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Eggshell-supported-Cu(II) salophen complex: An efficient and green catalyst for synthesis of propargylamines under solvent-free conditions

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ABSTRACT

In this report, the synthesis, characterization, and application of the eggshell-supported-Cu(II) salophen complex, as a novel and heterogeneous catalyst, is described. The catalyst is characterized by the UV, XRD, FT-IR, and SEM techniques. The eggshell-supported-Cu(II) salophen complex is a versatile, green, inexpensive, and simple catalyst used for the multi-component reactions (MCRs) of terminal alkynes, aldehydes, and secondary amines to give the corresponding propargylamines at 80 °C under the solvent-free conditions. The proposed methodology offers several advantages such as excellent product yield, simple procedure, and mild conditions. On the other hand, the synthesized catalyst could be removed from the reaction mixture by simple filtration and reused for up to six runs.

***Keywords**: Eggshell-supported-Cu(II) catalyst, Aldehyde, Amine, Alkyne, Propargylamine.*

1. Introduction

A multi-component reaction (MCR) is an attractive synthetic strategy used to generate multiple molecular scaffolds, and to increase structural as well as skeletal diversities from simple and easily-available molecules [1]. The development of novel MCRs to construct libraries of structurally-complex compounds for the evaluation of biological activities is a continuing interest at the forefront of synthetic organic chemistry. Among all the known MCRs, a three-component coupling of an aldehyde, an alkyne, and an amine (A^3-coupling) is an interesting approach to the synthesis of propargylamines [2-4], which has found broad applications as precursors for different nitrogen-containing compounds such as allylamines, pyrrolidines, oxazoles, and pyrroles.

The importance of propargylamine motifs can be best understood by the discovery of rasagiline (Fig. 1), which contains a propargylamine moiety (trade name, azilect), an FDA-approved drug that is prescribed for use as monotherapy in early Parkinson's disease [5]. Traditionally, propargylamines have been prepared by the amination of propargylic halides [6], propargylic phosphates [7], and propargylic triflates [8] or through the nucleophilic attack of lithium acetylides or Grignard reagents on imines or their derivatives [9]. However, these methods suffer from issues such as the moisture sensitivity and the requirement for strictly-controlled reaction conditions. Recently, A^3-coupling has been reported to be a convenient and general approach for the preparation of propargylamines [10-13]. Different complexes and salts of the transition metals such as ruthenium, copper [14], silver [15], indium [16], iridium [17], and gold [18] have been employed for the synthesis of propargylamines. Although several catalytic methods have been reported for the construction of propargylamines, most of them require an inert gas, an organic solvent, a high temperature, and an expensive metal such as Au, Ag, Ir, and Ru as the catalyst. Thus, the development of a milder, cheaper, reusable, and highly-efficient as well as an environmentally-benign method is desirable for constructing propargylamines.

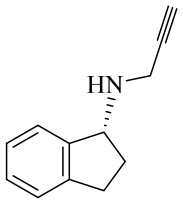

Fig. 1. Rasagiline.

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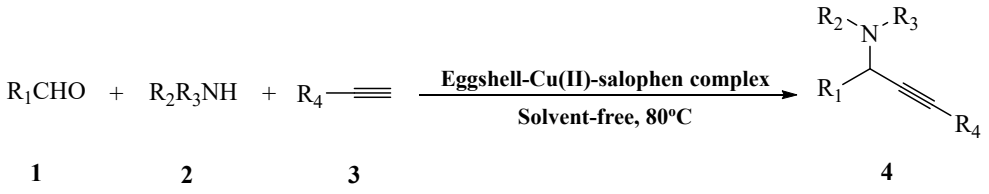
Despite the advantages of homogeneous metal catalysts, difficulties in recovering the catalyst from the reaction mixture severely inhibit their wide use in the industry. Heterogeneous catalysis supplies the opportunity for easy separation and recycling of the catalyst, minimization of the metallic waste, easy product purification, and, possibly, continuous or multiple processing of compounds. It is also relevant to note that the recent environmental concerns about solvent-based chemistry have stimulated a renewed interest in the study of chemical reactions under the solvent-free conditions [19]. In recent years, a great deal of efforts has been made for the application of eggshell as value-added products. These major applications include the coating pigments used for inkjet printing paper [20], starting materials used for preparing calcium phosphate bio-ceramics (e.g. hydroxyapatite) [21], and use as an active heterogeneous catalyst for a bio-diesel synthesis [22]. Xu et al. have reported that waste eggshell could be used as an active heterogeneous catalyst for the bio-diesel synthesis [23]. They have also described the synthesis of dimethyl carbonate catalyzed by eggshell [24]. Moreover, Sharma and co-workers have proved that eggshell is an interesting unconventional heterogeneous basic catalyst used in the bio-diesel synthesis [25]. Except for the bio-diesel synthesis, only one reaction, lactose isomerization, has been reported utilizing eggshell as a basic catalyst [26]. However, base catalysis is important in chemical industry, where it is widely applied [27]. Investigation of eggshell as a catalyst for base-catalyzed reactions is not only helpful for recycling solid eggshell waste but also could make the reaction process environmentally-benign. In view of this consideration, herein, for the first time, we report a green protocol for the synthesis of the propargylamine derivatives catalyzed by the eggshell-supported-copper(II) salophen complex under the solvent-free conditions (Scheme 1).

