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Divergent Syntheses of Silicon-Containing Alkanes by Iron-Catalysed Intermolecular 1,2-Difunctionalizations of Styrenes and Conjugated Alkenes with Silanes and Nucleophiles

Yuan Yang, Ren-Jie Song*, Xuan-Hui Ouyang, Cheng-Yong Wang, Jin-Heng Li*, and Shenglian Luo*

Dedicated to Professor Jiannan Xiang on the occasion of his 60th birthday

Abstract: The first iron-catalysed 1,2-difunctionalizations of styrenes and conjugated alkenes with silanes and *N*- or *C*-nucleophiles using an oxidative radical strategy is described. Employing $FeCl_2$ and di-*tert*-butyl peroxide (DTBP) allows divergent alkene 1,2-difunctionalizations, including 1,2-aminosilylation, 1,2-arylsilylation and 1,2-alkylsilylation, which rely on a wide range of nucleophiles, namely, amines, amides, indoles, pyrrole and 1,3-dicarbonyls, thus providing a powerful platform for producing diverse silicon-containing alkanes.

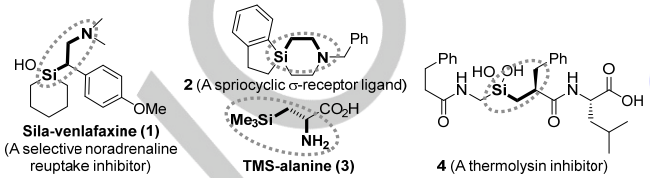
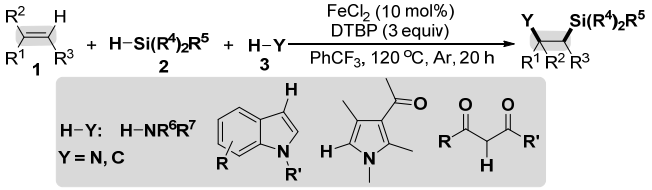


Figure 1. Examples of medicinal interest molecules comprising silicon.

Organosilicon chemistry has attracted increased attention from scientific researchers because organosilicon compounds have significant chemical, physical and bioactive properties, which grant them wide applications in organic chemistry, materials science, agrochemistry and medicinal chemistry.[1,2] Specifically, the recently expanding studies of both silicon analogues of known drugs and entirely new silicon-containing compounds have become an emerging leading research field in the pharmaceutical industry. For example, 1-amino-2-silylalkanes exhibit fascinating biological activities that exist in many potential pharmaceuticals and drug lead compounds,[2] such as Sila-venlafaxine (**1**),[2a-b] compound **2**[2c] and TMS-alanine (**3**)[2d-e] (Figure 1). Traditionally, synthesis of such 1-amino-2-silylalkanes and other silicon-containing amino compounds relies on the introduction of amino or silicon functional groups into the corresponding silicon-based or amino-based frameworks;[1-3] however, these methods suffer from harsh reaction conditions with strong bases, narrow substrate scope, multiple steps and/or use of expensive silicon reagents. Thus, new general and divergent strategies for producing silicon-containing compounds in a straightforward manner, especially 1-amino-2-silylalkanes, are desirable and urgently needed.

Recently, transformations of alkenes with silanes have emerged as a powerful tool to assemble silicon-containing molecules in syntheses,[4-7] with the vast majority of examples concerning the hydrosilylation or dehydrogenative silylation of alkenes through alkyl-metal or alkyl radical intermediates.[4,5]

Alternatively, 1,2-difunctionalization of alkenes, such as 1,2-bis-silylation,[6a-c] 1,2-arylsilylation[6d-f] and 1,2-hydroxysilylation,[6g] is particularly attractive in that it allows the simultaneous introduction of a silicon group and the other functional group beyond the hydrogen atom across the C=C bond to prepare complex functional silicon-containing molecules. However, examples of such alkene difunctionalizations are quite rare and challenging probably due to complications from dominant competitive reactions including hydrosilylation, dehydrogenative silylation, silane redistribution, and silane dehydrocoupling.[4-6] To the best of our knowledge, there is no report of intermolecular 1,2-aminosilylation of alkenes for the synthesis of 1-amino-2-silylalkanes. Herein, we report a new iron-catalysed intermolecular 1,2-aminosilylation of styrenes and conjugated alkenes with silanes and amines or amides for the preparation of diverse 1-amino-2-silylalkanes using a DTBP oxidant (Scheme 1),[7,8] wherein a silicon group and an amino group are simultaneously incorporated across the C=C bond. Interestingly, the reaction is expanded to 1,2-carbosilylation of alkenes with silanes and a wide range of carbon nucleophiles, such as indoles, pyrrole and 1,3-dicarbonyls.



