Supplementary Materials: Syntheses, Structures, and Catalytic Hydrocarbon Oxidation Properties of *N*-Heterocycle-Sulfonated Schiff Base Copper(II) Complexes

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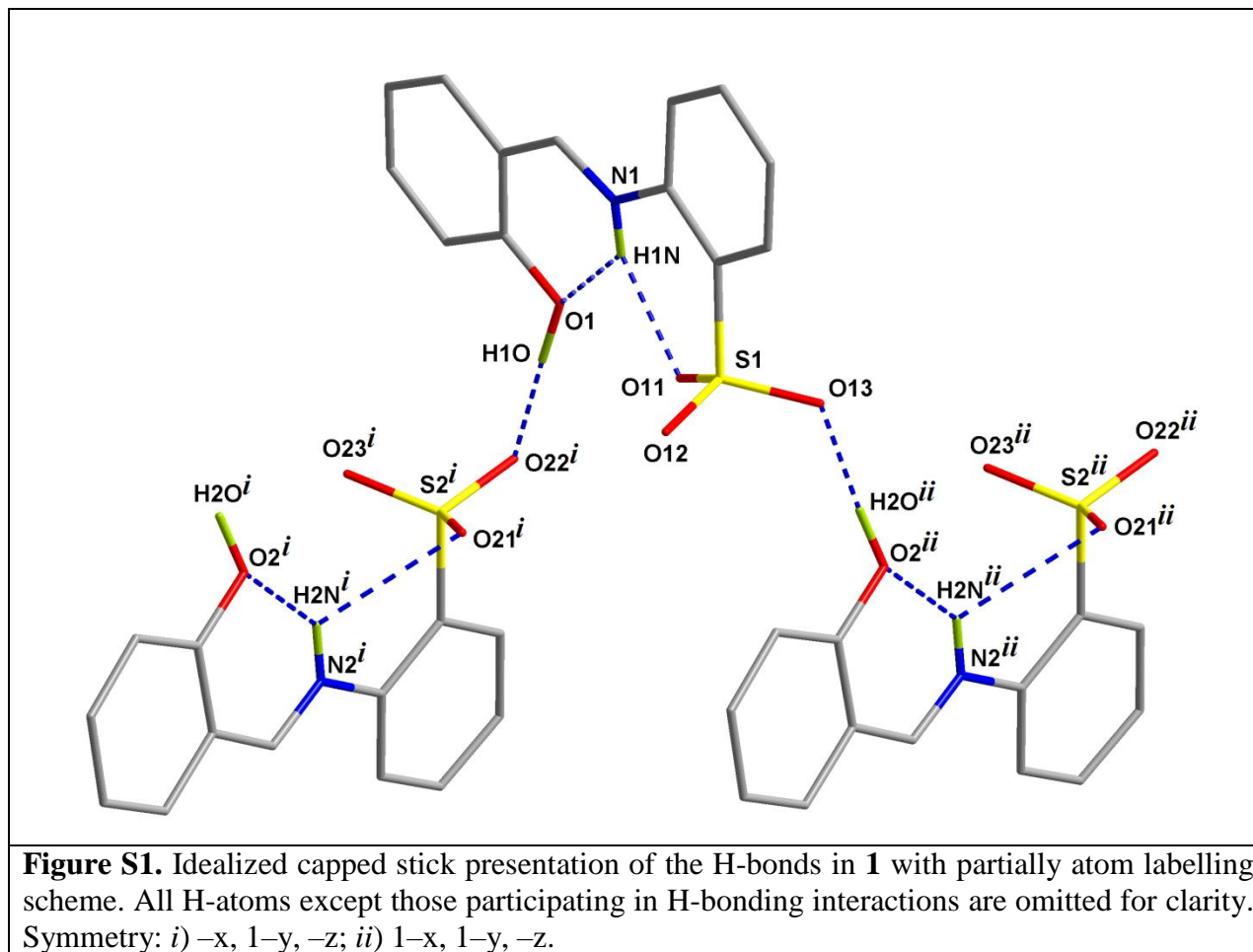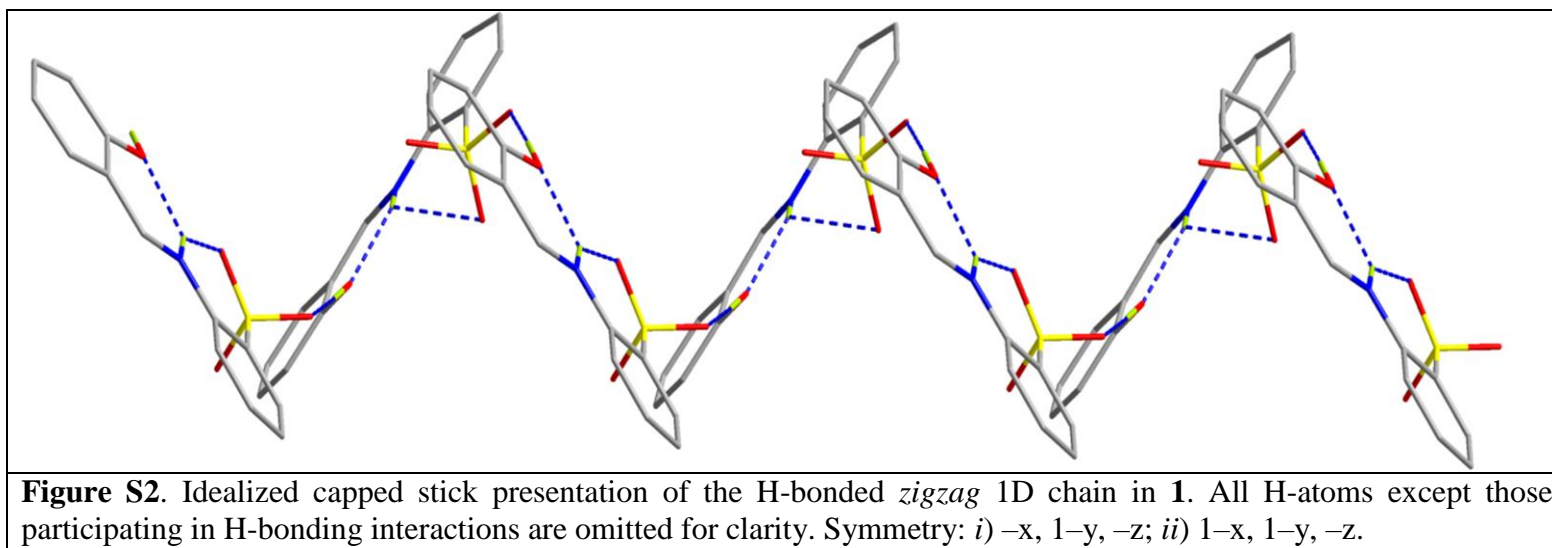
H-Bonded Networks in 1–5

