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无金属条件下可见光催化与溴盐协同促进烯烃的氢硅化反应研究

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摘要 开发了一种无金属条件下可见光促进的通过选择性硅-氢键活化实现的烯烃的氢硅化反应. 该反应使用催化量的、便宜易得的溴盐作为氢原子转移试剂. 该策略展现了非常好的官能团兼容性和广泛的底物范围, 并在温和、氧化还原中性的条件下, 以中等到优秀的收率合成了有机硅化合物. 同时, 该策略也能成功地将硅基引入到生物活性分子中.

关键词 光催化; 氢原子转移催化; 硅基自由基; 有机硅化合物

A Metal-Free Photocatalytic Hydrosilylation of Alkenes Using Bromide Salt as a Hydrogen Atom Transfer Reagent

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Abstract A metal-free photocatalytic hydrosilylation of alkenes through the selective activation of Si—H bond has been developed utilizing the readily available and cheaper bromide salt as the catalytic hydrogen atom transfer (HAT) reagent. This protocol features excellent functional group tolerance and broad substrate scope, affording the organosilicon compounds in moderate to excellent yields under a mild and redox-neutral process. This strategy was successfully applied for the introduction of the silyl group into bio-relevant active molecules.

Keywords photocatalysis; hydrogen atom transfer catalysis; silyl radical; organosilicon compound

1 Introduction

Organosilicons have a widespread application in the fields of life science, functional material science, drug discovery and organic synthesis,[1] owing to their unique, fine phy-chemical properties, such as hypotoxicity, fire insulation, high temperature resistance and inoxidizability. Research has shown that, in the development of medical research, many silicon-containing compounds serve as the biological isomers of hydrocarbons, exhibiting more excellent pharmaceutical activity[1d-1e] (Figure 1). In the context, in recent years, the direct and efficient synthesis of organosilicons has become a research focus in organic synthesis,[2] which is a promising and significant task for chemists.

Silyl radical is identified as an important radical intermediate in organic synthesis, from which many useful silicon-containing compounds can be easily reached through various chemical transformations.[3] So, it stimulates the research interest of a group of organic synthesis workers. Traditionally, the silyl radicals are generated by the oxidation of silanes, usually utilizing the stoichiometric radical initiators [*e.g.* peroxides, 2,2-azobisisobutyronitrile (AIBN)] under elevated temperature.[4] Beyond that, in 2017, the Stoltz group[5] disclosed that the alkali metal compound, such as KO^{t}Bu, could promote the formation of silyl radicals from silanes, realizing the C—H silylation of het-

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† 共同第一作者(These authors contributed equally to this work).

eroaromatics.

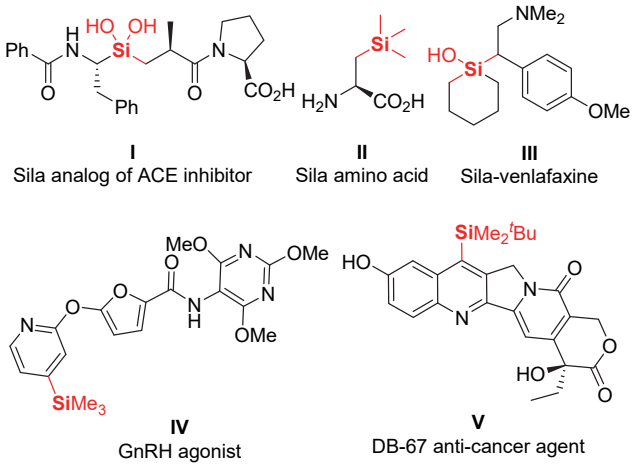


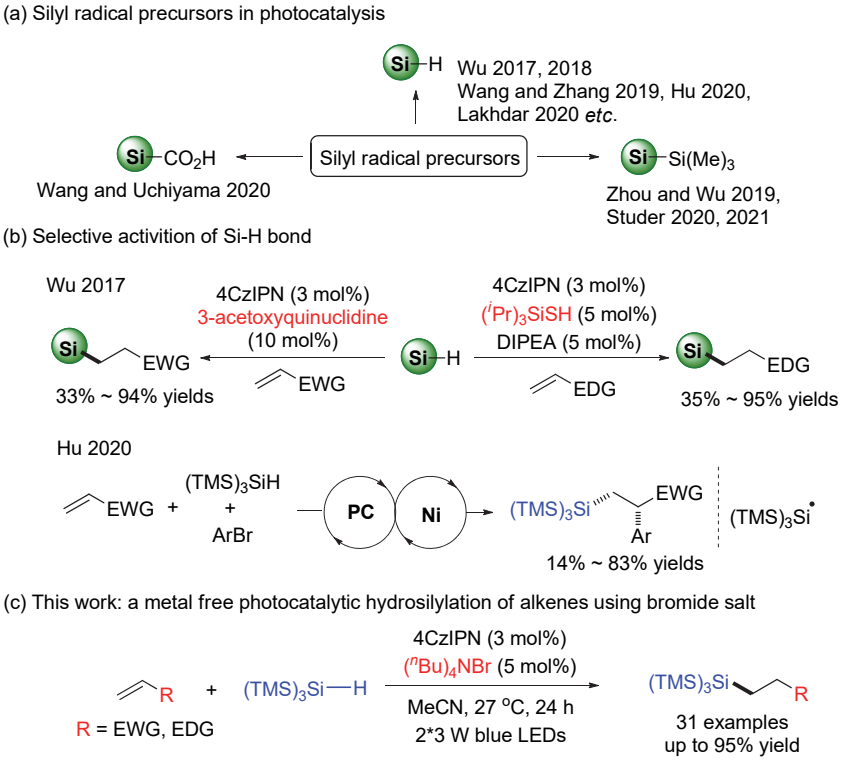
Figure 1 Examples of biologically active silicon-containing compounds

Over the last decade, visible-light-induced photoredox catalysis has been recognized as a powerful organic synthetic methodology.[6] Recently, some significant advances have been achieved in the field of photocatalytic silylation (Scheme 1, a).[7] For instance, in 2020, the Wang and Uchiyama group[8] developed the photocatalytic hydrosilylation of alkenes using the silacarboxylic acids as silyl radical precursor, which formed silyl radical though the decarboxylation oxidation. More recently, Studer and coworkers successfully developed the visible-light-driven hydrosilylation[9a] of electron-deficient alkenes, and the synthesis of α-aminosilanes[9b] via the oxidative cleavage of a trimethylsilyl-polysilanyl Si—Si bond.[10] Despite these impressive advances, the direct and selective activation of Si—H bond involving a hydrogen atom transfer (HAT) process from the commercial available silanes would provide a straightforward, atom- and step-economic process to gain the silicon-containing compounds (Scheme 1, b).[11] In regards, a metal-free photocatalytic hydrosilylation of alkenes has been introduced by the Wu group in 2017.[12a] The same group[12b] also applied this strategy to realize the silacarboxylation of alkenes with CO_2. In 2020, Hu and coworkers[13] have disclosed the arylsilylation of electron-deficient alkenes via cooperative photoredox and Ni catalysis. They implied that the NiBr complex plays a key role in the formation of silyl radical.

Inspired by these impressive advances, we anticipated that a metal-free photocatalytic hydrosilylation of alkenes using the readily available and cheaper bromide salt as a HAT reagent, would provide a facile and alternative synthetic technology to silicon-containing compounds (Scheme 1, c).

