Copper-Catalyzed γ-Selective and Stereospecific Allylic Cross-Coupling with Secondary Alkylboranes

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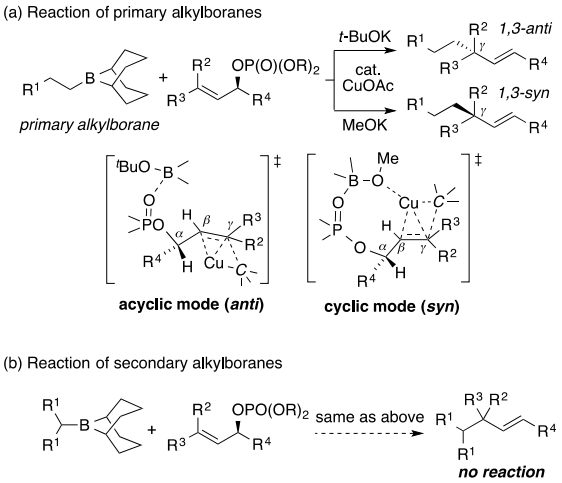
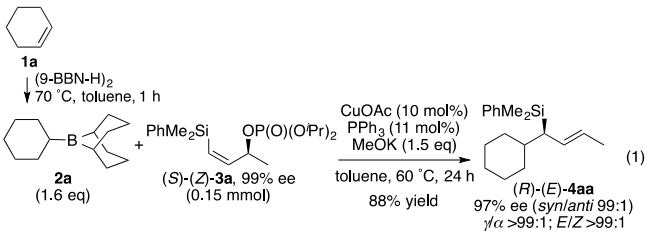
Abstract: The scope of the copper-catalyzed coupling reaction between organoboron compounds and allylic phosphates was expanded significantly by employing triphenylphosphine as a ligand for copper, allowing the use of *secondary* alkylboron compounds (alkyl-9-BBN). The reaction proceeded with complete γ-*E*-selectivity and preferential 1,3-*syn* stereoselectivity. Reaction of γ-silicon-substituted allylic phosphates afforded enantio-enriched α-stereogenic allylsilanes.

Copper-catalyzed allylic substitutions with organoboron compounds are of interest due to their broad substrate scope.[1,2] Previous reports have shown that sp^3-alkylboron compounds (alkyl-9-BBN) can be coupled with internal allylic systems with complete γ-selectivity using a catalytic amount of a copper(I) salt and a stoichiometric potassium alkoxide base.[3–5] Interestingly, the stereochemical cross-coupling between enantio-enriched chiral allylic phosphates and alkylboranes could be switched between the 1,3-*anti* and 1,3-*syn* forms relative to the leaving group by choosing the appropriate achiral alkoxide base with a specific steric demand: *t*-BuOK and MeOK showed 1,3-*anti* and 1,3-*syn* stereochemistry, respectively.[3c] Acyclic and cyclic bimodal participation of alkoxyborane species generated *in situ* in an organocopper addition–elimination sequence was proposed to account for the phenomenon of the *anti*-*syn* stereochemical reversal (Scheme 1a). However, only *primary* alkylboron compounds could be used as nucleophilic coupling partners. Neither the 1,3-*anti* and 1,3-*syn* form was effective in the reaction of *secondary* alkylboranes, probably due to increased steric demands of the transferring groups (Scheme 1b).

The present study describes the dramatic ligand effects of tertiary monophosphines, such as Ph_3P, Cy_3P, and tBu_3P, which enabled copper-catalyzed allylic cross-coupling between secondary alkylboron compounds (alkyl-9-BBN) and (*Z*)-acyclic or cyclic allylic phosphates. These ligand effects were most pronounced when the ligands were used as additives for the 1,3-*syn*-selective protocol (CuOAc/MeOK/toluene) in a previous study.[6] This new copper catalysis using secondary alkylboranes proceeded with complete γ-*E*-selectivity and preferential 1,3-*syn* stereoselectivity. These methods significantly broadened the scope of allylic C–C bond-forming cross-coupling reactions.



