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Synthesis of α-(Pentafluorosulfanyl)- and α-(Trifluoromethyl)-substituted Carboxylic Acid Derivatives by Ireland-Claisen Rearrangement

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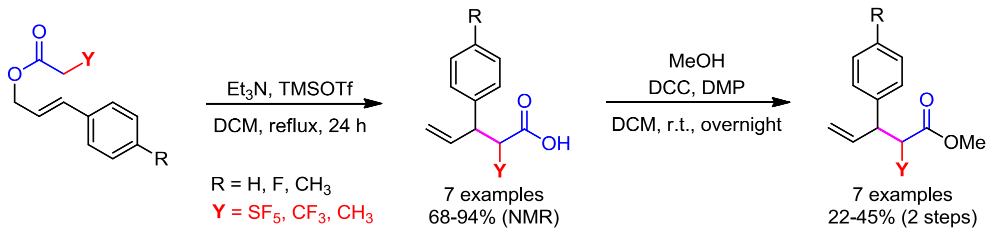
Keywords: C-C bond formation • DFT calculation • [3,3]-sigmatropic rearrangement • SF_5-chemistry • synthesis.



Abstract: Earlier studies have shown that [3,3]-sigmatropic rearrangements of allyl esters are useful for the construction of fluorine-containing carboxylic acid derivatives. This paper describes the synthesis of 3-aryl-pent-4-enoic acid derivatives bearing either a pentafluorosulfanyl (SF_5) or a trifluoromethyl (CF_3) substituent in the 2-position by treatment of corresponding SF_5 or CF_3 acetates of *p*-substituted cinnamyl alcohols with trimethylamine followed by trimethylsilyl triflate (TMSOTf). This Ireland-Claisen rearrangement delivered approximate 1:1 mixtures of *syn/anti*-diastereoisomers due to tiny differences (<0.5 kcal/mol) both in the energy of (*Z*)/(*E*)-isomeric ester enolates and in the alternative Zimmermann-

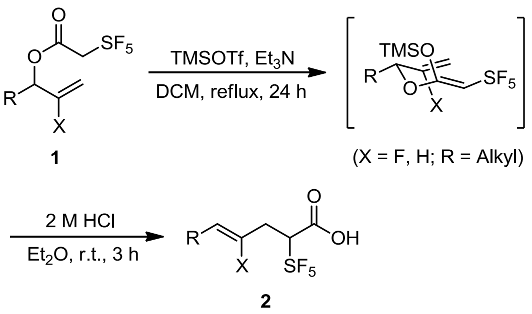
Traxler transition states of model compounds as shown by DFT calculations. Acidic reaction conditions have to be avoided since addition of the reagents in opposite sequence (first TMSOTf then Et_3N) led to oligomerization of the cinnamyl SF_5- and CF_3-acetates. Treatment of the corresponding regioisomeric 1-phenyl-prop-2-en-1-yl acetates under the latter conditions resulted in [1,3]-sigmatropic rearrangement and subsequent oligomerization of the intermediately formed cinnamyl esters. When Et_3N was added first followed by TMSOTf, no further reaction of the formed ester was detected.

Introduction

Rearrangement reactions belong to the most widely used methods to achieve an extension of the carbon scaffold of a given molecule. Here [3,3]-sigmatropic rearrangement reactions of the Claisen-type are of significant importance.[1] In 1912 Claisen described both the thermally induced rearrangement of an allyl aryl ether as well as the conversion of an allyl vinyl ether to the corresponding allyl phenol and carbonyl compounds, respectively.[2] As of now, several variations of the original Claisen rearrangements have been developed. The Ireland-Claisen rearrangement is one of the well-known and most frequently employed variants. In this reaction, which was discovered in 1972, an allylic ester is initially transformed into the corresponding ester enolate. This 3-oxa-1,5-diene system then rearranges to form a γ,δ-unsaturated carboxylic acid.[3] Like the aromatic and aliphatic Claisen rearrangements, the Ireland-Claisen variant can be performed in a stereoselective fashion. Thereby, the stereochemistry of the product(s) is determined by the geometry of the intermediately formed ester enolate(s) as well as by the conformation of the six-membered transition state(s).[3b] Additional advantages of the Ireland-Claisen rearrangement are mild reaction conditions and the tolerance of various functional groups.[1c,1d,4]

Due to the general interest in organofluorine compounds,[5] Ireland-Claisen rearrangement reactions of substrates containing fluorine or the CF_3-group have been previously studied by us[6] and others.[7] Likewise, in recent years the pentafluorosulfanyl (SF_5)-group became increasingly interesting[8] as a potential substitute for the CF_3-group. However, all our attempts to involve different 3-pentafluorosulfanyl allylic esters with an SF_5-group as part of the allylic system in the rearrangement step failed.[9] In contrast, Ireland-Claisen rearrangement of allylic SF_5-acetates **1** derived from aliphatic allylic alcohols with either a fluorine atom or a hydrogen atom in the 2-position were converted into the corresponding carboxylic acids **2** using trimethylsilyltriflate (TMSOTf) and triethylamine in dichloromethane.[10] (Scheme 1).

Scheme 1. Stereoselective synthesis of *trans*-configurated α-SF_5-substituted γ,δ-unsaturated carboxylic acids 2 by Ireland-Claisen rearrangements.[10]



The *trans*-configurated products were formed exclusively, although both (*Z*)- and (*E*)-ketene trimethylsilyl acetals were formed intermediately as proved in time-dependent NMR experiments. While the (*Z*)-ketene trimethylsilyl acetals rearranged smoothly, the (*E*)-isomers were stable under these and even more forcing conditions.[10] During aqueous work-up, the starting allylic esters are regenerated from the latter intermediates. As a consequence, incomplete conversion of the starting material **1** was observed in all cases. The (*Z*)-ketene trimethylsilyl acetals most likely rearrange *via* an energetically favored six-membered transition state to give the *trans*-configurated carboxylic acids **2**. For the first time, SF_5-substituted ester enolates were verified and characterized by NMR spectroscopy. Esters **1** with a phenyl group (R = Ph) could not be converted into the corresponding carboxylic acids under the conditions shown in Scheme 1. Instead complex mixtures of unidentified products were obtained.[10] Very recently, aldol-type reactions of SF_5-substituted acetic acid esters with aldehydes proceeding via analogous ester enolates have been described.[11]

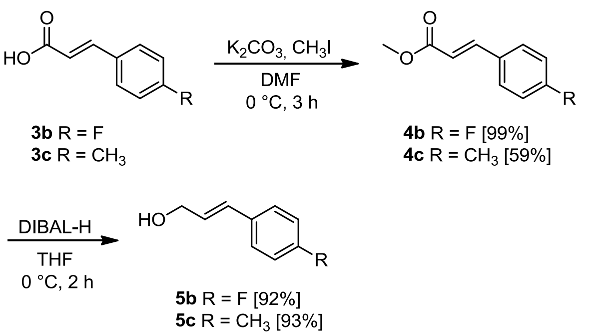
Herein, we would like to present our recent results on Ireland-Claisen rearrangements of 2-(pentafluorosulfanyl)acetic acid cinnamyl esters. Moreover, we compare these reactions concerning reactivity and selectivity with those of the corresponding allylic CF_3- and CH_3-substituted acetates and illuminate the importance of the particular reaction conditions. Furthermore, two earlier attempts to rearrange SF_5-substituted acetates of secondary allyl alcohols[10] were repeated under the new optimized conditions.

Results and Discussion

Synthesis of cinnamyl SF_5- and CF_3-acetates

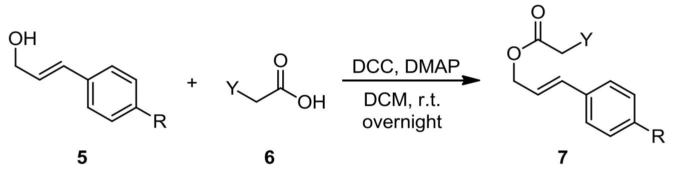
For the [3,3]-sigmatropic rearrangements besides cinnamyl alcohol (**5a**) itself, also the 4-fluoro and 4-methyl derivatives **5b** and **5c**[12] were synthesized by a two-step procedure starting from the commercial acids **3b** and **3c** according to known procedures (Scheme 2).[13,14] Direct reduction of the acids with either lithium aluminum hydride (LAH)[15] or the borane dimethylsulfide complex[16] were not successful.

Scheme 2. Preparation of cinnamyl alcohols 5b and 5c.



Esterification of the alcohols **5** with 2-(pentafluorosulfanyl)acetic acid (**6a**)[17] and commercially available 3,3,3-trifluoromethyl-propionic acid (**6b**) in the presence of *N,N′*-dicyclohexyl carbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) according to the protocol independently developed by Neises and Steglich[18a] and Hassner and Alexanian[18b] gave the desired SF_5- and CF_3-substituted allylic esters **7a**, **7b**, and **7d-g**. For the purpose of comparison in the Ireland-Claisen rearrangement, the known propionate **7c**[19] was prepared analogously starting from cinnamyl alcohol (**5a**) and propionic acid (**6c**) (Table 1).

Table 1. Synthesis of allylic esters



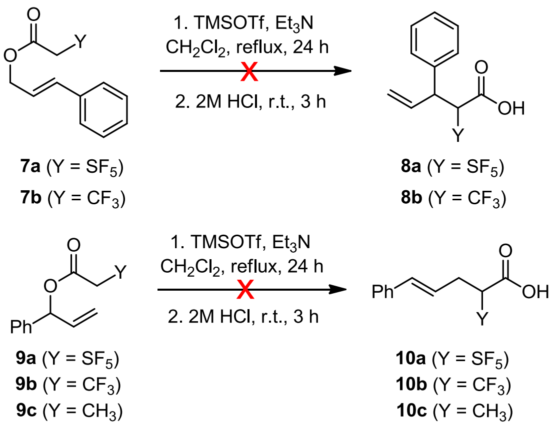
Entry	Alcohol	Y	R	Ester	Yield [%]
1	**5a**	SF_5	H	**7a**	88
2	**5a**	CF_3	H	**7b**	87
3	**5a**	CH_3	H	**7c**	89
4	**5b**	SF_5	F	**7d**	60
5	**5b**	CF_3	F	**7e**	59
6	**5c**	SF_5	CH_3	**7f**	83
7	**5c**	CF_3	CH_3	**7g**	85

The seven esters **7a-7g** produced in this way were isolated in high purity after column chromatography in yields between 59 and 89%. No significant difference in yields of the SF_5- and the CF_3-substituted compounds has been observed.

Attempts of Ireland-Claisen rearrangements

Having allylic esters **7a** and **7b** in hand, Ireland-Claisen rearrangements were attempted under the conditions (1. TMSOTf, 2. Et_3N, DCM, reflux) originally developed for intermediate formation of (trifluoromethyl)ketene silyl acetals (α-CF_3-ester enolate equivalents) in aldol-type reactions and ester enolate Claisen rearrangements[20] and optimized for rearrangements of allylic SF_5-acetates of type **1** derived from aliphatic allylic alcohols with either a fluorine atom or a hydrogen atom in the 2-position.[10] Surprisingly, the expected α,β-disubstituted carboxylic acids **8a** and **8b** were not obtained. Instead an oligomerization of the starting allylic esters occurred (see below). Interestingly, compound **9a** and the corresponding CF_3 and even the CH_3 analogues **9b** and **9c** also failed to rearrange to the expected products **10a**, **10b**, and **10c** (Scheme 3), respectively. Under the same conditions they oligomerized as well. Also, the *p*-fluorophenyl and the 1-naphthyl analogues **9d** and **9e** (Y = CF_3, not shown in Scheme 3) have been synthesized. Likewise, these allylic esters oligomerized under the aforementioned conditions.

