Improvements of Efficiency and Regioselectivity in the Iridium(I)-Catalyzed Aromatic C−H Silylation of Arenes with Fluorodisilanes

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The aromatic C−H silylation of arenes (10 equiv) with 1,2-di-*sec*-butyl-1,1,2,2-tetrafluorodisilane was carried out in octane at 120 °C in the presence of a catalytic amount of iridium(I) complexes (3.0 mol %) generated from 1/2[Ir(OMe)(COD)]$_2$ and 2,9-diisopropyl-1,10-phenanthroline. The reactions of many arenes resulted in the formation of corresponding arylfluorosilanes in high yields with excellent regioselectivities.

Introduction

The development of catalytic and selective functionalization of inactive C−H bonds in organic molecules by transition metal complexes is a research area of considerable interest in both organic and organometallic chemistry.[1] Since aromatic silicon compounds are versatile synthetic intermediates in organic synthesis,[2−5] an extension of the methodology to silylation of arenes would have significant synthetic value. Indeed, there have been several studies on this type of transformation with disilanes[6] or hydrosilanes;[7] however, the methods have been limited to the synthesis of less reactive aromatic triorganosilicon derivatives. Recently, we demonstrated that the aromatic C−H silylation of neat arenes with 1,2-di-*tert*-butyl-1,1,2,2-tetrafluorodisilane (*t*-BuF_2Si)$_2$ was catalyzed by iridium(I) complexes generated from 1/2[Ir(OMe)(COD)]$_2$ and 4,4′-di-*tert*-butyl-2,2′-bipyridine (dtbpy) at 120 °C.[8,9] Although this was the first example of preparing synthetically useful aromatic fluorosilanes directly from arenes, the protocol suffers from low regioselectivities especially for functionalized arenes and from the requirement of a large excess of arenes (60 equiv) to achieve high yields. Here we report a highly regioselective and more efficient protocol for iridium-catalyzed aromatic C−H silylation of arenes with fluorodisilanes. The use of 2,9-diisopropyl-1,10-phenanthroline (dipphen) as a ligand and 1,2-di-*sec*-butyl-1,1,2,2-tetrafluorodisilane (*s*-BuF_2Si)$_2$ as a silylation reagent

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Scheme 1. Iridium(I)-Catalyzed Aramatic C—H Silylation of Arenes

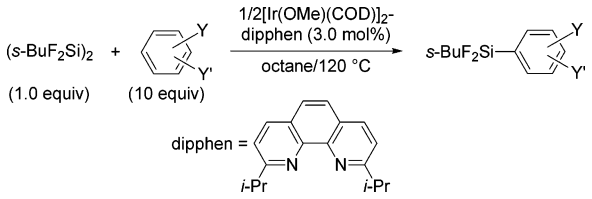
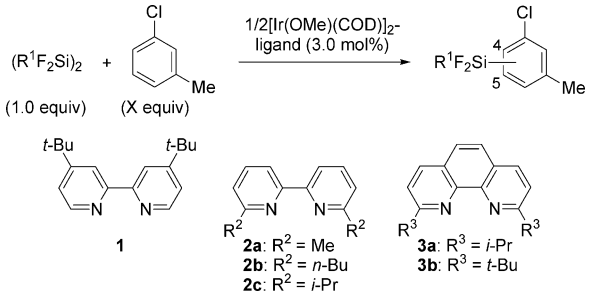


Table 1. Reaction Conditions for 3-Chlorotoluene[a]



entry	R^1	X	ligand	solvent	temp (°C)	time (h)	yield (%)[b]	5-:4-[c]
1	*t*-Bu	60	**1**	none	120	16	72	87:13
2	*t*-Bu	60	**2a**	none	120	16	60	99:1
3	*t*-Bu	60	**2b**	none	120	16	56	99:1
4	*t*-Bu	60	**2c**	none	120	16	20	>99:<1
5	*t*-Bu	60	**3a**	none	120	16	42	>99:<1
6	*t*-Bu	60	**3b**	none	120	16	0	—
7	*t*-Bu	10	**3a**	octane	120	16	28	>99:<1
8	*n*-Bu	10	**3a**	octane	120	16	32	>99:<1
9	*s*-Bu	10	**3a**	octane	120	16	99	>99:<1
10	*s*-Bu	5.0	**3a**	octane	120	16	74	>99:<1
11	*s*-Bu	10	**3a**	octane	80	16	30	>99:<1
12	*s*-Bu	10	**3a**	octane	120	32	99	>99:<1

[a] A mixture of a disilane (1.0 mmol), 3-chlorotoluene, $[Ir(OMe)(COD)]_2$ (0.015 mmol), a ligand (0.030 mmol), and octane (6 mL) was stirred in a sealed tube. [b] GC yields based on disilanes. [c] Isomer ratios were determined by GC and ^1H NMR.

allows the formation of regioisomerically pure arylfluorosilanes in high yields from a reduced amount of arenes (10 equiv) in octane at 120 °C (Scheme 1).

Results and Discussion

Our initial efforts were focused on improvement of regioselectivity (entries 1−6 in Table 1). As reported previously, the C—H silylation of neat 3-chlorotoluene (60 mmol) with (*t*-$BuF_2Si)_2$ (1.0 mmol) in the presence of a $1/2[Ir(OMe)(COD)]_2$−dtbpy (**1**) catalyst (0.030 mmol) at 120 °C for 16 h afforded a regioisomeric mixture of 5- and 4-silylated products in a ratio of 87:13 (entry 1).[8] This result indicates that the iridium species ligated by **1** is insufficient to recognize the steric environment of the substrate. Thus, we examined bulky 2,2′-bipyridine (bpy) ligands. The selectivity was improved to 99:1 when using 6,6′-di-Me-bpy (**2a**) and 6,6′-di-*n*-Bu-bpy (**2b**) (entries 2 and 3). Sterically more hindered 6,6′-di-*i*-Pr-bpy (**3b**) produced the desired 5-silylated product as a single isomer, but the reaction resulted in only a 20% yield (entry 4). Presumably, twisting between two pyridyl units arising from steric hindrance around the iridium center leads to the low activity because of low coordinating ability of the ligand to the iridium. On the basis of this hypothesis, we investigated the reaction by using structurally rigid 1,10-phenanthroline (phen) derivatives as ligands. As we expected, 2,9-di-*i*-Pr-phen (dipphen) (**3a**) displayed higher reactivity and the yield was improved to 42% (entry 5), while the use of sterically more hindered 2,9-di-*t*-Bu-phen (**3b**) led to no reaction (entry 6).

