102. Glycosylidene Carbenes

Part 23

Regioselective Glycosidation of Deoxy- and Fluorodeoxy-*myo*-Inositol Derivatives

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Dedicated to *Edgar Heilbronner* on the occasion of his 75th birthday

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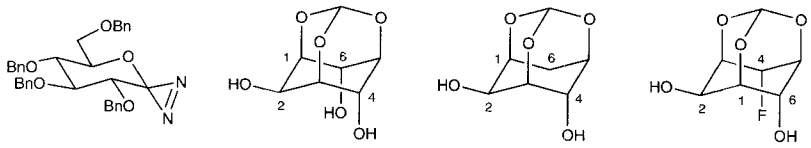
To demonstrate the relevance of the kinetic acidity of individual OH groups for the regioselectivity of glycosylation by glycosylidene carbenes, we compared the glycosylation by **1** of the known triol **2** with the glycosylation of the diol D-**3** and the fluorodiol L-**4**. Deoxygenation with Bu_3SnH of the phenoxythiocarbonyl derivative of **5** (*Scheme 1*) or the carbonothioate **6** gave the racemic alcohol (±)-**7**. The enantiomers were separated *via* the allophanates **9a** and **9b**, and desilylated to the deoxydiols D- and L-**3**, respectively. The assignment of their absolute configuration is based upon the CD spectra of the bis(4-bromobenzoates) D- and L-**10**. The (+)-(*R*)-1-phenylethylcarbamates **13a** and **13b** (*Scheme 2*) were prepared from the fluoroinositol (±)-**11** *via* (±)-**4** and the silyl ether (±)-**12** and separated by chromatography. The absolute configuration of **13a** was established by X-ray analysis. Decarbamoylation of **13a** (→ L-**12**) and desilylation afforded the fluorodiol L-**4**. The H-bonds of D-**3** and L-**4** in chlorinated solvents and in dioxane were studied by IR and ^{1}H-NMR spectroscopy (*Fig. 2*). In both diols, HO–C(2) forms an intramolecular, bifurcated H-bond. There is an intramolecular H-bond between HO–C(6) and F in solutions of L-**4** in CH_2Cl_2, but not in 1,4-dioxane; the solubility of L-**4** in CH_2Cl_2 is too low to permit a meaningful glycosidation in this solvent. Glycosidation of D-**3** in dioxane by the carbene derived from **1** (*Scheme 3*) followed by acetylation gave predominantly the pseudodisaccharides **18**/**19** (38%), derived from glycosidation of the axial OH group besides the pseudodisaccharides **16**/**17** (13%) and the epoxides **20**/**21** (7%), derived from protonation of the carbene by the equatorial OH group. Similarly, the reaction of L-**4** with **1** (*Scheme 4*) led to the pseudodisaccharides **28**/**29** (46%) and **26**/**27** (14%), derived from deprotonation of the axial and equatorial OH groups, respectively. Formation of the epoxides involved deprotonation of the intramolecularly H-bonded tautomer, followed by intramolecular alkylation, elimination, and substitution (*Scheme 4*). The regio- and diastereoselectivities of the glycosidation correlate with the H-bonds in the starting diols.

Introduction. – The glycosylation of alcohols by glycosylidene diazirines (for reviews, see [1–3]) is a reactivity-based method for the analysis of intramolecular H-bonds in solution, complementing the analysis by IR (see *e.g.* [4–7]) and NMR spectroscopy (see *e.g.* [8–12]). The regio- and stereoselectivity of the glycosidation of diols and triols by glycosylidene diazirines is determined by the relative kinetic acidity of the individual OH groups and depends mainly on intramolecular H-bonds [13–20]. A case in point is the glycosidation of the *myo*-inositol derivative **2**. This triol possesses an intramolecular H-bond between HO–C(4) and HO–C(6) both in solution and in the solid state [19], and (in relatively unpolar solvents) a bifurcated H-bond from HO–C(2) to O–C(1) and O–C(3). The kinetically most highly acidic OH group in dilute solutions is the one accepting an intramolecular H-bond. In keeping with this analysis, glycosidation of **2** with the diazirine **1** led in 90% to a 1:1 mixture of 4-*O*- and 6-*O*-β-D-glucosides.

We intended to check this interpretation by glycosylating the deoxy analogue **3** and to extend the study of H-bonding to the fluorinated deoxy analogue **4**. In dilute solutions in apolar solvents, the axial[1]) OH group of **3** is expected to be free, while the axial OH of **4** should be involved in a weak intramolecular H-bond, since F is a weak H-bond acceptor, but not a H-bond donor[2]).



1 **2** **3** **4**

The dependence of the reactivity of the individual OH groups of **2**–**4** upon H-bonding should be revealed by a comparative glycosidation with **1**.

Results and Discussion. – 1. *Synthesis of the Deoxydiol* D-**3** *and of the Fluorodeoxydiol* L-**4**. Stannylidenation of the diol **5** [33] followed by acylation with phenoxythiocarbonyl chloride (= phenyl carbonochloridothioate) and deoxygenation [34] gave 55% of the alcohol (±)-**7** (*Scheme 1*). Alternatively, (±)-**7** was prepared (60%) by deoxygenation [35] of the carbonothioate **6**, obtained in 51% yield from **5** and 1,1′-thiocarbonylbis[1*H*-imidazole]. Treatment of the Li salt of (±)-**7** with (+)-(*R*)-1-phenylethyl isocyanate at −78° [36] gave a 2:1 mixture of the diastereoisomeric carbamates **8a**/**8b** (38%, separated by prep. HPLC) and the allophanates **9a** (24%) and **9b** (22%). (+)-(*R*)-1-Phenylethyl isocyanate transformed **8a**/**8b** completely to **9a** and **9b**. Transesterification of each of the allophanates **9a** and **9b** with NaOEt in EtOH gave the alcohols D-**7** (97%, $[\alpha]_D^{25} = +0.2$) and L-**7** ($[\alpha]_D^{25} = -0.2$) that were desilylated to the enantiomerically pure diols D- and L-**3** (95%), respectively.

The absolute configuration of D-**3** was deduced from the CD spectra [37] [38] of the bis(4-bromobenzoate) D-**10**. The spectra showed a positive first *Cotton* effect [39] in MeCN (252 nm, $\Delta\varepsilon = +18.7$; 233 nm, $\Delta\varepsilon = -2.7$), indicating a clockwise arrangement of the $ArCO_2$ groups. The enantiomer L-**10**, derived from L-**3**, showed a negative first *Cotton* effect (252 nm, $\Delta\varepsilon = -19.2$; 233 nm, $\Delta\varepsilon = +1.3$).

The ^{1}H- and ^{13}C-NMR signals of the CH_2 groups of the deoxyinositols **3** and **7**–**10** appear at high field (H_{eq}–C(6) at 2.13–2.83 ppm, H_{ax}–C(6) of **3**, **7**, **8a**, **8b**, and **10** at 1.66–2.13 ppm, H_{ax}–C(6) of **9a** at 1.15 ppm, H_{ax}–C(6) of **9b** at 0.46 ppm, C(6) at 27–29 ppm). Both H_{eq}–C(6) and H_{ax}–C(6) show characteristic long-range couplings of *ca.* 1.5 Hz, the former with H–C(4) and the latter with the orthoformyl H. At room temperature, NMR signals of the (*E*)- and the (*Z*)-rotamers of **8a** and **8b** are observed in a ratio of *ca.* 4:1. The (*E*)-configuration (= *trans*-arrangement of NR and OR) is assumed for the main rotamer (*cf.* [40]). Aryl *N*-methylcarbamates prefer this configuration in solution [41]. This configuration is also preferred in the solid state; > 95% of the *N*-monosubstituted carbamates recorded in the *Cambridge Database* adopt it. This assignment is strongly supported by the X-ray analysis of the fluorocarbamate **13a** (see below). The allophanates **9a** and **9b** show NMR signals of a single rotamer. This is due to the intramolecular H-bond between N–H and the more distant C=O group, as depicted in *Scheme 1*. This H-bond is evidenced by the NH band at 3338 cm^{-1}, the low field shifts of NH in $CDCl_3$ solution (**9a**:

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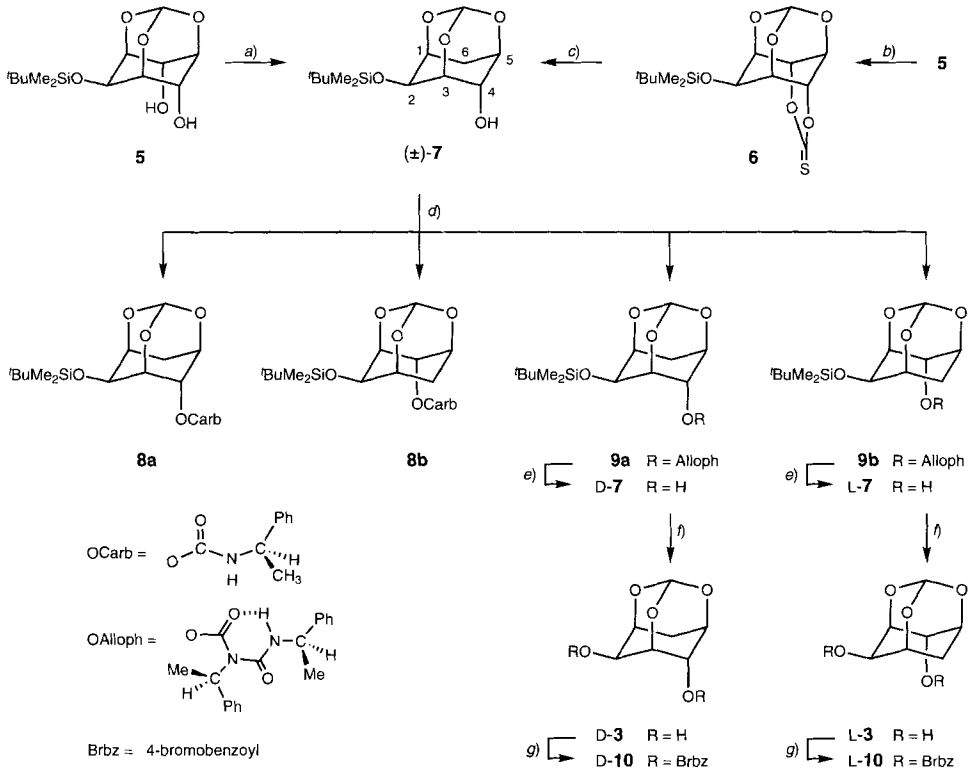
[1]) 'Axial' and 'equatorial' relate to the carbocyclic ring of the trioxatricyclodecane system.

[2]) F often replaces OH groups of drugs. For investigations of the interaction between OH and F groups, see *e.g.* [21–28]. For an extensive list of fluorinated analogues of natural compounds, see [29–32].

Scheme 1

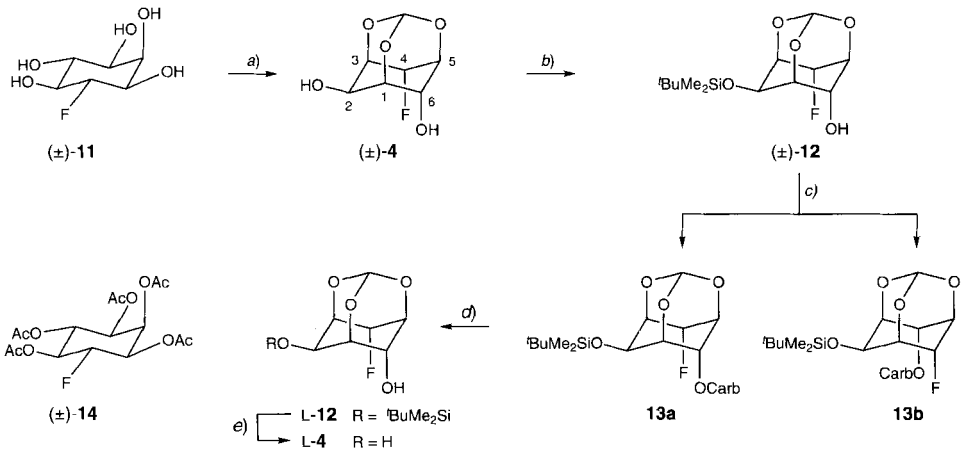


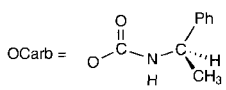
a) Bu_2SnO, MeOH, reflux; PhOC(S)Cl, dioxane, r.t.; Bu_3SnH, 2,2′-azobis[isobutyronitrile] (AIBN), toluene, reflux; 55%. *b*) 1,1′-Thiocarbonylbis[1*H*-imidazole], toluene, 80°; 51%. *c*) Bu_3SnH, AIBN, toluene, reflux; 65%. *d*) (+)-(*R*)-1-Phenylethyl isocyanate, BuLi, THF, −78°. *e*) Na, EtOH, reflux; 97.5% of D-**7**; 94% of L-**7**. *f*) $Bu_4NF \cdot 3\ H_2O$, THF, r.t.; 95% of D-**3**; 99% of L-**3**. *g*) 4-Bromobenzoyl chloride, AgOTf, 4-(dimethylamino)pyridine (DMAP), pyridine, 70°; 61% of D-**10**; 54% of L-**10**.

8.98, **9b**: 9.06 ppm), and the good solubility of the allophanates in apolar solvents [42–45]. The upfield shift of H_{ax}–C(6) of **9a** and **9b** (see above) indicates its location in the shielding zone of the imido moiety. Models suggest that the carbonyl rather than the large *N*-phenethyl group is oriented below the plane of the ring and that rotation around the C(4)–O bond is restricted.

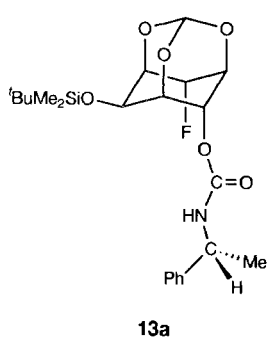
The racemic fluorodeoxy analogue (±)-**4** was prepared by acid-catalyzed orthoesterification of 4-deoxy-4-fluoro-*myo*-inositol ((±)-**11**) [46] (see also [47]) with excess triethyl orthoformate (*Scheme 2*) and isolated in a yield of 50% besides 33% of the starting material (±)-**11**, characterized as the peracetate (±)-**14** [46]. The diol (±)-**4** was selectively silylated with *t*-$BuMe_2SiOTf$ in the presence of 2,6-lutidine to give the axial monoalcohol (±)-**12** (81%). Treatment of (±)-**12** with (+)-(*R*)-1-phenylethyl isocyanate, Et_3N, and 4-(dimethylamino)pyridine afforded the distereoisomeric carbamates **13a** (41%) and **13b** (35%). X-Ray analysis of **13a** (*Fig. 1*) established its L-*myo*-configuration[3]). Decar-

Scheme 2





a) Triethyl orthoformate, $TsOH \cdot H_2O$, DMSO, 100°; 50%.
b) *t*-$BuMe_2SiOTf$, 2,6-lutidine, DMF; 81%.
c) (+)-(*R*)-1-Phenylethyl isocyanate, Et_3N, DMAP, CH_2Cl_2.
d) Na, MeOH, 65°; 72%.
e) $Bu_4NF \cdot 3\ H_2O$, THF, r.t.; 85%.



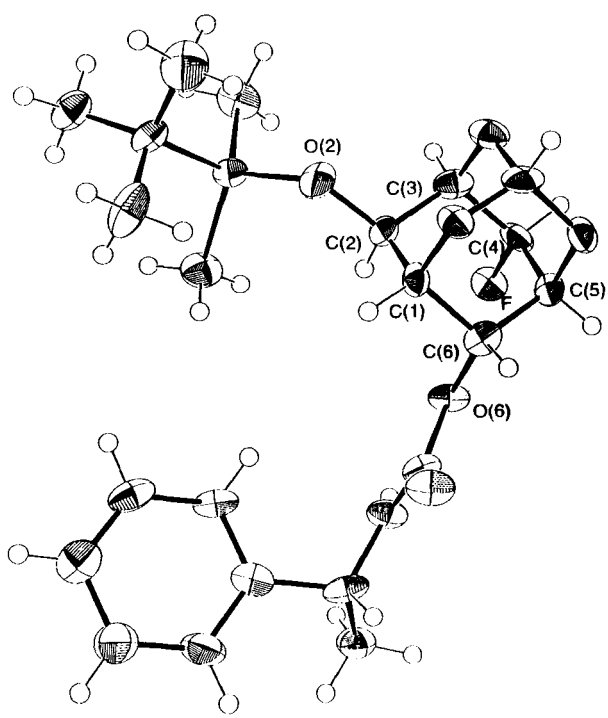


Fig. 1. *X-Ray structure of* **13a**

bamoylation of **13a** with NaOMe in MeOH gave L-**12** (72%), which was desilylated to the enantiomerically pure diol L-**4** (85%, $[\alpha]_D^{25} = +6$).

The F-substituent in **4**, **12**, **13a**, and **13b** is evidenced by the downfield shift of H–C(4) (5.2–5.4 ppm) and C(4) (84.9–86.9 ppm) and their characteristic coupling with F (^2J(F,H) = 47.5–47.9 Hz, ^1J(F,C) = 187–190 Hz). Vicinal couplings with F are observed for H–C(3) and H–C(5) (^3J(F,H) ≈ 1.5 Hz) and geminal couplings for C(3) (^2J(F,C) = 22–23 Hz) and C(5) (^2J(F,C) = 19–20.5 Hz). The axial position of F is revealed by long-range couplings between F and H–C(2) (^4J(F,H) ≈ 2 Hz, probably 'through space'), between F and the orthoformyl H (^5J(F,H) = 4.2–4.7 Hz), and between H–C(4) and H–C(6) (^4J(H,H) ≈ 2 Hz). The carbamoyl moiety of **13a** is (*E*)-configurated in the solid state. In $CDCl_3$ solution, **13a** and **13b** are *ca.* 5:1 mixtures of (*E*)- and (*Z*)-conformers, as it has been observed for the carbamates **8a** and **8b**. The equilibrium of conformers is evidenced by the coalescence, above 50°, of the ^{1}H-NMR signals of **8a** and **8b**.

2. *Hydrogen Bonds of the Diols* **3** *and* **4**. The FT-IR spectrum of D-**3** (CH_2Cl_2, 0.001M) shows OH bands at 3604 and 3573 cm^{-1} (*Table 1*). The band at 3573 cm^{-1} was assigned to

Table 1. *IR Bands* [cm^{-1}] *of the OH Groups of the Diols* D-**3** *and* (±)-**4** *and the Alcohols* (±)-**7**, (±)-**12**, *and* **26–29**

	Solvent	Concentration	HO–C(2)	HO–C(6)[a])
D-**3**	CH_2Cl_2	< 0.005M	3573	3604
D-**3**	dioxane	0.005M	3533	3412 (br.)
(±)-**7**	CH_2Cl_2	0.2M	–	3605, 3487 (br.)
(±)-**4**	CCl_4	0.0005M	3582	3620, 3608[b])
(±)-**4**	CH_2Cl_2	< 0.005M	3568	3602
(±)-**4**	dioxane	0.005M	3533	3414
(±)-**12**	CH_2Cl_2	0.0035M	–	3606
26	CCl_4	0.02M	–	3620
27	CCl_4	0.02M	–	3619
28	CCl_4	0.014M	3585	–
29	CCl_4	0.018M	3585	–

[a]) HO–C(4) of D-**3** and (±)-**7**. [b]) Broad bands for intermolecular H-bonds at 3500–3200 cm^{-1}.

