Palladium-Catalyzed Cross-Coupling Reaction of Alkyltrifluorosilanes with Aryl Halides#

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A cross-coupling reaction of alkyltrifluorosilanes with aryl halides was achieved using a catalytic amount of tetrakis(triphenylphosphine)palladium(0) and excess of tetrabutylammonium fluoride (TBAF) at 100 °C with high chemoselectivity. Functional groups like nitro, ketone carbonyl, and formyl tolerated the coupling conditions. Because potassium(18-crown-6) alkyltetrafluorosilicates also underwent a cross-coupling reaction in the presence of an additional molar amount of TBAF, the active species of the coupling reaction was assumed to be pentacoordinate silicates. TBAF in excess was considered to be required for trapping the tetrafluorosilane produced in the catalytic cycle of the cross-coupling reaction.

The palladium-catalyzed cross-coupling reaction has now grown to be the most versatile synthetic method for carbon–carbon bond construction and is widely used for the syntheses of both natural and unnatural organic products. Thus, bonds between the sp^2–sp^2, sp^2–sp^3, or sp^2–sp carbons are conveniently constructed straightforwardly.[1] Regarding the alkyl-type cross-coupling reaction, alkylmetals of Mg,[2] B,[3] Zn,[4] Sn,[5] Li,[6] and Zr[7] have been employed very often. However, the reaction when applied to organic synthesis sometimes encounters problems in respect to the selectivity and/or availability of the reagents (Eq. 1).

$$\text{R–M} + \text{R}'\text{–X} \xrightarrow{\text{Pd cat.}} \text{R–R}' \quad (1)$$

We have demonstrated that various types of organosilicon compounds can be used for the palladium-catalyzed cross-coupling reaction.[8] Recently, alkyltrifluorosilanes as the alkylmetal reagent were disclosed to be applicable to the cross-coupling reaction.[9] In this article we describe synthetic details of the cross-coupling reaction of alkylsilanes and discuss the mechanistic aspects (Eq. 2).

$$\text{Ar–X} + \text{F}_3\text{Si–R} \xrightarrow[\text{F}^-]{\text{Pd cat.}} \text{Ar–R} \quad (2)$$

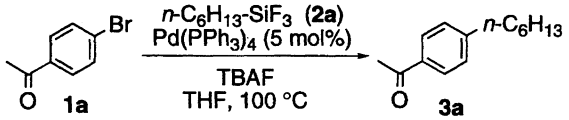
R = *n*-C_6H_{13}, CH_2CH_2Ph, CH_2CH_2COOMe, $CHMeCH_2COOMe$, CH_2CH_2CN, $CH_2CH_2CH_2CN$, $CH_2CH_2CH_2CH_2COMe$

As compared with alkylmetals of the main-group elements, alkyltrifluorosilanes have the following advantages: 1) stability to heat, air, and moisture, 2) facile handling, 3) less toxicity than other organometallics, and 4) ready availability of various types of alkylsilanes, for example, by the hydrosilylation of olefins.

Results and Discussion

Optimization of Reaction Conditions. We first studied the reaction of 4-bromoacetophenone (**1a**) and hexyltrifluorosilane (**2a**) in the presence of $Pd(PPh_3)_4$ as a catalyst and tetrabutylammonium fluoride (TBAF) in tetrahydrofuran (THF) at 100 °C and found that the amount of TBAF was critical, as shown in Table 1. The reaction using **2a** (2 mol) and TBAF (2 mol) for **1a** (1 mol) proceeded slowly; after 48 h the expected cross-coupled product **3a** was obtained in 20% yield along with the recovered **1a** (50% yield, Run 1). By using TBAF in excess (Run 2), the yield of **1a** was improved. The highest yield was obtained when the reaction was carried out using 4 molar amounts of TBAF from the

Table 1. Influence of Mol Ratio of **2a** and TBAF



Run	2a (mol amt.)	TBAF (mol amt.)	Time / h	Yield of 3a/%	Recovered 2a/%
1	2	2	48	20	50
2	2	2+1	18	49	20
3	2	4	22	65	
4	2	6	22	50	
5	4	4	22	34	

Dedicated to Professor Yoshito Kishi on the occasion of his 60th birthday.

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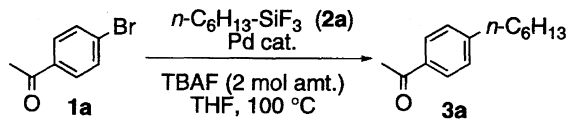
beginning (Run 3). With a 4 : 4 mol ratio of **2a** and TBAF, **3a** was produced in a yield similar to that in Run 1, but 4,4′-diacetylbiphenyl was coproduced as the major side product at the expense of the recovery of **1a** (Run 5).

We then examined the influence of the kind of Pd catalyst and ligand; the results are summarized in Table 2. In contrast to $Pd(PPh_3)_4$, a phosphine-free palladium complex afforded **3a** in a lower yield (Run 2). The use of $Pd_2(dba)_3 \cdot CHCl_3$ in combination with such a monodentate ligand as P(*o*-tol)$_3$, P(2-furyl)$_3$, or $AsPh_3$ was ineffective (Runs 3 to 5). Instead, significant amounts of by-products, such as a homo-coupled product and a reduced product, were formed. Pd(II) complexes also exhibited poor catalytic activity (Runs 6 and 7). Consequently, $Pd(PPh_3)_4$was concluded to be the best catalyst. A solvent also affected the reaction remarkably. THF was found to be superior medium. Both an aprotic polar solvent (DMF, DMSO, and MeCN) and a less polar solvent (1,2-dichloroethane and benzene) suppressed the reactivity of the catalyst and decreased the yield of **3a**.

The Reaction of Various Alkyltrifluorosilanes with Aryl Halides. In contrast to the cross-coupling reactions of alkylmagnesium halides, the chemoselectivity of the reaction of alkyltrifluorosilanes with aryl halides is remarkable: The ketone carbonyl, formyl, and nitro groups remained intact under the reaction conditions, as summarized in Table 3. Hexyltrifluorosilane (**2a**) reacted with various electron-deficient aryl halides to give the corresponding alkylated products (**3a**—**3g**). However, aryl halides substituted by an electron-donating group, such as methyl, methoxyl, or amino, gave, in place of the expected coupled product, homo-coupled and unidentified products. Similarly, 2-phenethyltrifluorosilane (**2b**) coupled with 4-bromo- or 4-iodoacetophenone to give the coupled product **4a**.

