Supplementary Information (SI) for Inorganic Chemistry Frontiers.

Electronic Supplementary Information (ESI)

Copper Pyridinedicarboxylates: Assembly, Structures, and Catalytic Oxidation of Terpenes

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ESI includes additional data on the synthesis, characterization, and catalytic application of **1**−**3** (Figures S1−36, Tables S1−S20).

Section 1 – Characterization of Compounds 1, 2 and 3.

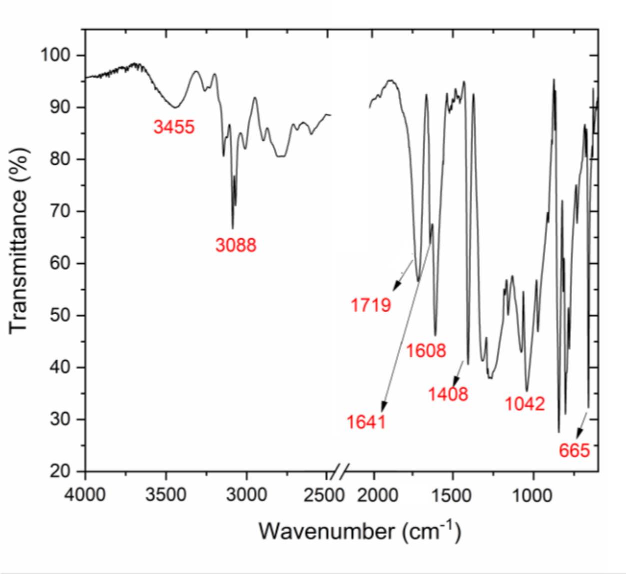

Figure S1. FT-IR spectrum of 3,4-Pyridinedicarboxylic acid.

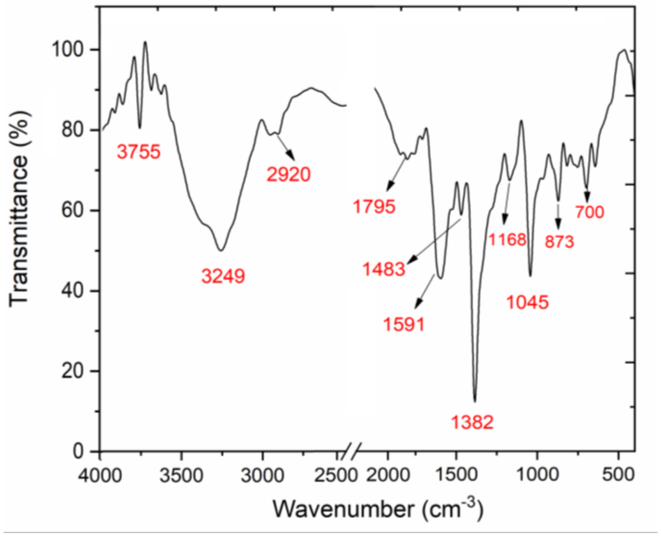

Figure S2. FT-IR spectrum of **1**.

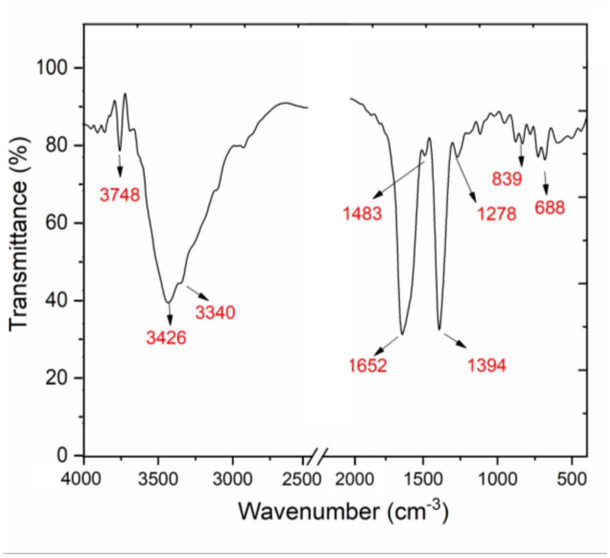

Figure S3. FT-IR spectrum of **2**.

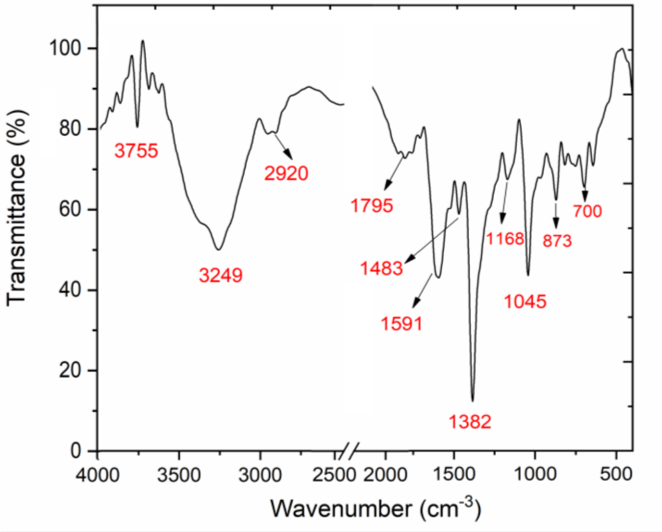

Figure S4. FT-IR spectrum of **3**.

Materials and Methods. All chemicals and solvents were acquired commercially and utilized without any prior preparation.

Characterization. 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. GC (gas chromatography) analyses were conducted using an Agilent Technologies 7820A series gas chromatograph with helium as the carrier gas and a flame ionization detector. GC-MS analyses were performed on a Scion 436-GC equipped with an electron impact ionization source and a single quadrupole analyzer. Both instruments were fitted with a polar BP20/SGE column (30 m × 0.25 mm × 0.25 μm).

The thermogravimetric analysis (TGA) of **1** and **2** reveals distinct temperatures for the initial endothermic effect. For **1**, it occurs between 130 and 200 °C, whereas for **2**, it is observed at a lower temperature range of 60–110 °C (see Figures S5 and S6). This endothermic event corresponds to the release of all water molecules, resulting in a mass loss of 4.4% (calcd. 4.4%) for **1** and 14.1% (calcd. 14.2%) for **2**. Subsequent thermal effects indicate a gradual decomposition of the samples, beginning at ~190–200 °C and ending by ~380–450 °C. This decomposition leads to the formation of CuO in **1** (remaining sample weight: exp. 19.0%, calcd. 19.3%) and 2CuO in **2** (remaining sample weight: exp. 24.7%, calcd. 25.1%). Additionally, the experimental powder X-ray diffraction (PXRD) patterns of **1** and **2** (Figures S7 and S8) closely match the diffractograms simulated from the CIF files.

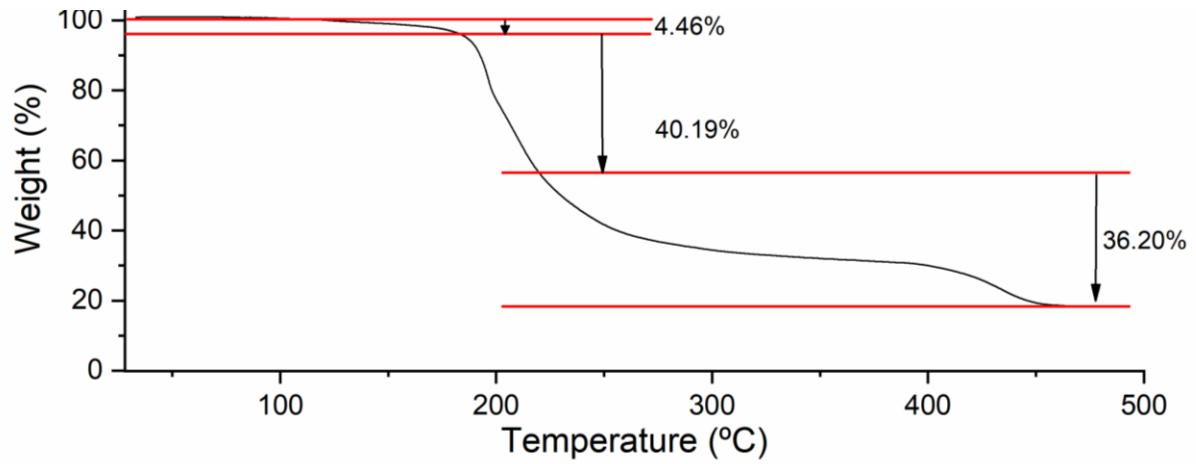

Figure S5. Thermogravimetric analysis of **1**.

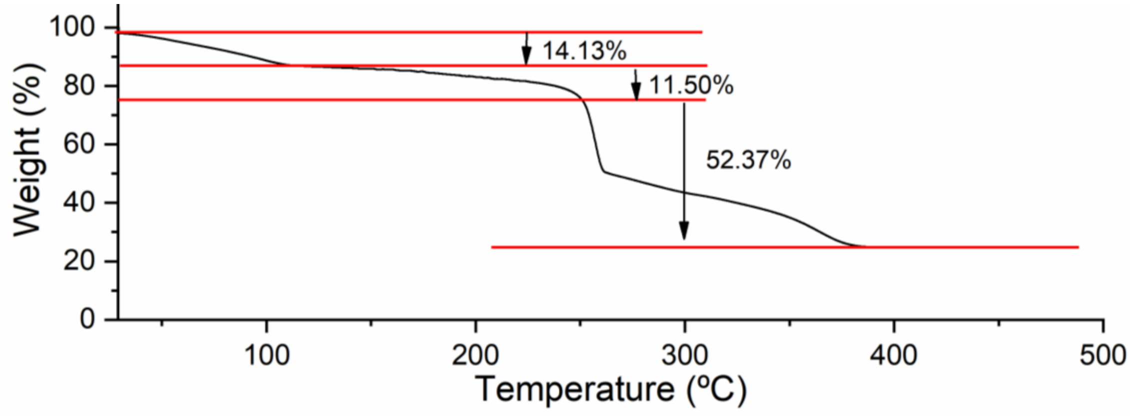

Figure S6. Thermogravimetric analysis of **2**.

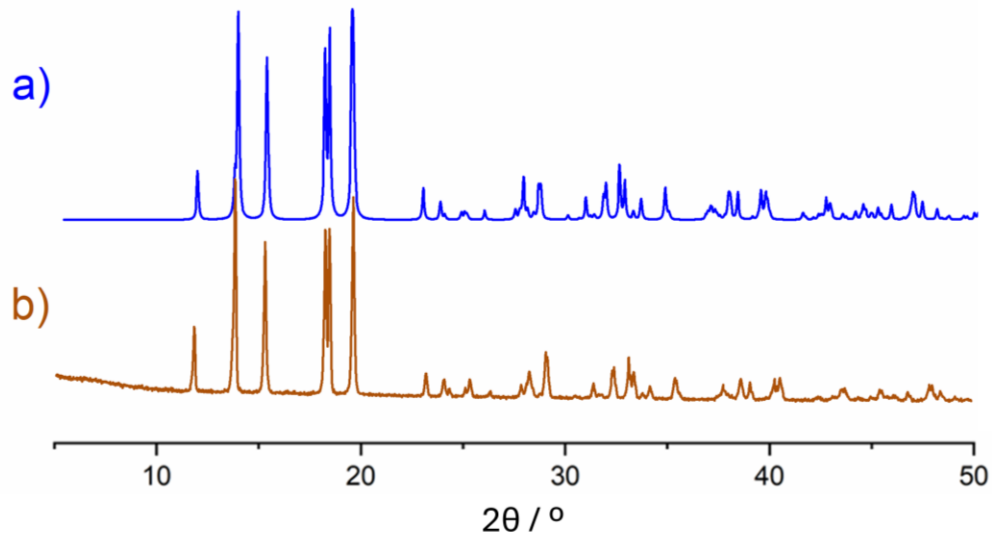

Figure S7. PXRD patterns for **0D** (a) simulated and (b) experimental.

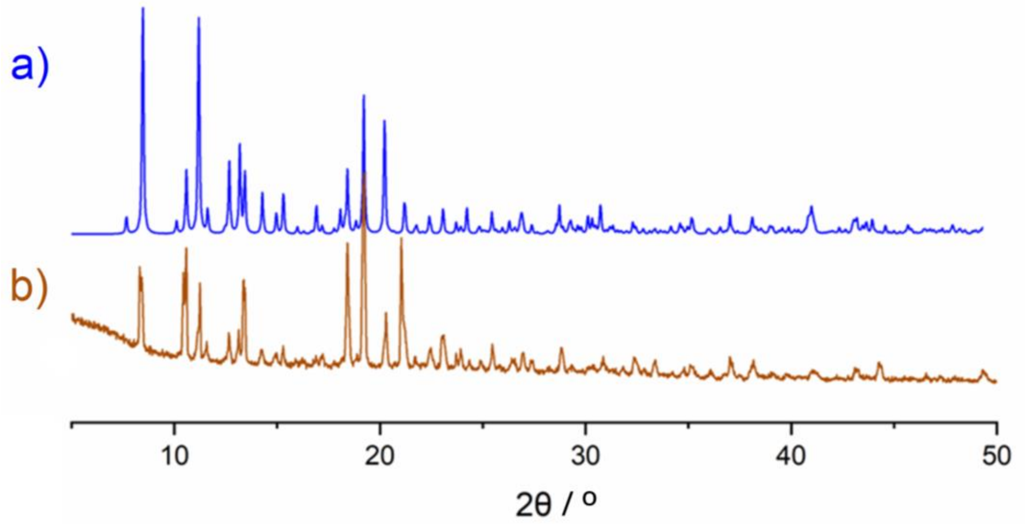

Figure S8. PXRD patterns for **2** (a) simulated and (b) experimental.

