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Halogenated salt assisted Cu-catalyzed asymmetric 1,4-borylstannation of 1,3-enynes: enantioselective synthesis of allenylstannes†

Jialin Ye,[a] Yang Liao,[bc] Hao Huang,[bc] Yang Liu,[bc] Dongmei Fang,[bc] Min Wang,*[bc] Lianrui Hu*[d] and Jian Liao *[abc]

An enantioselective 1,4-borylstannation of 1,3-enynes employed a chiral sulfoxide phosphine (**SOP**)/Cu complex as a catalyst, and the desired products, chiral allenylstannes, were first synthesized by asymmetric catalysis with satisfactory yields and enantioselectivies. In this protocol, a catalytic amount of additive, a halogenated salt, plays a crucial role in the success. Control experiments and theoretical studies disclosed that the four-membered ring transmetallation transition states which were stabilized by a halide anion are the key to yields and stereochemical outcomes.

Introduction

Developing novel and efficient methods to prepare axially chiral allenes, an important class of skeletons broadly present in natural products, pharmaceuticals, and other materials and which serve as synthetic intermediates, is of great interest.[1] Compared to classically predominant strategies, *e.g.* resolution[2] and stereospecific transformation of chiral substrates,[3] accessing chiral axial allenes *via* efficient asymmetric catalysis (transition metal catalysis and organocatalysis) of prochiral substrates is a long-standing challenge and highly desirable.

Transition metal-catalyzed 1,4-functionalizations of unactivated 1,3-enynes is becoming a valuable and straightforward option to prepare allenes,[4] mainly because of the ready availability of the starting materials, and two (mostly, different) functional groups can be installed for the construction of more complex multisubstituted allenes in a step-economic way. However, to date, the majority of reported methods have focused on racemic versions and there are only sporadically successful examples of asymmetric catalysis.[5,6] Until more recently, Cu-catalyzed 1,4-functionalization of unactivated 1,3-enynes has attracted significant attention with respect to the synthesis of axially chiral allenes. Representative examples by Hoveyda, Ge, Engle, Buchwald and their co-workers showed that, *via* the addition of chiral LCu–H species to 1,3-enynes, the *in situ* generated enantioenriched Cu-allenyl intermediates were immediately trapped by appropriate electrophiles (Bpin, proton and quinolone) to afford the corresponding chiral allenes efficiently (Scheme 1a).[6] These protocols could be termed enantioselective 1,4-hydrofunctionalization/semi-reduction;[6e] that is, one proton and another functional group were introduced into the allenyl frameworks. Despite these eminent advances, practical enantioselective 1,4-difunctionalization of 1,3-enynes dealing with two non-protonic functional groups has rarely been achieved. In 2018, Liu and co-workers disclosed an efficient radical 1,4-addition to access CF_3-containing allenyl nitriles. However, in their enantioselective version, an unsatisfactory stereochemical outcome, which could be caused by poor remote stereocontrol, was delivered (Scheme 1b).[7] We considered that a protocol involving trapping enantioenriched copper allenyl species generated by the addition of chiral Cu–Bpin species to the carbon–carbon double bond of 1,3-enynes, once appropriate electrophiles had been engaged, would afford chiral allenes.[8] In general, pursuing suitable electrophiles, particularly non-protonic electrophiles, is a challenging task.[9,10]

Recently, our lab reported a cooperative Cu/Pd-catalyzed enantioselective 1,4-borylarylation to synthesise chiral allenes. In that catalysis, apart from the exclusive 1,4-selectivities, it is notable that the stereochemical outcome benefited from the excessive usage of palladium catalyst (15 mol% Pd *vs.* 5 mol% Cu), due to ready racemization of enantioenriched copper–allenyl species (Scheme 1c).[8] This racemization process represents a serious challenge to access polyfunctional chiral allenes *via* this strategy. Instead of bimetal catalysis, we envisaged that the enantioenriched copper–allenyl species could be stabilized and, as a consequence, chiral allenes would be afforded with highly stereochemical outcomes. We imagined that this goal could be achieved through the identification of an appropriate additive, which is frequently presented in various asymmetric

