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Heterobiaryl Cross-Coupling

Highly Reactive, Single-Component Nickel Catalyst Precursor for Suzuki–Miyuara Cross-Coupling of Heteroaryl Boronic Acids with Heteroaryl Halides**

*Shaozhong Ge and John F. Hartwig**

The Suzuki–Miyaura (S-M) cross-coupling reaction is the most frequently conducted catalytic process to construct C–C bonds in medicinal chemistry,[1] and these coupling reactions are conducted most frequently with palladium catalysts.[2] The replacement of the precious metal palladium with the first-row, abundant metal nickel for S-M couplings could significantly reduce the cost of the catalyst. S-M couplings catalyzed by nickel complexes, because of the high reactivity of nickel(0) toward chloroarenes could allow some of the more challenging coupling reactions to occur with catalysts containing simple ligands. Several nickel catalysts have been reported for this class of cross-coupling reaction,[3] and these nickel catalysts are unusually active for the coupling of phenol derivatives[4] such as sulfonates,[5] ethers,[6] esters,[7] carbamates,[8] carbonates, and sulfamates.[8b] However, there are two general drawbacks to the existing nickel catalysts for S-M cross-couplings: high catalyst loading (3–10 mol% Ni) is required to achieve the coupling in high yield, and the scope of these cross-couplings does not encompass reactions that form hetero-biaryl products, which are important for medicinal and agrochemical applications.

Catalytic syntheses of the hetero-biaryl compounds are challenging because the ligation of the heteroaryl coupling partner can poison the catalyst. The majority of such catalytic hetero-biaryl syntheses have been achieved by palladium-catalyzed Suzuki–Miyaura or Stille–Migita cross-couplings with a 2–4 mol% palladium loading.[9] Nickel catalysts have also been employed to conduct such coupling reactions. However, the scope of the couplings between two heteroaryl reagents catalyzed by a nickel complex is limited to the specific reactions of 2- or 3-thienyl neopentylglycolboronate with pyrid-3-yl mesylate or sulfamate.[5d,e] No nickel catalyst that reacts with high turnover numbers and couples two heteroaryl substrates has been reported.

We report a single-component nickel catalyst that addresses these current limitations. The dppf-ligated cinnamylnickel(II) chloride (dppf = 1,1′-bis(diphenylphosphanyl)-ferrocene) couples a range of nitrogen- and sulfur-containing heteroaryl halides with five-membered heteroaryl boronic acids. These coupling reactions occur in high yields with only 0.5 mol% of nickel and no added ligand. Moreover, the low reactivity of this nickel precatalyst to air and moisture makes these reactions practical to conduct on large or small scale.

Our studies on nickel-catalyzed S-M cross-couplings were based on recent findings that a single-component, nitrile-ligated nickel catalyst improved the enantioselectivity of the α arylation of ketones.[10] Most of the prior nickel-catalyzed S-M reactions were conducted with a precatalyst and excess of an added ligand, such as $[Ni(cod)_2]$ (cod = cyclo-1,5-octadiene) with PCy_3 or PPh_3,[3g,5a,d,6] or the nickel(II) precatalysts $[(dppf)NiCl_2]$, $[(dppp)NiCl_2]$, and $[(PCy_3)_2NiCl_2]$ (dppf = 1,1′-bis(diphenylphosphanyl)ferrocene, dppp = 1,3-bis(diphenylphosphanyl)propane) with 0–2 equivalents of added PCy_3.[3a–c,5c,7,8] Even the aryl/nickel(II) chloride complex [*trans*-$(PPh_3)_2$NiCl(1-naphthyl)], which is a potential reaction intermediate, required high catalyst loading (5–10 mol% Ni) and 1–2 equivalents of added ligand per catalyst for the coupling of aryl tosylates and mesylates with aryl boronic acids or esters.[5b,e]

We initiated our studies of S-M cross-coupling reactions of heteroaryl boronic acids with heteroaryl halides by exploring reactions catalyzed by [(binap)Ni(η^2-NCPh)] (binap = 2,2′-bis(diphenylphosphanyl)-1,1′-binaphthyl). The use of a catalyst that couples these reagents under mild reaction conditions is important because of the instability of many heteroaryl boronic acids. The coupling reactions catalyzed by this nitrile complex did occur, but with limited scope (for details, see the Supporting Information). We investigated reactions catalyzed by the analogous dppf-ligated nickel(0) nitrile complex, but this complex was too unstable to isolate in pure form.

