Enantioselective Synthesis of Homoallylic Amines through Reactions of (Pinacolato)allylborons with Aryl-, Heteroaryl-, Alkyl- or Alkene-Substituted Aldimines Catalyzed by Chiral *C*₁-Symmetric NHC–Cu Complexes

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Abstract

A catalytic method for enantioselective synthesis of homoallylamides through Cu-catalyzed reactions of stable and easily accessible (pinacolato)allylborons with aryl-, heteroaryl-,alkyl- or alkenyl-substituted *N*-phosphinoylimines is disclosed. Transformations are promoted by 1–5 mol % of readily accessible NHC–Cu complexes, derived from *C*₁-symmetric imidazolinium salts, which can be prepared in multi-gram quantities in four steps from commercially available materials. Allyl additions deliver the desired products in up to quantitative yield and 98.5:1.5 enantiomeric ratio and are amenable to gram-scale operations. A mechanistic model accounting for the observed selectivity levels and trends is proposed.

Homoallylic amines are imbedded within structures of many biologically active agents and can serve as entities for preparation of myriad N-containing molecules.[1,2] Development of efficient and enantioselective allyl additions to aldimines, a direct approach for accessing chiral homoallylic amines, is thus a compelling objective in chemical synthesis. Enantiomerically pure allyl-containing reagents, used in stoichiometric quantities, react efficiently and diastereoselectively with aldimines; the utility of these strategies has been demonstrated in complex molecule synthesis.[3] Substrates containing a chiral auxiliary can participate in highly diastereoselective allyl additions.[4] Such an approach, however, requires especially reactive allylmetals (e.g., Grignard reagents[4a] or allylzincs[4g]) that could be intolerant of a number of key functional groups and/or preparation of which might be complicated; alternatively, stoichiometric quantities of costly allylindiums[4b–f] and/or Pd-based catalysts are needed.[4b,e] Several notable reports have demonstrated that chiral catalysts promote additions of allyl groups to aldimines.[5,6,7,8] Nonetheless, such protocols also demand precious indium salts (at times in stoichiometric amounts or more)[6] or require allyl reagents that are highly toxic[8a] or relatively unstable (so that high reactivity is achieved);[7b] some reported catalytic enantioselective approaches are operative with imines derived from activated aldehydes (e.g., glyoxylates)[5–7] or furnish products that necessitate somewhat harsh or costly conditions for conversion to the unprotected amine.[5–8] A reasonably general, cost effective and functional group tolerant catalytic enantioselective process thus remains lacking. We wish to outline a method for synthesis of enantiomerically enriched homoallylamides by reactions of stable allylboron reagents that can either be

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purchased or easily prepared. Transformations are performed with an inexpensive Cu salt and 1–5 mol % of chiral C_1-symmetric imidazolinium salts,[9] multi-gram quantities of which can be synthesized from commercially available materials by a straightforward four- to five-vessel protocol (~30% overall yield). Complete conversion is observed in 6–18 hours; the desired products are isolated in 61% to >98% yield and in up to 98.5:1.5 enantiomer ratio (er). Conversion of the resulting N-phosphinoylamides to the derived amines can be effected under aqueous acidic conditions, as amply demonstrated previously.[10]

The present investigations were conceived as a result of our interest in designing catalytic transformations promoted by N-heterocyclic carbene (NHC) copper complexes generated in situ by initial reaction with a boron-based reagent.[9b–c][11] We surmised that reaction of Cu-alkoxide **i** with (pinacolato)allylboron **1** should afford NHC–Cu-allyl **ii** (Scheme 1), a process driven by the formation of the energetically favorable B–O bond. We have previously adopted a similar strategy with B–B[11] and B–Si[9b] reagents to generate NHC–Cu–B complexes or the corresponding silanes, which participate in enantioselective C–B or C–Si bond forming reactions. We sought to examine whether the above approach might be utilized such that the B–C bond reacts with an NHC–Cu-alkoxide to yield a catalytically active NHC–Cu–C system (vs NHC–Cu–B or NHC–Cu–Si).[12] The resulting NHC–Cu–allyl **ii** could undergo reaction with an N-phosphinoylimine to initiate C–C bond formation, furnishing **iii**. Catalyst release might occur either by σ-bond metathesis between Cu–O bond of **iii** and the C–B of another molecule of **1** to generate the boronic ester derivative of the desired product,[13] or through the agency of an alcohol additive.[14]

