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ARTICLE

Picolinoyl functionalized MOF ligands for an air-promoted secondary alcohol oxidation with CuBr

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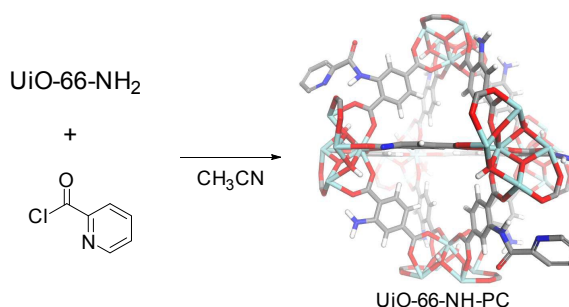
A novel Zr-derived metal-organic framework (MOF) ligand was designed and synthesized for an efficient Cu(I)-catalyzed secondary alcohol oxidation. The UiO-66-NH-PC solid ligand was utilized as an efficient oxidation reaction ligand. Several secondary alcohols were selectively transformed to ketones in good yields, using air as the oxidant, and under mild reaction conditions. In order to broaden the applicability of the method, a variety of primary alcohols and benzylic compounds was also tested in the oxidation reaction, affording the corresponding aldehydes and ketones in very high yields. Finally, the recyclability of the synthesized UiO-66-NH-PC ligand was confirmed by reusing the same batch of catalyst up to five times without observing any decrease in reactivity.

1. Introduction

Selective oxidation of alcohols to aldehydes or ketones is a fundamental step in the synthesis of countless useful organic compounds and important synthetic intermediates.¹ Utilizing molecular oxygen as the oxidizer is the most environmentally friendly and economically advantageous; it is green, readily available and inexpensive.² Air contains about 21% of oxygen and its obvious abundance makes it an ideal oxidant.³ However, the activation of air toward selective oxidations remains a challenge in synthetic chemistry, due to its inert nature. In literature, copper(I) salt have overcome other noble metals such as Pd,⁴ Au,⁵ Ru⁶ and Rh⁷ as an environmentally friendlier, inexpensive transitional metal for oxygen activation in catalytic reactions.⁸ Markó developed an aerobic catalytic system using 1,10-phenanthroline as the ligand and CuCl as the catalyst, which smoothly transformed secondary alcohols into the desired ketones in good yields.⁹ Stahl reported aerobic catalytic systems formed by [Cu(MeCN)₄]X (X = TfO, BF₄, or PF₆) and 2,2'-bipyridine (bpy) ligand for primary alcohol oxidation in presence of air.¹⁰ Other nitrogen derived ligands were also studied with copper salts in oxidation reactions.¹¹ However, there has been a very limited amount of reported successful systems for the aerobic oxidations of secondary alcohols.¹² The efficient oxidation of secondary alcohols using oxygen or air remains a major challenge for the synthetic community.

It is known that solid recyclable microporous materials can sever as ideal ligands.¹³ Recently, metal-organic frameworks (MOFs) have been applied in drug delivery, chemical sensing, molecular

separation, gas absorption and catalysis.¹⁴ MOFs have been used as versatile ligands for a variety of transition metal-based systems.¹⁵ Post-synthetic modifications can be efficiently utilized for the generation of a variety of MOFs ligands.¹⁶ Recyclable MOF/N,N'-ligands are desirable for oxidation reactions from a green chemistry point of view since commonly used N,N'-bidentate ligands are often toxic and carcinogenic.¹⁷ In order to develop an efficient aerobic secondary alcohol oxidation system, the synthesis of an ideal solid ligand for copper salt immobilization featuring an N,N'-chelating ligand is crucial.¹⁸



Scheme 1. Synthesis of the UiO-66-NH-PC ligand through post-synthetic modification.

In this manuscript, we are reporting a novel UiO-66-derived solid ligand for the efficient secondary alcohol oxidation reaction using air as the green oxidant (Scheme 1). A novel pyridine-containing UiO-66-NH-PC ligand was utilized for the complexation of a copper(I) salt to generate the Cu(I)/UiO-66-NH-PC complex. To our knowledge, it is the first example of a pyridine-derived MOF ligand employed in the aerobic oxidation of secondary alcohols. This novel oxidation methodology can be easily extended to the highly efficient oxidation of primary alcohols and benzylic carbon atoms. In addition, the UiO-66-NH-PC solid ligand can be recycled without compromising its catalytic activity.

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2. Experimental section

2.1 Materials

All the chemicals were used as acquired from vendors, and without need for further purification.

