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Mild C–H functionalization of alkanes catalyzed by bioinspired copper(II) cores†

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Three new copper(II) coordination compounds formulated as $[Cu(H_{1.5}bdea)_2](hba)\cdot2H_2O$ (**1**), $[Cu_2(\mu\text{-}Hbdea)_2(aca)_2]\cdot4H_2O$ (**2**), and $[Cu_2(\mu\text{-}Hbdea)_2(\mu\text{-}bdca)]_n$ (**3**) were generated by aqueous medium self-assembly synthesis from $Cu(NO_3)_2$, *N*-butyldiethanolamine (H_2bdea) as a main N,O-chelating building block and different carboxylic acids [4-hydroxybenzoic (Hhba), 9-anthracenecarboxylic (Haca), or 4,4′-biphenyldicarboxylic (H_2bdca) acid] as supporting carboxylate ligands. The structures of products range from discrete mono- (**1**) or dicopper(II) (**2**) cores to a 1D coordination polymer (**3**), and widen a family of copper(II) coordination compounds derived from H_2bdea. The obtained compounds were applied as bioinspired homogeneous catalysts for the mild C–H functionalization of saturated hydrocarbons (cyclic and linear C_5–C_8 alkanes). Two model catalytic reactions were explored, namely the oxidation of hydrocarbons with H_2O_2 to a mixture of alcohols and ketones, and the carboxylation of alkanes with $CO/S_2O_8^{2-}$ to carboxylic acids. Both processes proceed under mild conditions with a high efficiency and the effects of different parameters (*e.g.*, reaction time and presence of acid promoter, amount of catalyst and solvent composition, substrate scope and selectivity features) were studied and discussed in detail. In particular, an interesting promoting effect of water was unveiled in the oxidation of cyclohexane that is especially remarkable in the reaction catalyzed by **3**, thus allowing a potential use of diluted, *in situ* generated solutions of hydrogen peroxide. Moreover, the obtained values of product yields (up to 41% based on alkane substrate) are very high when dealing with the C–H functionalization of saturated hydrocarbons and the mild conditions of these catalytic reactions (50–60 °C, H_2O/CH_3CN medium). This study thus contributes to an important field of alkane functionalization and provides a notable example of new Cu-based catalytic systems that can be easily generated by self-assembly from simple and low-cost chemicals.

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Introduction

Alkanes represent an abundant and inexpensive class of hydrocarbon substrates for the synthesis of different value-added chemicals such as alcohols, ketones, aldehydes, and carboxylic acids.[1–3] However, the transformation of saturated hydrocarbons into useful products usually requires several reaction steps and harsh reaction conditions (elevated temperatures and pressures) owing to an intrinsic inertness of alkanes. Hence, the development of novel and effective reaction protocols capable of functionalizing saturated hydrocarbons under mild conditions constitutes a long-term objective in the fields of organic synthesis, catalysis, and biomolecular chemistry.[1–6]

In fact, much research was dedicated to the investigation of biological and bioinspired C–H functionalization reactions[7–10] using alkanes as abundant substrates including renewable feedstocks (*e.g.*, biogas).[11] These reactions require the use of enzymatic catalysts such as methane monooxygenases or their bioinspired analogues based on coordination compounds of iron and copper.[8–10] In particular, the design of Cu-based catalytic systems for the bioinspired oxidative functionalization of hydrocarbons and other substrates has been especially attractive, given rich coordination versatility and bioinorganic chemistry of copper along with its presence in the N,O-active sites of different oxidation enzymes.[9–12]

Following our general interest in the design and exploration of new Cu-based catalytic systems for the C–H functionalization of alkanes,[13] the main objectives of the present study have consisted in (1) the self-assembly generation of novel

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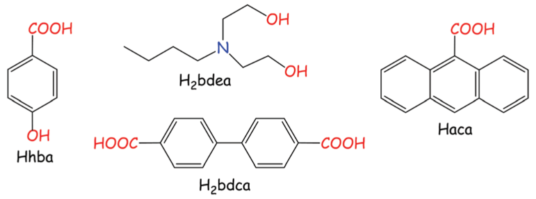
† Electronic supplementary information (ESI) available: Detailed description of catalytic experiments, additional structural representations (Fig. S1–S3) and catalysis data (Fig. S4 and S5), H-bonding details (Table S1) and bonding parameters (Tables S2–S4) for **1–3**; gas chromatograms (Fig. S6–S52). CCDC 1936224–1936226. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9ob01442j



Scheme 1 Formulae of ligands used for synthesis of **1–3**.

bioinspired copper cores with N,O-environments and (2) evaluation of their catalytic activity in the mild homogeneous oxidation and carboxylation of C_5–C_8 alkanes to give alcohols, ketones, or carboxylic acids. For achieving an N,O-environment around Cu centers, we selected a combination of the aminoalcohol and carboxylic acid ligands, wherein *N*-butyldiethanolamine (H_2bdea) was used as a principal building block that features water solubility, three potential coordination sites, and combines hydrophilic and hydrophobic functionalities. Various carboxylic acids having one, two, or three aromatic rings and thus a varying degree of steric hindrance and hydrophobicity were applied as supporting ligands. For catalytic tests, cyclic and linear C_5–C_8 hydrocarbons were used as typical substrates.

Hence, this study reports the synthesis by aqueous medium self-assembly, isolation and characterization, as well as crystal structures and catalytic properties of three new copper(II) coordination compounds, namely [Cu($H_{1.5}$bdea)$_2$](hba)·$2H_2O$ (**1**), [Cu_2(μ-Hbdea)$_2$(aca)$_2$]·$4H_2O$ (**2**), and [Cu_2(μ-Hbdea)$_2$(μ-bdca)]$_n$ (**3**) [*N*-butyldiethanolamine, H_2bdea; 4-hydroxybenzoic acid, Hhba; 9-anthracenecarboxylic acid, Haca; 4,4′-biphenyldicarboxylic acid, H_2bdca] (Scheme 1). Compounds **1–3** behave as effective catalysts for the oxidation of alkanes with H_2O_2 to alcohols and ketones, and for the carboxylation of alkanes with CO and persulfate oxidant to carboxylic acids.

