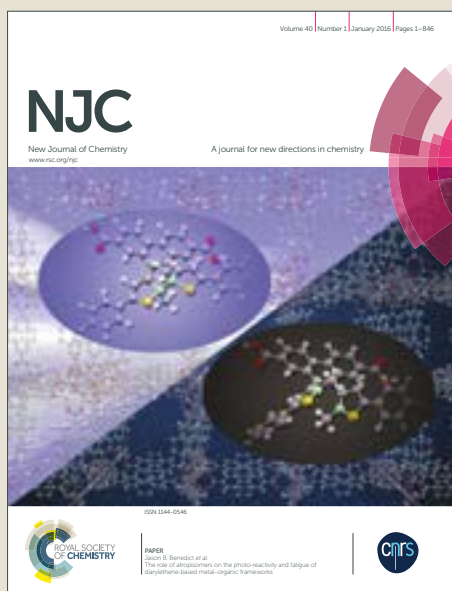


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## Efficient Heterogeneous Hydroboration of Alkynes: Enhancing the Catalytic Activity by Cu(0) Incorporated CuFe<sub>2</sub>O<sub>4</sub> Nanoparticles

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The CuFe<sub>2</sub>O<sub>4</sub> magnetic nanoparticles (NPs) are typically further calcined at high temperature to eliminate the reduced state of the Cu(0) source. Here we report the discovery of Cu(0) incorporated in CuFe<sub>2</sub>O<sub>4</sub> that enable enhancing the catalytic activity for hydroboration of alkynes. This catalyst system is of low working temperature and short reacting time, and wide tolerating substitution alkynes such as ynolate, ynamide and ynone. The Cu-CuFe<sub>2</sub>O<sub>4</sub> catalyst was prepared by a simple hydrothermal method and well characterized by SEM, TEM, PXRD, XPS and EDS. Recycling of the catalyst was also achieved without the loss of obvious activity after six runs. Furthermore, the mechanism of this reaction was also investigated.

### 1. Introduction

Owing to their unique properties, vinylboronates are valuable synthetic building blocks in organic semiconductors and pharmaceuticals chemistry.<sup>1</sup> A number of effective transitionmetal catalysts have been developed for hydroboration carbon-carbon triple bonds to generate vinylboronates with high regioselectivity.<sup>2</sup> Generally, transition metal-catalyzed hydroboration of alkynes proceed through homogeneous catalytic systems.<sup>3</sup> However, these methods require high catalyst loading and ligands to furnish high yield and selectivity, which limit its application in the industry. Therefore, the search for new routes for the efficient and environmentally friendly hydroboration of alkynes has continued to be of interest in chemical research. Transition-metal nanoparticles, which have larger surface areas and higher density of active sites, have been considered to be an important nanocatalyst towards heterogeneous catalysis.<sup>4</sup>

Recently, the nanocatalysis hydroboration of alkynes into vinylboronates with high selectivity has received increasing attention because it reduces metal contamination of products and avoids the use of toxic ligands. For example, Sreedhar and co-workers reported the hydroboration of aromatic and aliphatic alkynes used magnetically separable Fe<sub>3</sub>O<sub>4</sub> NPs.<sup>5</sup> Park's group reported that magnetic CuFe<sub>2</sub>O<sub>4</sub> NPs catalyzed hydroboration of alkynes with low catalyst loading under air.<sup>6</sup> However, these methods have common drawbacks such as

requirement of high working temperature, moderate yields for aliphatic alkynes and low functional group tolerance compared to homogeneous catalytic systems. To this end, there is a need to develop an efficient nanocatalyst to hydroboration of alkynes.

