Glycosylidene Carbenes

Part 26[1])

The Intramolecular F···HO Hydrogen Bond of 1,3-Diaxial 3-Fluorocyclohexanols

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According to *ab-initio* calculations, the CF···HO H-bond in 1,3-diaxial 3-fluorocyclohexanol is characterized by d(F···H) = 2.08 Å, d(F,O) = 2.88 Å, and ∠ (F···H–O) = 138°, and by ΔE between 1.2 and 4.1 kcal/mol, depending upon the reference system. Relative to the OH stretching frequency of axial cyclohexanol, the OH stretching frequency of 1,3-diaxial 3-fluorocyclohexanol is shifted by $\Delta\omega = 7\ cm^{-1}$. The rigid fluoro diols D-**4** and L-**4** were prepared from tetrahydroxy-*p*-benzoquinone in 11 steps and 1% overall yield. The IR spectrum of **4** in CCl_4 soln. is characterized by $\Delta\nu = 7\ cm^{-1}$ for the axial and $\Delta\nu = 44\ cm^{-1}$ for the equatorial OH group. A relatively strong intramolecular CF···HO bond of **4** in CCl_4 is evidenced by the large through-space coupling ^5J(F,HO) of 9.3 Hz. Nevertheless, this F···HO bond is disrupted in ethereal solvents, while the bifurcated O···HO bond subsists. In CCl_4, the carbene generated from the glucosylidene-derived diazirine **5** reacted more rapidly with the axial OH group of D-**4** and L-**4** than with the equatorial one. This regioselectivity is in keeping with the weaker H-bond of the axial OH group. The regioselectivity is lower in ethers, but its solvent dependence does not parallel solvent basicity. This is not satisfactorily explained by the differential interaction of the ether solvents with the axial and equatorial OH groups, as evidenced by the solvent dependence of their chemical shift, but must also reflect the different interaction of the solvents with the carbene derived from **5**, leading to ylides. The lower solvent dependence of the anomeric selectivity for the glycosidation of the equatorial OH group is a consequence of the coordination of the intermediate oxycarbenium ion with O–C(1) and O–C(3) rather than with the solvent. Under conditions of competitive glycosylation in CCl_4, the fluoro alcohol D-**22** reacted more slowly than the alcohol L-**24**, evidencing the intramolecular F···HO H-bond.

Introduction. – Intramolecular CF···HO H-bonds have been much debated. The conformation of simple fluorohydroxy compounds, such as 2-fluoroethanol (**1**), *trans*-2-fluorocyclohexanol, and *o*-fluorophenol (**2**) has been extensively studied to find possible effects of H-bonding. Microwave [2], IR [2–4], ^{1}H-NMR [4], and electron diffraction spectroscopy [5] as well as *ab-initio* calculations [4][6] indicate that 2-fluoroethanol prefers the Gg′ conformation (**1**)[2]), the only one geometrically compatible with such a H-bond; the second energetically most favourable conformer (A*g*) is less stable by 2 kcal/mol [4–8]. Similar observations and calculations were reported for *trans*-2-fluorocyclohexanol [9]. The conformational behaviour of *o*-fluorophenol could not be satisfactorily analysed by IR [10][11], ^{1}H-NMR [12–14], or ^{17}O-NMR spectroscopy [15]. Two conformers, presumably the s-*trans* (**2a**) and the s-*cis* one (**2b**), were observed by FIR (200–500 cm^{-1}, OH torsion) [16] and by fluorescence spectroscopy [17]. The FIR data

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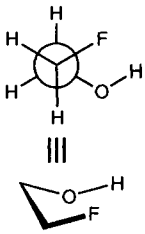
[2]) The Gg′ conformation is characterized by a *gauche* orientation about the C–C (G) and the C–O bond (*g*), the corresponding torsion angles (+ 60° and −60°) having opposite signs (′). This leads to a parallel orientation of the C–F and O–H bonds.

[16] and *ab-initio* calculations [18] suggest an enthalpy difference (ΔH) between the two conformers of 1.4–1.7 kcal/mol, the s-*cis*-conformer being the more stable one. The proximity of the F-atom and the hydroxy H-atom in these fluorohydroxy compounds has often been taken to reflect an intramolecular F···HO bond, although F and H can only weakly overlap. Microwave spectroscopy [2][19], electron diffraction [5], and *ab-initio* calculations [4][6] indicate a F···H distance of 2.5 Å in 2-fluoroethanol and of 2.3 Å in *o*-fluorophenol [18], barely less than the sum of the *van der Waals* radii of H and F (2.67 Å). Apart from H-bonding, other factors favour the observed conformations, *e.g.*, the dipole-dipole attraction between the nearly antiparallel dipoles of the O–H and C–F bonds [19], the *gauche* effect [5][20][21], and the destabilization of other conformers by lone-pair repulsion between O and F [4]. Taking one or the other of these corrections into account, H-bond contributions of 0 [4] to 1.8 kcal/mol [6] have been proposed.



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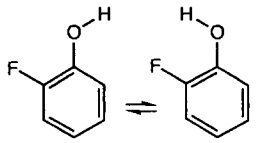
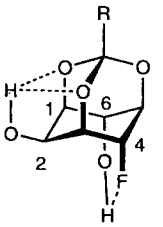
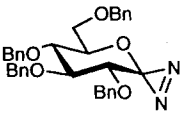


2a **2b**



D-**3** R = H
D-**4** R = Bu



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Intermolecular F···HO interactions are weak but significant. The enthalpy of formation ΔH[3]) of the 1-fluoroheptane···phenol complex in $Cl_2C{=}CCl_2$ is −2.54 kcal/mol [22]. For the fluorocyclohexane···phenol complex in CCl_4, $\Delta H = -3.1$ kcal/mol [23]. *Ab-initio* calculations for the H-bond in $HOH\cdots FCH_3$ yield $\Delta E = -2.38$ kcal/mol, with $d(H\cdots F) = 1.9$ Å [24]. For comparison, the ΔH of an OH···O bond is typically comprised between −4 and −6 kcal/mol [25][26]. Examples of F···HO short contacts in crystal structures are scarce, and have been reviewed [24][27–29].

For intramolecular F···HO bonds, one may expect a better F···H overlap and a stronger H-bond when the ring including the H-bond is larger than the one of the 2-fluoro alcohols discussed above. For fluoro alcohols, this has not been studied systematically, but such a behaviour is known for alkoxy alcohols of the type $HO(CH_2)_nOMe$ [30].

We wished to study intramolecular F···HO bonds engaged in a six-membered ring. The 1,3-diaxial conformer of *cis*-3-fluorocyclohexanol appeared to be well-suited for the formation of such a bond [31]. We have prepared the rigid fluorocyclohexanol **3** (R = H), but its poor solubility in apolar solvents restricted the investigations of the F···HO bond [31]. We now report the *ab-initio* calculations of 3-fluorocyclohexanol and related systems, the preparation of the highly soluble fluorocyclohexanediol **4** (R = Bu), and the analysis of the F···HO bond of **4** by IR and ^{1}H-NMR spectroscopy. We also report the

[3]) We refer to the enthalpy of formation of the H-bonded complex, which is not necessarily the same as the enthalpy contribution of the H-bond.

effect of this F···HO bond on the reactivity of the diol **4** towards the carbene generated from the glycosylidene-derived diazirine **5**.

Results and Discussion. – 1. *Calculations.* The calculations were performed on the MeF···HOMe and MeOH···HOMe complexes (*Table 1*) as well as on 1,3-diaxial 3-fluorocyclohexanol and related alcohols (*Table 2*) using the Gaussian 94 programme [32] and the B3LYP/6-31+G* hybrid density functional method (*cf.* [33] and ref. cit. therein)[4]). The 6-311+G** basis set was used as a check when possible. The IR frequencies were calculated in the harmonic approximation using analytical derivatives, and are referred to as ω, to distinguish them from the experimental (anharmonic) frequencies $\tilde{\nu}$. For the MeF···HOMe complex, the 6-31 + G* (*Table 1, Entry 1*) and 6-311 + G** (*Entry 2*) basis set yielded similar results. The energy of complex formation (ΔE) is −3.63 kcal/mol, the F···H distance is 2.0 Å, and the O–H···F angle 148°. As compared to the MeF···HOMe adduct, the MeOH···HOMe dimer (*Entries 3* and *4*) is more stable (ΔE = − 5.92 kcal/mol), more compact (d(O···H) = 1.9 Å), and characterized by a more highly linear H-bond (O–H···O angle = 176°). The (harmonic) ω values calculated for the MeOH dimer are much larger than the (anharmonic) $\tilde{\nu}$ values found for the gas-phase [34]. The overestimated frequency shift of the H-bonded OH stretching mode is a known deficiency of the B3LYP functional density method [33]. However, the

Table 1. *B3LYP Calculations of the Energy, Geometry, and OH Stretching Frequency ω of the MeF···HOMe and MeOH···HOMe Complexes, as Compared to the Experimental OH Stretching Frequencies $\tilde{\nu}$*

1)	6-31 + G*	MeF	+	MeOH	→	MeF···HOMe	ΔE = − 3.67 kcal/mol
	ω [cm^{-1}]	–		3763		3730	d(F···H) = 1.98 Å
	$\Delta\omega$[a]) [cm^{-1}]					33	d(F,O) = 2.88 Å
							∠(O···H–O) = 153.1°
2)	6-311 + G**	MeF	+	MeOH	→	MeF···HOMe	ΔE = − 3.63 kcal/mol
	ω [cm^{-1}]	–		3842		3800	d(F···H) = 2.02 Å
	$\Delta\omega$[a]) [cm^{-1}]					42	d(F,O) = 2.88 Å
							∠(F···H–O) = 147.6°
3)	6-31 + G*	MeOH	+	MeOH	→	MeOH···HOMe	ΔE = − 6.24 kcal/mol
	ω [cm^{-1}]	3763		3763		3764, 3615	d(O···H) = 1.89 Å
	$\tilde{\nu}$ [cm^{-1}]	3681		3681		3684, 3574	d(O,O) = 2.86 Å
	$\Delta\omega$[a]) [cm^{-1}]					+1, −148	∠(O···H–O) = 173.6°
	$\Delta\tilde{\nu}$[a]) [cm^{-1}]					+3, −107	
4)	6-311 + G**	MeOH	+	MeOH	→	MeOH···HOMe	ΔE = − 5.92 kcal/mol
	ω [cm^{-1}]	3842		3842		3844, 3689	d(O···H) = 1.90 Å
	$\tilde{\nu}$ [cm^{-1}]	3681		3681		3684, 3574	d(O,O) = 2.87 Å
	$\Delta\omega$[a]) [cm^{-1}]					+2, −153	∠(O···H–O) = 176.2°
	$\Delta\tilde{\nu}$[a]) [cm^{-1}]					+3, −107	

[a]) For the definition of $\Delta\omega$ and $\Delta\tilde{\nu}$, see *Footnote 5*.

[4]) We thank Dr. *Martin Suhm*, Laboratorium für Physikalische Chemie, ETH-Zürich, for the calculations and for valuable discussions.

calculated $\Delta\omega$ values[5]) of the MeOH dimer (+ 2; $-153\ cm^{-1}$) are in rather good agreement with the experimental $\Delta\tilde{\nu}$ (+ 3; $-107\ cm^{-1}$) [34] due to error compensation.

While a particular H-bond may be defined in geometric terms, the energy associated with it is defined as the energy difference between the H-bonded system and a non-H-bonded reference system. Thus, the energy of the H-bond depends on the reference system. We have, on the one hand, calculated the energy difference ΔE between the '*endo*'- and the '*exo*'-conformers of diaxial 3-fluorocyclohexanol (O → H vector pointed towards and away from the ring, respectively; *Table 2*, *Entry 2*) and, on the other hand, ΔE for the isodesmic reaction of axial fluorocyclohexane with axial '*endo*'-cyclohexanol to 1,3-diaxial '*endo*'-3-fluorocyclohexanol and cyclohexane (*Entry 4*). ΔE for the '*endo*'/'*exo*'-conformers is expected to express an upper limit for the energy associated with the H-bond, as it combines the disappearance of destabilizing interactions in the '*exo*'-conformer (such as lone-pair repulsion) with the appearance of stabilizing interactions in the '*endo*'-conformer. It amounts to 3.3 kcal/mol in favour of the '*endo*'-conformer (*Entry 2*). Taking into account the energy difference of −0.80 kcal/mol favouring the '*exo*'-conformation of axial cyclohexanol (*Entry 1*), the energy associated to the F···HO bond reaches an upper limit of 4.13 kcal/mol. ΔE for the isodesmic reaction is expected to express a lower limit for the energy associated with the H-bond. There are no destabilizing interactions in the starting compounds (except the one associated with the '*endo*'-conformer of axial cyclohexanol, also present in the product), while 3-fluorocyclohexanol is destabilized by the parallel orientation of the C–O and C–F bonds. This energy difference amounts to 1.24 kcal/mol. Thus, the calculated energy associated with the intramolecular F···HO bond of diaxial 3-fluorocyclohexanol is comprised between 1.24 and 4.13 kcal/mol.

For the sake of comparison, we have also calculated the energy difference for the '*endo*'- and '*exo*'-conformers of cyclohexane-1,3-diol (*Entry 3*). Similarly to diaxial 3-fluorocyclohexanol, diaxial cyclohexane-1,3-diol prefers the H-bonded '*endo*'-conformation. The energy difference between these conformers is 5.85 kcal/mol, leading to an upper limit for the O···HO bond of 0.80 + 5.85 = 6.65 kcal/mol. The isodesmic reaction of axial '*endo*'-cyclohexanol with axial '*exo*'-cyclohexanol to 1,3-diaxial '*endo,exo*'-cyclohexane-1,3-diol and cyclohexane (*Entry 5*) is exothermic by 3.85 kcal/mol. Thus, the calculated energy associated with the intramolecular O···HO bond of diaxial cyclohexane-1,3-diol is comprised between 3.85 and 6.65 kcal/mol.

The relative positions of F, H, and O in the MeF···HOMe complex are very similar to those in the H-bonded *cis*-3-fluorocyclohexanol. The amount of energy gained upon formation of the MeF···HOMe complex (3.63 kcal/mol) is within the energy limits associated to the F···HO bond of *cis*-3-fluorocyclohexanol (1.24–4.13 kcal/mol). It is,

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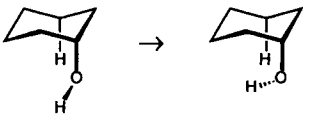
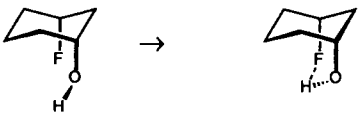
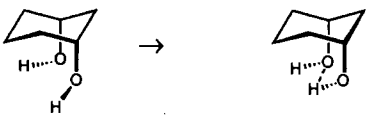
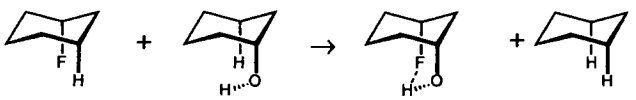
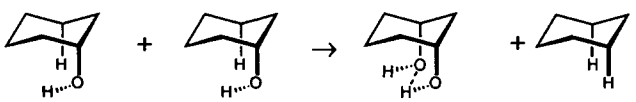
[5]) $\Delta\omega$ is defined as $\omega^{ref} - \omega^{b}$, with ω^{ref} and ω^{b} being the calculated OH stretching frequency of a reference alcohol lacking the H-bond and of the H-bonded alcohol under scrutiny. Similarly, $\Delta\tilde{\nu} = \tilde{\nu}^{ref} - \tilde{\nu}^{b}$ [35]. For the intermolecularly H-bonded MeOH···FMe and MeOH···HOMe complexes (*Table 1*), free MeOH was taken as the reference alcohol, with $\omega^{ref} = 3763$ (6-31 + G*) or $3842\ cm^{-1}$ (6-311 + G**), and $\tilde{\nu}^{ref} = 3681\ cm^{-1}$ (gas phase) [34]. For the intramolecularly H-bonded diaxial 3-fluorocyclohexanol and diaxial cyclohexane-1,3-diol (*Table 2*), $\omega^{ref} = 3743\ cm^{-1}$, the frequency of the calculated most stable conformer of axial cyclohexanol. For the intramolecularly OH···X bonded (X = F, OH, $OSiMe_2(^tBu)$) substituted cyclohexanols of *Table 3*, the reference is the alcohol where X is substituted by H: $\tilde{\nu}^{ref} = 3605$ (deoxyinositol **24**, CH_2Cl_2) or $3628\ cm^{-1}$ (**24**, CCl_4). This is in line with the value $\tilde{\nu}^{ref} = 3638$ to $3628\ cm^{-1}$ proposed for secondary alcohols in CCl_4 [36].

Table 2. *B3LYP/6-31 + G* Calculations of the Energy, Geometry, and OH Stretching Frequency of Cyclohexanol, 3-Fluorocyclohexanol, and Cyclohexane-1,3-diol*

1)				$\Delta E = +0.80$ kcal/mol
θ(H–C–O–H) [°]	63.3	179.9		
ω [cm^{-1}]	3743	3747		
$\Delta\omega$[a]) [cm^{-1}]	≡0	−4		
2)				$\Delta E = -3.33$ kcal/mol
θ(H–C–O–H) [°]	60.8	−158.8	d(F···H) = 2.08 Å	
ω [cm^{-1}]	3739	3736	d(F,O) = 2.88 Å	
$\Delta\omega$[a]) [cm^{-1}]	4	7	∠(F···H–O) = 138.0°	
3)				$\Delta E = -5.85$ kcal/mol
θ(H–C–O–H) [°]	59.7	−155.4	d(O···H) = 2.00 Å	
ω [cm^{-1}]	3737; 3737	3742; 3674	d(O,O) = 2.83 Å	
$\Delta\omega$[a]) [cm^{-1}]	6; 6	1; 69	∠(O···H–O) = 141.4	
4)				$\Delta E = -1.24$ kcal/mol
5)				$\Delta E = -3.85$ kcal/mol

[a]) For the definition of $\Delta\omega$ and $\Delta\tilde{\nu}$, see *Footnote 5*.

