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Enantioselective Copper-Catalyzed Three-Component Carboboronation of Allenes: Access to Functionalized Dibenzo[*b,f*][1,4]oxazepine Derivatives

Hao Deng[a], Ziwei Meng[a], Sifan Wang[a], Zheming Zhang[a], Yaqi Zhang[a], Yu Shangguan[a], Fazhou Yang[a], Dekai Yuan[a], Hongchao Guo[a], and Cheng Zhang[a]*

[a] Department of Applied Chemistry, China Agricultural University, 2 Yuanmingyuan West Road, Beijing 100193, China. Email: zhangc9711@cau.edu.cn or cheunggilbert@gmail.com

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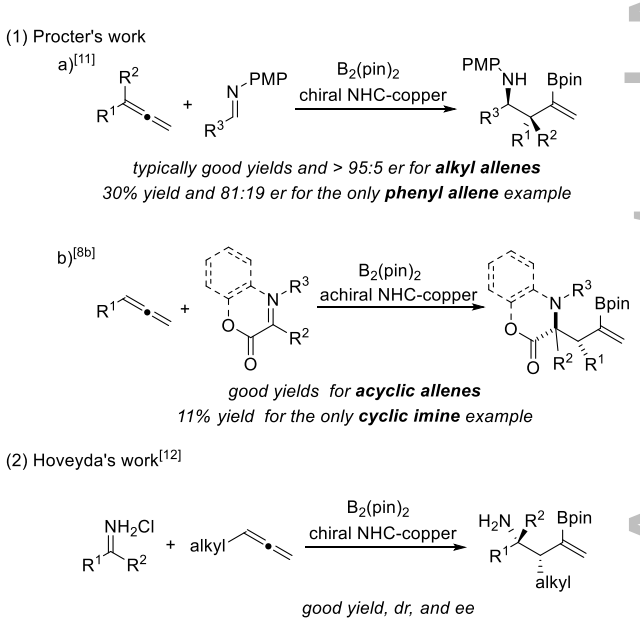
Abstract. A copper-catalyzed enantioselective three-component difunctionalization of allenes with seven-membered cyclic imines and bis(pinacolato)diboron ($B_2(Pin)_2$) to approach functionalized dibenzo[*b,f*][1,4]oxazepine derivatives is developed. The chiral products are obtained in up to 81% yield, >20:1 dr, and 98% ee when either a chiral diphosphine ligand or a chiral ferrocenyl-based P,N-ligand is used. Furthermore, the reaction exhibits reversed diastereoselectivities when the chiral diphosphine ligand and the chiral P,N-ligand are used respectively.

Keywords: cross-coupling; difunctionalization of allenes ; copper-catalyzed; asymmetric catalysis; boron

Homoallylic amines are important organic synthons to make natural products and biologically active compounds, and the development of synthetic methods to obtain such compounds has always been one of the interested research fields.[1] Boron-substituted homoallylic amine is of great interest for synthetic chemists, because they are able to be converted into diverse valuable motifs concisely. However, such highly functionalized boron-substituted homoallylic amines are hard to be obtained by traditional strategies, and it was not until 2006 that the first example for the synthesis of enantioselective boron-substituted homoallylic amines via a sequential palladium-catalyzed three-component method was reported by Morken and coworkers.[2] In spite of its effectiveness, the method suffered from complex procedures and high-cost catalysts.

In 2006, Sadighi made a seminal report that a boryl copper(I) complex could insert into alkenes and form boron-substituted alkyl copper species[3] which would undergo further nucleophilic addition or substitution reaction with electrophiles.[4] Alkynes are also reported being suitable substrates to undergo such three-component reactions.[5] Surprisingly, only recently have allenes been investigated to generate the allyl copper species reacting with electrophiles[6], such as carbonyl compounds[7], imines[8], electron deficient alkenes[9], and others[10]. Among these, boron-substituted homoallylic amines were obtained when imines were employed as electrophiles, and its asymmetric versions were also achieved when specific chiral ligands were used.

