

Fluoride Ion-Catalyzed Generation and Carbonyl Addition of α -Halo Carbanions Derived from α -Halo Organosilicon Compounds

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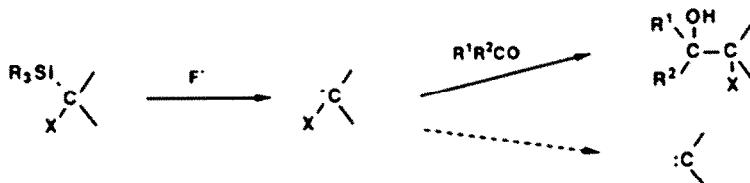
(Received in UK 9 September 1987)

Abstract: The title carbanion species are generated from the corresponding α -halo-organosilicon compounds by the action of a catalytic amount of tris(diethylamino)sulfonium difluorotrimethylsilicate and are found to undergo addition to aldehyde carbonyl efficiently at ambient temperature. The synthetic potential of the reaction is demonstrated by application to the synthesis of some insecticides.

Organometallic compounds having such leaving groups as halogen(s) at the α -position to the metal are called carbenoids and are in general thermally unstable to undergo α -elimination readily to give rise to carbenes.¹ Thus, for synthetic purpose, these must be generated and handled at extremely low temperatures:² for example, chloromethylithium decomposes even at -130 °C and preparation of dichloro- and trichloromethylithium should be carried out at -110 °C or -78 °C, respectively. The instability is attributed to intramolecular coordination by the halogen to the metal.¹ In order to weaken the intramolecular coordination, basic solvents³ or lithium salt additives⁴ have been employed. Another modification of the procedure for mono- and polyhalomethylithiums is reported: lithium dicyclohexylamide^{5a} or butyllithium^{5b} was added to a mixture of ketone and excess polyhalomethane at -95 °C to 0 °C. In spite of such efforts, however, handling of them still requires careful experimentation. We reasoned that, if the counter cation is well separated, the intramolecular coordination diminishes largely or disappears, and therefore the corresponding carbenoid anions should have enough life-times to undergo synthetic reactions before decomposition.

The strategy to generate the metal-free carbenoid anions is illustrated in Scheme 1. The key precursors are the corresponding α -haloorganosilanes. Reaction of α -haloalkylsilanes with tetrabutylammonium fluoride (TBAF) or tris(diethylamino)sulfonium difluorotrimethylsilicate (TASF) is expected to generate the desired carbanion species.⁶ The ammonium and sulfonium ions exist only as a charge neutralizer which does not form covalent bond with the carbanions.

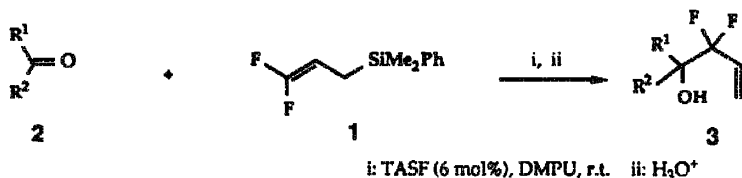
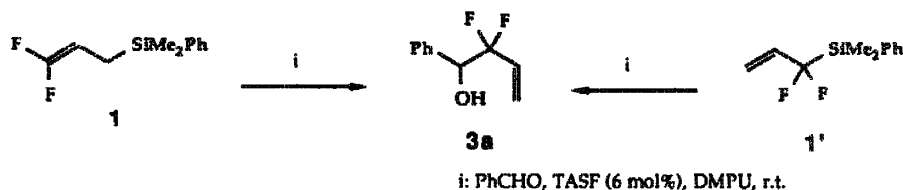
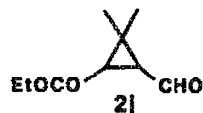
Scheme 1



$F^- = n-Bu_4N^+ F^-$ (TBAF), $(R_2N)_3S^+ Me_3SiF_2^-$ (TASF)

The working hypothesis discussed above originates from our earlier observation⁷ that γ,γ - and α,α -difluoroallyl(dimethyl)phenylsilanes (**1** and **1'**) react with benzaldehyde (**2a**) to afford 2,2-difluoro-1-phenyl-3-buten-1-ol (**3a**) under TASF catalysis at room temperature in 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU) and that an equilibrium between **1** and **1'** was not observed under the reaction

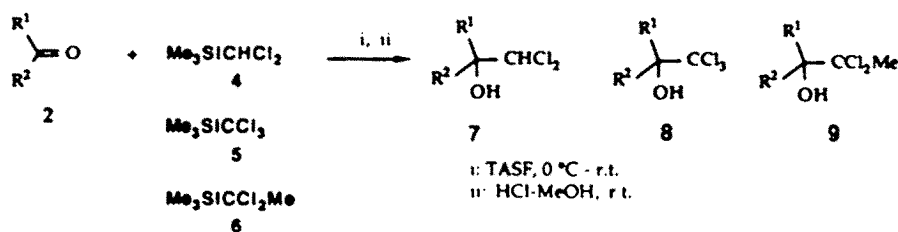
conditions. These experimental evidences suggest a metal free *gem*-difluoroallyl anion as the common intermediate, though *gem*-difluoroallyllithium exists only at low temperature of $-95\text{ }^{\circ}\text{C}$.⁸ In addition to benzaldehyde, the difluoroallylsilane **1** underwent addition to a variety of aldehydes and ketones at room temperature (Table 1).

a: R¹ = Ph, R² = Hc: R¹ = PhCH=CH, R² = He: R¹ = *t*-Bu, R² = Hg: R¹ = PhCH(Me), R² = Hi: R¹ = Me₂C=CH, R² = Hb: R¹ = 4-Cl-C₆H₄, R² = Hd: R¹ = *n*-C₁₀H₂₁, R² = Hf: R¹ = R² = Phh: R¹ = 3,4-Cl₂-C₆H₃, R² = HTable 1 TASF-Catalyzed Carbonyl Addition of **1** and **1**^a

Run	Aldehyde or Ketone	Solvent	Product	% Yield ^b
1	2a	DMPU	3a	93
2	2a	THF	3a	100
3	2a	DMPU	3^ac	98
4	2b	DMPU	3b	100
5	2c	DMPU	3c	52
6	2d	DMPU	3d	44
7	2d	THF	3d	42
8	2e^d	DMPU	3e	53
9	2f^e	THF	3f	34

^aThe reaction was carried out at room temperature with 0.06 eq of TASF. ^bIsolated yield.

^cCF₂=C(Me)CH₂SiMe₂Ph (**1**^{*}) was used instead of **1**. ^dIsolated as the dimethylphenylsilyl ether without acidic workup. ^eRecovered benzophenone was 50%.



In order to get further support for our working hypothesis, we subjected (dichloromethyl)-trimethylsilane (4) to the reaction with benzaldehyde under the similar conditions. Indeed, 4 afforded the expected adduct 7a in 77% yield in tetrahydrofuran (THF) in the presence of TASF⁹ catalyst (25 mol%) at room temperature. TBAF was less active,¹⁰ and aprotic polar solvents like hexamethylphosphoric triamide (HMPA) or dimethylformamide (DMF) were slightly inferior.

The reaction conditions were applied to other chlorinated silanes and various aldehydes under the optimized conditions. Though (chloromethyl)trimethylsilane and (difluoromethyl)dimethylphenylsilanes did not give the adducts, di- or trichlorinated alkylsilanes (5 and 6) gave the corresponding adducts in high yields. Noteworthy is that the carbonyl addition of polychloromethyl anion proceeds at room temperature in sharp contrast to the reaction of polychloromethylolithiums. The failure of $\text{PhMe}_2\text{SiCHF}_2$ may be attributed to fluorine substituents which destabilize the negative charge at α -carbon.¹¹ Ketones like cyclohexanone did not give the desired products. Instead, formation of enol silyl ether predominated as observed in the reaction with acetophenone. The carbanions generated in this system seems to be basic enough to induce enolization.¹²

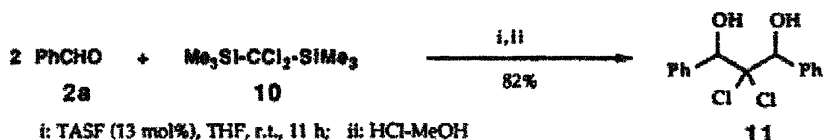
Table 2 Aldehyde Addition of 4, 5, and 6

Run	Aldehyde	Silane ^a	TASF (mol%)	Conditions	Product	% Yield ^{b,c}
1	2a	4	25	THF, r.t., 8 h	7a	74 ^d
2	2a	4	25	DMF, r.t., 20 h	7a	66 ^e
3	2a	4	25	HMPA, r.t., 20 h	7a	41 ^e
4	2a	4	100	THF, r.t., 12 h	7a	59 ^e
5	2c	4	25	THF, r.t., 18 h	7c	95
6	2d	4	25	THF, r.t., 18 h	7d	72
7	2g	4	25	THF, 0 °C, 9 h	7g	62
8	2h	4	25	THF, r.t., 3 h	7h	75
9	2j	4	25	THF, r.t., 6 h	7j	67
10	2a	5	10	THF, r.t., 8 h	8a	77
11	2d	5	10	THF, 0 °C, 12 h	8d	79
12	2i	5	5	THF, r.t., 4 h	8i	88
13	2a	6	25	THF, r.t., 12 h	9a	97

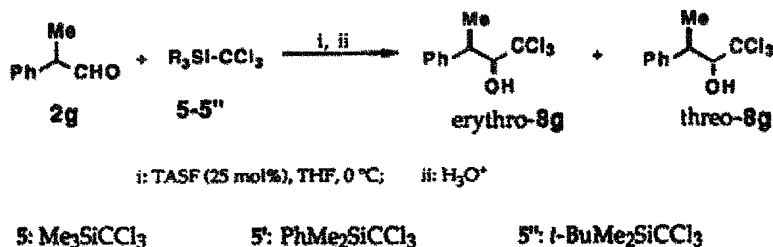
^aThe silane (1.2 mol equiv) was used. ^bIsolated after desilylation (1 M HCl-MeOH, r.t., 0.25-0.5 h).