Thus, we sought alternative discrete nickel precatalysts containing bis(phosphine)s besides binap. We considered that dppf-ligated allylnickel complexes could readily generate the reactive nickel(0) intermediate. Well-defined palladium allyl complexes ligated by phosphine ligands are more active for cross-coupling reactions that form C-C and C-N bonds than those generated in situ by combining $[Pd_2(dba)_3]$ (dba = dibenzylideneacetone) or $Pd(OAc)_2$ with phosphine ligands.[11] Phosphine-ligated allylnickel complexes are well known,[12] but their potential as catalysts for cross-coupling reactions has not been tapped.[13]

The new nickel complex [(dppf)Ni(cinnamyl)Cl] (**1**) was prepared by a one-pot reaction of cinnamyl chloride with [(dppf)Ni(cod)], which was generated in situ from $[Ni(cod)_2]$ and dppf in THF [Eq. (1)]. This reaction afforded complex

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[*] Dr. S. Ge, Prof. J. F. Hartwig
Department of Chemistry, University of California, Berkeley
CA, 94720-1460 (USA)
E-mail: jfhartwig@berkeley.edu
Homepage: http://www.cchem.berkeley.edu/jfhgrp/index.html

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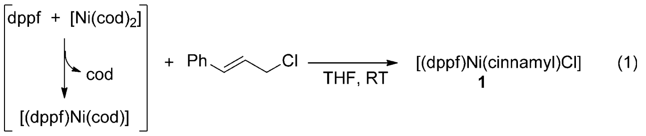
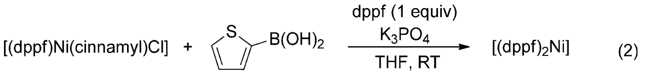


1 as a brown solid in 86% yield upon isolation. Compound **1** was stable under air in a closed vial at 0 °C for at least two weeks without noticeable decomposition, as determined by ^{1}H and ^{31}P NMR spectroscopy.

The rate of generation of nickel(0) from **1** was studied with 2-thienyl boronic acid as a nucleophile and K_3PO_4 as a base in THF in the presence of 1 equivalent of dppf to trap the resulting nickel(0) [Eq. (2)]. This reaction afforded

