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Nickel-catalyzed arylative substitution of homoallylic alcohols†

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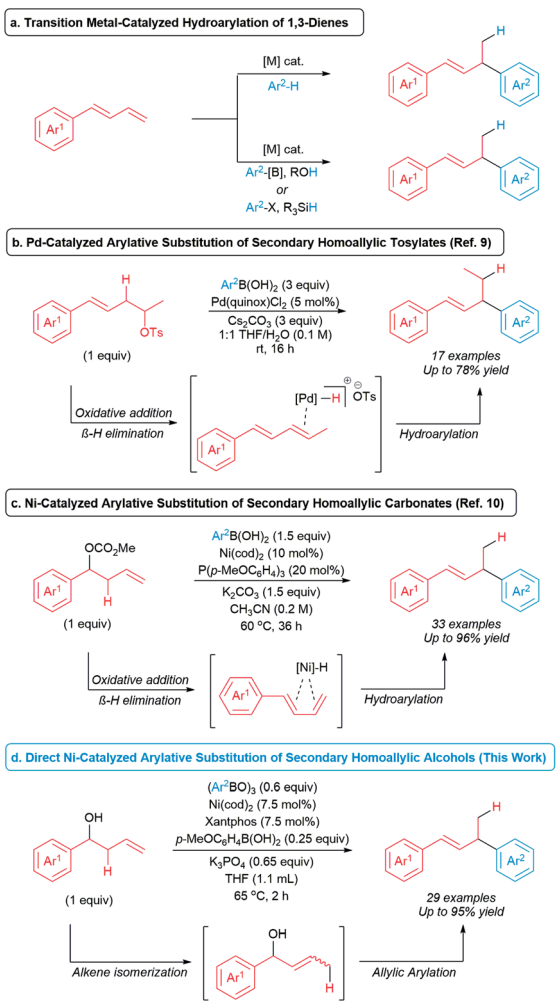
Direct coupling of unactivated alcohols remains a challenge in synthetic chemistry. Current approaches to cross-coupling of alcohol-derived electrophiles often involve activated alcohols such as tosylates or carbonates. We report the direct arylative substitution of homoallylic alcohols catalyzed by a nickel-bisphosphine complex as a facile method to generate allylic arenes. These reactions proceed *via* formation of an allylic alcohol intermediate. Subsequent allylic substitution with arylboroxine nucleophiles enables the formation of a variety of allylic arenes. The presence of *p*-methoxyphenylboronic acid is crucial to activate the allylic alcohol to achieve high product yields.

Introduction

Alkanols are among the most common and accessible functional groups in organic synthesis and are attractive as potential C(sp^3) coupling partners to form C(sp^3)–C bonds. However, due to the relatively strong bond dissociation energy of the C–O bond and poor leaving group ability of the OH group,[1] alcohols are rarely used directly as alkylating agents in cross-coupling chemistry.[2] Although numerous alcohol derivatives (*i.e.* tosylates, carbonates, *etc.*) have been extensively explored in redox-neutral cross-coupling reactions,[3,4] these derivatives typically require one or more preparation steps from the corresponding alcohol precursors. Therefore, processes that form C(sp^3)–C bonds directly from unactivated alcohols have the potential to streamline synthetic routes.

Transition metal-catalyzed hydroarylations of 1,3-dienes are privileged synthetic methods to generate allylic arenes and allylic heteroarenes.[5–8] Traditionally, hydro(hetero)arylation of 1,3-dienes involves activation of an aryl C–H bond (Scheme 1a, top).[5,6] Alternatively, hydro(hetero)arylations of 1,3-dienes have been developed by employing alcohols or silanes as external hydride sources (Scheme 1a, bottom).[7,8] In the past decade, approaches to tandem transition metal-catalyzed hydro(hetero)arylation of 1,3-dienes generated *in situ* from homoallylic electrophiles have been reported.[9–11] Sigman and co-workers developed Pd-catalyzed arylative substitutions of primary and secondary homoallylic tosylates with arylboronic acids (Scheme 1b).[9] In 2020, Kawatsura and co-workers developed the arylative substitution of secondary homoallylic carbonates with



Scheme 1 Transition metal-catalyzed formation of allylic arenes *via* hydroarylation and arylative substitutions.