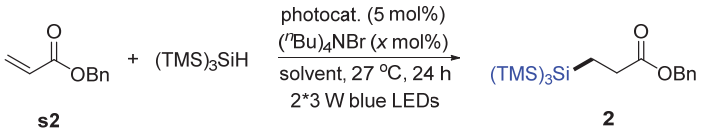
2 Results and discussion

The investigation of photocatalytic hydrosilylation began with benzyl acrylate **s2** and $(TMS)_3SiH$ as model substrates, 5 mol% 4CzIPN as photocatalyst, 15 mol% $(^nBu)_4NBr$ as the HAT reagent and CH_3CN as solvent under irradiation of 2×3 W blue LEDs for 24 h (Table 1). To our delight, under this mild condition, the desired product **2** was got in 97% yield determined by ^1H NMR and 95% isolated yield. When



Scheme 1 Photocatalytic silylation reactions

Table 1 Reaction optimization[a]



s2 2

Entry	Photocat.	*x*	Solvent	Yield[b]/%
1	4CzIPN	15	MeCN	97 (95)
2	Eosin Y	15	MeCN	92
3	Rhodamin	15	MeCN	96
4	4CzIPN (3 mol%)	15	MeCN	98
5	4CzIPN (3 mol%)	5	MeCN	98 (94)
6	4CzIPN (3 mol%)	5	THF	81
7	4CzIPN (3 mol%)	5	DCM	91
8[c]	4CzIPN (3 mol%)	5	MeCN	64
9[d]	No	5	MeCN	0
10[e]	4CzIPN (3 mol%)	5	MeCN	0
11[f]	4CzIPN (3 mol%)	5	MeCN	59

[a] Reaction conditions: **s-1** (0.2 mmol), $(TMS)_3SiH$ (0.3 mmol), PC (5 mol%) and $(^nBu)_4NBr$ (*x* mol%) in solvent (2.0 mL), irradiated by a 2×3 W blue LEDs under argon atmosphere for 24 h; [b] Yields were determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard, isolated yield in parentheses; [c] Air was replaced by argon atmosphere; [d] Without photocatalyst. [e] Without visible light irradiation, [f] Without the $(^nBu)_4NBr$.

other metal-free photocatalysts, such as eosin Y, Rhodamin, rose bangel, fluorescein and bromocresol green, were screened, it was found that the photocatalyst 4CzIPN gave the best result (Entries 1～3). Then, when 3 mol% 4CzIPN was added to this system, the desired product **2** was obtained in 98% yield. When the amount of $(^nBu)_4NBr$ was decreased to 5 mol%, product **2** was got in 94% isolate yield (Entry 5). Subsequently, a series of solvents, including tetrahydrofuran (THF), dichloromethane (DCM), *N*,*N*-dimethylformamide (DMF) and acetone, were examined, and CH_3CN was found to be the best solvent in this system (Entries 6, 7). The use of air replaced with Ar atmosphere led to a significant change in the reaction efficiency in 64% yield (Entry 8). Control experiments of this photocatalytic hydrosilylation were performed, either without the photocatalyst, or the lack of visible light irradiation, none of **2** was observed, indicating that this hydrosilylation reaction was a photocatalytic process (Entries 9, 10). In the absence of $(^nBu)_4NBr$, the desired product **2** could be got in 59% yield, which brought a bigger reduction than the formal reaction condition (Entry 11), which suggested that $(^nBu)_4NBr$ plays a role in this reaction.

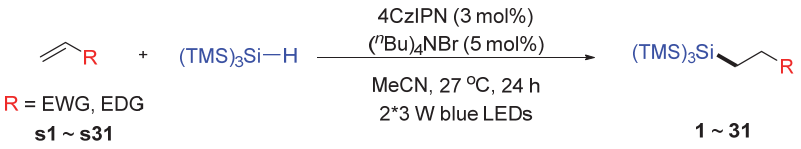
With the optimized reaction conditions in hand, the substrate scope for the hydrosilylation reaction of alkenes with $(TMS)_3SiH$ was examined (Table 2). Firstly, a diverse range of electron-deficient alkenes were investigated (Table 2, a). The acrylates with different electronic effect, including methyl ester (**1**), benzyl ester (**2**), menaphthyl (**3**), phenolic ester (**4**) and other alkyl esters, were well tolerated (**2**～**8**), affording the corresponding hydrosilylation products in 69%～94% yields. Especially, the *L*-mentholic acrylate carrying a big steric hindrance group, could smoothly work to obtain the desired product **6** in 78% yield. Lactone and dimethyl maleates were fine substrates, delivering the desired products (**9** and **10**) in 85% and 86% yields, respectively. Furthermore, acrylamides (**11**～**13**), could successfully undergo the hydrosilylation with silane to give these good results. Notably, compared to the Si—H bond of silane, acrylamide containing an active N—H bond was also a viable substrate in this transformation. The cyclic and acyclic enones (**14** and **15**) were all accommodated in the hydrosilylation reaction. Note that the large steric hindrance of substrate **s17** would influence the reaction efficiency of hydrosilylation in comparison with substrate **s16**. Subsequently, dihydrosilylation of diacrylates with silanes were performed to obtain **18** and **19** both in 69% yields.

Owing to the biological relevance of silyl group as the biological isomers of hydrocarbons, a mild and alternative route for late-stage introduction of silyl group into complex molecules will be highly desired in drug modification. Accordingly, to verify the practicability of this strategy, some common and natural molecules, such as cholesterol (**20**), androstone (**21**), vanillylacetone (**22**) and estrone (**23**), were selected as stones to subject to our hydrosilylation protocol. Luckily, all of them underwent the silylation to give the corresponding products with good to excellent yields and regioselectivity.

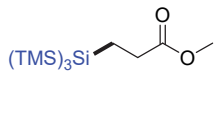
At the same time, other silanes, such as $(Me)_2PhSiH$, $(Et)_3SiH$, and $^tBu(Me)_2SiH$, were tried, and no corresponding products were found in these reactions. So, we think these silanes were not suitable in this photocatalytic hydrosilylation reaction, just only $(TMS)_3SiH$ can be applied in this reaction. Because as we all known, $(TMS)_3SiH$ was a better and more active silicon than common other silicon source.[3c]

Our attention was next turned to extend this visible-light-induced metal-free hydrosilylation protocol to electron-donating alkenes (Table 2, b). It was found that the hydrosilylation of a series of electron-rich alkenes with $(TMS)_3$-

Table 2 Scope of photocatalytic hydrosilylation of alkenes[a,b]



(a) electron-deficient alkenes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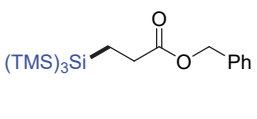
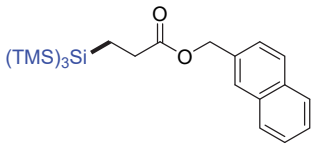

