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A novel efficient method for synthesis of propargylamines via three-component coupling of aryl azide, aldehyde, and alkyne promoted by iron–iodine–copper(I) bromide

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ABSTRACT

A novel, efficient method has been developed for the synthesis of propargylamines through a three-component coupling of aryl azides, aldehydes, and alkynes in the presence of iron–iodine–copper(I) bromide as catalyst. This method is the first example for directly using aryl azides as an amino component in a three-component coupling reaction. Some of the major advantages of this protocol are: good yields, the involvement of a less-expensive and non-toxic catalyst, mild reaction conditions, and a wide range of substrates.

Propargylamines are an attractive class of compounds owing to their potent biological activities which can act as enzyme inhibitors,[1] antitumor antibiotics,[2] herbicides,[3] and pharmaceutical agents.[4] In addition, they are versatile intermediates for organic synthesis and important structural elements of natural products and potential drug molecules.[5] Thus, the development of new synthetic methods for propargylamines has attracted the attention of medicinal/organic chemists. Recently, various methods have been developed for the synthesis of propargylamines. There are four common approaches for the preparation of propargylamines: (1) the direct nucleophilic attack of lithium acetylides or Grignard reagents to imines or their derivatives;[5d,6] (2) the direct C–C bond formation of terminal alkynes with tertiary amines via C–H activation;[7] (3) the amination of propargylic halides, propargylic phosphates, or propargylic triflates;[8] and (4) the three-component coupling of aldehydes, amines, and alkynes (A^3 coupling).[9] Among these methods, the direct addition of lithium acetylides or Grignard reagents to imines is limited by the stoichiometric reagents and highly moisture-sensitive conditions. The C–H activation of tertiary amines and the amination of propargylic halides are limited by its range of substrates. The last one is a powerful tool for the synthesis of propargylamines in a single operation. Thus, considerable efforts have been made to develop the A^3 coupling reactions catalyzed by various transition metal catalysts such as copper salts,[10] silver salts,[11] gold salts,[12] and zinc salts.[13] However, these methods were usually limited by the secondary amine as an amine component,[10b–f,11b,13b,c,14] and few of the approaches were suitable for the primary amines.[10g,15] Thus, there is still a need to develop a more efficient method for the preparation of propargylamines from readily available starting materials.

Although azides are versatile intermediates in organic synthesis,[16] the use of aromatic azides in organic synthesis has received relatively modest interest until recently, especially since those azides have been mostly prepared from the anilines via their diazonium salts.[17] Recently, aryl azides as the precursor of many nitrogen-containing compounds have become highly attracting due to the finding that aryl azides can be prepared in very good yields through copper-catalyzed coupling reaction of the corresponding aryl halides or aryl boronic acids with sodium azide under mild conditions.[18] To the best of our knowledge, we reported a novel three-component coupling reaction for the preparation of propargylamines from the readily available starting materials aryl azides for the first time.

An initial study was performed by the treatment of 4-chlorophenyl azide **1a** (1 mmol), benzaldehyde **2a** (1 mmol), and phenylacetylene **3a** (1 mmol) in THF (2 mL) in the presence of iron powder (1 mmol), iodine (0.2 mmol), and CuBr (2 mmol) at room temperature for 24 h (Table 1), only trace **4a** was obtained and this result encouraged us to continue to study this reaction. After optimizing the reaction temperature, to our delight, when the reaction was performed at 50 °C, we observed the formation of product **4a** in 74% isolated yield after 24 h.

With this result, other reaction parameters were studied for the preparation of product **4a** at 50 °C and the results are summarized in Table 1. The copper salts such as CuBr, CuI, CuCl, CuCN, and $CuSO_4{\cdot}5H_2O$ (commercial) were screened for the A^3 coupling. As a result, CuBr was found to be the most effective catalyst (Table 2, entry 1). As shown in Table 2, the solvents also played an important role in this reaction. THF (1 mL) gave the product in a high yield (84%). Thus, the optimum reaction conditions were determined as following: THF (1 mL) was used as solvent, the catalyst system was iron/iodine/copper bromide (1:0.2:1), the reaction temperature was 50 °C and the reaction time was 12 h.

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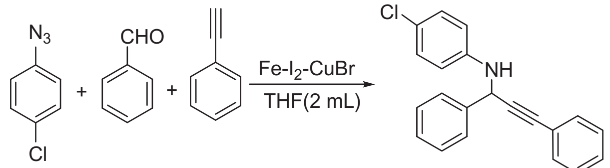
Table 1

Fe–I_2–CuBr-promoted three-component coupling reaction[a]



1a **2a** **3a** **4a**

Entry	Fe/I_2/CuBr	Temp (°C)	Yield[b,c] (%)
1	1:0.2:2	25	Trace
2	1:0.2:2	50	74
3	1:0.2:2	Reflux	56
4	1:0.2:1.5	50	44
5	1:0.2:1	50	39

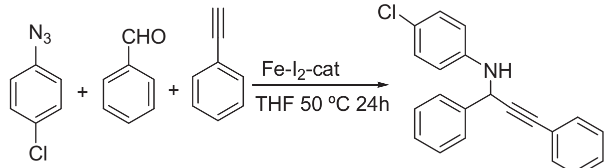
[a] Reaction conditions: 4-chlorophenyl azide/benzaldehyde/phenylacetylene (1:1:1).

[b] Reaction time was 24 h.

[c] Isolated yield was based on 4-chlorophenyl azide.