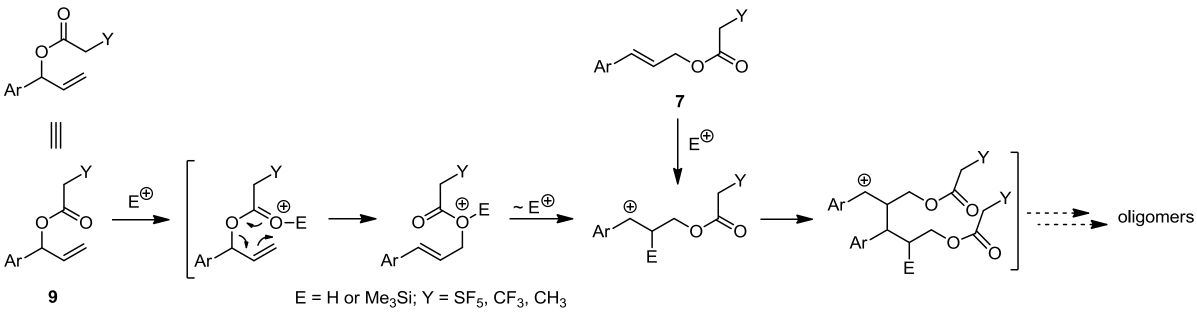
Scheme 3. Failure of [3,3]-sigmatropic rearrangement of cinnamyl 7a and 7b and substituted 1-phenylprop-2-en-1-yl-acetates 9a-9c.



This is surprising since, in the latter cases, extension of the π-system from benzenes **9a-9c** to styrene derivatives **10a-10c** and formation of a disubstituted double bond from a monosubstituted terminal one in the starting materials were expected to be driving forces for the [3,3]-sigmatropic rearrangement. Instead of the target products, mixtures of oligomers were formed according to the ESI-mass spectra, which show products with *m/z* values between 500 and 1200. Moreover, in the ^{1}H NMR spectra of the crude product mixtures, broad multiplets and absence of signals of vinylic protons provide hints on oligomeric structures (see SI).

Comparing the spectra of the mixtures of oligomeric products formed from either the cinnamyl acetates **7a** and **7b** or the secondary allyl acetates **9a** and **9b**, we realized that they looked almost identical. Consequently, we anticipated that slightly acidic conditions are created when TMSOTf is added to the allylic esters in methylene chloride before Et_3N addition. In case of esters **9** this gives rise to the possibility of an electrophilic attack of a proton or a trimethylsilyl cation equivalent E^+ on the carbonyl oxygen initiating a [1,3]-sigmatropic shift of the ester function. This leads to the formation of benzylic cations of the corresponding cinnamyl esters **7**, which oligomerize under the acidic conditions (Scheme 4).

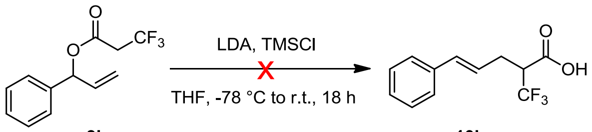
Scheme 4. Anticipated mechanism of [1,3]-sigmatropic rearrangement of substituted 1-phenylprop-2-en-1-yl-acetates 9 and subsequent oligomerization of the benzylic cations of the corresponding cinnamyl acetates 7.



TMSOTf is known to have some ionic character in dry, fairly non-polar solvents like methylene chloride, but it is more ionic in a polar environment.[21] Moreover, the reagent is useful as a Lewis acid in many carbonyl reactions[22] and has been used as a catalyst in cationic polymerization reactions.[23]

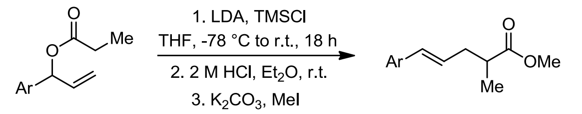
In order to test whether standard Ireland-Claisen conditions[3,6,7] might work, we treated compound **9b** with LDA (1.2 equiv) and TMSCl (1.2 equiv) in THF at -78 °C to room temperature in an attempt to obtain **10b** (Scheme 5). However, only the starting allylic ester **9b** was recovered after workup. No products with a CF_3 group were found in the ^{19}F NMR spectrum of the crude product. Treatment of **9b** with 2.5 equiv of LDA led to decomposition.

Scheme 5. Failure of Ireland-Claisen rearrangement of 1-phenylprop-2-en-1-yl-(3,3,3-trifluoropropionate) (9b).



In contrast, 1-(phenylprop-2-en-1-yl) propionate (**9c**) and its *p*-fluorophenyl- and 1-naphthyl derivatives **9f** and **9g** formed from the corresponding allylic alcohols underwent [3,3]-sigmatropic rearrangements under identical conditions, and the corresponding methyl esters **10c**, **10f**, and **10g** were isolated after methylation of the initially formed carboxylic acids with methyl iodide (Scheme 6).

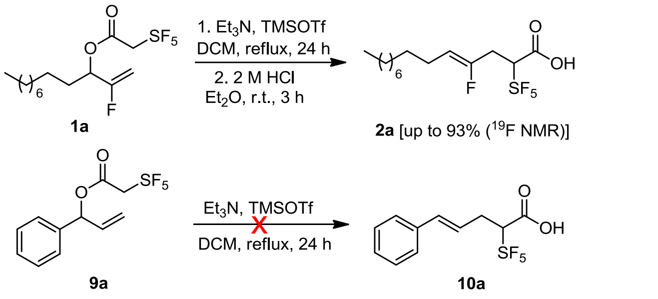
Scheme 6. [3,3]-Sigmatropic rearrangement of substituted 1-arylprop-2-en-1-yl-propionates 9.



Rearrangements under the new reaction conditions

From the results described in the former section, we concluded that an initial acidic environment is responsible for the failure of rearrangement of compounds **9a**, **9b**, and the substituted cinnamyl acetates **7**. Therefore, we hypothesized that basic conditions from the beginning might facilitate the rearrangement. We first chose compound **1a** to study the reaction by ^{19}F NMR spectroscopy. Indeed, when the order of addition of the reagents to compound **1a** in dichloromethane-d$_2$ was reversed, i.e. first addition of triethylamine followed by TMSOTf, the formation of the intermediate (*Z*)-ketene trimethylsilyl acetal was faster (^{19}F NMR spectroscopy, see SI) and after refluxing for 24 hours and work-up, the yield of **2a** was increased from 65% under the original conditions[10] to 93% (^{19}F NMR spectroscopy) (Scheme 7, Figure 1).

Scheme 7. Results of the treatment of 1a and 9a under the optimized reaction conditions.



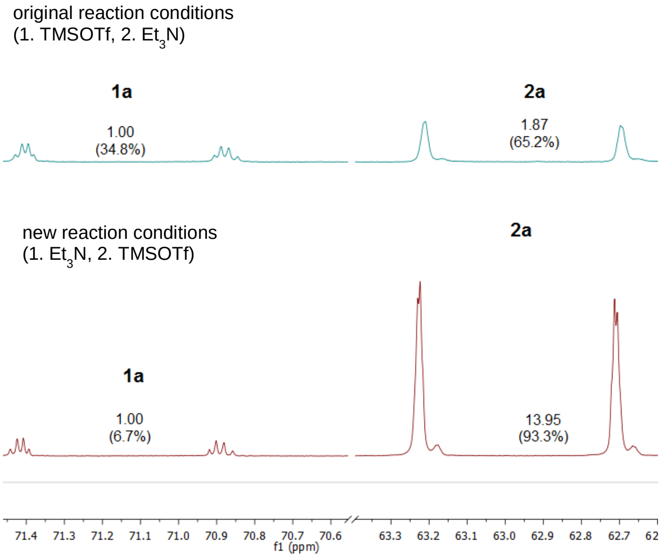
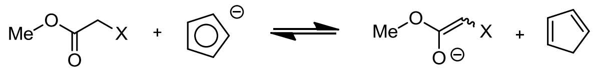


Figure 1. Comparison of the results of [3,3]-sigmatropic rearrangement of 1a under the original (1. TMSOTF, 2. Et_3N, top) and the new (1. Et_3N, 2. TMSOTf, bottom) reaction conditions (SF_5-part of ^{19}F NMR spectra after work up).

In contrast, the allylic ester **9a**, which yielded oligomeric products under the original conditions,[10] did not react under these new conditions (Scheme 7).

It is surprising that **9a** and also **9b** did not rearrange with Et_3N/TMSOTf since DFT calculations (TPSS-D3/def2-TZVP + COSMO) show that the methylene protons of **9a** and **9b** should be significantly more acidic than those of **9c**. This was estimated by the free energies of proton transfer from the model esters **C**, **D**, and **E** to the cyclopentadienyl anion (cyclopentadiene: pK_a = 18, in CH_2Cl_2) forming ester enolates (Table 2, for details see SI).

Table 2. Calculated free energies of proton transfer [kcal/mol, 298 K] to model (*E*)- and (*Z*)-ester enolates and p*K*a values of substituted acetic acid esters in CH_2Cl_2.

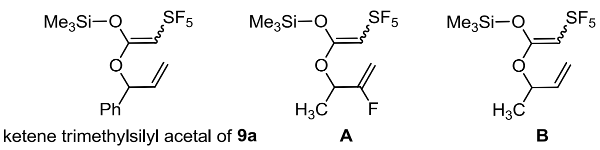


C (X = CH_3); **D** (X = CF_3); **E** (X = SF_5)

Anion	Ester enolates **C**		Ester enolates **D**		Ester enolates **E**	
	(*E*)	(*Z*)	(*E*)	(*Z*)	(*E*)	(*Z*)
pK_a	33.4	32.6	19.9	19.6	16.1	16.5
ΔG_{298}	20.97	19.86	2.54	2.18	-2.58	-2.01

Moreover, when comparing the activation energies for the [3,3]-sigmatropic rearrangements of the ketene silylacetal of **9a** with that of model compounds **A** and **B** (derived from the SF_5-acetic esters of 2-fluoro-but-1-en-3-ol and but-1-en-3-ol, see SI), it becomes clear that all rearrangements should proceed. In all cases the (*E*)-ketene trimethylsilyl acetals are thermodynamically favored by 1-2 kcal/mol over the (*Z*)-ketene trimethylsilyl acetals (Table 3).

