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# Solvent-induced selectivity switching: intermolecular allylsilylation, arylsilylation, and silylation of alkynes over montmorillonite catalyst

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ABSTRACT

Proton-exchanged montmorillonite showed catalytic activity for intermolecular allylsilylation, arylsilylation, and terminal silylation of alkynes with allylsilanes. The reaction selectivity greatly depended on the solvent used. Reactions proceeded with various terminal alkynes and allylsilanes in good to moderate yields. The reaction pathways involving cationic Si species on the montmorillonite surface were also investigated.

## Introduction

Carbosilylation of alkynes is a method to create both C–C and C–Si bonds on the triple bonds of alkynes to give substituted vinyl silanes, which are useful intermediates for organic transformations.[1] Among the carbosilylation reactions of alkynes, allyl- and arylsilylations are known reactions which are catalyzed by several homogeneous Lewis acids.[2–4] For example, $AlCl_3$, $EtAlCl_2$, and $HfCl_4$ have been reported as catalysts for the intermolecular allylsilylation of alkynes.[2] $HfCl_4$ and $EtAlCl_2$ have also been found to be a catalyst for intramolecular arylsilylation.[4a] In almost all cases, these Lewis acids activate the carbon–carbon triple bond for nucleophilic addition of allyl and aryl groups.

Recently, our group has reported allylsilylation of alkenes using proton-exchanged montmorillonite ($H^+$-montmorillonite) as a heterogeneous catalyst.[5] The allylsilylation of alkenes is initiated by the formation of a cationic silyl species on the montmorillonite surface ($[Si]^+$-montmorillonite) from a protonic acid site and allylsilane.[5,6] If the $[Si]^+$-montmorillonite can react not only with alkenes but also alkynes to give β-silyl cations, catalytic allylsilylation of alkynes should be possible, as shown in Scheme 1. Herein, allylsilylation of alkynes with allylsilanes was examined using $H^+$-montmorillonite (Scheme 2A). In addition, during the course of our study on allylsilylations, we found that arylsilylation and silylation proceeded selectively in the presence of solvents having relatively high nucleophilicity (Scheme 2B and C). In this Letter, we describe (i) novel methodologies to introduce allyl, aryl, and silyl groups to alkynes and (ii) the effect of solvents on the reaction pathways.

## Results and discussion

### Reactions of alkyne with allylsilane in various solvents

To investigate the effect of solvent on the product selectivity of the reaction between alkynes and allylsilane, the reaction of phenylacetylene (**1a**) with allyltrimethylsilane (**2a**) in various solvents was examined using $H^+$-montmorillonite, as shown in Table 1. *trans*-Allylsilylation of **1a** selectively proceeded to afford the product **3aa** in non-polar solvents, such as *n*-heptane and toluene (entries 1–3). In the case of aromatic solvents with relatively high nucleophilicity due to the presence of electron-donating functions, such as mesitylene and anisole, both the silyl group and the aromatic solvent were introduced to the carbon–carbon triple bond of **1a** (entries 4–6). For example, the reaction of **1a** with mesitylene and **2a** afforded the corresponding *trans*-arylsilylation product (**4aa**) in 66% yield (entry 5). In the presence of solvents with ether functions, terminal silylation of **1a** proceeded selectively, giving the product **5aa** (entries 7 and 8). In the case of other solvents having high polarity, such as DMF and DMSO, the reactions hardly occurred.

