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Visible-Light-Mediated Divergent Silylfunctionalization of Alkenes

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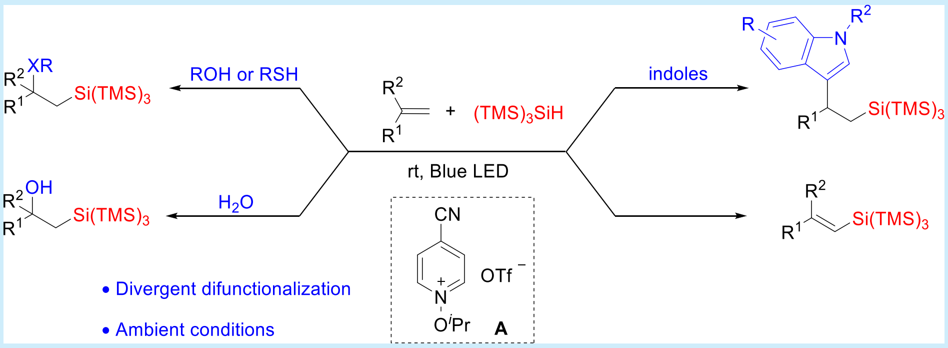
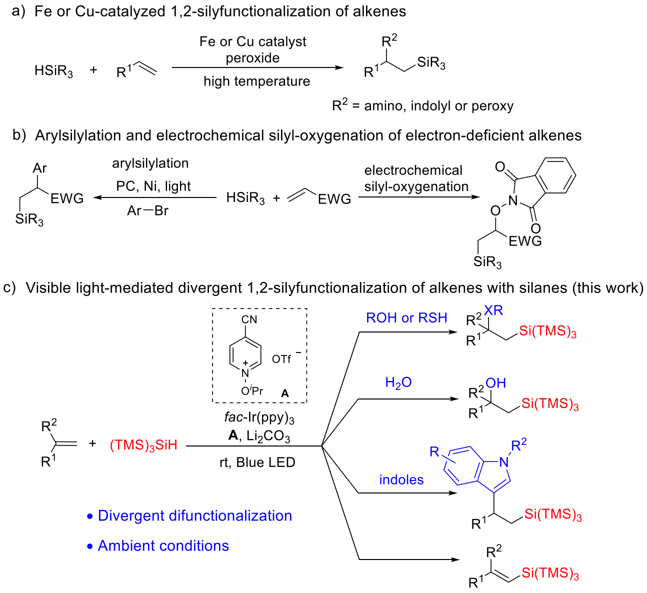


ABSTRACT: 1,2-Silylfunctionalization of alkenes is an efficient way to construct highly functionalized silicon-containing compounds. However, examples of 1,2-silylfunctionalization of alkenes using readily available hydrosilanes are limited. Herein, we present a visible-light-mediated divergent 1,2-silylfunctionalization of alkenes using hydrosilane under ambient conditions. A series of β-alkoxy, β-alkylthio, β-hydroxy, and β-indolyl silanes was obtained in good to excellent yields. Moreover, vinylsilanes were successfully prepared in the absence of an additional nucleophile.

Silicon-containing scaffolds are important building blocks that are present in a wide range of materials and pharmaceuticals.[1] Thus, the development of efficient and atom economic approaches to assemble organosilicon compounds has attracted significant attention. 1,2-Silylfunctionalization of alkenes with readily available hydrosilanes is a promising method that enables the rapid construction of complex silicon-containing motifs via the simultaneous introduction of a silicon group and another functional group. However, compared with the hydrosilylation of alkenes, which has been extensively studied, examples of the silylfunctionalization of alkenes are still limited. 1,2-Carbosilylation, 1,2-aminosilylation, and 1,2-peroxysilylation of alkenes triggered by the addition of silyl radicals have been developed using Fe or Cu as the catalyst (Scheme 1a).[2] In 2020, Kondo and co-workers reported the metal-free intramolecular carboxysilylation of alkenes using di-*tert*-butyl peroxide (DTBP) as a radical initiator.[3] However, these systems require high temperatures. Visible-light-promoted hydrogen atom transfer of hydrosilanes has been developed to generate silyl radicals under ambient conditions.[4] On the basis of the photoinduced strategy, silylcarboxylation and arylsilylation of alkenes have been demonstrated by the Wu and Hu groups, respectively.[5] Recently, He and co-workers reported the elegant oxysilylation of electron-deficient alkenes employing an electrochemical Si–H activation strategy (Scheme 1b).[6] Despite these advances, catalytic 1,2-hydroxysilylation and 1,2-alkoxysilylation of alkenes using hydrosilanes remain challenging. In 2003, Ishii