Scheme 1. Previous work (ref 3c).



In numerous studies for finding reaction conditions enabling the region- and stereoselective coupling between secondary alkylboron compounds and chiral secondary allylic electrophiles, we found critical effects of phosphine ligands for promoting this transformation. Specifically, the reaction between cyclohexylborane **2a**, which was prepared *via* hydroboration of cyclohexene (**1a**) and an enantio-enriched chiral γ-silylated allylic phosphate [(*S*)-(*Z*)-**3a** (99% ee)] containing a diisopropyl phosphate leaving group in the presence of CuOAc (10 mol%), PPh_3 (11 mol%), and MeOK (1.5 eq) in toluene at 60 °C for 24 h afforded allylsilane (*R*)-(*E*)-**4aa** with 97% ee in 88% yield with complete γ- and *E*-selectivities (Eq 1 and Table 1, entry 3).[7] The absolute configuration of the coupling product indicated that the reaction occurred with 1,3-*syn* stereochemistry (*syn*:*anti* 99:1). The reported phosphine-free conditions, which gave 1,3-*syn* (CuOAc/MeOK/toluene) or 1,3-*anti* (CuOAc/^{t}BuOK/THF) stereochemical outcomes in a previous study on the reaction of primary alkylboranes (Scheme 1a), did not produce any coupling

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product, leaving the substrates almost unreacted (Table 1, entries 1 and 2).[3c,8]

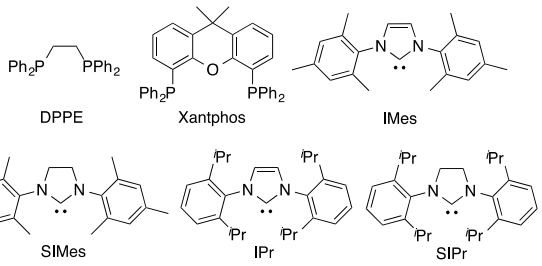
The effect of ligands on the reaction between **2a** and **3a** are shown in Table 1. Use of tri(4-methoxyphenyl)phosphine resulted in a significantly lower product yield and *syn*-stereoselectivity compared to PPh_3 (entry 4). No reaction occurred with the electron-deficient $P[3,5\text{-}(CF_3)C_6H_3]_3$ phosphine was used (entry 5). Use of PMe_3 produced a very low yield with moderate *syn* selectivity (*syn*:*anti* 88:12) (entry 6). The PEt_3 and PBu_3 promoted coupling efficiently, but *syn*-selectivity was decreased slightly compared to the excellent selectivity obtained with PPh_3 (entries 7 and 8). Interestingly, the bulkier monodentate trialkylphosphines, such as PCy_3 and P^tBu_3, were as effective as PPh_3 in terms of both product yield and *syn*-selectivity (entries 9 and 10). In contrast, bisphosphines such as DPPE and Xantphos, produced no reaction (entries 11 and 12). *N*-Heterocyclic carbene (NHC) monodentate ligands, such as IMes, SIMes, IPr, and SIPr, also did not promote the reaction (entries 13–16). Thus, PPh_3 was selected as the most useful additive for cost-effectiveness and handling ease (Eq. 1 and Table 1, entry 3).[9]

The effect of the stoichiometric base also is shown in Table 1. The use of EtOK instead of MeOK in the presence of PPh_3 resulted in a slight decrease in *syn*-stereoselectivity (entry 17). No reaction occurred with the sterically more demanding base *t*BuOK, which induced 1,3-*anti* stereochemistry under phosphine-free conditions in the reaction of primary alkylboranes (entry 18).[10]

