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# Access to Stereodefined (*E*)-2-Silylallylboronates via Regioselective Chloroboration of Allenylsilanes

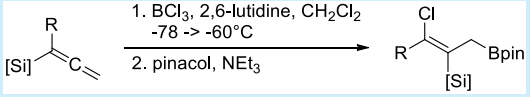
Zhantao Yang,[†,‡] Tingjie Liu,[†,§] Xixi Chen,[†,§] Ranran Wan,[†] Yang Li,[†] Xianzhen Wang,[†] Chun-Hua Yang,*[,†] and Junbiao Chang*[,‡]

[†]Henan Key Laboratory of New Optoelectronic Functional Materials, College of Chemistry and Chemical Engineering, Anyang Normal University, 436 Xian'ge Road, Anyang 455000, P. R. China

[‡]School of Pharmaceutical Sciences, Zhengzhou University, Zhengzhou, Henan 450001, P. R. China

Supporting Information

**ABSTRACT:** A catalyst-free method for the highly regioselective chloroboration of allenylsilanes is described. In the presence of $BCl_3$ and 2,6-lutidine, chloroboration of allenylsilanes proceeds smoothly without any catalyst, and the product could be treated with pinacol to afford the corresponding pinacol borates in one-pot reaction. This reaction provides a direct approach to construct valuable 2-silylallylboronate frameworks with operational simplicity and high atom-economy.

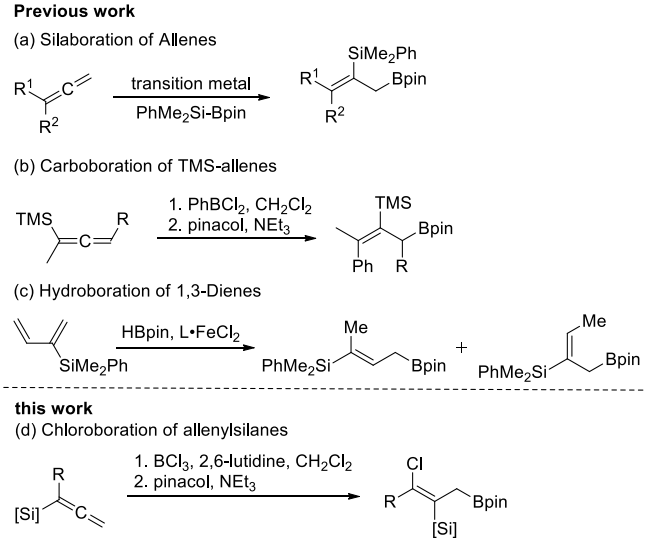



Silylallylboronates are widely used due to their high stability and lack of toxicity.[1] They have extensive functional compatibility and can be efficiently transformed to polyfunctional compounds through the reactions of C−Si and C−B bonds. Consequently, a variety of methods have been developed for the preparation of silylallylboronates.[2] Among them, there are some methods providing the preparation of 2-silylallylboronates, such as silaboration, carboboration, hydroboration, and so on.

Silaboration of allenes is one of the most useful and straightforward methods. However, this method usually gave a product in which the boron moiety was added to the central carbon atom and the silicon moiety was added to the unsubstituted terminal carbon atom of allenes producing allylsilanes.[3] Only few reported the silaboration of allenes to form allylborantes. Cheng et al. reported a method for the preparation of various 2-silylallylboronates by palladium-catalyzed silaboration of allenes with $PhMe_2SiBpin$ as the reagent and an organic iodide as the initiator (Scheme 1a).[4] This silaboration shows high regio- and stereoselectivity and provides the results that are completely different from the regiochemistry of the products reported previously. Stratakis et al. presented the first example of silaboration of terminal allenes catalyzed by Au nanoparticles with high yields and stereoselectivity (Scheme 1a).[5] The regioselectivity pattern of this method is unusual, with the boryl group adding to the terminal carbon atom. Ingleson et al. developed a method to construct 2-silylallylboronates via carboboration of TMS-substituted allenes (Scheme 1b).[6] Ritter et al. reported a Fe-catalyzed hydroboration of 2-dimethyl(phenyl)silylbutadiene. This reaction is chemo-, regio-, and stereoselective and gives 2-silylallylboronates (Scheme 1c).[7] However, the use of precious metals was often required for efficient catalytic turnover, and these requirements limit the actual utility of these methods.

