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# Cu-catalyzed highly selective reductive functionalization of 1,3-diene using $H_2O$ as stoichiometric hydrogen atom donor

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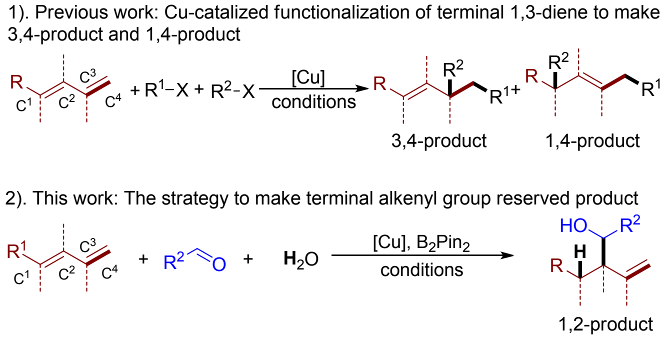
Qifan Li,[a] Xiaoyang Jiao,[a] Mimi Xing,[a] Penglin Zhang,[a] Qian Zhao[a] and Chun Zhang*[ab]

**A copper-catalyzed highly regio- and diastereo-selective reductive reaction of terminal 1,3-diene with water and aldehyde have been developed. This chemistry afforded the terminal alkenyl group containing product, which is a kind of versatile precursors for organic synthesis, with various substrate scopes. The present reaction system could realize catalytic transfer hydrogen to diene using water as a stoichiometric H atom donor. In this transformation, $B_2Pin_2$, a kind of mild and practical reductant was used as the mediator. The reaction pathway of this practical strategy was illustrated by control experiment.**

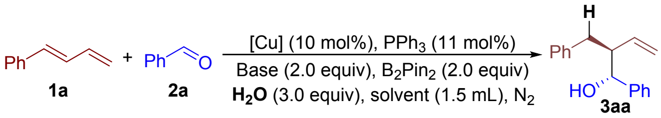
Develop new organic transform strategy to reserve active function group is important for the synthesis of drug, nature product and functional material molecule.[1] Among a lot of versatile starting compounds, 1,3-diene has caught more and more attention, because difunctionalization of conjugated diene with high regio- and diastereo-selectivity is an important class of transformation, which could control the formation of multiple complex isomeric product from simple precursor.[2,3] In recent several years, copper-catalyzed reaction systems have been extensively applied in such reaction, owing to the low price of copper-catalysts, ambient reaction conditions or practical reaction protocols.[4] With such powerful strategy, terminal diene could be converted into 1,4- or 3,4-functionalized product with good selectivity (1, Scheme 1). Comparing with above synthetic strategy, we developed a novel copper-catalyzed $B_2Pin_2$ mediated highly regio- and diastereo-selective functionalization of terminal 1,3-diene to afford 1,2-functionalized product (2, Scheme 1).

**Scheme 1**. Functionalization of terminal 1,3-diene.


1). Previous work: Cu-catalized functionalization of terminal 1,3-diene to make 3,4-product and 1,4-product

2). This work: The strategy to make terminal alkenyl group reserved product

**Table 1**. The effect of different reaction conditions. [a]



| entry | solvent | base | [Cu] | yield (%)[b] | dr |
|---|---|---|---|---|---|
| 1 | THF | LiO$^t$Bu | $Cu(OTf)_2$ | 76 | 5:1 |
| 2 | THF | NaO$^t$Bu | $Cu(OTf)_2$ | 52 | 4:1 |
| 3 | THF | KO$^t$Bu | $Cu(OTf)_2$ | 69 | 5:1 |
| 4 | THF | LiOMe | $Cu(OTf)_2$ | 66 | 2:1 |
| 5 | 1.4-dioxane | LiO$^t$Bu | $Cu(OTf)_2$ | 64 | 4:1 |
| 6 | toluene | LiO$^t$Bu | $Cu(OTf)_2$ | 80 | 9:1 |
| 7 | DCE | LiO$^t$Bu | $Cu(OTf)_2$ | 93 | >20:1 |
| 8 | DCE | LiO$^t$Bu | $Cu(acac)_2$ | 76 | >20:1 |
| 9 | DCE | LiO$^t$Bu | CuCl | 78 | >20:1 |
| 10 | DCE | LiO$^t$Bu | CuOAc | 23 | 13:1 |
| 11[c] | DCE | LiO$^t$Bu | $Cu(OTf)_2$ | 0 | -- |
| 12 | DCE | LiO$^t$Bu | none | 0 | -- |

[a] **1a** (0.25 mmol), **2a** (0.5 mmol), $B_2Pin_2$ (0.5 mmol), base (0.5 mmol), cat (10 mol %), $PPh_3$ (11 mol%), $H_2O$ (3.0 equiv), solvent (1.5 ml). [b] Isolated yield, diastereomers are inseparable, dr was determined by $^1H$-NMR. [c] Without $B_2Pin_2$.

