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Silaboration

trans-Silaboration of Terminal Alkynes Enabled by Development of a New Si—B Reagent

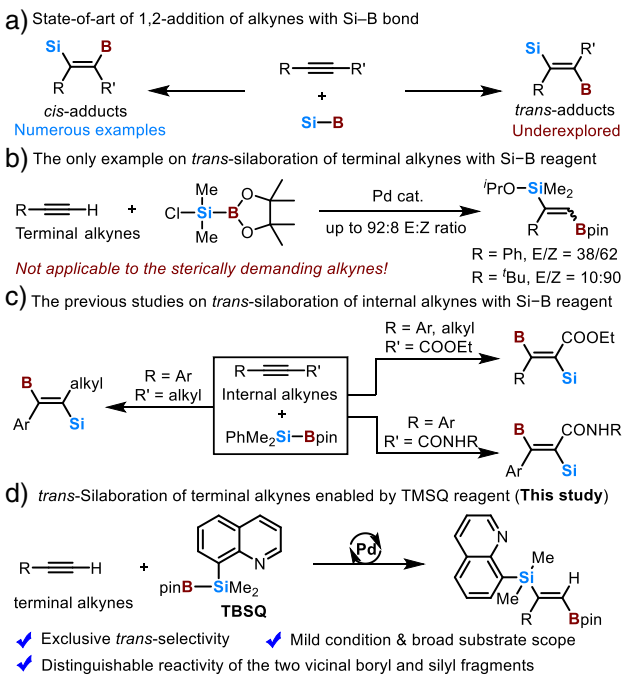
Song Chen[+], *Kailin Yin*[+], *Liangbo Zhu*,* *Chunming Cui*, *and Dongbing Zhao**

Abstract: The 1,2-silaboration of alkynes is a powerful strategy for regio- and stereoselective yielding versatile 1-boryl-2-silyl alkenes, which are ubiquitous synthons leveraging the orthogonal reactivity of boron and silicon for diverse downstream transformations. However, it dominantly features *cis*-selectivity. *trans*-Selective silaboration remains underdeveloped to date, especially for sterically hindered terminal alkynes. Herein, we report a Pd-catalyzed *trans*-silaboration of terminal alkynes using a novel Si—B reagent, TBSQ, bearing an 8-quinolinyl directing group on silicon. This strategy provides exclusive *E*-selectivity across a broad substrate scope, including bulky alkynes. Mechanistic studies suggest a combined *cis*-addition/Z→E isomerization pathway, with the directing group playing a crucial role. The resulting *trans*-1-boryl-2-silyl alkenes serve as valuable building blocks for selective downstream functionalization toward pharmaceutically relevant molecules.

The silaboration of alkynes,[1–3] which entails the 1,2-addition of Si—B reagents to alkynes, has proven to be one of the most efficient and atom-economical methods for the regio- and stereoselective simultaneous incorporation of boryl and silyl groups onto unsaturated carbon–carbon triple bonds. The resulting 1-boryl-2-silyl alkenes are valuable and versatile synthons in organic synthesis due to the orthogonal reactivity of the silicon and boron moieties. This unique property enables a variety of site-selective transformations, including Suzuki–Miyaura cross-couplings, Tamao–Fleming oxidations, and halogenations. Moreover, substituting functional groups with boron or silicon-containing moieties has become a fundamental strategy widely employed to enhance distinct physiological and optoelectronic properties in material science and medicinal chemistry.[4–9]

Since the initial realization of alkyne silaboration with Si—B compounds in 1996,[10] significant efforts have been directed toward broadening substrate diversity and modifying regioselectivity through the development of various catalytic systems and Si—B reagents.[11–22] Despite remarkable advances in the dimetalation of alkynes including silaboration, most documented cases have been restricted to *syn*-addition modes.[23–35] This limitation arises from the fact that the addition reactions catalyzed by transition metals typically involve the interaction between a vacant orbital of a transition metal and the π-orbital of acetylene. Consequently, direct access to *trans*-1-boryl-2-silyl alkenes from alkynes and Si—B reagents remains relatively uncommon.(Scheme 1)

In a notable study on the silaboration of terminal alkynes using (chlorodimethylsilyl) pinacolborane, Suginome achieved a reversal of stereochemistry, successfully yielding *trans*-1-boryl-2-silyl alkenes with an impressive *E*:*Z* ratio of up to 93:7.[36] However, this *trans*-silaboration protocol did not extend to sterically hindered alkynes; for example, both phenylacetylene and 3,3-dimethyl-1-butyne resulted in *Z*- and *E*-isomer mixtures with ratios of 62:38 and 90:10, respectively.



Scheme 1. Background and our study on *trans*-silaboration of alkynes.