Table 3. Relative energies of (*Z*/*E*)-isomeric ketene trimethylsilyl acetals and chair and boat transition states of [3,3]-sigmatropic rearrangements

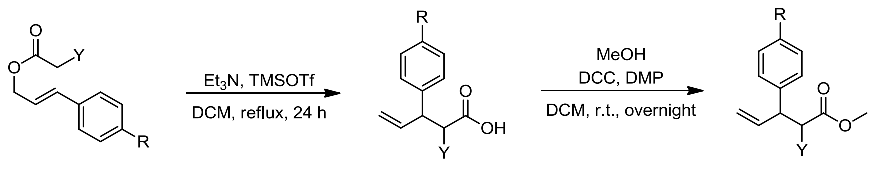


Ketene trimethylsilyl acetals	ΔG_{298} [kcal/mol] (*E*)	TS_{chair} [kcal/mol] (*E*)	TS_{boat} [kcal/mol] (*E*)	ΔG_{298} [kcal/mol] (*Z*)	TS_{chair} [kcal/mol] (*Z*)	TS_{boat} [kcal/mol] (*Z*)
9a	0.0	22.9	18.1	2.0	14.9	20.3
A	0.0	26.9	23.3	0.9	18.2	22.0
B	0.0	24.8	21.3	1.2	16.8	20.4

In all cases the activation energies for the transformation of the (*Z*)-ketene trimethylsilyl acetals to the favored chair transition states of [3,3]-sigmatropic rearrangements are 4-5 kcal/mol lower in energy than those of the boat transition states. Moreover, the activation energy for the transformation of the (*E*)-ketene trimethylsilyl acetals to the favored boat transition states is 3-5 kcal/mol higher in energy when compared to the activation energy for the transformation of the (*Z*)-ketene trimethylsilyl acetals to their chair transition states. As previously stated from NMR experiments with **1a**,[10] and proved by the present calculations, the rearrangement is proceeding exclusively *via* the corresponding (*Z*)-ketene trimethylsilyl acetal, while the (*E*)-ketene trimethylsilyl acetal did not rearrange. The latter was hydrolyzed to the starting ester **1a** during aqueous work up. Thus, from an energetic point of view, the phenyl-substituted ester **9a** should rearrange more easily, provided that the ester enolates were formed at all under the respective reaction conditions.

Fortunately, the undesired oligomerization reactions of cinnamyl acetates **7** occurring under the original reaction conditions[10] could be suppressed by using the new conditions and thereby avoiding an acidic environment. In this case [3,3]-sigmatropic rearrangements resulted in the formation of almost 1:1 mixtures of the target diastereoisomeric products **8** (Table 4). In analogy to our earlier studies,[10] the amount of the carboxylic acids **8** in the crude reaction mixture was determined by ^{19}F NMR spectroscopy. Subsequent conversion of the acids **8** into the methyl esters **15** allowed for a simpler isolation and purification of the γ,δ-unsaturated α-substituted carboxylic esters by column chromatography. Surprisingly, the initially used alkylation method (K_2CO_3, MeI, DMF, 0 °C, 3 h) did not exclusively give the target methyl esters **15**, since the SF_5-group served as a leaving group[24] and was partially substituted by a formate group, probably via an intermediate α-lactone (see SI). Therefore, the carboxylic acids **8** were treated with methanol in the presence of DCC and a catalytic amount of DMAP[18] (Table 4).

Table 4. Synthesis of α-substituted carboxylic acids 8 and by Ireland-Claisen rearrangements and esterification to 15.

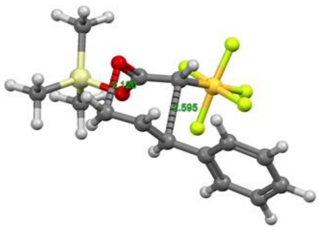


Entry	Esters **7**	Y	R	Acids **8**	Yield [%][a]	*dr*[a]	Esters **15**	Yield [%][b]	*dr*[a]
1	**7a**	SF_5	H	**8a**	92	62:38	**15a**	40	47:53
2	**7b**	CF_3	H	**8b**	94	54:46	**15b**	35	54:46
3	**7c**	CH_3	H	**8c**	-[c]	-[c]	**15c**	33	30:70[d]
4	**7d**	SF_5	F	**8d**	92	52:48	**15d**	45	39:61
5	**7e**	CF_3	F	**8e**	75	55:45	**15e**	30	56:44
6	**7f**	SF_5	CH_3	**8f**	68	63:37	**15f**	22	49:51
7	**7g**	CF_3	CH_3	**8g**	78	49:51	**15g**	22	52:48

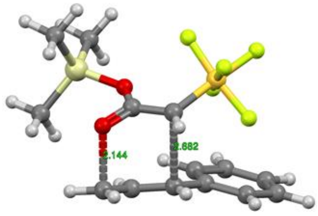
[a] Determined by ^{19}F NMR spectroscopy; [b] isolated yield over two steps; [c] not determined; [d] determined by GC.

The esters **7** were rearranged to the corresponding carboxylic acids **8** in 68-94% yields (^{19}F NMR spectroscopy), whereby no significant influence of the SF_5- and CF_3-substituents on the conversion of the starting materials has been observed. All carboxylic acids **8** were obtained as approximate 1:1-mixtures of both diastereomers. Unfortunately, we were not able to separate the acids or the esters in order to assign the *syn*/*anti*-configurations to specific compounds.

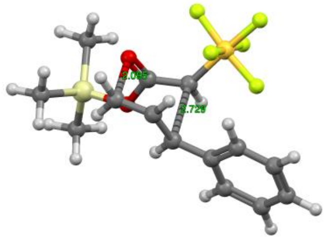
In order to find an explanation for the observed low diastereoselectivity, DFT calculations (PW6B95-D3//TPSS-D3/def2-TZVP + COSMO solvation model), were carried out (for details see SI). As a model system, the Ireland-Claisen rearrangement of the SF_5-substituted allylic ester **7a** to the corresponding carboxylic acids **8a** was chosen, and all four possible transition states – depending on the original geometry of the ketene trimethylsilyl acetal [(*Z*)-/(*E*)-configuration] as well as on the feasible geometry of the transition states itself (chair-/boat-conformation) – were determined (see SI). The four different transition states are shown in Figure 2 along with the relative energies and the corresponding free energy barriers ($\Delta G^{\ddagger}$) for the [3,3]-sigmatropic rearrangement reaction.



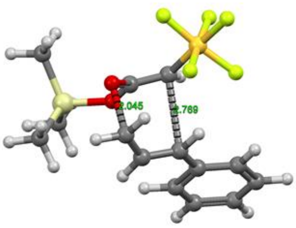
TS I (*Z*)/chair
0.0 kcal/mol
$\Delta G^{\ddagger}$ = +19.1 kcal/mol



TS II (*Z*)/boat
0.4 kcal/mol
$\Delta G^{\ddagger}$ = +19.5 kcal/mol



TS III (*E*)/chair
1.6 kcal/mol
$\Delta G^{\ddagger}$ = +20.6 kcal/mol

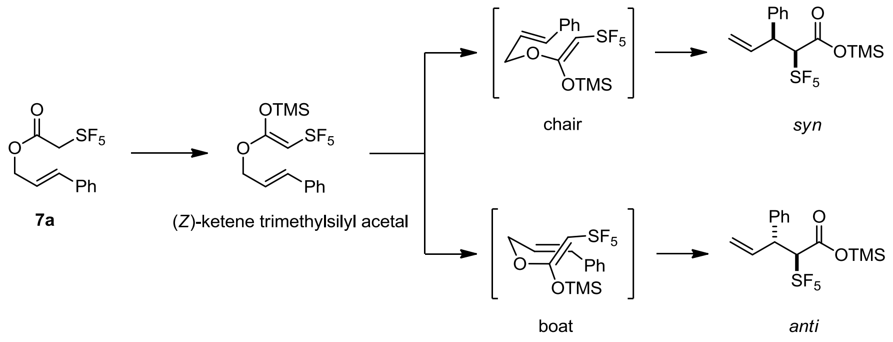


TS IV (*E*)/boat
0.5 kcal/mol
$\Delta G^{\ddagger}$ = +19.5 kcal/mol

Figure 2. Optimized transition states (DFT) of the Ireland-Claisen rearrangement of the model compound **7a** with Et_3N/TMSOTf to form diastereomeric acids **8a**.

The calculated relative energies indicate that the formation of acids **8** is generally possible via all four transition states, although the transition states **I**, **II**, and **IV** are energetically slightly favored. Furthermore, the free energy barriers suggest that the rearrangement reaction is more likely to proceed *via* the two (*Z*)-configurated transition states **I** and **II** with the lowest energy barriers resulting in either the *syn*- or the *anti*-diastereoisomer. However, transition states **III** and **IV** would lead to a similar product ratio of *syn*- and *anti*-isomers. Scheme 8 shows the anticipated mechanistic pathway – based on the DFT calculations – for the rearrangement of compound **7a** with the (*Z*)-ketene trimethylsilyl acetal as favored intermediate.

Scheme 8. Anticipated mechanistic pathway of the Ireland-Claisen rearrangement of compound 7a with Et_3N/TMSOTf.



Conclusions

Ireland-Claisen rearrangements of SF_5- and CF_3-substituted acetic acid cinnamyl esters **7** have been investigated. While treatment with trimethylsilyl triflate (TMSOTf) followed by Et_3N and subsequent refluxing in dichloromethane resulted in oligomerization, avoiding initial acidic conditions by reversing the addition sequence of reagents enabled the formation of the target diastereomeric 3-aryl-2-pentafluorosulfanylpent-4-enoic and 3-aryl-2-trifluoromethyl-pent-4-enoic acids **8** in good yields. The reaction products were obtained as approximate 1:1-mixtures of *syn*- and *anti*-isomers. The unexpected low diastereoselectivity is explained by similar energies of the intermediate (*E*)- and (*Z*)-ketene trimethylsilyl acetals and very tiny differences of energy barriers (DFT calculations) for the different transition states of the [3,3]-sigmatropic rearrangement reactions. Applying the new reaction conditions to the rearrangement of the SF_5-substituted acetic acid ester **1a** of 2-fluorododec-1-en-3-ol resulted in a higher yield of product **2a** due to faster formation of the rearranging (*Z*)-ketene trimethylsilyl acetal. The corresponding esters of 1-phenyl-prop-2-en-1-ol **9a** and **9b** failed to rearrange even under the new conditions.