Contrasted to other metal reagents, the organic boron-reagent is much more stable, ambient and practical, so preparation of this kind of compound has been studied intensely.[5] Among them, hydroboration of dienes could afford the important boron reagent, which is a kind of powerful intermediate for a lot of transformation.[6] However, some air or moisture sensitive reagents and catalysts, such as $Ni(cod)_2$

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[a] Department of Chemistry, Tianjin Key Laboratory of Molecular Optoelectronic Science, School of Sciences, Institute of Molecular Plus, Tianjin University, Weijin Rd. 92, Tianjin 300072, China.

[b] State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, China

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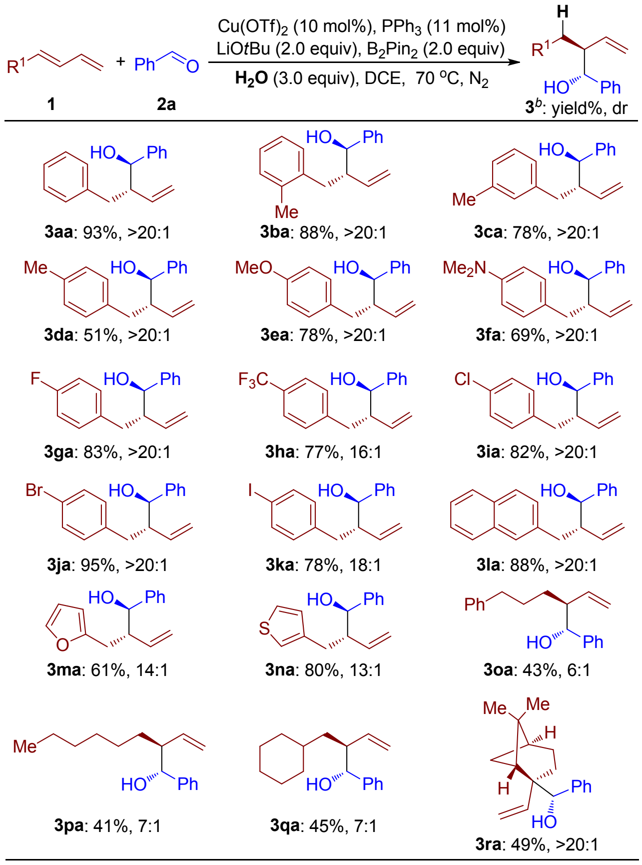
and HBPin, were usually used for those reactions. The present transformation could construct allyl boron intermediate with good regioselectivity by the copper-salt/$H_2O$/$B_2Pin_2$ system, which made this method more practical. Importantly, the examples of catalytic transfer hydrogenations of simple alkenes using $H_2O$ as the stoichiometric H atom donor is the sustainable strategy for organic synthesis.[7] Our work exploits a new way via using $H_2O$ as the safe and cost benefit hydrogen atom source for highly selective catalytic reductive transformation process.

Our study commenced with the copper-catalyzed reaction of (*E*)-buta-1,3-dien-1-ylbenzene (**1a**), benzaldehyde (**2a**), $B_2Pin_2$ and $H_2O$. Interestingly, this practical one pot reaction afforded 2-benzyl-1-phenylbut-3-en-1-ol (**3aa**) with 76% yield and 5:1 diastereoselectivity (entry 1, Table 1 and SI). The efficiency of this reaction was decreased by using other kinds of bases, such as $NaO^tBu$, $KO^tBu$, or LiOMe (entries 1-4, Table 1 and SI). We then surveyed the effect of different solvents. Compared with THF, 1,4-dioxane induced low yield and selectivity, but toluene and DCE afforded much better results (entry 5 to 7, Table 1). Especially, when DCE was chosen as solvent, the product could be given with 93% yield and better than 20:1 diastereoselectivity (entry 7, Table 1). Further studies indicated different kinds of copper-salts could affect the result of this reaction (entry 8 to 10, Table 1). Among them, $Cu(OTf)_2$ was the best choice. The data of entry 11 and 12 proved this reaction did not work without copper catalyst or $B_2Pin_2$ (Table 1).

