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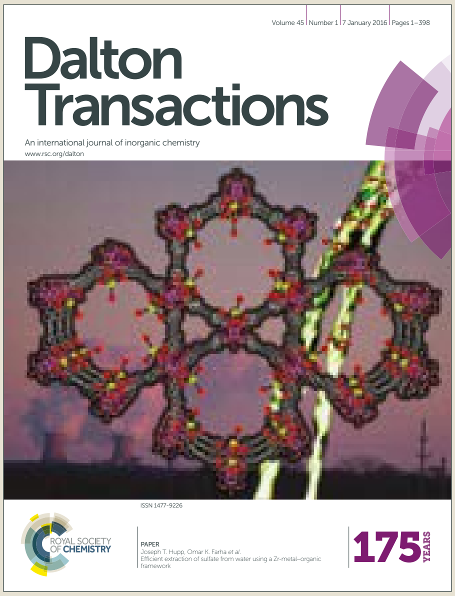

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A NbO type Cu(II) metal–organic framework showing efficient catalytic activity in Friedländer and Henry reactions

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Abstract: A three dimensional **NbO** type porous metal–organic framework **1** containing both tertiary amine groups and paddle wheel dinuclear $Cu_2(COO)_4$ secondary building units as active centre, was synthesized at room temperature. The activated framework **1′** can be used as efficient heterogeneous catalyst for the synthesis of quinoline derivatives by Friedländer and Henry (nitroaldol) reactions for the synthesis of β–nitroalcohols. This MOF-based heterogeneous catalyst is easily recycled and reused further without losing its structural integrity and catalytic activity.

Introduction

In recent years, there has been growing interest in the development of functional metal–organic frameworks (MOFs),[1] obtained by connecting metal ions/clusters with organic linkers.[2] The porosity, channel shape, pore size and functionality of MOFs can be easily tuned by judicious choice of metal nodes, organic ligands and synthetic strategies.[3] Due to these flexibilities, MOFs have emerged as novel porous materials with improved properties against its conventional competitors such as zeolites and activated carbon.[4] MOFs have shown enormous potential in a wide range of applications such as catalysis,[5] selective absorption and separation,[6] magnetism,[7] and molecular recognition.[8] Among them, the utility of MOFs in catalytic reactions

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is particularly interesting. Many organic reactions can be efficiently catalyzed by MOFs[9] due to accessibility of the active catalytic sites within the framework. MOFs can show its catalytic activity through two different components, *i.e.*, the metal ions and the coordinated linkers.[10,2b] These two components decide its nature: either it is Lewis acidic or basic in the catalytic medium.[11] A literature survey will show that there are lots of examples of Lewis acidic metal catalysis while the catalytic activity by Lewis basic nature of the MOFs remain scanty.[12] For example, Huh *et al.* reported a Lewis basic DABCO-functionalized Zn^{2+}-MOF that catalyzed the nitro-aldol reaction (known as Henry reaction) of 4-nitrobenzaldehyde with nitroalkanes.[13] There are various number of new methods being developed for functionalizing the linkers.[14] The heterogeneous catalysis by active Lewis basic organic functional groups in MOFs is still challenging.[15] Previously, our group reported a L-proline functionalized Cu^{2+}-MOF where the L-proline moiety with imidazole as a co-catalyst synergistically catalyzed the Baylis−Hillman reactions.[16]

Generally, porous MOFs with high specific surface area and coordinatively unsaturated metal centers (UMCs) are very good candidates for heterogeneous acidic catalysis.[17] Among a variety of MOFs, those with $[Cu_2(COO)_4]$ paddle-wheel units containing one or more solvents molecules loosely bound to the metals ions, have been explored as Lewis acidic catalysts in many organic reactions.[18] MOFs with basic functional groups, such as amido or amino groups in the linkers are capable of functioning as Lewis basic heterogeneous catalysts.[12] Besides, the basic groups in the MOF may also exhibit selective gas adsorption.[19]

Earlier, we reported[5b] a chiral piperazine-derived ligand incorporating isophthalate units at the terminals, i.e. 5,5′-(S)-(+)-2-methylpiperazine-1,4-diyl)diisophthalic acid. Herein, we report a similar ligand i.e. 5,5'-(piperazine-1,4-diyl)diisophthalic acid (**H_4L**; Scheme 1) that

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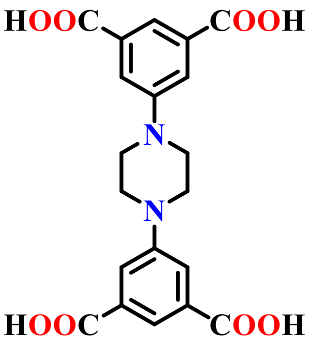
produces a 3D Cu^{2+}-MOF at room temperature and contains aqua bound paddle-wheel SBUs with piperazine units within the pores of the framework.