Rational design of transition-metal hybrid materials has become a fascinating and significant object of study nanotechnology and catalytic science. Recently, various copper ferrite (CuFe<sub>2</sub>O<sub>4</sub>) hybrid materials, Such as Cu-CuFe<sub>2</sub>O<sub>4</sub>@HKUST-1<sup>7</sup>, Cu<sub>2</sub>O-CuFe<sub>2</sub>O<sub>4</sub><sup>8</sup> and Al<sub>2</sub>O<sub>3</sub>-CuFe<sub>2</sub>O<sub>4</sub><sup>9</sup>, have been utilized as heterogeneous catalyst. Intrigued by these examples and literatures<sup>6,10</sup>, we anticipated that the Cu-CuFe<sub>2</sub>O<sub>4</sub> NPs catalyst might be able to exhibit better activity than a monocomponent catalytic system. Therefore, we here present the use of Cu-CuFe<sub>2</sub>O<sub>4</sub> NPs as heterogeneous catalysts for hydroboration of variety alkynes under an air atmosphere and at room temperature.

### 2. Results and discussion

#### 2.1 Preparation of Cu-CuFe<sub>2</sub>O<sub>4</sub> NPs

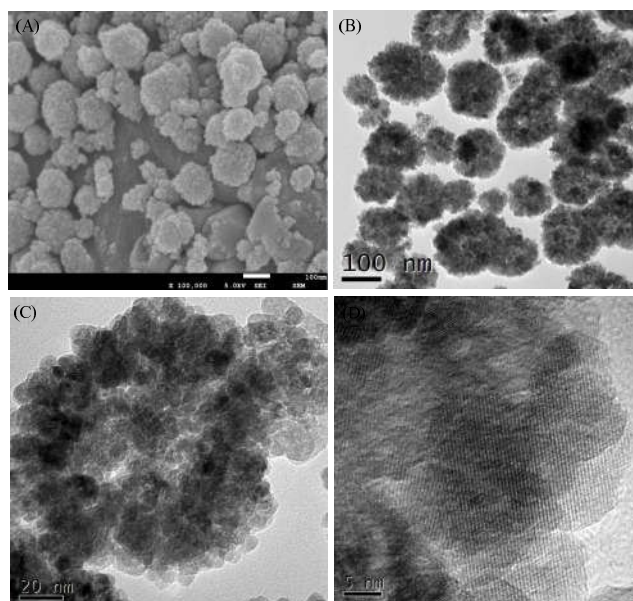
The Cu-CuFe<sub>2</sub>O<sub>4</sub> NP catalyst was synthesized as follows: FeCl<sub>3</sub>·6H<sub>2</sub>O, CuCl<sub>2</sub>·2H<sub>2</sub>O, NaAc, and Na<sub>3</sub>Cit were dissolved in ethylene glycol, and the obtained homogeneous solution was transferred to an autoclave and heated to 200 °C for 12 h. After cooling to room temperature, the final solid product was collected without further purification.

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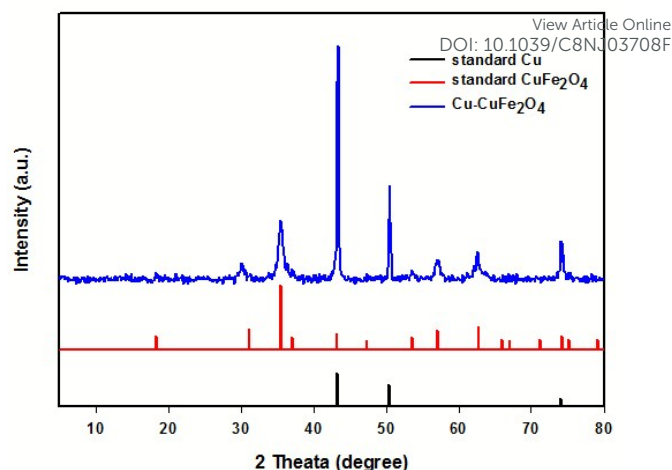
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Electronic Supplementary Information (ESI) available: <sup>1</sup>H, <sup>13</sup>C spectra. See  
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**Fig. 1.** SEM (A) and TEM (B) images of Cu-CuFe<sub>2</sub>O<sub>4</sub> MNPs. (C) TEM image at higher magnification. (D) Lattice-resolved HR-TEM images of Cu-CuFe<sub>2</sub>O<sub>4</sub> MNPs.

