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Copper-Catalyzed Enantioselective Allylic Substitution with Alkylboranes

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Supporting Information

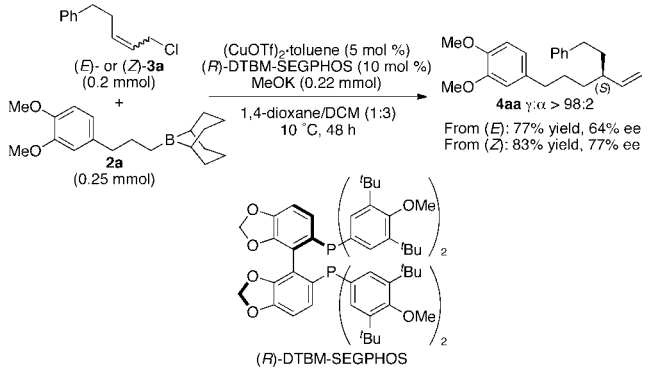
ABSTRACT: The first catalytic enantioselective allylic substitution reaction with alkylboron compounds has been achieved. The reaction between alkyl-9-BBN reagents and primary allylic chlorides proceeded with excellent γ-selectivities and high enantioselectivities under catalysis of a Cu(I)−DTBM-SEGPHOS system. The protocol produces terminal alkenes with an allylic stereogenic center branched with functionalized sp^3-alkyl groups. The reaction with a γ-silicon-substituted allyl chloride affords an efficient strategy for the enantioselective synthesis of functionalized α-stereogenic chiral allylsilanes.

Organoboron compounds are useful reagents for C−C bond formations because of their broad availability and excellent functional group compatibility.[1] Recently, enantioselective methods for C−C bond formation using organoboron compounds under the influence of chiral transition metal catalysts have made impressive progress.[2] Nevertheless, catalytic enantioselective allylic substitutions with organoboron compounds have not been well exploited.[3−7] Specifically, sp^3-alkylboron reagents have not yet been used successfully.

Herein, we report the first catalytic enantioselective allylic substitution reaction with alkylboron compounds.[8−10] The reaction between alkyl-9-BBN reagents and primary allylic chlorides proceeded with excellent γ-selectivities and high enantioselectivities under catalysis of a Cu(I)−DTBM-SEGPHOS system.[11] This protocol produces enantioenriched terminal alkenes with an allylic stereogenic center branched with functionalized sp^3-alkyl groups. The reaction with (*Z*)-1-dimethylphenylsilyl-3-chloro-1-pentene as an allylic substrate also proceeded selectively to afford enantioenriched α-stereogenic allylsilanes.[9b,c,12−14]

Earlier, we reported that the allyl−alkyl coupling between enantioenriched chiral secondary (*Z*)-allylic phosphates and alkyl-9-BBN reagents proceeded with excellent γ-selectivity and stereospecificity under the influence of a catalytic amount of a Cu(I) salt and a stoichiometric potassium alkoxide base.[9a−c] On the basis of this knowledge, we initiated a program to develop an unprecedented catalytic enantioselective allylic alkylation with alkylboranes. The initial screening with a substrate combination of alkylborane **2a** (0.25 mmol), which was prepared from dimethoxyallylbenzene (**1a**), and (*Z*)-allylic chloride **3a** (0.2 mmol) identified optimal reaction conditions using $(CuOTf)_2$·toluene (5 mol %), (*R*)-DTBM-SEGPHOS[11] (10 mol %), and MeOK (0.22 mmol) in 1,4-dioxane/dichloromethane (DCM) (1:3, 0.8 mL) at 10 °C for 48 h, which afforded the branched γ-substitution product (*S*)-**4aa** (γ/α > 98:2) with 77% ee in 83% yield (Scheme 1).[15,16] The enantioselection could be improved to 80% ee by reducing the reaction temperature to 5 °C at the expense of the yield (55%). The reaction of allylic chloride **3a** with *E*-configuration under otherwise identical conditions provided the product with the same absolute configuration with 64% ee (Scheme 1, *vide infra* for discussion on the effect of the alkene geometries).[17]

