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Synthesis of SF_5CF_2-Containing Enones and Instability of This Group in Specific Chemical Environments and Reaction Conditions

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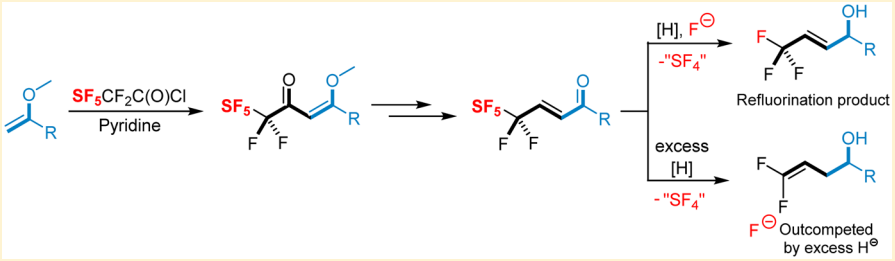
Supporting Information



ABSTRACT: The chemistry of the SF_5CF_2 moiety has been scarcely investigated. In this report, we present synthetic pathways to a variety of SF_5CF_2-substituted compounds starting from vinyl ethers and $SF_5CF_2C(O)Cl$. In specific chemical environments and under particular reaction conditions, the SF_5CF_2 moiety is unstable in downstream products resulting in the elimination of the SF_5^- anion and its decomposition to SF_4 and F^-. Surprisingly, the formed F^- can attack the intermediate difluorovinyl moiety to form trifluoromethyl substituted products. This appears to happen when an intermediate neighboring group participation involving a double bond is possible. Under slightly different conditions, the reaction stops at the stage of a difluorovinyl compound.

INTRODUCTION

The chemistry of the SF_5 group has been well explored, and a variety of compounds have been synthesized, especially aromatic derivatives.[1] Fewer examples exist on the synthesis and application of aliphatic SF_5 compounds as building blocks,[2] and only rare examples were reported where the SF_5 group is a leaving group. The examples we found in the literature involved the elimination of the SF_5 group under basic conditions[3] or its nucleophilic displacement by azide or formate, respectively.[4] Moreover, the addition of SF_5Cl to ethyl β,β-diethoxyacrylate resulted in the formation of diethyl chloromalonate. Sulfur tetrafluoride, SF_4, and EtF were detected with ^{19}F NMR spectroscopy giving evidence that the SF_5 group was probably incorporated in the β-position and then eliminated to give rise to SF_4 and F^-.[5a] Recently, Jubault, Bouillon et al. observed similar behavior (elimination of SF_5^-, decomposition, and fluoride addition) in the syntheses of isoxazolidines,[5b] and Beier et al. reported on the mild hydrolysis of the SF_5 group by water at room temperature.[5c] Previously, both an SF_5-containing carbanion and a nitrogen-based anion have been shown to eliminate SF_5^-, and both reactions resulted in crystal structure determinations of the SF_5^- anion, whereby in the latter case SF_5^- was stabilized and protected from further decomposition to SF_4 and F^- by a bulky cation, namely $Cs(18\text{-crown-}6)_2^+$.[5d,e]

We recently published syntheses of $SF_5CF_2C(O)OH$ and reactions of the corresponding acid chloride with amines and alcohols.[6] In order to further assess the utility of the acid in the preparation of more complex building blocks, we applied reactions of enol ethers **1** with $SF_5CF_2C(O)Cl$ as a starting point in further transformations. Friedel–Crafts-type acylations of ordinary alkenes using acyl chlorides or anhydrides with different Lewis acid catalysts are very well-known in the literature.[7] In addition, a series of trifluoroacetylations of electron-rich alkenes such as vinyl ethers and vinyl thioethers using trifluoroacetic anhydride have been reported.[8] In reactions with electron-deficient alkenes or arenes, decarbonylation of the acid chloride can occur as a competing process resulting in trifluoromethylation of the substrates.[9] In contrast, in the presence of particular Lewis acids, perfluoroacylation of ordinary alkenes becomes possible.[10] Our present study on reactions of $SF_5CF_2C(O)Cl$ with vinyl ethers revealed unexpected chemical behavior of the SF_5CF_2 group in the downstream products in specific structural environments and under particular reaction conditions leading to several undesired and foremost unexpected products initiated by elimination of the SF_5 group. This report might prove to be

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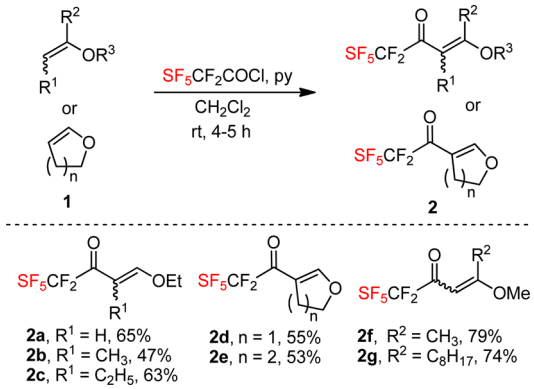
useful to other researchers attempting to introduce this interesting moiety into organic molecules as well as broaden our understanding of the chemistry of SF_5-containing structural motifs. This type of decomposition is not common for the analogous CF_3CF_2 substituent since CF_3 is not a leaving group. To the best of our knowledge, only one example (under forced conditions) has been mentioned in the literature: pyrolysis of di-α-pentafluoroethylbenzyl oxalate, via homolytic β scission, gave almost exclusively β,β-difluorostyrene in addition to trace amounts of high boiling components.[11]

RESULTS AND DISCUSSION

Compound $SF_5CF_2C(O)Cl$ was generated from the acid[6] with oxalyl chloride and reacted in situ with various vinyl ethers (**1**, R^3 = Me, Et) in the presence of pyridine to give compounds **2a**–**g** in moderate to good yields (Scheme 1).

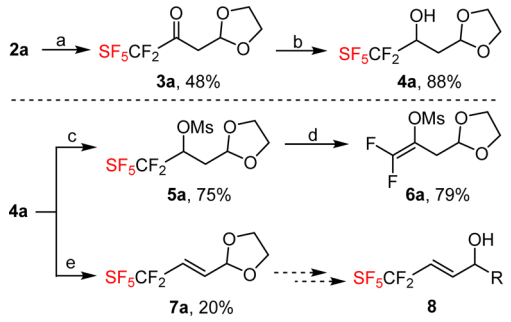
Scheme 1. Reactions of Vinyl Ethers (1, R^3 = Me, Et) with $SF_5CF_2C(O)Cl$ in the Presence of Pyridine



We focused our attention on compounds **2a**, **2f**, and **2g** in our further studies aiming to synthesize SF_5CF_2-substituted allylic alcohols **8**, which might be useful for [3,3]sigmatropic rearrangements.[12] Initially, we used compound **2a**, which after several transformations led to **7a** (Scheme 2).

After liberation of the aldehyde, different allylic alcohols **8** should be available via Grignard reactions (dashed arrows). First, **2a** was transformed to the cyclic acetal **3a** by reaction with ethylene glycol. Subsequently, the carbonyl group of **3a** was reduced with $NaBH_4$ to form **4a**, which would then be

Scheme 2. Initial Attempts Aiming To Synthesize Allylic Alcohols 8[a]

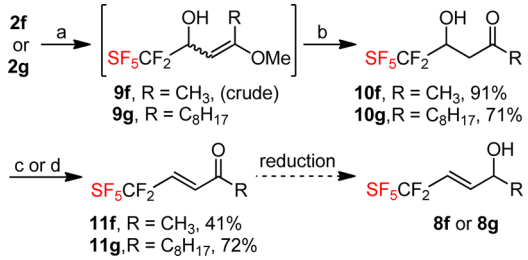


[a]Reaction conditions: (a) ethylene glycol, *p*-TsOH, PhMe; (b) $NaBH_4$, MeOH; (c) MsCl/Et_3N, CH_2Cl_2; (d) DBU, CH_2Cl_2, (e) P_2O_5, CH_2Cl_2.

dehydrated by conversion of the OH into a mesylate **5a** and its subsequent elimination with a base. Surprisingly, under these conditions, the SF_5 group was eliminated to give **6a** in 79% yield. Dehydration of **4a** under acidic conditions (P_2O_5), on the other hand, gave the desired product **7a**, but its high volatility limited the isolated yield to 20%. Presumably, after deprotection the aldehyde would be even more challenging to isolate. Therefore, we did not proceed further in this direction.

Instead, we changed our strategy and used compounds **2f** and **2g** where the R^2 substituent is present in the starting enol ether already and thus avoided highly volatile intermediates. As a model starting material, **2f**, which was prepared from 2-methoxypropene by reaction with $SF_5CF_2C(O)Cl$, was reduced to give **9f** as a crude product. After structural elucidation, the crude **9f** was hydrolyzed under acidic conditions to give the aldol **10f**, which was treated with MsCl/Et_3N to provide the crucial intermediate **11f** (via the corresponding mesylate, not shown) (Scheme 3).

Scheme 3. Synthesis of β-SF_5CF_2-Substituted α,β-Unsaturated Ketones 11[a]



[a]Reaction conditions: (a) $NaBH_4$, MeOH; (b) 2 M HCl, acetone (1:3); (c) MsCl/Et_3N, CH_2Cl_2 for **10f**; (d) P_2O_5, CH_2Cl_2 for **10g**.

It is noteworthy that comparison of the outcome of treatments of **4a** and **10f** with MsCl and an organic base proved the significant influence of different pK_a values of the C2 hydrogen atoms caused by the lack/presence of an activating carbonyl group. In contrast to the **10f** to **11f** transformation, a 2-fold excess of Et_3N was not sufficient to eliminate mesylate from **5a** in a one-pot reaction sequence. Therefore, DBU was used for this purpose as a separate step.

Subsequently, **11f** has been treated with $NaBH_4$ (0.6 equiv) in the presence of $CeCl_3{\cdot}7H_2O$ (1.0 equiv) in order to reduce the carbonyl group and to form the allylic alcohol **8f**. To our surprise, the formed product did not contain an SF_5 group anymore. The analysis of the crude reaction mixture with ^{19}F NMR spectroscopy strongly suggested formation of a CF_3 compound. This product, however, was difficult to isolate in reasonable yield. Therefore, the longer chain homologue **2g**, available from 2-methoxydec-1-ene and $SF_5CF_2C(O)Cl$, was used as the starting material in order to decrease the volatility of the final product. In this case, however, a partial formation of the CF_3 compound **11g′** occurred during synthesis of **11g** (^{19}F NMR spectrum, Figure 1). When MsCl/Et_3N or P_2O_5 was used for dehydration of **10g**, 2:1 and 3:1 mixtures of the desired **11g** and **11g′** were formed. When the reaction of **10g** with P_2O_5 in DCM was controlled by TLC and stopped immediately when all **10g** was consumed, the formation of **11g′** was prevented almost completely. The desired **11g** was isolated in 72% yield, and only a negligible amount of the undesired side product

