Novel C_1 Building Blocks for Fluoro Olefin Synthesis: $FC(SiMe_3)_3$ and $FC(SiMe_3)_2SnBu_3$

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Fluorotris(trimethylsilyl)methane reacted with 2 mol of aromatic aldehydes in the presence of KF/18-crown-6 to give 1,3-disubstituted 2-fluoro-2-propen-1-ols in one pot. On the other hand, treatment of fluoro(tributylstannyl)bis(trimethylsilyl)methane with BuLi, followed by addition of an aldehyde, produced (1-fluoroalkenyl)trimethylsilanes in moderate to good yields.

Fluorine-containing organometallic reagents are available from polyhalofluoroalkanes via a halogen–metal exchange reaction and are applicable to efficient and stereoselective synthesis of organofluorine compounds. This synthetic strategy is extremely versatile because various kinds of fluoropolyhaloalkanes are commercially available, and the halogen atoms in the initial products allow further functionalization and transformation.[1]

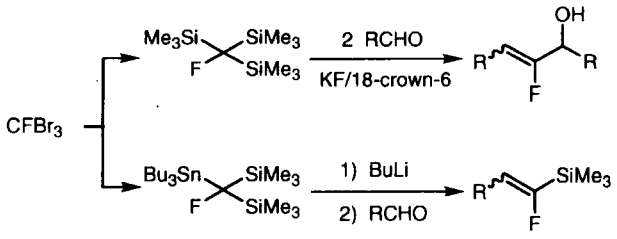
A typical example is zinc carbenoid reagent CF_3CCl_2ZnCl derived from 1,1,1-trichloro-2,2,2-trifluoroethane (chlorofluorocarbon-113a) and zinc metal in DMF. The reagent is thermally stable enough to react with aldehydes.[2] Use of zinc in excess in the presence of acetic anhydride leads to stereoselective in situ formation of 2-chloro-1,1,1-trifluoro-2-alkenes, a structural moiety found in highly potent insecticides. Another example is $LiCBr_2F$, generated by bromine–lithium exchange of tribromofluoromethane with butyllithium (BuLi); the carbenoid reagent undergoes carbonyl addition at -130 °C, giving rise to 1,1-dibromo-1-fluoro-2-alkanols that are versatile precursors for stereoselective synthesis of fluoro olefins and 2-bromo-2-fluoro-1,3-diols.[3] However, thermal instability of $LiCBr_2F$ has restricted its scope of utility.

In order to enhance the stability of the lithium carbenoid reagents,[4] we have studied the chemistry of silicon-substituted fluoromethyllithiums and found that a silyl substituent introduced to such a thermally labile fluorine-substituted carbenoid is effective for the enhancement of thermal stability and also for the extension of synthetic utility of labile carbenoid reagents.[5] We then focused our attention to more substitution with a silyl group on a carbon bearing a fluorine atom. In view of the facts that bis- or tris(triorganosilyl)-methanes are useful precursors for vinylsilane synthesis,[6] bis- or tris(triorganosilyl)fluoromethanes should be versatile precursors of fluoro olefins that are attracting much attention in the field of liquid crystalline materials,[7] peptide isosteres,[8] and enzyme inhibitors.[9] We report herein facile synthesis of fluoro olefins through the reaction of aldehydes with bis- or trissilylated fluoromethanes, all readily available from $CFBr_3$ (Scheme 1).[10]

Results and Discussion

Preparation of Fluorotris(trimethylsilyl)methane and Fluorobis(trimethylsilyl)methanes. Tris(trimethylsilyl)-fluoromethane (**1**) was prepared in 97% yield by treatment of $CFBr_3$ (1 mol) with BuLi (3.2 mol) in the presence of trimethylsilyl chloride (Me_3SiCl) (3.2 mol) in THF–Et_2O (2:1) at -130 °C, as shown in Scheme 2. Use of BuLi (2.0 mol) and Me_3SiCl (2.1 mol) under the same conditions yielded bromofluorobis(trimethylsilyl)methane (**2**) in 75% yield. Subsequent bromine–lithium exchange of **2** with *s*-BuLi[11] in the presence of tributylstannyl chloride (Bu_3SnCl, 1.2 mol) afforded fluoro(tributylstannyl)bis(trimethylsilyl)methane (**3**) that could alternatively be prepared in one pot by sequential treatment of $CFBr_3$ with Me_3SiCl (2 mol) and BuLi (2 mol) and then with Bu_3SnCl (1.1 mol) and *s*-BuLi (1 mol) in this order.

Fluoride Ion-Catalyzed Reaction of 1 with Aldehydes. At first, we examined the reaction of **1** with benzaldehyde using a fluoride ion catalyst. To a THF solution of **1** (1.0 mol) and PhCHO (1.0 mol), Bu_4NF (0.1 mol) was added at 0



Scheme 1. Synthesis of fluoro olefins using fluoropoly-(organosilyl)methanes.