Table 2. ^{1}*H-NMR* (300 MHz, $CDCl_3$) *Chemical Shifts* [ppm] *and Coupling Constants* [Hz] *for the OH Groups of the Diols* D-**3** *and* (±)-**4** *and the Alcohols* (±)-**7**, (±)-**12**, *and* **26–29**

	Solvent, concentration	HO–C(2)	J(H–C(2),OH)	HO–C(6)[a])	J(H–C(6),OH)[a])	J(F,OH)
D-**3**	$CDCl_3$, 0.001M	3.18	11.8	2.08	4.3	–
D-**3**	(D_8)dioxane, 0.03M	4.38	11.3	4.36–4.30	[b])	–
D-**3**	(D_6)DMSO, 0.05M	5.21	6.5	5.71	4.1	–
(±)-**7**	$CDCl_3$, 0.05M	–	–	2.00	4.6	–
(±)-**4**	$CDCl_3$, < 0.005M	3.09	11.8	2.17	7.8	*ca.* 8.8
(±)-**4**	(D_8)dioxane, 0.03M	4.55	10.5	4.13	5.0	[c])
(±)-**4**	(D_6)DMSO, 0.05M	5.45	5.8	5.59	3.8	[c])
(±)-**12**	$CDCl_3$, 0.016M	–	–	2.18	7.5	*ca.* 7.5
26	$CDCl_3$, 0.05M	–	–	2.10–2.04	[b])	[b])
27	$CDCl_3$, 0.05M	–	–	2.36	*ca.* 6	*ca.* 6
28	$CDCl_3$, 0.05M	3.00	11.1	–	–	–
29	$CDCl_3$, 0.05M	3.14	11.6	–	–	–

[a]) HO–C(4) of D-**3** and (±)-**7**. [b]) Not determined. [c]) Not visible (< 1 Hz).

[3]) Coordinates and thermal parameters were deposited with the *Cambridge Crystallographic Data Center*, 12 Union Road, Cambridge CB2 1EW, England.

the equatorial HO–C(2), involved in a bifurcated intramolecular H-bond to O–C(1) and O–C(3) [16] [19] [48], while the band at 3604 cm^{-1} is mainly due to the axial OH group. This assignment is supported by the IR spectrum of (±)-**7** (3605 cm^{-1}) in CH_2Cl_2 solution. A small contribution to the band at 3605 cm^{-1} of a tautomer of D-**3** possessing a free equatorial HO–C(2) appears probable. A free OH group and an analogous tautomer are evidenced by a weak band at a similar wave number in the FT-IR spectra of 4,6-di-*O*-benzyl-1,3,5-*O*-methylidyne-*myo*-inositol (3608 cm^{-1}) and 4-*O*-benzyl-1,3,5-methylidyne-*myo*-inositol (0.005M, 3608 cm^{-1}) in CH_2Cl_2 solution [19]. The FT-IR spectrum of 0.005M D-**3** in dioxane shows two OH bands, a strong one at 3412 and a weak one at 3533 cm^{-1}. The former is due to HO–C(4) in an intermolecular H-bond to the solvent and the latter to the bifurcated H-bond of HO–C(2) (solvated and hence tetracoordinated?). This assignment is confirmed by the ^{1}H-NMR spectra of D-**3** in $CDCl_3$ and (D_8)dioxane solution, where the presence of the bifurcated H-bond is evidenced by the large vicinal J(H–C(2), OH) (> 11 Hz, *Table 2*). In (D_6)DMSO solution, J(H–C(2), OH) = 6.5 Hz is only slightly larger than J(H, OH) = 4.2–5.7 Hz for equatorial cyclohexanols [10] [49], indicating that the bifurcated H-bond is mostly broken in favor of intermolecular H-bonds to the solvent. The values for J(H–C(4), OH) in $CDCl_3$ and (D_6)DMSO are similar and indicate a free rotation around the C(4)–O bond (*cf.* with the value of 3.0–4.2 Hz for axial cyclohexanols [10] [49]).

Evidence for F···HO H-bonds is available from X-ray analysis, and IR and NMR spectroscopy. In the solid state, a steroidal 1,2-*cis*-fluorocyclopentanol possesses an intramolecular F···HO H-bond (distance F···H: 2.17 Å, dihedral angle O–H···F: 114°) [50]. All other 1,2-*cis*-fluoro alcohols in the *Cambridge Database* (8 structures) are involved in bifurcated H-bonds, the OH group forming a strong intermolecular H-bond to O or N (distance H···O/N: 1.77–2.12 Å, dihedral angle O–H···O/N: 157–175°) combined with a weak intramolecular H-bond to F (distance H···F: 2.15–2.71 Å, dihedral angle O–H···F: 88–115°). No example of a 1,3-diaxial fluoro alcohol was found. A dimer, bonded by two intermolecular OH···F H-bonds, has been observed in the solid state of racemic 2-fluoro-1,1,2-triphenylethanol [51]. The F substituent – and not the OH group – of 4-fluorophenol is involved in an intermolecular H-bond with α-cyclodextrin [52].

In CCl_4 solution, intramolecular F···HO H-bonds have been detected by IR spectroscopy. The $\Delta\nu$ values between the free and the H-bonded tautomers are small (10–20 cm^{-1} [53] [54]). Very often, these bands are not separated, and it is difficult to decide if there is an intramolecular H-bond or not [55–57]. However, in favorable cases, vicinal J(H,OH) in NMR spectra indicate whether the O–H bond is directed towards F or not. In this way, a F···HO H-bond has been evidenced in an anancomeric 1,2-*cis*-fluorocyclohexanol in chlorinated solvents [53]. *Kobayashi* and *Hirota* [58] detected 'through-space' couplings between F and XH in solutions of 2-fluorophenol (J = 3.7–4.8 Hz) and 2-fluorothiophenol (J = 2 Hz) in $CDCl_3$ and CCl_4, but not in C_6D_6, nor in (D_6)acetone or (D_6)DMSO. This has been rationalized by assuming that intramolecular F···HX H-bonds exist only in these chlorinated solvents, while intermolecular H-bonds are more stable in the other solvents. The rationalization is supported by the observation of a 'through-space' J(F,H) coupling for solutions in CCl_4 or (D_6)acetone of 2-fluorotoluene, requiring a close contact between F and H [58]. Similarly, 'through-space' J(F,^{13}C=O) and J(F,^{15}N) couplings have been reported for 2-fluorobenzamides, requir-

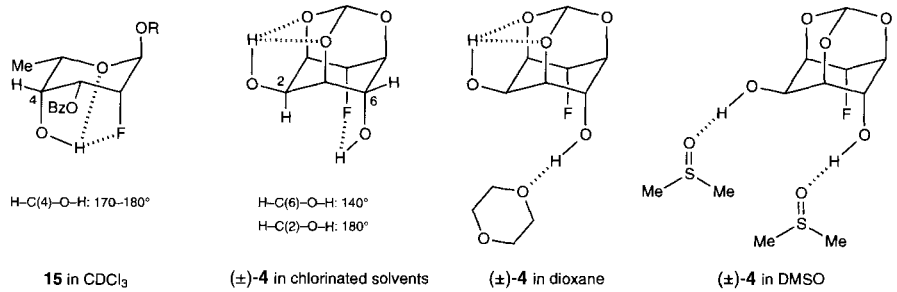


Fig. 2. *Preferred tautomers of* **15** *in* $CDCl_3$ *and of* (±)-**4** *in* $CDCl_3$, CD_2Cl_2, (D_8)*dioxane, and* (D_6)*DMSO*

ing an intramolecular F···HN H-bond [59]. A remarkable intramolecular H-bond has been observed in the ^{1}H-NMR spectrum ($CDCl_3$) of the α-L-talopyranoside **15** [60] (*Fig. 2*). The OH signal appears as a *t* with J(F,OH) of *ca.* 10 Hz and J(H,OH) = 10.5 Hz [61]. The large J(H,OH) indicates an antiperiplanar arrangement of H–C(4) and O–H and hence a bifurcated H-bond to the F-substituent and the ring-O-atom. Even inter-unit through-space J(F,H) couplings between F and H–O [60] or H–C groups [62] of oligosaccharides have been observed.

The structure of (±)-**4** in the solid state was established by X-ray analysis (*Fig. 3*)[3]). The C–F bond length (1.405 Å) is in agreement with the average value for this bond in deoxyfluoro carbohydrates. There are no F···HO H-bonds, although the O(6)···F distance (2.834 Å) in (±)-**4** is shorter than the O···F distances reported for short CF···HO intermolecular H-bonds [63]. HO–C(6) is involved in intermolecular H-bonds, as H-acceptor with HO–C(2′) (O···H′ distance 1.870 Å) and as H-donor to HO–C(2″) (H···O″ distance 1.823 Å). The absence of an intramolecular OH···F H-bond is not surprising,

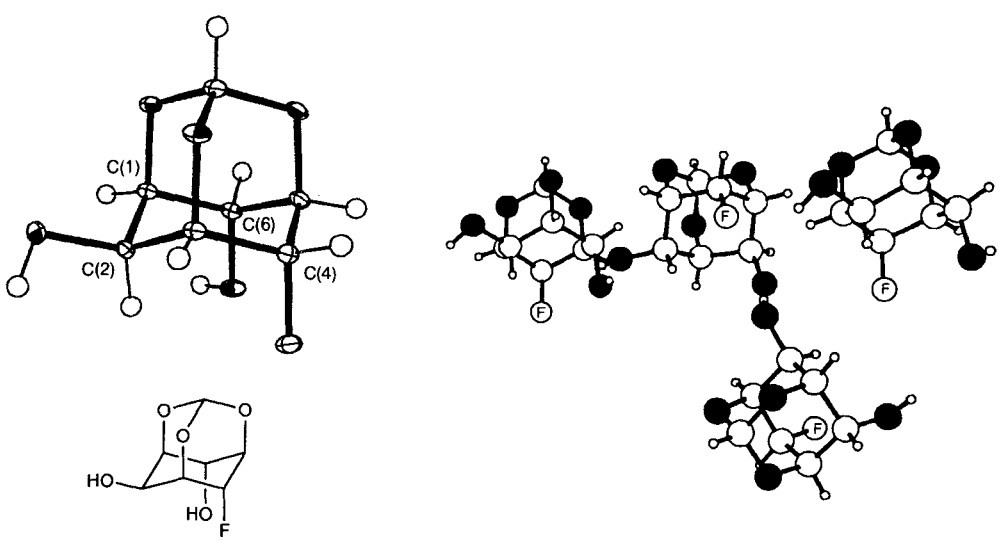


Fig. 3. *X-Ray structure of* (±)-**4**

considering that, as a rule, only strong intramolecular H-bonds are observed in the solid state [64], such as the H-bond between the two axial OH groups of **2** [19]. The F-substituent of (±)-**4** is, however, involved in a weak F···HC interaction with H–C(3‴) (F···H‴ distance 2.360 Å; for similar interactions, *cf.* [26] [65]).

The FT-IR spectrum of (±)-**4** in CH_2Cl_2 shows two OH bands, similar to L-**3** (*Table 1*). The band at 3568 cm^{-1} is assigned to the bifurcated H-bond. Strong intermolecular OH bands between 3500 and 3200 cm^{-1} in the FT-IR spectrum of (±)-**4** in CCl_4, even for a 0.0005M solution, prevent an unambiguous interpretation of the IR spectrum. No reference data are available for a ($CCl_4 \rightarrow CH_2Cl_2$) solvent shift of a OH···F absorption. Hence, no conclusions concerning the presence of free or OH···F H-bonded tautomers of (±)-**4** and (±)-**12** can be drawn.

In the ^{1}H-NMR spectrum of (±)-**4** in $CDCl_3$, HO–C(2) resonates at 3.09 ppm as *d* with a large coupling constant, evidencing a bifurcated H-bond (*Table 2*). The HO–C(6) signal of (±)-**4** and (±)-**12** appears at higher field as a broadened *t* with J(H,OH) ≈ 7.5 Hz and J(F,OH) ≈ 7.5–8.8 Hz. This strongly evidences the intramolecular H-bonds of (±)-**4** indicated in *Fig. 2*. Molecular-mechanics calculations (Macromodel V. 4.5, MM3* force field, gas phase) of L-**4** favor this H-bonded tautomer. The calculated dihedral angle H–C(6)–O–H of 140° corresponds to J(H,OH) = 7.5 Hz [61]. This is in keeping with the experimental values of (±)-**4** and (±)-**12**. An attempt to evidence the neighborhood of HO–C(6) and H–C(2) of (±)-**4** by a NOE failed due to saturation transfer from HO–C(6) *via* HDO to HO–C(2). Irradiation of HO–C(6) of the silyl ether (±)-**12** (in $CDCl_3$) led to NOE's for the signals of H–C(6) (4%), H–C(2) (3%), H–C(5) (2%), and H–C(1) (1%). This corroborates the presence of the intramolecular OH···F H-bond.

In (D_8)dioxane, the bifurcated H-bond of (±)-**4** is still present (J(2,OH) = 10.5 Hz), but the OH···F H-bond is broken (J(6,OH) = 5.0 Hz, no coupling between F and OH). J(6,OH) of (±)-**4** in (D_8)dioxane is slightly larger than J(4,OH) of D-**3** in (D_6)DMSO; this suggests a weak contribution of the OH···F H-bonded tautomer in dioxane.

In (D_6)DMSO, finally, the intramolecular OH···F H-bond of (±)-**4** is completely (J(6,OH) = 3.8 Hz) and the bifurcated H-bond mostly broken (J(2,OH) = 5.8 Hz)[4]. As dioxane is a medium strong H-bond acceptor and DMSO a strong one [66–71], the solvent dependence of the H-bonds shows that the bifurcated H-bond is stronger than the OH···F H-bond and that the OH···F H-bond is weak (as indicated by the small $\Delta\nu$ value of *ca.* 20 cm^{-1} for the IR spectrum in CCl_4). These conclusions have been confirmed by molecular-dynamics calculations.

The equatorial OH of D-**3** *and* L-**4** is involved in a rather strong bifurcated intramolecular H-bond, whereas the axial OH is either free (D-**3**) or engaged in a weak intramolecular H-bond (L-**4**). Therefore, glycosidation by **1** of the axial OH group of D-**3** and L-**4** should be preferred over glycosidation of the equatorial OH group, and glycosylation of the axial OH group in apolar solvents should be more pronounced for **3** than for **4**.

3. *Glycosidation of* D-**3** *and* L-**4**. The solubility of the diols D-**3** and L-**4** in apolar solvents proved too low for a meaningful glycosidation[5]. Glycosidation of D-**3** in 1,4-

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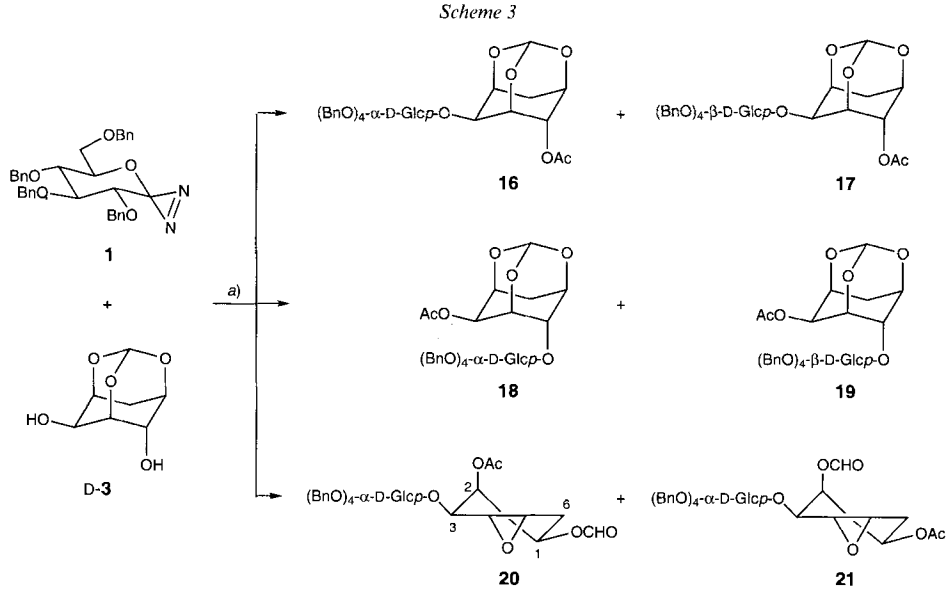
[4]) Complexes between alcohols and DMSO are bent as depicted in *Fig. 2*. The complexes found in the *Cambridge Database* show bond angles S=O···H of 109–144°.

[5]) ^{1}H-NMR Spectra (300 MHz) of saturated solutions of D-**3** and (±)-**4** in CD_2Cl_2, obtained by stirring the alcohols for 24 h in CD_2Cl_2 and filtering, required pulsing overnight.

dioxane with 1.1 equiv. of the diazirine **1** at room temperature followed by flash chromatography gave mixtures of the anomeric 1,2-linked pseudodisaccharides, of the anomeric 1,4-linked pseudodisaccharides, the α-D-1,3-linked epoxides, and of pseudotrisaccharides besides recovered D-**3** (26%; *Scheme 3*). Acetylation of the 1,2-linked pseudodisaccharides gave the anomers **16**/**17** (2:3; 13%). Acetylation of the mixture of 1,4-linked pseudodisaccharides and epoxides yielded the anomers **18**/**19** (1:5; 38%) and the regioisomeric epoxides **20**/**21** (53:47; 7%), separated by flash chromatography. The mixture of pseudotrisaccharides (8%), refractory to acetylation, was not analyzed. The ratio of the acetates **16**–**21** and of the corresponding alcohols (9:13:11:55:6:6) was determined by analytical HPLC and ^{13}C-NMR spectroscopy of the crude product and of the fractions resulting from flash chromatography before and after acetylation. Preparative HPLC afforded pure samples of **16**–**21**.

Scheme 3



a) Dioxane, 4-Å molecular sieves, r.t.; Ac_2O, Et_3N, DMAP, CH_2Cl_2; **16**/**17** 2:3 (13%), **18**/**19** 1:5 (38%), **20**/**21** 53:47 (7%).

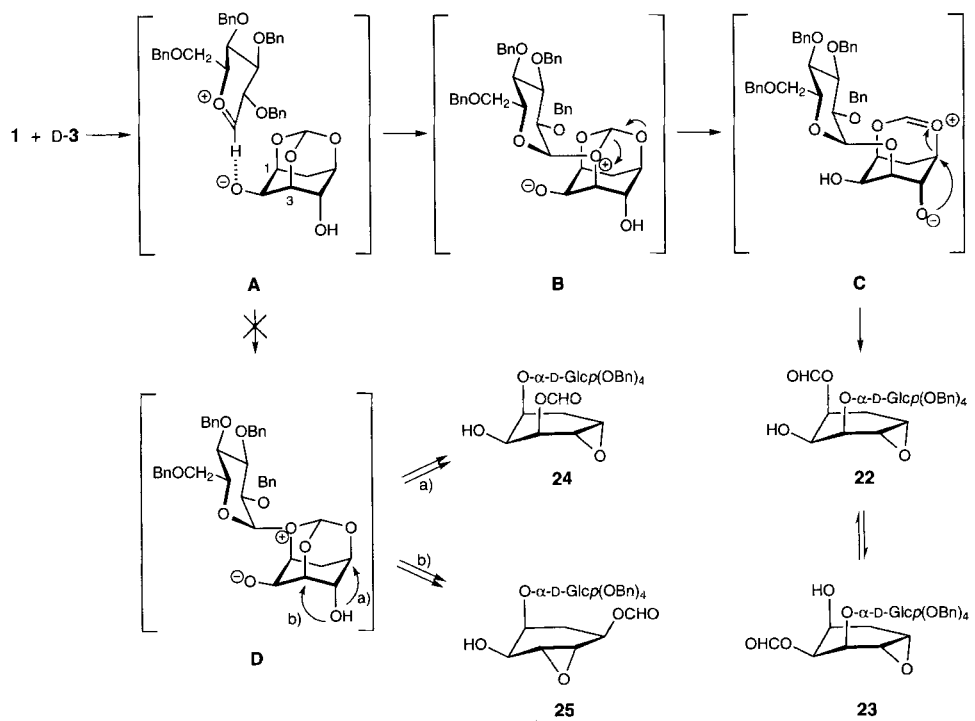
The constitution of **16**–**19** is deduced from the signal pattern of *H*–C(OAc): *td*($J \approx 4$ and 1.5 Hz) for H–C(4) of **16** and **17** at *ca.* 5.5 ppm and broad *q* ($J \approx 1.5$ Hz) for H–C(2) of **18** and **19** at *ca.* 5 ppm. The configuration at the anomeric center of **16**–**21** is easily deduced from the J(1′,2′) values, the chemical shifts of H–C(1′) and C(1′), and the characteristic downfield shift of H–C(3′) and H–C(5′) of the α-D-glucopyranosides (*cf.* [13] [15–18]).

