



Ruthenium-catalyzed nitrogen-directed ortho C–H borylation of aromatic imines with pinacolborane

Yuna Maeda^a, Masaru Sato^a, Shinsuke Okada^a, Miki Murata^{a,b,*}

^a Graduate School of Materials Science and Engineering, Kitami Institute of Technology, 165 Koen-Cho, Kitami, Hokkaido 090-8507, Japan

^b School of Earth, Energy and Environmental Engineering, Faculty of Engineering, Kitami Institute of Technology, 165 Koen-Cho, Kitami, Hokkaido 090-8507, Japan



ARTICLE INFO

Article history:

Received 12 April 2018

Revised 8 May 2018

Accepted 15 May 2018

Available online 16 May 2018

Keywords:

C–H functionalization

Borylation

Ruthenium catalysis

Imines

ABSTRACT

An efficient ruthenium catalyst system for the direct ortho C–H borylation of aromatic imines is described. The reaction of *tert*-butyl-1-arylmethanimines with pinacolborane in the presence of Ru(cod)(cot), followed by hydrolysis, to afford the ortho-formyl-substituted arylboronates. The borylation was achieved with complete mono-selectivity.

© 2018 Elsevier Ltd. All rights reserved.

Since organoboron compounds are an important class of organometallics for modern organic synthesis, the development of transition metal-catalyzed C–B bond-forming reactions has triggered ongoing interest.¹ During the past few years, considerable attention has been devoted to the functional group-directed C–H bonds through nearby heteroatom coordination to the metal center of the catalyst.² While the surface supported phosphine ligands, pioneered by Sawamura, demonstrated a broad scope for the functional group-directed borylations, the preparation of the catalyst could look somewhat cumbersome.^{3,4}

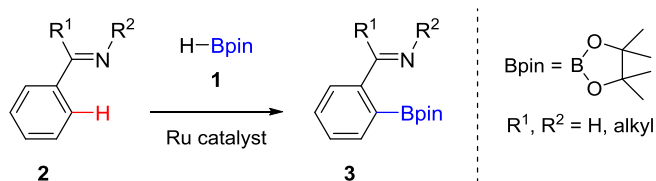
Recently, we and others demonstrated that the ruthenium-catalyzed C–H borylation of 2-arylpyridines took place at ortho-positions of the benzene ring.^{5–7} In these reports, relatively simple ruthenium complexes, e.g., commercially available RuH₂(CO)(PPh₃)₃, were used as a catalyst. During the course of further investigation of the site-selective aromatic C–H borylation, we expanded the ruthenium-catalyzed borylation protocol to other nitrogen-containing compounds. Herein, we wish to report an ortho-selective C–H borylation of aromatic imines **2** using pinacolborane (4,4,5,5-tetramethyl-1,3,2-dioxaborolane, **1**) as a boron source (Scheme 1).

At the outset of our studies, we tested reaction conditions for the dehydrogenative C–H borylation of (*E*)-*N*-*tert*-butyl-1-phenylmethanimine (**2a**) with pinacolborane (**1**). The results are summarized in Table 1. We started our experiments using similar conditions as reported in our C–H borylation procedure.⁶ When **2a** was treated with an excess amount of **1** (2 equiv) in the presence of 2 mol% of RuH₂(CO)(PPh₃)₃ in THF at 120 °C for 24 h, ca. 50% conversion of **2a** was reached (GC analysis). Although the resulting product **3a** could be observed by GC and ¹H NMR analyses of the crude reaction mixture, it was not able to avoid partially hydrolysis of **3a** during the analysis and isolation procedure.^{3c,8} The complete hydrolysis of the imine moiety of **3a** was achieved by subsequent treatment with hydrochloric acid to give the corresponding arylboronate bearing the formyl moiety **4a** in 48% yield (Entry 1). Under the condition, the reaction was completely ortho-regioselective. Furthermore, in contrast to our previous report with 2-arylpyridines, the formation of bis-borylated product **4a'** was completely suppressed at 120 °C (Entries 1 and 2).⁶

Although several ruthenium complexes, including Ru₃(CO)₁₂, Ru(cod)(cot), [Cp*RuCl]₄, and [RuCl₂(*p*-cymene)]₂, showed some catalytic activity for the C–H borylation (Entries 3–7), Ru(cod)(cot) was the catalyst of choice. Different reaction media were subsequently investigated, and THF proved to be the best solvent (Entries 3, 8, and 9). Thus, the optimized reaction conditions utilized Ru(cod)(cot) in THF. Under the condition, bis(pinacolato)di-

* Corresponding author at: School of Earth, Energy and Environmental Engineering, Faculty of Engineering, Kitami Institute of Technology, 165 Koen-Cho, Kitami, Hokkaido 090-8507, Japan.

