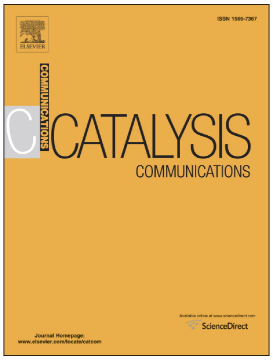

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A Polymer supported Cu(II) catalyst for oxidative amidation of benzyl alcohol and substituted amines in TBHP/H_2O

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Abstract: A new polymer supported copper complex of 2,6-bis(benzimidazolyl)pyridine Cu(PS-BBP)Cl_2 was prepared and characterized by elemental analyses, AAS, ESR, IR and UV-Vis spectral studies, magnetic moment measurement and thermogravimetric analyses. A facile oxidative coupling of alcohols and amines to synthesize amides was developed using Cu(PS-BBP)Cl_2 as a catalyst and tert-butyl hydroperoxide (TBHP) as an oxidant using water as a solvent in a one-pot process. The optimum conditions were determined for the reaction of benzyl alcohol and benzylamine by varying solvents, temperature, substrate to TBHP ratio and catalyst concentration and the yield resulted was found to be 95%. The catalyst showed excellent catalytic activity and reusability. A tentative reaction mechanism has been proposed.

Keywords: Oxidative amidation; Benzyl alcohol; Hemiaminal; Polymer supported Cu(II) complex; Substituted amines.

1. Introduction

The amide bond is an important linkage in natural products, synthetic polymers and pharmaceutical compounds, and amides are important class of compounds that are used as starting materials for engineering plastics, detergents and lubricants. In organic synthesis, primary amides are potent substrates for primary amines, nitriles, amino acid derivatives and heterocycle preparation. In nature, primary amides are present in numerous biologically active molecules [1-11]. The synthetic methods for amides can be achieved through the amidation of activated carboxylic acids, such as acid chlorides, esters and anhydrides [12-17]. Zinc salts catalyzed oxidative amidation of benzyl alcohols with aliphatic/aromatic amines using TBHP as oxidant under solvent free conditions have also been investigated [18]. $ZnBr_2$ catalyzed the oxidation of N-methylbenzylamine to benzamides in the presence of pyridine and TBHP, wherein pyridine stabilized the active species [19]. Ruthenium(II)diamine complex catalyzed the intramolecular cyclization of amino alcohols [20]. $Ru^{II}(\eta^6$-arene) complex with 1,2,3-triazolylidene ligands catalysed the reactions of primary alcohols and amines to imines and amides [21]. Ru and Pt metal complexes catalyzed amidation of nitriles [22,23], $[Rh(1,5\text{-cyclooctadiene})_2]BF_4$ catalyzed oxidative amination of aldehydes to give various aliphatic and aromatic amides [24]. $RhCl(PPh_3)_3$, $[Ir(Cp^*)Cl_2)]_2$, tributyltin hydride, Pd/C, $[PdCl_2(PMePh_2)_2]$ and $[Pd_2(\text{dibenzylideneacetone})_3]$ catalyzed conversion of aldoximes, alkynes and haloarenes to amides by utilising amines [26-30].

Several methods have been reported for the oxidative amidation using alcohols and amines as the starting materials [31-35]. Ruthenium complex based on 2-(di-tert-butylphosphinomethyl)-6-(diethylaminomethyl)pyridine ligand catalysed these reactions without acid or base promoters [36]. In situ generated complex from $[Ru(p\text{-cymene})Cl_2]_2$ or $[Ru(\text{benzene})Cl_2]_2$ with N-heterocyclic carbene and acetonitrile catalysed amide synthesis from alcohols and amines in high yields [37]. Ru complex with 1,3-diisopropylimidazol-2-ylidene in the presence of potassium tert-butoxide and tricycloalkylphosphine catalysed amidation from alcohols and amines [38]. These homogeneous catalytic systems have some disadvantages, such as they can be easily destroyed during the course of the reaction and cannot be recycled. Some heterogeneously metal catalyzed primary amide syntheses from primary alcohol have also been reported [39-42]. Polymer-supported palladium-N-heterocyclic carbene complex has been used as an efficient heterogeneous recyclable catalyst for coupling between aryl halides with alkyl/aryl isocyanides to give corresponding amides

[43]. A polymer-supported terpyridine-palladium(II) complex has been used for azidocarbonylation of aryl iodides with NaN_3 to yield primary aryl amides [44]. Heterogeneous Au and Au/Fe, Au/Ni or Au/Co catalysed oxidative amidation using molecular oxygen [45].

Since there are very few reports available for the oxidative amidation using polymer supported copper complex, an intriguing method of oxidative amidation was developed in the present work for promoting coupling of amines and benzyl alcohol in TBHP and water. This reaction proceeds in a clean economical manner without any acid, base or additives, and generates water and t-butanol as by-products. The use of water as solvent features many benefits such as improving reactivities and selectivities, simplifies the workup procedure and also environmental concerns. With increasing regulatory pressure focusing on organic solvents, the developments of nonhazardous alternatives are of great importance.

