Journal of Fluorine Chemistry 143 (2012) 189–197

Contents lists available at SciVerse ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Synthesis of α-trifluoromethylated amides by Eschenmoser–Claisen-type rearrangement of allylic alcohols

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ARTICLE INFO

Article history:
Received 16 April 2012
Received in revised form 19 July 2012
Accepted 24 July 2012
Available online 7 August 2012

Dedicated to Professor David O'Hagan on the occasion of receiving the ACS Award for Creative Work in Fluorine Chemistry.

Keywords:
Claisen rearrangement
Trifluoromethyl compounds
Amides
Allylic alcohols
Reaction mechanisms

ABSTRACT

A new, mild method to prepare α-trifluoromethylated amides bearing an additional *trans*-configured double bond in γ-position is described. Treatment at room temperature of fluorinated and non-fluorinated allylic alcohols **1** and **2** with the 1,1,3,3,3-pentafluoropropene–diethylamine adduct (**PFPDEA**) in the presence of triethylamine as base gave the products of [3,3]-sigmatropic Eschenmoser–Claisen-type rearrangements with good yields and excellent diastereoselectivity due to chair-like conformations of transition states. Starting with enantiomerically enriched allylic alcohols chirality transfer from carbon 3 of the allylic system to carbon 2 of the final α-trifluoromethyl carboxamides was observed. This methodology was applied to both simple and more complex, including terpenic, allylic alcohols and might be developed to an alternative strategy to the well-known electrophilic α-trifluoromethylation of carbonyl compounds.

1. Introduction

The steadily growing demand of fluoroorganic compounds both for the design of new biologically active compounds and new functional materials stimulated considerably interest in the development of new convenient and selective ways to introduce fluorine atom(s) into molecules. New methods of transformation of non-fluorinated into fluorinated groups were studied, e.g. methyl into trifluoromethyl group [1]. Hence, many reactions to construct organic fluoro compounds were developed, including Claisen-type rearrangements, which are powerful carbon–carbon bond-forming reactions frequently applied for transformations of carbon skeletons in organic synthesis [2]. These thermal [3,3]-sigmatropic rearrangements, according to the Woodward–Hoffmann rules proceed suprafacial. The highly ordered six-membered cyclic transition states along with the restrictions imposed by the orbital symmetry rules, allow one to expect excellent stereoselectivity [3]. Plenty of variants of this type of rearrangement have been developed until very recently. As the most common, regularly used in synthesis with non-fluorinated compounds, the Carroll [4], the Johnson [5], the Reformatsky [6], the ester enolate [7], the Ireland–Claisen [8] and the Eschenmoser [9] rearrangements should be mentioned.

This methodology, however, was also useful for the conversion of selectively fluorinated substrates and for the elaboration of simple fluorinated building blocks. For instance, Claisen rearrangements of polyfluorinated allylvinyl ethers [10], Johnson–Claisen rearrangements of allylic alcohols with a terminal difluorinated double bond [11], and Ireland–Claisen rearrangements with terminal difluorinated allylic esters have been described [12]. On the other hand, there are known less examples for rearrangements of monofluorinated olefins. A classical aromatic Claisen rearrangement of the bis-2-fluoroallyl ether of *p*-diphenol was applied to obtain a fluorinated derivative of the anti-malaria agent Bialamicol [13]. Several different examples of Johnson–Claisen rearrangement of 2-fluoro [14] and 3-fluoroallylic alcohols [15] as well as Ireland–Claisen rearrangement of vinyl fluorides [16] and the Kazmaier variant [17] of this rearrangement using amino acid esters of the fluorinated allylic alcohols [18,19] have been also published. As a result of the above-mentioned rearrangements formation of corresponding fluorinated γ,δ-unsaturated derivatives such as acids, esters or amino acids was observed. Claisen rearrangement had also been used to introduce a fluoro(trifluoromethyl)methylene moiety by treatment of allylic alcohols with the perfluoropropene-diethylamine adduct (PPDA) [20]. Such reaction led to the formation of γ,δ-unsaturated amides containing

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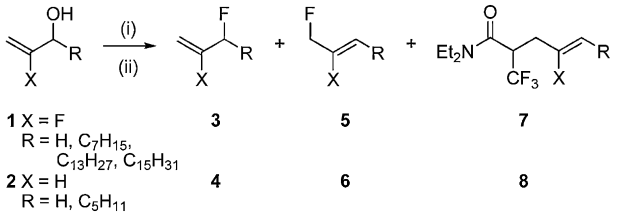
http://dx.doi.org/10.1016/j.jfluchem.2012.07.011



Scheme 1. Reagents and conditions: (i) (a) **PFPDEA** (2 equiv.), CH_2Cl_2, rt, 48 h; (b) Et_3N (2 equiv.), **PFPDEA** (2 equiv.), CH_2Cl_2, rt, 48 h; (ii) H_2O, excess.

at the α position a fluorine as well as a trifluoromethyl group. Although the PPDA [21] is one of the reagents used for the conversion of alcohols into alkylfluorides [22], the reaction of allylic alcohols in the presence of *N*,*N*-diisopropylethylamine did not produce the corresponding allylic fluorides but Eschenmoser–Claisen-type rearranged amides were formed.

Recently, the 1,1,3,3,3-pentafluoropropene diethylamine adduct (**PFPDEA**), a variation of Ishikawa's reagent, has been developed in our laboratory and applied as a new reagent for the direct transformation of alcohols to corresponding alkylfluorides [23]. Furthermore, we reported **PFPDEA** to produce 3,3,3-trifluoropropionic esters in the reaction with vicinal fluorohydrins [24]. In this paper, applications of this new fluorinating agent in reactions of both fluorinated and non-fluorinated allylic alcohols are described. We wish to report on stereoselective synthesis of γ-fluoro-α-trifluoromethyl-γ,δ-unsaturated amides under mild conditions by Eschenmoser–Claisen-type rearrangement. This might be developed as an alternative option to electrophilic α-trifluoromethylation reactions of carbonyl compounds [25].

2. Results and discussion

In our previous studies, we found that widening the field of application of **PFPDEA** to more complex molecules containing a hydroxyl group in different neighbourhood leads to formation of 3,3,3-trifluoropropionate derivatives as competing products in addition to the expected alkylfluorides [24]. Therefore, taking the advantage of esterification properties of this new fluorinating agent to obtain trifluoropropionic acid esters exclusively would be a convenient method of allylic alcohols esterification. Such esters were shown to undergo Ireland–Claisen rearrangements to give α-trifluoromethyl-γ,δ-unsaturated carboxylic acids [26].

Fluorinated allylic alcohols **1a–c** prepared according to a well-established three-step sequence [27] and **1d** [28] were subjected to the reaction with 2 equiv. of **PFPDEA** under mild conditions (i.e. in dichloromethane at room temperature). In contrast to the products we expected according to our earlier results [24], formation of trifluoropropionates was not observed. Instead, a complex mixture of products was formed. Among them the following three compounds were identified: 2,3-difluoroalk-1-enes **3**, 1,2-difluoroalk-2-enes **5** and (*Z*)-*N*,*N*-diethyl-4-fluoro-2-(trifluoro-methyl)alk-4-enamides **7** (Scheme 1 and Table 1). Compounds **3** and **5** were obtained as products of nucleophilic substitution without or with allylic rearrangement, while the amides **7** were formed via the [3,3]-sigmatropic rearrangement of an intermediary *N*,*N*-diethyl-3,3,3-trifluoro-1-(2-fluoroalk-1-en-3-yloxy)prop-1-en-1-amine (cf. discussion below and Scheme 5).

Simultaneously in competitive studies, the influence of a vinylic fluoride on the reactivity of allylic alcohols towards **PFPDEA** was investigated. The reaction of **PFPDEA** with oct-1-en-3-ol (**2**) applied as a model molecule, gave only substitution products, the allylfluorides 3-fluorooct-1-ene (**4**) and 1-fluorooct-2-ene (**6**). In contrast to its fluorinated analogues **1a–c**, there was no formation of a rearranged amide **8** observed under these conditions (Scheme 1 and Table 1).

Surprisingly, the reaction of both fluorinated (**1**) and non-fluorinated (**2**) allylic alcohols with **PFPDEA** in the presence of two equivalents of triethylamine led to the fluorinated γ,δ-unsaturated amides **7** or **8** exclusively. It seems that modification of the conditions by addition of 2 equiv. of the weak base Et_3N inhibits the nucleophilic substitution and favours amidation leading to the formation of amides **7** and **8** via Eschenmoser–Claisen-type rearrangement. The reaction has to be carried out by slow addition of the fluorinating agent (2 equiv.) to the mixture of the alcohol (1 equiv.) and triethylamine (2 equiv.) in the presence of inert solvents such as CH_2Cl_2 at room temperature. In contrast, according to the literature protocols, for Eschenmoser rearrangements of γ-trifluoromethylated allylic alcohols refluxing with *N*,*N*-dimethyl-acetamide dimethylacetal in high boiling solvents was required [29].

Claisen rearrangements proceed via highly ordered cyclic transition states (see Scheme 6). Along with the restrictions imposed by the orbital symmetry rules all the performed reactions gave the corresponding *trans*-configurated alk-4-enamides in fair to excellent yields (Table 2).

Having this method for complete control of the stereochemistry of double bond formation in position 4 in hand, a chirality transfer from carbon 3 of the allylic alcohol to carbon 2 of the formed amides should be possible. Thus, under the same conditions the enantiomerically enriched (*R*)-2-fluorooctadec-1-en-3-ol, (*R*)-**1c**, obtained by lipase-catalysed resolution [26] and optically pure (*R*)-oct-1-en-3-ol, (*R*)-**2a**, were subjected to the reaction with **PFPDEA**. Indeed, both allylic alcohols underwent rearrangement with transmission of chirality forming the corresponding optically active 2-trifluoromethylated *trans*-alk-4-enamides (*R*)-**7c** and (*R*)-**8** in good yields (Table 2). The enantiomeric excess of the products was determined by ^{19}F NMR using the enantiopure shift reagent (*R*)-(−)-*N*-(3,5-dinitrobenzoyl)-α-methylbenzylamine (DNBA) (Scheme 2).

However, in both cases decrease of the optical purity of the obtained products was observed. Three plausible explanations of such a partial racemization might be considered: (i) the initial basic reaction conditions may cause partial racemization of starting material; (ii) in the formed products the hydrogen at α-position to the amide function is quite acidic because of the electron withdrawing effect of the trifluoromethyl group and the

Table 1
Products distribution in reaction of allylic alcohols with 2 equiv. **PFPDEA** (reaction conditions A).