Methyl 3-(trifluorosilyl)propanoate (**2c**), readily derived from the commercially available trichlorosilyl derivative, also coupled with various aryl halides. Thus, **2c** is a synthetic equivalent of an ester homo-enolate. It is worth noting that **2c** reacted with 4-iodobenzaldehyde (**1b**) to give the expected cross-coupled product **5b** in 76% yield with the formyl group being intact (Run 13). Although zinc homo-enolates reportedly can undergo a cross-coupling reaction,[4] the chemoselectivity of the zinc reagents appears to be relatively inferior to alkyltrifluorosilanes. Trimethylsilyloxycyclopropanes are also employed as reagents equivalent to homo-enolates.[10]

Table 2. Optimization of Palladium Catalyst

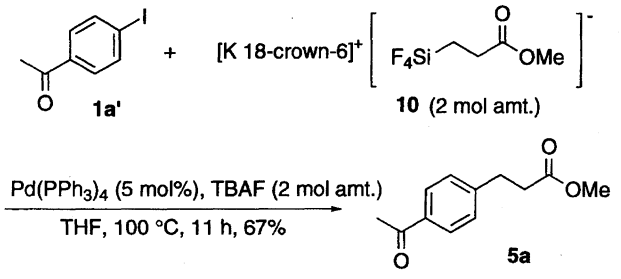


Run	Pd cat/mol% additive/mol%	Time h	Yield %
1	$Pd(PPh_3)_4$ (5)	38	62
2	$Pd_2(dba)_3 \cdot CHCl_3$ (2,5)	23	25
3	$Pd_2(dba)_3 \cdot CHCl_3$ (2,5) PPh_3 (10)	20	19
4	$Pd_2(dba)_3 \cdot CHCl_3$ (2,5) P(*o*-tol)$_3$ (10)	20	19
5	$Pd_2(dba)_3 \cdot CHCl_3$ (2,5) $AsPh_3$ (10)	25	15
6	$PdCl_2$(dppf) (5)	96	20
7	$PdCl_2$(dppe) (5)	96	31

Alkylsilanes with ester or nitrile functionality are, in general, more reactive than unfunctionalized ones. For example, **2c** reacted with 4-bromotoluene (**1j**) to give **5j** in 62% yield (Run 20), whereas **2a** failed to give the corresponding coupled product **3j**. Cyanoalkyltrifluorosilanes **2e** and **2f** were also prepared from the corresponding commercially available cyanoalkyltrichlorosilanes. 6-(Trifluorosilyl)hexan-2-one (**2g**), prepared by the hydrosilylation of 5-hexen-2-one with trichlorosilane, followed by fluorination, and stable enough to be stored in a refrigerator for months, gave **9a** upon a reaction with **1a′**.

Although we attempted to extend the cross-coupling of alkyltrifluorosilanes to alkenyl halides, allyl halides, or alkyl halides under various conditions, all attempts failed to give the expected products. Thus, the present reaction appears to be limited to aryl halides as the substrate.

Mechanistic Aspects. Palladium-catalyzed cross-coupling reactions of organosilicon compounds are, in general, successfully achieved using an *equimolar amount of* fluoride ion.[8] In these reactions pentacoordinate silicates are assumed to be the reactive species. Additional fluoride ions often convert pentacoordinate silicates into hexacoordinate silicates that are much less active. As described above, however, TBAF in excess was required to effect the cross-coupling reaction of alkyltrifluorosilane smoothly. To obtain insight into the mechanism, we examined the reaction of a well-defined alkyltetrafluorosilicate with aryl halide by means of ^{19}F NMR. Potassium (2-methoxycarbonylethyl)-tetrafluorosilicate (**10**) complexed by 18-crown-6 was prepared by treating methyl (3-trifluorosilyl)propanoate with KF and 18-crown-6.[11] Although the reaction of **10** with **1a′** in THF at 100 °C for 45 h in the presence of a catalytic amount of $Pd(PPh_3)_4$ did not give the expected cross-coupling product **5a** at all, the reaction carried out in the presence of TBAF proceeded immediately to give **5a** in 67% yield (Table 3). We also prepared potassium (2-methoxycarbonylethyl)pentafluorosilicate (**11**),[12] the corresponding hexacoordinate species, which turned out to be unreactive toward coupling with **1a′** using a catalyst $Pd(PPh_3)_4$ (5 mol%) in THF at 100 °C (Chart 1).



(3)

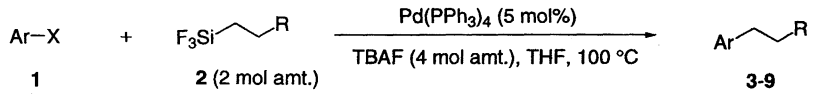


Table 3. Cross-Coupling of Alkyltrifluorosilane with Aryl Halide[a)]

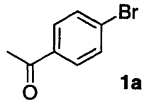
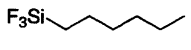
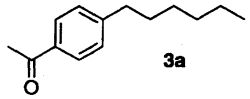
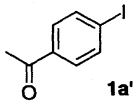
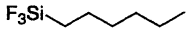
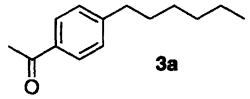
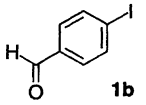
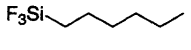
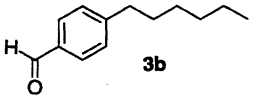
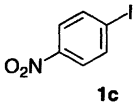
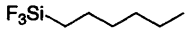
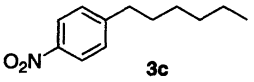
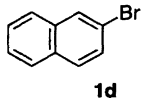
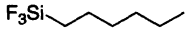
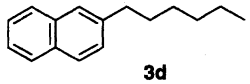
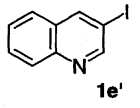
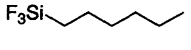
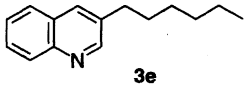
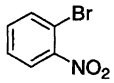
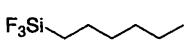
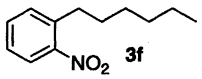
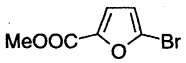
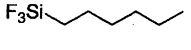
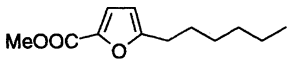
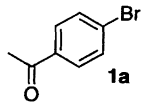
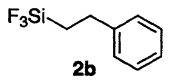
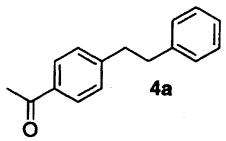
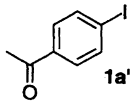
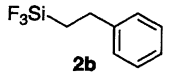
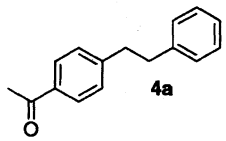
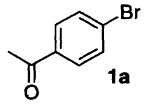
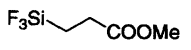
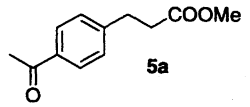
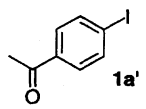
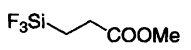
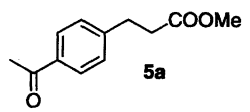
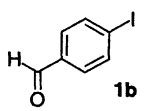
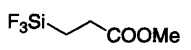
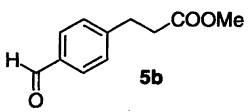
Run	Ar–X (1)	2	Time/h	Product (yield/%)	
1	 1a	 2a	22	 3a	65
2	 1a'	 2a	24[b)]	 3a	61
3	 1b	 2a	24	 3b	61
4	 1c	 2a	38[b)]	 3c	62
5	 1d	 2a	24[b)]	 3d	62
6	 1e'	 2a	37[c)]	 3e	70
7	 1f	 2a	37[c)]	 3f	53
8	 1g	 2a	27	 3g	34
9	 1a	 2b	34	 4a	71
10	 1a'	 2b	24	 4a	61
11	 1a	 2c	24	 5a	72
12	 1a'	 2c	10	 5a	77
13	 1b	 2c	10	 5b	76
14	1c	2c	9	5c	58