Experimental

Materials and methods

Commercially obtained reagents and solvents were used. Compounds **1–3** were self-assembled at room temperature (r.t., ∼25 °C) in air atmosphere. C, H, N elemental analyses were obtained from the Laboratory of Analyses of IST. IR spectra were measured using KBr discs and a JASCO FT/IR-4100 instrument (abbreviations: very strong: vs, strong: s, medium: m, weak: w, broad: br, shoulder: sh). ESI-MS(±) were measured using a LCQ Fleet mass spectrometer with an ESI source (Thermo Scientific).

Synthesis and analytical data for 1–3

All compounds were obtained following a general synthetic procedure. Aqueous solution of *N*-butyldiethanolamine (H_2bdea; 1 M, 1 mL, 1 mmol) was added to an aqueous 0.1 M solution of $Cu(NO_3)_2 \cdot 3H_2O$ (5 mL, 0.5 mmol for **1**; or 10 mL, 1 mmol for **2** and **3**) with continuous stirring. In a separate vial, a carboxylic acid [4-hydroxybenzoic acid (Hhba; 138.1 mg, 1 mmol) for **1**, 9-anthracenecarboxylic acid (Haca; 222.2 mg, 1 mmol) for **2**; or 4,4′-biphenyldicarboxylic acid (H_2bdca; 121.1 mg, 0.5 mmol) for **3**] was dissolved in an aqueous solution of NaOH (1 M, 3 mL, 3 mmol). The obtained solution was added dropwise to the main reaction mixture, which was then stirred overnight and filtered off. The filtrate was left to evaporate at room temperature in a beaker, producing blue crystals of products (including those of X-ray quality) in 2 weeks. These were collected manually or by filtration and dried in air to furnish **1–3** in ∼50% yields, based on $Cu(NO_3)_2 \cdot 3H_2O$.

[Cu($H_{1.5}$bdea)$_2$](hba)·$2H_2O$ (1). IR (KBr): 3478 (m br) ν(OH), 2951 (w) ν_{as}(CH), 2892 (w), 2873 (w) and 2846 (w) ν_s(CH), 1602 (s) and 1548 (s) ν_{as}(COO), 1468 (w), 1410 (s) and 1379 (s), ν_s(COO), 1355 (m), 1251 (s), 1172 (s), 1071 (s), 1059 (s), 1019 (m), 967 (w), 912 (m), 896 (m), 854 (m), 809 (w), 783 (s), 731 (w), 699 (w), 642 (s), 593 (m), 496 (m), 461 (w), 431 (w), 416 (w), and 404 (w) cm^{-1}. ESI-MS (H_2O), selected fragments: MS(−), *m*/*z*: 557 (32%) [{Cu(Hbdea)$_2$}(hba) + $2H_2O$]$^-$, 541 (25%) [{Cu(Hbdea)$_2$}(hba) + H_2O]$^-$. Anal. calcd for $C_{23}H_{46}CuN_2O_9$ (**1**, MW 557.9): C 49.47, H 5.02, N 8.31; found: C 49.18, H 4.96, N 8.14.

[Cu_2(μ-Hbdea)$_2$(aca)$_2$]·$4H_2O$ (2). IR (KBr): 3426 (s) ν(OH), 2960 (w) and 2930 (w) ν_{as}(CH), 2850 (w) ν_s(CH), 1585 (vs) ν_{as}(COO), 1521 (w), 1485 (w), 1444 (w), 1418 (m) and 1384 (s) ν_s(COO), 1317 (s), 1278 (m), 1222 (m), 1174 (w), 1142 (w), 1079 (m), 1015 (w), 892 (m), 733 (m), 692 (m), and 419 (m) cm^{-1}. ESI-MS (H_2O), selected fragments: MS(+), *m*/*z*: 891 (100%) [Cu_2(Hbdea)$_2$(aca)$_2$ + H]$^+$, 667 (12%) [Cu_2(Hbdea)$_2$(aca)]$^+$. Anal. calcd for $C_{46}H_{58}Cu_2N_2O_{10}$ (**2**·H_2O, MW 925.5): C 59.64, H 6.32, N 3.03; found: C 59.88, H 6.02, N 3.12.

[Cu_2(μ-Hbdea)$_2$(μ-bdca)]$_n$ (3). IR (KBr): 3441 (m br) ν(OH), 2962 (m) and 2932 (w) ν_{as}(CH), 2864 (w) ν_s(CH), 1604 (vs) and 1542 (s) ν_{as}(COO), 1468 (m), 1377 (vs br) ν_s(COO), 1259 (w), 1175 (w), 1141 (w), 1079 (s), 1027 (w), 982 (m), 895 (m), 866 (w), 775 (s), 701 (w), 677 (m), 645 (m), 575 (w) and 537 (w) cm^{-1}. ESI-MS (CH_3CN), selected fragments: MS(+), *m*/*z*: 1314 (70%) [{Cu_3(bdea)$_3$}(μ-bdca)$_2$ + H_2O + H]$^+$, 1154 (12%) [{Cu_2(μ-Hbdea)$_2$}$_2$(μ-bdca) + H_2O + H]$^+$, 1132 (15%) [{Cu_2(bdea)$_2$}$_2$(μ-bdca) + H]$^+$, 911 (45%) [Cu_3(bdea)$_3$(μ-bdca) + H]$^+$, 891 (100%) [{Cu_2(bdea)$_2$}$_2$ + H]$^+$. Anal. calcd for $C_{30}H_{44}Cu_2N_2O_8$ (**3**·$2H_2O$, MW 723.4): C 49.76, H 6.69, N 3.87; found: C 49.92, H 6.72, N 3.95.

X-ray crystallography

Single crystals of **1–3** were mounted with Fomblin oil in a cryoloop. Bruker AXS-KAPPA APEX II diffractometer (graphite-monochromated radiation, Mo Kα, λ = 0.71073 Å) was used for data collection, which was monitored with APEX2.[14] X-ray data were corrected for Lorentzian, polarization and absorption effects with SAINT and SADABS.[14] Structures were solved with SIR97 [15] and SHELXS-97.[16] SHELXL-97 was used for full matrix least-squares refinement on F^2.[16] All these programs are a part of WINGX-Version 2014.1.[17] Non-H atoms were refined anisotropically. Full-matrix least-squares refinement of the non-H atoms with anisotropic thermal parameters was applied. All the H atoms were placed in idealized positions and allowed to refine at a parent C or O atom, except for some OH groups and water moieties which were found from the electron density map. A twin matrix was applied to **1**. A disorder model was applied to butyl chain of the $Hbdea^-$ moiety in **2**. PLATON[18] was used for analysis of H-bond interactions. Structural data of **1–3** were deposited as CIF files within the Cambridge Crystallographic Data Base (CCDC 1936224–1936226†).

