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An Efficient Suzuki–Miyaura Coupling of Aryl Sulfamates and Boronic Acids Catalyzed by $NiCl_2$(dppp)

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Keywords: Nickel / Cross-coupling / Sulfur / Boronic acids / Biaryls

The Suzuki–Miyaura cross-coupling of aryl sulfamates and boronic acids was investigated by using [1,3-bis(diphenylphosphanyl)propane]nickel(II) chloride {$NiCl_2$(dppp)} as the catalyst. The results showed that $NiCl_2$(dppp) is a highly active and general catalyst that allows effective Suzuki–Miyaura cross-coupling of aryl sulfamates with a slight excess amount of the boronic acid (1.2 equiv.) in the presence of a low catalyst loading (generally 1.0–1.5 mol-%). The method also displays broad generality not only to various aryl sulfamates, but also to an array of boronic acids. Furthermore, various functional groups are tolerated. These apparent advantages make $NiCl_2$(dppp) a practical and reliable catalyst system for the Suzuki–Miyaura coupling of aryl sulfamates.

Introduction

Recently, the transition-metal-catalyzed cross-coupling of phenol/enol derivatives has received intense interest due to the wide availability and cheapness of phenolic compounds and the great importance of biaryl compounds in a broad range of areas.[1] Among various coupling reactions, the Suzuki–Miyaura cross-coupling is especially attractive because it involves the advantageous use of boronic acids as nucleophiles, which are stable to air and moisture and widely available, they show low toxicity and good functional group tolerance, and boron-containing byproducts can be easily purified.[2] One of the key efforts involved in this transformation is the development of an effective activating reagent that could activate the inert phenolic C–O bond for practical and reliable coupling by employing a stable, readily available, and cheap Ni-based catalyst. So far, numerous protocols have been developed including the use of an aryl triflate,[3] sulfonate,[4] ether,[4l,5] ester,[4l,6] carbamate,[4l,7] carbonate,[4l,7b] sulfamate,[4k,4l,7b–7d] phenolate,[8] sulfate,[9] phosphoramide,[10] phosphonium salt,[11] and phosphate,[12] and even more elegantly by the mutual activation of C–O and C–B bonds as developed very recently by Shi.[13]

In the above-mentioned coupling reactions, $NiCl_2(PCy_3)_2$ was the most frequently used catalyst owing to its ready availability and stability. However, most of these protocols required a high catalyst loading and a large excess amount of the boronic acids. In addition, some of the reactions necessitated the use of additional phosphane ligands. For instance, aryl sulfamate,[7b–7d] which has been shown to be the most competent electrophile discovered so far, required essentially 5–10 mol-% of $NiCl_2(PCy_3)_2$ associated with the use of 2.5–4.0 equiv. of boronic acids and 4.0–7.2 equiv. of K_3PO_4 base. More to the point, even under these severe conditions, the coupling efficiency for many of the phenol derivatives was only moderate except for aryl sulfamates. Thus, the development of a highly active catalyst system that allows the effective coupling of phenolic derivatives under more simplified conditions, for example, a significantly lowered catalyst loading and a low molar ratio of phenol derivative and boronic acid (ideally 1:1) remains an urgent demand for practical applications.

In our previous studies, we demonstrated that $NiCl_2$(dppp) was an efficient catalyst for the Suzuki–Miyaura cross-coupling of various phenol derivatives such as aryl phosphoramide,[10] phosphonium salt,[11] tosylate,[4j] mesylate,[4j] and halides.[14] Of particular note is that this catalyst is capable of catalyzing the cross-coupling of conventionally less reactive aryl tosylates, mesylates, and chlorides with a catalyst loading of lower than 1 mol-% without the need of an external supporting ligand. In addition to its high activity, $NiCl_2$(dppp) is also more stable and cheaper than $NiCl_2(PCy_3)_2$.[15] To best use this catalyst system, we initiated an investigation into the Suzuki–Miyaura coupling of aryl carbamates and sulfamates, as these substrates have the added advantages that they can direct the installation of functional groups onto the aromatic ring and they have good leaving ability.[7] Herein, we present that $NiCl_2$(dppp) is also a highly active catalyst for practical and reliable cross-coupling of aryl sulfamates and boronic acids. Our results showed that, under the optimized conditions, the re-

