An Expedient and Stereoselective Synthesis of Alkenyl Nonaflates from Silyl Enol Ethers: Optimization, Scope and Limitations

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The fluoride-catalysed reaction between silyl enol ethers **1** and nonafluorobutanesulfonyl fluoride (NfF) has been optimized, resulting in an expedient synthesis of the corresponding alkenyl nonaflates **3**. Tetra-*n*-butylammonium fluoride, dried either with molecular sieves or with potassium fluoride, and potassium fluoride in the presence of dibenzo-18-crown-6 were the best and most practical catalysts for this process. The reaction allows the synthesis of a wide variety of cyclic and acyclic alkenyl nonaflates **3** in good to excellent yields. For *E*/*Z* isomeric alkenes the configuration of the double bond is essentially retained. Remarkably, enolates derived from methyl ketones also provide *C*-sulfonylation products **4** as a side product; the desired alkenyl nonaflates **3l** and **3m** could, however, be prepared in good yields by further optimization.

Introduction

Since the discovery of their versatility in transition metal-catalysed or -mediated cross-coupling reactions, alkenyl triflates have attracted great attention. This in turn has had a powerful impact on the development of new methods for their synthesis. As a result, a number of new efficient triflating reagents have been introduced[1] and become commercially available,[2] and have been employed in highly chemo-, regio- and diastereoselective procedures.[3] The much broader use of alkenyl and aryl triflates (as compared with other perfluoroalkanesulfonates) in cross-coupling reactions is reflected in the titles of relevant reviews.[4] However, the synthetic potential of other alkenyl perfluoroalkanesulfonates seems to have been underestimated and still remains to be developed. This mainly concerns 1,1,2,2,3,3,4,4,4-nonafluorobutanesulfonic acid enol esters (hereafter abbreviated to alkenyl nonaflates), the successful application of which in Heck coupling reactions,[5] including a one-flask procedure starting from trimethylsilyl enol ethers,[5b] has already been reported. An advantage of the nonaflates is evident from comparison of the properties of trifluoromethanesulfonyl fluoride (TfF) and nonafluorobutanesulfonyl fluoride (NfF), which are industrial products[6] and precursors of all the other triflate and nonaflate derivatives. TfF is a toxic gas that requires special technique and precautions[4b] and therefore has to be transformed into more convenient but rather expensive triflating reagents.[2] NfF, on the other hand, is a stable and easily handled liquid[7] that is of considerable interest as a mild and efficient fluorinating[8] or nonaflating[8,9] reagent. However, no systematic studies on the preparation of alkenyl nonaflates with the aid of NfF has been reported to date.[8,10] In the context of our interest in the application of alkenyl nonaflates in Pd-catalysed cross-coupling reactions[5b,5d,5e] we present here the results of our studies on their synthesis with silyl enol ethers as starting material. For comparison, their preparation from the corresponding carbonyl compounds has been investigated in few representative cases.

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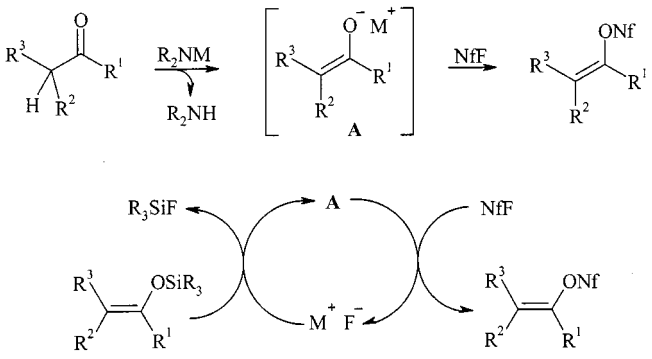
Results and Discussion

It is noteworthy that NfF is a moderately electrophilic reagent and cannot react directly with ketones or aldehydes (unless they contain C−H-activating electron-withdrawing substituents in the α-position) in the presence of conventional metal-free nitrogen bases[11] (R_3N, pyridine, 2,6-di-*tert*-butyl-4-methylpyridine), unlike the respective anhydride.[12] Therefore, activation of the enolizable carbonyl components by conversion into the appropriate enolates **A**[13] (commonly with iPr$_2$NLi[8] or (Me$_3$Si)$_2$NMet[10d]) is required, followed by addition of NfF (Scheme 1, top) or through the intermediacy of silyl enol ethers. Advantages of the latter approach are:

− Silyl enol ethers[14] are easily available chemo-, regio- and stereoselectively by various methods (including 1,4-additions and Diels−Alder and Hetero-Diels−Alder reac-



Scheme 1

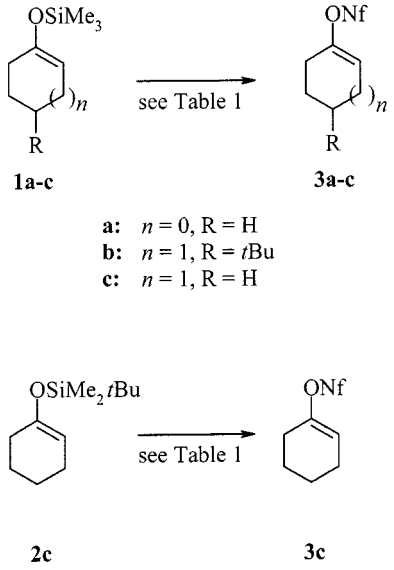
tions). Highly enantioselective methods for desymmetrization of cyclic ketones by use of homochiral lithium amide bases with successive[15] or internal[16] quenching with trimethylsilyl chloride have been developed.

– Once generated from a silyl enol ether, enolate **A** interacts with NfF in such a way that a fluoride anion is regenerated in each elementary step (Scheme 1, bottom), thus in principle permitting the use of substoichiometric or catalytic quantities of the initial fluoride source.

– The reaction routinely proceeds at high concentrations of the reactants (1–6 mmol per mL of solvent), which allows a subsequent reaction, such as a Pd-catalysed cross-coupling, to be carried out by simple dilution with the desired solvent, followed by addition of the required components.[5b]

Optimization of the Reaction Conditions

For optimization of the reaction conditions, cyclic silyl enol ethers **1a, 1b** and **2c** (Scheme 2) were used in the presence of different fluoride sources (Table 1). Thus, fluoro *ate* complexes (entries 1–4) and fluoride salts (entries 5–8) were employed, with variations in the solvent, the amounts and concentrations of the reacting components, the reaction temperature and the reaction time. Entries 1–4 and 6–8 represent optimal conditions for the corresponding fluoride source. As the nonaflation process involves the moisture-sensitive enolate **A** as a reactive intermediate,[17] careful protection from atmospheric moisture and dryness of the fluoride source have to be ensured. Use of the fluoro *ate* complexes (entries 1–4) is beneficial, as these can be obtained in anhydrous form. Tetra-*n*-butylammonium triphenyldifluorosilicate, a nonhygroscopic crystalline solid, provided the best result (entry 1), albeit giving Ph_3SiF as a side product. The analogous tin complex resulted in poorer yields of the nonaflate **3a** even when used in considerably higher molar amounts (entry 2), and also produced toxic, tin-containing side product(s). Tris(dimethylamino)sulfon-



Scheme 2

Table 1. Comparison of different nucleophilic activators in reactions of model trialkylsilyl enol ethers **1a, 1b** and **2c** with NfF to afford the nonaflates **3a-c** according to Scheme 2

Entry	Starting material	Solvent	NfF (equiv.)	Optimized reaction conditions: Activator	Amount (equiv.)	T (°C)	Time (h)	Product (yield, %)
1	**1a**	THF	1.2	[nBu$_4$N][$SiPh_3F_2$]	0.10	0 → room temp.	4	**3a** (85)
2	**1a**	CH_2Cl_2	2.0	[nBu$_4$N][$SnPh_3F_2$]	0.26	0 → room temp.	40	**3a** (55)
3	**1a**	THF/CH_2Cl_2[a]	2.0	[$(Me_2N)_3S$][$SiMe_3F_2$]	0.13	0 → room temp.	16	**3a** (75)
4	**1a**	CH_2Cl_2	1.2	[nBu$_4$N][HF_2][b]	0.07	0 → room temp.	16	**3a** (77)
5	**1a**	–	1.2	CsF	0.20	25	48	**3a** (10)
6	**1a**	PhH	2.0	{[$(Me_2N)_3P{=}N]_4P$}$^+$ F^-	0.12	0 → room temp.	16	**3a** (60)
7	**1a**	THF	1.2	[nBu$_4$N]F, method A[c]	0.18	0 → room temp.	16	**3a** (80)
8	**1b**	THF	1.2	[nBu$_4$N]F, method B[d]	0.05	−78 → room temp.	17	**3b** (85)
9	**1a**	THF	1.2	[nBu$_4$N]CN	0.20	0 → room temp.	16	**3a** (–[e])
10	**1a**	THF	1.2	MeLi, 1 h[f]	1.1	−78 → room temp.	16	**3a** (55)
11	**2c**	THF	1.2	MeLi, 18 h[f]	1.1	−78 → room temp.	16	**3c** (32)

[a] 1:1 ratio. [b] In the presence of 0.18 equiv. $Me_3SiSiMe_3$. [c] 1 molar [nBu$_4$N]F solution in THF dried with 4-Å molecular sieves (see ref.[29] for details). [d] Crystalline [nBu$_4$N]F·3H_2O pre-dried in vacuum, dissolved in THF and treated with dried KF (0.7–0.9 equiv.; see ref.[29] for details). [e] Traces of the product detected. [f] The silyl enol ether solution was stirred with MeLi at −5 to 0 °C for the time stated before the addition of NfF.

ium difluorotrimethylsilicate (entry 3) and tetra-*n*-butylammonium hydrogendifluoride[18] (entry 4) showed comparable efficiencies. However, the former reagent is extremely moisture-sensitive and cannot be stored as a stock solution, whilst the latter contains relatively acidic hydrogens and gives good results only after in situ treatment with hexamethyldisilane[19] by the procedure originally introduced by Vorbrüggen et al. for drying of [*n*Bu$_4$N]F solutions.[20]

