Multicomponent Catalysis

International Edition: DOI: 10.1002/anie.201605001
German Edition: DOI: 10.1002/ange.201605001

Catalytic Enantioselective Conjugate Additions of (pin)B-Substituted Allylcopper Compounds Generated in situ from Butadiene or Isoprene

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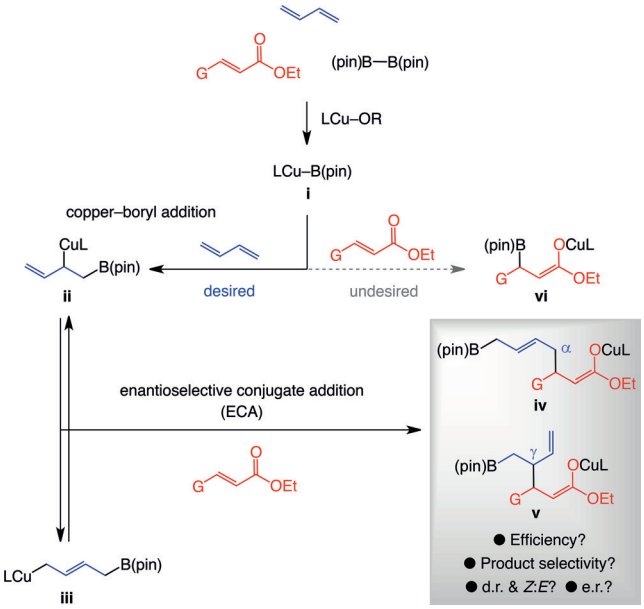
Abstract: *Multicomponent catalytic enantioselective transformations that entail the combination of butadiene or isoprene (common feedstock), an enoate (prepared in one step) and $B_2(pin)_2$ (commercially available) are presented. These processes constitute an uncommon instance of conjugate addition of an allyl moiety and afford the desired products in up to 83% yield and 98:2 enantiomeric ratio. Based on DFT calculations stereochemical models and rationale for the observed profiles in selectivity are provided.*

Multicomponent catalytic transformations can convert readily accessible starting materials to substantially more complex molecules.[1] One desirable scenario would involve 1,3-dienes and especially butadiene, a common feedstock produced in more than 10 million tons per year worldwide. However, catalytic enantioselective reactions with these unsaturated hydrocarbons, the majority of which are cycloadditions, are limited in number.[2] There are only the seminal contributions of Krische[3] regarding coupling of butadiene with alcohols or aldehydes, and the disclosures on reactions of 1-substituted butadienes with aldehydes[4a] and combination of aryl-based reagents and sodium dimethylmalonate.[4b,c]

Enantioselective processes have been recently developed that begin with the addition of a chiral Cu-B(pin) complex (pin = pinacolato) to an alkene,[5] affording organocopper species that may then react with another electrophile. Cu-based catalysts have accordingly been utilized to merge an allene and an aldehyde or ketone,[6] an allene and an allylic phosphate,[7] or an enyne and an aldehyde enantioselectively.[8] Related strategies, some with a Pd-based co-catalyst, entail the use of an aryl olefin and an aryl or benzyl halide (non-enantioselective)[9] or an allylic carbonate (enantioselective).[10]

A catalytic process with butadiene, $B_2(pin)_2$ and an enoate (Scheme 1) might be envisioned that constitutes enantioselective conjugate addition (ECA) of an allyl group, a class of valuable reactions that remains severely underdeveloped.[11] Further, the only reported multicomponent enantioselective conjugate additions[12] begin with initial addition to an alkynyl or alkenyl group followed by an intramolecular conjugate addition.[13]

The envisioned sequence would commence with the conversion of a 1,3-diene to allylcopper species **ii** and **iii**[14]



Scheme 1. The possibility of, and complications associated with, multicomponent Cu-catalyzed conjugate allyl addition processes involving butadiene, $B_2(pin)_2$ and an enoate. Abbreviations: L = chiral ligand; R, G = functional group; pin = pinacolato.

and then **iv** or **v** (α- vs. γ-addition). One possible complication would be competitive boryl conjugate addition (**i**→**vi**, Scheme 1).[15] This is a more formidable chemoselectivity challenge compared to when an allenyl,[6,7,13b] an alkynyl[13a] or a styrenyl[13] substrate is used because these latter species are either less hindered and/or more electrophilic (vs. a butadiene).

