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Insight into the Reactions of Trifluorovinylsilanes with Aromatic Aldehydes

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The conditions for the selective addition of trialkyl(trifluorovinyl)silanes to the C=O bond of aromatic aldehydes in the presence of cesium fluoride to give the corresponding "silylated" alcohols in high yields was performed. The reactivity of the "silylated" alcohols in the presence of nucleophilic reagents and Brönsted acids was studied. On the basis of isolated compounds and of intermediates detected by NMR spectroscopic methods, several reaction pathways are proposed. Significant differences between the reaction behaviour of triethyl(trifluorovinyl)silane and trimethyl(trifluoromethyl)silane under comparable conditions are pointed out; the differences can be attributed to the highly reactive trifluorovinyl group. The reactions of the "silylated" alcohols proceed with high stereoselectivity to give propenes, acid fluorides and acids of the (*E*) isomers in better than 98 % purity.

Introduction

Trifluoroallylic alcohols are of great interest as synthons in fluoroorganic chemistry. That is, (*Z*)-1,1-difluoro-1,2-dihalo-2-alkenes obtained by halogenation of 1,1-difluoro-2-halo-1-alkene-3-ols were applied in the construction of the C-3 side chain of polyfluorinated synthetic pyretroids.[1] The reaction of allylic alcohols with anhydrous hydrogen fluoride leads to the formation of 1,1,1,2-tetrafluoro-2-alkenes; some of them exhibit unique biological properties in the areas of agrochemicals, pharmaceuticals and material science.[2] Upon treatment with acids, trifluoroallylic alcohols give, together with alkenes, α-fluoroalkenoic acids and the corresponding acid fluorides, which serve as precursors to the fluoro analogues of retinals.[3] Starting from the ethers of trifluoroallylic alcohols, novel optically active partly *gem*-fluorinated allylic alcohols can be obtained by [2,3] Wittig rearrangement.[4]

The first attempt to synthesize trifluoroallylic alcohols starting from aldehydes and trifluorovinylmagnesium iodide was made by Knunyants et al. in 1958.[5] However, they succeeded to obtain only a fluoride of the corresponding α-fluoroalkenoic acid and proposed a route for its formation. These investigations were intensified by Tarrant et al. who synthesized some trifluoroallylic alcohols starting from aldehydes and ketones and trifluorovinyllithium or trifluorovinylmagnesium bromide and isolated them in low yields.[6] In 1975, Normant et al. found conditions for obtaining trifluoroallylic alcohols in high yields by the reaction of trifluorovinyllithium with aldehydes and ketones and for their conversion into α-fluoroalkenoic acid derivatives.[7] Later, Olah et al. reported an approach to phenyl(trifluorovinyl)-carbinol on the basis of the reaction of benzaldehyde with 1,3-bis(trimethylsilyl)-1,1,2,2-tetrafluoroethane in the presence of fluoride ions.[8] In 2002, Matsui et al. reported a method for synthesis of trifluoroallylic alcohols not by direct trifluorovinylation of aldehydes and ketones but by the reaction of 3,3,3,4-tetrafluoro-1-propenyl tosylate with arylmagnesium bromide.[9]

In contrast to trifluoroallylic alcohols, there are only two reports on the syntheses of the corresponding silyl ethers mentioned in the literature. In 1985 and 1988, Hiyama et al. showed that the reaction of benzaldehyde with triethyl-(trifluorovinyl)silane in the presence of a fluoride-ion source results in the formation of 3-triethylsiloxy-1,1,2-trifluoro-3-phenylpropene in low yield.[10] It should be noted that the reactivity of the product obtained was not investigated.

Herein, we report on a selective method to obtain *O*-trialkylsilyl aryl(trifluorovinyl)carbinols in high yields and the conversions of the synthesized compounds under the influence of fluoride ions. On the basis of the products isolated, we propose a reaction scheme for "silylated" alcohols in the presence of nucleophilic reagents and Brönsted acids.

Results and Discussion

We found that the reaction of *p*-substituted aromatic aldehydes **1** with triethyl(trifluorovinyl)silane ($Et_3SiCF=CF_2$)

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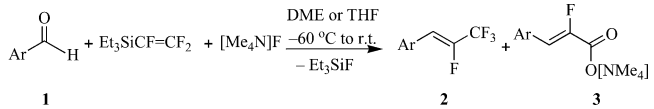
in the presence of tetramethylammonium fluoride ([Me_4N]F, 1 equiv.) in dimethoxyethane (DME) or tetrahydrofuran (THF) in the temperature range from –60 °C to room temperature results in the formation of 1-aryl-2,3,3,3-tetrafluoropropene **2** and the tetramethylammonium salt of *p*-substituted α-fluorocinnamic acid **3** (Scheme 1).



1 **2** **3**

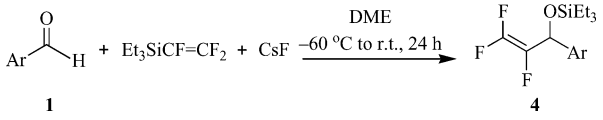
a: Ar = 4-$CH_3C_6H_4$
b: Ar = 4-FC_6H_4

Scheme 1.

It should be noted that a similar reaction of trimethyl(trifluoromethyl)silane (Me_3SiCF_3) with aromatic aldehydes in the presence of tetramethylammonium fluoride (1 equiv.) affords trifluoromethyl-containing tetramethylammonium alcoholates, [Me_4N]OCH(Ar)(CF_3); subsequent hydrolysis of the latter yields the corresponding secondary alcohols, Ar(CF_3)CHOH.[11]

Such essential differences between Me_3SiCF_3 and $Et_3SiCF{=}CF_2$ in similar conversions may be attributed to the highly reactive trifluorovinyl moiety being sensitive to further nucleophilic attack by the reaction products primarily formed. To confirm our assumption, we investigated the reaction of trialkyl(trifluorovinyl)silanes with aromatic aldehydes in the presence of fluoride-ion sources under different conditions.

