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Article

Cu(II) salen complex catalyzed synthesis of propargylamines by a three-component coupling reaction

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ABSTRACT

A one pot three-component coupling reaction of phenylacetylene, aldehyde, and amine derivatives in the presence of Cu(II) Salen complex as an efficient heterogeneous catalyst under solvent-free conditions is reported. The catalyst displayed high activity and afforded the corresponding propargylamines in good to excellent yields. This method provides a wide range of substrate applicability. The catalyst was reused several times without significant loss of its catalytic activity.

1. Introduction

Propargylamines are important synthetic intermediates for the synthesis of potential therapeutic drug molecules. Polyfunctional amino derivatives are versatile building blocks and are value-added intermediates in organic synthesis [1]. Traditionally, propargylamines have been prepared by the amination of propargylic halides [2], propargylic phosphates [3], and propargylic triflates [4] or through the nucleophilic attack of lithium acetylides and Grignard reagents on imines or their derivatives [5]. However, these methods suffer from issues such as moisture sensitivity and the requirement for strictly controlled reaction conditions. Recently, a three-component coupling among aldehyde, alkyne, and amine, commonly referred to as A^3 coupling, has been reported to be a convenient and general approach for the preparation of propargylamines [6]. Generally, the A^3 coupling reaction is catalyzed by transition metals by C–H activation. For example, Ag(I) salts [7], Au(I,III) salts [8], Au(III) salen complexes [9], Cu(I) salts [10], Ir complexes [11], Hg_2Cl_2 [12], Zn salts [13], $InCl_3$ [14], $InBr_3$ [15], and the Cu/Ru bimetallic system [16] under homogeneous conditions. Recently Ag(I) [17] and Cu(I) [18] in ionic liquids and supported Au(III) [19], Ag(I) [20], and Cu(I) [21] were successfully used to catalyze three-component coupling reactions under heterogeneous conditions with catalyst recycling and reuse. However, some of these methods require expensive metal catalysts (Ag, Au, Ir, etc.) [7,8,11], hazardous catalysts [12], inert conditions [16], harmful solvents [13,15], and long reaction times [9,21] and catalyst recycling can be difficult [7–14]. On the other hand, salen complexes are stable solid compounds that have been used as catalysts for various organic transformations [22–24]. Herein, we report a high yield synthesis of propargylamines catalyzed by the Cu(II) salen complex **1a** under solvent-free conditions at 80 °C (Scheme 1).

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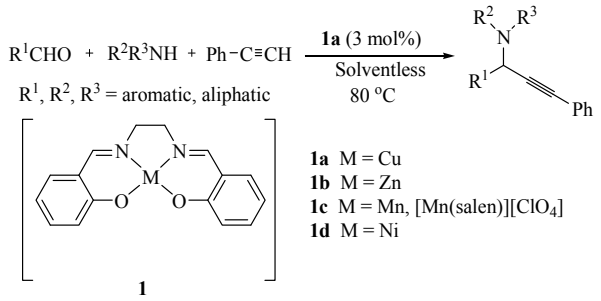


Scheme 1. Cu(II) salen complex catalyzed A^3-coupling leading to propargylamine.

2. Experimental

2.1. General experimental

All reagents were purchased from Merck and Aldrich and used without further purification. Melting points were measured on an Electrothermal 9100 apparatus. IR spectra were recorded on a Bruker Vector 22 spectrometer. ^{1}H and ^{13}C NMR spectra were measured with Bruker DRX-400 Avance spectrometers. Mass spectra and the purities of volatile compounds as well as gas chromatography (GC) analyses were recorded on a FINNIGAN-MATT 8430 mass spectrometer operating at an ionization potential of 20 eV. Elemental analyses were performed using a Perkin-Elmer 2400(II) CHN/O analyzer. Merck silica gel 60 (230–400 mesh) was used for column chromatography.

