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First cross-coupling reactions on halogenated 1*H*-1,2,4-triazole nucleosides

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Abstract—The halogenated 1*H*-1,2,4-triazole glycosides **6–10** were synthesized by BF_3-activated glycosylation of 3(5)-chloro-1,2,4-triazole (**2**), 3,5-dichloro-1,2,4-triazole (**3**), 3,5-dibromo-1,2,4-triazole (**4**), and 3(5)-bromo-5(3)-chloro-1,2,4-triazole (**5**) with 1,2,3,4-tetra-*O*-pivaloyl-β-D-xylopyranose (**1**). The β-anomeric major products 3-chloro-1-(2,3,4-tri-*O*-pivaloyl-β-D-xylopyranosyl)-1,2,4-triazole (**6**β), 3,5-dichloro-1-(2,3,4-tri-*O*-pivaloyl-β-D-xylopyranosyl)-1,2,4-triazole (**7**β), and 3,5-dibromo-1-(2,3,4-tri-*O*-pivaloyl-β-D-xylopyranosyl)-1,2,4-triazole (**8**β) were used as starting materials for transition metal catalyzed C–C-coupling reactions. Arylations of the triazole ring of **7**β, and **8**β were successful in 5-position with phenylboronic acid, 4-vinylphenylboronic acid, and 4-methoxyphenylboronic acid, respectively, under Suzuki cross-coupling conditions (products **11–17**). Moreover, a Cu-catalyzed perfluoroalkylation of **8**β is reported with 1-iodoperfluorohexane yielding 3-perfluorohexyl-1-(2,3,4-tri-*O*-pivaloyl-β-D-xylopyranosyl)-1,2,4-triazole (**18**). Compound **18** was depivaloylated to the trihydroxy derivative **19**. The copper-mediated reaction of **8**β with Rupert's reagent gave the bis(3-bromo-1-(2,3,4-tri-*O*-pivaloyl-β-D-xylopyranosyl)-1,2,4-triazol-5-yl) (**20**).

1. Introduction

Substituted 1,2,4-triazoles are of current interest because of their antiinflamatory, insecticide, antifungal, or antimicrobial activity.[1] Glycosylated triazole derivatives like 1-β-D-ribofuranosyl-1*H*-1,2,4-triazole-3-carboxamide (Virazol)[2] belong to the highly potent drugs against DNA- and RNA-viruses.[3] Moreover, this compound shows antitumor activity,[4] just as the anomeric 1-(2,3,4,6-tetra-*O*-acetyl-D-glucopyranosyl)-5-nitro-1*H*-1,2,4-triazoles.[5]

In order to broaden the approach for 1,2,4-triazole nucleoside analogues and animated by a recent excellent review[6] on regioselective cross-coupling reactions of halogenated heterocycles, we investigated first examples of cross-coupling reactions with this heterocycle (arylation and perfluoroalkylation). We focused our efforts on selected methods which allow the regioselective formation of carbon–carbon bonds by selective displacement of halogen atoms of halogenated 1*H*-1,2,4-triazole glycosides. In previous publications[7,8] it could be shown that a halogen atom linked to C-atom 5 of 1-substituted 1,2,4-triazole derivatives allows regioselective nucleophilic substitutions quite easy compared to a halogen atom linked to C-atom 3. The reason is a better mesomeric stabilization of the intermediate formed by attack of the nucleophilic reagent to C-atom 5.[8] For the C–C-coupling experiments within the scope of this paper, three different transition metal catalyzed methods (Fürstner-type coupling, Suzuki-type couplings and Ullmann-type couplings) were selected. Fürstner[9,10] used $Fe(acac)_3$ as catalyst. Suzuki cross-couplings are Pd-catalyzed C–C-couplings of organoboron compounds with carbon electrophiles (especially, aryl halogenides)[6,11,12] and Ullmann-type reactions[13] are catalyzed by Cu-catalysts.

