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Dithionite-Catalysed Addition of Perfluoroalkyl Iodides to Unsaturated Carbohydrates

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The perfluoroalkyl chains ($-C_4F_9$, $-C_6F_{13}$, $-C_8F_{17}$) were terminally connected to the 5-enopyranose **1**, and the 5-enofuranoses **8** and **23** by addition, in the presence of sodium dithionite, of the corresponding homologous perfluoroalkyl iodides to the double bond. Up to six products were separated from each reaction mixture and then fully characterised. The 5-iodo derivatives **9**, **10** (prepared from **8**), **24**, **25**, and **26** (prepared from **23**) were diastereomeric mixtures (5*R*/5*S*). Compounds **9**, **10**, and **25** were hydrodeiodinated to the methylene derivatives **17**, **18**, and **27**, respectively. Complete deprotection of the perfluoroalkyl-substituted pyranose **3** (prepared from **1**), and of the furanoses **17** and **18** led to the carbohydrate-based amphiphilic mesogens **29/30**, **21**, and **22**, respectively, with a perfluoroalkyl tail. These formed mesophases of the *smectic* A type.

Fluorocarbons are biochemically inert, dense, have a low surface tension and have a very high gas dissolving capacity. For use as "artificial blood" for drug delivery and targeting, and for use as contrast agents, fluorocarbons have to be emulsified with water. For stable emulsions a variety of biocompatible, strongly surface active fluorophilic/hydrophilic amphiphiles are needed. However, the higher the fluorine content of the amphiphile, the lower is its hemolytic activity[2]. Perfluoro-alkylated carbohydrates may serve as useful emulsifiers for "water-in-fluorocarbon" emulsions intended for biomedical uses, such as drug targeting, because their hydrophilic sugar head group may make them susceptible to recognition by specific receptors[3][4]. In most of the perfluoroalkyl-substituted carbohydrate amphiphiles which are already known, the perfluoroalkyl chain is attached to the carbohydrate via a hydrocarbon spacer and an ester, ether, amide, or phosphate bond[4][5]. In this paper we report on the syntheses of carbohydrate-based perfluoroalkyl amphiphiles, where the perfluoroalkyl chain is directly attached to the carbohydrate skeleton by a C−C bond.

Perfluoroalkyl halides are useful reagents for the introduction of perfluoroalkyl chains into organic molecules[6]. One of the simplest and most convenient methods for perfluoroalkylation is the radical addition of perfluoroalkyl iodides to double bonds. Such reactions are usually initiated by heating, light, use of radical initiators[7], or by the addition of metals such as nickel[8][9], copper[10], magnesium[11], zinc[12], titanium[13] and metal complexes[14]. Moreover, electrochemical initiation[15] and addition of triethyl borane[16][17], or sodium dithionite[18][19] have been described.

We tested several methods for the perfluoroalkylation of carbohydrates[20] with the aim of synthesizing a new group of "single tailed" amphiphilic liquid crystals. The most convenient, mild and inexpensive method seemed to be the dithionite initiated addition of perfluoroalkyl halides to unsaturated compounds in water/acetonitrile[18][19], which gave moderate and reproducible yields. The first applications of the dithionite initiation method in carbohydrate chemistry were reported by Portella and coworker[21] and Huang and coworkers[22]. We were unable to reproduce the results of the latter; a perfluoroalkylation of triacetylglucal. Nearly no glucal reacted in the course of the reaction. However, the addition of some perfluoroalkyl iodides to unsaturated monosaccharides with an exocyclic double bond in the 5-position did prove successful. Thus, the enopyranose **1** was reacted with perfluorohexyl iodide in the presence of sodium dithionite to give a product mixture (compounds **2**−**7**), where the perfluoroalkyl chain is regioselectively attached to the 6-position in all cases (Scheme 1). The introduction of iodine into the 5-position was not observed, probably for steric reasons. The main products were the two saturated diastereomers **2** (5%) and **3** (13%). In addition, the 5-eno isomers **4** and **5** (*E*- and *Z*-form, respectively) and the diastereomeric dimers **6** and **7** were isolated. All six products should be formed from the same radical intermediate.

The NMR spectra of the compounds **2**−**7** confirm that the isopropylidene protecting groups are not attacked under the reaction conditions. In agreement with the given structures, the proton spectra of the compounds **2** and **3** show seven, and the eno-pyranoses **4** and **5** only five, proton sig-

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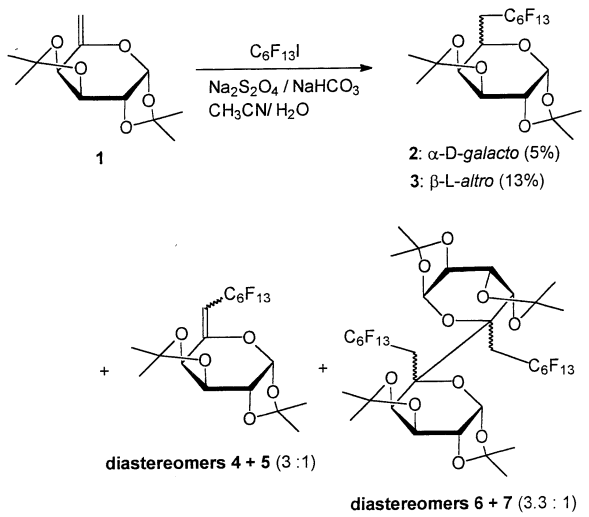
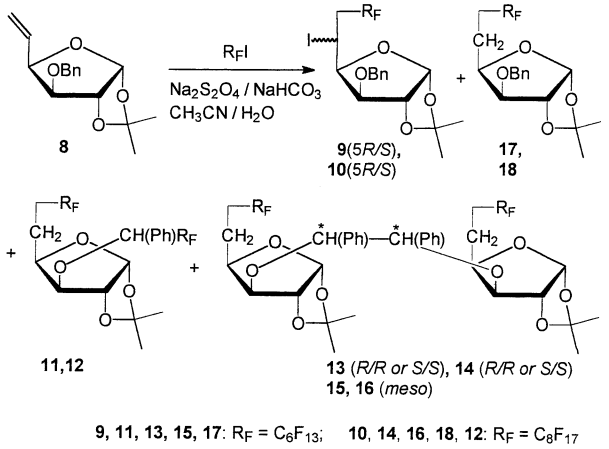
Scheme 1



nals of the sugar skeleton. The H,H-coupling constants of the diastereomer **2** correspond to the data for 6-bromo-6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose[23], whereas the couplings found for the diastereomer **3** correspond to 6-bromo-6-deoxy-1,2:3,4-di-*O*-isopropylidene-ß-L-altropyranose[23]. In this case, the differences of the $J_{4/5}$ coupling constants of **2** and **3** are characteristic. Because of the *cis*-arrangement of 4-H and 5-H in the galactose derivative **2**, the $J_{4/5}$ coupling is small (2.1 Hz). By contrast the diastereomer **3** has a $J_{4/5}$ coupling constant of 9.8 Hz indicating the *trans* arrangement of these two protons. Thus, the L-*altro* configuration is assigned to compound **3**. Moreover, the relatively small $J_{2/3}$ coupling constant of **3** (1.2 Hz) gives rise to speculation that the compound adopts a distorted $^1C_4$ conformation. Compound **2** has a $J_{2/3}$ coupling constant of 2.5 Hz, characteristic for di-*O*-isopropylidene-galactopyranose derivatives[23][24], which generally adopt a highly distorted conformation[25]. The NMR effects of fluorine were used to support the structures of the unsaturated diastereomers **4** and **5**. Thus, the 6-H signals of **4** and **5** split to two doublets (**4**: $J_{H/F} \approx 13.0$ Hz/15.1 Hz; **5**: $J_{H/F} \approx 14.6$ Hz/15.9 Hz) because of the coupling with neighbouring fluorine atoms. The C-5 signals of these compounds are significantly shifted ($\delta \approx 157$) to lower field. Furthermore, it is characteristic that the C-6 peaks of **4** and **5** are split by coupling with the fluorine atoms. Thus, the two doublets of **4** ($\delta = 99.1$, $^2J_{C\text{-}6/F} \approx 21.5$ Hz, $^2J_{C\text{-}6/F'} \approx 26.8$ Hz) indicate that the two α-fluorine atoms are diastereotopic in this compound. The dimers **6** and **7** (ratio 3.3:1), probably generated via a radical recombination reaction, could also be unambiguously characterised by NMR spectroscopy and MS. The crystalline dimer **7** is the 5-*meso* form, showing two different pyranose moieties in the ^{1}H- and ^{13}C-NMR spectra. The syrupy dimer **6** is either the (5*R*,5*R*) or the (5*S*,5*S*) isomer. In this case only one set of NMR signals is found for the two pyranoses, since various protons and C-atoms are homotopic. In agreement with the C-5 to C-5′ connection no proton is detectable in the 5-position within the dimers **6** and **7**.

In a second experiment we investigated the addition of perfluorohexyl and perfluorooctyl iodide to the 5-enofuranose **8**, which contains a double bond some distance from the ring (Scheme 2). Now the 5-iodo compounds **9**(5*R*/*S*) and **10**(5*R*/*S*) were formed as the major products when the reaction mixture was stirred for 24 h. Since the composition of the product mixture changed significantly, ultrasonic acceleration of the reaction (horn system, 13 mm, reaction time 1 h) did not give any advantage. Thus, the yield of **9**(5*R*/*S*) was decreased to 8%, while the amount of the minor products was increased (see Experimental Section); caused by activation of benzyl groups under sonochemical conditions.

Scheme 2



The compounds **9**(5*R*/*S*) and **10**(5*R*/*S*) represent diastereomeric mixtures of the corresponding (5*R*)- and (5*S*)-forms, respectively. The ratio of the diastereomers, determined by integration of the corresponding C-1 signals in the ^{13}C-NMR spectra, is in the range 3:1 to 15:1. In the ^{13}C-NMR spectra of the perfluorohexyl derivative **9**(5*R*/*S*) and the perfluorooctyl compound **10**(5*R*/*S*) the signals for C-5, where the iodo-atom is attached to, were found to be a multiplet at about $\delta = 10$, which is a typical ^{13}C shift for a −CHI− segment. Because of overlapping of the peaks of the minor diastereomer by the peaks of the major one, we report only the NMR data for the predominant component in the diastereomeric mixture of **9** and **10**. As mentioned some byproducts were formed in the reaction of the 5-enofuranose **8** with perfluorohexyl and perfluorooctyl iodide. Because benzyl groups are susceptible to a radical attack, products like **11** and **12**, having two perfluoroalkyl chains, or dimers like **13**, **14** and **15**, **16,** are formed in the course of the reaction (Scheme 2). An intact 3-*O*-benzyl group was proved in the ^{1}H-NMR spectra of the compounds **9**(5*R*/*S*), **10**(5*R*/*S*), **17**, and **18**, while an isopropylidene group was detectable for all the products **9**−**16** isolated from both reaction mixtures.

