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Claisen rearrangements based on vinyl fluorides

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Dedicated to Professor Gerd-Volker Röschenthaler on the occasion of his 60th birthday.

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Abstract

2-Fluoroalk-1-en-3-ols (**4**), available from terminal alkenes (**1**) by bromofluorination, subsequent dehydrobromination of the 1-bromo-2-fluoroalkanes (**2**) to form 2-fluoroalkenes (**3**) and selenium dioxide mediated allylic oxidation with *tert*-butylhydroperoxide, undergo Johnson-Claisen rearrangement on treatment with trimethyl orthoacetate to give methyl 4-fluoroalk-4-enoates (**7**) in high yields. In contrast Ireland-Claisen rearrangement of 3-acetoxy-2-fluorodec-1-ene (**9b**) with triethylamine and TMSOTf in ether failed. Instead of the expected formation of a carboxylic acid, selective C-silylation of the α-position to the carboxyl group to form **14** occurred. However, Ireland-Claisen rearrangement was successful with corresponding chloroacetates **10** and propionates **11** of four 2-fluoroalk-1-en-3-ols (**4**) to give 2-chloro-4-fluoroalk-4-enecarboxylic acids (**15**) or its 2-methyl derivatives **16**, respectively, in moderate yields. These [3,3]-sigmatropic rearrangements are diastereoselective giving *trans*-configured double bonds, exclusively. Corresponding esters derived from (*Z*)-2-fluorocyclododec-2-enol (**22**), did rearrange to yield mixtures of diastereomers much less selectively. Also 2-fluorodec-2-enol (**6**), which was prepared by rearrangement of 2-fluoro-2-octyloxirane (**5**) with TMSOTf and triethylamine, was successfully applied as a starting material for [3,3]-sigmatropic rearrangements. The corresponding 3-(1-fluoroethenyl)alkanoic acid derivatives **17** and **18** were formed in moderate yield.

Keywords: Fluorinated allylic esters; Vinyl fluorides; [3,3]-Sigmatropic rearrangement; Claisen rearrangement; Stereochemistry; Carboxylic acid derivatives

1. Introduction

Rearrangement reactions belong to the most frequently applied transformations of carbon skeletons in organic synthesis. Besides the Cope-rearrangement and its variants, the classical Claisen-rearrangement of allylphenyl ethers and particularly the aliphatic Claisen-rearrangements gained a very important position [1,2]. These reactions proceed as symmetry-allowed suprafacial thermal [3,3]-sigmatropic rearrangements through the lowest energy chair-like, six-membered transition states [3–5]. This allows to predict the stereochemistry of the formed main product. Most importantly, from the synthetic point of view, there were developed plenty of variants of this type of rearrangement. By way of example, the Carroll [6,7], the Johnson [8], the Eschenmoser [9,10] (including the Overman variant [11,12]), the Reformatsky [13,14], the ester enolate [15–17], and the Ireland-Claisen rearrangements [18–20] should be mentioned as some of the synthetically most useful variants regularly applied with non-fluorinated compounds.

Many examples of sigmatropic rearrangements with polyfluorinated compounds have also been described [21–23]. Among others there are Ireland-Claisen rearrangements with terminal difluorinated allylic esters [23–25], Johnson-Claisen rearrangements of allylic alcohols with terminal difluorinated double bonds [24–28], and Claisen rearrangements of polyfluorinated allylvinyl ethers [29–35]. In contrast, there is a relatively small number of examples for rearrangements with monofluorinated olefins. As early as in 1988 a one-pot cascade reaction of a Claisen and subsequent Cope-rearrangement of a vinyl fluoride was described [36].

As a typical example for a classical aromatic Claisen rearrangement, a fluorinated analogue of the anti-malaria agent Bialamicol was synthesized from a fluorinated

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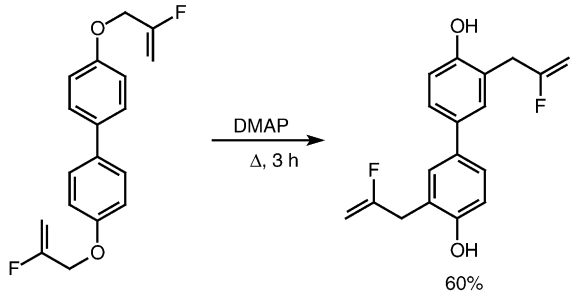
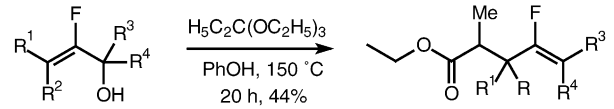


Scheme 1.



R^1 = H, Me, Ph; R^2 = H, Alk; R^3 = H, Alk; R^4 = H, Me

Scheme 2.

allylphenyl ether in the presence of *p*-dimethylamino pyridine (DMAP) (Scheme 1) [37].

Different examples of Johnson-Claisen rearrangements of 2-fluoroallylic alcohols by treatment with triethyl orthoacetate or triethyl orthopropionate in hot phenol leading to the corresponding ethyl esters have been published by Allmendinger et al. These transformations yielded 42–74% of the corresponding esters (Scheme 2) [38].

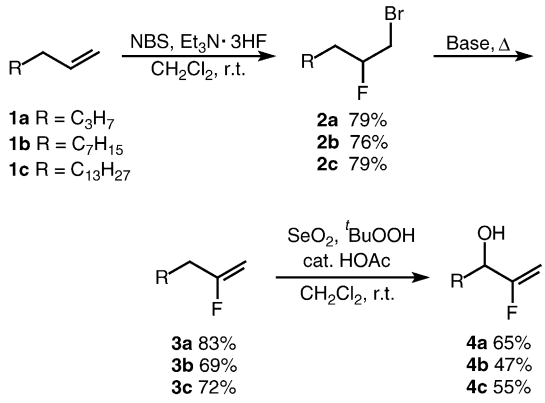
Analogously, several examples of Johnson-Claisen rearrangements involving 3-fluoroalk-2-enol derivatives have been published by Percy and coworkers [28,39] and similar reactions were used as key-step in syntheses of nucleosides [40–42].

In the frame of our interest in synthetic applications of vinyl fluorides, we discovered a simple and efficient access to 2-fluoroallylic alcohols some years ago consisting of bromofluorination of terminal alkenes [43,44], dehydrobromination of the formed 1-bromo-2-fluoroalkanes [45–47] and SeO_2-mediated allylic oxidation [48]. Now we investigated the application of these fluorinated allylic alcohols in different types of Claisen rearrangements.

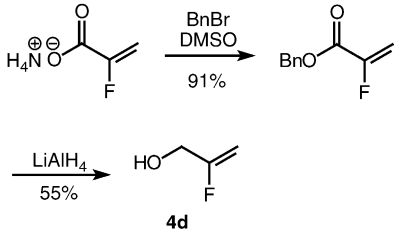
2. Results and discussion

Our well-established three-step sequence [47] of bromofluorination of 1-alkenes **1**, leading to 92:8 mixtures of 1-bromo-2-fluoroalkanes **2** and its regioisomers, HBr-elimination from the bromofluorides and selective allylic oxygenation of the vinyl fluorides **3** provided the desired fluorinated allylic alcohols **4a**–**4c** in 25–43% overall yield (Scheme 3). 2-Fluoroallylic alcohol (**4d**) was prepared from ammonium 2-fluoroacrylate (Scheme 4) [49].

Another fluorinated primary allylic alcohol, 2-fluorodec-2-enol (**6**), was prepared from the epoxide **5**, which was accessible from 2-fluorodecene (**3b**) by epoxidation with



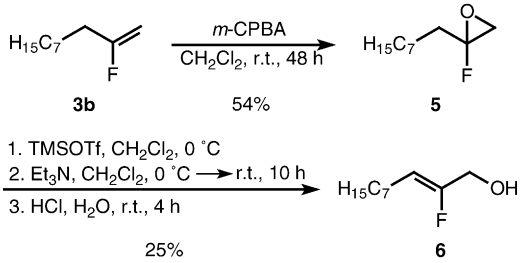
Scheme 3.



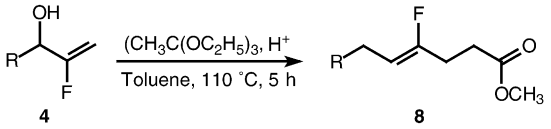
Scheme 4.

m-chloroperbenzoic acid. Epoxidation of vinyl fluorides has been described earlier by Elkik and Le Blanc [50] and Schlosser and Michel [51,52]. On the other hand it is known that non-fluorinated allylic alcohols can be prepared from epoxides by deprotonation of the 3-position with strong bases such as LDA or KO^{t}Bu through an E1cb mechanism [53]. Applying these and several similar conditions to the fluorinated epoxide **5** led to complicated mixtures of many fluorinated and non-fluorinated compounds in all cases. Alternatively, ring opening of epoxides by treatment with electrophiles such as butyldimethylsilyl iodide [54] or trimethylsilyl trifluoromethane sulfonates [55] in the presence of weak bases such as triethylamine has been described. Under the conditions shown in Scheme 5, the epoxide **5** was rearranged to **6** in low yield.

The mechanism of this reaction is not clear yet, but it is known that silyl iodides or silyl triflates with tertiary amines form ammonium salts, which are less active silylation reagents [56,57]. Probably these Lewis acids can activate the



Scheme 5.



Scheme 6.

Table 1
Results of Johnson-Claisen rearrangement of fluorinated allylic alcohols **4**

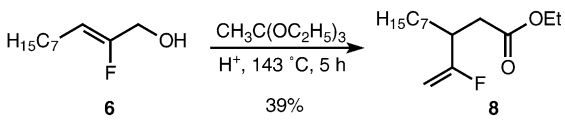
Alcohol	R^1	Ester	Yield (%)
4a	C_3H_7	**7a**	96
4b	C_7H_{15}	**7b**	84
4c	$C_{13}H_{27}$	**7c**	81
4d	H	**7d**	0

oxirane, which in the absence of nucleophiles is opened and subsequently deprotonated in the β-position. The thus-formed silylether could not be isolated, but acidic hydrolysis led to the desired allylic alcohol **6**. All attempts to increase the yield of this reaction failed until now.

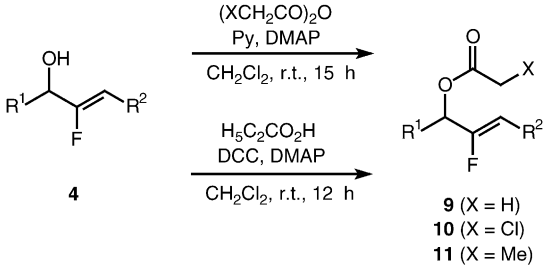
Having several fluorinated allylic alcohols in hand, we investigated Johnson-Claisen rearrangements of these compounds. Thus, the fluoroallylic alcohols **4a**–**4c** were refluxed with trimethyl orthoacetate in toluene in the presence of a catalytic amount of propionic acid for 5 h to give the corresponding *trans*-configured methyl 4-fluoroalk-4-enecarboxylates **7a**–**7c** in good to excellent yields (Scheme 6, Table 1). In contrast, compound **4d** did not give any of the expected ester under these conditions and heating with the orthoester in the absence of a solvent was unsuccessful as well. The reasons for this failure are not clear yet.

Under standard conditions, the reaction of 2-fluorodec-2-enol (**6**) with trimethyl orthoacetate was very slow (6% conversion of **6** after refluxing in toluene for 6 h). Therefore, compound **6** was refluxed in neat triethyl orthoacetate for 5 h to give the rearrangement product **8** in 39% yield (Scheme 7). Elongation of the reaction time led to side reactions and did not improve the yield. Steric reasons and the formation of a less stable terminal double bond might be responsible for the low yield of the latter reaction.

The fluorinated allylic alcohols **4** were subsequently esterified by treatment with acetic anhydride or chloroacetic anhydride, in the presence of DMAP (method A) according to a protocol developed by Steglich and Höfle [58] to give the corresponding esters **9**, **10** or **11**, respectively (Scheme 8).



Scheme 7.



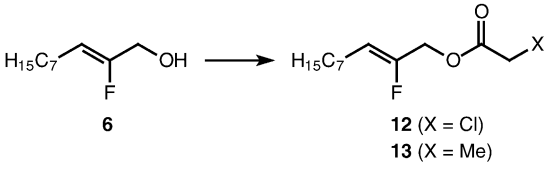
Scheme 8.

The corresponding propionates **11** were synthesized by treatment of **4** with propanoic acid in the presence of DCC/DMAP (method B) similarly to a protocol independently described by Neises and Steglich [59] and Hassner and Alexanian [60].

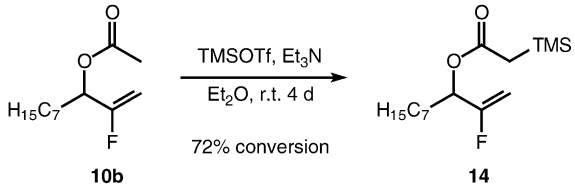
Similarly, also 2-fluorodec-2-enol (**6**) was acylated with chloroacetic anhydride in the presence of pyridine and a catalytic amount of DMAP or with propanoic acid/DCC/DMAP to give the corresponding chloroacetate **12** or the propionate **13**, respectively (Scheme 9).

At the beginning of our investigations only two examples [36,39] of Ireland-Claisen rearrangements of allylic acetates bearing a vinylic fluorine were described in literature. All our attempts towards rearrangement of **9b** under classical conditions of Ireland [19] failed and besides the starting material only complex mixtures of products were formed. Also under the conditions of a thermodynamically controlled enolization [61,62] the expected product of the Ireland-Claisen rearrangement was not formed. However, under these conditions a selective C-silylation of the α-carbon to the carbonyl group to form the α-silylated ester **14** was observed, though the transformation was not complete (Scheme 10).

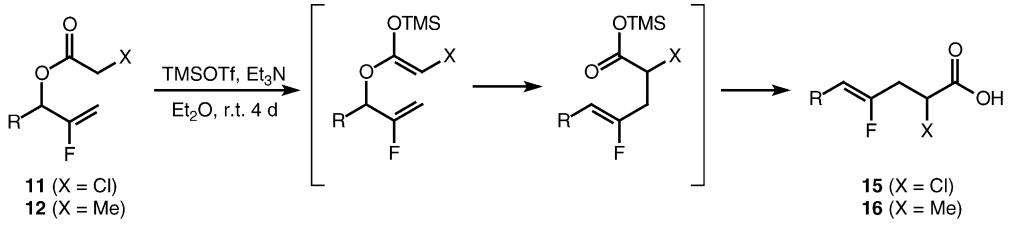
Such α-silylations were already observed in literature, particularly when TMSOTf was used instead of TMSCl [63]. Though, several Ireland-Claisen rearrangements have been described [18,19], this type of reactions seem not generally to be possible with acetates and several failures of such



Scheme 9.



Scheme 10.



Scheme 11.

Table 2
Synthesis of fluorinated allylic esters and 4-fluoroalk-4-enecarboxylic acid derivatives

Alcohol	R^1	R^2	X	Allylic ester (method)	Yield (%)	Carboxylic acid	Yield (%)
4b	C_7H_{15}	H	H	**9b** (A)	91	–[a]	0[a]
4a	C_3H_7	H	Cl	**10a** (A)	79	**15a**	29
4b	C_7H_{15}	H	Cl	**10b** (A)	92	**15b**	54
4c	$C_{13}H_{27}$	H	Cl	**10c** (A)	95	**15c**	66
4d	H	H	Cl	**10d** (A)	84	**15d**	86
6	H	C_7H_{15}	Cl	**12** (A)	99	**17**	60
4a	C_3H_7	H	Me	**11a** (B)	68	**16a**	32
4b	C_7H_{15}	H	Me	**11b** (B)	90	**16b**	70
4c	$C_{13}H_{27}$	H	Me	**11c** (B)	74	**16c**	72
4d	H	H	Me	**11d** (B)	50	**16d**	5
6	H	C_7H_{15}	Me	**13** (B)	94	**18**	52

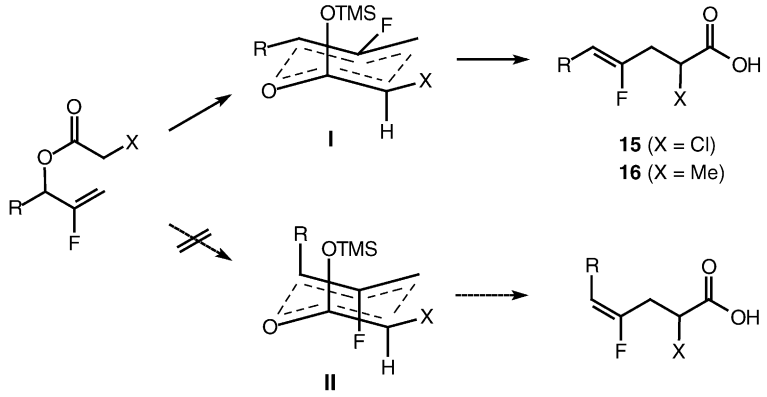
[a] Ethyl ester formed by Johnson-Claisen rearrangement.

reactions have been mentioned in literature [26]. Since the corresponding carboxylic esters are available by Johnson-Claisen rearrangement, these investigations were not continued.

