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ARTICLE

Synthesis and [3,3]-sigmatropic rearrangements of 5-(pentafluorosulfanyl)-pent-3-en-2-ol, its homologues, and trifluoromethyl analogues†

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The synthesis of aliphatic (pentafluoro-λ⁶-sulfanyl)(SF_5)-substituted compounds is more challenging than that of the related CF_3-substituted analogues. Previous investigations of [3,3]-sigmatropic rearrangements of γ-SF_5-substituted allylic alcohols failed to yield 3-SF_5-substituted carboxylic acid derivatives. Herein, we present the synthesis of a series of 1-SF_5-alk-1-en-3-ols and our efforts to apply them in Johnson-Claisen, ester enolate-Claisen, and Ireland-Claisen rearrangements. Unfortunately, these reactions failed to include the 1-SF_5-substituted 1,2-double bond, although successful reactions of analogous CF_3-allylic alcohols were reported. Further experiments revealed that bulkiness rather than electronic properties of the SF_5 group prevented [3,3]-sigmatropic rearrangements. Indeed, the introduction of a competing second vinyl group into the system (1-SF_5-penta-1,4-dien-3-ol) confirmed that a Johnson-Claisen rearrangement was successful (92% yield of methyl 7-SF_5-hepta-4,6-dienoate) with incorporation of the unsubstituted 4,5-double bond while the 1-SF_5-substituted 1,2-double bond remained unchanged. Efforts to apply 1-(SF_5CF_2)-substituted 1,2-double bond systems, which are similar to CF_3 analogues in steric requirements, in Johnson-Claisen or ester enolate-Claisen rearrangements failed because of the instability of the SF_5CF_2 substituent under various reaction conditions. On the other hand, when the SF_5 group was separated from the reaction center by a CH_2 group instead (5-SF_5-pent-3-en-2-ol), Johnson-Claisen rearrangements using six orthoesters provide the target 2-substituted 3-(CH_2SF_5)-hex-4-enoates in 55-76% yields as ~1:1 mixtures of diastereomers. As an example to demonstrate the utility of these products, methyl 3-(CH_2SF_5)-hex-4-enoate was reduced, and the formed alcohol was oxidized to the aldehyde. Finally, initial experiments showed that the synthetic sequence developed for SF_5 compounds is also applicable for analogous CF_3-substituted allylic alcohols (5-CF_3-pent-3-en-2-ol) and their Johnson-Claisen rearrangement.

Introduction

During the past couple of years, SF_5-substituted compounds have received considerable attention due to their peculiar properties. Results of SF_5 chemistry have been reviewed in 2012 and 2015, respectively, by Altamonte and Zanda[1] and Savoie and Welch.[2] Pentafluoro-λ⁶-sulfanyl compounds have attracted great interest in life sciences,[3] particularly in medicinal chemistry,[4] and agrochemistry[5] as well as in material sciences.[6] In most of these cited papers, the reactivity and properties of SF_5 compounds have been compared to those of CF_3-substituted analogues.

Generally aromatic SF_5 compounds have been prepared most frequently from thiophenols or diaryl disulfides by treatment with an oxidizer in the presence of an appropriate fluoride source.[1,2] The general method was reported by Sheppard already in 1960[7] and was modified and optimized later by many groups and applied to a broad variety of arenes and heteroarenes.[8] Recent results on the synthesis and application of SF_5-substituted heteroaromatic compounds have been reviewed by Kanishchev and Dolbier, and by Shibata et al.[9] On the other hand, the preparation of aliphatic SF_5 derivatives is generally less straightforward.[10] Currently, radical addition of SF_5X (X = Cl or Br) across multiple bond systems is the only practical and versatile option to generate a variety of simple aliphatic SF_5 compounds, serving as starting materials for the preparation of more complex structures. The electrophilic $SF_5^{\bullet}$ radical can be generated thermally, photochemically, or through chemical means. A tremendous step forward was made when Dolbier et al. discovered that $SF_5^{\bullet}$ radical formation can be mediated by triethylborane.[11] This method is currently the most frequently used approach to aliphatic SF_5 compounds, but it was also applied in multistep syntheses of SF_5 benzene itself and a couple of its derivatives.[12,13] Very recently, Paquin et al. published two new protocols for SF_5Cl addition towards alkenes and alkynes, based on the use of either an amine-borane complex or an electron donor-acceptor (EDA)-complex and

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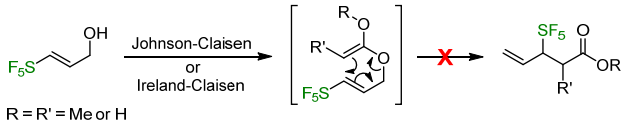
† Electronic supplementary information (ESI) available: Additional and optimization experiments, assigned NMR spectroscopic data, and copies of ^1H, ^{13}C, and ^{19}F NMR spectra of all new compounds. CCDC 1973261. For ESI and crystallographic data in CIF format. See DOI: 10.1039/x0xx00000x

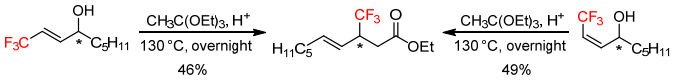
visible light irradiation to initiate the reaction.[14] The addition products of SF_5X (X = Cl, Br) to alkenes and alkynes, respectively, have been used to synthesize building blocks[10] such as for example SF_5-substituted alkenes and alkynes for cycloadditions,[15] arylations[16] or carbonyl compounds applicable for the preparation of more complex molecules.[17]

In our previous investigations, we used SF_5 acetates of fluorinated and non-fluorinated allylic alcohols for different types of [3,3]-sigmatropic rearrangements such as Johnson-Claisen and Ireland-Claisen rearrangements proceeding via SF_5-substituted enolates to prepare α-SF_5-substituted carboxylic acid derivatives.[18] Moreover, we[19] and others[20] used alkyl SF_5 acetates for aldol-type reactions with aldehydes proceeding via analogous SF_5-substituted ketene acetals. In contrast, when the SF_5 group is part of the allylic alcohol moiety, i.e., treatment of 3-SF_5-prop-2-enol with trimethyl (or triethyl) orthoacetate under Johnson-Claisen conditions[21] or the methyl propionate under Ireland-Claisen conditions, the expected [3,3]-sigmatropic rearrangements to the target β-SF_5-substituted methyl ester or the carboxylic acid, respectively, did not occur[22] (Scheme 1).



Scheme 1. Failed trials to involve 3-SF_5-substituted allylic alcohol in [3,3]-sigmatropic rearrangements[22]

In contrast, related γ-CF_3-substituted allylic alcohols have been involved in Claisen,[23] Johnson- and Eschenmoser-Claisen,[24] as well as in Ireland-Claisen rearrangements[25] to provide β-CF_3-substituted γ,δ-unsaturated carboxylic acid derivatives in good yields. Even quaternary CF_3-substituted carbon centers were created by Johnson-Claisen rearrangement.[26] However, in all cases, secondary allylic alcohols were used. For example, Johnson-Claisen rearrangements of both enantiomers of (*E*)- and (*Z*)-1-trifluoromethyl-oct-1-en-3-ols with triethyl orthoacetate in the presence of catalytic amount of propionic acid delivered the (*E*)-configured enantiomeric ethyl 3-trifluoromethyl-dec-4-enoates with complete chirality transfer[24b] (Scheme 2).

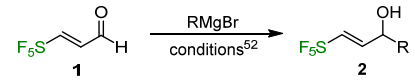


Scheme 2. Johnson-Claisen rearrangements of the enantiomeric (*E*)- and (*Z*)-1-trifluoromethyl-oct-1-en-3-ols with chirality transfer[24b]

Therefore, we expected that γ-SF_5-substituted secondary allylic alcohols might undergo Johnson-Claisen and related rearrangements. Herein, we report our results regarding SF_5-, SF_5CF_2-, and SF_5CH_2-substituted allylic alcohols and their CF_3 analogues in different types of [3,3]-sigmatropic rearrangement reactions.

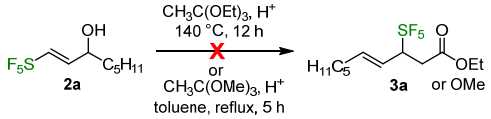
Results and Discussion

Initially, various γ-SF_5-substituted allylic alcohols **2** were prepared as starting materials by Grignard reactions of 3-SF_5-acrolein (**1**) (Scheme 3).[27] Compound **1** was synthesized from allyl acetate and SF_5Cl according to literature protocols.[15b]



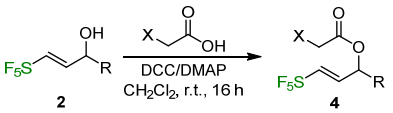
Scheme 3. Grignard reactions of 3-SF_5-acrolein (**1**)[27]

Having the SF_5-substituted secondary allylic alcohols **2** in hand, we attempted Johnson-Claisen rearrangements. Much to our regret, heating of compound **2a** with neat triethyl orthoacetate in the presence of catalytic amount of propionic acid in a sealed tube at 140 °C for 12 hours or refluxing **2a** with trimethyl orthoacetate and catalytic amount of propionic acid in toluene for 5 hours led to partial decomposition. No traces of target product **3a** or the methyl ester were identified in the crude reaction mixtures by ^{19}F NMR spectroscopy.



Scheme 4. Failed trials of Johnson-Claisen rearrangement of compound **2a**

Subsequently, we investigated Ireland-Claisen and ester enolate-Claisen rearrangements. The desired esters were prepared from the SF_5-substituted allylic alcohols **2** and the corresponding carboxylic acids or *N*-protected amino acids by Steglich/Hassner esterification[28] using dicyclohexyl carbodiimide (DCC) and dimethylamino pyridine (DMAP) (Scheme 5 and Table 1).



Scheme 5. Esterification reactions of allylic alcohols **2** with substituted acetic acids

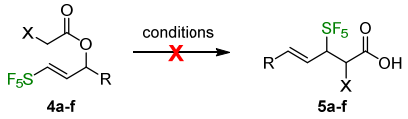
Table 1. Results of esterification reactions of allylic alcohols **2** to form allylic esters **4**

Product	R	X	Yield [%]
4a	H	CH_3	69
4b	C_5H_{11}	OCH_3	95[b]
4c	*cyclo*-C_6H_{11}	OCH_3	47[b]
4d[a]	H	NHBoc	87
4e	C_5H_{11}	NHBoc	83
4f	C_5H_{11}	NHTFA	69
4g	*cyclo*-C_6H_{11}	NHBoc	66
4h	*cyclo*-C_6H_{11}	NHPhth	90
4i	vinyl	NHBoc	63

[a] the structure of this compound was also elucidated by X-ray crystallography (CCDC 1973261, see Supporting Information); [b] pyridine in CH_2Cl_2 at room temperature was used instead of DCC/DMAP.

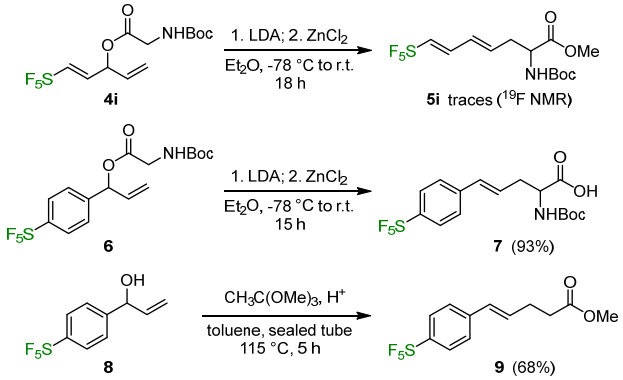
Selected compounds **4** were then treated with bases under the conditions for the corresponding [3,3]-sigmatropic rearrangements. In none of the cases were products **5** detected

in the crude product mixtures. At elevated temperature, decomposition occurred (Scheme 6).



Scheme 6. Failed trials of different Claisen-type rearrangements of compounds **4a-f**

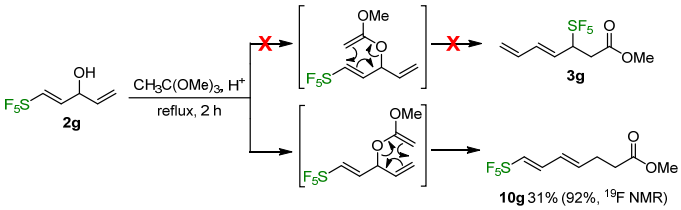
Compound **4a**, by treatment with bases such as Et_3N or LHMDS and TMSOTf or TMSCl in different solvents and at different temperatures, did not rearrange but decomposed at elevated temperature. In none of the experiments, were traces of the expected product **5a** detected in the crude product by ^{19}F NMR spectroscopy. Also, the methoxy-substituted allylic acetates **4b** and **4c** decomposed when treated with LHMDS/TMSCl in THF at room temperature or 60 °C, the conditions which were successfully used by Konno et al.[25a] for the Ireland-Claisen rearrangement of the corresponding CF_3 compounds. In none of the cases were the expected products **5b** and **5c** found in the reaction mixtures by ^{19}F NMR spectroscopy. Likewise, ester enolate-Claisen rearrangements of compounds **4d** and **4e** using LDA or LHMDS and $ZnCl_2$ in Et_2O or THF under various conditions failed. Also, compound **4f** could not be rearranged (for details see Supporting Information). Solely, the reaction of compound **4i** with LDA and $ZnCl_2$ in Et_2O under the conditions shown in Scheme 7, delivered a hint (^{19}F NMR) on the formation of traces of the expected product **5i** formed by incorporation of the unsubstituted double bond.



Scheme 7. Claisen-type rearrangements of compounds **4i**, **6,** and **8**

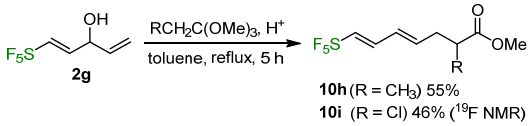
On the other hand, treatment of compound **6** (prepared from **8**) under the same conditions delivered the target *N*-Boc-protected amino acid **7** in 93% isolated yield. Also, the Johnson-Claisen rearrangement of the allylic alcohol **8** yielded 68% of the carboxylic acid methyl ester **9**.

Failure of the Johnson-Claisen rearrangement reaction of SF_5-substituted allylic alcohol **2a** with trialkyl orthoacetates might be explained by either the low nucleophilicity of the hydroxyl group caused by the strongly electron-withdrawing SF_5 group in the γ-position and/or its steric congestion, both of which could prevent the formation of the crucial ketene acetal intermediate. To test the first hypothesis, we introduced a competing vinyl group into our system. Refluxing 1-SF_5-penta-1,4-diene-3-ol (**2g**) with trimethyl orthoacetate in toluene for 5 hours provided methyl 7-SF_5-hepta-4,6-dienoate (**10g**), the rearrangement product involving the less sterically demanding and more electron-rich vinyl group (31% isolated yield). The alternative product **3g**, which might be formed by participation of the SF_5-substituted double bond, was not found in the crude product mixture. Solely **10g** (92%, ^{19}F NMR) was obtained by refluxing of **2g** in neat trimethyl orthoacetate (Scheme 8). For optimization experiments and reactions with triethyl orthoacetate see Supporting Information, Table S1.



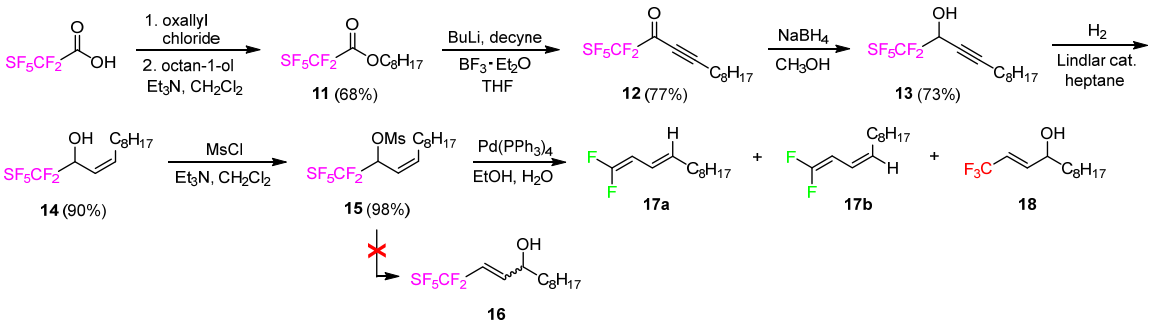
Scheme 8. Competing options of Johnson-Claisen rearrangement of compound **2g** involving either the SF_5-substituted (not occurring) or the unsubstituted vinyl moiety forming **10g**

In order to extend the applicability of this reaction, we refluxed compound **2g** with trimethyl orthopropionate in the presence of a catalytic amount of propionic acid in toluene for 5 hours and isolated 55% of the expected α-methyl derivative **10h**. With trimethyl orthochloroacetate, the rearrangement in the presence of propionic acid did not occur for unknown reasons, but it was successful using pivalic acid as catalyst. The desired product **10i** was found in the product mixture by ^{19}F NMR spectroscopy (46%), but could not be isolated (Scheme 9).



