78. *O*-(1-Phenyl-1*H*-tetrazol-5-yl) Glycosides: Alternative Synthesis and Transformation into Glycosyl Fluorides

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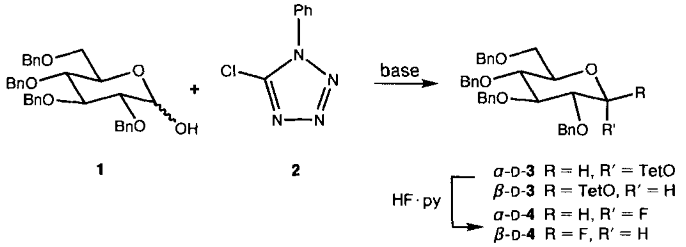
A number of new glycosyl donors, *O*-(1-phenyl-1*H*-tetrazol-5-yl) glycosides, are prepared from the corresponding hemiacetals, commercially available 5-chloro-1-phenyl-1*H*-tetrazole (**2**), and tetrabutylammonium fluoride (Bu_4NF) in either THF or DMF. The mild reaction conditions are compatible with a variety of protecting groups. The glycosyl donors are treated with hydrogen fluoride-pyridine complex (HF·py) to rapidly provide glycosyl fluorides in good-to-excellent yields, apparently by a (single or double) S_N2 mechanism as studied by both ^1H- and ^{19}F-NMR spectroscopy. Under acidic conditions, glycosyl fluorides equilibrate partially or completely, equilibration requiring a large excess of HF·py.

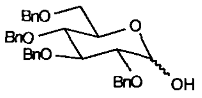
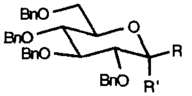
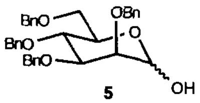
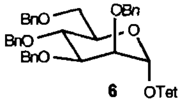
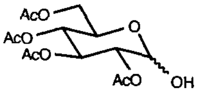
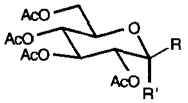
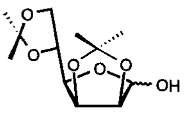
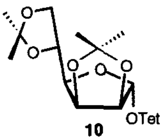
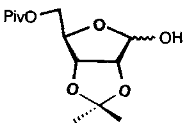
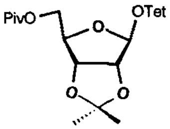
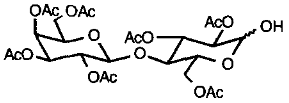
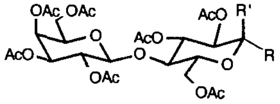
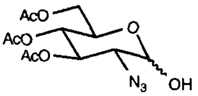
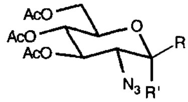
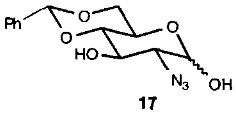
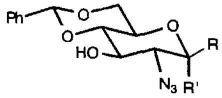
Introduction. – We have reported a glycosidation method using benzyl-protected *O*-(1-phenyl-1*H*-tetrazol-5-yl) glycosides such as α-D- and β-D-**3** as reactive glycosyl donors [1] (*Scheme*). These donors are accessible by the reaction of hemiacetals such as **1** [2] with commercially available 5-chloro-1-phenyl-1*H*-tetrazole (**2**). The strongly basic reaction conditions, however, have restricted the choice of protecting groups to those of the *O*-alkyl type.



We now report the preparation of variously protected *O*-(1-phenyl-1*H*-tetrazol-5-yl) (*O*Tet) glycosides under mild conditions, suitable for the introduction of the tetrazolyl group into *O*-acyl-protected hemiacetals. We also report the transformation of *O*Tet glycosides into glycosyl fluorides such as α-D- and β-D-**4**, which are valuable glycosyl donors in their own right [3–6].

Results and Discussion. – As heteroaryl fluorides are among the most reactive electrophiles in aromatic nucleophilic substitutions, we examined tetrabutylammonium fluoride (Bu_4NF) as a promoter for the preparation of *O*Tet glycosides from 5-chloro-1-phenyl-1*H*-tetrazole (**2**; *Scheme*), speculating that the corresponding fluorotetrazole will

Table 1. *Preparation of Tetrazolyl Glycosides from Hemiacetals and the Tetrazole* **2** *Using* Bu_4NF[a])

Hemiacetal	Tetrazolyl glycoside	Yield [%][b])	α-D/β-D[c])
 **1**	 α-D-**3** R = H, R′ = TetO β-D-**3** R = TetO, R′ = H	87	63:37
 **5**	 **6**	98	100:0
 **7**	 α-D-**8** R = H, R′ = TetO β-D-**8** R = TetO, R′ = H	91	91:9
 **9**	 **10**	95	100:0
 **11**	 **12**	95	100:0
 **13**	 α-D-**14** R = H, R′ = TetO β-D-**14** R = TetO, R′ = H	95	88:12
 **15** R = OH	 α-D-**16** R = H, R′ = TetO β-D-**16** R = TetO, R′ = H	89	88:12
 **17**	 α-D-**18** R = H, R′ = TetO β-D-**18** R = TetO, R′ = H	78	68:32

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[a] Reactions of **1**, **5**, **7**, **9**, **11**, and **13** were performed in THF at 22 ± 2°, and of **15** and **17** in DMF at −15°.

[b] Yields after column chromatography.

[c] Ratios of the anomers were determined by integration of appropriate signals in the ^{1}H-NMR spectrum of the mixture. For **6**, **10**, and **12**, only one anomer was detected by ^{1}H-NMR spectroscopy.

be formed as an intermediate[1]). Treatment of the hemiacetals **1** [2], **5** [9], **7** [10], **9** [11], **11** [12], and **13** [13] (*Table 1*) with 1.1 equiv. of **2** and 3 equiv. of Bu_4NF in THF at room temperature led indeed in high yield to the *O*Tet glycosides **3** [1], **6** [1], **8**, **10**, **12**, and **14**, respectively; the reactions were complete in less than 10 min. The *O*Tet glycosides were purified by column chromatography (1% Et_3N was added to the eluant). They can be stored under Ar at −10° for at least several weeks.

These glycosidation conditions were also suitable for the preparation of *O*Tet glycosides derived from 2-azido-2-deoxyaldoses. Thus, the azide **15** [14] obtained in 93% yield by selective deacetylation of 1,3,4,6-tetra-*O*-acetyl-2-azido-2-deoxy-D-glucopyranoside [15] [16] with hydrazine acetate [10], was treated with varying equivalents of Bu_4NF and the tetrazole **2** at a range of temperatures. The *O*Tet glycosides α-D- and β-D-**16** were obtained in yields of only up to 76% (3 equiv. of Bu_4NF, 0°, 10 min, α-D/β-D 93:7) using THF as the solvent; replacing THF by DMF, however, yielded 89% of α-D/β-D-**16** 88:12. The benzylidene derivative **17** was obtained in 77% yield by treating 2-azido-2-deoxy-D-glucopyranose [15] with benzaldehyde dimethyl acetal and camphor-10-sulfonic acid. Its rapid Bu_4NF-promoted reaction with a slight excess of **2** at −15° in DMF proceeded regioselectively and gave 78% of α-D/β-D-**18** 68:32.