Table S1. Bond Lengths for **1**.

Atoms	*Length/Å*	*Atoms*	*Length/Å*
Cu1—O3	2.0163 (18)	O7—C10	1.232 (3)
Cu1—O2	2.0131 (18)	O5—C7	1.220 (4)
Cu1—O4	2.3166 (19)	O8—C10	1.271 (3)
Cu1—N2	1.991 (2)	C7—O6	1.262 (3)
Cu1—N1	2.015 (2)		

Table S2. Bond Angles for **1**.

Atoms	*Angle/°*	*Atoms*	*Angle/°*
O3—Cu1—O4	88.56 (7)	N2—Cu1—O4	96.33 (7)
O2—Cu1—O3	166.95 (8)	N2—Cu1—N1	169.23 (9)
O2—Cu1—O4	87.29 (7)	N1—Cu1—O3	85.24 (8)
O2—Cu1—N1	82.73 (8)	N1—Cu1—O4	94.23 (8)
N2—Cu1—O3	97.13 (8)	O7—C10—O8	126.8 (3)
N2—Cu1—O2	95.62 (8)		

Table S3. Bond Lengths for **2**.

Atoms	*Length/Å*	*Atoms*	*Length/Å*
Cu1—N22	2.021 (7)	Cu2—O4	2.063 (6)
Cu1—N1	2.007 (7)	O2—C20	1.263 (11)
Cu1—O3	1.949 (6)	O5—C12	1.270 (11)
Cu1—O5	1.967 (6)	O6—C20	1.228 (11)
Cu1—O14	2.256 (8)	C11—O18	1.195 (12)
Cu2—O2	1.928 (6)	C12—O13	1.219 (12)
Cu2—O17	2.030 (8)	O1—C3	1.208 (11)
Cu2—O19	1.982 (8)	C3—O4	1.249 (11)

Table S4. Bond Angles for **2**.

Atoms	*Angle/°*	*Atoms*	*Angle/°*
N22—Cu1—O14	93.2 (3)	O5—Cu1—N1	89.4 (3)
N1—Cu1—N22	178.4 (3)	O5—Cu1—O14	93.4 (3)
N1—Cu1—O14	88.1 (3)	O2—Cu2—O17	91.6 (3)
O3—Cu1—N22	89.0 (3)	O2—Cu2—O19	164.5 (3)
O3—Cu1—N1	90.2 (3)	O2—Cu2—O4	93.7 (3)
O3—Cu1—O5	172.8 (3)	O17—Cu2—O4	167.2 (3)
O3—Cu1—O14	93.8 (3)	O19—Cu2—O17	88.2 (3)
O5—Cu1—N22	91.3 (3)	O19—Cu2—O4	89.7 (3)

Table S5. Bond Lengths for **3**.

Atoms	*Length/Å*	*Atoms*	*Length/Å*
Cu1—O3^{i}	1.974 (6)	O1—Cu2	2.306 (7)
Cu1—O3	1.974 (6)	O5—Cu2	2.387 (15)

Cu1—N1^{ii}	2.051 (7)	Cu2—O4^{iv}	2.258 (8)
Cu1—N1^{iii}	2.051 (7)	Cu2—O4^{ii}	2.258 (8)
Cu1—O6	2.240 (12)		

Symmetry codes: (i) y, x, −z+1; (ii) x−1/2, −y+3/2, −z+5/4; (iii) −y+3/2, x−1/2, z−1/4; (iv) y−1/2, −x+3/2, z+1/4.

Table S6. Bond Angles for **3**.

Atoms	***Angle/°***	***Atoms***	***Angle/°***
O3^{i}—Cu1—O3	165.4 (4)	O1^{vi}—Cu2—O5^{vi}	96.4 (4)
O3^{i}—Cu1—N1^{ii}	89.9 (3)	O1—Cu2—O5^{vi}	93.1 (4)
O3—Cu1—N1^{ii}	90.2 (3)	O1^{vi}—Cu2—O5	93.1 (4)
O3^{i}—Cu1—N1^{iii}	90.2 (3)	O1—Cu2—O5	96.4 (4)
O3—Cu1—N1^{iii}	89.9 (3)	O5^{vi}—Cu2—O5	166.9 (7)
O3—Cu1—O6	97.28 (19)	O4^{ii}—Cu2—O1	90.2 (3)
O3^{i}—Cu1—O6	97.28 (19)	O4^{iv}—Cu2—O1	175.5 (4)
N1^{ii}—Cu1—N1^{iii}	179.2 (5)	O4^{ii}—Cu2—O1^{vi}	175.5 (4)
N1^{ii}—Cu1—O6	89.6 (2)	O4^{iv}—Cu2—O1^{vi}	90.2 (3)
N1^{iii}—Cu1—O6	89.6 (2)	O4^{iv}—Cu2—O5^{vi}	83.3 (5)
C7—O3—Cu1	115.6 (6)	O4^{ii}—Cu2—O5^{vi}	87.7 (5)
C1—O1—Cu2	138.9 (6)	O4^{iv}—Cu2—O5	87.7 (5)
C5—N1—Cu1^{v}	118.6 (6)	O4^{ii}—Cu2—O5	83.3 (5)
C4—N1—Cu1^{v}	123.4 (6)	O4^{ii}—Cu2—O4^{iv}	92.3 (4)
O1—Cu2—O1^{vi}	87.5 (4)	C7—O4—Cu2^{vii}	164.3 (10)

Symmetry codes: (i) y, x, −z+1; (ii) x−1/2, −y+3/2, −z+5/4; (iii) −y+3/2, x−1/2, z−1/4; (iv) y−1/2, −x+3/2, z+1/4; (v) y+1/2, −x+3/2, z+1/4; (vi) −y+1, −x+1, −z+3/2; (vii) −y+3/2, x+1/2, z−1/4.

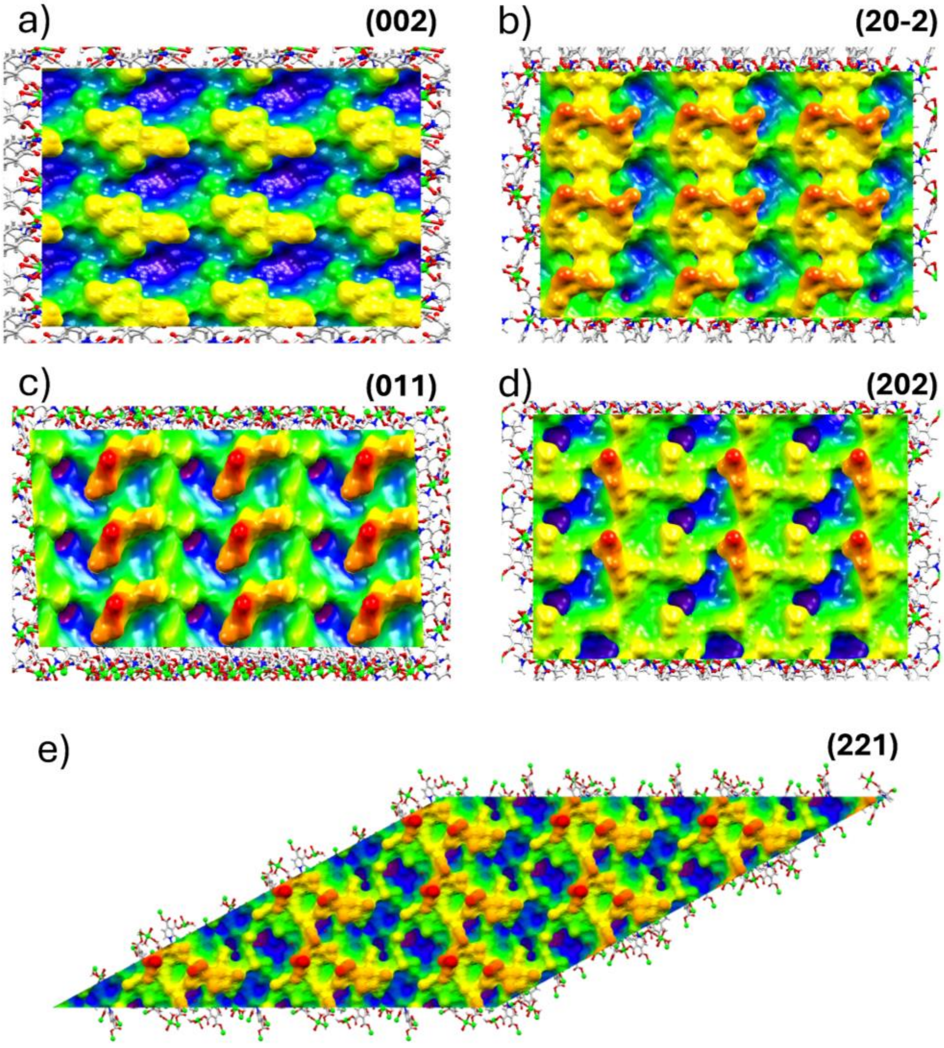

Figure S9. Surface coloring topology from different crystallographic faces of **2**, highlighting the distribution of $[Cu(DMF)]^{2+}$ $[Cu(H_2O)]^{2+}$. (a) Yellow regions for both copper centers. (b) Orange regions for $[Cu(H_2O)]^{2+}$ and yellow regions for $[Cu(DMF)]^{2+}$. (c - e) Red-orange regions for $[Cu(H_2O)]^{2+}$ and yellow region for $[Cu(DMF)]^{2+}$. The blue-purple regions represent the hollows features in all surfaces.

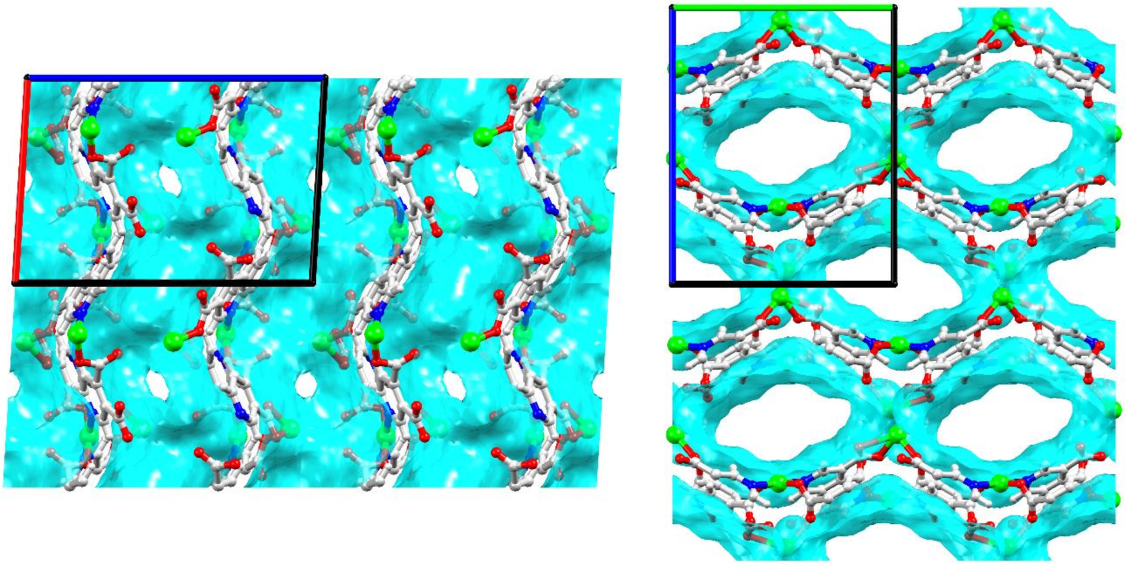

Figure S10. Representation of void regions between 2D metal-organic layers of **2** in two different views, where the porous areas (light blue color) account for 50.3% of the unit cell volume, calculated based on the 2×2×2 contact surface packing, excluding solvent molecules (H_2O and DMF). Color codes: Cu: green; O: red; N: blue; C: gray.

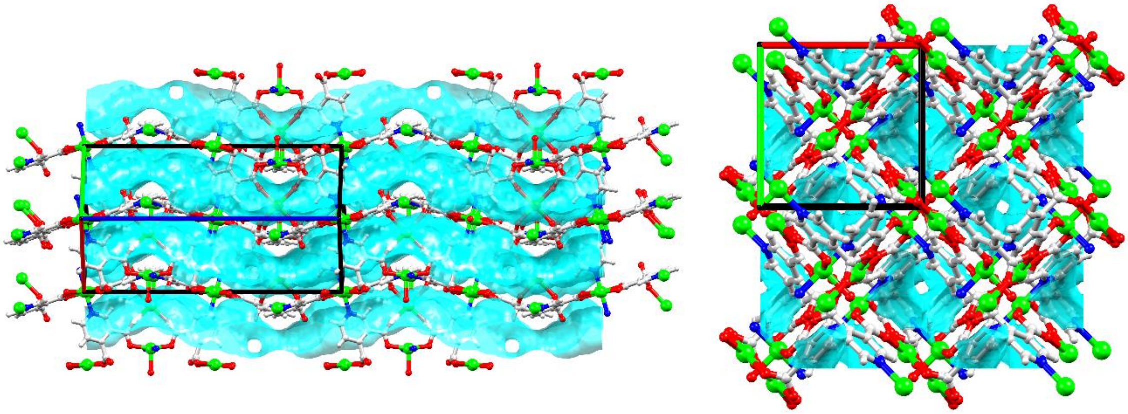

Figure S11. Representation of void regions of **3** in two different views, where the porous areas (light blue color) account for 33.0% of the unit cell volume, calculated based on the 2×2×2 contact surface packing, excluding solvent molecules (H_2O). Color codes: Cu: green; O: red; N: blue; C: gray.

