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NOVEL SYNTHESIS OF 1-FLUORO-1-SILYLOXIRANES USING BROMO(*tert*-BUTYLDIMETHYLSILYL)FLUORO-METHYLLITHIUM AND CARBONYL COMPOUNDS

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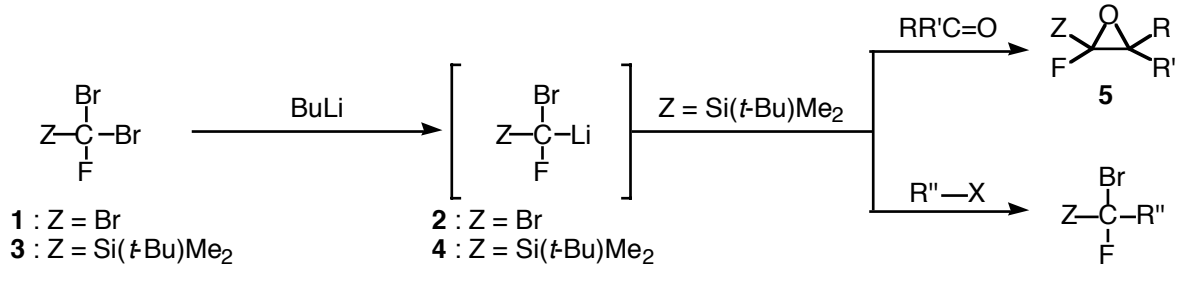
Abstract–Treatment of dibromo(*tert*-butyldimethylsilyl)fluoro-methane with BuLi in THF at -78 °C generated bromo(*tert*-butyldimethylsilyl)fluoromethyllithium, which reacted with aldehydes and ketones to give 1-fluoro-1-silyloxiranes in good yields. Alkylation of the carbenoid was also achieved efficiently.

Fluorine-substituted oxiranes are attractive synthetic intermediates[1] as useful building blocks for the synthesis of organofluorine compounds that are finding extensive applications in pharmaceutical and material sciences.[2] For example, hexafluoropropene oxide is utilized as a versatile precursor of hexafluoroacetone or difluorocarbene.[3]

In the course of our research concerning thermally labile fluorine-substituted carbenoid reagents derived from tribromofluoromethane (**1**),[4] we considered that the introduction of a silyl substituent to the reagent would enhance the stability and utility of the fluorine-substituted carbenoids, because a silicon atom could stabilize a geminal anionic center[5] and serve as a clue for further transformations.[6] Indeed, treatment of dibromo(*tert*-butyldimethylsilyl)fluoromethane (**3**) with BuLi generated the corresponding carbenoid (**4**), which was more stable than dibromofluoromethyllithium (**2**) and reacted with carbonyl compounds giving rise in good yields to 1-fluoro-1-silyloxiranes (**5**), a versatile building block for monofluoro compounds (Scheme 1). We describe here the detail of the generation of **4** followed by carbonyl addition and alkylation reaction .[7]



Scheme 1

This paper is dedicated to Professor Teruaki Mukaiyama on the occasion of his 73rd birthday.

Preparation of Dibromo(*tert*-butyldimethylsilyl)fluoromethane

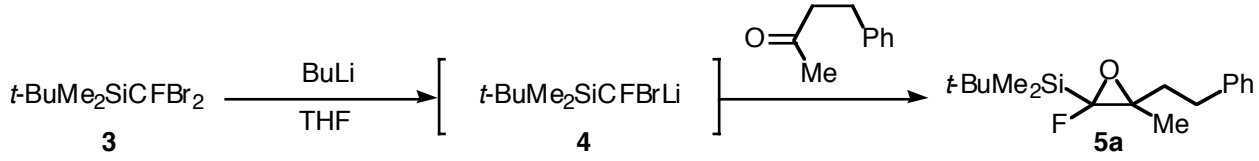
Dibromofluoro(trimethylsilyl)methane has been accessible *via* the reaction of Me_3SiCl with a reagent generated from **1** and tetrakis(dimethylamino)ethylene (eq. 1) and is found to be volatile and UV- and moisture-sensitive.[8] We envisaged that a *tert*-butyldimethylsilyl group instead of a trimethylsilyl group would facilitate the handling of the fluorosilylmethane reagent. Since the method depicted in eq. 1 is not applicable to *i*-Pr_3SiCl, *i*-$BuSiCl_3$, or *t*-$BuSiCl_3$,[8] silane (**3**) was alternatively prepared by the reaction of carbenoid (**2**) with *tert*-$BuMe_2SiCl$. Thus, treatment of **1** with BuLi in THF-Et_2O (2 : 1) at -130 °C in the presence of *t*-$BuMe_2SiCl$ gave **3** in 74% yield after purification by column chromatography on silica gel (eq. 2).