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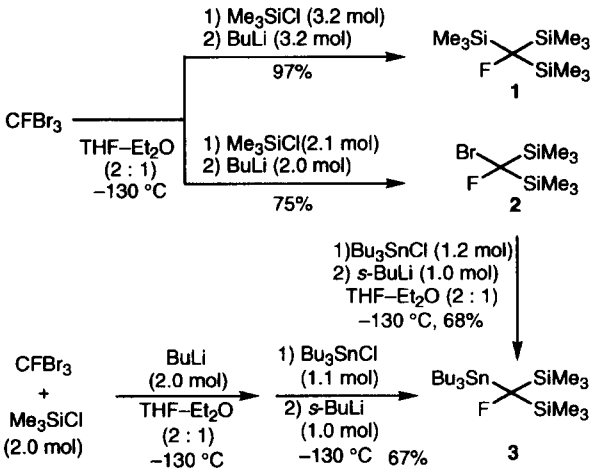
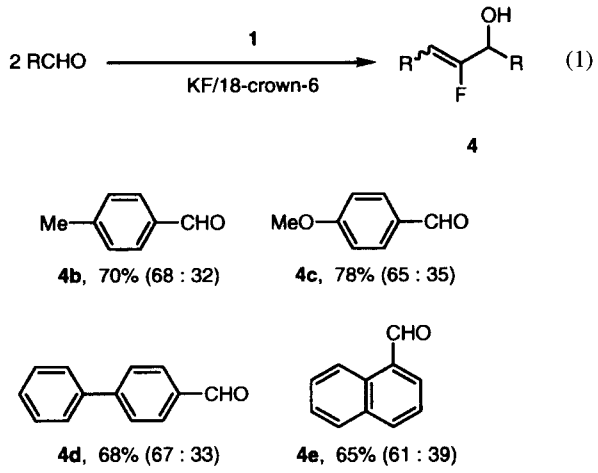


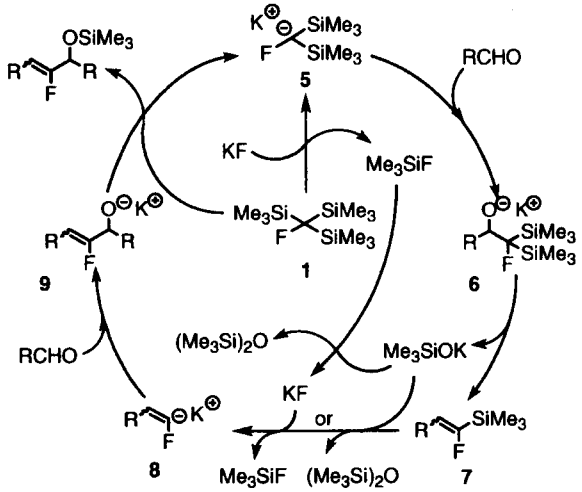
Scheme 2. Preparation of bis- and tris(silyl)fluoromethane **1**, **2**, and **3**.



°C to room temperature to give in 35% yield 2-fluoro-1,3-diphenyl-2-propen-1-ol (**4a**, $E : Z = 66 : 34$), a product derived from 1.0 mol of **1** and 2.0 mol of the aldehyde (Table 1, Run 1). When 2.5 mol of PhCHO was used, the yield of **4a** was slightly improved (Run 2). The formation of the 1 : 2 adduct was much improved with a KF/18-crown-6 reagent system (Runs 5 and 6).

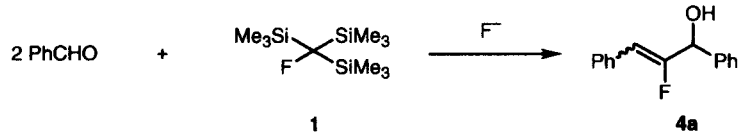
The conditions of Run 6 were applied to 4-MeC_6H_4CHO, 4-$MeOC_6H_4CHO$, 4-$C_6H_5C_6H_4CHO$, and 1-naphthaldehyde (Eq. 1), and the corresponding 1 : 2 adducts **4** were obtained in 65—78% yield with roughly 2 : 1 ratios of (*E*)- and (*Z*)-isomers. In contrast, cinnamaldehyde, 3-phenylpropanal, 4-CF_3–C_6H_4CHO, 4-NC–C_6H_4CHO, and C_6F_5CHO did not give the corresponding products. It is worthy to note that no (fluoroalkenyl)silanes were isolated; the second carbonyl addition occurred rapidly, in contrast to the fact that vinylsilane PhCH=CHSiMe$_3$ is produced upon the reaction of $(Me_3Si)_3CH$ with PhCHO in the presence of a fluoride catalyst.[6i]

We propose a mechanism illustrated in Scheme 3 for the formation of **4**. First, KF should activate **1** to generate fluoromethyl anionic reagent **5**, which reacts with an aldehyde, giving rise to potassium alkoxide **6**. The alkoxide undergoes the Peterson elimination to afford alkenylsilane **7** and Me_3SiOK, which would react with Me_3SiF to produce KF and $Me_3SiOSiMe_3$. Alkenylsilane **7** is attacked by the reproduced KF to generate alkenylpotassium reagent **8**, which reacts with another aldehyde to give adduct **9**. Nucleophilic activation of **7** by Me_3SiOK or alkoxide **9** might also be possible. Finally, silicon–potassium exchange between adduct **9** and starting silane **1** affords a silyl ether of **4** and generates



Scheme 3. Proposed mechanism.