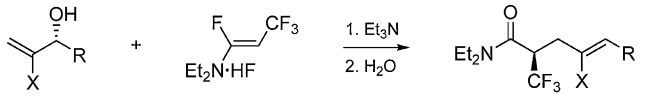
Alcohols	X	R	Products (yield [%])[a]		
1a	F	C_7H_{15}	**3a** (63)	**5a** (15)	**7a** (4)
1b	F	$C_{13}H_{27}$	**3b** (61)	**5b** (15)	**7b** (4)
1c	F	$C_{15}H_{31}$	**3c** (44)	**5c** (11)	**7c** (33)
2a	H	C_5H_{11}	**4a** (36)	**6a** (24)	–

[a] Yields of isolated products.

Table 2
Yield of alk-4-enamides **7** and **8** in the reaction of allylic alcohols with **PFPDEA** + Et_3N (reaction conditions B).

Alcohols	X	R	Products	Yield [%][a]
1a	F	C_7H_{15}	**7a**	88
1b	F	$C_{13}H_{27}$	**7b**	91
1c	F	$C_{15}H_{31}$	**7c**	72
1d	F	H	**7d**	41
2a	H	C_5H_{11}	**8a**	88
2b	H	H	**8b**	40
(*R*)-**1c** (65% ee)	H	$C_{15}H_{31}$	(*R*)-**7c**	76 (47% ee)
(*R*)-**2a** (>98.5% ee)	H	H	(*R*)-**8a**	93 (78% ee)

[a] Yields of isolated products.



(*R*)-**1c** (X = F, R = $C_{15}H_{31}$, 65% ee)
(*R*)-**2a** (X = H, R = C_5H_{11}, >98.5% ee)

(*R*)-**7c** (76%, 47% ee)
(*R*)-**8a** (93%, 78% ee)

Scheme 2. Chirality transfer in the reaction of enantioenriched allylic alcohols **1c** and **2a** with **PFPDEA** in the presence of triethylamine.

carboxamide function. Therefore, partial racemization might occur via the enolate. Eventually, least desirable alternative, (iii) the involved reaction mechanism, e.g. formation of the intermediate and rearrangement itself is not as stereoselective as to be expected. Essentially, Ireland–Claisen rearrangements of analogous 3,3,3-trifluoropropanoic acid allyl esters with triethylamine and trimethylsilyltriflate proceeded under complete racemization [26].

In order to prove the first of the preceding reasons for the observed decrease of enantiomeric excess in products **7c** and **8** (Scheme 2), blind experiments of allylic alcohol's behaviour in the presence of triethylamine by measuring the optical rotation revealed surprising results. Unexpectedly, within half an hour after addition of the base full racemization of the fluoroallylic alcohol (*R*)-**1c** (65% ee) was observed, whereas the same conditions caused only partial racemization of (*R*)-3-octenol (*R*)-**2a** after 24 h. Subsequently, the optical rotation measurements of the isolated enantiomerically enriched fluorinated amides (*R*)-**7c** and (*R*)-**8a** after treatment with triethylamine under ambient conditions did not show any changes.

At the next stage, we attempted to extend the method's field of application to other available nonfluorinated allylic alcohols. The developed procedure leading to the formation of desired Eschenmoser–Claisen rearranged products was employed in the reactions of more complex allylic derivatives containing hydroxyl group in different neighbourhood. Substrates possessing (i) primary hydroxyl group: geraniol (**9a**), farnesol (**9b**), perillil alcohol (**10**), 2-methyl-3-phenylprop-2-en-1-ol (**11**), myrtenol (**12**), furfuryl alcohol (**13**), (ii) secondary hydroxyl group: carveol (**14**), *trans*-pinocarveol (**15**), (iii) tertiary hydroxyl group: linalool (**16a**), *trans*-nerolidol (**16b**) were examined (Table 3).

Studies aimed at probing the efficiency of this methodology for the preparation of wider range of rearranged amides from alcohols **9–16** indicated that allylic alcohol's structure has a substantial influence on the desired rearranged product formation (Table 3).

Eschenmoser–Claisen type rearrangement has been also applied to introduce trifluoromethyl moiety by treatment of 5-(hydroxymethyl)uracil **17** with **PFPDEA** in the presence of triethylamine (Scheme 3). Such reaction led to exclusive formation of uracil derivative **37** containing a methyl group at position 5 and a 2-(*N*,*N*-diethyl-3,3,3-trifluoropropanamidyl) function at position 6.

The experimental results obtained in this work provided interesting insight into the general mechanism of action of the pentafluoropropene-diethylamine adduct towards different alcohols. The fluorination reactions with the use of **PFPDEA** or other

Table 3
Products of the reaction of allylic alcohols **9–16** with **PFPDEA** + Et_3N.

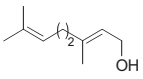
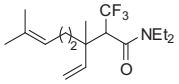
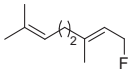
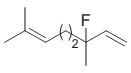
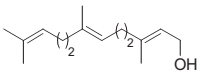
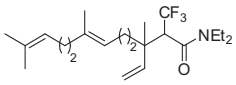
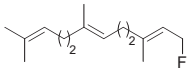
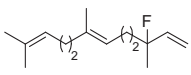
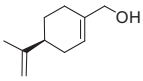
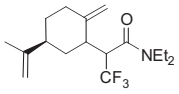
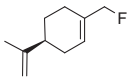
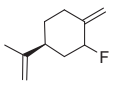
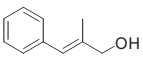
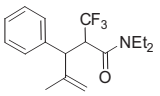
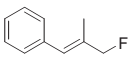
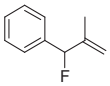
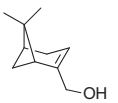
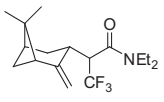
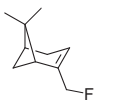
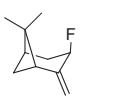
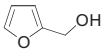
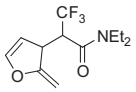
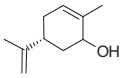
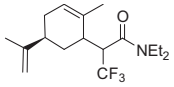
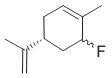
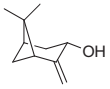
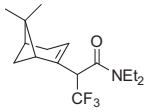
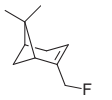
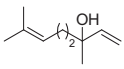
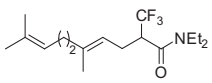
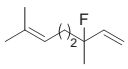
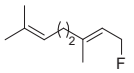
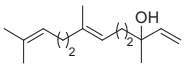
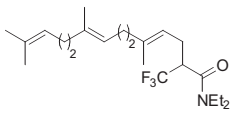
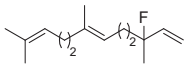
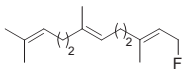
Substrate	Amide (yield)[a]	Structure	^{19}F NMR chemical shift [ppm][b]	Fluorides (yield)[a]	Structure	^{19}F NMR chemical shift [ppm][b]
9a 	**20a** (3%)		−67.5 (d, $^3J_{F,H}$ = 7.9 Hz, 3 F)	**18a** (26%)		−207.4 (t, $^2J_{F,H}$ = 47.9 Hz, 1 F)
				19a (32%)		−148.2 (m, 1 F)
9b 	**20b** (3%)		−67.5 (d, $^3J_{F,H}$ = 7.7 Hz, 1 F)	**18b** (22%)		−207.4 (t, $^2J_{F,H}$ = 47.9 Hz, 1 F)
				19b (36%)		−148.1 (m, 1 F)
10 	**23** (7%)		−67.4 (d, $^3J_{F,H}$ = 8.0 Hz, 3 F)	**21** (44%)		−211.7 (t, $^2J_{F,H}$ = 48.8 Hz, 1 F)
				22 (4%)		−180.7 (m, 1 F)
11 	**26** (8%)		−67.3 (d, $^3J_{F,H}$ = 7.9 Hz, 3 F)	**24** (28%)		−212.3 (t, $^2J_{F,H}$ = 47.4 Hz, 1 F)
				25 (26%)		−173.7 (d, $^2J_{F,H}$ = 47.4 Hz, 1 F)
12 	**29** (23%)		−67.9 (d, $^3J_{F,H}$ = 7.9 Hz, 3 F)	**27** (35%)		−214.4 (tdd, $^2J_{F,H}$ = 47.6 Hz, $^4J_{F,H}$ = 14.8 Hz, $^4J_{F,H}$ = 8.6 Hz, 1 F)
				28 (22%)		−137.2 (dddd, $^2J_{F,H}$ = 44.8 Hz, $^3J_{F,H}$ = 34.6 Hz, $^3J_{F,H}$ = 32.4 Hz, $^4J_{F,H}$ = 2.9 Hz, 1 F)

Table 3 (*Continued*)

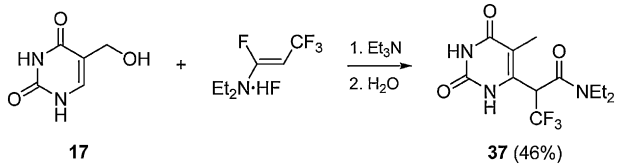
Substrate	Amide (yield)[a]	Structure	^{19}F NMR chemical shift [ppm][b]	Fluorides (yield)[a]	Structure	^{19}F NMR chemical shift [ppm][b]
13 	**30** (40%)		−68.4 (d, $^{3}J_{F,H}$ = 7.8 Hz, 3 F)	**31** (11%)		−201.3 (t, $^{2}J_{F,H}$ = 49.7 Hz, 1 F)
				32 (29%)		−109.3 (d, $^{2}J_{F,H}$ = 68.2 Hz, 1 F)
14 	**33** (0%)		–	**34** (55%)		−178.1 (ddd, $^{2}J_{F,H}$ = 50.1 Hz, $^{3}J_{F,H}$ = 15.7 Hz, $^{3}J_{F,H}$ = 4.6 Hz, 1 F); −166.8 (m, 1 F)
15 	**35** (86%)		−67.8 (d, $^{3}J_{F,H}$ = 8.0 Hz, 3 F)	**28** (3%)		−137.2 (dddd, $^{2}J_{F,H}$ = 44.8 Hz, $^{3}J_{F,H}$ = 34.6 Hz, $^{3}J_{F,H}$ = 32.4 Hz, $^{4}J_{F,H}$ = 2.9 Hz, 1 F)
				27 (3%)		−214.4 (tdd, $^{2}J_{F,H}$ = 47.6 Hz, $^{4}J_{F,H}$ = 14.8 Hz, $^{4}J_{F,H}$ = 8.6 Hz, 1 F)
16a 	**36a** (30%)		−67.7 (d, $^{3}J_{F,H}$ = 7.9 Hz, 3 F)	**19a** (<1%)		−148.2 (m, 1 F)
				18a (<1%)		−207.4 (t, $^{2}J_{F,H}$ = 47.9 Hz, 1 F)
16b 	**36b** (40%)		−68.2 (d, $^{3}J_{F,H}$ = 7.9 Hz, 3 F)	**19b** (<1%)		−148.1 (m, 1 F)
				18b (<1%)		−207.4 (t, $^{2}J_{F,H}$ = 47.9 Hz, 1 F)

[a] Yields determined by ^{19}F NMR using *m*-fluorotoluene as internal standard (^{19}F NMR (282 MHz, $CDCl_3$): δ = −114.1 (m, 1 F)).
[b] ^{19}F NMR (282 MHz, $CDCl_3$).

fluoro amino reagents (FARs) were reported to follow a S_Ni mechanism and go through a two-step process [30]. Formation of products obtained in the reaction of **PFPDEA** with allylic alcohols confirmed the suggested mechanism [24]. In the first step the fluorinating agent reacts with alcohols forming the intermediate hydrofluoride of a trifluoromethylated amide enolate (**TFMAE**) as a result of nucleophilic substitution of the vinylic fluorine by alcohol and hydrogen fluoride elimination (Scheme 4).