We found that the reaction of equimolar quantities of aromatic aldehydes **1**, $Et_3SiCF{=}CF_2$ and CsF affords "silylated" alcohols **4** in better than 95% yield. The reaction proceeds in DME between –60 °C and room temperature within 24 h (Scheme 2).

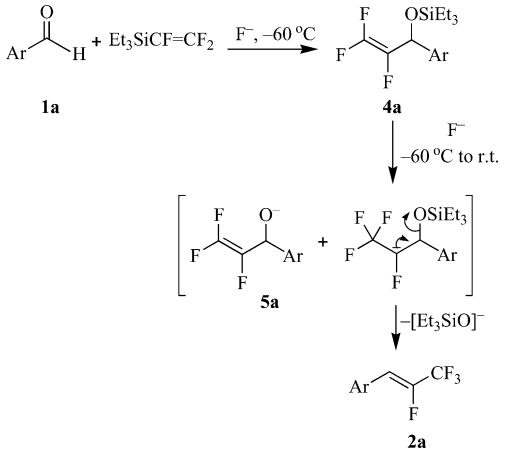


1 **4**

Scheme 2.

The reaction with a catalytic amount of CsF proceeds significantly slower, and even after one week 60% of aldehydes **1** were recovered unchanged. The use of a catalytic amount (10–15 mol-%) of [Me_4N]F which is, due to its better solubility, a stronger nucleophile than CsF for silane activation under similar conditions, yielded a complex product mixture containing only 50–60% of the targeted "silylated" alcohols **4**.

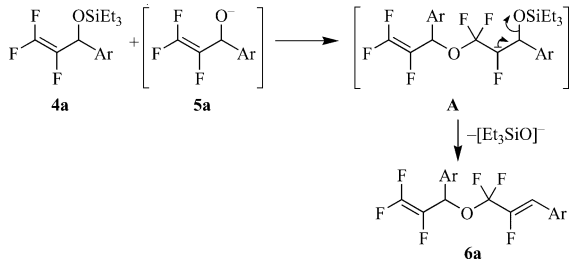
To understand the nature of these conversions, we investigated the reaction of equimolar quantities of aldehyde **1a** and $Et_3SiCF{=}CF_2$ in the presence [Me_4N]F (0.5 equiv.) by means of low-temperature ^{19}F NMR spectroscopic experiments. The selective formation of "silylated" alcohol **4a** in DME or THF at –60 °C was complete after a reaction time of 30 min. When the temperature is increased, [Me_4N]F attacks the two reactive positions of compound **4a**, that is, the terminal CF_2 group and the silicon atom. In contrast, the fluoride ion attacks the silicon atom and desilylates ether **4a** to afford alcoholate **5a**; the addition of the fluoride ion to the trifluorovinyl unit of **4a** is accompanied by simultaneous triethylsilanolate anion elimination with formation of olefin **2a** (Scheme 3).



1a **4a** **5a** **2a**

Scheme 3.

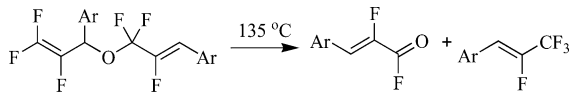
It should be noted that we were not able to detect the signals of alcoholate **5a** in the low-temperature ^{19}F NMR spectra. Concomitant with its formation, the extreme nucleophilic nature of **5a** results in its addition to the double bond of the trifluorovinyl group of "silylated" alcohol **4a** to give intermediate **A**, which again eliminates a triethylsilanolate anion to give "unsymmetrical" ether **6a** (Scheme 4).



4a **5a** **A** **6a**

Scheme 4.

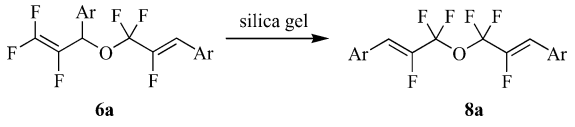
Keeping this reaction mixture at –45 °C for 80 min followed by the addition of water at the same temperature led to a product mixture of "silylated" alcohol **4a** (40%), "unsymmetrical" ether **6a** (50%) and unidentified fluorine-containing byproducts (10%). Ether **6a** was isolated from the mixture in 26% yield (relative to **1a**) with 94% purity. An attempt to purify **6a** by vacuum distillation failed. At 135 °C, the substance decomposed into **2a** and *p*-substituted α-fluorocinnamic acid fluoride **7a** as the major products (Scheme 5).



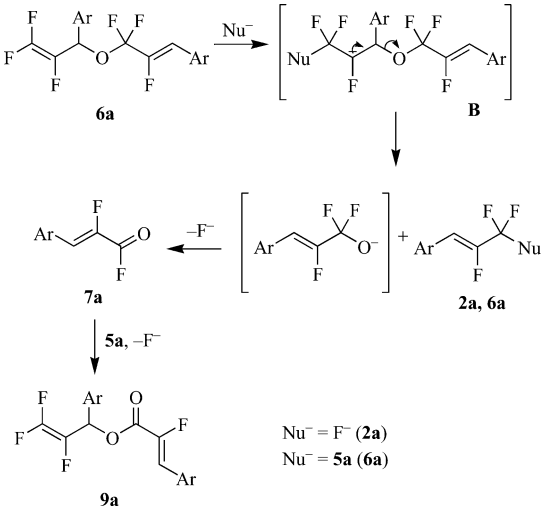
6a **7a** **2a**

Scheme 5.