2.2. General procedure for the preparation of propargylamine derivatives

In a 5-ml round-bottomed flask containing Cu(salen) (0.01 g, 3 mol%) in air, aldehyde (1 mmol), amine (1.2 mmol), and phenylacetylene (1.5 mmol) were added. The flask was then stoppered and the mixture was stirred at 80 °C (oil bath temperature). The completion of the reaction was monitored by TLC or GC. After reaction completion and cooling to room temperature, diethyl ether (5 ml) was added and the Cu salen was removed by filtration. The solvent was evaporated under reduced pressure, and the residue was purified by flash column chromatography on silica gel (eluent: hexane/ethyl acetate = 10) to give the corresponding product. Spectroscopic data for selected examples are as follows.

1,4-Bis(3-phenyl-1-(piperidin-1-yl)prop-2-ynyl)benzene (Table 2, entry 13). White solid, yield 95%; m.p.: 157–160 °C; IR (KBr): 3020, 2976, 2361, 1522, 1432, 1216, 772 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.67–7.60 (s, 2H), 7.56–7.51 (m, 2H), 7.37–7.31 (m, 3H), 4.83 (s, 1H), 2.68–2.5 (m, 4H), 1.69–1.59 (m, 4H), 1.52–1.44 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 139.72, 132.81, 128.33, 128.28, 128.05, 122.33, 87.78, 86.13, 62.14, 50.69, 26.15, 24.42; MS (EI, *m/z*): 471.3 (M^+), 388, 300, 232, 204, 130, 102, 77, 57; Anal. Calcd for $C_{34}H_{36}N_2$: C 86.40, H 7.68, N 5.93; Found: C 86. 37, H 7.69, N 5.89.

1,4-Bis(3-phenyl-1-(morpholin-1-yl)prop-2-ynyl)benzene (Table 2, entry 23). White solid, yield 95%; m.p.: 150–153 °C; IR (KBr): 3020, 2974, 2361, 1521, 1420, 1216, 772 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.69–7.61 (s, 2H), 7.56–7.51 (m, 2H), 7.39–7.31 (m, 3H), 4.81 (s, 1H), 3.81–3.65 (m, 4H), 2.77–2.69 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.36, 131.81, 128.50, 128.34, 128.31, 122.90, 88.50, 84.99, 67.17, 61.77, 49.86; MS (EI, *m/z*): 476.3 (M^+), 390, 304, 200, 152, 86, 56; Anal. Calcd for $C_{32}H_{34}N_2O_2$: C 80.30, H 7.16, N 5.85; Found: C 80. 27, H 7.12, N 5.80.

N-[1-(2,4-Dimethylphenyl)-3-phenyl-2-propynyl] piperidine (Table 2, entry 26). Yellow oil, yield 90%; IR (KBr): 3018, 2934, 2401, 1615, 1492, 1447, 1317, 1216, 771 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.62–7.58 (m, 1H), 7.58–7.54 (m, 1H), 7.53(d, *J* = 2 Hz, 1H), 7.40–7.31 (m, 3H), 7.08–6.98 (m, 2H), 4.83 (s, 1H), 2.65–2.52 (m, 4H), 2.45 (s, 3H), 2.35 (s, 3H), 1.62–1.50 (m, 4H), 1.49–1.40 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.42, 137.03, 133.88, 131.79, 131.45, 128.94, 128.27, 127.91, 125.76, 123.57, 87.84, 86.30, 59.94, 50.53, 26.35, 24.66, 21.05, 19.0; MS (EI, *m/z*): 302.1 (M^+), 219, 203, 115, 84, 55; Anal. Calcd for $C_{22}H_{25}N$: C 87.08, H 8.30, N 4.62; Found: C 86.98, H 8.34, N 4.58.

3. Results and discussion

We synthesized the salen complexes **1a**–**1d** and characterized them according to the literature [25,26]. In brief, **1a**, **1b**, and **1d** were prepared by the treatment of $M(OAc)_2$ (1.2 equiv.) with *N*,*N*-bis(salicylaldehyde) ethylenediamine as the ligand (1.2 equiv.) in refluxing ethanol over 2 h.