2, 94%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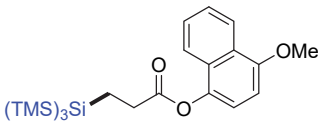
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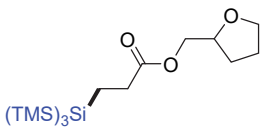
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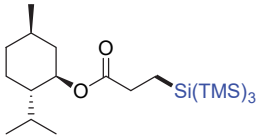
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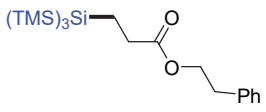
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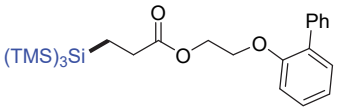
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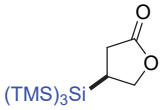
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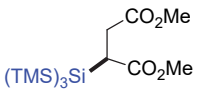
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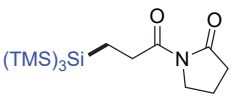
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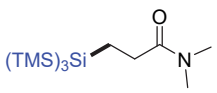
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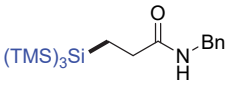
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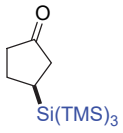
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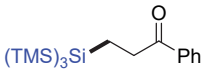
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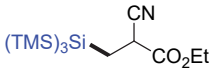
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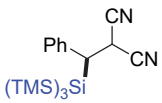
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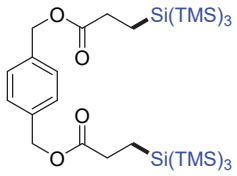
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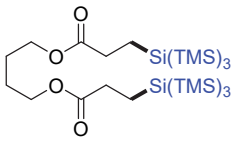
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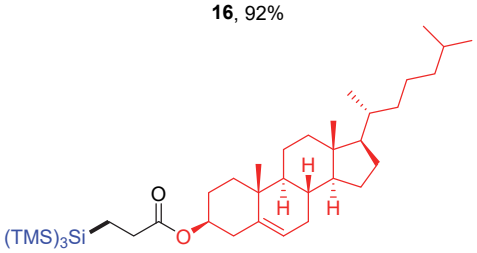
From Cholesterol derivative
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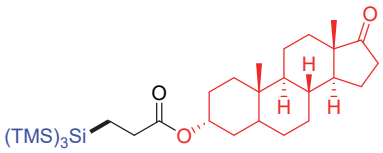
From androstone derivative
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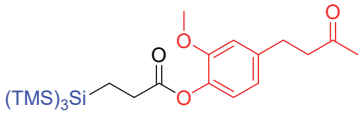
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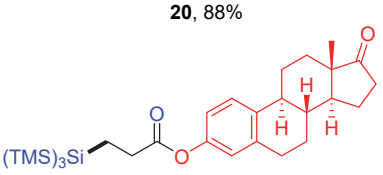
From estrone derivative
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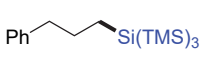
(b) electron-rich alkenes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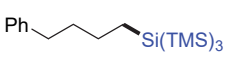
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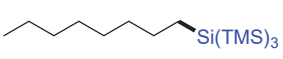
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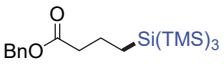
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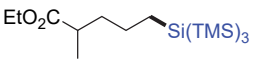
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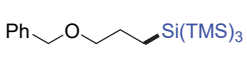
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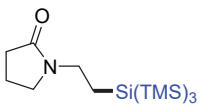
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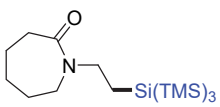
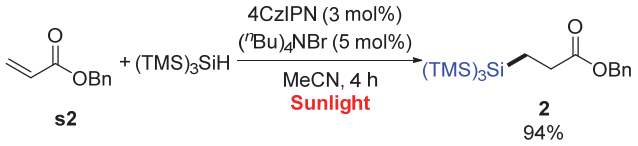

31, 68%

[a] Reactions were performed with alkenes (0.20 mmol), silane (0.3 mmol), 4CzIPN (3 mol%) and (^{n}Bu)$_4$NBr (5 mol%) in MeCN (2.0 mL), irradiated by a 2×3 W blue LEDs under Ar atmosphere for 24 h; [b] Isolated yield; [c] Silane (3.0 equiv., 0.6 mmol) in MeCN (1.0 mL).

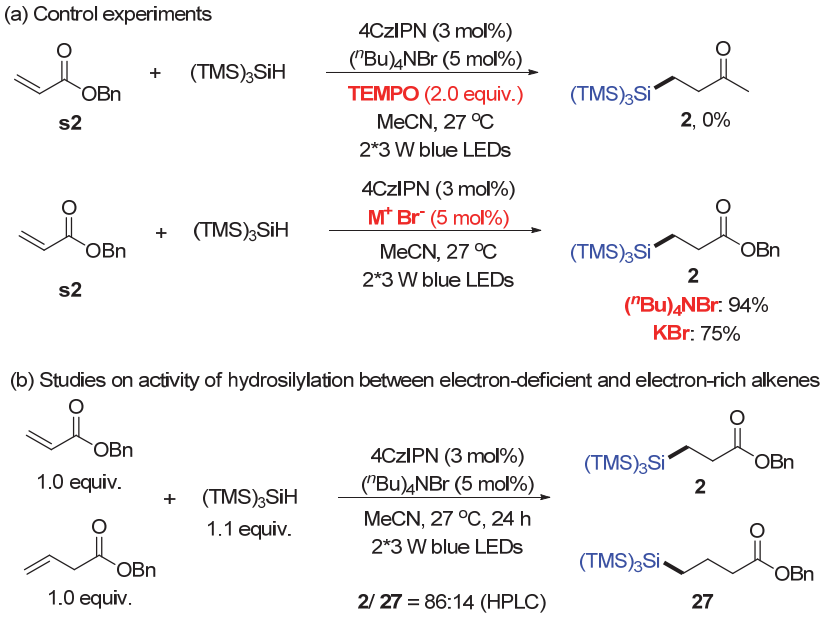
SiH were carried out under the same reaction condition with electron-deficient alkenes, and the desired products (**24**～**28**) were formed with excellent yields. Furthermore, other types of alkenes, including the allyl ether (**29**) and *N*-vinyl amide (**30**, **31**), were applied to the hydrosilylation protocol, delivering the corresponding products in 68%～86% yields.

Sunlight, as a clean and easily-access energy source, is extensively employed in organic synthesis.[14] So, to showcase the practicability of this photocatalytic hydrosilylation, the model reaction of **s2** and $(TMS)_3SiH$ was performed and irradiated by sunlight for 4 h, smoothly affording product **2** in 94% yield (Scheme 2).



Scheme 2 Photocatalytic hydrosilylation irradiated by sunlight

To gain further insight into the mechanism, some control experiments were performed, including addition of 2,2,6,6-tetramethylpiperidoxyl (TEMPO) as radical scavenger, and other bromide salt (*e.g.* KBr) as the HAT reagent (Scheme 3, a). The experimental results suggested that there was the existance of radical intermediates in this metal-free photocatalytic hydrosilylation and the Br^- played a key role in this HAT process and photocatalytic cycle.[13] Compared to the lower yield using KBr, $(^nBu)_4NBr$ may be attributed to its phase transfer property. Additionally, the hydrosilylation of the mixture alkenes with silane was also carried out to study the reaction activities of hydrosilylation between electron-deficient and electron-rich alkenes (Scheme 3, b). The final ratio of yield between **2** and **27** was determined by high performance liquid chromatography (HPLC).[15] And this result implied that there was a higher reaction activity of electron-deficient alkene than electron-rich one. There might be two reasons. The one was that silyl radical itself was easy to undergo nucleophilic addition, and the another was that the silyl radical adduct **2-1** with electron-deficient alkene was more stable and easy to be reduced by the reducing photocatalyst (PC^-).[11d,12a] Besides, the studies of fluorescence quenching experiments and Stern-Volmer linear supported that the obvious quenching of the excited photocatalyst (PC*) was observed by $(^nBu)_4NBr$ (Figure 2). In addition, for the photocatalyst 4CzIPN, its excited-state oxidation potential ($(E_{1/2}(PC^*/PC^-)=+1.35$ V vs SCE in MeCN)[15] is completely sufficient to oxidize bromine



Scheme 3 Mechanistic studies

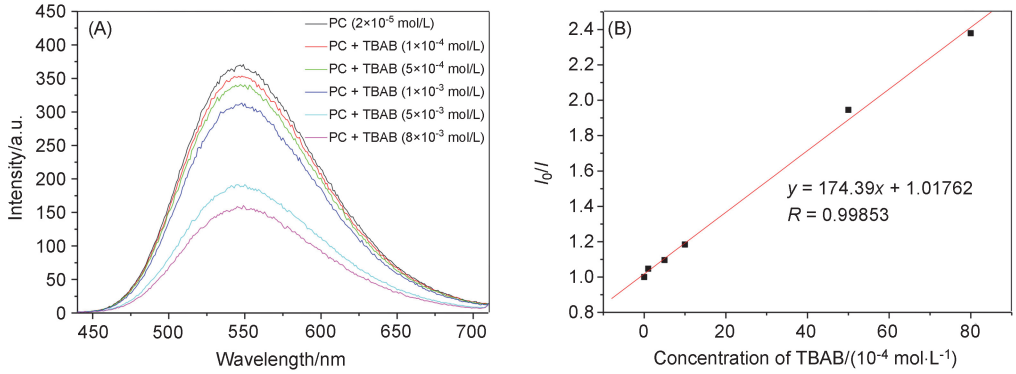


Figure 2 Fluorescence quenching experiments and Stern-Volmer liner

anion Br^- ($E^{red}_{1/2}$ = +0.8 V vs SCE in DME)[16] to bromine radical, suggesting that this process is thermodynamically favored.