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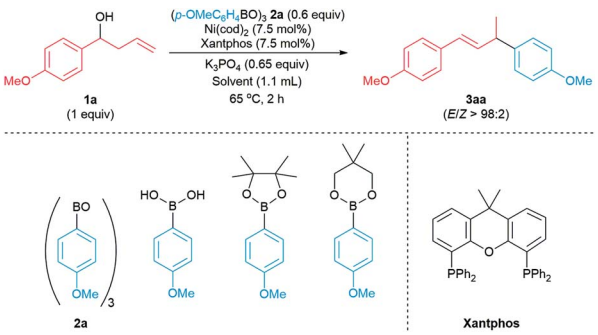
arylboronic acids catalyzed by a nickel complex of a monophosphine ligand (Scheme 1c).[10] These reactions proceed *via in situ* formation of a diene by a sequence of oxidative addition of the C–O bond to generate a metal-alkyl intermediate and subsequent β-hydride elimination. Alkene insertion to the metal-hydride bond, transmetallation with an arylboronic acid, and reductive elimination generate the allylic arene product. These formal hydroarylations of 1,3-dienes are attractive examples of coupling reactions involving secondary sp^3 electrophiles. However, the opportunity exists to improve these reactions by eliminating the need for an activated homoallylic electrophile. To this end, we now report the development of nickel-catalyzed arylative substitution of unactivated secondary homoallylic alcohols with arylboroxine nucleophiles (Scheme 1d). These arylative substitution reactions occur *via in situ* formation of allylic alcohols through alkene isomerization, followed by allylic arylation[12–14] to generate a variety of allylic arenes in short reaction times.

Results and discussion

Initially, reactions of 1-(*p*-methoxyphenyl)but-3-en-1-ol **1a** with common arylboron nucleophiles were evaluated to identify a suitable aryl coupling partner. Reactions did not occur when *p*-$MeOC_6H_4B(OH)_2$, *p*-$MeOC_6H_4Bpin$, and *p*-$MeOC_6H_4Bneop$ were used as the coupling partners (Table 1, entries 1–3). However, the reaction of 1 equiv. of *p*-methoxyphenylboroxine **2a** (12 : 1 mixture of arylboroxine : arylboronic acid) with **1a** formed the product **3aa** in 95% yield (entry 4). The yield of the reaction remained high upon lowering the loading of **2a** to 0.6 equiv. (entry 5). Interestingly, the reaction of **1a** with arylboroxine **2a** containing a higher ratio of boroxine to its corresponding boronic acid (arylboroxine : arylboronic acid = 16 : 1, entry 6) led to a drop in the yield of **3aa** to 71%. We hypothesized that the catalytic amount of *p*-methoxyphenylboronic acid could play a role in activating the homoallylic alcohol **1a**.[15] Indeed, adding 0.25 equiv. of *p*-$MeOC_6H_4B(OH)_2$ to the reaction of 0.6 equiv. of boroxine **2a** with **1a** led to the formation of the desired product **3aa** in 98% yield (entry 7). The addition of *p*-methoxyphenylboronic acid allowed the amount of arylboroxine **2a** to be lowered to 0.5, 0.4 or 0.33 equiv. without significant impact on the yield of **3aa** (entries 8–10). Since electron-deficient arylboronic acids are expected to activate the alcohol more effectively,[15a] we attempted to use *p*-trifluoromethylphenylboronic acid and *p*-methoxycarbonyphenylboronic acid as additives in the model reaction to activate the homoallylic alcohol. However, due to high content of corresponding arylboroxines in these commercially available, electron-deficient arylboronic acids, we observed the formation of the allylic arene byproducts derived from these

Table 1 Identification of reaction conditions[a]



Entry	Deviation from standard conditions	Yield **3aa**[b] (%)
1	2 equiv. *p*-$MeOC_6H_4B(OH)_2$ instead of **2a**	0
2	2 equiv. *p*-$MeOC_6H_4Bpin$ instead of **2a**	0
3	2 equiv. *p*-$MeOC_6H_4Bneop$ instead of **2a**	0
4	1 equiv. **2a** (arylboroxine : arylboronic acid = 12 : 1)	95
5	None (arylboroxine : arylboronic acid = 12 : 1)	93
6	None (arylboroxine : arylboronic acid = 16 : 1)	71
7[c]	**0.25 equiv. *p*-$MeOC_6H_4B(OH)_2$ added**	**98 (93)**[d]
8[c]	0.5 equiv. **2a**, 0.25 equiv. *p*-$MeOC_6H_4B(OH)_2$ added	90
9[c]	0.4 equiv. **2a**, 0.25 equiv. *p*-$MeOC_6H_4B(OH)_2$ added	88
10[c]	0.33 equiv. **2a**, 0.25 equiv. *p*-$MeOC_6H_4B(OH)_2$ added	84
11[e]	2 equiv. *p*-$MeOC_6H_4Bneop$ instead of **2a**	0
12[e]	2 equiv. *p*-$OMeC_6H_4Bpin$ instead of **2a**	0