Crystal data for 1. $C_{15}H_{28}Cu_{0.5}NO_7$, $M = 366.15$, $\lambda = 0.71073$ Å (Mo-Kα), $T = 293(2)$ K, monoclinic, space group $P2_1/n$, $a = 10.1856(14)$ Å, $b = 16.187(2)$ Å, $c = 11.0278(15)$ Å, $\alpha = 90°$, $\beta = 91.519(5)°$, $\gamma = 90°$, $V = 1817.5(4)$ Å^3, $Z = 4$, $D_c = 1.338$ g cm^{-3}, $\mu = 0.666$ mm^{-1}, 40 879 reflections collected, 3827 unique, $I > 2\sigma(I)$ ($R_{int} = 0.1208$), $R_1 = 0.0767$, $wR_2 = 0.2110$, GOF 1.061.

Crystal data for 2. $C_{23}H_{31}CuNO_6$, $M = 481.03$, $\lambda = 0.71073$ Å (Mo-Kα), $T = 293(2)$ K, monoclinic, space group $P2_1/c$, $a = 10.6013(6)$ Å, $b = 25.1550(13)$ Å, $c = 8.9311(4)$ Å, $\alpha = 90°$, $\beta = 109.342(2)°$, $\gamma = 90°$, $V = 2247.3(2)$ Å^3, $Z = 4$, $D_c = 1.422$ g cm^{-3}, $\mu = 1.011$ mm^{-1}, 14 787 reflections collected, 4455 unique, $I > 2\sigma(I)$ ($R_{int} = 0.0454$), $R_1 = 0.1015$, $wR_2 = 0.1928$, GOF 1.065.

Crystal data for 3. $C_{30}H_{44}Cu_2N_2O_8$, $M = 687.75$, $\lambda = 0.71073$ Å (Mo-Kα), $T = 293(2)$ K, monoclinic, space group $P2_1/c$, $a = 16.608(2)$ Å, $b = 11.434(4)$ Å, $c = 16.771(4)$ Å, $\alpha = 90°$, $\beta = 100.803(6)°$, $\gamma = 90°$, $V = 3128.3(14)$ Å^3, $Z = 4$, $D_c = 1.460$ g cm^{-3}, $\mu = 1.411$ mm^{-1}, 25 910 reflections collected, 5751 unique, $I > 2\sigma(I)$ ($R_{int} = 0.1301$), $R_1 = 0.0574$, $wR_2 = 0.1368$, GOF 0.900.

Catalytic experiments

Catalytic activity of **1–3** was evaluated in the oxidation[13] and carboxylation[19] of various saturated hydrocarbons under mild conditions, following our previously developed protocols. Agilent Technologies 7820A series gas chromatograph was used for gas chromatography (GC) analyses of the reaction mixtures (carrier gas: He; detector: FID; capillary column: BP20/SGE). Detailed description of catalytic experiments is given in ESI.†

Results and discussion

Synthesis of 1–3

Aiming at exploring the self-assembly generation of copper(II) coordination compounds bearing *N*-butyldiethanolamine (H_2bdea) as a principal building block, we attempted a series of aqueous-medium reactions between $Cu(NO_3)_2$, H_2bdea and different carboxylic acids containing one, two, or three aromatic rings [*i.e.*, 4-hydroxybenzoic (Hhba), 4,4′-biphenyldicarboxylic (H_2bdca), and 9-anthracenecarboxylic (Haca) acid, respectively]. As a result, three new products were generated, namely $[Cu(H_{1.5}bdea)_2](hba)\cdot 2H_2O$ (**1**), $[Cu_2(\mu\text{-}Hbdea)_2(aca)_2]\cdot 4H_2O$ (**2**), and $[Cu_2(\mu\text{-}Hbdea)_2(\mu\text{-}bdca)]_n$ (**3**), which range from discrete mono- or dicopper(II) cores to a 1D coordination polymer. All the compounds were obtained as stable crystalline solids and characterized by standard methods (IR spectroscopy, ESI-MS, elemental analysis) in addition to single crystal X-ray diffraction.

Structural description of 1–3

The crystal structure of $[Cu(H_{1.5}bdea)_2](hba)\cdot 2H_2O$ (**1**) is composed of a monocopper(II) $[Cu(H_{1.5}bdea)_2]^+$ cation, an hba^- anion, and two crystallization H_2O molecules (Fig. 1a). In the cation, the six-coordinate Cu1 atom possesses an octahedral $\{CuO_4N_2\}$ environment that is occupied by pairs of symmetry equivalent N and O atoms from two N,O_2-chelating aminoalcoholate moieties [Cu–N 2.050(4) Å; Cu–O 2.037(3) and 2.324(4) Å]. Several O–H⋯O hydrogen bonds provide an interlinkage of the $[Cu(H_{1.5}bdea)_2]^+$ cations with hba^- anions and of the latter with crystallization H_2O molecules, thus leading to an extension of the structure into a 3D H-bonded net (Fig. S1, ESI†).

The structure of $[Cu_2(\mu\text{-}Hbdea)_2(aca)_2]\cdot 4H_2O$ (**2**) contains a dicopper(II) aminoalcholate molecular unit and four H_2O molecules of crystallization (Fig. 1b). Two symmetry equivalent Cu1 atoms are five-coordinate and reveal a distorted square-pyramidal $\{CuO_4N\}$ environment. Its equatorial sites are taken by the two μ-O atoms and one N donor from two $Hbdea^-$ moieties [Cu–O 1.917(7) and 1.921(6) Å; Cu–N 2.031(7) Å] as well as one O donor from aca^- [Cu–O 1.940(5) Å]; the OH group from $Hbdea^-$ moiety occupies an axial site [Cu–O 2.303(9) Å]. In the dimer, the Cu1⋯Cu1 separation is 2.922(2) Å. An interesting feature of **2** concerns the H-bonding of crystallization water molecules into cyclic $(H_2O)_4$ clusters of the R4 type.[20,21] These water clusters interlink the dicopper $[Cu_2(\mu\text{-}Hbdea)_2(aca)_2]$·blocks into 1D H-bonded chains (Fig. S2, ESI†).

