Tris(pentafluorophenyl)silyl Triflate: Synthesis and Silylation of Carbonyl Compounds

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Tris(pentafluorophenyl)silyl triflate (**1**) was prepared by protodesilylation of phenyl-, allyl-, and isopropenyloxytris(pentafluorophenyl)silyl derivatives and characterized by X-ray crystallography. This reagent was employed for the silylation of carbonyl compounds. Aldehydes and ketones afforded the corresponding silyl enol ethers in good yields, while silylation of esters and lactones was dependent on the reaction conditions and on the substrate. A mechanism accounting for the observed phenomena is proposed. Studies of the relative reactivities of **1** and trimethylsilyl triflate are also presented.

Introduction

Silylating agents of general formula R_3SiX have found widespread use in synthetic chemistry for the modification of functional groups[1] and as Lewis-acidic mediators in carbon−carbon bond-forming reactions.[2] The primary factor determining the strength of a silylating species is the nature of the leaving group X as this affects the electrophilicity of the silicon atom. Although many compounds with different leaving groups have been described,[3] derivatives of triflic acid, such as silyl triflates, have turned out to be the most popular reagents for a wide variety of applications.[2,4] The reactivity of silyl triflates can be further controlled by varying the steric volume of the alkyl substituents. At the same time it would be interesting to consider carbon-centered groups which, besides being simple spectators, could also exert an electronic effect. Governed by this idea we decided to examine a silylating reagent bearing three pentafluorophenyl fragments at the silicon atom.[5]

Recently, Frohn has attempted to prepare tris(pentafluorophenyl)silyl fluorosulfonate (TPFS-OSO_2F), $(C_6F_5)_3SiOSO_2F$; he found this compound to be unstable as it decomposes into the corresponding fluorosilane $(C_6F_5)_3SiF$.[6] This instability is probably associated with the facile extrusion of sulfur trioxide driven by the silicon−fluorine bond formation. Nevertheless, one can expect that the analogous TPFS triflate, $(C_6F_5)_3SiOSO_2CF_3$ (**1**), will be more stable since it has no obvious degradation pathway.

The use of triflate **1** as a silylating reagent will allow the introduction of the TPFS fragment into a substrate. We have previously used TPFS chloride for the silylation of ketones.[7] This reaction was performed in refluxing dichloroethane and afforded TPFS enol ethers in moderate yields. The possibility of using TPFS enol ethers in aldol reactions[7] further justifies work to improve the procedure for this synthesis. The application of triflate **1** for the silylation of carbonyl compounds is expected to solve the latter problem, since in silylation reactions silyl triflates usually give better results than the corresponding chlorosilanes.[4a,4b]

In this paper we report the synthesis and characterization of silyl triflate **1** and demonstrate its efficiency in the silylation of aldehydes, ketones, and esters.

Results and Discussion

Synthesis of TPFS Triflate

The interaction of organosilanes with triflic acid is the most convenient way to form silyl triflates.[4a,4b] Based on extensive literature data, the propensity of a substituent to undergo protodesilylation should increase in the following order:[4a,4b,8] vinyl < phenyl < allyl < isopropenyloxy. We investigated the protodesilylation of several TPFS derivatives (Scheme 1).

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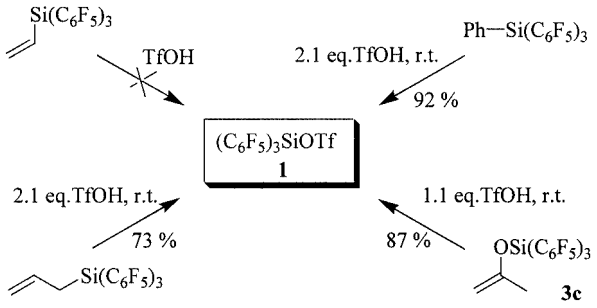


Scheme 1

A very slow reaction was observed between vinylsilane and TfOH, leading to less than 10% conversion in 24 hours. It is worthy to note that protodesilylation of triethylvinylsilane occurs instantaneously under the same conditions. Such a significant difference between TPFS and trialkylsilyl systems is apparently associated with the strong electron-withdrawing effect of the pentafluorophenyl groups.

The reaction of phenyl-TPFS with one equivalent of acid proceeded at room temperature in chlorinated solvents. However, as the conversion increased the rate of the process decreased dramatically, furnishing samples of triflate **1** that were always contaminated with the starting phenylsilane. We conjectured that TfOH is deactivated by complexation with the triflate **1**, but we could not observe any complex formation by ^{1}H and ^{19}F NMR spectroscopy. Complete conversion was achieved by using either 2.1 equivalents of TfOH at room temperature or with 1.6 equivalents and mixing the reagents at 60 °C in dichloroethane. In both cases the yield of TPFS triflate **1**, after purification by recrystallization from dichloroethane, was between 83 and 92%, although the latter procedure, which requires less acid, is more practical for larger scale syntheses.

Upon interaction of allyl-TPFS with one equivalent of TfOH in $CDCl_3$ the starting silane was consumed quite rapidly to afford moderate quantities of triflate **1** along with small amounts of isopropyl triflate and other unidentified species. The same reaction with 2.1 equivalents of TfOH gave a stoichiometric mixture of triflate **1** and isopropyl triflate, as judged by NMR spectroscopy, while a preparative run performed in dichloromethane provided triflate **1** in 73% yield.

Silyloxypropene (**3c**), which is believed to be the most active towards acid, reacts instantaneously with 1.1 equivalents of TfOH to afford only triflate **1** and acetone, according to NMR spectroscopy. The preparative experiment gave a yield of 87% of the desired triflate.

Thus, triflate **1** can be accessed from several TPFS precursors. Although the silyl enol ether gives shorter reaction times, the need to prepare it[7] renders this approach somewhat tedious. From a practical point of view, protodesilylation of the phenylsilane is recommended. Taking into account that the phenylsilane itself is easily synthesized from inexpensive bromopentafluorobenzene and phenyltrichlorosilane,[6] triflate **1** may be considered as readily available.

X-ray Structure of 1

The molecular structure of TPFS triflate was investigated by X-ray diffraction analysis (Figure 1). Analysis of the geometry of **1** showed that the silicon atom has an almost undistorted tetrahedral configuration. Of particular note is the length of the Si−O bond (1.663 Å), which is considerably shorter than that in analogous triphenylsilyl triflate (1.742 Å), and is the shortest Si−O distance known amongst other published silyl triflates.[9] A decrease of the Si−O bond length was also observed for the structure of the TPFS enol ether **3c**,[7] and seems to be a general phenomenon for TPFS derivatives. It may be due to the influence of the electron-withdrawing pentafluorophenyl groups.