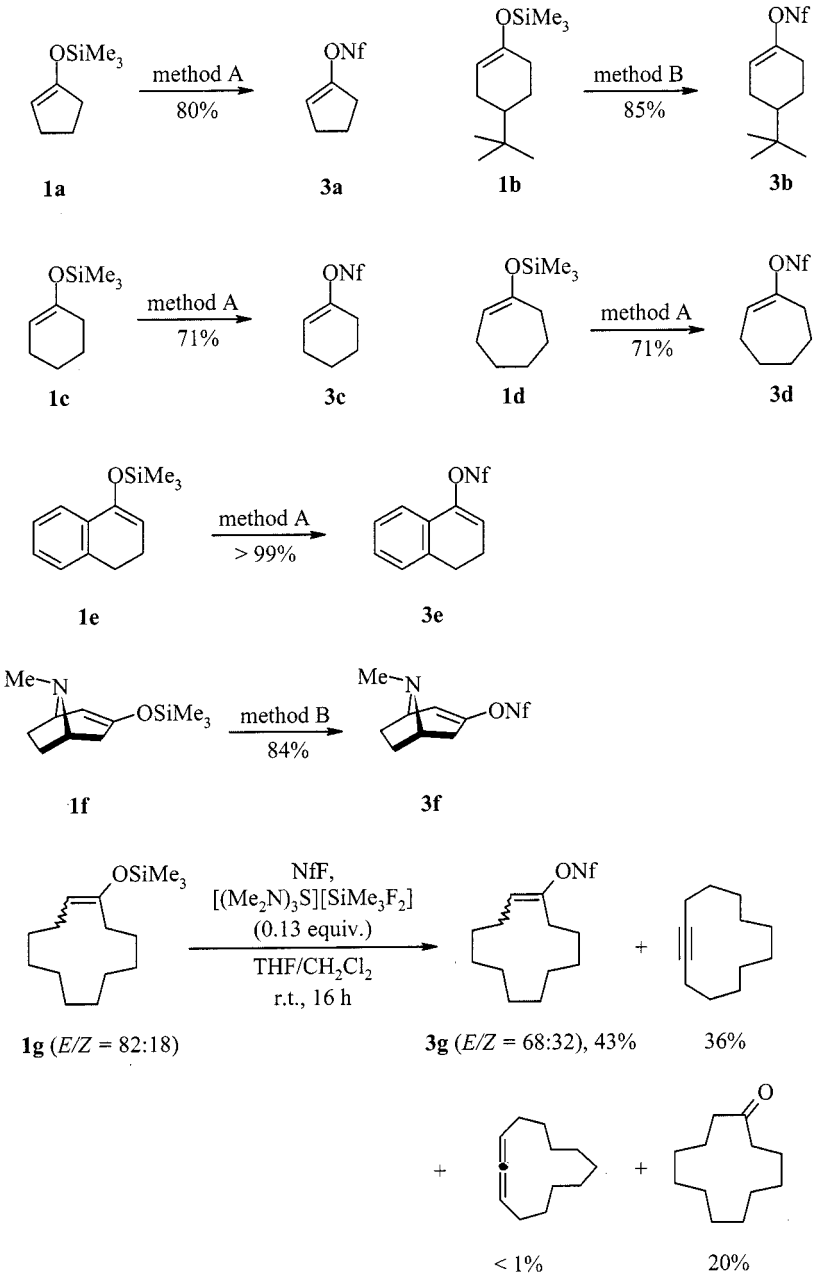
The results with fluoride salts are shown in entries 5−8 (Table 1). Cesium fluoride provided a disappointingly low yield of the nonaflate **3a** when used without solvent (entry 5), and gave only traces of the product if the reaction was conducted in THF, which may be due to the poor solubility of CsF in the reaction media.[21] Tetrakis[tris(dimethylamino)phosphoranylideneamino]phosphonium fluoride,[22] a highly soluble anhydrous fluoride source containing a dendritically branched, thermally very stable lipophilic counterion, gave satisfactory yields of the product only when applied in more than 10 mol % (entry 6). Unlike this phosphonium fluoride, tetra-*n*-butylammonium fluoride, a widely used fluoride salt highly soluble in organic solvents, is known to be unstable in completely anhydrous form.[23] However, both a commercially available solution of [*n*Bu$_4$N]F in THF containing ≤ 5% water and one prepared from crystalline [*n*Bu$_4$N]F·3H$_2$O gave low yields (15−21%) of the nonaflate **3c** in the model reaction **1c** → **3c** (see Scheme 2), together with considerable amounts of cyclohexanone, indicating hydrolysis.[24] A suitable drying was achieved by repeated treatment of the commercially available [*n*Bu$_4$N]F solution in THF with powdered molecular sieves 4 Å[25] (method A). The activation time and the number of consecutive dryings with fresh portions of the molecular sieves were both essential to attain satisfactory results (see Table 1, entry 7 and footnote). The molar quantity of the required fluoride source (ca. 15−20 mol %) was still relatively high and the drying procedure resulted in considerable loss (up to 50%) of the starting [*n*Bu$_4$N]F solution. We later succeeded in evading these drawbacks by use of a stock solution prepared from crystalline [*n*Bu$_4$N]F·3H$_2$O by drying at 45−48 °C (0.01 mbar) for 15 hours followed by dissolving in THF. The resulting solution was used in the presence of an excess of finely ground and thoroughly dried potassium fluoride (method B). According to the literature, drying of [*n*Bu$_4$N]F·3H$_2$O at 40−45 °C (< 0.13 mbar) for ca. 48 hours affords "anhydrous" [*n*Bu$_4$N]F containing 0.1−0.3 equiv. of water and ca. 10% of [*n*Bu$_4$N][HF$_2$].[26] Whatever the exact constitution of the resulting [*n*Bu$_4$N]F, we believe that a fine suspension of anhydrous KF in the solution of the predried [*n*Bu$_4$N]F serves as a heterogeneous inorganic scavenger of the residual water and/or hydrogen fluoride, acting as an inexpensive and efficient source of "anhydrous" fluoride in situ. The fluoride catalyst prepared by this method gave the best result with respect both to the molar quantity used (5 mol %) and to the yield of nonaflate **3b** from 4-*tert*-butyl(trimethylsiloxy)cyclohexene (**1b**) (entry 8).[27]

A few experiments in the nonaflation process were performed with other nucleophilic activators (Table 1, entries 9−11). Highly nucleophilic tetra-*n*-butylammonium cyanide was expected to initiate the process generating the enolate. This would release fluoride upon interaction with NfF and induce a sequence according to Scheme 1, bottom. However, only traces of the nonaflation product were observed (entry 9), together with recovered starting material **1a** and cyclopentanone resulting from hydrolysis. Methyllithium is known to generate lithium enolates from silyl enol ethers[28] in an amine-free procedure that gives unreactive tetraalkylsilane as the only side product. This procedure implies at least one equivalent of MeLi at 0 °C *prior to* the addition of the electrophile. The resulting lithium enolate of cyclopentanone was treated with NfF to give nonaflate **3a** in moderate yield (entry 10). Analogous in situ formation of the lithium enolate of cyclohexanone from *tert*-butyldimethylsilyl enol ether **2c** took considerably longer to be effected (entry 11); subsequent treatment with NfF resulted in a low yield of nonaflate **3c**.

Certain conclusions can be drawn from the data shown in Table 1 and from the following experiments. Suitably dried tetra-*n*-butylammonium fluoride (methods A or B, see above) appears to provide a desirable compromise concerning reactivity, stability in solutions, and price. Tetrakis[tris(dimethylamino)phosphoranylideneamino]-phosphonium fluoride and the studied tetra-*n*-butylammonium fluorosilicates can be used as purchased without any additional treatment, but give no appreciable benefit in reaction efficiency and are rather expensive.

Synthesis of Different Nonaflates

We synthesized nonaflates **3a**−**n**, varying the type, number and position of substituents at the C,C-double bond in the starting trimethylsilyl enol ethers **1a**−**n** under the optimized conditions. The results are summarized in Schemes 3−5. The method works well for the synthesis of cyclic nonaflates formally derived from cyclic ketones (Scheme 3), and for nonaflates with a terminal ONf group, arising from parent aldehyde precursors (Scheme 4). These nonaflates are reasonably stable, colourless or yellowish hydrophobic liquids, which can easily be purified either by distillation in vacuum or by column chromatography. We attribute the slightly lower yields of the simplest representatives − ethenyl nonaflate[29] and 1-propenyl nonaflate (**3h**) − to their higher volatility, whereas that of buta-1,3-dien-2-yl nonaflate **3n** (Scheme 5, Table 2, entry 9) may be due to lower stability.[30] With the exception of cyclododecanone derivatives (**1g** → **3g**), the reactions were clean and exclusively provided the nonaflates as isolated products. Nonaflate **3g** was not separated from the side products, which were cyclododecyne, cyclododeca-1,2-diene and cyclododecanone (36%, < 1% and 20% yields, respectively according to GC-MS data; see Scheme 3, bottom). Although base-induced elimination of perfluoroalkanesulfonic acids from alkenyl perfluoroalkanesulfonates is well documented in the literature,[12a] the reaction behaviour of **1g** represents the only case in which we actually observed alkyne or allene formation under our nonaflation conditions.

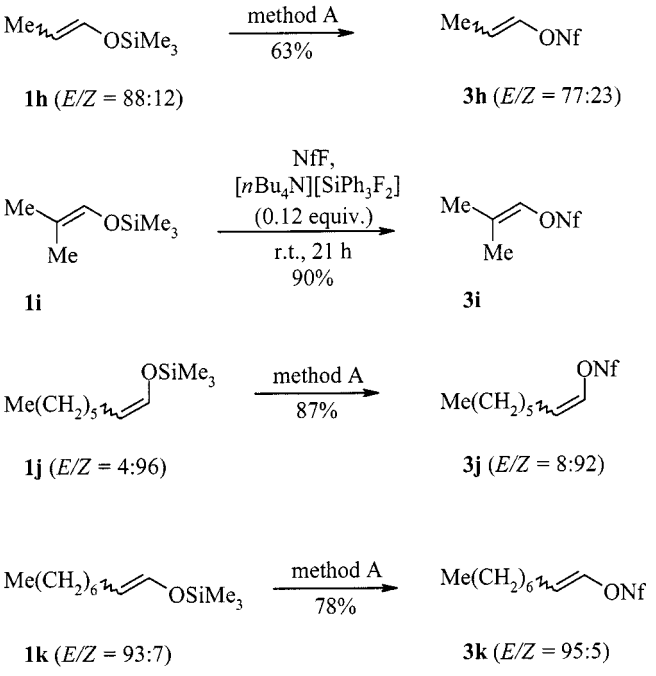


Scheme 3. Method A: [nBu$_4$N]F (0.15−0.29 equiv.), THF, NfF (1.1−2.0 equiv.), 0 °C → room temp., 16−18 h; Method B: [n-Bu$_4$N]F (0.04−0.05 equiv.), KF, THF, NfF (1.2 − 1.3 equiv.), −78 °C → room temp., 16−18 h

For aldehyde-derived nonaflates (Scheme 4), high degrees of retention of the initial configuration of C,C-double bonds were observed. The *E*/*Z* ratios in products **3h**, **3j** and **3k**, as well as in buta-1,3-dien-1-yl nonaflate,[29] were close to those in the corresponding starting silyl enol ethers. Hence the nonaflation procedure had occurred without *E*/*Z* isomerization of the intermediate enolate and may be termed a stereospecific process.