Table 3. (Continued)

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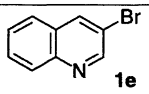
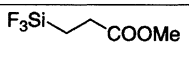
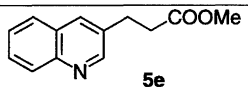
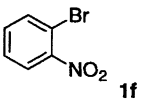
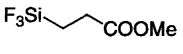
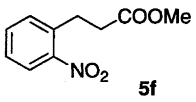
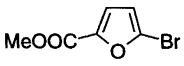
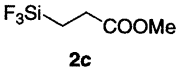
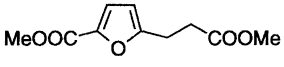
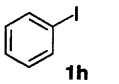
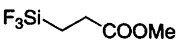
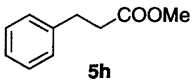
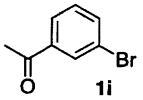
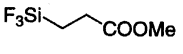
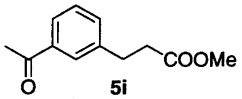
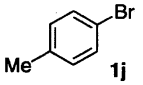
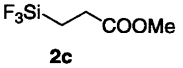
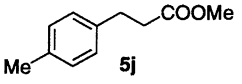
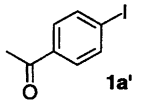
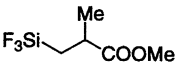
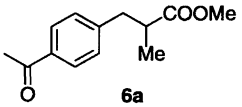
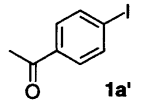
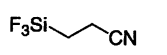
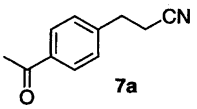
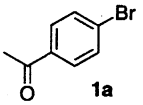
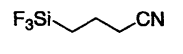
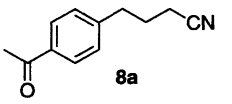
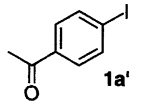
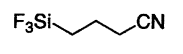
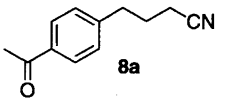
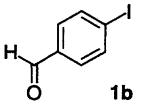
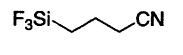
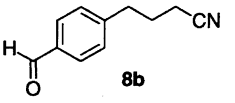
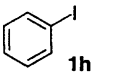
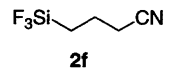
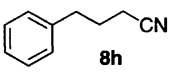
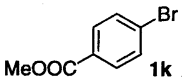
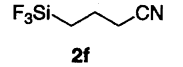
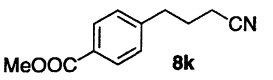
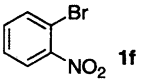
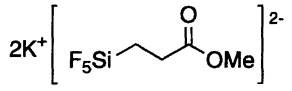
15	 **1e**	 **2c**	8	 **5e**	65
16	 **1f**	 **2c**	10	 **5f**	32
17	 **1g**	 **2c**	48	 **5g**	36
18	 **1h**	 **2c**	48	 **5h**	75
19	 **1i**	 **2c**	18	 **5i**	52
20	 **1j**	 **2c**	48	 **5j**	62
21	 **1a'**	 **2d**	18	 **6a**	42
22	 **1a'**	 **2e**	21	 **7a**	87
23	 **1a**	 **2f**	29	 **8a**	54
24	 **1a'**	 **2f**	24	 **8a**	86
25	 **1b**	 **2f**	21	 **8b**	84
26	 **1h**	 **2f**	32	 **8h**	84
27	 **1k**	 **2f**	22	 **8k**	77
28	 **1f**	**2f**	12	**8f**	37
29	**1a'**	**2g**	18	**9a**	66

a) Unless otherwise stated, all of the reaction was carried out using alkyltrifluorosilane (2 mol amt.), TBAF (4 mol amt.), and $Pd(PPh_3)_4$ (5 mol%). b) The reaction was started with 2 mol amt. of TBAF. After 8—12 h, another mol amt. of TBAF was added, and the reaction was continued for the specified total period. c) Double amounts of **2** and TBAF were used.

Table 4. ^{19}F NMR Data of **2a** and **12**[a)]

Run	Reagent and additive (mol amt.)	Chemical shift(s) (δ)	Ratio
1	**2a**	−137.6	—
2	**12**	−118.8	—
3	**2a**+TBAF (1)	−116.4, −151.9	20 : 1
4	**2a**+TBAF (2)	−116.3, −151.8	6.0 : 1
5	**2a**+TBAF (3)	−116.2, −151.7	2.6 : 1
6	TBAF only	−151.9	—

a) All spectra were measured in $CDCl_3$ at 27 °C with $CFCl_3$ as an internal standard (0 ppm).



11

K^+(18-crown-6) [n-$C_6H_{13}SiF_4$]$^-$

12

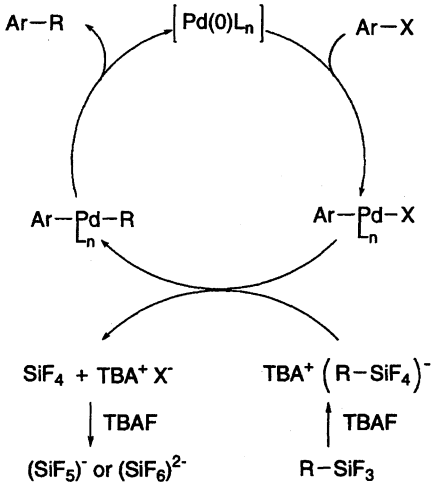
[n-$C_6H_{13}SiF_5$]$^{2-}$2M^+ (M = K and/or n-Bu_4N)

13

Chart 1.