### Allylsilylation of alkynes

The allylsilylation of alkynes with allylsilanes in toluene solvent is summarized in Table 2.[7] The reaction of crotyltrimethylsilane (**2c**:

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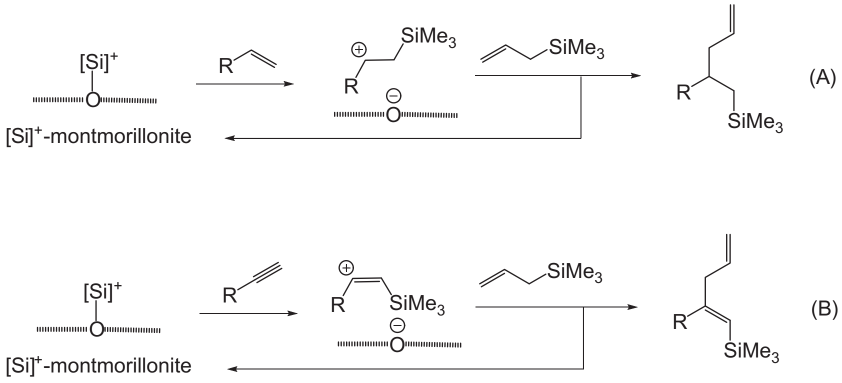
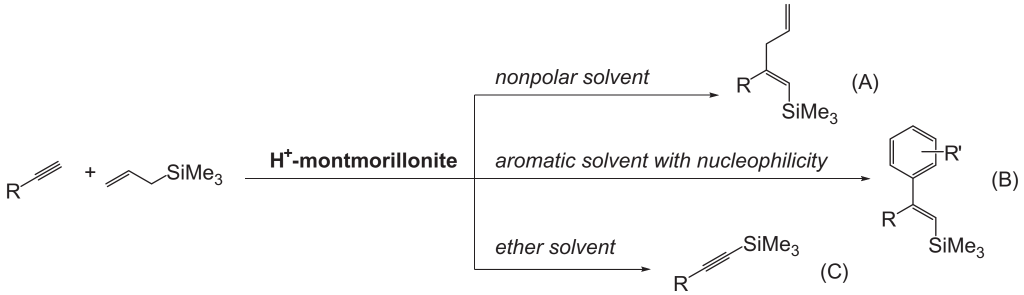


**Scheme 1.** Allylsilylations of (A) alkenes and (B) alkynes catalyzed by [Si]$^+$-montmorillonite.



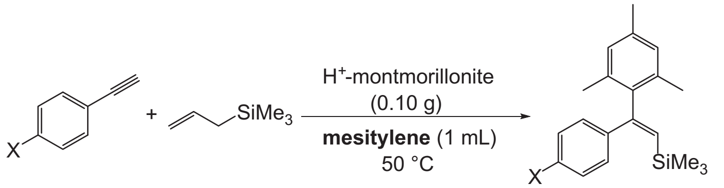
**Scheme 2.** Solvent-induced selectivity switching.

$R^2$ = Me, $R^3$ = H, $R^4$ = Me) afforded (*Z*)-trimethyl(3-methyl-2-phenylpenta-1,4-dienyl)silane (**3ac**) in 51% yield (entry 6). This result suggests that the reaction proceeded through acidic activation of the alkyne and nucleophilic addition of the allylsilane. As shown in Scheme 1, it can be expected that the [Si]$^+$-montmorillonite, which is formed from H$^+$-montmorillonite and allylsilane, reacts with alkynes. To confirm the direct activation of the alkyne by the cationic silyl species on montmorillonite, the reaction mixture of **1a** with **2a** was quenched with $H_2O$ (Scheme 3). If H$^+$ or another metal species such as Al$^{3+}$ initially activates the alkyne, diene compound **6** should be obtained via hydration of the intermediate (Scheme 3, dotted arrows).[2b] However, the formation of **6** was not detected. This result indicates direct activation of the cationic Si species on the montmorillonite surface. It can be expected that the activation of alkynes by a silyl cation induces the formation of β-silyl alkenyl cation **7**.[8] A proposed allylsilylation pathway involving **7** is shown in Scheme 4(A). Because an electron-withdrawing group on the *para*-position of phenylacetylene enhanced the reactivity (entries 1–3), increasing the electrophilicity of the β-silyl cationic intermediate **7**[8] is necessary to promote the reaction effectively.

