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ARTICLE

Selective oxidative cleavage of terminal olefins into aldehydes catalyzed by copper(II) complex

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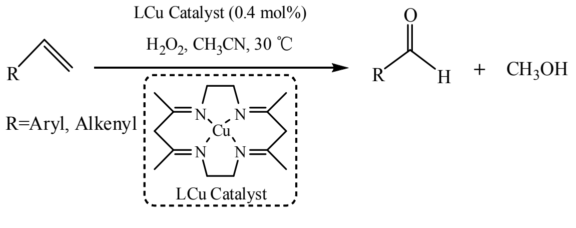
A simple method for oxidative C=C bond cleavage of terminal olefins to aldehydes with H_2O_2 catalyzed by copper(II) complex LCu consisted of copper(II) and macrocyclic ligand 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,7,11,14-tetraene (L) was described. This study indicated that the copper(II) complex displayed excellent catalytic ability for the selective oxidation of terminal olefins to aldehydes with high selectivity (S>90%) in CH_3CN at 30 ℃. The possible catalytic reaction mechanism of oxidation of terminal olefins was discussed.

1. Introduction

The selective functionalization of olefins is one of the most fundamental reactions in organic synthesis since it allows easy introduction of various hetero-atom(s) into the existing molecular framework.[1-3] The Aldehyde products are important precursors to acid and primary alcohol as well as widely used in medicine, agriculture and fine chemical industry.[4-6] At present, the oxidation of olefins into aldehydes is one of the bottlenecks and challenging problems in synthetic chemistry and petrochemical industry. Although some studies on oxidative cleavage of olefins into aldehydes through Fe,[7-11] Pd,[12-13] Ru,[14-16] Os,[17-18] Au[19] catalysts, biphasic PEG-300/scCO_2 catalyst[20] and supported catalysts[21-23] with sodium periodate or other oxidants have been reported, the problems of low activity, low selectivity, environment unfriendly and severe reaction conditions are still not resolved.[24-25] In recent years, the development of a simple and effective, environmentally benign oxidation methods is attracting growing interest,[26] with protocols based on cheap and abundant metal catalysts in combination with clean oxidants being highly sought. Herein, we describe an effective method to achieve aldehyde from terminal olefin through using H_2O_2 as an oxidant and a readily prepared copper complex LCu as catalyst, as illustrated in Scheme 1.



Scheme 1 LCu complex catalyzed oxidative cleavage of terminal olefins with H_2O_2 to aldehydes.

2. Experimental

2.1 Materials

$CuCl_2$•$2H_2O$, acetylacetone, ethylenediamine, 30% hydrogen peroxide, 1-(3,4-dimethoxyphenyl)ethanone, 1-(4-hydroxy-3-methoxyphenyl)ethanone, 4-methoxyacetophenone and the substrate olefins were analytical grade and purchased from commercial sources and used with certain purification. Acetonitrile was chromatographic pure grade and purchased from Adamas Company. The concentration of hydrogen peroxide was examined by titrating a standardized ceric sulfate solution to pale blue endpoint with a ferroin indicator.

2.2 Methods and instrumentations

The typical solution containing 0.5 $mol\cdot L^{-1}$ olefin, 2×10^{-3} $mol\cdot L^{-1}$ copper(II) complex LCu and 2.5 $mol\cdot L^{-1}$ hydrogen peroxide , was heated and kept at constant 30℃. The pH of solution was adjusted by hydrochloric acid and sodium hydroxide. The concentrations of reactant and product in the reaction solution were identified by GC-MS (Agilent 5973 Network 6890 N, Japan) with the standard samples and quantitatively detected by HLPC and GC. HPLC (waters1525) with a UV-vis detector and a C18 column with external standard method. Gas chromatography data was obtained using an FULI 9790 (China) FID gas chromatography system equipped with a KB-5 capillary column using p-nitrotoluene as internal standards and Agilent 6890 N (USA) with EC (TM)-WAX capillary column. Elemental analyses were implemented with a elemental analyzer (MOD 1106, Carlo Erba Company of Italy). NMR data were recorded on a Bruker spectrometer, using $CDCl_3$ as solvent with TMS as an internal standard. Multiplicities were given as: s (singlet), d (doublet), t (triplet), dd (doublets of doublet) or m (multiplets). Electrospray mass spectrometry (ESI-MS) measurements were performed with a TSQ Quantum Ultra. Ultraviolet–visible absorbance measurements were performed with a Hitachi U-2910 spectrophotometer (Tokyo, Japan).