Preliminary experiments with butadiene and phosphine or N-heterocyclic carbene (NHC) complexes of copper indicated that α,β-unsaturated mono-esters or related derivatives are not sufficiently reactive. However, commercially available diester **1a** (Scheme 2a) did undergo reaction with 5.0 mol% CuCl and PCy_3 with a slight preference for γ-addition product **4a** (**3a**:**4a** = 36:64), which was isolated in 60% yield as an equal mixture of diastereomers.[16] Follow-up studies revealed that reactions with other bis-phosphine ligands (**5a**–**h**, Scheme 2a) can be reasonably efficient (53:47–88:12 **3a**:**4a**; **3a** in up to 68% yield and >98% *E*), but enantiomeric ratio (e.r.) values were generally low (≤66:34).

Transformations were similarly effective with NHC–Cu complexes arising from **6a**–**h** (Scheme 2b); in some instances (cf. **6b**, **6e** and **6g**), probably as a result of the higher nucleophilicity of NHC–Cu–B(pin) species, boryl conjugate addition proved to be a major side reaction[15] (cf. **ii**, Scheme 1). There are other differences between phosphane-

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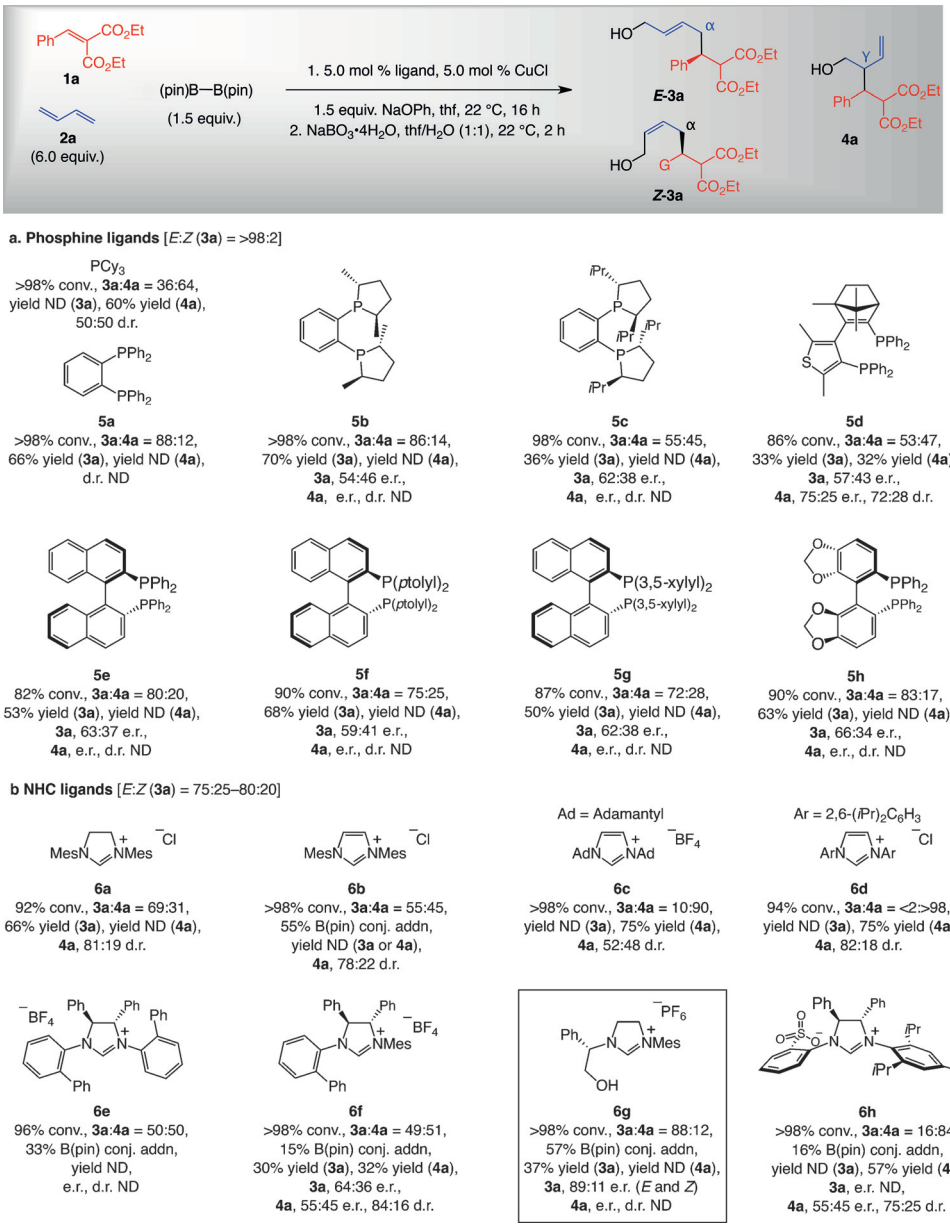
Supporting information for this article can be found under: http://dx.doi.org/10.1002/anie.201605001.