To determine the catalytic activity of **1a** during the preparation of propargylamine, a model reaction was conducted by heating **1a** (3 mol%), benzaldehyde (1 mmol), piperidine (1.2 mmol), and phenylacetylene (1.5 mmol) under solvent-free conditions at 80 °C for 2.5 h. Work-up of the reaction mixture afforded the expected product in 95% isolated yield (Table 1, entry 1). In the absence of catalyst no conversion was obtained even after 24 h (Table 1, entry 2). This observation shows the importance of catalyst **1a** in this reaction. To optimize the reac-

Table 1
Reaction conditions and reaction yields for synthesis of progargylamine.

Entry	Catalyst (mol%)	Solvent	*t*/°C	Isolated yield (%)
1	**1a** (3)	—	80	95
2	—	—	80	n.r. [a]
3	**1a** (1.5)	—	80	30
4	**1a** (5)	—	80	95
5	**1a** (3)	—	25	15
6	**1a** (3)	—	70	75
7	**1a** (3)	toluene	reflux	30/75 [a]
8	**1a** (3)	DMF	130	trace [a]
9	**1a** (3)	water	reflux	n.r./65 [a]
10	**1a** (3)	MeCN	reflux	50 [c]
11	**1d** (3)	—		75
12	**1b** (3)	—		30
13	**1c** (3)	—		5
14	$Cu(NO_3)_2{\cdot}H_2O$ (3)	—	80	40 [b,c]
15	$Cu(OAC)_2{\cdot}H_2O$ (3)	—	80	35 [b,c]
16	CuCl (3)	—	80	45 [b,c]

Reaction conditions: benzaldehyde 1 mmol, piperidine 1.2 mmol, phenylacetylene 1.5 mmol, 2.5 h ([a] 24 h, [b] 12 h). [c] Upon mixing without solvent, intense heat led to decomposition.

tion conditions, a model reaction was carried out under different reaction conditions. The results are summarized in Table 1. To determine the best catalyst loading, the reactions were carried out with various catalyst concentrations under solvent-free conditions (Table 1, entries 1, 3, and 4). Increasing the catalyst loading of **1a** from 3 to 5 mol% did not change the product yield (Table 1, entry 4), but lowering the catalyst loading to 1.5 mol% significantly reduced the isolated yield and only 30% of the product was collected (Table 1, entry 3). Poor results were obtained when the reaction was conducted at 25 and 70 °C (Table 1, entries 5 and 6).

To investigate the effect of solvents, model reactions were carried out in toluene, DMF, MeCN, and water under reflux conditions. All the screened solvents afforded a low product yield after 2.5 h (Table 1, entries 7–10). The best yield was obtained under solvent-free conditions at 80 °C (Table 1, entry 1). Therefore, solvent-free conditions were determined to be most effective for the generation of the desired product. The catalytic activities of the Zn(II), Mn(III), and Ni(II) salen complexes **1b**–**1d** were also investigated. The Ni(II) salen complex **1d** showed moderate catalytic activity (Table 1, entry 11), whereas the Zn(II) and Mn(III) salen complexes **1b** and **1c** gave a significantly lower product yield (Table 1, entries 12 and 13). The reason for this is not clear, but it is known that Cu ions can form stronger complexes with acetylenes than nickel [27]. To show the effect of the salen ligand on catalytic activity, model reactions were carried out under solvent-free conditions in the presence of the $Cu(NO_3)_2$, $Cu(OAc)_2$, and CuCl, and the product yields were 40%, 35%, and 45%, respectively, after 12 h (Table 1, entries 14, 15, and 16). These low yields could be due to decomposition because of intense heat evolution upon mixing the substrates under solvent-free conditions. However, for the conversion and yield of the product, a solvent-free reaction among an aldehyde, an amine, and phenylacetylene in the presence of **1a** (3 mol%) at 80 °C was performed as a general procedure for the preparation of propargylamine derivatives. Subsequently, various aldehydes, secondary amines, and phenylacetylene were coupled, and the results are summarized in Table 2. It indicates that aromatic aldehydes with both electron-donating and electron-withdrawing substituents give high

Table 2
Synthesis of propargylamines using Cu salen (Scheme 1). [a]