The second step – decomposition of **TFMAE**, however can proceed via different transition states leading to different products as depicted in Scheme 5. Most probably, allylic fluorides are generated when the intermediate **TFMAE** decomposes via either a six membered transition state **TS 2** or transition state **TS 1**. In this way the major fluorides are formed without allylic rearrangement by fluoride attack at carbon C-3 bearing the leaving group (Scheme 5, pathway b). These are examples of an intramolecular nucleophilic substitution, S_Ni, and typical nucleophilic substitution, S_N2, respectively.

Decomposition of the intermediate **TFMAE** through a less favoured, transition state **TS 3** is also possible (Scheme 5, pathway a). In this case the nucleophilic attack of fluoride occurs at carbon C-1 resulting in the formation of the minor product via an S_N2' reaction with allylic rearrangement.

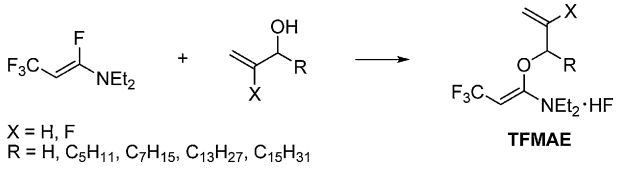


Scheme 3. Reaction of 5-(hydroxymethyl)uracil **17** with **PFPDEA** in the presence of triethylamine.

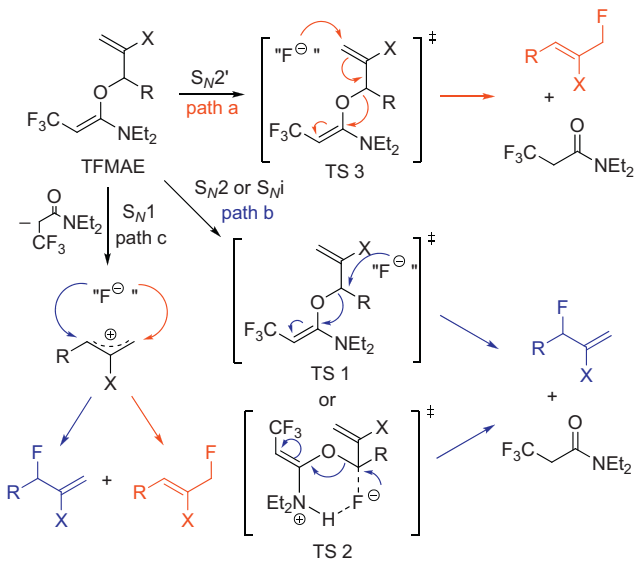
Since the formation of thermodynamically stable diethyl 3,3,3-trifluoropropionamide, $CF_3CH_2C(O)NEt_2$, is considered to be a driving force of fluoride substitution, decomposition of intermediate **TFMAE** can also generate stable allylic carbocation (Scheme 5, pathway c). Subsequent nucleophilic attack of fluoride at carbon C-1 or C-3 gives a mixture of two allylic fluorides as products. Therefore fluorination in an S_N1 reaction cannot be neglected.

Alternatively, the intermediates **TFMAE** can react as 1,5-diene systems. Consequently, *trans*-configurated 2-trifluoroalk-4-enamides are formed by [3,3]-sigmatropic Eschenmoser–Claisen-type rearrangement via a six-membered transition state (Scheme 6). Under the original conditions, only the reactions of the fluoroallylic alcohols **1a–c** with **PFPDEA** under standard conditions gave low amount of rearranged products (see Table 1). However, modification of the reaction conditions by addition of two equivalents of triethylamine resulted in exclusive formation of the rearranged products (see Table 2). Thus, in the absence of HF under more basic conditions, the rearrangement is favoured.

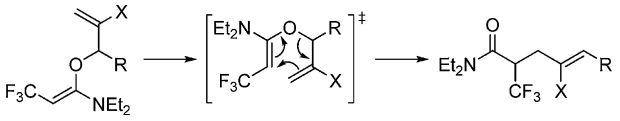
Subsequent investigations showed that the rearrangements of optically active fluorinated and non-fluorinated allylic alcohols with **PFPDEA** allowed the generation of enantioenriched amides through an intramolecular chirality transfer from carbon 3 of the allylic system to carbon 2 of the formed carboxyamides. Again, the



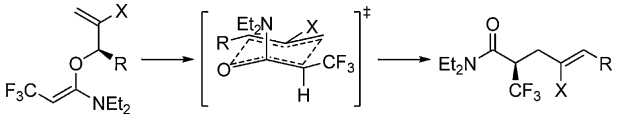
Scheme 4. Formation of the intermediate **TFMAE** from allylic alcohols and **PFPDEA**.



Scheme 5. Anticipated mechanisms for the formation of allylic fluorides.



Scheme 6. Eschenmoser–Claisen-type rearrangement of trifluoromethylated amide enolates **TFMAE**.



Scheme 7. Stereochemistry of the Eschenmoser–Claisen rearrangement of trifluoromethylated amide enolates **TFMAE**.

intermediate **TFMAE** is rearranged via a chair-like transition state where the long alkyl chain R attached to the stereogenic carbon adopts an equatorial conformation. Similarly, the trifluoromethyl group at the double bond also arranges in an equatorial position (Scheme 7).

Consequently, the (*R*)-configurations for both (*Z*)-4-fluoro-2-trifluoromethylicos-4-enoic acid amide (**7c**) and (*E*)-2-trifluoromethyldec-4-enoic acid amide (**8**) are assumed from the mechanism of the reaction. However, the determination of enantiomeric excess using enantiopure shift reagent in NMR revealed that not complete chirality transfer occurred (see discussion above).

3. Conclusion

This study on the application of the new fluorinating agent **PFPDEA** has shown, that one-pot reactions of fluorinated (**1**) and non-fluorinated (**2**) allylic alcohols with this pentafluoropropene-diethylamine adduct in the presence of two equivalents of triethylamine afforded *N,N*-diethyl-4-fluoro-2-(trifluoromethyl)alk-4-enamides **7** and *N,N*-diethyl-2-(trifluoromethyl)alk-4-enamides **8** with high stereoselectivity. These reactions involve Eschenmoser–Claisen-type rearrangements of an intermediary *N,N*-diethyl-3,3,3-trifluoro-1-(alk-1-en-3-yloxy)prop-1-en-1-amine (**TFMAE**). However, the optically active substrates (*R*)-**1c** and (*R*)-**2a** react with **PFPDEA** to give the corresponding enantiomerically enriched amides (*R*)-**7c** and (*R*)-**8a** with a lower enantiomeric excess than expected due to partial racemization of the starting fluorinated allylic alcohols **1c** and **2a**. Applying more complex allylic alcohols **9**–**17** the Eschenmoser–Claisen-type rearrangement competes with substitution of the OH group by fluoride without or with allylic rearrangement, leading to the allylic fluorides as major products in several cases. Depending on the structure of the allylic alcohol, the desired α-trifluoromethyl carboxamides were formed as main products in other cases. Nevertheless, all obtained results strongly support the postulated two-step mechanism of reactions of **PFPDEA** with alcohols. Presently, we are developing the described rearrangement as a new tool for the introduction of the trifluoromethyl moiety into organic molecules and will investigate the downstream chemistry of α-trifluoromethyl carboxamides in future.

4. Experimental

4.1. General methods

NMR spectra were recorded in deuterated solvents at 300 MHz (^{1}H), at 75 MHz (^{13}C) and at 282 MHz (^{19}F), calibrated using an internal reference: TMS (^{1}H), $CDCl_3$ (^{13}C), or $CFCl_3$ (^{19}F). Chemical shifts (δ) are quoted in parts per million (ppm) and coupling constants (J) are measured in Hertz (Hz). The following abbreviations are used to describe multiplicities s = singlet, d = doublet, t = triplet, q = quartet, b = broad, m = multiplet. For ^{13}C NMR data, additionally the multiplicity of the CH coupling determined by DEPT experiments are given. Optical rotations were measured at 20 °C (cell: diameter 3.5 mm × length 100 mm). Mass spectra were recorded by GC/MS coupling (EI, 70 eV). HRMS (EI) were recorded using a AMD-402 spectrometer. Gas chromatography analyses were performed using a column HP-5 (30 m, ∅ 0.32 mm, film 0.25 μm, carrier gas N_2). Thin-layer chromatography (TLC) was performed on coated silica gel plate Merck 60 F_{254}. Visualization of the reaction components was achieved using UV fluorescence (254 nm) and cerium(IV) ammonium nitrate or $KMnO_4$ solution stain. For purification of products column chromatography was carried out over Merck silica gel 60 (0.063–0.2 mm). All reagents purchased from suppliers were used without further purification. CH_2Cl_2 was dried and distilled over P_2O_5. Solvents for chromatography were distilled prior to use. Fluorinated allylic alcohols were prepared as described in the literature [27].

4.2. General procedures

4.2.1. Fluorination of allylic alcohols: general procedure (GP1)

To a solution of allylic alcohol **1** or **2** (1 equiv.) in dry CH_2Cl_2 (2.5 mL), a solution of pentafluoropropene-diethylamine adduct (**PFPDEA**, 2 equiv.) in dry CH_2Cl_2 (2.5 mL) was dropwise added. The resulting mixture was stirred at r.t. for 14 h and then quenched with water (10 mL). The organic layer was extracted with CH_2Cl_2 (3× 10 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ solution (10 mL) and brine (2× 10 mL). The organic phase was dried over $MgSO_4$ and the solvent was evaporated. The crude product was purified by column chromatography.

*4.2.1.1. Fluorination of 2-fluorodec-1-en-3-ol (**1a**).* According to the general procedure GP1, in the reaction of the fluorinating agent **PFPDEA** (1.450 g, 7.83 mmol) with 2-fluorodec-1-en-3-ol (**1a**, 1.001 g, 5.75 mmol) in dry CH_2Cl_2 (15 mL) a mixture of **3a**, **5a** and **7a** was obtained.