[a]*College of Chemical Engineering, Sichuan University, Chengdu 610065, China*
[b]*Natural Products Research Center, Chengdu Institute of Biology, Chinese Academy of Sciences, Chengdu 610041, China. E-mail: jliao@cib.ac.cn; wangmin@cib.ac.cn*
[c]*University of Chinese Academy of Sciences, Beijing 10049, China*
[d]*School of Science and Research Center for Advanced Computation, Xihua University, Chengdu 610039, China. E-mail: hulianrui@iccas.ac.cn*

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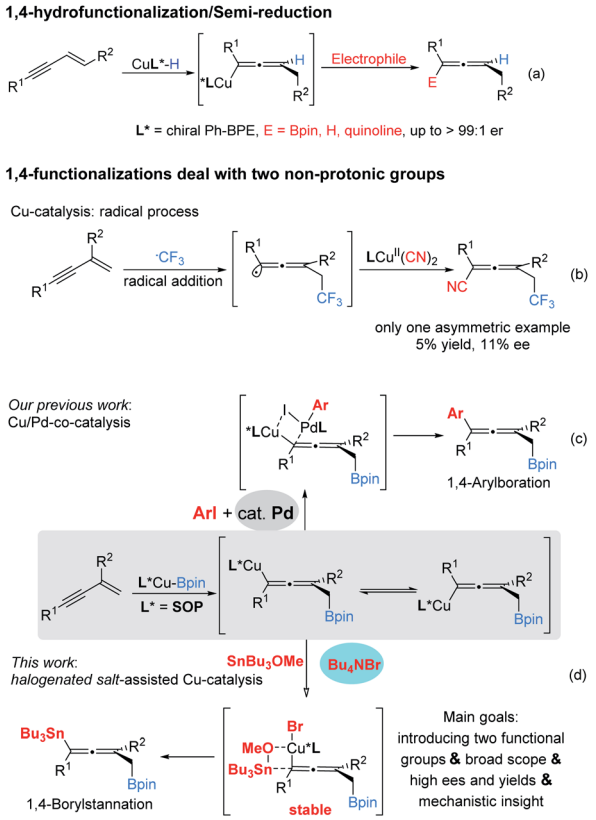


Scheme 1 Cu-catalyzed asymmetric 1,4-functionalization of 1,3-enynes.

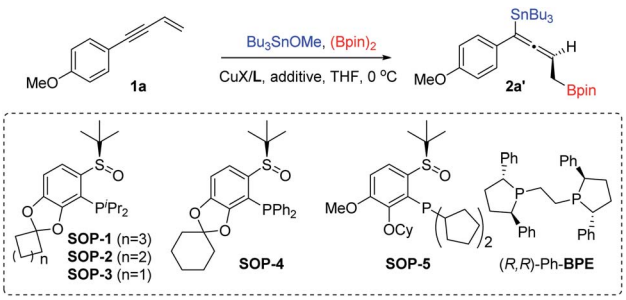
catalysis[11] and metal-catalyzed cross-couplings[12] and plays critical roles in stereocontrol, transformation efficiency and other outcomes. Meanwhile, a tin reagent was demonstrated to be a suitable electrophile in Cu-catalyed borylstannylation of alkynes (by Takaki *et al.*) and alkenes (by our group).[13]

Herein we report the first example of salt additive assisted copper catalyzed highly enantioselective 1,4-borylstannation of 1,3-enynes which was promoted by a chiral sulfoxide phosphine (**SOP**)[14] ligand. According to the present protocol, chiral allenylstannes,[15] which are very important synthetic intermediates due to their versatile transformation in many sophisticated reactions, were first synthesized *via* asymmetric catalysis; further, an added catalytic amount of additive plays a critical role in the stereochemical outcome; in addition, mechanistic investigations, including experimental and theoretical studies, which distinctly elucidate the role of additive salt (to date, an investigation of the mechanistic roles of additive remains a challenge)[11] are also presented in this article (Scheme 1d).

