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Synthesis of 3-perfluoroalkyl-propyl esters of L-(+)-tartaric acid

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Abstract

A convenient and effective method for the preparation of perfluoroalkyl-propanols (F–$(CF_2)_n$–$(CH_2)_3$–OH, $n = 6,8,10$) via boric acid esters is described. The radical addition of *F*-alkyl iodides to the C=C double bonds of triallyl borate is followed by the reduction step using tributylstannane hydride under one-pot conditions. Finally, the mild aqueous deprotection of the alcoholic function completes the reaction with an overall yield of 75–79%. The fluorophilicity (*f*) values of these and some other fluoroalcohols, which describe their phase preference, were determined by gas chromatography. *F*-alkyl-propanols are useful synthetic precursors of fluorinated esters of L-tartaric acid—potential chelating agents in fluorous biphase transformations.

Keywords: Perfluoroalkyl-propanols preparation; Reduction; Fluorinated esters of L-tartaric acid; Preparation; Esterification; Fluorophilicity; Gas chromatography

1. Introduction

The recent discovery of fluorous biphase systems (FBS) by Horváth and Rábai has provided novel methods for catalyst and reagent immobilization coupled with product separation [1]. In this pioneer work it was demonstrated that a phosphine ligand with suitable fluorinated 'ponytails' [$P(CH_2CH_2C_6F_{13})_3$] can be applied in hydroformylation reactions in a biphasic mixture of toluene and a fluorocarbon-type solvent, and simple phase separation sufficed to provide the products and the fluorous catalyst, which could be easily recycled. The benefits of application of this approach in homogeneous catalysis, fluorous synthesis—in which organic molecules are systematically rendered soluble in fluorocarbon solvents by the attachment of an adequate perfluorinated segment—and liquid-phase combinatorial synthesis are appearing [2–6]. However, a more extensive application of this novel phase separation and immobilization concept requires convenient and effective access to designed fluorous catalysts, reagents, ligands and labels. Fluorous partition coefficients [6–10] and fluorophilicity (*f*) values [11,12] have become preferred measurements of phase behaviour, thus aiding design of novel fluorophilic compounds. It has been a significant challenge for synthesis chemists over the past decade to synthesize optically pure products using chiral catalysts. Integrating the known enantioselective transformation methods with the FBS approach is a logical extension of both approaches. The first application of enantioselective reactions in the unique solvation environment provided by (per)fluorocarbons was recently reported by Pozzi et al. [13]. They synthesized two optically active perfluoroalkylated (salen)-MnIII complexes (Jacobsen–Katsuki catalysts) and successfully used them in chiral fluorous biphase epoxidation of alkenes (up to ee: 92%). In the present work, we describe a simple and efficient synthesis of perfluoroalkyl-propyl esters of L-tartaric acid as fluorinated analogues of alkyl tartrates which are widely used in enantioselective reactions as chelating ligands of transition metals [14].

Many preparations of the synthetic precursor *F*-alkyl-propanols are known in the literature [15–17], but we aimed at developing a more convenient and successful synthetic pathway. The first, a radical addition step of *F*-alkyl iodides (R_FI) to the C=C double bond of allyl alcohol produces higher conversions under more controllable conditions, if the hydroxyl group is protected [15,18–20]. The second, a reduction step can be suitably carried out with tributylstan-

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nane hydride in the presence of the radical initiator AIBN [15], and, finally, the deprotection of the hydroxyl function completes the procedure.

The trimethylene spacer unit in *F*-alkyl-propanols inserted in-between the hydroxyl group and the perfluorinated segment reduces the electron withdrawing effect and ensures usual reactivity of the functional group [1,21]. These fluorinated propanols are novel examples indicating that the experimental determination of fluorophilicity (*f*) values is essential for the understanding of how different constituents of a molecule affect its phase behaviour. It is also hoped that the systematic collection of fluorophilicity data could lead to the development of a structure–fluorophilicity correlation model, which then would allow the prediction of fluorophilicity values for the design of novel fluorous compounds.

