

## RESEARCH ARTICLE

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**Visible light-driven copper(II) catalyzed aerobic oxidative cleavage of carbon–carbon bonds: a combined experimental and theoretical study†**Sanliang Li,<sup>‡a</sup> Dong Tian,<sup>‡a</sup> Xiaowei Zhao,<sup>a</sup> Yanli Yin,<sup>b</sup> Richmond Lee \*<sup>c</sup> and Zhiyong Jiang \*<sup>a,b</sup>

By switching on visible blue light, aerobic oxidation of various substrates, such as  $\alpha$ -substituted,  $\beta$ -substituted and  $\alpha$ -halo styrenes, was first realized with a copper(II) catalyst. Subsequent Cu(II)-catalyzed photo-oxygenation of alkynes, aldehydes and carboxylic acids was extended and the new catalytic system was proven to be reliable towards functional group tolerance. For all classes of substrates examined, the oxidized products were isolated in good yields and were found to be highly chemoselective. Through computational studies employing density functional theory (DFT) and experimental support, the identity of the active catalytic species was proposed as a  $\mu_4$ -oxido copper chloride cluster [Cu<sub>4</sub>OCl<sub>6</sub>]. DFT modelling was engaged in examining the reactivity of this copper chloride cluster catalyst, outlining viable reaction pathways for the oxidative transformation of the styrenes.

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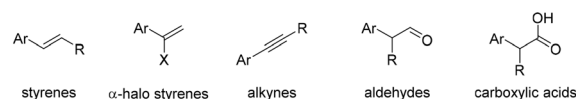
**Introduction**

Using visible light to drive homogeneous<sup>1–9</sup> and heterogeneous catalysis<sup>10,11</sup> is a synthetically sustainable and simple approach to organic transformations. The coupling of photocatalysis and aerobic oxidation as an innovative way of synthesizing diverse carbonyls has been developed by numerous research groups and is aptly termed photocatalytic oxygenation or photo-oxygenation.<sup>12</sup> As such, a number of elegant synthetic protocols have been developed to address the photo-oxygenation of sp<sup>3</sup> C–H bonds.<sup>13–18</sup> Selective oxygenation of carbon–carbon bonds constitutes an alternative procedure to incorporate oxygen into molecules,<sup>19,20</sup> which is also rapidly emerging.<sup>13,21–46</sup>

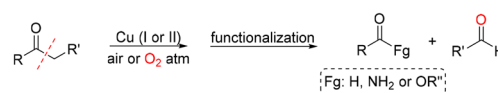
To date, a series of readily available chemical feedstocks, such as styrenes,  $\alpha$ -halo styrenes, alkynes, aldehydes and carboxylic acids, have been used to engage in photocatalytic oxygenation reactions (Scheme 1(A)), benefiting from the estab-

lishment of many useful methodologies that are often specific to one or two kinds of these substrates.<sup>21–46</sup> For example, in 2010, König and co-workers<sup>22</sup> introduced an elegant oxygenation reaction of *trans*-stilbene (carbon–carbon double bond) to benzaldehyde by employing riboflavin tetraacetate (RFT) as the catalyst *via* an energy transfer (ET) mechanism. The method also allowed oxidation of tolane (carbon–carbon triple bond) to benzil in 28% yield. In addition, oxidative scission of diphenylacetic acid could be carried out quantitatively. However, no satisfactory yields were found for other commonly used carboxylic acids. In 2016, Wolf and co-workers presented a cooperative RFT and non-heme Fe complex photocatalysis, allowing slightly enhanced yields for the oxygenation of *trans*-stilbene and tolane.<sup>13</sup> Photocatalyzed oxidation of alkenes to access ketones or aldehydes were limited either by yields or substrate scope when using short wavelength light

(A) Feedstocks in aerobic photo-oxygenation via C–C bond cleavage



(B) Cu-catalyzed oxidative cleavage of C(O)–C bonds

**Scheme 1** Visible light photo-oxygenation of carbon–carbon bonds and Cu-catalyzed oxidation of C(O)–C bonds.<sup>a</sup>Key Laboratory of Natural Medicine and Immuno-Engineering of Henan Province, Henan University, Kaifeng, Henan, 475004, P. R. China.

