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# Recent advances and perspectives in synthetic applications of silylboronates as silyl radical precursors†

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Silylboronates, as powerful and versatile reagents, have been widely used in synthetic chemistry over the past few decades, due to their ability to incorporate silicon and boron atoms into organic molecules. With the rapid development of radical chemistry, the use of silylboronates as silyl radical precursors has recently become a research focus in organic synthesis. Significant achievements have been made in the synthetic applications of silylboronates as silyl radical sources for various C–Si and C–X bond forming transformations. This review summarizes these recent advances, discusses their advantages and limitations, and illustrates the synthetic chances still open for further research and applications in this emerging area.

## 1 Introduction

Organosilicon compounds, owing to their unique chemical and physical properties, have found widespread applications in the fields of synthetic chemistry, pharmaceuticals, agrochemicals, and materials science.[1–3] Considerable efforts have hence been focused on synthesizing value-added organosilanes with structural diversity, and plenty of efficient silylation protocols have been accordingly developed by using various organosilicon reagents.[4] Among them, the use of silylboronates,[5] powerful and versatile reagents to incorporate silicon and/or boron atoms into organic molecules, has increased exponentially over the past few decades,[6] since the pioneering discovery that the Si–B bond could oxidatively add to low-valent transition metals (*e.g.* platinum, palladium, nickel, *etc.*) by the groups of Ito[7a,b] and Tanaka.[7c] Several major strategies for Si–B bond activation, including oxidative addition, transmetalation, Lewis base activation, and carbenoid insertion, have been subsequently established, which enabled a large number of elegant transformations involving silylboronates,[6a,d] such as 1,*n*-additions of C–C multiple bonds,[8] 1,2-additions of C=X bonds,[9] 1,4-

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† Dedicated to Professor Yong Tang on the occasion of his 60th birthday.

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additions of α,β-unsaturated carbonyl and related compounds,[10] allylic and propargylic substitution,[11] functionalization of strained-ring compounds or carbenoids and related compounds,[12] cycloadditions of multiple-bond systems,[13] C–H bond silylations,[14a,b] cross-coupling of C($sp^2$)–X or C($sp^3$)–X bonds,[14c,d] and others.[15]

In parallel with these impressive advances,[6] the synthetic applications of silylboronates as silyl radical precursors are also gaining increasing attention and become a hot research topic in recent years, along with the renaissance of radical chemistry,[16] because silyl radical species[17] are valuable intermediates for accessing diverse organosilanes *via* regio- and chemoselective silylation in organic synthesis.

As a consequence, a variety of silyl radical generation methods from silylboronates through photochemical, electrochemical or base activation strategies and their synthetic applications in various silyl radical involved transformations have been elegantly established for constructing C–Si or C–X bonds in the past few years. As illustrated in Fig. 1, these protocols can be classified into the following four categories, according to the kind of reaction developed: (1) hydrosilylation of alkenes or alkynes; (2) silyl radical involved silylfunctionalization; (3) selective radical silylation *via* C–X bond cleavage; (4) silyl radical mediated cross-coupling reactions.

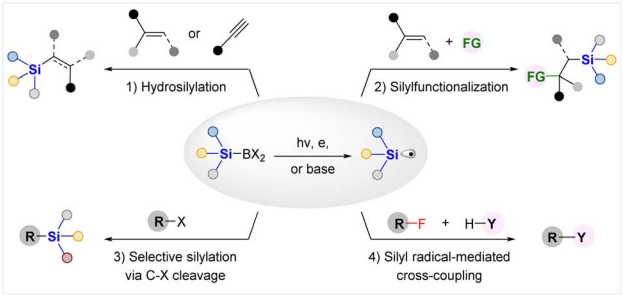


Fig. 1 Synthetic applications of silylboronates as silyl radical precursors.

Despite great advances made in this emerging area, there lacks a timely review article to summarize these latest advances

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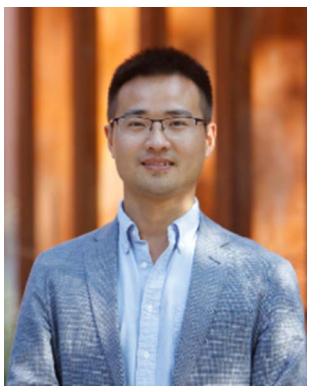

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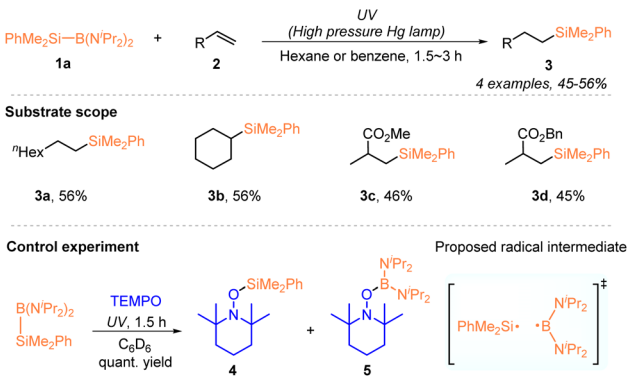
in exploring the synthetic potential of silylboronates as silyl radical precursors in organic synthesis; in sharp contrast, several elegant reviews have been published by Oestreich and coworkers to introduce the applications of silylboronates as silyl anion equivalents.[6a,d] In light of this, together with the flourishing of Si–B chemistry, we feel that it is necessary to present a review article that focuses on elucidating the latest technological innovations and the reactions for synthetic applications of silylboronates as silyl radical precursors, outlining the remaining synthetic opportunities, thereby facilitating the researchers with some references and inspiration to develop more efficient approaches for silyl radical generation from Si–B agents and diverse synthetic applications of the thus obtained silyl radicals. In this review, we will introduce the advances according to the classification shown in Fig. 1.

## 2 Hydrosilylation of alkenes or alkynes with silylboronates

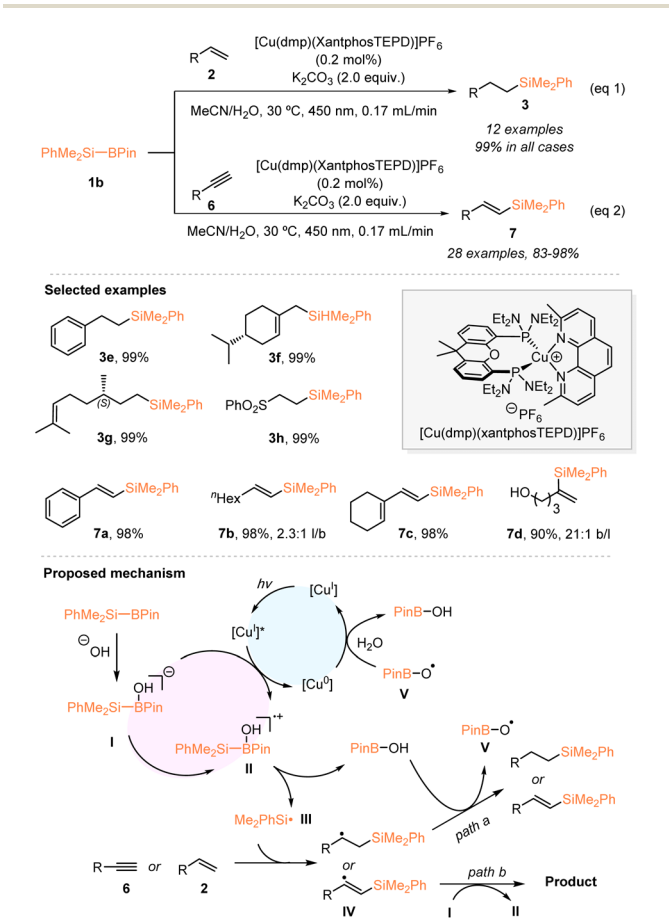
Hydrosilylation of alkenes or alkynes is an important and powerful way of preparing organosilicon compounds in industry and the laboratory.[18] With the rapid development of radical chemistry,[16] silyl radical-mediated hydrosilylation has been extensively explored in the past decade and has been one of the hot research areas in organic synthesis.[17a,b] In this context, the use of silylboronates as silyl radical precursors for developing hydrosilylation has recently received increasing attention, since the seminal work by Ito, who demonstrated the generation of silyl radicals from a silylaminoboronate *via* homolysis under UV irradiation.[19] Accordingly, a series of hydrosilylation reactions of alkenes or alkynes with silylboronates have been developed by using photochemical or electrochemical methods, allowing the access of various silylated alkanes or alkenes.

Early in 2000, the Ito group pioneered the generation of silyl radicals from organosilylboronate by using a photochemical method. Under UV irradiation of a high pressure Hg lamp, a dimethylphenylsilyl radical was effectively generated from $PhMe_2Si–B(N^iPr_2)_2$ (**1a**) *via* homolytic photolysis of the Si–B bond, which was confirmed by trapping experiments with TEMPO (Scheme 1).[19] The thus generated organosilyl radical enabled the regioselective hydrosilylation of monosubstituted alkenes **2** and delivered the desired organosilanes **3** with moderate yields. Interestingly, under UV irradiation, $PhMe_2Si–B(N^iPr_2)_2$ (**1a**) could promote the radical polymerization of vinyl acetate, methyl methacrylate and acrylate, affording the corresponding polymers containing a dimethylphenylsilyl at the polymer termini. Moreover, the radical pathway was confirmed by the experimental fact that no polymerization occurred in the presence of TEMPO or without irradiation.

In 2021, by using organosilylboronate as the radical precursor, Poisson and coworkers developed a copper-photocatalyzed hydrosilylation of alkenes under continuous flow (eqn (1), Scheme 2).[20] Under blue LED irradiation, the use of 0.2 mol% of their developed [Cu(dmp)(XantphosTEPD)]$PF_6$ effectively enabled the hydrosilylation of various monosubstituted alkenes **2** with the Suginome reagent $PhMe_2Si–Bpin$ (**1b**), in the presence of 2 equiv. $K_2CO_3$, which afforded the desired silylated alkanes **3** with 99% yields in all cases. Furthermore, the authors established the hydrosilylation of alkynes **6** with $PhMe_2Si–Bpin$ (**1b**) catalyzed by a Cu photocatalyst under blue LED irradiation and continuous flow conditions, allowing access to a variety of silylated alkenes **7** with excellent yields and good to excellent linear selectivities




Scheme 1 Photochemically induced silyl radical hydrosilylation of alkenes with $PhMe_2Si–B(N^iPr_2)_2$ (**1a**).

