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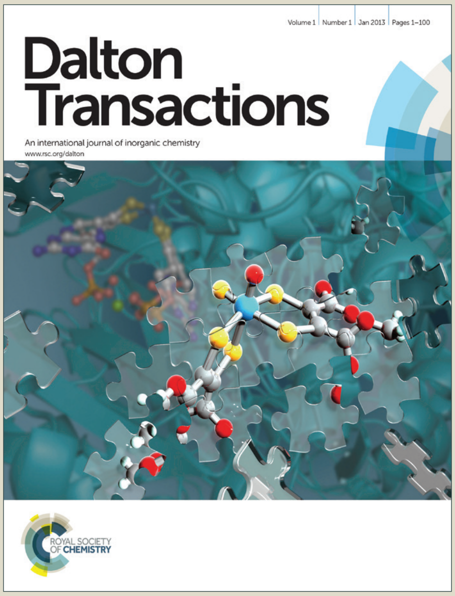

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Nitrogen Enriched Mesoporous Organic Polymer Anchored Copper(II) Material: an Efficient and Reusable Catalyst for the Synthesis of Esters and Amides From aromatic systems

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Abstract

A new copper-grafted mesoporous poly-melamine-formaldehyde (Cu-mPMF) has been synthesized from melamine and paraformaldehyde in DMSO medium, followed by grafting of Cu(II) at its surface. Cu-mPMF has been characterized by elemental analysis, powder XRD, HR TEM, FE-SEM, N_2 adsorption study, FT-IR, UV-vis DRS, TGA-DTA, EPR spectroscopy, Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). The Cu-grafted mesoporous material showed very good catalytic activity in methyl esterification of benzylic alcohols and amidation of nitriles. Moreover, the catalyst is easily recoverable and can be reused for seven times without appreciable loss of catalytic activity in the above reactions. The highly dispersed and strongly bound Cu(II) sites in the Cu-grafted mesoporous polymer could be responsible for the observed high activities of the Cu-mPMF catalyst. Due to strong binding with the functional groups of the polymer, no evidence of leached copper from the catalyst during the course of reaction occurred, suggesting true heterogeneity in the catalytic process.

Key words: Copper, mesoporous, poly-melamine, esterification, amidation, recoverable

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Introduction:

Arylated carbonyl compounds are important motifs in many natural products, pharmaceuticals and bioactive molecules, which have always drawn chemists attention in organic synthesis.[1] In particular, aryl esters and amides derivatives are found at the core of numerous important intermediates that are widely applied in the synthesis of bulk chemicals, drugs, synthetic materials and polymers.[2,3]

Traditionally, esters are prepared by the reaction of activated carboxylic acid derivatives with alcohols.[4] Recent developments in palladium-catalyzed three-component esterification reactions of alcohols, aryl halides, and CO provide a more direct approach for ester synthesis.[5,6] The oxidative esterification of aldehydes or alcohols is also reported for the synthesis of esters.[7] As the required aldehydes are normally synthesized by selective oxidation of alcohols,[8,9] the direct conversion of alcohols into esters in the presence of catalysts is certainly a step forward towards green, economic, and sustainable processes.[10-13] These one-pot procedures reported usually require the use of highly expensive noble metals such as gold,[10] palladium,[11] iridium,[12] or ruthenium[13] as catalysts.

On the other hand, one of the most common methods for amide synthesis employs activated derivatives of the carboxylic acid, such as esters[14] together with carbodiimides,

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phosphonium, or uronium salts as additives.[15] Other general procedures for amide synthesis include the well-established name reactions.[16-20] Besides, catalytic procedures have been developed including oxidative amidation of aldehydes[21] or alcohols,[22] aminocarbonylation of aryl halides[23]or terminal alkynes,[24] rearrangement of oximes and coupling with amines, cross coupling of amides with aryl and alkenyl halides,[25] and transamidation of amides with amines.[26] Besides these protocols, a less frequently reported synthetic method is the coupling of nitrile with a mine, which has been reported to be performed in the presence of ruthenium[27] or platinum[28] catalysts. The use of earth-abundant first-row transition metals instead of catalysts based on highly expensive noble metals is interesting and important from academic, industrial, and sustainability aspects.

Copper is one of the most abundant metals on the earth, and it is one of the most inexpensive and environmentally friendly. We describe our efforts on copper-catalyzed methyl esterification reactions with peroxides, which serve as both the oxidant and the source of the methyl group. To the best of our knowledge, copper-catalyzed direct esterification of benzylic alcohols in the absence of methanol and copper catalyzed secondary amides synthesis are rare to date.[29, 30] Previously reported most of these protocols used homogeneous copper catalysts. Homogeneous catalysts have some disadvantages, such as they may easily be destroyed during the course of the reaction and they cannot be easily recovered after the reaction for reuse.[31, 32] To get rid from these serious issues related to homogeneous catalyst, it is thus desirable to develop an efficient methodology to avoid all these difficulties.[33]

Various supports such as silica, carbon, and zeolites among have been used for the immobilization of homogeneous copper salt.[34] Among the different type of mesoporous materials, the organic mesoporous polymers are a class of advanced materials, which possess the

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textural porosities of mesoporous materials (well-ordered pores, large surface area and tunable structures) and simultaneously the advantages of organic polymers (high hydrophobicity, containing aromatic sections and higher stability in acid or base media in comparison to silicabased materials).[35]

In this context, mesoporous organic polymers carrying the reactive functional groups at the surface of the mesopores[36] can provide an ideal tethering agent for the active metals to bind at its surface strongly. Due to extensive cross-linking, polymeric materials are highly desirable material for long term stabilization of the entrapped metal centres, which reduces the possibility of leaching of the metal under reaction conditions.[37]

Herein, we report a novel copper doped mesoporous poly-melamine-formaldehyde (Cu-mPMF) material that exhibits superb activities towards esterification of benzyl alcohol and amidation of nitriles. The high activity of Cu-mPMF is attributed to its condensed network structure which contains large number of nitrogen atoms. Significant amounts of nitrogen have been incorporated into comparable inorganic framework materials[38] and this is found to be beneficial for the stabilization of copper acetate.

Experimental Section

Chemicals

Melamine and paraformaldehyde were purchased from Sigma-Aldrich. All other reagents and chemicals were purchased from commercial sources and were used without further purification. Solvents were dried and distilled through standard procedure.

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Physical measurements

The FT-IR spectra of the samples were recorded from 400 to 4000 cm^{-1} on a Perkins Elmer FT-IR 783 spectrophotometer using KBr pellets. UV-Vis spectra were taken using a Shimadzu UV- 2401PC doubled beam spectrophotometer having an integrating sphere attachment for solid samples. Thermogravimetric analysis (TGA) was carried out using a Mettler Toledo TGA/DTA 851e. Surface morphology of the samples was measured using a scanning electron microscope (SEM) (ZEISS EVO40, England) equipped with EDX facility. Powder X-ray diffraction (XRD) patterns of different samples were analyzed with a Bruker D8 Advance X-ray diffractometer using Ni–filtered Cu Kα (λ=0.15406 nm) radiation. High resolution transmission electron microscopy (HR-TEM) images of the mesoporous polymer were obtained using a FEI TECHNAI G20 transmission electron microscope operating at 200 kV. Specific surface area of the sample was measured by adsorption of nitrogen gas at 77 K and applying the Brunauer-Emmett-Teller (BET) calculation. X-ray photoelectron spectroscopy (XPS) was performed on an Omicron nanotech operated at 15 kV and 20 mA with a monochromatic Al K_{α} X-ray source. The EPR (electron paramagnetic resonance) spectrum of the copper catalyst was recorded for the solid sample at room temperature by a JES-FA200 ESR spectrometer (JEOL). NMR spectra were recorded on a Varian Mercury plus NMR spectrometer (^{1}H NMR at 300 and 500 MHz) in pure deuterated solvents.

Synthesis of mesoporous poly-melamine-formaldehyde polymer (mPMF): Melamine (0.378 g, 3 mmol) and paraformaldehyde (1.8 eq, 0.162 g, 5.4 mmol) were mixed with 3.36 ml (overall concentration of 2.5 M) of dimethyl sulfoxide (DMSO) in a 15 ml Teflon container secured in a steel reactor. The reaction mixture was heated to 120 ^{0}C in an oven for

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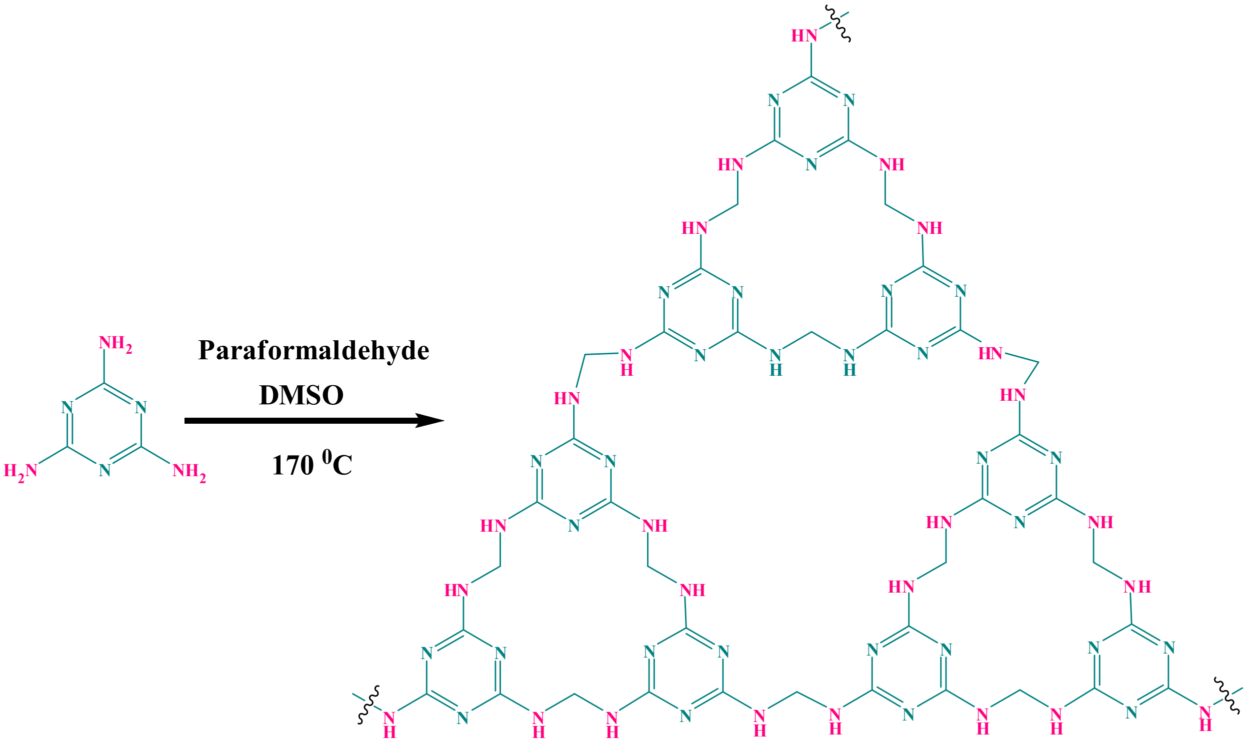
1 h. The reactor was then carefully removed from the oven for stirring on a magnetic stirrer plate to obtain a homogeneous solution. It was then heated in the oven to 170 ^{0}C for 72 h. The reaction was allowed to cool to room temperature, and the obtained solid was crushed, filtered, and washed with DMSO, acetone, tetrahydrofuran (THF) and CH_2Cl_2. The resulting white solid was dried under vacuum at 80 °C for 24 h.



Scheme1. Schematic diagram showing the formation of mesoporous polymer mPMF

Synthesis of Cu-mPMF catalyst: In typical synthesis, 1 gm mesoporous polymer in methanol (10 mL) was stirred along with $Cu(OAc)_2$ (300 mg). It was then heated to reflux for 24h and green coloured solid was filtered and dried under vacuum at 80 °C for 24 h. Copper(II) loading to the mPMF was determined to be 14.20% by AAS.