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2.3 Preparation of metal copper(II) complex LCu

The complex 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,7,11,14-tetraene copper(II) LCu was prepared according to the literatures.[27-28] Ethylenediamine (1.3 mL) was added dropwise to a stirred solution of the metal salt copper chloride dihydrate (1.65 g) in hot anhydrous butanol (30 mL). After the addition, the reaction mixture was stirred 3-5 min, and then the solution was refluxed for about eight hours after acetylacetone (2 mL) was added to the mixture. The complexes precipitated out on ice salt bath cooling the reaction mixture overnight and the light green desired product was gave after they were filtered, washed with hot water, methanol and dried in vacuum. Anal. Calcd. for $C_{14}H_{24}N_4CuCl_2$: C, 43.92; H, 6.28; N, 14.64; Cl, 18.56%. Found: C, 43.80; H, 6.19; N, 14.50; Cl, 19.01%. Mp: 208℃. The Cu loading was determined to be 2.60 mmol/g by inductively coupled plasma-atomic emission spectrometry (ICP-AES).

2.4 Syntheses of substrates 1c, 1d and 1e

1-methoxy-4-vinylbenzene (**1c**), 1-methoxy-4-vinylbenzene was prepared according to literatures.[29-31] A solution of 4-methoxyacetophenone (2.4 g) in absolute methanol (20 mL) was treated with $NaBH_4$ (3.02 g) added portionwise under ice water bath for 4 h. Then the reaction solution was refluxed for 10 h, the suspension gradually became a clear solution and adjusted to pH3.0 with hydrochloric acid. The most solvent was removed by vacuum distillation then the reaction mixture was poured into iced water (20 mL) and extracted with dichloromethane. The extract was eluted with ethyl acetate : n-hexane =1:1 (v/v) and then distilled to obtain the colorless oil which showed a single component on TLC. It was characterized by ESI-MS: m/z 135.08 (Calcd. for $[M^{+}+1]$: 135.07); ^{1}H NMR (400MHz, $CDCl_3$) δ 3.85 (s, 3H), 5.16-5.19 (dd, J=10.8 8.0 Hz, 1H), 5.64-5.68 (dd, J=17.6 8.0 Hz, 1H), 6.67-6.75 (m, 1H), 6.90-6.92 (m, 2H), 7.38-7.41 (m, 2H). ^{13}C NMR (100MHz, $CDCl_3$) δ 159.36, 136.23, 130.42, 127.41, 113.91, 111.60, 55.31. The NMR spectra in the ESI†.

1,2-dimethoxy-4-vinylbenzene (**1d**), 1,2-dimethoxy-4-vinylbenzene was prepared similar to the method of 1-methoxy-4-vinylbenzene (**1c**) synthesis. It was determined by checking with thin-layer chromatography and ESI-MS: m/z 165.07 (Calcd. for $[M^{+}+1]$: 165.08), ^{1}H NMR (400MHz, $CDCl_3$) δ 3.86 (s, 3H), 3.89 (s, 3H), 5.15 (d, J=8.0 Hz, 1H), 5.62 (d, J=8.0 Hz, 1H), 6.62-6.71 (m, 1H), 6.80 (d, J=8.0 Hz, 1H), 6.92-6.97 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 148.95, 136.49, 130.70, 119.45, 116.04, 111.76, 111.02, 108.60, 55.86, 55.76. The NMR spectra in the ESI†.

2-methoxy-4-vinylphenol (**1e**), The prepared of 2-methoxy-4-vinylphenol was similar to the method of 1-methoxy-4-vinylbenzene (**1c**) synthesis. The synthesized 2-methoxy-4-vinylphenol was determined by GC/MS and elemental analyses. Anal. Calcd. for $C_9H_{10}O_2$: C, 71.98; H, 6.71 %; found: C, 72.02; H, 6.70 %.