Furthermore, the esters **10** and **11** substituted by chlorine or a methyl group in α-position to the carboxyl function were treated with LDA and TMSCl using the classical conditions of Ireland-Claisen rearrangement at −78 °C. However, no rearrangement products were found after warming the reaction mixture to room temperature. The esters were partially recovered besides the allylic alcohols **4** produced by ester hydrolysis. Similar ester hydrolyses initiated by silylation reagents have already been observed for other types of reactions by Emde and Simchen [61]. Another reason for the failure of rearrangement might be a competing deprotonation in β-position to the fluorine substituent with strong bases. A comparable observation was made by Percy et al. in rearrangements of Ireland-Claisen systems bearing a γ-fluorine substituent [39].

Therefore, we used another method of enolization acting under less basic conditions and leading to the (*Z*)-enolate under thermodynamic control. Thus, treatment of the esters **11** or **12** with TMSOTf and triethylamine at room temperature in dichloromethane for 4 days gave the expected 4-fluoroalk-4-enecarboxylic acids **15** or **16** bearing a chlorine or a methyl substituent in 2-position in reasonable yields (except compound **16d**) (Scheme 11, Table 2).

From investigations of the crude product mixtures by GC and ^{19}F NMR spectroscopy it became obvious that the reaction, after >80% conversion of starting material yielded



Scheme 12.

exclusively the rearranged products **15** or **16**, respectively. The moderate yields are due to difficult isolation and purification of the products, which were partially destroyed during chromatographic separation (vide infra). Thus, the Ireland-Claisen rearrangement gave the (*Z*)-configured 4-fluoroalk-4-enecarboxylic acids. This stereochemistry becomes obvious from the big vicinal coupling constant $^{3}J_{H,F}$ of 37–38 Hz in the ^{1}H NMR spectra of compounds **15** and **16**.

The formation of these diastereomers can be rationalized from the most probable transition state **I** (Scheme 12). The alternative, **II**, with an axial R substituent is much less probable. This type of stereocontrol was already described by Ireland et al. [19].

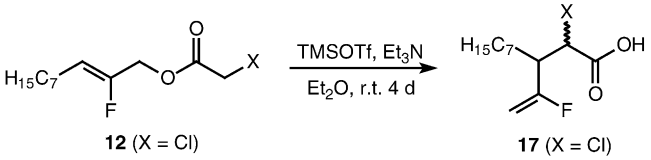
The carboxylic acids **15b** or **16b** were treated with methanol in the presence of DCC/DMAP to give the corresponding methyl esters in 86 or 67% yield, respectively.

Ireland-Claisen rearrangement of substituted carboxylic esters of the primary allylic alcohol 2-fluorodec-2-enol, namely the reactions of the chloroacetate **12** and the propionate **13** under the same conditions gave mixtures of diastereomers in 60 or 52% yield, respectively. Thus, from **12** a 1:1 mixture of compounds **17** was formed, while the rearrangement of **13** led to a 81:19 mixture of the diastereomers **18**. These diastereomers were not separated (Scheme 13, Table 2).

This type of an Ireland-Claisen rearrangement was much less efficient starting with a cyclic vinyl fluoride derived from (*E*)-cyclododecene (**19**) by bromofluorination and subsequent HBr-elimination from the formed *cis*-1-bromo-2-fluorocyclododecane (**20**) to form (*E*)-1-fluorocyclododecene (**21**). The allylic oxidation with selenium dioxide and *tert*-butylhydroperoxide occurred selectively in β-position to the fluorine substituent to give the (*Z*)-configured allylic alcohol **22** in low yield. The alcohol was esterified under the conditions described above to give the esters **23** or **24** in good yield.

Ireland-Claisen rearrangement under the above-mentioned standard conditions gave the corresponding carboxylic acids **25** or **26** in about 60% yields (GC) as about 70:30 mixtures of diastereomers (Scheme 14). The isomers could neither be separated from each other nor from the starting materials. Moreover, the formation of double bond isomers could not be excluded.

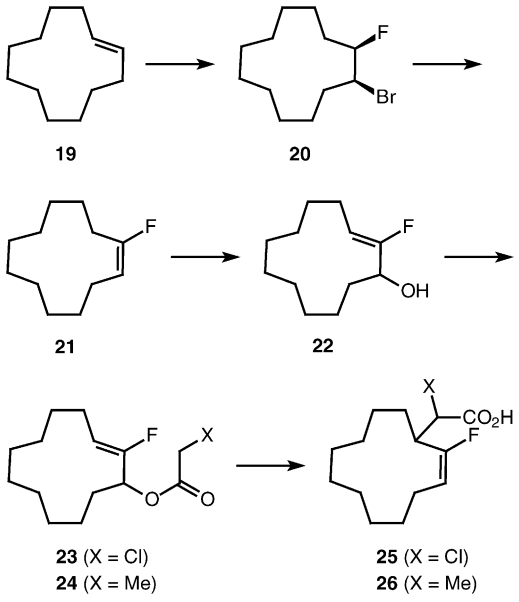
It has been mentioned already that purification of the 4-fluoroalk-4-enecarboxylic acids **15** and **16** by column



12 (X = Cl)
13 (X = Me)

17 (X = Cl)
18 (X = Me)

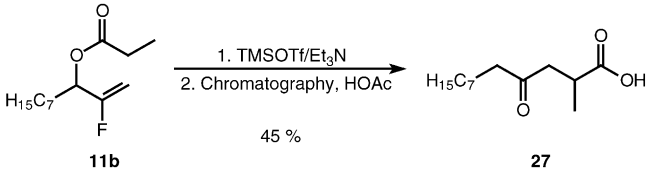
Scheme 13.



23 (X = Cl)
24 (X = Me)

25 (X = Cl)
26 (X = Me)

Scheme 14.



11b

27

Scheme 15.

chromatography was difficult and led to partial loss of material. When about 10% of acetic acid was added to the eluent, the vinyl moiety of compound **16b** was partially solvolyzed. We have shown earlier that this function is sensitive against strong acids [48]. Thus, the ester **11b** was rearranged according to the general procedure and the crude reaction product was subjected to column chromatography (silica gel) using a mixture of cyclohexane, ethyl acetate and acetic acid (10:1:1) as an eluent. In this way 2-methyl-4-oxododecanoic acid (**27**) was isolated in 45% overall yield (Scheme 15).

3. Conclusion

Based on vinyl fluorides **3** and **21** a series of fluorinated allylic alcohols **4**, **6** and **22** has been synthesized. Refluxing the allylic alcohols **4** or **6** with trimethyl- or triethyl orthoacetate in toluene Johnson-Claisen rearrangement occurred providing high-yielding access to (*Z*)-4-fluoroalk-4-enecarboxylic esters **7** or **8**, respectively. In agreement with the behaviour of non-fluorinated allylic acetates, also fluorinated analogues such as 3-acetoxy-2-fluorodec-2-ene (**9b**) seem not to be suitable to undergo Ireland-Claisen rearrangement on treatment with triethylamine and TMSOTf at room temperature. Under these conditions, C-silylation of

the α-position to the carbonyl group occurred. On the other hand, α-substituted acetates such as the α-chloroacetates **11** or the propionates **12** rearranged under the same conditions to give the corresponding 2-substituted (*Z*)-4-fluoroalk-4-enoic acids **15** or **16** in moderate yields. The esters **23** and **24** derived from (*Z*)-2-fluorocyclododec-2-enol (**22**) under similar conditions gave mixtures of diastereomers in low yield. The fluorovinylic moiety is hydrolysed to the keto group under acidic conditions.

4. Experimental

4.1. General remarks

NMR spectra were recorded at 300 MHz (^{1}H), 75 MHz (^{13}C) and 282 MHz (^{19}F) and are reported in ppm downfield from TMS (^{1}H and ^{13}C, $CDCl_3$ as internal standard, δ = 77.0 ppm), or $CFCl_3$ (^{19}F). Mass spectra were recorded by GC/MS coupling (EI, 70 eV) or by GC/MS/CI (chemical ionization). Gas chromatographic analyses were performed using a column HP-5 (30 m, Ø0.32 mm, film 0.25 μm, carrier gas N_2) or SPB-1 (30 m, Ø0.32 mm, film 0.25 μm, carrier gas N_2). Thin-layer chromatography was done on coated silica gel plate Merck 60 F_{254}. Column chromatography was done with silica gel Merck 60 (0.063–0.2 mm). All reactions involving air-sensitive agents were conducted under argon atmosphere applying Schlenk-technique. All reagents purchased from suppliers were used without further purification. CH_2Cl_2 was dried and distilled over P_2O_5, toluene was dried by azeotropic distillation, followed by distillation over sodium. Solvents for chromatography were distilled prior to use.

4.2. General procedure for bromofluorination

A solution of 100 mmol of the corresponding terminal alkene **1** and triethylamine trihydrofluoride (25 mL, 153 mmol) in CH_2Cl_2 (100 mL) under stirring at 0 °C was treated in portions with NBS (21.9 g, 120 mmol). The mixture was stirred overnight while warming up to room temperature. The yellowish suspension was poured into ice water (500 mL) and treated with a conc. ammonia solution until the pH was significantly basic. The aqueous phase was extracted with pentane (3 × 150 mL). The combined organic layer was washed with 2N HCl (2 × 150 mL) and with 5% $NaHCO_3$-solution (3 × 150 mL) and water (150 mL). After removing of the solvent the residue can be purified by column chromatography. Generally, the crude product was used for the next step.

4.2.1. 1-Bromo-2-fluorohexane (*2a*)

According to the general procedure **2a** was prepared from **1a** (8.40 g, 0.1 mol). Yield: 17.65 g (96%) (contaminated with 8% of the regioisomer and 4% of the 1,2-dibromide). The spectroscopic data agree with those published in Ref. [64].

4.2.2. 1-Bromo-2-fluorodecane (*2b*)

According to the general procedure **2b** was prepared from **1b** (14.00 g, 0.1 mol). Yield: 22.76 g (95%) (contaminated with 8% of the regioisomer and 3% of the 1,2-dibromide). The spectroscopic data agree with those published in Ref. [46].

4.2.3. 1-Bromo-2-fluorohexadecane (*2c*)

According to the general procedure **2c** was prepared from **1c** (22.40 g, 0.1 mol). Yield: 31.93 g (99%) (contaminated with 8% of the regioisomer and 3% of the 1,2-dibromide). ^{1}H NMR ($CDCl_3$): δ 0.88 (t, $^3J_{H,H}$ = 6.9 Hz, 3 H, 16-CH_3), 1.26 (m, 22 H, 5-CH_2–15-CH_2), 1.35–1.55 (m, 2 H, 4-CH_2), 1.60–1.80 (m, 2 H, 3-CH_2), 3.46 (dd, $^2J_{H,H}$ = 5.0 Hz, $^3J_{H,F}$ = 19.6 Hz, 2 H, 1-CH_2), 4.61 (dm, $^2J_{H,F}$ = 47.7 Hz, 1 H, 2-CHF). ^{13}C NMR ($CDCl_3$): δ 14.1 (q, C-16), 22.7 (t, C-15), 24.7 (dt, $^3J_{C,F}$ = 3.8 Hz, C-4), 29.2–29.8 (t, C-5–C-13), 31.9 (t, C-14), 33.3 (dt, $^2J_{C,F}$ = 16.5 Hz, C-3), 33.7 (dt, $^2J_{C,F}$ = 21.6 Hz, C-1), 92.1 (dd, $^1J_{C,F}$ = 175.5 Hz, C-2). ^{19}F NMR ($CDCl_3$) δ −178.0 (m). GC/MS (70 eV): *m/z* (%) 324/322 (0/0) [M^+], 304/302 (1/1) [M^+ − HF], 276/274 (1/1), 241 (1) [M^+ − HBr − H], 189 (2) [M^+ + H − HF − HBr], 163 (7), 111 (13) [$C_8H_{15}^+$], 97 (57) [$C_7H_{13}^+$], 85 (33) [$C_6H_{13}^+$], 83 (55) [$C_6H_{11}^+$], 71 (56) [$C_5H_{11}^+$], 69 (45) [$C_5H_9^+$], 57 (100) [$C_4H_9^+$], 55 (54) [$C_4H_7^+$], 43 (88) [$C_3H_7^+$], 41 (45) [$C_3H_5^+$].

4.3. Dehydrobromination of bromofluorides

4.3.1. 2-Fluorohex-1-ene (*3a*)

In a two-necked flask with a distillation bridge powdered KOH (13.00 g, 232 mmol) was treated drop wise with the mixture prepared in Section 4.2.1 (13.00 g, 63 mmol of **2a**) and heated to 95 °C until the formed vinyl fluoride **3a** distilled completely (4–48 h depending on the particle size of KOH). Yield: 5.27 g (82%, based on the part of **2a** contained in the starting material). The spectroscopic data agree with those published in Ref. [65].

The corresponding bromofluoride **2** (50.0 mmol) in pentane (500 mL) was refluxed with potassium *tert*-butanolate (6.74 g, 60 mmol) for 5 h. The mixture was poured into water (500 mL), the phases were separated and the organic layer was washed with water (200 mL) and 5% aqueous $NaHCO_3$ solution (200 mL). After drying of the organic phase over $MgSO_4$, the solvent was removed and the crude product was purified.

4.3.2. 2-Fluorodec-1-ene (*3b*)

The mixture from 4.2.2 (22.49 g, 94 mmol) was refluxed with potassium *tert*-butanolate (12.63 g, 113 mmol) in pentane (1200 mL) for 5 h. The mixture was poured into water (1000 mL), the phases were separated and the organic layer was washed with water (200 mL) and 5% aqueous $NaHCO_3$ solution (200 mL). After drying of the organic phase over $MgSO_4$, the solvent was removed and the crude product was distilled. Yield: 9.58 g (65%, mixture of 85% **3b**, 12% dec-1-yne, 3% of 1-fluorodecene, 69% yield of **3b**

based on **2b**). b.p. 71 °C at 27 mbar (Lit.: 95 °C at 133 mbar [48]). The spectroscopic data agree with those published in Ref. [46].

