



Highly efficient and recyclable catalyst for the direct chlorination, bromination and iodination of terminal alkynes



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ABSTRACT

Direct halogenation, including chlorination, bromination and iodination of terminal alkynes, are of great importance in organic synthesis. Here an efficient and recyclable nano-Ag/g-C₃N₄ catalyst system was developed and proved to be remarkably active with 39 examples varied from chlorination, bromination to iodination, of which 14 runs have yielded more than 95% of the product. Recycling of the catalyst was also achieved without obvious activity loss after several runs: 99% yield was observed even after 5 runs in the bromination of phenylacetylene. The catalysts system is of low cost and easy to be prepared, making this procedure versatile, convenient and economic.

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1. Introduction

1-haloalkynes are a series of important and powerful building blocks in organic chemistry. They are not only the precursors of a variety of advanced structures such as conjugated diynes, enynes, substituted alkenes, heterocycles and functional polymers, but also conceived as a dual functionalized molecules due to their unique structures involving both controllable electrophilic and nucleophilic properties [1–4], as shown in Fig. 1.

Considering about the importance of haloalkynes, different methods of the preparation of them are developed during decades [1]. Among these protocols, the most commonly and widely used methods are the direct halogenations of C–H bonds in terminal alkynes [5,6]. However, satisfactory results can be observed only for bromination and iodination in a long period [7–9]. The chlorination of terminal alkynes under mild conditions, however, remains a challenge. Typical procedures often require the involvement of highly unstable alkyl lithium reagents under –78 °C [10,11]. Other improvements of chlorination of terminal alkynes including using hypochlorites [12] or PTC (phase transfer catalyst) [13–15]. For example, Szafert et al. have reported a Silver nitrate catalyzed chlorination of terminal alkynes, using TBAF (tetrabutylammonium fluoride) as the PTC [16]. It is noteworthy that PTC in this process was crucial, and no reaction occurred in the absence of

the PTC. Organic base, such as DBU (1,8-Diazabicyclo[5.4.0]undec-7-ene) was also reported as the catalyst for the preparation of chloroalkynes using NCP (N-chlorophthalimide) as the chlorination reagent [9], although only limited examples were achieved. Recently our group have developed a practical method for the chlorination of terminal alkynes using Ag₂CO₃ as the catalyst and K₂CO₃ as the base [17]. Although the recycled silver salts have lost the catalytic activity, good to high isolated yields were achieved for a variety of terminal alkynes, encouraging us to further explore the halogenation of terminal alkynes. Despite of all the methods mentioned above, there is still a lack of a general and convenient method suitable for the bromination, iodination as well as chlorination, as Fig. 2 showed. Here we would like to report our latest discoveries on the halogenation (including chlorination, bromination and iodination) of terminal alkynes using a universal catalyst.

2. Results and discussions

2.1. Bromination of alkynes

During our exploration, the recycling of catalyst stands as the first priority to fulfill the purpose of sustainable chemistry. The immobilization of metal catalyst is one of the choices. Since g-C₃N₄ (graphitic carbon nitride) has shown a series of advantages such as low cost, easy to be prepared and functionalized, insoluble in most solvents and potential photocatalytic properties, and represents a series of heterogeneous catalyst in many fields [18–22],

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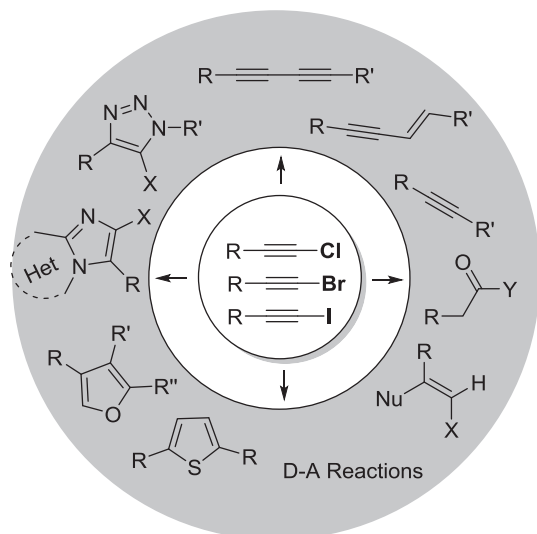


Fig. 1. Important organic structures from haloalkynes.

