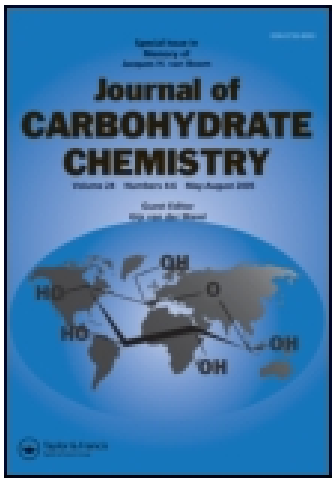

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SYNTHESIS OF (6-^{2}H)- AND 6-DEOXY-6-FLUORO-L-GALACTOSE DERIVATIVES[1]

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SYNTHESIS OF (6-^{2}H)- AND 6-DEOXY-6-FLUORO-L-GALACTOSE DERIVATIVES[1]

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ABSTRACT

The selective oxidation of trimethylsilylated D-galactose diethyl dithioacetal using Collins reagent provided the corresponding D-*galacto*-hexodialdo dithioacetal. Successive acid hydrolysis, isopropylidenation, and cleavage of the dithioacetal group gave the 1,2;3,4-di-*O*-isopropylidene-L-*galacto*-hexodialdo-1,5-pyranose as a key intermediate for the synthesis of 6-fluoro- and 6-deutero-substituted L-fucose derivatives.

INTRODUCTION

Our laboratory studies the synthesis of oligosaccharides, present in human milk, containing fucose residues with various markers. These labeled oligosaccharides may then be used as potential tools to clarify the role that high concentrations of complex carbohydrates in human milk play in infant nutrition.[2] As part of our ongoing interest in the preparation of L-fucose starting from D-galactose precursors, we previously developed a synthetic approach for L-fucose. This included the following synthetic steps: D-Galactose was converted into the D-galactose diethyl dithioacetal, which was then reduced with high active Raney nickel to give L-fucitol which was subsequently transformed into its 1,2,3,4,5-penta-*O*-trimethylsilyl derivative. The trimethylsilyl ether of the primary alcohol could be selectively oxidized in the presence of secondary alcohols by Collins reagent providing, after

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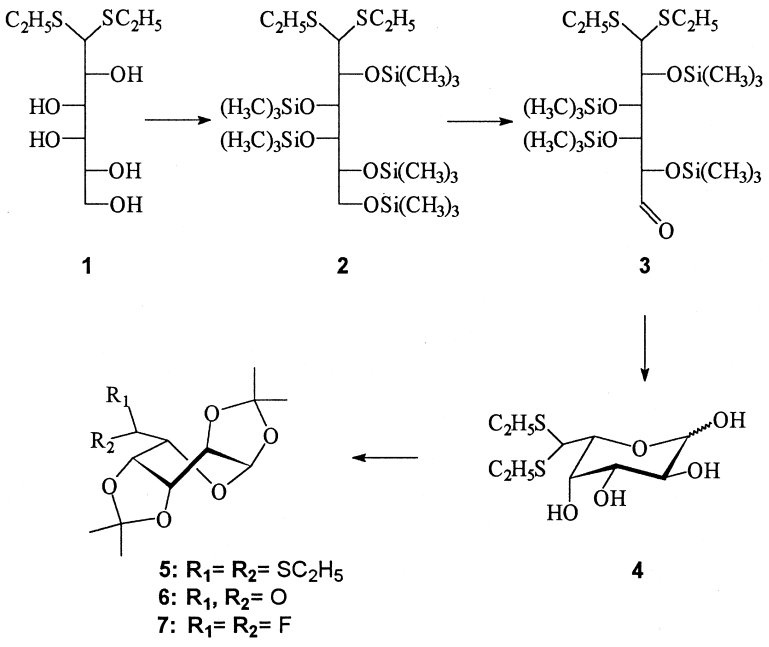
[1]Dedicated to Professor Peter Köll on the Occasion of His 60th Birthday.

acid hydrolysis, L-fucose in an overall yield of 87%.[3] Based on this strategy, we now report a route for the synthesis of L-galactose and L-fucose derivatives, respectively, substituted at the C-6 position by a fluorine or deuterium atom.

RESULTS AND DISCUSSION

For the preparation of the dialdo sugar **6**, suitable as a universal intermediate for further modification at C-6 position, it is possible to proceed from D-galactose diethyl dithioacetal **1** again (Scheme 1). In contrast to our previously reported approach to L-fucose,[3] the dithioacetal **1** was quantitatively converted into the 2,3,4,5,6-penta-*O*-trimethylsilyl derivative **2** which was then immediately oxidized by Collins reagent. Successive acid hydrolysis and isopropylidenation of the crude dialdo sugar **3**, which was formed as a result of the selective oxidation of a trimethylsilyl ether of a primary alcohol in the presence of secondary alcohols, provided the fully protected derivative **5** in an overall yield of 40%. Cleavage of the dithioacetal function was achieved by mercury salts in 86% yield. The analytical data for **5** and **6** fully agree with the proposed structures. In the ^{1}H NMR spectra the three-bond coupling constants within the pyranose ring amount to 5.0 ± 0.2 ($J_{1,2}$), 2.2 ± 0.1 ($J_{2,3}$), 7.9 ($J_{3,4}$), 1.8 ± 0.2 ($J_{4,5}$) and indicated the anticipated twist conformation (^2S_O) of the six-membered ring.[4]

According to a procedure reported by M. Sharma and coworkers[5] for 6-deoxy-6,6-difluoro-D-galactose, the key intermediate **6** was transformed into the 6,6-*gem*-difluoro derivative **7** by treatment with diethylaminosulfur trifluoride (DAST) in 63% yield (Scheme 1). The optical rotation of L-sugar **7**, $[\alpha]_D^{24}$ +41.5 (*c* 1.0,



Scheme 1.

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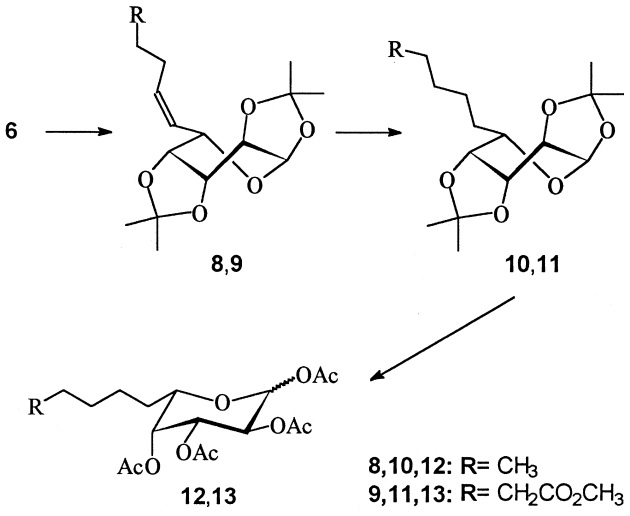
chloroform), and the corresponding D-sugar, $[\alpha]_D^{22}$ -42.3 (*c* 1.0, chloroform), prepared by Sharma et al.[5] confirm the enantiomeric relation between both sugars, whereas the minus sign of $[\alpha]_D^{25}$ -40.1 (*c* 1.02, chloroform) for the L-sugar in a paper of Sartorelli and co-workers[6] must be a printer's error.

