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Reversible 1,3-*anti*/*syn*-Stereochemical Courses in Copper-Catalyzed γ-Selective Allyl−Alkyl Coupling between Chiral Allylic Phosphates and Alkylboranes

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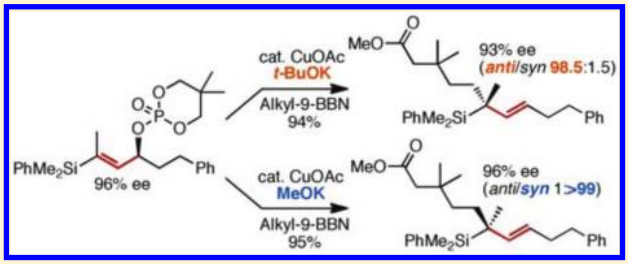
Supporting Information

ABSTRACT: The stereochemical courses of the copper-catalyzed allyl−alkyl coupling between enantioenriched chiral allylic phosphates and alkylboranes were switchable between 1,3-*anti* and 1,3-*syn* selectivities by the choice of solvents and achiral alkoxide bases with different steric demands. The reactions with γ-silylated allylic phosphates allow efficient synthesis of enantioenriched chiral allylsilanes with tertiary or quaternary carbon stereogenic centers. Cyclic and acyclic bimodal participation of alkoxyborane species in an organocopper addition−elimination sequence is proposed to account for the phenomenon of the *anti*/*syn*-stereochemical reversal.

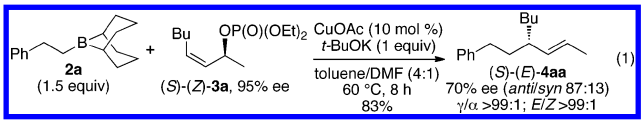


1. INTRODUCTION

Copper-mediated allylic substitutions of enantioenriched chiral allylic alcohol derivatives with organometallic reagents are powerful tools for constructing stereogenic carbon centers.[1] Typically, the reaction occurs with an 1,3-*anti*-stereochemistry (*anti*-S_N2') to deliver a new stereogenic center at the γ-position. In contrast, a switch of the stereochemical course from *anti* to *syn* is possible by employing reagent-directing leaving groups, such as benzothiazoles and carbamates (*syn*-S_N2').[2−4] Breit and co-workers introduced the *o*-diphenylphosphanyl benzoate (*o*-DPPB) group as a new reagent-directing leaving group,[5a−f] and furthermore realized the stereoselective conversion of chiral allylic substrates by employing the switchable *o*-DPPB/*o*-DPPB oxide leaving groups.[5g,h]

Herein, we report a new case for the reversibility of 1,3-*anti*/*syn*-stereochemical courses in allylic substitution, where the stereochemical courses are switchable by the choice of solvents and achiral alkoxide bases with different steric demands. The reactions allow efficient synthesis of enantioenriched chiral allylsilanes with tertiary or quaternary carbon stereogenic centers.[6−11] We note that examples of stereoselective conversion of one enantiomer of a substrate to both enantiomers of a product are still rare despite their usefulness in organic synthesis.[12]

Earlier, we reported the copper-catalyzed γ-selective allyl−alkyl coupling between allylic phosphates and alkylboranes (alkyl-9-BBN).[13,14] This reaction occurred preferentially with 1,3-*anti*-stereochemistry, but the stereoselectivity was only moderate with acyclic allylic substrates (eq 1).[13a] The sensitivity of the *anti*/*syn*-stereochemistry prompted us to explore the possibility of reversing the stereochemical course from *anti* to *syn* by the choice of reaction conditions.[15]