Scheme 1. Schematic diagram of the ligand, **H_4L.**

We show that the framework upon activation via heating forms **1′** having vacant coordination sites on Cu^{2+} that can act as an excellent heterogeneous catalyst for Friedländer reactions to synthesize quinoline derivative as well as for Henry reactions between aromatic aldehydes and nitroalkanes.

Experimental

Materials and physical measurements. The details of materials used, physicochemical characterization and X-ray structural investigation are given in the ESI†.

Synthetic methodology. The synthesis of the linker was achieved following previously reported method[20] and given in the ESI†.

Synthesis of $\{[Cu_2(L)(H_2O)_2]\cdot(3DMF)(4H_2O)\}_n$ (1). $Cu(NO_3)_2\cdot3H_2O$ (35 mg, 0.15 mmol) and **H_4L** (20 mg, 0.05 mmol) were taken in separate conical flasks and added 1mL water and 2mL DMF to each. These solutions heated on the hot plate till clear solutions were obtained. Then they were mixed and treated with two drops of conc. HCl and mixed well. The clear solution was

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allowed to slowly evaporate at room temperature for 7 d. Blue crystals of **1** were obtained after filtration. Yield = 57%. FT-IR (KBr pellets, cm^{-1}): 3431 (broad), 2937 (m), 1662 (s), 1589 (s), 1414 (s), 1381 (s), 1280 (m), 1241 (m), 1149 (m), 1099 (s), 1001 (s), 777 (s), 732 (s), 662(m); elemental analysis: calcd (%) for $C_{14.5}H_{23.5}N_{2.5}O_{8.5}Cu$: C 40.29, H 5.47, N 8.10; found: C 40.57, H 5.83, N 8.27.

Results and discussion

Blue block-shaped crystals of **1** were obtained at room temperature by reacting the ligand **H_4L** and $Cu(NO_3)_2 \cdot 3H_2O$ in aqueous DMF. The phase purity of the bulk sample was confirmed by its powder X-ray diffraction pattern (Fig. S9, ESI†). Single-crystal X-ray diffraction study revealed that **1** crystallized in the trigonal space group of *R*-3*m* (Table S1, ESI†) and was isoreticular to NOTT-101.[21] As expected, the framework was composed of paddle-wheel dinuclear $Cu_2(COO)_4$ SBUs. Four SBUs were bridged by the ligand **L^{4-}** to form a 3D **NbO** type structure. Each Cu(II) centre in the SBU coordinated to four carboxylate oxygen and one water molecule (Fig. 1a). The distances between Cu···O bonds lie in the range 1.930(5) Å to 2.160(6) Å and the Cu···Cu distance is 2.642(2) Å. The packing of **1** along the crystallographic *a* or *b* axis can be seen in Figure 1d. Two types of channels of different sizes could be seen along the *c* axis (Fig. 1b). While the larger channel is surrounded by six paddle-wheel SBUs, the smaller one is surrounded by three SBUs. There are two types of cages in the framework: one cage (pink) of about 13.765 Å in diameter and the other large oval shaped cage of about 24.749 × 18.604 $Å^2$ in dimension (Fig. 1c) occupied by DMF and water as guest molecule which are quite disordered and cannot be locate crystallographically. The solvent composition (1.5 DMF + 2 H_2O molecule per asymmetric unit) was confirmed from thermogravimetric and elemental analyses. The values

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are in well-accordance with the PLATON-calculated solvent-accessible void volume, which is found to be 68.64% of the unit-cell volume.