2,3-Difluorodec-1-ene (3a). Yield: 63% (GC). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.82 (ddt, $^2J_{H,F}$ = 45.3 Hz, $^3J_{H,F}$ = 13.5 Hz,

$^3J_{H,H}$ = 6.7 Hz, 1 H, C*H*F), 4.77 (m, $^3J_{H,F}$ = 16.9 Hz, 1 H, =C*H*′H″), 4.63 (m, $^3J_{H,F}$ = 48.5 Hz, 1 H, =CH′*H*″), 1.79 (m, 1 H, C*H*′H″), 1.40 (m, 1 H, CH′*H*″), 1.29 (m, 10 H, CH_2), 0.88 (m, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.7 (dd, $^1J_{C,F}$ = 261.1 Hz, $^2J_{C,F}$ = 21.9 Hz, =CF), 92.4 (dd, $^2J_{C,F}$ = 17.2 Hz, $^3J_{C,F}$ = 4.8 Hz, $=CH_2$), 89.5 (dd, $^1J_{C,F}$ = 172.5 Hz, $^2J_{C,F}$ = 30.8 Hz, CHF), 22.7–32.1 (CH_2), 14.1 (CH_3); ^{19}F NMR (282 MHz, $CDCl_3$): δ = −184.3 (ddd, $^2J_{F,H}$ = 45.3 Hz, $^3J_{F,F}$ = 25.6 Hz, $^3J_{F,H}$ = 20.9 Hz, 1 F, CHF), −113.6 (dddd, $^3J_{F,H}$ = 48.4 Hz, $^3J_{F,F}$ = 25.7 Hz, $^3J_{F,H}$ = 16.8 Hz, $^3J_{F,H}$ = 12.6 Hz, 1 F, =CF); GC MS (70 eV) *m*/*z* (%): 176 (3) [M^+], 156 (10) [M^+−HF], 136 (6) [156−HF], 127 (7) [156−C_2H_5], 121 (9) [136−CH_3], 113 (16) [127−CH_2], 107 (11) [127−HF], 99 (28) [113−CH_2], 69 (34) [$C_5H_9^+$], 56 (82) [$C_4H_8^+$], 43 (93) [$C_3H_7^+$], 41 (100) [$C_3H_5^+$]. HR MS (EI): *m*/*z* [M^+] calcd for $C_{10}H_{18}F_2$: 176.1337; found: 176.1335.

1,2-Difluorodec-2-ene (5a). Yield: 15% (GC). ^1H NMR (300 MHz, CDC): δ = 5.00 (ddt, $^3J_{H-F}$ = 35.1 Hz, $^3J_{H,H}$ = 7.6 Hz, $^4J_{H-F}$ = 5.4 Hz, 1 H, =CH), 4.76 (dd, $^2J_{H-F}$ = 48.1 Hz, $^3J_{H-F}$ = 18.4 Hz, 2 H, CH_2F), 2.12 (dt, $^3J_{H,H}$ = 7.2 Hz, $^3J_{H,H}$ = 7.0 Hz, 2 H, CH_2), 1.23–1.47 (m, 10 H, CH_2), 0.89 (m, $^3J_{H,H}$ = 6.5 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.2 (dd, $^1J_{C,F}$ = 261.6 Hz, $^2J_{C,F}$ = 18.3 Hz, =CF), 113.6 (dd, $^2J_{C,F}$ = 13.8 Hz, $^3J_{C,F}$ = 8.8 Hz, =CH), 80.4 (dd, $^1J_{C,F}$ = 168.2 Hz, $^2J_{C,F}$ = 33.2 Hz, CH_2F), 22.7–32.1 (CH_2), 14.1 (CH_3); ^{19}F NMR (282 MHz, $CDCl_3$): δ = −215.6 (tdd, $^2J_{F,H}$ = 48.2 Hz, $^3J_{F,F}$ = 31.4 Hz, $^4J_{F,H}$ = 5.6 Hz, 1 F, CH_2F), −122.0 (ddt, $^3J_{F,H}$ = 35.1 Hz, $^3J_{F,F}$ = 31.5 Hz, $^3J_{F,H}$ = 18.5 Hz, 1 F, =CF); GC MS (70 eV) *m*/*z* (%): 176 (2) [M^+], 156 (6) [M^+−HF], 143 (2) [M^+−CH_2F], 127 (7) [156−C_2H_5], 123 (9) [143−HF], 113 (16) [127−CH_2], 107 (11) [127−HF], 99 (28) [113−CH_2], 69 (27) [$C_5H_9^+$], 55 (53) [$C_4H_7^+$], 56 (41) [$C_4H_8^+$], 43 (100) [$C_3H_7^+$], 41 (77) [$C_3H_5^+$]. HR MS (EI): *m*/*z* [M^+] calcd for $C_{10}H_{18}F_2$: 176.1337; found: 176.1335.

*4.2.1.2. Fluorination of 2-fluorohexadec-1-en-3-ol (**1b**).* According to the general procedure, in the reaction of the fluorinating agent **PFPDEA** (0.992 g, 5.36 mmol) with 2-fluorohexadec-1-en-3-ol (**1b**, 1.003 g, 3.88 mmol) a mixture of **3b**, **5b** and **7b** was obtained.

2,3-Difluorohexadec-1-ene (3b). Yield: 61% (GC). ^1H NMR (300 MHz, $CDCl_3$): δ = 4.82 (ddt, $^2J_{H,F}$ = 47.3 Hz, $^3J_{H,F}$ = 12.9 Hz, $^3J_{H,H}$ = 6.5 Hz, 1 H, CHF), 4.76 (m, $^3J_{H,F}$ = 16.8 Hz, 1 H, =C*H*′H″), 4.61 (m, $^3J_{H,F}$ = 47.0 Hz, 1 H, =CH′*H*″), 1.77 (m, 1 H, C*H*′H″), 1.41 (m, 1 H, CH′*H*″), 1.29 (m, 22 H, CH_2), 0.88 (m, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.7 (dd, $^1J_{C,F}$ = 260.3 Hz, $^2J_{C,F}$ = 22.7 Hz, =CF), 92.4 (dd, $^2J_{C,F}$ = 16.4 Hz, $^3J_{C,F}$ = 4.3 Hz, $=CH_2$), 89.5 (dd, $^1J_{C,F}$ = 171.7 Hz, $^2J_{C,F}$ = 32.7 Hz, CHF), 22.7–32.1 (CH_2), 14.1 (CH_3); ^{19}F NMR (282 MHz, $CDCl_3$): δ = −184.3 (ddd, $^2J_{F,H}$ = 47.3 Hz, $^3J_{F,F}$ = 24.9 Hz, $^3J_{F,H}$ = 20.9 Hz, 1 F, CHF), −113.6 (dddd, $^3J_{F,H}$ = 47.0 Hz, $^3J_{F,F}$ = 25.4 Hz, $^3J_{F,H}$ = 16.7 Hz, $^3J_{F,H}$ = 12.4 Hz, 1 F, =CF); GC MS (70 eV) *m*/*z* (%): 260 (0) [M^+], 240 (3) [M^+−HF], 220 (4) [240−HF], 191 (1) [220−C_2H_5], 163 (2) [191−C_2H_4], 149 (3) [163−CH_2], 135 (7) [149−CH_2], 121 (10) [135−CH_2], 107 (9) [121−CH_2], 95 (23) [$C_7H_{11}^+$], 82 (21) [$C_6H_{10}^+$], 69 (26) [$C_5H_9^+$], 56 (57) [$C_4H_8^+$], 43 (63) [$C_3H_7^+$], 41 (100) [$C_3H_5^+$]. HR MS (EI): *m*/*z* [M^+] calcd for $C_{16}H_{30}F_2$: 260.2316; found: 260.2314.

1,2-Difluorohexadec-2-ene (5b). Yield: 15% (GC). ^1H NMR (300 MHz, $CDCl_3$): δ = 5.00 (ddt, $^3J_{H,F}$ = 35.2 Hz, $^3J_{H,H}$ = 7.6 Hz, $^4J_{H,F}$ = 5.3 Hz, 1 H, =CH), 4.75 (dd, $^2J_{H,F}$ = 48.1 Hz, $^3J_{H,F}$ = 18.5 Hz, 2 H, CH_2F), 2.13 (dt, $^3J_{H,H}$ = 6.9 Hz, $^3J_{H,H}$ = 6.7 Hz, 2 H, CH_2), 1.26–1.49 (m, 22 H, CH_2), 0.88 (t, ^3J(H,H) = 6.5 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.0 (dd, $^1J_{C,F}$ = 254.1 Hz, $^2J_{C,F}$ = 17.0 Hz, =CF), 113.3 (dd, $^2J_{C,F}$ = 13.8 Hz, $^3J_{C,F}$ = 8.8 Hz, =CH), 80.2 (dd, $^1J_{C,F}$ = 168.2 Hz, $^2J_{C,F}$ = 33.2 Hz, CH_2F), 22.7–32.1 (CH_2), 14.1 (CH_3); ^{19}F NMR (282 MHz, $CDCl_3$): δ = −215.6 (tdd, $^2J_{F,H}$ = 48.5 Hz, $^3J_{F,F}$ = 31.4 Hz, $^4J_{F,H}$ = 5.5 Hz, 1 F, CH_2F), −122.0 (ddt, $^3J_{F,H}$ = 35.3 Hz, $^3J_{F,F}$ = 31.5 Hz, $^3J_{F,H}$ = 18.8 Hz, 1 H, =CF); GC MS (70 eV) *m*/*z* (%): 260 (0) [M^+], 240 (1) [M^+−HF], 220 (4) [240−HF], 149 (3) [220−C_5H_{11}], 135 (8) [149−CH_2], 121 (10) [135−CH_2], 107 (14) [121−CH_2], 95 (39) [$C_7H_{11}^+$], 82 (61) [$C_6H_{10}^+$], 69 (57) [$C_5H_9^+$], 56 (31) [$C_4H_8^+$], 55 (88) [$C_4H_7^+$], 43 (98) [$C_3H_7^+$], 41 (100) [$C_3H_5^+$]. HR MS (EI): *m*/*z* [M^+] calcd for $C_{16}H_{30}F_2$: 260.2316; found: 260.2315.

*4.2.1.3. Fluorination of 2-fluorooctadec-1-en-3-ol (**1c**).* According to the general procedure a mixture of **3c**, **5c** and **7c** was obtained in the reaction of the fluorinating agent **PFPDEA** (0.963 g, 5.21 mmol) with 2-fluorooctadec-1-en-3-ol (**1c**, 0.738 g, 2.58 mmol).