To probe the feasibility of the envisioned catalytic cycle, we investigated the ability of various chiral NHC–Cu complexes to catalyze the reaction of **7a** and **1** (Table 1). Catalysts were formed and utilized in situ by treatment of the corresponding imidazolinium salts with NaO*t*-Bu and CuCl; MeOH filled the role of a proton source. Bidentate Cu complexes derived from phenol **2** or sulfonate **3** (entries 1–2, Table 1) readily promote transformation but deliver **8a** with minimal stereoselectivity. Similarly high efficiency and inferior enantioselectivity is obtained with C_2-symmteric **4a**–**4b** (entries 3–4). Enantiomeric purity is improved when C_1-symmetric NHC–Cu complexes derived from **5a**–**5c** or **6a** serve as catalysts (entries 5–8).

However, it is through the use of **6b** (entry 9, Table 1), bearing an *o*-substituted mesitylphenyl as its dissymmetric N-aryl group that, without any diminution in efficiency (>98% conv), significantly improved er is achieved (91:9 er). Incorporation of a *m*-isopropyl unit, beneficial in certain previous studies (**6c**, entry 10),[9b] does not enhance selectivity. Performing the reaction with 1.4 equivalents of **1** at −50 °C, under otherwise identical conditions, delivers **8a** in 95% yield and 97:3 er (entry 1, Table 2).

A variety of aryl-substituted substrates can be used; the resulting homoallylamides are isolated in 88% to >98% yield and 96:4–98.5:1.5 er (Table 2). Electron-deficient aldimines (entries 3–4, 7–10) as well as those containing an electron-donating substituent (entries 6 and 11), undergo facile transformation to afford products in ≥97:3 er. In the case of sterically congested aldimines **7b**, **7e**–**f** (entries 2, 5–6) and **7k**, the latter of which contains a *p*-methoxyphenyl unit (entry 11), higher enantioselectivity is achieved with the NHC–Cu complex derived from **6d** [**7b**, **7e**–**f** and **7k** in 84:16–87.5:12.5 er (>98% conv) with **6b**]. The catalytic protocol can also be performed with aldimines bearing a heteroaromatic unit (**9**–**11**, Scheme 2).

Similar to **6b**, **6d** is C_1-symmetric but bears two dissymmetric N-Ar units, existing as a 5:1 mixture of stereoisomers in solution (determined by analysis of 400 MHz ^{1}H NMR); imidazolinium salt **6d** is used as a mixture of isomers. The X-ray structure of the major

isomer of **6d** is shown in Figure 1; the same conformer is predominant in solution, as established by nOe experiments.[15] Whether both of the derived NHC–Cu complexes promote reaction and the facility with which the two stereoisomers undergo inter-conversion (after complexation) is unclear.[16]

A difficult class of substrates consists of alkyl-substituted N-imines,[5–8,17] which can be converted to the derived homoallylic amines in high enantiomeric purity (**13**–**16**, Scheme 3). Contrary to aldimines that bear a linear (e.g., **13** in 97:3 er) or *β*-branched (e.g., **14** in 96:4 er) group, enantioselectivity is diminished with an α-substituted alkyl unit (cf. **15** in 81:19 er). The highly enantioselective generation of diene **16** with the Cu complex derived from **6d** demonstrates that enal-derived aldimines are suitable substrates as well (85:15 er and >98% conv with **6b**).

Another class of allyl-containing agents that has received less attention in catalytic enantioselective imine additions is 2-substituted allylboronates such as methyl- and phenyl-containing **17a**–**b** (eq 1).[5,8a,18] Cu-catalyzed reactions are promoted, albeitwith higher catalyst loading and longer reaction times (5.0 mol % **6d** or **6b**), to deliver **18a** and **18b** in 96% and 91% yield and 95:5 and 91:9 er, respectively.[19] Transformations with *E*- or *Z*-crotylborons proceed efficiently and with appreciable enantioselectivity (85:15–90:10 er) but diastereoselectivities are low (~60:40 dr). Development of more stereoselective NHC–Cu-catalyzed variants with this latter set of B-based reagents is an objective of our future studies.
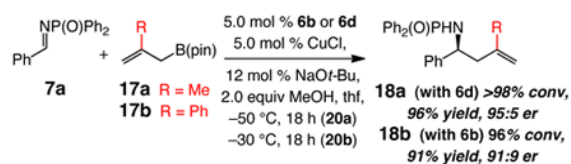
(1)

