

COPPER OXIDE CATALYZED AMIDES FROM OXIDATIVE AMIDATION OF BENZYL AMINE, STYRENE, AND PHENYL ACETIC ACIDS WITH DMF AS AMINE SOURCE

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ABSTRACT

Hydrothermal-assisted Copper oxide (CuO) nanocatalyst, which is found to be an efficient heterogeneous catalyst for the synthesis of amides through oxidative amidation of benzyl amine, styrene, and phenyl acetic acid with DMF as an amine source, respectively. The prepared CuO was further investigated using XRD, FTIR, and TEM which resulting monoclinic structure with a 27 nm was formed without impurities. Various substituted benzyl amines, styrenes, phenyl acetic acids, and formamides are well amidation and afforded the various N, N-substituted benzamides in moderate to good yields. The synthesized CuO nanocatalyst showed high reactivity with significant reusability for the synthesis of amides.

Keywords: Copper Oxide, Oxidative Amidation, Benzyl Amine, Amides.

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INTRODUCTION

The production of amides is one of the vital tools in synthetic organic chemistry,¹ because amides are unique functional groups and well recognized by nature. Amides are prevalent intermediates in the synthesis of biological molecules, drugs, peptide synthesis, proteins, and natural products.² Recently, it has been reported that 50 % of all drug compounds have at least one amide bond linkage; during the drug discovery 16 16 16% of all reported reactions are amide bond formation.³ In addition, amides have revealed significant applications in several fields, including natural products, biomolecules, agrochemicals, functional materials, colour pigments for inks, lubricants, intensifier of perfume, and polymer synthesis.⁴ Due to their favourable applications of amides, a series of simple and efficient methods has been highly needed.⁵ Conventionally, amides are constructed by the coupling of amines with carboxylic acids and their derivatives.⁶ However, in the reaction process, highly amount of activated reagents was required for the activation of carboxylic acids, which led to lower atom economy. Other alternative synthetic approaches, including rearrangement of aldoximes,⁷ carbonylation of alkenes⁸ and alkynes,⁹ cross-coupling of formamides with organohalides,¹⁰ amidation of thioacids,¹¹ hydration of nitriles,¹² acylation of aldehyde and alcohols with amines,¹³ were also developed for the amides synthesis. Unfortunately, all these methods suffer from some limitations, such as the production of excessive waste, harsh reaction conditions, and less readily available starting substrates. In recent years, DMF has emerged as an attractive tool for amide synthesis because it offers an amine ($-NH_2$) source,¹⁴ and as well as it acts as a good precursor for $-CO$, $-CH_3$, $-O$, $-CO(NH_3)_2$. Moreover, many organic reactions were carried out with DMF used as a polar solvent.¹⁴ In this regard, DMF was well coupled with various starting substrates such as aldehydes, benzyl alcohols, carboxylic acids, and toluenes to afford the amides in moderate to good yields by the researchers.¹⁵ After literature survey, amidation of benzyl amines, aryl alkenes, and phenylacetic acids with DMF has been rarely reported. In continuation of our research work herein, we wish to propose a simple and efficient protocol for the synthesis of amides from direct amidation of benzyl amines, aryl alkenes, and phenylacetic acids with DMF in the presence of copper as a nanocatalyst at 90 °C.

EXPERIMENTAL

All of the compounds were commercial grade and used without further purification. Organic extracts were dried over anhydrous Na_2SO_4 . Solvents were removed in a rotary evaporator under reduced pressure. Silica

gel (100–200 mesh size) was used for the column chromatography. Reactions were monitored by TLC on silica gel 60 F254 (0.25 mm). NMR spectra were recorded in DMSO-*d*₆ with tetramethyl silane as the internal standard for proton NMR (400 MHz) and DMSO-*d*₆ solvent as the internal standard for ¹³C NMR (100 MHz). LC-MS spectra were recorded using ESI mode. IR spectra were recorded in KBr pellets.

Preparation and Characterization of Nanocatalyst

The nanocatalyst Copper oxide (CuO) was obtained from a sonochemical approach using copper acetate as precursor. In brief, 100 mL of 0.25M [Cu(CH₃COO)₂] was stirred for 15 minutes, followed by the addition of 100mL NaOH (0.1M) and was further stirred for 30 min. A pinch of sodium borohydride was added to the reaction mixture and allowed to stir for 30 min. Then this mixture was transferred into Teflon-lined stainless steel and hydrothermally heated in an autoclave at 180 °C for 24h. The dark precipitate was formed as CuO, which was washed thoroughly with water and ethanol finally dried in a vacuum at room temperature. Further, the studies were conducted on a prepared nanocatalyst using XRD, TEM, and FTIR.