## Arylsilylation of alkynes

The reaction of **1a** with **2a** in mesitylene solvent was examined using various protonic acids, as shown in Table 3. Only protonic montmorillonites showed catalytic activity for the arylsilylation (entries 1 and 2). Other typical protonic acids, such as Nafion and $H_2SO_4$, did not show any catalytic activity for allylsilylation, arylsilylation, or silylation (entries 3–5). Because the reaction did not proceed at all with Na$^+$-montmorillonite (entry 6), the H$^+$ site on the montmorillonite surface must be necessary for the arylsilylation.

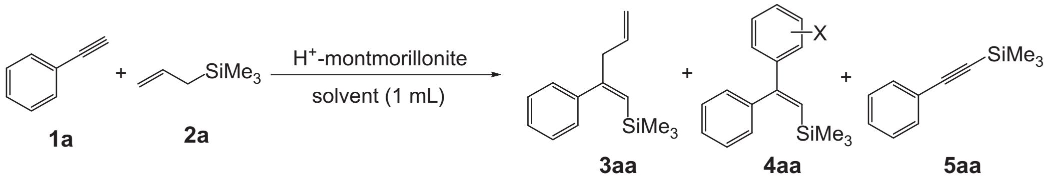
As shown in Eq. 1, the *para*-substitution effect on the arylsilylation was similar to that on the allylsilylation. The complete *trans*-selectivity of the Si and mesityl groups in the arylsilylation product indicates stepwise addition of the silyl and aryl groups to the triple bond. These results suggest that the reaction also proceeded through the β-silyl cation intermediate **7** as in the allylsilylation (Scheme 4). The proposed pathway for the arylsilylation is shown in Scheme 4(B). The reaction ceased completely by the addition of 2,6-di-*tert*-butyl pyridine. This result supports the formation of H$^+$ in the catalytic cycle.[9]

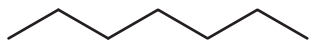
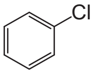
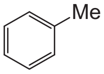
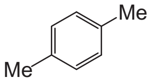
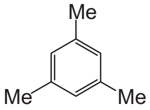
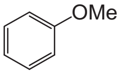
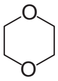
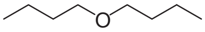


(1)

X=Cl: 79% yield (1.5 h)
X=H: 69% yield (8 h)
X=Me: 31% yield (32 h)

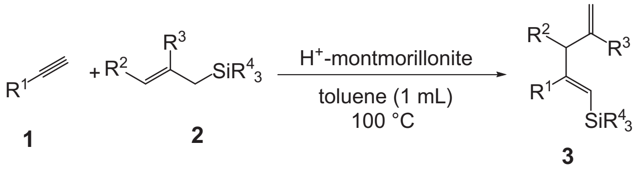
**Table 1**
Reactions between phenylacetylene (**1a**) and allylsilane (**2a**) using H$^+$-montmorillonite in various solvents[a]



| Entry | Solvent | Time (min) | Conv. of **1a** (%)[b] | Yield (%)[b] | | |
|---|---|---|---|---|---|---|
| | | | | **3aa** | **4aa** | **5aa** |
| 1 |  | 240 | 39 | 12 | – | 4 |
| 2 |  | 300 | 73 | 57 | <1 | 13 |
| 3 |  | 180 | >99 | 62 | <1 | 10 |
| 4 |  | 300 | >99 | 52 | 12 | 16 |
| 5 |  | 90 | >99 | 9 | 66 | 9 |
| 6 |  | 60 | >99 | 8 | 55[c] | 1 |
| 7 |  | 150 | 91 | <1 | – | 76 |
| 8 |  | 180 | 87 | <1 | – | 58 |

[a] Reaction conditions: **1a** (1.0 mmol), **2a** (3.0 mmol), H$^+$-montmorillonite (0.10 g), solvent (1 mL), 100 °C.
[b] Determined by GC and $^1$H NMR analysis using an internal standard. Based on **1a** used.
[c] (*o*/*p* = 23/77). In the reaction using aromatic solvent, the formation of small amount of hydroarylation product was detected.

