Bull. Chem. Soc. Jpn., *73*, 985—990 (2000)

Homo-Coupling Reactions of Alkenyl- and Arylfluorosilanes Mediated by a Copper(I) Salt

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(Received October 25, 1999)

Homo-coupling reactions of an alkenyl- or arylsilane readily occur with a copper(I) salt in an aprotic polar solvent such as *N*, *N*-dimethylformamide or dimethyl sulfoxide under an aerobic condition to give the corresponding conjugated dienes or biaryls, respectively. Optimization of a copper salt and a solvent for the homo-coupling reaction is discussed. The formation of the organocopper intermediates is evidenced by trapping experiments with iodine and by a conjugate addition to methyl vinyl ketone.

A large number of organometallic reagents have been employed for the oxidative homo-coupling reaction between sp^2-carbon centers. Indeed, several transition metal-mediated or catalyzed homo-coupling reactions with reagents of arylboronic acids[1] and arylstannanes[2] have been documented. On the other hand, the homo-coupling reaction of organosilanes is less familiar, even though various cross-coupling reactions of organosilanes with organic halides have been synthetically utilized.[3]

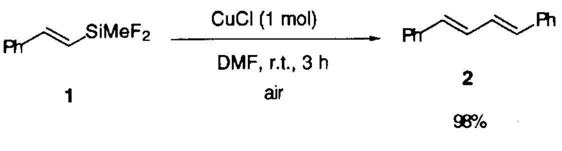
Cleavage of a carbon–silicon bond by a transition metal has been reported: A copper(II) halide CuX_2 (X = Cl, Br) has been reported to activate a carbon–silicon bond through a hexacoordinate organopentafluorosilicate to form the corresponding organic halides.[4] And, it has been documented that, in the presence of a stoichiometric amount of CuCl, homo-coupling reactions of alkenyl- and phenylhexacoordinate silicates of solid state at 200 to 300 °C afforded the symmetrical conjugated dienes and biphenyl, respectively.[5] The use of hexacoordinate organopentafluorosilicates is necessary to accomplish transmetalation from silicon to copper. Homo-coupling reactions of organosilanes with a copper(I) salt have recently appeared. However, it seems that a fluoride ion is necessary to induce the homo-coupling reaction via penta- or hexacoordinate silicate intermediates.[6] Accordingly, our research interest has centered on the possibility of homo-coupling reactions of aryl- and alkenylsilanes under mild conditions.

Herein, we report a convenient and efficient homo-coupling reactions of alkenyl- and arylsilanes and copper(I) salts in aprotic polar solvent *N*,*N*-dimethylformamide (DMF) or dimethyl sulfoxide (DMSO) under an aerobic condition. Mechanistic studies on an intermediate organocopper species derived from an organosilane and a copper salt is demonstrated by its iodination and conjugate addition to an α, β-unsaturated ketone.[7]

Results and Discussion

The conjugated dienes[8] are the major constituents of various biologically active compounds and materials having versatile physical properties. The preparation of conjugated dienes has been carried out using boron,[9] lithium/copper,[10] magnesium,[11] silver,[12] nickel,[13] and mercury/palladium.[14] For the homo-coupling reaction with alkenylsilanes, a readily available, inexpensive metal with a mild oxidant would be effective. The palladium-catalyzed homo-coupling reaction of alkenylsilanes has been reported to synthesize conjugated polyenes using $CuCl_2$ as an oxidant of a palladium catalyst.[15] With a need for general synthesis of conjugated dienes, we began to focus on optimizing the various conditions of copper-mediated homo-coupling reaction of difluoro(methyl)-[(*E*)-2-phenylethenyl]silane (**1**).

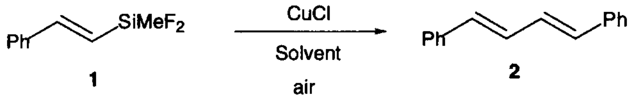
We first examined a reaction of difluoro(methyl)[(*E*)-2-phenylethenyl]silane (**1**) with a stoichiometric amount CuCl in dry DMF and KF as an activator at room temperature under an aerobic condition, and isolated a homo-coupled product, 1,4-diphenyl-1,3-butadiene (**2**), in 92% yield based on **1**. During this study, we found that the homo-coupling reaction did not require a fluoride ion activator for the organosilicon compound and that CuCl alone was effective enough for the formation of **2** in 98% yield (Eq. 1). This direct coupling of organosilanes without an additive activator such as a fluoride ion under such a simple system (with a Cu(I) salt, in DMF, in air) would be practical and attractive.[16]



(1)

We then studied the reaction of **1** with CuCl in a variety of solvent. Yields of the homo-coupled product **2** greatly depend on the nature of the solvent as summarized in Table 1.

