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Authors: Elavarasan Samaraj, Asim Bhaumik, and Sasidharan Manickam

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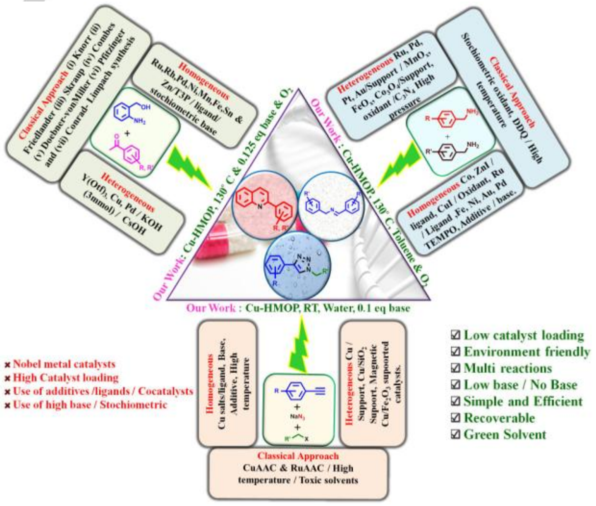
An efficient Cu–mesoporous organic nanorod for Frieldländer quinoline synthesis, and click reactions

Samaraj Elavarasan,[a] Asim Bhaumik,[b] and Manickam Sasidharan*[a]

Abstract: Within the green chemistry context, heterogeneous catalysis for the synthesis of N-heterocycles from renewable resources using non-precious metals has garnered great interest in terms of economic and environmental perspectives. Herein, we present a triazine functional hierarchical mesoporous organic polymer (HMOP) with nanorod morphology together with large BET surface area ~1218 m^{2}g^{-1}, huge pore volume > 6 mL.g^{-1} and dual micro/mesopore architectures. Subsequent Cu-coordination with nitrogen atoms of the HMOP provides a robust catalyst (Cu-HMOP) to accomplish multi-step cascade reactions for preparation of N-heterocycles by different routes. For instance, the Cu-HMOP efficiently catalyzes one-pot sequential multi-step oxidative dehydrogenative coupling of 2-aminobenzyl alcohol with diverse aromatic ketones to afford corresponding quinolines in excellent isolated yields (up to 97%). Secondly, the present catalyst exhibits good aerobic oxidative dehydrogenation activity of amines to imines. Thirdly, for "click" reaction involving azides-alkynes, the Cu-HMOP produced quantitative yield for 1,4-disubstituted 1,2,3-triazole derivatives at room temperature using water as solvent. Verification of active metal leaching by a hot filtration test as well as reusability of the retrieved Cu-HMOP catalysts shows a consistent activity in the multi-component quinoline synthesis as model reaction.

Introduction

The surge in the development of sustainable and atom-economical synthetic methodologies involving cascade organic synthesis is a fundamental challenge in chemical research.[1] Even more demanding is the advancement of heterogeneous catalysts based on base metals or metal oxide due to its facile product/catalyst separation, prospects of catalyst reusability, and environmental benignity. Accordingly, tremendous research efforts have been focused on new synthetic methodologies to design specific catalysts that enable the preparation of highly valuable N-heterocycles preferably in an atom-economical and sustainable fashion. Amines and nitrogen-containing heterocycles such as pyridines, quinolines, and pyrimidines are ubiquitous in biologically active core structures of many naturally occurring and biologically active molecules which are extensively used in pharmaceuticals, agrochemicals, and material chemistry.[2] In recent past, the tandem C–C and C–N bond forming reactions using cheap, abundant alcohols as coupling reagents have been effected with borrowing hydrogen or hydrogen autotransfer (BH/HA) approach.[3] In this context, Milstein and co-workers reported acceptorless dehydrogenative coupling of alcohols and amines to prepare imines.[4] Since then, several precious-metals based catalytic systems have been investigated extensively under homogeneous conditions.[5] Recently, intensive efforts were also devoted to replace noble metal catalysts by affordable, environmentally friendly earth-abundant base metals to accomplish N-heterocycles.[6] To synthesis N-heterocyclic compounds, several research groups including Beller, Kempe, Milstein, and Sato have demonstrated efficient Ir, and Ru based organometallic complexes by coupling the secondary alcohols, diols, and primary alcohols.[7] Initially, noble-metal supported mesoporous silica like MCM-41, SBA-15, porous zeolitic Cu-based metal organic frameworks (MOF) with 2-aminoaryl ketones were investigated for Friedländer reaction.[8a-c] Later on, Ru-complex mediated quinoline synthesis was reported by the group of Shim, Yus, and Verpoort via indirect Friedländer protocol involving oxidative cyclization of 2–aminobenzyl alcohol with either ketone or alcohols.[8d-f] Recently in 2016, Yan, Barta, Milstein and co-workers have introduced Fe, Co, and Mn based homogeneous catalysts to improve the sustainability by using inexpensive and widely abundant first row transition metals (Scheme 1).[9]



Scheme 1. Comparison of our work with recent reports on the synthesis of N-heterocycles and imines using different catalysts

In an alternate approach for achieving N-heterocyclic compounds, aerobic dehydrogenation of amines to imines via homocoupling, cross-coupling as well as (partially) saturated N-heterocyclic compounds as a complementary atom economical route was explored. In this strategy, several homogeneous

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[a] Mr. S. Elavarasan, Prof. Dr. M. Sasidharan
SRM Research Institute and Department of Chemistry, SRM Institute of Science and Technology, Kattankulathur, Chennai, 603203, India.
E-mail: sasidharan.m@res.srmuniv.ac.in
[b] Prof. Dr. A. Bhaumik
School of Materials Science, Indian Association for the Cultivation of Science, Jadavpur, Kolkata-700032, India.

