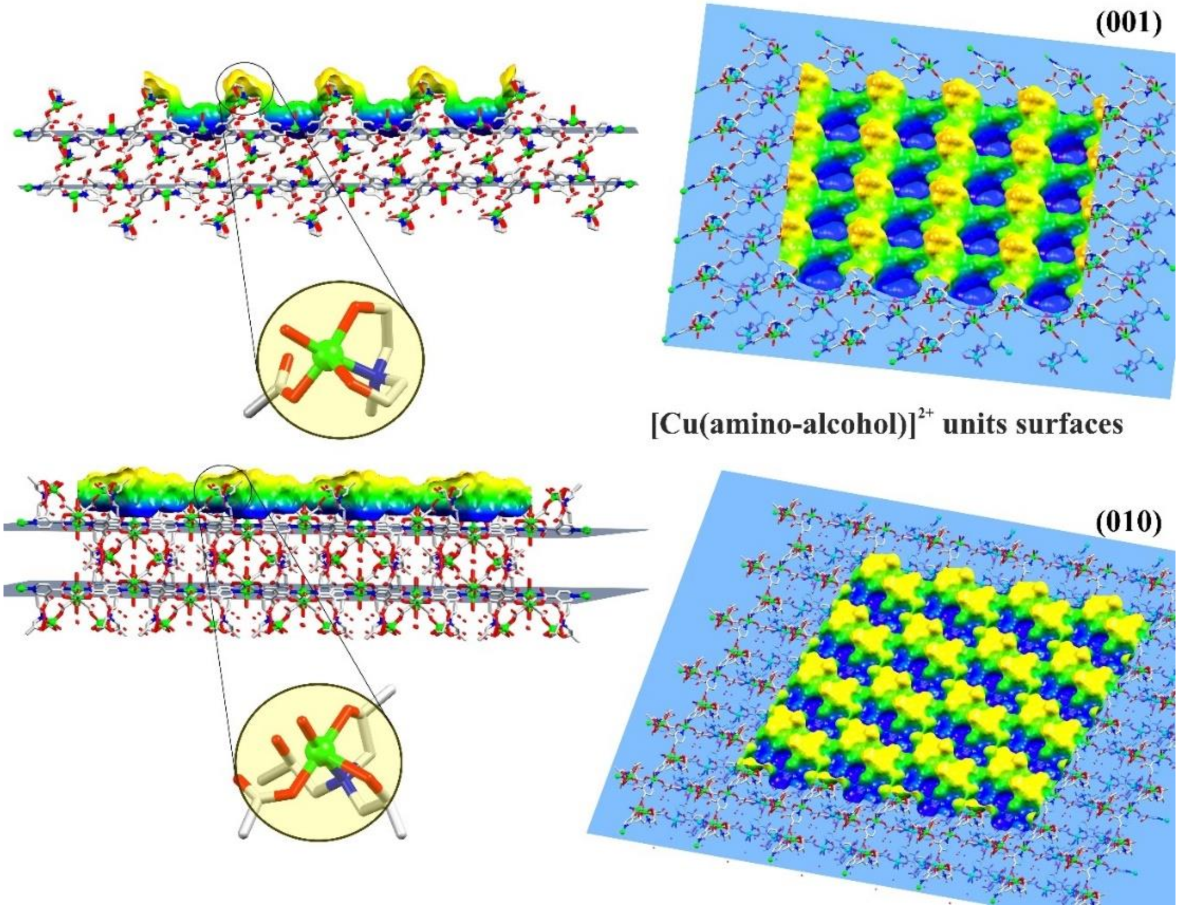


Figure S10. Representation of the 3D supramolecular arrangement of compounds as well as [Cu(aminoalcohol)]$^{2+}$ units in **Cu-mdea** (top; view along the *c*-axis) and **Cu-tipa** (bottom; view along the *b*-axis). On the right, the distribution of the respective [Cu(aminoalcohol)]$^{2+}$ unit surfaces for **Cu-mdea** and **Cu-tipa** is shown.

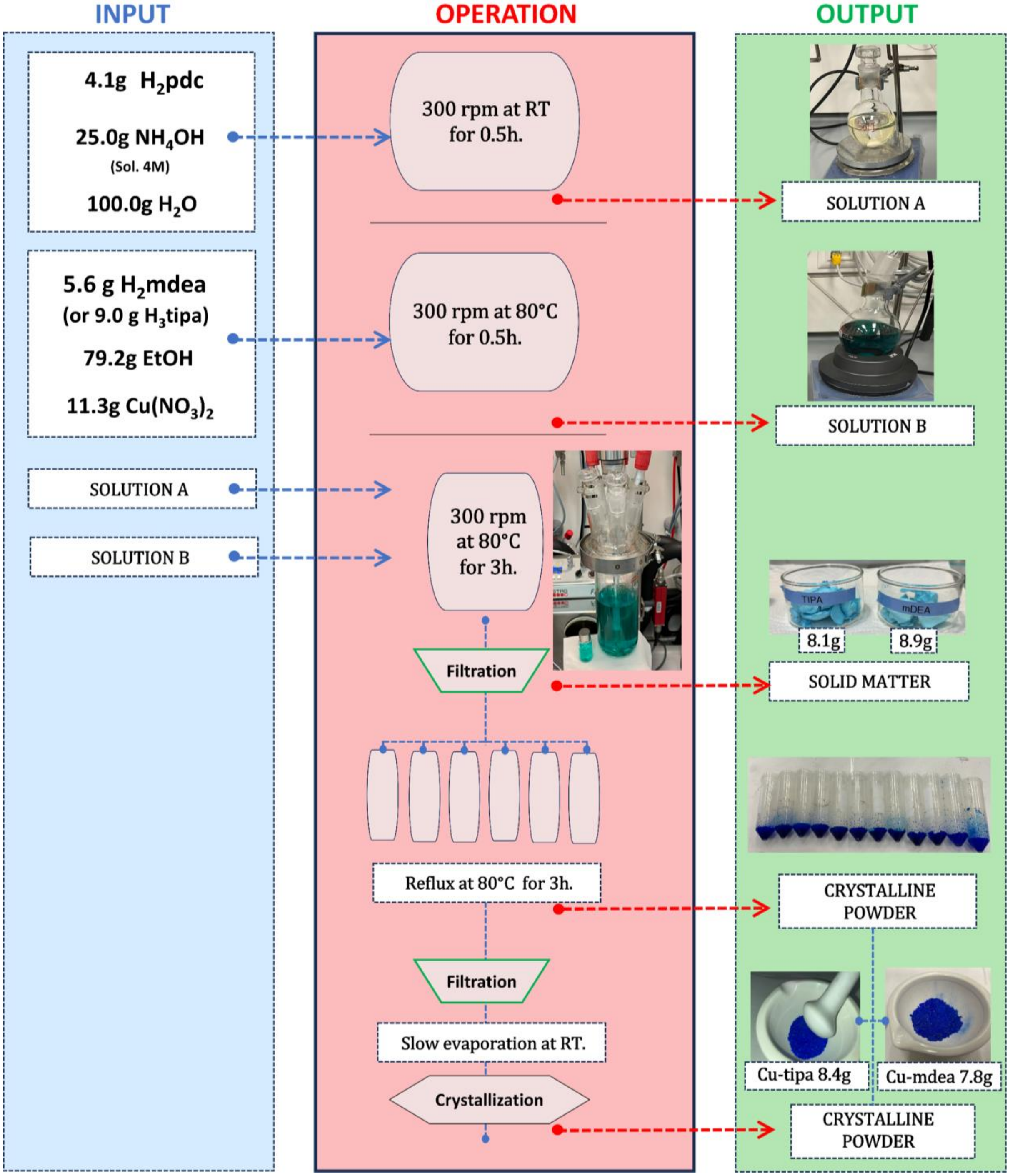


Figure S11. Block flow diagram of the scale-up process of **Cu-mdea** and **Cu-tipa**.

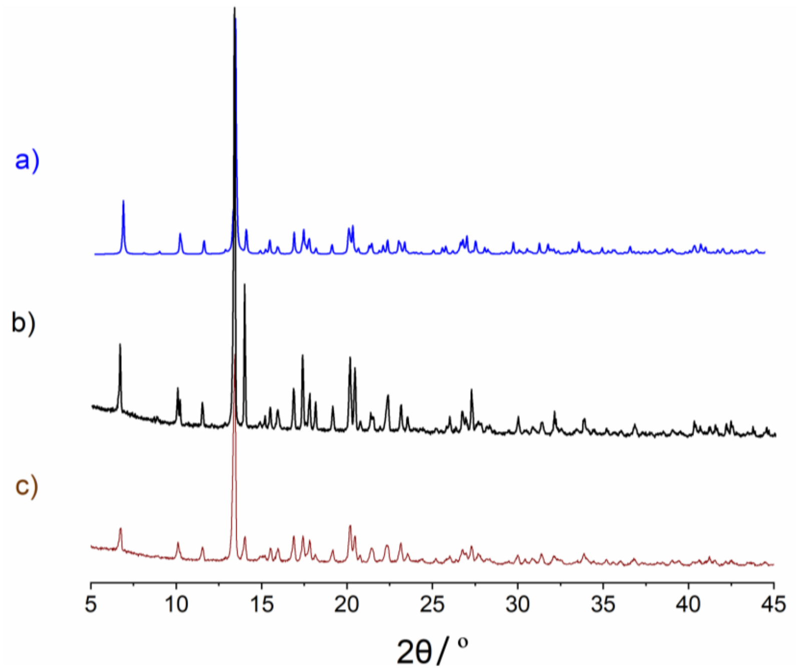


Figure S12. PXRD patterns of **Cu-tipa**: (a) simulated, (b) scale-up process (gram scale), and (c) beaker reactor (milligram scale).