2,3-Difluorooctadec-1-ene (3c). Yield: 44% (GC). ^1H NMR (300 MHz, $CDCl_3$): δ = 4.82 (ddt, $^2J_{H,F}$ = 47.3 Hz, $^3J_{H,F}$ = 12.8 Hz, $^3J_{H,H}$ = 6.5 Hz, 1 H, CHF), 4.76 (m, $^3J_{H,F}$ = 17.1 Hz, 1 H, =C*H*′H″), 4.62 (m, $^3J_{H,F}$ = 47.7 Hz, 1 H, =CH′*H*″), 1.79 (m, 1 H, C*H*′H″), 1.42 (m, 1 H, CH′*H*″), 1.29 (m, 26 H, CH_2), 0.88 (m, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.7 (dd, $^1J_{C,F}$ = 262.5 Hz, $^2J_{C,F}$ = 23.2 Hz, =CF), 92.4 (dd, $^2J_{C,F}$ = 16.5 Hz, $^3J_{C,F}$ = 5.3 Hz, $=CH_2$), 89.5 (dd, $^1J_{C,F}$ = 172.5 Hz, $^2J_{C,F}$ = 33.3 Hz, CHF), 22.7–32.1 (CH_2), 14.1 (CH_3); ^{19}F NMR (282 MHz, $CDCl_3$): δ = −184.3 (ddd, $^2J_{F,H}$ = 47.3 Hz, $^3J_{F,F}$ = 24.9 Hz, $^3J_{F,H}$ = 20.9 Hz, 1 F, CHF), −113.6 (dddd, $^3J_{F,H}$ = 47.0 Hz, $^3J_{F,F}$ = 25.4 Hz, $^3J_{F,H}$ = 16.7 Hz, $^3J_{F,H}$ = 12.4 Hz, 1 H, =CF); GC MS (70 eV) *m*/*z* (%): 288 (1) [M^+], 268 (2) [M^+−HF], 248 (1) [268−HF], 233 (1) [248−CH_3], 221 (1) [248−C_2H_3], 219 (1) [248−C_2H_5], 208 (3) [221−CH], 205 (0) [219−CH_2], 191 (0) [205−CH_2], 177 (1) [191−CH_2], 163 (2) [177−CH_2], 149 (3) [163−CH_2], 135 (7) [149−CH_2], 121 (10) [135−CH_2], 107 (9) [121−CH_2], 97 (42) [$C_7H_{13}^+$], 95 (29) [$C_7H_{11}^+$], 83 [$C_6H_{11}^+$], 82 (21) [$C_6H_{10}^+$], 69 (49) [$C_5H_9^+$], 57 (82) [$C_4H_9^+$], 55 (59) [$C_4H_7^+$], 43 (63) [$C_3H_7^+$], 41 (100) [$C_3H_5^+$]. HR MS (EI): *m*/*z* [M^+] calcd for $C_{16}H_{30}F_2$: 288.2629; found: 288.2627.

1,2-Difluorooctadec-2-ene (5c). Yield: 11% (CG). ^1H NMR (300 MHz, $CDCl_3$): δ = 5.00 (ddt, $^3J_{H,F}$ = 35.0 Hz, $^3J_{H,F}$ = 7.6 Hz, $^4J_{H,F}$ = 5.2 Hz, 1 H, =CH), 4.75 (dd, $^2J_{H,F}$ = 48.2 Hz, $^3J_{H,F}$ = 18.2 Hz, 2 H, CH_2F), 2.14 (dt, $^3J_{H,H}$ = 7.0 Hz, $^3J_{H,H}$ = 6.9 Hz, 2 H, CH_2), 1.19–1.51 (m, 26 H, CH_2), 0.88 (t, $^3J_{H,H}$ = 6.5 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.2 (dd, $^1J_{C,F}$ = 258.3 Hz, $^2J_{C,F}$ = 18.4 Hz, =CF), 113.2 (dd, $^2J_{C,F}$ = 13.9 Hz, $^3J_{C,F}$ = 9.2 Hz, =CH), 80.9 (ddt, $^1J_{C,F}$ = 166.8 Hz, $^2J_{C,F}$ = 31.8 Hz, CH_2F), 22.7–32.2 (CH_2), 14.1 (q, CH_3); ^{19}F NMR (282 MHz, $CDCl_3$): δ = −215.6 (tdd, $^2J_{F,H}$ = 48.5 Hz, $^3J_{F,F}$ = 31.1 Hz, $^4J_{F,H}$ = 5.5 Hz, 1 H, CH_2F), −122.0 (ddt, $^3J_{F,H}$ = 34.9 Hz, $^3J_{F,F}$ = 31.1 Hz, $^3J_{F,H}$ = 17.9 Hz, 1 H, =CF); GC MS (70 eV) *m*/*z* (%): 288 (1) [M^+], 268 (2) [M^+−HF], 248 (0) [268−HF], 235 (2) [268−CH_2F], 233 (0) [248−CH_3], 221 (0) [248−C_2H_3; 235−CH_2], 219 (0) [248−C_2H_5], 208 (3) [221−CH], 205 (1) [219−CH_2], 191 (1) [205−CH_2], 177 (3) [191−CH_2], 163 (2) [177−CH_2], 149 (4) [163−CH_2], 135 (7) [149−CH_2], 121 (10) [135−CH_2], 107 (9) [121−CH_2], 97 (42) [$C_7H_{13}^+$], 95 (29) [$C_7H_{11}^+$], 83 [$C_6H_{11}^+$], 82 (21) [$C_6H_{10}^+$], 69 (49) [$C_5H_9^+$], 57 (82) [$C_4H_9^+$], 55 (59) [$C_4H_7^+$], 43 (63) [$C_3H_7^+$], 41 (100) [$C_3H_5^+$]. HR MS (EI): *m*/*z* [M^+] calcd for $C_{16}H_{30}F_2$: 288.2629; found: 288.2625.

*4.2.1.4. Fluorination of oct-1-en-3-ol (**2**).* According to the general procedure mixture of **4** and **6** was obtained in the reaction of the fluorinating agent **PFPDEA** (1.965 g, 10.61 mmol) with oct-1-en-3-ol (**2**) (1.002 g, 7.80 mmol).

3-Fluorooct-1-ene (4a). Yield: 36% (GC). ^1H NMR (300 MHz, $CDCl_3$): δ = 5.88 (dddd, $^3J_{H,H}$ = 17.2 Hz, $^3J_{H,H}$ = 10.6 Hz, $^3J_{H,H}$ = 6.2 Hz, $^3J_{H,F}$ = 10.2 Hz, 1 H, =CH), 5.29 (ddd, $^3J_{H,H}$ = 17.4 Hz, $^2J_{H,H}$ = 1.3 Hz, $^4J_{H,F}$ = 3.6 Hz, 1 H, =C*H*′H″), 5.19 (ddd, $^3J_{H,H}$ = 10.7 Hz, $^2J_{H,H}$ = 1.2 Hz, $^4J_{H,F}$ = 1.2 Hz, 1 H, =CH′*H*″), 4.84 (ddtt, $^2J_{H,F}$ = 48.7 Hz, $^3J_{H,H}$ = 6.2 Hz, $^3J_{H,H}$ = 6.2 Hz, $^4J_{H,H}$ = 1.1 Hz, 1 H, CHF), 1.67 (m, 1 H, C*H*′H″), 1.56 (m, 1 H, CH′*H*″), 1.30 (m, 6 H, CH_2), 0.90 (t, $^3J_{H,H}$ = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.9 (d, $^2J_{C,F}$ = 21.3 Hz, =CH), 116.5 (d, $^3J_{C,F}$ = 10.7 Hz, $=CH_2$), 93.6 (d, $^1J_{C,F}$ = 166.7 Hz, CHF), 31.5 (dt, $^2J_{C,F}$ = 17.7 Hz, CH_2), 28.5 (CH_2), 24.3 (CH_2), 22.5 (CH_2), 13.9 (CH_3); ^{19}F NMR (282 MHz, $CDCl_3$): δ = −177.5 (m, 1 F, CHF); GC MS (70 eV) *m*/*z* (%): 130 (0) [M^+], 110 (27) [M^+−HF], 95 (8) [110−CH_3], 81 (33) [95−CH_2], 69 (100) [95−C_2H_2; $C_5H_9^+$], 67 (49) [81−CH_2; $C_5H_7^+$], 55 (53)

[69−CH_2], 54 (61) [69−CH_3], 41 (60) [$C_3H_5^+$]. HR MS (EI): *m/z* [M^+] calcd for $C_8H_{15}F$: 130.1158; found: 130.1156.

1-Fluorooct-2-ene (6a). Yield: 24% (GC). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.84 (dd, $^3J_{H,F}$ = 20.6 Hz, $^3J_{H,H}$ = 14.8 Hz, 1 H, =CH), 5.66 (dt, $^3J_{H,H}$ = 14.8 Hz, $^3J_{H,H}$ = 6.6 Hz, 1 H, =CH), 4.77 (ddd, $^2J_{H,F}$ = 47.5 Hz, $^3J_{H,H}$ = 6.3 Hz, $^4J_{H,H}$ = 0.7 Hz, 1 H, CH_2F), 2.07 (dt, $^3J_{H,H}$ = 6.7 Hz, $^3J_{H,H}$ = 6.5 Hz, 2 H, CH_2), 1.32 (m, 6 H, CH_2), 0.91 (t, $^3J_{H,H}$ = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.6 (d, $^3J_{C,F}$ = 13.5 Hz, =CH), 124.5 (d, $^2J_{C,F}$ = 16.3 Hz, =CH), 83.6 (d, $^1J_{C,F}$ = 159.9 Hz, CH_2F), 35.2 (CH_2), 32.1 (CH_2), 24.4 (CH_2), 22.5 (CH_2), 13.9 (CH_3); ^{19}F NMR (282 MHz, $CDCl_3$): δ = −208.4 (m, 1F, CH_2F). GC MS *m/z* (%) 130 (0) [M^+], 110 (25) [M^+−HF], 95 (11) [110−CH_3], 81 (40) [95−CH_2], 69 (63) [95−C_2H_2; $C_5H_9^+$], 67 (65) [81−CH_2; $C_5H_7^+$], 55 (53) [69−CH_2], 54 (79) [69−CH_3], 44 (100), 41 (60) [$C_3H_5^+$]. HR MS (EI): *m/z* [M^+] calcd for $C_8H_{15}F$: 130.1158; found: 130.1156.

4.2.2. Eschenmoser–Claisen-type rearrangement: general procedure (GP2)

To a solution of allylic alcohol (1 equiv.) and triethylamine (2 equiv.) in dry dichloromethane (5 mL), a solution of pentafluoropropene-diethylamine adduct (2 equiv.) in dry dichloromethane (5 mL) was dropwise added. The resulting mixture was stirred over 48 h at room temperature and then quenched with water (10 mL). The organic layer was extracted with dichloromethane (3× 10 mL). The combined organic layers were washed with saturated aqueous solutions of $NaHCO_3$ (1× 10 mL) and NaCl (2× 10 mL). The organic phase was dried over $MgSO_4$ and the solvent was evaporated. The crude product was purified by column chromatography.