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Additional supporting information can be found online in the Supporting Information section

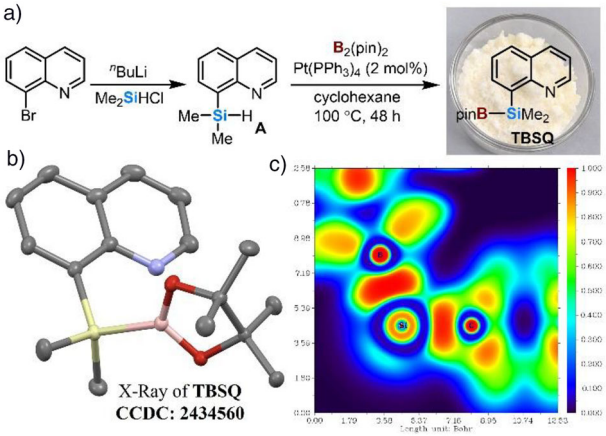


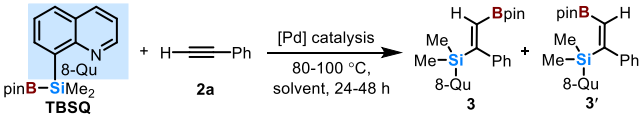
Figure 1. The new Si—B reagent TBSQ.

Subsequently, Sawamura,[37] Santos,[38] and Suginome[39] demonstrated transition metal-free or Cu-catalyzed *trans*-silaboration of alkynes, although these methods were limited to specific substrates such as internal alkynoates, propargylamides, and arylalkynes. Thus, the development of a *trans*-selective silaboration strategy for terminal alkynes that offers excellent compatibility with sterically demanding substrates and high stereoselectivity remains a significant and highly desirable goal.

With our sustained interest in the dimetalation of alkynes,[40–42] we have recently achieved the intermolecular *trans*-bis-silylation of terminal alkynes.[43] The incorporation of a coordinating group onto one of the silicon atoms in the disilane reagent proved essential for successfully reversing the stereochemistry. Motivated by this finding, we aimed to investigate whether *trans*-silaboration of alkynes could also be facilitated through the development of a new class of Si—B reagents featuring a directing group on the silicon atom. In this context, we have successfully accomplished the Pd-catalyzed *trans*-silaboration of terminal alkynes by introducing a Si—B reagent that contains an 8-quinolinyl group linked to the silicon atom: 8-(dimethyl(4,4,5,5-**t**etramethyl-1,3,2-dioxa**b**orolan-2-yl)**s**ilyl)**q**uinoline (TBSQ). This approach yields a diverse array of valuable *trans*-1-boryl-2-silyl alkenes. Experimental mechanistic investigations suggest that the reaction likely proceeds through a combination of *cis*-silaboration and *Z*/*E* isomerization processes, with TBSQ as the crucial Si—B reagent contributing to the desired reactivity. This transformation demonstrates excellent functional group tolerance and has been successfully applied to a wide variety of scaffolds bearing terminal alkyne groups, achieving exclusive *E*-selectivity, including instances with sterically demanding alkynes. Moreover, the utility of *trans*-1-boryl-2-silyl alkenes as versatile building blocks in organic synthesis has been highlighted through notable distinguishable and stepwise transformations of the silyl and boryl groups on the olefinic products, leading to a range of pharmaceutically relevant compounds.

Building upon this concept, we initiated the investigation into the synthesis of the proposed Si—B reagent, TBSQ. As illustrated in Figure 1a, the TBSQ reagent can be

Table 1: Condition Optimization[a)]



