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# Copper Pyrithione (CuPT)-Catalyzed Oxidation of Secondary and Primary Benzyl Alcohols with Molecular oxygen or Air Under Mild Conditions

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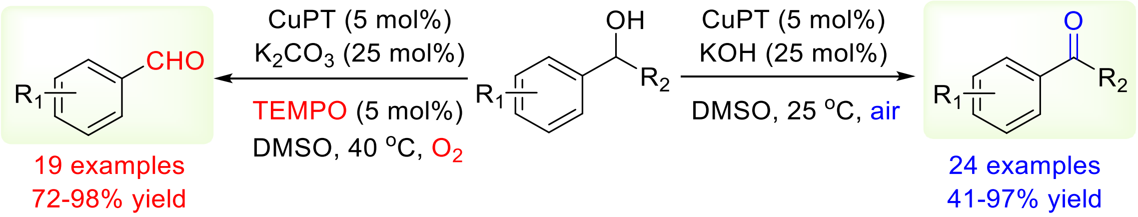
## Abstract

Copper pyrithione was used for the first time as the catalyst for oxidation secondary and primary benzyl alcohols to furnish corresponding carbonyl compounds in high yields of up to 98%. This type of reactions can be carried out in mild conditions, using molecular oxygen or air as the oxidant, and exhibiting a wide substrate scopes and selectivity.

## Graphical Abstract



**Keywords** Copper pyrithione · Oxidation · Green oxidant · Secondary and primary benzyl alcohols · Ketones and aldehydes

## 1 Introduction

Aromatic aldehydes and ketones are versatile synthetic intermediates for various C–C/O bond formation reactions, which are widely used in the preparation of natural products, biologically active molecules, and polymer materials [1]. Although several methodologies have been established for the synthesis of aromatic aldehydes and ketones, aerobic selective oxidation of primary or secondary alcohols to the corresponding carbonyl derivatives is one of the most effective protocols [2–6]. Traditional oxidation procedures for these transformations often involve the use of stoichiometric amount of oxidants such as Mn salts [7], Cr salts [8] and hypervalent iodines [9, 10], which usually cause the side reactions and over-oxidation of alcohols to carblic acids, as well as the formation of harmful gases and toxic heavy metal salts. Therefore, from the economic and environment viewpoint, development of cleaner catalytic oxidation systems for this reaction is highly desirable. In comparison to these conventional inorganic oxidants, molecular oxygen or air is an ideal oxidant because of its non-toxic, natural abundance, low cost and eco-friendly benign, and it has been successfully employed for various oxygenated chemicals synthesis.[11–14] However, due to the low reactivity and thermodynamically-stable of oxygen, the oxidation processes with oxygen or air generally have to rely on the presence of

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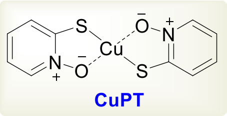
**Scheme 1** The structure of CuPT



transition-metal catalysts, such as Pd [15, 16], Ru [17–19], Au [20, 21] or other noble metals. In recent years, significant efforts have been made to achieve economic and environmental friendly reaction conditions, including the use of cheaper and earth-abundant metal (*e.g.* Cu [4, 22–29] or Ni [30, 31]), heterogeneous catalysts [32–34], or photocatalysts [35–37] and so on. Among the mentioned copper-based catalysts, (ligand)Cu/TEMPO (2,2,6,6-tetramethylpiperidinyl-1-l, and its derivatives)/base systems are proved to be efficient and selective for the oxidation of alcohols to aldehydes or ketones utilization of $O_2$ or air as the oxidant under mild conditions [23–29], [38–48], which have emerged as some of the most versatile bench scale methods for alcohol oxidation. Nevertheless, there is still a need to further develop a generally efficient catalytic system for this class of reactions.