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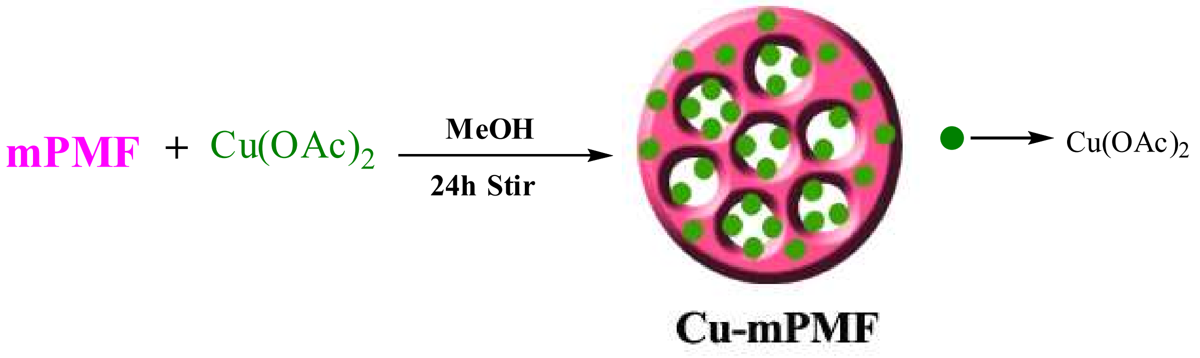

Scheme 2. Schematic diagram showing the formation of copper(II) grafted mesoporous mPMF

General Procedure for Cu-mPMF Catalyzed Esterification of Benzylic Alcohols: Benzylic alcohol (0.3 mmol), Cu-mPMF (20 mg), K_2CO_3 (0.6 mmol), TEAB (0.15 mmol), TBHP (2.4 mmol, 70% aqueous solution) and DMSO (2.0 mL) were added to a 50 mL round bottom flask and the reaction mixture was heated in an oil bath at 100 ^{0}C for 16h under 1 atm O_2 pressure. The reaction was quenched with a saturated solution of Na_2SO_3 (for removal of excess TBHP), and the mixture was extracted with ethyl acetate. The organic solvent was removed under vacuum, and purification by chromatography on a silica gel column using a mixture of petroleum ether and ethyl acetate afforded the desired product.

General Procedure for Cu-mPMF Catalyzed Esterification of Acids:

Acids (0.3 mmol), Cu-mPMF (20 mg), TBHP (1.8 mmol, 70% aqueous solution), and DMSO (2.0 mL) were added to a 50 mL round bottom flask in air, and the reaction mixture was heated in an oil bath at 100 ^{0}C for 16h. The reaction was quenched with a saturated solution of Na_2SO_3 (for removal of excess TBHP), and the mixture was extracted with ethyl acetate. The organic solvent was removed under vacuum, and purification by chromatography on a silica gel column using a mixture of petroleum ether and ethyl acetate afforded the desired product.

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General procedure for the secondary amide synthesis:

Nitriles (1 mmol), anilines (1.3 mmol) and Cu-mPMF (20 mg) in water (5mL) were put into a 50 mL round bottom flask. The reaction mixture was stirred at 80 ^{0}C for 14h and then cooled to room temperature and extracted with ethyl acetate. The organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by silica-gel column chromatography to afford the corresponding product.

Result and discussion

Characterization of Cu-mPMF material

X-ray diffraction: In Figure 1 powder X-ray diffraction pattern of mPMF and Cu-mPMF are shown. The mesoporous polymer, mPMF shows one broad diffraction peak cantered at $2\theta = 21$, which correspond to characteristic peak of the mPMF. Nevertheless, like other porous polymers based on cross-linking,[39] mPMF is mostly amorphous. In the XRD pattern of the Cu-mPMF shows the additional diffraction peaks at $2\theta = 10.67$, 12.85 and 25.74 degrees could be assigned to presence of crystalline features originated due to the binding of $Cu(OAc)_2$ at the pore surface.[39] Thus, overall intensity of the Cu-mPMF increased than mPMF due to the crystalline features of Cu-mPMF.

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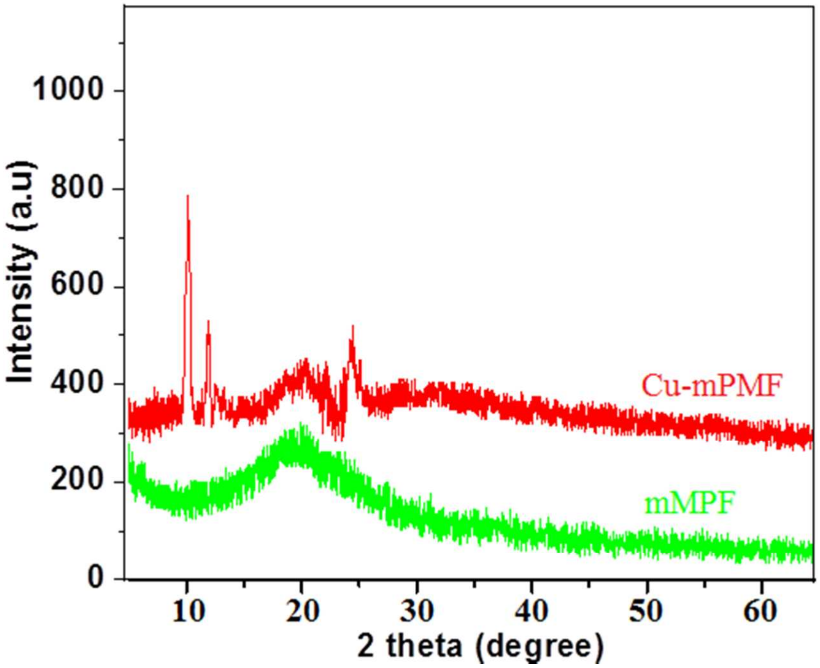

Figure 1 powder XRD pattern of mPMF and Cu-mPMF materials.

HR-TEM analysis: Fig. 2 demonstrates HR-TEM images of copper-grafted mesoporous poly-melamine-formaldehyde material. A foam-like interconnected mesoporous network structure was observed under HR-TEM images (2a and 2b). Figure 2c and 2d suggested the existence of high electron density dark spots of dimension *ca.* 7 nm throughout the specimen, which are assigned to copper(II)-particles in Cu-mPMF.

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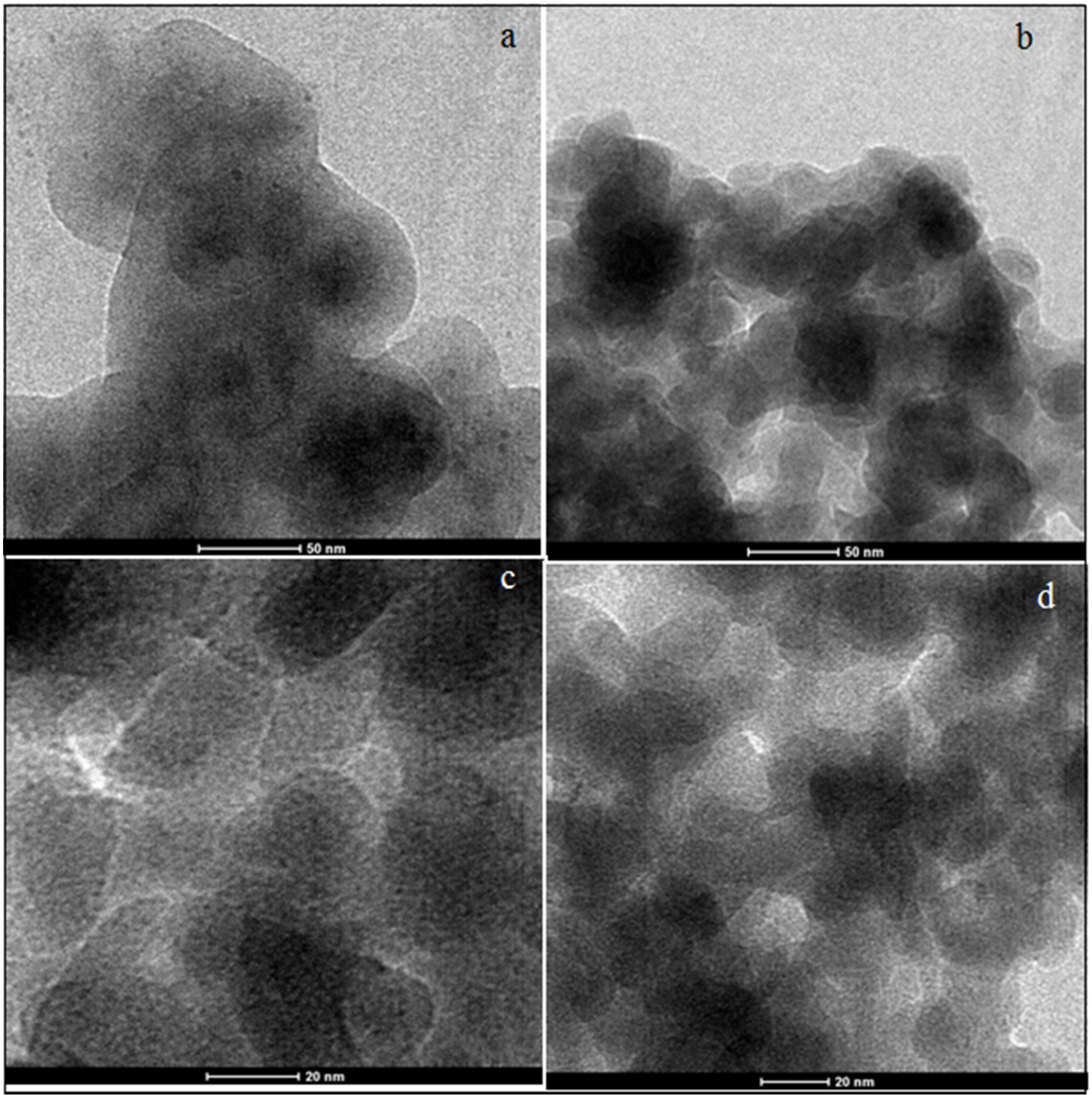

Figure 2 (a-d) HR-TEM images of Cu-mPMF material.

Scanning electron micrographs (SEM) analysis: The scanning electron micrographs of the Cu-mPMF are shown in Fig. 3A and B. This FE-SEM images indicates uniform spherical morphology of the polymer Cu-mPMF material and spherical particles get aggregated among themselves to form large assembly of particles. Energy dispersive spectroscopy analysis of X-

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rays (EDAX) data of the Cu-mPMF (Fig.S1) also inform that the attachment of metal on the surface of the polymer matrix. The elemental mapping (Fig. 3 c-f) indicates the presence of carbon, nitrogen, oxygen and Cu ions in the composites.