RESULTS AND DISCUSSION

Figure-1 shows the XRD pattern, shown corresponds to CuO, displaying characteristic peaks at specific 2θ values of 36°, 39°, 49°, and 63°. These peaks can be indexed to the (002), (111), (220), and (311) planes, confirming the crystalline nature of CuO and its monoclinic structure, which was compiled with standard JCPDS (File No. 45-0937).¹⁶ There were no impurity peaks observed for CuO NPs. The average crystallite size of *as*-prepared CuO NPs was calculated by the Debye-Scherrer equation ($k\lambda/\beta\cos\theta$) and found to be 27.62 nm.

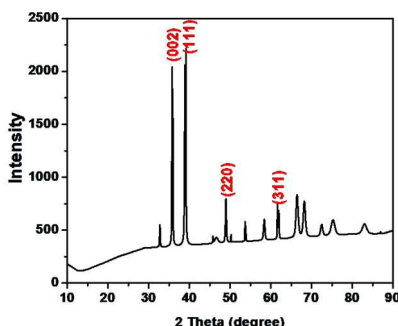


Fig.-1: XRD Patterns of Prepared CuO NPs

As shown in Fig.-2, the FTIR spectrum of CuO shows characteristic absorption bands that confirm the formation of CuO. Peaks at around 621 cm⁻¹, 586 cm⁻¹, and 536 cm⁻¹ correspond to the Cu–O stretching vibrations, indicative of CuO's monoclinic structure.¹⁶⁻¹⁷ The broad absorption in the 3500–3000 cm⁻¹ range corresponds to O–H stretching vibrations, likely due to adsorbed water or hydroxyl groups on the surface.¹⁷

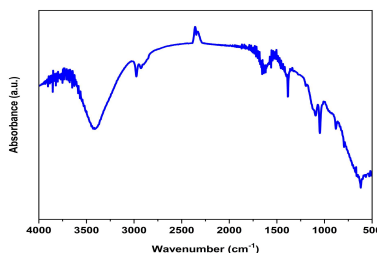


Fig.-2: FTIR Spectrum of Prepared CuO NPs

Figure-3 displays the TEM images that represent the morphology of synthesized CuO nanoparticles. The image on the left, at a scale of 500 nm, highlights the dispersed, well-defined nanostructures, indicating uniform particle distribution. The CuO nanoparticles exhibit irregular, quasi-spherical shapes with clear boundaries. The image on the right, at a higher magnification (100 nm scale), provides insights into the surface texture, showing agglomerated structures likely due to interparticle interactions. This aggregation could be attributed to the intrinsic high surface energy of CuO nanoparticles.¹⁷

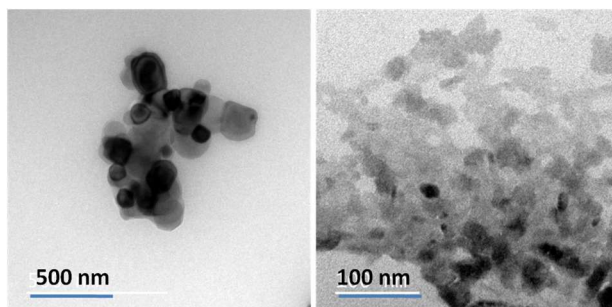
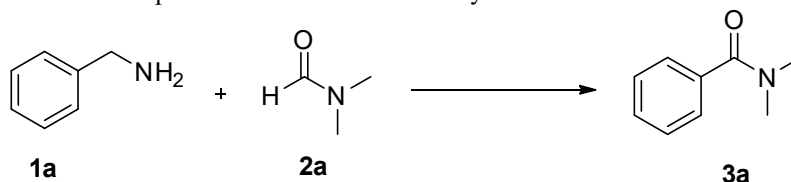