Copper pyrithione (bis(1-hydr-1*H*-pyridine-2-thionato-O,S)copper, CuPT), as an inexpensive, low toxicity and stable bivalent copper complex (Scheme 1), is often used as antifungal and antimicrobial agents in aquatic applications [49]. Very recently, we found that CuPT could act as an effective catalyst and/or coupled partner for selective C-N/C-S coupling reactions [50]. In order to further explore the scope of CuPT to other types of organic reactions, we herein report CuPT as a novel and high active catalyst for oxidation of secondary benzyl alcohols (without TEMPO) and primary benzyl alcohols (with TEMPO) to ketones and aldehydes under air or $O_2$ atmosphere.

## 2 Results and Discussion

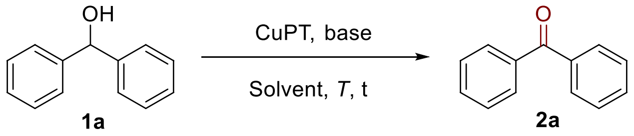
Our preliminary research began with diphenylmethanol (**1a**) as the model substrate for the oxidative reaction catalyzed by CuPT with air as the sole oxidant in DMSO at 70 °C for 30 min, and the results were illustrated in Table 1. Interestingly, the oxidation efficiency was found to be obviously dependent on the nature of inorganic base (entries 1–6). The bases with strong basicity demonstrated higher yields than the weak ones, and KOH was proved to be the best one with 97% yield (entry 6). No oxidated product was observed in the absence of base (entry 7). To our delight, decreasing the amount of CuPT and KOH to 5 mol% and 25 mol%, respectively, the yield of diphenylmethanone (**2a**) still remained constant at 97%. However, further decreasing the loading of CuPT and KOH all resulted in lower yields (entries 8–12). In different solvents other than DMSO, catalytic activities of the reactions were decreased significantly (entries 13–15). Fortunately, when the reaction temperature was reduced to 25 °C, a 97% yield was also obtained with only prolonging the reaction time to 40 min (entries 16–18). The reaction was investigated under Ar and no desired product was formed, indicating that air was the oxidant source (entry 19). The reaction yields were suppressed with other simple copper salts as the catalysts, such as $CuSO_4$ and $Cu(OAc)_2$ (entries 20 and 21). Finally, we obtained an optimal reaction conditions as follows: 5 mol% of CuPT and 25 mol% of KOH in DMSO under air at 25 °C.

With the optimized conditions in hand, the scope of secondary benzyl alcohols oxidation reactions was explored (Table 2). The results showed that the electronic effect of the substituents had slight effect on the reactivity. For example, the aromatic ring bearing electron-rich groups, such as Me, OMe and $NH_2$ (**2a**-**2f** and **2m**, 88–98% yields), gave the corresponding oxidative products in relatively higher yields than the cases containing electron-deficient groups, such as F or Cl (**2g**-**2l**, **2n** and **2o**, 49–90% yields). Notably, sterically 2-substituted substrate did not hamper the reaction. For example, excellent yields of 98% and 92% could be obtained when oxidation of 2-methyl or 2-amino diphenylmethanols (**2d** and **2e**). Because of incomplete conversion, lower yields for 1-aryl-ethan-1-ols were observed (**2p**-**2r**). The results might be due to their less reactivity than diarylmethanols, and more catalyst amount was needed. Moreover, 1,2,3,4-tetrahydronaphthalen-1-ol (**2s**), 2,3-dihydro-1H-inden- 1-ol (**2t**) and 9*H*-fluoren-9-ol derivatives (**2u**-**2w**) were also well-tolerated and produced the desired oxidation products in 43–91% yield. Gram-scale reaction was carried out with 10 mmol scale to generate the product in 98% yield (**2a**, 1.78 g), indicating the practical application of the present method.

The oxidation time on the product concentration of **2b** and **2j** were tested under the optimal conditions, and the results were shown in Fig. 1. Most of the raw materials were converted to the corresponding oxidation products within 1 h, and only a little improvement of the yield with further prolonging the reaction time to 4 h. These results suggested that the present oxidation proceeded rapidly under the established conditions.

