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Fluorine-containing β,β-disubstituted trimethylsilyl vinyl ethers: synthesis and reactions with *N*-(1,1,2,2-tetrafluoroethyl)dimethylamine

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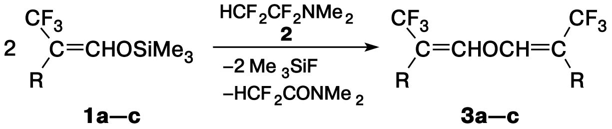
Fluorine-containing β,β-disubstituted trimethylsilyl vinyl ethers prepared by hydrosilylation of appropriate substituted trifluoromethylketenes react with *N*-(1,1,2,2-tetrafluoroethyl)dimethylamine to give β,β,β´,β´-tetrasubstituted divinyl ethers. Conditions for selective hydrofluorination of *tert*-butyl perfluoro-2-methylpent-2-enoate into the corresponding saturated ester were developed. Pyrolysis of the latter with P_2O_5 afforded perfluoromethyl(propyl)ketene.

Key words: fluorine-containing β,β-disubstituted trimethylsilyl vinyl ethers, fluorine-containing β,β,β´,β´-tetrasubstituted divinyl ethers, *N*-(1,1,2,2-tetrafluoroethyl)dimethylamine, fluorine-containing ketenes, hydrosilylation.

Earlier,[1] it has been demonstrated that hexafluoro-1-hydroisobutenyloxy(trimethyl)silane can be transformed into 2,2,2´,2´-tetrakis(trifluoromethyl)divinyl ether under the action of *N*-(α,α-difluoroalkyl)dialkylamines. In the present work, we studied reactions of other fluorine-containing β,β-disubstituted trimethylsilyl vinyl ethers **1a—c** with *N*-(1,1,2,2-tetrafluoroethyl)dimethylamine (**2**).

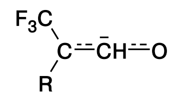
It turned out that silyl vinyl ethers **1a—c** are similarly transformed into divinyl ethers **3a—c** under the action of tetrafluoroethylamine **2** (Scheme 1)*.

Scheme 1



1, 3: R = EtOCO (**a**), C_2F_5CO (**b**), *n*-C_3F_7 (**c**)

2-Ethoxycarbonylvinyl ether **1a** smoothly reacts with amine **2** at room temperature for a day to give divinyl ether **3a** in high yield. 2-(Pentafluoropropionyl)vinyl ether **1b** is even more reactive: its reaction with tetrafluoroethylamine **2** proceeds exothermically. In contrast, heptafluoropropyl derivative **1c** reacts slowly. This refers both to the final cleavage of an intermediate amide acetal and even to initial detachment of the α-F atom from amine **2** in the form of Me_3SiF (for the detailed mechanism of the transformation **1**→**3**, see Ref. 1). An attempt to accelerate the reaction by increasing the reaction temperature was not very successful because the *in situ* generated 3,3,4,4,5,5,5-heptafluoro-2-trifluoromethylpent-1-enolate anion (**4c**) tends to eliminate the fluoride ion, in contrast to the hexafluoro-1-hydroisobutenolate anion (**4d**). This resulted in the formation of a number of by-products and a lowered yield of the target divinyl ether **3c**.



4a—d

R = EtOCO (**a**), C_2F_5CO (**b**), *n*-C_3F_7 (**c**), CF_3 (**d**)

Like 2,2,2´,2´-tetrakis(trifluoromethyl)divinyl ether, divinyl ethers **3a** and **3c** are very stable. In contrast, dioxo divinyl ether **3b**, which is sufficiently stable in the individual state, in the presence of diverse solvents (diethyl ether, acetone, and even *N*,*N*-dimethyldifluoroacetamide) undergoes further transformations at a more or less high rate, especially at elevated temperature. That is why the yield of divinyl ether **3b** upon the distillation of the reaction mixture was only 39%. The greater part of it seems to be rearranged into bicyclic diacetal **5** as a mixture of isomers **5A** and **5B** (**5A**/**5B** = 13/1). Its structure was confirmed by NMR spectra and GC-MS data (*cf.* Refs 2, 3) (Scheme 2).

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† Deceased.

* A substantially different result was obtained in reactions of α,α-difluoroalkylamines with pentafluoropropen-2-yl trimethylsilyl ether since the pentafluoropropen-2-olate anion arising from the elimination of Me_3SiF attacks, through its carbon atom, the conjugated α-fluoro iminium cation $[CF_2HCF{=}NR_2]^+$. The resulting aminopentanone $CF_3COCF_2CF(NR_2)CF_2H$ undergoes further transformations.

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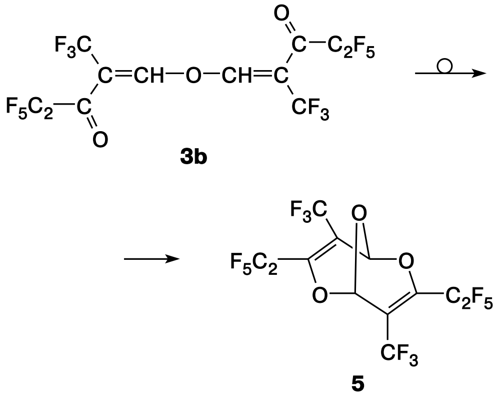
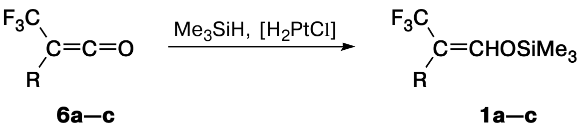
Scheme 2



The ratio of the *E*/*Z*-isomers in divinyl ethers **3a,b** is not the same as in the starting silyl vinyl ethers **1a,b**.* This is evidence for the stereochemical flexibility of intermediate enolate anions **4a,b**, which are the anions of β-dicarbonyl compounds (in contrast to the enolate anion **4c** with triad mesomerism). At the same time, the formation of only 1,1′-dihydrodivinyl ethers **3a,b** indicates that the reaction site of enolate anions **4a,b** is the formyl O atom, which is sterically least hindered and probably has the highest electron density.

The starting silyl vinyl ethers **1a**—**c** were prepared in high yields by hydrosilylation of appropriate ketenes **6a**—**c** according to a known procedure[1,4] (Scheme 3). The products were mixtures of *E*/*Z*-isomers, the *E*-structure being dominant.