In the ^{1}H- and ^{13}C-NMR spectra of **20** and **21**, one finds signals of an Ac and a CHO group (**20**: 2.06 (*s*) and 7.90 ppm (*d*, J = 0.8 Hz) and 169.76 (*s*), 20.77 (*q*), and 159.62 (*d*); **21**: 1.99 (*s*) and 8.05 ppm (*d*, J = 1.0 Hz) and 169.50 (*s*), 21.01 (*q*), and 159.51 (*d*)). Two signals at relatively high field in the ^{1}H-NMR spectra indicate the

presence of an oxiranyl moiety (**20**: 3.38 and 3.04 ppm; **21**: 3.40 and 3.07 pm). This is corroborated by two *d*'s in the ^{13}C-NMR spectra (**20**: 53.68 and 52.94 ppm; **21**: 53.97 and 52.64 ppm). The signals for *H*–C(OAcyl) appear at 4.8–5.08 ppm and for *H*–C(OGlc) at 4.2 ppm. Selective irradiations of **20** and **21** (see *Exper. Part*) show that the oxiranyl moiety is flanked by the CH_2 group on one side and by the (pyranosyloxy)methylene group on the other side, and that the two (acyloxy)methylene groups are located between the CH_2 and the (pyranosyloxy)methylene groups. The position of the HCO moiety is easily assigned by its long-range coupling. H–C(2) of **20** appears as a *d* and H–C(2) of **21** as a *dd* (^4J(H,CHO) = 1.0 Hz). The H–C(2) signal show a vicinal coupling with H–C(3) (**20**: 3.1 Hz, **21**: 3.5 Hz) but none to H–C(1). These assignments are confirmed by selective irradiations. The vicinal coupling constants of **20** and **21** are compatible with a $^1H_2$ conformation. Molecular-mechanics calculations (Macromodel V. 4.5, MM3* force field, gas phase) result in the $^1H_2$ conformer as the global minimum with calculated coupling constants similar to the observed ones.

The formation of the epoxides **20** and **21** is rationalized by postulating a protonation in the σ-plane of the carbene by the equatorial, intramolecularly H-bonded HO–C(2) group [16] leading to an ion pair, followed by alkylation of O–C(3) located in the π-plane of the oxycarbenium cation (*Scheme 4*, **A**→**B**). This postulate is in keeping with the exclusive formation of the α-D-configurated glycosides **20** and **21** [13] [14] [16]. The alkylation of O–C(3) is followed by an elimination to the 1,3-dioxenium ion **C** and, hence, by an intramolecular substitution leading to the epoxide **22**. Acyl migration in solution and during chromatography leads to the mixture **22**/**23**.

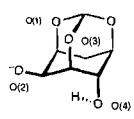
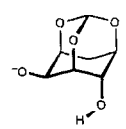
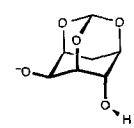
Scheme 4. *Reaction of the Carbene Derived from* **1** *with* D-**3**: *Mechanisms Leading to* **22** *and* **23**, *the Precursors of* **20** *and* **21**



Surprisingly, we could not detect any epoxides of the type **24** and **25**, expected from attack by the oxycarbenium cation at O–C(1) (**A**→**D**). This regioselectivity may result from geometric (repulsion between O–C(1) and the C(2)-OBn group?) and/or electronic factors. Depending on the relative importance of ionic and covalent interactions, either the difference of the partial charges at *O*–C(1) (= O(1)) *O*–C(3) (= O(3)) or the electron-density differences of the relevant occupied orbital may determine the regioselectivity of the C–O bond formation.

AM1 Calculations (AMPAC 5.0, gas phase) of the anion obtained by deprotonation of HO–C(2) of D-**3** shows, as expected, that the two highest occupied molecular orbitals possess the highest electron density at O(2) (*Table 3*). In view of this, the relatively large percentage of 1,3-linked pseudodisaccharides shows the deprotonation of the H-bonded HO–C(2), the formation of a 'tight' ion pair, and the importance of the double stereoelectronic control (protonation and C–O bond formation). The electron densities are

Table 3. *Data of the AM1 Calculations* (AMPAC 5.0 and SPARTAN 4.1, gas phase) *of the 2-Oxy Anion Derived from* **3**

Conformer	 **3A**			 **3B**			 **3C**		
AMPAC 5.0 program:									
< C(3)–C(4)–O(4)–H	43.0°			–58.4°			180°		
Final heat of formation	–231.3 kcal/mol[a])			–227.1 kcal/mol[b])			–224.8 kcal/mol[b])		
Orbital energy [eV]									
HOMO		–3.538			–3.307			–3.224	
HOMO-1		–3.603			–3.409			–3.337	
HOMO-2		–6.415			–6.435			–6.476	
Electron density [%] at	O(1)	O(2)	O(3)	O(1)	O(2)	O(3)	O(1)	O(2)	O(3)
HOMO	0.8	66.8	0.9	0.9	68.2	0.8	0.9	68.6	0.8
HOMO-1	2.3	62.5	2.1	2.1	62.7	2.1	2.0	63.2	2.0
HOMO-2	7.4	4.7	12.6	12.7	6.6	15.4	13.2	7.4	11.6
Partial charge	–0.297	–0.661	–0.296	–0.297	–0.661	–0.296	–0.297	–0.661	–0.296
Atom electron density	6.30	6.66	6.30	6.30	6.66	6.30	6.30	6.66	6.30
SPARTAN 4.1 program:									
< C(3)–C(4)–O(4)–H	62.3°			–60.7°			175.2°		
Final heat of formation	–207.9 kcal/mol[a])			–201.8 kcal/mol[c])			–200.9 kcal/mol[b])		
Orbital energy [eV]									
HOMO		–2.890			–2.752			–2.714	
HOMO-1		–2.943			–2.824			–2.790	
HOMO-2		–6.240			–6.174			–6.264	
Electron density [%] at	O(1)	O(2)	O(3)	O(1)	O(2)	O(3)	O(1)	O(2)	O(3)
HOMO	0.3	84.9	0.1	0.4	84.4	0.1	0.4	86.8	0.1
HOMO-1	0.7	82.3	0.9	0.7	82.4	0.8	0.7	82.5	0.8
HOMO-2	10.6	12.5	10.0	10.2	15.2	10.1	14.3	16.7	6.7
Partial charge	–0.289	–0.748	–0.288	–0.291	–0.756	–0.291	–0.291	–0.755	–0.289
Atom electron density	6.29	6.75	6.29	6.29	6.76	6.29	6.29	6.76	6.29

[a]) Global minimum. [b]) No minimum. Dihedral angle C(3)–C(4)–O(4)–H constraint during minimization. [c]) Relative minimum.

different at O(1) and O(3) for the rotamers **3A–C**. In dioxane solution, **3A** (global minimum) is not relevant, and both **3B** and **3C** are populated (as from J(H,OH), *cf.* discussion of H-bonds). Of these conformers, **3B** indeed shows a difference of electron density in favor of O(3) in the molecular orbital relevant for the C–O bond formation (HOMO-2). However, this difference is not reproduced when performing AM1 calculation (gas phase) with the SPARTAN 4.1 program, and its relevance is doubtful. The partial charges at O(1) and O(3) are very similar to each other. The calculations do not show a convincingly strong electronic influence on the regioselectivity.

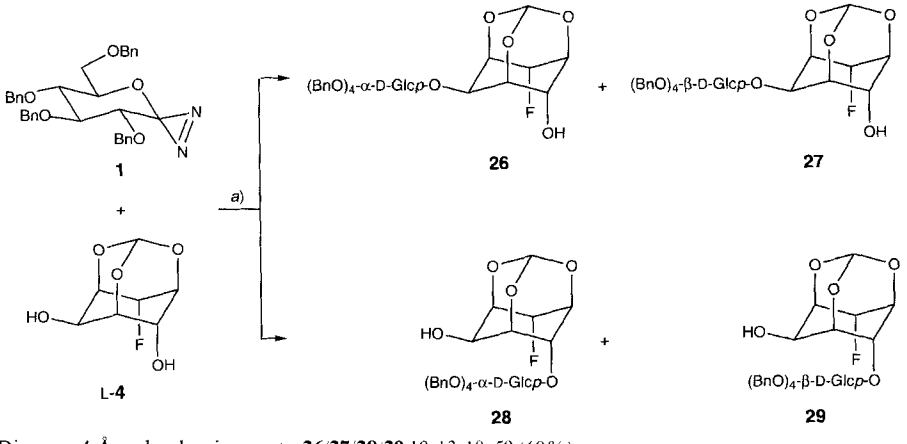
Both, formation of the epoxides **22** and **23** and of the orthoester pseudodisaccharides **16** and **17** require deprotonation of HO–C(2); *O*-alkylation of the (intimate) ion pair leads to the epoxides, while (partial) dissociation is required to form **16** and **17**.

Glycosidation of the fluorodiol L-**4** with 1.1 equiv. of **1** in 1,4-dioxane at room temperature under the conditions described for D-**3** (*Scheme 5*), followed by flash chromatography gave a mixture of the anomeric 1,2- and 1,4-linked pseudodisaccharides **26**/**27**/**28**/**29** (60%), a mixture of four pseudotrisaccharides, analyzed by ^{19}F-NMR spectroscopy (9%), and starting material L-**4** (26%). The ratio **26**/**27**/**28**/**29** 10:13:18:59 was determined by ^{19}F-NMR spectroscopy and analytical HPLC of the crude product. Preparative HPLC afforded pure samples of **26–29**.

The structures of **26–29** have been assigned by applying the criteria that have been used for **16–19**. Specifically, the 1,2-linkage of **26** and **27** and the 1,6-linkage of **28** and **29** are indicated by a downfield shift of C(2) and C(6), respectively, by *ca.* 6 ppm to lower field in the ^{13}C-NMR spectra. The bifurcated H-bond in **28** and **29** is revealed by the IR band at 3585 cm^{-1} (CCl_4; *Table 1*) and the vicinal J(H,OH) of 11.1 (**28**) and 11.6 Hz (**29**) ($CDCl_3$, *Table 2*). The *t* (J = 6 Hz) of HO–C(6) of **27** indicates the preponderant contribution of the F···HO H-bonded rotamer, whereas the *m* of HO–C(6) of **26** prevents the detection of the F···HO H-bond.

The regioselectivity of the glycosidation shows that, in dioxane, the carbene derived from **1** attacks preferentially the axial HO–C(4) of D-**3**. The ratio of protonation of the carbene by the axial *vs.* the equatorial OH of D-**3** is 65:35 (38% of **18**/**19** *vs.* 13% of **16**/**17** and 7% of **20**/**21**). For L-**4**, this ratio is raised to 77:23 (46% of **28**/**29** *vs.* 14% of **26**/**27**). The carbene is preferentially protonated by the axial OH (HO–C(4) or HO–C(6))

Scheme 5



a) Dioxane, 4-Å molecular sieves, r.t.; **26**/**27**/**28**/**29** 10:13:18:59 (60%).

involved in the weaker, intermolecular H-bond to the solvent. The substantial proportion of products derived from protonation by the intramolecularly H-bonded HO–C(2) is in keeping with the explanation of the exclusive glycosylation at the axial OH groups of the triol **1**, according to which the kinetic acidity of one axial H-bond is enhanced by the intramolecular H-bond donating second axial OH group [19].

The diastereoselectivity of the glycosidation of the equatorial OH group is low and in favor of the β-D-anomer (**17**/**16** 60:40, **27**/**26** 57:43). It is higher for the glycosidation of the axial OH group (**19**/**18** 83:17, **27**/**26** 77:23)[6]), in agreement with its higher kinetic acidity. The formation of the α-D-configurated epoxides **20**/**21** confirms earlier evidence for the protonation of the carbene by the H-bonded tautomers (see *Fig. 2*). No epoxides were formed in the reaction of **1** with L-**4**.

We thank Dr. *B. Schweizer* for the X-ray analyses, Mr. *T. Mäder* for excellent technical assistance (HPLC), the *Swiss National Science Foundation* and *F. Hoffmann-La Roche AG*, Basel, for generous support, and the *Ministerio de Educación y Ciencia* for a fellowship to *A. Zapata*.

Experimental Part

General. Solvents were freshly distilled, dioxane and (D_8)dioxane over Na and benzophenone. Anal. TLC: *Merck* precoated silica gel *60 F254* plates; detection by treatment with a soln. of 5% $(NH_4)_6Mo_7O_{26}\cdot 4\,H_2O$, and 0.1% $Ce(SO_4)_2\cdot H_2O$ in 10% H_2SO_4 soln. Flash chromatography (FC): silica gel *Merck 60* (40–63 μm). High-performance liquid chromatography (HPLC): anal. *Spherisorb Silica* (5 μm, 250 × 4.6 mm column), *Silica-NH*$_2$ (5 μm, 250 × 4 mm column), UV detection (220–254 nm), 2 ml/min; prep. *Spherisorb Silica* (5 μm, 250 × 20 mm column), prep. *Silica-NH*$_2$ (5 μm, 250 × 20 mm column), UV detection (220–254 nm); t_R in min. M.p.'s: uncorrected. Optical rotations: 1-dm cell at 25° at 589 nm. UV: λ_{max} (ε) in nm. CD: λ (Δε) in nm. FT-IR Spectra: in CCl_4, $CHCl_3$, or CH_2Cl_2 (concentration indicated for each compound (M)). NMR Spectra: at 200 and 300 MHz (^{1}H), 50 and 75 MHz (^{13}C), and 282 MHz (^{19}F); chemical shifts in ppm rel. to $SiMe_4$ (^{1}H, ^{13}C; for ^{1}H-NMR in (D_8)dioxane, the signal of the solvent was set at 3.53 ppm) or $CFCl_3$ (^{19}F) and coupling constants *J* in Hz; ^{1}H assignments based on selective homonuclear decoupling experiments. Mass spectra: CI, EI at 70 eV, and FAB in 3-nitrobenzyl alcohol (NBA) matrix. Calculations with the programs Macromodel V. 4.5 [72], AMPAC 5.0 [73], and SPARTAN 4.1 [74] were performed on a *IRIS Crimson-Elan*.

*2-O-[(*tert*-Butyl)dimethylsilyl]-1,3,5-*O*-methylidyne-4,6-*O*-thiocarbonyl*-myo*-inositol* (**6**). *a*) A soln. of **5** (200 mg, 0.66 mmol), Et_3N (0.9 ml, 6.60 mmol), and 4-(dimethylamino)pyridine (DMAP; 80 mg, 0.66 mmol) in CH_2Cl_2 (10 ml) was treated at 0° under N_2 with thiophosgene (160 μl, 1.91 mmol), warmed to r.t., and stirred for 48 h (additional DMAP (80 mg) and thiophosgene (50 μl) were added after 24 h). The soln. was diluted with CH_2Cl_2, washed with sat. aq. $NaHCO_3$ soln., H_2O, and brine, dried ($MgSO_4$), and evaporated. FC (hexane/AcOEt 8:1→6:1) gave **6** (98 mg, 43%).

b) A soln. of **5** (300 mg, 0.99 mmol) and 1,1′-thiocarbonylbis[^{1}*H*-imidazole] (264 mg, 1.48 mmol) in toluene (9 ml) was heated at 80° for 5 h. After evaporation, the residue was dissolved in CH_2Cl_2, the soln. washed with brine, dried ($MgSO_4$), and evaporated. FC (hexane/AcOEt 3:1) gave **6** (144 mg, 51%). Similarly, 8.9 g (29.2 mmol) of **5** yielded 2.2 g of **6** (32%). R_f (hexane/AcOEt 3:1) 0.48. M.p. 197–198° (hexane/AcOEt). FT-IR (0.05M, $CHCl_3$): 2958*m*, 2931*m*, 2899*w*, 2859*w*, 1723*w*, 1602*w*, 1472*w*, 1464*w*, 1379*m*, 1365*w*, 1350*m*, 1319*m*, 1303*m*, 1268*s*, 1166*s*, 1103*m*, 1080*m*, 1055*m*, 1035*m*, 1005*s*, 958*m*, 901*s*, 880*w*, 851*s*, 622*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.56 (*d*, *J* = 1.3, irrad. at 3.97→*s*, CHO_3); 5.18–5.12 (*m*, H–C(4), H–C(6)); 4.61 (*tt*, *J* = 4.3, 1.4, H–C(5)); 4.39 (*ddd*, *J* = 5.4, 2.2, 1.5, irrad. at 3.97→*dd*, *J* = 5.4, 1.5, H–C(1), H–C(3)); 3.97 (*q*, *J* = 1.4, H–C(2)); 0.94 (*s*, *t*-Bu); 0.15 (*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 184.75 (*s*, C=S); 101.88 (*d*, CHO_3); 71.79 (*d*, C(1), C(3), C(4), C(6)); 60.81, 59.65 (2*d*, C(2), C(5)); 25.71 (*q*, *Me*$_3$C); 18.24 (*s*, Me$_3$*C*); −4.75 (*q*, Me_2Si). CI-MS: 364 (10, $[M + NH_4]^+$), 349 (10), 348 (21), 347 (100, $[M + 1]^+$), 289 (10), 241 (9). Anal. calc. for $C_{14}H_{22}O_6SSi$ (346.48): C 48.53, H 6.40, S 9.25; found: C 8.54, H 6.42, S 9.08.

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[6]) The diastereoselectivity of the glycosidation of the axial OH group is similar to the one observed in the glycosidation of the axial HO–C(2) of methyl 4,6-*O*-benzylidene-α-D-altropyranoside [18].