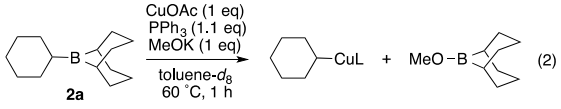
Table 1. Effects of ligands and bases[a,b]

entry	ligand	base	yield[c,d] (%)	*syn*:*anti*[e]
1	none	MeOK	0	–
2	none	^{t}BuOK	0	–
3	PPh_3 (eq 1)	MeOK	88	99.5:0.5
4	$P(4\text{-}MeOC_6H_4)_3$	MeOK	55	96.5:3.5
5	$P[3,5\text{-}(CF_3)C_6H_3]_3$	MeOK	0	–
6	PMe_3	MeOK	13	88:12
7	PEt_3	MeOK	95	98.5:1.5
8	PBu_3	MeOK	90	92:8
9	PCy_3	MeOK	93	99:1
10	$Pt\text{Bu}_3$	MeOK	83	99:1
11	DPPE	MeOK	0	–
12	Xantphos	MeOK	0	–
13	IMes	MeOK	0	–
14	SIMes	MeOK	0	–
15	IPr	MeOK	0	–
16	SIPr	MeOK	0	–
17	PPh_3	EtOK	99	98:2
18	PPh_3	^{t}BuOK	0	–

[a] Reaction was conducted using **3** (0.15 mmol), alkylborane **2** (0.24 mmol), CuOAc (10 mol%), ligand (11 mol%), and base (0.225 mmol) in toluene at 60 °C for 24 h. [b] Alkylborane **2** was prepared in advance by hydroboration of alkene **1** with 9-BBN dimer in toluene at 70 °C for 1 h and used without purification. [c] Isolated yield of product based on **3**. [d] Isomeric ratios (γ/α >99:1, E/Z >99:1). Determined by ^{1}H NMR or GC of the crude product. [e] Selectivity was determined by HPLC.



To gain understanding into the mechanism of Cu-catalyzed cross-coupling with secondary alkylboranes, the effect of PPh_3 on the stoichiometric reaction with CuOAc, MeOK and cyclohexylborane **2a** in toluene-d_8 at 60 °C for 1 h was investigated (Eq. 2). Reaction in the presence of PPh_3 caused the complete disappearance of the signal for **2a** (δ 86.4 ppm), confirmed by ^{11}B NMR spectroscopy, and a new signal for 9-BBN-OMe appeared at a higher magnetic field (δ 55.5 ppm). In contrast, reaction in the absence of PPh_3 did not result in formation of 9-BBN-OMe. Therefore, PPh_3 is essential for B/Cu transmetalation.



Molecular modelling studies suggested that tertiary monophosphines would not be able to coordinate to the copper center in the cyclic organocopper addition–elimination transition state due to steric effects (Scheme 1a).[11] Therefore, a catalytic cycle for the copper-catalyzed γ-*syn*-selective allylic cross-coupling with secondary alkylboranes should involve coordination and dissociation of the phosphine ligand as shown in Figure 1. According to these considerations, the reduction of yield and *syn* selectivity in the reaction with PMe_3 may suggest that the Cu–P interaction would be persistent in the addition–elimination step. This should be reasonable, considering the higher coordination ability of PMe_3 as a compact ligand. The marginal reduction of the syn selectivity in the reactions with PEt_3 and PBu_3 may be due to partial coordination of these ligands in the addition–elimination step. In this context, the common features of PPh_3, PCy_3, and $Pt\text{Bu}_3$, showing the high product yields and syn selectivities, may be due to their moderate coordination abilities toward Cu, allowing timely coordination/dissociation equilibriums.

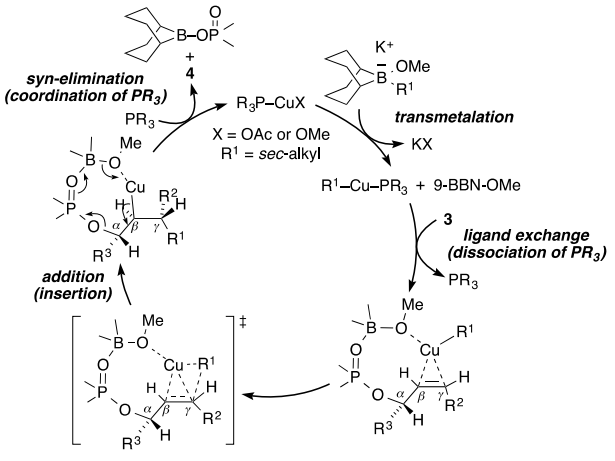
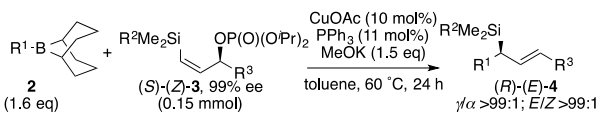