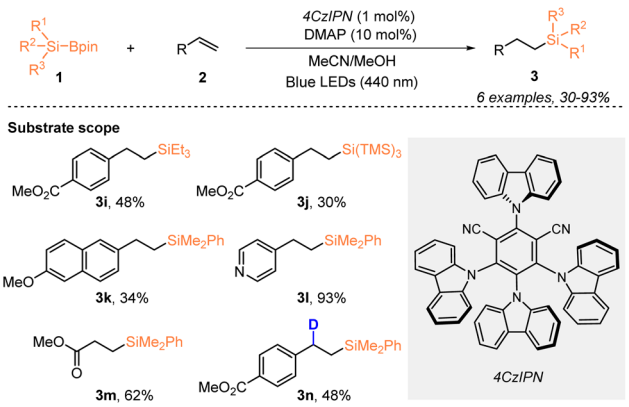



Scheme 2 Copper-photocatalyzed hydrosilylation of alkenes or alkynes with $PhMe_2Si–Bpin$.

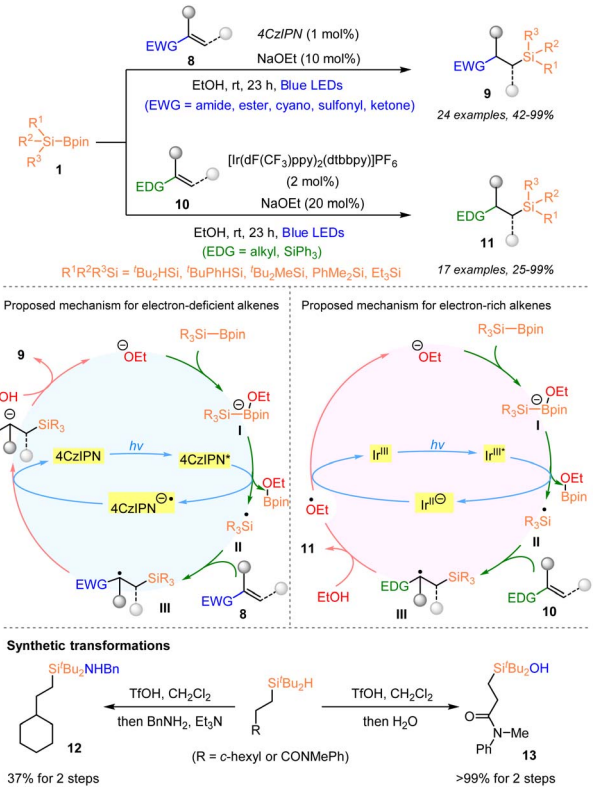
(eqn (2), Scheme 2). Based on the mechanistic studies, a possible reaction mechanism is proposed in Scheme 2. A borate species **I** was first generated from $PhMe_2Si$–Bpin under the action of the Lewis base hydroxide, which underwent oxidation with an excited Cu photocatalyst $[Cu^{I}]^*$ to give the radical cation **II**. Subsequently, the Si–B bond cleavage of intermediate **II** delivered the dimethylphenylsilyl radical **III**, which then reacted with alkenes or alkynes. The thus formed β-silylated carbon-centered radical species **IV** delivered the desired products after undergoing H-abstraction from HO–Bpin species or chain propagation.

One year later, Ohmiya, Sumida, and coworkers described a visible-light-driven organosilyl radical generation method from silylboronates (Scheme 3).[21] By using 1 mol% 4CzlPN, they realized the hydrosilylation of alkenes **2** with organosilylboronates **1** under blue LED irradiation, in the presence of 10 mol% Lewis base DMAP, affording the desired silylated products **3** in 30–93% yields. Notably, the corresponding deuterated organosilane **3n** was achieved with 48% yield and 95% deuterium incorporation, when methanol-$d_4$ was used instead of MeOH.

In 2023, Tanaka and Nagashima reported a photocatalytic protocol for *in situ* generation of both secondary and tertiary organosilyl radicals from silylboronates *via* one-electron oxidation of ate complexes of silylboronates and alkoxide co-catalysts (Scheme 4).[22] By employing such an "anionic SET strategy", highly efficient hydrosilylation and deuterosilylation of both electron-deficient alkenes **8** and electron-rich alkenes **10** with tertiary or secondary silylboronates **1** were achieved. It was found that a series of electron-deficient alkenes **8** reacted well with silylboronates by using a combination of 1 mol% 4CzlPN and 10 mol% NaOEt, under blue LED irradiation and afforded the corresponding organosilanes **9** with 42–99% yields, whilst the use of $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (2 mol%) and NaOEt (20 mol%) proved to be more efficient for the hydrosilylation of electron-rich alkenes **10**, furnishing the desired products **11** with 25–99% yields. Notably, such a catalytic system was suitable for the generation of secondary silyl radicals, although the use of secondary silyl radicals has been problematic in silylation



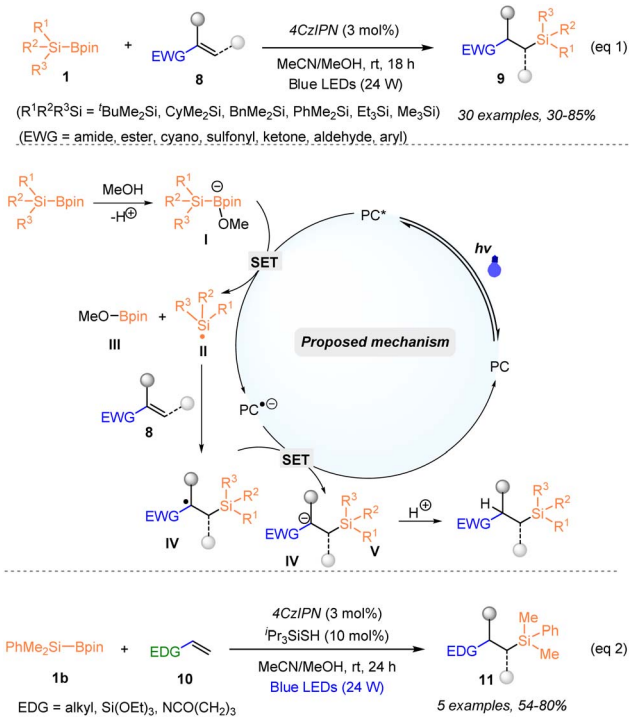

Scheme 3 Alkene hydrosilylation with silylboronate catalyzed by 4CzlPN.




Scheme 4 Organophotocatalytic hydrosilylation of electron-rich and -deficient alkenes with silylboronates.

due to their instability. As shown in Scheme 4, the plausible reaction mechanism was proposed according to the experimental results and DFT calculations. In addition, the elaboration of the product *via* the functionalization of the Si–H bond further highlighted the synthetic usefulness of this method.

Almost simultaneously, Zhang, Wang, and coworkers reported a visible light-induced organophotocatalytic hydrosilylation of electron-deficient alkenes **8** with organosilylboronates **1** (Scheme 5).[23] In the presence of 3 mol% 4CzlPN, a variety of hydrosilylation products **9** were obtained in 30–85% yields, under the irradiation of 24 W blue LEDs (eqn (1), Scheme 5). The necessity of both a photocatalyst and visible light was demonstrated by control experiments, since no target was detected in the absence of a photocatalyst or in darkness. The mild reaction conditions, broad substrate scope, and late-stage functionalization of three plant terpenoids further highlighted its practicability. A possible reaction mechanism was proposed, in which the *in situ* generated redox-active complex **I** from silylboronate and methanol *via* O → B coordination underwent a SET process with the photocatalyst in a photoexcited state (PC*) to deliver the silyl radical **II** and reduced $PC^{\bullet -}$ species, accompanied by the formation of MeO–Bpin (**III**). Subsequently, the formed silyl radical **II** reacted with alkenes to afford the desired products after photoreduction and protonation, along with the regeneration of the photocatalyst 4CzlPN. Moreover, this strategy was successfully extended to the hydrosilylation of electron-rich alkenes **10**, by slightly tuning the reaction conditions (eqn (2), Scheme 5). Notably, the authors

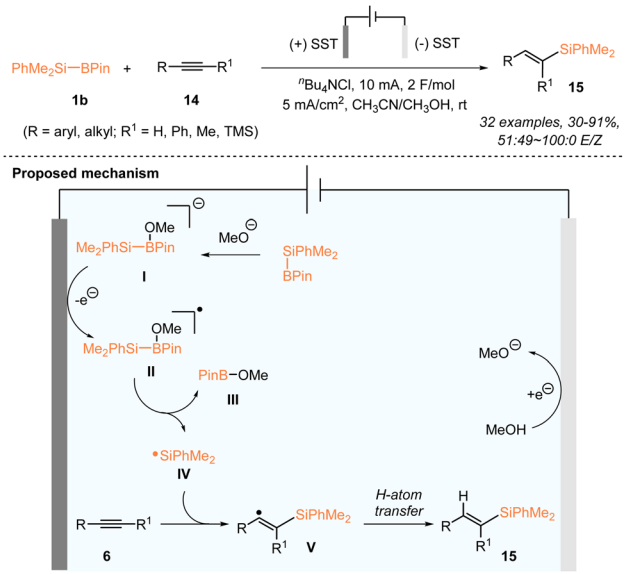



Scheme 5 Photochemically induced homolytic cleavage of Si–B bonds.

