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Nickel-Catalyzed Homo- and Cross-Coupling of Allyl Alcohols via Allyl Boronates

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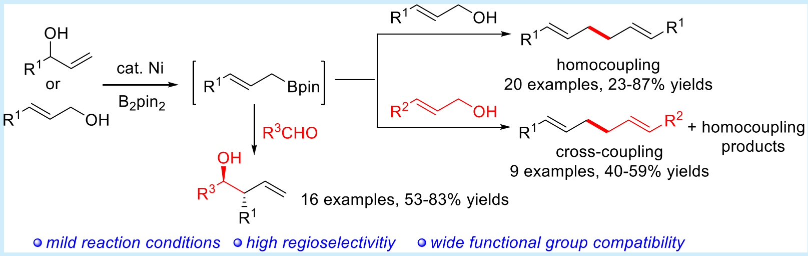
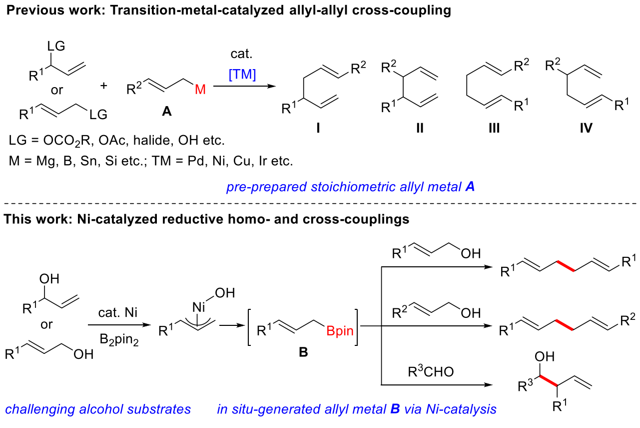


ABSTRACT: A nickel-catalyzed homo- and cross-coupling of allylic alcohols to 1,5-dienes in the presence of B$_2$pin$_2$ with excellent regioselectivity has been developed. Mechanistic studies indicate that the reaction proceeds via sequential nickel-catalyzed borylation of allyl alcohols followed by cross-coupling of the resulting allyl boronates with allyl alcohols. The method was effectively applied to nickel-catalyzed allylation of aldehydes using allylic alcohols directly.

Transition-metal-catalyzed allyl−allyl cross-coupling reactions between allylic electrophiles and allylmetal reagents such as allyl Grignard reagents,[1] allyl boronates,[2] allyl-silanes,[3] or allyl-stannanes[4] represent some of the most efficient methods for the synthesis of 1,5-dienes (Scheme 1), which are valuable building blocks in organic synthesis[5] and also found in many biologically active substances and naturally occurring terpenes[6] (Figure 1). Such allyl−allyl couplings are significantly challenging because both homo- and cross-couplings might be involved in these reactions; therefore, it is hard to obtain the desired products with high chemo- and regioselectivity and good yields. To date, transition metals such as palladium, nickel, copper, iridium, and gold have been used to catalyze allyl−allyl cross-couplings.[1−4] Notwithstanding the advances, these reactions require pre-prepared stoichiometric allyl organometallic reagents, which are usually sensitive to air and moisture and suffer from low stability and low functional-group tolerance. In addition, most of these studies use activated derivatives such as allylic halides, esters, and phosphates as the electrophiles.[1−4] These substrates are often prepared from allylic alcohols. The direct employment of allylic alcohols as the allylic electrophiles is much more attractive

Scheme 1. Metal-Catalyzed Allyl−Allyl Coupling Reactions



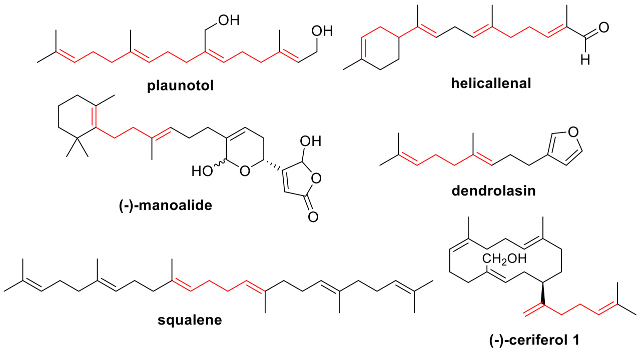


Figure 1. 1,5-Diene-containing terpenes.