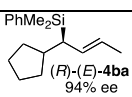
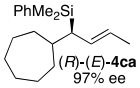
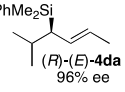
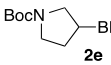
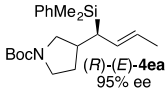
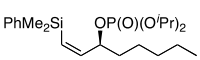
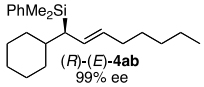
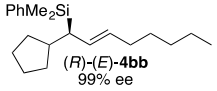
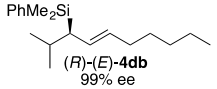
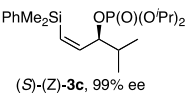
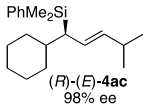
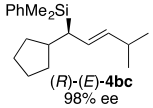
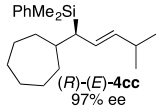
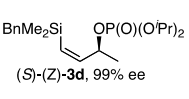
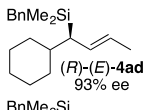
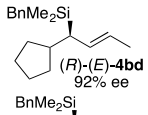
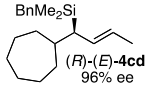
Figure 1. Proposed catalytic cycle for the copper-catalyzed γ-*syn*-selective allylic cross-coupling between secondary alkylboranes and secondary allylic phosphates.

The scope of copper-catalyzed regioselective and stereospecific cross-coupling reaction between secondary alkylboranes and enantio-enriched chiral γ-silylated allylic phosphates to afford enantio-enriched α-stereogenic chiral allylsilanes is summarized in Table 2.[12–14] Cyclic secondary alkylboranes **2b**,**c** with five- and seven-membered carbocycles underwent reaction with excellent *syn*-stereoselectivities (entries 1 and 2). Acyclic isopropylborane **2d** also was tolerated with a high level of stereoselectivity retained (entries 3 and 7). The heterocyclic secondary alkylborane **2e** with a carbamate group underwent stereospecific reaction resulting in a moderate product yield (entry 4).

The Me group at the α-position of **3a** could be replaced with *n*Pent (**3b**) or *i*Pr (**3c**) groups with excellent *syn*-selectivity retained (Table 2, entries 5–10). The allylic phosphate (*S*)-(*Z*)-**3d** with a $BnMe_2Si$ group at the γ-position reacted with cyclic secondary alkylboranes containing five-, six-, and seven-membered carbocycles with excellent *syn* selectivities (entries 11–13).

Table 2. Synthesis of chiral allylsilanes[a,b]