Scheme 1. 1,2-Silylfunctionalization of Alkenes Using Silanes



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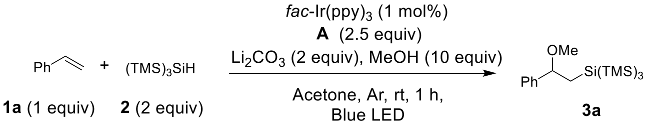
and co-workers accomplished the first 1,2-hydroxysilylation of alkenes using hydrosilanes and a catalytic amount of *N*-hydroxyphthalimide (NHPI) and $Co(OAc)_2$ under an oxygen atmosphere.[7] However, only limited alkenes bearing electron-withdrawing groups are suitable for this system. On the basis of the general mechanism of alkene silylfunctionalization using hydrosilanes, trapping the β-silyl carbon cation intermediate derived from the addition of the silyl radical to an alkene by H_2O or alcohol is a straightforward way to realize the 1,2-hydroxysilylation and 1,2-alkoxysilylation of alkenes. However, H_2O or alcohols have never been used as nucleophiles in these transformations. We suspect that this is the result of two challenges: (1) hydrosilanes can easily undergo hydrolysis and alcoholysis in the presence of transition metals at high temperatures, affording silanols and silyl ethers,[8] and (2) the α-H atom in alcohols can be abstracted by hydrogen atom transfer (HAT) reagents to generate carbon radicals, which inhibit activation of the Si−H bond.[9] Therefore, the development of a new and efficient protocol for alkene 1,2-hydrosilylation and 1,2-alkoxysilylation with hydrosilanes to access β-silyl alcohols and ethers using H_2O and alcohols as nucleophiles is of great interest.

The photoredox catalytic reduction of *N*-alkoxyazinium salts represents a facile approach for the synthesis of highly reactive alkoxy radicals.[10] In our previous work, we reported the photoinduced divergent difunctionalization of alkenes using *N*-alkoxyazinium salts as the source of an oxygen radical.[11] We envisioned that this strategy could allow the activation of the Si−H bond in hydrosilanes to provide silyl radicals, thereby realizing the 1,2-silylfunctionalization of alkenes under mild conditions. Herein, we report the visible-light-mediated divergent silylfunctionalization of alkenes using various nucleophiles, such as H_2O, alcohols, thiols, and indoles, to prepare a series of new functionalized silicon-containing compounds (Scheme 1c). Moreover, vinylsilanes were successfully prepared in the absence of an additional nucleophile.

We initiated our study on alkene 1,2-silylfunctionalization employing styrene (**1a**) and $(TMS)_3SiH$ (**2**) as substrates and utilizing methanol as the nucleophile. On the basis of our previous study, we chose *N*-isopropylazinium salt **A** as the precursor of the alkoxy radical because the sterically bulky isopropyl group can inhibit the direct addition of the alkoxy radical to **1a**. After careful evaluation, we found that the desired product **3a** was obtained in 93% yield in the presence of 1 mol % *fac*-$Ir(ppy)_3$ with 2 equiv of Li_2CO_3 as the base at room temperature (Table 1, entry 1). Changing the photocatalyst to $[Ir(dtbbpy)(ppy)_2][PF_6]$ or $Ru(bpy)_3Cl_2$ gave lower yields (entries 2 and 3). The 4-CzIPN could not catalyze this transformation (Table S2, entry 1). We reasoned that silyl radical species may be oxidized by the oxidized 4-CzIPN [$E_{1/2}(P^+/P) = +1.52$ V SCE in MeCN)] easily giving a silicon cation. Decreasing the amount of $(TMS)_3SiH$ or MeOH resulted in lower yields (entries 4 and 5). The addition of 1.5 equiv of **A** led to a lower product yield due to a decreased amount of isopropoxy radical formed during the reaction, which initiates the production of the silyl radical (entry 6). Conducting the reaction with or without other bases, such as KH_2PO_4 and K_2CO_3, sharply decreased the yield of **3a** (entries 7−9). When the reaction was carried out using TBHP as the oxidant, the yield of **3a** decreased to 15% (entry 10). Only a 42% yield of **3a** was obtained when acetone was replaced with dioxane as the reaction solvent (entry 11). The 1,2-silylfunctionalization was completely suppressed in the absence of **A**, photocatalyst, or light, revealing that all these components were essential for the reaction to occur (entries 12 and 13).