Although the silylation has been carried out in the presence of a large excess of neat arene, the reaction of a reduced amount of substrate in an inert solvent would be desirable for solid or expensive substrates. From this point of view, we attempted C—H silylation of 3-chlorotoluene (5.0−10 mmol) in octane (6 mL) by using optimized ligand **3a** (entries 7−12 in Table 1). The silylation by (*t*-$BuF_2Si)_2$ and by (*n*-$BuF_2Si)_2$ resulted in quite low yields (entries 7 and 8). On the other hand, (*s*-$BuF_2Si)_2$ unexpectedly displayed high reactivity to produce the corresponding silylated product in quantitative yield while maintaining high regioselectivity (entry 9). The reaction using 5.0 mmol of substrate and conducted at 80 °C resulted in a decreased yield (entries 10 and 11). Prolongation of the reaction time led to no increase in the yield, indicating that one of the two silyl groups in the disilane can be introduced to arene in the present silylation (entry 12).

Representative results of aromatic C—H silylation of arenes with (*s*-$BuF_2Si)_2$ catalyzed by the combination of $1/2[Ir(OMe)(COD)]_2$ and dipphen **3a** at 120 °C in octane are summarized in Table 2. Reactions occurred at C—H bonds located *meta* or *para* to a substituent in preference to those located in the *ortho* position. Thus, *o*- and *m*-xylene gave a single product (entries 1 and 2), but the reaction at *o*-carbon of *p*-xylene did not proceed at all due to steric hindrance of the substituent. Bicyclic substrates such as tetralin and indan yielded silylated products (entries 3 and 4). Both electron-rich and electron-poor arenes participated in silylation reactions (entries 5−8). The reactions of 1,3-disubstituted arenes selectively occurred only at the common *meta* position; therefore, regioisomerically pure arylsilanes were obtained even with two different substituents on the arene (entries 9−11). The silylation of indan and 1,3-dichlorobenzene by the previous protocol gave regioisomeric mixtures, but that by the present protocol yielded single isomers (entries 4 and 7), while 3-methylanisole unfortunately produced a mixture of two isomers probably due to small steric hindrance of the MeO group (entry 12).

C—H silylation by the present protocol was suitable for arenes possessing various functional groups, such as OMe, Cl, Br, CO_2-Me, and CF_3 or benzylic C—H bonds (entries 5−12). It is notable that aromatic C—H bonds were selectively silylated even in the presence of weaker benzylic C—H bonds or C—Br bonds.[10] Although the reactions of 1,2-diclorobenzene and 1,3-bis(trifluoromethyl) benzene by the previous protocol resulted in a low yield or led to no reaction, those by the present protocol gave the corresponding silylated products in high yields (entries 6 and 8).

In contrast to the control of regioselectivity of electrophilic and nucleophilic substitution of arenes by the electronic properties of substituents, the regiochemistry of C—H silylation of arenes is primarily controlled by the steric effects of these substituents. Both electron-rich and electron-poor monosubstituted arenes underwent smooth reaction with (*s*-$BuF_2Si)_2$ under the optimized conditions to produce regioisomeric mixtures of the *meta*- and *para*-silylated products in statistical ratios (ca. 2:1). An *ortho* isomer was not detected in any cases probably due to the steric effect of the substituents (Scheme 2).

Not only regioselectivity but also reactivity of the C—H silylation of arenes is not influenced by the electronic properties of substituents. When an equimolar mixture of toluene (5.0

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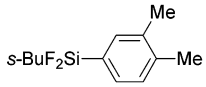
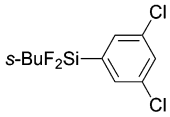
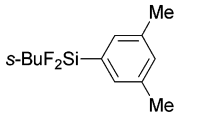
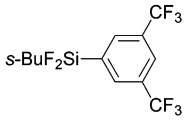
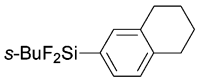
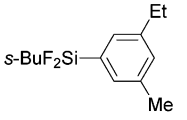
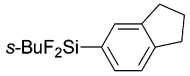
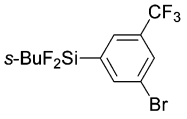
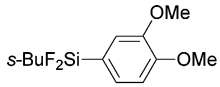
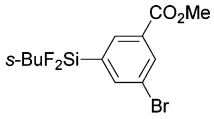
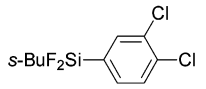
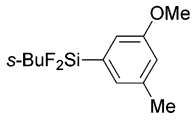
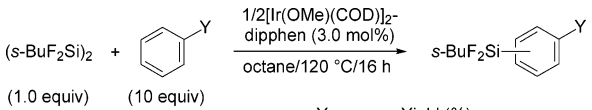
Table 2. Aromatic C—H Silylation of Disubstituted Arenes[a]

Entry	Product[b]	Yield (%)[c]	Entry	Product[b]	Yield (%)[c]
1		92	7		99
2		71	8		80
3		99	9		76
4		99	10		87
5		97	11		80
6		95	12		91[d]

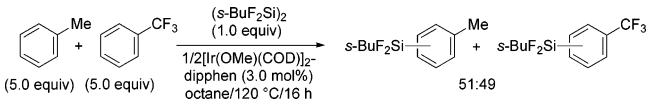
[a] All reactions were carried out at 120 °C for 16 h by using (*s*-$BuF_2Si)_2$ (1.0 mmol), an arene (10 mmol), $[Ir(OMe)(COD)]_2$ (0.015 mmol), dipphen (0.030 mmol), and octane (6 mL) in a sealed tube. [b]Isomeric purities over 99% were determined by GC and ^1H NMR. [c]GC yields based on (*s*-$BuF_2Si)_2$. [d]The reaction gave a mixture of 5- and 6-silylated products in a ratio of 87:13.