The crystal lattices of all the five compounds (**1–5**) are stabilized by H-bonding interactions. In the crystal lattice of the Schiff base (**1**), imine, phenolic (as acceptors and donors) and sulfonate groups (as donors) are involved in H-bonding interactions, whereas the coordinated (**2**, **4** and **5**) or non-coordinated (**3**) solvent molecules (methanol as donors) in addition to the sulfonate groups (as acceptors) are responsible for such a type of interactions in the lattices of the metal complexes.
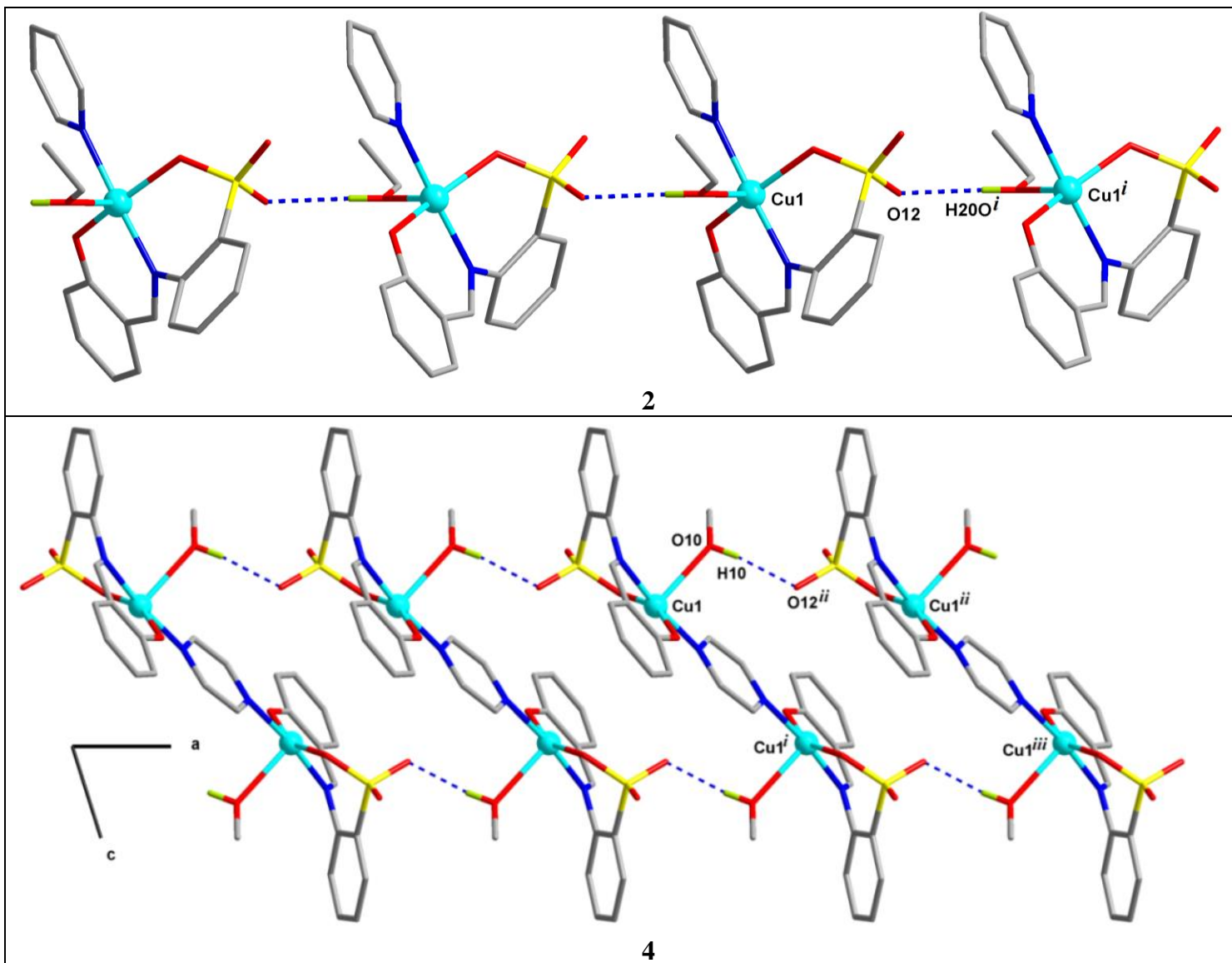
The molecular structure of the Schiff base (**1**) is stabilized by intramolecular H-bonds (Figures 1 and S1, Table S1) but the crystal lattice contains two additional intermolecular interactions, O1–H1O$^{...}$O22^i and O2^{ii}–H2O$^{ii...}$O13, which are responsible for the formation of a *zigzag* 1D chain as shown in Figures S1 and S2. In both cases the sulfonate oxygen atoms (O13 and O22^i) act as strong acceptors (Table S1) to the phenolic OH moieties (O1–H1O and O2^{ii}–H2O^{ii}) of two vicinal molecules.