Glycosyl fluorides are a useful class of glycosyl donors and have been prepared by a number of methods and from a range of starting materials [4–6] [17–20]. These methods include the transformation of hemiacetals with 2-fluoropyridinium tosylate [5], α-fluoroenamines [21], or diethyl(1,1,2,3,3,3-hexafluoropropyl)amine [3]. One of the best one-step methods consists in the reaction of hemiacetals with DAST (diethylaminosulfur trifluoride) [22] [23]; the reaction proceeds in high yield, but the reagent is relatively expensive.

In addition to hemiacetals, numerous glycosyl donors are used to prepare glycosyl fluorides. Interconversion of glycosyl donors increases flexibility in synthesis; for example, thioglycosides have been converted to glycosyl fluorides [4] [24] and pentenyl glycosides into glycosyl bromides [25]. Methods for the preparation of glycosyl fluorides from glycosyl donors include the reaction of 1-*O*-acyl glycosides with HF [26] and the reaction of glycosyl chlorides or bromides with AgF [27–29], ZnF_2 [30], or $AgBF_4$ [31–33]. Glycosyl fluorides are also accessible from the reaction of acyl glycosides or the corresponding hemiacetals with hydrogen fluoride-pyridine (HF·py) [6] [34] [35], a reagent introduced by *Olah et al.* in 1979 [36]. While this reagent is preferable to anhydrous HF, large excesses are required, reaction times range from 2–12 h, yields vary, and the method is not useful for acid-sensitive derivatives such as acetals. However, we found that glycosyl fluorides are rapidly obtained by treating *O*Tet glycosides with 5–10 equiv. of HF·py (*Table 2*). The low temperatures, short reaction times, and relatively small excess of reagent (*cf.* [6] [34] [35]) result, generally, in good-to-excellent yields and a high stereoselectivity. The reactions are best run at a glycoside concentration of 0.1M or higher in CH_2Cl_2. To obtain consistent results, vigorous stirring is necessary, as HF·py is not miscible with CH_2Cl_2.

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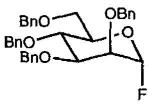
[1]) In contrast to the 5-bromo- and 5-iodo-1-phenyl-1*H*-tetrazoles [7], the fluoro analogue has not been described. The conversion of 5-chloro-1-(phenylmethyl)-1*H*-tetrazole to the corresponding fluorotetrazole using KF and [18]crown-6 in MeCN has been reported [8]; however, under these reaction conditions, 5-chloro-1-phenyl-1*H*-tetrazole was only partially converted to the corresponding fluorotetrazole, and we obtained inseparable mixtures of the chloro- and fluorotetrazoles (*ca.* 1:1, as determined by ^{13}C-NMR).

Table 2. *Preparation of Glycosyl Fluorides from Tetrazolyl Glycosides and HF·py*

Entry	*O*Tet Glycoside (α-D/β-D)	Equiv. of HF·py[a])	Temp. [°C]	Time [min]	Glycosyl fluoride (α-D/β-D)[b])	Yield [%][c])
1	**3** (100:0)[d])	160	−78	30	**4** (90:10)	93
2	**3** (100:0)	160	0	30	**4** (88:12)	95
3	**3** (82:18)	5	0	10	**4** (57:43)	89
4	**3** (63:37)	5	0	10	**4** (60:40)	90
5	**6** (100:0)	10	0	10	**19** (100:0)	76
6	**8** (89:11)	10	0	10	**20** (40:60)	85
7	**8** (89:11)	20	−20	20	**20** (50:50)	85
8	**10** (100:0)	5	0	3	**21** (100:0) **22** (100:0)	46 12
9	**10** (100:0)	5	−20	10	**21** (92:8) **22** (100:0)	72 10
10	**12** (0:100)[d])	5	−20	5	**23** (27:73)	82
11	**14** (88:12)	10	0	10	**24** (15:85)	86
12	**16** (90:10)	10	0	10	**25** (45:55)	95
13	**16** (90:10)	20	−20	30	**25** (56:44)	88

[a]) Approximate number of equiv. based on 70% HF in pyridine. [b]) Ratios of anomers were determined by integration of appropriate signals in the ^{1}H- and/or ^{19}F-NMR spectra of the mixture. [c]) Yields after column chromatography. [d]) The other anomer was not detected by ^{1}H-NMR spectroscopy.



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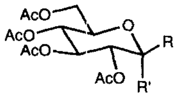
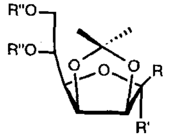
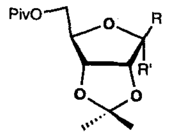


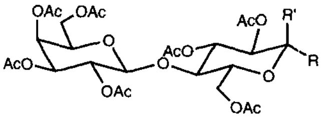
α-D-**20** R = H, R' = F
β-D-**20** R = F, R' = H



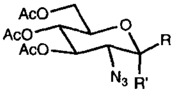
α-D-**21** R = H, R' = F, R'' = Me$_2$C
β-D-**21** R = F, R' = H, R'' = Me$_2$C
22 R = H, R' = F, R'' = H



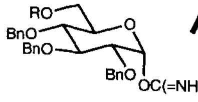
α-D-**23** R = H, R' = F
β-D-**23** R = F, R' = H



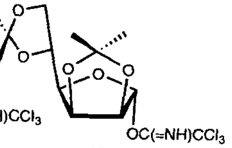
α-D-**24** R = H, R' = F
β-D-**24** R = F, R' = H



α-D-**25** R = H, R' = F
β-D-**25** R = F, R' = H



26 R = Bn
27 R = Ac



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Acid-stable protecting groups tolerate a large excess of HF·py, and **3** was converted in high yield to the fluorides **4** (α-D/β-D *ca.* 9:1, *Entries 1* and *2* of *Table 2*). Excellent yields of **4** were also obtained from the rapid reaction of **3** with only 5 equiv. of HF·py at 0° (*Entries 3* and *4*), although the stereoselectivity decreased. The ratio of the anomeric fluorides appears to depend on the amount of HF·py, the temperature, and the reaction time, but not on the ratio of the anomers of the *O*Tet glycosides (*Entries 3* and *4*). Not unexpectedly, the benzylated α-D-mannopyranoside **6** gave exclusively α-D-**19** (*Entry 5*), and the glycosyl fluoride **20** was obtained in high yield from the acetylated *O*Tet glycoside **8**, regardless, if the reaction was run at 0° or at lower temperature (*Entries 6* and *7*).

The mild conditions – fluorides are formed rapidly at 0° – are compatible with some acid-sensitive groups. Treatment of the di-*O*-isopropylidene-α-D-mannofuranoside **10** with 5 equiv. of HF · py at 0° for 3 min did provide 46% of the desired glycosyl fluoride **21**; however, 12% of the diol **22** were also produced (*Entry 8*), and the low yield suggests that the corresponding tetrol is also formed. Performing the reaction at −20° increased the yield of **21** to 72%; 10% of **22** were still isolated (*Entry 9*). Similarly, the *O*-isopropylideneribofuranoside **12** reacted with 5 equiv. of HF · py (5 min at −20°) to yield 82% of the glycosyl fluoride **23** (*Entry 10*). Conditions could not be found, however, for the satisfactory fluorination of either α-D- and β-D-**18** (see *Table 1*); cleavage of the benzylidene ring competed with fluoride formation even at −78°.