^cIsolated yields are given unless otherwise noted. ^dGLC yield was 77%. ^eGLC yield

Bis(trimethylsilyl)dichloromethane (10) reacted with 2 mol of benzaldehyde (2a) to give a 1 : 2 adduct 11 and thus can be regarded as a synthon of dichloromethylene dianion (CCl_2^-).



It remains uncertain whether a truly naked carbenoid anion is generated. To gain insight into the mechanism, we studied stereoselectivity of the carbonyl addition. The reaction of 2-phenylpropanal (2g) with 5 afforded erythro isomer of the adduct 8g as the major product (87% selectivity).¹³ The erythro : threo ratio (87 : 13) did not change significantly on employment of $\text{PhMe}_2\text{SiCCl}_3$ (5') (87 : 13) or $t\text{-BuMe}_2\text{SiCCl}_3$ (5'') (90 : 10). Thus, we concluded that the observed product ratio was the intrinsic selectivity of a naked trichloromethyl anion, and that a possible reactive intermediate pentavalent silicate species was safely rejected on the basis of the lack of the substituent effect at silicon. A paper by Shono and his coworkers¹⁴ disclosed a similar erythro : threo ratio (86 : 14) for the same transformation carried out under the electrochemical conditions (*e.*, CHCl_3 , CCl_4 , $\text{Et}_4\text{N}^+ \text{TsO}^-$).



The potential of the aldehyde addition of α -polyhaloalkylsilanes is demonstrated by the practical synthesis of some halogen containing insecticides. For example, addition of 4 to 3,4-dichlorobenzaldehyde (2h) gave an insecticide 7h,¹⁵ whereas the products 7j¹⁶ and 8i¹⁶ are precursors of 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylic acid, an acid part of permethrin and its derivatives.¹⁸

The concept of stabilizing carbenoid anions by removing the counter metal cations was extended to polyhaloethenyl anions,¹⁹ which might undergo β -elimination in addition to α -elimination. This extension was tested by the TASF-aided reaction of (polyhaloethenyl)silanes (12-17) with aldehydes at room temperature. Results summarized in Table 3 clearly show that β -elimination to acetylenes was relatively suppressed, and the carbonyl addition took place in fairly good yields. The successful C-C bond formation at ambient temperature contrasts sharply to the reaction of (trifluoroethenyl)lithium^{20,21} which is thermally extremely labile and should be handled below -78°C . Normant *et al.* recently reported potassium fluoride-mediated reaction of (polyfluoroethenyl)silane with electrophiles in dimethyl sulfoxide. Although protodesilylation of (trifluoroethenyl)silane proceeds smoothly, an aldehyde addition is apparently less effective: only one example reported therein is addition of 14 to 2e (yield unspecified). Evidently, replacing the counter metal cation to tris(diethylamino)sulfonium ion (TAS^+) is remarkably efficient for stabilizing the carbenoid anions and effecting the aldehyde addition.

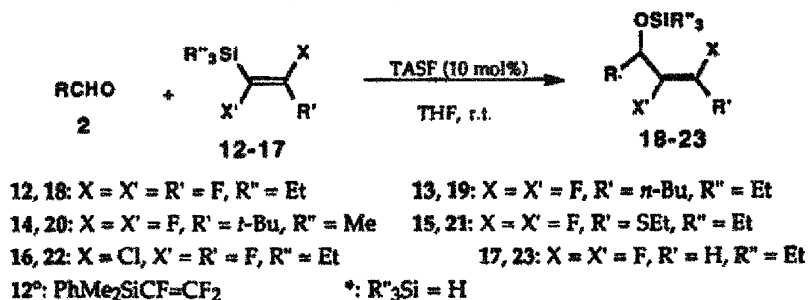
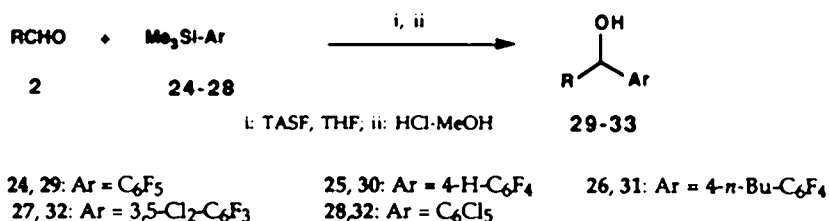


Table 3 Aldehyde Addition of Polyhaloethenylsilanes (12-17)^a

Run	Aldehyde	Silane ^b	TASF (mol%)	Reaction Time (h)	Product	% Yield
1	2a	12	20 ^c	5.5	18a	42
2	2a	12 ^d	10	24	18a	66
3	2a	12 ^e	10	7	18 ^g a ^f	61
4	2c	12	10	12	18c	43
5	2d	12 ^f	10	12	18d	59
6	2j	12	10	10	18j	39
7	2a	13	10	4	19a	84
8	2a	14	10	7	20a 20 ^h a	38 48
9	2a	15	10	8	21a	86
10	2a	16	10	12	22a	38
11	2d	16	10	24	22d	39
12	2d	17	10	24	23d	47

^aAll reactions were carried out in THF at room temperature. ^bThe silane (1.2 mol equiv) was used unless otherwise stated. ^cTBAF was employed in place of TASF. ^d2a/12 = 1.5. ^eIsolated after desilylation (HCl-MeOH, r.t.). ^f2d/12 = 1.2.

The extension applies also to polyhaloarylsilanes (24-28) whose Ar groups were smoothly introduced to aldehyde carbonyls (Table 4). Though a closely related reaction by means of potassium fluoride catalyst was reported by Ishikawa and his coworker,²³ the present system with TASF catalyst gave better yields. Again, decomposition to benzyne seems to be a minor pathway.



In conclusion, α - and β -haloorganosilanes are found to generate, with the aid of TASF catalyst, the corresponding α - and β -halo carbanion species which give the corresponding aldehyde adducts at ambient temperature. This methodology allows us to carry out synthetic reactions of versatile carbenoid anions conveniently and study the stability and reactivity of a wide variety of metal-free carbanion species whose organometallic compounds are unstable even at low temperatures.

Table 4 Aldehyde Addition of Polyhaloarylsilanes (24-28)

Run	Aldehyde	Arylsilane ^a	TASF (mol%)	Conditions	Product	% Yield ^b
1	2a	24	10	r.t., 12 h	29a	87
2	2a	25	10	0 °C, 12 h	30a	43
3	2a	26	10	r.t., 8 h	31a	89
4	2a	27	5	r.t., 2.5 h	32a	87
5	2a	28	10	r.t., 3 h	33a	87
6	2e	24	10	r.t., 12 h	29e	63
7	2e	25	10	0 °C, 12 h	30e	44

^aThe silane (1.2 mol) was used and the reaction was carried out in THF. ^bIsolated yield after desilylation with HCl-MeOH at room temperature.