Results and discussion

1,3-Enyne **1a**, Bu_3SnOMe and bis(pinacolato)diboron (B_2pin_2) were chosen as reaction partners to commence our investigation on the enantioselective 1,4-borylstannation (Table 1; for detailed information about condition screening, please see ESI†). By employing an *in situ* prepared chiral P-di-*i*Pr-sulfoxide phosphine (**SOP-1**)/CuCl complex (10 mol%) as a pre-catalyst, the reaction was carried in THF and at 0 °C for 12 hours. The desired product **2a′** was afforded in a moderate NMR yield and stereochemical outcome (73% NMR yield, 76% ee; entry 1; an unidentified side product was observed). Comparing this to our previous study,[8] we reasoned that the moderate result here was not a result of poor stereocontrol over the chiral ligand but was caused by racemization of the enantioenriched copper–allenyl intermediate. To find a solution to this issue, salt additives, which have been proven to play an important role in some metal-catalyzed crossing-couplings,[12] were employed in this reaction. To our delight, in the presence of LiCl, both yield and enantioselectivity were significantly enhanced to an excellent level (97% yield, 94% ee, entry 2), and it is notable that a catalytical amount of LiCl enables this efficiency. Encouraged by this result, we then turned our attention to ligand evaluation. All reactions with P-di-*i*Pr-sulfoxide phosphine ligands (**SOP-1**–**3**) bearing a benzodioxole skeleton produced **2a′** in excellent yields and the good to excellent stereocontrol outcomes were determined from the ring size (94–97% yield, 88–94% ee,

Table 1 Optimization of reaction conditions[a]