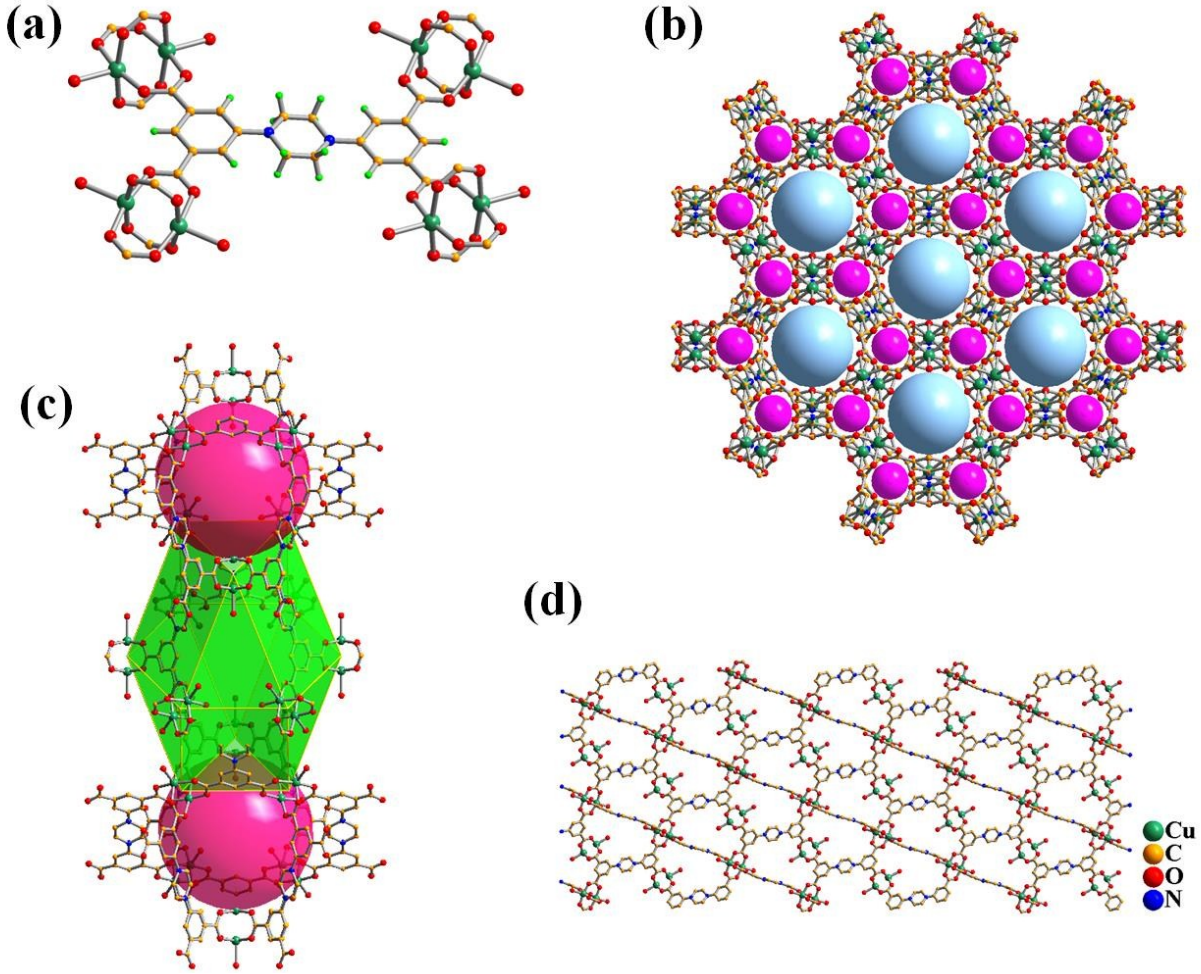

Fig. 1 Single-crystal X-ray diffraction structure showing (a) paddlewheel SBUs, (b) two types of channels along the *c*-axis, (c) two different types of cages, and (d) packing of **1** along *a*- or *b*-axis. The hydrogen atoms are omitted for clarity.

Catalytic activity towards the Friedländer and Henry reactions.

Recently, the MOF, **NJU-Bai 19** with exactly the same ligand and structure has just been reported, exhibiting enhanced CH_4 storage.[22] The permanent porosity of **NJU-Bai 19** was confirmed by N_2 isotherm measurements at 77 K of the acetone solvent-exchanged sample. The

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BET surface area of **NJU-Bai 19** was calculated to be around 2803 m^2 g^{-1}, which are comparable to those of NOTT-101[21] (2805 m^2 g^{-1}). Our MOF **1** having similar structure but different guest molecues in the voids was obtained via a different route and is expected to have similar BET surface area. Due to this permanent porosity, availability of Lewis acidic Cu^{2+} catalytic sites and amine group incorporated linker within the framework, we probed its catalytic activity towards Friedländer and Henry reactions.