$$Me_3SiCl + \underset{\mathbf{1}}{CFBr_3} + (Me_2N)_2C{=}C(NMe_2)_2 \xrightarrow[-20\ ^\circ C\ to\ rt]{CH_2Cl_2} \begin{array}{c} Me_3SiCFBr_2 \\ 54\% \\ + \\ [(Me_2N)_2CC(NMe_2)_2]^{2+}Cl^-Br^- \end{array} \quad (1)$$

$$t\text{-}BuMe_2SiCl + \underset{\mathbf{1}}{CFBr_3} \xrightarrow[-130\ ^\circ C]{\begin{array}{c} BuLi \\ THF\text{-}Et_2O\ (2:1) \end{array}} \underset{\begin{array}{c}\mathbf{3}\\ 74\%\end{array}}{t\text{-}BuMe_2SiCFBr_2} + BuBr + LiCl \quad (2)$$

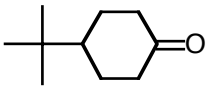
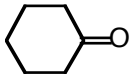
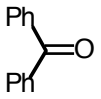
Generation and Carbonyl Addition of Silicon-substituted Lithium Carbenoid (4)

With **3** in hand, we first studied the generation and carbonyl addition of **4** using 4-phenyl-2-butanone as a carbonyl electrophile (Scheme 2). Treatment of **3** with BuLi *in the presence of* 4-phenyl-2-butanone in THF at -78 °C gave 1-fluoro-1-(*tert*-butyldimethylsilyl)-2-methyl-4-phenyl-2,3-epoxybutane (**5a**)[9] in 94% yield as a 64 : 36 mixture of diastereomers.[10] When 4-phenyl-2-butanone was added to the reaction mixture *after* the generation of **4** at -78°C, the yield of **5a** decreased drastically (16%, diastereomeric ratio = 68 : 32), while **5a** was obtained in 86% yield (diastereomeric ratio = 67 : 33) when the carbenoid was generated at -98 °C *followed* by the addition of 4-phenyl-2-butanone. Since **2** must be generated at –130°C *in the presence of* an electrophile, the above results show that substitution of a silyl group at a fluorine-attached carbon is effective for the stability enhancement of fluorinated carbenoid reagent (**2**). The *in-situ* procedure was applied to various aldehydes and ketones. The results are summarized in Table 1.



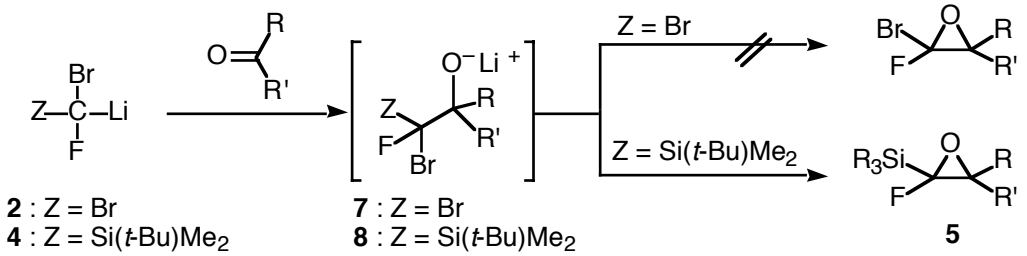
Scheme 2

Table 1. Carbonyl Addition of Lithium Carbenoid (**4**)

Entry	RR'CO	R	R'	Product	Yield (%)[a]	Diastereomeric ratio[b]
1	1-$C_{10}H_7CHO$	H	1-$C_{10}H_7$	**5b**	86	94 : 6
2	$Ph(CH_2)_2CHO$	H	$Ph(CH_2)_2$	**5c**	73	55 : 45
3	*n*-$C_7H_{15}CHO$	H	*n*-C_7H_{15}	**5d**	97	56 : 44
4		-$(CH_2)_2$CH(*t*-Bu)$(CH_2)_2$-		**5e**	98	73 : 27
5		-$(CH_2)_5$-		**5f**	97	———
6		Ph	Ph	**5g**	89	———

a) Isolated yield. b) The diastereomeric ratio was determined on the basis of ^1H and ^{19}F NMR spectroscopy. The stereochemistry was not determined.

Formation of 1-fluoro-1-silyloxiranes (**5**) proceeded in good to excellent yields with moderate to good diastereoselectivities and is attributed to a carbonyl addition of **4** to give alkoxide (**7**) followed by cyclization (Scheme 3). Noteworthy is that the substitution reaction took place at the fluorine-substituted carbon, a reaction considered to hardly take place intermolecularly.[11] Indeed, lithium alkoxide (**7**) derived from **2** did not cyclize even at a refluxing temperature of THF.[4] The ring-closure of **8** to give **5** should be attributed to the interaction of a Si-C σ* orbital with the *p*-orbital to stabilize the transition state of the nucleophilic substitution.[12] Thus, the silicon accelerating effect for the nucleophilic substitution at the α-carbon surpasses the fluorine retarding effect.