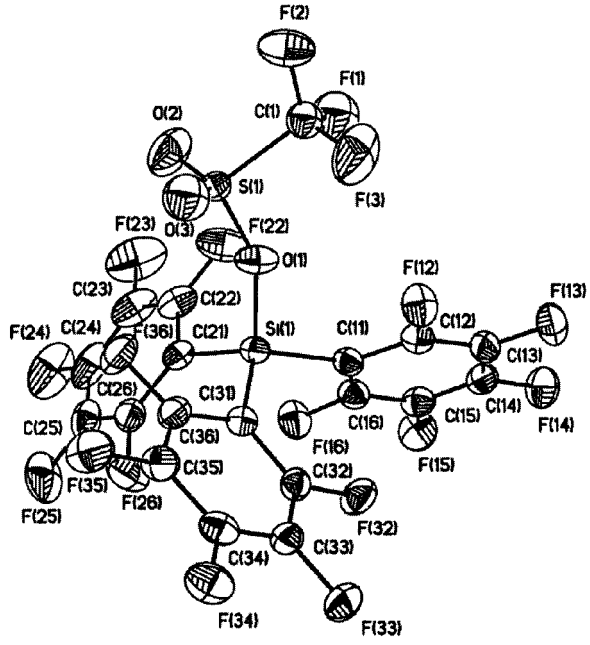


Figure 1. The molecular structure of TPFS triflate **1**; atoms are shown as thermal ellipsoids at 50% probability; selected bond lengths (Å): Si(1)−O(1) 1.663(2), Si−C (average) 1.858(3), S−O(1) (average) 1.510(2), S−O 1.433(3); bond angles (°) Si−O−S (average) 149.5, O−Si−C (average) 106.8, C−Si−C 112.0

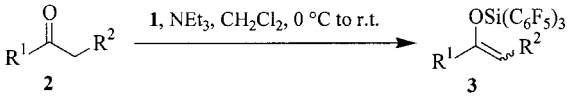
Silylation of Aldehydes and Ketones

Various carbonyl compounds can be silylated by triflate **1** in the presence of triethylamine in dichloromethane [Equation (1), Table 1]. The silylation is usually complete within 30 minutes at room temperature, although sterically hindered substrates may require slightly longer reaction times (entries 5 and 11)

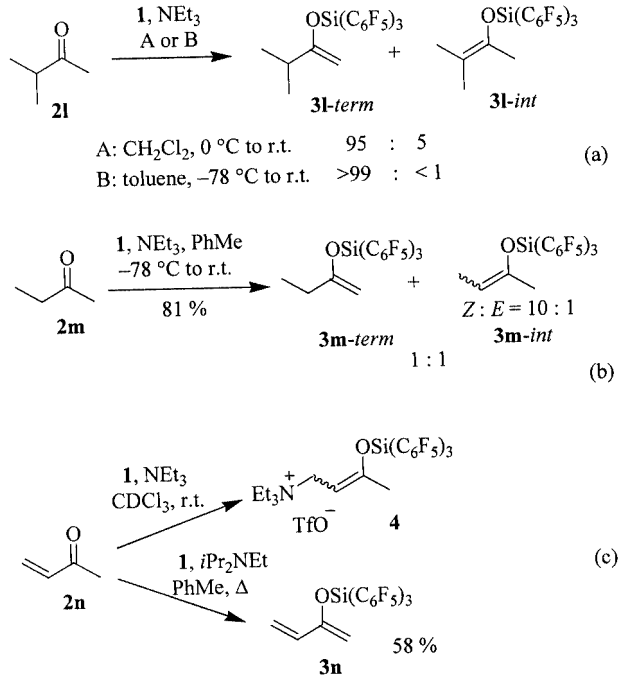
Table 1. Synthesis of TPFS enol ethers **3**

Entry	**2**	R^1	R^2	Time (h)	**3**	Yield of **3** (%)[a]	*E*:*Z*
1	**2a**	H	H	0.5	**3a**	72	
2	**2b**	H	Me	0.5	**3b**	82	1:10[b]
3	**2c**	Me	H	0.5	**3c**	92	
4	**2d**	Ph	H	0.5	**3d**	88	
5	**2e**	*t*Bu	H	1	**3e**	93	
6	**2f**[c]	cC_3H_5	H	0.5	**3f**	92	
7	**2g**	Et	Me	0.5	**3g**	87	1:3.3[d]
8	**2h**	Ph	Me	0.5	**3h**	89	1:8.5[d]
9	**2i**	$-(CH_2)_4-$		0.5	**3i**	94	
10	**2j**	$-(CH_2)_5-$		0.5	**3j**	95	
11	**2k**[e]	(+)-camphor		3	**3k**	86	

[a] Yield of distilled product. [b] Configuration was determined by comparison of H-H coupling constants in the HC=CH fragment. [c] Methyl cyclopropyl ketone was used. [d] Configuration was determined from the NOE spectrum. [e] (+)-Camphor was used.



(1)



Scheme 2

Since triflate **1** is moderately soluble and products **3** are usually well soluble in dichloromethane, the progress of the reaction can be followed by disappearance of the silylating agent. However, enol ether **3c** has limited solubility in dichloromethane and may precipitate on the surface of the triflate **1**, thereby preventing further dissolution of the latter and blocking the reaction. Fortunately, this problem can easily be overcome by using slightly more solvent.[10]

The silylation of substrates **2b,g,h**, all of which possess an ethyl group at the carbonyl carbon, afforded preferentially *Z*-isomers. Such a phenomenon has been observed for silylations with other silylating reagents and may originate from the greater thermodynamic stability of *Z*-isomers.[11] This stabilizing effect presumably comes from the interaction between the σ(C−H) and σ*(C−O) orbitals across the double bond, which are anti-oriented only in *Z*-configured compounds.

The silylation of 3-methylbutan-2-one (**2l**) under standard conditions afforded the silyl enol ether **3l**-*term* along with small amounts of the internal regioisomer (a in Scheme 2). Lowering the temperature, changing the solvent from dichloromethane to toluene, and performing the addition of a solution of triflate **1** to the mixture of ketone and triethylamine allowed us to isolate the terminal isomer **3l**-term as the only detectable product. Disappointingly, the silylation of butan-2-one (**2m**) under different conditions always gave approximately a 1:1 mixture of regioisomers (b in Scheme 2).

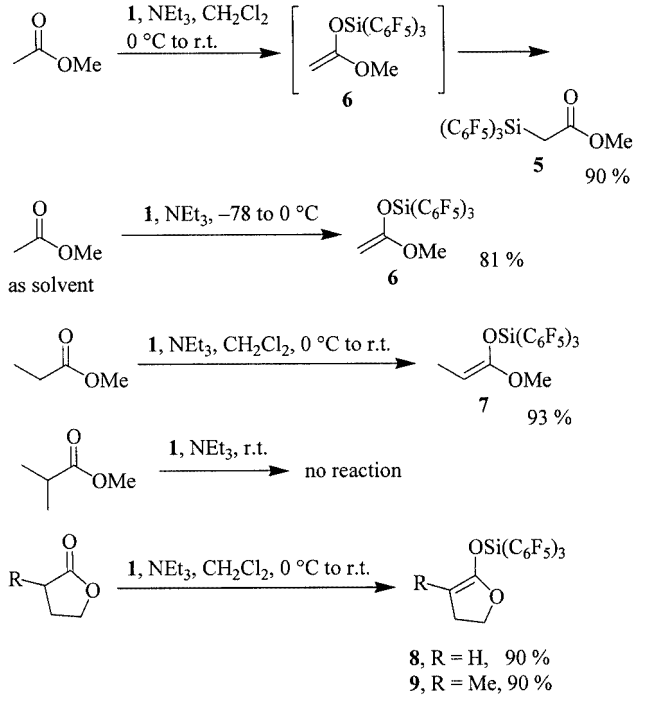
Attempts to silylate methyl vinyl ketone with triflate **1** and triethylamine at room temperature failed. According to NMR spectroscopic data, upon mixing the reagents the formation of ammonium salt **4** occurred rapidly instead of methyl group silylation[12] (c in Scheme 2). Nevertheless, silyl enol ether **3n** was obtained on silylation of **2n** using Hunig's base in refluxing toluene. Obviously, the steric hindrance of the base and high temperature favor the dissociation of the ammonium salt back to the ketone and the triflate **1**.

