Supporting material for

Cu_8Na_2-silsesquioxane/acetylacetonate precatalyst for the one pot cyclohexane to ε-caprolactone transformation

by

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General Experimental Considerations

All reagents were purchased from standard suppliers (Sigma and Fluka) and used without further purification. Elemental analyses were carried out with an XRF spectrometer VRA-30. IR spectra of the compounds were measured on a Shimadzu IRPrestige 21 FT-IR spectrophotometer in KBr pellets. UV−vis spectra of complexes **1** and **2** were recorded on a Cary 50 spectrophotometer.

Synthesis of 1−2.

0.30 g (1.53 mmol) of $PhSi(OMe)_3$ and 0.09 g (2.25 mmol) of NaOH were heated at reflux in 35 mL of ethanol for 2 h. Then, 0.267 g (4.54 mmol) of $Cu(acac)_2$ were added; the resulting mixture was heated at reflux for 12 h, cooled down to room temperature, and centrifuged to remove the insoluble precipitate.

For compound **1**: Crystallization in the presence of 20 mL of DMF gave crystalline material in ~5 days, and several single crystals were used for X-ray diffraction analysis. The rest of the crystalline material was dried in vacuum to calculate the yield. Anal. Calcd for $[(Ph_6Si_6O_{12})_2Cu_8Na_2(acac)_4(HO)_2]$: Cu, 19.32; Na, 1.75; Si, 12.8. Found: Cu, 19.20; Na, 1.66; Si, 12.1. Yield: 0.21 g (64%).

For compound **2**: Crystallization in the presence of 20 mL of acetone gave crystalline material in ~3 days, and several single crystals were used for X-ray diffraction analysis. The rest of the crystalline material was dried in vacuum to calculate the yield. Anal. Calcd for $[(Ph_6Si_6O_{12})_2Cu_8Na_2(acac)_4(HO)_2]$: Cu, 19.32; Na, 1.75; Si, 12.8. Found: Cu, 19.21; Na, 1.68; Si, 12.2. Yield: 0.20 g (60%).