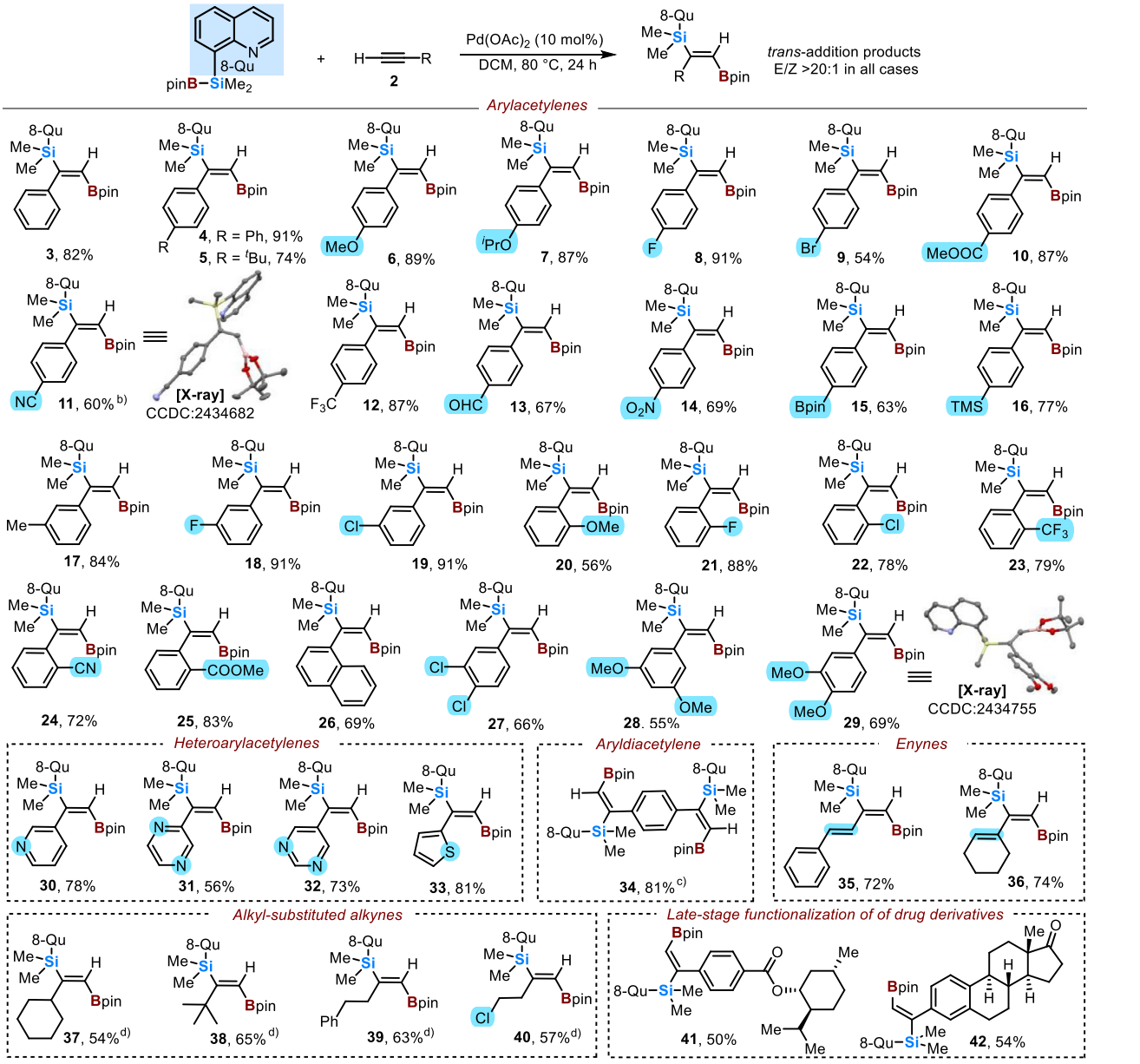
Entry	[Pd] cat.	Solvent	T (°C)	3:3′[b)]	Yield[%][b)]
1	$Pd(acac)_2$	toluene	100	0:100	83
2[c)]	$Pd(acac)_2$	toluene	100	0:100	84
3	$Pd(acac)_2$	cyclohexane	100	1:2.5	43
4	$Pd(OAc)_2$	cyclohexane	100	4:1	74
5	$Pd(dba)_2$	cyclohexane	100	0:100	68
6	$Pd(OAc)_2$	cyclohexane	60	6.7:1	62
7	$Pd(OAc)_2$	n-hexane	60	3.5:1	43
8	$Pd(OAc)_2$	DCM	60	>20:1	47
9	$Pd(OAc)_2$	DCM	80	>20:1	89 (82)
10[d)]	$Pd(OAc)_2$	DCM	80	>1:20	80
11[e)]	$Pd(OAc)_2$	DCM	80	6:1	83

[a)] Reactions were carried out by using Pd source (10 mol%), Si—B reagent TBSQ (0.2 mmol) and terminal alkyne (0.4 mmol) in solvent (2 mL) at 60–100 °C for 24 h. [b)] Yields and the ratio of **3** and **3′** were determined by GC analysis using 1-bromonaphthalene as the internal standard, the isolated yield is given in parentheses. [c)] Addition of 1,1,3,3-tetramethylbutyl isocyanide (40 mol%) as the ligand. [d)] Phenylacetylene **2a** (0.2 mmol; 1.0 equivalent) was used. [e)] Phenylacetylene **2a** (0.3 mmol; 1.5 equivalent) was used.

efficiently synthesized in two steps from the commercially available and inexpensive 8-bromoquinoline. The first step involves a lithium halogen exchange reaction between 8-bromoquinoline and sec-butyllithium, which is then followed by the addition of Me_2ClSiH to yield the corresponding hydrosilane **A**. In the next step, treatment of hydrosilane **A** with bis(pinacolato)diboron under an adapted version of Hajime Ito's Pt-catalyzed procedure[44] resulted in the formation of the desired silylborane, TBSQ, with a yield of 83%. Importantly, the TBSQ reagent is an air-stable, colorless solid that can be synthesized practically on a gram scale and is easily purified through recrystallization.The structure of TBSQ was definitively confirmed via single-crystal X-ray diffraction analysis (Figure 1b).[45] To further understand the bonding characteristics in TBSQ, density functional theory (DFT) calculations were conducted (Figures S1–S3 in Supporting Information). The Wiberg bond index (WBI) computed for the Si—B bond was found to be 0.934, indicating its nature as a single bond. Furthermore, the electron localization function (ELF) analysis of TBSQ suggests that the Si—B bond exhibits typical covalent bond characteristics (Figure 1c). Additionally, the natural population analysis (NPA) reveals charges of + 1.386 on the silicon atom and + 0.817 on the boron atom, underscoring its donor–acceptor character.