Scheme 2. Aromatic C—H Silylation of Monosubstituted Arenes



Y	Yield (%)	*o*-:*m*-:*p*-
Me	90	0:60:40
Cl	98	0:64:36
CF_3	98	0:67:33

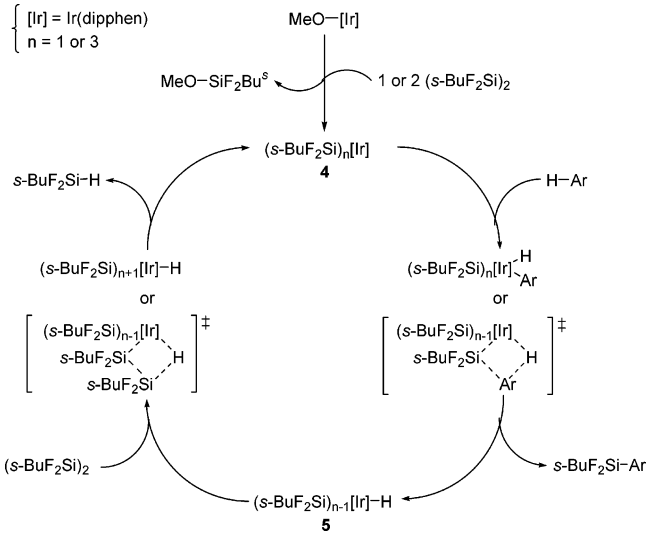
Scheme 3. Evaluation of Reactivity Difference between Toluene and Benzotrifluoride



equiv) and benzotrifluoride (5.0 equiv) was allowed to react with (*s*-$BuF_2Si)_2$ (1.0 equiv) under the optimized conditions, silylated products resulting from the reaction with both arenes were obtained in a ratio of 51:49 (Scheme 3).

Although we have not investigated the reaction mechanism yet, the present C—H silylation may proceed through (a) generation of a (silyl) iridium intermediate (**4**) by the reaction of (*s*-$BuF_2Si)_2$ with an iridium(I) complex, (b) oxidative addition of an aromatic C—H bond to **4** followed by reductive elimination of an arylsilane or direct σ-bond metathesis between an Ir—Si bond of **4** and an aromatic H—C bond to form an iridium hydride complex (**5**), and (c) oxidative addition of (*s*-$BuF_2Si)_2$ to **5** followed by reductive elimination of a hydrosilane or direct σ-bond metathesis between (*s*-$BuF_2Si)_2$ and **5** to regenerate a (silyl) iridium intermediate **4** (Scheme 4). It is unclear at this

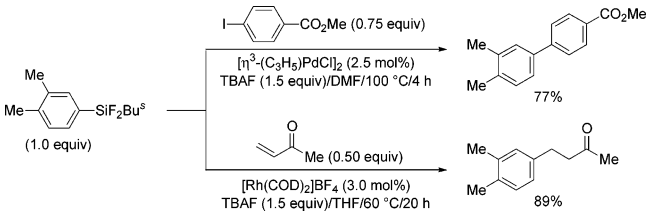
Scheme 4. Plausible Mechanism



moment whether the mechanism involves a mono(silyl) iridium(I) or a tris(silyl) iridium(III) intermediate, and it is not clear why two of the silyl groups in (*s*-$BuF_2Si)_2$ do not participate in the reaction.

Arylfluorosilanes thus obtained are useful reagents for carbon—carbon bond formation reactions (Scheme 5). For example, they cross-coupled with aryl halides in the presence of a palladium catalyst and a fluoride ion source in DMF to produce the corresponding unsymmetrical biaryls in high yields.[3a] Also, they participated in 1,4-addition to α,β-unsaturated ketones in the presence of a rhodium catalyst and a fluoride ion source in THF, giving β-arylketones in excellent yields.[4b]

Scheme 5. Synthetic Application of Arylfluorosilanes



Experimental Section

General Procedures. All the experiments were carried out under a nitrogen atmosphere. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solutions using a JEOL JNM-A400II spectrometer (400 or 100 MHz) and Me_4Si or residual protiated solvent as an internal standard. High-resolution mass spectra were obtained on a JEOL JMS-DX303. Elemental analyses were performed on a JSL Micro Corder JM10. GC analyses were conducted on a Hitachi G-3500 instrument equipped with a glass column (OV-101 on Uniport B, 2 m). 1,2-Di-*tert*-butyl-1,1,2,2-tetrafluorodisilane,[11] [Ir(OMe)(COD)]$_2$,[12] 6,6′-dibutyl-2,2′-bipyridine,[13] 6,6′-diisopropyl-2,2′-bipyridine,[14] and 2,9-di-*tert*-butyl-1,10-phenanthroline[15] were synthesized by the reported procedures. 1,2-Dibutyl-1,1,2,2-tetrafluorodisilane, 1,2-di-*sec*-butyl-1,1,2,2-tetrafluorodisilane, and 2,9-diisopropyl-1,10-phenanthroline were prepared by the methods similar to those for 1,2-di-*tert*-butyl-1,1,2,2-tetrafluorodisilane[11] and 2,9-di-*sec*-butyl-1,10-phenanthroline,[16] respectively. Arenes and octane were purified by distillation from appropriate drying agents. All of the other compounds were used as received.

1,2-Dibutyl-1,1,2,2-tetrafluorodisilane. Purity determined by NMR and GC analyses: >95%. Bp: 89 °C/38 mmHg. ^{1}H NMR: δ 0.90−0.98 (m, 4 H), 0.92 (t, 6 H, J = 7.3 Hz), 1.35−1.52 (m, 8 H). ^{13}C NMR: δ 13.50, 15.57−15.78 (m), 22.24, 25.61. HRMS: calcd for $C_8H_{18}F_4Si_2$ 246.0884, found 246.0873. Anal. Calcd for $C_8H_{18}F_4Si_2$: C, 39.00; H, 7.36. Found: C, 38.63; H, 7.37.

1,2-Di-*sec*-butyl-1,1,2,2-tetrafluorodisilane. Purity determined by NMR and GC analyses: >95%. Bp: 75 °C/30 mmHg. ^{1}H NMR: δ 0.97−1.07 (m, 2 H), 1.01 (t, 6 H, J = 7.3 Hz), 1.10 (d, 6 H, J = 7.3 Hz), 1.36−1.47 (m, 2 H), 1.62−1.72 (m, 2 H). ^{13}C NMR: δ 10.92, 12.80, 22.24, 22.72−22.82 (m). HRMS: calcd for $C_8H_{18}F_4Si_2$ 246.0884, found 246.0903. Anal. Calcd for $C_8H_{18}F_4Si_2$: C, 39.00; H, 7.36. Found: C, 38.71; H, 7.31.