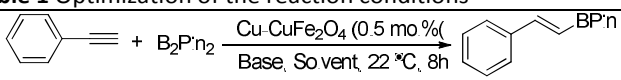
The detailed structure and morphology of the as-prepared Cu-CuFe<sub>2</sub>O<sub>4</sub> was characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and high resolution transmission electron microscopy (HR-TEM). As shown in Fig. 1, the Cu-CuFe<sub>2</sub>O<sub>4</sub> MNPs were nearly spherical in shape with a narrow size distribution (~200 nm). The status of the Cu on CuFe<sub>2</sub>O<sub>4</sub> NPs was confirmed by X-ray photoelectron spectroscopy (XPS) (Fig. S1). The binding energies of Cu 2p<sub>3/2</sub> and Cu 2p<sub>1/2</sub> shift to 932.43 and 952.22 eV, respectively, indicating that Cu(0) makes up of the CuFe<sub>2</sub>O<sub>4</sub> MNPs.<sup>11,12</sup> It was also confirmed by X-ray-diffraction (XRD) measurements (Fig. 2). The positions and relative intensities of all diffraction peaks for the resulting Cu-CuFe<sub>2</sub>O<sub>4</sub> NPs matched well with the data for standard CuFe<sub>2</sub>O<sub>4</sub> (JCPDS Card No. 77-0010) and Cu (JCPDS Card No. 85-1326). These peaks at 2θ = 18.2°, 29.9°, 35.3°, 43.4°, 53.5° and 62.7° are ascribed to the reflections of cubic CuFe<sub>2</sub>O<sub>4</sub>. In the same way, the characteristic peaks at 2θ = 43.4°, 50.53°, and 74.0° are attributable to the Cu(0).<sup>13</sup> The Cu(0) source came from Cu<sup>2+</sup> which was reduced by ethylene glycol under high temperature.<sup>14</sup> Furthermore, the structure and morphology of the Cu-CuFe<sub>2</sub>O<sub>4</sub> was characterized by scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) (Fig. S1D).



**Fig. 2.** XRD patterns of the as-prepared Cu-CuFe<sub>2</sub>O<sub>4</sub> nanoparticles, standard Cu and standard CuFe<sub>2</sub>O<sub>4</sub>.

## 2.2 Reaction design for the synthesis of vinylboronates

With the Cu-CuFe<sub>2</sub>O<sub>4</sub> NPs as a catalyst, the hydroboration of phenylacetylene (**1a**) was then selected as the prototype to start our investigation for the optimized reaction conditions, and the data were shown in Table 1. In the preliminary experiment, the hydroboration of phenylacetylene was carried out in various bases with 0.5 mol % Cu-CuFe<sub>2</sub>O<sub>4</sub> NPs as the catalyst, under air atmosphere at room temperature for 8 h (Table 1, entries 1–4). A moderate yield was observed when the reaction was carried out using K<sub>2</sub>CO<sub>3</sub> and Cs<sub>2</sub>CO<sub>3</sub> separately as bases. In contrast, the reaction proceeded well with MeONa and *t*-BuOK separately as bases, and it may be mainly affected by the solubility of the base. Some polar and non-polar solvents, such as DMF, MeCN and THF, were then examined in the reaction, and only lower yields were obtained (Table 1, entries 5–7). Subsequently, when shortening the reaction time and reducing the amount of catalyst and base, the product yield decreased (Table 1, entries 8–10). Moreover, we tested the hydroboration of phenylacetylene with CuFe<sub>2</sub>O<sub>4</sub> NPs and micro Cu powder as catalyst (Table 1, entries 11 and 12). It was found that the reactions were less productive. We also tested the reactions in the absence of the catalyst and base, and these reactions afforded the product of vinylboronate in poor yields (Table 1, entries 13 and 14). Based on the above results, it can be concluded that the enhanced catalytic activity of CuFe<sub>2</sub>O<sub>4</sub> NPs resulted from the incorporated Cu(0). Furthermore, the yield not decreased when the reaction was carried out under air as compared to that under nitrogen atmosphere (Table 1, entry 15).