Table 1. Optimization of the 1,2-Methoxysilylation of Styrene[a]



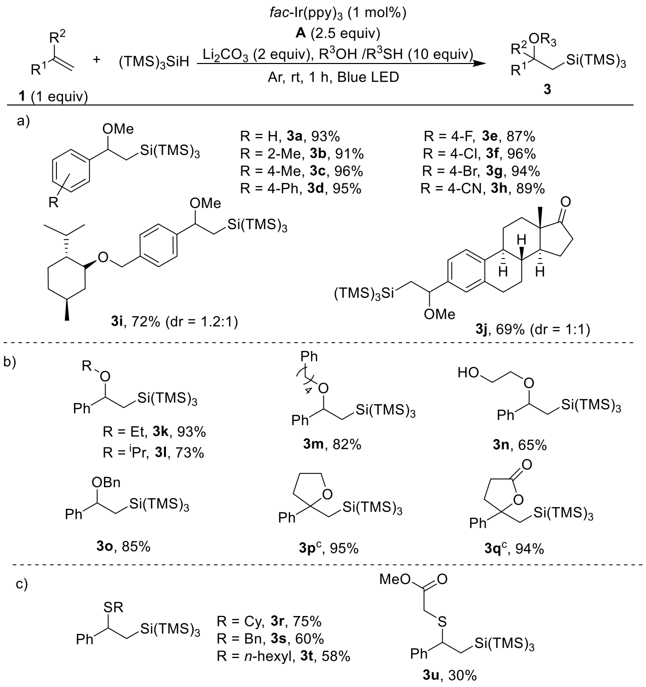
entry	deviation	yield[b] (%)
1	none	93
2	$[Ir(dtbbpy)(ppy)_2][PF_6]$ instead of *fac*-$Ir(ppy)_3$	20
3	$Ru(bpy)_3Cl_2$ instead of *fac*-$Ir(ppy)_3$	30
4	using 1.5 equiv of $(TMS)_3SiH$	53
5	5 equiv of CH_3OH as the additive	86
6	using 1.5 equiv of **A**	83
7	KH_2PO_4 instead of Li_2CO_3	0
8	K_2CO_3 instead of Li_2CO_3	66
9	without base	11
10	TBHP instead of **A**	15
11	1,4-dioxane instead of acetone	42
12	without **A**	N.D.
13	without light or *fac*-$Ir(ppy)_3$	N.D.

[a] Reaction conditions: **1a** (0.1 mmol), *fac*-$Ir(ppy)_3$ (1 mol %), $(TMS)_3SiH$ (0.2 mmol), MeOH (10 equiv), **A** (0.25 mmol), Li_2CO_3 (0.2 mmol), blue LED, Ar, rt, 1 h. [b] Isolated yield. N.D. = not detected.