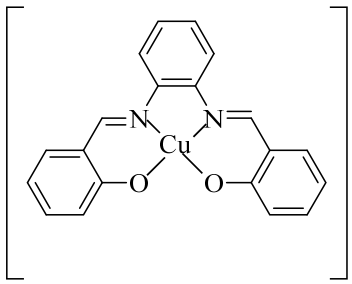
2. Experimental

All the chemicals used were purchased from the Merck or Fluka Companies. All the known compounds were identified by comparing their melting points and ^{1}HNMR data with the corresponding data reported in the literature. ^{1}H NMR spectra were recorded on a Bruker Advanced 300 MHz instrument. FT-IR spectra were obtained as potassium bromide pellets in the range of 400-4000 cm^{-1} on a Bomem MB series spectrometer. Powder X-ray diffraction (XRD) patterns were collected using a Philips PW-1800 or STOE diffractometer with Cu Kα radiation. Morphology of the products was determined using a scanning electron microscope (Hitachi, Japan, model s4160) at an accelerating voltage of 15 KV.

2.1. Eggshell powder preparation

Empty chicken eggshells were collected from a household, and washed with warm tap water. The adhering membranes were separated manually. The eggshells were subsequently washed with distilled water to clean them, and then dried at room temperature. Finally, the eggshells were crushed and ball-milled [28].





Cu(II) salophen complex

Scheme 1.

2.2. Typical procedure for preparation of eggshell-supported Cu(II) salophen complex

To a 100-mL round-bottomed flask equipped with a magnetic stirrer bar and containing ethanol (50 mL) were added eggshell powder (3.0 g) and salophen (10.0 mmol, 0.316 g). The reaction mixture was refluxed for 20 h, filtered and washed thoroughly with ethanol, and dried in vacuo for 10 h. Then, eggshell-salophen (3.0 g) was treated with $Cu(OAc)_2$ (10 mmol, 0.181 g) in DMF at room temperature for 5 h. The product formed was sequentially purified by Soxhlet extraction for 10 h with 200 mL of ethanol and acetonitrile in order to remove the residual reactants or complexes that were physically adsorbed on the external surface of the material. Finally, it was dried at 100 ºC for 10 h to give the eggshell-supported Cu(II) salophen complex. The copper content of the complex was found to be 2.6% (g/g) (0.4 mmol/g) according to the ICP measurements.

FT-IR (KBr): $\bar{\nu}$ = 1627 (C=N), 1585 (C=C), 1191 (C=O) cm^{-1}. UV-Visible: λ_{max}= 362 nm.

2.3. General procedure for synthesis of propargylamine derivatives

An aldehyde (1.0 mmol), an amine (1.2 mmol), and an alkyne (1.5 mmol) were successively added to the catalyst (0.2 g, 0.08 mmol of Cu). After stirring at 80°C for 4 h, the mixture was diluted with dichloromethane. After removing the catalyst by filtration, followed by solvent evaporation, the resulting crude product was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate = 10/2) to give the corresponding product. The recovered catalyst was thoroughly washed with ethanol and used for the next run.