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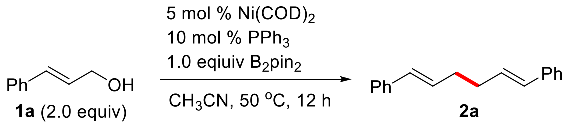
because of its easy availability, high stability, and atom economy.[7] There are very few examples using allylic alcohols in the allyl−allyl cross-couplings due to the poor leaving ability of the hydroxyl group. In 2011, Kobayashi et al.[2d] reported a Ni-catalyzed regioselective cross-coupling between allylic alcohols and terminal allyl boronates leading to linear products (type III). Later, Carreira[3b] and Yang[2h] reported Ir-catalyzed asymmetric coupling of branched allylic alcohols with allylsilanes or allyl boronates, which afforded branched products (type II). Herein, we report a nickel-catalyzed homo- and cross-coupling of allylic alcohols leading to linear 1,5-dienes. The nucleophilic allyl boronate is generated in situ by a Ni-catalyzed process, thus obviating the use of presynthesized stoichiometric allyl metals. In addition, the method can be extended successfully to highly regioselective coupling of allylic alcohols with aldehydes (Scheme 1).

During our study of nickel-catalyzed reductive coupling of allylic alcohols with other electrophiles, we found that 1,5-dienes derived from dimerization of allylic alcohols were always observed as the side products under various reaction conditions. According to the literature, Würtz-type dimerization of allylic halides and esters has been reported; however, the regioselectivity was often unsatisfactory.[8] A mild and regioselective dimerization by direct use of allylic alcohols remains to be developed. We then deeply evaluated this reaction. After extensive optimization studies, including the effects of the nickel source, ligands, reducing agents, reaction temperature, etc., we found that the additive B_2pin_2 played a key role in the effective transformation. Thus, 1,5-diene **2a** was obtained in 86% yield with excellent linear selectivity (>30:1) using 5 mol % $Ni(COD)_2$ and 10 mol % PPh_3 in the presence of 1.0 equiv of B_2pin_2 in CH_3CN at 50 °C (Table 1, entry 1). No apparent formation of other regioisomers was observed. Without B_2pin_2, only 4% of the desired product was obtained (entry 2). Other reducing agents such as Zn and Mn, which were widely used in Ni-catalyzed reductive coupling reactions,[9] failed to give the dimerization product (entry 3). The use of B_2nep_2 instead of B_2pin_2 provided **2a** in a lower yield (entry 4). We speculated that the allyl boronate intermediate derived from a diboron reagent might be formed, which facilitated the homocoupling of allyl alcohols. The effects of other ligands were also examined. Monodentate ligands such as $P(p\text{-}MeC_6H_4)_3$, $P(p\text{-}CF_3C_6H_4)_3$, $PMePh_2$, and PMe_2Ph provided **2a** in good yields of 68−81%, while P^nBu_3 gave **2a** in lower yield (entries 5−9). Bidentate ligands such as dppb and 2,2′-bipy resulted in lower yields (entries 10 and 11, respectively). $Ni(PPh_3)_4$, which has been shown to be an active catalyst in Ni-catalyzed cross-couplings between allyl alcohols and allyl boronates,[2d] failed to give the desired product (entry 12). The use of a Ni(II) complex such as $NiBr_2(DME)$ or $Ni(acac)_2$ was ineffective in this reaction (entry 13). In the absence of PPh_3, **2a** was formed in 23% yield (entry 14). In the absence of a nickel catalyst, no desired product was formed (entry 15).