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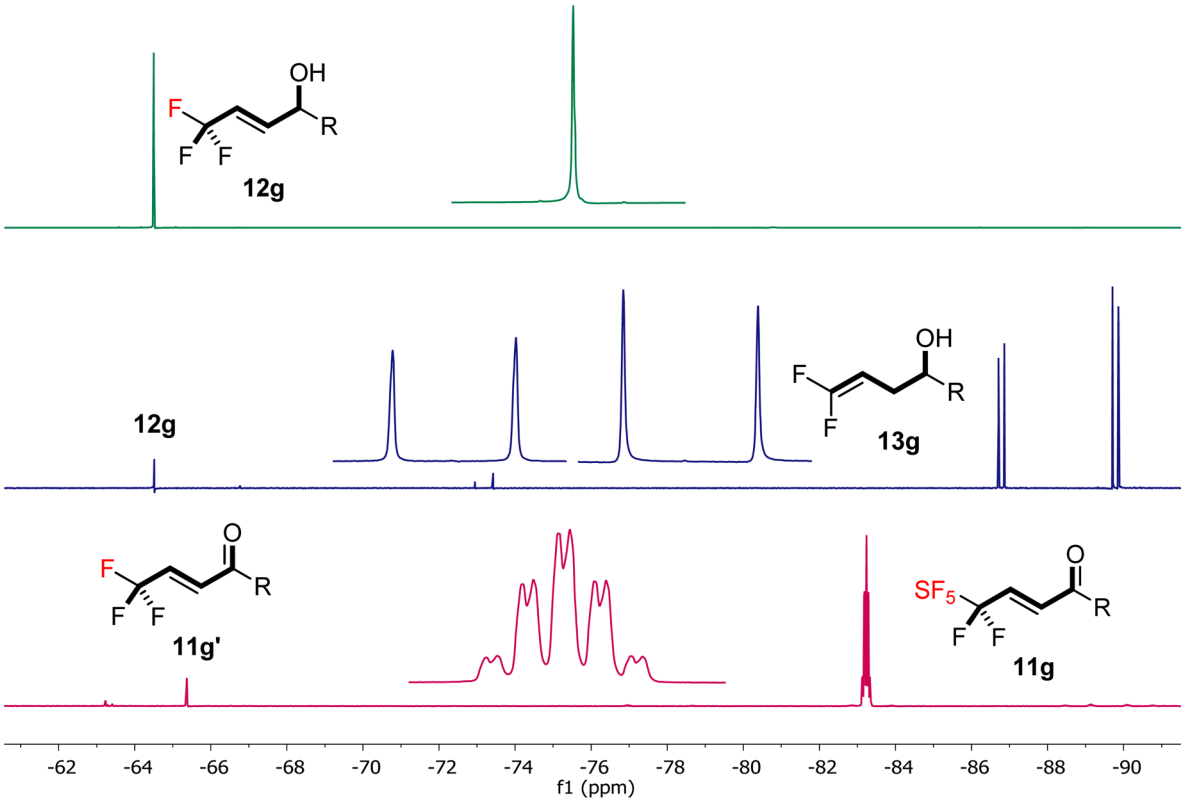


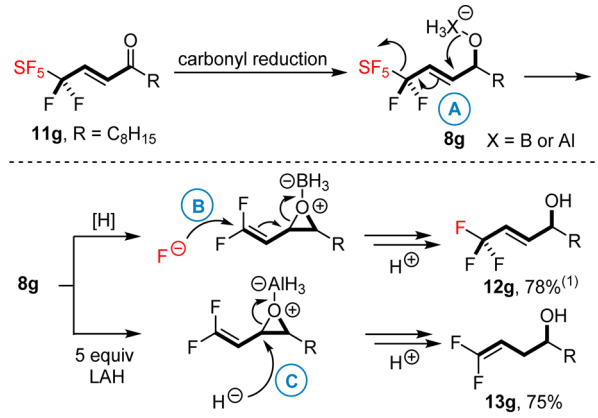
Figure 1. Selected $\{^1H\}^{19}F$ NMR data of the starting material **11g** with a characteristic quintet of multiplets belonging to the difluoromethylene group (negative part, with impurity of the CF3 compound **11g′**), reductively trapped intermediate **13g**, and the undesired substitution product **12g**.

11g′ was detected (the bottom ^{19}F NMR spectrum in Figure 1, signal at δ = −65.4 ppm).

Having **11g** in hand, it was reacted with 0.6 equiv of $NaBH_4$ in the presence of 1 equiv of $CeCl_3{\cdot}7H_2O$ in methanol in order to obtain **8g**. However, instead of the desired **8g**, the CF_3-substituted allylic alcohol **12g** was isolated with 78% yield (Scheme 4, Figure 1). The same result (58% yield) was observed when 0.6 equiv of LAH in diethyl ether was used as a reducing agent. In addition, the Meerwein−Ponndorf−Verley reduction was applied with similar results (5% yield of **12g**, see the Experimental Section for details). It is worth mentioning that reduction of the CF_3-containing analogue of compound **11f** under these conditions led to the allylic alcohol **12f**, while application of LAH in diethyl ether gave 5,5-difluoropent-4-en-2-ol (**13f**, R = Me).[13] We concluded that the basic conditions of those reactions caused the elimination of the SF_5 group. Therefore, our attention turned to acidic conditions, and $NaCNBH_3$ in methanol/HCl was used as the reducing agent, unfortunately giving the same undesired product **12g** (23% yield). These examples led us to consider that an epoxide might be involved in the formation of **12g** (Scheme 4).

We hypothesized that the formed alcoholate group (**8g**) attacks the vicinal sp^2 carbon atom, followed by double-bond migration and elimination of the SF_5^- group (A). The formed intermediate difluorovinyl oxirane reacts further with fluoride anion (B) (presumably formed by decomposition of SF_5^- to SF_4 and F^-) in an S_N2' fashion forming the CF_3 group, and the original double bond along with the hydroxyl group are recovered after quenching with a water solution to give **12g**. This uncommon mechanism[14] has been supported by using an excess of LAH in order to outcompete the fluoride anion by hydride, which opens the assumed intermediate epoxide in an S_N2 reaction (C) to give **13g** in 75% yield.

Scheme 4. Proposed Mechanism of the Formation of 12g (Top) and Experimental Support for the Assumed Formation of an Intermediate Epoxide Leading to 13g with Excess LAH (Bottom)[a]



[a][H] = (1) $NaBH_4/CeCl_3$/MeOH (**12g**, 78%); or (2) LAH (0.6 equiv)/Et_2O (**12g**, **13g** 5:1, 58%); or (3) $Al(iPrO)_3/i$PrOH (**12g**, **11g′** 1:1, 10%[b,c]); or (4) $NaBH_3CN$/MeOH/HCl (**12g**, 23%, **13g**, 4%[b]). Key: (b) by ^{19}F NMR, (c) by a different mechanism; see the explanation in the procedure in the Experimental Section.

Figure 1 depicts (from bottom to top) selected spectral data of the starting material **11g**, reductively trapped intermediate **13g**, and the undesired product **12g**.

We also carried out the reduction of **11g** with $LiBH_4$ in the presence of excess TMSCl in THF in order to trap the fluoride

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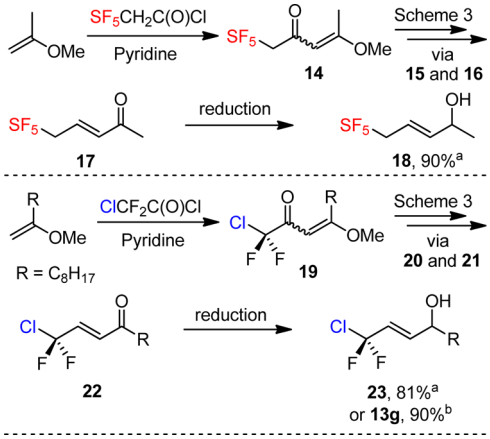
anion and to stop the reaction at the epoxide stage. Under these conditions, the epoxide was not found; however, substantial amounts of TMSF were detected by ^{19}F NMR spectroscopy alongside with several unidentified fluorinated products. Furthermore, our attempts to open the anticipated intermediate epoxide selectively by hydride in an S_N2' fashion using bulkier DIBALH was not successful and gave a 1:1 mixture of **12g** and **13g**. The DIBALH reduction in the presence of excess NaI in order to trap the epoxide (intermediate B) with iodide did not give the difluoroiodo analogue of **23**, but the homoallylic alcohol **13g** was formed exclusively.

In order to study the role of the difluoromethylene group of **11g** in all of these reactions, we prepared the methylene analogue **17** following the designed strategy (Scheme 1) using 2-methoxypropene and $SF_5CH_2C(O)Cl$[12,13b] as starting materials. Thus, enone **17**, prepared from the substitution product **14** analogously to the pathway shown in Scheme 3, was subjected to the same reduction conditions using $NaBH_4$ to give the SF_5CH_2-substituted allylic alcohol **18** in 90% yield (Scheme 5).

Scheme 5. Reductions of Compounds 17 and 22 to the Corresponding Allylic Alcohols 18, 23 or 13g[a]

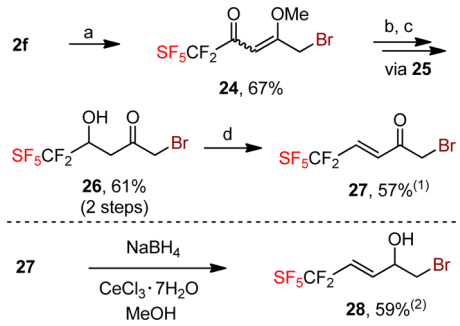


[a]Conditions: (a) $NaBH_4/CeCl_3$/MeOH; (b) LAH (5 equiv), THF.

Other SF_5-[15] as well as $ClCF_2$-substituted[16] allylic alcohols have been synthesized already under different basic conditions. For a direct comparison, nevertheless, compound **22** having the $ClCF_2$ group was prepared from **19** via **20** and **21** (see the Experimental Section) and, as it turned out, was successfully reduced to the corresponding allylic alcohol **23** in 81% isolated yield. However, elimination of chloride (via an epoxide) and its subsequent incorporation under these conditions is still possible. In order to prove whether such a process occurs, **22** has been treated with 5 equiv of LAH. The hydride opened the anticipated epoxide leading to **13g**. Thus, the difluoromethylene group plays a critical role in our systems facilitating the elimination of the SF_5 group. However, the allylic system **8g** shows similar properties to **23** in which elimination of the terminal substituent occurs. These processes are followed by reincorporation of the leaving group (Cl^-) or its decomposition products (F^- from SF_5^-) to the system (when no competing nucleophile is present).

Finally, we decided to test whether the nucleophilicity of the alcoholate (formed during reduction of **11g**) can be diminished by the inductive effect of a neighboring electron-withdrawing substituent. Hence, analogously to a recently published protocol for β-ethoxyvinyl polyfluoroalkyl ketones,[17] **2f** was reacted with bromine to give **24**. Then, following the previously used reduction/hydrolysis sequence (Scheme 3), compound **26** was synthesized. Its dehydration with P_2O_5 gave, in addition to the desired **27**, a minor amount of the CF_3-substituted **27′** already in an inseparable 18:1 mixture (Scheme 6). This

Scheme 6. β-Fluoroalkylated α,β-Unsaturated α'-Bromo Ketones[a]



[a]Reaction conditions: (a) Br_2, CH_2Cl_2; (b) $NaBH_4$, MeOH; (c) 2 M HCl, acetone (1:2), reflux; (d) P_2O_5, CH_2Cl_2, (1) 18:1 with CF_3 analogue; (e) $NaBH_4$, $CeCl_3\cdot 7H_2O$, MeOH, (2) 12:1 with CF_3 analogue.

mixture was subjected to the previously used reduction conditions. As we hoped, in this case the SF_5CF_2-substituted allylic alcohol was formed as a final product in 59% yield with minor erosion of the initial ratio of SF_5CF_2 and CF_3 products (from 18:1 in **27**:**27′** to 12:1 in **28**:**28′**). Similar results were obtained for the long-chain analogue; see the Experimental Section.