Scheme 3



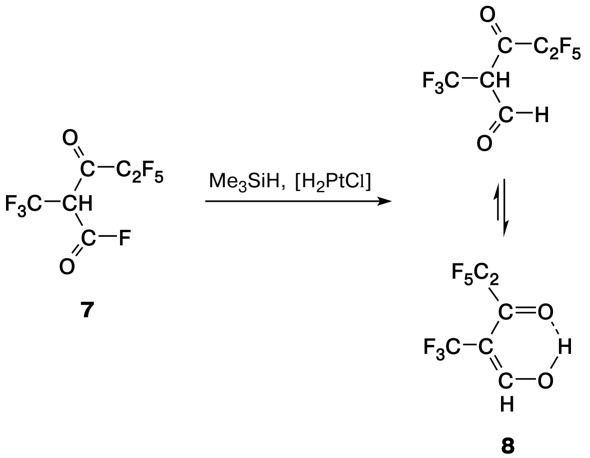
R = EtOCO (**a**), C_2F_5CO (**b**), *n*-C_3F_7 (**c**)

In the case of ether **1b**, which is a push-pull olefin with an obviously lowered energy of the C=C bond, distillation of the reaction mixture always gave an equilibrium mixture of isomers (*E*/*Z* = 1/1), although the crude product may occasionally have a nonequilibrium composition.

Known ethoxycarbonylketene **6a** was prepared according to a modified procedure.[5] Pyrolysis of diethyl trifluoromethylmalonate with P_2O_5 *in vacuo* afforded ketene **6a** in a lower yield (compared to the reported[5] one) but with required purity**.

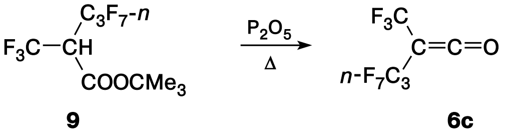
In contrast to the literature data,[7] the acylketene **6b** obtained in the present work contains a difficult-to-separate impurity of acid fluoride **7** (~12%) produced by hydrofluorination; the source of HF remains unclear. Nevertheless, we used crude oxo ketene **6b** in the next step because acid fluoride **7** is completely reduced under hydrosilylation conditions to oxo aldehyde **8** (ketone/enol = 1/10), which is simultaneously a hydrolyzate of silyl ether **1b** and can easily be separated from the latter by distillation (Scheme 4).

Scheme 4



Earlier unknown perfluoromethyl(propyl)ketene **6c** was obtained in high yield by pyrolysis of *tert*-butyl ester **9** with P_2O_5 according to a general procedure[5] (Scheme 5).

Scheme 5



Since saturated *tert*-butyl ester **9** has been isolated earlier[8] only by preparative GLC from its mixture with unsaturated *tert*-butyl ester **10**, here we found conditions for selective hydrofluorination of compound **10** without affecting the ester group*** (Scheme 6).

Such exhaustive hydrofluorination of unsaturated ester **10** is indispensable because pyrolysis with P_2O_5 results

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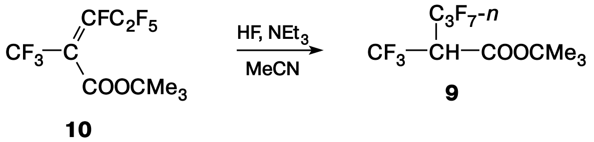
* *E*/*Z* Assignment of silyl vinyl and divinyl ethers **1a**—**c** and **3a**—**c** was made under the assumption that for the fragment $CF_3C{=}CH$, the coupling constant cis-$^4J_{\mathrm{C\underline{F}3,C\underline{H}}}$ is greater than $trans$-$^4J_{\mathrm{C\underline{F}3,C\underline{H}}}$ and the ^{19}F chemical shift for the CF_3 group $\delta_{cis\text{-}\mathrm{C\underline{F}_3C=CH}}$ is lesser than $\delta_{trans\text{-}\mathrm{C\underline{F}_3C=CH}}$.

** Ethoxycarbonylketene **6a** undergoes rapidly dimerization even at room temperature, like its methoxy analog.[6]

*** Attempted hydrofluorination of ester **10** with liquid HF in the presence of a catalytic amount of NEt_3 did not result in the expected addition to the C=C bond, causing only the decomposition of the ester group.

Scheme 6



in its decomposition to acylketene **6b**, which contaminates the target ketene **6c**.

To sum up, new fluorine-containing β,β-disubstituted (including functionalized) trimethylsilyl vinyl ethers **1a—c** were obtained and transformed, like hexafluoro-1-hydroisobutenyloxy(trimethyl)silane, into the corresponding β,β,β´,β´-tetrasubstituted divinyl ethers **3a—c** under the action of α,α-difluoroalkylamine **2**.

Experimental

^{1}H, ^{19}F, and ^{19}F{^{1}H} (with CF_3COOH as the external standard) NMR spectra were recorded on Bruker WP-200SY, Bruker Avance 300, Bruker Avance 400, and Bruker Avance 600 spectrometers. IR spectra were recorded on UR 20 and Carl Zeiss M-82 spectrophotometers in thin films. Raman spectra were recorded on Ramanor HG-2S and LabRAM spectrometers. MS and GC-MS measurements were performed on VG 7070E and Polaris/GCQ mass spectrometers (EI, 70 eV).

Dimethyl(tetrafluoroethyl)amine **2**,[9,10] diethyl trifluoromethylmalonate,[11] 1,3-dimethoxyperfluoro-2-methylpent-1-ene (with an impurity of pent-2-ene),[8] and trimethylsilane[12] were prepared according to known procedures. The other, commercial starting reagents and solvents were purified and dried, when necessary, according to standard procedures. Experiments involving ketenes **6a—c**, silyl vinyl ethers **1a—c**, and bis(2-acylvinyl) ether **3b** were carried out under dry argon. Unsaturated ester **10** was hydrofluorinated in a polyethylene vessel.

The characteristics of the compounds obtained are given in Tables 1—3. For mixtures of products, the molar ratio of the major components is always indicated.