Fig.-3: TEM Images of Prepared CuO Nanoparticles

Synthesis of Amides and Their Derivatives

The optimized conditions for this reaction were determined using alkene (1a) and *N,N*-dimethylformamide (2a) as model substrates. Initially, 1a was reacted with 2a in the presence of 5 mol% TBAI as a catalyst and 3 equivalents of TBHP as an oxidant at 90 °C for 15 hours, yielding the corresponding product 3a in 34% yield (Table-1, entry 1). Various catalysts, including a, b, and c, were screened for improved efficiency (Table-1, entries 2–4). Subsequently, other oxidants such as DTBP, TBPB, *m*-CPBA, and $K_2S_2O_8$ were evaluated. Among these, TBHP was identified as the most effective oxidant, providing a moderate yield (Table-1, entries 2–5). When the catalyst loading was increased to 10 mol%, the yield of product 3a improved to 64% (Table-1, entry 6). Notably, increasing the catalyst loading to 20 mol% resulted in a significant improvement, yielding 3a in 91% (Table-1, entry 7). However, further increasing the catalyst loading to 25 mol% did not lead to a substantial improvement in yield (Table-1, entry 8). These results indicate that 20 mol% of TBAI is optimal for this reaction.

Table-1: Optimized Conditions for the Synthesis of Amides



S. No	Catalyst (mol% %)	Oxidant (Eq.)	Temperature (T °C)	Yields ^a (%)
1	TBAI (5)	TBHP (3)	90	34
2	TBAI (5)	DTBP (3)	90	Trace
3	TBAI (5)	TBPB	90	Trace
4	TBAI (5)	<i>m</i> -CPBA	90	Trace
5	TBAI (5)	$K_2S_2O_8$	90	15
6	TBAI (10)	TBHP	90	64
7	TBAI (20)	TBHP (6)	90	93
8	TBAI (25)	TBHP	90	87
9	TBAI (20)	TBHP (5)	90	85
10	TBAI (20)	TBHP (2)	90	71
11	TBAI (20)	TBHP (3)	100	88
12	TBAI (20)	TBHP (3)	120	83
13	TBAI (20)	TBHP (3)	130	81
14	TBAI (20)	TBHP (3)	150	74
15	TBAI (20)	----	90	Trace
16		TBHP (3)	90	Trace

^aReaction conditions: benzyl amine 1a (1.8 mmol), *N,N*-Dimethylformamide (4 ml), catalyst (20 mol% %), oxidant (3eq.) at 90 °C for 15 h. Isolate yields

To further enhance the reaction yield, the oxidant quantity was increased to 5 equivalents; however, this resulted in unsatisfactory yields (Table-1, entry 9). Similarly, reducing the oxidant quantity to 2 equivalents led to a lower yield of the product (Table 1, entry 10). The influence of temperature on the reaction was

also investigated (Table-1, entries 11–14), revealing that higher temperatures resulted in decreased yields. No reaction was observed in the absence of either the catalyst or the oxidant (Table-1, entries 19–20). Based on these findings, the optimized reaction conditions were established as follows: 1.8 mmol of benzylamine (1a), 4 mL of N, N-dimethylformamide (2a), TBAI (20 mol%), and TBHP (3 equivalents) at 90 °C for 15 hours.

Moreover, a series of solvents were tested for better performance on reaction yield (Table-2, Entries 1-5). Unfortunately, DCE, Toulene, EtOH, and H₂O were not giving satisfactory yields (Entries 2-5). However, CH₃CN furnished a reasonable yield then to other solvents (Entry 1).

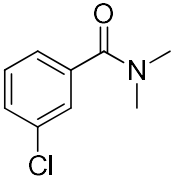
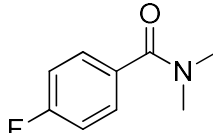
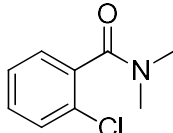
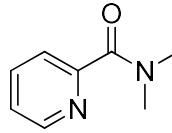
Table-2: Solvent Screening

S. No.	Solvent	Yields
1	CH ₃ CN	67
2	DCE	45
3	Toulene	42
4	EtOH	11
5	H ₂ O	Trace

With optimized conditions in hand, we started to investigate the scope of the reaction between various benzyl amines and DMF; all results are summarised in Table-2. Initially, neutral benzyl amine 1a was easily reacted with DMF and provided the N, N-dimethyl benzamide 3a in 94% good yield (Table-2, 3a). Benzyl amine bearing electron-donating groups such as *p*-methyl, *p*-methoxy, *m*-methyl, and *m*-methoxy substrates could be coupled with DMF to deliver the desired products in good yields (Table-3.3c,3d, 3f, and 3g). While *o*-substituted benzyl amines furnished the respective products in 83% and 82% yields (Table-3, 3b-3e). Encouraged by these results, we tested several halogen-substituted benzyl amines, such as -Cl and -F, were produced the amide products in moderate yields (Table-3, 3h-3k). But, chlorine *ato*-position of benzyl amine is slightly involved in the reaction and delivers the corresponding product in a lower yield than *meta* and *para*-substituted reactants (Table-3, 3k). Hetero aryl methyl amine could be efficiently converted to the desired amide product in 88% yield (Table-2, 3l).

