Asymmetric Catalysis

Deutsche Ausgabe: DOI: 10.1002/ange.201600148
Internationale Ausgabe: DOI: 10.1002/anie.201600148

# Catalytic Enantioselective Assembly of Homoallylic Alcohols from Dienes, Aryldiazonium Salts, and Aldehydes

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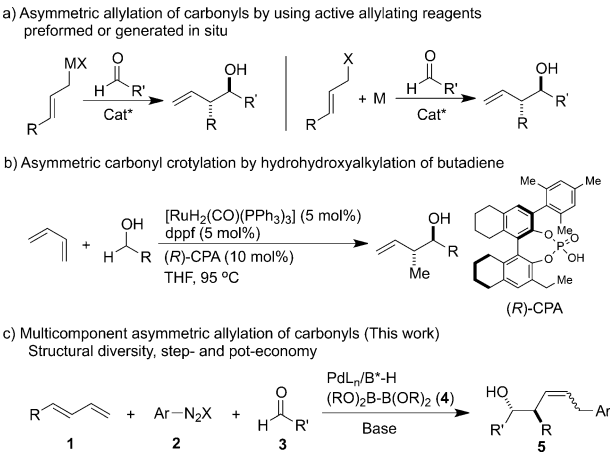
*Dedicated to Professor Yao-Zhong Jiang on the occasion of his 80th birthday*

***Abstract:*** *A highly selective multicomponent carbonyl allylation reaction of 1,3-butadienes, aryldiazonium tetrafluoroborates, and aldehydes has been established under the combined catalysis of palladium acetate and chiral anion phase transfer to render the favorable assembly of chiral Z-configured homoallylic alcohols in high yields and with excellent levels of enantioselectivity.*

Stereoselective carbonyl allylation represents one of the most useful classes of transformations, thus leading to homoallylic alcohols which can participate in a wide scope of transformations, occurring either at carbon–carbon double-bonds or hydroxy groups, to render them highly valuable intermediates in organic synthesis, in particular, in the total synthesis of natural products.[1] As such, the creation of new synthetic methods to access these molecules has long and continuously received widespread attention.[2–4] Traditionally, the most reliable methods rely on the stereoselective addition of allylic metal reagents to carbonyl groups, as demonstrated by many well-known and widely applicable reactions.[3] The carbonyl allylation reactions, based on the catalytic generation of either allylic metal species or umpolung process, have been promising alternatives (Scheme 1 a).[4] Recently, Krische and co-workers established a highly atom-economic C–H crotylation of primary alcohols by hydrohydroxyalkylation of butadiene enabled by a combined ruthenium(II) and chiral phosphoric acid catalysis (Scheme 1 b).[5] Very recently, we accomplished a highly stereoselective allylation of aldehydes with terminal alkenes based on allylic C–H activation enabled by combined palladium and Brønsted acid catalysis, albeit with moderate enantioselectivity.[6] Nowadays, the ideal synthesis, featuring the combination of step-, pot-, atom-economy, and increasing structural complexity from easily accessible starting materials, has been a target that synthetic chemists are continuously pursuing.[7] Multicomponent and domino reactions are actually among the most significant strategies which turn out to be very conceptually close to ideal synthesis.[8] However, the significance of either asymmetric multicomponent or domino processes for carbonyl allylation to access chiral homoallylic alcohols with high structural diversity has been much less recognized and hence they are highly desirable. Herein, we describe a highly regio- and stereoselective multicomponent carbonyl allylation reaction enabled by the combined catalysis[9] of a palladium complex and chiral anion phase transfer,[10,11] thus allowing for a highly efficient assembly of chiral homoallylic alcohols from easily accessible dienes, aryldiazonium salts, and aldehydes (Scheme 1 c).




***Scheme 1.*** General strategies for asymmetric carbonyl allylations. dppf = 1,1′-bis(diphenylphosphino)ferrocene, THF = tetrahydrofuran.