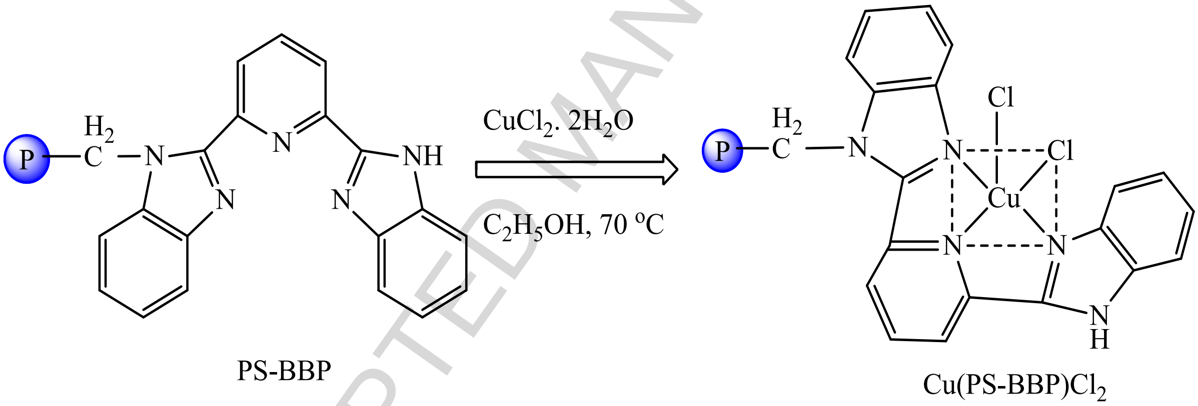
2. Experimental

2.1. Materials and methods

Chloromethylated polystyrene divinyl benzene (PS) was obtained as a gift from THERMAX Ltd. India. The $CuCl_2.2H_2O$, o-phenylenediamine, 2,6-pyridinedicarboxylic acid, TBHP (70%), benzene, ethylbenzene and cyclohexane were purchased from Merck and used without further purification. Solvents were used after purification by standard methods.
Elemental analyses were carried out with an Elementar Vario Micro Cube CHNS analyser. Diffuse reflectance UV-vis spectra were recorded as $BaSO_4$ disks on a Shimadzu UV-Vis-NIR model-3101P spectrophotometer. FT-IR spectra of solid compounds were taken using a Shimadzu 8,400 s FTIR spectrometer in the range of 4000-400 cm^{-1} using KBr disks. Thermogravimetric analyses was carried out with a TA instrument, SDT analyser model Q600. ESR measurements were carried out in the solid state at room temperature in a standard X band JES - FA200 spectrometer. The percentage of Cu in the supported complex was determined by using AAS, Avanta Pm, GF 3000. NMR spectra were recorded in $CDCl_3$ by using Bruker Avance spectrometer (^1H NMR at 500 MHz; ^{13}C NMR at 125 MHz). Tetramethysilane was used as reference, and the chemical shifts were reported in ppm. Spin multiplicities are described as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet) and br s (broad singlet).

2.2. Preparation of polymer supported complex Cu(PS-BBP)Cl_2 (Scheme 1)

2,6-bis(benzimidazolyl)pyridine (BBP) and functionalized polymer were prepared according to the literature methods [46, 47]. To the 1.0 g of functionalized polymer **(**PS-BBP), 10 mL of ethanol was added and kept for 1 h. To it, $CuCl_2.2H_2O$ (1 mmol; 0.17 g) in 10 mL of ethanol was added and stirred at 70 ºC for 48 h. The resulting green colored polymer supported complex was filtered, Soxhlet extracted with ethanol and dried for 24 h at 100 ºC.



Scheme 1. Preparation of the polymer anchored Cu(II) complex, Cu(PS-BBP)Cl_2.

3. Results and discussion

3.1. Characterization of Cu(PS-BBP)Cl_2

3.1.1. CHN analyses and AAS

Polymer supported complex Cu(PS-BBP)Cl_2 was synthesized by reacting PS-BBP with $CuCl_2.2H_2O$. The C, H and N% in Cu(PS-BBP)Cl_2 were found to be 86.8, 9.1 and 4.1%, respectively. The Cu in Cu(PS-BBP)Cl_2 was determined by AAS and was found to be 3.3%.

3.1.2. FT-IR and Electronic spectral studies

PS-BBP exhibited peaks due to ν(N-H) around 3190 cm^{-1} and the peak at 1623 cm^{-1} is assigned to ν(C=N) of benzimidazole/pyridine moieties in addition to polymer peaks. The IR spectrum of Cu(PS-BBP)Cl_2 displayed peaks due to ν(C=N) and ν(N-H) at 1612 and 3190 cm^{-1}, respectively. The shift of ν(C=N) peak in the supported complex as compared to PS-BBP indicated the coordination of copper through N of C=N moieties of pyridine and benzimidazole.