3. Results and discussion

3.1 Effect of solvents

Solvent system has crucial important influence on many olefin catalytic oxidation reactions.[32] The well-known Sharpless system uses periodate as the oxidant with $RuCl_3$ in various solvent, such as $ClCH_2CH_2Cl$,[33] CCl_4/CH_3CN[34] or EtOAc/MeCN,[35] which indicated the different effect on reaction time, selectivity and yield of product or other aspects. In this work the influence of five solvents N,N-Dimethylformamide (DMF), Benzyl cyanide (BC), N,N-Dimethylacet-amide (DMA), Acetonitrile and Water on this oxidation reaction was tested, the results were listed in Table 1. It can be seen that no reaction could be detected for the styrene oxidation when DMF, DMA and benzyl cyanide were used as solvent, respectively. Acetonitrile or water is efficient solvent for this oxidative cleavage reaction, and best reaction conversion of styrene and selectivity of benzaldehyde could be obtained when the oxidation reaction was carried out in acetonitrile.

Table 1 The conversion of styrene and selectivity of benzaldehyde for oxidative cleavage of styrene in various solvents.[a]

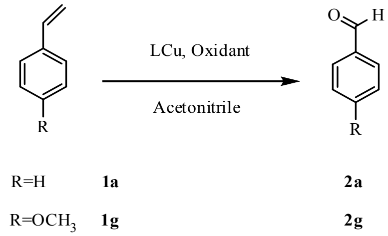
Entry	Solvents	Time (h)	Conversion (%)	Selectivity (%)
1	DMF	8	--	--
2	BC	2	--	--
3	DMA	4	--	--
4	Water[b]	3	72.5	81.2
5	Acetonitrile	1	84.1	94.6

[a] Reaction conditions: $[\text{styrene}]_0 = 0.05$ mol·L^{-1}, $[H_2O_2]_0 = 0.25$ mol·L^{-1}, [LCu] = 2×10^{-4} mol·L^{-1}, pH8.0, 30 ℃. [b] $[\text{styrene}]_0 = 0.01$ mol·L^{-1}, $[H_2O_2]_0 = 0.05$ mol·L^{-1}, [LCu] = 4×10^{-5} mol·L^{-1}. -- represent for no reaction.

3.2 Effect of oxidants

Oxidants 1, 4-benzoquinone (BQ), oxygen (O_2), Fe(III) showed excellent oxidation ability for the oxidation reactions of alkenes.[36-39] However, we found that in this catalytic system these oxidants hardly oxidized styrene to benzaldehyde, and H_2O_2 showed the best oxidation ability (Table 2), which implied the different catalytic mechanism. Furthermore, it can be found that for the oxidation reaction pH has great influence on yield and selectivity of benzaldehyde (Fig. S1 in the ESI†). From Fig. S1, initially the yield and selectivity of benzaldehyde increased gradually with increasing pH and the maximum values were achieved at pH8.0.

Table 2 Yields of oxidation of olefins to aldehydes by various oxidants.[a]



Entry	Oxidants	Time (h)	Yield of **2a** (%)	Yield of **2g** (%)
1	H_2O_2	1	79.6	74.3
2	m-CPBA	1	13.0	15.1
3	$FeCl_3$	2	2.2	3.0
4	BQ	20	--	--
5	O_2	2	--	--

[a] Reaction conditions: $[\text{substrate}]_0 = 0.05$ mol·L^{-1}, $[H_2O_2]_0 = 0.25$ mol·L^{-1}, [LCu] = 2×10^{-4} mol·L^{-1}, pH8.0, 30 ℃. -- represent for no reaction.

3.2 Oxidative cleavage reaction of styrene

Styrene is one of the most important raw materials in petrochemical industry.[40] The selective oxidation of styrene is also an elementary chemical reaction in organic synthesis. In recent years, some studies on oxidation of styrene have been reported.[37, 41-45] However, the slow reaction rate and low product selectivity are unsatisfactory. In this work, we employed metal complex LCu to catalyze the oxidation

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reaction of styrene with H_2O_2, and the complex LCu showed good catalytic activity. From Fig. 1, it is noted that the oxidation reaction proceeded cleanly, furnishing the benzaldehyde product with high selectivity except only a little amount of benzoic acid generated. Competing formation of other oxidation products, such as diols, phenylacetaldehyde, acetophenone, styrene oxide, were not observed. To understand the kinetics of styrene oxidation reaction, the variations of concentration of styrene and benzaldehyde versus time *t* were investigated (Fig. 2). From Fig. 2, it should be noted, however, that the oxidation of styrene to benzaldehyde with H_2O_2 did not occur in the absence of catalyst LCu. Based on the plot of $\ln(c_0(\text{styrene})/c_t(\text{styrene}))$ vs *t* (Fig. S2 in the ESI†), the apparent first-order reaction rate constant of oxidation of styrene was evaluated as 0.034 min^{-1} in the case of styrene concentration of 0.01 mol・L^{-1} and H_2O_2 concentration of 0.2 mol・L^{-1} at pH8.0 and 30 ℃.