Experimental

Melting points and boiling points are uncorrected. Bulb-to-bulb distillation was carried out by use of Büchi Kugelrohr or Glass Tube Oven (Shibata GTO 250R). ¹H NMR spectra (tetramethylsilane as an internal standard) were obtained with a Varian EM-390, Varian XL-100A, Hitachi R-90H, or Bruker AM-400 spectrometer, chemical shifts being given in ppm units. ¹⁹F NMR spectra (trichlorofluoromethane as an internal standard) with a Hitachi R-20B or Varian XL-100A spectrometer, ¹³C NMR spectra with a Bruker AM-400. IR data of neat liquid film samples (unless otherwise noted) were recorded with a JASCO A-202. Mass spectra (70 eV) were recorded with a RMU-6MG, high mass with a Hitachi M-80A spectrometer. GLC analyses were performed with a Shimadzu GC-7A chromatograph (FID detector). Preparative GLC were carried out with a Shimadzu GC-3BT chromatograph (TCD detector). TLC analyses were performed by means of Merck Silica Gel 60 F254 (0.25 mm thick). Preparative TLC plates were prepared with Merck Kiesel-Gel PF254. Column chromatography was carried out with silica-gel (Wakogel C-200) at atmospheric pressure. DMPU, HMPA, and DMF were distilled over calcium hydride and stored over Molecular Sieve 4A. (Dichloromethyl)trimethylsilane (4) and (chloromethyl)trimethylsilane were purchased from Aldrich Chemical Co. and distilled before use. Following halogenated silanes 3,3-difluoro-3-(dimethylphenylsilyl)propene (1),⁸ (trichloromethyl)trimethylsilane (5),²⁵ (1,1-dichloroethyl)trimethylsilane (6),²⁵ (difluoromethyl)dimethylphenylsilane,²⁸ bis(trimethylsilyl)dichloromethane (10),²³ (trichloromethyl)dimethylphenylsilane (5'),²⁵ (triethylsilyl)trifluoroethene (12),^{21c} trifluoro(trimethylsilyl)ethene,²¹ 1-chloro-1-(triethylsilyl)difluoroethene (16),²⁹ 1,2-difluoro-3,3-dimethyl-1-(trimethylsilyl)-1-butene (14),²² (pentafluoro)trimethylsilylbenzene (24),³⁰ and pentachloro(trimethylsilyl)benzene (28)³¹ were prepared according to the reported methods. (Dimethylphenylsilyl)trifluoroethene (12^a)^{21c} and 1-triethylsilyl-1,2-difluoro-1-hexene (13)²² were prepared by the modified literature procedure and showed following physical data. 12^a: bp 82-83 °C/17 Torr; ¹H NMR (CDCl₃) δ 0.47 (s, 6 H), 7.35-7.48 (m, 3 H), 7.58-7.72 (m, 2 H); ¹⁹F NMR (CDCl₃) δ 86.3 (dd, *J* = 65.6, 24.7 Hz, 1F), 114.0 (dd, *J* = 115.7 Hz, 1 F), 197.3 (dd, *J* = 115.7, 24.7 Hz, 1 F); IR 3090, 2975, 1725, 1425, 1265, 1255, 1130, 1115, 1040, 840, 815, 790, 730, 705, 695 cm⁻¹; MS *m/z* (rel intensity) 216 (M⁺, 7), 201 (13), 139 (45), 135 (88), 121 (25), 120 (35), 115 (38), 101 (81), 91 (34), 81 (100), 77 (50), 75 (41), 51 (33), 47 (38). Found: C, 55.79; H, 5.02%. Calcd for C₁₀H₁₁F₃Si: C, 55.54; H, 5.13%. 13: bp 100-120 °C (bath temp)/25 Torr; ¹H NMR (CDCl₃) δ 0.5-1.1 (m, 18 H), 1.1-1.7 (m, 4 H), 2.43 (ddt, *J* = 6, 7, 23 Hz, 2 H); ¹⁹F NMR (CDCl₃) δ = 145 (dt, *J* = 127, 23 Hz, 1 F), 172 (dt, *J* = 127, 6 Hz, 1 F); IR 2975, 2950, 2900, 1676, 1470, 1248, 1088, 1020, 741, 728 cm⁻¹; MS *m/z* (rel intensity) 234 (M⁺, 10), 107 (28), 105 (64), 95 (55), 81 (59), 79 (65), 77 (100), 67 (22), 55 (13), 53 (31), 49 (18), 47 (10), 41 (41). Found: C, 61.74; H, 10.50%. Calcd for C₁₂H₂₄F₂Si: C, 61.49; H, 10.32%.

1,1-Difluoro-3-(dimethylphenylsilyl)propene (1): A THF (2 ml) solution of pentamethylphenyldisilane (0.238 ml, 1 mmol) was treated with TBAF (0.5 M THF solution, 0.2 ml, 0.1 mmol), and the mixture was stirred for 5 min. Then, 3,3,3-trifluoropropene (TFP, 26.9 ml at 1 atm, 1.2 mmol) was bubbled at room temperature. The resulting reaction mixture was stirred for 6 h, then treated with water, and concentrated. Distillation at 120-130 (bath temp)/23 Torr gave 1 (0.181 g, 85% yield) as a colorless oil. ¹H NMR (CCl₄): δ 0.40 (s, 6 H), 1.55 (dt, *J* = 9 Hz, 2 H), 4.10 (ddt, *J* = 25, 2, 8 Hz, 1 H), 7.20-7.70 (m, 5 H);

^{19}F NMR (CCl_4): δ 89.85 (dd, $J = 50.8, 2.0$ Hz, 1 F), 93.00 (dd, $J = 50.8, 25.1$ Hz, 1 F). Found: C, 61.97; H, 6.40%. Calcd for $\text{C}_{11}\text{H}_{14}\text{F}_2\text{Si}$: C, 62.23; H, 6.65%.

By using 1,2-diphenyltetramethyldisilane (0.284 ml, 1 mmol) in HMPA (2 ml) and TBAF (0.1 mmol) and by treating the mixture with TFP as above, we obtained **1** (0.180 g, 85% yield).

Alternatively, **1** (9.14 g, 62% yield) was prepared by adding a THF (70 ml) solution of dimethylphenylsilyllithium (0.07 mol) to a THF (50 ml) solution of TFP (large excess) at room temperature and stirring the mixture overnight followed by workup and distillation as above.

3,3-Difluoro-2-methyl-2-propenyldimethylphenylsilane (1'): By using pentamethylphenyldisilane (0.238 ml, 1.0 mmol) and 2-methyl-3,3,3-trifluoropropene (26.9 ml at 1 atm, 1.2 mmol, 1° (0.167 g, 74% yield) was obtained after purification by distillation. Bp 130–140 °C (bath temp)/20 Torr. ^1H NMR (CCl_4) δ 0.32 (s, 6 H), 1.43 (t, $J = 3$ Hz, 3 H), 1.51 (t, $J = 2$ Hz, 2 H), 7.30–7.57 (m, 5 H). ^{19}F NMR (CCl_4) 97.40 (d, $J = 60$ Hz, 1 F), 99.42 (d, $J = 60$ Hz, 1 F); IR 1755, 1260, 1250, 1210, 1200, 1113, 1057, 965, 833, 710 cm^{-1} ; MS m/z (rel intensity) 139 (3), 136 (13), 135 (100), 107 (4), 105 (3), 91 (3), 77 (2), 43 (5). Found: C, 63.43; H, 7.27%. Calcd for $\text{C}_{12}\text{H}_{16}\text{F}_2\text{Si}$: C, 63.68; H, 7.12%.

Reaction of 1' with Benzaldehyde: TASf (20 mg, 0.06 mmol) was added to a mixture of **1** (0.208 ml, 1.0 mmol) and benzaldehyde (**2a**, 0.102 ml, 1.0 mmol) dissolved in DMPU (2 ml) at room temperature. The resulting mixture was stirred at room temperature overnight, treated with 1 M hydrochloric acid and extracted with diethyl ether. The ethereal extract was washed with sat. aq. NaCl solution, dried over magnesium sulfate, and concentrated in vacuo. Purification by preparative TLC (hexane-ethyl acetate 3 : 1, R_f 0.55) gave 2,2-difluoro-1-phenyl-3-buten-1-ol (**3a**, 0.172 g, 93% yield). ^1H NMR (CCl_4) δ 3.59 (d, $J = 5$ Hz, 1 H), 4.79 (dt, $J = 5, 10$ Hz, 1 H), 5.34–6.18 (m, 3 H), 7.20–7.40 (m, 5 H); ^{19}F NMR (CCl_4) δ 105.87 (dt, $J = 248, 10$ Hz, 1 F), 110.65 (dt, $J = 248, 10$ Hz, 1 F); IR 3440, 1650, 1500, 1421, 1200, 1160, 995, 965, 852, 703, 637 cm^{-1} ; MS m/z (rel intensity) 108 (9), 107 (100), 79 (68), 77 (36), 51 (14). Found: C, 65.01; H, 5.41%. Calcd for $\text{C}_{10}\text{H}_{10}\text{F}_2\text{O}$: C, 65.21; H, 5.47%.

Reaction of 1' with Benzaldehyde: TASf (5 mg, 0.015 mmol) was added to a mixture of **1'** (34 mg, 0.16 mmol) and benzaldehyde (**2a**, 16.3 μl , 0.16 mmol) dissolved in DMPU (1 ml), and the mixture was stirred overnight. Workup and TLC purification (hexane-ethyl acetate 5 : 1) gave **3a** (17 mg, 58% yield) as a colorless oil which exhibited the same ^1H NMR spectra as obtained above.

2,2-Difluoro-1-(4-chlorophenyl)-3-buten-1-ol (3b): TASf (20 mg, 0.06 mmol) was added to a mixture of **1** (0.21 g, 1.0 mmol) and 4-chlorobenzaldehyde (**2b**, 0.141 g, 1.0 mmol) and the reaction mixture was allowed to react overnight. Workup and preparative TLC (hexane-ethyl acetate 5 : 1, R_f 0.25) gave **3b** (0.222 g, 100% yield) as a colorless viscous oil. ^1H NMR (CCl_4) δ 2.39 (d, $J = 4$ Hz, 1 H), 4.79 (dt, $J = 4, 9$ Hz, 1 H), 5.30–6.07 (m, 3 H), 7.20–7.33 (m, 4 H); ^{19}F NMR (CCl_4) δ 107.20 (dt, $J = 250, 9$ Hz, 1 F), 10.70 (dt, $J = 250, 9$ Hz, 1 F); IR 3440, 1603, 1500, 1423, 1095, 1018, 855, 800, 770, 704 cm^{-1} ; MS m/z (rel intensity) 143 (33), 141 (100), 113 (21), 77 (85), 51 (15). Found: C, 55.01; H, 4.04%. Calcd for $\text{C}_{10}\text{H}_9\text{ClF}_2\text{O}$: C, 54.94; H, 4.15%.

