

## EDGE ARTICLE

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## Cu(I)-catalyzed enantioselective and stereospecific borylative annulation of cyclic 1,3-dione-tethered 1,3-enynes†

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A copper(I)-catalyzed, highly enantioselective, and diastereoselective borylative cyclization of prochiral cyclic 1,3-dione-tethered 1,3-enynes is reported. This stereospecific transformation exhibits a broad substrate scope, enabling access to bicyclic organoboron products containing four contiguous stereocenters with excellent enantioselectivity. Notably, the reaction rate is significantly influenced by the substrate's stereochemistry, with the (*Z*)-isomer undergoing borylative cyclization much faster than the (*E*)-isomer due to reduced steric interactions during C–C bond formation. Furthermore, treatment of the resulting products with sodium perborate yields the corresponding alcohols without compromising enantiomeric excess.

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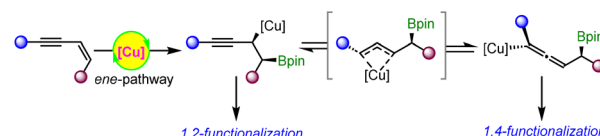
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## Introduction

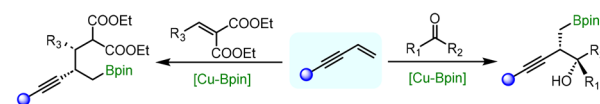
Conjugated enynes are highly reactive and valuable substrates in modern organic chemistry, widely utilized in the synthesis of complex aromatic molecules and materials.<sup>1</sup> While 1,3-enyne motifs can be readily accessed through several efficient methods, the catalytic cross-coupling of terminal alkynes stands out as the most convenient approach.<sup>2</sup> Recently, copper-catalyzed hydro- and borofunctionalizations, multicomponent reactions, radical functionalizations, and cyclizations of these  $\pi$ -systems have garnered significant attention from organic and medicinal chemists.<sup>3</sup> Among these methods, enantioselective Cu-catalyzed borylation of 1,3-enynes has also emerged as an elegant strategy, providing access to a diverse range of chiral organoboranes.<sup>4</sup> The resulting C–B bonds can be conveniently converted into C–C, C–O, and C–N bonds through stereospecific 1,2-migration.<sup>5</sup> However, achieving asymmetric chemo- and regioselective borylative difunctionalization of 1,3-enynes remains highly challenging due to the presence of multiple reactive sites.

In general, two pathways are possible for 1,3-enynes during hydro- or borofunctionalization. The reaction at the olefin can yield propargyl or allene products *via* the ene-pathway (Scheme 1a), whereas the reaction at the alkyne results in diene products through the yne-pathway.<sup>3</sup> In 2011, Ito and co-workers reported that the regioselectivity of borocupration is influenced by the nature of the ligand employed in the reaction and steric

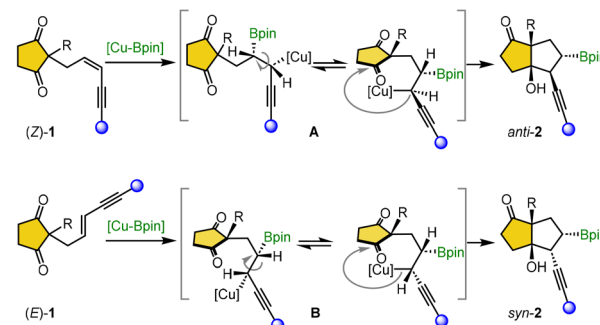
## a. Cu(I)-catalyzed selective functionalization of enynes



## b. Cu(I)-catalyzed 1,2-functionalization of enynes: previous work



## c. Highly enantioselective and stereospecific borylative cyclization: our work



Scheme 1 Cu(I)-catalyzed borylative functionalization of 1,3-enynes.