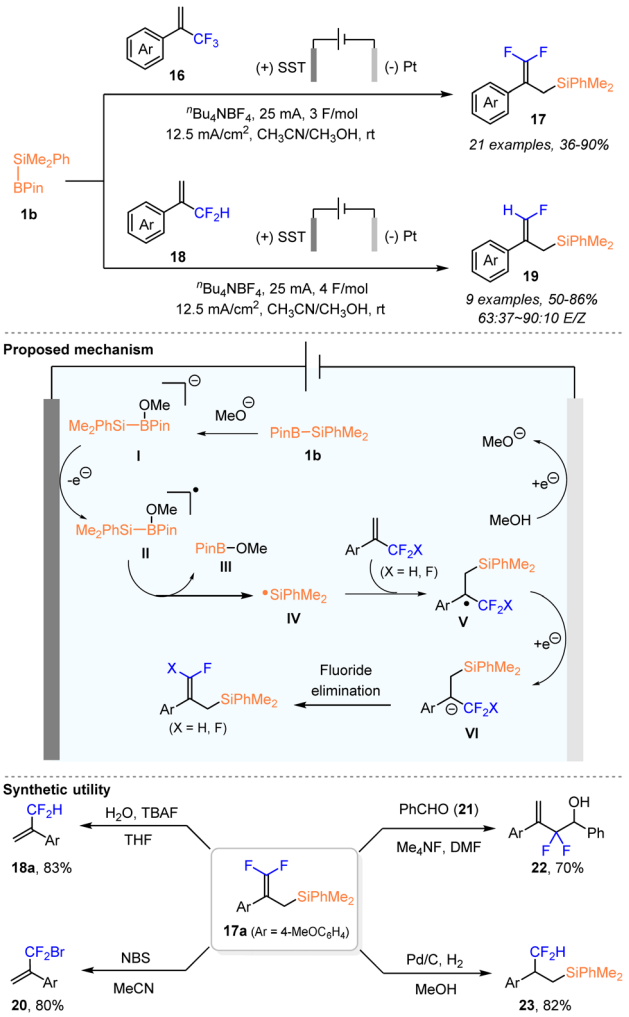
explored the hydrosilylation of alkynes with $PhMe_2Si$–Bpin, under the catalysis of 3 mol% 4CzIPN and blue LED irradiation, allowing the access of monosilylated alkenes *via* hydrosilylation or bis-silylated alkanes *via* bis-silylation depending on the amount of $PhMe_2Si$–Bpin employed.

In addition to photocatalysis, the generation of silyl radicals from silylboronates proves to be feasible under electrochemical conditions. The electrochemical hydrosilylation of both alkenes and alkynes with $PhMe_2Si$–Bpin (**1b**) has been accordingly established. In 2022, the Poisson group reported the electrochemical generation of silyl radicals from silylboronates for the first time and realized the electrochemical hydrosilylation of alkynes **14** with $PhMe_2Si$–Bpin (Scheme 6).[24]

Various terminal or internal alkynes **14** worked smoothly, in an undivided cell using stainless steel electrodes at both the anode and the cathode, at a constant current of 5 mA and a total charge of 2 F $mol^{-1}$ in a 0.1 M solution of $^nBu_4NCl$ in a mixed solvent of MeCN/MeOH, delivering a series of monosilylated alkenes **15** in 30–91% yields with a 51 : 49 ~ 100 : 0 *E*/*Z* ratio. The mechanistic study suggested the involvement of a dimethylphenylsilyl radical in this alkyne hydrosilylation. A plausible reaction mechanism is proposed in Scheme 6. The methoxide (MeO) anion, generated *in situ* from the reduction of MeOH at the cathode, first reacted with $PhMe_2Si$–Bpin to give a borate species **I**, which underwent anodic oxidation to give the radical species **II**. The silyl radical **IV** was subsequently generated from **II**, accompanied by the production of MeO–Bpin. The addition of the silyl radical to alkyne substrates **14** produced the reactive vinyl radical **V**, which delivered the targets **15** after undergoing H abstraction from MeOH.




Scheme 6 Electrochemical hydrosilylation of alkynes.




Scheme 7 Electrochemical synthesis of *gem*-difluoro- and γ-fluoroallyl silanes.

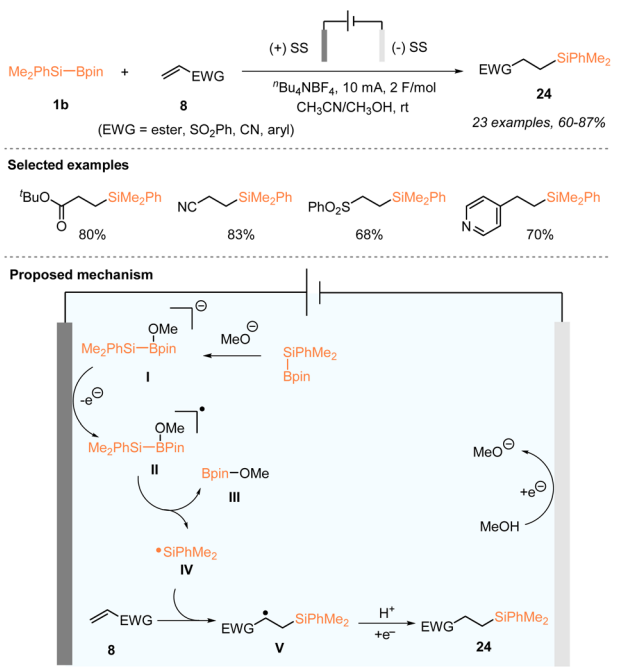
In the same year, Poisson and coworkers developed a facile electrochemical protocol for the synthesis of *gem*-difluoro and γ-fluoroallyl silanes **17** and **19** through a silyl radical mediated transformation between α-trifluoromethylstyrenes **16** or α-difluoromethylstyrenes **18** and $PhMe_2Si$–Bpin (Scheme 7).[25]

It was found that the *in situ* electro-generated silyl radical reacted smoothly with a series of α-trifluoromethylstyrenes **16** to afford the desired *gem*-difluoroallyl silanes **17** with 36–90% yields, in an undivided cell using a stainless steel electrode at the anode and a Pt electrode at the cathode, in a constant current of 25 mA and a total charge of 3 F $mol^{-1}$. By slightly varying the reaction conditions, α-difluoromethylstyrenes **18** could be effectively converted into the corresponding γ-fluoroallyl silanes **19** with 50–86% yields and a 63 : 37 ∼ 90 : 10 *E*/*Z* ratio. A similar mechanism is proposed in Scheme 7. Additionally, the excellent functional group tolerance, diversity and versatility of the thus obtained fluorinated building blocks further highlighted the synthetic value of this method, as exemplified by the preparation of α-difluoroalkyl substituted styrenes **18a** and **20**, difluoromethylated homoallylic alcohol **22**, and β-difluoromethyl silane **23**.

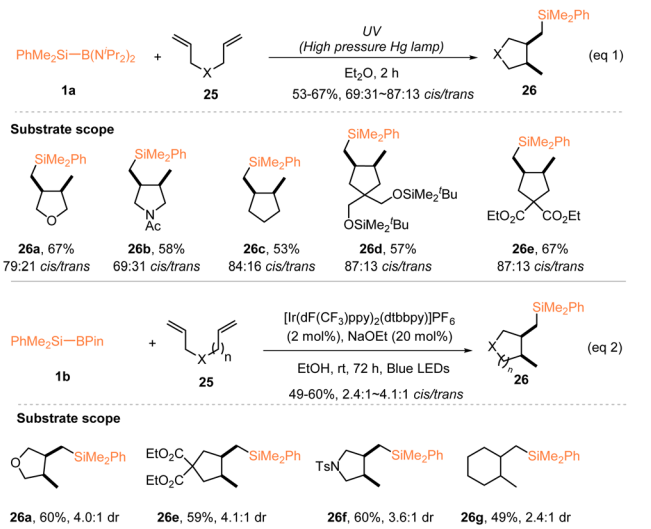
Later in 2023, also by using an electrochemical method, Tang, Pan, and coworkers realized a highly efficient radical hydrosilylation of electron-withdrawing alkenes **8** with $PhMe_2Si$–Bpin **1b** (Scheme 8).[26] In an undivided cell using stainless steel electrodes at both the anode and the cathode, a large panel of electron-withdrawing alkenes **8** successfully reacted with reactive dimethylphenylsilyl radical **IV**, which were electro-generated from $PhMe_2Si$–Bpin, enabling the formation of various hydrosilylated adducts **24** with 60–87% yields. This direct electrochemical hydrosilylation did not require exogenous oxidants and catalysts, making it a green, efficient and sustainable approach for the synthesis of organosilanes. In addition, this method was applied for the late-stage hydrosilylation of natural product acrylate derivatives such as piperitol, Boc-L-prolinol, and cholesterol, allowing the access of the corresponding silylated natural product derivatives. The mechanistic study revealed that a silyl radical was involved in this electrochemical alkene hydrosilylation. As depicted in Scheme 8, a reaction mechanism was proposed, which was similar to that of Poisson's work shown in Schemes 6 and 7.

## 3 Silyl radical involved silylfunctionalization with silylboronates

Along with the development of silyl radical hydrosilylations with silylboronates, a large number of radical silylfunctionalizations have been established using silylboronates as the radical sources, for the diverse synthesis of functionalized organosilanes. Early in 2000, Matsumoto and Ito investigated a photochemical intramolecular cyclization of 1,6-dienes **25** with $PhMe_2Si$–$B(N^iPr_2)_2$ (**1a**), during their study of the silyl radical-induced alkene hydrosilylation. In the presence of 1.2 equiv. $PhMe_2Si$–$B(N^iPr_2)_2$ (**1a**), irradiation of various 1,6-dienes **25** with a high pressure Hg lamp afforded 5-*exo*-cyclized products **26** exclusively in 53–67% yields with 69 : 31 ∼ 87 : 13 *cis*/*trans* selectivities (eqn (1), Scheme 9).[19] It should be mentioned that different functional groups, such as ester, silyl ether, ether, and amide, were tolerated in this radical-induced silylative cyclization. 23 years later, by using a combination of 2 mol% $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ and 20 mol% NaOEt, Tanaka and Nagashima reported a similar radical silylative cyclization of oxygen-, tosylamide-, and malonate-linked 1,6-dienes or methylene-linked 1,7-diene **25** with $PhMe_2Si$–Bpin **1b**, allowing the preparation of five- or six-membered cycles featuring




Scheme 8 Electrochemical hydrosilylation of alkenes with $PhMe_2Si$–Bpin.



