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New Application of 1,1,3,3,3-Pentafluoropropene-diethylamine Adduct (PFPDEA) as Fluorinating Agent. Synthesis of 3,3,3-Trifluoropropionates of Vicinal Fluorohydrins*

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Reaction of various ω-fluoro-(ω-1)-hydroxy and ω-hydroxy-(ω-1)-fluoro fatty acid methyl esters with adduct of 1,1,3,3,3-pentafluoropropene-diethylamine (PFPDEA) has been studied. As a products mixture of corresponding vicinal difluorides and vicinal fluoro-3,3,3-trifluoropropionates was obtained.

Key words: fluorohydrines, fluorination, nucleophilic fluorination, pentafluoropropene-amine adduct

The preparation of fluoroorganic compounds stimulated considerable interest in the development of convenient fluorinating reagents. Fluorinating agents such as hydrogen fluoride-pyridine complex (Olah's reagent) [1,2,3], sulfur tetrafluoride [1,4], dialkylaminotrifluorosulfuranes (DAST) [1,4] and α-fluoroamines [1,5] are widely employed in organic synthesis for the conversion of alcohols and carbonyl compounds into corresponding fluorides. Reagents being derivatives of fluoroamines such as 1,1,2,3,3,3-hexafluoropropyl-*N*,*N*-diethylamine (Ishikawa's reagent [1,5]) and 1,1,2,2-tetrafluoroethyl-*N*,*N*-dimethylamine (Petrov's reagent [8], both prepared by addition of dialkylamine to corresponding fluoro olefins) have been found as effective reagents for the conversion of alcohols into alkyl fluorides [7].

In our earlier studies 1,1,3,3,3-pentafluoropropyl-*N*,*N*-diethylamine was found to be a selective fluorinating agent replacing hydroxyl groups by fluorine [8]. In general, 1,1,3,3,3-pentafluoropropyl-*N*,*N*-diethylamine reacts with alcohols yielding fluorides and equimolar amounts of *N*,*N*-diethyl-3,3,3-trifluoropropionamide and hydrogen fluoride. In some cases, however, considerable amounts of by-products were formed, which causes lower yields of the fluorides, being major expected products. In general aliphatic primary alcohols including octanol and benzylic alcohol yield only alkyl fluorides. Secondary and tertiary alcohols react with PFPDEA giving the corresponding fluorides and usually considerably amounts of alkenes [8].

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* Dedicated to Prof. Dr. Z. Galus on the occasion of his 70th birthday.
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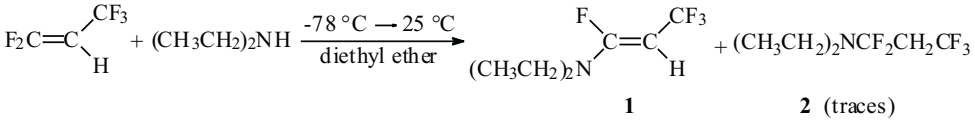
It is known, that similar fluoroamino reagents such as Ishikawa's reagent react with higher primary alcohols giving mixtures of fluorides and alkyl 2,3,3,3-tetrafluoropropionates [9–12]. Therefore, we have studied fluorination reactions with PFPDEA of more complex molecules containing a hydroxyl group in vicinal position to a fluorine substituent. As model compounds for replacing such hydroxyl groups methyl esters of fatty acids with terminal fluorohydrin moieties, *i.e.* ω-fluoro-(ω-1)-hydroxy and ω-hydroxy-(ω-1)-fluoro fatty acid methyl esters, were applied. These compounds were selectively prepared according to literature protocols [13,14].