Synthesis of divinyl ethers 3a—c

Bis[2-ethoxycarbonyl-2-(trifluoromethyl)vinyl] ether (3a). Silyl ether **1a** (*E*/*Z* = 8.1/1.0, 1.9466 g, 7.595 mmol) was added

Table 1. Boiling and melting points, IR and Raman spectra, and elemental analysis data for the compounds obtained

Compound	B.p./°C (*p*/Torr) [m.p./°C]	IR [Raman], ν/cm^{-1}	Found/Calculated (%)				Molecular formula
			C	H	F	Si	
1a[a]	48.0—48.5 (1)	[1640 s, 1709 m (C=C, C=O)][b]	41.9 42.2	5.58 5.90	22.3 22.2	10.80 10.96	$C_9H_{15}F_3O_3Si$
1b[c]	55 (2)	[1625 vs, 1703 vs (C=C, C=O)]	32.6 32.7	3.29 3.05	46.1 46.0	7.90 8.50	$C_9H_{10}F_8O_2Si$
1c[d]	55.5—56.5 (15)	[1652 s (C=C)]	30.4 30.7	2.91 2.86	54.2 53.9	7.53 7.97	$C_9H_{10}F_{10}OSi$
3a[e]	115—117 (1) [55—65]	[1628 m, 1675 vs, 1686 vs, 1721 m (C=C, C=O)][f]	41.2 41.2	3.44 3.45	32.5 32.6	—	$C_{12}H_{12}F_6O_5$
3b[g]	85—87 (1) [71—84]	[1681 vs, 1708 vs, 1722 s (C=C, C=O)]	28.9 29.0	0.51 0.40	60.9 61.0	—	$C_{12}H_2F_{16}O_3$
3c[h]	45—46 (1)	1652 vs, 1708 w [1652 w, 1710 vs] (C=C) (*cf.* Ref. 1)[i]	26.5 26.6	0.48 0.37	70.0 70.1	—	$C_{12}H_2F_{20}O$
6c	54—54.5 (760)	2185 vs [753 vs, 2182 w] (C=C=O)	26.1 25.9	0.00 0.00	68.7 68.3	—	$C_6F_{10}O$
8[j]	105—106 (760)	1584 vs, 1656 vs [1577 s, 1655 m] (C=C, C=O; enol), 1736 w, 1768 w [1708 vw, 1770 vw] (C=O; ketone)]	27.7 27.9	0.91 0.78	58.6 58.9	—	$C_6H_2F_8O_2$

[a] *E*/*Z* = 8.1/1.0.

[b] Contour splitting revealed the following lines: 1631 m, 1726 w (C=C, C=O; *Z*-isomer) and 1641 s, 1712 m (C=C, C=O; *E*-isomer).

[c] *E*/*Z* = 1/1.

[d] *E*/*Z* = 1.7/1.0.

[e] *E*,*E*/*E*,*Z*/*Z*,*Z* = 10.3/6.7/1.0.

[f] Contour splitting revealed the following lines: 1620 w, 1629 w, 1675 s, 1687 vs, 1720 w, 1727 w, 1739 vw (C=C, C=O).

[g] *E*,*E*/*E*,*Z*/*Z*,*Z* = 1/6/6.

[h] *E*,*E*/*E*,*Z*/*Z*,*Z* = 3/4/1.

[i] A misprint in Ref. 1: Table 1, compound **6**, IR (Raman) spectrum. Printed "1722 w, 1670 vs (1722 vs, 1666 vs) (C=C)". Should be printed "1722 w, 1670 vs (1722 vs, 1666 vw) (C=C)".

[j] Ketone/enol = 1/10.

Table 2. NMR spectra of the compounds obtained

Compound	Isomer	δ (*J*/Hz)	
		^1H	^{19}F
1a[a,b]	*E*	0.75 (s, 9 H, Me_3Si); 1.70 (t, 3 H, CH_3, $^3J_{CH_3,CH_2} = 7.15$); 4.61 (q, 2 H, CH_2, $^3J_{CH_2,CH_3} = 7.15$); 7.91 (q, 1 H, CH, $^4J_{CH,CF_3} = 1.65$)	16.4 (br.s, CF_3)
	Z	0.75 (s, 9 H, Me_3Si); 1.68 (t, 3 H, CH_3, $^3J_{CH_3,CH_2} = 7.15$); 4.61 (q, 2 H, CH_2, $^3J_{CH_2,CH_3} = 7.15$); 8.14 (q, 1 H, CH, $^4J_{CH,CF_3} = 1.28$)	19.5 (br.s, CF_3)
1b[c,d]	*E*	0.37 or 0.39 (both s, 9 H, Me_3Si); 7.70[e] (br.s, 1 H, CH)	−44.0 (s, 2 F, CF_2); −3.6 (s, 3 F, $C\underline{F}_3CF_2$); 16.5 (br.s, 3 F, $CF_3C=$)
	Z	0.37 or 0.39 (both s, 9 H, Me_3Si); 7.96 (br.s, 1 H, CH)	−37.4[f] (br.s, 2 F, CF_2); −4.3 (br.s, 3 F, $C\underline{F}_3CF_2$); 18.6[g] (br.s, 3 F, $CF_3C=$)
1c[h,i]	*E*	0.30 (s, 9 H, Me_3Si); 7.41 (br.q, 1 H, CH, $^4J_{CH,CF_3} = 1.81$)	−49.75 (m, 2 F, $CF_3C\underline{F}_2$); −32.9 (m, 2 F, $CF_2C=$); −4.6 (t, 3 F, $C\underline{F}_3CF_2$, $^4J_{CF_3,CF_2C=} = 9.82$); 17.1 (br.tt, 3 F, $CF_3C=$, $^4J_{CF_3,CF_2C=} = 8.92$, $^5J_{CF_3,CF_2} = 4.76$)
	Z	0.33 (s, 9 H, Me_3Si); 7.17 (br.tq, 1 H, CH, $^4J_{CH,CF_3} = {}^4J_{CH,CF_2C=} = 1.43$)	−49.79 (m, 2 F, $CF_3C\underline{F}_2$); −31.0 (m, 2 F, $CF_2C=$); −4.2 (t, 3 F, $C\underline{F}_3CF_2$, $^4J_{CF_3,CF_2C=} = 10.1$); 18.9 (br.tt, 3 F, $CF_3C=$, $^4J_{CF_3,CF_2C=} \approx {}^5J_{CF_3,CF_2} \approx 9.1$)
3a[c,j]	*E*,*E*	1.36 (t, 6 H, 2 CH_3, $^3J_{CH_3,CH_2} = 7.15$); 4.35 (q, 4 H, 2 CH_2, $^3J_{CH_2,CH_3} = 7.15$); 7.43 (q, 2 H, 2 CH, $^4J_{CH,CF_3} = 1.65$)	15.4 (br.s, 2 CF_3)
	E,*Z*	1.35 and 1.36 (both t, 6 H, 2 $CH_3(E + Z)$, $^3J_{CH_3,CH_2} = 7.15$); 4.32 (q, 2 H, $CH_2(Z)$, $^3J_{CH_2,CH_3} = 7.15$); 4.34 (q, 2 H, $CH_2(E)$, $^3J_{CH_2,CH_3} = 7.15$); 7.48 (br.q, 1 H, CH(*E*), $^4J_{CH,CF_3} = 1.65$); 7.80 (br.s, 1 H, CH(*Z*))	15.1 (br.s, $CF_3(E)$), 18.7 (s, $CF_3(Z)$)
	Z,*Z*	1.35 (t, 6 H, 2 CH_3, $^3J_{CH_3,CH_2} = 7.15$); 4.32 (q, 4 H, 2 CH_2, $^3J_{CH_2,CH_3} = 7.15$); 7.82 (br.s, 2 H, 2 CH)	18.4 (s, 2 CF_3)
3b[k,l]	*E*,*E*	8.60 (br.q, 2 H, 2 CH, $^4J_{CH,CF_3} = 1.59$)	−43.8 (br.s, 4 F, 2 CF_2); −3.81 (s, 6 F, 2 $C\underline{F}_3CF_2$); 18.3 (br.s, 6 F, 2 $CF_3C=$)
	E,*Z*	8.75 and 8.82 (both br.s, 1 H each, 2 CH(*E* + *Z*))	−44.1 (br.q, 2 F, $CF_2(E)$, $^9J_{CF_2,CF_3C=(Z)} = 7.8$); −38.3 (br.m, 2 F, $CF_2(Z)$); −3.75 (s, 3 F, $C\underline{F}_3CF_2(E)$); −3.71 (s, 3 F, $C\underline{F}_3CF_2(Z)$); 17.9 (br.s, 3 F, $CF_3C=(E)$); 19.26 (br.t, 3 F, $CF_3C=(Z)$, $^9J_{CF_3,CF_2(E)} = 7.8$)
	Z,*Z*	8.92 (br.s, 2 H, 2 CH)	−38.4 (br.s, 4 F, 2 CF_2); −3.71 (s, 6 F, 2 $C\underline{F}_3CF_2$); 19.30 (br.s, 6 F, 2 $CF_3C=$)
3c[c,m]	*E*,*E*	7.48 (br.q, 2 H, 2 CH, $^4J_{CH,CF_3} \approx 1.7$)	−48.79 (br.m, 4 F, 2 $CF_3C\underline{F}_2$); −33.03 (br.s, 4 F, 2 $CF_2C=$); −3.07 (t, 6 F, 2 $C\underline{F}_3CF_2$, $^4J_{CF_3,CF_2C=} = 11.0$); 17.13 (br.m, 6 F, 2 $CF_3C=$)
	E,*Z*	7.22 (br.s, 1 H, CH(*Z*)); 7.51 (br.q, 1 H, 2 CH(*E*), $^4J_{CH,CF_3} \approx 1.5$)	−48.66 (br.m, 2 F, $CF_3C\underline{F}_2(E)$); −47.9 (m, 2 F, $CF_3C\underline{F}_2(Z)$); −32.86 (m, 2 F, $CF_2C=(E)$); −30.9 (m, 2 F, $CF_2C=(Z)$); −3.01 and −2.76 (both t, both 3 F each, $C\underline{F}_3CF_2(E + Z)$, both $^4J_{CF_3,CF_2C=} = 10.4$); 16.99 (br.tt, 3 F, $CF_3C=(E)$, $^4J_{CF_3,CF_2C=} = 8.8$, $^5J_{CF_3,CF_2} = 6.1$); ~19.35 (br.m, 3 F, $CF_3C=(Z)$)