2.2 Preparation of UiO-66-NH-PC ligand

The synthesis of amino-functionalized UiO-66-NH₂ was done according to a literature procedure.¹⁹ 1.5 g of UiO-66-NH₂ (0.85 mmol based on MW of 1766 g/mol) were suspended in 20 mL of CH₃CN. 2.0 equiv. of picolinoyl chloride hydrochloride (303 mg, 1.7 mmol) were then added. The solution mixture was slowly stirred at 40 °C for 12 h, after which the CH₃CN solvent was decanted. Fresh CH₃CN (10 mL) was used to rinse the UiO-66-NH-PC crystals once a day for three days. The crystals were dried under vacuum at 40 °C before being used.

2.3 Catalytic selective oxidation of alcohols

In a typical process, a mixture of acetonitrile (5.0 mL) and alcohol (1.0 mmol) were added into a 10-mL round-bottom flask, together with 5 mol% of the Cu(I) species, 5 mol% of ligand (based on the nitrogen), 5 mol% of TEMPO, and 10 mol% of NMI. After a certain reaction time, *n*-dodecane (0.2 mmol) was added as an internal standard for the determination of yield and selectivity. The filtered liquid samples were analyzed by GC-MS or isolated for ¹H NMR.

2.4 UiO-66-NH-PC ligand recycling

At the end of each benzyl alcohol oxidation reaction cycle, the UiO-66-NH-PC ligand was recovered by centrifugation of the solution mixture followed by washing with 5 - 10 mL of CH₃CN. After being immersed in the CH₃CN for 12 h and dried at 40 °C under vacuum for 12 h, the UiO-66-NH-PC solid ligand was recovered and reused.

2.5 Material characterization

The phase composition of the products was characterized by X-ray powder diffraction (XRD, Cu K α radiation, $\lambda=0.1542$ nm) on a M21X diffractometer. Scanning electron microscope (SEM) images of samples were obtained with a ZEISS SUPRA 55. The BET surface area, pore volume and pore diameter were measured by an AUTOSORB-1C analyzer. Fourier transform infrared spectra (FT-IR) were collected by a Nicolet 6700 spectrometer. ¹H-NMR spectra were recorded on a Varian Unity Plus 400 instrument. Thermogravimetric analysis (TGA) was performed using an STA 449F3 instrument under nitrogen flow.

3. Results and discussion

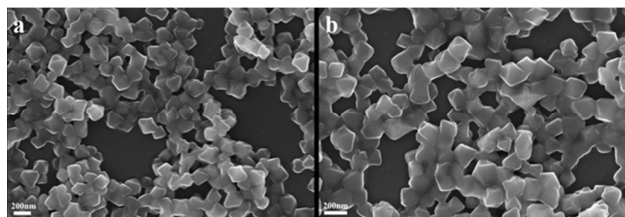


Fig. 1 SEM images of (a) UiO-66-NH₂ and (b) UiO-66-NH-PC.

Scanning electron microscopy (SEM) images of UiO-66-NH₂ and UiO-66-NH-PC are shown in Fig. 1. The crystals of UiO-66-NH₂ MOF appear to have an octahedral morphology with diameters of around 150 nm (Fig. 1a). The morphology of UiO-66-NH₂ MOF was retained after post-synthetic modification using picolinoyl chloride in CH₃CN solvent, as shown in Fig 1b. This observation indicates the strong chemical stability of UiO-66-NH₂ MOF in the presence of acidic acyl chloride reagents.

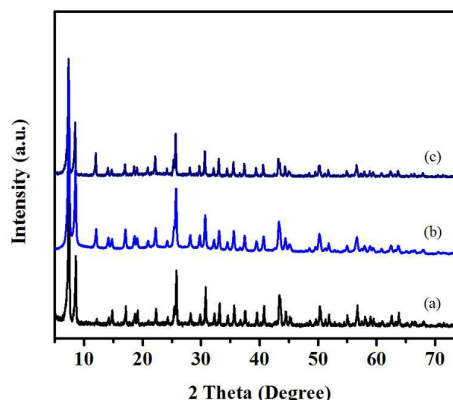


Fig. 2 PXRD patterns of (a) UiO-66-NH₂, (b) UiO-66-NH-PC and (c) recycled UiO-66-NH-PC.