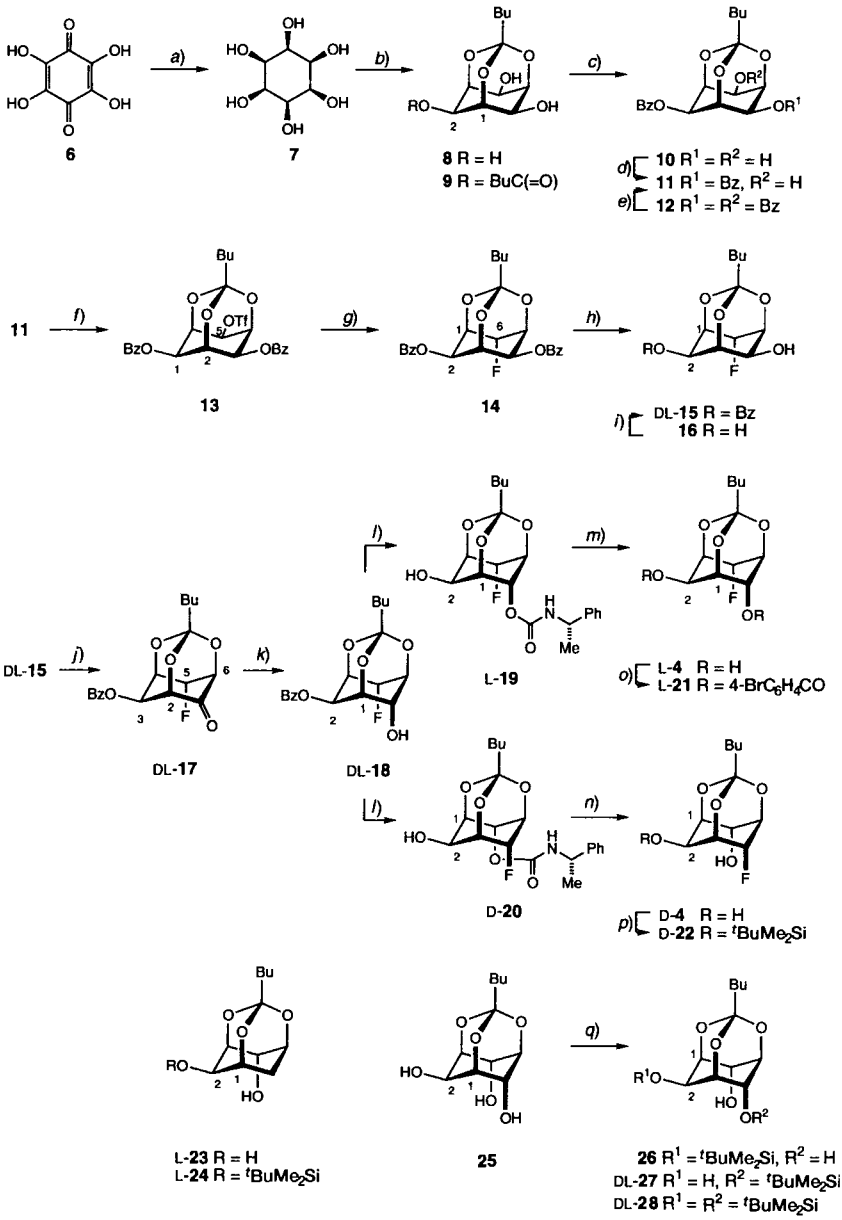
therefore, striking that $\Delta\omega$ for the MeF···HOMe complex ($\Delta\omega$ = 33–42 cm^{-1}) is so much larger than for the H-bonded conformer of *cis*-3-fluorocyclohexanol ($\Delta\omega$ = 7 cm^{-1}). It appears that $\Delta\omega$ is not only a function of the F···H distance and F···H–O angle, but also of the arrangement of the C–O and C–F bonds.

2. *Synthesis and Characterization of the Fluoro Diols* D-**4** *and* L-**4**. The orthoformate DL-**3** has been obtained by orthoesterification of DL-4-deoxy-4-fluoro-*myo*-inositol [31], for which only tedious preparations [37][38] were known at that time[6]). We envisaged to synthesize the enantiomeric orthopentanoates D-**4** and L-**4** by conversion of *cis*-inositol (**7**) into the triol **8** and subsequent introduction of the axial F and OH groups[7]), as this strategy may be applied to the synthesis of related diaxial cyclohexanes (*Scheme 1*).

[6]) Since then, a more attractive synthesis of DL-4-deoxy-4-fluoro-*myo*-inositol has been reported [39].

[7]) The descriptors 'axial' and 'equatorial' refer to the carbocyclic ring.

Scheme 1



a) H_2, 10%, Pd/C, H_2O, 23°; 16–20%. *b*) $BuC(OMe)_3$, TsOH · H_2O, DMSO, 60°; 86% of **8**, 10% of **9**. *c*) BzCl, Py, 23°; 21% of **10**, 55% of **11**, 20% of **12**. *d*) BzBr, Py, 23°; 42% of **10**, 31% of **11**, 17% of **12**. *e*) Et_3N, MeOH, THF, reflux; 19% of **10**, 50% of **11**, 16% of **12**. *f*) Tf_2O, Py, CH_2Cl_2, −10°; 95%. *g*) $[(Me_2N)_3P{=}N^+{=}P(NMe_2)_3]F^-$, toluene, reflux; 25–44%. *h*) Et_3N, MeOH, reflux; 5% of **14**, 58% of **15**, 31% of **16**. *i*) BzBr, Py. *j*) *Dess-Martin* periodinane, CH_2Cl_2, 23°. *k*) $LiBH_4$, THF, −10°; 84% from **15**, *l*) (*S*)-Phenylethyl isocyanate, 4-(dimethylamino)pyridine, CH_2Cl_2, 23°; MeONa, MeOH, 23°; 43% of L-**19**, 41% of D-**20**. *m*) $LiBHEt_3$, THF 0 → 23°; 91%, *n*) $LiBHEt_3$, THF, 0 → 23°; 79%. *o*) 4-Bromobenzoyl chloride, Py; quant. *p*) $^tBuMe_2SiOTf$, Py, CH_2Cl_2, 0 → 23°: 75–100%. *q*) $^tBuMe_2SiCl$, 1*H*-imidazole, DMF, 23°; 49% of **26**, 6% of **27**, 21% of **28**.

Hydrogenation [40][41] of commercially available tetrahydroxy-*p*-benzoquinone (**6**) provided 16–20% of *cis*-inositol (**7**), conveniently isolated [42] by ion-exchange chromatography (*Dowex 50W* × 2, Ca^{++} form). Acid-catalyzed transorthoesterification [43] with trimethyl orthopentanoate yielded 86% of the crystalline triol **8**, together with 10% of its monoester **9**. The structure of **8** was established by X-ray diffraction analysis of **8** · H_2O[8]). Benzoylation led to a mixture of the mono-, di-, and tribenzoates **10**–**12**, which were separated by chromatography. The desired dibenzoate **11** was isolated in 55% yield; the monobenzoate **10** (21%) and the tribenzoate **12** (20%) were recycled.

The stable crystalline triflate **13** was obtained in 95% yield from the dibenzoate **11**. Treatment of **13** with 1,1,1,3,3,3-hexakis(dimethylamino)diphosphazenium fluoride[9]) [56][57] led to the fluoro dibenzoate **14** (25–44%) together with a complex mixture. This transformation is evidenced in the ^{1}H-NMR spectrum by the disappearance of the broad *s* of H–C(5) of **13** at 5.15 ppm, and the appearance of a new signal for **14** at 5.31 ppm (J_{vic} = 4.4 Hz, typical of a *trans*-configuration [31]; J_{gem} = 48.1 Hz). Partial debenzoylation of **14** gave the fluoro alcohol DL-**15** and the readily recycled fluoro diol **16**. Attempts to invert the configuration at the HO–C moiety by triflation followed by nucleophilic displacement, or by *Mitsunobu* reaction resulted in extensive decomposition. However, oxidation of DL-**15** to the cyclohexanone DL-**17** (in equilibrium with its hydrate) followed by reduction with $LiBH_4$ yielded 84% of DL-**18**. The reduction proved highly selective; only signals of DL-**18** were observed in the ^{19}F-NMR spectrum of the crude. The diastereoselectivity is in agreement with *Cieplak*'s rule [58], according to which the transition state leading to DL-**18** is stabilized by electron delocalization from the σ(C(2),C(3)) and σ(C(5),C(6)) orbitals into the σ^*(H,C(1)) orbital associated to the incipient bond. Treatment of DL-**18** with (*S*)-phenylethyl isocyanate [59][60] followed by debenzoylation led to the diastereoisomeric carbamates L-**19** and D-**20** (82–85%), which were separated by HPLC. Decarbamoylation with $LiBHEt_3$, much easier to handle than the standard, volatile $HSiCl_3$ [61], gave the desired enantiomers D-**4** and L-**4**, respectively, in 79–91% yield.

The relative configuration of L-**4** was established by X-ray diffraction analysis (*Fig.*)[8]). The unit cell contains two conformers of L-**4** in a 1:1 ratio, L-**4a**, characterized by an ordered Bu side chain, and L-**4b**, characterized by an highly disordered Bu group. There are no intra- or intermolecular F···HO bonds, with the possible exception of an intermolecular F···HO–C(2) H-bond between two molecules of L-**4a** (d(H···F) = 2.25 Å, d(O,F) = 2.72 Å, ∠(O–H···F) = 109°). The proximity of these two groups may be a fortuitous consequence of the stronger adjacent intermolecular C(6)–O···HO–C(2) bond (d(H···O) = 1.91 Å, d(O,O) = 2.83 Å, ∠(O–H···O) = 160°). The absolute configuration of L-**4** was assigned on the basis of the positive first *Cotton* effect of the bis(4-bromobenzoate) L-**21** [62].

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[8]) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre*. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. (fax: + 44 (1223) 336 033; e-mail: deposit@ccdc.cam.ac.uk).'

[9]) Other fluorinating reagents such as 'anhydrous' tetrabutylammonium fluoride (TBAF, [44] [45]), the hypervalent silicon fluorides $[(Me_2N)_3S]^+[Me_3F_2Si]^-$ (TASF, [38] [46–48]) and $[^nBu_4N]^+[Ph_3F_2Si]^-$ (TBAT, [49]), and the hypervalent tin fluoride $[^nBu_4N]^+[Ph_3F_2Sn]^-$ [50] led to extensive decomposition (*cf.* [51–55]). We thank Prof. *Phil De Shong*, University of Maryland, for a generous gift of TBAT.

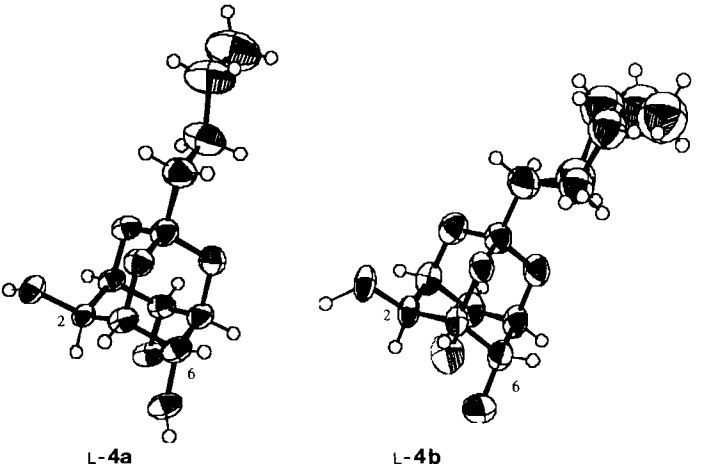


Figure. *ORTEP Representation of the X-ray structure of the fluoro diol* L-**4**. Two conformers, L-**4a** (ordered side chain) and L-**4b** (disordered side chain), are present in the unit cell.

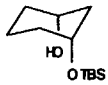
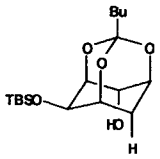
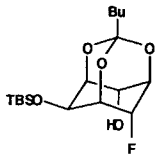
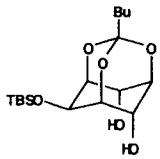
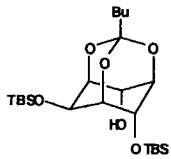
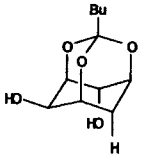
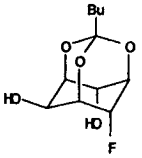
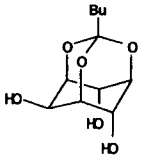
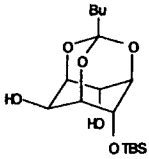
The alcohols **22**–**28** were required as reference compounds. The monosilyl ether D-**22** was obtained from the diol D-**4** (75%; *Scheme 1*). The preparation of **23**–**25** is described in the preceding paper [63]. The isomeric monosilyl ethers **26** (49%) and DL-**27** (6%), and the disilyl ether DL-**28** (21%) were obtained from the triol **25** (see *Exper. Part*).

According to vapour-pressure osmometry, D-**4** exists as a monomer in a 4 mM CH_2Cl_2 solution. In agreement with this, the position of the OH bands in the IR spectra of 0.05–15 mM solns. of D-**4** in CCl_4 is concentration independent. While the OH bands for solutions of D-**4** in chlorinated solvents (CCl_4, CH_2Cl_2) are characterized by sharp and well-resolved OH bands, those of D-**4** in ethereal solvents (Et_2O, *t*-BuOMe, 1,4-dioxane, THF) are strong and broad (3200–3700 cm^{-1}), showing local maxima. In *Table 3*, the (observed) OH stretching frequencies $\tilde{\nu}$ of D-**4** and of the related alcohols **22** and **23**–**28** [63] are compared to the (calculated) OH frequencies ω of cyclohexanols. The ω values are larger by 115–124 cm^{-1} than the $\tilde{\nu}$ values for CCl_4 solutions. The $\Delta\omega$ values, however, are in good agreement with the $\Delta\tilde{\nu}$ values.

For solns. in CCl_4, $\Delta\tilde{\nu}$ associated with the axial OH group of the fluoro alcohols D-**4** and D-**22** amounts to 7 cm^{-1}, equal to $\Delta\omega$. These small $\Delta\tilde{\nu}$ values show that the F···HO bond is weak. For solutions in CH_2Cl_2, $\Delta\tilde{\nu}$ drops to 0–1 cm^{-1} suggesting that even such a weak H-bond acceptor as CH_2Cl_2 competes with the CF group for the formation of a H-bond. The substitution of F by a OH or silyloxy group results in a much stronger H-bond; the HO···HO bond of the diaxial cyclohexane-1,3-diol **26** is characterized by $\Delta\tilde{\nu} = 88\ cm^{-1}$, and the *t*-$BuMe_2SiO$···HO bond of its silyl ether DL-**28** by $\Delta\tilde{\nu} = 119\ cm^{-1}$. The equatorial OH group of the fluoro diol D-**4** is involved in a bifurcated intramolecular O,O···HO bond of intermediate strength ($\Delta\tilde{\nu} = 28$–$45\ cm^{-1}$), similar to the bifurcated H-bond of the fluoro diol **3** [31] and the triol **25** [63].

The ^{1}H-NMR data relating to the CHOH groups of D-**4** are compiled in *Table 4*. For solutions of D-**4** in CCl_4, the axial OH appears as a *t*, due to ^3J(H,OH) = 9.3 Hz and ^5J(F,HO) = 9.3 Hz. The ^5J(F,HO) through-space coupling [64][65] which also appears in the ^{19}F-NMR spectrum of D-**4** is among the largest known for 3-fluoro alcohols, evidenc-

Table 3. *Calculated (in vacuo) and Experimental (≤ 15 mM solution) OH Stretching Frequencies* [cm^{-1}] *of Cyclohexanols.* TBS = $^tBuMe_2Si$.

					
OH_{ax}: *in vacuo*	ω	3743	3736	3742, 3674	–
OH_{ax}: *in vacuo*	$\Delta\omega$[5])	≡ 0	7	1, 69	–
					
		D-**24**	D-**22**	**26**	DL-**28**
OH_{ax}: CCl_4	$\tilde{\nu}$	3628	3621	3620, 3540	3509
OH_{ax}: CCl_4	$\Delta\tilde{\nu}$[5])	≡ 0	7	8, 88	119
OH_{ax}: CH_2Cl_2	$\tilde{\nu}$	3605	3605	3596, 3518a	3489
OH_{ax}: CH_2Cl_2	$\Delta\tilde{\nu}$	≡ 0	0	9, 87	116
					
		D-**23**	D-**4**	**25**	DL-**27**
OH_{ax}: CCl_4	$\tilde{\nu}$	3628	3621	3618, 3540	3508
OH_{ax}: CCl_4	$\Delta\tilde{\nu}$	0	7	10, 88	120
OH_{ax}: CH_2Cl_2	$\tilde{\nu}$	3605	3604	3597, 3516	3486
OH_{ax}: CH_2Cl_2	$\Delta\tilde{\nu}$	0	1	8, 89	119
OH_{eq}: CCl_4	$\tilde{\nu}$	3583	3584	3584	3584
OH_{eq}: CCl_4	$\Delta\tilde{\nu}$	45	44	44	44
OH_{eq}: CH_2Cl_2	$\tilde{\nu}$	3577	3575	3576	3571
OH_{eq}: CH_2Cl_2	$\Delta\tilde{\nu}$	28	30	29	34

ing the relatively strong F···HO bond [66][67]. Upon increasing the solvent basicity [68–73], the chemical shift for the axial OH increases from 1.89 to 4.52 ppm, and ^3J(H,HO) decreases from 9.3 to 4.6 Hz. The through-space ^5J(F,HO) decreases from 9.3 to 7.3 Hz in passing from CCl_4 to CD_2Cl_2, and is no longer visible in the ethereal solvents. This evidences that the F···HO bond is progressively weakened, and that the axial OH group is engaged in an increasingly stronger H-bond to the solvent. The chemical shift of the equatorial OH group increases from 2.71 to 4.27 ppm in passing from C_6D_6 to (D_8)THF, and ^3J(H,HO) decreases from 12.2 to 9.9 Hz. The intramolecular bifurcated O···HO bond is thus only partially broken in the more highly basic solvents, similarly to what has been observed for the related alcohol **3** [31]. These interpretations are in keeping with the temperature dependence of the chemical shift of the OH groups.

Table 4. *^{1}H-NMR Chemical Shifts* [ppm] *and Coupling Constants* [Hz] *for the OH Groups of the Fluoro Diol* D-**4** *in Solvents of Increasing Basicity*

	HO–C(2)	^3J(H–C(2), OH)	HO–C(6)	^3J(H–C(6), OH)	^5J(F,OH)
C_6D_6	2.71	11.7	buried	buried	buried
CCl_4[a])	2.71	12.2	1.89	9.3	9.3
$CDCl_3$	2.96	12.0	2.12	8.3	8.3
CD_2Cl_2	2.99	11.6	2.16	7.3	7.3
$(D_{10})Et_2O$	3.78	10.9	4.10	5.1	0
(D_8)dioxane	4.19	10.3	4.07	5.0	0
(D_8)THF	4.27	9.9	4.52	4.6	0

[a]) Containing 10 vol-% of CD_2Cl_2 for locking purposes.

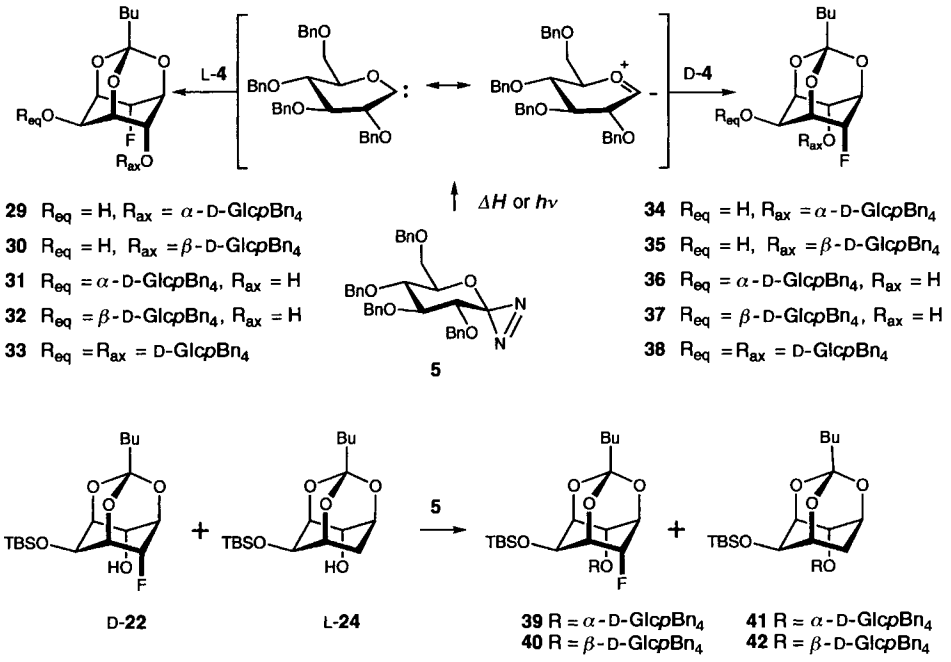
As a rule, the temperature dependence of the chemical shift ($\Delta\delta/\Delta T$) is larger for an inter- rather than intramolecularly H-bonded OH group [74–78]. For a solution of D-**4** in $CDCl_3$, $\Delta\delta/\Delta T$ is small for both the equatorial and axial OH groups (–1.7 and –2.3 ppb/°, resp.) For a solution of D-**4** in (D_8)dioxane, however, $\Delta\delta/\Delta T$ is large for both OH groups (–6.5 and –6.2 ppb/°). It may be concluded that, in $CDCl_3$, both OH groups are involved in intramolecular H-bonds, while in (D_8)dioxane both OH groups form H-bonds with the solvent. Remarkably, for D-**4** in dioxane, the temperature dependence of the chemical shift for the equatorial OH group (involved in both inter- and intramolecular H-bonds) is dominated by the intermolecular component.