The success of the above oxidation of secondary benzyl alcohols prompted us to investigate the feasibility of primary benzyl alcohols under the same condition. Unfortunately, only 41% yield of 4-bromo benzaldehyde was obtained with a 53% of carblic acid byproduct from over-oxidation. Therefore, we chose 2-naphthalenemethanol (**3a**) as a model substrate to optimize the oxidation reaction for primary benzyl alcohol (Table 3). First, we attempted to examine the effect of bases under the standard conditions for secondary benzyl alcohols. As we can see, higher yields were observed for KOH, NaOH and $Cs_2CO_3$ than $K_2CO_3$ and $K_3PO_4$ (entries 1–5). However, $K_2CO_3$ was the recommended base as its

**Table 1** Optimization study for oxidation of diphenylmethanol



| Entry | Cu catalyst (mol%) | Base (mol%) | Solvent | Temp. (°C) | Yield (%)[a] |
|---|---|---|---|---|---|
| 1 | CuPT (10) | $K_3PO_4$ (100) | DMSO | 70 | 26 |
| 2 | CuPT (10) | $NaHCO_3$ (100) | DMSO | 70 | 5 |
| 3 | CuPT (10) | $K_2CO_3$ (100) | DMSO | 70 | 8 |
| 4 | CuPT (10) | $Cs_2CO_3$ (100) | DMSO | 70 | 52 |
| 5 | CuPT (10) | NaOH (100) | DMSO | 70 | 96 |
| 6 | CuPT (10) | KOH (100) | DMSO | 70 | 97 |
| 7 | CuPT (10) | / | DMSO | 70 | 0 |
| 8 | CuPT (5) | KOH (100) | DMSO | 70 | 97 |
| 9 | CuPT (2.5) | KOH (100) | DMSO | 70 | 87 |
| 10 | – | KOH (100) | DMSO | 70 | 8 |
| 11 | CuPT (5) | KOH (25) | DMSO | 70 | 97 |
| 12 | CuPT (5) | KOH (15) | DMSO | 70 | 86 |
| 13 | CuPT (5) | KOH (25) | DMF | 70 | 73 |
| 14 | CuPT (5) | KOH (25) | MeCN | 70 | 85 |
| 15 | CuPT (5) | KOH (25) | DCE | 70 | 0 |
| 16 | CuPT (5) | KOH (25) | DMSO | 50 | 95 |
| 17 | CuPT (5) | KOH (25) | DMSO | 25 | 90 |
| 18 | CuPT (5) | KOH (25) | DMSO | 25 | 97[b] |
| 19 | CuPT (5) | KOH (25) | DMSO | 25 | 0[c] |
| 20 | $CuSO_4$ | KOH (25) | DMSO | 25 | 29 |
| 21 | $Cu(OAc)_2$ | KOH (25) | DMSO | 25 | 10 |

Reaction conditions: **1a** (0.5 mmol), catalyst, base, solvent (1 mL), air, 30 min