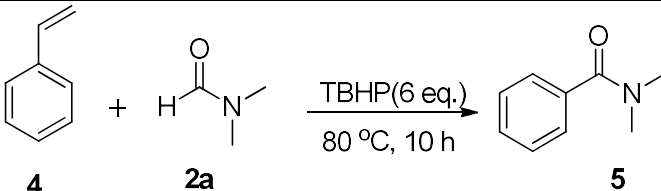
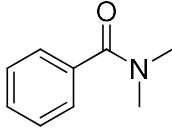
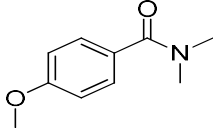
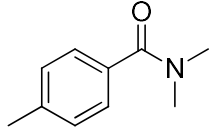
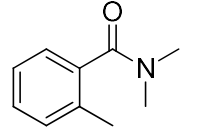
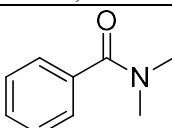
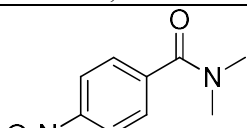
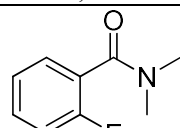
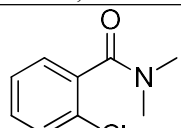
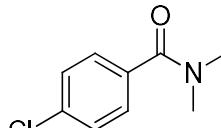
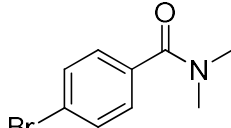
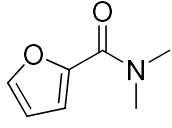
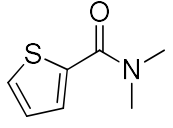
Table-2: Amidation of Various Benzylamines with DMF

3a, 91%	3b, 83%	3c, 88%	3d, 85%
3e, 82%	3f, 86%	3g, 84%	3h, 79%

 3i, 76%	 3j, 83%	 3k, 72%	 3l, 88%
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Further, we extended the scope of this method to a series of alkenes were tested for amides synthesis (Table-3). Alkene has different electron natures of functional groups on aromatic ring, which undergoes Amidation with moderate to good yields. With electron-rich (methyl and methoxy) groups at *para*/*meta*/*ortho* positions of the aromatic ring of alkene smoothly coupled and afforded their amide products in good yields (Table-3, 5b-5e). Strong electron deactivating substituent-nitro provided the corresponding product in lesser yield (Table-3, 5f). Halogen functional groups at *ortho*-position resulted in comparatively lesser yields of products than *para*-substituted alkene, due to the steric crowding (Table-3, 5g-5j). Furthermore, hetero aryl alkenes smoothly converted to their respective products in good yields under the optimized conditions (Table-3, 5k-5l).