As shown in eq 2, the enantioselective Cu-catalyzed transformation can be performed on reasonable laboratory scale (1.0 g) with only 1.0 mol % of the chiral catalyst. In the case of homoallylamide **8a**, material of high enantiomeric purity (97.5:2.5 er) is isolated in 75% yield by simple filtration without resorting to silica gel chromatography.
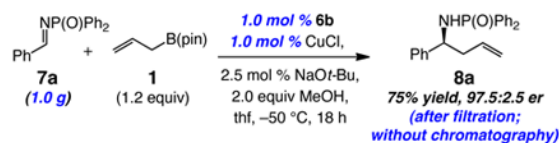
(2)

Several mechanistic issues merit a brief discussion. There is <5% conversion in the absence of MeOH under catalytic conditions. With stoichiometric amounts of the NHC–Cu complex, the desired homoallylamine is obtained without the protic additive. These observations indicate that the role of the additive is in connection with the release of the NHC–Cu catalyst (i.e., **iii**→**i** in Scheme 1 with ROH = MeOH). The facile formation of various homoallylamines under conditions that include 1–5 mol % catalyst loading but one and two equivalents of aldimine and MeOH, respectively, indicate that the rate of reaction of NHC–Cu-allyl complexes (cf. **ii**) with aldimines is substantially faster than adventitious

protonation of the C–Cu bond of the allylmetal intermediate. Reaction with d_2-(pinacolato)allylboron (labeled at C3) leads to complete scrambling of deuterium at C1 and C3, suggesting the intermediacy of π-allylcopper and providing a rationale for low diastereoselectivity with the crotylboron reagents.

Modes of reaction **I-II** (Figure 2) may be used to account for the stereochemical outcome of the Cu-catalyzed processes. Coordination of an N-phosphinoylimine's Lewis basic oxygen is likely the key contact point that brings substrate and catalyst together. The less Lewis basic N may be weakly associated with the transition metal center. Involvement of the Lewis basic P–O of the aldimine substrate offers a rationale for the high er values observed with *N*-phophinoyl-derived imines versus the corresponding *o*-anisidylimines, which react readily under the same conditions but deliver racemic products.[20] Molecular models suggests that preference for reaction via **I** versus the competing modes of reaction, such as that represented by **II**, might be due to subtle variations in catalyst-substrate interactions. Steric repulsion between the protruding Me unit and the aldimine substituent (G) in **I** appear to be less severe than that existing between a phenyl group of the phosphinoyl moiety in **II** (Figure 2); this difference might arise from tighter binding of the phosphinoyl oxygen with the Lewis acidic Cu, compared to the imine nitrogen. Superior enantioselectivities with **6d** (vs **6b**), particularly in the case of sterically congested aldimines, may be attributed to the tilt of the NAr moiety (Figure 1), lifting the resident *o*-Me group to accommodate the substrate molecule better.[21] Such conformational change leads to an improvement in enantioselectivity since it may not sufficiently reduce the more severe interaction in **II**. It should be noted that the identity of the stereochemistry-determining step has not been determined and the energetics of the catalytic cycle might vary with different substrates. The models in Figure 2 are meant to serve primarily for prediction of the stereochemical preferences.

Development of Cu-catalyzed enantioselective allyl additions to a wider range of imine substrates as well as other classes of electrophilic substrates are in progress.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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15. It is plausible that steric repulsion between the protruding Ph group of the imidizolinium backbone and the o-isopropyl substituent causes tilting of the N-aryl ($C_{carbene}$–N–C–C_{i-Pr} dihedral angle = 74.2°, $C_{carbene}$–N–C–C_{Me} dihedral angle = −103.4°) such that the other ortho unit of the N-Ar group (Me) and the backbone of the N-heterocyclic carbene (H_a in major **6d** isomer, Figure 1) are brought into a high degree of propinquity. It thus appears that the alternative orientation, where the Me is syn to the Ph group and the larger i-Pr oriented towards the rear, leads to a higher energy conformer. Related considerations have been put forward to explain similar stereochemical preferences, as substantiated by the X-ray structures of the Zn- and Al-based NHC complexes derived from sulfonate-based **3** (Table 1); see: Lee Y, Li B, Hoveyda AH. J Am Chem Soc. 2009; 131:11625. [PubMed: 19630406]

16. The identity of the alternative minor isomer (*o*-Me *syn* to NHC Ph) has been independently established by nOe experiments. The two isomers of **6d** readily interconvert in solution at ambient temperature. When a crystal consisting only of the major rotamer of the chiral imidazoliunium salt (used to obtain the X-ray structure in Figure 1) is placed in solution ($CDCl_3$, 22 °C), the original 5:1 ratio is observed within a few minutes.