2. RESULT AND DISCUSSION

2.1. Optimization of Conditions for the Reversal of 1,3-*anti*/*syn*-Stereochemical Courses in the Reaction of γ-Silylated Allylic Phosphate. Our initial study was focused on the reaction producing allylsilanes, because γ-silylated allylic phosphates appeared to be more suitable substrates in terms of the stereoselectivity compared with allylic phosphates having a hydrocarbon backbone (vida infra). Alkylborane **2a**, which was prepared via hydroboration of styrene (**1a**) with 9-borabicyclo[3.3.1]nonane (9-BBN-H) dimer, and γ-silylated allylic phosphate (*S*)-(*Z*)-**3b** (99% ee) bearing a cyclic phosphate leaving group[16] were subjected to the standard reaction conditions for the copper-catalyzed allyl−alkyl coupling (**2a**/**3b**/CuOAc/*t*-BuOK 1.6:1:0.1:1.5, THF, 40 °C) (Table 1, entry 1; conditions A).[13a] The reaction afforded allylsilane (*S*)-(*E*)-**4ab** in 94% yield with complete γ- and *E*-selectivities. The absolute configuration of (*S*)-(*E*)-**4ab** indicated that the reaction took place with 1,3-*anti*-stereochemistry and the enantiomeric excess was 94% ee (*anti*/*syn* 97.5:2.5).[17]

As shown in Table 1, entries 2−5, the natures of a base and a solvent have marked impacts on the *anti*/*syn*-selectivity. When *t*-BuOLi was used instead of *t*-BuOK in conditions A, the yield was low and the *anti*-selectivity decreased to 61% (entry 2).

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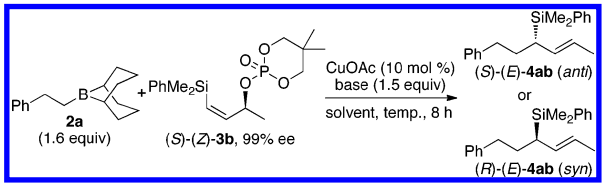
Table 1. Effect of Reaction Conditions on the *anti*/*syn*-Stereoselectivity of the Coupling between 2a and γ-Silylated Allylic Phosphate (*S*)-(*Z*)-3b[a]



entry	base	solvent	temp (°C)	yield (%)[b,c]	ee (%)[d]	*anti*/*syn*
1	*t*-BuOK	THF (cond A)	40	94	94 (*S*)	97.5:2.5
2	*t*-BuOLi	THF	40	14	22 (*S*)	61:39
3	EtOK	THF	40	86	56 (*R*)	22:78
4	MeOK	THF	40	99	59 (*R*)	20:80
5	*t*-BuOK	toluene	40	28	23 (*R*)	38:62
6	EtOK	toluene	40	90	80 (*R*)	9.5:90.5
7	MeOK	toluene	40	92	82 (*R*)	8.5:91.5
8	MeOK	toluene (cond B)	80	95	94 (*R*)	2.5:97.5

[a]The reaction was carried out with (*S*)-(*Z*)-**3b** (0.2 mmol), **2a** (0.32 mmol), CuOAc (10 mol %), and base (0.3 mmol) for 8 h. [b]Yield of the isolated product based on (*S*)-(*Z*)-**3b**. [c]Isomeric ratios (γ/α > 99:1, E/Z > 99:1). Determined by ^{1}H NMR or GC of the crude product. [d]The enantiomeric excess was determined by HPLC analysis.

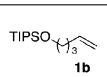
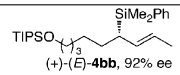
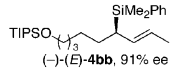
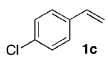
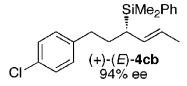
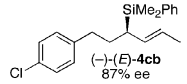
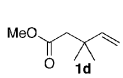
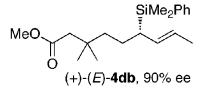
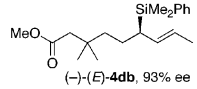
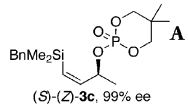
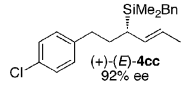
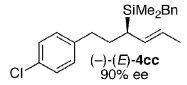
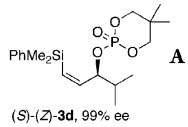
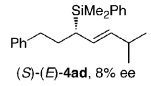
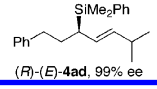
More pronounced effect on the stereoselectivity was observed when *t*-BuOK was changed to sterically less demanding EtOK: under otherwise same conditions, the stereochemical outcome was reversed to *syn*-selectivity, giving the *R* isomer of **4ab** with 56% ee (*anti*/*syn* 22:78) in 86% yield (entry 3). The *syn*-selectivity was further increased to 80% by the use of even smaller base MeOK (entry 4).