1,3-Butadiene and its derivatives are either bulk feedstock or easily accessible materials, which are versatile reagents capable of participating in a large number of fundamentally important and synthetically significant methodologies.[12] Very recently, Toste and co-workers showed that the chiral ion pair **2′** (Scheme 2), generated from a metathesis reaction of the insoluble aryldiazonium salt **2** and chiral phosphate salt by phase transfer (CAPT),[11] was able to undergo oxidative addition with the palladium(0) **A** species to give the chiral aryl palladium(II) phosphate **B**.[13] We and others previously found that the aryl palladium(II) species could undergo migratory insertion of a 1,3-diene to generate a π-allyl palladium intermediate.[14,15] Inspired by these leading findings, we envisioned that **B** would undergo a Heck insertion reaction with a 1,3-butadiene to form the chiral allylic palladium intermediate **C**, which could subsequently be

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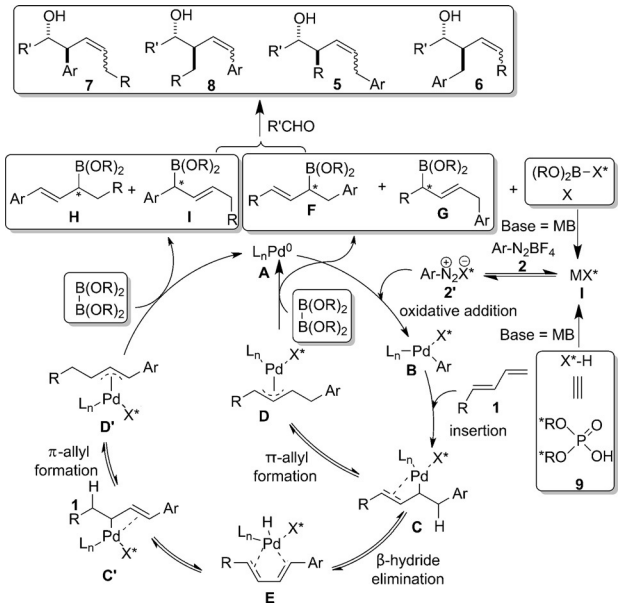
Supporting information for this article can be found under http://dx.doi.org/10.1002/anie.201600148.

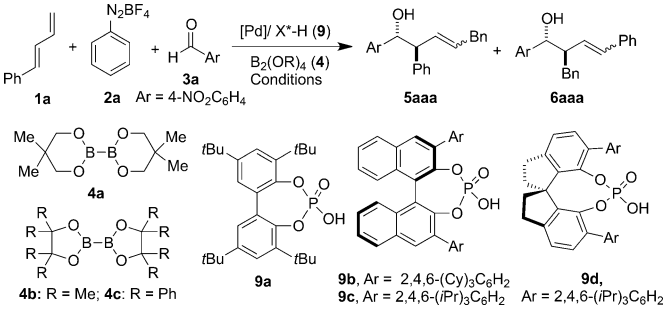



***Scheme 2.*** Mechanistic estimation of the multicomponent asymmetric carbonyl allylation reaction.

transformed into either the π-allyl palladium phosphate **D** or **D′**, as reported previously.[14] Both **D** and **D′** can principally undergo borylation with the diborate **4**,[6,16] thus theoretically leading to four different chiral allylboronates (**F**–**I**), which principally undergo an allylation reaction with aldehydes to give enantioenriched homoallylic alcohols (**5**–**8**; Scheme 2). However, since many isomers are principally generated, the control of the reaction to give a single product would bring formidable challenges to the proposed reaction.

In following up on the hypothesis, a multicomponent reaction of (*E*)-1-phenylbutadiene (**1a**) with phenyldiazonium tetrafluoroborate (**2a**), 4-nitrobenzaldehyde (**3a**), and a diborate **4** in the presence of catalytic amounts of $[Pd(dba)_2]$ and the achiral phosphoric acid **9a** was initially carried out in toluene with $NaHCO_3$ (Table 1, entry 1). Encouragingly, the proposed reaction was indeed able to successfully give the desired homoallylic alcohols **5aaa** and **6aaa**. However, with rather poor regio- and *Z*/*E*-selectivities (entry 1). Significantly, other regiomers were not observed. It has reported that the *Z*/*E* proportion of carbonyl allylation highly depends on the steric nature of diols attached to the α-substituted *E*-crotyl boronic esters,[17] thus the more stererically demanding diborates **4b** and **4c** were examined as borylation reagents, and indeed they led to enhanced regio- and *Z*/*E* selelectivities (entries 2 and 3). In particular, the bulkiest diborate **4c** resulted in a reaction to give **5aaa** in excellent regio- and *Z*/*E*-selectivities (entry 3). Then, the chiral phosphoric acids **9b–d** were evaluated to discover an asymmetric version of the multicomponent reaction. As anticipated, BINOL-based phosphoric acids indeed led to asymmetric induction albeit moderate (entries 4 and 5). In contrast, a SPINOL-derived Brønsted acid[18] turned out to be more promising and provided a much higher enantiomeric excess, and the regio- and *Z*/*E*-selectivities remained perfect (entry 6). Interestingly, the palladium complexes exerted considerable effect on

