RESEARCH ARTICLE

Microwave-assisted facile synthesis of propargylamine library by robust nitro functionalized cross-linked polystyrene resin supported Cu NPs

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Abstract

In the present investigation, we study catalytic activity of copper nanoparticles stabilized onto a nitro functionalized polystyrene resin (Cu NPs@ Nitro-Resin). The size of stabilized copper nanoparticles was found between 3 and 9 nm. This work reports a cost-effective and sustainable protocol for the synthesis of propargylamines. Herein, we have developed microwave-assisted synthesis of propargylamine from 3 components coupling of aldehyde, alkynes, and amines (A^3 coupling) in truly heterogeneous catalytic system. Reaction parameters, such as solvent, catalyst concentration reaction time, and recyclability, were investigated, and reaction conditions were optimized. The present method has advantages such as environmentally benign, ease to handle, short reaction time (≈ 25 min), excellent yields (98%), low E-factor (0.15), and high atom economy (94%).

KEYWORDS

A³ coupling, microwave heating, nanocatalysis, propargylamines, resin supported nanoparticles

1 | INTRODUCTION

In the 21st century, there has been an increased awareness towards green chemistry approach to synthesize of important organic moieties. The need for developing sustainable reaction protocols with state-of-the-art use of technology, alternate reaction media, energy saving, waste minimization, etc has become vital. One such technique that has gained attention is synergistic use of microwave reactors and nanoparticles as catalyst. In the last few decades, microwave radiation in synthetic organic chemistry became popular and attracted considerable practical and theoretical attention along with the development of resource friendly and environmentally benign processes in terms of sustainable chemistry.^[1,2] Although use of homogeneous and heterogeneous catalysts is common under microwave heating, there are some important parameters that need to be looked

carefully. During the reaction process, there is not only usual agglomeration and Ostwald ripening of nanoparticles but also increased chances of sintering and hot spot development even at low temperature as metal nanoparticles are efficient absorbers of microwave. So careful choice of solvents, supports, reaction temperature, etc needs to be evaluated.^[3-6]

Transition metal catalyzed multicomponent reactions are a powerful synthetic strategy to generate multiple molecular scaffolds and to increase structural as well as skeletal, diversity from simple and readily available molecules.^[7] Three components coupling of aldehyde, alkynes, and amines (A³ coupling) is one of the best examples of such a process, and this transformation has received much more attention in recent year. Propargylamine scaffolds show remarkable biological activity and are used in drugs such as rasagiline, a potent cardiovascular drug.^[8] Besides, they also act as enzyme inhibitors,^[9] antitumor,^[10] antibiotics,^[11] herbicides,^[12] and pharmaceutical agents.^[13] They are also useful as intermediate such as peptide isosters, oxotremorine analogues, β -lactams natural products, therapeutic drug molecules, and polyfunctional amino derivatives in organic synthesis as well as some drug molecules.^[14] One of the general and traditional ways of synthesizing propargylamine is through the amination of propargylic halides, propargylic phosphonates, or propargylic triflates and the nucleophilic addition of in situ generated metal acetylides to imines and enamines. However, all these methods require stoichiometric amounts of reagents that are highly moisture sensitive, poor atom economy, corrosive, generate large amounts of waste and require tedious workup during the reaction.^[15–20]

Recently, different homogenous catalysts such as CuCl,^[21] CuBr,^[22] CuI,^[23] Cu (I) PF₆-ligand,^[24] CuCl₂,^[25] Fe-I₂-CuBr,^[26] and Cu (I) pybox complex^[27] have been successfully used for the synthesis of propargylamine. However, to overcome disadvantages associated with homogenous catalysts such as poor recycling, stability, and handling in high scale industrial synthesis of propargylamine, heterogeneous catalysts have also been designed.^[28-44] They too consistently suffer from several problems such as sintering and Ostwald ripening. Tu et al reported an efficient tool to synthesize propargylamine under microwave irradiation by using CuI catalyst.^[45] Recently, Ermolatev et al have reported a microwaveassisted decarboxylative coupling of a 2-oxaacetic acid, an amine, and an alkyne to afford polysubstituted propargylamine by using CuBr as catalyst. However, the main disadvantage associated with both these methods is that it requires high amount of catalyst (15 mol%) and the recyclability issues of homogeneous catalyst could make this protocol less sustainable and accessible.^[46] Recently, Xiong et al have developed ovster shell waste supported CuCl₂ catalyst and investigated its activity towards A³ coupling under the microwave irradiations. Nevertheless, the issues of recyclability again reduced the adaptability of this catalyst.^[47] In our recent report, we reported the synthesis and characterization of copper nanoparticles stabilized onto a novel nitro functionalized polystyrene resin (Cu NPs@ Nitro functionalized Resin) and investigated its catalytic activity towards the C-N coupling of various aromatic amines with aryl halides and the oxidative C-C homocoupling of phenyacetylene.^[48] In the present investigation, we studied the feasibility and sustainability of this catalyst for the synthesis of propargylamine under microwave heating. The effect of various reaction parameters such as solvent, temperature, reaction time, catalyst quantity, etc was studied on the yield of products. To assess the generality of the protocol, we tested many substituted derivatives of aldehydes and phenyl acetylenes and analyzed the products by ¹H-NMR.