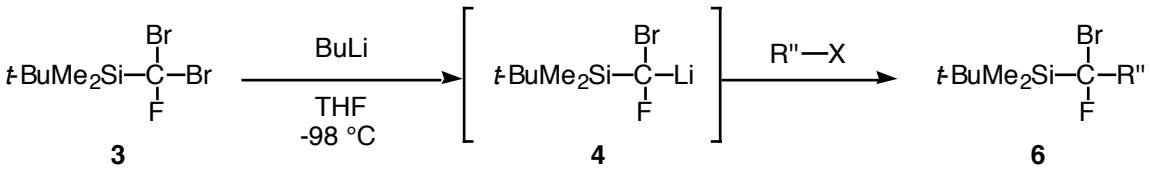


Scheme 3

Alkylation of Silicon-substituted Lithium Carbenoid (4)

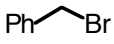
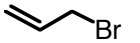
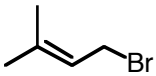
As described above, addition of a carbonyl electrophile can be performed *after* the generation of the carbenoid reagent at -98 °C. This observation suggests that **4** can be allowed to react with an electrophile that may competitively react with BuLi. Thus, alkylation was carried out by the addition of an alkylating reagent after **4** was generated at -98 °C. The results are shown in Table 2. The relatively reactive alkyl

halides and sulfonates as well as chlorotrimethylsilane were applicable and the alkylated or silylated products were isolated in good yields.[13]



3 **4** **6**

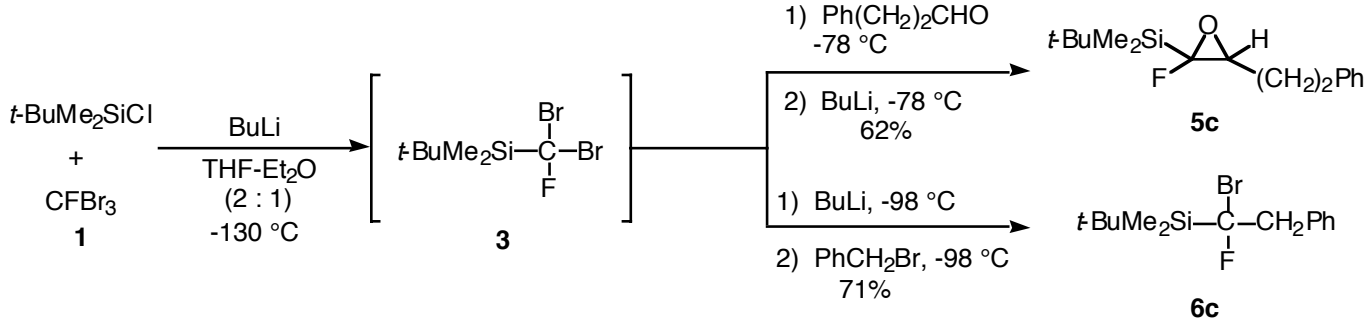
Table 2. Alkylation of Lithium Carbenoid (**4**)

R"—X	Product	Yield (%)[a]	R"—X	Product	Yield (%)[a]
MeI	**6a**	70 [b]		**6f**	trace
EtI	**6b**	85 [b]		**6f**	81
	**6c**	62		**6f**	83
	**6d**	69		**6g**	90
	**6e** [c]	66	Me_3SiCl	**6h**	74

a) Isolated yield. b) Yields were determined by ^1H NMR using 1,1,2-trichloroethylene as an internal standard. c) α-Alkylated product only.

One-pot Synthesis of 5 and 6 Starting with Tribromofluoromethane (1)

Synthetic utility of the fluorine-substituted carbenoid stabilized by a silyl substituent is demonstrated by sequential one-pot reactions involving preparation of **3**, generation of **4**, and carbonyl addition or alkylation (Scheme 4). Thus, **1** (1.5 mol) was treated with butyllithium (1.5 mol) in the presence of *tert*-butylchlorodimethylsilane (1.5 mol) in THF-Et_2O (2 : 1) at -130 °C. To the mixture, 3-phenylpropanal and additional BuLi were added in this order at -78 °C to afford **5c** in 62% yield. On the other hand, butyllithium (1.2 mol) and benzyl bromide (1 mol) were successively added to the solution of **3** at -98 °C, giving rise to **6c** in 71% yield.



Scheme 4

In summary, we have demonstrated that 1-fluoro-1-silyloxiranes are synthesized in good yields by the reaction of a fluorine- and silyl-substituted lithium carbenoid reagent with carbonyl compounds. In addition, alkylation of the fluorinated carbenoid with alkyl halides or triflates affords the corresponding products in yields of synthetic meaning. The present reagent provides us with a convenient tool for the synthesis of monofluoro compounds.

ACKNOWLEDGMENT

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EXPERIMENTAL SECTION

General. ^{1}H NMR spectra were measured on a Bruker AC 200 (200 MHz), or a Varian Mercury 200 (200 MHz) or 300 (300 MHz) spectrometer. The chemical shifts of ^{1}H NMR are expressed in parts per million downfield relative to the internal tetramethylsilane (δ = 0 ppm) or chloroform (δ = 7.26 ppm). Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; brs, broad singlet. ^{13}C NMR spectra were measured on a Bruker AC 200 (50 MHz) or a Varian Mercury 200 (200 MHz) spectrometer with tetramethylsilane as an internal standard (δ = 0 ppm). ^{19}F NMR spectra were measured on a Bruker AC 200 (188 MHz) or a Varian Mercury 200 (188 MHz) spectrometer with trichlorofluoromethane as an internal standard (δ = 0 ppm). The chemical-shift values are given in parts per million downfield relative to the internal standard. IR spectra were recorded on a Shimadzu FTIR-8100A spectrophotometer. GC-MS analyses were performed 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 ether were distilled from benzophenone and sodium before use under an argon atmosphere.