3. *Glucosylation of the Fluoro Diols* D-**4**, L-**4**, *and* DL-**4**, *the Monosilylated Fluoro Diol* D-**22**, *and the Monosilylated Diol* L-**24**. We have shown that the regioselectivity of the glycosylation of diols by glycosylidene diazirines such as **5** depends on the relative kinetic acidity of the OH groups, as conditioned by intra- and intermolecular H-bonds. Thus, the reactivity of OH groups functioning as H-bond donors is inversely proportional to the strength of the H-bond [79–81]. We, therefore, expected a preferential glycosylation in apolar solvents of the axial OH group of **4**, as this OH group is involved in at best a weak F···HO bond. Basic solvents should attenuate this preference, and the attenuation should be proportional to the basicity of the solvent, as the axial OH group should more readily form an intermolecular H-bond to a basic solvent than the equatorial OH group, already involved in a relatively strong (bifurcated) intramolecular H-bond.

The diols L-**4**, D-**4**, and DL-**4** (*Scheme 2*) were separately glucosylated at 23° with 1 mol-equiv. of diazirine **5** in the presence of powdered 3-Å molecular sieves, using a 7.5 mM initial concentration of each reactant in the chosen solvent (*Table 5*). Under these conditions, the glucosylation of L-**4** gave mostly the regioisomeric pairs of the anomeric monoglucosides **29** + **30**, and **31** + **32** (50–65%), besides 1–5% of a mixture of the bis-glucosides **33** and 35–50% of recovered starting material. Similarly, the glucosylation of D-**4** gave the regioisomeric pairs of the anomeric monoglucosides **34** + **35**, and **36** + **37**, besides a small amount of the bis-glucosides **38** and starting material. No other products were detected in the ^{19}F-NMR spectra of the crude mixtures. The ratios of the monoglucosides, as based on the ^{19}F-NMR spectra of the crudes, are reported in *Table 5*. In some cases, the (1→2)-linked monoglucosides were produced in too small amounts to precisely determine the α-D/β-D ratio. The isolation of the individual glucosides required extensive chromatography, and the material balance was only *ca.* 80%. Never-

theless, the ratio of the isolated glucosides corresponds to the one derived from the ^{19}F-NMR spectra. The degree of conversion of the starting material was increased to 83% by using 1.5 equiv. of the diazirine **5** (*Entry 9*) without significant effect on the regioselectivity, but the concomitant bisglucosylation complicated the interpretation of the spectra. The spectra of the monoglucosides are very similar to those of their analogues derived from the orthoformate **3** [31].

Scheme 2



TBS = ^{t}BuMe$_2$Si, D-GlcpBn$_4$= 2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl

With the exception of a marginal effect in the glucosylations in CCl_4, the regioselectivity did not depend on the absolute configuration of **4**. The results of the glucosylation of D-**4** (*Entry 4*) and L-**4** (*Entry 5*) were compared to those of DL-**4** (*Entry 6*). No significant difference was observed. The glucosylations performed in CCl_4 and CH_2Cl_2 (*Entries 1–3*) gave a ratio of (1→6)- *vs.* (1→2)-linked monoglucosides greater than or equal to 88:12. The axial OH group, involved in a weaker H-bond than the equatorial one, is kinetically more acidic and reacts faster. The glucosylations in ethereal solvents (*Entries 4–12*) led to lower regioselectivities. The diastereoselectivity of the glucosylation of the axial, but not of the equatorial OH group depended on the basicity of the solvent, with THF leading to the highest selectivity in favour of the β-D-anomer[10]). This is in keeping with earlier results [79].

[10]) In an exploratory experiment, L-**4** was glucosylated in THF at −60° under photolytic conditions. As expected, the diastereoselectivity increased for the (1→6)-linked monoglucosides (95:5) and for the (1→2)-linked monoglucosides (80:20).

Table 5. *Ratio of the Products of the Glucosylations of the Fluoro Diols* L-**4**, D-**4**, *and* DL-**4** *with 1.0 mol-equiv. of the Diazirine* **5**, *as Determined from the* ^{19}F-*NMR Spectra of the Crudes*[a])

Entry	Solvent	Abs. config. of **4**	Regioselectivity	Diastereoselectivity	
			$(1 \rightarrow 6)/(1 \rightarrow 2)$ (**29** + **30**)/(**31** + **32**) or (**34** + **35**)/(**36** + **37**)	α-D$(1 \rightarrow 6)/\beta$-D$(1 \rightarrow 6)$ **29**/**30** or **34**/**35**	α-D$(1 \rightarrow 2)/\beta$-D$(1 \rightarrow 2)$ **31**/**32** or **36**/**37**
1	CCl_4	D	92:08	30:70	(33:66)
2	CCl_4	L	89:11	34:66	(33:66)
3	CH_2Cl_2	D	88:12	29:71	(29:71)
4	1,4-dioxane	D	88:12	11:89	(25:75)
5	1,4-dioxane	L	86:14	18:82	(33:66)
6	1,4-dioxane	DL	87:13[b])	16:84[b])	(17:83)[b])
			86:14[c])	17:83[c])	(17:83)[c])
7	THF	D	82:18	11:89	20:80
8	THF	L	85:15	11:89	26:74
9	THF[d])	L	81:19	17:83	31:69
10	^{t}BuOMe	D	78:22	21:79	29:71
11	^{t}BuOMe	L	79:21	22:78	42:58
12	Et_2O	L	77:23	25:75	45:55

[a]) Ratios in parentheses indicate a relatively high error of the values, due to the low amount of $(1 \rightarrow 2)$-linked monoglucosides. [b]) For the monoglucosides derived from D-**4**. [c]) For the monoglucosides derived from L-**4**. [d]) 1.5 equiv. of the diazirine **5**; initial concentration of L-**4**, 50 mM.

To evaluate if the intramolecular F···HO bond has any effect upon the reactivity of the axial OH group, we compared the glucosylation of the monosilylated fluoro diol D-**22** and the monosilylated diol L-**24** (*Scheme 2*). In the absence of an intramolecular F···HO bond and of an H-bond to the solvent, one expects a higher kinetic acidity of the fluorinated alcohol D-**22**, and, therefore, a higher reactivity towards a glycosylidene carbene. A H-bond-accepting solvent would again attenuate this difference. However, the fluoro alcohol D-**22** proved less reactive than the alcohol L-**24** towards glucosylation by **5** in CCl_4 (*Table 6*, *Entry 1*). This difference disappears when 1,4-dioxane is the solvent (*Entry 2*). The result of the competitive glucosylation of D-**22** and L-**24** shows a clear-cut effect of the intramolecular F···HO bond on the reactivity of D-**22** towards the glucosylidene carbene generated from **5**.

For the glucosylation of **4**, surprisingly, the dependence of the regioselectivity on the solvent ($CCl_4 > CH_2Cl_2 >$ 1,4-dioxane $>$ THF $> Et_2O$) does not parallel solvent basic-

Table 6. *Ratio of the Products of the Glucosylation of* D-**22**/L-**24** *with 1.0 mol-equiv. of the Diazirine* **5**, *as Determined by Anal. HPLC of the Crudes*

Entry	Solvent	Regioselectivity	Diastereoselectivity (α-D/β-D)	
		(**39** + **40**)/(**41** + **42**)	**39**/**40**	**41**/**42**
1	CCl_4	40:60	23:77	25:75
2	1,4-dioxane	53:47	11:89	13:87

ity (CCl_4 < CH_2Cl_2 < 1,4-dioxane < Et_2O < THF [68–73]), the regioselectivity being higher for glucosylations in THF than in Et_2O (*Table 5*). Since the regioselectivity is the same for Et_2O and *t*-BuOMe, any steric effect is inoperative beyond the difference between THF and Et_2O. The solvent dependence could reflect a differential capability of THF and Et_2O to form H-bonds with the free axial OH group or the intramolecularly H-bonded equatorial OH group. That such an effect exists is evidenced by the different solvent dependence of the chemical shift δ for the axial *vs.* the equatorial OH group, δ increasing in the sequence CCl_4 < 1,4-dioxane < Et_2O < THF for the axial OH group, and in the sequence CCl_4 < Et_2O < 1,4-dioxane < THF for the equatorial OH group (*Table 4*). However, the $\Delta\delta$ values are moderate, and as the relative influence of Et_2O and THF remains unaltered, this cannot be the decisive factor[11]). Therefore, one has to consider the interaction of the solvent with the carbene. Nucleophilic solvents react with carbenes to form ylides [82], and THF should be more prone to do so than Et_2O. The basicity of such ylides derived from **5** may well be lower than the one of the parent carbene[12]), depend upon the structure (*i.e.*, on the solvent), and influence the regioselectivity of its reaction with the fluoro diol **4**.

That the solvent dependence of the anomeric selectivity is much larger for the glucosylation of the axial *vs.* the equatorial OH group of **4** (*Table 4*) is readily explained by pointing out that the oxycarbenium ion generated by deprotonation of the equatorial OH group is properly oriented to coordinate with O–C(1) and O–C(3) [31], independently of the solvent, while the oxycarbenium ion generated by deprotonation of the axial OH group will have to interact with the solvent.

We thank Drs. *V. Gramlich* and *B. Schweizer* for the X-ray analyses, and the *Swiss National Science Foundation* and *F. Hoffmann-La Roche Ltd.*, Basle, for generous support.

Experimental Part

General. Solvents were freshly distilled from CaH_2 or Na/benzophenone. Anal. TLC: *Merck* precoated silica gel *60 F254* plates; detection by treatment with a soln. of 5% $(NH_4)_6Mo_7O_{26} \cdot 4H_2O$, 0.1% $Ce(CO_4)_2 \cdot H_2O$, in 10% H_2SO_4. Flash chromatography (FC): silica gel *Merck 60* (40–63 μm). High-performance liquid chromatography (HPLC): *Spherisorb Silica* (5 μm; prep. column, 250 × 20 mm; anal. column, 250 × 4 mm), UV detection (255 nm), t_R in min. M.p.: uncorrected. Optical rotations: 1-dm cell at 25° at 589 nm. UV Spectra: λ_{max} (ε) in nm. CD Spectra: λ ($\Delta\varepsilon$) in nm. FT-IR Spectra: absorption in cm^{-1}; concentration of the CCl_4 or CH_2Cl_2 soln. in mM. NMR Spectra: chemical shifts in ppm rel. to $SiMe_4$ (^1H, ^{13}C) or $CFCl_3$ (^{19}F); *J* in Hz. Mass spectra: DCI at 70 eV; FAB in 3-nitrobenzyl alcohol (NBA) matrix. Calculations were performed using the programme Gaussian 94 [32] and the B3LYP density functional method [33].

Transorthoesterification. A soln. of *cis*-inositol (**7**; 1.50 g, 8.32 mmol) in DMSO (11 ml) was treated with trimethyl orthopentanoate (1.19 ml, 8.32 mmol) and TsOH · H_2O (168 mg, 0.88 mmol) for 2 h at 60°. Additional trimethyl orthopentanoate (0.56 ml, 1.66 mmol) was injected, and after 0.5 h, the soln. was neutralized with Et_3N (220 μl, 1.57 mmol). Evaporation and FC (AcOEt) gave **8** (1.76 g, 86%) as a white powder and **9** (269 mg, 10%) as a colourless oil. A colourless prism of **8** · H_2O suitable for X-ray diffraction was obtained by evaporation (8 weeks) of a H_2O/acetone/CH_2Cl_2 1:10:40 soln. (data deposited with the *Cambridge Crystallographic Database*).

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[11]) One notes that the solvent dependence of the regioselectivity parallels the solvent dependence of the $\Delta\delta$ values, as defined by $\delta(OH_{eq}) - \delta(OH_{ax})$, for each solvent. However, $\Delta\delta$ changes from + 0.89 to −0.32 ppm, while the regioselectivity is always in favour of OH_{ax}.

[12]) Evidence for the generation of such ylides has been described [83].

*1,3,5-O-Pentylidyne-*cis*-inositol* (**8**): White needles (pentane/AcOEt). R_f (AcOEt) 0.15. R_f (AcOEt/MeCN 3:1) 0.35. Prep. HPLC (AcOEt, 9 ml/min): t_R 14.8. M.p. 96–98°. IR (14 mM, CH_2Cl_2): 3574*m*, 2964*m*, 1405*m*, 1145*s*, 1103*m*, 1048*s*, 996*m*, 971*m*, 940*w*, 867*w*, 550*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 3.97 (*t*, *J* = 2.0, H–C(1), H–C(3), H–C(5)); 3.51 (*dt*, *J* = 11.6, 2.0, H–C(2), H–C(4), H–C(6)); 3.03 (*d*, *J* = 11.6, 3 OH); 1.77–1.63 (*m*, 2 H); 1.58–1.21 (*m*, 4 H); 0.90 (*t*, *J* = 7.3, Me). ^{1}H-NMR (200 MHz, CD_3OD): 3.97 (br. *s*, H–C(1), H–C(3), H–C(5)); 3.57 (br. *s*, H–C(2), H–C(4), H–C(6)); 1.72–1.65 (*m*, CH_2); 1.58–1.46 (*m*, CH_2); 1.31 (*sext.*, *J* = 7.3, CH_2); 0.90 (*t*, *J* = 7.3, Me). ^{13}C-NMR (50 MHz, CD_3OD): 111.67 (*s*, CO_3); 77.65 (*d*, C(1), C(3), C(5)); 65.30 (*d*, C(2), C(4), C(6)); 38.96 (*t*, CH_2); 25.28 (*t*, CH_2); 23.74 (*t*, CH_2); 14.39 (*q*, Me). DCI-MS (NH_4^+): 247 (100, $[M + 1]^+$), 157 (7), 115 (15), 102 (7). Anal. calc. for $C_{11}H_{18}O_6 \cdot 0.22\ H_2O$ (250.22): C 52.80, H 7.43; found: C 52.81, H 7.47.

*2-O-Pentanoyl-1,3,5-O-pentylidyne-*cis*-inositol* (**9**): Colourless oil. R_f (AcOEt) 0.65. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.60 (*t*, *J* = 1.7, H–C(2)); 4.16 (*q*, *J* = 1.8, H–C(1), H–C(3)); 4.11 (*quint.*, *J* = 1.8, H–C(5)); 3.59 (br. *d*, *J* = 11.2, H–C(4), H–C(6)); 3.30 (*d*, *J* = 11.3, 2 OH); 2.44 (*t*, *J* = 7.5, CH_2COO); 1.73–1.58 (*m*, 2 CH_2); 1.53–1.38 (*m*, 1 CH_2); 1.33 (*sext.*, *J* = 07.3, 2 CH_2); 0.91 (*t*, *J* = 7.3, Me); 0.89 (*t*, *J* = 7.3, Me). ^{13}C-NMR (75 MHz, $CDCl_3$): 173.47 (C=O); 110.54 (*s*, CO_3); 76.65 (*d*, C(5)); 74.43 (*d*, C(1), C(3)); 65.26 (*d*, C(2)); 64.24 (*d*, C(4), C(6)); 37.79 (*t*, CH_2); 33.93 (*t*, CH_2); 26.94 (*t*, CH_2); 24.10 (*t*, CH_2); 22.41 (*t*, CH_2); 22.15 (*t*, CH_2); 13.95 (*q*, Me); 13.68 (*q*, Me).

Benzoylation of **8**. A soln. of **8** (5.1 g, 20.7 mmol) in pyridine (50 ml) was treated with PhCOCl (4.8 ml, 41.4 mmol) at 22° under N_2 for 5 d. The mixture was filtered and the precipitate washed with AcOEt (50 ml). Evaporation and FC (hexane/AcOEt 5:1 → 0:1, then THF) gave **12** (2.29 g, 20%), **11** (5.20 g, 55%), and **10** (2.29 g, 21%).

Benzoylation of **10**. A soln. of **10** (476 mg, 1.36 mmol) in pyridine (3 ml) was treated with PhCOBr (162 µl, 1.36 mmol) at 23° under N_2. After 1 h, the mixture was diluted with AcOEt and washed with 20% aq. $CuSO_4$ soln., sat. aq. $NaHCO_3$ soln., and brine. Drying (Na_2SO_4) and FC (hexane/AcOEt 5:1 → 0:1) gave **12** (131 mg, 17%), **11** (193 mg, 31%), and **10** (202 mg, 42%).

Debenzoylation of **12**. A soln. of **12** (1.10 g, 3.13 mmol) in THF/Et_3N/MeOH 1:1:1 (15 ml) was heated to reflux under N_2 for 28 h. Evaporation and FC (hexane/AcOEt 5:1 → 0:1) gave **12** (179 mg, 16%), **11** (444 mg, 50%), and **10** (134 mg, 19%).

*2-O-Benzoyl-1,3,5-O-pentylidyne-*cis*-inositol* (**10**): Sturdy white needles from MeOH. R_f (hexane/AcOEt 1:1) 0.16. R_f (AcOEt) 0.67. M.p. 166–167°. IR (19 mM, CH_2Cl_2): 3570*m*, 2963*m*, 1722*s*, 1146*m*, 1113*m*, 995*m*, 969*m*. IR (40 mM, CCl_4): 3583*m*, 2963*m*, 1726*s*, 1269*s*, 1110*m*, 1053*m*, 996*m*, 970*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 8.13 (br. *d*, *J* = 7.5, 2 arom. H); 7.61 (br. *t*, *J* = 7.5, 1 arom. H); 7.48 (br. *t*, *J* = 7.5, 2 arom. H); 4.88 (*t*, *J* = 1.8, H–C(2)); 4.31 (*q*, *J* = 1.8, H–C(1), H–C(3)); 4.19 (*quint.*, *J* = 1.8, H–C(5)); 3.68 (br. *d*, *J* = 11.6, H–C(4), H–C(6)); 3.21 (*d*, *J* = 11.6, 2 OH); 1.83–1.75 (*m*, CH_2); 1.75–1.42 (*m*, CH_2); 1.35 (*sext.*, *J* = 7.9, CH_2); 0.92 (*t*, *J* = 7.1, Me). ^{13}C-NMR (75 MHz, $(CD_3)_2CO$): 166.65 (*s*, C=O); 134.52 (*d*, 1 arom. C); 131.27 (*s*, 1 arom. C); 130.69 (*d*, 2 arom. C); 129.73 (*d*, 2 arom. C); 111.28 (*s*, CO_3); 78.18 (*d*, C(5)); 74.97 (*d*, C(1), C(3)); 67.84 (*d*, C(2)); 64.86 (*d*, C(4), C(6)); 38.67 (*t*, CH_2); 25.19 (*t*, CH_2); 23.28 (*t*, CH_2); 14.42 (*q*, Me). FAB-MS: 701 (2.5, $[2M + 1]^+$), 351 (100, $[M + 1]^+$). Anal. calc. for $C_{18}H_{22}O_7$ (350.37): C 61.71, H 6.36; found: C 61.47, H 6.36.