**Table 1** Optimization of the reaction conditions<sup>[a]</sup>


Entry	Base	Solvent	Yield (%) <sup>[b]</sup>
1	K <sub>2</sub> CO <sub>3</sub>	EtOH	51
2	Cs <sub>2</sub> CO <sub>3</sub>	EtOH	60
3	MeONa	EtOH	95
4	<i>t</i> -BuOK	EtOH	92
5	MeONa	DMF	27
6	MeONa	MeCN	30
7	MeONa	THF	trace
8 <sup>[c]</sup>	MeONa	EtOH	80
9 <sup>[d]</sup>	MeONa	EtOH	90
10 <sup>[e]</sup>	MeONa	EtOH	80
11 <sup>[f]</sup>	MeONa	EtOH	45
12 <sup>[g]</sup>	MeONa	EtOH	27
13 <sup>[h]</sup>	-	EtOH	trace
14	-	EtOH	40
15 <sup>[i]</sup>	MeONa	EtOH	95

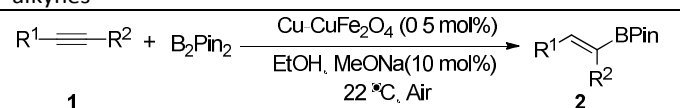
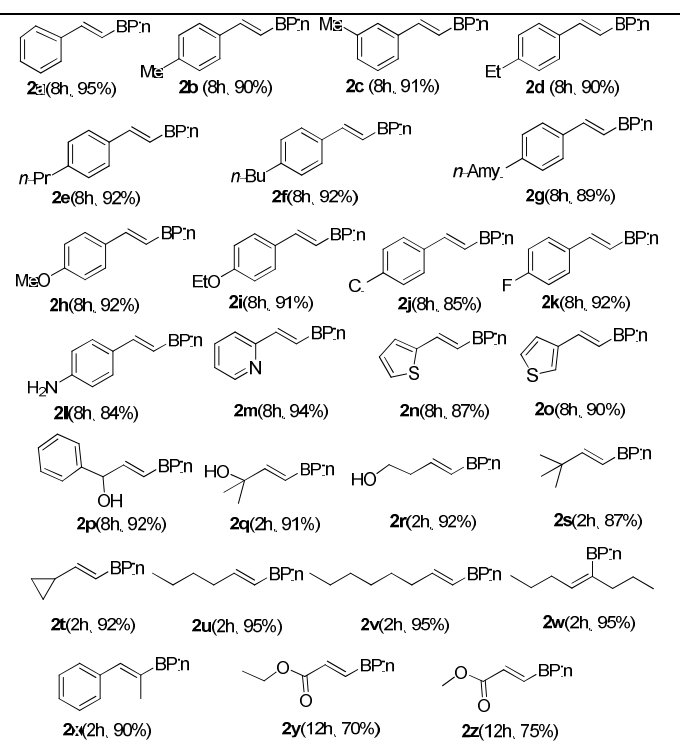
[a] Reaction conditions: Phenylacetylene (0.4 mmol), B<sub>2</sub>Pin<sub>2</sub> (0.44 mmol), Cu-CuFe<sub>2</sub>O<sub>4</sub> nanoparticles (0.6 mg, 0.5 mol%), Base (10 mol%), solvent (2 mL) under Air, 22 °C, 8h. [b] Isolated yield. [c] With Cu-CuFe<sub>2</sub>O<sub>4</sub> nanoparticles (0.3 mg, 0.25 mol%). [d] 6h. [e] 5 mol% of MeONa. [f] Using 0.5% mol of CuFe<sub>2</sub>O<sub>4</sub> NPs as catalyst. [g] Using 0.5% mol of micro Cu powder as catalyst. [h] Without catalyst. [i] Under N<sub>2</sub> atmosphere.