Scheme 1. Cu-Catalyzed Enantioselective Allylic Substitutions of 2a and 3a



The screening of chiral ligands revealed that introducing 3,5-di-*tert*-butyl-4-methoxyphenyl (DTBM) substituents on the phosphorus atoms of chiral bisphosphines was essential not only for the enantiocontrol but also for the catalytic activity with bisphosphine-based chiral Cu catalysts. Among various DTBM-substituted chiral bisphosphine ligands, (*R*)-DTBM-SEGPHOS was optimal (see Supporting Information (SI) for ligand effects). The introduction of the DTBM substituents may have induced the deaggregation of alkylcopper(I) species to form a catalytically active monomeric Cu complex.[18]

Effects of leaving groups and reaction conditions are summarized in Table 1.[16] In the earlier stage of the investigation, we used CuCl (5 mol %) as a Cu source for the reaction between **2a** and (*Z*)-**3a**. The reaction with (*R*)-DTBM-SEGPHOS (5 mol %) and MeOK in 1,4-dioxane at 35 °C proceeded with moderate yield and enantioselectivity (48% and 61% ee) (entry 1). Changing the leaving group to a bromide or phosphate caused drastic reductions of the product yield and enantioselectivity (entries 2 and 3).

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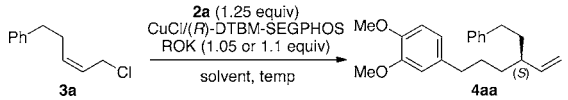
Table 1. Cu-Catalyzed Enantioselective Allylic Substitutions between 2a and 3a under Various Conditions[a]



entry	leaving group	Cu cat. (mol %)	ROK	solvent	temp (°C)	yield (%)[b,c]	ee (%)[d]
1	Cl	5	MeOK	dioxane	35	48	61
2	Br	5	MeOK	dioxane	35	18	34
3	OP(O)(OEt)$_2$	5	MeOK	dioxane	35	5	13
4	Cl	5	MeOK	THF	35	11	40
5	Cl	5	MeOK	toluene	35	7	41
6	Cl	5	MeOK	DCM	35	trace	–
7	Cl	10	MeOK	dioxane	10	23	74
8	Cl	10	MeOK	dioxane/DCM	10	81	77
9	Cl	5	*t*-BuOK	dioxane	35	39	57
10	Cl	5	PhOK	dioxane	35	0	–
11	Cl	5	MeOLi	dioxane	35	trace	–
12	Cl	5	MeONa	dioxane	35	0	–

[a]The reaction was carried out with **3a** (0.2 mmol), **2a** (0.25 mmol), Cu salt, ligand, and MeOK (0.21 mmol; entries 1–6 and 9–12, 0.22 mmol; entries 7 and 8) in solvent (0.8 mL) for 12 h (entries 1–6 and 9–12) or 48 h (entries 7 and 8). Alkylborane **2** was prepared in advance by hydroboration of **1** with the 9-BBN dimer at 60 °C (1 h) and used without purification. [b]The yield was determined by ^{1}H NMR. [c]Constitutional isomer ratio γ/α > 20:1 (determined by ^{1}H NMR analysis of the crude product). [d]The enantiomeric excess was determined by HPLC analysis.

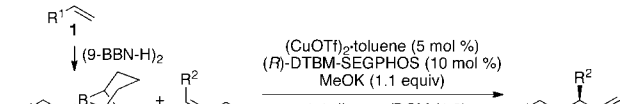
Solvents also showed marked influences on both yield and enantioselection. The use of THF or toluene as a solvent instead of 1,4-dioxane resulted in poor yields (11% and 7%) and lower enantioselectivities (40% and 41% ees) (Table 1, entries 4 and 5). Dichloromethane (DCM) as solvent inhibited the reaction almost completely (entry 6). The enantioselection was improved to 74% ee by carrying out the reaction at 10 °C with a 10 mol % catalyst loading in 1,4-dioxane, but with a serious reduction of the yield (23%, entry 7). Finally, we found that the reaction proceeded much more efficiently in a mixed solvent system, 1,4-dioxane/DCM (1:3). The reaction with a 10 mol % catalyst loading at 10 °C afforded (*S*)-**4aa** with 77% ee in 81% yield (entry 8). The slightly higher yield (83%) was obtained by changing CuCl to (CuOTf)$_2$·toluene with the enantioselectivity unchanged (Scheme 1).

