C–H Functionalization

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Nickel-Catalyzed Direct C–H Arylation and Alkenylation of Heteroarenes with Organosilicon Reagents**

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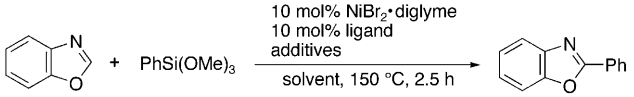
Organosilicon compounds are useful and ubiquitous synthetic reagents in modern organic chemistry. Among the versatile transformations involving them, transition metal catalyzed cross-coupling reactions of organic halides or pseudohalides, that is Hiyama cross-coupling, ranks as one of the most powerful and reliable C–C bond-forming reactions in organic synthesis.[1] Recent efforts by Nakao, Hiyama, and co-workers,[2] and Denmark et al.[3] introduce new types of stable and easy-to-handle silicon-based coupling reagents to enhance the generality of the reaction. In contrast, the development of new catalyst systems by Fu and co-workers[4] and Wu and co-workers[5] has expanded the scope of organic electrophiles into unactivated alkyl halides and arenesulfonates, respectively. In addition, the Hiyama coupling has significant benefits involving tractability, low toxicity, and environmentally benignity associated with organosilicon compounds, as well as organoboron reagents in the Suzuki–Miyaura coupling.

Meanwhile, metal-mediated C–C bond formation through direct C–H functionalization[6] has received much attention as a potentially more efficient and complementary process to the conventional cross-coupling methodology. Although the direct arylation of a variety of arenes and heteroarenes with arylboronic acids derivatives has been achieved,[7,8] the corresponding direct coupling with organosilanes still remains elusive. To the best of our knowledge, only two successful examples have been reported to date.[9] Moreover, these processes rely on the palladium catalysis, and substrates are limited to those containing an acetamide moiety as the chelation-assisted cyclopalladation step is crucial in the catalytic reaction. Herein we report a new nickel-based catalyst system for the direct C–H arylation and alkenylation of various heteroarenes with organosilanes.[10]

As an initial experiment, treatment of benzoxazole (**1a**, 0.50 mmol) with trimethoxyphenylsilane (**2a**, 1.0 mmol) in the presence of 10 mol% of $NiBr_2$·diglyme, 10 mol% of 1,10-phenanthroline (phen), and CsF in 3.0 mL of *N*,*N*-dimethylacetamide (DMAc) at 150 °C under air (O_2 as an oxidant) provided 2-phenylbenzoxazole (**3aa**) in 8% yield (GC) (Table 1, entry 1). Apparently, arylsilane **2a** participated in the reaction, and the desired cross-coupling involving C–H bond cleavage took place albeit in low yield. The interesting preliminary result encouraged us to optimize the reaction conditions based on the nickel catalyst. The replacement of air by a metal oxidant such as AgF or CuF_2 improved the reaction efficiency, with CuF_2 proving to be superior (Table 1, entries 2 and 3). Notably, the combination of CsF and CuF_2 was necessary for the satisfactory yield (Table 1, entry 4). The ligand effect was critical in this transformation. Whereas 2,2′-bipyridine (bpy) increased the yield to 70% (Table 1, entry 5), 2,9-dimethylphenanthroline (dmphen) and 4,4′-di(*tert*-butyl)-2,2′-bipyridine (dtbpy) resulted in a lower yield (Table 1, entries 6 and 7). Some investigations into the solvent revealed that other amide solvents such as *N*,*N*-dimethylformamide (DMF) resulted in a comparable yield, whereas the use of diglyme decreased the yield (Table 1, entries 8 and 9). As the nickel source, $NiBr_2$ or [Ni(acac)$_2$] instead of $NiBr_2$·diglyme showed lower performance (Table 1, entries 10 and 11).

Table 1: Optimization studies for nickel-catalyzed direct C–H phenylation of benzoxazole (**1a**) with trimethoxyphenylsilane (**2a**).[a]