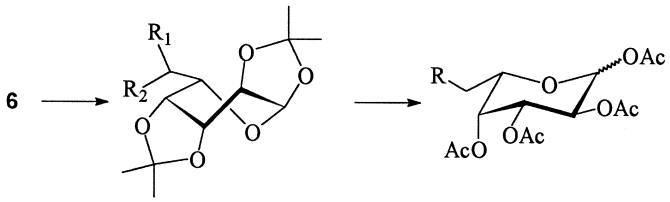
Next, an alternative route for the synthesis of carbon backbone elongated L-fucose derivatives[2] was investigated, starting from **6** (Scheme 2). The Wittig reaction with the alkylidene triphenylphosphorane of chain length C_4 gave the alkene **8** in 68% yield. Successive hydrogenation (**10**, 94%), deisopropylidenation and acetylation resulted in the target compound **12** in an overall yield of 19%, over eight synthetic steps from **1**.

The previously reported route involved the same number of synthetic steps and furnished **12** in overall yield of 31%. Thus, the former procedure seems to be superior compared with the latter one for the preparation of carbon backbone elongated L-fucose derivatives. In our new synthesis the crucial oxidation of **2** limited the overall yield. Nevertheless, the spacermodified L-fucose analogue **13** was prepared proceeding from **6** by introduction of an additional functional group at the end of the alkyl chain. Therefore, 4-carboxybutyl triphenylphosphonium bromide was used in the Wittig reaction and gave compound **13** in 20% yield related to **1**, after the same sequence of synthetic steps as for the preparation of **12**. The next publication in this series will describe the synthesis of **13** by the former procedure and its conversion into a GDP-L-fucose analogue.

Much more attractive is the introduction of fluorine or deuterium at the C-6 position of L-galactose and L-fucose, respectively, starting from key intermediate **6**. The reduction of the dialdo sugar **6** with lithium aluminium hydride or lithium aluminium deuteride gave the L-galactose derivatives **14** and **15** in 84% and 85%, respectively (Scheme 3). The introduction of a trifluoromethanesulfonyl group in **14** and **15** provided the C-6 activated derivatives **16** and **17** in



Scheme 2.



14: R_1= H R_2= OH
15: R_1= D R_2= OH
16: R_1= H R_2= OSO_2CF_3
17: R_1= D R_2= OSO_2CF_3
18: R_1= D R_2= H
19: R_1= H R_2= F

20: R= D
21: R= F

Scheme 3.

nearly quantitative yields. The reduction of **17** with sodium borohydride[7] gave the (6-H^2)-L-fucose derivative **18** in 85% yield, whereas the substitution of the triflyl group with fluorine resulted in the 6-deoxy-6-fluoro-L-galactose derivative **19** in an excellent 87% yield. By contrast, employing the *p*-toluenesulfonyl function as a leaving group furnished **19** in only 35% yield.[6] Both compounds **18** and **19** were deisopropylidenated and acetylated to provide the corresponding deuterium and fluorine substituted L-fucose derivatives **20** and **21**, respectively. The structures of the compounds **14** - **21** are in accordance with all analytical data and, as expected, the NMR data of these L-sugars are comparable with those of the D-sugars described in the literature.[8] In one of our next papers, we will describe the conversion of **20** and **21** into glycosyl donors and their coupling with D-lactose acceptors to provide both deuterium and fluorine substituted oligosaccharides of human milk.

EXPERIMENTAL

General Methods. Melting points were determined with a Boetius micro apparatus BHMK 05 (Rapido, Dresden) and are uncorrected. Optical rotations were measured for solutions in a 2-cm cell with an automatic polarimeter "GYROMAT" (Dr. Kernchen Co.). NMR spectra were recorded with Bruker AC-250 or ARX-300 spectrometers, at 250 MHz or 300 MHz for ^1H, and 62.9 MHz or 75.5 MHz for ^{13}C, respectively. Chemical shifts are given relative to the signal of internal tetramethylsilane ($\delta = 0$). First order chemical shifts and coupling constants were obtained from one-dimensional spectra, and assignment of proton resonances was based on COSY experiments. Thin-layer chromatography (TLC) on precoated plates of silica gel (Merck, Silica Gel 60, F_{254}, 0.25 mm) was performed with the following solvent systems (v/v): (A) heptane, (B) 10:1, (C) 9:1, (D) 8:1, (E) 5:1, (F) 4:1, (G) 3:1, (H) 2:1, (I) 4:3 heptane-ethyl acetate, and (J) 4:1 ethyl acetate-

methanol. The spots were made visible by spraying with methanolic 10% H_2SO_4 solution and charring them for 3-5 min with a heat gun. Detection of benzyl derivatives was effected by UV fluorescence. Preparative flash chromatography and HPLC was performed by elution from columns of slurry-packed Silica Gel 60 (Merck, 40-63 μm) and Nucleosil 100-7 (Knauer, 7.0 μm), respectively, with the above solvent systems. All solvents and reagents were purified and dried according to standard procedures.[9] After classical work up of the reaction mixtures, the organic layers as a rule, were dried over $MgSO_4$, and then concentrated under reduced pressure (rotary evaporator).

2,3,4,5,6-Penta-*O*-trimethylsilyl-D-galactose Diethyl Dithioacetal (**2**). To a solution of D-galactose diethyl dithioacetal (**1**, 2.86 g, 10 mmol) and hexamethyldisilazane (20.7 mL, 100 mmol) in dry pyridine (10 mL) was added chlorotrimethylsilane (6.3 mL, 50 mmol) under argon at room temperature. After stirring for 12 h (TLC solvent A R_f 0.21), the reaction mixture was diluted with diethyl ether (50 mL) and filtered. The filtrate was concentrated, the residue was dissolved in diethyl ether (50 mL) and the solution again filtered. After removing the solvent, the residue was codistilled with toluene (3 x 50 mL), and dried in high vacuum to yield **2** (6.1 g, 94%) as a colorless syrup: $[\alpha]_D^{23}$ +5.4° (*c* 1.0, chloroform); ^{1}H NMR ($CDCl_3$) δ 0.10 [s, 9H, $Si(CH_3)_3$], 0.14, [s, 18H, 2 x $Si(CH_3)_3$] , 0.15, 0.18 [2s, 18H, 2 x $Si(CH_3)_3$], 1.23, 1.24 (2t, 6H, J = 7.4 Hz, 2 x SCH_2CH_3), 2.64 (qd, 2H, J = 7.4 Hz, J =1.4 Hz, SCH_2CH_3), 2.74 (q, 2H, J = 7.4 Hz, SCH_2CH_3), 3.62 (dd, 1H, $J_{5,6}$ = 6.2 Hz, $J_{6,6'}$ = 10.3 Hz, H-6), 3.71 (d, 1H, $J_{1,2}$ = 4.2 Hz, H-1), 3.76-3.81 (m, 2H, H-5, H-6'), 3.98 (dd, 1H, $J_{2,3}$ = 2.5 Hz, H-2), 4.13-4.19 (m, 2H, H-3, H-4); ^{13}C NMR ($CDCl_3$) δ -0.49, 0.75, 1.27, 1.30, 1.61 (5 x $SiCH_3$), 14.41, 14.47 (2 x SCH_2CH_3), 24.37, 25.57 (2 x SCH_2CH_3), 55.30 (C-1), 64.05 (C-6), 74.04, 75.63, 76.05, 76.45 (C-2, C-3, C-4, C-5).