2,9-Diisopropyl-1,10-phenanthroline. Purity determined by NMR analyses: >95%. Mp: 98.8−99.2 °C. ^{1}H NMR: δ 1.47 (d, 12 H, J = 7.1 Hz), 3.50−3.61 (m, 2 H), 7.54 (d, 2 H, J = 8.3 Hz), 7.68 (s, 2 H), 8.14 (d, 2 H, J = 8.3 Hz). ^{13}C NMR: δ 22.89, 37.29, 120.07, 125.43, 127.25, 136.37, 145.24, 167.84. HRMS: calcd for $C_{18}H_{20}N_2$ 264.1626, found 264.1640. Anal. Calcd for $C_{18}H_{20}N_2$: C, 81.78; H, 7.63; N, 10.60. Found: C, 81.91; H, 7.66; N, 10.57.

Reaction Conditions for Aromatic C−H Silylation of 3-Chlorotoluene (entries 7−9 in Table 1). A resealable Schlenk tube containing [Ir(OMe)(COD)]$_2$ (9.9 mg, 0.015 mmol) and 2,9-diisopropyl-1,10-phenanthroline (7.9 mg, 0.030 mmol) was flushed with nitrogen and then charged with octane (6 mL), a disilane (246 mg, 1.0 mmol), and 3-chlorotoluene (1.27 g, 10 mmol). The tube was sealed with a Teflon screwcap, and the mixture was stirred at 120 °C for 16 h. The product was isolated by Kugelrohr distillation to give an analytically pure sample.

5-(*tert*-Butyldifluorosilyl)-3-chlorotoluene (entry 7). Purity determined by NMR and GC analyses: >95%. Bp: 58 °C/1.3 mmHg (Kugelrohr). ^{1}H NMR: δ 1.08 (s, 9 H), 2.37 (s, 3 H), 7.33 (s, 2 H), 7.42 (s, 1 H). ^{13}C NMR: δ 17.80 (t, J = 14.9 Hz), 21.11, 24.69, 129.54 (t, J = 18.2 Hz), 131.00, 132.48, 132.91, 134.49, 139.98. HRMS: calcd for $C_{11}H_{15}ClF_2Si$ 248.0600, found 248.0599. Anal. Calcd for $C_{11}H_{15}ClF_2Si$: C, 53.11; H, 6.08. Found: C, 52.89; H, 6.07.

5-(Butyldifluorosilyl)-3-chlorotoluene (entry 8). Purity determined by NMR and GC analyses: >95%. Bp: 62 °C/1.2 mmHg (Kugelrohr). ^{1}H NMR: δ 0.91 (t, 3 H, J = 7.2 Hz), 1.01−1.08 (m, 2 H), 1.35−1.53 (m, 4 H), 2.37 (s, 3 H), 7.31 (s, 1 H), 7.33 (s, 1 H), 7.40 (s, 1 H). ^{13}C NMR: δ 11.57 (t, J = 14.9 Hz), 13.53, 21.09, 23.43, 25.70, 130.36 (t, J = 2.1 Hz), 131.32 (t, J = 19.0 Hz), 132.22 (t, J = 2.1 Hz), 132.51, 134.52, 140.09. HRMS: calcd for $C_{11}H_{15}ClF_2Si$ 248.0600, found 248.0597. Anal. Calcd for $C_{11}H_{15}ClF_2Si$: C, 53.11; H, 6.08. Found: C, 53.11; H, 6.13.

5-(*sec*-Butyldifluorosilyl)-3-chlorotoluene (entry 9 in Table 1). Purity determined by NMR and GC analyses: >95%. Bp: 57 °C/1.2 mmHg (Kugelrohr). ^{1}H NMR: δ 0.99 (t, 3 H, J = 7.3 Hz), 1.08−2.20 (m, 1 H), 1.11 (d, 3 H, J = 5.8 Hz), 1.35−1.46 (m, 1 H), 1.61−1.72 (m, 1 H), 2.37 (s, 3 H), 7.31−7.33 (m, 2 H), 7.39−7.41 (m, 1 H). ^{13}C NMR: δ 12.24, 12.94, 19.47 (t, J = 14.1 Hz), 21.11, 23.21, 130.58 (t, J = 18.6 Hz), 130.58 (t, J = 2.1 Hz), 132.46, 132.48 (t, J = 2.1 Hz), 134.51, 140.06. HRMS: calcd for $C_{11}H_{15}ClF_2Si$ 248.0600, found 248.0609. Anal. Calcd for $C_{11}H_{15}ClF_2Si$: C, 53.11; H, 6.08. Found: C, 53.08; H, 5.85.

General Procedure for the Aromatic C−H Silylation (Table 2 and Scheme 2). A resealable Schlenk tube containing [Ir(OMe)(COD)]$_2$ (9.9 mg, 0.015 mmol) and 2,9-diisopropyl-1,10-phenanthroline (7.9 mg, 0.030 mmol) was flushed with nitrogen and then charged with octane (6 mL), 1,2-di-*sec*-butyl-1,1,2,2-tetrafluorodisilane (246 mg, 1.0 mmol), and an arene (10 mmol). The tube was sealed with a Teflon screwcap, and the mixture was stirred at 120 °C for 16 h. The product was isolated by Kugelrohr distillation to give an analytically pure sample.