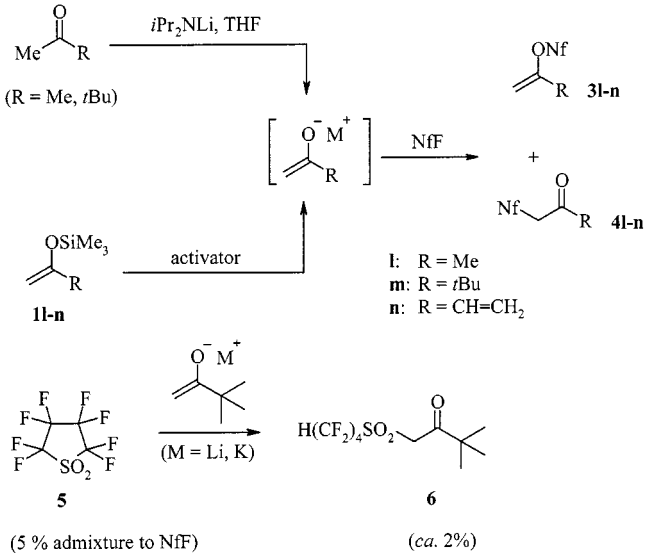
The enolates derived from methyl ketones require separate discussion, because a considerable amount of C-sulfonylation was observed. This formation of ketosulfones might be due to the considerably smaller steric hindrance at the terminal enolate carbon in comparison with that in the other enolates discussed above. As in our previous study,[10a] we again demonstrated the cation effect on *C*- versus *O*-regioselectivity of enolate sulfonylation, this time in more detail using NfF (Scheme 5). The lithium enolates were generated from the respective ketones, whereas for other enolates, trimethylsilyl enol ethers **1l**−**1n** were used as precursors (Table 2). The reactions showed trends similar to those described earlier for the sulfonylation of 3,3-dimethylbutan-2-one enolates with benzenesulfonyl fluoride:[10a] an increase in the ionic character of the enolate resulted in localization of the negative charge mainly at the enolate oxygen, which raised the relative proportion of alkenyl nonaflate as a result of charge-controlled *O*-nonaflation. Li-

thium enolates of acetone and 3,3-dimethylbutan-2-one gave considerable amounts of the nonafluorobutanesulfonyl ketones **4** (entries 1, 4). In the reaction of the lithium enolate of pinacolone we found ketosulfone **6** (2%) as a by-product, arising from perfluorinated cyclic sulfone **5**. This compound was present as an impurity in the NfF to an extent of 5%. In other nonaflation experiments we did not isolate the corresponding C-sulfonylation products. Although we cannot rigorously rule out their formation in these reactions, it seems that only the sterically less hindered enolates derived from methyl ketones are able to react as C-nucleophiles with **5**.



Scheme 4. Method A: $[n\mathrm{Bu_4N}]F$ (0.15−0.29 equiv.), THF, NfF (1.1−2.0 equiv.), 0 °C → room temp., 16−18 h unless otherwise noted

Use of the potassium enolate − generated by treatment of **1m** with an equimolar quantity of potassium ethoxide[31] − distinctly shifted the ratio in favour of the alkenyl nonaflate **3m** (*cf.* entries 5 and 4). The less coordinating tetra-*n*-butylammonium cation further enhanced the *O*-nonaflation rate, rendering alkenyl nonaflates **3l** and **3m** either highly predominant (entry 6) or virtually exclusive (entry 2). However, the preparative yields were not satisfactory (entries 2, 6, 7). ^{1}H NMR monitoring of the reaction mixtures showed considerable amounts of the parent ketones as by-products. A combination of thoroughly dried potassium fluoride (1.0 equivalent) and dibenzo-18-crown-6[32] delivered a fluoride source excluding a priori any adventitious acidic hydrogens during the reaction, but still favouring charge control in the nonaflation step. This provided exclusive *O*-nonaflation and good yields of nonaflates **3l** (entry 3) and **3m** (entry 8). For the preparation of **3m**, the use of a THF/DMF mixture was



Scheme 5

Table 2. Influence of the cation on *C*/*O*-regioselectivity of enolate nonaflation with NfF according to Scheme 5 (reactions were conducted in THF unless otherwise noted).

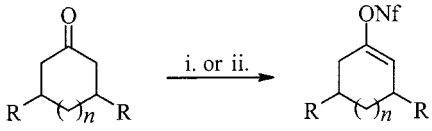
Entry	R	Activator for **1** (equiv.)	Cation	**3**:**4** ratio[a]	Yield **3** (%)	Yield **4** (%)
1	Me	−	Li^+	64:36	−	**4l** (25)
2	Me	$[n\mathrm{Bu_4N}][HF_2]$ (0.2) + KF (2.1)[b]	$n\mathrm{Bu_4N^+}$	> 95: < 5[c]	**3l** (32)	−
3	Me	dibenzo-18-crown-6 (0.2) + KF (1.0)	K^+ [d]	> 95:< 5[c]	**3l** (68)	−
4	*t*Bu	−	Li^+	31:69	−	**4m** (43)
5	*t*Bu	EtOK (1.0)	K^+	75:25	**3m** (47)	**4m** (17)
6	*t*Bu	$[n\mathrm{Bu_4N}][HF_2]$ (0.2)[e] + KF (2.1)[b]	$n\mathrm{Bu_4N^+}$	93:7	**3m** (40)	−
7	*t*Bu	$[n\mathrm{Bu_4N}]F$ (0.2)[e] − method B	$n\mathrm{Bu_4N^+}$	−[f]	**3m** (39)	−
8	*t*Bu	dibenzo-18-crown-6 (0.2) + KF (1.0)[g]	K^+[d]	> 95:< 5[c]	**3m** (64)	−
9	$CH=CH_2$	$[n\mathrm{Bu_4N}]F$ (0.18) − method A	$n\mathrm{Bu_4N^+}$	−[f]	**3n** (61)	−

[a] Determined for the crude mixture by ^{1}H NMR after acidic workup (aqueous H_3PO_4, pH = 2); only one of these components was usually isolated due to different workup procedures (see Exp. Sect.). [b] KF is expected to serve here as a heterogeneous inorganic scavenger of residual HF in the fluoride activator, analogously to Method B. [c] No clear signals of the nonafluorobutanesulfonyl ketones **4** were observed. [d] As a complex with dibenzo-18-crown-6. [e] 0.1 equiv. of the fluoride salt gave only 50−60% conversion of **1m** regardless of the reaction time. [f] No aqueous workup was performed. [g] In DMF/THF, 1:1 mixture.

advantageous, since the reaction in neat THF was rather sluggish. Considering the somewhat lower stability of buta-1,3-dienyl nonaflate **3n**,[30] we refrained from studying the counterion effect on buta-1,3-dien-2-olate nonaflation. The product **3n** (entry 9) was prepared and isolated in moderate yield by the general procedure without aqueous workup.[33]

The nonaflation reaction seemed to be sensitive to the electronic effects of substituents at the C,C-double bond and to steric effects of silyl substituents. Thus, attempts to prepare bisnonaflates from *cis*-1,2-bis(trimethylsiloxy)-ethene or 1,2-bis(trimethylsiloxy)cyclohexene with [*n*Bu$_4$N]F as a promoter have so far failed. Furthermore, none of the fluoride sources tested gave appreciable yields of nonaflates when silyl enol ethers bearing silyl groups bulkier than trimethylsilyl were employed; 1-(*tert*-butyldimethylsiloxy)cyclohexene (**2c**), 2-(*tert*-butyldimethylsiloxy)-cyclohexa-1,3-diene[34] and 2-(*n*-butyldimethylsiloxy)-3,3-dimethylbutene[5d] could not be converted into the corresponding nonaflates. This behaviour indicated that the mechanism as depicted in Scheme 1 may be oversimplified.[35] As expected, methyllithium can also cleave the *tert*-butyldimethylsilyl group upon prolonged treatment of the enol ether **2c** at 0 °C (Table 1, entry 11), to generate the respective lithium enolate, but this procedure can hardly be applied to polyfunctional substrates as very few functional groups are able to tolerate methyllithium under these harsh reaction conditions.

As mentioned above, generation of metal enolates is required to effect direct conversion of ketones into enol nonaflates with NfF (see Scheme 1, top). We therefore applied *i*Pr$_2$NLi followed by addition of NfF (Scheme 6). This approach was approximately as efficient as that of the "detour" via trimethylsilyl enol ethers when applied to the synthesis of the cyclic nonaflates **3c** and **3f** (*i* in Scheme 6; *cf.* Scheme 3 **1c** → **3c** or **1f** → **3f**). Use of DBU as base required considerably more drastic conditions[11] to effect nonaflation of ketones with NfF and resulted in lower yields of products. Synthesis of the model nonaflate **3c** was achieved in 48% yield by heating the reaction components in toluene.