Experimental Section

General remarks: All reactions involving air and/or moisture sensitive compounds were performed under argon atmosphere applying the Schlenk technique. DCM was dried over CaH_2 and distilled. THF was freshly distilled over sodium and benzophenone. TLC was performed on coated silica gel plates Merck 60 F_{254}. The spots were detected with alkaline $KMnO_4$ solution. For the purification of the compounds by column chromatography, silica gel Merck 60 (0.063-0.2 mm) was used. Solvents for chromatography were purified prior to use. The NMR spectra were recorded either at 300 MHz, 400 MHz, or 500 MHz spectrometers. ^{1}H NMR spectra were referenced to TMS, ^{13}C NMR spectra to the used deuterated solvent $CDCl_3$ or CD_2Cl_2, and ^{19}F NMR spectra to $CFCl_3$ as the internal standards. Actually, the SF_5 group is an AB_4 spin pattern, although with high-field NMR spectrometers this pattern moves toward AX_4 so that the A part, which is given by the single axial fluorine atom, is marked as a quintet (qn). In all cases the signal of the four equatorial fluorine atoms appeared as a doublet of multiplets (dm). The coupling between the axial and the equatorial fluorine atoms correlates with the doublet coupling constant. Electrospray ionization (ESI) mass spectrometry was performed on a MicroToF spectrometer. 1-Phenylprop-2-en-1-ol,[25] 1-(4-fluorophenyl)prop-2-en-1-ol,[26] 1-(naphthalen-1-yl)prop-2-en-1-ol,[27] and 1-phenylprop-2-en-1-yl-(2-pentafluorosulfanyl)acetate (**9a**)[10] were synthesized according to known procedures. The spectroscopic data are in agreement with published ones. The allylic alcohols **5b** and **5c**[12] were prepared in two-steps from the corresponding cinnamic acids **3b** and **3c** via the corresponding methyl esters **4b**[28]and **4c**.[29]

DFT Calculations: All calculations were performed with the TURBOMOLE program (6.6).[30] The structures were optimized without any geometry constraints using the TPSS functional[31] and an atom-pairwise dispersion correction (D3).[32,33] A flexible triple zeta basis set (def2-TZVP)[34] was used in all calculations. For the calculation of zero point vibrational energies and free enthalpy contributions, a rotor approximation was applied for vibrational modes with wavenumbers below 100 cm^{-1}.[35] In addition, in the Ireland-Claisen reactions, single point calculations were performed with the hybrid functional PW6B95(-D3).[36] Implicit solvation was taken into account in these single point calculations with the COSMO model[37] as implemented in Turbomole (ε = 9.08, CH_2Cl_2).

General procedure for the synthesis of allylic esters 7: DCC (1.2 equiv) was dissolved in dry DCM (8 mL) before the allylic alcohol **5** (1.2 mmol, 1.0 equiv) followed by the corresponding carboxylic acid (1.2 equiv) were added under argon atmosphere. A white precipitate was formed and a catalytic amount of DMAP was added. The mixture was stirred at rt overnight. The suspension was diluted with Et_2O (25 mL) before the formed urea derivative was filtered off. The remaining solution was washed with H_2O (3 × 10 mL), 5% acetic acid (3 × 10 mL), and brine (3 × 10 mL) and dried over $MgSO_4$ before the solvent was removed under reduced pressure. The crude products were purified by column chromatography as indicated below.

*Cinnamyl 2-(pentafluorosulfanyl)acetate (**7a**).* The allylic ester **7a** was prepared according to the aforementioned general procedure starting from cinnamyl alcohol (**5a**) (150 mg, 1.12 mmol) and 2-(pentafluorosulfanyl)acetic acid (**6a**)[17] (259 mg, 1.39 mmol). After column chromatography (cyclohexane/EtOAc, 5:1) the target product was obtained as a colorless oil. Yield: 297 mg (88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 – 7.17 (m, 5H), 6.70 (dt, J = 15.9 Hz, J = 1.4 Hz, 1H), 6.27 (dt, J = 15.7 Hz, J = 6.7 Hz, 1H), 4.85 (dd, J = 6.6 Hz, J = 1.3 Hz, 2H), 4.33 (qn, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.1 (qn, J = 4.5 Hz,), 135.9, 135.9, 128.8, 128.6, 126.9, 121.5, 70.7 (qn, J = 16.9 Hz), 67.3. ^{19}F NMR (282 MHz, $CDCl_3$): δ 79.0 (qn, 1F), 71.0 (dm, J = 147.8 Hz, 4F). MS-ESI: m/z 325.0292 $[M+Na]^+$ calcd. for $C_{11}H_{11}F_5O_2SNa^+$ 325.0292.

*Cinnamyl 3,3,3-trifluoropropanoate (**7b**).* The allylic ester **7b** was prepared according to the aforementioned general procedure starting from cinnamyl alcohol (**5a**) (150 mg, 1.12 mmol) and 3,3,3-trifluoropropanoic acid (**6b**) (178 mg, 1.39 mmol). After column chromatography (cyclohexane/EtOAc, 5:1) the target product was obtained as a colorless liquid. Yield: 236 mg (87%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45 – 7.22 (m, 5H), 6.68 (dt, J = 15.9 Hz, J = 1.3 Hz, 1H), 6.26 (dt, J = 15.9 Hz, J = 6.5 Hz, 1H), 4.82 (dd, J = 6.5 Hz, J = 1.3 Hz, 2H), 3.21 (q, J = 10.1 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.1 (q, J = 4.2 Hz), 136.0, 135.4, 128.8, 128.5, 126.8, 123.4 (q, J = 276.2 Hz,), 122.0, 66.5, 39.7 (q, J = 31.1 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ -63.4 (t, J = 10.1 Hz, 3F). MS-ESI: m/z 267.0602 $[M+Na]^+$ calcd. for $C_{12}H_{11}F_3O_2Na^+$ 267.0603.

*Cinnamyl propionate (**7c**).* The allylic ester **7c** was prepared according to the aforementioned general procedure starting from cinnamyl alcohol (**5a**) (219 mg, 1.63 mmol) and propionic acid (**6c**) (144 mg, 1.95 mmol). After column chromatography (cyclohexane/EtOAc, 10:1) the target product was obtained as a colorless liquid. Yield: 275 mg (89%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43 – 7.20 (m, 5H), 6.64 (dt, J = 15.9 Hz, J = 1.4 Hz, 1H), 6.28 (dt, J = 15.9 Hz, J = 6.4 Hz, 1H), 4.73 (dd, J = 6.4 Hz, J = 1.4 Hz, 2H), 2.37 (q, J = 7.6 Hz, 2H), 1.16 (t, J = 7.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.3, 136.3, 134.1, 128.7, 128.1, 126.7, 123.4, 65.0, 27.7, 9.2. The spectroscopic data agree with those given in the literature.[16] MS-ESI: m/z 213.0882 $[M+Na]^+$ calcd. for $C_{12}H_{14}O_2Na^+$ 213.0886.

*(E)-4-Fluorocinnamyl 2-(pentafluorosulfanyl)acetate (**7d**).* The allylic ester **7d** was prepared according to the aforementioned general procedure starting from (*E*)-3-(4-fluorophenyl)prop-2-en-1-ol (**5b**) (150 mg, 0.99 mmol) and 2-(pentafluorosulfanyl)acetic acid (**6a**) (221 mg, 1.19 mmol). After column chromatography (cyclohexane/EtOAc, 5:1) the target product was obtained as a clear liquid. Yield: 189 mg (60%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 – 7.29 (m, 2H), 7.10 – 6.93 (m, 2H), 6.67 (dt, J = 15.8 Hz, J = 1.3 Hz, 1H), 6.19 (dt, J = 15.9 Hz,

J = 6.7 Hz, 1H), 4.84 (dd, J = 6.7 Hz, J = 1.3 Hz, 2H), 4.34 (qn, J = 7.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.9 (d, J = 248.0 Hz), 162.1 (qn, J = 4.6 Hz), 134.7, 132.1, 128.5 (d, J = 8.2 Hz), 121.2 (d, J = 2.3 Hz), 115.8 (d, J = 21.8 Hz), 70.7 (qn, J = 16.9 Hz), 67.2. ^{19}F NMR (282 MHz, $CDCl_3$): δ 79.0 (qn, 1F), 71.0 (dm, J = 147.7 Hz, 4F), -113.6 (tt, J = 8.6 Hz, J = 4.3 Hz, 1F). MS-ESI: m/z 343.0203 $[M+Na]^+$ calcd. for $C_{11}H_{10}F_6O_2SNa^+$ 343.0198.

*(E)-4-Fluorocinnamyl 3,3,3-trifluoropropanoate (**7e**).* The allylic ester **7e** was prepared according to the aforementioned general procedure starting from (*E*)-3-(4-fluorophenyl)prop-2-en-1-ol (**5b**) (150 mg, 0.99 mmol) and 3,3,3-trifluoropropanoic acid (**6b**) (152 mg, 1.19 mmol). After column chromatography (cyclohexane/EtOAc, 5:1) the target product was obtained as a clear oil. Yield: 152 mg (59%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 – 7.31 (m, 2H), 7.09 – 6.95 (m, 2H), 6.64 (dt, J = 15.8 Hz, J = 1.3 Hz, 1H), 6.19 (dt, J = 15.9 Hz, J = 6.5 Hz, 1H), 4.81 (dd, J = 6.6 Hz, J = 1.3 Hz, 2H), 3.22 (q, J = 10.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.1 (q, J = 4.3 Hz), 162.9 (d, J = 247.8 Hz), 134.2, 132.2 (d, J = 3.3 Hz), 128.4 (d, J = 8.2 Hz), 123.5 (q, J = 276.2 Hz), 121.8 (d, J = 2.3 Hz), 115.8 (d, J = 21.7 Hz), 66.3, 39.8 (q, J = 31.1 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ -63.9 (t, J = 10.1 Hz, 3F), -113.6 – -113.8 (m, 1F). MS-ESI: m/z 285.0518 $[M+Na]^+$ calcd. for $C_{12}H_{10}F_4O_2Na^+$ 285.0509.

*(E)-4-Methylcinnamyl 2-(pentafluorosulfanyl)acetate (**7f**).* The allylic ester **7f** was prepared according to the aforementioned general procedure starting from (*E*)-3-(*p*-tolyl)prop-2-en-1-ol (**5c**) (150 mg, 1.01 mmol) and 2-(pentafluorosulfanyl)-acetic acid (**6a**) (150 mg, 1.01 mmol). After column chromatography (cyclohexane/EtOAc, 5:1) the target product was obtained as a clear liquid. Yield: 225 mg (83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 – 7.27 (m, 2H), 7.17 – 7.12 (m, 2H), 6.67 (dt, J = 15.7 Hz, J = 1.3 Hz, 1H), 6.22 (dt, J = 15.8 Hz, J = 6.7 Hz, 1H), 4.84 (dd, J = 6.8 Hz, J = 1.3 Hz, 2H), 4.32 (qn, J = 7.7 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.1 (qn, J = 4.5 Hz), 138.6, 135.9, 133.1, 129.5, 126.8, 120.4, 70.7

(qn, J = 17.0 Hz), 67.5, 21.3. ^{19}F NMR (282 MHz, $CDCl_3$): δ 79.0 (qn, 1F), 70.9 (dm, J = 147.7 Hz, 4F). MS-ESI: m/z 339.0449 $[M+Na]^+$ calcd. for $C_{12}H_{13}F_5O_2SNa^+$ 339.0449.

*(E)-4-Methylcinnamyl 3,3,3-trifluoropropanoate (**7g**).* The allylic ester **7g** was prepared according to the aforementioned general procedure starting from (*E*)-3-(*p*-tolyl)prop-2-en-1-ol (**5c**) (150 mg, 1.01 mmol) and 3,3,3-trifluoropropanoic acid (**6b**) (155 mg, 1.21 mmol). After column chromatography (cyclohexane/EtOAc, 5:1) the target product was obtained as a clear liquid. Yield: 221 mg (85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 – 7.26 (m, 2H), 7.18 – 7.07 (m, 2H), 6.65 (dt, J = 15.7 Hz, J = 1.3 Hz, 1H), 6.21 (dt, J = 15.8 Hz, J = 6.6 Hz, 1H), 4.81 (dd, J = 6.7 Hz, J = 1.3 Hz, 2H), 3.20 (q, J = 10.1 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.1 (q, J = 4.2 Hz), 138.4, 135.4, 133.2, 129.5, 126.7, 123.5 (q, J = 275.8 Hz), 120.9, 66.6, 39.7 (q, J = 30.9 Hz), 21.4. ^{19}F NMR (282 MHz, $CDCl_3$): δ -63.5 (t, J = 10.1 Hz, 3F). MS-ESI: m/z 281.0765 $[M+Na]^+$ calcd. for $C_{13}H_{13}F_3O_2Na^+$ 281.0760.