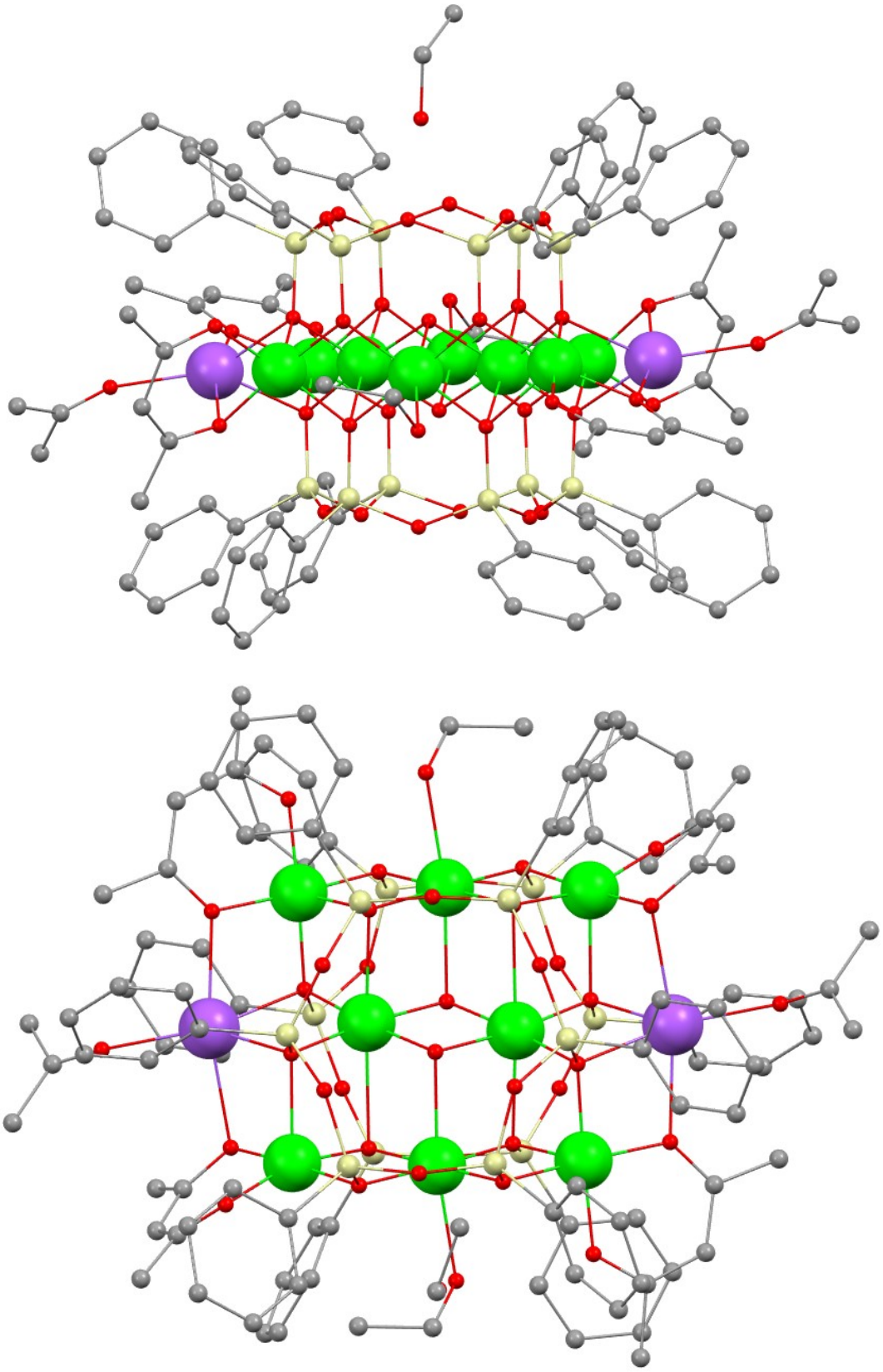

Figure S1. Two projections of molecular structures of **2**

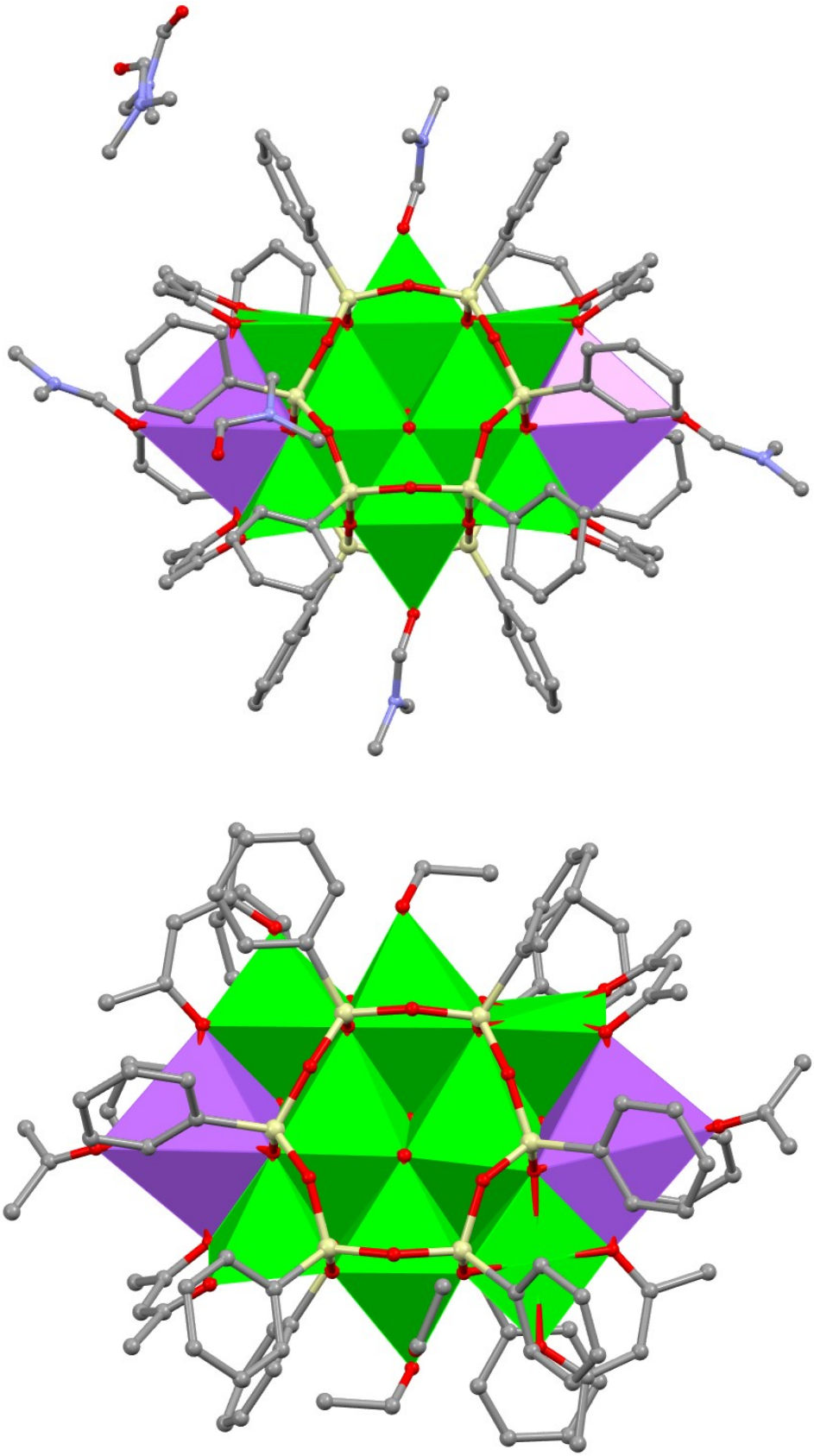

Figure S2. Molecular structures of **1** (top) and **2** (bottom) as polyhedrons

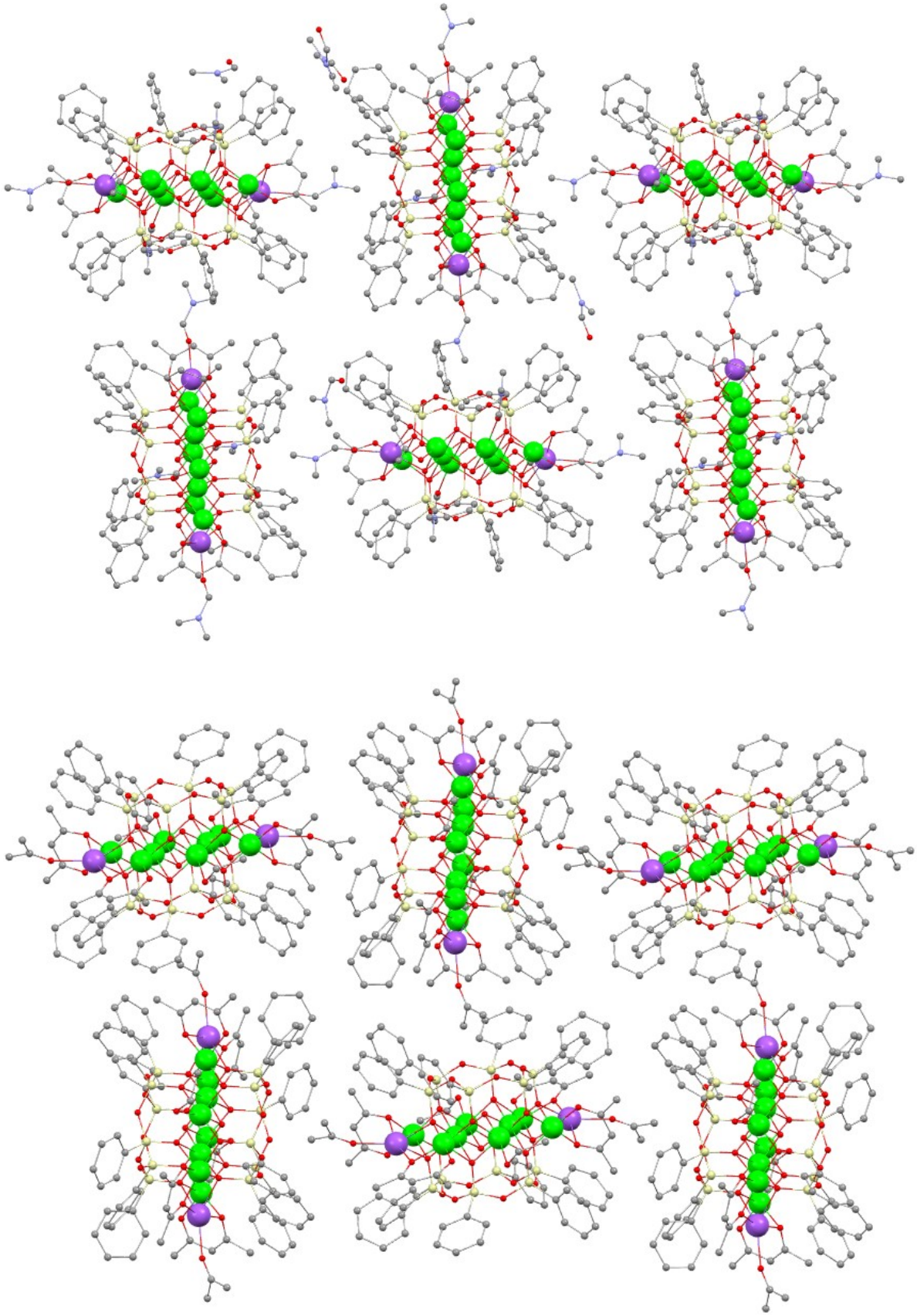

Figure S3. Packing of **1** (top) and **2** (bottom)

Table S1. Crystal data and structure refinement for compounds **1** and **2**.

Identification code	**1** • 4(Me_2NCHO)	**2** • ¾(EtOH)
Empirical formula	$C_{116}H_{146}Cu_8N_8Na_2O_{42}Si_{12}$	$C_{102.9}H_{237}Cu_8Na_2O_{38.75}Si_{12}$
Formula weight	3215.88	2866.74
Temperature, K	100.0(2)	100.0(2)
Crystal size, mm	0.10 × 0.11 × 0.12	0.06 × 0.08× 0.10
Wavelength, Å	0.71073	1.54184
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a, Å	14.7556(13)	17.0082(7)
b, Å	21.8329(19)	21.7596(6)
c, Å	22.221(2)	18.1345(7)