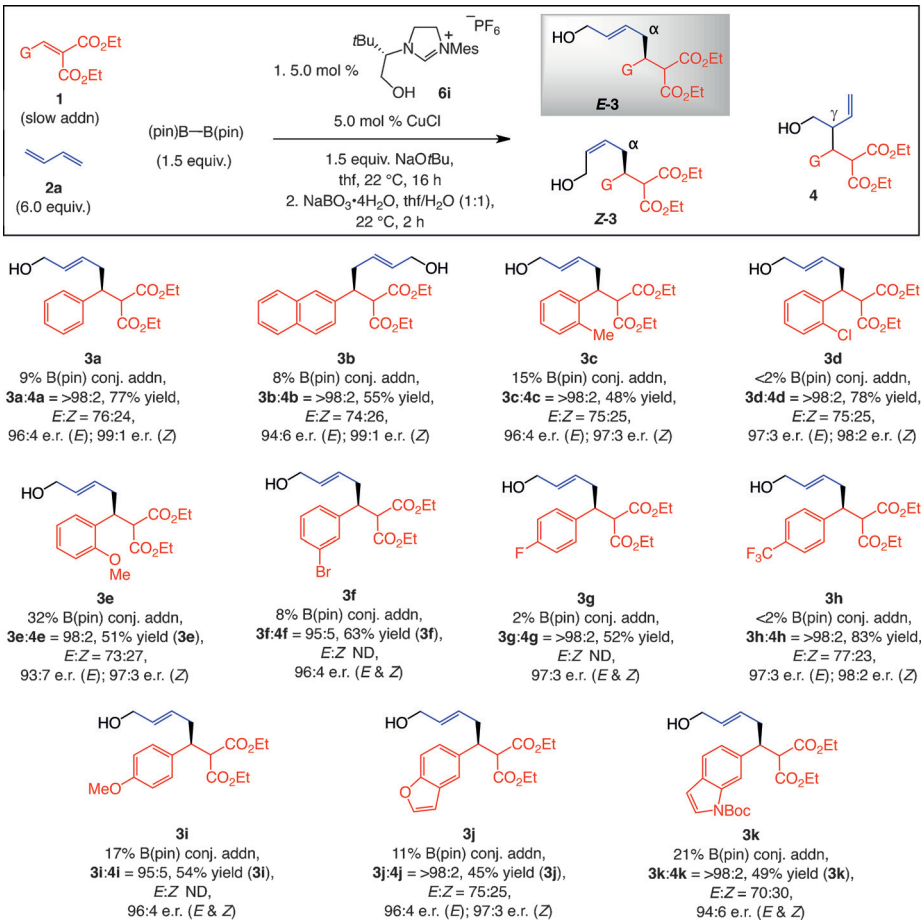


Scheme 2. Screening of different types of Cu-based catalysts. [a] Performed under N_2 atm. Conv. and d.r. was determined by analysis of ^{1}H NMR spectra of unpurified mixtures; conv. (±2%) refers to disappearance of **1a**. Yields are for isolated and purified products (±5%). In the case of **3a**, the e.r. values correspond to the *E* isomer, unless noted otherwise. Compound **4a** was formed in up to 80:20 d.r. (major diastereomer shown); the selectivity values indicated for this compound are for the predominant isomer. [d] E.r. values determined by HPLC (±1%). See the Supporting Information for details. Abbreviations: Mes = 2,4,6-$(Me)_3C_6H_2$; ND = not determined; Ad = adamantyl; pin = pinacolato.

and NHC–Cu-catalyzed processes: i) With the heterocyclic complexes, **3a**:**4a** ratios proved to be more sensitive to ligand structure. For instance (and remarkably), whereas there was minimal selectivity (**3a**:**4a** 55:45) when mesityl-substituted **6b**, when adamantyl-containing **6c** was used **3a** was produced preferentially (**3a**:**4a** 10:90). ii) Although *E*:*Z* selectivity was moderate with NHC–Cu complexes (75:25–80:20), use of phosphorous-based ligands afforded only *E*-alkenes (>98%).