Table 2

Optimization of the reaction conditions[a,b]



1a **2a** **3a** **4a**

Entry	Catalyst	Solvent	Yield[d] (%)
1	CuBr	THF (2 mL)	74
2	CuI	THF (2 mL)	3
3	CuCl	THF (2 mL)	24
4	CuCN	THF (2 mL)	6
5	$CuSO_4 \cdot 5H_2O$	THF (2 mL)	3
6	CuBr	Toluene (2 mL)	28
7	CuBr	Dioxane (2 mL)	8
8	CuBr	Acetonitrile (2 mL)	25
9	CuBr	Water (2 mL)	5
10	CuBr	THF (1 mL)	84
11	CuBr	THF (5 mL)	55
12	CuBr	THF (10 mL)	19
13[c]	CuBr	THF (1 mL)	83

[a] Reaction conditions: 4-chlorophenyl azide/benzaldehyde/phenylacetylene (1:1:1).

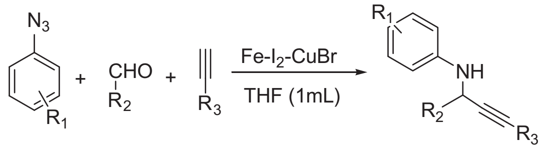
[b] Reaction time was 24 h.

[c] Reaction time was 12 h.

[d] Isolated yield was based on 4-chlorophenyl azide.

Table 3

The three-component coupling of aromatic azides, aldehydes, and alkynes promoted by Fe–I_2–CuBr[a,b]



1 **2** **3** **4**

Entry	R_1	R_2	R_3	Yield[c] (%)
1	*p*-Cl (**1a**)	C_6H_5– (**2a**)	C_6H_5– (**3a**)	81 (**4a**)
2	*p*-Cl (**1a**)	*p*-Cl–C_6H_5– (**2b**)	C_6H_5– (**3a**)	91 (**4b**)
3	*p*-Cl (**1a**)	*p*-F–C_6H_5– (**2c**)	C_6H_5– (**3a**)	84 (**4c**)
4	*p*-Cl (**1a**)	*o*-Cl–C_6H_5– (**2d**)	C_6H_5– (**3a**)	74 (**4d**)
5	H (**1b**)	C_6H_5– (**2a**)	C_6H_5– (**3a**)	72 (**4e**)
6	H (**1b**)	*p*-Me–C_6H_5– (**2e**)	C_6H_5– (**3a**)	72 (**4f**)
7	H (**1b**)	*p*-Cl–C_6H_5– (**2b**)	C_6H_5– (**3a**)	84 (**4g**)
8	H (**1b**)	*o*-Cl–C_6H_5– (**2d**)	C_6H_5– (**3a**)	82 (**4h**)
9	H (**1b**)	*m*-Cl–C_6H_5– (**2f**)	C_6H_5– (**3a**)	92 (**4i**)
10	H (**1b**)	*p*-F–C_6H_5– (**2g**)	C_6H_5– (**3a**)	95 (**4j**)
11	*p*-Me (**1c**)	*p*-Cl–C_6H_5– (**2b**)	C_6H_5– (**3a**)	89 (**4k**)
12	*p*-Me (**1c**)	C_6H_5– (**2a**)	C_6H_5– (**3a**)	81 (**4l**)
13	*p*-Me (**1c**)	*o*-Cl–C_6H_5– (**2d**)	C_6H_5– (**3a**)	82 (**4m**)
14	*p*-Me (**1c**)	*m*-Cl–C_6H_5– (**2f**)	C_6H_5– (**3a**)	78 (**4n**)
15	*p*-Me (**1c**)	*p*-OMe–C_6H_5– (**2h**)	C_6H_5– (**3a**)	64 (**4o**)
16	*o*-OMe (**1d**)	C_6H_5– (**2a**)	C_6H_5– (**3a**)	74 (**4p**)
17	*o*-OMe (**1d**)	*m*-Cl–C_6H_5– (**2f**)	C_6H_5– (**3a**)	84 (**4q**)
18	*o*-OMe (**1d**)	*o*-Cl–C_6H_5– (**2d**)	C_6H_5– (**3a**)	87 (**4r**)
19	*p*-Cl (**1a**)	Cyclohexane– (**2i**)	C_6H_5– (**3a**)	47 (**4s**)
20	*p*-Cl (**1a**)	Cyclohex-3-ene– (**2j**)	C_6H_5– (**3a**)	67 (**4t**)
21	H (**1b**)	C_6H_5– (**2a**)	*n*-Butyl- (**3b**)	74 (**4u**)
22	*p*-Cl (**1a**)	C_6H_5– (**2a**)	*n*-Butyl- (**3b**)	76 (**4v**)

[a] Reaction conditions: aryl azide/aldehyde/phenylacetylene (1:1:1).

[b] Reaction time was 12 h.

[c] Isolated yield was based on aryl azide.

To demonstrate the generality of this method, we investigated the scope of this reaction under the optimum conditions (THF, Fe–I_2–CuBr, 50 °C) and the results are summarized in Table 3. This method was generally effective for aromatic azides. A variety of aromatic azides **1a**–**d** reacted smoothly with aldehydes **2a**–**j** and alkyne **3a** and **b** to produce a range of propargylamines **4a**–**v**, and good to excellent isolated yields were observed for all substrates employed. We have also tried to employ alkyl azides, 4-methylbenzenesulfonyl azide, and benzoyl azide, however, we did not obtain the desired products. As shown in Table 3, we found that the substituents on the benzene ring had no significant steric and electric effects.

In conclusion, we have successfully developed a new efficient synthetic protocol for the preparation of propargylamine derivatives utilizing Fe–I_2–CuBr as the inexpensive and practical catalyst via three-component coupling reactions of aryl azides, aldehydes, and alkynes for the first time. This method not only provides an excellent complement to propargylamine synthesis, but also opens a new way to convert azides directly to useful amino compounds by new three-component coupling reactions.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.08.024.

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