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The Synthesis of Difluoromethylene-Linked C-Glycosides and C-Disaccharides

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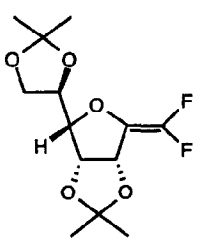
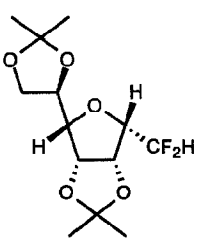
Abstract: Novel difluoromethylene linked C-glycosides and C-disaccharides were prepared by intermolecular addition of nucleophilic and electrophilic radicals to carbohydrate *gem*-difluoroenol ethers.

The diverse biology of glycosides, disaccharides and oligosaccharides has stirred considerable interest in the synthesis of non-natural analogues, particularly C-glycosides and C-disaccharides wherein the glycosidic oxygen is replaced by a methylene group.[1,2] Whilst techniques to effect this transposition proliferate,[3] the replacement of oxygen with the larger but tetrahedrally disposed isoelectronic difluoromethylene unit is rarely considered either as a carbohydrate modification or in the wider field of natural product analogues.[4] As part of a programme designed to achieve effective replacement of the anomeric oxygen of glycosides by the difluoromethylene moiety, we have recently described an efficient preparation of exocyclic difluoromethylene derivatives (e.g. **1**) of commonly available γ- and δ-lactones together with their reduction to *gem*-difluoromethyl C-glycosides (e.g. **2**).[5] For the purpose of brevity difluoromethylene- and methylene-linked C-glycosides will be referred to hereafter as CF_2- and CH_2-glycosides respectively.



1



2

With a view to expanding the little known chemistry of the *gem*-difluoroenol ether system we now report, in full detail, the extension of these studies towards the preparation of more highly functionalised CF_2-glycosides and disaccharides. We were particularly intrigued by the possibility of exploiting the mildness and selectivity of some free radical processes to elaborate these potentially sensitive molecules. It is to be acknowledged that workers in the area of CH_2-glycoside synthesis have developed elegant strategies which utilise radical additions in the key carbon-carbon bond forming step.[6-9]

For intermolecular bond forming reactions the kinetically favoured addition of a nucleophilic radical to an electron-deficient alkene is the most common approach, but the addition of such a radical to an electron-rich enol ether is seldom attempted. We performed AM1 molecular orbital calculations[10] on a set of illustrative molecules (**Table 1**) from which several interesting comparisons may be drawn: The HOMO energies of the difluoroenol ethers are very similar to those of the corresponding methylene analogues, while the LUMO energies are relatively lowered. Since the important frontier orbital interactions in the current instance would involve interaction of the radical SOMO with the LUMO of the alkene, such a lowering should lead to an increase in the rate of reactions with nucleophilic radicals.[11] Whilst it is understood that the absolute values for the LUMO energies are not to be taken as accurate, the relative differences are such that we were prompted to explore the reactions of difluoroenol ethers with nucleophilic radicals, in addition to their intuitively more suitable electrophilic counterparts.[12]

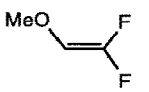
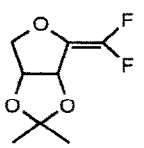
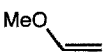
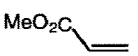
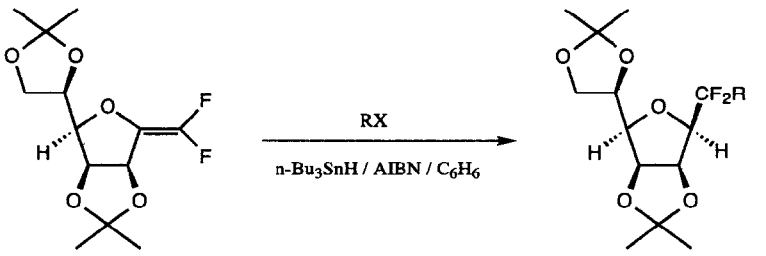
	HOMO Energy (eV)	LUMO Energy (eV)
	-10.8	0.7
	-10.7	0.6
	-10.8	1.9
	-13.0	0.2

Table 1: Orbital energies from AM1 calculations on energy minimised (MM2) structures.[13]

Reactions with Nucleophilic Radicals

The results from a series of simple alkyl halides, in the presence of tri-n-butyltinhydride with azobisisobutyronitrile (AIBN) as initiator, confirmed that such additions were possible (**Scheme 1**). In these reactions, radical addition occurred exclusively at the least hindered difluoromethylene terminus[14] with stereospecific capture from the unencumbered convex face of the bicyclic system. The sytheses of **4-6** typically required pseudo-high dilution conditions, with the addition over several hours of a solution of tin hydride and AIBN in degassed benzene to a refluxing benzene solution of **3** and excess halide. The stereochemistry at the anomeric centre in these compounds was confirmed by the typical 4Hz coupling constant between the anomeric proton and its vicinal neighbour. To the best of our knowledge the obtention of **5** represents the first example of a difluoromethylene linked glycolipid analogue.



3 **4-6**

RX	Yield (%)	Recovered **3** (%)
4 $CH_3(CH_2)_3Br$	33	23
5 $CH_3(CH_2)_{11}I$	24	25
6 	11	14

Scheme 1

With these results in hand, it was possible to demonstrate the potential for the synthesis of difluoromethylene-bridged disaccharides, using a series of primary carbohydrate radicals derived from 6-halo pyranosides[15,16] under standard tin hydride mediated conditions (**Table 2**). The CF_2-disaccharide adducts, **11-15**, were isolated together with unreacted difluoroenol ether and reduced halide. It could be ascertained by ^{19}F NMR of the crude reaction mixture that the only fluorine-containing products were the CF_2-disaccharides. It is uncertain whether the poor recovery of material is a consequence of the isolation procedure or hitherto undetected products. In the unusual case of **15**, isolation required repeated chromatography and it is worth noting that the volatility of the starting difluoroenol ether **20** may contribute to the generally reduced efficiency of this and other reactions in which it has been used. Nevertheless, we have thus demonstrated the unusual reactivity of the difluoroenol ether system towards nucleophilic radicals and applied this to the synthesis of a range of novel disaccharide analogues.