We measured the ^{19}F NMR spectra of a $CDCl_3$ solution of hexyltrifluorosilane (**2a**) in both the absence and presence of TBAF in varying ratios. The results are summarized in Table 4. The tetrahedral silane **2a** exhibited absorption at −137.6 ppm, whereas its pentacoordinate species **12**, prepared as described above, showed a single peak at −118.8 ppm.[13] An equimolar mixture of **2a** and TBAF showed a peak at −116.4 ppm along with a very weak one at −151.9 ppm, which was identical with TBAF. In addition, mixtures of **2a** and TBAF in ratios of 1 : 2 and 1 : 3 clearly exhibited two peaks corresponding to the respective ratios. Similar spectra were also given in THF-d_8. Consequently, we can conclude that TBAF cannot convert the pentacoordinate silicate **12** to the corresponding hexacoordinate silicate **13** at room temperature, even in the presence of excess TBAF.[14]

Based on the above observations, we may propose the reaction mechanism illustrated in Scheme 1. As is well known, the catalytic cycle should involve: (1) an oxidative addition of Pd(0)L_n to aryl halide to give Ar–Pd(L_n)–X complex, (2) transmetalation of this complex with pentacoordinate silicate to give Ar–Pd(L_n)–R, and finally (3) reductive elimination to give the coupled product and to regenerate the reactive catalyst.[1] Alkyltrifluorosilane should be converted into alkyltetrafluorosilicate to achieve transmetalation, as discussed above and previously.[8] The transmetalation of arylpalladium halide with alkyltetrafluorosilicate is naturally accompanied by the formation of tetrafluorosilane, which should react with TBAF to give pentafluoro- or hexafluorosilicate, because SiF_4 is apparently more reactive than alkyltrifluorosilane toward fluoride ion. The fact that an equimolar mixture of alkyltrifluorosilane and TBAF was not effective enough to give a coupled product should be attributed to the consumption of a fair amount of fluoride ion, giving SiF_5^- or SiF_6^{2-}. Indeed, the ^{19}F NMR spectrum of the reaction mixture after 24 h exhibited a signal at −129.4 ppm corresponding to neither TBAF nor SiF_4 (−162 ppm).[13,15] Also, the signal at −129.4 ppm, which should be attributed to pentafluorosilicate (−137.4 ppm) or hexafluorosilicate (−127.4), appeared.[13,15]



Scheme 1. Mechanism proposed for palladium-catalyzed cross-coupling of aryl halide with alkyltrifluorosilane using excess TBAF.

Conclusion

Alkyltrifluorosilanes, particularly those containing a cyano or alkoxycarbonyl group, were found to be applicable to a palladium-catalyzed cross-coupling reaction. Hereby the molar ratio of alkyltrifluorosilane to TBAF was disclosed to be crucial: the reaction with aryl halide took place using TBAF in excess and a $Pd(PPh_3)_4$ catalyst in THF at 100 °C. Although pentacoordinate alkyltetrafluorosilicate alone could not undergo a cross-coupling reaction, an additional mol of TBAF assisted the silicate to effect the reaction. An ^{19}F NMR study has revealed that TBAF does not convert the pentacoordinate silicate into the hexacoordinate silicate. Consequently, an additional amount of TBAF was concluded to be necessary for trapping the tetrafluorosilane produced from the catalytic cycle.

Experimental

All of the temperatures are uncorrected. NMR spectra were measured in a $CDCl_3$ solution, unless otherwise noted, the chemical shifts being given in ppm. ^{1}H NMR spectra (tetramethylsilane as an internal standard) were measured on a JEOL FX-100, EX-400,

or Bruker AC-200 spectrometer. ^{13}C NMR spectra ($CDCl_3$ as an internal standard) were measured on a JEOL FX-100, EX-400, or Bruker AC-200 spectrometer. ^{19}F NMR spectra ($CFCl_3$ as an internal standard) were measured on a JEOL FX-100 or Bruker AC-200 spectrometer. IR spectra were recorded with a Shimadzu FTIR-8000A spectrometer in neat, unless otherwise noted. Mass spectra were recorded with a Hitachi M-80 spectrometer or a Shimadzu QP-5000 GC-MS system. Elemental analyses were carried out at Elemental Analysis Center, Tokyo Institute of Technology, using Yanako MT2 CHN Corder. HRMS were performed at Sagami Chemical Research Center, using Hitachi M-80B spectrometer.

Silica-gel column chromatography was performed using a Merck Kieselgel 60 (70—230 mesh) or Wakogel C-200. Flash-column chromatography was performed using a Merck Kieselgel 60 (230—400 mesh). TBAF (1 M THF solution, 1 M=1 mol dm^{-3}) was purchased from Aldrich Chemical Inc. and used directly.

All of the reactions were carried out under an argon atmosphere. Diethyl ether, THF, and benzene were distilled from sodium/benzophenone prior to use. Hexane and pentane were distilled from sodium/benzophenone and stored over MS-4A under an argon atmosphere. Dichloromethane, DMF, DMSO, DMI, and HMPA were distilled from CaH_2 and stored over MS-4A under an argon atmosphere.

Palladium catalysts ($Pd(PPh_3)_4$,[16] $Pd_2(dba)_3\cdot CHCl_3$,[17] $PdCl_2$(dppe), and $PdCl_2$(dppf)[18]) were prepared according to the corresponding literature. Triphenylphosphine, P(*o*-tol)$_3$, and $AsPh_3$ were purchased from Tokyo Kasei Inc. and purified by recrystallization from an appropriate solvent. All of the alkyltrifluorosilanes were prepared by fluorination of the corresponding alkyltrichlorosilanes with $CuF_2\cdot 2H_2O$ by a modified procedure from the literature.[19] Hexyltrichlorosilane, methyl 3-(trichlorosilyl)propanoate, 3-(trichlorosilyl)propanenitrile, 4-(trichlorosilyl)butanenitrile, and 2-phenyl-1-(trichlorosilyl)ethane were purchased from Chisso Inc. and fluorinated. Other alkyltrichlorosilanes were prepared by hydrosilylation of terminal olefin with trichlorosilane using H_2PtCl_6 as a catalyst.[20] Silicates **10** and **11** were prepared according to the corresponding literature.[11,12] All aryl halides, except for **1b** and **1g**, were purchased from Tokyo Kasei Inc. or Aldrich Chemical Inc. and used without purification. 4-Iodobenzaldehyde (**1b**) was prepared by the reduction of 4-iodobenzonitrile with diisobutylaluminium hydride. Methyl 5-bromofuran-2-carboxylate (**1g**) was prepared by the esterification of 5-bromofuran-1-carboxylic acid with diazomethane.

Fluorination of Alkyltrichlorosilane.[19] **A General Procedure.** Alkyltrichlorosilane (50.0 mmol) was added dropwise to a suspension of $CuF_2\cdot 2H_2O$ (10.7 g, 78.0 mmol) in diethyl ether (50 ml) at 0 °C under vigorous stirring over a period of 40 min, while the reaction flask was kept below 5 °C. A blue suspension immediately turned to brown upon adding alkyltrichlorosilane. This suspension was allowed to warm to room temperature and was then stirred vigorously for 12—24 h. The reaction mixture finally became a light-greenish suspension. The mixture was diluted with pentane (50 ml) and stirred for an additional 30 min. All of the insoluble material was filtered with suction through a Celite pad and washed three times with pentane (ca. 5 ml). The combined filtrate was concentrated under reduced pressure, except for the synthesis of hexyltrifluorosilane (**2a**). The residue was distilled under vacuum to give the corresponding alkyltrifluorosilane. For the purification of **2a**, solvents were removed by distillation under atmospheric pressure. The fraction collected at bp 95—103 °C turned out to be pure **2a**:[21] ^{1}H NMR (100 MHz) δ=0.80—1.20 (m, 5H), 1.20—1.60 (m, 8H); ^{19}F NMR (96 MHz) δ=−137.60 (s).