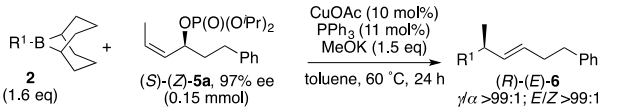


entry	borane	phosphate	product	yield[c,d] (%)	syn:anti[e]
1	 **2b**	(*S*)-(*Z*)-**3a** 99% ee	 (*R*)-(*E*)-**4ba** 94% ee	93	97.5:2.5
2	 **2c**	(*S*)-(*Z*)-**3a** 99% ee	 (*R*)-(*E*)-**4ca** 97% ee	80	99:1
3	 **2d**	(*S*)-(*Z*)-**3a** 99% ee	 (*R*)-(*E*)-**4da** 96% ee	94	98.5:1.5
4[f]	 **2e**	(*S*)-(*Z*)-**3a** 99% ee	 (*R*)-(*E*)-**4ea** 95% ee	47[f]	98:2
5	**2a**	 (*S*)-(Z)-**3b**, 99% ee	 (*R*)-(*E*)-**4ab** 99% ee	94	>99.5:0.5
6	**2b**	(*S*)-(*Z*)-**3b** 99% ee	 (*R*)-(*E*)-**4bb** 99% ee	93	>99.5:0.5
7	**2d**	(*S*)-(*Z*)-**3b** 99% ee	 (*R*)-(*E*)-**4db** 99% ee	88	>99.5:0.5
8	**2a**	 (*S*)-(Z)-**3c**, 99% ee	 (*R*)-(*E*)-**4ac** 98% ee	93	99.5:0.5
9	**2b**	(*S*)-(*Z*)-**3c** 99% ee	 (*R*)-(*E*)-**4bc** 98% ee	96	99.5:0.5
10	**2c**	(*S*)-(*Z*)-**3c** 99% ee	 (*R*)-(*E*)-**4cc** 97% ee	38	99:1
11	**2a**	 (*S*)-(Z)-**3d**, 99% ee	 (*R*)-(*E*)-**4ad** 93% ee	31	97:3
12	**2b**	(*S*)-(*Z*)-**3d** 99% ee	 (*R*)-(*E*)-**4bd** 92% ee	75	96.5:3.5
13	**2c**	(*S*)-(*Z*)-**3d** 99% ee	 (*R*)-(*E*)-**4cd** 96% ee	61	98.5:1.5

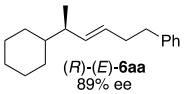
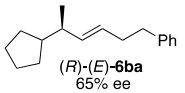
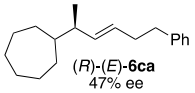
[a] Reaction was conducted with **3** (0.15 mmol), alkylborane **2** (0.24 mmol), CuOAc (10 mol%), PPh_3 (11 mol%), and MeOK (0.225 mmol) in toluene at 60 °C for 24 h. [b] Alkylborane **2** was prepared in advance by hydroboration of alkene **1** with 9-BBN dimer in toluene at 70 °C for 1 h and used without purification. [c] Isolated yield of the product based on **3**. [d] Isomeric ratios (γ/α >99:1, E/Z >99:1). Determined by ^{1}H NMR or GC of the crude product. [e] Enantiomeric excess was determined by HPLC. [f] Diastereomeric ratio (1:1).

The usefulness of this protocol was not limited to allylsilane synthesis but also could be applied to reaction of non-silicon-substituted acyclic allylic phosphates (Table 3). For example, reaction between allylic phosphate (*S*)-(*Z*)-**5a** (97% ee) and cyclohexylborane **2a** occurred with 96% *syn* selectivity to produce the Me-branched product (*R*)-(*E*)-**6aa** (entry 1). Reaction of cyclic secondary alkylboranes with a five- or a seven-membered ring also occurred, but 1,3-*syn* stereoselectivity was only moderate (entries 2 and 3).

Table 3. Allyl–alkyl coupling with non-silicon-substituted allylic phosphates[a,b]



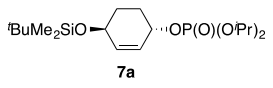
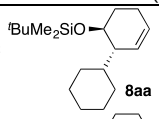
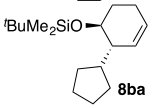
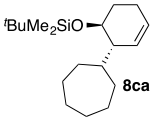
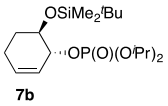
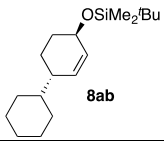
entry	borane	product	yield[c,d] (%)	syn:anti[e]

1	**2a**	 (*R*)-(*E*)-**6aa** 89% ee	88	96:4
2	**2b**	 (*R*)-(*E*)-**6ba** 65% ee	98	84:16
3	**2c**	 (*R*)-(*E*)-**6ca** 47% ee	78	74.5:25.5