We are interested in the synthesis and application of organoboron compounds,[8] and we have focused on the haloboration of C−C unsaturated bonds.[9] Suzuki realized bromoboration reaction of allenes with boron tribromide.[10] Chloroboration of allenes is the addition of a chlorine atom and a boron atom to a C=C double bond, and it provides a straightforward and atom-economical method for the synthesis of versatile allylboronates and vinylboronates. Chloroboration of allenylsilanes may provide a method to prepare silylallylboronates, but controlling the regioselectivity of this reaction is challenging. As far as is known, there are no reports about chloroboration of allenylsilanes. Herein, we describe the regioselective chloroboration of allenylsilanes (Scheme 1d).

**Scheme 1. Synthetic Strategies toward 2-Silylallylboronates**

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We initially prepared allenylsilanes (Scheme 2). Allenylsilanes were prepared from tetrahydro-2-(2-propynyloxy)-2*H*-pyran (**S1**) (see SI for details). The chloroboration of allenylsilane **1e** with $BCl_3$ was studied, giving the results in Table 1. As shown in this table, the reaction temperature was very crucial for the reaction. When the reaction was conducted at lower temperature, a higher conversion was obtained, and the chloroboration product was not detected when allenylsilane **1e** was treated with $BCl_3$/2,6-lutidine at room temperature. When the temperature was adjusted to −25 °C, the starting material was consumed. Then the reaction mixture was treated with pinacol/$NEt_3$ in one pot, and a new product was isolated by column chromatography. NMR spectra confirmed that this product was formed by chloroboration of the allenylsilane (**1e**), but only in 20% yield (Table 1, entry 2). The yield of the chloroboration product was 70% at −60 °C and was accompanied by the consumption of the starting material and formation of other products. The chloroboration product was formed as the only product in 50% yield at −78 °C, and the conversion did not increase with longer the reaction time. We reasoned that the starting material vigorously reacted with $BCl_3$ at high temperature, but when the reaction was conducted at −78 °C, and then slowly warmed to −60 °C, the reaction could be finished in 3 h at −60 °C. Thus, we successfully established the standard reaction conditions as allenylsilane (1.0 equiv), $BCl_3$ (1.5 equiv), 2,6-lutidine (1.5 equiv), and $CH_2Cl_2$ mixed at −78 °C and then slowly warmed to −60 °C where it was kept for 3 h. The reaction mixture was esterified with pinacol/$NEt_3$ for the exclusive formation of 2-silylallylboronate.

With the standard reaction conditions in Table 1 in hand, we turned our attention to the scope of the chloroboration reaction (Table 2). When [Si] = $SiMePh_2$ and R = a primary alkyl group, the reaction proceeded smoothly (entries 1−4).

**Scheme 2. Synthesis of Allenylsilanes**

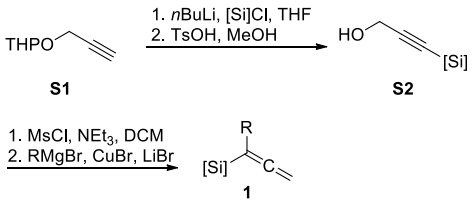
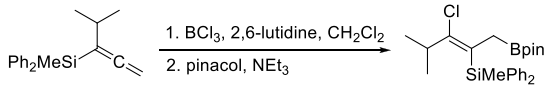



**Table 1. Optimization of the Reaction Conditions for Chloroboration of Allenylsilane 1e**[a]

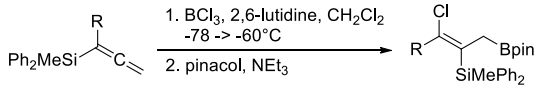



1e 2e

| Entry | Temp. | Reaction time | Yield[b] |
|---|---|---|---|
| 1 | rt. | 3 h | nd[c] |
| 2 | −25 °C | 3 h | 20% |
| 3 | −60 °C | 3 h | 70% |
| 4 | −78 °C | 12 h | 50% |
| 5 | −78 °C → −60 °C | 3 h | 80%[d] |

[a]Reaction conditions: (1) chloroboration: **1e** (0.1 mmol), $BCl_3$ (0.15 mmol), 2,6-lutidine (0.15 mmol), and $CH_2Cl_2$ (1 mL) under argon atmosphere; (2) esterification of the reaction mixture: pinacol (0.3 mmol) and $NEt_3$ (0.3 mmol). [b]Yields determined by $^1H$ NMR analysis. [c]nd = not detected. [d]The reaction was conducted at −78 °C, and then slowly warmed to −60 °C and kept for 3 h at −60 °C.