2. Results and discussion

The novel synthesis of perfluoroalkyl-propanols is based on a procedure described of Krahler using triallyl borate as starting material [19,20]. The protection of the alcoholic function via boric acid ester has two essential advantages compared to other methods. First, the deprotection of the product can be carried out under extremely mild conditions, simply by introducing water into the system. On the other hand, the radical addition of *F*-alkyl iodide to triallyl borate in the presence of AIBN is so effective (the complete conversion was checked by GC), that this provides the opportunity of direct reduction without isolation of the adduct formed. The preferred reagent for this reaction is tributylstannane hydride because it also functions under radical conditions and can be added directly to the reaction mixture. The method requires oxygen-free, anhydrous conditions and precise control of the reaction temperature. With this one-pot synthesis, an overall yield of 75–79% can be obtained based on the initial perfluoroalkyl iodides:

$$(CH_2{=}CH{-}CH_2{-}O)_3B + 3R_F^nI \xrightarrow{AIBN} (R_F^n{-}CH_2{-}CHI{-}CH_2{-}O)_3B \xrightarrow[-Bu_3SnI]{Bu_3SnH/AIBN} (R_F^n{-}CH_2{-}CH_2{-}CH_2{-}O)_3B \xrightarrow[-H_3BO_3]{H_2O} \underset{\mathbf{1-3}}{3R_F^n{-}CH_2{-}CH_2{-}CH_2{-}OH} \quad (n = 6, 8, 10)$$

The fluorophilicity value (f_a) of a compound 'a' has been defined from the partition coefficient (P_a) between two particular solvents, perfluoro(methylcyclohexane) and toluene at 25°C according to the following equation [11,12]:

$$f_a = \ln P_a \equiv \ln [c_a(CF_3C_6F_{11})/c_a(CH_3C_6H_5)].$$

According to this definition a molecule is 'fluorophilic' if its *f* value is positive. The measurement of this parameter in the case of a volatile fluorinated compound can be easily made by gas chromatography. If the volumes of the two phases and the sampled and injected volumes are the same, then the integrated areas (A_a) determine the fluorophilicity value:

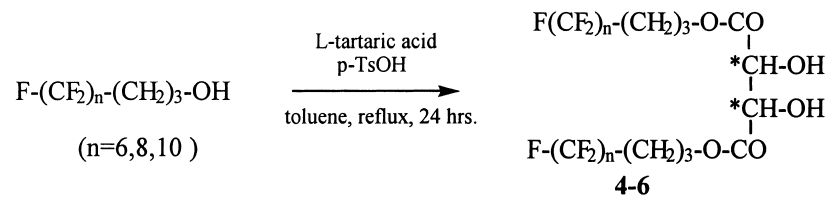
$$f_a = \ln [A_a(CF_3C_6F_{11})/A_a(CH_3C_6H_5)].$$

Table 1
The fluorophilicity (*f*) values of *F*-alkyl-propanols (F–$(CF_2)_n$–$(CH_2)_3$–OH) and some commercially available fluoroalcohols

F-alcohol	Fw	Fluorine content (%)	*f*
CF_3–CH_2–OH	100.0	57.0	-1.77 ± 0.16
$(CF_3)_2$CH–OH	168.0	67.8	-1.01 ± 0.08
F–$(CF_2)_6$–$(CH_2)_2$–OH	364.1	67.8	0.10 ± 0.03
F–$(CF_2)_6$–$(CH_2)_3$–OH	378.1	65.3	-0.23 ± 0.05
F–$(CF_2)_8$–$(CH_2)_2$–OH	464.1	69.6	1.02 ± 0.03
F–$(CF_2)_8$–$(CH_2)_3$–OH	478.2	67.6	0.59 ± 0.04
F–$(CF_2)_{10}$–$(CH_2)_3$–OH	587.2	69.0	1.42 ± 0.20

The fluorophilicity (*f*) values of *F*-alkyl-propanols and some commercially available fluoroalcohols were determined to compare their phase preference (Table 1). Trifluoroethanol, hexafluoroisopropyl alkohol and *F*-hexyl-propanol have negative *f* values in spite of their relatively high fluorine content, while the others with long perfluoroalkyl chains are fluorophilic. The *f* values of *F*-alkyl-alkanols increase with the size of the perfluorinated segment, as expected [22]. In case of the alcohols with the same size of perfluoroalkyl groups, the trimethylene spacer results in lower *f* values than the shorter ethylene unit.

