



Cu₆Se_{4.5} Nanoparticles from a single source precursor: Recyclable and efficient catalyst for cross-dehydrogenative coupling of tertiary amines with terminal alkynes



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ABSTRACT

The use of copper selenide nanocatalyst for an efficient and regioselective cross-dehydrogenative coupling (CDC) of tertiary amines with terminal alkynes in the presence of *tert*-butyl hydroperoxide as the oxidant is demonstrated for the first time. The catalyst comprising of unique Cu₆Se_{4.5} nanoparticles synthesized from a single source precursor CuSePh, is required in much lower amount (1 mol%), and is recyclable up to four reaction cycles with slight loss in activity. The reaction can be executed in the absence of solvent, is applicable to aromatic, benzylic, and aliphatic tertiary amines, and furnishes propargylamines in moderate to good yields.

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1. Introduction

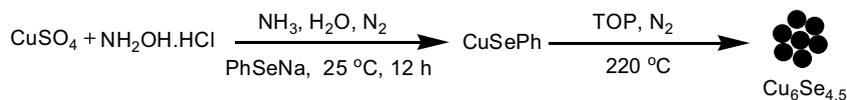
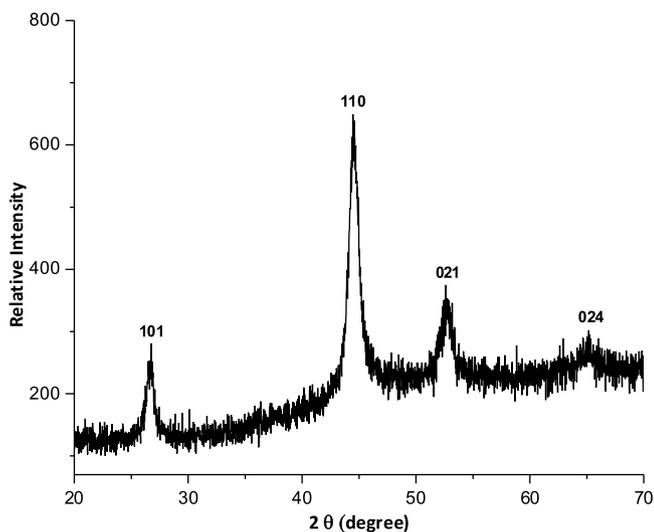
Cross Dehydrogenative Coupling (CDC) has emerged as a powerful tool in modern organic synthesis for the construction of carbon–carbon and carbon–heteroatom bonds in an atom economic and efficient manner [1]. The oxidative coupling of two different C–H bonds catalyzed by transition metals provides an access to a diverse array of aromatic and heterocyclic molecules without the need for their pre-functionalization [2]. CDC has been successfully demonstrated for a variety of alkylation, alkynylation, allylation, and arylation reactions [3]. Synthesis of propargylamines and their derivatives via CDC between amines and alkynes is an attractive route [4], and has been accomplished using copper [3a,5] iron [6] and silver [7] catalysts. This approach has significant advantages over the traditional methods for propargylamine synthesis such as nucleophilic alkynylation of functionalized amines, or transition metal catalysed addition of alkynes to imines [8] since they require the presence of a leaving group or the use of imines derived from pre-functionalized aldehydes and amines. While CDC route for propargylamine synthesis offers several merits, the reaction requires large quantity of catalyst resulting in

generation of vast amount of waste. Also, their scope of amine coupling partners is typically favorable for aryl amines [3a,4a,9] and tetrahydroisoquinoline derivatives [3a,4a,10] while CDC with the rather unreactive aliphatic tertiary amines has limited reports [4a–c]. These limitations challenge and demand the development of more efficient, economical and generalized routes for propargylamines as they are synthetically valuable intermediates for many biologically active compounds such as lactams [11], oxotremorine analogues [12], conformationally restricted peptides [13], and isosteres [14].

To enhance the efficiency of CDC, nanocatalysis offers a promising approach. In nanophase, the catalyst possesses high surface to volume ratio, has more catalytically active sites, and maintains the intrinsic features of a heterogeneous catalyst thus improving the overall efficiency of the system [15–17]. Although extensive efforts have been directed towards CuNP assisted reduction [18a] cross-couplings [18b–f], and other reactions, [18g–j] there are very few reports on CuNP mediated C–H bond activations [5g,19]. In our efforts directed towards developing synthetically useful strategies using copper [20], we explored the synthesis of propargylamines via CDC using copper nanocatalyst. Cu selenide NPs were synthesized through a single source precursor (SSP) route, since this approach permits an intrinsic control on reactivity and stoichiometry, and is free from issues related to air and moisture instability of the precursor [21]. We have previously reported the synthesis of Cu₂Se nanoflakes using selenated propylamine as Se source, and

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Scheme 1. Synthesis of $\text{Cu}_6\text{Se}_{4.5}$ NPs.Fig. 1. PXRD pattern of $\text{Cu}_6\text{Se}_{4.5}$ NPs.

used them for catalyzing Suzuki and Sonogashira reactions [22]. In the present work, we disclose for the first time the synthesis of $\text{Cu}_6\text{Se}_{4.5}$ NPs using SSP route, and their application in oxidative CDC of terminal alkynes and tertiary amines under solvent free conditions.