2 | RESULT AND DISCUSSION

The use of nanocatalysts has been rapidly increasing owing to their extraordinary efficiency as well as selectivity. In the past several years, supported metal nanoparticles have appeared as sustainable replacements to conventional homogeneous catalyst as they combine the ease of catalyst separation with high catalytic activity. The availability of, supported transition metal nanoparticles, has attracted excessive consideration because of their remarkable catalytic activity. The ideal supported nanocatalyst should be accessible, leach proof, stable, and highly recyclable.^[49] It is well known that the insoluble resins have been probably the most frequently used polymeric supports in heterogenous catalysis. Organic polymers, especially polystyrene-type resins, represent one of the most popular commercialized supports. As compared to some other supports used for the stabilization of active metal nanoparticles, polystyrene resin is a good candidate because of its commercially availability with low price. Its chemical and thermal stability, high surface area, inert nature, reusability, mechanical robustness, and plain filterability under microwave as well as conventional heating.^[50-53] In addition, the metal nanoparticles are highly stabilized in the polystyrene resin because of the electrostatic stabilization and steric stabilization. Supporting copper nanoparticles on polystyrene resin beads was performed in a 2-step process reported earlier by our group.^[48] High-resolution transmission electron microscopy (TEM) images indicated that the copper nanoparticles present in the interior of polymeric matrix of the polystyrene resin were of 3 to 9 nm dimension (Figure 1A). Copper loading on the resin as measured by atomic absorption spectroscopy was 0.21 mmol per gram of the resin. An X-ray photoelectron spectroscopy study was also performed to know the oxidation state of active sites in the catalyst. The high-resolution X-ray photoelectron spectroscopy of Cu 2p indicates the presence of a peak at 940 to 945 eV that is a characteristic of Cu^{+2} , mainly due to the formation of CuO. The presence of lower Cu 2P_{3/2} binding energy peaks (933 eV) indicated the presence of Cu(0) (Figure 1C). The stabilized copper nanoparticles present into the resin beads were of Cu(0) and Cu^{+2} state.

2.1 | Catalytic activity

Our initial investigation on the evaluation of the catalytic activity started with the coupling reaction of benzaldehyde, piperidine, and phenyl acetylene under microwave irradiation as model reaction (Scheme 1).



FIGURE 1 A, Transmission electron microscopy images of Cu NPs@ Resin. B, Histogram of Cu NPs@ Resin. C, High-resolution X-ray photoelectron spectroscopy of Cu 2p



100°C MW (100W), 25 min

The performance of metal supported heterogeneous catalysts in organic reactions mainly depends upon the accessibility of catalytic sites, which in turn depends on the choice of support material, the polarity of substrate, and solvents. To investigate the effect of solvent on the performance of reaction, the model reaction was performed in the presence of Cu NPs@ Nitro-Resin catalyst in different solvents such as toluene, acetonitrile, ethanol, *N*,*N*-dimethylformamide, dimethyl sulfoxide, 1,4 dioxane, and water. The results are shown in Table 1. The best yield of propargylamine (98%) was achieved in case of toluene. This can be attributed to the better swelling of resin in toluene and its nonreactive nature that decreases side reactions. We also tried solvent-free synthesis of

TABLE 1 Effect of solvents on synthesis of propargylamine using
 Cu NPs@ Nitro-Resin

Entry	Solvents	Yield, %
1 ^a	Toluene	Trace
2	Water	Trace
3	Ethanol	24
4	DMF	50
5	1,4 Dioxane	25
6	Acetonitrile	85
7	Toluene	98

Reaction condition: benzaldehyde (1 mmol), piperidine (1 mmol), phenyl acetylene (1.15 mmol), 180 mg catalyst (3.78 mmol% of Cu), 100°C, microwave (100 W), 25 min, solvent (1 mL).

propargylamine, but the resins beads were stuck on the surface of reaction vessel, and poor yield of product was obtained.