Table 1. Fluoride Ion-Catalyzed Reaction of **1** with Aldehydes



1 **4a**

Run	PhCHO (mol)	F^- (mol)	Solvent	Temp	Yield (%)	$E : Z$[a]
1	1.0	Bu_4NF (0.1)	THF	0 °C to r.t.	35	66 : 34
2	2.5	Bu_4NF (0.1)	THF	0 °C to r.t.	46	67 : 33
3	2.5	Bu_4NF (0.5)	THF	0 °C to r.t.	12	63 : 37
4	2.5	KF/18-crown-6 (0.1)	DMF	r.t.	26	56 : 44
5	2.5	KF/18-crown-6 (0.5)	DMF	r.t.	72	66 : 34
6	2.5	KF/18-crown-6 (1.0)	DMF	r.t.	74	65 : 35

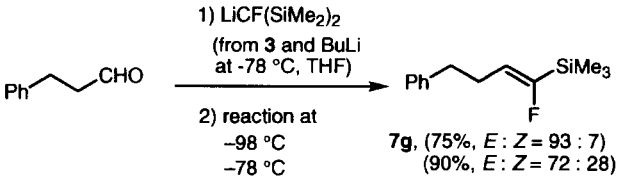
a) Stereochemistry was assigned on the basis of ^{19}F NMR spectroscopy: $^3J_{H-F}$ = 20.4 Hz for (*E*)-**4a** and 39.3 Hz for (*Z*)-**4a**.

anion **5** again.

Reaction of 3 with Aldehydes. Since the fluoride ion-catalyzed reaction of **1** with aldehydes gives fluorinated allylic alcohols **4** in one pot, we examined an alternative route for the generation of a fluorobis(trimethylsilyl)methyl anionic reagent from fluorobis(silyl)methane **2** or **3**, and the subsequent aldehyde addition in order to synthesize fluoroalkenylsilanes **7**, potential intermediates applicable to various kinds of synthetic transformations.[12] Although treatment of **2** with BuLi in THF at −78 °C, followed by the addition of 3-phenylpropanal at −98 °C, failed to give the desired alkenylsilane **7g**, tin–lithium exchange of **3** with BuLi in THF at −78 °C and subsequent treatment with 3-phenylpropanal at −98 °C gave successfully **7g** in 75% yield with 93% *E*-selectivity (Scheme 4). When the aldehyde addition was effected at −78 °C, the yield increased at the expense of the *E*/*Z* selectivity.

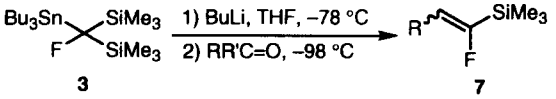
The reaction conditions (−98 °C) were applied to other aldehydes and a ketone as summarized in Table 2. Under these conditions, aldehydes that failed to give **4** gave products **7f**—**7j**. The configuration of the resulting olefins varied markedly depending on substituent R. Aromatic and α,β-unsaturated aldehydes preferred (*Z*)-olefins, whereas aliphatic and fluorine-substituted aldehydes gave (*E*)-olefins preferentially. The reason is not clear at present.

In summary, we have demonstrated that $FC(SiMe_3)_3$ and $FC(SiMe_3)_2SnBu_3$, both readily available from $CFBr_3$ (Eq. 2), can conveniently be employed for the transformation of aldehydes and a ketone to fluoro olefins by appropriate activation. The resulting fluoro olefins would serve as key precursors of bioactive molecules.

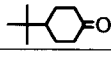


Scheme 4. Synthesis of 1-fluoro-1-silylalkene.

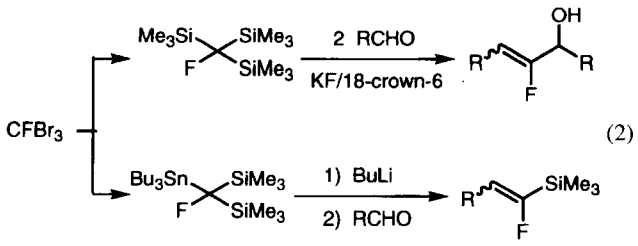
Table 2. Synthesis of **7** from **3**



3 **7**

PR′C=O	7	Yield (%)	*E* : *Z*[a]
PhCHO	**7a**	51	24 : 76
4-Me–C_6H_4CHO	**7b**	69	24 : 76
4-MeO–C_6H_4CHO	**7c**	98	15 : 85
4-C_6H_5–C_6H_4CHO	**7d**	87	28 : 72
(*E*)-PhCH=CHCHO	**7f**	90	20 : 80
$Ph(CH_2)_2CHO$	**7g**	75	93 : 7
C_6F_5CHO	**7h**	53	>99 : <1
4-CF_3–C_6H_4CHO	**7i**	98	57 : 43
	**7j**	52	—

a) Stereochemistry was assigned on the basis of ^{19}F NMR spectroscopy: $^3J_{H-F}$ = 45.7—52.6 Hz for (*E*)-**7** and 33.7—38.8 Hz for (*Z*)-**7**.



(2)

Experimental

General Remarks. Melting points were measured with a Yanagimoto micro melting point apparatus. IR spectra were recorded on a Shimadzu FTIR-8100A spectrometer and are expressed in wave numbers (cm^{-1}). ^1H NMR spectra were measured on a Varian Mercury 200 (200 MHz) or 300 (300 MHz) spectrometer with tetramethylsilane (δ = 0 ppm) or chloroform (δ = 7.26 ppm) as an internal standard; splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; brs, broad singlet. ^{13}C NMR spectra were measured on a Varian Mercury 200 (50 MHz) spectrometer with $CDCl_3$ as an internal standard (δ = 77.0 ppm). ^{19}F NMR spectra were measured on a Varian Mercury 200 (188 MHz) spectrometer with $CFCl_3$ as an internal standard (δ = 0 ppm). MS spectra were obtained with a Shimadzu GC-MS QP-5000 machine by electron impact ionization at 70 eV; high-resolution MS spectra were obtained with a JEOL JMS-700 spectrometer. TLC analyses were performed by means of Merck Kieselgel 60 F_{254}, and column chromatography was carried out using Merck Kieselgel 60 (230—400 mesh). THF and diethyl ether (Et_2O) were distilled from benzophenone and sodium before use under an argon atmosphere.