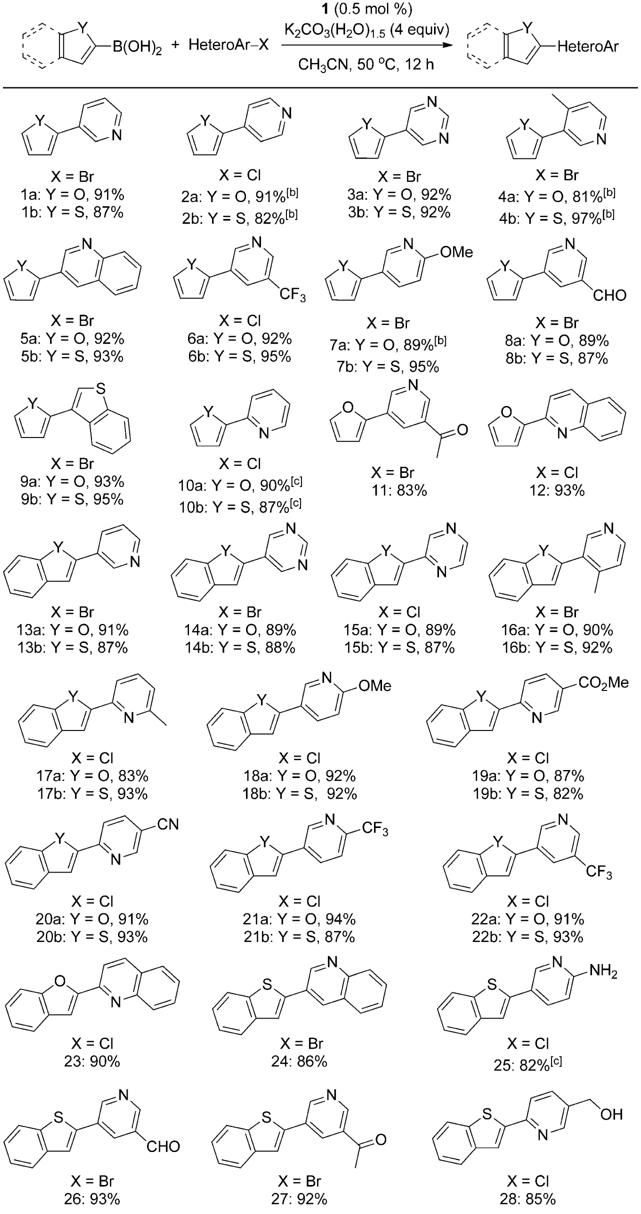


$[(dppf)_2Ni^0]$ quantitatively in 10 minutes at room temperature. On the basis of this rapid and quantitative generation of nickel(0), we evaluated **1** as the catalyst precursor (0.5 mol%) for the coupling of 2-thienyl boronic acid with 3-chloropyridine in the presence of $K_2CO_3(H_2O)_{1.5}$ in acetonitrile at 50 °C. This reaction afforded the coupling product in 81% yield upon isolation. For comparison, the reaction catalyzed by the nickel(II) precursors (e.g. $[(PPh_3)_2NiCl(1\text{-naphthyl})]/2\,PPh_3$ or $2\,PCy_3$ and $[(dppf)NiCl_2]/Zn$) used previously for S-M couplings of aryl boronic acids with aryl halides was conducted under the same reaction conditions. However, the reactions of these catalysts with the heteroaromatic substrates studied here gave the coupling product in less than 30% yield upon isolation (for details, see the Supporting Information).

To explore the scope of this catalyst for the preparation of hetero-biaryl compounds, we evaluated the coupling of a series of heteroaryl halides with several 2-heteroaryl boronic acids. These boronic acids undergo deboronation at elevated temperatures, and coupling of these boronic acids with (hetero)aryl halides has been achieved only recently with 2 mol% of the discrete [chloro(Xphos){2-(2-aminoethyl)phenyl}palladium(II)] precatalyst.[9d]

The results of the couplings catalyzed by **1** are summarized in Table 1. These reactions were conducted either with $K_2CO_3(H_2O)_{1.5}$ as a base in acetonitrile at 50 °C or with K_3PO_4 as base in 1,4-dioxane at 70 °C. Cross-couplings of 2-heteroaryl boronic acids with heteroaryl halides occurred with just 0.5 mol% of **1** and no added ligand. The 2-heteroaryl boronic acids that undergo this process include 2-furanyl (entries 1a–10a, 11, and 12), 2-thienyl (entries 1b–10b), benzo[*b*]furan-2-yl (entries 13a–22a and 23), and benzo[*b*]thien-2-yl (entries 13b–22b and 24–28) boronic acids. In general, these 2-heteroaryl boronic acids coupled with a range of unsubstituted and substituted pyridyl halides containing electron-donating groups (Me and OMe) or electron-withdrawing groups (CN, CF_3, CO_2Me) in good to excellent yields, despite the coordinating properties of pyridines. We presume that the catalyst is stable to the high concentrations of pyridines because of the chelating property of the dppf ligand. The coupling of these 2-heteroaryl boronic acids with 2-bromopyrimidine did not occur, even though these boronic acids reacted with 5-bromopyrimidine to form the corresponding hetero-biaryl in high yields (entries 3a, 3b, 14a, and 14b). This nickel-catalyzed S-M coupling tolerated unprotected NH_2 functionality (entry 25) and electrophilic functionalities such as an aldehydes (entries 8a, 8b, and 26), ketones with enolizable hydrogen atoms (entries 11 and 27), esters (entries 19a and 19b), and nitriles (entries 20a and 20b). In contrast to the coupling of aryl mesylates and aryl neopentylglycol-