Table 1. Reaction of Alkenylsilane **1** with CuCl in Various Solvents$^{a)}$



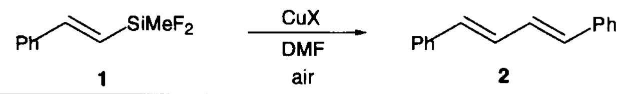
Entry	Solvent	Time (h)	Yield (%)$^{b)}$
1	DMF	3	98 (71)$^{c)}$
2	DMSO	6	99
3	DMA	0.25	82
4	THF/DMF (1 : 1)	6	81
5	NEt_3	1	79
6	THF/HMPA (1 : 1)	6	67
7	MeCN	24	41
8	EtOH	12	0
9	THF	12	0
10	Et_2O	12	0

a) A mixture of **1** (0.2 mmol) and CuCl (0.2 mmol) in a solvent (0.5 mL) was stirred at room temperature. b) GC yield based on **1** used. c) Isolated yield based on **1** used.

We found that aprotic polar solvents such as DMF, DMSO, *N*,*N*-dimethylacetamide (DMA), triethylamine, and acetonitrile were excellent to promote the reaction (Entries 1—3, 5, and 7). In particular, when DMF or DMSO was employed, the yield of **2** was quite high. The use of THF with DMF, or hexamethyphosphoric triamide (HMPA) also effected the reaction but with low yields (Entries 4 and 6). In a sharp contrast, no trace of the desired product was obtained in a protic or less polar solvent such as EtOH, THF or diethyl ether (Entries 8—10). Thus, the use of a polar solvent is essential to promote the reaction. We consider that the polar solvent would coordinate to an organosilicon reagent to form the pentacoordinate, but tetravalent species (vide infra), which may behave as a penta-valent organosilicate that is formed by the addition of a fluoride ion to the organosilane and is known to be highly active to transmetalation.

The results using various copper salts are listed in Table 2. Counter ions and the oxidation state of a copper salt dramatically affected the yield of **2**. CuCl and CuOTf efficiently accelerated the homo-coupling reaction (Entries 1—3). Although Cu_2O required heating at 60 °C, it furnished **2** in 81% yield after 24 h (Entry 4). Copper(I) cyanide[17] was also effective for the formation of **2**, albeit a longer reaction time (72 h) was required for the completion (Entry 5). Unlike CuCl or CuOTf, CuBr and CuI[18] that were reportedly effective for the coupling reactions using organotin reagents were less efficient for the present reaction (Entries 6 and 7). On the contrary, a copper(II) salt $CuCl_2$[19] was found to be inactive (Entry 8). In all of the following experiments, CuCl was employed because of easy handling in air compared with the triflate.

Table 2. Reaction of Alkenylsilane **1** with Copper Salts in DMF$^{a)}$

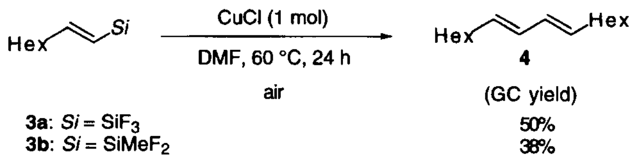


Entry	Copper salt	Temp (°C)	Time (h)	Yield (%)$^{b)}$
1	CuCl	R.T.	3	98
2	CuCl (10 mol%)		72	83
3	CuOTf		1	>99
4	Cu_2O	60	24	81
5	CuCN		72	75
6	CuI		72	36
7	CuBr		72	15
8	$CuCl_2$		72	0

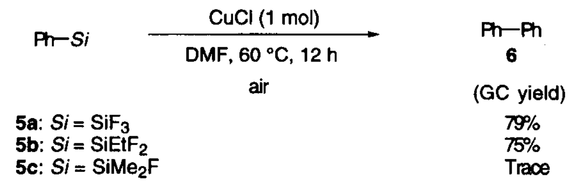
a) A mixture of **1** (0.2 mmol) and a copper salt (0.2 mmol) in DMF (0.5 mL). b) GC yield based on **1** used.

