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C−O Bond Silylation Catalyzed by Iron: A General Method for the Construction of Csp^2−Si Bonds

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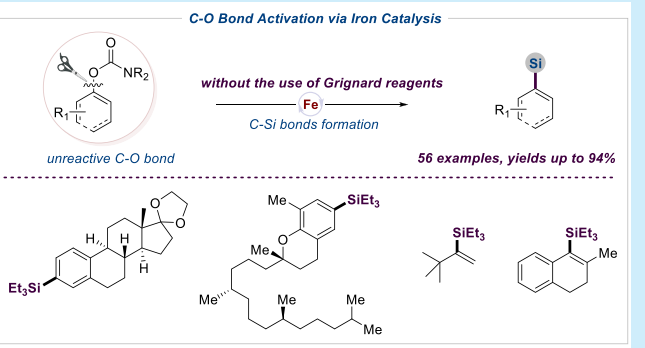
ABSTRACT: The iron-catalyzed construction of Csp^2−Si bonds via unreactive C−O bonds possesses a challenging topic in organic chemistry. Herein we report an iron-catalyzed silylation of aryl and alkenyl carbamates via C−O bond activation. This protocol features high efficiency and a broad substrate scope, enabling the late-stage silylation of biorelevant compounds and thus providing a good method to access valuable motifs in medicinal chemistry. Moreover, this protocol enables orthogonal transformations of phenol derivatives and also allows for the synthesis of multi-substituted arenes through the carbamate group as the directing group.



Iron catalysts have been widely used in cross-coupling reactions owing to their cheapness, abundance, and nontoxicity.[1] To facilitate the oxidative addition in iron-catalyzed cross-coupling reactions, a highly reactive, low-valent iron species always needs to be generated through sacrificial organometallic reagents via reductive elimination *in situ*.[2] Consequently, these reactions are mostly limited to the formation of C−C bonds through classical cross-coupling reactions,[3] and the iron-catalyzed construction of C−heteroatom bonds has lagged.[4] Organosilicon compounds are important reagents that are widely employed in organic synthesis, material science, as well as medicinal chemistry.[5] However, iron-catalyzed cross-coupling reactions to construct C−Si bonds have been less developed.[6,7] It is of great interest to develop an organometallic reagent-free and efficient iron-catalyzed method for the construction of C−Si bonds.

Compared with organohalides, oxygen-based electrophiles, such as phenol and ketone derivatives, have become increasingly more attractive as the coupling partners.[8] Not only are phenols and ketones commercially available and easily produced but also the halide-containing waste is avoided by using oxygen-based electrophiles. The silylation of unreactive C−O bonds has been carried out by the Martin group,[9] but the formation of alkenylsilanes has been less explored.[9b] The transmetalation process of silicon nucleophiles is more sluggish than that of other organometallic reagents. To address this issue, metal-based silicon nucleophiles are always used in cross-coupling reactions. For example, pioneering works were reported by the Oshima and Trost groups,[10] in which the aluminum-based silicon reagents were used (Scheme 1). Very recently, Oestreich and coworkers reported the copper-

Scheme 1. Transition-Metal-Catalyzed Construction of C−Si Bonds

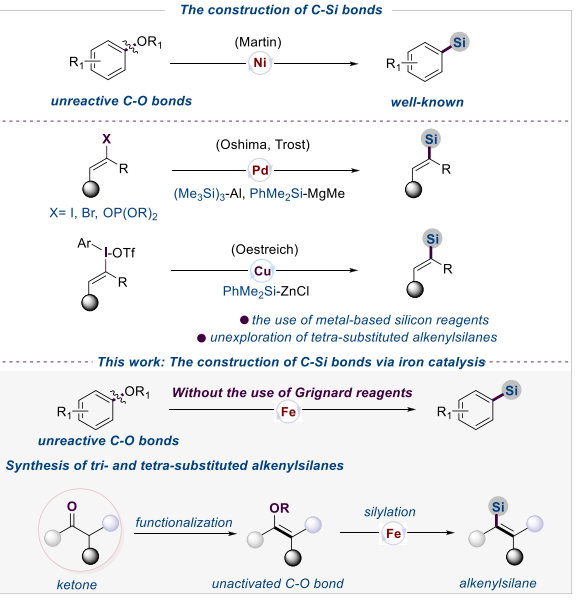


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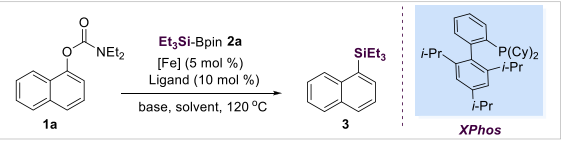
Table 1. Representative Results for the Optimization of the Iron-Catalyzed Silylation of Naphthalen-1-yl Diethylcarbamate 1a[a]