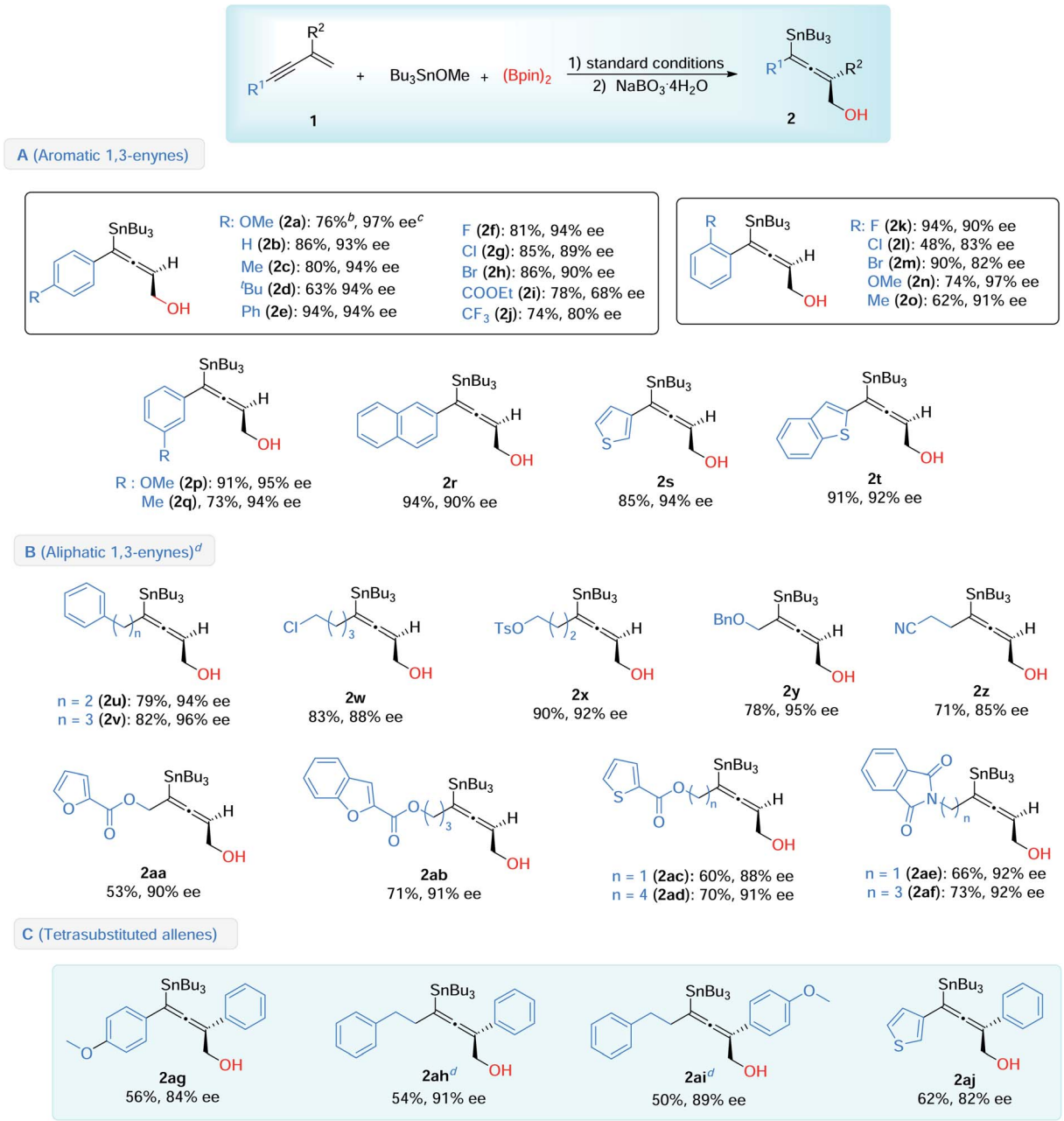


Entry	Ligand	CuX	Additive	Yield[b] (%)	ee[c] (%)
1	**SOP-1**	CuCl	None	73	76
2	**SOP-1**	CuCl	LiCl	97	94
3	**SOP-2**	CuCl	LiCl	95	91
4	**SOP-3**	CuCl	LiCl	94	88
5	**SOP-4**	CuCl	LiCl	75	82
6	**SOP-5**	CuCl	LiCl	80	88
7	**(*R*,*R*)-Ph-BPE**	CuCl	LiCl	n.r.	n.d.
8	**SOP-1**	CuCl	LiBr	95	92
9	**SOP-1**	CuCl	$Bu_4NF\cdot 3H_2O$	74	94
10	**SOP-1**	CuCl	$Bu_4NCl\cdot H_2O$	95	96
11	**SOP-1**	CuCl	Bu_4NBr	99	96
12	**SOP-1**	CuCl	Bu_4NI	99	95
13	**SOP-1**	CuBr	Bu_4NBr	99	97
14	**SOP-1**	CuI	Bu_4NBr	99	96
15[d]	**SOP-1**	CuBr	Bu_4NBr	99 (76)[e]	97

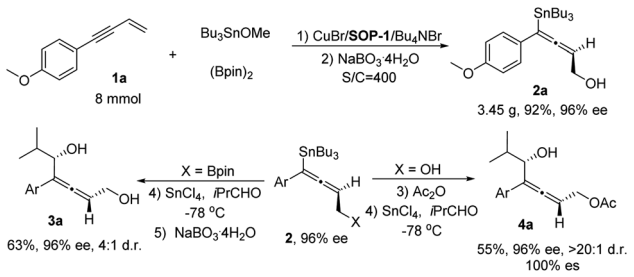
[a] Unless otherwise noted, reactions were carried out with **1a** (0.2 mmol), Bu_3SnOMe (0.3 mmol), $(Bpin)_2$ (0.3 mmol), **L** (12 mol%), Cu salt (10 mol%), additive (10 mol%) in THF (1.0 mL) at 0 °C for 12 h. [b] Determined by crude ^1H NMR analysis with dimethyl terephthalate as internal standard, n.r. = no reaction, n.d. = not determined. [c] The ee was determined by chiral HPLC analysis of compound **2a**, which was prepared *via* oxidation of the C–Bpin group of **2a′** to the corresponding primary alcohol (C–OH). [d] (CuBr1 mol%), **SOP-1** (1.2 mol%), Bu_4NBr (1 mol%). [e] In parentheses, isolated yield of **2a**.