The starting materials, compounds **6–10**, were synthesized by BF_3-activated glycosylations of 3-chloro-1*H*-1,2,4-triazole (**2**),[14] 3,5-dichloro-1*H*-1,2,4-triazole (**3**),[15] 3,5-dibromo-1*H*-1,2,4-triazole (**4**),[16] and 3-bromo-5-chloro-1,2,4-triazole (**5**)[16] with 1,2,3,4-tetra-*O*-pivaloyl-β-D-xylopyranose (**1**)[17] in acetonitrile (Scheme 1); for an alternative strategy to synthesize halogenated 1,2,4-triazole nucleosides by addition of *N*-halo-1,2,4-triazole derivatives to the double bond of glycals see our recent report in synthesis.[8]

The BF_3-activated glycosylation procedures of β-D-xylopyranose **1** with the azoles **2–5** required relatively long reaction times (3–6 days). The glycosidic linkages of the reactants occurred at N-1/N-2 of the triazole ring but never at N-atom 4. The dihalogen triazoles **3** and **4** gave α/β-anomeric mixtures of the glycosyl triazoles **7**α/β and **8**α/β, respectively, in which the corresponding β-anomers were

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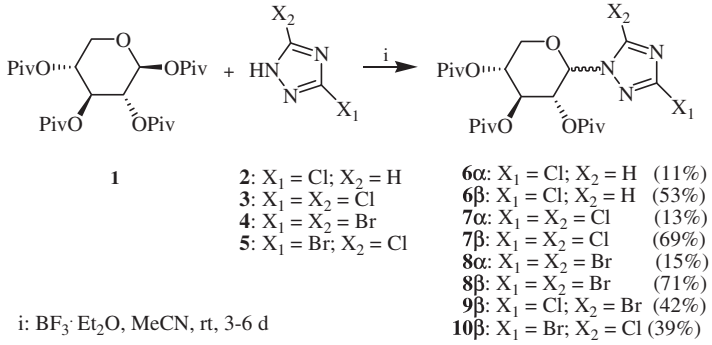


Scheme 1. Glycosylation of halogenated 1,2,4-triazoles with acylated sugars.

the major products (Scheme 1). When the reaction was carried out with 3-bromo-5-chloro-1,2,4-triazole (**5**), bearing different halogens at C-3 and C-5, only the regioisomeric β-glycosides (**9**β and **10**β) were formed, namely in similar amounts.

By contrast, 3-chloro-1*H*-1,2,4-triazole (**2**) likewise asymmetrically substituted in the positions 3 and 5, reacted regioselectively with 1,2,3,4-tetra-*O*-pivaloyl-β-D-xylopyranose (**1**), that is, the glycosyl donor attacked that N-atom of the triazole ring, which is 1,3-located to the Cl-substituted ring carbon. However, the product consisted of the two anomers **6**α and **6**β (Scheme 1).

There is abundant information about the tautomerism of azoles in solution. The knowledge on 1,2,4-triazoles indicates that only 1H tautomers are stable, that is, the NH-proton of the monochloro derivative **2** alternates between N1 and N2 of the triazole ring (Ref. 18 and papers cited therein). Moreover, Elguero et al.[18] postulate the preference of that tautomeric form of C-monohalogeno-1,2,4-triazoles in which the NH-proton and the halogen atom are 1,3-arranged.

The structures of the triazole nucleosides **6–10** are supported by their ^{1}H and ^{13}C NMR spectra. The assignment of signals was performed by recording DEPT, two-dimensional ^{1}H,^{1}H and ^{13}C,^{1}H correlation spectra. The ^{13}C NMR chemical shifts of the nucleosides **6**α/β were additionally compared to data from the literature.[7,8,19] Table 1 shows the chemical shifts of C-3 (triazole) and C-5 (triazole) for the nucleoside analogues **6–10**. For derivatives with identical substituents at the heteroaromatic C-atoms 3 and 5 is valid that the ^{13}C signal of C-atom 3 is shifted to lower field than that of C-atom 5. That is probably caused by the neighbourhood of two pyridine-type nitrogen atoms in the case of C-3, whereas C-atom 5 is linked to one pyridine- and one pyrrol-type nitrogen atom. Compared to triazole derivatives being unsubstituted at C-3 and C-5, the introduction of one or two chloro substituents does not significantly alter the chemical shifts of the C-atoms 3 and 5. By contrast, bromo substituents cause significant shifts (Table 1 and Refs. 7,8,19).