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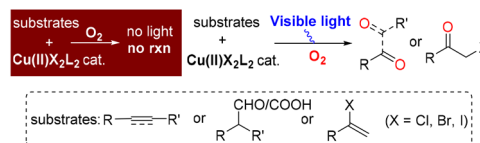
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sources.<sup>23–26</sup> Since then, many elegant visible-light-driven photocatalytic methods have been developed: a series of organic and inorganic compounds or materials such as disulfides,<sup>27</sup> Ag/AgBr/TiO<sub>2</sub> nanotubes,<sup>28</sup> polymeric carbon nitrides (PCN),<sup>29</sup> Acid Red 94,<sup>30</sup> tetrabutyl-ammonium decatungstate (TBADT),<sup>31</sup> CeCl<sub>3</sub>,<sup>32</sup> and a non-heme Mn(II) complex have been demonstrated as viable photocatalysts.<sup>33</sup> Among these examples, a Mn-catalyzed protocol<sup>33</sup> achieved the oxidation of aliphatic alkenes, thus successfully extending the limitations of viable substrate scope to include aryl alkenes. However, the practicability of these catalytic systems are undermined as the oxygenation of other carbon–carbon bonds has never been disclosed. In 2018, our group reported the aerobic oxidative transposition of vinyl halides,<sup>34</sup> avoiding the use of additional stoichiometric reagents,<sup>35,36</sup> or high temperature,<sup>37</sup> leading to a mild synthetic approach to  $\alpha$ -halo ketones. The groups of Sun and Chen,<sup>38,39</sup> reported successively the aerobic photo-oxygenation of alkynes to  $\alpha$ -diketones, but the generation of disulfide waste from excess 4-chlorobenzenethiol is not atom economical. Xia and co-workers in 2013 demonstrated the feasibility of the photocatalytic oxidative cleavage of the carbon–carbon single bond of aldehydes to produce carbonyls,<sup>40</sup> but since excess piperidine was required to generate the more easily oxidized enamine intermediate, the protocol is also not atom economical. Carboxylic acids are also important functional groups that can be transformed to carbonyl compounds *via* decarboxylation under an aerobic photocatalytic system.<sup>41–46</sup> Notably, toxic<sup>41</sup> or expensive<sup>43,44</sup> metal complexes were used as the photocatalysts in many examples, and a very recent contribution using Cu(OAc)<sub>2</sub><sup>46</sup> could not exclude the employment of an uneconomical ligand (*i.e.* neocuproine). Conceivably, the development of a general or unifying sustainable catalytic strategy for aerobic photo-oxygenation of these feedstocks is important (Scheme 1(A)).

Copper is a cheap and abundant transition metal being actively explored as a highly effective catalyst for aerobic oxidation reactions,<sup>47,48</sup> and the further development of efficient synthetic protocols to oxidatively cleave<sup>49–55</sup> and functionalize carbon–carbon bonds<sup>56–61</sup> has been investigated by various groups (Scheme 1(B)), and mechanistic studies involving experiment and computation have been carried out to understand the oxidative chemistry of C(O)–C bonds.<sup>62</sup> At the same time, a large body of work has examined well characterized mono- or multi-nuclear Cu–O<sub>2</sub> complexes,<sup>44,63–69</sup> providing key insights into the chemistry of catalytic species in biological oxidation reactions. However, recent investigations into the nature of Cu(II) cluster chemistry has also led to a better understanding of the identity of active catalytic species.<sup>70–74</sup> As an extension of our research interest in visible-light-driven photocatalysis,<sup>75–89</sup> we thus wondered if marrying the concept of photocatalysis and Cu-catalyzed carbon–carbon bond oxidation might accomplish the above-mentioned ideal aerobic photo-oxygenation.

Herein we report a new, atom economical and versatile method towards aerobic photo-oxidation of carbon–carbon bonds using a cheap and widely available metal salt, CuCl<sub>2</sub>·2H<sub>2</sub>O, as catalyst under visible light (3 W blue LED, see

## Design principle



Scheme 2 Design rationale for photo-activated Cu(II) catalysis.

Scheme 2). This synthetic strategy offers an effective way to oxidize a wide scope of substrates like alkenes, alkynes, aldehydes, and carboxylic acids to aldehydes, ketones and  $\alpha$ -diketones in modest to high yields with excellent chemoselectivity.  $\alpha$ -Halo-substituted styrenes are also compatible with the catalytic system, affording  $\alpha$ -halo acetophenones *via* oxidative halide migration with satisfactory results. Furthermore, through mechanistic studies involving quantum chemical calculations and experimental support, the identity of the active catalytic species was proposed as a  $\mu_4$ -oxido copper chloride cluster that is easily formed from CuCl<sub>2</sub>·2H<sub>2</sub>O. DFT modelling was also carried out to rationalize the reaction mechanisms for the oxidation of the styrenes.

## Results and discussion

## Cu(II)-Catalyzed aerobic photo-oxygenation of carbon–carbon double bonds

Optimal reaction condition screening was initiated with  $\alpha$ -methylstyrene **1a**, and 10 mol% of the copper(II) salt CuCl<sub>2</sub>·2H<sub>2</sub>O in MeCN solvent at 25 °C under irradiation with a 3 W blue LED (Table 1, entry 1). The product acetophenone **2a** was detected in 47% GC yield after 40 hours. Other

Table 1 Condition screening for the aerobic photo-oxygenation reaction of  $\alpha$ -methyl styrene<sup>a</sup>