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hindrance around the olefinic functionality of the enyne.<sup>6</sup> The first enantioselective Cu-catalyzed borylative 1,2-difunctionalization of 1,3-enynes was reported by the Hoveyda group in 2014 *via* the ene-pathway (Scheme 1b).<sup>7</sup> The borocupration of 1,3-enynes enables the formation of a chiral allenylcopper complex, which is readily captured by aldehydes to provide propargylated products with excellent diastereo- and enantioselectivities. In light of this report, Yin and co-workers disclosed similar consecutive protocols on ketones.<sup>8</sup> Later, Procter and co-workers disclosed a highly enantio- and diastereoselective borylative 1,2-coupling of 1,3-enynes with imines to provide chiral homopropargyl amines with excellent diastereo- and enantioselectivity.<sup>9</sup> Recently, Yun and co-workers reported a highly enantioselective 1,2-borylation/conjugate addition with  $\beta$ -substituted alkylidene malonates, enabling organoboranes bearing adjacent stereocentres.<sup>10</sup> In 2020, Hu, Wang, Liao, and co-workers developed a cooperative Cu/Pd-catalyzed 1,4-boroylation, wherein arylation occurs *via* transmetalation with palladium to access chiral tri- and tetra-substituted allenes.<sup>11</sup> Shortly thereafter, Xu *et al.* reported the 1,4-boroprotonation of trifluoromethyl-substituted conjugated enynes to access enantioenriched homoallenylboronates.<sup>12</sup> Similarly, CuH-catalyzed hydrofunctionalization of 1,3-enynes also allows the generation of chiral allenylcopper intermediates, which are readily captured by various electrophiles to yield the corresponding propargylic products and allenes with excellent stereoselectivities.<sup>13,14</sup> Among these elegant methods, 1,2-borofunctionalization is generally limited to terminal 1,3-enynes, with only two reports<sup>9,10</sup> exploring internal enynes due to their lower reactivity and other challenges related to regioselectivity and stereoselectivity. Here, *E/Z*-selectivity of the double bond controls the diastereoselectivity of the corresponding product in a stereospecific manner.

To the best of our knowledge, there are no intramolecular cyclizations reported *via* Cu-catalyzed borylative 1,2-difunctionalization of 1,3-enynes with internal electrophiles. Based on our interest in the area of enantioselective Cu-catalysis,<sup>15</sup> herein, we report a stereospecific annulation of 1,3-enyne-tethered cyclic 1,3-enones (Scheme 1c). This work describes an unprecedented intramolecular Cu(I)-catalyzed borylative difunctionalization of 1,3-enynes, delivering products with excellent diastereo- and enantioselectivity. The *E/Z* configuration of the substrates significantly influences the reaction rate and diastereoselectivity of products. We envisioned that stereospecific *syn*-addition of a borylcopper(I) intermediate on the double bond of (*Z/E*)-**1** could provide intermediate A/B. Subsequent intramolecular nucleophilic attack of organocuprate A/B could afford the corresponding product *anti*-**2** or *syn*-**2**, respectively with the retention of the configuration at the C–B bond. Notably, the reaction proceeds through highly regioselective 1,2-borocupration on the double bond adjacent to the sterically demanding quaternary prochiral center.

## Results and discussion

We began our investigation on Cu(I)-catalyzed borylative cyclization of *Z*-selective 1,3-enyne **1a** as a model substrate in the

presence of bis(pinacolato)diboron as the borylation source with various chiral bidentate phosphine ligands (Table 1). The reaction was initially conducted with 2.5 mol% of Cu(CH<sub>3</sub>CN)<sub>4</sub>PF<sub>6</sub>, 5 mol% of ligand, and 2.0 equivalents of base in THF at –78 °C for 2 hours. Notably, the BINAP ligands provided the desired product *anti*-**2a** in moderate yield with enantioselectivity ranging from 37% to 92%, whereas SEGPHOS ligands resulted in only trace amounts of the product (entries 1–5). In addition, the BDPP ligand L6, DUPHOS ligand L7, BIPHEP ligand L8, and iPr-BPE ligand L9 proved ineffective in the model reaction, resulting in no product formation. Fortunately, the reaction with (*S,S*)-Ph-BPE ligand L10 afforded **2a** in high yield with excellent enantioselectivity (>99% ee). The exclusive diastereoselectivity suggests that the borylative cyclization of (*Z*)-**1a** proceeds with high stereocontrol. The relative stereochemistry of *anti*-**2a** was confirmed by single crystal X-ray diffraction analysis (see Table 2).<sup>16</sup>

