

Synthesis and Heck Reactions of Ethenyl- and (Z)-Butadien-1-yl Nonaflate Obtained by the Fragmentation of Furan Derivatives

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Dedicated to Prof. Siegfried Hünig on the occasion of his 80th birthday

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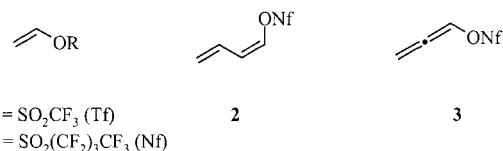
The nonaflation of lithium enolates or of silyl enol ethers, formally derived from acetaldehyde or crotonaldehyde, with nonafluorobutanesulfonyl fluoride gave ethenyl nonaflate (**1b**) and (Z)-buta-1,3-dien-1-yl nonaflate (**2**) in good yields. The required enolates were obtained by aldehyde-free routes by the lithiation of tetrahydrofuran or 2,5-dihydrofuran followed by the cyclofragmentation of the metallated heterocycles. The application of this approach to the synthesis of allenyl nonaflate **3** failed, presumably due to the intrinsic instability of this allene derivative. The nonaflates **1b** and **2** were also prepared by the fluoride-catalysed reaction of the

corresponding silyl enol ethers **5** and **7** with nonafluorobutanesulfonyl fluoride; however, the overall yields are slightly lower for these two-step pathways. The cyclofragmentation of lithiated 2,2-dimethyl-4-methylene-[1,3]dioxolane allowed the easy preparation of trimethylsiloxallene (**10**) in moderate yield. The nonaflates **1b** and **2** reacted smoothly with monosubstituted alkenes in the presence of a catalytic amount of palladium(II) acetate to give the anticipated Heck coupling products in good to moderate yields and with high stereoselectivities.

Introduction

The synthetic applicability of alkenyl triflates (trifluoromethanesulfonates) has been broadened tremendously since they were discovered to be highly reactive components in a wide variety of transition-metal-catalysed or -mediated cross-coupling reactions,^[1] thus providing a useful alternative to alkenyl bromides or iodides. Indeed, alkenyl triflates are easily available in one step from the corresponding carbonyl compounds under the action of a suitable base and an O-sulfonylating reagent,^[2,3] whereas the synthesis of alkenyl halides from carbonyl moieties often requires rather harsh reaction conditions or multi-step procedures. The strength of the base and R_FSO₂ donor can be widely varied [from LiN_iPr₂ to 2,6-di-*tert*-butyl-4-methylpyridine and from R_FSO₂F to (R_FSO₂)₂O respectively], which makes the transformation highly flexible with respect to regio- and diastereoselectivity,^[1b] and also compatible with most of the commonly used protecting groups in complex substrates.

However, despite these recent developments in the synthesis and application of perfluoroalkanesulfonates, of the simplest representatives of this subfamily, compounds **1–3**



Scheme 1

(Scheme 1), only ethenyl triflate (**1a**) and nonaflate (nonafluorobutanesulfonate) (**1b**) are described in the literature,^[4,5] with their behaviour in transition-metal-catalysed reactions not being studied at all. Moreover, neither method can be applied to the large scale preparation of **1a** and **1b**.

The enhanced leaving-group ability of R_FSO₂O (in particular of nonafluorobutanesulfonates NfO^[1b,2,6]) is well known and this property should have a promising effect on the transition-metal-catalysed C,C cross-coupling reactions of **1b–3**. For this reason, we aimed to elaborate simple and reliable methods for the preparation of **1b**, **2** and **3** in multi-gram quantities; we also performed a few typical Heck couplings to illustrate their reactivity.

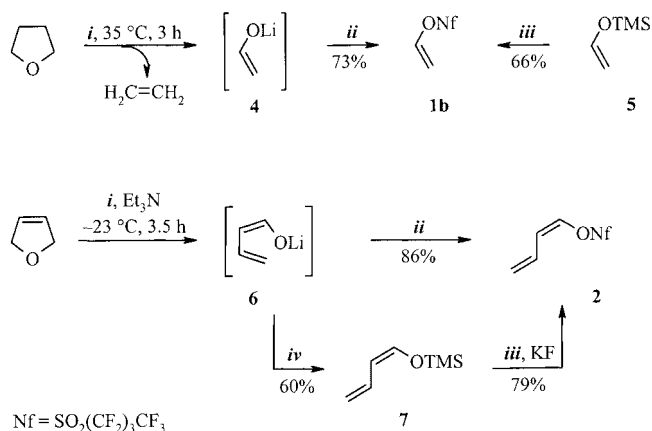
Results

Since clean preparation of the lithium enolates **4**, **6** or **8** by the direct deprotonation of the respective carbonyl precursors is known to be very difficult^[7] or impossible, we decided to generate them according to well-documented cyclofragmentations of lithiated oxygen-containing hetero-

