# A General and Selective Synthesis of Methylmonochlorosilanes from Di-, Tri-, and Tetrachlorosilanes

Yuki Naganawa,* Kei Sakamoto, and Yumiko Nakajima*
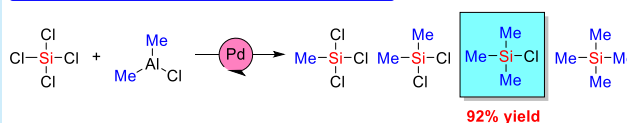
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**ABSTRACT:** Direct catalytic transformation of chlorosilanes into organosilicon compounds remains challenging due to difficulty in cleaving the strong Si−Cl bond(s). We herein report the palladium-catalyzed cross-coupling reaction of chlorosilanes with organoaluminum reagents. A combination of $[Pd(C_3H_5)Cl]_2$ and DavePhos ligand catalyzed the selective methylation of various dichlorosilanes **1**, trichlorosilanes **5**, and tetrachlorosilane **6** to give the corresponding monochlorosilanes.
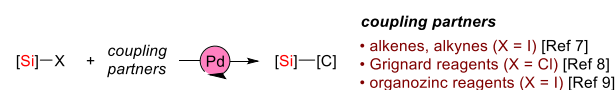
Organochlorosilanes are important raw materials in the silicon industry because they are widely applicable as precursors for the synthesis of various organosilicon materials.[1] In particular, chlorosilanes bearing different multiple organic substituents have recently been in great demand to produce high-performance organosilicon materials,[1] and thus further operations to introduce various organic groups into chlorosilanes are necessary. One of the classical but reliable approaches is the nucleophilic alkylation reaction of chlorosilanes with Grignard reagents (Kipping method).[2] However, the product selectivity of the Kipping method in the reactions with di-, tri-, and tetrachlorosilanes is generally poor due to the high reactivity of the organometallic species.[3] Therefore, the development of competent catalysts toward the introduction of various organic substituents on the silicon atom has been regarded as both an academically and industrially challenging task. Hydrosilylation of olefins has occupied an exclusive and reliable position as a methodology for the catalytic construction of silicon−carbon bonds.[4] However, this method is not applicable for the construction of a "Me−Si" moiety, which is an important core structure of various organosilicon materials, since olefins are utilized as reaction counterparts. As a result, the introduction of a methyl group on the silicon atom thus far predominantly relies on the Müller−Rochow "direct process,"[5] which proceeds via reaction of metal silicon with chloromethane mediated by a copper catalyst. Since the product selectivity of this direct process under the harsh reaction conditions is poor, the isolation of the target products is usually carried out through a distillation of the reaction residue.[5]
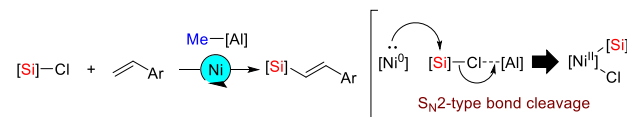
Apart from these established silicon−carbon bond forming reactions, transition-metal-catalyzed cross-coupling reactions of halosilanes[6] are attracting much attention after the seminal report on the palladium-catalyzed silyl-Heck reaction of iodosilanes by Watson and co-workers[7] (Scheme 1a). Furthermore, they applied this concept to the palladium-
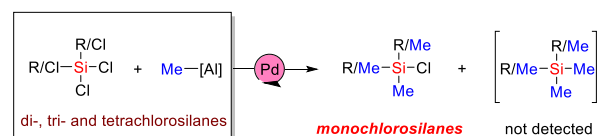
## Scheme 1. Catalytic Transformation of Si−X Bond to Si−C Bond