Scheme 9. Johnson-Claisen rearrangement of compound **2g** with methyl orthopropionate and methyl orthochloroacetate

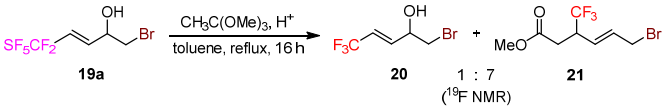
Thus, for the failure to incorporate the SF_5-substituted vinyl moiety in the rearrangement reactions, steric congestion rather than electronic effects of the SF_5 group seem to be more likely. The electron withdrawing effect of the SF_5 and the CF_3 groups are virtually the same,[30] while the steric demand of the SF_5 group is significantly greater than that of the CF_3 group and slightly lower than that of the *tert*-butyl group.[2] One also has to consider the approximate 90° bond angles around sulfur versus the tetraeder angle around the sp^3-hybridized carbon atoms. To gain further insight and assess whether the steric demand of the SF_5 group does solely prevent the rearrangement process, we decided to use an SF_5CF_2-substituted analogue. This system would retain (more or less) the electronic properties of the SF_5 group while decreasing the steric demand at the reaction center, which is expected to be more comparable to that of the CF_3 analogue. Previously, we found that such SF_5CF_2-substituted systems are challenging to prepare due to loss of the SF_5 group by nucleophilic displacement reactions under the influence of neighboring oxygen functions.[29] Therefore, we designed an alternative synthetic sequence starting from decyne and the *n*-octyl ester **11** (Scheme 10), prepared in two steps from SF_5CF_2COOH.[31]



Scheme 10. Synthesis of compounds **15** and trial of Pd(0)-catalyzed [1,3]-sigmatropic rearrangement of **15**

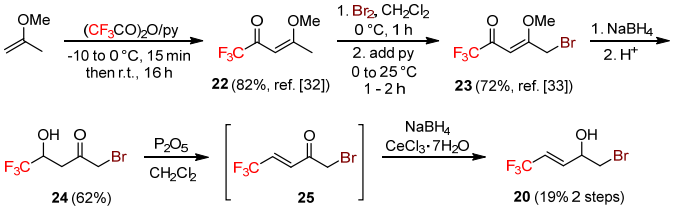
Accordingly, reaction of decyne with BuLi and subsequently with **11** gave the alkynyl ketone **12**, which was reduced with $NaBH_4$ to provide the propargyl alcohol **13**. Hydrogenation of the triple bond using the Lindlar catalyst gave 90% of the (*Z*)-allylic alcohol **14**, which was transformed to the mesylate **15** in almost quantitative yield. Unfortunately, the scheduled Pd(0)-catalyzed allylic rearrangement of **15** to access the target isomeric allylic alcohol **16** was not successful. Instead, a mixture of the diastereomeric geminal difluorinated 1,3-dienes **17a,b** (ratio 1:1) and approximately 12% (based on ^{19}F NMR spectrum of the crude product) of the CF_3-substituted allylic alcohol **18** was obtained from **15** (Scheme 10). For details, see the discussion in reference[29] and the Supporting Information.

In order to reduce the nucleophilicity of the oxygen functionality, the earlier prepared allylic alcohol **19a** (contaminated with 8% of the CF_3 analogue)[29] was subjected to the conditions of a Johnson-Claisen rearrangement using trimethyl orthoacetate. Analysis of the product mixture using ^{19}F NMR spectroscopy revealed absence of any SF_5CF_2-substituted compound and, together with other NMR data, strongly suggested formation of the CF_3-containing allylic alcohol **20** alongside with its rearrangement product **21** in a ratio of 1:7. The reaction was not allowed to reach completion and products were not isolated (Scheme 11). For a mechanistic interpretation of this type of reactions see the discussion in reference.[29]



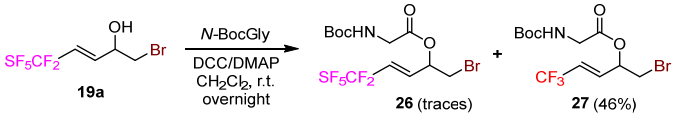
Scheme 11. Treatment of compound **19a** under the conditions of a Johnson-Claisen rearrangement leading to CF_3-substituted products **20** and **21**

These findings were confirmed by the independent synthesis of compounds **20** starting from 2-methoxypropene and trifluoroacetic acid anhydride via compounds **22-25** (Scheme 12) and its Johnson-Claisen rearrangement to form **21** (63%).



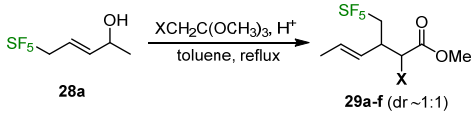
Scheme 12. Synthesis of compound **20** *via* **22**,[32] **23**[33]

Most probably, due to elevated temperature, the elimination of the SF_5 group preceded the rearrangement reaction. To avoid this undesired process, which was previously observed already,[29] we decided to synthesize the enolizable Boc-glycine ester as a presumably more stable precursor for a Kazmaier-type[34] ester enolate-Claisen rearrangement. Unfortunately, this project failed because treatment of allylic alcohol **19a** with *N*-Boc-Glycine and DCC/DMAP[28] besides traces of the target glycinate **26** gave mainly the CF_3-substituted allylic ester **27** (46% yield) (Scheme 13) by partial loss of the SF_5 group, presumably via the allylic alcohol **20**. Compound **27** decomposed under the conditions (see Scheme 7) of ester enolate-Claisen rearrangement.



Scheme 13. Formation of the *N*-protected glycine esters **26** and **27** from **19a**

The SF_5CF_2 group is obviously unstable under various reaction conditions, which had already been noticed in our previous investigations.[29] These undesired decomposition reactions forced us to test a SF_5CH_2-substituted allylic alcohol **28a**, which we had previously synthesized and found to be stable.[29] Gratifyingly, treatment of **28a** with trimethyl orthoacetate in the presence of catalytic amount of propionic acid in refluxing toluene resulted in rearrangement product **29a** (X = H, 55% yield), with the SF_5CH_2 group in β-position with regard to the carboxylate function (Scheme 14 and Table 2). This finding confirms that the steric demand of the SF_5 group rather than its strong electron withdrawing effect plays a critical role in the unsuccessful rearrangement processes involving the γ-SF_5-substituted allylic alcohols and esters **2** and **4**, respectively.



Scheme 14. Johnson-Claisen rearrangement of allylic alcohol **28a** with methyl orthoacetate and substituted analogues to form **29** as mixtures of diastereomers

Encouraged by the promising result involving the SF_5CH_2-substituted allylic alcohol **28a**, we explored the scope of this reaction by using various substituted orthoesters (Table 2). As a result, exclusively the (*E*)-isomers of α-methyl, α-ethyl, or α-propyl, β-SF_5CH_2-substituted, γ,δ-unsaturated methyl esters **29b-d** were formed in moderate yields as mixtures of diastereoisomers with a slight preference for the *syn* isomers.

Similarly, a bromoethyl group and chlorine substituent could be placed in the α-position of the methyl ester group forming products **29e,f**.

Table 2. Scope of the Johnson-Claisen rearrangement of allylic alcohol **28a** and various trimethyl orthoesters

Product	X	Yield [%]	*syn*/*anti* ratio
29a	H	55	83:17[a]
29b	CH_3	60	64:36
29c	C_2H_5	57	59:41
29d	C_3H_7	65	64:36
29e	C_2H_4Br	76	63:37
29f	Cl	63	55:45

[a] *E*/*Z* ratio

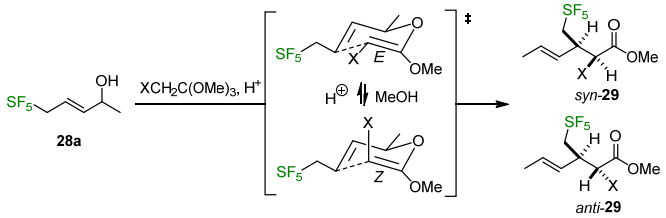
The assignment of the stereochemistry of the products (Figure 1) was based on the coupling constants between the H-C2 and H-C3 hydrogen atoms in the ^{1}H NMR spectra of the diastereomeric mixtures. For example, the spectrum of **29d** shows coupling values of 5.1 Hz for *syn*-**29d** and 8.0 Hz for *anti*-isomers.

29d *syn* $^3J_{H2-H3}$ = 5.1 Hz

29d *anti* $^3J_{H2-H3}$ = 8.0 Hz

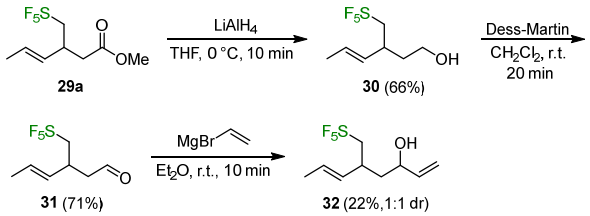
Figure 1. Structures of *syn* and *anti* diastereoisomers of **29d** with the relevant coupling constants.

The slight predominance for the *syn* product indicates a weak preference for the *E* isomer of the intermediary ketene acetal with the X substituent in an equatorial orientation (Scheme 15).



Scheme 15. Transition states leading to the *syn* and *anti* diastereoisomers

Furthermore, to show synthetic utility of this kind of products, we carried out some downstream transformations using **29a** as an example (Scheme 16). First, the ester group was reduced to the alcohol **30** using $LiAlH_4$ in THF. The alcohol **30** was oxidized to the corresponding aldehyde **31** by using the Dess-Martin reagent. Preliminary results of a Grignard reaction of formed **31** with vinylmagnesium bromide gave **32** as mixture of two diastereomers. However, these as well as the results of other carbonyl reactions exceed the scope of this work.

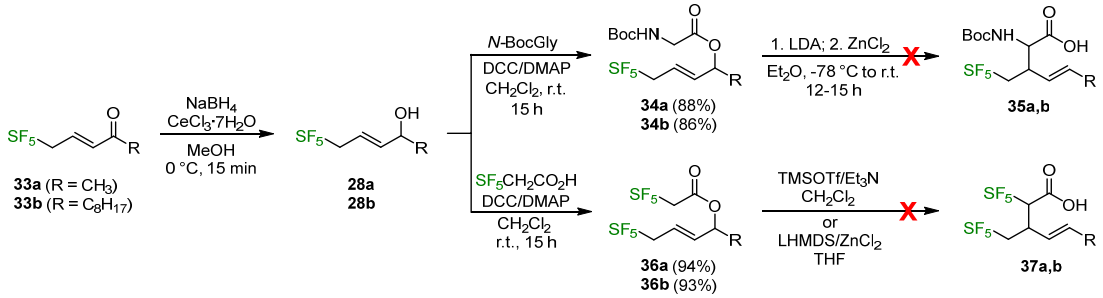


Scheme 16. Downstream chemistry of the rearrangement product **29a**.

In order to study ester enolate Claisen type rearrangements and having the synthesis of SF_5-substituted α-amino acids in mind, *N*-Boc protected glycine ester **34a** was prepared from **28a**[29] and Boc-glycine using the Steglich/Hassner DCC/DMAP esterification method.[28] Subsequently, **34a** was subjected to rearrangement conditions used by Konno et al.[25a] for rearrangement of analogous CF_3 compounds (Scheme 17). The substrate **34a** was consumed, but the target product **35a** was not formed and no other SF_5-substituted compounds were found in the crude product mixture by ^{19}F NMR spectroscopy. Probably, decomposition involving the acidic protons of the CH_2SF_5 group occurred. Products could not be isolated. Therefore, the long chain allylic alcohol **28b** was prepared from 2-methoxydec-1-ene and $SF_5CH_2CO_2H$ *via* **33b** analogously to the synthesis of **28a** from **33a**[29] and esterified with Boc-glycine to yield **34b**. By treatment of **34b** under the conditions shown in Scheme 17, we expected isolable products, but to our regret no reaction occurred.

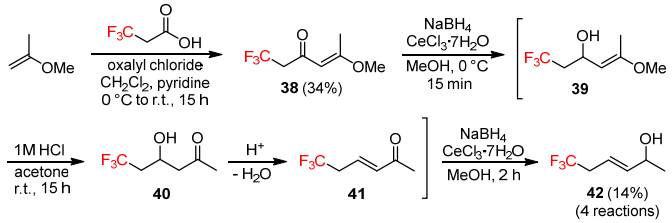
Our previous investigations on Ireland-Claisen rearrangements of SF_5-acetic acid esters of fluorinated allylic alcohols[18] led us to synthesize esters **36a,b** and to attempt rearrangement under the different conditions of our former studies. With TMSOTf/Et_3N in methylene chloride, no reaction occurred, and the esters were recovered, while application of LHMDS/$ZnCl_2$ to **36b** led to unidentified decomposition products. The target product **37b** was not identified in the crude product mixture by ^{19}F NMR spectroscopy.

Therefore, we prepared compound **42**, the CF_3 analogue of the allylic alcohol **28a** for comparison. Thus, reaction of methoxy propene with 3,3,3-trifluoropropionic acid chloride gave 34% of



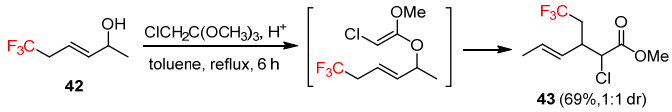
Scheme 17. Synthesis of esters **34a,b** and **36b**, and failed attempts of ester enolate type Claisen rearrangements to form carboxylic acids **35a,b** and **37b**, respectively

the addition/elimination product **38**. This compound was transformed to the allylic alcohol **42** in 14% overall yield via the enol ether **39**, the aldol **40** and the α,β-unsaturated ketone **41** without isolation of these intermediate compounds but followed by TLC (Scheme 18).



Scheme 18. Synthesis of (*E*)-6,6,6-trifluorohex-3-en-2-ol (**42**) as an analog of the SF_5-substituted allylic alcohol **28a**

Treatment of (*E*)-6,6,6-trifluorohex-3-en-2-ol (**42**) with trimethyl 2-chloroorthoacetate under the standard conditions resulted in the rearrangement product **43** in 69% yield with comparable results to the previous experiments with compounds **28**, i.e., 45:55 ratio of diastereomers (Scheme 19).



Scheme 19. Johnson-Claisen rearrangement of (*E*)-6,6,6-trifluorohex-3-en-2-ol (**42**)

Conclusions

Several reactions of different SF_5-substituted allylic alcohols have been investigated. Our experiments revealed that the SF_5 group in the vinylic γ position of an allylic alcohol prevented [3,3]-sigmatropic rearrangements due to its bulkiness rather than electronic properties. Indeed, the introduction of a competing second vinyl group into the system confirmed that the hydroxyl group remained sufficiently nucleophilic to react in the presence of an SF_5 group. However, instead of the SF_5-substituted double bond the unsubstituted one was involved in the Johnson-Claisen rearrangement. In order to decrease the steric congestion, (SF_5CF_2)-substituted allylic alcohols were synthesized. However, the SF_5CF_2 group in vinylic position was unstable under various reaction conditions. On the other hand, when the SF_5 group was separated from the reaction center by a CH_2 group instead of a CF_2 group, Johnson-Claisen rearrangement reactions were successful. Six commercially available orthoesters were used giving rise to new 3-(SF_5CH_2)-substituted (*E*)-alk-4-ene-carboxylates, which are useful for further modification, thereby providing building blocks such as alcohols and aldehydes for the construction of more complex molecules. Furthermore, initial experiments demonstrated that the developed synthetic sequence for SF_5 compounds is also useful for the analogous CF_3-substituted allylic alcohol and its application in Johnson-Claisen rearrangements. According to our earlier experience with β-fluorovinyl alcohols,[35] compounds bearing the SF_5 group in β-position of the allylic alcohol might rearrange successfully. This is subject of future research.

Experimental section

General remarks

Melting points were measured with a SMP 10 apparatus of Stuart Scientific Co. and are uncorrected. ^{1}H NMR spectra were recorded at room temperature at 300, 400, 500, or 600 MHz. ^{13}C and ^{19}F NMR spectra were likewise recorded at 75, 100, 126, or 151 MHz and 282 or 564 MHz, respectively. The spectra were calibrated with $CDCl_3$ (7.26 and 77.03 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. The assignment of signals was supported by the DEPT method and two-dimensional techniques (COSY, HMBC, and HSQC). The recorded ^{13}C NMR spectra were taken with broadband proton decoupling, so that multiplicities observed would have had to result from coupling to the ^{19}F nuclide. In the ^{19}F NMR spectra, the SF_5 group gives an AB_4 spin systems 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 (or HP1) column, 40 °C for 2 min, heated with 10 °C/min to 280 or 300 °C, then 5 min isotherm]. GC-MS (EI^+ Scan) were measured with a Micromass apparatus, while atmospheric pressure chemical ionization (APCI) mass spectra were recorded on an Orbitrap instrument with loop injection. Elemental analyses were obtained using a Foss Haraeus CHN-O-Rapid analyzer or a VarioEL III of Elementar Analysensysteme, Germany. All spectroscopic and analytical investigations were conducted by staff members of the Organic Chemistry Institute, University of Münster, Germany. All reactions requiring dry conditions were carried out in glassware that was either oven dried or prepared by Schlenk techniques under an argon atmosphere. All reagents were commercially obtained and used without further purification. Solvents were distilled and dried according to standard protocols if needed. TLC-plates (silica gel 60 F_{254}, Merck) 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 (Merck, particle size 0.040–0.063 mm).