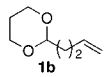
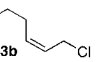
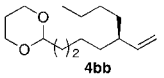
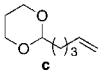
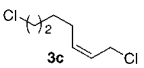
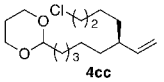
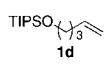
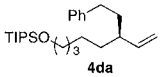
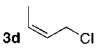
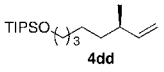
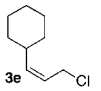
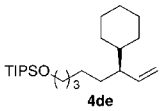
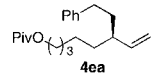
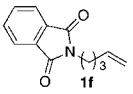
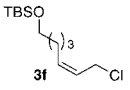
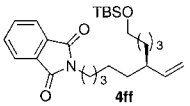
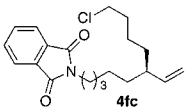
The nature of the base also had a strong impact on the yield and enantioselection. Changing the alkoxide base from MeOK to the bulkier *t*-BuOK caused a decrease in the yield (39%) and enantioselectivity (57% ee) (Table 1, entry 9). No reaction occurred with the weaker base PhOK (entry 10). The use of Li or Na methoxides also resulted in virtually no reaction (entries 11 and 12).

The inefficiency of the Li or Na methoxides may reflect higher solubilities of Li or Na salts, which may cause inhibitory effects in the hydrophobic solution phase of the reaction mixture. This assumption also explains the increase in the reaction efficiency when DCM was used as a cosolvent with 1,4-dioxane (Table 1, entry 8).

Various terminal alkenes and *Z*-allylic chlorides were subjected to the one-pot protocol involving the 9-BBN-hydroboration of terminal alkenes (**1**) and the subsequent enantioselective allylic substitution with the (CuOTf)$_2$·toluene/(*R*)-DTBM-SEGPHOS catalyst system (Table 2).[16,19] The reactions proceeded with excellent γ-selectivities (γ/α > 98:2) and high enantioselectivities (72–90% ee). Terminal alkenes having functional groups such as silyl ether, ester, acetal, and phthalimide moieties

Table 2. Scope of Enantioselective Allylic Substitution with Alkylboranes[a]



entry	terminal alkene	allylic chloride	product	yield (%)[b,c]	ee (%)[d]
1[e]	 1b	 3b	 4bb	93	88
2	 c	 3c	 4cc	71	83
3	 1d	3a	 4da	71	88
4	1d	 3d	 4dd	62	72
5	1d	 3e	 4de	53	76
6	 1e	3a	 4ea	73	88
7	 1f	 3f	 4ff	73	88
8	1f	3c	 4fc	72	90
9	 1g	3a	–	0	–

[a]The reaction was carried out with **3** (0.2 mmol), **2** (0.25 mmol), (CuOTf)$_2$·toluene (5 mol %), (*R*)-DTBM-SEGPHOS (10 mol %), and MeOK (0.22 mmol) in 1,4-dioxane/DCM (1:3, 0.8 mL) at 10 °C (entry 3) or 15 °C (entries 1, 2 and 4–9) for 48 h (entries 2, 3, 7, and 9) or 72 h (entries 1, 4–6, and 8). Alkylborane **2** was prepared in advance by hydroboration of **1** with the 9-BBN dimer at 60 °C (1 h) and used without purification. [b]The yield of the isolated product. [c]Constitutional isomer ratio γ/α > 98:2 (determined by ^{1}H NMR analysis of the crude product). [d]The enantiomeric excess was determined by HPLC analysis. [e]Reaction in 1.0 mmol scale.

at the terminal of the aliphatic chain were compatible with the hydroboration–enantioselective substitution protocol (entries 1–8). Functional groups such as silyl ether and chloro moieties in the allylic substrates were also tolerated (entries 2, 7, and 8).

The tolerance of this reaction toward smaller or sterically more demanding γ-substituents is demonstrated in the successful conversion of the γ-methyl or γ-cyclohexyl-substituted allyl chlorides (**3d**, **e**), although reductions in yield and enantioselection were observed (**4dd**, 62%, 72% ee; **4de**, 53%, 76% ee, Table 2, entries 4 and 5). Unfortunately, the attempt to use the alkylborane (**2g**) derived from styrene (**1g**) failed (entry 9).