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catalysts such as [Rh_2(caprolactamate)$_4$], [Cp*Ir(2-hydroxypyridine)], $Fe(NO_3)_3$/TEMPO, Fe/Co-pincer complexes, and $FeCl_2$/DMSO have been investigated to obtain quinolines albeit with moderate yield under homogeneous conditions.[10] The oxidative dehydrogenation has also been reported with Ru/Al_2O_3, Ru/Co_3O_4, Rh/MWCNT, and FeO_x@N-rGO under heterogeneous conditions to prove their efficacy.[11] Similarly, for aerobic dehydrogenation of amines to imines, precious metal based catalysts such as Pd, Pt, Au,[12a-f] Ru,[12g] metal organic frameworks,[12h], α-MnO_2[12i] and photocatalysts like TiO_2[12j] were investigated. However, most of these catalytic systems rely on noble metals, or either have cumbersome preparation methods or require the use of harsh reaction conditions like high pressure/temperature, light irradiation, and use of oxidative promoters. Therefore, development of inexpensive and facile catalytic system for dehydrogenative transformations is highly desirable. Yet another strategy to achieve N-heterocyclic compounds, is the “click” chemistry pioneered by Sharpless and Meldal, which involves the Cu(I) catalyzed [3+2] cycloadditon between terminal alkynes and azides.[13] Apart from the Cu-catalysts, other transition metals like Ag, Ru, Ir, etc. have also been extensively investigated to obtain 1,2,3-triazoles and its derivatives.[14] In order to improve the catalytic activity, a co-catalyst such as bases, auxillary ligands, and oxidizing or reducing agents depending on the Cu sources is often employed. Hence, the development of novel heterogeneous catalysts with improved catalytic activity devoid of any additives or ligands is quite important to meet the sustainability. In this context, immobilization of homogeneous Cu ions onto various heterogeneous supports like hyper-crosslinked polystyrene, zeolites, activated carbons, N-heterocyclic carbene (NHC)-modified silica, and MOFs has been reported.[15]

Recently, porous organic polymers (POP) have garnered considerable attention because of their potential applications in catalysis, gas separation, and sensors.[16] Owing to their high surface area, robust organic framework, and viability for functional group modification, porous polymers received great attention as a versatile platform in the field of heterogeneous catalysis. Despite of these advantages, the design of porous organic networks is often challenging and requires special ligands such as benzylamine, 2,2'-bipyridine or 4-diphenylphosphinostyrene etc. which limits the scope of these class of materials. Hence, exploration of a simple but facile protocol to create active sites on the solid support is quite critical. These POPs have outstanding properties over the already well-established inorganic silicate polymer with respect to molecular design flexibility to form various architectures, high surface area, and their stability against polar solvents. In this context, chemical process involving condensation of primary amine with carbonyl group of the aldehydes to form an imine or Schiff base is known to be beneficial for the interaction of polar gases or metal ions. In this perspective, Cu(I) supported over styrene-based polymeric beads, dimethylaminomethyl grafted polystyrene/divinylbenene resin (Amberlyst 21), melamine and tetraphathalaldehyde have been explored for “click reaction” under heterogeneous conditions.[17] Supported cuprous oxide nanoparticles also displayed good catalytic activity in alkyne–azide click cycloaddition reaction under mild conditions.[18]

Herein, we report a new triazine functional hierarchical mesoporous organic polymer (HMOP) platform through the polymerization of cyanuric chloride and melamines with nanorod morphology possessing high BET surface area ~1218 m^2g^{-1} and huge pore volume > 6 $mL.g^{-1}$ with dual micro/mesopore architectures. The present new Schiff base network serves as an efficient support due to abundance N sites for effective Cu-chelation (Cu-HMOP) that provides a ligand-free catalyst system to be used in diverse organic catalysis. Herein, we demonstrate for the first time, Cu-HMOP effectively catalyze multi-step cascade reaction of 2-aminobenzyl alcohol and aromatic ketones to diverse quinolines and aerobic dehydrogenation of partially (saturated) N-heterocyclic compounds to the corresponding heteroaromatics as well as aerobic oxidation of amines to imines (Scheme 1). The efficacy of the present Cu-HMOP also scrutinized for “click” chemistry to synthesize 1,2,3-triazole derivatives using water as green solvent at room temperature.

Results and Discussion

3.1. Catalyst characterization.

The triazine-based polymer was synthesized by modified literature report.[19] The cyanuric chloride effectively condenses with melamine monomer in a three dimensional network in presence of KOH to give polymer network comprising of exclusive triazine units connected through –NH functionality. Fig.1 exhibits the powder XRD patterns of Cu-HMOP and the appearance of diffraction peaks at ~24.3° and 43.9° corresponds to (*002*) and (*101*) planes, respectively, similar to amorphous carbon materials. The prominent reflection at 43.9° of HMOP confirms the hexagonal C_3N_3 structure similar to the literature report.[20]

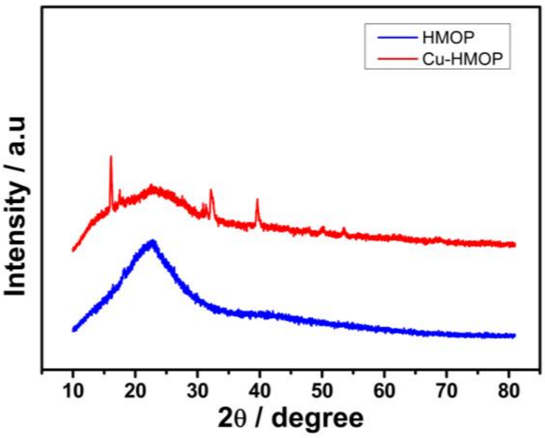

Fig. 1. X-ray diffractogram of hierarchical mesoporous organic polymer (HMOP) and Cu-loaded HMOP (Cu-HMOP).

The presence of a rather broad XRD peak feature at ~24.3° is attributed to the amorphous nature of polymer with exclusive hexagonal benzene-like triazine (C_3N_3) network.[21] The occurance of sharp reflections at 15.9, 17.0, 32.3, 33.1, and 40.3° suggest the existence of Cu species in the Cu-HMOP polymer (Fig.1). Fig.S1 (electronic supplementary, ESI†) shows a typical magnified TEM image of HMOP with nanorod or plate like morphological features with ~100 nm length and ~30 nm breath. High-resolution TEM micrograph of Cu-HMOP (Fig.2a-b) clearly confirms a sheet-like or nanotube-like morphology with plenty of mesopores in the range of ~3–7 nm in diameter. Fig. 2c-d confirms the presence of lattice fringes corresponding Cu metal with high degree of Cu dispersion in the triazine constructed polymer (Fig. 2c). The appearance of concentric bright spots against smooth background in the electron diffraction pattern (ED) further correlate the high crystallinity of Cu in the amorphous polymer network. To confirm the mesopores observed in TEM micrographs, we further employed N_2 adsorption/desorption measurements of HMOP and Cu-HMOP.