Section 2 – Catalytic Studies

Oxidation reactions: 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 taken from the reaction medium (12 μL in the case of α-pinene and 15 μL in the case of (+)-valencene mixed with CH_3NO_2 (9 μL, an internal standard), and diluted in 400 μL acetonitrile. Afterwards, 1 μL of this solution was injected in GC at a temperature of 240°C and at 1:50 split ratio. To monitor the oxidation of α-pinene, the temperature program of the oven was 100°C for 6 min and then gradually increase until 180°C with rate of 10°C min^{-1}. For the oxidation of valencene, the temperature program was 100°C for 4 min, 20°C min^{-1} until 180°C for 4 min and, 10°C min^{-1} until 220°C for 7 min. 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.

The number of mols (*n*) of α-pinene, pinene oxide, verbenone and valencene were determined by calibration curve, in which the angular coefficients (*a*) were 10.93, 9.38, 9.50, and 14.01 respectively. For verbenol, the (*a*) was considered the same as verbenone. The number of mols (*n*) of nootkatone the inverse function of angular coefficient was determined by correlation between the peak area of the isolated product (0.15 mmol) and (+)-valencene (0.15 mmol), i.e., $\left(\frac{1}{a}\right)_{Nootkatone} = 1.27 \times \left(\frac{1}{a}\right)_{Valencene}$.

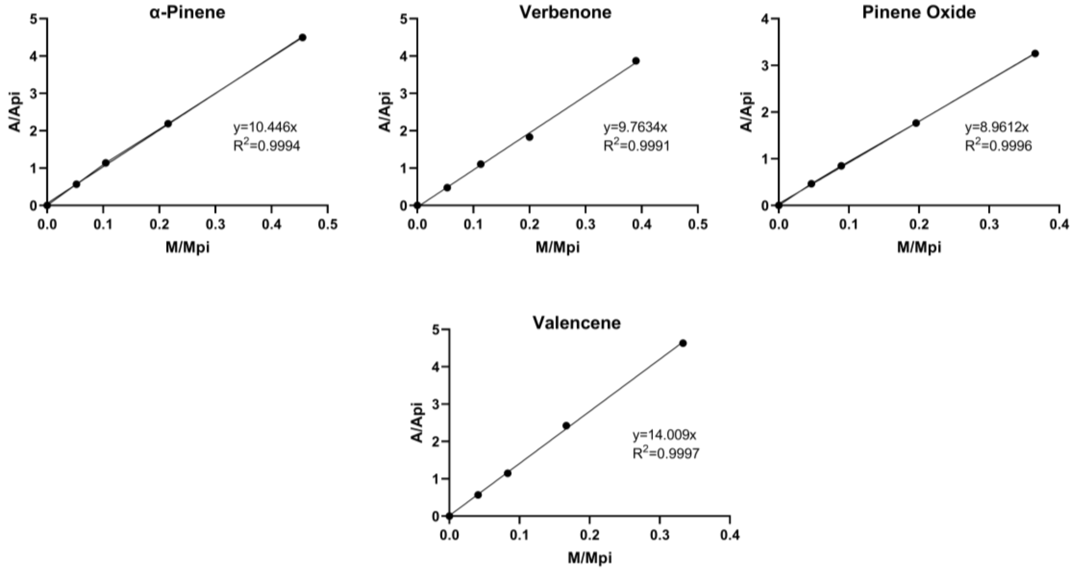

Figure S12. Calibration curves for α-pinene, pinene oxide, verbenone, and valencene.

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

A - peak area

n – number of mols

a – angular coefficient

$\boldsymbol{A_{IS}}$ - peak area of internal standard

$\boldsymbol{n_{IS}}$ – number of mols of internal standard

Purification of (+)-nootkatone by preparative TLC. A qualitative purification was performed using DC-Fertigplatten SIL G-25 pre-coated TLC plates with an eluent solution of dichloromethane, methanol (6:4 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 ^{1}H spectra were obtained on 400 MHz NMR spectrometers (Varian Inc.), using deuterated chloroform as solvent. The chemical shifts (δ) are relative to tetramethylsilane (TMS), used as the internal standard.

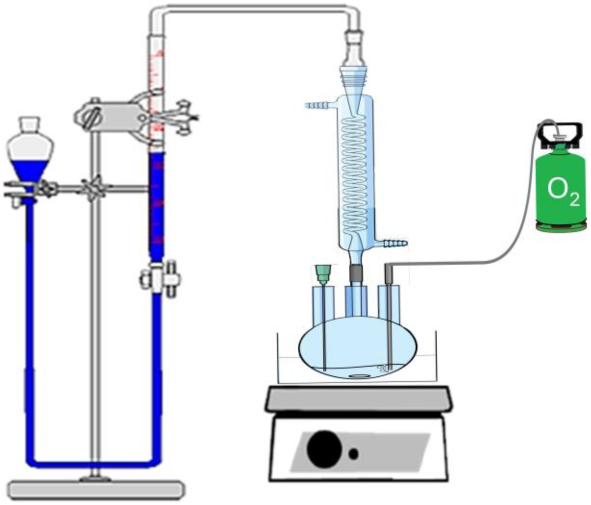

Figure S13. Schematic representation of the Apparatus used in the oxidation reactions with oxygen.

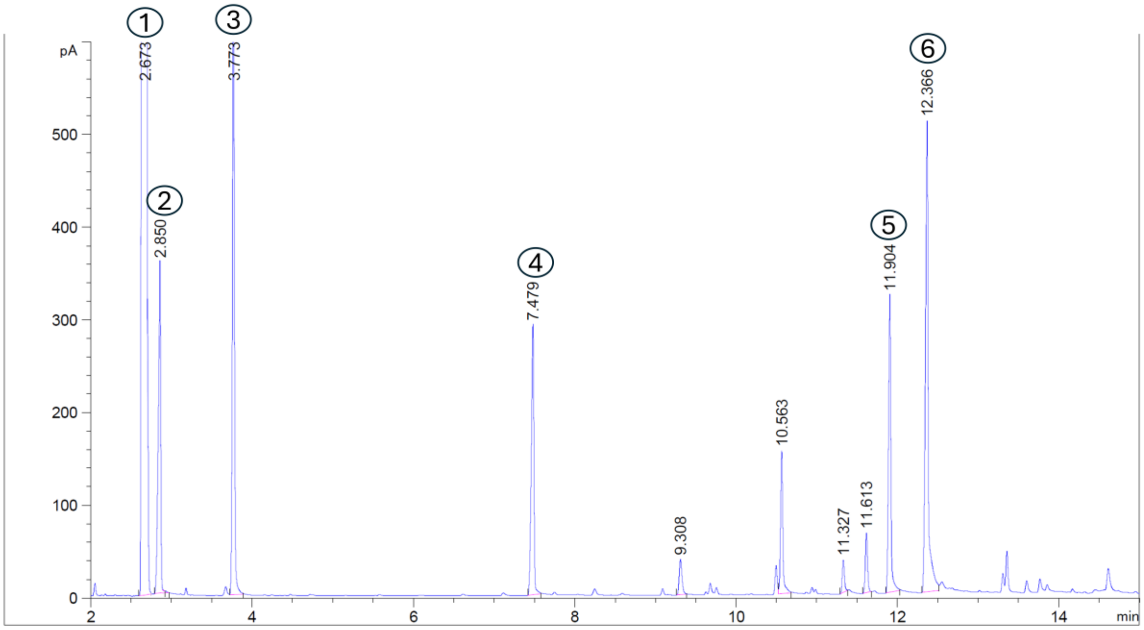

Figure S14. Fragment of a typical gas chromatogram of the reaction mixture in the Cu-catalyzed oxidation of α-pinene before addition of PPh_3. Conditions: α-pinene (1 mL), precatalyst (15 μmol), TBHP (70% in H_2O; 0.35 mmol), 9h, 800 rpm, 70 °C, O_2 (14 mL·min^{-1}). Identification: (1) CH_3CN (GC solvent), (2) α-pinene, (3) nitromethane (GC standard), (4) pinene oxide, (5) verbenol and (6) verbenone.

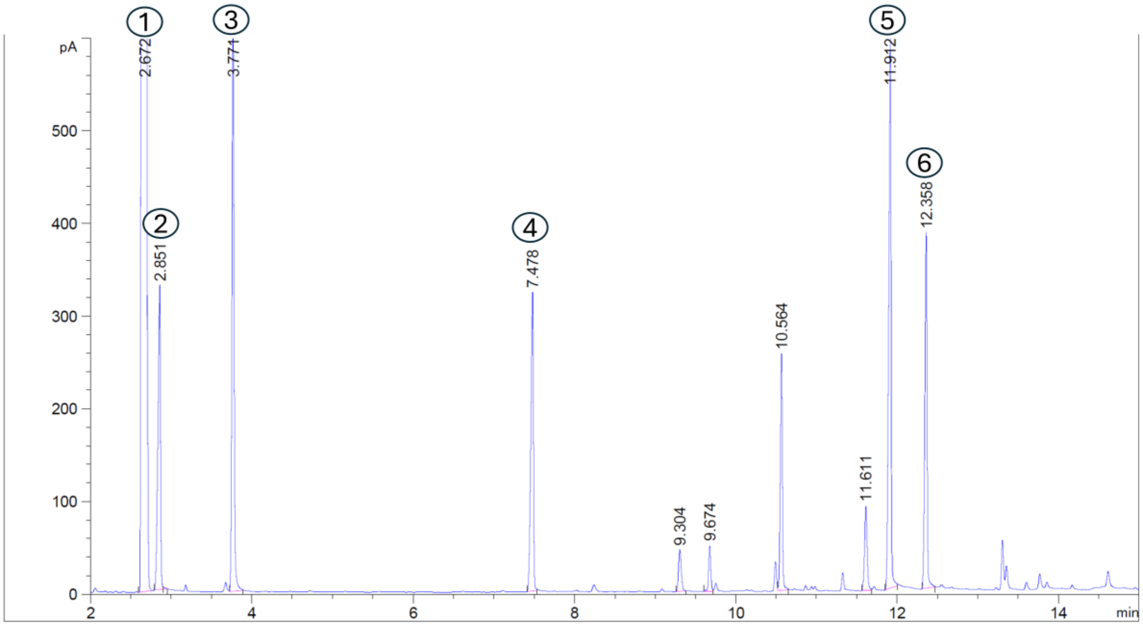

Figure S15. Fragment of a typical gas chromatogram of the reaction mixture (after the addition of PPh_3) in the Cu-catalyzed oxidation of α-pinene. Conditions: α-pinene (1 mL), precatalyst (15 μmol), TBHP (70% in H_2O; 0.35 mmol), 9h, 800 rpm, 70 °C, O_2 (14 mL·min^{-1}). Identification: (1) CH_3CN (GC solvent), (2) α-pinene, (3) nitromethane (GC standard), (4) pinene oxide, (5) verbenol and (6) verbenone.

Table S7. Cu-catalyzed Oxidation of α-Pinene-in the Presence of Compounds **1**, **2** and **3** in Comparison with Metal Free Reaction (Blank Test).[a]

Entry	Precatalyst (ID)	Time (h)	Conversion (%)[b]	Yield of the main products (%)[c]			
			A	**B**	**C**	**D**	**Total**
1	Blank	0	0	0	0	0	0
2		3	22.5	1.5	2.5	0.5	4.5
3		6	34.0	3.0	3.0	1.0	7.0
4		9	41.0	6.0	4.5	3.0	13.5
5	**1**	0	0	0	0	0	0
6		3	51.5	6.0	4.0	1.0	11.0
7		6	68.5	8.0	6.5	2.0	16.5
8		9	90.0	12.5	7.0	6.5	26.0
9	**2**	0	0	0	0	0	0
10		3	51.5	13.5	6.0	2.5	22.0
11		6	69.0	20.5	11.0	7.5	39.0
12		9	92.0	25.0	14.0	11.0	50.0
13	**3**	0	0	0	0	0	0
14		3	33.0	6.5	4.0	0.5	11.0
15		6	51.5	11.0	8.5	1.5	21.0
16		9	82.0	12.5	9.5	3.5	**25.5**

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[a] Conditions: α-pinene (1 mL), precatalyst (15 µmol), TBHP (70% in H_2O; 0.35 mmol), 9h, 800 rpm, 70 °C, O_2 (14 $mL\cdot min^{-1}$). [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: verbenone; C: pinene oxide; D: verbenol).