Activation of 1 to produce the active catalyst, 1′. To activate the framework, the as-synthesized sample was kept in acetone for 8 d at RT for solvent exchange. During this process, acetone was refreshed once a day. The acetone exchanged sample was then heated to 120 °C under ultra-high vacuum for 6 h to generate the fully de-solvated framework, **1′**. The PXRD pattern of **1′** (Fig. S11, ESI†) matches well with the as-synthesized MOF signifying that the overall architecture of the framework remained intact upon solvent removal. Also, the TGA curve showed the framework to be stable up to 280 ^{o}C like the as-synthesized sample (Fig. S8, ESI†)

Synthesis of quinoline derivatives via the Friedländer reaction. The large pore volume, chemical and thermal stability, and ability to form an UMC makes the MOF a potentially good heterogeneous catalyst. Here, we demonstrate the synthesis of quinoline derivatives via the Friedländer reaction, catalyzed by **1′** (Scheme 2). Quinoline is an ubiquitous backbone in various biologically and pharmaceutically active[23] molecules. A variety of quinoline derivatives show antibacterial, antimalarial, anti inflammatory agents besides exhibiting anti-asthmatic, anti-hypertensive and tyrokinase PDGF-RTK inhibiting properties.[24] Additionally, quinolines are used as synthons for the synthesis of nanostructures and polymers which accompany the optoelectronic or NLO properties with excellent mechanical strengths.[25] Due to their importance

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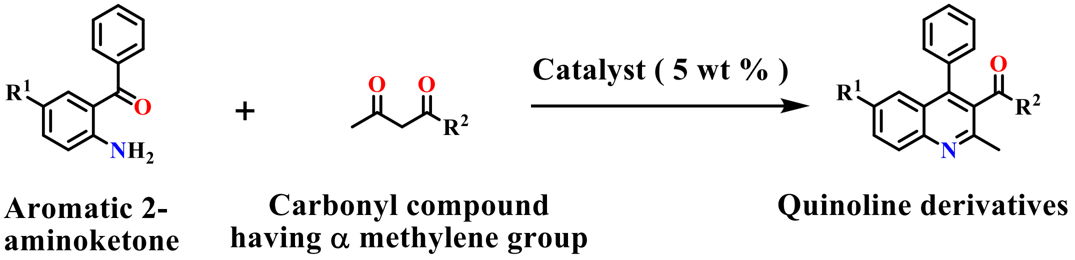
in industry, pharmacology and synthetic points of view, different versatile synthetic procedures have been reported for the preparation of quinoline derivatives.[26] Among these methods, Friedländer hetero-annulation is simple and a direct route for the preparation of quinoline derivatives through reaction between an aromatic 2-aminoaldehyde or ketone and a carbonyl compound containing a reactive α-methylene group.[27] Several new catalysts have been developed for its synthesis that avoid the use of the traditionally basic conditions. Apart from conventional protic acids, many other catalysts have also been used for the Friedländer synthesis.[28] Cu(BDC) and Cu(BTC) MOFs [BDC = 1,4-benzendicarboxylic acid, BTC = 1,3,5-benzentricarboxylic acid] having vacant Cu(II) sites as Lewis-acid, have already been showed catalytic activity for the Friedländer synthesis.[29]



Scheme 2. Synthesis of Quinoline derivatives through Friedländer reaction between aromatic 2-aminoketone and carbonyl compound having α-methylene group.

The present study concerns the catalytic behavior of **1′** showing its huge potential as a promising acidic heterogeneous catalyst for the synthesis of quinoline derivatives (Scheme 2). It is shown in the Table 1 that the various aromatic 2-aminoketone (0.5 mmol) and different carbonyl compounds containing a reactive α-methylene group (1-5 mmol) in presence of **1′** (5 wt %) as a catalyst, under solvent-free conditions (except the reaction mixture containing 1,3-cyclohexanedione), at 85 °C for 24 h, give the quinoline derivatives as the expected product in

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moderate to excellent yields. At first, we performed the reaction of 2-aminobenzophenone and ethyl acetoacetate in the presence of **1′** at 85 ºC for 24 h. This reaction gave the desired compound which was isolated with 94% yield (Table 1, Entry 1). The 4-chloro and 4-nitro substituted 2-aminobenzophenone gave the product with 92% and 36% yields respectively (Table 1, entries 2 and 3). Also, we tested the catalytic activity of **1′** with other ketones. 2-aminobenzophenone reacted with acetylacetone and 1,3-cyclohexanedione afforded the products with 91% and 87% yield, respectively (Table 1, entries 4 and 5). The heterogeneous catalytic activity of **1′** showed superiority over homogeneous copper salts i.e. copper acetate (Table 1, entry 6). The non-catalyst experiment showed that a very low yield (9%) was observed for 2-aminobenzophenone with ethyl acetoacetate (Table 1, entry 7). Further, when the reaction between 2-aminobenzophenone and ethyl acetoacetate was performed in the presence of $Cu(NO_3)_2.3H_2O$ and ligand (**H_4L**) under the same reaction condition, the desired compound was obtained in 17 % yield (Table 1, entry 8). The reason for such a low yield is that the blockage of the catalytic centers either by the nitrate anions, or by the ligands, which cannot be easily accessed by the reactant molecules.[29c] These data show that **1′** is a highly proficient Lewis-acid catalyst for Friedländer reactions with a wide variation of substrates. In each case, the desired product was characterized by the ^1H, ^{13}C NMR and ESI mass spectroscopy (Fig. S12‑S26, ESI†).