Entry	Conditions	Yield <sup>b</sup> (%)
1	CuCl <sub>2</sub> ·2H <sub>2</sub> O, MeCN	47
2	CuBr <sub>2</sub> or Cu(OTf) <sub>2</sub> , MeCN	N.R.
3	CuCl, MeCN	Trace
4	CuCl <sub>2</sub> ·2H <sub>2</sub> O, THF, DMF or toluene	N.R.
5	CuCl <sub>2</sub> ·2H <sub>2</sub> O, acetone	33
6	CuCl <sub>2</sub> ·2H <sub>2</sub> O, K <sub>3</sub> PO <sub>4</sub> , MeCN	20
7	CuCl <sub>2</sub> ·2H <sub>2</sub> O, Na <sub>3</sub> PO <sub>4</sub> , MeCN	46
8	CuCl <sub>2</sub> ·2H <sub>2</sub> O, Li <sub>3</sub> PO <sub>4</sub> , MeCN	40
9	CuCl <sub>2</sub> ·2H <sub>2</sub> O, LiH <sub>2</sub> PO <sub>4</sub> , MeCN	38
10	CuCl <sub>2</sub> ·2H <sub>2</sub> O, LiCl, MeCN	62
11	CuCl <sub>2</sub> ·2H <sub>2</sub> O, LiCl, MeCN, O <sub>2</sub>	72
12	LiCl, MeCN, O <sub>2</sub>	N.R.
13	No light, CuCl <sub>2</sub> ·2H <sub>2</sub> O, LiCl, MeCN, O <sub>2</sub>	N.R.
14	CuCl <sub>2</sub> ·2H <sub>2</sub> O, LiCl, MeCN, N <sub>2</sub>	N.R.
15	CuCl, LiCl, MeCN, O <sub>2</sub> (24 h)	55
16	CuCl <sub>2</sub> ·2H <sub>2</sub> O, LiCl, MeCN, O <sub>2</sub> (24 h)	61

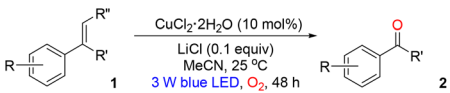
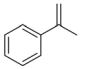
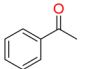
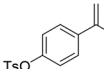
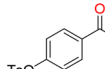
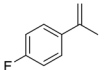
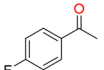
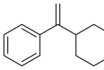
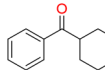
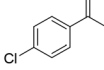
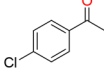
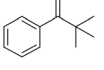
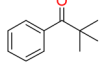
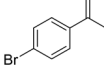
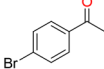
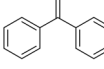
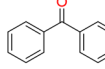
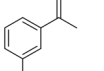
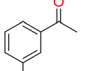
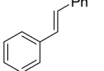
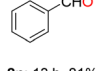
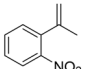
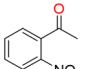
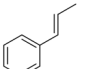
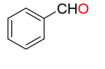
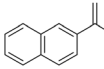
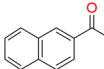
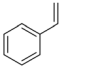
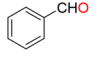
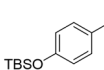
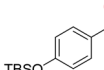
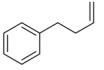
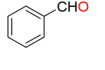
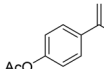
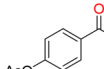
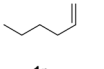
<sup>a</sup> 0.05 mmol scale in 0.5 mL solvent. <sup>b</sup> GC yield.

copper(II) salts,  $\text{CuBr}_2$  and  $\text{Cu}(\text{OTf})_2$ , were tested and found to be ineffective as catalysts (entry 2), as was the copper(I) salt  $\text{CuCl}$  (entry 3). No reaction was observed for other common organic solvents like THF, DMF, and toluene (entry 4), except for acetone (entry 5). We deduce that MeCN is the optimal solvent due to improved solubility of the reagents and its ability to bind to vacant sites on the copper catalyst. The addition of inorganic additives was examined next (entries 6–10) and 10 mol% of  $\text{LiCl}$  was found to increase the yield of **2a** to 62% (entry 10). Reactions conducted under oxygen further enhanced the yield of **2a** to 72% (entry 11). All three critical reaction ingredients – copper catalyst, light and oxygen (entries 12–14) – are required, thus implicating a mechanistic pathway that involves photo-activation of the Cu catalyst and oxygen. By repeating the reaction with  $\text{CuCl}$  under  $\text{O}_2$  instead of air for 24 h, **2a** was afforded in 55% yield (entry 15), being

only slightly lower compared to copper(II) chloride (61%, entry 16).

With the optimal reaction conditions established, the scope of this Cu(II)-catalyzed photo-oxygenation reaction was expanded to include other  $\alpha$ -substituted styrene derivatives (Table 2, entries 1–13). The reactions were completed within 21–48 hours, leading to ketones **2a–2m** in moderate to excellent yields. This method tolerated substrates with both electron-deficient (**1b–1f**) and relatively electron-rich substituents (**1g–1j**) in the *para*-, *meta*- and *ortho*-positions of the aryl groups. Substrates with *para* protecting groups, for instance *tert*-butyldimethylsilyl (TBS), acetyl (Ac) and tosyl (Ts), underwent the reaction without deprotection (entries 8–10). The reaction also proceeded with good yields when modifying the  $\alpha$ -methyl group to sterically bulkier alkyl groups (**1k** and **1l**) and a phenyl group (**1m**). The  $\beta$ -substituted styrenes **1n** and **1o**

**Table 2** Cu(II)-Catalyzed photo-oxygenation of olefins<sup>a</sup>

			
Substrate	Product (isol. yield%)	Substrate	Product (isol. yield%)
1 	 <b>2a</b> : 73%	10 	 <b>2j</b> : 22 h, 73%
2 	 <b>2b</b> : 70%	11 	 <b>2k</b> : 71%
3 	 <b>2c</b> : 56%	12 	 <b>2l</b> : 62%
4 	 <b>2d</b> : 72%	13 	 <b>2m</b> : 70%
5 	 <b>2e</b> : 75%	14 	 <b>2n</b> : 13 h, 81%
6 	 <b>2f</b> : 90%	15 	 <b>2o</b> : 62%
7 	 <b>2g</b> : 84%	16 	 <b>2p</b> : 33%
8 	 <b>2h</b> : 28 h, 62%	17 	 <b>2q</b> : 23%
9 	 <b>2i</b> : 21 h, 88%	18 	No reaction