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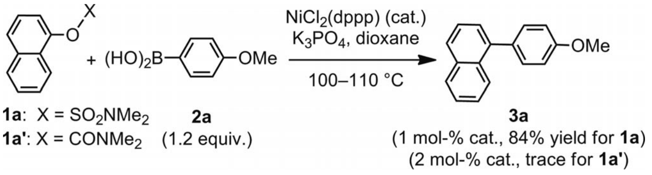
action proceeds smoothly with only a slight excess amount of the boronic acid (1.2 equiv.) in the presence of a significantly lowered catalyst loading (1–1.5 mol-%). These results provide an important advance for the Suzuki–Miyaura cross-coupling of aryl sulfamates.

Results and Discussion

At the outset, the catalytic activity of $NiCl_2$(dppp) for the cross-coupling of aryl sulfamates and carbamates was evaluated by employing the coupling of 1-naphthyl sulfamate (**1a**) or 1-naphthyl carbamate (**1a′**) with 4-methoxyphenyl boronic acid (**2a**) as the model reactions (Scheme 1).[16] After a brief optimization of the reaction conditions on the basis of our previous experiences,[4j,10,11,14] we quickly found that whereas the reaction of carbamate **1a′** and **2a** was inefficient, sulfamate **1a** could couple smoothly with only a slight excess amount of **2a** (1.2 equiv.) in the presence of 1 mol-% of $NiCl_2$(dppp) as catalyst and 4.0 equiv. of K_3PO_4 as base in dioxane at 100 °C. Under these conditions, desired product **3a** was obtained in 84% yield.

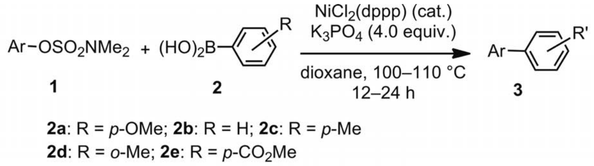


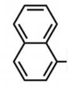
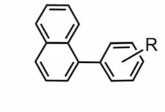
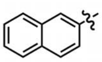
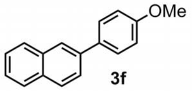
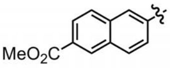
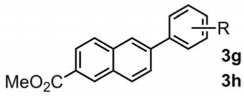
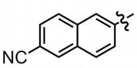
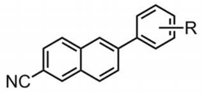
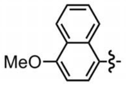
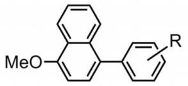
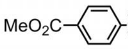
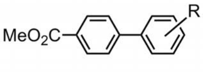
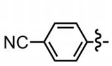
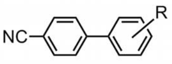
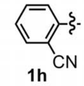
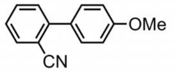
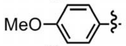
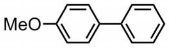
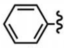
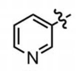
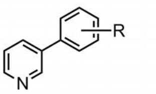
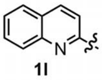
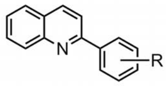
Scheme 1. Comparison of the reactivity of 1-naphthyl sulfamate and 1-naphthyl carbamate.

We then examined the substrate scope and limitation of these conditions. The results show that the reaction conditions exhibit good structural compatibility both to aryl sulfamates and boronic acids. As shown in Table 1, unsubstituted 1-naphthyl sulfamate (**1a**) and 2-naphthyl sulfamate (**1b**) coupled smoothly with a range of boronic acids, whose structures are decorated by electron-donating OMe (Table 1, Entry 1; **2a**), neutral H (Table 1, Entry 2; **2b**), and Me groups (Table 1, Entries 3 and 4; **2c** and **2d**), as well as electron-withdrawing CO_2Me groups (Table 1, Entry 5; **2e**) to afford desired products **3a**–**f** in high yields. Notably, a good yield (76%) for **3d** implies that the transformation is also tolerant of *ortho*-substituted boronic acid. In addition, efficient coupling was also observed for other naphthyl sulfamates modified by either an electron-deficient group such as CO_2Me (Table 1, Entries 7 and 8; **1c**) and CN groups (Table 1, Entries 9–11; **1d**) or an electron-rich group such as OMe (Table 1, Entries 12 and 13; **1e**), although a catalyst loading of 2 mol-% was required for electron-rich substrate **1e**.