General procedure for the Ireland-Claisen rearrangements: The corresponding allylic ester (1.00 mmol, 1.00 equiv) was dissolved in dry DCM (3 mL) and Et_3N (3.0 equiv) followed by TMSOTf (1.2 equiv) were added to a sealable tube. The tube was sealed, and the reaction mixture was heated at 40 °C for 24 h. The sealed tube was then opened and Et_2O (20 mL) and 2 M HCl (10 mL) were added to the solution, and the mixture was stirred at rt for 3 h (elimination of the TMS group). The phases were separated, and the aqueous layer was extracted with Et_2O (3 × 20 mL). The combined organic layers were washed with 2 M HCl (20 mL) and brine (20 mL) and dried over $MgSO_4$ before the solvent was removed under vacuum. The produced crude diastereomeric carboxylic acids **8** were investigated by ^{19}F NMR spectroscopy and by ESI mass spectrometry and used without purification for the esterification reaction to obtain the diastereomeric methyl esters **15**.

*2-(Pentafluorosulfanyl)-3-phenylpent-4-enoic acids (**8a**).* According to the general procedure cinnamyl 2-(pentafluorosulfanyl)acetate (**7a**) (0.151 g, 0.50 mmol, 1.0 equiv) was rearranged.

The formed product was analyzed and subsequently alkylated without purification. Yield: 0.172 g (crude, 93% of **8a**, ^{19}F NMR). ^{19}F NMR (282 MHz, $CDCl_3$): δ 67.7 and 67.9 (dm, $^2J_{F,F}$ = 147.2 Hz and $^2J_{F,F}$ = 146.9 Hz, 4F), 80.8 and 81.2 (qn, $^2J_{F,F}$ = 147.7 Hz or $^2J_{F,F}$ = 147.0 Hz, 1F). MS-ES(+)-EM: calcd for $C_{11}H_{11}F_5O_2SNa^+$: *m/z* = 325.0308 [M+Na]$^+$, found 325.0292. MS-ES(–)-EM calcd for $C_{11}H_{10}F_5O_2S^-$: *m/z* = 301.0316 [M-H]$^-$ found 301.0327.

*2-(Trifluoromethyl)-3-phenylpent-4-enoic acids (**8b**).* According to the general procedure (*E*)-cinnamyl 3,3,3-trifluoropropanoate (**7b**) (0.122 g, 0.50 mmol, 1.0 equiv) was rearranged. The formed product was analyzed and subsequently alkylated without purification. Yield: 0.118 g (crude, 52% of **8b**, ^{19}F NMR). ^{19}F NMR (282 MHz, $CDCl_3$): δ -64.2 and -63.8 (d or dd, $^3J_{H,F}$ = 7.5 Hz or $^3J_{H,F}$ = 7.7 Hz, $^4J_{H,F}$ = 1.3 Hz, 3F). MS-ES(+)-EM: calcd for $C_{12}H_{11}F_3O_2Na^+$: *m/z* = 267.0604 [M+Na]$^+$, found 267.0603. MS-ES(-)-EM calcd for $C_{12}H_{10}F_3O_2^-$: *m/z* = 243.0644 [M-H]$^-$, found 243.0638.

*3-(4-Fluorophenyl)-2-(pentafluorosulfanyl)pent-4-enoic acids (**8d**).* According to the general procedure (*E*)-4-fluorocinnamyl 2-(pentafluorosulfanyl)acetate (**7d**) (0.128 g, 0.40 mmol, 1.0 equiv) was rearranged. The formed product was analyzed and subsequently alkylated without purification. Yield: 0.153 g (crude, 90% of **8d**, ^{19}F NMR). ^{19}F NMR (282 MHz, $CDCl_3$): δ -115.3 and -114.6 (tt, $^3J_{H,F}$ = 8.5 Hz, $^4J_{H,F}$ = 5.2 Hz, 1F), 67.7 and 67.8 (dm, $^2J_{F,F}$ = 147.1 Hz or $^2J_{F,F}$ = 147.0 Hz, 4F), 80.8 and 81.3 (qn, $^2J_{F,F}$ = 148.2 Hz or $^2J_{F,F}$ = 146.9 Hz, 1F). MS-ES(+)-EM: calcd for $C_{11}H_{10}F_6O_2SNa^+$: *m/z* = 343.0210 [M+Na]$^+$, found 343.0198. MS-ES(-)-EM: calcd for $C_{11}H_9F_6O_2S^-$: *m/z* = 319.0239 [M-H]$^-$, found 319.0233.

*2-(Trifluoromethyl)-3-(4-fluorophenyl)pent-4-enoic acids (**8e**).* According to the general procedure (*E*)-4-fluorocinnamyl 3,3,3-trifluoropropanoate (**7e**) (0.262 g, 1.00 mmol, 1.0 equiv) was rearranged. The formed product was analyzed and subsequently alkylated without purification. Yield: 0.225 g (crude, 16% of **8e**, ^{19}F NMR). ^{19}F NMR (282 MHz, $CDCl_3$): δ -114.8 and -114.6 (tt, $^3J_{H,F}$ = 8.8 Hz, $^4J_{H,F}$ = 5.4 Hz or $^3J_{H,F}$ = 8.6 Hz, $^4J_{H,F}$ = 5.3 Hz, 1F, 9-CF), -64.7 and -64.4 (d or dd, $^3J_{H,F}$ = 7.6 Hz or $^3J_{H,F}$ = 7.8 Hz, $^4J_{H,F}$ = 1.3 Hz, 3F, 12-CF_3). MS-ES(+)-EM: calcd. for $C_{12}H_{10}F_4O_2Na^+$: *m/z* = 285.0514 [M+Na]$^+$, found 285.0509. MS-ES(-)-EM: calcd. for $C_{12}H_9F_4O_2^-$, *m/z* = 261.0543 [M-H]$^-$ found 261.0544.

*2-(Pentafluorosulfanyl)-3-(p-tolyl)pent-4-enoic acids (**8f**)*. According to the general procedure (*E*)-4-methylcinnamyl 2-(pentafluorosulfanyl)acetate (**7f**) (0.158 g. 0.50 mmol, 1.0 equiv) was rearranged. The formed product was analyzed and subsequently alkylated without purification. Yield: 0.135 g (crude, 84% of **8f**, ^{19}F NMR). ^{19}F NMR (282 MHz, $CDCl_3$): δ 67.7 and 67.8 (dm, $^2J_{F,F}$ = 147.3 Hz or $^2J_{F,F}$ = 146.9 Hz, 4F), 80.8 and 81.2 (qn, $^2J_{F,F}$ = 147.1 Hz or $^2J_{F,F}$ = 147.1 Hz, 1F). MS-ES(+)-EM: calcd. for $C_{12}H_{13}F_5O_2SNa^+$: *m/z* = 339.0447 [M+Na]$^+$, found 339.0449. MS-ES(-)-EM: calcd. for $C_{12}H_{12}F_5O_2S^-$: *m/z* = 315.0483 [M-H]$^-$, found 315.0484.

*2-(Trifluoromethyl)-3-(p-tolyl)pent-4-enoic acids (**8g**)*. According to the general procedure (*E*)-4-methylcinnamyl 3,3,3-trifluoropropanoate (**7g**) (0.258 g, 1.00 mmol, 1.0 equiv) was rearranged. The formed product was analyzed and subsequently alkylated without purification. Yield: 0.220 g (crude, 57% of **8g**, ^{19}F NMR). ^{19}F NMR (282 MHz, $CDCl_3$): δ -64.7 and -64.3 (d or dd, $^3J_{H,F}$ = 7.5 Hz or $^3J_{H,F}$ = 7.7 Hz, $^4J_{H,F}$ = 1.3 Hz, 3F). MS-ES(+)-EM: calcd for $C_{13}H_{13}F_3O_2Na^+$: *m/z* = 281.0758 [M+Na]$^+$, found 281.0760. MS-ES(-)-EM: calcd. for $C_{13}H_{12}F_3O_2^-$, *m/z* = 257.0805 [M-H]$^-$, found 257.0795.

Methylation of carboxylic acids 8 with K_2CO_3/MeI in DMF

The rearrangement products **8** have been difficult to isolate. Therefore, we preferred to methylate them with methyl iodide. First, we attempted methylation with potassium carbonate in DMF. However, under these conditions, the yields of the desired SF_5-substituted methyl esters **15** were rather low, and side products were formed in yields up to 50% (determined by GC). By way of example, the crude product mixture **8f** was treated with K_2CO_3/DMF/MeI, and the product mixture was separated by repeated column chromatography. Besides the fraction of the target diastereomeric SF_5-substituted esters **15f**, we also isolated a fraction of an 1:1 mixture of the diastereomeric methyl α-formyl carboxylates, which could not be separated. Thus, the SF_5 group is a leaving group under these conditions. In the literature, several examples have been reported where the SF_5 group served as a leaving group,[38] and we found other examples more recently.[24] The decomposition of the SF_5^- anion to generate fluoride and SF_4 and subsequent decomposition of SF_4 might be a driving force for the reaction.[39]

*Procedure for methylation of carboxylic acids **8f** with MeI/K_2CO_3 in DMF*. A stirred suspension of the diastereomeric acids **8f** (135 mg, 0.427 mmol) and K_2CO_3 (88 mg, 0.640 mmol) in DMF (2.0 mL) was cooled to 0 °C, and methyl iodide (0.05 mL, 0.854 mmol) was added slowly. Stirring was continued at 0 °C for 3 h. Then the reaction was stopped by the addition of water (10 mL). The mixture was extracted with diethyl ether (3 × 10 mL). The organic layers were combined, washed once with water (10 mL) and with brine (4 × 5 mL), and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the resulting crude clear oil (104 mg) was purified by column chromatography on silica gel (pentane/diethyl ether, 20:1). After three runs, a mixture of the SF_5-substituted esters **15f** (12 mg, 8%, see below) and a mixture of the formates **A** and **B** were isolated. Yield: 39 mg (37%). The relative configuration could not be assigned to the respective isomers **A** and **B**.

