

Nickel-Catalyzed Arylation of C(sp³)-O Bonds in Allylic Alkyl Ethers with Organoboron Compounds

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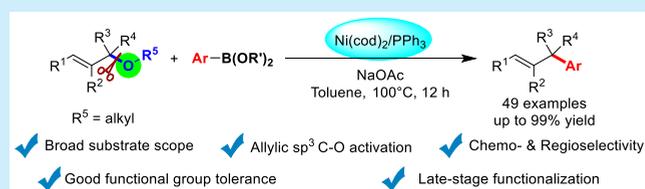
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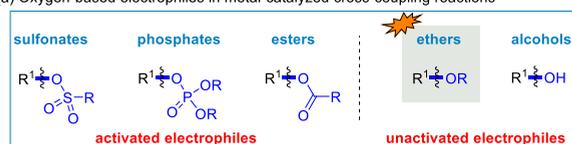
ABSTRACT: A nickel-catalyzed cross-coupling of allylic alkyl ethers with organoboron compounds through the cleavage of the inert C(sp³)-O(alkyl) bonds is described. Several types of allylic alkyl ethers can be coupled with various boronic acids or their derivatives to give the corresponding products in good to excellent yields with wide functional group tolerance and excellent regioselectivity. The gram-scale reaction and late-stage modification of biologically active compounds further prove the practicality of this synthetic method.



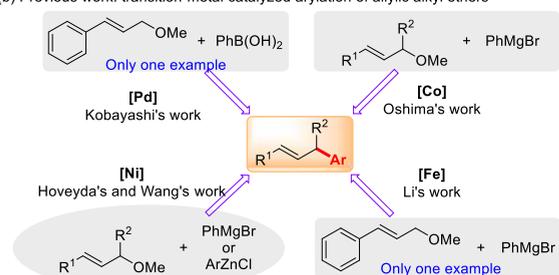
Transition-metal-catalyzed cross-coupling reactions have emerged as a powerful tool in the formation of C-C and C-heteroatom bonds for decades.¹ Organohalides as good electrophilic cross-coupling partners have been widely studied and applied.² With the development of high-efficiency catalytic systems, oxygen-based electrophiles have been shown to be a viable alternative to organohalides considering their natural abundance, ready availability, low toxicity, and excellent economic profile (Figure 1a).³ Based on their high reactivity,

sulfonates⁴ and phosphates⁵ were first used to construct C-C bonds in cross-coupling reactions, while moisture instability and high cost hindered their application. In recent years, considerable efforts have been made to explore some more stable and readily available C-O electrophiles, such as esters,⁶ ethers,⁷ and alcohols.⁸ In comparison with esters and alcohols, ethers usually act as solvents and protecting groups in organic synthesis owing to their higher chemical stability, and it is more challenging to utilize ethers as electrophiles in transition-metal-catalyzed cross-coupling reactions. The key challenges are related to the high activation energy required for the cleavage of the very electron-rich C(sp³)-O(alkyl) bonds and the low propensity of alkoxy residues to act as leaving groups. Thus, it is strategically important for C-O bond cleavage from allylic alkyl ethers to construct C-C bonds.

(a) Oxygen-based electrophiles in metal-catalyzed cross-coupling reactions



(b) Previous work: transition-metal catalyzed arylation of allylic alkyl ethers



(c) This work: nickel-catalyzed cross-coupling of allylic alkyl ethers with organoboron compounds

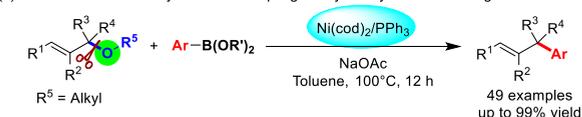


Figure 1. Transition-metal-catalyzed arylation of allylic ethers.

Over the last decades, some efforts to investigate the arylation of allyl alkyl ethers with nucleophilic coupling partners via transition-metal catalysis have been made (Figure 1b). In 2005, Kobayashi and co-workers reported an example of palladium-catalyzed allyl-aryl coupling between allyl methyl ether and phenylboronic acid.⁹ Then, Oshima and co-workers developed a phenylation reaction of allylic ethers with phenylmagnesium bromide (PhMgBr) catalyzed by cobalt.¹⁰ An example of iron-catalyzed phenylation of allyl methyl ether has also been shown by Li and co-workers with a low yield.¹¹ Recently, nickel-based catalysts have been attracting consid-