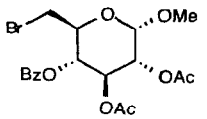
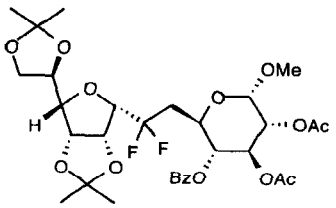
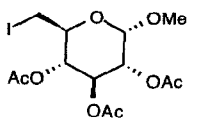
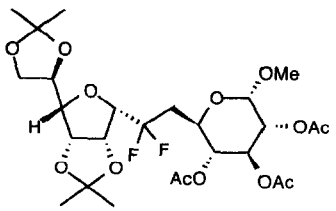
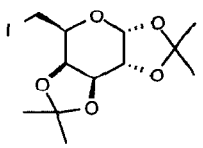
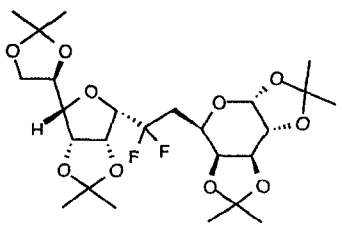
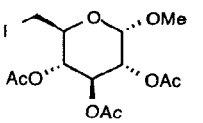
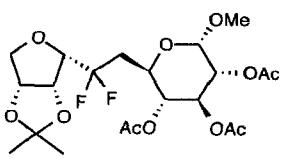
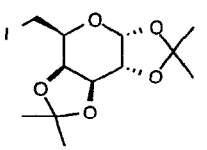
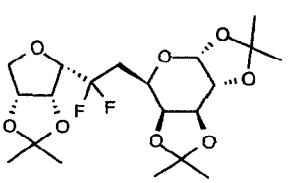
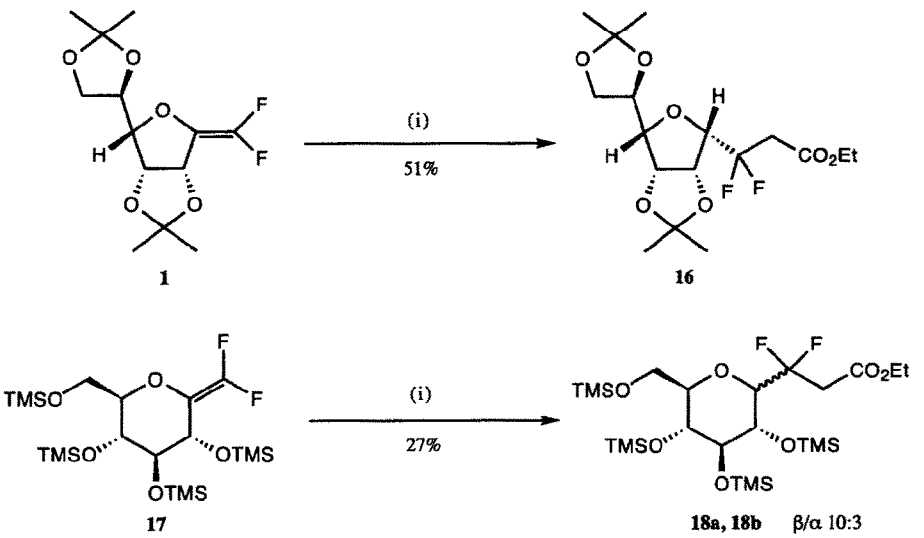
Difluoroenol ether	Halide	Disaccharide (yield)
1	 **8**	 **11** (25%)
1	 **9**	 **12** (40%)
1	 **10**	 **13** (20%)
20	 **9**	 **14** (23%)
20	 **10**	 **15** (14%)

Table 2 : Tri-n-butyltinhydride mediated additions of 6-halo pyranosides to difluoroenol ethers.

Reactions with Electrophilic Radicals

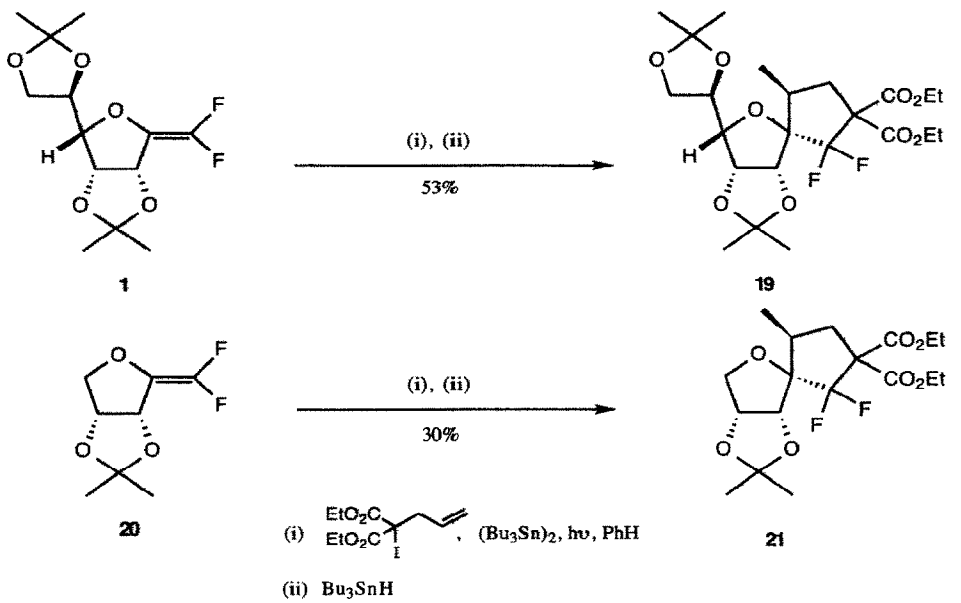
From the foregoing molecular orbital calculations, which show difluoroenol ether and enol ether systems to have relatively similar HOMO energies, it may also be anticipated that the carbohydrate difluoroenol ethers would be compatible with electrophilic radicals. It was found that addition to **1** of the radical derived from ethyl bromoacetate under the conditions described for nucleophilic radicals, proceeded more efficiently and with a similar regio- and stereospecificity to give CF_2-glycoside **16 (Scheme 2)**. Only a small quantity of starting material (6%) was recovered, in contrast to the simple alkyl radical additions. To date, we have been unable to obtain adducts between difluoroenol ether **17** and nucleophilic radicals. The enhanced reactivity of difluoroenol ethers towards electrophilic radicals is further indicated by the reaction of **17** with the radical from ethyl bromoacetate. The product **18** was isolated as a 10:3 mixture of isomers at the anomeric centre. The major isomer **18a** was assigned as the β-anomer on the basis of the typical diaxial coupling constant (8.4Hz) between the anomeric proton and its vicinal neighbour. The corresponding coupling constant for **18b** is 5.3Hz. The predominance of **18a** can be anticipated from the radical anomeric effect.[11]



Scheme 2

A powerful extension of this approach was found in the addition and cyclisation of diethyl allyliodomalonate to difluoroenol ethers **1** and **20** under the iodine atom transfer conditions developed by Curran,[17-19] affording spirofused difluorocarbocycles **19** and **21 (Scheme 3)**. In both instances the initially formed iodide products were reduced to facilitate isolation and characterisation. The reaction sequence to give difluoromethylene spiroacetal analogues involves addition of the malonate radical to the least hindered end of the difluoroenol ether, thereby giving an anomeric radical, which undergoes 5-*exo*-ring closure and iodine

atom transfer. That no evidence was found for products arising from quenching of the intermediate anomeric radical, can be attributed to the efficiency of the cyclisation.[20] From the ^{1}H, ^{13}C and ^{19}F NMR spectra of **19** and **21** it can be deduced that the cyclisations were stereoselective, resulting in a single orientation both at the anomeric centre and the methyl group. Tentative assignment of the stereochemistry was made on the basis of preliminary nOe difference experiments. The anomeric stereochemistry corresponds to cyclisation from the least hindered face of the [3,3,0]-bicyclic system.



