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PII: S0040-4039(16)30800-0
DOI: http://dx.doi.org/10.1016/j.tetlet.2016.06.121
Reference: TETL 47848

To appear in: *Tetrahedron Letters*

Received Date: 8 May 2016
Revised Date: 22 June 2016
Accepted Date: 27 June 2016

Please cite this article as: Horino, Y., Aimono, A., Minoshima, N., Abe, H., Facile Synthesis of (*Z*)-*anti*-Homoallylic Alcohols from 3-(Pinacolatoboryl)allyl Alcohols, Aldehydes, and Triorganoboranes via a Palladium-Catalyzed Three-Component Reaction, *Tetrahedron Letters* (2016), doi: http://dx.doi.org/10.1016/j.tetlet.2016.06.121

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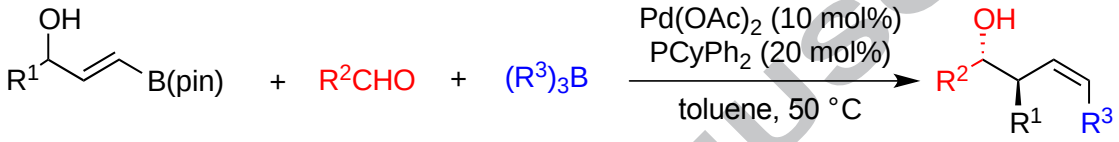

Tetrahedron Letters
journal homepage: www.elsevier.com

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ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

Keywords:
Allylation
Three-component reaction
Palladium catalysis
Homoallylic alcohols

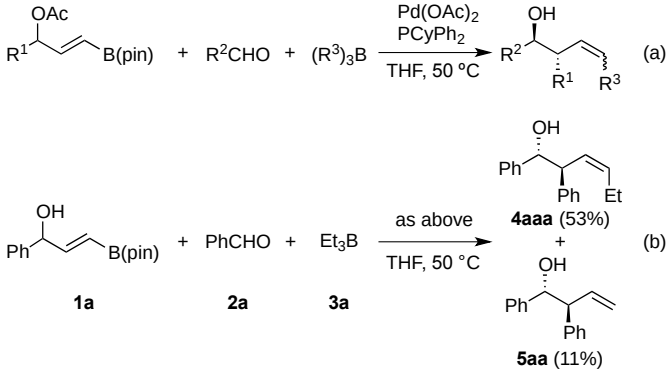
ABSTRACT

A palladium-catalyzed three-component reaction of 3-(pinacolatoboryl)allyl alcohols, aldehydes, and triorganoboranes was developed. The present protocol provides facile access to synthetically useful (*Z*)-*anti*-homoallylic alcohols with high diastereoselectivity and high levels of alkene stereocontrol. Furthermore, a single synthetic-step operation to synthesize (*Z*)-*anti*-homoallylic alcohols starting from propargyl alcohols by using palladium-catalyzed three-component reaction is successfully achieved.

Introduction

Recent advances have greatly increased the utility of allylic alcohols as allylating reagents in the σ-allylpalladium-mediated nucleophilic allylation reactions. These reactions differ from hitherto reported umpolung methods wherein π-allylpalladium complexes are used.[1-4] For instance, Zhou and co-workers applied Tamaru's umpolung allylation protocol,[5] wherein allylic alcohols are used as allylating reagents, to the palladium-catalyzed asymmetric umpolung allylation of carbonyl compounds and imines, wherein σ-allylpalladium intermediates generated from the triethylborane-mediated umpolung reaction of π-allylpalladium were proposed to serve as nucleophiles.[1] Furthermore, Sato and Mita have reported the σ-allylpalladium-mediated carboxylation of allylic alcohols with CO_2 in the presence of $ZnEt_2$.[6] These studies indicate the utility of a route to σ-allylpalladium-mediated nucleophilic allylation products using allylic alcohols as allylating reagents. However, a simple and convenient method for directly using allylic alcohols as allylating reagents is still highly desired from a step- and atom-economic point of view.[7]