Table 1. ^{13}C-Chemical shifts of C-atom 3 and C-atom 5 of the xylosyl triazoles **6–10**

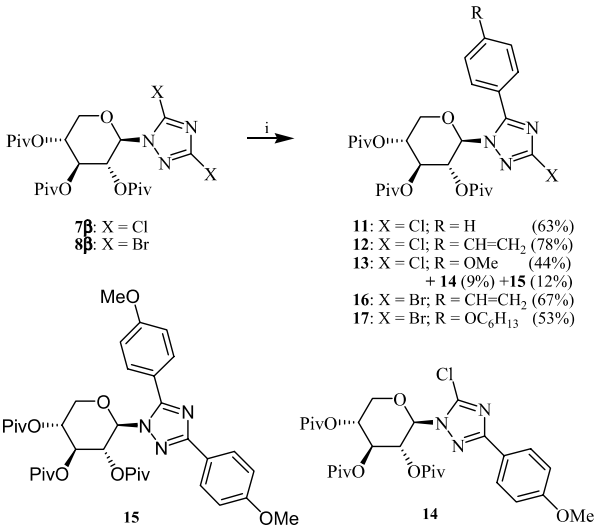
Compound	Triazole substituents (C-3, C-5)	δ (C-3) (ppm)	δ (C-5) (ppm)
6β	Cl, H	153.2	144.0
6α	Cl, H	153.6	146.2
7β	Cl, Cl	153.0	143.1
7α	Cl, Cl	152.5	143.9
8β	Br, Br	141.8	131.2
8α	Br, Br	141.3	132.0
9β	Cl, Br	154.4	131.0
10β	Br, Cl	140.5	143.5

The ^{13}C chemical shifts found for the C-atoms 5 of the anomeric monochloro derivatives **6**α and **6**β (146.2, 144.0 ppm) are similar to those of other 1-substituted 1,2,4-triazole derivatives with hydrogen in this position. As expected, the mixed halogenated glycoside **9**β shows one carbon atom with a shift similar to C-3 of dichloro derivative **7**β and another one with a shift similar to C-5 of dibromo derivative **8**β. Consequently, the mixed halogenated regioisomer **10**β shows one ^{13}C-signal matches with that of C-3 from **8**β and another one matches with that of C-5 from **7**β. This indicates, that **9**β is the 5-bromo-3-chloro- and **10**β the 3-bromo-5-chloro-derivative.

In the following, the behaviour of the glycosyl triazoles **6**β, **7**β, **8**β is described in different C–C-cross-coupling reactions. Firstly, we examined the Fürstner coupling reaction of **6**β and **7**β, respectively, with ethylmagnesium bromide in the presence of Fe(acac)$_3$. The 3-chloro derivative **6**β did not give any product,[9,10] whereas 3,5-dichloro derivative **7**β was hydrodechlorinated in 5-position under Fürstner conditions. However, a C–C-coupling product was likewise not found in this case. The product obtained from **7**β is identical with 3-chloro derivative **6**β.

In further cross-coupling experiments, we investigated reactions of the 3,5-dihalogeno-1,2,4-triazole glycosides **7**β and **8**β under Suzuki conditions. The compounds were reacted with different phenylboronic acids as shown in Scheme 2.

When diadamantyl-butylphosphine (pAd$_2$Bu), in situ prepared from the corresponding hydroiodide,[20] was used as ligand for the Pd-catalyst, compound 7β gave the desired product **11** in 63% yield. Further cross-couplings of the glycosides **7**β and **8**β were realized with differently substituted phenylboronic acids (Scheme 2). In all cases, the preferred position of arylation was C-atom 5 of the heteroaromatic ring. This position was also preferred in various nucleophilic substitution reactions of halogenated 1-alkyl, 1-aryl, and 1-glycosyl-1,2,4-triazoles.[7,8] It is known that also various transition metal catalysts can act as a

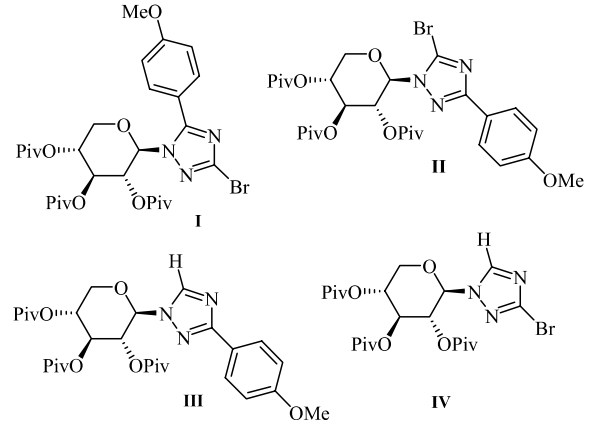


Scheme 2. Suzuki reactions of **7**β and **8**β with different phenylboronic acids. (i) Arylboronic acid, $Pd(OAc)_2$, $[HPAd_2Bu]^+I^-$, K_3PO_4, DMF, 100 °C, 20 h.