Table 1 Optimization of reaction conditions<sup>a,b,c,d</sup>

| Entry | Ligand                         | Yield [%] | 2a (ee) |
|-------|--------------------------------|-----------|---------|
| 1     | ( <i>R</i> )-SEGPHOS, L1       | <5        | —       |
| 2     | ( <i>S</i> )-BINAP, L2         | 54        | 92%     |
| 3     | ( <i>R</i> )-Tol-BINAP, L3     | 36        | 69%     |
| 4     | ( <i>S</i> )-DM-SEGPHOS, L4    | <5        | —       |
| 5     | ( <i>R</i> )-DM-BINAP, L5      | 31        | 37%     |
| 6     | ( <i>S,S</i> )-BDPP, L6        | <5        | —       |
| 7     | ( <i>R,R</i> )-Me-DUPHOS, L7   | —         | —       |
| 8     | ( <i>R</i> )-Cl-MeO-BIPHEP, L8 | —         | —       |
| 9     | ( <i>S,S</i> )-iPr-BPE, L9     | —         | —       |
| 10    | ( <i>S,S</i> )-Ph-BPE-L10      | 82%       | >99%    |

(*R*)-SEGPHOS, L1

(*S*)-BINAP, L2

(*R*)-Tol-BINAP, L3

(*S*)-DM-SEGPHOS, L4

(*S,S*)-BDPP, L6

(*R,R*)-Me-DUPHOS, L7

(*R*)-Cl-MeO-BIPHEP, L8

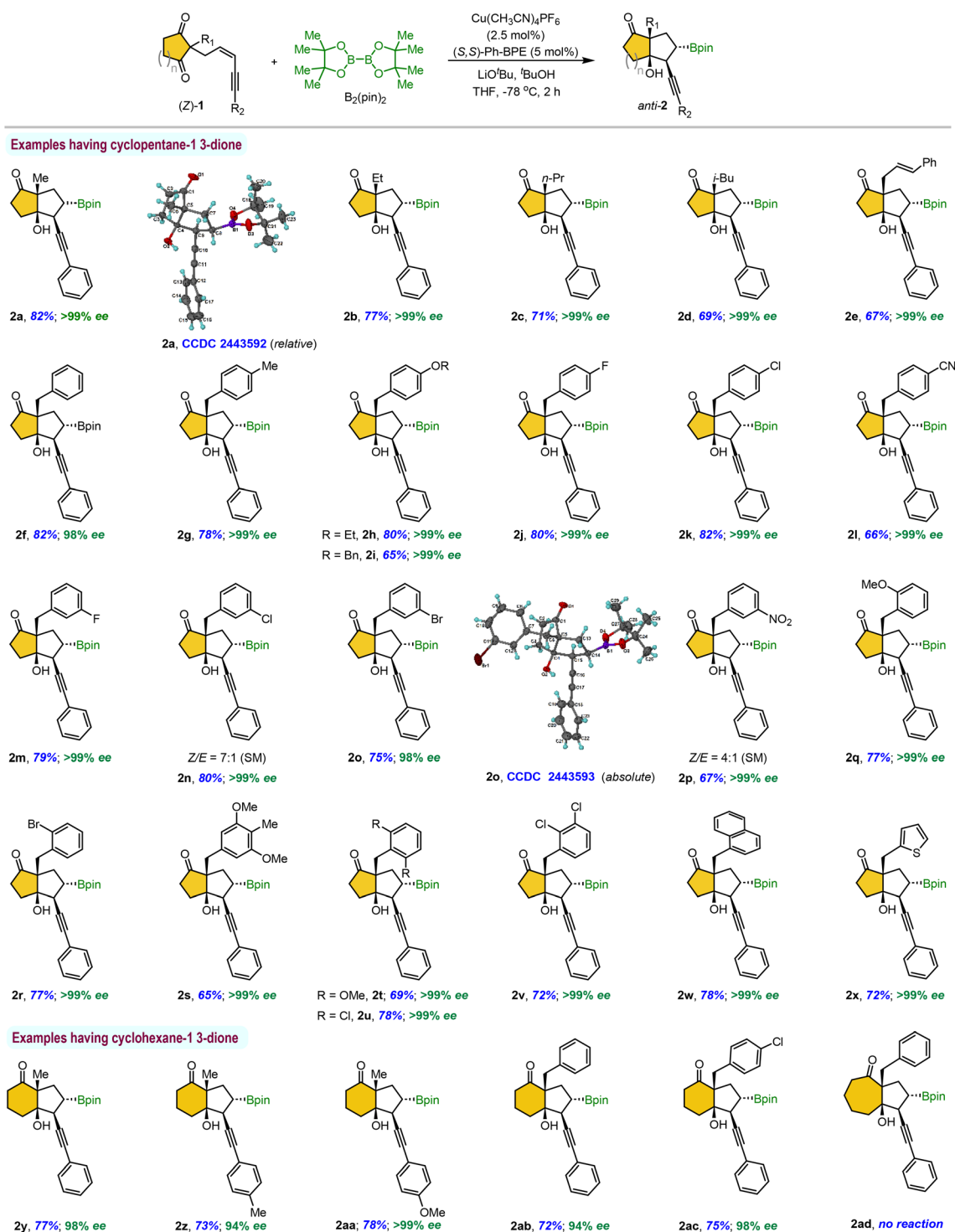
(*S,S*)-iPr-BPE, L9

(*S,S*)-Ph-BPE, L10

(*R*)-DM-BINAP, L5