We carried out the homo-coupling reaction using alkenylsilanes **3a** and **3b** as substrates using CuCl in DMF upon exposure to an atmospheric air. The results are summarized in Eq. 2. The number of fluorine atoms on silicon remarkably affected the reactivity of the organosilicon compounds. For example, the GC yield of **4** from trifluoro[(*E*)-1-octenyl]silane (**3a**) (50%) was better than that from difluoro(methyl)[(*E*)-1-octenyl]silane (**3b**) (38%). The isomeric purities of (*E*,*E*)-1,3-butadienes were higher than 99% when *E*-alkenylsilanes were used, as confirmed by coupling constants of ^{1}H NMR spectra.[20] It is well documented that the transmetalation from an alkaline metal to copper, followed by successive oxidative dimerization, takes place with complete retention of configuration.[21] The dimerization of an organocopper is suggested to proceed through a bimolecular or a concerted mechanism,[22] or alternatively by a radical mechanism.

On the other hand, symmetrical biaryls are also attractive molecules constructed by the sp^2-carbon centers and have been generally obtained by the Ullmann reaction[23] or by a Ni(0)[24] or Pd(0)[25]-catalyzed homo-coupling reaction of aryl halides. Recently, Pd-catalyzed homo-coupling reactions of arylsilanes are reported, but excess amounts of KF activator were required.[26] We then examined biaryl synthesis: Treatment of various phenylsilanes **5a**—**c** with an equimolar amount of CuCl gave biphenyl **6**, as shown in Eq. 3. Since phenylcopper species readily decompose giving biphenyl and copper metal,[27] the biphenyl formation from fluoro(phenyl)silane **5a** or **5b** is also ascribed to the transmetalation from silicon to copper to produce a phenylcopper intermediate. Comparison of the yield of **5b** by GC (75%) with that of **5c** (trace) indicates that at least two fluorine atoms on silicon are necessary to effect the reaction.



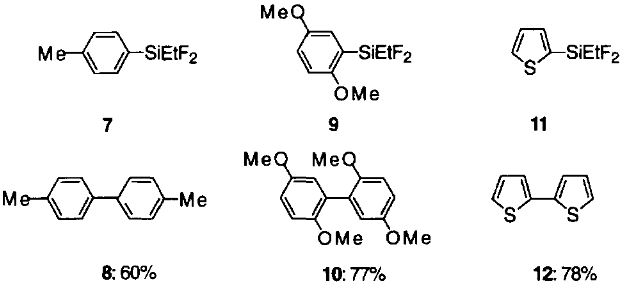
(2)



(3)

Because ethyldifluorosilane (**5b**) gave **6** in a yield comparable to trifluorosilane (**5a**), we thus investigated the homo-coupling reaction of variously substituted aryl(ethyl)difluorosilanes, as summarized in Eq. 4. Ethyldifluoro(4-methylphenyl)silane (**7**) and 2,5-dimethoxyphenylsilane (**9**) coupled smoothly to afford substituted biaryls **8** and **10** in 60 and 77% yields, respectively. A heterocycle such as 2-thienylsilane **11** also gave 2,2′-bithiophene (**12**) in 78% yield.

$$\underset{\mathbf{7,\,9,\,11}}{\text{Ar–SiEtF}_2} \xrightarrow[\text{DMF, 60 °C}\atop\text{air}]{\text{CuCl (1 mol)}} \underset{\mathbf{8,\,10,\,12}}{\text{Ar–Ar}} \qquad (4)$$