Compound **3** reveals a 1D linear chain coordination polymer structure, $[Cu_2(\mu\text{-}Hbdea)_2(\mu\text{-}bdca)]_n$, which is assembled from the dicopper(II) $[Cu_2(\mu\text{-}Hbdea)_2]^{2+}$ blocks and $\mu\text{-}bdca^{2-}$ linkers (Fig. 1c). Within the $[Cu_2(\mu\text{-}Hbdea)_2]^{2+}$ units,

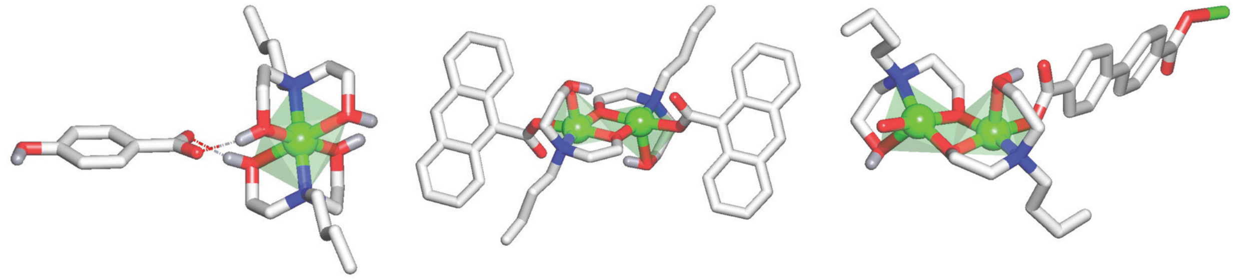


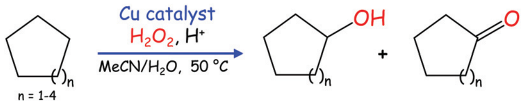
Fig. 1 Crystal structures of copper compounds **1** (a), **2** (b), and **3** (c). Crystallization H_2O molecules and CH hydrogen atoms are omitted. Colors: Cu, green balls; N, blue; O, red; C, gray; H, dark gray.

the Cu1 and Cu2 atoms are also 5-coordinate and feature distorted square-pyramidal {CuO_4N} geometries occupied by the equatorial N and O donors from the μ-$Hbdea^-$ and μ-$bdca^{2-}$ moieties and axial OH groups. The bonding parameters in **3** [Cu–O 1.910(3)–2.408(5) Å; Cu–N 2.048(4) Å, Cu1⋯Cu2 2.8908(9) Å] are comparable to those in **2** and related Cu-aminoalcoholate derivatives.[22] A major difference in these structures concerns a 1D polymeric nature of **3** due to the presence of 4,4′-biphenyldicarboxylate linkers (Fig. S3, ESI†).

Catalytic oxidation of cyclic C_5–C_8 hydrocarbons

All copper(II) compounds **1–3** exhibit good catalytic activity toward the oxidation of cyclohexane as a model substrate of industrial importance to give a mixture of cyclohexanol and cyclohexanone (intermediates in nylon production).[12,23] The reactions undergo in CH_3CN/H_2O mixture using H_2O_2 (50% in H_2O) at 50 °C and in the presence of acid promoter such as TFA, CF_3COOH (Fig. 2, Table 1). In the reaction catalyzed by **2**, the maximum total product yield of 22% was achieved in 1 h. The activities of **1** and **3** are comparable but the corresponding oxidation reactions are slightly slower, leading in 2 h to 22 and 18% total yields, respectively. Almost no yield decline was observed on increasing the reaction time up to 5 h (Fig. 2), indicating that an overoxidation of products does not occur.

Table 1 Mild oxidation of cycloalkanes to alcohols and ketones with H_2O_2 catalyzed by **1–3**[a]



			Product yield[b], %		
Entry	Cycloalkane	Catalyst	Ketone	Alcohol	Total
1	C_5H_{10}	**1**	3.4	5.6	9.0
2		**2**	4.4	4.9	9.3
3		**3**	6.6	3.5	10.1
4	C_6H_{12}	**1**	8.1	9.9	18.0
5		**2**	8.5	10.4	18.9
6		**3**	10.3	10.8	21.1
7	C_7H_{14}	**1**	15.2	8.1	23.3
8		**2**	13.5	8.2	21.7
9		**3**	14.5	10.0	24.5
10	C_8H_{16}	**1**	12.3	3.5	15.8
11		**2**	14.1	2.9	17.0
12		**3**	12.7	3.5	16.2

[a] Reaction conditions: Catalyst (0.01 mmol), TFA (0.1 mmol), cycloalkane (2.0 mmol), H_2O_2 (10.0 mmol; 50% in H_2O), CH_3CN (up to 5.0 mL total volume), 50 °C. [b] (Moles of product/moles of alkane) × 100%; GC yields (internal standard method).

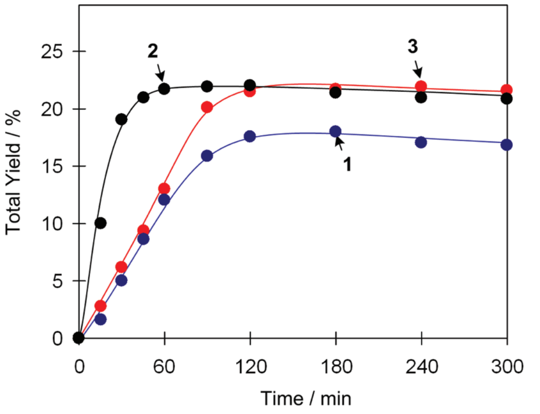


Fig. 2 Oxidation of cyclohexane (total yield of cyclohexanol and cyclohexanone *vs.* time) with H_2O_2 catalyzed by **1–3**. Reaction conditions: Catalyst (0.01 mmol), TFA (0.1 mmol), C_6H_{12} (2.0 mmol), H_2O_2 (10.0 mmol; 50% in H_2O), CH_3CN (up to 5.0 mL total volume), 50 °C.