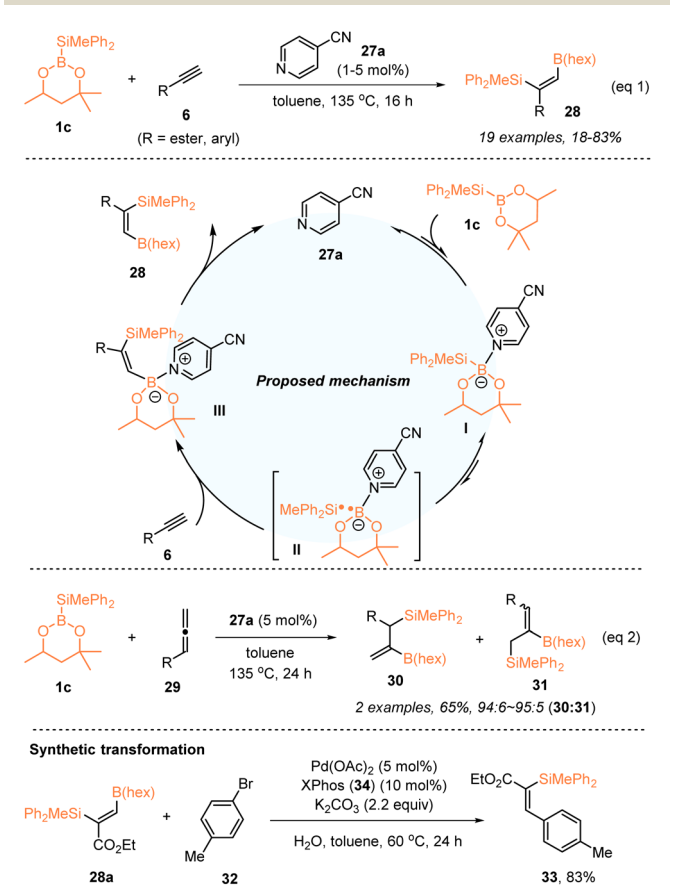

Scheme 9 Photochemical silylative cyclization of dienes with silylboronates.

a $PhMe_2Si$ group with 49–60% yields and 2.4 : 1 ~ 4.1 : 1 *cis*/*trans* selectivities, under the irradiation of blue LEDs (eqn (2), Scheme 9).[22]

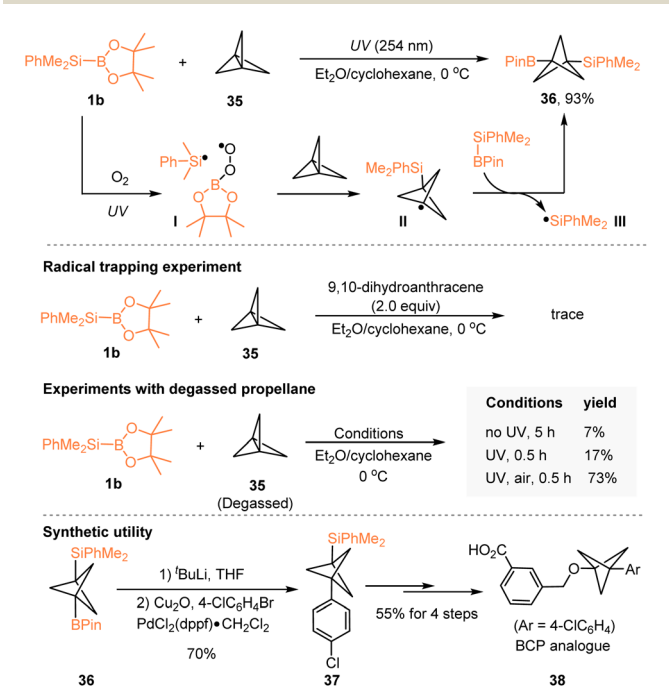
In 2019, Suginome, Ohmura, and coworkers developed a regioselective *syn*-1,2-silaboration of terminal alkynes **6** with hexylene glycol-derived silylboronic ester $PhMe_2Si$–B(hex) (**1c**) by using a pyridine-based organocatalyst (Scheme 10).[27] Under the catalysis of 1–5 mol% 4-cyanopyridine **27a**, a series of aromatic alkynes and alkyl propiolates **6** underwent regio- and stereoselective addition with $PhMe_2Si$–B(hex), to afford (*Z*)-3-boryl-2-silylacrylates **28** with 18–83% yields. Based on the initial experimental studies, a plausible reaction mechanism is proposed in Scheme 10. $PhMe_2Si$–B(hex) was first activated using 4-cyanopyridine **27a** *via* coordination with the B atom, leading to a homolytic cleavage of the Si–B bond to deliver a radical pair **II** consisting of a silyl radical and boron radical stabilized by 4-cyanopyridine. Subsequently, the radical pair was added to the C–C triple bond of alkynes **6** in a *syn* fashion, and the formed species **III** would deliver the targets **28**, accompanied by the regeneration of **27a**. The observed regioselectivity might stem from the fact that the more nucleophilic pyridine-boryl radical preferentially attacked the more electron-deficient alkyne terminus. Interestingly, terminal alkyl allenes were also suitable substrates in this 4-cyanopyridine catalysed silaboration with $PhMe_2Si$–B(hex) **1c**, furnishing β-borylallylsilanes **30** as the major products. Additionally, the thus obtained silaboration adducts were useful synthetic intermediates in the synthesis of stereo-defined functionalized organosilanes *via* the elaboration of the boryl group, as exemplified by the preparation of (*Z*)-3-aryl-2-silylacrylate **33** through Suzuki–Miyaura coupling.

In 2020, Uchiyama, Kanazawa, and coworkers reported a photochemical silaboration of [1.1.1]propellane **35** with $PhMe_2Si$–Bpin **1b**, which enabled the direct incorporation of B and Si functionalities onto the bicyclo[1.1.1]pentane (BCP) scaffold (Scheme 11).[28] Under UV irradiation, the generated dimethylphenylsilyl radical **I** from $PhMe_2Si$–Bpin **1b** and $O_2$ underwent the addition of [1.1.1]propellane **35** to give the BCP radical species **II**, which then reacted with another molecular $PhMe_2Si$–Bpin to deliver the product **36**, accompanied by the formation of silyl radical **III**. Control experiments, together with radical trapping experiments, demonstrated the involvement of a radical chain mechanism in this silaboration, probably initiated by oxygen. Remarkably, the synthetic utility of this methodology was highlighted by its diverse elaborations toward various BCP scaffolds featuring a silyl group. For example, a BCP analogue **38** of the bioactive compound, as a potential bioisostere of the biaryloxy scaffold,[29] was effectively prepared from **36** *via* six step reactions.

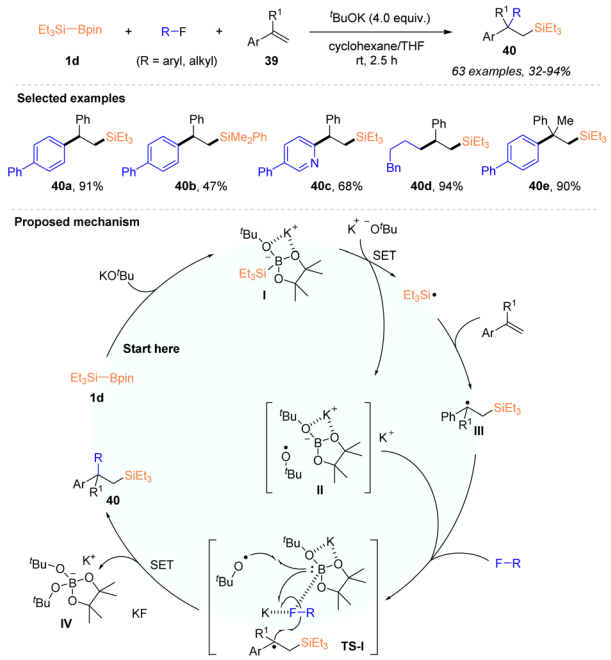
In 2021, the Shibata group disclosed a catalyst-free and $^t$BuOK enabled regioselective carbosilylation of alkenes using silylboronate and organic fluorides, allowing the introduction of silyl and carbon groups across the C–C double bond of alkenes (Scheme 12).[30] Under the action of 4 equiv. $^t$BuOK, a variety of silylated alkanes **40** with β-tertiary or quaternary carbon centers were synthesized in 32–94% yields from styrenes or α-substituted styrenes **39**, in the presence of $Et_3Si$–Bpin **1d**



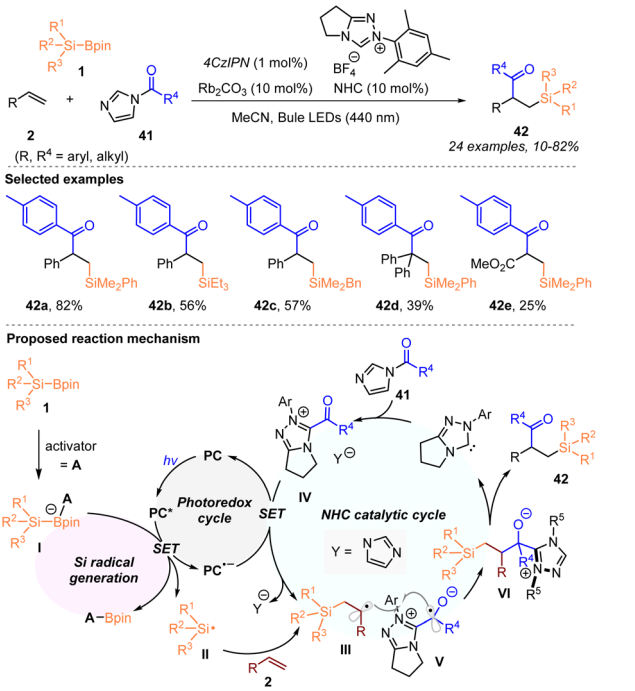

Scheme 10 Regioselective *syn*-1,2-silaboration of alkynes catalyzed by 4-cyanopyridine.