As expected, the interglycosidic bond of the lactose derivative **14** was stable to 10 equiv. of HF · py at 0° for 10 min, and the fluoride **24** [37] was isolated in 86% yield (*Entry 11*, *Table 2*). Finally, the azide **16** gave **25** in high yield (*Entries 12* and *13*), and a larger excess of the reagent and a longer reaction time resulted in the preferential formation of α-D-**25**.

Schmidt has reported a few examples of the rapid preparation of glycosyl fluorides from trichloroacetimidates using up to 10 equiv. of HF · py at room temperature [38]. The reaction of *O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)trichloroacetimidate (**26**) with 5 equiv. of HF · py at room temperature for 5 min in CH_2Cl_2 gave α-D/β-D-**4** 1:1 in 88% yield. When 10 equiv. of reagent were used, the anomeric ratio changed to 4:1, and 15 equiv. led to pure α-D-**4**. *Schmidt* has postulated that the β-D-fluoride is initially formed, and that it isomerizes to the α-D-anomer under the acidic reaction conditions. The stereoselectivity of the reaction of benzylated *O*Tet glucopyranosides with HF · py is consistent with this explanation. A large excess of reagent (> 150 equiv.) transforms α-D-**3** (*Table 2*, *Entries 1* and *2*) within 30 min almost exclusively into α-D-**4**. With 5 equiv. of HF · py and quenching with $NaHCO_3$ after 10 min, a mixture α-D/β-D-**4** was obtained (*Entries 3* and *4*). To determine whether β-D-fluorides are formed initially regardless of the anomeric configuration of the starting tetrazoles, or whether the reaction proceeds with inversion of the configuration, followed by isomerization, the progress of the reaction was monitored by ^1H- and ^{19}F-NMR spectroscopy.

When HF · py was directly added to a solution of α-D-**3** in either $CDCl_3$ or CD_2Cl_2 in an NMR tube (using a *Teflon*® liner within a standard glass NMR tube), two layers formed. Spinning the probe was not sufficient to mix them, and the two-phase system could be left for days with no evident reaction. Vigorous shaking of the tube, however, resulted in an immediate reaction at room temperature. Other common aprotic solvents suitable for low-temperature NMR studies also resulted in two-phase systems. Thus, the reactions were performed with vigorous stirring in a flask using a deuterated solvent at a low temperature. Periodically, samples were withdrawn and diluted in an NMR tube. ^1H-NMR and ^{19}F-NMR spectra were measured at room temperature. The reaction was stopped without addition of base and workup, simply by diluting the sample and avoiding to mix the two phases. NMR Spectra were measured immediately after withdrawing the sample from the reaction mixture. Storing the NMR samples for several hours at room temperature and remeasuring the spectra showed minimal change in sample composition.

Table 3 shows the time dependence of four reactions of *O*Tet glycosides with HF · py as observed by NMR spectroscopy. Interpretation of the ^1H- and ^{19}F-NMR spectra gave consistent results²). Integration of appropriate signals in both ^1H- and ^{19}F-NMR spectra were used to determine relative amounts of starting materials and products. The errors in these measurements were estimated at ±5%. After 0.5 min at −75° in CD_2Cl_2, the *O*Tet

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²) The ^1H-NMR data appeared more accurate. Presumably due to the *Teflon*® liner of the NMR tube, the baselines in the ^{19}F-NMR spectra were not straight.

Table 3. *Dependence of the Ratio of the Glycosyl Fluorides* **4**, **20**, *and* **25** *on Reaction Time: Determination by* ^{1}*H- and* ^{19}*F-NMR Spectroscopy*

Reaction	Time [min]	α-D/β-D-Fluoride (from ^{1}H-NMR)	α-D/β-D-Fluoride (from ^{19}F-NMR)
α-D-**3** → **4**[a]	0.5	47:53	45:55
	1	61:39	58:42
	2	72:28	65:35
	7	83:17	78:22
	33	90:10	90:10
	86[d]	90:10	91:9
8 (α-D/β-D 91:9) → **20**[b]	0.5	**8** (α-D/β-D 91:9)	**8** (α-D/β-D 91:9)
	1	0:100	0:100
	13	–	38:62
	20	–	45:55
	87[d]	–	43:57
α-D-**16** → **25**[c]	0.25	40:60	42:58
	1	40:60	45:55
	2	50:50	60:40
	15	50:50	60:40
	50	50:50	60:40
	90[d]	60:40	60:40
β-D-**16** → **25**[c]	0.25	100:0	100:0
	1	88:12	85:15
	2	–	80:20
	15	89:11	85:15
	50	86:14	82:18
	90[d]	90:10	90:10

[a] Reaction at −75° in CD_2Cl_2. [b] Reaction at −20° in $CDCl_3$. [c] Reaction at −40° in $CDCl_3$. [d] Workup.

glycoside α-D-**3** had disappeared according to ^{1}H-NMR spectroscopy, and a slight excess of β-D-**4** had formed (α-D/β-D-**4** *ca.* 47:53). Longer reaction times resulted in gradual anomerization to the more stable α-D-**4**. A final α-D/β-D ratio of 90:10 was observed. Clearly then, β-D-**4** isomerized to α-D-**4**; however, because the isomerization is fast at – 75°, it was not possible to determine if β-D-**4** was the exclusive first product.

Similarly, the conversion of **8** (α-D/β-D- 91:9) into α-D- and β-D-**20** was followed by NMR spectroscopy. After 0.5 min at −20° in $CDCl_3$, only starting material was observed by ^{1}H-NMR spectroscopy, and no fluorine signals were observed in the ^{19}F-NMR spectrum. After 1 min, all α-D/β-D-**8** was completely consumed, and only signals of β-D-**20** were present in both the ^{1}H- and ^{19}F-NMR spectra. Longer reaction times led to gradual conversion of β-D-**20** into α-D-**20** until a ratio of *ca.* 43:57 had been reached[3]. This experiment shows that β-D-**20** is initially formed (an expected result considering that **8** has a participating AcO–C(2) group) and that isomerization occurred under the reaction conditions.

The *O*Tet glycosides α-D- and β-D-**16**, lacking a participating group at C(2), appear to be well suited starting materials for the investigation of the retentive or inversive course of

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[3] By ^{19}F-NMR; signals in the ^{1}H-NMR spectra were not clearly separated.

the displacement. Pure samples of α-D- and β-D-**16** are available by HPLC. Both anomers were treated separately with 20 equiv. of HF·py in $CDCl_3$ at −40°, and formation of α-D/β-D-**25** was followed by both ^1H- and ^{19}F-NMR spectroscopy. After 0.25 min, α-D-**16** was transformed into α-D/β-D-**25** *ca.* 40:60 with subsequent isomerization to α-D/β-D-**25** *ca.* 60:40. In contrast, β-D-**16** gave, initially, exclusively α-D-**25** suggesting an S_N2 mechanism. Under the acidic reaction conditions, α-D-**25** isomerized quickly to a mixture α-D/β-D-**25** *ca.* 90:10. Although isomerization of the initially formed glycosyl fluoride occurred in both reactions starting from either anomer **16**, equilibration did not occur under the reaction conditions. The anomeric fluoride ratios changed only during the first 90 min, and they were different, depending upon which *O*Tet glycoside was used as starting material. Additional stirring for one week, as well as warming to room temperature did not change the ratios. Only after 2 more additions of 20 equiv. of HF·py each and stirring at room temperature did equilibration occur: only α-D-**25** was observed by both ^1H- and ^{19}F-NMR in both reactions starting either from α-D-**16** or from β-D-**16**.