catalyzed cross-coupling reactions of halosilanes with organometallic species such as Grignard reagents[8] and organozinc reagents[9] to obtain a variety of alkylsilanes (Scheme 1a). In this arena, our independent commitment is directed toward the development of the catalytic transformation of chlorosilanes, which are cheap and abundant silicon feedstocks. The major difficulty in realizing the target reactions lies in the catalytic activation of the strong silicon−chlorine bonds. To
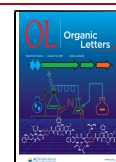
this end, we recently discovered that aluminum Lewis acids could electrophilically activate the silicon−chlorine bond,[10,11] facilitating its cleavage, which proceeds in an $S_N2$ fashion. With this strategy, we developed the first silyl-Heck reaction of chlorosilanes with styrenes catalyzed by electron-rich nickel catalysts (Scheme 1b).[12] During the course of this study, we became aware of the applicability of the organoaluminum reagent itself as a coupling partner of chlorosilanes. Thus, the nickel-catalyzed alkylation reaction of chlorosilanes with organoaluminum reagents was developed, which realized the selective synthesis of a series of alkylmonochlorosilanes starting from di- and trichlorosilanes.[13] However, the major drawback of this reaction was its narrow scope of substrates, especially the requirement for aryl substituents on the silicon atoms to achieve good product selectivity. In this context, we turned our attention to the development of novel catalyst systems for chlorosilanes to realize a general and selective methylation methodology. We herein report the high efficiency of palladium catalysis in selective cross-coupling of a broad range of di-, tri-, and tetrachlorosilanes with alkylaluminum reagents, thus furnishing various alkylated monochlorosilanes (Scheme 1c).

We selected inexpensive yet important silicone monomer $Me_2SiCl_2$ (**1a**) and undertook the optimization of reaction conditions for selective cross-coupling of **1a** with methyl-aluminum reagents (Table 1). As in the previous study, we

$Me_2AlCl$ led to the complete suppression of methylation (entry 2), we next investigated palladium catalysts, which have been reported for cross-coupling reactions utilizing organo-aluminum reagents.[14−16] Although the reaction of **1a** and $Me_3Al$ with $PdCl_2(PCy_3)_2$ went to completion, the formation of a mixture of **2a** and **3a** was observed (entry 3). In contrast, the use of $Me_2AlCl$ instead of $Me_3Al$ dramatically improved the product selectivity to furnish monomethylated product **2a** predominantly in 85% yield (entry 4). The catalyst prepared *in situ* from $[Pd(C_3H_5)Cl]_2$ (2.5 mol %) and monodentate electron-donating $PCy_3$ (10 mol %) showed similar activity to $PdCl_2(PCy_3)_2$ (entry 5). After the screening of various ligands, we revealed that a series of Buchwald ligands[17] could effectively facilitate the desired methylation reaction (entries 6−12). In particular, DavePhos (2-dicyclohexylphosphino-2′-(*N*,*N*-dimethylamino)biphenyl) was found to be the most efficient to give **2a** in quantitative yield (entry 12). Even at the elevated temperature of 120 °C, this reaction rarely provided **3a** (entry 13). Without any catalysts, no reaction proceeded (entry 14).

The palladium-catalyzed selective monomethylation of dichlorosilanes **1** with $Me_2AlCl$ could be applied to a broader range of substrates in comparison to the original nickel system as summarized in Scheme 2. We performed $^{29}Si\{^1H\}$ NMR spectroscopic analysis of the crude reaction mixture to calculate the NMR yields of **2** and the selectivity in the first methylation step. To determine the isolated yield, all monomethylated chlorosilanes **2** were transformed into the corresponding *p*-methoxybenzyloxysilanes **4**. Among the alkyl-