Synthesis of SF_5-substituted allylesters 4a-c

*(E)-3-(Pentafluoro-λ^6-sulfanyl)allyl propionate (**4a**).* In a flame dried flask under an argon atmosphere, DCC (7.47 g, 30.0 mmol) was dissolved in dry dichloromethane (100 mL) under stirring. Subsequently (*E*)-3-(pentafluoro-λ^6-sulfanyl)prop-2-en-1-ol[27] (1.84 g, 10.0 mmol) was added followed by propionic acid (0.83 mL, 11 mmol). Within 1 min, a white solid started to precipitate, and a catalytic amount of DMAP was added to the stirred suspension. After stirring overnight, the reaction mixture was diluted with pentane (100 mL), and the white precipitate was filtered off and washed thoroughly with dichloromethane (30 mL). The combined organic layers were washed with water (2 × 50 mL), 5% aq. acetic acid

(2 × 50 mL), and again water (2 × 50 mL). After drying with $MgSO_4$ the solvent was evaporated, and the yellowish crude product was purified on silica gel (pentane/diethyl ether, 20:1) affording the pure title product as a clear oil. Yield: 1.64 g (69%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.73–6.50 (m, 2H), 4.74 (m, 2H), 2.42 (q, $^3J_{H-H}$ = 7.6 Hz, 2H), 1.18 (t, $^3J_{H-H}$ = 7.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 173.5, 141.6 (dqu, $^2J_{C-F}$ = 21.2 Hz, $^2J_{C-F}$ = 1.2 Hz), 132.7 (qu, $^3J_{C-F}$ = 7.1 Hz), 60.6, 27.2, 8.9; ^{19}F NMR (282 MHz, $CDCl_3$): δ 82.42 (mqu, $^2J_{F-F}$ = 150.5 Hz 1F), 62.80 (dm, $^2J_{F-F}$ = 150.5 Hz, 4F); GC-MS 70eV *m/z* (rel. intens.): 240 (0) $[M]^+$, 127 (5) $[SF_5]^+$, 113 (10) $[M\text{-}SF_5]^+$, 89 (12) $[SF_3]^+$, 70 (2) $[SF_2]^+$, 57 (100) $[C_3H_5O]^+$.

*(E)-1-(Pentafluoro-λ^6-sulfanyl)oct-1-en-3-yl 2-methoxyacetate (**4b**).* Analogous to a procedure of Konno et al.,[25a] (*E*)-1-(pentafluoro-λ^6-sulfanyl)oct-1-en-3-ol (**2a**) (170 mg, 0.67 mmol) was dissolved in dry dichloromethane (4 mL) and cooled to 0 °C. Subsequently methoxyacetyl chloride (109 mg, 1.00 mmol) was added slowly, followed by the addition of dry pyridine (79 mg, 1.00 mmol). The mixture was warmed to r.t. and stirred for a further 2 h before quenching with 0.1 M HCl (4 mL). The layers were separated, and the aqueous layer was extracted with dichloromethane (3 × 15 mL). The combined organic layers were washed with water (10 mL) and dried with magnesium sulfate. After removal of the solvent, the crude brownish oil was purified by flash-chromatography (silica gel, 2 × 15 cm, pentane/diethyl ether, 15:1) giving the title product as a colorless clear oil. Yield: 207 mg (95%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.51 (dqu, $^3J_{H-H}$ = 14.7 Hz, $^3J_{H-F}$ = 6.2 Hz, 1H), 6.36 (ddqu, $^3J_{H-H}$ = 14.7 Hz, $^3J_{H-H}$ = 5.8 Hz, $^4J_{H-F}$ = 1.5 Hz, 1H), 5.42 (dt, $^3J_{H-H}$ = 5.8 Hz, $^4J_{H-H}$ = 1.5 Hz, 1H), 4.01 (s, 2H), 3.40 (s, 3H), 1.71–1.58 (m, 2H), 1.33–1.12 (m, 6H), 0.82 (t, $^3J_{H-H}$ = 6.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 169.2, 136.0 (dqu, $^3J_{C-F}$ = 21.1 Hz), 136.0 (dqu, $^4J_{C-F}$ = 6.9 Hz), 71.4, 69.6, 59.4, 33.6, 31.3, 24.4, 22.4, 13.9; ^{19}F NMR (282 MHz, $CDCl_3$): δ 82.48 (mqu, $^2J_{F-F}$ = 150.9 Hz, 1F), 63.08 (dm, $^2J_{F-F}$ = 150.9 Hz, 4F); MS-ES (+) *m/z*: calcd for: $C_{11}H_{19}F_5O_3SNa$ 349.0867, found: 349.0871.

*(E)-1-cyclohexyl-3-(pentafluoro-λ^6-sulfanyl)allyl 2-methoxyacetate (**4c**).* According to the above procedure, (*E*)-1-cyclohexyl-3-(pentafluoro-λ^6-sulfanyl)prop-2-en-1-ol (**2c**) (100 mg, 0.375 mmol) was esterified with methoxyacetylchloride (61.1 mg, 563 mmol), giving the title product as a colorless clear oil after flash-chromatography (1 × 15 cm, pentane/diethyl ether, 10:1). Yield: 60 mg (47%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.56 (m, 1H), 6.42 (ddm, $^3J_{H-H}$ = 14.7, $^3J_{H-H}$ = 6.1, $^4J_{H-F}$ = 1.0 Hz, 1H), 5.35–5.27 (m, 1H), 4.09 (s, 2H), 3.47 (s, 3H), 1.85–0.95 (m, 13H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.2, 142.1 (ddqu, $^2J_{C-F}$ = 20.7 Hz, $^2J_{C-F}$ = 1.0 Hz), 134.9 (dqu, $^3J_{C-F}$ = 7.0 Hz), 75.1, 69.5, 59.4, 41.3, 28.3, 28.1, 25.9, 25.6; ^{19}F NMR (282 MHz, $CDCl_3$): δ 82.00 (mqu, $^2J_{F-F}$ = 150.9 Hz, 1F), 62.59 (dm, $^2J_{F-F}$ = 150.9 Hz, 4F); MS-ES (+): calcd for: $C_{12}H_{19}F_5O_3SNa$ 361.0867, found: 361.0869.

Synthesis of the N-protected SF_5-substituted allyl glycinates 4d-i (General Procedure)

In a flame-dried Schlenk-flask under an argon atmosphere, DCC (3.0 mmol, 3 equiv) was dissolved in dry dichloromethane (10 mL). Under stirring, the corresponding alcohol[27] (1.0 mmol, 1.0 equiv) was added followed by the *N*-protected glycine (1.1 mmol, 1.1 equiv). Within one minute a white solid starts to precipitate, and a catalytic amount of DMAP was added to the stirred suspension. After stirring overnight, the precipitate was filtered off and washed with dichloromethane (2 × 10 mL). The combined organic layers were washed with water (2 × 10 mL), acetic acid (5%, 10 mL), and brine (2 × 10 mL), dried over magnesium sulfate, and the solvent was removed in vacuum. The crude product was purified by flash chromatography as specified for each product.

*(E)-3-(Pentafluoro-λ^6-sulfanyl)allyl (tert-butoxycarbonyl) glycinate (**4d**).* (*E*)-3-(Pentafluoro-λ^6-sulfanyl)prop-2-en-1-ol[27] (1.84 g, 10.0 mmol) was esterified with Boc-glycine (1.93 g, 11.0 mmol, 1.1 equiv) according to the general procedure. After diluting the reaction mixture with pentane (100 mL), the precipitated urea-derivative was filtered off and washed with pentane (50 mL). The combined organic layers were washed with water (2 × 50 mL), 5% acetic acid (2 × 50 mL), and again water (2 × 50 mL). After drying with $MgSO_4$, the solvent was evaporated, and the resulting solid was purified by flash chromatography (silica gel, 2 × 20 cm, cyclohexane/ethyl acetate, 6:1) giving the target product as a white solid. Yield: 3.17 g (87%). M.p. 62 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.67 (m, 1H), 6.55 (dqu, $^3J_{H-H}$ = 14.7 Hz, $^4J_{H-F}$ = 4.5 Hz, 1H), 5.08 (bs, 1H), 4.81 (m, 2H), 3.97 (bd, $^3J_{H-H}$ = 5.8 Hz, 2H), 1.46 (s, 9H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 169.7, 155.8, 142.2 (dqu, $^2J_{C-F}$ = 21.2 Hz), 132.0 (dqu, $^3J_{C-F}$ = 7.2 Hz), 80.4, 61.4, 42.4, 28.3 (×3); ^{19}F NMR (282 MHz, $CDCl_3$): δ 82.19 (mqu, $^2J_{F-F}$ = 149.1 Hz, 1F), 62.94 (dm, $^2J_{F-F}$ = 149.1 Hz, 4F); MS-ES (+) *m/z*: calcd for $C_{10}H_{16}F_5NO_4SNa$: 364.0612, found: 364.0613.

*(E)-1-(Pentafluoro-λ^6-sulfanyl)oct-1-en-3-yl (tert-butoxycarbonyl)glycinate (**4e**).* Along the lines of the general procedure, (*E*)-1-pentafluorosulfanyloct-1-en-3-ol (**2a**) (309 mg, 1.22 mmol) was esterified with Boc-glycine, giving the title product as a clear oil after flash-chromatography (cyclohexane/ethyl acetate, 7:1). Yield: 404 mg (83%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.62 (m, 1H), 6.42 (dd, 1H, $^3J_{H-H}$ = 14.7 Hz, $^3J_{H-H}$ = 5.5 Hz, 1H), 5.44 (dd, $^3J_{H-H}$ = 5.5 Hz, 1H), 5.10 (s, 1H), 3.94 (d, $^3J_{H-H}$ = 5.5 Hz, 2H), 1.87–1.58 (m, 2H), 1.45 (s, 9H), 1.40–1.19 (m, 6H), 0.89 (t, $^3J_{H-H}$ = 6.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 169.4, 155.7, 141.6 (qu, $^2J_{C-F}$ = 21.1 Hz), 135.9 (dqu, $^3J_{C-F}$ = 7.0 Hz), 80.2, 71.9, 42.4, 33.6, 31.2, 28.2 (×3), 24.3, 22.3, 13.8; ^{19}F NMR (282 MHz, $CDCl_3$): δ 84.67 (m, $^2J_{F-F}$ = 150.1 Hz, 1F), 62.89 (dm, $^2J_{F-F}$ = 150.1 Hz, 4F; MS-ES (+) *m/z*: calcd for $C_{15}H_{26}F_5NO_4SNa$: 434.1395, found: 434.1398.

*(E)-1-(Pentafluoro-λ^6-sulfanyl)oct-1-en-3-yl (2,2,2-trifluoroacetyl)glycinate (**4f**).* (*E*)-1-(Pentafluoro-λ^6-sulfanyl)oct-1-en-3-ol (**2a**) (254 mg, 1.0 mmol) was esterified with TFA-glycine according to the general procedure. The oily crude product was purified by flash-chromatography (2 × 15 cm, cyclohexane/ethyl acetate, 10:1) giving the pure product as a colorless oil. Yield: 253 mg (69%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.03 (bs, 1H), 6.67 – 6.54 (m, 1H), 6.42 (ddm, $^3J_{H-H}$ = 14.8 Hz, $^3J_{H-H}$ = 5.9 Hz, 1H), 5.45 (ddt, $^3J_{H-H}$ = 7.1 Hz, $^3J_{H-H}$ = 5.9 Hz, $^4J_{H-H}$ = 1.2 Hz, 1H), 4.17 (d, $^3J_{H-H}$ = 5.4 Hz, 2H), 1.80 – 1.64 (m, 2H), 1.40 – 1.24 (m, 6H), 0.89 (t, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$):

δ 167.4, 157.5 (q, $^2J_{C\text{-}F}$ = 38.2 Hz), 142.2 (dqu, $^2J_{C\text{-}F}$ = 21.3 Hz), 135.4 (dqu, $^3J_{C\text{-}F}$ = 7.0 Hz), 115.6 (q, $^1J_{C\text{-}F}$ = 287.3 Hz), 73.2, 41.3, 33.6, 31.3, 24.3, 22.4, 13.9; ^{19}F NMR (282 MHz, $CDCl_3$): δ 81.63 (m, $^2J_{F\text{-}F}$ = 150.7 Hz, 1F), 62.54 (dm, $^2J_{F\text{-}F}$ = 150.7 Hz, 4F), -76.35 (s, 3F); MS-ES (+) *m/z*: calcd for $C_{12}H_{17}F_8NO_3SNa$ 430.0694, found: 430.0696.

*(E)-1-Cyclohexyl-3-(pentafluoro-λ^6-sulfanyl)allyl (tert-butoxycarbonyl)glycinate (**4g**)*. According to the general procedure, (*E*)-1-cyclohexyl-3-(pentafluoro-λ^6-sulfanyl)prop-2-en-1-ol (**2c**) (100 mg, 0.375 mmol) was esterified with Boc-glycine. The formed ester **4g** was purified by flash-chromatography (2 × 15 cm, pentane/diethyl ether, 10:1) giving the title ester as a clear oil. Yield: 105 mg (66%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.57 (m, 1H), 6.40 (ddqu, $^3J_{H\text{-}H}$ = 14.7, $^4J_{H,H}$ = 5.9, $^4J_{H\text{-}F}$ = 0.9 Hz, 1H), 5.26 (m, 1H), 5.10 (s, 1H), 3.95 (dd, $^3J_{H\text{-}H}$ = 5.4, $^3J_{H\text{-}H}$ = 4.5 Hz, 2H), 1.80–1.60 (m, 5H, 4-CH), 1.46 (s, 9H), 1.35–0.82 (m, 6H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 169.5, 155.7, 142.2 (qu, $^2J_{C\text{-}F}$ = 20.4 Hz), 134.9 (qu, $^3J_{C\text{-}F}$ = 6.8 Hz), 80.2, 65.9, 42.5, 41.4, 28.3 (×2), 28.2 (×3), 26.0 (×2), 25.7; ^{19}F NMR (282 MHz, $CDCl_3$): δ 81.82 (m, $^2J_{F\text{-}F}$ = 150.1 Hz, 1F), 62.54 (dm, $^2J_{F\text{-}F}$ = 150.8 Hz, 4F); MS-ES (+) *m/z*: calcd for $C_{16}H_{26}F_5NO_4SNa$: 446.1395, found: 446.1386.

*(E)-1-Cyclohexyl-3-(pentafluoro-λ^6-sulfanyl)allyl 2-(1,3-dioxoisoindolin-2-yl)acetate (**4h**)*. To a stirred solution of (*E*)-1-cyclohexyl-3-(pentafluoro-λ^6-sulfanyl)prop-2-en-1-ol (**2c**) (152 mg, 0.570 mmol) in dry dichloromethane, DCC (125 mg, 0.627 mmol) and phthalimido-glycine (128 mg, 0.625 mmol) were added. When a white solid started to precipitate, a catalytic amount of DMAP was added and stirring was continued at r.t. overnight. The white urea derivative was filtered off and washed thoroughly with dichloromethane. The combined organic layers were washed, dried, and the solvent was removed in vacuum. The yellowish solid was purified by flash-chromatography (pentane/diethyl ether, 5:1) and the target product was obtained as a white solid. Yield: 232 mg (90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.95–7.73 (m, 4H), 6.53 (ddqu, $^3J_{H\text{-}F}$ = 20.7 Hz, $^3J_{H\text{-}H}$ = 6.1 Hz, $^4J_{H\text{-}H}$ = 1.2 Hz, 1H), 6.40 (ddqu, $^3J_{H\text{-}H}$ = 14.7 Hz, $^3J_{H\text{-}H}$ = 5.6 Hz, $^4J_{H\text{-}F}$ = 0.9 Hz, 1H), 5.35–5.25 (m, 1H), 4.50 (s, 2H), 1.85–0.80 (m, 11H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 167.4, 166.3 (×2), 142.1 (qu, $^2J_{C\text{-}F}$ = 20.6 Hz), 134.4 (qu, $^3J_{C\text{-}F}$ = 7.0 Hz), 134.4 (×2), 131.9 (×2), 123.7 (×2), 76.3, 41.4, 38.9, 28.4, 27.9, 26.0, 25.7 (×2); ^{19}F NMR (282 MHz, $CDCl_3$): δ 82.45 (m, $^2J_{F\text{-}F}$ = 150.0 Hz, 1F), 63.17 (dm, $^2J_{F\text{-}F}$ = 150.0 Hz, $^3J_{F\text{-}H}$ =1.9 Hz, 4F); GC-MS 70eV *m/z* (rel. intens.): 453 (2) $[M]^+$, 371 (41) $[M\text{-}C_6H_{12}]^+$, 326 (11) $[M\text{-}SF_5]^+$, 188 (99) $[C_{10}H_6NO_3]^+$, 160 (100), 83 (63) $[C_6H_{11}]^+$, 76 (44) $[C_6H_4]^+$, 55 (64) $[C_4H_4]^+$. MS-ES (+) *m/z*: calcd for $C_{19}H_{20}F_5NO_4SNa$ 476.0925, found: 476.0934 and calcd for $(C_{19}H_{20}F_5NO_4S)_2Na$ 929.1959, found: 929.1965.