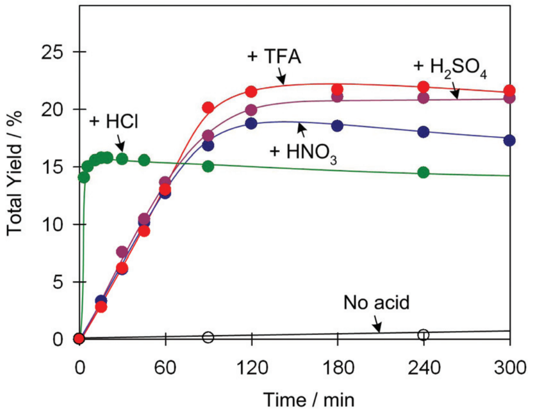


Fig. 3 Effect of the type of acid promoter on the total yield of products (cyclohexanol and cyclohexanone) in the cyclohexane oxidation with H_2O_2 catalyzed by **3**. Reaction conditions: Catalyst (0.01 mmol), acid promoter (0.1 mmol), C_6H_{12} (2.0 mmol), H_2O_2 (10.0 mmol; 50% in H_2O), CH_3CN (up to 5.0 mL total volume), 50 °C.

Oxidation of cyclohexane catalyzed by copper compounds proceeds in the presence of a small amount of acid promoter, which is needed to activate the catalyst and accelerate the reaction (Fig. 2 and 3),[12,13,24] thus affecting both the total product yield and the maximum initial reaction rate (W_0). We studied an effect of different acid promoters on the catalytic activity of **3** in cyclohexane oxidation (Fig. 3). In the presence of HNO_3 and H_2SO_4, the oxidations proceed similarly (the same initial reaction rates) to the system containing TFA, leading to the maximum product yields of 18–20% in 2 h. In a system containing HCl, there is a drastic acceleration of the reaction, which is completed in a few minutes with a product yield of 16% (TOF 380 h^{-1}). Such an accelerating effect of HCl can be explained by an ability of Cl^- anions to act as ligands and stabilize a Cu^I oxidation state or Cu–peroxo intermediates.[12]

We also studied an effect of the TFA amount on the total product yield and W_0 in the C_6H_{12} oxidation catalyzed by **3** (Fig. 4). The product yield gradually increases on changing the TFA concentration from 0 to 0.02 M, while higher amount of acid (0.03 M) does not accelerate the reaction. The dependence of the maximum initial rate (W_0) reveals an S-shape on the TFA concentration (Fig. 4b). A maximum value of W_0 is achieved at 0.01 M of TFA and above this concentration the reaction rate does not depend on the promoter amount.

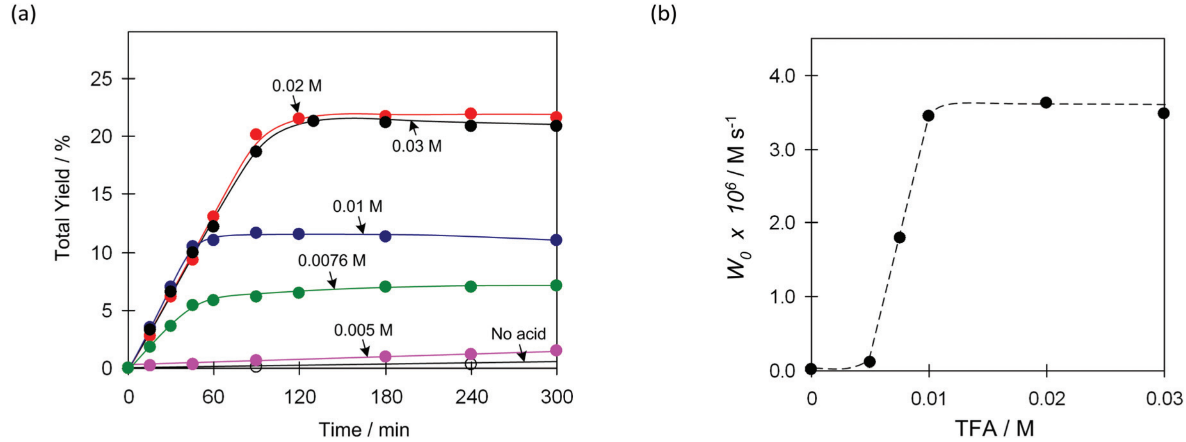


Fig. 4 Effect of TFA amount on (a) the total yield of products and (b) the maximum initial reaction rate (W_0) in the cyclohexane oxidation with H_2O_2 catalyzed by **3**. Reaction conditions: Catalyst (0.01 mmol), TFA (0.025–0.15 mmol), C_6H_{12} (2.0 mmol), H_2O_2 (10.0 mmol; 50% in H_2O), CH_3CN (up to 5.0 mL total volume), 50 °C.

The effects of catalyst amount on the total product yield and the maximum initial reaction rate in cyclohexane oxidation were investigated for all the catalysts in the presence of TFA promoter (Fig. S4 for **1** and **2**, ESI;† Fig. 5 for **3**). For catalysts **3** and **1**, the product yield and W_0 increase with catalyst amount in the studied range of concentrations up to 0.004 M. In the case of **2**, this effect was observed up to 0.002 M, and the following augmentation of the catalyst amount does not affect neither the product yield nor the initial reaction rate. The values of W_0 exhibit a first order dependence on the catalyst concentration for all the studied systems (Fig. 4d), thus suggesting an involvement of one Cu-containing catalytic species in the rate limiting stage of oxidation.

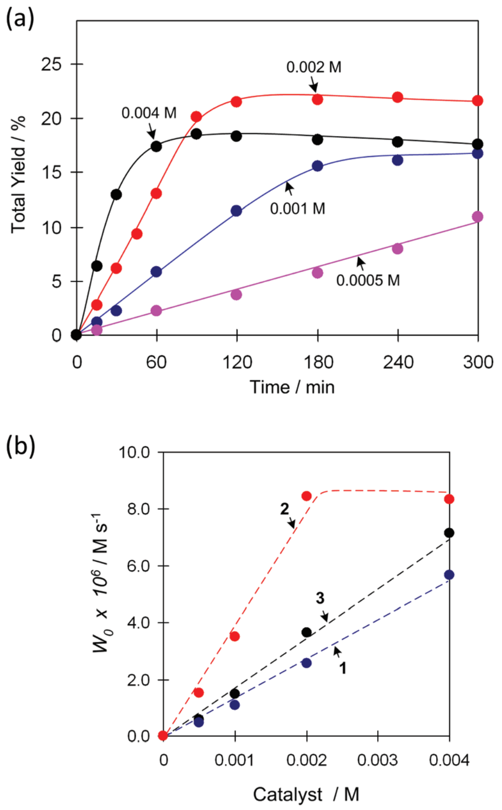


Fig. 5 Effect of catalyst amount on (a) the total product yield and (b) the maximum initial reaction rate (W_0) in the cyclohexane oxidation with H_2O_2 catalyzed by **3**. In (b), data for catalysts **1** and **2** are given for comparison. Reaction conditions: Catalyst (0.0025–0.02 mmol), TFA (0.1 mmol), C_6H_{12} (2.0 mmol), H_2O_2 (10.0 mmol; 50% in H_2O), CH_3CN (up to 5.0 mL total volume), 50 °C.