[a] NMR yield with 1,3,5-trimethbenzene as the standard

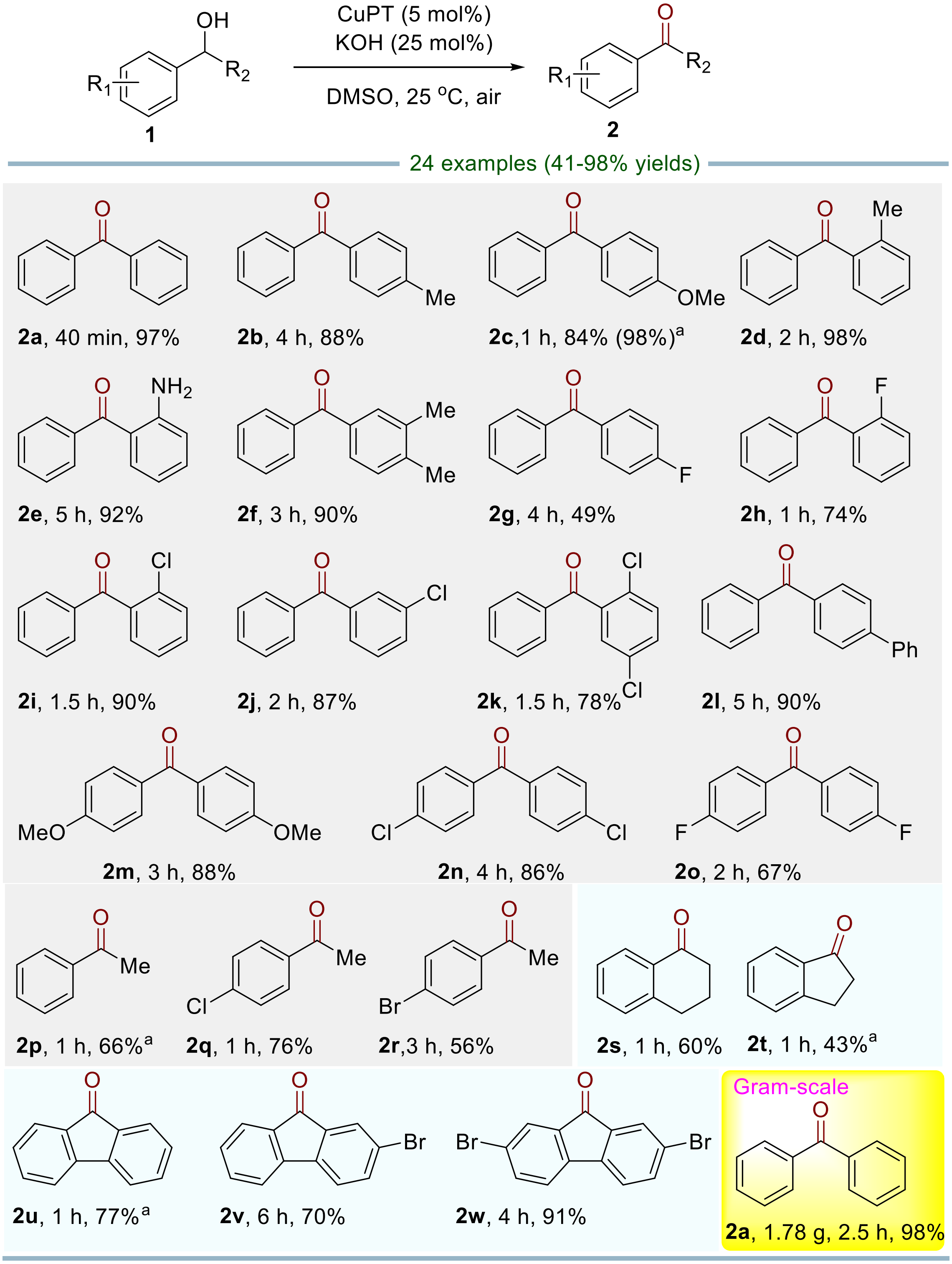
[b] 40 min

[c] Ar

weaker basicity and no over-oxidation 2-naphthoic acid byproduct formation. Slight improvement in the transformation of **3a** into **4a** was obtained by elevating the reaction temperature (entries 6–8). Replacing air with $O_2$ balloon provided a significant increased yield of **4a** (62%, entry 9). Considering the high catalytic efficiency of TEMPO in copper-catalyzed alcohol oxidation reaction, the reaction was then carried out with the addition of 5 mol% of TEMPO as the promoter in combination with $O_2$ balloon. As expected, the oxidation reaction proceeded to complete conversion of **3a** and gave a 95% yield of **4a**, whereas the yield reduced to 55% under air (entries 10 and 11). Lowering results were observed by decreasing the amount of CuPT or TEMPO (entries 12–14). Prolonging the reaction time to 12 h, the reaction was also worked well to give a yield of 96% even dropped the temperature to 40 °C (entries 15 and 16). Other simple copper salts still gave depressed yields similar with oxidation of secondary alcohols (entries 17 and 18). Finally, in the oxidation reaction of 2-naphthalenemethanol to 2-naphthaldehyde, the highest yield of 96% was gained when 5 mol% of CuPT as well as 5 mol% of TEMPO were used as the catalysts in DMSO at 40 °C for 12 h under $O_2$ atmosphere (entry 16).