An unexpected result was obtained upon purification of **6a** by column chromatography on silica gel: "unsymmetrical" ether **6a** rearranged into isomeric "symmetrical" ether **8a**, which was isolated in 45% yield and fully characterized (Scheme 6). However, an explanation for this rearrangement cannot be given. Furthermore, the trifluorovinyl group of **6a** appears to be the reactive centre in further transformations. Attack of the nucleophiles present in the reaction mixture, that is, alcoholate **5a** and the fluoride ion, at the double bond of **6a** initially affords intermediates of type **B**, which then decompose into **2a**, **6a** and **7a**. Acid fluoride **7a** also reacts with alcoholate **5a** to give ester **9a** (^{19}F NMR spectroscopy) (Scheme 7).

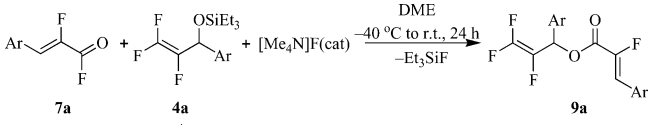


Scheme 6.



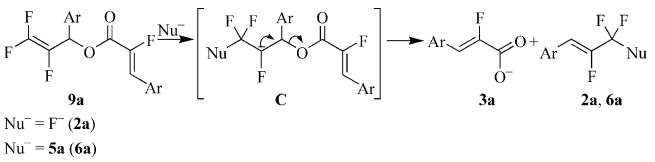
Scheme 7.

To confirm these assumptions, **7a** was synthesized by an alternative method[7] and treated with silyl ether **4a** in the presence of a catalytic amount of $[Me_4N]F$ (10–15 mol-%). The reaction conditions were chosen to be similar to those for the reaction of **1a** with $Et_3SiCF{=}CF_2$; through this reaction route, **9a** was formed in quantitative yield (^{19}F NMR spectroscopy) (Scheme 8).



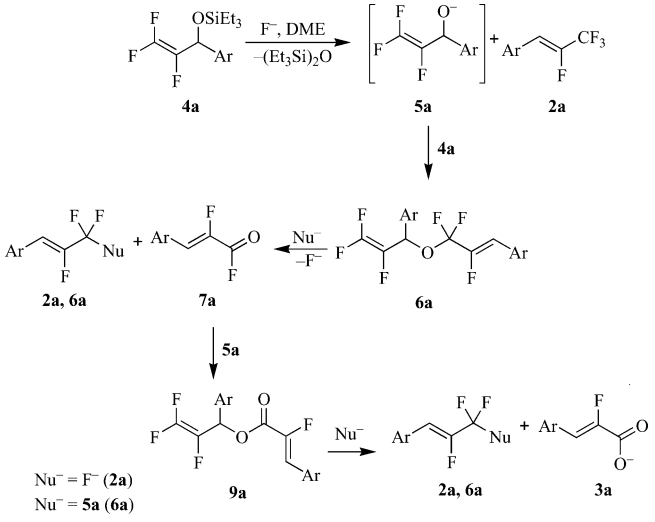
Scheme 8.

Compound **9a** was isolated in 67% yield and fully characterized. The ^{19}F NMR spectroscopic data of ester **9a** obtained as described above are in full accordance with those of the reaction product **9a** involved in Scheme 7. It should be noted that the trifluorovinyl group of compound **9a**, as well as that of the "silylated" alcohol **4a** and the "unsymmetrical" ether **6a**, is highly reactive toward nucleophiles. The following reactions of ester **9a** with alcoholate **5a** and fluoride ion led to the formation of intermediates of type **C**, which convert into products **2a**, **3a** and **6a** (Scheme 9).



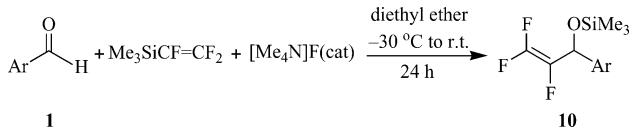
Scheme 9.

In parallel to the reaction of aldehyde **1a** with triethyl(trifluorovinyl)silane in the presence of fluoride-ion sources, we also studied the reaction of "silylated" alcohol **4a** with $[Me_4N]F$. By ^{19}F NMR spectroscopic methods, we detected the formation of the same products **2a**, **3a**, **6a** and **9a** in the course of the reaction. On the basis of the results obtained, we conclude that aldehyde **1a** reacts with $Et_3SiCF{=}CF_2$ in the presence of $[Me_4N]F$ probably to form "silylated" alcohol **4a**, which undergoes all reaction steps outlined above in a one-pot procedure (Scheme 10).



Scheme 10.

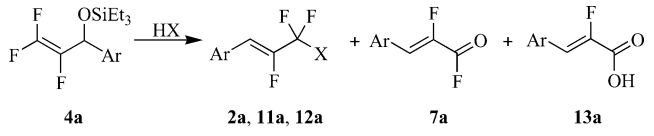
In comparative studies, $Me_3SiCF{=}CF_2$ was found to be much more reactive. Upon reaction with aldehyde **1a** in the presence of $[Me_4N]F$ (0.5 equiv.) in DME or THF, the exclusive formation of final products **2a**, **3a** and **7a** were confirmed by low-temperature ^{19}F NMR spectra recorded at –40 °C. However, in diethyl ether, the reaction of aldehyde **1** (1 equiv.) with $Me_3SiCF{=}CF_2$ (1.1 equiv.) and a catalytic amount of $[Me_4N]F$ afforded "silylated" alcohol **10** in better than 80% yield of the crude product (Scheme 11),



Scheme 11.

whereas the total amount of compounds **2**, **3**, **6** and **9** in the reaction mixture did not exceed 15%.