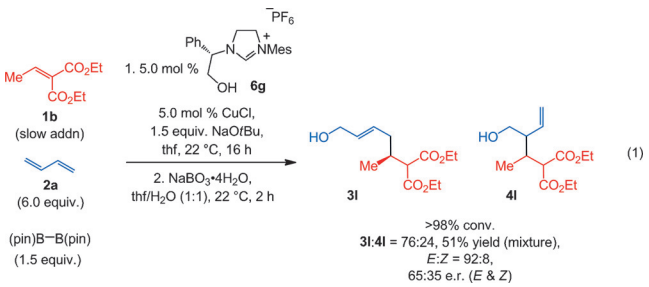
Enantioselectivity was highest with the complex derived from imidazolinium salt **6g**, furnishing *E*- and *Z*-**3a** in 89:11 e.r.; but this system also generated the largest amount of the β-boryl diester byproduct (57%; see Scheme 2). The key question therefore was: How could adventitious boryl conjugate addition be minimized along with further e.r. enhancement? It stands to reason that if enoate concentration were to be kept at a minimum, larger amounts of the desired allyl ECA product should be formed, and we hoped that a more enantioselective Cu complex would emerge by further screening. Accordingly, we found that by slow addition (syringe-pump)[17] of enoate **1a** and with imidazolinium salt **6i** (Scheme 3) and NaO*t*Bu as the base[18] **3a** may be generated exclusively (<2% **4a**) in 77% yield (*E* and *Z* alkenes) and 96:4 and 99:1 e.r. (for *E* and *Z* isomers, respectively; 76:24 *E*:*Z*).

A range of products can be directly synthesized from diesters that were either purchased or synthesized from simple starting materials in a single step (≈80% yield).[17] Aryl-substituted enoates, *ortho*-, *meta*- or *para*-substituted, including those with a sterically demanding (**3b–c**), electron withdrawing (**3d, 3f** or **3h**), or electron-donating substituent (**3e**, **3g**, **3i**) were suitable. With more electron-rich substrates (e.g., **3e** and **3i**) the amounts of the β-boryl carbonyl byproducts were formed, implying reaction of the allylcopper intermediate (cf. **iii–iv**, Scheme 1) is influenced more strongly by enoate electrophilicity compared to competing conjugate boryl addition. Products were isolated in 45–83% yield after oxidation, and the *E* isomer was generated predominantly (≈75:25). Enantioselectivities were uniformly high, irrespective of the unsaturated carbonyl reactant or the stereochemical identity of the alkene (93:7–99:1 e.r.). Enoates bearing a heteroaryl moiety were utilized as well: **3j** and **3k** were isolated in 45% and 49% yield and 94:6–97:3 e.r. (Scheme 3).



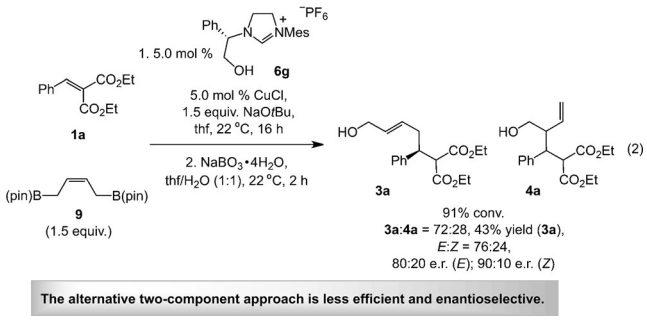
Scheme 3. Scope of the catalytic method. Complete (>98%) enoate consumption in all cases; *E*:*Z* ratios could not be determined in some cases due to overlapping signals in the ^{1}H NMR spectra. See the Supporting Information for details).

Reactions with alkyl-substituted enoates afforded larger amounts of the γ-addition product and were less enantioselective; the example in Equation (1) is illustrative. As will be detailed below, this difference is mechanistically revealing.



On the other hand, isoprene, another readily accessible diene, is an effective substrate (Scheme 4). The corresponding transformations proceeded with similar efficiency and chemo- and stereoselectivity as with butadiene.