<sup>a</sup> Reaction conditions: **1a** (50 mg, 0.2 mmol), B<sub>2</sub>(pin)<sub>2</sub> (60 mg, 0.24 mmol), Cu(CH<sub>3</sub>CN)<sub>4</sub>PF<sub>6</sub> (1.9 mg, 2.5 mol%), ligand (5.0 mol%), <sup>t</sup>BuOH (38  $\mu$ L, 0.4 mmol), LiO<sup>t</sup>Bu (36  $\mu$ L, 0.4 mmol, 1.0 M THF solution), in THF solvent (3 mL, 0.1 M). <sup>b</sup> Isolated yields. <sup>c</sup> Enantiomeric ratio (*er*) was determined by HPLC analysis using a chiral stationary phase. <sup>d</sup> >20 : 1 *dr* was observed from <sup>1</sup>H NMR analysis.



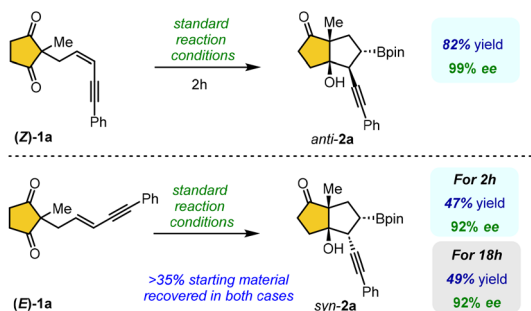
Table 2 Substrate scope of (Z)-isomer<sup>a,b,c,d</sup>

<sup>a</sup> Reaction conditions: **1** (0.3 mmol),  $B_2(\text{pin})_2$  (91 mg, 0.36 mmol),  $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$  (2.8 mg, 2.5 mol%), (S,S)-Ph-BPE (7.6 mg, 5.0 mol%),  $^t\text{BuOH}$  (57  $\mu\text{L}$ , 0.6 mmol),  $\text{LiO}^t\text{Bu}$  (54  $\mu\text{L}$ , 0.6 mmol, 1.0 M THF solution), in THF solvent (3 mL, 0.1 M). <sup>b</sup> Isolated yields after column chromatography. <sup>c</sup> Enantiomeric ratio (*er*) was determined by chiral HPLC analysis. <sup>d</sup> >20:1 *dr* was observed (unless otherwise mentioned) through  $^1\text{H}$  NMR analysis of a crude reaction mixture. SM = Starting material.