4.3.3. 2-Fluorohexadec-1-ene (**3c**)

Similar to the above-mentioned procedure **3c** was prepared from pure **2c** (16.12 g, 50 mmol). Yield: 12.50 g (mixture of 72% **2c**, 23% 1-bromohexadec-1-ene, 2% hexadec-1-yne). ^{1}H NMR ($CDCl_3$): δ 0.88 (t, $^3J_{H,H}$ = 6.9 Hz, 3 H, 16-CH_3), 1.26 (m, 22 H, 5-CH_2–15-CH_2), 1.50 (m, 2 H, 4-CH_2), 2.17 (m, 2 H, 3-CH_2), 4.17 (dd, $^3J_{H,F}$ = 50.3 Hz, $^2J_{H,H}$ = 2.4 Hz, 1 H, 1-CH_2), 4.47 (dd, $^3J_{H,F}$ = 17.4 Hz, $^2J_{H,H}$ = 2.4 Hz, 1 H, 1-CH_2). ^{13}C NMR ($CDCl_3$): δ 14.1 (q, C-16), 22.7 (t, C-15), 26.0 (t, C-4), 28.9, 29.4, 29.5, 29.6, 29.7 (t, C-5–C-13), 31.9 (dt, $^2J_{C,F}$ = 28.0 Hz, C-3), 31.9 (t, C-14), 89.1 (dt, $^2J_{C,F}$ = 21.6 Hz, C-1), 167.1 (d, $^1J_{C,F}$ = 256.9 Hz, C-2). ^{19}F NMR ($CDCl_3$): δ −95.0 (ddt, $^3J_{H,F}$ = 17.2 Hz, $^3J_{H,F}$ = 17.2 Hz, $^3J_{H,F}$ = 51.5 Hz). GC/MS (70 eV): *m/z* (%) 242 (0.2) [M^+], 222 (4) [M^+ − HF], 180 (7) [M^+ − HF − C_3H_6], 166 (6) [180 − CH_2], 152 (7) [180 − C_2H_4], 152 (6) [180 − C_3H_6], 138 (8) [180 − C_4H_8], 125 (11), 124 (9) [180 − C_5H_{10}], 110 (22) [180 − C_6H_{12}], 96 (64) [180 − C_7H_{14}], 85 (16) [$C_6H_{13}^+$], 82 (100) [180 − C_8H_{16}], 71 (35) [$C_5H_{11}^+$], 69 (84) [$C_5H_9^+$], 57 (88) [$C_4H_9^+$], 55 (81) [$C_4H_7^+$], 43 (100) [$C_3H_7^+$], 41 (62) [$C_3H_5^+$].

4.3.4. (*E*)-1-Fluorocyclododecene

Similar to the procedure mentioned above, (*E*)-1-fluorocyclododecene (**21**) was prepared from diastereopure *cis*-1-bromo-2-fluorocyclododecane (**20**) [43,44] (13.25 g, 50.0 mmol) by refluxing with KO^{t}Bu (11.23 g, 100 mmol) in cyclohexane (650 mL) for 5 h. Yield: 9.02 g (98%). The spectroscopic data agree with published ones [66].

4.4. General procedure for the allylic oxygenation of vinyl fluorides with selenium dioxide

A solution of selenium dioxide (5.55 g, 50 mmol) and 80% *tert*-butyl hydroperoxide in di-*tert*-butyl ether (25 mL, 200 mmol) in CH_2Cl_2 (100 mL) was treated with the corresponding fluorolefin **3** (20 mmol) and acetic acid (2.3 mL, 40 mmol). Subsequently, the mixture was stirred for 4–14 days at room temperature. Then toluene (10 mL) was added to precipitate SeO_2, which was separated. Then CH_2Cl_2 was removed without heating in vacuo. The residue was dissolved in diethyl ether (20 mL) and the solution was washed with 10% aqueous KOH (4 × 10 mL) in order to separate remaining SeO_2. To reduce the excess peroxide the solution was stirred with 5 g of $FeSO_4 \cdot 7H_2O$ at room temperature for 4 h. The colored suspension was filtered and the residue was washed with diethyl ether. The solution was washed with 2N HCl (20 mL) and with a sat. NaCl solution (30 mL). The solution was dried with $MgSO_4$ and the solvent was evaporated. The crude product was purified by column chromatography.

4.4.1. 2-Fluorohex-1-en-3-ol (**4a**)

Compound **3a** (9.30 g, 91 mmol) was reacted according to the general procedure. Due to the volatility of the product a different work-up was necessary. After completion of the reaction the mixture was treated with pentane (300 mL) and diethyl ether (90 mL). The organic phase was washed with 10% KOH (4 × 80 mL) and with a sat. NaCl solution (30 mL). After drying the solvent was evaporated and the residue was distilled. Yield: 7.00 g (65%). b.p. 33–35 °C at 80 mbar. ^{1}H NMR ($CDCl_3$): δ 0.95 (t, $^3J_{H,H}$ = 7.4 Hz, 3 H, 6-CH_3), 1.44 (m, 2 H, 5-CH_2), 1.65 (m, 2 H, 4-CH_2), 1.83 (br s, 1 H, OH), 4.13 (ddd, $^3J_{H,H}$ = 5.7 Hz, $^3J_{H,H}$ = 7.2 Hz, $^3J_{H,F}$ = 12.9 Hz, 1 H, 3-CH), 4.52 (dd, $^2J_{H,H}$ = 3.1 Hz, $^3J_{H,F}$ = 49.6 Hz, 1 H, 1-CH_2), 4.65 (dd, $^2J_{H,H}$ = 3.1 Hz, $^3J_{H,F}$ = 17.8 Hz, 1 H, 1-CH_2). ^{13}C NMR ($CDCl_3$): δ 13.7 (q, C-6), 18.4 (t, C-5), 36.1 (t, C-4), 70.1 (dd, $^2J_{C,F}$ = 30.5 Hz, C-3), 90.0 (dt, $^2J_{C,F}$ = 17.8 Hz, C-1), 166.9 (d, $^1J_{C,F}$ = 259.4, C-2). ^{19}F NMR ($CDCl_3$): δ −111.8 (ddd, $^3J_{H,F}$ = 11.5 Hz, $^3J_{H,F}$ = 17.2 Hz, $^3J_{H,F}$ = 49.6 Hz). GC/MS (70 eV): *m/z* (%) 118 (1) [M^+], 103 (2) [M^+ − CH_3], 90 (8) [M^+ + H − C_2H_5], 76 (25) [$C_3H_5OF^+$], 75 (100) [$C_3H_4OF^+$], 71 (14), 55 (11) [75 − HF], 43 (58) [$C_3H_7^+$], 41 (47) [$C_3H_5^+$].

4.4.2. 2-Fluorodec-1-en-3-ol (**4b**)

According to the general procedure **4b** was prepared from 9.42 g (59.6 mmol) **3b**. The product **4b** was purified by column chromatography with cyclohexane/ethyl acetate (10:1). Yield: 4.87 g (47%). The spectroscopic data agree with those published ones [48].

4.4.3. 2-Fluorohexadec-1-en-3-ol (**4c**)

According to the general procedure **4c** was prepared from 10.0 g (29.8 mmol) **3c**. The product **4c** was purified by column chromatography with cyclohexane/ethyl acetate (10:1). Yield: 4.25 g (55%). m.p. 30 °C (pentane). ^{1}H NMR ($CDCl_3$): δ 0.88 (t, $^3J_{H,H}$ = 6.9 Hz, 3 H, 16-CH_3), 1.26 (m, 22 H, 5-CH_2–15-CH_2), 1.54–1.76 (m, 2 H, 4-CH_2), 1.90 (br s, 1 H, OH), 4.10 (dddd, $^4J_{H,H}$ = 0.5 Hz, $^3J_{H,H}$ = 5.8 Hz, $^3J_{H,H}$ = 7.6 Hz, $^3J_{H,F}$ = 13.1 Hz, 1 H, 3-CH), 4.52 (ddd, $^4J_{H,H}$ = 0.5 Hz, $^3J_{H,F}$ = 49.4 Hz, $^2J_{H,H}$ = 3.1 Hz, 1 H, 1-CH_2), 4.64 (dd, $^3J_{H,F}$ = 17.4 Hz, $^2J_{H,H}$ = 3.1 Hz, 1 H, 1-CH_2). ^{13}C NMR ($CDCl_3$): δ 14.1 (q, C-16), 22.7 (t, C-15), 25.1 (t, C-5), 29.4, 29.5, 29.6, 29.7, 31.9, 34.0 (t, C-4 and C-6–C-14), 70.3 (dd, $^2J_{C,F}$ = 31.9 Hz, C-3), 90.0 (dd, $^2J_{C,F}$ = 18.0 Hz, C-1), 166.8 (d, $^1J_{C,F}$ = 260.8 Hz, C-2). ^{19}F NMR ($CDCl_3$): δ −111.7 (ddd, $^3J_{H,F}$ = 13.4 Hz, $^3J_{H,F}$ = 17.2 Hz, $^3J_{H,F}$ = 49.6 Hz). GC/MS (70 eV): *m/z* (%) 258 (1) [M^+], 240 (1) [M^+ − H_2O], 211 (11) [240 − C_2H_5], 182 (2) [$C_{13}H_{26}^+$ (McLafferty)], 166 (4), 137 (5), 114 (12), 113 (8) [$C_8H_{17}^+$], 99 (9) [$C_7H_{15}^+$], 97 (20) [$C_7H_{13}^+$], 86 (36), 85 (19) [$C_6H_{13}^+$], 83 (25) [$C_6H_{11}^+$], 76 (69) [$C_3H_5OF^+$], 75 (75) [$C_3H_4OF^+$], 71 (40) [$C_5H_{11}^+$], 69 (36) [$C_5H_9^+$], 57 (88) [$C_4H_9^+$], 55 (50) [$C_4H_7^+$], 43 (100) [$C_3H_7^+$], 41 (55) [$C_3H_5^+$]. Calcd. for $C_{16}H_{31}FO$ (258.24): C 74.37, H 12.09. Found: C 74.76, H 12.53.

*4.4.4. (Z)-2-Fluorocyclododec-2-en-1-ol (**22**)*

According to the general procedure **22** was prepared from (*E*)-1-fluorocyclododec-1-en (**21**) (7.00 g, 38 mmol). After 50% conversion of **21** the crude product was purified by column chromatography (cyclohexane/ethyl acetate, 10:1) to give a 92:8 mixture of **22** and its (*E*)-isomer. Yield: 1.96 g (27%). ^{1}H NMR ($CDCl_3$): δ 1.08–1.62 (m, 14 H, 5-CH_2–11-CH_2), 1.65–1.82 (m, 2 H, 12-CH_2), 1.90–2.10 and 2.30–2.43 (m, 2 H, 4-CH_2), 2.16 (s, 1 H, OH), 4.10 (ddd, $^3J_{H,H}$ = 4.5 Hz, $^3J_{H,H}$ = 9.5 Hz, $^3J_{H,F}$ = 21.7 Hz, 1 H, 1-CH), 4.84 (ddd, $^3J_{H,H}$ = 6.2 Hz, $^3J_{H,H}$ = 9.5 Hz, $^3J_{H,F}$ = 37.2 Hz, 1 H, 3-CH). ^{13}C NMR ($CDCl_3$): δ 22.2 (dt, $^3J_{C,F}$ = 3.8 Hz, C-4), 22.9, 24.0, 24.7, 25.4, 25.7, 25.8 (t, C-5–C-11), 31.9 (t, C-12), 71.7 (dd, $^2J_{C,F}$ = 30.5 Hz, C-1), 108.8 (dd, $^2J_{C,F}$ = 14.0 Hz, C-3), 158.2 (d, $^1J_{C,F}$ = 255.6 Hz, C-2). ^{19}F NMR ($CDCl_3$): δ −129.3 (m). GC/MS (70 eV): *m/z* (%) 201 (2) [M^+ + H], 200 (3) [M^+], 183 (1) [M^+ + H − H_2O], 180 (5) [M^+ − HF], 161 (2), 139 (5), 125 (8), 111 (13), 98 (16), 88 (100), 81 (23), 67 (28), 55 (30), 41 (39).

*4.4.5. 1-Fluoro-1-octyloxirane (**5**)*

A solution of 2-fluorodec-1-ene (**3b**) (5.64 g, 30.3 mmol **3b**, containing 15% dec-1-yne) in CH_2Cl_2 (100 mL) was stirred with *meta*-chloroperbenzoic acid (7.80 g, 29.8 mmol, 75% purity) at room temperature for 48 h, while the clear solution became muddy and *meta*-chlorobenzoic acid precipitated as a white solid. After filtration the colorless solution was extracted with a 0.1N $Na_2S_2O_3$-solution (50 mL) and a sat. $NaHCO_3$ solution (50 mL). After drying over $MgSO_4$ and evaporation of the solvent, the residue was distilled over a Vigreux column at 1.2–1.5 mbar. A fraction distilling between 45 and 65 °C was collected and analysed. Yield: 4.38 g (66% of compound **5**, 17% of starting material **3b** and 17% of dec-1-yne). ^{1}H NMR ($CDCl_3$): δ 0.88 (t, $^3J_{H,H}$ = 6.9 Hz, 3 H, 10-CH_3), 1.28 (m, 10 H, 5-CH_2–9-CH_2), 1.52 (m, 2 H, 4-CH_2), 1.97 (m, 2 H, 3-CH_2), 2.66 (dd, $^2J_{H,H}$ = 4.3 Hz, $^3J_{H,F}$ = 1.2 Hz, 1 H, 1-CH_2), 3.06 (dddd, $^2J_{H,H}$ = 4.3 Hz, $^3J_{H,F}$ = 1.2 Hz, $^4J_{H,H}$ = 1.7 Hz, $^4J_{H,H}$ = 0.5 Hz, 1 H, 1-CH_2). ^{13}C NMR ($CDCl_3$): δ 14.0 (q, C-10), 22.6 (t, C-4), 23.5 (t, C-9), 29.1, 29.2, 29.3 (t, C-5–C-7), 31.8 (t, C-8), 31.8 (dt, $^2J_{C,F}$ = 30.5 Hz, C-3), 50.8 (dt, $^2J_{C,F}$ = 22.9 Hz, C-1), 95.2 (d, $^1J_{C,F}$ = 261.9 Hz, C-2). ^{19}F NMR ($CDCl_3$): δ −134.8 (ps t, $^3J_{H,F}$ = 15.3 Hz). GC/MS (70 eV): *m/z* (%) 174 (0.07) [M^+], 145 (6) [$M^+ - C_2H_5$], 131 (10) [$M^+ - C_3H_7$], 123 (15), 103 (13) [$M^+ - C_5H_{11}$], 98 (20) [$C_7H_{14}^+$], 89 (100) [$M^+ - C_6H_{13}$], 81 (29), 76 (50) [$C_3H_5OF^+$], 55 (67) [$C_4H_7^+$], 43 (47) [$C_3H_7^+$], 41 (75) [$C_3H_5^+$].

*4.4.6. 2-Fluorodec-2-en-1-ol (**6**)*

In a dried Schlenk vessel the crude epoxide prepared above (4.38 g, containing 22.5 mmol of **5**) was dissolved in CH_2Cl_2 (10 mL) under argon. To this solution under stirring trimethylsilyl triflate (TMSOTf) (5.55 g, 25.0 mmol) in dry CH_2Cl_2 (20 mL) was dropped at 0 °C within 10 min. Then triethylamine (2.53 g, 25.0 mmol) was dropped to the red brown mixture at the same temperature within 30 min. The clear solution was stirred overnight while warming to room temperature. Then 2N HCl (150 mL) was added at room temperature and stirring was continued for 4 h. The layers were separated and the aqueous phase was extracted with CH_2Cl_2 (2 × 50 mL). The combined organic phases were washed with 2N HCl (2 × 100 mL) and a 5% $NaHCO_3$-solution (100 mL) and dried over $MgSO_4$. The solvent was removed in vacuo and the product was purified by column chromatography (cyclohexane/ethyl acetate, 10:1). Yield: 720 mg (25%). ^{1}H NMR ($CDCl_3$): δ 0.87 (t, $^3J_{H,H}$ = 6.7 Hz, 3 H, 10-CH_3), 1.20–1.43 (m, 10 H, 5-CH_2–9-CH_2), 1.65 (s, 1 H, OH), 2.10 (dt, $^3J_{H,H}$ = 6.9 Hz, $^3J_{H,H}$ = 6.9 Hz, 2 H, 4-CH_2), 4.10 (d, $^3J_{H,F}$ = 15.7 Hz, 2 H, 1-CH_2), 4.83 (dt, $^3J_{H,H}$ = 7.5 Hz, $^3J_{H,F}$ = 37.2 Hz, 1 H, 3-CH). ^{13}C NMR ($CDCl_3$): δ 14.0 (q, C-10), 22.6 (t, C-4), 23.3 (t, C-9), 29.0–29.1 (3 t, C-5–C-7), 31.7 (t, C-8), 61.4 (dt, $^2J_{C,F}$ = 30.5 Hz, C-1), 108.1 (dd, $^2J_{C,F}$ = 12.7 Hz, C-3), 157.5 (d, $^1J_{C,F}$ = 254.3 Hz, C-2). ^{19}F NMR ($CDCl_3$): δ −121.8 (dt, $^3J_{H,F}$ = 34.3 Hz, $^3J_{H,F}$ = 17.2 Hz). GC/MS (70 eV): *m/z* (%) 175 (2) [$M + H^+$], 174 (9) [M^+], 156 (3) [$M^+ - H_2O$], 154 (0) [M^+ − HF], 139 (0.5) [154 − CH_3], 123 (30) [154 − CH_2OH], 113 (10) [$C_8H_{17}^+$], 99 (15) [$C_7H_{15}^+$], 85 (14) [$M^+ - C_4H_6OF$], 84 (14) [$C_6H_{12}^+$ (McLafferty)], 81 (46), 70 (47) [$C_4H_6O^+$], 69 (67) [$C_5H_9^+$], 57 (53) [$C_4H_9^+$], 56 (69), 55 (68) [$C_4H_7^+$], 43 (100) [$C_3H_7^+$], 41 (84) [$C_3H_5^+$].