Changing the solvent (THF) in conditions A to toluene also caused the *anti*-to-*syn* reversal although the yield and the *syn*-selectivity were low (28% yield, *anti*/*syn* 38:62, Table 1, entry 5). The *syn*-selectivity was increased to 90.5% and 91.5% by the use of EtOK and MeOK, respectively, in place of *t*-BuOK (entries 6 and 7). Use of the smaller bases had a marked impact also on the increase in the yield. We were delighted to find that, when the reaction temperature was increased to 80 °C, the *syn*-selectivity became as high as 97.5% and the yield was excellent (entry 8; conditions B).

2.2. Reversible Stereochemistry in the Synthesis of Various Allylsilanes. Various enantioenriched allylsilanes can be synthesized through either 1,3-*anti*- or 1,3-*syn*-selective allyl−alkyl coupling reactions (Table 2). The alkylboranes (**2b−d**) bearing silyl ether, chloroaryl or ester moieties underwent the reactions with excellent stereoselectivity (Table 2, entries 1−6). The $PhMe_2Si$ group at the γ-position of **3b** could be replaced with $BnMe_2Si$ groups, affording the corresponding *R* and *S* isomers with excellent stereoselectivities (entries 7 and 8). For the reaction of (*S*)-(*Z*)-**3d** (99% ee), which has an α-*i*-Pr substituent using conditions A, the *anti*- and *syn*-stereochemical courses were comparable (entry 9). In contrast, conditions B resulted in a higher *syn*-selectivity than those with the other substrates (entry 10). This suggests that the bulkiness of the α-*i*-Pr substituent prompted the reactions toward the 1,3-*syn*-selectivity (vide infra for discussion).

The copper-catalyzed, 1,3-*anti*- and 1,3-*syn*-selective allyl−alkyl couplings can be extended to the synthesis of enantioenriched allylsilanes with a quaternary stereogenic center. The results are summarized in Table 3. We used γ,γ-disubstituted *E*-allylic phosphates, which are easier to prepare than the corresponding *Z*-isomers.[18] The reaction of γ,γ-disubstituted allylic phosphate (*S*)-(*E*)-**3e** (96% ee) using either conditions A or B afforded the corresponding quaternary chiral allylsilanes (*R*)-(*E*)-**4ae** (92% ee, *anti*/*syn* 98:2) and (*S*)-(*E*)-**4ae** (92% ee, *anti*/*syn* 2:98), respectively (entries 1 and 2).[19] The synthetic methods were compatible with an ester moiety in the alkenyl (alkylborane) substrate (entries 3 and 4). The reactions of allylic phosphate (*S*)-(*E*)-**3f** (99% ee) with a Bu group instead of the Me group at the γ-position by using either conditions A or B afforded (−)-(*E*)-**4af** (93% ee, *anti*/*syn* 97:3) and (+)-(*E*)-**4af** (96% ee, *anti*/*syn* 1.5:98.5), respectively (entries 5 and 6).