The crystal structure of UiO-66-NH₂ and UiO-66-NH-PC were further characterized by powder X-ray diffraction (PXRD). The PXRD spectra of UiO-66-NH₂ show the peaks at 7.43, 8.54, 17.08, 25.18, and 30.88 degrees, corresponds to the (1 1 1), (2 0 0), (4 0 0) and (6 0 0) planes in the XRD patterns of reported MOF²⁰ and simulated UiO-66 structures (Fig S1). The strong XRD peaks at $2\theta = 7.43^\circ$ and 8.54° are related to the octahedral and tetrahedral cages, respectively. The post-synthetic modification did not affect the crystalline structure of UiO-66-NH₂. As expected, the PXRD patterns observed for the UiO-66-NH-PC material possessed the same crystalline reflections as its precursor UiO-66-NH₂.²¹

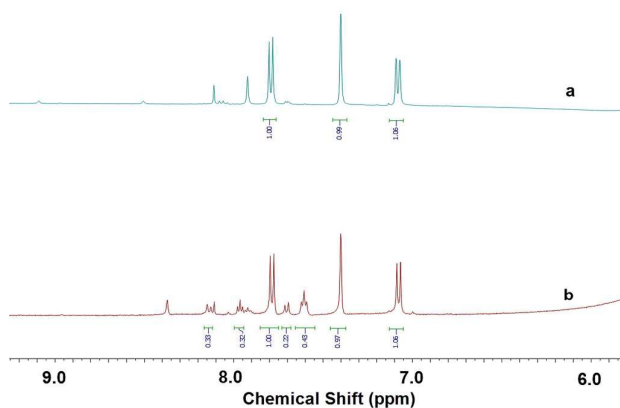


Fig. 3 ¹H NMR spectra of (a) UiO-66-NH₂ and (b) UiO-66-NH-PC.

The picolinoyl chloride modified UiO-66-NH-PC was digested and characterized by ^1H magnetic resonance (NMR) for the determination of the post-synthetic modification ratio (Fig. 3). The ^1H NMR spectra show that 25% of the amino groups are transformed to picolinamide groups. The modification ratio was utilized for the calculation of ligand usage in the catalysis evaluation. The ^1H NMR spectrum of UiO-66-NH-PC proved the chemical stability of UiO-66-NH $_2$ in the acidic chloride reagent. Also, the ESI-MS of the digested UiO-66-NH-PC showed a clear peak at MW 285 (negative mode), which suggested the successful post-synthetic modification of the amino MOF structure.

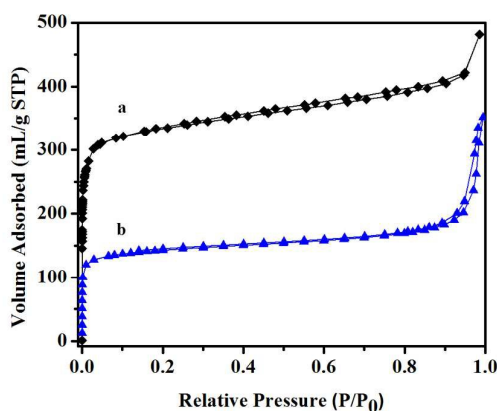


Fig. 4 Nitrogen adsorption/desorption isotherms of (a) UiO-66-NH $_2$ and (b) UiO-66-NH-PC.

The high porosity of the UiO-66-NH $_2$ was characterized by N $_2$ adsorption/desorption isotherms, which is shown in Fig. 4. The surface area of UiO-66-NH $_2$ was 1263 m 2 g $^{-1}$ as determined by the Brunauer-Emmett-Teller (BET) method. The isotherms in Fig. 4 were clearly shown to be of type I, which meets the expectations for a microporous MOF material. After post-synthetic modification using acyl chloride reagents, the BET surface area of UiO-66-NH-PC decreased due to the porous structure occupation. The surface area of UiO-66-NH-PC was determined to be 837 m 2 g $^{-1}$ and the decreased surface area did not reduce the activity of UiO-66-NH-PC.