1a **2a** **3aa**

Entry	Ligand	Additives (equiv)	Solvent	Yield of **3aa** [%][b]
1[c]	phen	CsF (4.0)	DMAc	8
2	phen	CsF (2.0) and AgF (2.0)	DMAc	16
3	phen	CsF (2.0) and CuF_2 (2.0)	DMAc	60
4	phen	CuF_2 (2.0)	DMAc	15
5	bpy	CsF (2.0) and CuF_2 (2.0)	DMAc	70
6	dmphen	CsF (2.0) and CuF_2 (2.0)	DMAc	24
7	dtbpy	CsF (2.0) and CuF_2 (2.0)	DMAc	36
8	bpy	CsF (2.0) and CuF_2 (2.0)	DMF	67
9	bpy	CsF (2.0) and CuF_2 (2.0)	diglyme	29
10[d]	bpy	CsF (2.0) and CuF_2 (2.0)	DMAc	31
11[e]	bpy	CsF (2.0) and CuF_2 (2.0)	DMAc	54
12[f]	bpy	CsF (3.0) and CuF_2 (2.0)	DMAc	80[g]
13	bpy	CsF (3.0) and $CuCl_2$ (2.0)	DMAc	2
14	bpy	CsF (3.0) and $Cu(OAc)_2·OH_2$ (2.0)	DMAc	5

[a] A mixture of $NiBr_2$·diglyme (0.050 mmol), ligand (0.050 mmol), additives, **1a** (0.50 mmol), and **2a** (1.0 mmol) in solvent (3.0 mL) was heated at 150 °C for 2.5 h under N_2. [b] Yield determined by GC methods. [c] Under air. [d] Used $NiBr_2$ instead of $NiBr_2$·diglyme. [e] Used [Ni(acac)$_2$] instead of $NiBr_2$·diglyme. [f] Used 1.0 mmol of H_2O. [g] Yield of isolated product.

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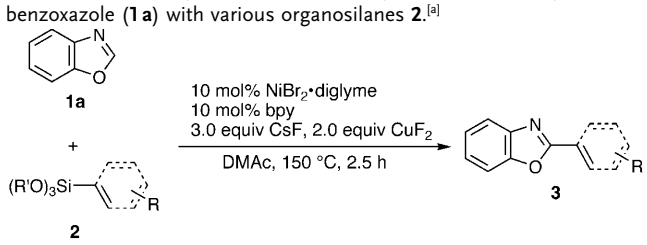
Finally, with 3.0 equivalents of CsF, 2.0 equivalents of CuF_2, and 2.0 equivalents of H_2O[11] as the additives, **3aa** was isolated in 80% yield (Table 1, entry 12). Notably, the use of $CuCl_2$ or $Cu(OAc)_2{\cdot}OH_2$ instead of CuF_2 was detrimental to the reaction (Table 1, entries 13 and 14).

With the reaction conditions employed for entry 12 in Table 1, we attempted the direct arylation of **1a** with various arylsilanes **2** (Table 2). However, we immediately found that

Table 2: Nickel-catalyzed direct C–H arylation and alkenylation of benzoxazole (**1a**) with various organosilanes **2**.[a]

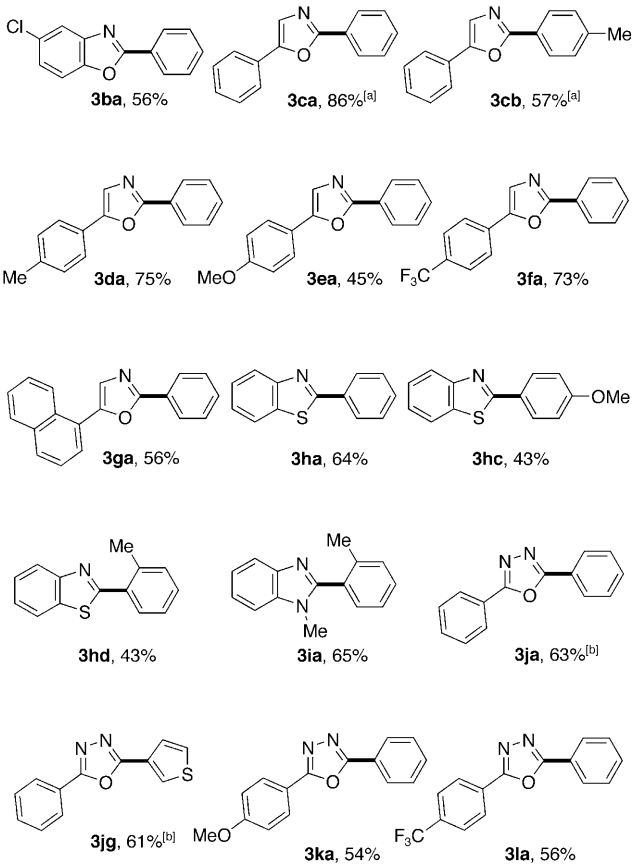


Entry		Organosilane **2**	Product **3**	Yield [%][b]
1[c]	**2a**	$(MeO)_3Si$	**3aa**	80
2[c]	**2b**	$(EtO)_3Si$–Me	**3ab**	(2)
3	**2b**	$(EtO)_3Si$–Me	**3ab**	77
4	**2c**	$(EtO)_3Si$–OMe	**3ac**	66
5	**2d**	Me, $(EtO)_3Si$	**3ad**	71
6	**2e**	$(EtO)_3Si$–F	**3ae**	52
7[d]	**2f** (E/Z= 13:87)	$(EtO)_3Si$–nC_6H_{13}	**3af**	70 (E/Z= 26:74)