Preparation of Dibromo(*tert*-butyldimethylsilyl)fluoromethane (3)

To a solution of tribromofluoromethane (**1**) (98 μL, 1.0 mmol) and *tert*-BuMe_2SiCl (0.150 g, 1.00 mmol) in THF (2 mL)-Et_2O (1 mL) was added a 1.60 M hexane solution of butyllithium (0.63 mL, 1.01 mmol) at -130 ℃ *via* a syringe over a period of 10 min. The resulting mixture was stirred for 0.5 h at -130 ℃ before quenching with a sat. aq. NH_4Cl solution. The aq. layer was extracted with ether (20 mL x 3). The combined extracts were dried over anhydrous sodium sulfate and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (hexane) to afford **3** (0.23 g, 74%). a colorless oil, R_f 0.66 (hexane). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.32 (s, 6H), 1.09 (s, 9H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ -6.6 (d, J = 1.1 Hz), 18.5, 27.4 (d, J = 1.1 Hz), 103.9 (d, J = 339.2 Hz); ^{19}F NMR ($CDCl_3$, 188 MHz) δ -70.7; IR (neat) 2967, 2934, 2863, 2361, 1472, 1464, 1397, 1368, 1256, 1032, 936, 841, 779, 745, 698, 662 cm^{-1}. Anal. Calcd for $C_7H_{15}Br_2FSi$: C, 27.47; H, 4.94. Found: C, 27.20; H, 4.90.

General Procedure for the Generation and Carbonyl Addition of 4

To a THF (2 mL) solution of dibromo(*tert*-butyldimethylsilyl)fluoromethane (**3**) (184 mg, 0.60 mmol) and an aldehyde or ketone (0.50 mmol) was added a 1.60 M hexane solution of butyllithium (3.1 mL, 0.50 mmol) at -78 °C. The resulting solution was stirred for 0.5 h at -78 °C and allowed to warm up to rt. The reaction mixture was quenched with a sat. aq. NH_4Cl solution. The aq. layer was extracted with ether (20 mL x 5); the combined organic layers were dried over anhydrous sodium sulfate. Concentration *in vacuo* gave a crude compound, which was purified by silica gel column chromatography (hexane-EtOAc = 20 : 1 ~ 5 : 1) to give oxirane **5**.

1-*tert*-Butyldimethylsilyl-1-fluoro-2-methyl-4-phenyl-1,2-epoxybutane (5a): a colorless oil, R_f 0.75 (hexane-EtOAc = 5 : 1). ^{1}H NMR ($CDCl_3$, 200 MHz) major isomer: δ 0.00-0.22 (m, 6H), 1.01 (s, 3H), 1.29 (d, *J* = 2.2 Hz, 9H), 1.60-2.19 (m, 2H), 2.77 (d, *J* = 7.4 Hz, 2H), 7.07-7.35 (m, 5 H); minor isomer: (assignable peak) δ 1.46 (s, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) major isomer: δ -6.8 (d, *J* = 2.7 Hz), -5.8 (d, *J* = 4.9 Hz), 16.5 (d, *J* = 1.1 Hz), 19.2 (d, *J* = 3.3 Hz), 26.6 (d, *J* = 1.9 Hz), 31.3 (d, *J* = 0.8 Hz), 35.2 (d, *J* = 0.8 Hz), 62.7 (d, *J* = 16.3 Hz), 100.6 (d, *J* = 290.0 Hz), 125.9, 128.3, 128.3, 141.4; minor isomer: δ -6.6 (d, *J* = 3.0 Hz), -5.8 (d, *J* = 4.2 Hz), 16.6 (d, *J* = 1.1 Hz), 16.8, 26.7 (d, *J* = 2.3 Hz), 30.7 (d, *J* = 1.5 Hz), 36.7 (d, *J* = 3.4 Hz), 63.1 (d, *J* = 16.7 Hz), 100.6 (d, *J* = 290.3 Hz), 126.0, 128.1, 128.5, 141.3; ^{19}F NMR ($CDCl_3$, 188 MHz) major isomer: δ -136.5; minor isomer: δ -139.1; IR (neat) 3029, 2955, 2932, 2860, 2361, 1605, 1497, 1474, 1464, 1381, 1364, 1252, 1050, 899, 841, 823, 808, 779, 749, 700, 683 cm^{-1}. Anal. Calcd for $C_{17}H_{27}OFSi$: C, 69.34; H, 9.24. Found: C, 69.63; H, 9.05.