entries 2–4). Similarly, P-di-Ph-(**SOP-4**) and P-di-cyclopentyl-sulfoxide phosphine (**SOP-5**) ligands also work well but slightly lower yields and enantioselectivities were afforded (75–80% yield, 82–88% ee, entries 5–6). A commercially available ligand (***R*,*R*)-Ph-BPE**, which has been successfully employed in the asymmetric 1,4-hydrofunctionalization of 1,3-enynes, failed to generate the desired product (entry 7).[16] We next examined the impact of salt additives on the reaction. LiBr furnished a similar result to LiCl. Ammonium salts (Bu_4NX, X = F, Cl, Br and I) were obviously beneficial both for yields and ees (entries 8–12). These results highlight the importance of chiral sulfoxide phosphine ligands (**SOP**s) and halogenated salts for significant outcomes (yield and ee). Other copper salts like CuBr and CuI had a slight influence on ee value (entries 13–14). Thus, **SOP-1**, CuBr and Bu_4NBr were selected as preferential ligand, copper source and additive, respectively. And this catalytic system worked well when the catalyst loading was reduced to 1 mol%: **2a′** was obtained with 99% NMR yield and 97% ee (entry 15). The absolute configuration of the product was assigned to be an (*S*)-configuration by comparing its electronic circular dichroism

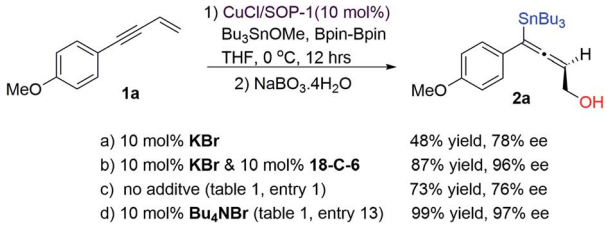
Table 2 Substrate scope[a]



[a] Reactions were performed with **1** (0.2 mmol), Bu_3SnOMe (0.3 mmol), $(Bpin)_2$ (0.3 mmol), **SOP-1** (1.2 mol%), CuBr (1 mol%), Bu_4NBr (1 mol%) in THF (1.0 mL) at 0 °C for 12 h. [b] Isolated yield. [c] Determined by chiral HPLC analysis. [d] Bu_3SnOMe was used (0.6 mmol).



Scheme 2 Gram-scale experiment and transformation of allenylstanne. Conditions: (1) **1a** (8 mmol), Bu_3SnOMe (12 mmol), $(Bpin)_2$ (12 mmol), **SOP-1** (0.024 mmol, 0.3 mmol%), CuBr (0.02 mmol, 0.25 mol%), Bu_4NBr (0.02 mmol, 0.25 mol%) in THF (4.0 mL) at 0 °C for 24 h. (2) $Na\ BO_3{\cdot}4H_2O$, THF-H_2O, rt, 2 h. (3) Ac_2O, TEA, DMAP, Et_2O, rt, 20 min. (4) −78 °C, $SnCl_4$, 30 min, then, *i*PrCHO, 30 min. (5) $NaBO_3{\cdot}4H_2O$, THF-H_2O, rt, 2 h. Ar = 4-Me-Ph.



Scheme 3 Control experiments.

(CD) spectrum with a theoretical simulated CD spectrum by the time-dependent DFT method (for details, see ESI†).