4.5. General procedure for the synthesis of acetates and chloroacetates (method A)

The corresponding allylic alcohol **4** (5 mmol) was dissolved in dry CH_2Cl_2 (5 mL) and treated with pyridine (0.44 g, 5.57 mmol). Then acetic anhydride (0.58 g, 5.5 mmol) or solid chloroacetic anhydride (0.94 g, 5.5 mmol) was dissolved under stirring and a catalytic amount of DMAP was added. After stirring overnight at room temperature the reaction mixture was dissolved in diethyl ether (30 mL) and washed with 2N aq. HCl (15 mL), a 5% $NaHCO_3$-solution (20 mL) and brine. The organic layer was dried over $MgSO_4$ and the solvent was removed. The product was purified by column chromatography.

*4.5.1. 3-Acetoxy-2-fluorodec-1-ene (**9b**)*

According to the general procedure 2-fluorohex-1-en-3-ol (**4b**) (174 mg, 1.0 mmol) was acetylated to give the ester **9b**. Yield: 210 mg (91%). ^{1}H NMR ($CDCl_3$): δ 0.88 (t, $^3J_{H,H}$ = 6.9 Hz, 3 H, 10-CH_3), 1.21–1.39 (m, 10 H, 5-CH_2–9-CH_2), 1.72 (m, 2 H, 4-CH_2), 2.08 (s, 3 H, 12-CH_3), 4.53 (dd, $^2J_{H,H}$ = 3.1 Hz, $^3J_{H,F}$ = 48.6 Hz, 1 H, 1-CH_2), 4.70 (dd, $^2J_{H,H}$ = 3.1 Hz, $^3J_{H,F}$ = 16.7 Hz, 1 H, 1-CH_2), 5.28 (dt, $^3J_{H,H}$ = 6.9 Hz, $^3J_{H,F}$ = 16.2 Hz, 1 H, 3-CH). ^{13}C NMR ($CDCl_3$): δ 13.9 (q, C-10), 20.8 (q, C-12), 22.5 (t, C-9), 24.9 (t, C-5), 29.0 (t, C-4), 29.1 (t, C-7), 31.0 (t, C-6), 31.7 (t, C-8), 71.3 (dd, $^2J_{C,F}$ = 30.5 Hz, C-3), 92.4 (dt, $^2J_{C,F}$ = 28.7 Hz, C-1), 163.0 (d, $^1J_{C,F}$ = 261.9 Hz, C-2), 169.8 Hz (s, C-11). ^{19}F NMR ($CDCl_3$): δ −111.5 (ddd, $^3J_{H,F}$ = 47.7 Hz, $^3J_{H,F}$ = 17.2 Hz, $^3J_{H,F}$ = 15.2 Hz). GC/MS (70 eV): *m/z* (%) 216 (0)

[M^+], 174 (7) [M^+ + H − CH_3CO], 156 (1) [M^+ − CH_3COOH (McLafferty)], 141 (1) [156 − CH_3], 127 (6), 118 (2) [$C_5H_7O_2F^+$ (McLafferty)], 113 (3), 99 (4) [156 − C_4H_9], 69 (5) [$C_5H_9^+$], 57 (8) [$C_4H_9^+$], 55 (15) [$C_4H_7^+$], 43 (100) [CH_3CO], 41 (21) [$C_3H_5^+$].

*4.5.2. 3-Chloroacetoxy-2-fluorohex-1-ene (**10a**)*

According to the general procedure the 2-fluorohex-1-en-3-ol (**4a**) (590 mg, 5.0 mmol) was esterified. Yield: 770 mg (79%). ^{1}H NMR ($CDCl_3$): δ 0.95 (t, $^3J_{H,H}$ = 7.4 Hz, 3 H, 6-CH_3), 1.39 (m, 2 H, 5-CH_2), 1.77 (m, 2 H, 4-CH_2), 4.08 (s, 2 H, 8-CH_2), 4.61 (dd, $^2J_{H,H}$ = 3.3 Hz, $^3J_{H,F}$ = 47.9 Hz, 1 H, 1-CH_2), 4.77 (dd, $^2J_{H,H}$ = 3.3 Hz, $^3J_{H,F}$ = 16.5 Hz, 1 H, 1-CH_2), 5.36 (dt, $^3J_{H,H}$ = 6.9 Hz, $^3J_{H,F}$ = 16.5 Hz, 1 H, 3-CH). ^{13}C NMR ($CDCl_3$): δ 13.5 (q, C-6), 18.1 (t, C-5), 32.9 (t, C-4), 40.7 (t, C-8), 73.1 (dd, $^2J_{C,F}$ = 28.0 Hz, C-3), 93.5 (dt, $^2J_{C,F}$ = 17.8 Hz, C-1), 161.8 (d, $^1J_{C,F}$ = 261.9 Hz, C-2), 166.4 (s, C-7). ^{19}F NMR ($CDCl_3$): δ −112.1 (ps dt, $^3J_{H,F}$ = 16.2 Hz, $^3J_{H,F}$ = 47.7 Hz). GC/MS (70 eV): *m/z* (%) 195 (1) [M^+ + H], 179 (1) [M^+ − CH_3], 167/165 (2/9) [M^+ − C_2H_5], 154/152 (6/15) [M^+ − C_3H_6], 118 (46) [$C_6H_{11}OF^+$ (McLafferty)], 100 (100) [118 − H_2O], 85 (55) [100 − CH_3], 79/77 (28/100) [$C_2H_2OCl^+$], 72 (16), 59 (18), 51/49 (6/21) [CH_2Cl^+], 41 (19) [$C_3H_5^+$].

*4.5.3. 3-Chloroacetoxy-2-fluorodec-1-ene (**10b**)*

According to the general procedure the 2-fluorodec-1-en-3-ol (**4b**) (870 mg, 5.0 mmol) was esterified to give **10b**. Yield: 1.14 g (92%). ^{1}H NMR ($CDCl_3$): δ 0.88 (t, $^3J_{H,H}$ = 6.9 Hz, 3 H, 10-CH_3), 1.28 (m, 10 H, 5-CH_2–9-CH_2), 1.77 (m, 2 H, 4-CH_2), 4.07 (s, 2 H, 12-CH_2), 4.60 (dd, $^2J_{H,H}$ = 3.3 Hz, $^3J_{H,F}$ = 47.9 Hz, 1 H, 1-CH_2), 4.76 (dd, $^2J_{H,H}$ = 3.3 Hz, $^3J_{H,F}$ = 16.5 Hz, 1 H, 1-CH_2), 5.34 (dt, $^3J_{H,H}$ = 6.9 Hz, $^3J_{H,F}$ = 16.5 Hz, 1 H, 3-CH). ^{13}C NMR ($CDCl_3$): δ 14.0 (q, C-10), 22.5 (t, C-9), 24.8 (t, C-5), 29.0 (dt, $^3J_{C,F}$ = 5.1 Hz, C-4), 29.2 (t, C-7), 30.8 (t, C-6), 31.6 (t, C-8), 40.7 (t, C-12), 73.4 (dd, $^2J_{C,F}$ = 30.5 Hz, C-3), 93.4 (dt, $^2J_{C,F}$ = 17.8 Hz, C-1), 161.8 (d, $^1J_{C,F}$ = 259.5, C-2), 166.3 (s, C-11). ^{19}F NMR ($CDCl_3$): δ −112.1 (ps dt, $^3J_{H,H}$ = 15.3 Hz, $^3J_{H,H}$ = 49.6 Hz). GC/MS (70 eV): *m/z* (%) 250 (0) [M^+], 215 (4) [M^+ − Cl], 201 (5) [M^+ − CH_2Cl], 174 (57) [M^+ + H − C_2H_2OCl], 152 (24) [M^+ + H − C_7H_{15}], 127 (31), 113 (27) [127 − CH_2], 99 (41) [127 − C_2H_4], 86 (54), 77 (100) [$C_2H_2OCl^+$], 57 (33) [$C_4H_9^+$], 55 (51) [$C_4H_7^+$], 43 (57) [$C_3H_7^+$], 41 (35) [$C_3H_5^+$].

*4.5.4. 3-Chloroacetoxy-2-fluorohexadec-1-ene (**10c**)*

According to the general procedure 2-fluorohexadec-1-en-3-ol (**4c**) (1.032 g, 4.0 mmol) was esterified. Yield: 1.26 g (95%). ^{1}H NMR ($CDCl_3$): δ 0.88 (t, $^3J_{H,H}$ = 6.4 Hz, 3 H, 16-CH_3), 1.31 (m, 22 H, 5-CH_2–15-CH_2), 1.77 (m, 2 H, 4-CH_2), 4.07 (s, 2 H, 18-CH_2), 4.60 (dd, $^2J_{H,H}$ = 3.2 Hz, $^3J_{H,F}$ = 47.9 Hz, 1 H, 1-CH_2), 4.76 (dd, $^2J_{H,H}$ = 3.2 Hz, $^3J_{H,F}$ = 16.5 Hz, 1 H, 1-CH_2), 5.33 (dt, $^3J_{H,H}$ = 6.9 Hz, $^3J_{H,F}$ = 16.5 Hz, 1 H, 3-CH). ^{13}C NMR ($CDCl_3$): δ 14.0 (q, C-16), 22.6 (t, C-15), 24.8 (t, C-5), 29.1–29.6 (t, C-7–C-13), 29.6 (dt, $^3J_{C,F}$ = 3.8 Hz, C-4), 30.9 (t, C-6), 31.9 (t, C-14), 40.7 (t, C-18), 73.4 (dd, $^2J_{C,F}$ = 30.5 Hz, C-3), 93.4 (dd, $^2J_{C,F}$ = 17.8 Hz, C-1), 161.8 (d, $^1J_{C,F}$ = 260.7 Hz, C-2), 166.3 (s, C-17). ^{19}F NMR ($CDCl_3$): δ −112.0 (d ps t, $^3J_{H,F}$ = 17.2 Hz, $^3J_{H,F}$ = 47.7 Hz). GC/MS (70 eV): *m/z* (%) 334 (0.1) [M^+], 317 (0.2) [M^+ − OH], 314 (0.3) [M^+ − HF], 299 (5) [M^+ − Cl], 285 (3) [M^+ − CH_2Cl], 258 (22) [M^+ + H − CH_2ClCOO], 240 (5) [M^+ − HO_2CH_2Cl], 211 (23), 180 (8), 152 (17) [M^+ + H − $C_{13}H_{27}$], 95 (47), 86 (100), 70 (65), 57 (83) [$C_4H_9^+$], 55 (84) [$C_4H_7^+$], 43 (100) [$C_3H_7^+$].

*4.5.5. 3-Chloroacetoxy-2-fluoropropene (**10d**)*

According to the general procedure 2-fluoroprop-2-enol (**4d**) (760 mg, 10.0 mmol) was esterified to give **6d**. Yield: 1.28 g (84%). ^{1}H NMR ($CDCl_3$): δ 4.12 (s, 2 H, 5-CH_2Cl), 4.68 (dd, $^2J_{H,H}$ = 3.3 Hz, $^3J_{H,F}$ = 46.7 Hz, 1 H, 3-CH_2), 4.71 (d, $^3J_{H,F}$ = 14.7 Hz, 2 H, 1-CH_2), 4.86 (dd, $^2J_{H,H}$ = 3.3 Hz, $^3J_{H,F}$ = 15.5 Hz, 1 H, 3-CH_2). ^{13}C NMR ($CDCl_3$): δ 40.4 (t, C-5), 62.6 (dt, $^2J_{C,F}$ = 33.1 Hz, C-1), 95.2 (dt, $^2J_{C,F}$ = 16.5 Hz, C-3), 159.3 (d, $^1J_{C,F}$ = 258.1 Hz, C-2), 166.6 (s, C-4). ^{19}F NMR ($CDCl_3$): δ −106.1 (ddt, $^3J_{H,F}$ = 15.3 Hz, $^3J_{H,F}$ = 15.3 Hz, $^3J_{H,F}$ = 47.7 Hz). GC/MS (70 eV): *m/z* (%) 154/152 (0.5/1) [M^+], 134/132 (0/1) [M^+ − HF], 117 (1) [132 − CH_3], 97 (2), 76 (94) [$C_3H_4OF^+$], 59 (100) [$C_3H_4F^+$], 51/49 (16/49) [CH_2Cl^+], 42 (27).

*4.5.6. 1-Chloroacetoxy-2-fluorodec-2-ene (**12**)*

According to the general procedure the fluoroallylic alcohol **6** (174 mg, 1.0 mmol) was esterified. Yield: 248 mg (99%). ^{1}H NMR ($CDCl_3$): δ 0.88 (t, $^3J_{H,H}$ = 6.7 Hz, 3 H, 10-CH_3), 1.28 (m, 10 H, 5-CH_2–9-CH_2), 2.12 (m, 2 H, 4-CH_2), 4.09 (s, 2 H, 12-CH_2), 4.67 (d, $^3J_{H,F}$ = 17.9 Hz, 2 H, 1-CH_2), 4.98 (dt, $^3J_{H,H}$ = 7.6 Hz, $^3J_{H,F}$ = 35.3 Hz, 1 H, 3-CH). ^{13}C NMR ($CDCl_3$): δ 14.0 (q, C-10), 22.6 (t, C-9), 23.6 (dt, $^3J_{C,F}$ = 3.8 Hz, C-4), 28.8, 29.0, 29.0 (t, C-5–C-7), 31.7 (t, C-8), 40.6 (t, C-12), 63.8 (dt, $^2J_{C,F}$ = 31.8 Hz, C-1), 113.0 (dd, $^2J_{C,F}$ = 12.7 Hz, C-3), 152.6 (d, $^1J_{C,F}$ = 253.0 Hz, C-2), 166.8 (s, C-11). ^{19}F NMR ($CDCl_3$): δ −119.8 (dt, $^3J_{H,F}$ = 19.1 Hz, $^3J_{H,F}$ = 36.2 Hz). GC/MS (70 eV): *m/z* (%) 252/250 (0/0) [M^+], 216 (1) [M^+ + H − Cl], 215 (4) [M^+ − Cl], 201 (3) [M^+ − CH_2Cl], 174 (4) [M^+ + H − $C_2H_2O_2Cl$], 167/165 (62/57) [M^+ − C_6H_{13}], 156 (5) [M^+ − $C_2H_3O_2Cl$], 136 (2) [156 − HF], 127 (9), 113 (13) [$C_8H_{17}^+$], 99 (23) [$C_7H_{13}^+$], 96 (24), 86 (35) [M^+ − $C_4H_4O_2FCl$], 77 (56) [C_2H_2OCl], 72 (46), 57 (21) [$C_4H_9^+$], 56 (441), 55 (51) [$C_4H_7^+$], 43 (100) [$C_3H_7^+$], 41 (54) [$C_3H_5^+$].