4,4-Difluoro-1-phenyl-1,5-hexadien-3-ol (3c): TASf (20 mg, 0.06 mmol) was added to **1** (0.21 ml, 1.0 mmol) and cinnamaldehyde (**2c**, 0.126 ml, 1.0 mmol) dissolved in DMPU (2 ml), and the resulting mixture was stirred overnight at room temperature. Workup and preparative TLC (hexane-ethyl acetate 5 : 1, R_f 0.35) gave **3c** (0.110 g, 52% yield) as a viscous oil. ^1H NMR (CCl_4) δ 2.07 (d, $J = 5$ Hz, 1 H), 4.20–4.65 (m, 1 H), 5.40–6.83 (m, 5 H), 7.12–7.45 (m, 5 H); ^{19}F NMR (CDCl_3) 108.17 (dt, $J = 250, 10$ Hz, 1 F), 111.57 (dt, $J = 250, 10$ Hz, 1 F); IR 3425, 1663, 1655, 1600, 1580, 1500, 1450, 1420, 1160, 1070, 970, 865, 746, 690 cm^{-1} ; MS m/z (rel intensity) 133 (100), 115 (24), 105 (9), 103 (9), 77 (19), 55 (36). Found: C, 68.49; H, 5.72%. Calcd for $\text{C}_{12}\text{H}_{12}\text{F}_2\text{O}$: C, 68.56; H, 5.75%.

3,3-Difluoro-1-tetradecen-4-ol (3d): Undecanal (**2d**, 0.206 ml, 1.0 mmol) in DMPU was subjected to the TASf-catalyzed reaction with **1** exactly as above. Purification of the crude product by column chromatography (hexane-ethyl acetate 10 : 1) gave **3d** (0.110 g, 44% yield) as colorless solid. Mp 38–38.5 °C; ^1H NMR (CCl_4) δ 0.89 (t, $J = 6$ Hz, 3 H), 1.15–1.70 (m, 18 H), 1.90 (br s, 1 H), 3.40–3.90 (m, 1 H), 5.37–6.17 (m, 3 H); ^{19}F NMR (CCl_4) δ 108.24 (dt, $J = 250, 9$ Hz, 1 F), 113.76 (dt, $J = 250, 9$ Hz, 1 F); IR (KBr) 3425, 1470, 1425, 1090, 990, 950, 810, 720 cm^{-1} ; MS m/z (rel intensity) 171 (37), 111 (27), 97 (100), 83 (95), 77 (10), 71 (27), 69 (94), 57 (42), 55 (98), 43 (64), 41 (47). Found: C, 67.95; H, 10.56%. Calcd for $\text{C}_{14}\text{H}_{26}\text{F}_2\text{O}$: C, 67.71; H, 10.55%.

3,3-Difluoro-5,5-dimethyl-4-(dimethylphenylsiloxy) 1-hexene (3e): Pivaldehyde (**2e**, 0.109 ml, 1.0 mmol) was allowed to react with **1** and TASf catalyst as above. Workup followed by GLC analysis revealed 53% yield of **3e** which showed ^1H NMR (CCl_4) δ 0.42 (s, 6 H), 0.90 (d, $J = 3$ Hz, 9 H), 3.49 (dd, $J = 6, 12$ Hz, 1 H), 5.25–6.35 (m, 3 H), 7.20–7.65 (m, 5 H); ^{19}F NMR (CCl_4) δ 87.74 (d, $J = 260$ Hz, 1 F), 107.22 (d, $J = 260$ Hz, 1 F); IR 1650, 1590, 1487, 1420, 1370, 1253, 1115, 860, 830, 783, 700, 650 cm^{-1} ; MS m/z (rel intensity) 283 (4), 227 (4), 221 (27), 136 (11), 135 (86), 77 (6), 57 (100). Found: C, 64.72; H, 8.21%. Calcd for $\text{C}_{16}\text{H}_{24}\text{F}_2\text{OSi}$: C, 64.39; H, 8.11%.

2,2-Difluoro-1,1-diphenyl-3-buten-1-ol (3f): Benzophenone (**2f**, 0.182 g, 1.0 mmol) was allowed to react with **1** and TASf catalyst as above. Workup and preparative TLC (hexane-ethyl acetate 5 : 1) gave a mixture of **3f** and benzophenone (0.180 g). The yield of **3f** was estimated to be 34%. Repeated TLC purification (hexane-ethyl acetate 3 : 1, R_f 0.65) gave analytically pure **3f** which exhibited ^1H NMR (CCl_4) δ 2.58 (br s, 1 H), 5.18–6.22 (m, 3 H), 7.10–7.70 (m, 5 H); ^{19}F NMR (CDCl_3 - CFCl_3) δ 105.36 (d, $J = 10$ Hz, 2 F); IR 3580, 1655, 1607, 1500, 1450, 1420, 1050, 760 cm^{-1} ; MS m/z (rel intensity) 184 (13), 183 (100), 106 (7), 105 (96), 77 (53), 51 (12). Found: C, 72.69; H, 5.22%. Calcd for $\text{C}_{16}\text{H}_{14}\text{F}_2\text{O}$: C, 72.83; H, 5.42%.

Reaction of 4 with Benzaldehyde. A Typical Procedure for TASf-Catalyzed Reaction of 1-Polyhaloalkylsilanes with Aldehydes: TASf (1 M THF solution, 0.25 ml, 0.25 mmol) was added to a mixture of benzaldehyde (**2a**, 0.107 g, 1.01 mmol) and **4** (0.193 g, 1.23 mmol) dissolved in THF (2 ml), and the reaction mixture was stirred for 8 h at room temperature before treatment with methanolic hydrogen chloride (1 M, 0.5 ml, 15 min, r.t.). Short path chromatography followed by GLC assay (pentadecane internal standard, Diasolid 1 m, 120 °C, N_2 50 ml/min, R_t 5.33 min) showed 77% yield of 2,2-dichloro-1-phenylethanol (**7a**). Isolation by column chromatography (dichloromethane-hexane 1 : 1) gave **7a** (0.141 g, 74% yield) as a colorless oil. ^1H NMR (CDCl_3) δ 2.87 (d, $J = 4$ Hz, 1 H), 4.93 (dd, $J = 4, 6$ Hz, 1 H), 5.78 (d, $J = 6$ Hz, 1 H), 7.39 (s,

5 H); IR (neat) 3440, 1496, 1452, 1192, 1050, 790, 734, 700 cm^{-1} ; MS m/z (rel intensity) 192 (M^+ + 2, trace), 190 (M^+ , trace), 106 (6), 107 (100), 91 (6), 79 (52), 78 (5), 77 (27), 51 (13).

In a parallel experiment void of acidic workup, we isolated, in addition to **7a**, the trimethylsilyl ether of **7a**: $^1\text{H NMR}$ (CDCl₃) δ 0.83 (s, 9 H), 4.65 (d, $J = 6$ Hz, 1 H), 5.45 (d, $J = 6$ Hz, 1 H), 7.10 (s, 5 H).

1,1-Dichloro-4-phenyl-3-buten-2-ol (7c): colorless oil. $^1\text{H NMR}$ (CDCl₃) δ 2.64 (br d, $J = 5$ Hz, 1 H), 4.55 (m, 1 H), 5.70 (d, $J = 4$ Hz, 1 H), 6.24 (dd, $J = 4, 16$ Hz, 1 H), 6.72 (d, $J = 16$ Hz, 1 H), 7.1-7.7 (m, 5 H); IR 3420, 1667, 1496, 1449, 1072, 969, 787, 754, 694 cm^{-1} ; MS m/z (rel intensity) 218 (M^+ + 2, 1), 216 (M^+ , 2), 134 (10), 133 (100), 115 (23), 105 (9), 91 (6), 79 (6), 77 (14), 55 (34), 51 (10). Found: C, 54.58; H, 4.68%. Calcd for C₁₀H₁₀Cl₂O·0.1 H₂O: C, 54.87; H, 4.70%.

1,1-Dichloro-2-dodecanol (7d): colorless oil. $^1\text{H NMR}$ (CDCl₃) δ 0.88 (br t, $J = 6$ Hz, 3 H), 1.1-1.8 (m, 18 H), 2.21 (br d, $J = 6$ Hz, 1 H), 3.80 (br s, 1 H), 5.65 (d, $J = 4$ Hz, 1 H); IR 3420, 2940, 2875, 1489, 1189, 786 cm^{-1} ; MS m/z (rel intensity) 171 (31), 111 (27), 98 (13), 97 (100), 88 (11), 85 (12), 84 (17), 83 (69), 82 (14), 81 (15), 71 (33), 70 (22), 69 (84), 67 (15), 58 (14), 57 (63), 56 (30), 55 (95), 43 (68), 42 (16), 41 (68). Found: C, 56.62; H, 9.39%. Calcd for C₁₂H₂₄Cl₂O: C, 56.47; H, 9.48%.

1,1-Dichloro-3-phenyl-2-butanol (7g): colorless oil. The ratio of erythro/threo was estimated to be 84 : 16. $^1\text{H NMR}$ (CDCl₃) δ 1.43 (d, $J = 7$ Hz, 3 H), 2.44 (d, $J = 6$ Hz, 1 H), 3.01 (dq, $J = 9, 7$ Hz, 1 H), 3.95 (ddd, $J = 9, 6, 2$ Hz, 1 H), 5.42 (d, $J = 2$ Hz, 1 H), 7.1-7.4 (m, 5 H) for the erythro isomer; δ 1.40 (d, $J = 7$ Hz, 3 H), 2.39 (d, $J = 6$ Hz, 1 H), 5.48 (d, $J = 6$ Hz, 1 H), 7.2-7.5 (m, 5 H) for the threo isomer. IR 3450, 1494, 1452, 1104, 1012, 768, 704, 546 cm^{-1} ; MS m/z (rel intensity) 220 (M^+ + 2, 2), 218 (M^+ , 2), 135 (7), 106 (10), 105 (100), 103 (6), 91 (6), 79 (10), 77 (11), 51 (5), 43 (7). Found: C, 54.64; H, 5.68%. Calcd for C₁₀H₁₂Cl₂O: C, 54.82; H, 5.52%.

