Asymmetric Catalysis

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Highly Diastereo- and Enantioselective Cu-Catalyzed Borylative Coupling of 1,3-Dienes and Aldimines

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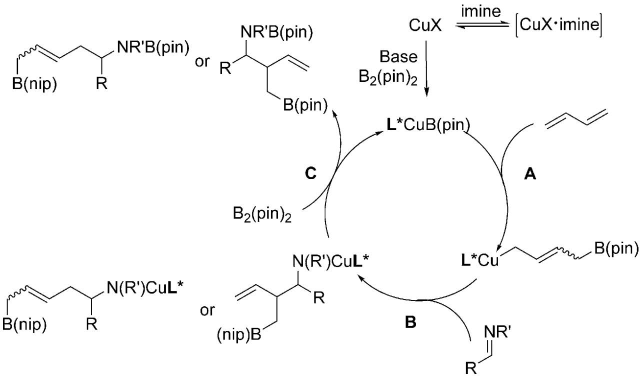
Dedicated to Professor Yaozhong Jiang on the occasion of his 80th birthday

Abstract: *A Cu-catalyzed diastereo- and enantioselective borylative coupling reaction of 1,3-dienes with imines was realized. Branched homoallylic amines are readily prepared in a syn-selective manner with high regio-, diastereo- and enantioselectivity. Moreover, these three-component coupling reactions feature good functional-group compatibility and easy access to the substrates and catalyst.*

Asymmetric allylation reactions[1] of imines have received increasing interests from the synthesis community[2] because enantioenriched homoallylic amine products are useful building blocks in organic synthesis and medicinal chemistry.[3] Copper catalysis is an efficient approach to promote the enantioselective addition of terminal allyl transmetalation reagents (e.g., with B, Si, and Sn) to imines,[4] however, Cu-catalyzed asymmetric, nucleophilic addition to imines with functionalized (e.g., γ-substituted) allyl metal reagents remain challenging. This is probably due to inefficiency of the transmetalation event arising from increased steric hindrance, the weak electrophilicity/reactivity of imines, and/or difficulties in predicting the regio- and stereochemical outcome of additions. New and efficient approaches to generating and utilizing functionalized allyl metal reagents in the presence of a copper catalyst hold promise for accessing complex homoallylic amines, and these methods will expand the application of catalytic asymmetric allylation chemistry.

Since the seminal work of borylcopper catalysis reported by the Ito[5] and the Miyaura[6] groups, Cu-catalyzed borylative coupling reactions have been recognized as an important method for generating boron-containing organocopper species in situ from an unsaturated hydrocarbon.[7] In this context, Hoveyda pioneered the use of boron-functional allylcopper intermediates in enantioselective allylation of aldehydes/ketones,[7f] allylic esters,[7i] and enoates.[7k] However, Cu-catalyzed borylative coupling of unsaturated hydrocarbon substrates and imines is less developed.[8] Conjugated dienes and especially 1,3-dienes, as a common feedstock, are ideal nucleophilic allyl metal precursors[9] and readily participate in allylic transformations of carbonyls and imines.[10] We envisioned merging the borylcupration of a conjugated diene[11] (Scheme 1, step A) and enantioselective imine allylation (Scheme 1, step B) in the presence of a suitable chiral copper catalyst. This approach could afford useful homoallylic amines containing an easily derivatizable boron motif. In this method, possible complications include the undesired borylation of imines,[12] poisoning of the metal catalyst by imines or products, and difficulty in controlling the regio- (linear vs. branched products)[7k,11a] and stereoselectivity (enantio- and/or diastereoselectivity).



Scheme 1. Cu-catalyzed borylative coupling of conjugated dienes and imines.

To test the feasibility of our proposed transformation, we chose a complex of CuCl and chiral sulfoxide-phophine (SOP, **L1**)[7j] as a catalyst in preliminary experiments. In the presence of isoprene (5 equiv), 1.5 equiv of $B_2(pin)_2$, and NaOtBu (40 mol %) as base, allylation of several imines (**3**–**7a** but not *N*-Boc imine **2**) proceeded smoothly to provide branched homoallylic amines. Interestingly, we found that the diastereoselectivity of the reaction increases with the bulkiness of the protecting groups on the imines (Ms < Ts < PMP < OMP < Dpp, Table 1, entries 2–6). With *N*-diphenylphosphinoyl (Dpp) as the protecting group, the homoallylic amine **8aa** was produced with 90:10 d.r., while the enantioselectivity was not satisfactory with our SOP ligand **L1** (Table 1, entry 6). We then turned our attention to commercially available chiral ligands. To our delight, (*R*)-BINAP (**L2**) gave **8aa** in 89 % *ee* and 86:14 d.r. (Table 1, entry 7). The observed selectivity