The preparation of potential chiral fluorinated complexing ligands derived from *F*-alkyl-propanols and L-tartaric acid is summarized in the following equation:



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The final separation of the unreacted alcohols from the products is worked out in all cases, because the recycling of the relatively expensive starting materials is a basic requirement. The average yield of the esterification procedure is 80%. While *F*-hexyl-propyl tartrate can be readily dissolved in organic solvents, such as diethyl ether, methanol and chloroform, the solubility properties of the other two analogues decrease drastically with the size of the *F*-alkyl unit. These esters are only slightly soluble in perfluorocarbons,

such as perfluoro(methylcyclohexane) and perfluoro(2-butyltetrahydrofuran), but can be easily dissolved in partially fluorinated alcohols like *F*-hexyl-ethanol or hexafluoroisopropyl alcohol.

3. Conclusions

The foregoing description of one-pot preparation of *F*-alkyl-propanols via boric acid esters is a convenient and noticeably effective method. The gas chromatographic measurement of the well-defined fluorophilicity values is a simple technique to express the fluorocarbon phase preference of volatile compounds. The collection of a vast amount of fluorophilicity data is necessary to understand the strategy of how to design systematically novel fluorous compounds. The tartaric acid esters derived from *F*-alkyl-propanols are practically insoluble in perfluorocarbons at room temperature presumably due to the strong ordering capacity of the hydroxyl functions forming hydrogen bonds. This effect is eliminated if these molecules chelate transition metals, thus hopefully increasing the solubility in fluorocarbon media and opening perspectives in the application of these ligands in chiral fluorous biphase transformations.

4. Experimental details

Triallyl borate was prepared from freshly distilled allyl alcohol (Merck) [20]. The following chemicals were used for the one-pot preparation of *F*-alkyl-propanols and the esterification procedures: perfluoroalkyl iodides (Fluorochem), AIBN (Fluka), tributylstannane hydride (Aldrich), L-(+)-tartaric acid and *p*-toluenesulfonic acid monohydrate (both Reanal, Hungary). For partition coefficient determinations *F*-octyl-ethanol (Fluka), *F*-hexyl-ethanol (PCR), trifluoroethanol and hexafluoroisopropyl alcohol (both Aldrich) reagent grade chemicals were used as received, while perfluoro(methylcyclohexane) (Fluorochem, 90%) was purified by refluxing with oleum (40% free SO_3, 6 h) followed by distillation, washing with water, drying ($MgSO_4$) and distilling to afford 98% purity by GC. Deuterated solvents and internal references for NMR analysis were originated from Merck. Melting points were determined on a Boetius micromelting point apparatus and are uncorrected. Sonications were performed using a Realsonic (RS-I6, 50/100 W) laboratory ultrasound cleaner. The structures of all products were proved by FT-IR (Bruker IFS 55), ^{1}H-, ^{13}C- and ^{19}F-NMR spectroscopy (Varian INOVA-300, 300 MHz for ^{1}H) using TMS and $CFCl_3$ as internal standards. Only ^{13}C-NMR spectra of nonfluorinated carbons were considered. Mass spectra were determined on a VG ZAB2-SEQ tandem mass spectrometer using electron impact (70 eV) for ionization and direct probe for sample introduction at a source temperature of 180 to 250°C. Mass range (*m/z*) from 25 to 1500 was considered. Both, in the case of perfluoroalkyl-propanols and their tartrates appropriate molecular ions were detected; however, the latter ions showed less intensity (ca. 1% of the base peak intensity). HRMS measurements were performed similarly, except using FAB technique for ionization of the tartrate samples. Optical rotation was determined by a Polamat A (Zeiss) polarimeter. The reaction steps of the one-pot synthesis of *F*-alkyl-propanols were monitored by gas chromatography (Hewlett–Packard 5890 Series II, Pona 50 m × 0.2 mm × 0.5 μm column, H_2 carrier gas, FID). The fluorophilicity values were also determined by GC in the following manner: In a 2.00-ml volumetric flask having conical bottom, the given compounds (10 mg) were extracted in a 1.00–1.00 ml mixture of pre-equilibrated perfluoro(methylcyclohexane) and toluene at 25°C. After standing overnight at this temperature, 0.5, 1 and 2 μl samples of the separated upper and lower phases were injected onto the capillary column. Then, volume ratios with best matching integrals for both phases were used. Due care was practised so as not to disturb the clean and transparent phases when sampled with a Hamilton syringe. An average of 5–5 injections for each run of three independent determinations resulted in the listed *f* values (Table 1).