Table 2. Synthesis of Various Enantioenriched Allylsilanes with a Tertiary Carbon Stereogenic Center[a,b]

entry	alkene	phosphate	conditions	product	yield (%)[c,d]	*anti*/*syn*[e,f]
1		(*S*)-(*Z*)-**3b** 99% ee	**A**	 (+)-(*E*)-**4bb**, 92% ee	89	96.5:3.5
2	**1b**	(*S*)-(*Z*)-**3b** 99% ee	**B**	 (−)-(*E*)-**4bb**, 91% ee	99	4:96
3		(*S*)-(*Z*)-**3b** 99% ee	**A**	 (+)-(*E*)-**4cb** 94% ee	91	97.5:2.5
4	**1c**	(*S*)-(*Z*)-**3b** 99% ee	**B**	 (−)-(*E*)-**4cb** 87% ee	99	6:94
5		(*S*)-(*Z*)-**3b** 99% ee	**A**	 (+)-(*E*)-**4db**, 90% ee	69	95.5:4.5
6	**1d**	(*S*)-(*Z*)-**3b** 99% ee	**B**	 (−)-(*E*)-**4db**, 93% ee	94	3:97
7	**1c**	 (*S*)-(*Z*)-**3c**, 99% ee	**A**	 (+)-(*E*)-**4cc** 92% ee	92	96.5:3.5
8	**1c**	(*S*)-(*Z*)-**3c** 99% ee	**B**	 (−)-(*E*)-**4cc** 90% ee	95	4.5:95.5
9	**1a**	 (*S*)-(*Z*)-**3d**, 99% ee	**A**	 (*S*)-(*E*)-**4ad**, 8% ee	96	54:46
10	**1a**	(*S*)-(*Z*)-**3d** 99% ee	**B**	 (*R*)-(*E*)-**4ad**, 99% ee	95	1:>99

[a]Conditions A: **3** (0.2 mmol), alkylborane **2** (0.32 mmol), CuOAc (10 mol %), *t*-BuOK (0.3 mmol, 1 M in THF), THF, 40 °C, 8 h. Conditions B: **3** (0.2 mmol), alkylborane **2** (0.32 mmol), CuOAc (10 mol %), MeOK (0.3 mmol), toluene, 80 °C, 8 h. [b]Alkylborane **2** was prepared in advance by hydroboration of **1** with 9-BBN dimer in THF (conditions A) or toluene (conditions B) at 60 °C for 1 h and used without purification. [c]Yield of the isolated 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. [f]The enantiomeric excess was determined by HPLC analysis.

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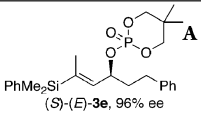
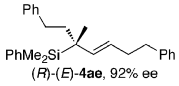
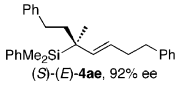
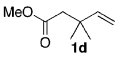
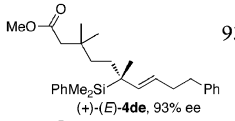
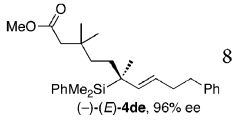
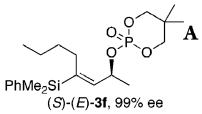
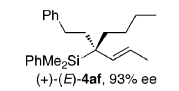
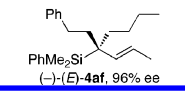
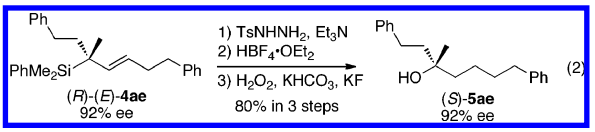
Table 3. Synthesis of Enantioenriched Allylsilanes with a Quaternary Carbon Stereogenic Center[a,b]

entry	alkene	phosphate	conditions	product	yield (%)[c,d]	*anti*/*syn*[e,f]
1	**1a**	 (*S*)-(*E*)-**3e**, 96% ee	**A**	 (*R*)-(*E*)-**4ae**, 92% ee	86	98:2
2	**1a**	(*S*)-(*E*)-**3e** 96% ee	**B**	 (*S*)-(*E*)-**4ae**, 92% ee	67	2:98
3	 **1d**	(*S*)-(*E*)-**3e** 96% ee	**A**	 (+)-(*E*)-**4de**, 93% ee	93	98.5:1.5
4	**1d**	(*S*)-(*E*)-**3e** 96% ee	**B**	 (−)-(*E*)-**4de**, 96% ee	81	1:>99
5	**1a**	 (*S*)-(*E*)-**3f**, 99% ee	**A**	 (+)-(*E*)-**4af**, 93% ee	70	97:3
6[g]	**1a**	(*S*)-(*E*)-**3f** 99% ee	**B**	 (−)-(*E*)-**4af**, 96% ee	56	1.5:98.5