Scheme 1. Three-component intermolecular 1,2-difunctionalization of alkenes.

As shown in Table 1, the three-component reaction of 4-methoxystyrene (**1a**) with $HSi(TMS)_3$ (**2a**) and morpholine (**3a**) was chosen for the optimization of the 1,2-aminosilylation conditions. Treatment of alkene **1a** with silane **2a**, amine **3a**, 10 mol% $FeCl_2$ and 3 equiv of DTBP in $PhCF_3$ at 120 °C for 20 h afforded the desired product **4aaa** in 67% yield (entry 1).

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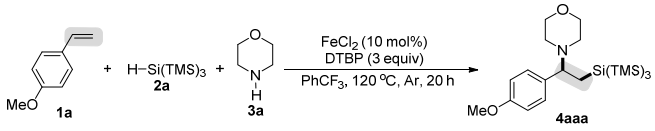
Inspired by these results, the amount of $FeCl_2$ was subsequently examined. The results revealed 10 mol% $FeCl_2$ as the best option (entries 1-4). Notably, without $FeCl_2$ the reaction could still occur, albeit with the yield diminished to 7% (entry 2). Other alternative Fe catalysts, such as $Fe(OTf)_2$ and $FeCl_3$, were tested (entries 5 and 6), but none were more efficient than $FeCl_2$. However, no desired reaction was observed in the absence of DTBP (entry 7), and both lower and higher amounts of DTBP had negative effects (Table S1 in Supporting Information). Gratifyingly, a reaction scale up to 1 mmol of alkene **1a** was successful at accessing **4aaa** in useful yield (entry 8).

Table 1. Screening of optimal reaction conditions[a]



Entry	Variation from the Standard Conditions	Isolated Yield [%]
1	none	67
2	without $FeCl_2$	7
3	$FeCl_2$ (5 mol %)	47
4	$FeCl_2$ (20 mol %)	68
5	$Fe(OTf)_2$ instead of $FeCl_2$	30
6	$FeCl_3$ instead of $FeCl_2$	48
7	without DTBP	0
8[b]	none	63

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (2 equiv), **3a** (2 equiv), $FeCl_2$ (10 mol%), DTBP (3 equiv), $PhCF_3$ (2 mL), argon, 120 °C, and 20 h. Some by-products, including the hydrosilylation product **4aa'** and dehydrogenative silylation product **4aa''**, were determined by GC-MS analysis. [b] **1a** (1 mmol) and 24 h.

Having optimized the reaction conditions, we set out to investigate the substrate scope of this alkene 1,2-aminosilylation protocol (Table 2). Initially, a wide range of terminal alkenes, including arylalkenes **1b-n**, alkylalkenes **1o-p**, 1,3-diene **1q** and 1-en-3-yne **1r**, were examined with silane **2a** and amine **3a** (**3baa-raa**). An array of substituents, namely, Me, Cl, Br, CN, CF_3 and MeO, on the aryl ring at the terminal alkene were well tolerated, and their electronic properties and positions affected the reactivity (**3baa-naa**). While alkene **1c** bearing an electron-donating 4-MeC_6H_4 group delivered **4caa** in 67% yield, alkenes **1d-g** and **1i** having a weak (Cl or Br) or a strong (CN or CF_3) electron-withdrawing group afforded **4daa-gaa** and **4iaa** with diminishing yields. Importantly, chloride and bromide groups were tolerated, thus providing the opportunity for subsequent modification of the halogenated position (**4daa-eaa**). Arylalkenes **1h** and **1j** with a MeO group on the *meta* and *ortho* position were highly reactive (**4haa** and **4jaa**). Using alkenes containing disubstituted phenyl (**1k-l**), naphthalen-2-yl (**1m**) and 3-methylthiophen-2-yl (**1n**) groups were successfully converted into **4kaa-naa** in 39%-72% yields. Unfortunately, aliphatic alkenes **1o** and **1p** both had no reactivity (**4oaa-paa**). Noted that conjugated alkenes **1q-r** were suitable substrates (**4qaa-raa**). Gratifyingly, the optimal conditions were applicable to a wide array of nitrogen nucleophiles, including secondary amines (**3b-d**), primary amines (**3e-1j**) and amides or an imide (**3k-n**), which underwent the aminosilylation reaction with alkene **1a** and $HSi(TMS)_3$ **2a** to afford **4aab-aan** in 40%-70% yields. Importantly, a number of silanes, such as *tert*-butyldimethylsilane (**2b**), triethylsilane (**2c**), tri*iso*propylsilane (**2d**), triphenylsilane (**2e**), methyldiphenylsilane (**2f**) and dimethyl(phenyl)silane (**2g**), were competent reaction partners for producing **4aba-aea** and **4afh-agh**, albeit giving decreased yields in comparison with those of $HSi(TMS)_3$ **2a**.