*(E)-1-(Pentafluoro-λ^6-sulfanyl)penta-1,4-dien-3-yl (tert-butoxycarbonyl)-glycinate (**4i**)*. (*E*)-1-(pentafluoro-λ^6-sulfanyl)penta-1,4-dien-3-ol (**2g**) (60.0 mg, 0.285 mmol) was esterified according to the general procedure. After purification by flash-chromatography (pentane/diethyl ether, 5:1) the target ester was obtained as a yellowish gummy oil. Yield: 66 mg (63%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.67 (dqud, $^3J_{H\text{-}H}$ = 14.7 Hz, $^3J_{H\text{-}F}$ = 6.2 Hz, $^4J_{H\text{-}H}$ = 1.0 Hz, 1H) 6.47 (dd, $^3J_{H\text{-}H}$ = 14.7 Hz, $^3J_{H\text{-}H}$ = 5.0 Hz, 1H), 5.95–5.86 (m, 2H) 5.80 (ddd, $^3J_{H\text{-}H}$ = 15.0, $^3J_{H\text{-}H}$ = 10.5, $^3J_{H\text{-}H}$ = 5.6 Hz, 1H), 5.08 (m, 1H), 3.97 (d, 2H, $^3J_{H\text{-}H}$ = 5.8 Hz), 1.45 (s, $^3J_{H\text{-}H}$ = 1.5 Hz, 9H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 169.2, 155.9, 142.3 (qu, $^2J_{C\text{-}F}$ = 20.0 Hz), 134.8 (qu, $^3J_{C\text{-}F}$ = 7.2 Hz), 132.2, 120.7, 80.4, 72.4, 42.6, 28.4 (×3); ^{19}F NMR (282 MHz, $CDCl_3$): δ 82.06 (m, $^2J_{F\text{-}F}$ = 151.1 Hz, 1F), 63.19 (dm, $^2J_{F\text{-}F}$ = 151.1 Hz, 4F); MS-ES (+) *m/z*: calcd. for $C_{12}H_{18}F_5NO_4SNa$ 390.0769, found: 390.0772; and calcd for $(C_{12}H_{18}F_5NO_4S)_2Na$ 757.1646, found: 757.1646.

Synthesis and ester enolate-Claisen Rearrangement of compound 6

*1-[4-(Pentafluoro-λ^6-sulfanyl)phenyl]prop-2-en-1-ol (**8**)*. 4-(Pentafluoro-λ^6-sulfanyl)benzaldehyde[36] (0.372 g, 1.6 mmol) was dissolved in dry diethyl ether (10 mL) under argon atmosphere. The solution was cooled to 0 °C and vinylmagnesium bromide (5.03 mL, 3.52 mmol, 2.20 equiv, 0.700 M solution in THF) was slowly added over a period of 5 min. The mixture was stirred for a further 10 min before being allowed to warm to room temperature and stirred for 4 h. To quench the reaction, 2 N HCl was added until the precipitate was dissolved. The layers were separated, and the aqueous layer was extracted with diethyl ether (3 × 20 mL). The combined organic layers were washed with brine (2 × 15 mL) and subsequently dried over magnesium sulfate, prior to removing the solvent in vacuum. The resulting yellowish oil was purified on silica gel (3 × 15 cm, pentane/ethyl acetate, 10:1), giving the target compound as a colorless clear oil. Yield: 281 mg (68%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.75 (dqu, $^3J_{H\text{-}H}$ = 8.2 Hz, $^3J_{H\text{-}F}$ = 2.0 Hz 1H), 7.46 (d, $^3J_{H\text{-}H}$ = 8.2 Hz, 1H), 5.97 (ddd, $^3J_{H\text{-}H}$ = 17.0 Hz, $^3J_{H\text{-}H}$ = 10.2 Hz, $^3J_{H\text{-}H}$ = 6.2 Hz, 1H), 5.37 (dd, $^3J_{H\text{-}H}$ = 17.0 Hz, $^4J_{H\text{-}H}$ = 1.2 Hz, 1H), 5.25 (dd, $^3J_{H\text{-}H}$ = 10.2 Hz, $^4J_{H\text{-}H}$ = 1.2 Hz, 1H), 5.23 (d, $^3J_{H\text{-}H}$ = 6.2 Hz, 1H), 2.34 (bs, 1H); ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): δ 153.2 (dqu, $^3J_{C\text{-}F}$ = 1.2 Hz, $^3J_{C\text{-}F}$ = 17.2 Hz), 146.1, 139.3, 126.4 (×2), 126.1 (dqu, $^4J_{C\text{-}F}$ = 4.6 Hz, ×2), 116.6, 74.6; ^{19}F NMR (282 MHz, $CDCl_3$): δ 84.60 (mp, $^2J_{F\text{-}F}$ = 149.9 Hz, 1F), 62.94 (d, $^2J_{F\text{-}F}$ = 149.9 Hz, 4F). Elemental analysis: calcd for $C_9H_9F_5OS$: C 41.54, H 3.49, found: C 41.10, H 3.57.

*1-[4-(Pentafluoro-λ^6-sulfanyl)phenyl]allyl (tert-butoxycarbonyl) glycinate (**6**)*. According to the general procedure 1-[4-(pentafluoro-λ^6-sulfanyl)phenyl]prop-2-en-1-ol (**8**) (550 mg, 2.12 mmol) was esterified with Boc-glycine. The crude product was purified on silica gel (5 × 11 cm, cyclohexane/ethyl acetate, 5:2) yielding a honey-like liquid. Yield: 542 mg (61%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.75 (dd, $^3J_{H\text{-}H}$ = 8.6 Hz, $^4J_{H\text{-}F}$ = 2.0 Hz, 2H), 7.45 (d, $^3J_{H\text{-}H}$ = 8.6 Hz, 2H), 6.32 (d, $^3J_{H\text{-}H}$ = 6.1 Hz, 1H), 5.96 (ddd, $^3J_{H\text{-}H}$ = 16.8 Hz, $^3J_{H\text{-}H}$ = 10.4 Hz, $^3J_{H\text{-}H}$ = 6.1 Hz, 1H), 5.35 (m, 2H), 5.02 (bs, 1H), 3.98 (m, 2H), 1.44 (s, 9H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 169.4, 155.7, 153.6 (qu, $^2J_{C\text{-}F}$ = 17.6 Hz), 142.1, 134.7 (×2), 127.3, 126.4 (dqu, $^3J_{C\text{-}F}$ = 4.7 Hz, ×2), 118.7, 80.2, 76.1, 42.6, 28.3 (×3); ^{19}F NMR (282 MHz, $CDCl_3$): δ 85.24–82.94 (m, $^2J_{F\text{-}F}$ = 150.0 Hz, 1F), 62.80 (d, $^2J_{F\text{-}$

$_F$ = 150.0 Hz, 4F); MS-ES (+) *m/z*: calcd for $C_{16}H_{20}F_5NO_4SNa$ 440.0925, found: 440.0925.

*(E)-2-[(tert-Butoxycarbonyl)amino]-5-[4-(pentafluoro-λ⁶-sulfanyl)phenyl]pent-4-enoic acid (**7**)*. The ester **6** (319 mg, 0.765 mmol) was dissolved in dry diethyl ether (14.0 mL) and cooled to -78 °C. LHMDS (2.31 mL, 2.31 mmol, 1 M in THF, 3.0 equiv) was added slowly to the stirring solution. After another 10 min, a solution of $ZnCl_2$ (2.1 mL, 1.53 mmol, 0.74 M in diethyl ether) was added, and the mixture was warmed to r.t. over night. After the addition of 2 N HCl (10 mL), the phases were separated, and the aqueous phase was extracted with diethyl ether (3 × 10 mL). The combined organic phases were washed with bicarbonate solution (5%, 10 mL), dried with $MgSO_4$, and the solvent was removed under vacuum to afford a white yellowish solid. Yield: 296 mg (93%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.77 (brs, 1H), 7.66 (d, $^3J_{H-H}$ = 8.5 Hz, 2H), 7.38 (d, $^3J_{H-H}$ = 8.5 Hz, 2H), 6.48 (d, $^3J_{H-H}$ = 15.8 Hz, 1H), 6.23 (td, $^3J_{H-H}$ = 15.7 Hz, $^3J_{H-H}$ = 7.5 Hz), 4.50 (q, $^3J_{H-H}$ = 6.4 Hz, 1H), 3.57 (bs, 1H), 2.90 – 2.60 (dm, 2H), 1.42 (s, 9H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 175.9, 155.4, 152.6 (qu, $^2J_{C-F}$ = 17.0 Hz), 140.0, 132.1, 127.5, 126.2 (qu, ×2), 126.1, 80.5, 52.9, 36.0, 28.2 (×3); ^{19}F NMR (282 MHz, $CDCl_3$): δ 84.37 (mqu, $^2J_{F-F}$ = 147.0 Hz, 1F), 62.47 (dm, $^2J_{F-F}$ = 147.0 Hz, 4F); MS-ES (+) *m/z*: calcd for $C_{16}H_{20}F_5NO_4SNa$ 440.0925, found: 440.0917.

Johnson-Claisen Rearrangements

*Methyl (E)-5-[4-(pentafluoro-λ⁶-sulfanyl)phenyl]pent-4-enoate (**9**)*. In a Young tube, the allyl alcohol **8** (70 mg, 0.27 mmol) was dissolved in dry toluene (0.6 mL) under an argon atmosphere. Trimethyl orthoacetate (0.4 mL) was added followed by a catalytic amount of propionic acid (2 drops). The mixture was heated at 115 ° C for 5 h. After cooling to room-temperature, water (30 mL) was added, and the phases were separated. The aqueous phase was extracted with diethyl ether (3 × 20 mL) before the combined organic phases were washed with brine (20 mL). After drying over $MgSO_4$, the solvent was removed in vacuum, affording a colorless oil. Yield: 57 mg (68%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.69–7.63 (dqu, $^3J_{H-H}$ = 8.6 Hz, $^3J_{H-F}$ = 1.8 Hz, 2H), 7.38 (d, $^3J_{H-H}$ = 8.6 Hz, 2H), 6.44 (d, $^3J_{H-H}$ = 16.0 Hz, 1H), 6.31 (dt, $^3J_{H-H}$ = 16.0 Hz, $^3J_{H-H}$ = 6.2 Hz, 1H), 3.69 (s, 3H), 2.54 (m, 4H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 173.1, 152.3 (qu, $^2J_{C-F}$ = 17.1 Hz), 140.6, 132.1 (×2), 129.2, 126.1 (qu, $^3J_{C-F}$ = 10.5 Hz, ×2), 126.0, 51.6, 33.3, 28.1; ^{19}F NMR (282 MHz, $CDCl_3$): δ 84.58 (mqu, $^2J_{F-F}$ = 149.6 Hz, 1F), 62.55 (dm, $^2J_{F-F}$ = 149.6 Hz, 4F); MS-ES (+) *m/z*: calcd for $C_{12}H_{13}F_5O_2SNa$ 339.0449 found: 339.0446. Elemental analysis: calcd for $C_{12}H_{13}F_5O_2S$, 316.31: C 45.57, H 4.14, found: C 45.54, H 4.10.

*Methyl (4E,6E)-7-(pentafluoro-λ⁶-sulfanyl)hepta-4,6-dienoate (**10g**)*. In a flame-dried Young tube, (*E*)-1-(pentafluoro-λ⁶-sulfanyl)penta-1,4-dien-3-ol (**2g**) (100 mg, 0.376 mmol) was dissolved in dry toluene (0.8 mL). Trimethyl orthoacetate (48 mg, 0.51 mL, 0.4 mmol, 1.06 equiv) was added followed by a catalytic amount of propionic acid (2 drops). The mixture was heated at 115 °C for 5 h. After cooling to room temperature, water (5 mL) was added, and the layers were separated. The aqueous layer was extracted with diethyl ether (3 × 5 mL) before the combined organic layers were washed with brine (2 × 2 mL). After drying over magnesium sulfate, the solvent was removed in vacuum. The crude product was purified on silica gel (pentane/diethyl ether, 10:1) giving the target compound as a colorless clear oil. Yield: 31 mg (31%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.83 (dd, $^3J_{H-H}$ = 14.4, $^3J_{H-H}$ = 10.0 Hz, 1H), 6.49 (dqu, 1H, $^3J_{H-H}$ = 14.4, $^3J_{H-F}$ = 6.7 Hz, 1H), 6.20 – 5.95 (m, 2H), 3.68 (s, 3H), 2.60 – 2.40 (m, 4H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 172.8, 142.3 (qu, $^4J_{C-F}$ = 2.2 Hz) 140.2 (qu, $^2J_{C-F}$ = 20.1 Hz), 136.2 (qu, $^3J_{C-F}$ = 7.5 Hz), 125.7, 51.7, 32.8, 28.0; ^{19}F NMR (282 MHz, $CDCl_3$): δ 85.64 – 83.47 (m, $^2J_{F-F}$ = 150.8 Hz, 1F), 64.09 (dm, $^2J_{F-F}$ = 150.8 Hz, 4F); MS-ES (+) *m/z*: calcd for $C_8H_{11}F_5O_2SNa$ 289.0292, found: 289.0293.

*Methyl (4E,6E)-2-methyl-7-(pentafluoro-λ⁶-sulfanyl)hepta-4,6-dienoate (**10h**)*. According to the above protocol (*E*)-1-(pentafluoro-λ⁶-sulfanyl)penta-1,4-dien-3-ol (**2g**) (50 mg, 0.19 mmol) was heated with trimethyl orthopropionate (27 mg, 0.20 mmol, 1.1 equiv) in toluene (0.5 mL). After purification on silica gel (pentane/diethyl ether, 10:1) the target product was afforded as a clear oil. Yield: 36 mg (55%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.83 (dd, $^3J_{H-H}$ = 14.4, $^3J_{H-H}$ = 9.7 Hz, 1H). 6.48 (md $^3J_{H-H}$ = 14.1 Hz, 1H), 6.10 – 5.95 (m, 2H, 6-CH), 3.69 (s, 3H), 2.58 (dd, $^2J_{H-H}$ = 13.4, $^3J_{H-H}$ = 6.6 Hz, 1H), 2.52 (dq, $^3J_{H-H}$ = 6.7 Hz, $^3J_{H-H}$ = 6.6 Hz, 1H), 2.31 (dt, $^2J_{H-H}$ = 13.4, $^3J_{H-H}$ = 6.6 Hz, 1H), 1.18 (d, $^3J_{H-H}$ = 6.7 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 175.9, 141.2, 140.2 (qu, $^2J_{C-F}$ = 20.5 Hz), 136.1 (qu, $^3J_{C-F}$ = 7.5 Hz), 126.7, 51.8, 38.9, 36.7, 16.8; ^{19}F NMR (282 MHz, $CDCl_3$): δ 84.51 (qu, $^2J_{F-F}$ = 150.8 Hz, 1F), 64.11 (dm, $^2J_{F-F}$ = 150.8 Hz, 4F); GC-MS 70eV *m/z* (rel. intens.): 280 (2) $[M]^+$, 249 (3) $[M\text{-}OMe]^+$, 221 (1) $[C_7H_{10}F_5S]^+$, 153 (1) $[M\text{-}SF_5]^+$, 93 (100) $[C_7H_{11}]^+$ 89 (11) $[SF_3]^+$, 59 (40) $[C_2H_3O_2]^+$, 51 (22) $[SF]^+$.

Efforts to synthesize the SF_5CF_2-substituted allylic alcohol 16.

*Octyl 2,2-difluoro-2-(pentafluoro-λ⁶-sulfanyl)acetate (**11**).* The carboxylic acid SF_5CF_2COOH[29] (564 mg, 2.54 mmol) was converted to the corresponding acyl chloride by using oxalyl chloride (484 mg, 3.81 mmol) and DMF (20 μL) in dry DCM (8 mL). When bubbling ceased (4 h), a mixture of octanol (597 μL, 2.99 mmol) and triethyl amine (527 μL, 2.99 mmol) in dry DCM (3 mL) was added at 0 °C. After stirring overnight, the reaction mixture was concentrated (under atmospheric pressure) and filtered through a silica pad using pentane as an eluent. The collected filtrate was concentrated under atmospheric pressure, and the residual solvent was removed by applying vacuum to give ester **11** as a colorless liquid. Yield: 581 mg (68%). Note: removal of the solvent must be carried out under atmospheric pressure, otherwise the isolated yield is significantly reduced to ~15%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.38 (t, $^3J_{H-H}$ = 6.7 Hz, 2H), 1.74 (dt, $^3J_{H-H}$ = 7.9, $^3J_{H-H}$ = 6.5 Hz, 2H), 1.45 – 1.24 (m, 10H), 0.95 – 0.84 (m, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 69.2, 31.7, 29.05, 28.96, 28.0, 25.4, 22.6, 14.1. The signals of the CF_2 and CO carbon atoms were not observed, as an insufficient number of transients were recorded, and these signals are expected to be highly coupled. ^{19}F NMR (282 MHz, $CDCl_3$): δ 65.99 (qum, $^2J_{F-F}$ = 148.0 Hz, 1F), 40.95 (dtm, $^2J_{F-F}$ = 148.0, $^3J_{F-F}$ = 12.0 Hz, 4F), -91.40 (qud, $^3J_{F-F}$ = 12.0, $^3J_{F-F}$ = 4.3 Hz,

2F); ESI MS (+) *m/z*: calcd for $C_{10}H_{17}F_7O_2SNa^+$, 357.0730, found: 357.0721.