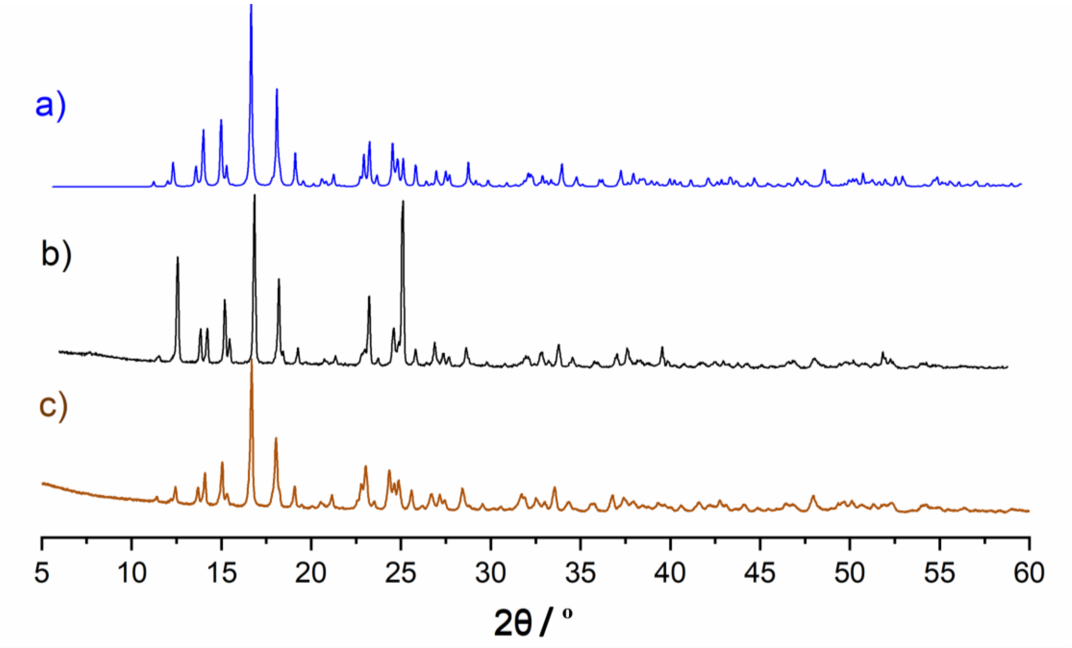


Figure S13. PXRD patterns for **Cu-mdea**: (a) simulated, (b) scale-up process (gram scale), and (c) beaker reactor (milligram scale).

Section 2 – Catalytic Studies

Materials and Methods. All chemicals and solvents were acquired commercially and utilized without any prior preparation. Elemental analyses for C, H and N were carried out on a PerkinElmer PE 2400 Series II analyzer (Laboratory of Analyses, IST). The infrared spectra were recorded on an FT-IR Shimadzu IRAffinity-1S apparatus spectrometer equipped with an ATR ZnSe Performance Crystal Plate accessory in the range of 4000–600 cm^{-1}, with an average of 64 scans and 2 cm^{-1} of spectral resolution. The thermogravimetric data were recorded on a Shimadzu DTG60 thermobalance with a heating rate of 5°C min^{-1} to a temperature of 500°C in a dynamic atmosphere of air.

Oxidation of α-Pinene: The GC (gas chromatography) analyses were performed on an Agilent Technologies 7820A series gas chromatograph (carrier gas, helium; detector, flame ionization; capillary column, BP20/SGE, 30m × 0.22 mm × 0.25 μm). The aliquots were diluted in 1:4 acetonitrile and a sample volume fraction of 1 μL was injected at a temperature of 280 °C and 1:50 split ratio. The temperature program was 100 °C for 6 min and then 10 °C min^{-1} until 180 °C. For characterization/guide of unidentified compounds, GC-MS analyses were performed on a Scion 436-GC equipped with a polar BP20/SGE column (30m × 0.25 mm × 0.25 μm), an electron impact ionization source, and a simple quadrupole analyser.

To conduct the test with $Cu(NO_3)_2 \cdot 3H_2O$, an aqueous stock solution (0.25 M) was prepared. A portion of this solution (24 μL, 6 μmol) was taken and transferred to a 2 mL catalytic vial, then left to dry at 100ºC for 10 min. The remaining $Cu(NO_3)_2 \cdot 3H_2O$ powder was used as a catalyst, following the general procedure for the oxidation of α-pinene.

The number of mols (n) of α-pinene, pinene oxide and verbenone were determined by calibration curve, in which the angular coefficients (a) were 10.93, 9.38 and 9.50, respectively. However, for *tert*-butylperoxy-2-pinene, which is not commercially available, the inverse function of angular coefficient was determined by correlation between the peak area of the isolated product (0.12 mmol) and verbenone (0.12mmol), i.e., $\left(\frac{1}{a}\right)_{4-tert-butylperoxy-2-pinene} = 1.62 \times \left(\frac{1}{a}\right)_{verbenone}$.

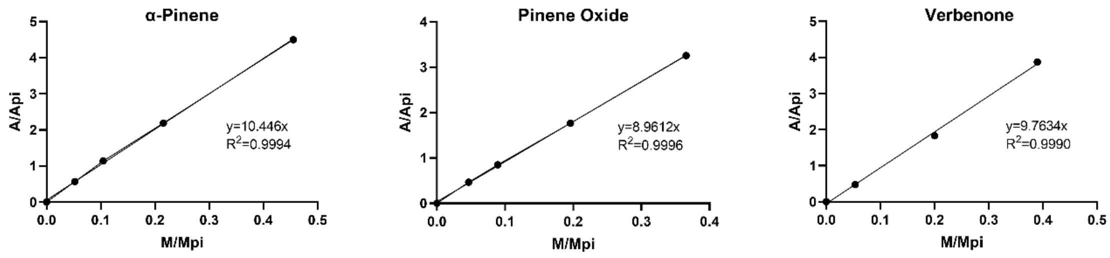


Figure S14. Calibration curves for α-pinene, pinene oxide, and verbenone.

Equation 1 $$n = \frac{A}{A_{IS}} \cdot \left(\frac{1}{a}\right) \cdot n_{IS}$$

A - peak area
A

Hot Filtration Test: In a 2 mL reactor, 1 mL of CH_3CN was initially placed, followed by the addition of 180 µL of TBHP (70% in H_2O, 1.2 mmol), which was stirred for 5 to 12 h at 60°C. After 20 min, the reaction mixture was subjected to hot filtration to remove the catalyst into another reactor containing 96 µL (0.6 mmol) of α-pinene at 60°C. Subsequently, aliquots were extracted from the mixture to monitor the progression of the reaction without the presence of catalyst.

Purification of Products by Preparative TLC. Purifications were performed using DC-Fertigplatten SIL G-25 pre-coated TLC plates with an eluent solution of hexane and ethyl acetate (10:0.5 ratio). After elution, each stain was revealed with UV light, then detached from the TLC plates. Multiple washes with dichloromethane were performed to ensure complete extraction of the isolated product, which was then dried and submitted to NMR analysis.

Characterization of Products by Nuclear Magnetic Resonance (NMR). The solution ^1H spectra were obtained on 500 MHz or 400 MHz NMR spectrometers (Varian Inc.), using deuterated chloroform as a solvent. The chemical shifts (δ) are relative to tetramethylsilane (TMS), used as the internal standard.

Copper Content in Solution by ICP-EOS. In different times of the catalytic reaction, 500 µL were collected and digested in 5 mL HNO_3 before analyzing by Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-EOS). The analyses were performed by the Laboratory of the Analyses of IST, University of Lisbon. The final amount of copper content in the reaction medium (ppm) was used to calculate the percentage of copper leaching from a given amount of catalyst.

Equation 1

$$Cu\,\% = \left[\frac{(ppm \cdot 1X10^{-3})}{mg/mL\ _{Cu\ amount\ in\ CP}}\right] \cdot 100$$

Equation 2

$$mol\,\% = \left[\frac{number\ of\ moles\ of\ catalyst)}{(number\ of\ moles\ of\ catalyst + number\ of\ moles\ ofsubstrate)}\right] \cdot 100$$

The determination of the copper content in the reaction solution was performed with a Perkin Elmer Optima 2000 DV inductively coupled plasma optical emission spectrometer (ICP-OES).

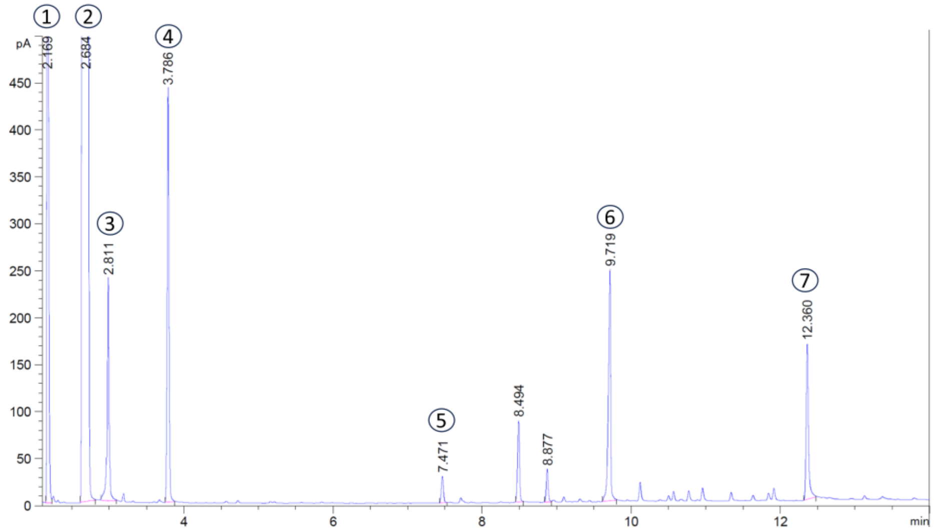


Figure S15. Typical gas chromatogram of the reaction mixture in the Cu-catalyzed oxidation of α-pinene. Conditions: α-pinene (0.6 mmol), catalyst (6 µmol), TBHP (70% in H_2O; 1.2 mmol), CH_3CN (1 mL), 12 h, 1200 rpm, 60°C, catalytic flask (2 mL). Identification: (1) *tert*-BuOH, (2) CH_3CN (3), α-pinene (4) nitromethane (GC standard), (5) pinene oxide, (6) 4-*tert*-butylperoxy-2-pinene and (7) verbenone.