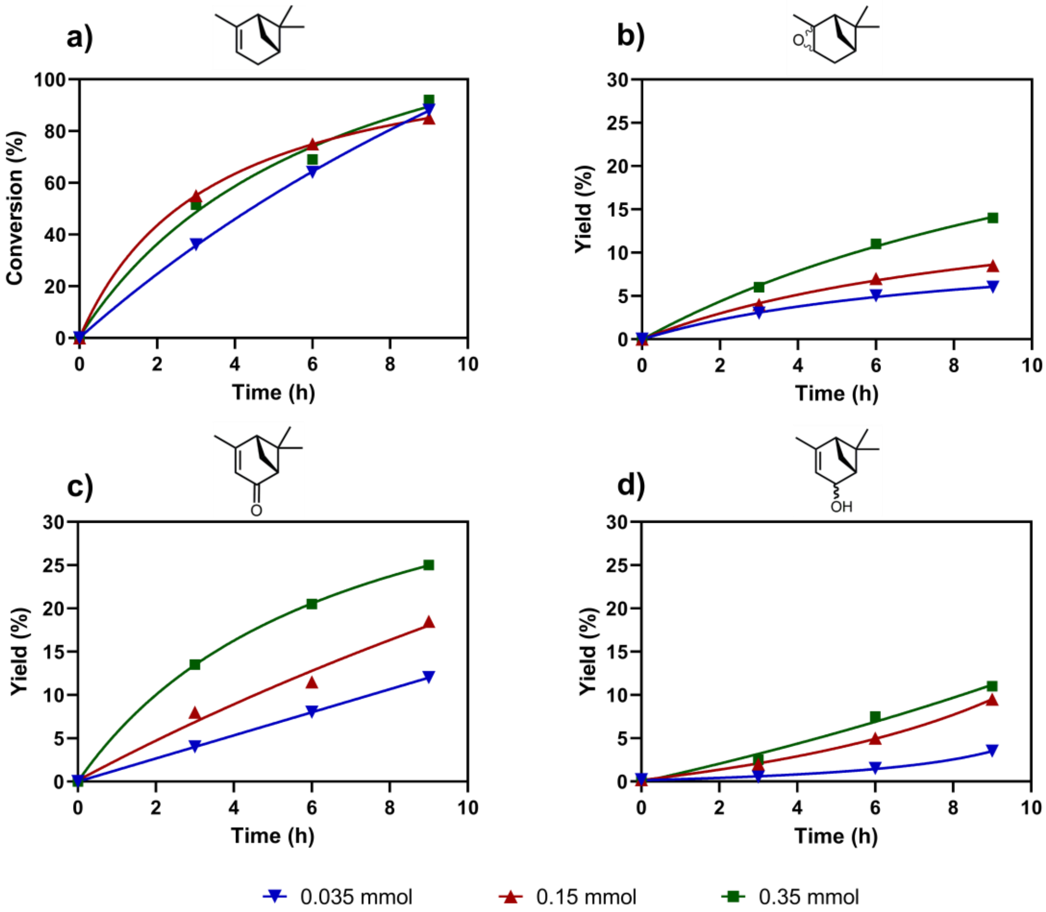

Figure S16. Cu-catalyzed oxidation of α-pinene with a varying amount of TBHP: 0.035 mmol (▼), 0.15 mmol (▲) and 0.35 mmol (■). Conditions: α-pinene (1 mL), **2** (15 µmol), TBHP (70% in H_2O; 0.035 − 0.35 mmol), 9 h, 800 rpm, 70 °C, O_2 (14 mL·min^{-1}).

Table S8. Cu-catalyzed Oxidation of α-Pinene: Effect of the Amount of TBHP.[a]

Entry	TBHP (mmol)	Time (h)	Conversion (%)[b]	Yield of the main products (%)[c]			
			A	**B**	**C**	**D**	**Total**
1	0.035	0	0	0	0	0	0
2		3	36.0	4.0	3.0	0.5	7.5
3		6	64.0	8.0	5.0	1.5	14.5
4		9	88.0	18.0	6.0	3.5	27.5
5	0.15	0	0	0	0	0	0
6		3	55.0	8.0	4.0	1.0	13.0
7		6	75.0	11.5	7.0	5.0	23.5
8		9	85.0	18.5	8.5	9.5	36.5
9	0.35	0	0	0	0	0	0
10		3	51.5	13.5	6.0	2.5	22.0
11		6	69.0	20.5	11.0	7.5	39.0
12		9	92.0	25.0	14.0	11.0	50.0

[a] Conditions: α-pinene (1 mL), **2** (15 µmol), TBHP (70% in H_2O; 0.035 − 0.35 mmol), 9h, 800 rpm, 70 °C, O_2 ($14\ mL\cdot min^{-1}$). [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: verbenone; C: pinene oxide; D: verbenol).

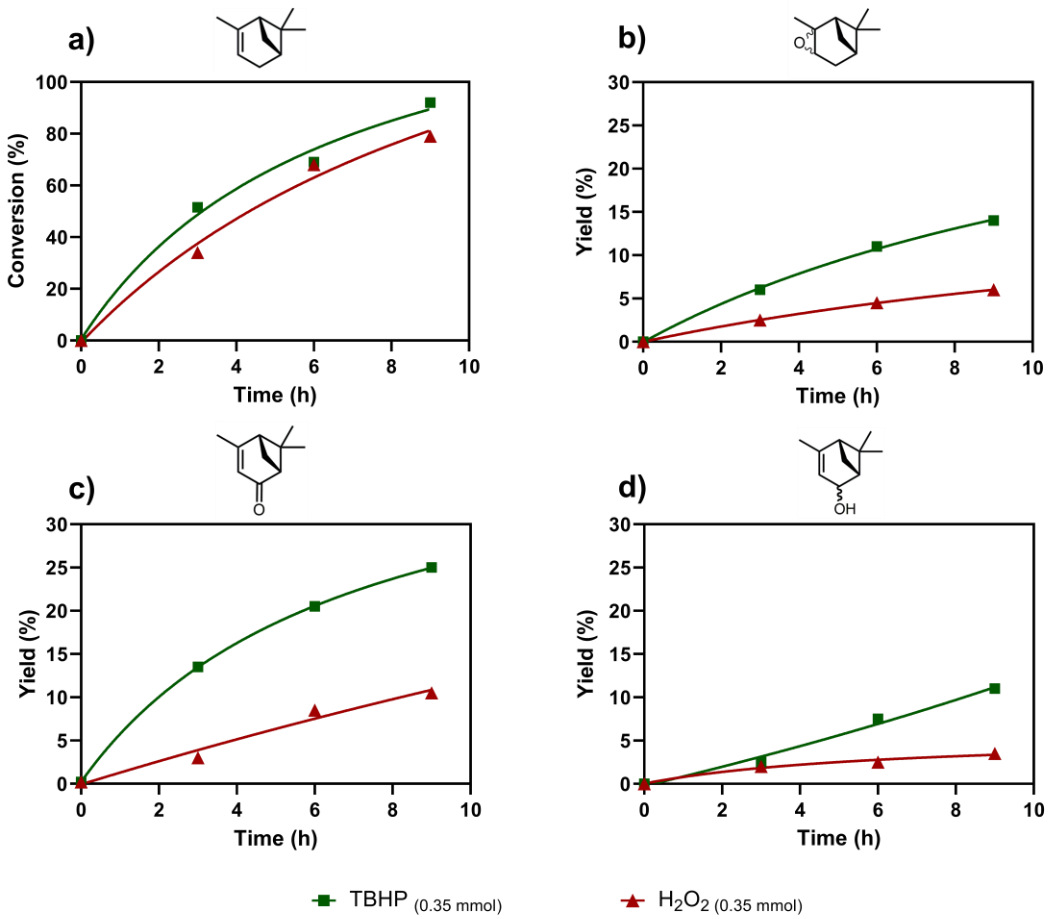

Figure S17. Cu-catalyzed oxidation of α-pinene varying initiator: H_2O_2 (60% in H_2O; 0.35 mmol) (▲) and TBHP (70% in H_2O; 0.35 mmol) (■).

Table S9. Cu-catalyzed Oxidation of α-Pinene in the Presence of Different Amounts of the Initiator: H_2O_2, TBHP, and TEMPO.[a]

Entry	Initiator (0.35 mmol)	Time (h)	Conversion (%)[b]	Yield of the main products (%)[c]			
			A	**B**	**C**	**D**	**Total**
1	H_2O_2	0	0	0	0	0	0
2		3	34.0	3.0	2.5	2.0	7.5
3		6	68.0	8.5	4.5	2.5	15.5
4		9	79.0	10.5	6.0	3.5	20.0
5	TBHP	0	0	0	0	0	0
6		3	51.5	13.5	6.0	2.5	22.0
7		6	70.0	20.5	11.0	7.5	39.0
8		9	92.0	25.0	14.0	11.0	50.0
9	TEMPO	0	0	0	0	0	0
10		3	28.0	3.0	4.0	3.5	10.0
11		6	39.0	3.5	4.0	3.0	10.5
12		9	45.0	4.0	4.0	3.5	11.5

[a]Conditions: α-pinene (1 mL), **2** (15 µmol), TBHP (70% in H_2O, H_2O_2 or TEMPO − 0.35 mmol), 9h, 800 rpm, 70 °C, O_2 (14 mL·min^{-1}). [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: verbenone; C: pinene oxide; D: verbenol).

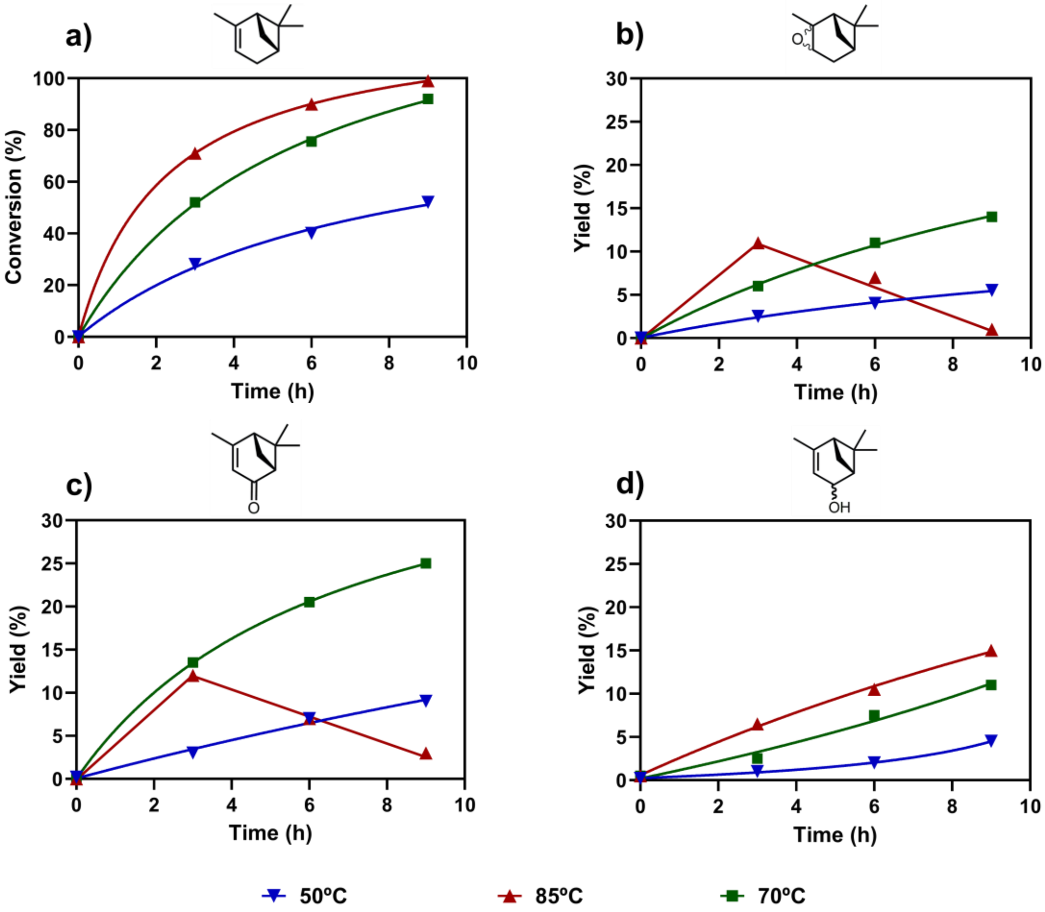

Figure S18. Cu-catalyzed oxidation of α-pinene at different temperatures: 50ºC (▼), 70ºC (■) and 85ºC (▲). Conditions: α-pinene (1 mL), **2** (15 µmol), TBHP (70% in H_2O; 0.35 mmol), 9h, 800 rpm, temperature (50−85ºC), O_2 (14 mL·min^{-1}).

Table S10. Cu-catalyzed Oxidation of α-Pinene at Varying Temperature: 50 ºC, 70 ºC and 85 ºC.[a]

Entry	T (ºC)	Time (h)	Conversion (%)[b]	Yield of the main products (%)[c]			
			A	**B**	**C**	**D**	**Total**
1	50ºC	0	0	0	0	0	**0**
2		3	28.0	3.0	2.5	0.5	**6.0**
3		6	40.0	7.0	4.0	2.0	**13.0**
4		9	52.0	9.0	5.5	4.5	**17.0**
5	70ºC	0	0	0	0	0	**0**
6		3	51.5	13.5	6.0	2.5	**22.0**
7		6	70.0	20.5	11.0	7.5	**39.0**
8		9	92.0	25.0	14.0	11.0	**50.0**
9	85ºC	0	0	0	0	0	**0**
10		3	71.0	12.0	11.0	6.5	**29.5**
11		6	90.0	7.0	7.0	10.5	**24.5**
12		9	99.0	3.0	0.0	15.0	**18.0**

[a] Conditions: α-pinene (1 mL), **2** (15 µmol), TBHP (70% in H_2O; 0.35 mmol), 9h, 800 rpm, temperature (50 − 85 °C), O_2 (14 mL·min^{-1}). [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: verbenone; C: pinene oxide; D: verbenol).