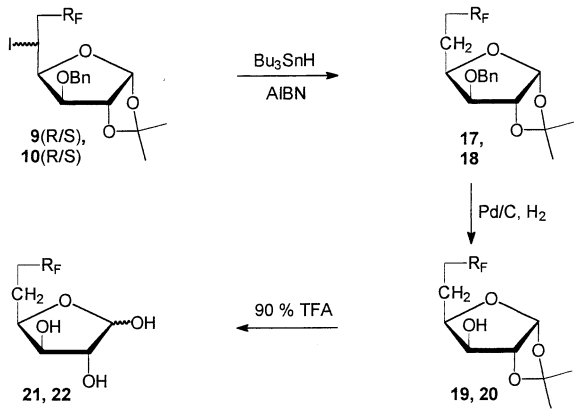
The corresponding signals of two different perfluoroalkyl chains are found in the NMR spectra of the furanoses **11**

and **12**. Furthermore, the double doublets at δ = 4.91 could be assigned to the 3-OCH proton in **11** ($J_{H/F} \approx 6.7$ Hz, $J_{H/F'} \approx 15.1$ Hz) and **12** ($J_{H/F} \approx 7.3$ Hz, $J_{H/F'} \approx 15.8$ Hz), respectively, because no H−H-coupling had been detected for these signals in a COSY experiment.

The dimers **13**, **14** show only one set of ^{1}H- and ^{13}C-NMR signals for the two halves of the molecule, indicating that various protons and C-atoms are homotopic and therefore their signals have the same chemical shift. It could not be decided, whether the (5*R*,5*R*) or the (5*S*,5*S*) configuration was present in these symmetrical compounds. The two aliphatic protons of the −CH−(Ph)−CH(Ph) bridge are represented by a singlet (**13**: δ = 4.44; **14**: δ = 4.45). Compared to **13** and **14** the crystalline dimers **15** and **16** are the corresponding *meso* forms, and two different carbohydrate rings are found in their NMR spectra. Here there is coupling with each other among the aliphatic protons of the −CH(Ph)−CH(Ph) segment (**15**: δ = 4.19, 4.42, $J \approx 8.6$ Hz; **16**: δ = 4.20, 4.42, $J \approx 8.4$ Hz).

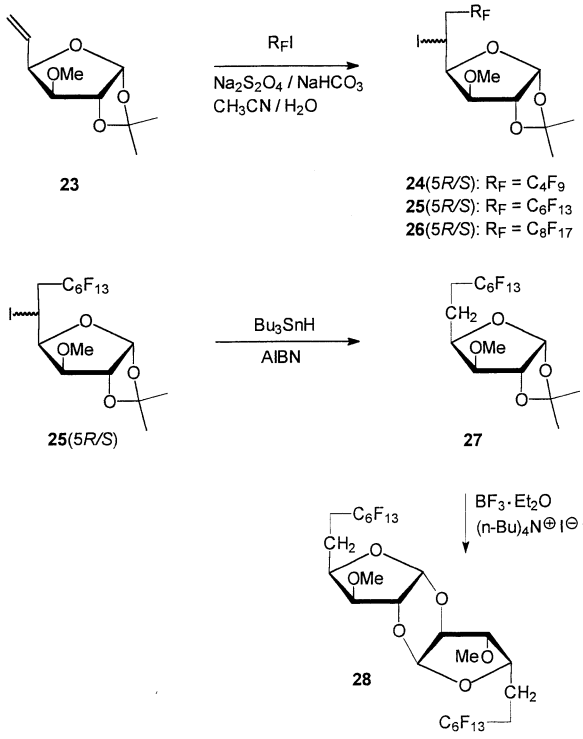
The diastereomeric mixtures **9**(5*R*/*S*) and **10**(5*R*/*S*) were not separated but were hydrodehalogenated with tributylstannane/AIBN[26][27][28] in moderate yields to form the 5-deoxy derivatives **17** and **18**, respectively (Scheme 3). Deprotection of the homologous furanoses **17** and **18** (debenzylation by hydrogen/palladium/charcoal (10%)[29] to **19** and **20**, respectively, and deacetalation by 90% TFA[30]) afforded the amphiphilic carbohydrates **21** and **22**, respectively (Scheme 3). These compounds are liquid crystals showing a narrow *smectic* A phase. Their mesogenic behaviour was investigated by polarising microscopy and DSC measurements and will be discussed in ref.[31] in more detail, together with further examples of this new type of perfluoroalkyl-substituted carbohydrate-based mesogens.

Scheme 3



In order to suppress side reactions and to increase the yield of the major products, we replaced the radical-sensitive benzyl group in **8** for a methyl group. Thus, the enofuranose **23** was treated with perfluorobutyl, perfluorohexyl, and perfluorooctyl iodide to give the addition products **24**(*R*/*S*), **25**(*R*/*S*), and **26**(*R*/*S*) in yields of 34%, 52%, and 32%, respectively (Scheme 4). The iodo derivative **25**(*R*/*S*) was hydrodeiodinated by treatment with tributylstannane/AIBN to form the 5-deoxy product **27**, which had also been a byproduct in the addition reaction of **23**. Attempts to deprotect both the isopropylidene and the methyl group simultaneously were not successful. Thus, treatment of **27** with the BF_3/tetrabutylammonium iodide reagent in dichloromethane, as recommended by Mandal et al.[32] for the cleavage of methyl ether functions, only led to the cleavage of the isopropylidene group. The active intermediate (probably an 1,2-anhydride of the furanose unit[33]) reacted to give the 1,2′: 2,1′-dianhydrofuranose **28** containing two furanose units in a yield of 28%. Because of the symmetry of compound **28**, various protons and C-atoms are homotopic so that only one set of signals for the two furanose rings is observed in the corresponding ^{1}H- and ^{13}C-NMR spectra. Treatment of 2-*O*-acetyl-D-furanosyl fluorides with methanolic sodium methoxide had led to similar dimerisation products[34]. The NMR data of these previously reported compounds are very similar to those of compound **28**.

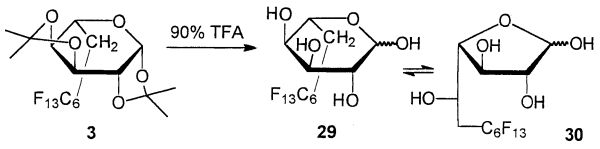
Scheme 4



Finally, the L-*altro*-pyranose **3** was deacetalated to a mixture of the anomeric L-*altro*-pyranoses **29** and -furanoses **30** containing four OH groups besides a perfluoroalkyl tail (Scheme 5). The ratio of the anomeric pyranoses and furanoses (see Table 2) was determined by integration of the signals of their anomeric protons. In order to assign the 1-H signals to the corresponding anomers, a C,H-correlation experiment (COSY) was used. The corresponding C-1 signals of the anomeric pyranoses and -furanoses could be easily found by comparison with ^{13}C-NMR data for D-altroses reported in ref.[35]. The mixture of the amphiphilic L-altroses **29**/**30** did show thermotropic mesogenic properties

with a range of about 30 K. Because the ratio of the anomeric pyranoses to furanoses in solution ([D$_6$]acetone) was 1.8:1, we assume that the content of anomeric furanoses is also relatively high in the liquid crystalline state.

Scheme 5



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Experimental Section

^{1}H and ^{13}C{^{1}H} NMR: Bruker AC 250; internal standard TMS, *J* values in Hz. − ^{19}F{^{1}H} NMR: external standard $CFCl_3$. − TLC: Silica gel foils 60 F_{254} (Merck). − Column chromatography: Silica gel 60 (63−200 μm) (Merck). − Melting points: Polarising microscope Leitz Laborlux 12 Pol equipped with a hot stage Mettler FP 90. Sonication: Vibracell horn system, 20 kHz, 400 W (30%), horn 13 mm diameter.

Perfluoroalkylation (General Procedure A): The corresponding perfluoroalkyl iodide (20 mmol) was slowly added, via a syringe, to a vigorously stirred mixture of 10 mmol of the unsaturated carbohydrate **1**, **8**, or **23**, $Na_2S_2O_4$ (3.48 g, 20 mmol) and $NaHCO_3$ (1.68 g, 20 mmol) in acetonitrile/H_2O (20 ml, 1:1 v/v), under an argon atmosphere at room temp. After completion of the reaction (monitored by TLC) the reaction mixture was diluted with 20 ml H_2O and extracted with Et_2O (2 × 20 ml). The organic layer was dried (Na_2SO_4), filtered and evaporated in vacuo to give a light yellow sirupy product mixture which was separated by column chromatography (eluent: heptane/AcOEt = 15:1).

Hydrogenation (General Procedure B): The 5-iodofuranose (2 mmol) and AIBN (25 mg) were dissolved in dry toluene (5 ml) and argon was passed through the solution for 30 min. Tributylstannane (0.6 ml, 2.2 mmol) was then added slowly via a syringe. The reaction mixture was kept at 60°C for 6 to 8 h until the starting material had disappeared (monitored by TLC). KF (0.3 g, 5 mmol), dissolved in water (2 ml) was added, and the mixture was stirred for 30 min at room temp. After filtration, the organic phase was separated, washed with water (10 ml), dried over Na_2SO_4, and evaporated under reduced pressure to give a colourless syrup which was purified by column chromatography [eluent: heptane/AcOEt (15:1)].

Debenzylation (General Procedure C): The corresponding carbohydrate (1 mmol) was dissolved in ethanol/methanol (5 ml, 1:1 v/v), a catalytic amount of 10% palladium/charcoal was added and the reaction mixture was stirred under 1 atm H_2 for 24 h. The mixture was filtered and evaporated under reduced pressure to give a white solid which was purified by column chromatography [eluent: heptane/AcOEt (6:1)] and/or recrystallisation.

Deisopropylidenation (General Procedure D): The carbohydrate (0.5 mmol) was dissolved in 90% aqueous trifluoroacetic acid (5 ml) and kept at room temp. for 60 h. The solvent was co-evaporated with toluene (10 ml, three to four times) and the resulting material was purified by column chromatography [eluent: toluene/AcOEt (1:1)] and recrystallisation.