As indicated in Table 4, various type of primary benzyl alcohols bearing electron-donating, electron-withdrawing, or electron-neutral groups at the *para*-, *meta*-, or *ortho*- positions of the aromatic ring could smoothly be converted to the corresponding aldehydes in 65–98% yield (**4a**–**4n**). It is clear that the reactions of electron-donating substituent substrates are faster and more efficient than the electron-withdrawing ones. The oxidation of cinnamaldehyde was occurred well in 94% yield and the conjugated C=C bond did not influence the activity under the optimized conditions, showing the high selectivity of the present catalytic system

**Table 2** CuPT-catalyzed aerobic oxidation of secondary benzyl alcohols to ketones



Reaction conditions: **1** (0.5 mmol), CuPT (5 mol%), KOH (25 mol%), DMSO (1 mL), 25 °C, air; isolated yield

[a] CuPT (10 mol%).

(**4o**). Notably, ferrocenemethanol was also a suitable case for this reaction, affording the desired ferrocenecarboxaldehyde (**4p**) in 64% yield, which highlighted that this oxidation is a useful approach for producing metal containing aldehyde. Moreover, heteroaromatic alcohol reacted excellently under our conditions to furnish the aldehyde in good yield (**4q**).

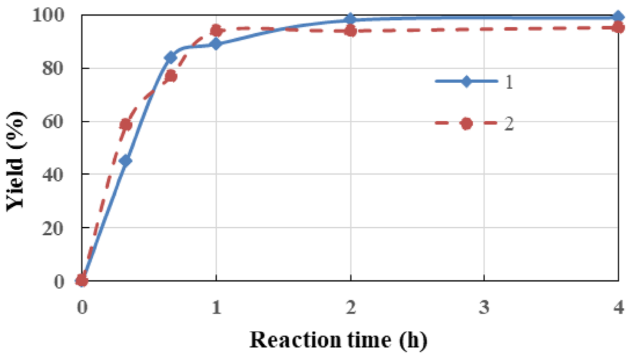


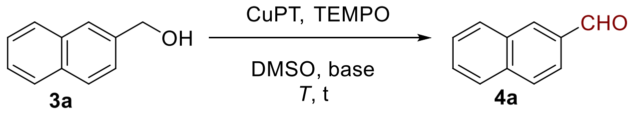
**Fig. 1** Time-concentration profile of the oxidation products of phenyl(*p*-tolyl)methanol (1, **2b**) and (3-chlorophenyl)(phenyl)methanol (2, **2j**)

We are pleased to find that treatment of double-oxidation of 1,4-benzenedimethanol proceeded without any difficulty to give **4r** in 80% yield. Compared to the absence of TEMPO, higher yield for 9*H*-fluoren-9-ol was delivered with the addition of TEMPO (**2u**, 85% vs 77%). In addition to these, the reaction could also be scaled to 10 mmol without loss of efficiency (91% yield).

We further attempted to investigate the scope of this reaction to some drug-like molecules **5** and **6a**-**6c**. However, all these substrates failed under the two optimized reaction conditions (Scheme 2).

Based on related reports [23, 51–54], a proposed mechanism for CuPT-catalyzed oxidation reaction was shown in Scheme 3. First, one ligand from the initial CuPT was cleaved and formed OH-copper complex **A** in alkaline media. Then, the intermolecular elimination was occurred between OH ligand and alcohol to generate copper-alkoxide complex **B** with a loss of one water molecule. Under the TEMPO-free conditions, carbonyl-copper(I) π complex **C** was formed via H-atom abstraction and one-electron transfer reaction of **B**. Oxidation reaction of **C** with $O_2$ produced ketones and **D**, which was easily reacted with water and regenerate **A**. In the presence of TEMPO, it preferred to coordinate with **B** to form **E**, followed by β-hydrogen transfer to TEMPO led to complex **F**. Intramolecular one-electron transfer provided aldehyde,