2,2-Dichloro-1-(3,4-dichlorophenyl)ethanol (7h): colorless oil. $^1\text{H NMR}$ (CDCl₃) δ 3.02 (br s, 1 H), 4.92 (br d, $J = 5$ Hz, 1 H), 5.76 (d, $J = 7$ Hz, 1 H), 7.1-7.6 (m, 3 H); IR (neat) 3450, 1474, 1032, 828, 793, 704, 672, 634 cm^{-1} .

2,2-Trichloro-1-phenylethanol (8a): colorless oil. $^1\text{H NMR}$ (CDCl₃) δ 3.33 (d, $J = 3$ Hz, 1 H), 5.13 (d, $J = 3$ Hz, 1 H), 7.2-7.45 (m, 3 H), 7.45-7.7 (m, 2 H); IR 3460, 1067, 860, 826, 781, 749, 702, 648, 606 cm^{-1} ; MS m/z (rel intensity) 125 (6), 108 (6), 107 (100), 79 (56), 78 (5), 77 (27), 51 (12), 50 (6). Found: C, 42.33; H, 2.83%. Calcd for C₈H₇Cl₃O: C, 42.61; H, 3.13%.

1,1,1-Trichloro-2-decan-2-ol (8d): colorless oil. $^1\text{H NMR}$ (CDCl₃) δ 0.88 (br t, $J = 6$ Hz, 3 H), 1.1-2.2 (m, 18 H), 2.72 (d, $J = 6$ Hz, 1 H), 3.85-4.10 (m, 1 H); IR 2970, 2940, 2870, 1469, 1093, 814, 787, 832 cm^{-1} ; MS m/z (rel intensity) 171 (31), 124 (12), 122 (19), 111 (27), 98 (12), 97 (100), 95 (12), 87 (11), 85 (12), 84 (14), 84 (90), 82 (13), 81 (13), 75 (29), 74 (23), 71 (35), 70 (19), 69 (90), 67 (14), 57 (63), 56 (24), 55 (93), 43 (96), 42 (16), 41 (74). Found: C, 49.85; H, 8.12%. Calcd for C₁₂H₂₃Cl₃O: C, 49.76; H, 8.00%.

1,1,1-Trichloro-3-phenyl-2-butanol (8g): a colorless oil in 75% yield from **2g** and **5**. The ratio of erythro to threo was estimated to be 87 : 13. $^1\text{H NMR}$ (CDCl₃) δ 4.23 (dd, $J = 7.0, 2.5$ Hz) for erythro-**8g** (lit.¹⁴ 4.21 (d, $J = 2.5$ Hz), 4.10 (br s) for threo-**8g** (lit.¹⁴ 4.13 (d, $J = 3$ Hz).

1,1,1-Trichloro-4-methyl-3-pentien-2-ol (8f): mp 82-83 °C (lit.³² 76-77 °C).

2,2-Dichloro-1-phenylpropanol (9a): colorless oil. $^1\text{H NMR}$ (CDCl₃) δ 2.02 (s, 3 H), 3.05 (d, $J = 4$ Hz, 1 H), 4.94 (d, $J = 4$ Hz, 1 H), 7.2-7.6 (m, 5 H); IR 3495, 1455, 1384, 1072, 1048, 1032, 766, 632, 706, 634, 604 cm^{-1} ; MS m/z (rel intensity) 206 (M^+ + 2, trace), 204 (M^+ , trace), 108 (6), 107 (100), 105 (9), 79 (59), 77 (26), 51 (10). Found: C, 52.48; H, 5.08%. Calcd for C₉H₁₀Cl₂O: C, 52.71; H, 4.91%.

2,2-Dichloro-1,3-diphenylpropane-1,3-diol (11): A mixture of two stereoisomers was produced in a ratio of 3 : 2 as colorless solid. $^1\text{H NMR}$ (CDCl₃) δ 3.63 (d, $J = 5$ Hz, 2 H), 5.25 (d, $J = 5$ Hz, 2 H), 7.2-7.6 (m, 10 H) for the major isomer, δ 3.11 (d, $J = 6$ Hz, 2 H), 5.01 (d, $J = 5$ Hz, 2 H), 7.2-7.6 (m, 10 H) for the minor isomer. Recrystallization from hexane afforded an 83 : 17 mixture, mp 134-137 °C. IR (KBr) 3450, 1457, 1209, 1063, 1048, 870, 764, 708, 678, 592 cm^{-1} ; MS m/z (rel intensity) 176 (11), 174 (65), 172 (100), 137 (5), 125 (5), 105 (5), 107 (57), 105 (10), 79 (48), 78 (7), 77 (38), 51 (12). Found: C, 60.68; H, 5.02%. Calcd for C₁₅H₁₄Cl₂O₂: C, 60.62; H, 4.75%.

(E)-1-Trithylsilyl-2-(ethylthio)difluoroethylene (15): To a solution of ethanethiol (0.185 ml, 11.0 mmol) in THF (10 ml) were added butyllithium (1.77 M hexane solution, 5.7 ml, 10.0 mmol) and **12** (10.0 mmol) at -78 °C. The solution was warmed to room temperature and stirred for 3 h at -78 °C, treated with dichloromethane (ca 1 ml) and water (1 drop), dried over magnesium sulfate, filtered and concentrated under reduced pressure. Purification by distillation gave **15** (0.84 g, 35% yield) as a colorless oil. Bp 80 °C (bath temp)/1 Torr. $^1\text{H NMR}$ (CDCl₃) δ 0.5-1.2 (m, 15 H), 1.32 (t, $J = 8$ Hz, 3 H), 2.77 (q, $J = 8$ Hz, 2 H), 1.9f; NMR (CDCl₃) δ 127 (d, $J = 148$ Hz, 1 F), 148 (d, $J = 148$ Hz, 1 F); IR 2875, 2800, 1150, 1090, 1020, 1007, 743, 730, 702 cm^{-1} ; MS m/z (rel intensity) 238 (M^+ , 14), 209 (52), 125 (24), 119 (16), 105 (43), 95 (42), 85 (13), 77 (100), 59 (12), 57 (10), 55 (30), 53 (36), 49 (26), 47 (19), 45 (14). Found: C, 50.38; H, 8.77%. Calcd for C₁₀H₂₀F₂SSi: C, 50.38; H, 8.46%.

(Z)-1-Trithylsilyl-1,2-difluoroethene (17): Lithium aluminum hydride (0.38 g, 10.0 mmol) was added portionwise to a THF (10 ml) solution of **12** (1.96 g, 10 mmol), and the resulting mixture was heated to reflux for 7 h. The excess hydride was quenched with wet dichloromethane and then with water (ca 1 ml) and dried over magnesium sulfate. Filtration, concentration in vacuo followed by distillation gave **17** (1.60 g, 90% yield) as a colorless oil. Bp 62 °C/33 Torr. $^1\text{H NMR}$ (CDCl₃) δ 0.5-0.9 (m, 6 H), 0.9-1.2 (m, 9 H), 7.58 (dd, $J = 12, 80$ Hz, 1 H); $^{19}\text{F NMR}$ (CDCl₃) δ 172 (dd, $J = 80, 128$ Hz, 1 F), 179 (dd, $J = 12, 128$ Hz, 1 F); IR 2970, 2930, 2900, 1650, 1466, 1148, 1130, 1093, 1022, 1008, 825, 748, 732 cm^{-1} ; MS m/z (rel intensity) 178 (M^+ , trace), 149 (6), 121 (19), 107 (5), 106 (10), 105 (100), 95 (8), 93 (6), 78 (6), 77 (61), 67 (5), 49 (13), 47 (11). Found: C, 54.23; H, 9.35%. Calcd for C₈H₁₆F₂Si: C, 53.89; H, 9.05%.

Reaction of 12 with Benzaldehyde. A Typical Procedure for TASF-Catalyzed Reaction of Polyfluoroethenylsilanes with Aldehydes. TASF (1 M THF solution, 0.2 ml, 0.2 mmol) was added to a THF (4 ml) solution of benzaldehyde (**2a**, 0.32

g, 3.0 mmol) and **12** (0.41 g, 2.1 mmol), and the solution was stirred for 24 h at room temperature. The reaction mixture was filtered through a short path column to remove the catalyst (elution with diethyl ether). Concentration under reduced pressure followed by distillation gave 3-triethylsiloxy-1,1,2-trifluoro-3-phenylpropene (**18a**) (0.41 g, 66% yield) as a colorless oil. Bp 100 °C (bath temp)/1 Torr. $^1\text{H NMR}$ (CDCl_3) δ 0.5-0.8 (m, 9 H), 0.8-1.1 (m, 6 H), 5.46 (ddd, $J = 2, 4, 25$ Hz, 1 H), 7.2-7.5 (m, 5 H); $^{19}\text{F NMR}$ (CDCl_3) δ 104 (ddd, $J = 2, 33, 80$ Hz, 1 F), 120 (ddd, $J = 4, 80, 115$ Hz, 1 F), 185 (ddd, $J = 25, 33, 115$ Hz, 1 F); IR 2965, 2890, 1792, 1308, 1260, 1112, 1100, 1066, 1004, 856, 840, 824, 740, 698 cm^{-1} ; MS m/z (rel intensity) 274 (11), 273 ($\text{M}^+ - \text{Et}$, 53), 171 (7), 151 (24), 149 (31), 121 (22), 106 (10), 105 (100), 103 (6), 101 (12), 87 (6), 78 (6), 77 (74), 75 (7), 59 (7), 49 (7), 47 (7), 45 (5). Found: C, 59.46; H, 6.99%. Calcd for $\text{C}_{15}\text{H}_{21}\text{F}_3\text{OSi}$: C, 59.58; H, 7.00%.