(*to be continued*)

Table 2 (*continued*)

Compound	Isomer	δ (*J*/Hz)	
		^{1}H	^{19}F
	Z,*Z*	7.25 (br.s, 2 H, 2 CH)	−47.9 (m, 4 F, 2 $CF_3C\underline{F}_2$); −30.9 (m, 4 F, 2 CF_2C=); −2.74 (t, 6 F, 2 $C\underline{F}_3CF_2$, $^4J_{CF_3,CF_2C=} = 10.4$); 19.41 (tt, 6 F, 2 CF_3C=, $^4J_{CF_3,CF_2C=} = {}^5J_{CF_3,CF_2} = 8.9$)
5[c,n]	**5A**	6.32 (br.s, 2 H, 2 CH)	−40.70 (dqm, 2 F, 2 $C\underline{F}_AF_B$, $^2J_{F(A),F(B)} = 287.9$, $^5J_{F(A),CF_3C=} = 14.2$) and −41.24 (d.q, 2 F, 2 $CF_A\underline{F}_B$, $^2J_{F(B),F(A)} = 287.9$, $^5J_{F(B),CF_3C=} = 19.8$); −5.15 (br.s, 6 F, 2 $C\underline{F}_3CF_2$); 20.9 (br.dd, 6 F, 2 CF_3C=, $^5J_{CF_3,F(A)} \approx {}^5J_{CF3,F(B)} \approx 17.9$)
5[c,n]	**5B**	6.32 (br.s, 1 H, CH); 7.69 (br.s, 1 H, CH´)	−45.08 (dq, 1 F, $C\underline{F}'_AF'_B$, $^2J_{F'(A),F'(B)} = 294.0$, $^5J_{F'(A),CF'_3C=} = 10.2$) and −47.12 (d.q, 1 F, $CF'_A\underline{F}'_B$, $^2J_{F'(B),F'(A)} = 294.0$, $^5J_{F'(B),CF'_3C=} = 16.4$); −38.49 (d.q, 1 F, $C\underline{F}_AF_B$, $^2J_{F(A),F(B)} = 289.4$, $^5J_{F(A),CF_3C=} =$ = 16.4) and −40.40 (d.q, 1 F, $CF_A\underline{F}_B$, $^2J_{F(B),F(A)} = 289.4$, $^5J_{F(B),CF_3C=} = 18.1$); −4.95 (br.s, 3 F, $C\underline{F}_3CF_2$); −1.57 (s, 3 F, $C\underline{F}'_3CF'_2$); 16.7 (br.ddm, 3 F, CF'_3C=, $^5J_{CF'_3,F'(B)} \approx 16$, $^5J_{CF'_3,F'(A)} \approx 10$); 21.3 (dddq, 3 F, CF_3C=, $^5J_{CF_3,F(B)} = 18.1$, $^5J_{CF_3,F(A)} = 16.4$, $^4J_{CF_3,CH} \approx$ ≈ $^6J_{CF_3,CF_3CF_2} \approx 2.6$)
6c[a]		—	−51.0 (m, 2 F, $CF_3C\underline{F}_2$); −27.2 (qq, 2 F, CF_2C=, $^4J_{CF_2,CF_3CF_2} = 10.5$, $^4J_{CF_2,CF_3C=} = 7.5$); −5.3 (t, 3 F, $C\underline{F}_3CF_2$, $^4J_{CF_3,CF_2C=} = 10.5$); 23.3 (tt, 3 F, CF_3C=, $^4J_{CF_3,CF_2C=} = 7.5$, $^5J_{CF_3,CF_2} = 4.5$)
7[o]		5.89 (qd, 1 H, CH, $^3J_{CH,CF_3} = 7.15$, $^3J_{CH,COF} = 2.75$)	−45.23 and −45.81 (both br.d, 1 F each, CF_AF_B, $^2J_{F(A),F(B)} = 301.4$); −5.8 (s, 3 F, $C\underline{F}_3CF_2$); 11.9 (m, 3 F, CF_3CH); 123.3 (br.q, 1 F, COF, $^4J_{COF,CF_3CH} = 9.54$)
8[a,p]	Ketone	5.34 (q, 1 H, $CHCF_3$, $^3J_{CH,CF_3} = 8.25$); 10.06 (br.m, 1 H, CHO)	−46.67 and −47.19 (both br.d, 1 F each, CF_AF_B, $^2J_{F(A),F(B)} = 296.6$); −5.3 (s, 3 F, $C\underline{F}_3CF_2$); 13.6 (br.d, 3 F, CF_3CH, $^3J_{CF_3,CH} = 8.59$)
	Enol	8.77[q] (br.s, 1 H, CH); 14.79[r] (br.s, 1 H, OH)	−43.4 (q, 2 F, CF_2, $^5J_{CF_2,CF_3C=} = 17.8$); −5.1 (s, 3 F, $C\underline{F}_3CF_2$); 18.4 (t, 3 F, CF_3C=, $^5J_{CF_3,CF_2} = 18.1$)
10[a,s]	*E*	~1.8[t] (Me_3C)	−43.4 (q.d, 2 F, CF_2, $^5J_{CF_2,CF_3C=} = 16.0$, $^3J_{CF_2,CF} =$ = 10.3); −36.3 (tqq, 1 F, CF, $^3J_{CF,CF_2} \approx {}^4J_{CF,CF_3C=} \approx$ ≈ 10, $^4J_{CF,CF_3CF_2} = 7.6$); ~−7.7[t] ($C\underline{F}_3CF_2$); 19.8 (tdq, 3 F, CF_3C=, $^5J_{CF_3,CF_2} = 15.6$, $^4J_{CF_3,CF} = 10.2$, $^6J_{CF_3,CF_3CF_2} = 3.0$)