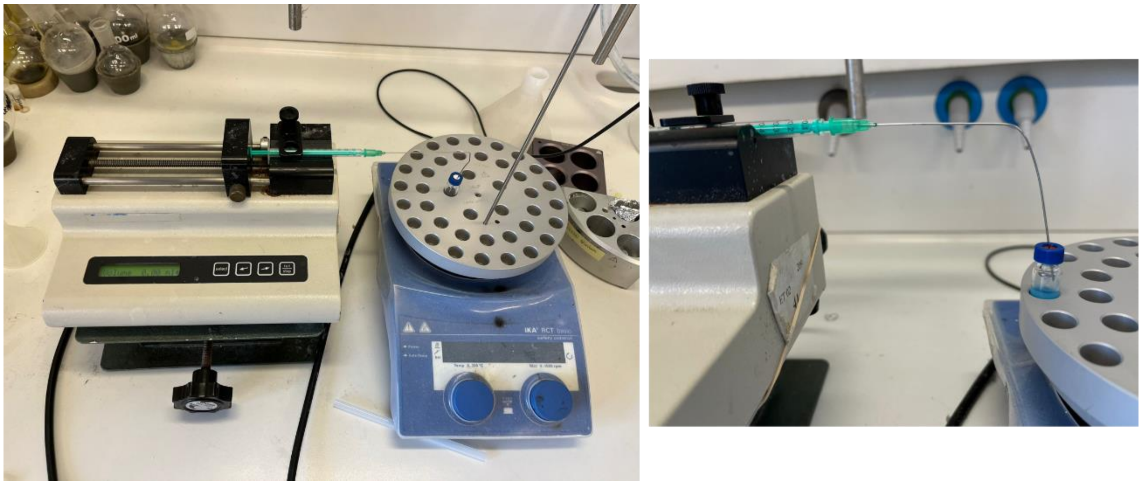


Figure S16. Apparatus for the slow addition of TBHP (70% in H_2O; 1.2 mmol) to the reaction medium.

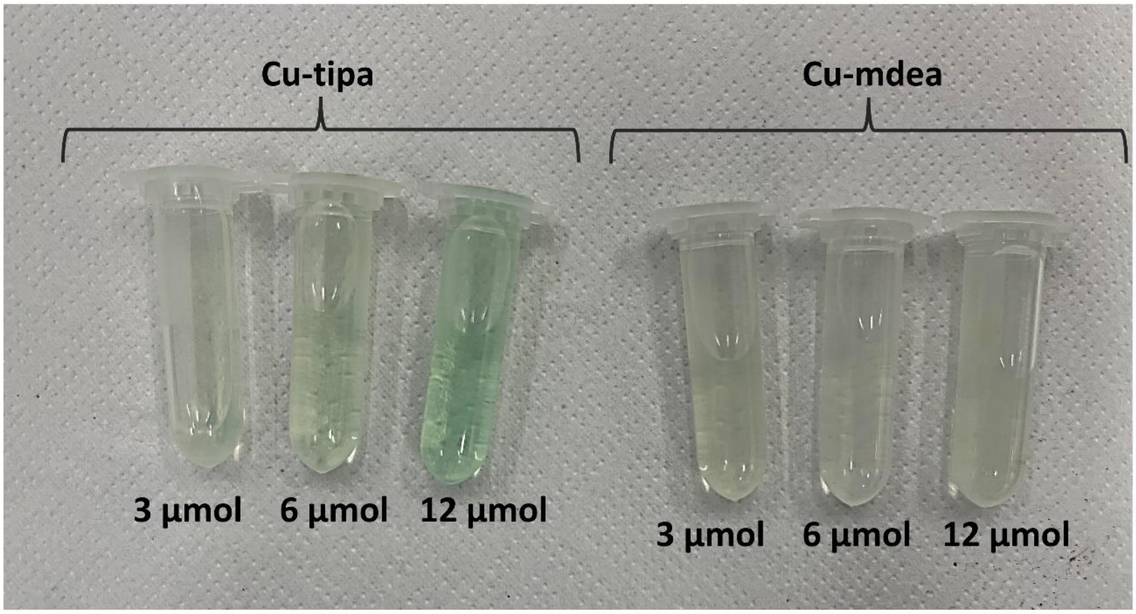
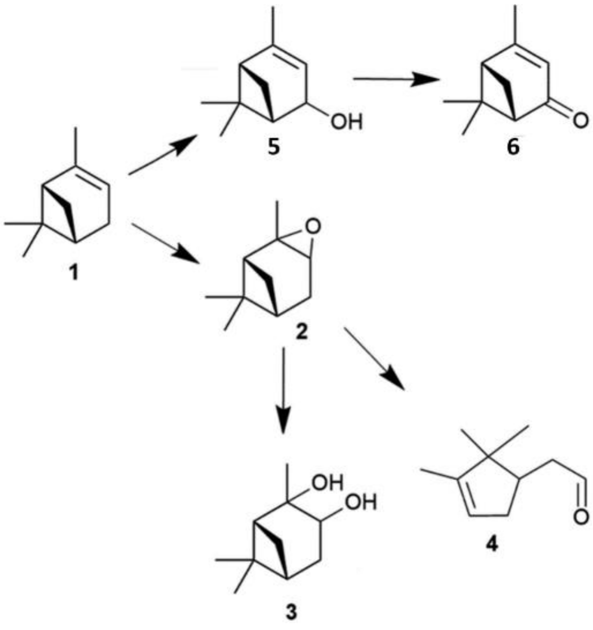


Figure S17. Solubility test for different concentrations of **Cu-mdea** and **Cu-tipa** in the oxidation reactions of α-pinene after 12 h at 60ºC. (Images correspond to the supernatant solutions after removing the catalyst from the reaction medium).



Scheme S1. Traces of products obtained from the oxidation of α-pinene catalyzed by **Cu-mdea** using different oxidants in CH_3CN: α-pinene **1**, α-pinene oxide **2**, pinanediol **3**, campholenic aldehyde 4, verbenol **5**, and verbenone **6**. (Adapted from ref.[S1]).

Table S5. Oxidation of α-pinene with TBHP catalyzed by **Cu-mdea** and blank test. Effect of oxidant-to-substrate molar ratio.[a]

Entry	Catalyst	Molar Ratio TBHP:Pinene	Conversion (%)[b]	Yield of the main products (%)[c]			
			A	**B**	**C**	**D**	**Total**
1	**Cu-mdea**	1:1	67.5	18.0	11.0	2.0	31.0
2		2:1	82.0	29.0	9.5	1.0	39.5
3		3:1	87.5	31.0	9.5	1.0	41.5

[a] Conditions: α-pinene (0.6 mmol), **Cu-mdea** (1 mol%), TBHP (70% in H_2O; 1.2 mmol), CH_3CN (1 mL), 5 h, 1200 rpm, 60°C, catalytic flask (2 mL). [b] *Conversion:* [moles of α-pinene initial - moles of α-pinene final) / (moles of α-pinene) × 100%]. [c] *Yield* was determined by GC based on α-pinene: (moles of product per initial mol of α-pinene) × 100. (A: α-pinene; B: 4-*tert*-butylperoxy-2-pinene; C: verbenone; D: pinene oxide).

Table S6. Oxidation of α-pinene catalyzed by different copper compounds with TBHP. Effect of time.[a]

Time (h)	**Cu-mdea**					**Cu-tipa**					**Blank**				
	Conv (%)[b]	Yield of the main products (%)[c]				Conv. (%)[b]	Yield of the main products (%)[c]				Conv. (%)[b]	Yield of the main products (%)[c]			
	A	**B**	**C**	**D**	**Total**	**A**	**B**	**C**	**D**	**Total**	**A**	**B**	**C**	**D**	**Total**
0	0	nd	nd	nd	**0**	0	nd	nd	nd	**0**	0	nd	nd	nd	**0**
1	59.0	16.5	4.0	0.5	**21.0**	60.0	13.5	6.0	0.5	**20.0**	6.0	0.5	0.5	nd	**1.0**
3	78.0	26.0	8.0	0.5	**34.5**	75.0	29.0	7.0	0.5	**36.5**	7.0	1.0	0.5	nd	**1.5**
6	83.0	29.0	9.5	0.5	**39.0**	87.5	31.0	9.5	0.5	**41.0**	15.0	1.5	2.0	nd	**3.5**
12	90.0	29.5	13.5	0.5	**43.5**	92.0	30.0	13.5	nd	**43.5**	25.5	4.5	2.0	nd	**6.5**

[a] Conditions: α-pinene (0.6 mmol), Catalysts (1 mol%), TBHP (70% in H_2O; 1.2 mmol), CH_3CN (1 mL), 12 h, 1200 rpm, 60°C, catalytic flask (2 mL). [b] *Conversion:* [moles of α-pinene initial - moles of α-pinene final) / (moles of α-pinene) × 100%]. [c] *Yield* was determined by GC based on α-pinene: (moles of product per initial mol of α-pinene) × 100. (A: α-pinene; B: 4-*tert*-butylperoxy-2-pinene; C: verbenone; D: pinene oxide).

Table S7. Oxidation of α-pinene catalyzed by **Cu-mdea** with TBHP. Effect of solvent type.[a]

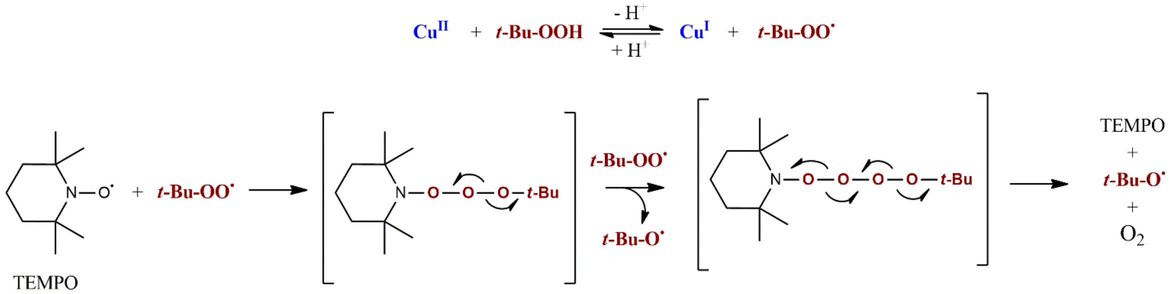
Entry	Solvent	Dielectric constant	Conversion (%)[b]	Yield of the main products (%)[c]			
			A	**B**	**C**	**D**	**Total**
1	Acetonitrile CH_3CN	37.5	89.0	30.0	13.5	0.5	**44.0**
2	Ethyl acetate $CH_3C(O)OCH_2CH_3$	6	13.0	2.5	2.0	nd	**4.5**
3	Acetone CH_3COCH_3	21	53.0	25.0	8.5	1.5	**35.0**
4	Dimethyl sulfoxide CH_3SOCH_3	47	83.0	19.0	10.5	3.5	**33.0**
5	Propan-2-ol $C_4H_{10}O$	19.9	10.5	1.5	1.5	1.0	**4.0**
6	Tetrahydrofuran $(CH_2)_4O$	7.5	14.0	3.0	2.5	nd	**5.5**

[a]Conditions: α-pinene (0.6 mmol), Catalysts (1 mol%), TBHP (70% in H_2O; 1.2 mmol), CH_3CN (1 mL), 9 h, 1200 rpm, 60°C, catalytic flask (2 mL). [b]*Conversion*: [moles of α-pinene initial - moles of α-pinene final) / (moles of α-pinene) × 100%]. [c]*Yield* was determined by GC based on α-pinene: (moles of product per initial mol of α-pinene) × 100. (A: α-pinene; B: 4-*tert*-butylperoxy-2-pinene; C: verbenone; D: pinene oxide).