With the new Si—B reagent TBSQ in hand, we proceeded to investigate the silaboration of phenylacetylene (**2a**) using TBSQ under Pd-catalyzed conditions that our group had previously reported for *trans*-bis-silylation of terminal alkynes (Table 1). Unfortunately, the initial reaction proceeded in a *cis*-fashion, yielding the *cis*-product **3aa'** with an 83% yield (Entry 1). The incorporation of 1,1,3,3-tetramethylbutyl isocyanide (^{t}OCNC) as a ligand did not alter the observed

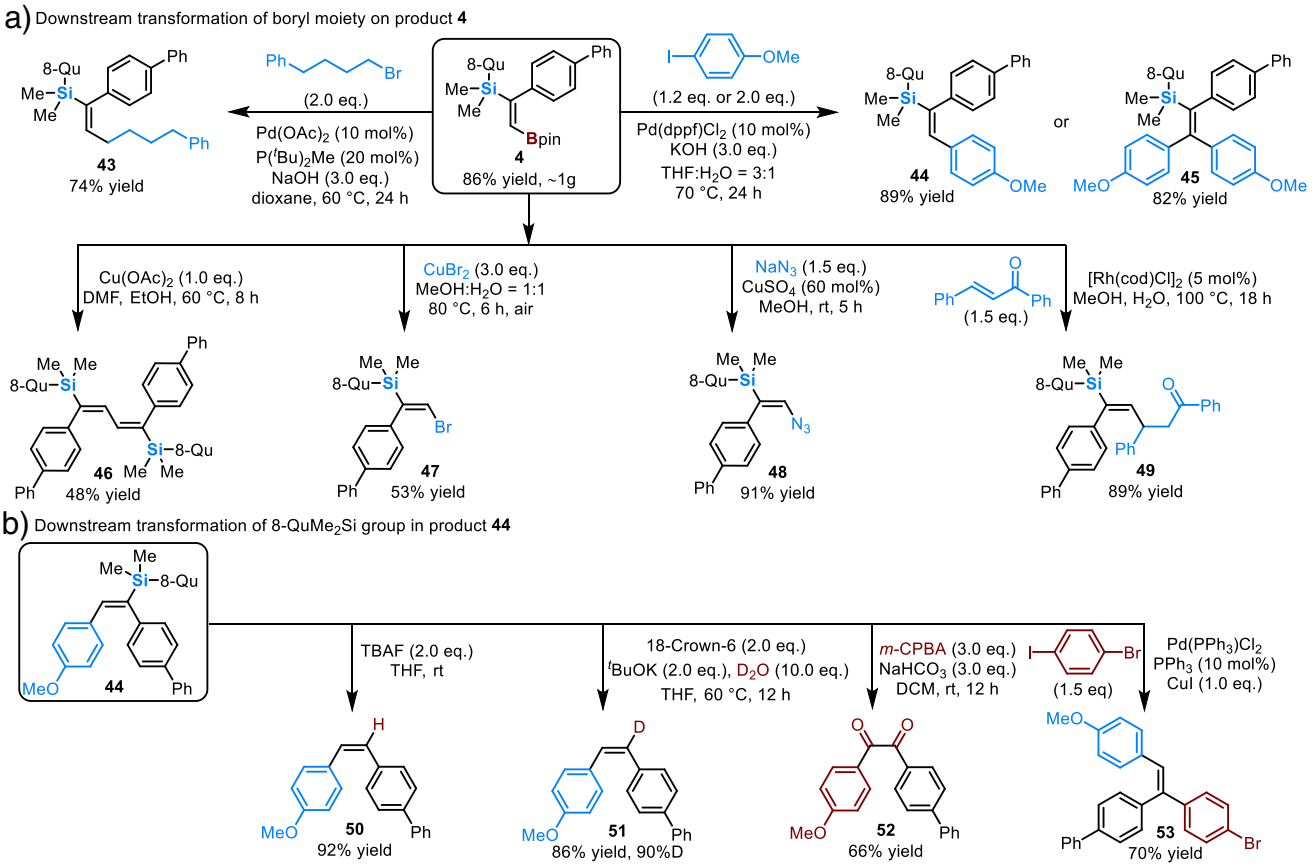
Table 2: Substrate scope[a)]



[a)] Reactions were carried out by using $Pd(OAc)_2$ (10 mol%), Si—B reagent **TBSQ** (0.2 mmol) and terminal alkyne (0.4 mmol) in DCM (2 mL) at 80 °C for 24 h. [b)] Reaction time: 48 h. [c)] Si—B reagent **TBSQ** (0.4 mmol) and aryldiacetylene (0.2 mmol). [d)] 5.0 Equivalent of alkyne was used under the reaction. Diastereomeric ratio (dr) were determined by the crude ^{1}H NMR.