*(±)-2-O-[(*tert*-Butyl)dimethylsilyl]-1,3,5-O-methylidyne-1,2,3,5/4-cyclohexanepentol* ((±)-**7**). *a*) A suspension of **5** (200 mg, 0.66 mmol) and Bu_2SnO (235 mg, 0.94 mmol) in MeOH (8 ml) was heated to reflux under N_2 until the mixture became clear. The soln. was boiled for 3 h an then evaporated. A soln. of the residue in dioxane (8 ml) was treated dropwise with PhOCSCl (0.1 ml, 0.72 mmol), stirred for 12 h at r.t., and evaporated. A soln. of the residue in toluene (10 ml) was heated to reflux, treated dropwise over 20 min with a soln. of Bu_3SnH (0.23 ml, 0.85 mmol) and 2,2′-azobis[isobutyronitrile] (AIBN; 4 mg, 0.036 mmol) in toluene (3 ml), and boiled under reflux for 2 h. The soln. was cooled to r.t. and treated with 5% aq. NaOH soln. (1 ml) for 1 h. The aq. layer was extracted with Et_2O; the combined org. phase washed with H_2O and brine, dried ($MgSO_4$), and concentrated to a syrup. FC (hexane/AcOEt 3:1) gave (±)-**7** (105 mg, 55%) and **5** (65 mg, 32%). An analogous reaction with 2 g (6.6 mmol) of **5** led to 0.98 g (52%) of (±)-**7** and 0.3 g (15%) of **5**.

b) A soln. of **6** (2.58 g, 7.46 mmol) in toluene (250 ml) was added over 100 min under N_2 to a boiling soln. of Bu_3SnH (4.19 ml, 15.80 mmol) and AIBN (92 mg, 0.82 mmol) in dry toluene (50 ml). The soln. was stirred for 1 h at reflux, hydrolyzed, and worked up as described above. FC (hexane/AcOEt 3:1) gave (±)-**7** (1.4 g, 65%). R_f (hexane/AcOEt 3:1) 0.24. M.p. 127–128° (hexane/AcOEt). FT-IR (0.2M, CH_2Cl_2): 3605*m*, 3487*w* (br.), 2930*s*, 2858*s*, 1472*m*, 1380*m*, 1362*m*, 1318*w*, 1167*s*, 1136*s*, 1114*s*, 1076*s*, 1002*s*, 937*s*, 910*w*, 878*s*, 856*s*, 838*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.42 (*t*, *J* = 1.2, CHO_3); 4.43 (*qd*, *J* = 4.4, 1.5, H–C(4)); 3.98 (*tq*, *J* = 3.6, 1.8, H–C(5)); 3.94 (br. *dq*, *J* = 3.8, 1.9, H–C(3)); 3.92–3.88 (*dquint*. *J* ≈ 4.0, 2.0, H–C(1)); 3.87 (*q*, *J* = 1.4, irrad. at 5.42 → *t*, *J* = 1.5, H–C(2)); 2.46 (*dtd*, *J* = 13.6, 4.1, 1.6, H_{eq}–C(6)); 2.00 (br. *d*, *J* = 4.6, HO–C(4)); 1.82 (*dq*, *J* = 13.6, 1.4, irrad. at 5.42 → *dt*, *J* = 13.6, 1.4, H_{ax}–C(6)); 0.80 (*s*, *t*-BuSi); 0.00 (*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 103.72 (*d*, CHO_3); 75.08 (*d*, C(3)); 71.15 (*d*, C(1)); 69.37 (*d*, C(5)); 66.27 (*d*, C(4)); 61.82 (*d*, C(2)); 27.31 (*t*, C(6)); 25.96 (*q*, *Me*$_3$C); 18.12 (*s*, Me$_3$*C*); –4.61 (*q*, Me_2Si). CI-MS: 290 (19, $[M + 2]^+$), 289 (100, $[M + 1]^+$). EI-MS: 289 (0.2, $[M + 1]^+$), 273 (0.3, $[M - Me]^+$), 257 (0.1, $[M - 31]^+$), 247 (0.8), 231 (41, $[M - (t\text{-Bu})]^+$), 185 (100), 167 (47), 157 (25), 143 (7), 129 (16), 103 (23), 83 (5), 75 (93), 55 (12), 45 (7), 29 (6). Anal. calc. for $C_{13}H_{24}O_5Si$ (288.42): C 54.14, H 8.39; found: C 54.24, H 8.17.

*Treatment (±)-***7** *with (+)-(*R*)-1-Phenylethyl Isocyanate*. A soln. of (±)-**7** (1.5 g, 5.39 mmol) in THF (21 ml) was added dropwise at –78° under Ar to a soln. of BuLi (4 ml of a 1.6M soln. in hexane, 6.47 mmol) in THF (4 ml). The mixture was stirred for 1 h, treated with a soln. of (+)-(*R*)-1-phenylethyl isocyanate (1.1 ml, 8.1 mmol) in THF (2.4 ml) within 30 min, and stirred for further 40 min at –78°. After the dropwise addition of a sat. aq. NH_4Cl soln. (50 ml), the mixture was warmed to r.t. and extracted with AcOEt (4 × 100 ml). The combined org. layers were washed with sat. aq. NH_4Cl soln. and brine, dried ($MgSO_4$), and evaporated. FC (hexane/AcOEt 6:1 → 5:1) gave **8a**/**8b** 2:1 (0.88 g, 38%; ratio determined by HPLC), **9a** (0.04 g, 1.3%), **9b** (0.57 g, 18%), and **9a**/**9b** (0.92 g, 29%). Prep. HPLC (hexane/AcOEt 85:15; *Si60*, 10 ml/min; t_R 11.7 (**9b**) and 15.3 (**9a**)) gave additional pure **9a** (0.72 g, 23%) and **9b** (0.12 g, 4%). Crystallization of **8a**/**8b** from hexane/AcOEt gave pure **8a**. Prep. HPLC (hexane/AcOEt 3:1; *Si60*, 10 ml/min; t_R 6.5 (**8b**)) of the mother liquors gave pure **8b**. The diastereoisomeric purity of **8a**, **8b**, **9a**, and **9b** was determined by anal. HPLC (*Spherisorb* silica gel; > 99%).

The mixture **8a**/**8b** was transformed into **9a**/**9b** by the following procedure: A soln. of **8a**/**8b** (1 mmol) in THF (4 ml) was added dropwise at –78° and under Ar to a soln. of BuLi (0.3 mmol) in THF (0.3 ml). The soln. was stirred for 1 h, treated dropwise with a soln. of (+)-(*R*)-1-phenylethyl isocyanate (2.7 mmol) in THF (0.5 ml), and stirred at –78° for 1 h. Usual workup, FC (hexane/AcOEt 6:1), and HPLC (see above) gave pure **9a** and **9b** (total yield 85–90%).

*1*D*-2-O-[(*tert*-Butyl)dimethylsilyl]-1,3,5-O-methylidyne-4-O-{[(*R*)-1-phenylethyl]carbamoyl}-1,2,3,5/4-cyclohexanepentol* (**8a**): M.p. 133–135° (hexane/AcOEt). R_f (hexane/AcOEt 3:1) 0.27. Anal. HPLC: t_R (hexane/Et_2O 4:1) 6.6. $[\alpha]_D^{25} = +43.3$ (*c* = 0.06, $CHCl_3$). FT-IR (0.02M, $CHCl_3$): 3444*w*, 3042*w*, 3007*w*, 2962*m*, 2931*m*, 2858*w*, 1728*s*, 1501*m*, 1470*w*, 1462*w*, 1451*w*, 1433*w*, 1390*w*, 1379*m*, 1351*w*, 1261*s*, 1167*s*, 1138*m*, 1104*s*, 1077*s*, 1066*s*, 938*m*, 879*w*, 855*s*, 838*m*, 823*m*. ^{1}H-NMR (300 MHz, CD_3OD; (*E*)/(*Z*) 82:18): 7.32–7.20 (*m*, 5 arom. H); 5.45 (br. *s*, 0.82 H), 5.38 (br. *s*, 0.18 H, CHO_3); 5.20 (br. *td*, *J* ≈ 3.9, 1.2 H–C(4)); 4.73 (*q*, *J* = 7.0, 0.82 H), 4.56 (*q*, *J* ≈ 7, 0.18 H, PhC*H*); 4.24–4.16 (*m*, 0.82 H); 4.16–4.06 (*m*, 1 H); 4.05–3.96 (*m*, 1 H); 3.91 (br. *s*, 0.82 H), 3.64 (br. *s*, 0.18 H, H–C(2)); 3.75–3.64 (*m*, 0.18 H); 2.59 (br. *dt*, *J* = 13.3, 3.8, H_{eq}–C(6)); 2.12 (br. *d*, *J* = 13.5, 0.18 H), 1.96 (br. *d*, *J* = 13.5, 0.82 H, H_{ax}–C(6)); 1.42 (*d*, *J* = 7.0, Me); 0.96 (*s*, 1.6 H), 0.88 (*s*, 7.4 H, *t*-BuSi); 0.16 (*s*, 1.1 H), 0.04 (*s*, 4.9 H, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$; (*E*)/(*Z*) 4:1): signals of (*E*)-**8a**: 153.61 (*s*, C=O); 142.93 (*s*); 128.80–124.92 (5*d*); 103.84 (*d*, CHO_3); 72.60 (*d*); 70.84 (*d*); 68.36 (*d*); 66.97 (*d*); 65.17 (*d*); 50.86 (*d*, PhC*H*); 28.12 (*t*, C(6)); 25.90 (*q*, *Me*$_3$C); 22.08 (*q*, Me); 18.41 (*s*, Me$_3$*C*); –4.6 (*q*, Me_2Si); signals of (*Z*)-**8a**: 154.07 (*s*, C=O); 144.3 (*s*); 72.2 (*d*); 66.53 (*d*); 52.30 (*d*, PhC*H*); 26.98 (*t*, C(6)); 23.95 (*q*, Me). FAB-MS: 871 (0.6, $[2M + 1]^+$), 813 (1.7, $[2M - 57]^+$), 571 (1.4), 531 (2.6), 436 (100, $[M + 1]^+$), 378 (70), 271 (20), 167 (36), 105 (87), 73 (84). Anal. calc. for $C_{22}H_{33}NO_6Si$ (435.59): C 60.66, H 7.64, N 3.22; found: C 60.59, H 7.51, N 3.17.

*1L-2-O-[(*tert*-Butyl)dimethylsilyl]-1,3,5-O-methylidyne-4-O-{[(*R*)-1-phenylethyl]carbamoyl}-1,2,3,5/4-cyclohexanepentol* (**8b**): $[\alpha]_D^{25} = +14.6$ ($c = 0.13$, $CHCl_3$). R_f (hexane/AcOEt 3:1) 0.32. Anal. HPLC: t_R (hexane/Et_2O 4:1) 5.4. FT-IR (0.02M, $CHCl_3$): 3443*w*, 3042*w*, 3007*w*, 2959*m*, 2931*m*, 2899*w*, 2858*w*, 1729*s*, 1604*w*, 1501*m*, 1472*w*, 1464*w*, 1452*w*, 1391*m*, 1380*m*, 1359*w*, 1317*w*, 1279*w*, 1260*m*, 1167*s*, 1139*m*, 1109*m*, 1076*m*, 1040*w*, 999*s*, 937*m*, 897*w*, 880*m*, 855*s*, 839*m*, 657*w*, 552*w*. ^{1}H-NMR (300 MHz, CD_3OD; (*E*)/(*Z*) 4:1): 7.30–7.19 (*m*, 5 arom. H); 5.45 (br. *s*, 0.8 H); 5.39 (br. *s*, 0.2 H, CHO_3); 5.20 (br. *t*, $J \approx 3.1$, 0.8 H); 5.14 (br. *t*, $J \approx 3$, 0.2 H, H–C(4)); 4.73 (*q*, $J = 7.0$, 0.8 H); 4.62 (*q*, $J \approx 7$, 0.2 H, PhC*H*); 4.22–4.12 (*m*, 1.8 H); 4.06–4.00 (*m*, 1 H); 3.98 (br. *s*, 1.8 H), 3.20 (br. *s*, 0.2 H, H–C(2)); 3.79 (br. *s*, 0.2 H); 2.55 (br. *d*, $J \approx 14.5$, 0.8 H), 2.52 (br. *d*, $J \approx 14.5$, 0.2 H, H_{eq}–C(6)); 1.93 (br. *d*, $J = 14.2$, 0.8 H), 1.66 (br. *d*, $J \approx 14$, 0.2 H, H_{ax}–C(6)); 1.43 (*d*, $J = 6.9$, 2.4 H), 1.37 (*d*, $J = 6.8$, 0.6 H, Me); 0.94 (*s*, 7.2 H), 0.84 (*s*, 1.8 H, *t*-BuSi); 0.14 (*s*, 4.8 H), –0.06 (*s*, 0.6 H), –0.08 (*s*, 0.6 H, Me_2Si). ^{13}C-NMR (75 MHz, (D_6)acetone; only signals of (*E*)-**8b** visible): 155.20 (*s*, C=O); 145.49 (*s*); 129.65 (2*d*); 128.22 (2*d*); 127.21 (*d*); 105.04 (*d*, CHO_3); 73.78 (*d*); 71.90 (*d*); 69.06 (*d*); 68.13 (*d*); 66.38 (*d*); 51.76 (*d*, PhCH); 29.03 (*t*, C(6)); 26.46 (*q*, Me_3C); 23.07 (*q*, Me); 19.03 (*s*, Me_3C); –4.26 (*q*, MeSi); –4.34 (*q*, MeSi). FAB-MS: 871 (1, $[2\,M + 1]^+$), 813 (1.5, $[2\,M - 57]^+$), 436 (100, $[M + 1]^+$), 378 (69), 271 (18), 225 (13), 167 (36), 136 (16), 105 (94), 73 (86). Anal. calc. for $C_{22}H_{33}NO_6Si$ (435.59): C 60.66, H 7.64, N 3.22; found: C 60.71, H 7.59, N 3.06.

*1D-2-O-[(*tert*-Butyl)dimethylsilyl]-1,3,5-O-methylidyne-4-O-{[(*R*)-1-phenylethyl]{[(*R*)-1-phenylethyl]-carbamoyl}carbamoyl}-1,2,3,5/4-cyclohexanepentol* (**9a**): R_f (hexane/AcOEt 3:1) 0.50. Anal. HPLC: t_R (hexane/Et_2O 4:1) 3.2. $[\alpha]_D^{25} = -8.9$ ($c = 1.05$, $CHCl_3$). FT-IR (0.002M, $CHCl_3$): 3338*w*, 3066*w*, 3042*w*, 3008*w*, 2959*m*, 2931*m*, 2886*w*, 2858*w*, 1719*s*, 1680*m*, 1603*w*, 1523*s*, 1497*m*, 1472*w*, 1463*w*, 1450*m*, 1407*s*, 1383*m*, 1362*w*, 1352*w*, 1328*w*, 1304*w*, 1288*w*, 1262*s*, 1166*s*, 1135*s*, 1111*m*, 1070*w*, 1000*s*, 937*m*, 909*w*, 894*w*, 854*m*, 839*m*, 823*m*, 646*w*, 606*w*, 552*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.98 (*d*, $J = 7.4$, NH); 7.38–7.20 (*m*, 10 arom. H); 6.18 (*q*, $J = 6.5$, PhC*H*); 5.46 (br. *s*, CHO_3); 5.16 (*td*, $J = 4.0$, 1.7, H–C(4)); 5.09 (*quint.*, $J = 7.0$, PhC*H*); 4.14 (*tq*, $J = 3.8$, 1.9, H–C(5)); 4.07 (*dq*, $J = 3.8$, 1.9, H–C(3)); 3.76–3.71 (br. *dquint.*, $J \approx 4$, 2, H–C(1)); 2.97 (br. *q*, $J \approx 1.3$, H–C(2)); 2.40 (*dtd*, $J \approx 13.7$, 4.0, 1.8, H_{eq}–C(6)); 1.64 (*d*, $J = 7.0$, Me); 1.58 (*d*, $J = 6.8$, Me); 1.15 (br. *dq*, $J \approx 13.8$, 1.7, H_{ax}–C(6)); 0.91 (*s*, *t*-BuSi); 0.07 (*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 155.21 (*s*, C=O); 153.46 (*s*, C=O); 143.44 (*s*); 142.20 (*s*); 128.78 (2*d*); 128.68 (2*d*); 127.40 (*d*); 126.88 (*d*); 125.99 (2*d*); 125.08 (2*d*); 103.92 (*d*, CHO_3); 71.79 (*d*); 71.47 (*d*); 70.31 (*d*); 66.48 (*d*); 64.55 (*d*); 51.05 (*d*, PhCH); 50.88 (*d*, PhCH); 27.74 (*t*, C(6)); 25.82 (*q*, Me_3C); 22.91 (*q*, Me); 18.29 (*s*, Me_3C); 17.57 (*q*, Me); –4.35 (*q*, MeSi); –4.45 (*q*, MeSi). FAB-MS: 583 (33, $[M - 1]^+$), 525 (10, $[M - (t\text{-Bu})]^+$), 479 (12), 436 (46), 421 (15), 378 (37), 271 (27), 225 (11), 209 (10), 185 (13), 167 (33), 137 (11), 120 (16), 105 (100), 73 (78). Anal. calc. for $C_{31}H_{42}N_2O_7Si$ (582.79): C 63.89, H 7.26, N 4.81; found: C 63.87, H 7.16, N 4.78.

*1L-2-O-[(*tert*-Butyl)dimethylsilyl]-1,3,5-O-methylidyne-4-O-{[(*R*)-1-phenylethyl]{[(*R*)-1-phenylethyl]-carbamoyl}carbamoyl}-1,2,3,5/4-cyclohexanepentol* (**9b**): R_f (hexane/AcOEt 3:1) 0.56. Anal. HPLC: t_R (hexane/Et_2O 4:1) 2.6. M.p. 127–128° (MeOH). $[\alpha]_D^{25} = -22.6$ ($c = 0.56$, $CHCl_3$). FT-IR (0.003M, $CHCl_3$): 3338*w*, 3042*w*, 3007*w*, 2959*m*, 2931*m*, 2858*w*, 1719*s*, 1680*m*, 1602*w*, 1523*s*, 1497*m*, 1472*w*, 1462*w*, 1449*w*, 1406*s*, 1380*m*, 1362*w*, 1352*w*, 1328*w*, 1306*w*, 1262*s*, 1166*s*, 1132*s*, 1109*s*, 1070*m*, 998*s*, 936*m*, 892*w*, 853*m*, 839*m*, 823*m*, 645*w*, 606*w*, 552*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 9.06 (*d*, $J = 7.4$, NH); 7.40–7.18 (*m*, 10 arom. H); 6.22 (*q*, $J = 6.5$, PhC*H*); 5.46 (br. *s*, CHO_3); 5.30 (*td*, $J = 4.0$, 1.8, H–C(4)); 5.10 (*quint.*, $J = 6.9$, PhC*H*); 4.13 (*dq*, $J = 3.8$, 1.9, H–C(3)); 3.76 (*dquint.*, $J = 4.2$, 2.1, H–C(1)); 3.62 (*tq*, $J = 3.6$, 1.8, H–C(5)); 3.55 (br. *q*, $J \approx 1.3$, H–C(2)); 2.13 (*dtd*, $J \approx 13.9$, 4.0, 1.9, irrad. at 5.30 → *dt*, $J = 13.9$, 4.0, H_{eq}–C(6)); 1.67 (*d*, $J = 7.0$, Me); 1.60 (*d*, $J = 6.9$, Me); 0.93 (*s*, *t*-BuSi); 0.46 (br. *dq*, $J \approx 13.9$, 1.4, H_{ax}–C(6)); 0.14 (*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 155.04 (*s*, C=O); 153.44 (*s*, C=O); 143.43 (*s*); 142.19 (*s*); 128.77 (2*d*); 128.67 (2*d*); 127.38 (*d*); 126.94 (*d*); 125.93 (2*d*); 124.87 (2*d*); 103.84 (*d*, CHO_3); 72.25 (*d*); 70.65 (*d*); 70.48 (*d*); 66.05 (*d*); 64.99 (*d*); 51.10 (*d*, PhCH); 50.71 (*d*, PhCH); 27.04 (*t*, C(6)); 25.82 (*q*, Me_3C); 22.95 (*q*, Me); 18.33 (*s*, Me_3C); 17.58 (*q*, Me); –4.42 (*q*, MeSi); –4.48 (*q*, MeSi). FAB-MS: 583 (40, $[M + 1]^+$), 525 (20, $[M - (t\text{-Bu})]^+$), 479 (24), 436 (64), 421 (29), 378 (53), 332 (10), 289 (6, $[M$ – allophanate$]^+$), 271 (45), 242 (11), 225 (20), 185 (21), 167 (44), 154 (11), 136 (18), 120 (28), 105 (100), 73 (95). Anal. calc. for $C_{31}H_{42}N_2O_7Si$ (582.79): C 63.89, H 7.26, N 4.81; found: C 64.05, H 7.06, N 4.75.