6-Deoxy-1,2:3,4-di-O-isopropylidene-6-C-perfluorohexyl-α-D-galactopyranose (**2**), *6-Deoxy-1,2:3,4-di-O-isopropylidene-6-C-perfluorohexyl-β-L-altropyranose* (**3**), *5,6,7,8,9,10,11,12-Octadeoxy-7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro-1,2:3,4-Di-O-isopropylidene-α-D-xylo-dodeca-5-enopyranoses* (**4** and **5**), *Bis-[6,7,8,9,10,11,12-heptadeoxy-7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro1,2:3,4-di-O-isopropylidene-β-L-arabino-dodecanopyranos-5-yl]* (**6**), *and Bis[6,7,8,9,10,11,12-heptadeoxy-7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro-1,2:3,4-di-O-isopropylidene-β-L-arabino-dodecanopyranos-5-yl]* (**7**): The unsaturated D-pyranose **1**[36] (2.42 g, 10 mmol) was perfluoro-alkylated with perfluorohexyl iodide as described in the General Procedure A (reaction time: under stirring 5 h; under sonication 1 h). The six pure products **2** (0.28 g, 5%), **3** (0.73 g, 13%), **4** (0.5 g, 9%), **5** (0.17 g, 3%), **6** (0.14 g, 3%), and **7** (0.46 g, 10%) were obtained after chromatographical separation.

2: Syrup, R_f = 0.66 [heptane/AcOEt (3:1)], $[\alpha]_D^{22}$ = −23.15 (*c* = 1.08, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.33, 1.34, 1.45, 1.53 (s, 3 H, CH_3), 2.34−2.53 (m, 2 H, 6,6′-H), 4.15 (dd, $J_{3/4} \approx$ 7.9 Hz, $J_{4/5} \approx$ 2.1 Hz, 1 H, 4-H), 4.25 (ddd, $J_{5/6} \approx$ 6.0 Hz, $J_{5/6'} \approx$ 5.8 Hz, 1 H, 5-H), 4.32 (dd, $J_{1/2} \approx$ 5.1 Hz, $J_{2/3} \approx$ 2.5 Hz, 1 H, 2-H), 4.63 (dd, 1 H, 3-H), 5.50 (d, 1 H, 1-H). − ^{13}C NMR (62 MHz, $CDCl_3$): δ = 24.4, 24.9, 25.8, 25.9 (CH_3), 32.1 (t, $J_{C\text{-}6/F} \approx$ 20.9 Hz, C-6), 61.7 (C-5), 70.1 (C-2), 70.8 (C-3), 72.9 (C-4), 96.4 (C-1), 109.0, 109.6 ($C(CH_3)_2$), 105−125 (m, 5 CF_2, CF_3). − ^{19}F NMR (235 MHz, $CDCl_3$/$CFCl_3$): δ = −126.0 (s, 2 F, CF_2−CF_3), −123.2, 122.7, 121.6 (s, 2 F, CF_2), −112.6 (s, 2 F, CF_2−CH_2), −80.6 (s, 3 F, CF_3). − MS, *m/z* (70 eV): 547 [M^+ − CH_3]. − $C_{18}H_{19}F_{13}O_5$ (562.3): calcd. C 38.41, H 3.38; found C 38.55, H 3.23.

3: Syrup, R_f = 0.64 [heptane/AcOEt (3:1)], $[\alpha]_D^{22}$ = −46.43 (*c* = 1.12, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.34, 1.35, 1.43, 1.49 (s, 3 H, CH_3), 2.13−2.34 (m, 1 H, 6-H), 2.34−2.61 (m, 1 H, 6′-H), 3.61 (m, 1 H, 5-H), 3.89 (dd, $J_{3/4} \approx$ 5.1 Hz, $J_{4/5} \approx$ 9.8 Hz, 1 H, 4-H), 4.26 (dd, $J_{1/2} \approx$ 2.4 Hz, $J_{2/3} \approx$ 1.2 Hz, 1 H, 2-H), 4.56 (dd, 1 H, 3-H), 5.26 (d, 1 H, 1-H). − ^{13}C NMR (62 MHz, $CDCl_3$): δ = 25.7, 25.8, 27.8, 27.8 (CH_3), 33.5 (t, $J_{C\text{-}6/F} \approx$ 21.7 Hz, C-6), 66.7 (C-5), 72.6 (C-4), 74.3 (C-3), 75.5 (C-2), 96.8 (C-1), 109.1, 111.1 ($C(CH_3)_2$), 105−125 (m, 5 CF_2, CF_3). − ^{19}F NMR (235 MHz, $CDCl_3$/$CFCl_3$): δ = −125.9 (s, 2 F, CF_2−CF_3), −123.2, −122.6, −121.5 (s, 2 F, CF_2), −112.4 (s, 2 F, CF_2−CH_2), −80.7 (s, 3 F, CF_3). − MS (70 eV): *m/z* 547 [M^+ − CH_3]. − $C_{18}H_{19}F_{13}O_5$ (562.3): calcd. C 38.41, H 3.38; found C 38.41, H 3.40.

4: Syrup, R_f = 0.56 [heptane/AcOEt (3:1)], $[\alpha]_D^{22}$ = −70.56 (*c* = 1.07, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.37, 1.37, 1.45, 1.48 (s, 3 H, CH_3), 4.26 (dd, $J_{1/2} \approx$ 3.1 Hz, $J_{2/3} \approx$ 1.8 Hz, 1 H, 2-H), 4.48 (d, $J_{3/4} \approx$ 6.4 Hz, 1 H, 4-H), 4.58 (dd, 1 H, 3-H), 5.06 (dd, $J_{F/6} \approx$ 13.0 Hz, $J_{F'/6} \approx$ 15.1 Hz, 1 H, 6-H), 5.68 (d, 1 H, 1-H). − ^{13}C NMR (62 MHz, $CDCl_3$): δ = 25.0, 25.4, 26.7, 26.8 (CH_3), 71.2 (C-3), 71.6 (C-4), 74.3 (C-2), 97.6 (C-1), 99.1 (dd, $J_{C\text{-}6/F} \approx$ 21.5 Hz, $J_{C\text{-}6/F'} \approx$ 26.8 Hz, C-6), 110.6, 111.6 ($C(CH_3)_2$), 105−125 (m, 5 CF_2, CF_3), 157.0 (dd, $J_{C\text{-}5/F} \approx$ 3.9 Hz, $J_{C\text{-}5/F'} \approx$ 7.8 Hz, C-5). − ^{19}F NMR (235 MHz, $CDCl_3$/$CFCl_3$): δ = −126.0 (s, 2 F, CF_2−CF_3), −123.1 (m, 2 F, CF_2), −122.7, −121.5 (s, 2 F, CF_2), −108.5−104.0 (m, 2 F, CF_2−CH_2), −80.8 (s, 3 F, CF_3). − MS (CI-isobutane): *m/z* 561 [M^+ + H]. − $C_{18}H_{17}F_{13}O_5$ (560.3): calcd. C 38.59, H 3.06; found C 39.20, H 3.02.

5 (minor diastereomer of **4**): Syrup, R_f = 0.60 [heptane/AcOEt (3:1)]. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.37, 1.37, 1.45, 1.45

(s, 3 H, CH_3), 4.33 (dd, $J_{1/2} \approx 3.7$ Hz, $J_{2/3} \approx 2.4$ Hz, 1 H, 2-H), 4.62 (dd, $J_{3/4} \approx 7.0$ Hz, 1 H, 3-H), 4.97 (dd, $J_{4/6} \approx 1.5$ Hz, 1 H, 4-H), 5.39 (ddd, $J_{F/6} \approx 14.6$ Hz, $J_{F'/6} \approx 15.9$ Hz, 1 H, 6-H), 5.68 (d, 1 H, 1-H). − ^{13}C NMR (62 MHz, $CDCl_3$): δ = 24.6, 25.4, 26.3, 26.4 (CH_3), 70.0, 72.6, 77.2 (C-2, C-3, C-4), 97.8 (C-1), 103.6 (t, $J_{C\text{-}6/F} \approx 24.6$ Hz, C-6), 110.8, 111.2 ($C(CH_3)_2$), 105−125 (m, 5 CF_2, CF_3), 157.8 (m, C-5). − ^{19}F NMR (235 MHz, $CDCl_3$/$CFCl_3$): δ = −125.8 (s, 2 F, CF_2−CF_3), −122.6 (s, 4 F, CF_2), −121.2 (s, 2 F, CF_2), −105.3 − 101.7 (m, 2 F, CF_2−CH_2), −80.6 (s, 3 F, CF_3).

6: Syrup, R_f = 0.68 [heptane/AcOEt (3:1)], $[\alpha]_D^{22}$ = −4.32 (*c* = 0.81, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.34, 1.36, 1.41, 1.47 (s, 3 H, CH_3), 2.83−3.31 (m, 2 H, 6,6′-H), 3.98 (d, $J_{1/2} \approx 3.2$ Hz, 1 H, 2-H), 4.64 (d, $J_{3/4} \approx 4.7$ Hz, 1 H, 3-H), 4.95 (d, 1 H, 4-H), 5.56 (d, 1 H, 1-H). − ^{13}C NMR (62 MHz, $CDCl_3$): δ = 25.7, 26.1, 26.4, 27.2 (CH_3), 36.7 (t, $J_{C\text{-}6/F} \approx 19.0$ Hz, C-6), 72.6 (m, C-4), 74.5 (m, C-3), 79.2 (C-2), 84.9 (m, C-5), 96.4 (C-1), 108.8, 110.8 ($C(CH_3)_2$), 105−125 (m, 5 CF_2, CF_3). − ^{19}F NMR (235 MHz, $CDCl_3$): δ = −125.8 (s, 2 F, CF_2−CF_3), −123.7, −122.5, −121.2 (s, 2 F, CF_2), −112.3 − 108.1 (m, 2 F, CF_2−CH_2), −80.6 (CF_3). In the NMR spectra of compound **6** only one set of signals appears owing to the symmetry of the molecule; the configuration at two homotopicC-5 atoms is (*R*,*R*) or (*S*,*S*). − MS (DCI {CH_2Cl_2} isobutane): *m*/*z* = 1123 [M^++H]. − $C_{36}H_{36}F_{26}O_{10}$ (1122.6): calcd. C 38.52, H 3.23; found C 39.13, H 3.45.