Notably, N_2 isotherm plots shown in Fig. 3A of HMOP obviously exhibits a characteristic Type I plateau up to $P/P_0 < 0.3$ indicating the presence of micropores of size below 2 nm. In depth inspection of adsorption/desorption isotherms revealed a narrow hysteresis loop at partial pressure $P/P_0 > 0.3$ and a prominent hysteresis loop (Type IV) is appeared at P/P_0 ~0.8-0.9 suggesting the presence of large mesopores in the polymer networks. The pore size features (Fig.3A, inset) were further obtained using the desorption branch of the isotherm employing Barret-Joyner-Halenda (BJH) model.[22]

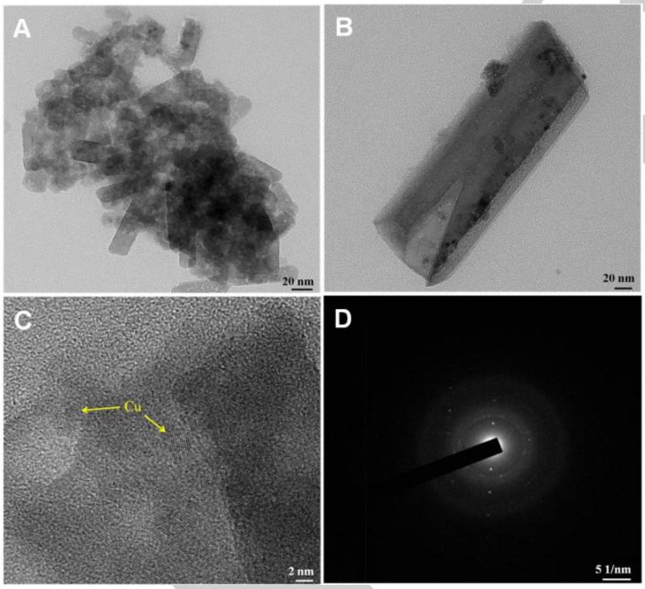

Figure 2. TEM micrographs of Cu-HMOP: (A) Nanorods at low magnification, (B) Magnified single strand, (C) HRTEM image showing lattice fringe of Cu-complex, and (D) Electron diffraction pattern.

A relatively sharp distribution curve centered at ~2.2 nm and a rather broad peak at ~5.0 nm in diameters are obvious. The narrow pores of ~2.2 nm could have originated from the intermolecular condensation between cyanuric chloride and melamine units to form micropores in short range order; whereas mesopores could have originated from the cross-linking of interlayers, interparticle's voids as well as incomplete condensation between the triazine subunits. The Brunner-Emmet-Teller (BET) surface area was found to be 1218 m^2g^{-1} with huge pore volume > 6 mLg^{-1} as evaluated from N_2 sorption isotherms at $P/P_0 = 0.99$. These dual pore architecture and robust textural properties are expected to promote facile diffusion of reactants and products during the catalytic reactions. Fig. 3B exhibits sorption measurements of Cu-HMOP (after Cu-complexation); a Type IV isotherm is clearly evident at $P/P_0 > 0.4$ and the mesopores become poly-dispersed in the range of 3-8 nm but the micropores located at 2.2 nm is relatively unchanged. Besides, the BET surface area and pore volumes were reduced to 550 m^2g^{-1} and ~0.52 $mL.g^{-1}$, respectively. All these textural properties involving reduction in the pore volume and BET surface area clearly confirms the presence of Cu inside the pores as well as channels of polymer networks.

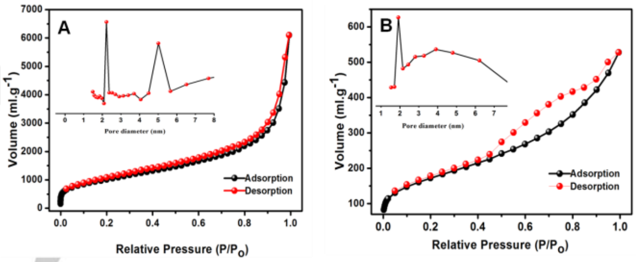

Figure 3. N_2 adsorption/desorption isotherms and BJH pore size distributions (inset figure) of pristine HMOP (A) and (B) Cu-HMOP.

The X-ray photoelectron spectroscopy (XPS) was employed to investigate the composition of various elements present in the pristine HMOP (Fig. S2A, ESI†). The survey spectrum of pristine HMOP material shows the presence of C, N, and O; the C 1s spectrum can be deconvoluted into two peaks, where the signal at 283.6 eV is ascribed to the sp^2-hybrized C-N bond present in the aromatic rings. The second high energy peak located at 286 eV that stem from the sp^2-hybridized C in an aromatic ring attached to side arm –NHR groups (Fig. S2B, ESI†).[23,24] The N 1s signal exhibits a single broad peak which can be deconvoluted into two signals located at 397.5 and 398.6 eV caused by pyridinic and urotropine-like N in a nitrogen-rich environment[23] which represent a nitrogen in triazine unit and bridging –NH–, respectively (Fig. S2c, ESI†). The full XPS survey spectrum of Cu-HMOP (Fig. 4A) displays the presence of C, N, Cu, O, and Cl elements in the Cu-HMOP. After Cu loading, the intensity of the signal at 286 eV corresponding to sp^2-hybridized C of aromatic ring attached to –NHR is just reversed (Fig. 4B) unlike pristine polymer indicating that the –NHR– interacts effectively with Cu(II) ions.

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Similar to pristine HMOP, the Cu-loaded counterpart shows N 1s XPS signals corresponding to pyridinic and –NH– bridging group in the polymer (Fig. 4C). The XPS signals at 932.0 eV, and 952.4 eV are due to the two types of Cu species assigned to the strong spin-orbit coupling of Cu $2p_{3/2}$ and Cu $2p_{1/2}$ which are in good agreement with the literature report.[25]

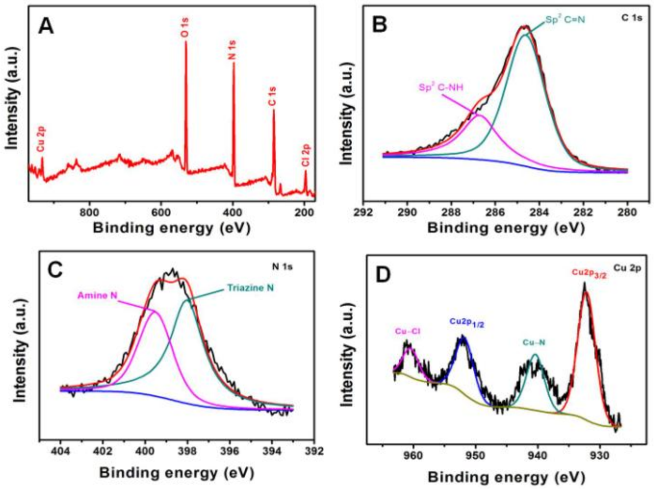


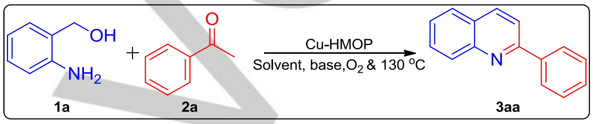
Figure 4. XPS spectra of Cu-HMOP: (A) Survey spectrum, (B) C 1s spectrum, (C) N 1s spectrum and (D) Cu 2p spectrum.