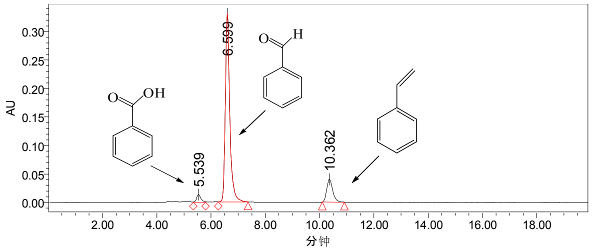


Fig. 1 HPLC profile of oxidative cleavage reaction of styrene in acetonitrile after 1 h. [LCu] = 2×10^{-3} mol·L^{-1}, [styrene]$_0$ = 0.5 mol·L^{-1}, [H_2O_2]$_0$ = 2.5 mol·L^{-1}, pH8.0, 30 ℃.

3.3 Oxidative cleavage reaction of various olefins

Under the optimized reaction conditions, the catalytic oxidations of aryl- and alkyl-substituted terminal olefins were investigated and the results were summarized in Table 3. Product aldehydes were isolated and purified with silica-gel column chromatography, and characterized by nuclear magnetic resonance (NMR) and high-resolution mass spectrometry (see ESI†). The olefins **1a-1l** were oxidized with H_2O_2 to corresponding aldehydes and simultaneously lost a carbon atom at a low catalyst loading of 0.4% mol ratio in acetonitrile under an aerial atmosphere at 30 ℃. In general, these terminal olefins **1a-1l** can be oxidized into the corresponding aldehydes in relatively short time with good selectivity. For the aryl-substituted terminal olefins **1a-1i**, the substituted group exhibited obvious influence on the oxidation reaction. Electron-rich styrene derivatives **1b-1e** gave the corresponding aldehydes along with fast reaction rate (conversion>80%) and good selectivity (S>90%) (Table 3, entries 2-5). Although electron-deficient styrene derivatives **1f-1i** gave lower conversion, the higher selectivity (S>96%) could be observed (Table 3, entries 6-9). Especially, 4-nitro-phenylethene (**1i**) afforded 67.8% conversion and 99% selectivity of 4-nitrobenzaldehyde. In addition, oxidation of 2-vinylnaphthalene (**1j**) also give relatively good conversion and selectivity as similar to styrene derivatives. More interestingly, although the oxidation of aliphatic olefins to aldehydes is not only difficult but also an urgent challenge,[46-47] the catalytic system in this work is also suitable to the oxidation of aliphatic olefins such as allylbenzene (**1k**) and 1-octene (**1l**) (Table 3, entries 11 and 12). As can be seen from Table 3, we can find that aryl-substituted terminal olefins has better conversion than aliphatic olefins. The experimental result is unexpected since the oxidation of aliphatic olefins to aldehydes is difficult and only aromatic alkenes were reported to be oxidized in many references.[19, 48] Some internal alkenes cyclohexene and trans-4-octene were employed as substrates. Unfortunately, the oxidation reaction did not occur (Table 3, entries 13 and 14). This might not be surprising, as selective oxidative cleavage of intramolecular alkene into aldehyde is known to be more difficult than aryl-substituted terminal alkene, especially, under mild conditions of catalytic system in this work.