7: M.p. 99−102°C (heptane); R_f = 0.52 [heptane/AcOEt (3:1)]; $[\alpha]_D^{22}$ = +4.24 (*c* = 1.01, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.28, 1.32 (s, 3 H, CH_3), 1.35 (s, 6 H, CH_3), 1.38 (s, 3 H, CH_3), 1.43 (s, 6 H, CH_3), 1.49 (s, 3 H, CH_3), 2.47−2.97 (m, 3 H, 6,6′-H), 3.14−3.44 (m, 1 H, 6′-H), 3.92 (d, $J_{1/2} \approx 2.9$ Hz, 1 H, 2-H_a), 3.98 (d, $J_{1/2} \approx 3.4$ Hz, 1 H, 2-H_b), 4.43 (d, $J_{3/4} \approx 5.4$ Hz, 1 H, 3-H_a), 4.57 (d, $J_{3/4} \approx 5.3$ Hz, 1 H, 3-H_b), 4.62 (d, 1 H, 4-H_b), 4.78 (d, 1 H, 4-H_a), 5.51 (d, 1 H, 1-H_b) 5.62 (d, 1 H, 1-H_a). − ^{13}C NMR (62 MHz, $CDCl_3$): δ = 24.8, 25.2, 25.3, 25.8, 26.1, 27.1, 27.4, 27.5 (CH_3), 31.4 (m, C-6), 34.7 (t, $J_{C\text{-}6/F} \approx 20.3$ Hz, C-6), 71.6 (m, C_b-4), 73.0 (m, C_b-3), 73.4 (C_a-4), 75.3 (C_a-3), 77.5 (C_b-2), 79.1 (C_a-2), 82.4 (C-5), 83.4 (C-5), 95.3 (m, C_a-1), 95.5 (C_b-1), 106.7, 109.7, 110.2, 110.3 ($C(CH_3)_2$), 105−125 (m, 10 CF_2, 2 CF_3). − ^{19}F NMR (235 MHz, $CDCl_3$): δ = −126.1 (s, 4 F, CF_2−CF_3), −123.5 (s, 2 F, CF_2), −123.1 (m, 2 F, CF_2), −122.7 (m, 4 F, CF_2), −121.5, −121.2 (s, 2 F, CF_2), −109.9 − 104.2 (m, 2 F, CF_2−CH_2), −80.9, −80.8 (CF_3). The two pyranose rings are indicated with a and b, the configuration at C_a-5, C_b-5 is (*R*,*S*) or (*S*,*R*). − MS (CI-isobutane): *m*/*z* = 1065 [M^+ − $(CH_3)_2CO$ + H]. − $C_{36}H_{36}F_{26}O_{10}$ (1122.6): calcd. C 38.52, H 3.23; found C 38.38, H 3.18.

3-O-Benzyl-5,6-dideoxy-5-iodo-1,2-O-isopropylidene-6-C-perfluorohexyl-α-"D-gluco"/"L-ido"-furanose (**9**), *5,6,7,8,9,10,11,12-Octadeoxy-7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro-1,2-O-isopropylidene-3-O-(perfluorohexyl-phenylmethyl)-α-D-xylo-dodecanofuranose* (**11**), *1,2-Bis(5,6,7,8,9,10,11,12-octadeoxy-7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro-1,2-O-isopropylidene-α-D-xylo-dodecanofuranos-3-O-yl)-1,2-diphenylethane* (**13**), *meso-1,2-Bis(5,6,7,8,9,10,11,12-octadeoxy-7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro.-1,2-O-isopropylidene-α-D-xylo-dodecanofuranos-3-O-yl)-1,2-diphenylethane* (**15**): The unsaturated D-furanose **8**[37] (2.76 g, 10 mmol) was perfluoro-alkylated with perfluorohexyl iodide under stirring (24 h) or under sonication (1 h) as described in the General Procedure A. After the given time no starting material **8** was detectable by TLC. Five products were chromatographically separated and characterised (see Table 1).

9: Syrup, R_f = 0.53 [heptane/AcOEt (3:1)], $[\alpha]_D^{22}$ = −29.8 (*c* = 0.28, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.31, 1.52 (s, 3 H, CH_3), 2.51−2.79 (m, 1 H, 6-H), 3.23−3.48 (m, 1 H, 6-H′), 4.27 (d, $J_{3/4} \approx 2.8$ Hz, 1 H, 3-H), 4.31−4.50 (m, 2 H, 4,5-H), 4.60 (d, $J_{1/2} \approx 3.7$ Hz, 1 H, 2-H), 4.66 (m, 2 H, CH_2−Ph), 5.96 (d, 1 H, 1-H), 7.30−7.39 (m, 5 H, Ph). − ^{13}C NMR (62 MHz, $CDCl_3$): δ = 11.5 (m, C-5), 26.2, 26.9 (CH_3), 37.0 (t, $J_{C\text{-}6/F} \approx 20.5$ Hz, C-6), 73.2 (CH_2−Ph), 81.5 (C-2), 82.5 (C-4), 83.9 (C-3), 105.9 (C-1), 112.2 ($C(CH_3)_2$), 105−125 (m, 5 CF_2, CF_3), 128.2, 128.2, 128.6, 137.0 (Ph). − ^{19}F NMR (235 MHz, $CDCl_3$/$CFCl_3$): δ = −125.8 (s, 2 F, CF_2−CF_3), −123.5, −122.6, −121.5 (s, 2 F, CF_2), −115.7−111.9 (m, 2 F, CF_2−CH_2), −80.6 (s, 3 F, CF_3). − MS, *m*/*z* (70 eV): 722 [M^+]. − $C_{22}H_{20}F_{13}IO_4$ (722.3): calcd. C 36.58, H 2.79; found C 36.90, H 2.73.

Table 1. Products from the perfluorination of the unsaturated D-furanose **8**[37] (2.76 g, 10 mmol) with perfluorohexyl iodide under stirring (24 h) or under sonication (1 h) as described in the General Procedure A

	9(*R*/*S*)[a]	**11**	**13**[b]	**15**	**17**
Stirring	1.59 g (22%)	traces	traces	traces	0.42 g (7%)
Sonication	0.58 g (8%)	0.46 g (5%)	1.31 g (11%)	1.43 g (12%)	traces

[a] Mixture of the (5*R*) and (5*S*) isomer. − [b]The configuration at the chiral centres of the ethane moiety is (1*R*,2*R*) or (1*S*,2*S*).

11: Syrup, R_f = 0.52 (heptane/AcOEt (3:1)]; $[\alpha]_D^{22}$ = −1.9 (*c* = 1.13, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.12, 1.42 (s, 3 H, CH_3), 1.92−2.52 (m, 4 H, 5,5′,6,6′-H), 4.08 (d, $J_{3/4} \approx 3.0$ Hz, 1 H, 3-H), 4.15 (d, $J_{1/2} \approx 3.7$ Hz, 1 H, 2-H), 4.19 (m, 1 H, 4-H), 4.91 (dd, $J_{H/F} \approx 6.7$ Hz, $J_{H/F'} \approx 15.1$ Hz, 1 H, C*H*−Ph), 5.62 (d, 1 H, 1-H), 7.43 (s, 5 H, Ph); the stereochemistry of the O−*C*H(Ph)R_F group in **11** was not noted. − ^{13}C NMR (62 MHz, $CDCl_3$): δ = 19.6 (C-5), 26.3, 26.9 (CH_3), 28.5 (t, $J_{C\text{-}6/F} \approx 22.5$ Hz, C-6), 79.3 (C-4), 79.6 (dd, $J_{C/F} \approx 21.9$ Hz, $J_{C/F'} \approx 28.2$ Hz, *C*H−Ph), 82.0 (C-3), 85.8 (C-2), 104.6 (C-1), 112.1 ($C(CH_3)_2$), 105−125 (m, 10 CF_2, 2 CF_3), 128.5, 129.1, 130.3, 133.2 (Ph). − ^{19}F NMR (235 MHz, $CDCl_3$/$CFCl_3$): δ = −126.0 (m, 3 F, CF_2), − 125.5−123.3 (m, 3 F, CF_2), −122.7 (s, 4 F, CF_2), −121.7 (m, 5 F, CF_2), −120.4 (s, 2 F, CF_2), −117.1−115.9 (m, 1 F, CF_2), −114.3 (s, 2 F, CF_2−CH), −80.7 (s, 6 F, CF_3). − MS, *m*/*z* (70 eV): 915 [M^+ + H]. − $C_{28}H_{20}F_{26}O_4$ (914.4): calcd. C 36.78, H 2.20; found C 37.43, H 2.20.

13 Syrup, R_f = 0.43 (heptane/AcOEt (3:1)], $[\alpha]_D^{23}$ = −29.26 (*c* = 1.15, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.28, 1.42 (s, 6 H, CH_3), 1.81−2.32 (m, 8 H, 5,5′,6,6′-H), 3.64 (d, $J_{3/4} \approx 3.0$ Hz, 2 H, 3-H_a, 3-H_b), 4.05 (m, 2 H, 4-H_a, 4-H_b), 4.44 (s, 2 H, C*H*−Ph), 4.52 (d, 2 H, $J_{1/2} \approx 4.0$ Hz, 2-H_a, 2-H_b), 5.81 (d, 2 H, 1-H_a, 1-H_b), 7.07 (m, 4 H, Ph), 7.20 (m, 6 H, Ph). − ^{13}C NMR (62 MHz, $CDCl_3$): δ = 19.5 (C_a-5, C_b-5), 25.8, 26.5 (CH_3), 27.9 (t, $J_{C\text{-}6/F} \approx$ 22.5 Hz, C_a-6, C_b-6), 78.6 (C_a-4, C_b-4), 80.7 (C_a-3, C_b-3), 82.0 (C_a-2, C_b-2), 83.6 (*C*H−Ph), 104.8 (C_a-1, C_b-1), 111.3 ($C(CH_3)_2$), 105−125 (m, 10 CF_2, 2 CF_3), 127.9, 128.2, 128.4, 137.2 (Ph), − ^{19}F NMR (235 MHz, $CDCl_3$/$CFCl_3$): δ = −125.9 (s, 4 F, CF_2−CF_3), −123.1, −122.6, −121.6 (s, 4 F, CF_2), −114.3 (s, 4 F, CF_2−CH_2), −80.6 (s, 6 F, CF_3). Because of the molecule symmetry, various atoms are homotopic. − MS (CI-isobutane) *m*/*z* = 1074 [M^+ − 2 $(CH_3)_2O$). − $C_{44}H_{40}F_{26}O_8$ (1190.8): calcd. C 44.36, H 3.39; found C 44.18, H 3.27.