These results show that the α-D-anomers of 2-*O*-benzyl- or 2-*C*-azidoglycopyranosyl fluorides are more stable by a least 1.4 kcal mol^{-1} under the specified reaction conditions. To our knowledge, the anomeric effect of fluoride has not been determined[4]), however, formation of several glycopyranosyl fluorides under equilibrating conditions show an anomeric ratio α-D/β-D ranging from 95:5 to > 99:1 [32] [35] [39–42], in accordance with our observations. Considering an *A* value of 0.15 kcal mol^{-1} [43], these equilibria show that the anomeric effect for fluoride ranges from 1.55 to 2.87 kcal mol^{-1}. (Values of 2.3 and 2.4 kcal mol^{-1} are given for the anomeric effect of Br and Cl, respectively [44].) In addition, the results show that fluorination with HF·py of *O*Tet glycosides results in initial inversion of configuration, followed by isomerization, although equilibration may require a large excess of reagent. The synthesis of most acetylated glycopyranosyl fluorides from the peracetates with anhydrous HF is thermodynamically controlled [26], and this appears to be the case also for the preparation of glycopyranosyl (and, most probably, glycofuranosyl) fluorides from *O*Tet glycosides and HF·py under appropriate conditions.

To our knowledge, the only other trichloroacetimidate that was treated with HF·py, besides the tetrabenzyl derivative **26**, is the trichloroacetimidate **27** [45]. As trichloroacetimidates are certainly more basic than *O*Tet glycosides, they might be particularly suitable for the preparation of glycosyl fluorides from acid-sensitive starting materials. Indeed, the trichloroacetimidate **28** [46] [47] reacted with 5 equiv. of HF·py at −20° in CH_2Cl_2 for 10 min to give 82% of α-D/β-D-**21** 19:1. Thus, both trichloracetimidates and *O*Tet glycosides are readily available, useful precursors for the preparation of glycosyl fluorides under mild conditions, and *O*Tet glycosides may prove valuable, alternative glycosyl donors [1].

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[4]) It has been calculated to be 0.86–3.1 kcal/mol [48] [49].

Experimental Part

1. *General.* All reactions were done under N_2 with exclusion of moisture. Ambient temperature of 22 ± 2° is implied by r.t. Solvents were distilled under an inert atmosphere before use: CH_2Cl_2, toluene, benzene, EtCN, and MeCN from CaH_2; Et_2O and THF from Na/benzophenone, and MeOH from Mg/I_2. K_2CO_3 was flame-dried and cooled under N_2 before use. Other commercial reagents were used as received. TLC: *Merck* precoated silica gel *60 F_{254}* plates; detection by spraying the plates with 5% $(NH_4)_6Mo_7O_{24} \cdot 4\,H_2O$ and 0.1% $Ce(SO_4)_2$ in 10% H_2SO_4 soln. followed by heating at *ca.* 200°. FC: silica gel *Merck 60* (0.040–0.063 mm). M.p.: *Büchi* apparatus; uncorrected. Optical rotations: *Jasco-DIP-370* digital polarimeter; 1-dm cell, at 25° and 589 nm. IR Spectra: *ca.* 3% soln. in $CHCl_3$ using a *Perkin-Elmer-1600* FT-IR apparatus. NMR Spectra: *Varian Gemini* instruments at 200, 300, or 500 MHz and at 50, 75, or 125 MHz for ^{1}H and ^{13}C, resp.

2. *Tetrazolyl Glycosides: General Procedure Using $Bu_4NF \cdot 3H_2O$ in THF.* To *ca.* 0.1M hemiacetal (1 equiv.) and **2** (1.1 equiv.) in THF at r.t. was added *ca.* 0.1M $Bu_4NF \cdot 3\,H_2O$ (3 equiv.) in THF. When TLC showed complete reaction (usually after 10 min or less), a sat. aq. $NaHCO_3$ soln. was added. Extraction with AcOEt (3×), washing with brine, and evaporation gave the crude tetrazolyl glycosides which were purified by FC (hexane/AcOEt with 1% added Et_3N). Results: *Table 1.*

*1-Phenyl-1*H*-tetrazol-5-yl 2,3,4,6-Tetra-*O*-acetyl-α-*D*- and -β-*D*-glucopyranosides* (α-D- and β-D-**8**, resp.): From α-D/β-D-**8** 91:9, a pure sample of α-D-**8** was obtained by HPLC (*Spherisorb S5W*, 5μ silica gel, 20 × 250 mm, 16 ml/min, hexane/CH_2Cl_2/Et_2O 3:1:1, UV detection (254 nm)).

Data of α-D-**8**: R_f (hexane/AcOEt 1:1) 0.27. $[\alpha]_D^{25} = +121.8$ ($c = 1.25$, $CHCl_3$). IR: 3008*w*, 1756*s*, 1597*m*, 1553*s*, 1506*m*, 1456*m*, 1369*m*, 1248*s*, 1041*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.78–7.48 (*m*, 5 arom. H); 6.51 (*d*, $J = 3.4$, H−C(1)); 5.53 (*t*, $J \approx 10$, H−C(3)); 5.27 (*dd*, $J = 10.4, 3.4$, H−C(2)); 5.21 (*t*, $J \approx 10$, H−C(4)); 4.27 (*dd*, $J = 13.0, 4.8$, H_A−C(6)); 4.12–4.02 (*m*, H−C(5), H_B−C(6)); 2.08 (*s*, Ac); 2.05 (*s*, Ac); 2.04 (*s*, Ac); 2.02 (*s*, Ac). ^{13}C-NMR (50 MHz, $CDCl_3$): 170.88, 170.42, 169.89, 169.64 (4*s*, 4 C=O); 159.20 (*s*, C(1′)); 133.26 (*d*); 130.24 (2*d*); 129.99 (*d*); 122.29 (2*d*); 99.62 (*d*, C(1)); 70.83, 69.67, 69.43, 67.59 (4*d*, C(2), C(3), C(4), C(5)); 61.38 (*t*, C(6)); 20.78–20.63 (4*q*, 4 Me). FAB-MS: 493 (3, $[M + 1]^+$), 433 (14, $[M - OAc]^+$), 331 (87, $[M - OTet]^+$), 169 (100), 109 (55). Anal. calc. for $C_{21}H_{24}N_4O_{10}$ (492.44): C 51.22, H 4.91, N 11.38; found: C 51.30, H 5.04, N 11.17.

Characteristic Data of β-D-**8**: ^{1}H-NMR (200 MHz, $CDCl_3$): 6.00 (*d*, $J = 8.1$, H−C(1)).