With the optimized conditions in hand, we subsequently explored the scope of this alkene 1,2-silylfunctionalization reaction (Scheme 2). An array of styrene substrates bearing electron-donating and electron-withdrawing substituents was efficiently converted into the corresponding β-methoxysilanes in good yields (**3a**−**3h**). Notably, the late-stage difunctionalization of natural product-derived alkenes could be realized under optimal conditions (**3i** and **3j**). When we used di- or trisubstituted styrenes as substrates, the intermolecular three-component reaction could not occur. Other alcohols, such as ethanol, 4-phenyl-1-butanol, benzyl alcohol, and ethylene glycol, were compatible with this transformation and smoothly delivered their corresponding alkoxysilylation products (**3k**−**3o**). Furthermore, intramolecular cyclization could occur when 4-aryl-4-pentenoic alcohol or 4-aryl-4-pentenoic acid were used as the substrate, affording silicon-containing epoxide (**3p**) or lactone (**3q**) products, respectively. Moreover, thiols were found to be appropriate nucleophiles, providing the desired product in good yields (**3r**−**3u**). However, when we used other hydrosilane substrates, such as Et_3SiH, $HSiMe_2Ph$, and $HSiPh_3$, no products were detected, and most of the substrates were recovered. We reasoned that the rate of hydrogen atom abstraction from the Si−H bond of other alkylsilanes was much slower than that of $(TMS)_3SiH$ because of a stronger bond energy.[12]

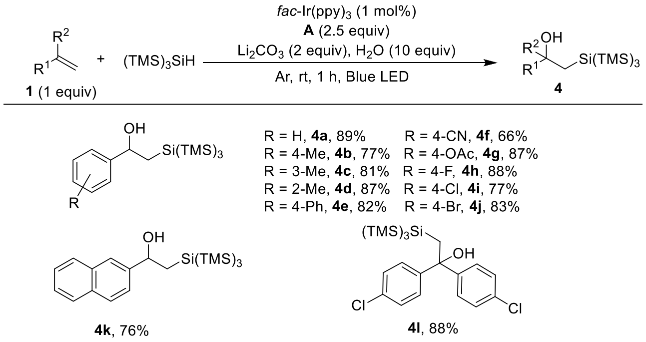
Subsequently, the silylfunctionalization of alkenes was investigated using H_2O as the nucleophile under the optimal reaction conditions (Scheme 3). We were delighted to find that the 1,2-hydroxysilylation of substituted styrenes proceeded well, leading to β-hydroxysilanes **4a**−**4k** in good yields. A 1,1-diphenyl alkene was also well tolerated in the reaction, affording tertiary benzylic alcohol **4l** in 88% yield. However, when α-methylstyrene was selected as the substrate, the

Scheme 2. Visible-Light-Mediated 1,2-Alkoxysilylation and 1,2-Alkylthiosilylation of Alkenes[a,b]



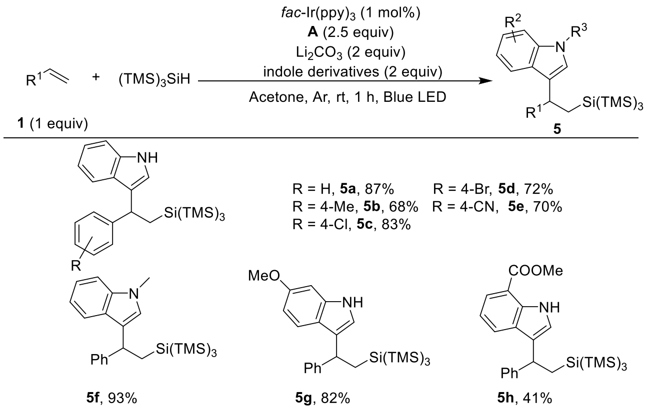
[a] Conditions: **1a** (0.1 mmol), (TMS)$_3$SiH (0.2 mmol), alcohol (1 mmol), **A** (2.5 equiv), *fac*-Ir(ppy)$_3$ (1 mol %), Li$_2$CO$_3$ (2 equiv), acetone (3 mL), Ar blue LED, rt, 1 h. [b] Isolated yield. [c] Reaction performed without external alcohols.

Scheme 3. Visible-Light-Mediated 1,2-Hydroxysilylation of Alkenes[a,b]



[a] Conditions: **1a** (0.1 mmol), (TMS)$_3$SiH (0.2 mmol), H$_2$O (1 mmol), **A** (2.5 equiv), *fac*-Ir(ppy)$_3$ (1 mol %), Li$_2$CO$_3$ (2 equiv), acetone (3 mL), Ar, blue LED, rt, 1 h. [b] Isolated yield.