Table 1: Coupling of sulfur- and oxygen-containing 2-heteroaryl boronic acids with heteroaryl halides catalyzed by **1**.[a]



X = Br
1a: Y = O, 91%
1b: Y = S, 87%

X = Cl
2a: Y = O, 91%[b]
2b: Y = S, 82%[b]

X = Br
3a: Y = O, 92%
3b: Y = S, 92%

X = Br
4a: Y = O, 81%[b]
4b: Y = S, 97%[b]

X = Br
5a: Y = O, 92%
5b: Y = S, 93%

X = Cl
6a: Y = O, 92%
6b: Y = S, 95%

X = Br
7a: Y = O, 89%[b]
7b: Y = S, 95%

X = Br
8a: Y = O, 89%
8b: Y = S, 87%

X = Br
9a: Y = O, 93%
9b: Y = S, 95%

X = Cl
10a: Y = O, 90%[c]
10b: Y = S, 87%[c]

X = Br
11: 83%

X = Cl
12: 93%

X = Br
13a: Y = O, 91%
13b: Y = S, 87%

X = Br
14a: Y = O, 89%
14b: Y = S, 88%

X = Cl
15a: Y = O, 89%
15b: Y = S, 87%

X = Br
16a: Y = O, 90%
16b: Y = S, 92%

X = Cl
17a: Y = O, 83%
17b: Y = S, 93%

X = Cl
18a: Y = O, 92%
18b: Y = S, 92%

X = Cl
19a: Y = O, 87%
19b: Y = S, 82%

X = Cl
20a: Y = O, 91%
20b: Y = S, 93%

X = Cl
21a: Y = O, 94%
21b: Y = S, 87%

X = Cl
22a: Y = O, 91%
22b: Y = S, 93%

X = Cl
23: 90%

X = Br
24: 86%

X = Cl
25: 82%[c]

X = Br
26: 93%

X = Br
27: 92%

X = Cl
28: 85%

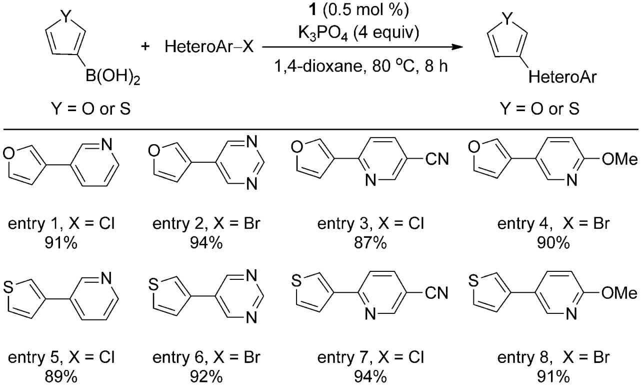
[a] Reaction conditions: heteroaryl halide (0.400 mmol), 2-heteroaryl boronic acid (0.800 mmol), compound **1** (2.0 μmol, 0.5 mol%), K_2CO_3-$(H_2O)_{1.5}$ (1.60 mmol), CH_3CN (1.0 mL), 50 °C, 12 h. Yields of isolated products are listed. [b] K_3PO_4 (1.60 mmol), 1,4-dioxane (1.0 mL), 70 °C. [c] 1 mol% compound **1**.

boronate catalyzed by 6 mol% [Ni(cod)$_2$] and 12 mol% PCy$_3$, which were reported to be intolerant of hydroxy functionality,[5d] the coupling of benzo[*b*]thien-2-yl boronic acid with 2-chloro-5-hydroxymethylpyridine, bearing a free hydroxy group, catalyzed by 0.5 mol% of **1** occurred in high yield (entry 28).