1-Phenyl-2-(trifluorosilyl)ethane (2b):[19] Bp 88—90 °C/72 mmHg (1 mmHg=133.322 Pa). ^{1}H NMR (100 MHz) δ=1.38 (m, 2H), 2.88 (t, J=8.2 Hz, 2H), 7.27 (m, 5H); ^{19}F NMR (96 MHz) δ=−137.19 (s).

Methyl-3-(trifluorosilyl)propanoate (2c): Bp 73—74 °C/75 mmHg. ^{1}H NMR (100 MHz) δ=1.25 (m, 2H), 2.60 (t, J=7.5 Hz, 2H), 3.77 (s, 3H); ^{19}F NMR (96 MHz) δ=−136.51 (s). Found: *m/z* 172.0140. Calcd for $C_4H_7F_3O_2Si$: M, 172.0167.

Methyl 2-Methyl-3-(trifluorosilyl)propanoate (2d): Bp 100—110 °C/30 mmHg. ^{1}H NMR (200 MHz) δ=1.25 (m, 2H), 1.32 (dd, J=7.2, 0.4 Hz, 3H), 2.83 (ddq, J=1.4, 7.2, 14.5 Hz, 1H), 3.77 (s, 3H); ^{19}F NMR (188 MHz) δ=−135.3.

3-(Trifluorosilyl)propanenitrile (2e): Purified by Kugelrohr distillation at 100 °C/20 mmHg. ^{1}H NMR (100 MHz) δ=1.42 (m, 2H), 2.60 (t, J=7.7 Hz, 2H); ^{19}F NMR (96 MHz) δ=−136.88 (s). Found: *m/z* 139.0034. Calcd for $C_3H_4NF_3Si$: M, 139.0065.

4-(Trifluorosilyl)butanenitrile (2f): Purified by Kugelrohr distillation at 90 °C/2—8 mmHg. ^{1}H NMR (100 MHz) δ=1.20 (m, 2H), 1.92 (m, 2H), 2.47 (t, J=6.5 Hz, 2H); ^{19}F NMR (96 MHz) δ=−137.08 (s). Found: *m/z* 153.0217. Calcd for $C_4H_6NF_3Si$: M, 153.0222.

6-(Trifluorosilyl)hexan-2-one (2g): Bp 86—87 °C/33 mmHg. ^{1}H NMR (100 MHz) δ=1.00 (m, 2H), 1.58 (m, 4H), 2.14 (s, 3H), 2.47 (t, J=6.8 Hz, 2H); ^{19}F NMR (96 MHz) δ=−137.55 (s). Found: *m/z* 184.0517. Calcd for $C_6H_{11}F_3OSi$: M, 184.0531.

Cross-Coupling Reaction of Alkyltrifluorosilane 2 with Aryl Halide 1. A General Procedure. To a solution of $Pd(PPh_3)_4$ (11.6 mg, 0.010 mmol) and aryl halide **1** (0.20 mmol) in THF (1 ml) placed in a screwed sealed glass tube were added sequentially alkyltrifluorosilane **2** (0.40 mmol) and TBAF (1 M THF solution, 0.80 ml, 0.80 mmol) at room temperature. The mixture was stirred for 30 min at room temperature and heated at 100 °C. The reaction was monitored by TLC or GC and allowed to continue until all of **1** was consumed. The reaction mixture was concentrated in vacuo, and the viscous residue was purified briefly by column chromatography (silica gel, CH_2Cl_2) to remove the Pd catalyst and tetrabutylammonium salt. The residue was further purified by flash column chromatography on silica gel to afford a spectrometrically pure product.

4-Hexylacetophenone (3a): ^{1}H NMR (200 MHz) δ=0.88 (m, 3H), 1.32 (m, 6H), 1.63 (m, 2H), 2.57 (s, 3H), 2.66 (t, J=7.5 Hz, 2H), 7.26 (d, J=8.5 Hz, 2H), 7.88 (d, J=8.5 Hz, 2H); ^{13}C NMR (50.3 MHz) δ=14.01, 22.52, 26.46, 28.87, 31.03, 31.61, 35.94, 128.41, 128.55, 134.88, 148.78, 197.80; IR 2930, 1684, 1606, 1412, 1267, 1182, 955, 818 cm^{-1}. Found: C, 82.10; H, 10.14%. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87%.

4-Hexylbenzaldehyde (3b):[22] ^{1}H NMR (200 MHz) δ=0.88 (m, 3H), 1.31 (m, 6H), 1.64 (m, 2H), 2.67 (t, J=7.5 Hz, 2H), 7.33 (d, J=8.0 Hz, 2H), 7.79 (d, J=8.0 Hz, 2H), 9.97 (s, 1H); ^{13}C NMR (50.3 MHz) δ=14.0, 22.5, 28.9, 31.0, 31.6, 36.2, 129.0, 129.9, 134.4, 150.5, 192.0.

4-Hexylnitrobenzene (3c): ^{1}H NMR (200 MHz) δ=0.88 (m, 3H), 1.32 (m, 6H), 1.64 (m, 2H), 2.71 (t, J=7.0 Hz, 2H), 7.32 (d, J=9.0 Hz, 2H), 8.13 (d, J=9.0 Hz, 2H); ^{13}C NMR (50.3 MHz) δ=14.00, 22.50, 28.81, 30.92, 31.56, 35.85, 123.54, 129.12, 150.83; IR 2930, 2859, 1599, 1518, 1466, 1347, 1109, 855, 749 cm^{-1}. Found: C, 69.40; H, 8.26; N, 6.68%. Calcd for $C_{12}H_{17}NO_2$: C, 69.54; H, 8.27; N, 6.76%.

2-Hexylnaphthalene (3d): ^{1}H NMR (200 MHz) δ=0.88 (t, J=6.0 Hz, 3H), 1.2—1.8 (m 8H), 2.77 (t, J=7.6 Hz, 2H), 7.16—7.48 (m, 3H), 7.60 (s, 1H), 7.73—7.82 (m, 3H); ^{13}C NMR (50.3 MHz) δ=14.1, 22.6, 29.0, 31.3, 31.7, 36.1, 124.9, 125.8, 126.3,

127.4, 127.7, 128.2, 128.4, 131.9, 133.7, 140.5; IR 3053, 2957, 2928, 2856, 1633, 1508, 1466, 1124, 816, 744 cm^{-1}. Found: C, 90.79; H, 9.36%. Calcd for $C_{16}H_{20}$: C, 90.51; H, 9.49%.