Scheme 3

Conclusions

We have thus demonstrated the reactivity of carbohydrate *gem*-difluoroenol ethers towards both nucleophilic and electrophilic radicals. The former was utilised in the synthesis of difluoromethylene-linked C-glycosides and disaccharides. A more efficient entry to simple CF_2-glycosides was found with electrophilic radicals. This has been extended, through radical atom transfer chemistry, to *gem*-difluorocarbocycles. Carbohydrate *gem*-difluoroenol ethers have proven to be versatile intermediates in the synthesis of novel difluoromethylene-containing carbohydrate structures and further exploration of their potential is currently underway.

Acknowledgements: We gratefully acknowledge the support of Glaxo Group Research for the award of a Studentship to MJT.

Experimental

Melting points were determined on a Kofler and a Reichert hot stage and are uncorrected. Infrared spectra were recorded on a Perkin Elmer 983G grating infrared spectrophotometer and a Perkin Elmer 1600 infrared spectrophotometer as thin film or dichloromethane solution. ^{1}H NMR and ^{13}C NMR spectra were recorded at 270MHz and 62.9MHz respectively on a Bruker WM-250, 400MHz and 100.6MHz respectively on a Varian VXR 400, at 500 and 125.8MHz respectively on a Bruker AM 500 instrument. ^{19}F NMR spectra were recorded at 84.3MHz on a Jeol FX90Q instrument and at 376.3MHz on a Varian VXR400 instrument, using fluorotrichloromethane as the internal standard. Mass spectra were recorded on a VG 7070B mass spectrometer, a VG 305 mass spectrometer and a VG ZAB SE mass spectrometer. Accurate mass measurements were made on a VG 7070b at Imperial College, by the SERC mass spectrometry service and by The School of Pharmacy mass spectrometry service. Optical rotations were measured on an Optical Activity AA1000 polarimeter. Elemental analyses were performed by the staff of the Imperial College microanalytical laboratory and by the staff of University College microanalytical laboratory. Petrol refers to redistilled light petroleum ether (b.p. 40-60°C), and ether to diethyl ether. Tetrahydrofuran and benzene were distilled from sodium-benzophenone ketyl under nitrogen. Preparative column chromatography was performed at low positive pressure on Merck Kiesel 60 (230-400 mesh) and Sorbsil C60 40/60 A. Preparative high pressure liquid chromatography was performed on a Gilson 305 apparatus with a Bischoff RI 8110 detector or a Shimadzu UV-VIS SPD-10A detector, using a Partisil 5 silica gel column. A MB/U Osram 400W Medium Pressure Mercury Arc Lamp was used for photolysis. All reactions were performed in oven dried glassware and under an inert atmosphere (nitrogen or argon).

Preparation of 2,5-anhydro-1-butyl-1-deoxy-1,1-difluoro-3,4;6,7-di-*O*-isopropylidene-D-*glycero*-D-*galacto*-heptitol (4). A solution of 2,5-anhydro-1-deoxy-1,1-difluoro-3,4;6,7-di-*O*-isopropylidene-D-*manno*-hept-1-enitol (**3**)[5] (18.4mg, 0.063mmol) and 1-bromobutane (0.20ml, 1.85mmol) in benzene (2ml) was degassed by heating at reflux for 30min. To the refluxing solution was added a degassed solution of tri-n-butyltinhydride (0.50ml, 1.85mmol) and AIBN (10mg) in benzene (1ml) over 12h by means of syringe pump. The reaction mixture was allowed to cool, ether (30ml) added and the mixture stirred with saturated potassium fluoride (10ml) for 30min. The organic phase was separated, filtered and dried over $MgSO_4$. The solvent was removed under reduced pressure and the oily residue adsorbed onto silica. Column chromatography (10-20% ether/petrol) furnished **3** (4.3mg, 23%) and 2,5-anhydro-1-butyl-1-deoxy-1,1-difluoro-3,4;6,7-di-*O*-isopropylidene-D-*glycero*-D-*galacto*-heptitol (**4**) (7.3mg, 33%) as a colourless oil. δ_H (270MHz; $CDCl_3$) 4.82(1H, dd, J=6.1, 3.7Hz, H-3), 4.78(1H, dd, J=6.0, 3.3Hz, H-4), 4.42(1H, dt, J=7.6, 5.4Hz, H-6), 4.12(1H, dd, J=8.8, 5.9Hz, H-7a), 4.05(1H, dd, J=8.8, 3.7Hz, H-7b), 3.69(1H, ddd, J=12.9, 5.1, 3.7Hz, H-2), 3.60(1H, dd, J=7.6, 3.7Hz, H-5), 2.06(2H, m, H-1'a, 1'b), 1.58-1.25(4H, m, 2xCH_2), 1.49(3H, s, Me), 1.44(3H, s, Me), 1.38(3H, s, Me), 1.33(3H, s, Me), 0.92(3H, t, J=7.2Hz, $CH_2\underline{CH_3}$); δ_F (84.3MHz; $CDCl_3$) -97.0(dm, J=260Hz), -106.4(dm, J=260Hz); δ_C (125.8MHz; $CDCl_3$) 122.5(t, J=242Hz), 113.7, 109.4, 82.3(t, J=33Hz), 81.6, 80.1, 80.0, 72.7, 66.8, 33.6(t, J=23Hz), 26.7, 26.3, 25.2, 25.0, 23.0, 22.6, 13.7; ν_{max}(film) 2935, 1456, 1380, 1260, 1210, 1119, 1070, 845cm^{-1}; m/z 350(M^+), 335(M^+-Me), 277, 197, 101, 43; Observed(M^+-Me): 335.1678; $C_{16}H_{25}F_2O_5$ requires: 335.1670.

Preparation of 2,5-anhydro-1-deoxy-1,1-difluoro-1-dodecyl-3,4;6,7-di-*O*-isopropylidene-D-*glycero*-D-*galacto*-heptitol (5). A solution of 2,5-anhydro-1-deoxy-1,1-difluoro-3,4;6,7-di-*O*-isopropylidene-D-*manno*-hept-1-enitol (**3**)[5] (173mg, 0.59mmol) and 1-iodododecane (530mg, 1.79mmol) in benzene (2ml) was degassed by heating at reflux for 30min. To the refluxing solution was added a degassed solution of tri-n-butyltinhydride (0.50ml, 1.85mmol) and AIBN (10mg) in benzene (2ml) over 6h by means of syringe pump. The reaction mixture was allowed to cool, ether (30ml) added and the mixture stirred with saturated potassium fluoride (10ml) for 30min. The organic phase was separated, filtered and dried over $MgSO_4$. The solvent was removed under reduced pressure and the oily residue adsorbed onto silica. Column chromatography (25% ether/petrol) furnished **3** (43.2mg, 25%) and 2,5-anhydro-1-deoxy-1,1-difluoro-1-dodecyl-3,4;6,7-di-*O*-isopropylidene-D-*glycero*-D-*galacto*-heptitol (**5**) (65.5mg, 24%) as a colourless oil. δ_H (270MHz; $CDCl_3$) 4.81(1H, dd, J=6.2, 3.5Hz, H-3), 4.77(1H, dd, J=6.1, 3.4Hz, H-4), 4.42(1H, dt, J=7.6, 5.4Hz, H-6), 4.09(2H, m, H-7a, 7b), 3.68(1H, ddd, J=13.2, 5.3, 3.5Hz, H-2), 3.56(1H, dd, J=7.5, 3.5Hz, H-5), 2.22-1.84(2H, m, H-1'a, 1'b), 1.60-1.25(CH_2 envelope), 1.49(3H, s, Me), 1.44(3H, s, Me), 1.38(3H, s, Me), 1.33(3H, s, Me), 0.87(3H, t, J=6.7Hz, $CH_2\underline{CH_3}$); δ_F (84.3MHz; $CDCl_3$) -97.0(m), -106.3(m); δ_C (125.8MHz; $CDCl_3$) 122.0(dd, J=248, 246Hz), 113.4, 109.4, 81.8, 80.4 (dd, J=31, 27Hz), 80.2, 79.9, 73.0, 66.9, 42.9(t, J=23Hz), 27.0, 26.0, 25.7, 25.6, 25.5, 25.4, 25.3, 25.2, 24.7; ν_{max}(film) 2935, 1456, 1380, 1260, 1210, 1119, 1070, 845cm^{-1}; m/z 462(M^+), 447(M^+-Me), 101, 43; Observed(M^+-Me): 447.2977; $C_{24}H_{41}F_2O_5$ requires: 447.2922.