CONCLUSIONS

We used $SF_5CF_2C(O)OH$ as a starting material for the preparation of new SF_5CF_2-substituted alkoxyvinyl ketones **2** by reaction of the corresponding acid chloride with vinyl ethers **1** in the presence of pyridine. Subsequent to reduction of the keto group, hydrolysis of the vinyl ether moiety formed an aldol **9**. Its careful dehydration with P_2O_5 or by treatment of an in situ formed mesylate with base delivered β-SF_5CF_2-substituted, α,β-unsaturated ketones **11**. All our attempts to reduce the carbonyl group of **11** retaining the SF_5CF_2 group failed and delivered secondary products such as CF_3-substituted allylic alcohols **12** formed by elimination of the SF_5 group and refluorination of intermediate terminal difluorovinyl structures. The corresponding homoallylic alcohol **13** could be isolated when an excess of the reducing agent was used. In addition to the literature examples of SF_5 group elimination under basic conditions mentioned in the introduction,[3−5] and SF_5 elimination from **5a** and **11** with a base, this seems to be also an intrinsic behavior of the SF_5CF_2 moiety of **11** under reducing conditions. In contrast the SF_5CH_2 and $ClCF_2$ analogues **17** or **22**, respectively, were reduced as expected under the same reaction conditions. Reducing the nucleophilicity of the intermediate alcoholate by a bromine substituent drastically reduced the elimination of the SF_5 group from **27** during reduction to **28**. Hence, this report might provide useful information for chemists interested in the introduction of the SF_5CF_2 group into organic molecules.

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EXPERIMENTAL SECTION

General Experimental Methods. ^{1}H NMR spectra were recorded at room temperature at 300 or 400 MHz. ^{13}C and ^{19}F NMR spectra were likewise recorded at 75 or 100 and 282 MHz, respectively. The spectra were calibrated with $CDCl_3$ (7.26 and 77.16 ppm for ^{1}H and ^{13}C, respectively) with respect to TMS (^{1}H and ^{13}C NMR) and CCl_3F (^{19}F NMR) as internal standards. In the ^{19}F NMR spectra, the SF_5 group gives an AB_4 spin system caused by the axial and equatorial fluorine atoms; when the chemical shifts of A and B are relatively close to each other, one might see an asymmetric nine-line pattern for the A fluorine atom, which we call a nonet. Mass spectra (ESI-MS) were measured with a MicroTof Mass spectrometer (the measured ions were produced mostly by addition of Na cations and are reported as $[M + Na]^+$ ions). In some cases, GC/MS was used (conditions −30 m HP5 column, 50 °C for 2 min, 15 °C/min to 300 °C). GC−MS (EI^+ scan) spectra were measured with a Micromass apparatus, while atmospheric pressure chemical ionization (APCI) mass spectra were recorded on an Orbitap instrument with loop injection. TLC plates (silica gel 60 F_{254}) were used for thin-layer chromatography (dipping the developed plate in an aqueous $KMnO_4$ solution followed by heating was used for visualization). Column chromatography was carried out on silica gel 60 (particle size 0.040−0.063 mm). All reactions requiring dry conditions were carried out in glassware that was either oven-dried or prepared by Schlenk techniques under argon atmosphere. Dry DCM was distilled from CaH_2; methanol, acetone, toluene were used as received from commercial suppliers; ethanol was used in its absolute form. All reagents were commercially obtained unless otherwise stated.

Typical Procedure for Synthesis of the Enones 2a−g. Under argon atmosphere, to a stirred solution of $SF_5CF_2C(O)OH$ in dry DCM was added a catalytic amount of DMF followed by oxalyl chloride at 0 °C. The cooling bath was removed, and when the bubbling ceased (approximately 4 h), a solution of pyridine and the enol ether in DCM was added at 0 °C. Stirring was continued for several hours. Then, silica was poured to the reaction mixture and solvents were removed in vacuum. This material was worked up by column chromatography (pentane/Et_2O, either 10:1 or 20:1).

*(E)-4-Ethoxy-1,1-difluoro-1-(pentafluoro-λ^6-sulfanyl)but-3-en-2-one (**2a**).* $SF_5CF_2C(O)OH$ (832 mg, 3.75 mmol), oxalyl chloride (800 μL, 9.40 mmol), ethyl vinyl ether **1a** (810 mg, 11.25 mmol), and pyridine (1.5 mL, 18.75 mmol) gave **2a** as a colorless oil after column chromatography (pentane/Et_2O, 10:1). Yield: 668 mg (65%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91 (d, $^3J_{H,H}$ = 12.1 Hz, 1H), 5.93 (dt, $^3J_{H,H}$ = 12.2 Hz, $^4J_{H,F}$ = 1.7 Hz, 1H), 4.11 (q, $^3J_{H,H}$ = 7.0 Hz, 2H), 1.40 (t, $^3J_{H,H}$ = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 180.6 (t, $^2J_{C,F}$ = 24.4 Hz), 168.4, 120.7 (t, $^1J_{C,F}$ = 309.8 Hz), 98.1, 69.5, 14.5. ^{19}F NMR (282 MHz, $CDCl_3$): δ 67.42 (quintm, $^2J_{F,F}$ = 146.4 Hz, 1F), 42.73 (dt, $^2J_{F,F}$ = 146.4, $^3J_{F,F}$ = 12.5 Hz, 4F), −92.92 (quintdd, $^3J_{F,F}$ = 12.5, $^3J_{F,F}$ = 4.5, $^4J_{H,F}$ = 1.6 Hz, 2F). GC/MS: *m/z* (rel int, ion): 276 (100, M^+), 261 (10, M^+ − Me), 71 (100, CH = $CHOEt^+$), 127 (2, SF_5^+), 99 (85, $M^+ - SF_5CF_2$) 89 (15, SF_3^+). APCI MS: *m/z* (rel abund, ion) [$FTMS^+$] calcd 277.0133, found 277.0127 (100, $C_6H_7F_7O_2SH^+$).

*4-Ethoxy-1,1-difluoro-3-methyl-1-(pentafluoro-λ^6-sulfanyl)but-3-en-2-one (**2b**).* The carboxylic acid $SF_5CF_2C(O)OH$ (316 mg, 1.42 mmol), oxalyl chloride (192 μL, 2.27 mmol), ethyl-1-propenyl ether **1b** (245 mg, 2.84 mmol), and pyridine (226 μL, 2.84 mmol) gave **2b** as a colorless oil after column chromatography (pentane/Et_2O, 10:1). Yield: 196 mg (47%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.68 (s, 1H), 4.21 (q, $^3J_{H,H}$ = 7.1 Hz, 2H), 1.81 (s, 3H), 1.39 (t, $^3J_{H,H}$ = 7.1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 180.4 (t, $^2J_{C,F}$ = 23.0 Hz), 164.6 (t, $^3J_{C,F}$ = 8.7 Hz), 121.6 (t, $^1J_{C,F}$ = 302.2 Hz), 113.8, 71.8, 15.4, 8.9. ^{19}F NMR (282 MHz, $CDCl_3$): δ 68.32 (quintm, $^2J_{F,F}$ = 146.0 Hz, 1F), 41.50 (dt, $^2J_{F,F}$ = 145.9, $^3J_{F,F}$ = 11.3 Hz, 4F), −84.53 (quintd, $^3J_{F,F}$ = 11.5, $^3J_{F,F}$ = 4.5 Hz, 2F). ESI MS ($C_7H_9F_7O_2SNa$): calcd 313.0109, found 313.0104.

*3-(Ethoxymethylene)-1,1-difluoro-1-(pentafluoro-λ^6-sulfanyl)-pentan-2-one (**2c**).* The compound $SF_5CF_2C(O)OH$ (237 mg, 1.07 mmol), oxalyl chloride (225 μL, 2.67 mmol), 1-butenyl ethyl ether **1c** (321 mg, 3.21 mmol), and pyridine (412 μL, 5.35 mmol) gave **2c** as a colorless oil after column chromatography (pentane/Et_2O, 10:1). Yield: 190 mg (63%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.65 (s, 1H), 4.20 (q, $^3J_{H,H}$ = 7.1 Hz, 2H), 2.34 (q, $^3J_{H,H}$ = 7.4 Hz, 2H), 1.38 (t, $^3J_{H,H}$ = 7.1 Hz, 2H), 0.93 (t, $^3J_{H,H}$ = 7.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 179.8 (t, $^2J_{C,F}$ = 22.1 Hz), 164.6, 121.9 (ttd, $^1J_{C,F}$ = 309.0, $J_{C,F}$ = 21.0, $J_{C,F}$ = 1.5 Hz) 120.4, 71.9, 17.2, 15.4, 12.4. ^{19}F NMR (282 MHz, $CDCl_3$): δ 66.03 (quintm, $^2J_{F,F}$ = 145.9 Hz, 1F), 41.50 (dt, $^2J_{F,F}$ = 145.9, $^3J_{F,F}$ = 11.5 Hz, 4F), −84.25 (quintd, $^3J_{F,F}$ = 11.5, $^3J_{F,F}$ = 4.5 Hz, 2F). ESI MS ($C_8H_{11}F_7O_2SNa$): calcd 327.0266, found 327.0260, [$(C_8H_{11}F_7O_2S)_2Na$] calcd 631.0634, found 631.0628.

*1-(4,5-Dihydrofuran-3-yl)-2,2-difluoro-2-(pentafluoro-λ^6-sulfanyl)ethan-1-one (**2d**).* The carboxylic acid $SF_5CF_2C(O)OH$ (238 mg, 1.07 mmol), oxalyl chloride (230 μL, 2.70 mmol), 2,3-dihydrofuran **1d** (224 mg, 3.21 mmol), and pyridine (430 μL, 5.35 mmol) gave **2d** as a yellow oil after column chromatography (pentane/Et_2O, 10:1). Yield: 160 mg (55%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.67 (s, 1H), 4.66 (t, $^3J_{H,H}$ = 9.8 Hz, 2H), 2.97 (t, $^3J_{H,H}$ = 9.8 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 176.3 (t, $^2J_{C,F}$ = 24.9 Hz), 164.0 (t, $^3J_{C,F}$ = 9.1 Hz), 120.8 (tm, $^1J_{C,F}$ = 309.5 Hz), 115.4, 73.9, 27.6. ^{19}F NMR (282 MHz, $CDCl_3$): δ 67.43 (quint, $^2J_{F,F}$ = 146.6 Hz, 1F), 41.77 (dm, $^2J_{F,F}$ = 146.6 Hz, 4F), −88.83 (quint, $^3J_{F,F}$ = 11.5 Hz, 2F). ESI MS ($C_6H_5F_7O_2SNa$): calcd 296.9796, found 296.9791.

*1-(3,4-Dihydro-2H-pyran-5-yl)-2,2-difluoro-2-(pentafluoro-λ^6-sulfanyl)ethan-1-one (**2e**).* The carboxylic acid $SF_5CF_2C(O)OH$ (249 mg, 1.12 mmol), oxalyl chloride (240 μL, 2.80 mmol), 3,4-dihydro-2*H*-pyran **1e** (282 mg, 3.36 mmol), and pyridine (450 μL, 5.60 mmol) gave **2e** as a colorless oil after column chromatography (pentane/Et_2O, 20:1). Yield: 170 mg (53%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.93 (s, 1H), 4.22−4.13 (m, 2H), 2.32 (t, $^3J_{H,H}$ = 6.4 Hz, 2H), 1.95 (quint, $^3J_{H,H}$ = 6.0 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 179.7 (t, $^2J_{C,F}$ = 23.6 Hz), 162.7 (t, $^3J_{C,F}$ = 10.0 Hz), 121.4 (ttd, $^1J_{C,F}$ = 307.5, $^2J_{C,F}$ = 22.5, $^3J_{C,F}$ = 2.3 Hz), 113.1, 67.9, 20.7, 18.8. ^{19}F NMR (282 MHz, $CDCl_3$): δ 67.68 (quintm, $^2J_{F,F}$ = 146.3 Hz, 1F), 41.53 (dt, $^2J_{F,F}$ = 146.3, $^3J_{F,F}$ = 11.5 Hz, 4F), −85.26 (quintd, $^3J_{F,F}$ = 11.4, $^3J_{F,F}$ = 4.3 Hz, 2F. ESI MS ($C_7H_7F_7O_2SNa$): calcd 310.9953, found 310.9947.