E-mail address: muratamk@mail.kitami-it.ac.jp (M. Murata).



Scheme 1. Ortho-selective C–H borylation of aromatic imines.

boron also participated in the C–H borylation, although a significant amount of **4a'** was obtained (Entries 10 and 11).

With optimal reaction conditions in hands, the substrate scope of the reaction was then examined in order to establish the generality of the ortho-selective C–H borylation of aromatic imines **2** with **1** (Table 2). At first, a series of *N*-alkyl benzaldimines **2b–d** were subjected to the optimized conditions. The *N*-*tert*-butyl substituent was necessary to achieve a satisfactory result. On the other hand, less sterically hindered substituents, such as *n*-butyl, benzyl and cyclohexyl, were unfavorable for the present borylation due to competitive reduction of the imino groups (Entries 1–3).⁹

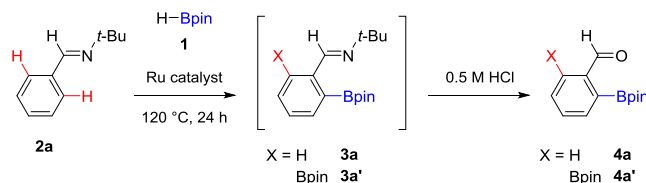
Next we investigated aromatic aldimine derivatives **2** bearing various substituents on the benzene ring. The values in parenthe-

ses show isolated yields by column chromatography. While the use of unmodified silica gel caused an undesired over-adsorption, we are pleased that the silica gel impregnated with boric acid gave satisfactory results.¹⁰ This borylation protocol tolerated para-substituted aldimines bearing not only electron-withdrawing (Entries 4 and 5) but also electron-donating groups (Entries 6 and 7). In addition, meta- and ortho-substituted aldimines also underwent the present borylation without any difficulties (Entries 8 and 9). The meta substituted aldimine **2i** underwent the C–H borylation only at the less hindered ortho position (Entry 8).

Subsequently, several aromatic ketimines were also surveyed under the optimized conditions. In contrast to aldimine analogs, *N*-benzyl ketimines underwent the ortho-selective C–H borylation with **1**, followed by hydrolysis, to afford the desired arylboronates containing an ortho acetyl moiety (Entries 10–12). In the case of **2m** bearing a methyl group at the meta position of the aromatic ring, the C–B bond formation took place only at the more sterically accessible position (Entry 12).

In conclusion, we have successfully applied aromatic imines **2** to the ruthenium-catalyzed ortho-selective C–H borylation using pinacolborane (**1**) as a boron source. The C–H borylation followed by hydrolysis gave the desired ortho-carbonyl-substituted arylboronates, which could be isolated by column chromatography on the boric-acid-impregnated silica gel. Further investigations to broaden the substrate scope are currently underway in our laboratory.

Table 1
Optimization of Ru-catalyzed borylation of **3a** with **1**^a.



Entry	Catalyst	Solvent	Yield% ^b	
			4a	4a'
1	RuH ₂ (CO)(PPh ₃) ₃	THF	48	0
2 ^c	RuH ₂ (CO)(PPh ₃) ₃	THF	44	4
3	Ru(cod)(cot)	THF	82	0
4 ^c	Ru(cod)(cot)	THF	70	22
5	Ru ₃ (CO) ₁₂	THF	2	0
6	[RuCl ₂ (<i>p</i> -cymene)] ₂	THF	8	0
7	[Cp*RuCl] ₄	THF	66	14
8	Ru(cod)(cot)	Cyclohexane	41	0
9	Ru(cod)(cot)	Toluene	57	0
10 ^d	Ru(cod)(cot)	THF	48	5
11 ^e	Ru(cod)(cot)	THF	4	64

^a Reaction conditions: **1** (0.5 mmol), **2a** (0.25 mmol), Ru catalyst (2 mol% Ru atom), and solvent (0.5 mL), 120 °C, 24 h.

^b GC yields are based on **2a**.

^c The reaction was carried out at 150 °C.

^d Bis(pinacolato)diboron (0.19 mmol) was used instead of **1**.

^e Bis(pinacolato)diboron (0.38 mmol) was used instead of **1**.

Download English Version:

<https://daneshyari.com/en/article/7828787>

Download Persian Version:

<https://daneshyari.com/article/7828787>

[Daneshyari.com](https://daneshyari.com)