Anal. Calcd for $C_{25}H_{62}O_5S_2Si_5$ (647.30): C, 46.39; H, 9.65; S, 9.91. Found: C, 46.27, H, 9.48, S, 10.03.

2,3,4,5-Tetra-*O*-trimethylsilyl-D-*galacto*-hexodialdose-1 Diethyl Dithioacetal (**3**). To dry pyridine (150 mL) was added chromium(VI)oxide (17.0 g, 170 mmol) in portions under argon with cooling (ice bath). After stirring for one hour at room temperature, a solution of compound **2** (22.0 g, 34.0 mmol) in dry pyridine (50 mL) was added dropwise to the Collins reagent. When the reaction was complete (2.5 h; TLC solvent B R_f 0.47), toluene (250 mL) was added, and the resulting solids were removed by filtration through silica gel. The filtrate was concentrated, the residue codistilled with toluene (150 mL), and dried *in vacuo*. The crude product **3** (13 g, brown syrup) was used in the next step without further purification. ^{1}H NMR ($CDCl_3$) δ 0.12 [s, 9H, Si $(CH_3)_3$], 0.14 [s, 18H, 2 x $Si(CH_3)_3$], 0.17 [s, 9H, $Si(CH_3)_3$], 1.20-1.28 (m, 6H, 2 x SCH_2CH_3), 2.65 (q, 2H, J = 7.2 Hz, SCH_2CH_3), 2.76 (q, 2H, J = 7.5 Hz, SCH_2CH_3), 3.88 (d, 1H, H-5), 3.94 (d, 1H, $J_{1,2}$ = 4.6 Hz, H-1), 4.05 (dd, 1H, $J_{2,3}$ = 2.2 Hz, H-2), 4.17 (dd, 1H, $J_{4,5}$ = 2.9 Hz, H-4), 4.32 (dd, 1H, $J_{3,4}$ = 8.0 Hz, H-3), 9.71 (s, 1H, H-6); ^{13}C NMR ($CDCl_3$) δ 0.25, 0.62, 0.94, 1.00 (4 x $SiCH_3$), 14.34, 14.41 (2 x SCH_2CH_3), 24.35, 25.95 (2 x SCH_2CH_3), 55.23 (C-1), 74.96, 75.47, 77.68, 79.39 (C-2, C-3, C-4, C-5), 199.44 (C-6).

1,2;3,4-Di-*O*-isopropylidene-L-*galacto*-hexodialdo-1,5-pyranose-6 Diethyl Dithioacetal (**5**). A solution of crude **3** (26 g) in tetrahydrofuran (330 mL), acetic acid (150 mL) and water (90 mL) was stirred for 24 h at room temperature (TLC solvent J R_f 0.59). The solution was then concentrated, the residue codistilled with toluene (3 x 300 mL), and dried in high vacuum. The crude D-*galacto*-hexodialdose-1-diethyl dithioacetal (**4**, 15 g, light brown syrup) was isopropylidenated without further characterization. Thus, to a solution of crude **4** (15 g) in dry acetone (200 mL) were added 2,2-dimethoxypropane (50 mL) and concd sulfuric acid (0.5 mL). The reaction mixture was stirred for two hours at room temperature under argon. When the reaction was complete (TLC solvent F R_f 0.42), sodium carbonate (3.0 g) was added, and the suspension was stirred for additional 15 min. The solids were then filtered off, and the filtrate was concentrated. The residue was purified by MPLC (eluent solvent B) to provide **5** (9.9 g, 40% related to **2**) as a colorless syrup: $[\alpha]_D^{23}$ +36.4° (*c* 1, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.25, 1.26 (2t, 6H, J = 7.5 Hz, 2 x SCH_2CH_3), 1.31, 1.34, 1.43, 1.51 [4s, 12H, 2 x $C(CH_3)_2$], 2.61-2.79 (m, 4H, 2 x SCH_2CH_3), 3.72 (dd, 1H, $J_{5,6}$ = 10.6 Hz, H-5), 4.11 (d, 1H, H-6), 4.30 (dd, 1H, $J_{2,3}$ = 2.2 Hz, H-2), 4.61 (dd, 1H, $J_{3,4}$ = 7.9 Hz, H-3), 4.66 (dd, 1H, $J_{4,5}$ = 1.6 Hz, H-4), 5.59 (d, 1H, $J_{1,2}$ = 5.2 Hz, H-1); ^{13}C NMR ($CDCl_3$) δ 13.94, 14.50 (2 x SCH_2CH_3), 24.26 (2 x SCH_2CH_3, two signals are isochronic), 24.51, 24.83 [$C(CH_3)_2$], 25.91 [$C(CH_3)_2$, two signals are isochronic], 69.73 (C-5), 70.57, 71.21, 71.33 (C-2, C-3, C-4), 97.03 (C-1), 108.70, 109.30 [2 x $C(CH_3)_2$].

Anal. Calcd for $C_{16}H_{28}O_5S_2$ (364.52): C, 52.72; H, 7.74; S, 17.59. Found: C, 52.58, H, 7.61; S, 17.68.