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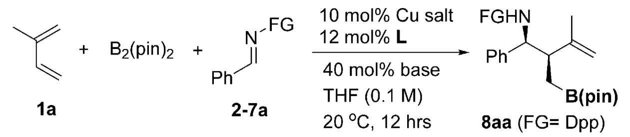
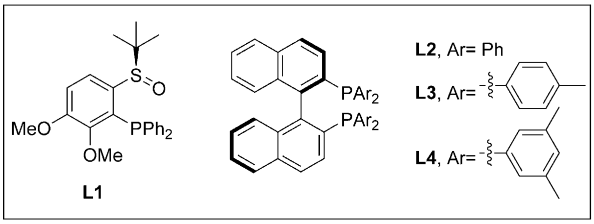
Table 1: Enantioselective borylative aminoalkylation of isoprene[a]

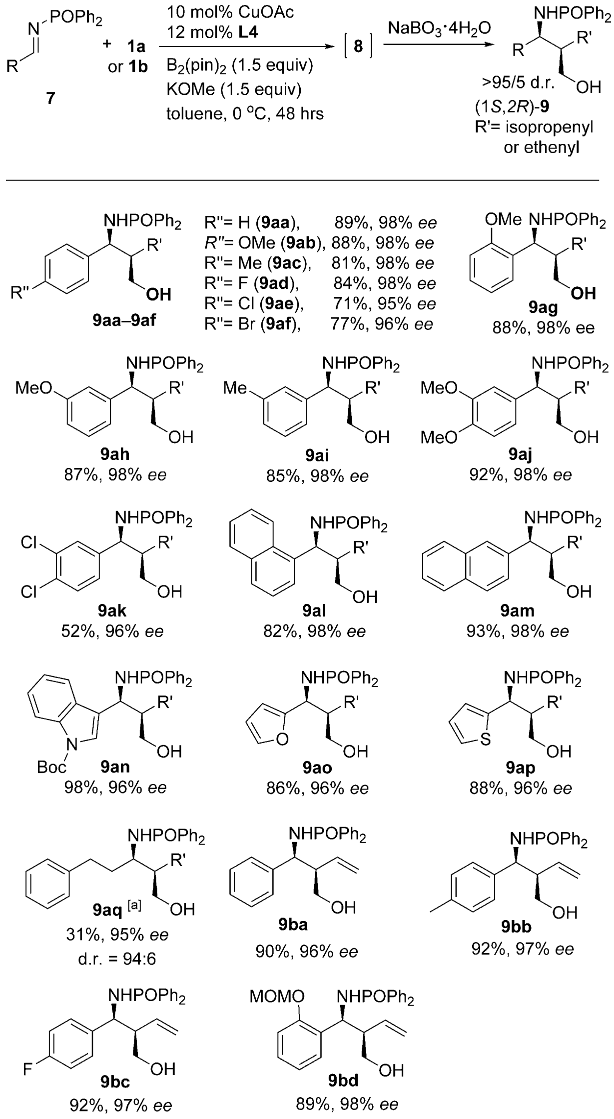


FG= Boc(2), Ms(3),Ts(4), PMP(5), OMP(6) and POPh$_2$(7a)



Entry	Imine	L	Copper salt + base	d.r.[b]	Yield[b]/ee[c] [%/%]
1	**2**	**L1**	CuCl + NaO^{t}Bu	–	0/–
2	**3**	**L1**	CuCl + NaO^{t}Bu	52:48	71/–
3	**4**	**L1**	CuCl + NaO^{t}Bu	57:43	70/–
4	**5**	**L1**	CuCl + NaO^{t}Bu	67:33	85/–
5	**6**	**L1**	CuCl + NaO^{t}Bu	73:27	76/–
6	**7a**	**L1**	CuCl + NaO^{t}Bu	90:10	95/23
7	**7a**	**L2**	CuCl + NaO^{t}Bu	86:14	72/89
8	**7a**	**L3**	CuCl + NaO^{t}Bu	89:11	89/93
9	**7a**	**L4**	CuCl + NaO^{t}Bu	93:7	87/94
10[d]	**7a**	**L4**	CuOAc + NaO^{t}Bu	96:4	92/95
11[d,e]	**7a**	**L4**	CuOAc + KOMe	96:4	98/97
12[e,f]	**7a**	**L4**	CuOAc + KOMe	98:2	98(40)/98