1-*tert*-Butyldimethylsilyl-1-fluoro-2-(1-naphthyl)-1,2-epoxyethane (5b): a colorless oil, R_f 0.67 (hexane-EtOAc = 4 : 1). ^{1}H NMR ($CDCl_3$, 200 MHz) major isomer: δ -0.53 (s, 3H), -0.22 (s, 3H), 0.93 (s, 9H), 4.51(s, 1H), 7.30-8.15 (m, 7H); minor isomer: (assignable peaks) δ 0.27 (s, 3H), 0.28 (s, 3H), 4.26 (s, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) major isomer: δ -7.3 (d, *J* = 5.0 Hz), -6.8 (d, *J* = 2.3 Hz), 16.8 (d, *J* = 1.5 Hz), 26.5 (d, *J* = 1.1 Hz), 97.5 (d, *J* = 294.7 Hz), 123.2, 123.7 (d, *J* = 2.7 Hz), 125.1, 126.1, 126.5, 128.3, 128.7, 130.1 (d, *J* = 1.9 Hz), 130.8, 133.0; ^{19}F NMR ($CDCl_3$, 188 MHz) major isomer: δ -129.0; minor isomer: δ -153.1; IR (neat) 3060, 2960, 2930, 2880, 2860, 1600, 1510, 1470, 1460, 1360, 1250, 1130, 975, 935, 885, 840, 800, 780, 680 cm^{-1}. Anal. Calcd for $C_{18}H_{23}OFSi$: C, 71.48; H, 7.66. Found: C, 71.60; H, 7.80.

1-*tert*-Butyldimethylsilyl-1-fluoro-4-phenyl-1,2-epoxybutane (5c): a colorless oil, R_f 0.69 (hexane-EtOAc = 10 : 1). ^{1}H NMR ($CDCl_3$, 200 MHz) major isomer: δ 0.03 (d, *J* = 0.4 Hz, 3H), 0.10 (s, 3H), 1.01 (d, *J* = 0.6 Hz, 9H), 1.58-2.23 (m, 2H), 2.64 (td, *J* = 5.9, 0.8 Hz, 1H), 2.70-2.96 (m, 2 H), 7.15-7.38 (m, 5H); minor isomer: (assignable peaks) δ 0.14 (d, *J* = 0.5 Hz, 3H), 0.20 (s, 3H), 3.05 (ddd, *J* = 1.9, 4.5, 8.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) major isomer: δ -8.7 (d, *J* = 3.0 Hz), -8.2 (d, *J* = 3.0 Hz), 16.5 (d, *J* = 0.8 Hz), 26.5 (d, *J* = 1.5 Hz), 28.4 (d, *J* = 2.3 Hz), 32.3, 58.2 (d, *J* = 145.2 Hz), 96.4 (d, *J* = 295.3 Hz), 126.1, 128.3, 128.4, 141.0; minor isomer: δ -7.0 (d, *J* = 3.0 Hz), -6.3 (d, *J* = 4.2 Hz), 16.6 (d, *J* = 1.1 Hz), 26.6 (d, *J* = 1.5 Hz), 30.8 (d, *J* = 2.7 Hz), 32.5 (d, *J* = 4.2 Hz), 58.6 (d, *J* =

140.2 Hz), 96.8 (d, J = 286.9 Hz), 126.2, 128.4, 128.6, 140.6; ^{19}F NMR ($CDCl_3$, 188 MHz) major isomer: δ -154.9; minor isomer: δ -131.7; IR (neat) 3029, 2955, 2932, 2861, 1605, 1497, 1472, 1366, 1254, 1127, 1086, 1009, 957, 891, 841, 824, 808, 781, 749, 698, 681 cm^{-1}. Anal. Calcd for $C_{16}H_{25}OFSi$: C, 68.52; H, 8.98. Found: C, 68.75; H, 9.17.

1-*tert*-Butyldimethylsilyl-1-fluoro-1,2-epoxynonane (5d): a colorless oil, R_f 0.40 (hexane-EtOAc = 5 : 1). ^{1}H NMR ($CDCl_3$, 200 MHz) major isomer: δ 0.05 (s, 3H), 0.11 (s, 3H), 0.80-1.10 (m, 12H), 1.15-1.80 (m, 12H), 2.93-3.05 (m, 1H); minor isomer: (assignable peak) δ 2.59 (t, J = 5.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) major isomer : (assignable peaks) δ -8.6 (d, J = 2.3 Hz), -6.4 (d, J = 4.2 Hz), 14.0, 16.6 (d, J = 1.1 Hz), 22.6, 31.7, 60.6 (d, J = 20,1 Hz), 96.7 (d, J = 285.8 Hz); minor isomer (assignable peaks) δ -8.2 (d, J = 3.0 Hz), -7.0 (d, J = 3.0 Hz), 16.5, 22.6, 31.7, 57.6 (d, J = 16.7 Hz), 96.3 (d, J = 294.2 Hz); ^{19}F NMR ($CDCl_3$, 188 MHz) major isomer: δ -132.0; minor isomer: δ -155.5; IR (neat) 2957, 2930, 2859, 1466, 1366, 1254, 961, 841, 826, 810, 779 ,681 cm^{-1}; MS (70 eV) m/z (rel intensity) 276 (M^++2, 0.9), 275 (M^++1, 1.6), 274 (M^+, 6.5), 133 (100). Anal. Calcd for $C_{15}H_{30}OFSi$: m/z 274.2128. HRMS Found: 274.2115.