*1,1-Difluoro-1-(pentafluoro-λ⁶-sulfanyl)dodec-3-yn-2-one (**12**)*. Decyne (539 mg, 2.99 mmol) in THF (8 mL) was treated with a 1.6 M solution of *n*-BuLi (1.80 mL) at -78 °C. After 30 min, a THF solution (4 mL) of ester **11** (500 mg, 1.50 mmol) and $BF_3 \bullet Et_2O$ (298 mg, 2.10 mmol) was added dropwise at -78 °C. Stirring was continued for 2 h at this temperature. The reaction was then quenched with a saturated aqueous solution of NH_4Cl (20 mL) and extracted with Et_2O (3 × 15 mL). The combined organic phases were washed with brine (50 mL), dried over Na_2SO_4, and concentrated. The crude product was purified by column chromatography using pentane as eluent to give **12** as a colorless oil. Yield: 512 mg (77%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.51 (t, $^3J_{H-H}$ = 7.0 Hz, 2H), 1.65 (q, $^3J_{H-H}$ = 7.0 Hz, 2H), 1.48 – 1.37 (m, 2H), 1.34 – 1.19 (m, 8H), 0.89 (t, $^3J_{H-H}$ = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 119.1 (tm), 106.4, 76.3 – 76.0 (m), 31.8, 29.1, 28.9, 28.7, 27.2, 22.6, 19.5, 14.0. The signal of the CO carbon atom was not observed, as an insufficient number of transients were recorded and this signal is expected to be highly coupled, which would further reduce its intensity. ^{19}F NMR (282 MHz, $CDCl_3$): δ 65.95 (qum, $^2J_{F-F}$ = 147.1 Hz, 1F), 43.88 (dtm, $^2J_{F-F}$ = 147.1, $^3J_{F-F}$ = 12.0 Hz, 4F), -91.52 (qum, $^3J_{F-F}$ = 12.3, $^3J_{F-F}$ = 4.1 Hz, 2F); ESI MS *m/z*: calcd for $C_{12}H_{17}F_7OSNaCH_3OH^+$ (methanol was the solvent): 397.1043, found: 397.1045.

*1,1-Difluoro-1-(pentafluoro-λ⁶-sulfanyl)dodec-3-yn-2-ol (**13**)*. Compound **12** (295 mg, 0.86 mmol) was treated with a solution of $NaBH_4$ (26 mg, 0.69 mmol) in methanol (10 mL) at 0 °C. After 15 min, the reaction was quenched with water (25 mL) and extracted with DCM (3 × 20 mL). The combined organic phases were washed with brine (15 mL), dried over Na_2SO_4, and concentrated. The crude product was purified by column chromatography using pentane/diethyl ether (10:1) as the eluent to give **13** as a colorless oil. Yield: 218 mg (73%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.88 (t, $^3J_{H-F}$ = 9.1 Hz, 1H), 2.69 (bs, 1H), 2.25 (td, $^3J_{H-H}$ = 7.0, $^5J_{H-H}$ = 2.1 Hz, 2H), 1.53 (qu, $^3J_{H-H}$ = 7.0 Hz, 2 H), 1.40 – 1.30 (m, 2H), 1.28 (m, 8H), 0.89 (t, $^3J_{H-H}$ = 7.0 Hz, 3H. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 127.2 (tm, $^1J_{C-F}$ = 304.4 Hz), 90.6, 71.8, 64.2 (t, $^2J_{C-F}$ = 25.6 Hz), 31.9, 29.2, 29.1, 28.8, 28.1, 22.7, 18.6, 14.1; ^{19}F NMR (282 MHz, $CDCl_3$): δ 68.73 (qum, $^2J_{F-F}$ = 145.6 Hz, 1F), 41.80 (dtm, $^2J_{F-F}$ = 146.7, $^3J_{F-F}$ = 15.1 Hz, 4F), AB spin system (J_{AB} = 188.3 Hz), -90.20 (bm, 1F) and -92.60 (bs, 1F). Molecular ion was not found in ESI MS.

*(Z)-1,1-Difluoro-1-(pentafluoro-λ⁶-sulfanyl)dodec-3-en-2-ol (**14**)*. Compound **13** (185 mg, 0.54 mmol) was dissolved in heptane (5 mL), and Lindlar's catalyst (28 mg) was added. The vessel was slightly evacuated, flushed with hydrogen (3 times), and filled with a hydrogen atmosphere using a balloon (3 times). The solution was stirred under hydrogen (balloon) at room temperature for two days. Then the reaction mixture was filtered through a short pad of celite to give **14** as a colorless oil. Yield: 186 mg (90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.89 (dt, $^3J_{H-H}$ = 10.6, $^3J_{H-H}$ = 7.6 Hz, 1H), 5.51 (t, $^3J_{H-H}$ = 9.8 Hz, 1H), 4.98 (ddd, *J* = 14.8, *J* = 8.6, *J* = 6.1 Hz, 1H), 2.41 (bs, 1H), 2.13 (q, $^3J_{H-H}$ = 7.3 Hz, 2H), 1.41 (qu, $^3J_{H-H}$ = 7.3 Hz, 1H), 1.28 (m, 10H), 0.88 (t, $^3J_{H-H}$ = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 140.0, 129.0 (t, $^1J_{C-F}$ = 304.0 Hz), 121.4, 68.3 (t, $^2J_{C-F}$ = 23.4 Hz), 31.9, 29.4, 29.24, 29.22, 29.1, 28.0, 22.7, 14.1; ^{19}F NMR (282 MHz, $CDCl_3$): δ 69.53 (qu, $^2J_{F-F}$ = 145.5 Hz, 1F), 40.41 (dtm, $^2J_{F-F}$ = 145.5, $^3J_{F-F}$ = 15.6 Hz, 4F), AB spin system (J_{AB} = 188.3 Hz), -89.06 (t, $^3J_{F-F}$ = 14.9 Hz, 1F) and -94.51 (bs, 1F). Molecular ion was not found in ESI MS.

*(Z)-1,1-Difluoro-1-(pentafluoro-λ⁶-sulfanyl)dodec-3-en-2-yl methanesulfonate (**15**)*. To a solution of **14** (150 mg, 0.43 mmol) in DCM (10 mL), MsCl (64 mg, 0.56 mmol) and Et_3N (57 mg, 0.56 mmol) were added successively under stirring at 0 °C. Stirring was continued for 1 h. Then, silica (2 g) was poured into the reaction mixture, the solvent was removed, and the solid was charged to the top of a column filled with silica gel (10 g). Elution with pentane/Et_2O (10:1) gave **15** as a colorless oil. Yield: 181 mg (98%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.09 (dt, $^3J_{H-H}$ = 11.0, $^3J_{H-H}$ = 7.6 Hz, 1H), 5.95 – 5.80 (m, 1H), 5.55 (t, $^3J_{H-H}$ = 10.3 Hz, 1H), 3.07 (s, 3H), 2.22 (qt, $^3J_{H-H}$ = 14.8, $^3J_{H-H}$ = 7.7 Hz, 2H), 1.47 – 1.38 (m, 2H), 1.36 – 1.20 (m, 10H), 0.89 (t, $^3J_{H-H}$ = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 143.7, 126.4 (m), 117.3, 74.0 (ddm, $^2J_{C-F}$ = 28.5, $^2J_{C-F}$ = 22.3 Hz), 39.9, 31.9, 29.4, 29.3, 29.2, 28.8, 28.2, 22.7, 14.1; ^{19}F NMR (282 MHz, $CDCl_3$): δ 67.91 (qut, $^2J_{F-F}$ = 148.0, $^3J_{F-F}$ = 5.0 Hz, 1F), 40.98 (dtm, $^2J_{F-F}$ = 146.6, $^3J_{F-F}$ = 15.2 Hz, 4F), AB spin system (J_{AB} = 195.7 Hz): -88.24 (qud, $^3J_{F-F}$ = 14.2, $^3J_{F-H}$ = 7.9 Hz, 1F*)* and -91.31 (qud, $^3J_{F-F}$ = 14.9 Hz, 1F); ESI MS *m/z*: calcd for $C_{13}H_{23}F_7O_3S_2Na^+$: 447.0869, found: 447.0878.

Attempted Palladium(0)-Catalyzed [1,3]-Sigmatropic Rearrangement of (*Z*)-1,1-Difluoro-1-(pentafluoro-λ⁶-sulfanyl)dodec-3-en-2-yl Methanesulfonate (15)

To a solution of **15** (33 mg, 0.08 mmol) in ethanol (1 mL), $Pd(PPh_3)_4$ (13 mg, 0.01 mmol) and Et_3N (16 mg, 0.16 mmol) were added under stirring at 0 °C. Stirring was continued for 30 min, and the reaction was quenched with water (3 mL), extracted with DCM (3 × 5 mL), and the combined organic phases were washed with 5% NH_4Cl solution (5 mL) and water (5 mL) and dried over Na_2SO_4. After evaporation of the solvent, the crude material was analyzed using NMR spectroscopy (see Supporting Information).

*(E)-1,1-difluorododeca-1,3-diene (**17a**)*. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.60 (dt, $^3J_{H-H}$ = 15.4, $^3J_{H-H}$ = 7.00 Hz, 1H), 4.90 (ddd, $^3J_{H-F}$ = 24.8, $^3J_{H-H}$ = 10.7, *J* = 1.8 Hz, 1H); ^{19}F NMR (282 MHz, $CDCl_3$): δ -87.97 (dd, $^2J_{F-F}$ = 35.3, $^3J_{F-H}$ = 24.7 Hz, 1F), -90.70 (d, $^2J_{F-F}$ = 35.3 Hz, 1F).

*(Z)-1,1-difluorododeca-1,3-diene (**17b**)*. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.45 (qd, $^3J_{H-H}$ = 8.7, $^4J_{H-H}$ = 1.5 Hz, 1H), 5.15 (dddd, $^3J_{H-F}$ = 24.2, *J* = 11.4 Hz, *J* = 2.2, *J* = 1.8 Hz, 1H); ^{19}F NMR (282 MHz, $CDCl_3$): δ -86.84 (dd, $^2J_{F-F}$ = 29.4, $^3J_{F-H}$ = 24.2 Hz, 1F), -87.75 (d, $^2J_{F-F}$ = 29.4 Hz, 1F).

*(E)-1,1,1-Trifluorododec-2-ene (**18**)*. ^{19}F NMR (282 MHz, $CDCl_3$): δ -63.17 (d, $^3J_{F-H}$ = 6.9 Hz, 3F).

Reaction of SF_5CF_2-allylic alcohol 19a with trimethyl orthoacetate

The allylic alcohol **19a**[29] (15 mg, 0.05 mmol), trimethyl orthoacetate (3.6 mg, 0.15), and propionic acid (10 μL) were

refluxed in dry toluene (1 mL) for 16 h. The reaction mixture was analyzed by ^{19}F NMR spectroscopy showing the formation of the CF_3-substituted allylic alcohol **20** (-64.45 ppm) and the CF_3-substituted rearrangement product **21** (-71.39 ppm) in a ratio of 1:7, respectively. The products were not isolated. Their structure was confirmed by independent synthesis of **20** from known compound **22**[32] *via* **23** and **24**. Compound **21** was synthesized independently from **20** by Johnson-Claisen rearrangement (see below).

Independent synthesis of compounds 20 and 21

*1-Bromo-5,5,5-trifluoro-4-hydroxypentan-2-one (**24**)*. Crude bromo enone **23** (950 mg, 3.87 mmol) (synthesized according to known procedures from methoxy propene and trifluoracetic acid anhydride in the presence of pyridine[32] followed by bromination of crude **22** analogous to ref.[33]) was treated with $NaBH_4$ (120 mg, 3.10 mmol) in methanol (15 mL) at 0 °C for 10 min. After quenching with water (50 mL), extraction with DCM (2 × 15 mL), and evaporation of the solvent, the crude material was refluxed with 1 M HCl in acetone (1:7, 25 mL) for 1 h. Then the reaction mixture was diluted with water, extracted with DCM, and dried over $MgSO_4$. Filtration over silica gel (10 g) and removal of solvents gave product **24** as a liquid. Yield: 560 mg (62%, 2 steps). ^1H NMR (300 MHz, $CDCl_3$): δ 4.55 (m, 1H), 4.16 (s, 2H), 3.44 (bd, $^3J_{H\text{-}H}$ = 5.0 Hz, 1H), AB spin system: 3.04 (dd, $^2J_{H\text{-}H}$ = 17.7, $^3J_{H\text{-}H}$ = 9.5 Hz, 1H) and 2.90 (dd, $^2J_{H\text{-}H}$ = 17.8, $^3J_{H\text{-}H}$ = 2.7 Hz, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 200.2, 124.4 (q, $^1J_{C\text{-}F}$ = 280.8 Hz), 66.4 (q, $^2J_{C\text{-}F}$ = 32.7 Hz), 48.4, 39.7; ^{19}F NMR (282 MHz, $CDCl_3$): δ -79.67 (d, $^3J_{F\text{-}H}$ = 6.7 Hz, 3F); ESI MS (+) *m/z*: calcd. for $C_5H_6O_2{}^{79}BrF_3Na^+$, 256.9395, found: 256.9386 and calcd for $C_5H_6O_2{}^{81}BrF_3Na^+$, 258.9375, found: 258.9362.

*(E)-1-Bromo-5,5,5-trifluoropent-3-en-2-ol (**20**)*. The bromine-containing hydroxyl ketone **24** (170 mg, 0.73 mmol) was stirred with P_2O_5 (830 mg, 2.92 mmol) in dry DCM (10 mL) overnight. The reaction mixture was decanted and washed with water (5 mL) and 5% bicarbonate solution (2 × 5 mL). Then, it was filtered through a short pad of silica. Concentration under atmospheric pressure afforded the crude enone **25**. This compound was directly reduced with $NaBH_4$ (28 mg, 0.73 mmol) in the presence of $CeCl_3{\cdot}7H_2O$ (271 mg, 0.73 mmol) in methanol (8 mL). The reaction was quenched with water (20 mL), the phases were separated, and the aqueous phase was extracted with DCM (3 × 15 mL). The combined organic phases were washed with water (2 × 15 mL), dried over magnesium sulfate, and the solvents were removed under atmospheric pressure. The obtained crude material was purified by column chromatography using pentane/Et_2O, 6:1 as eluent. The collected fractions containing **20** were concentrated under atmospheric pressure and finally under mild vacuum to give a light yellow liquid. Yield: 30 mg (19%, 2 steps). ^1H NMR (300 MHz, $CDCl_3$): δ 6.32 (ddq, $^3J_{H\text{-}H}$ = 15.6, $^3J_{H,H}$ = 4.1, $^4J_{H\text{-}F}$ = 2.0 Hz, 1H), 6.00 (dqd, $^3J_{H\text{-}H}$ = 14.7, $^3J_{H\text{-}F}$ = 6.4, $^4J_{H\text{-}H}$ = 1.9 Hz, 1H), 4.46 (bs, 1H), AB spin system: 3.64 (dd, $^2J_{H\text{-}H}$ =11.3, $^4J_{H\text{-}H}$ = 3.9 Hz, 1H), 3.47 (dd, $^3J_{H\text{-}H}$ = 11.3, $^4J_{H\text{-}H}$ = 6.9 Hz, 1H), 2.44 (bd, $^3J_{H\text{-}H}$ = 4.9 Hz, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 137.5 (q, $^3J_{C\text{-}F}$ = 6.3 Hz), 122.9 (q, $^1J_{C\text{-}F}$ = 275.0 Hz), 120.8 (q, $^2J_{C\text{-}F}$ = 34.4 Hz), 69.8, 48.4; ^{19}F NMR (282 MHz, $CDCl_3$): δ -64.46 (dt, $^3J_{F\text{-}H}$ = 6.2, $^4J_{F\text{-}H}$ = 2.1 Hz, 3F). Molecular ions were not found in ESI.