We have previously reported the palladium-catalyzed three-component reaction of 3-(pinacolatoboryl)allyl acetates, aldehydes, and triorganoboranes that stereoselectively provides (*Z*)-*anti*-homoallylic alcohols (Scheme 1a).[8] Although the reaction also proceeds via σ-allylpalladium intermediates, the reaction mechanism is different from the protocols mentioned above; the palladium atom in the formation of σ-allylpalladium ~~intermedi~~ates serves as a Lewis acid to coordinate with aldehydes, and an acetoxy group on the palladium atom acts as a Lewis base to intramolecularly activate the pinacolatoboryl group at the α-position. As a result, the nucleophilic allylation of aldehydes with allylboronates takes place via a putative *cis*-decaline-like cyclic transition state; the resulting vinylpalladium intermediates couple with triorganoboranes to give (*Z*)-*anti*-homoallylic alcohols. In mechanistic studies, we found that 3-(pinacolatoboryl)allyl alcohol **1a** was also able to take part in the palladium-catalyzed three-component reaction (Scheme 1b). However, the desired product **4aaa** was obtained in only moderate yield with a significant amount of the *β*-hydride elimination product **5aa**. As an effort toward the developing an atom-economical nucleophilic allylation reaction utilizing allylic alcohols as allylating reagents,[9] we herein report the facile synthesis of (*Z*)-*anti*-



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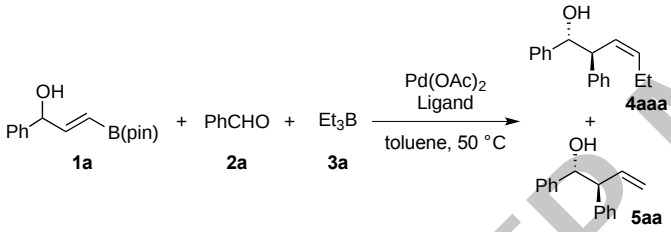
Scheme 1. Previous works

homoallylic alcohols from 3-(pinacolatoboryl)allyl alcohols, aldehydes, and triorganoboranes via a palladium-catalyzed three-component reaction. It is worth noting that (*Z*)-*anti*-homoallylic alcohols cannot be easily accessed via known catalytic conditions.[10-12]

Results and discussion

Initially, we screened the reaction conditions for the palladium-catalyzed three-component reaction of **1a**, benzaldehyde (**2a**), and triethylborane (**3a**) by evaluating various ligands (Table 1). The reaction of **1a** (1 equiv), **2a** (2.4 equiv), and **3a** (2.4 equiv) in the presence of $Pd(OAc)_2$ (10 mol%) and $PCyPh_2$ (20 mol%) in toluene under Ar atmosphere at 50 ºC afforded the corresponding product **4aaa** in 52% isolated yield along with **5aa** in 9% yield (entry 1). The chemical yield of **4aaa** and the ratio of **4aaa**/**5aa** improved when the 3.6 equivalents of triethylborane was used (entry 2). However, further addition of triethylborane did not ameliorate the reaction (entry 3). Among the monodentate phosphine ligand tested, $PCyPh_2$ showed the best result in terms of chemical yield of **4aaa** and the ratio of **4aaa**/**5aa** (entries 4–7). Moreover, changing the palladium source from $Pd(OAc)_2$ to $Pd_2(dba)_3CHCl_3$ did not efficiently promote the present reaction (entry 8).

Table 1. Optimization of reaction conditions[a]