[a] A mixture of $NiBr_2{\cdot}$diglyme (0.050 mmol), bpy (0.050 mmol), CsF (1.5 mmol), CuF_2 (1.0 mmol), **1a** (0.50 mmol), and **2** (1.0 mmol) in DMAc (1.5 mL) was heated at 150 °C for 2.5 h under N_2. [b] Yield of isolated product. Yield determined by GC methods given within parentheses. [c] The reaction was carried out under the conditions shown in entry 12 in Table 1. [d] Used 2.0 mmol of CsF.

the above conditions were not general: the coupling with (4-methylphenyl)silane **2b** proceeded sluggishly to afford the desired product **3ab** in only 2% GC yield (Table 2, entry 2). Additional investigation revealed that some adjustments were required for the other substrate combinations. Namely, an anhydrous reaction medium and higher concentration resulted in the formation of **3ab** in 77% yield (Table 2, entry 3).[12] Under the modified reaction conditions, electron-donating **2c** as well as sterically demanding **2d** coupled with **1a** without any difficulties to create the corresponding benzoxazole–aryl bonds in good yields (Table 2, entries 4 and 5). In contrast, the electron-withdrawing (4-fluorophenyl)silane **2e** showed moderate reactivity (Table 2, entry 6). Notably, alkenylsilane **2f** was also a suitable coupling partner albeit with the concomitant minor E/Z isomerization (Table 2, entry 7).

Our nickel-based catalyst system was robust and could be applied to the direct coupling of a variety of heteroarenes



Scheme 1. Products of the nickel-catalyzed direct coupling of heteroarenes **1** with organosilanes **2**. The formed C–C bonds are illustrated with a bold line. Reaction conditions: A mixture of $NiBr_2{\cdot}$diglyme (0.050 mmol), bpy (0.050 mmol), CsF (1.5 mmol), CuF_2 (1.0 mmol), **1** (0.50 mmol), and **2** (1.0 mmol) in DMAc (1.5 mL) was heated at 150 °C for 2–6 h under N_2. [a] Used 3.0 mL of DMAc. [b] Used 1.0 mmol of CsF.

with organosilanes. The results are summarized in Scheme 1. An array of heteroarenes involving 5-aryloxazole, benzothiazole, benzimidazole, and 1,3,4-oxadiazole underwent the arylation. In addition, electronically and sterically diverse groups such as methyl, methoxy, trifluoromethyl, chloro, and naphthyl substituents were tolerated under the reaction conditions, and the corresponding biaryls were produced in moderate to good yields.[13] Since these π-conjugate molecules containing heteroaryl–aryl bonds are often found in many natural products, pharmaceuticals, and functional materials, this type of coupling is quite important in organic synthesis.[14]

Next, to obtain information about the reaction mechanism, we performed the experiments shown below. The stoichiometric (to $NiBr_2$/bpy) reaction without CuF_2 led to the formation of 2-phenylbenzoxazole (**3aa**) in 53% yield. However, it required a prolonged reaction time (10 h) for the full conversion of the substrate [Eq. (1)]. The result and the interesting findings mentioned in entries 13 and 14 of Table 1 indicate that CuF_2 would work as not only an oxidant to Ni but also as the crucial accelerator in the catalytic cycle. Additional investigations involved using the isolated [PhNiCl(bpy)][15] complex **4**. Upon exposure of a stoichio-