Based on the above results and relevant literatures,[12-13] we took the electron-deficient alkene for example to propose a plausible mechanism for the photocatalytic hydrosilylation (Scheme 4). Firstly, the photocatalytic cycle begins with the excitation of ground state of photocatalyst (PC) under irradiation of visible light. Then, the excited state PC* undergoes a reductive quenching by the bromine anion via a single electron transfer (SET) process, giving the reducing photocatalyst (PC^-) and bromine radical. A hydrogen atom abstraction between this bromine radical and Si—H bond of silane happened, along with the release of HBr, affording the silyl radical intermediate. Next, the radical addition of the silyl radical to alkene occurs to produce the carbon-centered radical **2-1**, followed the reduction by the reducing photocatalyst (PC^-) [$E_{1/2}$(PC/PC^-) = −1.21 V vs SCE in MeCN],[15] completing the photocatalytic cycle. Finally, the forming carbanion intermediate **2-2** is protonated to afford the product **1**, closing the HAT cycle.

3 Conclusions

In summary, a meta-free hydrosilylation of alkenes employing photoredox-mediated HAT strategy has been successfully developed. This method utilized the bromide salt as HAT reagent to promote the selective activation of Si—H bond. This protocol features broad substrate scope and excellent functional group tolerance under a mild and redox-neutral process. The synthetic application of a late-stage functionalization has been demonstrated through the feasible introduction of silyl group into bio-relevant active molecules. The direct and efficient synthesis of organosilicons through this dual catalytic strategy is ongoing in our laboratory.

4 Experimental section

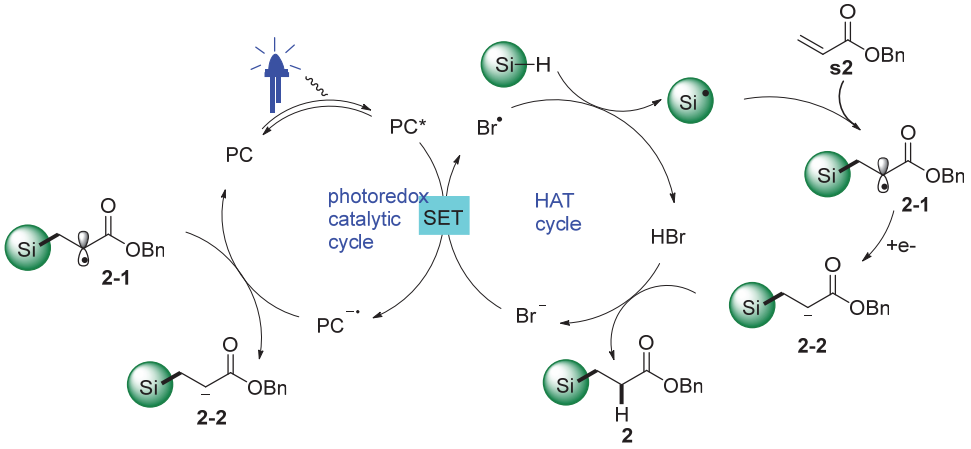
4.1 General information

^{1}H NMR spectra were recorded on a Bruker (400 MHz) NMR spectrometer. Chemical shifts (δ) are reported relative to tetramethylsilane (TMS). ^{13}C NMR were recorded on a JEOL JNM-ECZ400S (100 MHz) NMR spectrometer with complete proton decoupling spectrophotometers ($CDCl_3$ δ 77.0). The high-resolution mass spectroscopic (HRMS) data were obtained on a Solarix XR/AB Sciex 5800/Micorflex LRF/Trace 1300/Exactive GC mass spectrometer. The enantiomeric excesses (*ee*) were obtained by the angilent 1260 high performance liquid chromatography. Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All the solvents were used as received. Then those newly distilled solvents were conserved in 4 Å molecular sieves. Flash column chromatography was performed using 200～300 mesh silica gel. Further visualization was achieved by staining with $KMnO_4$.

4.2 General procedures for the preparation of unknown alkenes

To a stirring solution of alcohol (10 mmol, 1.0 equiv.) in anhydrous dichloromethane (70 mL), was added triethylamine (11 mmol, 1.1 eauiv.) in an ice-water bath under Ar atmosphere. And then acryloyl chloride (12 mmol, 1.2 equiv.) was added dropwise at the same temperature. Before the reaction completion, the reaction was monitored by thin layer chromatography (TLC). Solvent was removed by vacuum. The resulting residue was extracted with ethyl acetate (70 mL×3) and water (70 mL), washed with brine (100 mL). The organic phase was dried with anhydrous Na_2SO_4 and concentrated. The crude product was purified by column chromatography (petroleumether/ethyl acetate, V∶V=100∶1 to 20∶1), followed by recrystallization to give the desired products.

Naphthalen-2-ylmethyl acrylate (**s3**): Yellow solid, 63% yield. m.p. 25.2～27.1 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.86 (dt, J=6.6, 3.7 Hz, 4H), 7.50 (ddd, J=7.4, 3.7, 2.2 Hz, 3H), 6.49 (dd, J=17.3, 1.5 Hz, 1H), 6.21 (dd, J=17.3, 10.4 Hz, 1H), 5.87 (dd, J=10.5, 1.5 Hz, 1H), 5.38 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.0, 133.22, 133.15, 133.09, 131.2, 128.4, 128.3, 128.0, 127.7, 127.4, 126.3, 125.9, 66.4; HRMS (ESI) calcd for $C_{14}H_{13}O_2$ $[M+H]^+$ 213.0916, found 213.0912.



Scheme 4 Proposed mechanism

4-Methoxynaphthalen-1-yl acrylate (**s4**): Yellow oil, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.37～8.19 (m, 1H), 7.89～7.72 (m, 1H), 7.60～7.45 (m, 2H), 7.20 (d, J=8.3 Hz, 1H), 6.79 (d, J=8.3 Hz, 1H), 6.72 (dd, J=17.4, 1.3 Hz, 1H), 6.48 (dd, J=17.3, 10.4 Hz, 1H), 6.09 (dd, J=10.4, 1.3 Hz, 1H), 4.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.0, 153.6, 139.9, 132.6, 127.9, 127.5, 127.0, 126.3, 125.7, 122.4, 120.9, 117.7, 102.9, 55.7; HRMS (ESI) calcd for $C_{14}H_{12}O_3Na$ $[M+Na]^+$ 251.0684, found 251.0683.

(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl acrylate (**s6**): Colourless oil, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.38 (dd, J=17.3, 1.6 Hz, 1H), 6.10 (dd, J=17.3, 10.4 Hz, 1H), 5.79 (dd, J=10.4, 1.6 Hz, 1H), 4.76 (td, J=10.9, 4.4 Hz, 1H), 2.05～2.00 (m, 1H), 1.91～1.83 (m, 1H), 1.73～1.66 (m, 2H), 1.55～1.47 (m, 1H), 1.46～1.38 (m, 1H), 1.12～1.05 (m, 1H), 1.04～0.99 (m, 1H), 0.93～0.86 (m, 7H), 0.77 (d, J=7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.8, 130.2, 129.0, 74.3, 47.0, 40.8, 34.2, 31.4, 26.3, 23.5, 22.0, 20.7, 16.4; HRMS (ESI) calcd for $C_{13}H_{22}O_2Na$ $[M+Na]^+$ 233.1517, found 233.1514.