The use of triflate **1** for the silylation of carbonyl compounds offers significant advantages over TPFS chloride in terms of reaction times, temperature, as well as product yield and purity. Silylations with **1** usually proceed quite cleanly to give crude products of good purity that contain only traces of the starting substrate and triethylammonium triflate. If desired, TPFS enol ethers **3** can be distilled in vacuo.[13] In contrast to trialkylsilyl enol ethers, compounds **3** are extremely moisture-sensitive species that revert back to carbonyls on hydrolysis. While problematic at first glance, TPFS enol ethers can be conveniently stored and handled using traditional Schlenk techniques.

Silylation of Esters and Lactones

The silylation of methyl acetate under standard conditions afforded α-silyl ester **5** as the sole product (Scheme 3). NMR monitoring of this reaction revealed that the silyl ketene acetal **6** is initially formed, followed by rearrangement into **5**.[14] Importantly, the transformation of **6** to **5** begins when the starting methyl acetate and the silylating agent have not been completely consumed. This observation prompted us to propose that the conversion of the ketene acetal to the α-silyl ester is promoted by the silylating agent rather than occurring as a concerted silyl-group migration. If this is the case, to generate ketene acetal **6** as a major component it is necessary to accelerate its formation, which is most easily achieved by increasing the concen-

tration of starting substrate. Indeed, performing the silylation with methyl acetate as solvent at −78 °C to room temperature allowed us to isolate ketene acetal **6** as the sole product. Compound **6** is a somewhat labile species that is prone to rearrangement into the C-isomer at room temperature. However, it may be stored at −25 °C for at least twelve days with no signs of rearrangement. Thus, depending on the reaction conditions, it is possible to obtain either the C- or *O*-silyl derivatives of methyl acetate.



Scheme 3

Silylation of methyl propionate furnished the stable and distillable silyl ketene acetal **7** as the *Z*-isomer only.[15] Surprisingly, methyl isobutyrate did not undergo silylation under standard conditions.[16] Silylation of butyrolactone and α-methylbutyrolactone was quite rapid and clean, leading to silyl ketene acetals **8** and **9**, respectively. The molecular structure of **9** was studied by X-ray crystallography (Figure 2). This is the first structural characterization of a TPFS-ketene acetal. As expected, the Si−O bond length in **9** (1.632 Å) is shorter than that in non-fluorinated derivatives.[17]

Triflate **1** is a more selective reagent than conventional trialkylsilyl triflates for the silylation of esters and lactones. Indeed, silylation of esters with trimethylsilyl triflate usually provides either mixtures of *C*- and *O*-silyl derivatives or bis-silylated species.[4a,4b,18] The latter are also formed from butyrolactone.[4a,4b,18] In contrast, as shown in the present study, TPFS triflate always affords single products, and the problem of bis-silylation was not encountered.

The reactivity difference between methyl isobutyrate and α-methylbutyrolactone, both of which are α,α-disubstituted esters, is remarkable. To explain this observation it is necessary to consider the mechanism of the reaction. It is quite

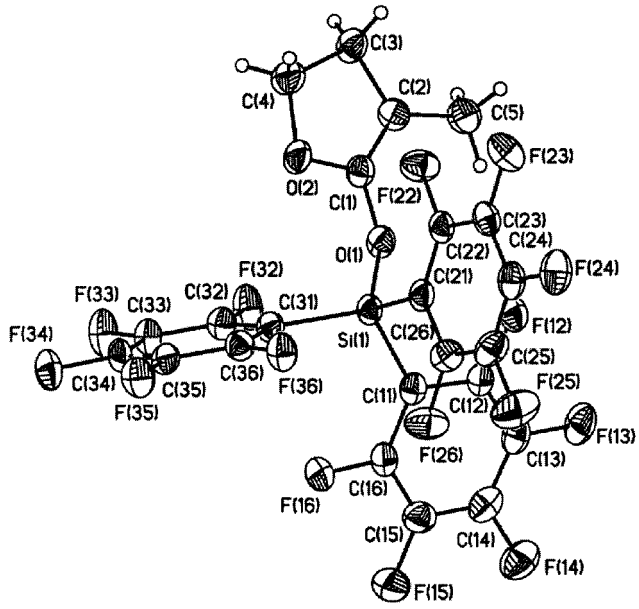
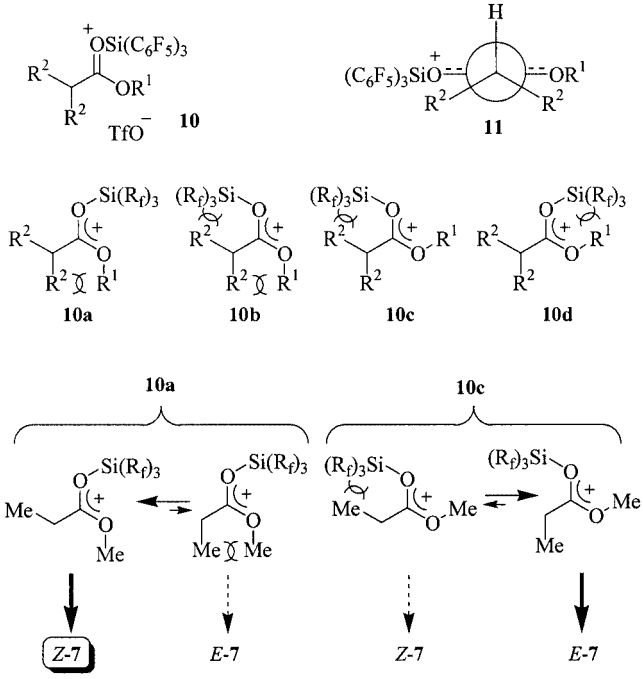


Figure 2. The molecular structure of **9**; non-hydrogen atoms are shown as thermal ellipsoids at 50% probability; selected bond lengths (Å): Si(1)−O(1) 1.632(3), O(1)−C(1) 1.347(5), Si−C (average) 1.886(5); bond angles (°): Si(1)−O(1)−C(1), C−Si−C 110.14, O−Si−C 108.66

likely that silylation proceeds through the silyloxycarbenium cation **10**, which is formed upon transfer of the TPFS group from the silylating agent to the substrate[19] (Scheme 4). Subsequent deprotonation should take place from conformation **11**, in which breaking of the C−H bond occurs parallel to the cationic π-system. Cation **10** may also exist in four different conformations **10a**−**d**.



Scheme 4

To account for the experimental data two hypotheses may be proposed:

Deprotonation occurs from conformation **10a**: In the reaction of methyl isobutyrate this structure is destabilized owing to repulsive interaction between the methyl groups (R^1, R^2 = Me), which becomes even more pronounced in the transition state (see projection **11**).

Deprotonation occurs from conformation **10c**: In this case, for methyl isobutyrate the steric repulsion between the α-methyl substituent (R^2) and the bulky silyl group is destabilizing.

Reaction of α-methylbutyrolactone probably proceeds via the conformation **10a**, which is devoid of unfavorable interactions. By applying this analysis to the silylation of methyl propionate we may expect that conformer **10a** should give the *Z*-isomer, while conformer **10c** should give the *E*-isomer of the silyl ketene acetal. In practice, (*Z*)-**7** was obtained exclusively, thereby supporting the first hypothesis implying **10a** as the product-determining conformation in the acyclic series.

Activity of Triflate 1

It is important to evaluate the activity of TPFS triflate **1** in comparison with its trialkylsilyl analogue, since this will give a measure of the influence of the pentafluorophenyl group. The propensity of TPFS enol ethers to hydrolyse, as well as their ability to undergo uncatalyzed coupling with aldehydes,[7] testifies in favor of the enhanced Lewis acidity of the TPFS fragment compared to its trialkylsilyl counterpart. In addition, the acceleration of the nucleophilic attack at the silicon atom upon the introduction of a pentafluorophenyl group has been documented in earlier investigations.[20] Accordingly, one can expect that TPFS triflate **1** should be more reactive than conventional trimethylsilyl triflate (TMSOTf, **12**).