**Table 2**
Allylsilylation of alkynes (**1**) with allylsilanes (**2**)[a]



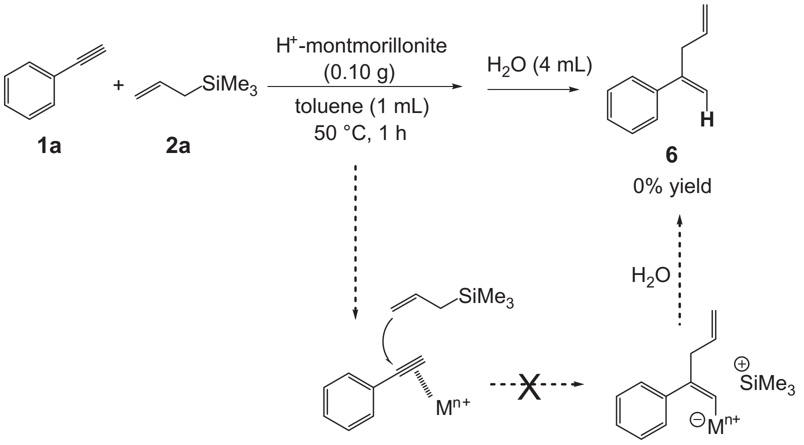
| Entry | R$^1$ | R$^2$ | R$^3$ | R$^4$ | Time (h) | Yield (%)[b] | Selectivity (%)[b] |
|---|---|---|---|---|---|---|---|
| 1 | *p*-Cl-Ph (**1b**) | H | H | Me (**2a**) | 0.5 | 66 (64[c]) | 67 |
| 2 | Ph (**1a**) | H | H | Me (**2a**) | 3 | 62 | 62 |
| 3 | *p*-Me-Ph (**1c**) | H | H | Me (**2a**) | 12 | 26 | 30 |
| 4 | *n*-$C_6H_{13}$ (**1d**) | H | H | Me (**2a**) | 0.5 | 30 | 30 |
| 5 | Ph (**1a**) | H | Me | Me (**2b**) | 1.5 | 72 (61[c]) | 74 |
| 6 | Ph (**1a**) | Me | H | Me (**2c**) | 4 | 51 | 53 |
| 7 | Ph (**1a**) | H | H | Et (**2d**) | 4 | 34 | 35 |

[a] Reaction conditions: **1** (1.0 mmol), **2** (3.0 mmol), H$^+$-montmorillonite (0.10 g), toluene (1 mL), 100 °C.
[b] Determined by GC and $^1$H NMR analysis using an internal standard. Based on **1** used.
[c] Isolated yield.