The crystal lattices of the copper(II) complexes (**2–5**) contain only a strong hydrogen bonding interaction involving a non-coordinated sulfonate oxygen (O12 or O12^{ii}) and the coordinated ethanol (in **2**) or methanol (in **3–5**) solvent molecule.

As shown in Figures 2 and S3, a non-coordinated oxygen atom (O12 in **2** and **4** and O13 in **3** and **5**) of the sulfonate group acts as a strong acceptor (Table S1) and interacts with the alcoholic (ethanol in **2** and methanol in **3–5**) proton of a vicinal molecule forming linear 1D (in **2**), hacksaw double chain 1D (in **4**), 2D motif (in **5**) but no dimensionality in **3**. The double coordination of 2,2'-bipyridine in compound **3** (Figure 2) prevents the coordination of methanol which makes H-bonds with the asymmetric unit but without interacting with any vicinal molecule, thus producing no dimensionality in the crystal lattice. In all the other complexes (**2**, **4** and **5**), the coordinated methanol makes the alcoholic proton easily available for the vicinal molecule and thus acts as strong donor to build interesting supramolecular structures with various dimensionalities (Figure S3).

Figure S1. Idealized capped stick presentation of the H-bonds in **1** with partially atom labelling scheme. All H-atoms except those participating in H-bonding interactions are omitted for clarity. Symmetry: *i)* –x, 1–y, –z; *ii)* 1–x, 1–y, –z.

Figure S2. Idealized capped stick presentation of the H-bonded *zigzag* 1D chain in **1**. All H-atoms except those participating in H-bonding interactions are omitted for clarity. Symmetry: *i*) –x, 1–y, –z; *ii*) 1–x, 1–y, –z.
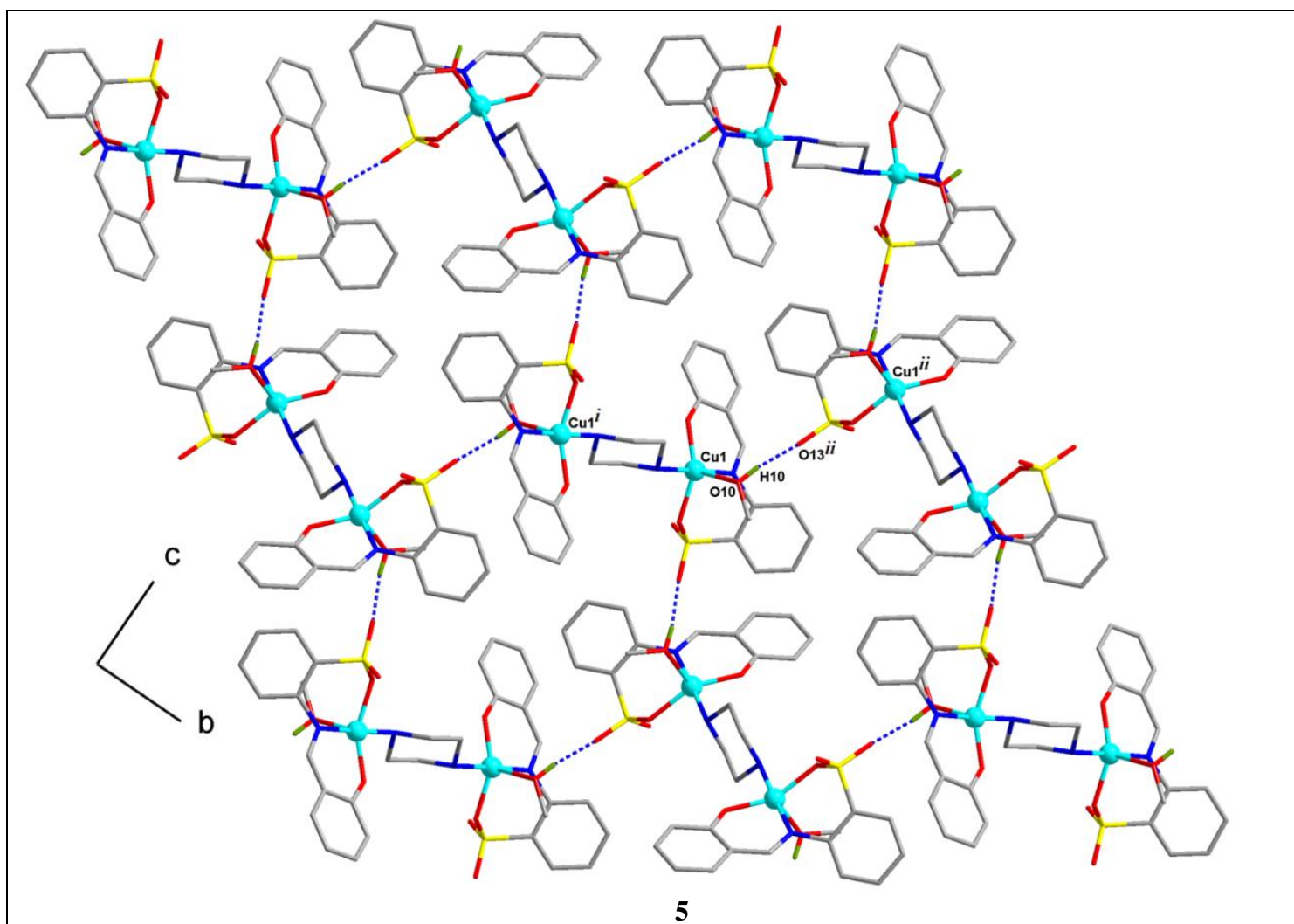
2