It was found that temperature has a prominent effect on synthesis of propargylamine. In our model reaction, the synthesis of propargylamine was conducted at different temperatures ranging from 60°C to 100°C shown in Figure 2. From the results, we have found that the yield of propargylamine increases significantly from 27% to 98% as temperature was raised from 60°C to 100°C. Thus,



FIGURE 2 Screening of temperature for the synthesis of propargylamine conditions: benzaldehyde (1 mmol), piperidine (1 mmol), phenyl acetylene (1.15 mmol), 180 mg catalyst (3.78 mmol% of Cu), 1 mL toluene, microwave (100 W), 25 min

100°C was selected as the optimum temperature to afforded higher yield of propargylamine (98%), and the effect of other important parameters such as quantity of catalyst, reaction time, and effect of solvents was studied at this temperature.

To ascertain the yield of propargylamine, reaction mixture was analyzed at intervals of 5 minutes. The reaction was quenched at different intervals of time and product isolated. The report indicates that after 5 minutes, the yield of propargylamine was 15%, which increased to 98% in 25 minutes. A time-verses-yield graph is shown in Figure 3.

The presence of catalyst was necessary for the progress of the reaction as in its absence trace amount of propargylamine formed (Table 1). To study the effect of catalyst concentration on reaction rate, we changed the amount of catalyst from 80 to 180 mg while keeping other parameters constant (Figure 4). As the quantity of catalyst increased from 80 to 180 mg, the yield of propargylamine enhanced up to 98%. Therefore, 180 mg of catalyst was sufficient to afforded high yield (98%) of propargylamine.

2.2 | Scope of different aldehydes and acetylenes for the synthesis of propargylamine

The generality of the protocol or substrate scope for the synthesis of propargylamine was also investigated. Under the optimized reaction conditions, different derivatives of propargylamine could be synthesized. The results are shown in Tables 2 and 3. To our delight,



FIGURE 3 Screening of time on the synthesis of propargylamine. Reaction conditions: benzaldehyde (1 mmol), piperidine (1 mmol), phenyl acetylene (1.15 mmol), 180 mg catalyst (3.78 mmol% of Cu), 1 mL toluene, 373 K, microwave (100 W)



FIGURE 4 Screening of quantity of catalyst on the synthesis of propargylamine. Reaction conditions: benzaldehyde (1 mmol), piperidine (1 mmol), phenyl acetylene (1.15 mmol), 180 mg catalyst (3.78 mmol% of Cu), 1 mL toluene, 373 K, microwave (100 W), 25 min

the reaction was uniform irrespective of the nature of the substituents (electron withdrawing or electron donating) on the aromatic ring. A wide range of substituted aldehydes that included -X (Br, Cl, I), -OH, -CH₃, -OCH₃, and -NO₂ groups were compatible with this procedure. Almost all screened substrates underwent A³ coupling smoothly to afford the corresponding products in 98 to 82% yields as summarized in Table 2. In case of furfuraldehyde, excellent product was obtained in short period (entry 13, Table 2). We also tried vanillin that also afforded excellent yield of product in short time (entry 7, Table 2). Different acetylene derivatives were also tried for the synthesis of propargylamine. All the derivatives gave corresponding products in 92 to 98% vields, and results are summarized in Table 3. Both aromatic and aliphatic acetylenes gave high yield of products. Different substituents (electron withdrawing and electron donation) of phenyl acetylene afford excellent yield. 1-Hexyne (entry 6, Table 3), ethynyl cyclopropane (entry 5, Table 3), and trimethyl silyl (entry 8, Table 3) also gave good yields. In addition, reaction was also tried with aliphatic aldehydes such as paraformaldehyde and acetaldehyde, and they afforded good yields of propargylamine (entries 17 and 18, Table 3). All the products were characterized by matching their ¹H-NMR spectra, summarized in Supporting Information. The proposed reaction mechanism of A³-coupling reaction is well known in literature. It has been reported that the reaction takes place by the activation of the Csp-H bond of the terminal alkyne by the Cu NPs@ Resin. After that alkynyl-Cu intermediate goes to react with