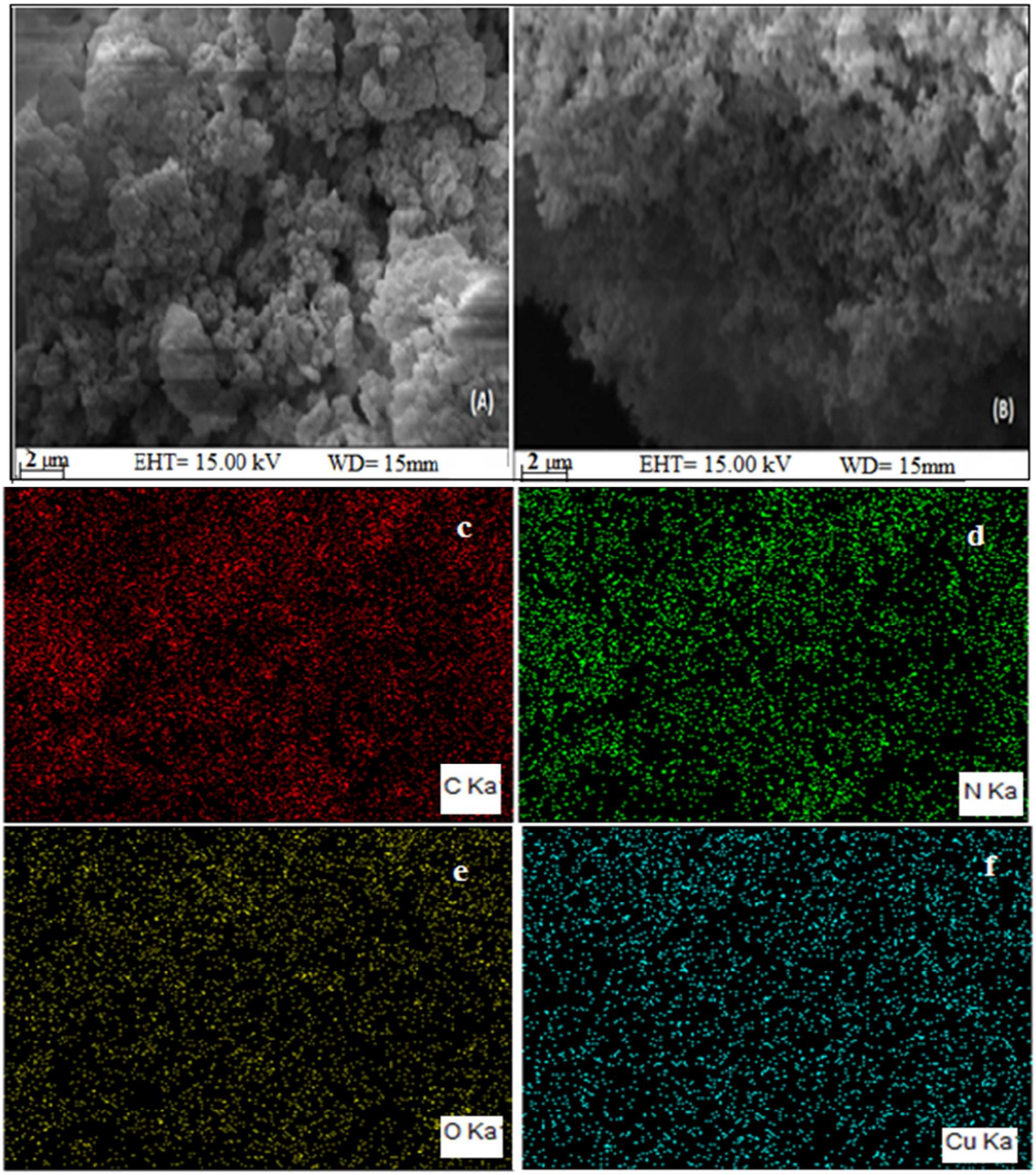

Figure 3 (a) - (b) scanning electron micrographs and (c)-(f) elemental mapping of the Cu-mPMF

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Specific surface area

The surface area of the Cu-mPMF determined by N_2-adsorption study reveals that Cu-mPMF exhibits specific surface area of about 170.4 m²/g (Fig.4). The BET surface areas of mPMF is 930.0 m^2 g^{-1} with an average pore size of 15.7 nm.[23] Considerable decrease in the surface area to 170.4 m²/g in Cu-mPMF suggests that copper acetate particles are anchored at the surface of the mPMF.

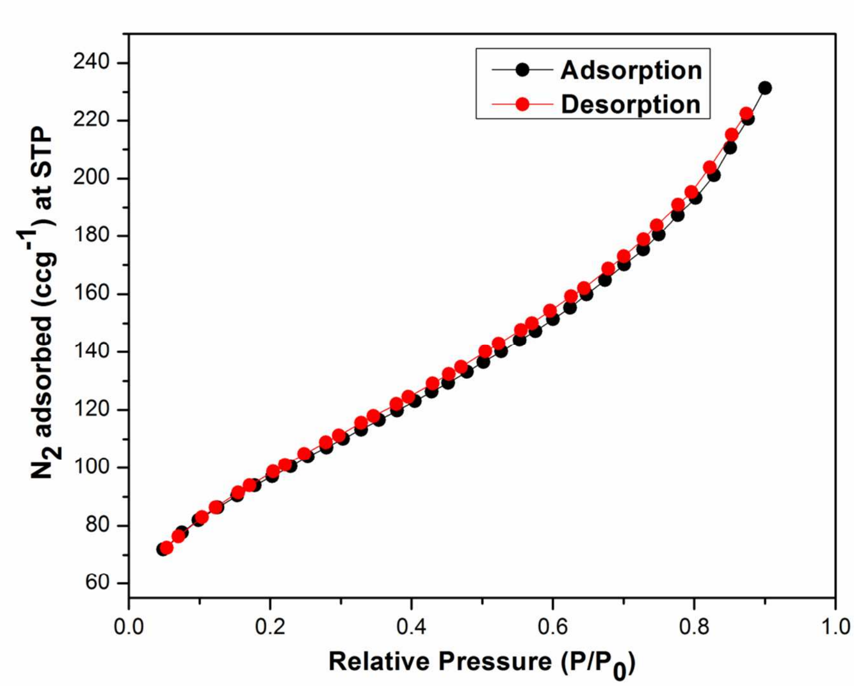

Figure 4 N_2 adsorption/desorption isotherms of Cu-mPMF

Raman spectroscopy

In addition to the optical spectroscopy, Raman spectroscopy also provides useful information regarding the interaction of metal and mesoporous mPMF. Raman spectra of the mPMF-Cu shows two well documented D and G band at 1412 and 1551 cm^{-1} respectively (Fig.5). The D band at 1412 cm^{-1} is attributed due to the defect or disorder in carbon atom and G band at 1551 cm^{-1} is attributed due to sp^2 in plane vibration of carbon atom. Raman spectroscopy

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of mesoporous Cu-mPMF showed different intensity peaks from each component. The peaks at 970 and 665cm^{-1} corresponded to T band and copper acetate respectively.[40]

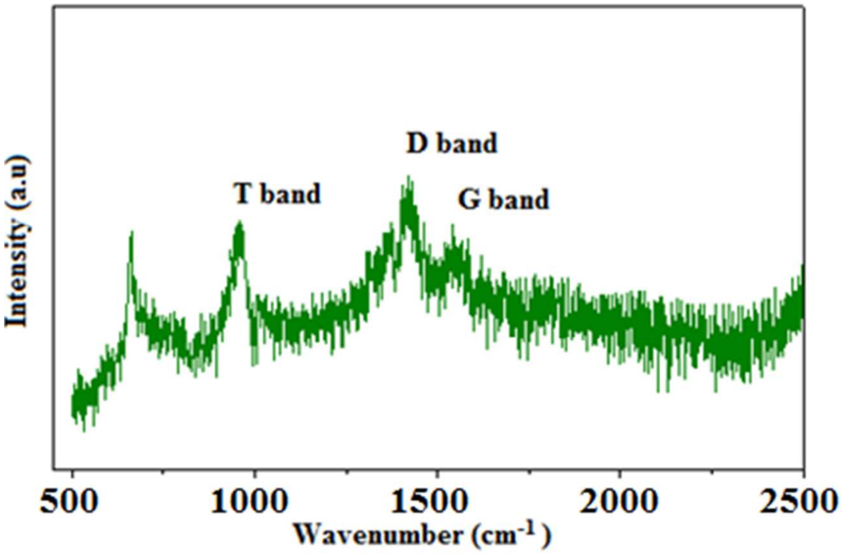

Figure 5 Raman spectroscopy of Cu-mPMF

Electron paramagnetic resonance study

Electron paramagnetic resonance (EPR) of copper-grafted mesoporous organic polymer Cu-mPMF at room temperature is shown in Figure 6. In the mesoporous organic polymer Cu is anchored at the surface of the polymer matrix through the donor nitrogen sites. The spectrum shows four well-defined hyperfine lines which arises due to the coupling of the unpaired electron with the nuclear spin of Cu(II).[41] The g and A values of the fresh catalyst are 2.05 and 326.8 mT respectively.

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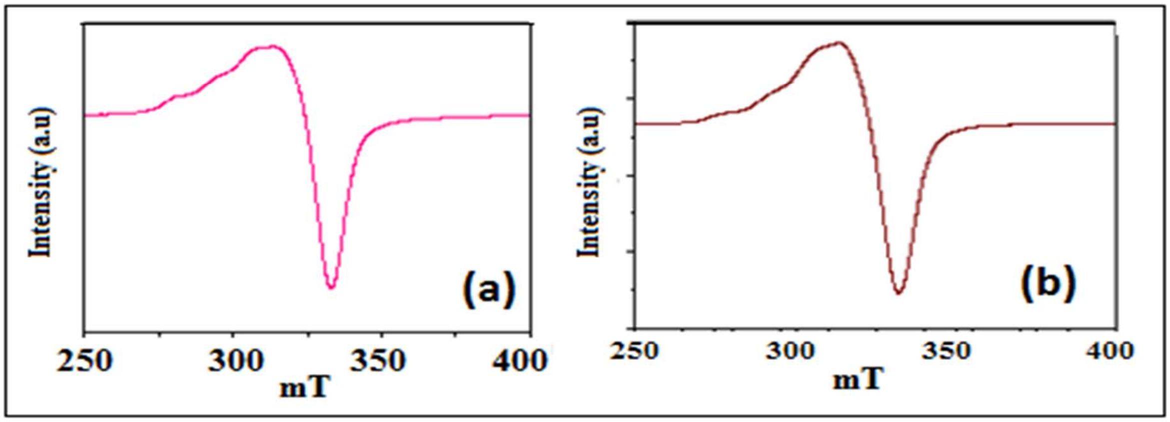

Figure 6 The X-band EPR spectrum of Cu(II) in (a) fresh and (b) used catalyst for Cu-mPMF

X-ray photoelectron spectroscopy (XPS): The mesoporous polymelamine formaldehyde grafted copper acetate sample contains carbon and nitrogen as the major elements. The XPS data showed peaks centred at 956.1, 936.6, 404.1 and 287.8 eV (Fig. 7). These binding energies correspond to Cu$2p_{1/2}$, Cu$2p_{3/2}$, N1s and C1s, respectively. The C peak at 287.8 eV is identified as sp^2-bonded carbon (C=N) in good agreement with literature. N1s spectrum signals centered at 404.1 corresponds to nitrogen present in copper grafted mPMF. The binding energy of the Cu$2p_{3/2}$ peak at 936.3 eV and indicates that copper species are only present as Cu(II) state in mesoporous Cu-mPMF. The binding energy values 936.6 and 956.1 eV corresponding to the spin orbit splitting components of Cu $2p_{3/2}$ and Cu $2p_{1/2}$ in the +2 oxidation state of copper agrees well with the reported literature values. There is also a satellite peak present in the XPS spectrum, which is a feature of 2p → 3d satellite peak of Cu in +2 oxidation state.[42]

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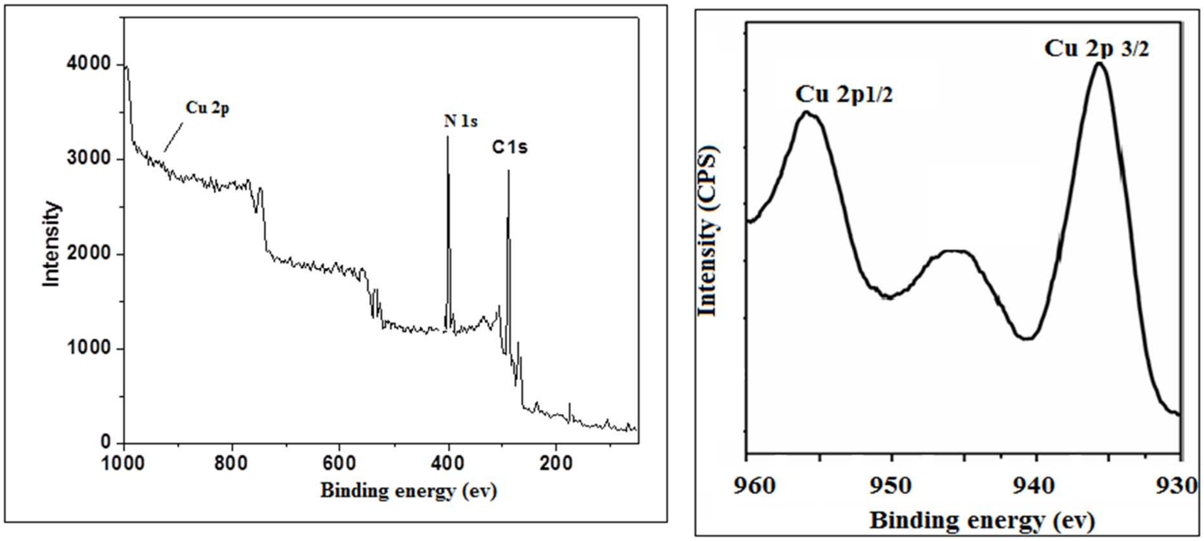

Figure 7 X-ray photoelectron spectroscopy (XPS) analysis of Cu-mPMF.