RESULTS AND DISCUSSION

Preparation of 1,1,3,3,3-pentafluoropropene-diethylamine adduct. 1,1,3,3,3-Pentafluoropropene - diethylamine adduct (PFPDEA) was synthesized by formal nucleophilic substitution of a fluoride with diethylamine (DEA) at the double bond of pentafluoropropene (PFP) similar to a procedure described previously by Ishikawa [5]. There are few protocols to prepare PFPDEA including a pressure reaction in an autoclave, which has been used in our case (Reaction 1). This reaction gave a mixture of two products, namely 1-diethylamino-1,3,3,3-tetrafluoropropene (**1**) and only traces of the desired *N,N*-diethyl-1,1,3,3,3-pentafluoropropylamine (**2**).



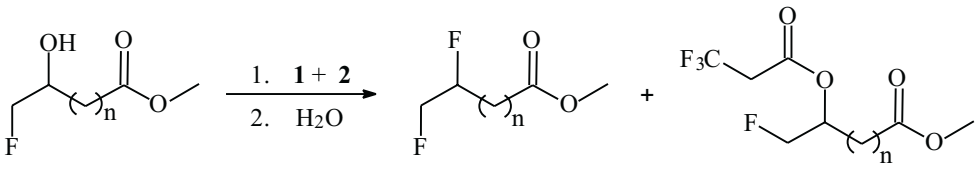
1 **2** (traces)

Reaction 1

Reaction of 1,1,3,3,3-pentafluoropropene-diethylamine adduct with fluorohydroxy fatty acid methyl esters. The above-mentioned fluorinating mixture of **1** and **2** was tested on several regioisomeric fluorohydrins, *i.e*. methyl 11-fluoro-10-hydroxyundecanoate, methyl 10-fluoro-11-hydroxyundecanoate, methyl 14-fluoro-13-hydroxytetradecanoate, and methyl 13-fluoro-14-hydroxytetradecanoate.

There were two series of fluorinating reactions of fluorohydrins **3** and **6** carried out to compare effectiveness of the fluorinating mixture under different conditions. In the first series, the reactions were done in CH_2Cl_2 at ambient temperature under air. Alternatively the reactions were run in THF at 65°C under an argon atmosphere. It was observed that reaction conditions did not significantly influence the yield of fluoride substitution. The general procedure for each reaction was as follows: the substrates were mixed in a molar ratio of 1:2 (fluorohydroxy compound:fluorinating mixture). Unexpectedly, in the reactions of 1,1,3,3,3-pentafluoropropene-diethylamine adduct (PFPDEA) with fluorohydroxy compounds **3** and **6**, apart from corresponding difluorides **4** and *N,N*-diethylamide of 3,3,3-trifluoropropionic acid

(by-product), also fluoro-*O*-3,3,3-trifluoropropionate derivatives **5** or **7** were produced. While the difluorides **4** were the major products of the secondary fluorohydrins **3** (Reaction 2), the trifluoropropionates **7** were formed exclusively or as the main product from the primary fluorohydrins **6** (Reaction 3).

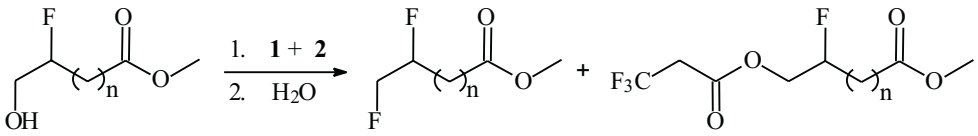


3a (n = 8)
3b (n = 11)

4a (41 %)
4b (49 %)

5a (26 %)
5b (42 %)

Reaction 2



6a (n = 8)
6b (n = 11)

4a (traces)
4b (17 %)

7a (89 %)
7b (73 %)

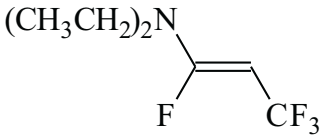
Reaction 3

CONCLUSIONS

The general mechanism of the nucleophilic substitution using PFPDEA is not clear yet. It was suggested previously that the process of replacing hydroxyl group by fluoride follows a S_Ni mechanism, which can be inhibited by neighboring bulky groups, giving rise for the formation of esters [6]. Our experimental results showed, however, that not only steric but also electronic influence of a vicinal fluorine could disturb the nucleophilic substitution leading to the formation of trifluoropropionic acid esters as major products. Nevertheless, it looks that use of PFPDEA could be adjusted to prepare both: fluorides or/and trifluoropropionates as the dominant products. It seems that one can also consider this procedure as an introduction of building block containing CF_3 moiety. Further mechanistic investigations are in progress.