1,4-Phenylenebis(methylene) diacrylate (**s18**): White solid, 88% yield. m.p. 70.2～72.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38 (s, 4H), 6.44 (dd, J=17.3, 1.5 Hz, 2H), 6.16 (dd, J=17.3, 10.4 Hz, 2H), 5.85 (dd, J=10.5, 1.5 Hz, 2H), 5.20 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.9, 135.9, 131.2, 128.4, 128.2, 65.9; HRMS (ESI) calcd for $C_{14}H_{14}O_4Na$ $[M+Na]^+$ 269.0790, found 269.0793.

(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl acrylate (**s20**): White solid, 46% yield. m.p. 118.2～119.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.38 (dd, J=17.3, 1.6 Hz, 1H), 6.10 (dd, J=17.3, 10.4 Hz, 1H), 5.79 (dd, J=10.4, 1.6 Hz, 1H), 5.39 (d, J=5.7 Hz, 1H), 4.65～4.73 (m, 1H), 2.36 (d, J=6.8 Hz, 2H), 2.05～1.77 (m, 5H), 1.68～1.43 (m, 7H), 1.40～1.24 (m, 4H), 1.22～1.05 (m, 7H), 1.05～0.95 (m, 6H), 0.91 (d, J=4.0 Hz, 3H), 0.86 (dd, J=6.6, 1.8 Hz, 6H), 0.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.6, 139.6, 130.1, 129.1, 122.7, 74.1, 56.7, 56.2, 50.1, 42.3, 39.8, 39.5, 38.1, 37.0, 36.6, 36.2, 35.8, 31.9, 31.9, 28.2, 28.0, 27.8, 24.3, 23.8, 22.8, 22.5, 21.0, 19.3, 18.7, 11.8; HRMS (ESI) calcd for $C_{30}H_{48}O_2Na$ $[M+Na]^+$ 463.3552, found 463.3563.

(3*R*,8*R*,9*S*,10*S*,13*S*,14*S*)-10,13-Dimethyl-17-oxohexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl-acrylate (**s21**): White solid, 42% yield. m.p. 146.2～148.1 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.39 (dd, J=17.3, 1.6 Hz, 1H), 6.13 (dd, J=17.3, 10.4 Hz, 1H), 5.80 (dd, J=10.4, 1.6 Hz, 1H), 5.10 (t, J=2.8 Hz, 1H), 2.43 (dd, J=19.2, 8.7 Hz, 1H), 2.12～2.01 (m, 1H), 1.96～1.89 (m, 1H), 1.83～1.74 (m, 3H), 1.73～1.63 (m, 2H), 1.61～1.45 (m, 6H), 1.35～1.16 (m, 7H), 1.06～0.96 (m, 1H), 0.84 (d, J=12.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 221.2, 165.7, 130.0, 129.3, 70.1, 54.4, 51.5, 47.8, 40.2, 36.0, 35.8, 35.0, 32.9, 32.8, 31.6, 30.8, 28.0, 26.1, 21.7, 20.1, 13.8, 11.3; HRMS (ESI) calcd for $C_{22}H_{33}O_3$ $[M+H]^+$ 345.2430, found 345.2436.

2-Methoxy-4-(3-oxobutyl)phenyl acrylate (**s22**): White solid, 93% yield. m.p. 68.1～72.0 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.96 (d, J=8.1 Hz, 1H), 6.81 (d, J=2.1 Hz, 1H), 6.75 (dd, J=8.0, 1.9 Hz, 1H), 6.59 (dd, J=17.3, 1.4 Hz, 1H), 6.33 (dd, J=17.3, 10.4 Hz, 1H), 5.99 (dd, J=10.4, 1.4 Hz, 1H), 3.80 (s, 3H), 2.88 (t, J=7.5 Hz, 2H), 2.76 (t, J=7.4 Hz, 2H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 207.7, 164.2, 150.9, 140.1, 137.7, 132.4, 127.6, 122.6, 120.3, 112.7, 55.8, 45.1, 30.1, 29.5; HRMS (ESI) calcd for $C_{14}H_{16}O_4Na$ $[M+Na]^+$ 271.0946, found 271.0945.

(8*R*,9*S*,13*S*,14*S*)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl acrylate (**s23**): White solid, 50% yield. m.p. 158.2～159.1 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.30 (d, J=8.5 Hz, 1H), 6.90 (dd, J=8.4, 2.6 Hz, 1H), 6.86 (d, J=2.5 Hz, 1H), 6.59 (dd, J=17.3, 1.3 Hz, 1H), 6.31 (dd, J=17.3, 10.4 Hz, 1H), 5.99 (dd, J=10.4, 1.4 Hz, 1H), 2.92 (dd, J=8.6, 3.8 Hz, 2H), 2.51 (dd, J=18.8, 8.6 Hz, 1H), 2.45～2.37 (m, 1H), 2.33～2.26 (m, 1H), 2.21～1.94 (m, 4H), 1.69～1.40 (m, 6H), 0.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 220.6, 164.8, 148.448, 138.0, 137.4, 132.3, 128.0, 126.3, 121.4, 118.6, 50.4, 47.9, 44.119, 38.0, 35.8, 31.5, 29.3, 26.3, 25.7, 21.5, 13.8; HRMS (ESI) calcd for $C_{21}H_{25}O_3$ $[M+H]^+$ 325.1804, found 325.1805.

Benzyl-but-3-enoate (**s27**): Pale yellow oil, 97% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.39～7.30 (m, 5H), 6.06～5.83 (m, 1H), 5.19 (dq, J=4.0, 1.4 Hz, 1H), 5.16 (dd, J=3.4, 1.6 Hz, 1H), 5.14 (s, 2H), 3.15 (dt, J=6.9, 1.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.4, 135.8, 130.1, 128.6, 128.2, 128.2, 118.7, 66.4, 39.1; HRMS (ESI) calcd for $C_{11}H_{12}O_2Na$ $[M+Na]^+$ 199.0735, found 199.0741.

4.3 General procedures for the synthesis of **1**～**17**, and **20**～**31**

To a dried Schlenk tube was treated with alkene (0.20 mmol, 1.0 equiv.), $(TMS)_3SiH$ (0.3 mmol, 1.5 equiv.), photocatalyst (0.006 mmol, 3 mol%), $(^nBu)_4NBr$ (0.01 mmol, 5 mol%), and MeCN (2.0 mL, bubbled by Ar for 30 min) were added under Ar atmosphere. After that, this resulting solution was stirred at a distance of ≈2 cm under irradiation by 2×3 W blue LEDs at 27 ℃ for 24 h. The solvent was evaporated, and the crude product was purified by column chromatography using hexane/ethyl acetate as eluent (V∶V=100∶1 to 50∶1), affording the desired product.

Methyl-3-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)propanoate (**1**): Colorless oil, 60.41 mg, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.67 (s, 3H), 2.36～2.32 (m, 2H), 1.13～1.08 (m, 2H), 0.17 (s, 27H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.1, 51.6, 33.0, 2.8, 1.0.

Benzyl-3-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)propanoate (**2**): Colorless oil, 77.12 mg, 94% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41～7.28 (m, 5H), 5.12 (s, 2H), 2.45～2.30 (m, 2H), 1.21～1.07 (m, 2H), 0.17 (s, 27H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.6, 136.1, 128.5, 128.2, 128.2, 66.3, 33.2, 2.8, 1.0; HRMS (ESI) calcd for $C_{19}H_{38}O_2NaSi_4$ $[M+Na]^+$ 433.1847, found 433.1851.