Catalytic activities:

Since supported copper systems exhibit catalytic activity in a wide range of the industrially important processes and have been extensively studied, we have decided to investigate the catalytic activity of Cu-mPMF in the field of esterification of benzylic alcohols and synthesis of secondary amides from nitriles and anilines.

Cu-mPMF catalyzed estrification:

To test the catalytic activity of the present catalyst, first esterification of benzylic alcohols was tested at 100 ^{0}C for 16h and TBHP was used as the methyl source as well as oxidant. For optimization of reaction conditions, we choose the benzyl alcohol as a substrate for the esterification reaction (Scheme 3). In this case benzyl alcohol is selectively converted to methyl benzoate in the presence of Cu-mPMF, *tert*-butyl hydroperoxide (TBHP) and TEAB in DMSO at 100 ^{0}C under oxygen atmosphere (1 atm). But the conversion of benzyl alcohol into desired product was increased when base was introduced.

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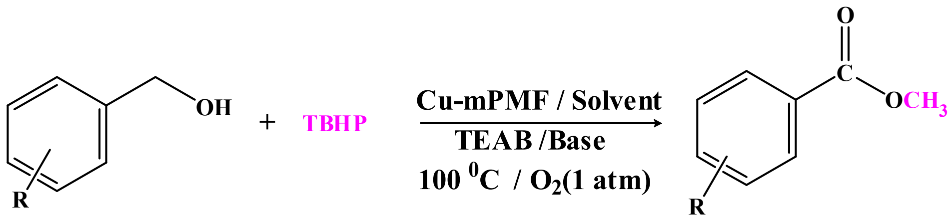

Scheme 3 Cu-mPMF catalyzed esterification of benzyl alcohol

It was found that sodiumethoxide afforded a 33 % yield of desired ester. But in the presence of potassium carbonate 85% desired ester was formed. From Table 1 it was cleared that DMSO was the only effective solvent for this reaction. Only a low yield was obtained when DMSO was replaced by DMF. No target product was observed in other solvents such as toluene and THF.

Table 1 effect of solvent and base on the esterification of benzyl alcohol

Entry	Solvent	Base	Yield (%)
1	DMSO	NaOEt	33
2	DMSO	Na_2CO_3	67
3	DMSO	K_2CO_3	85
4	DMF	K_2CO_3	6
5	THF	K_2CO_3	NR
6	Toluene	K_2CO_3	NR
7[a]	DMSO-D_6	K_2CO_3	82
8[b]	DMSO	K_2CO_3	NR
9[c]	DMSO	K_2CO_3	78

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10	DMSO	-	15

Reaction conditions: Benzyl alcohol (0.3 mmol), Cu-mPMF (20 mg), TBHP (2.4 mmol), TEAB (0.15 mmol), base (0.6 mmol), Solvent (2 mL), 100 ^{0}C, O_2 (1 atm), 16 h.

[a] TBHP in decane instead of its aqueous solution (70 wt % TBHP).

[b] DTBP or DCP oxidant used instead of TBHP.

[c] Reaction carried out at 90 ^{0}C.

The present esterification was very sensitive to the reaction temperature, when temperature was reduced to 90 ^{0}C from 100 ^{0}C a lower yield (78%) was obtained (Table 1, entry 9). Interestingly, no reaction occurred in the absence of TBHP or when TBHP was replaced with other oxidant like di-tert-butyl peroxide (DTBP) or dicumyl peroxide (DCP). Under the same conditions, the control experiment showed that the yield would be reduced in the absence of oxygen. The maximum yield was obtained in the presence of Cu-mPMF, K_2CO_3, TEAB in DMSO at100 ^{0}C and oxygen (1atm) (Table 1, entry 3). In this reaction benzyl alcohol first oxidized to acid under the reaction condition. Literature study suggests that in the presence of copper catalyst TBHP decomposes to generate the methyl radical. Next, acyloxyl radical is generated from benzoic acid by the reaction with *tert*-butoxyl or *tert*-butylperoxyl radical and then coupling of methyl radical and acyloxyl radical gives the corresponding ester. When other oxidants instead of TBHP (methyl source) were used no desired product was formed, only a mixture of aldehyde and acid were obtained. To confirm whether the methyl came from TBHP or DMSO, we carried out the control reaction in DMSO-d_6 with TBHP. An 82% yield of ester was obtained with no deuterated ester detected, thus demonstrating the methyl group came from TBHP.

To examine the scope of this esterification reaction, a variety of various benzylic alcohol derivatives were examined under optimized conditions. The experimental results are summarized in Table 2. As shown in Scheme 3, the protocol well tolerated diverse electronic and steric

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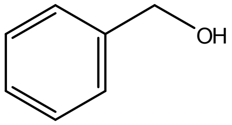
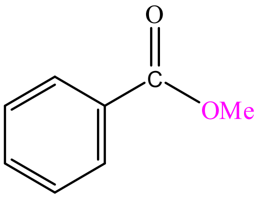
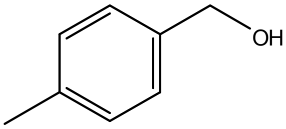
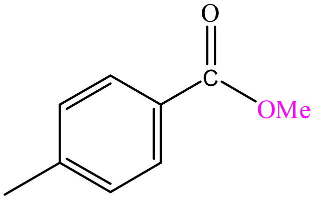
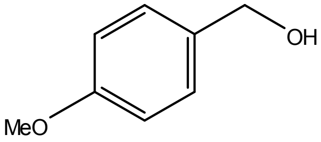
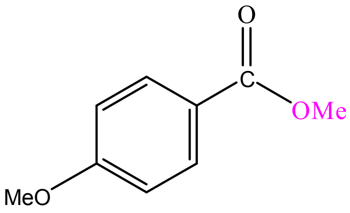
substituents of the benzylic alcohol, as well as heterocyclic substrates, all resulting in good to excellent yields. The substitution of electron withdrawing and electron donating groups on the aryl ring of alcohol has influence on the outcome of the reaction. Benzylic alcohols bearing either electron-donating or electron-withdrawing substituents, afforded the corresponding esters in good to excellent yields. Strong electron-donating groups such as methoxy group containing benzylic alcohol resulted in slightly excess yields than benzylic alcohol with electron-withdrawing groups, such as Cl, Br and NO_2 (Table 2, entries 6-8). Even heteroaromatic proved effective for this esterification reaction as depicted with the thiophene ring system leading to products (Table 2, entry 12). Unfortunately, the present catalytic system is less effective for aliphatic compound (Table 2, entry 15).

Table 2 Cu-mPMF Catalyzed Methyl Esterification of Various Benzylic Alcohols

Entry	Substrate	Product	Yield (%)
1			85
2			88
3			95

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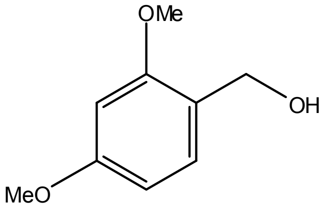
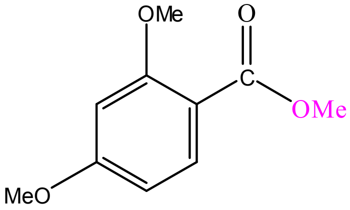
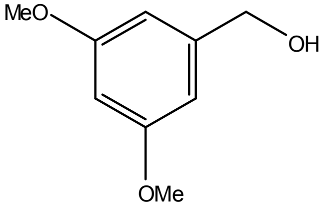
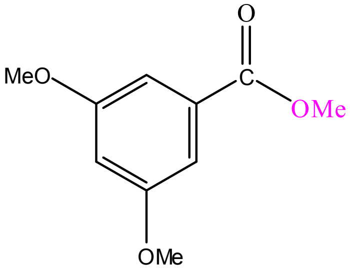
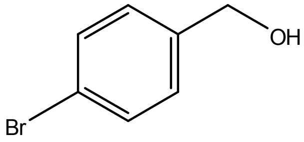
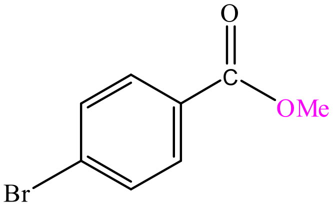
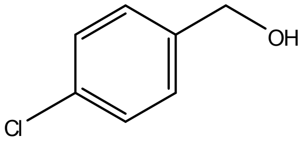
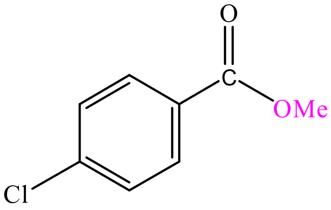
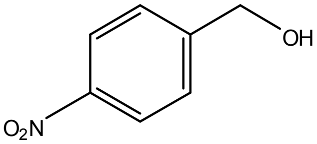
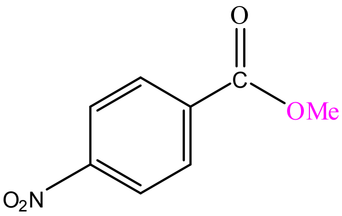
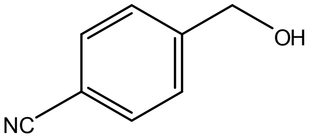
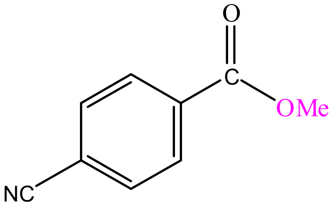
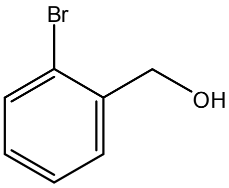
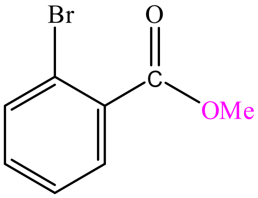
4			75
5			83
6			77
7			76
8			58
9			68
10			71

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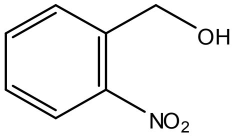
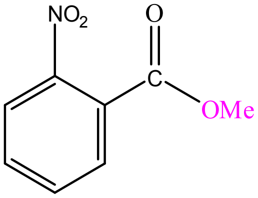
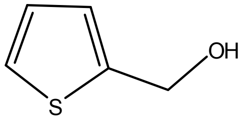
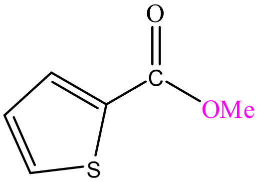
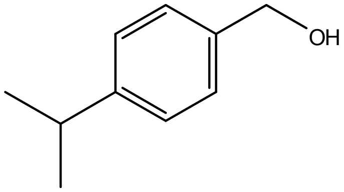
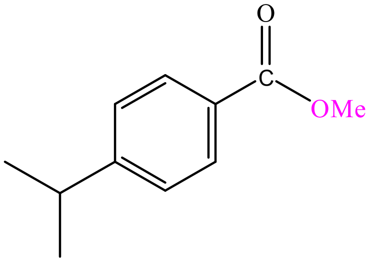
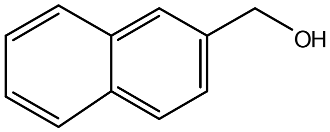
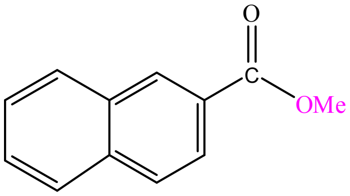
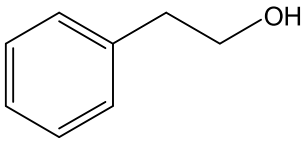
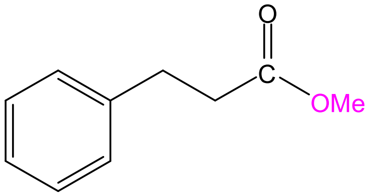
11			64
12			72
13			78
14			89
15			49

Reaction conditions: Alcohol (0.3 mmol), Cu-mPMF (20 mg), TBHP (2.4 mmol), TEAB (0.15 mmol), K_2CO_3 (0.6 mmol), DMSO (2 mL), 100 ^{0}C, O_2 (1 atm), 16 h.