Silylation of Tribromofluoromethane. Fluorotris(trimethylsilyl)methane (1): To a solution of $CFBr_3$ (0.98 ml, 10 mmol) and Me_3SiCl (4.2 ml, 33 mmol) in THF (20 ml)–Et_2O (10 ml) was added a 1.36 M hexane solution (1 M = 1 mol dm^{-3}) of BuLi (24 ml, 32 mmol) at −130 °C via a syringe over a period of 10 min. The resulting mixture was stirred for 30 min at −130 °C before quenching with a sat. aq NH_4Cl solution (30 ml). The organic layer was separated; the aqueous layer was extracted with Et_2O (50 ml×3). The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo. The residue was distilled under reduced pressure to afford **1** (2.4 g, 97% yield) as a colorless oil. Bp 80 °C/3 mmHg (1 mmHg = 133.322 Pa). ^1H NMR ($CDCl_3$) δ = 0.16 (s, 27H); ^{13}C NMR ($CDCl_3$) δ = 0.04 (d, J = 4.6 Hz), 96.0 (d, J = 119.6 Hz); ^{19}F NMR ($CDCl_3$) δ = −263.7; IR (neat) 2957, 2905, 1402, 1254, 1264, 870, 849, 810, 764, 681, 615 cm^{-1}; MS *m*/*z* 252 (M^++2; 0.1), 251 (M^++1; 0.1), 250 (M^+; 0.6), 235 (20), 143 (100). HRMS Found: *m*/*z* 250.1404. Calcd for $C_{10}H_{27}FSi_3$: M, 250.1405.

Bromofluorobis(trimethylsilyl)methane (2): To a solution of $CFBr_3$ (0.98 ml, 10 mmol) and Me_3SiCl (2.7 ml, 21 mmol) in THF (20 ml)–Et_2O (10 ml) was added a 1.59 M hexane solution of BuLi (12.6 ml, 20 mmol) dropwise at −130 °C under an argon atmosphere. The resulting mixture was stirred for 30 min at −130 °C, gradually warmed to room temperature and stirred for 12 h before quenching with a sat. aq NH_4Cl solution (30 ml). The organic layer was separated; the aqueous layer was extracted with Et_2O (50 ml×3). Work up and vacuum distillation gave **2** (1.94 g, 75% yield) as a colorless oil. Bp 100 °C/20 mmHg. ^1H NMR ($CDCl_3$) δ = 0.23 (s, 18H); ^{13}C NMR ($CDCl_3$) δ = −2.4 (d, J = 1.9 Hz), 113.0 (d, J = 260.6 Hz); ^{19}F NMR ($CDCl_3$) δ = −173.4; IR

(neat) 2961, 1905, 1410, 1254, 953, 901, 849, 812, 764, 704, 619 cm^{-1}; MS *m/z* 259 (M^++3; 0.06), 258 (M^++2; 0.36), 257 (M^++1; 0.07), 256 (M^+; 0.33) 73 (100). HRMS Found: *m/z* 256.0111. Calcd for $C_7H_{18}BrFSi_2$: M, 256.0114.

Fluoro(tributylstannyl)bis(trimethylsilyl)methane (3): To a mixture of **2** (87 mg, 0.34 mmol) and Bu_3SnCl (0.110 ml, 0.41 mmol) in THF (2 ml)–Et_2O (1 ml) was added 0.98 M cyclohexane solution of *s*-BuLi (0.36 ml, 0.35 mmol) dropwise at −130 °C under an argon atmosphere. The resulting mixture was stirred for 30 min at −130 °C, gradually warmed to room temperature, and stirred for 12 h before quenching with a sat. aq NH_4Cl solution (5 ml). The organic layer was separated; the aqueous layer was extracted with Et_2O (20 ml×3). The combined organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo to afford an oil which was purified by column chromatography (hexane) to give **3** (107 mg, 68% yield) as a colorless oil. R_f 0.56 (hexane). ^{1}H NMR ($CDCl_3$) δ = 0.11 (s, 18H), 0.90 (t, *J* = 7.5 Hz, 9H), 0.96—1.20 (m, 6H), 1.33 (q, *J* = 7.2 Hz, 6H), 1.42—1.55 (m, 6H); ^{13}C NMR ($CDCl_3$) δ = −0.4 (d, *J* = 4.0 Hz), 11.5 (d, *J* = 4.0 Hz), 13.6, 27.6, 29.2, 105.8; ^{19}F NMR ($CDCl_3$) δ = −263.7 (t, *J* = 76.1 Hz); IR (neat) 2960, 2920, 2850, 1460, 1420, 1375, 1070, 960, 880, 840, 760, 670, 590 cm^{-1}. Found: C, 48.96; H, 9.88%. Calcd for $C_{19}H_{45}FSi_2Sn$: C, 48.82; H, 9.70%.