4.1. Preparation of perfluoroalkyl-propanols

4.1.1. 4,4,5,5,6,6,7,7,8,8,9,9,9-Tridecafluoro-nonan-1-ol (1)

In a pre-dried, nitrogen purged reaction flask perfluorohexyl iodide (30.0 g, 67.3 mmol), triallyl borate (4.08 g, 22.4 mmol) and AIBN (0.10 g, 0.61 mmol) were mixed at room temperature. Continuous stirring and by-pass nitrogen flow was applied during the entire reaction. The temperature was raised to 70°C over 30 min and held at this temperature for 1 h. An additional amount of AIBN (0.1 g) was added to the mixture, which was then slowly heated to 80°C. After 3 h, a small sample was hydrolyzed and the ether extract was analyzed by GC (100% conversion). The reaction temperature was decreased to 70–73°C and AIBN (0.1 g) was added to the mixture. Tributylstannane hydride (20.2 g, 69.4 mmol) was added dropwise over 2 h. Additional AIBN (0.05 g) was introduced and the temperature was maintained for 1 h, then heated to 80°C for 30 min to complete the reduction (checked by GC). Finally, distilled water (50 ml) was added and the reaction mixture was stirred intensively for 20 min at the same temperature. The mixture was cooled to room temperature and the organic components were extracted with diethyl ether (3 × 50 ml). The ether phase was washed with water, separated, and dried over Na_2SO_4, and the solvent removed by rotary evaporation. The residue was distilled under reduced pressure (16 mmHg). The main fraction was collected over a temperature range of 90–100°C (93.3% purity by GC), the second one at 100–130°C (83.7% purity). Repeated distillation using a Vigreaux column (b.p. 91°C/16 mmHg, in accordance with

the literature [23]: 86–88°C/12 mmHg) gave 19.0 g of product **1** (74.7%, 97.1% purity by GC). NMR (CD_3OD) δ: ^1H: 1.76–1.86 m (2H) [H_2-2]; 2.15–2.37 m (2H) [H_2-3]; 3.64 t $^3J_{HH} = 6.0$ Hz (2H) [H_2-1]; ^{13}C: 24.6 ($^3J_{CF} < 4$ Hz) (C-2); 28.9 t ($^2J_{CF} = 22$ Hz) (C-3); 61.7 (C-1); ^{19}F: −81.3 m (3F) [CF_3]; CF_2 resonances are −114.1 m (2F), −121.7 m (2F), −122.7 m (2F), −123.3 m (2F), −126.1 m (2F). FT-IR (CCl_4) ν (cm^{-1}): 3640.3 (OH), 2958.9 (CH_{as}), 2882.7 (CH_s), 1240.8, 1207.8 (CF). MS (*m/z*, *I*%, M-X): 378, *5.3*, M; 377, *21*, M-1; 341, *12*, M-37; 295, *8.3*, M-83; 69, *26*, CF_3; 47, *51*, OCF; 31, *100*, CF. HRMS (*m/z*) calculated for $C_9H_7F_{13}O$, $M^+ = 378.0289$, found $M^+ = 378.0298$.

4.1.2. 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Heptadecafluoro-undecan-1-ol (2)

In a nitrogen-purged flask perfluorooctyl iodide (20.0 g, 36.6 mmol), triallyl borate (2.22 g, 12.2 mmol) and AIBN (0.05 g, 0.30 mmol) were dissolved in isooctane (25 ml) at room temperature. The addition and dehalogenation procedures using tributylstannane hydride (10.2 g, 35.0 mmol) were carried out as above (temperature programme, initiator addition). After hydrolysis with distilled water (50 ml), the crude product precipitated from the cold isooctane phase. It was filtered, dried and recrystallized twice from isooctane. Yield: 13.5 g (77.0%, 98.1% purity by GC), m.p. 42–43°C, (in accordance with the literature [24]: 42°C). NMR (CD_3OD) δ: ^1H: 1.76–1.86 m (2H) [H_2-2]; 2.15–2.37 m (2H) [H_2-3]; 3.64 t $^3J_{HH} = 6.0$ Hz (2H) [H_2-1]; ^{13}C: 24.6 ($^3J_{CF} < 4$ Hz) (C-2); 28.9 t ($^2J_{CF} = 22$ Hz) (C-3); 61.7 (C-1); ^{19}F: −81.3 m (3F) [CF_3]; CF_2 resonances are −114.2 m (2F), −121.7 m (6F), −122.5 m (2F), −123.3 m (2F), −126.1 m (2F). FT-IR (CCl_4) ν (cm^{-1}): 3640.3 (OH), 2958.7 (CH_{as}), 2882.8 (CH_s), 1242.2, 1215.1 (CF). MS (*m/z*, *I*%, M-X): 478, *3.9*, M; 477, *3.7*, M-1; 441, *9.3*, M-37; 395, *6.3*, M-83; 69, *24*, CF_3; 47, *22*, OCF; 31, *100*, CF. HRMS (*m/z*) calculated for $C_{11}H_7F_{17}O$, $M^+ = 478.0225$, found $M^+ = 478.0224$.