[a] Reaction conditions: **1a** (0.25 mmol), **2a** (0.15 mmol), $Ni(cod)_2$ (0.0188 mmol), Xantphos (0.0188 mmol), K_3PO_4 (0.162 mmol), THF (1.1 mL) at 65 °C for 2 h under a N_2 atmosphere. *E*/*Z* ratios were determined by ^1H NMR spectroscopy of crude mixtures. [b] Yields were determined by ^1H NMR spectroscopy of the crude reaction mixture using CH_2Br_2 as an internal standard. [c] **2a** with arylboroxine : arylboronic acid ratio = 16 : 1. [d] Isolated yield. [e] 0.25 equiv. *p*-$MeOC_6H_4B(OH)_2$ added.

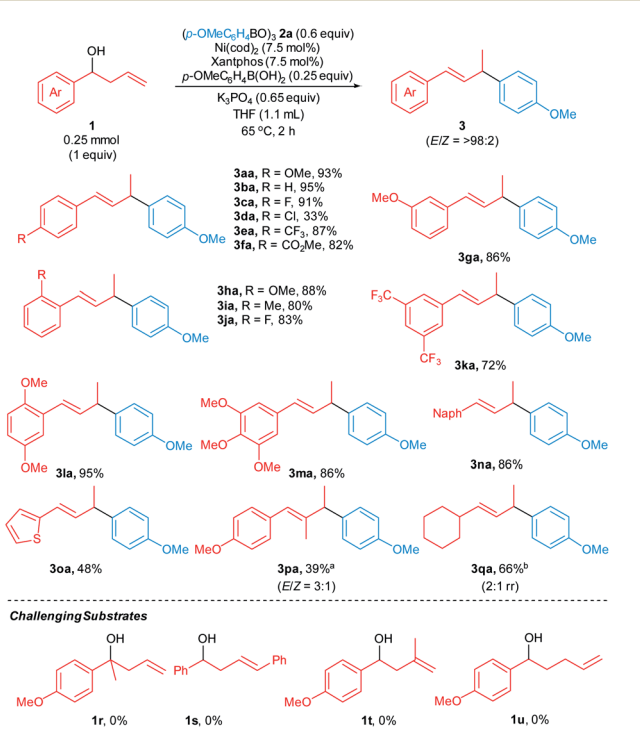
electron-deficient arylboroxines. In contrast, using *p*-methoxyphenylboronic acid as an additive, we did not observe the allylic arene byproduct derived from the *p*-methoxyphenylboroxine when evaluating the arylboroxine scope (see Scheme 4, below). Therefore, we chose *p*-methoxyphenylboronic acid as an additive in our arylative coupling reactions. In addition we re-evaluated the arylboronic ester nucleophiles with *p*-methoxyphenylboronic acid as an additive. Reactions did not occur when the arylboronic acid pinacol ester and arylboronic acid neopentylglycol ester were used as the coupling partner in the presence of 0.25 equiv. of *p*-$MeOC_6H_4B(OH)_2$ (entries 11–12).[16] We chose reaction conditions using 0.6 equiv. of **2a** with the addition of 0.25 equiv. of *p*-$MeOC_6H_4B(OH)_2$ to evaluate the scope of the arylative coupling reaction.