*Methyl (E)-6-bromo-3-(trifluoromethyl)hex-4-enoate (**21**)*. The allylic alcohol **20** (25 mg, 0.12 mmol), trimethyl orthoacetate (41 mg, 0.36 mmol), and C_2H_5COOH (10 μL) in toluene (0.8 mL) were refluxed overnight. The pure liquid product was isolated according to the usual work-up procedure used also for the other rearrangement reactions. Yield: 20 mg (63%). ^1H NMR (500 MHz, $CDCl_3$): δ 5.93 (dt, $^3J_{H\text{-}H}$ = 15.3, $^3J_{H\text{-}H}$ = 6.7 Hz, 1H), 5.66 (ddt, $^3J_{H\text{-}H}$ = 15.3, $^3J_{H\text{-}H}$ = 8.7, $^4J_{H\text{-}H}$ = 1.3 Hz, 1H), 4.03 (ddd, $^3J_{H\text{-}H}$ = 6.8, $J_{H\text{-}H}$ = 2.3, $^4J_{H\text{-}H}$ = 1.3 Hz, 2H), 3.71 (s, 3H), 3.40 (dqq, $^3J_{H\text{-}H}$ = 13.3, $^3J_{H\text{-}F}$ = 8.9, $J_{H\text{-}H}$ = 4.5 Hz, 1H), 2.76 (dd, $^2J_{H\text{-}H}$ = 16.0, $^3J_{H,H}$ = 4.4 Hz, 1H), 2.52 (dd, $^2J_{H\text{-}H}$ = 16.0, $^3J_{H\text{-}H}$ = 9.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.3, 132.9, 128.6-128.1 (m), 126.0 (q, $^3J_{C\text{-}F}$ = 2.6 Hz), 52.1, 43.6, 43.3 (q, $^2J_{C\text{-}F}$ = 28.3 Hz), 33.3 (q, $^3J_{C\text{-}F}$ = 2.4 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ -71.87 (d, $^3J_{F\text{-}H}$ = 8.7 Hz, 3F). Molecular ions were not found in APCI.

*(E)-1,1,1-Trifluorododec-2-en-4-yl-(tert-butoxycarbonyl) glycinate (**27**)*. The alcohol **19a**[29] (40 mg, 0.12 mmol), *N*-BocGly (32 mg, 0.18 mmol), DMAP (3 mg, 0.02 mmol), and DCC (38 mg, 0.18 mmol) were stirred in DCM (2 mL), at room temperature overnight. Silica was poured to the reaction mixture, and the solvent was removed under reduced pressure. The thus obtained material was subjected to column chromatography (silica gel, pentane/Et_2O, 2:1) to provide **27** as a colorless oil. Yield: 30 mg (46%). ^1H NMR (400 MHz, $CDCl_3$): δ 6.38 (ddq, $^3J_{H\text{-}H}$ = 15.8, $^3J_{H\text{-}H}$ = 4.3, $^4J_{H\text{-}F}$ = 2.0 Hz, 1H), 5.99 (dq, $^3J_{H\text{-}H}$ = 16.0, $^3J_{H\text{-}F}$ = 5.5 Hz, 1H), 5.68 – 5.61 (m, 1H), 4.00 (d, $^3J_{H\text{-}H}$ = 5.9 Hz, 2H), 5.03 (bs, 1H), 3.67 (dd, $^3J_{H\text{-}H}$ = 5.5, $^4J_{H\text{-}H}$ = 2.7 Hz, 2H), 1.46 (s, 9H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 169.2, 155.7, 133.7 (q, $^3J_{C\text{-}F}$ = 6.4 Hz), 122.4 (q, $^1J_{C\text{-}F}$ = 269.8 Hz), 122.3 (q, $^2J_{C\text{-}F}$ = 34.4 Hz), 80.4, 71.5, 44.0, 42.4, 28.3; ^{19}F NMR (282 MHz, $CDCl_3$): δ -65.27 (dt, $^3J_{F\text{-}H}$ = 6.3, $^4J_{F\text{-}H}$ = 2.1 Hz, 3F). ESI MS (+) *m/z*: calcd for $C_{12}H_{17}BrF_3NO_4Na^+$, 398.0185, found: 398.0185, and calcd 400.0165, found: 400.0169.

Johnson-Claisen-Rearrangements of (*E*)-5-(pentafluoro-λ⁶-sulfanyl)pent-3-en-2-ol (28). General Procedure.

(*E*)-5-(Pentafluoro-λ⁶-sulfanyl)pent-3-en-2-ol (**28a**)[29] (50 mg, 0.24 mmol), the corresponding orthoester (0.72 mmol, 3 equiv), and propionic acid (10 μL) were refluxed in dry toluene (1 mL) for 16 h. Then, the reaction was quenched with water (5 mL), extracted with Et_2O (3 × 3 mL), washed with brine (2 × 3 mL), dried over $MgSO_4$, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (pentane/Et_2O, 15:1).

*Methyl (E)-3-[(pentafluoro-λ⁶-sulfanyl)methyl]hex-4-enoate (**29a**)*. Yield: 35 mg (55%), colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ 5.62 (dqd, $^3J_{H\text{-}H}$ = 15.4, $^3J_{H\text{-}H}$ = 6.4, $^4J_{H\text{-}H}$ = 0.8 Hz, 1H), 5.33 (dd, $^3J_{H\text{-}H}$ = 15.3, $^3J_{H\text{-}H}$ = 8.4 Hz, 1H), 3.86 – 3.63 (m, 2H), 3.67 (s, 3H), 3.20 (sextet, $^3J_{H\text{-}H}$ = 6.9 Hz, 1H), 2.55 (AB, $^2J_{H\text{-}H}$ = 15.9, $^3J_{H\text{-}H}$ = 5.8 Hz, 1H), 2.43 (dd, $^2J_{H\text{-}H}$ = 15.9, $^3J_{H\text{-}H}$ = 7.6 Hz, 1H), 1.66 (dd, $^3J_{H\text{-}H}$ = 6.4, $^4J_{H\text{-}H}$ = 1.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 171.5, 129.6, 128.6, 75.5 (qu, $^2J_{C\text{-}F}$ = 11.2 Hz), 51.8, 38.5 (m), 36.9 (qu, $^3J_{C\text{-}F}$ = 3.3 Hz), 17.9; ^{19}F NMR (282 MHz, $CDCl_3$): δ 84.96 (nonet, $^2J_{F\text{-}F}$ = 147.6 Hz, 1F), 66.41 (dtd, $^2J_{F\text{-}F}$ = 147.7, $^3J_{F\text{-}H}$ = 8.6, *J*

= 2.1 Hz, 4F); ESI MS (+) *m/z*: calcd for ($C_8H_{13}F_5O_2SNa^+$), 291.0449, found: 291.0453.

*Methyl (E)-2-methyl-3-[(pentafluoro-λ⁶-sulfanyl)methyl]hex-4-enoates (**29b**)*. Yield (combined): 40 mg (60%), dr 64:36, colorless oil. ESI MS (+) *m/z*: calcd for $C_9H_{15}F_5O_2SNa^+$, 305.0605, found: 305.0608.

Syn-**29b**: ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.60 (dq, $^3J_{H\text{-}H}$ = 15.2, $^3J_{H\text{-}H}$ = 6.5 Hz, 1H), 5.31 (ddd, $^3J_{H\text{-}H}$ = 15.2, $^3J_{H\text{-}H}$ = 9.2, $^4J_{H\text{-}H}$ = 1.9 Hz, 1H), 3.74 (m, 2H), 3.69 (s, 3H), 2.89 (tt, $^3J_{H\text{-}H}$ = 8.8 Hz, $^3J_{H2\text{-}H3}$ = 4.6 Hz, 1H), 2.65 (qd, $^3J_{H\text{-}H}$ = 7.1, $^3J_{H2\text{-}H3}$ = 4.6 Hz, 1H), 1.69 (dd, $^3J_{H\text{-}H}$ = 6.5, $^4J_{H\text{-}H}$ = 1.7 Hz, 3H), 1.15 (d, $^3J_{H\text{-}H}$ = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 174.3, 129.9, 127.9, 75.0 (quint, $^2J_{C\text{-}F}$ = 11.6 Hz), 51.7, 43.3 (quint, $^3J_{C\text{-}F}$ = 3.3 Hz), 42.9, 17.95, 14.6; ^{19}F NMR (282 MHz, $CDCl_3$): δ 85.33 (nonet, $^2J_{F\text{-}F}$ = 144.0 Hz, 1F), 66.40 (dtd, $^2J_{F\text{-}F}$ = 144.0, $^3J_{F\text{-}H}$ = 8.5, ^4J = 2.0 Hz, 4F).

Anti-**29b**: ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.61 (dq, $^3J_{H\text{-}H}$ = 15.2, $^3J_{H\text{-}H}$ = 6.5 Hz, 1H), 5.24 (ddd, $^3J_{H\text{-}H}$ = 15.2, $^3J_{H\text{-}H}$ = 9.5, $^4J_{H\text{-}H}$ = 1.8 Hz, 1H), 3.94 (dpd, $^2J_{H\text{-}H}$ = 16.8, $^3J_{H\text{-}F}$ = 8.5, $^3J_{H\text{-}H}$ = 4.2 Hz, 2H), 3.71 (s, 3H), 3.07 (dq, $^3J_{H2\text{-}H3}$ = 9.0 Hz, $^3J_{H\text{-}H}$ = 6.5 Hz, 1H), 2.53 (quint, $^3J_{H\text{-}H}$ = 7.1, 1H), 1.69 (dd, $^3J_{H\text{-}H}$ = 6.5, $^4J_{H\text{-}H}$ = 1.7 Hz, 3H), 1.14 (d, $^3J_{H\text{-}H}$ = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 174.8, 129.8, 128.2, 74.7 (quint, $^2J_{C\text{-}F}$ = 11.1 Hz), 51.9, 43.1, 42.6 (quint, $^3J_{C\text{-}F}$ = 3.1 Hz), 17.9, 13.9; ^{19}F NMR (282 MHz, $CDCl_3$): δ 85.08 (nonet, $^2J_{F\text{-}F}$ = 144.0 Hz, 1F), 66.64 (dtd, $^2J_{F\text{-}F}$ = 144.0, $^3J_{F\text{-}H}$ = 8.5, J = 2.0 Hz, 4F).

*Methyl (E)-2-ethyl-3-[(pentafluoro-λ⁶-sulfanyl)methyl]hex-4-enoates (**29c**)*. Yield (combined): 40 mg (57%), dr 59:41, colorless oil. ESI MS (+) *m/z*: calcd for $C_{10}H_{17}F_5O_2SNa^+$ 319.0762, found: 319.0769. Assignment of the diastereoisomers is not certain in this case.

Major product: ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.59 (dq, $^3J_{H\text{-}H}$ = 15.4, $^3J_{H\text{-}H}$ = 6.3 Hz, 1H), 5.33 (ddd, $^3J_{H\text{-}H}$ = 15.2, $^3J_{H\text{-}H}$ = 9.2, $^4J_{H\text{-}H}$ = 1.9 Hz, 1H), 3.73 – 3.63 (m, 2H), 3.68 (s, 3H), 2.92 (tt, $^3J_{H2\text{-}H8}$ = $^3J_{H2\text{-}H3}$ = 9.1, $^3J_{H\text{-}H}$ = 4.8 Hz, 1H), 2.41 (dt, $^3J_{H2\text{-}H3}$ = 9.3, $^3J_{H\text{-}H}$ = 5.4 Hz, 1H), 1.69 (dd, $^3J_{H\text{-}H}$ = 6.4, $^4J_{H\text{-}H}$ = 1.6 Hz, 3H), 1.59 (m, 2H), 0.91 (t, $^3J_{H\text{-}H}$ = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 173.9, 129.7, 128.1, 75.2 (quint, $^2J_{C\text{-}F}$ = 11.1 Hz), 51.6, 50.7, 42.0 (quint, $^3J_{C\text{-}F}$ = 3.1 Hz), 22.8, 17.9, 12.0; ^{19}F NMR (282 MHz, $CDCl_3$): δ 85.30 (quint, $^2J_{F\text{-}F}$ = 145.5 Hz, 1F), 66.48 (dt, $^2J_{F\text{-}F}$ = 145.7, $^3J_{F\text{-}H}$ = 8.2 Hz, 4F).

Minor product: ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.59 (dq, $^3J_{H\text{-}H}$ = 15.4, $^3J_{H\text{-}H}$ = 6.3 Hz, 1H), 5.23 (ddd, $^3J_{H\text{-}H}$ = 15.2, $^3J_{H\text{-}H}$ = 9.3, $^4J_{H\text{-}H}$ = 1.8 Hz, 1H), 3.92 (dtt, $^2J_{H\text{-}H}$ = 21.6, $^3J_{H\text{-}H}$ = 8.4, $^3J_{H\text{-}H}$ = 4.6 Hz, 2H), 3.71 (s, 3H), 2.97 (qd, $^3J_{H\text{-}H}$ = $^3J_{H\text{-}H}$ = 8.4, $^3J_{H\text{-}H}$ = 4.0 Hz, 1H), 2.29 (dt, $^3J_{H\text{-}H}$ = 7.8, $^3J_{H\text{-}H}$ = 6.2 Hz, 1H), 1.70 (dd, $^3J_{H\text{-}H}$ = 6.4, $^4J_{H\text{-}H}$ = 1.6 Hz, 3H), 1.48 (dqd, $^2J_{H\text{-}H}$ = 14.8, $^3J_{H\text{-}H}$ = 7.4, $^3J_{H\text{-}H}$ = 5.4 Hz, 2H), 0.89 (t, $^3J_{H\text{-}H}$ = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 174.5, 129.4, 129.1, 74.8 (quint, $^2J_{C\text{-}F}$ = 11.3 Hz), 51.7, 51.0, 42.0 (quint, $^3J_{C\text{-}F}$ = 3.1 Hz), 23.2, 17.9, 11.7; ^{19}F NMR (282 MHz, $CDCl_3$): δ 85.24 (quint, $^2J_{F\text{-}F}$ = 145.9 Hz, 1F), 66.80 (dt, $^2J_{F\text{-}F}$ = 145.9, $^3J_{F\text{-}H}$ = 8.2 Hz, 4F).

*Methyl (E)-3-[(pentafluoro-λ⁶-sulfanyl)methyl]-2-propylhex-4-enoates (**29d**)*. Yield (combined): 48 mg (65%), dr 64:36, colorless oil. ESI MS (+) *m/z*: calcd for $C_{11}H_{19}F_5O_2SNa^+$, 333.0918, found: 333.0936; calcd for $(C_{11}H_{19}F_5O_2S)_2Na^+$ 643.1944, found: 643.1944.

Syn product: ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.58 (dq, $^3J_{H\text{-}H}$ = 15.2, $^3J_{H\text{-}H}$ = 6.5 Hz, 1H), 5.32 (dm, $^3J_{H\text{-}H}$ = 15.2 Hz, 1H, H-9), 3.74 – 3.62 (m, 2H), 3.67 (s, 3H), 2.90 (tt, $^3J_{H\text{-}H}$ = 9.1, $^3J_{H\text{-}H}$ = $^3J_{H\text{-}H}$ = 5.1 Hz, 1H), 2.50 (td, $^3J_{H\text{-}H}$ = 10.0, $^3J_{H\text{-}H}$ = 5.2 Hz, 1H), 1.69 (dt, $^3J_{H\text{-}H}$ = 6.9, $^4J_{H\text{-}H}$ = 1.7 Hz, 3H), 1.41 – 1.36 (m, 1H), 1.34 – 1.27 (m, 2H), 1.26 – 1.18 (m, 1H), 0.91 (t, $^3J_{H\text{-}H}$ = 7.3 Hz, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 174.0, 129.7, 128.2, 75.2 (quint, $^2J_{C\text{-}F}$ = 11.1 Hz), 51.6, 48.8, 42.3 (quint, $^3J_{C\text{-}F}$ = 3.2 Hz), 31.8, 20.7, 17.95, 13.9; ^{19}F NMR (282 MHz, $CDCl_3$): δ 85.28 (quint, $^2J_{F\text{-}F}$ = 145.5 Hz, 1F), 66.50 (dt, $^2J_{F\text{-}F}$ = 145.4, $^3J_{F\text{-}H}$ = 8.5 Hz, 4F).

Anti-product: ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.58 (dq, $^3J_{H\text{-}H}$ = 15.2, $^3J_{H\text{-}H}$ = 6.5 Hz, 1H), 5.22 (ddd, $^3J_{H\text{-}H}$ = 15.2, $^3J_{H\text{-}H}$ = 9.2, $^4J_{H\text{-}H}$ = 1.8 Hz, 1H), 3.91 (dquintd, $^2J_{H\text{-}H}$ = 21.3, $^3J_{H\text{-}F}$ = 8.4, $^3J_{H1\text{-}H2}$ = 4.1 Hz, 2H), 3.69 (s, 3H), 2.96 (ddt, $^3J_{H\text{-}H}$ = 12.3, $^3J_{H\text{-}H}$ = 8.0, $^3J_{H1\text{-}H2}$ = 4.3 Hz, 1H), 2.38 (ddd, $^3J_{H\text{-}H}$ = 10.6, $^3J_{H\text{-}H}$ = 7.6, $^3J_{H\text{-}H}$ = 4.2 Hz, 1H), 1.70 (td, $^3J_{H\text{-}H}$ = 6.9, $^4J_{H\text{-}H}$ = 1.7 Hz, 3H), 1.68 – 1.62 (m, 2H), 1.60 – 1.54 (m, 1H), 1.49 – 1.44 (m, 1H), 0.90 (t, $^3J_{H\text{-}H}$ = 7.3 Hz, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 174.7, 129.4, 129.1, 74.8 (quint, $^2J_{C\text{-}F}$ = 11.0 Hz), 51.7, 49.4, 42.3 (quint, $^3J_{C\text{-}F}$ = 3.2 Hz), 32.0, 20.6, 17.9, 13.9; ^{19}F NMR (282 MHz, $CDCl_3$): δ 85.24 (quint, $^2J_{F\text{-}F}$ = 145.5 Hz, 1F), 66.76 (dt, $^2J_{F\text{-}F}$ = 144.0, $^3J_{F\text{-}H}$ = 8.5 Hz, 4F).