*4.5.7. (Z)-3-Chloroacetoxy-2-fluorocyclododecene (**23**)*

According to the general procedure the fluoroallylic alcohol **22** (400 mg, 2.0 mmol) was esterified to give the ester (*Z*)-**23** after chromatography (silica gel, cyclohexane/ethyl acetate, 40:1). Yield: 0.35 g (63%). ^{1}H NMR ($CDCl_3$): δ 1.17–1.69 (m, 14 H, 5-CH_2–11-CH_2), 1.73–1.90 (m, 2 H, 4-CH_2), 1.93–2.07 (m, 1 H, 12-CH_2), 2.33–2.48 (m, 1 H, 12-CH_2), 4.05 (s, 2 H, 14-CH_2), 5.01 (ddd, $^3J_{H,H}$ = 5.7 Hz, $^3J_{H,H}$ = 10.3 Hz, $^3J_{H,F}$ = 36.2 Hz, 1 H, 3-CH), 5.28 (ddd, $^3J_{H,H}$ =

5.2 Hz, $^3J_{H,H}$ = 10.0 Hz, $^3J_{H,F}$ = 23.8 Hz, 1 H, 1-CH). ^{13}C NMR ($CDCl_3$): δ 22.7 (dt, $^3J_{C,F}$ = 3.8 Hz, C-4), 23.1, 24.1, 24.3, 24.5, 25.5, 25.7, 26.1, 28.5 (t, C-5–C-12), 40.9 (t, C-14), 75.3 (dd, $^2J_{C,F}$ = 29.3 Hz, C-1), 112.9 (dd, $^2J_{C,F}$ = 14.0 Hz, C-3), 154.0 (d, $^1J_{C,F}$ = 255.6 Hz, C-2), 166.3 (s, C-13). ^{19}F NMR ($CDCl_3$): δ −128.6 (dd, $^3J_{H,F}$ = 22.9 Hz, $^3J_{H,F}$ = 36.2 Hz).

4.6. General procedure for synthesis of propionates (method B)

The corresponding fluorinated allylic alcohol **4** (10 mmol) in CH_2Cl_2 (40 mL) under stirring was treated with dicyclohexylcarbodiimide (DCC) (2.28 g, 11.0 mmol) and subsequently with propionic acid (814 mg, 11.0 mmol). Then a catalytic amount of *N*,*N*-dimethylaminopyridine (DMAP) was added and the mixture was stirred at room temperature overnight. The reaction mixture was treated with diethyl ether (200 mL), the dicyclohexyl urea was filtered and the organic layer was washed with water (3 × 40 mL), 5% aq. acetic acid (3 × 40 mL) and again with water (3 × 40 mL). The organic layer was dried over $MgSO_4$, the solvent was removed and the residue was purified by distillation or column chromatography.

4.6.1. 2-Fluoro-3-propionoxyhexene (*11a*)

According to the general procedure **4a** (590 mg, 5.00 mmol) and propionic acid (407 mg, 5.5. mmol) were reacted. The crude product was filtered through a 10 cm column (silica gel, *n*-pentane) to give **11a** as a colorless liquid. Yield: 590 mg (68%). ^{1}H NMR ($CDCl_3$): δ 0.94 (t, $^3J_{H,H}$ = 7.4 Hz, 3 H, 6-CH_3), 1.16 (t, $^3J_{H,H}$ = 7.6 Hz, 3 H, 9-CH_3), 1.38 (m, 2 H, 5-CH_2), 1.73 (m, 2 H, 4-CH_2), 2.36 (q, $^3J_{H,H}$ = 7.6 Hz, 2 H, 8-CH_2), 4.53 (dd, $^2J_{H,H}$ = 3.1 Hz, $^3J_{H,F}$ = 48.4 Hz, 1 H, 1-CH_2), 4.70 (dd, $^2J_{H,H}$ = 3.1 Hz, $^3J_{H,F}$ = 16.7 Hz, 1 H, 1-CH_2), 5.30 (dt, $^3J_{H,H}$ = 6.9 Hz, $^3J_{H,F}$ = 15.7 Hz, 1 H, 3-CH). ^{13}C NMR ($CDCl_3$): δ 9.0 (q, C-9), 13.6 (q, C-6), 18.2 (t, C-5), 27.6 (t, C-8), 33.2 (t, C-4), 70.9 (dd, $^2J_{C,F}$ = 34.3 Hz, C-3), 92.3 (dt, $^2J_{C,F}$ = 17.8 Hz, C-1), 162.9 (d, $^1J_{C,F}$ = 260.7 Hz, C-2), 173.3 (s, C-7). ^{19}F NMR ($CDCl_3$):δ −111.5 (ddd, $^3J_{H,F}$ = 15.3 Hz, $^3J_{H,F}$ = 17.2 Hz, $^3J_{H,F}$ = 47.7 Hz). GC/MS (70 eV): *m*/*z* (%) 174 (3) [M^+], 145 (11) [$M^+ - C_2H_6$], 132 (8), 118 (24) [$C_6H_{11}OF^+$ (McLafferty)], 100 (38) [118 − H_2O], 85 (27) [100 − CH_3], 73 (8) [$C_3H_5O_2^+$], 57 (100) [$C_3H_5O^+$], 41 (7) [$C_3H_7^+$].

4.6.2. 2-Fluoro-3-propionoxydecene (*11b*)

According to the general procedure **4b** (1.74 g, 10.0 mmol) and propionic acid (814 mg, 11.0 mmol) were reacted. The crude product was filtered through a 10 cm column (silica gel, cyclohexane/ethyl acetate, 10:1) to give **11b** as a colorless liquid. Yield: 2.06 g (90%). ^{1}H NMR ($CDCl_3$): δ 0.89 (t, $^3J_{H,H}$ = 6.9 Hz, 3 H, 10-CH_3), 1.15 (t, $^3J_{H,H}$ = 7.6 Hz, 3 H, 13-CH_3), 1.29 (m, 10 H, 5-CH_2–9-CH_2), 1.73 (m, 2 H, 4-CH_2), 2.35 (q, $^3J_{H,H}$ = 7.6 Hz, 2 H, 12-CH_2), 4.52 (dd, $^2J_{H,H}$ = 3.1 Hz, $^3J_{H,F}$ = 48.4 Hz, 1 H, 1-CH_2), 4.69 (dd, $^2J_{H,H}$ = 3.1 Hz, $^3J_{H,F}$ = 16.7 Hz, 1 H, 1-CH_2), 5.28 (dt, $^3J_{H,H}$ = 6.7 Hz, $^3J_{H,F}$ = 16.0 Hz, 1 H, 3-CH). ^{13}C NMR ($CDCl_3$): δ 9.0 (q, C-13), 14.0 (q, C-10), 22.6 (t, C-9), 24.9 (t, C-5), 27.6 (t, C-12), 29.0 (t, C-4), 29.1 (t, C-7), 31.1 (t, C-6), 31.7 (t, C-8), 71.2 (dd, $^2J_{C,F}$ = 30.5 Hz, C-3), 92.3 (dt, $^2J_{C,F}$ = 17.8 Hz, C-1), 162.9 (d, $^1J_{C,F}$ = 259.4 Hz, C-2), 173.3 (s, C-11). ^{19}F NMR ($CDCl_3$): δ −111.5 (ddd, $^3J_{H,F}$ = 15.3 Hz, $^3J_{H,F}$ = 17.2 Hz, $^3J_{H,F}$ = 49.6 Hz). GC/MS (70 eV): *m*/*z* (%) 230 (0) [M^+], 174 (14) [$M^+ - C_3H_4O$], 156 (2) [$M^+ - C_3H_6O_2$], 145 (4) [$M^+ - C_6H_{13}$], 127 (6), 113 (3) [$C_8H_{17}^+$], 86 (10), 57 (100) [$C_3H_5O^+$] and [$C_4H_9^+$], 55 (18) [$C_4H_7^+$], 43 (17) [$C_3H_7^+$], 41 (23) [$C_3H_5^+$].

4.6.3. 2-Fluoro-3-propionoxyhexadec-1-ene (*11c*)

According to the general procedure **4c** (1.032 g, 4.00 mmol) and propionic acid (407 mg 5.5 mmol) were reacted. The crude product was filtered through a 10 cm column (silica gel, cyclohexane/ethyl acetate, 10:1) to give **11c** as a colorless liquid. Yield: 931 mg (74%). ^{1}H NMR ($CDCl_3$): δ 0.88 (t, $^3J_{H,H}$ = 6.9 Hz, 3 H, 16-CH_3), 1.16 (t, $^3J_{H,H}$ = 7.6 Hz, 3 H, 19-CH_3), 1.26 (m, 22 H, 5-CH_2–15-CH_2), 1.73 (m, 2 H, 4-CH_2), 2.36 (q, $^3J_{H,H}$ = 7.6 Hz, 2 H, 18-CH_2), 4.52 (dd, $^2J_{H,H}$ = 3.1 Hz, $^3J_{H,F}$ = 48.4 Hz, 1 H, 1-CH_2), 4.70 (dd, $^2J_{H,H}$ = 3.1 Hz, $^3J_{H,F}$ = 16.7 Hz, 1 H, 1-CH_2), 5.28 (dt, $^3J_{H,H}$ = 6.9 Hz, $^3J_{H,F}$ = 16.0 Hz, 1 H, 3-CH). ^{13}C NMR ($CDCl_3$): δ 9.0 (q, C-19); 14.0 (q, C-16), 22.7 (t, C-15), 24.9 (t, C-5), 27.6 (t, C-18), 29.2, 29.3, 29.4, 29.5, 29.6, 29.6, 31.5, 31.9 (t, C-4 and C-6–C-14), 71.2 (dd, $^2J_{C,F}$ = 31.8 Hz, C-3), 92.3 (dd, $^2J_{C,F}$ = 17.8 Hz, C-1), 163.0 (d, $^1J_{C,F}$ = 260.7 Hz, C-2), 173.3 (s, C-17). ^{19}F NMR ($CDCl_3$): δ −111.4 (ddd, $^3J_{H,F}$ = 17.2 Hz, $^3J_{H,F}$ = 15.3 Hz, $^3J_{H,F}$ = 47.7 Hz). GC/MS (70 eV): *m*/*z* (%) 314 (0.4) [M^+], 313 (0.4) [M^+ − H], 299 (0.5) [$M^+ - CH_3$], 285 (14) [$M^+ - C_2H_5$], 271 (0.8) [$M^+ - C_3H_7$], 258 (33) [$M^+ + H - C_3H_5O$], 229 (3), 211 (16), 180 (5), 173 (4), [$M^+ - C_{10}H_{21}$], 146 (15), 109 (11), 86 (44), 57 (100) [$C_3H_5O^+$], 43 (41) [$C_3H_7^+$].

4.6.4. 2-Fluoro-3-propionoxypropene (*11d*)

According to the general procedure **4d** (760 mg, 10.0 mmol) and propionic acid (814 mg, 11.0 mmol) were reacted to give **11d** after careful removing of the solvent using a Vigreux column and bulp-to-bulp distillation of the residue. Yield: 700 mg (50%). ^{1}H NMR ($CDCl_3$): δ 1.17 (t, $^3J_{H,H}$ = 7.6 Hz, 3 H, 6-CH_3), 2.39 (q, $^3J_{H,H}$ = 7.6 Hz, 2 H, 5-CH_2), 4.60 (d, $^3J_{H,F}$ = 14.1 Hz, 2 H, 1-CH_2), 4.61 (dd, $^2J_{H,H}$ = 3.3 Hz, $^3J_{H,F}$ = 47.5 Hz, 1 H, 3-CH_2), 4.79 (dd, $^2J_{H,H}$ = 3.3 Hz, $^3J_{H,F}$ = 16.9 Hz, 1 H, 3-CH_2). ^{13}C NMR ($CDCl_3$): δ 8.9 (q, C-6), 27.3 (t, C-5), 61.1 (dt, $^2J_{C,F}$ = 35.6 Hz, C-1), 94.0 (dt, $^2J_{C,F}$ = 17.8 Hz, C-3), 160.5 (d, $^1J_{C,F}$ = 256.9 Hz, C-2), 173.6 (s, C-4). ^{19}F NMR ($CDCl_3$): δ −105.9 (ddt, $^3J_{H,F}$ = 15.3 Hz, $^3J_{H,F}$ = 15.4 Hz, $^3J_{H,F}$ = 45.8 Hz). GC/MS (70 eV): *m*/*z* (%) 132 (1) [M^+], 75 (3) ($C_3H_4OF^+$], 57 (100) [$C_3H_5O^+$], 39 (4).

4.6.5. (Z)-2-Fluoro-1-propionoxydec-2-ene (*13*)

According to the general procedure **6** (174 mg, 1.00 mmol) was reacted with propionic acid (82 mg

1.10 mmol). After chromatographic purification (10 cm silica gel, cyclohexane/ethyl acetate, 10:1) the product **13** was isolated as a colorless oil. Yield: 216 mg (94%). ^{1}H NMR ($CDCl_3$): δ 0.88 (t, $^3J_{H,H}$ = 6.9 Hz, 3 H, 10-CH_3), 1.15 (t, $^3J_{H,H}$ = 7.6 Hz, 3 H, 13-CH_3), 1.28 (m, 10 H, 5-CH_2–9-CH_2), 2.11 (m, 2 H, 4-CH_2), 2.37 (q, $^3J_{H,H}$ = 7.6 Hz, 2 H, 12-CH_2), 4.56 (d, $^3J_{H,F}$ = 17.9 Hz, 2 H, 1-CH_2), 4.91 (dt, $^3J_{H,H}$ = 7.6 Hz, $^3J_{H,F}$ = 35.8 Hz, 1 H, 3-CH). ^{13}C NMR ($CDCl_3$): δ 8.9 (q, C-13), 14.0 (q, C-10), 22.6 (t, C-9), 23.5 (dt, $^3J_{C,F}$ = 4.0 Hz, C-4), 27.4 (t, C-12), 28.9, 29.0, 29.0 (t, C-5–C-7), 31.7 (t, C-8), 62.2 (dt, $^2J_{C,F}$ = 31.8 Hz, C-1), 111.6 (dd, $^2J_{C,F}$ = 14.0 Hz, C-3), 152.7 (d, $^1J_{C,F}$ = 253.0 Hz, C-2), 173.8 (s, C-11). ^{19}F NMR ($CDCl_3$): δ −119.5 (dt, $^3J_{H,F}$ = 19.1 Hz, $^3J_{H,F}$ = 36.2 Hz). GC/MS (70 eV): *m/z* (%) 230 (1) [M^+], 201 (2) [$M^+ - C_2H_9$], 187 (1) [$M^+ - C_3H_7$], 174 (6) [$M^+ + H - C_3H_5O_2$], 156 (7) [174 − H_2O], 145 (11), 127 (3), 113 (5) [$C_8H_{17}^+$], 99 (9) [$C_7H_{15}^+$], 86 (11), 72 (17), 67 (8), 57 (100) [C_3H_5O], 43 (17) [$C_3H_7^+$], 41 (16) [$C_3H_5^+$].

*4.6.6. (Z)-2-Fluoro-3-propionoxycyclododec-2-ene (**24**)*

According to the general procedure the allylic alcohol **22** (202 mg, 1.00 mmol) was esterified. After chromatographic purification (silica gel, cyclohexane/ethyl acetate, 10:1) the ester **24** was isolated as a viscous oil. Yield: 210 mg (82%). ^{1}H NMR ($CDCl_3$): δ 1.15 (t, $^3J_{H,H}$ = 7.4 Hz, 15-CH_3), 1.17–1.69 (m, 14 H, 5-CH_2–11-CH_2), 1.73–1.90 (m, 2 H, 4-CH_2), 1.93–2.07 (m, 1 H, 12-CH_2), 2.33 (q, $^3J_{H,H}$ = 7.4 Hz, 2 H, 14-CH_2), 2.33–2.48 (m, 1 H, 12-CH_2), 4.95 (ddd, $^3J_{H,H}$ = 5.7 Hz, $^3J_{H,H}$ = 10.0 Hz, $^3J_{H,F}$ = 36.5 Hz, 1 H, 3-CH), 5.23 (ddd, $^3J_{H,H}$ = 5.2 Hz, $^3J_{H,H}$ = 9.8 Hz, $^3J_{H,F}$ = 23.8 Hz, 1 H, 1-CH). ^{13}C NMR ($CDCl_3$): δ 9.0 (q, C-15), 22.6 (dt, $^3J_{C,F}$ = 3.8 Hz, C-4), 23.1, 24.2, 24.4, 24.5, 25.5, 25.8, 26.1, 27.7, 28.8 (t, C-5–C-12, C-14), 73.1 (dd, $^2J_{C,F}$ = 29.2 Hz, C-1), 111.6 (dd, $^2J_{C,F}$ = 14.0 Hz, C-3), 155.0 (d, $^1J_{C,F}$ = 255.6 Hz, C-2), 173.4 (s, C-13). ^{19}F NMR ($CDCl_3$): δ −127.9 (dd, $^3J_{H,F}$ = 24.8 Hz, $^3J_{H,F}$ = 36.2 Hz).