† See ref.^[14b]

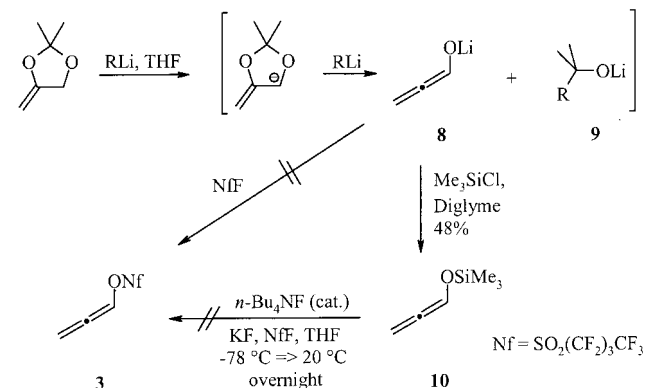
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Scheme 2. *i*: *n*BuLi, THF; *ii*: NfF, $-78\text{ }^{\circ}\text{C} \rightarrow 20\text{ }^{\circ}\text{C}$, overnight; *iii*: *n*Bu₄NF (cat.), NfF, THF, overnight; *iv*: Me₃SiCl, $-78\text{ }^{\circ}\text{C} \rightarrow 20\text{ }^{\circ}\text{C}$, overnight

cycles to give the lithium enolates **4**,^[8,9] **6**^[8,10] (Scheme 2), or **8**^[11] (Scheme 3). These enolates were directly trapped by nonafluorobutane-1-sulfonyl fluoride (NfF).^[12] We described earlier that trimethylsilyl enol ethers may be converted into the corresponding nonaflates by fluoride-catalysed reactions in the presence of NfF.^[13] This method should open up an alternative pathway to compounds **1b**, **2** and **3** via trimethylsilyl enol ethers **5**, **7**, and **10**, respectively.



Scheme 3

Our current studies towards the fluoride-catalysed nonaflation of silyl enol ethers^[14] demonstrated that the quality of the fluoride source, particularly its “dryness”, is essential for good yields of the resulting alkenyl nonaflates. To this end, commercially available *n*Bu₄NF (TBAF) appears to provide an optimum compromise concerning its price, stability in solution and reactivity. However, it cannot be prepared in an anhydrous form by thermal drying at high vacuum due to its instability at elevated temperatures.^[15] Therefore, we used freshly ground activated molecular sieves 4 Å^[16] or anhydrous potassium fluoride powder^[17] for drying the *n*Bu₄NF solutions (see the Exp. Sect.).

We prepared the nonaflates **1b** and **2** on a 20-gram scale by the direct nonaflation of the intermediate lithium enolates **4** and **6** in good to excellent yields (73% and 86%). In both cases the direct routes were superior to those with

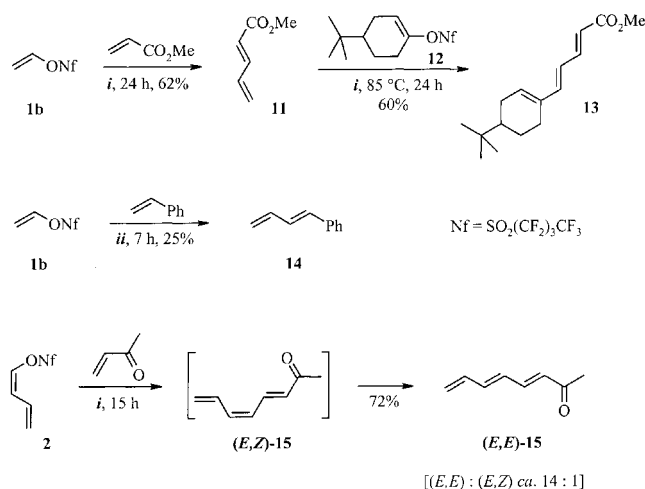
trimethylsilyloxyethene (**5**) (66% yield) or (*Z*)-1-trimethylsilyloxybuta-1,3-diene (**7**) (47% yield with respect to 2,5-dihydrofuran). Both pathways studied (see Scheme 2) resulted in the stereospecific formation of (*Z*)-buta-1,3-dien-1-yl nonaflate (**2**).^[18]

It should be noted that in an early experiment on the preparation of **2** by the interaction of intermediate **6** with NfF we obtained only about 30% yield of the desired product together with a large amount of a low-melting solid which was tentatively assigned as polytetrahydrofuran based on its ¹H NMR and ¹³C NMR spectroscopic data. This result indicated the formation of a highly electrophilic side product under the reaction conditions applied. We believe that this polymerization was induced by *n*-butyl nonaflate^[19] resulting from the interaction of NfF with lithium butoxide, which is in turn inevitably formed in commercial *n*BuLi solutions upon storage. However, the addition of triethylamine to the tetrahydrofuran solution of **6** prior to the NfF addition greatly improved the yield of **2** and completely suppressed the polymerization.^[20]