1,2;3,4-Di-*O*-isopropylidene-α-L-*galacto*-hexodialdo-1,5-pyranose (**6**). To a stirred solution of **5** (6.1 g, 16.7 mmol) in acetone (250 mL) were successively added yellow mercury(II)oxide (8.7 g, 40.2 mmol), mercury(II)chloride (8.7 g, 32.0 mmol), and water (25 mL). The resulting suspension was stirred for two hours at room temperature (TLC solvent F R_f 0.36). The suspension was then filtered through a layer of Celite, and the filtrate was concentrated. The residue was dissolved in chloroform (200 mL), successively washed with aq 1 N KI (2 x 70 mL), brine (2 x 70 mL), dried, and concentrated. The residue was codistilled with toluene (3 x 100 mL) to give **6** (3.7 g, 86%) as a colorless syrup, which was used immediately for the next reaction step without further purification. An analytically pure sample was obtained by HPLC (eluent solvent E): $[\alpha]_D^{25}$ +116.8 (*c* 1.0, chloroform); IR (KBr) 1741 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 1.30, 1.33, 1.42, 1.49 [4s, 12H, 2 x $C(CH_3)_2$], 4.17 (d, 1H, H-5), 4.36 (dd, 1H, $J_{2,3}$ = 2.3 Hz, H-2), 4.57 (dd, 1H, $J_{4,5}$ = 2.0 Hz, H-4), 4.64 (dd, 1H, $J_{3,4}$ = 7.9 Hz, H-3), 5.65 (d, 1H, $J_{1,2}$ = 4.8 Hz, H-1), 9.59 (s, 1H, H-6); ^{13}C NMR ($CDCl_3$) δ 24.21, 24.76, 25.76, 25.96 [2 x $C(CH_3)_2$], 70.39, 70.50, 71.71 (C-2, C-3, C-4), 73.18 (C-5), 96.22 (C-1), 108.98, 110.00 [2 x $C(CH_3)_2$], 200.13 (C-6).

Anal. Calcd for $C_{12}H_{18}O_6$ (258.27): C, 55.80; H, 7.02. Found: C, 55.63, H, 7.18.

6-Deoxy-6,6-difluoro-1,2;3,4-di-*O*-isopropylidene-α-L-galactopyranose (**7**). To a solution of **6** (439 mg, 1.7 mmol) in dry dichloromethane (10 mL) was added

dropwise diethylaminosulfur trifluoride (DAST, 0.6 mL, 4.54 mmol) under argon at 5 °C. After stirring for 24 h at ambient temperature (TLC solvent G R_f 0.44), water (2 mL) was added and, after a few minutes, the mixture was diluted with chloroform (50 mL). The organic layer was washed with cold sat aq $NaHCO_3$ (2 x 25 mL), water (2 x 25 mL), dried, and concentrated. The purification by HPLC (eluent solvent F) provided **7** (300 mg, 63%) as a light brown syrup, which crystallized after a few days in the refrigerator: mp 43-45 °C; $[\alpha]_D^{24}$ +41.5° (*c* 1.0, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.33, 1.34, 1.44, 1.53 [4 s, 12 H, 2 x $C(CH_3)_2$], 3.87 (m, 1H, H-5), 4.34 (dd, 1H, $J_{2,3}$ = 2.5 Hz, H-2), 4.36 (m, 1H, H-4), 4.64 (ddd, 1H, $J_{3,4}$ = 7.9 Hz, $^5J_{3,F}$ = 1.5 Hz, H-3), 5.54 (dd, 1H, $J_{1,2}$ = 4.9 Hz, $^5J_{1,F}$ = 1.9 Hz, H-1), 5.83 (ddd, 1H, $J_{5,6}$ = 6.7 Hz, $J_{6,F}$ = 54.0 Hz, $J_{6,F'}$ = 59.8 Hz, H-6); ^{13}C NMR ($CDCl_3$) δ 24.23, 24.83, 25.78, 25.97 [2 x $C(CH_3)_2$], 67.98 (dd, $J_{C,F}$ = 32.3 Hz, $J_{C,F'}$ = 24.0 Hz, C-5), 69.71 (d, $J_{C,F}$ = 7.4 Hz, C-4), 70.26 (C-2), 70.33 (C-3), 95.94 (C-1), 109.14, 109.95 [2 x $C(CH_3)_2$], 114.45 (dd, $J_{C,F}$ = 237.8 Hz, $J_{C,F'}$ = 245.1 Hz, C-6); ^{19}F NMR ($CDCl_3$) δ -55.8 (d, J= 279.4 Hz, F), -58.0 (d, J= 279.4, F').

Anal. Calcd for $C_{12}H_{18}O_5F_2$ (280.27): C, 51.42; H, 6.47. Found: C, 51.56, H, 6.42.

1,2;3,4-Di-*O*-isopropylidene-6,7,8,9,10-pentadeoxy-α-L-*galacto*-dec-6-enopyranose (**8**). To a suspension of butyl triphenylphosphonium bromide (2.4 g, 6.0 mmol) in dry tetrahydrofuran (15 mL) was added lithium hexamethyldisilazanate (6.0 mL of a 1N soln in tetrahydrofuran). After stirring for one hour under argon, a solution of **6** (1.0 g, 3.9 mmol) in dry tetrahydrofuran (6 mL) was dropwise added, and stirring was continued for 3 h (TLC solvent H R_f 0.63). Heptane (50 mL) was then added, and the mixture was concentrated. The residue was dissolved in heptane (100 mL) and the precipitating salts were filtered off. The filtrate was washed with water (2 x 50 mL), dried and concentrated. The residue was purified by MPLC (eluent ethyl acetate gradient 0%→11% in heptane) to yield **8** (780 mg, 68 %) as a colorless syrup: $[\alpha]_D^{23}$ +107.8° (*c* 1.0, chloroform); ^{1}H NMR ($CDCl_3$) δ 0.89 (t, 3H, J = 7.3 Hz, H-10, H-10′, H-10″), 1.32 [s, 6H, $C(CH_3)_2$], 1.39 (m, 2H, H-9, H-9'), 1.49, 1.55 [2 s, 6H, $C(CH_3)_2$], 2.06 (m, 2H, H-8, H-8'), 4.12 (dd, 1H, $J_{4,5}$ = 1.7 Hz, H-4), 4.29 (dd, 1H, $J_{2,3}$ = 2.2 Hz, H-2), 4.57 (dd, 1H, $J_{5,6}$ = 7.1, H-5), 4.59 (dd, 1H, $J_{3,4}$ = 7.8 Hz, H-3), 5.53 (d, 1H, $J_{1,2}$ = 5.2 Hz, H-1), 5.60 (m, 1H, H-7), 5.66 (m, 1H, H-6); ^{13}C NMR ($CDCl_3$) δ 13.71 (C-10), 22.55 (C-9), 24.24, 24.85, 25.89, 26.02 [2 x $C(CH_3)_2$], 30.11 (C-8), 63.66 (C-5), 70.17 (C-2), 70.80 (C-3), 73.46 (C-4), 96.50 (C-1), 108.24, 109. 6 [2 x $C(CH_3)_2$], 125.15 (C-7), 134.23 (C-6).

Anal. Calcd for $C_{16}H_{26}O_5$ (298.38): C, 46.40; H, 8.78. Found: C, 46.42; H, 8.69.