Table 1. Optimization of the Reaction Conditions

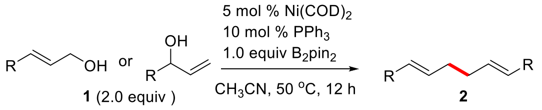


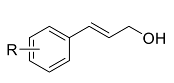
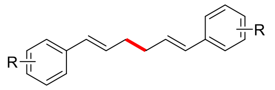
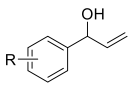
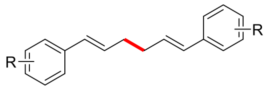
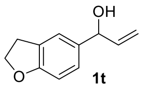
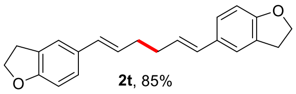
entry	derivation from standard conditions	yield (%)[a]
1	none	86 (82[b])
2	no B_2pin_2	4
3	Zn or Mn instead of B_2pin_2	3−4
4	B_2nep_2 instead of B_2pin_2	56
5	$P(p\text{-}MeC_6H_4)_3$ instead of PPh_3	81
6	$P(p\text{-}CF_3C_6H_4)_3$ instead of PPh_3	72
7	$PMePh_2$ instead of PPh_3	81
8	PMe_2Ph instead of PPh_3	68
9	P^nBu_3 instead of PPh_3	46
10	5 mol % dppb instead of 10 mol % PPh_3	24
11	5 mol % 2,2′-bipy instead of 10 mol % PPh_3	27
12	$Ni(PPh_3)_4$ instead of $Ni(COD)_2$, without PPh_3	0
13	$NiBr_2(DME)$ or $Ni(acac)_2$ instead of $Ni(COD)_2$	0
14	no PPh_3	23
15	no $Ni(COD)_2$	0

[a] NMR yields using 1,3,5-trimethoxybenzene as the internal standard. [b] Isolated yields.

Next, the scope of the nickel-catalyzed homocoupling of allylic alcohols was examined (Table 2). For cinnamyl alcohol derivatives, the phenyl ring bearing a 4-OMe or 4-CF_3 substituent worked well to afford product **2b** or **2c**, respectively, in 50−83% yields (Table 2, entry 2 or 3, respectively). However, treatment of **1d** possessing a 3-Cl

Table 2. Scope of the Ni-Catalyzed Homocoupling of Allyl Alcohols



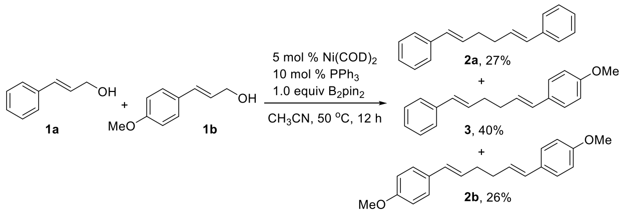
entry	allyl alcohol **1**	yield of product **2**[a]
		
1	R = 4-H (**1a**)	R = 4-H (**2a**), 82% (74%)[b]
2	R = 4-OMe (**1b**)	R = 4-OMe (**2b**), 83%
3	R = 4-CF_3 (**1c**)	R = 4-CF_3 (**2c**), 50%
4	R = 3-Cl (**1d**)	R = 3-Cl (**2d**), 52%[c,d]
5	R = 4-F (**1e**)	R = 4-F (**2e**), 80%[c]
		
6	R = 4-H (**1f**)	R = 4-H (**2a**), 83%
7	R = 4-Me (**1g**)	R = 4-Me (**2g**), 85%
8	R = 4-^{t}Bu (**1h**)	R = 4-^{t}Bu (**2h**), 86%
9	R = 4-NMe_2 (**1i**)	R = 4-NMe_2 (**2i**), 76%
10	R = 4-OPiv (**1j**)	R = 4-OPiv (**2j**), 84%[c]
11	R = 4-CN (**1k**)	R = 4-CN (**2k**), 78%
12	R = 4-CO_2Me (**1l**)	R = 4-CO_2Me (**2l**), 77%
13	R = 3-OTBS (**1m**)	R = 3-OTBS (**2m**), 72%
14	R = 3,5-diOMe (**1n**)	R = 3,5-diOMe (**2n**), 80%
15	R = 2-Me (**1o**)	R = 2-Me (**2o**), 87%
16	R = 2-OMe (**1p**)	R = 2-OMe (**2p**), 83%
17	R = 4-$SiMe_3$ (**1q**)	R = 4-$SiMe_3$ (**2q**), 78%
18	R = 4-Bpin (**1r**)	R = 4-Bpin (**2r**), 42%
19	R = 4-(trimethylsilyl)ethynyl (**1s**)	R = 4-(trimethylsilyl)ethynyl (**2s**), 23%
20	 **1t**	 **2t**, 85%

[a] Isolated yields. [b] On a 6 mmol scale. [c] With 10 mol % $Ni(COD)_2$ and 20 mol % PPh_3. [d] At 40 °C.