Lithiation of 2,2-dimethyl-4-methylene-[1,3]dioxolane with *s*BuLi followed by cyclofragmentation is known to lead to allenyloxyallene **8** and acetone, which in turn reacts quickly with a second equivalent of *s*BuLi resulting in an equimolar mixture of **8** and the lithium alkoxide **9** (Scheme 3).^[11] As the direct nonaflation of this mixture could cause undesirable complications in the reaction course owing to the intrinsic instability of the tertiary alkyl nonaflate formed, we first tried to synthesize and isolate pure 1-trimethylsilyloxy-1,2-propadiene (**10**), a potential precursor of the target allenyloxyallene **3**.^[21] Our optimisation of this process revealed *n*BuLi to be the reagent of choice producing a clean mixture of **8** and **9**.^[22] In order to facilitate the isolation of the low-boiling trimethylsilyl enol ether **10** by distillation, we replaced tetrahydrofuran with the considerably higher boiling diglyme before reaction^[23] of the **8**/**9** mixture with trimethylchlorosilane; this eventually allowed us to isolate pure trimethylsilyloxyallene (**10**) in 48% yield.

Not unexpectedly, all attempts to prepare the allenyloxyallene **3** were unsuccessful. The direct nonaflation of lithioxyallene **8** and the indirect route via trimethylsilyloxyallene **10** (Scheme 3) led to the complete consumption of the starting materials, but only decomposition products were isolated, indicating the inherent instability of nonaflate **3**. This may be attributed to the propensity of the C–ONf bond for easy heterolysis, which is strongly facilitated here by a $\pi_{\text{C}=\text{C}} \rightarrow \sigma^*_{\text{C}-\text{O}}$ interaction of the fixed, coplanar terminal $\pi_{\text{C}=\text{C}}$ bond with the C–O bond.^[24]

The alkenyl nonaflates **1b** and **2** are colourless, very hydrophobic, low viscosity liquids. Neat ethenyl nonaflate (**1b**) is stable upon storage at $-18\text{ }^{\circ}\text{C}$ for a long period (no visual or spectral changes), whereas buta-1,3-dien-1-yl nonaflate (**2**) gradually turns dark without any changes in the ¹H NMR spectrum. This sample decomposed violently during distillation evolving highly acidic decomposition product(s) (NfOH?). However, neat nonaflate **2** did not indicate any



Scheme 4. *i*: Pd(OAc)₂ (4–5 mol %), LiCl, Et₃N, DMF, room temp.; *ii*: Pd(OAc)₂ (4–5 mol %), KOAc, K₂CO₃, DMF, 70 °C

changes when stored over dry potassium carbonate powder at –18 °C for several months.

The nonaflates **1b** and **2** were found to react with mono-substituted alkenes under very mild phosphane-free conditions using 4–5 mol % palladium(II) acetate as catalyst leading to the anticipated coupling products **11**, **14** and **15** (Scheme 4). We were pleased to observe that the addition of **1b** and **2** to activated alkenes such as methyl acrylate or methyl vinyl ketone was effected in the presence of cheap and environmentally friendly lithium chloride^[25] as co-catalyst resulting in good yields and high (*E*)-selectivity of the products **11** and **15**. As is to be expected, nonaflate **2** seems to react with retention of the initial configuration of the C,C double bond to give (3*E*,5*Z*)-octa-3,5,7-trien-2-one (**15**) as the primary product. However, this compound is configurationally unstable under the reaction conditions and undergoes fast conversion into the thermodynamically more stable (3*E*,5*E*)-isomer of **15**.^[26] Interruption of the reaction after 3 h at room temperature (84% conversion of the starting nonaflate) reveals an (*E,E*):(*E,Z*) ratio of 2.3:1. The coupling of **1b** with styrene gave (*E*)-1-phenylbuta-1,3-diene (**14**) in lower yield, presumably owing to the competitive elimination of NfOH from **1b** under the reaction conditions (70 °C).^[27]

The nonaflate **1b** may be used as an (*E*)-CH=CH synthon in a three-component one-flask assemblage of a polyene backbone. Thus, synthesis of the double coupling product **13** was achieved simply by adding a second nonaflate **12** into the reaction mixture after the completion of the first reaction **1b** → **11**, followed by stirring for 24 h at 85 °C (Scheme 4). This three-component, one-pot method may have general importance for the synthesis of polyenes.