Scheme 11 Silaboration of [1.1.1]propellane with $PhMe_2Si$–Bpin.




Scheme 12 $^{t}$BuOK enabled regioselective carbosilylation of alkenes.




Scheme 13 Radical relay three-component coupling of alkenes with silylboronates and acylimidazoles.

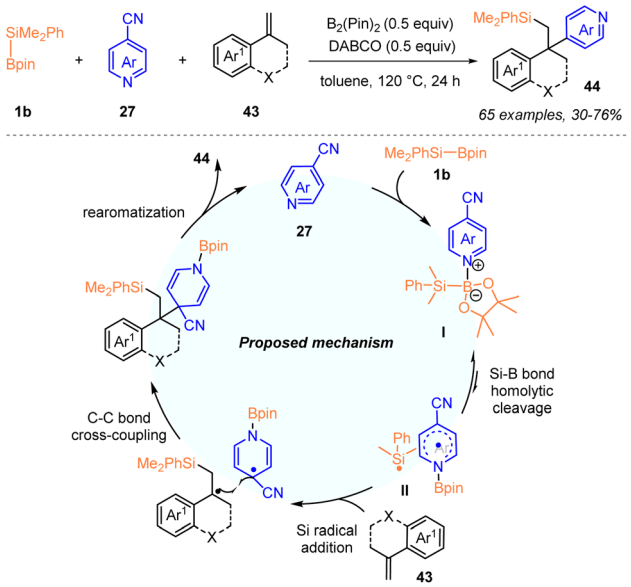
and aryl or alkyl fluorides. Moreover, an intramolecular carbosilylation of fluoroarenes featuring an alkenyl side chain with $Et_3Si$–Bpin **1d** was also established. The mild conditions at room temperature, broad substrate scope and excellent chemo- and site-selectivity demonstrated the practicability of this protocol. It should be mentioned that electron-deficient acrylates and acrylamides, as well as internal styrenes, were not suitable under this reaction system. As depicted in Scheme 12, the authors proposed a possible mechanism involving the silyl radical pathway, according to the initial mechanistic study. $Et_3Si$–Bpin **1d** was first activated by $^{t}$BuOK, and the formed intermediate **I** underwent a SET process with a *t*-butoxy anion ($^{t}BuO^{-}$) to deliver a triethylsilyl radical ($^{\bullet}SiEt_3$) *via* the cleavage of the Si–B bond, accompanied by the generation of boron species **II**. The addition of $^{\bullet}SiEt_3$ to styrene gave rise to a carbon-centered radical adduct **III**, which underwent radical reactions with fluorides, $^{\bullet}OBu^{t}$, and borate anions, as shown in the transition state **TS-I**, where the C–F bond of fluorides was activated by both $K^{+}$ and boron atoms. Finally, the desired carbosilylated adducts were obtained after forming a C–C bond, with the concomitant generation of a stable borate complex [Bpin($O^{t}Bu$)$_2$]K **IV** and KF.

In 2022, by combining visible-light-induced silyl radical generation from silylboronates with radical NHC catalysis, Ohmiya, Sumida, and coworkers accomplished the acylsilylation of alkenes **2** with silylboronates **1** and acylimidazoles **41** (Scheme 13).[21]

In the presence of 4CzIPN (1 mol%), the NHC catalyst and $Rb_2CO_3$ (10 mol%, each), the radical relay three-component coupling process involving a silyl radical allows the introduction of acyl and organosilyl moieties into alkenes, affording a variety of β-acyl substituted silanes **42** with 10–82% yields, under blue LED irradiation. A possible reaction mechanism is illustrated in Scheme 13, in which the silyl radical **II** was first formed *via* SET oxidation of the activated silylboronates **I** with the excited photocatalyst (PC*). The radical addition of silyl radical **II** to alkenes **2** led to the generation of carbon-centered radical species **III**. The generated acyl azolium complex **IV** underwent a SET reduction with the reduced photocatalyst ($PC^{\bullet-}$) in the NHC catalytic cycle, to deliver the persistent ketyl radical **V**. Subsequently, radical–radical coupling between **III** and **V** occurred to give the intermediate **VI**, which produced the targets **42** with the regeneration of the NHC catalyst. Notably, as mentioned by the authors, such acylsilylation was difficult to achieve with HAT-promoted silyl radical generation methods.

Also in 2022, Li, Wang and co-workers described a metal-free 1,2-silylpyridylation of alkenes **43** with $PhMe_2Si$–Bpin (**1b**) and 4-cyanopyridines **27** *via* pyridine-mediated B–B and B–Si bond activation (Scheme 14).[31a] In the presence of DABCO and $B_2pin_2$ (50 mol%, each), a wide range of alkenes **43** and substituted 4-cyanopyridines **27** were tolerated and provided various C4-silylalkylated pyridines **44** in 30–76% yields with excellent functional group compatibility.

More importantly, this method could be easily applied to the late-stage modification of complex bioactive molecules. A proposed mechanism with a silyl radical addition and sequential radical–radical coupling process is demonstrated in Scheme 14, in which the addition of the silyl radical to the alkene was the rate-limiting step. The author proposed that the 4-cyanopyridine might play dual roles in this 1,2-silylpyridylation, including the homolytic cleavage of the Si–B bond to give the silyl radical and pyridine-boryl radical, and the homolytic



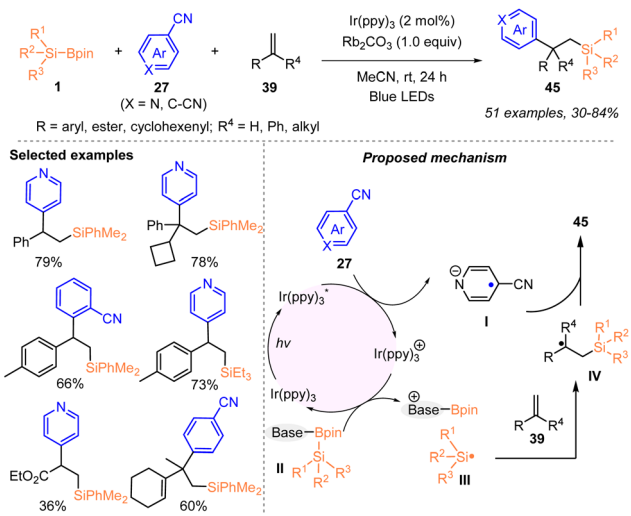

Scheme 14 1,2-Silylpyridylation of aryl alkenes with $PhMe_2Si$–Bpin.

cleavage of the B–B bond of $B_2pin_2$ to produce a persistent pyridine-boryl radical for the subsequent radical–radical coupling process. Additionally, the presence of DABCO might inhibit the competitive Si–C bonding events of the silyl radical and 4-cyanopyridinyl-boryl radical.

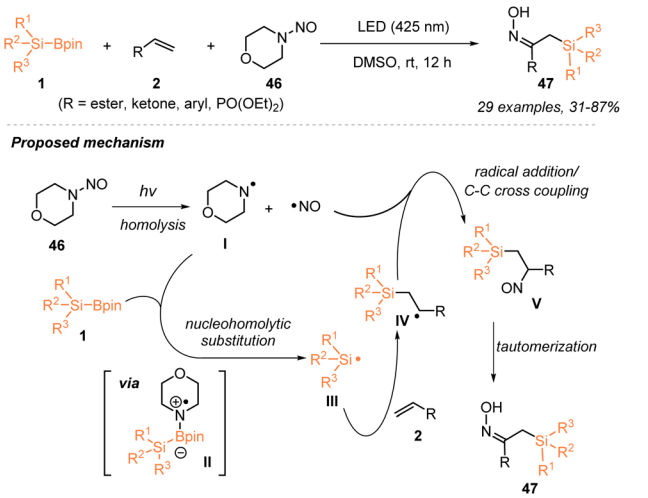
Later on, the same group reported a visible-light catalyzed arylsilylation of alkenes **39** with silylboronates **1** and (hetero) aryl nitriles **27**, which enabled the diverse construction of valuable silicon-containing 1,1-diaryl derivatives (Scheme 15).[31b] Under blue LED irradiation, the arylsilylation of mono- or di-substituted alkenes **39** proceeded smoothly to deliver various silylated 1,1-diaryl compounds **45** with 30–84% yields, in the presence of 2 mol% $Ir(ppy)_3$ and 1 equiv. $Rb_2CO_3$. Based on control experiments, the authors proposed a plausible mechanism, in which aryl nitriles underwent single-electron reduction with excited $Ir(ppy)_3^*$ to generate aryl nitrile radical anion **I** and oxidizing $Ir(ppy)_3^+$. The activated silylborane **II** was oxidized by $Ir(ppy)_3^+$ to afford the silyl radical **III** after undergoing Si–B bond cleavage, along with the regeneration of $Ir(ppy)_3$. Subsequently, the addition of silyl radical **III** to alkenes led to the formation of carbon-centered radical **IV**, which coupled with aryl nitrile radical anion **I** to give the desired products **45**.

In 2024, Wang, Jia and coworkers disclosed a novel strategy to generate silyl radicals from silylboronates **1** *via* nucleohomolytic substitution of boron with aminyl radicals and applied such a strategy to realize an efficient silyl-oximation of alkenes **2** utilizing silylboronates **1** and *N*-nitrosamine **46** (Scheme 16).[32] Under the irradiation of 425 nm LEDs, a variety of α-oximinoesters **47** bearing a silyl group were obtained in 31–87% yields. The radical-trapping experiment with TEMPO and the radical clock experiment with vinyl cyclopropane supported the involvement of a silyl radical intermediate in this visible-light-induced catalyst-free silyl-oximation of alkenes. Accordingly, a plausible mechanism is proposed in Scheme 16, whereby photo-induced homolytic cleavage of the N–NO bond in *N*-nitrosamine produces an amino radical **I** and a persistent NO˙ radical. Subsequently, a nucleohomolytic substitution of silylboronates with amino radical **I** released a silyl radical **III**, which then reacted with an alkene to afford carbon-centered radical **IV** that was captured by the persistent NO˙ radical to deliver the target after tautomerization.