4.7. General procedure for the Johnson-Claisen rearrangement

In a 10 mL round bottom flask a solution of the corresponding alcohol (1 mmol), trimethyl orthoacetate (1.47 mL) and one drop of propanoic acid was refluxed in dry toluene (2 mL) for 5 h. After cooling to room temperature, the mixture was poured into water (20 mL) and the aqueous phase was extracted with diethyl ether (3 × 10 mL). The combined ethereal extract was washed with brine (10 mL) and dried over $MgSO_4$. The product was purified by column chromatography (silica gel, cyclohexane/ethyl acetate, 20:1).

*4.7.1. Methyl (Z)-4-fluoroct-4-enecarboxylate (**7a**)*

According to the general procedure, from allylic alcohol **4a** (118 mg, 1.00 mmol), the ester **7a** was formed. Yield: 170 mg (96%). ^{1}H NMR ($CDCl_3$): δ 0.89 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, 8-CH_3), 1.35 (m, 2 H, 7-CH_2), 2.03 (m, 2 H, 6-CH_2), 2.48 (m, 4 H, 2-CH_2 and 3-CH_2), 3.68 (s, 3 H, 9-CH_3), 4.54 (dt, $^3J_{H,H}$ = 7.4 Hz, $^3J_{H,F}$ = 45.3 Hz, 1 H, 5-CH). ^{13}C NMR ($CDCl_3$): δ 13.4 (q, C-8), 22.5 (t, C-7), 25.4 (dt, $^3J_{C,F}$ = 5.1 Hz, C-6), 27.6 (dt, $^2J_{C,F}$ = 29.2 Hz, C-3), 31.2 (t, C-2), 51.5 (q, C-9), 105.8 (dd, $^2J_{C,F}$ = 15.3 Hz, C-5), 157.7 (d, $^1J_{C,F}$ = 251.8 Hz, C-4), 172.8 (s, C-1). ^{19}F NMR ($CDCl_3$): δ −112.0 (m). GC/MS (70 eV): *m/z* (%) 175 (3) [M^+ + H], 174 (21) [M^+], 154 (18) [M^+ − HF], 143 (23) [$M^+ - CH_3O$], 132 (10) [$M^+ + H - C_3H_7$], 111 (9), 101 (59) [$M^+ - C_3H_5O_2$], 97 (62), 85 (73), 74 (100), [$C_3H_6O_2^+$], 59 (31) [$C_2H_3O_2^+$], 55 (13), 43 (19) [$C_3H_7^+$], 41 (14) [$C_3H_5^+$].

*4.7.2. Methyl (Z)-4-fluorododec-4-enecarboxylate (**7b**)*

According to the general procedure, from allylic alcohol **4b** (174 mg, 1.00 mmol) the ester **7b** was formed. Yield: 194 mg (84%). ^{1}H NMR ($CDCl_3$): δ 0.80 (t, $^3J_{H,H}$ = 6.6 Hz, 3 H, 12-CH_3), 1.23 (m, 10 H, 7-CH_2–11-CH_2), 1.96 (m, 2 H, 6-CH_2), 2.40 (m, 4 H, 2-CH_2 and 3-CH_2), 3.61 (s, 3 H, 13-CH_3), 4.46 (dt, $^3J_{H,H}$ = 7.4 Hz, $^3J_{H,F}$ = 37.7 Hz, 1 H, 5-CH). ^{13}C NMR ($CDCl_3$): δ 13.9 (q, C-12), 22.5 (t, C-11), 23.4 (dt, $^3J_{C,F}$ = 5.1 Hz, C-6), 27.3 (t, C-2), 29.0, 31.1, 31.8 (t, C-7–C-10), 29.2 (dt, $^2J_{C,F}$ = 28.0 Hz, C-3), 51.5 (q, C-13), 106.0 (dd, $^2J_{C,F}$ = 15.3 Hz, C-5), 157.6 (d, $^1J_{C,F}$ = 251.8 Hz, C-4), 172.6 (s, C-1). ^{19}F NMR ($CDCl_3$): δ −112.1 (m). GC/MS (70 eV): *m/z* (%): 230 (10) [M^+], 211 (4) [M^+ − F], 210 (28) [M^+ − HF], 199 (3) [$M^+ - OCH_3$], 178 (20) [210 − CH_4O], 150 (20) [178 − CO], 145 (30), 136 (51) [$M^+ - HF - C_3H_6O_2$], 97 (45) [$C_7H_{15}^+$], 85 (53) [$C_6H_{13}^+$], 74 (100) [$C_3H_6O_2^+$ (McLafferty)], 59 (21) [$CO_2CH_3^+$], 57 (11) [$C_4H_9^+$], 55 (22) [$C_4H_7^+$], 43 (36) [$C_3H_7^+$], 41 [$C_3H_5^+$].

*4.7.3. Methyl (Z)-4-fluorooctadec-4-enoate (**7c**)*

According to the general procedure, from allylic alcohol **4c** (258 mg, 1.00 mmol) the ester **7c** was formed as a white waxy solid. Yield: 248 mg (81%). m.p. 32 °C. ^{1}H NMR ($CDCl_3$): δ 0.88 (t, $^3J_{H,H}$ = 6.9 Hz, 3 H, 18-CH_3), 1.26 (m, 22 H, 7-CH_2–17-CH_2), 2.15 (m, 2 H, 6-CH_2), 2.68 (m, 4 H, 2-CH_2 and 3-CH_2), 3.67 (s, 3 H, 19-CH_3), 4.53 (dt, $^3J_{H,F}$ = 37.7 Hz, $^3J_{H,H}$ = 7.4 Hz, 1 H, 5-CH). ^{13}C NMR ($CDCl_3$): δ 14.0 (q, C-18), 22.7 (t, C-17), 23.5 (dt, $^3J_{C,F}$ = 5.1 Hz, C-6), 27.5 (dt, $^2J_{C,F}$ = 29.3 Hz, C-3), 29.1, 29.3, 29.4, 29.6, 29.6, 31.2, 31.9 (t, C-7–C-16 and C-2), 51.5 (q, C-19), 106.1 (dd, $^2J_{C,F}$ = 15.3 Hz, C-5), 157.6 (d, $^1J_{C,F}$ = 253.0 Hz, C-4), 172.7 (s, C-1). ^{19}F NMR ($CDCl_3$): δ −112.1 (m). GC/MS (70 eV): *m/z* (%) 314 (1) [M^+], 294 (8) [M^+ − HF], 262 (4), 220 (13), 180 (6), 145 (24) [$M^+ - C_{12}H_{25}$], 132 (21) [$M^+ + H - C_{13}H_{27}$], 97 (34) [$C_7H_{13}^+$], 85 (42) [$C_6H_{13}^+$], 74 (100) [$C_3H_6O_2^+$], 69 (23) [$C_5H_{11}^+$], 67 (17) [$C_6H_9^+$], 57 (27) [$C_4H_9^+$], 55 (25) [$C_4H_7^+$], 43 (41) [$C_3H_7^+$], 41 (33) [$C_3H_5^+$]. Calcd. for $C_{19}H_{35}FO_2$ (314.26): C 72.57, H 11.22. Found: C 72.50, H 11.43.

*4.7.4. Ethyl 3-(1-fluoroethenyl)-decanoate (**8**)*

According to the general procedure, the allylic alcohol **6** (174 mg, 1.00 mmol) was refluxed with triethyl orthoacetate (1 mL) and one drop of propanoic acid for 20 h. After work-

up the residue was purified by HPLC using a RP-18 column and methanol to give the ester **8** as a colorless liquid. Yield: 94 mg (39%). ^{1}H NMR ($CDCl_3$): δ 0.79 (t, $^3J_{H,H}$ = 6.7 Hz, 3 H, 12-CH_3), 1.16 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, 14-CH_3), 1.18 (m, 12 H, 6-CH_2–11-CH_2), 2.28 (dd, $^2J_{H,H}$ = 15.5 Hz, $^3J_{H,H}$ = 6.9 Hz, 1 H, 2-CH_2), 2.41 (dd, $^2J_{H,H}$ = 15.5 Hz, $^3J_{H,H}$ = 7.6 Hz, 1 H, 2-CH_2), 2.61 (m, 1 H, 3-CH), 4.04 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, 13-CH_2), 4.18 (dd, $^2J_{H,H}$ = 2.9 Hz, $^3J_{H,F}$ = 50.3 Hz, 1 H, 5-CH_2), 4.45 (ddd, $^2J_{H,H}$ = 2.9 Hz, $^3J_{H,F}$ = 16.7 Hz, $^4J_{H,H}$ = 0.5 Hz, 1 H, 5-CH_2). ^{13}C NMR ($CDCl_3$): δ 14.0 (q, C-12), 14.2 (q, C-14), 22.6 (t, C-11), 26.8 (t, C-6), 29.1, 29.3 (t, C-7 and C-9), 31.5 (t, C-8), 31.8 (t, C-10), 37.4 (t, C-2), 39.2 (dd, $^2J_{C,F}$ = 25.4 Hz, C-3), 60.4 (t, C-13), 90.5 (dt, $^2J_{C,F}$ = 20.4 Hz, C-5), 167.1 (d, $^1J_{C,F}$ = 260.7 Hz, C-4), 171.8 (s, C-1). ^{19}F NMR ($CDCl_3$): δ −106.2 (ddd, $^3J_{H,F}$ = 19.1 Hz, $^3J_{H,F}$ = 22.9 Hz, $^3J_{H,F}$ = 51.5 Hz). GC/MS (70 eV): *m/z* (%) 244 (0) [M^+], 224 (1) [M^+ − HF], 216 (0) [M^+ − C_2H_4 (McLafferty)], 201 (1) [216 − CH_3], 195 (2), 181 (2) [216 − HF − CH_3], 167 (5) [M^+ − HF − C_4H_9], 156 (1) [$C_{10}H_{17}F^+$ (McLafferty)], 146 (28) [M^+ − C_7H_{14}], 156 (16) [156 − HF], 111 (19), 99 (17) [$C_7H_{15}^+$], 95 (19), 93 (20), 81 (27), 73 (100) [$C_3H_5O_2^+$], 57 (29) [$C_4H_9^+$], 55 (56) [$C_4H_7^+$], 43 (61) [$C_3H_7^+$], 41 (72) [$C_3H_5^+$].

4.8. General procedure for the Ireland-Claisen rearrangement

In a dried Schlenk vessel the respective allylic ester (2.00 mmol) in CH_2Cl_2 (4 mL) was treated under argon with triethylamine (0.60 g, 6.0 mmol) and TMSOTf (0.46 g, 2.4 mmol) and stirred at room temperature for 4 days, while the solution turned from colorless to dark red-brown. Then 2N HCl (15 mL) was added and the mixture was stirred vigorously for 4 h. The phases were separated and the aqueous was extracted with diethyl ether (3 × 15 mL). Further work-up was different for the respective products and will be mentioned below.

4.8.1. 3-(Trimethylsilylacetoxy)-2-fluorodecene (*14*)

According to general procedure for the Ireland-Claisen rearrangement, the ester **9b** (0.43 g, 2.0 mmol) in dry diethyl ether (4 mL) was stirred with triethylamine (0.61 g, 6.0 mmol) and TMSOTf (0.46 g, 2.4 mmol) at room temperature for 4 days. The brown mixture was hydrolysed with water (20 mL) and extracted with diethyl ether (2 × 20 mL). After washing the combined ethereal phase with water (20 mL) and drying over $MgSO_4$, the solvent was evaporated and the residue was filtered through a silica gel column (pentane/diethyl ether, 15:1) to get a colorless oil. Yield: 0.42 g containing 28% of starting material **9b** and 72% of **14**. This mixture could not be separated. NMR spectroscopic data of compound **14** were extracted from the spectra of this mixture. ^{1}H NMR ($CDCl_3$): δ 0.00 (s, 9 H, 13-CH_3), 0.75 (t, $^3J_{H,H}$ = 6.7 Hz, 3 H, 10-CH_3), 1.14 (m, 10 H, 5-CH_2–9-CH_2), 1.59 (m, 2 H, 4-CH_2), 1.80 (d, $^2J_{H,H}$ = 1.9 Hz, 2 H, 12-CH_2), 4.42 (dd, $^2J_{H,H}$ = 3.1 Hz, $^3J_{H,F}$ = 48.4 Hz, 1 H, 1-CH_2), 4.57 (dd, $^2J_{H,H}$ = 3.1 Hz, $^3J_{H,F}$ = 16.7 Hz, 1 H, 1-CH_2), 5.13 (dt, $^3J_{H,H}$ = 6.9 Hz, $^3J_{H,F}$ = 18.1 Hz, 1 H, 3-CH). ^{13}C NMR ($CDCl_3$): δ −2.9 (q, C-13), −1.4 (q, C-13), 14.1 (q, C-10), 22.6 (t, C-9), 25.0 (t, C-5), 26.9 (t, C-12), 29.1 (t, C-7), 29.1 (t, C-6), 31.1 (t, C-4), 31.8 (t, C-8), 71.0 (ds, $^2J_{C,F}$ = 30.5 Hz, C-3), 92.8 (dt, $^2J_{C,F}$ = 17.8 Hz, C-1), 162.9 (d, $^1J_{C,F}$ = 262.0 Hz, C-2), 171.9 (s, C-11). ^{19}F NMR ($CDCl_3$): δ −112.1 (m). GC/MS (70 eV): *m/z* (%) 288 (0.2) [M^+], 273 (0.7) [M^+ − CH_3], 259 (4) [M^+ − C_2H_5], 246 (18) [M^+ − C_3H_6], 204 (14), 156 (6) [$C_{10}H_{17}F^+$ (McLafferty)], 115 (100) [$C_5H_{11}OSi^+$], 75 (38) [$C_2H_7OSi^+$], 73 (77) [$C_3H_9Si^+$], 55 (19) [$C_4H_7^+$], 43 (38) [$C_3H_7^+$].

4.8.2. (Z)-2-Chloro-4-fluorooct-4-enoic acid (*15a*)

According to general procedure the ester **10a** (398 mg, 2.00 mmol) was rearranged. Different from the general procedure the combined ethereal phase was extracted with 1N NaOH (3 × 15 mL) and the ethereal phase was trashed. The basic solution was acidified with conc. HCl and extracted with diethyl ether (3 × 15 mL). The combined ethereal layer was washed with water (15 mL) and dried over $MgSO_4$. After evaporation of the solvent the product **15a** was isolated without further purification. Yield: 110 mg (29%). ^{1}H NMR ($CDCl_3$): δ 0.90 (t, $^3J_{H,H}$ = 7.4 Hz, 3 H, 8-CH_3), 1.38 (tq, $^3J_{H,H}$ = 7.4 Hz, $^3J_{H,H}$ = 7.2 Hz, 2 H, 7-CH_2), 2.07 (m, 2 H, 6-CH_2), 2.71 (ddd, $^2J_{H,H}$ = 15.0 Hz, $^3J_{H,H}$ = 7.8 Hz, $^3J_{H,F}$ = 22.7 Hz, 1 H, 3-CH_2), 2.96 (ddd, $^2J_{H,H}$ = 15.0 Hz, $^3J_{H,H}$ = 6.2 Hz, $^3J_{H,F}$ = 15.0 Hz, 1 H, 3-CH_2), 4.49 (dd, $^3J_{H,H}$ = 7.8 Hz, $^3J_{H,H}$ = 6.4 Hz, 1 H, 2-CHCl), 4.72 (dt, $^3J_{H,H}$ = 7.5 Hz, $^3J_{H,F}$ = 37.3 Hz, 1 H, 5-CH), 10.50 (br s, 1 H, COOH). ^{13}C NMR ($CDCl_3$): δ 13.5 (q, C-8), 22.4 (t, C-7), 25.6 (dt, $^3J_{C,F}$ = 3.8 Hz, C-6), 37.9 (dt, $^2J_{C,F}$ = 28.0 Hz, C-3), 53.1 (d, C-2), 110.1 (dd, $^2J_{C,F}$ = 14.0 Hz, C-5), 153.3 (d, $^1J_{C,F}$ = 251.8 Hz, C-4), 174.7 (s, C-1). ^{19}F NMR ($CDCl_3$): δ −114.3 (ddd, $^3J_{H,H}$ = 17.2 Hz, $^3J_{H,F}$ = 22.9 Hz, $^3J_{H,F}$ = 38.1 Hz). GC/MS (70 eV) (TMS-Ester): *m/z* (%) 267 (1) [M^+ + H], 266 (1) [M^+], 253/251 (5/1) [M^+ − CH_3], 231 (32) [M^+ − Cl], 215 (31) [M^+ − HCl − CH_3], 187 (6), 173 (12), 168/166 (12/6) [$C_5H_{11}O_2SiCl^+$ (McLafferty)], 150 (15), 141 (36) [M^+ − HCl − $(CH_3)_3SiO$], 121 (9) [141 − HF], 99 (12), 93 (32), 77 (39), 73 (100) [$(CH_3)_3Si^+$], 45 (12).