α, deg.	90	90
β, deg.	108.970(2)	112.040(5)
γ, deg.	90	90
V, Å^3	6769.9(10)	6221.0(4)
Z	2	2
Density (calc.), Mg/m^3	1.578	1.530
μ, mm^{-1}	1.428	3.305
F(000)	3312	2935.8
Theta range, deg.	2.102 – 30.620	3.039 – 80.166
Index ranges	$-21 \le h \le 20$, $-31 \le k \le 31$, $-31 \le l \le 31$	$-21 \le h \le 21$, $-22 \le k \le 27$, $-22 \le l \le 22$
Reflections collected	103341	67488
Independent reflections, R_{int}	20686, 0.1146	13147, 0.0922
Reflections observed	12259	7910
R_1 / wR_2 ($I > 2\sigma(I)$)	0.0787 / 0.1878	0.0745 / 0.1908
R_1 / wR_2 (all data)	0.1403 / 0.2216	0.1200 / 0.2167
Goodness-of-fit on F^2	1.024	1.136
Extinction coefficient	0.0015(1)	—
T_{min} / T_{max}	0.835 / 0.862	0.150 / 1.00
$\Delta\rho_{max}$ / $\Delta\rho_{min}$, e·Å^{-3}	1.804 / -1.948	1.544 / -1.523

X-ray crystal structure determination

The single-crystal X-ray diffraction data for **1** were collected on a three-circle Bruker D8 QUEST diffractometer equipped with a PHOTON-III area-detector (T = 100 K, λ(Mo$K\alpha$)-radiation, graphite monochromator, φ and ω-scanning mode). The data were indexed and integrated using the SAINT program [S1] and then scaled and corrected for absorption (semi-empirical from equivalents) using the SADABS program [S2]. The single-crystal X-ray diffraction study of **2** was carried out on a four-circle Rigaku Synergy-S diffractometer equipped with a HyPix6000HE area-detector (T = 100 K, λ(Cu$K\alpha$)-radiation, graphite monochromator, shutterless ω-scanning mode). The data were integrated and corrected for absorption (semi-empirical from equivalents) by the *CrysAlisPro* program [S3]. For details, see **Table S1**.