The coupling of heteroaryl halides with 3-heteroaryl boronic acids also occurred with broad scope. However, the appropriate combination of base and solvent is critical for these couplings to occur in high yields. For example, 3-furanyl or 3-thienyl boronic acid coupled with 3-chloropyridine in high yields when the coupling reactions were conducted with K$_3$PO$_4$ as a base in 1,4-dioxane at 80 °C. However, either no coupling (for 3-thienyl boronic acid) or very low yield (37% for 3-furanyl boronic acid) were obtained when these reactions were conducted in acetonitrile with K$_2$CO$_3$(H$_2$O)$_{1.5}$ as a base.

The reactions of 3-heteroaryl boronic acids with heteroaryl halides occurred with a scope similar to that of the reactions of 2-heteroaryl boronic acids in Table 1, and selected examples are summarized in Table 2. Unsubstituted 3-chloropyridine reacted with these boronic acids in high yields (entries 1 and 5). Heteroaryl halides containing two nitrogen atoms, for example, 5-bromopyrimidine, also reacted with these boronic acids in high yields (entries 2 and 6). The reactions of these boronic acids with substituted chloropyridines bearing electron-withdrawing groups (entries 3 and 7) or electron-donating groups (entries 4 and 8) also occurred in high yields.

Table 2: Coupling of five-membered 3-heteroaryl boronic acids with heteroaryl halides catalyzed by **1**.[a]

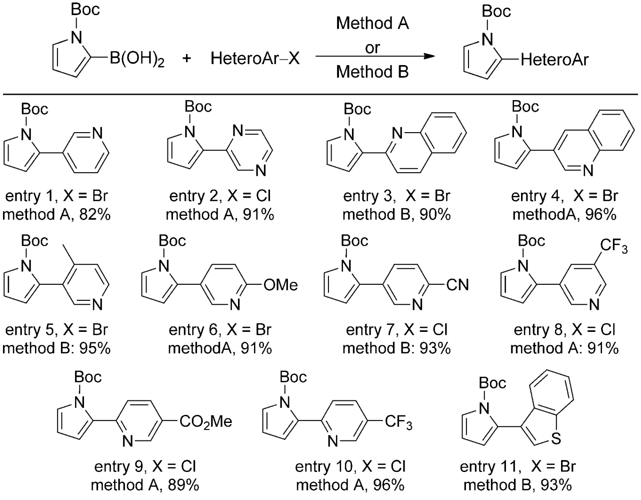


[a] Reaction conditions: heteroaryl halide (0.400 mmol), 3-heteroaryl boronic acid (0.800 mmol), **1** (2.0 μmol, 0.5 mol%), K$_3$PO$_4$ (1.60 mmol), 1,4-dioxane (1.0 mL), at 80 °C for 8 h. Yields of isolated products are listed.

The S-M coupling between two nitrogen-containing heterocyclic coupling partners is challenging, presumably because of the instability of azole boronic acids, the electron-rich nature and instability of many haloazoles, and the coordinating property of pyridines. Such coupling has been realized only recently with palladium catalysts.[9a,b] Nickel-catalyzed S-M couplings of azine and azole electrophiles have been reported previously, but the coupling of two nitrogen-containing heterocycles has not been achieved with nickel catalysts.