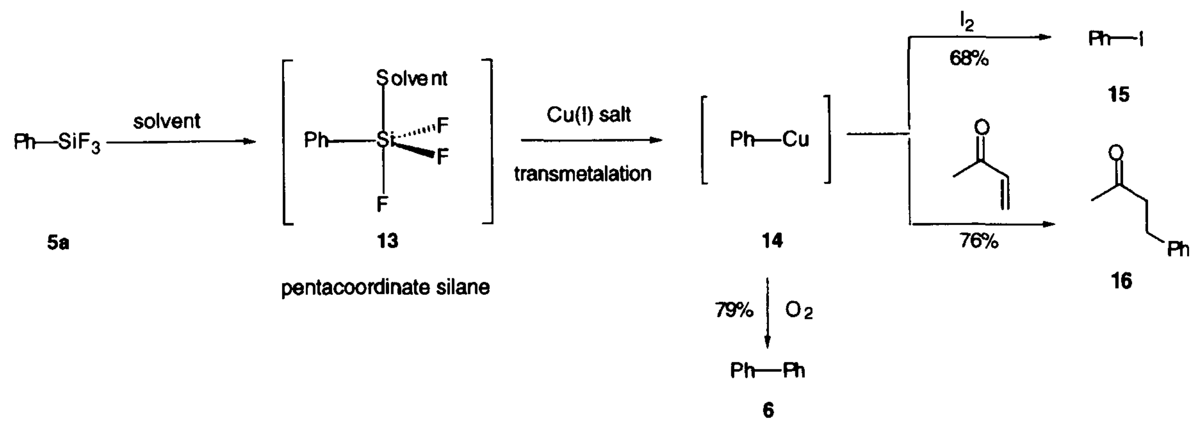
To gain insight into the reaction mechanism, we carried out the reaction of (trifluoro)phenylsilane (**5a**) using an equimolar amount of CuCl in DMF *under an argon atmosphere* at room temperature for 3 h (Scheme 1). The color of the reaction mixture immediately became reddish orange. The monitoring experiment by GC revealed that **5a** was completely consumed, albeit the formation of only a trace amount of biphenyl (**6**) was detected. At this stage, introducing air into the resulting suspension furnished **6** in 79% yield. This result strongly indicates that **5a** first reacted with CuCl to form an intermediate, presumably organocopper species, which oxidatively coupled under an aerobic condition to afford **6**.

We next performed experiments for trapping the postulated organocopper intermediate with various reagents. When iodine was added to the resulting mixture of **5a** with CuCl under an argon atmosphere, iodobenzene (**15**) was isolated in 68% yield. In a manner similar to the conjugate addition of an organocopper to an α,β-unsaturated ketone,[28] methyl vinyl ketone was introduced to the reaction mixture of **5a** with a Cu(I) salt under an argon atmosphere to afford 4-phenyl-2-butanone (**16**) in 76% yield. These results support, although indirectly, the formation of organocopper species during the course of the homo-coupling.

The process for the generation of organocopper species is postulated as follows: A polar solvent DMF first coordinates to (trifluoro)phenylsilane (**5a**) in a manner similar to the attack of a fluoride ion which has been considered likely in the Pd-catalyzed cross-coupling reaction to produce pentacoordinate phenylsilane as an active species.[3] Since the reaction of allyltrichlorosilane with an aldehyde without catalyst is well explained by the coordination of a polar solvent, DMF or HMPA, the present transmetalation would also be triggered by such coordination.[29] Via the pentacoordinate intermediate **13**, the phenyl group would transfer from silicon to copper to give organocopper species **14**, which would then oxidatively dimerize to furnish the homo-coupled product under exposure to atmospheric air. Although mechanistic details of the homo-coupling process remain unclear, since the organocopper species could neither be isolated nor detected, the above observed results should give a clue for the formation of the organocopper species by the transmetalation from silicon to copper.

Conclusion

The reactions of alkenyl- and arylsilanes with a copper(I) salt in DMF were demonstrated to be synthetically useful because the methodology opens the novel and preparative homo-coupling reactions for the generation of symmetrical conjugated dienes or biaryls. The number of fluorine atom on silicon is shown to be highly crucial: Two or three fluorine atoms on silicon are essential for the success of the homo-coupling. In these reactions, DMF plays an important role to activate the organosilicon compounds and oxygen is employed as a mild oxidant. Thereby, the new carbon–carbon bond formation of organosilanes with a copper salt in DMF under the condition is rather convenient. Trapping experiments implicated the transmetalation of an organic group from silicon to copper to form organocopper species. In principle, organocopper species are useful intermediates in the synthesis of a variety of compounds via cross-coupling reactions and conjugate additions.



Scheme 1.

Experimental

All temperatures are uncorrected. The melting points were measured with a Yanagimoto micro melting-point apparatus. NMR spectra were measured on a Varian Mercury 300 spectrometer and on a Bruker AC-200 NMR spectrometer. $CHCl_3$: 7.26 ppm for ^1H NMR and $CDCl_3$: 77.0 ppm for ^{13}C NMR were used as internal standards. The IR spectra were recorded on a Shimadzu FTIR-8000A spectrometer in neat liquid or KBr. GC analyses were performed on a Shimadzu GC-14A equipped with a flame ionization detector using Shimadzu Capillary Column (CBP1-M25-025). The GC yields were determined using suitable hydrocarbon internal standards. For thin-layer chromatography (TLC) analyses throughout this work, Merck precoated TLC plate (silica gel 60 GF_{254}, 0.25 mm) was used. Flush column chromatography was performed using Merck Kieselgel 60 (70—230 mesh and 230—400 mesh) or Wakogel C-200.