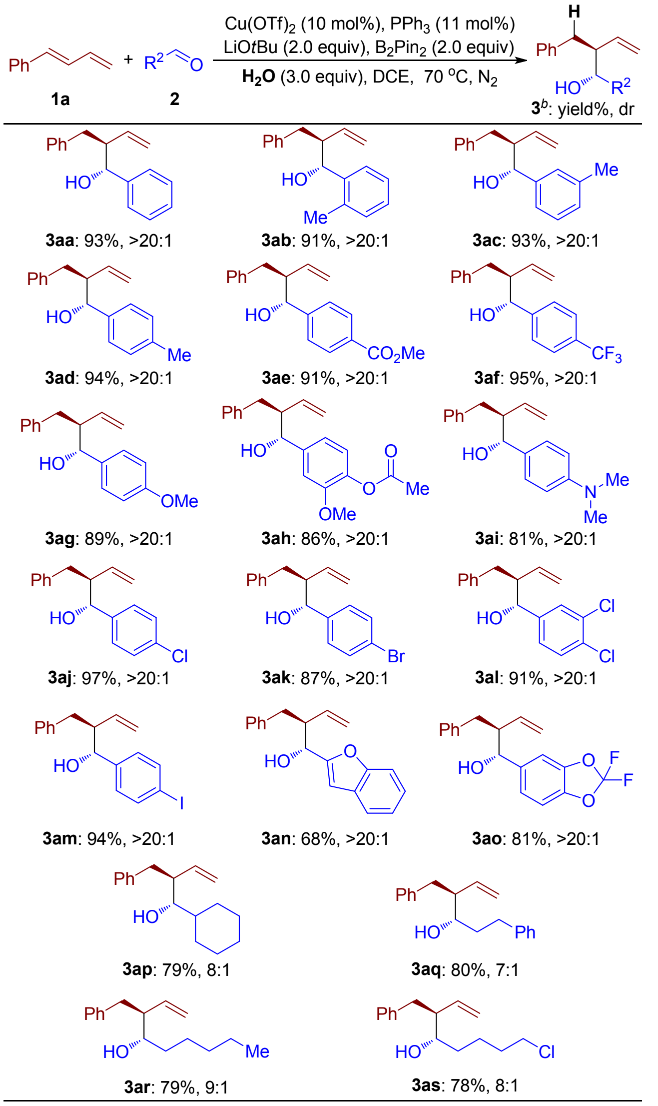
**Table 2**. Cu-catalyzed $B_2Pin_2$ mediated reductive reaction of **2a** with different terminal 1,3-diene (**1**).[a]



**3aa**: 93%, >20:1
**3ba**: 88%, >20:1
**3ca**: 78%, >20:1
**3da**: 51%, >20:1
**3ea**: 78%, >20:1
**3fa**: 69%, >20:1
**3ga**: 83%, >20:1
**3ha**: 77%, 16:1
**3ia**: 82%, >20:1
**3ja**: 95%, >20:1
**3ka**: 78%, 18:1
**3la**: 88%, >20:1
**3ma**: 61%, 14:1
**3na**: 80%, 13:1
**3oa**: 43%, 6:1
**3pa**: 41%, 7:1
**3qa**: 45%, 7:1
**3ra**: 49%, >20:1

[a] Standard Reaction Conditions: **1** (0.25 mmol), **2a** (0.5 mmol), $B_2Pin_2$ (0.5 mmol), $LiO^tBu$ (0.5 mmol), $Cu(OTf)_2$ (10 mol%), $PPh_3$ (11 mol%), $H_2O$ (3.0 equiv), DCE (1.5 ml), 70 °C, under $N_2$ condition. [b] Isolated yield, diastereomers are inseparable, dr was determined by $^1H$-NMR.

**Table 3**. Cu-catalyzed $B_2Pin_2$ mediated reductive reaction of **1a** with different aldehyde (**2**).[a]



**3aa**: 93%, >20:1
**3ab**: 91%, >20:1
**3ac**: 93%, >20:1
**3ad**: 94%, >20:1
**3ae**: 91%, >20:1
**3af**: 95%, >20:1
**3ag**: 89%, >20:1
**3ah**: 86%, >20:1
**3ai**: 81%, >20:1
**3aj**: 97%, >20:1
**3ak**: 87%, >20:1
**3al**: 91%, >20:1
**3am**: 94%, >20:1
**3an**: 68%, >20:1
**3ao**: 81%, >20:1
**3ap**: 79%, 8:1
**3aq**: 80%, 7:1
**3ar**: 79%, 9:1
**3as**: 78%, 8:1

[a] Standard reaction conditions: **1a** (0.25 mmol), **2** (0.5 mmol), $B_2Pin_2$ (0.5 mmol), $LiO^tBu$ (0.5 mmol), $Cu(OTf)_2$ (10 mol%), $PPh_3$ (11 mol%), $H_2O$ (3.0 equiv), DCE (1.5 ml), 70 °C, under $N_2$ condition. [b] Isolated yield, diastereomers are inseparable, dr was determined by $^1H$-NMR.