Isomer A: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08 (t, $^4J_{H,H}$ = 0.9 Hz, 1H), 7.18-7.10 (m, 4H), 6.17 (ddd, $^3J_{H,Htrans}$ = 17.0, $^3J_{H,Hcis}$ = 10.3, $^3J_{H,H}$ = 8.7 Hz, 1H), 5.43 (dd, $^3J_{H,H}$ = 6.8 Hz, $^4J_{H,H}$ = 1.0 Hz, 1H), 5.23 (ddd, $^3J_{H,Hcis}$ = 10.3, $^2J_{H,Hgem}$ = 1.5 Hz, $^4J_{H,H}$ = 0.8 Hz, 1H), 5.19 (ddd, $^3J_{H,Htrans}$ = 16.9, $^2J_{H,Hgem}$ = 1.3 Hz, $^4J_{H,H}$ = 1.3 Hz, 1H,), 3.92-3.88 (m, 1H, 3-CH), 3.67

(s, 3H, 6-CH_3), 2.30 (s, 3H) ppm. ^{13}C NMR (121 MHz, $CDCl_3$): $\delta = 168.9$ (s), 160.1 (s), 137.2 (s), 135.7 or 132.2 (s),134.9 (d), 129.5 (d), 128.4 or 128.0 (d,), 118.7 (t), 74.8 (d), 52.5 or 52.3 (q), 50.9 (d), 21.2 (q).

Isomer B: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.05$ (t, $^{4}J_{H,H} = 0.9$ Hz, 1H), 7.18-7.10 (m, 4H), 6.03 (ddd, $^{3}J_{H,Htrans} = 17.0$, $^{3}J_{H,Hcis} = 10.3$, $^{3}J_{H,H} = 8.0$ Hz), 5.41 (dd, $^{3}J_{H,H} = 4.8$ Hz, $^{4}J_{H,H} = 1.0$ Hz, 1H), 5.16 (ddd, $^{3}J_{H,Hcis} = 10.3$, $^{2}J_{H,Hgem} = 1.1$ Hz, $^{4}J_{H,H} = 1.1$ Hz, 1H), 5.14 (ddd, $^{3}J_{H,Htrans} = 16.9$, $^{2}J_{H,Hgem} = 1.3$ Hz, $^{4}J_{H,H} = 1.3$ Hz, 1H), 3.97-3.91 (m, 1H) 3.67 (s, 3H), 2.30 (s, 3H) ppm. ^{13}C NMR (121 MHz, $CDCl_3$): $\delta = 168.8$ (s), 160.1 (s), 137.2 (s), 136.1 (d), 135.7 (s) or 132.2 (s), 129.5 (d), 128.4 (d) or 128.0 (d), 117.8 (t), 75.2 (d), 52.5 (q) or 52.3 (q), 50.6 (d), 21.2 (q).

ESI-MS$^+$ (for isomers A and B): calcd. for $[C_{14}H_{16}O_4+Na]^+$ $m/z = 271.0941$, found: 271.0951 $[M+Na]^+$.

Therefore, the methyl esters **15** were prepared analogously to the allylic esters. DCC (1.2 equiv) was dissolved in dry DCM (5 mL) before MeOH (1.0 equiv) followed by the corresponding carboxylic acids **8** (0.5 mmol, 1.0 equiv) were added under argon atmosphere. A white precipitate was formed and a catalytic amount of DMAP was added. The mixture was stirred at rt overnight. The suspension was diluted with Et_2O (20 mL) before the formed urea derivative was filtered off. The remaining solution was washed with H_2O (3 × 10 mL), 5% acetic acid (3 × 10 mL), and brine (3 × 10 mL) and dried over $MgSO_4$ before the solvent was removed under reduced pressure, and the mixture of diastereomeric methyl esters **15** was purified as described for the particular compounds.

*Methyl 2-(pentafluorosulfanyl)-3-phenylpent-4-enoates (**15a**).* The title compounds were prepared according to the aforementioned general procedure starting from cinnamyl 2-(pentafluorosulfanyl)acetate (**7a**) (120 mg, 0.40 mmol) over two steps. After column chromatography (cyclohexane/EtOAc, 10:1) the target product was obtained as a clear oil.

Yield: 51 mg (40%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37 – 7.13 (m, 5H), 6.16 – 5.98 (m, 1H), 5.20 – 5.07 (m, 2H), 4.89/4.88 (qn/dqn, J = 5.9 Hz/J = 11.2 Hz, J = 5.9 Hz, 1H), 4.29 – 4.19 (m, 1H), 3.74/3.43 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.2/164.8 (qn, J = 3.1 Hz/J = 3.5 Hz), 139.7 (qn, J = 1.5 Hz)/139.2, 137.9 (qn, J = 1.4 Hz)/135.9, 129.2/129.0, 128.0/127.7, 127.8/127.5, 118.6/116.6, 89.3/88.8 (qn, J = 9.2 Hz), 53.2/53.0, 51.8/51.4 (qn, J = 2.2 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ 81.8/81.3 (qn, 1F), 67.3/67.1 (dm, J = 146.8 Hz/J = 147.1 Hz). MS-ESI: m/z 339.0456 $[M+Na]^+$ calcd. for $C_{12}H_{13}F_5O_2SNa^+$ 339.0449.

Methyl 3-phenyl-2-(trifluoromethyl)pent-4-enoates ***(15b)***. The diastereomeric target compounds were prepared according to the aforementioned general procedure starting from cinnamyl 3,3,3-trifluoropropanoate (**7b**) (157 mg, 0.64 mmol) over two steps. After column chromatography (cyclohexane/EtOAc, 10:1) the target product was obtained as a clear oil. Yield: 44 mg (35%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37 – 7.15 (m, 5H), 6.10 – 5.91 (m, 1H), 5.26 – 5.06 (m, 2H), 4.02 – 3.88 (m, 1H), 3.74/3.43 (s, 3H), 3.61/3.59 (dq, J = 10.7 Hz, J = 7.7 Hz/ J = 11.2 Hz, J = 7.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.2/166.9 (q, J = 3.5 Hz/J = 3.4 Hz), 139.3/139.2, 136.9, 129.0/129.0, 127.9/127.8, 127.6/127.6, 124.2/124.1 (q, J = 281.5 Hz), 117.6/117.5, 56.0/56.0 (q, J = 25.9 Hz/J = 25.8 Hz), 52.7/52.6, 48.9/48.4 (q J = 1.9 Hz/J = 1.5 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ -64.8/-64.4 (d/dd, J = 7.6 Hz/J = 7.8 Hz, J = 1.3 Hz, 3F). MS-ESI: m/z 281.0767 $[M+Na]^+$ calcd. for $C_{13}H_{13}F_3O_2Na^+$ 281.0760.

Methyl 2-methyl-3-phenylpent-4-enoates ***(15c)***. The diastereomeric target compounds were prepared according to the aforementioned general procedure starting from cinnamyl propionate (**7c**) (125 mg, 0.66 mmol) over two steps. After column chromatography (cyclohexane/EtOAc, 10:1) the target product was obtained as a clear oil. Yield: 45 mg (33%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 – 7.15 (m, 5H), 6.00/5.93 (ddd, J = 17.1, *J* = 10.3 Hz, *J* = 8.4 Hz/ *J* = 17.3, *J* = 10.4 Hz, *J* = 9.7 Hz 1H), 5.13/5.05 (ddd/dt, *J* = 16.9 Hz, *J* = 1.6 Hz, *J* = 0.9 Hz/*J* = 10.0 Hz, *J* = 1.3 Hz, 1H), 5.11/5.01 (dd/ddd, *J* = 10.0 Hz, *J* = 1.5 Hz/*J* = 10.1 Hz, *J* = 1.6 Hz, *J* = 0.8 Hz), 3.53 – 3.40 (m, 1H), 3.68/3.43 (s, 3H), 1.22/0.97 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.2/175.9, 142.4/141.4, 139.9/138.7, 128.9/128.6, 128.2/127.7, 126.9/126.7, 116.9/115.6, 53.9/53.8, 51.6/51.5, 45.4/45.1, 16.0/15.7. MS-ESI: *m*/*z* 227.1057 $[M+Na]^+$ calcd. for $C_{13}H_{16}O_2Na^+$ 227.1043.

*Methyl 3-(4-fluorophenyl)-2-(pentafluorosulfanyl)pent-4-enoates (**15d**).* The diastereomeric target compounds were prepared according to the aforementioned general procedure starting from (*E*)-3-(4-fluorophenyl)allyl 2-(pentafluorosulfanyl)acetate (**7d**) (150 mg, 0.47 mmol) over two steps. After column chromatography (cyclohexane/EtOAc, 10:1) the target product was obtained as a clear oil. Yield: 70 mg (45%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.23 – 6.94 (m, 4H), 6.13 – 5.95 (m, 1H), 5.19 – 5.08 (m, 2H), 4.83/4.82 (qn/dqn, *J* = 5.8 Hz/*J* = 11.7 Hz, *J* = 5.9 Hz, 1H), 4.30 – 4.19 (m, 1H), 3.75/3.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.0/164.7 (qn, *J* = 3.0 Hz/*J* = 3.2 Hz), 162.1/162.1 (d, *J* = 247.3 Hz/*J* = 246.4 Hz), 137.6/135.8, 135.4/135.1, 129.7/129.4 (d, *J* = 8.2 Hz/*J* = 8.1 Hz), 118.7/116.8, 116.1/115.9 (d, *J* = 21.6 Hz), 89.2/88.8 (qn, *J* = 8.9 Hz), 53.2/53.0, 51.0/50.6 (qn, *J* = 2.6 Hz/*J* = 2.2 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ 81.6/81.3 (qn, 1F), 67.4/67.2 (dm, *J* = 146.8 Hz/*J* = 147.0 Hz, 4F), -114.6/-115.3 (tt, *J* = 8.4 Hz, *J* = 5.2 Hz/*J* = 8.5 Hz, *J* = 5.2 Hz, 1F). MS-ESI: *m*/*z* 357.0367 $[M+Na]^+$ calcd. for $C_{12}H_{12}F_6O_2SNa^+$ 357.0354.

*Methyl 3-(4-fluorophenyl)-2-(trifluoromethyl)pent-4-enoates (**15e**).* The diastereomeric target compounds were prepared according to the aforementioned general procedure starting from (*E*)-3-(4-fluorophenyl)allyl 3,3,3-trifluoropropanoate (**7e**) (150 mg, 0.57 mmol) over two steps. After column chromatography (cyclohexane/EtOAc, 10:1) the target product was obtained as a clear oil. Yield: 47 mg (30%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.24 – 7.12 (m, 2H), 7.07 – 6.96 (m, 2H), 6.06 – 5.89 (m, 1H), 5.22 – 5.08 (m, 2H), 4.02 – 3.88 (m, 1H), 3.55/3.55 (dq, J = 11.2 Hz, J = 7.0 Hz/J = 10.6 Hz, J = 7.6 Hz, 1H), 3.76/3.47 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.0/166.8 (q, J = 3.3 Hz/ J = 3.5 Hz), 162.1/162.1 (d, J = 245.9 Hz/ J = 246.4 Hz), 136.6, 135.1/134.9, 129.5 (d, J = 7.8 Hz), 124.1/124.0 (q, J = 281.4 Hz/ J = 281.6 Hz), 117.7, 115.9/115.9 (d, J = 21.4 Hz/ J = 21.5 Hz), 56.1 (q, J = 26.0 Hz), 52.8/52.6, 48.1/47.6 (q, J = 1.9 Hz/J = 1.7 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ -64.4/-64.9 (dd/d, J = 7.8 Hz, J = 1.2 Hz/J = 7.6 Hz, 3F), -115.2/-115.5 (tt, J = 8.5 Hz, J = 5.2 Hz/J = 8.6 Hz, J = 5.2 Hz, 1F). MS-ESI: m/z 299.0677 $[M+Na]^+$ calcd. for $C_{13}H_{12}F_4O_2Na^+$ 299.0666.