entry	[Fe]	ligand	solvent	base	yield (%)[b]
1	$Fe(OTf)_2$	P(*t*-Bu)$_3$	toluene	MeOK	0
2	$Fe(OTf)_2$	P(*p*-MePh)$_3$	toluene	MeOK	28
3	$Fe(OTf)_2$	XPhos	toluene	MeOK	36
4	$Fe(OTf)_2$	XPhos	toluene	*t*-BuONa	23
5	$Fe(OTf)_2$	XPhos	toluene	MeONa	60
6	$Fe(OTf)_2$	XPhos	(*i*-Pr)$_2$O	MeONa	28
7	$Fe(OTf)_2$	XPhos	1,4-dioxane	MeONa	64
8	$FeBr_2$	XPhos	1,4-dioxane	MeONa	78
9	$Fe(OAc)_2$	XPhos	1,4-dioxane	MeONa	93 (89)
10	$Fe(OAc)_2$		1,4-dioxane	MeONa	0
11		XPhos	1,4-dioxane	MeONa	0

[a]Reaction conditions (unless otherwise specified): **1a** (0.3 mmol, 1.0 equiv), silylborane **2a** (0.75 mmol, 2.5 equiv), [Fe] (0.015 mmol, 0.05 equiv), ligand (0.03 mmol, 0.1 equiv), solvent (1.5 mL), base (1.05 mmol, 3.5 equiv), 120 °C, 15 h. [b]Determined by ^{1}H NMR using mesitylene as an internal standard. The isolated yield is shown in parentheses.

catalyzed silylation of vinyliodonium triflate with silylzinc reagents (Scheme 1).[11] Although those achievements have been made, it should be noted that the synthesis of tetra-substituted alkenylsilanes remains challenging. Moreover, the iron-catalyzed formation of C−Si bonds with unreactive C−O bonds has yet to be achieved, owing to the problematic oxidative addition step with iron catalysts due to their strong bond dissociation energy.[12] To continue our interest in transition-metal catalysis,[13] herein we describe an example of the construction of Csp^2−Si bonds from phenol and ketone derivatives through iron-catalyzed C−O bond activation without Grignard reagents,[14] thus providing a facile and efficient route to the synthesis of tri- and tetra-substituted alkenylsilanes.

With these considerations in mind, we began to search for the potential oxygen-based electrophiles for the iron-catalyzed silylation. Among the oxygen-based electrophiles, aryl carbamates are rather attractive due to their ease of preparation and high stability.[15] Moreover, the carbamate group has been widely employed as the directing group to realize regioselective C−H bond functionalization or electrophilic aromatic substitution, providing the chance for orthogonal transformations.[16] Accordingly, we began our investigations by subjecting aryl carbamate **1a** to silylborane **2a** in the presence of various bases and electron-rich ligands, such as P(*t*-Bu)$_3$ and P(Cy)$_3$, but no desired product was observed. (For details, see the Supporting Information.) To our delight, after extensive investigations, the silylated product **3** was observed in 28% yield when P(*p*-MePh)$_3$ was used as a ligand (Table 1, entry 2). Encouraged by these results, other parameters were evaluated (Table 1, entries 3−5), and the desired product **3** was obtained in a promising 60% yield when sodium methanolate was used as a base in the presence of XPhos as the ligand (Table 1, entry 5). Switching the solvent from toluene to ethers provided the corresponding compound in moderate yield (Table 1, entries 5−7). After testing other iron sources, we found that $FeBr_2$ could promote this reaction, providing **3** in 78% yield. Furthermore, $Fe(OAc)_2$ could drastically improve the reaction efficiency, delivering **3** in 89% isolated yield (Table 1, entries 8 and 9; for details, see the Supporting Information). Control experiments revealed the necessity for both an iron catalyst and a ligand, and no desired product was observed in the absence of an iron catalyst or XPhos. These results suggest that electron-rich ligand XPhos plays a crucial role in promoting this reaction. This is probably because the electron-rich ligand could facilitate the oxidative addition of an unreactive C−O bond to the iron catalyst.