3. Results and Discussion

3.1. IR analysis

A comparison made between the FT-IR spectrum of the encapsulated complex and that for the ‘‘free complex’’ indicated the presence of the complex inside the eggshell cavities and pores. The IR spectrum of eggshell showed major adsorption bands at 3410, 2509, 1425, 875, and 711 cm^{-1}. Strong characteristic phosphate and carbonate bands with absorbed H_2O were observed in the IR spectra. The band related to the stretching vibration $\bar{\nu}$ (OH) of uncoordinated H_2O was observed, as expected, at ~3000 cm^{-1}. A broad band at around 3410 cm^{-1} shows the presence of absorbed H_2O. The broad band at this region results from overlapping of the hydrogen vibrations in the phosphate group: stretching vibrations of structural–OH and absorbed H_2O. A low-intensity band could be observed at 711 cm^{-1}, which is due to the stretching vibration of the P–OH group [29]. Also, a strong broad band was observed at 1425 cm^{-1}, which was assigned to the stretching vibration of the C–O group. Moreover, an out-of-plane vibration (OCO) was observed at 875 cm^{-1} as a strong band. The medium broad band at 2509 cm^{-1} shows the presence of HCO_3. This data confirms the presence of $CaCO_3$ in the eggshell powder [30]. The IR spectra for the eggshell-supported-Cu(II) salophen complex show major bands at 1627 cm^{-1} $\bar{\nu}$ (C=N), 1585 cm^{-1} $\bar{\nu}$ (C=C), and 1191 cm^{-1} $\bar{\nu}$ (C=O), which are absent in the eggshell IR spectrum (Fig. 2) [31].

3.2. UV analysis

The UV-visible spectra provided further evidence for the presence of the Cu(I) salophen complex on the support (Fig. 3). The UV-visible spectrum of the eggshell-salophen ligand in ethanol showed a typical absorption at 362 nm, attributable to the ligand π-π* charge transfer band. The emission peak for the eggshell-supported-Cu(II) salophen complex appeared at around 410 nm. This red shift might be related to the coordination of the copper atom with the ligand, which makes the conjugated system larger [32].

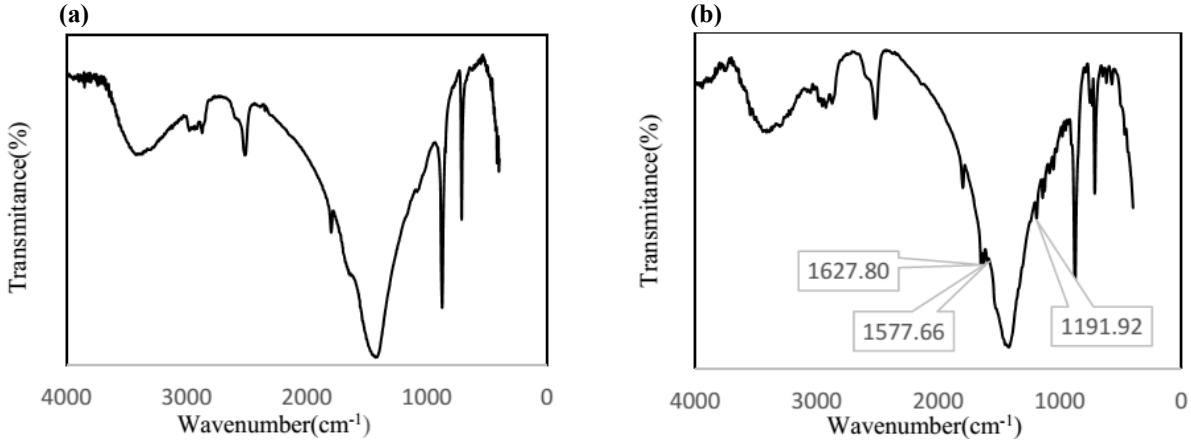


Fig. 2. FT-IR spectra for eggshell (a) and eggshell-supported-Cu(II) salophen complex (b).