*2,4-Di-O-benzoyl-1,3,5-O-pentylidyne-*cis*-inositol* (**11**): Colourless prisms from pentane/^{i}Pr$_2$O. R_f (hexane/AcOEt 4:1) 0.06. R_f (hexane/AcOEt 1:1) 0.63. M.p. 138–140°. IR (22 mM, CH_2Cl_2): 3568*w*, 2962*w*, 1725*s*, 1098*m*, 998*m*, 976*m*, 912*w*. IR (31 mM, CCl_4): 3580*w*, 2962*m*, 1728*s*, 1269*s*, 1104*m*, 1096*m*, 999*m*, 978*m*, 909*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.15–8.13 (*m*, 4 arom. H); 7.61 (*tt*, *J* = 7.5, 1.4, 2 arom. H); 7.48 (*t*, *J* = 7.5, 4 arom. H); 5.00 (br. *s*, H–C(2), H–C(4)); 4.57 (*quint.*, *J* = 1.8, H–C(3)); 4.41 (br. *d*, *J* = 1.8, H–C(1), H–C(5)); 3.83 (br. *d*, *J* = 11.5, H–C(6)); 3.24 (br. *d*, *J* = 11.5, OH); 1.83–1.78 (*m*, CH_2); 1.63–1.53 (*m*, CH_2); 1.42 (*sext.*, *J* = 7.4, CH_2); 0.93 (*t*, *J* = 7.3, Me). ^{13}C-NMR (50 MHz, $CDCl_3$): 166.25 (*s*, 2 C=O); 133.93 (*d*, 2 arom. C); 130.35 (*d*, 4 arom. C); 129.71 (*s*, 2 arom. C); 128.85 (*d*, 4 arom. C); 110.90 (*s*, CO_3); 74.20 (*d*, C(1), C(5)); 71.15 (*d*, C(3)); 65.99 (*d*, C(2), C(4)); 64.58 (*d*, C(6)); 37.99 (*t*, CH_2); 24.50 (*t*, CH_2); 22.64 (*t*, CH_2); 14.19 (*q*, Me). FAB-MS: 909 (11, $[2M + 1]^+$), 455 (100, $[M + 1]^+$). Anal. calc. for $C_{25}H_{26}O_8$ (454.48): C 66.07, H 5.77; found: C 66.10, H 5.72.

*1,3,5-Tri-O-benzoyl-2,4,6-O-pentylidyne-*cis*-inositol* (**12**): Colourless prisms from pentane/^{i}Pr$_2$O. R_f (hexane/AcOEt 4:1) 0.35. M.p. 168–170°. IR (18 mM, CH_2Cl_2): 2962*w*, 1727*s*, 1452*m*, 1107*s*, 995*m*, 989*m*, 913*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 8.20 (br. *d*, *J* = 7.3, 6 arom. H); 7.62 (br. *t*, *J* = 7.3, 3 arom. H); 7.48 (br. *t*, *J* = 7.3, 6 arom. H); 5.40 (br. *s*, H–C(1), H–C(3), H–C(5)); 4.78 (br. *s*, H–C(2), H–C(4), H–C(6)); 2.20–1.95 (*m*, CH_2); 1.82–1.62 (*m*, CH_2); 1.43 (*sext.*, *J* = 7.3, CH_2); 1.00 (*t*, *J* = 7.3, Me). ^{13}C-NMR (50 MHz, $CDCl_3$): 165.50 (*s*, 3 C=O); 133.26 (*d*, 3 arom. C); 129.75 (*d*, 6 arom. C); 129.08 (*s*, 3 arom. C); 128.21 (*d*, 6 arom. C); 110.17 (*s*, CO_3); 71.08 (*d*, C(2), C(4), C(6)); 65.34 (*d*, C(1), C(3), C(5)); 37.45 (*t*, CH_2); 24.11 (*t*, CH_2); 22.22

(*t*, CH_2); 13.83 (*q*, Me). FAB-MS: 1117 (2.8, $[2M + 1]^+$), 559 (100, $[M + 1^+$). Anal. calc. for $C_{32}H_{30}O_9$ (558.58): C 68.81, H 5.41; found: C 68.53, H 5.59.

*1,3-Di-*O*-benzoyl-2,4,6-*O*-pentylidyne-5-*O*-[(trifluoromethylsulfonyl]-*cis*-inositol* (**13**). A vigourously stirred soln. of **11** (2.60 g, 5.72 mmol) and pyridine (2.80 ml, 34.3 mmol) in CH_2Cl_2 (60 ml) was cooled to $-10°$ under N_2. Freshly distilled Tf_2O (0.89 ml, 8.58 mmol) was added, and after 10 min, the reaction was quenched at $-10°$ with aq. phosphate buffer (pH 6.8, 1M; 10 ml). The mixture was diluted with Et_2O (300 ml), and washed with 20% aq. $CuSO_4$ soln. (3 × 30 ml), sat. aq. $NaHCO_3$ soln. (3 × 20 ml), and brine (50 ml). Drying (Na_2SO_4) and evaporation afforded **13** (3.20 g, 95%) as a pale-yellow powder containing no impurity by NMR. The triflate was stable during FC (silica gel, hexane/CH_2Cl_2 1:3 → 0:1). Flat colourless prisms from pentane/$^iPr_2O$. R_f (hexane/AcOEt 3:1) 0.55. R_f (hexane/CH_2Cl_2 1:4) 0.63. M.p. 158–159°. IR (17 mM, CCl_4): 2963*w*, 1730*s*, 1425*m*, 1270*s*, 1247*s*, 1221*s*, 1146*s*, 1106*m*, 975*s*, 918*m*, 616*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 8.14 (br. *d*, *J* = 7.5, 4 arom. H); 7.63 (br. *t*, *J* = 7.5, 2 arom. H); 7.49 (br. *t*, *J* = 7.5, 4 arom. H); 5.18 (br. *s*, H–C(1), H–C(3)); 5.15 (br. *s*, H–C(5)); 4.71 (br. *s*, H–C(4), H–C(6)); 4.66 (br. *s*, H–C(2)); 1.90–1.77 (*m*, CH_2); 1.67–1.50 (*m*, CH_2); 1.41 (*sext.*, *J* = 7.2, CH_2); 0.95 (*t*, *J* = 7.2, Me). ^{13}C-NMR (50 MHz, $CDCl_3$): 166.17 (*s*, 2 C=O); 134.19 (*d*, 2 arom. C); 130.41 (*d*, 4 arom. C); 129.24 (*s*, 2 arom. C); 128.94 (*d*, 4 arom. C); 110.93 (*s*, CO_3); 76.63 (*d*, C(2)); 71.59 (*d*, C(4), C(6)); 70.95 (*d*, C(5)); 64.81 (*d*, C(1), C(3)); 37.57 (*t*, CH_2); 24.25 (*t*, CH_2); 22.54 (*t*, CH_2); 14.14 (*q*, Me). ^{19}F-NMR (282 MHz, $CDCl_3$): −74.61 (*s*). FAB-MS: 691 (7, $[M + 105]^+$), 587 (100, $[M + 1]^+$), 105 (26).

*2,4-Di-*O*-benzoyl-6-deoxy-6-fluoro-1,3,5-*O*-pentylidyne*-epi-*inositol* (**14**). A soln. of **13** (1.19 g, 2.03 mmol) and 1,1,1,3,3,3-hexakis(dimethylamino)diphosphazenium fluoride (0.5M in C_6H_6, 6.0 ml, 3.00 mmol) in toluene (12 ml) was heated for 5 h under reflux and N_2. After cooling to r.t., the mixture was diluted with Et_2O (150 ml) and washed with H_2O (2 × 40 ml) and brine (40 ml). Drying (Na_2SO_4), evaporation, and FC (hexane/CH_2Cl_2 1:3 → 1:4) afforded **14** (407 mg, 44%) as a glassy material. Fibrous white needles from pentane/$^iPr_2O$. R_f (hexane/CH_2Cl_2 1:4) 0.36. M.p. 125–128°. IR (13 mM, CH_2Cl_2): 2965*w*, 1725*s*, 1602*w*, 1452*w*, 1112*s*, 997*m*, 980*m*. ^{1}H-NMR (200 MHz, C_6D_6): 8.23 (*dd*, *J* = 8.0, 1.6, 4 arom. H); 7.16–7.05 (*m*, 6 arom. H); 5.06 (br. *s*, H–C(2), H–C(4)); 4.78 (*dt*, ^2J(H,F) = 48.0, *J* = 4.5, H–C(6)); 4.41 (br. *t*, *J* = 1.8, H–C(3)); 4.36–4.28 (*m*, H–C(1), H–C(5)); 1.90–1.77 (*m*, CH_2); 1.67–1.50 (*m*, CH_2); 1.48 (*sext.*, *J* = 7.2, CH_2); 0.81 (*t*, *J* = 7.2, Me). ^{1}H-NMR (300 MHz, $CDCl_3$): 8.14 (br. *d*, *J* = 7.6, 4 arom. H); 7.61 (br. *t*, *J* = 7.6, 2 arom. H); 7.48 (br. *t*, *J* = 7.6, 4 arom. H); 5.36 (*dt*, ^2J(H,F) = 48.4, *J* = 4.5, H–C(6)); 5.26 (br. *s*, H–C(2), H–C(4)); 4.63 (br. *s*, H–C(1), H–C(3), H–C(5)); 1.82–1.76 (*m*, CH_2); 1.60–1.50 (*m*, CH_2); 1.40 (sext., *J* = 7.5, CH_2); 0.93 (*t*, *J* = 7.2, Me). ^{13}C-NMR (75 MHz, $CDCl_3$): 165.68 (*s*, 2 C=O); 133.54 (*d*, 2 arom. C); 130.00 (*d*, 4 arom. C); 129.43 (*s*, 2 arom. C); 128.51 (*d*, 4 arom. C); 110.04 (*s*, CO_3); 82.99 (*dd*, ^1J(C,F) = 187.5, C(6)); 71.08 (*d*, C(3)); 69.46 (*dd*, ^2J(C,F) = 21.8, C(1), C(5)); 64.43 (*d*, C(2), C(4)); 37.04 (*t*, CH_2); 24.57 (*t*, CH_2); 22.43 (*t*, CH_2); 14.02 (*q*, Me). ^{19}F-NMR (282 MHz, $CDCl_3$): −196.79 (*d*, ^2J(H,F) = 49). FAB-MS: 457 (100, $[M + 1]^+$), 399 (40), 340 (36), 105 (78). Anal. calc. for $C_{25}H_{25}FO_7$ (456.47): C 65.78, H 5.52; found: C 65.68, H 5.70.

Debenzoylation of **14**. A soln. of **14** (400 mg, 0.875 mmol) in MeOH/Et_3N 2:3 (10 ml) was heated for 16 h under reflux and N_2. Evaporation and FC (hexane/AcOEt 4:1 → 1:2) afforded **14** (20 mg, 5%), DL-**15** (95.3 mg, 31%), and **16** (125.7 mg, 58%). Diol **16** was transformed into **14**/DL-**15**/**16** by overnight treatment at r.t. with 1 equiv. of BzBr in pyridine.

DL-*2-*O*-Benzoyl-6-deoxy-6-fluoro-1,3,5-*O*-pentylidyne*-epi-*inositol* (DL-**15**): White needles from pentane/hexane/AcOEt 6:4:1 at −20°. R_f (hexane/AcOEt 2:1) 0.42. M.p. 119–120°. IR (57 mM, CH_2Cl_2): 3569*w*, 2963*m*, 1724*s*, 1452*w*, 1279*s*, 1112*s*, 1052*s*, 996*s*, 979*s*, 904*w*, 884*w*, 865*w*. IR (57 mM, CCl_4): 3583*w*, 2964*m*, 1728*s*, 1452*w*, 1267*s*, 1110*m*, 1060*m*, 997*m*, 980*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.14 (br. *d*, *J* = 7.8, 2 arom. H); 7.62 (br. *t*, *J* = 7.5, 1 arom. H); 7.49 (br. *t*, *J* = 7.5, 2 arom. H); 5.31 (*dt*, ^2J(H,F) = 48.1, *J* = 4.4, H–C(6)); 5.16–5.12 (*m*, H–C(2)); 4.58–4.54 (*m*, 1 H), 4.41–4.36 (*m*, 2 H, H–C(1), H–C(3), H–C(5)); 3.92 (br. *d*, *J* = 11.7, H–C(4)); 3.14 (*d*, *J* = 11.7, OH); 1.77–1.71 (*m*, CH_2); 1.53–1.46 (*m*, CH_2); 1.32 (*sext.*, *J* = 7.4, CH_2); 0.92 (*t*, *J* = 7.4, Me). ^{13}C-NMR (75 MHz, $CDCl_3$): 165.76 (*s*, C=O); 133.55 (*d*, 1 arom. C); 130.00 (*d*, 2 arom. C); 129.44 (*s*, 1 arom. C); 128.51 (*d*, 2 arom. C); 110.11 (*s*, CO_3); 83.07 (*dd*, ^1J(C,F) = 186.3, C(6)); 73.71 (*d*, C(3)); 71.70 (*dd*, ^2J(C,F) = 23.3), 69.06 (*dd*, ^2J(C,F) = 21.8, C(1), C(5)); 64.54 (*d*, C(2)); 62.73 (*d*, C(4)); 37.10 (*t*, CH_2); 24.50 (*t*, CH_2); 22.41 (*t*, CH_2); 13.98 (*q*, Me). ^{19}F-NMR (282 MHz, $CDCl_3$): −198.32 (*d*, ^2J(H,F) = 49). FAB-MS: 353 (100, $[M + 1]^+$), 105 (22). HR-FAB-MS: 353.1403 ($[M + H]^+$; calc. 353.1401). Anal. calc. for $C_{18}H_{21}FO_6$ (352.36): C 61.36, H 6.01; found: C 61.16, H 5.77.

*6-Deoxy-6-fluoro-1,3,5-*O*-pentylidyne*-epi-*inositol* (**16**): Colourless prisms from pentane/$^iPr_2O$. R_f (hexane/AcOEt 1:1) 0.21. M.p. 123–124°. IR (19 mM, CH_2Cl_2): 3573*m*, 2964*m*, 1408*w*, 1132*m*, 1052*s*, 999*m*, 978*m*. IR (19 mM, CCl_4): 3585*m*, 2965*m*, 1407*w*, 1264*s*, 1133*m*, 1054*s*, 999*m*, 978*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.27 (*dt*, ^1J(H,F) = 48.2, *J* = 4.5, H–C(6)); 4.33–4.31 (*m*, H–C(1), H–C(5)); 4.19 (br. *t*, *J* = 2.1, H–C(3)); 3.78

(br. *d*, *J* = 11.7, H–C(2), H–C(4)); 3.17 (*d*, *J* = 11.7, 2 OH); 1.73–1.66 (*m*, CH_2); 1.53–1.46 (*m*, CH_2); 1.32 (*sext.*, *J* = 7.1, CH_2); 0.91 (*t*, *J* = 7.1, Me). ^{13}C-NMR (50 MHz, $CDCl_3$): 110.17 (*s*, CO_3); 83.16 (*dd*, ^1J(C,F) = 185.2, C(6)); 76.46 (*d*, C(3)); 71.27 (*dd*, ^2J(C,F) = 24.0, C(1), C(5)); 62.69 (*d*, C(2), C(4)); 37.04 (*t*, CH_2); 24.25 (*t*, CH_2); 22.25 (*t*, CH_2); 13.71 (*q*, Me). ^{19}F-NMR (282 MHz, $CDCl_3$): –199.84 (*d*, ^2J(H,F) = 49). DCI-MS (NH_4^+): 249 (100, $[M + 1]^+$), 219 (7), 117 (18), 85 (46), 57 (31), 49 (50). Anal. calc. for $C_{11}H_{17}FO_5$ (248.25): C 53.22, H 6.90; found: C 53.04, H 6.83.

DL-*2-O-Benzoyl-4-deoxy-4-fluoro-1,3,5-O-pentylidyne*-myo-*inositol* (DL-**18**). A soln. of DL-**15** (727 mg, 2.06 mmol) and *Dess-Martin* periodinane (= 1,1,1-tris(acetyloxy)-1,1-dihydro-1,2-benziodoxol-3(1*H*)-one; (1.8 g, 4.12 mmol) in CH_2Cl_2 (12 ml) was stirred overnight at 23°. TLC Analysis indicated that the reaction was incomplete, but no progress occurred upon further addition of periodinane (0.6 g, 1.41 mmol). After 2 h, the mixture was diluted with Et_2O/AcOEt 1:2 (150 ml) and washed with sat. aq. $Na_2S_2O_3$/sat. aq. $NaHCO_3$ soln. The org. phase was dried (Na_2SO_4) and evaporated. The residue was dissolved in CH_2Cl_2 (20 ml) and treated with more periodinane (1.0 g, 2.35 mmol). After 1 h, the analogous workup and filtration (SiO_2 plug, Et_2O) afforded a crude colourless oil (595 mg, *ca.* 82%), which was dissolved in THF (12 ml), and treated with 0.54M $LiBH_4$ in THF (2.48 mmol) for 20 min at –10° (*caution*: fizz). The mixture was diluted with dry ^{t}BuOMe (40 ml) and treated with 1M phosphate buffer (pH 7.0, 10 ml) and H_2O_2 (1 ml). After vigourously stirring for 10 min at 23°, the org. layer was diluted with AcOEt, washed with brine (6 ×), and dried (Na_2SO_4). FC (hexane/AcOEt 2:1 → 1:1) afforded DL-**18** (605 mg, 84% from DL-**15**) as a white foam. White needles from pentane/^{i}Pr$_2$O. R_f (hexane/AcOEt 2:1) 0.39. M.p. 136–137°. IR (71 mM, CH_2Cl_2): 3604*w*, 2964*m*, 1721*s*, 1452*m*, 1356*m*, 1330*m*, 1315*m*, 1178*w*, 1112*s*, 1090*s*, 1072*s*, 1046*m*, 1025*m*, 995*s*, 978*s*, 900*w*, 883*w*. IR (14 mM, CCl_4): 3620*w*, 2962*m*, 1723*s*, 1452*w*, 1269*s*, 1247*m*, 1111*m*, 1086*m*, 995*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 8.20 (*dd*, *J* = 8.4, 1.3, 2 arom. H); 7.60 (br. *t*, *J* = 7.4, 1 arom. H); 7.48 (*t*, *J* = 7.4, 2 arom. H); 5.47 (*q*, ^4J(H,F) = *J* = 2.1, H–C(2)); 5.36 (*dtd*, ^2J(H,F) = 48.0, *J* = 4.3, 2.2, H–C(4)); 4.63–4.59 (*m*, H–C(3), H–C(6)); 4.46 (*dq*, *J* = 4.2, 2.1, H–C(1)); 4.43 (*tq*, *J* ≈ 4, 2, ^3J(H,F) ≈ 2, H–C(5)); 2.29 (*t*, ^5J(OH,F) = *J* = 7.2, OH); 1.73–1.70 (*m*, CH_2); 1.50–1.44 (*m*, CH_2); 1.34 (*sext.*, *J* = 7.3, CH_2); 0.90 (*t*, *J* = 7.3, Me). ^{13}C-NMR (75 MHz, $CDCl_3$): 165.97 (*s*, C=O); 133.48 (*d*, 1 arom. C); 130.00 (*d*, 2 arom. C); 129.59 (*s*, 1 arom. C); 128.48 (*d*, 2 arom. C); 109.56 (*s*, CO_3); 86.15 (*dd*, ^1J(C,F) = 187.0, C(4)); 72.31 (*d*, C(1)); 69.78 (*dd*, ^2J(C,F) = 22.7), 68.22 (*dd*, ^2J(C,F) = 17.8 (C(3), C(5)); 67.31 (*d*, C(2)); 62.31 (*d*, C(6)); 36.57 (*t*, CH_2); 24.77 (*t*, CH_2); 22.43 (*t*, CH_2); 13.97 (*q*, Me). ^{19}F-NMR (282 MHz, $CDCl_3$): –196.69 (*dd*, ^2J(H,F) = 49, ^5J(OH,F) = 7). FAB-MS: 353 (71, $[M + 1]^+$), 231 (8), 179 (13), 161 (11), 137 (19), 136 (14), 104 (100). Anal. calc. for $C_{18}H_{21}FO_6$ (352.36): C 61.36, H 6.01; found: C 61.28, H 5.86.