3c (R = H, *n* = 1, i. 65%, ii. 48%)
3f (R,R = –N(Me)–, *n* = 2, i. 86%)
3o (R,R = –N(CO$_2$Et)–, *n* = 2, i. 94%)

Scheme 6. i. 1) *i*Pr$_2$NLi in THF, −78 °C; 2) NfF, −78 °C → room temp., overnight; ii. DBU in toluene at 85 °C, NfF, 85 °C overnight

Conclusion

We have developed a general and expedient method for synthesis of alkenyl nonaflates **3** from trimethylsilyl enol ethers **1** and the industrial product nonafluorobutanesulfonyl fluoride (NfF). For the crucial fluoride-induced desilylation step, tetra-*n*-butylammonium fluoride was found to be a good fluoride source, provided that a suitable drying procedure was performed. Potassium fluoride/dibenzo-18-crown-6 gave better results when applied to silyl enol ethers derived from methyl ketones. The reaction is applicable to a wide range of silyl enol ethers derived from ketones or aldehydes and enables alkenyl nonaflates to be synthesised with a high degree of stereoretention if *E*/*Z* isomeric alkenes are involved. With the exception of compound **3g** (see Scheme 3), alkenyl nonaflates **3** were isolated as the exclusive products. The explicit advantage of our method is the use of trimethylsilyl enol ethers as starting materials. Their chemo-, regio- and stereoselective syntheses, as well as their isolation and purification, are comprehensively documented in the literature. The nonaflation method is suitable for the synthesis of pure alkenyl nonaflates **3**, but also for one-pot coupling procedures (such as Heck or Suzuki reactions) in which the generated nonaflates are directly used without purification. This will be reported in a subsequent account.[5e]

Experimental Section

General Methods: NMR spectra were recorded on Bruker AC 500, WH 270 or AC 250 instruments, in $CDCl_3$ as solvent unless stated otherwise. ^{1}H and ^{13}C chemical shifts are expressed as ppm downfield from tetramethylsilane (δ = 0) used as an internal standard. ^{19}F chemical shifts are given in ppm upfield from $CFCl_3$ (δ = 0) used as an internal standard. ^{13}C signals of the $CF_3(CF_2)_3$ groups are not given, as no unambiguous assignments were possible, due to strong splitting by coupling with the ^{19}F nuclei. Mass spectra were registered with a Varian MAT 711 spectrometer. GS/MS analysis was performed with a Hewlett−Packard (HP) 5890 Series II and a HP 5972 MS-Selective Detector. IR spectra were measured with Beckman IR Acculab 4, Beckman IR 5A, Perkin−Elmer IR 1420 or Perkin−Elmer FT-IR spectrometers Nicolet 5 SXC. TLC analysis was performed with Merck 60 F_{254} silica gel plates. Column chromatography (hereafter abbreviated as CC) was conducted on 60 silica gel (40−63 μm, Fluka).

The lithiation, silylation and nonaflation reactions were carried out under atmosphere of argon in heat-gun-dried reaction flasks, adding the components by syringe. Solvents for reactions were dried by standard procedures. Nonafluorobutanesulfonyl fluoride was obtained from Bayer AG; it can also be purchased from Aldrich.

The preparation and drying of [*n*Bu$_4$N]F solution in THF (Aldrich or Fluka, contains 3% water), *n*Bu$_4$NF·3H$_2$O (Merck−Schuchardt) and KF used in *Methods A* and *B* are described by us in our preceding publication.[29] A 50% solution of [*n*Bu$_4$N][HF$_2$] in CH_2Cl_2 (1.93 mmol·mL^{-1}) was purchased from Fluka. Potassium ethoxide was purchased from Aldrich. Dibenzo-18-crown-6 (Merck−Schuchardt) was stored over CaH_2 in a tightly closed vial.

Methyl vinyl ketone (Fluka, assay ca. 95%, contains ca. 0.5% hydroquinone, ca. 0.5% AcOH and ca. 5% water) was treated with P_2O_5 at −78 °C and recondensed under high vacuum into a cold (−78 °C) trap containing a few crystals of hydroquinone and kept at −18 °C. *N*-Ethoxycarbonyl-4-tropinone was purchased from Acros Organics. The starting silyl enol ethers were obtained by the standard procedures described in the literature. 1-Trimethylsiloxy-non-1-ene (**1k**, *E*/*Z* = 93:7),[36] and 1-trimethylsiloxyoct-1-ene (**1j**,

E/*Z* = 25:75)[37] were synthesized stereoselectively as described in the literature. The latter compound was further enriched up to 4:96 *E*/*Z* ratio by a kinetic resolution exploiting the considerably higher reactivity of the *E* isomer in a hetero-Diels−Alder reaction.[38] 8-Methyl-3-trimethylsiloxy-8-azabicyclo[3.2.1]oct-2-ene (*rac*-**1f**) was prepared from tropinone (Acros Organics) and isolated without aqueous workup as described in ref.[24] Commercially available 2.5 molar *n*BuLi (Aldrich) was titrated by the [1,10]phenanthroline method.[39]

Experimental details on optimization of the nonaflation procedure with different nucleophilic activators (Table 1) are given in ref.[5d]

Alkenyl Nonaflates 3. General Procedures. Method A: A 1 M solution of "dry" [*n*Bu$_4$N]F in THF[29] was added at 0 °C, with vigorous stirring, to the neat silyl enol ether **1**. No dilution of the reaction mixture with extra solvent was made prior to the addition of the [*n*Bu$_4$N]F unless otherwise noted. Once the fluoride source had been added, the neat NfF was injected dropwise by syringe to give a two-phase, yellowish-to-brown reaction mixture, which soon afterwards became homogeneous. Stirring (at ambient temperature for 16−18 h unless otherwise noted), removal of the volatiles in vacuum and subsequent kugelrohr distillation of the residue afforded the pure products.
Method B: A 1.05 molar [*n*Bu$_4$N]F solution in THF[29] was added to a suspension of the thoroughly dried KF in THF, and the resulting mixture was stirred at 0−5 °C for 15−20 min before being cooled to −78 °C. The silyl enol ether and NfF were subsequently added at −78 °C, and the resulting mixture was allowed to warm to ambient temperature over 2−3 h and stirred overnight. Aqueous workup, extraction with hexane, drying of the combined organic phase ($MgSO_4$), and subsequent column chromatography or kugelrohr distillation of the residue furnished the pure nonaflates **3**.

Cyclopent-1-enyl Nonaflate (3a): According to Method A, **1a** (0.390 g, 2.50 mmol), [*n*Bu$_4$N]F solution (0.45 mmol) and NfF (0.906 g, 3.00 mmol) provided 0.725 g (80%) of **3a** as a colourless liquid (b.p. 80 °C/24 mbar). The physical and spectroscopic data of **3a** agreed with those described in the literature.[10a]

***rac*-4-*tert*-Butylcyclohex-1-enyl Nonaflate (3b):** According to Method B, *rac*-**1b** (0.180 g, 0.80 mmol), [*n*Bu$_4$N]F solution (0.04 mmol) and NfF (0.910 g, 3.01 mmol) in THF (0.2 mL) in the presence of KF (0.040 g, 0.70 mmol), after purification by CC (hexane), provided 0.295 g (85%) of **3b** as a colourless oil (b.p. 100 °C/2 mbar). ^{1}H NMR (270 MHz): δ = 0.89 (s, 9 H, *t*Bu), 1.26−1.45, 1.88−2.02, 2.15−2.45 (2 m, 2 H, 2 H, 3 H, 4-H, 5-H, 6-H), 5.76 (dt, *J* = 5.8, 2.2 Hz, 1 H, 2-H). ^{13}C NMR (75.5 MHz): δ = 27.2 (q, C*Me*$_3$), 24.1, 25.4, 28.6 (3 t, C-3, C-5, C-6), 32.1 (s, *C*Me$_3$), 42.9 (d, C-4), 118.5 (d, C-2), 149.3 (s, C-1). IR (film): $\tilde{\nu}$ = 3100−3000 cm^{-1} (=C−H), 2965, 2930, 2875, 2850 (C−H), 1420, 1145 (SO_2), 1240, 1200 (C−F). GC/MS-data: retention time: 9.02 min (79 °C). MS (EI, 70 eV): *m*/*z* (%) = 435 (9) [M$^+$ − 1], 379 (19), 218 (10), 131 (10), 83 (16), 69 (35, CF_3^+), 57 (100) [$C_4H_9^+$], 55 (21), 41 (19). $C_{14}H_{17}F_9O_3S$ (436.3): calcd. C 38.54, H 3.93, S 7.34; found C 38.53, H 3.94, S 7.19.

Cyclohex-1-enyl Nonaflate (3c): According to Method A, **1c** (1.70 g, 10.0 mmol), [*n*Bu$_4$N]F solution (1.50 mmol) and NfF (6.04 g, 20.0 mmol) provided 1.54 g (71%) of **3c** as a colourless liquid (120 °C/24 mbar). The physical and spectroscopic data of **3c** agreed with those described in the literature.[10a]

Cyclohept-1-enyl Nonaflate (3d): According to Method A, **1d** (0.920 g, 5.00 mmol), [*n*Bu$_4$N]F solution (0.90 mmol) and NfF (3.02 g, 10.0 mmol) provided 1.40 g (71%) of **3d** as a colourless liquid (130 °C/4 mbar). The physical and spectroscopic data of **3d** agreed with those described in the literature.[10c]

3,4-Dihydronaphthalen-1-yl Nonaflate (3e): According to Method A, silyl enol ether **1e** (0.270 g, 1.24 mmol), [*n*Bu$_4$N]F solution (0.36 mmol) and NfF (0.725 g, 2.40 mmol), after purification by CC (hexane/EtOAc, 10:1), provided 0.531 g (> 99%) of **3e** as a colourless, viscous oil. ^{1}H NMR (300 MHz): δ = 2.51 (td, *J* = 8.0, 5.7 Hz, 2 H, 3-H), 2.87 (t, *J* = 8.0 Hz, 2 H, 4-H), 6.02 (t, *J* = 5.7 Hz, 1 H, 2-H), 7.18−7.15, 7.28−7.23, 7.37−7.34 (3 m, 4 H, Ar). ^{13}C NMR (75.5 MHz): δ = 22.3, 26.8 (2 t, C-3, C-4), 117.7, 121.3, 126.9, 127.8, 129.3 (5 d, C-5 to C-8, C-2), 128.7 (s, C-1), 136.2 (s, C-4a), 146.6 (s, C-8a). IR (film): $\tilde{\nu}$ = 3150 cm^{-1} (=C−H), 2950, 2840 (CH_2), 1655, 1485 (C=C), 1420, 1145 (SO_2), 1235, 1200 (C−F). GC/MS-data: retention time: 10.5 min (81 °C). MS (EI, 70 eV): *m*/*z* (%) = 428 (33) [M$^+$], 219 (24), [C_4F_9], 145 (54) [M$^+$ − $C_4F_9SO_2$], 131 (16), 115 (100) [C_9H_7], 100 (12), 91 (33) [C_7H_7], 69 (32) [CF_3], 48 (3) [SO]. $C_{14}H_9F_9O_3S$ (428.3): calcd. C 39.26, H 2.12, S 7.49; found C 39.54, H 2.08, S 7.18.