4-(*sec*-Butyldifluorosilyl)-1,2-dimethylbenzene (entry 1 in Table 2). Purity determined by NMR and GC analyses: >95%. Bp: 75 °C/2.5 mmHg (Kugelrohr). ^{1}H NMR: δ 0.99 (t, 3 H, J = 7.4 Hz), 1.11−1.20 (m, 1 H), 1.12 (d, 3 H, J = 5.4 Hz), 1.35−1.46 (m, 1 H), 1.63−1.73 (m, 1 H), 2.30 (s, 6 H), 7.22 (d, 1 H, J = 7.3 Hz), 7.39 (d, 1 H, J = 7.8 Hz), 7.41 (s, 1 H). ^{13}C NMR: δ 12.38, 12.98, 19.66, 19.66 (t, J = 14.5 Hz), 20.00, 23.37, 125.53 (t, J = 18.2 Hz), 129.59, 131.55, 134. 96, 136.61, 140.70. HRMS: calcd for $C_{12}H_{18}F_2Si$ 228.1146, found 228.1133. Anal. Calcd for $C_{12}H_{18}F_2Si$: C, 63.12; H, 7.95. Found: C, 62.89; H, 8.06.

5-(*sec*-Butyldifluorosilyl)-1,3-dimethylbenzene (entry 2 in Table 2). Purity determined by NMR and GC analyses: >95%. Bp: 55 °C/2.5 mmHg (Kugelrohr). ^{1}H NMR: δ 0.99 (t, 3 H, J = 7.3 Hz), 1.11−1.21 (m, 1 H), 1.11 (d, 3 H, J = 4.9 Hz), 1.32−1.46 (m, 1 H), 1.63−1.73 (m, 1 H), 2.34 (s, 6 H), 7.16 (s, 1 H), 7.26 (s, 2 H). ^{13}C NMR: δ 12.35, 12.97, 19.58 (t, J = 14.9 Hz), 21.27, 23.31, 128.25 (t, J = 18.2 Hz), 131.44 (t, J = 2.1 Hz), 133.41, 137.71. HRMS: calcd for $C_{12}H_{18}F_2Si$ 228.1146, found 228.1136. Anal. Calcd for $C_{12}H_{18}F_2Si$: C, 63.12; H, 7.95. Found: C, 62.73; H, 7.84.

6-(*sec*-Butyldifluorosilyl) tetralin (entry 3 in Table 2). Purity determined by NMR and GC analyses: >95%. Bp: 65 °C/1.3 mmHg (Kugelrohr). ^{1}H NMR: δ 1.00 (t, 3 H, J = 7.3 Hz), 1.13−1.19 (m, 4 H), 1.38−1.45 (m, 1 H), 1.64−1.72 (m, 1 H), 1.80−1.84 (m, 4 H), 2.80 (br s, 4 H), 7.14 (d, 1 H, J = 8.1 Hz), 7.36 (s, 1 H), 7.36 (d, 1 H, J = 7.6 Hz). ^{13}C NMR: δ 12.38, 12.99, 19.64 (t, J = 14.5 Hz), 22.90, 23.06, 23.36, 29.25, 29.59, 125.10 (t, J = 18.6 Hz), 129.11, 130.73, 134.86, 137.21, 141.30. HRMS: calcd for $C_{14}H_{20}F_2Si$ 254.1302, found 254.1295. Anal. Calcd for $C_{14}H_{20}F_2Si$: C, 66.10; H, 7.92. Found: C, 66.15; H, 7.69.

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5-(*sec*-Butyldifluorosilyl) indan (entry 4 in Table 2). Purity determined by NMR and GC analyses: >95%. Bp: 53 °C/1.2 mmHg (Kugelrohr). ^{1}H NMR: δ 1.01 (t, 3 H, J = 7.3 Hz), 1.13−1.21 (m, 1 H), 1.14 (d, 3 H, J = 5.1 Hz), 1.37−1.48 (m, 1 H), 1.65−1.75 (m, 1 H), 2.06−2.13 (m, 2 H), 2.96 (t, 4 H, J = 7.4 Hz), 7.32 (d, 1 H, J = 7.3 Hz), 7.44 (d, 1 H, J = 7.3 Hz), 7.54 (s, 1 H). ^{13}C NMR: δ 12.39, 13.00, 19.67 (t, J = 14.5 Hz), 23.36, 25.05, 32.65, 33.12, 124.50, 125.70 (t, J = 18.2 Hz), 129.75 (t, J = 2.1 Hz), 131.81 (t, J = 2.1 Hz), 144.19, 148.40. HRMS: calcd for $C_{13}H_{18}F_2Si$ 240.1146, found 240.1146. Anal. Calcd for $C_{13}H_{18}F_2Si$: C, 64.96; H, 7.55. Found: C, 64.64; H, 7.62.

4-(*sec*-Butyldifluorosilyl)-1,2-dimethoxybenzene (entry 5 in Table 2). Purity determined by NMR and GC analyses: >95%. Bp: 73 °C/1.2 mmHg (Kugelrohr). ^{1}H NMR: δ 0.99 (t, 3 H, J = 7.4 Hz), 1.10−1.21 (m, 1 H), 1.12 (d, 3 H, J = 5.6 Hz), 1.35−1.46 (m, 1 H), 1.62−1.73 (m, 1 H), 3.91 (s, 6 H), 6.95 (d, 1 H, J = 8.1 Hz), 7.09 (d, 1 H, J = 1.2 Hz), 7.24 (dd, 1 H, J = 1.3 and 7.9 Hz). ^{13}C NMR: δ 12.38, 12.94, 19.62 (t, J = 14.9 Hz), 23.33, 55.68, 55.83, 111.06, 115.49, 119.73 (t, J = 19.0 Hz), 127.69 (t, J = 2.1 Hz), 148.84, 151.90. HRMS: calcd for $C_{12}H_{18}F_2O_2Si$ 260.1044, found 260.1042. Anal. Calcd for $C_{12}H_{18}F_2O_2Si$: C, 55.36; H, 6.97. Found: C, 55.12; H, 6.84.

4-(*sec*-Butyldifluorosilyl)-1,2-dichlorobenzene (entry 6 in Table 2). Purity determined by NMR and GC analyses: >95%. Bp: 60 °C/1.2 mmHg (Kugelrohr). ^{1}H NMR: δ 0.99 (t, 3 H, J = 7.3 Hz), 1.10−1.21 (m, 1 H), 1.11 (d, 3 H, J = 6.8 Hz), 1.35−1.46 (m, 1 H), 1.60−1.71 (m, 1 H), 7.46 (d, 1 H, J = 7.8 Hz), 7.54 (d, 1 H, J = 8.1 Hz), 7.71 (s, 1 H). ^{13}C NMR: δ 12.20, 12.92, 19.44 (t, J = 14.1 Hz), 23.19, 128.99 (t, J = 19.0 Hz), 130.72, 132.86 (t, J = 2.1 Hz), 133.22, 135.65 (t, J = 2.1 Hz), 136.47. HRMS: calcd for $C_{10}H_{12}Cl_2F_2Si$ 268.0053, found 268.0048. Anal. Calcd for $C_{10}H_{12}Cl_2F_2Si$: C, 44.62; H, 4.49. Found: C, 44.61; H, 4.46.