EXPERIMENTAL

1)Reaction of (2H)-pentafluoropropene with diethylamine. Diethylamine (10.5 g, 0.14 mol) and dry diethylether (30 ml) were placed in a Carius tube equipped with magnetic stirring bar, and the tube was cooled to –70°C by means of dry ice/acetone bath. (2H)-Pentafluoropropene (21 g, 0.16 mol) was transferred to the tube from balloon *via* a needle valve (over 3 h). Then the cooling bath was removed and the mixture was brought to room temperature with magnetic stirring. After overnight stirring the solvent was evaporated and the resulting residue was subjected to distillation under vacuum. Yellowish liquid, (13.4 g, 41%) bp 95°C/72 mmHg, was obtained. The ^{19}F NMR spectrum revealed that this oil was a mixture of 1-diethylamino-1,3,3,3-tetrafluoropropene (**1**) and *N,N*-diethyl-1,1,3,3,3-pentafluoropropylamine (**2**) (traces).



1

^{19}F NMR ($CDCl_3$): δ [ppm]: –51.8 (dd, 3F, 3-F, $^3J_{FH}$ = 7 Hz, $^4J_{FF}$ = 15 Hz), –93.3 (dq, 1F, 1-F, $^3J_{FH}$ = 34 Hz, $^4J_{FF}$ = 15 Hz).

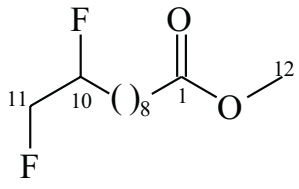
2)Reaction of the fluorinating mixture with fluorohydroxy fatty acid methyl esters. Two different procedures (a) and (b) were used in fluorinating reactions of fluorohydrins. No significant differences were observed in the yield of products related to different reaction conditions.

(a) The solution of the corresponding fluorohydroxy fatty acid methyl ester in dry CH_2Cl_2 was added dropwise into a solution of the mixture of **1** and **2** in dry CH_2Cl_2 at room temperature. After stirring for 14 h, the solution was poured into water and the mixture was extracted three times with small amount of CH_2Cl_2. The merged organic layer was repeatedly washed with water and dried over $MgSO_4$. Removal of the solvent gave a mixture of products as yellow oil. Crude products were purified by silica gel column chromatography.

(b) The solution of fluorohydroxy fatty acid methyl ester in dry THF was added dropwise into an argon-covered solution of **1** and **2** in refluxing dry THF. After stirring overnight under reflux, the solvent was removed giving a mixture of products as yellow oil. Crude products were purified by silica gel column chromatography.

2.1 Fluorination reaction of 11-fluoro-10-hydroxyundecanoate (3a). 11-Fluoro-10-hydroxyundecanoate (**3a**) (200 mg, 0.86 mmol) in 5 ml of CH_2Cl_2 or THF and fluorinating mixture (350 mg, 1.71 mmol) in 5 ml of CH_2Cl_2 or THF. After column chromatography (cyclohexane/ethylacetate, 9:1) two new products were isolated: methyl 10,11-difluoroundecanoate (**4a**) (82 mg, 41 %) and methyl 11-fluoro-10-*O*-(3,3,3-trifluoroporpionate)undecanoate (**5a**) (75 mg, 26%).

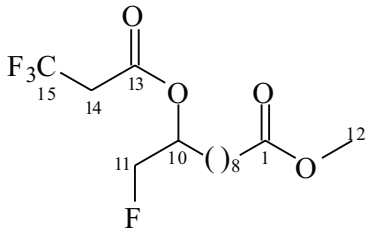
2.1.1 Methyl 10,11-difluoroundecanoate (4a).