*1D-2-O-[(*tert*-Butyl)dimethylsilyl]-1,3,5-O-methylidyne-1,2,3,5/4-cyclohexanepentol* (D-**7**). A soln. of Na (225 mg, 9.79 mmol) in EtOH (6.75 ml) was added dropwise at r.t. under Ar to a soln. of **9a** (490 mg, 0.84 mmol) in EtOH (4.5 ml). The soln. was heated at reflux for 45 min, cooled to 0°, treated with sat. aq. NH_4Cl soln., and extracted with AcOEt. The org. layer was washed with sat. aq. NH_4Cl soln. and brine, dried ($MgSO_4$), and evaporated. FC (hexane/AcOEt 4:1 → 3:1) gave D-**7** (230 mg, 97.5%). Spectroscopic data: identical to those of (±)-**7**. M.p. 122–123° (hexane/AcOEt). $[\alpha]_D^{25} = +0.2$ ($c = 0.70$, $CHCl_3$). Anal. calc. for $C_{13}H_{24}O_5Si$ (288.42): C 54.14, H 8.39; found: C 53.96, H 8.12.

1D-1,3,5-O-Methylidyne-1,2,3,5/4-cyclohexanepentol (D-**3**). A soln. of D-**7** (257 mg, 0.89 mmol) in THF (6 ml) was treated at 0° under Ar with $Bu_4NF \cdot 3\,H_2O$ (849 mg, 2.69 mmol). The soln. was stirred for 4 h at r.t., diluted with

AcOEt, filtered through SiO_2, and evaporated. FC (hexane/AcOEt 1:4) gave D-**3** (148 mg, 95%). R_f (hexane/AcOEt 1:5) 0.33. M.p. > 265° (dec.; hexane/AcOEt). $[\alpha]_D^{25} = +5.7$ ($c = 1.01$, MeOH). IR (CH_2Cl_2, < 0.005M): 3604*w*, 3573*w*, 3068*w*, 2986*m*, 1711*w*, 1422*s*, 1233*w*, 1164*s*, 1123*w*, 1084*m*, 1054*m*, 989*s*, 933*w*, 896*s*, 882*w*, 828*w*, 802*w*. IR (dioxane, 0.03M): 3421*s*. IR (dioxane, 0.005M): 3533*w*, 3412*s*. ^{1}H-NMR (300 MHz, $CDCl_3$, 0.001M): 5.51 (br. *t*, $J = 1.2$, irrad. at 3.89→*d*, $J \approx 1.2$, CHO_3); 4.59 (br. *q*, $J \approx 4$, addn. of CD_3OD→br. *t*, $J \approx 4$, H–C(4)); 4.17–4.11 (*m*, H–C(1), H–C(3), H–C(5)); 3.89 (br. *d*, $J = 11.8$, irrad. at 3.18→br. *s*, addn. of CD_3OD→br. *s*, H–C(2)); 3.18 (*d*, $J = 11.9$, exchange with CD_3OD, HO–C(2)); 2.61 (*dtd*, $J = 13.8$, 4.1, 1.2, irrad. at 4.59→*dt*, $J = 13.8$, 4.1, H_{eq}–C(6)); 2.08 (*d*, $J = 4.3$, exchange with CD_3OD, HO–C(4)); 2.05 (*dq*, $J = 13.8$, 1.4, H_{ax}–C(6)). ^{1}H-NMR (300 MHz, (D_8)dioxane, 0.03M): 5.40 (br. *s*, CHO_3); 4.38 (*d*, $J = 11.3$, exchange with D_2O, HO–C(2)); 4.36–4.30 (*m*, 1 H exchanged with D_2O, addn. of D_2O→*t*, $J = 3.3$, H–C(4), HO–C(4)); 3.99–3.91 (*m*, H–C(1), H–C(3), H–C(5)); 3.89 (*dq*, $J = 11.8$, 1.5, addn. of D_2O→*q*, $J = 1.5$, H–C(2)); 2.42 (br. *dt*, $J = 13.5$, 3.5, H_{eq}–C(6)); 1.93 (*dq*, $J = 13.8$, 1.5, H_{ax}–C(6)). ^{1}H-NMR (300 MHz, (D_6)DMSO, 0.05M); 5.71 (*d*, $J = 4.1$, HO–C(4)); 5.43 (*t*, $J = 1.2$, CHO_3); 5.21 (*d*, $J = 6.5$, HO–C(2)); 4.20 (*qd*, $J = 4.1$, 1.4, H–C(4)); 3.96 (*tq*, $J \approx 4$, 2, H–C(5)); 3.92–3.87 (*m*, H–C(1), H–C(3)); 3.70 (br. *dq*, $J = 6.2$, 1.2, H–C(2)); 2.30 (*dtd*, $J = 13.4$, 3.9, 1.4, H_{eq}–C(6)); 1.87 (*dq*, $J = 13.4$, 1.5, H_{ax}–C(6)). ^{1}H-NMR (300 MHz, CD_3OD, 0.05M): 5.43 (*t*, $J = 1.3$, CHO_3); 4.38 (*td*, $J \approx 3.4$, 1.2, H–C(4)); 4.07–3.98 (*m*, H–C(1), H–C(3), H–C(5)); 3.86 (br. *s*, H–C(2)); 2.49 (*dddd*, $J = 13.7$, 4.0, 3.2, 1.5, H_{eq}–C(6)); 2.02 (*dq*, $J = 13.6$, 1.4, H_{ax}–C(6)). ^{13}C-NMR (75 MHz, CD_3OD): 105.33 (*d*, CHO_3); 76.20 (*d*); 72.58 (*d*); 70.82 (*d*); 67.00 (*d*); 65.13 (*d*); 28.19 (*t*, C(6)). EI-MS: 174 (0.2, M^+), 156 (0.2, $[M - H_2O]^+$), 149 (0.1), 130 (4), 128 (4), 110 (3), 99 (26), 73 (100), 57 (22), 43 (11), 32 (10), 28 (34), 18 (10). CI-MS: 175 (100, $[M + 1]^+$), 111 (6), 99 (26), 83 (6), 73 (27), 57 (5), 43 (3). Anal. calc. for $C_7H_{10}O_5$ (174.16): C 48.28, H 5.79; found: C 48.35, H 5.93.

*1*D*-2,4-Bis-*O*-(4-bromobenzoyl)-1,3,5-*O*-methylidyne-1,2,3,5/4-cyclohexanepentol* (D-**10**). At r.t., 4-bromobenzoyl chloride (40 mg, 0.18 mmol), AgOTf (50 mg, 0.19 mmol), and DMAP (2 mg, 0.016 mmol) were added under Ar to a soln. of D-**3** (10 mg, 0.057 mmol) in pyridine (1 ml). The mixture was heated to 70° for 36 h (additional 4-bromobenzoyl chloride (40 mg) and AgOTf (50 mg) were added after 15 h) and then treated with MeOH. Evaporation and FC (hexane/AcOEt 4.5:1) gave D-**10** (19 mg, 61%). R_f (hexane/AcOEt 4:1) 0.35. M.p. 195° (EtOH/AcOEt). $[\alpha]_D^{25} = +113.9$ ($c = 0.28$, $CHCl_3$). UV (MeCN, $2.2 \cdot 10^{-5}$ M): 246 (34303). CD (MeCN, $2.2 \cdot 10^{-5}$ M): 233 (−2.7), 239 (0), 252 (18.7). FT-IR (0.005M, $CHCl_3$): 3043*w*, 2962*w*, 2853*w*, 1726*s*, 1592*s*, 1528*w*, 1486*m*, 1435*w*, 1400*m*, 1368*w*, 1346*w*, 1261*s*, 1163*s*, 1116*s*, 1100*s*, 1071*m*, 1012*s*, 1001*s*, 958*w*, 941*m*, 888*w*, 860*w*, 847*m*, 833*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.01 (*d*, $J = 8.6$, 2 arom. H); 7.94 (*d*, $J = 8.7$, 2 arom. H); 7.63 (*d*, $J = 8.7$, 2 arom. H); 7.62 (*d*, $J = 8.6$, 2 arom. H); 5.81 (*td*, $J = 4.1$, 1.6, irrad. at 2.83→*t*, $J = 4.1$, H–C(4)); 5.69 (*t*, $J = 1.2$, CHO_3); 5.24 (br. *q*, $J \approx 2$, H–C(2)); 4.61 (*dq*, $J \approx 4$, 2, H–C(3)); 4.50 (*tq*, $J \approx 4.1$, 1.8, H–C(5)); 4.49–4.45 (*m*, H–C(1)); 2.83 (*dtd*, $J = 14.0$, 4.5, 1.7, irrad. at 5.81→*dt*, $J = 14.0$, 4.5, H_{eq}–C(6)); 2.13 (*dq*, $J = 14.0$, 1.5, H_{ax}–C(6)). ^{13}C-NMR (75 MHz, $CDCl_3$): 165.53 (*s*, C=O); 164.15 (*s*, C=O); 132.15 (2*d*); 131.91 (2*d*); 131.48 (2*d*); 131.23 (2*d*); 129.22 (*s*); 128.82 (*s*); 128.34 (*s*); 127.61 (*s*); 104.10 (*d*, CHO_3); 69.69 (*d*); 67.95 (*d*); 67.85 (*d*); 67.23 (*d*); 66.67 (*d*); 27.91 (*t*, C(6)). CI-MS: 541 (28, M^+), 340 (5), 294 (7), 185 (96), 183 (100), 105 (10), 49 (6). Anal. calc. for $C_{21}H_{16}Br_2O_7$ (540.16): C 46.70, H 2.99; found: C 46.81, H 3.19.

*1*L*-2-O-[(*tert*-Butyl)dimethylsilyl]-1,3,5-*O*-methylidyne-1,2,3,5/4-cyclohexanepentol* (L-**7**). As described for D-**7** with Na (84 mg, 3.65 mmol) in EtOH (2.5 ml) and **9b** (185 mg, 0.32 mmol) in EtOH (1.7 ml). FC (hexane/AcOEt 4:1) gave L-**7** (86 mg, 94%). M.p. 122–123° (hexane/AcOEt). $[\alpha]_D^{25} = -0.2$ ($c = 0.88$, $CHCl_3$). Spectroscopic data: identical to those of (±)-**7**. Anal. calc. for $C_{13}H_{24}O_5Si$ (288.42): C 54.14, H 8.39; found: C 54.32, H 8.37.

*1*L*-1,3,5-O-Methylidyne-1,2,3,5/4-cyclohexanepentol* (L-**3**). As described for D-**3**, with L-**7** (45 mg, 0.16 mmol), THF (dried; 2 ml), and $Bu_4NF \cdot 3\,H_2O$ (314 mg, 0.99 mmol; 3 h): L-**3** (27 mg, 99%). R_f (hexane/AcOEt 5:1) 0.33. M.p. > 270° (dec.; hexane/AcOEt). Spectroscopic data: identical to those of D-**3**.

*1*L*-2,4-Bis-O-(4-bromobenzoyl)-1,3,5-O-methylidyne-1,2,3,5/4-cyclohexanepentol* (L-**10**). As described for D-**10**, with the same amounts of reagents and solvent and L-**3** (9 mg, 0.05 mmol): L-**10** (15 mg, 54%). R_f (hexane/AcOEt 4:1) 0.35. M.p. 195–196° (EtOH/AcOEt). $[\alpha]_D^{25} = -116.7$ ($c = 0.21$, $CHCl_3$). UV (MeCN, $2.2 \cdot 10^{-5}$ M): 246 (34277). CD (MeCN, $2.2 \cdot 10^{-5}$ M): 233 (1.33), 238 (0), 252 (−19). Spectroscopic data: identical to those of D-**10**. Anal. calc. for $C_{21}H_{16}Br_2O_7$ (540.16): C 46.70, H 2.99; found: C 46.73. H 3.10.

*(±)-4-Deoxy-4-fluoro-1,3,5-O-methylidyne-*myo*-inositol* ((±)-**4**). TsOH · H_2O (210 mg, 1.13 mmol) was added at r.t. under N_2 to a soln. of (±)-**11** [46] (330 mg, 1.81 mmol) and triethyl orthoformate (0.6 ml, 3.6 mmol) in dry DMSO (30 ml). The soln. was heated at 100° for 5 h, cooled, neutralized with Et_3N, and evaporated. The residue was dissolved in the minimum amount of MeOH and purified by FC (CH_2Cl_2/MeOH 25:1→6:1). The resulting syrup (199 mg) was triturated with $CHCl_3$ to give (±)-**4** (173 mg, 50%) as a white solid. Starting material (±)-**11** was recovered as the acetate (±)-**14** (247 mg, 33%) by elution with CH_2Cl_2/MeOH 2:1, evaporation, acetylation (Ac_2O/pyridine 1:2, r.t., 12 h), and FC (hexane/AcOEt 3:1). (±)-**4**: R_f ($CHCl_3$/MeOH 10:1) 0.36. M.p. > 270°

(dec.; MeOH/AcOEt). FT-IR (CH_2Cl_2, < 0.005M): 3602*w*, 3568*w*, 2986*w*, 2963*m*, 2904*w*, 1605*w*, 1423*m*, 1162*m*, 1095*s*, 1012*s*, 957*w*, 896*m*, 865*m*, 807*s*. FT-IR (CCl_4, 0.0005M): 3620*s*, 3608*m*, 3582*s*, 3420*m* (br.), 3360*m* (br.), 3290*m* (br.). FT-IR (dioxane, 0.03M): 3416*s* (br.). FT-IR (dioxane, 0.005M): 3533*w*, 3414*s* (br.). ^{1}H-NMR (300 MHz, $CDCl_3$, < 0.005M): 5.49 (*dd*, ^5J(H,F) = 4.7, J = 1.4, CHO_3); 5.38 (*dtd*, ^2J(H,F) = 47.5, J = 4.1, 2.2, H–C(4)); 4.63 (*dtd*, J = 7.8, 3.9, 1.9, H–C(6)); 4.44 (*tq*, $J \approx 3.7$, 1.6, ^3J(H,F) ≈ 1.6, H–C(5)); 4.39 (*dquint.*, $J \approx 3.5, 1.2$, ^3J(H,F) ≈ 1.2, H–C(3)); 4.26 (*dq*, $J \approx 4.0, 2.0$, H–C(1)); 4.12 (br. *dquint.*, J = 11.8, 1.8, ^4J(H,F) ≈ 1.8, H–C(2)); 3.09 (*d*, J = 11.8, HO–C(2)); 2.17 (*t*, $J \approx 8.3$, J(H,F) ≈ 8.3, HO–C(6)). ^{1}H-NMR (300 MHz, (D_8)dioxane, 0.03M): 5.42 (*dd*, ^5J(H,F) = 4.4, J = 1.3, CHO_3); 5.19 (*dtd*, ^2J(H,F) = 47.8, J = 4.0, 1.8, H–C(4)); 4.55 (*d*, J = 10.5, HO–C(2)); 4.41 (br. *q*, $J \approx 3.8$, H–C(6)); 4.25 (*tq*, J = 3.4, 1.7, ^3J(H,F) ≈ 1.7, H–C(5)); 4.21 (br. *dquint.*, $J \approx 3.6, 1.8$, ^3J(H,F) ≈ 1.8, H–C(3)); 4.13 (*d*, J = 5.0, HO–C(6)); 4.01 (*dq*, J = 3.8, 1.9, H–C(1)); 3.94 (br. *dquint.*, J = 10.5, 1.8, ^4J(H,F) ≈ 1.8, H–C(2)). ^{1}H-NMR (300 MHz, (D_6)DMSO, < 0.05M): 5.59 (br. *d*, J = 3.8, HO–C(6)); 5.51 (*dd*, ^5J(H.F) = 4.3, J = 1.2, CHO_3); 5.45 (*d*, J = 5.8, HO–C(2)); 5.15 (*dtd*, ^5J(H,F) = 47.5, J = 4.0, 1.9, H–C(4)); 4.32–4.27 (*m*, H–C(6)); 4.26 (*tq*, $J \approx 3.5$, 1.8, ^3J(H,F) ≈ 1.8, H–C(5)); 4.16 (*dquint.*, $J \approx 3.4$, 1.8, ^3J(H,F) ≈ 1.8, H–C(3)); 3.98–3.92 (*m*, H–C(1), H–C(2)). ^{1}H-NMR (300 MHz, CD_3OD): 5.43 (*dd*, ^5J(H,F) = 4.5, J = 1.3, CHO_3); 5.21 (*dtd*, ^2J(H,F) = 47.8, J = 4.1, 1.8, H–C(4)); 4.47 (br. *td*, $J \approx 3.6$, 1.6, H–C(6)); 4.30 (*tq*, $J \approx 3.2$, 1.6, ^3J(H,F) ≈ 1.6, H–C(5)); 4.24 (*dquint.*, $J \approx 3.5$, 2.0, ^3J(H,F) ≈ 2.0, H–C(3)); 4.10–4.07 (*m*, H–C(2)); 4.06 (*dq*, $J \approx 3.8$, 1.9, H–C(1)). ^{13}C-NMR (75 MHz, CD_3OD): 104.14 (*d*, CHO_3); 86.85 (*dd*, ^1J(C,F) = 190, C(4)); 75.76 (*d*, C(1)); 73.40 (*dd*, ^2J(C,F) = 23, C(3)); 70.27 (*dd*, ^2J(C,F) = 19, C(5)); 67.99 (*d*, C(6)); 60.98 (*d*, C(2)). ^{19}F-NMR (282 MHz, $CDCl_3$, < 0.005M): −195.44 (br. *dt*, $J \approx 47.7$, 6.3). ^{19}F-NMR (282 MHz, CD_3OD): −194.44 (br. *d*, J = 47.5). CI-MS: 193 (100, $[M + 1]^+$), 175 (6), 117 (41), 99 (5), 73 (69), 29 (6). Anal. calc. for $C_7H_9FO_5$ (192.14): C 43.76, H 4.72, F 9.89; found: C 44.03, H 4.85, F 9.98.

*X-Ray Analysis of (±)-***4**: Crystals were obtained from MeOH/AcOEt. $C_7H_9FO_5$ (192.14). Orthorhombic *Pbcn*; a = 18.859 (4), b = 8.135 (3), c = 9.370 (3); V = 1437.5 (8) Å^3; D_{calc} = 1.776 Mg/m^3; Z = 8. The crystals were measured in the $\omega/2\theta$ mode on an *Enraf-Nonius-CAD4* diffractometer (graphite monochromator, MoK_α, λ = 0.71073 Å) at 100 K. Of the total of 2816 collected reflections, 2628 were independent, R = 0.0393, R_w = 0.1060. The structures were solved with the direct-methods routine of SHELXS-86 and the refinement was performed with SHELXL-93 [75].