***Table 1:*** Optimization of reaction conditions.[a]




| Entry | 4 | X*-H | [Pd] | Base | Yield [%][b] | 5/6[c] | *Z*/*E*[d] | *ee* [%][e] |
|---|---|---|---|---|---|---|---|---|
| 1 | **4a** | **9a** | $[Pd(dba)_2]$ | $NaHCO_3$ | 70 | 1.3:1 | 1:2 | – |
| 2 | **4b** | **9a** | $[Pd(dba)_2]$ | $NaHCO_3$ | 90 | 2.7:1 | 1.7:1 | – |
| 3 | **4c** | **9a** | $[Pd(dba)_2]$ | $NaHCO_3$ | 99 | >20:1 | >20:1 | – |
| 4 | **4c** | **9b** | $[Pd(dba)_2]$ | $NaHCO_3$ | 99 | >20:1 | >20:1 | 52 |
| 5 | **4c** | **9c** | $[Pd(dba)_2]$ | $NaHCO_3$ | 99 | 17:1 | >20:1 | 54 |
| 6 | **4c** | **9d** | $[Pd(dba)_2]$ | $NaHCO_3$ | 99 | >20:1 | >20:1 | 82 |
| 7 | **4c** | **9d** | $Pd(OAc)_2$ | $NaHCO_3$ | 99 | >20:1 | >20:1 | 93 |
| 8 | **4c** | **9d** | $Pd(TFA)_2$ | $NaHCO_3$ | 99 | >20:1 | >20:1 | 65 |
| 9[f] | **4c** | **9d** | $Pd(OAc)_2$ | $NaHCO_3$ | 80 | 10:1 | >20:1 | 11 |
| 10[g] | **4c** | **9d** | $Pd(OAc)_2$ | $NaHCO_3$ | 96 | 13:1 | 13:1 | 81 |
| 11[h] | **4c** | **9d** | $Pd(OAc)_2$ | $NaHCO_3$ | 99 | >20:1 | >20:1 | 76 |
| 12[i] | **4c** | **9d** | $Pd(OAc)_2$ | $NaHCO_3$ | 99 | >20:1 | >20:1 | 92 |
| 13[j] | **4c** | **9d** | $Pd(OAc)_2$ | $NaHCO_3$ | 99 | >20:1 | >20:1 | 86 |
| 14 | **4c** | **9d** | $Pd(OAc)_2$ | $Li_2CO_3$ | 98 | 13:1 | >20:1 | 91 |
| 15 | **4c** | **9d** | $Pd(OAc)_2$ | $K_2CO_3$ | 74 | 9:1 | >20:1 | 87 |
| 16 | **4c** | **9d** | $Pd(OAc)_2$ | $K_3PO_4$ | 39 | 9:1 | >20:1 | 73 |

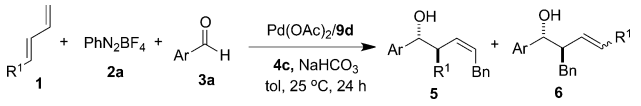
[a] Unless noted otherwise, the reaction of **1a** (0.12 mmol) with **2a** (0.12 mmol), **3a** (0.1 mmol), and **4** (0.12 mmol) was carried out with a palladium complex (0.01 mmol), **9** ( 0.01 mmol), and a base (0.2 mmol) in toluene (1.0 mL) at 25 °C for 24 h. [b] Yield of isolated product. [c] The ratio of **5aaa**/**6aaa** was determined by $^1$H NMR analysis of the crude reaction products (see Figure S1 in the Supporting Information) for details. [d] The ratio of (*Z*)-**5aaa**/(*E*)-**5aaa** was determined by $^1$H NMR analysis of the crude reaction mixture (see Figure S1). [e] The *ee* value of (*Z*)-**5aaa** was determined by HPLC analysis. [f] In THF. [g] In $Et_2O$. [h] In DCM. [i] In PhF. [j] In $PhCF_3$. dba = dibenzylidene acetone, DCM = dichloromethane, TFA = trifluoroacetate.