Enantiomerically Pure Carbamates L-**19** *and* D-**10**. A mixture of DL-**18** (119.0 mg, 0.338 mmol), sublimed 4-(dimethylamino)pyridine (120.8 mg, 0.989 mmol), and 3-Å powdered molecular sieves (131 mg) in CH_2Cl_2 (3.0 ml) was stirred for 30 min at 23° under N_2 and then treated with (*S*)-1-phenylethyl isocyanate (143 µl, 1.01 mmol). After 20 h, filtration (fritted glass) and FC (hexane/AcOEt 4:1) gave an non-separated 1:1 mixture of diastereoisomers as a colourless oil (164.9 mg, 98%). The mixture was dissolved in MeOH (3 ml), debenzoylated with 2.8M MeONa in MeOH (120 µl, 0.336 mmol) for 40 min at 23°, filtered (silica gel plug, Et_2O) and evaporated. Methyl benzoate was removed azeotropically with toluene/H_2O 1:1 (16 ml). HPLC (hexane/AcOEt 4:1) afforded D-**20** (54.7 mg, 41%) and L-**19** (56.7 mg, 43%) as colourless oils.

L-*4-Deoxy-4-fluoro-1,3,5-O-pentylidyne-6-O-{[(S)-1-phenylethyl]carbamoyl}*-myo-*inositol* (L-**19**): Colourless oil. R_f (hexane/AcOEt 2:1) 0.37. Prep. HPLC (hexane/AcOEt 4:1, 10 ml/min): t_R 32.0. $[\alpha]_D^{25} = -44.6 \pm 0.3$ (*c* = 0.80, $CHCl_3$). IR (9 mM, CH_2Cl_2): 3568*w*, 3435*w*, 2963*m*, 1732*s*, 1506*s*, 1217*s*, 1083*s*, 1001*m*, 978*m*. IR (13 mM, CCl_4): 3585*w*, 3448*w*, 2964*m*, 1734*s*, 1497*m*, 1216*m*, 1083*s*, 1002*m*, 979*m*, 909*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.42–7.26 (*m*, 5 arom. H); 5.40 (*td*, *J* = 3.7, 1.2, 0.8 H, H–C(6)); 5.35 (*td*, *J* = 4.1, 1.6, 0.2 H, H–C(6)); 5.22 (*dtd*, ^2J(H,F) = 49.4, *J* = 4.1, 1.2, H–C(4)); 5.08 (br. *d*, *J* ≈ 6.9, H–N); 4.86 (*quint.*, *J* = 7.0, PhC*H*); 4.48 (*td*, *J* = 4.1, 1.2, H–C(5)); 4.40–4.20 (*m*, H–C(1), H–C(3)); 3.99 (br. *d*, *J* = 11.6, H–C(2)); 3.03 (*d*, *J* = 11.6, OH); 1.75–1.62 (*m*, CH_2); 1.58–1.38 (*m*, CH_2); 1.52 (*d*, *J* = 7.0, Me); 1.35 (*sext.*, *J* = 7.0, CH_2); 0.90 (*t*, *J* = 7.0, Me). ^{13}C-NMR (50 MHz, $CDCl_3$): main rotamer: 153.88 (*s*, C=O); 143.04 (*s*, 1 arom. C); 128.80 (*d*, 2 arom. C); 127.56 (*d*, 2 arom. C); 125.95 (*d*, 1 arom. C); 109.95 (*s*, CO_3); 84.79 (*dd*, ^1J(C,F) = 189.9, C(4)); 72.03 (br. *d*, C(1)); 72.09 (*dd*, ^2J(C,F) = 30.3, C(3) or C(5)); 67.51 (*d*, C(6)); 66.33 (*dd*, ^2J(C,F) = 19.2, C(3) or C(5)); 60.15 (*d*, C(2)); 50.81 (*d*, PhCH); 36.50 (*t*, CH_2); 24.56 (*t*, CH_2); 22.31 (*t*, CH_2); 22.31 (*q*, Me); 13.77 (*q*, Me). ^{19}F-NMR (282 MHz, $CDCl_3$; (*E*)/(*Z*) 4:1): –199.64 (*d*, ^2J(H,F) = 49, (*Z*)); –200.03 (*d*, ^2J(H,F) = 49, (*E*)). FAB-MS: 791 (2, $[2M + 1]^+$), 530 (7), 396 (100, $[M + 1]^+$), 307 (22), 289 (8), 231 (11). Anal. calc. for $C_{20}H_{26}FNO_6$ (395.43): C 60.75, H 6.63, N 3.54; found: C 60.88, H 6.38, N 3.56.

D-*4-Deoxy-4-fluoro-1,3,5-O-pentylidyne-6-O-{[(S)-1-phenylethyl]carbamoyl}*-myo-*inositol* (D-**20**): Colourless oil. R_f (hexane/AcOEt 2:1) 0.41. Prep. HPLC (hexane/AcOEt 4:1, 10 ml/min): t_R 26.6. $[\alpha]_D^{25} = -19.3 \pm 0.8$ (*c* = 0.80, $CHCl_3$). IR (9 mM, CH_2Cl_2): 3567*w*, 3434*w*, 2963*m*, 1732*s*, 1506*s*, 1230*s*, 1083*s*, 1002*m*, 978*m*.

IR (13 mM, CCl_4): 3585*w*, 3448*w*, 2964*m*, 1738*s*, 1497*m*, 1215*m*, 1084*s*, 1002*m*, 978*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): main rotamer: 7.41–7.29 (*m*, 5 arom. H); 5.39 (br. *s*, H–C(6)); 5.28–5.24 (*m*, H–C(4)); 5.08 (br. *d*, $J \approx 9$, H–N); 4.85 (*quint.*, $J = 6.6$, PhC*H*); 4.54 (br. *s*), 4.33 (br. *s*), 4.25 (br. *s*, H–C(1), H–C(3), H–C(5)); 3.96 (br. *d*, $J = 12.0$, H–C(2)); 3.01 (*d*, $J = 12.0$, OH); 1.73–1.64 (*m*, CH_2); 1.58–1.38 (*m*, CH_2); 1.52 (*d*, $J = 6.6$, Me); 1.35 (*sext.*, $J = 6.8$, CH_2); 0.91 (*t*, $J = 7.0$, Me). ^{13}C-NMR (75 MHz, $CDCl_3$): 154.06 (*s*, C=O); 143.16 (*s*, 1 arom. C); 129.00 (*d*, 2 arom. C); 127.84 (*d*, 2 arom. C); 126.22 (*d*, 1 arom. C); 110.11 (*s*, CO_3); 84.97 (*dd*, ^1J(C,F) = 189.2, C(4)); 72.49 (*d*, C(1)); 72.17 (*dd*, ^2J(C,F) = 24.4, C(3) or C(5)); 67.62 (*d*, C(6)); 66.47 (*dd*, ^1J(C,F) = 20.8, C(3) or C(5)); 60.3 (*d*, C(2)); 51.00 (*d*, PhCH); 36.66 (*t*, CH_2); 24.70 (*t*, CH_2); 22.44 (*t*, CH_2); 22.24 (*q*, Me); 13.91 (*q*, Me). ^{19}F-NMR (282 MHz, $CDCl_3$; (*E*)/(*Z*) *ca.* 16:1): −199.82 (*d*, ^2J(H,F) = 49, (*Z*)); −200.16 (*d*, ^2J(H,F) = 49, (*E*)). FAB-MS: 791 (3, $[2M + 1]^+$), 530 (12, $[M + 135]^+$), 396 (100, $[M + 1]^+$), 307 (5), 289 (3), 231 (16). Anal. calc. for $C_{20}H_{26}FNO_6$ (395.43): C 60.75, H 6.63, N 3.54; found: C 60.82, H 6.57, N 3.65.

D-*4-Deoxy-4-fluoro-1,3,5-*O*-pentylidyne*-myo-*inositol* (D-**4**). A soln. of D-**20** (56.7 mg, 0.143 mmol) in THF (1.0 ml) was cooled to 0°, and 1.0M $LiBHEt_3$ in THF (430 µl, 0.430 mmol) was injected dropwise over 3 min (*caution*: fizz). The soln. was stirred at 23° for 80 min, diluted with dry ^{t}BuOMe (10 ml), cooled to 0°, and treated with 1.0M aq. phosphate buffer (pH 7.0, 6 ml; *caution*: fizz), followed by 30% aq. H_2O_2 soln. (0.5 ml; *caution*: exothermic). After 10 min of vigourous stirring at 23°, extraction (2 × 20 ml of AcOEt), washing (3 × 10 ml of brine), drying (Na_2SO_4), and FC (hexane/AcOEt 2:1) afforded D-**4** (28.3 mg, 79%) as a white solid. Colourless prisms from pentane/AcOEt or $CHCl_3$. R_f (hexane/AcOEt 1:1) 0.24. M.p. 145–146°. $[\alpha]_D^{25} = -0.7 \pm 0.7$ ($c = 0.56$, $CHCl_3$). IR (40 mM, CH_2Cl_2): 3607*w*, 3575*w*, 2964*m*, 1093*s*, 1078*s*, 1058*m*, 1000*s*, 977*s*, 894*w*. IR (13.3 mM, CCl_4): 3621*w*, 3585*w*, 2963*m*, 1267*w*, 1248*w*, 1080*s*, 999*s*, 976*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.31 (*dtd*, ^2J(H,F) = 48.1, $J = 4.2$, 1.8, H–C(4)); 4.55–4.51 (*m*, H–C(2)); 4.36–4.33 (*m*, H–C(3), H–C(5)); 4.22 (*dq*, $J = 4.0$, 2.0, H–C(1)); 4.43 (*dq*, ^4J(H,F) = 2.0, $J = 11.7$, 2.0, H–C(2)); 2.96 (*d*, $J = 12.0$, HO–C(2)); 2.12 (*t*, ^5J(OH,F) = $J = 8.3$, HO–C(6)); 1.73–1.70 (*m*, CH_2); 1.50–1.44 (*m*, CH_2); 1.34 (*sext.*, $J = 7.3$, CH_2); 0.90 (*t*, $J = 7.3$, Me). ^{13}C-NMR (75 MHz, $CDCl_3$): 109.83 (*s*, CO_3); 86.67 (*dd*, ^1J(C,F) = 185.6, C(4)); 74.80 (*d*, C(1)); 72.13 (*dd*, ^2J(C,F) = 23.2), 67.80 (*d*, ^2J(C,F) = 17.0, C(3), C(5)); 67.30 (*d*), 59.71 (*d*, C(2), C(6)); 36.66 (*t*, CH_2); 24.75 (*t*, CH_2); 22.46 (*t*, CH_2); 13.91 (*q*, Me). ^{19}F-NMR (282 MHz, $CDCl_3$): −199.84 (*d*, ^2J(H,F) = 49). DCI-MS (NH_4^+): 333 (1, $[M + BuCO]^+$), 249 (100, $[M + 1]^+$), 117 (14), 85 (21, $[BuCO]^+$). Anal. calc. for $C_{11}H_{17}FO_5$ (248.25): C 53.22, H 6.90; found: C 53.29, H 6.67. Vapour-pressure osmometry (3.94 mM, CH_2Cl_2): 251.3 ± 8.9 g/mol (calc. for $C_{11}H_{17}FO_5$, 248.25 g/mol).

L-*4-Deoxy-4-fluoro-1,3,5-*O*-pentylidyne*-myo-*inositol* (L-**4**). The same procedure applied to L-**19** (54.7 mg, 0.138 mmol) afforded L-**4** (31.3 mg, 91%): $[\alpha]_D^{25} = +0.7 \pm 0.7$ ($c = 0.43$, $CHCl_3$).

L-*2,6-Bis-*O*-(4-bromobenzoyl)-4-deoxy-4-fluoro-1,3,5-*O*-pentylidyne*-myo-*inositol* (L-**21**). A soln. of L-**4** (1.5 mg, 6.04 µmol) in pyridine (0.5 ml) was treated with 4-bromobenzoyl chloride (30 mg, 137 µmol) for 12 h at 23°, whereupon a white precipitate was formed. The suspension was dissolved with AcOEt, washed with sat. aq. $NaHCO_3$ soln., 20% aq. $CuSO_4$ soln., sat. aq. $NaHCO_3$ soln., and brine. The AcOEt layer was dried (Na_2SO_4), evaporated, and filtered through SiO_2 (hexane/Et_2O 2:1) to give L-**21** (3.7 mg, 100%). White powder. R_f (hexane/AcOEt 9:1) 0.59. UV (MeCN, 29 µM): 245 (37000). CD (MeCN, 29 µM): 234 (−4.7), 241 (0), 253 (+16.6). IR (6.5 mM, CH_2Cl_2): 2963*m*, 1728*s*, 1591*m*, 1103*s*, 1070*s*. ^{1}H-NMR: (200 MHz, $CDCl_3$): 8.02 (*d*, $J = 8.8$, 2 arom. H); 7.93 (*d*, $J = 8.2$, 2 arom. H); 7.71 (*d*, $J = 8.6$, 1 arom. H); 7.64 (*d*, $J = 8.2$, 1 arom. H); 7.63 (*d*, $J = 8.8$, 2 arom. H); 5.79 (br. *s*), 5.51 (br. *s*, H–C(2), H–C(6)); 5.37 (*dtd*, $J \approx 49$, 4, 2, H–C(4)); 4.68–4.63 (*m*, H–C(1), H–C(3), H–C(5)); 1.83–1.75 (*m*, CH_2); 1.57–1.28 (*m*, 2 CH_2); 0.94 (*t*, $J = 7.1$, Me). FAB-MS: 617 (42, $[M(^{81}Br) + 1]^+$), 615 (70), 613 (36), 185 (44, $^{81}BrC_6H_4CO^+$), 183 (44), 133 (100).

D-*2-*O*-[(*tert*-Butyl)dimethylsilyl]-4-deoxy-4-fluoro-1,3,5-*O*-pentylidyne*-myo-*inositol* (D-**22**). A soln. of D-**4** (6.6 mg, 26.6 µmol) and 2,6-dimethylpyridine (6.2 µl, 53.2 µmol) in CH_2Cl_2 (0.75 ml) was treated with ^{t}BuMe$_2$SiOTf (9.1 µl, 39.9 µmol) for 4 h at 0°. The mixture was evaporated, the residue dissolved in Et_2O, and the soln. filtered through SiO_2. FC (hexane/AcOEt 4:1) afforded D-**4** (9.7 mg, 100%) as a white solid. White fibrous needles from hexane. R_f (hexane/AcOEt 1:1) 0.50. M.p. 87–88°. Anal. HPLC (hexane/AcOEt 16:1, 2 ml/min): t_R 10.1. $[\alpha]_D^{25} = +0.6 \pm 0.5$ ($c = 1.36$, CH_2Cl_2). IR (4.0 mM, CH_2Cl_2): 3604*w*, 2858*m*, 1605*w*, 1083*s*, 1007*s*, 847*s*. IR (4.0 mM, CCl_4): 3621*w*, 2959*m*, 1471*w*, 1389*w*, 1256*m*, 1144*m*, 1082*m*, 1007*m*, 888*m*, 842*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.30 (*dtd*, ^2J(H,F) = 48.2, $J = 4.0$, 1.7, H–C(4)); 4.50 (*dtd*, $J \approx 8$, 4, 2, H–C(6)); 4.31 (*tq*, $J = 3.6$, 1.8, ^3J(H,F) = 1.8, H–C(5)); 4.30 (*dq*, $J = 4.2$, 2.1, H–C(3)); 4.16–4.12 (*m*, H–C(1), H–C(2)); 2.10 (*t*, ^5J(OH,F) = $J = 8.1$, OH); 1.69–1.63 (*m*, CH_2); 1.45–1.36 (*m*, CH_2); 1.30 (*sext.*, $J = 7.2$, CH_2); 0.93 (*s*, *t*-BuSi); 0.87 (*t*, $J = 7.2$, Me); 0.13 (*s*, MeSi); 0.07 (*s*, MeSi). ^{13}C-NMR (75 MHz, $CDCl_3$): 109.42 (*s*, CO_3); 87.17 (*dd*, ^1J(C,F) = 185.2, C(4)); 74.92 (*d*, C(1)); 72.55 (*dd*, ^2J(C,F) = 25.1), 68.20 (*d*, ^2J(C,F) = 20.3, C(3), C(5)); 67.75 (*d*, C(6)); 59.59 (*d*, C(2)); 36.54 (*t*, CH_2); 25.65 (*q*, Me_3C); 24.75 (*t*, CH_2); 22.46 (*t*, CH_2); 18.08 (*s*, Me_3C); 13.91 (*q*, Me); −4.84 (*q*, Me_2Si). ^{19}F-NMR (282 MHz, $CDCl_3$): −196.46 (*dd*, ^2J(H,F) = 49,

^5J(OH,F) = 7). DCI-MS (NH_4^+): 363 (100, $[M + 1]^+$), 305 (10, $[M - {}^t\text{Bu}]^+$), 225 (6), 202 (27), 183 (56). Anal. calc. for $C_{17}H_{31}FO_5Si$ (362.51): C 56.33, H 8.62; found: C 56.61, H 8.40.

Silylation of the Triol **25**. A soln. of the triol **25** [63] (19.2 g, 78.0 mmol), 1*H*-imidazole (13.7 g, 200 mmol), and *t*-BuMe$_2$SiCl (15.7 g, 100 mmol) in DMF (60 ml) was stirred for 30 min at 23°, evaporated (46°/ < 1 Torr), diluted with hexane/AcOEt 1:3, washed (H_2O, brine), and dried (Na_2SO_4). FC (hexane/AcOEt 1.4 → 1:2) gave the disilyl ether **28** (8.39 g, 21%), the monosilyl ethers **27** (1.64 g, 6%) and **26** (14.4 g, 49%), and the triol **25** (2.50 g, 13%).