One-Pot Procedure for the Preparation of 3. A 1.52 M hexane solution of BuLi (6.6 ml, 10 mmol) was added to a solution of $CFBr_3$ (0.49 ml, 5.0 mmol) and Me_3SiCl (1.27 ml, 10 mmol) in THF (10 ml)–Et_2O (5 ml) at −130 °C via a syringe over a period of 10 min. The mixture was stirred for 30 min before treatment with Bu_3SnCl (1.49 ml, 5.5 mmol) and then with *s*-BuLi (0.74 M cyclohexane solution, 6.8 ml, 5.0 mmol) at −130 °C. The resulting solution was stirred for 30 min at −130 °C and quenched with a sat. aq NH_4Cl solution (30 ml). The organic layer was separated; the aqueous layer was extracted with Et_2O (40 ml×3). Work up and purification by column chromatography gave **3** (1.56 g, 67% yield).

Reaction of 1 with Aldehydes. A General Procedure with KF and 18-Crown-6. To a solution of KF (1.00 mmol) and 18-crown-6 (1.00 mmol) in DMF (2 ml) were added an aldehyde (2.5 mmol) and **1** (1.00 mmol) successively at room temperature. The reaction mixture was stirred for 12 h and then quenched with 3 M HCl (5 ml). The organic layer was separated; the aqueous layer was extracted with Et_2O (20 ml×3). The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography to give **4**. (*E*)- and (*Z*)-Isomers of **4a** and **4b** were separable.

(*E*)-2-Fluoro-1,3-diphenyl-2-propen-1-ol ((*E*)-4a): Prepared in 48% yield as a colorless oil, R_f 0.53 (hexane–ethyl acetate = 4 : 1). ^{1}H NMR ($CDCl_3$) δ = 2.37 (brs, 1H), 5.68 (dd, *J* = 7.2, 26.7 Hz, 1H), 6.51 (d, *J* = 20.4 Hz, 1H), 7.20—7.80 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ = 69.2 (d, *J* = 25.7 Hz), 111.2 (d, *J* = 25.7 Hz), 126.4 (2 peaks), 127.5, 128.2, 128.6 (2 peaks), 132.6 (d, *J* = 12.6 Hz), 139.2, 159.2 (d, *J* = 256.4 Hz); ^{19}F NMR ($CDCl_3$) δ = −120.1 (dd, *J* = 20.4, 26.7 Hz); IR (neat) 3400, 1680, 1495, 1449, 1219, 1144, 1024, 920, 893, 756, 698 cm^{-1}. Found: C, 79.14; H, 5.79%. Calcd for $C_{15}H_{13}FO$: C, 78.93; H, 5.74%.

(*Z*)-2-Fluoro-1,3-diphenyl-2-propen-1-ol ((*Z*)-4a): This alcohol was isolated in 26% yield as a colorless solid, mp 61—62 °C. ^{1}H NMR ($CDCl_3$) δ = 2.45 (brs, 1H), 5.33 (dd, *J* = 4.5, 12.0 Hz, 1H), 5.90 (d, *J* = 39.3 Hz, 1H), 7.20—7.60 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ = 73.2 (d, *J* = 32.0 Hz), 106.9 (d, *J* = 6.3 Hz), 126.8, 127.4 (d, *J* = 2.2 Hz), 128.4, 128.5, 128.6, 128.7 (d, *J* = 7.5 Hz), 132.6 (d, *J* = 2.3 Hz), 139.3, 159.2 (d, *J* = 266.6 Hz); ^{19}F NMR ($CDCl_3$) δ = −115.6 (dd, *J* = 12.0, 39.3 Hz); IR (KBr) 3400, 1686, 1495, 1449, 1231, 1275, 1157, 1022, 895, 862, 725, 695 cm^{-1}. Found: C, 78.95; H, 5.69%. Calcd for $C_{15}H_{13}FO$: C, 78.93; H, 5.74%.

(*E*)-2-Fluoro-1,3-bis(4-methylphenyl)-2-propen-1-ol ((*E*)-4b): Obtained in 48% yield as a colorless solid, mp 80—81 °C. ^{1}H NMR ($CDCl_3$) δ = 2.25 (d, *J* = 11.3 Hz, 1H), 2.35 (s, 3H), 2.37 (s, 3H), 5.65 (dd, *J* = 7.5, 26.4 Hz, 1H), 6.45 (d, *J* = 20.5 Hz, 1H), 7.10—7.45 (m, 8H); ^{19}F NMR ($CDCl_3$) δ = −120.7 (dd, *J* = 20.5, 26.4 Hz); IR (nujor) 3300, 1510, 1145, 1040, 900 cm^{-1}; MS *m/z* 258 (M^++2; 2), 257 (M^++1; 18), 256 (M^+; 100), 241 (42), 221 (78), 119 (78). HRMS Found: *m/z* 256.1275. Calcd for $C_{17}H_{17}FO$: M, 256.1263.

(*Z*)-2-Fluoro-1,3-bis(4-methylphenyl)-2-propen-1-ol ((*Z*)-4b): Isolated in 22% yield as a colorless solid, mp 48—49 °C. ^{1}H NMR ($CDCl_3$) δ = 2.24 (brs, 1H), 2.34 (s, 3H), 2.37 (s, 3H), 5.37 (d, *J* = 11.5 Hz, 1H), 5.87 (d, *J* = 39.3 Hz, 1H), 7.10—7.55 (m, 8H); ^{19}F NMR ($CDCl_3$) δ = −116.5 (dd, *J* = 11.5, 39.3 Hz); IR (nujor) 3300, 1520, 1150, 1020, 810 cm^{-1}; MS *m/z* 258 (M^++2; 2), 257 (M^++1; 19), 256 (M^+; 100), 241 (45), 221 (83), 119 (93). HRMS Found: *m/z* 256.1255. Calcd for $C_{17}H_{17}FO$: M, 256.1263.