15: M.p. 103−106°C (heptane), R_f = 0.34 (heptane/AcOEt (3:1)], $[\alpha]_D^{22}$ = −15.22 (*c* = 1.34, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.09, 1.10, 1.33, 1.34 (s, 3 H, CH_3), 1.54−2.27 (m, 8

H, 5,5′,6,6′-H), 3.49 (m, 2 H, 3-H_a, 3-H_b), 3.52 (d, $J_{1/2} \approx 4.0$ Hz, 1 H, 2-H_b), 3.86 (m, 2 H, 4-H_a, 4-H_b), 4.14 (d, 1 H, $J_{1/2} \approx 4.0$ Hz, 2-H_a), 4.19 (d, 1 H, $J \approx 8.6$ Hz, C*H*−Ph), 4.42 (d, 1 H, $J \approx 8.6$ Hz, C*H*−Ph), 5.13 (d, 1 H, 1-H_b), 5.57 (d, 1 H, 1-H_a), 7.34−7.40 (m, 10 H, Ph). The furanose rings were marked with a and b.− ^{13}C NMR (62 MHz, $CDCl_3$): δ = 19.4 (C_a-5, C_b-5), 25.7, 26.0, 26.5, 26.6 (CH_3), 27.4−29.0 (m, C_a-6, C_b-6), 78.5, 79.1 (C_a-4, C_b-4), 79.9, 81.5 (C_a-3, C_b-3), 82.0 (C_a-2), 84.1, 84.4 (*C*H−Ph), 84.8 (C_b-2), 104.4, 104.7 (C_a-1, C_b-1), 111.3, 111.5 (*C*(CH_3)$_2$), 105−125 (m, 10 CF_2, 2 CF_3), 127.2−128.9, 138.2 (Ph). − ^{19}F NMR (235 MHz, $CDCl_3$/$CFCl_3$): δ = −125.9 (s, 4 F, C*F*$_2$−CF_3), −123.1, −122.6, −121.6 (s, 4 F, CF_2), −114.1 (s, 4 F, CF_2−CH_2), −80.6 (s, 6 F, CF_3). − MS (CI-isobutane) *m/z* = 1191 [M^+ + H). − $C_{44}H_{40}F_{26}O_8$ (1190.8): calcd. C 44.36, H 3.39; found C 44.35, H 3.06.

3-O-Benzyl-5,6-dideoxy-5-iodo-1,2-O-isopropylidene-6-C-perfluorooctyl-"D-gluco"/"L-ido"-furanose (**10**), *5,6,7,8,9,10,11,12,13,14-Decadeoxy-7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-heptadecafluoro-1,2-O-isopropylidene-3-O-(perfluorooctyl-phenylmethyl)-α-D-xylo-tetradecanofuranose* (**12**), *1,2-Bis(5,6,7,8,9,10,11,12,13,14-decadeoxy-7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-heptadecafluoro-1,2-O-isopropylidene-α-D-xylo-tetradecanofuranos-3-O-yl)-1,2-diphenyl-ethane* (**14**), *meso-1,2-Bis(5,6,7,8,9,10,11,12,13,14-decadeoxy-7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-heptadecafluoro-1,2-O-isopropylidene-α-D-xylo-tetradecanofuranos-3-O-yl)-1,2-diphenylethane* (**16**): The unsaturated 3-*O*-benzyl-D-furanose **8**[37] (2.76 g, 10 mmol) was perfluoro-alkylated with perfluorooctyl iodide under stirring (reaction time: 20 h) as described in the General Procedure A. The five pure products **10** (0.66 g, 8%, mixture of the (5*R*) and (5*S*) isomer), **12** (0.78 g, 7%), **14** (0.42 g, 3%), **16** (1.39 g, 10%), and **18** (traces) were obtained after chromatographical separation.

10: Syrup, R_f = 0.52 (heptane/AcOEt (3:1)], $[\alpha]_D^{22}$ = −22.64 (*c* = 0.27, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.32, 1.52 (s, 3 H, CH_3), 2.52−2.80 (m, 1 H, 6-H), 3.25−3.50 (m, 1 H, 6-H′), 4.28 (d, $J_{3/4} \approx 2.8$ Hz, 1 H, 3-H), 4.32−4.50 (m, 2 H, 4,5-H), 4.61 (d, $J_{1/2} \approx 3.7$ Hz, 1 H, 2-H), 4.67 (m, 2 H, CH_2−Ph), 5.97 (d, 1 H, 1-H) , 7.31−7.45 (m, 5 H, Ph). − ^{13}C NMR (62 MHz, $CDCl_3$): δ = 11.6 (m, C-5), 26.2, 26.9 (CH_3), 37.2 (t, $J_{C\text{-}6/F} \approx 20.9$ Hz, C-6), 73.2 (*C*H_2−Ph), 81.5 (C-2), 82.5 (C-4), 83.9 (C-3), 106.0 (C-1), 112.2 (*C*(CH_3)$_2$), 105−125 (m, 7 CF_2, CF_3), 128.2, 128.2, 128.6, 137.0 (Ph). − ^{19}F NMR (235 MHz, $CDCl_3$/$CFCl_3$): δ = −125.8 (s, 2 F, C*F*$_2$−CF_3), −123.4, −122.5 (s, 2 F, CF_2), −122.0−121.1 (m, 6 F, CF_2), −115.7−111.7 (m, 2 F, CF_2−CH_2), −80.5 (s, 3 F, CF_3). − $C_{24}H_{20}F_{17}IO_4$ (822.3): calcd. C 35.06, H 2.45; found C 34.83, H 2.19.

12: M.p. 93−95°C (heptane), R_f = 0.49 (heptane/AcOEt (3:1)], $[\alpha]_D^{22}$ = +0.79 (*c* = 1.26, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.12, 1.42 (s, 3 H, CH_3), 1.91−2.50 (m, 4 H, 5,5′,6,6′-H), 4.08 (d, $J_{3/4} \approx 3.0$ Hz, 1 H, 3-H), 4.15 (d, $J_{1/2} \approx 3.8$ Hz, 1 H, 2-H), 4.19 (m, 1 H, 4-H), 4.91 (dd, $J_{H/F} \approx 7.3$ Hz, $J_{H/F'} \approx 15.8$ Hz, 1 H, C*H*−Ph), 5.62 (d, 1 H, 1-H), 7.43 (s, 5 H, Ph). The stereochemistry of the O−*C*H(Ph)R_F group in **12** was not noted. − ^{13}C NMR (62 MHz, $CDCl_3$): δ = 19.3 (m, C-5), 26.0, 26.6 (CH_3), 28.2 (t, $J_{C\text{-}6/F} \approx 22.5$ Hz, C-6), 79.1 (C-4), 79.3 (dd, $J_{C/F} \approx 22.0$ Hz, $J_{C/F'} \approx 28.5$ Hz, *C*H−Ph), 81.6 (C-3), 85.5 (C-2), 104.3 (C-1), 111.8 (*C*(CH_3)$_2$), 105−125 (m, 14 CF_2, 2 CF_3), 128.2, 128.2, 128.8, 128.8, 130.0, 132.8 (Ph). − ^{19}F NMR (235 MHz, $CDCl_3$/$CFCl_3$): δ = −126.1 (s, 4 F, CF_2), −123.2 (s, 2 F, CF_2), −122.7 (s, 4 F, CF_2), −121.8 (s, 13 F, CF_2), −120.4 (s, 2 F, CF_2), −117.1−115.8 (m, 1 F, CF_2−CH), −114.3 (s, 2 F, CF_2−CH_2), −80.8 (m, 6 F, CF_3). − $C_{32}H_{20}F_{34}O_4$ (1114.5): calcd. C 34.49, H 1.81; found C 34.53, H 1.69.

14: Syrup, R_f = 0.46 (heptane/AcOEt (3:1)], $[\alpha]_D^{23}$ = −24.59 (*c* = 1.05, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.27, 1.42 (s, 6 H, CH_3), 1.81−2.38 (m, 8 H, 5,5′,6,6′-H), 3.64 (d, $J_{3/4} \approx 3.2$ Hz, 2 H, 3-H_a, 3-H_b), 4.05 (m, 2 H, 4-H_a, 4-H_b), 4.45 (s, 2 H, C*H*−Ph), 4.49 (d, $J_{1/2} \approx 4.0$ Hz, 2 H, 2-H_a, 2-H_b), 5.80 (d, 2 H, 1-H_a, 1-H_b), 7.07−7.12 (m, 4 H, Ph), 7.18−7.21 (m, 6 H, Ph). − ^{13}C NMR (62 MHz, $CDCl_3$): δ = 19.5 (m, C_a-5, C_b-5), 25.8, 26.5 (CH_3), 27.9 (t, $J_{C\text{-}6/F} \approx 22.7$ Hz, C_a-6, C_b-6), 78.6 (C_a-4, C_b-4), 80.7 (C_a-3, C_b-3), 81.9 (C_a-2, C_b-2), 83.6 (*C*H−Ph), 104.8 (C_a-1, C_a-1), 111.3 (*C*(CH_3)$_2$), 105−125 (m, 14 CF_2, 2CF_3), 127.9, 128.3, 128.4, 137.3 (Ph). − ^{19}F NMR (235 MHz, $CDCl_3$/$CFCl_3$): δ = −126.0 (s, 4 F, C*F*$_2$−CF_3), −123.2, −122.5 (s, 4 F, CF_2), −121.9−121.4 (m, 12 F, CF_2), −114.5 (s, 2 F, CF_2−CH_2), −80.7 (s, 6 F, CF_3). The configuration at the chiral centres of the ethane moiety is (1*R*,2*R*) or (1*S*,2*S*). Because of the molecule symmetry, various atoms are homotopic. − $C_{48}H_{40}F_{34}O_8$ (1390.8): calcd. C 41.45, H 2.90; found C 42.04, H 2.74.

16: M.p. 111−113°C (heptane), R_f = 0.41 (heptane/AcOEt (3:1)], $[\alpha]_D^{23}$ = −13.52 (*c* = 1.79, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.09, 1.09, 1.32, 1.34 (s, 3 H, CH_3), 1.55−2.28 (m, 8 H, 5,5′,6,6′-H), 3.50 (m, 2 H, 3-H_a, 3-H_b), 3.52 (d, $J_{1/2} \approx 3.9$ Hz, 1 H, 2-H_b), 3.86 (m, 2 H, 4-H_a, 4-H_b), 4.15 (d, $J_{1/2} \approx 3.9$ Hz, 1 H, 2-H_a), 4.20 (d, $J \approx 8.4$ Hz, 1 H, C*H*−Ph), 4.42 (d, $J \approx 8.4$ Hz, 1 H, C*H*−Ph), 5.13 (d, 1 H, 1-H_b), 5.57 (d, 1 H, 1-H_a), 7.31−7.43 (m, 10 H, Ph) The two furanose rings were marked with a and b. − ^{13}C NMR (62 MHz, $CDCl_3$): δ = 19.4 (m, C_a-5, C_b-5), 25.6, 26.0, 26.5, 26.6 (CH_3), 27.7 (t, $J_{C\text{-}6/F} \approx 22.4$ Hz, C-6), 28.4 (t, $J_{C\text{-}6/F} \approx 22.2$ Hz, C-6), 78.6, 79.2 (C_a-4, C_b-4), 79.9, 81.6 (C_a-3, C_b-3), 82.0 (C_a-2), 84.2, 84.4 (*C*H−Ph), 84.6 (C_b-2), 104.4, 104.7 (C_a-1, C_b-1), 111.3, 111.5 (*C*(CH_3)$_2$), 105−125 (m, 14 CF_2, 2 CF_3), 127.3, 127.3, 128.2, 128.2, 128.3, 128.3, 128.3, 128.6, 128.6, 128.9, 138.2, 141.1 (Ph). − ^{19}F NMR (235 MHz, $CDCl_3$/$CFCl_3$): δ = −126.1 (s, 4 F, C*F*$_2$−CF_3), −123.3, −122.7 (s, 4 F, CF_2), −122.2−121.4 (m, 12 F, CF_2), −114.5, −114.3 (s, 2 F, CF_2−CH_2), −80.9 (s, 6 F, CF_3) . − $C_{48}H_{40}F_{34}O_8$ (1390.8): calcd. C 41.45, H 2.90; found C 41.46, H 2.82.