Methyl 2-(pentafluorosulfanyl)-3-(p-tolyl)pent-3-enoates ***(15f)***. The diastereomeric target compounds were prepared according to the aforementioned general procedure starting from (*E*)-3-(*p*-tolyl)allyl 2-(pentafluorosulfanyl)acetate (**7f**) (130 mg, 0.41 mmol) over two steps. After column chromatography (cyclohexane/EtOAc, 10:1) the target product was obtained as a clear oil. Yield: 31 mg (22%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.17 – 7.02 (m, 4H), 6.12 – 6.02 (m, 1H), 5.17 – 5.05 (m, 2H), 4.88 – 4.81 (m, 1H), 4.23 – 4.18 (m, 1H), 3.74/3.46 (s, 3H), 2.33/2.30 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.2/164.8 (qn, J = 2.7 Hz/ J = 3.6 Hz), 138.1/136.7, 137.5/137.3, 136.2/136.2, 129.9/129.7, 127.8/127.6, 118.3/116.3, 89.4/88.9 (qn, J = 8.4 Hz/J = 8.9 Hz), 53.1/53.0, 51.5/51.0 (qn, J = 2.4 Hz), 21.2/21.2. ^{19}F NMR (471 MHz, $CDCl_3$): δ 82.4/82.0 (qn, 1F), 67.7/67.5 (dm, J = 147.2 Hz/J = 146.1 Hz, 4F). MS-ESI: m/z 353.0607 $[M+Na]^+$ calcd. for $C_{13}H_{15}F_5O_2SNa^+$ 353.0605.

Methyl 3-(p-tolyl)-2-(trifluoromethyl)pent-4-enoates ***(15g)***. The diastereomeric target compounds were prepared according to the aforementioned general procedure starting from (*E*)-3-(*p*-tolyl)allyl 3,3,3-trifluoropropanoate (**7g**) (130 mg, 0.50 mmol) over two steps. After column chromatography (cyclohexane/EtOAc, 10:1) the target product was obtained as a clear oil. Yield: 30 mg (22%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.16 – 7.03 (m, 4H), 6.04 – 5.93 (m, 1H), 5.20 – 5.06 (m, 2H), 3.96 – 3.87 (m, 1H), 3.76/3.47 (s, 3H), 3.63 – 3.54 (m, 1H), 2.33/2.31 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.2/166.9 (q, J = 3.3 Hz/ J = 3.6 Hz), 137.3/137.2, 137.2/137.1, 136.4/136.2, 129.7/129.7, 127.7/127.6, 124.3/124.1 (q, J = 281.5 Hz), 117.3/117.2, 56.1/56.1 (q, J = 25.8 Hz/J = 25.7 Hz), 52.7/52.5, 48.5/48.1 (q, J = 1.8 Hz/J = 1.9 Hz), 21.2/21.2. ^{19}F NMR (471 MHz, $CDCl_3$): δ -64.4/-64.8 (dd/d, J = 7.9 Hz, J = 1.3 Hz/J = 7.6 Hz, 3F). MS-ESI: m/z 295.0924 $[M+Na]^+$ calcd. for $C_{14}H_{15}F_3O_2Na^+$ 295.0916.

General procedure for synthesis of propionic and trifluoropropionic acid allylic esters

DCC (1.2 equiv) is dissolved in dry DCM (8 mL) before the allylic alcohol (1.2 mmol, 1.0 equiv) and the corresponding carboxylic acid (1.2 equiv) are added under an argon atmosphere. A white precipitate is formed, and a catalytic amount of DMAP is added. The mixture is stirred at rt overnight. The suspension is diluted with Et_2O (25 mL) before the formed urea derivative is filtered off. The remaining solution is washed with H_2O (3 × 10 mL), 5% acetic acid (3 × 10 mL), and brine (3 × 10 mL) and dried over $MgSO_4$ before the solvent is removed under reduced pressure. The crude products are purified by column chromatography (silica gel) as indicated below.

*1-Phenylprop-2-en-1-yl 3,3,3-trifluoropropionate (**9b**)*. According to the above general procedure 1-phenylprop-2-en-1-ol (170 mg, 1.27 mmol) was reacted with 3,3,3-trifluoropropionic acid. The crude product was purified by column chromatography (cyclohexane/EtOAc, 5:1) to give the product as a colorless liquid. Yield: 248 mg (80%). ^1H NMR (300 MHz, $CDCl_3$): δ 3.21 (q, $^3J_{H,F}$ = 10.0 Hz, 2H), 5.21 – 5.39 (m, 2H), 6.00 (ddd, $^3J_{H,H}$ = 16.5 Hz, $^3J_{H,H}$ = 10.4 Hz, $^3J_{H,H}$ = 6.0 Hz, 1H), 6.32 (dt, $^3J_{H,H}$ = 6.0 Hz, $^4J_{H,H}$ = 1.3 Hz, 1H), 7.24 – 7.44 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 40.0 (qt, $^2J_{C,F}$ = 31.0 Hz), 77.9 (d), 117.8 (t), 123.4 (q, $^1J_{C,F}$ = 276.9 Hz), 127.3 (d), 128.7 (d), 128.8 (d), 135.4 (d), 138.0 (s), 163.2 (q, $^3J_{C,F}$ = 4.2 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ -63.3 (t, $^3J_{H,F}$ = 10.1 Hz, 3F). MS-ES(+)-EM: m/z calcd for $C_{12}H_{11}F_3O_2Na^+$ 267.0603; found 267.0610 $[M+Na]^+$.

*1-Phenylprop-2-en-1-yl propionate (**9c**)*. According to the above general procedure 1-phenylprop-2-en-1-ol (500 mg, 3.73 mmol) was reacted with propionic acid. The crude product was purified by column chromatography (cyclohexane/EtOAc, 5:1) to give the product as a colorless liquid. Yield: 556 mg (78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.15 (t, $^{3}J_{H,H}$ = 7.6 Hz, 3H), 2.39 (2q, $^{3}J_{H,H}$ = 7.5 Hz u. $^{3}J_{H,H}$ = 7.6 Hz, 2H), 5.23 (dt, $^{3}J_{H,H}$ = 10.4 Hz, $^{2}J_{H,H}$ = $^{4}J_{H,H}$ = 1.3 Hz, 1H), 5.29 (dt, $^{3}J_{H,H}$ = 17.1 Hz, $^{2}J_{H,H}$ = $^{4}J_{H,H}$ = 1.4 Hz, 1H), 6.00 (ddd, $^{3}J_{H,H}$ = 17.2 Hz, $^{3}J_{H,H}$ = 10.4 Hz, $^{3}J_{H,H}$ = 5.9 Hz, 1H), 6.28 (dt, $^{3}J_{H,H}$ = 5.9 Hz, $^{4}J_{H,H}$ = 1.4 Hz, 1H), 7.25 – 7.39 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 9.2 (q), 27.9 (t), 76.1 (d), 116.9 (t), 127.2 (d), 128.2 (d), 128.6 (d), 136.5 (d), 139.1 (s), 173.4 (s).

The compound was mentioned in the literature, but no spectroscopic data were given.[40]

*1-(4-Fluorophenylprop-2-en-1-yl) 3,3,3-trifluoropropionate (**9d**)*. According to the above general procedure 1-(4-fluorophenyl)prop-2-en-1-ol (200 mg, 1.31 mmol) was reacted with 3,3,3-trifluoropropionic acid. The crude product was purified by column chromatography (cyclohexane/EtOAc, 10:1) to give a colorless liquid. Yield: 240 mg (70%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.22 (q, $^{3}J_{H,F}$ = 10.1 Hz, 2H), 5.30 (dt, $^{3}J_{H,H}$ = 10.5 Hz, $^{2}J_{H,H}$ = $^{4}J_{H,H}$ = 1.2 Hz, 1H), 5.32 (dt, $^{3}J_{H,H}$ = 17.2 Hz, $^{2}J_{H,H}$ = $^{4}J_{H,H}$ = 1.3 Hz, 1H), 5.98 (ddd, $^{3}J_{H,H}$ = 17.1 Hz, $^{3}J_{H,H}$ = 10.5 Hz, $^{3}J_{H,H}$ = 5.8 Hz, 1H), 6.31 (dt, $^{3}J_{H,H}$ = 5.8 Hz, $^{4}J_{H,H}$ = 1.4 Hz, 1H), 7.00 – 7.13 (m, 2H), 7.28 – 7.39 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 40.0 (qt, $^{2}J_{C,F}$ = 31.1 Hz), 77.2 (d), 115.8 (dd, $^{2}J_{C,F}$ = 21.7 Hz), 118.0 (t), 123.4 (q, $^{1}J_{C,F}$ = 275.3 Hz), 129.2 (dd, $^{3}J_{C,F}$ = 8.3 Hz), 133.8 (d, $^{4}J_{C,F}$ = 3.2 Hz), 135.2 (d), 162.8 (d, $^{1}J_{C,F}$ = 247.5 Hz), 163.2 (q, $^{3}J_{C,F}$ = 4.3 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ -113.1 (tt, $^{3}J_{H,F}$ = 8.6 Hz, $^{4}J_{H,F}$ = 5.3 Hz, 1F), -63.3 (t, $^{3}J_{H,F}$ = 10.1 Hz, 3F). MS-ES(+)-EM: *m*/*z* calcd for $C_{12}H_{10}F_4O_2Na^+$ 285.0509; found 285.0511 $[M+Na]^+$.

*1-(Naphthalenylprop-2-en-1-yl) 3,3,3-trifluoropropionate (**9e**)*. According to the above general procedure 1-(naphthalenyl)prop-2-en-1-ol (200 mg, 1.09 mmol) was reacted with

3,3,3-trifluoropropionic acid. The crude product was purified by column chromatography (cyclohexane/EtOAc, 10:1) to give a colorless oil. Yield: 260 mg (81%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.22 and 3.23 (q, $^{3}J_{H,F}$ = 10.1 Hz, 2H), 5.32 (dt, $^{3}J_{H,H}$ = 10.4 Hz, $^{2}J_{H,H}$ = $^{4}J_{H,H}$ = 1.2 Hz, 1H), 5.34 (dt, $^{3}J_{H,H}$ = 17.2 Hz, $^{2}J_{H,H}$ = $^{4}J_{H,H}$ = 1.3 Hz, 1H), 6.17 (ddd, $^{3}J_{H,H}$ = 17.1 Hz, $^{3}J_{H,H}$ = 10.5 Hz, $^{3}J_{H,H}$ = 5.4 Hz, 1H), 7.04 (dt, $^{3}J_{H,H}$ = 5.5 Hz, $^{4}J_{H,H}$ = 1.5 Hz, 1H), 7.40 – 7.63 (m, 4H), 7.76 – 7.93 (m, 2H), 8.02 – 8.16 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 40.0 (qt, $^{2}J_{C,F}$ = 31.0 Hz), 75.5 (d), 118.2 (t), 123.5 (q, $^{1}J_{C,F}$ = 276.2 Hz), 123.7 (d), 125.4 (d), 125.7 (d), 126.0 (d), 126.6 (d), 129.0 (d), 129.5 (d), 130.6 (s), 133.6 (s), 134.0 (s), 135.1 (d), 163.3 (q, $^{3}J_{C,F}$ = 4.3 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ -63.2 (t, $^{3}J_{H,F}$ = 10.1 Hz, 3F). MS-ES(+)-EM: *m/z* calcd for $C_{16}H_{13}F_3O_2Na^+$ 317.0760; found 317.0759 $[M+Na]^+$.