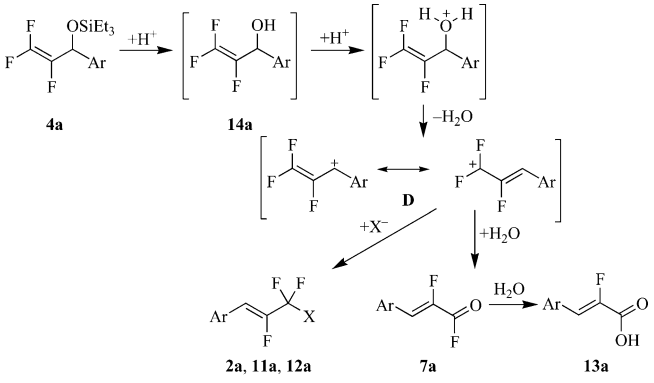
Our studies on the conversions of "silylated" alcohol **4a** under action of fluoride ions were accompanied by investigations of its reactivity towards Brönsted acids. As it is known, the "silylated" alcohols are deprotected by acids to give the free alcohols. However, when "silylated" alcohol **4a** is treated with $H[BF_4]$, HCl or HBr, it is converted into propenes **2a**, **11a** or **12a**, respectively. In this case, minor amounts of **7a** and **13a** are always detected in the reaction mixtures (^{19}F NMR spectroscopy) (Scheme 12).



HX: $H[BF_4]$ (**2a**), HCl (**11a**), HBr(**12a**)

Scheme 12.

We suppose that "silylated" alcohol **4a** in the presence of an acid is initially converted into free alcohol **14a**. Further protonation of the oxygen atom induces the elimination of water to give carbocation **D** as an intermediate. The stabilization of the latter can be accomplished either by the reaction with a halide ion to form the corresponding propene or with water to give acid fluoride **7a** and finally acid **13a** (Scheme 13).



X-: F^- (**2a**), Cl^- (**11a**), Br^- (**12a**)

Scheme 13.

It should be noted that in reactions of **4a** with acids under anhydrous conditions the corresponding propene is formed nearly exclusively. Earlier, this fact was noticed in the reaction of alcohol **14** with water-free complex HF·THF,[2] which resulted in propene **2**. A similar reaction of "silylated" alcohol **4a** with gaseous HCl afforded propene **11a** as a major product.

Conclusions

The reaction of equimolar amounts of aromatic aldehydes **1**, $Et_3SiCF{=}CF_2$ and CsF proceeds selectively to afford "silylated" alcohols **4** in excellent yields. Compounds **4** attract significant attention as synthons for further conversions under the action of both nucleophilic and electrophilic reagents. Products **4** are unique due to the presence of two reactive centres; both of them can be involved in conversions depending on the purpose. The presence of a silyl protecting group for the hydroxy functionality makes compounds **4** absolutely stable upon storage, unlike the free alcohols. It also should be noted that all reactions of "silylated" alcohols **4** studied are highly stereoselective; the obtained propenes, acid fluorides and acids are (*E*) isomers with more than 98% purity. This reaction peculiarity can be also used for the purposeful synthesis of compounds with definite steric configuration.

Experimental Section

General Remarks: All reactions were carried out under a dry argon atmosphere by using Schlenk techniques. The following products were synthesized according to literature procedures: $Me_3SiCF{=}CF_2$,[12] $Et_3SiCF{=}CF_2$,[12] $[Me_4N]F$,[13] 2-fluoro-3-*p*-tolylallylic acid fluoride (**7a**).[7] All solvents were purified according to literature procedures.[14] R_f values refer to TLC carried out on 25-mm silica-gel plates (Merck F254). ^1H, ^{13}C, ^{19}F and ^{29}Si NMR were recorded with Bruker Avance300 and Avance400 spectrometers. The assignment of quaternary C, CH, CH_2 and CH_3 as well as C, CF, CF_2 and CF_3 atoms were made on the basis of DEPT experiments. Chemical shifts are referenced relative to external standards Me_4Si (for ^1H, ^{13}C and ^{29}Si) and CCl_3F (for ^{19}F and ^{29}Si). Mass spectra (EI, 20 eV) were obtained with a Finnigan MAT 95 spectrometer. Melting points were measured in one-end-open glass capillaries and are uncorrected. Column chromatography was carried out by using 60–240 mesh silica gel at atmospheric pressure. C, H, N and F analyses were performed with HEKAtech Euro EA 3000 and Analytikjena Spekol 1100 instruments.

General Procedure for the Synthesis of 1-Triethylsiloxy-2,3,3-trifluoro-1-aryl-2-propenes (4): To a solution of **1** (10 mmol) in dimethoxyethane (DME) (50 mL) at –60 °C was added $Et_3SiCF{=}CF_2$ (2.16 g, 11 mmol) and CsF (1.52 g, 10 mmol). The mixture was stirred for 1 h at –30 °C and then for 23 h at room temperature. Cesium fluoride was filtered off and the filtrate was concentrated in vacuo. The residue was purified by distillation under reduced pressure.

1-Triethylsiloxy-2,3,3-trifluoro-1-(4-tolyl)prop-2-ene (4a): Yield 2.75 g (87%). B.p. 80 °C/0.09 Torr. ^1H NMR (300.13 MHz, $CDCl_3$, 25 °C): δ = 0.69 (q, $^3J_{H,H}$ = 7.7 Hz, 6 H, CH_2Si), 1.00 (t, $^3J_{H,H}$ = 7.7 Hz, 9 H, CH_3CH_2), 2.40 (s, 3 H, $CH_3C_6H_4$), 5.52 [dm, $^3J_{H,F}$ = 32.2 Hz, 1 H, CH], 7.21 (m, 2 H, Ar-H_{ortho}), 7.25 (m, 2 H, Ar-H_{meta}) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$, 25 °C): δ = 4.6 (CH_2Si), 6.5 (CH_3CH_2), 21.1 ($CH_3C_6H_4$), 67.8 (CH), 126.0 (2 C, Ar-C_{ortho}), 129.1 (2 C, Ar-C_{meta}), 129.7 (ddd, $^1J_{C,F}$ = 241 Hz, $^2J_{C,F}$ = 48 Hz, $^2J_{C,F}$ = 12 Hz, =CF), 136.0 (Ar-C_{ipso}), 137.9 (Ar-C_{para}), 153.5 (ddd, $^1J_{C,F}$ = 318 Hz, $^1J_{C,F}$ = 276 Hz, $^2J_{C,F}$ = 45 Hz, $=CF_2$) ppm. ^{19}F NMR (282.4 MHz, $CDCl_3$, 25 °C): δ = –104.3 (dd, $^2J_{F,F}$ = 80.6 Hz, $^3J_{F,Fcis}$ = 31.7 Hz, =C*F*F), –120.8 (dd, $^2J_{F,F}$ = 80.6 Hz, $^3J_{F,Ftrans}$ = 115 Hz, =CF*F*), –186.3 (ddd, $^3J_{F,Ftrans}$ = 115 Hz, $^3J_{F,H}$ = 32.2 Hz, $^3J_{F,Fcis}$ = 31.7 Hz, =CF-) ppm. ^{29}Si NMR (59.63 MHz, $CDCl_3$, 25 °C): δ = 22.6 (s) ppm. MS (EI): *m*/*z* (%) = 287 (100) $[M - C_2H_5]^+$. $C_{16}F_3H_{23}OSi$ (316.43): calcd. C 60.73, F 18.01, H 7.33; found C 60.61, F 17.93, H 7.28.