Next, we extended the technology to non-fused aromatic sulfamates. This is far more challenging because of the less delocalized nature of the aromatic ring (i.e., less electron-deficient system). The results show consistently with the general observations[5–11] that non-fused aryl sulfamates were

Table 1. Suzuki–Miyaura cross-coupling of various sulfamates and boronic acids.[a]



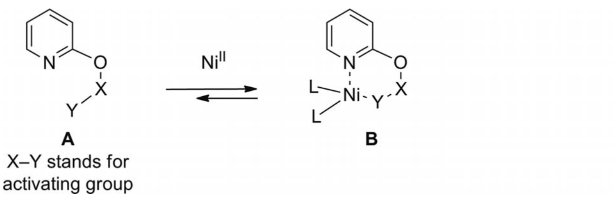
Entry	Ar	ArB(OH)2	Product	Yield[b] [%]
1	 **1a**	**2a**	 **3a** R = *p*-OMe	84
2		**2b**	**3b** R = H	76[c]
3		**2c**	**3c** R = *p*-Me	93[c]
4		**2d**	**3d** R = *o*-Me	76[c]
5		**2e**	**3e** R = CO_2Me	64
6	 **1b**	**2a**	 **3f**	77
7	 **1c**	**2a**	 **3g** R = *p*-OMe	76
8		**2e**	**3h** R = *p*-CO_2Me	71
9	 **1d**	**2a**	 **3i** R = *p*-OMe	95
10		**2b**	**3j** R = H	82
11		**2e**	**3k** R = *p*-CO_2Me	90
12	 **1e**	**2a**	 **3l** R = *p*-OMe	75[d]
13		**2b**	**3m** R = H	61[d]
14	 **1f**	**2a**	 **3n** R = *p*-OMe	74
15		**2b**	**3o** R = H	84
16	 **1g**	**2a**	 **3p** R = *p*-OMe	96
17		**2b**	**3q** R = H	81
18		**2d**	**3r** R = *o*-Me	87
19		**2e**	**3s** R = *p*-CO_2Me	80
20	 **1h**	**2a**	 **3t**	77[e]
21	 **1i**	**2b**	 **3u**	35
22	 **1j**	**2a**	**3u**	38
23	 **1k**	**2a**	 **3v** R = *p*-OMe	99
24		**2b**	**3w** R = H	88
25		**2e**	**3x** R = *p*-CO_2Me	85
26	 **1l**	**2a**	 **3y** R = *p*-OMe	84[e]
27		**2b**	**3z** R = H	88[e]

[a] Reaction conditions: Aryl sulfamate **1** (0.5 mmol), boronic acid **2** (0.6 mmol), K_3PO_4 (2.0 mmol, 4.0 equiv.), dioxane (3 mL), 100–110 °C, 12–24 h; unless otherwise noted, 1.0 and 1.5 mol-% of $NiCl_2$(dppp) loading, respectively, for the naphthyl-based sulfamates and non-fused aromatic sulfamates. [b] Isolated yield. [c] Yield was determined by ^1H NMR spectroscopy due to the contamination of a small amount of hard-to-separate byproduct derived from homocoupling of the boronic acid. [d] A catalyst loading of 2 mol-% was used. [e] A catalyst loading of 3 mol-% was used.

somewhat less reactive than the fused aromatic analogues. However, efficient coupling could be achieved under conditions that were otherwise identical to those used to couple naphthyl sulfamates except that the catalyst loading was increased from 1.0 to 1.5 mol-%. Under these slightly altered conditions, aryl sulfamates activated by electron-withdrawing groups such as ester (Table 1, Entries 14 and 15; **1f**) and cyano groups (Table 1, Entries 16–19; **1g**) were viable coupling partners. They were coupled smoothly with an array of boronic acids substituted by electron-donating OMe, simple H, and electron-withdrawing CO_2Me groups, as well as sterically hindered boronic acid (Table 1, Entry 18; **3r**). Moreover, *ortho*-cyano substituted substrate **1h** (Table 1, Entry 20) could also be coupled smoothly to give **3t** in high yield in the presence of 1.2 equiv. of boronic acid and 3 mol-% of the catalyst. The effective coupling of sterically hindered **1h** is important, because it can be potentially used for synthesizing the key intermediate of antihypertensive sartan drugs.[7d,14] However, deactivated (Table 1, Entry 21; **1i**) and non-activated (Table 1, Entry 22; **1j**) substrates were somewhat challenging, affording the coupled product in significantly lower yields.