*Methyl (E)-2-(2-bromoethyl)-3-[(pentafluoro-λ⁶-sulfanyl)methy]hex-4-enoates (**29e**)*. Yield (combined): 67 mg (76%), dr 63:37, colorless oil. ESI MS (+) *m/z*: calcd for $C_{10}H_{16}{}^{79}BrF_5O_2SNa^+$: 396.9867, found: 396.9872, calcd for $C_{10}H_{16}{}^{81}BrF_5O_2SNa^+$: 398.9846, found: 398.9851. Assignment of the diastereomers is not certain in this case.

Major product: ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.62 (dq, $^3J_{H\text{-}H}$ = 15.1, $^3J_{H\text{-}H}$ = 6.0 Hz, 1H), 5.28 (dd, $^3J_{H\text{-}H}$ = 15.3, $^3J_{H\text{-}H}$ = 9.3 Hz, 1H), 3.71 (s, 3H), 3.71 – 3.64 (m, 2H), 3.45 (t, $^3J_{H\text{-}H}$ = 6.5 Hz, 1H), 3.34 (dtd, $^3J_{H\text{-}H}$ = 10.3, $^3J_{H\text{-}H}$ = 8.4, $^3J_{H\text{-}H}$ = 6.1 Hz, 1H), 2.91 (dt, $^2J_{H\text{-}H}$ = 8.9, $^3J_{H\text{-}H}$ = 4.6 Hz, 1H), 2.83 (dt, $^2J_{H\text{-}H}$ = 9.1, $^3J_{H\text{-}H}$ = 4.5 Hz, 1H), 2.28 (ddt, $^2J_{H\text{-}H}$ = 15.2, $^3J_{H\text{-}H}$ = 9.4, $^3J_{H\text{-}H}$ = 5.9 Hz, 1H), 1.90 (dddd, 1H, $^2J_{H\text{-}H}$ = 14.7, $^3J_{H\text{-}H}$ = 8.3, $^3J_{H\text{-}H}$ = 6.6, $^3J_{H\text{-}H}$ = 4.6 Hz, 1H), 1.70 (ddd, $^3J_{H\text{-}H}$ = 6.4, $^4J_{H\text{-}H}$ = 4.5, $^5J_{H\text{-}H}$ = 1.6 Hz, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 172.8, 130.5, 127.1, 74.9 (quint, $^2J_{C\text{-}F}$ = 11.6 Hz), 52.0, 46.9, 42.2 (quint, $^3J_{C\text{-}F}$ = 3.4 Hz), 32.8, 30.8, 18.0; ^{19}F NMR (564 MHz, $CDCl_3$): δ 84.94 (quint, $^2J_{F\text{-}F}$ = 145.9 Hz, 1F), 66.35 (dt, $^2J_{F\text{-}F}$ = 145.9, $^3J_{F\text{-}H}$ = 8.3 Hz, 4F).

Minor product: ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.61 (dq, $^3J_{H\text{-}H}$ = 15.1, $^3J_{H\text{-}H}$ = 6.3 Hz, 1H), 5.21 (ddd, $^3J_{H\text{-}H}$ = 15.3, $^3J_{H\text{-}H}$ = 9.2 Hz, $^4J_{H\text{-}H}$ = 1.8 Hz, 1H), 3.94 (m, 2H), 3.72 (s, 1H), 3.47 (td, $^3J_{H\text{-}H}$ = 6.7, $J_{H\text{-}H}$ = 1.7 Hz, 1H), 3.28 (dtd, $^3J_{H\text{-}H}$ = 10.3, $^3J_{H\text{-}H}$ = 8.9, $^3J_{H\text{-}H}$ = 6.2 Hz, 1H), 3.08 (dt, $^2J_{H\text{-}H}$ = 9.0, $^3J_{H\text{-}H}$ = 6.8 Hz, 1H), 2.67 (ddd, $^2J_{H\text{-}H}$ = 10.5, $^3J_{H\text{-}H}$ = 7.1, $^3J_{H\text{-}H}$ = 3.5 Hz, 1H), 2.20 (m, 1 H), 1.98 (dddd, $^2J_{H\text{-}H}$ = 14.5, $^3J_{H\text{-}H}$ = 8.9, $^3J_{H\text{-}H}$ = 7.0, $^3J_{H\text{-}H}$ = 3.5 Hz, 1H), 1.70 (ddd, $^3J_{H\text{-}H}$ = 6.4, $^4J_{H\text{-}H}$ = 4.5, $^5J_{H\text{-}H}$ = 1.6 Hz, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 173.4, 130.4, 128.1, 74.5 (quint, $^2J_{C\text{-}F}$ = 11.4 Hz), 52.1, 47.7, 41.9 (quint, $^3J_{C\text{-}F}$ = 3.6 Hz), 32.1, 30.6, 17.97; ^{19}F NMR (564 MHz, $CDCl_3$): δ 84.74 (quint, $^2J_{F\text{-}F}$ = 146.4 Hz, 1F), 66.83 (dt, $^2J_{F\text{-}F}$ = 146.4, $^3J_{F\text{-}H}$ = 8.3 Hz, 4F).

*Methyl (E)-2-chloro-3-[(pentafluoro-λ⁶-sulfanyl)methyl]hex-4-enoates (**29f**)*. Yield (combined): 45 mg (63%), dr 55:45, colorless oil. ESI MS (+) *m/z*: calcd for $C_8H_{12}ClF_5O_2SNa^+$: 325.0059, found: 325.0062.

Syn product: ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.71 (dq, $^3J_{H\text{-}H}$ = 15.2, $^3J_{H\text{-}H}$ = 6.5 Hz, 1H), 5.37 (m, 1H), 4.62 (d, $^3J_{H2\text{-}H3}$ = 3.5 Hz, 1H), 3.86 – 3.68 (m, 2H), 3.78 (s, 3H), 3.50 (tdd, $^3J_{H\text{-}H}$ = 9.2, $^3J_{H\text{-}H}$ = 6.3, $^3J_{H2\text{-}H3}$ = 3.3 Hz, 1H), 1.71 (ddd, $^3J_{H\text{-}H}$ = 8.4, $^3J_{H\text{-}H}$ = 6.5, $^4J_{H\text{-}H}$ = 1.7 Hz, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 167.9, 132.2, 124.9, 73.0 (quint, $^2J_{C\text{-}F}$ = 12.2 Hz), 60.5 (quint, $^4J_{C\text{-}F}$ = 1.7 Hz), 53.2, 43.8 (quint, $^3J_{C\text{-}F}$ = 3.5 Hz), 18.1; ^{19}F NMR (564 MHz, $CDCl_3$): δ 84.69 (quint, $^2J_{F\text{-}F}$ = 146.0 Hz, 1F), 66.92 (dt, $^2J_{F\text{-}F}$ = 146.0, $^3J_{F\text{-}H}$ = 8.4, 4F).

Anti product: ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.73 (dq, $^3J_{H\text{-}H}$ = 15.2, $^3J_{H\text{-}H}$ = 6.5 Hz, 1H), 5.36 (m, 1H), 4.17 (d, $^3J_{H2\text{-}H3}$ = 7.3 Hz, 1H), 4.15 – 4.01 (m, 2H), 3.78 (s, 3H), 3.32 (qd, $^3J_{H\text{-}H}$ = $^3J_{H\text{-}H}$ = 9.4, $^3J_{H\text{-}H}$ = 2.7 Hz, 1H), 1.71 (ddd, $^3J_{H\text{-}H}$ = 8.4, $^3J_{H\text{-}H}$ = 6.5, $^4J_{H\text{-}H}$ = 1.7 Hz, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 168.2, 132.3, 126.4, 72.9 (quint, $^2J_{C\text{-}F}$ = 12.8 Hz), 59.3, 53.1, 44.2 (quint, $^3J_{C\text{-}F}$ = 3.7 Hz), 18.04; ^{19}F NMR (564 MHz, $CDCl_3$): δ 84.67 (quint, $^2J_{F\text{-}F}$ = 146.2 Hz, 1F), 67.98 (dt, $^2J_{F\text{-}F}$ = 146.8, $^3J_{F\text{-}H}$ = 8.3 Hz, 4F).

Downstream transformations starting from methyl ester 29a

*(E)-3-[(Pentafluoro-λ^6-sulfanyl)methyl]hex-4-en-1-ol (**30**)*. The methyl ester **29a** (180 mg, 0.67 mmol) was added under stirring at 0 °C to a suspension of $LiAlH_4$ (51 mg, 1.34 mmol) in THF (5 mL), and the reaction mixture was stirred for an additional 10 min. The reaction was then quenched with water (15 mL), the phases were separated, and the aqueous was extracted with Et_2O (3 × 10 mL). The combined organic phases were washed with 5% NH_4Cl solution (5 mL), water (5 mL), and dried over $MgSO_4$. Evaporation of the solvents afforded the target alcohol **30** as a liquid. Yield: 106 mg (66%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.61 (dq, $^3J_{H\text{-}H}$ = 15.3, $^3J_{H\text{-}H}$ = 6.4 Hz, 1H), 5.22 (ddd, $^3J_{H\text{-}H}$ = 15.2, $^3J_{H\text{-}H}$ = 9.1, $^4J_{H\text{-}H}$ = 1.8 Hz, 1H), 3.74 – 3.59 (m, 4H), 2.90 (ttd, $^3J_{H\text{-}H}$ = 10.2, $J_{H\text{-}H}$ = 6.6, $J_{H\text{-}H}$ = 4.1 Hz, 1H), 1.81 (dddd, $^3J_{H\text{-}H}$ = 14.1, $^3J_{H\text{-}H}$ = 8.0, $^3J_{H\text{-}H}$ = 6.3, $J_{H\text{-}H}$ = 4.1, 1H), 1.70 (dd, $^3J_{H\text{-}H}$ = 6.5, $^4J_{H\text{-}H}$ = 1.7 Hz, 3H), 1.57 – 1.44 (m, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 130.9, 128.5, 77.2 (quint, $^2J_{C\text{-}F}$ = 10.2 Hz), 60.2, 37.6 (quint, $^3J_{C\text{-}F}$ = 3.2 Hz), 36.7, 17.9; ^{19}F NMR (282 MHz, $CDCl_3$): δ 85.53 (quint, $^2J_{F\text{-}F}$ = 145.8 Hz, 1F), 66.42 (dtd, $^2J_{F\text{-}F}$ = 145.8, $^3J_{F\text{-}H}$ = 8.6, $^4J_{F\text{-}H}$ = 2.0 Hz, 4F); ESI MS (+) *m/z*: calcd for $C_7H_{13}OSF_5Na^+$ 263.0499, found: 263.0493.

*(E)-3-[(Pentafluoro-λ^6-sulfanyl)methyl]hex-4-enal (**31**)*. The alcohol **30** (50 mg, 0.21 mmol), dissolved in DCM (2 mL), was treated with Dess-Martin reagent (106 mg, 0.25 mmol), and the reaction mixture was stirred at r.t. for 20 min. Silica (2 g) was then added to the reaction mixture, which was concentrated, charged to the top of a column with 10 g silica gel, and eluted with pentane. Evaporation of the solvent gave the title compound **31** as a yellowish liquid. Yield: 35 mg (71%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.70 (t, $^3J_{H\text{-}H}$ = 1.4, 1H), 5.70 – 5.58 (m, 1H), 5.34 (dd, $^3J_{H\text{-}H}$ = 15.2, $^3J_{H\text{-}H}$ = 8.2 Hz, 1H), 3.73 (quintd, $^3J_{H\text{-}F}$ = 8.5, $^3J_{H\text{-}H}$ = 6.5 Hz, 2H), 3.31 (m, 1H), 2.75 – 2.56 (AB, 2H), 1.68 (dd, $^3J_{H\text{-}H}$ = 6.4, $^4J_{H\text{-}H}$ = 1.6 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 199.8, 129.7, 129.0, 75.6 (quint, $^2J_{C\text{-}F}$ = 11.3 Hz), 47.3 (quint, $^3J_{C\text{-}F}$ = 1.5 Hz), 35.0 (quint, $^3J_{C\text{-}F}$ = 3.0 Hz), 17.9; ^{19}F NMR (282 MHz, $CDCl_3$): δ 84.85 (quint, $^2J_{F\text{-}F}$ = 145.6 Hz, 1F), 66.38 (dtd, $^2J_{F\text{-}F}$ = 145.6, $^3J_{F\text{-}H}$ = 8.5, J = 2.1 Hz, 4F); ESI MS (+) *m/z*: calcd for $C_7H_{11}OSF_5Na^+$, 261.0370, found: 261.0343; calcd for $C_7H_{11}OSF_5NaCH_3OH^+$, 293.0605, found: 293.0631; calcd for $C_7H_{11}OSF_5NaC_2H_5OH^+$ 307.0762, found: 307.0788.

*(E)-5-[(pentafluoro-λ^6-sulfanyl)methyl]octa-1,6-dien-3-ol (**32**)*. Analogously to the procedure used for the synthesis of compound **8**, the aldehyde **31** (24 mg, 0.1 mmol) was reacted with vinylmagnesium bromide (0.32 mL, 0.22 mmol, 2.2 equiv, 0.7 M solution in THF) to provide a 1:1 mixture of the diastereomeric Grignard products **32**. Yield: 5.9 mg (22%). The products could not be isolated in pure form.

Synthesis of starting materials for ester enolate Claisen type rearrangements of compounds 34 and 36

*(E)-1-(Pentafluoro-λ^6-sulfanyl)dodec-2-en-4-one (**33b**)*. SF_5CH_2COOH (478 mg, 2.57 mmol), oxalyl chloride (348 μL, 4.11 mmol), 2-methoxydec-1-ene (1,092 mg, 6.42 mmol), and pyridine (512 μL, 6.42 mmol) gave the addition/elimination product, which was purified by column chromatography (pentane/Et_2O, 90:1). This intermediate β–methoxy-α,β-unsaturated ketone was reacted with $NaBH_4$ (130 mg, 3.40 mmol) in methanol (25 mL) at 0 °C. The reaction mixture was quenched with water (50 mL) and extracted with DCM (3 × 30 mL). The extract containing the 3-methoxy allylic alcohol was concentrated and dissolved in 3:1 mixture of acetone/2M HCl (8 mL), and stirred overnight. The reaction mixture was diluted with water (20 mL) and extracted with DCM (3 × 30 mL). After drying over Na_2SO_4, the concentrated γ-hydroxy ketone was dissolved in DCM (10 mL) and treated with MsCl (300 mg, 2.67 mmol) and Et_3N (566 mg, 5.61 mmol) at 0 °C for 15 min. Silica was poured to the reaction mixture and dried. This material was subjected to the column chromatography (pentane). Evaporation of the solvents afforded **33b** as a yellow oil. Yield: 200 mg (25% over 4 steps). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.83 (dt, $^3J_{H\text{-}H}$ = 15.6, $^3J_{H\text{-}H}$ = 7.8 Hz, 1H), 6.31 (dt, $^3J_{H\text{-}H}$ = 15.8, $^4J_{H\text{-}H}$ = 1.3 Hz, 1H), 4.39 (sextetd, $^3J_{H\text{-}H}$ = $^3J_{H\text{-}F}$ = 7.4, $^4J_{H\text{-}H}$ = 1.2 Hz, 2H), 2.59 (m, 2H), 1.62 (quint, $^3J_{H\text{-}H}$ = 7.2 Hz, 2H), 1.31 – 1.24 (m, 10H), 0.88 (t, $^3J_{H\text{-}H}$ = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 199.4, 136.0, 132.2 (quint, $^3J_{C\text{-}F}$ = 4.3 Hz), 72.0 (quint, $^2J_{C\text{-}F}$ = 16.2 Hz), 41.0, 31.9, 29.4, 29.2, 29.2, 23.9, 22.7, 14.2; ^{19}F NMR (282 MHz, $CDCl_3$): δ 81.06 (nonet, $^2J_{F\text{-}F}$ = 146.0 Hz, 1F), 66.17 (dt, $^2J_{F\text{-}F}$ = 146.0, $^3J_{F\text{-}H}$ = 7.4 Hz, 4F); ESI MS (+) *m/z*: calcd for $C_{12}H_{21}F_5OSNa^+$, 331.1125, found: 331.1133.