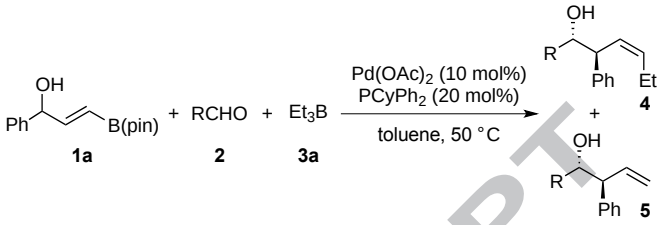


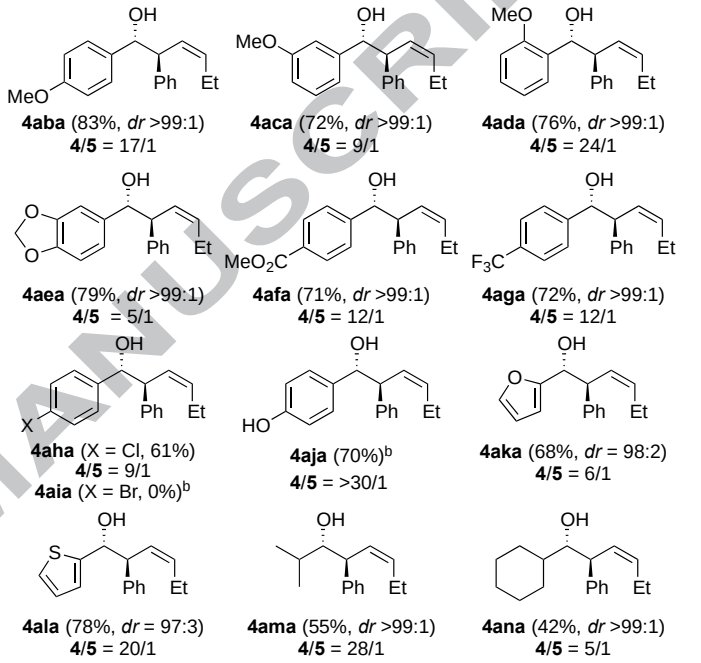
Entry	Ligand	Time (h)	**4aaa** (%)[b]	*Z*/*E*[c]	**5aa** (%)[b]
1[d]	$PCyPh_2$	4	52	>20/1	9
2	$PCyPh_2$	4	60	>20/1	6
3[e]	$PCyPh_2$	4	51	>20/1	7
4	$P(n\text{-}Bu)_3$	5	35	>20/1	31
5	PPh_3	4.5	52	>20/1	17
6	$P(p\text{-}MeOC_6H_4)_3$	4.5	54	>20/1	14
7	$P(p\text{-}CF_3C_6H_4)_3$	7	57	>20/1	7
8[f]	$PCyPh_2$	6	58	>20/1	4

[a] Conditions: **1a** (0.5 mmol), **2a** (1.2 mmol), **3a** (1 M in hexane sol., 1.8 mmol), $Pd(OAc)_2$ (0.05 mmol), and $PCyPh_2$ (0.1 mmol) in toluene (2 mL) at 50 °C.
[b] Isolated yield.
[c] The ratio of *Z*/*E* was determined by NMR analysis of the crude mixtures.
[d] **3a** (1 M in hexane sol., 1.2 mmol) was used.
[e] **3a** (1 M in hexane sol., 2.4 mmol) was used.
[f] $Pd_2(dba)_3CHCl_3$ (5 mol%) and $PCyPh_2$ (20 mol%) were used.

Having determined the optimal conditions, we subsequently explored the reaction scope using various aldehydes and **1a** and **3a** (Table 2). It was found that a wide array of electronically and sterically diverse aromatic aldehydes **2b**–**2h** was tolerant to produce **4aba**–**4aha** in good-to-high yields with high diastereoselectivities and high levels of alkene stereocontrol. While *p*-bromobenzaldehyde **(2i)** and *p*-hydroxybenzaldehyde (**2j**) did not afford the corresponding products under optimized reaction condition, to our delight, **4aja** was formed in 70% yield when the amount of **3a** was increased. On the other hand,

Table 2. Scope of Aldehydes[a]





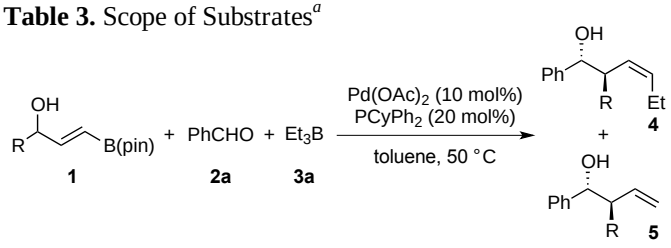
[a] Conditions: **1a** (0.5 mmol), **2** (1.2 mmol), **3a** (1 M in hexane sol., 1.8 mmol), $Pd(OAc)_2$ (0.05 mmol), and $PCyPh_2$ (0.1 mmol) in toluene (2 mL) at 50 °C.
[b] **3a** (1 M in hexane sol., 2.4 mmol) was used.