*1-Phenyl-1*H*-tetrazol-5-yl 2,3:5,6-Di-*O*-isopropylidene-α-*D*-mannofuranoside* (**10**): R_f (hexane/AcOEt 1:1) 0.53. M.p. 157–158°. $[\alpha]_D^{25} = +19.0$ ($c = 0.5$, $CHCl_3$). IR: 3008*m*, 1597*w*, 1552*s*, 1505*s*, 1456*w*, 1385*m*, 1375*m*, 1120*m*, 1104*m*, 1083*m*, 1069*m*, 924*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.65–7.45 (*m*, 5 arom. H); 6.37 (*s*, H−C(1)); 4.97 (*d*, $J = 5.8$, H−C(2)); 4.92 (*dd*, $J = 5.8, 3.2$, H−C(3)); 4.44 (*m*, H−C(5)); 4.13–4.06 (*m*, H_A−C(6), H−C(4)); 3.99 (*dd*, $J = 7.0, 4.3$, H_B−C(6)); 1.51 (*s*, Me); 1.41 (*s*, Me); 1.36 (br. *s*, 2 Me). ^{13}C-NMR (50 MHz, $CDCl_3$): 158.84 (*s*, C(1′)); 133.36 (*s*); 130.07 (2*d*); 129.64 (*d*); 122.32 (2*d*); 114.17, 114.02 (2*s*, Me_2C); 109.65 (*d*, C(1)); 85.40 (*d*, C(4)); 83.55 (*d*, C(2)); 79.28 (*d*, C(3)); 72.88 (*d*, C(5)); 66.85 (*t*, C(6)); 27.07, 26.12, 25.25, 24.85 (4*q*, 4 Me). EI-MS: 389 (100, $[M - 15]^+$), 185 (39), 119 (38), 101 (51), 49 (48), 43 (62). Anal. calc. for $C_{19}H_{24}N_4O_6$ (404.42): C 56.43, H 5.98, N 13.85; found C 56.57, H 5.94, N 13.85.

*1-Phenyl-1*H*-tetrazol-5-yl 2,3-*O*-Isopropylidene-5-*O*-pivaloyl-β-*D*-ribofuranoside* (**12**): R_f (hexane/AcOEt 2:1) 0.31. M.p. 111–112°. $[\alpha]_D^{25} = -31.1$ ($c = 1.4$, $CHCl_3$). IR: 2981*m*, 1729*s*, 1597*w*, 1552s, 1506*w*, 1480*w*, 1459*w*, 1281*m*, 1139*s*, 1118*s*, 1094*s*, 924*m*, 869*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.65–7.48 (*m*, 5 arom. H); 6.47 (*s*, H−C(1)); 4.99 (*d*, $J = 5.9$, H−C(2)); 4.72 (*d*, $J = 5.9$, H−C(3)); 4.66 (t, $J \approx 7.2$, H−C(4)); 4.13 (*dd*, $J = 11.6, 7.6$, H_A−C(5)); 4.01 (*dd*, $J = 11.6, 6.7$, H_B−C(5)); 1.54 (*s*, Me); 1.36 (*s*, Me); 1.11 (*s*, *t*-Bu). ^{13}C-NMR (50 MHz, $CDCl_3$): 178.22 (*s*, C=O); 158.78 (*s*, C(1′)); 133.35 (*s*); 130.09 (2*d*); 129.74 (*d*); 122.62 (2*d*); 114.12 (*s*, Me_2C); 111.00 (*d*, C(1)); 86.71, 85.57, 81.30 (3*d*, C(2), C(3), C(4)); 63.74 (*t*, C(5)); 38.88 (*s*, Me_3C); 27.17 (*q*, Me_3C); 26.59, 25.22 (2*q*, 2 Me). FAB-MS: 419 (4, $[M - 1]^+$), 403 (4, $[M - 15]^+$), 257 (100, $[M - OTet]^+$), 57 (86). Anal. calc. for $C_{20}H_{26}N_4O_6$ (418.45): C 57.41, H 6.26, N 13.39; found: C 57.60, H 6.28, N 13.26.

*1-Phenyl-1*H*-tetrazol-5-yl 2,3,6,2′,3′,4′,6′-Hepta-*O*-acetyl-α-*D*- and -β-*D*-lactosides* (α-D- and β-D-**14**, resp.): From α-D/β-D-**14** 88:12, a pure sample of α-D-**14** was obtained by HPLC (conditions as for α-D-**8**).

Data of α-D-**14**: R_f (hexane/AcOEt 2:1) 0.34. M.p. 90–92°. $[\alpha]_D^{25} = +74.9$ ($c = 0.55$, $CHCl_3$). IR: 3038*w*, 1755*s*, 1553*m*, 1370*m*, 1248*m*, 1062*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.75–7.48 (*m*, 5 arom. H); 6.42 (*d*, $J = 3.6$, H−C(1)); 5.54 (*dd*, $J = 10.2, 8.8$, H−C(3)); 5.36 (*d*, $J = 3.1$, H−C(4′)); 5.19 (*dd*, $J = 10.3, 3.5$, H−C(2)); 5.11 (*dd*, $J = 10.5, 7.8$, H−C(2′)); 4.95 (*dd*, $J = 10.4, 3.5$, H−C(3′)); 4.49 (*d*, $J = 8.0$, H−C(1′)); 4.42 (*dd*, $J = 12.2, 2.0$, 1 H); 4.15–4.03 (*m*, 3 H); 4.00–3.82 (*m*, 3 H); 2.15 (*s*, Ac); 2.11 (*s*, Ac); 2.09 (*s*, Ac); 2.06 (*s*, Ac); 2.01 (*s*, Ac); 2.00 (*s*, Ac); 1.97 (*s*, Ac). ^{13}C-NMR (50 MHz, $CDCl_3$): 170.70, 170.58, 170.46, 170.41, 170.05, 169.91, 169.41 (7*s*, 7 C=O); 159.21 (*s*, C(1′)); 133.25 (*s*); 130.37 (2*d*); 130.03 (*d*); 122.25 (2*d*); 101.53 (*d*, C(1)); 99.55 (*d*, C(1′)); 75.73, 71.72, 71.23, 71.06, 69.80, 69.36, 69.23, 66.84 (8*d*, C(2), C(2′), C(3), C(3′), C(4), C(4′), C(5), C(5′)); 61.48, 61.02 (2*t*, C(6), C(6′));

20.94–20.65 (7*q*, 7 Me). FAB-MS: 721 (3, $[M - \text{OAc}]^+$), 619 (47, $[M - \text{OTet}]^+$), 331 (95), 169 (100), 109 (79). Anal. calc. for $C_{33}H_{40}N_4O_{18}$ (780.70): C 50.77, H 5.16, N 7.18; found: C 50.60, H 4.95, N 6.90.

Characteristic Data of β-D-**14**: ^{1}H-NMR (300 MHz, $CDCl_3$): 5.93 (*d*, *J* = 10.4, H–C(1)).

3. *Tetrazolyl Glycosides: General Procedure Using* $Bu_4NF \cdot 3\ H_2O$ *in DMF.* To *ca.* 0.1M hemiacetal (1 equiv.) and **2** (1.1–1.2 equiv.) in DMF at −15° was added solid $Bu_4NF \cdot 3\ H_2O$ (3–4 equiv.). When TLC showed complete reaction, workup and purification was done as described above. Results: *Table 1.*

*1-Phenyl-1*H*-tetrazol-5-yl 3,4,6-Tri-*O*-acetyl-2-azido-2-deoxy-α-D- and -β-D-glucopyranoside* (α-D- and β-D-**16**): The mixture α-D/β-D-**16** 88:12 was separated by HPLC (*Spherisorb S5W*, 5 μ silica gel, 20 × 250 mm, 10 ml/min, hexane/CH_2Cl_2/Et_2O 2:1:1, UV detection (220 nm)).