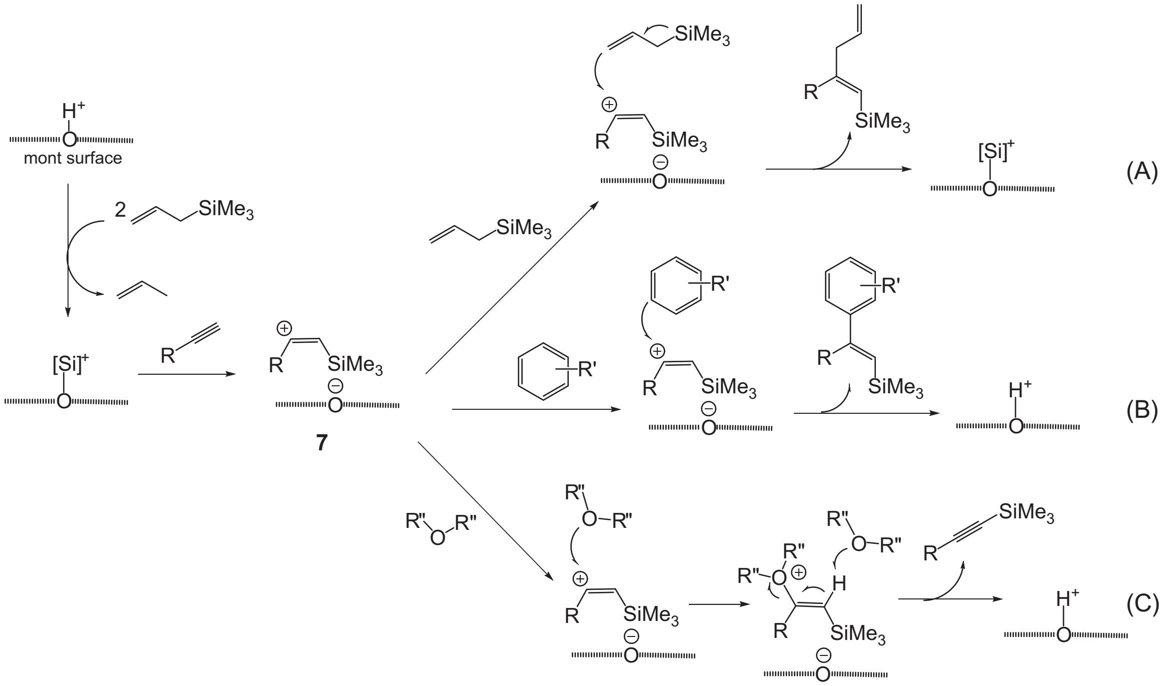
## Terminal silylation of alkynes

It is known that the terminal silylation of alkynes is catalyzed by bases, which abstract the terminal proton of the alkyne.[10] As shown in Table 1, terminal silylation of **1a** proceeded selectively in ether solvents.[11] Even though the oxygen atom of ethers acts as a weak Lewis base, the reaction did not proceed in the absence of the H$^+$-montmorillonite. From these facts, both the ether solvent and montmorillonite acted as catalysts. A proposed reaction pathway of the terminal silylation is shown in Scheme 4(C). The cationic intermediate **7** may react easily with Lewis basic ethers to form the silylated product and H$^+$.

The generality of alkynes for the terminal silylation was investigated by using 1,4-dioxane solvent and H$^+$-montmorillonite as a catalyst, as shown in Table 4. Good to moderate yields were obtained in the case of both aromatic and aliphatic terminal alkynes.



**Scheme 3.** Quench experiment.



**Scheme 4.** Proposed reaction pathways using (A) nonpolar solvent, (B) aromatic solvent with relatively high nucleophilicity, and (C) ether solvent.

In the terminal silylation, phenylacetylene having electron-donating group (entry 3) showed higher reactivity than that of the electron-withdrawing group (entry 1). On the other hand, substrates having electron-withdrawing group showed high reactivity in allyl- and arylsilyaltion (Table 2 and Eq. 1). It can be expected that the electron-donating effect of the substituent enhances adsorption of the alkyne on the cationic Si species even in the presence of ether solvent which may also adsorb on the active cationic site.

## Summary

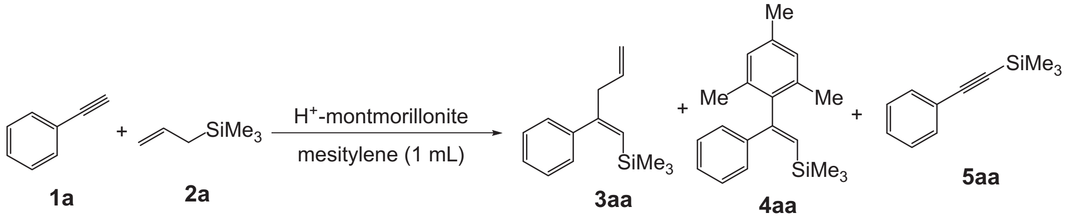
Solvent-induced selectivity switching of montmorillonite-catalyzed allylsilylation, arylsilylation, and silylation of alkynes was discovered. These three reaction pathways included the same β-silyl cation as an intermediate, which was generated by the reaction between the cationic silyl species on the montmorillonite surface and the alkyne. The reaction selectivity changed depending on the reactivity between the intermediate and the solvent used.