Under standard conditions, the borylative cyclization of 1,3-ene (Z)-**1a** proceeded with complete *anti*-selectivity, affording the bicyclic product **2a** in 82% yield with >99%

enantioselectivity (Scheme 2). In contrast, the reaction of 1,3-ene (E)-**1a** yielded the *syn*-selective bicyclic product **2a** with moderate yield and 92% enantioselectivity. Besides, prolonging



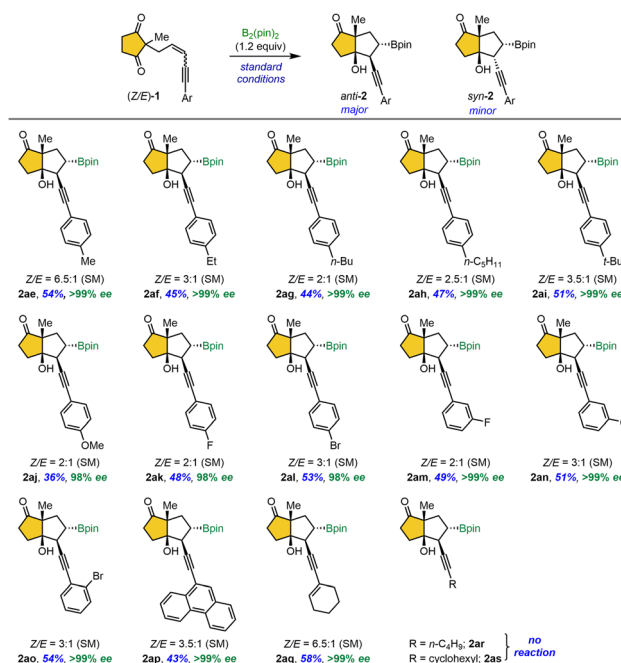


Scheme 2 Comparative study of reaction rates.

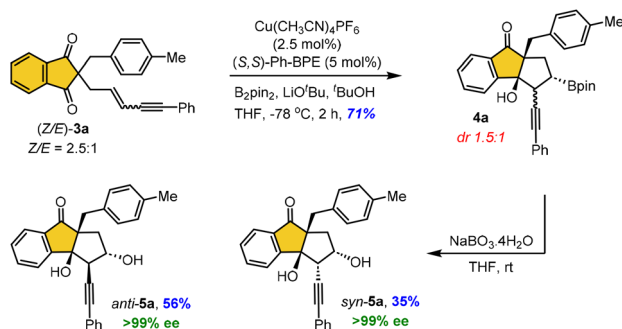
the reaction time did not enhance the conversion, and over 35% of the starting material (*E*)-1a remained unreacted in both cases. The reaction rates and *syn/anti* selectivity of the reaction were significantly influenced by the *E* or *Z* configuration of the 1,3-enyne substrates.<sup>17</sup> Notably, the borylative cyclization of (*Z*)-1a proceeded much faster than that of (*E*)-1a, affording the desired product in high yield with exclusive enantioselectivity. This enhanced reactivity is likely attributed to reduced steric interaction between the Bpin and alkyne groups in Int-A compared to Int-B during C–C bond formation (see Scheme 1c).

Later, the scope of the borylative cyclization in the presence of B<sub>2</sub>pin<sub>2</sub> was explored using various prochiral (*Z*)-selective 1,3-enyne-tethered cyclic 1,3-diones **1** under optimized reaction conditions, unless otherwise specified for the *Z/E* ratio of the substrate. Our initial investigation focused on phenyl-