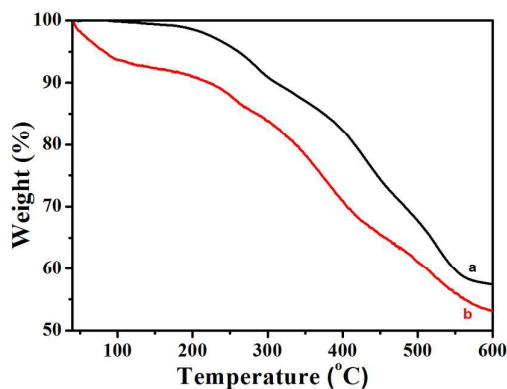
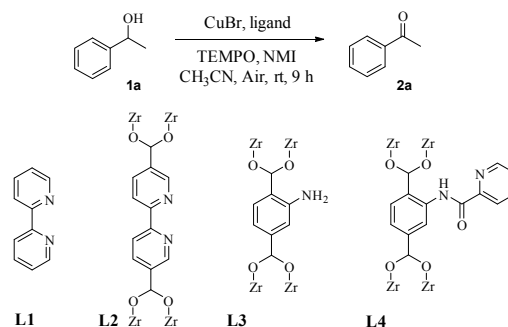


Fig. 5 TGA plots of (a) UiO-66-NH $_2$ and (b) UiO-66-NH-PC.

The synthesized UiO-66-NH $_2$ and UiO-66-NH-PC were examined by thermal gravimetric analysis (TGA) to confirm the thermal and structural identities of Zr-derived MOFs. A 10% weight loss for UiO-66-NH $_2$ occurred at around 310 °C, which indicates good thermal

stability. For the UiO-66-NH-PC, a 10% weight loss occurred at around 230 °C, which is attributed to the departure of the guest molecules. This observation indicates that the post-synthetic modification with picolinoyl chloride did not affect the thermal stability of the UiO-66-NH $_2$ framework.

Table 1. Cu(I) catalyzed secondary alcohol oxidation reaction scheme.^a



Entry	Cu(I) source	Ligand	Solvent	Yield ^b
1	CuBr	-	CH $_3$ CN	16%
2	CuBr	L1	CH $_3$ CN	96%
3	CuBr	L2	CH $_3$ CN	26%
4	CuBr	L3	CH $_3$ CN	33%
5	CuBr	L4	CH $_3$ CN	99%
6 ^c	CuBr	L4	CH $_3$ CN	62%
7	CuBr	L4	PhCH $_3$	34%
8	CuBr	L4	THF	53%
9	CuBr	L4	CH $_2$ Cl $_2$	69%
10	CuI	L4	CH $_3$ CN	91%
11	CuCl	L4	CH $_3$ CN	48%

^a 5 mol% Cu(I) catalyst, 5 mol% ligand, 5 mol% TEMPO, 10 mol% NMI in the presence of air at room temperature for 9 h, ^b Yields were calculated based on the GC-MS conversion and selectivity, ^c No NMI additive added.

A variety of copper(I) sources and organic ligands were tested in order to optimize the oxidation reaction of secondary alcohols. Very poor yields were observed in the absence of an organic ligand, which demonstrates the crucial role of the ligand in the reaction (Table 1, entry 1). 4,4'-bipyridine was tested as the bidentate pyridine ligand and it functioned well under our reaction conditions (Table 1, entry 2). However, homogeneous nitrogen ligands, such as 4,4'-bipyridine, suffered from the difficulty in recycling. At this point, we expected that converting the 4,4'-bipyridine ligand to the relative MOF bipyridine ligand would solve the ligand recycling issue. The UiO-67 MOF **L2** was synthesized according to the literature procedure. However, only low yields were observed when the UiO-67 ligand **L2** was utilized (Table 1, entry 3). It is postulated that the carboxylate functional group was withdrawing electron density from the pyridine's nitrogen atom. The electron deficiency on the aromatic ring resulted in low oxidation activity. Furthermore, UiO-66-NH $_2$ **L2** only gave a poor yield since the aromatic amino group is not a good coordinating functional group for Cu(I) (Table 1, entry 4). As we learnt from model ligand studies, we intended to design a MOF structure as the heterogeneous ligand for CuBr. In the aromatic region on the MOF structure, the pyridine moiety should not be affected by the presence of electron-withdrawing carboxylate groups. The **L4** ligand, which used picolinoyl chloride as the PSM reagent, was the most effective solid ligand during our reaction optimization (Table 1, entry 5). Yield of up to 99% were achieved in presence of air at room temperature. This result is in