Naphthalen-2-ylmethyl-3-(1,1,1,3,3,3-hexamethyl-2-(tri-

methylsilyl)trisilan-2-yl)propanoate (**3**): Colorless oil, 81.2 mg, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.85 (dd, J=8.9, 3.9 Hz, 4H), 7.52～7.46 (m, 3H), 5.29 (s, 2H), 2.49～2.37 (m, 2H), 1.22～1.11 (m, 2H), 0.18 (s, 27H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.6, 133.4, 133.1, 133.0, 128.3, 128.0, 127.7, 127.4, 126.3, 126.2, 126.0, 66.4, 33.2, 2.8, 1.0; HRMS (ESI) calcd for $C_{23}H_{41}O_2Si_4$ $[M+H]^+$ 461.2184, found 461.2191.

4-Methoxynaphthalen-1-yl-3-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)propanoate (**4**): Colorless oil, 65.71 mg, 69% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.27 (dd, J=7.4, 1.6 Hz, 1H), 7.77 (dd, J=7.4, 1.4 Hz, 1H), 7.57～7.46 (m, 2H), 7.15 (d, J=8.3 Hz, 1H), 6.77 (d, J=8.3 Hz, 1H), 4.01 (s, 3H), 2.79～2.69 (m, 2H), 1.38～1.32 (m, 2H), 0.24 (s, 27H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.6, 153.3, 140.0, 127.5, 126.9, 126.2, 125.7, 122.4, 120.8, 117.6, 102.8, 55.7, 33.4, 3.2, 1.1; HRMS (ESI) calcd for $C_{23}H_{40}O_3NaSi_4$ $[M+Na]^+$ 499.1952, found 499.1953.

(Tetrahydrofuran-2-yl)methyl-3-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)propanoate (**5**): Colorless oil, 71.14 mg, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.20～4.08 (m, 2H), 4.05～3.96 (m, 1H), 3.91～3.86 (m, 1H), 3.84～3.75 (m, 1H), 2.43～2.32 (m, 2H), 2.07～1.95 (m, 1H), 1.95～1.82 (m, 2H), 1.61～1.56 (m, 1H), 1.17～1.05 (m, 2H), 0.16 (s, 27H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.7, 76.5, 68.5, 66.6, 33.0, 28.0, 25.6, 2.7, 1.0; HRMS (ESI) calcd for $C_{17}H_{40}O_3NaSi_4$ $[M+Na]^+$ 427.1952, found 427.1953.

(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl-3-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)propanoate (**6**): Colorless oil, 71.49 mg, 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.65 (td, J=10.8, 4.4 Hz, 1H), 2.36～2.23 (m, 2H), 2.04～1.95 (m, 1H), 1.89～1.82 (m, 1H), 1.73～1.63 (m, 2H), 1.54～1.44 (m, 1H), 1.41～1.34 (m, 1H), 1.14～1.06 (m, 2H), 1.05～0.99 (m, 1H), 0.99～0.94 (m, 1H), 0.90 (dd, J=6.7, 3.8 Hz, 7H), 0.77 (d, J=7.0 Hz, 3H), 0.17 (s, 27H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.4, 74.1, 47.0, 40.9, 34.2, 33.6, 31.4, 26.4, 23.6, 22.0, 20.7, 16.5, 2.9, 1.0; HRMS (ESI) calcd for $C_{22}H_{50}O_2NaSi_4$ $[M+Na]^+$ 481.2786, found 481.2784.

Phenethyl-3-(1,1,1,3,3,3-Hexamethyl-2-(trimethylsilyl)-trisilan-2-yl)propanoate (**7**): Colorless oil, 79.75 mg, 94% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.29 (dd, J=9.3, 5.4 Hz, 2H), 7.23 (t, J=6.0 Hz, 3H), 4.29 (t, J=7.1 Hz, 2H), 2.95 (t, J=7.1 Hz, 2H), 2.41～2.25 (m, 2H), 1.15～0.99 (m, 2H), 0.17 (s, 27H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.6, 137.8, 129.0, 128.5, 126.5, 64.9, 35.1, 33.3, 2.9, 1.0; HRMS (ESI) calcd for $C_{20}H_{40}O_2NaSi_4$ $[M+Na]^+$ 447.2003, found 447.1995.

2-([1,1'-Biphenyl]-2-yloxy)ethyl-3-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)propanoate (**8**): Colorless oil, 97.05 mg, 94% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.63～7.52 (m, 2H), 7.44～7.35 (m, 3H), 7.35～7.28 (m, 2H), 7.08 (t, J=4.0 Hz, 1H), 7.00 (d, J=9.5 Hz, 1H), 4.36 (t, J=4.0 Hz, 2H), 4.18 (t, J=4.0 Hz, 2H), 2.46～2.23 (m, 2H), 1.22～1.01 (m, 2H), 0.19 (s, 27H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.5, 155.3, 138.2, 131.2, 131.0, 129.5, 128.5, 127.9, 126.9, 121.6, 113.1, 66.5, 62.7, 33.0, 2.7, 1.1; HRMS (ESI) calcd for $C_{26}H_{44}O_3NaSi_4$ $[M+Na]^+$ 539.2265, found 539.2267.

4-(1,1,1,3,3,3-Hexamethyl-2-(trimethylsilyl)trisilan-2-yl)dihydrofuran-2(3*H*)-one (**9**): White solid, 56.46 mg, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.50 (t, J=8.6 Hz, 1H), 4.15 (dd, J=11.8, 8.9 Hz, 1H), 2.61 (dd, J=17.2, 8.5 Hz, 1H), 2.35 (dd, J=17.2, 13.3 Hz, 1H), 2.20～2.05 (m, 1H), 0.22 (s, 27H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 178.0, 74.1, 34.5, 19.4, 1.5; HRMS (ESI) calcd for $C_{13}H_{32}O_2NaSi_4$ $[M+Na]^+$ 355.1377, found 355.1376.

Dimethyl-2-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)-trisilan-2-yl)succinate (**10**): Colorless oil, 67.45 mg, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.67 (s, 3H), 3.64 (s, 3H), 2.99 (dd, J=17.0, 12.7 Hz, 1H), 2.74 (dd, J=12.7, 2.7 Hz, 1H), 2.42 (dd, J=17.0, 2.7 Hz, 1H), 0.22 (s, 27H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.2, 173.2, 51.9, 51.4, 35.4, 25.9, 1.4; HRMS (ESI) calcd for $C_{15}H_{36}O_4Si_4Na$ $[M+Na]^+$ 415.1580, found 415.1586.

1-(3-(1,1,1,3,3,3-Hexamethyl-2-(trimethylsilyl)trisilan-2-yl)propanoyl)pyrrolidin-2-one (**11**): Pale yellow oil, 42.59 mg, 55% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.80 (t, J=7.2 Hz, 2H), 3.01～2.90 (m, 2H), 2.59 (t, J=8.1 Hz, 2H), 2.09～1.96 (m, 2H), 1.14～1.02 (m, 2H), 0.18 (s, 27H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.4, 175.3, 45.5, 35.9, 33.7, 17.2, 1.7, 1.0; HRMS (ESI) calcd for $C_{16}H_{38}NO_2Si_4$ $[M+H]^+$ 388.1980, found 388.1988.

3-(1,1,1,3,3,3-Hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-*N*,*N*-dimethylpropanamide (**12**): Colorless oil, 45.13 mg, 65% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.96 (d, J=11.5 Hz, 6H), 2.42～2.25 (m, 2H), 1.18～1.01 (m, 2H), 0.17 (s, 27H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.0, 37.1, 35.5, 32.5, 2.6, 1.1; HRMS (ESI) calcd for $C_{14}H_{38}NOSi_4$ $[M+H]^+$ 348.2030, found 348.2037.