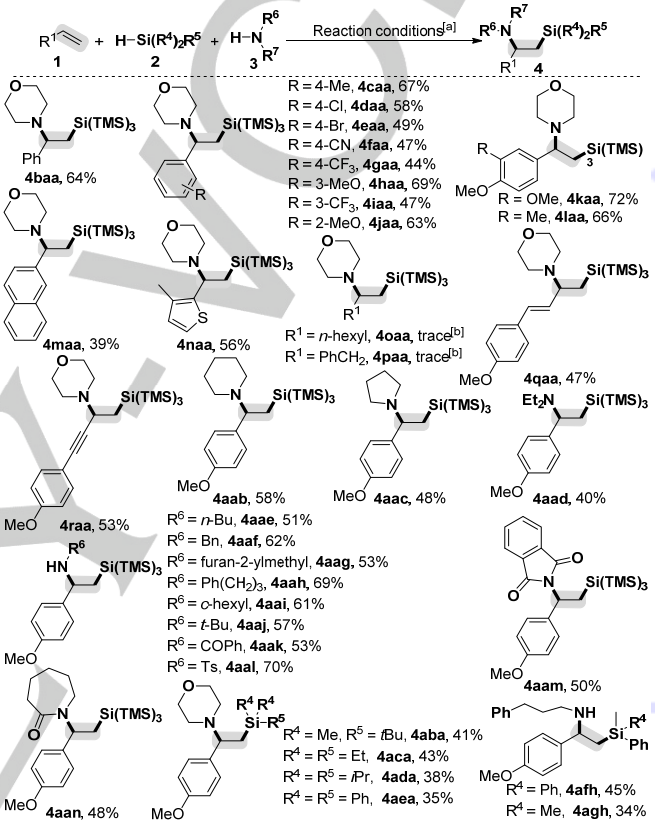


Table 2. Variation of the Alkenes (**1**), Silanes (**2**) and *N*-Nucleophiles (**3**). [a] Reaction conditions: see Table 1. [b] >90% of alkene **1** was recovered.

Next, the scope with respect to carbon nucleophiles was explored under the optimal conditions (Table 3). Indole **3o** as a suitable *C*-nucleophile smoothly underwent the 1,2-arylsilylation reaction with various alkenes **1a-g, 1h, 1j-k, 1q-r** and **1s** providing **5aao-gao**, **5hao**, **5jao-kao**, **5qao-rao** and **5sao** in 44%-67% yields.[9] 1-Methyl-1-phenylethene (**1t**) also exhibited reactivity and delivered **5tao** in moderate yield. For internal alkenes, 1,2-dihydronaphthalene (**1u**) and prop-1-en-1-ylbenzene (**1v**), both were viable for the 1,2-arylsilylation reaction (**5uao-vao**). Subsequently, a series of indoles **3p-v** bearing different substitution patterns were tested by reacting with alkene **1a** and $HSi(TMS)_3$ **2a** (**5aap-aav**). 1-Methyl-1*H*-indole (**3p**) was transformed to **5aap** with 57% yield. Several substituents, such as 5-Me, 5-MeO, 5-CN, 7-CO_2Me, 4-CHO and 2-Me, on the indole core were perfectly tolerated (**5aaq-aav**). Other tertiary silane **2b-c**, secondary silane **2h** and primary silane **2i** were also suitable for preparing **5abo-aco** and **5aho-**

aio. Further exploitation of *C*-nucleophiles revealed that pyrrole **3w** and 1,3-dicarbonyls **3x-y** were viable *C*-nucleophiles. Using pyrrole **3w** could furnish useful fully-substituted pyrrole **5aaw** in 62% yield. Pleasingly, both pentane-2,4-dione (**3x**) and ethyl 3-oxo-3-phenylpropanoate (**3y**) could succeed to furnish **5aax** and **5aay** in moderate yields.