<sup>a</sup> 0.2 mmol scale in 2.0 mL MeCN.

were chosen next, affording benzaldehyde **2n** in moderate to good yields (entries 14 and 15). Styrene **1p** was also oxidized to benzaldehyde although in much lower yield (entry 16). We also attempted to use aliphatic olefins as substrates (entries 17 and 18). It was found that an aryl group is also crucial to the transformation taking place: but-3-en-1-ylbenzene **1q** could afford benzaldehyde **2n** in 23% yield, but no reaction of hex-1-ene **1r** was observed. Therefore, compared to previous reports,<sup>27–33</sup> this method features a similar catalytic ability for styrene-type olefins, and has a slightly broader substrate scope than most other works.<sup>27–32</sup>

Subsequently, we evaluated the compatibility of vinyl halides with this catalytic system. A variety of vinyl halides, including vinyl bromides (**3a–3e**), vinyl chlorides (**3f–3i**) and vinyl iodide (**3j**) were screened in the absence of LiCl (Table 3), and all the substrates were photo-oxidized to the  $\alpha$ -halo substituted acetophenones **4a–4j** in 63–83% yield. It is worth noting that the compatibility of vinyl iodides robustly supports the broader utility of this sustainable method than that of our previously established Fe-catalysis.<sup>34</sup>

### Cu(II)-Catalyzed aerobic photo-oxygenation of carbon–carbon triple bonds

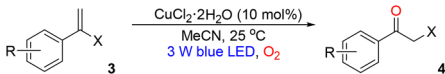




















Convinced by the potential of this catalytic system for oxidizing various aryl alkenes, the focus was next shifted to target alkynes. Tolane **5a**, being the first alkyne to be selected, gave benzil **6a** in 36% yield with sluggish reactivity under the previous optimal reaction conditions. Increasing the catalyst loading marginally to 15 mol%  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , 15 mol%

of additive LiBr, and changing to a solvent mixture (acetone : MeCN : DMF = 10 : 5 : 2), the yield of **6a** was visibly improved to 77% (Table 4, entry 1). A series of alkynes were then reacted under the new conditions, and various  $\alpha$ -diketones **6b–6h** could be obtained in 56–73% yield (entries 2–9). Functional groups with electron-withdrawing or electron-donating substituents on the aryl group were well tolerated. Alkynes with electron-withdrawing groups were also evaluated, but no reaction was observed.<sup>90</sup> Nevertheless, avoiding the use of other stoichiometric reagents is sustainable and is also the synthetic advantage of this method.<sup>38,39</sup>

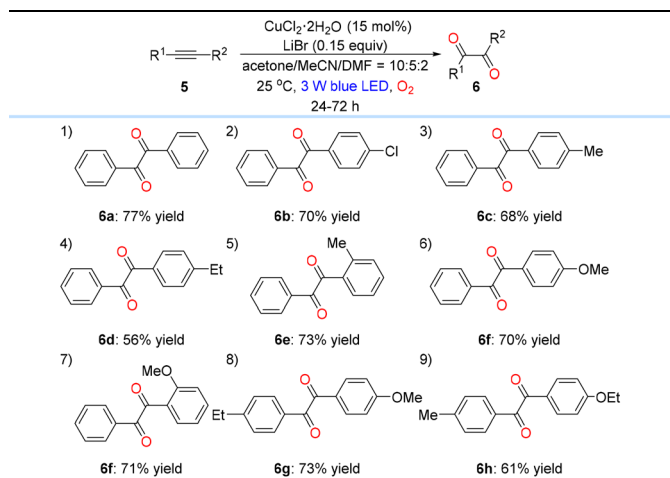
### Cu(II)-Catalyzed aerobic photo-oxygenation of C(O)–C bonds

With the method developed to photo-oxidize carbon–carbon (double and triple) unsaturated bonds, the envelope was further pushed to include C(O)–C single-bond-like aldehydes under the same reaction conditions as styrenes. The first three aldehydes that were investigated, 2-phenylpropanal (**7a**), cyclohexanecarbaldehyde (**7b**), and 2-phenylacetaldehyde (**7c**), were oxidatively transformed to the corresponding acetophenone (**2a**), cyclohexanone (**2o**) and benzaldehyde (**2n**) in high yields (Table 5, entries 1–3). These promising results encouraged us to broaden the substrate scope and branch out to use carboxylic acids, *viz*  $\alpha$ -aryl- $\alpha$ -methyl acetic acids (**8a–8e**),  $\alpha$ , $\alpha$ -diaryl acyclic (**8f** and **8g**) and cyclic (**8h** and **8i**) acetic acids,  $\alpha$ -phenyl acetic acid (**8j**) and cyclohexanecarboxylic acid (**8k**). The oxidatively cleaved products, *i.e.*, ketones and aldehydes, were isolated in 40–97% yield (entries 4–14). It is worth mentioning that aliphatic olefins was fully consumed in the reaction, but

**Table 3** Cu(II)-Catalyzed photo-oxygenation of vinyl halides<sup>a</sup>

			
Substrate	Product (isol. yield%)	Substrate	Product (isol. yield%)
1 	 4a: 20 h, 82%	6 	 4f: 25 h, 74%
2 	 4b: 21 h, 80%	7 	 4g: 22 h, 73%
3 	 4c: 17 h, 83%	8 	 4h: 24 h, 60%
4 	 4d: 22 h, 84%	9 	 4i: 24 h, 72%
5 	 4e: 24 h, 74%	10 	 4j: 72 h, 63%

<sup>a</sup> 0.2 mmol scale in 2.0 mL MeCN.