Scheme 4. Visible-Light-Mediated 1,2-Carbosilylation of Alkenes[a,b]

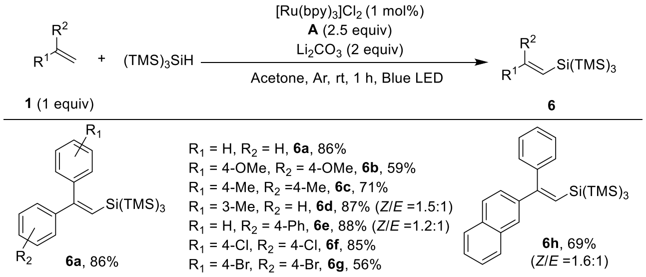


[a] Conditions: **1a** (0.1 mmol), (TMS)$_3$SiH (0.2 mmol), indole (2 equiv), **A** (2.5 equiv), *fac*-Ir(ppy)$_3$ (1 mol %), Li$_2$CO$_3$ (2 equiv), acetone (3 mL), Ar, blue LED, rt, 1 h. [b] Isolated yield.

corresponding tertiary benzyl alcohol product was not obtained. Indole derivatives are important motifs in synthetic chemistry.[13] It is important to efficiently access indoles with multifunctional groups. Therefore, we employed a variety of substituted indoles as carbon nucleophiles in the silylfunctionalization reaction (Scheme 4). To our delight, the unprotected indole smoothly underwent the 1,2-arylsilylation reaction with various alkenes, providing the corresponding products (**5a**–**5e**) in moderate to good yields. Moreover, indoles bearing methyl, methoxy, and ester groups were also suitable for the difunctionalization reaction (**5f**–**5h**).

Vinylsilanes are valuable synthetic intermediates.[14] We found that vinylsilanes could be successfully prepared using Ru(bpy)$_3$Cl$_2$ as the catalyst and 1,1-diaryl alkenes as substrates in the absence of an additional nucleophile. As shown in Scheme 5, a variety of 1,1-diaryl alkenes bearing electron-donating and electron-withdrawing substituents such as methoxy, methyl, aryl, chloro, and bromo groups were amenable to the vinylsilylation reaction, giving products **6a**–**6h**.

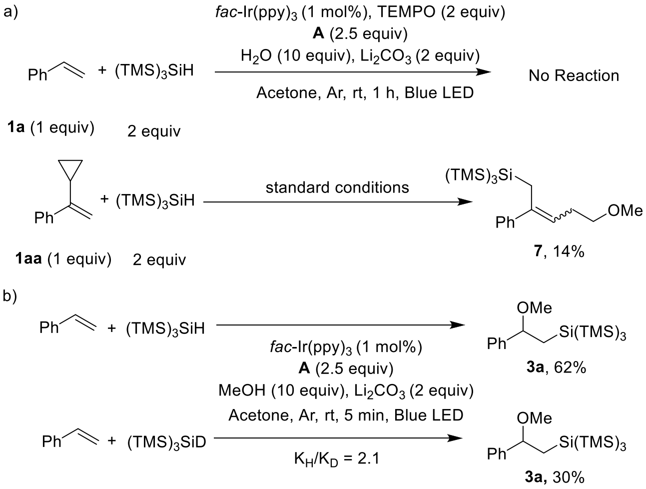
Scheme 5. Visible-Light-Mediated Vinylsilylation of Alkenes[a,b]



[a] Conditions: 1a (0.1 mmol), (TMS)$_3$SiH (0.2 mmol), **A** (2.5 equiv), [Ru(bpy)$_3$]Cl$_2$ (1 mol %) Li$_2$CO$_3$ (2 equiv), acetone (3 mL), Ar, blue LED, rt, 1 h. [b] Isolated yield.