Conclusion

We have developed convenient methods for the synthesis of ethenyl nonaflate (**1b**) and of the previously unknown (*Z*)-buta-1,3-dien-1-yl nonaflate (**2**) on a 20-gram scale us-

ing the commercially available product nonafluorobutanesulfonyl fluoride. We also successfully demonstrated their utilisation in phosphane-free Heck-coupling reactions with monosubstituted alkenes. Other transition-metal-catalysed reactions such as Suzuki or Sonogashira couplings should also be possible with **1b** or **2** as the precursor. Although our attempts to prepare allenyl nonaflate **3** were unsuccessful, this effort led to the elaboration of a convenient procedure for the synthesis of trimethylsilyoxyallene (**10**), which should behave as a potentially valuable acrolein α -anion synthon^[11,28] and which might also be an interesting building block for cycloadditions.^[29]

Experimental Section

General Methods: NMR spectra were recorded on Bruker AC 500, WH 270, AC 250 instruments with CDCl₃ as the solvent, unless stated otherwise. ¹H and ¹³C chemical shifts are expressed in ppm downfield from tetramethylsilane ($\delta = 0$). The ¹³C signals of the CF₃(CF₂)₃ groups were not assigned due to their complex coupling with the ¹⁹F nuclei. Mass spectra were recorded with a Varian MAT 711 spectrometer. GS/MS analysis was performed with a Hewlett–Packard (HP) 5890 Series II and HP 5972 MS-Selective Detector. IR spectra were measured with Beckman IR Acculab 4, Beckman IR 5A, Perkin–Elmer IR 1420 or a Perkin–Elmer FT-IR spectrometer Nicolet 5 SXC.

The lithiation, silylation and nonaflation reactions were carried out under an atmosphere of argon in heat-gun-dried reaction flasks adding the components with a syringe. Solvents were dried by standard procedures. Methyl vinyl ketone (Fluka, assay ca. 95%, contains ca. 0.5% hydroquinone, ca. 0.5% AcOH and ca. 5% water) was treated with P₂O₅ at –78 °C and recondensed under high vacuum into a cold trap (–78 °C) containing a few crystals of hydroquinone and kept at –18 °C. Nonafluorobutanesulfonyl fluoride was obtained from Bayer AG; it can also be purchased from Aldrich. Commercially available “dry” KF (ca. 20 g) was placed in a mortar and maintained in an oven at 200 °C for 5 h. Then, whilst still hot, it was thoroughly ground into a fine powder using a hot pestle (thick leather gloves!). This pre-dried KF was used for further activation to be a co-catalyst in the following nonaflation reactions. Commercially available 2.5 M *n*BuLi and 1.3 M *s*BuLi (both from Aldrich) were titrated using the [1,10]phenanthroline method.^[30] (*Z*)-1-trimethylsilyloxybuta-1,3-diene (**7**)^[31] and 4-*tert*-butyl-1-(trimethylsilyloxy)cyclohexene were prepared according to literature procedures (ref.^[10,32] respectively). TLC analysis was performed on Merck silica gel 60 F₂₅₄ plates. Column chromatography (hereafter abbreviated as CC) was conducted on silica gel 60 (40–63 μ m, Fluka).

Preparation of the *n*Bu₄NF (TBAF) catalyst. Method 1: Drying of the 1.0 M Solution in THF: Molecular sieves (4 Å, pellets) were dried at 400 °C for 24 h and then thoroughly ground in a mortar. The fine powder obtained (approximately 15 g) was placed in a round-bottom flask (50 mL), and further activated by heating with a heat gun for a few minutes under high vacuum. A commercially available (Aldrich or Fluka, contains 3% water) 1.0 M solution of *n*Bu₄NF in THF (30 mL) was added with a syringe under an argon atmosphere. The resulting suspension was stirred vigorously at ambient temperature for 24 h, and the powder was then allowed to precipitate. The supernatant *n*Bu₄NF solution was collected by syringe, placed in another round-bottomed flask (50 mL) containing

molecular sieves (4 Å, approximately 15 g), prepared as described above, vigorously stirred at ambient temperature for at least 24 h, and the powder was again allowed to precipitate. The dried TBAF solution was collected by syringe, stored in a refrigerator and used as a catalyst in the following nonaflation reaction.

Method 2: Drying of Crystalline $n\text{Bu}_4\text{NF}\cdot 3\text{H}_2\text{O}$: $n\text{Bu}_4\text{NF}\cdot 3\text{H}_2\text{O}$ (5.60 g, 18.9 mmol) as an off-white crystalline solid (Merck) was dried in a kugelrohr apparatus at 45–48 °C (0.01 mbar) for 15 h (the temperature should not exceed 50 °C!) gradually converting into a yellowish viscous oil (4.75 g) that turns out to be a waxy yellowish solid upon storage in anhydrous conditions at 4 °C. The amount of this residue (4.75 g, quantitative yield) is in good agreement with the formula $n\text{Bu}_4\text{NF}\cdot 0.5\text{H}_2\text{O}$. The residue was then dissolved in dry THF producing a 1.05 M solution of $n\text{Bu}_4\text{NF}\cdot 0.5\text{H}_2\text{O}$ (overall volume 20 mL) which was used as a catalyst for the preparation of nonaflates from trimethylsilyl enol ethers. This solution seems to be stable upon storage in a tightly closed vial at 4 °C since its efficiency in the standard reaction (conversion of 4-*tert*-butyl-1-(trimethylsilyloxy)cyclohexene into the respective nonaflate **12**^{[14b])} remains constant for several months.