We studied initially the coupling of 1-Boc-pyrrole-2-boronic acid with heteroaryl halides catalyzed by **1**, and the results are summarized in Table 3. The scope of heteroaryl halides that underwent this process encompassed a range of 3-pyridyl (entries 5–8) and 2-pyridyl (entries 9 and 10) halide derivatives bearing electron-donating (OMe and Me) and electron-withdrawing (CF$_3$, CN, CO$_2$Me) groups. In general, these coupling reactions afforded the corresponding heterobiaryl products in good to excellent yields (82–96%) upon isolation. This coupling also occurred in high yields with 2-chloropyrazine (entry 2) and quinolinyl halides (entries 3 and 4). The *ortho*-substituted 3-bromo-4-methylpyridine reacted with this boronic acid in 92% yield (entry 5). A sulfur-containing heteroaryl bromide also coupled with this boronic acid in high yield (entry 11).

Table 3: Coupling of 1-Boc-pyrrole-2-boronic acid with heteroaryl halides catalyzed by **1**.[a]



[a] Reaction conditions: heteroaryl halide (0.400 mmol), 1-Boc-pyrrole-2-boronic acid (0.800 mmol), **1** (2.0 μmol, 0.5 mol%), 12 h. Method A: K$_2$CO$_3$(H$_2$O)$_{1.5}$ (1.60 mmol), CH$_3$CN (1.0 mL), 50 °C, 12 h. Method B: K$_3$PO$_4$ (1.60 mmol), 1,4-dioxane (1.0 mL), 70 °C, 12 h. Yields of isolated products are listed.

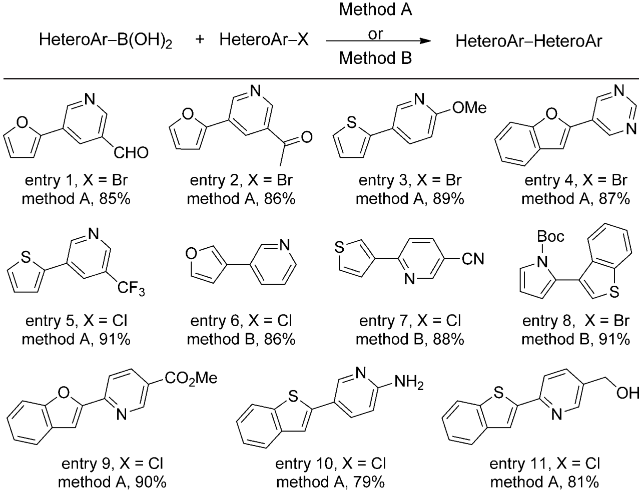
Although the cross-couplings of five-membered heteroaryl boronic acids with heteroaryl halides occurred in high yields in almost all cases we examined, the few limitations on this reaction we observed should be noted. Among all of the five-membered ring heteroaryl halides tested, only 2-chlorobenzoxazole and 2-chlorobenzothiazole did not form the coupled product from reactions with any of the five-membered ring heteroaryl boronic acids employed in this study. Among six-membered ring heteroaryl halides, 2-halopyrimidine did not react, as noted earlier in this paper. Although each five-membered ring heteroaryl boronic acid we investigated coupled in high yield with good scope, pyridyl boronic acids did not react under either conditions A (K$_2$CO$_3$(H$_2$O)$_{1.5}$ as base in acetonitrile) or conditions B (K$_3$PO$_4$ as base in 1,4-dioxane). Nickel-catalyzed coupling of pyridylboronates will be the subject of future studies.

Compared with the air-sensitive and thermally unstable nickel(0) precursor [Ni(cod)$_2$], the single-component nickel precursor **1** is convenient to use. It is stable indefinitely when stored under nitrogen at room temperature, and it is sufficiently stable to air and moisture to be weighed on the benchtop. Reactions catalyzed by **1**, which was stored for more than six months under a nitrogen atmosphere, were indistinguishable from those conducted with the freshly prepared **1**. For example, the reaction of 2-thienyl boronic acid with 3-chloropyridine catalyzed by 0.5 mol% of **1** (stored in a nitrogen-filled dry box for more than six months) afforded 3-(thien-2-yl)pyridine in 84% yield, and this result is comparable to that catalyzed by the freshly prepared **1**.