With the optimized conditions in hand, we then explored the scope of this enantioselective 1,4-borylstannation (Table 2). Firstly, we examined the aromatic 1,3-enynes. A wide range of enynes with different functional groups like alkyl (Me, *t*Bu, CF_3), halogens (F, Cl, Br), ether (OMe), aryl (Ph), ester (COOEt) and cyanide, at *para*-, *meta*-, and *ortho*-positions, could be readily converted into the corresponding products with generally good to excellent enantioselectivities (68–97% ee) (Table 2, A). Among these, a sensitive functional group (COOEt) was tolerated in this borylstannation process, with modest results (**2i**, 78% yield, 68% ee). Enynes with electron-withdrawing groups (4-CF_3, 2-Cl, 2-Br) showed inferior reactivities, giving the corresponding products with slightly lower ee values (**2j**, **2l**, **2m**). In addition, 2-naphthyl (**2r**) and heteroaromatic 1,3-enynes (**2s**, **2t**) were accommodated with excellent results (85–94% yields, 90–94% ee).

For the aliphatic scope of 1,3-enyne, different chain lengths and functional groups were investigated, and good enantioselectivities were observed in the process (85–96% ee) (Table 2, B). The chain lengths have little effect on the results (**2u** *vs.* **2v**, **2ac** *vs.* **2ad**, **2ae** *vs.* **2af**). Various functional groups, including halogen (**2w**), ether (**2y**), esters (**2x**, with aromatic heterocycles, **2aa–2ad**), nitrile (**2z**) and imides (**2ae** and **2af**), were compatible under these conditions, and the desired products were afforded with high enantioselectivities.

We further showed that this reaction could be used to access chiral tetrasubstituted allenes (Table 2, C). 2-Arylsubstituted 1,3-enynes were employed as substrates, under the standard conditions, and the desired tetrasubstituted chiral allenes were successfully obtained with satisfactory yields and enantioselectivities (**2ag–2aj**, 54–62% yields, 82–91% ee).

Finally, a gram-scale experiment and transformation of chiral allenylstanne product was carried out (Scheme 2). This protocol can be readily scaled up: with 8 mmol of **1a**, in the presence of 0.25 mol% of catalyst (S/C = 400) and a longer reaction time (24 h), the desired product **2a** (3.45 g) was obtained in 92% isolated yield and 96% ee. In the presence of $SnCl_4$ as Lewis acid,[17] the chiral allenylstanne **2a′** was transformed into allenylcarbinol, which was oxidized by $NaBO_3{\cdot}4H_2O$ to give the corresponding chiral allenyldiol **3a** with high enantioselectivity but moderate diastereoselectivity. Interestingly, treating the chiral allenylstanne **2a** with Ac_2O, the acetyl

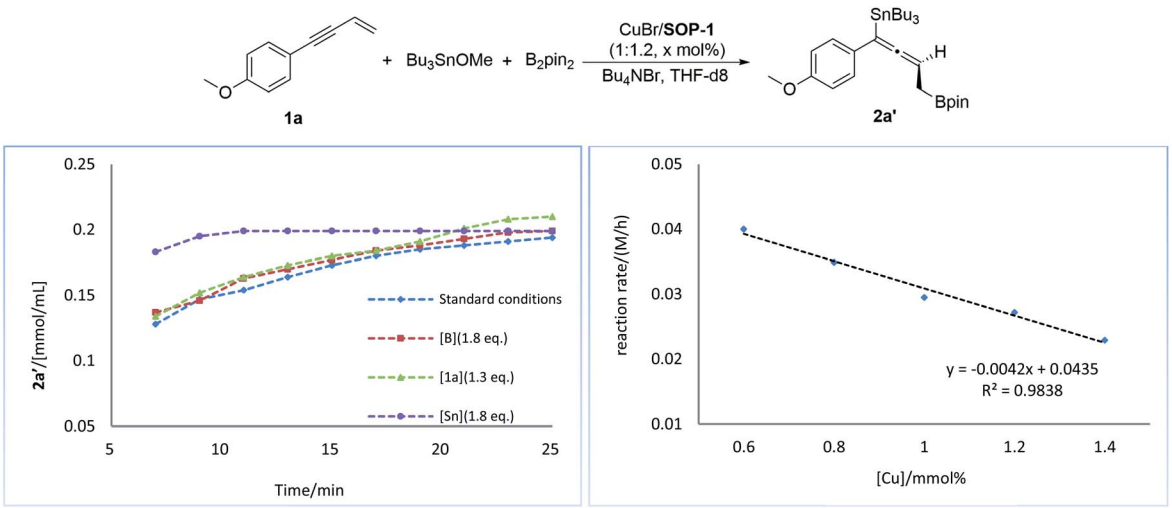


Fig. 1 Kinetic profiles of the reaction (left plot). Rate dependence on catalyst loading (right plot).