Preparation of 2,5-anhydro-1-cyclohexyl-1-deoxy-1,1-difluoro-3,4;6,7-di-*O*-isopropylidene-D-*glycero*-D-*galacto*-heptitol (6). A solution of 2,5-anhydro-1-deoxy-1,1-difluoro-3,4;6,7-di-*O*-isopropylidene-D-*manno*-hept-1-enitol (**3**)[5] (466mg, 1.6mmol) and iodocylcohexane (0.65ml, 5.0mmol) in benzene (5ml) was degassed by heating at reflux for 30min. To this refluxing solution was added a degassed solution of tri-n-butyltinhydride (1.48ml, 5.5mmol) and AIBN (10mg) in benzene (5ml) over 6h by means of syringe pump. The reaction mixture was allowed to cool, ether (50ml) and carbon tetrachloride were added and the mixture stirred for 15min. A dilute solution of iodine in ether was added until the iodine colour persisted. The mixture was shaken with 5% potassium fluoride. The organic phase was separated, washed with water and dried over $MgSO_4$. The solvent was removed under reduced pressure and the oily residue adsorbed onto silica. Column chromatography (25% ether/petrol) furnished **3** (65mg, 14%) and 2,5-anhydro-1-cyclohexyl-1-deoxy-1,1-difluoro-3,4;6,7-di-*O*-isopropylidene-D-*glycero*-D-*galacto*-heptitol (**6**) (68mg, 11%) as a colourless oil. δ_H (270MHz; $CDCl_3$) 4.84(1H, dd, J=6.1, 3.7Hz, H-3), 4.77(1H, dd, J=6.1, 3.4Hz, H-4), 4.44(1H, dt, J=7.8, 5.1Hz, H-6), 4.10(2H, m, H-7a, 7b), 3.69(1H, ddd, J=12.2, 8.6, 3.7Hz, H-2), 3.52(1H, dd, J=7.6, 3.7Hz, H-5), 2.20-1.10(CH envelope), 1.49(3H, s, Me), 1.44(3H, s, Me), 1.37(3H, s, Me), 1.33(3H, s, Me); δ_F (84.3MHz; $CDCl_3$) -111.7(m); ν_{max}(film) 2940, 1456, 1380, 1260, 1210, 1119, 1070cm^{-1}; m/z 361(M^+-Me), 101, 43; Observed(M^+-Me): 361.1825; $C_{18}H_{27}F_2O_5$ requires: 361.1827.

Preparation of methyl 2,3-di-*O*-acetyl-8,11-anhydro-4-*O*-benzoyl-6,7-dideoxy-9,10;12,13-di-*O*-isopropylidene-7,7-difluoro-D-*glycero*-L-*galacto*-α-D-*gluco*-tridecopyranoside (11). A solution of 2,5-anhydro-1-deoxy-1,1-difluoro-3,4;6,7-di-*O*-isopropylidene-D-*gulo*-hept-1-enitol (**1**)[5] (120mg, 0.41mmol) and methyl 2,3-di-*O*-acetyl-4-*O*-benzoyl-6-bromo-6-deoxy-α-D-glucopyranoside (**8**)[16] (548mg, 1.23mmol) in benzene (5ml) was degassed by heating at reflux for 30min. To the refluxing solution was added a degassed solution of tri-n-butyltinhydride (0.40ml, 1.50mmol) and AIBN (30mg) in benzene (2ml) over 12h by means

of syringe pump. The reaction mixture was allowed to cool and the solvent removed under reduced pressure to give an oily residue. Column chromatography (25% ether/petrol) furnished **1** (30mg, 25%) and 2,3-di-*O*-acetyl-8,11-anhydro-4-*O*-benzoyl-6,7-dideoxy-9,10;12,13-di-*O*-isopropylidene-7,7-difluoro-D-*glycero*-L-*galacto*-α-D-*gluco*-tridecopyranoside (**11**) (68mg, 25%) as a colourless oil, which became a crystalline solid on storage at ambient temperature under argon for several weeks (m.p. 82-85°C). δ_H (270MHz; $CDCl_3$) 8.00-7.40(5H, m, Ph), 5.67(1H, t, J=9.8Hz, H-3), 5.13(1H, t, J=7.8, H-4), 4.96(1H, d, J=3.7Hz, H-1), 4.94(1H, dd, J=10.0, 3.7Hz, H-2), 4.78(1H, dd, J=6.1, 3.9Hz, H-9), 4.60(1H, dd, J=5.6, 4.2Hz, H-10), 4.36(1H, ddd, J=9.8, 1.2, 0.7Hz, H-5), 4.18(2H, m, H-13a, 12), 3.78(1H, ddd, J=14.2, 4.4, 3.9Hz, H-8), 3.65(1H, t, J=7.6Hz, H-13b), 3.55(1H, dd, J=7.5, 4.0Hz, H-11), 3.46(3H, s, OMe), 2.65-2.25(2H, m, H-6a, 6b), 2.09(3H, s, OAc), 1.88(3H, s, OAc), 1.56(3H, s, CMe), 1.39(6H, s, CMe_2), 1.28(3H, s, CMe); δ_F (84.3MHz; $CDCl_3$) -96.7(dm, J=264Hz), -102.3(dt, J=263, 20Hz); δ_C (67.9MHz; $CDCl_3$) 170.3, 169.9, 165.7, 133.6, 130.0, 129.0, 128.6, 121.0(dd, J=248, 243Hz), 113.7, 109.9, 96.7, 84.0, 82.5(dd, J=34, 26Hz), 80.5, 79.9, 75.4, 72.4, 71.2, 69.8, 65.9, 64.1(d, J=7Hz), 55.7, 35.4(t, J=23Hz), 26.7, 25.4, 24.4, 20.9, 20.7; ν_{max}(CH_2Cl_2) 2937, 1748, 1731, 1405, 1372, 1221, 1162, 1112, 1065, 978, 907, 848cm^{-1}; m/z 658(M^+), 643(M^+-Me), 571, 313, 269, 105, 81; Observed(M^+-Me): 643.2205; $C_{30}H_{37}F_2O_{13}$ requires: 643.2202; $[\alpha]_D^{20}$=+56.8 (c=1.30, $CHCl_3$); Found: C56.56, H5.91%; $C_{31}H_{40}F_2O_{13}$ requires: C56.53, H6.12%.