Synthesis of Ethenyl Nonaflate (1b) by direct Nonaflation of Enolate 4: A 2.20 M solution of *n*-butyllithium in hexane (40.0 mL, 88.0 mmol) was added to THF (100 mL), and the reaction mixture was stirred for 3 h at 35 °C. The resultant yellow solution was cooled (–78 °C) and neat nonafluorobutanesulfonyl fluoride (34.5 g, 114 mmol) was added with a syringe (15 min.), the temperature being maintained below –70 °C. The reaction mixture was stirred for 2 h at –78 °C, allowed to warm to 20 °C for 2 h and was stirred for a further 12 h (20 °C). The resultant brown homogeneous solution was then poured into pentane (600 mL), and an ice/satd. aq. NaHCO_3 mixture (200 mL) was added quickly with vigorous stirring. The aqueous phase was extracted with pentane (3 × 100 mL), and the combined organic phase was washed with brine (200 mL), dried (Na_2SO_4) and filtered. Pentane was evaporated from the filtrate at atmospheric pressure until the temperature of the residue rose to 72 °C. The residue was then subjected to fractional distillation to give ethenyl nonaflate **1b** (21.1 g, 73%) as a colourless liquid (b.p. 75–76 °C/80 mbar) which is sufficiently stable upon storage at –18 °C.

Synthesis of 1b Starting from Trimethylsilyloxyethene (5): NfF (0.91 g, 3.00 mmol) was added to trimethylsilyloxyethene (**5**; 0.31 g, 2.70 mmol) at 0 °C. A solution of 1 M $n\text{Bu}_4\text{NF}$ in THF (0.45 mL, 0.45 mmol, prepared by method 1) was then carefully added to the resulting two-phase mixture. This was then gradually warmed up to ambient temperature and stirred overnight (16 h). The volatile components were removed in vacuum, and the product **1b** was isolated as a colourless liquid (0.58 g, 66% yield) by kugelrohr distillation at 25 °C (40 mbar). ^1H NMR (270 MHz, C_6D_6): δ = 4.99 (dd, J = 3.6, 5.7 Hz, 1 H, 2-H), 5.26 (dd, J = 3.6, 13.2 Hz, 1 H, 2-H), 6.77 (dd, J = 5.7, 13.2 Hz, 1 H, 1-H). – ^{13}C NMR (75.5 MHz, C_6D_6): δ = 104.0 (t, C-2), 142.5 (d, C-1). – IR (film): $\tilde{\nu}$ = 3115 cm^{-1} (=C–H), 1645 (C=C), 1430, 1145 (SO_2), 1240, 1205 (C–F). – $\text{C}_6\text{H}_3\text{F}_9\text{O}_3\text{S}$ (326.1): calcd. C 22.10, H 0.93, S 9.83; found C 22.15, H 0.94, S 9.38.

Synthesis of (Z)-buta-1,3-dien-1-yl Nonaflate (2) by Direct Nonaflation of (Z)-dienolate 6: A 2.28 M solution of *n*-butyllithium in hexane (26.0 mL, 59.3 mmol) was added to a solution of 2,5-dihydrofuran (4.17 g, 59.5 mmol) in THF (40 mL) at –78 °C, and the reaction mixture was stirred for 3.5 h at –23 °C. After cooling again to –78 °C, neat Et_3N (9.10 g, 89.9 mmol) and NfF (23.6 g, 78.0 mmol) were added consecutively with a syringe within 20 min. to the resultant yellow solution, and the reaction mixture was

stirred for 2 h at –78 °C. The solution was then allowed to warm to 20 °C for 2 h and stirring was continued for a further 12 h at 20 °C. The resultant brown solution was then poured into a vigorously stirred mixture of hexane (150 mL) and ice/satd. aq. NaHCO_3 (150 mL). The aqueous phase was extracted with hexane (2 × 20 mL) and the combined organic phase was washed with a cold (0–5 °C) solution of H_3PO_4 (6.1 mL commercially available 85% H_3PO_4 in 50 mL ice/water), then with brine (100 mL), and dried (Na_2SO_4). Filtration, removal of volatiles in vacuo (up to 20 mbar) followed by fractional distillation of the residue gave (Z)-buta-1,3-dien-1-yl nonaflate (**2**) (18.1 g, 86%) as a pure colourless liquid, b.p. 67–68 °C (12.4 mbar).