5-(*sec*-Butyldifluorosilyl)-1,3-dichlorobenzene (entry 7 in Table 2). Purity determined by NMR and GC analyses: >95%. Bp: 47 °C/1.2 mmHg (Kugelrohr). ^{1}H NMR: δ 1.00 (t, 3 H, J = 7.3 Hz), 1.11−1.23 (m, 1 H), 1.12 (d, 3 H, J = 6.8 Hz), 1.36−1.47 (m, 1 H), 1.61−1.71 (m, 1 H), 7.49 (d, 2 H, J = 2.0 Hz), 7.52 (t, 1 H, J = 2.0 Hz). ^{13}C NMR: δ 12.16, 12.91, 19.37 (t, J = 14.1 Hz), 23.13, 131.75 (t, J = 2.1 Hz), 131.80, 132.77 (t, J = 19.0 Hz), 135.60. HRMS: calcd for $C_{10}H_{12}Cl_2F_2Si$ 268.0053, found 268.0050. Anal. Calcd for $C_{10}H_{12}Cl_2F_2Si$: C, 44.62; H, 4.49. Found: C, 44.46; H, 4.45.

5-(*sec*-Butyldifluorosilyl)-1,3-bis(trifluoromethyl)benzene (entry 8 in Table 2). Purity determined by NMR and GC analyses: >95%. Bp: 68 °C/26 mmHg (Kugelrohr). ^{1}H NMR: δ 1.02 (t, 3 H, J = 7.4 Hz), 1.14 (d, 3 H, J = 7.3 Hz), 1.21−1.30 (m, 1 H), 1.39−1.50 (m, 1 H), 1.64−1.74 (m, 1 H), 8.04 (s, 1 H), 8.08 (s, 2 H). ^{13}C NMR: δ 12.11, 12.89, 19.28 (t, J = 13.6 Hz), 23.08, 123.10 (q, J = 272.9 Hz), 125.38−125.52 (m), 131.65 (q, J = 33.6 Hz), 131.90 (t, J = 19.4 Hz), 133.75. HRMS: calcd for $C_{12}H_{12}F_8Si$ 336.0580, found 336.0586. Anal. Calcd for $C_{12}H_{12}F_8Si$: C, 42.86; H, 3.60. Found: C, 42.69; H, 3.57.

5-(*sec*-Butyldifluorosilyl)-3-ethyltoluene (entry 9 in Table 2). Purity determined by NMR and GC analyses: >95%. Bp: 42 °C/1.2 mmHg (Kugelrohr). ^{1}H NMR: δ 0.99 (t, 3 H, J = 7.3 Hz), 1.11−1.20 (m, 1 H), 1.12 (d, 3 H, J = 5.4 Hz), 1.23 (t, 3 H, J = 7.7 Hz), 1.37−1.46 (m, 1 H), 1.63−1.71 (m, 1 H), 2.36 (s, 3 H), 2.63 (q, 2 H, J = 7.6 Hz), 7.18 (s, 1 H), 7.28 (s, 2 H). ^{13}C NMR: δ 12.36, 12.98, 15.59, 19.60 (t, J = 14.5 Hz), 21.35, 23.32, 28.74, 128.32 (t, J = 17.8 Hz), 130.36 (t, J = 2.1 Hz), 131.73 (t, J = 2.1 Hz), 132.23, 137.77, 144.07. HRMS: calcd for $C_{13}H_{20}F_2Si$ 242.1302, found 242.1309. Anal. Calcd for $C_{13}H_{20}F_2Si$: C, 64.42; H, 8.32. Found: C, 64.42; H, 8.37.

3-Bromo-5-(*sec*-butyldifluorosilyl) benzotrifluoride (entry 10 in Table 2). Purity determined by NMR and GC analyses: >95%. Bp: 43 °C/2.5 mmHg (Kugelrohr). ^{1}H NMR: δ 1.01 (t, 3 H, J = 7.4 Hz), 1.13 (d, 3 H, J = 7.3 Hz), 1.17−1.28 (m, 1 H), 1.37−1.48 (m, 1 H), 1.62−1.72 (m, 1 H), 7.80 (t, 1 H, J = 0.7 Hz), 7.92 (s, 1 H), 7.94 (s, 1 H). ^{13}C NMR: δ 12.13, 12.89, 19.34 (t, J = 13.7 Hz), 23.11, 122.91 (q, J = 273.5), 123.43, 128.77−128.93 (m), 131.57 (q, J = 3.6 Hz), 132.57 (q, J = 32.8 Hz), 132.71 (t, J = 19.0 Hz), 139.91 (q, J = 1.7 Hz). HRMS: calcd for $C_{11}H_{12}BrF_5Si$ 345.9811, found 345.9805. Anal. Calcd for $C_{11}H_{12}BrF_5Si$: C, 38.05; H, 3.48. Found: C, 38.08; H, 3.44.

Methyl 3-bromo-5-(*sec*-butyldifluorosilyl)benzoate (entry 11 in Table 2). Purity determined by NMR and GC analyses: >95%. Bp: 79 °C/1.2 mmHg (Kugelrohr). ^{1}H NMR: δ 0.99 (t, 3 H, J = 7.4 Hz), 1.11 (d, 3 H, J = 7.3 Hz), 1.16−1.26 (m, 1 H), 1.36−1.47 (m, 1 H), 1.61−1.71 (m, 1 H), 3.94 (s, 3 H), 7.93 (dd, 1 H, J = 2.0 and 1.0 Hz), 8.22 (dd, 1 H, J = 1.5 and 1.0 Hz), 8.31 (t, 1 H, J = 1.7 Hz). ^{13}C NMR: δ 12.16, 12.89, 19.33 (t, J = 13.7 Hz), 23.12, 52.58, 123.17, 131.78 (t, J = 19.0 Hz), 132.02, 133.22 (t, J = 2.1 Hz), 135.58, 140.59 (t, J = 2.1 Hz), 165.25. HRMS: calcd for $C_{12}H_{15}BrF_2O_2Si$ 335.9992, found 335.9988. Anal. Calcd for $C_{12}H_{15}BrF_2O_2Si$: C, 42.74; H, 4.48. Found: C, 42.71; H, 4.34.