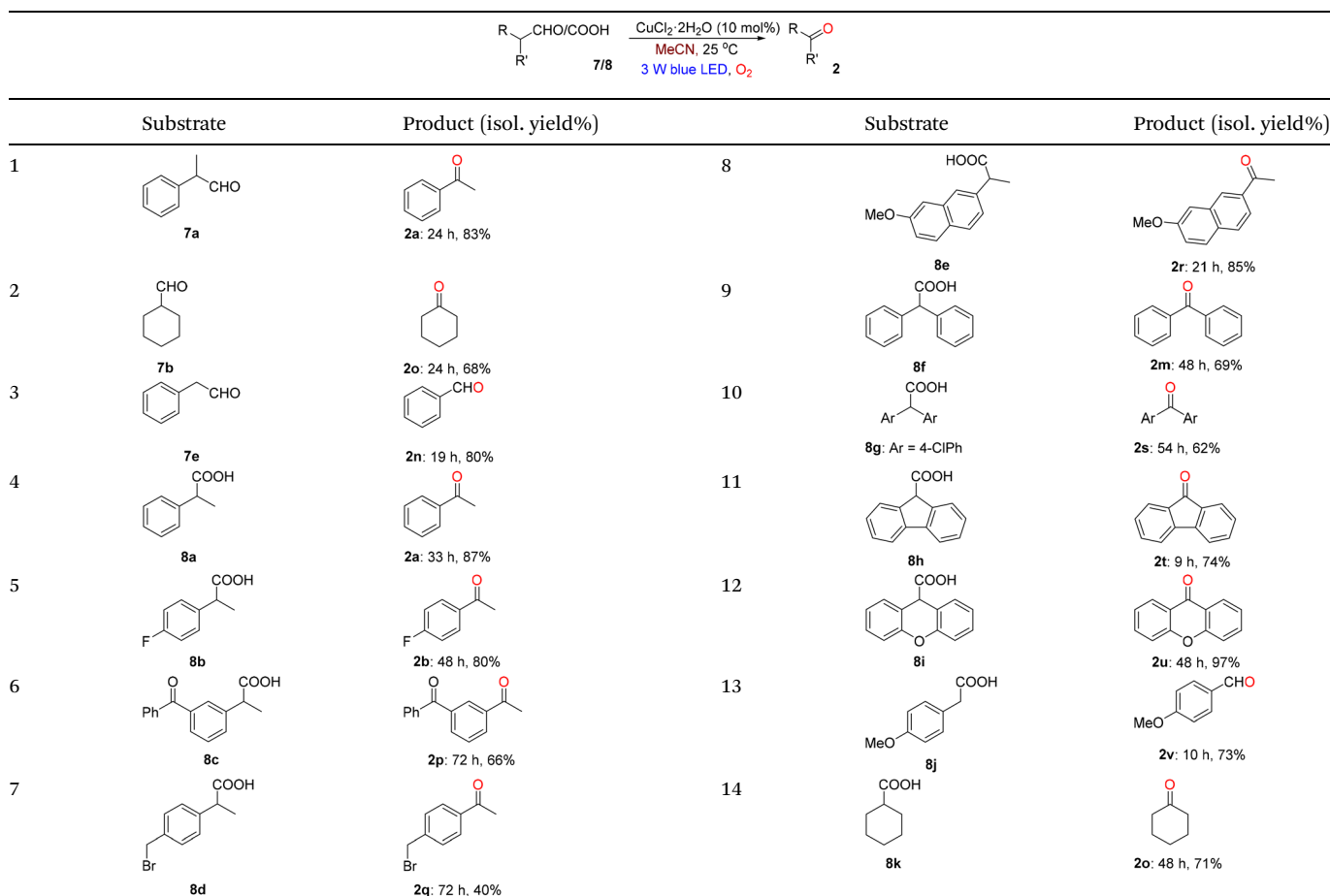
Table 4 Cu(II)-catalyzed photo-oxygenation of alkynes<sup>a</sup><sup>a</sup> 0.2 mmol scale in 2.0 mL MeCN.