2-Fluoro-1,3-bis(4-methoxyphenyl)-2-propen-1-ol (4c): This alcohol was prepared in 78% yield as a mixture of stereoisomers (*E* : *Z* = 65 : 35), a pale yellow oil, R_f 0.17 (hexane–ethyl acetate = 4 : 1). ^{1}H NMR ($CDCl_3$) (*E*)-isomer: δ = 2.35 (brs, 1H), 3.81 (s, 3H), 3.82 (s, 3H), 5.62 (d, *J* = 26.0 Hz, 1H), 6.42 (d, *J* = 20.4 Hz, 1H), 6.85—7.50 (m, 8H), (*Z*)-isomer: δ = 5.30 (d, *J* = 11.4 Hz, 1H), 5.83 (d, *J* = 39.3 Hz, 1H); ^{19}F NMR ($CDCl_3$) (*E*)-isomer: δ = −123.2 (dd, *J* = 20.4, 26.0 Hz), (*Z*)-isomer: δ = −118.3 (dd, *J* = 11.4, 39.3 Hz); IR (neat) 3470, 3000, 2950, 2930, 2900, 2840, 1680, 1610, 1510, 1460, 1300, 1250, 1180, 1140, 1030, 830, 755 cm^{-1}; MS *m/z* 290 (M^++2; 2), 289 (M^++1; 11), 288 (M^+; 49), 272 (100). HRMS Found: *m/z* 288.1186. Calcd for $C_{17}H_{17}FO_3$: M, 288.1162.

2-Fluoro-1,3-bis(4-biphenylyl)-2-propen-1-ol (4d): This allylic alcohol was isolated in 68% yield as a mixture of stereoisomers (*E* : *Z* = 67 : 33), a yellow solid, mp 71—72 °C. ^{1}H NMR ($CDCl_3$) (*E*)-isomer: δ = 2.10 (brs, 1H), 5.81 (d, *J* = 26.8 Hz, 1H), 6.58 (d, *J* = 20.2 Hz, 1H), 7.20—7.90 (m, 18 H), (*Z*)-isomer: 5.44 (d, *J* = 11.8 Hz, 1H), 6.02 (d, *J* = 38.8 Hz, 1H); ^{19}F NMR ($CDCl_3$) (*E*)-isomer: δ = −119.4 (dd, *J* = 20.2, 26.8 Hz), (*Z*)-isomer: δ = −115.1 (dd, *J* = 11.8, 38.8 Hz); IR (nujor) 3300, 1510, 1150, 720 cm^{-1}; MS *m/z* 381 (M^++1; 2.3), 380 (M^+; 7.2), 207 (100), 309 (18). HRMS Found: *m/z* 380.1586. Calcd for $C_{27}H_{21}FO$: M, 380.1576.

2-Fluoro-1,3-bis(1-naphtyl)-2-propen-1-ol (4e): Obtained in 65% yield as a mixture of stereoisomers (*E* : *Z* = 61 : 39), a yellow viscous oil, R_f 0.43 (hexane–ethyl acetate = 4 : 1). ^{1}H NMR ($CDCl_3$) (*E*)-isomer: δ = 2.50 (brs, 1H), 6.22 (dd, *J* = 17.6, 25.3 Hz, 1H), 6.96 (d, *J* = 19.0 Hz, 1H), 7.30—8.50 (m, 14H), (*Z*)-isomer: δ = 6.60 (d, *J* = 36.8 Hz, 1H), 7.09 (ddd, *J* = 1.6, 7.0, 8.6 Hz, 1H); ^{19}F NMR ($CDCl_3$) (*E*)-isomer: δ = −115.2 (dd, *J* = 19.0, 25.2 Hz), (*Z*)-isomer: δ = −113.6 (dd, *J* = 7.0, 36.8 Hz) ; IR (nujor) 3350, 1700, 1600, 1300, 1220, 1080, 1010, 840, 780, 700 cm^{-1}; MS (70 eV) *m/z* 330 (M^++2; 3), 329 (M^++1; 26), 328 (M^+; 100). HRMS Found: *m/z* 328.1268. Calcd for $C_{23}H_{17}FO$: M, 328.1263.

Reaction of 3 with Aldehydes. To a solution of **3** (1.00 mmol) in THF (2 ml) was added BuLi (1.05 mmol) at −78 °C; the resulting mixture was stirred for 20 min at −78 °C. An aldehyde or a ketone (1.2 mmol) was added to the reagent solution at −98 °C; the resulting mixture was allowed to warm to room temperature before quenching with a sat. aq NH_4Cl solution. The organic layer was

separated; the aqueous layer was extracted with Et_2O (20 ml×3). The combined organic layer was dried over anhydrous $MgSO_4$. Concentration in vacuo followed by column chromatography gave **7**.