[a] The reaction was carried out with **1a** (1.0 mmol), imine (0.2 mmol), and B$_2$(pin)$_2$ (0.3 mmol) in THF (2 mL). [b] Determined by ^{1}H NMR spectroscopy. [c] The enantiomeric excess was determined by HPLC analysis of the oxidized product **9aa** (for details, see the Supporting Information). [d] Reacted for 17 h. [e] Toluene as the solvent. [f] In the presence of 1.5 equiv of KOMe (0.3 mmol) at 0 °C for 48 h. The yield of isolated **8aa** is shown in parentheses. PMP = *p*-methoxylphenyl, OMP = *o*-methoxylphenyl.



Scheme 2. Scope with respect to the aldmines. The reaction was performed with isoprene or 1,3-butadiene (1.0 mmol), imine (0.2 mmol), and B$_2$(pin)$_2$ (0.3 mmol), the diastereoselectivity was determined by ^{1}H NMR analysis of the crude product. Yields of isolated product are shown. The *ee* values were determined by HPLC analysis. [a] The reaction was performed in the presence of 20 mol% of MeOK at 25 °C.

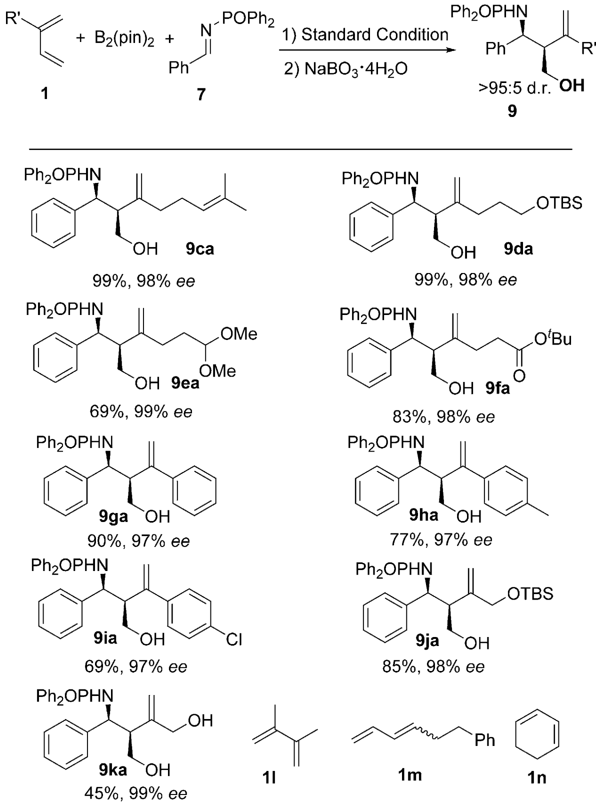
values were enhanced when the more bulky biphosphine ligands (*R*)-Tol-BINAP (**L3**; 93 % *ee*, 89:11 d.r.) and (*R*)-DM-BINAP (**L4**; 94 % *ee*, 93:7 d.r.) were employed (Table 1, entries 8 and 9; for other chiral ligands screened, see the Supporting Information.) The selectivity profiles and reaction efficiency were further improved by using CuOAc as the copper source (entry 10), KOMe as the base, and toluene as the solvent (entry 11). Excellent yields and selectivity were achieved by lowering the reaction temperature to 0 °C and increasing the KOMe loading to 1.5 equiv (entry 12).