**Table 3** Optimization study for oxidation of 2-naphthalenemethanol



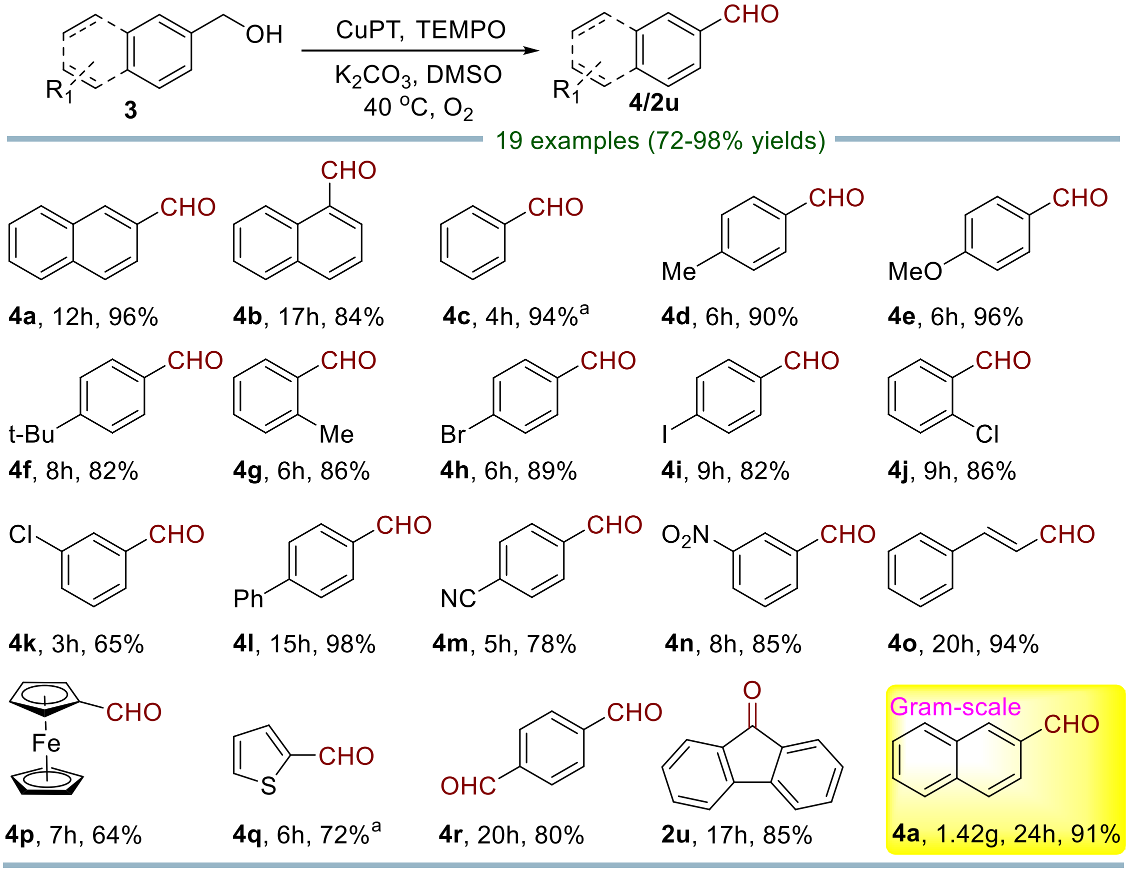
| Entry | Cu catalyst (mol%) | TEMPO mol%) | Base (mol%) | T (℃) | T (h) | Yield (%)[a] |
|---|---|---|---|---|---|---|
| 1 | CuPT (5) | 0 | KOH (25) | 25 | 6 | 51 |
| 2 | CuPT (5) | 0 | NaOH (25) | 25 | 6 | 33 |
| 3 | CuPT(5) | 0 | $Cs_2CO_3$ (25) | 25 | 6 | 38 |
| 4 | CuPT (5) | 0 | $K_2CO_3$ (25) | 25 | 6 | 24 |
| 5 | CuPT (5) | 0 | $K_3PO_4$ (25) | 25 | 6 | 16 |
| 6 | CuPT (5) | 0 | $K_2CO_3$ (25) | 40 | 6 | 26 |
| 7 | CuPT (5) | 0 | $K_2CO_3$ (25) | 60 | 6 | 32 |
| 8 | CuPT (5) | 0 | $K_2CO_3$ (25) | 80 | 6 | 40 |
| 9 | CuPT (5) | 0 | $K_2CO_3$ (25) | 60 | 6 | 62[b] |
| 10 | CuPT (5) | 5 | $K_2CO_3$ (25) | 60 | 6 | 95[b] |
| 11 | CuPT (5) | 5 | $K_2CO_3$ (25) | 60 | 6 | 55 |
| 12 | CuPT (2.5) | 5 | $K_2CO_3$ (25) | 60 | 6 | 87[b] |
| 13 | CuPT (0) | 5 | $K_2CO_3$ (25) | 60 | 6 | 12[b] |
| 14 | CuPT (2.5) | 2.5 | $K_2CO_3$ (25) | 60 | 6 | 64[b] |
| 15 | CuPT (5) | 5 | $K_2CO_3$ (25) | 40 | 6 | 87[b] |
| 16 | CuPT (5) | 5 | $K_2CO_3$ (25) | 40 | 12 | 96[b] |
| 17 | $CuSO_4$ (5) | 5 | $K_2CO_3$ (25) | 40 | 12 | 57[b] |
| 18 | $Cu(OAc)_2$ (5) | 5 | $K_2CO_3$ (25) | 40 | 12 | 78[b] |