(*Z*)-*N*,*N*-Diethyl-4-fluoro-2-(trifluoromethyl)dodec-4-enamide (7a). According to the general procedure GP2 **7a** was obtained in the reaction of the fluorinating agent **PFPDEA** (1.098 g, 5.93 mmol) with 2-fluorodec-1-en-3-ol (**1a**) (0.504 g, 2.89 mmol) and triethylamine (0.675 g, 6.67 mmol). The product **7a** was purified by column chromatography with cyclohexane/ethyl acetate (15:1). Yield: 80% (0.788 g, 2.31 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.68 (dt, $^3J_{H,F}$ = 38.2 Hz, $^3J_{H,H}$ = 7.6 Hz, 1 H, =CH), 3.63 (ddq, $^3J_{H,H}$ = 11.1 Hz, $^3J_{H,F}$ = 7.9 Hz, $^3J_{H,H}$ = 3.6 Hz, 1 H, $CHCF_3$), 3.40 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, CH_2), 3.33 (q, $^3J_{H,H}$ = 7.1 Hz, 2 H, CH_2), 2.90 (ddd, $^2J_{H,H}$ = 14.3 Hz, $^3J_{H,F}$ = 28.5 Hz, $^3J_{H,H}$ = 10.6 Hz, 1 H, C*H*′H″), 2.60 (ddd, $^2J_{H,H}$ = 13.2 Hz, $^3J_{H,F}$ = 13.3 Hz, $^3J_{H,H}$ = 3.4 Hz, 1 H, CH′*H*″), 2.01 (dt, $^3J_{H,H}$ = 6.9 Hz, $^3J_{H,H}$ = 6.7 Hz, 2 H, CH_2), 1.28 (m, 12 H, CH_2), 1.19 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_3), 1.12 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H), 0.88 (t, $^3J_{H,H}$ = 6.8 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.8 (CO), 154.3 (d, $^1J_{C,F}$ = 250.1 Hz, =CF), 124.9 (q, $^1J_{C,F}$ = 280.7 Hz, CF_3), 109.5 (dd, $^2J_{C,F}$ = 10 Hz, =CH), 43.1 (dq, $^2J_{C,F}$ = 29.6 Hz, *C*HCF$_3$), 42.6 (CH_2), 41.4 (CH_2), 31.8 (CH_2), 30.4 (dq, $^2J_{C,F}$ = 28.1 Hz, $^3J_{C,F}$ = 2.4 Hz, CH′H″), 22.7–29.4 (CH_2), 14.4 (CH_3), 14.1 (CH_3), 12.8 (CH_3); ^{19}F NMR (282 MHz, $CDCl_3$): δ = −114.2 (ddd, $^3J_{F,H}$ = 38.4 Hz, $^3J_{F,H}$ = 28.5 Hz, $^3J_{F,H}$ = 13.3 Hz, 1 F, =CF), −68.4 (d, $^3J_{F,H}$ = 8.3 Hz, 3 F, CF_3); GC MS *m/z* (%) 339 (6) [M^+], 324 (3) [M^+−CH_3], 310 (32) [M^+−C_2H_5], 296 (8) [M^+−C_3H_7], 282 (4) [M^+−C_4H_9], 268 (12) [M^+−C_5H_{11}], 254 (100) [M^+−C_6H_{13}], 226 (6) [254−C_2H_4], 206 (3) [226−HF], 183 (25) [254 +H−$C_4H_{10}N$], 168 (15) [183−CH_3], 154 (10) [183−H−CO], 115 (2) [183+H−CF_3], 100 (32) [$H_{10}C_4NCO^+$], 72 (23) [100−CO], 58 (16) [$C_3H_8N^+$], 41 (8) [$C_3H_5^+$]. Anal. calcd for $C_{17}H_{29}F_4NO$: C, 60.16; H, 8.61; N, 4.13. Found: C, 60.38; H, 8.67; N, 4.22.

(*Z*)-*N*,*N*-Diethyl-4-fluoro-2-(trifluoromethyl)octadec-4-enamide (7b). According to the general procedure **7b** was obtained in the reaction of the fluorinating agent **PFPDEA** (0.735 g, 3.97 mmol) with 2-fluorohexadec-1-en-3-ol **1b** (0.485 g, 1.88 mmol) and triethylamine (0.458 g, 4.53 mmol). The product **7b** was purified by column chromatography with cyclohexane/ethyl acetate (35:1). Yield: 91% (0.723 g, 1.69 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.68 (dt, $^3J_{H,F}$ = 38.2 Hz, $^3J_{H,H}$ = 7.6 Hz, 1 H, =CH), 3.63 (ddq, $^3J_{H,F}$ = 7.9 Hz, $^3J_{H,H}$ = 3.6 Hz, $^3J_{H,H}$ = 10.6 Hz, 1 H, $CHCF_3$), 3.40 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, CH_2), 3.33 (q, $^3J_{H,H}$ = 7.0 Hz, 2 H, CH_2), 2.90 (ddd, $^2J_{H,H}$ = 14.3 Hz, $^3J_{H,F}$ = 28.6 Hz, $^3J_{H,H}$ = 10.6 Hz, 1 H, C*H*′H″), 2.60 (ddd, $^2J_{H,H}$ = 14.3 Hz, $^3J_{H,F}$ = 13.3 Hz, $^3J_{H,H}$ = 3.4 Hz, 1 H, CH′*H*″), 2.01 (dt, $^3J_{H,H}$ = 6.8 Hz, $^3J_{H,H}$ = 6.7 Hz, 2 H, CH_2), 1.26 (m, 22 H, CH_2), 1.19 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_3), 1.12 (t, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 0.88 (t, $^3J_{H,H}$ = 6.7 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.8 (s, CO), 154.3 (d, $^1J_{C,F}$ = 250.7 Hz, =CF), 124.8 (q, $^1J_{C,F}$ = 280.7 Hz, CF_3), 109.4 (d, $^2J_{C,F}$ = 15.5 Hz, =CH), 43.0 (q, $^2J_{C,F}$ = 25.9 Hz, *C*HCF$_3$), 42.6 (CH_2), 41.4 (CH_2), 31.9 (CH_2), 30.3 (dq, $^2J_{C,F}$ = 28.2 Hz, $^3J_{C,F}$ = 2.4 Hz, CH_2), 22.7–29.4 (CH_2), 14.3 (CH_3), 14.1 (CH_3), 12.8 (CH_3); ^{19}F NMR (282 MHz, $CDCl_3$): δ = −114.3 (ddd, $^3J_{F,H}$ = 38.1 Hz, $^3J_{F,H}$ = 13.3 Hz, $^3J_{F,H}$ = 28.6 Hz, 1 F, =CF), −68.4 (d, $^3J_{F,H}$ = 8.2 Hz, 3 F, CF_3); GC MS (70 eV) *m/z* (%): 423 (4) [M^+], 408 (2) [M^+−CH_3], 394 (2) [M^+−C_2H_5], 380 (3) [M^+−C_3H_7], 366 (6) [M^+−C_4H_9], 352 (4) [M^+−C_5H_{11}], 338 (3) [M^+−C_6H_{13}], 324 (7) [M^+−C_7H_{15}], 310 (27) [M^+−C_8H_{17}], 296 (7) [310+H−CH_3], 282 (4) [310+H−C_2H_5], 268 (12) [310+H−C_3H_7], 254 (100) [310+H−C_4H_9], 226 (4) [254−C_2H_4], 206 (2) [226−HF], 183 (24) [254+H^+−$C_4H_{10}N$], 168 (10) [183−CH_3], 154 (7) [183−H−CO], 115 (2) [183+H−CF_3], 113 (0) [$C_8H_{17}^+$], 100 (20) [$H_{10}C_4NCO^+$], 99 (0) [$C_7H_{15}^+$], 85 (2) [$C_6H_{13}^+$], 72 (14) [100−CO], 58 (16) [$C_3H_8N^+$], 57 (5) [$C_4H_9^+$], 43 (10) [$C_3H_7^+$], 41 (8) [$C_3H_5^+$]. Anal. calcd for: $C_{23}H_{41}F_4NO$: C, 65.22; H, 9.76; N, 3.31. Found: C, 65.43; H, 9.84; N, 3.14.

(*Z*)-*N*,*N*-Diethyl-4-fluoro-2-(trifluoromethyl)icos-4-enamide (7c). According to the general procedure **7c** was obtained in the reaction of the fluorinating agent **PFPDEA** (0.548 g, 2.96 mmol) with 2-fluorooctadec-1-en-3-ol **1c** (0.404 g, 1.41 mmol) and triethylamine (0.356 g, 2.52 mmol). The product **7c** was purified by column chromatography with cyclohexane/ethyl acetate (40:1). Yield: 72% (0.459 g, 1.02 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.68 (dt, $^3J_{H,F}$ = 38.4 Hz, $^3J_{H,H}$ = 7.6 Hz, 1 H, =CH), 3.63 (ddq, $^3J_{H,H}$ = 10.5 Hz, $^3J_{H,F}$ = 7.8 Hz, $^3J_{H,H}$ = 3.6 Hz, 1 H, $CHCF_3$), 3.40 (q, $^3J_{H,H}$ = 7.3 Hz, 2 H, CH_2), 3.33 (q, $^3J_{H,H}$ = 7.1 Hz, 2 H, CH_2), 2.90 (ddd, $^2J_{H,H}$ = 14.3 Hz, $^3J_{H,F}$ = 28.6 Hz, $^3J_{H,H}$ = 10.5 Hz, 1 H, C*H*′H″), 2.60 (ddd, $^2J_{H,H}$ = 14.3 Hz, $^3J_{H,F}$ = 13.3 Hz, $^3J_{H,H}$ = 3.6 Hz, 1 H, CH′*H*″), 2.01 (dt, $^3J_{H,H}$ = 6.9 Hz, $^3J_{H,H}$ = 6.9 Hz, 2 H, CH_2), 1.26 (m, 26 H, CH_2), 1.19 (t, $^3J_{H,H}$ = 7.3 Hz, 3 H, CH_3), 1.12 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_3), 0.88 (t, $^3J_{H,H}$ = 6.7 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.7 (s, CO), 154.2 (d, $^1J_{C,F}$ = 252.0 Hz, =CF), 124.9 (q, $^1J_{C,F}$ = 280.4 Hz, CF_3), 109.3 (d, $^2J_{C,F}$ = 14.2 Hz, =CH), 43.0 (q, $^2J_{C,F}$ = 25.5 Hz, *C*HCF$_3$), 42.5 (CH_2), 41.3 (CH_2), 31.9 (CH_2), 30.3 (dq, $^2J_{C,F}$ = 28.3 Hz, $^3J_{C,F}$ = 2.6 Hz, CH_2), 22.6–29.6 (CH_2), 14.3 (CH_3), 14. (CH_3), 12.8 (CH_3); ^{19}F NMR (282 MHz, $CDCl_3$): δ = −114.3 (ddd, $^3J_{F,H}$ = 38.4 Hz, $^3J_{F,H}$ = 13.3 Hz, $^3J_{F,H}$ = 28.6 Hz, 1 F, =CF), −68.4 (d, $^3J_{F,H}$ = 9.4 Hz, 3 F, CF_3); GC MS (70 eV) *m/z* (%): 451 (4) [M^+], 436 (1) [M^+−CH_3], 422 (3) [M^+−C_2H_5], 408 (2) [M^+−C_3H_7], 394 (3) [M^+−C_4H_9], 380 (5) [M^+−C_5H_{11}], 366 (7) [M^+−C_6H_{13}], 352 (4) [M^+−C_7H_{15}], 338 (4) [M^+−C_8H_{17}], 324 (9) [M^+−C_9H_{19}], 310 (25) [M^+−$C_{10}H_{21}$], 296 (8) [310+H−CH_3], 282 (6) [310+H−C_2H_5], 268 (13) [310+H−C_3H_7], 254 (100) [310+H−C_4H_9], 226 (4) [254−C_2H_4], 206 (1) [226−HF], 183 (27) [254+H−$C_4H_{10}N$], 168 (9) [183−CH_3], 154 (7) [183−H−CO], 115 (1) [183+H−CF_3], 113 (0) [$C_8H_{17}^+$], 100 (20) [$H_{10}C_4NCO^+$], 99 (0) [$C_7H_{15}^+$], 85 (1) [$C_6H_{13}^+$], 72 (17) [100−CO], 71 (3) [$C_5H_{11}^+$], 58 (9) [$C_3H_8N^+$], 57 (8) [$C_4H_9^+$], 43 (11) [$C_3H_7^+$], 41 (9) [$C_3H_5^+$]. Anal. calcd for $C_{25}H_{45}F_4NO$: C, 66.49; H, 10.04; N, 3.10. Found: C, 66.62; H, 10.34; N, 3.26.