substituent resulted in a trace of product (determined by TLC), possibly due to the fact that the C−Cl bond is susceptible to oxidative cleavage in nickel catalysis. Gratifyingly, a moderate yield of **2d** could be achieved by doubling the amounts of Ni(COD)$_2$ and PPh$_3$ and decreasing the reaction temperature to 40 °C (entry 4). A high yield of **2e** with a 4-F substituent was also achieved (entry 5). Allyl alcohol **1f**, a regioisomer of **1a**, worked well to afford the same product **2a** in 83% yield (entry 6), indicating that a common π-allyl nickel intermediate was involved in the reaction. A range of branched alcohols bearing either electron-donating (4-Me, 4-^{t}Bu, 4-NMe$_2$, and 4-OPiv) or electron-withdrawing (4-CN and 4-CO$_2$Me) groups on the phenyl ring were converted to the corresponding linear 1,5-dienes **2g**−**2l** in 76−86% yields (entries 7−12, respectively). It was noted that increasing the amounts of the nickel catalyst and ligand was also required to achieve a better yield of **2j** bearing a pivalate group (entry 10). The results indicated that the electronic nature of aryl substituents had little influence on the reaction. The 3-OTBS and 3,5-diOMe groups on the aryl ring were tolerated well (entries 13 and 14, respectively). Moreover, when the sterically congested allyl alcohols bearing 2-methyl and 2-methoxy groups on the phenyl ring were employed, the corresponding **2o** and **2p**, respectively, were formed in high yields, indicating that the reaction was not sensitive to steric effects (entries 15 and 16, respectively). A silyl group on the phenyl ring was also suitable (**2q**). Substrate **1r**, which included a 4-Bpin-phenyl moiety, gave **2r** in a lower yield of 42%. Allyl alcohol **1s** bearing an internal alkynyl group provided **2s** in 23% yield (entry 19). The gram-scale synthesis of 1,5-diene **2a** was also performed (entry 1), which demonstrated the practicality of this method.

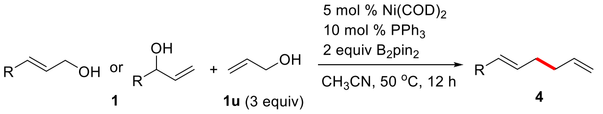
When different allyl alcohols **1a** and **1b** were subjected to this catalytic system, cross-coupling product **3** was obtained in 40% yield, together with homocoupling products **2a** and **2b** in 26−27% yields (Scheme 2). To our delight, no apparent branched isomers were observed in this reaction.

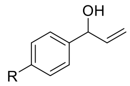
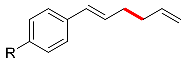
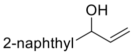
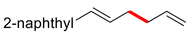
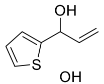
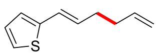
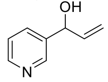
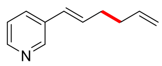
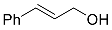
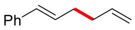
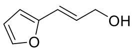
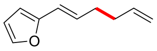
Scheme 2. Nickel-Catalyzed Reaction of Allyl Alcohols 1a and 1b



The cross-coupling of branched alcohol **1h** with terminal allyl alcohol **1u** proceeded efficiently to give **4a** in 55% yield using excess **1u** and 2.0 equiv of B$_2$pin$_2$ (Table 3, entry 1). The homocoupling products of **2h** (33% yield) and **2u** (∼55% NMR yield, based on **1u**) could also be observed. **2u** could easily be removed by evaporation. This method was applied to various allyl alcohols, and in all cases, the desired 1,5-dienes were formed in moderate yields with excellent linear selectivity. The allyl alcohols with either electron-poor or electron-rich aryl rings coupled well with **1u** (**4b** and **4c**). Reactions of thienyl- or pyridyl-substituted allyl alcohols were also suitable (**4e** and **4f**). Linear alcohols such as cinnamyl alcohol **1a** and 2-furanyl-substituted alcohol **1z** transformed smoothly into **4g** and **4h**, respectively.