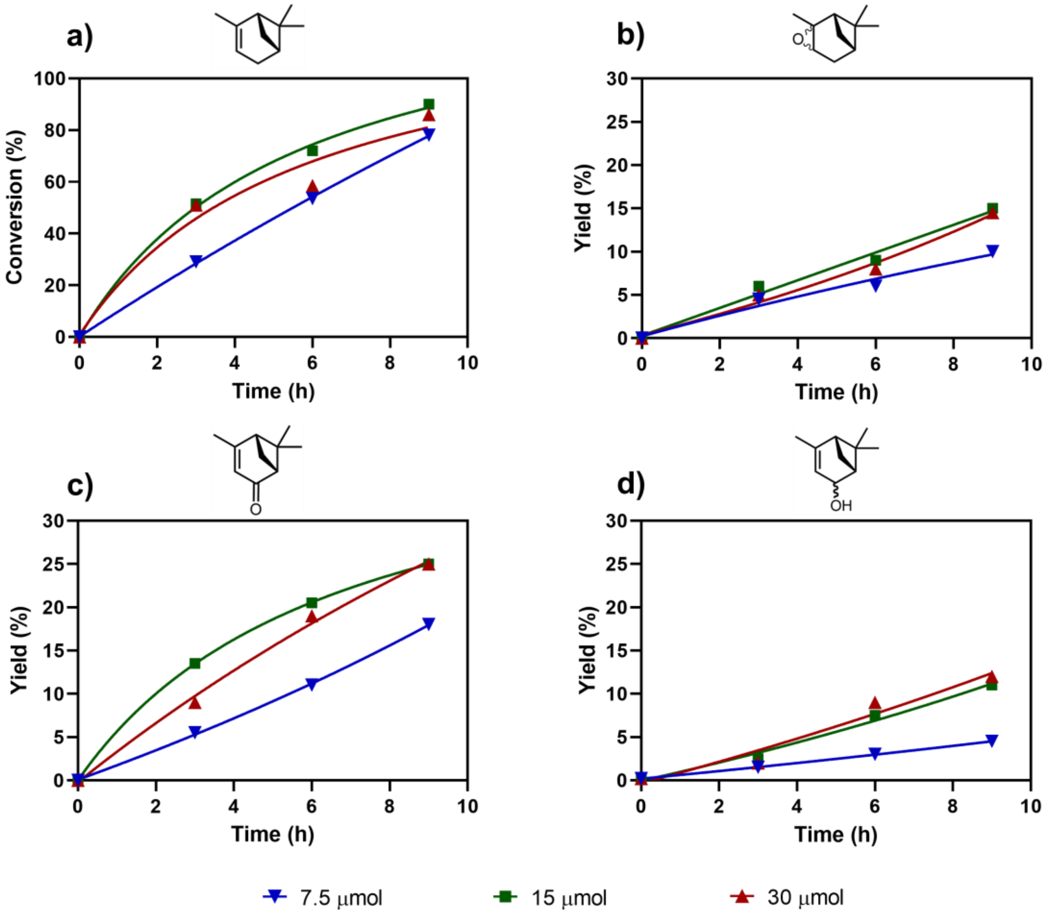

Figure S19. Cu-catalyzed oxidation of α-pinene using different amounts of **2**: 7.5 µmol (▼), 15 µmol (■), and 30 µmol (▲).

Table S11. Cu-catalyzed Oxidation of α-Pinene Using Different Amounts of **2**: 7.5 µmol, 15 µmol, and 30 µmol.[a]

Entry	**2** (µmol)	Time (h)	Conversion (%)[b]	Yield of the main products (%)[c]			
			A	**B**	**C**	**D**	**Total**
1	7.5	0	0	0	0	0	0
2		3	29.0	5.5	4.5	1.5	14.0
3		6	53.5	11.0	6.0	3.0	20.0
4		9	78.0	18.0	10.0	4.5	32.5
5	15	0	0	0	0	0	0
6		3	51.0	13.5	6.0	2.5	22.0
7		6	73.0	20.5	9.0	7.5	37.0
8		9	91.0	25.0	15.0	11.0	51.0
9	30	0	0	0	0	0	0
10		3	51.0	9.0	5.0	2.0	16.0
11		6	58.5	19.0	8.0	9.0	36.0
12		9	88.0	25.0	14.5	12.0	51.5

[a] Conditions: α-pinene (1 mL), **2** (7.5 – 30 µmol), TBHP (70% in H_2O; 0.35 mmol), 9h, 800 rpm, temperature (70 °C), O_2 (14 mL·min^{-1}). [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: verbenone; C: pinene oxide; D: verbenol).

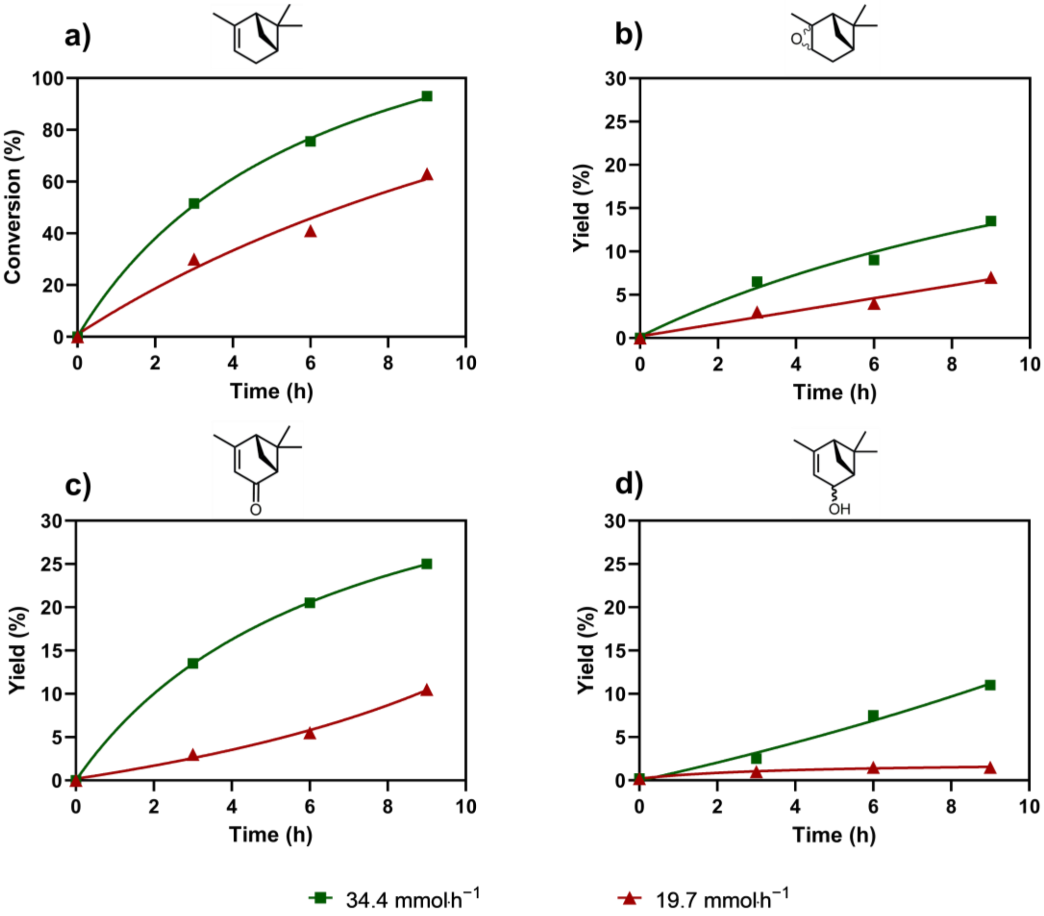

Figure S20. Cu-catalyzed oxidation of α-pinene at different amounts of oxygen: 19.7 mmol·h^{-1} (8 mL·min^{-1}) (▲) and 34.4 mmol·h^{-1} (14 mL·min^{-1}) (■).

Table S12. Cu-catalyzed Oxidation of α-Pinene at Different Amounts of Oxygen: 19.7 mmol·h^{-1} and 34.4 mmol·h^{-1}.[a]

Entry	Oxygen Flow (mmol·h^{-1})	Time (h)	Conversion (%)[b]	Yield of the main products (%)[c]			
			A	**B**	**C**	**D**	**Total**
1	19.7	0	0	0	0	0	0
2		3	30.0	3.0	3.0	1.0	6.0
3		6	41.0	5.5	4.0	1.5	11.0
4		9	63.0	10.5	7.0	1.5	19.0
5	34.4	0	0	0	0	0	0
6		3	51.5	13.5	6.0	2.5	22.0
7		6	75.0	20.5	11.0	7.5	39.0
8		9	93.0	25.0	13.5	11.0	49.5

[a] Conditions: α-pinene (1 mL), **2** (15 µmol), TBHP (70% in H_2O; 0.35 mmol), 9h, 800 rpm, temperature (70 °C), O_2 (19.7 − 34.4 mmol·h^{-1}). [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: verbenone; C: pinene oxide; D: verbenol).

Table S13. Oxidation of α-Pinene catalyzed by **2** (effect of treatment with PPh_3).[a]

Entry	Time (h)	Conversion (%)[b]	Yield of the main products (%)[c]						**D**[d]	**TOF** (h^{-1})[e]
			Before PPh_3			After PPh_3				
		A	**B**	**C**	**D**	**B**	**C**	**D**		
1	0	0.0	0	0	0	0	0	0	0	-
2	1	11.0	2.0	2.0	1.0	1.0	2.0	2.0	1.0	46.5
3	2	25.0	4.0	4.5	3.0	2.0	5.0	5.0	3.0	52.5
4	3	35.5	6.0	6.0	4.0	-	-	-	-	49.5
5	4	45.0	9.0	11.0	6.0	2.5	10.0	13.5	11.0	47.5
6	5	54.0	12.0	13.5	8.0	4.0	13.0	16.0	12.0	45.5
7	7	70.0	18.0	15.0	10.0	7.5	15.0	20.5	13.0	49.0
8	8	81.0	20.5	14.5	12.5	12.0	14.0	21.0	9.0	49.0
9	9	90.0	23.0	14.0	13.0	11.0	14.0	25.0	14.0	47.5

[a] Conditions: α-pinene (1 mL), **2** (15 µmol), TBHP (70% in H_2O; 0.35 mmol), 9h, 800 rpm, temperature (70 °C), O_2 (14 mL·min^{-1}). [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. [d] D - Estimated yield of verbenyl hydroperoxide: yield of verbenol (**C** after PPh_3) – yield of verbenone (**D** after PPh_3). [e] *TOF:* [(mols of substrate $_{(t=0)}$ × Conv. (%)] / (mols of catalyst × t(h) x 100)].
(A: α-pinene; B: verbenone; C: pinene oxide; D: verbenol).

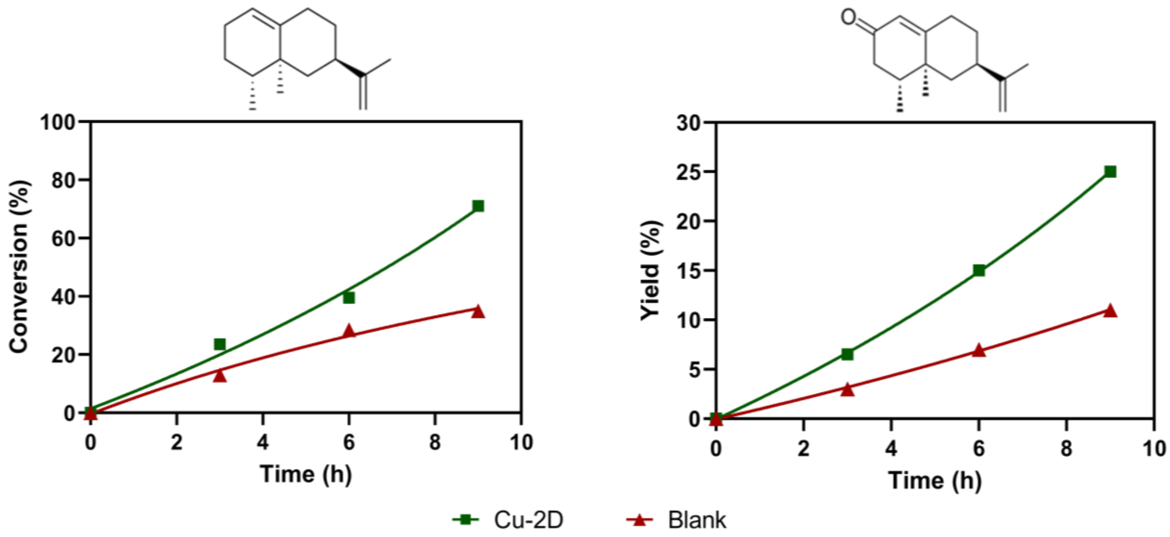

Figure S21. Cu-catalyzed oxidation of (+)-valencene: blank (▲) and **2** (15μmol) (■).

Table S14. Cu-Catalyzed Oxidation of (+)-Valencene.[a]

Entry	Precatalyst (15 μmol)	Time (h)	Conversion (%)[b]	Nootkatone Yield (%)[c]	Nootkatone Yield (%, after PPh_3)[d]
1	-	0	0	0	-
2		3	13.0	3.0	-
3		6	28.5	7.0	-
4		9	35.0	11.0	-
5	**2**	0	0	0	0
6		3	23.5	6.5	6.0
7		6	39.5	15.0	13.0
8		9	71.0	25.0	24.0

---

[a] Conditions: (+)-valencene (1 mL), **2** (15 μmol), TBHP (70% in H_2O; 0.35 mmol), 9h, 800 rpm, temperature (70 °C), O_2 (14 mL·min^{-1}). [b] *Conversion*: [moles of valencene initial − moles of valencene final) / (moles of valencene) × 100]. [c] *Yield* of nootkatone was determined by GC based on valencene: (moles of product per initial mol of α-pinene) × 100. [d] Estimated yield of nootkatone after the treatment of aliquot with PPh_3 before injecting to GC. (F: (+)-valencene; G: nootkatone).