1-Fluoro-2-phenyl-1-trimethylsilylethene (7a): This olefin was prepared in 51% yield as a mixture of stereoisomers ($E:Z$ = 24:76), a colorless oil, R_f 0.70 (hexane). ^{1}H NMR ($CDCl_3$) (*Z*)-isomer: δ = −0.03 (s, 9H), 7.04 (d, J = 35.0 Hz, 1H), 6.98—7.49 (m, 5H), (*E*)-isomer: δ = 0.24 (s, 9H), 5.85 (d, J = 52.2 Hz, 1H); ^{19}F NMR ($CDCl_3$) (*Z*)-isomer: δ = −106.6 (d, J = 35.0 Hz), (*E*)-isomer: δ = −114.0 (d, J = 52.2 Hz); IR (neat) 2960, 2930, 2850, 1460, 1330, 1250, 840, 665 cm^{-1}; MS *m/z* 196 (M^++2; 3), 195 (M^++1; 10), 194 (M^+; 60), 77 (100). HRMS Found: *m/z* 194.0920. Calcd for $C_{11}H_{15}FSi$: M, 194.0927.

1-Fluoro-2-(4-methylphenyl)-1-trimethylsilylethene (7b): This was isolated in 69% yield as an $E:Z$ = 24:76 mixture of stereoisomers, a colorless oil, R_f 0.67 (hexane). ^{1}H NMR ($CDCl_3$) (*Z*)-isomer: δ = 0.09 (s, 9H), 2.35 (s, 3H), 7.03 (d, J = 38.8 Hz, 1H), 7.08—7.50 (m, 4H), (*E*)-isomer: δ = 0.25 (s, 9H), 5.83 (d, J = 52.6 Hz, 1H); ^{19}F NMR ($CDCl_3$) (*Z*)-isomer: δ = −107.5 (d, J = 38.8 Hz), (*E*)-isomer: δ = −115.3 (d, J = 52.6 Hz); IR (neat) 3025, 2960, 1510, 1250, 1040, 850, 810, 760 cm^{-1}; MS *m/z* 210 (M^++2; 5), 209 (M^++1; 21), 208 (M^+; 100). HRMS Found: *m/z* 208.1083. Calcd for $C_{12}H_{17}FSi$: M, 208.1084.

1-Fluoro-2-(4-methoxyphenyl)-1-trimethylsilylethene (7c): Prepared in 98% yield as a mixture of stereoisomers ($E:Z$ = 15:85), a colorless oil, R_f 0.24 (hexane). ^{1}H NMR ($CDCl_3$) (*Z*)-isomer: δ = 0.08 (s, 9H), 3.81 (s, 3H), 6.80—7.60 (m, 5H), (*E*)-isomer: δ = 0.24 (s, 9H), 5.79 (d, J = 52.6 Hz, 1H); ^{19}F NMR ($CDCl_3$) (*Z*)-isomer: δ = −108.2 (d, J = 35.2 Hz), (*E*)-isomer: δ = −117.6 (d, J = 51.9 Hz); IR (neat) 2980, 2950, 1600, 1500, 1245, 1170, 1030, 840, 750 cm^{-1}; MS *m/z* 226 (M^++2; 5), 225 (M^++1; 19), 224 (M^+; 100). HRMS Found: *m/z* 224.1036. Calcd for $C_{12}H_{17}FOSi$: M, 224.1033.

1-Fluoro-2-(4-biphenylyl)-1-trimethylsilylethene (7d): Obtained in 87% yield, as a mixture of stereoisomers ($E:Z$ = 28:72), a colorless oil, R_f 0.67 (hexane). ^{1}H NMR ($CDCl_3$) (*Z*)-isomer: δ = 0.13 (s, 9H), 7.06 (d, J = 35.2 Hz, 1H), 7.22—7.80 (m, 9H), (*E*)-isomer: δ = 0.27 (s, 9H), 5.90 (d, J = 52.0 Hz, 1H); ^{19}F NMR ($CDCl_3$) (*Z*)-isomer: δ = −105.8 (d, J = 35.2 Hz), (*E*)-isomer: δ = −113.4 (d, J = 52.0 Hz); IR (neat) 2960, 2930, 1490, 1460, 1250, 1040, 850, 760, 700 cm^{-1}; MS *m/z* 272 (M^++2; 11), 271 (M^++1; 41), 270 (M^+; 100). HRMS Found: *m/z* 270.1230. Calcd for $C_{12}H_{19}FSi$: M, 270.1240.

(3*E*)-1-Fluoro-4-phenyl-1-trimethylsilyl-1,3-butadiene (7f): This diene was prepared in a 20:80 mixture of (1*E*, 3*E*)- and (1*Z*, 3*E*)-isomers in 90% yield, a pale yellow oil, R_f 0.34 (hexane). ^{1}H NMR ($CDCl_3$) (*Z*)-isomer: δ = 0.34 (s, 9H), 5.70—7.50 (m, 8H), (*E*)-isomer: δ = 0.22 (s, 9H); ^{19}F NMR ($CDCl_3$) (*Z*)-isomer: δ = −107.3 (d, J = 33.7 Hz), (*E*)-isomer: δ = −116.6 (d, J = 45.7 Hz); IR (neat) 3050, 2960, 1500, 1450, 1250, 1040, 960, 840, 750, 690 cm^{-1}; MS *m/z* 222 (M^++2; 5), 221 (M^++1; 21), 220 (M^+; 100). HRMS Found: *m/z* 220.1087. Calcd for $C_{13}H_{17}FSi$: M, 220.1084.