Table S8. Oxidation of α-pinene over **Cu-mdea** and blank. Effect of catalyst loading.[a]

Entry	Catalyst	Amount (mol%)[b]	Conversion (%)[c]	Yield of the main products (%)[d]			
			A	**B**	**C**	**D**	**Total**
1	**Cu-mdea**	0.5	74.5	32.0	11.5	4.5	**48.0**
2	**Cu-mdea**	1.5	85.0	37.0	14.5	3.0	**54.5**
3	**Cu-mdea**	3.0	93.0	42.0	18.5	3.0	**63.5**
4	Blank	-	9.5	1.5	1.5	1.0	**4.0**

[a]Conditions: α-pinene (0.6 mmol), **Cu-mdea** (0.5−3.0 mol%), TBHP (70% in H_2O; 1.2 mmol), CH_3CN (1 mL), 5 h, 1200 rpm, 60°C, catalytic flask (2 mL). [b] mol%: [moles of catalyst / (moles of catalyst + moles of α-pinene) × 100%]. [c]*Conversion:* [moles of α-pinene initial - moles of α-pinene final) / (moles of α-pinene) × 100%]. [d]*Yield* was determined by GC based on α-pinene: (moles of product per initial mol of α-pinene) × 100. (A: α-pinene; B: 4-*tert*-butylperoxy-2-pinene; C: verbenone; D: pinene oxide).



Scheme S2. Mechanism of TEMPO reaction with $tBuOO^{\bullet}$ to catalyze the formation of O_2 and $tBuO^{\bullet}$.[S2]

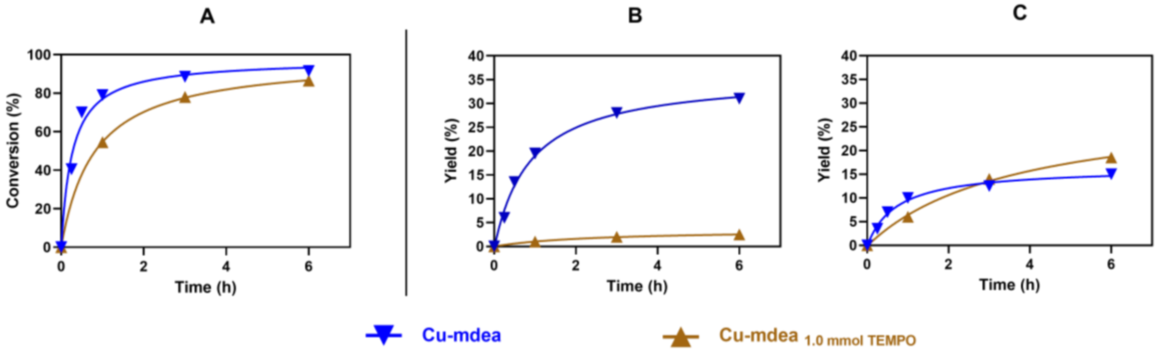


Figure S18: Cu-catalyzed oxidation of α-pinene over **Cu-mdea** in the presence of TEMPO (light brown) and without TEMPO (gray). (A: α-pinene; B: 4-*tert*-butylperoxy-2-pinene: C: verbenone).

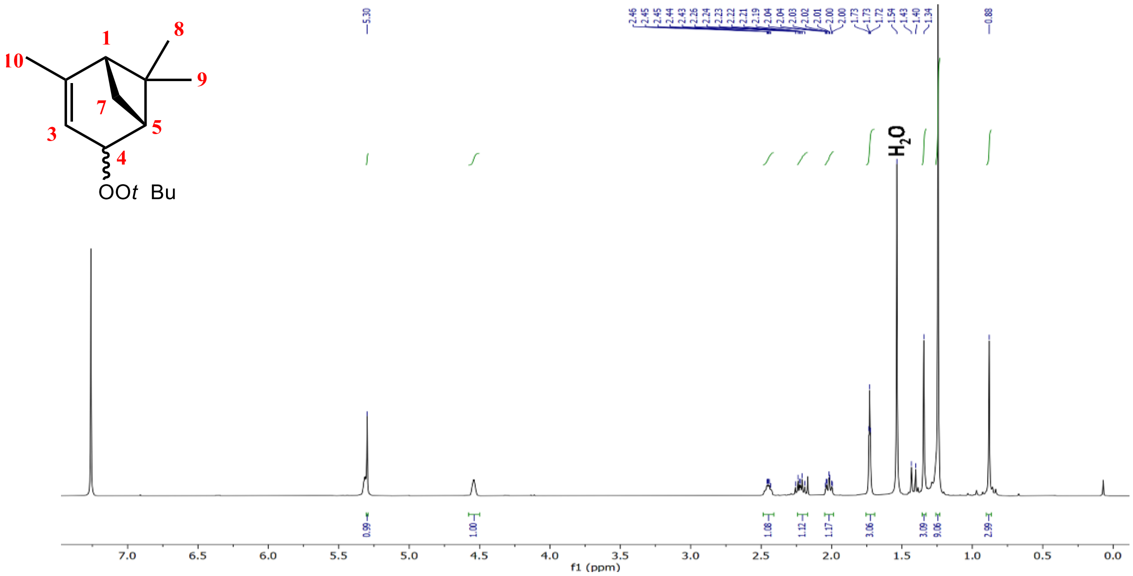


Figure S19. ^{1}H NMR spectrum of the isolated 4-*tert*-butylperoxy-2-pinene in chloroform-d.

4-*tert*-butylperoxy-2-pinene *(26mg, 32%):* ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.88 (s, 3H, CH_3, H-9), 1.23 (s, 9H, *t*-Bu), 1.33 (s, 3H, CH_3, H-8), 1.40 (dt, 1H, H-7*exo*, J = 8.9, 1.4 Hz), 1.73 (t, 3H, CH_3, H-10, J = 1.7 Hz), 2.0 (td, 1H, H-1, J = 6.6, 1.6 Hz), 2.21 (dt, 1H, H-7, J = 8.9, 5.6 Hz), 2.45-2.50 (m, 1H, H-5), 4.52-4.56 (m, 1H, H-4), 5.30 (m, 1H, H-3).[S3]

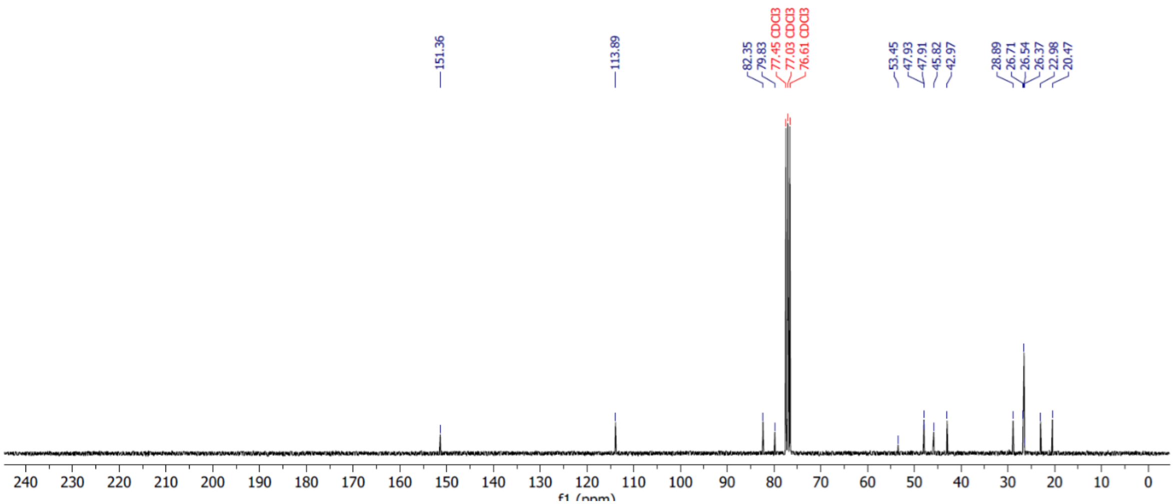


Figure S20. ^{13}C NMR spectrum of the isolated 4-*tert*-butylperoxy-2-pinene in chloroform-d.

^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.5 (C-9), 23.0 (C-10), 26.4 (*t*-Bu), 26.7 (C-8), 28.9 (C-7), 43.0 (C-5), 45.8 (C-6), 47.9 (C-1), 79.8 (C-O), 82.4 (C-4), 113.9 (C-3), 151.4 (C-2).