[a] Without a solvent.
[b] *E*/*Z* = 8.1/1.0.
[c] In $CDCl_3$.
[d] *E*/*Z* = 1/1.
[e] In the reaction mixture, 8.23 (br.q, $^4J_{CH,CF3C=} \approx 1.5$ Hz).
[f] In C_6D_6, −37.4 (q, $^5J_{CF2,CF3C=} = 3.37$ Hz).
[g] In C_6D_6, 18.1 (br.t, $^5J_{CF3,CF2} = 3.43$ Hz).
[h] In CD_2Cl_2.
[i] *E*/*Z* = 1.7/1.0.
[j] *E*,*E*/*E*,*Z*/*Z*,*Z* = 10.3/6.7/1.0.
[k] In acetone-d_6.
[l] *E*,*E*/*E*,*Z*/*Z*,*Z* = 1/6/6.
[m] *E*,*E*/*E*,*Z*/*Z*,*Z* = 3/4/1.
[n] **5A**/**5B** = 13/1.
[o] In ketene **6b**.
[p] Ketone/enol = 1/10.
[q] In the reaction mixture, 8.81 (br.d, $^3J_{CH,OH} = 12.65$ Hz).
[r] In the reaction mixture, 14.92 (br.d, $^3J_{OH,CH} = 12.65$ Hz).
[s] *E*/*Z* = 1/22.
[t] The signal is masked by the corresponding signal for the *Z*-isomer of ester **10**.