(*sec*-Butyldifluorosilyl)-3-methylanisole (entry 12 in Table 2). Purity determined by NMR and GC analyses: >95%. Bp: 47 °C/1.2 mmHg (Kugelrohr). ^{1}H NMR: δ (5-silyl isomer) 0.99 (t, 3 H, J = 7.4 Hz), 1.11−1.19 (m, 1 H), 1.12 (d, 3 H, J = 5.4 Hz), 1.37−1.44 (m, 1 H), 1.62−1.71 (m, 1 H), 2.36 (s, 3 H), 3.81 (s, 3 H), 6.87 (s, 1 H), 6.96 (d, 1 H, J = 2.2 Hz), 7.04 (s, 1 H), (6-silyl isomer) 0.95 (t, 3 H, J = 8.1 Hz), 1.07 (d, 3 H, J = 7.3 Hz), 1.11−1.19 (m, 1 H), 1.37−1.44 (m, 1 H), 1.62−1.71 (m, 1 H), 2.38 (s, 3 H), 3.83 (s, 3 H), 6.70 (s, 1 H), 6.84 (d, 1 H, J = 7.6 Hz), 7.43 (d, 1 H, J = 7.6 Hz). ^{13}C NMR: δ (5-silyl isomer) 12.37, 13.00, 19.56 (t, J = 14.5 Hz), 21.48, 23.32, 55.20, 115.77 (t, J = 2.1 Hz), 118.28, 126.79 (t, J = 2.1 Hz), 129.54 (t, J = 18.2 Hz), 139.75, 159.30, (6-silyl isomer) not assigned. HRMS: calcd for $C_{12}H_{18}F_2OSi$ 244.1095, found 244.1092. Anal. Calcd for $C_{12}H_{18}F_2OSi$: C, 58.98; H, 7.42. Found: C, 58.68; H, 7.33.

(*sec*-Butyldifluorosilyl)toluene (Scheme 2). Purity determined by NMR and GC analyses: >95%. Bp: 64 °C/30 mmHg (Kugelrohr). ^{1}H NMR: δ (3-silyl isomer) 1.00 (t, 3 H, J = 7.3 Hz), 1.11−1.22 (m, 1 H), 1.12 (d, 3 H, J = 5.4 Hz), 1.36−1.47 (m, 1 H), 1.63−1.73 (m, 1 H), 2.39 (s, 3 H), 7.34 (d, 2 H, J = 5.1 Hz), 7.45 (t, 1 H, J = 4.3 Hz), 7.47 (s, 1 H), (4-silyl isomer) 0.99 (t, 3 H, J = 7.4 Hz), 1.11−1.22 (m, 1 H), 1.12 (d, 3 H, J = 5.4 Hz), 1.35−1.46 (m, 1 H), 1.62−1.72 (m, 1 H), 2.39 (s, 3 H), 7.26 (d, 2 H, J = 7.6 Hz), 7.55 (d, 2 H, J = 8.1 Hz). ^{13}C NMR: δ (3-silyl isomer) 12.34, 12.97, 19.59 (t, J = 14.9 Hz), 21.43, 23.32, 128.17, 128.40 (t, J = 18.6 Hz), 130.91 (t, J = 2.1 Hz), 132.47, 134.38 (t, J = 1.7 Hz), 137.79, (4-silyl isomer) 12.35, 12.97, 19.65 (t, J = 14.9 Hz), 21.67, 23.35, 125.02 (t, J = 18.2 Hz), 129.05, 133.92 (t, J = 2.1 Hz), 141.95. HRMS: calcd for $C_{11}H_{16}F_2Si$ 214.0989, found 214.0979. Anal. Calcd for $C_{11}H_{16}F_2Si$: C, 61.64; H, 7.52. Found: C, 61.42; H, 7.52.

(*sec*-Butyldifluorosilyl) chlorobenzene (Scheme 2). Purity determined by NMR and GC analyses: >95%. 68 °C/30 mmHg (Kugelrohr). ^{1}H NMR: δ (3-silyl isomer) 0.99 (t, 3 H, J = 7.4 Hz), 1.11−1.23 (m, 1 H), 1.12 (d, 3 H, J = 6.6 Hz), 1.36−1.47 (m, 1 H), 1.61−1.73 (m, 1 H), 7.39 (t, 1 H, J = 7.7 Hz), 7.49−7.54 (m, 2 H), 7.61−7.62 (m, 1 H), (4-silyl isomer) 0.99 (t, 3 H, J = 7.4 Hz), 1.10−1.22 (m, 1 H), 1.11 (d, 3 H, J = 6.3 Hz), 1.35−1.46 (m, 1 H), 1.60−1.71 (m, 1 H), 7.43 (d, 2 H, J = 8.3 Hz), 7.59 (d, 2 H, J = 8.5 Hz). ^{13}C NMR: δ (3-silyl isomer) 12.21, 12.90, 19.48 (t, J = 14.1 Hz), 23.23, 129.83, 131.00 (t, J = 18.6 Hz), 131.81 (t, J = 2.5 Hz), 131.84, 133.63 (t, J = 2.1 Hz), 134.80, (4-silyl isomer) 12.25, 12.92, 19.54 (t, J = 14.1 Hz), 23.27, 126.83 (t, J = 19.0 Hz), 128.68, 135.25 (t, J = 2.1 Hz), 138.28. HRMS: calcd for $C_{10}H_{13}ClF_2Si$ 234.0443, found 234.0446. Anal. Calcd for $C_{10}H_{13}ClF_2Si$: C, 49.24; H, 4.88. Found: C, 49.11; H, 4.87.