Once the reaction was over, the reaction mixture was filtered to collect the catalyst. It was washed by acetone and then heated at 120 ºC under vacuum for 2 h to regenerate the active catalyst. We further used it for subsequent runs and checked its recyclability. The regenerated

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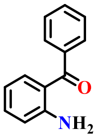
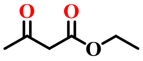
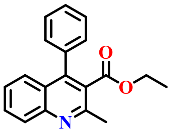
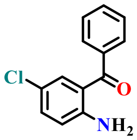
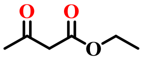
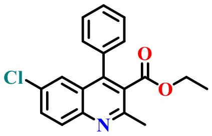
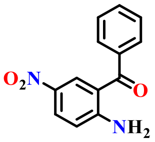
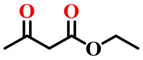
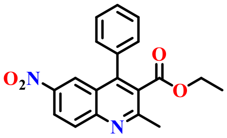
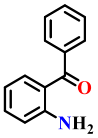
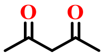
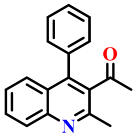
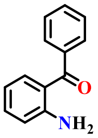
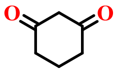
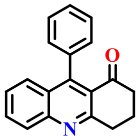
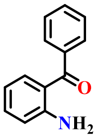
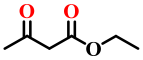
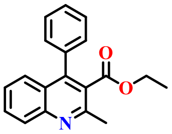
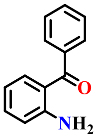
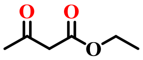
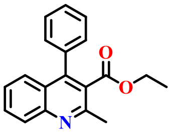
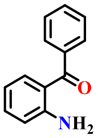
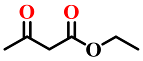
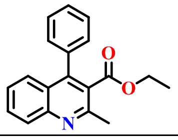
Table 1. Screening for the **1′** catalysed Friedländer reaction between different aromatic 2-aminoketone and different ketones at 80 ºC[a]

Entry	Catalyst	Aromatic 2-aminoketone	Carbonyl with α-methylene group	Quinoline derivatives	Yield (%)b
1	**1′**				94
2	**1′**				92
3	**1′**				36
4	**1′**				91
5	**1′**				87
6	$Cu(OAc)_2\cdot H_2O$				47
7	No Catalyst				9
8	$Cu(NO_3)_2\cdot 3H_2O$ + H_4L				17

[a] Reaction conditions: 2-aminoaryl ketones (0.5 mmol), carbonyl compound having α-methylene group (1-5 mmol), and catalyst **1′** (5 wt %), sealed tube 85 ºC for 24 h. [b] Yield of the isolated product after flash chromatography.

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catalyst showed similar activity till at least four cycles (Fig. 2a); after that, it showed partial loss in framework integrity as observed in the PXRD pattern (Fig. S27, ESI†). The heterogeneous nature of **1′** was demonstrated by the hot filtration experiment (Fig. 2b).