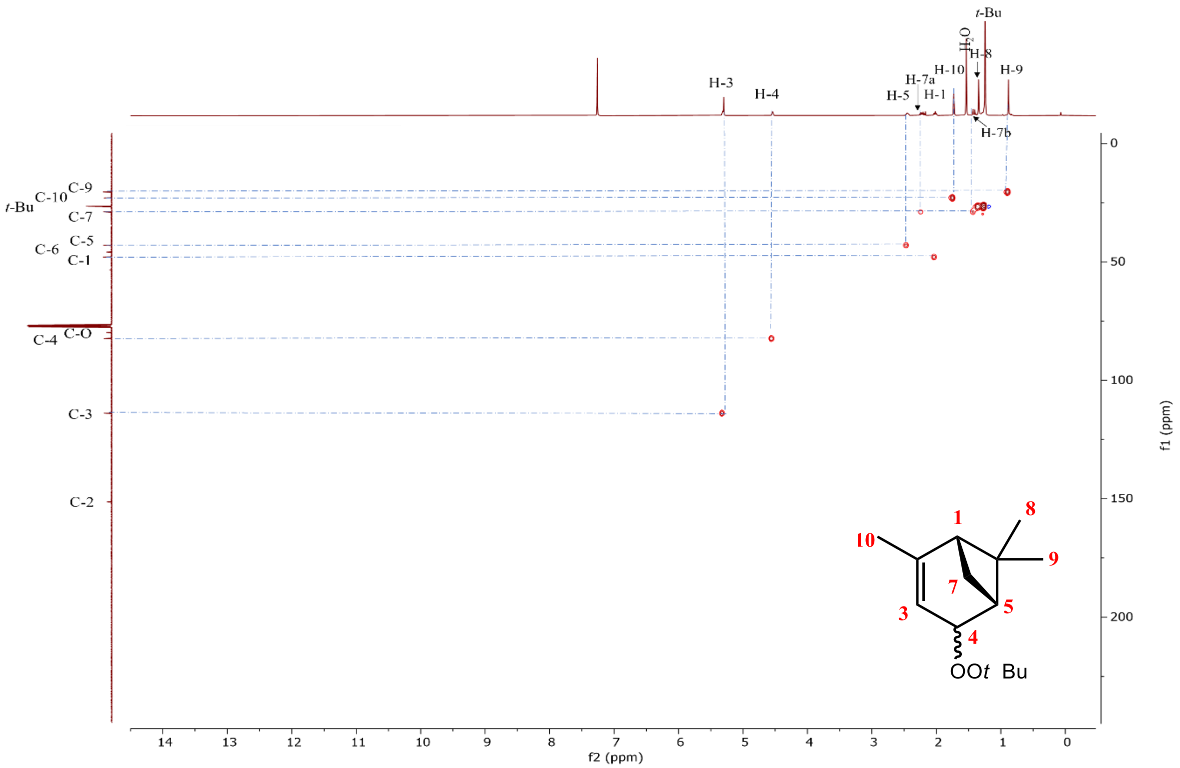


Figure S21. 2D HSQC NMR spectrum of the isolated 4-*tert*-butylperoxy-2-pinene in chloroform-d.

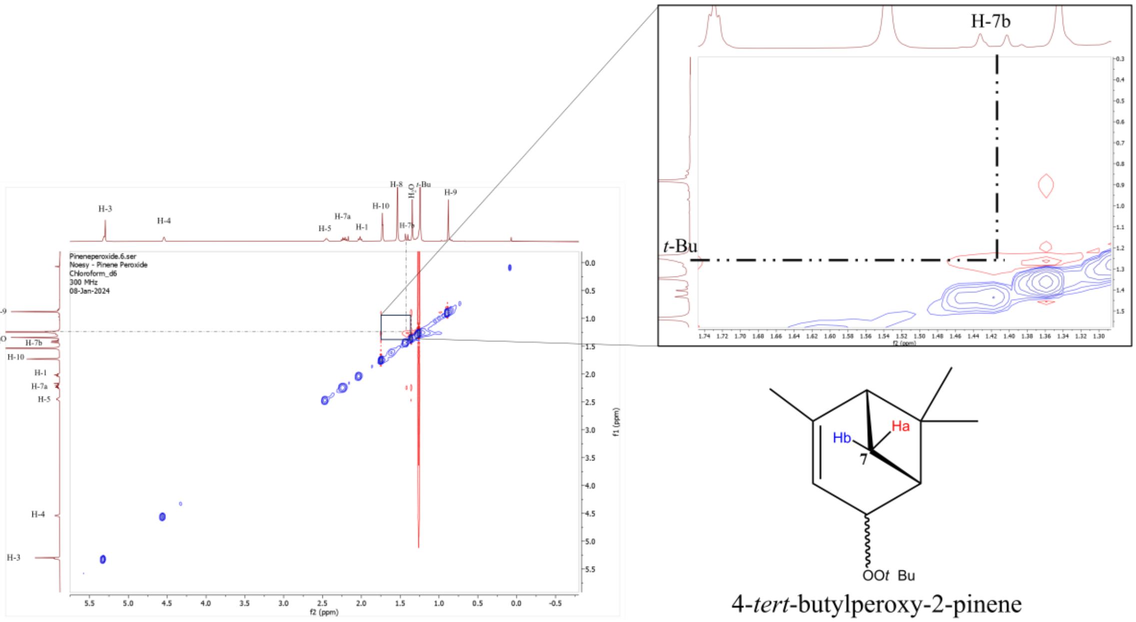


Figure S22. 2D NOESY NMR spectrum of the isolated *tert*-butylperoxy-2-pinene in chloroform-d.

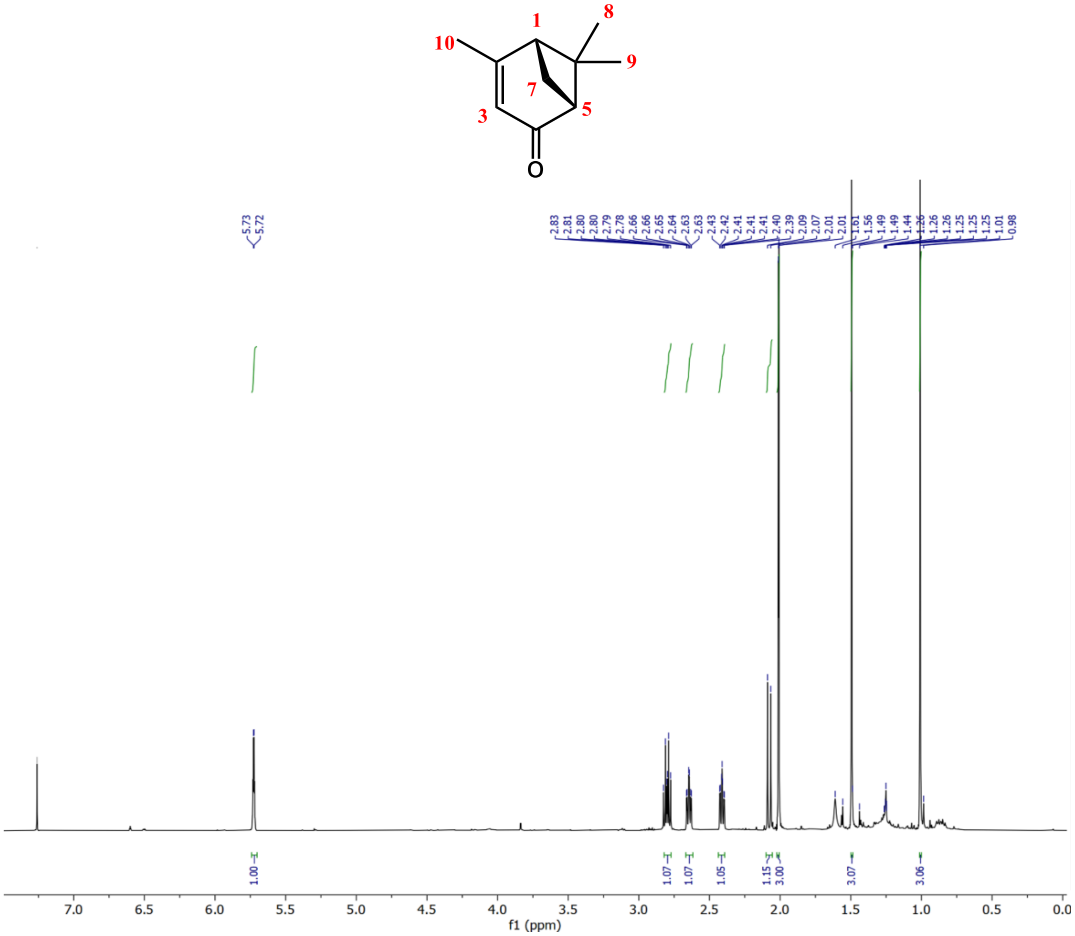


Figure S23. 1H NMR spectrum of the isolated verbenone obtained in the oxidation of α-pinene.

Verbenone - (9.3 mg, 9.7% yield); 1H NMR ($CDCl_3$, 300 MHz) δ 1.00 (s, 3H, CH3, H-9), 1.49 (s, 3H, CH3, H-8), 2.01 (d, 3H, H-10, CH3, J = 1.5 Hz), 2.07 (d, 1H, H-1, J = 9.5 Hz), 2.39–2.41 (m, 1H, H-7), 2.63–2.66 (m, 1H, m), 2.77–2.83 (m, 1H, H-5), 5.72–5.73 (m, 1H, H-3).[S4]

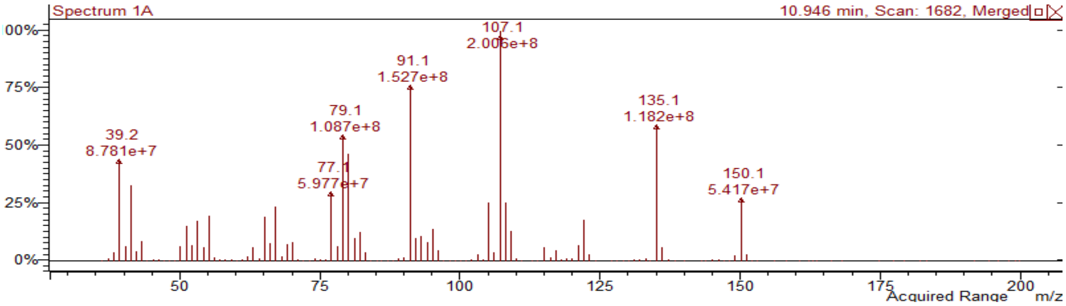


Figure S24. Mass spectrum of verbenone obtained in the oxidation of α-pinene. GC–MS (EI): m/z 150, 107 (C_4H_9O).