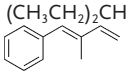
the stereoselectivity. For instance, in comparison with other palladium sources, $Pd(OAc)_2$ provided similar yields, regio- and *Z*/*E*-selectivities, but offered a much higher enantioselectivity, and thus appeared to be the best metal catalyst (entries 6–8). A general evaluation of solvents suggested that toluene was the most suitable reaction media (entry 7 versus 9–13). Both regio- and enantioselectivities are sensitive to the inorganic bases, among which $NaHCO_3$ led to the best results in terms of stereoselectivity (entries 14–16 versus 7).

With the optimal reaction conditions in hand, the substrate scope with regard to 1,3-butadiene derivatives was first probed by reactions with **2a** and **3a** (Table 2). Basically, the multicomponent arylborylation and carbonyl allylborylation cascade of aryl 1,3-butadienes proceeded successfully to generate homoallylic alcohols in excellent yields, and regio- and *Z*/*E*-selectivities, together with high levels of enantioselectivity (entries 1–9), whereas, the diene substrates bearing a phenyl group with a strong electron-withdrawing substituent at the *para*-position provided diminished *ee* values

***Table 2:*** Scope with respect to 1,3-butadienes.[a]




| Entry | 1 | $R^1$ | 5 | Yield [%][b] | 5/6[c] | Z/E[d] | ee [%][e] |
|---|---|---|---|---|---|---|---|
| 1[f] | **1b** | 1-naphthyl | **5baa** | 99 | >20:1 | >20:1 | 92 |
| 2 | **1c** | 2-naphthyl | **5caa** | 98 | >20:1 | >20:1 | 88 |
| 3 | **1d** | 2-$MeC_6H_4$ | **5daa** | 99 | >20:1 | >20:1 | 93 |
| 4 | **1e** | 3-$MeC_6H_4$ | **5eaa** | 99 | >20:1 | >20:1 | 89 |
| 5 | **1f** | 4-$MeC_6H_4$ | **5faa** | 97 | 19:1 | >20:1 | 93 |
| 6 | **1g** | 4-$MeOC_6H_4$ | **5gaa** | 99 | >20:1 | >20:1 | 92 |
| 7 | **1h** | 2-$FC_6H_4$ | **5haa** | 99 | >20:1 | >20:1 | 91 |
| 8 | **1i** | 4-$ClC_6H_4$ | **5iaa** | 99 | 16:1 | >20:1 | 93 |
| 9 | **1j** | 2-$BrC_6H_4$ | **5jaa** | 99 | >20:1 | >20:1 | 90 |
| 10[f] | **1k** | 4-$CO_2MeC_6H_4$ | **5kaa** | 99 | >20:1 | >20:1 | 84 |
| 11 | **1l** | 4-$CF_3C_6H_4$ | **5laa** | 63 | 12:1 | >20:1 | 85 |
| 12 | **1m** | cyclohexyl | **5maa** | 96 | >20:1 | >20:1 | 88 |
| 13 | **1n** | $(CH_3CH_2)_2CH$ | **5naa** | 74 | >20:1 | >20:1 | 88 |
| 14 | **1o** |  | **5oaa** | 99 | >20:1 | >20:1 | 86 |

[a] Reactions of **1** (0.12 mmol) with **2a** (0.12 mmol), **3a** (0.1 mmol) and **4c** (0.12 mmol) was carried out with $Pd(OAc)_2$ (0.01 mmol), **9d** (0.01 mmol), and $NaHCO_3$ (0.2 mmol) in toluene (1.0 mL) at 25 °C for 24 h. [b] Yield of isolated product. [c] The ratio of **5**/**6** was determined by $^1$H NMR analysis of the crude reaction mixture. [d] The ratio of (*Z*)-**5**/(*E*)-**5** was determined by $^1$H NMR analysis of the crude reaction mixture. [e] The *ee* value of (*Z*)-**5** was determined by HPLC analysis. [f] The *Z*/*E* ratio of **1** was about 1:1.

(entries 10 and 11). More significantly, the extension of the optimal reaction conditions to alkyl dienes led to a similarly successful reaction to afford the desired products in high yields with perfect regio- and *Z*/*E*-selectivity, and good enantioselectivities (entries 12 and 13). Notably, the C3-substituted diene **1o** was also able to provide an almost perfect yield as well as regio- and *Z*/*E*-selectivities, albeit with a relatively lower enantioselectivity (entry 14). The configuration of **5jaa** was assigned by X-ray analysis (see the Supporting Information).