### Table 1. Optimization of Reaction Conditions for Methylation of 1a[a]



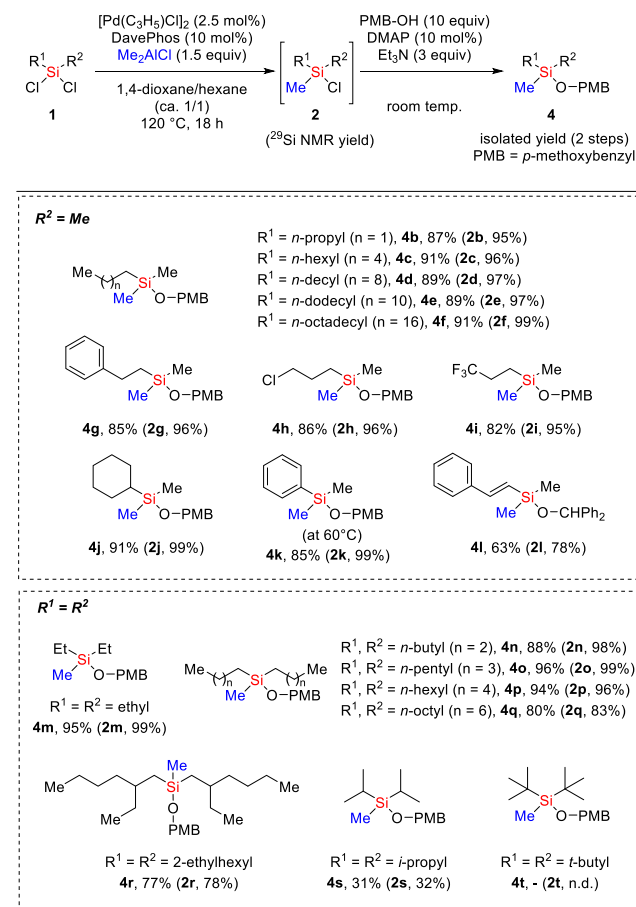| entry | catalyst | ligand | Me-[Al][b] | % conv (1a)[c] | % yield (2a/3a)[c] |
|---|---|---|---|---|---|
| 1 | $NiCl_2(PCy_3)_2$ | none | $Me_3Al$ | 78 | 22/43 |
| 2 | $NiCl_2(PCy_3)_2$ | none | $Me_2AlCl$ | <5 | <5/<5 |
| 3 | $PdCl_2(PCy_3)_2$ | none | $Me_3Al$ | >99 | 50/35 |
| 4 | $PdCl_2(PCy_3)_2$ | none | $Me_2AlCl$ | >99 | 85/n.d. |
| 5 | $[Pd(C_3H_5)Cl]_2$ | $PCy_3$ | $Me_2AlCl$ | >99 | 85/n.d. |
| 6 | $[Pd(C_3H_5)Cl]_2$ | $PPh_3$ | $Me_2AlCl$ | 28 | 28/n.d. |
| 7 | $[Pd(C_3H_5)Cl]_2$ | $PtBu_3$ | $Me_2AlCl$ | <5 | <5/<5 |
| 8 | $[Pd(C_3H_5)Cl]_2$ | dcpe[d] | $Me_2AlCl$ | 59 | 9/32 |
| 9 | $[Pd(C_3H_5)Cl]_2$ | IPr | $Me_2AlCl$ | 35 | 16/5 |
| 10 | $[Pd(C_3H_5)Cl]_2$ | XPhos | $Me_2AlCl$ | >99 | 95/n.d. |
| 11 | $[Pd(C_3H_5)Cl]_2$ | SPhos | $Me_2AlCl$ | 92 | 82/n.d. |
| 12 | $[Pd(C_3H_5)Cl]_2$ | DavePhos | $Me_2AlCl$ | >99 | >99/n.d. |
| 13[e] | $[Pd(C_3H_5)Cl]_2$ | DavePhos | $Me_2AlCl$ | >99 | 85/<5 |
| 14 | none | none | $Me_2AlCl$ | <5 | n.d./n.d. |

[a]Reaction conditions: Catalyst (5 mol %/M), ligand (10 mol %), **1a** (0.5 mmol), methylaluminum reagent (0.75 mmol) in dioxane (0.5 mL), 60 °C, 18 h. [b]Concentration of methylaluminum reagents: $Me_3Al$ (1.4 M in hexane), $Me_2AlCl$ (1.1 M in hexane). [c]Determined by $^{29}Si\{^1H\}$ NMR spectroscopic analysis with trimethyl(phenyl)silane (0.5 mmol) as an internal standard. [d]5 mol %. [e]Performed at 120 °C.

initially confirmed that the reaction of **1a** and 1.5 equiv of $Me_3Al$ with previously reported $NiCl_2(PCy_3)_2$ (5 mol %)[12,13] in 1,4-dioxane at 60 °C for 18 h did not successfully give the target monomethylated product $Me_3SiCl$ (**2a**) with the coproduction of $Me_4Si$ (**3a**) resulting from the undesired dimethylation (entry 1). Since the exchange of $Me_3Al$ for