*(E)-1-(Pentafluoro-λ^6-sulfanyl)dodec-2-en-4-ol (**28b**)*. $NaBH_4$ (25 mg, 0.65 mmol) was added to a solution of ketone **33b** (200 mg, 0.65 mmol) and $CeCl_3{\cdot}7H_2O$ (240 mg, 0.65 mmol) in MeOH (10 mL) at 0 °C. After stirring for 15 min, the reaction was quenched with water (15 mL) and extracted with DCM (3 × 15 mL). The combined organic phases were washed with brine (40 mL), dried over Na_2SO_4 and concentrated to give **28b** as a colorless oil. Yield: 190 mg (94%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.90 – 5.80 (m, 2H), 4.28 (ddt, $^2J_{H\text{-}H}$ = 13.7, $^3J_{H\text{-}H}$ = 9.6, $J_{H\text{-}H}$ = 5.2 Hz, 2H), 4.17 (m, $^3J_{H\text{-}H}$ = 6.3 Hz, 1H), 2.11 (bs, 1H), 1.53 (tt, $^3J_{H\text{-}H}$ = 9.7, $^3J_{H\text{-}H}$ = $^4J_{H\text{-}H}$ = 6.7 Hz, 2H), 1.31 – 1.24 (m, 12H), 0.89 (t, $^3J_{H\text{-}H}$ = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 143.0, 119.5 (quint, $^3J_{C\text{-}F}$ = 4.1 Hz), 73.5 (quint, $^2J_{C\text{-}F}$ = 14.4 Hz), 71.8, 37.0, 32.0, 29.6, 29.6, 29.3, 25.3, 22.8, 14.2; ^{19}F NMR (282 MHz, $CDCl_3$): δ 82.60

(nonet, $^2J_{F-F}$ = 144.5 Hz, 1F), 63.50 (dt, $^2J_{F-F}$ = 144.5, $^3J_{F-H}$ = 7.4 Hz, 4F); ESI-MS (+): Molecular ion was not found.

*(E)-5-(Pentafluoro-λ⁶-sulfanyl)pent-3-en-2-yl (tert-butoxycarbonyl)glycinate (**34a**)*. The alcohol **28a** (80 mg, 0.38 mmol), *N*-BocGly (99 mg, 0.57 mmol), DMAP (9 mg, 0.07 mmol), DCC (116 mg, 0.56 mmol) were stirred in DCM (4 mL), overnight at room temperature. Silica was poured to the reaction mixture, solvents were removed under reduced pressure, and the obtained material was subjected to column chromatography (pentane/Et_2O, 1:1). Evaporation of the solvents gave **34a** as a colorless oil. Yield: 122 mg (88%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.94 – 5.85 (m, 1H), 5.80 (dd, $^3J_{H-H}$ = 15.3, $^3J_{H-H}$ = 5.0 Hz, 1H), 5.41 (quint, $^3J_{H-H}$ = $^3J_{H-H}$ = 6.4 Hz, 1H), 5.08 (bt, $^3J_{H-H}$ = 5.8 Hz, 1H), 4.23 (sextet, $^3J_{H-H}$ = $^3J_{H-F}$ = 7.1, 2H), 3.87 (d, $^3J_{H-H}$ = 5.3 Hz, 2H), 1.41 (s, 9H), 1.33 (d, $^3J_{H-H}$ = 6.6 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 169.5, 155.7, 138.4, 121.2 (quint, $^3J_{C-F}$ = 4.1 Hz), 80.0, 72.9 (quint, $^2J_{C-F}$ = 14.8 Hz), 70.5, 42.5, 28.2 (×3), 19.6; ^{19}F NMR (282 MHz, $CDCl_3$): δ 82.22 (nonet, $^2J_{F-F}$ = 144.7 Hz, 1F), 63.99 (dt, $^2J_{F-F}$ = 144.6, $^3J_{F-H}$ = 7.2 Hz, 4F); ESI MS (+) *m/z*: calcd for $C_{12}H_{20}F_5NO_4SNa^+$, 392.0925, found: 392.0921.

*(E)-1-(Pentafluoro-λ⁶-sulfanyl)dodec-2-en-4-yl-(tert-butoxycarbonyl)glycinate (**34b**)*. The alcohol **28b** (52 mg, 0.17 mmol), *N*-BocGly (44 mg, 0.25 mmol), DMAP (4 mg, 0.03 mmol), DCC (51 mg, 0.25 mmol) were stirred in DCM (4 mL), overnight at room temperature. Silica was poured to the reaction mixture, solvents were removed under reduced pressure, and thus obtained material was subjected to column chromatography (pentane/Et_2O, 3:1). Evaporation of the solvents afforded **34b** as a colorless oil. Yield: 67 mg (86%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.89 (dt, $^3J_{H-H}$ = 14.9, $^3J_{H-H}$ = 7.3 Hz, 1H), 5.76 (dd, $^3J_{H-H}$ = 15.5, $^3J_{H-H}$ = 6.3 Hz, 1H), 5.30 (q, $^3J_{H-H}$ = $^3J_{H-H}$ = 6.5 Hz, 1H), 5.01 (bs, 1H), 4.24 (ddt, $^3J_{H-H}$ = 13.7, $^3J_{H-F}$ = 9.5, $^3J_{H-H}$ = 6.4 Hz, 2H), 3.89 (s, 2H), 1.63 (tdd, $^3J_{H-H}$ = 14.6, $^3J_{H-H}$ = 10.8, $^4J_{H-H}$ = 6.3 Hz, 2H), 1.44 (s, 9H), 1.31 – 1.24 (m, 12H), 0.89 (t, $^3J_{H-H}$ = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 169.6, 155.6, 137.7, 122.1 (quint, $^3J_{C-F}$ = 3.8 Hz), 80.0, 74.4, 72.9 (quint, $^2J_{C-F}$ = 14.9 Hz), 42.5, 33.9, 31.8, 29.3, 29.2, 29.1, 28.2 (×3), 24.7, 22.6, 14.1; ^{19}F NMR (282 MHz, $CDCl_3$): δ 82.22 (nonet, $^2J_{F-F}$ = 144.5 Hz, 1F), 64.03 (dt, $^2J_{F-F}$ = 144.5, $^3J_{F-H}$ = 7.0 Hz, 4F); ESI MS (+) *m/z*: calcd for $C_{19}H_{34}F_5O_4SNa^+$, 490.2021, found: 490.2033.

*(E)-1-(Pentafluoro-λ⁶-sulfanyl)pent-2-en-4-yl 2-(pentafluoro-λ⁶-sulfanyl)acetate (**36a**)*. The alcohol **28a** (40 mg, 0.19 mmol), SF_5CH_2COOH (53 mg, 0.28 mmol), DMAP (3.5 mg, 0.029 mmol), DCC (58 mg, 0.28 mmol) were stirred in DCM (5 mL), overnight at room temperature. Silica was poured to the reaction mixture, then solvents were removed under reduced pressure, and thus obtained material was subjected to column chromatography (pentane/Et_2O, 15:1). Evaporation of the solvents afforded **36a** as a yellow liquid. Yield: 68 mg (94%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.96 (dt, $^3J_{H-H}$ = 14.9, $^3J_{H-H}$ = 5.8 Hz, 1H), 5.84 (dd, $^3J_{H-H}$ = 15.5, $^3J_{H-H}$ = 5.9 Hz, 1H), 5.47 (quint, $^3J_{H-H}$ = 6.4 Hz, 1H), 4.40 – 4.20 (m, 4H), 1.40 (d, $^3J_{H-H}$ = 6.5 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 161.2 (quint, $^3J_{C-F}$ = 4.5 Hz), 137.3 (broad), 122.3 (quint, $^3J_{C-F}$ = 4.1 Hz), 72.7 (quint, $^2J_{C-F}$ = 15.6 Hz), 72.2, 70.8 (quint, $^2J_{C-F}$ = 16.9 Hz), 19.3; ^{19}F NMR (282 MHz, $CDCl_3$): δ 81.53 (nonet, $^2J_{F-F}$ = 148.4 Hz, 1F), 78.88 (nonet, $^2J_{F-F}$ = 145.0 Hz), 70.95 (dm, $^2J_{F-F}$ = 148.4, $^3J_{F-H}$ = 7.6 Hz, 4F), 63.68 (dm, $^2J_{F-F}$ = 145.0, $^3J_{F-H}$ = 7.8 Hz, 4F); ESI MS (+) *m/z*: calcd for $C_7H_{10}F_{10}O_2S_2Na^+$, 402.9885, found: 402.9879.

*(E)-1-(Pentafluoro-λ⁶-sulfanyl)dodec-2-en-4-yl 2-(pentafluoro-λ⁶-sulfanyl)acetate (**36b**)*. The alcohol **28b** (63 mg, 0.20 mmol), SF_5CH_2COOH (45 mg, 0.24 mmol), DMAP (4 mg, 0.03 mmol), and DCC (50 mg, 0.24 mmol) were stirred in DCM (5 mL) overnight at room temperature. Workup according to the previous protocol afforded **36b** as a yellow oil. Yield: 90 mg (93%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.95 (dt, $^3J_{H-H}$ = 15.3, $^3J_{H-H}$ = 7.6 Hz, 1H), 5.78 (dd, $^3J_{H-H}$ = 15.5, $^3J_{H-H}$ = 6.8 Hz, 1H), 5.33 (q, $^3J_{H-H}$ = $^3J_{H,H}$ = 6.7 Hz, 1H), 4.30 (quint, $^3J_{H-H}$ = 7.7 Hz, 2H), 4.23 (sext, $^3J_{H-F}$ = $^3J_{H-H}$ = 7.0 Hz, 2H), 1.75 – 1.56 (m, 2H), 1.31 – 1.24 (m, 12H), 0.89 (t, $^3J_{H-H}$ = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 161.4 (quint, $^3J_{C-F}$ = 4.3 Hz), 136.7, 123.2 (quint, $^3J_{C-F}$ = 4.1 Hz), 76.2, 72.8 (quint, $^2J_{C-F}$ = 14.8 Hz), 71.0 (quint, $^2J_{C-F}$ = 16.8 Hz), 33.7, 31.9, 29.4, 29.23, 29.18, 24.7, 22.7, 14.1; ^{19}F NMR (282 MHz, $CDCl_3$): δ 81.55 (nonet, $^2J_{F-F}$ = 147.3 Hz, 1F), 78.94 (nonet, $^2J_{F-F}$ = 144.6 Hz, 1F), 71.03 (dm, $^2J_{F-F}$ = 147.3, $^3J_{F-H}$ = 7.5 Hz, 4F), 63.69 (dt, $^2J_{F-F}$ = 144.6, $^3J_{F-H}$ = 7.7 Hz, 4F); ESI MS (+) *m/z*: calcd for $C_{14}H_{24}F_{10}O_2S_2Na^+$), 501.0950, found: 501.0958.

Synthesis and Johnson-Claisen rearrangement of (*E*)-6,6,6-trifluorohex-3-en-2-ol (42)

*(Z)-1,1,1-Trifluoro-5-methoxyhex-4-en-3-one (**38**)*. 3,3,3-Trifluoropropionyl chloride was prepared from CF_3CH_2COOH (2625 mg, 20.52 mmol), oxalyl chloride (3900 mg, 30.77 mmol), and DMF (20 μL) in DCM (40 mL). Methoxypropene (3000 mg, 41.00 mmol) and pyridine (3200 mg, 41.00 mmol) in DCM (15 mL) were then added to the reaction mixture at 0 °C, and the reaction mixture was stirred for 15 h. Work up provided the title compound as a yellowish liquid. Yield: 1280 mg (34%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.46 (s, 1H), 3.68 (s, 3H), 3.18 (q, $^3J_{H-F}$ = 10.8 Hz, 3H), 2.31 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 187.5, 176.2, 124.3 (q, $^1J_{C-F}$ = 276.7 Hz), 98.3, 55.8, 47.7 (q, $^2J_{C-F}$ = 27.4 Hz), 20.3; ^{19}F NMR (282 MHz, $CDCl_3$): δ -62.92 (t, $^3J_{F-H}$ = 10.8 Hz, 3F); ESI MS (+) *m/z*: calcd for $C_7H_9O_2F_3H^+$, 183.0627, found: 183.0629, calcd for $C_7H_9O_2F_3Na^+$, 205.0447, found: 205.0460; calcd for $C_7H_9O_2F_3NaCH_3OH^+$ 237.0709, found: 237.0723.

*(E)-6,6,6-Trifluorohex-3-en-2-ol (**42**)*. (*Z*)-1,1,1-Trifluoro-5-methoxyhex-4-en-3-one (**38**) (1000 mg, 5.49 mmol) was treated with $NaBH_4$ (209 mg, 5.49 mmol) and $CeCl_3$•$7H_2O$ (2044 mg, 5.49 mmol) in methanol (25 mL) at 0 °C. After 2 h the reaction was quenched with 1 M HCl (50 mL) and extracted with EtOAc (3 × 40 mL). The crude solution of **39** was concentrated and subsequently dissolved in a 3:1 acetone/1 M HCl mixture (10 mL) and stirred overnight, whereupon compound **41** was formed via **40**. The reaction mixture was diluted with H_2O (20 mL) and extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with brine (40 mL), dried over $MgSO_4$ and the solvent was evaporated. The obtained crude, α,β-unsaturated ketone **41** (which proved to be unstable on silica) was immediately reduced with $NaBH_4$ (209 mg, 5.49 mmol) and $CeCl_3$ • $7H_2O$ (2044 mg, 5.49 mmol) in methanol (25 mL) at 0 °C. After 2 h the reaction was quenched with 1 M HCl (50 mL) and extracted with EtOAc (3 × 40 mL). Work up provided

crude material, which was purified by column chromatography (pentane/Et_2O, 2:1) to give the pure allylic alcohol **42** as a colorless liquid. Yield: 120 mg (14% overall, 4 steps). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.78 (dd, $^3J_{H-H}$ = 15.8, $^3J_{H-H}$ = 6.0 Hz, 1H), 5.65 – 5.55 (dtd, $^3J_{H-H}$ = 15.4, $^3J_{H-H}$ = 7.0, $^3J_{H-H}$ = 1.2 Hz, 1H), 4.32 (quint, $^3J_{H-H}$ = 6.3 Hz, 1H), 2.80 (qd, $^3J_{H-F}$ = 10.7, $^3J_{H-H}$ = 7.1 Hz, 3H), 1.85 (bs, 1H), 1.27 (d, $^3J_{H-H}$ = 6.5 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 141.5, 125.9 (q, $^1J_{C-F}$ = 276.4 Hz), 117.6 (q, $^3J_{C-F}$ = 3.7 Hz), 68.1, 36.9 (q, $^2J_{C-F}$ = 29.8 Hz), 23.1; ^{19}F NMR (282 MHz, $CDCl_3$): δ -66.95 (t, $^3J_{F-H}$ = 10.8 Hz, 3F). Molecular ion was not found in ESI-MS.

*Methyl syn-(E)-2-chloro-3-(2,2,2-trifluoroethyl)hex-4-enoate and methyl anti-(E)-2-chloro-3-(2,2,2-trifluoroethyl)hex-4-enoate (**43**)*. According to the general procedure, the allylic alcohol **42** (25 mg, 0.16 mmol), methyl chloroorthoacetate (75 mg, 0.49 mmol), propionic acid (10 μL), and toluene (1 mL) were refluxed for 6 h. After workup the crude product was purified by column chromatography (silica gel, pentane/Et_2O, gradient 30:1 to 10:1) to give the liquid **43**, as a mixture of diastereomers (ratio *syn*/*anti* = 55:45). Yield: 27 mg (69%). ^{1}H NMR (300 MHz, $CDCl_3$): δ overlap 5.75-5.58 (m, 1H), 5.42-5.23 (m, 1H), 4.47 (d, 1H, $^3J_{H-H}$ = 3.9 Hz), 4.17 (d, 1H, $^3J_{H-H}$ = 7.5 Hz), 3.78 (s, 3H), 3.77 (s, 3H), 3.12 (dq, $^3J_{H-H}$ = 12.5, $^3J_{H-H}$ = 4.4 Hz, 1H), 3.00 (qd, $^3J_{H-H}$ = 10.1, $^3J_{H-H}$ = 3.0 Hz, 1H), overlap 2.66-2.10 (m, 2H), 1.68 (d, $^3J_{H-H}$ = 6.5, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 168.6, 168.2, 131.3, 130.9, 129.4 (q, $^1J_{C-F}$ = 275 Hz), 127.0, 126.2, 61.2, 60.3, 53.1, 53.0, 41.6 (q, $^3J_{C-F}$ = 2.5 Hz), 41.1 (q, $^3J_{C-F}$ = 2.8 Hz), 36.0 (d, $^2J_{C-F}$ = 27.8 Hz), 35.3 (d, $^2J_{C-F}$= 27.0 Hz), 18.1. ^{19}F {^{1}H} NMR (282 MHz, $CDCl_3$): δ -64.16 (s, 3F) and -63.62 (s, 3F). ESI MS (+) *m/z*: calcd for $C_9H_{12}O_2ClF_3Na^+$: 267.0370, found: 267.0367.

Author Contributions

The manuscript was compiled through contributions from all of the authors. P.D., W.S.H., and A.V.M. executed the experiments and assigned structures of the products. J.S.T. and G.H. developed the concept, supervised the work and compiled the manuscript. All of the authors have given approval to the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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