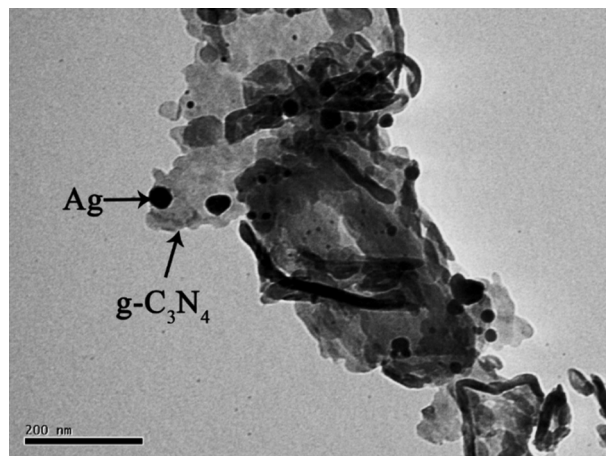
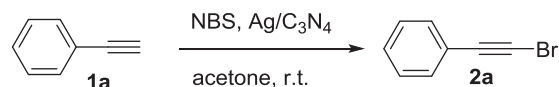


Fig. 3. TEM image of Ag@C₃N₄-10.8 wt%.



entry	cat. loading (mol%)	time (h)	yield (%)
1	2	3	22
2	4	3	99
3	6	3	91
4	8	3	99
5	10	3	95
6	4	0.5	38
7	4	1	56
8	4	1.5	76
9	4	2	93
10	4	2.5	99
11	4	10	93

conditions: 0.5 mmol phenylacetylene, 0.5 mmol NBS, 2 mL acetone, GC yield.

Scheme 1. Bromination of phenylacetylene under different conditions.

withdrawing or electron-donating ones, do not have obvious influences on the yields. Heteroaryl substituted alkynes, such as **2m** and **2n**, also gave excellent isolated yields. Terminal diynes, which are less stable than ordinary terminal alkynes, also gave excellent yields (**2o** and **2p**).

2.2. Iodination of alkynes

We have then further applied the catalyst in the iodination experiments, and found that the catalyst performed excellently again. Using NIS (N-iodosuccinimide) as the iodination reagent, high yields of 1-iodoalkynes were observed in all runs, ranging from 88% to 99% with 12 different examples, and details are listed in Scheme 3. Aryl substituents on the alkynes with either electron withdrawing or donating groups all gave satisfactory yields (**3b–3e**). The positions of the substitution group on the aryl ring of

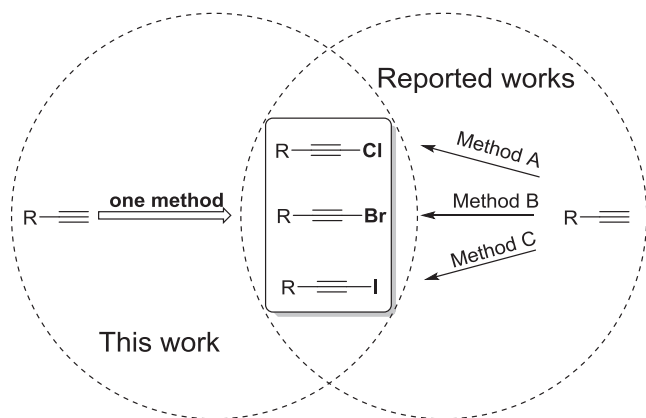


Fig. 2. Direct halogenation of terminal alkynes.

we have also applied it as the co-catalyst in our study. Ag was chosen as the metal catalyst due to the high activities in alkyne synthesis [6,17,23], and we have thus prepared the Ag/g-C₃N₄ to initialize our research. The g-C₃N₄ catalyst can be easily prepared by one-step polymerization of urea at 550 °C for 2 h in a muffle furnace with a heating rate of 5 °C/min. Ag (10.8 wt%) was introduced through a chemical deposition method, using NaBH₄ as the reductant, and the residue was dried at 60 °C for 12 h, resulting a light yellow powder as the final form. TEM image (Fig. 3) shows that the Ag particles are immobilized at the surface of C₃N₄ as small nanoparticles with diameter of about 10–40 nm.

To test the catalytic activity of the prepared catalyst, we initiate the investigation with the bromination of terminal alkynes with NBS (N-bromosuccinimide), which yields 1-bromoalkynes, a kind of important and widely used precursors in organic synthesis [24–28]. Phenylacetylene (**1a**) was used as the substrate to optimize the reaction conditions, and the results are shown in Scheme 1. The catalyst has shown excellent activities even under room temperature, with 4 mol% of the catalyst loading (catalyst loading is calculated according to Ag) to generate 99% of the product **2a** in less than 3 h.

Different substrates were then used under the optimized conditions, and we are pleased to observe that all the substrates we tested have achieved excellent results, and the yields are listed in Scheme 2. The substituents on the aryl moieties, either electron-

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