3-Hexylquinoline (3e): ^{1}H NMR (200 MHz) δ=0.89 (m, 3H), 1.33 (m, 6H), 1.72 (m, 2H), 2.79 (t, J=7.5 Hz, 2H), 7.50 (ddd, J=1.5, 7.0, 8.0 Hz, 1H), 7.64 (ddd, J=1.5, 7.0, 8.5 Hz, 1H), 7.76 (dd, J=1.0, 8.0 Hz, 1H), 7.90 (d, J=1.0 Hz, 1H), 8.07 (br d, J=8.5 Hz, 1H), 8.78 (d, J=1.5 Hz, 1H); ^{13}C NMR (50.3 MHz) δ=14.03, 22.54, 28.83, 31.06, 31.61, 33.18, 126.45, 127.26, 128.18, 128.42, 129.13, 134.03, 135.36, 152.13; IR 2955, 2928, 2857, 1570, 1495, 1466, 955, 907, 860, 781, 750 cm^{-1}. Found: m/z 213.1533. Calcd for $C_{15}H_{19}N$: M, 213.1517.

2-Hexylnitrobenzene (3f):[23] ^{1}H NMR (100 MHz) δ=0.4—1.8 (m, 11H), 2.7—3.0 (m, 2H), 7.1—7.6 (m, 3H), 7.7—7.9 (m, 1H).

Methyl 5-Hexyl-2-furancarboxylate (3g): ^{1}H NMR (200 MHz) δ=0.88 (t, J=6.4 Hz, 3H), 1.24—1.43 (m, 6H), 1.59—1.71 (m, 2H), 2.68 (t, J=7.6 Hz, 2H), 3.87 (s, 3H), 6.10 (d, J=3.3 Hz, 1H), 7.09 (d, J=3.3 Hz, 1H); ^{13}C NMR (50.3 MHz) δ=14.0, 22.5, 27.7, 28.3, 28.8, 31.4, 51.7, 107.5, 119.3, 142.8, 159.3, 161.6; IR 2955, 2932, 2861, 1732, 1531, 1520, 1308, 1206, 1140, 1021, 762 cm^{-1}. Found: m/z 210.1255. Calcd for $C_{12}H_{18}O_3$: M, 210.1256.

4-Phenethylacetophenone (4a): ^{1}H NMR (200 MHz) δ=2.57 (s, 3H), 2.95 (m, 4H), 7.12—7.32 (m, 7H), 7.86 (d, J=8.0 Hz, 2H); ^{13}C NMR (50.3 MHz) δ=26.48, 37.33, 37.76, 126.05, 128.35, 128.38, 128.45, 128.65, 135.12, 141.02, 147.39, 197.77; IR 1676, 1601, 1412, 1273, 959, 866, 826 cm^{-1}. Found: m/z 224.1216. Calcd for $C_{16}H_{16}O$: M, 224.1201.

Methyl 3-(4-Acetylphenyl)propanoate (5a): ^{1}H NMR (200 MHz) δ=2.58 (s, 3H), 2.66 (t, J=7.5 Hz, 2H), 3.01 (t, J=7.5 Hz, 2H), 3.67 (s, 3H), 7.29 (d, J=8.5 Hz, 2H), 7.89 (d, J=8.5 Hz, 2H); ^{13}C NMR (50.3 MHz) δ=26.47, 30.75, 35.02, 51.63, 128.46, 128.59, 135.41, 146.11, 172.83, 197.65; IR 2953, 1786, 1682, 1608, 1414, 1269, 1183, 957, 841 cm^{-1}. MS m/z (rel intensity) 206 (M^+; 30), 191 (100), 131 (34), 103 (20), 77 (22). Found: C, 69.76; H, 6.59%. Calcd for $C_{12}H_{14}O_3$: C, 69.89; H, 6.84%.

Methyl 3-(4-Formylphenyl)propanoate (5b): ^{1}H NMR (200 MHz) δ=2.66 (t, J=7.5 Hz, 2H), 3.02 (t, J=7.5 Hz, 2H), 3.65 (s, 3H), 7.35 (d, J=8.5 Hz, 2H), 7.79 (d, J=8.5 Hz, 2H), 9.95 (s, 1H); ^{13}C NMR (50.3 MHz) δ=30.94, 34.92, 51.67, 128.95, 129.99, 134.82, 147.73, 172.75, 191.80; IR 2953, 1736, 1701, 1437, 1213, 1170, 847, 830 cm^{-1}. MS m/z (rel intensity) 192 (M^+; 42), 132 (100), 103 (29), 91 (59), 77 (43). Found: C, 68.85; H, 6.50%. Calcd for $C_{11}H_{12}O_3$: C, 68.74; H, 6.29%.

Methyl 3-(4-Nitrophenyl)propanoate (5c): ^{1}H NMR (200 MHz) δ=2.68 (t, J=8 Hz, 2H), 3.06 (t, J=8 Hz, 2H), 3.68 (s, 3H), 7.37 (d, J=8 Hz, 2H), 8.15 (d, J=8 Hz, 2H); ^{13}C NMR (50.3 MHz) δ=30.6, 34.8, 51.8, 123.8, 129.2, 146.7, 148.2, 172.5; IR 3114, 3083, 2959, 2857, 1732, 1609, 1579, 1520, 1431, 1348, 855, 752 cm^{-1}. Found: C, 57.42; H, 5.06; N, 6.68%. Calcd for $C_{10}H_{11}NO_4$: C, 57.41; H, 5.30; N, 6.70%.

3-(2-Methoxycarbonylethyl)quinoline (5e):[24] ^{1}H NMR (200 MHz) δ=2.75 (t, J=7.5 Hz, 2H), 3.16 (t, J=7.5 Hz, 2H), 3.68 (s, 3H), 7.49—8.10 (m, 5H), 8.81 (d, J=2.3 Hz, 1H), 9.95 (s, 1H); ^{13}C NMR (50.3 MHz) δ=28.2, 35.1, 51.7, 126.7, 127.4, 128.0, 128.9, 129.2, 133.1, 134.4, 147.0, 151.6, 172.3; IR 2951, 1736, 1605, 1570, 1495, 1437, 1331, 1127, 986, 897, 789, 752 cm^{-1}.

Methyl 3-(2-Nitrophenyl)propanoate (5f): ^{1}H NMR (200 MHz) δ=2.73 (t, J=7.5 Hz, 2H), 3.23 (t, J=7.5 Hz, 2H), 3.68 (s, 3H), 7.34—7.59 (m, 3H), 8.94 (d, J=8 Hz, 1H); ^{13}C NMR (50.3 MHz) δ=28.3, 34.6, 51.7, 124.9, 127.6, 132.1, 133.2, 135.5, 149.2, 172.7; IR 2953, 1736, 1525, 1437, 1348, 1290, 1197, 1172, 746 cm^{-1}. Found: C, 57.43; H, 5.09; N, 6.66%. Calcd for $C_{10}H_{11}NO_4$: C, 57.41; H, 5.30; N, 6.70%.