4

5

Figure S3. Idealized capped stick presentations of the H-bonded linear 1D in **2**, double chain 1D in **4** and 2D motif in **5**. All H-atoms except those participating in H-bonding are omitted for clarity. Symmetry: (*i*) 0.5+x, 0.5–y, –0.5+z (in **2**); *i*) 1–x, –y, 1–z; *ii*) 1+x, y, z; *iii*) 2–x, –y, 1–z (in **4**) and *i*) 2–x, –y, –z; *ii*) *i*) 0.5+x, 0.5 –y, 0.5+z (in **5**).

Table S1. Geometries [distances in (Å) and angles in (°)] of the H-bonds in **1–5**.

Compound	D–H···A	D···A	H···A	D–H···A
1	N1–H1N···O1	2.647	1.98	131.4
	N1–H1N···O11	2.725	1.99	140.1
	O1–H1O···O22^i	2.593	1.62	174.0
	N2^i–H2N^i···O2^i	2.626	1.95	133.0
	O2^{ii}–H2O^{ii}···O13	2.606	1.69	174.0
	N2^i–H2N^i···O21^i	3.015	2.48	119.3
2	O20^i–H20O^i···O12	2.807	2.02	170.2
3	O40^i–H40^i···O13	2.792	1.97	175.5
4	O10–H10···O12^{ii}	2.760	1.95	172.0
5	O10–H10···O13^{ii}	2.730	1.85	171.0

Table S2. Tests concerning the oxidation of cyclooctane in the presence of H_2L (**1**) and in the absence of any metal catalyst (blank tests).[a]

Entry	Time (h)	No additive		Py		HNO$_3$	
		Yield[b], %	TON[c]	Yield[b], %	TON[c]	Yield[b], %	TON[c]
1	0	0	0	0	0	0	0
2	2	0.01	0	0	0	1.14	3
3	4	0.31	1	0	0	1.83	5
4	8	0.28	1	0.17	0	2.13	5
5	24	0.19	0	0.52	1	2.30	6
6	32	0.17	0	0.84	2	2.70	7

[a] Reaction conditions: cyclooctane (0.25 M), **1** (10^{-3} M), additive (0.072 M), H_2O_2 (1.2 M) in acetonitrile at 60 °C; total volume of reaction mixture is 10 mL. [b] Amounts of cyclooctanone and cyclooctanol were determined after reduction of the aliquots with PPh$_3$; when the yield was above zero, only cyclooctanol was detected in a measurable amount. [c] Turnover number of the catalyst (sum of moles of all products per mole of **1**).

Table S3. Results obtained before the reduction with PPh$_3$ of the aliquots of the oxidation of cyclooctane catalyzed by **3**.[a]

Entry	Time (min)	Yield[b], %	Selectivity[c]	TON[d]
1	0	0	-	0
2	4	3	82:18	8
3	9	8	84:16	20
4	120	19	85:15	48

[a] Reaction conditions: cyclooctane (0.25 M), complex **3** (10^{-3} M per copper), H_2O_2 (1.2 M) in acetonitrile at 60 °C; total volume of reaction mixture is 10 mL. [b] Amounts of cyclooctanone and cyclooctanol were determined before reduction of the aliquots with PPh$_3$ (for this method see ref. 19). [c] Cyclooctanone/cyclooctanol ratio. [d] Turnover number of the catalyst (sum of moles of all products per mole of **3**).

Table S4. Crystallographic Data for **1**–**5**.