Table-3: Substrate Scope of the Various Alkenes

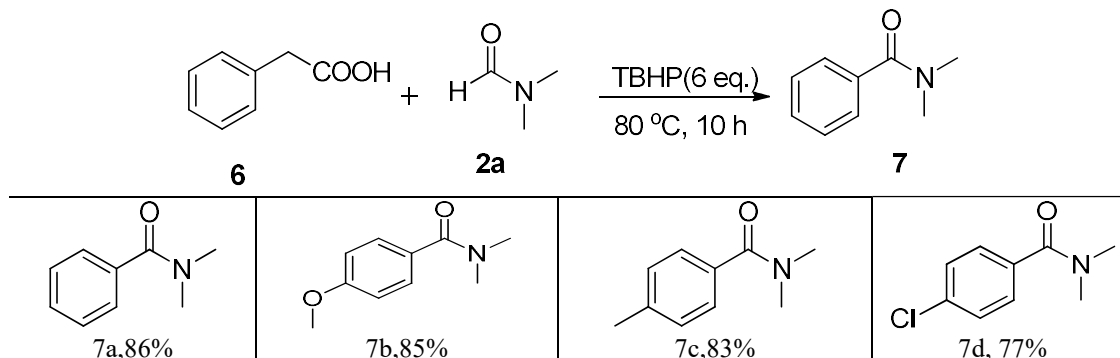
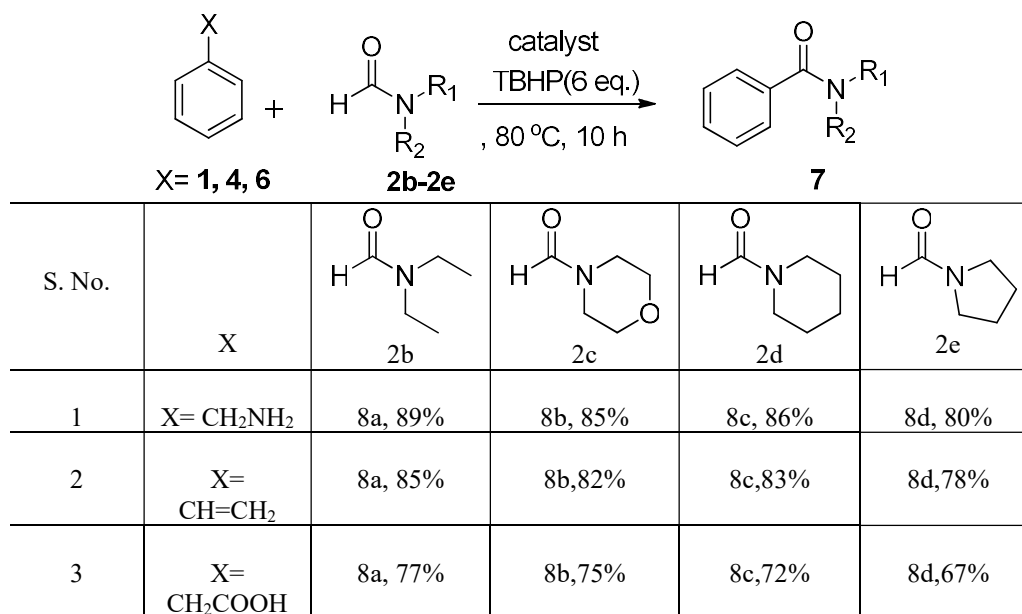
			
 5a, 88%	 5b, 87%	 5c, 84%	 5d, 80%
 5e, 85%	 5f, 63%	 5g, 69%	 5h, 66%
 5i, 73%	 5j, 75%	 5k, 85%	 5l, 83%

Next, we also studied the reactivity of various phenyl acetic acids for the synthesis of amides under the above-optimized conditions. To our delight, all phenyl acetic acids were well amidation with DMF, affording the corresponding amide products in satisfactory yields (Table-4). Methoxy and methyl-substituted phenyl acetic acids were smoothly involved in amidation reaction, and the corresponding products were obtained in good yields (7b-7c). As well as, reaction with *p*-cl acids was compatible with DMF under optimized conditions, the respective amide product in moderate yield (7d).

After successfully synthesizing *N,N*-dimethyl benzamides from benzyl amine, alkenes, and phenyl acetic acids. Further, we extended this method to investigate the scope and limitations of various *N*-substituted formamides. *N,N*-diethyl formamide (2b) and cyclic secondary formamides (2c-2e) acted as an amino source, afforded the corresponding *N,N*-substituted benzamides in moderate to good yields (Table-5, 8a-

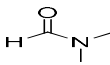
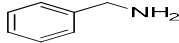
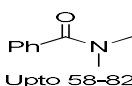
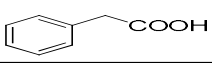
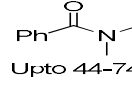
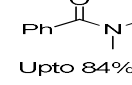
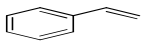
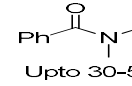
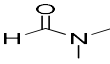
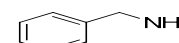
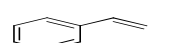
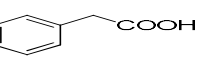
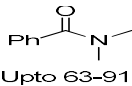
8d). The oxidative amidation of benzyl amine and aryl alkene with *N*, *N*-ethyformamide and cyclic secondary formamides delivered the corresponding products up to 78-89% good yields (Table-5, entry 1-2). Phenyl acetic acid produced the corresponding product in low yield compared to benzyl amine and aryl alkene (Table-5, entry 3).