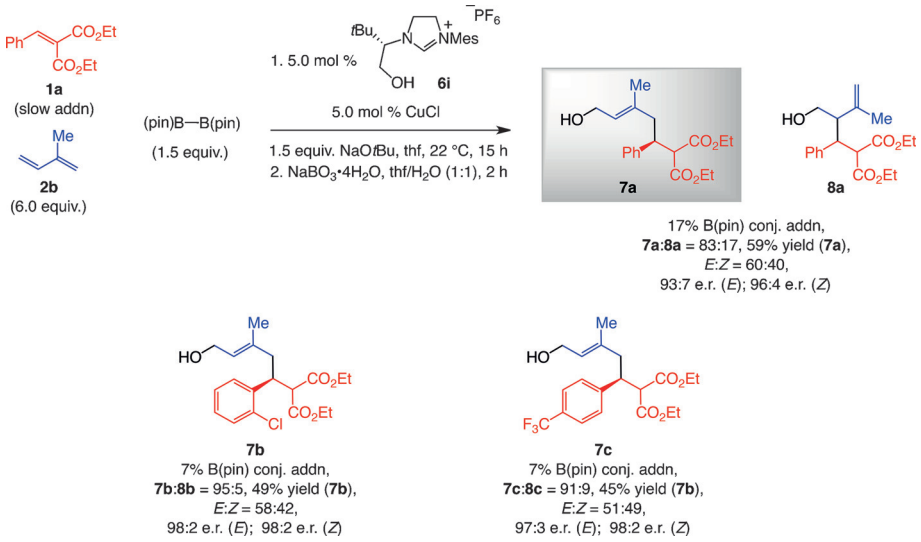
Several issues regarding the reactions in Schemes 3 and 4 merits brief discussion. One is that the alternative two-step/two-component strategy presented in Equation (2) with



The alternative two-component approach is less efficient and enantioselective.

allylboron reagent **9** is significantly less effective. This is probably because of a comparatively efficient background process catalyzed solely by metal alkoxide, a possibility confirmed by the appropriate control experiments. What is more, diboryl reagent **9** is somewhat sensitive and must be handled with care. Another point is that although products are at times obtained in what may be viewed as moderate yield (range: 45–83%), a C–B as well as a C–C bond is generated by a single process with robust, easily accessible and inexpensive starting materials (e.g., butadiene vs. bis(allyl)boronate **9**[19]). Even if the alternative approaches entailing two (or more) steps were competitive in terms of overall yield and enantioselectivity, the present method offers direct access to the desired products without the need for initial synthesis and purification of an appropriate precursor that would then be converted to the requisite reagent (e.g., **9**).

Development of a mechanistic model was next. DFT calculations, performed at the wB97XD/Def2TZVPP$_{thf(SMD)}$// wB97XD/Def2SVP$_{thf(PCM)}$ level,[17] indicate that a nucleophilic NHC–Cu–allyl complex[20] associates with the enoate alkene through back-bonding[21] (see **I**–**II**, Figure 1). The sodium cation of the metal alkoxide resulting from deprotonation of the chiral ligand's hydroxy group is at the center of a complex that contains the enoate's carbonyl oxygen atoms. This is consistent with the fact that masking the hydroxy group in **6i** as *tert*-butyldimethylsilyl ether results in substantial loss in enantioselectivity (e.g., **3a** in 60:40 e.r.). Analysis of different structural parameters indicates that edge-to-face affinity[22] between the aryl ring of the chiral ligand and that of the enoate in **I** is critical: there appears to

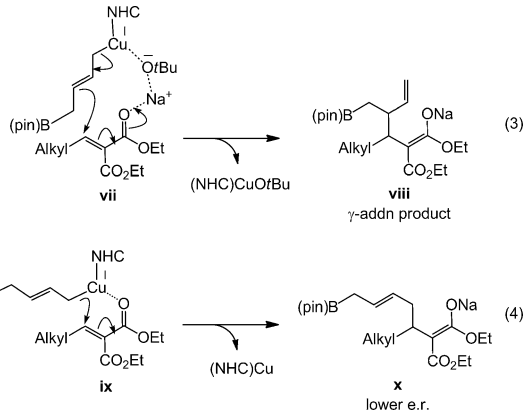


Scheme 4. Conjugate additions with isoprene (>98% enoate consumption in all cases; see the Supporting Information for details).