[a] The reaction was carried out with **5** (0.15 mmol), alkylborane **2** (0.24 mmol), CuOAc (10 mol %), PPh_3 (11 mol %), and MeOK (0.225 mmol) in toluene at 60 °C for 24 h. [b] Alkylborane **2** was prepared in advance by hydroboration of alkene **1** with 9-BBN dimer in toluene at 70 °C for 1 h and used without purification. [c] Yield of the isolated product based on **5**. [d] Isomeric ratios (γ/α >99:1, E/Z >99:1). Determined by ^{1}H NMR or GC of the crude product. [e] The enantiomeric excess was determined by HPLC.

Cyclic allylic phosphates also could serve as substrates (Table 4). Coupling reactions between *trans*-2-cyclohexene-1,4-diol derivative **7a** and **2a** proceeded with excellent γ-selectivity and 1,3-*syn* selectivity relative to the leaving group, giving *trans*-1,2-isomer **8aa** (entry 1). Reactions with cyclopentyl or cycloheptylboranes also occurred with excellent 1,3-*syn* selectivity (entries 2 and 3). *Trans*-3-cyclohexene-1,2-diol derivative **7b** underwent coupling with excellent 1,3-*syn* selectivity (entry 4).

Table 4. Allyl–alkyl coupling with cyclic allylic phosphates[a,b]

entry	borane	phosphate	product	yield[c,d] (%)	syn:anti[e]
1	**2a**	 **7a**	 **8aa**	85	>99:1
2	**2b**	**7a**	 **8ba**	90	>99:1
3	**2c**	**7a**	 **8ca**	73	>99:1
4	**2a**	 **7b**	 **8ab**	49	93:7

[a] Reaction was conducted with **7** (0.15 mmol), alkylborane **2** (0.24 mmol), CuOAc (10 mol%), PPh_3 (11 mol%), and MeOK (0.225 mmol) in toluene at 60 °C for 24 h. [b] Alkylborane **2** was prepared in advance by hydroboration of alkene **1** with 9-BBN dimer in toluene at 70 °C for 1 h and used without purification. [c] Isolated yield of the product based on **7**. [d] Isomeric ratios (γ/α >99:1, E/Z >99:1). Determined by ^{1}H NMR or GC of the crude product. [e] The syn:anti selectivity was determined by ^{1}H NMR.

In summary, the scope of the copper-catalyzed coupling reaction between organoboron compounds and allylic phosphates was broadened significantly by employing triphenylphosphine as a ligand for copper, allowing the use of secondary alkylboron compounds (alkyl-9-BBN). The reaction proceeded with complete γ-*E*-selectivity and preferential 1,3-*syn* stereoselectivity. This is the first catalytic allylic substitution reaction with secondary alkylboron derivatives.

Experimental Section

Equation 1 shows a representative reaction. $(9\text{-BBN-H})_2$ (30.2 mg, 0.12 mmol) was placed in a vial containing a magnetic stirring bar. The vial was sealed with a Teflon®-coated silicon rubber septum followed by evacuation of the vial, which was then filled with argon. Cyclohexene (**1a**) (0.027 mL, 0.27 mmol) and toluene (0.3 mL) were added to the vial, and the mixture stirred at 70 °C for 1 h to prepare a secondary alkylborane. Then, CuOAc (1.8 mg, 0.015 mmol), PPh_3 (4.0 mg, 0.0165 mmol), and MeOK (15.7 mg, 0.225 mmol) were placed in another vial, which was sealed with a Teflon®-coated silicon rubber septum, and then evacuated and filled with argon. Next, the alkylborane solution was transferred to the vial containing the Cu salt, followed by addition of (*S*)-(*Z*)-**3a** (55.6 mg, 0.15 mmol). After 24 h stirring at 60 °C, the mixture was filtered through a short plug of aluminum oxide, which was then washed with diethyl ether. After the solvent was removed under reduced pressure, flash chromatography on silica gel (hexane) gave (*R*)-(*E*)-**4aa** (35.6 mg, 0.132 mmol) in 88% yield.