N-Benzyl-3-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)-trisilan-2-yl)propanamide (**13**): Pale yellow solid, 53.20 mg, 65% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42～7.25 (m, 5H), 5.69 (s, 1H), 4.45 (d, J=5.7 Hz, 2H), 2.40～2.19 (m, 2H), 1.20～1.07 (m, 2H), 0.18 (s, 27H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.7, 138.4, 128.7, 128.0, 127.5, 43.7, 35.6, 3.4, 1.1; HRMS (ESI) calcd for $C_{19}H_{40}NOSi4$ $[M+H]^+$ 410.2187, found 410.2188.

3-(1,1,1,3,3,3-Hexamethyl-2-(trimethylsilyl)trisilan-2-yl)cyclopentan-1-one (**14**): Colorless oil, 34.33 mg, 52% yield. ^{1}H NMR (400 MHz, CDCl3) δ: 2.50～2.35 (m, 1H), 2.33～2.22 (m, 2H), 2.19～2.04 (m, 1H), 1.99 (dd, J=18.1, 13.7 Hz, 1H), 1.77 (s, 1H), 1.70～1.60 (m, 1H), 0.21 (s, 27H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 221.1, 44.8, 39.6, 30.4, 19.6, 1.7; HRMS (ESI) calcd for $C_{14}H_{34}ONaSi_4$ $[M+Na]^+$ 353.1584, found 353.1591.

3-(1,1,1,3,3,3-Hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-1-phenylpropan-1-one (**15**): Colorless oil, 44.86 mg, 59% yield. 1H NMR (400 MHz, $CDCl_3$) δ: 7.98～7.86 (m, 2H), 7.60～7.52 (m, 1H), 7.47 (t, J=7.6 Hz, 2H), 3.10～2.90 (m, 2H), 1.22～1.12 (m, 2H), 0.21 (s, 27H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 200.7, 136.7, 132.9, 128.7, 128.0, 37.6, 1.8, 1.2; HRMS (ESI) calcd for $C_{18}H_{36}ONaSi_4$ [M+

Na]$^+$ 403.1741, found 403.1746.

Ethyl-2-Cyano-3-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)propanoate (**16**): Colorless oil, 68.66 mg, 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.26 (q, J=7.1 Hz, 2H), 3.37 (dd, J=10.2, 4.7 Hz, 1H), 1.58～1.52 (m, 1H), 1.46～1.40 (m, 1H), 1.33 (t, J=7.1 Hz, 3H), 0.23 (s, 27H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.4, 118.0, 62.8, 36.4, 14.0, 9.9, 1.1; HRMS (ESI) calcd for $C_{15}H_{35}NO_2NaSi_4$ [M+Na]$^+$ 396.1643, found 396.1633.

((1,1,1,3,3,3-Hexamethyl-2-(trimethylsilyl)trisilan-2-yl)(phenyl)methyl)malononitrile (**17**): White solid, 42.24 mg, 55% yield. m.p. 60.1～62.2 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.39～7.30 (m, 5H), 4.05 (d, J=4.8 Hz, 1H), 3.01 (d, J=4.8 Hz, 1H), 0.20 (s, 27H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.4, 129.7, 129.1, 128.0, 113.2, 113.0, 34.5, 29.7, 1.6; HRMS (ESI) calcd for $C_{19}H_{34}N_2NaSi_4$ [M+Na]$^+$ 425.1697, found 425.1704.

(3*S*,8*S*,10*R*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-3-yl-3-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)propanoate (**20**): White solid, 121.45 mg, 88% yield. m.p. 102.2～124.2 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.37 (d, J=4.6, 1H), 4.67～4.52 (m, 1H), 2.44～2.16 (m, 4H), 2.06～1.92 (m, 2H), 1.91～1.79 (m, 3H), 1.62～1.43 (m, 7H), 1.37～1.24 (m, 4H), 1.22～1.06 (m, 9H), 1.05～0.95 (m, 6H), 0.92 (d, J=6.5 Hz, 3H), 0.86 (dd, J=6.6, 1.8 Hz, 6H), 0.68 (s, 3H), 0.17 (s, 27H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.2, 139.8, 122.5, 73.9, 56.7, 56.1, 50.0, 42.3, 39.7, 39.5, 38.1, 37.0, 36.6, 36.2, 35.8, 33.5, 31.9, 31.8, 28.2, 28.0, 27.8, 24.3, 23.8, 22.8, 22.6, 21.0, 19.3, 18.7, 11.8, 2.7, 1.1; HRMS (ESI) calcd for $C_{39}H_{77}O_2Si_4$ [M+H]$^+$ 689.5001, found 689.5009.

(3*R*,8*R*,9*S*,10*S*,13*S*,14S)-10,13-Dimethyl-17-oxohexadecahydro-1*H*-cyclopenta[a]phenanthren-3-yl-3-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)propanoate (**21**): Colorless oil, 106.62 mg, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.00 (t, J=2.7 Hz, 1H), 2.44 (dd, J=19.2, 8.8 Hz, 1H), 2.35～2.26 (m, 2H), 2.07 (dt, J=18.7, 9.0 Hz, 1H), 1.97～1.90 (m, 1H), 1.84～1.70 (m, 3H), 1.70～1.62 (m, 2H), 1.62～1.47 (m, 6H), 1.31～1.17 (m, 7H), 1.15～1.07 (m, 2H), 1.07～0.94 (m, 1H), 0.86 (s, 3H), 0.82 (s, 3H), 0.18 (s, 27H); ^{13}C NMR (100 MHz, $CDCl_3$) δ:221.4, 174.2, 69.8, 54.4, 51.5, 47.8, 40.1, 35.9, 35.8, 35.0, 33.7, 32.9, 32.8, 31.5, 30.8, 28.0, 26.0, 21.7, 20.0, 13.8, 11.3, 3.2, 1.0; HRMS (ESI) calcd for $C_{31}H_{61}O_3Si_4$ [M+H]$^+$ 593.3698, found 593.3684.

2-Methoxy-4-(3-oxobutyl)phenyl-3-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)propanoate (**22**): Colorless oil, 62.82 mg, 63% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.92 (d, J=8.0 Hz, 1H), 6.82～6.68 (m, 2H), 3.80 (s, 3H), 2.87 (t, J=7.4 Hz, 2H), 2.81～2.70 (m, 2H), 2.66～2.49 (m, 2H), 2.14 (s, 3H), 1.27～1.20 (m, 2H), 0.20 (s, 27H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 207.7, 172.9, 151.0, 139.8, 138.3, 122.6, 120.3, 112.7, 55.8, 45.1, 32.9, 30.1, 29.6, 3.0, 1.1; HRMS (ESI) calcd for $C_{23}H_{44}O_4Si_4N$ [M+H]$^+$ 519.2214, found 519.2218 .

(8*R*,9*S*,13*S*,14*S*)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-yl-3-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)propanoate (**23**): Colorless oil, 72.68 mg, 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.28 (d, J=8.4 Hz, 1H), 6.86 (dd, J=8.4, 2.6 Hz, 1H), 6.82 (d, J=2.4 Hz, 1H), 2.95～2.87 (m, 2H), 2.59～2.46 (m, 3H), 2.45～2.37 (m, 1H), 2.32～2.26 (m, 1H), 2.20～1.94 (m, 4H), 1.68～1.41 (m, 6H), 1.27～1.20 (m, 2H), 0.91 (s, 3H), 0.21 (s, 27H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 221.0, 173.5, 148.8, 138.0, 137.3, 126.5, 121.7, 118.8, 50.5, 48.0, 44.2, 38.1, 36.0, 33.5, 31.6, 29.5, 26.4, 25.8, 21.7, 13.9, 3.0, 1.2. 1.20; HRMS (ESI) calcd for $C_{30}H_{53}O_3Si_4$ [M+H]$^+$ 573.3072, found 573.3068.