1,2;3,4-Di-*O*-isopropylidene-10-methoxycarbonyl-6,7,8,9,10-pentadeoxy-α-L-*galacto*-dec-6-enopyranose (**9**). To a suspension of 4-carboxybutyl triphenylphosphonium bromide (2.65 g, 6.0 mmol) in dry tetrahydrofuran (15 mL) was added lithium hexamethyldisilazanate (12.0 mL of a 1 N soln in tetrahydrofuran). After stirring for one hour under argon, a solution of **6** (1.0 g, 3.9 mmol) in dry tetrahydrofuran (6 mL) was dropwise added and stirring was continued for 3 h. As

soon as aldehyde **6** was consumed (TLC solvent H), water (100 mL) and heptane (30 mL) were added, and the solution were filtered. The aqueous layer was washed with heptane (2 x 25 mL) and concentrated to a volume of 20 mL. For esterification of the free carboxy function, dichloromethane (30 mL), iodomethane (2.6 mL, 40 mmol) and tertrabutylammonium bromide (1.6 g, 5.0 mmol) were added, and the mixture was stirred vigorously for 20 h (TLC solvent G R_f 0.28). The layers were separated, and the aqueous layer was extracted with dichloromethane (2 x 15 ml). Finally, the combined organic layers were dried, and concentrated. The residue was purified by MPLC (eluent ethyl acetate gradient 0%→20% in heptane) to provide **9** (965 mg, 70%) as a colorless syrup: $[\alpha]_D^{23}$ +89.1° (*c* 1.0, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.31, 1.44, 1.53 [3s, 12H, 2 x C(CH_3)$_2$], 1.71, 2.13 (2m, 4H, H-8, H-8′,H-9, H-9′), 2.29 (t, 2H, J = 7.3 Hz, H-10, H-10′), 3.63 (s, 3H, CO_2CH_3), 4.11 (dd, 1H, $J_{4,5}$ = 2.0 Hz, H-4), 4.28 (dd, 1H, $J_{2,3}$ = 2.3 Hz, H-2), 4.52 (dd, 1H, $J_{5,6}$ = 7.3, H-5), 4.58 (dd, 1H, $J_{3,4}$ = 7.9 Hz, H-3), 5.52 (d, 1H, $J_{1,2}$ = 5.0 Hz, H-1), 5.58 (m, 1H, H-7), 5.62 (m, 1H, H-6); ^{13}C NMR ($CDCl_3$) δ 24.59 (C-9), 24.31, 24.90, 25.96, 26.15 [2 x C(*C*H_3)$_2$], 27.44 (C-8), 33.40 (C-10), 51.53 (CO_2*C*H_3), 63.66 (C-5), 70.20 (C-2), 70.84 (C-3), 73.39 (C-4), 96.53 (C-1), 108.36, 109.18 [2 x *C*(CH_3)$_2$], 126.16 (C-7), 133.21 (C-6), 173.82 (*C*O_2CH_3).

Anal. Calcd for $C_{18}H_{28}O_7$ (356.41): C, 61.35; H, 6.86. Found: C, 61.21; H, 6.70.

Hydrogenation of the Alkenes **8** and **9**. To a solution of alkene **8** or **9** (4.0 mmol) in heptane (10 mL) palladium-on-charcoal (120 mg) was added. The solution was stirred in an atmosphere of hydrogen for 20 h at ambient temperature. When the reaction was complete (TLC controlled), the mixture was filtered over Celite, the filtrate was concentrated, and the analytically pure residue dried *in vacuo*.

1,2;3,4-Di-*O*-isopropylidene-6,7,8,9,10-pentadeoxy-α-L-*galacto*-decopyranose (**10**). (1.13 g, 94%; TLC solvent H R_f 0.64), colorless syrup: $[\alpha]_D^{23}$ +61.2° (*c* 1.0, chloroform); ^{1}H NMR ($CDCl_3$) δ 0.86 (t, 3H, J = 6.2 Hz, H-10, H-10'), 1.22-1.68 (m, 8H, H-6,H-6′,H-7,H-7′,H-8,H-8',H-9, H-9'), 1.31, 1.33, 1.44, 1.50 [4s, 12H, 2 x C(CH_3)$_2$], 3.69 (m, 1H, H-5), 4.11 (dd, 1H, $J_{4,5}$ = 1.7 Hz, H-4), 4.27 (dd, 1H, $J_{2,3}$ = 2.3 Hz, H-2), 4.56 (dd, 1H, $J_{3,4}$ = 8.0 Hz, H-3), 5.52 (d, 1H, $J_{1,2}$ = 5.2 Hz, H-1); ^{13}C NMR ($CDCl_3$) δ 14.09 (C-10), 22.56 (C-9), 25.36 (C-7), 24.33, 24.94, 26.00, 26.03 [2 x C(*C*H_3)$_2$], 30.08, 31.70 (C-6,C-9), 67.37 (C-5), 70.55 (C-2), 70.90 (C-3), 72.86 (C-4), 96.61 (C-1), 108.22, 108.91 [2 x *C*(CH_3)$_2$].

Anal. Calcd for $C_{16}H_{28}O_5$ (300.39): C, 63.97; H, 9.39. Found: C, 64.05; H, 9.31.

1,2;3,4-Di-*O*-isopropylidene-10-methoxycarbonyl-6,7,8,9,10-pentadeoxy-α-L-*galacto*-undecopyranose (**11**). (1.33 g, 93%; TLC solvent G R_f 0.32), colorless syrup: $[\alpha]_D^{25}$ +46.6° (*c* 1.0, chloroform); ^{1}H NMR (CDC_{l3}) δ 1.26-1.69 (m, 8H, H-6,H-6′,H-7,H-7′,H-8,H-8′,H-9, H-9′), 1.29, 1.30, 1.41, 1.48 [4s, 12H, C(CH_3)$_2$], 2.27 (t, 2H, J = 7.6, H-10, H-10', H-10″), 3.62 (s, 3H, CO_2CH_3), 3.67 (m, 1H, H-5), 4.08 (dd, 1H, $J_{4,5}$ = 1.8 Hz, H-4), 4.25 (dd, 1H, $J_{2,3}$ = 2.3 Hz, H-2), 4.54 (dd, 1H, $J_{3,4}$ = 7.9 Hz, H-3), 5.49 (d, 1H, $J_{1,2}$ = 5.3 Hz, H-1); ^{13}C NMR ($CDCl_3$) δ

24.32, 24.82, 25.98, 26.03 [2 x C(CH$_3$)$_2$], 24.92, 25.34 (C-7,C-8) 28.94, 29.92 (C-6,C-9), 34.01 (C-10), 51.43 (CO_2CH_3), 67.26 (C-5), 70.51 (C-2), 70.88 (C-3), 72.81 (C-4), 96.57 (C-1), 108.22, 108.93 [2 x C(CH$_3$)$_2$], 174.20 (CO_2CH_3).

Anal. Calcd for $C_{18}H_{30}O_7$ (358.42): C, 60.31; H, 8.43. Found: C, 60.22; H, 8.51.