[a]Conditions A: **3** (0.2 mmol), alkylborane **2** (0.32 mmol), CuOAc (10 mol %), *t*-BuOK (0.3 mmol, 1 M in THF), THF, 40 °C, 18 h. Conditions B: **3** (0.2 mmol), alkylborane **2** (0.32 mmol), CuOAc (10 mol %), MeOK (0.3 mmol), toluene, 80 °C, 8 h. [b]Alkylborane **2** was prepared in advance by hydroboration of **1** with 9-BBN dimer in THF (conditions A) or toluene (conditions B) at 60 °C for 1 h and used without purification. [c]Yield of the isolated 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. [f]The enantiomeric excess was determined by HPLC analysis. [e]The reaction was carried out in toluene/DCE (3:1) solvent.

The α-quaternary allylsilane (*R*)-(*E*)-**4ae** (92% ee) was readily derivatized to the chiral tertiary carbinol **5ae** (92% ee) by alkene reduction followed by Fleming−Tamao oxidation with retention of configuration (eq 2).[20]

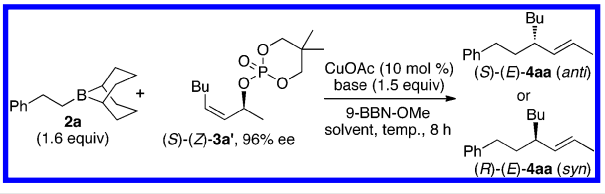


2.3. Allyl−Alkyl Coupling with Non-Silicon-Substituted Allylic Phosphates. The phenomenon of *anti*/*syn*-stereochemical reversal is not limited to cases with silylated allylic phosphates (Table 4). For instance, the reaction between the allylic phosphate (*S*)-(*Z*)-**3a′** (96% ee) and **2a** under conditions A occurred with 97% 1,3-*anti*-selectivity (entry 1). In contrast, the copper-catalyzed reaction of the same substrate pair under conditions B proceeded with 85% *syn*-selectivity, giving (*R*)-(*E*)-**4aa** with 66% ee in 31% yield (entry 2). The addition of 9-BBN-OMe (1.5 equiv to **3a′**) increased the *syn*-selectivity to 89% and the product yield to 55% (entry 3) (see section 2.4 for the role of 9-BBN-OMe). The use of 9-BBN-OMe in a larger quantity (3 equiv) improved the yield to 74% (entry 4; conditions C).

Various combinations of allylic phosphates having a hydrocarbon backbone and alkylboranes were examined, and the results are summarized in Table 5. The 1,3-*anti*-selectivity was generally high with conditions A (*anti*/*syn* > 95:5) (entries 1, 3, 5, 7, and 9). Although the efficiency of 1,3-*syn*-selectivity under conditions C was relatively low with the phosphates (*S*)-(*Z*)-**3a′**, which has a Me group at the α-position (entry 2, *anti*/*syn* 11:89), higher *syn*-selectivities (92−95%) were observed when the steric demand of the α-substituent is larger than that of the Me group (entries 4, 6, 8 and 10). The selectivity trend biased toward the 1,3-*syn*-stereochemical course by the bulkiness of the α-substituent is similar to that observed in the reaction with γ-silylated allylic substrates. The reactions were compatible with acetal or 3,4-dimethoxyphenyl moieties in the alkenyl (alkylborane) substrates (entries 1, 2, and 5−8).