Table 3. Mass spectra of the compounds obtained

Compound	Isomer	m/z (I_{rel} (%))
1a[a]	*E*	257 $[M + H]^+$ (1.8); 241 $[M - Me]^+$ (13.7); 213 $[C_6H_8F_3O_3Si]^+$ (37.0); 211 $[M - OEt]^+$ (15.9); 193 $[C_6H_7F_2O_3Si]^+$ (100); 149 $[C_5H_7F_2OSi]^+$ (24.9); 119 $[C_4HF_2O_2]^+$ (27.4); 91 $[C_3HF_2O]^+$ (14.0); 77 $[Me_2SiF]^+$ (26.1); 73 $[Me_3Si]^+$ (13.2)[b]
	Z	257 $[M + H]^+$ (3.3); 241 $[M - Me]^+$ (17.1); 213 $[C_6H_8F_3O_3Si]^+$ (40.8); 211 $[M - OEt]^+$ (9.9); 193 $[C_6H_7F_2O_3Si]^+$ (100); 149 $[C_5H_7F_2OSi]^+$ (16.0); 119 $[C_4HF_2O_2]^+$ (27.7); 91 $[C_3HF_2O]^+$ (26.2); 77 $[Me_2SiF]^+$ (21.1); 73 $[Me_3Si]^+$ (10.9); 69 $[CF_3]^+$ (11.6)[b]
1b[c,d]	*E*+*Z*	315 $[M - Me]^+$ (9.8); 311 $[M - F]^+$ (1.7); 219 $[C_6HF_6O_2]^+$ (17.8); 211 $[M - C_2F_5]^+$ (41.9); 119 $[C_4HF_2O_2$ and/or $C_2F_5]^+$ (100); 91 $[C_3HF_2O]^+$ (50.4); 77 $[Me_2SiF]^+$ (24.2); 75 $[C_3HF_2]^+$ (15.4); 73 $[Me_3Si]^+$ (39.6); 69 $[CF_3]^+$ (11.2)[b]
1c[e]	*E*	352 $[M]^+$ (2.7); 337 $[M - Me]^+$ (22.8); 333 $[M - F]^+$ (2.8); 241 $[C_6HF_8O]^+$ (28.0); 233 $[M - C_2F_5]^+$ (5.2); 213 $[C_5HF_8]^+$ (17.8); 193 $[C_5F_7]^+$ (42.9); 77 $[Me_2SiF]^+$ (100); 73 $[Me_3Si]^+$ (80.6)[b]
	Z	352 $[M]^+$ (0.9); 337 $[M - Me]^+$ (23.9); 333 $[M - F]^+$ (1.0); 241 $[C_6HF_8O]^+$ (13.4); 233 $[M - C_2F_5]^+$ (5.2); 213 $[C_5HF_8]^+$ (11.6); 193 $[C_5F_7]^+$ (30.0); 77 $[Me_2SiF]^+$ (100); 73 $[Me_3Si]^+$ (76.3)[b]
3a[f]	*E,E*	351 $[M + H]^+$ (1.3); 350 $[M]^+$ (0.7); 305 $[M - OEt]^+$ (5.4); 278 $[C_9H_8F_6O_3]^+$ (9.1); 250 $[C_7H_4F_6O_3]^+$ (14.9); 248 $[C_7H_2F_6O_3]^+$ (13.5); 184 $[C_6H_7F_3O_3]^+$ (15.0); 167 $[C_6H_6F_3O_2]^+$ (100); 139 $[C_4H_2F_3O_2]^+$ (63.9); 119 $[C_4HF_2O_2]^+$ (39.3); 91 $[C_3HF_2O]^+$ (62.6)
	E,Z	351 $[M + H]^+$ (2.3); 350 $[M]^+$ (1.6); 305 $[M - OEt]^+$ (3.5); 302 $[M - C_2H_5F]^+$ (4.4); 278 $[C_9H_8F_6O_3]^+$ (12.1); 250 $[C_7H_4F_6O_3]^+$ (23.5); 248 $[C_7H_2F_6O_3]^+$ (30.5); 233 $[C_7H_3F_6O_2]^+$ (51.8); 213 $[C_7H_2F_5O_2]^+$ (39.5); 167 $[C_6H_6F_3O_2]^+$ (100); 156 $[C_4H_3F_3O_3]^+$ (44.4); 139 $[C_4H_2F_3O_2]^+$ (84.7); 119 $[C_4HF_2O_2]^+$ (60.5); 91 $[C_3HF_2O]^+$ (90.0)
	Z,Z	351 $[M + H]^+$ (2.9); 350 $[M]^+$ (1.6); 305 $[M - OEt]^+$ (43.1); 250 $[C_7H_4F_6O_3]^+$ (36.3); 248 $[C_7H_2F_6O_3]^+$ (34.2); 233 $[C_7H_3F_6O_2]^+$ (51.6); 213 $[C_7H_2F_5O_2]^+$ (100); 191 $[C_8H_6F_3O_2]^+$ (53.0); 167 $[C_6H_6F_3O_2]^+$ (85.7); 156 $[C_4H_3F_3O_3]^+$ (57.5); 139 $[C_4H_2F_3O_2]^+$ (79.0); 119 $[C_4HF_2O_2]^+$ (69.9); 91 $[C_3HF_2O]^+$ (74.8)
3b[g,h]	*E,E*/*E,Z* /*Z,Z*	499 $[M + H]^+$ (3.5); 498 $[M]^+$ (0.4); 479 $[M - F]^+$ (2.2); 379 $[M - C_2F_5]^+$ (60.2); 351 $[M - C_2F_5CO]^+$ (46.8); 219 $[C_6HF_6O_2]^+$ (40.6); 209 $[C_5F_7O]^+$ (44.4); 191 $[C_5HF_6O]^+$ (62.3); 141 $[C_4HF_4O]^+$ (100); 123 $[C_4H_2F_3O]^+$ (38.4); 119 $[C_2F_5$ and/or $C_4HF_2O_2]^+$ (31.8); 97 $[C_2F_3O]^+$ (36.3); 91 $[C_3HF_2O]^+$ (34.5); 75 $[C_3HF_2]^+$ (42.2); 69 $[CF_3]^+$ (50.7)
3c[i]	*E,E*	542 $[M]^+$ (0.1); 523 $[M - F]^+$ (13.3); 423 $[M - C_2F_5]^+$ (21.0); 263 $[C_6HF_{10}]^+$ (67.1); 243 $[C_6F_9]^+$ (9.9); 163 $[C_4HF_6]^+$ (100); 75 $[C_3HF_2]^+$ (6.2); 69 $[CF_3]^+$ (8.0)
	E,Z	523 $[M - F]^+$ (18.5); 423 $[M - C_2F_5]^+$ (20.5); 263 $[C_6HF_{10}]^+$ (65.5); 243 $[C_6F_9]^+$ (8.4); 163 $[C_4HF_6]^+$ (100); 75 $[C_3HF_2]^+$ (7.3); 69 $[CF_3]^+$ (7.1)
	Z,Z	523 $[M - F]^+$ (14.7); 423 $[M - C_2F_5]^+$ (19.6); 263 $[C_6HF_{10}]^+$ (63.9); 243 $[C_6F_9]^+$ (7.3); 163 $[C_4HF_6]^+$ (100); 75 $[C_3HF_2]^+$ (7.5); 69 $[CF_3]^+$ (6.5)
5[j]	**5A**	499 $[M + H]^+$ (0.8); 479 $[M - F]^+$ (40.6); 379 $[M - C_2F_5]^+$ (13.2); 351 $[M - C_2F_5CO]^+$ (21.7); 223 $[C_6H_2F_7O]^+$ (21.0); 213 $[C_5HF_8]^+$ (55.0); 123 $[C_4H_2F_3O]^+$ (100); 119 $[C_2F_5$ and/or $C_4HF_2O_2]^+$ (29.5)
	5B	499 $[M + H]^+$ (0.2); 479 $[M - F]^+$ (30.1); 389 $[C_9H_2F_{13}O_2]^+$ (8.6); 379 $[M - C_2F_5]^+$ (15.2); 351 $[M - C_2F_5CO]^+$ (29.6); 223 $[C_6H_2F_7O]^+$ (28.1); 213 $[C_5HF_8]^+$ (82.9); 123 $[C_4H_2F_3O]^+$ (100); 119 $[C_2F_5$ and/or $C_4HF_2O_2]^+$ (58.1)
6c		278 $[M]^+$ (12.5); 259 $[M - F]^+$ (59.0); 209 $[M - CF_3]^+$ (25.5); 181 $[M - CF_3 - CO]^+$ (9.0); 159 $[M - C_2F_5]^+$ (69.0); 112 $[C_3F_4]^+$ (12.5); 93 $[C_3F_3]^+$ (30.0); 69 $[CF_3]^+$ (100)
8[k]		259 $[M + H]^+$ (0.6); 257 $[M - H]^+$ (0.3); 239 $[M - F]^+$ (13.3); 219 $[M - HF_2]^+$ (5.0); 210 $[C_5HF_7O]^+$ (7.2); 193 $[C_5F_7]^+$ (9.2); 139 $[M - C_2F_5]^+$ (24.7); 119 $[C_2F_5$ and/or $C_4HF_2O_2]^+$ (34.2); 91 $[C_3HF_2O]^+$ (100); 71 $[C_3FO]^+$ (26.0); 69 $[CF_3]^+$ (18.6)

[a] *E*/*Z* = 8.1/1.0.