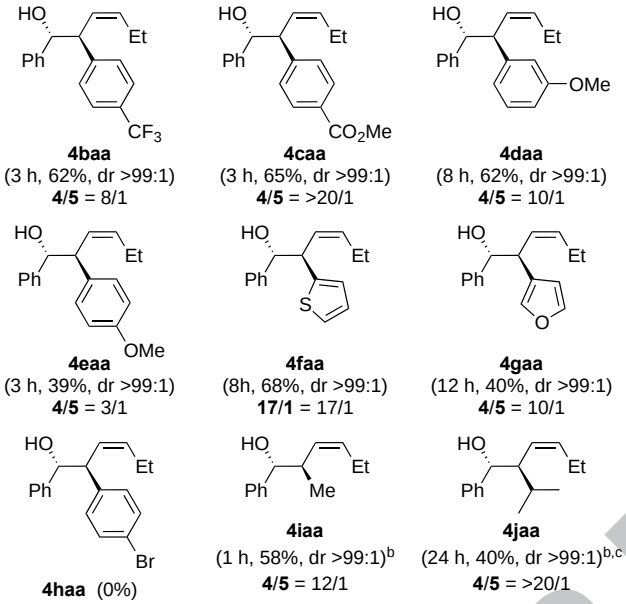
2i did not take part in the reaction. Furthermore, we investigated the reaction of heterocyclic aldehydes and observed that the reactions of furfural and 2-thienylaldehydes smoothly proceeded to produce **4aka** and **4ala**, respectively, in good yields. Nevertheless, it is noteworthy that the aliphatic aldehydes such as isobutyraldehyde (**2m**) and cyclohexanecarbaldehyde (**2n**) successfully participated in the reaction to produce **4ama** and **4ana** in 55% and 42% yields, respectively. The high diastereoselectivity and high levels of alkene stereocontrol were observed for all aldehydes examined.

Next, the three-component reaction was applied to 3-(pinacolatoboryl)allyl alcohol **1** having various simple or functionalized aryl substituents using **2a** and **3a** (Table 3). 3-(Pinacolatoboryl)allyl alcohols possessing an electron-withdrawing group on the aromatic ring afforded **4baa**, **4caa**, and **4daa** in 62%–65% yields. Conversely, an electron-donating group on the aromatic ring resulted in decreased yields, giving **4eaa** in 39% yield with a significant amount of *β*-hydride elimination product **5ea**. In addition, when heteroaryl-substituted substrates were subjected to the reaction, the reaction time required to achieve full conversion was longer, providing **4faa** and **4gaa** in 68% and 40% yields, respectively. In contrast to our previous study,[8] the present protocol is not applicable to 3-(pinacolatoboryl)allyl alcohol having a *p*-bromophenyl

substituent. In the case of methyl-substituted substrate **1i**, the reaction smoothly proceeded to provide **4iaa** in 58% yield. The

Table 3. Scope of Substrates[a]



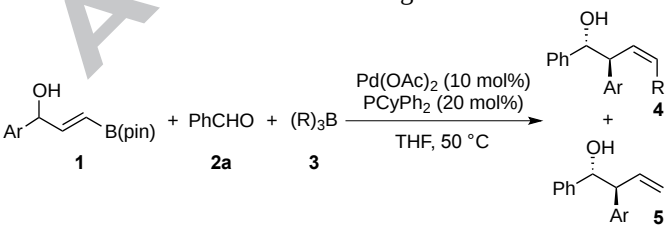


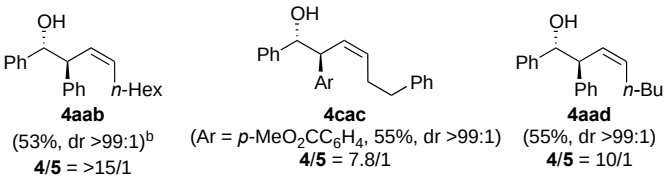
[a] Conditions: **1** (0.5 mmol), **2a** (1.2 mmol), **3a** (1 M in hexane sol., 1.8 mmol), $Pd(OAc)_2$ (0.05 mmol), and $PCyPh_2$ (0.1 mmol) in toluene (2 mL) at 50 °C.
[b] Reaction was performed at 70 °C.
[c] $Pd(OAc)_2$ (0.1 mmol) and $PCyPh_2$ (0.2 mmol) were used.