*1,1-Difluoro-4-methoxy-1-(pentafluoro-λ^6-sulfanyl)pent-3-en-2-one (**2f**).* The carboxylic acid $SF_5CF_2C(O)OH$ (1.41 g, 6.36 mmol), oxalyl chloride (1.35 mL, 15.89 mmol), methoxypropene **1f** (1.37 g, 19.08 mmol), and pyridine (2.54 mL, 31.8 mmol) gave **2f** as a pale yellow oil after column chromatography (pentane/Et_2O, 10:1). Yield: 1.37 g (79%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.74 (s, 1H), 3.80 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 182.1, 179.1 (t, $^2J_{C,F}$ = 22.6 Hz), 120.8 (tm, $^1J_{C,F}$ = 309.8 Hz), 92.2, 56.7, 21.3. ^{19}F NMR (282 MHz, $CDCl_3$): δ 67.49 (quintt, $^2J_{F,F}$ = 146.0, $^3J_{F,F}$ = 4.7 Hz, 1F), 42.11 (dt, $^2J_{F,F}$ = 146.0, $^3J_{F,F}$ = 12.7 Hz, 4F), −92.48 (quintdd, $^3J_{F,F}$ = 12.7, $^3J_{F,F}$ = 4.6, $J_{H,F}$ = 1.6 Hz, 2F). ESI MS ($C_6H_7F_7O_2SNa$): calcd 298.9953, found 298.9947.

*1,1-Difluoro-4-methoxy-1-(pentafluoro-λ^6-sulfanyl)dodec-3-en-2-one (**2g**).* The carboxylic acid $SF_5CF_2C(O)OH$ (213 mg, 0.96 mmol), oxalyl chloride (200 μL, 2.40 mmol), the methyl vinyl ether **1g**[18] (350 mg, 2.05 mmol), and pyridine (380 μL, 4.80 mmol) gave **2g** as a yellow oil after column chromatography (pentane). Yield: 267 mg (74%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.69 (s, 1H), 3.79 (s, 3H), 2.80−2.73 (m, 2H), 1.53 (quint, $^3J_{H,H}$ = 7.3 Hz, 2H) 1.42−1.18 (m, 10H), 0.87 (t, $^3J_{H,H}$ = 6.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 186.1, 178.6 (t, $^2J_{C,F}$ = 22.1 Hz), 121.1 (t, $^1J_{C,F}$ = 292.0 Hz), 91.6, 56.7, 34.2, 31.9, 29.5, 29.3, 29.3, 26.9, 22.8, 14.2. ^{19}F NMR (282 MHz, $CDCl_3$): δ 68.0 (quint, $^2J_{F,F}$ = 146.2, 1F), 42.5 (dt, $^2J_{F,F}$ = 146.2, $^3J_{F,F}$ = 10.9 Hz, 4F), −92.0 (quint, $^3J_{F,F}$ = 12.6 Hz, 2F). ESI MS ($C_{13}H_{21}F_7O_2SNa$): calcd 397.1048, found 397.1049.

Attempted Synthesis of the Allylic Alcohols 8 Starting from 2a. *3-(1,3-Dioxolan-2-yl)-1,1-difluoro-1-(pentafluoro-λ^6-sulfanyl)-propan-2-one (**3a**).* Compound **2a** (409 mg, 1.48 mmol) was dissolved in toluene (8 mL). Ethylene glycol (637 mg, 5.92 mmol) and *p*-TsOH (57 mg, 0.30 mmol) were added, and the mixture was refluxed for 6 h. After the completion of the reaction (TLC analysis), the mixture was diluted with water (25 mL) and extracted with DCM (3 × 20 mL), and the combined organic phases were washed with brine (50 mL). After being dried with Na_2SO_4 and concentrated under

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vacuum, the obtained crude product was purified by column chromatography (pentane/Et_2O, 15:1) to afford **3a** as a colorless oil. Yield: 208 mg (48%). ^1H NMR (300 MHz, $CDCl_3$): δ 5.37 (t, $^3J_{H,H}$ = 4.8 Hz, 1H), 4.04−3.96 (m, 2H), 3.96−3.89 (m, 2H), 3.14 (d, $^3J_{H,H}$ = 4.8 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 188.1 (t, $^2J_{C,F}$ = 25.7 Hz), 119.4 (t, $^1J_{C,F}$ = 300 Hz), 99.3, 65.1, 42.5−42.0 (m). ^{19}F NMR (282 MHz, $CDCl_3$): δ 68.0 (quintt, $^2J_{F,F}$ = 146.3 Hz, $^3J_{F,F}$ = 4.0 Hz, 1F), 43.8 (dt, $^2J_{F,F}$ = 146.3, $^3J_{F,F}$ = 11.9 Hz, 4F), −93.7 (quintd, $^3J_{F,F}$ = 11.9, $^3J_{F,F}$ = 4.0 Hz, 2F). ESI MS ($C_6H_7F_7O_3SNa$): calcd 314. 9902, found 314.9900.

*3-(1,3-Dioxolan-2-yl)-1,1-difluoro-1-(pentafluoro-λ⁶-sulfanyl)-propan-2-ol (**4a**).* Compound **3a** (208 mg, 0.71 mmol) was dissolved in EtOH (8 mL). At 0 °C, $NaBH_4$ (22 mg, 0.57 mmol) was added, and stirring was continued for 30 min at that temperature. After being quenched with 1 M HCl (20 mL), the reaction mixture was extracted with DCM (3 × 20 mL), washed with brine (50 mL), dried over $MgSO_4$, and concentrated. The crude product was purified by column chromatography (pentane/Et_2O, 4:1) to afford **4a** as a yellow oil. Yield: 183 mg (88%). ^1H NMR (300 MHz, $CDCl_3$): δ 5.14 (t, $^3J_{H,H}$ = 4.3 Hz, 1H), 4.54 (ddt, $^3J_{H,F}$ = 17.0, $^3J_{H,F}$ = 8.0, $^3J_{H,H}$ = 4.8 Hz, 1H), 4.03−3.91 (m, 2H), 3.91−3.79 (m, 2H), 3.49 (bs, 1H), 2.16−2.09 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 128.9 (t, $^1J_{C,F}$ = 307 Hz), 101.8, 69.1−68.2 (m), 65.1 and 64.9, 33.7. ^{19}F NMR (282 MHz, $CDCl_3$): δ 69.8 (quintm, $^2J_{F,F}$ = 146.8 Hz, 1F), 40.46 (dt, $^2J_{F,F}$ = 146.8, $^3J_{F,F}$ = 16.0 Hz, 4F), −89.3 and −95.1 (ABX_4 spin system, J_{AB} = 189, $^3J_{F,F}$ = 16.0 Hz, 2F). ESI MS ($C_6H_9F_7O_3SNa$): calcd 317.0058, found 317.0053.

*3-(1,3-Dioxolan-2-yl)-1,1-difluoro-1-(pentafluoro-λ⁶-sulfanyl)-propan-2-yl Methanesulfonate (**5a**).* Mesyl chloride (23 mg, 0.20 mmol) was added to a solution of the alcohol **4a** (45 mg, 0.15 mmol) and TEA (30 mg, 0.30 mmol) in dry DCM (5 mL) at 0 °C, and the reaction mixture was allowed to reach room temperature. After 2 h, the reaction was quenched with water, and the reaction mixture was extracted with DCM (3 × 8 mL). The combined organic phases were dried over $MgSO_4$ and concentrated. The crude product was purified by column chromatography (pentane/Et_2O, 4:1) to give **5a** as yellow oil. Yield: 42 mg (75%). ^1H NMR (300 MHz, $CDCl_3$): δ 5.52−5.37 (m, 1H), 5.08 (dd, $^3J_{H,H}$ = 4.7, $^3J_{H,H}$ = 3.2 Hz, 1H), 4.03−3.92 (m, 2H), 3.91−3.80 (m, 2H), 3.09 (s, 3H), 2.38−2.27 (m, 1H), 2.27−2.18 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 127.1 (tm, $^1J_{C,F}$ = 303.7 Hz), 100.2, 74.5 (t, $^2J_{C,F}$ = 24.1 Hz), 65.3 and 65.0, 39.3, 33.2. ^{19}F NMR (282 MHz, $CDCl_3$): δ 68.39 (quintm, $^2J_{F,F}$ = 146.0 Hz, 1F), 42.57 (dt, $^2J_{F,F}$ = 146.1, $^3J_{F,F}$ = 14.4 Hz, 4F), AB spin system, J_{AB} = 194 Hz, −86.72 (quintd, $^3J_{F,F}$ = 14.9, $^3J_{F,F}$ = 4.9 Hz, 1F and −89.62 (m, 1F). GC/MS: *m*/*z* (rel int, ion): 371 (<1, M^+ − H), 277 (<1, M^+ - MsO), 293 (<1, M^+ − Ms), 89 (10, SF_3^+), 79 (20, Ms^+), 73 (100, $C_3H_5O_2^+$). ESI MS ($C_7H_{11}F_7O_5S_2Na$): calcd 394.9834, found 394.9828.

*3-(1,3-Dioxolan-2-yl)-1,1-difluoroprop-1-en-2-yl Methanesulfonate (**6a**).* Compound **5a** (52 mg, 0.14 mmol) was treated with DBU (25 mg, 0.17 mmol) in DCM (2 mL). After 1 h, the reaction was quenched with water (5 mL) and extracted with DCM (3 × 5 mL). The DCM extract was washed with brine (10 mL), dried over $MgSO_4$, concentrated, and purified by column chromatography (pentane/Et_2O, 4:1) to give **6a** as a yellow oil. Yield: 27 mg (79%). ^1H NMR (300 MHz, $CDCl_3$): δ 5.12 (t, $^3J_{H,H}$ = 4.5 Hz, 1H), 4.04−3.95 (m, 2H), 3.95−3.87 (m, 2H), 3.18 (s, 3H), 2.70 (ddd, $^3J_{H,H}$ = 4.5, $^4J_{H,F}$ = 3.7, $^4J_{H,F}$ = 2.5 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.4 (dd, H, $^1J_{C,F}$ = 285.9, $^1J_{C,F}$ = 258.8 Hz), 109.2 (dd, H, $^2J_{C,F}$ = 48.5, 16.6 Hz), 101.0 (t, H, $^4J_{C,F}$ = 3.5 Hz), 65.1, 38.8 ($^5J_{C,F}$ = 2.2 Hz), 32.7 (d, H, $^3J_{C,F}$ = 2.6 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −92.2 (dt, $^2J_{F,F}$ = 49.6, $^4J_{H,F}$ = 2.6 Hz, 1F), −105.7 (dt, $^2J_{F,F}$ = 49.6, $^4J_{H,F}$ = 3.7 Hz, 1F). ESI MS ($C_7H_{10}F_2O_5SNa$): calcd 267.0115, found 267.0109.