Acknowledgements

This work was supported by Grants-in-Aid for Young Scientists (A) and Challenging Exploratory Research, JSPS to H.O. and by ACT-C, JST to M.S. and S.M. and by CREST, JST to M.S. K.N. thanks JSPS for scholarship support.

Keywords: Copper catalysis • Secondary alkylborane • Coupling • Allylic substitution • Stereoselectivity

[1] For a review on transition-metal-catalyzed allylic substitutions with organoboron compounds, see: Pigge, F. C. *Synthesis* **2010**, 1745–1762.

[2] For reviews on Cu-catalyzed enantioselective allylic substitutions with organomagnesium, organozinc or organoaluminum reagents, see: a) A. H. Hoveyda, A. W. Hird, M. A. Kacprzynski, *Chem. Commun.* **2004**, 1779–1785; b) C. A. Falciola, A. Alexakis, *Eur. J. Org. Chem.* **2008**, 3765–3780; c) A. Alexakis, J. E. Bäckvall, N. Krause, O. Pàmies, M. Diéguez, *Chem. Rev*. **2008**, *108*, 2796–2823; d) S. R. Harutyunyan, T. den Hartog, K. Geurts, A. J. Minnaard, B. L. Feringa, *Chem. Rev*. **2008**, *108*, 2824–2852.

[3] For Cu-catalyzed γ-selective and stereospecific allylic substitutions between primary alkyl-9-BBN and enantio-enriched secondary allylic phosphates, see: a) H. Ohmiya, U. Yokobori, Y. Makida, M. Sawamura, *J. Am. Chem. Soc.* **2010**, *132,* 2895–2897; b) K. Nagao, H. Ohmiya, M. Sawamura, *Synthesis* **2012**, *44*, 1535–1541; c) K. Nagao, U. Yokobori, Y. Makida, H. Ohmiya, M. Sawamura, *J. Am. Chem. Soc.* **2012**, *134,* 8982–8987. See also: d) A. M. Whittaker, R. P. Rucker, G. Lalic, *Org. Lett.* **2010**, *12,* 3216–3218

[4] For Cu-catalyzed enantioselective allylic substitutions between alkyl-9-BBN and prochiral primary allyl chlorides, see: a) Y. Shido, M. Yoshida, M. Tanabe, H. Ohmiya, M. Sawamura, *J. Am. Chem. Soc.* **2012**, *134,* 18573–18576. b) K. Hojoh, Y. Shido, H. Ohmiya, M. Sawamura, *Angew. Chem. Int. Ed.* **2014**, *53,* 4954.

[5] For Cu-catalyzed γ-selective allylic substitutions with aryl-, alkenyl-, and allenylboronates, see: a) H. Ohmiya, N. Yokokawa, M. Sawamura, *Org. Lett.* **2010**, *12,* 2438–2440. b) R. Shintani, K. Takatsu, M. Takeda, T. Hayashi, *Angew. Chem.* **2011**, *123*, 8815–8818; *Angew. Chem. Int. Ed.*

2011, *50*, 8656–8659; c) B. Jung, A. H. Hoveyda, *J. Am. Chem. Soc.* **2012**, *134,* 1490–1493; d) F. Gao, J. L. Carr, A. H. Hoveyda, *Angew. Chem.* **2012**, *124*, 6717–6721; *Angew. Chem. Int. Ed.* **2012**, *51*, 6613–6617; e) M. Takeda, K. Takatsu, R. Shintani, T. Hayashi, *J. Org. Chem.* **2014**, *79,* 2354–2367.

[6] For a review on copper-mediated 1,3-syn selective allylic substitutions of organometallic reagents by employing reagent-directing leaving groups, see: B. Breit, Y. Schmidt, *Chem. Rev*. **2008**, *108*, 2928–2951.