### 2.3 Substrate scope

Under the optimal conditions in hand, we first investigated the aromatic and aliphatic alkynes (Table 2). Both electron-rich and -deficient substituents on the aromatic rings of arylacetylenes **1** worked well with B<sub>2</sub>Pin<sub>2</sub> under standard conditions to realize desired products in moderate to excellent yields with high regioselectivity (Table 2, **2b–2l**). The reaction exhibited good tolerance to halo-substitutions (Table 2, **2j** and **2k**) and aminos (Table 2, **2l**). In addition, heteroalkynes, including 2-ethynyl pyridine, 2-ethynyl thiophene and 3-ethynyl thiophene were well tolerated, providing excellent yields and selectivities (Table 2, **2m–2o**). Moreover, extending the synthetic utility of the reaction to challenging aliphatic alkynes, including sterically demanding, hydroxyl, and long-chain alkynes gave target product with excellent yields in high selectivities (Table 2, **2p–2x**). More importantly, this method was also effective for methyl propiolate and ethyl propiolate (Table 2, **2y** and **2z**).

We next surveyed the functionalized alkynes and alkenes (Scheme 1). The ynamide and ynone were reduced to **3a** and **3b** in high yields, respectively. To our delight, when the same reaction condition was applied to  $\alpha,\beta$ -unsaturated carbonyl compounds, such as carvone and ethyl butadienoate, the  $\beta$ -boration products **3c** and **3d** were obtained in excellent yields with high selectivities. The structure of **3c** had been characterized by X-ray. This proved this system has a very high

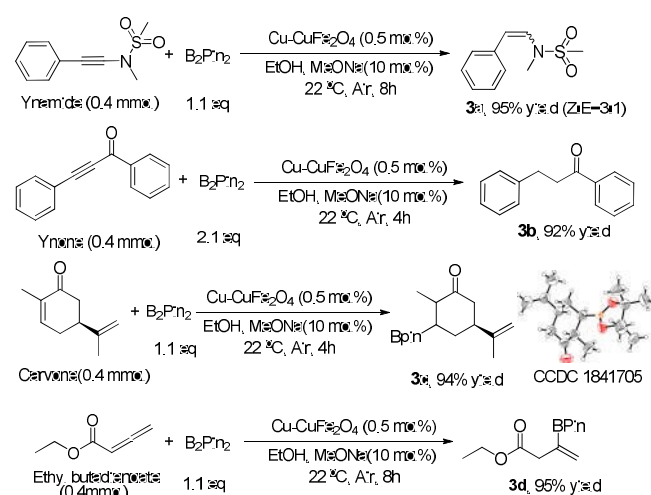
chemical selectivity, which probably has many important applications in organic synthesis. DOI: 10.1039/C8NJ03708F

**Table 2** Substrate scope of the aromatic and aliphatic alkynes<sup>[a,b]</sup>



Yields and reaction times for products **2a–2z**:

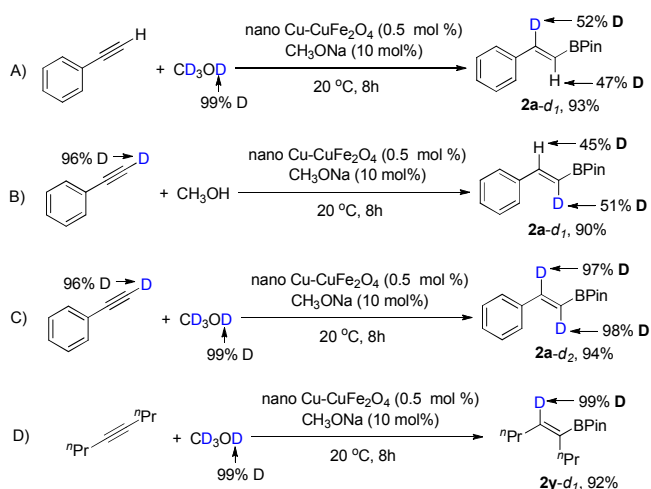
- 2a** (8h, 95%), **2b** (8h, 90%), **2c** (8h, 91%), **2d** (8h, 90%), **2e** (8h, 92%), **2f** (8h, 92%), **2g** (8h, 89%), **2h** (8h, 92%), **2i** (8h, 91%), **2j** (8h, 85%), **2k** (8h, 92%), **2l** (8h, 84%), **2m** (8h, 94%), **2n** (8h, 87%), **2o** (8h, 90%), **2p** (8h, 92%), **2q** (2h, 91%), **2r** (2h, 92%), **2s** (2h, 87%), **2t** (2h, 92%), **2u** (2h, 95%), **2v** (2h, 95%), **2w** (2h, 95%), **2x** (2h, 90%), **2y** (12h, 70%), **2z** (12h, 75%)