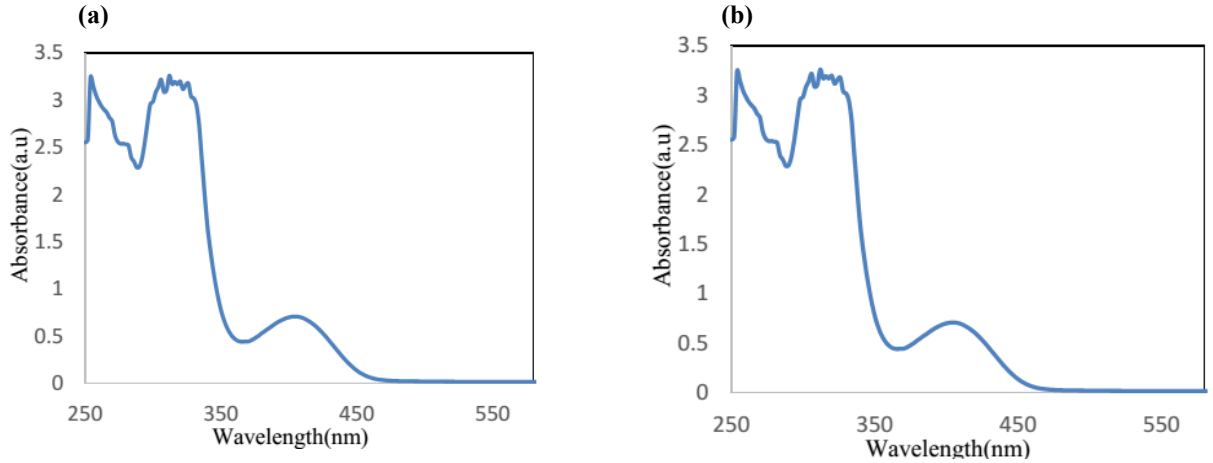


Fig. 3. UV-visible spectra for eggshell-salophen ligand (a) and eggshell-supported-Cu(II) salophen complex (b).

3.3. Powder X-ray diffraction

XRD was used to determine the structures of the eggshell and the eggshell-supported-Cu(II) salophen complex (Fig. 4). The peak positions and intensity distributions in the XRD pattern for the eggshell-supported-Cu(II) salophen complex catalyst are similar to those for the eggshell powder.

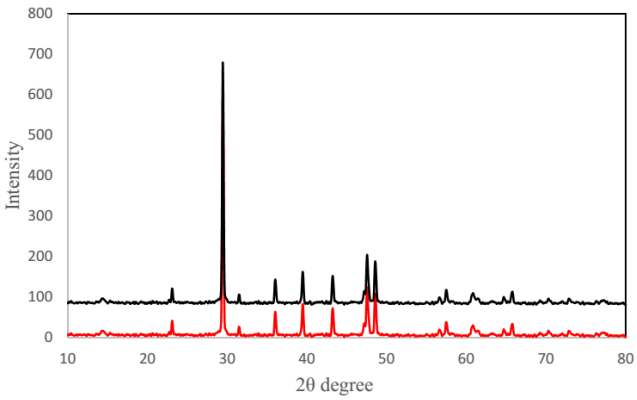


Fig. 4. XRD patterns for eggshell: (a) red line and eggshell-supported-Cu(II) salophen complex (b) black line.

3.4. Microscopic analysis

The scanning electron micrograph analysis is another useful tool used for the analysis of the surface morphology of a catalyst. It can easily be seen in Fig. 5 that the high porosity of the micro porous catalyst contain Cu(II) salophen complex provides a large contact area for catalyzing the reaction.

3.5. Catalytic activity

A test-reaction was performed using benzaldehyde (1 mmol), piperidine (1.2 mmol), and phenylacetylene (1.5 mmol) under the solvent-free conditions at 80°C in the absence of catalyst in order to establish the effectiveness of the catalyst. No conversion to the product was obtained even after 10 h of heating. To optimize the reaction conditions, the above model reaction was carried out under different reaction conditions. The results obtained are summarized in Table 1.

To determine the best catalyst loading, the reactions were carried out with various catalyst concentrations under the solvent-free conditions (entries 1, 2, and 3). Increasing the catalyst loading from 0.2 g to 0.3 g did not change the product yield (entry 2) but lowering the catalyst loading to 0.1 g reduced the isolated yield, and only 80% of the product was collected (entry 3). It was found that at lower temperatures, the reactions proceeded slowly, giving lower yields (entries 4 and 5). To check the solvent effect on the reaction outcome, the above model reaction was carried out with 0.2 g of the catalyst in solvents such as THF, CH_3CN, and ethanol at 80 ºC (entries 6, 7, and 8).

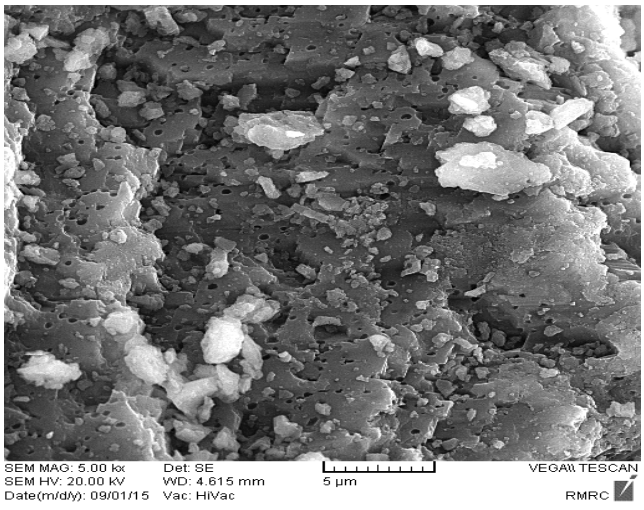


Fig. 5. Scanning electron micrographs for eggshell-supported-Cu(II) salophen complex.

