



# Superparamagnetic copper ferrite nanoparticles catalyzed aerobic, ligand-free, regioselective hydroboration of alkynes: Influence of synergistic effect

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## ABSTRACT

We discovered a general and comprehensive approach for the regioselective hydroboration of terminal and internal alkynes to synthesize vinylboronates using inexpensive and magnetically separable copper ferrite nanoparticles at low catalyst loading using Bis(pinacolato)diboron in the absence of ligand and additives, under mild and greener conditions. A diverse range of functional groups was tolerated in the reaction, including allene and enones, and the corresponding boronates were obtained in high yields under air. Moreover, the as-synthesized alkenylboronates were used as precursors to prepare wide variety of vinylorgano chalcogenides regioselectively, in high yields. The present protocol enable the conversion of  $C_{sp}-H$  bonds to make  $C_{sp}^2-B$  bonds via activation of  $B-B$  bond, followed by formation of  $C_{sp}^2-Se$  (Te or S) bonds via activation of  $Se$  (Te or S)- $Se$  (Te or S) bonds in a regioselective manner. Deuterium isotope labeling studies showed that the proton source of vinyl boronate stem from the solvent employed.

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## 1. Introduction

Suzuki-Miyaura coupling is the most widely used organic reaction among synthetic chemists to form various kinds of bonds especially C–C, C–O, and C–N, so on [1–4]. Undoubtedly, C–Se (Te or S) bonds exhibit important biological properties, especially antiviral, anticancer and antitumor properties [5–8]. Suzuki coupling involves the use of boronic acids or analogues with different partners and transition-metal catalysts, which allows for the synthesis of a wide range of important organic molecules. The high stability, nontoxic nature, easy of handling, and substrate compatibility of organoboron compounds make them powerful and promising synthons in organic synthesis. Although numerous successful catalytic processes to synthesize vinylboronates have been established, attempts to increase the catalytic efficiency and to control reaction selectivity with broad substrate scope are still in place. Borylation of carbon-carbon triple bonds, followed by protonation, is one of the most attractive routes to generate vinylboronates with high regioselectivity. So far, significant efforts have been made to develop practical methods to synthesize this scaffold [9–14]. Among these, several methods based on transition-metal catalysis have been reported during the past decade [15–39]. In particular,

copper catalyzed hydroboration of alkynes are considered to be a cost-effective and straightforward approach to obtain alkenylboronic esters with high regioselectivity. However, most of the copper catalyzed reactions are homogeneous and require high catalyst loading, ligands, and long reaction times to furnish high yields and selectivity. Recycling of the catalyst is highly desirable, as it can contribute significantly to cost reduction and the environment protection. Recently, Li and co-workers reported that micro copper powder promoted heterogeneous version of hydroboration of alkynes under inert atmosphere [40]. It is known that reducing the size from micro to nano could lead to different properties. Because of their large surface area, nano particles can adsorb a greater number of reactant molecules, which in turn undergo effective collisions to furnish the desired products in high yields, even at low catalyst loading. Our literature survey showed that very few nanoparticle catalysts have been used for the preparation of vinylboronates in the absence of phosphine ligands and those protocols require high temperature to accomplish high conversion [22,41].

During the past decade, significant improvements have been made in the field of nanotechnology and nano science, which have led to the design and production of new nanostructured catalytic systems. Among these catalytic systems, transition-metal nanoparticles (NPs) have attracted much attention because of their larger surface areas and higher density of active sites as compared to their bulk-metal equivalents; such properties enable their use for catalytic applications in various organic transformations [42–45]. NPs

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are promising heterogeneous catalysts that are effective even at low concentrations, allows easy isolation of the product, ligand free, and can be easily recovered and recycled. These intriguing features of NPs are highly desirable in the context of environmental and industrial concerns. In addition, it has been reported that supported metal NPs should have inherent advantages over their counterparts because of easy dissolution under experimental conditions, efficient recycling, aggregation, metal dispersion, synergistic effects between the metal and support, so on. Among various metal supports for NPs, magnetic materials have drawn much attention because the easy and complete recovery makes them for several recycles after the reaction by using external magnet and also eliminate metal contamination with products that are especially biologically important molecules [46–56]. Copper ferrite ( $\text{CuFe}_2\text{O}_4$ ) NPs with a spinel structure have been used widely in batteries, fuel cells, biology and catalytic studies owing to their advantages such as environment friendliness, moisture insensitivity, high dispersity, and easy recovery using an external magnetic field [57–63]. However, to the best of our knowledge, the composition-effect of the copper ferrite nanocatalysts on the catalytic performance for hydroboration of alkynes has not been reported.

Herein, we report the hydroboration of alkynes with a bis(pinacolato)diboron using  $\text{CuFe}_2\text{O}_4$  NPs as catalyst to prepare vinylboronates regioselectively in high yield under air. We demonstrate that the catalyst is selective, efficient and the synergistic effect is the key parameter to its high catalytic activity. One-pot synthesis of biologically important arylchalcogenide derivatives was also demonstrated.

## 2. Experimental

### 2.1. Materials and instrumentation

All commercial reagents and starting materials were purchased from Sigma-Aldrich and TCI and used without further purification. Methanol- $d_4$  was procured from Acros Organics. The products reported are known and their mass splitting pattern were consistent with the preceding literature. The mass spectra were determined by using Shimadzu GCMS-QP 2010 Ultra (Pusan National University). The NMR spectra were recorded on an Agilent 300 MHz spectrometer.