To estimate the relative activity of triflates **1** and **12** as silylating agents we carried out a series of experiments. The silylation reactions of camphor using either **1** or **12** and triethylamine in $CDCl_3$ were monitored by NMR spectroscopy.[21] In the experiment with TMSOTf 65% conversion was observed in 12 h, while in the tube containing triflate **1** conversion into silyl enol ether was only 30% during the same time. Qualitatively similar results were obtained in experiments with methyl *tert*-butyl ketone, where with TMSOTf more than 75% of the ketone was consumed by the time of first acquisition (<1 min), whereas in the tube with triflate **1** 45% conversion was observed in five minutes.

These studies unambiguously demonstrate that, contrary to our expectations, TPFS triflate **1** is a weaker silylating agent than TMSOTf for the silylation of carbonyl compounds. Such a phenomenon supports the conclusion that, for the present system, the electronic effect of the pentafluorophenyl groups is overcompensated by steric factors.

Conclusion

We have described a new representative of the silyl triflate family. TPFS triflate, which is readily accessible, serves as a very convenient reagent for the introduction of a TPFS group by silylation, as demonstrated by its use for the synthesis of TPFS enol ethers and ketene acetals. The availability of the latter species provides a further stimulus for the elaboration of their chemistry. Based on the results presented in this paper, two general directions for further investigation may be identified: employment of triflate **1** for the silylation of functional groups, and utilization of TPFS derivatives in synthetic methodology. Studies along these lines are in progress in our laboratories.

Experimental Section

General Remarks: All reactions were performed under an argon atmosphere. Dichloromethane (DCM) and dichloroethane (DCE) were refluxed over anhydrous $AlCl_3$ for two days followed by distillation, then refluxed and distilled from NaOH, and finally distilled from CaH_2 prior to use. Hexane was distilled from $LiAlH_4$ and stored over 4-Å molecular sieves. Toluene was distilled from CaH_2 and stored over 4-Å molecular sieves. All NMR measurements were carried out in $CDCl_3$ which was distilled from CaH_2 and stored over 4-Å molecular sieves. Melting points were determined in a sealed capillary. The starting compounds TPFS phenyl,[6,22] TPFS allyl,[22] **3c**,[7] and α-methylbutyrolactone[23] were obtained according to literature procedures.

TPFS Triflate (1). From TPFS Phenyl: Triflic acid (1.12 mL, 12.56 mmol) was added dropwise to a stirred solution of TPFS phenyl (4.76 g, 7.85 mmol) in DCE (5 mL) at 60 °C. The flask was wrapped with cotton wool and allowed to stand at room temperature for 6 hours without stirring, and then was kept in the freezer (−23 °C) overnight. The cold liquid was decanted off and the crystals were washed with cold DCE (ca. −20 °C, 2 × 2.5 mL). Alternatively, the crystals could be washed with a room temperature DCE/hexane mixture (1:2; 3 × 2.5 mL). Subsequent recrystallization from DCE (10 mL) afforded 4.92 g of product as white crystals (92% yield). M.p. 133−136 °C. ^{13}C NMR: δ = 101.5 (tm, $J_{C,F}$ = 25.3 Hz), 118.7 (q, $J_{C,F}$ = 317.8 Hz), 138.4 (dm, $J_{C,F}$ = 258.9 Hz), 146.1 (dm, $J_{C,F}$ = 263.1 Hz), 150.1 (dm, $J_{C,F}$ = 248.4 Hz) ppm. ^{19}F NMR: δ = −158.82 (m), −142.86 (tt, $J_{F,F}$ = 19.4, 5.6 Hz), −126.96 (dm, $J_{F,F}$ = 16.8 Hz), −76.94 (s). $C_{19}F_{18}O_3SSi$ (678.32): calcd. C 33.64; found C 33.58.

From TPFS Allyl: Triflic acid (0.31 mL, 3.57 mmol) was added to a solution of TPFS allyl (0.98 g, 1.74 mmol) in DCM (1 mL). After stirring for 20 min the solvent was evaporated, and the residue was washed with hexane (3 × 2 mL) and recrystallized from DCE (2 mL) to give 0.87 g of **1** (73% yield).

From TPFS Enol Ether 3c: Triflic acid (0.62 mL, 6.97 mmol) was added to a solution of **3c** (3.71 g, 6.33 mmol) in DCM (5.5 mL). After stirring for 5 min the solvent was evaporated, and the residue recrystallized from DCE (8 mL) to give 3.72 g of **1** (87% yield).

Silyl Enol Ethers 3a−k. General Procedure: Triethylamine (0.83 mL, 6 mmol) and carbonyl compound **2a−k** (4 mmol) were successively added, at 0 °C, to a suspension of triflate **1** (2.71 g, 4 mmol) in DCM (5.4 mL for **2a−c,f**, 2.7 mL for **2d,e,g-k**). The cooling bath was then removed and the mixture was stirred at room temperature for the time indicated in Table 1. The solvent was evaporated, the residue was extracted with hexane (3 × 5 mL) under argon with the removal of the hexane phase through a cannula covered with filter paper (for the extraction of **3a,f** warm hexane, ca. 50 °C, was used). The combined hexane solutions were concentrated, and the residue was distilled in vacuo.

[Tris(pentafluorophenyl)silyloxy]ethylene (3a): B.p. 122−124 °C/0.08 Torr. M.p. 109−112 °C. ^{1}H NMR: δ = 4.43 (dd, J = 5.6, 1.6 Hz, 1 H, CH_AH$_B$=), 4.70 (dd, J = 13.5, 1.6 Hz, 1 H, CH$_A$$H_B$=), 6.42 (dd, J = 13.5, 5.6 Hz, 1 H, CHO) ppm. ^{13}C NMR: δ = 99.4, 104.2 (tm, $J_{C,F}$ = 28.4 Hz), 137.8 (dm, $J_{C,F}$ = 255.5 Hz), 142.9, 144.2 (dm, $J_{C,F}$ = 258.3 Hz), 149.5 (dm, $J_{C,F}$ = 246.9 Hz) ppm. ^{19}F NMR: δ = −160.38 (m), −147.16 (t, $J_{F,F}$ = 19.4 Hz), −128.51 (dm, $J_{F,F}$ = 19.4 Hz) ppm. $C_{20}H_3F_{15}OSi$ (572.30): calcd. C 41.97, H 0.53; found C 42.15, H 0.55.

1-[Tris(pentafluorophenyl)silyloxy]prop-1-ene (3b): E:Z = 1:10. B.p. 120−122 °C/0.4 Torr. M.p. 95−100 °C. ^{1}H NMR: Z-isomer: δ = 1.61 (dd, J = 7.2, 1.6 Hz, 3 H, CH$_3$), 4.86−4.75 (m, 1 H, CHCH$_3$), 6.19 (d, J = 6.6 Hz, 1 H, CHO) ppm; E-isomer: δ = 1.52 (dd, J = 7.2, 1.7 Hz, CH$_3$), 5.26 (dq, J = 11.8, 7.2 Hz, 1 H, CHCH$_3$) ppm. ^{13}C NMR: Z-isomer: δ = 9.1, 104.2 (tm, $J_{C,F}$ = 26.9 Hz), 110.0, 135.8, 137.8 (dm, $J_{C,F}$ = 256.7 Hz), 144.4 (dm, $J_{C,F}$ = 258.5 Hz), 149.5 (dm, $J_{C,F}$ = 247.7 Hz) ppm. ^{19}F NMR: Z-isomer: δ = −160.37 (m), −146.76 (tt, $J_{F,F}$ = 19.4, 5.6 Hz), −128.23 (dm, $J_{F,F}$ = 19.4 Hz) ppm. The configuration of the double bond was determined by comparison of H-H coupling constants in the HC=CH fragment (6.6 Hz in the Z-isomer vs. 11.8 Hz in the E-isomer). $C_{21}H_5F_{15}OSi$ (586.33): calcd. C 43.02, H 0.86; found C 42.84, H 1.00.