### Scheme 2. Scope of Monomethylation of Dichlorosilanes 1

methyldichlorosilanes, the reactions of dichloromethylsilanes **1b−f** bearing different *n*-alkyl chains were initially carried out to examine the size influence of the alkyl chains. Regardless of the carbon numbers, methylations of **1b−f** resulted in the exclusive formation of the corresponding monochlorosilanes **2b−f** with 95−99% yields. After alcoholysis workup, dimethyl-monoalkoxysilanes **4b−f** could be isolated in 87−91% yields in two steps. Considering the functional group tolerance, the reactions with dichloromethylsilanes **1g−i** with 2-phenethyl, 3-chloropropyl and 3,3,3-trifluoropropyl groups uniformly proceeded to give the products **2g−i** (95−96% yields) and **4g−i** (82−86% yields). The reaction of dichloromethylsilane **1j** having a cyclohexyl group quantitatively gave **2j** (99% yield) and **4j** (91% yield). We then subjected dichloromethyl-phenylsilane **1k** to the present catalytic system, even though aryl-substituted dichlorosilanes were already identified as suitable substrates in the previous nickel catalysis.[13] At the standard reaction temperature (120 °C), **1k** was converted to **2k** (89% yield) in conjunction with **3k** (11% yield). However, we could completely control the selectivity at a lower reaction temperature (60 °C) to obtain **2k** (99% yield) and **4k** (85% yield), respectively. Since alkenylsilanes are useful synthetic intermediates and readily accessed via the silyl-Heck reaction,[9,12] the reaction of dichlorostyrylmethylsilane **1l** was performed to provide the corresponding product **2l** (78% yield). Since the corresponding *p*-methoxybenzyloxysilane was slightly decomposed during the isolation process, we determined the isolated yield as 63% after transformation to the more stable diphenylmethoxysilane **4l**. We next investigated the scope of dichlorosilanes with two identical alkyl chains. The methylation of **1m−r** with various *n*-alkyl chains and a branched 2-ethylhexyl group gave **2m−r** (78−99% yields) and **4m−r** (77−96% yields). In contrast, the reaction of dichlorosilanes **1s** and **1t** having bulky secondary and tertiary alkyl groups led to poorer reactivity (32% conversion for **1s** and almost no reaction for **1t**) due to the steric hindrance. As shown in Table 2, no substrates gave detectable dimethylated products.

We also demonstrated a gram-scale synthesis starting from dichlorodihexylsilane (**1p**) (40 mmol) to furnish the target monochlorosilane **2p** in 78% isolated yield (7.79 g) after purification by simple distillation (Scheme 3a). A preparation of **2p** was previously reported by a 3-step synthesis starting from **1c**, in 42% overall yield (Scheme 3b).[18]

**Scheme 3. (a) Gram-Scale Synthesis of 2p Utilizing Selective Monomethylation of 1p with Me₂AlCl; (b) Reported Synthesis of 2p in 3 Steps**
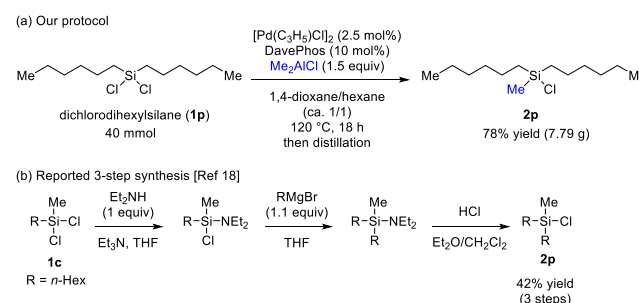


Not limited to the methylation reaction, we were able to conduct the selective introduction of other alkyl chains into **1a** with trialkylaluminum reagents (see Supporting Information (SI)).

To further expand the utility of the Pd-catalyzed selective methylation of chlorosilanes, modification of the reaction conditions for dichlorosilanes was performed in the model reaction using MeSiCl₃ (**5a**) (Table 2). The reaction of **5a** with 1.5 equiv of Me₂AlCl under the same conditions for **1a** led to the formation of **1a** and **2a** in a ratio of 39:61 without the detection of Me₄Si **3a** (entry 1). However, switching the product selectivity between mono- and dimethylation was enabled by changing the amount of Me₂AlCl. Namely, the reaction with 0.8 equiv of Me₂AlCl gave **1a** as a major product in 92% yield (entry 2), while the reaction with 2.5 equiv of Me₂AlCl at an elevated temperature gave **2a** as a major product in 95% yield (entry 3). The byproduct **3a** was not detected even at 120 °C (entry 4).[19] In contrast, the reaction without any catalysts and nickel-catalyzed reaction of **5a** failed (entries 5 and 6).