17. Alkyl-substituted aldimines are prepared in situ through generation of the corresponding α-amino sulfones according to previously developed procedures: (a) Côté A, Boezio AA, Charette AB. Proc Natl Acad Sci. 2004; 101:5405. [PubMed: 15064400] (b) Yamaguchi A, Matsunaga S, Shibasaki M. Tetrahedron Lett. 2006; 47:3985. See the Supporting Information for details.

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19. At −50 °C (vs −30 °C), under otherwise identical conditions, reaction of **17b** affords **18b** in 54% yield (57% conv) and 94:6 er.

20. See the Supporting Information for details.

21. Additionally, molecular models indicate that, in **II**, the tilt of the aryl unit causes steric repulsion between the N-aryl's *i*-Pr and the other phenyl of the phosphinoyl group. In **I**, it is only the methylene of the allylcopper that interacts with the *ortho* substituent.
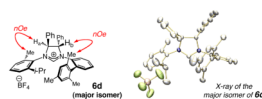
Figure 1.
Nuclear Overhauser effect (nOe) experiments and X-ray structure, indicating the identity of the major isomer of imidazolinium salt **6d** (5:1, see the Supporting Information for details).
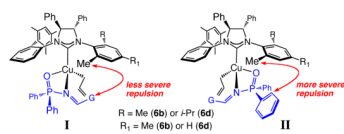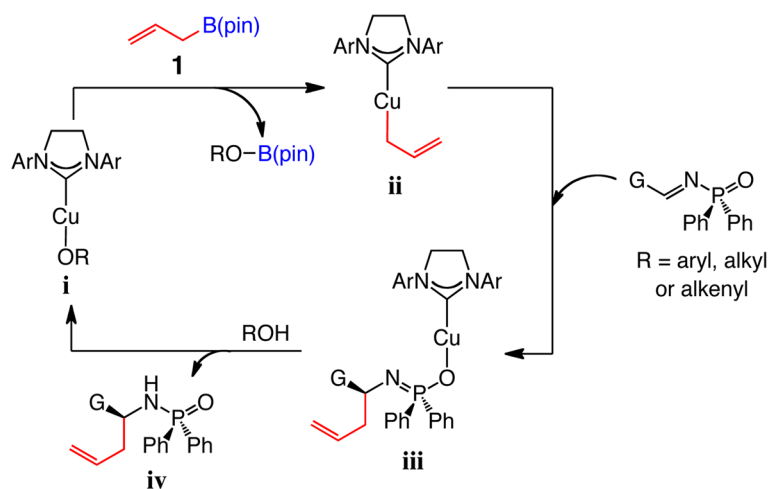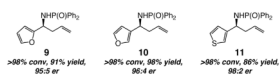
Figure 2.
Model for origin of enantioselectivity in NHC–Cu-catalyzed allyl additions to *N*-phosphinoylimines.
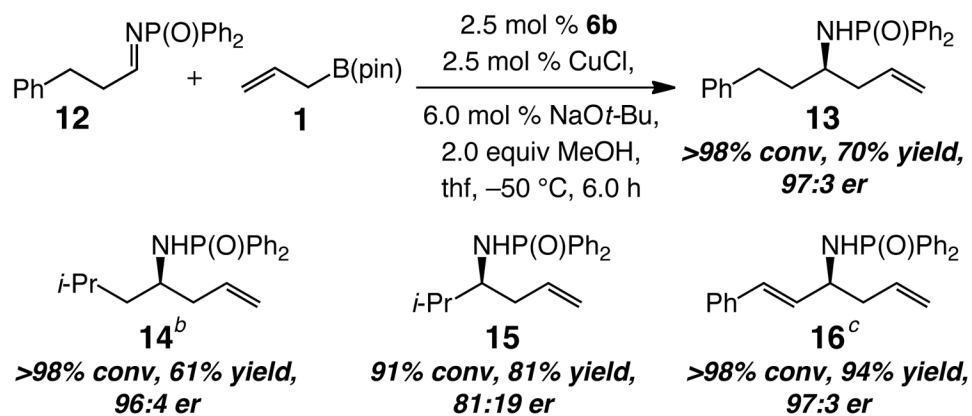
Scheme 1.
Catalytic Cycle for Reaction of (Pinacolato)allylboron with Aldimines Promoted by an NHC–Cu Complex[a]

[a] B(pin) = pinacolatoboron.