[a] Reaction conditions: Alkyne (0.4 mmol), B<sub>2</sub>Pin<sub>2</sub> (0.44 mmol), Cu-CuFe<sub>2</sub>O<sub>4</sub> nanoparticles (0.6 mg, 0.5 mol%), MeONa (10 mol%), ethanol (2 mL), under air, 22 °C. [b] Isolated yield.

**Scheme 1.** Substrate scope of the functionalized alkynes and alkenes

### 2.4 Mechanistic studies

To get some insights on this Cu-CuFe<sub>2</sub>O<sub>4</sub> NPs catalyzed hydroboration of alkynes, we conducted a series of deuterium labeling experiments, and the results are summarized in Scheme 2. Performing phenylacetylene and B<sub>2</sub>Pin<sub>2</sub> to the catalytic reaction in methanol-d<sub>4</sub> under air atmosphere lead to formation of the vinylboronate with deuterium at α- and β-vinyl carbon as well in 93% isolated yield (Scheme 2A). Similar results were obtained for the hydroboration reaction of phenylacetylene-d<sub>1</sub> with B<sub>2</sub>Pin<sub>2</sub> in methanol (Scheme 2B). We also studied the hydroboration of phenylacetylene-d<sub>1</sub> or oct-4-yne with B<sub>2</sub>Pin<sub>2</sub> in methanol-d<sub>4</sub> under the standard conditions. These reactions afforded vinylboronates **2a-d<sub>2</sub>** and **2y-d<sub>1</sub>** in high isolated yields, and the deuterium atoms of **2a-d<sub>2</sub>** and **2y-d<sub>1</sub>** are located at the α-vinyl carbon (Scheme 2C and 2D). The results of these deuterium-labeling experiments suggest that the proton source arise from the solvent used in the reaction.