Successive Deisopropylidenation and Acetylation of **10** and **11**. A solution of **10** (901 mg, 3.0 mmol) or **11** (1.08 g, 3.0 mmol) in 90% trifluoroacetic acid (20 mL) was stirred for two hours at room temperature (TLC solvent J). The mixture was then concentrated, the residue codistilled with toluene (3 x 30 mL), and dried in high vacuum. The residue was dissolved in acetic anhydride (20 mL), and the solution was cooled to 4 °C. After addition of 70% perchloric acid (0.2 mL), the solution was stirred for 3.5 h at 4 °C under argon. When the reaction was complete (TLC solvent H), the mixture was poured into ice-water (350 mL). After stirring for one hour, the aqueous layer was extracted with chloroform (2 x 150 mL). The combined organic layers were washed with cold sat aq $NaHCO_3$ (2 x 150 mL), water (2 x 150 mL), dried, and concentrated. The crude products were purified by MPLC (eluent ethyl acetate gradient 0% → 25% in heptane).

1,2,3,4-Tetra-*O*-acetyl-6,7,8,9,10-pentadeoxy-α?β-L-*galacto*-decopyranose (**12**). (851 mg, 73%), colorless syrup: For analytical data see lit.[2]

1,2,3,4-Tetra-*O*-acetyl-10-methoxycarbonyl-6,7,8,9,10-pentadeoxy-α-L-*galacto*-decopyranose (**13**α). (700 mg, 52%; TLC solvent H R_f 0.42), colorless syrup: $[\alpha]_D^{27}$ -111.3° (*c* 1.0, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.24, 1.33, 1.50, 1.40, 1.55, 1.59 (6m, 8H, H-6,H-6′,H-7, H-7′,H-8, H-8′,H-9, H-9′), 1.96, 1.98, 2.11, 2.13 (4s, 12H, 4 x $OCOCH_3$), 2.24 (t, 2H, H-10, H-10'), 3.62 (s, 3H, CO_2CH_3), 3.99 (m, 1H, H-5); 5.26 (m, 1H, H-4), 5.27 (m, 1H, H-3), 5.34 (m, 1H, H-2), 6.30 (d, 1H, 0.1 Hz, H-1); ^{13}C NMR ($CDCl_3$) δ 20.44, 20.54, 20.64, 20.78 (4 x $OCOCH_3$), 24.54 (C-9), 24.74 (C-7), 28.75 (C-8) 29.78 (C-6), 33.78 (C-10), 51.33 (CO_2CH_3), 68.13 (C-4), 69.25 (C-3), 70.92 (C-2, C-5, two signals are isochronic), 89.90 (C-1), 168.96, 169.31, 170.03, 170.31 (4 x $OCOCH_3$), 173.86 (CO_2CH_3).

Anal. Calcd for $C_{20}H_{30}O_{11}$ (446.45): C, 53.81; H, 6.77. Found: C, 53.69; H, 6.56.

1,2,3,4-Tetra-*O*-acetyl-10-methoxycarbonyl-6,7,8,9,10-pentadeoxy-β-L-*galacto*-decopyranose (**13**β). (350 mg, 26%; TLC solvent H R_f 0.40), colorless crystals: mp 75 °C (from ethyl acetate-heptane); $[\alpha]_D^{22}$ -24.0° (*c* 1.5, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.28, 1.37, 1.30, 1.40, 1.55, 1.60 (6m, 8H, H-6,H-6′,H-7, H-7',H-8, H-8′,H-9, H-9′), 1.94, 1.99, 2.07, 2.13 (4s, 12H, 4 x $OCOCH_3$), 2.24 (t, 2H, H-10, H-10′), 3.61 (s, 3H, CO_2CH_3), 3.68 (m, 1H, H-5), 5.01 (m, 1H, $J_{3,4}$ = 3.6 Hz, H-3), 5.26 (m, 1H, H-4), 5.27 (dd, 1H, $J_{2,3}$ =10.4 Hz, H-2), 5.60 (d, 1H, $J_{1,2}$ = 8.2 Hz, H-1); ^{13}C NMR ($CDCl_3$) δ 20.45, 20.54, 20.64, 20.73 (4 x $OCOCH_3$), 24.56 (C-9), 24.83 (C-7), 28.64 (C-8), 29.84 (C-6), 33.81 (C-10), 51.34 (CO_2CH_3), 68.16(C-2), 69.04 (C-4), 71.33 (C-3), 74.16 (C-5), 92.34 (C-1), 168.99, 169.32, 169.87, 170.31 (4 x $OCOCH_3$), 173.89 (CO_2CH_3).

Anal. Calcd for $C_{20}H_{30}O_{11}$ (446.45): C, 53.81; H, 6.77. Found: C, 53.82; H, 6.49.

Reduction of the Dialdo Sugar **6** to the Corresponding L-Galactose Derivatives **14** and **15**. To a suspension of lithium aluminium hydride (1.20 g, 31.6 mmol) or lithium aluminium deuteride (1.33 g, 31.6 mmol) in dry tetrahydrofuran (100 mL) was added a solution of **6** (6.3 g, 24.4 mmol) in dry tetrahydrofuran (50 mL). The mixture was then stirred for 3.5 h at room temperature under argon (TLC solvent I R_f 0.30). The workup involved first destroying the hydride excess by addition of sat aq ammonium chloride (approximately 20 mL). After filtration, the solution was concentrated to a volume of about 20 mL, and chloroform (300 mL) was added. The organic layer was then extracted with brine (2 x 100 mL), dried, and concentrated.The crude products were purified by MPLC (eluent ethyl acetate gradient 0%→45% in heptane).

1,2;3,4-Di-*O*-isopropylidene-α-L-galactopyranose (**14**). (5.32 g, 84%), colorless syrup: $[\alpha]_D^{23}$ +54.3° (*c* 1.0, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.32, 1.33, 1.44, 1.52 [4s, 12H, 2 x $C(CH_3)_2$], 2.21 (brs, OH), 3.73 (dd, 1H, $J_{5,6}$ = 7.3 Hz, $J_{6,6'}$ = 14.9 Hz, H-6), 3.79-3.91 (m, 2H, H-5,H-6'), 4.26 (dd, 1H, $J_{4,5}$ = 1.5 Hz, H-4), 4.26 (dd, 1H, $J_{2,3}$ = 2.4 Hz, H-2), 4.60 (dd, 1H, $J_{3,4}$ = 7.9 Hz, H-3), 5.55 (d, 1H, $J_{1,2}$ = 4.9 Hz, H-1); ^{13}C NMR ($CDCl_3$) δ 24.23, 24.89, 25.87, 25.98 [2 x $C(CH_3)_2$], 62.30 (C-6), 68.01 (C-5), 70.48, 70.68 (C-2,C-3), 71.55 (C-4), 96.24 (C-1), 108.64, 109.42 [2 x $C(CH_3)_2$].

Anal. Calcd for $C_{12}H_{20}O_6$ (260.29): C, 55.37; H, 7.74. Found: C, 55.46; H, 7.63.