Scheme 2.
NHC–Cu-Catalyzed Enantioselective Allyl Addition to Heteroaryl-Substituted Phosphinoylimines[a]
[a]Performed under the conditions shown in Table 2 with **6b** (for **9** and **11**) or **6d** (for **10**) as the imidazolinium salt. Conversions and selectivities determined as indicated in Table 2; yields of isolated and purified products (±5%).

Scheme 3.
NHC–Cu-Catalyzed Enantioselective Allyl Addition to Alkyl-Substituted Phosphinoylimines[a]

[a]Performed under identical conditions for *R*-**13**. Conversions and selectivities determined as indicated in Table 2; yields are of the purified products (±5%). [b] With catalyst derived from **6d**. [c] Performed with 5.0 mol % of **6d** and CuCl and 12 mol % NaO*t*-Bu.

Table 1

Screening of Chiral NHC Complexes[a]
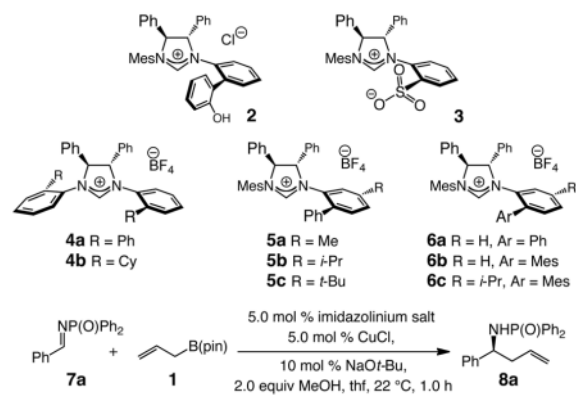
entry	imidazolinium salt	conv (%)[b]	er[c]
1	**2**	>98	57.5:42.5
2	**3**	70	47.5:52.5
3	**4a**	84	55.5:44.5
4	**4b**	>98	56:44
5	**5a**	>98	72.5:27.5
6	**5b**	>98	70:30
7	**5c**	>98	67.5:32.5
8	**6a**	>98	73.5:26.5
9	**6b**	***>98***	***91:9***
10	**6c**	>98	88:12

[a]Reactions performed under N_2 atm with 2.0 equiv of **1**.

[b]Values determined by analysis of 400 MHz ^{1}H NMR spectra of unpurified mixtures.

[c]Values determined by HPLC analysis; see the Supporting Information for details. Mes = 2,4,6-$(Me)_3C_6H_2$.

Table 2

NHC–Cu-Catalyzed Enantioselective Allyl Addition to Aryl-Substituted Phosphinoylimines[a]

entry	substrate (aryl)		imid. salt	conv (%)[b]	yield (%)[c]	er[d]
1	7a	Ph	6b	>98	95	97:3
2	7b	2-naphthyl	6d	>98	89	97:3
3	7c	o-FC$_6$H$_4$	6b	>98	95	98:2
4	7d	o-BrC$_6$H$_4$	6b	>98	92	98:2
5	7e	o-MeC$_6$H$_4$	6d	>98	98	96:4
6	7f	o-MeOC$_6$H$_4$	6d	>98	98	97:3
7	7g	m-BrC$_6$H$_4$	6b	>98	88	96:4
8	7h	p-ClC$_6$H$_4$	6b	>98	92	98:2
9	7i	p-BrC$_6$H$_4$	6b	>98	92	98.5:1.5
10	7j	p-CF$_3$C$_6$H$_4$	6b	97	95	98.5:1.5
11	7k	p-OMeC$_6$H$_4$[e]	6d	>98	>98	98:2

[a] Reactions performed under N$_2$ atm with 1.4 equiv of (pinacolato)allylboron **1**.

[b] Values determined by analysis of 400 MHz ^{1}H NMR spectra of unpurified mixtures (9-methylanthracene as internal standard).

[c] Yields of isolated products after purificaton (±5%).

[d] Values determined by HPLC analysis; see the Supporting Information for details.

[e] Carried out at −15 °C.