



Nickel(0) powder catalysis in Suzuki–Miyaura cross-coupling reaction

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ABSTRACT

Iodo- and bromoarenes are cross-coupled with arylboronic acids in the presence of a catalytic amount of nickel(0) powder along with a base in PEG-400 at 110 °C to afford biaryls in high yields.

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1. Introduction

The transition metal-catalyzed carbon–carbon bond forming reaction by the cross-coupling of aryl, vinyl and alkyl electrophiles with organoboranes is well known as Suzuki–Miyaura cross-coupling reaction [1–5]. This protocol has been widely used as a powerful synthetic tool for the synthesis of pharmaceuticals and organic materials. Many elegant catalytic systems which facilitate such a coupling under the milder and cheaper conditions have been developed by the tuning of a ligand combined with the kind of palladium catalysts. In connection with this report, a number of homogeneous and heterogeneous nickel catalysts have also been used for Suzuki–Miyaura coupling [6–11]. For representative examples, Miyaura et al. have reported that chloroarenes are readily coupled with arylboronic acids in the presence of nickel(0) catalyst in situ prepared from $\text{NiCl}_2(\text{dppf})$ and BuLi to give biaryls [12]. It is also worthy to note that nickel on charcoal and graphite precursors can be easily activated and used to catalyze the cross-coupling of haloarenes with arylboronic acids [13,14]. It was also disclosed by Monteiro that $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ can be directly used for such a coupling without further addition of a phosphine ligand [15]. Unactivated alkyl halides were found to be cross-coupled with arylboronic acids in the presence of a nickel catalyst combined with amino alcohols as ligands [16]. Under these circumstances, as a nickel catalyst alternative for Suzuki–Miyaura cross-coupling, herein this report

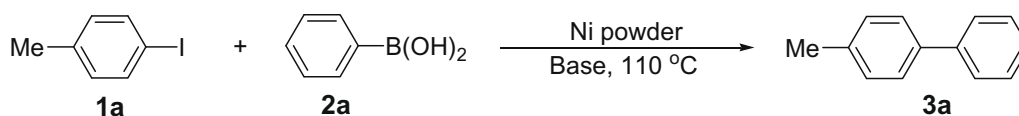
describes a nickel powder-catalyzed cross-coupling reaction between haloarenes and arylboronic acids leading to biaryls.

2. Results and discussion

The results of several attempted cross-coupling reactions of 4-iodotoluene (**1a**) with phenylboronic acid (**2a**) for the optimization of conditions are listed in Table 1. Treatment of **1a** with 1.2 equiv. of **2a** in PEG-400 in the presence of a catalytic amount of nickel(0) powder (10 mol% based on **1a**) along with K_3PO_4 for 1 h afforded 4-phenyltoluene (**3a**) in 79% yield with incomplete conversion of **1a** on GLC (run 1). Biphenyl formed by the homocoupling of **2a** was not obtained at all. The yield of **3a** increases with prolonging the reaction time up to 5 h (runs 1–3). The reaction proceeded similarly even in the presence of a smaller amount of nickel(0) powder under the employed conditions (runs 2 and 4). Among the bases examined, K_2CO_3 and Cs_2CO_3 revealed to be as similarly effective as K_3PO_4 (runs 4–6). However, NaOAc was not effective for the formation of **3a** (run 7). On the other hand, the kind of solvent was critical for the formation of **3a**. It is reported by several groups that poly(ethylene glycol) (PEG) is used as an efficient medium in transition metal-catalyzed reactions [17–26]. Performing the reaction combined with CsCO_3 in solvents such as toluene and dioxane resulted in only 0–10% yields of **3a** (runs 8 and 9). However, DMF could be alternatively used (run 10). As a result, after further elaborated tuning with reaction time, the best result in terms of both product **3a** yield and complete conversion of **1a** is best accomplished by the standard set of reaction conditions

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Table 1
Optimization of conditions for the reaction of 4-iodotoluene (**1a**) with phenylboronic acid (**2a**).



Run	Ni powder (mmol)	Bases	Solvents	Time (h)	Yield (%)
1	0.1	K ₃ PO ₄	PEG-400	1	79
2	0.1	K ₃ PO ₄	PEG-400	5	93
3	0.1	K ₃ PO ₄	PEG-400	10	93
4	0.05	K ₃ PO ₄	PEG-400	5	90
5	0.05	K ₂ CO ₃	PEG-400	5	88
6	0.05	Cs ₂ CO ₃	PEG-400	5	90
7	0.05	NaOAc	PEG-400	5	44
8	0.05	Cs ₂ CO ₃	Toluene	5	0
9	0.05	Cs ₂ CO ₃	Dioxane	5	10
10	0.05	Cs ₂ CO ₃	DMF	5	89
11	0.05	K ₃ PO ₄	PEG-400	10	94
12	0.05	K ₂ CO ₃	PEG-400	10	99
13	–	K ₂ CO ₃	PEG-400	10	0

Reaction conditions: **1a** (1 mmol), **2a** (1.2 mmol), base (2 mmol), solvent (2 ml), at 110 °C, under N₂.

shown in run 12 of Table 1. Finally, in order to identify the possibility of the contamination of Pd in the reagents, we carried out the reaction in the absence of nickel powder in new reaction tube and magnetic bar and confirmed that **3a** was not formed at all (run 13). We also confirmed that no Pd in nickel powder was observed by ICP-OES (<1 ppm).