Synthesis of 2 Starting from (Z)-1-trimethylsilyloxybuta-1,3-diene (7): Pre-dried KF (1.00 g) was dried further at 210–220 °C (0.03–0.05 mbar) for 2 h and allowed to cool to ambient temperature. THF (4.0 mL) and a $n\text{Bu}_4\text{NF}$ (1.05 M) solution in THF (0.95 mL, 1.00 mmol, prepared by method 2) were subsequently added. The resulting suspension was vigorously stirred at ambient temperature for 20 min before cooling to –78 °C. (Z)-1-Trimethylsilyloxybuta-1,3-diene (**7**; 2.84 g, 20.0 mmol), Et_3N (0.50 mL, 3.6 mmol) and NfF (7.91 g, 26.0 mmol) were subsequently added to the vigorously stirred reaction mixture at –78 °C. This was then gradually warmed to ambient temperature, stirred overnight and subjected to aqueous workup (50 mL hexane/30 mL satd. aq. NH_4Cl + 30 g ice). The aqueous phase was extracted with hexane (2 × 10 mL), the combined organic phase was washed with brine (20 mL) and dried (Na_2SO_4). Volatile components were removed in vacuo (up to 25 mbar) and the residue was subjected to fractional distillation to give nonaflate **2** (5.54 g, 79% yield) as a colourless liquid, b.p. 56 °C (7.1 mbar). The product should be stored at –18 °C over dry K_2CO_3 powder. Otherwise, it turns gradually dark presumably owing to the traces of NfOH slowly releasing from the product (no changes in ^1H NMR spectrum). Distillation of this dark product causes its violent decomposition accompanied by liberation of NfOH . ^1H NMR (270 MHz, C_6D_6): δ = 4.82–4.93 (m, 2 H, 4-H), 5.03 (dd, J = 5.7, 10.9 Hz, 1 H, 2-H), 6.00 (d*, J = 5.7 Hz, 1 H, 1-H), 6.35 (dddd, J = 1.0, 10.4, 10.9, 17.0 Hz, 1 H, 3-H); *further splitting by long range couplings. – ^{13}C NMR (67.5 MHz, CDCl_3): δ = 118.7, 126.5 (2 d, C-3, C-2), 122.2 (t, C-4), 134.8 (d, C-1). – IR (film): $\tilde{\nu}$ = 3120 cm^{-1} (=C–H), 1660 (C=C), 1435, 1145 (SO_2), 1250–1200 (C–F). – MS (EI, 80 eV): m/z (%) = 353 (6) [$\text{M} + 1$]⁺, 352 (57) [M^+], 288 (12) [$\text{M} - \text{SO}_2$]⁺, 219 (23) [$\text{CF}_3(\text{CF}_2)_3$]⁺, 169 (3) [C_3F_7]⁺, 150 (3) [C_3F_6]⁺, 142 (4), 131 (66) [$\text{CF}_2 = \text{CF}_2$]⁺, 119 (35) [C_2F_5]⁺, 100 (38) [C_2F_4]⁺, 69 (100) [CF_3^+] or [$\text{C}_4\text{H}_5\text{O}^+$], 53 (24) [C_4H_5^+], 41 (73) [C_3H_5^+], 39 (40) [C_3H_3^+], 27 (6) [C_2H_3^+]. – HRMS ($\text{C}_8\text{H}_5\text{F}_9\text{O}_3\text{S}$): calcd. 351.98157; found 351.98245.

Improved Synthesis of 2,2-Dimethyl-4-methylene-[1,3]dioxolane: 3-Chloropropane-1,2-diol (18.8 g, 170 mmol) was added at 0 °C to neat 2-methoxypropene (25.7 g, 357 mmol) with stirring. The reaction mixture was allowed to warm up to ambient temperature for 2 h and then stirred for an additional 15 h. Volatile components were removed in vacuo (up to 35 mbar) for 4 h at 30 °C. Solid KOH (25.2 g, 450 mmol) and DBU (5.19 g, 34.0 mmol) were added consecutively to the resulting 4-chloromethyl-2,2-dimethyl-[1,3]dioxolane, the reaction flask was equipped with a short-path Vigreux column, and the mixture was gradually warmed with vigorous stirring and subjected to fractional distillation, the desired product (b.p. 103–105 °C^[33]) being collected into a flask containing solid KOH pellets. The physical constants of the product were in good agreement with those described in the literature.^[11,33] The obtained 2,2-dimethyl-4-methylene-[1,3]dioxolane (14.0 g, 72% yield) was stored neat over KOH pellets in a tightly closed vial at –18 °C.