Entry	R1	Amine	Time (h)	Isolated yield (%)	Ref.
1	C_6H_5	piperidine	2.5	95	[28]
2	4-BrC_6H_5	piperidine	1.45	100	[29]
3	4-MeC_6H_4	piperidine	1.15	95	[28]
4	4-ClC_6H_4	piperidine	2	95	[28]
5	3-ClC_6H_4	piperidine	1.15	90	[21]
6	4-$MeOC_6H_4$	piperidine	2	80	[28]
7	2-$MeOC_6H_4$	piperidine	2	85	[32]
8	3-$MeOC_6H_4$	piperidine	2	80	[8]
9	2-BrC_6H_4	piperidine	1.25	100	[33]
10	3-BrC_6H_4	piperidine	0.5	90	[32]
11	4-CNC_6H_4	piperidine	1	85	[30]
12	2-OHC_6H_4	piperidine	1	100	[30]
13	4-$CHOC_6H_4$	piperidine	1	95 [b]	this work
14	Furyl	piperidine	3	90	[29]
15	Thiophyl	piperidine	2.75	85	[30]
16	C_6H_5	morpholine	2.5	85	[28]
17	4-CNC_6H_4	morpholine	1	80	[30]
18	4-FC_6H_4	morpholine	1.25	85	[33]
19	4-$CF_3C_6H_4$	morpholine	1	98	[30]
20	3-OHC_6H_4	morpholine	1	85	[30]
21	2-OHC_6H_4	morpholine	1	100	[30]
22	3-BrC_6H_5	morpholine	1	80	[30]
23	4-$CHOC_6H_4$	morpholine	0.75	95 [b]	this work
24	2-Naphthyl	piperidine	1.5	90	[30]
25	$PhCH=CH_2$	morpholine	1.25	100	[33]
26	2,4-$DiMeC_6H_3$	piperidine	3	90	this work
27	$CH_3CH_2CH_2$	morpholine	0.45	90	[31]
28	$CH_3CH_2CH_2$	piperidine	0.45	95	[31]
29	C_6H_5	pyrrolidine	2	80	[28]
30	2-Naphthyl	pyrrolidine	0.75	100	[30]
31	$(CH_3)_2CH$	morpholine	0.25	100	[30]
32	C_6H_5	dibenzylamine	2	85	[8]
33	C_6H_5	diethylamine	2	60 [c]	[31]
34	4-FC_6H_4	diethylamine	1	70 [c]	[31]

[a] Aldehyde:phenylacetylene:amine (1:1.5:1.2). [b] Disubstituted product. [c] Reaction temperature was 60 °C under N_2.

reactivity and generate the desired products in good yields (Table 2, entries 2–13 and 17–23). Similarly, heteroaromatic aldehydes such as thiophene-2-carbaldehyde and furan-2-carbaldehyde participate well in this reaction (Table 2, entries 14 and 15). Aliphatic aldehydes react efficiently and afford excellent yields of the corresponding propargylamines (Table 2, entries 27, 28, and 31). Conjugated aldehydes such as cinnamaldehyde react well with morpholine and phenylacetylene, leading to a high yield of the expected product (Table 2, entry 25).