***rac*-8-Methyl-8-azabicyclo[3.2.1]oct-2-en-3-yl Nonaflate (3f):** According to Method B, *rac*-**1f** (0.850 g, 4.00 mmol), [*n*Bu$_4$N]F solution (0.15 mmol) and NfF (1.57 g, 5.20 mmol) in the presence of KF (0.200 g, 3.40 mmol) in THF (0.7 mL), after purification by kugelrohr distillation (105−108 °C/0.3 mbar), provided 1.42 g (84%) of **3f** as an orange oil. ^{1}H NMR (270 MHz): δ = 1.57−1.68, 1.88−2.27, 2.82 (2 m, d*, *J* = 17.5 Hz, 1 H, 4 H, 1 H, 4-H, 6-H, 7-H), 2.41 (s, 3 H, MeN), 3.39−3.50 (m, 2 H, 1-H, 5-H), 5.86 (d*, *J* = 5.4 Hz, 1 H, 2-H); * further splitting by multiple couplings. ^{13}C NMR (67.5 MHz): δ = 29.9, 33.0, 34.3 (3 t, C-4, C-6, C-7), 35.0 (q, MeN), 57.4, 58.2 (2 d, C-1, C-5), 120.8 (d, C-2), 146.0 (s, C-3). IR (film): $\tilde{\nu}$ = 3500−3300 cm^{-1} (=C−H), 2950, 2875, 2805 (C−H), 1420, 1145 (SO_2), 1240, 1200 (C−F). MS (EI, 80 eV): *m*/*z* (%) = 421 (4) [M$^+$], 392 (1) [M$^+$ − CH_3N], 138 (12) [M$^+$ − $CF_3(CF_2)_3SO_2$], 131 (1) [CF_2=$CFCF_2$]$^+$, 122 (5) [M$^+$ − $CF_3(CF_2)_3SO_3$], 110 (23) [M$^+$ − $CF_3(CF_2)_3SO_2$ − C_2H_4], 96 (15), 69 (6) [CF_3^+], 18 (100) [H_2O^+ or NH_4^+]. $C_{12}H_{12}F_9NO_3S$ (421.3): calcd. C 34.21, H 2.87, N 3.32; found C 33.93, H 2.85, N 3.50.

Nonaflation of 1-Trimethylsiloxycyclododec-1-ene (1g): The reaction was performed according to Method A, by treatment of **1g** (1.27 g, 5.00 mmol; *E*/*Z* = 82:18) with [$(Me_2N)_3S$][$SiMe_3F_2$] (0.65 mmol, 0.25 molar in THF/CH_2Cl_2) and NfF (3.02 g, 10.0 mmol), followed by kugelrohr distillation at 120 °C/0.001 mbar to afford a mixture of products (1.34 g). Repeated fractional distillation at 80 °C/2 mbar furnished a fraction (0.890 g) enriched in nonaflate **3g** but complete separation was not achieved, and the content of the resulting mixture of products, established by GC-MS, was: (*E*)-**3g** (29%), (*Z*)-**3g** (14%), cyclododecyne[40] (36%), cyclododeca-1,2-diene[40] (< 1%) and cyclododecanone (20%).
(*E*)-Cyclododec-1-enyl Nonaflate (3g): ^{1}H NMR (300 MHz): δ = 1.20−1.74, 2.10−2.47 (2 m, 20 H, 3-H − 12-H), 5.49 (t, *J* = 8.3 Hz, 1 H, 2-H). ^{13}C NMR (75.5 MHz): δ = 22.0, 22.9, 24.0, 24.2, 24.3, 24.7, 25.3, 25.4, 26.0, 26.4 (10 t, C-3 − C-12), 124.0 (d, C-2), 148.6 (s, C-1).
(*Z*)-Cyclododec-1-enyl Nonaflate (3g): ^{1}H NMR (300 MHz): δ = 1.20−1.74, 2.10−2.47, (2 m, 20 H, 3-H − 12-H), 5.37 (t, *J* = 7.7 Hz, 1 H, 2-H). ^{13}C NMR (75.5 MHz): δ = 22.1, 22.5, 23.9, 24.0, 24.2, 24.3, 24.4, 24.9, 25.4, 26.1 (10 t, C-3 − C-12), 123.0 (d, C-2), 150.5 (s, C-1).

Prop-1-enyl Nonaflate (3h): According to Method A, **1h** (0.355 g, 2.72 mmol; *E*/*Z* = 88:12), [*n*Bu$_4$N]F solution (0.45 mmol) and NfF (0.906 g, 3.00 mmol), after purification by kugelrohr distillation at

70 °C/20 mbar, provided 0.582 g (63%) of **3h** as a colourless oil (*E*/*Z* = 77:23). **(*E*)-3h:** ^{1}H NMR (300 MHz): δ = 1.73 (dd, *J* = 7.0, 1.8 Hz, 3 H, Me), 5.29 (qd, *J* = 7.0, 5.7 Hz, 1 H, 2-H), 6.58 (dq*, *J* = 5.7, 1.8 Hz, 1 H, 1-H); * the signal partially overlaps with signals of the *Z* isomer. ^{13}C NMR (75.5 MHz): δ = 9.6 (q, C-3), 115.1 (d, C-2), 136.5 (d, C-1). **(*Z*)-3h:** ^{1}H NMR (300 MHz): δ = 1.69 (dd, *J* = 7.2, 1.8 Hz, 3 H, Me), 5.79 (dq, *J* = 7.2, 4.6 Hz, 1 H, 2-H), 6.52 (m_c*, 1 H, 1-H); * the signal partially overlaps with the signals of the *E* isomer. ^{13}C NMR (75.5 MHz): δ = 11.7 (q, C-3), 117.5 (d, C-2), 136.7 (d, C-1). IR (film): $\tilde{\nu}$ = 3125 cm^{-1} (=C−H), 2935 (C−H), 1675 (C=C), 1390, 1145 (SO_2), 1240, 1200 (C−F). GC/MS-data: (*E*)-**3h**, retention time: 1.71 min (72 °C). MS (EI, 70 eV): *m*/*z* (%) = 340 (15) [M$^+$], 276 (8) [M$^+$ − SO_2], 219 (8) [$C_4F_9^+$], 131 (33), 119 (12) [$C_2F_5^+$], 100 (23) [$C_2F_4^+$], 69 (100) [CF_3^+], 57 (6), 41 (88) [$C_3H_5^+$], 29 (75). − (*Z*)-**3h**, retention time: 1.84 min (72 °C). MS (EI, 70 eV): *m*/*z* (%) = 340 (38) [M$^+$], 276 (15) [M$^+$ − SO_2], 219 (12) [$C_4F_9^+$], 131 (38), 119 (13) [$C_2F_5^+$], 100 (25) [$C_2F_4^+$], 69 (100) [CF_3^+], 57 (6), 41 (92) [$C_3H_5^+$], 29 (77). $C_7H_5F_9O_3S$ (340.2): calcd. C 24.72, H 1.48, S 9.43; found C 25.04, H 1.50, S 9.43.

2-Methylprop-1-enyl Nonaflate (3i): According to Method A, **1i** (0.600 g, 4.17 mmol), diluted with THF (4 mL), [*n*Bu$_4$N][$SiPh_3F_2$] solution (0.50 mmol; 0.25 molar solution in THF) and NfF (1.81 g, 6.00 mmol), after 21 h at room temp. and purification by kugelrohr distillation at 80 °C/10 mbar, provided 1.34 g (90%) of **3i** as a colourless oil. ^{1}H NMR (300 MHz): δ = 1.69 (d, *J* = 1.3 Hz, 3 H, *E*-Me), 1.75 (d, *J* = 1.1 Hz, 3 H, *Z*-Me), 6.42 (m_c, 1 H, 1-H). ^{13}C NMR (75.5 MHz): δ = 15.6, 19.0 (2 q, 2 Me), 125.9 (s, C-2), 130.8 (d, C-1). The physical and spectroscopic data of **3i** were consistent with those described in the literature.[10a]

Oct-1-enyl Nonaflate (3j): According to Method A, **1j** (0.500 g, 2.50 mmol; *E*/*Z* = 4:96), [*n*Bu$_4$N]F solution (0.45 mmol) and NfF (0.906 g, 3.00 mmol), after purification by kugelrohr distillation at 100 °C/1 mbar, provided 0.893 g (87%) of **3j** as a colourless oil (*E*/*Z* = 8:92). **(*Z*)-3j:** ^{1}H NMR (300 MHz): δ = 0.82−1.00, 1.21−1.48 (2 m, 4 H, 7 H, 4-H − 8-H), 2.19 (q, *J* = 7.5 Hz, 2 H, 3-H), 5.23 (td, *J* = 7.5, 5.7 Hz, 1 H, 2-H), 6.57 (d, *J* = 5.7 Hz, 1 H, 1-H). ^{13}C NMR (75.5 MHz): δ = 13.9 (q, C-8), 22.5, 24.1, 28.4, 28.7, 31.5 (5 t, C-3 − C-7), 120.3 (d, C-2), 135.5 (d, C-1). **(*E*)-3j:** ^{1}H NMR (300 MHz): δ = 0.82−1.00, 1.58−1.71 (2 m, 4 H, 7 H, 4-H − 8-H); 2.05 (q, *J* = 7.8 Hz, 2 H, 3-H), 5.78 (td, *J* = 12.1, 7.8 Hz, 1 H, 2-H), 6.56 (d*, 1 H, 1-H); * the coupling constant could not be determined owing to very low intensity. ^{13}C NMR (75.5 MHz): δ = 13.8 (q, C-8), 20.4, 26.5, 28.5, 29.0, 31.5 (5 t, C-3 − C-7), 122.5 (d, C-2), 136.2 (d, C-1). IR (film): $\tilde{\nu}$ = 3120 cm^{-1} (=C−H), 2960, 2935, 2860 (C−H), 1669 (C=C), 1430, 1130 (C−F), 1240, 1205 (SO_2). GC/MS-data: (*Z*)-**3j**, retention time: 9.67 min (167 °C). MS (EI, 70 eV): *m*/*z* (%) = 410 (< 1) [M$^+$], 274 (10), 218 (19), 131 (23), 109 (21), 81 (40), 69 (100) [CF_3^+], 55 (52) [$C_4H_9^+$], 43 (52) [$C_3H_7^+$], 29 (24) [$C_2H_5^+$]. **(*E*)-3j:** retention time: 10.02 min (170 °C). MS (EI, 70 eV): *m*/*z* (%) = 410 (< 1) [M$^+$], 274 (25), 218 (28), 131 (30), 109 (12), 100 (13), 81 (26), 69 (100) [CF_3^+], 55 (43) [$C_4H_9^+$], 43 (32) [$C_3H_7^+$], 29 (17) [$C_2H_5^+$]. $C_{12}H_{15}F_9O_3S$ (410.3): calcd. C 35.13, H 3.68, S 7.81; found C 35.55, H 3.79, S 7.32.