Table 3. Scope of the Ni-Catalyzed Cross-Coupling of Allyl Alcohols

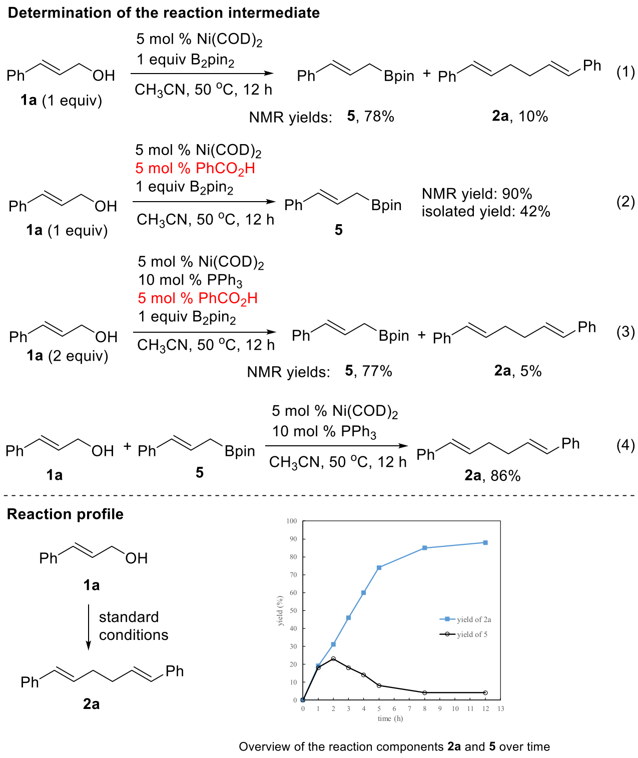


entry	allyl alcohol 1	product 4	yield (%)[a]
			
1	R = ^{t}Bu (**1h**)	R = ^{t}Bu (**4a**)	55
2	R = CO$_2$Me (**1l**)	R = CO$_2$Me (**4b**)	59
3	R = morpholino (**1v**)	R = morpholino (**4c**)	52
4	 **1w**	 **4d**	50
5	 **1x**	 **4e**	54[b]
6	 **1y**	 **4f**	46
7	 **1a**	 **4g**	53
8	 **1z**	 **4h**	57[c]

[a] Isolated yields. [b] Containing a trace of byproduct. [c] Containing 9% isomer, possibly a Z-isomer.

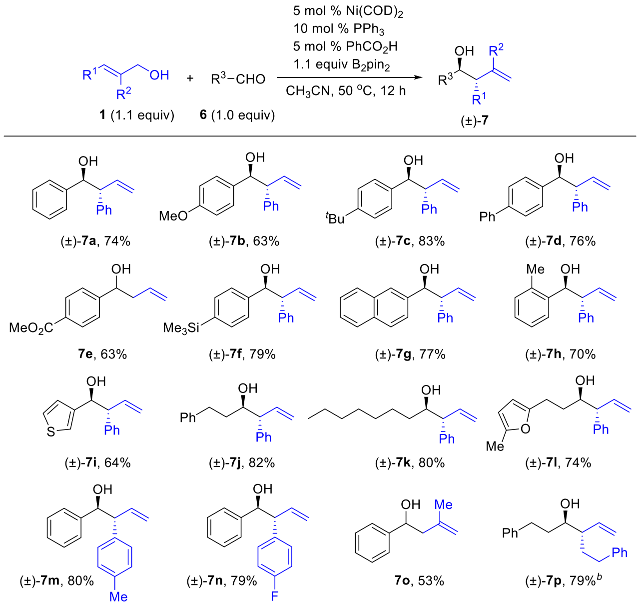
We next tried to isolate the possible reaction intermediate. To our delight, without the ligand, allyl boronate **5** could be formed in 78% yield, along with dimer **2a** in 10% yield (Scheme 3, eq 1). The yield of **5** could be dramatically improved to 90% upon addition of 5 mol % PhCO$_2$H to the reaction mixture, and the dimerization could be completely

Scheme 3. Mechanistic Studies



inhibited (Scheme 4, eq 2). In addition, addition of 5 mol % $PhCO_2H$ to the reaction mixture under the standard conditions resulted in a trace of dimer **2a**; thus, $PhCO_2H$ plays a role in inhibiting the dimerization (Scheme 4, eq 3). It was noted that boronate **5** was unstable during isolation; thus, an only 42% isolated yield was obtained. To the best of our knowledge, there has been no report of boroylation of allylic alcohols using economic nickel as the catalyst,[10,11] and our reaction provided a simple route for aryl allyl boronates. The reaction of allylic alcohol **1a** with allyl boronate **5** under standard reaction conditions afforded the desired **2a** in 86% yield (Scheme 4, eq 4). It should be noted that most of the metal-catalyzed allyl−allyl coupling involved boranes limited to terminal allyl boronates, and there have been few reports using substituted allyl boronates;[2a,e,f] in particular, coupling with aryl allyl boronates such as **5** has not been reported. The reaction shown in eq 4 may provide an efficient way to selectively prepare unsymmetrically substituted 1,5-dienes. We also monitored the reaction by ^{1}H NMR spectroscopy. These studies showed that 4−23% of allyl boronate **5** was present throughout the reaction. The amounts of allyl boronate **5** reached a maximum value after 2 h and then steadily decreased. These results strongly suggest that the reactions proceed via an allyl boronate intermediate.