Preparation of methyl 2,3,4-tri-*O*-acetyl-8,11-anhydro-6,7-dideoxy-9,10;12,13-di-*O*-isopropylidene-7,7-difluoro-D-*glycero*-L-*galacto*-α-D-*gluco*-tridecopyranoside (12). A solution of 2,5-anhydro-1-deoxy-1,1-difluoro-3,4;6,7-di-*O*-isopropylidene-D-*gulo*-hept-1-enitol (**1**)[5] (200mg, 0.68mmol) and methyl 2,3,4-tri-*O*-acetyl-6-deoxy-6-iodo-α-D-glucopyranoside (**9**)[15] (880mg, 2.04mmol) in benzene (7ml) was degassed at reflux under nitrogen for 0.5h. To the refluxing solution was added a degassed solution of AIBN (56mg, 0.34mmol) and tri-n-butyltinhydride (0.663ml, 2.48mmol) in benzene (3.5ml) over 10h by means of syringe pump. The reaction mixture was refluxed for 3h and allowed to cool to room temperature. Iodine (30mg, 0.12mmol) and carbon tetrachloride (0.5ml) were added and the mixture was evaporated. The residue was taken up in ethyl acetate (15ml), stirred vigorously with a saturated solution of potassium fluoride (20ml) for 2h and filtered. The organic phase was separated, washed with saturated potassium fluoride (3x 20ml), water (20ml), brine (20ml), dried over $MgSO_4$ and concentrated *in vacuo*. Chromatography (25% petrol/ether) afforded the title compound (162mg, 40%) as white crystals (m.p. 68°C, ether/petrol). δ_H (400MHz, $CDCl_3$) 5.46(1H, dd, J=10.1, 9.1Hz, H-3), 4.88(3H, m, H-4, 2, 1), 4.80(1H, dd, J=6.0, 3.7Hz, H-9), 4.65(1H, dd, J=5.8, 3.9Hz, H-10), 4.36(1H, q, J=7.5Hz, H-5), 4.24(2H, m, H-13a, 12), 3.80(1H, dt, J=14.6, 3.6Hz, H-8), 3.71(1H, dd, J=8.5, 7.7Hz, H-13b), 3.61(1H, dd, J=7.9, 4.0Hz, H-11), 3.42(3H, s, OMe), 2.55-2.22(2H, br m, H-6a, 6b) 2.07, 2.05, 2.00(9H, 3s, 3xOAc), 1.46, 1.45, 1.39, 1.28(12H, 4s, 4xMe); δ_F (376.3MHz, $CDCl_3$) -96.2(dm, J=262Hz), -102.8(ddd, J=262, 29, 11Hz); ν_{max} (CH_2Cl_2) 2989, 2940, 1750, 1382, 1266, 1248, 1225, 1163, 1122, 1109, 1047cm^{-1}; FAB/MS m/z 595(M^+-H), 581(M^+-Me), 565, 539, 345 100, 84, 57, 41; $[\alpha]_D^{20}$=+72.7 (c=0.22, $CHCl_3$); Observed(M^+-Me): 581.2037; $C_{25}H_{35}F_2O_{13}$ requires: 581.2045.

Preparation of 1,2;3,4;9,10;12,13-tetra-*O*-isopropylidene-6,7-dideoxy-7,7-difluoro-8,11-anhydro-D-*glycero*-L-*galacto*-α-D-*galacto*-tridecopyranose (13). A solution of 2,5-anhydro-1-deoxy-1,1-difluoro-3,4;6,7-di-*O*-isopropylidene-D-*gulo*-hept-1-enitol (**1**)[5] (200mg, 0.68mmol) and 1,2;3,4-di-*O*-isopropylidene-6-deoxy-6-iodo-α-D-galactopyranose (**10**)[15] (760mg, 2.04mmol) in benzene (7ml) was degassed by heating at reflux under nitrogen for 0.5h. To the refluxing solution was added a degassed solution of AIBN (56mg,

0.34mmol) and tri-n-butyltinhydride (0.663ml, 2.48mmol) in benzene (3.5ml) over 10h by means of syringe pump. The reaction mixture was refluxed for 3h and allowed to cool to room temperature. Iodine (30mg, 0.12mmol) and carbon tetrachloride (0.5ml) were added and the mixture was evaporated. The residue was taken up in ethyl acetate (15ml), stirred vigorously with a saturated solution of potassium fluoride (20ml) for 2h and filtered. The organic phase was separated, washed with saturated potassium fluoride (3x20ml), water (20ml), brine (20ml), dried over $MgSO_4$ and concentrated. Chromatography (40% ethyl acetate/petrol) afforded the title compound (70 mg, 21%) as white crystals (m.p. 158°C, ethanol). δ_H (400MHz, $CDCl_3$) 5.46(1H, d, J=5.0Hz, H-1), 4.81(1H, dd, J=6.1, 3.7Hz, H-9), 4.59(2H, m, H-10, 3), 4.39(1H, q, J=6.0Hz, H-5), 4.26(1H, dd, J=5.0, 2.5Hz, H-2), 4.18(1H, dd, J=8.4, 6.7Hz, H-13a), 4.10(2H, m, H-12, 4), 3.86(1H, dt, J=15.5, 4.2Hz, H-8), 3.68(1H, t, J=8.2Hz, H-13b), 3.60(1H, dd, J=7.8, 3.9Hz, H-11), 2.55-2.22(2H, br m, H-6a, 6b), 1.50(3H, s, Me), 1.43(3H, s, Me), 1.42(6H, s, 2xMe), 1.37, 1.31, 1.29, 1.24 (12H, 4s, 4xMe); δ_F (376.3MHz, $CDCl_3$) -97.0(dd, J=258, 23Hz), -101.5(dt, J=258, 18Hz); δ_C (100.6MHz, $CDCl_3$) 121(t, J=241Hz), 113.3, 109.8, 109.2, 108.7, 96.4, 83.6, 82.0(t, J=26Hz), 80.5, 80.0, 75.4, 73.4, 70.8, 70.1, 65.9, 63.4, 35.3(t, J= 23Hz), 26.6, 26.0, 25.9, 25.5, 25.3, 24.9, 24.5, 24.4; $\nu_{max}(CH_2Cl_2)$ 2976, 2934, 2884, 1444, 1382, 1350, 1121, 1075, 739cm^{-1}; FAB/MS m/z 535(M^+-H), 521(M^+-Me), 479, 113, 101, 85, 59, 43; $[\alpha]_D^{20}$=-43.8 (c=0.14, $CHCl_3$); Found: C55.91, H7.14%; $C_{25}H_{38}F_2O_{10}$ requires: C55.96, H7.11%.