### 2.2. General procedure for the synthesis of vinylboronates

A 10 mL aluminium capped vial equipped with a stir bar was charged with a mixture of alkyne (1 mmol), bis(pinacolato)diboron (1.2 mmol), 0.5 mol%  $\text{CuFe}_2\text{O}_4$ , potassium *tert*-butoxide (10 mol%) and methanol (2 mL). The mixture was stirred at 50 °C for 12 h in air. Afterwards, the mixture was diluted with diethyl ether, filtered through celite bed, and extracted with water three times. The combined organic extract was dried with anhydrous magnesium sulfate followed by filtration and rotary evaporated of the solvent, the residue obtained was subjected to analyze GC–MS and the crude product was purified by column chromatography on silica with hexane as eluent.

### 2.3. Typical procedure for the synthesis of unsymmetrical vinyl chalcogenides from alkenylboronates and diaryl chalcogenides

To a 10 mL sealed aluminium capped glass vial with septum, charged diphenyl dichalcogenide (0.55 eq.), phenylvinyl boronate (1 eq.), DMSO:H<sub>2</sub>O (2:1) and  $\text{CuFe}_2\text{O}_4$ ·bpy (5 mol%). The mixture was heated at 100 °C under vigorous magnetic stirring for 12 h. After stirring for appropriate time, mixture was cooled to RT, diluted with diethyl ether, filtered through celite bed, and extracted with water three times. The combined organic extract was dried

with anhydrous magnesium sulfate followed by filtration and rotary evaporation of the solvent and the residue obtained was analyzed by GC–MS.

### 2.4. Typical procedure for the synthesis of phenylvinyl selenides from phenylselenium chloride

To a schlenk tube, phenylselenium chloride (1 eq.) and pentenylboronate (1.2 eq.) were charged followed by 1 mL of BMIM.BF<sub>4</sub> and the mixture was stirred at RT for 24 h. After stirring, the reaction mixture was extracted with diethyl ether and washed with water several times until complete removal of ionic liquid has achieved. The combined ether extracts were dried with anhydrous magnesium sulfate, filtered and rotary evaporated. The residue obtained was analyzed by GC–MS.

### 2.5. Recycle test

A 10 mL aluminium capped vial equipped with a stir bar was charged with a mixture of alkyne (1 mmol), bis(pinacolato)diboron (1.2 mmol), 0.5 mol%  $\text{CuFe}_2\text{O}_4$ , potassium *tert*-butoxide (10 mol%) and methanol (2 mL). The mixture was stirred at 50 °C for 12 h in air. After the reaction, the catalyst was recovered by an external magnetic field followed by washing with methanol and dried in a vacuum for 12 h. The recovered nanoparticle was then reused four times in subsequent reactions under identical conditions without any significant loss of catalytic activity.

## 3. Results and discussion

### 3.1. Optimization of reaction conditions

In continuation of our studies on copper-catalyzed transformations and exploration of new nanocatalytic systems [64–69], we report commercially available [70]  $\text{CuFe}_2\text{O}_4$  NPs catalyze hydroboration of alkynes in the presence of bis(pinacolato)diboron ( $\text{B}_2\text{Pin}_2$ ) and base, under mild conditions.  $\text{B}_2\text{Pin}_2$  is an environmental friendly, benchmark reagent and more stable towards oxygen and moisture compared to other boron sources that cannot be handled in air owing to oxidative and hydrolytic reactions of the B–H bonds. In addition, lower catalyst loadings of an inexpensive catalyst, no phosphine or NHC-ligands, effective conversion of challenging alkynes, high yields, excellent regioselectivity, heterogeneous etc., are important factors in the context of green chemistry.

So, keeping these aspects in mind, we initiated our studies by investigating the hydroboration of 4-tolylacetylene (**1a**) as the model substrate in the presence of  $\text{B}_2\text{Pin}_2$  (**2a**, 1.2 equiv) and base, using  $\text{CuFe}_2\text{O}_4$  NPs as the catalyst, to optimize the reaction conditions. Initially, the base (potassium *tert*-butoxide) and temperature (50 °C) were kept constant while the other parameters were varied. The solvents acetonitrile, toluene, tetrahydrofuran, and dimethyl sulfoxide afforded less satisfactory results (Table 1, entries 1–4), whereas methanol produced the highest yield (Table 1, entry 5) of the borylated product (**3aa**). A drop in yield was observed when the reaction was performed at room temperature (Table 1, entry 6). A control experiment with no catalyst has failed to increase the rate of the reaction and as a consequence, the yield was diminished (Table 1, entry 7). Among the bases tested, potassium carbonate and potassium hydroxide were less effective as compared to potassium *tert*-butoxide (Table 1, entries 8 and 9). The hydroboration could also be carried out successfully in the absence of base with a satisfactory yield (Table 1, entry 10). To the best of our knowledge, this is the first report of a heterogeneous catalyzed hydroboration of terminal alkynes to obtain high product yields in the absence of a base, at low catalyst copper loading. Interestingly,  $\text{CuFe}_2\text{O}_4$  nanoparticles were much more catalytically active than

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