With reaction conditions identified that lead to high yields in our model reaction, we sought to establish the scope of the reaction by evaluating arylative substitutions of a variety of homoallylic alcohols (Scheme 2). An array of α-aryl-substituted homoallylic alcohols **1** react with *p*-methoxyphenylboroxine **2a** to generate allylic arene products **3** in modest-to-high yields (33–95%). The reaction of chlorinated homoallylic alcohol (**1d**) furnished the product **3da** in 33% yield with isomerization of **1d** to a mixture of allylic alcohols accounting for the balance of the mass. It is likely that oxidative addition of the Ni catalyst to the C_{aryl}–Cl bond is competitive with the desired arylate substitution. However, Suzuki–Miyaura coupling products are not observed. Notably, a homoallylic alcohol bearing an ester substituent at the aryl moiety (**1f**) was tolerated under the standard reaction conditions, furnishing the allyic arene **3fa** in 82% yield. Homoallylic alcohols with polysubstituted α-aryl groups **1k–m** and α-naphthyl homoallylic alcohol **1n** react to form allylic arenes **3ka–3na** in good-to-high yields (72–95%). Moreover, the reaction of α-thienyl homoallylic alcohol **1o** generated the corresponding heteroarene-containing product **3oa** in 48%. Additionally, the reaction of homoallylic alcohol **1p** bearing a β-substituent furnished the corresponding allylic arene **3pa** in 39% yield with 3 : 1 *E*/*Z* ratio. The reaction of α-alkyl-substituted homoallylic alcohol **1q** with boroxine **2a** formed the corresponding product **3qa** in 63% yield with 2 : 1 rr. However, reactions of tertiary homoallylic alcohol **1r**, homoallylic alcohols containing 1,2- and 1,1-disubstituted alkenes (**1s** and **1t**), and bishomoallylic alcohol **1u** did not occur under our reaction conditions.

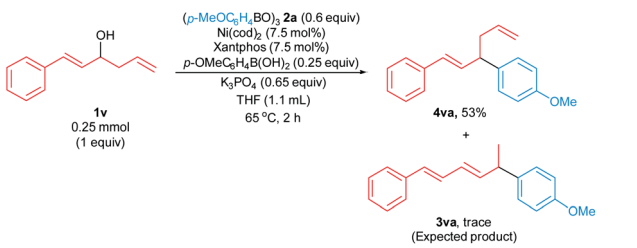
We attempted to extend the arylative substitution reaction to encompass α-styrenyl homoallylic alcohols (Scheme 3). Interestingly, the reaction of α-styrenyl homoallylic alcohol **1v** with boroxine **2a** did not generate the desired allylic arene **3va**. Instead, product **4va** was isolated in 53% yield. The observation of the aryl nucleophile replacing the OH at the α-position in product **4va** *in lieu* of the γ-position like products **3aa–3qa** suggests our arylative substitution reactions might proceed *via* a different mechanism compared to the previously reported formal hydroarylations of homoallylic alcohol derivatives (Scheme 1b and c).

Next, we examined the scope of the arylative substitution reactions with respect to arylboroxine coupling partners (Scheme 4). Reactions of 1-(*p*-methoxyphenyl)but-3-en-1-ol **1a** with a variety of substituted boroxines **2** generated allylic arenes **3** in modest-to-high yields (43–94%). The scope of these arylative substitution reactions encompasses a variety of *para*-, *meta*-, *ortho*-, and disubstituted arylboroxines. Notably, arylboroxines containing fluoride (**2d**), ester (**2e**), chloride (**2h**), and acetal (**2j**) substituents were tolerated under our reaction conditions. Moreover, furanyl-3-boroxine **2m** reacts with homoallylic alcohol **1a** to form the corresponding allylic heteroarene in 53% yield.

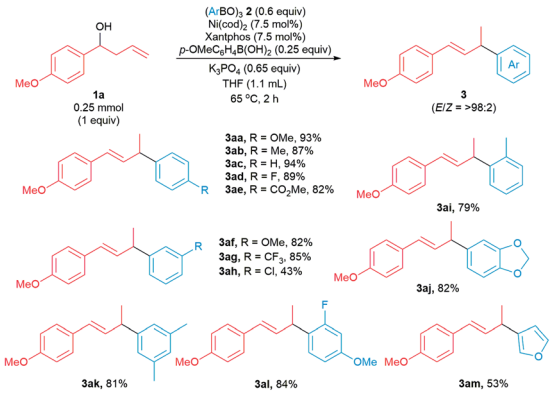
We examined the scalability of the arylative substitution in a 5 mmol scale reaction of homoallylic alcohol **1a** (Scheme 5). This reaction formed the desired product **3aa** in 84% yield when conducted in the presence of 5 mol% nickel precatalyst and 5 mol% Xantphos ligand. In addition, the synthetic utility was



Scheme 2 Homoallylic alcohol substrate scope. Reactions were carried out on a 0.25 mmol scale. **2a** with arylboroxine : arylboronic acid = 16 : 1. *E*/*Z* ratios were determined by ^{1}H NMR spectroscopy of crude mixtures. Yields of isolated products are shown. [a] Homoallylic alcohol **1p** (*syn* : *anti* = 1 : 1). [b] Isolated yield of a mixture of 3,4- and 1,4-isomers.