*(E)-2-[3,3-Difluoro-3-(pentafluoro-λ⁶-sulfanyl)prop-1-en-1-yl]-1,3-dioxolane (**7a**).* Compound **4a** (40 mg, 0.14 mmol) was treated with P_2O_5 (57 mg, 0.40 mmol) in DCM (4 mL) overnight. Then the mixture was filtered and concentrated under atmospheric pressure to give **7a** (contaminated with trace amounts of several unidentified SF_5CF_2 compounds). Yield: 7 mg (20%), colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ 6.42 (ddt, $^3J_{H,H}$ = 15.7, *J* = 3.6, *J* = 1.8 Hz, 1H), 6.26−6.09 (m, 1H), 5.49 (dt, *J* = 3.3, *J* = 1.7 Hz, 1H), 3.98 (tt, *J* = 3.2, *J* = 1.6 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.3 (t, $^3J_{C,F}$ = 9.0 Hz, C3), 122.5 (t, $^2J_{C,F}$ = 21.0 Hz), 100.3, 65.1. ^{19}F NMR (282 MHz, $CDCl_3$): δ 68.71 (quintm, $^2J_{F,F}$ = 144.4 Hz, 1F), 37.79 (dt, $^2J_{F,F}$ = 144.5, $^3J_{F,F}$ = 15.1 Hz, 4H), −82.17 (dquintm, $^3J_{F,F}$ = 15.1, $^3J_{F,F}$ = 5.0 Hz 2F). GC/MS: *m*/*z* (rel int, ion) 276 (25, M^+), 149 (25, $M^+ - SF_5$), 89 (25, SF_3^+), 73 (60, $M^+ - SF_5CF_2CH$ = CH). APCI MS: *m*/*z* (rel abund, ion) [FTMS$^-$] calcd 126.9641, found 126.9639 (100, SF_5^-), [FTMS$^+$] calcd 274.9971, found 274.9966 (35, $C_6H_6O_2SF_7^+$).

Attempted Synthesis of the Allylic Alcohols 8 Starting from 2f and 1g. *5,5-Difluoro-4-hydroxy-5-(pentafluoro-λ⁶-sulfanyl)-pentan-2-one (**10f**).* Compound **2f** (374 mg, 1.35 mmol) and $NaBH_4$ (26 mg, 0.68 mmol) were placed in MeOH (10 mL) at 0 °C. After 15 min, the reaction mixture was quenched with water and extracted with DCM (3 × 30 mL). The DCM extract was then dried over $MgSO_4$ and concentrated. The resulting hydroxyl enol ether **9f** (confirmed by NMR spectroscopy) was subsequently hydrolyzed by treatment with a 1:3 2 M HCl/acetone mixture (10 mL) for 12 h at room temperature. Column chromatography (pentane/Et_2O, 4:1) afforded **10f**. Yield: 270 mg (91% over two steps). White solid. Mp: 70−71 °C. ^1H NMR (300 MHz, $CDCl_3$): 4.87−4.71 (m, 1H), 3.85 (bs, 1H), AB spin system: 2.94 (dd, $^2J_{H,H}$ = 17.8, $^3J_{H,H}$ = 9.0 Hz, 1H) and 2.83 (dt, $^2J_{H,H}$ = 17.8, $^4J_{H,F}$ = 2.3 Hz, 1H), 2.24 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 206.1, 129.0 (tm, $^1J_{C,F}$ = 300.1 Hz), 69.9−66.0 (m), 43.6, 30.8. ^{19}F NMR (282 MHz, $CDCl_3$): δ 69.56 (quintm, $^2J_{F,F}$ = 145.5 Hz, 1F), 40.5 (dt, $^2J_{F,F}$ = 145.5, $^3J_{F,F}$ = 15.8 Hz, 4F). AB spin system: −88.8 and −94.6 (J_{AB} = 191 Hz, 2F). ESI MS ($C_5H_7F_7O_2SNa$): calcd 286.9953, found 286.9947, [$(C_5H_7F_7O_2S)_2Na$] calcd 551.0008, found 551.0002.

*1,1-Difluoro-2-hydroxy-1-(pentafluoro-λ⁶-sulfanyl)dodecan-4-one (**10g**).* Compound **2g** (250 mg, 0.67 mmol) was treated with $NaBH_4$ (15 mg, 0.40 mmol) in MeOH (10 mL) at 0 °C for 15 min. The reaction mixture was quenched with water and extracted with DCM (3 × 15 mL). The DCM extract was dried over $MgSO_4$ and concentrated. The resulting hydroxyl enol ether **9g** was subsequently hydrolyzed by treatment with a 1:3 2 M HCl/acetone mixture (10 mL) overnight. Column chromatography (pentane/Et_2O, 10:1) afforded **10g** as a yellow oil. Yield: 172 mg (71% over two steps). ^1H NMR (300 MHz, $CDCl_3$): δ 4.90−4.72 (m, 1H), 3.99 (bs, 1H), AB spin system: 2.91 (dd, $^2J_{H,H}$ = 17.6, $^3J_{H,H}$ = 9.1 Hz, 1H) and 2.71 (dt, $^2J_{H,H}$ = 17.6, $^4J_{H,F}$ = 2.4 Hz, 1H), 2.48 (t, $^3J_{H,H}$ = 7.4 Hz, 2H), 1.58 (quint, $^3J_{H,H}$ = 7.2 Hz, 2H), 1.26 (m, 10H), 0.87 (t, $^3J_{H,H}$ = 6.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 208.6, 129.1 (t, $^1J_{C,F}$ = 303.6 Hz), 68.6−67.4 (m), 43.9, 42.7, 31.9, 29.4, 29.2, 29.2, 23.6, 22.8, 14.2. ^{19}F NMR (282 MHz, $CDCl_3$): δ 68.0 (quintm, $^2J_{F,F}$ = 146.2, 1F), 42.5 (dt, $^2J_{F,F}$ = 146.2, $^3J_{F,F}$ = 10.9 Hz, 4F), AB spin system: −88.8 and −94.4 (J_{AB} = 190 Hz, 2F). ESI MS ($C_{12}H_{21}F_7O_2SNa$): calcd 385.1048, found 385.1043.

*(E)-5,5-Difluoro-5-(pentafluoro-λ⁶-sulfanyl)pent-3-en-2-one (**11f**).* To a solution of the alcohol **10f** (650 mg, 2.46 mmol) in dry DCM (25 mL) was added TEA (497 mg, 4.92 mmol) followed by MsCl (336 mg, 2.95 mmol) at 0 °C. The reaction mixture was stirred for 30 min. It was then quenched with water (50 mL) and extracted with DCM (3 × 30 mL). The organic phase was dried over $MgSO_4$. Careful removal of solvents and filtration through a short silica pad afforded **11f**. Yield: 250 mg (41%). Volatile yellow oil. ^1H NMR (300 MHz, $CDCl_3$): δ 6.81−6.70 (m, 2H), 2.39 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 195.1 (*C4*), 135.4 (t, $^3J_{C,F}$ = 7.5 Hz), 130.3 (t, $^2J_{C,F}$ = 22.6 Hz), 126.4 ($^1J_{C,F}$ = 296.6 Hz), 28.7. ^{19}F NMR (282 MHz, $CDCl_3$): δ 67.7 (quintm, $^2J_{F,F}$ = 145.3 Hz, 1F), 38.7 (dtd, $^2J_{F,F}$ = 145.3, $^3J_{F,F}$ = 14.5, *J* = 1.5 Hz, 4F), −83.41 (quintdd, $^3J_{F,F}$ = 14.5, $^3J_{H,F}$ = 10.1, $^3J_{F,F}$ = 4.9 Hz, 2F). GC/MS: *m*/*z* (rel int, ion) 246 (50, M^+), 231 (98, [M − CH_3]$^+$), 127 (20, SF_5^+), 119 (85, [*M*-SF_5]$^+$). APCI MS: *m*/*z* (rel abund, ion) [FTMS$^-$] calcd 126.9641, found 126.9642 (30, SF_5^-), calcd 247.0033, found 247.0034 (10, $C_5H_6F_7OS^-$), calcd 267.0095, found 267.0094 (5, $C_5H_7F_8OS^-$).

*(E)-1,1-Difluoro-1-(pentafluoro-λ⁶-sulfanyl)dodec-2-en-4-one (**11g**).* Compound **10g** (190 mg, 0.52 mmol) was treated with P_2O_5 (594 mg, 2.10 mmol) in DCM (4 mL). After 3 h, the reaction mixture was filtered and purified by column chromatography (pentane) to give **11g** as a yellow oil. Yield: 130 mg (72%).

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Note: It is very important to control the progress of the reaction and to quench after complete consumption of aldol **10g** to avoid decomposition of **11g** caused by the hydroxyl tautomer. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.83−6.53 (m, 2H), 2.64 (t, $^{3}J_{H,H}$ = 7.3 Hz, 2H), 1.65 (quint, $^{3}J_{H,H}$ = 7.2 Hz, 2H), 1.33−1.23 (m, 10H), 0.87 (t, $^{3}J_{H,H}$ = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.5, 134.8 (t, $^{3}J_{C,F}$ = 7.3 Hz), 129.5 (t, $^{2}J_{C,F}$ = 22.6 Hz), 42.2, 31.7, 29.2, 29.0, 29.0, 23.4, 22.6, 14.0, the CF_2 group was not recorded. ^{19}F NMR (282 MHz, $CDCl_3$): δ 67.83 (quintm, $^{2}J_{F,F}$ = 145.1 Hz, 1F), 38.71 (dt, $^{2}J_{F,F}$ = 145.1, $^{3}J_{F,F}$ = 14.2 Hz, 4F), −83.21 (quintdd, $^{3}J_{F,F}$ = 14.4, $^{3}J_{H,F}$ = 10.6, $^{3}J_{F,F}$ = 4.9 Hz, 2F). ESI MS ($C_{12}H_{19}F_7OSH$): calcd 345.1123, found 345.1118.

*(E)-1,1,1-Trifluorododec-2-en-4-one (**11g′**).* Compound **11g′** was prepared in order to ensure its formation during synthesis of **11g**.

Compound **12g** (15 mg, 0.06 mmol) was oxidized with Dess−Martin periodinane (32 mg, 0.08 mmol) in DCM (1 mL). After completion of the reaction, silica was poured into the reaction vessel, solvents were removed under reduced pressure, and the material was further worked up by column chromatography (pentane → pentane/Et_2O, 90:10). Yield: 13 mg (87%), colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.72 (dq, $^{3}J_{H,H}$ = 15.9, $^{4}J_{H,F}$ = 1.6 Hz, 1H), 6.59 (dq, $^{3}J_{H,H}$ = 15.9, $^{4}J_{H,F}$ = 1.4 Hz, 1H), 2.61 (t, $^{3}J_{H,H}$ = 7.3 Hz, 2H), 1.71−1.55 (m, 2H), 1.36−1.21 (m, 10H), 0.87 (t, $^{3}J_{H,H}$ = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 198.2, 134.1 (q, $^{3}J_{C,F}$ = 5.5 Hz), 128.3 (q, $^{2}J_{C,F}$ = 35.2 Hz), 122.4 (q, $^{1}J_{C,F}$ = 270.2 Hz), 41.9, 31.8, 29.3, 29.1, 29.0, 23.5, 22.6, 14.1. ^{19}F NMR (282 MHz, $CDCl_3$): δ −65.2 (dd, $^{3}J_{H,F}$ = 6.1, $^{4}J_{H,F}$ = 1.6 Hz, 2F). ESI MS ($C_{12}H_{19}F_3ONa$): calcd 259.1286, found 259.1279.

*(E)-1,1,1-Trifluorododec-2-en-4-ol (**12g**).* Compound **11g** (65 mg, 0.19 mmol) was treated with $CeCl_3{\cdot}7H_2O$ (70 mg, 0.19 mmol) and $NaBH_4$ (4 mg, 0.11 mmol) in MeOH (2 mL) at 0 °C, 15 min. The reaction was quenched with water and extracted with DCM (2 × 10 mL), and the combined organic phases were washed with brine (20 mL), dried over $MgSO_4$, and concentrated. Column chromatography (pentane/Et_2O, 10:1) gave **12g** as a colorless oil. Yield: 35 mg (78%).

To an ice-cooled solution of **11g** (30 mg, 0.09 mmol) in Et_2O (2 mL) was added dropwise a Et_2O (1 mL) suspension of LAH (2 mg, 0.05 mmol, 0.6 equiv) at 0 °C. After 10 min, the reaction was quenched with water (5 mL) and extracted with DCM (3 × 5 mL). The combined organic phases were concentrated to give a mixture of **12g**, **13g** (5:1). Yield: 15 mg (around 58% combined).

