



Short communication

Phosphine and palladium-free synthesis of aryl and alkenyl boronates: A nano-catalytic approach

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ARTICLE INFO

Article history:

Received 31 March 2016

Received in revised form 8 July 2016

Accepted 19 July 2016

Available online 22 July 2016

Keywords:

Borylation

Copper

Deuterium

Ligand-free

Nanoparticles

ABSTRACT

Superparamagnetic copperferrite nanoparticle is employed as an environmentally benign and efficient catalyst to affect the borylation of aryl iodides yielding the corresponding arylboronates at low catalyst loading under mild reaction conditions. This protocol tolerates various substituents present in aryl iodides and also could be extended to beta bromostyrenes in the absence of phosphine and palladium.

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1. Introduction

Arylboronic esters are important class of benchmark reagents with broad utility in the area of organic synthesis. Because of their unique chemical properties such as broad functional group availability, air stability, and ease of handling, they have been considered as important building blocks in organic synthesis, and as a consequence, they undergo a wide range of transformations that lead to the formation of C–C and C–X (X = heteroatom) bonds. The phenylboronic acid skeleton is a privileged structure in medicinal chemistry for the discovery of pharmaceutical leads. Boron-based compounds exhibit various important biological activities [1]. Kong and colleagues utilized boronic acids as antimetabolic agents (I and II) and bortezomib (III), a proteasome inhibitor, has been well known for anticancer therapy (Fig. 1) [2].

The traditional synthesis of arylboronic acids was accomplished via the reaction of aromatic organomercury compounds with borane solution followed by hydrolysis furnish arylboronic acids [3]. Various studies have reported that direct synthesis of arylboronic acids from aryl halides employing homogeneous palladium complex [4–9]. Compared to boronic acids, boronates are environmental friendly, easy to handle, air and chromatography-stable.

Heise et al. successfully prepared the boronate derivatives with the reaction of glycol borates and Grignard reagents at room temperature under mild conditions [10]. Chavant et al. described the synthesis of aryl boronic esters through metal-halogen exchange reaction between $i\text{PrMgCl}\cdot\text{LiCl}$ and aryl iodides at 0 °C using cyclic borate esters [11]. Alternate approaches admit transition-metal catalysts for syntheses of arylboronic acid esters via activation of C–H and C–X bonds. Among those, palladium, nickel, iridium and recently copper complexes or salts in combination with toxic phosphine ligands was employed for borylation to take place [12–21]. Notably, Zhang and co-workers were noticed the borylation of aryl iodides through cesium effect under transition-metal free conditions [22], followed by Kiatiesevi et al. employed palladium as catalyst along with copper co-catalyst and triphenylphosphine to effect borylation take place at C–I bond of aromatics [23].

Conversely, there is significant interest in the development of transition metal nanoparticles for technological applications in various areas such as chemical sensors, electrocatalysts for fuel cells, and heterogeneous catalysts for organic transformations. We wondered if the nanocatalytic system could be complementary to aforementioned protocols that involved phosphine and overcome by means of a spinel bimetallic nanoparticles as catalysts to effect borylation of haloarenes. Since the catalytic activities of nanoparticles largely dependent on the surface design of the support along with the size and shape of the metal nanoparticles, the quest for more suitable solid supports for copper nanoparticles to provide highly active and selective catalyst is a challenging problem.

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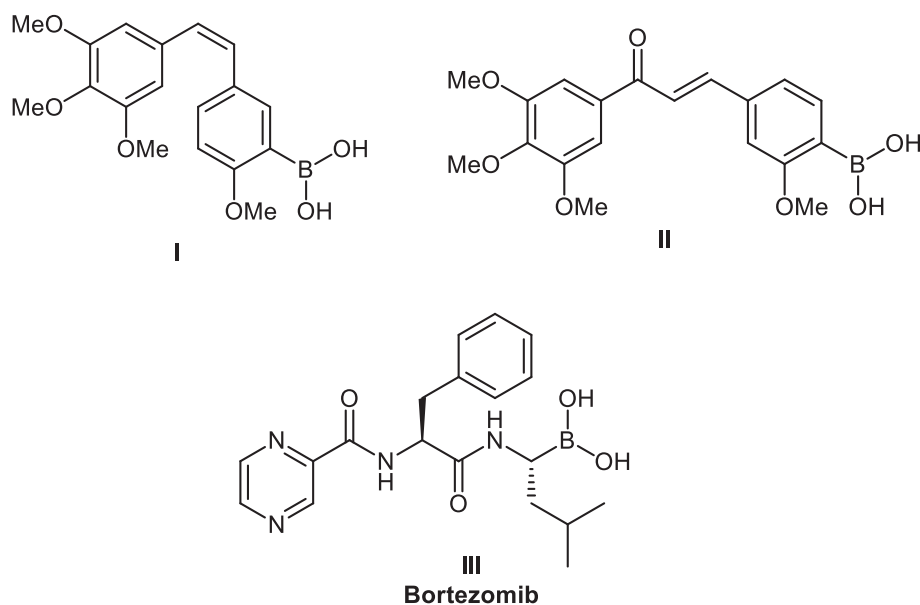


Fig. 1. Some biologically active organoboron compounds.

In the course of a program devoted to the discovery in designing a new nanoparticle catalysts for efficient organic transformations [24–31], we were interested in the synthesis of arylboronates using cost-

effective, readily available and magnetically recoverable copper ferrite nanoparticles is used as a catalyst to prepare arylboronates from aryl iodides under mild conditions. Of particular importance, we discovered

Table 1
Optimization of reaction conditions.

Entry	Cat. (mol%)	Solvent	Base	Yield (%) ^a
1	–	dmf	(CH ₃) ₃ COK	NR
2	2.5	dmf	(CH ₃) ₃ COK	77
3	5	dmf	(CH ₃) ₃ COK	90
4	5	dmf	(CH ₃) ₃ COLi	57
5	5	dmf	(CH ₃) ₃ CONa	44
6	5	dmf	MeOLi	80
7	5	dmpu	(CH ₃) ₃ COK	Trace
8	5	dmso	(CH ₃) ₃ COK	2
9	5	thf	(CH ₃) ₃ COK	3
10	5	Acetonitrile	(CH ₃) ₃ COK	2
11	5	Toluene	(CH ₃) ₃ COK	1
12	5	dma	(CH ₃) ₃ COK	53
13	5	nmp	(CH ₃) ₃ COK	20
14 ^b	5	dmf	(CH ₃) ₃ COK	8
15 ^c	5	dmf	(CH ₃) ₃ COK	13
16 ^d	5	dmf	(CH ₃) ₃ COK	48
17 ^e	5	dmf	(CH ₃) ₃ COK	55
18 ^f	5	dmf	(CH ₃) ₃ COK	41
19 ^g	5	dmf	(CH ₃) ₃ COK	ND

^a Determined by GC–MS.

^b Reaction with micro copper powder catalyst.

^c CuO nanopowder.

^d CuO hollow spheres.

^e Cu₂O nanocubes.

^f Copper nanoparticles.

^g Iron oxide nanoparticles.

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