Methyl 5-(2-Methoxycarbonylethyl)furan-2-carboxylate (5g): ^{1}H NMR (200 MHz) δ=2.70 (t, J=7.5 Hz, 2H), 3.02 (t, J=7.5 Hz, 2H), 3.68 (s, 3H), 3.86 (s, 3H), 6.16 (dt, J=3.5, 0.5 Hz, 1H), 7.07 (d, J=3.5 Hz, 1H); ^{13}C NMR (50.3 MHz) δ=23.64, 31.94, 51.73, 51.79, 108.17, 119.12, 143.31, 158.87, 159.09, 172.40; IR 2999, 2953, 1740 (br), 1534, 1522, 1437, 1307, 1207, 1136, 1022 cm^{-1}. Found m/z 212.0675. Calcd for $C_{10}H_{12}O_5$: M, 212.0685.

Methyl 3-Phenylpropanoate (5h):[25] ^{1}H NMR (200 MHz) δ=2.64 (dt, J=1.0, 7.5 Hz, 2H), 2.96 (t, J=7.5 Hz, 2H), 3.68 (s, 3H), 7.15—7.35 (m, 5H); ^{13}C NMR (50.3 MHz) δ=30.92, 35.67, 51.57, 126.24, 128.24, 128.48, 140.49, 173.31; IR 2953, 1740, 1454, 1165, 986, 752 cm^{-1}.

Methyl 3-(3-Acetylphenyl)propanoate (5i): ^{1}H NMR (200 MHz) δ=2.58 (s, 3H), 2.66 (t, J=7.5 Hz, 2H), 3.01 (t, J=7.5 Hz, 2H), 3.66 (s, 3H), 7.40 (m, 2H), 7.79 (m, 2H); ^{13}C NMR (50.3 MHz) δ=26.61, 30.68, 35.38, 51.63, 126.45, 127.99, 128.71, 133.09, 137.37, 141.02, 172.95, 198.08; IR 2953, 1736, 1686, 1603, 1437, 1360, 1273, 1196, 800, 733 cm^{-1}. Found: C, 69.88; H, 6.64%. Calcd for $C_{12}H_{14}O_3$: C, 69.89; H, 6.84%.

Methyl 3-(4-Methylphenyl)propanoate (5j):[26] ^{1}H NMR (200 MHz) δ=2.32 (s, 3H), 2.62 (t, J=8.0 Hz, 2H), 2.93 (t, J=8.0 Hz, 2H), 3.67 (s, 3H), 7.10 (s, 4H); ^{13}C NMR (50.3 MHz) δ=20.96, 30.50, 35.82, 51.54, 128.11, 129.15, 135.72, 137.41, 173.39; IR 2951, 1740, 1516, 1437, 1364, 1196, 1169, 988, 837 cm^{-1}. MS m/z (rel intensity) 178 (M^+; 24), 118 (94), 105 (100), 91 (24), 77 (17).

Methyl 3-(4-Acetylphenyl)-2-methylpropanoate (6a): ^{1}H NMR (200 MHz) δ=1.18 (d, J=6 Hz, 3H), 2.58 (s, 3H), 2.68—2.83 (m, 2H), 3.06—3.15 (m, 1H), 3.64 (s, 3H), 7.26 (d, J=7 Hz, 2H), 7.88 (d, J=7 Hz, 2H); ^{13}C NMR (50.3 MHz) δ=16.9, 26.5, 39.6, 41.1, 51.7, 128.5, 129.1, 135.5, 145.1, 176.0, 197.7; IR 2977, 2953, 2878, 1736, 1682, 1609, 1360, 1269, 1169, 884, 816 cm^{-1}. Found: C, 71.00; H, 7.32%. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32%.

3-(4-Acetylphenyl)propanenitrile (7a): ^{1}H NMR (200 MHz) δ=2.60 (s, 3H), 2.66 (t, J=7.5 Hz, 2H), 3.12 (t, J=7.5 Hz, 2H), 7.34 (d, J=8.5 Hz, 2H), 7.94 (d, J=8.5 Hz, 2H); ^{13}C NMR (50.3 MHz) δ=18.90, 26.54, 31.35, 118.62, 128.52, 128.91, 136.19, 143.23, 197.50; IR 2938, 2247, 1682, 1609, 1414, 1360, 1269, 1186, 959, 839 cm^{-1}. Found: C, 76.41; H, 6.54; N, 8.04%. Calcd for $C_{11}H_{11}NO$: C, 76.28; H, 6.40; N, 8.09%.

4-(4-Acetylphenyl)butanenitrile (8a): ^{1}H NMR (200 MHz) δ=2.01 (tt, J=7.0, 7.5 Hz, 2H), 2.35 (t, J=7.0 Hz, 2H), 2.59 (s, 3H), 2.85 (t, J=7.5 Hz, 2H), 7.29 (d, J=8.5 Hz, 2H), 7.91 (d, J=8.5 Hz, 2H); ^{13}C NMR (50.3 MHz) δ=16.35, 26.41, 26.46, 34.21, 119.10, 128.57, 128.68, 135.57, 145.29, 197.55; IR 2938, 2245, 1682, 1607, 1414, 1269, 1184, 959, 839 cm^{-1}. MS m/z (rel intensity) 187 (M^+; 11), 172 (100), 116 (11), 77 (12). Found: C, 76.75; H, 6.92; N, 7.31%. Calcd for $C_{12}H_{13}NO$: C, 76.98; H, 7.00; N, 7.48%.

4-(4-Formylphenyl)butanenitrile (8b): ^{1}H NMR (200 MHz) δ=1.95—2.10 (m, 2H), 2.36 (t, J=7.0 Hz, 2H), 2.88 (t, J=7.5 Hz, 2H), 7.34 (d, J=7 Hz, 2H), 7.84 (d, J=7 Hz, 2H), 9.99 (s, 1H); ^{13}C NMR (50.3 MHz) δ=16.5, 26.5, 34.5, 119.0, 129.1, 130.2, 135.1, 146.9, 191.7; IR 2936, 2741, 2245, 1698, 1607, 1306, 1213, 1171, 826 cm^{-1}. Found m/z 173.0825. Calcd for $C_{11}H_{11}NO$: M, 173.0841.

4-Phenylbutanenitrile (8h): Identical with the authentic sample purchased from Aldrich.