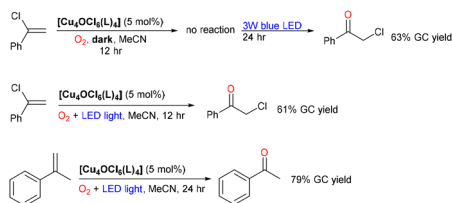
the identities of products formed were difficult to determine using crude <sup>1</sup>H-NMR analysis.<sup>90</sup> Meanwhile, benzoic acids are incompatible as no reaction was observed.<sup>90</sup>

## Mechanistic studies

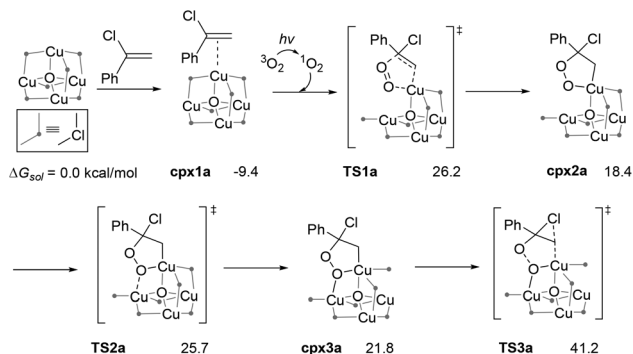
In recent works by Becker and Schindler, μ<sub>4</sub>-oxido copper clusters [Cu<sub>4</sub>OCl<sub>6</sub>] generated *in situ* from copper chloride have been proposed as the active species responsible for catalysis.<sup>73,74</sup> As such, the complex of [Cu<sub>4</sub>OCl<sub>6</sub>(L)<sub>4</sub>], where L = benzylamine, was synthesized according to the literature and was assessed in our reaction protocol.<sup>71,72</sup> The results were indicative of the μ<sub>4</sub>-oxido Cu cluster complex being the catalytically active species (Scheme 3).

Density functional theory (DFT) was performed to model and propose a mechanism based on this μ<sub>4</sub>-oxido Cu chemistry and model styrenes (Scheme 3 and see the ESI† for DFT methods). The DFT model was first directed towards understanding the Cl migration and tandem oxidation of α-chlorostyrene with the [Cu<sub>4</sub>OCl<sub>6</sub>] cluster as the active species (see Scheme 4). The complexation of the chlorostyrene forming **cpx1a** lowered the solution free energy significantly by −9.4 kcal mol<sup>−1</sup> relative to the free starting species. Addition of O<sub>2</sub> aided by light further required overcoming a large barrier of 35.6 kcal mol<sup>−1</sup> relative to **cpx1a**, through **TS1a**, forming the peroxy intermediate **cpx2a**. The subsequent steps involving rearrangement of **TS2a** and Cl migration to **TS3a** are

Table 5 Cu(II)-Catalyzed photo-oxygenation of C(O)–C bonds<sup>a</sup><sup>a</sup> 0.2 mmol scale in 1.0 mL MeCN.



**Scheme 3**  $\mu_4$ -Oxido Cu cluster catalyzed photo-oxidation of model alkenes. L = benzylamine.

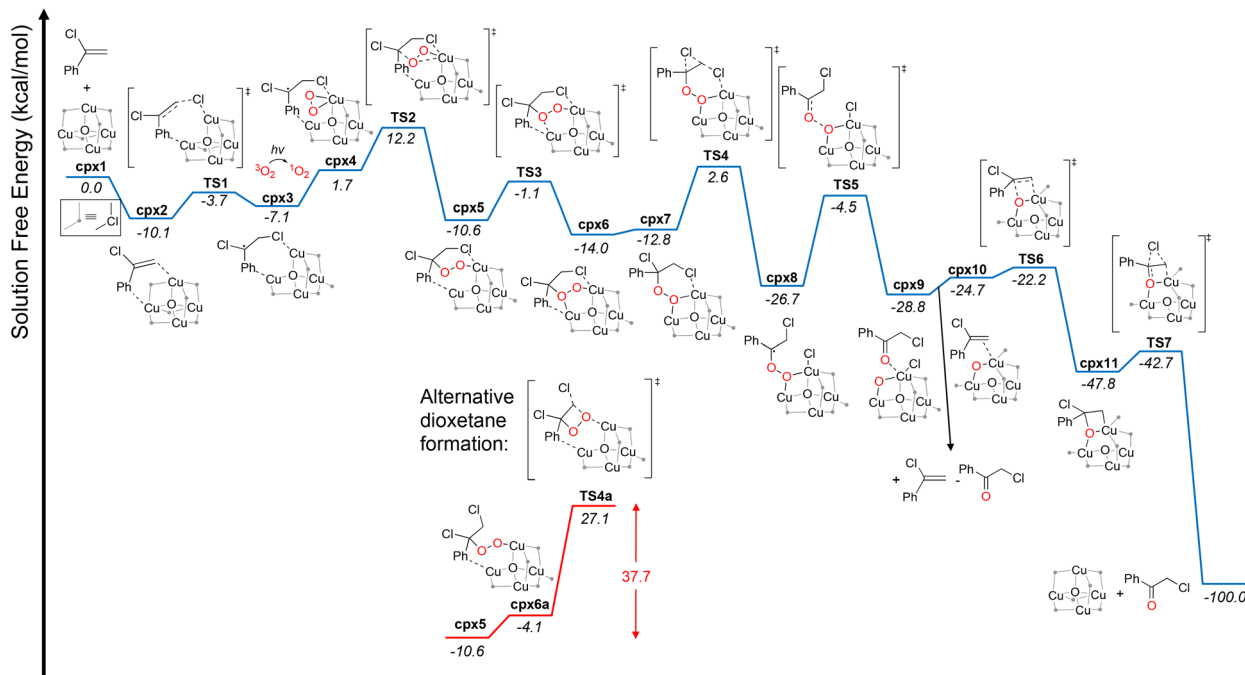


**Scheme 4** First DFT model investigating Cl atom migration and oxidation of  $\alpha$ -chlorostyrene. Solution free energy values are in  $\text{kcal mol}^{-1}$ .