*1-(4-Fluorophenylprop-2-en-1-yl) propionate (**9f**)*. According to the above general procedure 1-(4-fluorophenyl)prop-2-en-1-ol (200 mg, 1.31 mmol) was reacted with propionic acid. The crude product was purified by column chromatography (cyclohexane/EtOAc, 10:1) to give a colorless liquid. Yield: 225 mg (82%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.15 (t, $^{3}J_{H,H}$ = 7.6 Hz 3H), 2.38 and 2.39 (q, $^{3}J_{H,H}$ = 7.5 Hz and $^{3}J_{H,H}$ = 7.6 Hz, 2H), 5.25 (dt, $^{3}J_{H,H}$ = 10.4 Hz, $^{2}J_{H,H}$ = $^{4}J_{H,H}$ = 1.3 Hz, 1H), 5.28 (dt, $^{3}J_{H,H}$ = 17.1 Hz, $^{2}J_{H,H}$ = $^{4}J_{H,H}$ = 1.4 Hz, 1H), 5.98 (ddd, $^{3}J_{H,H}$ = 17.2 Hz, $^{3}J_{H,H}$ = 10.4 Hz, $^{3}J_{H,H}$ = 5.7 Hz, 1H), 6.25 (dt, $^{3}J_{H,H}$ = 5.9 Hz, $^{4}J_{H,H}$ = 1.4 Hz, 1H), 6.98 – 7.09 (m, 2H), 7.29 – 7.37 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 9.2 (q), 27.9 (t), 75.3 (d), 115.5 (dd, $^{2}J_{C,F}$ = 21.5 Hz), 117.0 (t), 129.1 (dd, $^{3}J_{C,F}$ = 8.2 Hz), 135.0 (d, $^{4}J_{C,F}$ = 3.2 Hz), 136.3 (d), 162.6 (d, $^{1}J_{C,F}$ = 246.6 Hz), 173.4 (s). ^{19}F NMR (282 MHz, $CDCl_3$): δ -114.0 (tt, $^{3}J_{H,F}$ = 8.6 Hz, $^{4}J_{H,F}$ = 5.3 Hz, 1F). MS-ES(+)-EM: *m/z* calcd for $C_{12}H_{13}FO_2Na^+$ 231.0792; found 231.0794 $[M+Na]^+$.

*(1-Naphthalenylprop-2-en-1-yl) propionate (**9g**)*. According to the above general procedure 1-(naphthalenyl)prop-2-en-1-ol (200 mg, 1.09 mmol) was reacted with propionic acid. The crude product was purified by column chromatography (cyclohexane/EtOAc, 10:1) to give a

colorless oil. Yield: 221 mg (84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.15 (t, $^{3}J_{H,H}$ = 7.6 Hz, 3H), 2.40 and 2.42 (q, $^{3}J_{H,H}$ = 7.5 Hz or $^{3}J_{H,H}$ = 7.6 Hz, 2H), 5.27 (dt, $^{3}J_{H,H}$ = 10.6 Hz, $^{2}J_{H,H}$ = $^{4}J_{H,H}$ = 1.3 Hz, 1H), 5.30 (dt, $^{3}J_{H,H}$ = 17.3 Hz, $^{2}J_{H,H}$ = $^{4}J_{H,H}$ = 1.4 Hz, 1H), 6.18 (ddd, $^{3}J_{H,H}$ = 17.1 Hz, $^{3}J_{H,H}$ = 10.5 Hz, $^{3}J_{H,H}$ = 5.3 Hz, 1H), 7.00 (dt, $^{3}J_{H,H}$ = 5.4 Hz, $^{4}J_{H,H}$ = 1.7 Hz, 1H), 7.42 – 7.54 (m, 3H), 7.56 – 7.61 (m, 1H), 7.77 – 7.88 (m, 2H), 8.10 – 8.16 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 9.2 (q), 27.9 (t), 73.5 (d), 117.2 (t), 123.9 (d), 125.4 (d), 125.5 (d), 125.8 (d), 126.4 (d), 128.9 (d), 129.1 (d), 130.8 (s), 134.0 (s), 134.7 (s), 136.1 (d), 173.5 (s). MS-ES(+)-EM: *m*/*z* calcd for $C_{16}H_{16}O_2Na^+$ 263.1043; found 263.1050 $[M+Na]^+$.

Ireland-Claisen rearrangement of 1-arylprop-2-en-1-yl propionates

General procedure

In an oven-dried Schlenk vessel, the respective ester (0.5 mmol, 1.0 equiv) is dissolved in dry THF (5 mL) and cooled down to -78 °C. Then LDA (1.8 M solution in THF/heptane/ethyl benzene, 2.5 equiv) is added dropwise under stirring. The mixture is stirred at this temperature for 10 min before TMSCl (1.2 equiv) is added. Stirring is continued overnight, while the solution is allowed to warm up to rt. The mixture is diluted with diethyl ether (15 mL), 2 M HCl (7.5 mL) is added, and stirring at r.t. is continued for 3 h. The phases are separated, and the aqueous phase is extracted with diethyl ether (3 × 15 mL). The combined organic layers are washed with 2 M HCl (15 mL) and brine (15 mL) and dried over magnesium sulfate. The solvent is removed under reduced pressure. The crude carboxylic acid is dissolved in DMF (20 mL), and potassium carbonate (1.5 mmol) is added. Methyl iodide (2.0 equiv) is added, and the suspension is stirred at 0 °C for 3 h. After warming to r.t., water (100 mL) is added, and the aqueous phase is extracted with ethyl acetate (3 × 50 mL). The combined organic phase is washed with saturated bicarbonate solution (50 mL) and brine (50 mL). The organic solution is dried over magnesium sulfate, and the solvent is removed under reduced pressure. The crude product is purified by column chromatography.

*Methyl (E)-2-methyl-5-phenylpent-4-en-yl-carboxylate (**10c**).*[41] According to the general procedure 1-(phenylpent-2-en-1-yl) propionate (**9c**) (50 mg, 0.26 mmol) was transformed to the product, which was purified by column chromatography (pentane/diethyl ether, 10:1) to be isolated as a colorless liquid. Yield: 19 mg (28%, over two steps). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.20 (d, $^{3}J_{H,H}$ = 6.8 Hz, 3H), 2.29 – 2.49 (m, 1H), 2.51 – 2.66 (m, 2H), 3.68 (s, 3H), 6.14 (ddd, $^{3}J_{H,H}$ = 15.7 Hz, $^{3}J_{H,H}$ = 7.4 Hz, $^{3}J_{H,H}$ = 6.8 Hz, 1H), 6.42 (d, $^{3}J_{H,H}$ = 15.9 Hz, 1H), 7.17 – 7.23 (m, 1H), 7.26 – 7.37 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.8 (q), 37.2 (t), 39.7 (d), 51.8 (q), 126.2 (d), 127.3 (d), 127.3 (d), 128.6 (d), 132.3 (d), 137.5 (s), 176.7 (s). MS-ES(+)-EM: *m*/z calcd for $C_{13}H_{16}O_2Na^+$ 227.1043; found 227.1050 $[M+Na]^+$.

*Methyl (E)-2-methyl-5-(4-fluorophenyl)pent-4-en-yl-carboxylate (**10f**).* According to the general procedure 1-(4-fluorophenylpent-2-en-1-yl) propionate (**9f**) (150 mg, 0.72 mmol) was transformed to the product, which was purified by column chromatography (pentane/diethyl ether, 10:1) to be isolated as a colorless liquid. Yield: 52 mg (32%, over two steps). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.20 (d, $^{3}J_{H,H}$ = 6.8 Hz, 3H), 2.25 – 2.41 (m, 1H), 2.48 – 2.68 (m, 2H), 3.68 (s, 3H), 6.05 (dt, $^{3}J_{H,H}$ = 15.7 Hz, $^{3}J_{H,H}$ = $^{3}J_{H,H}$ = 7.0 Hz, 1H), 6.38 (d, $^{3}J_{H,H}$ = 16.0 Hz, 1H), 6.90 – 7.03 (m, 2H), 7.23 – 7.36 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 37.1 (t), 39.7 (d), 51.8 (q), 115.5 (dd, $^{2}J_{C,F}$ = 21.5 Hz), 127.0 (dd, $^{6}J_{C,F}$ = 2.3 Hz), 127.6 (dd, $^{3}J_{C,F}$ = 8.0 Hz), 131.0 (d), 133.6 (d, $^{4}J_{C,F}$ = 3.3 Hz), 162.2 (d, $^{1}J_{C,F}$ = 246.0 Hz), 176.6 (s). ^{19}F NMR (282 MHz, $CDCl_3$): δ -115.3 (tt, $^{3}J_{H,F}$ = 8.6 Hz, $^{4}J_{H,F}$ = 5.4 Hz, 1F). MS-ES(+)-EM: *m*/z calcd for $C_{13}H_{15}FO_2Na^+$ 245.0948; found 245.0953 $[M+Na]^+$.

*Methyl (E)-2-methyl-5-(naphthalene-1-yl)pent-4-en-yl-carboxylate (**10g**).* According to the general procedure 1-[(naphthalene-1-yl)pent-2-en-1-yl] propionate (**9g**) (150 mg, 0.62 mmol) was transformed to the product, which was purified by column chromatography (pentane/diethyl ether, 10:1) to be isolated as a colorless liquid. Yield: 100 mg (63%, over two steps). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.26 (d, $^{3}J_{H,H}$ = 6.7 Hz, 3H), 2.39 – 2.53 (m, 1H), 2.59 – 2.76 (m, 2H), 3.69 (s, 3H), 6.14 (dt, $^{3}J_{H,H}$ = 15.5 Hz, $^{3}J_{H,H}$ = $^{3}J_{H,H}$ = 7.1 Hz, 1H), 7.15 (d, $^{3}J_{H,H}$ = 15.2 Hz, 1H), 7.35 – 7.60 (m, 4H), 7.69 – 7.90 (m, 2H), 8.01 – 8.16 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.9 (q), 37.6 (t), 39.8 (d), 51.8 (q), 123.9 (d), 124.0 (d), 125.7 (d), 125.8 (d), 126.0 (d), 127.7 (d), 128.6 (d), 129.6 (d), 130.6 (d), 131.2 (s), 133.7 (s), 135.4 (s), 176.6 (s). MS-ES(+)-EM: *m*/*z* calcd for $C_{17}H_{18}O_2Na^+$ 277.1199; found 277.1198 $[M+Na]^+$.

Supporting Information

Copies of ^{1}H, ^{13}C, ^{19}F NMR spectra for all isolated new compounds; DFT calculations of energies of intermediates and transition states; mechanistic discussion of side reactions (PDF). The Supporting Information is available free of charge on the ASC Publications webside at DOI: 10.1021/acs.joc. xxx

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Notes

The authors declare no competing financial interest.

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