Methyl 4-(3-Cyanopropyl)benzoate (8k): ^{1}H NMR (200 MHz) δ=1.93—2.08 (m, 2H), 2.34 (t, J=7.0 Hz, 2H), 2.84 (t,

J=7.0 Hz, 2H), 3.91 (s, 3H), 7.26 (d, J=6.0 Hz, 2H), 7.98 (d, J=6.0 Hz, 2H); ^{13}C NMR (50.3 MHz) δ=16.4, 26.5, 34.3, 52.0, 119.1, 128.4, 128.6, 130.0, 145.1, 166.9; IR 2957, 2940, 2869, 2242, 1717, 1441, 1281, 1179, 1115, 762 cm^{-1}. Found: *m/z* 203.0952. Calcd for $C_{12}H_{13}NO_2$: M, 203.0946.

4-(2-Nitrophenyl)butanenitrile (8f): ^{1}H NMR (200 MHz) δ=1.95—2.13 (m, 2H), 2.44 (t, J=7.0 Hz, 2H), 3.04 (t, J=7.5 Hz, 2H), 7.31—7.45 (m, 2H), 7.54—7.62 (m, 1H), 7.98 (d, J=8 Hz, 1H); ^{13}C NMR (50.3 MHz) δ=16.9, 26.2, 32.1, 119.1, 125.1, 127.8, 132.1, 133.3, 135.0, 149.2; IR 3069, 2936, 2874, 2247, 1610, 1578, 1348, 1167, 860, 789, 741, 702, 666 cm^{-1}. Found: C, 63.34; H, 5.37; N, 14.66%. Calcd for $C_{10}H_{10}N_2O_2$: C, 63.15; H, 5.30; N, 14.73%.

6-(4-Acetylphenyl)hexan-2-one (9a): ^{1}H NMR (200 MHz) δ=1.62 (m, 4H), 2.12 (s, 3H), 2.45 (m, 2H), 2.57 (s, 3H), 2.68 (m, 2H), 7.26 (d, J=8.5 Hz, 2H), 7.87 (d, J=8.5 Hz, 2H); ^{13}C NMR (50.3 MHz) δ=23.33, 26.54, 29.91, 30.50, 35.74, 43.40, 128.54, 128.60, 135.09, 148.03, 197.81, 208.69; IR 2938, 1714, 1682, 1607, 1414, 1360, 1269, 1182, 957, 818 cm^{-1}. Found: C, 76.76; H, 8.20%. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31%.

Preparation of Potassium[18-crown-6] Tetrafluoro(2-methoxycarbonylethyl)silicate (10).[11] Methyl 3-(trifluorosilyl)-propanoate (**2c**, 0.46 ml, 3.0 mmol) was added in one portion to a well-stirred suspension of anhydrous potassium fluoride (174 mg, 3.0 mmol) and 18-crown-6 (0.79 g, 3.0 mmol) in toluene (10 ml) at room temperature. The resulting suspension was stirred for 28 h. The precipitated material was filtered under vacuum, washed twice with toluene and then with pentane, and dried in vacuo at room temperature for 12 h. Thus, pure **10** was obtained as colorless crystals by recrystallization from dichloromethane.

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References

1) R. F. Heck, "Palladium Reagents in Organic Synthesis," Academic Press, New York (1985).

2) M. Kumada, *Pure Appl. Chem.*, **52**, 669 (1980); K. Tamao, "Comprehensive Organic Synthesis," ed by B. M. Trost, Pergamon Press, Oxford (1991), Vol. 3, p. 435.

3) N. Miyaura, T. Ishiyama, H. Sasaki, M. Sato, and A. Suzuki, *J. Am. Chem. Soc.*, **111**, 314 (1989).

4) P. Knochel and R. D. Singer, *Chem. Rev.*, **93**, 2117 (1993).

5) J. K. Stille, *Angew. Chem., Int. Ed. Engl.*, **25**, 508 (1986).

6) S. -I. Murahashi, M. Yamamura, K. Yanagisawa, N. Mita, and K. Kondo, *J. Org. Chem.*, **44**, 2408 (1979).

7) E. Negishi, *Acc. Chem. Res.*, **15**, 340 (1982).

8) Y. Hatanaka and T. Hiyama, *Synlett*, **1991**, 845; T. Hiyama and Y. Hatanaka, *Pure Appl. Chem.*, **66**, 1471 (1994).

9) H. Matsuhashi, M. Kuroboshi, Y. Hatanaka, and T. Hiyama, *Tetrahedron Lett.*, **35**, 6507 (1994).

10) E. Nakamura, S. Aoki, K. Sekiya, H. Oshino, and I. Kuwajima, *J. Am. Chem. Soc.*, **109**, 8056 (1987); S. Aoki, E. Fujimura, E. Nakamura, and I. Kuwajima, *J. Am. Chem. Soc.*, **110**, 3296 (1988).

11) S. E. Johnson, R. O. Day, and R. R. Holms, *Inorg. Chem.*, **28**, 3182 (1989); S. E. Johnson, J. S. Payne, R. O. Day, J. M. Holms, and R. R. Holms, *Inorg. Chem.*, **28**, 3190 (1989).

12) J. Yoshida, K. Tamao, H. Yamamoto, T. Kakui, T. Uchida, and M. Kumada, *Organometallics*, **1**, 542 (1982).

13) F. Klanberg and E. L. Muetterties, *Inorg. Chem.*, **7**, 155 (1968).

14) J. J. Moscony and A. G. McDiarmid, *J. Chem. Soc., Chem. Commun.*, **1996**, 307.

15) R. K. Marat and A. F. Janzen, *Can. J. Chem.*, **55**, 3845 (1977).

16) D. R. Coulson, *Inorg. Synth.*, **13**, 121 (1972).

17) T. Ukai, H. Kawazura, and Y. Ishii, *J. Organomet. Chem.*, **65**, 253 (1974).

18) T. Hayashi, M. Konishi, and M. Kumada, *Tetrahedron Lett.*, **1979**, 1871.

19) K. Tamao, T. Kakui, M. Akita, T. Iwahara, R. Kanatani, J. Yoshida, and M. Kumada, *Tetrahedron*, **39**, 983 (1983).

20) J. L. Speier, *Adv. Organomet. Chem.*, **17**, 407 (1979).

21) S. D. Fazio, S. A. Tomellini, S. H. Hsu, J. B. Crowther, T. V. Raglione, T. R. Floyd, and R. A. Hartwick, *Anal. Chem.*, **57**, 1559 (1985).

22) M. A. Osman, *Helv. Chim. Acta*, **65**, 2448 (1982).

23) E. M. Genies and P. Noel, *J. Electroanal. Chem. Interfacial Electrochem.*, **310**, 89 (1991).

24) W. Danho, J. W. Tilley, S. J. Shiuey, I. Kulesha, J. Swistok, R. Kakofske, J. Michalewsky, R. Wagner, and J. Triscari, *Int. J. Pept. Protein Res.*, **39**, 337 (1992); *Chem. Abstr.*, **117**, 143640 (1992).

25) C. W. Lee and H. Alper, *J. Org. Chem.*, **60**, 250 (1995).

26) H. I. Tashtoush and R. Sustmann, *Chem. Ber.*, **126**, 1759 (1993).