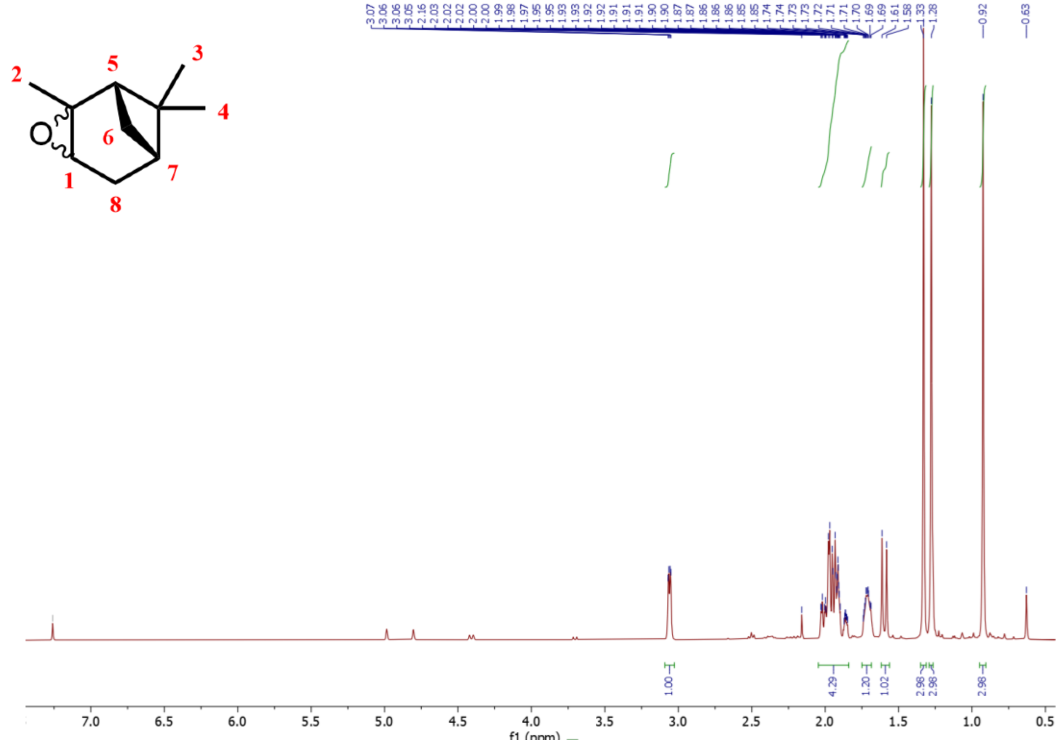


Figure S25. ^{1}H NMR spectrum of the isolated pinene oxide obtained in the oxidation of α-pinene.

Pinene oxide (GC reference): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.93 (s, 3H, H-4, CH_3), 1.28 (s, 3H, H-3, CH_3), 1.33 (s, 3H, H-2, CH_3), 1.62 (d, 2H, CH_2, H-8, *J* = 9.2 Hz), 1.68-1.74 (m, 1H, CH, H-7), 1.85-2.03 (m, 5H, CH_2, CH_2, CH correlate to H-8, H-6, H-5, respectively), 3.04 (d, 1H, CH, H-1, *J* = 3.9 Hz).[S5]

Table S9. Oxidation of α-pinene catalyzed by **Cu-mdea** and **Cu-tipa** with TBHP at 40ºC.[a]

Time (h)	**Cu-mdea**					**Cu-tipa**					**Blank**				
	Conv (%)[b]	Yield of the main products (%)[c]				Conv. (%)[b]	Yield of the main products (%)[c]				Conv. (%)[b]	Yield of the main products (%)[c]			
	A	**B**	**C**	**D**	**Total**	**A**	**B**	**C**	**D**	**Total**	**A**	**B**	**C**	**D**	**al**
0	0	nd	nd	nd	0	0	nd	nd	nd	0	0	nd	nd	nd	0
1	40.0	4.5	2.5	1.5	8.5	36.5	4.5	4.5	0.5	9.5	4.0	nd	0.5	nd	0.5
3	46.0	9.0	5.0	0.5	14.5	39.5	10.0	5.5	1.0	16.5	6.0	0.5	0.5	nd	1.0
6	53.5	15.0	5.5	0.5	21.0	42.0	13.0	5.0	0.5	18.5	8.5	1.5	0.5	nd	2.0
12	63.0	18.0	6.0	0.5	24.5	48.0	12.5	5.0	0.5	18.0	12.0	2.0	0.5	nd	2.5

[a]Conditions: α-pinene (0.6 mmol), **Cu-mdea** (1.0 mol%), TBHP (70% in H_2O; 1.2 mmol), CH_3CN (1 mL), 12 h, 1200 rpm, 40°C, catalytic flask (2 mL). [b] *Conversion*: [moles of α-pinene initial - moles of α-pinene final) / (moles of α-pinene) × 100%]. [c]*Yield* was determined by GC based on α-pinene: (moles of product per initial mol of α-pinene) × 100. (A: α-pinene; B: 4-*tert*-butylperoxy-2-pinene; C: verbenone; D: pinene oxide).

Table S10. Oxidation of α-pinene catalyzed by **Cu-mdea** and **Cu-tipa** with TBHP at 50ºC.[a]

Time (h)	**Cu-mdea**					**Cu-tipa**					**Blank**				
	Conv (%)[b]	Yield of the main products (%)[c]				Conv. (%)[b]	Yield of the main products (%)[c]				Conv. (%)[b]	Yield of the main products (%)[c]			
	A	**B**	**C**	**D**	**Total**	**A**	**B**	**C**	**D**	**Total**	**A**	**B**	**C**	**D**	**Total**
0	0	nd	nd	nd	0	0	nd	nd	nd	0	0	nd	nd	nd	0
1	50.5	9.5	5.5	1.0	16.0	55.0	8.5	5.0	0.5	14.0	4	nd	0.5	1.5	2.0
3	65.0	22.5	8.0	0.5	31.0	68.0	16.0	6.5	1.0	23.5	6.5	1.0	0.5	0.5	2.0
6	75.0	27.5	7.5	1.0	36.0	72.5	18.5	6.0	1.0	25.5	11.5	1.5	0.5	nd	2.0
12	74.5	32.5	8.5	1.0	42.0	69.5	23.5	6.0	0.5	30.0	20.0	2.0	0.5	nd	2.5

[a] Conditions: α-pinene (0.6 mmol), **Cu-mdea** (1.0 mol%), TBHP (70% in H_2O; 1.2 mmol), CH_3CN (1 mL), 12 h, 1200 rpm, 50°C, catalytic flask (2 mL). [b] *Conversion*: [moles of α-pinene initial - moles of α-pinene final) / (moles of α-pinene) × 100%]. [c] *Yield* was determined by GC based on α-pinene: (moles of product per initial mol of α-pinene) × 100. (A: α-pinene; B: 4-*tert*-butylperoxy-2-pinene; C: verbenone; D: pinene oxide).

Table S11. Oxidation of α-pinene catalyzed by **Cu-mdea** and **Cu-tipa** with TBHP at 60ºC.[a]

Time (h)	**Cu-mdea**					**Cu-tipa**					**Blank**				
	Conv (%)[b]	Yield of the main products (%)[c]				Conv. (%)[b]	Yield of the main products (%)[c]				Conv. (%)[b]	Yield of the main products (%)[c]			
	A	**B**	**C**	**D**	**Total**	**A**	**B**	**C**	**D**	**Total**	**A**	**B**	**C**	**D**	**Total**
0	0	nd	nd	nd	0	0	nd	nd	nd	0	0	nd	nd	nd	0
1	59.0	16.5	4.0	0.5	21.0	60.0	13.5	6.0	0.5	20.0	6.0	0.5	0.5	nd	1.0
3	78.0	26.0	8.0	0.5	34.5	75.0	29.0	7.0	0.5	36.5	7.0	1.0	0.5	nd	1.5
6	83.0	29.0	9.5	0.5	39.0	87.5	31.0	9.5	0.5	41.0	15.0	1.5	2.0	nd	3.5
12	90.0	29.5	13.5	0.5	43.5	92.0	30.0	13.5	nd	43.5	25.5	4.5	2.0	nd	6.5

[a]Conditions: α-pinene (0.6 mmol), **Cu-mdea** (1.0 mol%), TBHP (70% in H_2O; 1.2 mmol), CH_3CN (1 mL), 12 h, 1200 rpm, 60°C, catalytic flask (2 mL). [b]*Conversion*: [moles of α-pinene initial - moles of α-pinene final) / (moles of α-pinene) × 100%]. [c]*Yield* was determined by GC based on α-pinene: (moles of product per initial mol of α-pinene) × 100. (A: α-pinene; B: 4-*tert*-butylperoxy-2-pinene; C: verbenone; D: pinene oxide).

Table S12. Oxidation of α-pinene catalyzed by **Cu-mdea** and **Cu-tipa** with TBHP at 70 ºC.[a]

Time (h)	**Cu-mdea**					**Cu-tipa**					**Blank**				
	Conv (%)[b]	Yield of the main products (%)[c]				Conv. (%)[b]	Yield of the main products (%)[c]				Conv. (%)[b]	Yield of the main products (%)[c]			
	A	**B**	**C**	**D**	**Total**	**A**	**B**	**C**	**D**	**Total**	**A**	**B**	**C**	**D**	**Total**
0	0	nd	nd	nd	0	0	nd	nd	nd	0	0	nd	nd	nd	0
0.25	40.5	6.0	3.5	4.0	13.5	40.0	6.5	2.5	3.0	12.0	3.0	nd	0.5	nd	0.5
0.5	70.0	13.5	7.0	4.5	25.0	75.0	11.5	8.5	4.5	24.5	7.0	nd	1.0	nd	1.0
1	79.0	19.5	10.0	4.0	33.5	79.0	17.0	9.5	4.0	30.5	12.0	0.5	4.0	nd	4.5
3	88.5	28.0	12.5	3.0	43.5	87.0	30.0	12.0	4.0	46.0	17.0	1.0	3.0	2.0	6.0
6	91.5	31.0	15.0	0.5	46.5	92.5	31.0	14.0	nd	45.0	25.5	1.5	2.0	0.5	4.0
12	92.5	30.0	14.5	0.5	45.0	92.5	30.0	14.5	nd	45.5	29.5	4.5	2.0	0.5	7.0

[a]Conditions: α-pinene (0.6 mmol), **Cu-mdea** (1.0 mol%), TBHP (70% in H_2O; 1.2 mmol), CH_3CN (1 mL), 12 h, 1200 rpm, 70°C, catalytic flask (2 mL). [b]*Conversion:* [moles of α-pinene initial - moles of α-pinene final) / (moles of α-pinene) × 100%]. [c]*Yield* was determined by GC based on α-pinene: (moles of product per initial mol of α-pinene) × 100. (A: α-pinene; B: 4-*tert*-butylperoxy-2-pinene; C: verbenone; D: pinene oxide).