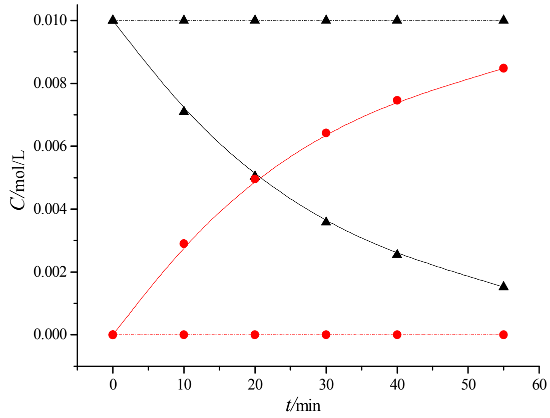
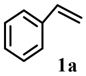
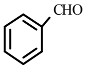
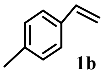
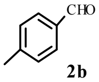
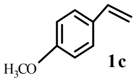
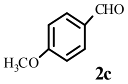
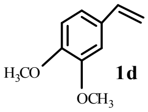
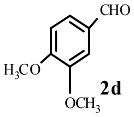
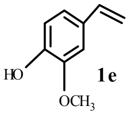
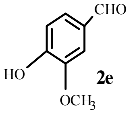
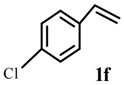
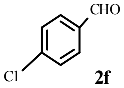
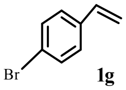
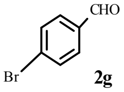
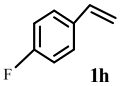
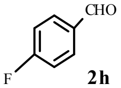
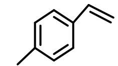
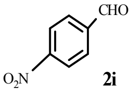
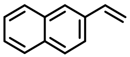
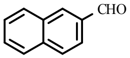
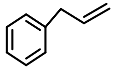
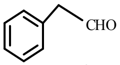
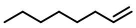
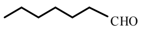
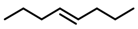


Fig. 2 The variations of concentration *c* (mol·L^{-1}) of styrene (▲) and benzaldehyde (●) versus time *t* (min). [styrene]$_0$ = 0.01 mol·L^{-1}, [H_2O_2]$_0$ = 0.2 mol·L^{-1}, pH8.0, 30 ℃. Solid line —: theoretical fitting curves based on the Eqns. $C_{\text{Styrene}} = C_0\exp(-kt)$ and $C_{\text{Benzaldehyde}} = C_0(1-\exp(-kt))$, *k* was the apparent first-order reaction rate constant and C_0 was the initial concentration of styrene. [LCu] = 4×10^{-5} mol·L^{-1}. Dot line ---: without catalyst.

Table 3 Oxidative cleavage of various olefins with H_2O_2 catalyzed by LCu complex in CH_3CN.[a]

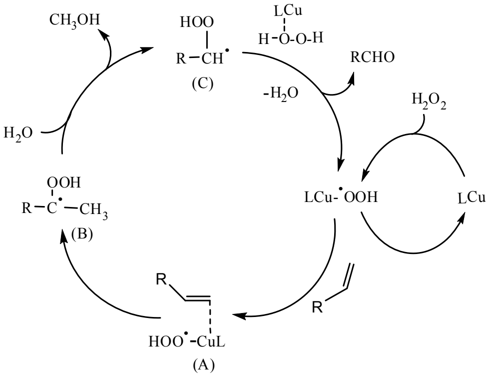
Entry	Substrate	Product	Selectivity (%)	Yield (%)[b]
1	 **1a**	 **2a**	94.3	73.2
2	 **1b**	 **2b**	92.3	72.2
3	 **1c**	 **2c**	91.3	70.3
4	 **1d**	 **2d**	90.2	73.0
5	 **1e**	 **2e**	92.7	70.1
6	 **1f**	 **2f**	96.5	74.1
7	 **1g**	 **2g**	97.3	68.8

8	 **1h**	 **2h**	96.3	76.7
9	 **1i**	 **2i**	99.0	61.9
10	 **1j**	 **2j**	91.4	76.0
11	 **1k**	 **2k**	87.6	51.1
12	 **1l**	 **2l**	99.2	56.5
13[c]	 **1m**	--	--	--
14[c]	 **1n**	--	--	--

[a] Reaction conditions: $[\text{substrate}]_0 = 0.5\ \text{mol}\cdot\text{L}^{-1}$, $[\text{LCu}] = 2\times10^{-3}\ \text{mol}\cdot\text{L}^{-1}$, $[H_2O_2]_0 = 2.5\ \text{mol}\cdot\text{L}^{-1}$, 30 ℃, pH8.0, 60 min. See ESI for details. [b] Isolated yields are given. [c] 150 min. -- represent for no reaction.