We also observed an unusual acceleration effect of the added water on the initial reaction rate in cyclohexane oxidation (Fig. S5 for **1** and **2**, ESI;† Fig. 6 for **3**). In the reaction catalyzed by **3**, W_0 linearly increases with addition of water (up to 12.9 M), thus indicating a first order dependence and demonstrating the direct involvement of H_2O in the rate limiting step of oxidation. Such an unusual promoting behavior of water well contrasts with other catalytic systems for alkane oxidation, wherein additional amounts of H_2O in the system decrease the substrate solubility, diminish the concentration of oxidant, and decelerate the reactions.[4,5,12] Similar acceleration effect of water on the W_0 was observed for the reactions catalyzed **1** and **2** (Fig. S5†). However, the total yield is lower in these cases and a yield drop can be observed after achieving the maximum. This can be associated with lowering of cyclohexane solubility and oxidant concentration in the presence of higher amounts of water. It should be noted that the crystallization water molecules present in the structures of **1** and **2** do not affect the observed behavior due to their very low amount, which is three orders of magnitude lower in comparison with the amount of H_2O present in the system due to the use of 50% H_2O_2 aqueous solution as oxidant (reaction conditions of Fig. S5†).

To check the substrate versatility of the present catalytic systems, the oxidation of other cycloalkanes apart from cyclohexane (*i.e.*, cyclopentane, cycloheptane, and cyclooctane) was investigated (Table 1). All compounds exhibit comparable activity with cycloheptane being the most reactive sub-

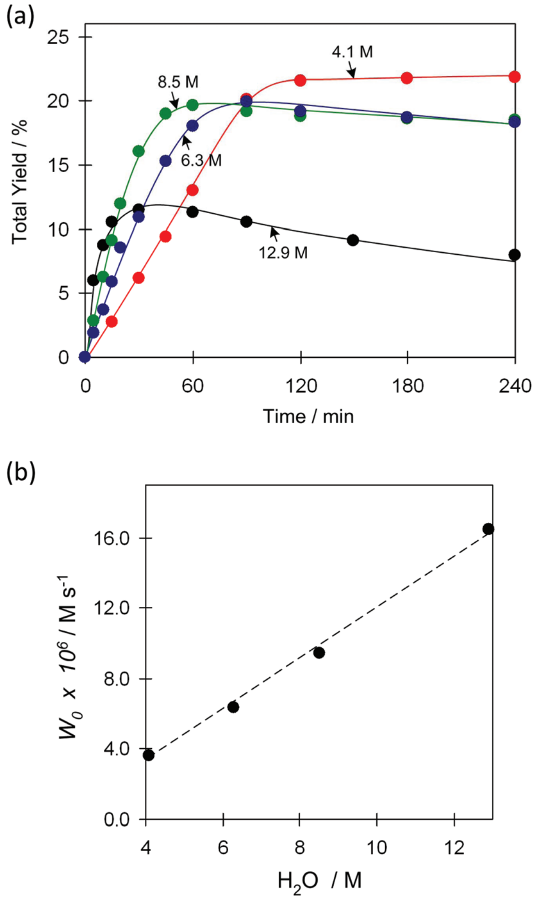


Fig. 6 Effect of total H_2O amount in the reaction system on (a) the total product yield and (b) the maximum initial reaction rate (W_0) in the cyclohexane oxidation with H_2O_2 catalyzed by **3**. Reaction conditions: Catalyst **3** (0.01 mmol), TFA (0.10 mmol), C_6H_{12} (2.0 mmol), H_2O_2 (10.0 mmol; 50% in H_2O), added H_2O (up to 0.8 mL), CH_3CN (up to 5.0 mL total volume), 50 °C.

strate (up to 25% product yields), followed by cyclohexane (up to 21% yields) and cyclooctane (up to 17% yields). The oxidation of cyclopentane is less efficient (10% product yields) due to its volatility under the reactions conditions (low boiling point).

To understand some mechanistic aspects of these oxidation reactions, we investigated other model substrates to obtain different types of selectivity parameters (Table 2). Thus, the oxidation of linear C_7 and C_8 hydrocarbons (*n*-heptane and *n*-octane) undergoes with a generally moderate regioselectivity in terms of the C(1) : C(2) : C(3) : C(4) values. For *n*-C_7H_{16}, these are 1 : 4 : 4 : 5 (for **2**), 1 : 5 : 5 : 6 (for **3**), and 1 : 9 : 12 : 15 (for **1**). A higher regioselectivity of **1** can be related to a more sterically hindered Cu center within the bis-aminoalcohol $[Cu(H_{1.5}bdea)_2]^+$ cation. Moreover, compound **1** is cationic and contains two chelating aminoalcohol blocks per Cu center (there is one aminoalcohol ligand per Cu center in **2** and **3**), in addition to featuring a 6-coordinate Cu atom in comparison to the 5-coordinate Cu atoms in **2** and **3**. However, this trend in different selectivities is not seen when oxidizing methylcyclohexane, wherein the normalized reactivities of hydrogen atoms at primary, secondary and tertiary carbon centers are rather similar in **1–3**, as attested by the bond selectivity 1° : 2° : 3° values of 1 : 5 : 16, 1 : 6 : 19, and 1 : 5 : 9, respectively. For the oxidation of adamantane, the bond selectivity 3°/2° parameters are within the 2.6–3.4 range, which is common for reactions occurring with participation of very powerful oxidizing species like $HO^•$ radicals.[1,3,13,25] Besides, no stereoselectivity was observed in the oxidation *cis*- and *trans*-1,2-dimethylcyclohexane.