4a

^{1}H NMR ($CDCl_3$): δ [ppm]: 1.31 (m, 10 H, 4-H to 8-H), 1.56 (m, 2 H, 9-H), 1.62 (m, 2 H, 3-H), 2.31 (t, 2 H, 2-H, $^3J_{H,H}$ = 7.5 Hz), 3.67 (s, 3 H, 12-H), 4.41 (ddd, 1 H, 11-H, $^2J_{H,F}$ = 47.5 Hz, $^2J_{H,H}$ = 10.3 Hz, $^3J_{H,H}$ = 5.4 Hz), 4.48 (ddd, 1 H, 11-H, $^2J_{H,F}$ = 47.5 Hz, $^2J_{H,H}$ = 10.3 Hz, $^3J_{H,H}$ = 3.1 Hz), 4.66 (ddm, 1 H, 10-H, $^2J_{H,F}$ = 48.6 Hz, $^3J_{H,F}$ = 23.5 Hz); ^{13}C NMR ($CDCl_3$): δ [ppm]: 25.1–29.6 (6 t, 3-C to 8-C), 30.4 (ddt, 9-C, $^2J_{C,F}$ = 20.3 Hz, $^3J_{C,F}$ = 6.4 Hz), 34.5 (t, 2-C), 51.8 (q, 12-C), 84.5 (ddd, 10-C, $^1J_{C,F}$ = 174.3 Hz, $^2J_{C,F}$ = 22.9 Hz), 92.2 (ddt, 11-C, $^1J_{C,F}$ = 171.7 Hz, $^2J_{C,F}$ = 19.1 Hz,), 180 (s, 1-C); ^{19}F NMR ($CDCl_3$): δ [ppm]: –189.78 (m, 1 F, 10-F), –230.83 (tdd, 1 F, 11-F, $^2J_{F,H}$ = 47.5 Hz, $^3J_{F,F}$ = 23.5 Hz, $^3J_{F,H}$ = 15.1 Hz); MS (EI/MS, 70 eV): m/z (%): 236 (1) [M^+], 205 (5) [M^+-OCH_3], 203 (0) [M^+-CH_2F], 172 (1) [205-CH_2F; 203-OCH_3], 171 (1) [203-CH_2F], 144 (2) [172-CO], 143 (1) [171-C_2H_4], 124 (2) [144-HF], 101 (5) [$C_5H_8O_2^+$], 88 (4) [172-C_5H_8O], 87 (33) [$C_4H_7O_2^+$], 75 (10) [88-CH], 74 (100) [$C_3H_6O_2^+$], 68 (3) [$C_5H_8^+$], 55 (17) [$C_4H_7^+$]; HRMS: calculated for $C_{12}H_{22}O_2F_2$ 236.15878, found 236.15859.