[7] Reaction of (*S*)-(*E*)-**3a** proceeded with significantly decreased E-selectivity (*E*/*Z* 59:41), consistent with the concept of allylic 1,3-strain in acyclic stereocontrol. See: R. W. Hoffmann, *Chem. Rev*. **1989**, *89*, 1841–1860.

[8] The use of $Cu(acac)_2$ or CuTC instead of CuOAc under phosphine-free conditions (Table 1, entry 1) resulted in no reaction.

[9] The effect of ligands on the reaction of primary alkylborane also was examined (CuOAc/MeOK/toluene/60 °C). Reaction between 2-phenylethyl-9-BBN and (*S*)-(*Z*)-**3a** with PPh_3 or PCy_3 gave moderate 1,3-s*yn* selectivity (*syn*:*anti* 79:21, 81% yield and *syn*:*anti* 89:11, 84% yield). In contrast, phosphine-free conditions resulted in greater 1,3-syn selectivity (s*yn*:*anti* 97.5:2.5, 95% yield).

[10] Several observations concerning the optimum reaction conditions should be noted. Reaction with cyclohexylboronic acid and its pinacolate ester instead of secondary alkyl-9-BBN reagents did not produce any coupling product, leaving unreacted substrates. Using diethyl phosphate instead of diisopropyl phosphate as a leaving group was useful, although it produced a slightly decreased stereoselectivity (*syn*:*anti* 98:2, 87%).

[11] Details of the DFT calculations will be reported elsewhere.

[12] For reviews on the synthesis of allylsilanes, see: a) C. E. Masse, J. S. Panek, *Chem. Rev.* **1995**, *95*, 1293–1316; b) I. Fleming, A. Barbero, D. Walter, *Chem. Rev.* **1997**, *97*, 2063–2192; c) L. Chabaund, P. James, Y. Landais, *Eur. J. Org. Chem.* **2004**, 3173–3199.

[13] For the synthesis of enantio-enriched allylsilanes through Cu-catalyzed enantioselective allylic substitutions of prochiral γ-silylated primary allylic alcohol derivatives with organozinc or organoaluminum reagents, see: a) M. A. Kacprzynski, T. L. May, S. A. Kazane, A. H. Hoveyda, *Angew. Chem.* **2007**, *119*, 4638–4642; *Angew. Chem. Int. Ed.* **2007**, *46*, 4554–4558; b) F. Gao, K. P. McGrath, Y. Lee, A. H. Hoveyda, *J. Am. Chem. Soc*. **2010**, *132*, 14315–14320. For the synthesis of allylsilanes *via* copper-catalyzed allylic substitutions with silylating reagents, see: c) D. J. Vyas, M. Oestreich, *Chem. Commun.* **2010**, 568–570; d) D. J. Vyas, M. Oestreich, *Angew. Chem.* **2010**, *122*, 8692–8694; *Angew. Chem. Int. Ed.* **2010**, *49,* 8513–8515.

[14] For the synthesis of enantio-enriched allylsilanes through palladium-catalyzed allylic substitutions of enantio-enriched γ-silylated secondary allylic alcohol derivatives with organoboronic acids, see: D. Li, T. Tanaka, H. Ohmiya, M. Sawamura, *Org. Lett*. **2010**, *12*, 3344–3347.

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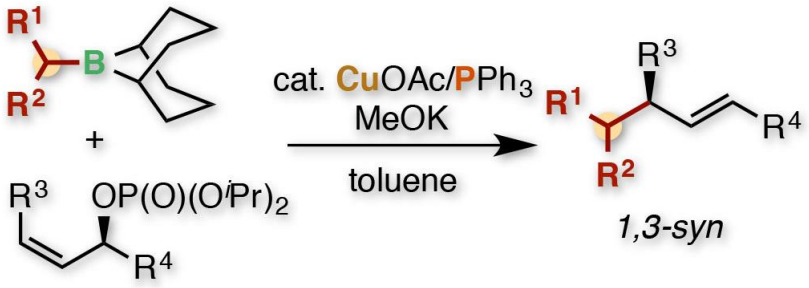

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