The other two low intensity peaks at 939.8 and 960.6 eV (Fig. 4D) might be due to newly formed Cu–N and Cu–Cl bonds on the polymer surface.[26] The survey spectrum also clearly indicates the presence of Cl atom from the appearance of a signal at ~200 eV, which is mainly due to the strong spin-orbit coupling of Cl $2p_{3/2}$ and Cl $2p_{1/2}$. Thus the XPS studies clearly reflect that –NHR- and triazine network effectively complexes with Cu(II) chloride on the polymer surface, which could serve as an efficient catalyst for organic transformation. The amount of Cu estimated by XPS analysis was found to be 1.1 wt% and further analysis for trace metals by ICP showed 1.24 wt% copper in the Cu-HMOP material.

3.2. Activity of Cu-HMOP in quinoline synthesis

We first examined the efficacy of Cu-HMOP catalytic system for dehydrogenative oxidative coupling to synthesize quinoline derivatives, an alternative to conventional homogeneous Frieldländer quinoline synthesis.[27] Elena Pérez-Mayoral and Miroslav Polozij have synthesized quinoline using Cu-catalyst from 2-aminoaryl ketones and aldehydes with 41 - 99% yield[28] Inspired by the catalytic activity of Cu-species, we have investigated 2-aminobenzyl alcohols as precursor to afford quinolines by aerobic oxidation of alcohols followed by cyclization. Treatment of 1 (1.0 mmol) with slight excess of 2 (1.1 mmol) in presence of catalytic Cu-HMOP and t–BuOK as base in toluene (2.0 mL) at 130 °C resulted in 96% isolated yield of quinoline after 24 h without any traces of side products (Table 1, entry 2). Screening of different bases indicated that t-BuOK was an effective base for oxidative cyclization in presence of O_2 (Table 1, entries 2–5). Among the different solvents scrutinized (Table 1, entries 2, 6–9), the multistep cascade reaction proceeds smoothly with non-polar solvent like toluene and thus, toluene was used for further investigation. Screening of reaction temperatures (Table 1, entries 2,10–12) indicated that 130 °C is the optimal temperature to attain high reactant conversion and product selectivity. By lowering the reaction time (entries 13 & 14) or catalyst loading (entries 15 & 16) under identical reaction conditions decreased the yield of the quinoline. Further, optimization for Cu-grafted catalyst was achieved with 15 wt% (entry 2). The reactions performed without base or catalyst did not afford the desired product (Table 1, entries 1 & 17), whereas 29% of quinoline was obtained using the HMOP polymer (entry 18). The yield of quinoline was reduced when the reactions was performed in argon or air atmosphere (Table 1, entries 19 & 20).

Table 1. Reaction optimization using Cu-HMOP[a]



Entry	Catalyst Wt.%	Base / solvents / temperature	Time, h	Yield, %
1	15	no base	24	Nil
2	15	t-BuOK	24	96
3	15	KOH	24	77
4	15	K2CO3	24	21
5	15	Et3N	24	trace
6	15	DMF	24	68
7	15	ethanol	24	42
8	15	H2O	24	23
9	15	acetonitrile	24	28
10	15	120 °C	24	79
11	15	110 °C	24	54
12	15	90 °C	24	23
13	15	t-BuOK	18	76
14	15	t-BuOK	12	73
15	10	t-BuOK	24	84
16	5	t-BuOK	24	30
17	No catalyst	t-BuOK	24	21
18	Pristine polymer	t-BuOK	24	29
19b	15	t-BuOK	24	26
20c	15	t-BuOK	24	44

[a]Reaction conditions: 2-aminobenzyl alcohol, (1, 1.0 mmol), acetophenone, (2a, 1.10 mmol), Base (0.25 mmol) and toluene (2.0 mL) were stirred at 130 °C unless otherwise noted. [b]Under Argon. [c]Under air.

With the optimized reaction conditions in hand for the cascade synthesis of quinoline, we next examined the substrate scope of various substituted ketones (2a–o) having electron-donating and electron-withdrawing groups with 2-amino benzyl alcohol 1 as summarized in Table 2. When the R^2–, R^3–, and R^4– functionalities on the aromatic ring was appended with electron-donating groups such as 4-Et-Ph (2c), 4-Me-Ph (2d), 4-MeO-Ph (2e), 4-EtO-Ph (2f), 3,4-di-MeO-Ph (2g), 2,5-di-MeO-Ph (2h) and 3,4,5-tri-MeO-Ph (2i) the reaction underwent smooth conversion to afford the desired quinoline derivatives 3c-3i in

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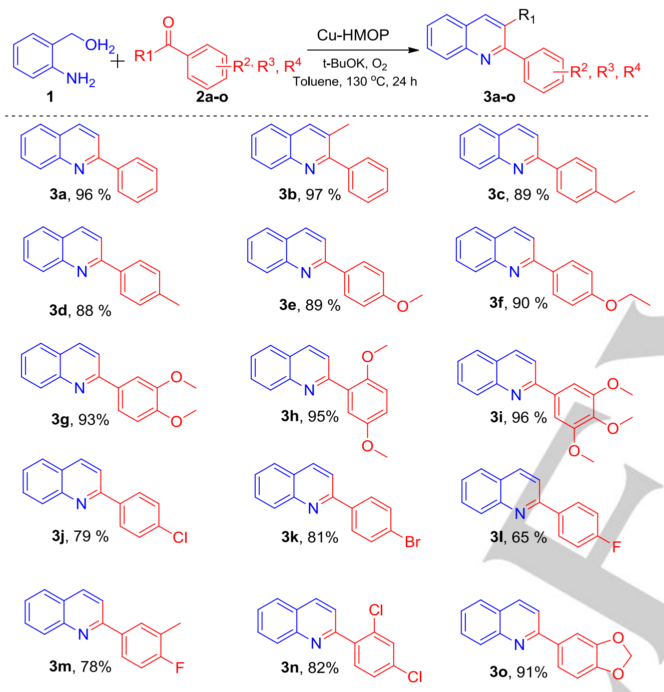
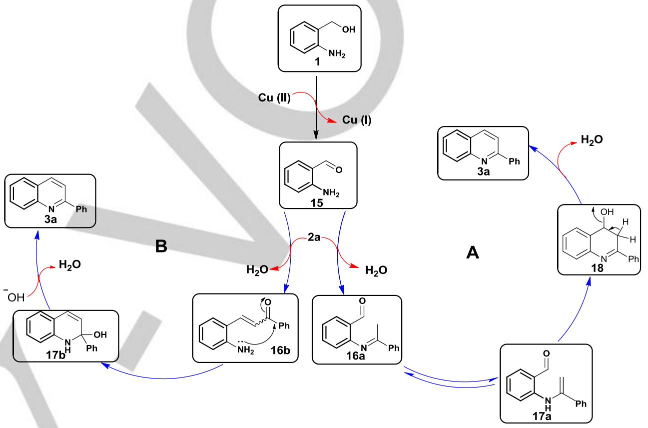
89%-95% yields. On the other hand, When the R^2– and R^3–functionalities on the aromatic ring was appended with halogen derivatives such as 4-Cl-Ph (2j), 4-Br-Ph (2k), 4-F-Ph (2l), 4-F-2-Me-Ph (2m) and 2,3-di-Cl-Ph (2n), the reaction proceeded smoothly to produce the desired quinolines in 65%-82% yields. The electronic nature of the substitutents such as ethyl, methoxy, ethoxy, and halides on the aromatic ring of ketones had less effect over the quinoline formation (Table 2, 3a-i). The potential steric nature of di- or tri–substituted groups on aryl ketones did not hamper the oxidative cyclization to the corresponding quinoline derivatives (Table 2, 3g-3i). Noteworthy feature of this methodology is that the sterically hindered, m,p–dimethoxy, o,m,p–trimethoxy, o,p–dichloro, and o,p–dimethoxy derivatives gave excellent yields (82-96%). To our delight, propiophenone (2b) and 1,3–dioxalone-substituted arylmethyl ketones (2o) also gave complete conversion to generate the corresponding products in 91-97% (Table 2, 3b and 3o).