Table 2 Different selectivity parameters in the oxidation of saturated hydrocarbons catalyzed by **1–3** [a]

	Catalyst		
Selectivity parameter	**1**	**2**	**3**
Regioselectivity			
C(1) : C(2) : C(3) : C(4)[b] (*n*-heptane)	1 : 9 : 12 : 15	1 : 4 : 4 : 5	1 : 5 : 5 : 6
C(1) : C(2) : C(3) : C(4)[b] (*n*-octane)	1 : 9 : 11 : 10	1 : 7 : 6 : 6	1 : 6 : 6 : 6
Bond selectivity 1° : 2° : 3° (methylcyclohexane)[c]	1 : 5 : 16	1 : 6 : 19	1 : 5 : 9
3°/2° (adamantane)[d]	2.6	3.2	3.4
Stereoselectivity			
trans/*cis*[e] (*cis*-1,2-dimethylcyclohexane)	1.00	0.97	0.97
trans/*cis*[e] (*trans*-1,2-dimethylcyclohexane)	0.79	0.87	0.95

[a] Reaction conditions: Catalyst **1–3** (5 μmol), TFA (0.05 mmol), alkane substrate (1.0 mmol), H_2O_2 (5.0 mmol; 50% in H_2O), MeCN (up to 2.5 mL total volume), 3 h, 50 °C. All selectivity parameters were calculated on the basis of the ratios of isomeric alcohol products; normalization for the number of hydrogen atoms at each C center was also performed. [b] C(1) : C(2) : C(3) : C(4) refers to reactivity of H atoms at C(1), C(2), C(3), and C(4) atoms. [c] 1° : 2° : 3° refers to reactivity of H atoms at primary/secondary/tertiary carbon atoms. [d] 3°/2° referrers to reactivity of H atoms at tertiary/secondary carbon atoms. [e] *trans*/*cis* refers to a ratio of stereoisomeric alcohol products with mutual *trans* and *cis* orientation of CH_3 groups.

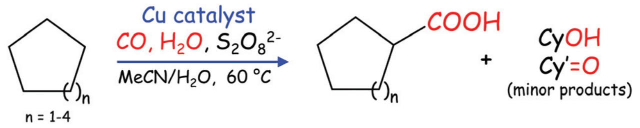
Therefore, these specific selectivity parameters as well as the analysis of prior studies[1,12,24–26] indicate that the present reactions catalyzed by **1–3** proceed with participation of hydroxyl radicals as principal hydrocarbon oxidizing species. These radicals are formed when hydrogen peroxide reacts with a copper catalyst. Then, hydroxyl radicals activate the cycloalkane substrate *via* H-abstraction with the generation of cycloalkyl radicals ($Cy^•$). The latter easily react with dioxygen to give cycloalkyl peroxo radicals ($CyOO^•$) and then cycloalkyl hydroperoxides (CyOOH) as intermediate products.

In fact, the presence of cycloalkylhydroperoxides as intermediate products in cycloalkane oxidation was detected using the method of Shul'pin,[3,26] namely by analyzing by gas chromatography the selected reaction mixtures before and after their treatment with solid triphenylphosphine; this reagent allows a selective reduction of CyOOH to alcohols.[3,26] Cycloalkylhydroperoxides are not very stable in the reaction mixture at 50 °C and undergo thermal or Cu-catalyzed decomposition to give cyclic alcohols (CyOH) and ketones (Cy′=O) as final reaction products.[1,12,24–26]

Catalytic carboxylation of cyclic and linear C_5–C_8 hydrocarbons

We also explored compounds **1–3** as catalysts for the carboxylation of both cyclic and linear C_5–C_8 alkanes with CO to form monocarboxylic acids as major products (Tables 3 and 4). In these reactions, a hydrocarbon reacts with carbon monoxide as a source of carbonyl functionality and water as a source of hydroxyl group to generate a carboxylic acid product in a single step.[19] The reactions also require a peroxodisulfate oxidant, copper catalyst, and proceed in H_2O/MeCN medium at 60 °C.

Table 3 Mild carboxylation of cycloalkanes to cycloalkanecarboxylic acids catalyzed **1–3** [a]



Entry	Cycloalkane	Catalyst	Product yield[b], % Carboxylic acid	Ketone	Alcohol	Total
1	C_5H_{10}	1	27.7	0.7	0.3	28.7
2		2	27.9	0.8	0.5	29.2
3		3	28.6	1.1	0.6	30.2
4	C_6H_{12}	1	40.6	2.0	0.5	43.1
5		2	39.3	2.1	0.6	42.0
6		3	40.0	1.8	0.5	42.3
7	C_7H_{14}	1	21.1	6.7	2.6	30.4
8		2	26.5	7.4	3.8	37.7
9		3	27.4	7.6	2.5	37.5
10	C_8H_{16}	1	9.8	9.8	8.8	28.4
11		2	10.9	12.0	6.6	29.5
12		3	11.2	10.5	7.5	29.2

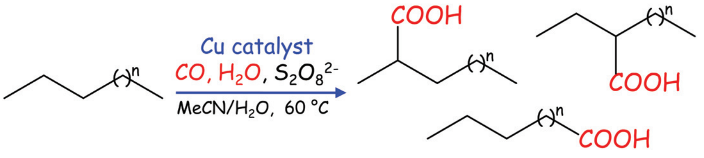
[a] Cyclic ketones and alcohols are formed as byproducts in minor amounts. Reaction conditions: Catalyst (10 μmol), cycloalkane substrate (1.00 mmol), p(CO) = 20 atm, $K_2S_2O_8$ (1.50 mmol), H_2O (2.0 mL)/MeCN (4.0 mL), 60 °C, 4 h in autoclave (20.0 mL volume). [b] (Moles of products/moles of cycloalkane) × 100%; GC yields (internal standard method).

Compounds **1–3** act as very efficient catalysts in carboxylation of cyclic C_5–C_8 hydrocarbons to produce the corresponding C_6–C_9 cycloalkanecarboxylic acids as principal products in up to 41% total yields based on cycloalkane (Table 3). As expected for cycloalkane substrates, there is only one cycloalkanecarboxylic acid product, whereas for linear alkanes the formation of isomeric monocarboxylic acids was observed (Table 4). In addition, the generation of alcohols and ketones (and aldehydes for linear alkane substrates) in minor quantities was also detected due to competing oxidation reactions.