Non-1-enyl Nonaflate (3k): According to Method A, **1k** (0.535 g, 2.50 mmol; *E*/*Z* = 93:7), [*n*Bu$_4$N]F solution (0.45 mmol) and NfF (0.906 g, 3.00 mmol), after purification by kugelrohr distillation at 80 °C/1 mbar, provided 0.827 g (78%) of **3k** as a colourless oil (*E*/*Z* = 95:5). **(*E*)-3k:** ^{1}H NMR (300 MHz): δ = 0.87 (t, *J* = 6.0 Hz, 3 H, 9-H), 1.27−1.46 (m, 10 H, 4-H − 8-H), 2.03 (qd, *J* = 7.7, 1.2 Hz, 2 H, 3-H), 5.76 (dt, *J* = 11.9, 7.7 Hz, 1 H, 2-H), 6.53 (br. d, *J* = 11.9 Hz, 1 H, 1-H). ^{13}C NMR (75.5 MHz): δ = 14.0 (q, C-9), 22.5, 26.5, 28.7, 28.8, 28.9, 31.7 (6 t, C-3 − C-8), 122.5 (d, C-2), 136.2 (d, C-1). The following signals can be assigned to the nonaflate **(*Z*)-3k:** ^{1}H NMR (300 MHz): δ = 0.92 (t*, *J* = 6.0 Hz, 3 H, 9-H), 5.21 (td, *J* = 7.7, 5.5 Hz, 1 H, 2-H), 6.54 (m_c*, 1 H, 1-H); * the signal partially overlaps with the signals of the *E* isomer. IR (film): $\tilde{\nu}$ = 3150 cm^{-1} (=C−H), 2960, 2930, 2860 (C−H), 1665 (C=C), 1430, 1145 (SO_2), 1240, 1205 (C−F). GC/MS-data: (*E*)-**3k**, retention time: 6.99 min (140 °C). MS (EI, 70 eV): *m*/*z* (%) = 424 (< 1) [M$^+$], 219 (8) [$C_4F_9^+$], 131 (21), 95 (23), 82 (38), 69 (100) [CF_3^+], 55 (63) [$C_4H_9^+$], 43 (67) [$C_3H_7^+$], 29 (37) [$C_2H_5^+$]. (*Z*)-**3k**, retention time: 6.49 min (135 °C). MS (EI, 70 eV): *m*/*z* (%) = 424 (38) [M$^+$], 219 (10) [$C_4F_9^+$], 131 (23), 95 (23), 82 (38), 69 (100) [CF_3^+], 55 (48) [$C_4H_9^+$], 43 (80) [$C_3H_7^+$], 29 (38) [$C_2H_5^+$]. $C_{13}H_{17}F_9O_3S$ (424.3): calcd. C 36.80, H 4.04, S 7.56; found C 37.07, H 4.07, S 7.21.

3,3-Dimethylbuten-2-yl Nonaflate (3m): According to Method B, **3m** was prepared from **1m** (0.170 g, 1.00 mmol), [*n*Bu$_4$N]F solution (0.20 mmol) and NfF (0.400 g, 1.30 mmol) in the presence of KF (0.120 g, 2.10 mmol) in THF (0.3 mL). No aqueous workup was performed. Instead, the reaction mixture was diluted with pentane, filtered through celite and concentrated in vacuum (up to 100 mbar), and the residue was subjected to CC (pentane) to give the nonaflate **3m** (0.150 g, 39%) as a colourless liquid. The physical and spectroscopic data of **3m** agreed with those described in the literature.[10a]

Buta-1,3-dien-2-yl Nonaflate (3n): According to Method A, **1n** (0.355 g, 2.50 mmol), [*n*Bu$_4$N]F solution (0.45 mmol) and NfF (0.906 g, 3.00 mmol), after purification by kugelrohr distillation at 25 °C/20 mbar, provided 0.538 g (61%) of **3n** as a colourless, volatile liquid. ^{1}H NMR (270 MHz): δ = 5.17 (d, *J* = 3.5 Hz, 1 H, 1-H), 5.28 (dd, *J* = 3.5, 1.3 Hz, 1 H, 1-H), 5.41 (dq, *J* = 11.1, 0.7 Hz, 1 H, 4-H), 5.65 (d, *J* = 17.1 Hz, 1 H, 4-H), 6.29 (dd, *J* = 17.1, 11.1 Hz, 1 H, 3-H). ^{13}C NMR (75.5 MHz): δ = 107.0 (t, C-1), 118.7 (t, C-4), 129.1 (d, C-3), 152.1 (s, C-2). IR (film): $\tilde{\nu}$ = 3050 cm^{-1} (=C−H), 1650 (C=C), 1425, 1145 (SO_2), 1240, 1205 (C−F). GC/MS-data: retention time: 4.16 min (74 °C). MS (EI, 70 eV): *m*/*z* (%) = 352 (12) [M$^+$], 219 (10) [$C_4F_9^+$], 153 (100), 131 (27), 119 (13) [$C_2F_5^+$], 100 (20) [$C_2F_4^+$], 69 (100) [CF_3^+], 53 (50) [$C_4H_5^+$], 41 (35) [$C_3H_5^+$], 27 (16) [$C_2H_3^+$]. $C_8H_5F_9O_3S$ (352.2): calcd. C 27.28, H 1.43, S 9.10; found C 27.09, H 1.57, S 8.13.

Cation Effect on *C*- vs. *O*-Nonaflation of NfF of Enolates Derived from Methyl Ketones. 1-(Nonafluorobutanesulfonyl)propan-2-one (4l): A solution of *n*-butyllithium in hexane (2.44 molar, 4.9 mL, 12.0 mmol) was added at −78 °C to a solution of *i*Pr$_2$NH (1.58 g, 16.0 mmol) in THF (19 mL). The cooling bath was removed, the resulting mixture was allowed to warm to room temp. and then recooled to −78 °C, neat acetone (0.590 g, 10.0 mmol) was added dropwise, and the resulting mixture was stirred for 0.5 h at −78 °C. Then neat NfF (4.54 g, 15.0 mmol) was added to the generated solution of lithium propen-2-olate. The reaction mixture was stirred at −78 °C for 2 h, gradually allowed to warm to room temp. and stirred for an additional 15 h. The resultant brownish solution was then poured into a vigorously stirred mixture of pentane (100 mL) and ice/aq. H_3PO_4 (100 mL, pH = 2), the aqueous phase was extracted with pentane (3×20 mL), and the combined organic phase was dried ($MgSO_4$). ^{1}H NMR monitoring after removal of volatiles in vacuum (up to 100 mbar) showed a ratio of **3l**/**4l** of 64:36. The residue was subjected to CC (gradient elution: hexane → hexane/Et$_2$O/AcOH, 200:10:1 → hexane/Et$_2$O/AcOH, 50:10:1) to give 0.850 g (25%) of the pure sulfonyl ketone **4l** as yellowish crystals, m.p. 53−57 °C. The compound **4l** existed in $CDCl_3$ solution as a 90:10 mixture of keto and enol forms. Keto tautomer, ^{1}H NMR

(270 MHz): δ = 2.49 (s, 3 H, 3-H), 4.32 (br. s, 2 H, 1-H). ^{13}C NMR (67.5 MHz): δ = 31.5 (q, C-3), 61.7 (t, C-1), 191.5 (s, C-2). Enol tautomer, ^{1}H NMR (270 MHz): δ = 2.16 (s, 3 H, 3-H), 5.25 (br. s, 1 H, 1-H), 10.16 (br. s, 1 H, OH). ^{13}C NMR (67.5 MHz): δ = 22.8 (q, C-3), 87.5 (d, C-1); C-2 signal was not observed due to its low intensity. IR (KBr): $\tilde{\nu}$ = 3445 cm^{-1} (br., OH), 2980, 2930 (C−H), 1730 (C=O), 1360, 1140 (SO_2), 1205 (br., C−F). MS (EI, 80 eV): *m*/*z* (%) = 340 (< 1) [M^+], 325 (3) [$M^+ - CH_3$], 219 (11) [$CF_3(CF_2)_3]^+$, 200 (< 1) [$C_4F_8]^+$, 181 (< 1) [$C_4F_7]^+$, 169 (1) [$CF_3(CF_2)_2]^+$, 131 (13) [CF_2=$CFCF_2]^+$, 121 (41) [$M^+ - CF_3(CF_2)_3$], 119 (4) [$CF_3CF_2]^+$, 105 (1), 100 (8) [$C_2F_4]^+$, 69 (29) [CF_3^+], 57 (6) [$M^+ - CF_3(CF_2)_3SO_2$], 42 (100) [CH_2=C=O]$^+$. $C_7H_5F_9O_3S$ (340.2): calcd. C 24.72, H 1.48; found C 24.92, H 1.34.