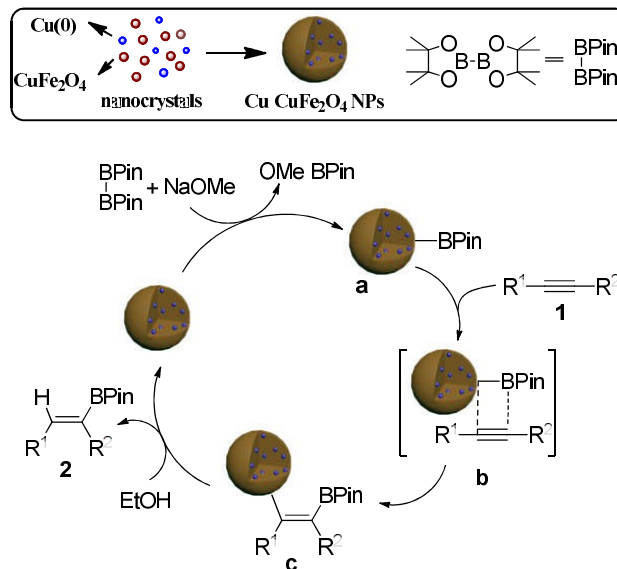


**Scheme 2.** Deuterium-Labeling Experiments

To demonstrate if the reaction was catalyzed by heterogeneous Cu-CuFe<sub>2</sub>O<sub>4</sub> NPs, we studied the structural variation of the catalyst before and after the reaction by transmission electron microscopy (TEM). As shown in Fig. S2, the shape and size of the Cu-CuFe<sub>2</sub>O<sub>4</sub> NPs still remained. In addition, the colour of the final reaction solution didn't turn to green or blue, which indicated that the catalyst had not been oxidized (Fig. S3).<sup>[8]</sup> This phenomenon was consistent with the previous result that the reaction performed well under nitrogen atmosphere (Table 1, entry 15). Subsequently, we tested the metal residue in the reaction solution by using ICP-MS. The copper concentration in the solution of the Cu-CuFe<sub>2</sub>O<sub>4</sub> system was about 0.07 ppm, which was much lower than that of common CuCl/PPh<sub>3</sub> catalyst system (35.63 ppm). These evidences completely implied the hydroboration catalyzed by Cu-CuFe<sub>2</sub>O<sub>4</sub> NPs was not under homogeneous reactions.

Based on the previous work of heterogeneous catalyst catalyzed hydroboration of alkenes,<sup>[6,10]</sup> and the results of the series of deuterium labeling experiments, a proposed catalytic cycle is depicted in Scheme 3. Key to the success of this

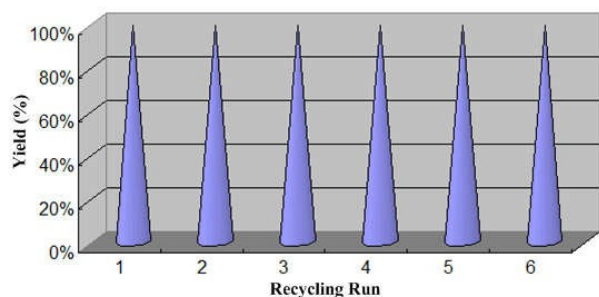
catalytic cycle is generate intermediate **a** by reaction of Cu-CuFe<sub>2</sub>O<sub>4</sub> with bis(pinacolato)diboron (B<sub>2</sub>Pin<sub>2</sub>) in the presence of NaOMe. Intermediate **a** through adsorption of alkyne **1** gives intermediate **b**, which subsequently transformed to **c**. Finally, treatment of **c** with ethanol yields the final product **2** and regenerates the Cu-CuFe<sub>2</sub>O<sub>4</sub> catalyst.



**Scheme 3.** Proposed Mechanism

### 2.5 Recycling and discussion of the catalyst

The recycling tests of the catalyst activity for the hydroboration of alkynes have also been explored. After the reaction was complete, the catalyst was separated by using an external magnet and reused for the hydroboration of the next batch of phenylacetylene and B<sub>2</sub>Pin<sub>2</sub> in the presence of MeONa. This procedure was repeatedly conducted with the recovered catalyst and the yield of the product was monitored in every cycle. As shown in Fig. 3, the products were isolated in 90-96% yields consistently for the reactions performed over six times. The recycled catalyst was subjected to XRD and TEM analysis (Fig. S4 and S5), and it was found that the structure and morphology of catalyst was unchanged. The leaching of the Cu was also discussed. ICP-MS analysis showed that the Cu lost was 0.015% after one catalytic circle. From these results, it was concluded that the Cu-CuFe<sub>2</sub>O<sub>4</sub> catalyst showed good stability in the hydroboration of alkynes.



**Fig.3** Recycling of Cu-CuFe<sub>2</sub>O<sub>4</sub>-catalyst for the synthesis of vinylboronates (Reaction conditions: Phenylacetylene (16 mmol), B<sub>2</sub>Pin<sub>2</sub>(17.6 mmol), Cu-CuFe<sub>2</sub>O<sub>4</sub> nanoparticles (24mg, 0.5 mol%), MeONa ( 10 mol%), ethanol (20 mL), under Air, room temperature, t =8h.)

### 3. Conclusions

In summary, a Cu-CuFe<sub>2</sub>O<sub>4</sub> NPs was prepared and utilized as a highly efficient and environmentally friendly catalyst for the hydroboration of alkynes. Broad functional group tolerance and good to excellent yields with high selectivities were observed under mild conditions. The catalyst shows good recyclability and can be recovered simply by a magnetic field and reused six times without significant loss in its catalytic activities. Furthermore, the heterogeneous catalytic mechanism was also discussed.