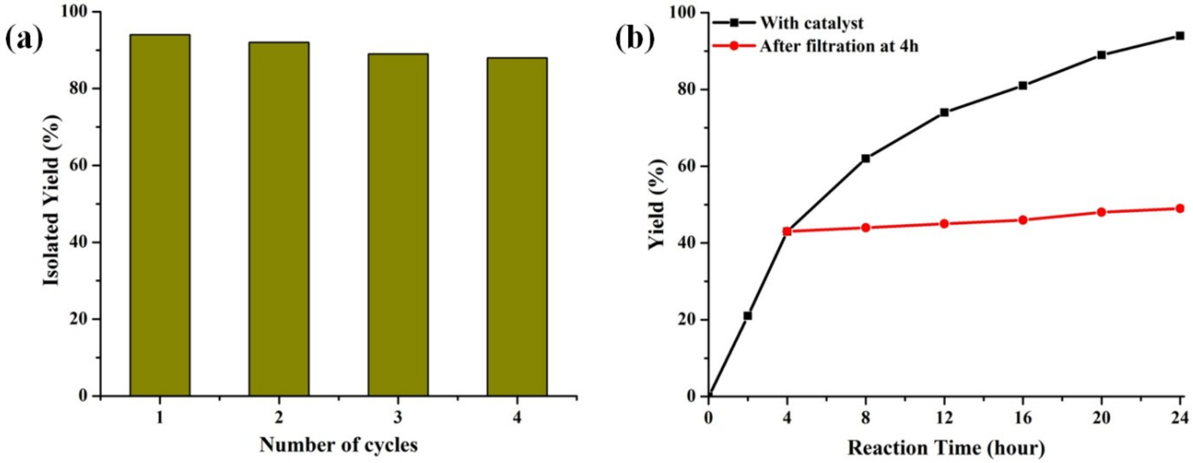

Fig. 2 (a) Catalyst recyclability test and (b) hot filtration test showing heterogeneous nature of **1′,** in Friedländer reaction.

β−nitroalcohols Synthesis via carbon−carbon bond formation (Henry reaction). Further, the catalytic activity of **1′** was evaluated in the Henry (or nitroaldol) reactions for the synthesis of β−nitroalcohols. This reaction is an important C−C bond forming reaction.[30] Besides, β−nitroalcohols are often used as important starting materials for the synthesis of various polyfunctional compounds having pharmaceutical significance.[31] Generally, the Henry reaction is efficiently catalyzed by basic catalysts[32] and often leads a dehydrative nitro-olefin as a minor byproduct.[33] In addition, many homogenous catalyst based on homo / heterobimetallic[34] and transition-metal complexes have been applied in this reaction.[35] Among them, the Cu(II) complexes were proved to be one of the most efficient catalysts.[36] However, only a few heterogeneous catalysts for this reaction are reported till date.[37] There are, also a few examples of MOF-based heterogeneous catalysts for the Henry reaction.[38] Since in our MOF, tertiary

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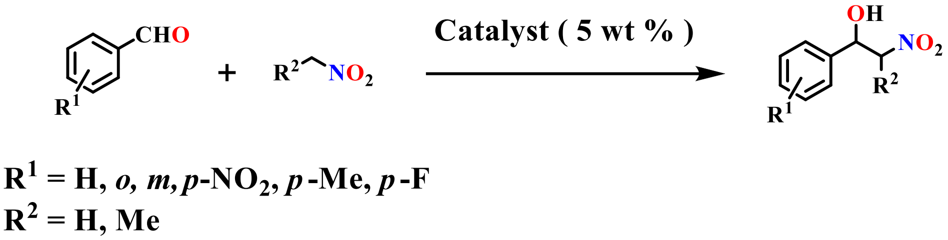
amine group is incorporated in the linker and axially aqua bound Cu metal centre can be activated to form active centre, which synergistically showed high efficiency for Henry reaction under mild conditions.



Scheme 3 Henry reaction of substituted benzaldehydes with nitroalkanes catalyzed by **1′**.

Here, we report the Henry (nitroaldol) reaction for the synthesis of β−nitroalcohols, heterogeneously catalyzed by **1′** (Scheme 3). The screening results shows that the different aromatic aldehyde (0.5 mmol) react with the nitroalkanes (10 mmol) in presence of **1′** (5 wt %) under solvent free condition at 50 ºC for 48 h, to produce the corresponding product in good yields, are summarized in Table 2. Initially we performed the reaction by using 4-nitrobenzaldehyde as model substrate with nitromethane, and catalyst **1′**. We observed that the reaction afforded the corresponding nitroalcohol after 48 h in 89% yield (Table 2, entry 1). To know the optimized reaction condition (Reaction time, catalyst's amount, temperature), we carried out the reaction between 4-nitrobenzaldehyde and nitromethane with **1′**. The optimization experiments revealed that the catalyst amount is 5 wt% and reaction time and temperature is 48 h and 50 ºC, respectively (Fig. S50, ESI†). We also demonstrated the catalytic activity of **1′** with others substituted aromatic aldehydes and nitromethane and nitroethane. Table 2 shows that on reaction with nitromethane the product yield is 67% by benzaldehyde, 58% by 4-methylebenzaldehyde, and 68% by 4-fluorobenzaldehyde (Table 2, entries 4-6 respectivily) while reaction with nitroethane the product yield is 81% by 4-nitrobenzaldehyde (Table 2, entry