1,1,1,3,3,3-Hexamethyl-2-(3-phenylpropyl)-2-(trimethylsilyl)trisilane (**24**): Colorless oil, 57.86 mg, 79% yield. 1H NMR (400 MHz, $CDCl_3$) δ: 7.28 (d, J=6.3 Hz, 2H), 7.22～7.13 (m, 3H), 2.64 (t, J=7.6 Hz, 2H), 1.79～1.66 (m, 2H), 0.88～0.78 (m, 2H), 0.15 (s, 27H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.4, 128.4, 128.2, 125.6, 40.5, 30.9, 7.4, 1.1; HRMS (ESI) calcd for $C_{18}H_{38}NaSi_4$ [M+Na]$^+$ 389.1948, found 389.1940.

1,1,1,3,3,3-Hexamethyl-2-(4-phenylbutyl)-2-(trimethylsilyl)trisilane (**25**): Colorless oil, 64.18 mg, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27 (t, J=7.5 Hz, 2H), 7.18 (d, J=7.1 Hz, 3H), 2.62 (t, J=7.6 Hz, 2H), 1.66 (p, J=7.4 Hz, 2H), 1.48～1.39 (m, 2H), 0.84～0.75 (m, 2H), 0.15 (s, 27H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.7, 128.4, 128.2, 125.5, 35.9, 35.5, 28.8, 7.4, 1.1; HRMS (ESI) calcd for $C_{19}H_{40}NaSi_4$ [M+Na]$^+$ 403.2105, found 403.2107.

1,1,1,3,3,3-Hexamethyl-2-octyl-2-(trimethylsilyl)trisilane (**26**): Colorless oil, 60.52 mg, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.41～1.23 (m, 12H), 0.88 (t, J=6.8 Hz, 3H), 0.81～0.71 (m, 2H), 0.16 (s, 27H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 34.3, 31.9, 29.3, 29.2, 22.7, 14.1, 7.5, 1.2; HRMS (ESI) calcd for $C_{17}H_{44}NaSi_4$ [M+Na]$^+$ 383.2418, found 383.2417.

Benzyl 4-(1,1,1,3,3,3-Hexamethyl-2-(trimethylsilyl)-trisilan-2-yl)butanoate (**27**): Colorless oil, 79.75 mg, 94% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47～7.27 (m, 5H), 5.12 (s, 2H), 2.40 (t, J=7.0 Hz, 2H), 1.82～1.68 (m, 2H), 0.85～0.73 (m, 2H), 0.15 (s, 27H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.1, 136.1, 128.5, 128.2, 66.0, 38.5, 24.7, 7.5, 1.1; HRMS (ESI) calcd for $C_{20}H_{41}O_2Si_4$ [M + H]$^+$ 425.2184, found 425.2190.

Ethyl-5-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-2-methylpentanoate (**28**): Colorless oil, 74.14 mg, 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.11 (q, J=7.1 Hz, 1H), 2.48～2.39 (m, 1H), 1.73～1.64 (m, 1H), 1.47～1.34 (m, 3H), 1.25 (t, J=7.1 Hz, 3H), 1.12 (d, J=6.9 Hz, 3H), 0.79～0.70 (m, 2H), 0.15 (s, 27H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.9, 60.1, 39.2, 38.4, 26.9, 17.0, 14.3, 7.5, 1.1; HRMS (ESI) calcd for $C_{17}H_{42}O_2Si4Na$ [M+Na]$^+$ 413.2160, found 413.2161.

2-(3-(Benzyloxy)propyl)-1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane (**29**): Colorless oil, 64.98 mg, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38～7.23 (m, 5H), 4.51 (s, 2H), 3.42 (t, J=6.8 Hz, 2H), 1.74～1.66 (m, 2H),

0.85～0.67 (m, 2H), 0.16 (s, 27H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.7, 128.3, 127.6, 127.5, 73.5, 72.8, 29.0, 3.5, 1.1; HRMS (ESI) calcd for $C_{19}H_{40}ONaSi_4$ $[M+Na]^+$ 419.2054, found 419.2051.

1-(2-(1,1,1,3,3,3-Hexamethyl-2-(trimethylsilyl)trisilan-2-yl)ethyl)pyrrolidin-2-one (**30**): Pale yellow oil, 61.78 mg, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.38 (t, J=7.0 Hz, 2H), 3.35～3.25 (m, 2H), 2.35 (t, J=8.1 Hz, 2H), 2.00 (p, J=7.4 Hz, 2H), 1.08～0.96 (m, 2H), 0.19 (s, 27H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.9, 46.2, 42.1, 31.2, 17.7, 6.5, 1.1; HRMS (ESI) calcd for $C_{15}H_{37}NONaSi_4$ $[M+Na]^+$ 382.1850, found 382.1855.

1-(2-(1,1,1,3,3,3-Hexamethyl-2-(trimethylsilyl)trisilan-2-yl)ethyl)azepan-2-one (**31**): Pale yellow oil, 52.66 mg, 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.46～3.36 (m, 2H), 3.34～3.27 (m, 2H), 2.54～2.43 (m, 2H), 1.77～1.64 (m, 6H), 1.09～1.02 (m, 2H), 0.19 (s, 27H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.8, 49.1, 48.2, 37.4, 30.1, 28.9, 23.3, 7.3, 1.1; HRMS (ESI) calcd for $C_{17}H_{41}NONaSi_4$ $[M+Na]^+$ 410.2163, found 410.2163.

4.4 General procedures for the dihydrosilylative synthesis of **18** and **19**

To a dried Schlenk tube was treated with alkene (0.20 mmol, 1.0 equiv.), $(TMS)_3SiH$ (0.5 mmol, 3.0 equiv.), photocatalyst (0.006 mmol, 3 mol%), $(^nBu)_4NBr$ (0.01 mmol, 5 mol%), and MeCN (1.0 mL, bubbled by Ar for 30 min) were added under Ar atmosphere. After that, this resulting solution was stirred at a distance of ≈1 cm under irradiation by 2×3 W blue LEDs at 27 ℃ for 24 h. The solvent was evaporated, and the crude product was purified by column chromatography using hexane/ethyl acetate (V∶V=100∶1 to 50∶1) as eluent, affording the desired product.

1,4-Phenylenebis(methylene)-bis(3-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)propanoate) (**18**): White solid, 102.44 mg, 69% yield. m.p. 91.1～93.1 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36 (s, 4H), 5.11 (s, 4H), 2.43～2.32 (m, 4H), 1.19～1.06 (m, 4H), 0.16 (s, 54H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 174.5, 136.1, 128.5, 65.9, 33.1, 2.8, 1.0; HRMS (ESI) calcd for $C_{32}H_{71}O_4Si_8$ $[M+H]^+$ 743.3506, found 743.3513.

Butane-1,4-diyl-bis(3-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)propanoate) (**19**): Colourless oil, 95.82 mg, 69% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.17～4.05 (m, 4H), 2.40～2.26 (m, 4H), 1.73～1.70 (m, 4H), 1.17～1.03 (m, 4H), 0.18 (s, 54H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.7, 63.9, 33.2, 25.3, 2.8, 1.0; HRMS (ESI) calcd for $C_{28}H_{70}O_4NaSi_8$ $[M+Na]^+$ 717.3326, found 717.3334.

4.5 General procedures for the hydrosilylation irradiated by sunlight

To a dried Schlenk tube was treated with **s2** (0.20 mmol, 1.0 equiv.), $(TMS)_3SiH$ (0.3 mmol, 1.5 equiv.), photocatalyst (0.006 mmol, 3 mol%), $(^nBu)_4NBr$ (0.01 mmol, 5 mol%), and MeCN (2.0 mL, bubbled by Ar for 30 min) were added under Ar atmosphere. After that, this resulting solution was stirred and irradiated by sunlight at 27～34 ℃ for 4 h. The solvent was evaporated, and the crude product was purified by column chromatography using hexane/ethyl acetate (V∶V=100∶1 to 50∶1) as eluent, affording the desired product **2** in 94% yield.

Supporting Information Experimental procedures and full spectroscopic data for all new compounds. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn.

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