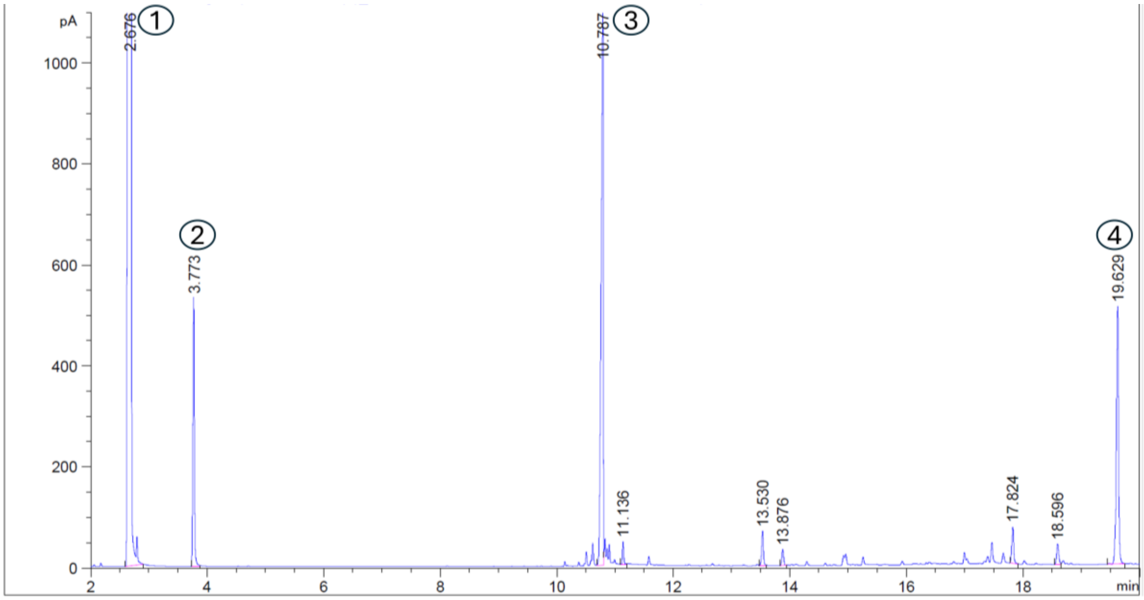

Figure S22. A fragment of a typical gas chromatogram of the reaction mixture in Cu-catalyzed oxidation of (+)-valencene. Conditions: (+)-valencene (1 mL), precatalyst (15 µmol), TBHP (aq. 70%, 0.35 mmol) (50 µL), 9h, 800 rpm, 70 °C, O_2 (14 mL·min^{-1}). Identification: (1) CH_3CN (GC solvent), (2) nitromethane (GC standard), (3) (+)-valencene and (4) (+)-nootkatone.

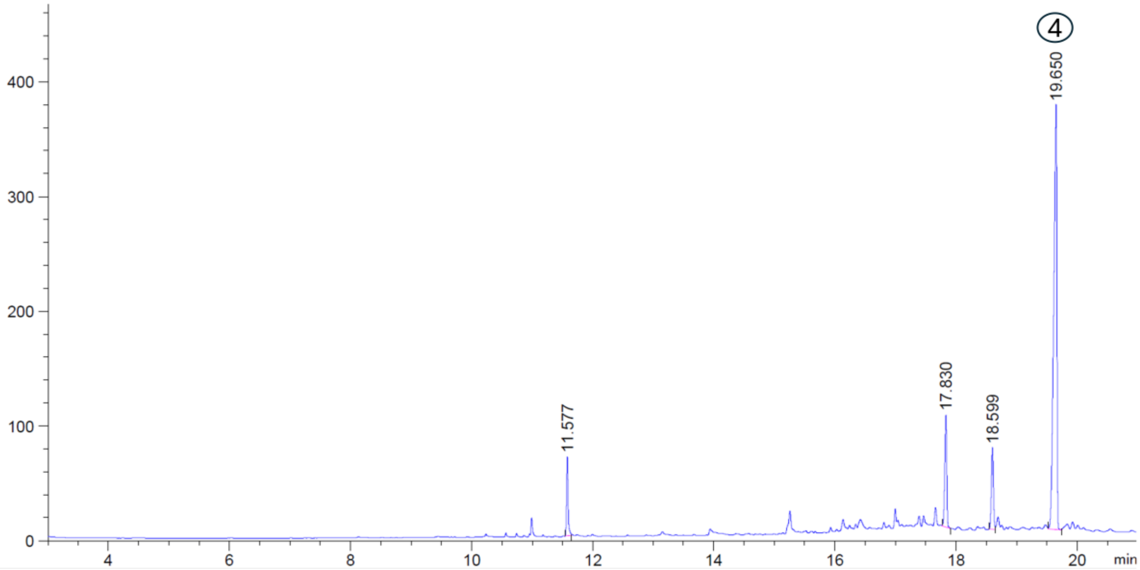

Figure S23. Chromatogram of the 75% isolated nootkatone from the Cu-catalyzed oxidation of (+)-valencene. Estimated Purity (%) = [Area of nootkatone (4) / (Area of all peaks) × 100].

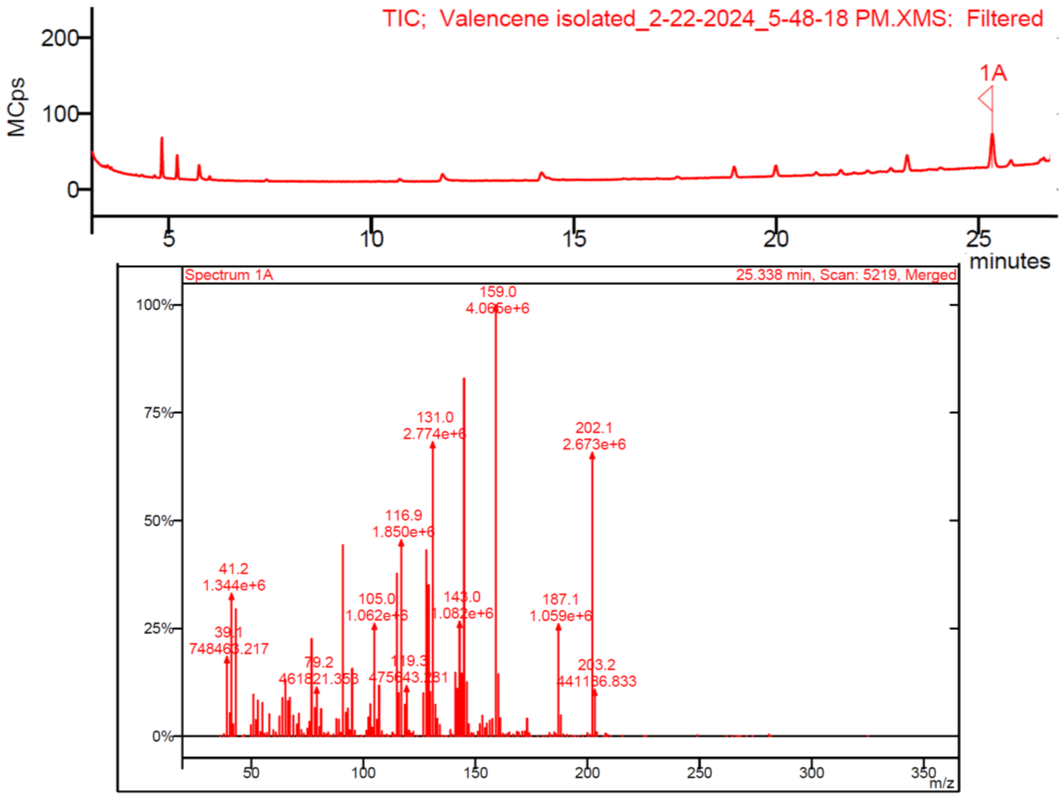

Figure S24. Mass spectrum of (+)-nootkatone obtained in the oxidation of (+)-valencene. GC–MS (EI).[1]

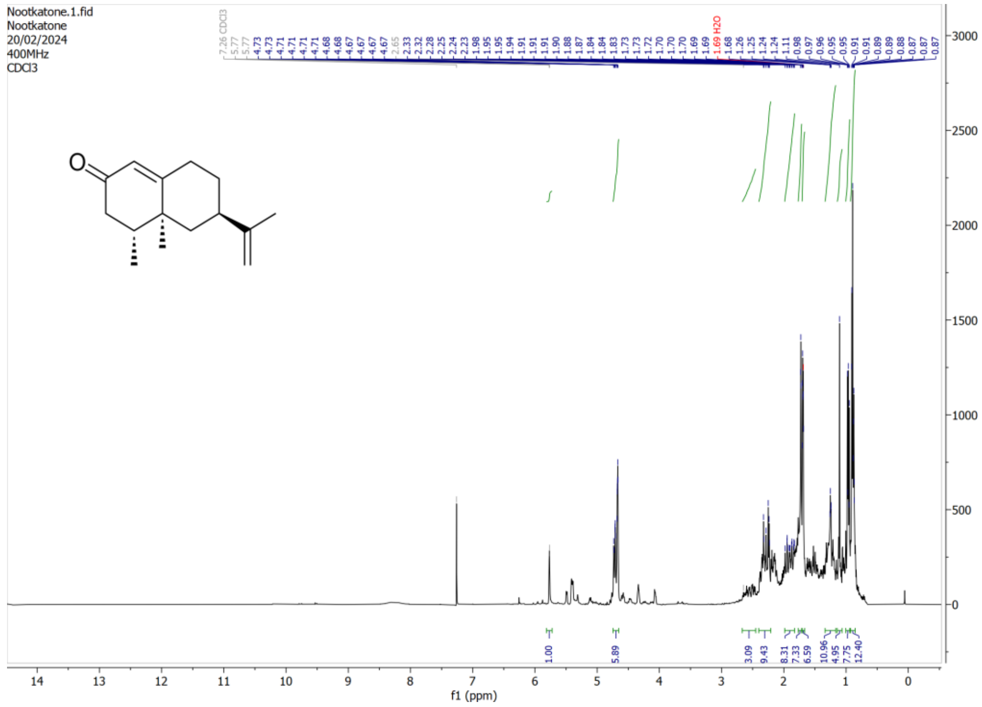

Figure S25. ^{1}H NMR spectrum of the 75% isolated (+)-nootkatone in chloroform-d.

(+)-Nootkatone: 1H NMR ($CDCl_3$, 400 MHz) δ: 5.77 (s, 1H), 4.72 (m, 1H), 4.71 (m, 1H), 1.74 (s, 3H), 1.11 (s, 3H), 0.96 (d, 3H).[2]

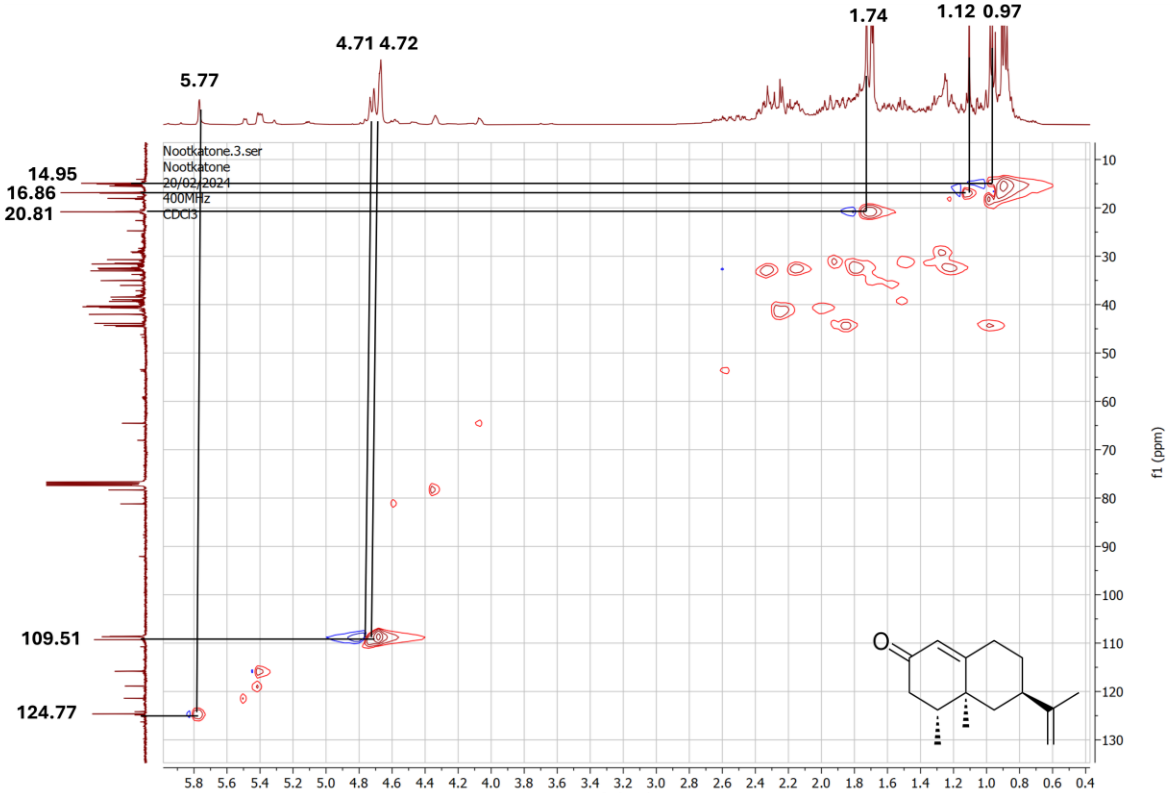

Figure S26. 2D HSQC spectrum of the 75% isolated nootkatone in chloroform-d.