1-*tert*-Butyldimethyl[6-*tert*-butyl-2-fluoro-1-oxaspiro[2.5]oct-2-yl]silane (5e): a colorless oil, R_f 0.43 (hexane-EtOAc = 20 : 1). ^{1}H NMR ($CDCl_3$, 200 MHz) major isomer: δ 0.16 (s, 3H), 0.18 (s, 3H), 0.875 (s, 9H), 1.04 (s, 9H), 1.10-2.00 (m, 9H); minor isomer: δ 0.11 (s, 3H), 0.24 (s, 3H), 0.876 (s, 9H), 1.01 (d, J = 4.3 Hz, 9H), 1.08-1.95 (m, 9H); ^{13}C NMR (C_6D_6, 50 MHz) major isomer : (assignable peak) δ -6.2 (d, J = 3.8 Hz), -5.7 (d, J = 3.8 Hz), 17.1 (d, J = 1.5 Hz), 47.1, 101.3 (d, J = 288.7 Hz); minor isomer: (assignable peaks) δ -6.5 (d, J = 2.7 Hz), -5.5 (d, J = 5.3 Hz), 16.7, 47.9, 101.4 (d, J = 287.2 Hz); ^{19}F NMR ($CDCl_3$, 188 MHz) major isomer: δ -139.0; minor isomer: δ -141.7; IR (neat) 2950, 2860, 1470, 1450, 1410, 1390, 1365, 1250, 1210, 1030, 985, 910, 905, 885, 840, 820, 805, 780, 680, 570 cm^{-1}. Anal. Calcd for $C_{17}H_{33}OFSi$: C, 68.03; H, 10.77. Found: C, 67.94; H, 11.07.

1-*tert*-Butyldimethyl[2-fluoro-1-oxaspiro[2.5]oct-2-yl]silane (5f): a colorless oil, R_f 0.77 (hexane-EtOAc = 5 : 1). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.13 (d, J = 0.2 Hz, 3H), 0.18 (s, 3H), 1.01 (d, J = 0.1 Hz, 9H), 1.30-1.85 (m, 10H); ^{13}C NMR (C_6D_6, 50 MHz) δ -6.3 (d, J = 3.4 Hz), -5.7 (d, J = 4.2 Hz), 16.9, 24.6, 24.9, 25.9, 26.9, 31.7 (d, J = 3.4 Hz), 64.8 (d, J = 17.0 Hz), 101.5 (d, J = 287.9 Hz); ^{19}F NMR ($CDCl_3$, 188 MHz) δ -140.7; IR (neat) 2934, 2861, 2361, 2342, 1802, 1649, 1584, 1464, 1451, 1364, 1250, 1167, 1134, 1075, 1017, 957, 905, 891, 864, 839, 773, 675 cm^{-1}; MS (70 eV) m/z (rel intensity) 246 (M^++2, 0.3), 245 (M^++1, 0.6), 244 (M^+, 2.3), 226 (45), 169 (97), 75 (100). Anal. Calcd for $C_{13}H_{25}OFSi$: m/z 244.1659. HRMS Found: 244.1652.

1-*tert*-Butyldimethylsilyl-1-fluoro-2,2-diphenyl-1,2-epoxyethane (5g): a colorless oil, R_f 0.68 (hexane-EtOAc = 5 : 1). ^{1}H NMR ($CDCl_3$, 200 MHz) δ -0.37 (s, 3H), -0.12 (s, 3H), 1.01 (s, 9H), 7.20-7.55 (m, 10H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ -7.4 (d, J = 4.2 Hz), -7.0 (d, J = 2.3 Hz), 17.1 (d, J = 1.9 Hz), 26.8 (d, J = 1.9 Hz), 67.3 (d, J = 17.8 Hz), 100.5 (d, J = 299.4 Hz), 127.2 (d, J = 1.1 Hz), 127.6 (d, J = 1.5 Hz), 127.7, 127.9, 128.1, 128.2, 137.6 (d, J = 4.2 Hz), 137.9 (d, J = 3.8 Hz); ^{19}F NMR ($CDCl_3$, 188 MHz) δ -132.5; IR (neat) 3063, 3033, 2932, 2861, 1813, 1497, 1472, 1449, 1364, 1254, 1051, 926, 905, 876, 839, 808, 783, 754, 702 cm^{-1}; MS (70 eV) m/z (rel intensity) 329 (M^++1, 0.3), 328 (M^+, 0.8), 253 (0.4), 214 (0.2), 194 (19), 166 (100), 77 (39). Anal. Calcd for $C_{20}H_{25}OFSi$: C,

73.13; H, 7.67. Found: C, 73.09; H, 7.73.