Synthesis of 1-Trimethylsiloxy-1,2-propadiene (10): A 2.43 M solution of *n*-butyllithium in hexane (47.0 mL, 114 mmol) was slowly added to a solution of 2,2-dimethyl-4-methylene-[1,3]dioxolane (6.85 g, 60.0 mmol) in THF (50 mL) at -78°C . The reaction mixture was gradually warmed to -23°C and stirred at this temperature for 2 h. Diglyme (20 mL) was then added and the volatile components were evaporated in vacuo (0.04–0.05 mbar) keeping the flask in a cooling bath. At the end of the evaporation, the cooling bath temperature rose to 0°C . It was then recooled to -30°C and trimethylchlorosilane (14.9 g, 137 mmol) was added with vigorous stirring. The reaction mixture was allowed to warm to ambient temperature for 2 h, stirred for further 15 h and then evaporated in vacuo (3 \rightarrow 2 mbar) into a -78°C cold trap. After warming to ambient temperature, the contents of the trap were subjected to fractional distillation to give trimethylsilyoxyallene **10** (3.65 g, 48% yield) as a colourless liquid, b.p. $50^{\circ}\text{C}/104$ mbar. ^1H NMR (270 MHz): $\delta = 0.21$ (s, 9 H, SiMe₃), 5.27 (d, $J = 6.0$ Hz, 2 H, 3-H), 6.57 (t, $J = 6.0$ Hz, 1 H, 1-H); cf. ref.^[21] ^{13}C NMR (67.5 MHz): $\delta = -0.2$ (q, SiMe₃), 87.1 (t, C-3), 114.7 (d, C-1), 204.8 (s, C-2).

Attempts to Prepare 1,2-Propadienyl nonaflate (3): An interaction of NfF with lithioxyallene **8** ($-78^{\circ}\text{C} \rightarrow 20^{\circ}\text{C}$, overnight) using both direct and reverse order of component mixing (slow addition of NfF to the THF solution of **8** and **9** and vice versa) led to the complete consumption of the starting materials but only a complex mixture of decomposition products was observed by NMR spectroscopy. The same is true of attempts to prepare the nonaflate **3** from trimethylsilyoxyallene **10** as described above for the synthesis of nonaflate **2** from the enol ether **7**.

Synthesis of Methyl (*E*)-penta-2,4-dienoate (11): LiCl (0.50 g, 11.7 mmol), Et₃N (1.58 g, 15.6 mmol), methyl acrylate (1.35 g, 15.6 mmol) and Pd(OAc)₂ (88 mg, 0.39 mmol) were added to a solution of ethenyl nonaflate (**1b**) (2.55 g, 7.80 mmol) in DMF (5.8 mL). The reaction flask was closed tightly, and the reaction mixture was vigorously stirred at ambient temperature (24 h). After consumption of the starting nonaflate (^1H NMR control) the mixture was subjected to aqueous workup (40 mL pentane/25 mL satd. aq. NH₄H₂PO₄ + 25 g ice). The water phase was then extracted with pentane (3 \times 10 mL) and the combined organic phase was washed with brine (20 mL) and dried (MgSO₄). After filtration, the volatile components were removed in vacuo (up to 30 mbar) and the product was recondensed at 0.05 mbar in a -78°C cold trap. The spectroscopic data of **11** (0.54 g, 62% yield) were consistent with those described in the literature.^[34]

Synthesis of Methyl (2*E*,4*E*)-5-(4-*tert*-butylcyclohex-1-enyl)penta-2,4-dienoate (13): Methyl (*E*)-penta-2,4-dienoate (**11**) was prepared in situ (see above) from ethenyl nonaflate (**1b**) (0.93 g, 2.90 mmol) and methyl acrylate (0.19 g, 2.20 mmol) in DMF (1.5 mL), in the presence of LiCl (0.11 g, 2.60 mmol), Et₃N (0.55 g, 5.40 mmol) and Pd(OAc)₂ (20 mg, 0.09 mmol). Then, 4-*tert*-butylcyclohex-1-enyl nonaflate (**12**) (0.78 g, 1.80 mmol) was added, and the resulting mixture was stirred for 24 h at 85°C . It was then subjected to aqueous workup (20 mL hexane/10 mL satd. aq. NaHCO₃ + 10 mL water). The water phase was extracted with hexane (2 \times 10 mL), and the combined organic phase was washed with brine (20 mL) and dried (MgSO₄). Filtration, removal of volatiles in vacuo, followed by CC (gradient elution: hexane \rightarrow hexane/Et₂O 100:1) of the residue gave product **13** (0.27 g, 60% yield) as a yellowish crystalline solid, m.p. $71-75^{\circ}\text{C}$. ^1H NMR (270 MHz): $\delta = 0.88$ (s, 9 H, CMe₃), 1.10–1.35, 1.89–2.40 (2 m, 2 H, 5 H, 3 CH₂, CH), 3.74 (s, 3 H, OMe), 5.86 (d, $J = 15.3$ Hz, 1 H, 2-H), 5.99 (m, 1 H, 2'-H), 6.20 (dd, $J = 11.2, 15.3$ Hz, 1 H, 4-H), 6.56 (d, $J =$

15.3 Hz, 1 H, 5-H), 7.34 (dd, $J = 11.2, 15.3$ Hz, 1 H, 3-H). ^{13}C NMR (67.5 MHz): $\delta = 23.6, 25.6, 28.0$ (3 t, CH₂), 27.1, 32.1 (q, s, CMe₃), 44.0 (d, CH), 51.3 (q, OMe), 119.0, 122.9, 135.6, 144.0, 145.7 (5 d, CH), 135.7 (s, C-1'), 167.7 (s, C-1). $-\text{C}_{16}\text{H}_{24}\text{O}_2$ (248.4): calcd. C 77.38, H 9.74; found C 77.26, H 9.68.