***N*,*N*-Diethyl-4-fluoro-2-(trifluoromethyl)pent-4-enamide (7d)**. According to the general procedure **7d** was obtained in the reaction of the fluorinating agent **PFPDEA** (1.10 g, 6.00 mmol) with 2-fluoroprop-1-en-3-ol 1d (0.230 g, 3.00 mmol) and triethylamine (0.607 g, 6.00 mmol). The product **7d** was purified by column chromatography with cyclohexane/ethyl acetate (10:1). Yield: 40% (0.290 g, 1.20 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.55 (dd, $^3J_{H,F}$ = 16.9 Hz, $^2J_{H,H}$ = 3.0 Hz, 1 H, =CH′H″), 4.35 (dd, $^3J_{H,F}$ = 49.8 Hz,

$^2J_{H,H}$ = 3.0 Hz, 1 H, =CH′H″), 3.59 (m, 1 H, $CHCF_3$), 3.30 (m, 4 H, CH_2), 2.93 (ddd, $^3J_{H,F}$ = 27.4 Hz, $^2J_{H,H}$ = 14.4 Hz, $^3J_{H,H}$ = 10.6 Hz, 1 H, CH′H″), 2.57 (ddd, $^2J_{H,H}$ = 14.4 Hz, $^3J_{H,F}$ = 12.2 Hz, $^3J_{H,H}$ = 3.7 Hz, 1 H, CH′H″), 1.13 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_3), 1.05 (t, $^3J_{H,H}$ = 7.1 Hz 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.3 (CO), 161.4 (d, $^1J_{C,F}$ = 255.7 Hz, =CF), 124.7 (q, $^1J_{C,F}$ = 280.6 Hz, CF_3), 93.5 (d, $^2J_{C,F}$ = 18.8 Hz, $=CH_2$), 42.7 (qd, $^2J_{C,F}$ = 26.4 Hz, $^3J_{C,F}$ = 1.6 Hz, $CHCF_3$), 42.5 (CH_2), 41.3 (CH_2), 30.0 (dq, $^2J_{C,F}$ = 27.3 Hz, $^3J_{C,F}$ = 2.7 Hz, CH_2), 14.3 (CH3), 12.7 (CH3); ^{19}F NMR (282 MHz, $CDCl_3$): δ = −99.4 (dddd, $^3J_{F,H}$ = 49.8 Hz, $^3J_{F,H}$ = 27.4 Hz, $^3J_{F,H}$ = 16.9 Hz, $^3J_{F,H}$ = 12.2 Hz, 1 F, =CF), −68.4 (d, $^3J_{F,H}$ = 7.8 Hz, 3 F, CF_3). Anal. calcd for $C_{10}H_{15}F_4NO$: C, 49.79; H, 6.27; N, 5.81. Found: C, 49.85; H, 6.34; N, 5.96.

(2*R*)-*N*,*N*-Diethyl-4-fluoro-2-(trifluoromethyl)icos-4(*Z*)-enamide ((*R*)-7c). According to the general procedure (*R*)-**7c** was obtained in the reaction of the fluorinating agent **PFPDEA** (0.391 g, 2.11 mmol) with (*R*)-2-fluorooctadec-1-en-3-ol (65% ee) (*R*)-**1c** (0.301 g, 1.05 mmol) and triethylamine (0.213 g, 2.10 mmol). The product (*R*)-**7c** was purified by column chromatography with cyclohexane/ethyl acetate (40:1). Yield: 76% (0.361 g, 0.80 mmol). $[\alpha]_D^{25}$ +8.8 (c 0.51, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.68 (dt, $^3J_{H,F}$ = 38.4 Hz, $^3J_{H,H}$ = 7.6 Hz, 1 H, =CH), 3.63 (ddq, $^3J_{H,H}$ = 10.5 Hz, $^3J_{H,F}$ = 7.8 Hz, $^3J_{H,H}$ = 3.6 Hz, 1 H, $CHCF_3$), 3.40 (q, $^3J_{H,H}$ = 7.3 Hz, 2 H, CH_2), 3.33 (q, $^3J_{H,H}$ = 7.1 Hz, 2 H, CH_2), 2.90 (ddd, $^2J_{H,H}$ = 14.3 Hz, $^3J_{H,F}$ = 28.6 Hz, $^3J_{H,H}$ = 10.5 Hz, 1 H, C*H*′H″), 2.60 (ddd, $^2J_{H,H}$ = 14.3 Hz, $^3J_{H,F}$ = 13.3 Hz, $^3J_{H,H}$ = 3.6 Hz, 1 H, CH′*H*″), 2.01 (dt, $^3J_{H,H}$ = 6.9 Hz, $^3J_{H,H}$ = 6.9 Hz, 2 H, CH_2), 1.26 (m, 26 H, CH_2), 1.19 (t, $^3J_{H,H}$ = 7.3 Hz, 3 H, CH_3), 1.12 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_3), 0.88 (t, $^3J_{H,H}$ = 6.7 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.7 (s, CO), 154.2 (d, $^1J_{C,F}$ = 252.0 Hz, =CF), 124.9 (q, $^1J_{C,F}$ = 280.4 Hz, CF_3), 109.3 (d, $^2J_{C,F}$ = 14.2 Hz, =CH), 43.0 (q, $^2J_{C,F}$ = 25.5 Hz, *C*HCF$_3$), 42.5 (CH_2), 41.3 (CH_2), 31.9 (CH_2), 30.3 (dq, $^2J_{C,F}$ = 28.3 Hz, $^3J_{C,F}$ = 2.6 Hz, CH_2), 22.6–29.6 (CH_2), 14.3 (CH_3), 14. (CH_3), 12.8 (CH_3); ^{19}F NMR (282 MHz, $CDCl_3$): δ = −114.3 (ddd, $^3J_{F,H}$ = 38.4 Hz, $^3J_{F,H}$ = 13.3 Hz, $^3J_{F,H}$ = 28.6 Hz, 1 F, =CF), −68.4 (d, $^3J_{F,H}$ = 9.4 Hz, 3 F, CF_3); GC MS (70 eV) *m*/*z* (%): 451 (4) [M^+], 436 (1) [M^+-CH_3], 422 (3) [$M^+-C_2H_5$], 408 (2) [$M^+-C_3H_7$], 394 (3) [$M^+-C_4H_9$], 380 (5) [$M^+-C_5H_{11}$], 366 (7) [$M^+-C_6H_{13}$], 352 (4) [$M^+-C_7H_{15}$], 338 (4) [$M^+-C_8H_{17}$], 324 (9) [$M^+-C_9H_{19}$], 310 (25) [$M^+-C_{10}H_{21}$], 296 (8) [310+H−CH_3], 282 (6) [310+H−C_2H_5], 268 (13) [310+H−C_3H_7], 254 (100) [310+H−C_4H_9], 226 (4) [254−C_2H_4], 206 (1) [226−CF], 183 (27) [254+H−$C_4H_{10}N$], 168 (9) [183−CH_3], 154 (7) [183−H−CO], 115 (1) [183+H−CF_3], 113 (0) [$C_8H_{17}^+$], 100 (20) [$H_{10}C_4NCO^+$], 99 (0) [$C_7H_{15}^+$], 85 (1) [$C_6H_{13}^+$], 72 (17) [100−CO], 71 (3) [$C_5H_{11}^+$], 58 (9) [$C_3H_8N^+$], 57 (8) [$C_4H_9^+$], 43 (11) [$C_3H_7^+$], 41 (9) [$C_3H_5^+$]. Anal. calcd for $C_{25}H_{45}F_4NO$: C, 66.49; H, 10.04; N, 3.10. Found: C, 66.62; H, 10.34; N, 3.26.

(*E*)-*N*,*N*-Diethyl-2-(trifluoromethyl)dec-4-enamide (8a). According to the general procedure **8** was obtained in the reaction of the fluorinating agent **PFPDEA** (1.730 g, 9.30 mmol) with oct-1-en-3-ol **2** (0.500 g, 3.90 mmol) and triethylamine (0.811 g, 8.01 mmol). The product **8** was purified by column chromatography with cyclohexane/ethyl acetate (10:1). Yield: 88% (1.001 g, 3.43 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.59 (ddd, $^3J_{H,H}$ = 14.9 Hz, $^3J_{H,H}$ = 7.3 Hz, $^3J_{H,H}$ = 6.8 Hz, 1 H, =CH), 5.28 (dt, $^3J_{H,H}$ = 14.9 Hz, $^3J_{H,H}$ = 7.2 Hz, 1 H, =CH), 3.41 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, CH_2), 3.32 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, CH_2), 3.30 (m, 1 H, $CHCF_3$), 2.72 (ddd, $^2J_{H,H}$ = 13.4 Hz, $^3J_{H,H}$ = 10.5 Hz, $^3J_{H,H}$ = 7.1 Hz, $^4J_{H,H}$ = 0.8 Hz, 1 H, C*H*′H″), 2.43 (ddd, $^2J_{H,H}$ = 13.3 Hz, $^3J_{H,H}$ = 7.2 Hz, $^3J_{H,H}$ = 4.8 Hz, 1 H, CH′*H*″), 1.96 (dt, $^3J_{H,H}$ = 6.8 Hz, $^3J_{H,H}$ = 6.8 Hz, 2 H, CH_2), 1.23–1.37 (m, 6 H, CH_2), 1.18 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_3), 1.13 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_3), 0.87 (t, $^3J_{H,H}$ = 6.9 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.9 (s, CO), 135.4 (=CH), 125.5 (q, $^1J_{C,F}$ = 280.9 Hz, CF_3), 124.5 (=CH), 46.6 (tq, $^2J_{C,F}$ = 25.5 Hz, *C*HCF$_3$), 42.8 (CH_2), 41.5 (CH_2), 32.7 (CH_2), 31.7 (CH_2), 30.5 (q, $^3J_{C,F}$ = 2.6 Hz, CH_2), 29.2 (CH_2), 22.8 (CH_2), 15.0 (CH_3), 14.3 (CH_3), 13.2 (CH_3); ^{19}F NMR (282 MHz, $CDCl_3$): δ = −68.2 (d, $^3J_{F,H}$ = 9.7 Hz, 3 F, CF_3); GC MS (70 eV) *m*/*z* (%): 293 (10) [M^+], 278 (6) [M^+-CH_3], 264 (4) [$M^+-C_2H_4$], 250 (10) [$M^+-C_3H_7$], 236 (100) [$M^+-C_4H_9$], 224 (63) [M^+-CF_3], 183 (45) [236+H−C_4H_6], 168 (28) [183−CH_3], 154 (22) [183−C_2H_5], 140 (5) [183−C_3H_8], 126 (9) [183−C_3H_8N], 100 (52) [$H_{10}C_4NCO^+$], 72 (39) [100−CO], 58 (28) [$C_3H_8N^+$]. Anal. calcd for $C_{15}H_{26}NOF_3$: C, 61.41; H, 8.93; N, 4.77. Found: C, 61.52; H, 9.09; N, 4.75.