After the optimal conditions were established, the scope of this iron-catalyzed silylation reaction was explored. As shown in Scheme 2, when naphthyl phenol derivatives were used as substrates, this reaction proceeded well, providing the corresponding silylated products in good to excellent yield (**3**−**10**, 68−94%). Substrates bearing a strong electron-donating group afforded the desired products in good yield (**5**−**7**, 68−74%). In addition, the naphthyl carbamates containing an aryl group on the aromatic ring proceeded smoothly, and the corresponding products were obtained in good yield (**8**−**10**, 72−89%). Polycyclic aromatic substrates also showed good reactivity, affording the silylated products in moderate to good yield (**11**−**14**, 66−81%), and the *N*-heteroaromatic carbamate could undergo this transformation as well, producing **15** in a synthetically useful yield. Biphenyl substrates were demonstrated to be good reaction partners, resulting in the corresponding products in moderate yield (**16** and **17**, 57−64%). To our delight, relatively inert monophenyl substrates also proceeded smoothly, yielding the corresponding products in moderate to good yield (**18**−**31**, 50−81%). Moreover, the silyl and alkynyl groups were well-tolerated, and **18** was afforded in an excellent yield (81%), providing an opportunity for the further modification of aryl silanes. Importantly, this silylation reaction could be extended to alkenyl carbamates, and the corresponding silylated products were obtained in moderate to good yield. For a carbamate group located at the one- or two-position of cyclic styrene derivatives, the transformation proceeded smoothly (**32**−**48**). Functional groups such as CF_3, Cl, F, OBn, carbamate, and 2-pyridyloxy could be well-tolerated (**45**, **46**, **47**, **50**, **51**, and **52**). It is worth noting that the relatively unreactive alkenyl carbamates without the π-extended conjugated system could react well (**49**−**53**). Linear carbamate bearing a bulky group

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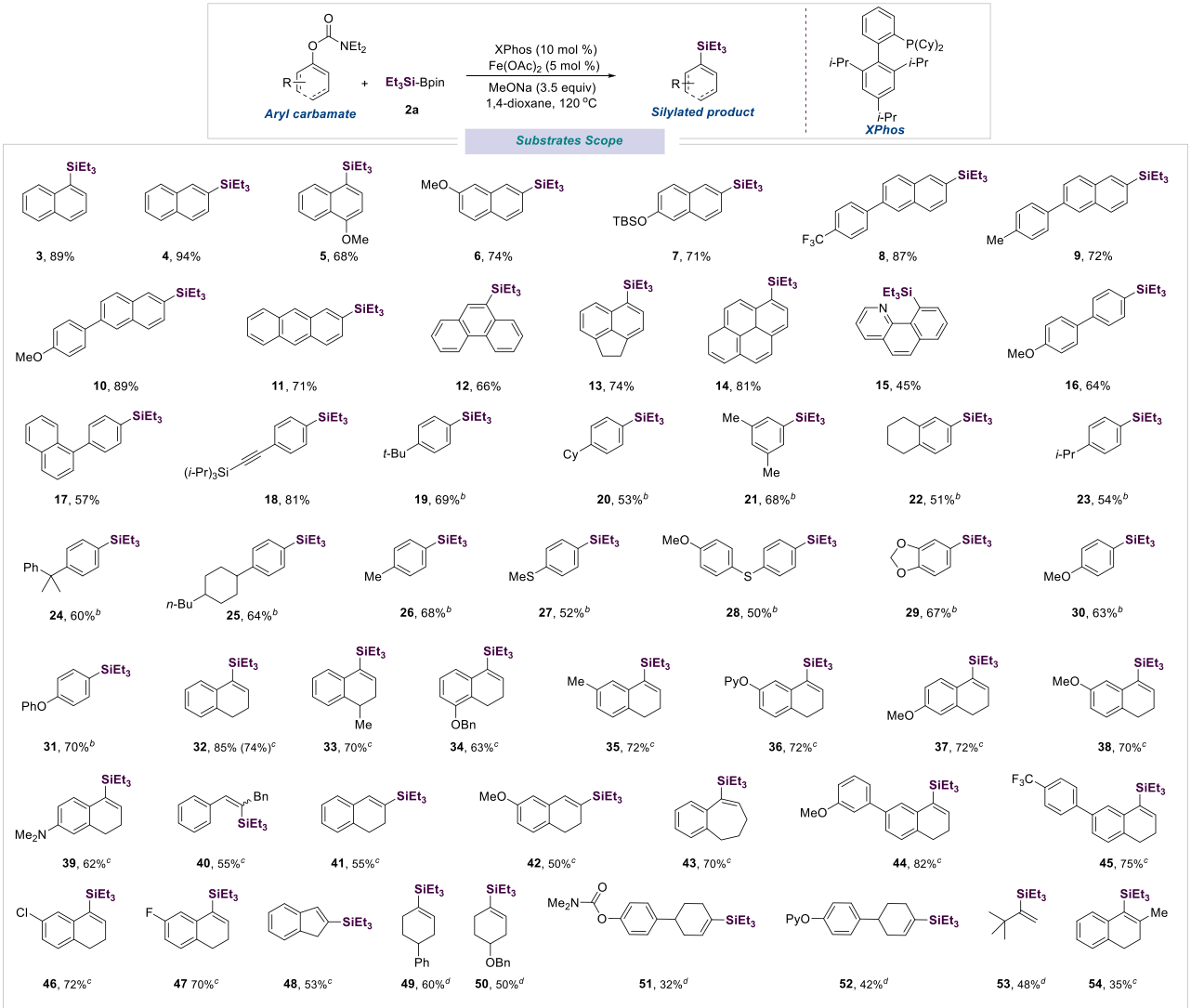
Scheme 2. Scope of the Iron-Catalyzed Silylation of Aryl and Alkenyl Carbamates[a]