*(±)-2-*O*-[(*tert*-Butyl)dimethylsilyl]-4-deoxy-4-fluoro-1,3,5-*O*-methylidyne-*myo*-inositol* ((±)-**12**). A soln. of (±)-**4** (335 mg, 1.74 mmol) and 2,6-lutidine (= 2,6-dimethylpyridine; 0.5 ml, 4.35 mmol) in dry DMF (3.5 ml) was treated at 0° under N_2 with (*t*-Bu)Me_2SiOTf (0.49 ml, 2.10 mmol), stirred for 10 min, warmed to r.t., and stirred for 1 additional h. The soln. was diluted with CH_2Cl_2, washed with sat. aq. $NaHCO_3$ soln., H_2O, and brine, dried ($MgSO_4$), and evaporated. FC (hexane/AcOEt 3:1) gave (±)-**12** (435 mg, 81%). R_f (hexane/AcOEt 2:1) 0.41. M.p. 107–108° (hexane/AcOEt). FT-IR (CH_2Cl_2, 0.0035M): 3606*m*, 2958*m*, 2931*m*, 2887*w*, 2858*m*, 1605*w*, 1472*w*, 1403*w*, 1378*w*, 1362*w*, 1349*w*, 1310*w*, 1288*w*, 1165*s*, 1138*s*, 1109*s*, 1065*s*, 1039*m*, 1005*s*, 971*s*, 946*m*, 897*m*, 880*m*, 848*s*, 667*w*, 582*w*, 520*m*, 508*w*. ^{1}H-NMR (300 MHz, $CDCl_3$, 0.016M): 5.52 (*dd*, ^5J(H,F) = 4.6, J = 1.4, CHO_3); 5.33 (*dtd*, ^2J(H,F) = 47.5, J = 4.2, 1.8, H–C(4)); 4.59 (*dtd*, J = 7.5, 3.8, 1.8, irrad. at 2.18 → NOE of 4%, H–C(6)); 4.40 (*tq*, $J \approx 3.3$, 1.6, ^3J(H,F) ≈ 1.6, irrad. at 2.18 → NOE of 2%, H–C(5)); 4.29 (br. *dq*, $J \approx 4.3$, 1.2, ^3J(H,F) < 1, H–C(3)); 4.23 (*dq*, ^4J(H,F) ≈ 3.3, $J \approx 1.9$, irrad. at 2.18 → NOE of 3%, H–C(2)); 4.16 (*dq*, $J \approx 3.9$, 1.9, irrad. at 2.18 → NOE of 1%, H–C(1)); 2.18 (*t*, J = 7.5, J(H,F) ≈ 7.5, HO–C(6)); 0.96 (*s*, *t*-BuSi); 0.17 (*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 102.45 (*d*, CHO_3); 86.5 (*dd*, ^1J(C,F) = 187.2, C(4)); 74.50 (*d*, C(1)); 72.01 (*dd*, ^2J(C,F) = 21.9, C(3)); 68.02 (*dd*, ^2J(C,F) = 18.3, C(5)); 67.58 (*d*, C(6)); 60.42 (*d*, C(2)); 25.88 (*q*, Me_3C); 18.36 (*s*, Me_3C); −4.71 (*q*, Me_2Si). ^{19}F-NMR (282 MHz, $CDCl_3$, 0.016M): −194.00 (br. *ddt*, $J \approx 47.9$, 7.4, 3.7). CI-MS: 324 (2, $[M + NH_4]^+$), 307 (100, $[M + 1]^+$), 249 (33, $[M - 57]^+$), 225 (4), 203 (53), 183 (52), 155 (8), 129 (3), 81 (3), 75 (7). Anal. calc. for $C_{13}H_{23}FO_5Si$ (306.40): C 50.96, H 7.57; found: C 51.15, H 7.61.

*Treatment of (±)-***12** *with (+)-(*R*)-1-Phenylethyl Isocyanate.* A soln. of (±)-**12** (380 mg, 1.24 mmol), Et_3N (340 µl, 2.48 mmol), and DMAP (150 mg, 1.24 mmol) in dry CH_2Cl_2 (19 ml) was treated at r.t. under N_2 with (+)-(*R*)-1-phenylethyl isocyanate (180 µl, 1.43 mmol) and stirred for 48 h (additional (+)-(*R*)-1-phenylethyl isocyanate (56 µl, 23 µl) was added after 12 and 24 h, resp.). The soln. was treated with sat. aq. NH_4Cl soln. and extracted with CH_2Cl_2. The combined org. layers were washed with brine, dried ($MgSO_4$), and evaporated. FC (hexane/AcOEt 5:1) yielded **13a**/**13b** (485 mg, 82%) and (±)-**12** (45 mg, 11%). HPLC (hexane/Et_2O 4:1, *Si 60-NH_2*) gave **13a** (245 mg) and **13b** (205 mg).

*2-*O*-[(*tert*-Butyl)dimethylsilyl]-4-deoxy-4-fluoro-1,3,5-*O*-methylidyne-6-*O*-{[(*R*)-1-phenylethyl]carbamoyl}-*L*-myo-inositol* (**13a**). $[\alpha]_D^{25}$ = +37.6 (c = 0.76, $CHCl_3$). M.p. 100° (hexane/AcOEt). Anal. HPLC: t_R (hexane/Et_2O 9:1) 28.4. FT-IR (0.04M, $CHCl_3$): 3441*w*, 3009*m*, 2958*m*, 2931*m*, 2886*w*, 2858*m*, 1729*s*, 1603*w*, 1505*s*, 1472*m*, 1463*m*, 1453*m*, 1398*m*, 1378*m*, 1362*w*, 1307*m*, 1278*m*, 1261*s*, 1165*s*, 1145*s*, 1107*s*, 1077*s*, 1005*s*, 968*s*, 946*m*, 890*m*, 882*m*, 851*s*, 582*w*, 552*w*, 519*m*, 503*w*. ^{1}H-NMR (300 MHz, $CDCl_3$, 23°; (*E*)/(*Z*) 85:15): 7.38–7.26 (*m*,

5 arom. H); 5.52 (*dd*, ^5J(H,F) = 4.2, *J* = 1.3, CHO_3); 5.40 (br. *td*, *J* = 3.7, 1.7, H–C(6)); 5.24 (br. *d*, ^2J(H,F) ≈ 47.9, H–C(4)); 5.02 (br. *d*, *J* ≈ 7.7, 0.85 H); 4.72–4.60 (br. *s*, 0.15 H, NH); 4.85 (br. *quint.*, *J* ≈ 7.2, PhC*H*); 4.57–4.51 (br. *s*, 0.85 H), 4.50–4.40 (br. *s*, 0.15 H, H–C(5)); 4.26–4.22 (*m*, H–C(3), 0.15 H–C(1)); 4.20–4.17 (*m*, 0.85 H–C(1)); 4.09 (br. *s*, H–C(2)); 1.55 (*d*, *J* = 6.8, Me); 0.93 (*s*, *t*-BuSi); 0.11 (*s*, Me_2Si). ^{1}H-NMR (300 MHz, $CDCl_3$, 70°): only one set of signals. ^{13}C-NMR (75 MHz, $CDCl_3$; only signals of (*E*)-**13a** visible): 153.68 (*s*, C=O); 142.93 (*s*); 128.74 (2*d*); 127.58 (2*d*); 125.98 (*d*); 102.74 (*d*, CHO_3); 85.02 (*dd*, ^1J(C,F) = 189.3, C(4)); 72.15 (*d*, C(1)); 71.94 (*dd*, ^2J(C,F) = 22.8, C(3)); 68.11 (*d*, C(6)); 66.72 (*dd*, ^2J(C,F) = 20.4, C(5)); 60.96 (*d*, C(2)); 50.86 (*d*, PhCH); 25.84 (*q*, Me_3C); 22.09 (*q*, Me); 18.35 (*s*, Me_3C); –4.74 (*q*, Me_2Si). ^{19}F-NMR (282 MHz, $CDCl_3$ 23°; (*E*)/(*Z*) 87:13): *ca.* –195.56 (br. *d*, *J* ≈ 45, 0.13 F); –195.73 (br. *d*, *J* = 47.5, 0.87 F). FAB-MS: 907 (1.7, [2 *M* + 1]$^+$), 850 (0.9, [2 *M* – 56]$^+$), 454 (100, [*M* + 1]$^+$), 396 (68, [*M* – 58]$^+$), 350 (8), 292 (18), 231 (6), 185 (14), 137 (25), 105 (79), 73 (81). Anal. calc. for $C_{22}H_{32}FNO_6Si$ (453.58): C 58.26, H 7.11, N 3.09; found: C 58.29, H 7.32, N 2.90.

*2-O-[(*tert*-Butyl)dimethylsilyl]-4-deoxy-4-fluoro-1,3,5-O-methylidyne-6-O-{[(*R*)-1-phenylethyl]carbamoyl}-*D*-myo-inositol* (**13b**). $[\alpha]_D^{25}$ = +8 (*c* = 0.46, $CHCl_3$). Anal. HPLC: t_R (hexane/Et_2O 9:1) 30.6. FT-IR (0.02M, $CHCl_3$): 3441*w*, 2958*s*, 2931*m*, 2886*w*, 2858*w*, 1728*s*, 1603*w*, 1505*m*, 1472*w*, 1463*w*, 1452*w*, 1398*w*, 1379*w*, 1362*w*, 1307*w*, 1278*w*, 1261*m*, 1165*s*, 1145*m*, 1107*m*, 1075*m*, 1005*s*, 968*m*, 947*m*, 900*w*, 882*w*, 851*s*, 594*w*, 520*m*, 506*w*. ^{1}H-NMR (300 MHz, $CDCl_3$, 23°; (*E*)/(*Z*) 4:1): 7.36–7.29 (*m*, 5 arom. H); 5.52 (br. *dd*, ^5J(H,F) ≈ 4.2, *J* ≈ 1.2, CHO_3); 5.41 (br. *s*, H–C(6)); 5.22 (br. *d*, ^2J(H,F) ≈ 47.9, H–C(4)); 5.05 (*d*, *J* = 7.9, NH); 4.85 (br. *quint.*, *J* = 7.1, 0.8 H), 4.66 (br. *quint.*, *J* ≈ 7, 0.2 H, PhC*H*); 4.58–4.51 (br. *s*, 0.2 H), 4.51–4.45 (br. *s*, 0.8 H, H–C(5)); 4.28–4.20 (br. *s*, 1.8 H), 4.08–4.02 (br. *s*, 0.2 H, H–C(1), H–C(3)); 4.16–4.10 (br. *s*, 0.8 H), 3.94–3.88 (br. *s*, 0.2 H, H–C(2)); 1.51 (*d*, *J* = 6.8, 2.4 H); 1.50–1.40 (br. *d*, 0.6 H, Me); 0.96 (*s*, 7.2 H), 0.87 (*s*, 1.8 H, *t*-BuSi); 0.17 (*s*, 4.8 H), 0.00 (*s*, 1.2 H, Me_2Si). ^{1}H-NMR (300 MHz, $CDCl_3$, 60°): one set signals. ^{13}C-NMR (300 MHz, $CDCl_3$; only signals of (*E*)-**13b** visible): 153.63 (*s*, C=O); 142.74 (*s*); 128.72 (2*d*); 127.54 (2*d*); 125.90 (*d*); 102.69 (*d*, CHO_3); 84.94 (*dd*, ^1J(C,F) = 190.2, C(4)); 72.13 (*d*, C(1)); 71.90 (*dd*, ^2J(C,F) = 22.7, C(3)); 68.09 (*d*, C(6)); 66.60 (*dd*, ^2J(C,F) = 20.3, C(5)); 60.84 (*d*, C(2)); 50.78 (*d*, PhCH); 25.83 (*q*, Me_3C); 22.14 (*d*, Me); 18.35 (*s*, Me_3C); –4.65 (*q*, Me_2Si). ^{19}F-NMR (282 MHz, $CDCl_3$; (*E*)/(*Z*) ≈ 4:1): *ca.* –195.52 (br. *d*, *J* ≈ 45, 0.2 F); –195.68 (br. *d*, *J* = 47.6, 0.8 F). ^{19}F-NMR (282 MHz, $CDCl_3$, 60°): –195.65 (br. *d*, *J* = 47.9). FAB-MS: 907 (0.85, [2 *M* + 1]$^+$), 849 (2, [2 *M* – 57]$^+$), 454 (95, [*M* + 1]$^+$), 396 (66, [*M* – 58]$^+$), 350 (7), 292 (14), 185 (12), 137 (14), 105 (100), 73 (93). Anal. calc. for $C_{22}H_{32}FNO_6Si$ (453.58): C 58.26, H 7.11, N 3.09; found: C 58.50, H 7.07, N 3.21.

X-Ray Analysis of **13a**: Crystals were obtained from AcOEt/hexane. $C_{22}H_{32}FON_6Si$ (453.58). Orthorhombic $P2_12_12_1$; *a* = 9.877, *b* = 9.994, *c* = 47.649 (3); *V* = 4703.8 Å^3; D_{calc} = 1.281 Mg/m^3; *Z* = 8. The crystals were measured in the $\omega/2\theta$ mode on an *Enraf-Nonius-CAD4* diffractometer (graphite monochromator, MoK_α, λ = 0.71073 Å) at 123 K. Of the 4718 total collected reflections, 4679 were independent, *R* = 0.0884, R_w = 0.2565. The structures were solved with the direct-methods routine of SHELXS-86, and the refinement was performed with SHELXL-93 [75].

*2-O-[(*tert*-Butyl)dimethylsilyl]-4-deoxy-4-fluoro-1,3,5-O-methylidyne-*L*-myo-inositol* (*L*-**12**). A soln. of NaOMe (1.95M, 2 ml) was added dropwise at r.t. under Ar to a soln. of **13a** (140 mg, 0.32 mmol) in MeOH (1 ml). The soln. was heated at 65° for 2 h, cooled to 0°, treated with a sat. aq. NH_4Cl soln., and extracted with Et_2O (4×). The combined org. layers were washed with sat. aq. NH_4Cl soln. and brine, dried ($MgSO_4$), and evaporated. FC (CH_2Cl_2) gave *L*-**12** (68 mg, 72%). Spectroscopic data: identical to those of (±)-**12**.

*4-Deoxy-4-fluoro-1,3,5-O-methylidyne-*L*-myo-inositol* (*L*-**4**). A soln. of *L*-**12** (45 mg, 0.19 mmol) in THF (1.5 ml) was treated at 0° under Ar with $Bu_4NF \cdot 3\ H_2O$ (140 mg, 0.44 mmol) and stirred for 150 min at r.t. Evaporation and FC (AcOEt) gave *L*-**4** (32 mg, 85%). $[\alpha]_D^{25}$ = +6 (*c* = 0.3, MeOH). M.p. 240° (dec.; MeOH/AcOEt). Spectroscopic data: identical to those of (±)-**4**. Anal. calc. for $C_7H_9FO_5$ (192.14): C 43.76, H 4.72; found: C 43.74, H 4.86.

Glycosidation of *D*-**3** *with* **1**. A suspension of *D*-**3** (70 mg, 0.40 mmol) and dried powdered 4-Å molecular sieves (200 mg) in 1,4-dioxane (8 ml, 0.05M) was stirred for 1 h at r.t. under Ar, treated with **1** (242 mg, 0.44 mmol), stirred for 4.5 h, and filtered through *Celite*. Evaporation of the filtrate and FC (hexane/AcOEt 3:1) gave *Fractions A* (58 mg), *B* (145 mg), and *C* (59 mg), besides recovered *D*-**3** (18 mg, 26%). *Fr. A* was acetylated (Et_3N/DMAP/Ac_2O 2:1:2, CH_2Cl_2, 0°, 1 h); usual workup, evaporation, and FC (hexane/AcOEt 2:1) afforded **16**/**17** 2:3 (37 mg, 13%). Similarly, *Fr. B* was acetylated; usual workup, evaporation, and FC (hexane/AcOEt 3:1) afforded **18**/**19** 1:5 (113 mg, 38%) and **20**/**21** 53:47 (21 mg, 7%). The ratios were determined by ^{1}H- and ^{13}C-NMR and HPLC of the crude product (before and after acetylation) and of each fraction. Prep. HPLC (**16**/**17**, hexane/Et_2O 2:1, 14 ml/min; **18**/**19** and **20**/**21**, hexane/AcOEt 4:1, 14 ml/min) afforded pure samples of **16**–**21**. *Fr. C* could not be acetylated (mixture of pseudotrisaccharides) and was purified by prep. HPLC (hexane/AcOEt 2:1, 14 ml/min) to give *Fr. D* (39 mg, 8%) as a mixture of at least three compounds (anal. HPLC). *Fr. D* was analyzed by NMR, but not further purified.

1D-4-O-Acetyl-1,3,5-O-methylidyne-2-O-(2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl)-1,2,3,5/4-cyclohexanepentol (**16**): R_f (hexane/AcOEt 2:1) 0.24. Anal. HPLC: t_R (hexane/AcOEt 2:1) 11.3. M.p. 142–143° (MeOH/EtOH). $[\alpha]_D^{25} = +46.7$ ($c = 0.12$, $CHCl_3$). FT-IR (0.01M, $CHCl_3$): 3089*w*, 3067*w*, 3042*w*, 3007*m*, 2964*m*, 2927*m*, 2869*m*, 1754*m*, 1496*w*, 1454*m*, 1374*m*, 1262*s*, 1167*s*, 1091*s*, 1028*s*, 1004*s*, 941*m*, 869*m*, 822*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.41–7.11 (*m*, 20 arom. H), 5.57 (br. *s*, irrad. at 3.53→*d*, $J = 1.2$, CHO_3); 5.46 (br. *td*, $J = 4.0$, 1.6, irrad. at 2.66→*t*, $J \approx 4.0$, H–C(4)); 5.02 (*d*, $J = 10.9$, PhC*H*); 4.91 (*d*, $J = 3.7$, H–C(1′)); 4.85 (*d*, $J \approx 12.2$, PhC*H*); 4.845 (*d*, $J = 11.0$, PhC*H*); 4.83 (*d*, $J = 10.9$, PhC*H*); 4.61 (*d*, $J = 12.2$, PhC*H*); 4.60 (*d*, $J = 12.1$, PhC*H*); 4.46 (*d*, $J = 10.7$, PhC*H*); 4.46–4.41 (*m*, H–C(3)); 4.43 (*d*, $J = 12.0$, PhC*H*); 4.29–4.22 (*m*, H–C(1), H–C(5)); 4.13 (*t*, $J = 9.3$, H–C(3′)); 4.05 (*ddd*, $J = 10.1$, 3.8, 1.8, H–C(5′)); 3.72 (*dd*, $J = 10.5$, 3.8, 1 H–C(6′)); 3.64 (br. *t*, $J \approx 9.2$, H–C(4′)); 3.60 (*dd*, $J = 10.5$, 1.7, 1 H–C(6′)); 3.60 (*dd*, $J = 9.6$, 3.6, H–C(2′)); 3.53 (br. *q*, $J \approx 1.2$, H–C(2)); 2.66 (*dtd*, $J = 13.9$, 4.2, 1.8, H_{eq}–C(6)); 2.02 (*s*, Ac); 1.79 (br. *dq*, $J = 13.8$, 1.5, H_{ax}–C(6)). ^{13}C-NMR (75 MHz, $CDCl_3$): 168.96 (*s*, C=O); 138.91 (*s*); 138.69 (*s*); 138.14 (*s*); 137.82 (*s*); 128.36–127.53 (several *d*); 103.93 (*d*, CHO_3); 97.17 (*d*, C(1′)); 81.73 (*d*, C(3′)); 80.43 (*d*, C(2′)); 77.66 (*d*, C(4′)); 75.68 (*t*, PhCH_2); 75.10 (*t*, PhCH_2); 73.41 (*t*, PhCH_2); 73.22 (*t*, PhCH_2); 71.08 (*d*); 70.59 (*d*, C(5′)); 70.47 (*d*); 68.54 (*t*, C(6′)); 67.59 (*d*); 67.51 (*d*); 66.55 (*d*); 27.77 (*t*, C(6)); 20.74 (*q*, Me). FAB-MS: 737 (0.9, $[M-1]^+$), 532 (1), 461 (1.6), 385 (1.2), 327 (3.6), 307 (1.5), 181 (11), 154 (13), 147 (11), 133 (40), 107 (14), 91 (100), 73 (60), 55 (36). Anal. calc. for $C_{39}H_{40}O_{11}$ (738.83): C 69.90, H 6.28; found: C 69.94, H 6.53.