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7). The result summary unveiled that (i) aromatic aldehyde containing electron withdrawing substituents affords higher yield (Table 2, entries 1, 2, 3 and 6) while aromatic aldehyde containing electron donating substituents affords lower yield (Table 2, entry 5) with respect to the benzaldehyde (Table 2, entry 4). (ii) the size of the nitroalkane chain also alter the reactivity due to steric factor,[13] for example, on reaction with 4-nitrobenzaldehyde, nitromethane gave the product in 89% yield while nitroethane gave the product in 81% yield (Table 2, entries 1 and 7). Here we also checked the effect of substituents position, on the catalytic activity. The *ortho*, *meta*, and *para* substituted nitrobenzaldehyde reacted with nitromethane and give the product in 82%, 86% and 89% yield respectively (Table 2, entries 2, 3, and 1). Also, we were performed blank reaction (in absence of catalyst source; Table 2, entry 10) by using 4-nitrobenzaldehyde and nitromethane as substrate at same reaction condition, very small amount of desired product was obtained. The nitroaldol reaction also take place when using $Cu(OAc)_2{\cdot}H_2O$ and **H$_4$L** as an alternative of **1′** (Table 2, entries 8 and 9). Another set of reaction was examined between 4-nitrobenzaldehyde and nitromethane in the presence of both $Cu(NO_3)_2.3H_2O$ and **H$_4$L** at the same reaction condition which gave the desired compound in 19% yield (Table 2, entry 11). This result shows that the synergistic effect has been lost by the blocking of the catalytic sites on the metal. Here, presumably only the basic nature of the ligand is operative for the reaction. These results indicated the superiority over homogeneous copper salt and also showing the synergistic effect of **1′** leading to high efficiency for Henry reaction.

The catalyst **1′** could be reused and recycled at least for four consecutive runs (Fig. 3a). Crystallinity almost remains unchanged for three catalytic cycles and a slight degradation was observed in the fourth cycle as proved by the PXRD analysis after each cycle (Fig. S49, ESI†). The heterogeneous behavior of **1′** was confirmed using hot filtration test. The reaction mixture

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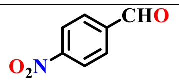
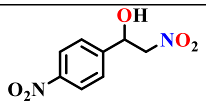
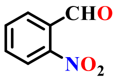
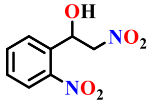
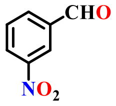
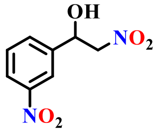
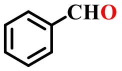
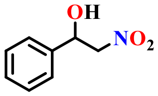
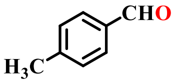
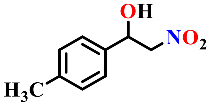
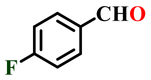
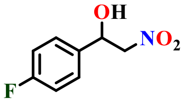
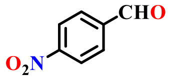
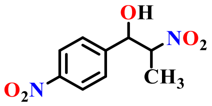
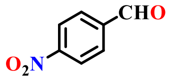
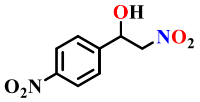
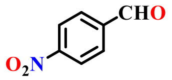
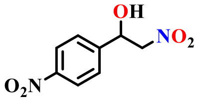
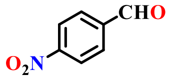
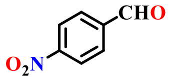
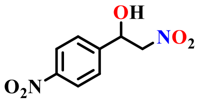
Table 2. β–nitroalcohols synthesis of substituted benzaldehydes with nitroalkanes catalyzed by **1′**.[c]

Entry	Catalyst	Ar–CHO	Nitroalkanes	Product	Yield (%)[d]
1	**1′**		CH_3NO_2		89
2	**1′**		CH_3NO_2		82
3	**1′**		CH_3NO_2		86
4	**1′**		CH_3NO_2		67
5	**1′**		CH_3NO_2		58
6	**1′**		CH_3NO_2		68
7	**1′**		$CH_3CH_2NO_2$		81
8	$Cu(OAc)_2{\cdot}H_2O$		CH_3NO_2		65
9	H_4L		CH_3NO_2		18
10	No Catalyst		CH_3NO_2	–	< 5
11	$Cu(NO_3)_2{\cdot}3H_2O$ + H_4L		CH_3NO_2		19

[c] Reaction Conditions: 5 mol% catalyst **1′**, substituted benzaldehyde (0.5 mmol) and nitroalkane (10 mmol), Reaction tube, 50 ºC for 48 h.

[d] Yield of the isolated product after flash chromatography.

was filtered after 6 h to separate the catalyst. At same reaction condition, no further conversion was observed in the filtrate part suggesting the heterogeneous nature of the **1′** (Fig. 3b). The

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product formation was confirmed by the ^{1}H, ^{13}C NMR and ESI mass spectroscopy (Fig. S28–S48, ESI†).