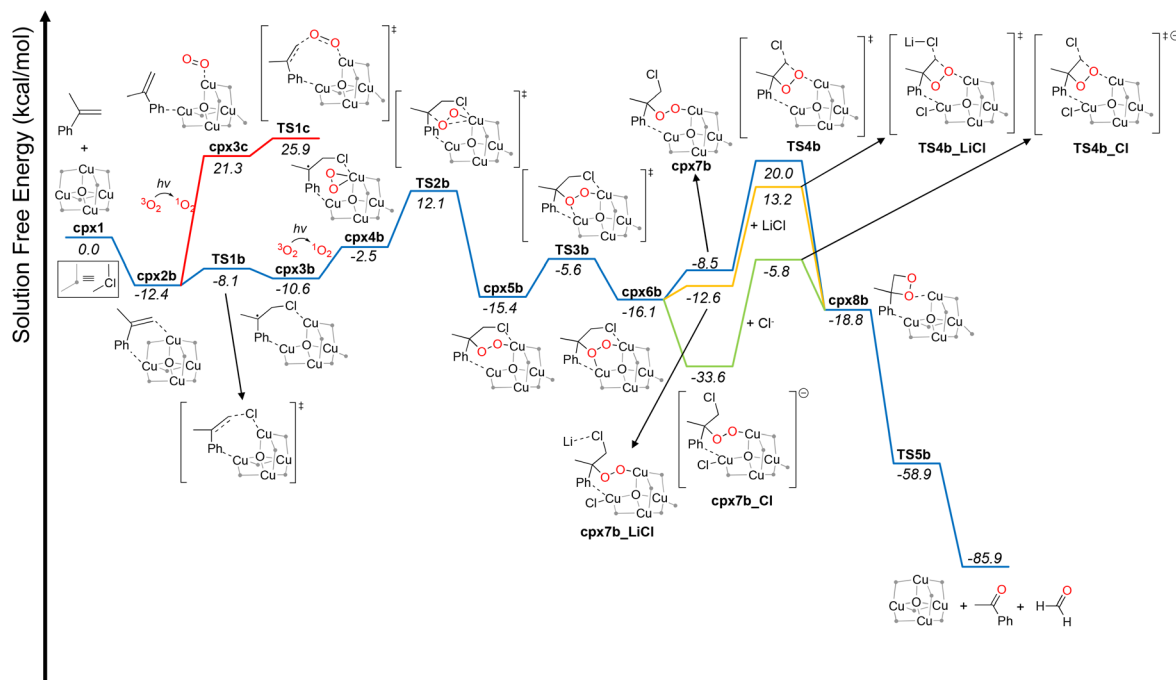
highly endergonic, *i.e.*, 36.1 and 50.6  $\text{kcal mol}^{-1}$ , respectively, all relative to **cpx1a**. As such the first DFT model suggests that the pathway through direct  $\text{O}_2$  oxidation of the chlorostyrene is not feasible.

Another pathway was considered whereby the chlorine on the  $[\text{Cu}_4\text{OCl}_6]$  cluster first activates the chlorostyrene at the  $\text{C}_\beta$  position, generating a  $\text{C}_\alpha$  radical center that may be more susceptible to oxidation (Fig. 1). When the aromatic phenyl of chlorostyrene was also  $\pi$ -bound to the Cu cluster, a more stable complex **cpx2** was generated, where  $\Delta G_{\text{sol}} = -10.1 \text{ kcal mol}^{-1}$ . A Cl atom transfer from the Cu cluster to chlorostyrene is energetically feasible through **TS1**,  $\Delta G_{\text{sol}}^\ddagger = 6.4 \text{ kcal mol}^{-1}$  relative to **cpx2**, forming **cpx3** ( $\Delta G_{\text{sol}} = -7.1 \text{ kcal mol}^{-1}$ ) with the  $\text{C}_\alpha$  radical center stabilized by conjugation into the phenyl ring. Subsequent oxidation of the Cu cluster with  $\text{O}_2$  assisted by light forms the peroxy intermediate **cpx4**, and attack of the  $\text{CuO}_2$  to  $\text{C}_\alpha$  center through **TS2**,  $\Delta G_{\text{sol}}^\ddagger = 22.3 \text{ kcal mol}^{-1}$ , forms stable **cpx5** ( $\Delta G_{\text{sol}} = -10.6 \text{ kcal mol}^{-1}$ ). The rearrangement of **cpx5** via **TS3** results in a more stable first resting state endoperoxy **cpx6**,  $\Delta G_{\text{sol}} = -14.0 \text{ kcal mol}^{-1}$ .