Materials. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium/benzophenone prior to use. DMF, DMA, DMSO, HMPA, acetonitrile, and triethylamine were distilled from CaH_2 and stored over MS-4A under an argon atmosphere. Methanol was distilled from magnesium methoxide. Copper(I) chloride, bromide, and iodide were purified by the literature method.[30] Alkenylfluorosilanes (**1**, **3a**, and **3b**)[31] were prepared by the hydrosilylation of the corresponding alkyne with $HSiCl_3$ or $HSiMeCl_2$ in the presence of a platinum catalyst $(Bu_4N)_2PtCl_6$[32] followed by fluorination with $CuF_2 \cdot 2H_2O$.[33] (Trifluoro)phenylsilane (**5a**) was purchased and used without further purification. Ethyl(difluoro)phenylsilane (**5b**), fluoro(dimethyl)phenylsilane (**5c**), ethyl(difluoro)(4-methylphenyl)silane (**7**), ethyl(difluoro)(2,5-dimethoxyphenyl)silane (**9**), and ethyl(difluoro)(2-thienyl)silane (**11**) were prepared by the fluorination of the corresponding arylchlorosilanes as described above.

A General Procedure for the Homo-Coupling Reaction of Organosilanes. (1*E*,3*E*)-1,4-Diphenyl-1,3-butadiene (2). A glass tube was degassed and evacuated prior to the introduction of air through a $CaCl_2$ drying tube. To the reaction vessel was successively added CuCl (330 mg, 3.3 mmol), DMF (10 mL) and **1** (500 μL, 3.3 mmol). After being stirred for 3 h at room temperature the reaction mixture was quenched with 1 M hydrochloric acid (30 mL, 1 M = 1 mol dm^{-3}) and extracted with diethyl ether (20 mL). The organic layer was collected and aqueous layer was extracted with diethyl ether (10 mL×3). The combined ethereal layer was washed with $NaHCO_3$ aq and brine, and dried over Na_2SO_4. Filtration and concentration afforded pale yellow solid, which was purified by column chromatography to give 241 mg (1.17 mmol, 71% yield) of **2** as a white solid. GC yield was 98%. $R_f = 0.70$ (hexane : AcOEt = 9 : 1). Mp 150—152 °C (lit,[34] 152—153 °C); IR (KBr) 3164, 3232, 3056, 3017, 2958, 2931, 2924, 2849, 1951, 1836, 1769, 1733, 1593, 1491, 1445, 1075, 992, 741, 691 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) $\delta = 6.59$—6.73 (m, 2 H), 6.88—7.03 (m, 2 H), 7.16—7.50 (m, 10 H); ^{13}C NMR (50.3 MHz, $CDCl_3$) $\delta = 126.36$, 127.54, 128.64, 129.24, 132.81, 137.35.

(7*E*,9*E*)-7,9-Hexadecadiene (4): Isolated in 42% yield as a colorless oil;[35] GC yield was 50%; IR (neat) 3015, 2957, 2957, 2855, 1466, 1379, 1115, 986, 725 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) $\delta = 0.88$ (t, $J = 5.3$ Hz, 6 H), 1.15—1.55 (m, 16 H), 2.04 (q, $J = 6.8$ Hz, 4 H), 5.45—5.64 (m, 2 H), 5.97 (d, $J = 14.5$ Hz, 2 H); ^{13}C NMR (50.3 MHz, $CDCl_3$) $\delta = 14.07$, 22.61, 28.89, 29.40, 31.74, 32.62, 130.33, 132.42.

Biphenyl (6): Isolated in 56% yield as a colorless solid; GC yield was 79%; mp 70—72 °C (lit,[36] 69.5—70 °C); IR (KBr) 3087, 3055, 3045, 3028, 3012, 1479, 1429, 729, 696 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) $\delta = 7.21$—7.60 (m, 10 H); ^{13}C NMR (50.3 MHz, $CDCl_3$) $\delta = 127.11$, 127.20, 128.71, 141.18.