With the optimized conditions for dimethylation of **5a** in hand, we investigated the scope of substrates (Scheme 4). A variety of alkyltrichlorosilanes **5** with *n*-alkyl groups, primary alkyl groups, halogenated alkyl groups, secondary alkyl groups, and a phenyl group were all tolerated to give the corresponding products **2** (83−99% yields) and **4** (77−94% yields), respectively. The selective introduction of other alkyl chains into **5a** with trialkylaluminum reagents were also demonstrated (see SI).

In the category of chlorosilanes, considerable amounts of tetrachlorosilane (**6**) are inexpensively produced as a byproduct of the polysilicon industry or from the chlorination of ferrosilicon with chlorine.[20] Therefore, **6** is obviously the most basic and attractive starting material to synthesize various organosilicon compounds. However, to the best of our knowledge, there have been no satisfactory examples for catalytic conversion of **6** into organosilicon compounds. The present palladium catalyst could be applied to **6** to achieve selective triple methylation, furnishing **2a** in 92% NMR yield (Scheme 5a). In contrast, the nickel-catalyzed reaction of **6** led to the formation of **5a** and **3a** with poor selectivity (Scheme 5b).

A possible reaction mechanism for the palladium-catalyzed cross-coupling of chlorosilanes and methylaluminum species is shown in Scheme 6. The initial step is the generation of the
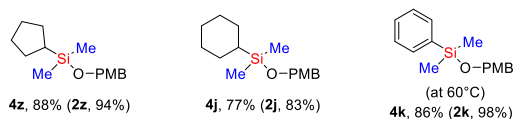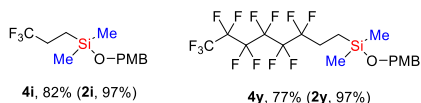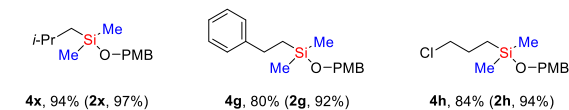
**Table 2. Optimization of Reaction Conditions for Methylation of 5a**[a]



| entry | *x* (equiv) | *T* (°C) | % conv (5a)[b] | % yield (1a/2a/3a)[b] |
|---|---|---|---|---|
| 1 | 1.5 | 60 | >99 | 39/61/n.d. |
| 2 | 0.8 | 60 | >99 | 92/8/n.d. |
| 3 | 2.5 | 90 | >99 | n.d./95/n.d. |
| 4 | 2.5 | 120 | >99 | n.d./86/n.d. |
| 5[c] | 2.5 | 90 | <5 | n.d./n.d./n.d. |
| 6[d] | 2.5 (Me₃Al) | 90 | 41 | n.d./6/32 |

[a]Reaction conditions: [Pd(C₃H₅)Cl]₂ (2.5 mol %), DavePhos (10 mol %), **5a** (0.5 mmol), Me₂AlCl in dioxane, 18 h. [b]Determined by ²⁹Si{¹H} NMR spectroscopic analysis with trimethyl(phenyl)silane (0.5 mmol) as an internal standard. [c]Without catalyst. [d]NiCl₂(PCy₃)₂ was used as catalyst.

## Scheme 4. Scope of Double Methylation of Trichlorosilanes 5



(²⁹Si NMR yield)

isolated yield (2 steps)
R' = Ph₂CH or PMB

R = ethyl
**4u**, 92% (**2u**, 98%)