cis-selectivity (Entry 2). Fortunately, when using cyclohexane as the solvent, the *trans*-product **3aa** was formed, achieving a *cis*/*trans* ratio of 2.5:1 (Entry 3). Substituting $Pd(acac)_2$ with $Pd(OAc)_2$ as the precursor significantly enhanced the *cis*/*trans* ratio of **3aa′**/**3aa** to 1:4 (Entry 4). However, when $Pd(dba)_2$ was employed as the catalyst, exclusive *cis*-selectivity was observed (Entry 5). Lowering the reaction temperature to 60 °C further improved the *trans*-selectivity, yielding a *cis*/*trans* ratio of 1:6.7 (Entry 6). Upon switching to hexane as the solvent, we noted a marked decrease in the *cis*/*trans* ratio (Entry 7, 3.5:1). To our surprise, using dichloromethane (DCM) as the solvent led to the exclusive formation of the *trans*-product **3** at a yield of 47% (Entry 8). Increasing the temperature to 80 °C further improved the yield while maintaining excellent *trans*-selectivity, resulting in an isolated yield of 82% (Entry 9). Decrease of the amount of phenylacetylene to 1.0 equivalent under the reaction support high *cis*-selectivity (Entry 10). With 1.5 equivalent of phenylacetylene, the reaction delivered the mixture of **3** and **3′** (**3**: **3′** = 6:1) in 83% yield (Entry 11).

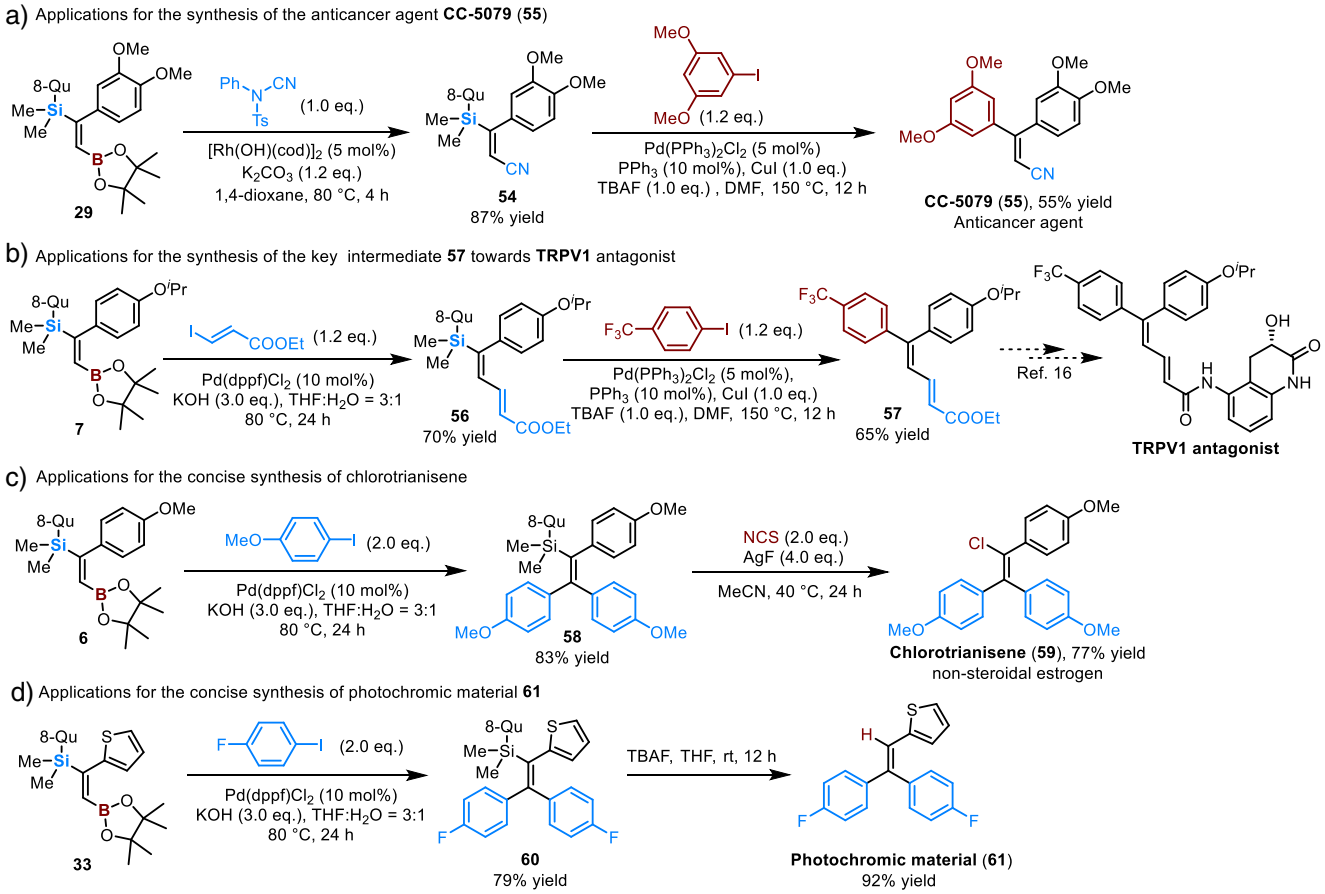
With the optimal reaction conditions established, we set out to explore the generality of this *trans*-silaboration of