4.1.3. 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-Heneicosafluoro-tridecan-1-ol (3)

The following quantities of reagents were used: perfluorodecyl iodide (10.0 g, 15.5 mmol), triallyl borate (0.941 g, 5.17 mmol) and AIBN (0.03 g, 0.18 mmol) in isooctane (25 ml). Tributylstannane hydride (4.95 g, 17.0 mmol) was used for the reduction. The reaction conditions and work-up procedure were as in the case of compound **2**. Yield: 7.10 g (79.2%, 98.0% purity by GC), m.p. 86–89°C. NMR (CD_3OD) δ: ^1H: 1.76–1.86 m (2H) [H_2-2]; 2.15–2.37 m (2H) [H_2-3]; 3.63 t $^3J_{HH} = 6.0$ Hz (2H) [H_2-1]; ^{13}C: 24.6 ($^3J_{CF} < 4$ Hz) (C-2); 28.9 t ($^2J_{CF} = 22$ Hz) (C-3); 61.6 (C-1); ^{19}F: −81.2 m (3F) [CF_3]; CF_2 resonances are −114.1 m (2F), −121.5 m (10F), −122.5 m (2F), −123.3 m (2F), −126.0 m (2F). FT-IR (CCl_4) ν (cm^{-1}): 3639.8 (OH), 2958.5 (CH_{as}), 2872.1 (CH_s), 1242.4, 1217.4 (CF). MS (*m/z*, *I*%, M-X): 578, *2.7*, M; 577, *7.3*, M-1; 541, *25*, M-37; 495, *14*, M-83; 69, *56*,, CF_3; 47, *48*, OCF; 31, *100*, CF. HRMS (*m/z*) calculated for $C_{13}H_7F_{21}O$, $M^+ = 578.0162$, found $M^+ = 578.0154$; calculated. for $C_{13}H_5F_{20}O$, $(M\text{-}H_2F)^+ = 557.0021$, found $(M\text{-}H_2F)^+ = 557.0026$; calculated for $C_{13}H_5F_{20}$, $(M\text{-}OH_2F)^+ = 541.0072$, found $(M\text{–}OH_2F)^+ = 541.0081$; calculated for $C_{13}H_6F_{19}O$, $(M\text{–}HF_2)^+ = 539.0115$, found $(M\text{–}HF_2)^+ = 539.0132$.

4.2. Esterification procedures

4.2.1. 2R,3R-dihydroxy-succinic acid bis-(4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-nonyl) ester (4)

In a reaction flask fitted with a Dean–Stark trap for the removal of water during the reaction a mixture of **1** (5.00 g, 13.2 mmol), L-tartaric acid (0.795 g, 5.30 mmol) and *p*-toluenesulfonic acid monohydrate (0.190 g, 1.00 mmol) in toluene (50 ml) was refluxed at an oil bath of 145°C for 24 h. Toluene was removed and the residue extracted with ether and washed twice with distilled water. The ether layer was separated, dried over Na_2SO_4 and the solvent removed. Unreacted **1** was recovered using a short-path distillation apparatus (0.512 g, 92.5% purity by GC). The distillation residue was recrystallized from toluene (50 ml), resulting in 3.72 g product (80.7%), m.p. 78–80°C, $[\alpha]_{546}{}^{25} = 12.4$ ($c = 2.50$ g/100 ml, *F*-hexyl-ethanol). NMR (CD_3OD) δ: ^1H: 1.95–2.08 m (4H) [H_2-2]; 2.21–2.43 m (4H) [H_2-3]; 4.24–4.38 m (4H) [$H_{x,y}$-1]; 4.59 s (2H) [H–(CH–O)]; ^{13}C: 21.3 t ($^3J_{CF}$ <4 Hz) (C-2); 28.8 t ($^2J_{CF} = 22$ Hz) (C-3); 65.2 (C-1), 74.1 (C–(CH–O)), 172.9 (C=O); ^{19}F: −81.3 m (3F) [CF_3]; CF_2 resonances are −114.2 m (2F), −121.7 m (2F), −122.7 m (2F), −123.2 m (2F), −126.1 m (2F). FT-IR (KBr) ν (cm^{-1}): 3540.4 (OH), 2979.3 (CH), 1741.8 (C=O); 1235.8, 1192.6 (CF). HRMS (FAB, *m/z*) calculated for $C_{22}H_{17}F_{26}O_6$, $(M + H)^+ = 871.0610$, found $(M + H)^+ = 871.0591$.