3.4 Possible reaction mechanism of oxidative cleavage of terminal olefins

To gain some insight into the reaction mechanism, we employed epoxy ethyl benzene as substrate to carry out the oxidation reaction under the same reaction conditions. It can be found that the yield of benzaldehyde was only 19.3% after 1 h. The value was far less than that of 78.6% when styrene was used as substrate and no epoxy ethyl benzene was detected during the process of catalytic oxidation of styrene. These implied that the epoxy ethyl benzene could not be the main reaction intermediate, and the oxidation reaction may involve other reaction course. Besides aldehyde, the other C1 product derived from the cleavage of C=C bond was also investigated (Fig. S3 in the ESI†). From Fig. S3, it is noted that methanol was detected in reaction solution. Based on quantitative analyses, 64.7% yield of methanol was found under the conditions as described in Fig. S3. However, the value is somewhat lower than the yield 79.6% of benzaldehyde, which may be ascribed that the volatile of methanol led to the lower measured value, and/or a small amount of methanol was further oxidized to formaldehyde or formic acid. Active copper-oxo species played an important role in catalytic oxidation reaction.[46, 49] In order to obtain the information of the copper-oxo species, the generation and property of the species were investigated. The reaction of copper(II) complex with H_2O_2 were monitored by UV-vis and the spectral change was shown in Fig. S4 in the ESI†. It can be observed that an optic feature with $\lambda_{\max} = 324$ nm appeared after adding H_2O_2 to the LCu complex solution. This indicated that a new species formed. Further the formation kinetics showed that the new species could be readily generated within 30 min and then could stably exist for more than 1.5 h. Methylene blue dye test, which could quantify hydroxyl radical, was also performed by detecting the variation of concentration of methylene blue by UV-vis spectrophotometer at $\lambda = 660$ nm. When the copper complex and hydrogen peroxide were added into methylene blue solution the absorbance of methylene blue at $\lambda = 660$ nm had no change, which indicated that free radical •OH was not the predominant reactive species. Recently, we found copper complex can activate H_2O_2 and consequently form "associated radical LCu-•OOH". This kind of active oxo species is different from other unstable free radicals such as •OH, •OOH[50-51] or metal-oxo species[52-55] and it possesses relatively high reduction potential and is stable in aqueous solution at ambient temperature.[56-57] Thus, this kind of LCu-•OOH species was also regarded as the predominant active oxo species in this work's catalytic oxidation of terminal olefins with H_2O_2. In order to further understand the reaction mechanism, we used density functional theory (DFT) method to calculate the NBO charge distributions of substrate styrene (Fig.S5 in the ESI†). From the calculated result, it can be seen that the atoms C_α and C_β of C=C alkene group all show negative charge, which implies that it is impossible the negative charge oxygen atom attack directly the C_α. Therefore, taking together the observations made above, a possible reaction mechanism of oxidative cleavage of terminal olefins catalyzed by complex LCu was proposed as illustrated in Scheme 2. Initially, the LCu-•OOH species, which generated through the reaction of copper complex LCu with H_2O_2, might associate with the olefins to generate A. Subsequently, the peroxy radica intermediate B formed from A by the rearrangement and transferring of hydrogen atom. Then one water molecule might add to the intermediate B and lead to form of the intermediate C as well as other product methanol. Finally, the intermediate C reacts with LCu-H_2O_2 to form aldehyde through losing one water and rearrangement of oxygen atom. Thus the catalytic reaction cycle completed.



Scheme 2 The possible mechanism for the catalytic oxidative cleavage of terminal olefins

4. Conclusions

In summary, a simple and effective method for the selective oxidative cleavage of terminal olefins to aldehydes by using cheap and a small amount (0.4 mol%) copper(II) complex as catalyst under mild conditions has been reported. The copper(II) complex can rapidly oxidized many styrene derivatives to corresponding aldehydes with high selectivity (S>90%). Interestingly, the catalytic system in this work is also suitable to the aliphatic terminal olefins such as allylbenzene and 1-octene. Under the conditions developed so far, the catalyst is, however,

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ineffective toward intramolecular alkenes. On the basis of various researches, a possible mechanism involving associated radical active oxo species seems in operation, which gives rise to peroxy radical intermediate and subsequently the cleavage products. However, further studies are needed to broaden the scope of the substrate as well as substantiate the proposed mechanism.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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