Scheme 2. Downstream transformations of our product **4** based on the boryl and silyl moieties.

alkynes. Our initial investigation focused on the influence of substituents on the benzene ring of aryl acetylenes (Table 2). We found that the electronic effects had minimal impact on the regio- and stereoselectivity. Various aryl acetylenes, both those bearing electron-donating and electron-withdrawing groups, were efficiently transformed into the corresponding *trans*-1-boryl-2-silyl alkenes with high yields, while no detectable amounts of *Z*-isomers were formed. Additionally, steric hindrance arising from substituents at the *para*-, *meta*-, or *ortho*-positions of aryl alkynes had little effect on the stereocontrol and reactivity, leading to the formation of products with excellent *trans*-selectivity and good to excellent yields. The reactions exhibited robust functional group tolerance; substituents such as methoxy (**6**, **20**, **28**, **29**), halogen (**8**, **9**, **18**, **19**, **21**, **22**, **27**), trifluoromethyl (**12**, **23**), ester (**10**, **25**), formyl (**13**), nitro (**14**), and cyano (**11**, **24**) were all found to be well compatible. Furthermore, alkynes with two different substituents on the benzene ring performed effectively under the standard conditions (**27**, **28**, **29**). Beyond a variety of phenylacetylenes, alkynes featuring fused-ring naphthalene were successfully converted into the desired product **26** with a yield of 69%. We also observed that heteroaryl acetylenes, including 3-pyridyl, 2-pyrazinyl, 5-pyrimidinyl, and 2-thienyl, produced the corresponding products **30**–**33** with yields ranging from 56% to 81%, while maintaining excellent *trans*-selectivity. Additionally, substrates bearing two ethynyl groups were thoroughly coupled with the Si–B reagent TBSQ, yielding product **34** in 81% yield. Encouragingly, our reaction conditions were also applicable to conjugated enynes possessing a terminal acetylene group (Table 2). The internal C=C double bond remained intact, while the terminal C≡C triple bond was the sole site for *trans*-silaboration, providing the corresponding products **35** and **36** in satisfactory yields. Moreover, alkyl-substituted alkynes participated effectively in *trans*-silaboration under our Pd-catalyzed conditions (Table 2). In contrast to Suginome's *trans*-silaboration protocol, we observed exclusive *anti*-selectivity for sterically hindered alkyl alkynes, such as cyclohexylacetylene and 3,3-dimethyl-1-butyne, producing the corresponding *E*-products **37** in 54% yield and **38** in 65% yield, respectively. Primary aliphatic substituents also yielded good quantities of *E*-products, as demonstrated by compounds **39** and **40**. We further evaluated the practicality of our method for late-stage functionalization of alkyne-bearing multifunctional medicinal compounds. Terminal alkenes derived from *d*-menthol and estrone were successfully utilized as substrates, resulting in the formation of corresponding *trans*-products **41** and **42** with yields of 50% and 54%, respectively. Importantly, the structure and spatial configuration of the products were definitively confirmed through X-ray diffraction analysis of crystals **11** and **29**.[45]

To illustrate the practical applications of our method, we successfully scaled up the reaction to produce approximately 1 gram of product **4**, achieving an impressive yield of 86%



Scheme 3. Applications of our products for the concise synthesis of pharmaceutical agents and photochromic materials.

(Scheme 2a). We then employed product **4** as a substrate for synthesizing a variety of structurally diverse building blocks through further transformations. Generally, the boryl moiety preferentially undergoes transformations to generate various organosilicon structures, while the 8-QuMe_2Si group remains largely unaltered (Scheme 2a). We first demonstrated that the boryl moiety effectively coupled with both alkyl and aryl halides. Specifically, the coupling of **4** with (4-bromobutyl)benzene under Pd-catalyzed conditions yielded product **43** in 74% yield. Additionally, it successfully coupled with 1.0 or 2.0 equivalents of 1-iodo-4-methoxybenzene, producing compound **44** in 89% yield and compound **45** in 82% yield, respectively. The homocoupling reaction of **4** using $Cu(OAc)_2$ gave bissilyl butadiene **46** in 48% yield. Furthermore, treatment of **4** with $CuBr_2$ in a methanol–water mixture afforded product **47** in 53% yield. The reaction of compound **4** with NaN_3 in the presence of $CuSO_4$ resulted in the synthesis of compound **48** in 91% yield. Additionally, compound **4** can react with α,β-unsaturated ketones under Rh-catalyzed conditions to produce compound **49** in 89% yield. Next, we demonstrated that the remaining 8-QuMe_2Si group in product **44** could be further utilized as a masked nucleophile (Scheme 2b). Protodesilylation of **44** using TBAF was accomplished easily yielding compound **50** in 92% yield. The mono-deuterated diarylethylene **51** was efficiently synthesized in 86% yield by treating compound **44** with KO^{t}Bu in the presence of 18-crown-6 in THF, followed by quenching with D_2O. We also showed that compound **44** could be oxidized using *m*-CPBA, providing the 1,2-diketone **52** in 66% yield. Moreover, the 8-QuMe_2Si group in product **44** was capable of coupling with aryl iodide, leading to the formation of triaryl-substituted olefin **53**.