4.2.2. 2R,3R-dihydroxy-succinic acid bis-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoro-undecyl) ester (5)

Initial quantities were the following: compound **2** (3.35 g, 7.00 mmol), L-tartaric acid (0.420 g, 2.80 mmol) and *p*-toluenesulfonic acid monohydrate (0.133 g, 0.70 mmol) in toluene (50 ml). The experimental conditions and the work-up procedure were the same as in the previous case. The amount of **2** recovered was 0.482 g (GC pure). The product was recrystallized from toluene. Yield: 2.36 g (78.7%), m.p. 109–110°C, $[\alpha]_{546}{}^{25} = 10.9$ ($c = 2.58$ g/100 ml, *F*-hexyl-ethanol). NMR ($(CF_3)_2CDOD$) δ: ^1H: 2.05–2.21 m (4H) [H_2-2]; 2.21–2.38 m (4H) [H_2-3]; 4.33–4.47 m (4H) [$H_{x,y}$-1]; 4.54 s (2H) [H–(CH–O)]; ^{13}C: 21.6 t ($^3J_{CF}$ <4 Hz) (C-2); 29.6 ($^2J_{CF} = 22$ Hz) (C-3); 68.5 (C-1), 74.2 (C–(CH–O)), 174.4 (C=O); ^{19}F: −81.6 m (3F) [CF_3]; CF_2 resonances are −114.5 m (2F), −121.5 m (2F), −121.7 m (4F), −122.6 m (2F), −123.4 m (2F), −126.3 m (2F). FT-IR (KBr) ν (cm^{-1}): 3540.6 (OH),

2978.1 (CH), 1741.4 (C=O); 1237.5, 1204.8 (CF). HRMS (FAB, *m/z*) calculated for $C_{26}H_{17}F_{34}O_6$, $(M + H)^+ = 1071.0482$, found $(M + H)^+ = 1071.0331$.

4.2.3. *2R,3R-dihydroxy-succinic acid bis-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-heneicosafluoro-tridecyl) ester (**6**)*

Compound **3** (3.00 g, 5.19 mmol), L-tartaric acid (0.312 g, 2.08 mmol) and *p*-toluenesulfonic acid monohydrate (0.095 g, 0.50 mmol) in toluene (30 ml). The experimental conditions were the same as described above. The mixture was cooled to room temperature. The solidified mixture was filtered and sonicated in 50 ml of methanol for 10 min. The solid was filtered and the sonication procedure was repeated with another 50 ml of methanol. The crude product was filtered again and dried. From the combined filtrates, 0.211 g **3** was recovered (97.6% purity by GC). The dry product was recrystallized from boiling toluene. Yield: 2.09 g (79.0%), m.p. 133–134°C, $[\alpha]_{546}{}^{25} = 8.68$ (c = 2.42 g/100 ml, *F*-hexyl-ethanol). NMR ($(CF_3)_2CDOD$) δ: ^{1}H: 2.05–2.35 m (8H) [H_2-2 and H_2-3]; 4.33–4.48 m (4H) [$H_{x,y}$-1]; 4.54 s (2H) [H–(CH–O)]; ^{13}C: 21.6 t ($^3J_{CF}$ <4 Hz) (C-2); 29.5 ($^2J_{CF}$ = 22 Hz) (C-3); 68.5 (C-1), 74.1 (C–(CH–O)), 174.4 (C=O); ^{19}F: −81.6 m (3F) [CF_3]; CF_2 resonances are −114.5 m (2F), −121.5 m (10F), −122.6 m (2F), −123.5 m (2F), −126.3 m (2F). FT-IR (KBr) ν (cm^{-1}): 3540.7 (OH), 2966.1 (CH), 1743.2 (C=O); 1210.0 (CF). HRMS (FAB, *m/z*) calculated for $C_{30}H_{17}F_{42}O_6$, $(M + H)^+ = 1271.0354$, found $(M + 1)^+ = 1271.0308$.

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