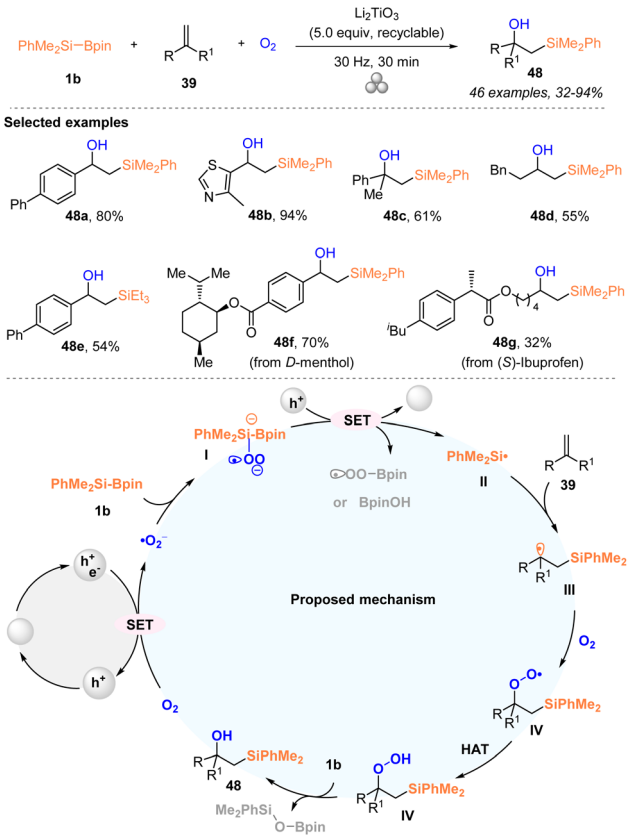
Very recently, Lian and coworkers developed a triphasic 1,2-hydroxysilylation of alkenes **39** with $PhMe_2Si$–Bpin **1b** under an oxygen atmosphere by mechanically piezoelectric catalysis through a single-electron-transfer (SET) pathway (Scheme 17).[33] A series of aromatic and aliphatic alkenes **39** worked well with $PhMe_2Si$–Bpin **1b** under an oxygen atmosphere to deliver the corresponding 1,2-hydroxysilylation products **48** with 32–94% yields. Moreover, this method could be used for the late-stage modification of drug-derived alkenes. Notably, this strategy pioneers the research in mechanic force-induced solid–liquid–




Scheme 15 Visible light-catalyzed arylsilylation of alkenes.



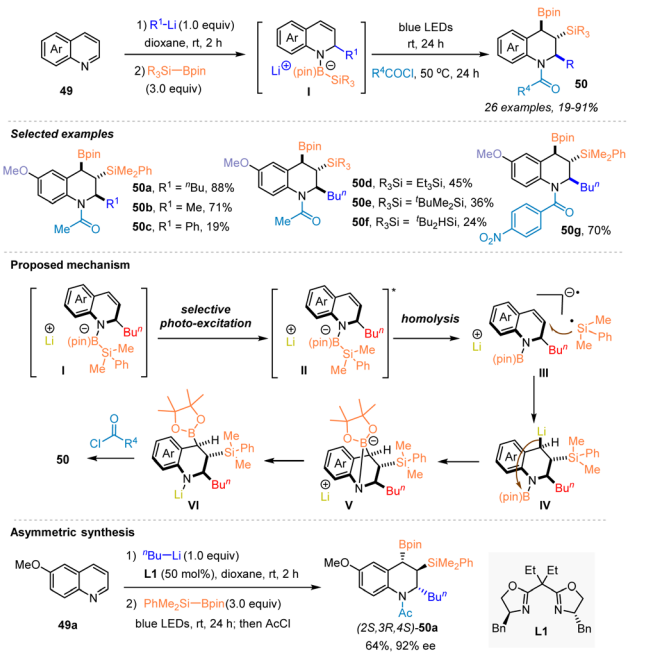

Scheme 16 Silyl-oximation of alkenes with silylboronate and *N*-nitrosamine.




Scheme 17 Triphasic hydroxysilylation of alkenes by mechanically piezoelectric catalysis.

gas triphase reactions under ambient conditions and indicates that silylboronate can be transformed into a silyl radical by highly polarized $Li_2TiO_3$ particles and oxygen under ball-milling conditions for the first time. The excellent substrate scope with good functionality tolerance, simple operation, multiple recycles of the catalyst, and solvent-free conditions further highlighted the practicability of the current protocol. A silyl radical process involving reaction pathway was proposed according to the mechanistic studies, as illustrated in Scheme 17. The highly polarized $Li_2TiO_3$ particles were first generated by agitating $Li_2TiO_3$ particles *via* ball-milling, which reduced oxygen to give superoxide radicals ($^{\bullet}O_2^-$). Subsequently, the intermediate **I**, which was produced from superoxide radicals ($^{\bullet}O_2^-$) *via* coordinating with the boron center of silylboronate **1b**, underwent SET oxidation to afford the silyl radical species **II**, accompanied by the reduction of the oxidized $Li_2TiO_3$ particles. The trapping of the silyl radical **II** with alkenes delivered alkyl radical intermediate **III**, which then interacted with triplet oxygen to give the peroxyl radical species **IV** *via* the formation of the C–O bond. Finally, the target **48** was generated from intermediate **IV** after undergoing a HAT process and reduction with silylboronate.

In 2023, Tanaka and coworkers developed a chemo-, regio- and stereo-selective dearomatic triple elementalization (carbo-sila-boration) of quinolines through the addition of organolithium and sequential visible light-induced silaboration, allowing the efficient synthesis of various carbo-sila-borated

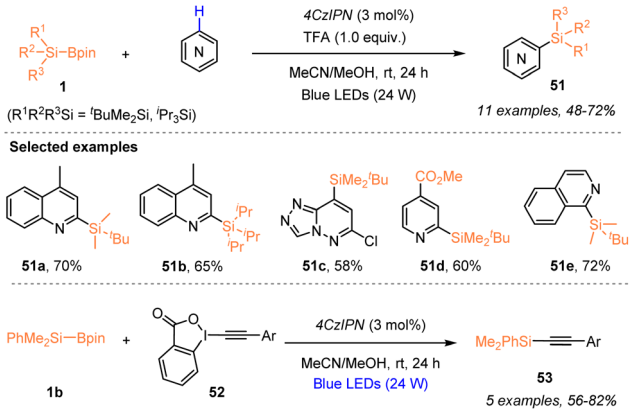



Scheme 18 Dearomative triple elementalization (carbo-sila-boration) of quinolines.

tetrahydroquinolines **50** that are expected to be versatile synthetic platforms (Scheme 18).[34] The tandem sequence started with the addition of organolithium to quinolines **49**. The generated lithium anilides then reacted with silylboronates to afford the anilide-silylborane ate complexes **II**, which underwent Si–B bond cleavage to form silyl radicals under blue LED irradiation, thus enabling the occurrence of carbo-sila-boration to deliver the desired products **50**. Control experiments and DFT calculation studies revealed the involvement of a Si–B bond activation process in this sequence, in which visible light excitation of anilide–silylborane ate complexes **II** produced a silyl radical rather than a silyl anion. Notably, the synthetic utility of this method was highlighted by the potential of carbo-sila-borated tetrahydroquinolines as synthetic platforms, as exemplified by the chemo- and stereospecific conversions of C–B/C–Si bonds to C–C, C–O, and C–H/D bonds. In addition, the asymmetric carbo-sila-boration of quinoline was explored by combining an asymmetric alkylation of quinoline with *n*-BuLi enabled by chiral ligand **L1**, delivering chiral carbo-sila-borated tetrahydroquinoline (2*S*,3*R*,4*S*)-**50a**.

## 4 Selective silylation *via* C–X bond cleavage

Aside from the radical silylfunctionalization of unsaturated hydrocarbons, *e.g.* alkenes or alkynes, the use of silylboronate as a silyl radical precursor has recently been applied for selective silylation *via* C–X bond cleavage. In 2023, Zhang, Wang, and coworkers employed a visible-light-induced organophotocatalytic strategy to realize a radical Minisci-type C–H silylation of N-heteroarenes with silylboronates **1** (Scheme 19).[23]



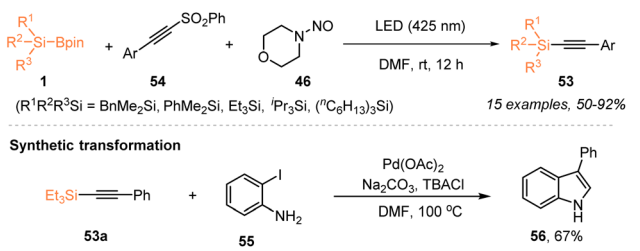

Scheme 19 Organophotocatalytic silylation *via* C–H or C–I bond cleavage.

The use of 3 mol% 4CzIPN enabled the facile synthesis of silylated N-heteroarenes **51** with 48–72% yields, in the presence of TFA (1.0 equiv.), under 24 W blue LED irradiation. Moreover, the authors found that the silyl radicals generated *via* such an organophotocatalytic strategy could react with ethynylbenziodoxolones (EBXs) **52** through C–I bond cleavage, thus realizing the alkynylation of silylboronates **1** with EBXs **52** for the preparation of alkynylsilanes **53** with 56–82% yields.