After the successful application of the oxidative methyl esterification from benzylic alcohols, we tried to extend this methodology to carboxylic acids as substrates. It was found that base and additive TEAB were not necessary in the methyl esterification of the acids and 1.8 mmol of TBHP was sufficient for the reaction. Subsequently, various acid derivatives were

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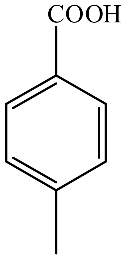
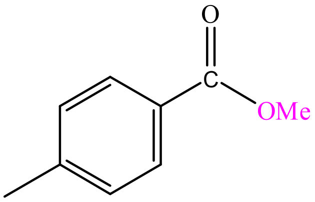
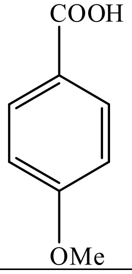
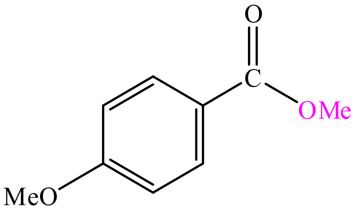
examined, and representative results are listed in Table 3. Similar to benzylic alcohols different substituted acids were subjected to the esterification reactions, as shown in Table 3. The results indicate that acids with electron-withdrawing or electron-donating groups were all well-tolerated and provided the corresponding products in good to excellent yields. As shown in Table 3, benzoic acid with methoxyl groups at different positions on the phenyl ring all worked smoothly under Cu-mPMF/ TBHP catalytic system, giving 84–97% yields of the desired esters (Table 3, entries 2-4). The electron-withdrawing group substituted acids (Table 3, entries 5-9) could also be efficiently converted to the expected esters. The hetero cyclic substrates were reacted smoothly under the optimized conditions (Table 3, entries 13, 14). The use of acids instead of alcohols provides almost similar yield of desired product. This observation also suggests that the above reaction (Scheme 3) may follow the following reaction sequence, alcohol → acid → acyloxyl radical → ester.

Table 3 Cu-mPMF Catalyzed Methyl Esterification of Various Acids

Entry	Substrate	Product	Yield (%)
1			92
2			97

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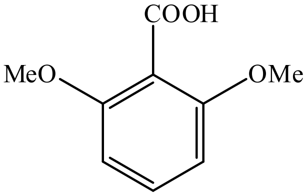
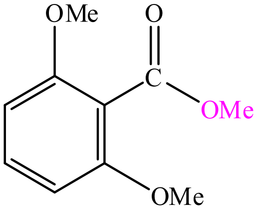
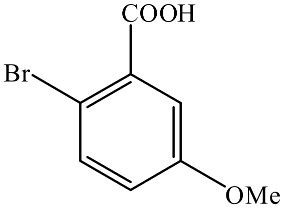
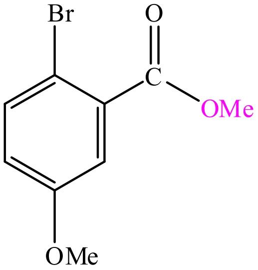
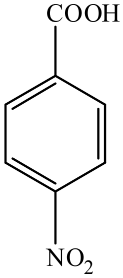
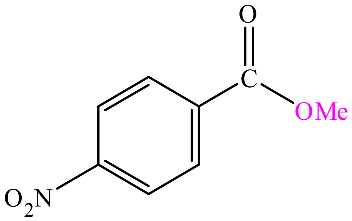
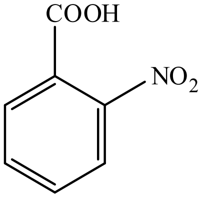
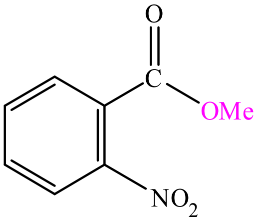
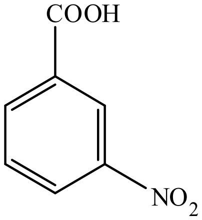
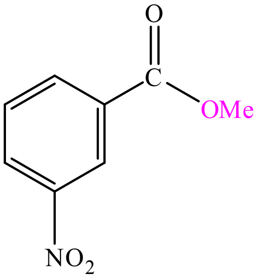
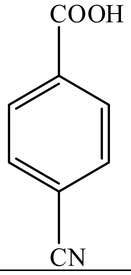
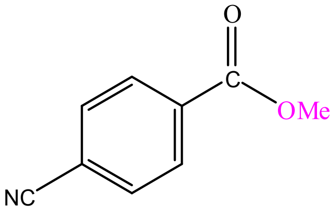
3			84
4			87
5			55
6			64
7			66
8			67

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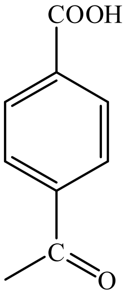
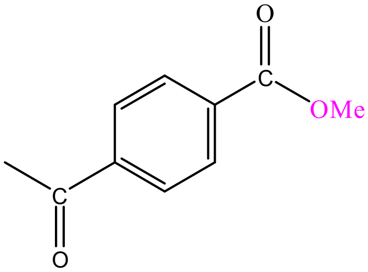
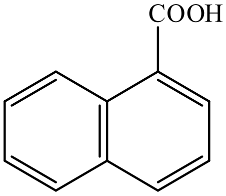
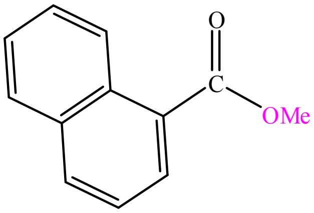
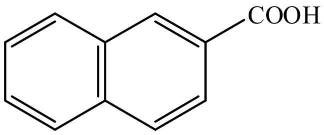
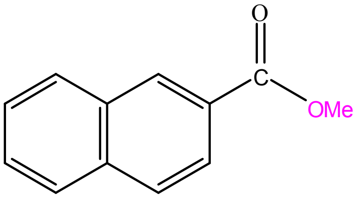
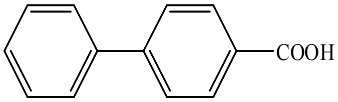
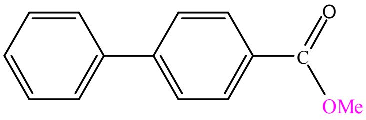
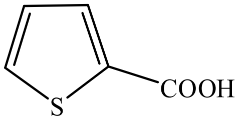
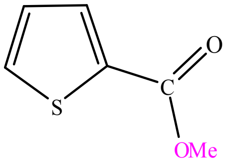
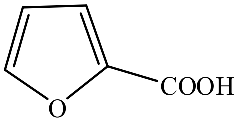
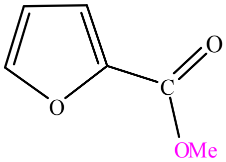
9			74
10			77
11			91
12			89
13			73
14			65

Reaction conditions: Alcohol (0.3 mmol), Cu-mPMF (20 mg), TBHP (1.8 mmol), DMSO (2 mL), 100 ^{0}C, 16 h.

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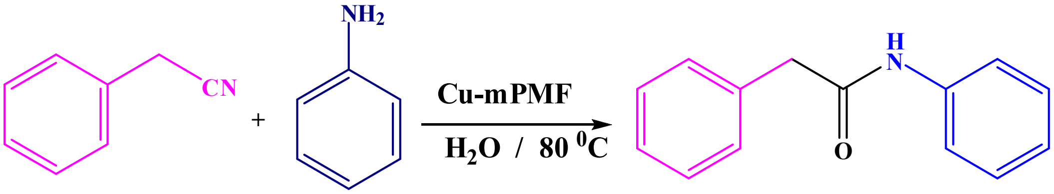
Cu-mPMF catalyzed amides synthesis

After successful synthesis of various esters from benzylic alcohols, we have extended the applications of our newly synthesized Cu-mPMF for the synthesis of secondary amides from various nitriles and anilines.



Scheme 4 Cu-mPMF catalyzed secondary amide synthesis

At the initial stage, a model reaction of phenylacetonitrile and aniline was carried out in aqueous acetonitrile solvent at 80 ^{0}C. A yield of 48 % N, 2-diphenylacetamide was obtained. Less polar solvent like toluene was less effective. When this reaction was carried out in water medium 85 % yield was obtained and thus water was chosen as the most effective solvent. This coupling reaction was found to be highly sensitive to the reaction temperature. At lower temperatures (50-65 ^{0}C) only low to moderate yield was obtained. A reaction temperature of 80 ^{0}C was found to be optimal for the model reaction. Also the reaction was carried out for different time ranging from 10 h to 16 h and it was found that at 14 h the conversion was 77% at given conditions. Literature study showed that nitrile directly reacted with amine to form an unstable amidine intermediate which can be easily hydrolyzed to give corresponding amide.[43]

To understand the substrate scope of this reaction, a wide range of phenylacetonitriles and anilines were reacted under the optimized reaction conditions (Table 4). Good to excellent yields of secondary amides were obtained in most cases. Electron donating or electron-withdrawing substituents on nitriles or anilines produce good to excellent yields of secondary

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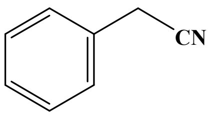
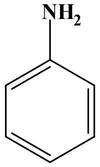
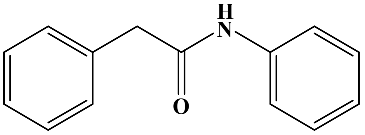
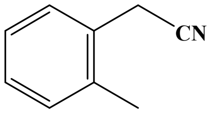
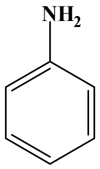
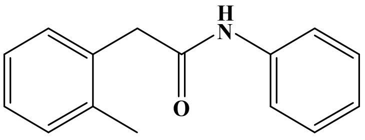
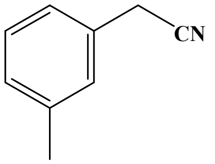
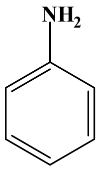
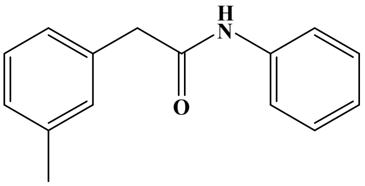
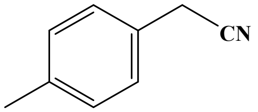
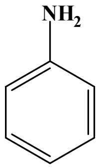
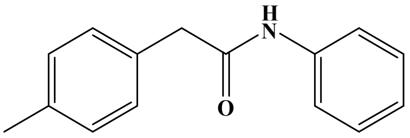
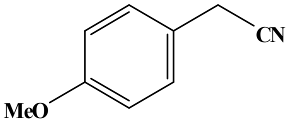
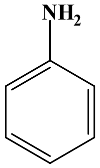
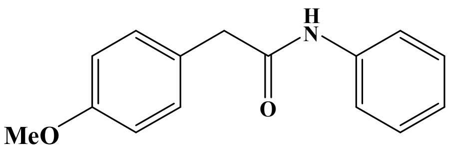
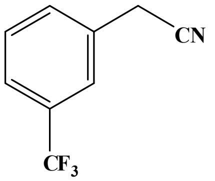
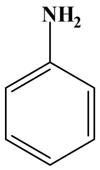
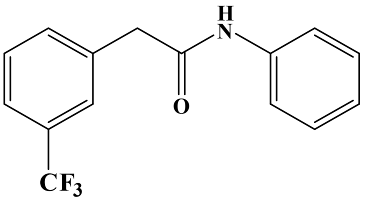
amides, electron donating groups are more effective than electron withdrawing, indicating that the reaction is slightly sensitive to electronic effects. Anilines or nitriles bearing substituent at *ortho* position resulted in lower yields than substituents at *meta* or *para* position. For example, 4-methoxyaniline gave the desired product in 92% and, while 4-chloro and fluoroaniline resulted in 76% and 72% yields, respectively (Table 4, entries 11, 12).