Table S13. Oxidation of α-pinene catalyzed by **Cu-mdea** and **Cu-tipa** with TBHP at 80ºC.[a]

Time (h)	**Cu-mdea**					**Cu-tipa**					**Blank**				
	Conv (%)[b]	Yield of the main products (%)[c]				Conv. (%)[b]	Yield of the main products (%)[c]				Conv. (%)[b]	Yield of the main products (%)[c]			
	A	**B**	**C**	**D**	**Total**	**A**	**B**	**C**	**D**	**Total**	**A**	**B**	**C**	**D**	**Total**
0	0	nd	nd	nd	0	0	nd	nd	nd	0	0	nd	nd	nd	0
0.25	65.5	9.5	6.5	4.0	20.0	43.0	7.5	3.5	4.5	15.5	6.0	nd	1.0	nd	1.0
0.5	78.0	17.0	10.5	4.5	32.0	76.0	13.5	9.0	4.5	27.0	8.0	0.5	1.5	nd	2.0
1	82.5	27.0	12.0	3.5	42.5	80.5	23.5	10.0	5.0	38.5	15.5	1.0	5.0	nd	6.0
3	91.0	32.0	14.0	2.0	48.0	89.5	30.0	15.0	0.5	45.5	22.5	1.5	4.0	2.5	8.0
6	91.5	33.0	15.5	0.5	49.0	92.0	36.5	18.0	nd	54.5	27.5	2.0	3.0	1.0	6.0
12	90.5	32.0	17.0	nd	49.0	94.0	28.5	17.5	nd	46.0	34.0	5.5	3.0	0.5	9.0

[a] Conditions: α-pinene (0.6 mmol), **Cu-mdea** (1.0 mol%), TBHP (70% in H_2O; 1.2 mmol), CH_3CN (1 mL), 12 h, 1200 rpm, 80°C, catalytic flask (2 mL). [b] *Conversion:* [moles of α-pinene initial - moles of α-pinene final) / (moles of α-pinene) × 100%]. [c] *Yield* was determined by GC based on α-pinene: (moles of product per initial mol of α-pinene) × 100. (A: α-pinene; B: 4-*tert*-butylperoxy-2-pinene; C: verbenone; D: pinene oxide).

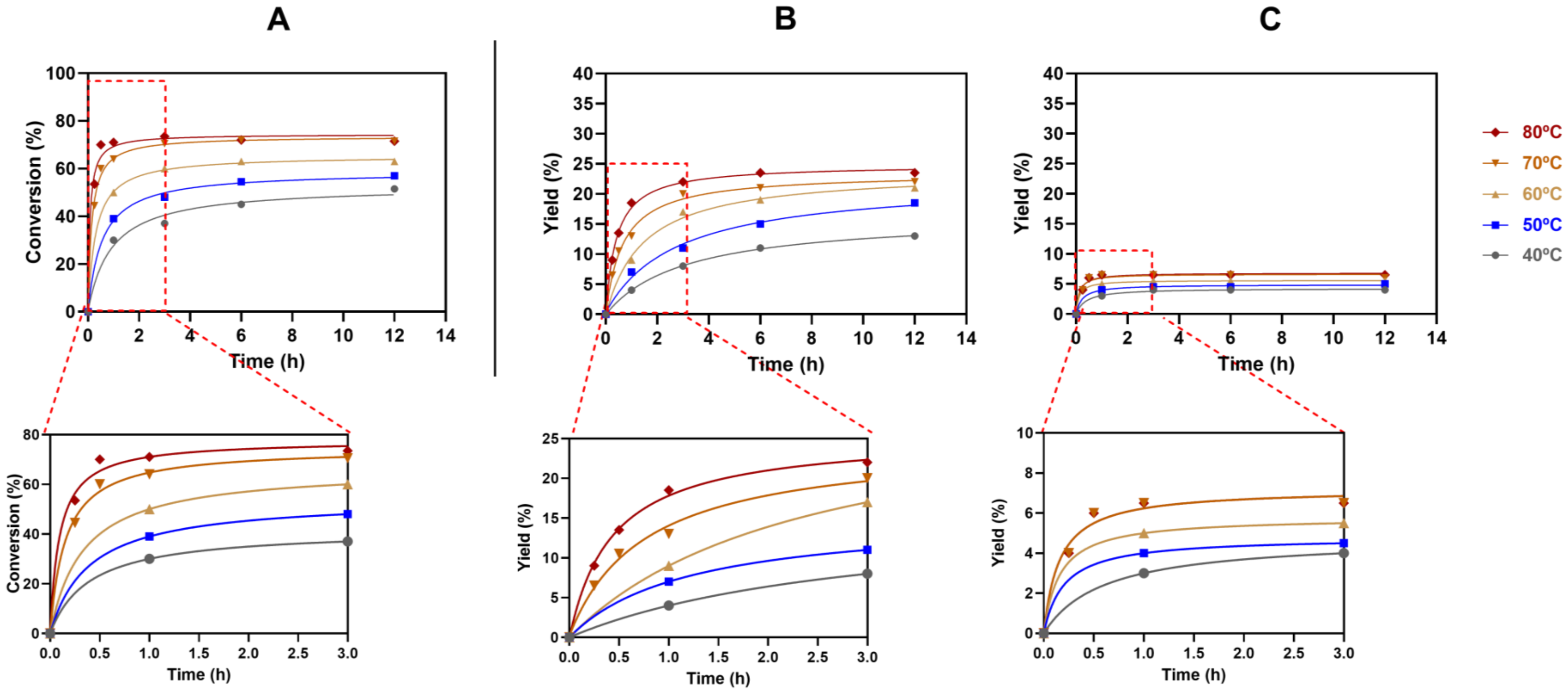


Figure S26. Cu-catalyzed oxidation of α-pinene over **Cu-mdea** with temperature ranging from 40ºC to 80ºC. (A) Conversion of α-pinene. Accumulation of 4-*tert*-butylperoxy-2-pinene (B) and verbenone (C). Conditions: α-pinene (0.6 mmol), **Cu-mdea** (1 mol%), TBHP (70% in H_2O; 1.2 mmol), CH_3CN (1 mL), 12 h, 1200 rpm, catalytic flask (2 mL).

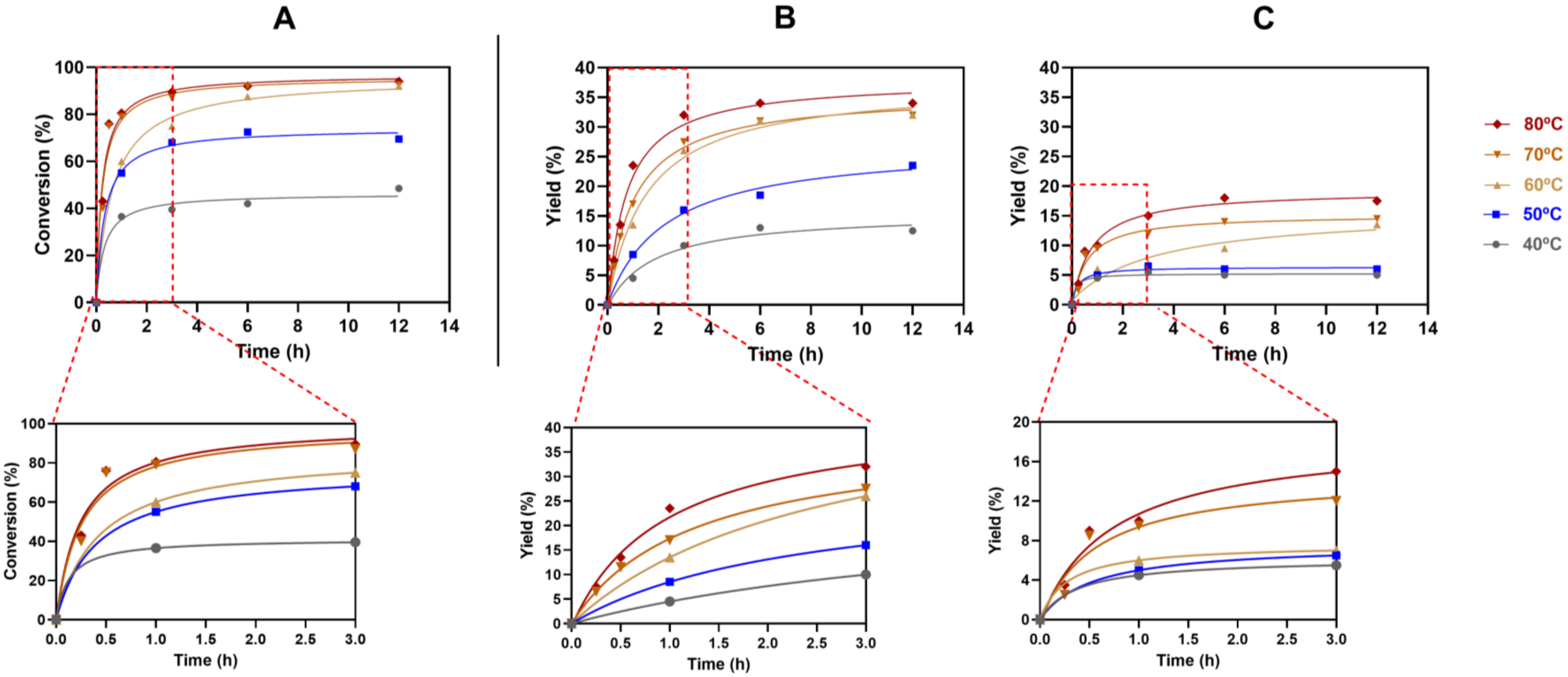


Figure S27. Cu-catalyzed oxidation of α-pinene over **Cu-tipa** with temperature ranging from 40ºC to 80ºC. (A) Conversion of α-pinene. Accumulation of 4-*tert*-butylperoxy-2-pinene (B) and verbenone (C). Conditions: α-pinene (0.6 mmol), **Cu-tipa** (1 mol%), TBHP (70% in H_2O; 1.2 mmol), CH_3CN (1 mL), 12 h, 1200 rpm, catalytic flask (2 mL).