nucleophile and preferentially attack the most electron-deficient position of a substrate.[6]

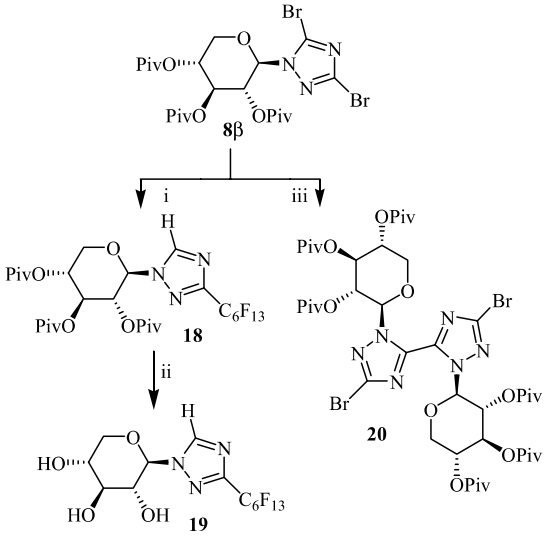
Some side products were found in the arylations of the nucleosides **7**β and **8**β with 4-methoxyphenylboronic acid. Thus, compound **7**β gave 9% yield of the 3-arylated product **14** and 12% yield of the 3,5-diarylated product **15** beside the major product **13** (44%) (Scheme 2). The analogous conversion of the bromo derivative **8**β proceeded still less selective. The result was 25% yield of the slightly contaminated 5-arylated 3-bromo derivative **I** beside mixtures containing the 3-arylated derivatives **II** and **III**, 3,5-diaryl compound **15**, and 3-bromo-1-(2,3,4-tri-*O*-pivaloyl-β-D-xylopyranosyl)-1,2,4-triazole (**IV**), respectively (Scheme 3). These products could not be fully characterized. On the other hand, the conversion of 4-hexyloxyphenylboronic acid did not work well with **7**β, whereas the bromo derivative **8**β yielded 53% of the desired product **17** (Scheme 2).

Besides coupling reactions with arylboronic acids, we were interested in the introduction of trifluoromethyl- and perfluoroalkyl groups into the heteroaromatic 5-position of glycosyl triazoles. Perfluoroalkylcopper reagents are the most studied perfluoroalkyl organometallic reagents, readily prepared from halogeno perfluoroalkanes by copper metal insertion using a coordinating solvent.[21]



Scheme 3. Products of the conversion of bromo derivative **8**β with 4-methoxyphenylboronic acid.

For the perfluoroalkylation of the glycosides **7**β and **8**β we used such a copper-mediated procedure.[22] No perfluoroalkylation was observed on heating of dichloro derivative **7**β with 1-iodo-perfluorohexane in the presence of copper powder at 110 °C in DMSO for 20 h. Under the same conditions, dibromo derivative **8**β reacted to 3-perfluorohexyl-1-(2,3,4-tri-*O*-pivaloyl-β-D-xylopyranosyl)-1,2,4-triazole (**18**) in a yield of 37% (Scheme 4). In addition, traces of a compound were detected, which is probably the 3,5-di-perfluorohexylated derivative. This result indicates that the hydrodebromination, competing with the C–C-cross-coupling reaction for the more reactive 5-position of the triazole ring of **8**β, proceeded faster. Consequently, the cross-coupling can only occur in 3-position. Products reduced in 5-position were also formed from compound **8**β in the Suzuki coupling with 4-methoxyphenylboronic acid (Scheme 3). Compound **18** was deprotected by treatment with 1% methanolic potassium *tert*butoxide yielding **19** (yield 75%). Attempts to introduce a trifluoromethyl group into the 5-position of **8**β applying the reagent combination $(CH_3)_3SiCF_3$–KF–CuI as precursor of a trifluoromethylcopper(I) species,[23] were not successful in DMF. The only product observed was compound **20**, which can be discussed as a result of an Ullmann-type coupling reaction. Leave out of only one component of the reagent combination resulted in no conversion of **8**β.