We further demonstrated that *trans*-1-boryl-2-silyl alkenes serve as valuable synthetic intermediates, providing new pathways for the streamlined preparation of various pharmaceutical agents and materials. One notable transformation involves the conversion of compound **29** into the anticancer and antitumor agent **CC-5079** through the cyanation of the boryl group, followed by an organosilicon-based cross-coupling (Scheme 3a). In contrast, the conventional synthetic route for **CC-5079** and related 3,3-diarylacrylonitrile analogs, starting from commercially available acid chlorides, typically relies on a Friedel–Crafts reaction and Horner–Wadsworth–Emmons (HWE) alkenylation, resulting in a 1:1 mixture of geometric isomers that must be separated via preparative HPLC.[46] Additionally, we showed that product **7** can be readily transformed into diene **56** with a yield of 70% through a Pd-catalyzed Suzuki–Miyaura coupling with ethyl (*E*)-3-iodoacrylate, followed by a Pd-catalyzed organosilicon-based cross-coupling with 1-iodo-4-(trifluoromethyl)benzene, yielding compound **57** in 65%. This compound serves as a key intermediate in the synthesis of a TRPV1

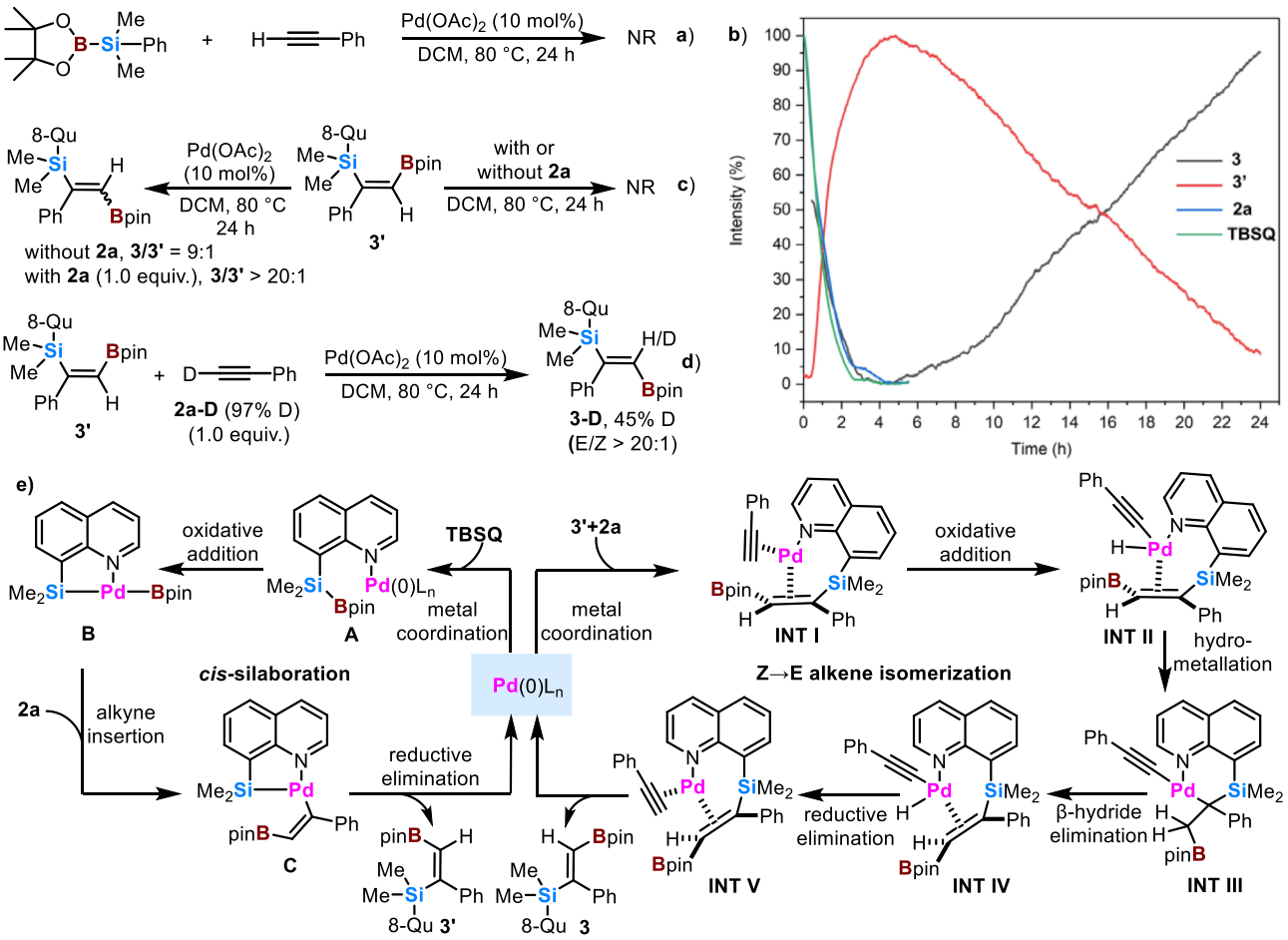


Figure 2. Mechanistic studies.