protected allene was obtained in quantitative yield, which could be stereospecifically transformed into allenylcarbinol **4a** with excellent diastereoselectivity (100% ee and >20 : 1 dr) under the same conditions. The Still-coupling of the Sn–C bond also worked with a moderate stereospecific transformation (see ESI† for details).

What concerned us next was the mechanism, particularly the mechanistic role of an additive in this metal-catalyzed asymmetric protocol. It is worth noting again that the additive (halogenated salts) was added in a catalytic amount in this protocol, which indicates that the role of the additive should be different from that in the previous transition metal-catalyzed cross-couplings.[12] An important task is to determine whether it is the cation or anion of Bu_4NBr, or the synergy between cation and anion that promotes the excellent stereochemical outcome in this protocol. We set up two control experiments (Scheme 3). Experiment a was conducted by adding KBr (10 mol%, equal to the Cu-catalyst) into this catalytic system and product **2a** was obtained with 48% NMR yield and 78% ee (similar to the results obtained by the reaction without an additive, see Table 1, entry 1); experiment b was conducted by adding KBr (10 mol%) and the equivalent crown ether (10 mol% 18-C-6), it is interesting that in the presence of 18-C-6, the yield and ee of product **2a** were greatly enhanced (87%, 96% ee). The difference between these two experiments (a and b) could be reasoned to be the solubility of the additive (KBr is poorly soluble in THF). In experiment b, the entrapment of potassium cation by 18-C-6 enables KBr to be soluble in THF. According to these data (experiments a, b, c and d), we could reason that, in this protocol, in the presence of a soluble halide anion, the racemization process could be avoided or slowed down dramatically *via* the coordination of a halide anion to the copper(I) intermediate, generating the desired chiral allene with high yields and excellent stereochemical outcomes.

Next, we conducted a series of experiments under synthetically relevant conditions. The progress of the reaction was monitored by *in situ* ^1H NMR spectroscopy (Fig. 1, left plot) (see ESI† for details). We first conducted a standard experiment, and we plotted the formation of product **2a′** as a function of time (blue line). We then performed the same experiment with changed amounts of **1a**, $(Bpin)_2$, and Bu_3SnOMe, respectively.

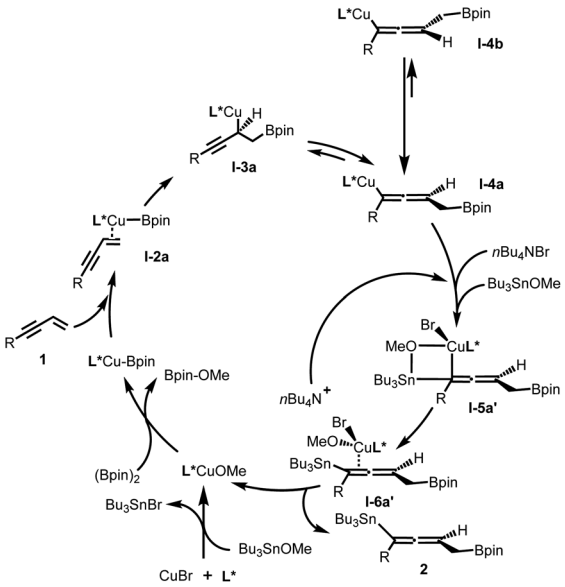


Fig. 3 Proposed catalytic cycle.