substituted enynes with various substituents at the all-carbon prochiral center, and the results are summarized in Table 2. Substrates bearing sterically diverse alkyl groups and a cinnamyl group at the quaternary center were well-tolerated, undergoing borylative enantioselective desymmetrization to afford the corresponding products **2a–2e** in 67–82% yield with excellent enantioselectivity. Next, a range of benzyl groups with electronically and sterically tuned substituents at the prochiral center were evaluated. These 1,3-enyne-tethered cyclopenta-1,3-diones proved to be highly suitable, delivering bicyclo[3.3.0]octane products **2f–2v** in good yields with uniformly >99% ee across all cases. Particularly, the reaction was carried out on the substrates as an inseparable mixture of (*Z/E*)-isomers, with the major (*Z*)-1,3-enyne predominantly yielding the corresponding products *anti*-2n and *anti*-2p, along with trace amounts of *syn*-products derived from the (*E*)-isomer. Beyond benzyl groups, a similar range of yields and enantioselectivities was observed with other substituents, including 1-naphthyl and thiophen-2-ylmethylene groups at the quaternary prochiral center, furnishing products **2w** and **2x**, respectively. Next, the generality of the present approach was evaluated using *Z*-selective enyne-tethered cyclohexa-1,3-diones under standard conditions, which provided the corresponding products **2y–2ac** in comparable yields and enantioselectivities. However, the cycloheptane-1,3-dione substrate failed to afford the desired product (**2ad**), and most of the starting material was recovered. The absolute stereochemistry of the bicyclic ketone *anti*-2o was unambiguously established by single-crystal X-ray diffraction

Table 3 Substrate scope of the (*Z/E*)-isomer<sup>a,b,c,d,e</sup>

<sup>a</sup> Reaction conditions same as in Table 2. <sup>b</sup> Isolated yields of the major product *anti*-2. <sup>c</sup> Diastereoselectivity was observed to be >20:1 for the major isomer, which was confirmed by <sup>1</sup>H NMR analysis. <sup>d</sup> Unable to find the ratio of major and minor products in the crude <sup>1</sup>H NMR analysis. <sup>e</sup> Enantioselectivity of the major isomer. SM = starting material.



Scheme 3 Borylative cyclization of 1,3-indandiones.

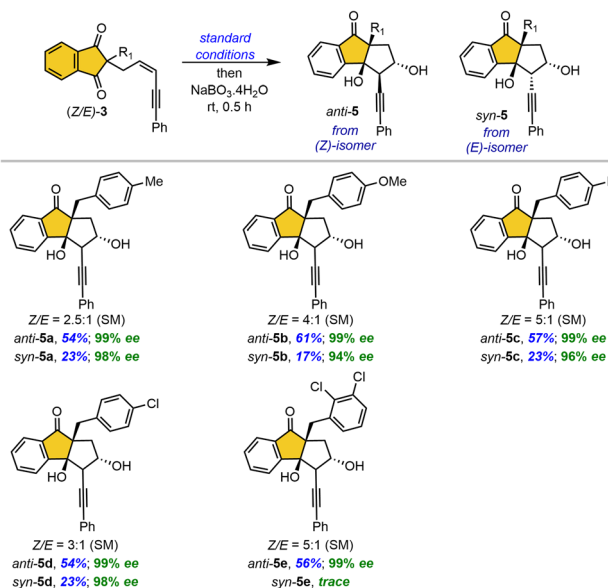
analysis.<sup>16</sup> The stereochemical assignments of the remaining products were assumed by analogy.

Next, we explored the scope of 1,3-enynes bearing various aromatic substituents (Table 3). The reaction was carried out on a mixture of (*Z/E*)-isomers under standard conditions, yielding product *anti*-2 predominantly from (*Z*)-1,3-enyne as the major diastereomer due to its higher reaction rate. Only trace amounts of the *syn*-product 2 (<5% yield) were identified from (*E*)-1 in a few examples, highlighting the strong stereochemical influence on the reaction outcome. The transformation proceeded with good diastereoselectivity, and excellent enantioselectivity. Aromatic 1,3-enynes with diverse substituents, regardless of their electronic properties, were well-tolerated under the standard conditions. Substituents such as alkyl, alkoxy, and halogen groups at the para-, meta-, or ortho-positions of the phenyl ring afforded the corresponding products (**2ae–2ao**) in moderate

yields with excellent enantioselectivity (97–99% ee). Additionally, 9-phenanthryl and 1-cyclohexenyl groups on 1,3-enynes were readily converted into the desired products (**2ap** and **2aq**) in good yields with >99% enantioselectivity. Unfortunately, 3-enyne substrates bearing aliphatic substituents failed to afford the desired products, and most of the starting material was recovered (entries **2ar** and **2as**).