1-Triethylsiloxy-2,3,3-trifluoro-1-(4-fluorophenyl)prop-2-ene (4b): Yield: 2.76 g (86%). B.p. 75 °C/0.3 Torr. ^1H NMR (300.13 MHz,

$CDCl_3$, 25 °C): δ = 0.69 (q, $^3J_{H,H}$ = 7.7 Hz, 6 H, CH_2Si), 0.99 (t, $^3J_{H,H}$ = 7.7 Hz, 9 H, CH_3CH_2), 5.51 (dm, $^3J_{H,F}$ = 25.2 Hz, 1 H, CH), 7.08 (m, 2 H, Ar-H_{ortho}), 7.42 (m, 2 H, Ar-H_{meta}) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$, 25 °C): δ = 4.5 (CH_2Si), 6.5 (CH_3CH_2), 67.4 (CH), 127.8 (2 C, Ar-C_{ortho}), 115.3 (2 C, Ar-C_{meta}), 130.8 (=CF), 134.7 (Ar-C_{ipso}), 162.5 (Ar-C_{para}), 152.4 (=CF_2) ppm. ^{19}F NMR (282.4 MHz, $CDCl_3$, 25 °C): δ = –103.9 (dd, $^2J_{F,F}$ = 80.5 Hz, $^3J_{F,Fcis}$ = 32 Hz, =C*F*F), –114.3 (m, 4-FC_6H_4), –120.7 (dd, $^2J_{F,F}$ = 80.5, $^3J_{F,Ftrans}$ = 114.5 Hz, =CF*F*), –186.1 (ddd, $^3J_{F,Ftrans}$ = 114.5, $^3J_{F,Fcis}$ = 32, $^3J_{F,H}$ = 25 Hz, =CF-) ppm. ^{29}Si NMR (59.63 MHz, $CDCl_3$, 25 °C): δ = 22.8 (d, $^1J_{Si,C}$ = 60 Hz) ppm. MS (EI): *m*/*z* (%) = 291 (100) $[M - C_2H_5]^+$. $C_{15}F_4H_{20}OSi$ (320.40): calcd. C 56.23, F 23.72, H 6.29; found C 56.34, F 23.77, H 6.31.

General Procedure for the Synthesis of 2,3,3-Trifluoro-1-trimethylsiloxy-1-aryl-2-propenes (10): To a solution of **1** (1.4 mmol) in diethyl ether (7 mL) at –30 °C was added $Me_3SiCF{=}CF_2$ (0.24 g, 1.54 mmol) and $[Me_4N]F$ (13 mg, 0.14 mmol). The mixture was stirred for 1 h at –30 °C and then overnight at room temperature. The precipitate formed was filtered off, the solvent was evaporated in vacuo and pentane (6 mL) was added to the residue. The pentane solution was decanted and concentrated in vacuo. The residue was purified by distillation under reduced pressure.

2,3,3-Trifluoro-1-trimethylsiloxy-1-(4-tolyl)prop-2-ene (10a): Yield: 0.29 g (75%). B.p. 65–66 °C/2 Torr. ^1H NMR (300.13 MHz, *c*-C_6D_{12}, 25 °C): δ = 0.15 (s, 9 H, C*H*$_3$Si), 2.29 (s, 3 H, C*H*$_3C_6H_4$), 5.46 (dm, $^3J_{H,F}$ = 25 Hz, 1 H, CH), 7.07 (m, 2 H, Ar-H_{ortho}), 7.27 (m, 2 H, Ar-H_{meta}) ppm. ^{13}C NMR (75.47 MHz, *c*-C_6D_{12}, 25 °C): δ = –0.3 (*C*H$_3$Si), 21.2 (*C*H$_3C_6H_4$), 68.8 (dt, $^2J_{C,F}$ = 22 Hz, $^3J_{C,F}$ = 3 Hz, CH), 126.7 (2 C, Ar-C_{ortho}), 129.5 (2 C, Ar-C_{meta}), 130.1 (ddd, $^1J_{C,F}$ = 244 Hz, $^2J_{C,F}$ = 48 Hz, $^2J_{C,F}$ = 12 Hz, =CF), 136.6 (Ar-C_{ipso}), 138.1 (Ar-C_{para}), 153.5 (ddd, $^1J_{C,F}$ = 318 Hz, $^1J_{C,F}$ = 276 Hz, $^2J_{C,F}$ = 45 Hz, =CF_2) ppm. ^{19}F NMR (282.4 MHz, *c*-C_6D_{12}, 25 °C): δ = –105.5 (ddd, $^2J_{F,F}$ = 82 Hz, $^3J_{F,Fcis}$ = 33 Hz, $^4J_{F,H}$ = 2 Hz, =C*F*F), –122.1 (ddd, $^2J_{F,F}$ = 82 Hz, $^3J_{F,Ftrans}$ = 115 Hz, $^4J_{F,H}$ = 3 Hz, =CF*F*), –185.7 (ddd, $^3J_{F,Ftrans}$ = 115 Hz, $^3J_{F,Fcis}$ = 33 Hz, $^3J_{F,H}$ = 25 Hz, =CF) ppm. ^{29}Si NMR (59.63 MHz, *c*-C_6D_{12}, 25 °C): δ = 19.3 (d, $^1J_{Si,C}$ = 59 Hz) ppm. MS (EI): *m*/*z* (%) = 274 (45) $[M]^+$, 259 (100) $[M - CH_3]^+$. $C_{13}F_3H_{17}OSi$ (274.35): calcd. C 56.91, F 20.78, H 6.25; found C57.02, F 20.83, H 6.28.