Electronic spectra of PS, BBP, PS-BBP and Cu(PS-BBP)Cl_2 complex are depicted in Fig. S1. The peaks in the range 200-334 nm are observed in free ligand as well as in the complex, and PS-BBP have been assigned to intraligand $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of benzimidazole groups. The electronic spectrum of the Cu(PS-BBP)Cl_2 complex showed two characteristic bands at 412 and 765 nm assigned to the dxz, dyz → dx^2-y^2 ($^2B_{1g} \rightarrow {}^2Eg$) and dxy → dx^2-y^2 ($^2B_{1g} \rightarrow {}^2B_{2g}$) transitions, respectively. Because of the low intensity of $dz^2 \rightarrow dx^2$-y^2 ($^2B_{1g} \rightarrow {}^2A_{1g}$) transition, this band is usually not observed as a separate band in the distorted square pyramidal complex.

3.1.3. TGA studies

Thermograms of Cu(PS-BBP)Cl_2 and PS were obtained at the heating rate of 10 °C min^{-1} under nitrogen atmosphere up to 550 °C. PS showed decomposition of 34% due to loss of chloride in the range of 279-410 °C and loss of polymer occurred above 410 °C. The thermal decomposition of Cu(PS-BBP)Cl_2 occured in three steps; first step involved the removal of two chlorides with weight loss of ~ 3.7% in the temperature range of 180-195 °C, while the second decomposition step occurred in the range 195-386 °C accompanied with a weight loss of ~ 20.1%, and which could be ascribed to the decomposition of BBP ligand. The polymer decomposed above 386 °C (Fig. 1).

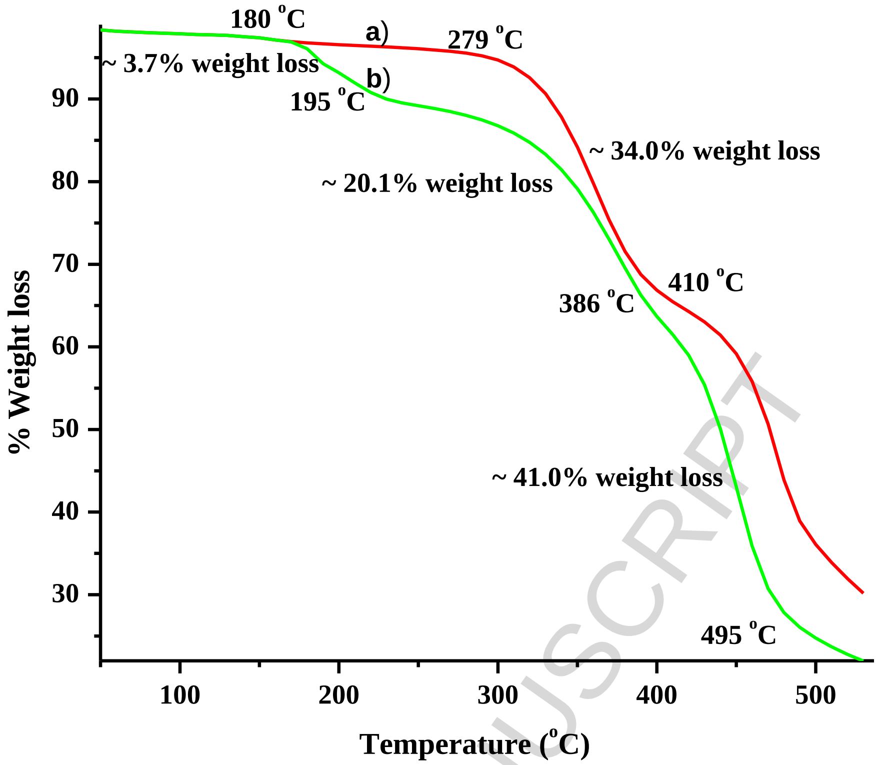


Fig. 1. Thermograms of a) PS and b) Cu(PS-BBP)Cl_2.

3.1.4. EPR and magnetic moment measurements

The EPR spectrum of Cu(PS-BBP)Cl_2 recorded in polycrystalline state at room temperature revealed the coordination environment around copper(II). The EPR spectrum of Cu(PS-BBP)Cl_2 displayed three g values at 2.49, 2.30 and 2.07 due to g_1, g_2 and g_3, respectively (Fig. 2). The value of $g_1 > g_2 > g_3 > 2.0023$ and the ratio of $g_2\text{-}g_1/g_3\text{-}g_2 = R$ was found to be 0.82. The values of $R < 1$ for the complex suggest a distorted square pyramidal geometry around Cu with $dx^2\text{-}y^2$ as the ground state. Room temperature magnetic moment of Cu(PS-BBP)Cl_2 was measured using a vibrating sample magnetometer (VSM). It exhibited a value of 1.74 BM, which is very consistent with the expected spin-only magnetic moment S = ½, d^9 copper (II) system.