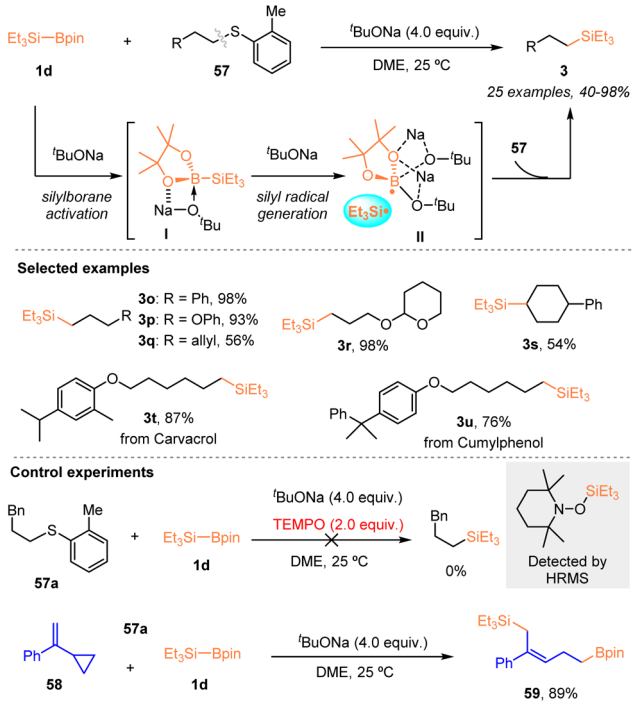
A year later, Wang and Jia *et al.* also reported the preparation of synthetically useful alkynylsilanes by using silyl radicals generated from silylboronates *via* nucleohomolytic substitution of boron with aminyl radicals (Scheme 20).[32] Under 425 nm LED irradiation, the alkynylation of silylboronates **1** with ethynyl phenyl sulfones (EPSs) **54** proceeded smoothly to afford a series of silylated alkynes **53** with 50–92% yields, in the presence of *N*-nitrosamine **46**. The process for silyl radical generation was the same as the pathway of Scheme 16. The transformation of alkynylsilane **53a** into 3-phenylindole further highlighted the utility of this protocol.

In 2023, Feng, Xue, and Liu accomplished a $^{t}$BuONa enabled site-selective silylation of alkyl/aryl thioethers **57** with $Et_3Si$–Bpin (**1d**) *via* C(alkyl)–S bond cleavage (Scheme 21).[35]

It was found that a series of primary or secondary alkyl aryl sulfides **57** were tolerated and afforded various alkylsilanes **3** with 40–98% yields, in the presence of 4.0 equiv. $^{t}$BuONa. $Et_3Si$–Bpin was activated by $^{t}$BuONa to form complex **I**, which further interacted with another $^{t}$BuONa molecule to produce the active silyl radical *via* a single-electron transfer process. Subsequently,




Scheme 20 Visible light-induced alkynylation of silylboronates.

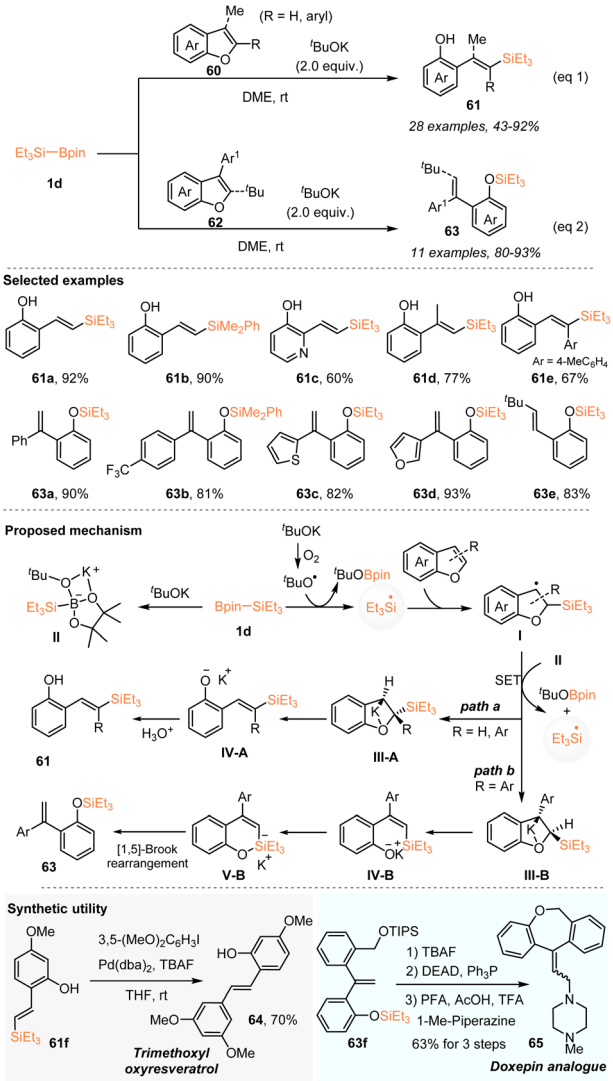



Scheme 21 Site-selective silylation of thioethers with $Et_3Si$–Bpin *via* C–S bond cleavage.

the resulting silyl radical prefers to work with the C(alkyl)–S bond, facilitating the C(alkyl)–S bond cleavage to yield alkylsilanes. Furthermore, the gram scale synthesis and late-stage silylation of bioactive molecules highlighted the usefulness of this protocol. Radical inhibition and radical clock experiments confirmed the involvement of silyl radical species in this reaction system.

Also in 2023, Cui, Cao, Shi, and coworkers reported a dearomatization silylation of benzofurans or furopyridines *via* silyl radical addition and subsequent C–O bond scission (Scheme 22).[36] Under the action of 2.0 equiv. $^{t}$BuOK, a series of benzofurans or furopyridines without substituents at the C2 or C3 position worked well with $Et_3Si$–Bpin **1d** to deliver the ring-opening vinylsilanes **61** with 43–92% yields. Benzofurans, featuring an aryl at the C2 position or a methyl at the C3 position, were tolerated as well and afforded the corresponding vinylsilanes with moderated to good yields.

It should be mentioned that benzofurans with a bulky *tert*-butyl group at the C2-position or an aryl group at the C3-position underwent[1,5] Brook rearrangement following silyl radical addition and subsequent C–O bond scission, producing vinylphenoxyl silanes **63** with 80–93% yields. Based on initial mechanistic studies, the authors proposed a reaction mechanism, as shown in Scheme 22. The triethylsilyl radical EtSi˙ was first generated *via* the reaction of $Et_3Si$–Bpin with a $^{t}$BuO radical that was formed from $^{t}$BuOK and $O_2$. The addition of EtSi˙ to benzofurans or furopyridines proceeded to give the carbon-centered radical species **I**, whilst the direct interaction of $Et_3Si$–Bpin with $^{t}$BuOK led to the formation of complex **II**. Subsequently, radical species **I** underwent a SET process with

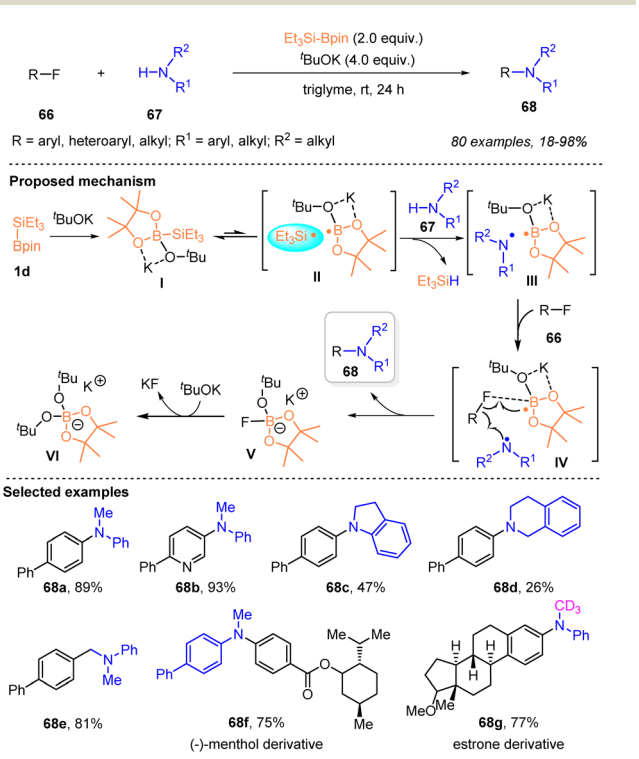



Scheme 22 Dearomatization radical silylation of benzofurans or furopyridines.

complex **II** to afford intermediate **III-A** or **III-B**. Then **III-A** underwent β-elimination to give the product **61** after protonation, while **III-B** underwent sequential β-elimination and [1,5]-Brook rearrangement to furnish vinylphenoxyl silanes **63**. Moreover, the diverse product elaboration demonstrated the practicability of this protocol, as evidenced by the preparation of trimethoxyl oxyresveratrol **64** and doxepin analogue **65**.

## 5 Silyl radical mediated cross-coupling with silylboronates

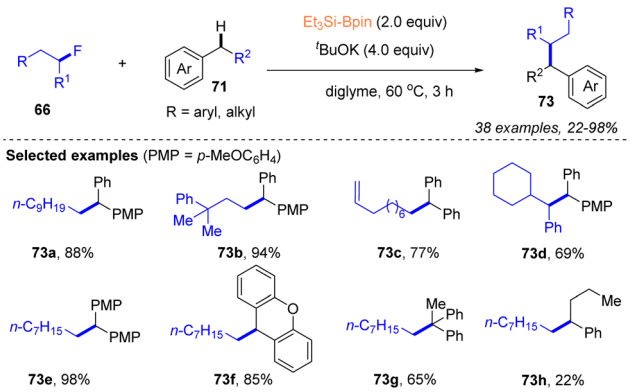
With the application of silylboronates as silyl radical precursors for constructing organosilanes *via* C–Si bond forming reactions, silylboronates have also been identified as an effective medium for enabling C–F bond cleavage of organic fluorides to enable cross coupling reactions. In 2023, the Shibata group pioneered this study and established a transition metal-free silylboronate-mediated cross-coupling of organic fluorides **66** with amines **67** *via* inert C–F bond activation under mild conditions (Scheme 23).[37] A series of (hetero)aryl or alkyl fluorides reacted smoothly with cyclic or acyclic *N*-alkylanilines or secondary dialkylamines **67**, in the presence of 2 equiv. $Et_3Si$–Bpin and 4 equiv. $^t$BuOK, to afford various tertiary amines **68** with 18–98% yields. The coordination of $Et_3Si$–Bpin and $^t$BuOK enabled the cross-coupling to proceed at room temperature, thus avoiding the high potential barriers associated with thermally induced $S_N2$ or $S_N1$ amination. A single-electron-transfer/radical-mediated defluorinative amination involving a frustrated radical pair chemistry mechanism is illustrated in Scheme 23, according to the mechanistic studies. The intermediate **I** was first generated from $Et_3Si$–Bpin with KO$^t$Bu, which then produced a frustrated radical pair **II** that comprises $Et_3Si^{\bullet}$ and a boron-radical species *via* the homolytic cleavage of the Si–B bond. The formed $Et_3Si^{\bullet}$ underwent hydrogen abstraction from amines **67** to provide a frustrated radical pair **III** consisting of an amino radical and the boron radical species, along with the generation of $HSiEt_3$. The frustrated radical pair **III** subsequently interacted with organic fluorides **66** *via* transition state **IV**, where the C–F bond was activated by the interaction between the F atom and B center, and the amino radical selectively attacked the carbon center of the C–F bond, to deliver the desired cross-coupling product, accompanied by the formation of stable [Bpin(O$^t$Bu)$_2$]K (**VI**). The significant feature of this transformation included the selective activation of the C–F bond of organofluorides by silylboronate without affecting potentially cleavable C–O, C–Cl, C–H or C–N bonds and the $CF_3$ group, mild reaction conditions, broad substrate scope, and late-stage modification of fluorine-containing drugs.