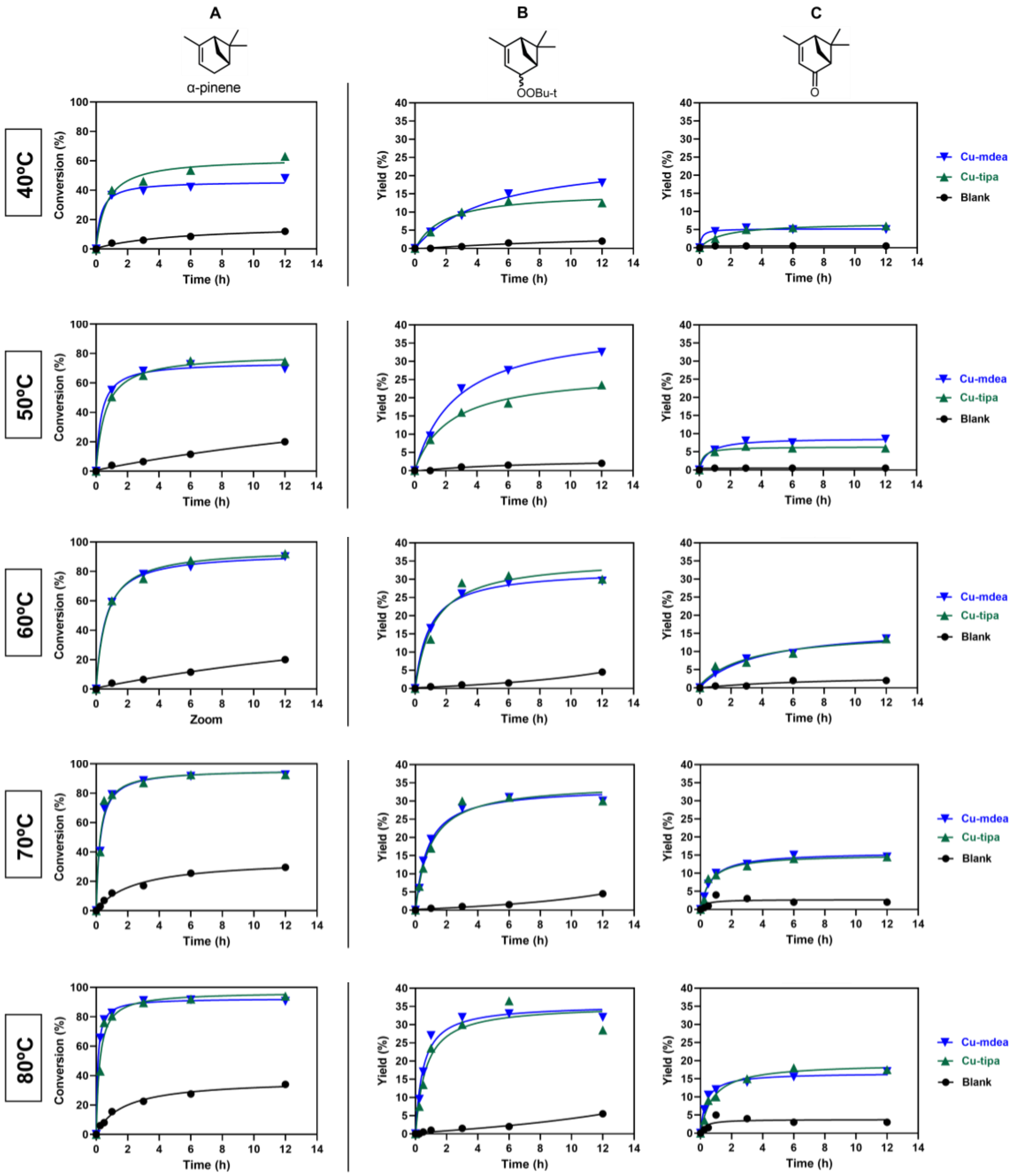


Figure S28. Cu-catalyzed oxidation of α-pinene over different copper-containing compounds and blank, ranging temperature from 40ºC to 80ºC. (A) Conversion of α-pinene. Accumulation of 4-*tert*-butylperoxy-2-pinene (B) and verbenone (C). Conditions: α-pinene (0.6 mmol), Catalyst (1 mol%), TBHP (70% in H_2O; 1.2 mmol), CH_3CN (1 mL), 12 h, 1200 rpm, catalytic flask (2 mL).

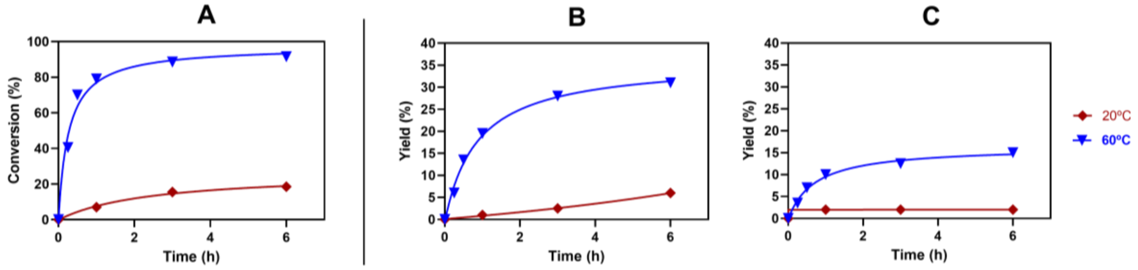


Figure S29. Cu-catalyzed oxidation of α-pinene over **Cu-mdea** at room temperature (blue) and at 60ºC. (A) Conversion of α-pinene. Accumulation of 4-*tert*-butylperoxy-2-pinene (B) and verbenone (C). Conditions: α-pinene (0.6 mmol), **Cu-mdea** (1 mol%), TBHP (70% in H_2O; 1.2 mmol), CH_3CN (1 mL), 12 h, 1200 rpm, 60°C, catalytic flask (2 mL).

Table S14. Catalyst recycling test of **Cu-mdea** and **Cu-tipa**.[a]

Entry	Catalyst (1 mol%)[b]	Cycles	Conv. (%)[c]	Yield of the main products (%)[d]				TOF[e] (h^{-1})
			A	**B**	**C**	**D**	**Total**	
1	**Cu-mdea**	2x	82.0	31.0	16.0	1.0	48.0	13.6
2		3x	80.0	31.0	16.0	1.0	48.0	13.4
3		4x	75.5	31.0	14.0	0.5	45.0	12.6
4	**Cu-tipa**	2x	86.0	31.0	13.0	1.0	45.0	14.3
5		3x	78.5	30.0	11.5	0.5	42.0	13.8
6		4x	72.5	16.0	8.5	1.0	25.5	12.1

[a]Conditions. Catalyst recycling test of **Cu-mdea** and **Cu-tipa**. Conditions: α-pinene (0.6 mmol), $Cu(NO_3)_2$ (1 mol%), TBHP (70% in H_2O; 1.2 mmol), CH_3CN (1 mL), 6 h, 1200 rpm, 60°C, catalytic flask (2 mL). [b]*mol%:* [moles of catalyst / (moles of catalyst + moles of α-pinene) × 100%]. [c]*Conversion:* [moles of α-pinene initial - moles of α-pinene final) / (moles of α-pinene) × 100%]. [d]*Yield* was determined by GC based on α-pinene: (moles of product per initial mol of α-pinene) × 100. [e]*TOF:* [(mols of substrate $_{(t=0)}$ × Conv. (%)] / (mols of catalyst × t(h) x 100)]. (A: α-pinene; B: 4-*tert*-butylperoxy-2-pinene; C: verbenone; D: pinene oxide).

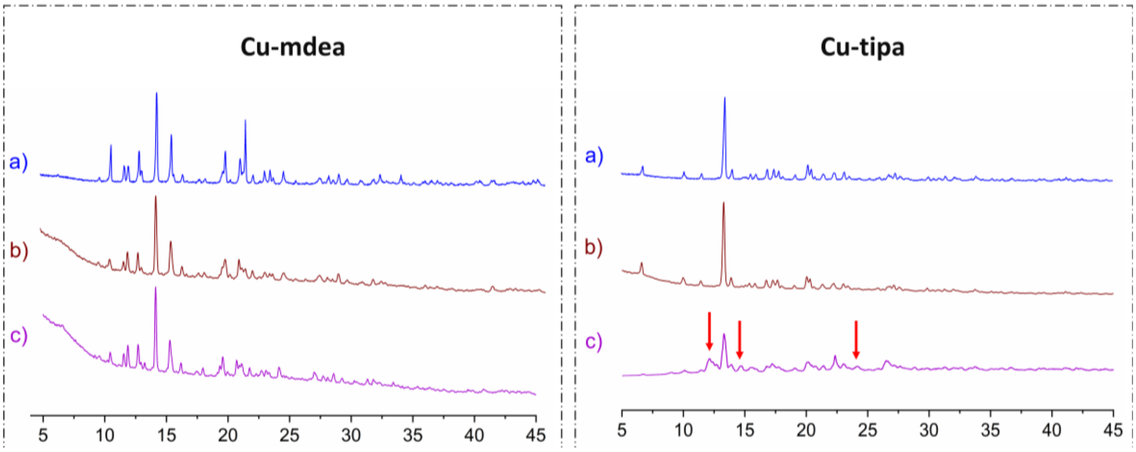


Figure S30. PXRD patterns of **Cu-tipa** (left) and **Cu-mdea** (right): (a) prior to the initial reaction, (b) after the first catalytic run, and (c) after four consecutive runs. (The red arrows highlight the additional crystallographic phases encountered in **Cu-tipa**).

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