After the reaction conditions have been established, various aryl iodides **1** were subjected to the reaction with arylboronic acids **2** in order to investigate the reaction scope and several representative results are summarized in Table 2. An array of aryl iodides (**1a–g**) having electron-donating and -withdrawing substituents on the aromatic ring reacted with **2a** and the corresponding coupled biaryls (**3a–g**) were produced in the range of 75–99% isolated yields. The product yield was not significantly affected by the position of the substituent on **1a–g**, whereas the electronic nature of that had some relevance to the product yield. Lower reaction rate and yield were observed with 4-iodoanisole (**1e**). In the reaction of iodobenzene (**1d**) with various arylboronic acids (**2b–f**) having electron-donating and -withdrawing substituents, the corresponding biaryls were also obtained in quantitative yields. From the reactions between substituted iodobenzenes (**1a** and **1f**) and 4-tolylboronic acid (**2b**), the corresponding biaryls were also produced in similar yields.

Similar treatment of bromobenzene (**4a**) with **2a** under the employed conditions afforded biphenyl (**3d**) in only 5% yield with incomplete conversion of **4a** on GLC. However, when 0.2 equiv. of I₂ was further added, the reaction rate was dramatically enhanced and **3d** was obtained in 95% yield with complete conversion of **4a** (Table 3) [27,28]. Several aryl bromides (**4b–e**) were also readily cross-coupled with arylboronic acids under the I₂ introduced conditions to give the corresponding biaryls in the range of 70–95% yields.

Finally, strongly electron withdrawing group substituted chloroarene, 4-chloronitrobenzene (**5**) was also found to be coupled with **2a** under the conditions used in the reaction with bromoarenes to give 4-nitrobiphenyl (**3o**) in 92% isolated yield (Scheme 1). However, neither 4-iodotoluene (**1a**) nor 1-iodooctane was coupled with **2a** under the employed conditions.

3. Experimental

3.1. General

¹H and ¹³C NMR (400 and 100 MHz) spectra were recorded on a Bruker Avance Digital 400 spectrometer using TMS as an internal

standard. Melting points were determined on a Stanford Research Inc. MPA100 automated melting point apparatus. GLC analyses were carried out with a Shimadzu GC-17A instrument equipped with a CBP10-S25-050 column (Shimadzu, fused silica capillary column, 0.33 mm × 25 m, 0.25 μm film thickness) using nitrogen as carrier gas. The isolation of pure products was carried out via column (silica gel 60, 70–230 mesh, Merck) or thin layer (silica gel 60 GF₂₅₄, Merck) chromatography. Nickel powder (100 mesh, 99.99%) was purchased from Aldrich. Commercially available organic and inorganic compounds were used without further purification except for toluene, which was distilled by known method before use.

3.2. General procedure for Ni powder-catalyzed cross-coupling reaction of iodo- and bromoarenes with arylboronic acids

To an organic reactor (Radleys Discovery Technologies) were added haloarene (**1** and **4**) (1 mmol), arylboronic acid **2** (1.2 mmol), nickel powder (0.05 mmol), K₂CO₃ (0.276 g, 2 mmol) and PEG-400 (2 ml). In the reaction with bromoarene **4**, I₂ (0.051 g, 0.2 mmol) was further added. After the system was flushed with N₂, the mixture was stirred at 110 °C for 10 h. The reaction mixture was cooled down to room temperature, poured into water and extracted with ethyl acetate (30 ml × 3). The combined organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mixture was purified by thin layer chromatography (silica gel, ethyl acetate–hexane mixture) to give biaryls **3**. All biaryls prepared by the above procedure were characterized by GLC and melting point comparison with authentic samples synthesized by known methods and purchased from chemical companies. Spectroscopic data for several selected biaryls are shown below.

4-Acetyl-4'-methylbiphenyl (3k): Solid; m.p. 119 °C (chloroform) (lit. [29] 119–120 °C); ¹H NMR (400 MHz, CDCl₃) δ 2.40 (s, 3H), 2.61 (s, 3H), 7.26 (d, *J* = 8.1 Hz, 2H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 2H), 8.00 (d, *J* = 8.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 21.33, 26.80, 127.08, 127.24, 129.06, 129.85, 135.71, 137.06, 138.39, 145.84, 197.93.

4-Acetyl-4'-fluorobiphenyl (3l): Solid; m.p. 103.2–103.5 °C (hexane) (lit. [30] 102–104 °C); ¹H NMR (400 MHz, CDCl₃) δ 2.62 (s, 3H), 7.12–7.16 (m, 2H), 7.55–7.59 (m, 2H), 7.62 (d, *J* = 8.3 Hz, 2H), 8.01 (d, *J* = 8.3 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 26.80, 116.06 (d, *J* = 21.1 Hz), 127.19, 129.07 (d, *J* = 8.0 Hz), 129.13, 135.97, 136.12 (d, *J* = 2.9 Hz), 144.84, 163.14 (d, *J* = 246.6 Hz), 197.83.

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