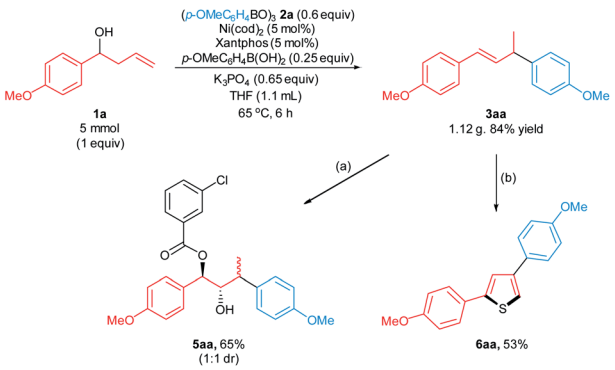
Scheme 3 Arylative substitution of α-styrenyl homoallylic alcohol. Reaction was carried out on a 0.25 mmol scale. Yield of isolated product **4va** is shown.



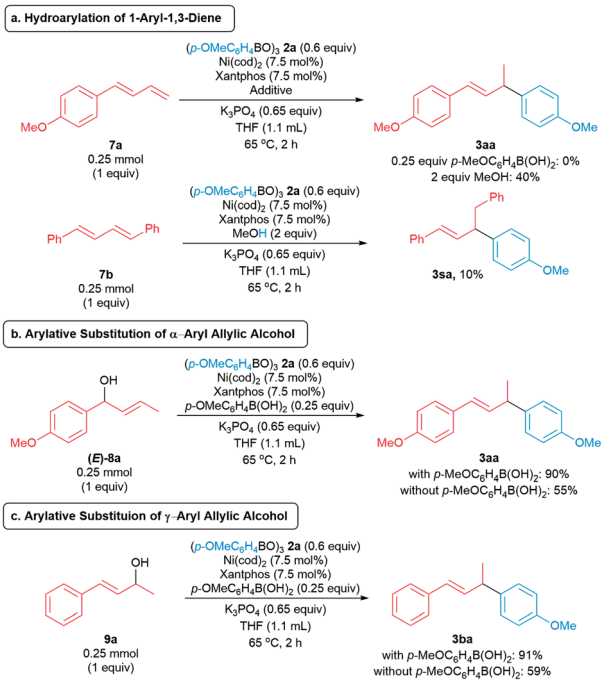
Scheme 4 Arylboroxine substrate scope. Reactions were carried out on a 0.25 mmol scale. **2** with arylboroxine : arylboronic acid > 10 : 1. *E*/*Z* ratios were determined by ^{1}H NMR spectroscopy of crude mixtures. Yields of isolated products are shown.

demonstrated by subjecting the allylic arene **3aa** to alkene functionalization transformations. The reaction of **3aa** with *m*CPBA, followed by workup with saturated aq. $NaHCO_3$ furnished the hydroxyester **5aa** in 65% yield as a 1 : 1 ratio of separable diastereomers. Transition metal-free sulfuration/annulation[17] of **3aa** formed thiophene **6aa** in 53% yield.

To gain insights into the reaction mechanism, we conducted a series of control experiments. In previous studies reported by the Sigman (Scheme 1b)[9] and Kawatsura groups (Scheme 1c),[10] a 1,3-diene is proposed to be generated *in situ*. To probe whether our arylative substitution proceeds *via* a similar mechanism, we subjected the diene **7a** to the standard reaction conditions. Compound **7a** was recovered in 97% yield, and the allylic arene **3aa** was not detected (Scheme 6a, top). In the presence of MeOH as a hydride source,[7b,8c,18] the hydroarylation of diene **7a** formed the allylic arene **3aa** in 40% yield. We also conducted the hydroarylation of 1,4-diphenyl-1,3-diene **7b**, furnishing the allylic arene **3sa** in 10% (Scheme 6a, bottom).[7b] In contrast, the reaction of homoallylic alcohol **1s** with boroxine **2a** did not generate **3sa** (Scheme 2). These observations suggest the