2.4. Mechanistic Consideration. As we proposed in the previous report, it is conceivable that the copper-catalyzed allyl−alkyl coupling proceeds through the addition−elimination mechanism of a neutral organocopper species.[13a] The generality and completeness of the γ-regioselectivity (>99:1) strongly supports this assumption. On the basis of this assumption, the 1,3-*anti*-stereochemical outcome, which was preferred under conditions A, can be rationalized by the mechanism involving B/Cu transmetalation between trialkyl(alkoxy)borate **A** and CuX [X = OP(O)(OR^4)$_2$ or OAc], and the addition of alkylcopper(I) species **B** across the C−C double bond of **3**

Table 4. Effect of Reaction Conditions on the *anti*/*syn*-Stereoselectivity of the Coupling between 2a and Allylic Phosphate (*S*)-(*Z*)-3a′[a]



entry	base	solvent	9-BBN-OMe (equiv)	temp (°C)	yield (%)[b,c]	ee (%)[d]	*anti*/*syn*
1	*t*-BuOK	THF	none (cond A)	40	87	90 (*S*)	97:3
2	MeOK	toluene	none (cond B)	80	31	66 (*R*)	15:85
3	MeOK	toluene	1.5	80	55	74 (*R*)	11:89
4	MeOK	toluene	3.0 (cond C)	80	74	74 (*R*)	11:89

[a]The reaction was carried out with (*S*)-(*Z*)-**3a′** (0.2 mmol), **2a** (0.32 mmol), CuOAc (10 mol %), and MeOK (0.3 mmol) for 8 h. [b]Yield of the isolated product based on (*S*)-(*Z*)-**3a′**. [c]Isomeric ratios (γ/α > 99:1, E/Z > 99:1). Determined by ^{1}H NMR or GC of the crude product. [d]The enantiomeric excess was determined by HPLC analysis.

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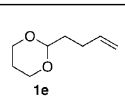
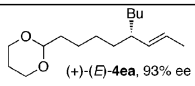
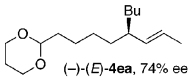
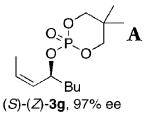
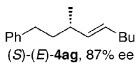
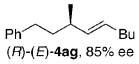
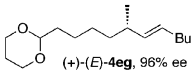
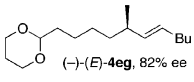
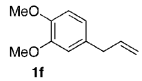
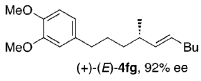
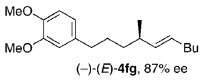
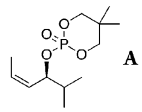
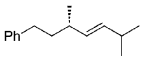
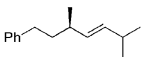
Table 5. Scope of Stereospecific Allyl−Alkyl Coupling[a,b]

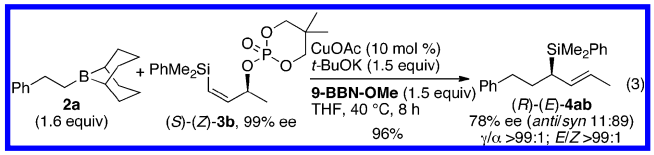
entry	alkene	phosphate	conditions	product	yield (%)[c,d]	*anti*/*syn*[e]
1	 **1e**	(*S*)-(*Z*)-**3a'A** 96% ee		 (+)-(*E*)-**4ea**, 93% ee	65	98.5:1.5
2	**1e**	(*S*)-(*Z*)-**3a'C** 96% ee		 (−)-(*E*)-**4ea**, 74% ee	67	11:89
3	**1a**	 **A** (*S*)-(*Z*)-**3g**, 97% ee		 (*S*)-(*E*)-**4ag**, 87% ee	70	95:5
4	**1a**	(*S*)-(*Z*)-**3g C** 97% ee		 (*R*)-(*E*)-**4ag**, 85% ee	74	6:94
5	**1e**	(*S*)-(*Z*)-**3g A** 97% ee		 (+)-(*E*)-**4eg**, 96% ee	80	99.5:0.5
6	**1e**	(*S*)-(*Z*)-**3g C** 97% ee		 (−)-(*E*)-**4eg**, 82% ee	84	8:92
7	 **1f**	(*S*)-(*Z*)-**3g A** 97% ee		 (+)-(*E*)-**4fg**, 92% ee	74	97.5:2.5
8	**1f**	(*S*)-(*Z*)-**3g C** 97% ee		 (−)-(*E*)-**4fg**, 87% ee	95	5:95
9[f]	**1a**	 **A** (*S*)-(*Z*)-**3h**, 99% ee		 (*S*)-(*E*)-**4ah**, 94% ee	29	97.5:2.5
10[f]	**1a**	(*S*)-(*Z*)-**3h C** 99% ee		 (*R*)-(*E*)-**4ah**, 83% ee	70	8:92