Preparation of methyl 2,3,4-tri-*O*-acetyl-9,10-*O*-isopropylidene-6,7-dideoxy-7,7-difluoro-8,11-anhydro-D-*arabino*-α-D-*gluco*-undecopyranoside (14). To a solution of 2,5-anhydro-1-deoxy-1,1-difluoro-3,4-*O*-isopropylidene-D-*erythro*-penta-1-enitol (**20**) (200mg, 1.04mmol) and methyl-2,3,4-tri-*O*-acetyl-6-deoxy-6-iodo-α-D-glucopyranoside (**9**)[15] (1.34g, 3.12mmol) in degassed benzene (10ml) was added a solution of AIBN (85mg, 0.52mmol) and tri-n-butyltinhydride (1.02ml, 3.8mmol) in degassed benzene (4ml) over 12h by means of syringe pump. The reaction mixture was refluxed for 2h and allowed to cool to room temperature. Iodine (30mg, 0.12mmol) and carbon tetrachloride (0.5ml) were added and the mixture was concentrated. The residue was taken up in ethyl acetate (15ml), stirred vigorously with a saturated solution of potassium fluoride (20ml) for 2h and filtered. The organic phase was separated, washed with saturated potassium fluoride (3x20ml), water (20ml), brine (20ml), dried over $MgSO_4$ and concentrated. Chromatography (30% petrol/ether) afforded the title compound (119mg, 23%) as white crystals (m.p. 55 °C, ether-petrol). δ_H (400MHz, $CDCl_3$) 5.42(1H, t, J=10.2Hz, H-3), 4.89(1H, d, J=3.6Hz, H-1), 4.85-4.70(4H, m, H-10, 9, 4, 2), 4.22(1H, t, J=9.8Hz, H-5), 4.10(1H, d, J= 10.7Hz, H-11a), 3.67(1H, dt, J=14.6, 3.6Hz, H-8), 3.53(1H, dd, J=10.8, 3.6Hz, H-11b), 3.40(3H, s, OMe), 2.65-2.25(2H, br m, H-6a, 6b), 2.04, 2.00, 1.97(3H, 3s, 3xOAc), 1.45, 1.28(6H, 2s, 2xMe); δ_F (376.3MHz, $CDCl_3$) -96.0(dm, J=265Hz), -103.0(ddd, J=265, 28, 12Hz); δ_C (100.6MHz, $CDCl_3$) 170.2, 169.95, 169.91, 121.3(t, J=243 Hz), 113, 96.4, 82.9(dd, J= 34, 27Hz), 80.4, 79.4, 72.9, 71.8, 70.8, 70.0, 63.5, 55.4, 35.3(t, J=22Hz), 25.6, 24.4, 20.7, 20.6 ; $\nu_{max}(CH_2Cl_2)$ 2989, 2941, 2753, 1372, 1266, 1240, 1225, 1165, 1121, 1074, 1047, 993, 738, 704cm^{-1}; FAB/MS m/z 495(M^+-H), 481(M^+-Me), 465, 303, 245, 137; $[\alpha]_D^{20}$=+71.4 (c=0.7, $CHCl_3$); Observed(M^+-H): 495.1685 $C_{21}H_{29}F_2O_{11}$ requires: 495.1678.

Preparation of 2,5-anhydro-1-deoxy-1,1-difluoro-3,4-*O*-isopropylidene-D-*erythro*-penta-1-enitol (20). Dibromodifluoromethane (4.19ml, 45.8mmol) and hexamethylphosphorous triamide (8.34ml, 45.8mmol) were added to a solution of (-)2,3-*O*-isopropylidene-D-erythronolactone (1.45g, 9.2mmol) in tetrahydrofuran (80ml) at -20°C. A white precipitate formed and the mixture was allowed to warm to room temperature for 20min.

Zinc powder (3g, 45.8mmol) was added along with another portion of hexamethylphosphorous triamide (1.6ml, 9.2mmol) and the mixture was refluxed for 4h. The mixture was poured into ether (300ml), washed with aqueous copper sulphate (4x100ml), water (100ml), brine (100ml), dried over $MgSO_4$ and evaporated. Chromatography (15% ether/petrol) afforded the title compound (896mg, 51%) as a pale yellow oil. δ_H (400MHz, $CDCl_3$) 5.30(1H, dd, J=6.3, 3.0Hz, H-3), 4.85(1H, m, H-4), 4.28(1H, d, J=10.5Hz, H-5a), 3.93(1H, dd, J=10.5, 4.2Hz, H-5b), 1.46(3H, s, Me), 1.35(3H, s, Me); δ_F (376.3MHz, $CDCl_3$) -102.5(d, J=85Hz), -118.0(d, J=85Hz); δ_C (100.6MHz, $CDCl_3$) 150.2(dd, J= 288, 273Hz), 119.4(dd, J=49, 14Hz), 113.2, 79.0, 77.0, 75.2, 26.4, 25.2; ν_{max}(film) 2992, 2943, 1790, 1384, 1275, 1277, 1232, 1211, 1159, 1114, 1061, 1031, 982, 885, 866cm^{-1}; m/z 192(M^+), 177(M^+-Me), 109, 76; $[\alpha]_D^{20}$=-206.0 (c=2.15, CH_2Cl_2); Observed (M^+): 192.0591; $C_8H_{10}F_2O_3$ requires: 192.0598.

Preparation of 1,2;3,4;9,10-tri-*O*-isopropylidene-6,7-dideoxy-7,7-difluoro-8,11-anhydro-D-*arabino*-α-D-*galacto*-undecopyranose. (15) To a solution of 2,5-anhydro-1-deoxy-1,1-difluoro-3,4-*O*-isopropylidene-D-*erythro*-penta-1-enitol (**20**) (165mg, 0.85mmol) and 1,2;3,4-di-*O*-isopropylidene-6-deoxy-6-iodo-α-D-galactopyranose (**10**)[15] (950mg, 2.55mmol) in degassed benzene (7ml), heated to reflux, was added a solution of AIBN (70mg, 0.42mmol) and tri-n-butyltinhydride (0.663ml, 3.1mmol) in degassed benzene (3.5 ml) over 10h by means of syringe pump. The reaction mixture was refluxed for 3h and allowed to cool to room temperature. Iodine (30mg, 0.12mmol) and carbon tetrachloride (0.5ml) were added and the mixture was evaporated. The residue was taken up in ethyl acetate (15ml), stirred vigorously with a saturated solution of potassium fluoride (20ml) for 2h and filtered. The organic phase was separated, washed with saturated potassium fluoride (3x20ml), water (20ml), brine (20ml), dried over $MgSO_4$ and concentrated *in vacuo*. Chromatography (50% petrol/ether) afforded the title compound (51mg, 13%) as white crystals (m.p. 93-97°C, ethanol). δ_H (400MHz, $CDCl_3$) 5.46(1H, d, J=5.0Hz, H-1), 4.81(2H, m, H-10, 9), 4.58(1H, dd, J=7.5, 2.5Hz, H-3), 4.26(1H, dd, J=5.0, 2.5Hz, H-5), 4.12(3H, m, H-11a, 4, 2), 3.75(1H, dt, J=14.8, 5.0Hz, H-8), 3.53(1H, dd, J=10.4, 3.9Hz, H-11b), 2.65-2.22(2H, br m, H-6a, 6b), 1.50, 1.46, 1.42, 1.31, 1.29, 1.28(18H, 6s, 6xMe); δ_F (376.3MHz, $CDCl_3$) -98.0(dq, J=256, 17Hz), -101.5(dtd, J=256, 21, 6Hz); δ_C (100.6MHz, $CDCl_3$) 121.5(dd, J=247, 241Hz), 112.8, 109.3, 108.8, 96.44, 82.5(dd, J=29, 24Hz), 80.6, 79.7, 73.5, 72.7, 70.7, 70.2, 62.8, 35.6(t, J=23.2Hz), 26.0, 25.9, 25.7, 25.0, 24.7, 24.5; ν_{max} (CH_2Cl_2) 2989, 2938, 1379, 1287, 1212, 1166, 1120, 1100, 1068, 994, 913, 862, 744, 703cm^{-1}; FAB/MS m/z 437(M^++H), 421(M^+-Me), 379, 113, 85, 59, 43; $[\alpha]_D^{20}$=-62.8 (c=0.18, $CHCl_3$); Found: C54.61, H6.90%; $C_{20}H_{30}F_2O_8$ requires: C55.04, H6.93%.