TABLE 2 Scope of various aldehydes for the synthesis ofpropargylamine

TABLE 2 (Continued)



(Continues)

(Continues)

TABLE 2 (Continued)



Reaction condition: aldehyde (1 mmol), secondary amine (1 mmol), acetylene (1.15 mmol), 180 mg catalyst (3.78 mmol% of Cu), 100°C, microwave (100 W), 25 min, toluene (1 mL).

the immonium ion generated from the reaction of aromatic aldehyde and secondary amine to afford the propargylamine and regenerate the catalytic active sites for another reaction.^[32,33] In addition, Cu NPs@ Nitro-Resin exhibited high activity, environmentally begins protocol, with negligible waste generation from the reaction mixture after the workup. The green chemistry metrics calculation for the model reaction provided very small E-factor (0.15) and high atom economy (94%) (see Supporting Information for calculations).^[54,55]

2.3 | Recyclability

Recyclability is one of the biggest advantages of a heterogeneous catalyst and an important parameter that is required for evaluation of catalytic performance. The recovery and reusability of the Cu NPs@ Nitro-Resin catalyst was studied for coupling reaction of benzaldehyde, secondary amine, and acetylene under optimized reaction conditions. To attempt this, the Cu NPs@ Nitro-Resin was easily isolated from the reaction mixture by filtration and washed with methanol and hot deionized water 3 times to removed adsorbed organic products from its surface. After cleaning and drying of the catalyst, it was ready to use for the 6 catalytic batches. As shown in Figure 5, it was found that the Cu NPs@ Nitro-Resin catalyst could be reused for 5 runs with some loss of its activity after several runs. Nitro functionalization is mainly responsible for enhancing the stability by restricting the metal leaching from the resin beads. Also, it enhances the polarity of resin that facilitates the movement of reactant towards the resin and hence the catalyst. Additionally, the filtrate was analyzed for the presence of copper by atomic absorption

TABLE 3 Scope of various acetylenes for the synthesis of propargylamine

Entry	Substrate	Product	Time, min	Yield, %
1		N N	25	98
2	CH3	N CH3	15	97
3	OCH3	C C C H3	18	95
4	NO ₂		25	92
5			20	92
6	<u>∽_</u> ≡		20	95
7	Br		20	98
8	∖si—≡		20	94

Reaction condition: aldehyde (1 mmol), secondary amine (1 mmol), acetylene (1.15 mmol), 180 mg catalyst (3.78 mmol% of Cu), 100°C, microwave (100 W), 25 min, toluene (1 mL).



FIGURE 5 Recycling studies of the Cu NPs@ Nitro-Resin for synthesis of propargylamine

spectrometer and the concentration of copper in the filtrate was estimated to be 65 ± 10 ppb. Further, we also checked the stability of the support; Fourier transform infrared spectra of the fresh and spent catalyst were taken and compared (Figure S6). It was observed that in fresh catalyst, the stretching frequencies of nitro group appeared at 1523 and 1335 cm⁻¹ (see Supporting Information). It was noted that there is no change in the functional groups of the resin during coupling reaction among benzaldehyde, secondary amine, and phenyl acetylene.

3 | CONCLUSION

An efficient Cu NPs@ Nitro-Resin catalyst has been developed for 1-step 3-component coupling of aldehyde, amines, and alkynes. We have developed convenient and simple protocol to afford higher yield of propargylamines in short period. The reaction has high atom efficiency, since water is the by-product. This method offers advantages such as environmentally benign low E-factor (0.15) and high atom economy (94%), mildness of the reaction conditions, ease to handle, widely applicable for various substrates, selectivity, and excellent yields. The present catalyst shows higher activity, and the most important is its reusability that makes this catalyst so efficient. So a wide scope of the substrates and cheap catalyst permit us to anticipate a good future for this protocol in academic as well as industry.

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SUPPORTING INFORMATION

Additional Supporting Information may be found online in the supporting information tab for this article.

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