Data of α-D-**16**: R_f (hexane/AcOEt 1:1) 0.38. $[\alpha]_D^{25} = +120.4$ ($c = 0.85$, $CHCl_3$). IR: 3008*w*, 2115*s*, 1754*s*, 1597*w*, 1552*s*, 1506*m*, 1456*m*, 1368*m*, 1153*m*, 1018*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.73–7.49 (*m*, 5 arom. H); 6.48 (*d*, *J* = 3.5, H–C(1)); 5.46 (*t*, *J* ≈ 10.5, H–C(3)); 5.16 (*t*, *J* ≈ 9.6, H–C(4)); 4.27 (*dd*, *J* = 13.0, 4.6, H_A–C(6)); 4.06–4.00 (*m*, H–C(5), H_B–C(6)); 3.97 (*dd*, *J* = 10.5, 3.5, H–C(2)); 2.12 (*s*, Ac); 2.04 (*s*, Ac); 2.01 (*s*, Ac). ^{13}C-NMR (50 MHz, $CDCl_3$): 170.81, 170.22, 169.80 (3*s*, 3 C=O); 159.01 (*s*, C(1′)); 133.11 (*s*); 130.38 (2*d*, 2 arom. CH); 130.04 (*d*, arom. CH); 122.85, 122.47 (2*d*, 2 arom. CH); 100.09 (*d*, C(1)); 70.77, 70.76, 67.70 (3*d*, C(3), C(4), C(5)); 61.34 (*t*, C(6)); 61.29 (*d*, C(2)); 20.76–20.65 (3*q*, 3 Me). FAB-MS: 476 (34, $[M + 1]^+$), 314 (49), 184 (51), 166 (56), 163 (71), 154 (58), 138 (100). Anal. calc. for $C_{19}H_{21}N_7O_8$ (475.42): C 48.00, H 4.45, N 20.62; found: C 48.23, H 4.70, N 20.48.

Data of β-D-**16**: R_f (hexane/AcOEt 1:1) 0.38. $[\alpha]_D^{25} = -56.9$ ($c = 0.48$, $CHCl_3$). IR: 3004*w*, 2944*w*, 2115*s*, 1756*s*, 1598*w*, 1551*s*, 1508*m*, 1458*m*, 1368*m*, 1075s. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.70–7.65 (*m*, 2 arom. H); 7.60–7.50 (*m*, 3 arom. H); 5.81 (*d*, *J* = 8.4, H–C(1)); 5.19 (*t*, *J* ≈ 9.3, H–C(3)); 5.11 (*t*, *J* ≈ 9.3, H–C(4)); 4.37 (*dd*, *J* = 12.7, 4.7, H_A–C(6)); 4.13 (*dd*, *J* = 12.6, 2.2, H_B–C(6)); 3.98 (*ddd*, *J* = 9.7, 4.7, 2.2, H–C(5)); 3.90 (*dd*, *J* = 9.7, 8.4, H–C(2)); 2.11 (*s*, Ac); 2.07 (*s*, Ac); 2.05 (*s*, Ac). ^{13}C-NMR (75 MHz, $CDCl_3$): 170.44, 169.65, 169.59 (3*s*, 3 C=O); 158.60 (*s*, C(1′)); 132.62 (*s*); 129.79 (2*d*, 2 arom. CH); 129.76 (*d*, arom. CH); 122.53 (2*d*, 2 arom. CH); 100.55 (*d*, C(1)); 73.08, 72.51, 67.51, 63.12 (4*d*, C(2), C(3), C(4), C(5)); 61.10 (*t*, C(6)); 20.68, 20.59, 20.55 (3*q*, 3 Me). FAB-MS: 476 (44, $[M + 1]^+$), 314 (31), 184 (25), 166 (28), 163 (66), 154 (55), 138 (70), 118 (61), 69 (68), 55 (100). Anal. calc. for $C_{19}H_{21}N_7O_8$ (475.42): C 48.00, H 4.45; found: C 48.27, H 4.61.

*2-Azido-2-deoxy-4,6-*O*-benzylidene-D-glucopyranose* (**17**): To a soln. of 2-azido-2-deoxy-D-glucopyranose [15] (1.14 g, 5.6 mmol) in DMF (25 ml) was added benzaldehyde dimethyl acetal (0.92 ml, 6.2 mmol) and camphorsulfonic acid (0.065 g, 0.28 mmol). The mixture was heated at 50° with continual removal of MeOH (*Büchi* rotary evaporator, 30 mbar). After 3 h, Et_3N was added, followed by an aq. $NaHCO_3$ soln. Extraction with AcOEt (3×), washing with H_2O (3×), and removal of the solvent gave crude **17** which was purified by FC (hexane/AcOEt 1:1). R_f (hexane/AcOEt 1:1) 0.30. IR: 3442*s*, 3311*s*, 2883*m*, 2107*s*, 1500*m*, 1450*m*, 1377*s*, 1292*m*, 1097*s*, 1030*s*, 988*s*, 965*s*, 751*s*, 699*s*. ^{1}H-NMR (300 MHz, CD_3OD, α-D/β-D-**17** 13:87): 7.51–7.29 (*m*, 5 arom. H); 5.58 (*s*, PhC*H*); 5.21 (*d*, *J* = 3.8, 0.13 H, H–C(1)); 4.63 (*d*, *J* = 8.0, 0.87 H, H–C(1)); 4.25 (*dd*, *J* = 10.3, 4.9, 0.87 H, H_A–C(6)); 4.17 (*dd*, *J* = 10.0, 4.9, 0.13 H, H_A–C(6)); 4.12–3.92 (*m*, 0.26 H); 3.76 (*t*, *J* ≈ 10.0, 0.87 H, H_B–C(6)); 3.74 (*t*, *J* ≈ 10.0, 0.13 H, H_B–C(6)); 3.60 (*t*, *J* ≈ 9.1, 0.87 H, H–C(3)); 3.50 (*t*, *J* ≈ 9.1, 0.87 H, H–C(4)); 3.46–3.38 (*m*, 1.13 H, H–C(5)); 3.23 (*dd*, *J* = 8.0, 3.5, 0.13 H, H–C(2)); 3.20 (*dd*, *J* = 9.3, 8.0, 0.87 H, H–C(2)). ^{13}C-NMR (50 MHz, $CDCl_3$, α-D/β-D-**17** 1:1): 137.17, 137.04 (2*s*); 129.87, 128.82, 136.69, 126.64 (4*d*); 102.50, 102.34 (2*d*, C(1)); 96.87, 92.98 (2*d*, Ph*C*H); 82.08, 80.86, 72.26, 69.23, 67.71, 66.58, 63.96, 62.65 (8*d*, C(2), C(3), C(4), C(5)); 69.10, 68.64 (2*t*, C(6)). EI-MS: 293 (1, M^+), 179 (31), 107 (100), 101 (30), 79 (28), 77 (27). Anal. calc. for $C_{13}H_{15}N_3O_5$ (293.28): C 53.24, H 5.16, N 14.33; found: C 53.06, H 5.05, N 14.09.