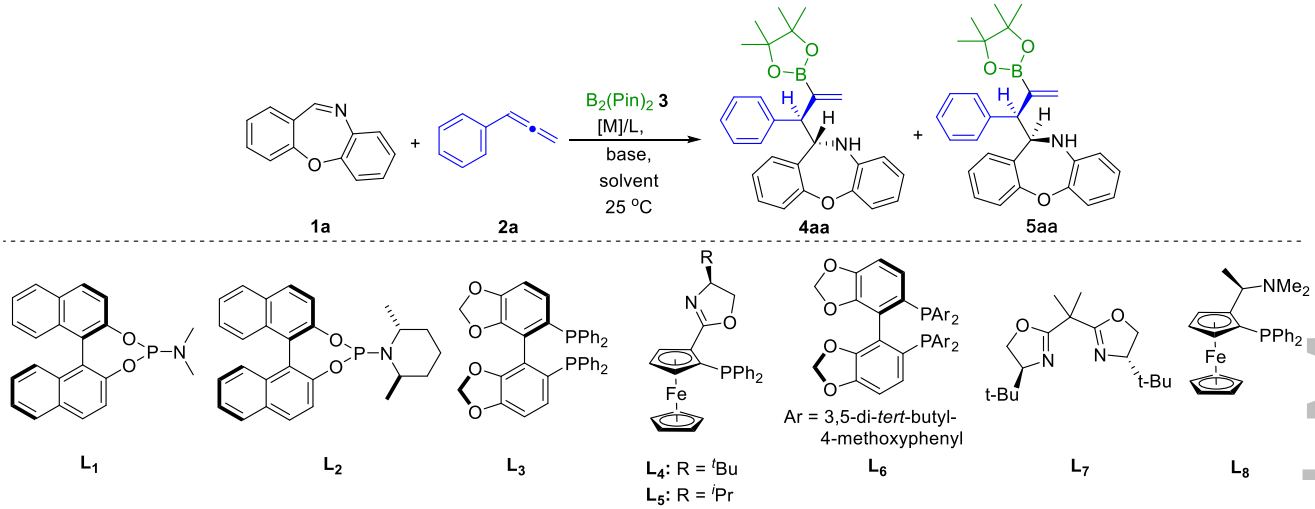


Scheme 1. Previous work for copper-catalyzed three component carboboronation of allenes.

In 2016, Procter group disclosed a highly chemoselective and diastereoselective N-heterocyclic carbene (NHC)/Cu-catalyzed three-component borylcarbonation of allenes with $B_2(Pin)_2$ and

imines.[8a] Latterly, they achieved an enantioselective version of the reaction by employing a chiral NHC-ligand combined with copper iodide, and it afforded the chiral homoallylic amines with moderate to high diastereoselectivities and enantioselectivities (Scheme 1a).[11] Very recently, Hoveyda et al developed an effective method to synthesize homoallylic primary amine with exclusive diastereoselectivities and high enantioselectivities via three-component coupling reactions of $B_2(Pin)_2$, alkyl allenes, and NH-ketimine salts (Scheme 1c).[12] However, among these, only the type of chiral NHC-ligands was employed to control diastereoselectivities and enantioselectivities for the homoallylic amines. In addition, the substrate scope is confined to acyclic imines and mostly alkyl allenes, while cyclic imines[8b] and phenyl allenes[11] showed sluggish reactivity and low selectivity. As a result, expanding the substrate scope to phenyl allenes and cyclic imines, as well as the developement of diverse effective chiral ligands are highly desired. Given the prevalence of the scaffold of dibenzo-1,4-oxazepines in therapeutic drug development,[13] we are interested to incorporate such chiral boron-substituted homoallylic amines into the dibenzo-1,4-oxazepines by using seven-membered heterocyclic imines as electrophiles. Herein, we report a diastereo- and enantioselective copper-catalyzed three-component difunctionalization of allenes with $B_2(Pin)_2$ and seven-membered heterocyclic imines in the presence of a chiral diphosphine- or P,N-ligand , and the diastereoselectivity for the reaction is reversed when the two chiral ligands are switched.

Table 1. Optimization of reaction conditions[a]