## Experimental section

Proton nuclear magnetic resonance ($^1$H NMR) and carbon nuclear magnetic resonance ($^{13}$C NMR) spectra were recorded in $CDCl_3$ with a JNM-AL300 spectrometer operating at 300 and 75 MHz, respectively. Analytical GLC was measured using a Shimadzu GC-8A equipped with a Silicon SE-30 column and a flame ionization detector. A Shimadzu QP5000 GC-MS equipped with DB-1 column was used. The products were confirmed by comparison with the reported NMR and MS data. To determine yields and conversions, *n*-propylbenzene and *p*-xylene were used as internal standards for GC and $^1$H NMR analysis.

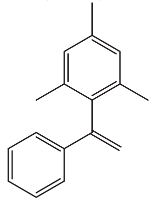
$Na^+$-montmorillonite [$Na_{0.66}(OH)_4Si_8(Al_{3.34}Mg_{0.66}Fe_{0.19})O_{20}$; Kunipia F] was obtained from Kunimine Industry. Proton-exchanged montmorillonite was prepared from $Na^+$-montmorillonite using the reported ion exchange procedure with aqueous hydrogen chloride.[12] The prepared $H^+$-montmorillonite was stored under 30% humidity. $H^+$-montmorillinite was dried under vacuum (ca.

**Table 3**
Reactions between phenylacetylene (**1a**) and allylsilane (**2a**) in the presence of mesitylene using various acids[a]



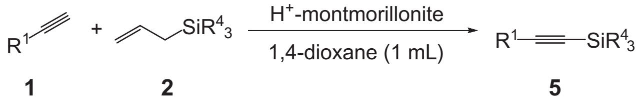
| Entry | Acid | Conv. of **1a** (%)[b] | Yield (%)[b] | | |
|---|---|---|---|---|---|
| | | | **3aa** | **4aa** | **5aa** |
| 1[c] | H$^+$-montmorillonite | 98 | 4 | 69 | 3 |
| 2 | Mont K10 | 79 | <1 | 35 | <1 |
| 3 | Amberlyst | 26 | <1 | <1 | <1 |
| 4 | Nafion | 16 | <1 | <1 | <1 |
| 5 | $H_2SO_4$ | 9 | <1 | <1 | <1 |
| 6 | Na$^+$-montmorillonite | 15 | <1 | <1 | <1 |
| 7 | None | 8 | <1 | <1 | <1 |

[a] Reaction conditions: **1a** (1.0 mmol), **2a** (3.0 mmol), H$^+$-montmorillonite (0.10 g), mesitylene (1 mL), 50 °C, 8 h.
[b] Determined by GC and $^1$H NMR analysis using an internal standard. Based on **1a** used.
[c] 5% Yield of 1,3,5-trimethyl-2-(1-phenylvinyl)-benzene (**8**) was obtained via hydroarylation of **1a** with mesitylene.



**8**

**Table 4**
Terminal silylation of alkynes (**1**) with allylsilanes (**2**)[a]



| Entry | R$^1$ | R$^4$ | Time (h) | Yield of **5** (%)[b] | Selectivity of **5** (%)[b] |
|---|---|---|---|---|---|
| 1 | *p*-Cl-Ph (**1b**) | Me (**2a**) | 3 | 65 | 93 |
| 2 | Ph (**1a**) | Me (**2a**) | 2.5 | 76 | 84 |
| 3 | *p*-Me-Ph (**1c**) | Me (**2a**) | 5 | 87 (78[c]) | 91 |
| 4 | $PhCH_2$ (**1e**) | Me (**2a**) | 3 | 40 | 99 |
| 5 | *n*-$C_6H_{13}$ (**1d**) | Me (**2a**) | 3 | 62 | 71 |
| 6 | Ph (**1a**) | Et (**2d**) | 9 | 82 (77[c]) | 92 |

[a] Reaction conditions: **1** (1.0 mmol), **2** (3.0 mmol), H$^+$-montmorillonite (0.10 g), 1,4-dioxane (1 mL), 100 °C.
[b] Determined by GC and $^1$H NMR analysis using an internal standard. Based on **1** used.
[c] Isolated yield.