Table 2. Quinoline synthesis using various aryl ketones and 2-aminobenzyl alcohol over Cu-HMOP[a]



[a] Reaction conditions: 2-aminobenzyl alcohol (1, 1.0 mmol), aryl ketones (2a-o, 1.10 mmol), base (0.25 mmol) and toluene (2.0 mL) was stirred at 130 °C.

Based on the previous literature reports, a plausible reaction mechanism is proposed as depicted in Scheme 2. The initial oxidation of o-aminobenyl alcohol 1 with catalytic Cu-HMOP in the presence of oxygen gave the o-amino benzaldehyde intermediate 15. Subsequent reaction of intermediate 15 with acetophenone 2a generated the desired Friedlander product 3a in two possible pathways (A & B). In the pathway A, the reaction proceed through three step sequence (i) Schiff base formation 16a; (ii) amine-enamine tautomerization 17a; (iii) intramolecular annulation 18 and dehydration. In pathway B, the reaction proceeds through a base catalyzed intermolecular aldol adduct 17b followed by water elimination and intramolecular condensation reaction. Based on previous theoretical studies, aldolic condensation is quite feasible than the initial imine formation, hence pathway B would be more favorable to form quinolines from the intermediate 15.[27,28]



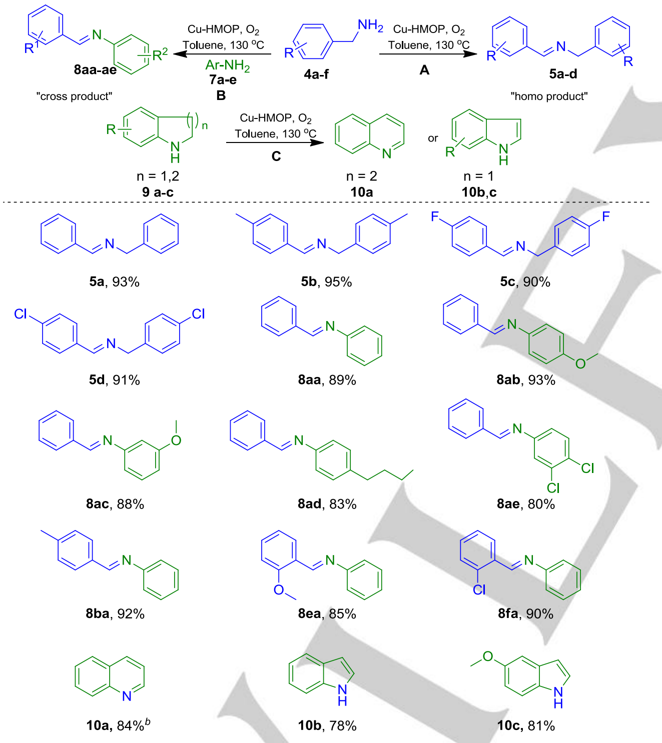
Scheme 2. Plausible reaction pathway for formation of quinoline by oxidative dehydrogenation using Cu-HMOP.

3.3. Cu-HMOP catalyzed aerobic dehydrogenative coupling

The coupling reaction was first surveyed with different solvents of varying polarity and the toluene emerged as the best solvent (Table S1, ESI†, entries 1-4). A series of experiments with different temperatures ranging from 110-140 °C (Table S1, ESI†, entries 1, 5-7) revealed that 130 °C as critical temperature for achieving a maximum yield of imines (94% isolated yield). Using toluene solvent at 130 °C, the optimal reaction time was found to be 30 h to attain maximum conversion and selectivity (Table S1, ESI†, entries 1, 8-11). The gradual increase in activity with catalyst loading (Table S1, ESI†, entries 1, 12,13) suggests that the present catalyst system is not suffering from adsorption/desorption governed mass transfer limitation. Both the pristine polymer (HMOP) and absence of catalysts, led to lower yields signifying the importance of catalysts in the aerobic dehydrogenative coupling (Table S1, ESI†, entries 14, 15). To probe the role of oxidant, the reaction was carried out under argon atmosphere instead of O_2. Interestingly, decreased conversion was observed, indicating the importance of oxygen in the reactions (Table S1, ESI†, entry 16). However, the air ambience shows moderate activity (Table S1, ESI†, entry 17) than that of pure O_2 (entry 1). Therefore, after extensive screening of various reaction parameters, we chose aerobic conditions using toluene at 130 °C as the optimal reaction conditions for further investigation. With the above optimized reaction conditions for N-benzylidene benzylamine (5a, Table 3, reaction A), the substrate scope was verified for reactions involving homo-coupling, cross-coupling, and unsaturated heterocyclic compounds. Table 3, runs 5a–5d show the catalytic aerobic oxidation of various benzylamines bearing 4-Me-Bn (4b), 4-F-Bn (4c) and 4-Cl-Bn (4d) substituents with excellent yields (90%-94%). The electron withdrawing as well as donating groups had marginal impact (< 5% conversion under otherwise identical conditions).