Scheme 4. Scope of the Ni-Catalyzed Allylation of Aldehydes[a]

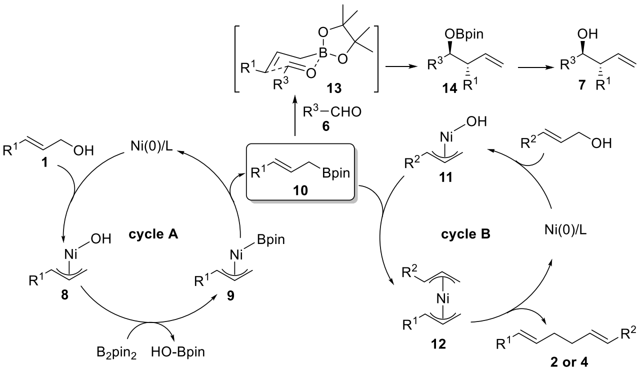


[a]Isolated yieds with >20:1 dr. [b]Containing small amounts of an impurity.

The results presented above also suggest that the current process could be extended to other catalytic transformations involving allyl boronate. We then performed the allylation of aldehydes using allylic alcohols.[12] After briefly screening the conditions, we found that the desired allylation occurred efficiently with excellent regio- and stereoselectivity using 5 mol % $PhCO_2H$ as the additive (Scheme 4). Without $PhCO_2H$, an only moderate yield of **7a** was formed. The reaction proved to be quite general with respect to substitution of allylic alcohols and aldehydes, because aryl or alkyl groups were all suitable for these substrates, showing a broad diversity of the products. For example, the allylation of aliphatic aldehydes such as 3-phenylpropanal (**6j**), octanal (**6k**), and 3-(5-methylfuran-2-yl)propanal (**6l**) proceeded well to provide **7j**−**7l**, respectively, in good yields. The reaction of aliphatic allyl alcohol and aldehyde also took place smoothly (**7p**). Control experiments indicated that benzaldehydes **6a** could react with allyl boronate **5** without the need for a nickel catalyst in the presence or absence of $PhCO_2H$, leading to **7a** in 56−60% yields, indicating that allyl boronate **5** served as the intermediate for this reaction.

On the basis of the previous reports and the results presented above,[13] a plausible reaction mechanism is depicted in Scheme 5. Oxidative addition of allylic alcohol to Ni(0) generates a π-allylnickel(II) complex **8**. In this process, B_2pin_2 may function as a Lewis acid to facilitate the elimination of the OH group. Transmetalation of **8** with B_2pin_2 occurs to give complex **9**, which delivers allyl boronate **10** by reductive elimination (cycle A). In cycle B, **10** reacts with π-allylnickel(II) complex **11** to give a diallylnickel intermediate **12**. Reductive elimination of **12** via a bis(η^1-allyl)nickel complex affords linear product **2** or **4** (cycle B). In the presence of aldehyde **6**, allyl boronate **10** reacts with **6** via transition state **13**[14] to give homoallylic alcohols **7** stereoselectively.

Scheme 5. Possible Reaction Mechanism



In summary, we have developed a nickel-catalyzed homo- and cross-coupling of allylic alcohols to 1,5-dienes with excellent regioselectivity. The reaction proceeds via sequential nickel-catalyzed borylation of allylic alcohols followed by cross-coupling of the resulting allyl boronates with allyl alcohols. The key intermediate of allyl boronates was found to be formed in high NMR yields under very simple conditions without the need for a ligand. The method was effectively applied to nickel-catalyzed allylation of aldehydes using allylic alcohols directly.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c01424.

Experimental details and spectroscopic characterization of all products and new substrates (PDF)

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Notes

The authors declare no competing financial interest.

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