Reaction conditions: **3a** (0.5 mmol), Cu catalyst, base, DMSO (1 mL), air

[a] NMR yield with 1,3,5-trimethbenzene as the standard

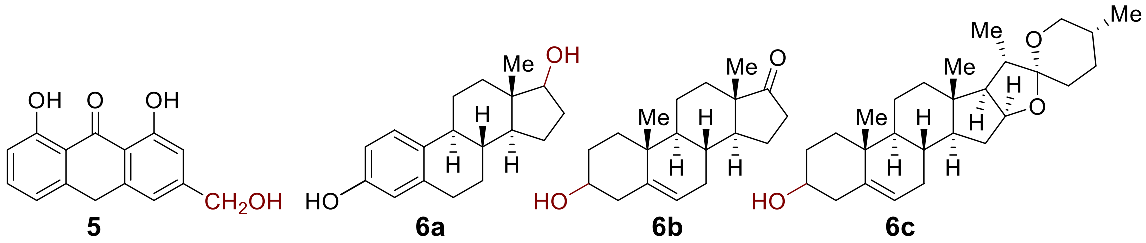
[b] $O_2$ balloon

**Table 4** CuPT-catalyzed aerobic oxidation of primary benzyl alcohols to aryl aldehyde.



Reaction conditions: **3a** (0.5 mmol), CuPT (5 mol%), TEMPO (5 mol%), $K_2CO_3$ (25 mol%), DMSO (1 mL), $O_2$ balloon, isolated yield