(6*R*,*S*)- 1,2;3,4-Di-*O*-isopropylidene-α-L-(6-^{2}H)-galactopyranose (**15**). (5.42 g, 85 %), colorless syrup: $[\alpha]_D^{23}$ +53.4° (*c* 1.0, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.29, 1.30, 1.41, 1.49 [4s, 12H, 2 x $C(CH_3)_2$], 2.34 (brs, OH), 3.65-3.85 (m, 2H, H-5,H-6*R*,H-6*S*), 4.23 (dd, 1H, $J_{4,5}$ = 1.8 Hz, H-4), 4.29 (dd, 1H, $J_{2,3}$ = 2.5 Hz, H-2), 4.57 (dd, 1H, $J_{3,4}$ = 7.9 Hz, H-3), 5.52 (d, 1H, $J_{1,2}$ = 5.1 Hz, H-1); ^{13}C NMR ($CDCl_3$) δ 24.31, 24.91, 25.91, 26.00 [2 x $C(CH_3)_2$], 61.85 (t, $J_{C,D}$ = 21.9 Hz, C-6), 68.12 (C-5), 70.58, 70.75 (C-2,C-3), 71.50 (C-4), 96.27 (C-1), 108.64, 109.42 [2 x $C(CH_3)_2$]; CI mass spectrum (isobutane): *m/z* 261 ($C_{12}H_{19}O_6D^+$, 3%), 246 ($C_{11}H_{16}O_6D^+$, 100%], 204 (96%).

Anal. Calcd for $C_{12}H_{19}O_6D$ (261.28): C, 55.16. Found: C, 55.04.

Introduction of the Trifluoromethanesulfonyl Group in **14** and **15**. To a solution of **14** (7.50 g, 28.8 mmol) or **15** (7.52g, 28.8 mmol) and collidine (7.5 mL, 56.6 mmol) in dry dichloromethane (300 mL) was added a solution of trifluoromethanesulfonic acid anhydride (7.5 mL, 45.8 mmol) in dry dichloromethane (30 mL). The reaction mixture was stirred for two hours at room temperature under argon (TLC controlled). The mixture was then poured into ice-water (300 mL), the organic layer separated, and the aqueous layer extracted with chloroform (2 x 100 ml). The combined organic layers were washed with cold aq 15% $NaHSO_4$ (2 x 250 mL), ice-water (2 x 250 mL), cold sat aq $NaHCO_3$ (2 x 250 mL), water (2 x 250 mL), dried, and concentrated. After drying in high vacuum, the crude compounds **16** and **17** were used in the next step without further purification.

1,2;3,4-Di-*O*-isopropylidene-6-*O*-trifluoromethanesulfonyl-α-L-galactopyranose (**16**). (10.7 g, 95%; TLC solvent F R_f 0.38), colorless crystals: mp 47 °C; $[\alpha]_D^{24}$ +47.4° (*c* 1.0, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.29, 1.30, 1.44, 1.53 [4s,

12H, 2 x C(CH_3)$_2$], 4.10 (ddd, 1H, $J_{5,6}$ = 4.9 Hz, $J_{5,6'}$ = 6.7 Hz, H-5), 4.23 (d, 1H, $J_{4,5}$ = 2.1 Hz, H-4), 4.35 (dd, 1H, $J_{2,3}$ = 2.7 Hz, H-2), 4.57 (dd, 1H, $J_{6,6'}$ = 10.5 Hz, H-6), 4.63 (dd, 1H, H-6'), 4.64 (dd, 1H, $J_{3,4}$ = 8.0 Hz, H-3), 5.55 (d, 1H, $J_{1,2}$ = 4.9 Hz, H-1); ^{13}C NMR ($CDCl_3$) δ 24.38, 24.86, 25.85, 26.94 [2 x C(*C*H_3)$_2$], 66.06 (C-5), 70.20, 70.37, 70.63 (C-2,C-3,C-4), 74.67 (C-6), 96.12 (C-1), 109.14, 110.14 [2 x *C*(CH_3)$_2$], 118.53 (q, $J_{C,F}$ = 314.5 Hz, CF_3).

(6*R*,*S*)-1,2;3,4-Di-*O*-isopropylidene-6-*O*-trifluoromethanesulfonyl-α-L-(6-^{2}H)-galactopyranose (**17**). (10.65 g, 94%; TLC solvent F R_f 0.39, analytical sample by HPLC eluent solvent D), light brown syrup: $[\alpha]_D^{23}$ +44.6° (*c* 1.0, chloroform); ^{1}H NMR ($CDCl_3$) δ?1.31, 1.42, 1.51 [3s, 12H, C(CH_3)$_2$], 4.09 (m, 1H, H-5), 4.23 (d, 1H, $J_{4,5}$ = 2.1 Hz, H-4), 4.34 (dd, 1H, $J_{2,3}$ = 2.7 Hz, H-2), 4.55, 4.60 (2d, 1H, J = 7.7 Hz, J = 4.4 Hz, (*R*,*S*)H-6), 4.63 (dd, 1H, $J_{3,4}$ = 7.6 Hz, H-3), 5.52 (d, 1H, $J_{1,2}$ = 4.8 Hz, H-1); ^{13}C NMR ($CDCl_3$) δ 24.35, 24.82, 25.82, 26.90 [2 x C(*C*H_3)$_2$], 65.99 (C-5), 70.20, 70.37, 70.63 (C-2,C-3,C-4), 74.39 (t, $J_{C,D}$ = 24.0 Hz, C-6), 96.10 (C-1), 109.11, 110.11 [2 x *C*(CH_3)$_2$], 118.63 (q, $J_{C,F}$ = 319.6 Hz, CF_3).

6-Deoxy-1,2;3,4-di-*O*-isopropylidene-α-L-(6-^{2}H)-galactopyranose (**18**). To a solution of **17** (6.9 g, 17.5 mmol) in dry acetonitrile (250 mL) was added sodium borohydride (2.06 g, 54.4 mmol), and the mixture was stirred for 48 h at room temperature under argon. When the reaction was complete (TLC solvent D R_f 0.53), the mixture was filtered through a layer of silica gel and poured into ice-water (250 ml). The aqueous layer was extracted with chloroform (2 x 150 mL), and the combined organic layers were washed with water, dried, and concentrated. Purification by MPLC (eluent solvent D) provided **18** (3.66 g, 85%) as colorless syrup: $[\alpha]_D^{24}$ +52.7° (*c* 1.0, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.23 (d, 2H, $J_{5,6}$ = 7.7 Hz, H-6, H-6′), 1.30, 1.33, 1.43, 1.49 [4s, 12H, 2 x C(CH_3)$_2$], 3.88 (m, 1H, H-5), 4.05 (dd, 1H, $J_{4,5}$= 1.7 Hz, H-4), 4.26 (dd, 1H, $J_{2,3}$ = 2.0 Hz, H-2), 4.56 (dd, 1H, $J_{3,4}$ = 7.9 Hz, H-3), 5.49 (d, 1H, $J_{1,2}$ = 5.3 Hz, H-1); ^{13}C NMR ($CDCl_3$) δ 15.54 (t, $J_{C,D}$ = 19.6 Hz, C-6), 24.41, 24.87 [C(*C*H_3)$_2$], 25.99 [C(*C*H_3)$_2$ two signals are isochronic], 63.40 (C-5), 70.34, 70.94 (C-3,C-4), 73.51 (C-2), 96.52 (C-1), 108.16, 108.89 [2 x *C*(CH_3)$_2$]; CI mass spectrum (isobutane): *m/z* 246 ($C_{12}H_{20}O_5D^+$, 100%), 230 ($C_{11}H_{16}O_5D^+$, 95%), 188 (90%).