Finally, the coupling efficiency of N-heteroaromatic sulfamates was investigated as represented by N-3 (Table 1, Entries 23–25; **1k**) and N-2 heteroarenes (Table 1, Entries 26 and 27; **1l**). Both 3- and 2-pyridyl derivatives **1k** and **1l** could be coupled uneventfully with electron-rich (i.e., **2a**), neutral (i.e., **2b**), and electron-deficient boronic acids (i.e., **2e**). These results suggest that the method is also applicable to heteroaryl sulfamates.

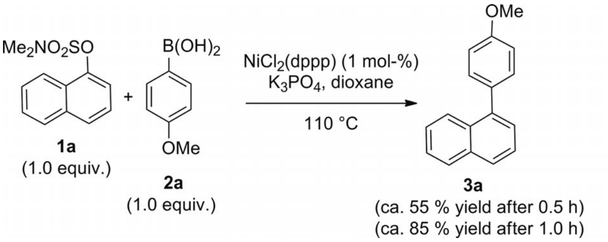
Here, a little more attention should be given to 2-quinolyl sulfamate (**1l**): a somewhat higher catalyst loading of 3 mol-% was required for this substrate compared with other substrates. Of the Ni-catalyzed Suzuki–Miyaura cross-coupling reactions of N-heterophenolic derivatives, the 3- and 4-pyridyl derivatives have been extensively studied, and the reactions proved to be successful.[4j,7a,10,11a] However, only very few examples of 2-OH pyridine analogues have been reported, and these couplings were unsuccessful. This is in sharp contrast to the great importance of 2-arylated pyridyl compounds in a wide spectrum of areas such as catalysis, coordination, and functional materials. In fact, we[11b] and other groups[7a] have experienced problems in Ni-catalyzed Suzuki–Miyaura couplings of 2-OH pyridine derivatives. Most possibly, this is due to the unique structural features of the 2-pyridyl scaffold, which is ready to form an N-containing six-membered chelate with the Ni catalyst[11b] [e.g., **B** in Equation (1)], and thereby, suppressing the activity of the catalyst. Indeed, similar coordination effects have also been observed in Pd-catalyzed Heck coupling of 2-halopyridines.[17] Nevertheless, herein we showed that 2-pyridyl sulfamates would be viable substrates to couple with boronic acids in the presence of a low loading of $NiCl_2$(dppp) as the catalyst.



(1)

Having exemplified the high activity and the broad substrate scope of $NiCl_2$(dppp) for the Suzuki–Miyaura cross-coupling of aryl sulfamates, we became interested in obtaining further insight into the reactivity difference between aryl sulfamates and tosylates or mesylates. The two classes of substrates have shown to be competent electrophiles[18] in the presence of the $NiCl_2$(dppp) catalyst and are readily available and markedly stable for handling, but each class of substrate has their distinctive advantages. Typically, as an important advantage, the sulfamyl group may serve as a latent directing group for the installation of other functional groups onto the aromatic ring at the *ortho*/*para* position prior to cross-coupling.[7] Aryl tosylates or mesylates are much cheaper than aryl sulfamates due to the considerably lower cost of tosyl chloride or mesyl chloride in comparison to the cost of *N*,*N*-dimethylsulfamoyl chloride.[19] Furthermore, the preparation of aryl sulfonates is more convenient than that of aryl sulfamates, because triethylamine is used as the base instead of sodium hydride for the preparation of aryl sulfonates. Therefore, an investigation into the reactivity difference between aryl sulfamates and sulfonates would provide important information for choosing suitable activating reagents when a particular synthetic application is under consideration.