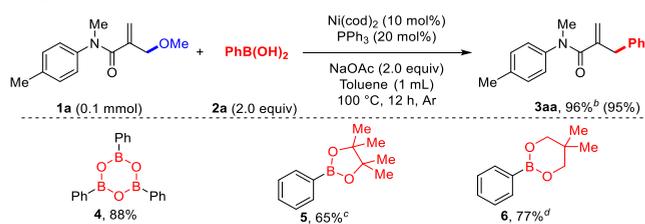
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erable attention in the transformations of $C(sp^3)-O$ bonds because of their low cost, wide availability, and unique reaction properties. Under nickel-catalyzed conditions, Hoveyda and Wang et al. employed $PhMgBr$ or arylzinc chlorides ($ArZnCl$) as the nucleophiles to couple with allyl ethers, respectively.¹² However, to the best of our knowledge, nickel-catalyzed allyl-aryl cross-coupling between allylic alkyl ethers and organoboron compounds was still unknown.

Compared with organozinc or Grignard reagents, organoboron compounds have emerged as more attractive nucleophilic coupling partners because of their advantages, such as commercial availability, stability to air and moisture, and low toxicity.¹³ Herein, we develop a highly efficient protocol for the direct cross-coupling between allylic alkyl ethers and organoboron compounds in good to excellent yields.

Initially, 2-(methoxymethyl)-*N*-methyl-*N*-(*p*-tolyl)acrylamide (**1a**) and phenylboronic acid (**2a**) were chosen as the model substrates, and a series of experiments aimed at identifying optimal conditions for selective arylation were conducted (see the Supporting Information). To our delight, we found that in the presence of bis(1,5-cyclooctadiene)nickel ($Ni(cod)_2$) (10 mol %), triphenylphosphine (20 mol %), and sodium acetate (2.0 equiv) the desired product **3aa** could be obtained in 95% yield in 1 mL of toluene at 100 °C (Scheme 1). In addition, under these conditions, by using 2,4,6-

Scheme 1. Optimized Conditions^a and Scope of Organoboron Compounds

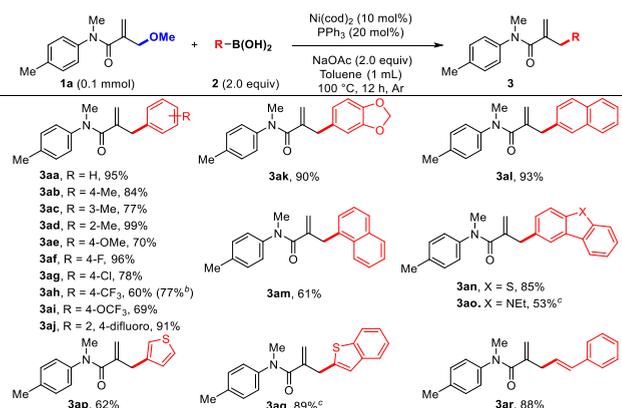


^aIsolated yield. ^bGC yield with adamantane as the internal standard. ^c(*p*-OMe- C_6H_5)₃P (20 mol %) was used instead of PPh_3 for 24 h. ^dReaction performed at 120 °C for 24 h.

triphenylboroxin **4** and phenylboronic acid esters **5** and **6** instead of **2a**, the product **3aa** could also be generated in high isolated yields (65–88%).

With the optimized conditions in hand, the substrate scope of boronic acids was explored (Scheme 2). Both electron-rich and electron-poor arylboronic acids could react with **1a** to afford the corresponding products **3aa–ak** in good to excellent yields with excellent regioselectivities (60–99%). A wide range of functional groups, such as methyl (**3ab–ad**), methoxyl (**3ae**), fluoro (**3af** and **3aj**), chloro (**3ag**), trifluoromethyl (**3ah**), trifluoromethoxyl (**3ai**), and even acetal (**3ak**), were all well tolerated. Notably, the steric hindrance did not affect the high efficiency of this method, and *p*-, *m*-, and *o*-tolylboronic acids were converted to their desired products with comparable reactivities (**3ab–ad**, 77–99% yields). Both 2- and 1-naphthylboronic acids could serve as the nucleophiles to give the corresponding **3al** and **3am** in 93% and 61% yield, respectively. Furthermore, some (hetero)arylboronic acids