4.8.3. (Z)-2-Chloro-4-fluorododec-4-enoic acid (*15b*)

According to general procedure the ester **10b** (625 mg, 2.50 mmol) was rearranged and the product **15b** was isolated as described for compound **15a**. Yield: 340 mg (54%). ^{1}H NMR ($CDCl_3$): δ 0.88 (t, $^3J_{H,H}$ = 6.9 Hz, 3 H, 12-CH_3), 1.27 (m, 10 H, 7-CH_2–11-CH_2), 2.07 (m, 2 H, 6-CH_2), 2.71 (m, 1 H, 3-CH_2), 2.97 (m, 2 H, 3-CH_2), 4.49 (dd, $^3J_{H,H}$ = 7.6 Hz, $^3J_{H,H}$ = 6.7 Hz, 1 H, 2-CHCl), 4.71 (dt, $^3J_{H,H}$ = 7.5 Hz, $^3J_{H,F}$ = 37.4 Hz, 1 H, 5-CH). ^{13}C NMR ($CDCl_3$): δ 14.0 (q, C-12), 22.6 (t, C-11), 23.6 (dt, $^3J_{C,F}$ = 5.1 Hz, C-6), 29.0, 29.1, 29.5 (t, C-7–C-9), 31.8 (t, C-10), 37.9 (dt, $^2J_{C,F}$ = 28.0 Hz, C-3), 53.0 (d, C-2), 110.5 (dd, $^2J_{C,F}$ = 15.3 Hz, C-5), 153.1 (d, $^1J_{C,F}$ = 251.8 Hz, C-4), 174.4 (s, C-1). ^{19}F NMR ($CDCl_3$): δ −114.5 (ddd, $^3J_{H,F}$ = 15.3 Hz, $^3J_{H,F}$ = 22.9 Hz, $^3J_{H,F}$ =

38.2 Hz). GC/MS (70 eV) (TMS-Ester): *m/z* (%) 322 (1) [M^+], 307 (4) [$M^+ - CH_3$], 287 (42) [$M^+ - Cl$], 271 (17) [$M^+ - HCl - CH_3$], 250 (1) [$M^+ + H - TMS$], 227 (1), 197 (11), 166 (33), 150 (23), 73 (100) [$(CH_3)_3Si^+$], 42 (26) [$C_3H_7^+$].

4.8.3.1. Methyl (Z)-2-chloro-4-fluorododec-4-enoate. (*Z*)-2-Chloro-4-fluorododec-4-enoic acid (**15b**) (250 mg, 1.00 mmol) and methanol (35.2 mg, 1.10 mmol) were dissolved in pentane (50 mL). DCC (228 mg, 1.1 mmol) and a catalytic amount of DMAP were added and the mixture was stirred at room temperature overnight. The resulting suspension was filtered and the colorless solution was washed with water (3 × 20 mL), 5% aqueous acetic acid (3 × 20 mL) and again with water (20 mL). The solution was dried over $MgSO_4$, the solvent was removed and the residue was purified by column chromatography (silica gel, cyclohexane/ethyl acetate, 20:1) and the ester was isolated as a colorless liquid. Yield: 228 mg (86%). ^{1}H NMR ($CDCl_3$): δ 0.88 (t, $^3J_{H,H}$ = 6.9 Hz, 3 H, 12-CH_3), 1.27 (m, 10 H, 7-CH_2–11-CH_2), 2.05 (m, 2 H, 6-CH_2), 2.70 (ddd, $^2J_{H,H}$ = 15.3 Hz, $^3J_{H,H}$ = 8.1 Hz, $^3J_{H,F}$ = 22.7 Hz, 1 H, 3-CH_2), 2.92 (ddd, $^2J_{H,H}$ = 15.3 Hz, $^3J_{H,H}$ = 6.7 Hz, $^3J_{H,F}$ = 15.3 Hz, 1 H, 3-CH_2), 3.79 (s, 3 H, 13-CH_3), 4.44 (dd, $^3J_{H,H}$ = 6.7 Hz, $^3J_{H,H}$ = 7.9 Hz, 1 H, 2-CH), 4.68 (dt, $^3J_{H,H}$ = 7.6 Hz, $^3J_{H,F}$ = 37.4 Hz, 1 H, 5-CH). ^{13}C NMR ($CDCl_3$): δ 14.0 (q, C-12), 22.6 (t, C-11), 23.6 (dt, $^3J_{C,F}$ = 3.1 Hz, C-6), 29.0, 29.0, 29.2 (t, C-7–C-9), 31,8 (t, C-10), 51.6 (d, C-2), 53.1 (q, C-13), 110.1 (dd, $^2J_{C,F}$ = 14.0 Hz, C-5), 153.5 (d, $^1J_{C,F}$ = 251.8 Hz, C-4), 176.0 (s, C-1). ^{19}F NMR ($CDCl_3$): δ −114.2 (ddd, $^3J_{H,F}$ = 15.3 Hz, $^3J_{H,F}$ = 21.0 Hz, $^3J_{H,F}$ = 38.2 Hz). GC/MS (70 eV): *m/z* (%) 266/264 (1/2) [M^+], 229 (93) [$M^+ - Cl$], 228 (23) [$M^+ - HCl$], 209 (4) [$M^+ - HF - Cl$], 208 (4) [$M^+ - HF - HCl$], 177 (5), 157 (8) [$C_{10}H_{18}F^+$], 131 (40), 110/108 (28/100) [$C_3H_5O_2Cl^+$ (McLafferty)], 81 (26), 59 (29) [$C_2H_3O_2^+$], 55 (34) [$C_4H_7^+$], 43 (56) [$C_3H_7^+$], 41 (32) [$C_3H_5^+$].

*4.8.4. (Z)-2-Chloro-4-fluorooctadec-4-enoic acid (**15c**)*

According to general procedure the ester **10c** (541 mg, 1.61 mmol) was rearranged. The combined ethereal extract was washed with brine (2 × 15 mL), dried over $MgSO_4$, and the solvent was removed. The crude product was purified by HPLC using an RP-18 column and methanol as the solvent. The carboxylic acid **15c** was isolated as a white solid. Yield: 353 mg (66%). m.p. 48 °C. ^{1}H NMR ($CDCl_3$): δ 0.88 (t, $^3J_{H,H}$ = 6.6 Hz, 3 H, 18-CH_3), 1.26 (m, 22 H, 7-CH_2–17-CH_2), 2.08 (dt, $^3J_{H,H}$ = 6.7 Hz, $^3J_{H,H}$ = 6.9 Hz, 2 H, 6-CH_2), 2.72 (ddd, $^2J_{H,H}$ = 15.0 Hz, $^3J_{H,H}$ = 7.9 Hz, $^3J_{H,F}$ = 21.9 Hz, 1 H, 3-CH_2), 2.96 (ddd, $^2J_{H,H}$ = 15.0 Hz, $^3J_{H,H}$ = 6.2 Hz, $^3J_{H,F}$ = 21.2 Hz, 1 H, 3-CH_2), 4.47 (dd, $^3J_{H,H}$ = 6.2 Hz, $^3J_{H,H}$ = 7.9 Hz, 1 H, 2-CH), 4.71 (dt, $^3J_{H,H}$ =7.6 Hz, $^3J_{H,F}$ = 37.2 Hz, 1 H, 5-CH), 9.45 (br s, 1 H, COOH). ^{13}C NMR ($CDCl_3$): δ 14.1 (q, C-18), 22.7 (t, C-17), 23.6 (dt, $^3J_{C,F}$ = 3.8 Hz, C-6), 29.1, 29.1, 29.4, 29.6, 29.6, 29.7 (t, C-7–C-15), 31.9 (t, C-16), 38.0 (dt, $^2J_{C,F}$ = 29.2 Hz, C-3), 53.1 (d, C-2), 110.4 (dd, $^2J_{C,F}$ = 14.0 Hz, C-5), 153.2 (d, $^1J_{C,F}$ = 251.8 Hz, C-4), 174.3 (s, C-1). ^{19}F NMR ($CDCl_3$): δ −114.4 (ddd, $^3J_{H,F}$ = 17.2 Hz, $^3J_{H,F}$ = 22.9 Hz, $^3J_{H,F}$ = 38.2 Hz). GC/MS (70 eV) (TMS-Ester): *m/z* (%) 406 (1) [M^+], 391 (3) [$M^+ - CH_3$], 371 (34) [$M^+ + H - Cl$], 370 (6) [$M^+ - Cl$], 355 (22) [370 − CH_3], 311 (1), 281 (6), 252 (2), 233 (2), 173 (8), 166 (43) [$C_5H_{11}O_2Si^+$], 150 (28), 117 (14) [$COOSiCH_3^+$], 73 (100) [$SiCH_3^+$], 57 (22) [$C_4H_9^+$], 55 (26) [$C_4H_7^+$], 43 (32) [$C_3H_7^+$], 41 (23) [$C_3H_5^+$].

*4.8.5. 2-Chloro-4-fluoropent-4-enoic acid (**15d**)*

According to general procedure the ester **10d** (152 mg, 1.00 mmol) was rearranged and the product **15d** was isolated without further purification. Yield: 130 mg (86%). ^{1}H NMR ($CDCl_3$): δ 2.79 (ddd, $^2J_{H,H}$ = 15.3 Hz, $^3J_{H,H}$ = 8.1 Hz, $^3J_{H,F}$ = 23.1 Hz, 1 H, 3-CH_2), 3.01 (ddd, $^2J_{H,H}$ = 14.6 Hz, $^3J_{H,H}$ = 6.0 Hz, $^3J_{H,F}$ = 14.6 Hz, 1 H, 3-CH_2), 4.36–4.59 (m, 2 H, 2-CHCl and 5-CH_2), 4.75 (dd, $^2J_{H,H}$ = 3.1 Hz, $^3J_{H,F}$ = 16.7 Hz, 1 H, 5-CH_2), 7.61 (br s, 1 H, COOH). ^{13}C NMR ($CDCl_3$): δ 37.6 (dt, $^2J_{C,F}$ = 29.2 Hz, C-3), 52.6 (d, C-2), 94.1 (dt, $^2J_{C,F}$ = 19.1 Hz, C-5), 160.4 (d, $^1J_{C,F}$ = 256.9 Hz, C-4), 173.4 (s, C-1). ^{19}F NMR ($CDCl_3$): δ −99.2 (m). GC/MS (70 eV) (TMS-Ester): *m/z* (%) 226/224 (0.5/1) [M^+], 211/209 (3/7) [$M^+ - CH_3$], 189 (15) [$M^+ - Cl$], 173 (4) [$M^+ - HCl - CH_3$], 167 (1), 137 (2), 117 (5) [$C_4H_9O_2Si^+$], 99 (7) [$M^+ - HCl - (CH_3)_3SiO$], 93 (39), 73 (100) [$(CH_3)_3Si^+$], 53 (23).

*4.8.6. 2-Chloro-3-(1-fluoroethenyl)-decanoic acid (**17**)*

According to the general procedure the ester **12** (250 mg, 1.00 mmol) was rearranged. After chromatography (silica gel, cyclohexane/ethyl acetate/acetic acid) the 1:1 mixture of **17** was isolated as a colorless liquid. Yield: 150 mg (60%). ^{1}H NMR ($CDCl_3$): δ 0.88 (t, $^3J_{H,H}$ = 6.9 Hz, 3 H, 12-CH_3), 1.28 (m, 10 H, 7-CH_2–11-CH_2), 1.35–1.51 and 1.51–1.68 (m, 2 H, 6-CH_2), 2.82 (m, 1 H, 3-CH), 4.31 and 4.38 (d, $^3J_{H,H}$ = 8.6 Hz and $^3J_{H,H}$ = 8.1 Hz, 1 H, 2-CH), 4.43 and 4.45 (dd, $^2J_{H,H}$ = 3.1 Hz, $^3J_{H,F}$ = 49.8 Hz and $^2J_{H,H}$ = 3.1 Hz, $^3J_{H,F}$ = 49.8 Hz, 1 H, 5-CH_2), 4.75 and 4.78 (dd, $^2J_{H,H}$ = 3.1 Hz, $^3J_{H,F}$ = 17.4 Hz and ddd, $^2J_{H,H}$ = 3.1 Hz, $^3J_{H,F}$ = 17.6 Hz, $^4J_{H,H}$ = 0.5 Hz, 1 H, 5-CH_2), 9.81 (br s, 1 H, COOH). ^{13}C NMR ($CDCl_3$): δ 14.0 (q, C-12), 22.6, 26.6, 27.0, 27.6, 28.5, 29.0, 29.1, 29.2, 31.7, 31.7 (t, C-6–C-11), 46.8 (dd, $^2J_{C,F}$ = 25.4 Hz, C-3), 47.1 (dd, $^2J_{C,F}$ = 25.4 Hz, C-3), 56.9 (d, C-1), 58.5 (d, C-2), 94.2 (dt, $^2J_{C,F}$ = 19.1 Hz, C-5), 95.7 (dt, $^2J_{C,F}$ = 19.1 Hz, C-5), 162.2 (d, $^1J_{C,F}$ = 260.5 Hz, C-4), 162.9 (d, $^1J_{C,F}$ = 260.7 Hz, C-4), 174.1 (s, C-1), 174.3 (s, C-1). ^{19}F NMR ($CDCl_3$): δ −107.8 (ddd, $^3J_{H,F}$ = 19.1 Hz, $^3J_{H,F}$ = 24.8 Hz, $^3J_{H,F}$ = 51.5 Hz, 0.5 F), −105.2 (ddd, $^3J_{H,F}$ = 17.2 Hz, $^3J_{H,F}$ = 22.9 Hz, $^3J_{H,F}$ = 49.6 Hz, 0.5 H). GC/MS (70 eV) (TMS-Ester): *m/z* (%) 325/323 (0/1) [$M^+ + H$], 324/322 (0/1) [M^+], 287 (10) [$M^+ - Cl$], 265 (3) [$M^+ - H - HCl - HF$], 252 (2), 223 (13) [$M^+ - C_7H_{15}$], 189 (6), 173 (3), 166 (2) [$C_5H_{11}O_2SiCl^+$ (McLafferty)], 150 (6), 131 (9) [166 − Cl], 73 (100) [$(CH_3)_3Si^+$], 55 (18) [$C_4H_7^+$], 41 (17) [$C_3H_5^+$].

*4.8.7. (Z)-4-Fluoro-2-methyloct-4-enoic acid (**16a**)*

According to general procedure the ester **11a** (348 mg, 2.00 mmol) was rearranged. After work-up as described for

compound **15a** the product **16a** was isolated without further purification. Yield: 110 mg (32%). ^{1}H NMR ($CDCl_3$): δ 0.89 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, 8-CH_3), 1.22 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, 9-CH_3), 1.30–1.44 (m, 2 H, 7-CH_2), 2.03 (m, 2 H, 6-CH_2), 2.15–2.79 (br m, 3 H, 2-CH and 3-CH_2), 4.57 (dt, $^3J_{H,H}$ = 7.5 Hz, $^3J_{H,F}$ = 37.5 Hz, 1 H, 5-CH), 9.75 (br s, 1 H, COOH). ^{13}C NMR ($CDCl_3$): δ 13.5 (q, C-8), 16.2 (q, C-9), 22.5 (t, C-7), 25.5 (dt, $^3J_{C,F}$ = 4.0 Hz, C-6), 35.8 (dt, $^2J_{C,F}$ = 28.0 Hz, C-3), 36.9 (d, C-2), 107.6 (dd, $^2J_{C,F}$ = 15.3 Hz, C-5), 156.6 (d, $^1J_{C,F}$ = 251.8 Hz, C-4), 182.0 (s, C-1). ^{19}F NMR ($CDCl_3$): δ −111.8 (ddd, $^3J_{H,F}$ = 17.2 Hz, $^3J_{H,F}$ = 21.0 Hz, $^3J_{H,F}$ = 38.1 Hz). GC/MS (70 eV) (TMS-Ester): *m/z* (%) 246 (3) [M^+], 231 (6) [$M^+ - CH_3$], 211 (7) [$M^+ - HF - CH_3$], 203 (1) [$M^+ - C_3H_7$], 175 (8), 146 (60) [$C_6H_{14}O_2Si^+$], 130 (34) [$M^+ + H - COOTMS$], 109 (10) [$M^+ - HF - COOTMS$], 99 (22), 73 (100) [$(CH_3)_3Si^+$], 56 (24), 41 (13) [$C_3H_5^+$].