To a solution of **11g** (24 mg, 0.07 mmol) in MeOH/HCl 10:1 (1 mL) was added $NaCNBH_3$ (4 mg, 0.07 mmol). After 1 h, the reaction was quenched with water (5 mL) and extracted with DCM (3 × 5 mL). The combined organic phases were dried over $MgSO_4$ and concentrated. Yield (^{19}F NMR spectroscopy): **12g** (23%), **13g** (4%).

A solution of **11g** (17 mg, 0.05 mmol) and $Al(iPrO)_3$ (21 mg, 0.1 mmol) was refluxed in *i*PrOH (1 mL). After filtration, the mixture was concentrated and analyzed by NMR spectroscopy. Compounds **12g** and **11g′** were formed as a 1:1 mixture in 10% combined yield. This indicates that (i) formation of the CF_3 group occurred, (ii) the ketone formed was reduced to the allylic alcohol, and (iii) the reaction was not rerun to reach complete reduction. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.41 (ddq, $^{3}J_{H,H}$ = 15.7, $^{3}J_{H,H}$ = 4.2, $^{4}J_{H,F}$ = 2.1 Hz, 1H), 5.89 (dqd, $^{3}J_{H,H\ trans}$ = 15.7, $^{3}J_{H,F}$ = 6.5, $^{4}J_{H,H}$ = 1.7 Hz, 1H), 4.28 (tdq, $^{3}J_{H,H}$ = 7.1, $^{3}J_{H,H}$ = 4.2, $^{5}J_{H,F}$ = 2.3 Hz, 1H), 1.59−1.53 (m, 2H), 1.28 (m, 12H), 0.87 (t,, $^{3}J_{H,H}$ = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.4 (q, $^{3}J_{C,F}$ = 6.0 Hz), 123.4 (q, $^{1}J_{C,F}$ = 269.2 Hz), 117.6 (q, $^{2}J_{C,F}$ = 33.9 Hz), 70.4, 36.6, 31.8, 29.4, 29.4, 29.2, 25.1, 22.6, 14.1. ^{19}F NMR (282 MHz, $CDCl_3$): δ −64.0 (dt, $^{3}J_{H,F}$ = 6.5, $^{4}J_{H,F}$ = 2.2, $^{5}J_{H,F}$ = 2.2 Hz, 3F). ESI MS ($C_{12}H_{21}F_3ONa$): calcd 261.1442, found 261.1437.

*1,1-Difluorododec-1-en-4-ol (**13g**).* To an ice-cooled solution of **11g** (47 mg, 0.14 mmol) in THF (2 mL) was added dropwise a THF (1 mL) suspension of LAH (26 mg, 0.68 mmol, 5 equiv) at 0 °C. After 10 min, the reaction was quenched with water (5 mL) and extracted with DCM (3 × 5 mL). The combined organic phases were concentrated, and the crude product was purified by column chromatography (pentane/Et_2O, 10:1) to give **13g** as a colorless oil. Yield: 22 mg (75%).

To an ice-cooled solution of **22** (13 mg, 0.05 mmol) in THF (1 mL) was added dropwise a THF (0.5 mL) suspension of LAH (9 mg, 0.25 mmol, 5 equiv) at 0 °C. After 10 min, the reaction was quenched with water (5 mL) and extracted with DCM (3 × 5 mL). The combined organic phases were concentrated to give **13g**. Yield: 10 mg (90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.25 (dtd, $^{3}J_{H,F\ trans}$ = 25.4, $^{3}J_{H,H}$ = 8.0, $^{3}J_{H,F\ cis}$ = 2.5 Hz, 1H), 3.70−3.56 (m, 1H), 2.25−2.03 (m, 2H), 1.53 (bs, 1H), 1.49−1.43 (m, 2H), 1.35−1.21 (m, 12H), 0.88 (t, $^{3}J_{H,H}$ = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 74.4 (dd, $^{2}J_{C,F}$ = 23.2, $^{2}J_{C,F}$ = 20.6 Hz), 71.1 (t, $^{4}J_{C,F}$ = 2.4 Hz), 36.7, 31.8, 30.3 (d, $^{3}J_{C,F}$ = 4.2 Hz), 29.6, 29.5, 29.2, 25.6, 22.7, 14.1. The CF_2═CH− group was not recorded. ^{19}F NMR (282 MHz, $CDCl_3$): δ −87.22 (dq, $^{2}J_{F,F}$ = 45.2, $^{3}J_{H,F\ cis}$ = $^{4}J_{H,F}$ = 1.9 Hz, 1F), −90.35 (ddt, $^{2}J_{F,F}$ = 45.1, $^{3}J_{H,F\ trans}$ = 25.4, $^{4}J_{H,F}$ = 2.0 Hz, 1F). ESI MS ($C_{12}H_{22}F_2ONa$): calcd 243.1536, found 243.1530.

Synthesis and Reduction of the SF_5CH_2- and $ClCF_2$-Substituted Analogues 17 and 22. *4-Methoxy-1-(pentafluoro-λ^6-sulfanyl)pent-3-en-2-one (**14**).* According to the already used procedure: $SF_5CH_2C(O)OH$ (309 mg, 1.17 mmol), oxalyl chloride (225 μL, 2.65 mmol), methoxy propene (191 mg, 2.65 mmol), pyridine (210 μL, 2.65 mmol). Yield: 225 mg (56%) of **14** as a yellow oil after column chromatography (Et_2O/pentane, 10:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.57 (s, 1H), 4.28 (quint, $^{3}J_{H,F}$ = 8.2 Hz, 2H), 3.70 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 184.5 (quint, $^{3}J_{C,F}$ = 3.5 Hz), 177.6, 99.1 (quint, $^{4}J_{C,F}$ = 2.5 Hz, 78.4 (quint, $^{2}J_{C,F}$ = 11.2 Hz), 56.1, 20.5. ^{19}F NMR (282 MHz, $CDCl_3$): δ 82.23 (nonet, $^{2}J_{F,F}$ = 149.0 Hz, 1F), 71.61 (dtt, $^{2}J_{F,F}$ = 149.0, $^{3}J_{H,F}$ = 8.1, J = 3.8 Hz, 4F). ESI MS ($C_6H_9F_5O_2SNa$): calcd 263.0141, found 263.0136.

*4-Hydroxy-5-(pentafluoro-λ^6-sulfanyl)pentan-2-one (**16**).* Compound **14** (871 mg, 3.63 mmol) was treated with $NaBH_4$ (206 mg, 5.44 mmol) in MeOH (25 mL) at 0 °C for 4 h. The reaction mixture was quenched with water and extracted with DCM (3 × 70 mL), and the DCM extracts were dried over $MgSO_4$, and concentrated. The resulting hydroxyl enol ether **15** was subsequently hydrolyzed by treatment with a 1:3 2 M HCl/acetone mixture (50 mL) overnight. Column chromatography (pentane/Et_2O, 1:2) afforded **16** as a colorless oil. Yield: 750 mg (90% over two steps). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.66 (tt, $^{3}J_{H,H}$ = 11.7, $^{3}J_{H,H}$ = 6.0 Hz, 1H), AB spin system: 3.79 (m, 2H, H1 and 3.71 (m, 1H), 3.19 (bs, 1H), 2.72 (d, $^{3}J_{H,H}$ = 5.8 Hz, 2H), 2.21 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 207.7, 75.7 (quint, $^{2}J_{C,F}$ = 11.8 Hz), 64.3 (quint, $^{3}J_{C,F}$ = 4.1 Hz), 48.1 (quint, $^{4}J_{C,F}$ = 1.5 Hz), 30.8. ^{19}F NMR (282 MHz, $CDCl_3$): δ 84.32 (nonet, $^{2}J_{F,F}$ = 148.2 Hz, 1F), 66.91 (dtd, $^{2}J_{F,F}$ = 148.2, $^{3}J_{H,F}$ = 8.36, $^{4}J_{H,F}$ = 4.18 Hz, 4F). ESI MS ($C_5H_9F_5O_2SNa$): calcd 251.0141, found 251.0136.

*(E)-5-(Pentafluoro-λ^6-sulfanyl)pent-3-en-2-one (**17**).* Compound **16** (48 mg, 0.21 mmol) was treated with MsCl (31 mg, 0.27 mmol) and TEA (55 mg, 0.54 mmol) in DCM (4 mL) for 1 h at 0 °C, silica was poured into the reaction flask, and **17** was obtained as a colorless oil after column chromatography (pentane/Et_2O, 4:1). Yield: 36 mg (81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.81 (dt, $^{3}J_{H,H}$ = 15.6, $^{3}J_{H,H}$ = 7.7 Hz, 1H), 6.29 (dt, $^{3}J_{H,H}$ = 15.8, $^{4}J_{H,H}$ = 1.3 Hz, 1H), 4.41 (h, $^{3}J_{H,F}$ = $^{3}J_{H,H}$ = 7.3 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 197.1, 136.8, 133.3 (quint, $^{3}J_{C,F}$ = 4.5 Hz), 72.0 (quint, $^{2}J_{C,F}$ = 16.5 Hz), 27.7. ^{19}F NMR (282 MHz, $CDCl_3$): δ 80.96 (nonet, $^{2}J_{F,F}$ = 145.8 Hz, 1F), 66.26 (dtd, $^{2}J_{F,F}$ = 145.8, $^{3}J_{H,F}$ = 7.3, J = 2.4 Hz, 4F). ESI MS ($C_5H_7F_5OSNa$): calcd 233.0035, found 233.0030.

*(E)-5-(Pentafluoro-λ^6-sulfanyl)pent-3-en-2-ol (**18**).* A solution of $NaBH_4$ (2 mg, 0.06 mmol) in MeOH (1 mL) was added to a MeOH (2 mL) solution of **17** (22 mg, 0.10 mmol) and $CeCl_3{\cdot}7H_2O$ (38 mg, 0.10 mmol) at 0 °C. After 15 min, the reaction was quenched with water (6 mL) and extracted with DCM (3 × 6 mL). The combined organic phases were washed with brine (15 mL), dried over Na_2SO_4, and concentrated to give **5b** as a colorless oil. Yield: 20 mg (90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.97−5.81 (m, 2H), 4.39 (qt, $^{3}J_{H,H}$ = 6.4, $J_{H,H}$ = 3.8 Hz, 1H), 4.28 (h, $^{3}J_{H,F}$ = $^{3}J_{H,H}$ = 7.4 Hz, 2H), 1.66 (bs, 1H), 1.31 (d, $^{3}J_{H,H}$ = 6.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.6, 118.7 (quint, $^{3}J_{C,F}$ = 3.9 Hz), 73.3 (quint, $^{2}J_{C,F}$ = 14.7 Hz), 67.6, 22.9.

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^{19}F NMR (282 MHz, $CDCl_3$): δ 82.06 (nonet, $^2J_{F,F}$ = 144.6 Hz, 1F), 63.61 (dtd, $^2J_{F,F}$ = 144.6, $^3J_{H,F}$ = 7.7, J = 3.9 Hz, 4F). ESI MS ($C_5H_9F_5OSNa$): calcd 235.0192, found 235.0186.