2.1.2 Methyl 11-fluoro-10-O-(3,3,3-trifluoropropionate)undecanoate (5a).

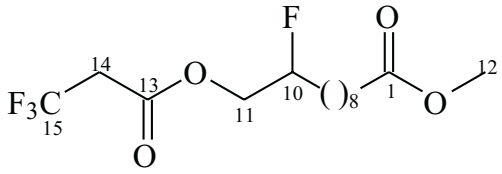


5a

^{1}H NMR ($CDCl_3$): δ [ppm]: 1.29 (m, 10 H, 4-H to 8-H), 1.62 (m, 4 H, 3-H and 9-H), 2.30 (t, 2 H, 2-H, $^3J_{H,H}$ = 7.5 Hz), 3.21 (q, 2 H, 14-H, $^3J_{H,F}$ = 10.1 Hz), 3.66 (s, 3 H, 12-H), 4.41 (ddd, 1 H, 11-H, $^2J_{H,F}$ = 47.5 Hz, $^2J_{H,H}$ = 10.3 Hz, $^3J_{H,H}$ = 5.4 Hz), 4.48 (ddd, 1 H, 11-H, $^2J_{H,F}$ = 47.5 Hz, $^2J_{H,H}$ = 10.3 Hz, $^3J_{H,H}$ = 3.1 Hz) 5.14 (dm, 1 H, 10-H, $^3J_{H,F}$ = 20.5 Hz); ^{13}C NMR ($CDCl_3$): δ [ppm]: 25.3–29.6 (7 t, 3-C to 9-C), 34.4 (t, 2-C), 40.2 (qt, 14-C, $^2J_{C,F}$ = 30.5 Hz), 51.8 (q, 12-C), 74.4 (dd, 10-C, $^2J_{C,F}$ = 19.1 Hz), 83.5 (dt, 11-C, $^1J_{C,F}$ = 175.5 Hz), 118.9 (q, 15-C, $^1J_{C,F}$ = 340.8 Hz), 174.6 (s, 1-C), 179.7 (m, 13-C); ^{19}F NMR ($CDCl_3$): δ [ppm]: –63.68 (t, 3 F, 15-F, $^3J_{F,H}$ = 10.1 Hz), –230.36 (td, 1 F, 11-F, $^2J_{F,H}$ = 47.5 Hz, $^3J_{F,H}$ = 20.5 Hz); MS (EI/MS, 70 eV): m/z (%): 345 (1) [HM^+], 313 (14) [M^+-OCH_3], 280 (3) [313-CH_2F], 217 (1) [M^+-$OC(O)CH_2CF_3$], 186 (8) [217-OCH_3], 173 (10) [$C_5H_5O_2F_3^+$], 164 (20) [186-HF-H_2], 136 (10) [164-CO], 128 (12) [$C_3H_3O_2F_3^+$], 111 (19) [128-OH; $C_3H_2OF_3^+$], 98 (25), 87 (19) [$C_4H_7O_2^+$], 74 (100) [$C_3H_6O^+$], 55 (23) [$C_4H_7^+$]; HRMS: calculated for $C_{15}H_{25}O_4F_4$ 345.16888, Found 345.16754.

2.2 Fluorination reaction of 10-fluoro-11-hydroxyundecanoate (6a). 10-Fluoro-11-hydroxyundecanoate (**6a**) (50 mg, 0.21 mmol) in 3 ml of CH_2Cl_2 or THF and fluorinating mixture (90 mg, 0.44 mmol) in 2 ml of CH_2Cl_2 or THF were mixed together. Following the previously described procedure, after column chromatography (cyclohexane/ethylacetate, 9:1) only one new product was isolated: methyl 10-fluoro-11-*O*-(3,3,3-trifluoroporpionate)undecanoate (**7a**) (66 mg, 89%).