Scheme 2. Scope of Boronic Acids^a

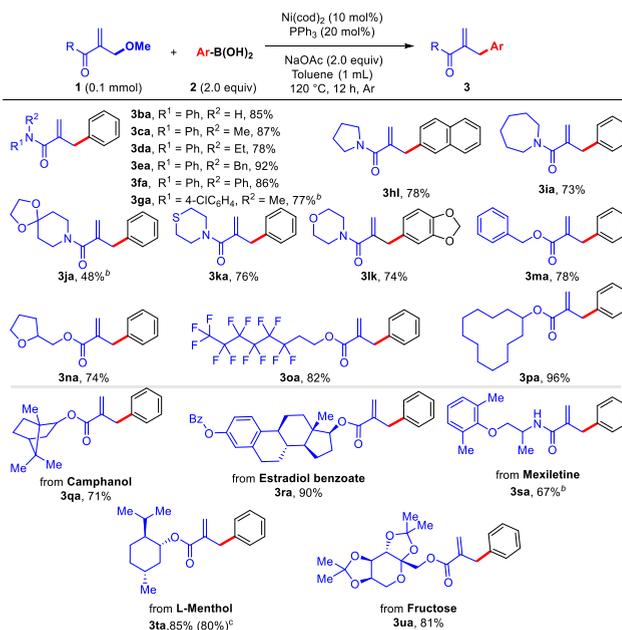


^aIsolated yield. ^b(*p*-OMe- C_6H_5)₃P (20 mol %) was used for 24 h. ^cReaction performed at 120 °C for 24 h.

bearing dibenzothiophene, carbazole heterocycles, thiophene, and benzothiophene groups could also be successfully applied in this process, manufacturing **3an–aq** in 53–89% yields. These results further expanded the scope of boronic acids. The *trans*- β -styreneboronic acid **2u** also proved to be a suitable substrate, to afford the desired product **3ar** in good yield (88%).

Next, the broad scope of this protocol with respect to various allylic ethers was observed (Scheme 3). By employing

Scheme 3. Scope of Allylic Ethers^a



^aIsolated yield. ^b(*p*-OMe- C_6H_5)₃P (20 mol %) was used for 24 h. ^cReaction was carried out at the 1 mmol scale.

arylboronic acid **2a** as the nucleophilic coupling partner, acrylamide substrate **1b** with an unprotected *N*-H group was efficiently transformed into the desired product **3ba** in 85% yield. Notably, a series of 2-(methoxymethyl)acrylamides with alkyl and aryl groups located at the nitrogen core could be readily applied in this reaction, generating the corresponding products **3ca–ga** in good to excellent yields (77–92%). In addition, the substrate scope toward heterocyclic unsaturated

dialkylamides was also screened under the optimized conditions. The formation of **3hl**, **3ia–ka**, and **3lk** indicated that these substrates containing five-, six-, and seven-membered heterocycles could be effectively transformed to their desired products with satisfactory results (48–78% yields). Subsequently, various 2-(methoxymethyl)acrylates were tested. Benzyl 2-(methoxymethyl)acrylamide **1m** and (tetrahydrofuran-2-yl)methyl 2-(methoxymethyl)acrylate **1n** were well-tolerated in our conditions, producing the arylation products in high yields. Substrates with a bulky group were compatible reaction partners and could generate coupling products **3oa** and **3pa** in 82% and 96% yield, respectively. To demonstrate the potential utility of this coupling reaction, we evaluated the method in the late-stage modification of complex and/or biologically active compounds, including the derivatives of camphanol, estradiol benzoate, mexiletine, *L*-menthol, and fructose. The results showed that these substrates were transformed into the target molecules successfully with good yields (**3qa–ua**, 67–90%). Moreover, this transformation was scaled up to 1 mmol to generate **3ta** in 80% yield without sacrificing yield.

To broaden the generality of the method, we turned our attention to other C–O electrophiles. As shown in Table 1,

Table 1. Scope of Other C–O Electrophiles^a

Substrate	Product	Yield
		76%
		28%
		78% ^b
		83%
		47%
		35%
		70%
		72%

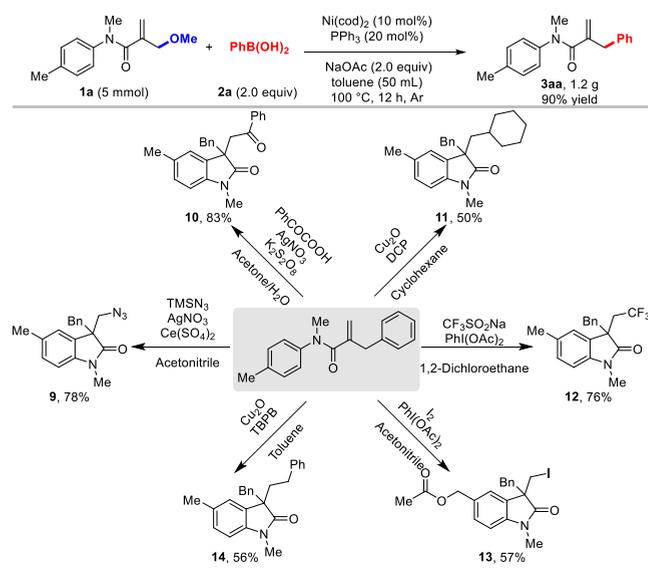
^aIsolated yield. ^b**2a** (3.0 equiv) and (*p*-OMe-C₆H₅)₃P (20 mol %) were used for 24 h.