The rate of product formation in this experiment was represented. When the amount of **1a** and $(Bpin)_2$, was changed, the rate of product formation (green line and red line) was almost identical to that in the standard reaction (blue line), while the rate of product formation was sensitive to the concentration of Bu_3SnOMe (purple line), suggesting that this reaction has a zeroth order of dependence on **1a** and $(Bpin)_2$, and has a first order of dependence on Bu_3SnOMe. We next carried out initial rate experiments to probe kinetic information about the catalyst for this reaction, and the data demonstrated that the reaction can be promoted faster when the catalyst loading is increased, and the reaction rate showed a negative order on the catalyst (Fig. 2, right plot, and see ESI† for details). We then investigated the effect of salt (Bu_4NBr) on the reaction (Fig. 2, left plot) and an inhibiting effect on the reaction was observed when Bu_4NBr was overloaded (compared to CuBr). The nonlinear effect experiment indicated that this reaction follows a single-metal catalyzed model (Fig. 2, right plot). According to these results, we speculated that the inhibiting effect of the salt and the

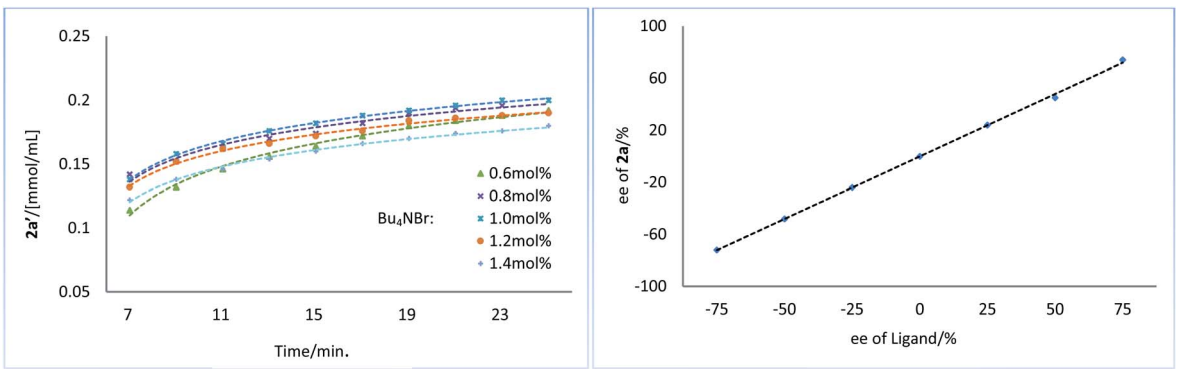


Fig. 2 Kinetic profiles of Bu_4NBr on reaction (left plot). Nonlinear effect experiment (right plot).

aforementioned negative order is probably caused by partial dimerization of the copper complex.[18]

Based on experimental and theoretical studies (see ESI† for details), a catalytic cycle of this protocol is proposed in Fig. 3. It is notable that, first, the bromide ion of the copper source (CuBr) was consumed in the process of formation of **SOP**Cu–OMe species with Bu_3SnBr as the side product; second, the added bromide ion (from Bu_4NBr) quickly coordinates with copper–allenyl species **I-4a** and Bu_3SnOMe to form a stable **I-5a′** intermediate *via* a four-membered ring transition state, before the racemization process (**I-4a** to **I-4b**) happened; third, the chirality-preserving transmetallation intermediate **I-6a′** released the bromide ion and desired product **2**, and subsequently turned over the catalytic cycle.

Conclusions

In summary, we reported an enantioselective Cu-catalyzed 1,4-borylstannation of unactivated 1,3-enynes, as the desired products, chiral allenylstannes, for the first time, were achieved *via* asymmetric catalysis. The achievements (introducing two functional groups, excellent yields and ees, broad substrate scope and high reactivity) of this protocol could be highlighted by chiral sulfoxide phosphine ligands (**SOP**s) and salt additives (halogenated salts). Mechanistic investigations, including control experiments and DFT calculations, disclosed that the halide anion played an important role in this protocol for stereochemical outcome by stabilizing the key copper–allenyl intermediate *via* a four-membered ring transition state to avoid the facile racemization of enantioenriched copper–allenyl species.

Conflicts of interest

There are no conflicts to declare.

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