1-(Nonafluorobutanesulfonyl)-3,3-dimethylbutan-2-one (4m): As described above, a solution of *n*-butyllithium in hexane (2.40 molar, 5.0 mL, 12.0 mmol), *i*Pr$_2$NH (1.58 g, 16.0 mmol), 3,3-dimethylbutan-2-one (1.00 g, 10.0 mmol) and NfF (4.54 g, 15.0 mmol) in THF (19 mL) at −78 °C provided **4m**, which was isolated by CC (gradient elution: hexane → hexane/Et$_2$O/AcOH, 200:10:1) as colourless crystals, m.p. 55−57 °C in 47% yield (1.80 g). The compound existed in $CDCl_3$ solution as an 82:18 mixture of keto and enol forms. Keto tautomer, ^{1}H NMR (270 MHz): δ = 1.231 (s, 9 H, CMe_3), 4.47 (t, *J* = 1.2 Hz*, 2 H, 1-H). ^{13}C NMR (125 MHz): δ = 25.4 (q, C*Me*$_3$), 45.9 (s, *C*Me$_3$), 55.5 (t, C-1), 199.8 (s, C-2) . ^{19}F NMR (470 MHz): δ = −126.37 (t**, *J* = 13.8 Hz, 2 F, C^3*F*$_2$), −121.69 (m, 2 F, 2 F, C^2*F*$_2$), −112.38 (br. t, *J* = 13.8 Hz, 2 F, C^1*F*$_2$), −81.18 (tt, *J* = 9.7, 2.2 Hz, 3 F, C*F*$_3$); * long range coupling with ^{19}F nuclei; ** further complex splitting by ^{19}F−^{19}F and/or ^{1}H−^{19}F couplings. Enol tautomer, ^{1}H NMR (270 MHz): δ = 1.227 (s, 9 H, CMe_3), 5.30 (s, 1 H, 1-H), 10.33 (s, 1 H, OH). ^{13}C NMR (125 MHz): δ = 27.1 (q, C*Me*$_3$), 38.8 (s, *C*Me$_3$), 84.2 (d, C-1), 188.9 (s, C-2). ^{19}F NMR (470 MHz): δ = −126.50 (t*, *J* = 14.0 Hz, 2 F, C^3*F*$_2$), ca. −121.7** (m, 2 F, 2 F, C^2*F*$_2$), −115.29 (t*, *J* = 13.7 Hz, 2 F, C^1*F*$_2$), −81.22 (tt, *J* = 9.7, 2.4 Hz, 3 F, C*F*$_3$); * further complex splitting by ^{19}F−^{19}F couplings. ** the exact chemical shift could not be determined owing to shielding by the corresponding signal of the keto tautomer. IR (KBr): $\tilde{\nu}$ = 3420 cm^{-1} (br., OH), 2980, 2925 (C−H), 1930, 1720 (C=O), 1365, 1140 (SO_2), 1235, 1205 (C−F). MS (EI, 80 eV): *m*/*z* (%) = 382 (3) [M^+], 367 (3) [$M^+ - CH_3$], 325 (4) [$M^+ - t$Bu], 219 (2) [$CF_3(CF_2)_3]^+$, 177 (3), 163 (100) [$M^+ - CF_3(CF_2)_3$], 131 (4) [CF_2=$CFCF_2]^+$, 121 (3), 119 (2) [$CF_3CF_2]^+$, 105 (2), 100 (2) [$C_2F_4]^+$, 99 (3) [$M^+ - CF_3(CF_2)_3SO_2$], 85 (3) [*t*BuCO]$^+$, 69 (12) [CF_3^+], 57 (67) [*t*Bu$^+$]. $C_{10}H_{11}F_9O_3S$ (382.3): calcd. C 31.42, H 2.90; found C 31.22, H 2.65.

Reaction between Potassium 3,3-Dimethylbut-1-en-2-olate and NfF: Potassium ethoxide (0.510 g, 6.00 mmol) was dried at 100 °C (0.04 mbar) for 1 h, after which THF (10 mL) was added. Silyl enol ether **1m** (1.04 g, 6.00 mmol) was added dropwise at −40 °C to the resulting suspension. The mixture was allowed to warm to 5 °C over 1 h, resulting in a nearly homogeneous, bright yellow solution of the potassium enolate. After the mixture had been cooled to −70 °C, neat NfF (2.20 g, 7.20 mmol) was added, and the reaction mixture was allowed to warm to 10 °C over 2 h and stirred at this temperature for 7 h. The resultant yellow solution was then poured into a vigorously stirred mixture of pentane (100 mL) and ice/aq. H_3PO_4 (100 mL, pH = 2), the aqueous phase was extracted with pentane (3×20 mL), and the combined organic phase was dried ($MgSO_4$). ^{1}H NMR monitoring after removal of volatiles in vacuum (up to 100 mbar) showed the **3m**/**4m** ratio to be 75:25. The residue was subjected to CC (gradient elution: pentane → hexane/Et$_2$O/AcOH, 200:10:1) to give the pure nonaflate **3m** (1.07 g, 47%), sulfonyl ketone **4m** (0.380 g, 17%) and 3,3-dimethyl-1-(1,1,2,2,3,3,4,4-octafluorobutane-1-sulfonyl)butan-2-one (**6**, 0.051 g, 2%). Compound **6** (yellowish oil, slowly crystallized upon storage in a refrigerator) existed in $CDCl_3$ solution as an 84:16 mixture of keto and enol forms. Keto tautomer, ^{1}H NMR (270 MHz): δ = 1.23 (s, 9 H, CMe_3), 4.45 (t, *J* = 1.2 Hz*, 2 H, 1-H), 6.09 [tt, $^2J(^1H-^{19}F)$ = 51.8, $^3J(^1H-^{19}F)$ = 5.0 Hz, 1 H, CF_2H]. ^{13}C NMR (125 MHz): δ = 25.5 (q, C*Me*$_3$), 45.9 (s, *C*Me$_3$), 55.4 (t, C-1), 107.4 [dtt, $^1J(^{13}C-^{19}F)$ = 255, $^2J(^{13}C-^{19}F)$ = 32 Hz, *C*F$_2$H], 199.8 (s, C-2). ^{19}F NMR (470 MHz): δ = −137.49 [d**, $^2J(^1H-^{19}F)$ = 51.8 Hz, 2 F, C*F*$_2$H], −129.36, −122.19 (2 s**, 2 F, 2 F, C^2*F*$_2$, C^3*F*$_2$), −112.48 (br. t, *J* = 12.8 Hz, 2 F, C^1*F*$_2$); * long range coupling with ^{19}F nuclei; ** further complex splitting by ^{19}F−^{19}F and/or ^{1}H−^{19}F couplings. Enol tautomer, ^{1}H NMR (270 MHz): δ = 1.22 (s, 9 H, CMe_3), 5.29 (s, 1 H, 1-H), 6.07 [tt, $^2J(^1H-^{19}F)$ = 51.8, $^3J(^1H-^{19}F)$ = 5.1 Hz, 1 H, CF_2H], 10.32 (s, 1 H, OH). ^{13}C NMR (125 MHz): δ = 27.1 (q, C*Me*$_3$), 38.7 (s, *C*Me$_3$), 84.3 (d, C-1), 188.7 (s, C-2); *C*F$_2$H signal was not observed due to its low intensity or shielding by the corresponding signal of the keto tautomer. ^{19}F NMR (470 MHz): δ = −137.53 [d*, $^2J(^1H-^{19}F)$ = 51.8 Hz, 2 F, C*F*$_2$H], −129.74, −122.33 (2 s*, 2 F, 2 F, C^2*F*$_2$, C^3*F*$_2$), −115.30 (t*, *J* = 12.7 Hz, 2 F, C^1*F*$_2$); * further complex splitting by ^{19}F−^{19}F and/or ^{1}H−^{19}F couplings.

Nonaflations of 1l and 1m Promoted by Tetrabutylammonium Hydrogen Difluoride: As described for Method B, 1 mmol scale in THF (0.3 mL), in the presence of KF (0.120 g, 2.10 mmol), [*n*Bu$_4$N][HF_2] (0.105 mL) in place of [*n*Bu$_4$N]F and NfF (0.400 g, 1.30 mmol). After acidic aqueous workup, pentane extraction, drying and evaporation as described above, the contents of the organic phases were analysed by ^{1}H NMR. CC (pentane) provided 0.110 g (32%) of **3l** or 0.150 g (40%) of **3m** as pure, colourless liquids.

Dibenzo-18-crown-6/KF as a Fluoride Promoter. Propen-2-yl Nonaflate (3l): Potassium fluoride (0.058 g, 1.00 mmol) was dried at 230 °C (0.04 mbar) for 1 h. After this had cooled to room temp., dibenzo-18-crown-6 (0.072 g, 0.20 mmol) was added, and the mixed powder was heated at 120 °C (0.04 mbar) for 10 min, after which THF (1 mL) and silyl enol ether **1l** (0.134 g, 1.00 mmol) were added consecutively at room temp. The reaction mixture was stirred for 10 min at room temp., cooled to 0 °C, and NfF (0.404 g, 1.30 mmol) was added dropwise. After warming up to room temp., the mixture was stirred for 70 h. Acidic aqueous workup as described in the procedure for the synthesis of **3m**/**4m**, filtration through celite, pentane extraction, drying and evaporation (up to 100 mbar) gave crude **3l** (no signals of the ketone **4l** were detected by ^{1}H NMR). Pure nonaflate **3l** was isolated by CC (pentane) in 68% yield (0.231 g) as a colourless, volatile liquid. ^{1}H NMR (270 MHz): δ = 2.10 (d, *J* = 1.1 Hz, 3 H, 3-H), 4.95 (dq, *J* = 3.4, 1.1 Hz, 1 H, 1-H), 5.09 (d, *J* = 3.4 Hz, 1 H, 1-H). ^{13}C NMR (67.5 MHz): δ = 20.1 (q, C-3), 105.4 (t, C-1), 153.3 (s, C-2). IR (film): $\tilde{\nu}$ = 3000−2935 cm^{-1} (C−H), 1679 (C=C), 1422, 1145 (SO_2), 1240, 1207 (C−F). MS (EI, 80 eV): *m*/*z* (%) = 340 (5) [M^+], 276 (6) [$M^+ - SO_2$], 219 (7) [$CF_3(CF_2)_3]^+$, 131 (100) [CF_2=$CFCF_2]^+$, 119 (7) [$CF_3CF_2]^+$, 100 (10) [$C_2F_4]^+$, 81 (13) [$C_2F_3]^+$, 77 (8) [$FCH_2C(Me)$=$OH]^+$, 75 (13) [$C_3H_4FO]^+$, 73 (50) [O=$CHC(Me)$=$OH]^+$, 69 (58) [CF_3^+], 64 (4) [SO_2^+], 57 (6) [$M^+ - CF_3(CF_2)_3SO_2$], 43 (3) [MeC≡O]$^+$, 42 (16) [CH_2=C=O]$^+$, 41 (5) [CH_2=$CHCH_2]^+$, 40 (75) [MeC≡CH]$^+$ or [CH_2=C=$CH_2]^+$, 39 (4) [$C_3H_3]^+$, 38 (10) [$C_3H_2]^+$ or [F_2^+], 31 (18) [$CH_3O]^+$ or [CF^+], 28 (8) [CO^+] or [$C_2H_4]^+$, 27 (51) [$C_2H_3]^+$, 26 (8) [$C_2H_2]^+$. HRMS: calcd. for $C_7H_5F_9O_3S$ 339.98157; found 339.98333.