[b] For Si-containing ions, data are given only for the ^{28}Si isotope.

[c] *E*/*Z* = 1/1.

[d] The *E*/*Z*-isomers cannot be separated by chromatography.

[e] *E*/*Z* = 1.7/1.0.

[f] *E,E*/*E,Z*/*Z,Z* = 10.3/6.7/1.0.

[g] *E,E*/*E,Z*/*Z,Z* = 1/6/6.

[h] Direct inlet probe.

[i] *E,E*/*E,Z*/*Z,Z* = 3/4/1.

[j] **5A**/**5B** = 13/1.

[k] Ketone/enol = 1/10.

at ~20 °C to tetrafluoroethylamine **2** (0.4546 g, 3.133 mmol). The reaction mixture was kept in a sealed glass tube for a day. According to NMR data, the final reaction mixture contained divinyl ether **3a** (*E,E*/*E,Z*/*Z,Z* = 10.1/6.4/1.0), *N*,*N*-dimethyldifluoroacetamide, Me_3SiF, the starting silyl ether **1a** (*E*/*Z* = 2.2/1.0) (1.0 : 0.99 : 1.9 : 0.42), and an insignificant amount of impurities. Divinyl ether **3a** was isolated by distillation. The yield of compound **3a** was 0.975 g (88.9%), colorless liquid solidifying into a white solid (≥95% purity, *E*,*E*/*E*,*Z*/*Z*,*Z* = = 10.3/6.7/1.0 (NMR)).

Bis[2-pentafluoropropionyl-2-(trifluoromethyl)vinyl] ether (3b) and 3,7-bis(pentafluoroethyl)-4,8-bis(trifluoromethyl)-2,6,9-trioxabicyclo[3.3.1]nona-3,7-diene (5). Silyl ether **1b** (*E*/*Z* = 1/1, 8.6548 g, 26.207 mmol) was added at <0 °C to tetrafluoroethylamine **2** (1.7808 g, 12.273 mmol). The reaction mixture was carefully warmed to room temperature and kept in a sealed glass tube for a day. According to NMR data, the final reaction mixture contained divinyl ether **3b** (*E*,*E*/*E*,*Z*/*Z*,*Z* = 1.0/5.5/5.0), *N*,*N*-dimethyldifluoroacetamide, Me_3SiF, the starting silyl ether **1b** (*E*/*Z* = 1/1), bicyclic compound **5** (1.0 : 1.1 : 1.9 : 0.1 : 0.05), and small amounts of insignificant impurities. Trimethylsilyl fluoride (≥96% purity, 2.28 g, ~100% (NMR)) and a fraction (1.14 g) with b.p. 45—49 °C (8 Torr) were collected in a trap (–78 °C) upon heating the reaction mixture *in vacuo* (8 Torr) to ≤75 °C. The collected fraction contained *N*,*N*-dimethyldifluoroacetamide and bicyclic compound **5** (1.0 : 0.06) (NMR). Distillation of the residue *in vacuo* (1 Torr) gave bicyclic compound **5** (3.16 g, **5A**/**5B** = 13/1, ≥77% purity) as a colorless, moderately viscous liquid with b.p. 45—85 °C (1 Torr) and crude divinyl ether **3b** (3.03 g, ~90% purity) as a slightly yellowish viscous, fast-solidifying liquid with b.p. 85—87 °C (1 Torr). Main impurities included silyl ether **1b**, *N*,*N*-dimethyldifluoroacetamide, and divinyl ether **3b** for compound **5** and bicyclic compound **5** and *N*,*N*-dimethyldifluoroacetamide for compound **3b** (NMR). Crude ether **3b** was washed twice with hexane and dried *in vacuo* (1 Torr). The yield of compound **3b** was 2.39 g (39.1%), white solid (≥99% purity, *E*,*E*/*E*,*Z*/*Z*,*Z* = 1/6/6 (NMR)).

Bis[2-heptafluoropropyl-2-(trifluoromethyl)vinyl] ether (3c). Silyl ether **1c** (*E*/*Z* = 1.7/1.0, 16.22 g, 46.05 mmol) was added at room temperature to tetrafluoroethylamine **2** (3.06 g, 21.09 mmol). The reaction mixture was kept in a sealed glass tube at 20 °C for 79 h, at 40 °C for 5 h, and at 50—60 °C for 7 h. According to NMR data, the final reaction mixture contained divinyl ether **3c** (*E*,*E*/*E*,*Z*/*Z*,*Z* = 3/4/1), *N*,*N*-dimethyldifluoroacetamide, Me_3SiF (1.0 : 0.75 : 2.5), a number of insignificant impurities, and no silyl ether **1c**. Fractional distillation gave ~96% divinyl ether **3c** (9.08 g, 79.4%) with b.p. 38—39 °C (<1 Torr). The main impurity was *N*,*N*-dimethyldifluoroacetamide (3.5%). An ethereal solution of 96% divinyl ether **3c** was repeatedly washed with water, dried over $MgSO_4$, concentrated, and redistilled to give analytically pure ether **3c** (≥99% purity, *E*,*E*/*E*,*Z*/*Z*,*Z* = 3/4/1 (NMR)) as a colorless, moderately viscous liquid.

Synthesis of trimethylsilyl vinyl ethers 1a—c

2-Ethoxycarbonyl-3,3,3-trifluoropropenyloxy(trimethyl)silane (1a). A mixture of Me_3SiH (1.22 g, 16.5 mmol), ketene **6a** (2.60 g, 14.3 mmol), and a catalytic amount of $H_2PtCl_6 \cdot 6H_2O$ was stirred at –78 °C and then allowed to warm in air. After a strongly exothermic reaction was completed, the mixture was cooled to room temperature (35—40 min). Distillation gave silane **1a** (3.04 g, 83.1%) as a colorless, moderately viscous liquid (≥98% purity, *E*/*Z* = 8.1/1.0 (NMR)).