With the excellent activities of Cu-HMOP mediated homo-coupling, we further scrutinized the feasibility of this present protocol in the synthesis of un-symmetrical imines synthesis (Table 3, reaction B). Reactions between benzylamine and different substituted anilines were carried out to achieve unsymmetrical imines (Table 3, runs 8aa-8ae). The presence of electron-donating groups such as 4-MeO-Ph (7b), 3-MeO-Ph (7c) and 4-n-Bu-Ph (7d) had less impact on the product selectivity (83-93%, 8ab-8ad). When the functionality was electron withdrawing group like 3,4-di-Cl-Ph (7e), the reaction produced 80% yield. Further varying benzylamine functionalities like electron-donating groups such as 4-Me-Bn (4b), 2-MeO-Bn (4e) and halogen group like 2-Cl-Bn (4f) in cross-coupling reaction produced good yields 92%, 85% and 90%, respectively. The present Cu-HMOP catalyst protocol is even better than the mesporous Cs/MnOx (77% maximum yield) catalysts.[29]

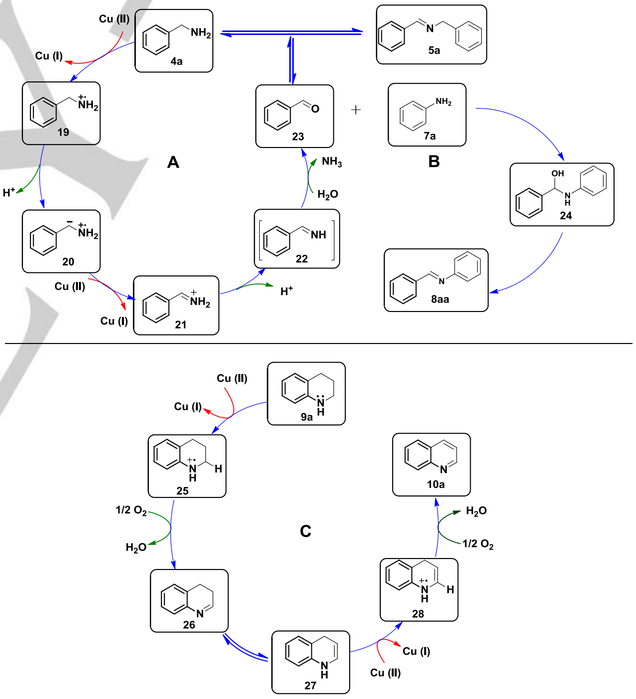
Table 3. Aerobic oxidative dehydrogenation of amines by homocoupling, and cross-coupling over Cu-HMOPa.



[a] Reaction conditions: Amines (4a-d, 9a-c 1.0 mmol) and Toluene (2.0 mL) was stirred at 130 °C for 30 h. bDMF (2.0 mL)

The scope of current methodology is also extended to N-containing aromatic heterocycles (Table 3, reaction C). The 1,2,3,4-tetrahydroquinoline readily underwent smooth conversion with excellent isolated yield (84%, 10a). Similarly, indoline leads to high yield (78%, 10b) under identical conditions indicating the robustness of present catalytic protocol. More importantly, the catalyst is highly suitable for compounds containing electron lone pairs on oxygen atom like –OMe which gives impressive yield of 81% (10c) that can be interpreted as a measure of the susceptibility of the catalytic efficiency to substituent effects.

Based on the preceding literature reports for dehydrogenative imine formation over the metal-complexes and metal-oxides,[12h,j] herein, a plausible reaction mechanism is proposed as shown in Scheme 3. Initial oxidation of compound 4a in the presence of Cu-HOMP followed by the benzylic proton elimination gave the zwitterion intermediate 20. Then the oxidation of the intermediate 20 and a proton elimination resulted in the key imine intermediate 22. Subsequent hydrolysis of intermediate 22 produced the oxidation compound 23. Next, the coupling of aldehyde 23 with another molecule of benzyl amine obtained the desired homo-coupled imine compound 5a.



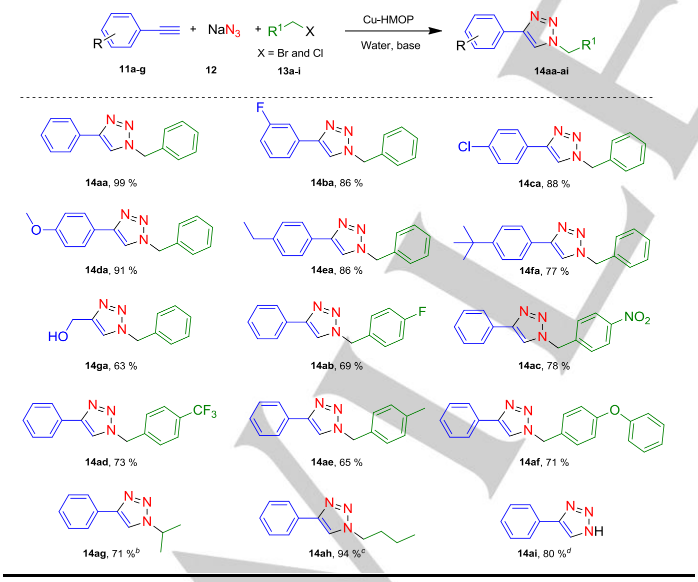
Scheme 3. (A,B) Aerobic oxidative dehydrogenative homo- and cross-coupling and (C) dehydrogenative aromatization of heterocycles.

On the other hand, when a two-component reaction was introduced with aniline as a substrate under the same reaction conditions, the cross-coupled imine was obtained through the intermediate 24. A similar oxidative strategy was employed for the synthesis of quinoline 10a from tetrahyroquinoline as the substrate under the standard reaction conditions.

3.4. Cu-HMOP catalyzed [3+2] cycloaddition of terminal alkynes and azides

Encouraged with the catalytic performance of previous reactions, we have also extended the utility of present Cu-HMOP catalytic protocol for synthesis of 1,2,3-triazole (14aa) by three component system comprising terminal alkynes, sodium azides, and benzyl halides involving *in-situ* alkyl/arylazide generation followed by [3+2] cycloaddition (Table S2, ESI†). Preliminary control experiments with a mixture of phenyl acetylene (1.0 mmol), benzyl halides (1.10 mmol), and sodium azide (1.50 mmol) in presence of triethylamine base (0.10 mmol) and water at room temperature resulted in 99% yield for 14aa (run 3). Further optimization with various bases and solvents, proved water as the best solvent at room temperature in presence of triethylamine as an ideal base (runs 2-8). Next, screening of reaction duration as well as catalyst loading under standard conditions (runs 9-12) indicated 10 wt% critical catalyst loading with 18 h reaction time to achieve high conversion and good product selectivity. Notably, the absence of base as well as pristine HMOP polymer under identical conditions lead to poor yield, (35 & 8% for runs 1 & 14) and no reaction was observed in the absence of catalyst (run, 13). Next, using the above optimized reaction conditions involving water as green solvent at room temperature, we have explored the scope of this protocol for the synthesis of 1,4-disubstituted-1,2,3-triazoles. As shown in Table 4, compounds 14aa-14ga show influence of substitutents on phenyl-ring of alkynes over the [3+2] cycloaddition. Electron-donating as well as electron withdrawing groups gave good to excellent isolated yields (typically 63-99%).