2-[Tris(pentafluorophenyl)silyloxy]propene (3c): Analytical and spectroscopic data are identical to those reported previously.[7]

1-Phenyl-1-[tris(pentafluorophenyl)silyloxy]ethylene (3d): Viscous pale-yellow oil. B.p. 145−150 °C/0.4 Torr. $C_{24}H_7F_{15}OSi$ (648.39): calcld. C 48.16, H 1.09; found C 48.25, H 1.23. Spectral data are identical to those reported previously.[7]

3,3-Dimethyl-2-[tris(pentafluorophenyl)silyloxy]but-1-ene (3e): B.p. 128−130 °C/0.45 Torr. M.p. 105−106 °C. ^{1}H NMR: δ = 1.08 (s, 9 H, tBu), 3.78 (d, J = 3.0 Hz, 1 H, CH_AH$_B$=), 4.12 (d, J = 3.0 Hz, 1 H, CH$_A$$H_B$=) ppm. ^{13}C NMR: δ = 27.8, 36.6, 88.7, 104.5 (tm, $J_{C,F}$ = 27.4 Hz), 137.6 (dm, $J_{C,F}$ = 256.8 Hz), 144.2 (dm, $J_{C,F}$ = 258.9 Hz), 149.3 (dm, $J_{C,F}$ = 246.3 Hz), 165.3 ppm. ^{19}F NMR: δ = −160.45 (m), −147.10 (tt, $J_{F,F}$ = 20.4, 4.5), −127.97 (dm, $J_{F,F}$ = 20.4 Hz) ppm. $C_{24}H_{11}F_{15}OSi$ (628.41): calcd. C 45.87, H 1.76; found C 46.06, H 2.02.

1-Cyclopropyl-1-[tris(pentafluorophenyl)silyloxy]ethene (3f): B.p. 140−142 °C/0.5 Torr. M.p. 117−119 °C. ^{1}H NMR: δ = 0.56−0.70 (m, 4 H, CH$_2$CH$_2$), 1.41−1.54 (m, 1 H, CH), 3.70 (d, J = 2.6 Hz, 1 H, CH_AH$_B$=), 4.23 (d, J = 2.6 Hz, 1 H, CH$_A$$H_B$=) ppm. ^{13}C NMR: δ = 4.9, 15.1, 90.4, 104.4 (tm, $J_{C,F}$ = 27.8 Hz), 137.7 (dm, $J_{C,F}$ = 254.9 Hz), 144.3 (dm, $J_{C,F}$ = 260.3 Hz), 149.4 (dm, $J_{C,F}$ = 252.2 Hz), 157.6 ppm. ^{19}F NMR: δ = −160.60 (m), −147.23 (tt, $J_{F,F}$ = 19.4, 5.5), −128.12 (dm, $J_{F,F}$ = 19.4 Hz) ppm. $C_{24}H_{11}F_{15}OSi$ (612.36): calcd. C 45.11, H 1.15; found C 45.23, H 1.22.

3-[Tris(pentafluorophenyl)silyloxy]pent-2-ene (3g): E:Z = 1:3.3. B.p. 120−122 °C/0.35 Torr. M.p. 36−45 °C. ^{1}H NMR: Z-isomer: δ = 0.97 (t, J = 7.2 Hz, 3 H, CH_3CH$_2$), 1.34 (d, J = 6.9 Hz, 3 H, CH_3CH), 2.00 (q, J = 7.2 Hz, 2 H, CH$_2$), 4.62 (q, J = 6.9 Hz, 1 H, CH) ppm; E-isomer: δ = 1.01 (t, J = 7.5 Hz, 3 H, CH_3CH$_2$), 1.46 (d, J = 6.6 Hz, 3 H, CH_3CH), 2.14 (q, J = 7.5 Hz, 2 H, CH$_2$), 4.49 (q, J = 6.9 Hz, 1 H, CH) ppm. ^{13}C NMR: Z-isomer: δ = 11.1, 23.6, 28.1, 103.1, 105.2 (m), 137.8 (dm, $J_{C,F}$ = 254.0 Hz), 144.0 (dm, $J_{C,F}$ = 259.4 Hz), 149.4 (dm, $J_{C,F}$ = 247.7 Hz), 150.9 ppm; E-isomer: δ = 10.3, 102.4, 151.9 ppm. ^{19}F NMR: δ = −160.59 (m), −147.29 (tt, $J_{F,F}$ = 19.4, 5.6), −127.98 (dm, $J_{F,F}$ = 19.4 Hz) ppm. In the major isomer an NOE between the CH$_2$ and CH protons was observed. $C_{23}H_9F_{15}OSi$ (614.38): calcd. C 44.96, H 1.48; found C 44.91, H 1.50.

1-Phenyl-1-[tris(pentafluorophenyl)silyloxy]prop-1-ene (3h): E:Z = 1:8.5. B.p. 140−142 °C/0.15 Torr. M.p. 103−111 °C. ^{1}H NMR: Z-isomer: δ = 1.65 (d, J = 6.9 Hz, 3 H, CH$_3$), 5.31 (q, J = 6.8 Hz, 1 H, CH), 7.12−7.33 (m, 5 H, Ph) ppm; E-isomer: δ = 5.24 (q, J = 7.5 Hz, 1 H, CH) ppm. ^{13}C NMR: Z-isomer: δ = 11.1, 105.0 (t, $J_{C,F}$ = 28.7 Hz), 108.3, 125.2, 128.0, 128.2, 137.46 (dm, $J_{C,F}$ = 257.6 Hz) 137.52, 143.9 (dm, $J_{C,F}$ = 259.4 Hz), 148.5, 149.0 (dm, $J_{C,F}$ = 244.1 Hz) ppm; E-isomer: δ = 107.5 ppm. ^{19}F NMR: δ = −160.63 (m), −147.32 (tt, $J_{F,F}$ = 19.4, 5.5), −127.61 (dm, $J_{F,F}$ = 16.8 Hz) ppm. In the major isomer an NOE between the aromatic protons and CH was observed. $C_{26}H_9F_{15}OSi$ (662.42): calcd. C 48.96, H 1.37; found C 49.03, H 1.57.

1-[Tris(pentafluorophenyl)silyloxy]cyclohex-1-ene (3i): B.p. 122−125 °C/0.3 Torr. M.p. 71−72 °C. $C_{24}H_9F_{15}OSi$ (626.39): calcd. C 46.02, H 1.45; found C 45.88, H 1.47. Spectral data are identical to those reported earlier, except that the compound obtained here has none of the impurities reported previously.[7]

1-[Tris(pentafluorophenyl)silyloxy]cyclohept-1-ene (3j): B.p. 144−146 °C/0.31 Torr. M.p. 62−64 °C ^{1}H NMR: δ = 1.39−1.74 [m, 6 H, (CH$_2$)$_3$], 1.94 (q, J = 5.5 Hz, 2 H, CH$_2$), 2.29−2.40 (m, 2 H, CH$_2$), 5.02 (t, J = 6.6 1 H, CH) ppm. ^{13}C NMR: δ = 25.0, 25.1, 27.5, 31.0, 34.5, 105.4 (tm, $J_{C,F}$ = 28.4 Hz), 111.1, 137.7 (dm, $J_{C,F}$ = 255.5 Hz), 144.3 (dm, $J_{C,F}$ = 258.3 Hz), 149.6 (dm, $J_{C,F}$ = 248.4 Hz), 154.4 ppm. ^{19}F NMR: δ = −161.62 (m), −148.18 (t, $J_{F,F}$ = 19.4 Hz), −128.30 (dm, $J_{F,F}$ = 19.4 Hz) ppm.