(*sec*-Butyldifluorosilyl) benzotrifluoride (Scheme 2). Purity determined by NMR and GC analyses: >95%. Bp: 48 °C/50

mmHg (Kugelrohr). ^{1}H NMR: δ (3-silyl isomer) 1.00 (t, 3 H, J = 7.3 Hz), 1.13 (d, 3 H, J = 7.1 Hz), 1.16−1.25 (m, 1 H), 1.39−1.46 (m, 1 H), 1.64−1.71 (m, 1 H), 7.56 (t, 1 H, J = 7.7 Hz), 7.78 (d, 1 H, J = 7.8 Hz), 7.84 (d, 1 H, J = 7.3 Hz), 7.90 (d, 1 H, J = 0.7 Hz), (4-silyl isomer) 1.00 (t, 3 H, J = 7.3 Hz), 1.12 (d, 3 H, J = 7.1 Hz), 1.15−1.25 (m, 1 H), 1.36−1.47 (m, 1 H), 1.62−1.72 (m, 1 H), 7.70 (d, 2 H, J = 8.3 Hz), 7.79 (d, 2 H, J = 7.8 Hz). ^{13}C NMR: δ (3-silyl isomer) 12.19, 12.89, 19.44 (t, J = 14.1 Hz), 23.20, 123.92 (q, J = 272.3), 128.38 (t, J = 3.8 Hz), 128.72, 129.95 (t, J = 19.0 Hz), 130.35−130.51 (m), 130.71 (q, J = 32.5 Hz), 137.20 (q, J = 0.8 Hz), (4-silyl isomer) 12.15, 12.87, 19.48 (t, J = 14.1 Hz), 23.20, 123.77 (q, J = 272.3 Hz), 124.88 (q, J = 3.3 Hz), 133.13 (t, J = 17.8 Hz), 133.5 (q, J = 32.8 Hz), 134.32 (t, J = 2.1 Hz). HRMS: calcd for $C_{11}H_{13}F_5Si$ 268.0706, found 268.0707. Anal. Calcd for $C_{11}H_{13}F_5Si$: C, 49.24; H, 4.88. Found: C, 49.11; H, 4.87.

Competition Experiments (Scheme 3). A resealable Schlenk tube containing $[Ir(OMe)(COD)]_2$ (9.9 mg, 0.015 mmol) and 2,9-diisopropyl-1,10-phenanthroline (7.9 mg, 0.030 mmol) was flushed with nitrogen and then charged with octane (6 mL), 1,2-di-*sec*-butyl-1,1,2,2-tetrafluorodisilane (246 mg, 1.0 mmol), toluene (0.46 g, 5.0 mmol), and benzotrifluoride (0.73 g, 5.0 mmol). The tube was sealed with a Teflon screwcap, and the mixture was stirred at 120 °C for 16 h. Volatile materials were removed under reduced pressure, and mesitylene (40 mg, 0.33 mmol) was added as an internal standard. The resulting mixture was analyzed by ^{1}H NMR spectroscopy in $CDCl_3$. The mole ratio of arylfluorosilanes produced was as follows: toluene/benzotrifluoride (51:49).

Cross-Coupling of 4-(*sec*-Butyldifluorosilyl)-1,2-dimethylbenzene with Methyl 4-Iodobenzoate (Scheme 4). A mixture of 4-(*sec*-butyldifluorosilyl)-1,2-dimethylbenzene (228 mg, 1.0 mmol), 1.0 M TBAF in THF (1.5 mL, 1.5 mmol), and DMF (0.5 mL) was stirred at rt for 10 min. Methyl 4-iodobenzoate (197 mg, 0.75 mmol), $[\eta^3$-$(C_3H_5)PdCl]_2$ (7.0 mg, 0.019 mmol), and DMF (2.5 mL) were added, and the resulting mixture was stirred at 100 °C for 4 h. Isolation by column chromatography over silica gel gave an analytically pure sample.

Methyl 4-(3,4-dimethylphenyl)benzoate. Purity determined by NMR and GC analyses: >95%. Mp: 100.7−100.9 °C. ^{1}H NMR: δ 2.31 (s, 3 H), 2.33 (s, 3 H), 3.93 (s, 3 H), 7.22 (d, 1 H, J = 7.8 Hz), 7.36 (d, 1 H, J = 7.8 Hz), 7.40 (s, 1 H), 7.63 (d, 2 H, J = 8.3 Hz), 8.08 (d, 2 H, J = 8.3 Hz). ^{13}C NMR: δ 19.48, 19.90, 52.05, 124.58, 126.75, 128.43, 130.00, 130.17, 136.76, 137.12, 137.49, 145.66, 167.05. HRMS: calcd for $C_{16}H_{16}O_2$ 240.1150, found 240.1153. Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.62; H, 6.78.

1,4-Addition of 4-(*sec*-Butyldifluorosilyl)-1,2-dimethylbenzene to Methyl Vinyl Ketone (Scheme 4). A mixture of 4-(*sec*-butyldifluorosilyl)-1,2-dimethylbenzene (228 mg, 1.0 mmol) and 1.0 M TBAF in THF (1.5 mL, 1.5 mmol) was stirred at rt for 10 min. $[Rh(COD)_2]BF_4$ (6.1 mg, 0.015 mmol), methyl vinyl ketone (35 mg, 0.50 mmol), and THF (1 mL) were added, and the resulting mixture was stirred at 60 °C for 20 h. Isolation by column chromatography over silica gel and Kugelrohr distillation gave an analytically pure sample.

4-(3,4-Dimethylphenyl)butan-2-one. Purity determined by NMR and GC analyses: >95%. 52 °C/1.5 mmHg (Kugelrohr). ^{1}H NMR: δ 2.13 (s, 3 H), 2.21 (s, 3 H), 2.22 (s, 3 H), 2.72 (t, 2 H, J = 7.0 Hz), 2.82 (t, 2 H, J = 7.0 Hz), 6.91 (d, 1 H, J = 7.6 Hz), 6.95 (s, 1 H), 7.03 (d, 1 H, J = 7.6 Hz). ^{13}C NMR: δ 19.21, 19.66, 29.20, 29.97, 45.32, 125.49, 129.55, 129.65, 134.14, 136.51, 138.29, 208.07. HRMS: calcd for $C_{12}H_{16}O$ 176.1201, found 176.1186. Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.75; H, 9.15.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectral analyses of products. This material is available free of charge via the Internet at http://pubs.acs.org.

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