The structures were solved by intrinsic phasing modification of direct methods [S4] and refined by a full-matrix least-squares technique on F^2 with anisotropic displacement parameters for all non-hydrogen atoms. The hydrogen atoms of the OH-groups were localized in the difference-Fourier maps and included in the refinement within the riding model with fixed isotropic displacement parameters [U_{iso}(H) = 1.5U_{eq}(O)]. The other hydrogen atoms were placed in calculated positions and refined within the riding model with fixed isotropic displacement parameters [U_{iso}(H) = 1.5U_{eq}(C) for the CH_3-groups and 1.2U_{eq}(C) for the other groups]. All calculations were carried out using the *SHELXTL* program [S5, S6].

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center, CCDC 2551737 (**1**) and CCDC 2551738 (**2**). Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

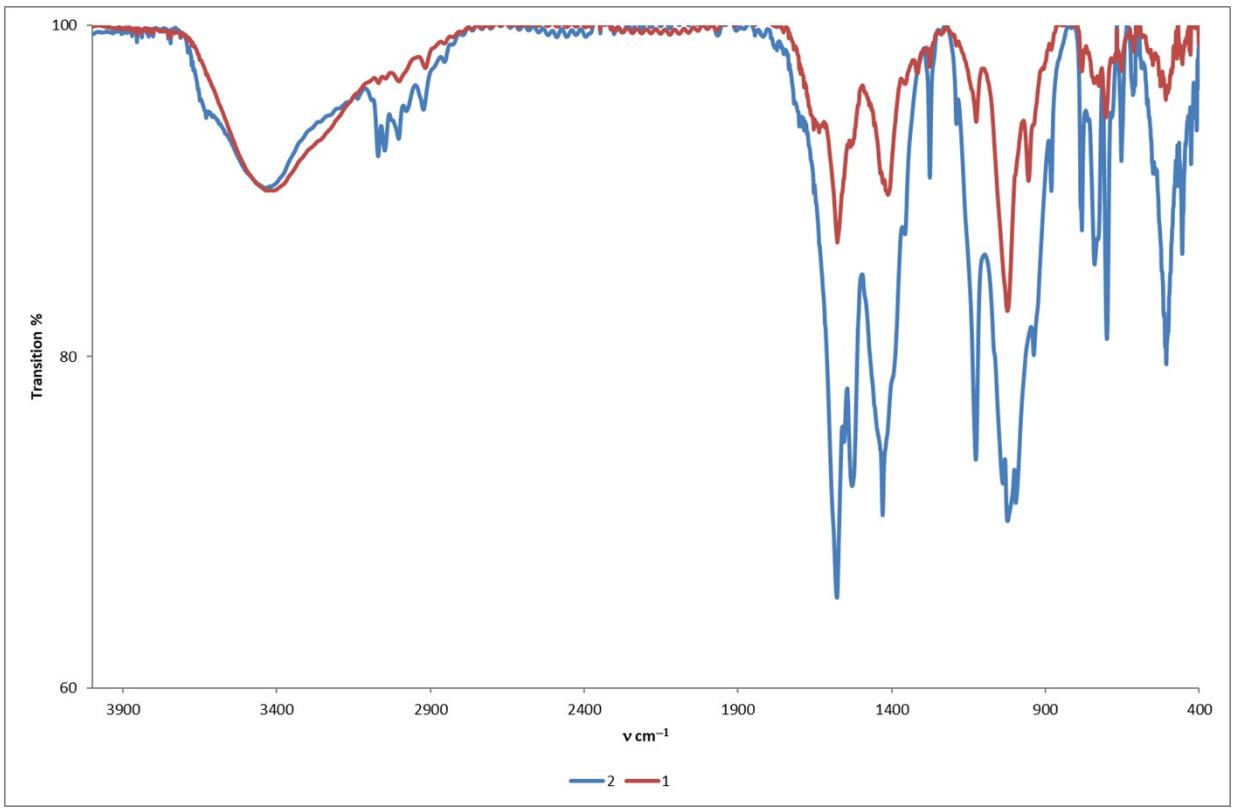

Figure S4. IR spectra of **1-2**

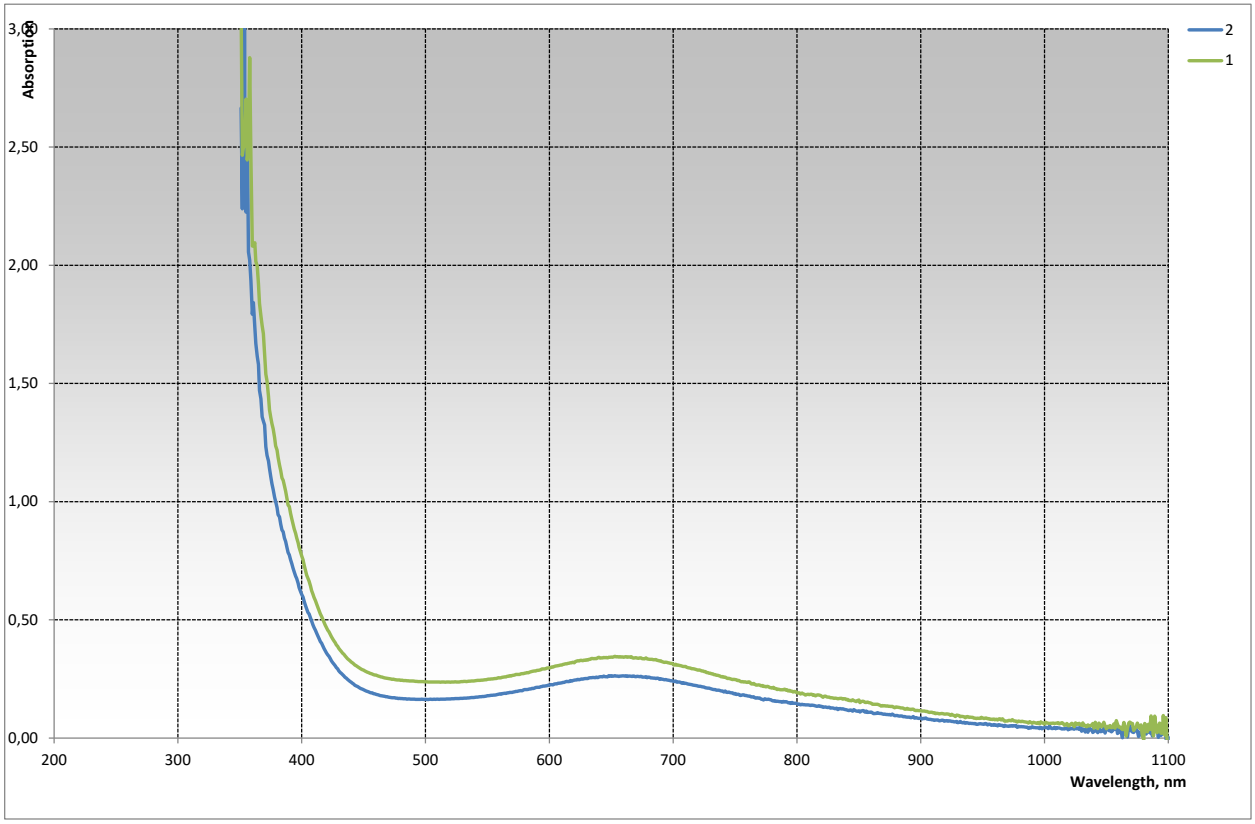

Figure S5. UVvis spectra of **1-2**

Experimental Section for tandem cyclohexane oxidation by mCPBA