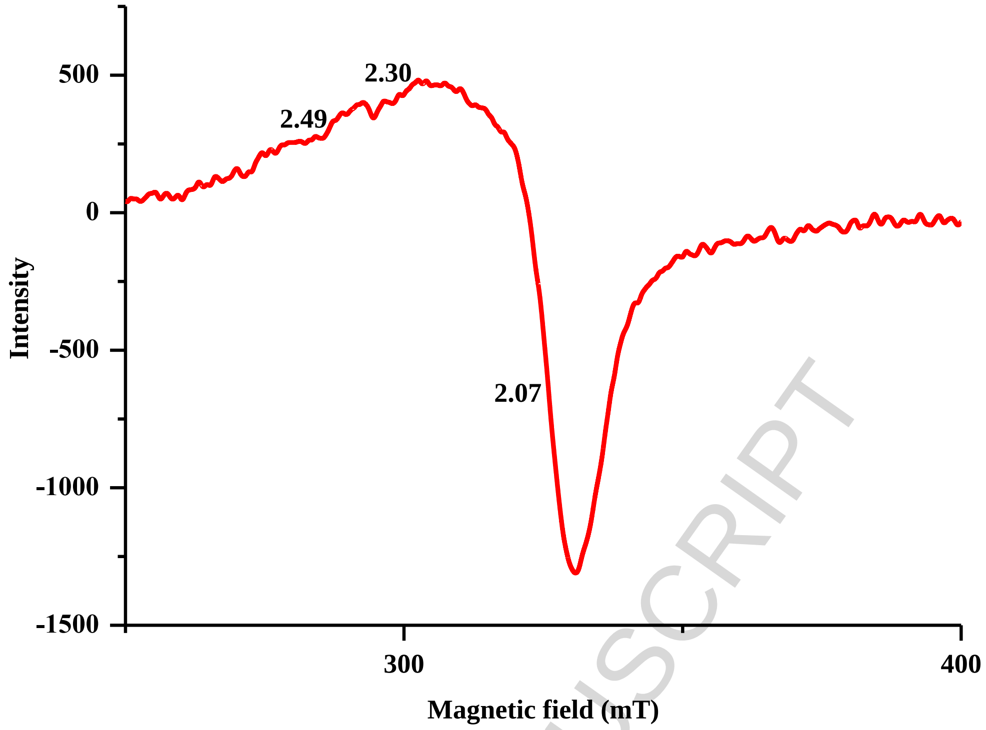


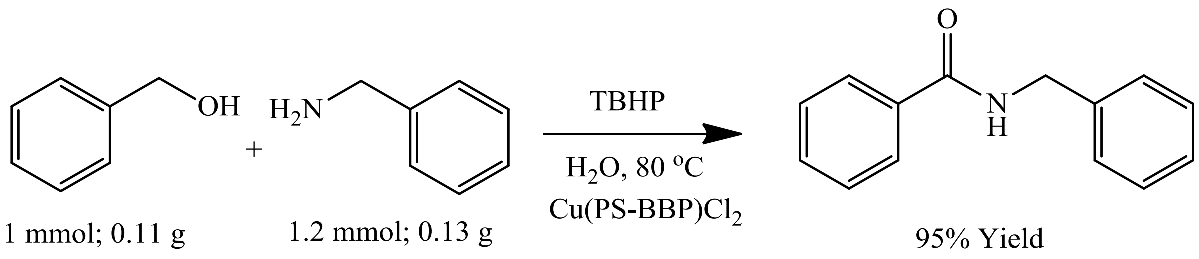
Fig. 2. X band EPR spectrum of Cu(PS-BBP)Cl_2 at room temperature.

Based on the above results, square pyramidal geometry was suggested for polymer anchored Cu(II) complex.

3.2. Catalytic activity measurements

3.2.1 General procedure for the preparation of amides

The reaction was carried out using 1 mmol benzyl alcohol, 1.2 mmol benzyl amine and 40 mg Cu(PS-BBP)Cl_2 (0.0210 mmol of Cu) in the presence of TBHP (2 mmol) in 2 mL of water at 80 °C for 10 h (Scheme 2). The reaction was monitored by TLC. The product was extracted with ethyl acetate and purified by column chromatography. The oxidative amidation of benzyl alcohol with benzyl amine was chosen as a model reaction to optimize the reaction conditions (Scheme 2).



Scheme 2. Oxidative amidation of benzyl alcohol and benzylamine.

To find out the optimum reaction conditions, the reaction was carried out by varying the temperature, solvents, substrate to oxidant ratio and the catalyst concentration (Table 1). The amidation reaction was carried out by varying the reaction temperature from 60 to 90 °C with 40 mg (0.0210 mmol) of Cu(PS-BBP)Cl_2 catalyst in 2 mL water for 10 h. The product yield increased with rise in temperature up to 80 °C (78% at 60 °C, 82% at 70 °C and at 80 °C, 95%) but after a further increase to 90 °C the yield of amide decreased to 79%. This might be due to the enhanced decomposition of TBHP at higher temperature. In acetonitrile (85%), tetrahydrofuran (60%), ethyl alcohol (89%) and 1:1 mixture of water and ethyl alcohol (92%), the conversion was lower than that in water (95%). Water being a highly polar molecule renders benzyl alcohol, amine and oxidant (70 % TBHP in water) soluble to give homogeneous clear solution, except polymer supported catalyst. This facilitates the insertion of TBHP into polymer supported Cu(II) complex.