1-Fluoro-4-phenyl-1-trimethylsilyl-1-butene (7g): Prepared in 75% yield as a 93:7 mixture of (*E*)- and (*Z*)-isomers, a colorless oil, R_f 0.34 (hexane). ^{1}H NMR ($CDCl_3$) (*E*)-isomer: δ = 0.13 (s, 9H), 2.30—2.70 (m, 4H), 5.06 (dt, J = 49.6, 7.4 Hz, 1H), 7.10—7.40 (m, 5H), (*Z*)-isomer: δ = 0.17 (s, 9H), 5.86 (dt, J = 36.8, 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) (*E*)-isomer: δ = −2.6 (d, J = 1.1 Hz), 25.3 (d, J = 10.7 Hz), 35.3, 120.7 (d, J = 4.2 Hz), 125.9, 128.3, 128.4, 141.7, 168.3 (d, J = 276.2 Hz), (*Z*)-isomer (only characteristic peaks are shown): δ = −1.5 (d, J = 3.1 Hz), 27.4 (d, J = 12.9 Hz), 36.7, 122.9 (d, J = 13.3 Hz), 126.0, 128.4, 128.5; ^{19}F NMR ($CDCl_3$) (*E*)-isomer: δ = −123.2 (d, J = 49.6 Hz), (*Z*)-isomer: δ = −112.4 (d, J = 36.8 Hz); IR (neat) 3030, 2960, 2860, 1650, 1605, 1500, 1450, 1250, 1090, 1030, 1000, 980, 940, 840, 750, 700, 630 cm^{-1}; MS *m/z* 224 (M^++2; 0.4), 223 (M^++1; 1.4), 222 (M^+; 7.3), 91 (100). Found: C, 70.28; H, 8.91%. Calcd for $C_{13}H_{19}FSi$: C, 70.22; H, 8.61%.

(*E*)-1-Fluoro-2-(pentafluorophenyl)-1-trimethylsilylethene (7h): Obtained in 53% yield as a single isomer, a colorless oil, R_f 0.61 (hexane). ^{1}H NMR ($CDCl_3$) δ = 0.28 (s, 9H), 5.79 (d, J = 47.6 Hz, 1H); ^{19}F NMR ($CDCl_3$) δ = −99.0 (dt, J = 47.6, 24.3 Hz), −138.1 (td, J = 22.7, 9.2 Hz), −156.2 (t, J = 21.4 Hz), 163.4 (td, J = 21.4, 7.5 Hz); IR (neat) 2970, 2930, 1660, 1520, 1500, 1255, 1130, 1080, 990, 970, 850, 760 cm^{-1}; MS *m/z* 286 (M^++2; 2), 285 (M^++1; 6), 284 (M^+; 35), 269 (100). HRMS Found: *m/z* 284.0460. Calcd for $C_{11}H_{10}F_6Si$: M, 284.0456.

1-Fluoro-2-(4-trifluoromethylphenyl)-1-trimethylsilylethene (7i): This was isolated in 98% yield as a mixture of stereoisomers ($E:Z$ = 57:43), a colorless oil, R_f 0.24 (hexane). ^{1}H NMR ($CDCl_3$) (*E*)-isomer: δ = 0.26 (s, 9H), 5.79 (d, J = 52.6 Hz, 1H), 7.30—7.70 (m, 4H), (*Z*)-isomer: δ = 0.09 (s, 9H), 7.01 (d, J = 34.8 Hz, 1H); ^{19}F NMR ($CDCl_3$) (*E*)-isomer: δ = −63.1, −110.0 (d, J = 52.6 Hz), (*Z*)-isomer: δ = −63.0, −102.7 (d, J = 34.8 Hz); IR (neat) 2960, 1620, 1410, 1320, 1250, 1160, 1120, 1065, 1020, 850, 760 cm^{-1}; MS *m/z* 264 (M^++2; 3), 263 (M^++1; 12), 262 (M^+; 62), 151 (100). HRMS Found: *m/z* 262.0794. Calcd for $C_{12}H_{14}F_4Si$: M, 262.0801.

4-*t*-Butyl-1,1-(1-fluoro-1-trimethylsilylmethylene)cyclohexane (7j): Isolated in 52% yield, a colorless oil, R_f 0.50 (hexane). ^{1}H NMR ($CDCl_3$) δ = 0.20 (s, 9H), 0.85 (s, 9H), 0.90—1.20 (m, 3H), 1.45—1.96 (m, 4H), 2.36 (dd, J = 2.0, 13.6 Hz, 1H), 3.04 (dd, J = 1.6, 13.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = −0.9 (d, J = 3.1 Hz), 25.7 (d, J = 13.7 Hz), 27.6, 27.8 (d, J = 1.5 Hz), 28.5 (d, J = 9.1 Hz), 28.7 (d, J = 2.7 Hz), 32.5, 48.2, 134.1 (d, J = 6.1 Hz), 157.8 (d, J = 263.3 Hz); ^{19}F NMR ($CDCl_3$) δ = −125.2; IR (neat) 2950, 2860, 2830, 1645, 1475, 1440, 1360, 1245, 1050, 875, 840, 755 cm^{-1}; MS *m/z* 245 (M^++3; 0.4), 244 (M^++2; 4), 243 (M^++1; 15), 242 (M^+; 72), 227 (M^+−Me; 1) 57 (100). HRMS Found: *m/z* 242.1866. Calcd for $C_{14}H_{27}FSi$: M, 242.1876.

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