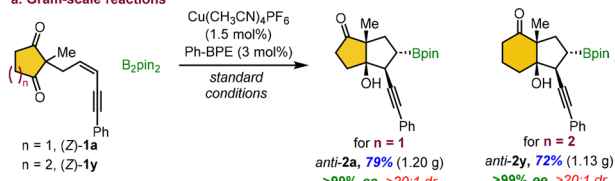
The enantioselective desymmetrization of  $\alpha,\alpha$ -disubstituted 1,3-indandione (*Z/E*)-**3a** (*dr* = 2.5 : 1) proceeded efficiently under the optimized reaction conditions, affording the desired product **4a** as a mixture of inseparable diastereomers in a 1.5 : 1 ratio with a 71% yield (Scheme 3). Subsequent oxidation of the Bpin group using  $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$  yielded the corresponding alcohols *anti*-**5a** (56%) and *syn*-**5a** (35%) as separable diastereomers, which were easily purified *via* simple column chromatography. It is interesting to observe that the (*E*)-isomer of the 1,3-indandione substrate reacts just as effectively as the (*Z*)-isomer.

For ease of handling, we performed a one-pot borylative cyclization/oxidation of 1,3-indandiones under standard reaction conditions, followed by the sequential addition of  $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$  (Table 4). We briefly screened this reaction with substrates featuring various benzyl groups at the prochiral quaternary center, yielding separable diastereomeric products *anti*-5 and *syn*-5. Electronically diverse substituents on the benzyl group provided high yields and excellent enantioselectivities (**5a–5d**). However, a sterically demanding ortho-substituted benzyl group resulted in only a trace amount of *syn*-product from the (*E*)-isomer and predominantly *anti*-5e from the (*Z*)-isomer.

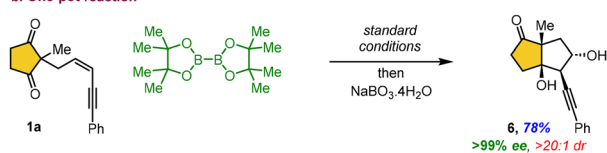
Table 4 One-pot borylative cyclization/oxidation of 1,3-indandiones<sup>a,b,c,d</sup>

<sup>a</sup> Reaction conditions: Same as in Table 2 and then  $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$  (150 mg, 1.5 mmol, 5.0 equiv.) was added in the same reaction. <sup>b</sup> Isolated yields of respective diastereomers. <sup>c</sup> Enantiomeric excess (ee) was determined by chiral HPLC analysis. <sup>d</sup> The *dr* was observed from <sup>1</sup>H NMR analysis of the crude reaction mixture. SM = starting material.

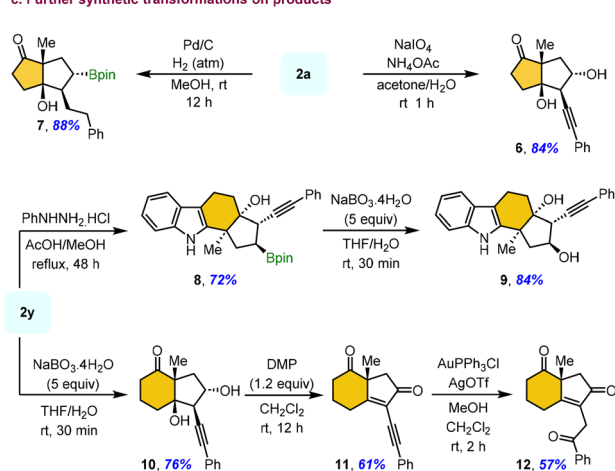
## a. Gram-scale reactions



## b. One-pot reaction



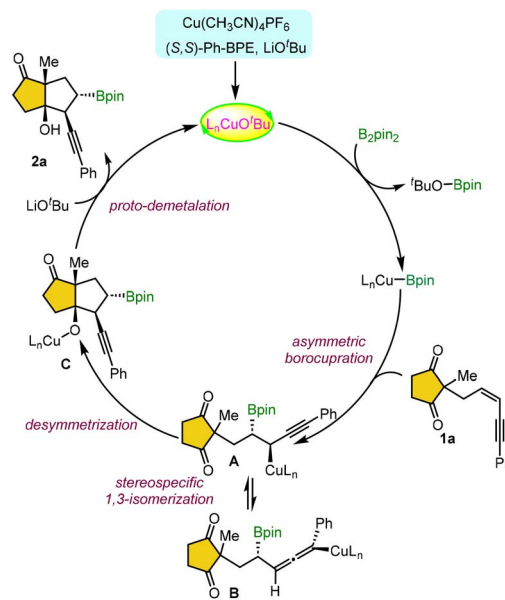
## c. Further synthetic transformations on products