The effect of oxidant concentration on reaction was monitored using three different amounts of aqueous 70% TBHP viz. 1, 2 and 3 mmol for a fixed amount of reactants (1 mmol of benzyl alcohol and 1.2 mmol of benzyl amine) and Cu(PS-BBP)Cl_2 (0.0210 mmol) in 10 mL H_2O at 80 °C. When the molar ratio of reactant to oxidant was 1:1, product yield was 48%. Reactions at 1:2 and 1:3 molar ratio gave same % of product (95%). These results suggest that 1:2 molar ratio of reactants to TBHP is ideal for the maximum yield. The reaction was carried out by varying four different amounts viz. 0.0104, 0.5157, 0.0210 and 0.0262 mmol of Cu(PS-BBP)Cl_2 at 80 °C using 1:2 molar ratio of substrate to TBHP. As 0.0210 mmol of catalyst gave maximum yield, this concentration was considered sufficient to carry out the reaction.

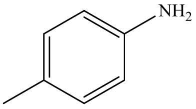
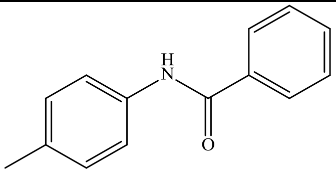
Table 1. Optimization of the reaction conditions.

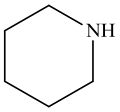
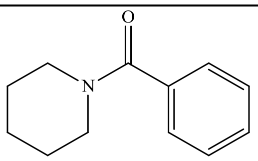
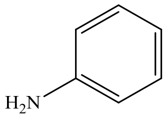
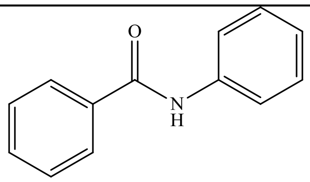
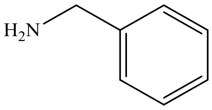
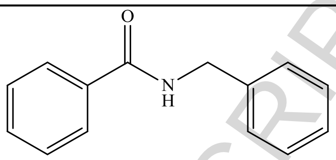
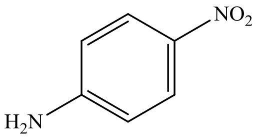
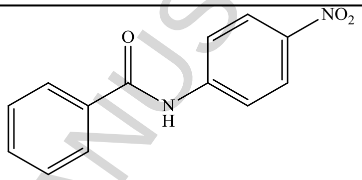
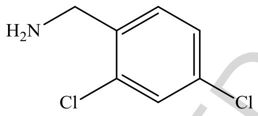
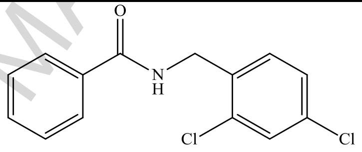
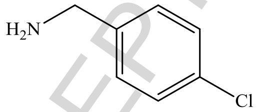
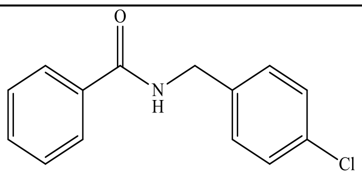
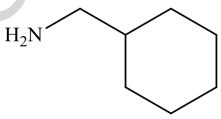
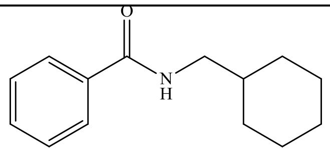
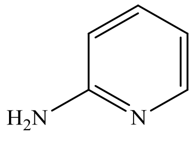
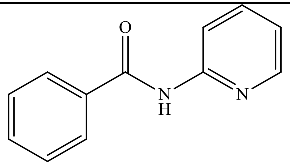
Entry	Temperature (°C)	Solvent	Substate:TBHP	Catalyst concentration (mmol X 10^{-2})	Yield (%)
1	60	H_2O	1:2	2.10	78
2	70	H_2O	1:2	2.10	82
3	**80**	**H_2O**	**1:2**	**2.10**	**95**
4	90	H_2O	1:2	2.10	89
5	80	CH_3CN	1:2	2.10	75
6	80	THF	1:2	2.10	80
7	80	$H_2O + C_2H_5OH$(1:1)	1:2	2.10	92
8	80	C_2H_5OH	1:2	2.10	89
9	80	H_2O	1:2	1.04	43

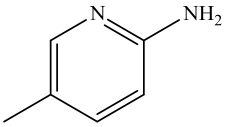
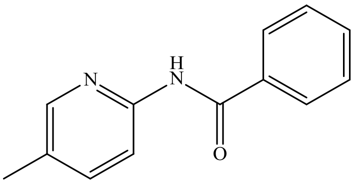
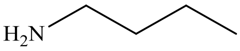
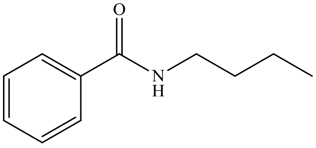
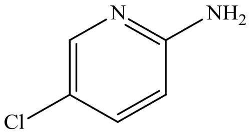
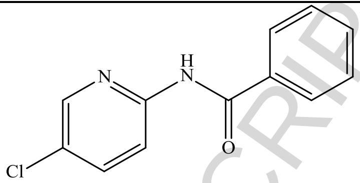
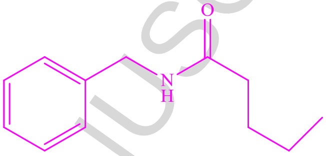
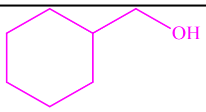
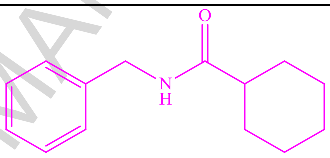
10	80	H_2O	1:2	1.57	73
11	80	H_2O	1:2	2.62	90
12	80	H_2O	1:1	2.10	48
13	80	H_2O	1:3	2.10	95