Table 4 Cu-mPMF Catalyzed secondary amides synthesis from nitriles and anilline

Entry	Nitriles	Anilines	Product	Yield (%)
1				77
2				80
3				83
4				85
5				92
6				61

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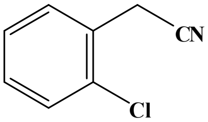
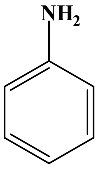
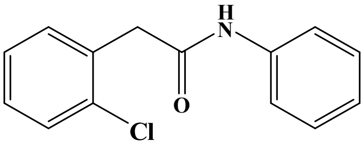
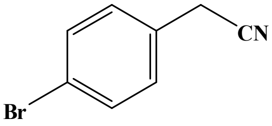
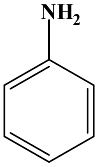
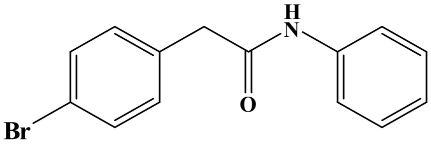
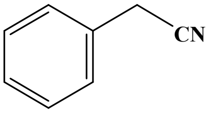
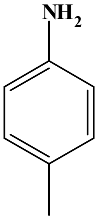
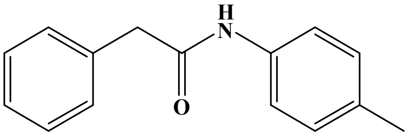
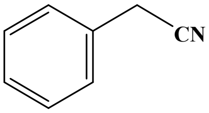
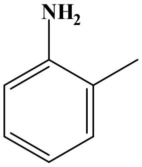
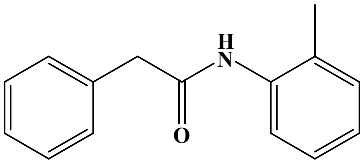
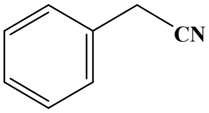
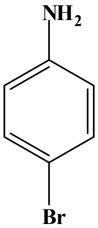
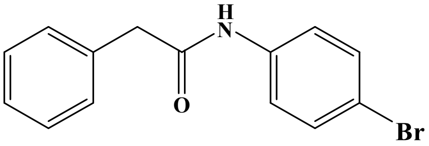
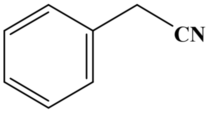
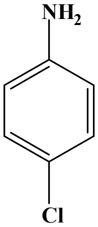
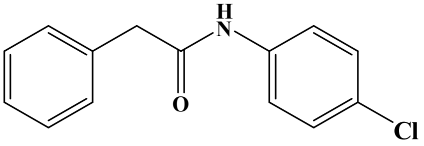
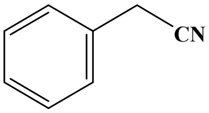
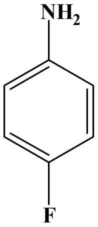
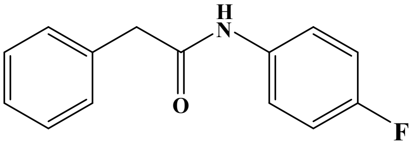
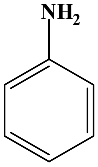
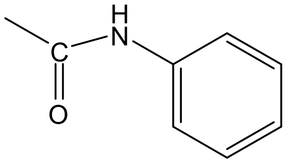
7				68
8				63
9				86
10				84
11				76
12				72
13				68
14	H_3C—CN			58

Reaction conditions: Nitriles (1 mmol), Anilines (1.3 mmol), Cu-mPMF (0.1 mmol) in H_2O (5 mL) at 80 ^{0}C for 14 h.

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Possible reaction mechanism:

Although the exact reaction sequence was not determined, based on our experimental results and former mechanistic studies[44-49], the reaction mechanisms of these reactions are proposed in Scheme 5. In case of methyl esterification reaction various literatures suggested that TBHP can produce methyl radical *via tert*-butoxyl and *tert*-butylperoxyl radicals. In the presence of oxidants and additive benzyl alcohol is transformed into corresponding acid. Subsequently, the acyloxyl radical is generated from benzoic acid by the reaction with tert-butoxyl or tert-butylperoxyl radical. Finally, coupling of the acyloxyl and methyl radicals gives the desired ester. But in case of amide synthesis reaction, exact reaction pathway is not clear to us. Various literatures[47-49] suggest that initially nitrile is hydrolyzed to give primary amide then it reacts with amine to give secondary amide. On the other hand, some groups suggested that nitrile first reacts with amine to give an unstable intermideate (amidine) which can be easily hydrolyzed to secondary amide.

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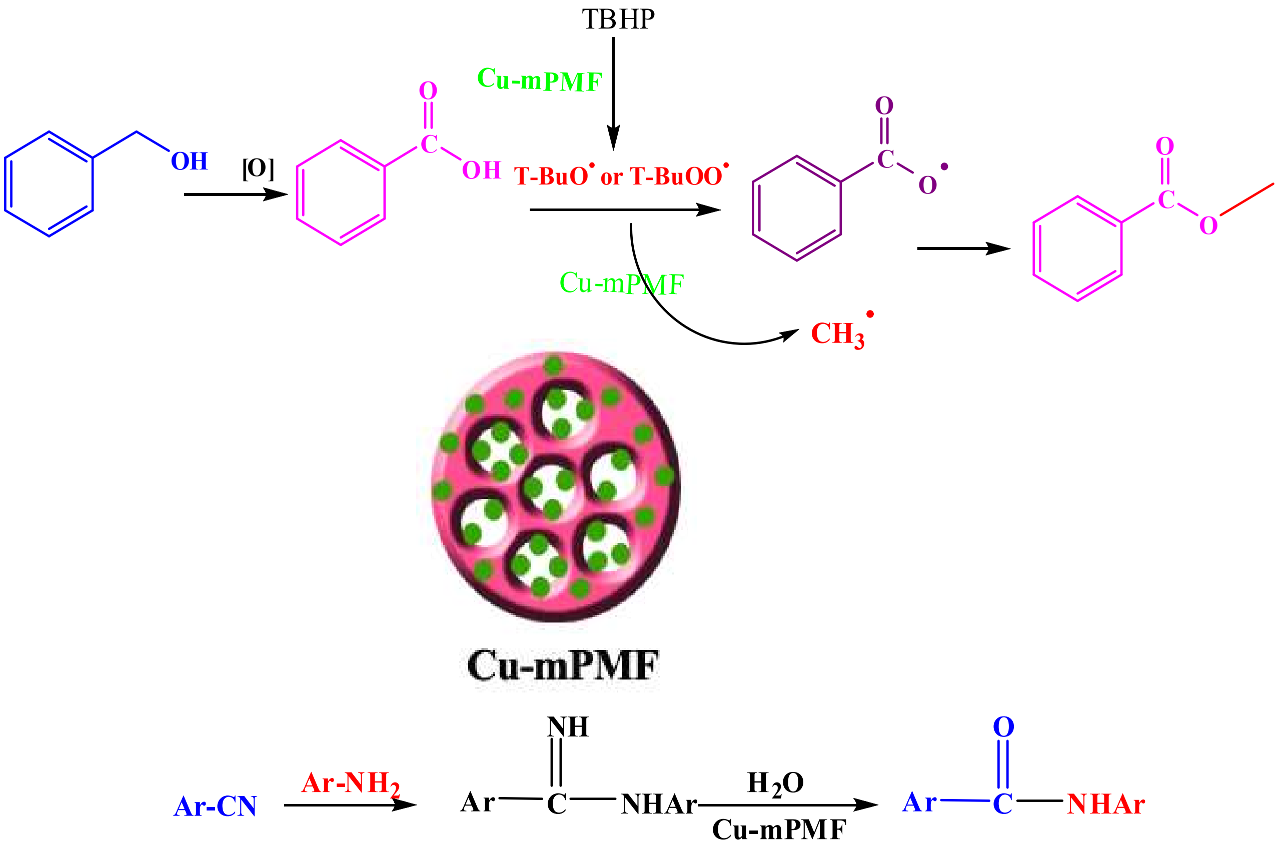

Scheme 5 Proposed reaction mechanism of Cu-mPMF catalyzed esterification and amidation

Catalyst reusability

Recovery and catalyst reuse are important issues in the heterogeneous catalysis. We studied the reusability of the present heterogeneous copper catalyst in the esters and amides synthesis reactions (Fig. 8). After completion of the reaction, the catalyst was recovered by simple filtration and washed with ethyl acetate followed by acetone then dried in reduced pressure at 40 ^{0}C. The recovered catalyst was employed in the next run with further addition of substrates in appropriate amount under optimum reaction conditions. The catalyst show almost

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same activity up to 7 reaction cycles. No catalyst deterioration was observed, confirming the high stability of the heterogeneous catalyst under the reaction conditions. Further, no evidence for leaching of copper or decomposition of the catalyst was observed during the catalytic reaction and no metal could be detected by atomic absorption spectroscopic measurement of the filtrate after removal of catalyst. These studies clearly demonstrated that metal was intact to a considerable extent with the heterogeneous support, and there is no significant amount of leaching occurred during reaction.

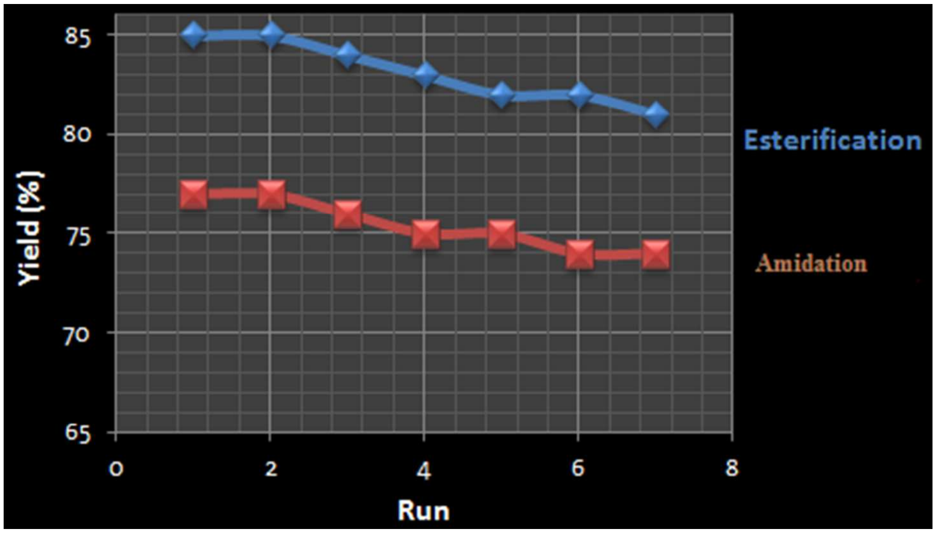

Figure 8 Catalyst reusability test of the mPMF supported copper catalyst.

Conclusions

In conclusion, we have reported the preparation and characterization of mesoporous polymer supported Cu(II) complex and its successful applications for the methyl esterification of benzylic alcohols in the presence of TBHP, which use as the methyl source. Both electron-rich and electron-deficient benzylic alcohols could be applied and the nature of the base, temperature and the solvent system proved crucial for the transformation. The present system is highly air and moisture stable and the catalyst can be synthesized readily from inexpensive and

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commercially available starting materials. Moreover, the catalyst was reused for six consecutive cycles with consistent catalytic activity. Further work is in progress to broaden the scope of this catalytic system for other organic transformation. A protocol, which allows expansion of this chemistry to other aromatic halides and mechanistic pathway of this reaction are currently under investigation.

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References

[1] (a) D. Lednicer and L. A. Mitscher, The Organic Chemistry of Drug Synthesis, *John Wiley, New York*, 1980, vol. 2, p. 62; (b) S. Edmondson, S. J. Danishefsky, L. Sepp-Lorenzino and N. Rosen, *J. Am. Chem. Soc*., 1999, **121**, 2147–2155; (c) S. Simon and J. Petrasek, *Plant Sci.,* 2011, **180**, 454–460.

[2] (a) K. Ishihara, *Tetrahedron*, 2009, **65**, 1085-1109; (b) J. Otera, Esterification: Methods, Reactions, and Applications, *Wiley-VCH, Weinheim*, 2003; (c) T. W. Greene and P. G. M. Wuts, in Protective Groups in Organic Synthesis, *Wiley-VCH, New York*, 1991.