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agreement with our catalyst's design, which provided an unaffected pyridine moiety in the MOF structure. The same reaction was performed in the absence of basic NMI additive and only 62% yield was obtained (Table 1, entry 6). The NMR additive strongly facilitate the deprotonation of the secondary alcohol, which leads to faster formation of the desired ketone product. A solvent screening was performed in order to determine the optimal reaction conditions for the oxidation of 1-phenylethan-1-ol at room temperature (Table 1, entries 7-9). It was not surprising to observe the low to modest yield of the oxidation reaction when run in toluene or THF (Table 1, entries 7 and 8). The low polarity of toluene solvent and strong coordination ability of THF solvent were the main reason of the reduced catalytic activity. Furthermore, dichloromethane solvent failed to provide satisfied yield either (Table 1, entry 9). Moreover, CuI showed comparable yield, while CuCl only gave a poor yield of the desired acetophenone product (Table 1, entries 10 and 11). Both CuI and CuCl were excluded from further oxidation activity studies. As a result, UiO-66-NH-PC/CuBr was chosen as the most optimal combination for further oxidation reaction studies. Our Cu(I)/MOF system demonstrated great catalytic efficiency under mild reaction conditions using air as the green oxidant. The catalytic activity of our system proved enhanced, when compared to that of several previously reported systems; the comparison is summarized in Table S1.

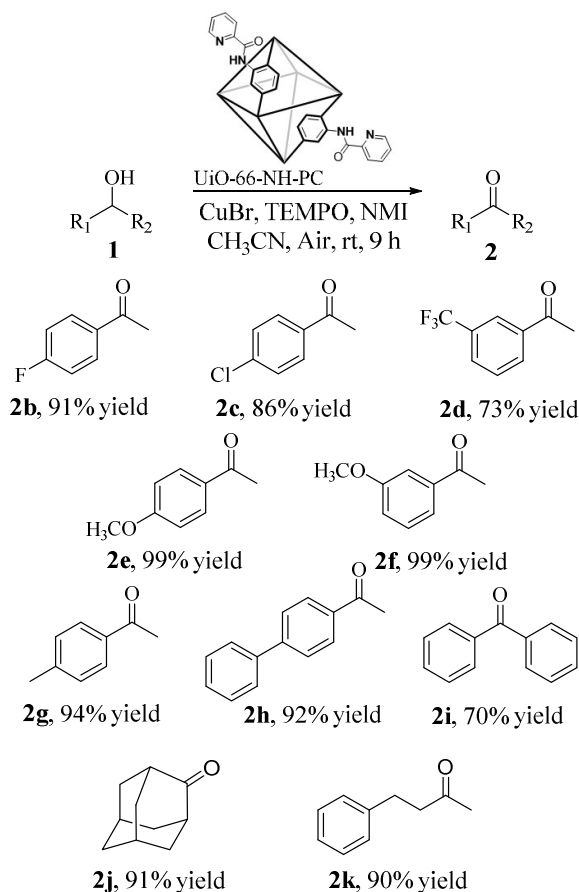


Fig. 6 Secondary alcohol oxidation employing CuBr/UiO-66-NH-PC.

A variety of substituted secondary alcohols were further tested using the CuBr/UiO-66-NH-PC system. TEMPO and *N*-methylimidazole (NMI) were used as organic additives under open-

air conditions. Electron-deficient phenylethanols gave good to modest yields under our reaction conditions (Fig. 6, 2b-2d). This is likely due to the reduced electron-density on the benzylic carbon center. In addition, electron-rich phenylethanols were transformed to their desired ketones in good yields (Fig. 6, 2e and 2f). Para-methyl phenylethanol showed a similar reactivity to the parent secondary alcohol (Fig. 6, 2g). Furthermore, 1-(*para*-phenylphenyl)ethanol was tested as an electron-rich bulky alcohol (Fig. 6, 2h). Good yield and selectivity were observed. This observation proved that large molecule are tolerated in our oxidation reaction system. However, reduced yield was observed for the biphenylmethanol substrate, which provided the desired benzophenone in only 70% yield (Fig. 6, 2i). It is possibly due to the steric effect during the secondary alcohol oxidation. Furthermore, adamantan-2-ol and 4-phenylbutan-2-ol were tested as aliphatic secondary alcohols. They both gave the corresponding ketone products **2j** and **2k** in good yield and high selectivity (Fig. 6, 2j and 2k).

Table 2. Cu(I)/Air/UiO-66-NH-PC promoted oxidation of primary alcohols and benzylic compounds.^a

Entry	Substrate	Product	Yield ^b	Sel.
1			99%	99%
2			99%	99%
3			74%	99%
4			68%	99%

^a 5 mol% CuBr catalyst, 5 mol% UiO-66-NH-PC, 5 mol% TEMPO, 10 mol% NMI in the presence of air at room temperature for 1 h, ^b Yield was calculated based on the GC-MS conversion and selectivity.

