



# CuO/Fe<sub>2</sub>O<sub>3</sub> NPs: robust and magnetically recoverable nanocatalyst for decarboxylative A3 and KA2 coupling reactions under neat conditions



Upasana Gulati, U. Chinna Rajesh, Diwan S. Rawat\*

Department of Chemistry, University of Delhi, Delhi 110007, India

## ARTICLE INFO

### Article history:

Received 13 June 2016

Revised 20 August 2016

Accepted 20 August 2016

Available online 22 August 2016

### Keywords:

Decarboxylative strategies

A3 and KA2 coupling reactions

Green and sustainable chemistry

Magnetically recoverable

Propargylamines

## ABSTRACT

CuO/Fe<sub>2</sub>O<sub>3</sub> NPs were found to be robust, green and sustainable nanocatalysts for the synthesis of trisubstituted propargylamines by the reaction of propiolic acid, secondary amines and aldehydes via decarboxylative A3 coupling reaction under solvent free conditions. Further, we explored the wide applicability of the present methodology by replacing the more reactive aldehydes with less reactive ketones to afford the tetrasubstituted propargylamines via decarboxylative KA2 reaction. The present method showed several advantages such as usage of magnetically recoverable with six times recyclability of nanocatalyst, follows green chemistry principles including low E-factor and high atom economy for the A3 and KA2 reactions as well as high turnover numbers through easy catalyst recycling.

© 2016 Elsevier Ltd. All rights reserved.

## Introduction

Chemical pollution has been the major environmental issue since the time of industrial revolution. In order to solve this problem, green chemistry principles have been introduced in the last decade of twentieth century. These principles mainly deal with the minimization of waste production rather than focusing on waste treatment.<sup>1</sup> Nanocatalysis has been considered to be an efficient approach to achieve sustainable chemistry with various advantages such as high surface area, recovery and reusability of catalyst with minimum waste generation.<sup>2</sup> Magnetically recoverable nanocatalysts (MRNCs) have attracted great attention due to their intriguing catalytic properties along with rapid and robust magnetic separation by external magnet.<sup>3</sup> Recently, we reported green approach for the one-step synthesis of CuO/Fe<sub>2</sub>O<sub>3</sub> MRNC to afford heterocycles such as aminoindolizines and pyrrolo[1,2-a]quinolones.<sup>4</sup> Moreover, our group has reported that Cu(II)/HM as a versatile nanocatalyst for the synthesis of tetrasubstituted propargylamines and pyrrolo[1,2-a]quinolines via KA2, A3 coupling reactions and also included some preliminary results on their decarboxylative coupling strategies.<sup>5</sup> Decarboxylative coupling reactions have attracted significant attention in organic synthesis due to in-situ formation of organometallic species which elimi-

nates the requirement of expensive and toxic organometallic reagents.<sup>6–9</sup> The decarboxylative C–C bond formation involves usage of relatively neutral reaction conditions as compared to organometallic reagents.<sup>7,10–16</sup>

However, there have been very limited reports on the utilization of decarboxylative coupling strategies for the synthesis of heterocycles and value-added chemicals such as imidazo[1,2-a]pyridines, substituted propargylamines, oxazolidin-2-ones, 3-amino-1,4-enynes and 1,4-diamino-2-butyne using copper based homogeneous catalysts.<sup>17–23</sup> To the best of our knowledge there is no report on decarboxylative A3 and KA2 coupling reactions using MRNCs. With this background and in continuation of our interest towards green and sustainable chemistry,<sup>4,5,24–27</sup> we herein report the catalytic potential of CuO/Fe<sub>2</sub>O<sub>3</sub> NPs for decarboxylative A3 and KA2 coupling reactions under solvent free conditions for the first time (Scheme 1).

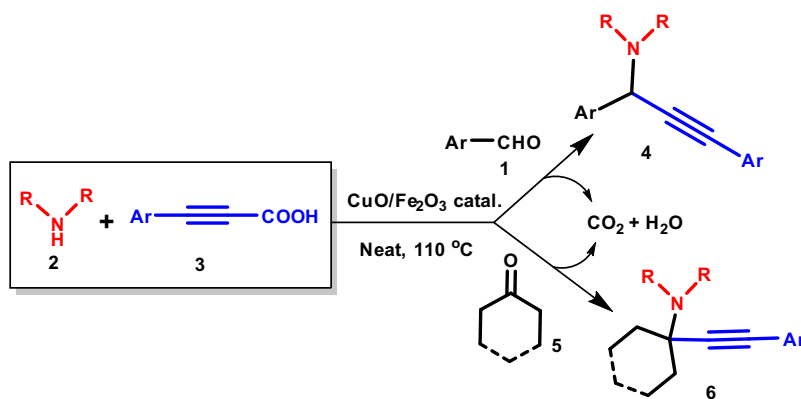
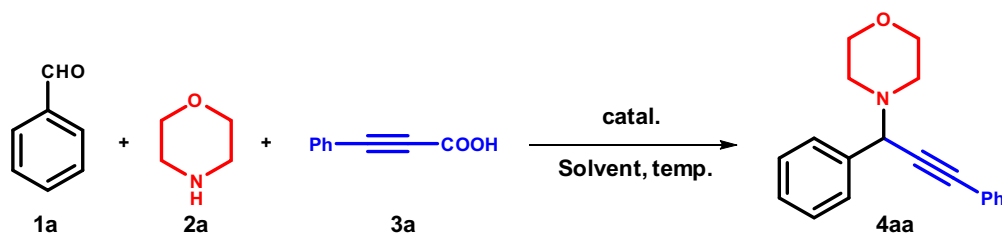
## Results and discussion