Moreover, these coupling reactions can be conducted with catalyst weighed in air. The coupling of 2-thienyl boronic acid with 5-bromopyrimidine conducted on a 4.0 mmol scale in degassed acetonitrile catalyzed by 0.5 mol% of **1** (stored under air in a closed vial at 0°C for 15 days and weighed in air) afforded 5-(thien-2-yl)pyrimidine in 89% yield (this reaction was set up outside a dry box; see the Supporting Information). The result of this reaction was indistinguishable from that conducted with 0.5 mol% of the freshly prepared **1** (0.400 mmol scale, carried out inside a dry box), and it delivered the product in 92% yield (entry 3b; Table 1).

To assess the generality of the procedure for conducting reactions outside a dry box, we conducted 11 examples of couplings to evaluate the scope of the reactions under these reaction conditions with different boronic acids and functionalized aryl halides. We compared these results to those of reactions conducted under fully anaerobic conditions. The results of the reactions with catalysts weighed in air are shown in Table 4. These reactions include the coupling of heteroaryl halides containing aldehyde, enolizable ketone, nitrile, amino, ester, and hydroxy functionality with oxygen-, sulfur-, and nitrogen-containing heteroaryl boronic acids. The rates and yields of these reactions were comparable to those of the corresponding reactions assembled inside a dry box. Thus, these coupling reactions can be conducted in a manner suitable for practical applications.

Table 4: Coupling of five-membered heteroaryl boronic acids with heteroaryl halides catalyzed by **1** that was weighed in air.[a]



[a] Reaction conditions: see reaction conditions listed in Table 3. All the reagents were weighed in air. The air in the reaction vessels was replaced with nitrogen by vacuum/nitrogen sequences.

In summary, we have prepared the new, discrete nickel(II) complex [(dppf)Ni(cinnamyl)Cl] (**1**) by the oxidative addition of cinnamyl chloride to [(dppf)Ni(cod)], and this nickel precursor catalyzes the couplings of five-membered heteroaryl boronic acids with a range of nitrogen- and sulfur-containing heteroaryl halides. The desired hetero-biaryl products were obtained in good to excellent yields upon isolation, with only a 0.5 mol% loading of **1**. This coupling reaction was easily conducted on large scale without a dry box. Such efficient coupling reactions result from the rapid generation of the catalytically active nickel(0) species from the nickel precursor [(dppf)Ni(cinnamyl)Cl] under mild S-M coupling conditions. Further studies of other classes of cross-coupling reactions catalyzed by related single-component nickel precatalysts are ongoing in our laboratory.

Experimental Section

Procedure for coupling of heteroaryl boronic acids with heteroaryl halides catalyzed by **1** (For Table 4): In air, a 4 mL screw-capped vial was charged with the heteroaryl halide (0.400 mmol, if solid), the heteroaryl boronic acid (0.800 mmol), $K_2CO_3(H_2O)_{1.5}$ or K_3PO_4 (1.60 mmol), **1** (2.0 μmol), and a magnetic stirring bar. The vial was then sealed with a screw-cap containing a PTFE septum and the air in the vial was replaced with nitrogen using a vacuum/nitrogen sequence (three times). Degassed CH_3CN or 1,4-dioxane (1 mL) and heteroaryl halides (0.400 mmol, if liquid) were added using an air-tight syringe, and the mixture was heated at 50°C or 70°C for 12 h and then quenched with H_2O (0.5 mL). The mixture was extracted with diethyl ether (3 mL × 2), and the combined ether fraction was dried over Na_2SO_4. All the volatile materials were evaporated under reduced pressure, and the residue was purified by chromatography on silica with a CombiFlash system. Detailed procedures on the purification of the hetero-biaryl products and data on the characterization of them are contained in the Supporting Information.

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Keywords: biaryls · cross-coupling · homogeneous catalysis · nickel · synthetic methods

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