*1-Phenyl-1*H*-tetrazol-5-yl 2-Azido-4,6-*O*-benzylidene-2-deoxy-α-D- and -β-D-glucopyranoside* (α-D- and β-D-**18**, resp.): The anomers were separated by column chromatography (hexane/CH_2Cl_2/AcOEt 2:1:1): 53% of α-D-**18** and 25% of β-D-**18**.

Data of α-D-**18**: R_f (hexane/AcOEt 1:1) 0.37. $[\alpha]_D^{25} = +74.0$ ($c = 0.50$, $CHCl_3$). IR: 3599*w*, 3356*w*, 3008*w*, 2872*w*, 2117*s*, 1597*m*, 1552*s*, 1506*s*, 1457*m*, 1377*w*, 1294*m*, 1143*s*, 1091*s*, 1006*s*, 990*s*. ^{1}H-NMR (300 MHz, CD_3OD): 7.80–7.25 (*m*, 10 arom. H); 6.36 (*d*, *J* = 3.6, H–C(1)); 5.60 (*s*, PhC*H*); 4.18 (*m*, 1 H); 4.05 (*m*, 1 H); 3.86 (*dd*, *J* = 9.9, 3.6, H–C(2)); 3.80–3.65 (*m*, 3 H). ^{13}C-NMR (50 MHz, CD_3OD): 160.49 (*s*, C(1′)); 138.76, 134.35 (2*s*, 2 arom. C); 131.00 (*d*, 2 arom. CH); 130.89, 130.11 (2*d*, 2 arom. CH); 129.14 (*d*, 2 arom. CH); 127.54 (*d*, 2 arom. CH); 123.76 (*d*, 2 arom. CH); 103.16, 102.65 (2*d*, C(1), Ph*C*H); 81.82 (*d*, C(4)); 70.85 (*d*, C(3)); 67.08 (*d*, C(2)); 64.95 (*d*, C(5)); 69.18 (*t*, C(6)). FAB-MS: 438 (43, $[M + 1]^+$), 163 (57), 154 (97), 136 (98), 107 (94), 91 (91), 77 (100).

Data of β-D-**18**: R_f (hexane/AcOEt 1:1) 0.45. $[\alpha]_D^{25} = -91.0$ ($c = 0.42$, $CHCl_3$). IR: 3604*w*, 3407*w*, 3008*w*, 2117*s*, 1598*m*, 1551*w*, 1507*m*, 1457*m*, 1296*m*, 1100*m*, 1024*s*. ^{1}H-NMR (300 MHz, CD_3OD): 7.80–7.25 (*m*, 10 arom. H); 5.78 (*d*, *J* = 8.2, H–C(1)); 5.61 (*s*, PhC*H*); 4.34 (*dd*, *J* = 10.1, 4.4, H_A–C(6)); 3.89 (*t*, *J* ≈ 9.1, 1 H); 3.81–3.76 (*m*, 2 H); 3.71 (*m*, H–C(2)); 3.62 (*t*, *J* = 8.9, 1 H). ^{13}C-NMR (75 MHz, CD_3OD): 160.81 (*s*, C(1′)); 139.17, 134.43

(2*s*); 131.33–124.22 (several *d*, arom. CH); 103.39, 103.11 (2*d*, C(1), Ph*C*H); 81.74 (*d*, C(4)); 73.53 (*d*, C(3)); 68.74, 67.95 (2*d*, C(2), C(5)); 69.33 (*t*, C(6)). FAB-MS: 438 (26, $[M + 1]^+$), 163 (45), 145 (100), 136 (93), 107 (81), 77 (66). Anal. calc. for $C_{20}H_{19}N_7O_5$ (437.42): C 54.92, H 4.38, N 22.42; found: C 55.10, H 4.52, N 22.15.

4. *Glycosyl Fluorides from Tetrazolyl Glycosides: General Procedure.* HF · C_6H_5N was added to 0.1M tetrazolyl glycoside in CH_2Cl_2 under the conditions indicated in *Table 2*. When TLC showed complete reaction or after the given time, the mixture was cautiously poured into a sat. aq. $NaHCO_3$ soln. Extraction with CH_2Cl_2 (3 ×) and evaporation gave the crude product which was purified by FC (hexane/AcOEt). Results: *Table 2*.

For the NMR experiments, 0.1M tetrazolyl glycoside in a deuterated solvent ($CDCl_3$ or CD_2Cl_2) at the specified temp. was treated with 20 equiv. of HF · C_6H_5N. Samples were withdrawn (0.3–0.5 ml), diluted with 0.2–0.3 ml of deuterated solvent in a *Teflon®* liner within a standard glass NMR tube, and spectra were measured immediately. After workup as described above, a final spectrum was measured. Results: *Table 3*.

Glycosyl fluorides **4** [17] [29] [35] [41] [50] [51], **19** [29] [41], **20** [26–29] [32] [35] [52], **21** [4] [22] [35] [51], and **24** [37] all showed characteristics consistent with those reported in the literature.

*2,3-*O*-Isopropylidene-α-*D*-mannofuranosyl Fluoride* (**22**): R_f (hexane/AcOEt 1:1) 0.08. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.71 (*d*, ^2J(H,F) = 59.3, H–C(1)); 4.93 (*dd*, *J* = 5.9, 3.7, H–C(3)); 4.78 (*t*, *J* = 6.1, ^3J(H,F) = 6.1, H–C(2)); 4.19 (*dd*, *J* = 8.3, 3.7, H–C(4)); 4.10–3.98 (*m*, H–C(5)); 3.88 (*dd*, *J* = 11.5, 3.1, H_A–C(6)); 3.74 (*dd*, *J* = 11.5, 5.7, H_B–C(6)); 2.75 (br. *s*, OH); 2.05 (br. *s*, OH); 1.48 (*s*, Me); 1.35 (*s*, Me). ^{13}C-NMR (50 MHz, $CDCl_3$): 113.87 (*dd*, ^1J(C,F) = 222, C(1)); 113.66 (*s*, Me_2*C*); 84.79 (*dd*, ^2J(C,F) = 42.2, C(2)); 81.87 (*d*, C(3)); 79.37 (*d*, C(4)); 70.21 (*d*, C(5)); 64.33 (*t*, C(6)); 26.09, 24.84 (2*q*, 2 Me). ^{19}F-NMR (282 MHz, $CDCl_3$): −129.08 (*dd*, *J* = 59.3, 6.1).

*2,3-*O*-Isopropylidene-5-*O*-pivaloyl-α-*D*- and -β-*D*-ribofuranosyl Fluoride* (α-D- and β-D-**23**, resp.): FC (hexane/AcOEt 9:1) provided 60% of α-D-**23** and 22% of β-D-**23**.