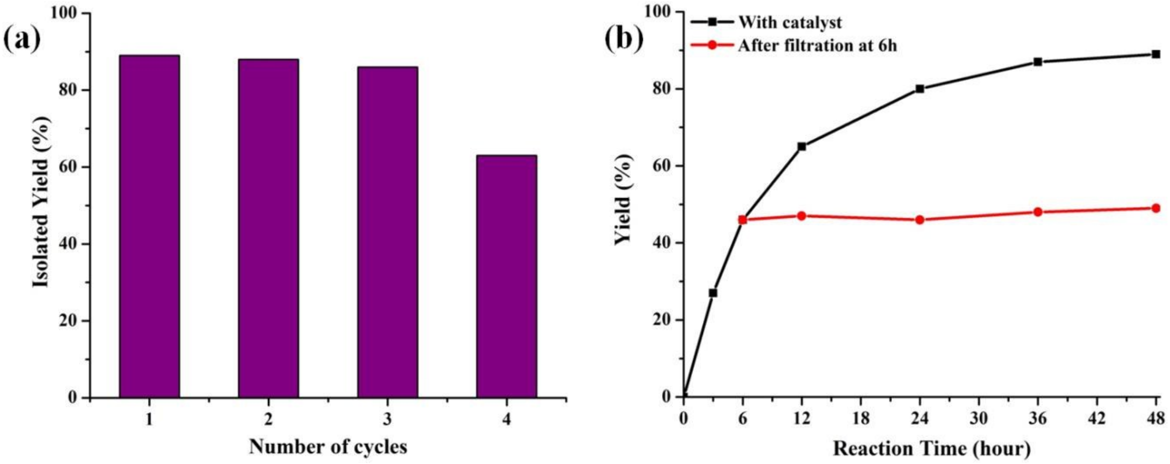

Fig. 3 (a) Reacyclability test of the nitroaldol reaction between 4-nitrobenzaldehyde and nitromethane catalysed by **1′**. (b) Plot of β−nitroalcohol yield *vs* time for the reaction between 4-nitrobenzaldehyde and nitromethane in presence of **1′** (Black curve) and after filtering off the catalyst **1′** (Red color).

Conclusions

In summary, a porous three dimensional NbO type metal−organic framework, **1** has been synthesized in single crystal form from the assembly of a semi-rigid piperazine-derived ligand and Cu(II) ion. The framework is isoreticular to NOTT-101 and is composed of paddle- wheel dinuclear $Cu_2(COO)_4$ secondary building units. Coordinatively unsaturated Cu(II) sites, suitable framework cages surrounded by tertiary nitrogen-containing ligands, and porosity, robustness endow the framework **1′** as efficient heterogeneous catalyst for the synthesis of quinoline derivatives by Friedländer reaction and β−nitroalcohols synthesis through the Henry (or nitroaldol) reaction of substituted benzaldehydes with nitroalkanes.

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†Electronic supplementary information (ESI) available: The details of materials used, physicochemical characterization and X-ray structural investigation. CCDC 1542257 for **1**. For ESI and crystallographic data in CIF or other electronic format see DOI:

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A NbO type Cu(II) metal–organic framework showing efficient catalytic activity in Friedländer and Henry reactions

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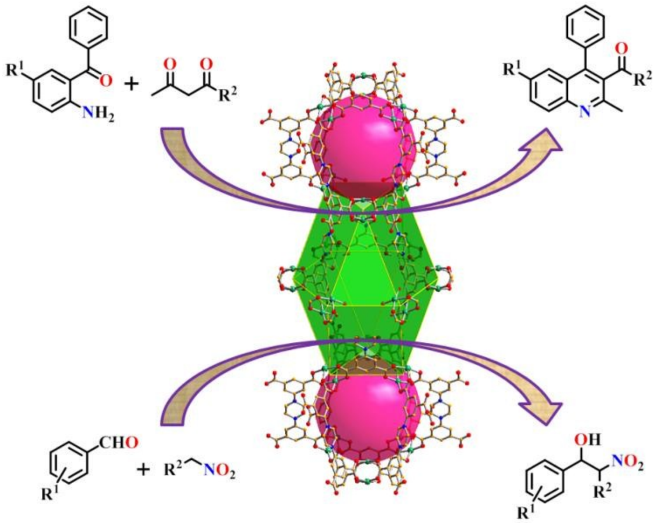

A three dimensional *NbO* type Cu(II)-MOF, **1** shows excellent and efficient heterogeneous catalytic activity for Friedländer reaction as well as Henry reaction.