2.2.1 Methyl 10-fluoro-11-O-(3,3,3-trifluoropropionate)undecanoate (7a).

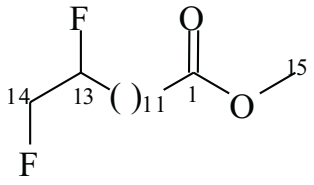


7a

^{1}H NMR ($CDCl_3$): δ [ppm]: 1.31 (m, 10 H, 4-H to 8-H), 1.56 (m, 2 H, 9-H), 1.62 (m, 2 H, 3-H), 2.30 (t, 2 H, 2-H, $^3J_{H,H}$ = 7.5 Hz), 3.24 (q, 2 H, 14-H, $^3J_{H,F}$ = 10.1 Hz), 3.66 (s, 3 H, 12-H), 4.28 (dm, 2 H, 11-H, $^3J_{H,F}$ = 23.5 Hz), 4.67 (dm, 1 H, 10-H, $^2J_{H,F}$ = 48.8 Hz); ^{13}C NMR ($CDCl_3$): δ [ppm]: 25.2–29.7 (7 t, 3-C to 9-C), 34.4 (t, 2-C), 39.4 (qt, 14-C, $^2J_{C,F}$ = 29.6 Hz), 51.8 (q, 12-C), 70.8 (dt, 11-C, $^2J_{C,F}$ = 19.1 Hz), 83.5 (dd, 10-C, $^1J_{C,F}$ = 174.2 Hz), 118.9 (q, 15-C, $^1J_{C,F}$ = 340.8 Hz), 174.6 (s, 1-C), 179.8 (m, 13-C); ^{19}F NMR ($CDCl_3$): δ [ppm]: –63.75(t, 3 F, 15-F, $^3J_{H,F}$ = 9.5 Hz), –187.56(m, 1 F, 10-F); MS (EI/MS, 70 eV): m/z (%): 345 (1) [HM^+], 313 (10) [M^+-OCH_3], 280 (1) [313-CH_2F], 217 (1) [M^+-$OC(O)CH_2CF_3$], 186 (1) [217-OCH_3], 173 (1) [$C_5H_5O_2F_3^+$], 164 (12) [186-HF-H_2], 136 (3) [164-CO], 128 (2) [$C_3H_3O_2F_3^+$], 111 (15) [128-OH; $C_3H_2OF_3^+$], 98 (23), 87 (24) [$C_4H_7O_2^+$], 74 (100) [$C_3H_6O^+$], 55 (16) [$C_4H_7^+$]; HRMS: calculated for $C_{15}H_{25}O_4F_4$ 345.16888, found 345.16954.

2.3 Fluorination reaction of 14-fluoro-13-hydroxytetradecanoate (3b). 14-Fluoro-13-hydroxytetradecanoate (**3b**) (200 mg, 0.86 mmol) in 5 ml of CH_2Cl_2 or THF and fluorinating mixture (350 mg, 1.71 mmol) in 5 ml of CH_2Cl_2 or THF were mixed together as described above. After column chromatography (cyclohexane/ethylacetate, 19:1) two new products were isolated: methyl 13,14-difluorotetradecanoate (**4b**) (98 mg, 49 %) and methyl 14-fluoro-13-*O*-(3,3,3-trifluoropropionate)tetradecanoate (**5b**) (117 mg, 42%).

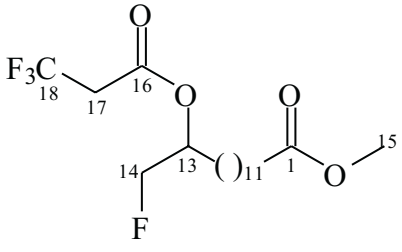
2.3.1 Methyl 13,14-difluorotetradecanoate (4b).



4b

^{1}H NMR ($CDCl_3$): δ [ppm]: 1.26–1.36 (m, 18 H, 3-H to 10-H), 1.56 (m, 2 H, 11-H), 1.62 (m, 2 H, 3-H), 2.30 (t, 2 H, 2-H, $^3J_{H,H}$ = 7.5 Hz), 3.66 (s, 3 H, 15-H), 4.41 (ddd, 1 H, 14-H, $^2J_{H,F}$ = 47.5 Hz, $^2J_{H,H}$ = 10.3 Hz, $^3J_{H,H}$ = 5.4 Hz), 4.48 (ddd, 1 H, 14-H, $^2J_{H,F}$ = 47.5 Hz, $^2J_{H,H}$ = 10.3 Hz, $^3J_{H,H}$ = 3.1 Hz), 4.66 (ddm, 1 H, 13-H, $^2J_{H,F}$ = 48.6 Hz, $^3J_{H,F}$ = 23.5 Hz); ^{13}C NMR ($CDCl_3$): δ [ppm]: 25.1– 29.9 (9 t, 3-C to11-C), 30.4 (ddt, 12-C, $^2J_{C,F}$ = 20.3 Hz, $^3J_{C,F}$ = 6.0 Hz), 34.5 (t, 2-C), 51.7 (q, 15-C), 84.5 (ddd, 10-C, $^1J_{C,F}$ = 172.9 Hz, $^2J_{C,F}$ = 22.9 Hz,), 92.2 (ddt, 11-C, $^1J_{C,F}$ = 172.9 Hz, $^2J_{C,F}$ = 19.1 Hz,), 174.7 (s, 1-C); ^{19}F NMR ($CDCl_3$): δ [ppm]: –189.78 (m, 1 F, 13-F), –230.83 (tdd, 1 F, 14-F, $^2J_{F,H}$ = 47.5 Hz, $^3J_{F,F}$ = 23.5 Hz, $^3J_{F,H}$ = 15.1 Hz); MS (EI/MS, 70 eV): m/z (%): 278 (7) [M^+], 247 (7) [M^+-OCH_3], 245 (1) [M^+-CH_2F], 227 (2) [247-HF], 214 (2) [247-CH_2F; 245-OCH_3], 207 (4) [227-HF] 186 (2) [214-CO], 166 (1) [186-HF], 143 (5) [$C_8H_{15}O_2^+$], 112 (2) [$C_7H_{12}O^+$], 98 (7), 87 (45) [$C_4H_7O_2^+$], 74 (100) [$C_3H_6O_2^+$], 68 (11) [$C_5H_8^+$], 55 (24) [$C_4H_7^+$]; HRMS: calculated for $C_{15}H_{28}O_2F_2$ 278.20575, found 278.20487.