2,3,3-Trifluoro-1-(4-fluorophenyl)-1-trimethylsiloxyprop-2-ene (10b): Yield: 0.30 g (77%). B.p. 85 °C/12 Torr. ^1H NMR (300.13 MHz, $CDCl_3$, 25 °C): δ = 0.19 (s, 9 H, CH_3Si), 5.49 (dm, $^3J_{H,F}$ = 25 Hz, 1 H, CH), 7.08 (m, 2 H, Ar-H_{ortho}), 7.40 (m, 2 H, Ar-H_{meta}) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$, 25 °C): δ = –0.3 (CH_3Si), 67.3 (CH), 115.3 (2 C, Ar-C_{meta}), 127.8 (2 C, Ar-C_{ortho}), 128.8 (=CF), 134.4 (Ar-C_{ipso}), 152.4 (=CF_2), 162.6 (Ar-C_{para}) ppm. ^{19}F NMR (282.4 MHz, $CDCl_3$, 25 °C): δ = –103.3 (ddd, $^2J_{F,F}$ = 80 Hz, $^3J_{F,Fcis}$ = 33 Hz, $^4J_{F,H}$ = 2 Hz, =C*F*F), –114.2 (m, 4-FC_6H_4), –120.3 (ddd, $^2J_{F,F}$ = 80 Hz, $^3J_{F,Ftrans}$ = 116 Hz, $^4J_{F,H}$ = 4 Hz, =CF*F*), –186.5 (ddd, $^3J_{F,Ftrans}$ = 116 Hz, $^3J_{F,Fcis}$ = 33 Hz, $^3J_{F,H}$ = 25 Hz, =CF) ppm. MS (EI): *m*/*z* (%) = 278 (50) $[M]^+$, 263 (100) $[M - CH_3]^+$. $C_{12}F_4H_{14}OSi$ (278.32): calcd. C 51.78, F 27.31, H 5.07; found C 51.67, F 27.37, H 5.04.

Preparation of 1,1,2-Trifluoro-3-(4-methylphenyl)prop-2-enyl 2,3,3-Trifluoro-1-(4-methylphenyl)prop-2-enyl Ether (6a): To a solution of **1a** (0.6 g, 5 mmol) in DME (20 mL) at –60 °C was added $Et_3SiCF{=}CF_2$ (1.08 g, 5.5 mmol) and $[Me_4N]F$ (0.23 g, 2.5 mmol). The mixture was stirred for 80 min at –45 ± 5 °C, then cold water (8 mL) was added, and the products were extracted with diethyl ether (2 × 6 mL). The combined ether phases were washed with water (6 mL), dried ($MgSO_4$) and concentrated in vacuo. The residue (1.05 g) was dissolved in $CHCl_3$ (5 mL), and 35% aqueous HCl (2 mL) was added to convert byproducts **4a** and **9a** into **7a**, **11a** and **13a**. The mixture was stirred for ca. 4 d at room temperature until the reaction was complete (monitored by ^{19}F NMR spectroscopy). All volatile compounds were evaporated in vacuo (0.4 Torr) at 40 °C. The residue was dissolved in THF (10 mL) and aqueous NaOH (10%, 5 mL) and Bu_4NHSO_4 (30 mg) were added to neutralize acrylic acid **13a** and the corresponding fluoride **7a**. The mixture was stirred for ca. 2 h at room temperature. After the reaction was complete (monitored by TLC on silica-gel-coated plates by using pentane as eluent), THF was evaporated, and the product was extracted with hexane (5 mL). The extract was washed with water (2 × 5 mL), dried ($MgSO_4$) and concentrated in vacuo to yield 0.5 g (26%) of **6a** (94% purity). ^1H NMR [300.13 MHz, $(CD_3)_2CO$, 25 °C]: δ = 2.30 (s, 3 H, C*H*$_3C_6H_4$), 2.31 (s, 3 H, C*H*$_3C_6H_4$),6.03 (dtm, $^3J_{H,F}$ = 24.8 Hz, $^4J_{H,H}$ = 2.3 Hz, 1 H, CH-CF), 6.25 (d, $^3J_{H,F}$ = 35.6 Hz, 1 H, CH=CF), 7.08 (m, 2 H, Ar-H_{meta}), 7.12 (m, 2 H, Ar-H_{meta}), 7.28 (m, 2 H, Ar-H_{ortho}), 7.37 (m, 2 H, Ar-H_{ortho}) ppm. ^{13}C NMR [75.47 MHz, $(CD_3)_2CO$, 25 °C]: δ = 20.3 (1 C, *C*H$_3C_6H_4$), 20.5 (1 C, *C*H$_3C_6H_4$), 69.6 (1 C, *C*H-CF), 109.8 (1 C, *C*H=CF), 118.1 (1 C, CF_2-O), 126.2 (1 C, CF_2=*C*F), 126.2 (2 C, Ar-C_{ortho}), 127.8 (1 C, Ar-C_{ipso}), 128.9 (4 C, Ar-C_{meta}), 129.1 (2 C, *Ar*-C_{ortho}), 131.1 (1 C, *Ar*-C_{ipso}), 138.4 (2 C, Ar-C_{para}), 146.2 (1 C, CH=*C*F), 152.4 (1 C, *C*F_2=CF) ppm. ^{19}F NMR [282.4 MHz, $(CD_3)_2CO$, 25 °C]: δ = –76.9 (ddd, $^2J_{F,F}$ = 154 Hz, $^3J_{F,F}$ = 12.7 Hz, $^4J_{F,H}$ = 3.6 Hz, C*F*FO; ABX spin system), –77.7 (dd, $^2J_{F,F}$ = 154 Hz, $^3J_{F,F}$ = 14.0 Hz, CF*F*O), –102.5 (ddd, $^2J_{F,F}$ = 71.9 Hz, $^3J_{F,Fcis}$ = 33.3 Hz, $^4J_{F,H}$ = 1.7 Hz, =C*F*F), –119.0 (dd, $^2J_{F,F}$ = 71.9 Hz, $^3J_{F,Ftrans}$ = 115.7 Hz, =CF*F*), –130.3 (dt, $^3J_{F,H}$ = 35.6 Hz, $^3J_{F,F}$ = 13.2 Hz, CF=CH), –186.7 (ddd, $^3J_{F,Ftrans}$ = 115.7 Hz, $^3J_{F,Fcis}$ = 33.3 Hz, $^3J_{F,H}$ = 24.8 Hz, =CF) ppm. MS (EI): *m*/*z* (%) = 386 (20) $[M]^+$, 294 (100) $[M - C_6H_4CH_3]^+$, 185 (40) $[CH_3C_6H_4 - CH(CF{=}CF_2)]^+$.