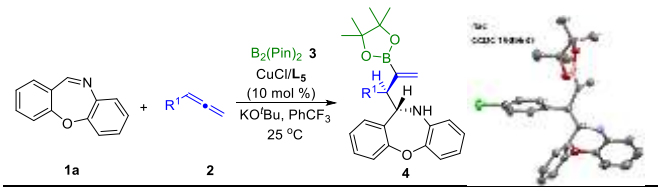


Entry	[M]/**L** (x mol %)	Base	Solvent	Yield (%)[b]	Dr (**4aa**:**5aa**)[c]	Ee (%, major)[d]
1	CuCl/**L**$_1$ (10)	KO^{t}Bu	$PhCF_3$	14	-	0
2	CuCl/**L**$_2$ (10)	KO^{t}Bu	$PhCF_3$	57	-	0
3	CuCl/**L**$_3$ (10)	KO^{t}Bu	$PhCF_3$	91	2:1	67
4	CuCl/**L**$_4$ (10)	KO^{t}Bu	$PhCF_3$	78	>20:1	72
5	**CuCl/L$_5$ (10)**	**KO^{t}Bu**	**$PhCF_3$**	**77**	**5:1**	**87**
6	**CuCl/L$_6$ (10)**	**KO^{t}Bu**	**$PhCF_3$**	**54**	**1:4**	**96**
7	CuCl/**L**$_7$ (10)	KO^{t}Bu	$PhCF_3$	32	-	3
8	CuCl/**L**$_8$ (10)	KO^{t}Bu	$PhCF_3$	26	-	0
9	CuBr/**L**$_5$ (10)	KO^{t}Bu	$PhCF_3$	15	-	-
10	CuI/**L**$_5$ (10)	KO^{t}Bu	$PhCF_3$	10	-	-
11	CuCl/**L**$_5$ (10)	LiO^{t}Bu	$PhCF_3$	70	4:1	49
12	CuCl/**L**$_5$ (10)	NaO^{t}Bu	$PhCF_3$	57	4.2:1	87
13	CuCl/**L**$_5$ (10)	KOMe	$PhCF_3$	59	4:1	86
14	CuCl/**L**$_5$ (10)	KO^{t}Bu	THF	trace	-	-
15	CuCl/**L**$_5$ (10)	KO^{t}Bu	1,4-dioxane	trace	-	-
16	CuCl/**L**$_5$ (10)	KO^{t}Bu	Toluene	73	5:1	86
17	CuCl/**L**$_5$ (15)	KO^{t}Bu	$PhCF_3$	57	4:1	80
18	CuCl/**L**$_5$ (5)	KO^{t}Bu	$PhCF_3$	27	-	52
19[e]	CuCl/**L**$_5$ (10)	KO^{t}Bu	$PhCF_3$	52	5:1	88

[a] Unless otherwise indicated, all reactions were carried out with **1a** (0.1 mmol), **2a** (0.3 mmol), **3** (0.11 mmol), and base (0.1 mmol) with copper salt/ligand in 1 mL of solvent at 25 °C for 12 hours. [b]Total isolated yield. [c] Determined by ^{1}H NMR. [d] Determined by HPLC analysis using a chiral stationary phase. [e] Reaction was carried out at 10 °C.

At the outset of the experiment, phenyl allene **1a**, seven-membered heterocyclic imine **2a**, and $B_2(pin)_2$ were subjected to various copper salts, ligands, bases, and solvents, to probe optimal reaction conditions (Table 1).[14] First, CuCl, $PhCF_3$, and KO^{t}Bu were selected as the copper salt, solvent, and base respectively, and various chiral ligands are subjected to the reaction to investigate their catalytic efficacy (Table 1, entries 1-8). Monophosphoramidite ligands (**L$_1$** and **L$_2$**) gave sluggish to moderate yields of **4aa** but they did not exhibit any activity for the chiral induction of products (Table 1, entries 1-2). To great delights, the diphosphine ligand **L$_3$** affords the final product **4aa** in 91% total yields, 2/1 dr, and 67% ee (Table 1, entry 3). Ferrocene-based chiral P,N-ligand **L$_4$** afforded the product with improved yield, diastereoselectivity and enantioselectivity (Table 1, entry 4), and replacement of **L$_4$** with **L$_5$** made the best performance when it furnished product **4aa** in 77% yield, 5/1 dr, and 87% ee (Table 1, entry 5). Interestingly, the reaction gave reversed diastereoselectivity when the stereo-bulky diphosphine ligand **L$_6$** was used, and product **5a** was obtained in 54% yield and 96% ee (Table 1, entry 6). However, N,N-ligand **L$_7$** and P,N-ligand **L$_8$** were not suitable ligands when they gave poor yields of products and low enantioslectivities (Table 1, entries 7-8). Replacing CuCl with CuBr or CuI greatly impaired the reaction when the product was obtained in extremely low yield (Table 1, entries 9-10). The reason for this phenomenon might be that NHC/Cu complexes formed from CuBr and CuI are prone to be affected by trace of water in $PhCF_3$. Various bases were then examined as well (Table 1, entries 11-13), and ^{t}BuOK still gave the best performance, and other bases, such as ^{t}BuOLi, ^{t}BuONa, and MeOK, gave decreased yields, diastereoselectivities, and enantioselectivities of the product. Finally, different kinds of solvents were screened (Table 1, entries 14-16), and it showed that THF and 1,4-dioxane were unfavorable solvents when trace of product **4aa** was detected. Toluene showed relatively inferior result to $PhCF_3$. Increasing or decreasing the loading amounts of the copper salt and the ligand gave harmful results to the reaction (Table 1, entries 17-18). Lowered temperature did not show better diastereoselectivity and enantioselectivity, but afforded the product in much lower yield (Table 1, entry 19).