Scheme 5 Large-scale reaction and synthetic transformations. Yields of isolated products are shown. Reaction conditions for (a): **3aa** (0.3 mmol), *m*CPBA (0.45 mmol), DCM (3 mL), rt, 24 h then sat. $NaHCO_3$ (2 mL), rt, 5 min. Reaction conditions for (b): **3aa** (0.3 mmol), K_2S (0.9 mmol), DMSO (2 mL), 140 °C, 24 h under air.

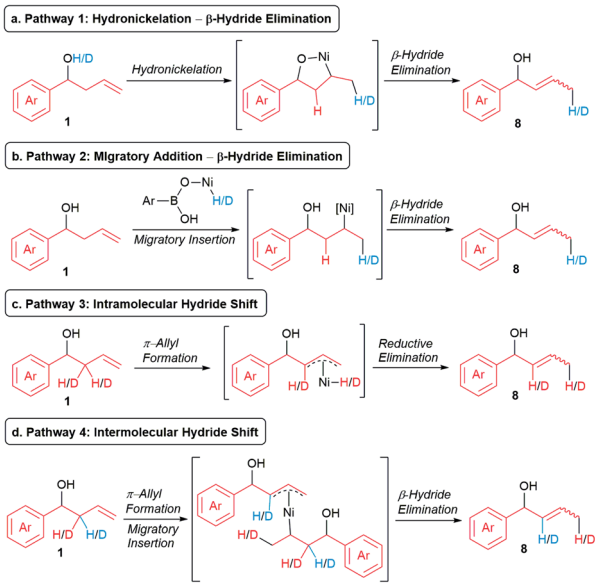


Scheme 6 Control experiments. Yields were determined by ^{1}H NMR spectroscopy of the crude reaction mixture using CH_2Br_2 as an internal standard.

mechanism involving *in situ* generation of a 1,3-diene is not likely in our arylative substitution reactions.

We then turned our focus to the potential for *in situ* formation of an allylic alcohol *via* isomerization of the homoallylic alcohol, followed by allylic arylation to form the allylic arene products **3**. The reaction of allylic alcohol (***E***)**-8a** and boroxine **2a** under the standard conditions produced allylic arene **3aa** in 90% (with *p*-$MeOC_6H_4B(OH)_2$) and 55% (without *p*-$MeOC_6H_4B(OH)_2$) yields, suggesting the arylative substitution may occur *via* an allylic alcohol intermediate (Scheme 6b). In addition, allylic alcohol **9a** reacts with boroxine **2a** under standard reaction conditions to form allylic arene **3ba** in 90% yield (Scheme 6c). These observations suggest the arylative substitutions of allylic alcohols (***E***)**-8a** and **9a** proceed *via* π-allylnickel(II) intermediates.[13,19] Furthermore, the reactions of these allylic alcohols produce the corresponding allylic arenes in higher yields in the presence of *p*-methoxyphenylboronic acid, suggesting *p*-methoxyphenylboronic acid is involved in activation of the allylic alcohols.[15]

We continued our mechanistic studies by probing the *in situ* formation of the allylic alcohol. We envisioned four potential pathways to form the allylic alcohol. Pathway 1 involves the intramolecular hydronickelation of homoallylic alcohol **1** to form the oxanickelacycle, followed by β-hydride elimination (Scheme 7a).[20] Pathway 2 consists of the oxidative addition of nickel catalyst to the O–H bond of *p*-$MeOC_6H_4B(OH)_2$, subsequent migratory insertion of the alkene present in **1**, and β-hydride elimination (Scheme 7b). Pathway 3 comprises an intramolecular hydride shift involving the formation of a π-allyl-Ni(II) to enable the migration of a hydride from the