*2-*O*-[(*tert*-Butyl)dimethylsilyl]-1,3,5-*O*-pentylidyne*-myo-*inositol* (**26**): Colourless prisms (hexane/AcOEt). R_f (hexane/AcOEt 4:1) 0.19. M.p. 103–105°. IR (17 mM, CCl_4): 3620*w*, 3539*w*, 3391*w*, 2958*m*, 2858*m*, 1471*m*, 1388*m*, 1258*m*, 1144*m*, 1111*m*, 1082*s*, 1005*m*, 988*m*, 889*m*, 849*m*, 837*m*. IR (28 mM, CH_2Cl_2): 3596*w*, 3518*w*, 2959*m*, 2858*w*, 1140*m*, 1108*m*, 1081*s*, 985*m*, 887*m*, 838*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.51 (*dt*, *J* = 7.6, 3.8, with D_2O → *t*, *J* = 3.9, H–C(4), H–C(6)); 4.22–4.18 (*m*, H–C(2), H–C(5)); 4.14 (*dd*, *J* = 3.8, 2.3, H–C(1), H–C(3)); 3.08 (*d*, *J* = 7.2, with D_2O → no signal, HO–C(4), HO–C(6)); 1.68–1.63 (*m*, CH_2); 1.49–1.39 (*m*, CH_2); 1.30 (*sext.*, *J* = 7.2, CH_2); 0.94 (*s*, *t*-BuSi); 0.87 (*t*, *J* = 7.2, Me); 0.13 (*s*, Me_2Si). ^{13}C-NMR (50 MHz, $CDCl_3$): 109.09 (*s*, CO_3); 75.15 (*d*, C(1), C(3)); 68.84 (*d*, C(5)); 68.46 (*d*, C(4), C(6)); 59.76 (*d*, C(2)); 36.81 (*t*, CH_2); 25.74 (*q*, Me_3C); 24.72 (*t*, CH_2); 22.34 (*t*, CH_2); 18.18 (*s*, Me_3C); 13.80 (*q*, Me); −4.77 (*q*, Me_2Si). DCI-MS (NH_4^+): 417 (6, $[M + {}^t\text{Bu}]^+$), 361 (89, $[M + 1]^+$), 359 (11), 345 (4, $[M - \text{Me}]^+$), 303 (27, $[M - {}^t\text{Bu}]^+$), 225 (13), 201 (11), 187 (21), 183 (63), 167 (32), 159 (17), 151 (26), 131 (29), 110 (8), 94 (13), 85 (21), 75 (100). Anal. calc. for $C_{17}H_{32}O_6Si$ (360.52): C 56.64, H 8.95; found: C 56.57, H 8.67.

DL-*4-*O*-[(*tert*-Butyl)dimethylsilyl]-1,3,5-*O*-pentylidyne*-myo-*inositol* (**27**): Colourless oil. R_f (hexane/AcOEt 4:1) 0.32. IR (14 mM, CCl_4): 3584*w*, 3508*m*, 2958*m*, 1549*w*, 1470*w*, 1259*m*, 1092*s*, 1002*m*, 978*m*, 839*s*. IR (28 mM, CH_2Cl_2): 3571*w*, 3486*m*, 2959*m*, 2861*w*, 1470*w*, 1092*s*, 1001*m*, 975*m*, 839*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.56 (*dt*, *J* = 4.0, 1.9, H–C(4)); 4.40 (*dtd*, *J* = 10.1, 4.0, 2.2, H–C(6)); 4.21 (*dq*, *J* = 4.0, 2.0, 1 H), 4.14–4.09 (*m*, 2 H, H–C(1), H–C(3), H–C(5)); 4.04 (*dt*, *J* = 11.8, 2.0, H–C(2)); 3.85 (*d*, *J* = 10.3, HO–C(6)); 3.01 (*d*, *J* = 11.8, HO–C(2)); 1.68–1.62 (*m*, CH_2); 1.47–1.36 (*m*, CH_2); 1.29 (*sext.*, *J* = 7.3, CH_2); 0.90 (*s*, ^{t}BuSi); 0.88 (*t*, *J* = 7.2, Me); 0.17 (*s*, Me_2Si); 0.15 (*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 109.28 (*s*, CO_3); 75.27 (*d*), 74.65 (*d*, C(1), C(3)); 69.09 (*d*, C(5)); 68.60 (*d*), 68.0 (*d*, C(4), C(6)); 59.78 (*d*, C(2)); 36.78 (*t*, CH_2); 25.42 (*q*, Me_3C); 24.61 (*t*, CH_2); 22.32 (*t*, CH_2); 17.64 (*s*, Me_3C); 13.78 (*q*, Me); −5.26 (*q*, Me_2Si); −5.49 (*q*, Me_2Si). DCI-MS (NH_4^+): 361 (100, $[M + 1]^+$), 303 (62, $[M - {}^t\text{Bu}]^+$), 229 (15), 187 (65), 183 (17), 159 (16), 155 (12), 129 (20), 109 (15), 92 (12), 85 (40), 73 (43). Anal. calc. for $C_{17}H_{32}O_6Si$ (360.52): C 56.64, H 8.95; found: C 56.78, H 9.02.

DL-*2,4-Bis*-O-*[(*tert*-butyl)dimethylsilyl]-1,3,5-*O*-pentylidyne*-myo-*inositol* (**28**): Colourless oil. R_f (hexane/AcOEt 4:1) 0.68. IR (13 mM, CCl_4): 3509*m*, 2956*m*, 2859*m*, 1549*w*, 1471*w*, 1389*w*, 1257*m*, 1144*m*, 1091*s*, 992*m*, 890*m*, 847*s*. IR (13 mM, CH_2Cl_2): 3490*m*, 2958*m*, 2859*w*, 1471*w*, 1389*w*, 1141*m*, 1091*s*, 990*m*, 842*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.55 (*dt*, *J* = 3.9, 2.1, H–C(4)); 4.40 (*dtd*, *J* = 10.0, 4.2, 2.1, H–C(6)); 4.20 (*t*, *J* = 1.7, H–C(2)); 4.17–4.10 (*m*, 2 H), 4.05 (*dq*, *J* = 4.2, 1.8, 1 H, H–C(1), H–C(3), H–C(5)); 3.82 (*d*, *J* = 10.0, OH); 1.72–1.64 (*m*, CH_2); 1.50–1.25 (*m*, 2 CH_2); 0.96 (*s*, *t*-BuSi); 0.93 (*s*, *t*-BuSi); 0.90 (*t*, *J* = 7.0, Me); 0.19 (*s*, Me_2Si); 0.17 (*s*, Me_2Si); 0.15 (*s*, Me_2Si); 0.14 (*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 109.03 (*s*, CO_3); 75.56 (*d*), 75.02 (*d*, C(1), C(3)); 69.67 (*d*, C(5)); 69.07 (*d*), 68.62 (*d*, C(4), C(6)); 59.72 (*d*, C(2)); 36.86 (*t*, CH_2); 25.71 (*q*, Me_3C); 25.44 (*q*, Me_3C); 24.77 (*t*, CH_2); 22.35 (*t*, CH_2); 18.10 (*s*, Me_3C); 17.61 (*s*, Me_3C); 13.81 (*q*, Me); −4.75 (*q*, Me_2Si); −4.84 (*q*, Me_2Si); −5.25 (*q*, Me_2Si); −5.47 (*q*, Me_2Si). DCI-MS (NH_4^+): 475 (17, $[M + 1]^+$), 417 (10, $[M - {}^t\text{Bu}]^+$), 301 (7), 297 (13), 183 (15), 159 (5), 84 (15), 75 (18), 49 (100). Anal. calc. for $C_{23}H_{46}O_6Si_2$ (474.78): C 58.19, H 9.77; found: C 58.18, H 9.73.

Stock Solution of Diazirine **5** [84]. All manipulations, including the filtration, were performed under Ar. A suspension of 1,5-anhydro-2,3,4,6-tetra-*O*-benzyl-1-hydrazi-D-glucitol (186 mg, 0.337 mmol) [84], Me_3N (*ca.* 0.5 ml, 5.33 mmol), and powdered 3-Å molecular sieves (186 mg) in CH_2Cl_2 (4.0 ml) was stirred at 23° for 1 h, and cooled to −50°. A soln. of I_2 (85.4 mg, 0.673 mmol) in CH_2Cl_2 (17 ml) was added at −50° over 30 min, until persistence of a faint yellow colour. The mixture was stirred for 15 min at −40°, and rapidly filtered through an oven-dried plug of SiO_2 and Na_2SO_3, eluting with cold (−20°) anh. CH_2Cl_2 (20 ml). The filtrate was concentrated *in vacuo* at −10° to 6.6 ml, as determined by weighing the soln. (8.7 g). This afforded a 46.5 mM stock soln. of diazirine **5**, which was stored at −80° and used without further purification.

Glucosylation of **4**. At −10°, 46.5 mM diazirine **5** in CH_2Cl_2 (0.86 ml, 0.0403 mmol) was evaporated, and a suspension of DL-, D-, or L-**4** (10.0 mg, 0.0403 mmol), and powdered 3-Å molecular sieves (100–200 mg) in the desired solvent (5.4 ml) was injected. After stirring for 20 min at −10°, the mixture was rapidly warmed to 23° by means of a water bath and under vigorous agitation. Typically, glycosylations were completed in 3 h, but stirring was continued overnight at 23°. Filtration through a *Celite* pad and FC (hexane/AcOEt 1:6 → 1:0) led to mixtures of the diglucosides **33** and **38**, mixtures of monoglucosides **29**/**30**, **31**/**32**, **34**/**35**, and **36**/**37**, and the

recovered fluoro diols D-**4** and L-**4**. HLPC of **29**/**30** and **34**/**35** (hexane/AcOEt 2:1), **31**/**32** (hexane/CH_2Cl_2/Et_2O 70:15:15), and **36**/**37** (hexane/AcOEt 20:9) gave pure samples of the anomers. The crude mixtures were analysed by ^{19}F-NMR (*Table 5*).

L-*4-Deoxy-4-fluoro-1,3,5*-O-*pentylidyne-6*-O-*(2,3,4,6-tetra*-O-*benzyl*-α-D-*glucopyranosyl)*-myo-*inositol* (**29**): R_f (hexane/AcOEt 2:1) 0.60. Prep. HPLC (hexane/AcOEt 2:1, 10 ml/min): t_R 16.0. IR (3.1 mM, CCl_4): 3586*w*, 3010*m*, 1070*s*, 1001*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.32–7.23 (*m*, 18 arom. H); 7.12–7.09 (*m*, 2 arom. H); 5.21 (*dtd*, ^2J(H,F) = 47.9, J = 4.1, 1.7, H–C(4)); 4.92 (*d*, J = 3.8, H–C(1′)); 4.91 (*d*, J = 10.8, PhC*H*); 4.80 (*d*, J = 10.8, PhC*H*); 4.75 (*d*, J = 10.8, PhCH); 4.68 (*d*, J = 11.8, PhC*H*); 4.61 (*d*, J = 11.8, PhC*H*); 4.58 (*d*, J = 12.0, PhC*H*); 4.45 (*d*, J = 12.0, PhC*H*); 4.43 (*d*, J = 10.8, PhC*H*); 4.43–4.40 (*m*, H–C(6)); 4.39–4.36 (*m*, H–C(5)); 4.32–4.29 (*m*, H–C(3)); 4.24 (*dq*, J = 4.0, 2.0, H–C(1)); 4.06 (*dq*, J = 11.3, 2.0, ^4J(H,F) = 2.0, H–C(2)); 3.86 (*t*, J = 9.3, H–C(3′)); 3.72–3.62 (*m*, H–C(5′), 2 H–C(6′)); 3.57 (*t*, J = 9.3, H–C(4′)); 3.53 (*dd*, J = 9.3, 3.8, H–C(2′)); 2.85 (*d*, J = 11.3, OH); 1.67–1.63 (*m*, CH_2); 1.43–1.36 (*m*, CH_2); 1.34–1.24 (*sext.*, J = 7.5, CH_2); 0.86 (*t*, J = 7.3, Me). ^{13}C-NMR (75 MHz, $CDCl_3$): 138.94, 138.49, 138.28, 137.98 (4*s*, 4 arom. C); 128.67–127.86 (several *d*); 110.08 (*s*, CO_3); 97.47 (*d*, C(1′)); 84.88 (*dd*, ^1J(C,F) = 191.6, C(4)); 81.57 (*d*, C(3′)); 79.97 (*d*, C(2′)); 77.51 (*d*, C(4′)); 75.83 (*t*, PhCH_2); 75.34 (*t*, PhCH_2); 73.99 (*d*, C(1) or C(6)); 73.71 (*t*, PhCH_2); 73.21 (*t*, PhCH_2); 72.46 (*d*, C(1) or C(6)); 72.38 (*dd*, ^2J(C,F) = 24.4, C(3) or C(5)); 71.56 (*d*, C(5′)); 68.47 (*t*, C(6′)); 66.76 (*dd*, ^2J(C,F) = 20.8, C(3) or C(5)); 60.19 (*d*, C(2)); 36.77 (*t*, CH_2); 24.77 (*t*, CH_2); 22.49 (*t*, CH_2); 13.95 (*q*, Me). ^{19}F-NMR (282 MHz, $CDCl_3$): −199.19 (*d*, ^2J(H,F) = 47). FAB-MS: 771 (100, $[M + 1]^+$), 679 (22, $[M - Bn]^+$), 663 (31, $M - BnO]^+$), 587 (53).

L-*4-Deoxy-4-fluoro-1,3,5*-O-*pentylidyne-6*-O-*(2,3,4,6-tetra*-O-*benzyl*-β-D-*glucopyranosyl)*-myo-*inositol* (**30**): R_f (hexane/AcOEt 2:1) 0.60. Prep. HPLC (hexane/AcOEt 2:1, 10 ml/min): t_R 17.0. IR (7.8 mM, CCl_4): 3586*w*, 3032*m*, 1261*s*, 1095*s*, 1015*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.32–7.24 (*m*, 18 arom. H); 7.22–7.13 (*m*, 2 arom. H); 5.19 (*dtd*, ^2J(H,F) = 46.5, J = 4.0, 1.4, H–C(4)); 4.88 (*d*, J = 11.0, PhC*H*); 4.78 (*d*, J = 11.2, PhC*H*); 4.77 (*d*, J = 10.8, PhC*H*); 4.76 (*d*, J = 11.2, PhC*H*); 4.68 (*d*, J = 11.1, PhC*H*); 4.59 (buried *m*, H–C(6)); 4.59 (*d*, J = 12.1, PhC*H*); 4.52 (*d*, J = 10.8, PhC*H*); 4.52–4.50 (*m*, H–C(5)); 4.51 (*d*, J = 12.1, PhC*H*); 4.47 (*d*, J = 7.8, H–C(1′)); 4.31–4.27 (*m*, H–C(3)); 4.22 (*dq*, J = 4.0, 1.9, H–C(1)); 3.98 (br. *dt*, J = 11.8, 2.1, H–C(2)); 3.70 (*dd*, J = 10.8, 2.2, H–C(6′)); 3.65 (*dd*, J = 10.8, 4.6, H–C(6′)); 3.60 (*t*, J = 8.9), 3.56 (*t*, J = 8.8, H–C(3′), H–C(4′)); 3.46–3.42 (*m*, H–C(5′)); 3.41 (*t*, $J \approx$ 8.3, H–C(2′)); 2.83 (*d*, J = 11.8, OH); 1.72–1.64 (*m*, CH_2); 1.49–1.36 (*m*, CH_2); 1.35–1.24 (*m*, CH_2); 0.88 (*t*, J = 7.3, Me). ^{13}C-NMR (75 MHz, $CDCl_3$): 138.78 (*s*), 138.36 (*s*), 138.26 (*s*, 2 C, 4 arom. C); 128.72–127.84 (several *d*); 110.03 (*s*, CO_3); 103.04 (*d*, C(1′)); 84.95 (*dd*, ^1J(C,F) = 90.4, C(4)); 84.66 (*d*, C(3′)); 81.96 (*d*, C(2′)); 77.79 (*d*, C(4′)); 75.78 (*t*, PhCH_2); 75.22 (*t*, PhCH_2); 75.22 (*d*, C(5′)); 75.06 (*t*, PhCH_2); 73.58 (*t*, PhCH_2); 72.89 (*d*), 72.68 (*d*, C(1), C(6)); 72.42 (*dd*, ^2J(C,F) = 25.6, C(3) or C(5)); 68.92 (*t*, C(6′)); 68.42 (*dd*, ^2J(C,F) = 19.5, C(3) or C(5)); 60.23 (*d*, C(2)); 36.79 (*t*, CH_2); 24.79 (*t*, CH_2); 22.49 (*t*, CH_2); 13.93 (*q*, Me). ^{19}F-NMR (282 MHz, $CDCl_3$): −198.74 (*d*, ^2J(H,F) = 49). FAB-MS: 1541 (7, $[2M + 1]^+$), 771 (100, $[M + 1]^+$), 679 (10, $[M - Bn]^+$), 663 (14, $M - BnO]^+$), 587 (7), 231 (6), 181 (16), 91 (84, Bn^+).

L-*4-Deoxy-4-fluoro-1,3,5*-O-*pentylidyne-2*-O-*(2,3,4,6-tetra*-O-*benzyl*-α-D-*glucopyranosyl)*-myo-*inositol* (**31**): R_f (hexane/AcOEt 2:1) 0.16. Prep. HPLC (hexane/CH_2Cl_2/Et_2O 70:15:15, 10 ml/min): t_R 28.5. IR (6.5 mM, CCl_4): 3620*w*, 3032*w*, 2960*m*, 1454*w*, 1084*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.37–7.25 (*m*, 18 arom. H); 7.16–7.15 (*m*, arom. H); 5.27 (*dtd*, ^2J(H,F) = 48.5, J = 4.3, 1.8, H–C(4)); 4.99 (*d*, J = 10.9, PhC*H*); 4.96 (*d*, J = 3.7, H–C(1′)); 4.85 (*d*, J = 11.2, PhC*H*); 4.83 (*d*, J = 10.9, PhC*H*); 4.81 (*d*, J = 11.9, PhC*H*); 4.63 (*d*, J = 11.9, PhC*H*); 4.60 (*d*, J = 12.0, PhC*H*); 4.50 (*d*, J = 11.2, PhC*H*); 4.44 (*d*, J = 12.0, PhC*H*); 4.47–4.45 (*m*, 2 H), 4.44–4.38 (*m*, 1 H, H–C(1), H–C(3), H–C(6)); 4.31 (*tq*, J = 4.0, 2.0, ^3J(H,F) = 2.0, H–C(5)); 4.08 (*t*, J = 9.3, H–C(3′)); 4.06 (*ddd*, J = 10.6, 4.0, 2.2, H–C(5′)); 3.87–3.86 (*m*, H–C(2)); 3.72 (*dd*, J = 10.6, 4.0, H–C(6′)); 3.64 (*dd*, J = 10.6, 2.2, H–C(6′)); 3.63 (*t*, J = 9.6, H–C(4′)); 3.60 (*dd*, J = 9.0, 3.7, H–C(2′)); 1.95 (*t*, ^5J(OH,F) = J = 7.2, OH); 1.68–1.64 (*m*, CH_2); 1.34–1.24 (*m*, CH_2); 1.29 (*sext.*, J = 7.5, CH_2); 0.85 (*t*, J = 7.3, Me). ^{19}F-NMR (282 MHz, $CDCl_3$): −196.39 (*d*, ^2J(H,F) = 49). FAB-MS: 771 (100, $[M + 1]^+$), 91 (56, Bn^+).