Preparation of Bis[1,1,2-trifluoro-3-(4-methylphenyl)prop-2-enyl] Ether (8a): 6a (0.3 g, 0.78 mmol) in pentane was passed through the column with silica gel to yield 0.135 g of **8a** (45%). R_f = 0.29 (pentane). ^1H NMR (300.13 MHz, $CDCl_3$, 25 °C): δ = 2.40 (s, 6 H, $CH_3C_6H_4$), 6.38 (d, $^3J_{H,F}$ = 36 Hz, 2 H, CH), 7.23 (m, 4 H, Ar-H_{ortho}), 7.49 (m, 4 H, Ar-H_{meta}) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$, 25 °C): δ = 21.4 (2 C, $CH_3C_6H_4$), 111.0 (q, $^2J_{C,F}$ = $^3J_{C,F}$ = 3 Hz, 2 C, CH), 116.8 (td, $^1J_{C,F}$ = 271 Hz, $^2J_{C,F}$ = 43 Hz, 2 C, CF_2), 123.6 (d, $^4J_{C,F}$ = 7 Hz, 4 C, Ar-C_{ortho}), 127.2 (d, $^3J_{C,F}$ = 3.5 Hz, 2 C, Ar-C_{ipso}), 129.5 (4 C, Ar-C_{meta}), 139.6 (d, $^6J_{C,F}$ = 2.5 Hz, 2 C, Ar-C_{para}), 145.8 (dt, $^1J_{C,F}$ = 268 Hz, $^2J_{C,F}$ = 36 Hz, 2 C, CF) ppm. ^{19}F NMR (282.4 MHz, $CDCl_3$, 25 °C): δ = –74.6 (dm, $^3J_{F,F}$ = 10 Hz, 4 F, CF_2; ABX spin system), –131.3 (dtm, $^2J_{F,H}$ = 36 Hz, $^3J_{F,F}$ = 10 Hz, 2 F, CF) ppm. MS (EI): *m*/*z* (%) = 386 (20) $[M]^+$, 294 (100) $[M - C_6H_4CH_3]^+$, 185 (40) $[CH_3C_6H_4 - CH(CF{=}CF_2)]^+$. $C_{20}F_6H_{16}O$ (386.33): calcd. C 62.18, F 29.51, H 4.17; found C 62.03, F 29.44, H 4.13.

Preparation of 2,3,3-Trifluoro-1-(4--tolyl)allyl 2-Fluoro-3-(4-tolyl)-acrylate (9a): To a mixture of **7a** (0.46 g, 2.5 mmol) and **4a** (0.79 g, 2.5 mmol) in DME (20 mL) at –40 °C was added $[Me_4N]F$ (30 mg, 0.32 mmol). The mixture was stirred for 1 h at –20 °C and then overnight at room temperature. The precipitate formed was filtered off, the filtrate was concentrated, and the residue was dissolved in a minimum amount of pentane and precipitated upon cooling to yield 0.61 g (67%) of **9a**. M.p. 64–66 °C. ^1H NMR [300.13 MHz, $(CD_3)_2CO$, 25 °C]: δ = 2.37 (s, 3 H, C*H*$_3C_6H_4$), 2.39 (s, 3 H, C*H*$_3C_6H_4$), 6.77 (dm, $^3J_{H,F}$ = 26 Hz, 1 H, CH-CF), 7.17 (d, $^3J_{H,F}$ = 36 Hz, 1 H, CH=CF), 7.3 (2 H, Ar-H_{meta}), 7.31 (2 H, Ar-H_{meta}), 7.49 (2 H, Ar-H_{ortho}), 7.67 (2 H, Ar-H_{ortho}) ppm. ^{13}C NMR [75.47 MHz, $(CD_3)_2CO$, 25 °C]: δ = 20.2 (1 C, *C*H$_3C_6H_4$), 20.5 (1 C, *C*H$_3C_6H_4$), 69.3 (1 C, *C*H-CF), 118.8 (1 C, *C*H=CF), 125.8 (1