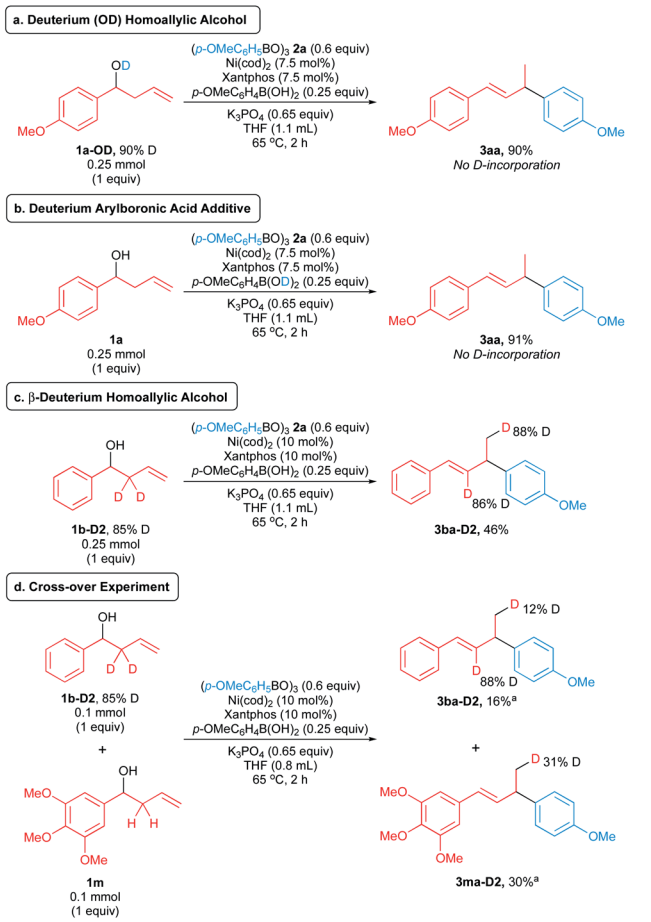


Scheme 7 Possible pathways for the *in situ* formation of allylic alcohol.

β position to the terminal position (Scheme 7c).[21,22] Pathway 4 comprises an intermolecular hydride shift involving a sequential formation of a π-allyl-Ni(II), migratory insertion, and β-hydride elimination (Scheme 7d).[22]

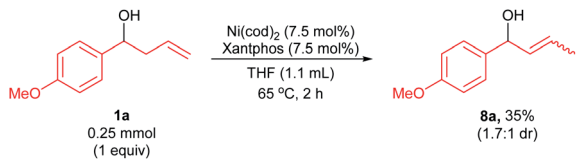
We conducted experiments with deuterium-labelled substrates to evaluate these pathways. The reaction of deuterated homoallylic alcohol **1a-OD** with boroxine **2a** produced allylic arene **3aa** in 90% yield without any deuterium incorporation (Scheme 8a). Similarly, homoallylic alcohol **1a** reacted with boroxine **2a** in the presence of deuterated *p*-methoxyphenylboronic acid to form **3aa** in 91% yield without any deuterium incorporation (Scheme 8b). These observations rule out the *in situ* formation of allylic alcohol *via* pathways 1 and 2. Notably, in the reaction of β-deuterated homoallylic alcohol **1b-D2**, we observed deuterium incorporation (88% D) to the terminal position of product **3ba-D2** (Scheme 8c), suggesting that the pathways 3 and 4 are feasible in our arylative substitution reaction. To further distinguish these pathways, we performed the cross-over experiment using β-deuterated homoallylic alcohol **1b-D2** and nondeuterated homoallylic alcohol **1m** (Scheme 8d). We observed deuterium incorporation into products arising from both homoallylic alcohol substrates. Higher amounts of deuterium were incorporated into the terminal position (31% D) of product **3ma-D2** derived from the nondeuterated homoallylic alcohol **1m** compared to the product **3ba-D2** derived from the deuterated homoallylic alcohol **1b-D2** (12% D). This result indicates that the *in situ* formation of allylic alcohol can proceed through the intermolecular hydride shift mechanism (pathway 4, Scheme 7d), but we cannot rule out formation of the allylic alcohol *via* the intramolecular hydride shift mechanism (pathway 3, Scheme 7c) as a competing reaction pathway.