L-*4-Deoxy-4-fluoro-1,3,5*-O-*pentylidyne-2*-O-*(2,3,4,6-tetra*-O-*benzyl*-β-D-*glucopyranosyl)*-myo-*inositol* (**32**): R_f (hexane/AcOEt 2:1) 0.16. Prep. HPLC (hexane/CH_2Cl_2/Et_2O 70:15:15, 10 ml/min): t_R 42.8. IR (5.1 mM, CCl_4): 3619*w*, 3032*w*, 2961*m*, 1454*w*, 1358*m*, 1082*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.39–7.37 (*m*, 2 arom. H); 7.32–7.26 (*m*, 16 arom. H); 7.18–7.17 (*m*, 2 arom. H); 5.30 (*dtd*, ^2J(H,F) = 48.2, J = 4.2, 1.8, H–C(4)); 5.10 (*d*, J = 11.0, PhC*H*); 4.95 (*d*, J = 11.0, PhC*H*); 4.82 (*d*, J = 11.0, PhC*H*); 4.78 (*d*, J = 11.0, PhC*H*); 4.75 (*d*, J = 11.0, PhC*H*); 4.62–4.61 (*m*, H–C(3)); 4.61 (*d*, J = 7.5, irrad. at 3.58 → *s*, H–C(1′)); 4.59 (*d*, J = 12.1, PhC*H*); 4.55 (*d*, J = 11.0, PhC*H*); 4.56–4.54 (*m*, H–C(6)); 4.52 (*d*, J = 12.1, PhC*H*); 4.38 (*dq*, 4.3, 2.1, irrad. at 4.61 → *m*, H–C(1)); 4.36 (*tq*, J = 3.6, 1.8, ^3J(H,F) = 1.8, irrad. at 4.61 → *m*, H–C(5)); 4.20 (br. *q*, ^4J(H,F) = J = 2.5, irrad. at 4.61 → br. *t*, J = 2.5, H–C(2)); 3.72 (*dd*, J = 10.6, 2.0, irrad. at 3.47 → *d*, J = 10.6, H–C(6′));

3.67 (*dd*, J = 10.6, 4.6, irrad. at 3.47 → *d*, J = 10.6, H–C(6′)); 3.65 (*t*, $J \approx$ 8.9, irrad. at 3.47 → change, H–C(4′)); 3.60 (*t*, J = 9.0, H–C(3′)); 3.58 (*dd*, J = 9.0, 7.5, irrad. at 4.61 → *d*, J = 9.0, H–C(2′)); 3.47 (*ddd*, J = 9.4, 4.6, 2.0, H–C(5′)); 2.17 (*td*, ^5J(OH,F) = 8.4, J = 8.4, 2.2, OH); 1.69–1.66 (*m*, CH_2); 1.45–1.39 (*m*, CH_2); 1.25 (*sext.*, J = 7.4, CH_2); 0.82 (*t*, J = 7.3, Me). ^{19}F-NMR (282 MHz, $CDCl_3$): −196.30 (*dd*, ^5J(OH,F) = 47, ^2J(H,F) = 7). FAB-MS: 771 (100, $[M + 1]^+$), 415 (16), 181 (96).

D-*4-Deoxy-4-fluoro-1,3,5-*O*-pentylidyne-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α-*D*-glucopyranosyl)*-myo-*inositol* (**34**): R_f (hexane/AcOEt 2:1) 0.65. Prep. HPLC (hexane/AcOEt 2:1, 10 ml/min): t_R 16.4. IR (9.0 mM, CCl_4): 3586*w*, 3032*w*, 2961*m*, 1454*m*, 1361*w*, 1084*s*, 980*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.35–7.26 (*m*, 18 arom. H); 7.21–7.13 (*m*, 2 arom. H); 5.24 (*dtd*, ^2J(H,F) = 46.9, $J \approx$ 3, 2, H–C(4)); 4.92 (*d*, J = 10.8, PhC*H*); 4.82 (*d*, J = 11.4, PhC*H*); 4.79 (*d*, J = 10.8, PhC*H*); 4.78 (*d*, J = 11.4, PhC*H*); 4.76 (*d*, J = 3.9, H–C(1′)); 4.57 (*d*, J = 9.6, PhC*H*); 4.57 (*d*, J = 12.3, PhC*H*); 4.47 (*d*, J = 9.6, PhC*H*); 4.46 (*d*, J = 12.3, PhC*H*); 4.36–4.34 (*m*, 2 H), 4.34–4.29 (*m*, 1 H), 4.20–4.12 (*m*, 2 H, H–C(1), H–C(2), H–C(3), H–C(5), H–C(6)); 3.86 (br. *d*, J = 9.3), 3.83 (br. *d*, J = 9.3, H–C(3′), H–C(4′)); 3.67 (*dd*, J = 9.3, 3.9, H–C(6′)); 3.59 (*dd*, J = 9.3, 2.3, H–C(6′)); 3.57 (buried *m*, H–C(5′)); 3.51 (*dd*, J = 9.6, 3.3, H–C(2′)); 2.84 (*d*, J = 11.8, OH); 1.72–1.64 (*m*, CH_2); 1.49–1.36 (*m*, CH_2); 1.35–1.24 (*m*, CH_2); 0.89 (*t*, J = 7.2, Me). ^{13}C-NMR (50 MHz, $CDCl_3$): 138.77, 138.26 (2 C), 137.94 (3 *s*, 4 arom. C); 128.68–127.66 (several *d*); 109.82 (*s*, CO_3); 98.81 (*d*, C(1′)); 84.79 (*dd*, ^1J(C,F) = 190.0, C(4)); 81.54 (*d*, C(3′)); 79.76 (*d*, C(2′)); 77.41 (*d*, C(4′)); 75.60, 75.00, 73.57, 73.47 (4*t*, 4 PhCH_2); 73.16 (*d*), 72.94 (*d*, C(1), C(6)); 72.33 (*dd*, ^2J(C,F) = 25.5, C(3) or C(5)); 70.98 (br. *d*, C(5′)); 68.43 (*t*, C(6′)); 67.73 (*dd*, ^2J(C,F) = 19.1, C(3) or C(5)); 59.86 (*d*, C(2)); 36.62 (*t*, CH_2); 24.63 (*t*, CH_2); 22.34 (*t*, CH_2); 13.80 (*q*, Me). ^{19}F-NMR (282 MHz, $CDCl_3$): −198.54 (*d*, ^2J(H,F) = 49). FAB-MS: 771 (64, $[M + 1]^+$), 663 (65, $[M - BnO]^+$), 647 (43), 531 (59), 277 (14), 231 (49), 181 (100).

D-*4-Deoxy-4-fluoro-1,3,5-*O*-pentylidyne-6-*O*-(2,3,4,6-tetra-*O*-benzyl-β-*D*-glucopyranosyl)*-myo-*inositol* (**35**): R_f (hexane/AcOEt 2:1) 0.70. Prep. HPLC (hexane/AcOEt 2:1, 10 ml/min): t_R 13.0. IR (13.0 mM, CCl_4): 3585*w*, 3032*w*, 2961*m*, 1497*w*, 1454*m*, 1360*m*, 1306*m*, 1086*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.35–7.26 (*m*, 18 arom. H); 7.18–7.15 (*m*, 2 arom. H); 5.24 (*dtd*, ^2J(H,F) = 48.2, J = 3.4, 1.5, H–C(4)); 4.93 (*d*, J = 11.0, PhC*H*); 4.86 (*d*, J = 11.0, PhC*H*); 4.80 (*d*, J = 10.7, PhC*H*); 4.78 (*d*, J = 10.7, PhC*H*); 4.64 (*d*, J = 10.8, PhC*H*); 4.57 (*d*, J = 10.8, PhC*H*); 4.57 (*d*, $J \approx$ 10.0, PhC*H*); 4.56 (buried *m*, H–C(6)); 4.55 (*d*, $J \approx$ 10.0, PhC*H*); 4.52 (*d*, J = 7.5, H–C(1′)); 4.48 (*tq*, $J \approx$ 4, 2, ^3J(H,F) ≈ 2, H–C(5)); 4.35 (br. *s*, H–C(1), H–C(3)); 4.17 (*dq*, $J \approx$ 11.2, 2.1, ^4J(H,F) ≈ 2.1, H–C(2)); 3.71 (*dd*, J = 10.5, 1.8, H–C(6′)); 3.65 (*dd*, J = 10.5, 4.8, H–C(6′)); 3.60 (*t*, J = 8.7), 3.57 (*t*, J = 8.4, H–C(3′), H–C(4′)); 3.49–3.43 (*m*, H–C(5′)); 3.43 (*t*, $J \approx$ 8.3, H–C(2′)); 2.90 (*d*, J = 11.7, OH); 1.72–1.64 (*m*, CH_2); 1.49–1.36 (*m*, CH_2); 1.35–1.24 (*m*, CH_2); 0.90 (*m*, J = 7.2, Me). ^{13}C-NMR (75 MHz, $CDCl_3$): 138.81, 138.57, 138.33, 138.24 (4*s*, 4 arom. C); 128.70–127.86 (several *d*); 110.00 (*s*, CO_3); 104.42 (*d*, C(1′)); 85.07 (*dd*, ^1J(C,F) = 190.4, C(4)); 84.55 (*d*, C(3′)); 82.01 (*d*, C(2′)); 77.72 (*d*, C(4′)); 75.83 (*t*, PhCH_2); 75.22 (*t*, PhCH_2); 74.88 (br. *d*, C(1), C(6)); 74.58 (*t*, PhCH_2); 74.07 (*d*, C(5′)); 73.69 (*t*, PhCH_2); 72.54 (*dd*, ^2J(C,F) = 24.4, C(3) or C(5)); 68.99 (*t*, C(6′)); 67.36 (*dd*, ^2J(C,F) = 20.8, C(3) or C(5)); 60.14 (*d*, C(2)); 36.81 (*t*, CH_2); 24.82 (*t*, CH_2); 22.51 (*t*, CH_2); 13.95 (*q*, Me). ^{19}F-NMR (282 MHz, $CDCl_3$): −198.69 (*d*, ^2J(H,F) = 49). FAB-MS: 771 (96, $[M + 1]^+$), 679 (10, $[M - Bn]^+$), 663 (14, $[M - BnO]^+$), 231 (53), 181 (100).

D-*4-Deoxy-4-fluoro-1,3,5-*O*-pentylidyne-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-*D*-glucopyranosyl)*-myo-*inositol* (**36**): R_f (hexane/AcOEt 2:1) 0.18. Prep. HPLC (hexane/AcOEt 20:9, 10 ml/min): t_R 14.8. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.35–7.23 (*m*, 18 arom. H); 7.15–7.13 (*m*, 2 arom. H); 5.17 (*dtd*, ^2J(H,F) = 48.2, J = 4.3, 1.8, H–C(4)); 4.98 (*d*, J = 10.8, PhC*H*); 4.97 (*d*, J = 3.9, H–C(1′)); 4.83 (*d*, J = 10.8, PhC*H*); 4.80 (*d*, J = 10.8, PhC*H*); 4.78 (*d*, J = 12.2, PhC*H*); 4.62 (*d*, J = 12.2, PhC*H*); 4.61–4.59 (buried *m*, H–C(1) or H–C(3)); 4.57 (*d*, J = 12.0, PhC*H*); 4.53–4.48 (buried *m*, H–C(6)); 4.48 (*d*, J = 10.8, PhC*H*); 4.42 (*d*, J = 12.0, PhC*H*); 4.37 (*dq*, J = 4.0, 2.0, H–C(1) or H–C(3)); 4.31 (*tq*, $J \approx$ 4, 2, ^3J(H,F) ≈ 2, H–C(5)); 4.08 (*t*, J = 9.3, H–C(3′)); 4.06 (*ddd*, J = 10.0, 4.2, 2.5, H–C(5′)); 3.85 (*dt*, ^4J(H,F) = 2.7, J = 1.8, H–C(2)); 3.70 (*dd*, J = 10.5, 4.2, H–C(6′)); 3.62 (*dd*, J = 10.5, 2.5, H–C(6′)); 3.61 (*dd*, J = 10.0, 9.0, H–C(4′)); 3.58 (*dd*, J = 9.7, 3.7, H–C(2′)); 2.08 (br. *s*, OH); 1.68–1.63 (*m*, CH_2); 1.44–1.36 (*m*, CH_2); 1.27 (*sext.*, J = 7.3, CH_2); 0.83 (*t*, J = 7.3, Me). ^{19}F-NMR (282 MHz, $CDCl_3$): −196.35 (*d*, ^2J(H,F) = 49).

D-*4-Deoxy-4-fluoro-1,3,5-*O*-pentylidyne-2-*O*-(2,3,4,6-tetra-*O*-benzyl-β-*D*-glucopyranosyl)*-myo-*inositol* (**37**): R_f (hexane/AcOEt 2:1) 0.18. Prep. HPLC (hexane/AcOEt 20:9, 10 ml/min): t_R 16.0. IR (6.5 mM, CCl_4): 3621*w*, 3032*w*, 2961*m*, 1497*w*, 1454*m*, 1356*m*, 1084*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.38–7.36 (*m*, 2 arom. H); 7.34–7.27 (*m*, 16 arom. H); 7.19–7.17 (*m*, 2 arom. H); 5.30 (*dtd*, ^2J(H,F) = 48.4, J = 4.1, 1.7, H–C(4)); 5.09 (*d*, J = 11.0, PhC*H*); 4.95 (*d*, J = 11.0, PhC*H*); 4.82 (*d*, J = 11.0, PhC*H*); 4.79 (*d*, J = 11.0, PhC*H*); 4.75 (*d*, J = 11.0, PhC*H*); 4.59 (*d*, J = 7.4, H–C(1′)); 4.58 (*d*, J = 12.0, PhC*H*); 4.56 (*d*, J = 11.0, PhC*H*); 4.52 (*d*, J = 12.0, PhC*H*); 4.49–4.45 (*m*, H–C(1), H–C(3), H–C(6)); 4.35 (*tq*, J = 3.4, 1.7, ^3J(H,F) = 1.7, H–C(5)); 4.20 (*q*, ^4J(H,F) = J = 2.5, H–C(2)); 3.73 (*dd*, J = 11.0, 2.0, H–C(6′)); 3.67 (*dd*, J = 11.0, 5.2, H–C(6′)); 3.65 (*t*, J = 8.9, H–C(4′)); 3.58

(*t*, *J* = 8.9, H–C(3')); 3.58 (*dd*, *J* = 8.9, 7.4, H–C(2')); 3.47 (*ddd*, *J* = 9.8, 5.2, 2.0, H–C(5')); 2.16 (br. *s*, OH); 1.69–1.66 (*m*, CH_2); 1.45–1.39 (*m*, CH_2); 1.25 (*sext.*, *J* = 7.4, CH_2); 0.82 (*t*, *J* = 7.3, Me). ^{19}F-NMR (282 MHz, $CDCl_3$): −196.60 (*d*, ^2J(H,F) = 49).

Glycosylation of D-**22** *and* L-**24**. At −10°, 45.0 mM **5** in CH_2Cl_2 (0.78 ml, 35.2 μmol) was evaporated and the vacuum released with Ar. A mixture of D-**22** (6.3 mg, 17.6 μmol), L-**24** (17.6 mg μmol), and powdered 3-Å molecular sieves (121 mg) in either CCl_4 or 1,4-dioxane (4.7 ml) was injected, and the mixture was rapidly brought to 23° by means of a water bath. After 6 h, the mixture was filtered through *Celite* and concentrated. The mixture was analysed by ^{1}H- and ^{19}F-NMR and by anal. HPLC (hexane/AcOEt 1:16) with parallel UV and refractive-index detection: *Table 6*. The glycosides **39** and **40** were isolated by FC (hexane/AcOEt 1:16 → 1:1) and HPLC (hexane/AcOEt 93:7). Pure samples of **41** and **42** were isolated by prep. HPLC (hexane/AcOEt 91:9) of the crude product of a separate glycosidation of L-**24**.

D-*2*-O-*[(*tert-*Butyl)dimethylsilyl]-4-deoxy-4-fluoro-1,3,5*-O-*pentylidyne-6*-O-*(2,3,4,6-tetra*-O-*benzyl*-α-D-*glucopyranosyl)*-myo-*inositol* (**39**): R_f (hexane/AcOEt 9:1) 0.23. Anal. HPLC (hexane/AcOEt 16:1, 2 ml/min): t_R 13.1. Prep. HPLC (hexane/AcOEt 93:7, 10 ml/min): t_R 43.5. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.30–7.26 (*m*, 18 arom. H); 7.14–7.12 (*m*, 2 arom. H); 5.24 (*dtd*, ^2J(H,F) = 46.9, *J* ≈ 4, 2, H–C(4)); 4.89 (*d*, *J* = 10.9, PhC*H*); 4.84 (*d*, *J* = 3.6, H–C(1')); 4.80 (*d*, *J* = 11.9, PhC*H*); 4.78 (*d*, *J* = 11.1, PhC*H*); 4.72 (*d*, *J* = 12.0, PhC*H*); 4.62 (*d*, *J* = 12.0, PhC*H*); 4.56 (*d*, *J* = 12.2, PhC*H*); 4.47 (*d*, *J* = 11.0, PhC*H*); 4.45 (*d*, *J* = 12.2, PhC*H*); 4.36–4.33 (*m*, H–C(5)); 4.31–4.29 (*m*, H–C(6)); 4.23–4.21 (*m*, H–C(2), H–C(3)); 4.15 (*dq*, *J* = 4.1, 2.1, H–C(1)); 3.91–3.82 (*m*, H–C(5')); 3.83 (*t*, *J* = 9.4, H–C(3')); 3.67 (*dd*, *J* = 10.6, 3.8, H–C(6')); 3.58 (*dd*, *J* = 10.6, 2.1, H–C(6')); 3.57 (*t*, *J* = 9.6, H–C(4')); 3.50 (*dd*, *J* = 9.7, 3.7, H–C(2')); 1.68–1.65 (*m*, CH_2); 1.44–1.39 (*m*, CH_2); 1.31 (*sext.*, *J* = 7.4, CH_2); 0.91 (*s*, ^{t}BuSi); 0.88 (*t*, *J* = 7.3, Me); 0.10 (*s*, MeSi); 0.09 (*s*, MeSi). ^{19}F-NMR (282 MHz, $CDCl_3$): −196.72 (^2J(H,F) = 49.0).

D-*2*-O-*[(*tert-*Butyl)dimethylsilyl]-4-deoxy-4-fluoro-1,3,5*-O-*pentylidyne-6*-O-*(2,3,4,6-tetra*-O-*benzyl*-β-D-*glucopyranosyl)*-myo-*inositol* (**40**): R_f (hexane/AcOEt 9:1) 0.29. Anal. HPLC (hexane/AcOEt 16:1, 2 ml/min): t_R 11.1. Prep. HPLC (hexane/AcOEt 93:7, 10 ml/min): t_R 32.7. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.33–7.26 (*m*, 18 arom. H); 7.15–7.13 (*m*, 2 arom. H); 5.20 (*dtd*, ^2J(H,F) = 49.8, *J* = 3.9, 1.7, H–C(4)); 4.93 (*d*, *J* = 10.9, PhC*H*); 4.89 (*d*, *J* = 10.9, PhC*H*); 4.80 (*d*, *J* = 10.8, PhC*H*); 4.77 (*d*, *J* = 10.9, PhC*H*); 4.64 (*d*, *J* = 10.8, PhC*H*); 4.54 (*d*, *J* = 11.9, PhC*H*); 4.53–4.51 (*m*, H–C(6)); 4.52 (*d*, *J* = 7.9, H–C(1')); 4.52 (*d*, *J* = 10.3, PhC*H*); 4.52 (*d*, *J* = 12.0, PhC*H*); 4.38 (*dq*, *J* = 3.9, 1.9, H–C(3)); 4.33 (*tq*, *J* ≈ 4, 2, ^3J(H,F) ≈ 2, H–C(5)); 4.30–4.23 (*m*, H–C(2), H–C(1)); 3.73 (*dd*, *J* = 10.6, 2.0, H–C(6')); 3.67 (*dd*, *J* = 10.6, 4.7, H–C(6')); 3.63 (*t*, *J* = 8.9), 3.59 (*t*, *J* = 8.4, H–C(3'), H–C(4')); 3.46 (*ddd*, *J* = 9.3, 4.6, 1.8, H–C(5')); 3.40 (*dd*, *J* = 9.0, 7.6, H–C(2')); 1.70–1.65 (*m*, CH_2); 1.47–1.41 (*m*, CH_2); 1.35 (*sext.*, *J* = 7.4, CH_2); 0.91 (*s*, ^{t}BuSi); 0.88 (*t*, *J* = 7.3, Me); 0.11 (*s*, Me_2Si). ^{19}F-NMR (282 MHz, $CDCl_3$): −197.15 (^2J(H,F) = 46.8).