### 4. Experimental

**Materials and instrumentation.** Copper(II) chloride dihydrate (CuCl<sub>2</sub>·2H<sub>2</sub>O), ferric chloride hexahydrate (FeCl<sub>3</sub>·6H<sub>2</sub>O), sodium acetate (NaAc), trisodium citrate dihydrate (Na<sub>3</sub>Cit), ethyleneglycol (EG), bis(pinacolato)diboron (B<sub>2</sub>Pin<sub>2</sub>), sodium methoxide and all alkenes were purchased from Energy Chemical Reagent Company. Petroleum ether, ethyl acetate and other compounds were supplied by Sinopharm Chemical Reagent Co., Ltd. All reagents used in this work were used without further purification. The NMR spectra were recorded on an Varian 400 MHz spectrometer. GC-MS analysis was performed on Agilent7890-5975c G3440A 7890 instrument.

#### 4.1 Procedure for the preparation of Cu-CuFe<sub>2</sub>O<sub>4</sub> catalysts

FeCl<sub>3</sub>·6H<sub>2</sub>O (4.050 g, 15 mmol), CuCl<sub>2</sub>·2H<sub>2</sub>O (1.4488 g, 8.5 mmol), NaAc (8.2 g, 100 mmol), and Na<sub>3</sub>Cit (26.1 mg, 0.1 mmol) were dissolved in ethylene glycol (100 mL). After the mixture was stirred at room temperature for 4 h, the obtained homogeneous solution was transferred to an autoclave and heated to 200 °C for 12 h. When the reaction was completed and cooled to room temperature, the solid product was filtered, and then rinsed with water and ethanol three times, and dried at room temperature.

#### 4.2 General procedure for the preparation of vinylboronates

CH<sub>3</sub>CH<sub>2</sub>OH (2 mL), the alkyne (0.4 mmol), B<sub>2</sub>Pin<sub>2</sub> (112mg, 0.44 mmol), sodium methoxide (2.2 mg, 0.04 mmol) and Cu-CuFe<sub>2</sub>O<sub>4</sub> nanoparticles (0.6 mg, 0.5 mol %) were added to a

Schlenk tube under air atmosphere. The mixture was then stirred at room temperature for 8 h. Next, the solvents were evaporated under vacuum, and 3 mL of water added into the tube. Then the aqueous solution was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 mL three times). The combined organic phase was dried over anhydrous MgSO<sub>4</sub> and concentrated, and the residue was purified by column chromatography using petroleum ether/ethyl acetate (v/v=20:1) as an eluent. Evaporation of the volatiles under vacuum resulted in the corresponding product.

#### 4.3 Procedure for catalyst recycling

The recycling of the catalyst was carried out for the synthesis of vinylboronate under the same procedure given in the section 3.2 under reaction conditions: Phenylacetylene (16 mmol), B<sub>2</sub>Pin<sub>2</sub> (17.6 mmol), Cu-CuFe<sub>2</sub>O<sub>4</sub> nanoparticles (24mg, 0.5 mol%), MeONa ( 10 mol%), ethanol (20 mL), under air, room temperature, t = 8h. In each run, after the reaction the catalyst was separated by filtration, washed thoroughly with ethyl acetate, water, ethanol and dried by vacuum. Then, the dried catalyst was used further, without any purification or reactivation. The filtrate was evaporated under vacuum, and the residue was purified by column chromatography. The main text of the article should appear here with headings as appropriate.

### Conclusions

The conclusions section should come in this section at the end of the article, before the acknowledgements.

### Conflicts of interest

The authors declare no conflict of interest.

### Acknowledgements

Financial support from the National Natural Science Foundation of China (21771088, 21371078, 21401077), the Natural Science Foundation of Zhejiang Province (LY17B030011) and the open research fund of FJIRSM, CAS (20170034) is gratefully acknowledged.T

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Nano-copper ferrite supported Cu catalysts are active for hydroboration of alkynes to vinylboronates.