Synthesis of (*E*)-1-phenyl-1,3-butadiene (14): A mixture of KOAc (0.17 g, 1.7 mmol), K₂CO₃ (0.30 g, 2.2 mmol) and Pd(OAc)₂ (20 mg, 0.09 mmol) was added to a mixture of ethenyl nonaflate (**1b**) (0.82 g, 2.50 mmol) and DMF (5 mL). Styrene (0.27 g, 2.60 mmol) was then added, and the resulting suspension was stirred at 70°C (7 h). After cooling to ambient temperature, it was subjected to aqueous workup (ethyl acetate/water). The aqueous phase was then extracted with ethyl acetate, and the combined organic phase was washed with brine (20 mL) and dried (Na₂SO₄). Filtration, removal of volatiles in vacuo followed by CC (hexane/EtOAc 20:1) of the residue gave a colourless oil, which was further exposed to vacuum to remove residual styrene, resulting in product **14** (81 mg, 25% yield). The spectroscopic data of the product **14** were consistent with those described in the literature.^[35]

Synthesis of (3*E*,5*E*)-octa-3,5,7-trien-2-one (15): LiCl (1.29 g, 30.5 mmol), Et₃N (2.91 g, 28.8 mmol), methyl vinyl ketone (1.47 g, 21.0 mmol) and Pd(OAc)₂ (0.10 g, 0.45 mmol) were added to an emulsion of (*Z*)-buta-1,3-dien-1-yl nonaflate (**2**; 3.70 g, 10.5 mmol) in DMF (11 mL). The reaction flask was then flushed with argon for 2–3 min, closed tightly, and the reaction mixture was vigorously stirred at ambient temperature for 15 h (complete conversion of the starting nonaflate). After aqueous workup (hexane/satd. aq. NH₄Cl + ice), and triple extraction of the aqueous phase with hexane, the combined organic phase was washed with brine and dried (Na₂SO₄). After filtration and evaporation of the volatile components in vacuum, the crude product was purified by kugelrohr distillation at $65-70^{\circ}\text{C}$ (0.04 mbar) to give (3*E*,5*E*)-octa-3,5,7-trien-2-one (**15**) [0.92 g, 72% yield, (5*E*):(5*Z*) ratio ca. 14:1] as a yellowish liquid^[36] which crystallises in the freezer at -18°C .^[37] The crystalline material melts below room temperature. ^1H NMR (500 MHz): $\delta = 2.29$ (s, 3 H, Me), 5.35 (d, $J = 10.0$ Hz, 1 H, 8-H), 5.45 (d, $J = 16.8$ Hz, 1 H, 8-H), 6.17 (d, $J = 15.5$ Hz, 1 H, 3-H), 6.35 (dd, $J = 11.1, 15.0$ Hz, 1 H, 5-H), 6.45 (ddd, $J = 10.0, 10.8, 16.8$ Hz, 1 H, 7-H), 6.61 (dd, $J = 10.8, 15.0$ Hz, 1 H, 6-H), 7.16 (dd, $J = 11.1, 15.5$ Hz, 1 H, 4-H); the coupling constants indicate an (*E*)-configuration of the C-3,C-4 and C-5,C-6 double bonds. ^{13}C NMR (125 MHz): $\delta = 27.3$ (q, Me), 122.0 (t, C-8), 130.6, 130.8, 136.1, 141.7, 142.9 (5 d, CH), 198.4 (s, C-2).

Evidence for the initial formation of the expected (3*E*,5*Z*)-**15** (see Scheme 4) was obtained by an experiment at room temperature which was interrupted after 3 h [84% conversion of the starting nonaflate, (5*E*):(5*Z*) = 2.3:1]. Formation of (3*E*,5*Z*)-**15** is indicated by a downfield signal at $\delta = 7.60$ (ddd, $J = 0.9, 11.7, 15.3$ Hz, 1 H, 4-H) with a larger coupling constant (15.3 Hz), which is due to the (*E*)-configuration of the C-3,C-4 double bond. As a consequence, the remaining possibility for the second isomer [other than (3*E*,5*E*)-**15**] is (3*E*,5*Z*)-**15**. The conversion and *E/Z* ratio were determined by ^1H NMR spectroscopy on the crude reaction mixtures just after aqueous workup.

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