*4.8.8. (Z)-4-Fluoro-2-methyldodec-4-enoic acid (**16b**)*

According to general procedure the ester **11b** (920 mg, 4.00 mmol) was rearranged. The ethereal solution was extracted with 1N NaOH (3 × 30 mL) and the organic layer was discarded. The basic solution was acidified with conc. HCl and extracted with diethyl ether (3 × 30 mL). The combined ethereal phase was dried and the solvent was evaporated. The product **16b** was isolated without further purification. Yield: 640 mg (70%). ^{1}H NMR ($CDCl_3$): δ 0.88 (t, $^3J_{H,H}$ = 6.9 Hz, 3 H, 12-CH_3), 1.21 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, 13-CH_3), 1.27 (m, 10 H, 7-CH_2–11-CH_2), 2.05 (dt, $^3J_{H,H}$ = 6.9 Hz, $^3J_{H,H}$ = 6.7 Hz, 6-CH_2), 2.23 (ddd, $^2J_{H,H}$ = 14.5 Hz, $^3J_{H,H}$ = 7.6 Hz, $^3J_{H,F}$ = 22.2 Hz, 1 H, 3-CH_2), 2.65 (m, 2 H, 2-CH and 3-CH_2), 4.57 (dt, $^3J_{H,H}$ = 7.4 Hz, $^3J_{H,F}$ = 37.7 Hz, 1 H, 5-CH), 11.51 (br s, 1 H, COOH). ^{13}C NMR ($CDCl_3$): δ 14.0 (q, C-12), 16.1 (q, C-13), 22.6 (t, C-11), 23.5 (dt, $^3J_{C,F}$ = 5.1 Hz, C-6), 29.1, 29.4 (t, C-7–C-9), 31.8 (t, C-10), 35.8 (dt, $^2J_{C,F}$ = 28.0 Hz, C-3), 36.9 (d, C-2), 107.9 (dd, $^2J_{C,F}$ = 15.3 Hz, C-5), 156.4 (d, $^1J_{C,F}$ = 251.8 Hz, C-4), 182.3 (s, C-1). ^{19}F NMR ($CDCl_3$): δ −112.2 (ddd, $^3J_{H,F}$ = 15.3 Hz, $^3J_{H,F}$ = 21.0 Hz, $^3J_{H,F}$ = 38.1 Hz). GC/MS (70 eV): *m/z* (%) 230 (12) [M^+], 210 (5) [$M^+ - HF$], 157 [$C_{10}H_{18}F^+$], 137 (38) [157 − HF], 125 (24) [$C_9H_{17}^+$], 97 (10) [$C_7H_{13}^+$], 95 (41), 81 (49), 74 (62) [$C_3H_6O^+$], 55 (100) [$C_4H_7^+$], 43 (53) [$C_3H_7^+$], 41 (51) [$C_3H_5^+$]. Calcd. for $C_{13}H_{23}FO_2$ (230.17): C 67.79, H 10.07; Found: C 67.63, H 10.41.

4.8.8.1. Methyl (Z)-4-fluoro-2-methyldodec-4-enoate. (*Z*)-4-Fluoro-2-methyldodec-4-enoic acid (**16b**) (230 mg, 1.00 mmol) and methanol (35 mg, 1.10 mmol) were dissolved in pentane (50 mL). DCC (228 mg, 1.1 mmol) and a catalytic amount of DMAP were added and the mixture was stirred at room temperature overnight. The resulting suspension was filtered and the colorless solution was washed with water (3 × 20 mL), 5% aqueous acetic acid (3 × 20 mL) and again with water (20 mL). The solution was dried over $MgSO_4$, the solvent was removed and the residue was purified by column chromatography (silica gel, cyclohexane/ethyl acetate, 20:1) and the ester was isolated as a colorless liquid. Yield: 163 mg (67%). ^{1}H NMR ($CDCl_3$): δ 0.88 (t, $^3J_{H,H}$ = 6.9 Hz, 3 H, 12-CH_3), 1.18 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, 13-CH_3), 1.27 (m, 10 H, 7-CH_2–11-CH_2), 2.05 (m, 2 H, 6-CH_2), 2.21 (ddd, $^2J_{H,H}$ = 14.6 Hz, $^3J_{H,H}$ = 7.6 Hz, $^3J_{H,F}$ = 21.7 Hz, 1 H, 3-CH_2), 2.54 (ddd, $^2J_{H,H}$ = 14.6 Hz, $^3J_{H,H}$ = 6.7 Hz, $^3J_{H,F}$ = 17.2 Hz, 1 H, 3-CH_2), 2.71 (m, 1 H, 2-CH), 3.67 (s, 3 H, 14-CH_3), 4.53 (dt, $^3J_{H,H}$ = 7.4 Hz, $^3J_{H,F}$ = 37.7 Hz, 5-CH). ^{13}C NMR ($CDCl_3$): δ 14.0 (q, C-12), 16.4 (q, C-13), 22.6 (t, C-11), 23.5 (dt, $^3J_{C,F}$ = 5.1 Hz, C-6), 29.0, 29.0, 29.4 (t, C-7–C-9), 31.8 (t, C-10), 36.2 (dt, $^2J_{C,F}$ = 29.2 Hz, C-3), 36.9 (d, C-2), 51.6 (q, C-14), 107.5 (dd, $^2J_{C,F}$ = 15.3 Hz, C-4), 156.7 (d, $^1J_{C,F}$ = 251.8 Hz, C-5), 176.0 (s, C-1). ^{19}F NMR ($CDCl_3$): δ −111.8 (ddd, $^3J_{H,F}$ = 17.2 Hz, $^3J_{H,F}$ = 21.0 Hz, $^3J_{H,F}$ = 38.2 Hz). GC/MS (70 eV): *m/z* (%) 244 (12) [M^+], 224 (2) [$M^+ - HF$], 213 (1) [$M^+ - CH_3O$], 209 (4) [224 − CH_3], 175 (2), 159 (9) [$M^+ - C_6H_{13}$], 157 (13) [$C_{10}H_{18}F^+$], 137 (21) [157 − HF], 111 (29), 88 (100) [$C_4H_8O_2^+$ (McLafferty)], 81 (39), 59 (18) [$C_2H_3O_2^+$], 57 (15) [$C_4H_9^+$], 55 (30) [$C_4H_7^+$], 43 (27) [$C_3H_7^+$], 41 (28) [$C_3H_5^+$]. Calcd. for $C_{12}H_{25}O_2F$ (244.18): C 68.85, H 10.25. Found: C 68.88, H 10.34.

*4.8.9. 2-Methyl-4-oxododecanoic acid (**27**)*

According to the above-mentioned procedure the ester **11b** (829 mg, 3.60 mmol) was rearranged and the crude product **16b** was subjected to column chromatography under acidic conditions (silica gel, cyclohexane/ethyl acetate/acetic acid, 10:1:1) to get **27** as a colorless oil. Yield: 370 mg (45%). ^{1}H NMR ($CDCl_3$): δ 0.88 (t, $^3J_{H,H}$ = 6.6 Hz, 3 H, 12-CH_3), 1.21 (d, $^3J_{H,H}$ = 7.2 Hz, 3 H, 13-CH_3), 1.27 (m, 12 H, 6-CH_2–11-CH_2), 1.57 (m, 2 H, 5-CH_2), 2.43 (m, 2 H, 3-CH_2), 2.95 (m, 1 H, 2-CH). ^{13}C NMR ($CDCl_3$): δ 14.0 (q, C-12), 16.8 (q, C-13), 22.6 (t, C-11), 23.7 (t, C-6), 29.0, 29.1, 29.3 (t, C-7–C-9), 33.5 (d, C-2), 34.5 (t, C-10), 42.9 (t, C-5), 45.4 (t, C-3), 181.5 (s, C-1), 208.9 (s, C-4). GC/MS (70 eV) (TMS ester): *m/z* (%) 300 (1) [M^+], 285 (27) [M^+-CH_3], 257 (7), 202 (37), 187 (46) [M^+-C_8H_{17}], 112 (100) [$C_8H_{16}^+$], 75 (47) [$C_2H_7OSi^+$], 73 (100) [$C_3H_9Si^+$], 57 (31) [$C_4H_9^+$], 55 (14) [$C_4H_7^+$], 43 (26) [$C_3H_7^+$], 41 (21) [$C_3H_5^+$].

*4.8.10. (Z)-4-Fluoro-2-methyloctadec-4-enoic acid (**16c**)*

According to general procedure the ester **11c** (314 mg, 1.00 mmol) was rearranged. The combined ethereal extract was washed with brine (2 × 15 mL), dried over $MgSO_4$, and the solvent was removed. The crude product was purified by HPLC using an RP-18 column and methanol as the solvent. The carboxylic acid **16c** was isolated as a white solid. Yield: 225 mg (72%). m.p. 33 °C. ^{1}H NMR ($CDCl_3$): δ 0.88 (t, $^3J_{H,H}$ = 6.7 Hz, 3 H, 18-CH_3), 1.22 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, 19-CH_3), 1.26 (m, 22 H, 7-CH_2–17-CH_2), 2.04 (m, 2 H, 3-CH), 2.22 (ddd, $^3J_{H,H}$ = 7.6 Hz, $^2J_{H,H}$ = 14.6 Hz, $^3J_{H,F}$ = 21.9 Hz, 1 H, 3-CH_2), 2.53–2.80 (m, 2 H, 3-CH_2 and 2-CH), 4.55 (dt, $^3J_{H,H}$ = 7.4 Hz, $^3J_{H,F}$ = 37.4 Hz, 1 H, 5-CH). ^{13}C NMR ($CDCl_3$): δ 14.1 (q, C-18), 16.2 (q, C-19), 22.7 (t, C-17), 23.5 (dt, $^3J_{C,F}$ = 3.8 Hz, C-6), 29.1, 29.1, 29.3, 29.4, 29.4, 29.6, 29.7 (t, C-7–C-15), 31.9 (t, C-16), 35.8 (dt, $^2J_{C,F}$

= 28.0 Hz, C-3), 36.8 (d, C-2), 107.9 (dd, $^2J_{C,F}$ = 15.3 Hz, C-5), 156.4 (d, $^1J_{C,F}$ = 251.8 Hz, C-4), 181.7 (c, C-1). ^{19}F NMR ($CDCl_3$): δ −111.9 (ddd, $^3J_{H,F}$ = 17.2 Hz, $^3J_{H,F}$ = 22.9 Hz, $^3J_{H,F}$ = 38.2 Hz). GC/MS (70 eV) (TMS-Ester): *m/z* (%) 386 (5) [M^+], 371 (3) [$M^+ - CH_3$], 366 (2) [M^+ − HF], 351 (18) [366 − CH_3], 315 [$M^+ - C_4H_{10}Si$], 287 (1), 217(3), 183 (4) [$C_{13}H_{27}^+$], 169 (5) [$C_{12}H_{25}^+$], 146 (100) [$C_6H_{14}O_2Si^+$], 131 (16) [146 − CH_3], 130 (38), 117 (5) [$C_5H_9O_2Si^+$], 73 (69) [$(CH_3)_3Si^+$], 43 (21) [$C_3H_7^+$].

*4.8.11. 4-Fluoro-2-methylpent-4-enoic acid (**16d**)*

According to general procedure the ester **11d** (350 mg, 3.20 mmol) was rearranged. The reaction mixture was worked up as described for compound **15a** and the product **16d** was isolated without further purification. Yield: 17 mg (5%). ^{1}H NMR ($CDCl_3$): δ 1.18 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, 6-CH_3), 2.22 (ddd, $^2J_{H,H}$ = 15.0 Hz, $^3J_{H,H}$ = 7.6 Hz, $^3J_{H,F}$ = 22.4 Hz, 1 H, 3-CH_2), 2.63 (m, 2 H, 3-CH_2 and 2-CH), 4.24 (dd, $^2J_{H,H}$ = 2.6 Hz, $^3J_{H,F}$ = 49.6 Hz, 1 H, 5-CH_2), 4.53 (dd, $^2J_{H,H}$ = 2.9 Hz, $^3J_{H,F}$ = 17.2 Hz, 1 H, 5-CH_2), 10.75 (br s, 1 H, COOH). ^{19}F NMR ($CDCl_3$): δ −96.7 (ddd, $^3J_{H,F}$ = 15.3 Hz, $^3J_{H,F}$ = 22.9 Hz, $^3J_{H,F}$ = 49.6 Hz).

*4.8.12. 3-(1-Fluoroethenyl)-2-methyldecanoic acid (**18**)*

According to the general procedure the ester **13** (216 mg, 0.94 mmol) was rearranged. The acid **18** was isolated as a colorless liquid by column chromatography (silica gel, cyclohexane/ethyl acetate/acetic acid, 10:1:2) as a 81:19 mixture of diastereomers. The isomers could not be separated by HPLC. Yield: 120 mg (56%); 62% de. ^{1}H NMR ($CDCl_3$): δ 0.88 (t, $^3J_{H,H}$ = 6.9 Hz, 3 H, 12-CH_3), 1.19 (d, $^3J_{H,H}$ = 7.2 Hz, 3 H, 13-CH_3), 1.27 (m, 10 H, 7-CH_2–11-CH_2), 1.45 (m, 2 H, 6-CH_2), 2.53 (m, 1 H, 3-CH), 2.70 (m, 1 H, 2-CH), 4.30 (dd, $^2J_{H,H}$ = 2.9 Hz, $^3J_{H,F}$ = 50.3 Hz, 1 H, 5-CH_2), 4.62 (dd, $^2J_{H,H}$ = 2.6 Hz, $^3J_{H,F}$ = 17.9 Hz, 1 H, 5-CH_2), 10.31 (br s, 1 H, COOH). ^{13}C NMR ($CDCl_3$): δ 13.4 (q, C-13), 14.0 (q, C-12), 22.6, 27.1, 27.5, 29.1, 29.5, 31.8 (t, C-6–C-11), 41.8 (d, C-2), 45.0 (dd, $^2J_{C,F}$ = 24.2 Hz, C-3), 91.8 (dt, $^2J_{C,F}$ = 20.3 Hz, C-5), 166.3 (d, $^1J_{C,F}$ = 260.7 Hz, C-4), 181.4 (s, C-1). ^{19}F NMR ($CDCl_3$): δ −103.2 (ddd, $^3J_{H,F}$ = 17.2 Hz, $^3J_{H,F}$ = 22.9 Hz, $^3J_{H,F}$ = 49.6 Hz), −107.3 (ddd, $^3J_{H,F}$ = 17.2 Hz, $^3J_{H,F}$ = 26.7 Hz, $^3J_{H,F}$ = 49.6 Hz). GC/MS (70 eV) (TMS-Ester): *m/z* (%) 302 (1) [M^+], 287 (6) [$M^+ - CH_3$], 267 (1) [M^+ − HF − CH_3], 259 (1) [$M^+ - C_3H_7$], 245 (3) [$M^+ - C_4H_9$], 04 (8) [$C_9H_{17}O_2FSi^+$ (McLafferty)], 203 (61) [M^+ H or $M^+ - C_7H_{15}$], 146 (6) [204 − C_3H_3F], 130 (8), 111 (35), 95 (15), 73 (100) [$(CH_3)_3Si^+$], 55 (17) [$C_4H_7^+$], 43 (12) [$C_3H_7^+$], 41 (14) [$C_3H_5^+$].

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