(+)-Nootkatone: 1H NMR ($CDCl_3$, 300 MHz) δ: 5.77 (s, 1H), 4.72 (m, 1H), 4.71 (m, 1H), 1.74 (s, 3H), 1.11 (s, 3H), 0.96 (d, 3H). 13C NMR ($CDCl_3$, 300 MHz) δ: 199.7, 170.6, 149.1, 124.7, 109.2, 43.9, 42.1, 40.4, 39.3, 33.0, 31.6, 20.8, 16.9, 14.9.[2]

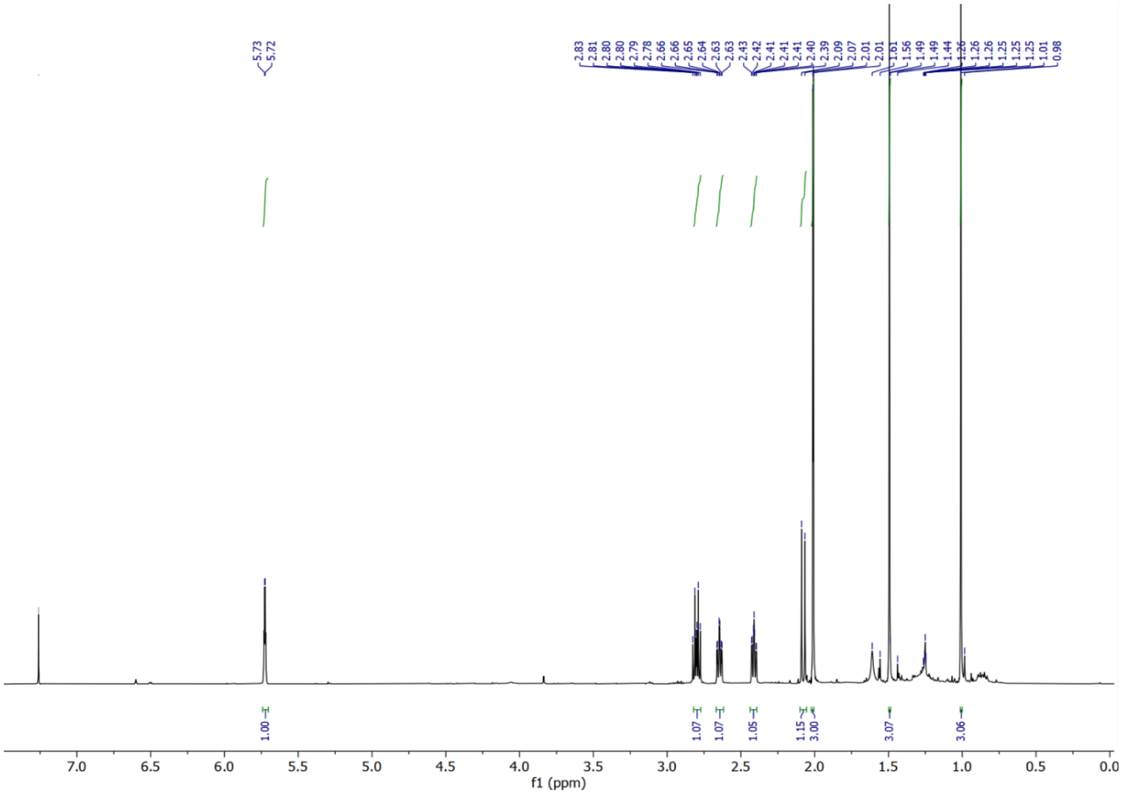

Figure S27. 1H NMR spectrum of verbenone.

Verbenone - (GC reference) 1H NMR ($CDCl_3$, 300 MHz) δ 1.00 (s, 3H, CH_3, H-9), 1.49 (s, 3H, CH_3, H-8), 2.01 (d, 3H, H-10, CH_3, 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).[3]

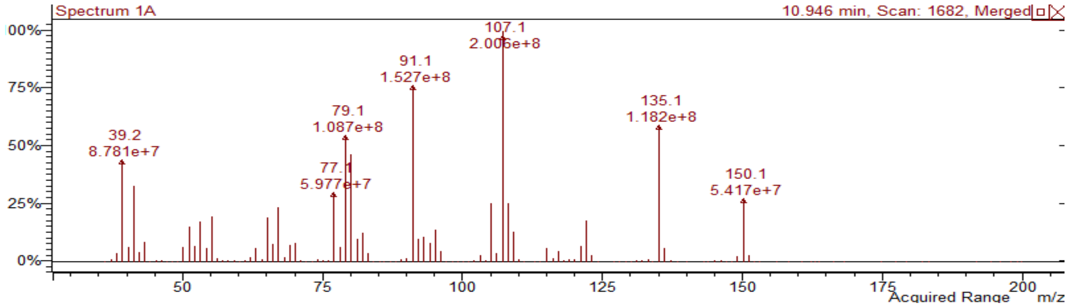

Figure S28. Mass spectrum of verbenone obtained in the oxidation of α-pinene. GC–MS (EI): m/z 150, 107 (C_4H_9O).

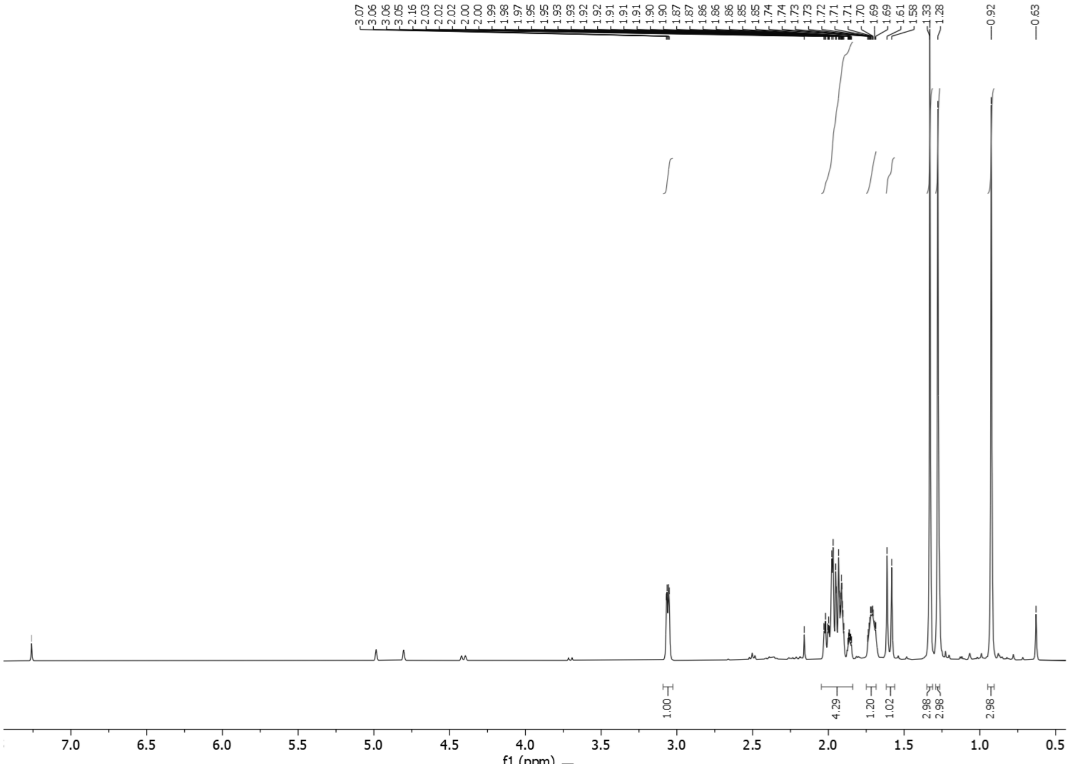

Figure S29. 1H NMR spectrum of pinene oxide.

Pinene oxide (GC reference): 1H 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).[4]

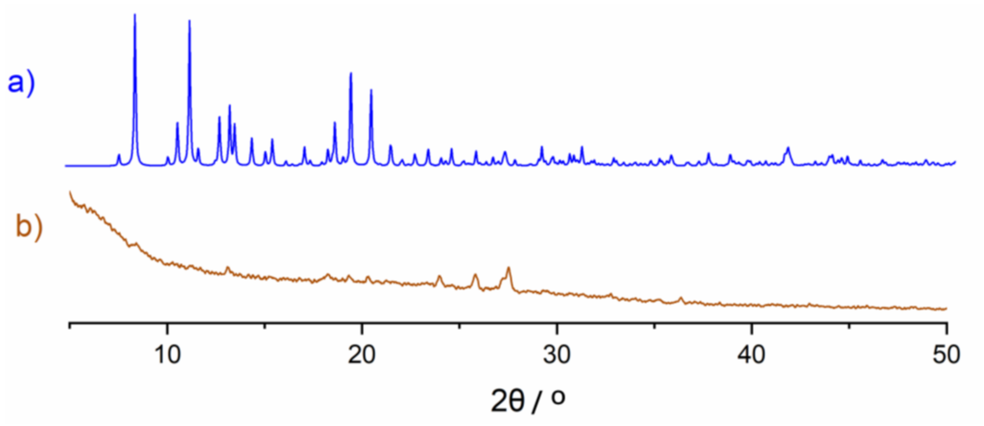

Figure S30. PXRD patterns of **2**: (a) simulated and (b) after Cu-catalyzed oxidation of α-pinene.

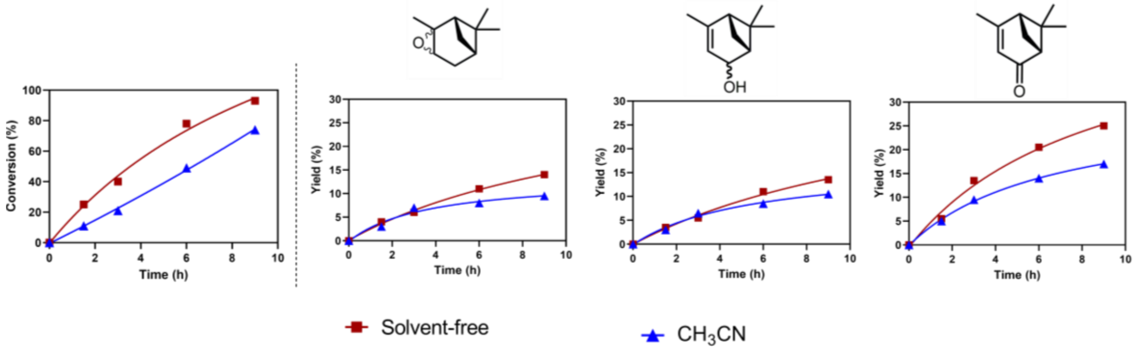

Figure S31. Cu-catalyzed oxidation of α-pinene in the presence of CH_3CN solvent (▲). compared to solvent-free reaction (■). Conditions for solvent-free reaction: α-pinene (1 mL), **2** (15 µmol), TBHP (70% in H_2O; 0.35 mmol), 9 h, 800 rpm, 70 °C, O_2 (34.4 $mmol \cdot h^{-1}$). Conditions for reaction in CH_3CN: α-pinene (1 mL), **2** (8 µmol), TBHP (70% in H_2O; 0.35 mmol), 9 h, 800 rpm, 70 °C, O_2 (34.4 $mmol \cdot h^{-1}$) CH_3CN (3 mL).

Table S15. Cu-catalyzed Oxidation of α-Pinene in the CH_3CN medium compared to added-solvent-free Reaction.

Entry	Reaction	Time (h)	Conversion (%)[c]	Yield of the main products (%)[d]			
			A	**B**	**C**	**D**	**Total**
1	Added-solvent-free[a]	0	0	0	0	0	0
2		1.5	25.0	5.5	4.0	3.5	13.0
3		3.0	40.0	13.5	6.0	5.5	25.0
4		6.0	78.0	20.5	11.0	11.5	43.0
5		9.0	93.0	25.0	13.0	12.5	50.5
6	CH_3CN[b]	0	0	0	0	0	0
7		1.5	11.0	5.0	3.0	2.5	10.5
8		3.0	21.0	9.5	7.0	6.5	23.0
9		6.0	49.0	14.0	7.5	8.5	30.0
10		9.0	74.5	17.0	9.5	10.5	37.0

[a] Conditions: α-pinene (1 mL), **2** (15 µmol), TBHP (70% in H_2O; 0.35 mmol), 9 h, 800 rpm, 70 °C, O_2 (34.4 $mmol \cdot h^{-1}$), [b] Conditions: α-pinene (1 mL), **2** (8 µmol), TBHP (70% in H_2O; 0.35 mmol), 9 h, 800 rpm, 70 °C, O_2 (34.4 $mmol \cdot h^{-1}$) CH_3CN (3 mL). [c] *Conversion*: [moles of α-pinene initial − moles of α-pinene final) / (moles of α-pinene initial) × 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: verbenone; C: pinene oxide; D: verbenol).