[3] (a) T. Cupido, J. T. Puche, J. Spengler and F. Albericio, *Curr. Opin. Drug Discovery Dev*. 2007, **10**, 768-783; (b) J. W. Bode, *Curr. Opin. Drug Discovery Dev*., 2006, **9**, 765-775; (c) J. M. Humphrey, A. R. Chamberlin, *Chem. Rev.,* 1997, **97**, 2243-2266.

[4] (a) J. McNulty, A. Capretta, V. Laritchev, J. Dyck and A. J. Robertson, *Angew. Chem.,* 2003, **115**, 4185-4188; (b) P. Gopinath, S. Nilaya and K. M. Muraleedharan, *Org. Lett.,* 2011, **13**, 1932-1935; (c) K. C. K. Swamy, N. N. B. Kumar, E. Balaraman and K. V. P. P. Kumar, *Chem. Rev.,* 2009, **109**, 2551-2661.

DOI: 10.1039/C4DT03838J

[5] (a) A. Brennführer, H. Neumann and M. Beller, *Angew. Chem.,* 2009, **121**, 4176-4196; (b) C. M. Kormos and N. E. Leadbeater, *Org. Biomol. Chem.,* 2007, **5**, 65-68; (c) Y. Yamamoto, *Adv. Synth. Catal.,* 2010, **352**, 478-492; (d) Z. Xin, T. M. Gogsig, A. T. Lindhardt and T. Skrydstrup, *Org. Lett.,* 2012, **14**, 284-287.

[6] H. Zhang, R. Shi, A. Ding, L. Lu, B. Chen and A. Lei, *Angew. Chem.,* 2012, ***124***, 12710-12713.

[7] (a) K. Ekoue-Kovi, C. Wolf, *Chem. Eur. J.*, 2008, **14**, 6302-6315; (b) X. F. Wu, C. Darcel, *Eur. J. Org. Chem.,* 2009, 1144-1147; (c) R. Gopinath, B. Barkakaty, B. Talukdar and B. K. Patel, *J. Org. Chem.,* 2003, **68**, 2944-2947; (d) A. S. K. Hashmi, C. Lothschuetz, M. Ackermann, R. Doepp, S. Anantharaman, B. Marchetti, H. Bertagnolli and F. Rominger, *Chem. Eur. J.,* 2010, **16**, 8012-8019; (e) B. R. Travis, M. Sivakumar, G. O. Hollist and B. Borhan, *Org. Lett.,* 2003, **5**, 1031-1034; (f) R. Gopinath and B. K. Patel, *Org. Lett.,* 2000, **2**, 577-579; (g) C. Marsden, E. Taarning, D. Hansen, L. Johansen, S. K. Klitgaard, K. Egeblad and C. H. Christensen, *Green Chem.,* 2008, **10**, 168-170; (h) G. A. Hero-poulos, C. V. Barber, *Tetrahedron Lett.,* 2011, **52**, 5319-5322; (i) S. Yamada, D. Morizono and K. Yamamoto, *Tetrahedron Lett.,* 1992, **33**, 4329-4332; (j) C. Liu, S. Tang, L. Zheng, D. Liu and H. Zhang, A. Lei, *Angew. Chem.,* 2012, **124**, 5760-5764; (n) W. J. Yoo and C. J. Li, *J. Org. Chem.,* 2006, **71**, 6266-6268; (k) W. J. Yoo, C. J. Li, *Tetrahedron Lett.,* 2007, **48**, 1033-1035.

[8] (a) D. I. Enache, J. K. Edwards, P. Landon, B. Solsona-Espriu, A. F. Carley, A. A. Herzing, M. Watanabe, C. J. Kiely, D. W. Knight and G. J. Hutchings, *Science* 2006, **311**, 362-365; (b) R. A. Sheldon, W. C. E. Arends, G.-J. ten Brink and A. Dijksman, *Acc. Chem. Res.,* 2002, **35**, 774-781; (c) M. S. Sigman and D. R. Jensen, *Acc. Chem. Res.,* 2006, **39**, 221-229; (d) R. Liu, C. Dong, X. Liang, X. Wang and X. Hu, *J. Org. Chem.,* 2005, **70**, 729-731; (e) R. Liu, X. Liang, C. Dong, X. Hu, *J. Am. Chem. Soc.,* 2004, **126**, 4112; (f) T. Mallat, A. Baiker, *Chem. Rev.,* 2004, **104**, 3037; (g) M. J. Schultz, M. S. Sigman, *Tetrahedron* 2006, **62**, 8227-8241.

[9] (a) M. F. Semmelhack, C. R. Schmid, D. A. Cortés and C. S. Chou, *J. Am. Chem. Soc.,* 1984, **106**, 3374-3376; (b) I. E. Markó, P. R. Giles, M. Tsukazaki, S. M. Brown and C. J. Urch, *Science* 1996, **274,** 2044-2046; (c) I. A. Ansari, R. Gree, *Org. Lett.,* 2002, **4**, 1507-1509; (d) P. Gamez, I. W. C. E. Arends, J. Reedijk and R. A. Sheldon, *Chem.*

View Article Online
DOI: 10.1039/C4DT03838J

Commun., 2003, 2414-2415; (e) I. E. Markó, A. Gautier, R. Dumeunier, K. Doda, F. Philippart and S. M. Brown, C. J. Urch, *Angew. Chem.,* 2004, **116**, 1614; (f) N. Jiang, A. J. Ragauskas, *J. Org. Chem.,* 2006, **71**, 7087-7090; (g) O. Onomura, H. Arimoto, Y. Matsumura, Y. Demizu, *Tetrahedron Lett.,* 2007, **48**, 8668-8672; (h) C. Liu, J. Han and J. Wang, *Synlett* 2007, 643;(i) P. J. Figiel, M. N. Kopylovich, J. Lasri, M. F. C. Guedes da Silva, J. J. R. Fraústo da Silva and A. J. L. Pombeiro, *Chem. Commun.,* 2010, **46**, 2766-2768; (j) J. M. Hoover, S. S. Stahl, *J. Am. Chem. Soc.,* 2011, **133**, 16901-169010; (k) C. Han, M. Yu, W. Sun, X. Yao, *Synlett,* 2011, 2363-2368.

[10] (a) B. Xu, X. Liu, J. Haubrich, R. J. Madix, C. M. Friend, *Angew. Chem.,* **2009**, *121*, 4270-7273; (b) R. L. Oliveira, P. K. Kiyohara, L. M. Rossi, *Green Chem.,* **2009**, *11*, 1366-1370; c) H. Miyamura, T. Yasu-kawa, S. Kobayashi, *Green Chem.,* **2010**, *12*, 776-778.

[11] (a) S. Gowrisankar, H. Neumann and M. Beller, *Angew. Chem.,* 2011, **123**, 5245-5249; (b) C. Liu, J. Wang, L. Meng, Y. Deng, Y. Li and A. Lei, *Angew. Chem.,* 2011, **123**, 5250-5254; *(*c) C. Liu, S. Tang and A. Lei, *Chem. Commun.,* 2013, **49**, 1324-1326.

[12] (a) T. Suzuki, K. Morita, M. Tsuchida and K. Hiroi, *J. Org. Chem.,* 2003, **68**, 1601-1602; (b) T. Suzuki, K. Morita, Y. Matsuo and L. Hiroi, *Tetrahedron Lett.,* 2003, **44**, 2003-2006; (c) A. Izumi, Y. Obora, S. Sakaguchi, and Y. Ishii, *Tetrahedron Lett.,* 2006, **47**, 9199-9204; (d) S. Arita, T. Koike, Y. Kayaki and T. Ikariya, *Organometallics,* 2008, **27** 2795-2802; (e) S. Arita, T. Koike, Y. Kayaki and T. Ikariya, *Chem. Asian J.* 2008, **3**, 1479-1485.

[13] (a) J. Zhang, G. Leitus, Y. Ben-David and D. Milstein, *J. Am. Chem. Soc.,* 2005, **127**, 10840-10841; b) J. Zhang, M. Gandelman, L. J. W. Shimon and D. Milstein, *Dalton Trans.,* 2007, 107-113; (c) C. Gunanathan, L. J. W. Shimon and D. Milstein, *J. Am. Chem. Soc.,* 2009, **131**, 3146-3147; (d) N. A. Owston, A. J. Parker and J. M. J. Williams, *Chem. Commun.,* 2008, 624-625; (e) N. A. Owston, T. D. Nixon, A. J. Parker, M. K. Whittlesey and J. M. J. Williams, *Synthesis,* 2009, 1575-1578; (f) T. Zweifel, J.-V. Naubron and H. Grútzmacher, *Angew. Chem.,* 2009, **121**, 567-571.

[14] (a) B. C. Ranu and P. Dutta, *Synth. Commun.,* 2003, **33**, 297–301; (b) R. Arora, S. Paul, R. Gupta, *Can. J. Chem*., 2005, **83**, 1137–1140.

View Article Online
DOI: 10.1039/C4DT03838J

[15] E. Valeur and M. Bradley, *Chem. Soc. Rev.*, 2009, **38**, 606–631.

[16] (a) R. G. Kalkhambkar, S. N. Waters and K. K. Laali, *Tetrahedron Lett.,* 2011, **52**, 867–871; (b) J. J. Ritter and P. P Minieri, *J. Am. Chem. Soc*., 1948, **70**, 4045–4048.

[17] (a) F. Macleod, S. Lang and J. A. Murphy, *Synlett* 2010, 529–534; (b) J. S. Yadav, B. V. S. Reddy and K. Praneeth, Tetrahedron Lett., 2008, **49**, 4742–4745.

[18] (a) D. Gnanamgari, R. H. Crabtree, *Organometallics* 2009, **28**, 922–924; (b) N. A. Owston, A. J. Parker and J. J. M Williams, *Org. Lett*., 2007, **9**, 3599–3601; (c) J. K. Augustine, R. Kumar, A. Bombrun, A. B. Mandal, *Tetrahedron Lett*., 2011, **52**, 1074–1077; (d) S. Chandrasekhar and K. Gopalaiah, *Tetrahedron Lett*., 2003, **44**, 7437–7439.

[19] (a) A. Domling and I. Ugi, *Angew. Chem., Int. Ed.,* 2000, **39**, 3168–3210; (b) S. Santra, P. R. Andreana, *J. Org. Chem*., 2011, **76**, 2261–2264; (c) J. Isaacson and Y. Kobayashi, *Angew. Chem., Int. Ed*., 2009, **48**, 1845–1848; (d) S. C. Pan and B. List, *Angew. Chem., Int. Ed*., 2008, **47**, 3622–3625.

[20] (a) H. Meier and K. P. Eller, *Angew. Chem., Int. Ed.,* 1975, **14**, 32–43; (b) W. Kirmse, *Eur. J. Org. Chem*., 2002, 2193–2256; (c) R. R. Julian, J. A. May, B. M. Stoltz and J. L. Beauchamp, *J. Am. Chem. Soc*., 2003, **125**, 4478–4486.

[21] (a) W. J. Yoo, C J. Li, *J. Am. Chem. Soc*., 2006, **128**, 13064–13065; (b) J. W. Bode, S. S. Sohn, *J. Am. Chem. Soc.,* 2007, **129**, 13798–13799; (c) K. E. Kovi, C. Wolf, *Chem. Eur. J.,* 2008, **14**, 6302–6315; (d) Y. Suto, N. Yamagiwa, Y. Torisawa, *Tetrahedron Lett.,* 2008, **49**, 5732–5735; (e) C. L. Allen, S. Davulcu and J. J. M. Williams, *Org. Lett*., 2010, **12**, 5096–5099.

[22] (a) S. C. Ghosh and S. H Hong, *Eur. J. Org. Chem*., 2010, 4266–4270; (b) J. H. Dam G. Osztrovszky, L. U. Nordstr and R. Madsen, *Chem. Eur. J.,* 2010, **16**, 6820–6827; (c) Y. Wang, D. P. Zhu, L. Tang, S. J. Wang and Z. Y. Wang, *Angew. Chem., Int. Ed*., 2011, **50**, 8917–8921; (d) S. C. Ghosh, S. Muthaiah, Y. Zhang, X. Y. Xu and S. H. Honga, *Adv. Synth. Catal*., 2009, 351, 2643–2649; (e) L. U. Nordstrøm, H. Vogt and R. Madsen, *J. Am. Chem. Soc*., 2008, **130**, 17672–17673.