2.3.2 Methyl 14-fluoro-13-O-(3,3,3-trifluoropropionate)tetradecanoate (5b).

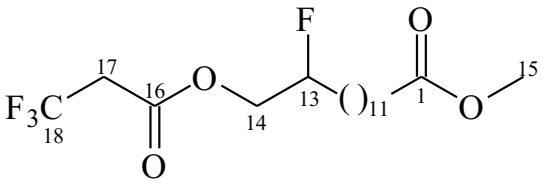


5b

^{1}H NMR ($CDCl_3$): δ [ppm]: 1.20–1.38 (m, 14 H, 4-H to 10-H), 1.56-1.70 (m, 4 H, 3-H and 11-H), 2.30 (t, 2 H, 2-H, $^{3}J_{H,H}$ = 7.5 Hz), 3.22 (q, 2 H, 17-H, $^{3}J_{H,F}$ = 10.1 Hz), 3.66 (s, 3 H, 12-H), 4.40 (ddd, 1 H, 14-H, $^{2}J_{H,F}$ = 47.5 Hz, $^{2}J_{H,H}$ = 10.3 Hz, $^{3}J_{H,H}$ = 5.4 Hz), 4.47 (ddd, 1 H, 14-H, $^{2}J_{H,F}$ = 47.5 Hz, $^{2}J_{H,H}$ = 10.3 Hz, $^{3}J_{H,H}$ = 3.1 Hz), 5.14 (dm, 1 H, 13-H, $^{3}J_{H,F}$ = 20.5 Hz); ^{13}C NMR ($CDCl_3$): δ [ppm]: 25.3–29.9 (10 t, 3-C to 12-C), 34.5 (t, 2-C), 40.1 (qt, 17-C, $^{2}J_{C,F}$ = 29.2 Hz), 51.8 (q, 15-C), 74.5 (dd, 13-C, $^{2}J_{C,F}$ = 19.1 Hz), 83.6 (dt, 14-C, $^{1}J_{C,F}$ = 175.5 Hz), 116 (q, 18-C, $^{1}J_{C,F}$ = 336.4 Hz), 174.6 (s, 1-C), 179.9 (m, 16-C); ^{19}F NMR ($CDCl_3$): δ [ppm]: –63.83 (t, 3 F, 18-F, $^{3}J_{F,H}$ = 10.1 Hz), –230.23 (td, 1 F, 14-F, $^{2}J_{F,H}$ = 47.5 Hz, $^{3}J_{F,H}$ = 20.5 Hz); MS (EI/MS, 70 eV): m/z (%): 386 (1) [M^+], 355 (10) [M^+-OCH_3], 322 (3) [355-CH_2F], 259 (1) [M^+-$OC(O)CH_2CF_3$], 228 (8) [259-OCH_3], 206 (8) [228-HF-H_2], 178 (2) [206-CO], 173 (10) [$C_5H_5O_2F_3^+$], 128 (10) [$C_3H_3O_2F_3^+$], 111 (27) [128-OH; $C_3H_2OF_3^+$], 98 (67), 87 (29) [$C_4H_7O_2^+$], 74 (100) [$C_3H_6O^+$], 55 (31) [$C_4H_7^+$]; HRMS: calculated for $C_{18}H_{30}O_4F_4$ 386.20801, Found 386.20951.