Aldehyde adducts of **12-17** were obtained in a similar manner involving purification by preparative TLC (silica-gel, dichloromethane-hexane 1 : 1 to 1 : 2).

2,3,3-Trifluoro-1-phenyl-2-propen-1-ol (18^a): TASF (1 M THF solution, 0.1 ml, 0.1 mmol) was added to a THF (2 ml) solution of benzaldehyde (**2a**, 0.107 g, 1.01 mmol) and **12^a** (0.26 g, 1.21 mmol), and the solution was stirred for 6.5 h at room temperature. Then, methanolic hydrogen chloride (1 M solution, 1 ml) was added, and the whole was stirred for 0.5 h at room temperature. The reaction mixture was filtered through a short-path column, and the filtrate was concentrated under reduced pressure. Purification by column chromatography (dichloromethane-hexane 1 : 2) gave **18^a** (0.115 g, 61% yield) as a colorless oil. $^1\text{H NMR}$ (CDCl_3) δ 2.50 (br s, 1 H), 5.46 (ddd, $J = 1, 4, 25$ Hz, 1 H), 7.2-7.6 (m, 5 H); $^{19}\text{F NMR}$ (CDCl_3) δ 102 (ddd, $J = 1, 32, 76$ Hz, 1 F), 119 (ddd, $J = 3, 76, 115$ Hz, 1 F), 187 (ddd, $J = 25, 32, 115$ Hz, 1 F); IR 3350, 1790, 1308, 1253, 1090, 1074, 1032, 1216, 833, 735, 698 cm^{-1} ; MS m/z (rel intensity) 188 (M^+ , 35), 151 (22), 138 (28), 137 (100), 109 (43), 79 (27), 78 (25), 77 (35), 51 (28).

3-Triethylsiloxy-1,1,2-trifluoro-5-phenyl-1,4-pentadiene (18c): colorless oil, $^1\text{H NMR}$ (CDCl_3) δ 0.5-0.8 (m, 9 H), 0.8-1.1 (m, 6 H), 5.03 (dm, $J = 24$ Hz, 1 H), 6.21 (dd, $J = 6, 15$ Hz, 1 H), 6.63 (d, $J = 15$ Hz, 1 H), 7.2-7.5 (m, 5 H); $^{19}\text{F NMR}$ (CDCl_3) δ 103 (dd, $J = 31, 79$ Hz, 1 F), 119 (ddd, $J = 4, 79, 115$ Hz, 1 F), 185 (ddd, $J = 24, 31, 115$ Hz, 1 F); IR 2970, 2890, 1793, 1308, 1260, 1118, 1080, 1046, 1006, 802, 747, 694 cm^{-1} ; MS m/z (rel intensity) 328 (M^+ , 2), 300 (12), 299 (55), 197 (23), 178 (10), 177 (75), 175 (50), 155 (24), 147 (42), 146 (33), 133 (10), 128 (16), 127 (44), 115 (11), 106 (10), 105 (100), 87 (24), 77 (91), 75 (15), 59 (20), 47 (14). Found: C, 62.22; H, 7.34%. Calcd for $\text{C}_{17}\text{H}_{23}\text{F}_3\text{OSi}$: C, 62.17; H, 7.06%.

3-Triethylsiloxy-1,1,2-trifluoro-1-tridecene (18d): colorless oil, $^1\text{H NMR}$ (CDCl_3) δ 0.4-0.75 (m, 6 H), 0.75-1.1 (m, 12 H), 1.27 (s, 16 H), 1.4-1.8 (m, 2 H), 4.28 (dm, $J = 26$ Hz, 1 H); $^{19}\text{F NMR}$ (CDCl_3) δ 104 (ddd, $J = 1, 33, 83$ Hz, 1 F), 120 (ddd, $J = 3, 83, 114$ Hz, 1 F), 187 (ddd, $J = 26, 33, 114$ Hz, 1 F); IR 2970, 2940, 1793, 1471, 1308, 1262, 1096, 1006, 750, 732 cm^{-1} ; MS m/z (rel intensity) 337 ($\text{M}^+ - \text{Et}$, 37), 225 (18), 211 (24), 183 (19), 145 (10), 117 (10), 115 (22), 107 (14), 105 (51), 103 (16), 95 (11), 87 (100), 83 (18), 81 (15), 77 (50), 75 (40), 73 (15), 69 (26), 67 (13), 59 (23), 57 (26), 55 (39), 47 (15), 43 (47), 41 (29). Found: C, 62.52; H, 10.05%. Calcd for $\text{C}_{19}\text{H}_{27}\text{F}_3\text{OSi}$: C, 62.25; H, 10.17%.

Ethyl 3-(1-Triethylsiloxy-2,3,3-trifluoro-2-propenyl)-2,2-dimethylcyclopropanecarboxylate (18f): colorless oil obtained as the *trans*- and *cis*-isomeric mixture. $^1\text{H NMR}$ (CDCl_3) δ 0.4-0.75 (m, 6 H), 0.8-1.1 (m, 9 H), 1.1-1.4 (m, 9 H), 1.48 (m, 1 H), 1.87 (m, 1 H), 3.8-4.3 (m, 1 H), 4.12 (q, 2 H) for the *trans*-isomer, δ 0.4-0.8 (m, 6 H), 0.8-1.16 (m, 9 H), 1.18 (s, 3 H), 1.22 (s, 3 H), 1.28 (t, $J = 7$ Hz, 3 H), 1.58-1.77 (m, 2 H), 3.95-4.25 (m, 1 H), 4.11 (q, $J = 7$ Hz, 2 H) for the *cis*-isomer.

1-Triethylsiloxy-2,3-difluoro-1-phenyl-2-heptene (19a): colorless oil, $^1\text{H NMR}$ (CDCl_3) δ 0.47-0.80 (m, 6 H), 0.80-1.13 (m, 12 H), 1.13-1.74 (m, 4 H), 2.08-2.64 (m, 2 H), 5.77 (dd, $J = 27, 4$ Hz, 1 H), 7.20-7.48 (m, 5 H); $^{19}\text{F NMR}$ (CDCl_3) δ 152 (ddt, $J = 125, 4, 22$ Hz, 1 F), 193 (ddt, $J = 125, 27, 5$ Hz, 1 F); IR 2970, 2890, 1453, 1214, 1174, 1091, 1068, 1004, 856, 745, 733, 700 cm^{-1} ; MS m/z (rel intensity) 312 (10), 311 ($\text{M}^+ - \text{Et}$, 37), 211 (2), 159 (25), 147 (47), 133 (20), 117 (93), 115 (26), 105 (87), 91 (49), 85 (29), 77 (48), 75 (25), 57 (30), 43 (31), 41 (21). Found: C, 66.72; H, 9.12%. Calcd for $\text{C}_{19}\text{H}_{23}\text{F}_2\text{OSi}$: C, 67.02; H, 8.88%.

1-Ethylthio-1,2-difluoro-3-triethylsiloxy-3-phenylpropene (21a): colorless oil, $^1\text{H NMR}$ (CDCl_3) δ 0.47-0.85 (m, 6 H), 0.85-1.14 (m, 9 H), 1.27 (t, $J = 7$ Hz, 3 H), 2.76 (dq, $J = 1, 7$ Hz, 2 H), 5.82 (dd, $J = 4, 25$ Hz, 1 H), 7.16-7.50 (m, 5 H); $^{19}\text{F NMR}$ (CDCl_3) δ 131 (dd, $J = 4, 142$ Hz, 1 F), 149 (dd, $J = 25, 142$ Hz, 1 F); IR 2975, 2900, 1258, 1097, 1070, 1008, 858, 838, 749, 732, 701, 574 cm^{-1} ; MS m/z (rel intensity) 345 ($\text{M}^+ + 1, 1$), 344 (M^+ , 8), 316 (19), 315 (79), 283 (52), 213 (20), 183 (20), 151 (97), 149 (63), 135 (35), 129 (36), 105 (100), 91 (22), 87 (23), 77 (42), 59 (20). Found: C, 59.11; H, 7.84%. Calcd for $\text{C}_{17}\text{H}_{26}\text{F}_2\text{OSi}$: C, 59.26; H, 7.61%.