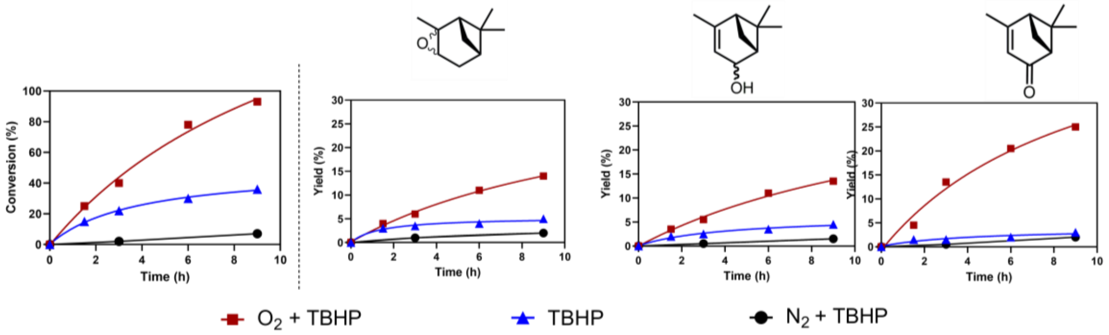

Figure S33. Cu-catalyzed oxidation of α-pinene with TBHP as initiator, with O_2 (■), without O_2 (▲), and with N_2 (●). Conditions: α-pinene (1 mL), **2** (15 µmol), TBHP (70% in H_2O; 0.35 mmol), 9 h, 800 rpm, 70 °C, O_2 (34.4 mmol·h^{-1}, when applied).

Table S17. Cu-catalyzed Oxidation of α-Pinene with TBHP as Initiator, with O_2, without O_2, and with N_2.[a]

Entry	TBHP (70% in H_2O; 0.35 mmol)	Time (h)	Conversion (%)[b]	Yield of the main products (%)[c]			
			A	**B**	**C**	**D**	**Total**
1	O_2	0	0	0	0	0	0
2		1.5	25.0	5.5	4.0	3.5	13.0
3		3.0	40.0	13.5	6.0	5.5	25.0
4		6.0	78.0	20.5	11.0	11.5	43.0
5		9.0	93.0	25.0	13.0	12.5	50.5
6	-	0	0	0	0	0	0
7		1.5	15.0	1.5	3.0	2.0	6.5
8		3.0	22.0	1.5	3.5	2.5	7.5
9		6.0	30.0	2.0	4.0	3.5	9.5
10		9.0	36.0	3.0	5.0	4.5	12.5
11	N_2	0	0	0	0	0	0
12		3.0	2.0	0.5	0.5	1.0	2.0
13		9.0	7.0	2.0	1.5	2.0	5.5

[a] Conditions: α-pinene (1 mL), **2** (15 µmol), TBHP (70% in H_2O; 0.35 mmol), 9h, 800 rpm, temperature (70 °C), O_2 (34.4 mmol·h^{-1}, when applied). [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: verbenone; C: pinene oxide; D: verbenol).

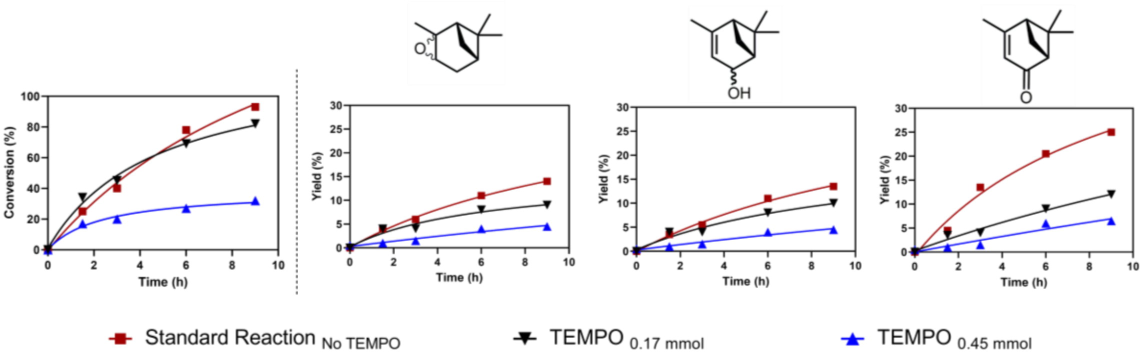

Figure S34. The effect of TEMPO as a radical scavenger in the Cu-catalyzed oxidation of α-pinene: Standard reaction (no TEMPO) (🟥), TEMPO (0.17 mmol) (▼), and TEMPO (0.45 mmol) (▲). Conditions: α-pinene (1 mL), **2** (15 µmol), TBHP (70% in H_2O; 0.35 mmol), 9 h, 800 rpm, 70 °C, O_2 (14 mL·min^{-1}), (TEMPO 0.17–0.45 mmol, when applied).

Table S18. The effect of TEMPO as a Radical Scavenger in the Cu-catalyzed Oxidation of α-Pinene: Standard Reaction (no TEMPO), TEMPO (0.17 mmol), and TEMPO (0.45 mmol).[a]

Entry	**TEMPO** (mmol)	Time (h)	Conversion (%)[b]	Yield of the main products (%)[c]			
			A	**B**	**C**	**D**	**Total**
1	-	0	0	0	0	0	0
2		1.5	25.0	5.5	4.0	3.5	13.0
3		3.0	40.0	13.5	6.0	5.5	25.0
4		6.0	78.0	20.5	11.0	11.5	43.0
5		9.0	93.0	25.0	13.0	12.5	50.5
6	0.17[d]	0	0	0	0	0	0
7		1.5	34.0	3.5	4.0	4.0	11.5
8		3.0	45.0	4.0	6.0	4.0	14.0
9		6.0	69.0	9.0	8.0	8.0	25.0
10		9.0	82.0	12.0	11.0	10.0	33.0
11	0.45[d]	0	0	0	0	0	0
12		1.5	17.0	0.5	1.5	0.5	2.5
13		3.0	20.5	1.5	1.5	1.5	4.5
14		6.0	27.0	6.0	5.5	4.0	15.5
15		9.0	32.0	6.5	5.5	4.5	16.5

[a] Conditions: α-pinene (1 mL), **2** (15 µmol), TBHP (70% in H_2O; 0.35 mmol), 9h, 800 rpm, temperature (70 °C), O_2 (14 mL·min^{-1}), (TEMPO 0.17–0.45 mmol). [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: verbenone; C: pinene oxide; D: verbenol).
[d] TEMPO was added immediately before the reaction started.

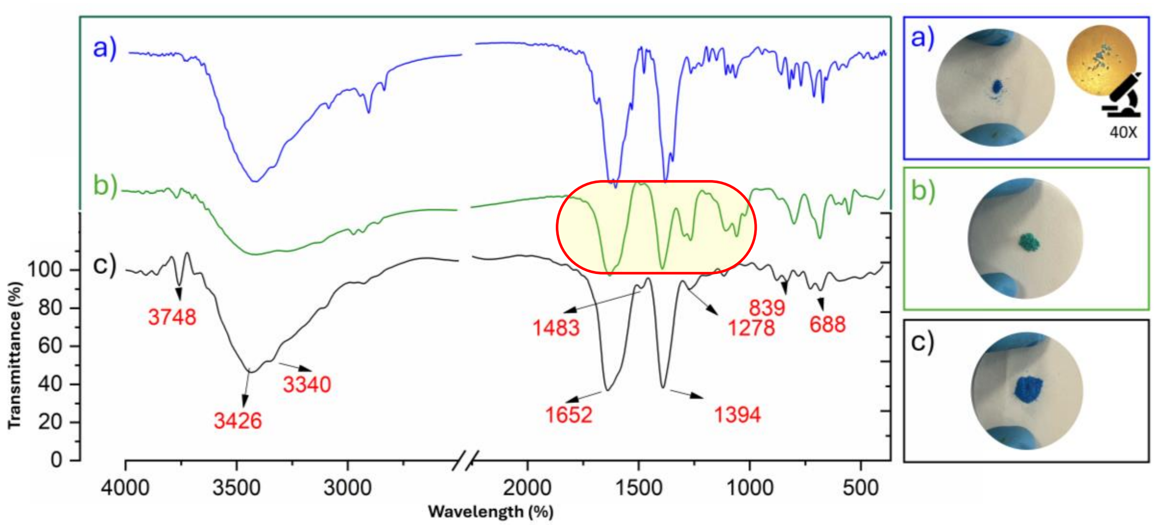

Figure S35. FT-IR spectra of compound **2**: (a) crystalline blue powder obtained from the recrystallization of the recovered sample after catalysis; (b) green powder recovered from the reaction medium; and (c) as-synthesized sample: crystalline blue powder. The highlighted region in (b) shows a decrease in intensity of the ν(C=O), 1652 (s) and ν(C-H) 1394(s) bands, compared to spectra (a) and (c). This can be attributed to the release of DMF from the Cu-DMF moiety in compound **2** during the catalyst recycling.

Table S19. α-Pinene oxidation with O_2. Comparison of Various Catalysts Under Solvent-free Conditions.

Entry	Catalyst	T (°C)	Conversion (%)[f]	Selectivity (%)[g]			Ref
				Verbenone	Verbenol	Epoxide	
1	Compound **2**[a]	70	93	39	21	20	This work
2	Cr-MCM-41[b]	60	40	26	33	8	(6)
3	Cr-MIL-101[c]	60	26	31	39	8	(7)
4	Fe-MIL-101[c]	40	12	33	-	9	(7)
5	Lotus-shaped MnO_2 [d]	75	94	87	-	-	(8)
6	Mn–Fe_3O_4 [e]	60	32	37	23	28	(9)
7	Co–Fe_3O_4 [e]	60	36	40	24	26	(9)

Reaction Conditions: [a] α-Pinene (8.3 mmol), precatalyst (15 µmol), TBHP (70% aq., 0.35 mmol), 9h, 800 rpm, 70 °C, O_2 (14 mL·min^{-1}). [b] Catalyst (3.5 wt%), 60 °C, O_2 (1 atm), 7 h. [c] α-Pinene (8.3 mmol), O_2 (1 atm), 13 or 26 mg of catalyst activated at 70 °C (Fe) or 100 °C (Cr), TBHP 0.02 mmol, 16 h. [d] α-Pinene (25.2 mmol), catalyst (55 mg), O_2 (1 atm), 75 °C. [e] catalyst (1.2 wt%), 60 °C, O_2 (1 atm), 7 h. [f] Conversion of α-pinene, determined by GC analysis. [g] Selectivity was determined by GC analysis

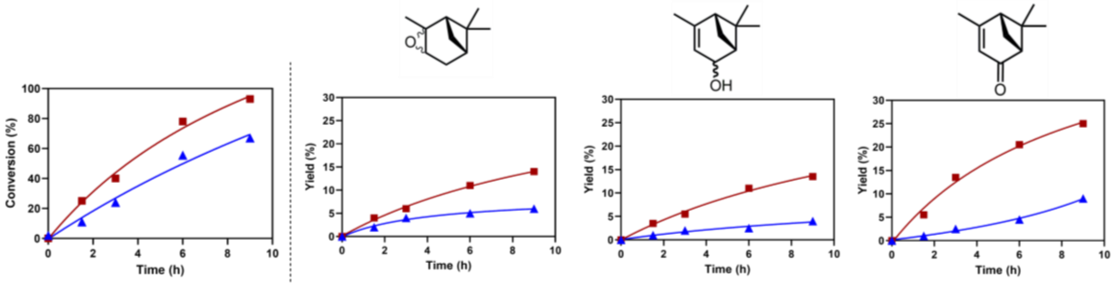

Figure S36. Cu-catalyzed oxidation of α-pinene with **2** under different conditions: heterogeneous system (■), homogeneous system (in the presence of trifluoroacetic acid, TFA) (▲). Conditions for the standard reaction (heterogeneous conditions): α-pinene (1 mL), **2** (15 µmol), TBHP (70% in H_2O; 0.35 mmol), 9 h, 800 rpm, 70 °C, O_2 (34.4 mmol·h^{-1}). Conditions for reaction under homogeneous conditions: α-pinene (1 mL), **2** (15 µmol), TFA (0.3 mmol), TBHP (70% in H_2O; 0.35 mmol), 9 h, 800 rpm, 70 °C, O_2 (34.4 mmol·h^{-1}).

Table S20. Cu-catalyzed oxidation of α-pinene with **2** under heterogeneous vs. homogeneous reaction conditions.

Entry	Compound **2** (15 µmol)	Time (h)	Conversion (%)[c]	Yield of the main products (%)[d]			
			A	**B**	**C**	**D**	**Total**
1	Precatalyst in heterogeneous system[a]	0	0	0	0	0	0
2		1.5	25.0	5.5	4.0	3.5	13.0
3		3.0	40.0	13.5	6.0	5.5	25.0
4		6.0	78.0	20.5	11.0	11.5	43.0
5		9.0	93.0	25.0	13.0	12.5	50.5
6	Precatalyst in homogeneous system[b] (0.3 mmol TFA)	0	0	0	0	0	0
7		1.5	11.0	1.0	0.5	1.0	2.5
8		3.0	24.0	2.5	4.0	2.0	8.5
9		6.0	55.5	4.5	5.0	2.5	12.0
10		9.0	67.0	9.0	6.0	4.0	19.0

[a] Conditions: α-pinene (1 mL), **2** (15 µmol), TBHP (70% in H_2O; 0.35 mmol), 9 h, 800 rpm, 70 °C, O_2 (34.4 mmol·h^{-1}), [b] Conditions: α-pinene (1 mL), **2** (15 µmol), TFA (0.3 mmol), TBHP (70% in H_2O; 0.35 mmol), 9 h, 800 rpm, 70 °C, O_2 (34.4 mmol·h^{-1}). [c] *Conversion*: [moles of α-pinene initial − moles of α-pinene final) / (moles of α-pinene initial) × 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: verbenone; C: pinene oxide; D: verbenol).

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