various allylic substrates were tested with arylboronic acid **2** under the optimized reaction conditions. We were pleased to find that allylic isopropyl ether **7a** was well applicable for the current transformation, delivering **3aa** in 76% yield. Moreover, a range of cinnamyl methyl ethers were also suitable substrates for this transformation (**7b–e**). In contrast to primary ether, methyl-substituted secondary and tertiary ethers reacted more efficiently with **2a**, affording the corresponding products (**8b** and **8c**) in 78% and 83% yield, respectively. In addition, when there is a methyl substituent on the alkene of the cinnamyl methyl ether, moderate yield was obtained (**8d**). It is noted that a branched allylic ether substrate **7f** coupling with **2a** was found to produce the linear product **8e**, albeit with somewhat low yield. Alkyl-substituted allylic ethers could also react with

arylboronic acid, yielding the desired products **8f** and **8g** in good yields.

To further demonstrate the practicality of this method, a gram-scale reaction of **1a** (5 mmol) with **2a** was carried out under the standard reaction conditions, affording product **3aa** (1.2 g) in 90% yield (Scheme 4, top). Furthermore, several

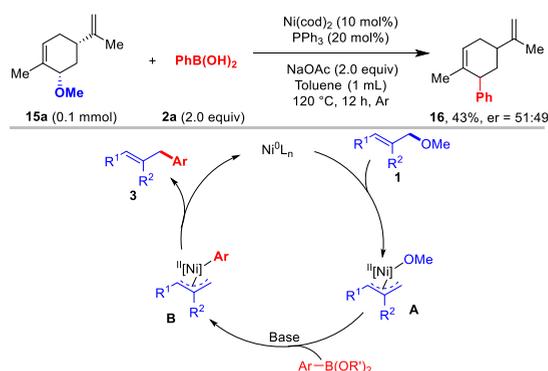
Scheme 4. Gram-Scale Synthesis and Transformation of **3aa**



transformations of **3aa** were performed (Scheme 4, bottom). In the presence of various coupling partners and oxidants, the carbocyclization of **3aa** proceeded successfully, providing a series of functionalized 3,3-disubstituted oxindoles **9–14** in moderate to good yields. Azido,¹⁴ benzoyl,¹⁵ cyclohexyl,¹⁶ trifluoromethyl,¹⁷ iodo,¹⁸ and benzyl groups¹⁹ were well-tolerated. Notably, when **3aa** was treated with iodine (I₂) and iodobenzene diacetate (PhI(OAc)₂) in acetonitrile at room temperature, an unexpected difunctional product **13** was formed in 57% yield.

To gain insights into the reaction mechanism, a control experiment was carried out. Under the standard reaction conditions, chiral allylic alkyl ether **15a** can react with **2a**, yielding racemic products **16** in 43% yield (er = 51:49) (Scheme 5, top). It is very likely that an allylic nickel intermediate was formed. Therefore, according to the previous reports^{3c} and the result of our experiments, we proposed a possible mechanism for this reaction (Scheme 5, bottom).

Scheme 5. Mechanistic Study and Proposed Catalytic Cycle



Assisted by the coordination with alkene **1**, a key allylic intermediate **A** is formed by oxidative addition of nickel(0) to a C–O bond. Transmetalation followed by reductive elimination gives the desired product **3**.

In summary, we have established an efficient and practical nickel-catalyzed cross-coupling of allylic alkyl ethers with organoboron compounds through the cleavage of the inert C(sp³)–O bond. This protocol is distinguished by its wide substrate scope, providing the desired products in good to excellent yields with excellent regioselectivity and good functional group compatibility. The application in the late-stage modification of biologically active molecules, gram-scale synthesis, and product transformation proves the synthetic utility of this method.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.orglett.1c01879>.

Experimental procedures and characterization of all compounds (PDF)

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Notes

The authors declare no competing financial interest.

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