### CuO/Fe<sub>2</sub>O<sub>3</sub> catalyzed decarboxylative A3 coupling reaction

Initially, a model reaction was performed among benzaldehyde (**1a**), morpholine (**2a**) and phenylpropionic acid (**3a**) using 5 mg of CuO/Fe<sub>2</sub>O<sub>3</sub> as catalyst in the presence of various solvents and under neat condition at 110 °C as shown in Table 1. Product (**4aa**) was obtained in 60% yield in the presence of water (entry 1, Table 1),

\* Corresponding author. Tel.: +91 11 27662683; fax: +91 11 27667501.

E-mail address: [dsrawat@chemistry.du.ac.in](mailto:dsrawat@chemistry.du.ac.in) (D.S. Rawat).

**Table 1**Optimization study for CuO/Fe<sub>2</sub>O<sub>3</sub> catalyzed decarboxylative A3 coupling reaction<sup>a</sup>

S. No.	Catal. (mg)	Solvent	Temp. (°C)	Time (h)	Yield of <b>4aa</b> <sup>b</sup> (%)
1	CuO/Fe <sub>2</sub> O <sub>3</sub> (5)	Water	100	3.5	60
2	CuO/Fe <sub>2</sub> O <sub>3</sub> (5)	EG	110	3.5	78
3	CuO/Fe <sub>2</sub> O <sub>3</sub> (5)	PEG	110	3.5	78
4	CuO/Fe <sub>2</sub> O <sub>3</sub> (5)	DMF	110	3.5	85
5	CuO/Fe <sub>2</sub> O <sub>3</sub> (5)	DMSO	110	3.5	82
<b>6</b>	<b>CuO/Fe<sub>2</sub>O<sub>3</sub> (5)</b>	<b>Neat</b>	<b>110</b>	<b>3.5</b>	<b>92</b>
7	CuO/Fe <sub>2</sub> O <sub>3</sub> (10)	Neat	110	3.5	92
8	CuO/Fe <sub>2</sub> O <sub>3</sub> (3)	Neat	110	3.5	88
9	CuO/Fe <sub>2</sub> O <sub>3</sub> (5)	Neat	90	5	79
10	CuO/Fe <sub>2</sub> O <sub>3</sub> (5)	Neat	70	8	60
11	CuO/Fe <sub>2</sub> O <sub>3</sub> (5)	Neat	50	21	35
12	CuO/Fe <sub>2</sub> O <sub>3</sub> (5)	Neat	rt	21	—
13	Fe <sub>2</sub> O <sub>3</sub> (5)	Neat	110	8	30
14	CuO NPs (5)	Neat	110	6	81
15	CuCl <sub>2</sub> (5)	Neat	110	4	76
16	Neat	Neat	110	4	—

Bold value indicate the optimized reaction condition.

<sup>a</sup> Reaction conditions: benzaldehyde **1a** (1 mmol), morpholine **2a** (1 mmol), phenylpropionic acid **3a** (1 mmol), catalyst (5 mg) and solvent (2 mL) were stirred at appropriate temperature.<sup>b</sup> Isolated yield.

whereas in other green solvents such as ethylene glycol and polyethylene glycol, the product was isolated in 78% yield (entries 2 and 3, Table 1). Moreover, polar organic solvents such as DMF and DMSO afforded product (**4aa**) in 85% and 82% yields respectively (entries 4 and 5, Table 1). To our delight, product (**4aa**) was obtained in 92% yield under neat condition (entry 6, Table 1). Next, we studied the effect of catalyst loading under neat condition. Upon increasing the catalyst amount to 10 mg, there was no further improvement in the yield of product (entry 7, Table 1), whereas upon decreasing the catalyst amount to 3 mg the yield was dropped to 88% (entry 8, Table 1). The yield of product (**4aa**) was dropped gradually upon decreasing the temperature to 50 °C

(entries 9–11, Table 1). There was no product formation at room temperature even after prolonged reaction time (entry 12, Table 1).

Next, we screened Fe<sub>2</sub>O<sub>3</sub> and CuO NPs alone as catalysts under optimized reaction conditions. The results showed that Fe<sub>2</sub>O<sub>3</sub> gave product in 30% yield while CuO NPs gave 81% yield (entries 13 and 14, Table 1). On the other hand, CuCl<sub>2</sub> yielded product in 76% (entry 15, Table 1). There was no product formation in the absence of catalyst under optimized reaction conditions (entry 16, Table 1). Therefore, the optimized condition was found to be usage of 5 mg of CuO/Fe<sub>2</sub>O<sub>3</sub> catalyst at 110 °C under neat condition to afford the trisubstituted propargylamines (**4aa**) in 92% yield.

Download English Version:

<https://daneshyari.com/en/article/5258561>

Download Persian Version:

<https://daneshyari.com/article/5258561>

[Daneshyari.com](https://daneshyari.com)