1,7,7-Trimethyl-2-[tris(pentafluorophenyl)silyloxy]bicyclo[2.2.1]hept-2-ene (3k): B.p. 147−149 °C/0.08 Torr. M.p. 77−79 °C. $[\alpha]_D^{20}$ = +10.3 (c = 3.60, CH$_2$Cl$_2$). ^{1}H NMR: δ = 0.72 (s, 3 H, CH$_3$), 0.77 (s, 3 H, CH$_3$), 0.89 (m, 1 H), 0.94 (s, 3 H, CH$_3$), 1.13 (m, 1 H), 1.54 (m, 1 H), 1.82 (m, 1 H), 2.16 (t, J = 3.3 Hz, 1 H, CH$_2$CH$_2$CH), 4.47 (d, J = 3.3 Hz, 1 H, CH=CO) ppm. ^{13}C NMR (CDCl$_3$): δ = 9.6, 19.2, 20.0, 27.0, 30.9, 49.9, 53.7, 55.6, 104.5 (tm, $J_{C,F}$ = 31.2 Hz), 105.7, 137.7 (dm, $J_{C,F}$ = 258.3 Hz), 144.4 (dm, $J_{C,F}$ = 266.8 Hz), 149.5 (dm, $J_{C,F}$ = 245.6 Hz), 158.0 ppm. ^{19}F NMR: δ = −161.16 (m), −147.16 (tt, $J_{F,F}$ = 19.4, 5.6 Hz), −128.01 (dm, $J_{F,F}$ = 19.4 Hz) ppm. $C_{28}H_{15}F_{15}OSi$ (680.48): calcd. C 49.42, H 2.22; found C 49.33, H 2.44.

Synthesis of 3l-*term* and 3m: A solution of triflate **1** (1.78 g, 2.62 mmol) in toluene (18 mL) was added with a cannula over 20 min to a solution of ketone **2l** or **2m** (2.62 mmol) and triethylamine (0.55 mL, 3.93 mmol) in toluene (18 mL) at −78 °C. The mixture was stirred for 6 hours at −78 °C, diluted with hexane (18 mL), and allowed to warm to room temperature by removing the cooling bath. The solution phase was decanted and concentrated in vacuo. The residue was extracted twice with hexane (18 and 7 mL). The combined organic layers were concentrated to give a crude product, which was either recrystallized or distilled.

3-Methyl-2-[tris(pentafluorophenyl)silyloxy]but-1-ene (3l−*term*): The crude product had a purity of about 95% which corresponds to a yield of about 90%. As partial isomerization occurs upon distillation, the crude product was first recrystallized from hexane (4 mL) and then distilled to give 1.33 g of **3l**-*term* (63% yield). B.p. 120−124 °C/0.03 Torr. M.p. 100−102 °C. ^{1}H NMR: δ = 1.05 (d, J = 6.6 Hz, 6 H, 2CH$_3$), 2.33 (sept, J = 6.6 Hz, 1 H, CH), 3.83 (d, J = 2.9 Hz, 1 H, CH_ACH$_B$=), 4.14 (d, J = 2.9 Hz, 1 H, CH$_A$CH_B=) ppm. ^{13}C NMR: δ = 20.2, 34.2, 89.9, 104.6 (tm, $J_{C,F}$ = 26.3 Hz), 137.7 (dm, $J_{C,F}$ = 256.7 Hz), 144.3 (dm, $J_{C,F}$ = 260.3 Hz), 149.4 (dm, $J_{C,F}$ = 247.7 Hz), 162.9 ppm. ^{19}F NMR: δ =

−160.84 (m), −147.51 (tt, $J_{F,F}$ = 19.4, 5.5 Hz), −128.10 (dm, $J_{F,F}$ = 19.2 Hz) ppm. $C_{24}H_9F_{15}OSi$ (614.38): calcd. C 44.96, H 1.48; found C 44.77, H 1.14.

Mixture of 2-[Tris(pentafluorophenyl)silyloxy]but-1-ene (3m−*term*) and 2-[Tris(pentafluorophenyl)silyloxy]but-2-ene (3m−*int*): The crude product was distilled to give 1.88 g of a 1:1 mixture of terminal and internal regioisomers in 81% yield; **3m**-*int* is present as a 1:10 mixture of *E* and *Z* regioisomers. B.p. 112−115 °C/0.05 Torr. M.p. 83−85 °C. ^{1}H NMR: **3m**-*term*: δ = 1.05 (t, J = 7.9 Hz, 3 H, CH_3), 2.15 (q, J = 7.9 Hz, 2 H, CH_2CH_3), 3.96 (d, J = 2.6 Hz, 1 H, CH_ACH_B=), 4.17 (d, J = 2.6 Hz, 1 H, CH_ACH_B=) ppm; (*Z*)-**3m**-*int*: δ = 1.37 (dq, J = 6.6, 1.3 Hz, 3 H, CH_3), 1.74 (s, 3 H, CH_3), 4.63 (q, J = 6.6 Hz, 1 H, CH) ppm; (*E*)-**3m**-*int*: δ = 1.47 (dq, J = 7.2, 1.3 Hz, 3 H, CH_3), 1.80 (s, 3 H, CH_3) ppm. ^{13}C NMR: δ = 10.2, 11.1, 21.2, 28.6, 91.5 (*term*), 105.7 (*Z*-*int*), 137.5 (dm, $J_{C,F}$ = 252.7 Hz), 144.0 (dm), 145.3, 149.2 (dm, $J_{C,F}$ = 248.4 Hz), 159.1 ppm. ^{19}F NMR: δ = −160.70 (m), −147.34 (t, $J_{F,F}$ = 19.4 Hz), −128.09 (m) ppm. In the major stereoisomer of **3m**-*int* an NOE between the CH_3C(OSi) and CH protons was observed. $C_{26}H_9F_{15}OSi$ (600.35): calcd. C 44.01, H 1.18; found C 43.88, H 1.39.

2-[Tris(pentafluorophenyl)silyloxy]buta-1,3-diene (3n): Toluene (2.2 mL), *i*Pr$_2$NEt (0.66 mL, 3.78 mmol), and **2n** (256 μL, 3.15 mmol) were successively injected into a flask containing triflate **1** (2.16 g, 3.15 mmol) at room temperature. The mixture was refluxed for 4 hours, then allowed to cool to 50 °C, diluted with hexane (2.2 mL), and cooled to room temperature. The solution phase was filtered under argon through a cannula covered with filter paper, followed by washing the solid with hexane (2 × 5 mL). The combined hexane solution was concentrated, and the residue was distilled in vacuo to afford 1.09 g of **3n** as white crystals (58% yield). B.p. 158−161 °C/0.55 Torr. M.p. 93−95 °C. ^{1}H NMR: δ = 4.25 (d, J = 2.3 Hz, 1 H, CH_ACH_B=CO), 4.43 (d, J = 2.3 Hz, 1 H, CH_ACH_B=CO), 5.14 (d, J = 10.7 Hz, 1 H), 5.51 (d, J = 17.0 Hz, 1 H), 6.16 (dd, J = 17.0, 10.5 Hz, 1 H) (CH_2=CH) ppm. ^{13}C NMR: δ = 97.7, 104.4 (tm, $J_{C,F}$ = 27.0 Hz), 116.1, 132.4, 137.7 (dm, $J_{C,F}$ = 251.2 Hz), 144.3 (dm, $J_{C,F}$ = 249.8 Hz), 149.5 (dm, $J_{C,F}$ = 249.8 Hz), 153.2 ppm. ^{19}F NMR: δ = −160.40 (m), −146.85 (tt, $J_{F,F}$ = 19.4, 5.6 Hz), −127.85 (dm, $J_{F,F}$ = 19.4 Hz) ppm. $C_{22}H_5F_{15}OSi$ (598.34): calcd. C 44.16, H 0.84; found C 43.83, H 0.90.