Using $H_2O$ as hydrogen atom donor and $B_2Pin_2$ as mediator for this reductive transformation, the substrate scope of terminal 1,3-diene was investigated (Table 2). In general, modest to good yields and diastereoselectivity using either electron-rich (MeO- and $Me_2N$-), or electron-deficient (F-, $CF_3$- and Cl-) aryl substituted 1,3-diene were observed (**3aa** to **3ka**, table 2). And the substituents at *ortho*-position positions of the arene group did not affect the efficiency (**3ba**, table 2). Notably, when bromo-substituted aromatic 1,3-diene was employed as substrate, the corresponding product could be afforded with 95% yield and great selectivity, which could be used for further transformation (**3ja**, Table 2). The iodo-

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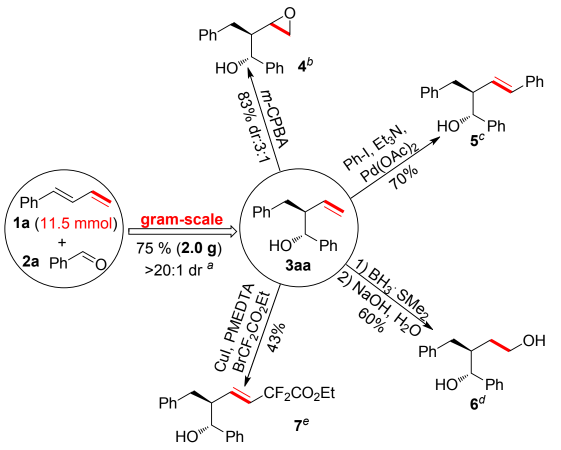
substituted aromatic 1,3-diene still worked, but with lower efficiency (**3ka**, Table 2). To our delight, the naphthyl, furyl and thienyl group could be survival under this reductive reaction condition (**3la** to **3na**, Table 2). Importantly, alkyl 1,3-diene could be transfered into the corresponding products smoothly (**3oa** to **3ra**, table 2). The 1,2-disubstituted 1,3-diene still worked well, which gave the quaternary carbon atom containing product (**3ra**, table 2).

The substrate scope of the Cu-catalyzed $B_2Pin_2$ mediated highly selective reductive transformation was further expanded to a variety of substituted aldehydes (**2**) (Table 3). These results indicated that aryl aldehyde with both electron-donating and electron-withdrawing groups proceeded well with good yields and great diastereoselectivity (**3aa** to **3ap**, Table 3). The substrate group at *para*-, *meta*-, and *ortho*-position of arene ring did not affect the efficiency (**3ab** to **3ad**, Table 3). Notably, even when *bromo*-substituted or *iodo*-substituted arylaldehyde was employed as starting material, good results were afforded (**3ak** and **3am**, Table 3). These products could be used for further coupling reaction to make complicated molecules. Moreover, under this ambient reaction condition, the substrates with hetero-cycle groups could be converted into desired products with good efficiency, which exhibited the good substrate tolerance of this method (**3an** and **3ao**, Table 3). Furthermore, the substrate scope could expand to alkyl aldehydes which afforded good yields and moderate diastereoselectivity (**3ap** to **3as**, table 3).

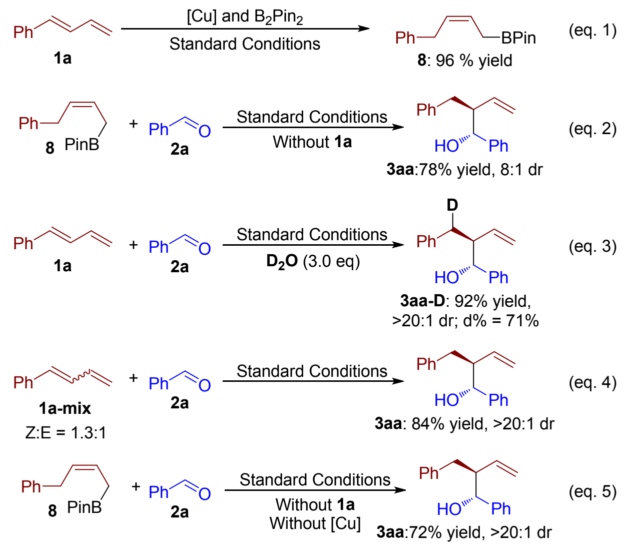
**Scheme 2**. Large scale reaction and further transformation of product.