*(Z)-1-Chloro-1,1-difluoro-4-methoxydodec-3-en-2-one (**19**).* According to the previously used procedure, $ClCF_2C(O)OH$ (500 mg, 3.85 mmol), oxalyl chloride (488 μL, 5.77 mmol), the methyl vinyl ether **1g**[1] (900 mg, 5.40 mmol), and pyridine (850 μL, 6.15 mmol) gave **19** as a yellow oil after column chromatography (pentane). Yield: 578 mg (53%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.61 (t, $^4J_{H,F}$ = 1.1 Hz, 1H), 3.77 (s, 3H), 2.79−2.74 (m, 2H), 1.53 (quint, $^3J_{H,H}$ = 7.3 Hz, 2H) 1.31−1.23 (m, 10H), 0.85 (t, $^3J_{H,H}$ = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 185.4, 179.7 (t, $^2J_{C,F}$ = 27.4 Hz), 120.9 (t, $^1J_{C,F}$ = 306.4 Hz), 90.1, 56.5, 33.9, 31.9, 29.5, 29.3, 29.3, 27.1, 22.7, 14.2. ^{19}F NMR (282 MHz, $CDCl_3$): δ −66.6 (d, $^4J_{H,F}$ = 1.1 Hz, 2F). ESI MS ($C_{13}H_{21}F_2O_2ClNa$): calcd 305.1096, found 305.1090, [$(C_{13}H_{21}F_2O_2Cl)_2Na$] calcd 587.2288, found 587.2294.

*1-Chloro-1,1-difluoro-2-hydroxydodecan-4-one (**21**).* Compound **19** (578 mg, 2.05 mmol) was treated with $NaBH_4$ (62 mg, 1.64 mmol) in MeOH (25 mL) at 0 °C for 15 min. The reaction mixture was quenched with water and extracted with Et_2O (3 × 40 mL), and the Et_2O extracts were dried over $MgSO_4$ and concentrated. The resulting hydroxyl enol ether **20** was subsequently hydrolyzed by treating with a 1:3 2 M HCl/acetone mixture (20 mL) overnight. Column chromatography (pentane/Et_2O, 10:1) afforded **21** as a colorless oil. Yield: 292 mg (53% over two steps). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.53 (td, $^3J_{H,F}$ = 7.8, $^3J_{H,H}$ = 4.3 Hz, 1H), 3.43 (bs, 1H), 2.85 (d, $^2J_{H,H}$ = 9.0, $^3J_{H,H}$ = 4.2 Hz, 1H), 2.78 (dd, $^2J_{H,H}$ = 9.0, $^3J_{H,H}$ = 4.2 Hz, 1H′), 2.48 (t, $^3J_{H,H}$ = 7.4 Hz, 2H), 1.58 (quint, $^3J_{H,H}$ = 7.3 Hz, 2H), 1.32−1.22 (m, 10H), 0.87 (t, $^3J_{H,H}$ = 6.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 208.9, 129.1 (t, $^1J_{C,F}$ = 295.3 Hz), 71.4 (t, $^2J_{C,F}$ = 27.9 Hz), 43.9, 42.7, 31.9, 29.4, 29.2, 29.1, 23.5, 22.7, 14.2. ^{19}F NMR (282 MHz, $CDCl_3$): δ AB spin system: J_{AB} = 165 Hz: −64.0 (dd, $^3J_{H,F}$ = 8.0, $^4J_{H,F}$ = 2.0 Hz) and −65.7 (dt, $^3J_{H,F}$ = 8.0, $^4J_{H,F}$ = 1.8 Hz, 2F). ESI MS ($C_{12}H_{21}ClF_2O_2Na$): calcd 293.1096, found 293.1090.

*(E)-1-Chloro-1,1-difluorododec-2-en-4-one (**22**).* Compound **21** (240 mg, 0.89 mmol) was treated with MsCl (122 mg, 1.07 mmol) and TEA (260 mg, 2.56 mmol) in DCM (10 mL) for 1 h at 0 °C. Silica was poured into the reaction mixture. After drying, this material was applied on a short pad of silica and filtered with pentane/Et_2O (10:1) to give **22** as a yellowish oil. Yield: 189 mg (84%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.74 (dt, $^3J_{H,H}$ = 15.7, $^3J_{H,F}$ = 8.8 Hz, 1H), 6.58 (dt, $^3J_{H,H}$ = 15.7, $^3J_{H,H}$ = 1.4 Hz, 1H), 2.60 (t, $^3J_{H,H}$ = 7.3 Hz, 1H), 1.62 (quint, $^3J_{H,H}$ = 7.1 Hz, 2H), 1.31−1.23 (m, 10H), 0.86 (t, $^3J_{H,H}$ = 6.7 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.5, 133.0 (t, $^2J_{C,F}$ = 28.4 Hz), 129.9 (t, $^3J_{C,F}$ = 5.6 Hz), 123.1 (t, $^1J_{C,F}$ = 287.6 Hz), 41.1, 30.9, 28.4, 28.2, 28.1, 22.6, 21.7, 13.1. ^{19}F NMR (282 MHz, $CDCl_3$): δ −53.5 (dt, $^3J_{H,F}$ = 8.9, $^4J_{H,F}$ = 1.4 Hz, 2F). ESI MS ($C_{12}H_{19}ClF_2ONa$): calcd 275.0990, found 275.0985.

*(E)-1-Chloro-1,1-difluorododec-2-en-4-ol (**23**).* A solution of $NaBH_4$ (12 mg, 0.31 mmol) in MeOH (3 mL) was added to a solution of **22** (78 mg, 0.31 mmol) and $CeCl_3{\cdot}7H_2O$ (115 mg, 0.31 mmol) in MeOH (2 mL) at 0 °C. After 15 min, the reaction was quenched with water (6 mL) and extracted with DCM (3 × 6 mL). The combined organic phases were washed with brine (15 mL), dried over Na_2SO_4, and concentrated to give **23** as colorless oil. Yield: 64 mg (81%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.29 (ddt, $^3J_{H,H}$ = 15.5, $^3J_{H,H}$ = 4.3, $^4J_{H,F}$ = 2.0 Hz, 1H), 6.04 (dtd, $^3J_{H,H}$ = 15.5, $^3J_{H,F}$ = 9.0, $^3J_{H,H}$ = 1.6 Hz, 1H), 4.25 (tdd, $^3J_{H,H}$ = 8.8, $^3J_{H,H}$ = 4.3, $^4J_{H,H}$ = 2.1 Hz, 1H), 2.10 (bs, 1H), 1.59−1.51 (m, 2H), 1.35−1.23 (m, 12H), 0.88 (t, $^3J_{H,H}$ = 6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 139.6 (t, $^3J_{C,F}$ = 6.4 Hz), 125.1 ($^1J_{C,F}$ = 286.5 Hz), 123.9 (t, $^2J_{C,F}$ = 27.1 Hz), 70.4, 36.8 (t, $^5J_{C,F}$ = 1.4 Hz), 31.9, 29.6, 29.5, 29.3, 25.3, 22.7, 14.2. ^{19}F NMR (282 MHz, $CDCl_3$): δ −50.0 (dm, $^3J_{H,F}$ = 9.0, 2F). GC/MS: m/z (rel int, ion): 254 (1, M^+), 237 (3, $[M-OH]^+$), 211 (3, $[M\text{-}Pr]^+$), 169 (70, $[M\text{-}CF_2Cl]^+$), 143 (20, $C_9H_{19}O^+$), 141 (65, $[M\text{-}C_8H_{17}]^+$), 43 (90, Pr^+). APCI MS: m/z (rel abund, ion): [FTMS$^+$] calcd 271.1271, found 271.1266 (20, $C_{12}H_{21}OClF_2OH^+$), [FTMS$^-$] calcd 289.0943, found 289.0915 (100, $C_{12}H_{21}OClF_2Cl^-$), calcd 305.0892, found 305.0863 (100, $C_{12}H_{21}OClF_2ClO^-$).

Synthesis and Reduction of the Bromide-Substituted Derivatives 27. *5-Bromo-1,1-difluoro-4-methoxy-1-(pentafluoro-λ^6-sulfanyl)pent-3-en-2-one (**24**).* Analogous to reference,[18] a DCM solution (25 mL) of **2f** (1043 mg, 3.78 mmol) was slowly treated with bromine (605 mg, 7.45 mmol) at 0 °C for 20 min. The reaction was quenched with solid $Na_2S_2O_3$ until the residual bromine had vanished. Then silica was poured into this mixture, solvents were evaporated, and this material was applied for column chromatography (pentane/Et_2O, 10:1). Yield: 900 mg (67%) (contaminated with the hydrolysis product, ratio 4:1). Pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.81 (t, $^4J_{H,F}$ = 1.5 Hz, 1H), 4.42 (s, 2H), 3.89 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 178.5 (t, $^2J_{C,F}$ = 23.6 Hz), 176.7, 92.7, 57.4, 25.5. ^{19}F NMR (282 MHz, $CDCl_3$): δ 67.44 (quintm, $^2J_{F,F}$ = 146.4 Hz, 1F), 43.04 (dt, $^2J_{F,F}$ = 146.4, $^3J_{F,F}$ = 12.4 Hz, 4F), −92.48 (quintdd, $^3J_{F,F}$ = 12.4, $^3J_{F,F}$ = 4.5, $^4J_{H,F}$ = 1.5 Hz, 2F). ESI MS ($C_6H_6BrF_7SO_2Na$): calcd 376.9058, found 376.9052, calcd 378.9037, found 378.9032 (calcd for ^{79}Br and ^{81}Br, respectively).

*1-Bromo-5,5-difluoro-4-hydroxy-5-(pentafluoro-λ^6-sulfanyl)-pentan-2-one (**26**).* Compound **24** (860 mg, 2.43 mmol) was treated with $NaBH_4$ (74 mg, 1.94 mmol) in MeOH (20 mL) at 0 °C. After 5 min, the reaction was quenched with water (40 mL) and extracted with DCM (3 × 50 mL). The crude material **25** was refluxed in an acetone/2 M HCl (3:1) mixture (12 mL) for 1 h. Then it was diluted with water (30 mL), extracted with DCM (3 × 30 mL), washed with brine (50 mL), and dried over $MgSO_4$. Column chromatography (pentane/Et_2O, 2:1) gave **26** as a white solid. Yield: 510 mg (61%). Mp: 61−62 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.87 (tt, $^3J_{H,F}$ = 10.9, $^3J_{H,H}$ = 5.2 Hz, 1H), 4.18 (d, 2H, $^4J_{H,H}$ = 1.4 Hz), 3.34 (d, $^3J_{H,H}$ = 6.2 Hz, 1H), 3.15 (dd, $^2J_{H,H}$ = 17.8, $^3J_{H,H}$ = 9.3 Hz, 1H), 3.00 (dt, $^2J_{H,H}$ = 17.8, $^3J_{H,H}$ = 2.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 199.9, 128.7 (tquint, $^1J_{C,F}$ = 301.9, $^2J_{C,F}$ = 20.5 Hz), 68.0 (dd, $^2J_{C,F}$ = 25.3, $^2J_{C,F}$ = 21.0 Hz), 48.5, 40.4 (dd, $^3J_{C,F}$ = 2.9, $^3J_{C,F}$ = 1.5 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ 69.37 (quintm, $^2J_{F,F}$ = 145.6 Hz, 1F), 40.64 (dt, $^2J_{F,F}$ = 145.6, $^3J_{F,F}$ = 15.5 Hz, 4F), AB spin system, J_{AB} = 192 Hz, −88.78 (quint, $^3J_{F,F}$ = 15.5 Hz, 1F) and −94.63 (quint, $^3J_{F,F}$ = 15.5 Hz, 1F). ESI MS ($C_5H_6BrF_7SO_2Na$): calcd 364.9058, found 364.9054, calcd 366.9037, found 366.9032, for ^{79}Br and ^{81}Br, respectively.