Anal. Calcd for $C_{12}H_{19}O_5D$ (245.29): C, 58.76; H. Found: C, 58.73.

6-Deoxy-6-fluoro-1,2;3,4-di-*O*-isopropylidene-α-L-galactopyranose (**19**). To a solution of **16** (10.7 g, 27.3 mmol) in dry dichloromethane (300 mL) was dropwise added a 1 M solution of tetrabutylammonium fluoride in dry tetrahydrofuran (100 mL). After stirring for 18 h at room temperature under argon (TLC solvent D R_f 0.20), the reaction mixture was concentrated, and the residue dissolved in chloroform (400 ml). The organic phase was extracted with water (3 x 100 ml), dried and concentrated. Purification by MPLC (eluent ethyl acetate gradient 0%→12% in heptane) gave **19** (6.24g, 87%) as a colorless syrup: $[\alpha]_D^{24}$ +44.3° (*c* 1.0, chloroform); lit.[6] $[\alpha]_D^{25}$ +44.7° (*c* 1.0, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.32, 1.33, 1.43, 1.53 [4s, 12H, 2 x C(CH_3)$_2$], 4.06 (m, 1H, H-5), 4.21 (dd, 1H, $J_{3,4}$ = 8.0 Hz, H-3), 4.32 (dd, 1H, $J_{2,3}$ = 2.4 Hz, H-2), 4.51 (ddd, 1H, $J_{5,6}$ = 6.8 Hz, $J_{6,6'}$ = 9.5 Hz, $J_{F,6}$ = 48.2 Hz, H-6), 4.57 (ddd, 1H, $J_{5,6'}$ = 5.5 Hz, $J_{F,6'}$ = 46.1 Hz, H-6′),

4.62 (ddd, 1H, $J_{4,5}$ = 2.5 Hz, $J_{4,F}$ = 1.2 Hz, H-4), 5.53 (d, 1H, $J_{1,2}$ = 4.9 Hz, H-1); ^{13}C NMR ($CDCl_3$) δ 24.43, 24.90, 25.98 [2 x C(CH_3)$_2$ two signals are isochronic], 66.58 (d, $J_{C,F}$ = 22.9 Hz, C-5), 70.41, 70.49 (C-2,C-3), 70.56 (d, $J_{C,F}$ = 7.6 Hz, C-4), 80.64 (d, $J_{C,F}$ = 168.1 Hz, C-6), 96.22 (C-1), 108.78, 109.44 [2 x $C(CH_3)_2$]; ^{19}F NMR ($CDCl_3$) δ -230.9.

Anal. Calcd for $C_{12}H_{19}O_5F$ (262.27): C, 54.95; H, 7.30. Found: C, 54.82; H, 7.18.

Successive Deisopropylidenation and Acetylation of **18** and **19**. Compounds **18** (736 mg, 3.0 mmol) and **19** (787 mg, 3.0 mmol) were processed as described for the syntheses of **12** and **13**.

1,2,3,4-Tetra-*O*-acetyl-6-deoxy-α/β-L-(6-^{2}H)-galactopyranose (**20**). (720 mg, 72%; α/β ratio 2.5:1; TLC solvent H R_f 0.20), colorless syrup: ^{1}H NMR of the α-anomer ($CDCl_3$) δ 1.09 (d, 2H, H-6, H-6′), 1.95, 1.96, 2.10, 2.13 (4s, 12H, 4 x $OCOCH_3$), 4.22 (t, 1H, $J_{5,6}$ = $J_{5,6'}$ = 6.4 Hz, H-5), 5.27-5.30 (m, 3H, H-2,H-3,H-4), 6.28 (d, 1H, $J_{1,2}$ = 2.8 Hz, H-1); ^{13}C NMR of the α-anomer ($CDCl_3$) δ 15.55 (t, $J_{C,D}$ = 19.1 Hz, C-6), 20.42, 20.46, 20.52, 20.77 (4 x OCOCH_3), 66.41 (C-2), 67.14 (C-5), 68.76 (C-3), 70.51 (C-4), 89.87 (C-1), 169.51, 170.32, 170.54, 170.91 (4 x OCOCH_3); CI mass spectrum (isobutane): *m/z* 274 ($C_{12}H_{16}O_7D^+$, 98%], 153 [100%].

Anal. Calcd for $C_{14}H_{19}O_9D$ (333.31): C, 50.44. Found: C, 50.29.

1,2,3,4-Tetra-*O*-acetyl-6-deoxy-6-fluoro-α?β-L-galactopyranose (**21**). (883 mg, 84%; α/β ratio 3:1, TLC solvent H R_f 0.20), colorless syrup: ^{1}H NMR of the α-anomer ($CDCl_3$) δ 1,98, 2.01, 2.14, 2.15 (4s, 12H, 4 x $OCOCH_3$), 4.25-4.40 (m, 2H, H-5,H-6,H-6'), 4.44 (dd, 0.5H, $J_{5,6}$ = 5.3 Hz, $J_{6,6'}$ = 9.3 Hz, H-6), 4.51 (dd, 0.5H, $J_{5,6'}$ = 6.4 Hz,H-6'), 5.33-5.35 (m, 2H, H-2,H-3), 5.54 (s, 1H, H-4), 6.34 (d, 1H, $J_{1,2}$ = 2.7 Hz, H-1); ^{13}C NMR of the α-anomer ($CDCl_3$) δ?20.56, 20.59, 20.65, 20.89 (4 x OCOCH_3), 66.38 (C-2), 67.28 (C-5), 67.45 (d, $J_{C,F}$ = 7.6 Hz, C-4), 69.52 (d, $J_{C,F}$ = 23.8 Hz, C-5), 81.10 (d, $J_{C,F}$ = 172.6 Hz, C-6), 89.64 (C-1), 169.20, 170.20, 170.37, 170.40 (4 x OCOCH_3); ^{19}F NMR of the α-anomer ($CDCl_3$) δ?-231.6.

Anal. Calcd for $C_{14}H_{19}O_9F$ (350.30): C, 48.00; H, 5.46. Found: C, 47.79, H, 5.30.

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