	1	2	3	4	5
Formula	$C_{13}H_{11}NO_4S$	$C_{20}H_{20}CuN_2O_5S$	$C_{24}H_{21}CuN_3O_5S$	$C_{32}H_{30}Cu_2N_4O_{10}S_2$	$C_{32}H_{36}Cu_2N_4O_{10}S_2$
FW	277.29	463.98	527.04	821.80	827.85
Crystal colour	Yellow	Green	Green	Green	Green
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	*P*-1	*P*21/*n*	*P*21/*n*	*P*-1	*P*21/*n*
a/Å	9.0847(6)	9.5036(4)	8.1099(2)	7.4426(4)	6.9512(9)
b/Å	10.5878(8)	18.3619(8)	29.4538(7)	10.2904(6)	18.534(2)
c/Å	13.3058(9)	11.3390(5)	10.5303(3)	11.4557(7)	13.4906(15)
α/°	70.313(3)	90.00	90.00	75.615(2)	90.00
β/°	82.104(3)	91.883(2)	109.3950(9)	71.959(3)	100.283(3)
γ/°	76.733(3)	90.00	90.00	85.198(2)	90.00
V/Å^3	1170.35(14)	1977.63(15)	2372.60(11)	808.05(8)	1710.1(4)
Z	4	4	4	1	2
T/K	150(2)	150(2)	296(2)	296(2)	150(2)
2θ/°	5.48 – 50.70	4.22 – 50.72	4.94 – 52.74	4.92– 52.82	3.78 – 52.84
μ (Mo Kα)/mm^{-1}	0.286	1.245	1.049	1.512	1.429
ρ_{calcd}/g cm^{-3}	1.574	1.558	1.475	1.689	1.608
F(000)	576	956	1084	420	852
Absorption-correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan	Multi-scan
Index ranges	−10<*h*<10	−11<*h*<11	−9<*h*<10	−9<*h*<9	−8<*h*<7
	−12<*k*<12	−21<*k*<22	−36<*k*<34	−12<*k*<12	−23<*k*<22
	−13<*l*<16	−13<*l*<10	−13<*l*<13	−14<*l*<14	−16<*l*<16
Reflections collected	9969	14180	24195	15098	13661
Independent reflections	4194	3629	4826	3327	3506
R_{int}	0.0560	0.0555	0.0350	0.0183	0.1286
$R_1{}^a$/ w$R_2{}^b$ [I > 2σ(I)]	0.0510/0.0991	0.0373/0.0759	0.0398/0.0963	0.0349/0.0932	0.0526/0.0901
$R_1{}^a$/ w$R_2{}^b$ [for all $F_o{}^2$]	0.1101/0.1129	0.0594/0.0838	0.0534/0.1028	0.0371/0.0952	0.1145/0.1035
GOF on F^2	0.919	1.017	1.007	1.098	0.920

Table S5. Effect of the presence of diphenylamine on the oxidation of cyclooctane catalyzed by **3**.[a]

Entry	Time (min)	Yield[b], %	Selectivity[c]	TON[d]	Yield drop[e] owing to Ph_2NH, %
1	0	0	-	0	0
2	5	3	0:100	8	5
3	9	6	3:97	14	29
4	120	10	16:84	25	53

[a] Reaction conditions: cyclooctane (0.25 M), complex **3** (10^{-3} M per copper), H_2O_2 (1.2 M), Ph_2NH (1.2 M) in acetonitrile at 60 °C; total volume of reaction mixture is 10 mL. [b] Amounts of cyclooctanone and cyclooctanol were determined after reduction of the aliquots with PPh_3 (for this method see ref. 19). [c] Cyclooctanone/cyclooctanol ratio. [d] Turnover number of the catalyst (sum of moles of all products per mole of **3**). [e] (1 – total yield with Ph_2NH / total yield without Ph_2NH) x 100

Table S6. Effect of the presence of bromotrichloromethane on the oxidation of cyclooctane catalyzed by **3**.[a]

Entry	Time (h)	Yield[b], %	Selectivity[c]	TON[d]	Yield drop[e] owing to $CBrCl_3$, %
1	0	0	-	0	0
2	5	3	0:100	8	8
3	9	6	4:96	14	32
4	2	9	17:83	24	54

[a] Reaction conditions: cyclooctane (0.25 M), complex **3** (10^{-3} M per copper), H_2O_2 (1.2 M), $CBrCl_3$ (0.25 M) in acetonitrile at 60 °C; total volume of reaction mixture is 10 mL. [b] Amounts of cyclooctanone and cyclooctanol were determined after reduction of the aliquots with PPh_3 (for this method see ref. 19). [c] Cyclooctanone/cyclooctanol ratio. [d] Turnover number of the catalyst (sum of moles of all products per mole of **3**). [e] (1 – total yield with $CBrCl_3$/ total yield without $CBrCl_3$) x 100