In line with previous studies on copper systems, the catalytic reactions were performed under both conventional heating and microwave irradiation. Conventional experiments were carried out in sealed tubes at 50 °C for 4 h, while microwave-assisted reactions were conducted in 10 mL closed vials at 80 °C for 30 min with continuous stirring. The standard reaction mixture consisted of cyclohexane (0.5 mmol, 54 μL), the catalyst (introduced from a 0.0007 M stock solution in CH_3CN, prepared by dissolving 30.00 mg of the precatalyst in 7 mL of CH_3CN), mCPBA dissolved in 1 mL of CH_3CN, and HNO_3 (25 μmol; 50 μL of a 0.5 M stock solution in CH_3CN). Acetonitrile was added to adjust the final reaction volume to 2.055 mL. In a selected run, TEMPO (0.5 mmol, 78.1 mg) was also introduced as a radical trap. Upon completion, the reaction mixtures were cooled to ambient temperature and spiked with cycloheptanone (60 μL) as an internal GC standard. The total volume was then brought to 5.06 mL with CH_3CN, and the solutions were homogenized before transferring 1 mL aliquots into plastic vials. Quenching was performed by adding triphenylphosphine (PPh_3), following the Shulpin protocol, and allowing at least 10 min for complete reaction.[9] Analytical GC measurements were carried out on a Clarus 500 instrument equipped with an SGE BP20 column (30 m × 0.22 mm × 0.25 μm). Samples (0.5 μL) were injected under the following temperature program: initial 100 °C (2 min), ramp to 220 °C at 20 °C min^{-1}, hold for 4 min, then increase to 240 °C at the same rate and hold for another 4 min. The total run time was 18 min. Injector and detector temperatures were 200 °C and 250 °C, respectively, with a carrier gas pressure of 14 psi. Products (cyclohexanol, cyclohexanone, and ε-caprolactone) were identified by comparison with authentic standards, while quantitative analysis was performed using response factors determined from standard solutions (0.1 M in CH_3CN) and the internal standard method with cycloheptanone.

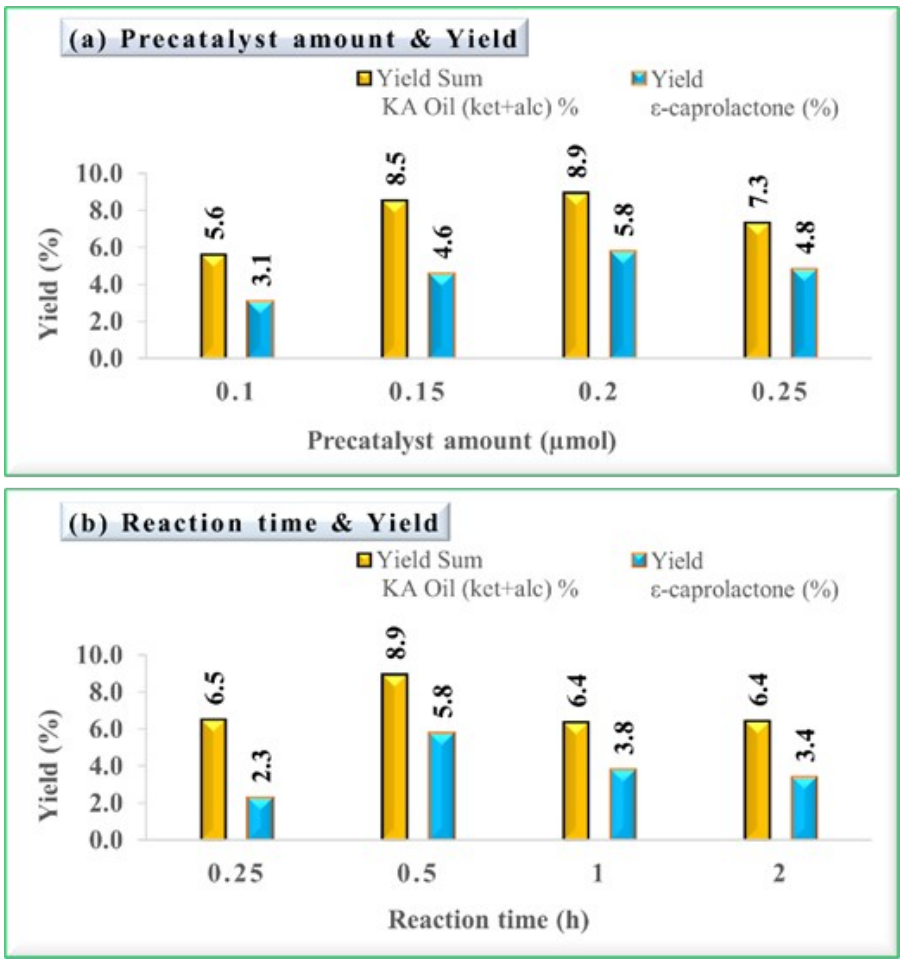

Figure S6. Influence of the precatalyst amount (a) and reaction time (b) on the yield.