Data of α-D-**23**: R_f (hexane/AcOEt 2:1) 0.43. $[\alpha]_D^{25}$ = +21.5 (*c* = 0.55, $CHCl_3$). IR: 3008*w*, 2983*m*, 1732*s*, 1284*m*, 1160*s*, 1140*s*, 1106*s*, 1052*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.63 (*dd*, *J* = 3.5, ^2J(H,F) = 64.5, H–C(1)); 4.80–4.58 (*m*, H–C(2), H–C(3), H–C(4)); 4.30 (*dd*, *J* = 12.1, 3.5, H_A–C(5)); 4.17 (*dd*, *J* = 12.1, 3.5, H_B–C(5)); 1.56 (*s*, Me); 1.37 (*s*, Me); 1.20 (*s*, *t*-Bu). ^{13}C-NMR (50 MHz, $CDCl_3$): 177.58 (*s*, C=O); 115.68 (*s*, Me_2*C*); 107.75 (*dd*, ^1J(C,F) = 236, C(1)); 81.46 (*dd*, ^3J(C,F) = 2.2, C(3)); 80.76 (*dd*, ^2J(C,F) = 20.6, C(2)); 79.11 (*d*, C(4)); 63.24 (*t*, C(5)); 38.53 (*s*, Me_3*C*); 26.92 (*q*, Me); 26.87 (2*q*, 2 Me); 26.82 (*q*, Me); 25.42 (*q*, Me). ^{19}F-NMR (282 MHz, $CDCl_3$): −130.02 (*dd*, *J* = 64.5, 15.1). EI-MS: 277 (0.2, $[M + 1]^+$), 261 (100, $[M - Me]^+$), 159 (8), 85 (13), 57 (59). Anal. calc. for $C_{13}H_{21}FO_5$ (276.30): C 56.51, H 7.66; found: C 56.45, H 7.49.

Data of β-D-**23**: R_f (hexane/AcOEt 2:1) 0.50. $[\alpha]_D^{25}$ = +1.4 (*c* = 2.7, $CHCl_3$). IR: 2977*m*, 1730*s*, 1480*m*, 1282*m*, 1160*s*, 1131*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.76 (*d*, ^1J(H,F) = 61.9, H–C(1)); 4.80 (*t*, *J* ≈ 6.0, H–C(3)); 4.72 (*d*, *J* = 6.0, H–C(2)); 4.52 (*m*, H–C(4)); 4.20–4.05 (*m*, 2 H–C(5)); 1.46 (*s*, Me); 1.32 (*s*, Me); 1.21 (*s*, *t*-Bu). ^{13}C-NMR (50 MHz, $CDCl_3$): 178.35 (*s*, C=O); 115.56 (*dd*, ^1J(C,F) = 223, C(1)); 113.40 (*s*, Me_2*C*); 86.62 (*dd*, ^3J(C,F) = 2.7, C(3)); 85.28 (*dd*, ^2J(C,F) = 40.6, C(2)); 81.15 (*d*, C(4)); 64.38 (*t*, C(5)); 39.01 (*s*, Me_3*C*); 27.30 (*q*, *Me_3*C); 26.50, 25.08 (2*q*, 2 Me). ^{19}F-NMR (282 MHz, $CDCl_3$): −116.41 (*dm*, *J*(H,F) = 62.0). EI-MS: 261 (100, $[M - Me]^+$), 159 (12), 86 (13), 57 (62), 43 (12). Anal. calc. for $C_{13}H_{21}FO_5$ (267.30): C 56.51, H 7.66; found: C 56.66, H 7.52.

*3,4,6-Tri-*O*-acetyl-2-azido-2-deoxy-α-*D*- and -β-*D*-glucopyranosyl Fluoride* (α-D- and β-D-**25**, resp.). From α-D/β-D-**15**, a pure sample of each anomer was obtained by HPLC (*Spherisorb S5W*, 5 μ silica gel, 20 × 250 mm, 2 ml/min, hexane/CH_2Cl_2/Et_2O 3:3:14, UV detection (220 nm)).

Data of α-D-**25**: R_f (hexane/AcOEt 2:1) 0.27. $[\alpha]_D^{25}$ = +157 (c = 0.21, $CHCl_3$). M.p. 91–92°. IR: 3008*w*, 2115*s*, 1753*s*, 1368*m*, 1161*m*, 1038*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.72 (*dd*, ^2J(H,F) = 51.9, *J* = 2.6, H–C(1)); 5.48 (*dd*, *J* = 10.5, 9.4, H–C(3)); 5.14 (*t*, *J* ≈ 9.6, H–C(4)); 4.32 (*dd*, *J* = 12.3, 4.1, H_A–C(6)); 4.21 (*m*, H–C(5)); 4.14 (*dd*, *J* = 12.4, 2.1, H_B–C(6)); 3.51 (*ddd*, ^3J(H,F) = 25.6, *J* = 10.5, 2.6, H–C(2)); 2.11 (*s*, Ac); 2.10 (*s*, Ac); 2.06 (*s*, Ac). ^{13}C-NMR (75 MHz, $CDCl_3$): 170.46, 169.82, 169.56 (3*s*, 3 C=O); 105.62 (*dd*, ^1J(C,F) = 230, C(1)); 70.08 (*d*, C(3)); 70.02 (*d*, C(5)); 67.35 (*d*, C(4)); 61.18 (*t*, C(6)); 61.04 (*dd*, ^2J(C,F) = 21.9, C(2)); 20.68, 20.63, 20.55 (3*q*, 3 Me). ^{19}F-NMR (282 MHz, $CDCl_3$): −147.27 (*dd*, *J* = 51.5, 25.5). EI-MS: 334 (0.2, $[M + 1]^+$), 274 (0.3, $[M - OAc]^+$), 168 (3), 143 (22), 115 (22), 86 (11), 43 (100). Anal. calc. for $C_{12}H_{16}FN_3O_7$ (333.27): C 43.25, H 4.84, N 12.61; found: C 43.55, H 4.97, N 12.73.

Data of β-D-**25**: R_f (hexane/AcOEt 2:1) 0.27. $[\alpha]_D^{25}$ = −7.3 (*c* = 0.15, $CHCl_3$). IR: 3038*w*, 2918*w*, 2117*s*, 1756*s*, 1368*m*, 1104*m*, 1052*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.17 (*dd*, ^2J(H,F) = 51.5, *J* = 7.4, H–C(1)); 5.12–5.03 (*m*, H–C(3), H–C(4)); 4.30 (*ddd*, *J* = 12.6, 4.9, 1.0, H_A–C(6)); 4.18 (*dd*, *J* = 12.6, 2.5, H_B–C(6)); 3.81 (*m*, H–C(5)); 3.67 (*m*, H–C(2)); 2.11 (*s*, Ac); 2.10 (*s*, Ac); 2.04 (*s*, Ac). ^{13}C-NMR (50 MHz, $CDCl_3$): 170.90, 170.17, 169.90 (3*s*, 3 C=O); 107.84 (*dd*, ^1J(C,F) = 218, C(1)); 72.33 (*dd*, ^3J(C,F) = 5.8, C(3)); 72.02 (*d*, C(5)); 67.90 (*d*, C(4)); 63.87 (*dd*, ^2J(C,F) = 23.3, C(2)); 61.75 (*t*, C(6)); 20.85, 20.78, 20.71 (3*q*, 3 Me). ^{19}F-NMR (282 MHz, $CDCl_3$): −139.4 (*dd*, *J* = 51.6, 12.1). EI-MS: 334 (0.1, $[M + 1]^+$), 274 (0.1, $[M - OAc]^+$), 256 (9), 143 (14), 115 (16), 86 (12), 43 (100). Anal. calc. for $C_{12}H_{16}FN_3O_7$ (333.27): C 43.25, H 4.84, N 12.61; found: C 43.52, H 4.86, N 12.33.

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