Table 2. Substrate scope expansion for allenes[a]



Entry	R^1	**4**	Yield (%)[b]	Dr (**4:5**)[c]	Ee (%)[d]
1	Ph (**2a**)	**4aa**	77	5:1	87
2	4-BrPh (**2b**)	**4ab**	76	3.4:1	85
3	4-ClPh (**2c**)	**4ac**	75	4:1	87
4	4-MePh (**2d**)	**4ad**	57	3:1	85
5	4-EtPh (**2e**)	**4ae**	50	3.2:1	88
6	4-CF_3Ph (**2f**)	**4af**	65	4.6:1	81
7	2-MePh (**2g**)	**4ag**	65	16:1	92
8	3-MePh (**2h**)	**4ah**	68	4.6:1	88
9	2-MeOPh (**2i**)	**4ai**	64	6.6:1	92
10	3,4-$Me_2C_6H_4$ (**2j**)	**4aj**	64	4:1	89
11	2,6-$Me_2C_6H_4$ (**2k**)	**4ak**	81	10:1	94
12[e]	Cy (**2l**)	**4al**	65	>20:1	98
13	$PhCH_2CH_2$ (**2m**)	**4am**	50	10:1	76

[a] Unless otherwise indicated, all reactions were carried out with **1a** (0.1 mmol), **2** (0.3 mmol), **3** (0.11 mmol), and KO^{t}Bu (0.1 mmol) with CuCl/**L$_5$** (10 mmol %) in 1 mL of $PhCF_3$ at 25 °C for 12 hours. [b]Total isolated yield. [c] Determined by ^{1}H NMR. [d] Determined by HPLC analysis using a chiral stationary phase. [e] **L$_6$** was used as the ligand.

After the determination of optimal reaction conditions, we then evaluated the efficiency of the catalytic method by expanding the substrate scope of allenes. Allenes bearing various substituents as well as diverse substituted patterns were subjected to the optimal reaction conditions (Table 2). With respect to phenyl allenes, no matter electron-withdrawing groups or electron-donating groups substituted phenyl allenes, corresponding products are obtained in moderate to good yields and diastereoselectivities, along with high enantioselectivities (Table 2, entries 1-11). Strong electron-withdrawing group CF_3 on 4-position of the phenyl ring showed corrosive effect on the enantioselectivity of corresponding product (Table 2, entry 6). Regarding substituted positions on the phenyl ring, 2-substituted phenyl allene gave much higher diastereoselectivity than the 3- or 4-substituted counterparts (Table 2, entries 4, 7 and 8). Interestingly, the 2,6-dimethylphenyl allene afforded the corresponding product with much better yields and diatereoselectivity, along with higher enantioselectivity than the 3,4-dimethylphenyl allene (Table 2, entry 11). The alkyl allene **2l** is a suitable substrate for the reaction since it formed the corresponding product **4al** in excellent diastereoselectivity and enantioselectivity albeit in moderate yield (Table 2, entry 12). However, when phenylethyl allene **2m** is subjected to the reaction, both the diastereoselectivity and enantioselectivity of the product were greatly decreased (Table 2, entry 13). In addition, the absolute configuration of product **4ac** was determined by X-ray crystallography.[15]

Table 3. Substrate scope expansion for imines[a-d]