From Fig. 1, the Cl 1,2-shift from **cpx7** via **TS4** overcomes a small barrier of 16.6  $\text{kcal mol}^{-1}$  relative to **cpx6**. This pathway, much lower in free energy compared to **TS4a**, requires the halide on  $\text{C}_\alpha$  to migrate to the  $\text{C}_\beta$  position, displacing another Cl in concert. The proceeding intermediate **cpx8** is very exergonic,  $\Delta G_{\text{sol}} = -26.7 \text{ kcal mol}^{-1}$ . Next, O–O cleavage through **TS5** proceeds within a reasonable barrier of  $\Delta G_{\text{sol}}^\ddagger = 22.2 \text{ kcal mol}^{-1}$  relative to **cpx8**, forming a Cu  $\mu$ -oxo cluster and  $\alpha$ -chloroketone product, which is further exergonic by  $-28.8 \text{ kcal mol}^{-1}$  (**cpx9**). Dissociation of product and the binding of another  $\alpha$ -chlorostyrene substrate (**cpx10**) instigates the Cu  $\mu$ -oxo cluster to oxidize the double bond through a low-energy barrier of  $\Delta G_{\text{sol}}^\ddagger = 6.6 \text{ kcal mol}^{-1}$ , **TS6** relative to **cpx9**, and generates a highly exergonic **cpx11** ( $\Delta G_{\text{sol}} = -47.8 \text{ kcal mol}^{-1}$ ).



**Fig. 1** Free energy profile for the proposed mechanism of a Cu cluster catalyzed oxidation of  $\alpha$ -chlorostyrene. Solution free energy values are in  $\text{kcal mol}^{-1}$ .



**Fig. 2** Free energy profile for the proposed mechanism of a Cu cluster catalyzed oxidation of  $\alpha$ -methylstyrene. Solution free energy values are in  $\text{kcal mol}^{-1}$ .

Finally, Cl 1,2-migration *via* **TS7**,  $\Delta G_{\text{sol}}^{\ddagger} = 5.1 \text{ kcal mol}^{-1}$  relative to **cpx11**, affords another  $\alpha$ -chloroketone product. An alternative product formation lies in the possibility of dioxetane formation, which cleaves to give acyl chloride and aldehyde. This pathway was considered *via* the direct displacement of Cl from the  $C_{\beta}$  position through **TS4a** from **cpx6a** (Fig. 1). However, this pathway was calculated to be unfavorable due to the high energy barrier of  $37.7 \text{ kcal mol}^{-1}$ . Bearing this in mind, the mechanism for  $\alpha$ -methylstyrene was examined next with DFT.

For  $\alpha$ -methylstyrene (Fig. 2), the barrier for direct addition of  $\text{O}_2$  to styrene was calculated to be  $\Delta G_{\text{sol}}^{\ddagger} = 38.3 \text{ kcal mol}^{-1}$  *via* **TS1c** relative to **cpx2b**. The barrier for Cl addition through **TS1b** is lower at  $4.3 \text{ kcal mol}^{-1}$  followed by  $\text{O}_2$  addition through **TS2b** or  $24.5 \text{ kcal mol}^{-1}$  relative to **cpx2b**. The oxidized **cpx5b** is exergonic by  $-15.4 \text{ kcal mol}^{-1}$  followed by rearrangement *via* **TS3b** to **cpx6b** ( $\Delta G_{\text{sol}} = -16.1 \text{ kcal mol}^{-1}$ ). Since the product formed is acetophenone, the next plausible step would be dioxetane formation *via* **TS4b**,  $\Delta G_{\text{sol}}^{\ddagger} = 36.1 \text{ kcal mol}^{-1}$  relative to **cpx6b**, forming a more stable dioxetane **cpx8b** ( $\Delta G_{\text{sol}} = -18.8 \text{ kcal mol}^{-1}$ ). The DFT calculations also revealed that LiCl as additive plays an important role in lowering the free energy barrier for dioxetane formation (Fig. 2 yellow and green pathways) *via* transition states **TS4b\_LiCl** and **TS4b\_Cl**, which are  $29.3 \text{ kcal mol}^{-1}$  relative to **cpx6b** and  $27.8 \text{ kcal mol}^{-1}$  relative to **cpx6b\_Cl**, respectively. Decomposition of the dioxetane intermediate **cpx8b** was calculated to be very spontaneous *via* **TS5b** resulting in the acetophenone and formaldehyde products, which are highly exergonic.

## Conclusions

In summary, we have disclosed a new and versatile synthetic methodology for the photo-oxygenation of various styrenes, alkynes, aldehydes and carboxylic acids catalyzed by  $\text{CuCl}_2$ . The oxidation products are isolated in good yields with high chemoselectivity. The simplicity of this reaction protocol, using blue LED as a visible light source,  $\text{O}_2$  and employing an economical Cu catalyst, easily allows a highly effective catalytic system tolerable of different functional groups to be set up. Furthermore, the first DFT modelling was performed to elucidate a feasible chemical pathway for the oxidative transformation of styrenes through an active catalytic species proposed as the  $\mu_4$ -oxido copper chloride cluster  $[\text{Cu}_4\text{OCl}_6]$ .

## Author contributions

Z.J. conceived and designed the experiments. R.L. designed the mechanistic studies and performed the DFT calculations. S.L., D.T. and X.Z. performed the experiments. S.L., Y.Y., R.L. and Z.J. prepared the Supplementary Information. Z.J., Y.Y. and R.L. wrote the paper. S.L. and D.T. contributed equally to this work. All authors discussed the results and commented on the manuscript.

## Conflicts of interest

There are no conflicts to declare.

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