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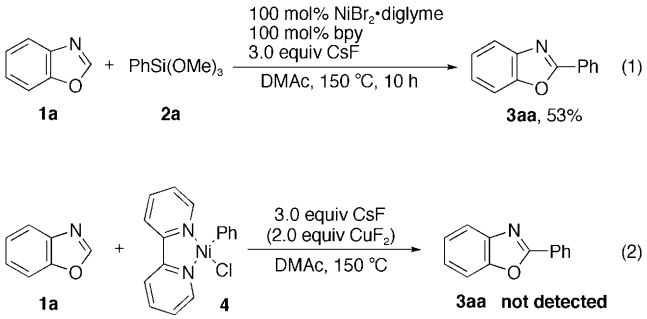
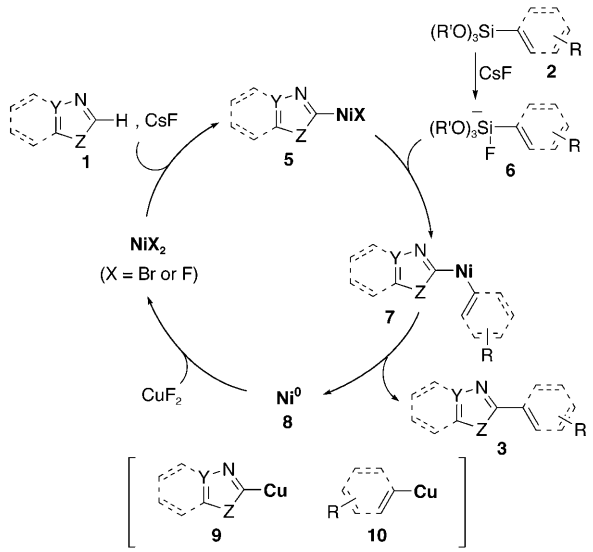
metric amount of **4** to a mixture of benzoxazole (**1a**) and CsF, no corresponding coupling product **3aa** was detected in the presence or absence of CuF_2 [Eq. (2)], which was suggestive of the importance of the formation of [(heteroaryl)$Ni^{II}X$] rather than [(aryl)$Ni^{II}X$] (X = halide) as a key intermediate under the catalytic conditions.



On the basis of these outcomes, we are tempted to assume the reaction mechanism of the catalytic direct coupling as illustrated in Scheme 2. Initial nickelation of heteroarene **1**



Scheme 2. Plausible reaction mechanism.

with the aid of the basic nature of CsF gives the [(heteroaryl)Ni]X intermediate **5**.[16] The subsequent transmetalation with aryl or alkenylsilicate **6**, generated in situ by the action of CsF, and the subsequent productive reductive elimination furnishes the biaryl **3** and the zerovalent Ni species **8**. Reoxidation of **8** with CuF_2 regenerates the divalent NiX_2 to complete the catalytic cycle. Although additional elucidation is essential for the clarification of the additional role of CuF_2, it could enhance the nickelation or transmetalation step through the formation of heteroaryl **9**[17] or aryl **10**[18] copper species. These organocuprates may undergo the transfer of organic group to the Ni center much more readily.

In conclusion, we have demonstrated the efficient nickel catalyst system for the direct Hiyama-type cross-coupling of heteroarenes with organosilanes through C–H bond cleavage leading to the π-extended heterocycles. The nickel-based strategy could complement the precedented palladium-mediated processes[8] and additionally contribute to develop the synthetic utility of organosilicon compounds in the field of C–H functionalization chemistry.

Experimental Section

Nickel-catalyzed direct C–H phenylation of benzoxazole (**1a**) with trimethoxyphenylsilane (**2a**) (Table 2, entry 1): $NiBr_2$·diglyme (18 mg, 0.050 mmol) was placed in a 20 mL two-necked reaction flask equipped with a reflux condenser and dried with a heat gun under high vacuum for 5 min. 2,2′-Bipyridine (7.8 mg, 0.050 mmol), CsF (228 mg, 1.5 mmol), CuF_2 (102 mg, 1.0 mmol), and dibenzyl (ca. 50 mg, internal standard) were then added to the reaction flask, which was then filled with nitrogen by using the standard Schlenk technique. DMAc (1.0 mL) was added dropwise, and the solution was stirred for 10 min at room temperature. Finally, a solution of benzoxazole (**1a**, 60 mg, 0.50 mmol) and trimethoxyphenylsilane (**2a**, 198 mg, 1.0 mmol) in DMAc (2.0 mL) and H_2O (18 mg, 1.0 mmol) were added. The solution was stirred at 150 °C for 2.5 h. The consumption of **1a** was confirmed by GC analysis, and the resulting mixture was then quenched with water. The mixture was extracted with ethyl acetate, and the combined organic layers were dried over sodium sulfate. Concentration in vacuo and subsequent chromatography on silica gel with *n*-hexane/ethyl acetate (20:1, v/v) gave 2-phenylbenzoxazole (**3aa**, 78 mg, 0.40 mmol) in 80% yield.

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[13] However, the reaction with other arenes such as benzothiophene, 2-(methoxycarbonyl)thiophene, and pentafluorobenzene was unsuccessful. Only $<2\%$ yields of the products were detected.

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