Scheme 4 Large-scale reactions and further transformations.

Gram-scale reactions using (Z)-1a and (Z)-1y were carried out with reduced catalyst loading under standard conditions, affording the desired products *anti*-2a and *anti*-2y, respectively, without any significant loss in yield or enantioselectivity (Scheme 4a). The one-pot borylative cyclization, followed by the sequential addition of the mild oxidizing agent sodium perborate, afforded the corresponding alcohol **6** in a similar yield with exclusive enantioselectivity (Scheme 4b). Interestingly, the reaction with the strong oxidizing agent sodium periodate also afforded alcohol **6** in high yield, instead of undergoing boronic ester hydrolysis (Scheme 4c). The Pd/C-catalyzed hydrogenolysis of compound **2a** successfully reduces the triple bond, providing bicyclic ketone **7** in 88% yield. The Fischer cyclization of compound **2y** with phenylhydrazine furnished a highly functionalized tetracyclic fused indole **8** in 72% yield. Subsequent oxidation of **8** with sodium perborate afforded the corresponding alcohol **9** in 84% yield. Interestingly, direct oxidation of **2y** with sodium perborate yielded alcohol **10**, which upon Dess–Martin periodinane (DMP) oxidation provided the  $\alpha$ -alkynyl enone **11** via sequential alcohol oxidation and *tert*-alcohol elimination in good yield. This highly reactive, fused, electron-deficient enyne **11** serves as a promising intermediate for diverse cycloaddition reactions. In addition, Au(I)-catalyzed hydration of enyne **11** in methanol afforded aryl ketone **12** in 57% yield.

Based on the proposed copper catalytic cycle, the ligated copper alkoxide complex  $\text{LnCuOtBu}$  is generated *in situ* in the presence of a chiral ligand and base (Scheme 5). This complex



Scheme 5 Plausible reaction mechanism.

undergoes  $\sigma$ -bond metathesis with a diboron reagent, yielding the  $\text{LnCu-Bpin}$  species. The enantioselective and regioselective 1,2-*syn*-addition of  $\text{LnCu-Bpin}$  to the 1,3-enyne-tethered cyclic-1,3-dione **1a** leads to the formation of a propargylic copper intermediate A. This intermediate exists in equilibrium with an axially chiral allenyl-copper intermediate B via a stereospecific isomerization. Subsequent desymmetrization through annulation of propargylic intermediate A furnishes the desired product **2a**, while the catalytic cycle is completed by regenerating  $\text{LnCu-OtBu}$  via a copper alkoxide intermediate C in the presence of a base.

## Conclusions

In summary, we have developed a stereospecific, enantioselective copper(I)-catalyzed borylative cyclization of prochiral 1,3-enyne-tethered cyclic-1,3-diones with excellent diastereoselectivity. This asymmetric desymmetrization reaction efficiently delivers highly functionalized chiral octahydropentalenes bearing four contiguous stereocenters. Notably, the use of a BPE-ligand resulted in >99% ee for most examples. Additionally, (Z)-1,3-enyne substrates react more rapidly than their (*E*)-isomers, affording borylation products in high yields under standard reaction conditions. Ongoing studies in our laboratory are focused on further Cu(I)-catalyzed stereoselective transformations.

## Data availability

The data supporting this article have been included as part of the ESI.†

## Author contributions

G. R. and V. B. P. performed the experiments and analyzed the experimental data; J. B. N. conducted the single X-ray

crystallographic analysis; R. C. designed and supervised the project and wrote the manuscript with the assistance of co-authors.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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