2-Chloro-3-triethylsiloxy-1,1-difluoro-3-phenylpropene (22a): colorless oil, $^1\text{H NMR}$ (CDCl_3) δ 0.47-0.82 (m, 6 H), 0.82-1.11 (m, 9 H), 5.67 (t, $J = 3$ Hz, 1 H), 7.23-7.50 (m, 5 H); $^{19}\text{F NMR}$ (CDCl_3) δ 88 (dd, $J = 3, 45$ Hz, 1 F), 92 (dd, $J = 3, 45$ Hz, 1 F); IR 2975, 2900, 1744, 1287, 1093, 1060, 1014, 834, 748, 730, 703 cm^{-1} ; MS m/z (rel intensity) 291 (30), 290 (16), 289 (76), 187 (10), 167 (48), 166 (11), 165 (100), 152 (10), 151 (27), 139 (32), 137 (92), 105 (55), 102 (19), 77 (73), 75 (11), 59 (12), 47 (10). Found: C, 56.62; H, 6.68%. Calcd for $\text{C}_{15}\text{H}_{21}\text{ClF}_2\text{OSi}$: C, 56.50; H, 6.64%.

2-Chloro-3-triethylsiloxy-1,1-difluoro-1-tridecene (22d): colorless oil, $^1\text{H NMR}$ (CDCl_3) δ 0.45-0.8 (m, 6 H), 0.8-1.15 (m, 12 H), 1.30 (s, 16 H), 1.45-1.85 (m, 2 H), 4.35-4.65 (m, 1 H); $^{19}\text{F NMR}$ (CDCl_3) δ 88 (d, $J = 44$ Hz, 1 F), 92 (d, $J = 44$ Hz, 1 F); IR 2950, 1747, 1470, 1286, 1100, 1002, 750, 730 cm^{-1} ; MS m/z (rel intensity) 355 (38), 354 (25), 353 ($\text{M}^+ - \text{Et}$, 96), 241 (27), 115 (26), 109 (16), 105 (72), 104 (11), 103 (100), 97 (35), 95 (37), 91 (15), 89 (35), 87 (38), 83 (42), 81 (33), 77 (63), 75 (85), 71 (15), 69 (43), 67 (28), 59 (26), 57 (32), 55 (58), 47 (26), 43 (59), 41 (35). Found: C, 60.02; H, 9.44%. Calcd for $\text{C}_{19}\text{H}_{27}\text{ClF}_2\text{OSi}$: C, 59.58; H, 9.74%.

3-Triethylsiloxy-1,2-difluoro-1-tridecene (23d): colorless oil, $^1\text{H NMR}$ (CDCl_3) δ 0.4-0.8 (m, 6 H), 0.8-1.1 (m, 12 H), 1.27 (s, 16 H), 1.4-1.8 (m, 2 H), 4.57 (dm, $J = 27$ Hz, 1 H), 6.83 (dd, $J = 5, 74$ Hz, 1 H); $^{19}\text{F NMR}$ ($\text{CDCl}_3\text{-CFC}_2\text{Cl}_2$) δ 175 (ddd, $J = 6, 27, 127$ Hz, 1 F), 180 (ddd, $J = 7, 74, 127$ Hz, 1 F); IR 2970, 2945, 2900, 2875, 1033, 1097, 1007, 749, 732 cm^{-1} ; MS m/z (rel intensity) 319 ($\text{M}^+ - \text{Et}$, 37), 207 (25), 193 (46), 123 (27), 115 (32), 113 (24), 107 (37), 105 (86), 99 (26), 95 (33), 93 (36), 87 (39), 83 (34), 81 (35), 79 (27), 77 (85), 75 (41), 69 (100), 67 (30), 59 (28), 57 (40), 55 (74), 47 (25), 43 (75), 41 (93). Found: C, 65.59; H, 11.01%. Calcd for $\text{C}_{19}\text{H}_{28}\text{F}_2\text{OSi}$: C, 65.47; H, 10.99%.

Reaction of 14 with Benzaldehyde. TASF (1 M THF solution, 0.1 ml, 0.1 mmol) was added to a THF (2 ml) solution of **2a** (0.106 g, 1.00 mmol) and **14** (0.233 g, 1.21 mmol), and the mixture was stirred for 7 h at room temperature. Workup and preparative TLC (dichloromethane-hexane 1 : 2) gave **[E]-1-trimethylsiloxy-2,3-difluoro-4,4-dimethyl-1-phenyl-2-pentene (20a)** (0.112 g, 36% yield) along with **[E]-1-phenyl-2,3-difluoro-4,4-dimethyl-2-penten-1-ol (20*a)** (0.106 g, 48% yield) both as colorless oils. The product **20a** exhibited following spectra. $^1\text{H NMR}$ (CDCl_3) δ 0.19 (s, 9 H), 1.23 (t, $J = 2$ Hz, 9 H), 5.77 (dd, $J = 5, 26$ Hz, 1 H), 7.16-7.49 (m, 5 H); $^{19}\text{F NMR}$ (CDCl_3) δ 154 (d, $J = 123$ Hz, 1 F), 169 (dd, $J = 26, 123$ Hz, 1 F); IR 2975, 1252, 1234, 1120, 1090, 1066, 880, 856, 840, 749, 708, 698 cm^{-1} ; MS m/z (rel intensity) 242 (18), 241 ($\text{M}^+ - t\text{-Bu}$, 100), 189 (11), 179 (10), 174 (13), 149 (31), 143 (10), 129 (11), 117 (10), 105 (12), 91 (10), 77 (26), 75 (11), 73 (71), 57 (15), 45 (10), 43 (10), 41 (11). Found: C, 64.29; H, 8.25%. Calcd for $\text{C}_{16}\text{H}_{24}\text{F}_2\text{OSi}$: C, 64.39; H, 8.11%. **20*a**: $^1\text{H NMR}$ (CDCl_3) δ 1.25 (dd, $J = 2, 2$ Hz, 9 H), 2.66 (br s, 2 H), 5.73 (dd, $J = 5, 25$ Hz, 1 H), 7.15 (7.47 (m, 5 H); $^{19}\text{F NMR}$ (CDCl_3) δ 153 (d, $J = 126$ Hz, 1 F), 169 (dd, $J = 25, 126$ Hz, 1 F); IR 3380 (br), 2980, 1233, 1124, 1026, 958, 730, 700 cm^{-1} ; MS m/z (rel intensity) 227 ($\text{M}^+ + 1, 3$), 226 (M^+ , 22), 169 (74), 143 (254), 138 (100), 109 (39), 107 (62), 105 (59), 91 (29), 79 (59), 78 (36), 77 (64), 59 (43), 57 (70), 51 (30), 41 (27). Found: C, 68.73; H, 7.28%. Calcd for $\text{C}_{13}\text{H}_{16}\text{F}_2\text{O}$: C, 69.01; H, 7.13%.

(2,3,5,6-Tetrafluorophenyl)trimethylsilane (25): Lithium aluminum hydride (0.198 g, 5.2 mmol) was added portionwise to a solution of **24** (1.24 g, 5.2 mmol) in THF (20 ml), and the mixture was stirred for 7 h at room temperature. The excess hydride was carefully quenched with aq sat sodium sulfate solution and the reaction mixture was diluted with diethyl ether. The resulting mixture was dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. Distillation gave **25** (0.86 g, 78% yield) as a colorless oil. Bp 80-85 °C (bath temp)/20 Torr; $^1\text{H NMR}$ (CDCl_3) δ 0.41 (t, $J = 1.5$ Hz, 9 H), 6.96 (t, $J = 8, 10$ Hz, 1 H); $^{19}\text{F NMR}$ (CDCl_3) δ 128 (m, 2 F), 139 (m, 2 F); IR 1470, 1260, 1242, 1228, 1172, 912, 887, 850, 832, 772, 712, 634 cm^{-1} ; MS m/z (rel intensity) 224 ($\text{M}^+ + 2, 2$), 223 ($\text{M}^+ + 1, 7$), 222 (M^+ , 46), 208 (8), 207 (38), 125 (6), 111 (25), 108 (5), 107 (62), 101 (20), 81 (42), 78 (7), 77 (100), 75 (8), 73 (10), 63 (15), 62 (5), 61 (8), 57 (13), 51 (6), 49 (22), 47 (23). Found: C, 48.84; H, 4.61%. Calcd for $\text{C}_9\text{H}_{10}\text{F}_4\text{Si}$: C, 48.64; H, 4.54%.

1-Butyl-4-(trimethylsilyl)tetrafluorobenzene (26): Butyllithium (1.77 M hexane solution, 2.8 ml, 5.0 mmol) was added to a solution of **24** (1.20 g, 5.0 mmol) dissolved in THF (10 ml) at -78 °C, and the reaction mixture was stirred for 0.5 h at room temperature before quenching with dichloromethane (10 ml) and water (ca 0.5 ml). The resulting mixture was dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure. Distillation gave **26** (1.11 g, 80% yield) as a colorless oil. Bp 80 °C (bath temp)/1 Torr; $^1\text{H NMR}$ (CDCl_3) δ 0.40 (t, $J = 1.5$ Hz, 9 H), 0.8-1.1 (m, 3 H), 1.1-1.7 (m, 4 H), 2.68 (t, $J = 7$ Hz, 2 H); $^{19}\text{F NMR}$ (CDCl_3) δ 128 (m, 2 F), 145 (m, 2 F); IR 2980, 1448, 1256, 967, 774 cm^{-1} ; MS m/z (rel intensity) 279 ($\text{M}^+ + 1, 5$), 278 (M^+ , 24), 263 (14), 222 (16), 221 (100), 155 (14), 101 (30), 81 (19), 77 (33), 57 (11), 55 (13), 49 (11), 43 (24), 41 (28). Found: C, 55.98; H, 6.68%. Calcd for $\text{C}_{13}\text{H}_{18}\text{F}_4\text{Si}$: C, 56.08; H, 6.52%.