3,3-Dimethylbut-2-enyl Nonaflate (3m): A mixture of KF (0.058 g, 1.00 mmol) and dibenzo-18-crown-6 (0.072 g, 0.20 mmol) was

dried as described above, and a mixture of DMF/THF 1:1 (1 mL) was added. After this had been cooled to 0 °C, silyl enol ether **1m** (0.170 g, 1.00 mmol) was added, and the resulting suspension was stirred at 0−5 °C for 10 min. Neat NfF (0.440 g, 1.40 mmol) was added dropwise, and the resulting mixture was allowed to warm to room temp. and stirred at this temperature for 70 h. Workup and purification as described above provided 0.244 g (64%) of nonaflate **3m**.

Synthesis of Nonaflates from Ketones. Deprotonation with LDA. Cyclohex-1-enyl Nonaflate (3c): A solution of *n*-butyllithium in hexane (2.2 molar, 2.32 mL, 5.10 mmol) was added at −78 °C to a solution of *i*Pr_2NH (0.516 g, 5.10 mmol) in THF (80 mL). After this had remained for 1 h at −78 °C, cyclohexanone (0.490 g, 5.00 mmol) was added, followed by stirring for a further 1 h at −78 °C. Neat NfF (3.02 g, 10.0 mmol) was added dropwise, and the reaction mixture was allowed to warm up to room temp. overnight and then poured into the saturated aq. NH_4Cl. The water phase was extracted with EtOAc, and the combined organic phase was washed consecutively with saturated aq. NaCl and water, dried (Na_2SO_4) and filtered. The volatiles were removed in vacuum, and the residue was subjected to kugelrohr distillation to furnish **3c** (1.23 g, 65%).

***rac*-8-Methyl-8-azabicyclo[3.2.1]oct-2-en-3-yl Nonaflate (3f):** A solution of *n*-butyllithium in hexane (2.5 molar, 5.6 mL, 14.0 mmol) was added to a solution of *i*Pr_2NH (1.54 g, 15.0 mmol) in THF (12 mL) at −78 °C. The cooling bath was removed, the resulting mixture was allowed to warm to room temp. and then once more cooled to −78 °C, and a solution of 8-methyl-8-azabicyclo[3.2.1]octan-3-one (tropinone) (1.43 g, 10.2 mmol) in THF (10 mL) was added. After warming to −50 °C for 0.5 h, it was again cooled to −78 °C, and neat NfF (6.04 g, 20.0 mmol) was added. The reaction mixture was stirred at −78 °C for 2 h, allowed gradually to warm to room temp. and stirred for additional 15 h. The resultant brown solution was then poured into a vigorously stirred mixture of hexane (100 mL) and ice/satd. aq. $NaHCO_3$ (100 mL), the aqueous phase was extracted with hexane (3×30 mL), and the combined organic phase was dried (Na_2SO_4). Filtration, removal of volatiles in vacuo and subsequent CC (gradient elution: hexane → hexane/Et_2O, 20:1 → hexane/Et_2O/Et_3N, 8:2:1) gave **3f** (3.72 g, 86%).

***rac*-8-Ethoxycarbonyl-8-azabicyclo[3.2.1]oct-2-en-3-yl Nonaflate (3o):** As described above, a solution of *n*-butyllithium in hexane (2.24 molar, 5.3 mL, 11.9 mmol), *i*Pr_2NH (1.43 g, 14.3 mmol), *N*-carbethoxy-4-tropinone (1.87 g, 9.48 mmol, added dropwise as a solution in 1.5 mL THF followed by stirring at −78 °C before the addition of NfF) and NfF (4.30 g, 14.3 mmol) in THF (20 mL) at −78 °C provided **3o**, which was isolated by CC (gradient elution: hexane → hexane/Et_2O, 20:1 → hexane/Et_2O, 8:1 → hexane/Et_2O, 4:1) in 94% yield (4.27 g) as a yellow oil. ^{1}H NMR (270 MHz): δ = 1.24 (t, *J* = 7.1 Hz, 3 H, OCH_2*Me*), 1.69−1.81, 1.98−2.06, 2.11, 2.16−2.31, 3.02 (2 m, br. d, *J* = 17.2 Hz, m, br. m, 1 H, 2 H, 1 H, 1 H, 1 H, 4-H, 6-H, 7-H), 4.13 (br. q, *J* = 7.1 Hz, 2 H, OCH_2Me), 4.40−4.66 (br. m, 2 H, 1-H, 5-H), 6.09 (br. d, *J* = 5.4 Hz, 1 H, 2-H). ^{13}C NMR (67.5 MHz): δ = 14.5 (q, OCH_2*Me*), 28.9, 34.8, 36.5 (3 br. t, C-4, C-6, C-7), 51.8, 51.9 (2 d, C-1, C-5), 61.4 (t, OCH_2Me), 123.2 (br. d, C-2), 154.1 (s, C-3 or C=O); one of the carbon signals (C-3 or C=O) was not observed due to overlapping or strong broadening. IR (film): $\tilde{\nu}$ = 3600−3400 cm^{-1} (=C−H), 3075, 2985, 2920, 2880 (C−H), 1710 (br., C=O), 1420, 1145 (SO_2), 1240, 1200 (C−F). MS (EI, 80 eV): *m*/*z* (%) = 479 (40) [M^+], 450 (5) [M^+ − Et], 434 (3) [M^+ − OEt], 406 (< 3) [M^+ − CO_2Et], 391 (5) [M^+ − CF_4], 378 (7) [M^+ − CH_2NCO_2Et], 314 (4) [M^+ − CH_2NCO_2Et − SO_2], 219 (5) [$CF_3(CF_2)_3]^+$, 196 (21) [M^+ − $CF_3(CF_2)_3SO_2$], 180 (9) [M^+ − $CF_3(CF_2)_3SO_3$], 168 (28) [M^+ − $CF_3(CF_2)_3SO_2$ − CO], 154 (100) $[C_8H_{12}NO_2]^+$, 140 (4) $[C_7H_{10}NO_2]^+$, 131 (5) $[CF_2{=}CFCF_2]^+$, 126 (4) $[C_8H_{12}NO_2 - C_2H_4]^+$, 124 (4) $[C_8H_{12}NO_2 - C_2H_4 - H_2]^+$, 100 (4) $[C_2F_4^+]$, 96 (17) $[C_5H_6NO]^+$, 82 (19) $[C_5H_8N]^+$, 80 (7) $[C_5H_6N]^+$, 79 (7) $[C_5H_5N]^+$, 69 (17) $[CF_3^+]$, 68 (8) $[C_4H_6N]^+$, 67 (6) $[C_4H_5N]^+$, 28 (20) $[HC{\equiv}NH]^+$ or $[CO^+]$ or $[C_2H_4]^+$, 27 (5) $[C_2H_3]^+$ or $[HCN]^+$, 26 (5) $[C_2H_2]^+$ or $[CN^+]$. $C_{14}H_{14}F_9NO_5S$ (479.3): calcd. C 35.08, H 2.94, N 2.92; found C 35.07, H 2.74, N 2.72.

Nonaflation in the Presence of DBU. Cyclohex-1-enyl Nonaflate (3c): A solution of cyclohexanone (0.245 g, 2.50 mmol) and DBU (0.456 g, 3.00 mmol) in toluene (5 mL) was warmed, and neat NfF (0.906 g, 3.00 mmol) was added at 85 °C over 3.5 h, followed by stirring at this temperature overnight. Direct kugelrohr distillation of the reaction mixture gave **3c** (0.439 g, 48%).

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[1] *N,N*-Bis(trifluoromethanesulfonyl)aniline (*N*-phenyltriflimide) is perhaps the most popular tool for transfer of a triflyl group to an enolate oxygen, although *N*-(5-chloro-2-pyridyl)triflimide and *N*-(2-pyridyl)triflimide appear to be more efficient at low temperature; see ref.[4b] and references cited therein.

[2] According to recent catalogues of chemical suppliers, the prices of these aryl triflimides are approximately 5−15 times higher than that of Tf_2O.

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[7] Nonafluorobutanesulfonyl fluoride is slightly cheaper per mmol than Tf_2O.

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[34] The observed inertness of the *tert*-butyldimethylsilyl enol ethers in fluoride-induced nonaflation with NfF provides evidence of high chemoselectivity of the reaction, which may be useful in synthesis when the selective transformation of a trimethyl silyl enol functionality in the presence of a TBDMS ether is required.

[35] The sulfur atom in nonafluorobutanesulfonyl fluoride is surrounded with highly electronegative substituents and so may be prone to form intermediate five-coordinated *S*-centred *ate* complexes followed by C−S bond cleavage: $CF_3(CF_2)_3SO_2F + F^- \rightarrow [CF_3(CF_2)_3SO_2F_2]^- \rightarrow [CF_3(CF_2)_2CF_2]^- + SO_2F_2$. This kind of precomplexation followed by fragmentation may interfere the enolate nonaflation process when fluoride-induced enolate generation is hampered by bulky substituents at a *Si* centre, as in *tert*-butyldimethylsilyl enol ethers. For the formation of a stable five-coordinated *ate* complex from a sulfonic ester, see: C. W. Perkins, S. R. Wilson, J. C. Martin, *J. Am. Chem. Soc.* **1985**, *107*, 3209−3218. Fluoride-induced C−S bond cleavage in 2,2,2-trifluoro(1-trifluoromethyl)ethyl nonaflate, resulting in 1,1,2,2,3,3,4,4,4-nonafluorobutane, is documented in the literature: M. Hanack, J. Ullmann, *J. Org. Chem.* **1989**, *54*, 1432−1435.

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