Trimethyl[3,3,3-trifluoro-2-(pentafluoropropionyl)propenyloxy]silane (1b) and 4,4,5,5,5-pentafluoro-3-oxo-2-trifluoromethylpentanal (8). Crude ketene **6b** (8.99 g) containing besides ketene **6b** (7.82 g, 30.5 mmol) acid fluoride **7** (1.05 g, 3.8 mmol) was added dropwise at ≤0 °C to a stirred mixture of Me_3SiH (3.18 g, 43.0 mmol) and a catalytic amount of $H_2PtCl_6 \cdot 6H_2O$. The addition rate was such as to ensure only very slight boiling of the reaction mixture (reflux condenser, –78 °C) and to maintain its temperature at ≤26 °C. Stirring was continued until the reaction mixture was cooled to room temperature (~1.5 h). Distillation *in vacuo* gave silane **1b** (9.42 g, 93.5% with respect to the ketene content in the initial mixture) as a colorless, moderately viscous liquid (≥99% purity, *E*/*Z* = 1/1 (NMR)). The low-boiling fraction collected in a trap (–78 °C) during the vacuum distillation was distilled twice to give oxo aldehyde **8** (0.41 g, 41.8% with respect to the acid flouride content in the initial mixture) as a colorless, mobile, volatile liquid (≥95% purity, ketone/enol = 1/10 (NMR)).

3,3,4,4,5,5,5-Heptafluoro-2-trifluoromethylpent-1-enyloxy-(trimethyl)silane (1c) was obtained from Me_3SiH (3.43 g, 46.2 mmol) and ketene **6c** (11.30 g, 40.6 mmol, ≥97% purity) as described for compound **1b**. Self-heating of the reaction mixture to ≤37 °C was observed; the total reaction time was 3 h. Distillation gave silane **1c** (12.73 g, 88.9%) as a colorless, moderately viscous liquid (97% purity, *E*/*Z* = 1.7/1.0 (NMR)).

Synthesis of trifluoromethylketenes 6a—c

Ethoxycarbonyl(trifluoromethyl)ketene (6a). Ketene **6a** was prepared according to a modified procedure.[5] A mixture of P_2O_5 (25.09 g, 176.8 mmol) and diethyl trifluoromethylmalonate (10.21 g, 44.75 mmol) was heated *in vacuo* (150 Torr) at 120—150 °C (bath temperature) for 1 h. A fraction with b.p. 64—69 °C (150 Torr) was collected in a cooled receiving flask (<0 °C). The yield of ketene **6a** was 3.17 g (38.9%) (≥98% purity (NMR)). Pure ketene **6a** dimerized by 20% at room temperature in a day.

Dimer of ketene **6a**. ^{1}H NMR (solvent-free), δ: 1.63 and 1.86 (both t, 3 H each, 2 CH_3, $^3J_{CH_3,CH_2}$ = 7.15 Hz); 4.70 and 5.10 (both q, 2 H each, 2 CH_2, $^3J_{CH_2,CH_3}$ = 7.15 Hz). ^{19}F NMR (solvent-free), δ: 10.7 (s, CF_3); 19.4 (s, CF_3) (*cf.* Ref. 6).

Pentafluoropropionyl(trifluoromethyl)ketene (6b) and 4,4,5,5,5-pentafluoro-3-oxo-2-trifluoromethylpentanoyl fluoride (7). Ketene **6b** was obtained according to a known procedure.[7] A freshly distilled mixture of 1,3-dimethoxyperfluoro-2-methylpent-1-ene and -pent-2-ene (90% purity, 15.02 g, 41.7 mmol) was added dropwise with slight heating and stirring to SbF_5 (0.75 g, 3.46 mmol). A fraction with b.p. ≤62 °C was collected. After the addition was completed, all products with b.p. ≤85 °C were removed. Redistillation over SbF_5 (~0.2 g, ~0.9 mmol) gave crude ketene **6b** (9.26 g) containing besides ketene **6b** (8.05 g, 75.4%) acid fluoride **7** (1.08 g, 9.4%) (NMR), b.p. 81—83 °C.

Perfluoromethyl(propyl)ketene (6c). A mixture of P_2O_5 (43.03 g, 303.1 mmol) and *tert*-butyl ester **9** (18.23 g, 51.77 mmol) was heated at 100—150 °C (bath temperature) for 1.5 h. A fraction with b.p. 49—55 °C was collected in a cooled receiving flask (<0 °C). The yield of ketene **6c** was 11.51 g (80.0%), a colorless mobile volatile liquid fuming in air, ≥97% purity. Impurities (2—3%) included alkanes C_5H_{12}—C_9H_{20} and alkenes (and/or cycloalkanes) C_5H_{10}—C_8H_{16} (^{1}H NMR, GLC-MS). Analytically pure ketene **6c** was obtained by separation of the lower liquid phase at –100 °C. Ketene **6c** is stable under moisture-free conditions and can be stored in glass containers.

***tert*-Butyl perfluoro-2-hydro-2-methylpentanoate (9).**[8] A mixture of Bu^{t}OH (31.1 g, 0.420 mol) and perfluoro-2-methylpent-2-ene (92% purity, 32.9 g, 0.101 mol) was refluxed with stirring in NEt_3 (22.3 g, 0.220 mol) for 7 h. The reaction mixture was cooled and poured into ice water. The organic phase was separated, washed with water, dried over $CaCl_2$, and distilled *in vacuo*. Fractions with b.p. 47—56 °C (30 Torr) and 44—48 °C (15 Torr) were collected. The former fraction (19.20 g) was a 1.0 : 4.65 mixture of esters **9** and **10** ($E/Z = 1/22$), ≥97% purity. The latter fraction (1.65 g) was a 1.0 : 0.14 mixture of esters **9** and **10** ($E/Z = 1/3.7$), ≥96% purity (NMR, GLC). The total yield was 59.4%. The parameters of the ^{1}H and ^{19}F NMR spectra of ester **9** and the *Z*-isomer of ester **10** agree with the literature data.[8]

A mixture of *tert*-butyl esters **9** and **10** (1.0 : 4.65, ≥97% purity, 19.20 g, 0.056 mol) was added at <0 °C to a solution of HF (~14 mL, 14.36 g, 0.718 mol) and NEt_3 (~30 mL, 21.65 g, 0.214 mol) in MeCN (60 mL). The reaction mixture was stirred at 30—35 °C for 6 h. On cooling (<0 °C), HF (~1 mL, 0.91 g, 0.045 mol) was added and stirring was continued at 30—35 °C for 5 h. Then the mixture was cooled and poured into water. The organic phase was separated, washed with water, and dried over $CaCl_2$. Distillation gave ester **9** (17.76 g, 90.1%), b.p. 45.5—47 °C (15 Torr), ≥99% purity (NMR, GLC).

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