The Cu-catalyzed protocol is applicable to the reaction between a γ-silylated allyl chloride (**3g**) and alkylboranes, which affords enantioenriched α-stereogenic chiral allylsilanes (Table 3).[16] For instance, the reaction between alkylborane **2h**, which

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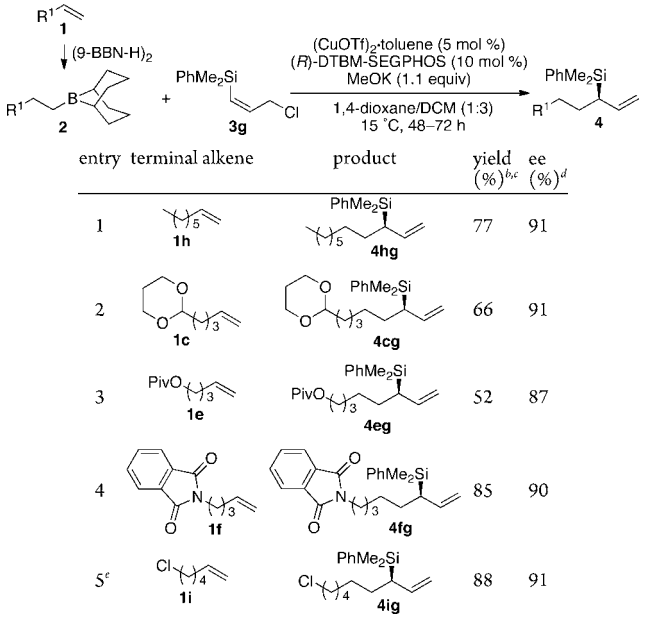
Table 3. Synthesis of Chiral Allylsilanes[a]



[a]The reaction was carried out with **3g** (0.2 mmol), **2** (0.25 mmol), $(CuOTf)_2$·toluene (5 mol %), (*R*)-DTBM-SEGPHOS (10 mol %), and MeOK (0.22 mmol) in 1,4-dioxane/DCM (1:3, 0.8 mL) at 15 °C for 48 h (entries 1, 2, 4 and 5) or 72 h (entry 3). Alkylborane **2** was prepared in advance by hydroboration of **1** with the 9-BBN dimer at 60 °C (1 h) and used without purification. [b]The yield of the isolated product. [c]Linear isomer was not detected: γ/α > 99:1 (^{1}H NMR). [d]The enantiomeric excess was determined by HPLC analysis. [e]Reaction in 1.0 mmol scale.

was derived from terminal alkene **1h**, and **3g** under the conditions optimized for the reaction of (*Z*)-**3a** (Scheme 1) proceeded with complete γ-selectivity and afforded chiral allylsilane **4hg** with 91% ee in 77% yield (Table 3, entry 1).[20] The terminal alkenes (**1c,e,f,i**) bearing acetal, ester, phthalimide, or chloro moieties were also compatible with the protocol with comparable enantioselectivities (entries 2–5).

A possible catalytic cycle for the present Cu catalysis can be postulated as illustrated in Figure 1. It would involve addition–β-elimination of a neutral organocopper(I) species **C** as proposed for the Cu-catalyzed allyl–alkyl coupling between secondary allylic phosphates and alkylboranes.[9a–c] During this addition–elimination pathway [**D** → **E-TS** → **F** → **4**], methoxyborane (9-BBN-OMe), which is derived from the transmetalation between

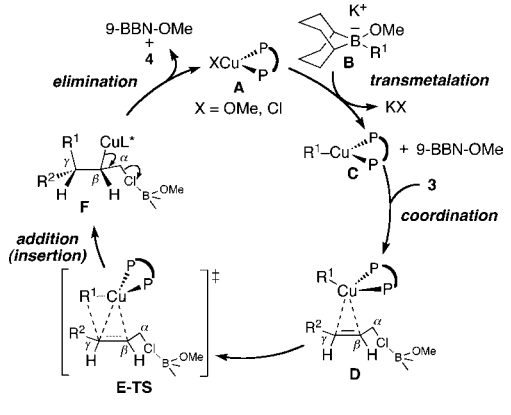


Figure 1. Possible catalytic cycle.

CuX(DTBM-SEGPHOS) [**A**, X = OMe or Cl] and a trialkyl(alkoxo)borate **B**, may play a role in activating the chloride leaving group through its Lewis acidic character.[9c] The addition of alkylcopper(I) species **C** would occur with *anti* stereochemistry with respect to the leaving group, being followed by *anti*-β-elimination.

Earlier, we reported that the stereochemical courses of the Cu-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 achiral alkoxide bases with different steric demands: *t*-BuOK and MeOK showed 1,3-*anti* and 1,3-*syn* stereochemistry, respectively.[9c] For the reaction with the sterically less hindered MeOK base, it was proposed that *in situ* generated 9-BBN-OMe bridges the leaving group and the Cu atom through Lewis acid/base bifunctional participation. Nevertheless, in the present enantioselective catalysis with the chiral bisphosphine ligand, the coordination of 9-BBN-OMe to the Cu center is ruled out because the Cu center bearing the alkyl group and the chiral bisphosphine ligand is coordinatively saturated upon alkene coordination.