Preparation of ethyl 4,7-anhydro-2,3-dideoxy-3,3-difluoro-5,6;8,9-di-*O*-isopropylidene-D-*glycero*-L-*galacto*-nononate (16). A solution of 2,5-anhydro-1-deoxy-1,1-difluoro-3,4;6,7-di-*O*-isopropylidene-D-*gulo*-hept-1-enitol (**1**)[5] (153mg, 0.52mmol) and ethyl bromoacetate (0.58ml, 5.2mmol) in benzene (5ml) was degassed by heating at reflux for 30min. To this refluxing solution was added a degassed solution of tri-n-butyltinhydride (1.40ml, 5.0mmol) and AIBN (10mg) in benzene (2.5ml) over 12h by means of syringe pump. The reaction mixture was allowed to cool, ether (30ml) added and the mixture stirred with saturated potassium fluoride (10ml) for 30min. The organic phase was separated, filtered and dried over $MgSO_4$. The solvent was removed under reduced pressure to give a yellow oil. Column chromatography (50% ether/petrol) furnished **1** (6mg, 4%) and ethyl 4,7-anhydro-2,3-dideoxy-3,3-difluoro-5,6;8,9-di-*O*-isopropylidene-D-*glycero*-L-*galacto*-nononate (**16**) (100mg, 51%) as a colourless oil. δ_H (270MHz; $CDCl_3$) 4.83(1H, dd, J=6.1, 3.7Hz, H-5), 4.66(1H, ddd, J=6.1, 4.2, 0.7Hz, H-6), 4.38(1H, dd J=14.6, 7.1Hz, H-8), 4.22(1H, dd, J=8.5, 6.8Hz, H-9a),

4.18(2H, qd, J=7.1, 1.5Hz, $OC\underline{H}_2CH_3$), 3.94(1H, ddd, J=13.4, 4.4, 3.9Hz, H-4), 3.71(1H, dd, J=8.5, 7.3Hz, H-9b), 3.62(1H, dd, J=8.0, 4.2Hz, H-7), 3.24(2H, m, H-2), 1.48(3H, s, Me), 1.44(3H, s, Me), 1.39(3H, s, Me), 1.28(3H, s, Me), 1.27(3H, t, J=7.1Hz, $OCH_2C\underline{H}_3$); δ_F (84.3MHz; $CDCl_3$) -93.6(ddd, J=266, 34, 15Hz), -103.3(dd, J=266, 17Hz); δ_C (67.9MHz; $CDCl_3$) 167.1(t, J=4Hz), 119.5(dd, J=247, 244Hz), 113.6, 110.1, 84.2, 81.8(dd, J=34, 28Hz), 80.5, 79.9(d, J=6Hz), 75.4, 66.0, 61.0, 39.7(t, J=24Hz), 26.7, 25.5, 25.4, 24.3, 14.1; $\nu_{max}(CH_2Cl_2)$ 2938, 1738, 1373 1211, 1162, 1109, 1064cm^{-1}; m/z 365(M^+-Me), 277, 201, 185, 101, 43; Observed(M^+-Me): 365.1407; $C_{16}H_{23}F_2O_7$ requires: 365.1412.

Preparation of ethyl 4,8-anhydro-2,3-dideoxy-3,3-difluoro-5,6,7,9-tetra-*O*-(trimethylsilyl)-D-*glycero*-D-*gulo*-nononate (18a) and 4,8-anhydro-2,3-dideoxy-3,3-difluoro-5,6,7,9-tetra-*O*-(trimethylsilyl)-D-*glycero*-D-*ido*-nononate (18b). Ethyl bromoacetate (0.132ml, 1.2mmol) was added to a solution of 2,6-anhydro-1-deoxy-1,1-difluoro-3,4,5,7-tetra-*O*-(trimethylsilyl)-D-*gluco*-hept-1-enitol (**17**)[5] (200mg, 0.4mmol) in degassed benzene (7ml) and to this mixture was added at reflux a solution of AIBN (32.5mg, 0.2mmol) and tri-n-butyltinhydride (0.390ml, 1.46mmol) in degassed benzene (3.5ml) over 12h by means of syringe pump. The crude mixture was concentrated, taken up in undistilled ether (25ml), diazabicyclo[5.4.0]undec-7-ene (0.3ml, 2mmol) was added and a white precipitate formed. The mixture was titrated with iodine, filtered through a short silica column, eluting with ether, and concentrated. Chromatography (10% ether/petrol) afforded a mixture of the title compounds (64mg, 27%) as a colourless oil. High pressure liquid chromatography (5% ethyl acetate/hexane) enabled separation of the two isomers, which existed as a 10:3 mixture. Major isomer **18a**: δ_H (400MHz, toluene-d_8) 3.95(1H, ddd, J=21.1, 8.4, 4.7Hz, H-4), 3.86(1H, m, H-5), 3.83(2H, q, J=7.4Hz, $O\underline{CH}_2CH_3$), 3.61(2H, m, H-9a, 9b), 3.58(1H, t, J=8.6Hz, H-7), 3.50(1H, t, J=8.6Hz, H-6), 3.14(2H, m, H-8, 2a), 2.81(1H, td, J=15.1, 8.5Hz, H-2b), 0.87(3H, t, J=7.1Hz, $OCH_2\underline{CH}_3$), 0.25-0.06(36H, m, 4xTMS) ; δ_F (376.3MHz, toluene-d_8) -101.5(dddd, J=258, 21, 10, 5Hz), -106(ddt, J=258, 20, 10Hz); δ_C (100.6MHz, $CDCl_3$) 167.1, 120.6(t, J=248Hz), 81.5, 79, 77.8(t, J=25Hz), 71.0, 70.9, 62.1, 60.9, 40.1(t, J=26Hz), 14.2, 1.4, 1.1, 0.9, 0.3; $[\alpha]_D^{20}$=+9.9 (c=0.6, CH_2Cl_2). Minor isomer **18b**: δ_H (400MHz, toluene-d_8) 4.54(1H, ddd, J=20.2, 10.9, 5.3Hz, H-4), 4.0(1H, t, J=6.1Hz, H-7), 3.92(1H, dd, J=7.3, 5.4Hz, H-5), 3.84(2H, q, J=7.2Hz, $O\underline{CH}_2CH_3$), 3.66(4H, m, H-9a, 9b, 8, 6), 3.15(1H, br m, H-2a), 2.95(1H, td, J=16.6, 11.2Hz, H-2b), 0.9(3H, t, J=7.2Hz, $OCH_2\underline{CH}_3$), 0.34-0.08(36H, m, 4xTMS); δ_F (376.3MHz, $CHCl_3$) -95.4(ddd, J=260, 30, 20Hz), -101.5(dm); $[\alpha]_D^{20}$=+11.1 (c=0.2, CH_2Cl_2). Mixture: $\nu_{max}(CH_2Cl_2)$ 2958, 1745, 1401, 1378, 1264, 1251, 1154, 1106, 1026.5, 966, 870, 844, 742cm^{-1}; FAB/MS m/z 589(M^++H), 574 , 498, 483, 463, 409, 393, 373, 353, 319, 305, 299, 275, 249, 217, 191, 147, 129; Observed(M^++H): 589.2680; $C_{23}H_{51}F_2O_7Si_4$ requires: 589.2679.