In fact, the highest reactivity among all the cyclic substrates was observed for cyclohexane, resulting in 41% yield of $C_6H_{11}COOH$, followed by cyclopentane (28% of C_5H_9COOH) and cycloheptane (27% of $C_7H_{13}COOH$). The yield of carboxylic acid drops to 10–11% when using cyclooctane as substrate (Table 3). The total yield of the oxidation byproducts (ketone is formed predominantly to alcohol) increases with the hydrocarbon ring size, namely from 1.0% for C_5H_{10} to 19% for C_8H_{16}. Interestingly, the oxidation of cyclooctane is a more preferable reaction in comparison with its carboxylation.

Linear C_5–C_8 hydrocarbons containing both secondary (more reactive) and primary carbon atoms are carboxylated into a mixture of isomeric carboxylic acids (Table 4). The branched carboxylic acids are formed as main products, while the yields of the linear acids are negligible (0.2–0.5%) due to low reactivity of primary carbon atoms. The carboxylation of n-pentane into a mixture of C_6-isomeric carboxylic acids cata-

Table 4 Mild carboxylation of linear alkanes to carboxylic acids catalyzed **1–3** [a]



Entry	Alkane	Products	Catalyst	Product yield[b], % (1)	(2)	(3)	(4)	Total
1	n-C_5H_{12}	$C_5H_{11}COOH$ (*1*) $C_3H_7CH(COOH)CH_3$ (*2*)	1	tr[c]	13.6	6.1	—	19.7
2		$C_2H_5CH(COOH)C_2H_5$ (*3*)	2	tr	20.5	8.0	—	28.5
3			3	tr	16.1	4.2	—	20.3
4	n-C_6H_{14}	$C_6H_{13}COOH$ (*1*) $C_4H_9CH(COOH)CH_3$ (*2*)	1	tr	6.4	11.6	—	18.0
5		$C_3H_7CH(COOH)C_2H_5$ (*3*)	2	tr	12.0	18.1	—	30.1
6			3	tr	11.2	16.2	—	27.4
7	n-C_7H_{16}	$C_7H_{15}COOH$ (*1*) $C_5H_{11}CH(COOH)CH_3$ (*2*)	1	tr	7.9	8.9	3.4	20.2
8		$C_4H_9CH(COOH)C_2H_5$ (*3*) $C_3H_7CH(COOH)C_3H_7$ (*4*)	2	tr	15.6	10.4	3.5	29.5
9			3	tr	13.6	9.7	3.1	26.4
10	n-C_8H_{18}	$C_8H_{17}COOH$ (*1*) $C_6H_{12}CH(COOH)CH_3$ (*2*)	1	tr	6.3	5.7	3.8	15.8
11		$C_5H_{11}CH(COOH)C_2H_5$ (*3*) $C_4H_9CH(COOH)C_3H_7$ (*4*)	2	tr	9.0	6.8	4.2	20.0
12			3	tr	15.6	7.7	4.6	27.6

[a] Reaction conditions are those of Table 3. [b] (Moles of products/moles of alkane) × 100%; GC yields (internal standard method). [c] Only traces of this acid were observed (<0.5% yield); traces of oxidation byproducts (alcohols, ketones, aldehydes; <1.0% total yield) were observed in some cases.

lyzed by **2** proceeds with yields up to 29%, whereas in the presence of **1** and **3** it results in 20% yields. For *n*-hexane and *n*-heptane carboxylation, the highest activity (up to 30% total yield) was also observed for **2**, followed by **3** and **1** (up to 27% and 20%, respectively). The carboxylation of *n*-octane into a mixture of C_9 isomeric carboxylic acids proceeds with a total yield of 28, 20, and 16%, when catalyzed by compounds **3**, **2**, and **1**, respectively.

The observed difference in the catalytic behavior of compounds **1–3** (Tables 3 and 4) is primarily associated with their distinct structures and activity toward the carboxylation of different types of substrates. It should also be noted that the crystallization water present in the structures of **1** and **2** has no influence on the observed catalysis since its amount is negligibly low in comparison with the quantity of water solvent present in the system.

The selectivity parameters observed in the carboxylation of *n*-alkanes (Table 4) as well as previous data[12,19] suggest a free radical mechanism in these carboxylation reactions. Briefly, a sulfate radical anion ($SO_4^{\bullet-}$) is generated *via* the thermolysis of $K_2S_2O_8$. It then abstracts an H atom from a hydrocarbon substrate producing an alkyl radical ($R^{\bullet}$), which then easily reacts with carbon monoxide to form an acyl radical ($RCO^{\bullet}$). The latter undergoes oxidation to an acyl cation (RCO^+), which is then hydrolyzed by H_2O to give a carboxylic acid product (RCOOH).[12,19]

Conclusions

We showed herein that facile self-assembly reactions between copper(II) nitrate, *N*-butyldiethanolamine, and different carboxylic acids in water (all the reagents used are rather simple and commercially available chemicals) resulted in the generation of three new coordination compounds **1–3**. The type of the carboxylic acid applied as a supporting ligand appears to influence the resulting structures, which range from a discrete cationic monocopper core in **1** to a neutral dicopper(II) complex **2** and a linear chain 1D coordination polymer **3**. These products also widen a family of water-soluble aminoalcoholate copper(II) derivatives that find a noteworthy application in homogeneous bioinspired catalysis, namely in the C–H functionalization of saturated hydrocarbons under mild conditions.[12]

Actually, all compounds **1–3** catalyze the oxidation with hydrogen peroxide of C_5–C_8 cycloalkanes, resulting in the formation of cyclic alcohols and ketones in up to 22% total product yields. Interesting effects of acid promoter and catalyst loading as well as H_2O-accelerating role and substrate scope were investigated. Besides, the obtained catalysts are also active in the mild carboxylation with carbon monoxide and persulfate oxidant of both cyclic and linear C_5–C_8 saturated hydrocarbons to produce the corresponding carboxylic acids in up to 41% yields based on alkane substrate.

It is important to highlight that the present values of product yields are very high when dealing with the C–H functionalization of alkanes (particularly inert substrates) and the mild conditions of these catalytic reactions.[1–3,12,23–29] Besides, a very interesting promoting effect of water was unveiled in the oxidation of cycloalkanes that is especially remarkable in the reaction catalyzed by **3**. This feature might be of particular practical importance given a possibility of using the diluted solutions of hydrogen peroxide as oxidant that can be generated *in situ via* an electrochemical pathway.

The research on further widening the substrate scope and exploration of other types of C–H functionalization reactions[30–32] using the present copper(II) catalysts will be continued.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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