reaction is slower with increasing size of the alkyl substituent. When the isopropyl-substituted substrate **1j** was used, desired product **4jaa** was obtained in 40% yield at 70 °C for 24 h. In all cases, high levels of (*Z*)-stereo- and diastereoselectivity were observed.

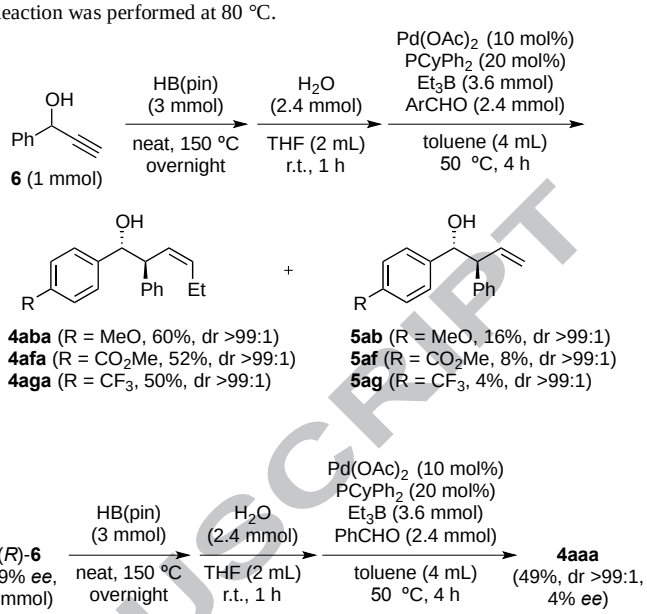
To further investigate the scope of the present process, tri-*n*-alkylboranes were surveyed under the optimized reaction conditions; Tri-*n*-hexylborane and triphenethylborane prepared from 1-hexene and styrene with $BH_3 \cdot SMe_2$ nicely participated in

Table 4. Reaction with Various Triorganoboranes[a]





[a] Conditions: **1** (0.5 mmol), **2a** (1.2 mmol), **3** (1.8 mmol), $Pd(OAc)_2$ (0.05 mmol), and $PCyPh_2$ (0.1 mmol) in toluene (2 mL) at 50 °C.
[b] Reaction was performed at 80 °C.



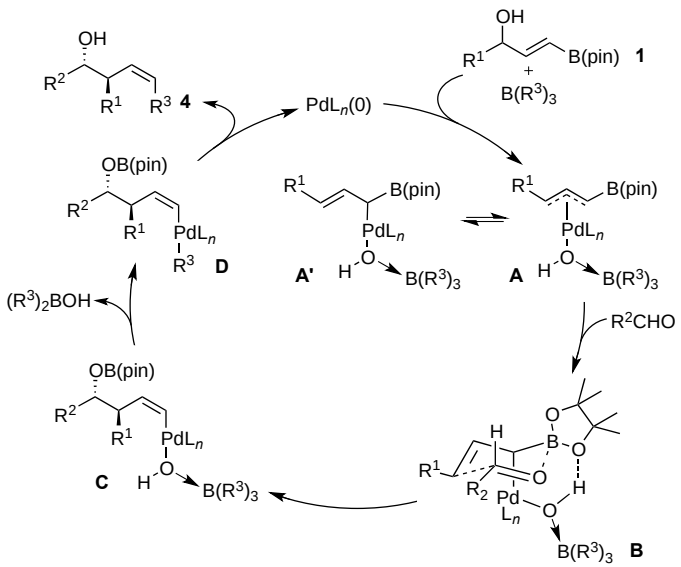
Scheme 2. A single synthetic-step operation via hydroboration/three-component reaction

the three-component reaction to give **4aab** and **4cac** in 53% and 55% yields, respectively, with high diastereo- and (*Z*)-selectivity. In addition, the commercially available tri-*n*-butylborane afforded **4aad** in 55% yield with high *Z*-selectivity. As a limitation, triphenylborane, tri-*sec*-alkylboranes, *B*-alkyl-9-BBN, and alkyl boronate esters are not suitable coupling partners at the current level of development.