A series of control experiments was conducted to elucidate the possible mechanism of the reaction. The results of Stern–Volmer quenching studies indicated that the excited photocatalyst [$E_{1/2}$(P$^+$/*P) = −1.73 V vs SCE in MeCN][15] can be oxidized by the *N*-isopropylazinium salt [$E_{1/2}$ = −0.15 V vs SCE in MeCN, Figure S2].[11] The 1,2-hydroxysilylation reaction was completely inhibited by 2,2,6,6-tetramethylpiperidinooxy (TEMPO, Scheme 6a), which acts as a radical scavenger. Furthermore, a radical clock experiment was performed using **1aa** as the substrate under our standard reaction conditions, which gave ring-opening product 7 in 14% yield (Scheme 6a). These results suggest the presence of radical intermediates. The kinetic isotope effect (KIE) was also investigated, and the result (k_H/k_D = 2.1) clearly showed that the cleavage of the Si−H bond may be involved in the rate-determining step (Scheme 6b). Therefore, the reason other alkyl silanes do not participate in this transformation may be the slow cleavage rate of the Si−H bond, which is consistent

Scheme 6. Control Experiments



with our hypothesis. Notably, styrene was obtained when we treated the 1,2-methoxysilylation product **3a** with **A**, indicating that the *N*-isopropylazinium salt promoted the decomposition of **3a**. In contrast, **3a** was stable when using Li_2CO_3 as the additive, suggesting that carbonates not only participate in the reaction as base but also can suppress the decomposition of desired products (Figure S4). The same results were observed for the products obtained from the 1,2-hydroxysilylation of alkenes (Figure S5). A plausible mechanism is proposed on the basis of the results of the control experiments (Figure 1). *N*-Isopropylazinium salt **A** can oxidize the photoactivated *fac*-Ir(ppy)$_3$ catalyst to afford *fac*-Ir^{IV}(ppy)$_3$ (**I**) and isopropoxy radical (**II**). Then, oxygen radical species **II** can abstract the hydrogen atom from $(TMS)_3SiH$ to deliver silyl radical **III**, which can add to the alkene to provide intermediate **IV**. Subsequently, adduct **IV** ($E_{1/2}{}^{ox}$ = +0.73 V vs SCE for benzyl radical)[16] can be oxidized by **I** [$E_{1/2}(P^+/P)$ = +0.77 V vs SCE in MeCN] to furnish carbocation intermediate **V**. Finally, intermediate **V** can trap nucleophiles to produce the difunctionalization product. In the absence of an additional nucleophile, deprotonation of **V** can occur to generate the vinylsilane product.

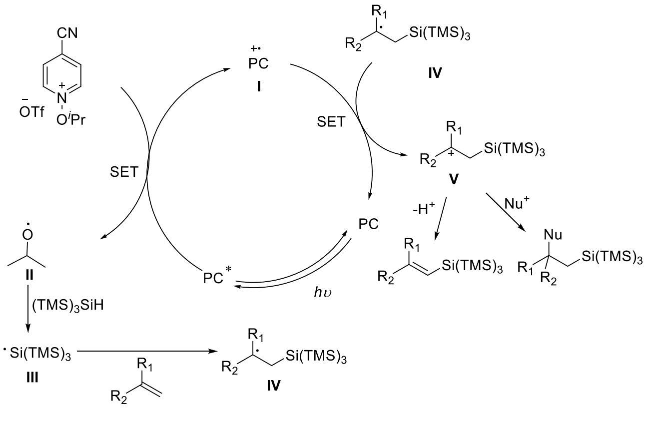


Figure 1. Proposed mechanism.

In summary, we have demonstrated the unprecedented divergent intermolecular 1,2-silylfunctionalization of alkenes using $(TMS)_3SiH$. Various nucleophiles, such as alcohols, H_2O, thiols, and indoles, are compatible with the catalytic system, providing *β*-alkoxy, *β*-alkylthio, *β*-hydroxy, and *β*-indolyl silanes in good to excellent yields under mild conditions. Moreover, vinylsilanes were successfully produced in the absence of additional nucleophiles. We expect that this approach may offer intriguing opportunities for the synthesis of new bioactive and useful silicon-containing molecules.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c01658.

> Experimental procedures, detailed mechanistic studies, characterization data, and ^1H NMR and ^{13}C NMR spectra for all new products (PDF)

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Notes

The authors declare no competing financial interest.

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