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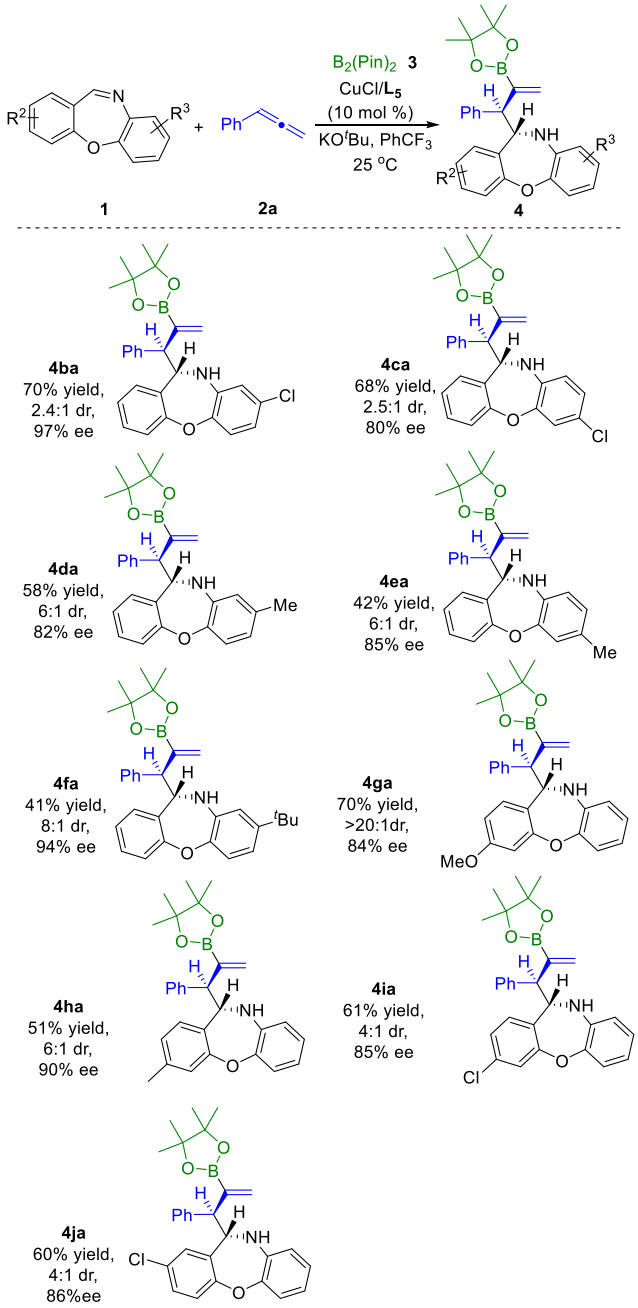
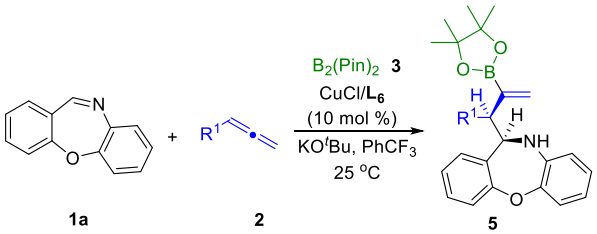


[a] All reactions were carried out with **1** (0.1 mmol), **2a** (0.3 mmol), **3** (0.11 mmol), and KO^{t}Bu (0.1 mmol) with CuCl/**L$_5$** (10 mmol %) in 1 mL of $PhCF_3$ at 25 °C for 12 hours. [b]Total isolated yield. [c] Determined by ^{1}H NMR. [d] Determined by HPLC analysis using a chiral stationary phase.

We then examined the substituent effects of the seven-membered heterocyclic imines on the reaction (Table 3). Typically, imines bearing electron-withdrawing group on both sides of phenyl rings afforded higher yields of corresponding products (**4ba**, **4ca**, and **4ja**) than that with electron-donating groups (**4da-4fa,** and **4ha**), except for **4ga**. The reason might be that electron-withdrawing groups make the imines more electrophilic to undergo nucleophilic attack by allyl copper intermediates. With respects to diastereoselectivities, however, imines with electron-donating groups gave better results (**4da-4ha**). Position of substituent on the phenyl ring of imines did not affect the diastereoselectivity and enantioselectivity too much for the reaction.

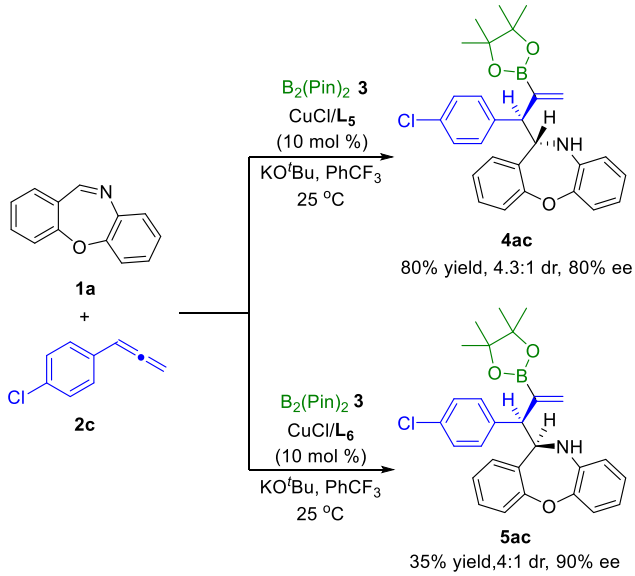
Table 4. Substrate scope for reversed diastereoselectivities using **L$_6$** as the ligand[a]