R = n-propyl (n = 1), **4b**, 81% (**2b**, 95%)
R = n-octyl (n = 6), **4v**, 91% (**2v**, 99%)
R = n-decyl (n = 8), **4d**, 92% (**2d**, 96%)
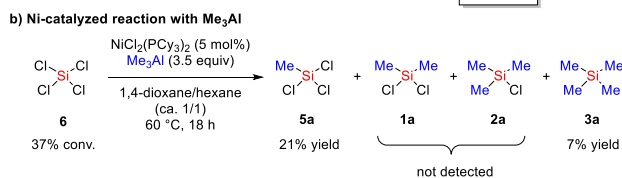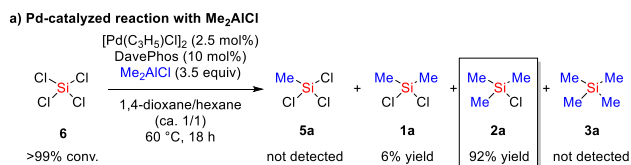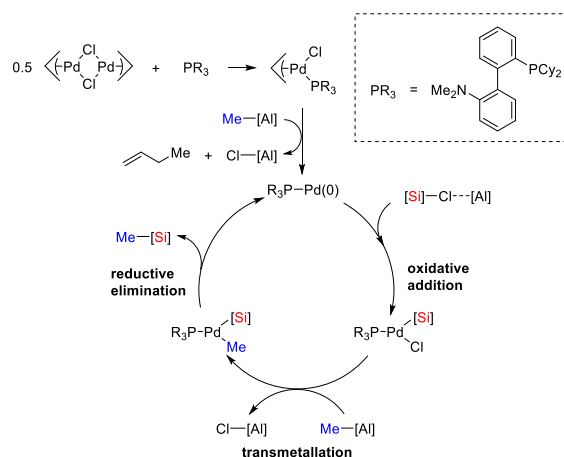R = n-dodecyl (n = 10), **4e**, 89% (**2e**, 93%)
R = n-hexadecyl (n = 14), **4w**, 93% (**2w**, 98%)
R = n-octadecyl (n = 16), **4f**, 90% (**2f**, 96%)

**4x**, 94% (**2x**, 97%)    **4g**, 80% (**2g**, 92%)    **4h**, 84% (**2h**, 94%)

**4i**, 82% (**2i**, 97%)    **4y**, 77% (**2y**, 97%)

**4z**, 88% (**2z**, 94%)    **4j**, 77% (**2j**, 83%)    (at 60°C) **4k**, 86% (**2k**, 98%)
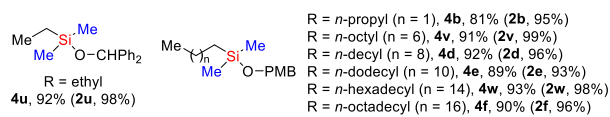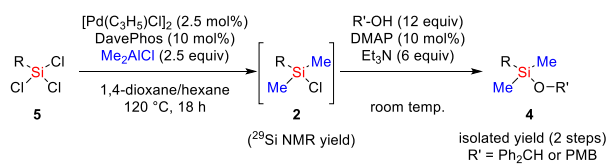
## Scheme 5. Selective Triple Methylation of Tetrachlorosilane 6



a) Pd-catalyzed reaction with Me₂AlCl

**6** >99% conv.    **5a** not detected + **1a** 6% yield + **2a** 92% yield + **3a** not detected

b) Ni-catalyzed reaction with Me₃Al

**6** 37% conv.    **5a** 21% yield + **1a** **2a** not detected + **3a** 7% yield

## Scheme 6. Plausible Catalytic Cycle



Pd(π-allyl)(Davephos)Cl complex from the reaction of [Pd(C₃H₅)Cl]₂ and DavePhos. Upon activation by methyl-aluminum species, the resultant Pd(0) species is formed to initiate the catalytic cycle.[17b] The oxidative addition of

chlorosilanes, the subsequent transmetalation with methyl-aluminum species, and the reductive elimination should occur to afford methylsilanes and the regeneration of "Pd(0)" species. As in the previous nickel catalysis,[12,13] we suppose that the oxidative addition of the Si–Cl bond to Pd(0) species could proceed via the $S_N2$-type pathway with the aid of the Lewis acidic aluminum reagents.[10] Presumably, the reason for the high selectivity in the production of the monochlorosilanes is that the lower Lewis acidity of the silicon center[21] could suppress the oxidative addition through the occurrence of the $S_N2$-type reaction.

In summary, selective introduction of methyl groups into chlorosilanes has been demonstrated via palladium-catalyzed cross-coupling reactions with methylaluminum reagents. In contrast to the previous nickel systems, a much broader scope of di-, tri-, and tetrachlorosilanes was tolerated to give the corresponding methylmonochlorosilanes with excellent selectivity. Since the characteristics between nickel and palladium catalysis were clearly differentiated in the present research, studies to clarify and organize the appropriate catalyst systems to access a wide range of the corresponding organosilicon compounds via cross-coupling reactions of chlorosilanes with various coupling partners are currently in progress.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c04175.

Detailed experimental procedures, characterization data, and copies of $^1H$, $^{13}C$ NMR spectra (PDF)

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### Notes

The authors declare no competing financial interest.

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