3-O-Benzyl-5,6,7,8,9,10,11,12-octadeoxy-7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro-1,2-O-isopropylidene-α-D-xylo-dodecano-furanose (**17**): The iodofuranose **9** (1.44 g, 2.0 mmol) was hydrodehalogenated as described in the General Procedure B; yield of **17** 0.63 g (53%).

17: Syrup, R_f = 0.47 (heptane/AcOEt (3:1)], $[\alpha]_D^{22}$ = −20.7 (*c* = 1.04, $CHCl_3$). − ^{1}H NMR (250 MHz , $CDCl_3$): δ = 1.32, 1.48 (s, 3 H, CH_3), 1.81−2.40 (m, 4 H, 5,5′,6,6′-H), 3.80 (d, $J_{3/4} \approx 3.3$ Hz, 1 H, 3-H), 4.20 (ddd, $J_{4/5} \approx 5.1$ Hz, $J_{4/5} \approx 8.0$ Hz, 1 H, 4-H), 4.48 (d, $J \approx 11.8$ Hz, 1 H, 1 CH_2−Ph), 4.63 (d, $J_{1/2} \approx 3.8$ Hz, 1 H, 2-H), 4.71 (d, 1 H, 1 CH_2−Ph), 5.91 (d, 1 H, 1-H), 7.28−7.37 (m, 5 H, Ph). − ^{13}C NMR (62 MHz, $CDCl_3$): δ = 19.4 (m, C-5), 26.1, 26.6 (CH_3), 37.9 (t, $J_{C\text{-}6/F} \approx 22.4$ Hz, C-6), 71.7 (*C*H_2−Ph), 78.9 (C-4), 81.8 (C-3), 82.2 (C-2), 104.8 (C-1), 111.5 (*C*(CH_3)$_2$), 105−125 (m, 5 CF_2, CF_3), 127.9, 128.1, 128.6, 137.1 (Ph). − ^{19}F NMR (235 MHz, $CDCl_3$/$CFCl_3$): δ = −125.9 (s, 2 F, C*F*$_2$−CF_3), −123.2, −122.6, −121.6 (s, 2 F, CF_2), −114.3 (s, 2 F, CF_2−CH_2), −80.6 (s, 3 F, CF_3). − $C_{22}H_{21}F_{13}O_4$ (596.4): calcd. C 44.31, H 3.55; found C 44.32, H 3.56.

3-O-Benzyl-5,6,7,8,9,10,11,12,13,14-decadeoxy-7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-heptadecafluoro-1,2-O-isopropylidene-α-D-xylo-tetradecano-furanose (**18**): The iodofuranose **10** (0.41 g, 0.5 mmol) was hydrodehalogenated as described in the General Procedure B; yield of **18** 0.17 g (50%). **18**: Syrup, R_f = 0.45 (heptane/AcOEt (3:1)], $[\alpha]_D^{23}$ = −18.95 (*c* = 0.57, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.32, 1.48 (s, 3 H,

CH_3), 1.81−2.40 (m, 4 H, 5,5′,6,6′-H), 3.80 (d, $J_{3/4} \approx 3.3$ Hz, 1 H, 3-H), 4.15 (m,1 H, 4-H), 4.47 (d, $J \approx 11.9$ Hz, 1 H, CH_2−Ph), 4.63 (d, $J_{1/2} \approx 3.9$ Hz, 1 H, 2-H), 4.71 (d, 1 H, CH_2−Ph), 5.91 (d, 1 H, 1-H), 7.28−7.36 (m, 5 H, Ph). − ^{13}C NMR (62 MHz, $CDCl_3$): δ = 19.5 (t, $J_{C\text{-}5/F} \approx 4.0$ Hz, C-5), 26.2, 26.7 (CH_3), 27.9 (t, $J_{C\text{-}6/F} \approx 22.2$ Hz, C-6), 71.8 (*C*H_2−Ph), 79.0 (C-4), 81.8 (C-3), 82.3 (C-2), 104.8 (C-1), 111.6 (*C*$(CH_3)_2$), 105−125 (m, 7 CF_2, CF_3), 127.9, 128.2, 128.6, 137.2 (Ph). − ^{19}F NMR (235 MHz, $CDCl_3$/$CFCl_3$): δ = −125.9 (s, 2 F, CF_2−CF_3), −123.2, −122.5 (s, 2 F, CF_2), −121.6 (m, 6 F, CF_2), −114.2 (s, 2 F, CF_2−CH_2), −80.7 (s, 3 F, CF_3). − $C_{24}H_{21}F_{17}O_4$ (696.4): calcd. C 41.39, H 3.04; found C 41.61, H 2.86.

5,6,7,8,9,10,11,12-Octadeoxy-7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro-1,2-O-isopropylidene-α-D-xylo-dodecanofuranose (**19**): The furanose **17** (0.60 g, 1.0 mmol) was debenzylated as described in the General Procedure C to yield the crystalline derivative **19** (0.46 g, 91%), m.p. 113°C (heptane), R_f = 0.27 [heptane/AcOEt (3:1)], $[\alpha]_D^{22}$ = −6.8 (*c* = 1.11, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.30, 1.48 (s, 3 H, CH_3), 1.81−2.47 (m, 4 H, 5,5′,6,6′-H), 4.08−4.18 (m, 2 H, 3-H, 4-H), 4.51 (d, $J_{1/2} \approx 3.8$ Hz, 1 H, 2-H), 5.90 (d, 1 H, 1-H). − ^{13}C NMR (62 MHz, $CDCl_3$): δ = 19.3 (t, $J_{C\text{-}5/F} \approx 4.0$ Hz, C-5), 26.1, 26.6 (CH_3), 28.1 (t, $J_{C\text{-}6/F} \approx 22.6$ Hz, C-6), 75.6 (C-4), 79.0 (C-3), 85.5 (C-2), 104.4 (C-1), 111.7 (*C*$(CH_3)_2$), 105−125 (m, 5 CF_2, CF_3). − ^{19}F NMR (235 MHz, $CDCl_3$/$CFCl_3$): δ = −125.9 (s, 2 F, CF_2−CF_3), −123.2, −122.6, −121.6 (s, 2 F, CF_2), −114.3 (s, 2 F, CF_2−CH_2), −80.6 (s, 3 F, CF_3). − $C_{15}H_{15}F_{13}O_4$ (506.3): calcd. C 35.59, H 2.99; found C 35.58, H 2.80.

5,6,7,8,9,10,11,12,13,14−Decadeoxy-7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-heptadecafluoro-1,2-O-isopropylidene-α-D-xylo-tetradecanofuranose (**20**): The furanose **18** (0.14 g, 0.2 mmol) was debenzylated as described in the General Procedure C giving the crystalline derivative **20** in a yield of 0.11 g (90%), m.p. 121−122°C (heptane), R_f = 0.22 (heptane/AcOEt (3:1)], $[\alpha]_D^{23}$ = −10.19 (*c* = 0.53, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.31, 1.49 (s, 3 H, CH_3), 1.81−2.46 (m, 4 H, 5,5′,6,6′-H), 4.08−4.18 (m, 2 H, 3-H, 4-H), 4.51 (d, $J_{1/2} \approx 3.8$ Hz, 1 H, 2-H), 5.90 (d, 1 H, 1-H). − ^{13}C NMR (62 MHz, $CDCl_3$): δ = 19.3 (t, $J_{C\text{-}5/F} \approx 4.7$ Hz, C-5), 26.1, 26.6 (CH_3), 28.1 (t, $J_{C\text{-}6/F} \approx 22.4$ Hz, C-6), 75.6 (C-4), 79.0 (C-3), 85.5 (C-2), 104.4 (C-1), 111.7 (*C*$(CH_3)_2$), 105−125 (m, 7 CF_2, CF_3). − ^{19}F NMR (235 MHz, $CDCl_3$/$CFCl_3$): δ = −125.8 (s, 2 F, CF_2−CF_3), −123.1, −122.4 (s, 2 F, CF_2), −121.5 (m, 6 F, CF_2), −114.3 (m, 2 F, CF_2−CH_2), −80.5 (s, 3 F, CF_3) . − $C_{17}H_{15}F_{17}O_4$ (606.3): calcd. C 33.68, H 2.49; found C 33.76, H 2.40.

5,6,7,8,9,10,11,12-Octadeoxy-7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro-D-xylo-dodecanose (**21**): The isopropylidene furanose **19** (0.25 g, 0.5 mmol) was deacetalated as described in the General Procedure D yielding 0.19 g (83%) of the liquid crystalline product (S_A) **21**, m.p. 131−132°C (heptane/acetone), c.p. 146−147°C, R_f = 0.07 (heptane/AcOEt (1:1)]. - ^{1}H NMR (250 MHz, [D_6]acetone): δ = 1.80−2.08 (m, 4 H, 5-$H_{\alpha,\beta}$, 5′-$H_{\alpha,\beta}$) 2.18−2.49 (m, 4 H, 6-$H_{\alpha,\beta}$, 6′-$H_{\alpha,\beta}$), 3.96 (dd, $J_{1/2} \approx 4.0$ Hz, $J_{2/3} \approx 2.5$ Hz, 1 H, 2-H_α), 3.99 (dd, $J_{2/3} \approx 2.0$ Hz, $J_{3/4} \approx 4.0$ Hz, 1 H, 3-H_β), 4.01 (dd, $J_{1/2} \approx 1.0$ Hz, 1 H, 2-H_β), 4.08 (dd, $J_{3/4} \approx 4.0$ Hz, 1 H, 3-H_α), 4.14 (dd, $J_{4/5} \approx 6.1$ Hz, 1 H, 4-H_α), 4.17 (dd, $J_{4/5} \approx 6.2$ Hz, 1 H, 4-H_β), 5.04 (d, 1 H, 1-H_β), 5.34 (d, 1 H, 1-H_α). − ^{13}C NMR (62 MHz, [D_6]acetone): δ = 21.4 (t, $J_{C\text{-}5/F} \approx 4.6$ Hz, C-5), 22.2 (t, $J_{C\text{-}5/F} \approx 4.1$ Hz, C-5), 28.5 (t, $J_{C\text{-}6/F} \approx 22.2$ Hz, C-6), 28.6 (t, $J_{C\text{-}6/F} \approx 22.2$ Hz, C-6), 77.0 (C_β-3), 77.3 (C_α-3), 78.2 (C_α-2), 78.3 (C_β-4), 81.4 (C_α-4), 82.0 (C_β-2), 97.0 (C_α-1), 103.8 (C_β-1), 105−125 (m, 5 CF_2, CF_3). − ^{19}F NMR (235 MHz , [D_6]acetone/$CFCl_3$): δ = −126.4 (s, 2 F, CF_2−CF_3), −123.7, −123.1, −122.1 (s, 2 F, CF_2), −114.5 (m, 2 F, CF_2−CH_2), −81.4 (s, 3 F, CF_3). − $C_{12}H_{11}F_{13}O_4$ (466.2): calcd. C 30.92, H 2.38; found C 30.95, H 2.24.