Finally, we examined a single synthetic-step operation to synthesize (*Z*)-*anti*-homoallylic alcohols starting from propargyl alcohols by using palladium-catalyzed three-component reaction (Scheme 2).[13] Propargyl alcohol **6** was treated with pinacolborane at 150 °C for 12 h. H_2O and THF were then added, and the mixture was stirred at room temperature for 1 h. After the volatile materials were removed under reduced pressure, *p*-anisaldehyde, a toluene solution of the prepared Pd-$PCyPh_2$ catalyst, and Et_3B (1 M in hexane) were successively added to the residue. The reaction was completed in 4 h, and the corresponding (*Z*)-*anti*-homoallylic alcohol **4aba** was obtained in 60% isolated yield along with **5ab** in 16%. Similarly, the present sequential procedure allowed the use of *p*-(trifluoromethyl)benzaldehyde and methyl 4-formylbenzoate to give **4afa** and **4aga**, respectively, in good overall yields. Next, a chirality transfer experiment was examined using (*R*)-**6** in a single synthetic-step operation. In contrast to our previous work,[8] an efficient chirality transfer was not observed, and **4aaa** was produced in 49% yield as a nearly racemic mixture.[14] In all cases, high levels of (*Z*)-stereo- and diastereoselectivity were observed.

Based on the results described above, a preliminary reaction mechanism is proposed in Scheme 3. First, triorganoborane may coordinate to the oxygen atom of **1** to help it undergo oxidative addition to Pd(0), which then leads to the formation of η^3-allylpalladium intermediate **A**. The allylboronate in the allylic *gem*-palladium/boryl intermediate **A′**[15] (depicted in another η^1-allyl form for simplicity) undergoes nucleophilic allylation of an aldehyde via a closed transition state **B** to form (*Z*)-vinylpalladium intermediate **C**. In the transition state **B**, palladium complex predominantly locates at the axial position due to gauche strain of the palladium complex with pinacol ester

over A[1,3] strain. Transmetalation of **C** with a triorganoborane followed by reductive elimination from a vinylpalladium intermediate **D** gives the desired product **4**.[16, 17]



Scheme 3. A plausible reaction mechanism

In summary, we have developed a palladium-catalyzed three-component reaction that provides access to a wide variety of (*Z*)-*anti*-homoallylic alcohols starting from easily accessible and stable 3-(pinacolatoboryl)allyl alcohols, aldehydes, and triorganoboranes. Both the stereochemistry of the alkene and diastereoselectivity associated with the catalysis are well controlled.

Acknowledgments

We thank Prof. Ryuta Miyatake (University of Toyama) for his assistance with HRMS measurements. This work was financially supported by the JSPS KAKENHI Grant Number 15K05496.

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15. Intramolecular protonation of the boronate oxygen by the Brønsted-acid hydroxyl group on palladium might preferentially lead to the formation of **A'**. In addition, it would increase boron's electrophilicity. For related examples, see: (a) Jain, P.; Antilla, J. C. *J. Am. Chem. Soc.* **2010**, *132*, 11884–11886 and ref 12e.
16. The transmetallation step is not clear at the moment.
17. Another possible reaction path based on Zhou's observations might be considered, see; ref 2.

Supplementary Material

Supplementary material that may be helpful in the review process should be prepared and provided as a separate electronic file. That file can then be transformed into PDF format and submitted along with the manuscript and graphic files to the appropriate editorial office.

Highlights

Allylic alcohols can be utilized directly as an allylating agent.

(*Z*)-anti-Homoallylic alcohols can be readily synthesized.

Triorganoboranes are used as a coupling reagent.

Pd/R_3B induces the formation of π-allylpalladium species from allylic alcohols.