[a]Reaction conditions: aryl carbamates (0.3 mmol, 1.0 equiv), silylborane **2a** (0.75 mmol, 2.5 equiv), $Fe(OAc)_2$ (0.015 mmol, 0.05 equiv), XPhos (0.03 mmol, 0.1 equiv), 1,4-dioxane (1.5 mL), MeONa (1.05 mmol, 3.5 equiv), 120 °C, 15 h. [b]Aryl carbamates (0.2 mmol, 1.0 equiv), silylborane **2a** (0.64 mmol, 3.2 equiv), [Fe] (0.02 mmol, 0.1 equiv), dtbpy (0.02 mmol, 0.1 equiv), MTBE (1.5 mL), MeONa (0.8 mmol, 4.0 equiv) was used. (For details, see the Supporting Information.) [c]Alkenyl carbamates (0.2 mmol, 1.0 equiv), silylborane **2a** (0.5 mmol, 2.5 equiv), $Fe(OAc)_2$ (0.02 mmol, 0.1 equiv), Xantphos (0.024 mmol, 0.12 equiv), MTBE (2.0 mL), MeONa (0.8 mmol, 4.0 equiv), 100 °C, 15 h. The isolated yield on a 1 mmol scale is shown in parentheses. [d]Alkenyl carbamates (0.2 mmol, 1.0 equiv), silylborane **2a** (0.6 mmol, 3.0 equiv), FeI_2 (0.02 mmol, 0.1 equiv), BINAP (0.024 mmol, 0.12 equiv), MTBE (1.0 mL), MeONa (0.8 mmol, 4.0 equiv), 100 °C, 15 h. (For details, see the Supporting Information.)

was also suitable for this reaction, providing the silylated product in moderate yield (**53**, 48%). Moreover, this transformation could be used to synthesize tetra-substituted alkenylsilane, providing the desired product in an acceptable yield (**54**, 35%).

To further demonstrate the inherent value of this protocol, the late-stage silylation of biorelevant compounds, such as estrone and vitamin E carbamates, was conducted (Scheme 3). The desired products were delivered in moderate yield (**55** and **56**, 48−58%), providing facile access to diversified bioactive molecules from phenol structures. Most remarkably, the versatile utilities of this protocol can be demonstrated by meta-arylation through C−H bond activation using carbamate as the directing group, followed by silylation via iron catalysis. The introduction of a *meta*-aryl group on naphthyl carbamates via C−H bond activation followed by silylation via iron catalysis allows for the synthesis of the silylated compounds in moderate yield (**57** and **58**, 44−72%).[17] These results suggest that these iron-catalyzed silylation protocols could not only enable the diversification of phenol derivatives but also provide an efficient method to synthesize valuable molecules, meta-substituted arenes in medicinal chemistry.