1-Bromo-1-(*tert*-butyldimethylsilyl)-1-fluoroethane (6a): a colorless oil, R_f 0.78 (hexane). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.18 (s, 3H), 0.24 (s, 3H), 1.02 (d, *J* = 2.6 Hz, 9H), 2.20 (d, *J* = 24.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ -7.0 (d, *J* = 2.7 Hz), -6.9 (d, *J* = 1.5 Hz), 17.8, 27.4 (d, *J* = 1.1 Hz), 29.7 (d, *J* = 20.6 Hz), 112.2 (d, *J* = 264.7 Hz); ^{19}F NMR ($CDCl_3$, 188 MHz) δ -115.3 (d, *J* = 24.2 Hz); IR (neat) 2960, 2930, 2850, 1460, 1370, 1250, 1150, 1075, 1040, 1000, 895, 840, 820, 775, 690, 670, 570 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 161(M^+-Br, 1.6), 143 (24), 141 (24), 125 (29), 115 (6), 77 (100), 73 (65), 57 (96). Anal. Calcd for $C_8H_{18}FSi$ (M^+-Br): *m/z* 161.1162. HRMS Found: 161.1153.

1-Bromo-1-(*tert*-butyldimethylsilyl)-1-fluoropropane (6b): a colorless oil, R_f 0.61 (hexane). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.19 (s, 3H), 0.25 (s, 3H), 1.03 (d, *J* = 0.6 Hz, 9H), 1.19 (t, *J* = 7.2 Hz, 3H), 1.92-2.42 (m, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ -6.6 (d, *J* = 2.7 Hz), -6.5 (d, *J* = 1.5 Hz), 8.7 (d, *J* = 7.6 Hz), 17.9, 27.5 (d, *J* = 1.1 Hz), 35.6 (d, *J* = 19.3 Hz), 117.9 (d, *J* = 266.8 Hz); ^{19}F NMR ($CDCl_3$, 188 MHz) δ -125.8 (dd, *J* = 10.2, 33.9 Hz); IR (neat) 2963, 2934, 2886, 2863, 1472, 1464, 1395, 1366, 1252, 1111, 1076, 1007, 965, 839, 801, 777, 725, 673 cm^{-1}. Anal. Calcd for $C_9H_{20}OFSi$: C, 42.35; H, 7.90. Found: C, 42.56; H, 7.98.

1-Bromo-1-(*tert*-butyldimethylsilyl)-1-fluoro-2-phenylethane (6c): a colorless oil, R_f 0.39 (hexane). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.25 (s, 3H), 0.28 (s, 3H), 1.11 (d, *J* = 0.6 Hz, 9H), 3.22 (dd, *J* = 14.7, 39.7 Hz, 1H), 3.69 (dd, *J* = 9.8, 14.5 Hz, 1H), 7.26-7.43 (m, 5H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ -6.7 (d, *J* = 2.3 Hz), -6.5 (d, *J* =1.5 Hz), 18.1, 27.7 (d, *J* = 1.1 Hz), 47.5 (d, *J* = 18.3 Hz), 113.7 (d, *J* = 269.2 Hz), 127.2, 127.9, 131.2 (d, *J* = 1.5 Hz), 134.9 (d, *J* = 2.3 Hz); ^{19}F NMR ($CDCl_3$, 188 MHz) δ -127.6; IR (neat) 3088, 3065, 3034, 2961, 2932, 2886, 2861, 1605, 1497, 1472, 1464, 1456, 1414, 1395, 1366, 1254, 1208, 1046, 1030, 1009, 995, 932, 839, 824, 812, 779, 729, 696, 673, 590, 567 cm^{-1}. Anal. Calcd for $C_{14}H_{22}BrFSi$: C, 52.99; H, 6.99. Found: C, 52.85; H, 7.03.

1-Bromo-1-(*tert*-butyldimethylsilyl)-1-fluorobut-3-ene (6d): a colorless oil, R_f 0.56 (hexane). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.20 (s, 3H), 0.25 (s, 3H), 1.04 (s, 9H), 2.70-3.20 (m, 2H), 5.10-5.35 (m, 2H), 5.90-6.10 (m, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ -6.6 (d, *J* = 2.3 Hz), -6.9 (d, *J* = 2.0 Hz), 17.9, 27.5, 46.8 (d, *J* = 19.0 Hz), 114.3 (d, *J* = 267.1 Hz), 119.5, 131.6 (d, *J* = 7.6 Hz); ^{19}F NMR ($CDCl_3$, 188 MHz) δ -125.0 (dd, *J* = 10.2, 30.5 Hz); IR (neat) 3083, 2963, 2932, 2863, 1642, 1472, 1466, 1410, 1395, 1366, 1254, 1235, 1134, 1057, 1007, 990, 922, 839, 826, 777, 673, 629 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 187 (M^+-Br, 1), 151 (0.4), 139 (28), 137 (28), 115 (18), 77 (73), 57 (100). Anal. Calcd for $C_{10}H_{20}FSi$ (M^+-Br): *m/z* 187.1318. HRMS Found: 187.1322.