Accordingly, the reactivity of 1-naphthyl sulfamate (**1a**) and 1-naphthyl tosylate (**4**) was compared through the coupling with 4-methoxyphenyl boronic acid (**2a**) under identical reaction conditions [Equations (2) and Equation (3)]. The results showed that in the presence of only 1.0 equiv. of boronic acid and 1 mol-% of $NiCl_2$(dppp) as catalyst, the two different substrates display equally high reactivity with ca. 55% yield of product **3a** observed for both reactions after heating the reaction mixture for 0.5 h.[20] Complete conversion as well as high yields (85 and 80%, respectively)



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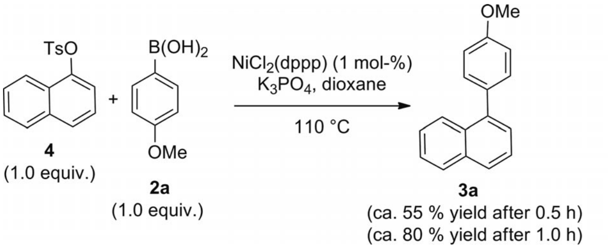

(3)

was observed when the reaction time was elongation to 1 h. These results indicate that aryl sulfamates and tosylates display similar high reactivity in the presence of the $NiCl_2$(dppp) catalyst.

Conclusions

In summary, we have clearly demonstrated that $NiCl_2$(dppp) is a highly active and generally applicable catalyst for the Suzuki–Miyaura cross-coupling of aryl sulfamates and boronic acids, although deactivated and non-activated phenyl sulfamates are somewhat less reactive. This catalyst offers several advantages over the frequently used $NiCl_2(PCy_3)_2$ catalyst. Namely, effective coupling proceeds smoothly with only a slight excess amount of the boronic acid (1.2 equiv.) as well as a significantly lowered catalyst loading of 1–1.5 mol-% for most of the substrates. In contrast, 2.5–4.0 equiv. of the boronic acid in the presence of a catalyst loading of 5–10 mol-% was essentially required when $NiCl_2(PCy_3)_2$ was employed as catalyst. In addition to the high catalytic efficiency, the $NiCl_2$(dppp) complex is more stable towards air and moisture than $NiCl_2(PCy_3)_2$, which can be attributed to a combination of the bidentate and aromatic nature of the dppp ligand. Finally, dppp is much cheaper than the PCy_3 ligand.[15] Owing to the aforementioned advantages, $NiCl_2$(dppp) presented herein would be a more appealing catalyst for the transition-metal-catalyzed Suzuki–Miyaura cross-coupling of aryl sulfamate when large-scale synthesis is carried out.

Experimental Section

General Procedure for the Suzuki–Miyaura Cross-Coupling Reaction of Aryl Sulfamates with Arylboronic Acids: To a 25-mL Schlenk tube equipped with a magnetic bar was added $NiCl_2$(dppp) (amount indicated in Table 1), the aryl sulfamate (0.5 mmol, 1.0 equiv.), the arylboronic acid (0.6 mmol, 1.2 equiv.), and anhydrous K_3PO_4 (2.0 mmol, 4.0 equiv.). The tube was then evacuated (3 × 10 min) under vacuum and backfilled with N_2. Dried dioxane (3.0 mL) was injected by syringe, and the reaction mixture was stirred at 100–110 °C until the aryl sulfamate had disappeared as monitored by TLC. The reaction mixture was then poured into water (20 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layer was dried with anhydrous Na_2SO_4, filtered, and concentrated to dryness. The crude material was purified by flash chromatography (silica gel, hexane/CH_2Cl_2 or hexane/ethyl acetate) to give the desired cross-coupled products.

Supporting Information (see footnote on the first page of this article): General information and reaction procedure, product characterization, copies of the ^{1}H NMR and ^{13}C NMR spectra.

Acknowledgments

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[1] For very recent reviews, see: a) D.-G. Yu, B.-J. Li, Z.-J. Shi, *Acc. Chem. Res.* **2010**, *43*, 1486–1495; b) B. M. Rosen, K. W. Quasdorf, D. A. Wilson, N. Zhang, A.-M. Resmerita, N. K. Garg, V. Percec, *Chem. Rev.* **2011**, *111*, 1346–1416; c) B.-J. Li, D.-G. Yu, C.-L. Sun, Z.-J. Shi, *Chem. Eur. J.* **2011**, *17*, 1728–1759; d) J. D. Sellars, P. G. Steel, *Chem. Soc. Rev.* **2011**, *40*, 5170–5180.

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[20] The yields was determined by using HPLC with compound **3e** (see Table 1, Entry 5) as external standard.

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