Under similar conditions, and over reduced reaction times, the CuBr/UiO-66-NH-PC system was employed in the aerobic oxidation of primary alcohols (Table 2). Benzyl alcohol reacted smoothly using the combination of CuBr/UiO-66-NH-PC in presence of air for 1 h (Table 2, entry 1). An enol substrate, such as (*E*)-3-phenylprop-2-en-1-ol was tested and a yield of 99% was achieved (Table 2, entry 2). Cyclohexylmethanol and octan-1-ol were both evaluated as aliphatic primary alcohols, however, only moderate yields were observed (Table 2, entries 3 and 4). This is due to the reduced electron density around the aliphatic primary carbon.

The UiO-66-NH-PC solid ligand was recycled for five times in order to examine its recyclability and chemical stability. After each reaction cycle, the solid ligand was centrifuged from the reaction mixture and then washed with CH₃CN. The re-evaluation of UiO-66-NH-PC ligand indicated that the high efficiency of UiO-66-NH-PC was maintained at least after five cycles (Fig. 7). This observation further proved that the strong covalent bond ensures the chemical stability

of the pyridine ligand during the oxidation reaction. Furthermore, a hot filtration test of the UiO-66-NH-PC solid was performed and the oxidation reaction stopped after the UiO-66-NH-PC ligand was isolated from the CH₃CN solution (Fig. S3). This indicated that the UiO-66-NH-PC ligand is crucial for the reaction and that there was no leaching of the acyl pyridine moiety. In addition, SEM image and XRD pattern of the UiO-66-NH-PC ligand remained unvaried even after five oxidation cycles (Fig S2 and 2c). These results clearly demonstrate that there was no alteration in the internal UiO-66 porous structure over the aerobic oxidation process.

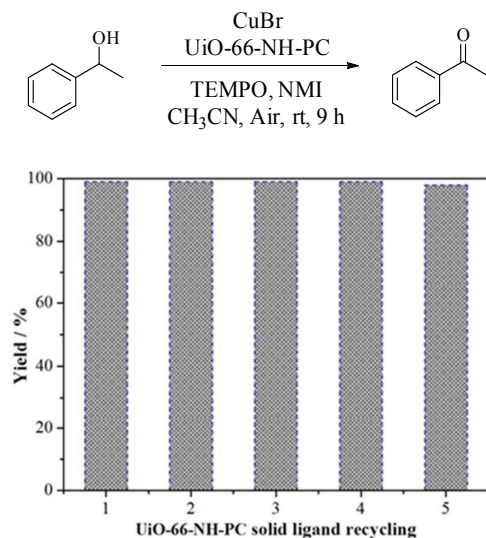


Fig. 7 UiO-66-NH-PC recycling test.

4. Conclusions

In summary, a picolinoyl chloride post-synthetically modified UiO-66 MOF was obtained and utilized as a solid and reusable ligand for a selective secondary alcohol oxidation reaction. A highly efficient aerobic oxidation system for secondary alcohols was achieved using air as the oxidant and CuBr as the copper source. Several secondary alcohols were transformed to their corresponding ketones in high yield under mild reaction conditions. To the best of our knowledge, this is the very first example of secondary alcohol oxidation using a combination of copper(I) salt, recyclable ligand and air as the oxidant. The reaction methodology was further extended to the oxidation of primary alcohols and benzylic compounds.

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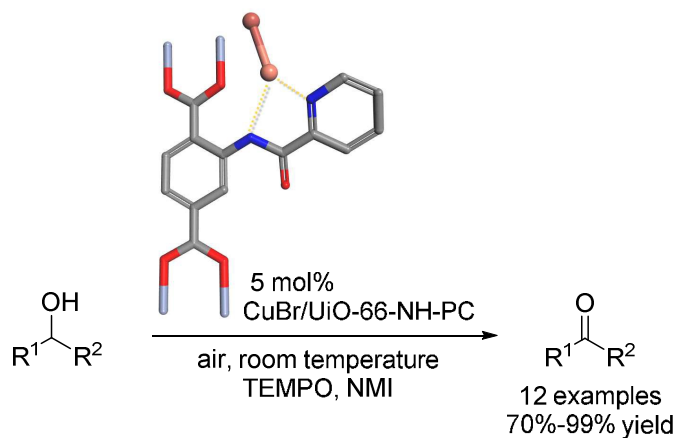
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Picolinoyl functionalized MOF ligands for an air-promoted secondary alcohol oxidation with CuBr

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A novel Zr-derived pyridine MOF ligand was designed and synthesized for an efficient Cu(I)-catalyzed secondary alcohol oxidation.