1D-4-O-Acetyl-1,3,5-O-methylidyne-2-O-(2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyl)-1,2,3,5/4-cyclohexanepentol (**17**): R_f (hexane/AcOEt 2:1) 0.29. Anal. HPLC: t_R (hexane/AcOEt 2:1) 10.7. M.p. 126–127° (hexane/AcOEt). $[\alpha]_D^{25} = +14.5$ ($c = 0.22$, $CHCl_3$). FT-IR (0.01M, $CHCl_3$): 3090*w*, 3066*w*, 3042*w*, 3007*w*, 2963*m*, 2911*w*, 2869*w*, 1754*m*, 1497*w*, 1454*m*, 1434*w*, 1374*m*, 1307*w*, 1262*s*, 1167*s*, 1068*s*, 1028*s*, 1004*s*, 938*m*, 910*w*, 882*w*, 869*m*, 822*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.38–7.19 (*m*, 20 arom. H); 5.65 (br. *s*, irrad. at 3.84→*d*, $J \approx 1$, CHO_3); 5.53 (*td*, $J = 4.1$, 1.5, irrad. at 2.65→*t*, $J = 4.1$, H–C(4)); 5.06 (*d*, $J = 10.6$, PhC*H*); 4.97 (*d*, $J = 10.9$, PhC*H*); 4.84 (*d*, $J = 10.9$, PhC*H*); 4.81 (*d*, $J = 10.9$, PhC*H*); 4.79 (*d*, $J = 10.6$, PhC*H*); 4.59 (*d*, $J = 7.5$, H–C(1′)); 4.54 (*d*, $J = 10.6$, PhC*H*); 4.54 (br. *s*, PhCH_2); 4.49 (br. *dquint.*, $J \approx 4.2$, 2.2, H–C(1)); 4.37 (*dt*, $J = 4.0$, 1.9, H–C(3)); 4.28 (br. *tq*, $J \approx 4.0$, 1.7, H–C(5)); 3.84 (br. *d*, $J \approx 0.8$, H–C(2)); 3.70–3.48 (*m*, H–C(2′), H–C(3′), H–C(4′), H–C(5′), 2 H–C(6′)); 2.65 (*dtd*, $J = 13.9$, 4.0, 1.8, H_{eq}–C(6)); 2.05 (*s*, Ac); 1.84 (*dq*, $J = 13.8$, 1.5, H_{ax}–C(6)). ^{13}C-NMR (75 MHz, $CDCl_3$): 169.12 (*s*, C=O); 138.47 (*s*); 138.21 (*s*); 138.09 (*s*); 137.90 (*s*); 128.41–127.68 (several *d*); 104.03 (*d*, CHO_3); 130.75 (*d*, C(1′)); 84.54 (*d*, C(3′)); 81.87 (*d*, C(2′)); 77.82 (*d*, C(4′)); 75.70 (*t*, PhCH_2); 75.09 (*t*, 2 PhCH_2); 74.92 (*d*, C(5′)); 73.41 (*t*, PhCH_2); 72.49 (*d*); 69.89 (*d*); 69.49 (*d*); 69.36 (*t*, C(6′)); 67.62 (*d*); 66.55 (*d*); 27.67 (*t*, C(6)); 20.83 (*q*, Me). FAB-MS: 1476 (0.8, $[2\ M]^+$), 1262 (2.9, $[2\ M - C_9H_{10}O_6]^+$), 878 (2), 739 (7.6, $[M+1]^+$), 523 (4, $[M - C_9H_{10}O_6]^+$), 307 (46), 181 (61), 154 (100), 137 (88), 120 (29), 107 (48), 91 (96), 76 (41), 68 (23). Anal. calc. for $C_{39}H_{40}O_{11}$ (738.83): C 69.90, H 6.28; found: C 69.61, H 6.27.

1D-2-O-Acetyl-1,3,5-O-methylidyne-4-O-(2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl)-1,2,3,5/4-cyclohexanepentol (**18**): R_f (hexane/AcOEt 2:1) 0.44. Anal. HPLC: t_R (hexane/Et_2O 2:1) 11.3. $[\alpha]_D^{25} = +59.2$ ($c = 0.51$, $CHCl_3$). FT-IR (0.01M, $CHCl_3$): 3089*w*, 3067*w*, 3042*w*, 3007*m*, 2961*m*, 2927*m*, 2868*w*, 1737*s*, 1604*w*, 1497*w*, 1454*m*, 1436*w*, 1373*m*, 1318*w*, 1261*m*, 1166*s*, 1070*s*, 1028*s*, 1001*s*, 942*m*, 912*w*, 885*w*, 862*w*, 822*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.37–7.13 (*m*, 20 arom. H); 5.57 (br. *s*, CHO_3); 4.94 (br. *q*, $J = 1.3$, H–C(2)); 4.94 (*d*, $J = 10.8$, PhC*H*); 4.83 (*d*, $J = 10.6$, PhC*H*); 4.83 (*d*, $J = 10.9$, PhC*H*); 4.81 (*d*, $J = 3.8$, H–C(1′)); 4.78 (*d*, $J = 11.9$, PhC*H*); 4.60 (*d*, $J = 12.1$, PhC*H*); 4.55 (*d*, $J = 11.9$, PhC*H*); 4.49 (*d*, $J = 10.6$, PhC*H*); 4.47 (*d*, $J = 12.1$, PhC*H*); 4.41 (*td*, $J = 4.0$, 1.8, H–C(4)); 4.30–4.22 (*m*, H–C(1), H–C(3)); 4.13 (*tq*, $J \approx 4.0$, 1.8, H–C(5)); 3.88 (*t*, $J \approx 9.1$, H–C(3′)); 3.86–3.78 (*m*, H–C(5′)); 3.75 (*dd*, $J = 10.8$, 3.2, 1 H–C(6′)); 3.69 (*t*, $J = 10$, H–C(4′)); 3.63 (*dd*, $J = 10.9$, 1.9, 1 H–C(6′)); 3.55 (*dd*, $J = 9.6$, 3.7 H–C(2′)); 2.55 (*dtd*, $J = 13.3$, 4.0, 1.3, H_{eq}–C(6)); 2.18 (*s*, Ac); 2.14 (*dq*, $J = 13.7$, 1.3, H_{ax}–C(6)). ^{13}C-NMR (75 MHz, $CDCl_3$): 170.68 (*s*, C=O); 138.70 (*s*); 138.10 (2*s*); 137.87 (*s*); 128.66–127.72 (several *d*); 103.88 (*d*, CHO_3); 97.62 (*d*, C(1′)); 81.62 (*d*, C(3′)); 79.69 (*d*, C(2′)); 77.32 (*d*, C(4′)); 75.66 (*t*, PhCH_2); 75.19 (*t*, PhCH_2); 73.82 (*t*, PhCH_2); 73.50 (*t*, PhCH_2); 71.64 (*d*); 71.27 (*d*); 71.17 (*d*, C(5′)); 68.30 (*t*, C(6′)); 68.06 (*d*); 67.02 (*d*); 66.92 (*d*); 27.15 (*t*, C(6)); 21.06 (*q*, Me). FAB-MS: 737 (2, $[M-1]^+$), 647 (1, $[M - C_7H_7]^+$), 531 (4), 415 (4), 391 (4), 307 (3), 181 (29), 109 (30), 91 (10), 69 (62), 55 (76). Anal. calc. for $C_{39}H_{40}O_{11}$ (738.83): C 69.90, H 6.28; found: C 69.98, H 6.57.

1D-2-O-Acetyl-1,3,5-O-methylidyne-4-O-(2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyl)-1,2,3,5/4-cyclohexanepentol (**19**): R_f (hexane/AcOEt 2:1) 0.46. Anal. HPLC: t_R (hexane/Et_2O 2:1) 13.3. M.p. 75–76° (MeOH/EtOH). $[\alpha]_D^{25} = +6.2$ ($c = 0.95$, $CHCl_3$). FT-IR (0.01M, $CHCl_3$): 3067*w*, 3042*w*, 3008*m*, 2963*m*, 2869*w*, 1737*m*, 1497*w*, 1454*w*, 1414*w*, 1374*m*, 1362*m*, 1309*w*, 1262*s*, 1167*s*, 1094*s*, 1006*s*, 942*w*, 911*w*, 884*w*, 866*m*, 823*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.39–7.17 (*m*, 20 arom. H); 5.59 (br. *s*, irrad. at 5.0→*d*, $J \approx 1$, CHO_3); 5.00 (br. *q*, $J \approx 1.4$, irrad. at 5.59→*t*, $J \approx 1$, H–C(2)); 4.90 (*d*, $J = 10.9$, PhC*H*); 4.87 (*d*, $J = 11.3$, PhC*H*); 4.82 (*d*, $J = 10.8$, PhC*H*); 4.81 (*d*, $J = 11$, PhC*H*); 4.75 (*d*, $J = 11$, PhC*H*); 4.57 (*d*, $J = 12$, PhC*H*); 4.56 (*d*, $J = 11.7$, PhC*H*); 4.55

(*d*, J = 7.8, H–C(1′)); 4.53 (*td*, J = 4.0, 1.5, H–C(4)); 4.52 (*d*, J = 12, PhC*H*); 4.43 (*tq*, $J \approx 4.0$, 1.4, H–C(5)); 4.29 (*dq*, J = 4.0, 1.6, H–C(3)); 4.29–4.24 (*m*, (H–C(1)); 3.70–3.60 (*m*, H–C(3′), H–C(4′), 2 H–C(6′)); 3.50–3.44 (*m*, H–C(2′), H–C(5′)); 2.60 (*dtd*, J = 13.7, 4.0, 1.6, H_{eq}–C(6)); 2.19 (*s*, Ac); 2.13 (*dq*, J = 13.8, 1.4, H_{ax}–C(6)). ^{13}C-NMR (75 MHz, $CDCl_3$): 170.44 (*s*, C=O); 138.38 (*s*); 138.15 (*s*); 137.93 (2*s*); 128.36–127.67 (several *d*); 103.85 (*d*, CHO_3, C(1′)); 84.55 (*d*, C(3′)); 81.91 (*d*, C(2′)); 77.43 (*d*, C(4′)); 75.69 (*t*, PhCH_2); 75.00 (*t*, 2 PhCH_2); 74.84 (*d*, C(5′)); 73.93 (*d*); 73.41 (*t*, PhCH_2); 70.38 (*d*); 68.82 (*d*); 68.56 (*t*, C(6′)); 68.29 (*d*); 66.78 (*d*); 27.39 (*t*, C(6)); 21.13 (*q*, Me). FAB-MS: 1476 (0.7, [2 M]$^+$), 1262 (2.6, [2 M – $C_9H_{10}O_6$]$^+$), 829 (1.9), 739 (22, [M + 1]$^+$), 647 (3.7, [M – C_7H_7]$^+$), 523 (2.1, [M – $C_9H_{11}O_6$]$^+$), 415 (11), 307 (17), 289 (11), 271 (17), 253 (19), 242 (13), 217 (15), 199 (40), 193 (12), 181 (83), 165 (17), 154 (62), 149 (21), 136 (61), 129 (13), 120 (19), 107 (44), 91 (100), 67 (27), 59 (35). Anal. calc. for $C_{39}H_{40}O_{11}$ (738.83): C 69.90, H 6.28; found: C 69.79, H 6.41.

*1*D*-2-*O*-Acetyl-4,5-anhydro-1-*O*-formyl-3-O-(2,3,4,6-tetra-*O*-benzyl-α-*D*-glucopyranosyl)-1,2,3/4,5-cyclohexanepentol* (**20**): R_f (hexane/AcOEt 2:1) 0.39. Anal. HPLC: t_R (hexane/Et_2O 2:1) 16.5. $[\alpha]_D^{25}$ = +53.9 (c = 0.38, $CHCl_3$). FT-IR (0.07M, $CHCl_3$): 3090*w*, 3064*w*, 3042*w*, 3007*m*, 2962*w*, 2933*w*, 2866*w*, 1736*s*, 1602*w*, 1497*w*, 1454*m*, 1366*m*, 1310*w*, 1261*s*, 1161*s*, 1070*s*, 1028*s*, 930*w*, 903*w*, 861*w*, 822*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.90 (*d*, J = 0.8, CHO); 7.35–7.25 (*m*, 18 arom. H); 7.18–7.14 (*m*, 2 arom. H); 5.25 (*d*, J = 3.5, H–C(1′)); 5.00–4.94 (*m*, strong irrad. at 2.51→change, H–C(1)); 4.98 (*d*, J = 10.9, PhC*H*); 4.98 (*d*, J = 3.4, irrad. at 4.18→*s*, H–C(2)); 4.86 (*d*, J = 10.7, PhC*H*); 4.84 (*d*, J = 10.9, PhC*H*); 4.74 (br. *s*, PhCH_2); 4.61 (*d*, J = 12, PhC*H*); 4.52 (*d*, J = 10.8, PhC*H*); 4.47 (*d*, J = 12.1, PhC*H*); 4.18 (*dd*, $J \approx 3.3$, 1.8, irrad. at 4.98→*d*, $J \approx 1.5$, irrad. at 3.04→*d*, $J \approx 3.0$, H–C(3)); 4.08 (*dt*, $J \approx 9.6$, 2.8, H–C(5′)); 3.99 (*t*, J = 9.4, H–C(3′)); 3.74 (*dd*, J = 10.3, 3.4, 1 H–C(6′)); 3.69 (*t*, J = 9.5, H–C(4′)); 3.61 (*dd*, J = 10.3, 2.1, 1 H–C(6′)); 3.59 (*dd*, J = 9.7, 3.5, H–C(2′)); 3.38 (*dt*, J = 3.6, 1.9, irrad. at 3.04→br. *s*, strong irrad. at 2.51→br. *d*, $J \approx 3.5$, H–C(5)); 3.04 (*dd*, J = 3.6, 1.5, irrad. at 4.18→*d*, J = 3.6, H–C(4)); 2.51 (*ddd*, J = 14.2, 10.4, 2.4, irrad. at 4.98→*dd*, $J \approx 14$, 2, H_a–C(6)); 2.33 (*ddd*, J = 14.3, 5.6, 1.2, irrad. at 4.98→*dd*, $J \approx 14$, 1.5, H_b–C(6)); 2.06 (*s*, Ac). ^{1}H-NMR (300 MHz, C_6D_6): 7.38–7.04 (*m*, 20 arom. H, CHO); 5.23 (*d*, J = 3.4, H–C(1′)); 5.02 (*d*, J = 10.8, PhC*H*); 5.00 (*d*, $J \approx 3$, irrad. at 4.11→*s*, H–C(2)); 4.98 (*d*, J = 11.2, PhC*H*); 4.87 (*ddd*, J = 10.6, 5.8, 0.8, H–C(1)); 4.85 (*d*, J = 11.2, PhC*H*); 4.68 (*d*, J = 11.2, PhC*H*); 4.50 (br. *s*, PhCH_2); 4.47 (*d*, J = 12.2, PhC*H*); 4.39 (*d*, J = 12.2, PhC*H*); 4.32 (*ddd*, J = 10.0, 3.8, 1.8, H–C(5′)); 4.23 (*t*, J = 9.4, H–C(3′)); 4.11 (*d*, J = 3.4, H–C(3)); 3.85 (*t*, J = 10.0, H–C(4′)); 3.80 (*dd*, J = 10.4, 3.8, 1 H–C(6′)); 3.69 (*dd*, J = 10.5, 1.8, 1 H–C(6′)); 3.53 (*dd*, J = 9.7, 3.6, H–C(2′)); 2.87 (*s*, H–C(4), H–C(5)); 2.39 (*dd*, J = 13.5, 10.9, H_a–C(6)); 2.10 (*dd*, J = 13.7, 6.0, H_b–C(6)); 1.90 (*s*, Ac). ^{13}C-NMR (50 MHz, $CDCl_3$): 169.76 (*s*, C=O); 159.62 (*d*, CHO); 138.78 (*s*); 138.33 (*s*); 138.20 (*s*); 137.82 (*s*); 128.45–127.66 (several *d*); 96.96 (*d*, C(1′)); 81.34 (*d*, C(3′)); 80.20 (*d*, C(2′)); 77.20 (*d*, C(4′)); 75.50 (*t*, PhCH_2); 75.11 (*t*, PhCH_2); 73.63 (*t*, PhCH_2); 73.35 (*t*, PhCH_2); 71.95 (*d*, C(3)); 70.75 (*d*, C(5′)); 69.52 (*d*); 69.00 (*d*, C(1), C(2)); 68.42 (*t*, C(6′)); 53.68 (*d*), 52.94 (*d*, C(4), C(5)); 24.14 (*t*, C(6)); 20.77 (*q*, Me). FAB-MS: 1262 (0.4, [2 M – $C_9H_{10}O_6$]$^+$), 738 (2.5, M^+), 523 (0.9, [M – $C_9H_{11}O_6$]$^+$), 307 (11), 181 (30), 154 (42), 147 (18), 136 (46), 133 (20), 120 (15), 107 (25), 91 (100), 81 (14), 77 (23), 73 (44), 54 (23). Anal. calc. for $C_{39}H_{40}O_{11}$ (738.83): C 69.90, H 6.28; found: C 69.93, H 6.34.

*1*D*-1-*O*-Acetyl-4,5-anhydro-2-*O*-formyl-3-O-(2,3,4,6-tetra-*O*-benzyl-α-*D*-glucopyranosyl)-1,2,3/4,5-cyclohexanepentol* (**21**): R_f (hexane/AcOEt 2:1) 0.42. Anal. HPLC: t_R (hexane/Et_2O 2:1) 15.9. $[\alpha]_D^{25}$ = +60 (c = 0.17, $CHCl_3$). FT-IR (0.02M, $CHCl_3$): 3066*w*, 3042*w*, 3007*w*, 2927*s*, 2855*s*, 1732*m*, 1497*w*, 1455*m*, 1366*m*, 1261*m*, 1164*m*, 1100*m*, 1070*m*, 1028*m*, 910*w*, 861*w*, 822*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.05 (*d*, J = 1.0, CHO); 7.35–7.25 (*m*, 18 arom. H); 7.16–7.12 (*m*, 2 arom. H); 5.24 (*d*, J = 3.7, H–C(1′)); 5.08 (*dd*, J = 3.1, 1.0, irrad. at 8.05→*d*, J = 3.1, H–C(2)); 4.96 (*d*, J = 10.9, PhC*H*); 4.88 (br. *dd*, J = 10.5, 5.6, strong irrad. at 2.52→br. *s*, H–C(1)); 4.84 (*d*, J = 10.6, PhC*H*); 4.83 (*d*, J = 10.9, PhC*H*); 4.825 (*d*, J = 11.5, PhC*H*); 4.69 (*d*, J = 11.5, PhC*H*); 4.59 (*d*, J = 12.1, PhC*H*); 4.49 (*d*, J = 10.7, PhC*H*); 4.485 (*d*, J = 12.0, PhC*H*); 4.20 (br. *dd*, $J \approx 3.2$, 1.5, irrad. at 5.08→br. *s*, irrad. at 3.07→*d*, $J \approx 3$, H–C(3)); 4.13 (*ddd*, J = 10.0, 4.0, 2.3, H–C(5′)); 3.97 (*t*, J = 9.4, H–C(3′)); 3.70 (*dd*, J = 10.3, 4.0, 1 H–C(6′)); 3.60 (*dd*, J = 10.5, 2.2, 1 H–C(6′)); 3.60 (br. *t*, $J \approx 9.7$, H–C(4′)); 3.59 (*dd*, J = 9.7, 3.7, H–C(2′)); 3.40 (br. *dt*, $J \approx 3.4$, 1.8, irrad. at 3.07→br. *s*, irrad. at 2.52→*d*, $J \approx 3.5$, H–C(5)); 3.07 (*dd*, J = 3.7, 1.5, H–C(4)); 2.52 (*ddd*, J = 14.1, 10.7, 2.3, H_a–C(6)); 2.32 (*ddd*, J = 13.9, 5.7, 1.3, H_b–C(6)); 1.99 (*s*, Ac). ^{1}H-NMR (300 MHz, C_6D_6): 7.57 (*d*, J = 0.8, CHO); 7.40–7.02 (*m*, 20 arom. H); 5.18 (*d*, J = 3.6, H–C(1′)); 5.03 (br. *s*, irrad. at 7.57→*d*, J = 2.5, irrad. at 4.17→*s*, H–C(2)); 5.01 (*d*, J = 10.6, PhC*H*); 4.98 (*d*, J = 10.8, PhC*H*); 4.91 (*dd*, J = 10.7, 5.7, strong irrad. at 2.44→change, H–C(1)); 4.85 (*d*, J = 11.3, PhC*H*); 4.64 (*d*, J = 11.2, PhC*H*); 4.62 (*d*, J = 11.6, PhC*H*); 4.47 (*d*, J = 11.4, PhC*H*); 4.45 (*d*, J = 12.1, PhC*H*); 4.37 (*d*, J = 12.0, PhC*H*); 4.35 (*ddd*, J = 10.0, 4.2, 1.5, H–C(5′)); 4.20 (*t*, J = 9.3, H–C(3′)); 4.17 (br. *s*, H–C(3)); 3.76 (*dd*, J = 10.4, 4.3, 1 H–C(6′)); 3.73 (*t*, J = 9.3, H–C(4′)); 3.67 (*dd*, J = 10.4, 1.6, 1 H–C(6′)); 3.53 (*dd*, J = 9.8, 3.6, H–C(2′)); 2.88 (br. *dt*, $J \approx 3.5$, 1.8, strong irrad. at 2.44→*d*, J = 3.5, H–C(5)); 2.81 (*dd*, J = 3.5, 1.3, irrad. at 4.17→*d*, J = 3.5, H–C(4)); 2.44 (*ddd*, J = 13.7, 10.7, 2.2, H_a–C(6)); 2.18 (*ddd*, J = 13.8, 5.7, 1.3, H_b–C(6)); 1.81 (*s*, Ac). ^{13}C-NMR (75 MHz, $CDCl_3$): 169.50 (*s*, C=O); 159.51 (*d*, CHO); 138.66 (*s*); 138.08 (*s*); 138.00 (*s*); 137.72