2.4 Fluorination reaction of 13-fluoro-14-hydroxytetradecanoate (6b). 13-Fluoro-14-hydroxy-tetradecanoate (**6b**) (200 mg, 0.86 mmol) in 5 ml of CH_2Cl_2 or THF and fluorinating mixture (350 mg, 1.71 mmol) in 5 ml of CH_2Cl_2 or THF. After column chromatography (cyclohexane/ethylacetate, 19:1) two new products were isolated: methyl 13,14-difluorotetradecanoate (**4b**) (35 mg, 17%) and (**7b**) methyl 13-fluoro-14-*O*-(3,3,3-trifluoropropionate)tetradecanoate (205 mg, 73%).

2.4.1 Methyl 13-fluoro-14-O-(3,3,3-trifluoropropionate)tetradecanoate (7b).



7b

^{1}H NMR ($CDCl_3$): δ [ppm]: 1.20–1.38 (m, 14 H, 4-H to 10-H), 1.56-1.70 (m, 4 H, 3-H and 11-H), 2.30 (t, 2 H, 2-H, $^{3}J_{H,H}$ = 7.5 Hz), 3.24 (q, 2 H, 17-H, $^{3}J_{H,F}$ = 10.1 Hz), 3.66 (s, 3 H, 12-H), 4.28 (dm, 2 H, 14-H, $^{3}J_{H,F}$ = 23.5 Hz), 4.67 (dm, 1 H, 13-H, $^{2}J_{H,F}$ = 48.8 Hz); ^{13}C NMR ($CDCl_3$): δ [ppm]: 24.8–29.7 (9 t, 3-C to 11-C), 31.1 (dt, 12-C, $^{2}J_{C,F}$ = 20.3 Hz), 34.4 (t, 2-C), 39.4 (qt, 17-C, $^{2}J_{C,F}$ = 29.6 Hz), 51.8 (q, 15-C), 71.7 (dt, 14-C, $^{2}J_{C,F}$ = 19.1 Hz), 83.5 (dd, 13-C, $^{1}J_{C,F}$ = 172.4 Hz), 118.9 (q, 18-C, $^{1}J_{C,F}$ = 340.8 Hz), 174.6 (s, 1-C), 180.4 (m, 16-C); ^{19}F NMR ($CDCl_3$): δ [ppm]: –63.93 (t, 3 F, 18-F, $^{3}J_{H,F}$ = 9.5 Hz), –187.64 (m, 1 F, 13-F); MS (EI/MS, 70 eV): m/z (%): 386 (1) [M^+], 355 (10) [M^+-OCH_3], 335 (3) [355-HF], 259 (1) [M^+-$OC(O)CH_2CF_3$], 228 (5) [259-OCH_3], 206 (10) [228-HF-H_2], 178 (2) [206-CO], 173 (1) [$C_5H_5O_2F_3^+$], 128 (3) [$C_3H_3O_2F_3^+$], 111 (18) [128-OH; $C_3H_2OF_3^+$], 98 (51), 87 (33) [$C_4H_7O_2^+$], 74 (100) [$C_3H_6O^+$], 55 (22) [$C_4H_7^+$]; HRMS: calculated for $C_{18}H_{30}O_4F_4$ 386.20801, found 386.21056.

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