[a] Volatile substrates, NMR yield with 1,3,5-trimethbenzene as the standard

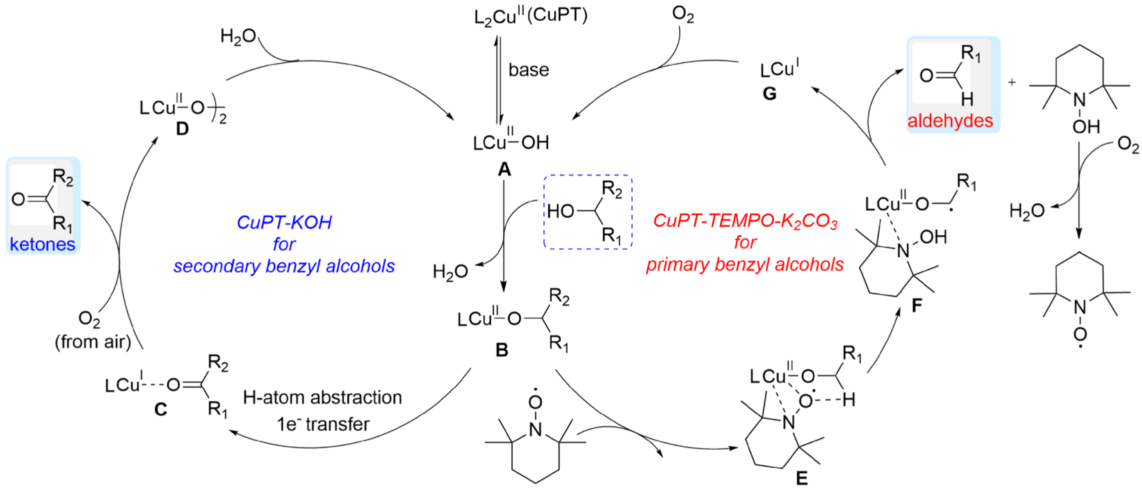


**Scheme 2** Failed examples of some drug-like molecules

TEMPOH and Cu(I) species **G**. Finally, **A** and TEMPO were all regenerated by the aerobic oxidation with $O_2$.

## 3 Conclusion

In summary, we have for the first time established a very simple and efficient protocol for CuPT-catalyzed oxidation



**Scheme 3** Possible reaction mechanism

of secondary and primary benzyl alcohols with air or $O_2$ as the oxidant under mild conditions. In the process, ketones were obtained in good to excellent yields in the presence of CuPT-KOH catalytic system, while CuPT-TEMPO-$K_2CO_3$ was more suitable for selective oxidation of primary benzyl alcohols to aldehydes. The low-cost, broad substrate tolerance with green oxidant will make it attractive both in lab research and industrial applications.

## 4 Experimental

### 4.1 Materials and Instruments

Unless otherwise stated, CuPT and other reagents were purchased from Adamas and Energy-Chemical, and used without further purification. Column chromatography and thin-layer chromatography were performed with silica gel (200–300 mesh) and $GF_{254}$ plates purchased from Qingdao Haiyang Chemical Co. Ltd. $^1$H NMR and $^{13}$C NMR were recorded on a Bruker Avance III HD 400 instrument using TMS as the internal standard and DMSO-$d_6$ or $CDCl_3$ as the solvent.

### 4.2 General Procedure for CuPT-Catalyzed Oxidation of Secondary Benzyl Alcohols

To a 10 mL reaction tube was added secondary alcohol (0.5 mmol), CuPT (0.025 mmol, 5 mol%), KOH (0.125 mmol, 25 mol%) and DMSO (1 mL). The reaction tube was stirred at 25 °C in an open air for the mentioned time in Table 2. The reaction solution was diluted with 10 mL saturated brine, and then extracted with ethyl acetate (3 × 10 mL). Combined the organic phases, washed with saturated brine for twice, dried over anhydrous $Na_2SO_4$, and concentrated in *vacuo*. The residue was purified by silica gel column chromatography (petroleum ether-ethyl acetate) to afford the target compound **2a**-**2w** in Table 2.

### 4.3 General Procedure for CuPT- Catalyzed Oxidation of Primary Benzyl Alcohols

To a 10 mL reaction tube was added benzyl alcohol (0.5 mmol), CuPT (0.025 mmol, 5 mol%), $K_2CO_3$ (0.125 mmol, 25 mol%), TEMPO (0.025 mmol, 5 mol%) and DMSO (1 mL). The reaction tube was stirred at 40 °C under $O_2$ balloon for the mentioned time in Table 4. The reaction solution was diluted with 10 mL saturated brine, and then extracted with ethyl acetate (3 × 10 mL). Combine the organic phases, washed with saturated brine for twice, dried over anhydrous $Na_2SO_4$, and concentrated in *vacuo*. The residue was purified by silica gel column chromatography (petroleum ether-ethyl acetate) to afford the target compound **4a**-**4r** and **2u** in Table 4.

### 4.4 General Procedure for Time-Concentration Experiments

Five parallel experiments were conducted for **2b** and **2j** under CuPT-KOH catalytic system condition, respectively. The reactions were stopped after 20 min, 40 min, 1 h, 2 h and 4 h, and then the reactions mixture were purified to afford the target products in corresponding yields. The time-concentration curves were next drawn as shown in Fig. 1.

**Supplementary Information** The online version contains supplementary material available at https://doi.org/10.1007/s10562-022-04172-3.

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## Declarations

**Conflict of interest** There are no conflicts to declare.

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