Table 1. Optimization of reaction conditions[a].

Entry	Catalyst (g)	Solvent	Time (h)	Temp. (ºC)	Yield (%)
1	0.2	-	4	80	95
2	0.3	-	4	80	95
3	0.1	-	4	80	80
4	0.2	-	4	50	65
5	0.2	-	4	25	30
6	0.2	THF	10	80	40
7	0.2	CH3CN	10	80	50
8	0.2	EtOH	10	80	45
9	0.2	H2O	10	100	25
10	0.2	Toluene	10	100	60

[a]Reaction conditions: benzaldehyde (1 mmol), piperidine (1.2 mmol), phenylacetylene (1.5 mmol).

Furthermore, the above model reaction was performed in high boiling point solvents such as water and toluene at 100ºC (entries 9 and 10). All the screened solvents afforded a low product yield after 10 h. It is noteworthy that when water was used as the solvent, a lower product yield was observed (entry 9). The best yield was obtained under the solvent-free conditions at 80°C (entry 1). Thus, all the reactions were performed in the presence of 0.2 g of the catalyst at 80 °C under the solvent-free conditions.

Once the catalytic activity was proven, the scope of the reaction was tested (Table 2), finding excellent results for the reaction independency from the nature of the substituents on the alkyne 3 and secondary amine 2, and aldehyde used. The results tabulated in Table 2 indicate that the aromatic aldehydes with both the electron-donating and electron-withdrawing substituents display high reactivities, and generate the desired products in good-to-excellent yields. Interestingly, when the reaction was conducted with terephthalaldehyde using 3 equiv. of phenylacetylene and 2.4 equiv. of amine piperidine, morpholine or dimethylamine, only disubstituted products (Fig. 6) were obtained in 92, 88, and 87% yields, respectively, without the formation of any mono-substituted propargylamine (Table 2, entries 22-24).

In order to show the merit of this catalytic method, the results obtained for the reactions of piperidine, benzaldehyde, and phenylacetylene (Table 3) were compared with those obtained for some other catalysts used for the same reactions. Most of the listed methodologies suffer from some limitations such as prolonged reaction times, elevated temperatures, and use of hazardous materials. For example, preparation of propargylamine was carried out in the hazardous toluene or CH_3CN (Table 3, entries 1, 2, 3, 6, 7). Additionally, the present protocol was effective in the synthesis of propargylamine **4a** in a reaction time of 4 h. The same transformation required 6-24 h for completion by using other catalysts. Furthermore, in some of the reactions, an expensive metal such as gold or silver was used (Table 3, entries 10, 11, and 12). As it is evident in the results tabulated in Table 3, eggshell-supported-Cu(II) is more efficient than the other catalysts.

3.6. Catalyst reusability

One of the purposes for designing this heterogeneous catalyst was to enable recycling of the catalyst for use in the subsequent reactions. The catalyst reusability was tested upon the reaction of benzaldehyde, piperidine, and phenylacetylene, as the representative reactants, and in the presence of 0.2 g of the eggshell-supported-Cu(II) salophen complex in order to study the recyclability of this heterogeneous catalyst. Similarly, the reactions for the repeated runs were conducted after separation of the organic compounds from the reaction mixture by extraction, and the recovered solid catalyst was recycled for another run. The recycling process was repeated for six more cycles with some decrease in the catalytic activity of the catalyst (Table 4).

Table 2. A^3-coupling of aldehydes, amines, and alkynes catalyzed by eggshell-Cu(II)-salophen[a].