(a) Reaction conditions: cyclohexane (0.5 mmol, 54 µL), precatalyst **1**, HNO_3 (25 µmol), oxidant (2 mmol), reaction in CH_3CN, total volume 2055 µL. MW irradiation, 80 °C for 30 min.

(b) Reaction conditions: same as in (a) but employing 0.2 µmol of precatalyst **1** and different reaction times.

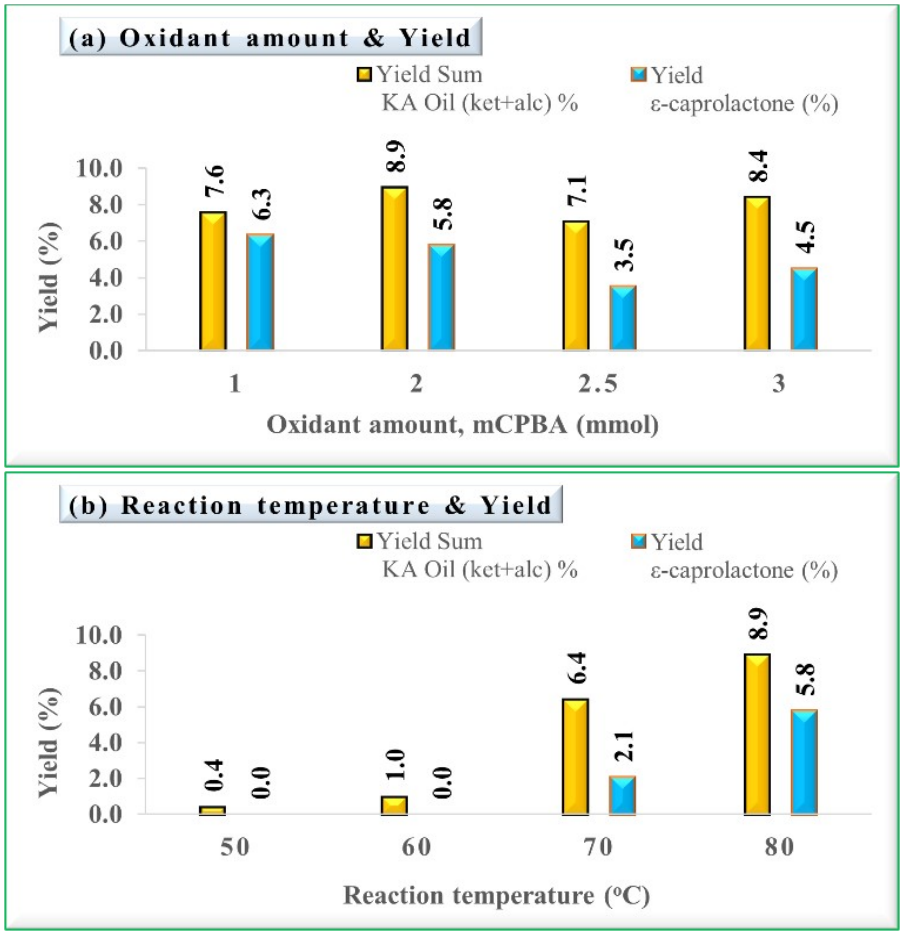

Figure S7**.** Influence of the oxidant amount (a) and reaction temperature (b) on the yield.
(a) Reaction conditions: same as in (a, Fig. 2) but using 0.2 µmol of precatalyst **1** and different oxidant amounts.
(b) Reaction conditions: same as in (a, Fig. 2), although with 0.2 µmol of precatalyst **1** and different temperatures.

References

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[S2] Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., *J. Appl. Cryst.*, **2015**, *48*, 3-10.

[S3] Rigaku, *CrysAlisPro Software System, v. 1.171.41.106a*, Rigaku Oxford Diffraction, **2021**.

[S4] Sheldrick, G.M. *Acta Crystallogr.* **2015**, *A71*, 3-8.

[S5] Sheldrick, G.M. *Acta Crystallogr.* **2008**, *A64*, 112-122.

[S6] Sheldrick, G.M. *Acta Crystallogr.* **2015**, *C71*, 3-8.