2. Results and discussion

The $\text{Cu}_6\text{Se}_{4.5}$ NPs (Scheme 1) were prepared by thermolysis of CuSePh , synthesized by modifying the reported procedure for synthesis of CuSPh^{23} and characterized using ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy (see spectrum 1 and 2 in Supporting information).

The NPs were authenticated by PXRD, SEM-EDX, and HRTEM data. PXRD pattern of $\text{Cu}_6\text{Se}_{4.5}$ NPs exhibited diffraction lines (hkl) at 101, 110, 021, and 024 (Fig. 1). These diffraction peaks were indexed to the hexagonal phase of $\text{Cu}_6\text{Se}_{4.5}$ NPs, as they showed good agreement with the literature data (JCPDS 72-2130). TEM images revealed the particles to have spherical morphology with a size of ~ 5 – 7 nm (Fig. S1, Supporting information). SEM-energy-dispersive X-ray spectral data confirmed the presence of Cu and Se in these NPs in the ratio 6:4.5 (Fig. S2, Supporting information). The oxidation states of Cu and Se in $\text{Cu}_6\text{Se}_{4.5}$ NPs have been assigned with the help of XPS analysis. As shown in Fig. 2, the sample consists of copper and selenium only. The Cu 2p spectrum illustrates that the peaks for binding energies for Cu 2p_{3/2} and 2p_{1/2} appearing at 931.5 and 951.5 eV respectively are symmetric, narrow, and devoid of satellite. These values of binding energies indicate the oxidation state of Cu in $\text{Cu}_6\text{Se}_{4.5}$ NPs to be (+1) (Fig. 2a), in accordance with a recent literature report [24a]. In the Se 3d XPS spectrum (Fig. 2b), the binding energy peak corresponding to 53.85 eV is characteristic of Se^{-2} [23b].

Cross-dehydrogenative coupling between model substrates *N,N*-dimethylbenzylamine (1a) and phenylacetylene (2a) was initiated using *tert*-butyl hydroperoxide (TBHP), and $\text{Cu}_6\text{Se}_{4.5}$ NPs as the catalyst. We were pleased to see that the synthesized NPs were effective in catalyzing the reaction, and yielded the desired product Benzyl-methyl-(3-phenyl-prop-2-ynyl)-amine (3a) in 62% yield

Table 1
Optimization of reaction conditions for CDC^a.

Entry No.	Catalyst mol%	Solvent	Time (h)	Yield ^b %
1	1	–	3	62
2	1	H ₂ O	3	nd
3	1	DMSO	3	54
4	1	DCE	3	51
5	1	Toluene	3	26
6	1	Dioxane	3	23
7	0.5	–	3	19
8	–	–	12	nd
9 ^c	1	–	12	nd
10 ^d	1	–	3	7
11 ^e	1	–	3	nd
12 ^f	1	–	3	nd
13	1	–	2	43
14	1	–	10	62
15 ^g	1	–	3	42
16 ^h	1	–	3	46
17 ⁱ	1	–	3	58
18 ^j	1	–	3	53
19 ^k	1	–	10	48

^a Reaction Conditions: 1a (1.0 mmol), 2a (1.0 mmol), Catalyst $\text{Cu}_6\text{Se}_{4.5}$ NPs, TBHP in water (1.5 mmol), N₂, 100 °C.

^b isolated yields.

^c without TBHP.

^d NBS as oxidant.

^e benzoquinone as oxidant.

^f K₂S₂O₈ as oxidant.

^g temp. 70 °C.

^h TBHP (3.0 mmol).

ⁱ 1a (1.5 mmol).

^j 1a (2.0 mmol).

^k reaction with CuSePh as catalyst.

(Table 1, entry 1). Encouraged with the finding, we next optimized the reaction conditions by varying the solvent, time, and catalyst loading. It was found that addition of solvents such as water, DMSO, DCE, toluene, and dioxane to the reaction mixture containing equivalent amounts of 1a and 2a, $\text{Cu}_6\text{Se}_{4.5}$ NPs, and TBHP resulted in a significant drop in the yield of 3a (Table 1, entries 2–6). Since the reaction gave the highest product yield under neat conditions (Table 1, entry 1), it was decided to carry out further studies in the absence of added solvent. Lowering the catalyst loading to 0.5 mol% decreased the yield of 3a to 19% (Table 1, entry 7). It was also found that the reaction did not proceed in the absence of copper catalyst or TBHP (Table 1, entry 8 and 9). Use of NBS as the oxidant did not help the reaction either, and the yield of 3a decreased to only 7% (Table 1, entry 10). With other oxidants such as benzoquinone and K₂S₂O₈, 3a was not formed at all (Table 1, entries 11 and 12). Further, reducing the reaction time to 2 h resulted in a lower conversion to product, while increasing it up to 10 h did not alter the product yield (entries 13 and 14, Table 1). Furthermore, lowering the reaction temperature to 70 °C or increasing the amount of TBHP to 0.4 mL also led to decreased product yields (entries 15 and 16, Table 1). It was also seen that increasing the amount of 1a to 1.5 and 2.0 equivalents, reduced the yield of 3a to 58 and 53% respectively (entries 17 and 18, Table 1). Notably, the reaction was carried out under nitrogen atmosphere, since the presence of air converted 1a into benzaldehyde, and the desired coupled product was not

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