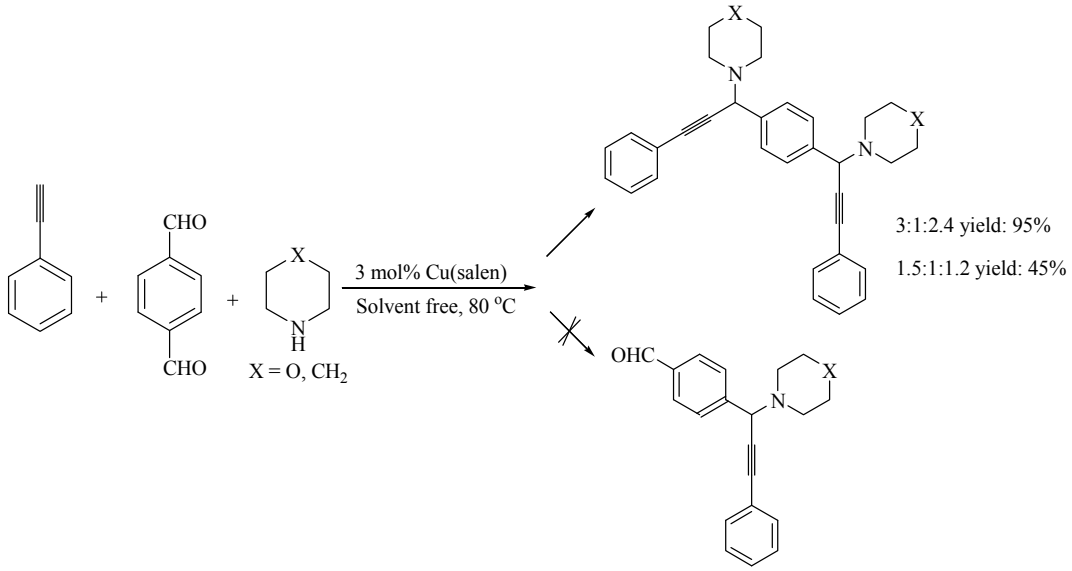
Interestingly, when the reaction was conducted with terephthalaldehyde using 3 equiv. of phenylacetylene and 2.4 equiv of amine piperidine or morpholine (Scheme 2), only disubstituted products were obtained in 95% yield without the formation of any monosubstituted propargylamines (Table 2, entries 13 and 23).

A tentative mechanism for this reaction is proposed in Scheme 3 based on previous studies [7,18,34]. It is assumed that the aldehyde is first condensed in situ with the secondary amine to give an iminium ion. The Cu(salen) complex activates the C–H bond of phenylacetylene to generate a copper acetylide intermediate, which is then added to the iminium ion to afford propargylamine. Such a coordination/deprotonation/acetylide formation sequence has been demonstrated for Ag ions [35].

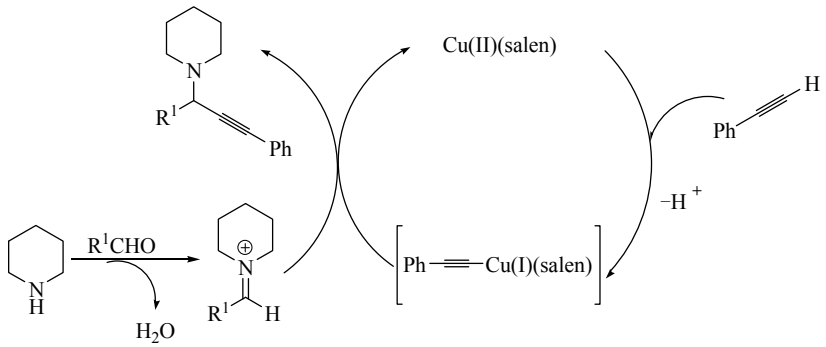
To compare our results with those of other researchers, the model reaction was compared with those reported in the literature on the basis of reaction conditions, reaction time, and percentage yield (Table 3). As shown in Table 3, our method gives a higher yield of product in a shorter reaction time under solventless conditions.

The reusability of the catalyst was determined in the reaction between benzaldehyde, piperidine, and phenylacetylene under solvent-free conditions (Table 2, entry 1). After the completion of the reaction, which was monitored by TLC, the catalyst was removed by filtration and washed twice with diethyl ether (5 ml). It was dried in an oven and reused six times without any significant loss of activity toward the synthesis of 1-(1,3-diphenylprop-2-ynyl)piperidine. These results confirm the practical recyclability of this catalyst and thus confirm its potential role in modern organic synthesis (Table 4).

Although a similar catalytic reaction has been reported before [9], the Cu(II) salen complex has lower cost and higher catalytic activity and is reusable, and the reaction is not sensitive to electron-donating or electron-withdrawing substituents. The yields are attractive, and various cyclic and acyclic amines such as piperidine, morpholine, pyrrolidine, dibenzylamine, and diethylamine are tolerated. All the obtained results demonstrate that the Cu(II) salen complex is an efficient catalyst for the synthesis of propargylamines.