Preparation of [2S(1R)3R4R5S9S] 2-(1,2-isopropylenedioxy-ethyl)-3,4-isopropylenedioxy-6,6-difluoro-7,7-di-ethoxycarbonyl-9-methyl-1-oxaspiro[4,4]nonane (19). To a solution of 2,5-anhydro-1-deoxy-1,1-difluoro-3,4,6,7-di-*O*-isopropylidene-D-*gulo*-hept-1-enitol (**1**)[5] (200mg, 0.684mmol) and diethyl allyliodomalonate[17] (670mg, 2mmol) in degassed benzene (7ml) was added hexabutylditin (0.103ml, 0.20mmol) and the solution was irradiated for 1.5h. Tri-n-butyltinhydride (0.667ml, 2.40mmol) was added, the mixture was refluxed overnight and allowed to cool to room temperature. Iodine (30mg, 0.12mmol) and carbon tetrachloride (0.5ml) were added and the mixture was concentrated. The residue was taken up in ethyl acetate (15 ml), stirred vigorously with a saturated solution of potassium fluoride (20 ml) for 2h and filtered. The organic phase was separated, washed with saturated potassium fluoride (3x20ml), water (20ml), brine

(20ml), dried over $MgSO_4$ and concentrated. Chromatography (40% ether/petrol) afforded the title compound (177mg, 52%) as a colourless oil. δ_H (400MHz, $CDCl_3$) 4.88(1H, d, J=5.9Hz, H-4), 4.62(1H, dd, J=5.9, 4.3Hz, H-3), 4.30(5H, m, H-1', 2xO$\underline{CH_2}CH_3$), 4.16(1H, dd, J=8.6, 6.8Hz, H-2'a), 3.66(1H, t, J=8.5Hz, H-2'b), 3.62(1H, dd, J=7.6, 4.3Hz, H-2), 2.87(1H, m, H-8a), 2.29(1H, m, H-9), 1.80(1H, ddd, J=12.9, 9.3, 3.1Hz, H-8b), 1.50(3H, s, CMe_2), 1.39(3H, s, CMe_2), 1.31-1.28(12H, m, CMe_2, 2xOCH$_2\underline{CH_3}$), 1.07(3H, d, J=7.4Hz, Me); δ_F (376.3MHz, $CDCl_3$) -109.5(d, J=252Hz), -112.3(d, J=253Hz); δ_C (100.6MHz, $CDCl_3$) 165.8, 165.0, 123.0(dd, J=288, 249Hz), 113.6, 109.4, 89.3(dd, J=31, 17Hz), 81.4, 80.6, 75.5, 66.1, 63.3(dd, J=41, 18Hz), 62.7, 62.1, 36.4, 35.7, 26.9, 25.8, 25.4, 24.9, 18.8, 14.0, 13.8; ν_{max}(CH_2Cl_2) 2986, 1742, 1382, 1372, 1265, 1211, 1109, 1069, 738, 704cm^{-1}; FAB/MS m/z 493(M^++H), 477(M^+-Me), 435, 137, 101; $[\alpha]_D^{20}$=-22.2 (c=0.9, CH_2Cl_2); Observed(M^++H): 493.2244; $C_{23}H_{35}F_2O_9$ requires: 493.2249.

Preparation of [3R4R5S9S] 3,4-isopropylenedioxy-6,6-difluoro-7,7-di-ethoxycarbonyl-9-methyl-1-oxaspiro[4,4]nonane (21). To a solution of 2,5-anhydro-1-deoxy-1,1-difluoro-3,4-*O*-isopropylidene-D-*erythro*-penta-1-enitol (**20**) (200 mg, 1.04mmol) and diethyl allyliodomalonate[17] (1.01g, 3.1mmol) in degassed benzene (10ml) was added hexabutylditin (0.158ml, 0.3mmol) and the solution was irradiated for 1.5h. Tri-n-butyltinhydride (1.022ml, 3.8mmol) was added and the mixture was heated at reflux overnight. Iodine (30mg, 0.12mmol) and carbon tetrachloride (0.5 ml) were added and the mixture was concentrated. The residue was taken up in ethyl acetate (15ml), stirred vigorously with a saturated solution of potassium fluoride (20ml) for 2h and filtered. The organic phase was separated, washed with saturated potassium fluoride (3x20ml), water (20ml), brine (20ml), dried over $MgSO_4$ and concentrated *in vacuo*. Chromatography (50% ether/petrol) afforded the title compound (122mg, 30%) as a yellow oil. δ_H (400MHz, $CDCl_3$) 4.84(1H, d, J=5.9Hz, H-4), 4.77(1H, dd, J=5.4, 4.4Hz, H-3), 4.23(4H, m, OEt), 3.70(1H, d, J=10.8Hz, H-2a), 3.66(1H, dd, J=10.4, 4.1Hz, H-2b), 2.80(1H, m, H-8a), 2.24(1H, m, H-9), 1.87(1H, ddd, J=9.2, 5.3, 3.1Hz, H-8b), 1.54(3H, s, CMe), 1.35(3H, s, CMe), 1.27(6H, m, 2xOCH$_2\underline{CH_3}$), 1.08(3H, d, J=7.3Hz, Me); δ_F (376.3MHz, $CDCl_3$) -107.5(d, J=255Hz), -112.5(d, J=255Hz); δ_C (100.6MHz, $CDCl_3$) 165.8, 165.3, 123.5(dd, J=288, 249Hz), 113.4, 90.2(dd, J=31, 17Hz), 81.2, 80.4, 71.4, 63.3(dd, J=42, 19Hz), 62.3, 62.1, 36.2, 35.9, 26.1, 25.3, 18.6, 14.0, 13.8; ν_{max}(CH_2Cl_2) 2984, 1743, 1300, 1267, 1232, 1101, 1069, 737cm^{-1}; FAB/MS m/z 393(M+H+), 377(M^+-Me), 347, 289, 121, 93, 59, 43, 29; Observed(M^++Na): 415.1548 $C_{18}H_{26}F_2O_7Na$ requires: 415.1544; $[\alpha]_D^{20}$=-34.7 (c=0.6, CH_2Cl_2).

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