**Table 2. Regioselective Chloroboration of Allenylsilanes**[a]




1 2

| Entry | R | Yield[b] |
|---|---|---|
| 1 | Me (**1a**) | 76% |
| 2 | Et (**1b**) | 71% |
| 3 | $nC_4H_9$ (**1c**) | 66% |
| 4 | $nC_8H_{17}$ (**1d**) | 68% |
| 5 | *i*Pr (**1e**) | 75% |
| 6 | Cy (**1f**) | 75% |
| 7 | *i*Bu (**1g**) | 62% |

[a]Reaction conditions: (1) chloroboration: **1** (0.1 mmol), $BCl_3$ (0.15 mmol), 2,6-lutidine (0.15 mmol) and $CH_2Cl_2$ (1 mL) under argon atmosphere; (2) esterification of the reaction mixture: pinacol (0.3 mmol) and $NEt_3$ (0.3 mmol). [b]Yield of isolated product.

When [Si] = $SiMePh_2$ R = secondary alkyl substituents (entries 5−6), the reaction provided 2-silylallylboronates (**2e**) and (**2f**), respectively. In addition, the substrate with an isobutyl group could be subjected to the chloroboration reaction providing the product (**2g**) with high regioselectivity (entry 7).

Then we studied the scope of allenes (Table 3). When R = $CH_3$ and [Si] = $SiMe_2Ph$, $SiPh_3$, or $SiHPh_2$ (Table 3, entries 1−3), the reactions proceeded readily, providing the corresponding (*E*)-2-silylallylboronates in good yields with high regioselectivity. Moreover, R might be Et, *i*Pr, Cy, or $nC_8H_{17}$ (entries 4−9). For R = H, the desired chloroboration product was not detected (entry 10). When dimethyl(5-methylhexa-2,3-dien-2-yl)(phenyl)silane (**1r**) was subjected to the reaction, the chloroboration product was not detected when the substrate disappeared (entry 11). When monosubtituted allene (**1s**) and 1,1-disubtituted allenes (**1t**−**1u**) were subjected to the reaction, the chloroboration reactions did not proceed (Table 3, entries 12−14). These results indicated that the silyl group was dedicated to the chloroboration reaction. A gram scale reaction of **1n** (1.7 g, 5 mmol) proceeded in 78% yield with the same selectivity (entry 7). The regioselectivity of 2-silylallylboronates was confirmed by X-ray diffraction analysis of (*E*)-**2i** (Figure 1).

Finally, to demonstrate the synthetic utility of our reaction, several functional group transformation reactions were carried out (Scheme 3). (*E*)-2-Silylallylboronate (**2n**) was transformed to (*E*)-(3-chloro-1-iodo-4-methylpent-2-en-2-yl)-triphenylsilane (**3**) by treatment with *n*BuLi/NIS.[11] Allylboronate **2n** was treated with aqueous $KHF_2$ and gave potassium (*E*)-(3-chloro-4-methyl-2-(triphenylsilyl)pent-2-en-1-yl)-trifluoroborate (**4**) in 83% yield. Iodinolysis of vinyl-Si of **2n** with iodine chloride afforded vinyl iodide (**5**).[12]

Results in Table 3 showed that the chloroboration of nonsilyl substituted allenes did not proceed. These results indicated that a silyl group was dedicated to the chloroboration reaction. In order to examine the reaction mechanism, DFT calculations were carried out using silylated allene (**1h**) (see SI). Based on our preliminary studies, we propose a possible mechanism for the chloroboration of allenylsilanes (Scheme 4). When $BCl_3$ is mixed with silylated allene (**1h**), chloroboration of silylated allene undergoes with silyl group


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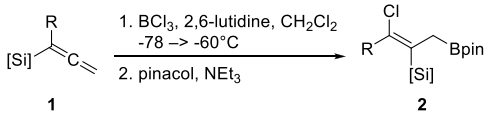
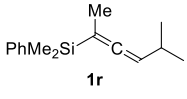
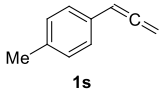
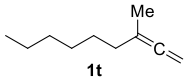
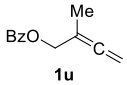
**Table 3. Regioselective Chloroboration of Allenylsilanes Using Various Silyl Substituents**[a]




1 2

| Entry | R | [Si] | Yield[b] |
|---|---|---|---|
| 1 | Me (**1h**) | $SiMe_2Ph$ | 83% |
| 2 | Me (**1i**) | $SiPh_3$ | 80% |
| 3 | Me (**1j**) | $SiHPh_2$ | 76% |
| 4 | Et (**1k**) | $SiMe_2Ph$ | 77% |
| 5 | Et (**1l**) | $SiPh_3$ | 82% |
| 6 | *i*Pr (**1m**) | $SiMe_2Ph$ | 75% |
| 7 | *i*Pr (**1n**) | $SiPh_3$ | 78%[c] |
| 8 | Cy (**1o**) | $SiMe_2Ph$ | 79% |
| 9 | $nC_8H_{17}$ (**1p**) | $SiMe_2Ph$ | 78% |
| 10 | H (**1q**) | $SiPh_3$ | nr[d] |
| 11 |  **1r** | | nd[e] |
| 12 |  **1s** | | nr[d] |
| 13 |  **1t** | | nr[d] |
| 14 |  **1u** | | nr[d] |