be close contact between H^1 and $C^{1'}$ and $C^{2'}$ of the 2,6-dimethyl aryl moiety (2.82 and 2.75 Å, respectively). This attractive interaction situates the phenyl ring in plane with the Cu–C^4 bond (Cu–C^4–C^5–C^6 dihedral angle = −3.4°), causing the NHC ligand to tilt; this offers a rationale for why the Cu–C^3 distance in **I** is shorter (5.00 vs. 5.25 Å in **II**) and the N_{Ar}–C_{NHC}–Cu angle is smaller (121.6° vs. 124.8° in **II**). The position of the allyl group in **II** causes a less favorable tilt of the 2,6-dimethylphenyl ring. Further, aryl–aryl interaction translates to a shorter average Na–O distance in **I** (2.24 vs. 2.27 Å in **II**) and a more robust metal bridge. Placement of Cu–C^{Allyl} proximal to C^1 thus leads to a strong preference for the formation of the α product isomer (95:5 to >98:2 α:γ).

The moderate *E*:*Z* ratios probably originate from the allylcopper stereoisomers being generated with similar selectivity from reaction of NHC–Cu–B(pin) with a diene. The reduced enantioselectivity of alkyl-substituted enoates [see Eq. (1)] may be attributed to two factors: a) The absence of an attractive aryl-aryl interaction. b) The more electron donating alkyl substituent means a higher energy π* orbital, weaker back-bonding and less favorable Cu–π complexation. As such, either mode of addition affording the γ-addition products become competitive [see **vii**→**viii**, Eq. (3)], and/or a less rigid structure leads to lower e.r. [see **ix**→**x**, Eq. (4)].

Enantiomerically enriched diesters may be converted to a range of other valuable compounds (Scheme 5). Oxidation converts the 76:24 *E*/*Z* mixture to the enal in purely the *E* form (**10** in 98% yield; Scheme 5a). The initial allyl-



boron product may be utilized in catalytic cross-coupling, as represented by the reaction of **11** with aryl bromide,[23] affording **12** in 67% yield and as only the *E* stereoisomer; the increase in *E*:*Z* ratio (>98% vs. ≈75% *E*) suggests that isomerization of the π-allyl palladium intermediate is faster than C–C bond formation. α-Olefin **13** was isolated in 84% yield by direct treatment of **11** with KHF_2 and *para*-toluenesulfonic acid.[24] Allylic alcohol **14** was obtained in >98:2 diastereomeric ratio (d.r.; readily separable diastereomers) and 51% yield after a straightforward two-step procedure.[25]