We also subjected homoallylic alcohol **1a** to the standard reaction conditions in the absence of arylboroxine nucleophile,

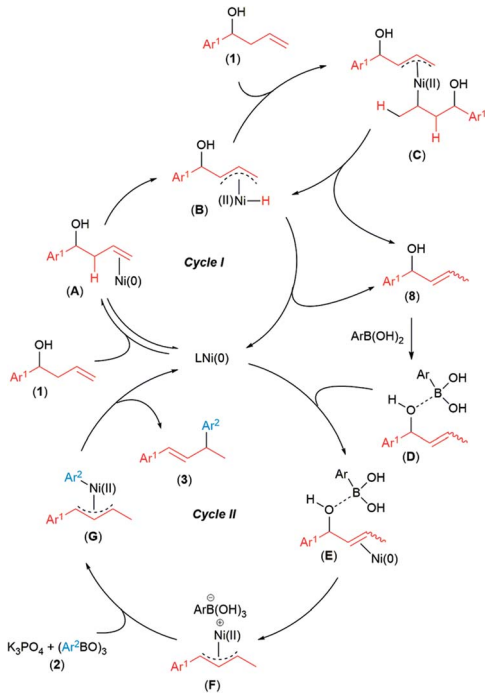


Scheme 8 Deuterium-labelling experiments. Yields and deuterium ratios were determined by ^{1}H NMR spectroscopy of the crude reaction mixture. [a] Isolated yields.

p-methoxyphenylboronic acid additive, and K_3PO_4 (Scheme 9). The reaction formed the allylic alcohol **8a** in 35% yield with 1.7 : 1 dr. This experiment, in combination with the allylic arylation of **8a** (Scheme 6b) and the reactions of deuterium-labelled homoallylic alcohol **1b-D2** (Schemes 8c and d), is consistent with *in situ* formation of the allylic alcohol intermediate by pathways 3 and/or 4 (Schemes 7c and d). In addition, the 1,3-diene was not observed in the isomerization reaction of homoallylic alcohol (Scheme 9), which further suggests the mechanism involving the *in situ* generation of 1,3-diene is not active in our arylative substitutions of homoallylic alcohols.



Scheme 9 Isomerization of homoallylic alcohol **1a**. Yield was determined by ^{1}H NMR spectroscopy of the crude reaction mixture using CH_2Br_2 as an internal standard.



Scheme 10 Proposed mechanism.

Based on these control experiments, we propose the tandem catalytic cycles in Scheme 10. In cycle I, the isomerization of the homoallylic alcohol is proposed to occur *via* formation of a π-allyl-Ni(II) **B** from LNi(0) catalyst and homoallylic alcohol **1**.[21,22] Intermediate **B** undergoes migratory insertion to another homoallylic alcohol **1** to form intermediate **C**, followed by β-hydride elimination to generate allylic alcohol **8**. Intermediate **B** can also undergo reductive elimination to form allylic alcohol **8**. Next, the allylic alcohol **8** generated in cycle I is activated *in situ* (intermediate **D**) by coordination of the oxygen atom to the boron atom of *p*-methoxyphenylboronic acid.[15] Intermediate **D** undergoes oxidative addition with Ni(0) catalyst in cycle II to produce π-allylnickel(II) intermediate **F**. Subsequent transmetallation with arylboroxine **2** facilitated by K_3PO_4[23] and reductive elimination forms the desired product **3** and regenerates the Ni(0) catalyst.[12a] In a recent study, Fang and coworkers proposed a related isomerization/substitution mechanism for nickel-catalyzed hydrocyanation of alkenyl alcohols.[24]

Conclusions

We have developed an arylative substitution of homoallylic alcohols catalyzed by a nickel complex prepared *in situ* from $Ni(cod)_2$ and Xantphos ligand to generate allylic arenes under mild reaction conditions. These reactions are fast and proceed *via* a tandem isomerization/allylic arylation mechanism. The use of *p*-methoxyphenylboronic acid to activate the *in situ* generated allylic alcohol leads to the formation of products in higher yields. These arylative substitutions demonstrate the utility of unactivated alcohols in transition metal-catalyzed cross-coupling chemistry, and the requirement of preactivated alcohols is not necessary. Additional studies on the use of unactivated alcohols in nickel-catalyzed cross-coupling reactions are ongoing.

Data availability

Experimental data associated with this article are provided in the ESI.†

Author contributions

H. N. T. and L. M. S. conceived the project. H. N. T. optimized the reactions conditions, performed the experimental mechanistic studies, and completed the synthetic applications. H. N. T. and C. M. N. synthesized starting materials and evaluated the scope. H. N. T. and L. M. S. wrote the manuscript with input from C. M. N. M. T. K. and D. D. Y. performed the deuterium-labelling experiments during the revision of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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