Scheme 23 Silylboronate-mediated radical cross-coupling of fluorides and amines.

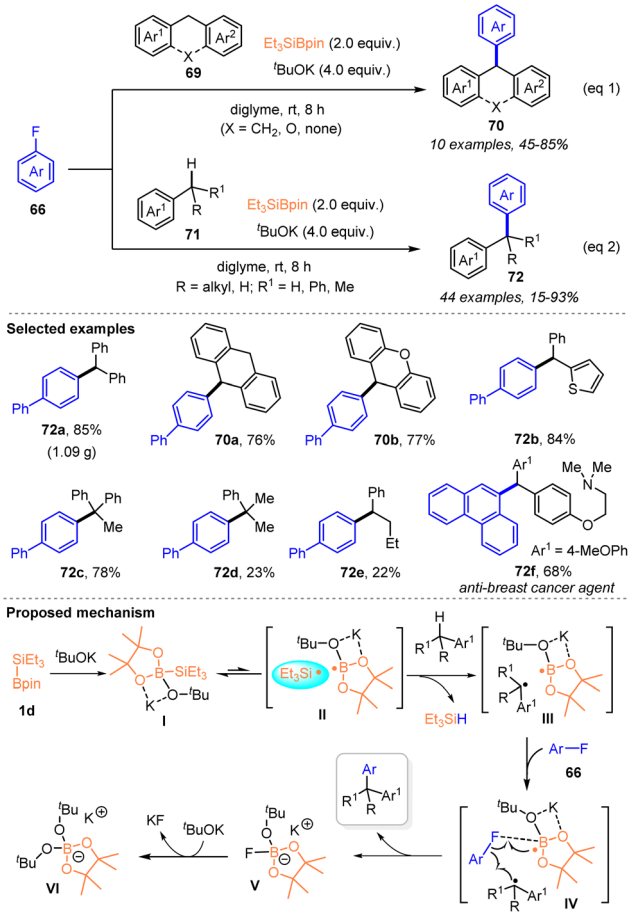
Shortly after, by employing the strategy of silyl radical-mediated cross-coupling of fluorides, the same group realized an efficient cross-coupling of aryl fluorides **66** with arylalkanes **69** or **71** enabled by a combination of $Et_3Si$–Bpin **1d** with $^t$BuOK, allowing the diverse access of various triaryl- or diarylalkanes **70** or **72**, which are promising scaffolds for pharmaceuticals and functional materials, with moderate to excellent yields under very mild reaction conditions (Scheme 24).[38] A salient feature of this protocol was that the activation of the C–F and C–H bonds occurred at room temperature. The practicability was further highlighted by the fact that no transition metal and specialized ligands with high temperature, which are usually required in common cross-coupling reactions, were used in this method. A similar silyl radical-involved reaction mechanism is proposed in Scheme 24, based on the ESR analysis and experimental studies.

Subsequently, they further utilized a silylboronate-mediated cross-coupling strategy to enable the cross coupling of alkyl fluorides and aryl alkanes for the formation of $C(sp^3)$–$C(sp^3)$ bonds (Scheme 25).[39] Under the action of $Et_3Si$–Bpin with $^t$BuOK, a variety of alkyl fluorides **66** could react efficiently with mono- or diaryl alkanes **71** at 60 °C, producing diaryl or aryl alkanes **73** bearing a tertiary or quaternary carbon center in 22–98% yields. Moreover, alkyl chlorides, bromides, and iodides were also suitable substrates for this transformation. Although a radical-involving pathway was supported by radical trapping and ESR experiments, radical ring-opening experiments and DFT calculations suggested that an ionic process might occur in this cross-coupling. Notably, mechanistic studies using DFT calculations were conducted on silylboronate-mediated cross-coupling for the first time and supported the crucial role of diglyme in enhancing the reaction efficiency *via* encapsulation of potassium cations (Scheme 25).

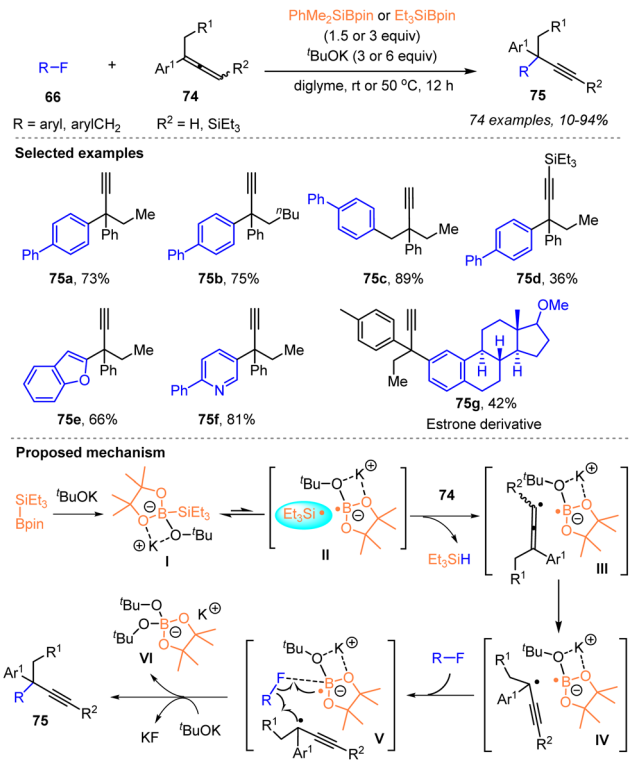



Scheme 25 Silylboronate-mediated cross-coupling of alkylfluorides and aryl alkanes.

More recently, Shibata and coworkers developed an efficient silylboronate-mediated cross-coupling between organic fluorides **66** and allenes **74** *via* a catalyst-free silyl radical relay strategy, which provided a facile protocol for the construction of α-alkynyl substituted all-carbon quaternary centers (Scheme 26).[40]




Scheme 24 Silylboronate-mediated cross-coupling of benzylic C–H with arylfluorides.




Scheme 26 Radical cross-coupling of organic fluorides and allenes mediated by silylboronates.

Under the action of $^{t}$BuOK and $Et_3Si$–Bpin **1d** or $PhMe_2Si$–Bpin **1b**, a variety of aryl or benzyl fluorides **66** worked well with disubstituted allenes **74** to afford a library of coupling products **75** featuring an α-ethynyl-containing all-carbon quaternary center with up to 94% yields. The key to success was *in situ* radical rearrangement of the formed allenyl radicals to give bulky tertiary propargyl radicals. A salient feature of this cross-coupling was the ability of the *in situ* generated silyl radical to abstract a proton directly from the C($sp^2$)–H bond of allenes to form an allenyl radical, which was subsequently isomerized to a propargylic radical, as depicted in the proposed mechanism of Scheme 26. Furthermore, mild reaction conditions without a transition metal, wide substrate scope, the late-stage functionalization of bioactive molecules and the modification of a liquid crystalline material demonstrated the practical utility of the current protocol.

# 6 Conclusion and outlook

The past few years have witnessed significant advancements in synthetic applications of silylboronates as silyl radical precursors, with the rapid development of radical chemistry. As summarized in this review article, a variety of C–Si or C–X bond forming transformations have been established for the diverse construction of organosilanes or other valuable molecules (*e.g.* tertiary amines, triaryl- or diarylalkanes and α-alkynyl substituted quaternary centers), including hydrosilylation of alkenes or alkynes; silyl radical involved silylfunctionalization; selective radical silylation *via* C–X bond cleavage; silyl radical mediated cross-coupling.

Despite these impressive achievements, there is still ample room for further exploration in synthetic applications of silylboronates as silyl radical precursors toward valuable chemicals. First, more successful and diverse transformations are needed to demonstrate the synthetic practicability and potential of silylboronates as silyl radical precursors, since most of the currently reported examples focus on the hydrosilylation or silylfunctionalization. Second, the generation of silyl radical species from silylboronates mainly relies on the use of photochemical, electrochemical or stoichiometric base activation. Therefore, the development of new and efficient methods for the generation of silyl radicals from silylboronates will be highly desirable. Third, no asymmetric reactions using silylboronates as silyl radical sources have been reported, which provides another important direction to explore radical asymmetric transformations involving silylboronates for accessing chiral organosilanes, in particular, silicon-stereogenic chiral silanes.[41] With the continuous emergence of new silylboronate reagents, catalytic systems, and synthetic strategies, it can be anticipated that more and more attractive and facile silyl radical transformations involving silylboronates will be explored, which will greatly broaden the synthetic applications of silylboronates in the area of radical chemistry.

# Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

# Author contributions

All authors co-wrote the manuscript.

# Conflicts of interest

There are no conflicts to declare.

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