4,4′-Dimethylbiphenyl (8): Isolated in 60% yield as a colorless solid; mp 120—123 °C (lit,[37] 118—121 °C); IR (KBr) 3050, 3025, 2969, 2942, 2917, 2853, 1503, 1489, 1456, 1113, 1007, 804 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) $\delta = 2.39$ (s, 6 H), 7.24 (d, $J = 8.4$ Hz, 4 H), 7.48 (d, $J = 8.4$ Hz, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 21.07$, 126.77, 129.40, 136.66, 138.26.

2,2′,5,5′-Tetramethoxybiphenyl (10): Isolated in 77% yield as a colorless solid; $R_f = 0.60$ (CH_2Cl_2); mp 100—101 °C (lit,[38] 103—104 °C); IR (KBr) 2992, 2953, 2941, 2905, 2832, 1509, 1501, 1470, 1416, 1225, 1142, 1051, 1040, 808, 752 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) $\delta = 3.73$ (s, 6 H), 3.78 (s, 6 H), 6.83—6.94 (m, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 55.70$, 56.49, 112.47, 113.37, 117.12, 128.61, 151.27, 153.30.

2,2′-Bithiophene (12): Isolated in 78% yield as a colorless solid; GC yield was 80%; $R_f = 0.50$ (hexane); mp 32—34 °C (lit,[39] 30 °C); IR (KBr) 3016, 3071, 1501, 1418, 1235, 1206, 1048, 828, 816, 693 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) $\delta = 7.02$ (dd, $J = 5.1$, 3.6 Hz, 2 H), 7.18 (dd, $J = 3.6$, 1.1 Hz, 2 H), 7.22 (dd, $J = 5.1$, 1.1 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 123.72$, 124.30, 127.71, 137.35.

The Reaction of Phenylsilane (5a) with CuCl under Argon. To a DMF (0.5 mL) solution of CuCl (15 mg, 0.15 mmol) placed in a Schlenk tube was added **5a** (20 μL, 0.15 mmol) *under an argon atmosphere*. The colorless reaction mixture turned into a reddish orange suspension. The reaction mixture was stirred for 3 h at room temperature to confirm that **5a** was completely consumed by GC analysis, while no formation of **6** was detected.

i) Introduction of Air: Formation of Biphenyl (6). The argon atmosphere was replaced by air through a drying $CaCl_2$ tube. The reddish orange reaction mixture changed into a blue suspension and finally into a pale green solution after 24 h at an ambient temperature. GC indicated the formation of biphenyl (**6**) in 79% yield.

ii) Addition of Iodine: Formation of Iodobenzene (15). Iodine (57 mg, 0.22 mmol) was added to the reaction mixture under an argon atmosphere and stirring was continued for 24 h at an ambient temperature. GC showed the formation of iodobenzene (**15**) in 68% yield.

The Conjugate Addition to Methyl Vinyl Ketone: Formation of 4-Phenyl-2-butanone (16). To a suspension of LiI (43 mg, 0.23 mmol) and $(CuOTf)_2 \cdot C_6H_6$ (116 mg, 0.23 mmol) in DMF (1.5 mL) was added trifluorophenylsilane (27 mL, 0.20 mmol) at room temperature under an argon atmosphere. Methyl vinyl ketone (25 mL, 0.30 mmol) was added to the mixture at room temperature. The reaction mixture was stirred for 15 h at 60 °C and quenched with 3 M HCl (20 mL). Diethyl ether (10 mL) was added and separated. The aqueous layer was extracted with diethyl ether (10 mL×3). The combined ethereal layers were washed with $NaHCO_3$ aq and brine, and dried over $MgSO_4$. Filtration and evaporation provided colorless oily substances, which were purified by column chromatography on silica gel to give **16** (22 mg, 76%) as a colorless liquid.[40] IR (neat) 3029, 2926, 1719, 1497, 1454, 1163, 750, 700 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): $\delta = 2.12$ (s, 3 H), 2.70—2.94 (m, 4 H), 7.13—7.35 (m, 5 H); ^{13}C NMR (50.3 MHz, $CDCl_3$) $\delta = 29.48$, 29.74, 44.82, 125.85, 128.04, 128.24, 140.77, 207.54.

The authors are indebted to Shin-Etsu Chemical Co., Ltd. for the generous donation of organosilicon reagents. The present research was partially supported by Grants-in-Aid for Scientific Research Nos. 07405042 and 09239102 from the Ministry of Education, Science, Sports and Culture.

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