Ammonium Salt 4: $CDCl_3$ (0.45 mL), triethylamine (35 μL, 0.25 mmol) and **2n** (14.5 μL, 0.18 mmol) were successively added to an NMR tube containing triflate **1** (115 mg, 0.17 mmol). The tube was shaken and introduced into the NMR spectrometer. Salt **4** was formed as a 5:1 mixture of isomers. ^{1}H NMR: major: δ = 1.20−1.35 (br. t, 9 H, 3 CH_3CH_2), 1.95 (s, 3 H, CH_3C=C), 3.10−3.35 (br. q, 6 H, 3 CH_3CH_2), 3.81 (d, J = 7.6 Hz, 2 H, CH_2CH=C), 4.73 (t, J = 7.5 Hz, 1 H, CH) ppm; minor: δ = 1.84 (s, 3 H, CH_3C=C), 4.88 (t, J = 7.5 Hz, 1 H, CH) ppm. ^{13}C NMR: major: δ = 7.4, 17.6, 52.5, 55.3, 96.9, 156.9 ppm; minor: δ = 7.1, 52.7, 96.7 ppm. ^{19}F NMR: major: δ = −159.87 (m), −145.86 (tt, $J_{F,F}$ = 19.4 Hz), −128.54 (d, $J_{F,F}$ = 19.4 Hz), −79.90 (s) ppm; minor: δ = −159.31 (m), −145.18 (m) ppm.

Methyl 2-Tris(pentafluorophenyl)silyl Acetate (5): This compound was obtained according to the general procedure using 2.7 mL of DCM for every 4 mmol of triflate **1**; reaction time: 1 h. Yield: 90%. B.p. 130−135 °C/0.35 Torr. M.p. 75−78 °C. ^{1}H NMR: δ = 2.98 (s, 2 H, CH_2), 3.58 (s, 3 H, CH_3) ppm. ^{13}C NMR: δ = 24.1, 52.5, 103.6 (tm, $J_{C,F}$ = 28.5 Hz), 137.6 (dm, $J_{C,F}$ = 254.7 Hz), 143.9 (dm, $J_{C,F}$ = 258.9 Hz), 149.4 (dm, $J_{C,F}$ = 244.1 Hz), 169.7 ppm. ^{19}F NMR: δ = −160.35 (m), −147.40 (tt, $J_{F,F}$ = 20.4, 4.5 Hz) −127.34 (dm, $J_{F,F}$ = 18.1 Hz) ppm. $C_{24}H_9F_{15}OSi$ (602.32): calcd. C 41.88, H 0.84; found C 41.88, H 0.85.

1-Methoxy-1-[tris(pentafluorophenyl)silyloxy]ethene (6): A solution of triflate **1** (0.687 g, 1.01 mmol) in methyl acetate (3.5 mL) was added over 15 min to a solution of triethylamine (0.28 mL, 2.03 mmol) in methyl acetate (3.5 mL) at −78 °C. After stirring for 30 min at −78 °C the reaction flask was connected to a vacuum pump and the low-temperature bath was replaced by an ice/water bath. After concentration, the residue was extracted with hexane at 0 °C (3 × 5 mL). The combined extracts were concentrated in vacuo at 0 °C to give 0.492 g of **6** as a colorless viscous oil (81% yield). ^{1}H NMR: δ = 3.29 (d, J = 3.3 Hz, 1 H, CH_ACH_B=), 3.49 (s, 3 H, CH_3), 3.57 (d, J = 3.3 Hz, 1 H, CH_ACH_B=) ppm. ^{13}C NMR: δ = 55.9, 62.7, 105.0 (td, $J_{C,F}$ = 28.2, 3.1 Hz), 137.8 (dm, $J_{C,F}$ = 253.3 Hz), 144.3 (dm, $J_{C,F}$ = 257.9 Hz), 149.6 (dm, $J_{C,F}$ = 247.2 Hz), 159.9 ppm. ^{19}F NMR: δ = −159.71 (m), −146.44 (t, $J_{F,F}$ = 19.4 Hz), −126.78 (dm, $J_{F,F}$ = 19.4 Hz).

1-Methoxy-1-[tris(pentafluorophenyl)silyloxy]prop-1-ene (7): This compound was obtained according to the general procedure using 5.4 mL of DCM for every 4 mmol of triflate **1**; reaction time: 1.5 h. Yield: 93%. Pale-yellow oil. B.p. 120−123 °C/0.3 Torr. ^{1}H NMR: δ = 1.58 (d, J = 6.6 Hz, 3 H, CH_3CH), 3.37 (s, 3 H, OCH_3), 3.66 (q, J = 6.6 Hz, 1 H, CH) ppm. ^{13}C NMR: δ = 8.9, 55.4, 72.7, 105.3 (tm, $J_{C,F}$ = 28.4 Hz), 137.6 (dm, $J_{C,F}$ = 255.5 Hz), 144.1 (dm, $J_{C,F}$ = 258.3 Hz), 149.4 (dm, $J_{C,F}$ = 251.2 Hz), 154.7 ppm. ^{19}F NMR: δ = −161.25 (m), −148.18 (tt, $J_{F,F}$ = 20.8, 5.6 Hz), −128.56 (dm, $J_{F,F}$ = 18.1 Hz) ppm. An NOE was observed between the OMe and CH protons.

2-[Tris(pentafluorophenyl)silyloxy]-4,5-dihydrofuran (8): This compound was obtained according to the general procedure using 5.4 mL of DCM for every 4 mmol of triflate **1**; reaction time: 1.5 h. Yield: 90%. The product decomposes upon distillation. M.p. 82−83 °C. ^{1}H NMR: δ = 2.62 (td, J = 8.9, 2.0 Hz, 2 H, CH_2CH_2O), 3.96 (t, J = 2.0 Hz, 1 H, CH), 4.22 (t, J = 8.9 Hz, 2 H, CH_2CH_2O) ppm. ^{13}C NMR: δ = 28.2, 69.3, 71.4, 104.1 (tm, $J_{C,F}$ = 28.4 Hz), 137.2 (dm, $J_{C,F}$ = 254.1 Hz), 144.2 (dm, $J_{C,F}$ = 255.5 Hz), 149.3 (dm, $J_{C,F}$ = 249.8 Hz), 155.5 ppm. ^{19}F NMR: δ = −161.39 (m), −147.20 (tt, $J_{F,F}$ = 19.4, 5.6 Hz), −128.15 (dm, $J_{F,F}$ = 19.4 Hz) ppm.