View Article Online
DOI: 10.1039/C4DT03838J

[23] (a) A. Schoenberg and R. F Heck, *J. Org. Chem.,* 1974, **39**, 3327–3331; (b) J. R. Martinelli, D. A. Watson, D. M. M. Freckmann, T. E. Barder, S. L. Buchwald, *J. Org. Chem.,* 2008, **73**, 7102–7107; (c) A. Brennfuhrer, H. Neumann and M. Beller, *Angew. Chem., Int. Ed*., 2009, **48**, 4114–4133; (d) O. Lagerlund, M. L. H. Mantel, M. Larhed, *Tetrahedron*, 2009, **65**, 7646–7652.

[24] (a) U. Matteoli, A. Scrivanti, V. Beghetto, *J. Mol. Catal. A: Chem*., 2004, **213**, 183-186; (b) S. M. Lu and H. Alper, *J. Am. Chem. Soc.,* 2008, **130**, 6451–6455.

[25] (a) J. D. Hicks, A. M. Hyde, A. M. Cuezva, S. L. Buchwald, *J. Am. Chem. Soc*., 2009, **131**, 16720–16734; (b) M. C. Willis, G. N. Brace, I. P. Holmes, *Angew. Chem., Int. Ed*., 2005, **44**, 403–406.

[26] (a) S. Calimsiz and M. A Lipton, *J. Org. Chem.,* 2005, **70**, 6218–6221; (b) N. A. Stephenson, J. Zhu, S. H. Gellman, S. S. Stahl, *J. Am. Chem. Soc*., 2009, **131**, 10003-10008; (C) M. Zhang, S. Imm, S. Bahn, L. Neubert, H. Neumann and M. Beller, *Angew. Chem., Int. Ed*., 2012, **51**, 3905–3909.

[27] S. I. Murahashi, T. Naota, E. Saito, *J. Am. Chem. Soc*., 1986, **108**, 7846–7847.

[28] (a) C. J. Cobley, M. van den Heuvel, A. Abbadi and J. G. de Vries, *Tetrahedron Lett.,* 2000, **41**, 2467–2470; (b) C. L. Allen, A. A. Lapkin and J. M. J. Williams, *Tetrahedron Lett.,* 2009, **50**, 4262–4264.

[29] (a)Y. Zhu, H. Yan, L. Lu, D. Liu, G. Rong, and J. Mao. *J. Org. Chem.,* 2013, **78**, 9898−9905, (b) Pan Li, Jingjing Zhao, Rui Lang , Chungu Xia , Fuwei Li, *Tetrahedron Lett*., 2014, 55, 390–393.

[30] X. Li, Z. Li, H. Deng, X. Zhou, *Tetrahedron Lett.,* 2013, **54**, 2212–2216; (b) C. Hu, X. Yan, X. Zhoua, and Z. Li, *Org. Biomol. Chem.,* 2013, **11**, 8179–8182.

[31] S. M. Islam, R. A. Molla, A. S. Roy and K. Ghosh, *RSC Adv.,* 2014, **4**, 26181–26192.

[32] (a) K. R. Gruenwald, A. M. Kirillov, M. Haukka, J. Sanchiz and A. J. L. Pombeiro, *Dalton Trans*., 2009, 2109–2120; (b) M. Singla, M. Gupta, P. Mathur and M. S. Hundal, *Transition Met. Chem*., 2008, **33**, 175–182; (c) S. M. Islam, R. A. Molla, A. S.

DOI: 10.1039/C4DT03838J

Roy, K. Ghosh, N. Salam, Md. A. Iqubal, K. Tuhina, *J. Org. met. Chem.*, 2014, 761, 169-178.

[33] (a) N. Salam. S. K. Kundu, A. S. Roy, P. Mondal, S. Roy, A. bhaumik and S. M. Islam, *Catal. Sci. Technol.*, 2013, **3**, 3303-3316; (b) U. Mandi, M. Pramanik, A. S. Roy, N. Salam, A. Bhaumik and S. M. Islam, *RSC Adv.*, 2014, **4**, 15431-15440; (c) N. Salam. B. Banerjee, A. S. Roy, P. Mondal, S. Roy, A. bhaumik and S.M.Islam, *App. Catal. A: Gen.* 2014, **477**, 184-194; (d) K. Ghosh, Md. A. Iqubal, R. A. Molla, A. Mishra, Kamaluddin and S. M. Islam, *Catal. Sci. Technol..*, DOI: 10.1039/c4cy01278j; (e) R. A. Molla, K. Ghosh, K. Tuhina and S. M. Islam, *New. J. Chem.*, DOI: 10.1039/C4NJ01457J; (f) R. A. Molla, K. Ghosh, A. S. Roy and S. M. Islam, *J. Mol.Catal A: Chem.,* 2015, **396**, 268-274.

[34] (a) T. Miao and L. Wang, *Synthesis*, 2008, 363-368. (b) J. Mondal, A. Modak, M. Nandi, H. Uyama and A. Bhaumik, *RSC Adv.*, 2012, **2**, 11306-11317. (c) K. Saito, K. Hirose, T. Okayasu, H. Nishide and M. T. W. Hearn, *RSC Adv.*, 2013, **3**, 9752-9756. (d) B. H. Lipshutz and B. R. Taft, *Angew. Chem., Int. Ed.*, 2006, **45**, 8235-8238. (e) S. Chassaing, M. Kumarraja, A. S. S. Sido, P. Pale and J. Sommer, *Org. Lett.*, 2007, **9**, 883-886.

[35] (a) D. E. De Vos, M. Dams, B. F. Sels and P. A. Jacobs, *Chem. Rev.*, 2002, **102**, 3615-3640; (b) J. A. Melero, R. V. Grieken and G. Morales, *Chem. Rev.*, 2006, **106**, 3790-3812; (c) S. Angelos, E. Johansson, J. F. Stoddart and J. I. Zink, *Adv. Funct. Mater*, 2007, **17**, 2261-2271; (d) M. Vallet-Regı´, F. Balas and D. Arcos, *Angew. Chem., Int. Ed.*, 2007, **46**, 7548-7558; (e) F. Zhang, Y. Meng, D. Gu, Y. Yan, C. Yu, B. Tu and D. Zhao, *J. Am. Chem. Soc.*, 2005, **127**, 1350813509; (g) Y. Meng, D. Gu, F. Zhang, Y. Shi, H. Yang, Z. Li, C. Yu, B. Tu and D. Zhao, *Angew. Chem., Int. Ed.*, 2005, **44**, 7053-7059.

[36] (a) Y. Meng, D. Gu, F. Zhang, Y. F. Shi, L. Cheng, D. Feng, Z.X. Wu, Z. X. Chen, Y. Wan, A. Stein and D. Zhao, *Chem. Mater.*, 2006, **18**, 4447–4464; (b) B. Karimi, H. M. Mirzaei and A. Mobaraki, *Catal. Sci. Technol.,* 2012, **2**, 828–834. (c) D. Chandra, B. K. Jena, C. R. Raj and A. Bhaumik, *Chem. Mater.*, 2007, **19**, 6290–6296. (d)M. Nandi, R. Gangopadhyay and A. Bhaumik, *Micropor. Mesopor. Mater*. 2008,

109, 239–247; (e) M. Pramanik, M. Nandi, H. Uyama and A. Bhaumik, *Catal. Sci. Technol.,* 2012, **2**, 613–620. (f) J. Schuster, R. Koehn, A. Keilbach, M. Doeblinger, H. Amenitsch and T. Bein, *Chem. Mater*, 2009, **21**, 5754–5762; (g) Y. L. Zhang, S. Wei, F. J. Liu, Y. C. Du, S. Liu, Y. Y. Ji, T. Yokoi, T. Tatsumi and F. S. Xiao, *Nano Today*, 2009, **4**, 135–142; (b) E. Poli, R. De Sousa, F. Je´rome, Y. Pouilloux and J. M. Clacens, *Catal. Sci. Technol.,* 2012, **2**, 910–914.

[37] J. K. Cho, R. Najman, T. W. Dean, O. Ichihara, C. Muller and M. Bradley, *J. Am. Chem. Soc*., 2006, **128**, 6276–6277.

[38] (a) P. Pandey, A. P. Katsoulidis, I. Eryazici, Y. Wu, M. G. Kanatzidis and S. T. Nguyen, *Chem. Mater.*, 2010, **22**, 4974–4979. (b) J. Germain, F. Svec and J.M. J. Fr´echet, *Chem.Mater,* 2008, **20**, 7069–7076. (c) P. Kuhn, A. Thomas and M. Antonietti, *Macromolecules*, 2009, **42**, 319–326. (d) M. G. Schwab, B. Fassbender, H. W. Spiess, A. Thomas, X. Feng and K. M. ullen, *J. Am. Chem. Soc.*, 2009, **131**, 7216–7217.

[39] M. K. Bhunia, S. K. Das, P. Pachfule, R. Banerjee and A. Bhaumik, *Dalton Trans.*, 2012, 41, 1304-1311; (b) S. Roy, T. Chatterjee, B. Banerjee, N. Salam, A. Bhaumik and S. M. Islam, *RSC Adv.*, 2014, **4**, 46075-46083.

[40] (a) A. C. Ferrari and J. Robertson, *Physical Review B*, 2001, **64**, 075414. (b) C. M. S. Izumi, Vera R. L. Constantino, and Marcia L. A. Temperini *J. Phys. Chem., B* 2005, **109***,* 22131-22140.

[41] S. Roy, T. Chatterjeec, M. Pramanikd, A. S. Roy, A Bhaumik and S. M Islam, *J. Mol. Catal. A: Chem*., 2014, **386**, 78–85.

[42] (a) Q. Guo, Y. Xie, X. Wang, S. Zhang and T.S. Hou, *Chem. Commun*., 2004**,** 26-27; (b) C.-B. Cao, Q. Lv and H.-S. Zhu, *Diamond Related Mater*, 2003, **12**, 1070-1074; (c) G. Zhang, J. Long, X. Wang, W. Dai, Z. Li, L. Wu and X. Su, *New J. Chem*., 2009, **33**, 2044–2050. (d) A. Narani, R. K. Marella, E. Ramudu, K. S. Rama-Rao and D. R. Burri, *RSC Adv*., 2014, **4**, 3774-3781.

[43] (a) J. H. Forsberg, V. T. Spaziano, T. M. Balasubramian, G. K. Lui, S. A. Kinsley, C. A. Duckworth, J. J. Poteruca and P. S. Brown, J. L. Miller, *J. Org. Chem*., 1987, **52**,

View Article Online
DOI: 10.1039/C4DT03838J

1017–1021; (b). R. L. Shriner and F. W. Neumanw, *Chem. Rev.,* 1944, **35**, 351–425.

[44] L. Chen, E. Shi, Z. Liu, S. Chen, W. Wei, H. Li, K. Xu, X. Wan, *Chem. Eur. J.* 2011, **17**, 4085−4089.

[45] Z. Liu, J. Zhang, S. Chen, E. Shi, Y. Xu and X. Wan, *Angew. Chem., Int. Ed.*, 2012, **51**, 1−6.

[46] R. T. Gephart, C. L. McMullin, N. G. Sapiezynski, E. S. Jang, M. J. B. Aguila, T. R. Cundari and T. H. Warren, *J. Am. Chem. Soc.*, 2012, **134**, 17350−17353.

[47] W. O Siegl, *J. Org. Chem.,* 1977, **42**, 1872–1877.

[48] J. H. Forsberg, V. T. Spaziano, T. M. Balasubramian, G. K. Lui, S. A. Kinsley, C. A. Duckworth, J. J. Poteruca, P. S. Brown and J. L. Miller, *J. Org. Chem.*, 1987, **52**, 1017–1021.

[49] R. L Shriner and F. W Neumanw, *Chem. Rev*. 1944, **35**, 351-425.

View Article Online
DOI: 10.1039/C4DT03838J

Nitrogen Enriched Mesoporous Organic Polymer Anchored Copper(II) Material: an Efficient and Reusable Catalyst for the Synthesis of Esters and Amides From aromatic systems

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New mesoporous polymer anchored copper acetate (Cu-mPMF) has been synthesized and well characterized. The catalytic performance of this complex has been tested for esterification of benzylic alcohols with TBHP and amidation of nitrile with anilines. This catalyst showed excellent catalytic activity, recyclability and reused more than six times.