3,5-Dichloro-2,4,6-trifluoro-1-(trimethylsilyl)benzene (27): An ethereal solution (3 ml) of 1,3,5-trichlorotrifluorobenzene (2.35 g, 10.0 mmol) was added to a mixture of butyllithium hexane solution (1.70 M, 5.9 ml, 10 mmol) and diethyl ether (5 ml) at -78 °C over 15 min, and the mixture was stirred for 1 h at -78 °C. Chlorotrimethylsilane (1.27 ml, 10.0 mmol) was added to the reaction mixture at -78 °C, and stirring was continued for 0.5 h at -78 °C and 0.5 h at room temperature. Workup and purification by column chromatography (hexane-dichloromethane 5 : 1) gave **27** (2.49 g, 96% yield) as colorless crystals, mp 43-44 °C, $^1\text{H NMR}$ (CDCl_3) δ 0.40 (t, $J = 1.7$ Hz, 9 H); $^{19}\text{F NMR}$ (CDCl_3) δ 99 (m, 2 F), 109 (t, $J = 4$ Hz, 1 F); IR 1600, 1406, 1254, 1070, 848, 792, 769 cm^{-1} ; MS m/z (rel intensity) 274 ($\text{M}^+ + 2, 28$), 272 (M^+ , 41), 259 (39), 257 (57), 191 (20), 159 (19), 157 (29), 143 (32), 141 (96), 101 (27), 97 (41), 81 (39), 77 (100), 73 (26), 49 (35), 47 (35). Found: C, 39.21; H, 3.07%. Calcd for $\text{C}_9\text{H}_9\text{Cl}_2\text{F}_3\text{Si}$: C, 39.57; H, 3.32%.

Reaction of 24 with Benzaldehyde. A Typical Procedure for TASF-Catalyzed Aldehyde Addition of Polyhaloarylsilanes. TASF (1 M THF solution, 0.1 ml, 0.1 mmol) was added to a THF (2 ml) solution of benzaldehyde (**2a**, 0.111 g, 1.05 mmol) and **24** (0.29 g, 1.19 mmol) at 0 °C. The mixture was stirred for 20 min at 0 °C and for 12 h at room temperature before treatment with 1 M HCl methanol solution (1 ml). Workup as before followed by preparative TLC (dichloromethane-hexane 1 : 1) gave **1-(pentafluorophenyl)-1-phenylmethanol (29a)**, 0.25 g, 87% yield) as colorless crystals: mp 49 °C. $^1\text{H NMR}$ (CDCl_3) δ 3.20 (br s, 1 H), 6.13 (br s, 1 H), 7.2-7.4 (m, 5 H); $^{19}\text{F NMR}$ (CDCl_3) δ 142 (m, 2 F), 154 (m, 1 F), 161 (m, 2 F); IR 3400, 1528, 1508, 1127, 996, 950, 706, 648 cm^{-1} ; MS m/z (rel intensity) 275 ($\text{M}^+ + 1, 7$), 274 (M^+ , 51), 273 (6), 267 (10), 197 (12), 195 (38), 167 (8), 107 (20), 105 (11), 80 (7). Found: C, 56.75; H, 2.54%. Calcd for $\text{C}_{13}\text{H}_7\text{F}_5\text{O}$: C, 56.95; H, 2.57%.

1-(2,3,5,6-Tetrafluorophenyl)-1-phenylmethanol (30a): colorless viscous oil, $^1\text{H NMR}$ (CDCl_3) δ 2.88 (br s, 1 H), 6.21 (br s, 1 H), 6.94 (t, $J = 7, 10$ Hz, 1 H), 7.2-7.5 (m, 5 H); IR 3400, 1508, 1253, 1097, 932, 710 cm^{-1} ; MS m/z (rel intensity) 257 ($\text{M}^+ + 1, 10$), 256 (M^+ , 63), 219 (11), 179 (10), 177 (40), 149 (10), 107 (28), 105 (14), 79 (100), 78 (27), 77 (33), 51 (17). Found: C, 60.75; H, 3.10%. Calcd for $\text{C}_{13}\text{H}_9\text{F}_4\text{O}$: C, 60.95; H, 3.15%.

1-(4-Butyltetrafluorophenyl)-1-phenylmethanol (31a): colorless oil, $^1\text{H NMR}$ (CDCl_3) δ 0.93 (t, $J = 7$ Hz, 3 H), 1.1-1.8 (m, 4 H), 2.69 (t, $J = 7$ Hz, 2 H), 2.98 (d, $J = 8$ Hz, 1 H), 6.17 (d, $J = 8$ Hz, 1 H), 7.13-7.50 (m, 5 H); $^{19}\text{F NMR}$ (CDCl_3) δ 145 (s), IR 3390, 2975, 1489, 1280, 976, 702, 640 cm^{-1} ; MS m/z (rel intensity) 313 ($\text{M}^+ + 1, 11$), 312 (M^+ , 60), 311 (11), 235 (18), 233 (30), 107 (27), 105 (36), 79 (100), 78 (59), 78 (59), 77 (24), 43 (32), 41 (14). Found: C, 65.12; H, 5.31%. Calcd for $\text{C}_{17}\text{H}_{16}\text{F}_4\text{O}$: C, 65.38; H, 5.16%.

1-(3,5-Dichloro-2,4,6-trifluorophenyl)-1-phenylmethanol (32a): colorless oil, $^1\text{H NMR}$ (CDCl_3) δ 2.80 (br d, $J = 6$ Hz, 1 H), 6.18 (br d, $J = 6$ Hz, 1 H), 7.32 (s, 5 H); $^{19}\text{F NMR}$ (CDCl_3) δ 111 (t, $J = 2$ Hz, 1 F), 115 (d, $J = 2$ Hz, 2 F); IR 3360, 1612, 1449, 1210, 1190, 1092, 1066, 1040, 1025, 788, 727, 697, 593 cm^{-1} ; MS m/z (rel intensity) 308 ($\text{M}^+ + 2, 19$), 307 ($\text{M}^+ + 1, 7$), 306 (M^+ , 29), 229 (19), 227 (17), 107 (27), 105 (13), 79 (100), 78 (34), 77 (26), 51 (14). Found: C, 50.70; H, 2.27%. Calcd for $\text{C}_{13}\text{H}_7\text{Cl}_2\text{F}_3\text{O}$: C, 50.84; H, 2.30%.

1-(Pentachlorophenyl)-1-phenylmethanol (33a): colorless crystals, mp 99 °C; $^1\text{H NMR}$ (CDCl_3) δ 3.46 (br d, $J = 10$ Hz, 1 H), 6.67 (br d, $J = 10$ Hz, 1 H), 7.1-7.4 (m, 5 H); IR (KBr) 3200-3600 (br), 1358, 1118, 1042, 1026, 727, 693, 656, 552 cm^{-1} ; MS m/z (rel intensity) 358 ($\text{M}^+ + 4, 20$), 356 ($\text{M}^+ + 2, 32$), 354 (M^+ , 20), 277 (23), 107 (69), 79 (100), 78 (33), 77 (36). Found: C, 43.71; H, 1.88%. Calcd for $\text{C}_{13}\text{H}_7\text{Cl}_5\text{O}$: C, 43.80; H, 1.98%.

1-Pentafluorophenyl-1-undecanol (28a): mp 28 °C. ^1H NMR (CDCl_3) δ 0.87 (br t, $J = 6$ Hz, 3 H), 1.25 (br s, 16 H), 1.4-2.1 (m, 2 H), 2.1-2.3 (m, 1 H), 5.00 (m, 1 H); ^{19}F NMR (CDCl_3) δ 143 (m, 2 F), 155 (m, 1 F), 162 (m, 2 F); IR 3400, 2940, 2870, 1526, 1507, 1133, 1118, 994, 979 cm^{-1} ; MS m/z (rel intensity) 338 (M^+ , trace), 198 (8), 197 (100), 194 (6), 57 (12), 55 (9), 43 (24), 41 (15). Found: C, 60.43; H, 6.82%. Calcd for $\text{C}_{17}\text{H}_{23}\text{F}_5\text{O}$: C, 60.35; H, 6.85%.

1-(2,3,5,6-Tetrafluorophenyl)-1-undecanol (30e): colorless crystals, mp 50-51 °C. ^1H NMR (CDCl_3) δ 0.88 (br t, $J = 6$ Hz, 3 H), 1.27 (br s, 16 H), 1.5-2.2 (m, 2 H), 2.2-2.4 (m, 1 H), 5.03 (br s, 1 H), 6.97 (t, $J = 8, 10$ Hz, 1 H); ^{19}F NMR (CDCl_3) δ 138 (m, 2 F), 143 (m, 2 F); IR 3430, 2935, 2870, 1508, 1253, 1172, 912, 846 cm^{-1} ; MS m/z (rel intensity) 320 (M^+ , 1), 180 (10), 179 (100), 167 (8), 75 (6), 71 (6), 69 (5), 57 (15), 55 (10), 43 (25), 41 (15). Found: C, 63.65; H, 7.67%. Calcd for $\text{C}_{17}\text{H}_{24}\text{F}_4\text{O}$: C, 63.73; H, 7.55%.

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