Thus, it was observed that with 1:2 molar ratio of substrate to TBHP, 0.0210 mmol Cu(PS-BBP)Cl_2, 2 mL water at 80 ºC in 10 h was the optimal reaction condition to afford the desired amide in good yield. When the blank reaction was carried out in the presence of reactants and TBHP without catalyst, even after 10 h, the yield was 10%. No amide formation was found in the absence of TBHP. Thus, it was concluded that Cu(PS-BBP)Cl_2 and TBHP were essential to obtain the desired amide product. By using this optimum reaction conditions, the reaction was carried out for different amines. It was found that the electron donating groups (Table 2, entries 1 and 10) on the aromatic ring substituted amines reacted more efficiently with benzyl alcohol than those with electron withdrawing groups (Table 2, entries 5-7 and 12). Secondary amines are poor substrates in this reaction, showing lower yield (Table 2, entry 2). The oxidative amidation was also conducted using aliphatic alcohols, such as pentanol, and cyclohexylmethanol, with the yield of benzylamineto be 68 and 72 %, respectively (Table 2, entry 13 and 14). Progress of the reactions was monitored by thin layer chromatography (TLC). Products were isolated by extracting the reaction mixture in ethyl acetate and purified by column chromatography and subjected to ^{1}H and ^{13}C NMR spectral analyses.

Table 2. Oxidative amidation of benzyl alcohol (1-12) with primary and secondary amines.

No.	Amines	Products	% Yield[a]
1			86

2			87
3			80
4			95
5			73
6			70
7			76
8			92
9			82

10			87
11			92
12			78
13^{b}			68
14^{c}			72

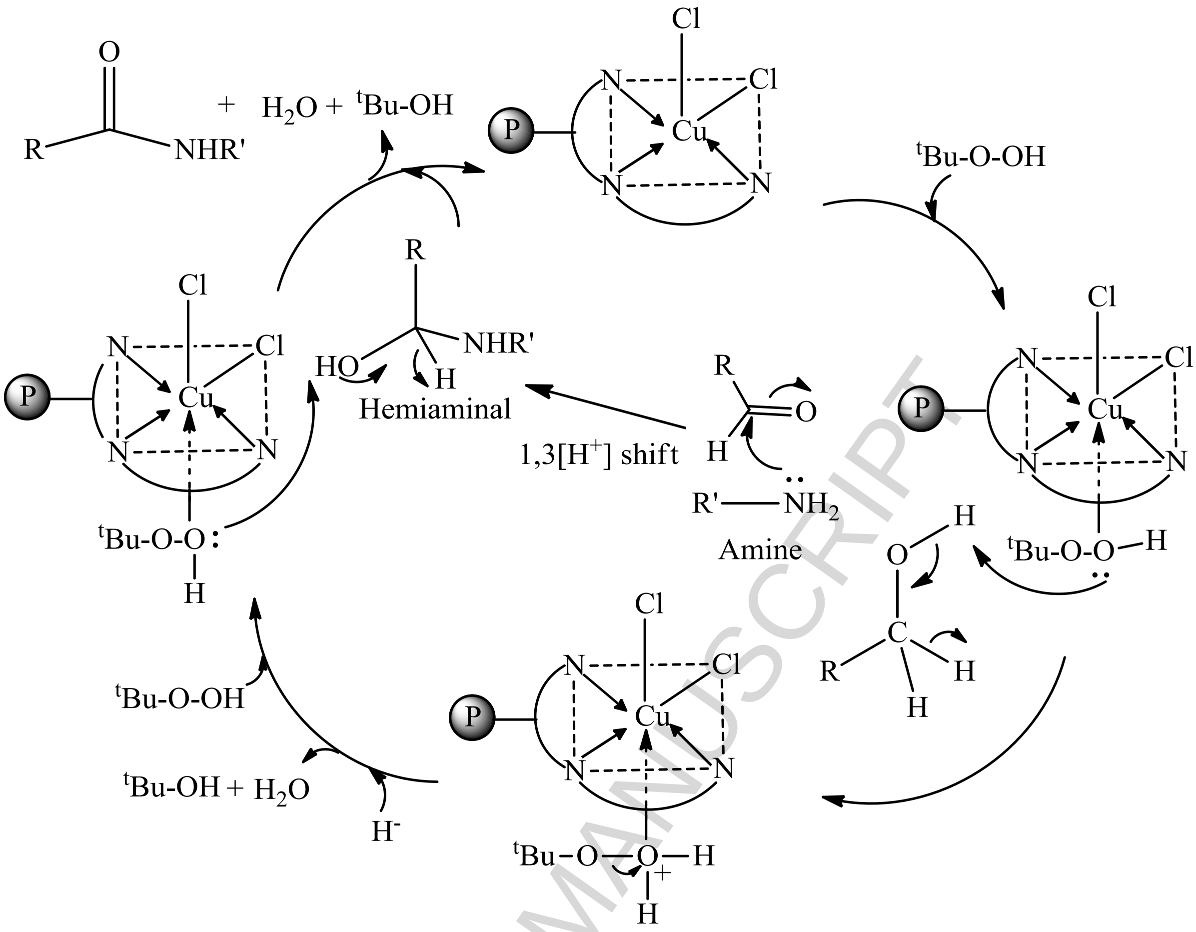
Reaction conditions: Benzyl alcohol (1 mmol), amine (1.2 mmol), Cu(PS-BBP)Cl$_2$ (0.0210 mmol), TBHP (2 mmol) in Water (2 mL) at 80 °C in 10 h . ^{a}Isolated yield.