Scheme 2. Selective synthesis of disubstituted products from terephthalaldehyde, phenylacetylene, and morpholine or piperidine.



Scheme 3. Tentative mechanism of progargylamine synthesis.

Table 3
Propargylamine formation by Cu(II)salen and other reported catalysts [a].

Entry	Catalyst	Reaction conditions	Time (h)	Yield (%)	Ref.
1	$Fe(HSO_4)_3$ (10 mol%)	CH_3CN, reflux	4	94	[28]
2	Gold(III) salen (0.05 mol%)	H_2O, N_2, 40 °C	24	94	[9]
3	nano Co_3O_4 (10 mol%)	toluene, 130 °C	15	87	[36]
4	SiO_2-Py-CuI (5 mol%)	CH_3CN, 90 °C, N_2	6	90	[37]
5	$Zn(OAC)_2{\cdot}2H_2O$ (10 mol%)	toluene, reflux	7	92	[30]
6	Nafion®NR50 (0.25 g)	CH_3CN, 70–80 °C, N_2	5	96	[29]
7	$NiCl_2$ (5 mol%)	toluene, 111 °C	8	95	[38]
8	$[Au(C^N)Cl_2]$ [b] (1mol%)	H_2O, N_2, 40 °C	24	82	[39]
9	SiO_2-NH-Cu, (2 mol%)	solventless, r.t.	24	79	[21]
10	$FeCl_3$ (10 mol%)	solventless, 70 °C	14	52	[40]
11	CuI (10 mol%)	2 ml [bmim][PF_6], 100 °C	5	78	[18]
13	$CuCl_2$ (10 mol%)	solventless, 80 °C	3	85	[42]
14	Fe_3O_4 nanoparticle (20 mol%)	toluene, 110 °C	16	75	[41]
15	Cu(II) salen complex (3 mol%)	solventless, 80 °C	2.5	95	this work

[a] A^3 coupling reaction between benzaldehyde (1 mmol), piperidine (1.2 mmol), and phenylacetylene (1.5 mmol). [b] Gold (III) (C^N) complex $[Au(C^N)Cl_2]$ (N^CH = 2-phenylpyridine).

Table 4
Reusability of the catalyst for the synthesis of propargylamine (Table 2, entry 1).

Run	Isolated yield (%)
Fresh	95
1	94
2	92
3	92
4	90
5	90

Reaction conditions: benzaldehyde 1 mmol, piperidine 1.2 mmol, phenylacetylene 1.5 mmol, 80 °C, 2.5 h.

4. Conclusions

We report an efficient synthesis of propargylamines through a three-component coupling between aldehydes, amines, and phenylacetylene via C–H activation by a Cu(II) salen complex as a suitable catalyst. Advantages of this method are the recyclability of the catalyst without a significant loss of catalytic activity, an easy procedure and work-up, broad substrate applicability, and high yields in short reaction times. Finally, this approach could make a valuable contribution to existing processes in the field of propargylamine synthesis.

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Graphical Abstract

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Cu(II) salen complex catalyzed synthesis of propargylamines by a three-component coupling reaction

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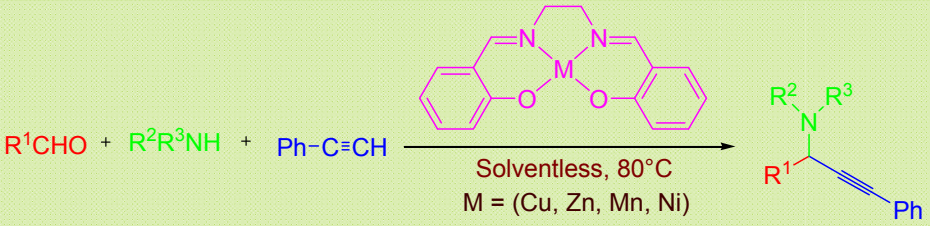

A Cu(II) salen complex showed excellent catalytic activity toward the synthesis of propargylamines through the three-component coupling of aldehydes, amines, and phenylacetylene. Highlights are excellent yields, short reaction times, and a recyclable catalyst.

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