5,6,7,8,9,10,11,12,13,14-Decadeoxy-7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-heptadecafluoro-D-xylo-tetradecanose (**22**): The isopropylidene furanose **20** (0.07 g, 0.11 mmol) was deacetalated as described in the General Procedure D yielding 0.06 g (79%) of the liquid crystalline product (S_A) **22**, m.p. 136−137°C (heptane/acetone), c.p. 149−150°C, R_f = 0.07 (heptane/AcOEt (1:1)]. − ^{1}H NMR (250 MHz, [D_6]acetone): δ = 1.80−2.08 (m, 4 H, 5-$H_{\alpha,\beta}$, 5′-$H_{\alpha,\beta}$), 2.18−2.49 (m, 4 H, 6-$H_{\alpha,\beta}$, 6′-$H_{\alpha,\beta}$), 3.96 (dd, $J_{1/2} \approx 4.0$ Hz, $J_{2/3} \approx 2.5$ Hz, 1 H, 2-H_α), 3.99 (dd, $J_{2/3} \approx 2.0$ Hz, $J_{3/4} \approx 4.0$ Hz, 1 H, 3-H_β), 4.01 (dd, $J_{1/2} \approx 1.0$ Hz, 1 H, 2-H_β), 4.08 (dd, $J_{3/4} \approx 4.0$ Hz, 1 H, 3-H_α), 4.14 (dd, $J_{4/5} \approx 6.1$ Hz, 1 H, 4-H_α), 4.17 (dd, $J_{4/5} \approx 6.2$ Hz, 1 H, 4-H_β), 5.04 (d, 1 H, 1-H_β), 5.34 (d, 1 H, 1-H_α). − ^{13}C NMR (62 MHz, [D_6]acetone): δ = 21.5 (t, $J_{C\text{-}5/F} \approx 4.1$ Hz, C-5), 22.3 (t, $J_{C\text{-}5/F} \approx 3.9$ Hz, C-5), 28.6 (t, $J_{C\text{-}6/F} \approx 22.2$ Hz, C-6), 28.7 (t, $J_{C\text{-}6/F} \approx 22.1$ Hz, C-6), 77.0 (C_β-3), 77.3 (C_α-3), 78.2 (C_α-2), 78.4 (C_β-4), 81.4 (C_α-4), 82.1 (C_β-2), 97.1 (C_α-1), 103.9 (C_β-1), 105−125 (m, 7 CF_2, CF_3). − ^{19}F NMR (235 MHz, [D_6]acetone/$CFCl_3$): δ = −126.3 (s, 2 F, CF_2−CF_3), −123.6, −122.9 (s, 2 F, CF_2), −122.1 (s, 6 F, CF_2), −114.4 (m, 2 F, CF_2−CH_2), −81.3 (s, 3 F, CF_3). − $C_{14}H_{11}F_{17}O_4$ (566.2): calcd. C 29.70, H 1.96; found C 30.10, H 1.82.

5,6-Dideoxy-5-iodo-1,2-O-isopropylidene-3-O-methyl-6-C-perfluorobutyl-α-"D-gluco"/"L-ido"-furanose (**24**): The unsaturated 3-*O*-methyl-D-furanose **23**[37] (2.0 g, 10 mmol) was perfluoro-alkylated with perfluorobutyl iodide (reaction time: 7 h) as described in the General Procedure A. Yield of **24** (1.86 g, 34%). **24**: Syrup (mixture of the (5*R*) and (5*S*)-isomer), R_f = 0.48 (heptane/AcOEt (3:1)], $[\alpha]_D^{22}$ = −39.11 (*c* = 0.53, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.31, 1.50 (s, 3 H, CH_3), 2.50−2.75 (m, 1 H, 6-H), 3.18−3.44 (m, 1 H, 6′-H), 3.47 (s, 3 H, OCH_3), 3.99 (d, $J_{3/4} \approx 2.9$ Hz, 1 H, 3-H), 4.24−4.43 (m, 2 H, 4,5-H), 4.57 (d, $J_{1/2} \approx 3.9$ Hz, 1 H, 2-H), 5.94 (d, 1 H, 1-H). − ^{13}C NMR (62 MHz, $CDCl_3$): δ = 11.5 (m, C-5), 26.2, 26.9 (CH_3), 37.1 (t, $J_{C\text{-}6/F} \approx 21.0$ Hz, C-6), 58.4 (OCH_3), 80.9 (C-2), 83.7 (C-4), 84.2 (C-3), 105.9 (C-1), 112.2 (*C*$(CH_3)_2$), 105−125 (m, 3 CF_2, CF_3). − ^{19}F NMR (235 MHz, $CDCl_3$/$CFCl_3$): δ = −125.7 (m, 2 F, CF_2−CF_3), −124.5 (s, 2 F, CF_2), −112.1 − 116.9 (m, 2 F, CF_2−CH_2), −80.8 (s, 3 F, CF_3). − $C_{14}H_{16}F_9IO_4$ (546.2): calcd. C 30.79, H 2.95; found C 31.00, H 2.87.

5,6-Dideoxy-5-iodo-1,2-O-isopropylidene-3-O-methyl-6-C-perfluorohexyl-α-"D-gluco"/"L-ido"-furanose (**25**): The unsaturated 3-*O*-methyl-D-furanose **23**[37] (2.0 g, 10 mmol) was perfluoro-alkylated with perfluorohexyl iodide (reaction time: 7 h) as described in the General Procedure A. Yield of **25** (3.36 g, 52%)**. 25**: Syrup, R_f = 0.51 (heptane/AcOEt (3:1)], $[\alpha]_D^{22}$ = −31.23 (*c* = 1.05, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.32, 1.51 (s, 3 H, CH_3), 2.51−2.75 (m, 1 H, 6-H), 3.23−3.44 (m, 1 H, 6′-H), 3.47 (s, 3 H, OCH_3), 3.99 (d, $J_{3/4} \approx 3.0$ Hz, 1 H, 3-H), 4.29 (ddd, $J_{4/5} \approx 10.7$ Hz, $J_{5/6} \approx 9.8$ Hz, $J_{5/6'} \approx 1.8$ Hz, 1 H, 5-H), 4.38 (dd, 1 H, 4-H), 4.57 (d, $J_{1/2} \approx 3.7$ Hz, 1 H, 2-H), 5.94 (d, 1 H, 1-H). − ^{13}C NMR (62 MHz, $CDCl_3$): δ = 11.4 (C-5), 26.2, 26.9 (CH_3), 37.3 (t, $J_{C\text{-}6/F} \approx 20.6$ Hz, C-6), 58.4 (OCH_3), 81.0 (C-2), 83.8 (C-4), 84.2 (C-3), 106.0 (C-1), 112.1 (*C*$(CH_3)_2$), 105−125 (m, 5 CF_2, CF_3). − ^{19}F NMR (235 MHz, $CDCl_3$/$CFCl_3$): δ = −125.8 (s, 2 F, CF_2−CF_3), −123.4, −122.5, −121.4 (s, 2 F, CF_2), −113.7 (m, 2 F, CF_2−CH_2), −80.7 (s, 3 F, CF_3). − MS, *m/z* (CI-isobutane): 647 [M^++H]. − $C_{16}H_{16}F_{13}IO_4$ (646.2): calcd. C 29.74, H 2.50; found C 29.93, H 2.65.

5,6-Dideoxy-5-iodo-1,2-O-isopropylidene-3-O-methyl-6-C-perfluorooctyl-α-"D-gluco"/"L-ido"-furanose (**26**): The unsaturated 3-

O-methyl-D-furanose **23**[37] (2.0 g, 10 mmol) was perfluoro-alkylated with perfluorooctyl iodide as described in the General Procedure A (reaction time: 2.5 h). Yield of **26** (2.39 g, 32%). **26**: Syrup, R_f = 0.47 (heptane/AcOEt (3:1)], $[\alpha]_D^{23}$ = −23.75 (*c* = 1.46, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.32, 1.51 (s, 3 H, CH_3), 2.49−2.77 (m, 1 H, 6-H), 3.20−3.44 (m, 1 H, 6′-H), 3.47 (s, 3 H, OCH_3), 3.99 (d, $J_{3/4} \approx$ 2.6 Hz, 1 H, 3-H), 4.24−4.44 (m, 2 H, 4,5-H), 4.58 (d, $J_{1/2} \approx$ 3.6 Hz, 1 H, 2-H), 5.94 (d, 1 H, 1-H), other diastereomer: δ = 5.98 (d, $J_{1/2} \approx$ 3.9 Hz, 1 H, 1-H). − ^{13}C NMR (62 MHz, $CDCl_3$): δ = 11.4 (m, C-5), 26.2, 26.9 (CH_3), 37.2 (t, $J_{C\text{-}6/F} \approx$ 20.3 Hz, C-6), 58.4 (OCH_3), 80.9 (C-2), 83.7 (C-4), 84.2 (C-3), 106.0 (C-1), 112.2 ($C(CH_3)_2$), 105−125 (m, 7 CF_2, CF_3); other diastereomer: δ = 105.6 (C-1). − ^{19}F NMR (235 MHz, $CDCl_3$/$CFCl_3$): δ = −125.8 (s, 2 F, CF_2−CF_3), −123.4, −122.4 (s, 2 F, CF_2), −121.6 (s, 4 F, CF_2), −121.3 (s, 2 F, CF_2), −116.6 − 111.8 (m, 2 F, CF_2−CH_2), −80.6 (s, 3 F, CF_3) . − $C_{18}H_{16}F_{17}IO_4$ (746.2): calcd. C 28.97, H 2.16; found C 29.11, H 2.09.