b: Pentanol (1 mmol), benzylamine (1.2 mmol).

c: Cyclohexylmethanol (1 mmol), benzylamine (1.2 mmol).

3.3. Reaction mechanism

The non-free radical nature of this reaction was confirmed by the addition of a free radical inhibitor 2,6-di-t-butyl-4-methylphenol (BHT, 1 equiv) to the reaction mixture wherein amide formation was not inhibited. A tentative mechanism for the oxidative amidation by the coupling of an alcohol with an aromatic amine is expected to proceed via oxidation of the alcohol to an aldehyde and formation of an intermediate hemiaminal. Further oxidation of the hemiaminal would lead to the amide, with elimination of water and t-butanol (Scheme 3).



Scheme 3. A tentative mechanism for oxidative amidation.

3.4. ^{1}H and ^{13}C-NMR spectral data of amides

1. N-p-Tolylbenzamide

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.39 (s, 3H), 6.39 (br s, 1H), 7.21-7.29 (d, 2H), 7.30-7.36 (m, 5H), 7.69 (d, 2H). ^{13}C NMR (125 MHz): δ 21.49, 127.10, 127.50, 127.88, 128.74, 129.23, 131.58, 138.50, 141.93, 167.47.

2. Phenyl(piperidin-1-yl)methanone

^{1}H NMR (500 MHz, CDCl$_3$): δ 1.48-1.63 (br s, 6H), 3.30 (br s, 2H),), 3.67 (br s, 2H), 7.35 (s, 5H). ^{13}C NMR (125 MHz): δ 24.55, 25.59, 26.50, 43.06, 48.70, 126.73, 128.35, 129.29, 136.49, 170.24.

3. N-Phenylbenzamide

^{1}H NMR (500 MHz, CDCl$_3$): δ 6.50 (br s, 1H), 7.42-7.52 (m, 5H), 7.79-7.85 (m, 5H). ^{13}C NMR (125 MHz): δ 127.10, 127.50, 127.88, 128.74, 129.23, 131.58, 138.50, 141.93, 167.47.

4. N-Benzylbenzamide

^{1}H NMR (500 MHz, CDCl$_3$): δ 4.64-4.65 (d, 2H), 6.44 (br s, 1H), 7.26-7.32 (m, 5H), 7.35-7.36 (t, 2H), 7.41-7.51 (t, 1H), 7.79 (d, 2H). ^{13}C NMR (125 MHz): δ 44.24, 114.57, 125.02, 125.22, 135.50, 135.76, 147.13, 147.15, 149.21, 165.06.

5. N-(4-Nitrophenyl)benzamide

^{1}H NMR (500 MHz, CDCl$_3$): δ 6.45 (br s, 1H), 7.34 (m, 5H), 7.54-7.56 (m, 2H), 7.64-7.66 (m, 2H).^{13}C NMR (125 MHz): δ 126.77, 126.91, 127.97, 128.49, 131.42, 134.38, 135.46, 148.31, 167.26.

6. N-(2,4-Dichlorobenzyl)benzamide

^{1}H NMR (500 MHz, CDCl$_3$): δ 4.68 (d, 2H), 6.64 (br s 1H), 7.23 (dd, 1H), 7.45-7.40 (m, 4H), 7.51 (t, 1H), 7.77 (d, 2H). ^{13}C NMR (125 MHz): δ 41.32, 126.94, 127.24, 128.52, 129.23, 130.76, 131.64, 133.86, 133.91, 134.06, 134.23, 167.51.

7. N-(4-chlorobenzyl)benzamide

^{1}H NMR (500 MHz, CDCl$_3$): δ 4.60-4.62 (dd, 2H), 6.50 (br s, 1H), 7.26-7.32 (m, 4H), 7.41-7.45 (t, 2H), 7.49-7.52 (t, 1H), 7.78-7.79 (d, 2H). ^{13}C NMR (125 MHz): δ 44.24, 125.02, 125.23, 135.50, 135.76, 147.14, 149.21, 149.50, 151.18, 169.06.