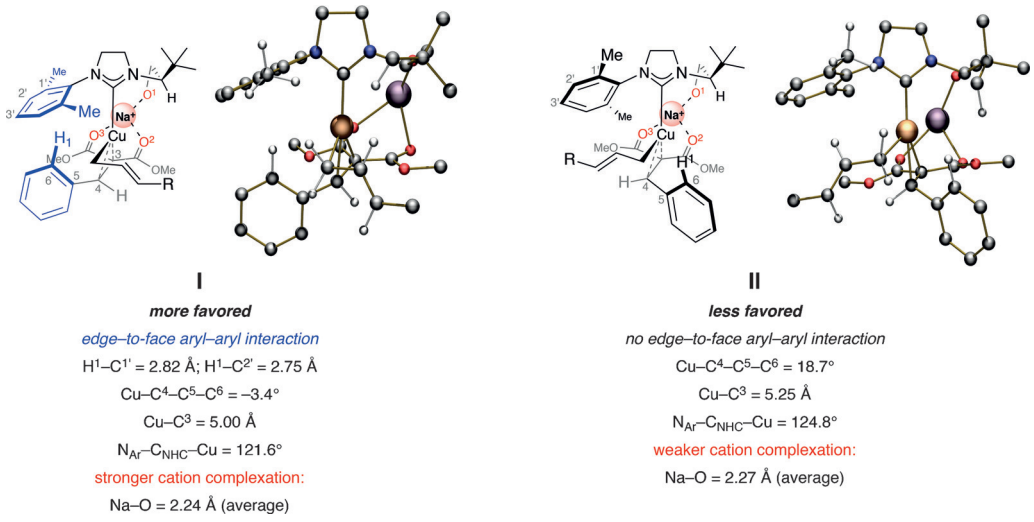
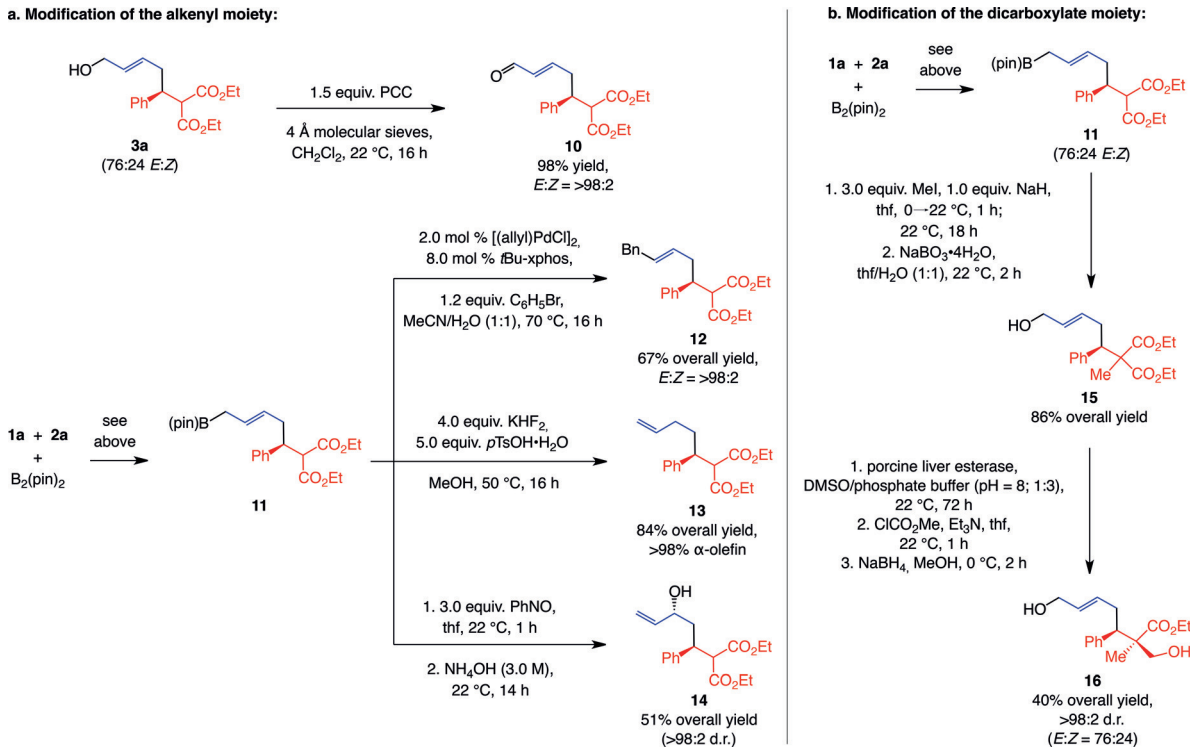


Figure 1. Stereochemical models derived from DFT calculations. See the Supporting Information for details.



Scheme 5. Functionalization of products. See the Supporting Information for details.

The diester moiety allows for enhanced utility. For instance, alkylation of enantiomerically enriched allylboron **11** followed by enzymatic desymmetrization[26] of **15** delivered the desired mono-acid with complete stereoselectivity (> 98:2 d.r.; Scheme 5b); chemoselective reduction of the carboxylic acid moiety afforded alcohol **16** in 40% overall yield. Functionalized organic molecules containing a quaternary carbon stereogenic center can therefore be secured with exceptional stereochemical purity.[27]

We thus introduce catalytic ECA reactions of allyl moieties that can be performed with feedstock butadienes, α,β-unsaturated carbonyl compounds and commercially available $B_2(pin)_2$. The enantiomerically enriched products may serve as precursors to other useful derivatives that would otherwise be more cumbersome to prepare. Development of additional catalytic multicomponent transformations, mechanistic studies and applications to preparation of biologically relevant target molecules are underway.

Acknowledgements

Financial support was provided by the NIH (GM-47480) and the NSF (CHE-1362763).

Keywords: boron · conjugate additions · copper · enantioselective catalysis · synthetic methods

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 9997–10002
Angew. Chem. **2016**, *128*, 10151–10156

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[17] See the Supporting Information for details.
[18] Optimization studies led us to establish that use of NaO*t*Bu in place of NaOPh led so significantly higher α:γ and enantiomeric ratios (e.g., in the case of **3a**: >98:2 vs. 80:20 α:γ and 96:4 vs. 92:8 e.r. for NaOPh and NaO*t*Bu, respectively). The reasons for these variations are under investigation.
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Received: May 21, 2016
Published online: July 20, 2016