(*s*); 128.42–127.59 (several *d*); 97.20 (*d*, C(1′)); 81.33 (*d*, C(3′)); 80.14 (*d*, C(2′)); 77.80 (*d*, C(4′)); 75.52 (*t*, PhCH_2); 75.32 (*t*, PhCH_2); 73.61 (*t*, PhCH_2); 73.01 (*t*, PhCH_2); 72.80 (*d*, C(3)); 70.81 (*d*, C(5′)); 69.08 (*d*); 68.92 (*d*, C(1), C(2)); 68.63 (*t*, C(6′)); 53.97 (*d*), 52.64 (*d*, C(4), C(5)); 25.06 (*t*, C(6)); 21.01 (*q*, Me). FAB-MS: 737 (3.8, $[M-1]^+$), 647 (0.7, $[M-\text{BnO}]^+$), 572 (1), 531 (1), 523 (1, $[M-C_9H_{11}O_6]^+$), 482 (1.7), 415 (5), 391 (10), 307 (6), 181 (28), 154 (25), 149 (20), 136 (24), 107 (18), 95 (16), 91 (100), 81 (17), 75 (17), 71 (14), 54 (27). Anal. calc. for $C_{39}H_{40}O_{11}$ (738.83): C 69.90, H 6.28; found: C 69.67, H 6.03.

Glycosidation of L-**4** *with* **1**. A suspension of L-**4** (65 mg, 0.34 mmol) and dried powdered 4-Å molecular sieves (188 mg) in 1,4-dioxane (6.8 ml, 0.05M) was stirred at r.t. under Ar for 1 h, treated with **1** (200 mg, 0.36 mmol), stirred for 4.5 h at r.t. and filtered through *Celite*. Evaporation and FC (hexane/AcOEt 3:1) gave **26**/**27**/**28**/**29** 10:13:18:59 (147 mg, 60%; ratio determined by ^{19}F-NMR and HPLC of the crude product), L-**4** (18 mg, 28%), and a mixture of 4 trisaccharides (37 mg, 9%; determined by ^{19}F-NMR). Prep. HPLC (*Si 60*; hexane/AcOEt 7:3, 15 ml/min, for **27** and **28**; hexane/THF 4:1, 10 ml/min, for **26** and **29**) afforded pure samples of **26**–**29**.

*4-Deoxy-4-fluoro-1,3,5-*O*-methylidyne-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-*D*-glucopyranosyl)-*L*-*myo*-inositol* (**26**): $[\alpha]_D^{25} = +37.5$ ($c = 0.08$, $CHCl_3$). Anal. HPLC: t_R (hexane/THF 3:1) 4.17, t_R (hexane/AcOEt 3:1) 4.91. FT-IR (0.02M, CCl_4): 3620*w*, 3460*w*, 3090*w*, 3066*w*, 3032*m*, 2962*m*, 2924*m*, 2865*m*, 1946*w*, 1870*w*, 1806*w*, 1741*w*, 1606*w*, 1497*w*, 1454*m*, 1382*m*, 1362*m*, 1310*w*, 1261*s*, 1208*m*, 1166*s*, 1093*s*, 1028*s*, 1007*s*, 971*m*, 945*s*, 922*w*, 898*w*, 604*w*, 553*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.39–7.14 (*m*, 20 arom. H); 5.50 (*dd*, ^5J(H,F) = 4.5, $J = 1.2$, CHO_3); 5.31 (*dtd*, ^2J(H,F) = 44.3, $J = 3.3$, 1.2, H–C(4)); 5.03 (*d*, $J = 10.9$, PhC*H*); 4.91 (*d*, $J = 3.7$, H–C(1′)); 4.86 (*d*, $J = 10.6$, PhC*H*); 4.85 (*d*, $J = 10.8$, PhC*H*); 4.85 (*d*, $J = 12.7$, PhC*H*); 4.62 (*d*, $J = 12.1$, PhC*H*); 4.61 (*d*, $J = 11.9$, PhC*H*); 4.49 (*d*, $J = 10.8$, PhC*H*); 4.44 (*d*, $J = 11.9$, PhC*H*); 4.47–4.40 (*m*, H–C(1), H–C(3), 2 H–C(6)); 4.37 (br. *tq*, $J \approx 3$, 1.5, ^3J(H,F) ≈ 1.5, H–C(5)); 4.12 (*t*, $J = 9.3$, H–C(3′)); 4.09 (*ddd*, $J = 10.3$, 4.3, 2.1, H–C(5′)); 3.93 (br. *s*, H–C(2)); 3.72 (*dd*, $J = 10.6$, 4.2, 1 H–C(6′)); 3.65 (*dd*, $J = 10.6$, 2.2, 1 H–C(6′)); 3.62 (br. *t*, $J \approx 9.5$, H–C(4′)); 3.60 (*dd*, $J = 9.8$, 3.7, H–C(2′)); 2.10–2.04 (*m*, OH). ^{13}C-NMR (75 MHz, $CDCl_3$): 138.90 (*s*); 138.45 (*s*); 138.15 (*s*); 137.95 (*s*); 128.54–127.59 (several *d*); 102.53 (*d*, CHO_3); 97.96 (*d*, C(1′)); 86.02 (*dd*, ^1J(C,F) = 186.9, C(4)); 81.84 (*d*, C(3′)); 80.38 (*d*, C(2′)); 77.79 (*d*, C(4′)); 75.74 (*t*, PhCH_2); 75.17 (*t*, PhCH_2); 73.43 (*t*, 2 PhCH_2); 72.54 (*d*, C(1)); 70.68 (*d*, C(5′)); 69.36 (*dd*, ^2J(C,F) = 22.8, C(3)); 68.79 (*t*, C(6′)); 68.00 (*dd*, ^2J(C,F) = 18.3, C(5)); 67.29 (*d*), 67.17 (*d*, C(2), C(6)). ^{19}F-NMR (282 MHz, $CDCl_3$): −193.89 (br. *d*, $J = 47.1$). FAB-MS: 713 (3, $[M-1]^+$), 181 (18), 107 (12), 91 (94). Anal. calc. for $C_{41}H_{43}FO_{10}$ (714.78): C 68.90, H 6.06; found: C 69.07, H 6.31.

*4-Deoxy-4-fluoro-1,3,5-*O*-methylidyne-2-*O*-(2,3,4,6-tetra-*O*-benzyl-β-*D*-glucopyranosyl)-*L*-*myo*-inositol* (**27**): $[\alpha]_D^{25} = +6$ ($c = 0.33$, $CHCl_3$). Anal. HPLC: t_R (hexane/AcOEt 3:1) 5.33. FT-IR (0.02M, CCl_4): 3619*w*, 3426*w*, 3090*w*, 3066*w*, 3032*m*, 2960*m*, 2906*m*, 2867*m*, 1946*w*, 1869*w*, 1806*w*, 1742*m*, 1606*w*, 1497*w*, 1454*m*, 1360*m*, 1307*w*, 1261*m*, 1208*m*, 1167*s*, 1073*s*, 1029*s*, 1005*s*, 953*m*, 900*w*, 832*w*, 697*s*, 602*w*, 556*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.39–7.17 (*m*, 20 arom. H); 5.56 (*dd*, ^5J(H,F) = 4.6, $J = 1.3$, CHO_3); 5.32 (*dtd*, ^2J(H,F) = 47.9, $J = 4.2$, 1.8, H–C(4)); 5.08 (*d*, $J = 10.7$, PhC*H*); 4.96 (*d*, $J = 11$, PhC*H*); 4.83 (*d*, $J = 10.8$, PhC*H*); 4.81 (*d*, $J = 10.9$, PhC*H*); 4.78 (*d*, $J = 10.6$, PhC*H*); 4.70–4.66 (*m*, H–C(3)); 4.63 (*d*, $J = 7.5$, H–C(1′)); 4.63–4.58 (*m*, 2 H–C(6)); 4.59 (*d*, $J = 12$, PhC*H*); 4.56 (*d*, $J = 10.6$, PhC*H*); 4.53 (*d*, $J = 12$, PhC*H*); 4.42 (*tq*, $J \approx 3.4$, 1.7, ^3J(H,F) ≈ 1.7, H–C(5)); 4.34 (*dq*, $J \approx 2.3$, 1.9, H–C(1)); 4.25–4.21 (*m*, H–C(2)); 3.73 (*dd*, $J = 10.8$, 1.7, 1 H–C(6′)); 3.71–3.58 (*m*, 1 H–C(6′), H–C(4′), H–C(3′)); 3.52–3.48 (*m*, H–C(5′)); 2.36 (br. *t*, $J \approx 6$, J(H,F) ≈ 6, OH). ^{13}C-NMR (75 MHz, $CDCl_3$): 138.56 (*s*); 138.36 (*s*); 138.10 (*s*); 138.02 (*s*); 128.43–127.67 (several *d*); 103.38 (*d*, CHO_3); 102.61 (*d*, C(1′)); 86.20 (*dd*, ^1J(C,F) = 186.6, C(4)); 84.58 (*d*, C(3′)); 81.92 (*d*, C(2′)); 77.69 (*d*, C(4′)); 75.74 (*t*, PhCH_2); 75.08 (*t*, PhCH_2); 75.02 (*t*, PhCH_2); 74.94 (*d*, C(5′)); 73.39 (*t*, PhCH_2); 71.78 (*d*, C(1)); 70.78 (*dd*, ^2J(C,F) = 22.6, C(3)); 68.95 (*t*, C(6′)); 67.78 (*dd*, ^2J(C,F) = 18, C(5)); 67.38 (*d*), 67.26 (*d*, C(2), C(6)). ^{19}F-NMR (282 MHz, $CDCl_3$): −193.80 (br. *d*, $J = 47.5$). FAB-MS: 1427 (0.08, $[2M-1]^+$), 1237 (0.15, $[2M-191]^+$), 713 (2.7, $[M-1]^+$), 531 (1.5), 415 (3), 271 (3), 253 (5), 181 (26), 91 (100). Anal. calc. for $C_{41}H_{43}FO_{10}$ (714.78): C 68.90, H 6.06; found: C 68.78, H 6.19.

*4-Deoxy-4-fluoro-1,3,5-*O*-methylidyne-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α-*D*-glucopyranosyl)-*L*-*myo*-inositol* (**28**): $[\alpha]_D^{25} = +51.2$ ($c = 0.29$, $CHCl_3$). Anal. HPLC: t_R (hexane/AcOEt 3:1) 4.45. FT-IR (0.014M, CCl_4): 3585*w*, 3090*w*, 3066*w*, 3032*w*, 2963*m*, 2926*w*, 2865*w*, 1946*w*, 1737*w*, 1606*w*, 1497*w*, 1454*w*, 1402*w*, 1362*w*, 1320*w*, 1301*w*, 1261*s*, 1208*w*, 1163*s*, 1095*s*, 1012*s*, 955*w*, 891*w*, 866*w*, 832*m*, 697*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.36–7.11 (*m*, 20 arom. H); 5.49 (*dd*, ^5J(H,F) = 4.3, $J = 1.3$, CHO_3); 5.28 (*dtd*, ^2J(H,F) = 47.6, $J = 4.1$, 1.7, H–C(4)); 4.95 (*d*, $J = 10.8$, PhC*H*); 4.94 (*d*, $J = 3.7$, H–C(1′)); 4.83 (*d*, $J = 11.3$, PhC*H*); 4.79 (*d*, $J = 11.9$, PhC*H*); 4.60 (*d*, $J = 12$, PhC*H*); 4.73 (*d*, $J = 11.9$, PhC*H*); 4.60 (*d*, $J = 12.0$, PhC*H*); 4.55 (*d*, $J = 12.1$, PhC*H*); 4.52–4.48 (*m*, H–C(3)); 4.47 (*d*, $J = 10.8$, PhC*H*); 4.46–4.42 (*m*, 2 H–C(6)); 4.36–4.32 (*m*, H–C(5)); 4.28 (*dq*, $J = 3.8$, 1.9, H–C(1)); 4.15 (*dquint.*, $J \approx 11.3$, 1.5, ^4J(H,F) ≈ 1.5, H–C(2)); 3.89 (br. *t*, $J \approx 9.3$, H–C(3′)); 3.76–3.70 (*m*, H–C(5′)); 3.71–3.64 (*m*, 2 H–C(6′)); 3.60 (br. *t*, $J \approx 9.6$, H–C(4′)); 3.57 (*dd*, $J = 9.7$, 3.7, H–C(2′)); 3.00 (*d*, $J = 11.1$, OH). ^{13}C-NMR

(75 MHz, $CDCl_3$): 138.67 (*s*); 138.22 (*s*); 137.98 (*s*); 137.66 (*s*); 128.46–127.64 (several *d*); 102.92 (*d*, CHO_3); 97.57 (*d*, C(1′)); 84.39 (*dd*, ^1J(C,F) = 191.6, C(4)); 81.42 (*d*, C(3′)); 79.86 (*d*, C(2′)); 77.39 (*d*, C(4′)); 75.69 (*t*, Ph*C*H_2); 75.22 (*t*, Ph*C*H_2); 73.60 (*t*, Ph*C*H_2); 73.40 (*d*, C(6)); 73.20 (*t*, Ph*C*H_2); 72.55 (*d*, C(1)); 71.72 (*dd*, ^2J(C,F) = 25.8, C(3)); 71.53 (*d*, C(5′)); 68.40 (*t*, C(6′)); 66.70 (*dd*, ^2J(C,F) = 20, C(5)); 60.74 (*d*, C(2)). ^{19}F-NMR (282 MHz, $CDCl_3$): −196.38 (br. *d*, *J* = 47.5). FAB-MS: 713 (5, $[M-1]^+$), 623 (1.2, $[M-91]^+$), 569 (0.7), 530 (1.1), 415 (4), 325 (1.2), 271 (4), 253 (3), 181 (31), 91 (100). Anal. calc. for $C_{41}H_{43}FO_{10}$ (714.78): C 68.90, H 6.06; found: C 68.63, H 6.21.

*4-Deoxy-4-fluoro-1,3,5-*O*-methylidyne-6-*O*-(2,3,4,6-tetra-*O*-benzyl-β-*D*-glucopyranosyl)-*L*-*myo*-inositol* (**29**): $[\alpha]_D^{25}$ = +9.9 (*c* = 0.78, $CHCl_3$). Anal. HPLC: t_R (hexane/AcOEt 3:1) 4.91, t_R (hexane/THF 3:1) 4.96. FT-IR (0.018M, CCl_4): 3585*w*, 3090*w*, 3067*w*, 3032*m*, 2963*m*, 2906*m*, 2865*m*, 1946*w*, 1868*w*, 1806*w*, 1742*w*, 1606*w*, 1497*w*, 1454*m*, 1402*m*, 1380*w*, 1361*m*, 1323*w*, 1300*m*, 1277*w*, 1261*s*, 1238*w*, 1209*w*, 1163*s*, 1082*s*, 1028*s*, 1011*s*, 995*s*, 958*m*, 948*m*, 910*w*, 894*w*, 872*w*, 832*w*, 697*s*, 605*w*, 570*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.38–7.18 (*m*, 20 arom. H); 5.51 (*dd*, ^5J(H,F) = 4.3, *J* = 1.2, CHO_3); 5.28 (*dtd*, ^2J(H,F) = 47.6, *J* = 4.0, 1.6, H–C(4)); 4.94 (*d*, *J* = 11, PhC*H*); 4.84 (*d*, *J* = 11.3, PhC*H*); 4.83 (*d*, *J* = 11.3, PhC*H*); 4.82 (*d*, *J* = 10.9, PhC*H*); 4.74 (*d*, *J* = 11, PhC*H*); 4.69–4.65 (*m*, 2 H–C(6)); 4.66–4.56 (*m*, 3 PhC*H*); 4.63–4.59 (*m*, H–C(5)); 4.53 (*d*, *J* ≈ 7.2, H–C(1′)); 4.36–4.31 (*m*, H–C(3)); 4.27 (*dt*, *J* ≈ 3.7, 1.8, H–C(1)); 4.08 (br. *d*, *J* ≈ 10.8, H–C(2)); 3.77–3.70 (*m*, 2 H–C(6′)); 3.68–3.60 (*m*, H–C(3′), H–C(4′)); 3.51–3.44 (*m*, H–C(5′)); 3.47 (br. *t*, *J* ≈ 7.8, H–C(2′)); 3.14 (*d*, *J* = 11.6, OH). ^{13}C-NMR (75 MHz, $CDCl_3$): 138.50 (*s*); 138.09 (2*s*); 138.00 (*s*); 128.46–127.66 (several *d*); 102.84 (*d*, CHO_3, C(1′)); 84.51 (*d*, C(3′)); 84.46 (*dd*, ^1J(C,F) = 191.5, C(4)); 81.82 (*d*, C(2′)); 77.62 (*d*, C(4′)); 75.68 (*t*, Ph*C*H_2); 75.08 (*d*, C(5′)); 75.08 (*t*, Ph*C*H_2); 74.98 (*t*, Ph*C*H_2); 73.45 (*t*, Ph*C*H_2); 72.47 (*d*), 72.29 (*d*, C(1), C(6)); 71.81 (*dd*, ^2J(C,F) = 24.4, C(3)); 68.75 (*t*, C(6′)); 68.34 (*dd*, ^2J(C,F) = 19.5, C(5)); 60.79 (*d*, C(2)). ^{19}F-NMR (282 MHz, $CDCl_3$): −195.82 (br. *d*, *J* = 47.6). FAB-MS: 713 (8, $[M-1]^+$), 623 (1.6, $[M-BnO]^+$), 513 (1), 415 (7), 271 (9), 253 (11), 221 (6), 181 (65), 91 (100). Anal. calc. for $C_{41}H_{43}FO_{10}$ (714.78): C 68.90, H 6.06; found: C 68.63, H 5.90.

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