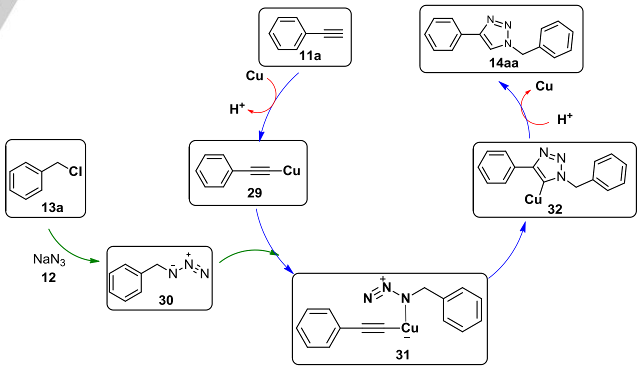
Table 4. Click reactions of various substituted benzyl halides with different alkynes over Cu-HMOP.[a]



[a]Reaction conditions: Phenyl acetylene (11a-g, 1.0 mmol), benzyl halides (13a-i), 1.1 mmol, sodium azide (12, 1.50 mmol), base (0.10 mmol) and H2O (5.0 mL) was stirred at room temperature for 18 h. [b]Alkyl halide (13a, 2.0 mmol), sodium azide (12, 2.50 mmol). [c]Reaction was stirred at 80 °C. [d]Reaction carried out only with sodium azide (12, 2.0 mmol).

Electron withdrawing functionalities like 3-F-Ph (11b) and 4-Cl-Ph (11c) afforded slightly lower yields 86% & 88% (14ba & 14ca) as compared to 99% (14aa) without any substituents. Similarly, 4-MeO-Ph (11d), 4-Me-Ph (11e), and 4-t-Bu-Ph (11f) also led to good yields in the range of 77-91% (14da-14fa). More importantly, aliphatic derivative such as propargyl alcohol reacted under optimized reaction condition to give the corresponding product in 63% selectivity (14ga). Entries 14ab-14af show the effect of various substitutents present on the aromatic ring of benzyl halide and exhibit pronounced decrease in the yield (65-78%) unlike influence of substituents on terminal alkynes as mentioned above. For instance, the 4-F-Bn (13b), 4-NO_2-Ph (13c), and 4-CF_3-Ph (13d) afford moderate yield 69-78% (14ab-14ad), attributed to the electronic effect of strongly electron withdrawing nature. Similarly, the electron donating 4-Me-Ph (13e), and 4-PhO-Ph (13f) substituents (14ae, 14af) also led to lower yield despite its electron-donating nature and the lower yield is partly ascribed to the steric nature of aromatic rings. More importantly, the aliphatic substrates like iso-propyl (13g), n-propyl (13h) derivative, and simple sodium azide (12) gave the corresponding 1,2,3-triazole derivatives (14ag-14ai) in good to excellent yields.

A plausible reaction pathway for the Cu-HOMP-catalysed three-component click chemistry was proposed as shown in Scheme 4.[30] In-situ reduction of Cu(II)-HOMP using trimethylamine gave the active Cu(I) species, which on further reaction with phenyl acetylene produced the copper acetylide intermediate 29. Reaction of intermediate 29 with in-situ generated azide (from benzyl halide) afford the 1,4-regioselective vinyl copper species 32 via alkyne-azide click cyclization. Protolysis of intermediate 32 resulted in the desired triazole 14aa and the active catalyst was regenerated for the next catalytic cycle.



Scheme 4. Proposed reaction pathway [3+2] cycloaddition of terminal alkynes and azides using Cu-HMOP.

3.5. Catalyst leaching test and recyclability

Catalyst deactivation possibly due to primary particles agglomeration and leaching of active metals from solid matrix into solution under operating conditions is often a challenge for heterogeneous catalytic systems. Investigation of active metal leaching was carried out from the reaction system involving

2–aminobenzyl alcohols (1) and acetophenone (2) to form quinoline as model system under identical conditions (Fig. S3, ESI†). In a typical hot-filtration leaching test reaction, the Cu-HMOP solid catalyst was removed from the reaction system after 10 h (~35% conversion) and the reaction was continued with filtrate under the same reaction conditions for another 14 h. Analysis of the filtrate revealed no further progress in the reaction. Furthermore, trace metal analysis of the filtrate by ICP technique confirmed the absence of Cu in the solution phase and therefore, catalysis by Cu-species in solution phase is safely ruled out. To evaluate the reusability of Cu-HMOP for quinoline synthesis as model reaction, the catalyst was separated from the reaction mixture by centrifugation, washed thoroughly with toluene and ethanol. Prior to each recycle runs, the catalyst was reactivated at 100 °C in a vacuum oven for 6 h to remove any surface adsorbed reactants/product molecules. It is seen from Fig. S4, ESI†, the catalyst can be reused for a minimum of 5 trials albeit with a minor loss of ~6% activity from its initial performance. Furthermore, the re-used Cu-HMOP catalyst retained a rod like morphology (Fig. S5, ESI†) after the liquid-phase reaction. Hence, the present Cu-loaded triazine based porous polymer serves as truly heterogeneous catalyst with high active site stability.

Conclusions

In summary, we have successfully demonstrated a nanoporous hierarchical Cu-chelated porous organic polymer consisting of exclusive triazine units (C_3N_3) connected through –NH groups as robust catalysts for the synthesis of N-heterocycles by different synthetic strategies. The robust textural properties, high BET surface area ~1218 m^2g^{-1}, huge pore volume $>$ 6 $mL.g^{-1}$ and multimodal micro/mesopore architectures are expected to favor high catalytic activity for the synthesis of N-heterocycles. The Cu-HMOP efficiently catalyzed one-pot sequential multi-step oxidative dehydrogenative coupling of 2-aminobenzyl alcohol with diverse aromatic ketones to afford quinolines in excellent yields (up to 97%). The Cu-HMOP/O_2 catalyst system also furnished excellent oxidative dehydrogenation activity of (partially) saturated N-heterocycles to the corresponding aromatic analogues and amines to imines. Scrutinization of Cu-HMOP for “click” chemistry produced quantitative yield for diverse 1,2,3-triazole derivatives at room temperature using water as green solvent without any additives or ligands. Verification of leaching of the active metal by a hot filtration test as well as reusability of the retrieved Cu-HMOP catalysts suggested its sustainable catalytic activity in the multi-step quinoline synthesis. All experimental results demonstrated the robustness of present Cu-HMOP catalyst in terms of versatility, recovery/reusability, and potential impact in green heterogeneous catalysis.