*1*L-*2*-O-*[(*tert-*Butyl)dimethylsilyl]-1,3,5*-O-*pentylidyne-4*-O-*(2,3,4,6-tetra*-O-*benzyl*-α-D-*glucopyranosyl)-1,2,3,5/4-cyclohexanepentol* (**41**): R_f (hexane/AcOEt 9:1) 0.23. Anal. HPLC (hexane/AcOEt 16:1, 2 ml/min): t_R 19.0. Prep. HPLC (hexane/AcOEt 91:9, 10 ml/min): t_R 28.0. $[\alpha]_D^{25}$ = + 32.1 ± 1.1 (*c* = 0.68, CCl_4). IR (7.7 mM, CCl_4): 3033*w*, 2959*m*, 2859*m*, 1454*w*, 1389*w*, 1362*w*, 1260*m*, 1073*s*, 1028*m*, 886*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.34–7.26 (*m*, 18 arom. H); 7.13–7.10 (*m*, 2 arom. H); 4.92 (*d*, *J* = 11.2, PhC*H*); 4.91 (*d*, *J* = 2.8, irrad. at 3.61 → *s*, H–C(1')); 4.81 (*d*, *J* = 10.9, 2 PhC*H*); 4.74 (*d*, *J* = 12.1, PhC*H*); 4.64 (*d*, *J* = 12.1, PhC*H*); 4.59 (*d*, *J* = 12.1, PhC*H*); 4.46 (*d*, *J* = 11.8, 2 PhC*H*); 4.31 (br. *t*, *J* = 3.4, H–C(4)); 4.18–4.14 (*m*, 2 H), 4.09–4.05 (*m*, 1 H, H–C(1), H–C(3), H–C(5)); 3.95 (br. *s*, H–C(2)); 3.84 (*t*, *J* = 8.9, H–C(3')); 3.73–3.56 (*m*, H–C(2'), H–C(3'), H–C(5'), H–C(6')); 3.52 (*dd*, *J* = 9.7, 3.7, H–C(6')); 2.42 (br. *dt*, *J* ≈ 13.7, 4, H_{eq}–C(6)); 1.86 (*d*, *J* = 13.4, H_{ax}–C(6)); 1.68–1.62 (*m*, CH_2); 1.49–1.40 (*m*, CH_2); 1.31 (*sext.*, *J* = 7.0, CH_2); 0.91 (*s*, *t*-BuSi); 0.88 (*t*, *J* = 7.2, Me); 0.07 (*s*, Me_2Si). ^{13}C-NMR (50 MHz, $CDCl_3$): 138.69, 138.17, 138.07, 137.86 (4*s*, 4 arom. C); 128.62–127.77 (several *d*); 109.95 (*s*, CO_3); 98.16 (*d*, C(1')); 81.90 (*d*, C(3')); 79.07 (*d*, C(2')); 77.19 (*d*, C(4')); 75.61 (*t*, PhCH_2); 75.30 (*t*, PhCH_2); 73.57 (*t*, PhCH_2); 73.57 (*d*); 73.19 (*t*, PhCH_2); 73.19 (*d*); 71.71 (*d*); 71.35 (*d*); 68.90 (*d*, C(5')); 68.22 (br. *t*, C(6')); 64.24 (*d*, C(2)); 37.80 (*t*, CH_2); 27.38 (*t*, C(6)); 25.74 (*q*, Me_3C); 24.58 (*t*, CH_2); 22.45 (*t*, CH_2); 18.10 (*s*, Me_3C); 13.86 (*q*, Me); −4.63 (*q*, MeSi); −4.70 (*q*, MeSi). FAB-MS: 867 (100, $[M + 1]^+$), 809 (27, $[M - {}^t\text{Bu}]^+$), 759 (16), 327 (7), 181 (6), 91 (47, Bn^+).

*1*L-*2*-O-*[(*tert-*Butyl)dimethylsilyl]-1,3,5*-O-*pentylidyne-4*-O-*(2,3,4,6-tetra*-O-*benzyl*-β-D-*glucopyranosyl)-1,2,3,5/4-cyclohexanepentol* (**42**): R_f (hexane/AcOEt 9:1) 0.25. Anal. HPLC (hexane/AcOEt 16:1, 2 ml/min): t_R 18.2. Prep. HPLC (hexane/AcOEt 91:9, 10 ml/min): t_R 24.8. $[\alpha]_D^{25}$ = + 2.5 ± 0.3 (*c* = 1.07, CCl_4). IR (12.3 mM, CCl_4): 3032*w*, 2958*m*, 2859*m*, 1454*w*, 1389*w*, 1362*w*, 1260*m*, 1142*m*, 1083*s*, 980*m*, 886*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.34–7.26 (*m*, 18 arom. H); 7.17–7.13 (*m*, 2 arom. H); 4.89 (*d*, *J* = 10.9, PhC*H*); 4.81 (*d*, *J* = 9.7, 2 PhC*H*); 4.78 (*d*, *J* = 9.6, PhC*H*); 4.73 (*d*, *J* = 11.2, PhC*H*); 4.54 (*d*, *J* = 12.4, PhC*H*); 4.58 (*d*, *J* = 11.8, PhC*H*); 4.54 (*d*, *J* = 10.9, PhC*H*); 4.49 (*d*, *J* = 7.8, irrad. 3.45 → *s*, H–C(1')); 4.46 (*td*, *J* = 4.0, 1.3, H–C(4)); 4.30

(*dq*, J = 4.2, 2.1, H–C(3)); 4.18–4.15 (*m*, H–C(5)); 4.07–4.03 (*m*, H–C(1)); 3.91 (*t*, J = 1.9, H–C(2)); 3.74–3.60 (*m*, H–C(3′), H–C(4′), H–C(5′), H–C(6′)); 3.49–3.39 (*m*, H–C(2′), H–C(6′)); 2.40 (*dtd*, J = 13.4, 3.6, 1.6, H_{eq}–C(6)); 1.78 (*d*, J = 13.4, H_{ax}–C(6)); 1.68–1.63 (*m*, CH_2); 1.52–1.42 (*m*, CH_2); 1.33 (*sext.*, J = 7.3, CH_2); 0.92 (*s*, ^{t}BuSi); 0.89 (*t*, J = 7.2, Me); 0.09 (*s*, Me_2Si). ^{13}C-NMR (50 MHz, $CDCl_3$): 138.51, 138.10 (2 C), 138.04 (3*s*, 4 arom. C); 128.55–127.72 (several *d*); 109.88 (*s*, CO_3); 103.25 (*d*, C(1′)); 84.68 (*d*, C(3′)); 82.24 (*d*, C(2′)); 77.63 (*d*, C(4′)); 75.70 (*t*, $PhCH_2$); 75.06 (*t*, $PhCH_2$); 74.97 (*t*, $PhCH_2$); 74.97 (*d*, C(5′)); 74.78 (*d*); 73.89 (*d*); 73.48 (*t*, $PhCH_2$); 71.82 (*d*); 68.75 (*t*, C(6′)); 67.89 (*d*); 64.24 (*d*, C(2)); 37.83 (*t*, CH_2); 27.17 (*t*, C(6)); 25.77 (*q*, Me_3C); 24.59 (*t*, CH_2); 22.47 (*t*, CH_2); 18.12 (*s*, Me_3C); 13.87 (*q*, Me); –4.61 (*q*, MeSi); –4.74 (*q*, MeSi). FAB-MS: 957 (5, $[M + Bn]^+$), 867 (100, $[M + 1]^+$), 809 (23, $[M - {}^tBu]^+$), 759 (9), 327 (13), 181 (15), 91 (68, Bn^+). Anal. calc. for $C_{51}H_{66}O_{10}Si$ (867.16): C 70.64, H 7.67; found: C 70.82, H 7.56.

REFERENCES

[1] M. Weber, A. Vasella, *Helv. Chim. Acta* **1997**, *80*, 2352.
[2] K. S. Buckton, R. G. Azrak, *J. Chem. Phys.* **1970**, *52*, 5652.
[3] C. L. Brummel, S. W. Mork, L. A. Philips, *J. Chem. Phys.* **1991**, *95*, 7041.
[4] J. M. Bakke, L. H. Bjerkeseth, E. C. L. Rønnow, K. Steinsvoll, *J. Mol. Struct.* **1994**, *321*, 205.
[5] J. Huang, K. Hedberg, *J. Am. Chem. Soc.* **1989**, *111*, 6909.
[6] D. A. Dixon, B. E. Smart, *J. Phys. Chem.* **1991**, *95*, 1609.
[7] P. J. Krueger, H. D. Mettee, *Can. J. Chem.* **1964**, *42*, 326.
[8] P. Buckley, P. A. Giguère, D. Yamamoto, *Can. J. Chem.* **1968**, *46*, 2917.
[9] R. J. Abraham, T. A. D. Smith, W. A. Thomas, *J. Chem. Soc., Perkin Trans. 2* **1996**, 1949.
[10] T.-S. Lin, E. Fishman, *Spectrochim. Acta, Part A*, **1967**, *23*, 491.
[11] J. Gebicki, A. Krantz, *J. Chem. Soc. Perkin Trans. 2* **1984**, 1617.
[12] E. A. Allan, L. W. Reeves, *J. Phys. Chem.* **1963**, *67*, 591.
[13] T. Kobayashi, M. Hirota, *Chem. Lett.* **1972**, 975.
[14] S. R. Salman, A. R. Kudier, *Spectrochim. Acta, Part A*, **1990**, *46*, 1147.
[15] D. W. Boykin, S. Chandrasekaran, A. L. Baumstark, *Magn. Reson. Chem.* **1993**, *31*, 489.
[16] G. L. Carlson, W. G. Fateley, A. S. Manocha, F. F. Bentley, *J. Phys. Chem.* **1972**, *76*, 1553.
[17] M. Ito, S. Yamamoto, T. Aota, T. Ebata, *J. Mol. Struct.* **1990**, *237*, 105.
[18] S. W. Dietrich, E. C. Jorgensen, P. A. Kollman, S. Rothenberg, *J. Am. Chem. Soc.* **1976**, *98*, 8311.
[19] R. G. Azrak, E. B. Wilson, *J. Chem. Phys.* **1970**, *52*, 5299.
[20] K. Hagen, K. Hedberg, *J. Am. Chem. Soc.* **1973**, *95*, 8263.
[21] J. Pourcin, G. Davidovics, H. Bodot, L. Abouaf-Marguin, B. Gauthier-Roy, *J. Mol. Spectrosc.* **1985**, *109*, 186.
[22] A. D. K. Jones, J. G. Watkinson, *J. Chem. Soc.* **1964**, 2366.
[23] R. West, D. L. Powell, L. S. Whatley, M. K. T. Lee, P. v. R. Schleyer, *J. Am. Chem. Soc.* **1962**, *84*, 3221.
[24] J. A. K. Howard, V. J. Hoy, D. O'Hagan, G. T. Smith, *Tetrahedron* **1996**, *52*, 12613.
[25] S. N. Vinogradov, R. H. Linnell, in 'Hydrogen-Bonding', Van Nostrand Reinhold Company, New York, 1970, p. 121.
[26] T. Bürgi, T. Droz, S. Leutwyler, *Chem. Phys. Lett.* **1995**, *246*, 291.
[27] P. Murray-Rust, W. G. Stallings, C. T. Monti, R. K. Preston, J. P. Glusker, *J. Am. Chem. Soc.* **1983**, *105*, 3206.
[28] L. Shimoni, J. P. Glusker, *Struct. Chem.* **1994**, *5*, 383.
[29] J. D. Dunitz, R. Taylor, *Chem.-Eur. J.* **1997**, *3*, 89.
[30] L. P. Kuhn, R. A. Wires, *J. Am. Chem. Soc.* **1964**, *86*, 2161.
[31] A. Zapata, B. Bernet, A. Vasella, *Helv. Chim. Acta* **1996**, *79*, 1169.
[32] M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzales, J. A. Pople, 'Gaussian 94 {Revision C.3}', Gaussian Inc., Pittsburgh, PA, 1995.
[33] C. Maerker, P. von R. Schleyer, K. R. Liedl, T.-K. Ha, M. Quack, M. A. Suhm, *J. Comput. Chem.* **1997**, *18*, 1695.
[34] F. Huisken, A. Kulcke, C. Laush, J. M. Lisy, *J. Chem. Phys.* **1991**, *95*, 3924.
[35] M. Tichy, *Adv. Org. Chem.* **1965**, *5*, 115.
[36] A. R. H. Cole, G. T. A. Müller, D. W. Thornton, R. L. S. Willix, *J. Chem. Soc.* **1959**, 1218.

[37] C. Jiang, J. D. Moyer, D. C. Baker, *J. Carbohydr. Chem.* **1987**, *6*, 319.
[38] S. V. Ley, M. Parra, A. J. Redgrave, F. Sternfeld, *Tetrahedron* **1990**, *46*, 4995.
[39] S. Ballereau, P. Guédat, B. Spiess, N. Rehnberg, G. Schlewer, *Tetrahedron Lett.* **1995**, *36*, 7449.
[40] L. Odier, 'Procédé de préparation du *cis*-inositol', Eur. Patent 0 523 082 A1, 1992.
[41] S. J. Angyal, L. Odier, M. E. Tate, *Carbohydr. Res.* **1995**, *266*, 143.
[42] K. Sasaki, K. B. Hicks, G. Nagahaski, *Carbohydr. Res.* **1988**, *183*, 1.
[43] H. W. Lee, Y. Kishi, *J. Org. Chem.* **1985**, *50*, 4402.
[44] D. P. Cox, J. Terpinski, W. J. Lawrynowicz, *J. Org. Chem.* **1984**, *49*, 3216.
[45] D. Landini, A. Maia, A. Rampoldi, *J. Am. Chem. Soc.* **1989**, *54*, 328.
[46] W. Middleton, *Org. Synth.* **1986**, *64*, 221.
[47] W. A. Szarek, G. W. Hay, B. Doboszewski, *J. Chem. Soc., Chem. Commun.* **1985**, 663.
[48] B. Doboszewski, G. W. Hay, W. A. Szarek, *Can. J. Chem.* **1987**, *65*, 412.
[49] A. S. Pilcher, H. L. Ammon, P. DeShong, *J. Am. Chem. Soc.* **1995**, *117*, 5166.
[50] M. Gingras, *Tetrahdron Lett.* **1991**, *32*, 7381.
[51] J. A. Wilkinson, *Chem. Rev.* **1992**, *92*, 505.
[52] O. A. Mascaretti, *Aldrichim. Acta* **1993**, *26*, 47.
[53] A. A. E. Penglis, *Adv. Carbohydr. Chem. Biochem.* **1981**, *38*, 195.
[54] N. F. Taylor, 'Fluorinated Carbohydrates', in 'ACS Symposium Series', American Chemical Society, Washington, DC, 1988, No. 374.
[55] W. A. Szarek, 'New Synthetic Methods Emphasizing Deoxyfluoro Sugars and Protective Group Strategy', in 'Trends in Synthetic Carbohydrate Chemistry', Eds. D. Horton, L. D. Hawkins, and G. J. McGarvey, American Chemical Society, Washington DC, 1989, p. 2.
[56] R. Schwesinger, R. Link, G. H. Rotter, D. Honert, H.-H. Limbach, F. Männle, *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1372.
[57] L. A. Paquette, 'Encyclopedia of Reagents for Organic Synthesis', Wiley, New York, 1995.
[58] A. S. Cieplak, *J. Am. Chem. Soc.* **1981**, *103*, 4540.
[59] W. H. Pirkle, M. S. Hoekstra, *J. Org. Chem.* **1974**, *39*, 3904.
[60] W. H. Pirkle, J. R. Hauske, *J. Org. Chem.* **1977**, *42*, 1839.
[61] W. H. Pirkle, J. R. Hauske, *J. Org. Chem.* **1977**, *42*, 2781.
[62] M. Chang, H. V. Meyers, K. Nakanishi, M. Ojita, J. H. Parker, M. H. Parker, R. Takeda, J. T. Vázquez, W. T. Wiesler, *Pure Appl. Chem.* **1989**, *61*, 1193.
[63] M. A. Biamonte, A. Vasella, *Helv. Chim. Acta* **1998**, *81*, 688.
[64] E. Abushanab, *J. Am. Chem. Soc.* **1971**, *93*, 6532.
[65] J. Hilton, L. H. Sutcliffe, *Prog. Nucl. Magn. Reson. Spectrosc.* **1975**, *10*, 27.
[66] P. C. Myhre, J. W. Edmonds, J. D. Kruger, *J. Am. Chem. Soc.* **1966**, *88*, 2459.
[67] A. D. Cross, P. W. Landis, *J. Am. Chem. Soc.* **1964**, *86*, 4005.
[68] C. Reichardt, 'Solvents and Solvent Effects in Organic Chemistry', VCH, Weinheim, 1988.
[69] M. M. Davis, 'Acid-Base Behavior in Aprotic Organic Solvents.', Natl. Bur. Std. (U.S.), 1968.
[70] C. Laurence, M. Queignec-Cabatos, T. Dziembowska, R. Queignec, B. Wojtkowiak, *J. Am. Chem. Soc.* **1981**, *103*, 2567.
[71] G. J. Martin, M. L. Martin, *J. Chim. Phys. Chim. Biol.* **1964**, *61*, 1222.
[72] P.-C. Maria, J.-F. Gal, *J. Phys. Chem.* **1985**, *89*, 1296.
[73] I. Persson, M. Sandström, P. L. Goggin, *Inorg. Chim. Acta* **1987**, *129*, 183.
[74] B. Casu, M. Reggiani, G. G. Galo, A. Vigevani, *Tetrahedron* **1966**, *22*, 3061.
[75] T. Schaefer, G. Kotowycz, *Can. J. Chem.* **1968**, *46*, 2865.
[76] F. Heatley, J. E. Scott, B. Casu, *Carbohydr. Res.* **1979**, *72*, 13.
[77] F. Heatley, J. E. Scott, R. W. Jeanloz, E. Walker-Nasir, *Carbohydr. Res.* **1982**, *99*, 1.
[78] B. R. Leeflang, J. F. G. Vliegenthart, L. M. J. Kroon-Batenburg, B. P. V. Eijick, J. Kroon, *Carbohydr. Res.* **1992**, *230*, 41.
[79] A. Vasella, *Pure Appl. Chem.* **1993**, *65*, 731.
[80] K. Briner, B. Bernet, J.-L. Maloisel, A. Vasella, *Helv. Chim. Acta* **1994**, *77*, 1969.
[81] A. Vasella, in 'Topics in Bioorganic and Biological Chemistry', Ed. S. M. Hecht, Oxford University Press, Vol. 2, in press.
[82] A. Padwa, S. F. Hornbuckle, *Chem. Rev.* **1991**, *91*, 263.
[83] C. Waldraff, Ph. D. Thesis, University of Zürich, 1995.
[84] K. Briner, A. Vasella, *Helv. Chim. Acta* **1989**, *72*, 1371.

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