The generality for aryldiazonium tetrafluoroborates was then investigated (Table 3). A broad scope of aryldiazonium derivatives was tolerated. High regio- and *Z*/*E*-selectivities were obtained for most of 4-substituted aryldiazonium salts investigated, with the exception of 4-methoxybenzenediazonium tetrafluoroborate (entries 1–4 and 6–10 versus 5). However, the reaction conversion was considerably influenced by the electronic nature of the substituent (entries 1–10). For instance, considerably lower yields were observed for the cases involving aryldiazonium salts bearing highly electron-deficient phenyl groups (entries 8–10). In addition, the substitution pattern had some impact on the selectivities, as found in cases involving 2-, 3- and 4-acetylbenzenediazonium tetrafluoroborates (**2h**, **2l** and **2m**; entries 7, 11, and 12). The configuration of **5aga** was again assigned by X-ray analysis (see the Supporting Information).

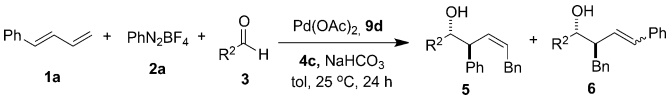
The substrate scope of the multicomponent reaction with respect to aldehydes was finally explored (Table 4). A wide spectrum of aldehydes turned out to be excellent substrates

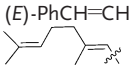
***Table 3:*** Scope with respect to aryldiazonium tetrafluoroborates.[a]


| Entry | 2 | $Ar^1$ | 5 | Yield [%][b] | 5/6[c] | Z/E[d] | ee [%][e] |
|---|---|---|---|---|---|---|---|
| 1 | **2b** | 4-$FC_6H_4$ | **5aba** | 99 | >20:1 | >20:1 | 91 |
| 2 | **2c** | 4-$ClC_6H_4$ | **5aca** | 99 | >20:1 | >20:1 | 90 |
| 3 | **2d** | 4-$BrC_6H_4$ | **5ada** | 91 | >20:1 | >20:1 | 89 |
| 4 | **2e** | 4-$MeC_6H_4$ | **5aea** | 97 | >20:1 | >20:1 | 90 |
| 5 | **2f** | 4-$MeOC_6H_4$ | **5afa** | 99 | 17:1 | 19:1 | 87 |
| 6 | **2g** | 4-$CO_2EtC_6H_4$ | **5aga** | 99 | >20:1 | >20:1 | 90 |
| 7 | **2h** | 4-$AcC_6H_4$ | **5aha** | 94 | >20:1 | >20:1 | 92 |
| 8 | **2i** | 4-$CF_3C_6H_4$ | **5aia** | 40 | >20:1 | >20:1 | 90 |
| 9 | **2j** | 4-$CNC_6H_4$ | **5aja** | 68 | >20:1 | >20:1 | 89 |
| 10 | **2k** | 4-$NO_2C_6H_4$ | **5aka** | 64 | >20:1 | >20:1 | 88 |
| 11 | **2l** | 2-$AcC_6H_4$ | **5ala** | 90 | >20:1 | >20:1 | 94 |
| 12 | **2m** | 3-$AcC_6H_4$ | **5ama** | 98 | 19:1 | 18:1 | 85 |

[a] The reactions were carried out with **1a** (0.12 mmol), **2** (0.12 mmol), **3a** (0.1 mmol), **4c** (0.12 mmol), $Pd(OAc)_2$ (0.01 mmol), **9d** (0.01 mmol), $NaHCO_3$ (0.2 mmol) in toluene (1.0 mL) at 25 °C for 24 h. [b] Isolated yield. [c] The ratio of **5**/**6** was determined by $^1$H NMR analysis of the crude reaction mixture. [d] The ratio of (*Z*)-**5**/(*E*)-**5** was determined by $^1$H NMR analysis of the crude reaction mixture. [e] The *ee* value of (*Z*)-**5** was determined by HPLC analysis.