The enantioselection likely occurs at transition states of the R^1–Cu addition across the C–C double bond. Enantioselection models for the reaction of (*Z*)-**3** are given in Figure 2 (**E-TS-1** and **E-TS-2**). In this model, the Cu adopts tetrahedral coordination geometry, the axis of the C–C double bond is coplanar with the Cu–R^1 bond, and Ar^1 and Ar^3 are equatorial and Ar^2 and Ar^4 are axial. Importantly, Ar^1 points toward the allyl chloride substrate more significantly than the other equatorial aryl group (Ar^3). The axial aryl groups (Ar^2 and Ar^4) are much more distal to the substrate. According to these assumptions, **E-TS-1** has less steric strain than **E-TS-2**, because Ar^1 is close to both the R^2 and $ClCH_2$ substituents in **E-TS-2**, while **E-TS-1** encounters the corresponding steric repulsions only between Ar^3 and the R^2 substituent, which should be relatively small due to the distal location of Ar^3.

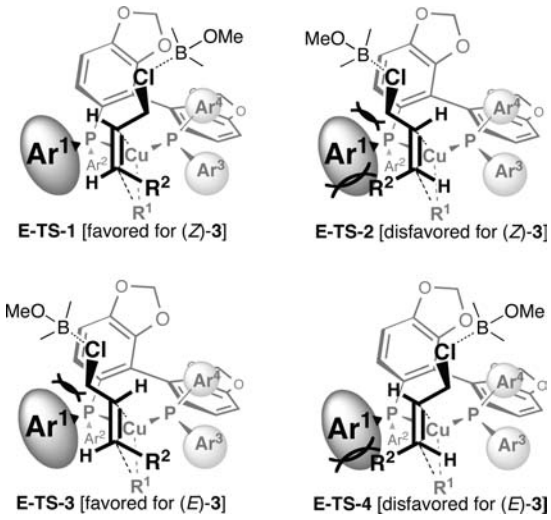


Figure 2. Models for enantiodiscrimination.

In the case of the reaction with (*E*)-**3**, Ar^1 causes steric repulsions toward either the $ClCH_2$ (**E-TS-3**) or R^2 substituents (**E-TS-4**). Consequently, the energy difference between **E-TS-3** and **E-TS-4** is smaller than that between **E-TS-1** and **E-TS-2**. These considerations explain the more efficient enantioselection in the reaction with the allylic substrate with *Z*-configuration (Scheme 1). The observed stereoconvergency from the *Z* and *E*

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allylic substrates affording the product with the identical absolute configuration suggests Ar^1 has greater steric interaction with the R^2 substituent (**E-TS-4**) than with the $ClCH_2$ substituent (**E-TS-3**).

In summary, we demonstrated the enantioselective reaction between alkylboron compounds (alkyl-9-BBN) and allylic chlorides under catalysis of the Cu(I)−DTBM-SEGPHOS system that proceeds with excellent γ-selectivities and high enantioselectivities. Introducing the DTBM substituents to the chiral ligand is crucial for promotion of the reaction. To our knowledge, this is the first catalytic enantioselective allylic substitution reaction of alkylboron derivatives. The protocol produces enantioenriched chiral terminal alkenes with an allylic stereogenic center branched with functionalized sp^3-alkyl groups and affords an efficient strategy for the enantioselective synthesis of α-stereogenic chiral allylsilanes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and characterization data for all 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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(15) The yields of **4aa** in Scheme 1 were determined by ^{1}H NMR analysis of the crude products.

(16) For Scheme 1 and Tables 1−3, unreacted allylic chloride (**3**) was detected in the crude materials after removal of the catalyst.

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(19) The absolute configuration of **4bb** was determined by transforming it to a known compound. See SI for details. Absolute configurations of **4aa** and the other products listed in Table 2 were assigned by consideration of the stereochemical pathway.

(20) The absolute configuration of allylsilane **4hg** was determined by transforming it to a chiral secondary alcohol by alkene reduction, followed by Fleming−Tamao oxidation with retention of configuration. See SI for details. Absolute configurations of the other allylsilanes were assigned by consideration of the stereochemical pathway.