To gain insight into the mechanism of this iron-catalyzed C−O bond activation reaction, radical inhibition experiments were conducted. Drastically diminished yields were observed when one equivalent of a radical scavenger **TEMPO** or a radical inhibitor **BHT** was added under the standard silyation reaction conditions (Scheme 4A), indicating that a radical pathway might be involved. In these reactions, the adduct of **TEMPO** with an aryl radical was not observed by LC−MS. Furthermore, the electron paramagnetic resonance experiments were also conducted, which suggested that a free radical

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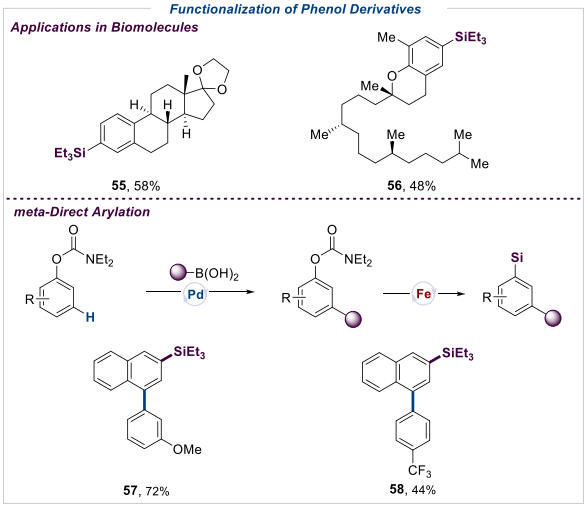
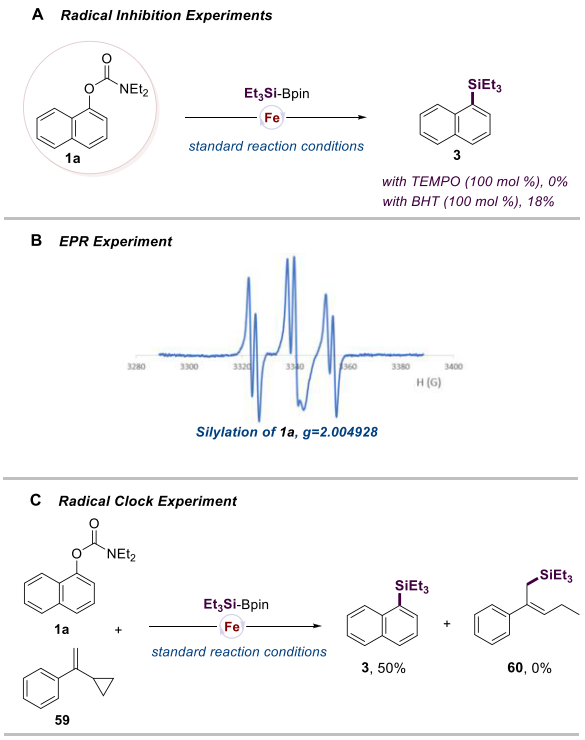
Scheme 3. Late-Stage Functionalization of Biomolecules and Orthogonal Transformations of Phenols



Scheme 4. Mechanistic Studies



was involved in this catalytic system (Scheme 4B; for details, see the Supporting Information). Moreover, a radical clock experiment was carried out as well (Scheme 4C). The radical ring-opening product **60** was not observed, suggesting that a silane radical species may not be involved in this catalytic system.

In conclusion, we have developed the first example of the iron-catalyzed silylation of aryl and alkenyl carbamates via C−O bond activation. This reaction features simple operation, high efficiency, and a broad substrate scope. It could be applied for the late-stage silylation of bioactive compounds, offering potential applications in drug discovery and development. Furthermore, the carbamate directing group could facilitate the C−H bond functionalization of aromatic rings, providing good opportunities for the diversification of silylated derivatives. Further studies to illustrate the mechanism and expand this novel transformation are under way in our lab, and the results will be reported in due course.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c00633.

Experimental data and copies of ^{1}H NMR and ^{13}C NMR spectra for all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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