With optimized reaction conditions in hand, the scope with respect to the imine partners was first investigated. The isolated yields and *ee* values of the three-component reaction products were measured following oxidation to the γ-hydroxy branched amines **9**.[13] As shown in Scheme 2, an array of Dpp-protected aryl and heteroaryl aldimines react with isoprene under the reaction conditions, and homoallylic amines were obtained with good to excellent *ee* (95–98 %) and excellent d.r. (> 95:5). The electronic and steric properties of the aryl substituents on the imine partner have little effect on the observed selectivity of the reaction but a pronounced impact on the reactivity. For example, arylimines with *para*- or *meta*-methyl, methoxy, or fluorine substituents gave good yields (81–88 %), and *o*-methoxylphenyl aldimine (the product **9ag**) also showed high reactivity. On the other hand, those with electron-withdrawing substituents gave comparatively lower yields of products (71 % for *p*-Cl and 77 % for *p*-Br), and the use of 3,4-dichlorophenyl imine gave **9ak** in only 52 % yield. Electron-rich imines apparently display higher reactivity, probably owing to facile coordination to the allylic copper intermediate, which accelerates the allylation process. Indeed, the tested electron-rich 3,4-dimethoxyl phenyl, indolyl, furyl, and thienyl substrates all gave high yields (86–98 %) and excellent *ee* (96–98 %). Alkyl aldimines were also examined and were found to decompose under the standard reaction conditions.

Nonetheless, 3-phenylpropionaldimine reacted to give **9aq** in moderate yield with high diastereo- and enantioselectivity when we decreased the amount of base (20 mol%) and increased the reaction temperature (25 °C).

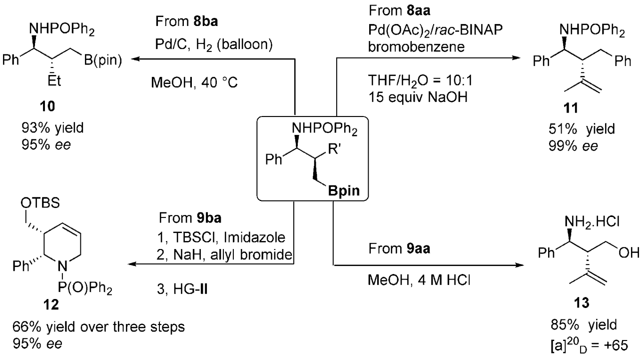
The borylative coupling of the parent 1,3-butadiene (**1b**) and aryl aldimines was also investigated (Scheme 2). Homoallylic amines (**9ba**–**9bd**) were obtained in high yields (89–92%) with excellent *ee* (96–98%) and diastereoselectivity (> 95:5). The absolute configuration of **9ba** was confirmed by X-ray diffraction analysis[14] and the borylative coupling products are accordingly assigned as the (1*S*,2*R*)-configuration resulting from a *syn*-addition event.

This three-component coupling reaction is also effective for an array of 2-substituted 1,3-dienes (Scheme 3). For example, myrcene (**1c**) and its derivatives (**1d**–**1f**) were quite reactive and afforded **9ca**–**9fa** with excellent enantiomeric excess. 2-Aromatic dienes also reacted smoothly (**9ga**–**9ia**). Notably, this reaction is also tolerant of heteroatom-containing functional groups [CH_2OTBS and CH_2B(pin)], albeit with lower yields in some cases (**9ja** and **9ka**). However, 2,3-dimethyl butadiene (**1l**) and non-terminal conjugated dienes (**1m** and **1n**) did not afford the desired three-component adducts but rather hydroboration products,[11] probably due to the low reactivity of the corresponding borylcopper species to imines.



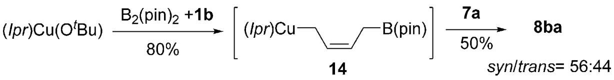
Scheme 3. Scope with respect to the conjugated dienes. The reaction was performed with isoprene (1.0 mmol), **7a** (0.2 mmol), and $B_2(pin)_2$ (0.3 mmol), and the diastereoselectivity was determined by ^1H NMR analysis of the crude product. Yields of isolated product are shown. The *ee* values were determined by HPLC analysis.

To demonstrate the versatility and potential of this method, several transformations of enantioenriched B(pin)- or hydroxy-funtionalized homoallylic amines were performed to access more complex building blocks (Scheme 4). For example, the Pd/C-catalyzed hydrogenation of **8ba** afforded γ-aminoboronic ester **10** in high yield without any loss of *ee* or d.r.. The selective transformation of the C−B bond in **8aa** by Suzuki–Miyaura coupling was also implemented to give branched homoallylic amine **11**. Other transformations, namely N-allylation and ring-closing metathesis (RCM), allowed the construction of chiral tetrahydropyridine **12**[15] with a high level of optical purity. Furthermore, the N-Dpp group of the hydroxy homoallylic amine (**9aa**) was easily removed under mild conditions. These derivatization processes demonstrate the promise of this method in organic synthesis.