1-Bromo-1-(*tert*-butyldimethylsilyl)-1-fluoro-4-methylpent-3-ene (6e): a colorless oil, R_f 0.69 (hexane). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.20 (s, 3H), 0.24 (s, 3H), 1.03 (s, 9H), 1.64 (s, 3H), 1.78 (d, *J* = 1.2 Hz, 3H), 2.67-3.14 (m, 2H), 5.32-5.43 (m, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ -6.6 (d, *J* = 2.7 Hz), -6.3 (d, *J* = 1.9 Hz), 17.9, 18.4 (d, *J* = 0.8 Hz), 25.9, 27.5 (d, *J* = 1.1 Hz), 41.3 (d, *J* = 19.0 Hz), 116.0 (d, *J* = 266.8 Hz), 117.5 (d, *J* = 6.8 Hz), 135.8; ^{19}F NMR ($CDCl_3$, 188 MHz) δ -124.2 (dd, *J* = 11.9, 32.2 Hz); IR (neat) 2965, 2932, 2886, 2861, 1676, 1472, 1464, 1451, 1414, 1377, 1366, 1254, 1181, 1113, 1046, 936, 839, 823, 812, 777, 739, 673 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 181 (M^++2-$SiMe_2$(*tert*-Bu), 0.4), 179 (M^+-$SiMe_2$(*tert*-Bu), 0.3), 160 (0.7), 139 (22), 137 (22), 115 (9), 77 (100), 57

(35). Anal. Calcd for C_6H_9BrF (M^+-Si(*tert*-Bu)Me_2): *m/z* 178.9872. HRMS Found: 178.9980.

1-Bromo-1-(*tert*-butyldimethylsilyl)-1-fluoro-4-phenylbutane (6f): a colorless oil, R_f 0.50 (hexane). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.16 (s, 3H), 0.22 (s, 3H), 0.99 (d, *J* = 0.6 Hz, 9H), 1.90-2.35 (m, 4H), 2.68 (t, *J* = 6.6 Hz, 2H), 7.05-7.35 (m, 5H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ -6.6 (d, *J* = 3.0 Hz,), -6.5 (d, *J* = 1.9 Hz), 17.9, 26.0 (d, *J* = 5.7 Hz), 27.5 (d, *J* = 0.8 Hz), 35.4, 41.9 (d, *J* = 19.0 Hz), 116.9 (d, *J* = 266.5 Hz), 125.9, 128.4 (2 peaks), 141.7; ^{19}F NMR ($CDCl_3$, 188 MHz) δ -123.9 (dd, *J* = 6.6, 30.5 Hz); IR (neat) 3029, 2959, 2932, 2861, 1605, 1497, 1472, 1464, 1366, 1254, 1084, 1007, 955, 839, 810, 777, 747 cm^{-1}. Anal. Calcd for $C_{16}H_{26}BrFSi$: C, 55.64; H, 7.59. Found: C, 55.51; H, 7.63.

1-Bromo-1-(*tert*-butyldimethylsilyl)-1-fluorohex-5-ene (6g): a colorless oil, R_f 0.65 (hexane). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.19 (s, 3H), 0.24 (s, 3H), 1.02 (s, 9H), 1.70-2.35 (m, 6H), 4.90-5.22 (m, 2H), 5.82 (ddt, *J* = 10.2, 17.0, 6.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ -6.6 (d, *J* = 2.7 Hz), -6.5 (d, *J* = 1.5 Hz), 17.9, 23.5 (d, *J* = 5.7 Hz), 27.5 (d, *J* = 1.1 Hz), 33.3, 41.7 (d, *J* = 18.6 Hz), 115.1, 117.0 (d, *J* = 266.4 Hz), 138.03; ^{19}F NMR ($CDCl_3$, 188 MHz) δ -124.1 (dd, *J* = 10.2, 33.9 Hz); IR (neat) 3079, 2959, 2934, 2861, 1642, 1509, 1474, 1464, 1366, 1254, 949, 912, 839, 824, 777, 673 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 181 (M^++2-Si(*tert*-Bu)Me_2, 0.7), 179 (M^+-$SiMe_2$(*tert*-Bu), 0.7), 159 (0.5), 139 (52), 137 (52), 115 (15), 77 (100), 73 (97), 57 (100). Anal. Calcd for C_6H_9BrF (M^+-Si(*tert*-Bu)Me_2): *m/z* 178.9872. HRMS Found: 178.9885.

Bromo(*tert*-butyldimethylsilyl)fluoro(trimethylsilyl)methane (6h): a colorless oil, R_f 0.58 (hexane). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.18 (s, 3H), 0.19 (s, 3H), 0.25 (s, 9H), 1.06 (d, *J* = 0.6 Hz, 9H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ -5.0 (d, *J* = 1.1 Hz), -4.9 (d, *J* = 4.2 Hz), -2.0 (d, *J* = 2.3 Hz), 18.9 (d, *J* = 0.8 Hz), 113.9 (d, *J* = 264.3 Hz); ^{19}F NMR ($CDCl_3$, 188 MHz) δ -169.7. IR (neat) 2959, 2932, 2861, 2361, 1474, 1464, 1412, 1366, 1254, 949, 885, 847, 804, 787, 776, 745, 702, 619 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 302 (M^++4, 0.01), 301 (M^++3, 0.02), 300 (M^++2, 0.07), 299 (M^++1, 0.01), 298 (M^+, 0.05),151 (46), 149 (45), 139 (58), 137 (58), 85 (57), 73 (100), 57 (81). Anal. Calcd for $C_{10}H_{24}BrFSi_2$: C, 40.12; H, 8.08. Found: C, 39.97; H, 7.83.

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