[a]Reaction conditions: (1) chloroboration: **1** (0.1 mmol), $BCl_3$ (0.15 mmol), 2,6-lutidine (0.15 mmol) and $CH_2Cl_2$ (1 mL) under argon atmosphere; (2) esterification of the reaction mixture: pinacol (0.3 mmol) and $NEt_3$ (0.3 mmol). [b]Yield of isolated product. [c]5 mmol scale. [d]nr = no reaction. [e]nd = not detected.

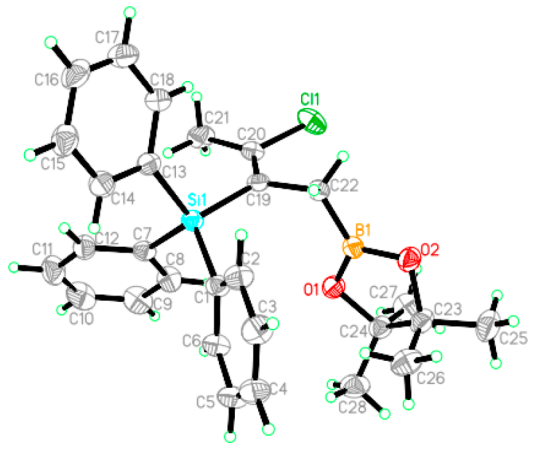
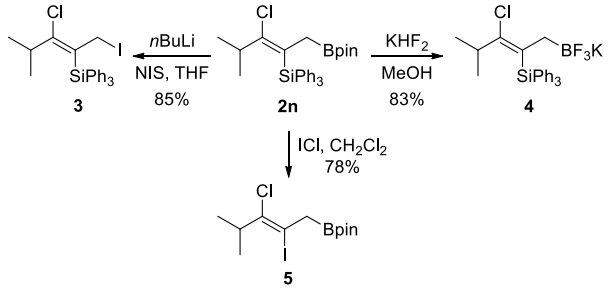


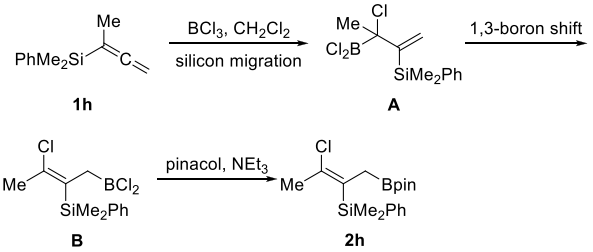

**Figure 1.** Structure of (*E*)-**2i**.

migration producing the intermediate allyl$BCl_2$ **A**.[6] The chloroboration of nonsilyl substituted allenes did not proceed.

**Scheme 3. Derivatization of Chloroboration Products**




**Scheme 4. Proposed Mechanism**




It is in accordance with the mechanism. Then sigmatropic 1,3-boron shift of allyl$BCl_2$ **A** forms the allyl$BCl_2$ species **B**, which is less hindered and more thermodynamically stable.[6,13] This can be transformed to boronate ester **2h** upon the treatment with pinacol. There is another possible mechanism for this reaction (see SI for details).

In summary, a regioselective chloroboration of allenylsilanes is reported. This provides a direct and one-pot approach to construct valuable 2-silylallylboronate frameworks with operational simplicity and high atom-economy under metal-free conditions. This is the first reported chloroboration of silylated allenes and leads unexpectedly to regio-reversed silylallylboronates with an *E* geometry.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b03720.

Representative experimental procedures, characterization data of substrates and products, and NMR spectra (PDF)

### Accession Codes

CCDC 1951271 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

## ■ AUTHOR INFORMATION

### Corresponding Authors

*E-mail: changjunbiao@zzu.edu.cn.
*E-mail: 09yangchunhua@163.com.

### ORCID

Zhantao Yang: 0000-0003-1575-3665
Chun-Hua Yang: 0000-0002-3770-9887



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Junbiao Chang: 0000-0001-6236-1256

## Author Contributions

[§]Tingjie Liu and Xixi Chen contributed equally.

## Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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