3-Methyl-2-[tris(pentafluorophenyl)silyloxy]-4,5-dihydrofuran (9): This compound was obtained according to the general procedure using 5.4 mL of DCM for every 4 mmol of triflate **1**; reaction time: 1 h. The product decomposes upon distillation. Yield: 90%. M.p. 73−78 °C. ^{1}H NMR: δ = 1.56 (s, 3 H, CH_3), 2.54 (t, J = 8.5 Hz, 2 H, CH_2CH_2O), 4.08 (t, J = 8.5 Hz, 2 H, CH_2CH_2O) ppm. ^{13}C NMR: δ = 9.4, 33.1, 67.4, 79.8, 104.7 (tm, $J_{C,F}$ = 27.8 Hz), 137.6 (dm, $J_{C,F}$ = 255.5 Hz), 144.3 (dm, $J_{C,F}$ = 259.8 Hz), 149.5 (dm, $J_{C,F}$ = 248.4 Hz), 149.5 ppm. ^{19}F NMR: δ = −161.10 (m), −147.60 (tt, $J_{F,F}$ = 19.4, 5.6 Hz), −128.23 (dm, $J_{F,F}$ = 19.4 Hz) ppm.

X-ray Crystallographic Study: The diffraction data for **1** and **9** were collected using Syntex P2$_1$ and Bruker Smart CCD 1000 diffractometers, respectively (Mo-K_α radiation, λ = 0.71073 Å). The structures were solved by direct methods and refined by full-matrix least-squares methods against F^2 using the SHELXTL 5.1 program.[24] The positions of the hydrogen atoms were calculated geometrically and included in the refinement in a rigid-body approximation. The high thermal displacement parameters of the triflate group in the structure of **1** allowed us to split it into two positions in a ratio of 7:3 and then refine them with the use of geometrical restraints (SADI instruction).

Crystal Data for 1: The crystal of $C_{19}F_{18}O_3SSi$ was triclinic at 163 K, space group $P\bar{1}$, a = 10.158(2), b = 11.228(2), c = 11.284(2) Å, α = 61.96(3)°, β = 89.64(3)°, γ = 74.84(3)°, V = 1086.1(4) Å^3, Z = 2, M = 678.34, d_{calc} = 2.074 g·cm^{-3}, μ(Mo-K_α) = 3.84 cm^{-1}, $F(000)$ = 660. 5503 Reflections were measured, of which 5220 were unique. R_1 = 0.0590 was calculated against F^2 for 4523 reflections with $I > 2\sigma(I)$.

Crystal Data for 9: The crystal of $C_{23}H_7F_{15}O_2Si$ was triclinic at 120 K, space group $P\bar{1}$, a = 10.107(5), b = 10.187(5), c = 11.897(6) Å, α = 80.255(10)°, β = 81.481(11)°, γ = 71.232(9)°, V = 1137.3(10) Å^3, Z = 2, M = 628.38, d_{calc} = 1.835 g·cm^{-3}, μ(Mo-K_α) = 2.49 cm^{-1}, $F(000)$ = 620. 6249 Reflections were measured, of which 4292 were unique. R_1 = 0.0686 was calculated against F^2 for 2832 reflections with $I > 2\sigma(I)$.

CCDC-245733 (for **1**) and -245734 (for **9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Supporting Information (see also the footnote on the first page of this article): ^{1}H, ^{13}C, and ^{19}F NMR spectra of **3j**−**l** and **5**−**9**.

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[9] [9a] For the structure of Ph_3SiOTf see: A. Asadi, A. G. Avent, C. Eaborn, M. S. Hill, P. B. Hitchcock, M. M. Meehan, J. D. Smith, *Organometallics* **2002**, *21*, 2183−2188. CCDC ref code AGELED. [9b] According to the CCDC, the Si−O bond length in four-coordinate silyl triflates ranges from 1.742 to 1.760 Å, see structures AGELAZ, AGELED, KAVLAU, PODNEB, XITFEL.

[10] The problem of triflate passivation may become very important if silylation is performed at temperatures at which the TPFS-containing product may be poorly soluble.

[11] [11a] P. Cazeau, F. Duboudin, F. Moulines, O. Babot, J. Dunogues, *Tetrahedron* **1987**, *43*, 2075−2088. [11b] H. Emde, A. Götz, K. Hofmann, G. Simchen, *Liebigs Ann. Chem.* **1981**, 1643−1657. [11c] For a pertinent discussion see: S. E. Denmark, S. M. Pham, *J. Org. Chem.* **2003**, *68*, 5045−5055.

[12] Formation of salts similar to **4** has been reported in the literature, see ref. 11a.

[13] Vacuum distillation of **3** usually posed no problems. However, compound **3l**-*term*, produced as a single regioisomer, underwent partial isomerization into **3l**-*int* upon distillation, presumably due to the presence of traces of triethylammonium triflate. Therefore, **3l**-*term* had to be recrystallized before distillation.

[14] [14a] Rearrangement of trichlorosilyl ketene acetals to α-trichlosilyl esters has been reported, see: I. F. Lutsenko, Yu. I. Baukov, G. S. Burlachenko, B. N. Khasapov, *J. Organomet. Chem.* **1966**, *5*, 20−28. [14b] The structural assignment between isomers **5** and **6** was unequivocally made by ^{13}C NMR spectroscopy, where the chemical shifts of the α-carbon atom differ by 39 ppm (sp^3 vs. sp^2), see: G. L. Larson, V. G. de Maldonado, L. M. Fuentes, L. E. Torres, *J. Org. Chem.* **1988**, *53*, 633−639.

[15] The configuration was determined by an NOE experiment.

[16] In $CDCl_3$ solution no reaction was observed at room temperature after 5 h. After 48 h 25% of methyl isobutyrate had disappeared, although not to give the silyl ketene acetal or α-silyl ester, but to some other species, which were tentatively identified as TPFS isobutyrate and methyltriethylammonium triflate.

[17] Only two structures of silyl ketene acetals were found in the Cambridge database: [17a] (*E*)-*t*BuPh$_2$SiO(*t*BuO)C=CHMe, Si−O 1.660 Å, CCDC ref code VAKYUB; R. E. Babston, V. Lynch, C. S. Wilcox, *Tetrahedron Lett.* **1989**, *30*, 447−450. [17b] 1,1,2,2-Tetrakis(2,4,6-triisopropylphenyl)-1,2-dihydrofuro[3,2-*d*][1,2,3]oxadisilol-5(6*H*)-one, Si−O 1.725 Å, CCDC ref code QOXDIQ: S. Boomgaarden, W. Saak, M. Weidenbruch, H. Marsmann, *Organometallics* **2001**, *20*, 2451−2453.

[18] H. Emde, G. Simchen, *Synthesis* **1977**, 867−869.

[19] Cations similar to **10**, containing a trialkylsilyl fragment, have been previously identified by NMR spectroscopy when using a non-coordinating counterion, see: G. K. S. Prakash, Q. Wang, G. Rasul, G. A. Olah, *J. Organomet. Chem.* **1998**, *550*, 119−123.

[20] A. L. Klebanskii, Yu. A. Yuzhelevskii, E. G. Kagan, G. A. Nikolaev, A. V. Harlamova, *Zh. Obsch. Khim.* **1968**, *38*, 914−918 (*Russ. J. Gen. Chem.* **1968**, *38*, 878−882).

[21] For quantitative NMR studies a homogeneous solution of TPFS triflate **1** was used at a concentration of about 50 mg of **1** per 0.5 mL of $CDCl_3$.

[22] A. D. Dilman, D. E. Arkhipov, A. A. Korlyukov, V. P. Ananikov, V. M. Danilenko, V. A. Tartakovsky, unpublished work.

[23] F. N. Stepanov, *Zh. Obshch. Khim.* **1955**, *25*, 2480−2485 (*Chem. Abstr.* **1956**, 50:9291f).

[24] G. M. Sheldrick, *SHELXTL-97*, V5.10, **1997**, Bruker AXS Inc., Madison, WI-53719, USA.

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