Table-4: Substrate Scope of the Various Phenyl Acetic Acids

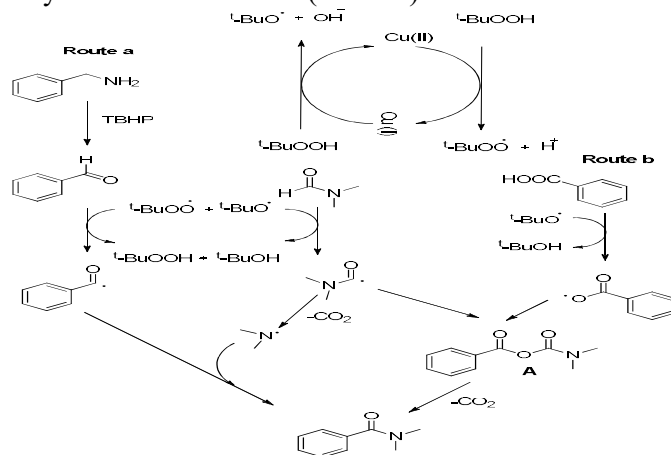
Table-5: Synthesis of Various *N*-substituted Formamides

Other hand, we investigated the comparative study between the present synthesised heterogeneous catalyst and various previously reported catalysts for the synthesis of *N*, *N*-substituted benzamides from the benzyl amine, aryl alkene, and phenyl acetic acid with DMF (Chart 1). In recent years, benzyl amine was Amidation with DMF in the presence of various catalysts, such as I₂,¹⁸ afforded the corresponding amide products up to 58-82% yields, and Cu-Fe based nano catalyst¹⁹ furnished the amides up to 44-74% yields (Chart 1, a,b). In 2013-year, copper catalyst gave the corresponding amide products up to 84% yields from oxidative Amidation of phenyl acetic acid with DMF (Chart 1, c).²⁰In last year, styrene coupled with DMF the desired amide products formed in 30-52% limited yields by the employing an orderedmesoporous HKUST-1-CuO as a heterogeneous catalyst (Chart 1, d).²¹Allthe above established methods clearly showed that the production of amide products in limited yields. The present synthesized CuO nanocatalyst showed the highest reactivity with substrates, affording the amide products up to yields comparable to CuO (Chart 1, e).

Chart-1: Comparison Study for the Reaction of Benzyl Amine, Phenyl Acetic Acid, and Aryl Alkene with DMF by Employing Various Catalysts

R1	R2	Catalyst	Product & yield	Reference
Previous methods				
		a) I ₂	 Upto 58-82%	16
		b) Cu-Fe MO	 Upto 44-74%	17
		c) Cu(ClO ₄)·6H ₂ O	 Upto 84%	18
		d) HKUST-1-Cu	 Upto 30-52%	19
Prasent method				
e) 	  		 Upto 63-91%	This work

Based on the earlier reports,²¹ the plausible mechanism of this reaction was shown in Scheme-2. Initially, benzylamine was oxidized and converted to benzyl aldehyde in the presence of tetrabutyl hydrogen peroxide. After, *t*-butoxyl and *t*-butylperoxyl radicals abstract the protons from the generated benzyl aldehyde and DMF, forming an acyl radical and aminyl radicals. Finally, these two radicals were cross-coupling with each other to deliver the corresponding amide product (Route a). Styrene was provided with the aldehyde by the *in situ* oxidative reaction in the presence of TBHP; it was again oxidised with NANO/TBHP, forming an acid derivative. After, carbamic anhydride intermediate A was formed by the coupling of radical 1 and radical 2, respectively. Finally, the formation of amide derivatives by the loss of CO₂ from the carbamic anhydride intermediate A (Route b).



Scheme-2: A Plausible Reaction Mechanism for the Amides from Benzyl Amines, Aryl Alkenes, and Phenylacetic Acids in the Presence of Copper Catalyst

CONCLUSION

In conclusion, CuO nanoparticles were obtained through a hydrothermal approach, and analytical instruments were used to characterize their properties. Further, we have developed a new efficient method for the synthesis of amides in the presence of CuO nanocatalyst *via* oxidative amidation of benzyl amine, styrene, and phenyl acetic acid with DMF as an amine source. Various benzyl amines, styrenes, phenyl

acetic acids, and formamides were involved in an amidation reaction afforded the different N, N-substituted benzamides in moderate to good yields. The synthesized CuO nano catalyst showed high reactivity with significant reusable for six times for the synthesis of amides.

CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

The present work is related to *SDG-9: Industry, Innovation and Infrastructure*. All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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