antagonist (Scheme 3b). In contrast, the conventional synthetic protocol requires four steps starting from ethyl (*E*)-4-oxobut-2-enoate.[47] In another application, we utilized product **6** in a concise synthesis of chlorotrianisene **59**, achieved through a two-step process involving Pd-catalyzed coupling with 1-iodo-4-methoxybenzene and subsequent chlorination of the silyl group. Chlorotrianisene is recognized as a long-acting non-steroidal estrogen and an orally active estrogen receptor modulator (Scheme 3c).[48] Moreover, we explored the synthesis of photochromic material **61**,[49] employing *trans*-1-boryl-2-silyl alkene **33**. This was first subjected to Pd-catalyzed Suzuki–Miyaura coupling conditions, followed by a straightforward protodesilylation (Scheme 3d).

To gain a deeper insight into the reaction mechanism and the origins of *trans*-selectivity, we conducted a series of experiments. Initially, we investigated the impact of the 8-quinolinyl group on the Si–B reagent TBSQ in the *trans*-silaboration reaction under standard conditions. When we replaced the TBSQ with the commercially available silylborane Me_2PhSi–Bpin, the *trans*-silaboration reaction was completely inhibited under the same conditions (Figure 2a). This finding emphasizes that the presence of the 8-quinolinyl group in the silylborane is essential for both reactivity and *trans*-selectivity in the silaboration process. Next, we employed in situ FTIR spectroscopy to monitor the model reaction of Si–B reagent TBSQ with phenylacetylene **2a** under optimized conditions (Figure 2b). We observed that the concentration of the *Z*-product **3′** increased rapidly at the reaction outset, while only trace amounts of the *E*-product **3** were detected until the complete consumption of the Si–B reagent TBSQ. Subsequently, the *cis*-1-boryl-2-silyl alkene **3aa′** underwent rapid and complete *Z*/*E* isomerization to yield the *trans*-1-boryl-2-silyl alkene **3**. This suggests that the *trans*-silaboration reaction proceeds via two independent steps: *cis*-silaboration and *Z*/*E* isomerization, aligning with our previous findings on the *trans*-disilylation of terminal alkynes. To further elucidate this reaction, we conducted control experiments using *Z*-product **3′** (Figure 2c). When treated under standard conditions, **3′** underwent partial isomerization, resulting in a mixture of **3** and **3′** with a 9:1 trans/cis ratio. Notably, *Z*/*E* isomerization did not occur in the absence of the Pd source. Introducing 1.0 equivalent of phenylacetylene **2a** under Pd-catalyzed conditions allowed full isomerization of *Z*-product **3′** to *E*-product **3** (*E*/*Z* > 20:1). These results indicate that 1) the Pd catalyst and the 8-quinolinyl group on silicon are essential for initiating the *Z*/*E* isomerization; and 2) while alkynes are not strictly necessary for the reaction, their presence significantly accelerates the rate of *Z*/*E* isomerization. We also conducted a deuterium labeling experiment to examine the role of alkynes in the *Z*/*E* isomerization step

(Figure 2d). The H/D exchange between the alkyne and **3′** was observed when deuterated phenylacetylene **2a-D** was used as an additive under standard isomerization conditions, suggesting that the *Z/E* isomerization may involve a reversible addition/elimination process. Based on these experimental findings, we propose that the catalytic cycle as shown in Figure 2e for this *trans*-silaboration reaction aligns well with our previously developed *trans*-disilylation reaction involving terminal alkynes.

In conclusion, we have synthesized a novel air-stable Si—B reagent, TBSQ, by incorporating an 8-quinolinyl directing group onto the silicon atom. Utilizing TBSQ as the Si—B reagent in the silaboration of terminal alkynes has enabled us to successfully address the challenge of achieving *trans*-silaboration, particularly with sterically hindered alkynes under Pd-catalyzed conditions. This approach yields a diverse array of *trans*-1-boryl-2-silyl alkenes in an exclusive manner. Notably, this transformation demonstrates a broad substrate scope and exceptional functional group tolerance. The chemically discernible silyl and boryl groups are introduced effectively, facilitating subsequent stepwise derivatizations. This capability paves the way for the modular and robust synthesis of densely functionalized biologically active compounds. The introduction of the 8-quinolinyl directing group in this Si—B reagent is crucial for achieving *trans*-selectivity. We expect that the new Si—B reagent TBSQ, endowed with a coordinating group, will find broader applications in both organosilicon and boron chemistry.

Supporting Information

Experiment details, spectra data, copies of ^{1}H and ^{13}C NMR spectra, and X-ray crystallographic data have been given in Supporting Information (SI).

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

Keywords: Alkynes · Si—B reagent · Silaboration · *Trans*-selectivity

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