Entry	R^1	5	Yield (%)[b]	Dr (**5:4**)[c]	Ee (%)[d]
1	Ph (**2a**)	**5aa**	54	4:1	96
2	4-BrPh (**2b**)	**5ab**	58	7:1	97
3	4-ClPh (**2c**)	**5ac**	50	>20:1	93
4	4-MePh (**2d**)	**5ad**	56	10:1	94
5	Cy	**5ae**	-	<1:20	-

[a] All reactions were carried out with **1**a (0.1 mmol), **2** (0.3 mmol), **3** (0.11 mmol), and KO^{t}Bu (0.1 mmol) with CuCl/**L$_6$** (10 mmol %) in 1 mL of $PhCF_3$ at 25 °C for 12 hours. [b]Total isolated yield. [c] Determined by ^{1}H NMR. [d] Determined by HPLC analysis using a chiral stationary phase.

Since the reaction with ligand **L$_6$** gave reversed diastereoselectivity during optimization of reaction conditions (Table 1, entry 6), we then tried to obtain the diastereoisomers for other substrates by switching the ligand from **L$_5$** to **L$_6$** (Table 4). Results showed that phenyl allenes bearing substituents with different electronic properties (Br, Cl, and Me) were all suitable substrates, and the corresponding diastereoisomers are obtained in moderate yields, good to excellent diastereoselectivities, along with excellent enantioselectivities (Table 4, entries 2-4). However, when alkyl allene **2l** is subjected to the same conditions, the reaction did not show reversed diastereoselectivity (Table 4, entry 5 and Table 2, entry 12). Reactions underwent sluggishly when imines bearing substituents on the phenyl ring are employed in the reaction, and the corresponding diastereoselectivity-reversed products **5** are obtained in low yields.[14]



Scheme 2. Scale-up synthesis of product **4ac** and **5ac**.

In the end, scale-up syntheses of **4ac** and **5ac** were also performed (Scheme 2). Under optimal reaction conditions by using $\mathbf{L_5}$ as the ligand, product **4ac** is obtained in 80% yield, 4.3:1 dr, along with 80% ee. As expected, replacing ligand $\mathbf{L_5}$ with Ligand $\mathbf{L_6}$ resulted in product **5ac** in 40% yield, >20:1 dr, and 90% ee.

In summary, we have developed an enantioselective copper-catalyzed three-component coupling reaction of allenes with $B_2(pin)_2$ and seven-membered cyclic imines to synthesize highly functionalized chiral dibenzo[*b*,*f*][1,4]oxazepine derivatives. The reaction provides desired products in up to 81% yield, >20:1 dr, and 98% ee when either a chiral diphosphine ligand or a chiral ferrocenyl-based P,N-ligand is used. In addition, the reaction exhibited reversed diastereoselectivities when the chiral diphosphine ligand and the chiral P,N-ligand are used respectively.

Experimental Section

General procedure for asymmetirc carboboronation of allenes: CuCl (1 mg, 0.01 mmol, 10 mol %), a ligand (0.01 mmol, 10 mol %), KO^{t}Bu (11.2 mg, 0.1mmol) , dibenzo[*b*,*f*][1,4]oxazepine **1** (0.1mmol) and allene **2** (0.3mmol) were placed in an oven dried 20 mL Schlenk flask. The flask was evacuated for 0.5 h and backfilled with argon. $PhCF_3$ (0.5 mL) were added at room temperature under argon atmosphere. Then, $B_2(pin)_2$ (28 mg, 0.11 mmol) in 0.5 ml $PhCF_3$ was added and the resulting mixture was stirred at 25 ºC for 12 h. After the reaction is finished, the mixture was filtered through a short silica column and concentrated, and diastereoselectivities of products were determined by ^{1}H-NMR analysis. Finally, boron-subsituted dibenzo[*b*,*f*][1,4]oxazepine derivative **4** or **5** was obtained after the mixture was purified by silica gel column chromatography (hexane : EtOAc=10:1).

Acknowledgements

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[14] Please see supporting information for more information.

[15] CCDC 1909637 (**4ac**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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UPDATE

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