Scheme 4. Further transformation of the products.

We performed studies to probe the mechanism and rationalize the stereochemical outcome of this three-component reaction. Our initial attempt to prepare the corresponding (BINAP)Cu−allyl intermediate from 1,3-diene was unfruitful. Considering that N-heterocyclic carbenes (NHC) are effective ligands for stabilizing the Cu−Bpin species [16] and the corresponding adducts with styrene [17] and allene,[11b] we decided to make NHC-ligated allylcopper species [(NHC)Cu−allyl] from 1,3-diene. Fortunately, when exposing butadiene to a mixture of (Ipr)Cu(O^{t}Bu) and $B_2(pin)_2$, σ-allylcopper complex **14** was isolated and the olefinic configuration was confirmed as *Z* by analysis of the coupling constant of the two olefinic hydrogens[18] [$J_3 \approx 10$ Hz, Eq. (1)].



(1)

Allyllation of imine **7a** with **14** afforded the *syn* product (**8ba**) in moderate d.r. (56:44),[19] and this selectivity is consistent with the catalytic reaction (see the Supporting Information). Thus, the formal 1,4-migratory insertion of 1,3-dienes into borylcopper should release the (*Z*)-allylcopper species.[20] In the imine allylation event, a closed 6-centered transition structure could possibly be formed. In N-Dpp (*E*)-imine allylation, the observed excellent *syn* selectivity might arise from an unusual boat-like transition state,[21] where the steric repulsion between bulky *N*-diphenylphosphinoyl group and the γ-substituent group [e.g., -CH_2B(pin)] of the allylcopper complex is avoided, although chair-like transition states that involve the participation of Z-conformed imine[20b] or the coordination of phosphinoyl oxygen to Lewis acidic Cu[4b] could not be excluded. Moreover, a boat-like stereochemical model based on analysis of the X-ray crystal structures of Cu^I–(*R*)-BINAP complexes[22] is proposed to account for the observed enantioselectivity, wherein the *N*-diphenylphosphinoyl group resides far away from either of the axial P-aryl groups of (*R*)-DM-BINAP. (Figure 1) This model can also explain the positive effects of the steric hindrance from the N-protecting group of the imines and P-aryl groups of the BINAPs on the stereochemical outcome (see Table 1, entries 2–10).

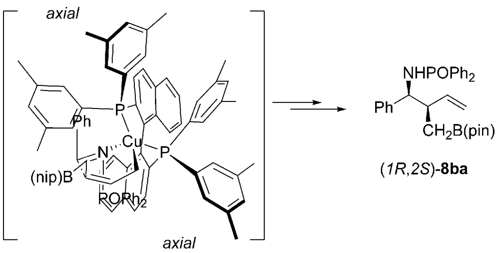


Figure 1. A model for the stereochemical outcome of the Cu-catalyzed enantioselective borylative coupling of butadiene (**1b**) and *N*-Dpp imine (**7a**).

In summary, a highly diatereo- and enantioselective borylative coupling reaction of 1,3-dienes and *N*-Dpp aldimines was realized by using a simple chiral biphosphine/copper catalyst. The favored *syn* selectivity, unlike that found for the borylative coupling of allenes and imines, is unexpectedly observed. Transition-state models were proposed to rationalize the enantio- and diastereoselectivity. This three-component coupling reaction represents a useful method for the asymmetric allylation of imines. More detailed mechanistic studies and applications to the preparation of biologically relevant target molecules are underway.

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Keywords: 1,3-dienes · asymmetric catalysis · borylative coupling · copper · imines

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[14] CCDC 1500573 (**9ba**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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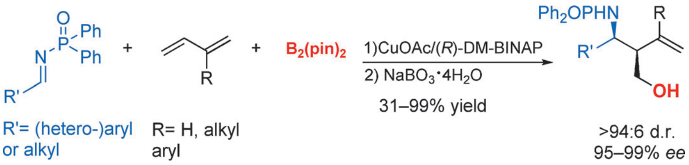
Communications

Asymmetric Catalysis



A multitude of *syns*: A Cu-catalyzed borylative coupling reaction of 1,3-dienes with imines was realized. Branched homoallylic amines are readily prepared in a *syn*-selective manner with high regio-, diastereo- and enantioselectivity. Moreover, these three-component coupling reactions feature good functional-group compatibility and easy access to the substrates and catalyst.