Experimental Section

Materials and Methods

Cyanuric chloride, melamine, dimethyl sulfoxide (DMF) $CuCl_2.2H_2O$, NaN_3, triethylamine, KOH, K_2CO_3, and t-BuO^-K^+ with AR grade were purchased from Sigma-Aldrich and used without any further purification. All solvents like hexane, ethylacetate, ethanol, and methanol were obtained from Fisher scientific and used as received. Reaction progress was monitored by thin-layer chromatography (TLC) using Merck 60 F254 pre-coated silica gel plate. Column chromatography separations were performed using 100-200 mesh silica gel and ethylacetate/hexane solvents as mobile phase. ^1H and ^{13}C NMR spectral data were acquired on Bruker 500 MHz instrument. Powder X-ray diffraction (XRD) pattern was recorded with a Bruker diffractometer (D8 Advance, Davinci) with CuKα rays (λ = 1.5418 Å). The morphology was explored using transmission electron microscopic (HRTEM) images acquired with a JEOL (JEM-2100 Plus) operating at 200 kV by coating test samples on a copper grid. Specific surface area, pore size distribution, and pore volume details were obtained from N_2 sorption isotherms using autosorb IQ series (Quantachrome Instruments).

Synthesis of hierarchical mesoporous organic polymer (HMOP) and Cu-HMOP

In a typical synthesis of HMOP, melamine (5.0 mmol) dissolved in 100 mL DMSO was magnetically stirred using a 250 mL round bottom flask. To the above content, cyanuric chloride (5.0 mmol) dissolved in DMSO (100 mL) was added drop wise followed by the addition of KOH (10.0 mmol). The reaction mixture was heated to 160 °C for 24 h under a refluxing condenser. After the completion of reaction, the precipitate was filtered off, washed thoroughly with water and methanol to remove solvent as well as unreacted precursors. The polymer was dried at 80 °C for 24 h to obtain a hierarchical mesoporous organic polymer (HMOP). For the synthesis of Cu-HMOP, an appropriate amount of $CuCl_2.2H_2O$ was dissolved in ethanol (10 mL) and 1.0 g HMOP was added to the above solution and stirred vigorously for an hour. The resultant turbid mixture was sonicated for 10 min followed by overnight stirring. Finally the material was filtered off and washed thoroughly with water, ethanol, and dried at 80 °C to obtain Cu-HMOP.

Synthesis of quinoline

A 60 mL pressure tube was charged with a magnetic bar, Cu-HMOP (15 wt%), t-BuOK (0.12 mmol), toluene (2.0 mL), 2-aminobenzylalcohol (1.0 mmol), and arylketones (1.10 mmol). Then the tube was purged with O_2, and stirred at 130 °C in a preheated oil bath for a period of 24 h. The reaction mixture was diluted with ethylacetate (5.0 mL), filtered through celite material, and washed with solvent. The combined solvent was evaporated and the crude product was purified by column chromatography technique using ethylacetate/hexane as an eluent system.

Aerobic dehydrogenative coupling of amines

A 60 mL pressure tube was charged with magnetic bar, Cu-HMOP (10 wt%), saturated amines (1.0 mmol), and Toluene (2.0 mL). Finally, the tube was purged with O_2, followed by stirring at 130 °C in a preheated oil bath for 24 h. The reaction mixture was diluted with ethylacetate (5.0 mL) filtered through celite bed and washed thoroughly. The collected solvents were evaporated and the crude product was purified using column chromatography technique with ethylacetate/hexane solvent system.

Protocol for 1,2,3-triazole synthesis (Click chemistry)

In a typical synthesis, a 15 mL tube was charged with a magnetic bar, Cu-HMOP (10 wt%), phenyl acetylene (1.0 mmol), benzyl chloride (1.10 mmol), sodium azide (1.50 mmol), and triethylamine (0.10 mmol) and stirred at room temperature for 18 h using water as a solvent. After the completion, ethylacetate (5.0 mL) was added to the reaction mixture and the aqueous layer was separated and partitioned again with ethylacetate (5mL x 2). Then the combined organic layer were dried over Na_2SO_4 and evaporated, the resultant crude product was purified using column chromatography with ethylacetate/hexane as the solvent system.

Leaching and recycling test

To study leaching of any active copper metal into solution, hot filtration test was performed considering quinoline synthesis as a test reaction. As described in section 2.3, an identical experiment was performed between 2-aminobenzylalcohol (1 mmol), and arylketones (1.1 mmol) for inital period of 10 h by maintaining all other reaction parameters identical. The catalyst was recovered from the reaction system and the filtrate was kept under the same reaction conditions to further continue for 14 h. The course of reaction was followed by monitoring conversion and product formation using gas chromatography (GC). For catalyst recyclability test, the catalyst recovered from the first reaction run between 2-aminobenzylalcohol (1 mmol), and arylketones (1.1 mmol) was separated by centrifugation, washed thoroughly with ethanol and acetone, dried in a vacuum oven at 100 °C for overnight to remove any occluded organics on the catalyst surface. The activated catalyst was reused for quinoline synthesis as a model reaction for another 5 successive cycles under identical conditions as described above experimental details.

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Keywords: Click reaction • Dehydrogenation • Hierarchical structures • Porous organic polymer • Quinoline synthesis

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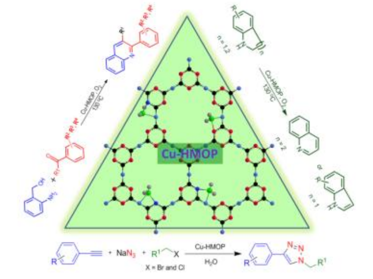
Entry for the Table of Contents

Layout 1:

FULL PAPER

Cu-hierarchical mesoporous organic polymer (Cu-HMOP) with nanorod morphology serves as an efficient catalyst for Friedländer quinoline synthesis by one-pot sequential multi-step oxidative dehydrogenative coupling of 2-aminobenzyl alcohol with diverse aromatic ketones. The Cu-HMOP also catalyze aerobic oxidative dehydrogenation of amines to imines and "click" reaction involving azides-alkynes. Active metal leaching by a hot filtration confirmed heterogeneous nature of catalysts.



1)Green solvents. 2)45 examples. 3)Multiple applications. 4)Low catalyst loading. 5)Recyclable catalyst.

*Samaraj Elavarasan, Asim Bhaumik, and Manickam Sasidharan**

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