*(E)-1-Bromo-5,5-difluoro-5-(pentafluoro-λ^6-sulfanyl)pent-3-en-2-one (**27**).* Compound **26** (220 mg, 0.64 mmol) was added to a suspension of P_2O_5 (916 mg, 6.45 mmol) in dry CH_2Cl_2 (20 mL). The resulting mixture was stirred for 2 days at room temperature. Next it was filtered, concentrated, and filtered through a short pad of silica. Yield: 120 mg (57%, contaminated with the CF_3 analogue **27′** in the ratio of 18:1), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.08 (dt, $^3J_{H,H}$ = 15.7, $^4J_{H,F}$ = 1.7 Hz, 1H), 6.94 (dddquint, $^3J_{H,H}$ = 15.3, $^3J_{H,F}$ = 13.3, $^3J_{H,F}$ = 11.6, $^4J_{H,F}$ = 1.6 Hz, 1H), 4.26 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 189.2, 132.6 (t, $^2J_{C,F}$ = 23.0 Hz), 131.0 (t, $^3J_{C,F}$ = 7.6 Hz), 125.9 (tquint, $^1J_{C,F}$ = 295.2, $^2J_{C,F}$ = 26.7 Hz), 47.4. ^{19}F NMR (282 MHz, $CDCl_3$): δ 67.42 (quintm, $^2J_{F,F}$ = 145.3 Hz, 1F), 39.12 (dt, $^2J_{F,F}$ = 145.3, $^3J_{F,F}$ = 14.2 Hz, 4F), −83.70 (quint, $^3J_{F,F}$ = 14.1 Hz, 2F). APCI MS: m/z (rel abund, ion) [FTMS$^-$] calcd 126.9646, found 126.9644 (100, SF_5^-).

*(E)-1-Bromo-5,5-difluoro-5-(pentafluoro-λ^6-sulfanyl)pent-3-en-2-ol (**28**).* To compound **27** (25 mg, 0.08 mmol) in methanol (1.5 mL) was added $CeCl_3{\cdot}7H_2O$ (28 mg, 0.08 mmol). Then the mixture was cooled to 0 °C, and a methanol (1 mL) solution of $NaBH_4$ (3 mg, 0.08 mmol) was added dropwise. After 5 min, the reaction was quenched with 0.5 M HCl (3 mL) and extracted with CH_2Cl_2 (3 × 6 mL), and the DCM extracts were washed with brine (15 mL) and dried over $MgSO_4$. Yield: 15 mg (60%, contaminated with the CF_3 analogue **27′** in the ratio of 12:1). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.48 (ddt, $^3J_{H,H}$ = 15.6, $^3J_{H,H}$ = 3.9, $^4J_{H,F}$ = 2.0 Hz, 1H), 6.23 (dtquint, $^3J_{H,H}$ = 15.5, $^3J_{H,F}$ = 12.0, $^4J_{H,H}$ = 1.8 Hz, 1H), 4.59 (s, 1H), 3.72 (dd, $^2J_{H,H}$ = 11.3, $^3J_{H,H}$ = 4.0 Hz, 1H), 3.56 (dd, $^2J_{H,H}$ = 11.3, $^3J_{H,H}$ = 6.7 Hz, 1H), 2.50 (d, $^3J_{H,H}$ = 5.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 139.3 (t, $^3J_{C,F}$ = 8.5 Hz), 127.0 (tm, $^1J_{CF}$ = 294.0 Hz), 121.8 (t, $^2J_{C,F}$ = 21.6 Hz), 70.0, 48.3. CF_2 was not detected. ^{19}F NMR (282 MHz, $CDCl_3$): δ 68.44 (quintm, $^2J_{F,F}$ = 145.5 Hz, 1F), 39.19 (dt, $^2J_{F,F}$ = 145.5, $^3J_{F,F}$ = 15.2 Hz, 4F), −82.00 − −82.35 (m, 2F). APCI MS: m/z

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(rel abund, ion): [FTMS$^-$] calcd 126.9646, found 126.9642 (100, SF_5^-).

*5-Bromo-1,1-difluoro-4-methoxy-1-(pentafluoro-λ^6-sulfanyl)-dodec-3-en-2-one (**24b**).* Compound **2g** (560 mg, 1.50 mmol) was treated with bromine (240 mg, 3.00 mmol) in dry DCM (10 mL). After 30 min, the reaction was quenched with solid $Na_2S_2O_3$ until the residual bromine had vanished. Then silica was poured into this mixture, solvents were evaporated, and this material was applied for column chromatography (pentane/Et_2O, 4:1). Yield: 615 mg, (91%). ^{1}H NMR (400 MHz, $CDCl_3$): 5.81 (t, $^3J_{H,H}$ = 7.6 Hz, 1H), 5.72 (t, $^4J_{H,F}$ = 1.6 Hz, 1H), 3.89 (s, 3H), 1.99 (q, $^3J_{H,H}$ = 6.2 Hz, 2H), 1.34−1.21 (m, 10H), 0.88 (t, $^3J_{H,H}$ = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 179.0, 178.8 (t, $^2J_{C,F}$ = 23.2 Hz), 120.7 (tm, $^1J_{CF}$ = 312 Hz), 91.6, 57.4, 45.0, 34.8, 31.7, 29.0, 28.9, 27.4, 22.7, 14.1. ^{19}F NMR (282 MHz, $CDCl_3$): δ 67.50 (quintm, $^2J_{F,F}$ = 146.4 Hz, 1F), 42.98 (dt, $^2J_{F,F}$ = 146.4, $^3J_{F,F}$ = 12.4 Hz, 4F), −92.36 (quintdd, $^3J_{F,F}$ = 12.4, $^3J_{F,F}$ = 4.5, $^4J_{H,F}$ = 1.6 Hz, 2F). ESI MS ($C_{13}H_{20}BrF_7SO_2Na$): calcd 475.0153, found 475.0147, calcd 477.0133, found 477.0127 for ^{79}Br and ^{81}Br, respectively.

*5-Bromo-1,1-difluoro-2-hydroxy-1-(pentafluoro-λ^6-sulfanyl)-dodecan-4-one (**26b**).* Compound **24** (220 mg, 0.49 mg) was treated with $NaBH_4$ (18 mg, 0.49 mmol) in MeOH (6 mL) at 0 °C. After 5 min, the reaction was quenched with water (15 mL) and extracted with DCM (3 × 15 mL). The crude material **26** was dissolved in acetone/2 M HCl (3:1) mixture (4 mL) for 1 h. Then it was diluted with water (10 mL), extracted with DCM (3 × 15 mL), washed with brine (30 mL), and dried over $MgSO_4$. Yield: 52 mg (52%) of **26** (with large excess of one diastereoisomer). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.85 (tdd, $^3J_{H,F}$ = 16.1, $^3J_{H,H}$ = 8.5, $^3J_{H,H}$ = 4.2 Hz, 1H), 4.25 (td, J = 8.5, 5.6 Hz, 1H), AB spin system: 3.22 (dd, $^2J_{H,H}$ = 18.0, $^3J_{H,H}$ = 9.3 Hz, 1H) and 3.12−3.00 (m, 1H), 2.06−1.77 (m, 2H), 1.34−1.22 (m, 10H), 0.88 (t, $^3J_{H,H}$ = 6.7 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 202.7, 68.5−67.8 (m), 63.9, 39.4, 33.7, 31.6, 28.9, 28.8, 25.9, 22.6, 14.0. CF_2 was not detected. ^{19}F NMR (282 MHz, $CDCl_3$): δ 69.56 (quintm, $^2J_{F,F}$ = 145.6 Hz, 1F), 40.60 (dm, $^2J_{F,F}$ = 145.6 Hz, 4F), AB spin system, J_{AB} = 191 Hz, −88.61 (m, 1F) and −94.63 (bs, 1F). ESI MS ($C_{12}H_{20}BrF_7SO_2Na$): calcd 463.0148, found 463.0151, calcd 465.0127, found 465.0130, for ^{79}Br and ^{81}Br, respectively.

*(E)-5-Bromo-1,1-difluoro-1-(pentafluoro-λ^6-sulfanyl)dodec-2-en-4-one (**27b**) and (E)-5-Bromo-1,1,1-trifluorododec-2-en-4-one (**27b′**).* Compound **26** (24 mg, 0.05 mmol) was added to a suspension of P_2O_5 in dry CH_2Cl_2 (5 mL). The resulting mixture was stirred overnight at room temperature. Next it was filtered, concentrated, and filtered through a short pad of silica. Yield: 10 mg (43%, 6:1 mixture with **27′**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.17 (dt, $^3J_{H,H}$ = 15.7, $^4J_{H,F}$ = 1.8 Hz, 1H), 7.04−6.83 (m, 1H), 4.36 (dd, $^3J_{H,H}$ = 8.3, $^3J_{H,H}$ = 5.9 Hz, 1H), 2.02−1.85 (m, 2H, AB spin system), 1.39−1.16 (m, 13H), 0.88 (t, $^3J_{H,H}$ = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 191.1, 132.2 (t, $^2J_{C,F}$ = 23.6 Hz), 131.0 (t, $^3J_{C,F}$ = 8.7 Hz), 62.8, 33.1, 31.6, 28.9, 28.9, 25.9, 22.6, 14.0. CF_2 was not detected. ^{19}F NMR (282 MHz, $CDCl_3$): δ 67.17 (quinttm, $^2J_{F,F}$ = 145.3, $^3J_{F,F}$ = 4.9 Hz, 1F), 39.05 (dt, $^2J_{F,F}$ = 145.3, $^3J_{F,F}$ = 14.5 Hz, 4F), −83.40 (quintdd, $^3J_{F,F}$ = 14.0, $J_{F,F}$ = 8.2, $^3J_{F,F}$ = 4.7 Hz, 2F). APCI MS: *m*/*z* (rel abund, ion) [FTMS$^-$] calcd 126.9646, found 126.9639 (28, SF_5^-).

*(E)-5-Bromo-1,1-difluoro-1-(pentafluoro-λ^6-sulfanyl)dodec-2-en-4-ol (**28b**) and (E)-5-Bromo-1,1,1-trifluorododec-2-en-4-ol (**28b′**).* To the 6:1 mixture of **27** and **27′** (10 mg, 0.02 mmol) in methanol (1 mL) was added $CeCl_3{\cdot}7H_2O$ (9 mg, 0.02 mmol). Then the mixture was cooled to 0 °C, and a methanol (1 mL) solution of $NaBH_4$ was added dropwise. After 5 min, the reaction was quenched with 0.5 M HCl (3 mL) and extracted with CH_2Cl_2 (3 × 5 mL), and the DCM extracts were washed with brine (10 mL) and dried over $MgSO_4$. Yield: 9 mg (89%, 5:1 mixture with **28′**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.52 (ddt, $^3J_{H,H}$ = 15.7, $^3J_{H,H}$ = 3.8, $^4J_{H,F}$ = 1.9 Hz, 1H), 6.21−6.12 (m, 1H), 4.44 (dh, $^3J_{H,H}$ = 4.4, J = 2.3 Hz, 1H), 3.96 (ddt, J = 9.0, 7.4, $^3J_{H,H}$ = 4.5 Hz, 1H), 2.29 (s, 1H), 1.87−1.74 (m, 2H, AB spin system), 1.33−1.25 (m, 10H), 0.85 (t, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.6 (t, $^3J_{C,F}$ = 8.6 Hz), 121.5 (t, $^2J_{C,F}$ = 22.1 Hz), 72.8, 66.6, 34.3, 31.8, 29.1, 29.0, 26.6, 22.7, 14.2. CF_2 was not detected. ^{19}F NMR (282 MHz, $CDCl_3$): δ 69.05 (quintm, $^2J_{F,F}$ = 144.5, 1F), 37.66 (dt, $^2J_{F,F}$ = 144.5, $^3J_{F,F}$ = 15.1 Hz, 4F), −81.51 (quintd, $^3J_{F,F}$ = 15.6, $^3J_{F,F}$ = 5.4 Hz, 2F). APCI MS: *m*/*z* (rel abund, ion): [FTMS$^-$] calcd 78.9183, found 78.9188 (10, Br^-), calcd 126.9646, found 126.9648 (100, SF_5^-); [FTMS$^+$] calcd 345.1123, found 345.1116 (30, $C_{12}H_{20}F_7OS^+$).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00550.

^{1}H, ^{13}C, and ^{19}F NMR spectra for all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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