***N*,*N*-Diethyl-2-(trifluoromethyl)pent-4-enamide (8b)**. According to the general procedure **8b** was obtained in the reaction of the fluorinating agent **PFPDEA** (1.10 g, 6.00 mmol) with 2-fluoroprop-1-en-3-ol **2b** (0.230 g, 3.00 mmol) and triethylamine (0.607 g, 6.00 mmol). The product **8b** was purified by column chromatography with cyclohexane/ethyl acetate (10:1). Yield: 40% (0.290 g, 1.20 mmol). 1H NMR (300 MHz, $CDCl_3$): δ = 5.69 (ddt, $^3J_{H,H}$ = 17.2 Hz, $^3J_{H,H}$ = 10.0 Hz, $^3J_{H,H}$ = 7.1 Hz, 1 H, =CH), 5.18 (ddd, $^2J_{H,H}$ = 1.6 Hz, $^3J_{H,H}$ = 17.2 Hz, $^3J_{H,H}$ = 3.6 Hz, 1 H, =C*H*′H″), 5.09 (ddt, $^2J_{H,H}$ = 1.6 Hz, $^3J_{H,H}$ = 10.0 Hz, $^3J_{H,H}$ = 1.0 Hz, 1 H, =CH′*H*″), 3.42 (m, 4 H, CH_2), 3.35 (m, 1 H, $CHCF_3$), 2.81 (ddddd, $^2J_{H,H}$ = 13.2 Hz, $^3J_{H,H}$ = 10.5 Hz, $^3J_{H,H}$ = 7.1 Hz, $^3J_{H,H}$ = 1.4 Hz, $^3J_{H,H}$ = 1.0 Hz, 1 H, C*H*′H″), 2.50 (ddd, $^2J_{H,H}$ = 13.2 Hz, $^3J_{H,H}$ = 7.5 Hz, $^3J_{H,H}$ = 3.6 Hz, 1 H, CH′*H*″), 1.19 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_3), 1.13 (t, $^3J_{H,H}$ = 7.1 Hz 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.2 (CO), 132.9 (=CH), 125.0 (q, $^1J_{C,F}$ = 280.6 Hz, CF_3), 118.7 ($=CH_2$), 45.6 (q, $^2J_{C,F}$ = 25.6 Hz, *C*HCF$_3$), 42.4 (CH_2), 41.1 (CH_2), 31.2 (CH_2), 14.6 (CH_3), 12.8 (CH_3); ^{19}F NMR (282 MHz, $CDCl_3$): δ = −68.2 (d, $^3J_{F,H}$ = 7.9 Hz, 3 F, CF_3). Anal. calcd for $C_{10}H_{16}F_3NO$: C, 53.80; H, 7.22; N, 6.27. Found: C, 53.92; H, 7.41; N, 6.41.

(2*R*)-*N*,*N*-Diethyl-2-(trifluoromethyl)dec-4(*E*)-enamide ((*R*)-8a). According to the general procedure (*R*)-**8a** was obtained in the reaction of the fluorinating agent **PFPDEA** (0.578 g, 3.12 mmol) with (*R*)-oct-1-en-3-ol (*R*)-**2a** (0.200 g, 1.56 mmol) and triethylamine (0.316 g, 3.12 mmol). The product (*R*)-**8a** was purified by column chromatography with cyclohexane/ethyl acetate (10:1). Yield: 93% (0.423 g, 1.45 mmol). $[\alpha]_D^{25}$ +36.8 (*c* 0.75, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.59 (ddd, $^3J_{H,H}$ = 14.9 Hz, $^3J_{H,H}$ = 7.3 Hz, $^3J_{H,H}$ = 6.8 Hz, 1 H, =CH), 5.28 (dt, $^3J_{H,H}$ = 14.9 Hz, $^3J_{H,H}$ = 7.2 Hz, 1 H, =CH), 3.41 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, CH_2), 3.32 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, CH_2), 3.30 (m, 1 H, $CHCF_3$), 2.72 (ddd, $^2J_{H,H}$ = 13.4 Hz, $^3J_{H,H}$ = 10.5 Hz, $^3J_{H,H}$ = 7.1 Hz, $^4J_{H,H}$ = 0.8 Hz, 1 H, C*H*′H″), 2.43 (ddd, $^2J_{H,H}$ = 13.3 Hz, $^3J_{H,H}$ = 7.2 Hz, $^3J_{H,H}$ = 4.8 Hz, 1 H, CH′*H*″), 1.96 (dt, $^3J_{H,H}$ = 6.8 Hz, $^3J_{H,H}$ = 6.8 Hz, 2 H, CH_2), 1.23–1.37 (m, 6 H, CH_2), 1.18 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_3), 1.13 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_3), 0.87 (t, $^3J_{H,H}$ = 6.9 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.9 (s, CO), 135.4 (=CH), 125.5 (q, $^1J_{C,F}$ = 280.9 Hz, CF_3), 124.5 (=CH), 46.6 (tq, $^2J_{C,F}$ = 25.5 Hz, *C*HCF$_3$), 42.8 (CH_2), 41.5 (CH_2), 32.7 (CH_2), 31.7 (CH_2), 30.5 (q, $^3J_{C,F}$ = 2.6 Hz, CH_2), 29.2 (CH_2), 22.8 (CH_2), 15.0 (CH_3), 14.3 (CH_3), 13.2 (CH_3); ^{19}F NMR (282 MHz, $CDCl_3$): δ = −68.2 (d, $^3J_{F,H}$ = 9.7 Hz, 3 F, CF_3); GC MS (70 eV) *m*/*z* (%): 293 (10) [M^+], 278 (6) [M^+-CH_3], 264 (4) [$M^+-C_2H_4$], 250 (10) [$M^+-C_3H_7$], 236 (100) [$M^+-C_4H_9$], 224 (63) [M^+-CF_3], 183 (45) [236+H−C_4H_6], 168 (28) [183−CH_3], 154 (22) [183−C_2H_5], 140 (5) [183−C_3H_8], 126 (9) [183−C_3H_8N], 100 (52) [$H_{10}C_4NCO^+$], 72 (39) [100−CO], 58 (28) [$C_3H_8N^+$]. Anal. calcd for $C_{15}H_{26}NOF_3$: C, 61.41; H, 8.93; N, 4.77. Found: C, 61.62; H, 9.17; N, 4.69.

***N*,*N*-Diethyl-3,3,3-trifluoro-2-(5-methyl-2,6-dioxo-1,2,3,6-tetra-hydropyrimidin-4-yl)-propanamide (37)**. According to the general procedure **37** was obtained in the reaction of the fluorinating agent **PFPDEA** (0.741 g, 4.00 mmol) with 5-(hydroxymethyl)uracil **17** (0.284 g, 2.00 mmol) and triethylamine (0.437 g, 4.00 mmol). The product **37** was purified by column chromatography with chloroform/methanol (95:5). Yield: 46% (0.283 g, 0.92 mmol). ^{1}H NMR (300 MHz, DMSO-d_6): δ = 11.3 (s, 1 H, NH), 10.9 (s, 1 H, NH), 3.95, (m, 1 H, $CHCF_3$), 3.35 (s, 3 H, CH_3), 3.26 (m, 2 H, CH_2), 2.67 (m, 2 H, CH_2), 1.01 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_3), 0.93 (t, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$):

δ = 164.6 (CO), 164.5 (=C(*C*O)NH), 151.1 (NH(*C*O)NH) 140.6 (=*C*(NH)CH), 125.3 (q, $^{1}J_{C,F}$ = 280.7 Hz, CF_3), 106.3 (=*C*(CO)CH_3), 42.8 (q, $^{2}J_{C,F}$ = 24.5 Hz, *C*HCF_3), 41.9 (CH_2), 40.3 (CH_2), 24.7 (CH_3), 14.3 (CH_3), 12.8 (CH_3); ^{19}F NMR (282 MHz, DMSO-d_6): δ = −65.6 (d, $^{3}J_{F,H}$ = 8.3 Hz, 3 F, CF_3); GC MS (70 eV) *m*/*z* (%): 307 (12) [M^+], 238 (6) [M^+-CF_3], 235 (4) [$M^+-NC_4H_{10}$], 215 (16) [235−HF], 207 (5) [235−CO], 187 (10) [207−HF], 182 (2) [$C_7H_{11}NOF_3^+$], 165 (9), 137 (7) 125 (28) [$C_5H_5N_2O_2^+$], 100 (7) [$H_{10}C_4NCO^+$], 72 (100) [$H_{10}C_4N^+$], 58 (35) [$C_3H_8N^+$]. Anal. calcd for $C_{12}H_{16}N_3O_3F_3$: C, 46.91; H, 5.25; N, 13.68. Found: C, 46.97; H, 5.30; N, 13.69.

Acknowledgements

Financial support by the Deutsche Forschungsgemeinschaft is gratefully acknowledged (Sonderforschungsbereich 424 stipends for J.W.). We are indebted to DSc Marcin Hoffmann for advice and fruitful discussions on the DFT calculations results. Part of this work was supported also by Polish Ministry of Science and National Education (grant No. N N204 027738 to M.T.-S.). Pentafluoropropene sample (PFP) was kindly provided to us by SynQuest Laboratories Ltd.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jfluchem.2012.07.011.

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