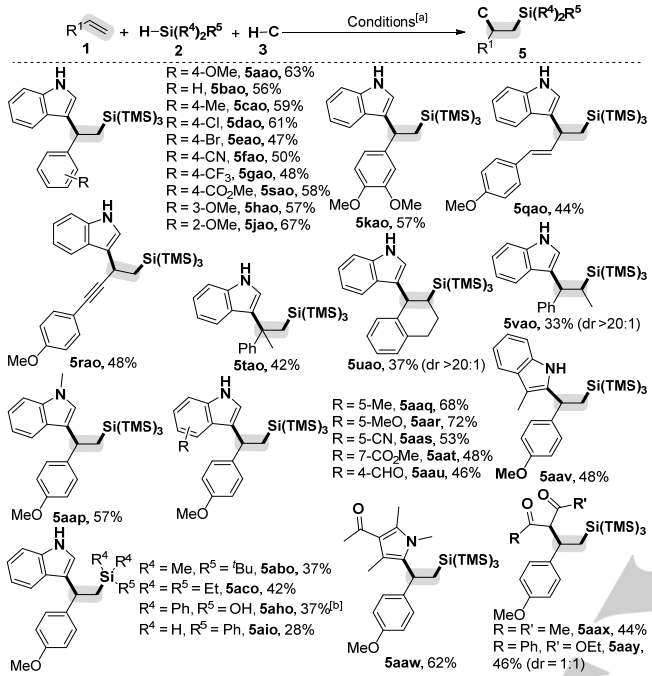
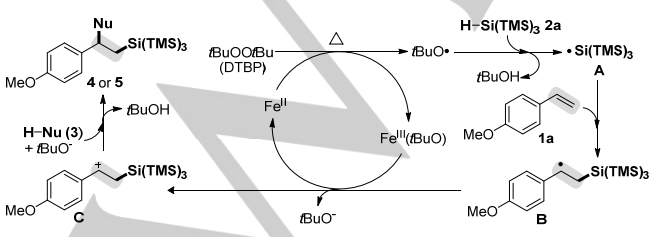


Table 3. Variation of the Alkenes (**1**), Silanes (**2**) and *C*-Nucleophiles (**3**). [a] Reaction conditions: see Table 1. [b] Diphenylsilane (**2h**) was used.

On the basis of the above results, a possible mechanism for the alkene difunctionalization reaction was proposed (Scheme 2 and Scheme S1 in Supporting Information).[4-8] Initially, DTBP is split by the active Fe^{II} species under heating takes place to afford the *tert*-butoxyl radical and the Fe^{III}(*t*BuO) species.[6,7] Hydrogen-abstraction from $HSi(TMS)_3$ **2a** by the *t*-butoxyl radical gives the silicon-centred radical **A**,[6,7] which sequentially adds across the C=C bond of alkene **1a** to grant the alkyl radical intermediate **B**. Oxidation of the intermediate **B** by the Fe^{III}(*t*BuO) species delivers the alkyl cation intermediate **C**. Finally, reaction of the intermediate **C** with *N*- or *C*-nucleophile **3** provides the desired product **4** or **5**.



Scheme 2. Possible Reaction Mechanism.

In summary, we have developed the first iron-catalysed intermolecular 1,2-difunctionalization of styrenes and conjugated alkenes with silanes and *N*- or *C*-nucleophiles. The reaction is initiated by a key silicon-centred radical from oxidative cleavage of the Si-H bond followed by addition across the C=C bond in addition to N-H oxidative functionalization cascades, thus building the 1-amino-2-silylalkane cores. Moreover, the reaction can be expanded to three-component 1,2-carbosilylation of alkenes via Si-H/C-H oxidative functionalization. Notably, the reaction exhibits high selectivity, excellent tolerance of functional groups and broad scope of substrates, including a wide range of alkenes, silanes, and *N*- and *C*-nucleophiles. Further studies on mechanism and applications are currently underway.

Acknowledgements

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Conflict of interest

The authors declare no conflict of interest.

Keywords: iron • difunctionalization • alkenes • silanes • nucleophiles

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[9] CCDC 1535711 (**5aao**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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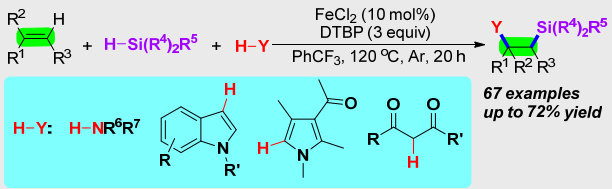

Employing $FeCl_2$ and DTBP divergent alkene 1,2-difunctionalization reactions, including 1,2-aminosilylation, 1,2-arylsilylation and 1,2-alkylsilylation, are achieved by using different nucleophiles, thereby providing straightforward and practical access to 1-amino-2-silylalkanes and other functionalized silicon-containing alkanes with broad substrate scope and high selectivity.

Y. Yang, R.-J. Song, X.-H. Ouyang, C.-Y. Wang, J.-H. Li*, and S. Luo**

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Divergent Syntheses of Silicon-Containing Alkanes by Iron-Catalysed Intermolecular 1,2-Difunctionalizations of Styrenes and Conjugated Alkenes with Silanes and Nucleophiles