[a]Conditions A (entries 1, 3, 5, 7, 9): **3** (0.2 mmol), alkylborane **2** (0.32 mmol), CuOAc (10 mol %), *t*-BuOK (0.3 mmol, 1 M in THF), THF, 40 °C, 8 h. Conditions C (entries 2, 4, 6, 8, 10): **3** (0.2 mmol), alkylborane **2** (0.32 mmol), CuOAc (10 mol %), MeOK (0.3 mmol), 9-BBN-OMe (0.6 mmol), toluene, 80 °C, 8 h. [b]Alkylborane **2** was prepared in advance by hydroboration of **1** with 9-BBN dimer in THF (conditions A) or toluene (conditions C) at 60 °C for 1 h and used without purification. [c]Yield of the isolated 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]The enantiomeric excess was determined by HPLC analysis. [f]The reaction was carried out for 18 h.

followed by *anti*-β-elimination from alkylcopper complex **E** (Figure 1, path a). In contrast, the 1,3-*syn*-stereochemical outcome, which was preferred under conditions B and C, can be attributed to the pathway involving the addition of alkylcopper species **B** with *syn*-stereochemistry with respect to the leaving group followed by *syn*-β-elimination (Figure 1, path b).

The switch of the selectivity would likely rely on the nature of the alkoxyboranes (9-BBN-OR, R = *t*-Bu or Me), which are derived from the transmetalation between CuX [X = OMe, $OP(O)(OR^4)_2$ or OAc] and the alkylborates (**A** or **F**). Regardless of the R groups, the alkoxyboranes would play a role in activating the phosphate leaving group through their Lewis-acidic character at the boron atom.[21,22] When the R group in the alkoxyborane is compact enough (R = Me), the alkoxy oxygen would be able to coordinate to the copper atom, enabling path b, which proceeds through a cyclic transition state **H-TS** (**G** → **H-TS** → **I**). This results in 1,3-*syn*-stereochemistry. In contrast, when the R group is as bulky as the *t*-Bu group, steric factors would prevent the coordination of the alkoxy oxygen to the copper atom. Accordingly, the acyclic mechanism as in path a is preferred (**C** → **D-TS** → **E**). Use of a potentially coordinating solvent such as THF may also render the O−Cu coordination less favorable.

The assumed participation of 9-BBN-OMe in the 1,3-*syn* allylic substitution was strongly supported by an additional experiment that used an external 9-BBN-OMe reagent (eq 3). Thus, the *anti*-to-*syn* reversal occurred upon adding 9-BBN-OMe (1.5 equiv) to the reaction between **2a** and (*S*)-(*Z*)-**3b** under otherwise 1,3-*anti* reaction conditions.



The proposed acyclic and cyclic mechanisms for the 1,3-*anti*- and 1,3-*syn*-stereochemical courses may be consistent with the general observation that the sterically more demanding α-substituents in the allylic phosphates biased the reaction toward 1,3-*syn*-stereoselectivity. Thus, assuming the stereodifferentiating transition state **D-TS** for the *anti*-stereochemical course so that the Cu−C(β) bond and the C(α)−O bond are antiperiplanar as illustrated in Figure 2a, a steric repulsion between the organocopper moiety and the bulky α-substituent (R^3) would be significant. On the other hand, such a steric repulsion could be avoided in the cyclic transition state **H-TS** leading to the 1,3-*syn*-stereochemical outcome as shown in Figure 2b.