1 mmHg) at 120 °C for 1 h before the catalytic reaction. Amberlyst was purchased from Organo Co. as Amberlyst® 15DRY. Nafion was purchased from Aldrich Inc. as Nafion® NR50. Unless otherwise noted, all other materials were purchased from Wako Pure Chemicals, Tokyo Kasei Co., Kanto Kagaku Co., and Aldrich Inc.

## Allylsilylation of alkynes

The typical procedure for allylsilylation of phenylacetylene (**1a**) with allyltrimethylsilane (**2a**) is as follows. Into a glass reactor were placed the H$^+$-montmorillonite (0.10 g), toluene (1.0 mL), **1a** (1.0 mmol), and **2a** (3.0 mmol) under a dry Ar atmosphere using Schlenk techniques. The resulting mixture was vigorously stirred at 100 °C. After 180 min, the catalyst was separated by filtration. GC analysis of the filtrate showed a 62% yield of (*Z*)-trimethyl (2-phenylpenta-1,4-dien-1-yl)silane (**3aa**). The filtrate was evaporated and the crude product was purified by column chromatography using silica (*n*-hexane as eluant) to afford a pure product. The product was identified by comparison with the reported $^1$H and $^{13}$C NMR and mass spectral data.

## Arylsilylation of alkynes

The typical procedure for arylsilylation of phenylacetylene (**1a**) with allyltrimethylsilane (**2a**) and mesitylene is as follows. Into a glass reactor were placed the H$^+$-montmorillonite (0.10 g), mesitylene (1.0 mL), **1a** (1.0 mmol), and **2a** (3.0 mmol) under a dry Ar atmosphere using Schlenk techniques. The resulting mixture was vigorously stirred at 50 °C. After 8 h, the catalyst was separated by filtration. GC analysis of the filtrate showed a 69% yield of (*E*)-(2-mesityl-2-phenylvinyl)trimethylsilane (**4aa**). The filtrate was evaporated and the crude product was purified by column chromatography using silica (*n*-hexane as eluant) to afford a pure product: $^1$H NMR (400 MHz, $CDCl_3$): 0.03 (s, 9H), 2.15 (s, 6H), 2.27 (s, 3H), 5.65 (s, 1H), 6.84 (s, 2H), 7.22 (m, 5H); $^{13}C\{^1H\}$ NMR (100.61 MHz. $CDCl_3$): 0.39, 20.5, 21.0, 127.4, 127.7, 128.2, 128.5, 133.1, 134.9, 136.0, 142.2, 142.8, 156.7; MS (EI) *m/z* (%): 59, 73(100), 135, 177, 207, 220, 279, 294($M^+$). The *trans* relationship of the mesityl and silyl groups was confirmed by H–H NOESY.

## Terminal silylation of alkynes

The typical procedure for terminal silylation of phenylacetylene (**1a**) with allyltrimethylsilane (**2a**) is as follows. Into a glass reactor were placed the $H^+$-montmorillonite (0.10 g), 1,4-dioxane (1.0 mL), **1a** (1.0 mmol), and **2a** (3.0 mmol) under a dry Ar atmosphere using Schlenk techniques. The resulting mixture was vigorously stirred at 100 °C. After 150 min, the catalyst was separated by filtration. GC analysis of the filtrate showed a 76% yield of trimethyl(phenylethynyl)silane (**5aa**). The product was identified by comparison with the reported $^1H$ and $^{13}C$ NMR and mass spectral data.[13]

## Acknowledgments

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