C, CF_2=*C*F), 126.8 (2 C, Ar-C_{ortho}), 128.1 (1 C, Ar-C_{ipso}), 129.4 (2 C, Ar-C_{meta}), 129.6 (2 C, Ar-C_{meta}), 130.5 (2 C, Ar-C_{ortho}), 130.9 (1 C, Ar-C_{ipso}), 139.2 (1 C, Ar-C_{para}), 140.7 (1 C, Ar-C_{para}), 145.7 (1 C, CH=*C*F), 153.4 (1 C, *C*F_2=CF), 159.6 (d, $^2J_{C,F}$ = 35 Hz, 1 C, C=O) ppm. ^{19}F NMR [282.4 MHz, $(CD_3)_2CO$, 25 °C]: δ = –102.2 (ddd, $^2J_{F,F}$ = 70 Hz, $^3J_{F,Fcis}$ = 32 Hz, $^4J_{F,H}$ = 2 Hz, C*F*F), –116.6 (ddd, $^2J_{F,F}$ = 70 Hz, $^3J_{F,Ftrans}$ = 114 Hz, $^4J_{F,H}$ = 3 Hz, CF*F*), –127.8 (d, $^3J_{F,H}$ = 36 Hz, CH=CF), –187.0 (ddd, $^3J_{F,Ftrans}$ = 114 Hz, $^3J_{F,Fcis}$ = 32 Hz, $^3J_{F,H}$ = 26 Hz, C*F*=CF_2) ppm. MS (EI): *m*/*z* (%) = 364 (20) $[M]^+$, 272 (100) $[M - C_6H_4CH_3]^+$, 185 (40) $[CH_3C_6H_4 - CH(CF=CF_2)]^+$. $C_{20}F_4H_{16}O_2$ (364.33): calcd. C 65.93, F 20.86, H 4.43; found C 66.08, F 20.79, H 4.40.

Preparation of 2,3,3,3-Tetrafluoro-1-(4-tolyl)prop-1-ene (2a) and 2-Fluoro-3-(4-tolyl)acrylic Acid (13a): To a mixture of **1a** (1 g, 8.3 mmol) and $Et_3SiCF=CF_2$ (1.82 g, 9.1 mmol) in DME (40 mL) at –55 ± 5 °C was portionwise added $[Me_4N]F$ (0.78 g, 8.3 mmol) over 1.5 h. The mixture was stirred for 1 h at –30 °C and then overnight at room temperature. The precipitate formed (tetramethylammonium salt of 2-fluoro-3-*p*-tolylacrylic acid, **3a**) was filtered, washed with aqueous HCl (5%, 7 mL) and water (2 × 7 mL), then dissolved in aqueous NaOH (10%, 7 mL). Insoluble impurities were filtered off, and the filtrate was acidified with 5% aqueous HCl to the isotonic point. The precipitate formed was filtered and dried to yield 0.70 g (47%) of **13a**. Physical and spectral characteristics of **13a** correspond to literature data.[15] The filtrate of the reaction mixture was concentrated in vacuo, and pentane (6 mL) was added to the residue. The pentane solution was decanted, and the solvent was evaporated in vacuo. The residue was purified by distillation under reduced pressure to yield 0.53 g (31%) of **2a** (*E*/*Z* = 98:2). B.p. 78 °C/12 Torr. (*E*) isomer: ^{1}H NMR (300.13 MHz, $CDCl_3$, 25 °C): δ = 2.44 (s, 3 H, $CH_3C_6H_4$), 6.38 (d, $^3J_{H,F}$ = 36 Hz, 1 H, CH), 7.26 (d, $^3J_{H,H}$ = 8 Hz, 2 H, Ar-H_{ortho}), 7.52 (d, $^3J_{H,H}$ = 8 Hz, 2 H, Ar-H_{meta}) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$, 25 °C): δ = 21.3 ($CH_3C_6H_4$), 111.4 (quint, $^2J_{C,F}$ = $^3J_{C,F}$ = 3.5 Hz, CH), 119.0 (qd, $^1J_{C,F}$ = 271 Hz, $^2J_{C,F}$ = 41 Hz, CF_3), 126.9 (d, $^3J_{C,F}$ = 3.9 Hz, Ar-C_{ipso}),129.6 (Ar-C_{meta}), 129.7 (d, $^4J_{C,F}$ = 7.4 Hz, Ar-C_{ortho}), 144.4 (dq, $^1J_{C,F}$ = 266 Hz, $^2J_{C,F}$ = 38 Hz, CF) ppm. ^{19}F NMR (282.4 MHz, $CDCl_3$, 25 °C): δ = –72.0 (d, $^3J_{F,F}$ = 11 Hz, 3 F, CF_3), –133.3 (dq, $^2J_{F,H}$ = 36 Hz, $^3J_{F,F}$ = 11 Hz, 1 F, CF) ppm. (*Z*) isomer: ^{19}F NMR (282.4 MHz, $CDCl_3$, 25 °C): δ = –66.8 (d, $^3J_{F,F}$ = 10 Hz, 3 F, CF_3), –125.7 (dq, $^2J_{F,H}$ = 21 Hz, $^3J_{F,F}$ = 11 Hz, 1 F, CF) ppm. MS (EI): *m*/*z* (%) = 204 (100) $[M]^+$. $C_{10}F_4H_8$ (204.16): calcd. C 58.83, F 37.23, H 3.95; found C 58.69, F 37.38, H 3.88.

General Procedure for the Reactions of 4a with Brönsted Acids: To a solution of **4a** (0.40 g, 1.26 mmol) in diethyl ether or dioxane (10 mL) was added an excess amount of the appropriate acid (HBF_4, HCl or HBr). The mixture was stirred at room temperature until the reaction was complete. Reaction control was monitored by ^{19}F NMR spectroscopy. Spectral data of **11a**[16] and **12a**[17] correspond with literature data.

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