***Table 4:*** Scope with respect to aldehydes.[a]




| Entry | 3 | $R^2$ | 5 | Yield [%][b] | 5/6[c] | Z/E[d] | ee [%][e] |
|---|---|---|---|---|---|---|---|
| 1 | **3b** | $C_6H_5$ | **5aab** | 99 | >20:1 | >20:1 | 90 |
| 2 | **3c** | 4-$MeOC_6H_4$ | **5aac** | 86 | >20:1 | >20:1 | 93 |
| 3 | **3d** | 2-furanyl | **5aad** | 99 | >20:1 | >20:1 | 92 |
| 4 | **3e** | 2-thienyl | **5aae** | 95 | >20:1 | >20:1 | 92 |
| 5 | **3f** | (*E*)-PhCH=CH | **5aaf** | 99 | >20:1 | >20:1 | 93 |
| 6 | **3g** |  | **5aag** | 98 | >20:1 | >20:1 | 93 |
| 7 | **3h** | cyclohexyl | **5aah** | 99 | >20:1 | >20:1 | 92 |
| 8 | **3i** | $PhCH_2CH_2$ | **5aai** | 99 | >20:1 | >20:1 | 93 |
| 9 | **3j** | $TBSOCH_2CH_2$ | **5aaj** | 93 | >20:1 | >20:1 | 92 |
| 10[f] | **3k** | $BocNHCH_2$ | **5aak** | 99 | >20:1 | >20:1 | 94 |
| 11[f] | **3l** | $BnOCH_2$ | **5aal** | 81 | >20:1 | >20:1 | 94 |
| 12[f] | **3m** | $CO_2Et$ | **5aam** | 93 | >20:1 | >20:1 | 92 |

[a] Unless noted otherwise, reactions were carried out with **1a** (0.12 mmol), **2a** (0.12 mmol), **3** (0.1 mmol), **4c** (0.12 mmol), $Pd(OAc)_2$ (0.01 mmol), **9d** (0.01 mmol), and $NaHCO_3$ (0.2 mmol) in toluene (1.0 mL) at 25 °C for 24 h. [b] Yield of isolated product. [c] The ratio of **5**/**6** was determined by $^1$H NMR analysis of the crude reaction mixture. [d] The ratio of (*Z*)-**5**/(*E*)-**5** was determined by $^1$H- NMR analysis of the crude reaction mixture. [e] The *ee* value of (*Z*)-**5** was determined by HPLC analysis. [f] Aldehyde was added after the mixture was stirred for 24 h, and then stirred for another 24 h. Boc = *tert*-butoxycarbonyl, TBS = *tert*-butyldimethylsilyl.

for undergoing clean reactions and to give homoallylic alcohols in very high yields and with excellent levels of regio-, enantio-, and *Z*/*E*-selectivities. For aromatic alde-

hydes, the installation of substituents or heteroatoms on the aryl group was allowed, thus resulting in high yields and excellent selectivities (entries 1–4). Notably, the successful multicomponent reaction of unsaturated aldehydes proceeded with excellent results (entries 5 and 6). More significantly, aliphatic aldehydes performed well in the reaction (entries 7–12). In particular, the introduction of different functionalities to the aliphatic aldehydes was nicely accommodated and yielded multiply functionalized chiral homoallylic alcohols with excellent selectivities (entries 9–12). Definitely, the densely functionalized homoallylic alcohols provide an opportunity for structural modifications in organic synthesis.

In conclusion, we have established a highly regio- and enantioselective multicomponent reaction of 1,3-butadienes, aryldiazonium tetrafluoroborates, and aldehydes in the presence of octaphenyl-2,2′-bi(1,3,2-dioxaborolane), thus favoring the generation of *Z*-configured homoallylic alcohols in high yields, by using a combined palladium and chiral anion phase-transfer catalysis, wherein the phosphoric acid is sole chiral element to control the stereoselectivity. The protocol tolerates a wide range of substrates and therefore provides an efficient method to access enantioenriched homoallylic alcohols with high structural diversity. It also features both step- and pot-economy. More importantly, the concept presented herein points to a new strategy for asymmetric functionalization of 1,3-dienes.

## Acknowledgements

We are grateful for financial support from MOST (973 project 2015CB856600), NSFC (21232007), and SRG-HSC (2015SRG-HSC044).

**Keywords:** allylic compounds · asymmetric catalysis · multicomponent reactions · palladium · phase-transfer catalysis

**How to cite:** *Angew. Chem. Int. Ed.* **2016**, *55*, 4322–4326
*Angew. Chem.* **2016**, *128*, 4394–4398

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Received: January 6, 2016
Published online: February 25, 2016

  