[a] **1a** (11.5 mmol), **2a** (23 mmol), $B_2Pin_2$ (23 mmol), LiO$^t$-Bu (23 mmol), $PPh_3$ (11 mol%), $Cu(OTf)_2$ (10 mol%), DCE (69 ml), isolated yield. [b] **3aa** (0.25 mmol), *m*-CPBA (0.375 mmol), DCM(1.3 ml), isolated yield. [c] **3aa** (0.185 mmol), Ph-I (0.37 mmol), $Pd(OAc)_2$ (10 mol%), $Et_3N$ (1.85 mmol), $CH_3CN$ (1.8 ml), isolated yield. [d] **3aa** (0.2 mmol), $BH_3{\cdot}SMe_2$ (0.6 mmol), NaOH (0.9 mmol), $H_2O_2$ (1.2 mmol), THF (2.0 ml), isolated yield. [e] **3aa** (0.2 mmol), $BrCF_2CO_2Et$ (0.3 mmol), CuI (10 mol%), PMDETA (0.3 mmol), $CH_3CN$ (1.0 ml), isolated yield.

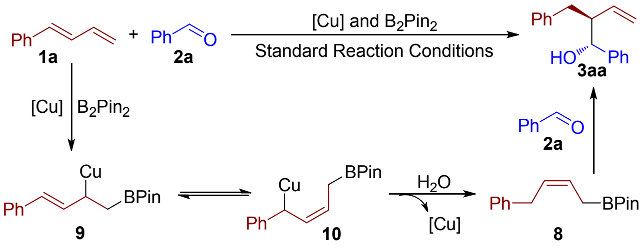
To test the feasibility of a large-scale reaction, the reaction of (*E*)-buta-1,3-dien-1-ylbenzene (**1a**) (11.5 mmol) and benzaldehyde (**2a**) (23 mmol) was investigated. The reaction could afford 2.0 g **3aa** (75% yield) with great diastereoselectivity (a, Scheme 2). The product of this chemistry, which installed terminal alkenyl group, is a kind of versatile intermediate for chemical synthesis. As shown in scheme 2, the product **3aa** could go through epoxidation reaction,[8] Heck reaction,[9] hydroboration-oxidation reaction[10] and radical coupling reaction[11] to afford the desired complex products smoothly (b, c, d and e, Scheme 2).

**Scheme 3**. Control experiments



To investigate the mechanism of this transformation, the control experiments were designed. Firstly, without benzaldehyde (**2a**), compound **8** could be separated with 96% yield (eq. 1, Scheme 3). This result suggested **8** should be the key intermediate of the present transformation. Furthermore, when it was put into the similar standard conditions, the desired product **3aa** was afforded with good yield (eq. 2, Scheme 3). A slight difference of the reaction system might affect the diastereoselectivity and yield, which exhibited the advantage of this one pot reaction strategy. The reaction of **1a** and **2a** was tested in the presence of $D_2O$, the D-labeled product could be detected (eq. 3, Scheme 3). This result could prove $H_2O$ is the stoichiometric H atom donor of Cu-catalyzed $B_2Pin_2$ mediated highly selective reductive transformation. Importantly, when *Z* and *E* version mixed buta-1,3-dien-1-ylbenzene was selected as starting material, this chemistry afforded as similar result as the example of **3aa** from table 1 (eq. 4, Scheme 3). This data suggested the isomerization process of allyl copper intermediate could be involved in this transformation. Furthermore, without copper-catalyst, **8** react with **2a** could afford **3aa** with good yield and diastereoselectivity (eq. 5, Scheme 3). This result suggested copper did not participate in this step of the reaction.

**Scheme 4**. The proposed reaction mechanisum.



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On the basis of the above control experiments, a proposed mechanism for the high selective reductive reaction was illustrated in Scheme 4. The first step of this reaction was the formation of the tautomer copper complex **9** and **10**.[4c, 4f, 12] The intermediate **10** reacted with water to give the intermediate **8**, which have been proved by the control experiment.[4f] Further reaction of **8** with benzaldehyde (**2a**) afforded the product **3aa**.[13]

In summary, we have demonstrated a novel Cu-catalyzed $B_2Pin_2$ mediate highly selective reductive functionalization of 1,3-diene using $H_2O$ as hydrogen donor. This practical chemistry could afford the terminal alkenyl group containing product with various substrate scopes, which is a kind of useful block for organic synthesis. Furthermore, this method could support gram-scale preparation without diminish diastereoselectivity. Further studies for synthetic applications are ongoing in our laboratory.

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## Conflicts of interest

The authors declare no competing financial interest.

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