8. N-(Cyclohexylmethyl)benzamide

^{1}H NMR (500 MHz, CDCl$_3$): δ 0.97-1.04 (q, 2H), 1.14-1.29 (m, 3H), 1.55-1.63 (m, 1H), 1.65-14.69 (m, 2H), 1.73-1.80 (m, 4H), 3.31 (t, 2H), 6.19 (br s, 1H), 7.43 (t, 2H), 7.49 (t, 1H), 7.75-7.77 (d, 2H). ^{13}C NMR (125 MHz): δ 28.93, 29.81, 31.32, 32.15, 47.00, 125.75, 128.23, 129.55, 135.62, 175.31.

9. N-(Pyridin-2-yl)benzamide

^1H NMR (500 MHz, $CDCl_3$): δ 6.45 (br s, 1H), 7.34-7.56 (m, 5H), 7.64 (m, 2H), 7.66 (m, 2H). ^{13}C NMR (125 MHz): δ 114.53, 114.57, 125.02, 125.22, 135.50, 135.76, 147.13, 149.21, 149.50, 167.06.

10. N-(5-methylpyridin-2-yl)benzamide

^1H NMR ($CDCl_3$, 500 MHz): δ 2.33 (s, 3H), 7.12-7.17 (m, 3H), 7.52 (br s, 1H), 7.59-7.61 (d, 1H), 7.67-7.69 (m, 2H), 8.38-8.43 (m, 1H). ^{13}C NMR (125 MHz): δ 19.36, 117.92, 120.08, 121.00, 123.90, 124.86, 125.75, 125.91, 131.28, 131.90, 165.86.

11. N-Butylbenzamide

^1H NMR (500 MHz, $CDCl_3$): δ 0.94-0.97 (t, 3H), 1.37-1.45 (m, 2H), 1.57-1.63 (m, 2H), 3.43-3.47 (m, 2H), 6.23 (br s, 1H), 7.27-7.43 (m, 2H), 7.47-7.50 (m, 1H), 7.75-7.77 (m, 2H). ^{13}C NMR (125 MHz): δ 13.67, 20.06, 31.63, 39.72, 126.80, 128.36, 131.11, 134.80, 167.53.

12. N-(5-Chloropyridin-2-yl)benzamide

^1H NMR (500 MHz, $CDCl_3$): δ 6.50-6.51 (m, 1H), 6.64 (br s, 1H), 7.15 (m, 1H), 7.16 (d, 1H), 7.26-7.36 (m, 4H), 7.42 (d, 1H). ^{13}C NMR (125 MHz): δ 126.94, 128.43, 128.79, 129.40, 129.93, 131.45, 133.44, 134.11, 135.53, 167.43.

13. N-benzylpentanamide

^1H NMR (500 MHz, $CDCl_3$): δ 0.91 (t, 3H), 1.62 (m, 2H), 1.34 (m, 2H), 2.20 (t, 2H), δ 4.41 (d, 2H), 5.97 (br s, 1H), 7.22-7.36 (m, 5H). ^{13}C NMR (125 MHz): δ 13.73, 19.11, 35.50, 38.57, 43.45, 127.38, 127.72, 128.60, 138.35, 172.90.

14. N-benzylcyclohexanecarboxamide

^{1}H NMR (500 MHz, $CDCl_3$): δ 0.96-1.03 (m, 2H), 1.13-1.29 (m, 2H), 1.54 (m, 1H), 1.59-1.80 (m, 6H), 3.29-3.31 (m, 2H), 6.19 (br s, 1H), 7.41-7.50 (m, 3H), 7.76 (m, 2H).^{13}C NMR (125 MHz): δ 25.76, 26.33, 30.85, 37.97, 46.16, 126.80, 128.43, 131.19, 134.86, 167.55.

3.5. Recycling ability

The recycling ability of the catalyst was also examined for the probe reaction under optimized reaction conditions. After the reaction, catalyst was filtered and dried in vacuum and reused for the oxidative amidation reaction. The %-yield remained almost constant up to three runs and slightly decreased for the fourth cycle. The recycled catalyst was subjected to AAS and the results indicated that metal complex was not leached out from the support (Fig. S2).

4. Conclusions

A Cu(PS-BBP)Cl_2 catalyst was synthesized and characterized and its activity was investigated towards oxidative amidation of benzyl alcohols with aromatic amine surrogates using TBHP in water. Both secondary and tertiary benzamides can be prepared without using any noxious reagents. The electronic effects of the substituent can also perturb the amidation reaction. The tolerance of the reaction to water creates the potential for the conversion of biomolecules. A plausible reaction mechanism for the oxidative amidation reaction was suggested. The catalyst showed excellent activity and recycled up to three runs.

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Highlights

- A novel polymer supported Cu(II) complex was prepared and characterized physico-chemical methods.
- Elegant method for the preparation of amides using TBHP as oxidant in water
- Non free radical mechanism was studied
- Catalyst was reused for three times