Entry	R^1	Amine	R^4	Product	Isolated yield (%)	[Ref.]
1	C_6H_5	piperidine	Ph	**4a**	95 (oil)	[33]
2	C_6H_5	morpholine	Ph	**4b**	90 (oil)	[33]
3	C_6H_5	pyrrolidine	Ph	**4c**	90 (oil)	[34]
4	C_6H_5	diethylamine	Ph	**4d**	70 (oil)	[35]
5	C_6H_5	aniline	Ph	**4e**	65 (oil)	[36]
6	4-ClC_6H_4	morpholine	Ph	**4f**	92 (oil)	[35]
7	4-ClC_6H_4	pyrrolidine	Ph	**4g**	90 (oil)	[33]
8	4-ClC_6H_4	morpholine	CH_2OH	**4h**	83 (oil)	This work
9	4-ClC_6H_4	diethylamine	CH_2OH	**4i**	75 (oil)	This work
10	2-ClC_6H_4	morpholine	Ph	**4j**	80 (oil)	[36]
11	2-ClC_6H_4	piperidine	Ph	**4k**	78 (oil)	[33]
12	4-$CH_3C_6H_4$	morpholine	Ph	**4l**	93 (m.p. 78-80 ºC)	[32] (m.p. 80-82 ºC)
13	4-$CH_3C_6H_4$	pyrrolidine	Ph	**4m**	85 (oil)	[33]
14	3-$NO_2C_6H_4$	morpholine	Ph	**4n**	85 (oil)	[35]
15	3-$NO_2C_6H_4$	piperidine	Ph	**4o**	88 (oil)	[33]
16	2-$MeOC_6H_4$	piperidine	Ph	**4p**	83 (oil)	[34]
17	2-OHC_6H_4	morpholine	Ph	**4q**	80 (oil)	[34]
18	2-OHC_6H_4	piperidine	Ph	**4r**	88 (oil)	[34]
19	4-BrC_6H_4	morpholine	Ph	**4s**	85 (oil)	[34]
20	4-BrC_6H_4	piperidine	Ph	**4t**	87 (oil)	[32]
21	2,4-$Cl_2C_6H_3$	morpholine	Ph	**4u**	90 (oil)	[33]
22	4-$CHOC_6H_4$	morpholine	Ph	**4v**	92[b] (oil)	[34]
23	4-$CHOC_6H_4$	piperidine	Ph	**4w**	88[b] (oil)	[34]
24	4-$CHOC_6H_4$	dimethylamine	Ph	**4x**	87[b] (oil)	This work

[a]Reaction conditions: aldehyde (1 mmol), amine (1.2 mmol), alkyne (1.5 mmol), catalyst (0.2 g), 80 °C for 4 h.
[b]Disubstituted product.

4. Conclusions

The eggshell-supported-Cu(II) salophen complex was found to be an excellent catalyst for the multi-component reactions (MCRs) of terminal alkynes, secondary amines, and aldehydes. The reactions had high atomic efficiencies since the only reaction by-product was water. The absence of a solvent implied both a very low energetic cost and a very low environmental impact. All these facts together with the simplicity of the protocol, wide scope of substrates, and their simple recycling permitted us to anticipate a good future for this process hereby documented not only in academia but also in industry.

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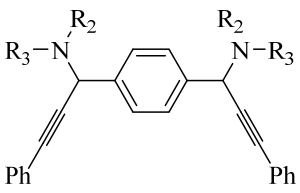

Fig. 6.

Table 3. Comparison of protocols for synthesis of propargylamine from benzaldehyde, piperidine, and phenylacetylene.

Entry	Catalyst	Solvent	Time (h)	Temp. (ºC)	Yield (%)	[Ref.]
1	Cu-HAP	CH_3CN	6	reflux	85	[37]
2	Fe_3O_4	Toluene	16	reflux	75	[38]
3	$Si(CH_2)_3SO_3CuCl$	H_2O	10	reflux	86	[39]
4	$Zn(OAc)_2.2H_2O$	Toluene	7	reflux	92	[40]
5	$NiCl_2$	Toluene	8	reflux	95	[33]
6	Silica-CHDA-Cu	-	12	80	92	[41]
7	$AuBr_3$	H_2O	12	100	99	[42]
8	AgI	H_2O	14	100	70	[43]
9	PS-NHC-Ag(I)	-	24	rt	92	[44]
10	Eggshell-supported-Cu(II)salophen	-	4	80	95	This work

Table 4. Synthesis of propargylamine **4a** catalyzed by recycled catalyst[a].

Entry	Catalyst	Yield[b]
1	first run	95
2	second run	93
3	third run	90
4	fourth run	85
5	fifth run	80
6	sixth run	75

[a]Reaction conditions: benzaldehyde (1 mmol), piperidine (1.2 mmol), phenylacetylene (1.5 mmol), 80ºC for 4h.
[b]Isolated yield.

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