5,6,7,8,9,10,11,12-Octadeoxy-7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro-1,2-O-isopropylidene-3-O-methyl-α-D-xylo-dodecanofuranose (**27**): The iodofuranose **25** (1.29 g, 2.0 mmol) was dehalogenated as described in the General Procedure B to yield the syrupy product **27** (1.04 g, 63%), R_f = 0.45 (heptane/AcOEt (3:1)], $[\alpha]_D^{22}$ = −20.76 (*c* = 1.05, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.31, 1.48 (s, 3 H, CH_3), 1.81−2.45 (m, 4 H, 5,5′,6,6′-H), 3.41 (s, 3 H, OCH_3), 3.59 (d, $J_{3/4} \approx$ 3.2 Hz, 1 H, 3-H), 4.16 (ddd, $J_{4/5} \approx$ 4.8 Hz, $J_{4/5'} \approx$ 8.1 Hz, 1 H, 4-H), 4.58 (d, $J_{1/2} \approx$ 3.7 Hz, 1 H, 2-H), 5.86 (d, 1 H, 1-H). − ^{13}C NMR (62 MHz, $CDCl_3$): δ = 19.4 (t, $J_{C\text{-}5/F} \approx$ 4.1 Hz, C-5), 26.1, 26.7 (CH_3), 28.1 (t, $J_{C\text{-}6/F} \approx$ 22.1 Hz, C-6), 57.8 (OCH_3), 78.9 (C-4), 81.6 (C-2), 84.7 (C-3), 104.7 (C-1), 111.4 ($C(CH_3)_2$), 105−125 (m, 5 CF_2, CF_3). − ^{19}F NMR (235 MHz, $CDCl_3$/$CFCl_3$): δ = −125.9 (s, 2 F, CF_2−CF_3), −123.2, −122.6, −121.6 (s, 2 F, CF_2), −114.2 (m, 2 F, CF_2−CH_2), −80.6 (s, 3 F, CF_3). − MS, *m/z* (CI-isobutane): 521 [M^++H]. − $C_{16}H_{17}F_{13}O_4$ (520.3): calcd. C 36.94, H 3.29; found C 36.99, H 3.23.

1,2′:1′,2-Di-anhydro-bis[5,6,7,8,9,10,11,12-octadeoxy-7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro-3-O-methyl-D-xylo-dodecano-furanose] **(28)**: Tetrabutylammonium iodide (0.32 g, 1.0 mmol) and BF_3−diethyl ether (0.12 ml) were added to a solution of compound **27** (0.42 g, 0.8 mmol) in dichloromethane (5 ml). The mixture was stirred under argon for 4.5 h at room temp. and then neutralised with solid $NaHCO_3$, filtered, diluted with chloroform (5 ml), and successively washed with aq. $Na_2S_2O_3$ solution (5 ml) and water (5 ml). The organic layer was separated, dried with Na_2SO_4, filtered and the solvents were evaporated under reduced pressure. The residue was purified by column chromatography (eluent: heptane/AcOEt (5:1)] and recrystallized to give 0.10 g (28%) of **28**; R_f = 0.28 (heptane/AcOEt 3:1), m.p. 42−44°C (heptane/acetone). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.81−2.48 (m, 4 H, 5,5′,6,6′-H), 3.40 (s, 3 H, OCH_3), 3.73 (d, $J_{3/4} \approx$ 3.7 Hz, 1 H, 3-H), 3.95 (d, $J_{1/2} \approx$ 3.9 Hz, 1 H, 2-H), 4.27 (ddd, $J_{4/5} \approx$ 5.0 Hz, $J_{4/5'} \approx$ 8.5 Hz, 1 H, 4-H), 5.13 (d, 1 H, 1-H). − ^{13}C NMR (62 MHz, $CDCl_3$): δ = 19.4 (t, $J_{C\text{-}5/F} \approx$ 4.0 Hz, C-5), 28.0 (t, $J_{C\text{-}6/F} \approx$ 22.1 Hz, C-6), 57.5 (OCH_3), 75.8 (C-2), 79.8 (C-4), 85.5 (C-3), 97.2 (C-1), 105−125 (m, 5 CF_2, CF_3). − ^{19}F NMR (235 MHz, $CDCl_3$/$CFCl_3$): δ = −125.9 (s, 2 F, CF_2−CF_3), −123.2, −122.7, −121.7 (s, 2 F, CF_2), −114.4 − 114.2 (m, 2 F, CF_2−CH_2), −80.6 (s, 3 F, CF_3). − MS (CI-isobutane): *m/z* = 925 (M^++H). − $C_{26}H_{22}F_{26}O_6$ (924.4): calcd. C 33.78, H 2.40, found C 33.84, H 2.25.

6-Deoxy-6-C-perfluorohexyl-L-altrose (**29/30**): The pyranose derivative **3** (0.22 g, 0.4 mmol) was deacetalated as described in the General Procedure D (20 h, room temp.). The residue was purified by column chromatography (eluent: AcOEt; R_f = 0.43). The product is an equilibrium mixture of the pyranoses **29**α,β and the furanoses **30**α,β (yield: 0.04 g, 21%) showing thermotropic liquid crystalline properties (S_A): m.p. 136−139°C; c.p. 171−172°C. The ratio of the anomeric pyranoses and furanoses dissolved in [D_6]acetone was determined by ^{1}H-NMR measurements (see Table 2). − ^{19}F NMR (235 MHz, $CDCl_3$): δ = −126.4 (s, 2 F, CF_2−CF_3), −123.7, −123.1, −121.0 (s, 2 F, CF_2), −114.5−110.7 (m, 2 F, CF_2−CH_2), −81.3 (s, 3 F, CF_3). − $C_{12}H_{11}F_{13}O_5$ (482.2): C 29.89, H 2.30; found C 29.90, H 2.30.

Table 2. The ratio of the anomeric pyranoses and furanoses dissolved in [D_6]acetone as determined by ^{1}H-NMR measurements

Components	Percentage	δ (1-H)[a]	$J_{1/2}$ (Hz)	δ (C-1)[a]
α-pyranose (29α)	33.2%	4.84	≈ 1.7	95.1
β-pyranose (29β)	30.3%	4.98	≈ 1.5	92.5
α-furanose (30α)	23.5%	5.14	≈ 1.8	103.0
β-furanose (30β)	13.0%	5.19	≈ 4.5	96.6

[a] ^{1}H NMR (250 MHz, [D_6]acetone); ^{13}C NMR (62 MHz, [D_6]acetone).

[1] Part 18: R. Miethchen, Chr. Hager, M. Hein, *Synthesis* **1997**, 159−161.
[2] J. G. Riess, *New J. Chem.*, **1995**, *19*, 891−909.
[3] J. G. Riess, *Colloids Surfaces A, Physicochemical and Engineering Aspects,* **1994**, *84*, 33−48.
[4] J. G. Riess, J. Greiner, in *Carbohydrates as Organic Raw Materials II* (Descotes, Ed.), VCH, Weinheim, **1993**, p.209−259.
[5] *Organofluorine compounds in medical chemistry and biomedical applications* (Eds.: R. Filler, Y. Kobayashi, L.M. Yagupolski), Elsevier, Amsterdam, **1993**.
[6] R. N. Haszeldine, *J. Fluorine Chem.*, **1986**, *33*, 307−313.
[7] D. J. Burton, Z.-Y. Yang, *Tetrahedron*, **1992**, *48*, 189−275.
[8] Q. Y. Chen, Z. Y. Yang, *J. Chem. Soc., Chem. Commun.*, **1986**, 498−499.
[9] Q. S. Hu, C. M. Hu, *J. Fluorine Chem.*, **1996**, *76*, 117−119.
[10] Q. Y. Chen, Z. Y. Yang, *J. Fluorine Chem.*, **1985**, *28*, 399−411.
[11] Q. Y. Chen, Z. M. Qiu, Z. Y. Yang, *J. Fluorine Chem.*, **1987**, *36*, 149−161.
[12] N. Requirand, H. Blancou, A. Commeyras, *Bull. Soc. Chim. Fr.*, **1993**, *130*, 798−806.
[13] C. R. Davis, D. J. Burton, Z.-Y. Yang, *J. Fluorine Chem.*, **1995**, *70*, 135−140.
[14] K. von Werner, DE 4 234 458 (1992); C.A. **1994**, *121*, 25626
[15] C. Dapremont, P. Calas, A. Commeyras, *J. Fluorine Chem.*, **1992**, *56*, 249−258.
[16] Y. Takeyama, Y. Ichinose, K. Oshima, K. Utimoto, *Tetrahedron Lett.*, **1989**, *30*, 3159−3162.
[17] G. Foulard, T. Brigaud, C. Portella, *Tetrahedron*, **1996**, *52*, 6187−6200.
[18] W.-Y. Huang, *J. Fluorine Chem.*, **1992**, *58*, 1−8.
[19] G. Rong, R. Keese, *Tetrahedron Lett.*, **1990**, *31*, 5615−5616.
[20] C. Zur, Dissertation, Univ. Rostock, 1997.
[21] S. Bergeron, T. Brigaud, G. Foulard, R. Plantier-Royon, C. Portella, *Tetrahedron Lett*. **1994**, *35*, 1985−1988.
[22] W.-Y. Huang, Y. Xie, *Chinese J. Chem.*, **1991**, *9*, 351−359.
[23] J.-R. Neeser, L. D. Hall, J. A. Balatoni, *Helv. Chim. Acta* **1983**, *66*, 1018−1027.
[24] B. E. Stacey, B. Tierney, *Carbohydr. Res.* **1976**, *49*, 129−140.
[25] P. Koell, W. Saak, S. Pohl, B. Steiner, M. Koos, *Carbohydr. Res.* **1994**, *265*, 237−248.
[26] M. Van Der Puy, R. K. Belter, R. J. Borowski, L. A. S. Ellis, P. J. Persichini, A. J. Poss, T. P. Rygas, H. S. Tung, *J. Fluorine Chem.*, **1995**, *71*, 59−63.
[27] J. Auge, S. David, *Carbohydr. Res.*, **1977**, *59*, 255−257.
[28] P. Kocienski, C. Pant, *Carbohydr. Res.*, **1982**, *110*, 330−332.
[29] C. H. Heathcock, R. Ratcliffe, *J. Am. Chem. Soc.*, **1971**, *93*, 1746−1757.
[30] D. Cabaret, R. Kazandjan, M. Wakselman, *Carbohydr. Res.*, **1986**, *149*, 464−470.

[31] C. Zur, A. O. Miller, R. Miethchen, *Liquid Cryst.* **1997**, in press.
[32] A. K. Mandal, N. R. Soni, K. R. Ratnam, *Synthesis*, **1985**, 274−275.
[33] Y. V. Voznyi, I. S. Kalicheva, A. A. Galoyan, *Bioorg. Khim* **1985**, *11*, 970.
[34] R. Miethchen, T. Gabriel, *J. Fluorine Chem.* **1994**, *67*, 11−15.
[35] K. Bock, C. Pedersen, *Adv. Carbohydr. Chem. Biochem.* **1983**, *41*, 27−66.
[36] H. B. Mereyala, B. R. Gaddam, *J. Chem. Soc., Perkin Trans 1*, **1994**, 2187−2190.
[37] J. S. Josan, F. W. Eastwood, *Carbohydr. Res.* **1968**, *7*, 161−166.
[97278]