3. CONCLUSION

In summary, we demonstrated a new case of the reversibility of 1,3-*anti*/*syn*-stereochemical courses in allylic substitution, where the stereochemical courses are switchable by the choice of solvents and achiral alkoxide bases with different steric demands. The protocols allowed the stereoselective conversion of silicon-substituted allylic phosphates into enantioenriched chiral allylsilanes with tertiary or quaternary carbon stereogenic centers. Thus, both enantiomers of the allylsilanes with high enantiomeric purities are readily available from one enantiomer of the substrate. The protocols are versatile and useful for the synthesis of functionalized allylsilanes because alkylboranes are widely available via in situ alkene hydroboration with a broad functional compatibility.[23] Furthermore, the use of secondary allylic alcohol derivatives as substrates is advantageous to the preparation of allylsilanes that are substituted at the alkene terminus.[6−11] The reversible nature of the *anti*/*syn*-stereoselectivity provides clues to understanding the mechanism of the copper-catalyzed allyl−alkyl coupling reactions. Although elucidation of the mechanism must await further detailed studies aided by theoretical calculations, the experimental results obtained in the present study strongly suggest the critical participation of alkoxyboranes in acyclic and cyclic modes during the organocopper addition−elimination pathways.

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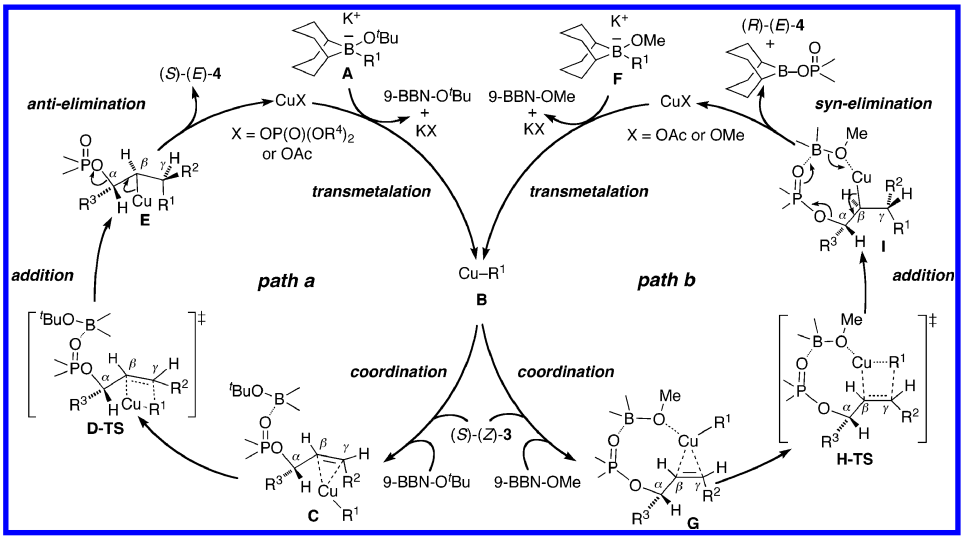

Figure 1. Possible pathways for the copper-catalyzed allyl−alkyl coupling between allylic phosphates and alkylboranes.

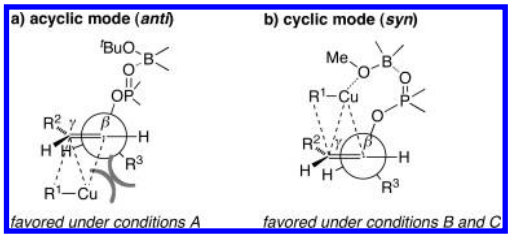

Figure 2. Stereoelectronic effect models.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details and characterization data for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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