Scheme 4. Conversion of **8**β with 'perfluorohexylcopper(I)' and 'trifluoromethylcopper(I)' and following deprotection of the perfluorohexylated compound. (i) $C_6F_{13}I$, Cu, DMSO, 110 °C, 20 h. (ii) $KOBu^t$, MeOH, rt, 4–5 days. (iii) $(CH_3)_3SiCF_3$, KF, CuI, DMF, 80 °C, 24 h.

The formation of bis-heterocycles was also observed in other organometal cross-couplings, for example, in a reaction of 2,4-dibromothiazole.[6]

In summary, halogenated 1-glycosyl-1,2,4-triazoles synthesized by a BF_3-activated glycosylation procedure with a relatively high β-selectivity are suitable substrates in transition metal catalyzed cross-coupling reactions. In Suzuki reactions with a modified Pd-catalyst, a preferred substitution at C-5 of the triazole ring was observed, which is in accordance with results of nucleophilic substitutions at similar substrates.[8] In perfluoroalkylations the brominated precursor **8**β proved to be more suitable than the corresponding chloro derivative, when the reaction was carried out with in situ formed perfluoroalkylcopper(I) reagent. The reaction proceeded to the 3-substituted derivative **18** accompanied by hydrodebromination at C-atom 5.

2. Experimental

2.1. General

Chemicals were obtained from Aldrich, Fluka and Merck KGaA and used without further purification. Solvents were dried according to standard procedures. Melting points were determined with a Leitz polarizing microscope (Laborlux 12 Pol) equipped with a hot stage (Mettler FP 90) and are uncorrected. Microanalyses were carried out with a C/H/N/S-analyzer Thermoquest Flash EA 1112. Standard ^{1}H, ^{13}C NMR and DEPT spectra were recorded on a Bruker spectrometer AC 250. For the correlation spectra (COSY, NOESY, HMBC) we used a Bruker Spectrometer AVANCE 500. ^{1}H and ^{13}C NMR chemical shifts are given in ppm, and refer to tetramethylsilane (^{1}H, 0 ppm) and $CDCl_3$ (^{13}C, 77.00 ppm), CD_3OD (^{13}C, 49.05 ppm), C_6D_6 (^{13}C, 128.02 ppm), respectively. Optical rotations were measured on a Polar LμP (IBZ Meßtechnik). Column chromatography was carried out with Merck Silica Gel 60 (63–200 μm) and TLC on Merck Silica Gel 60 F_{254} sheets. TLC was carried out on a silica gel 60 GF_{250} (Merck) by charring with 5% H_2SO_4 in methanol.

2.1.1. 3-Chloro-1-(2,3,4-tri-*O*-pivaloyl-α-D-xylopyranosyl)-1,2,4-triazole (6α) and 3-chloro-1-(2,3,4-tri-*O*-pivaloyl-β-D-xylopyranosyl)-1,2,4-triazole (6β). To a solution of 1,2,3,4-tetra-*O*-pivaloyl-β-D-xylopyranose (**1**) (3.0 g, 6.2 mmol) and 3-chloro-1*H*-1,2,4-triazole (**2**)[14] (1.28 g, 12.4 mmol) in anhyd acetonitrile (50 mL), 3–5 equiv of $BF_3\cdot Et_2O$ were added. The mixture was stirred for about 6 days at room temperature (TLC control). Then, it was poured into a saturated aqueous solution of $NaHCO_3$ (50 mL) and extracted three times with chloroform. After washing of the chloroform phase with water and brine, the solution was dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by column chromatography (eluent: heptane/diethyl ether, v:v=3:1; **6**α: R_f=0.12, **6**β: R_f=0.08) yielding 0.32 g (11%) of **6**α and 1.6 g (53%) of **6**β.

Compound **6**β: colorless crystals; mp 166–168 °C (cyclohexane); $[\alpha]_D^{20}$ −18.43 (*c* 1.09, $CHCl_3$). ^{1}H NMR (250 MHz, C_6D_6): δ=7.67 (s, 1H, H-triazole); 5.38–5.24 (m, 2H, H-2, H-3); 5.00 (ddd, 1H, $^3J_{4,5a}$=5.8 Hz, $^3J_{3,4}$=9.1 Hz, $^3J_{4,5b}$=10.3 Hz, H-4); 4.71 (d, 1H, $^3J_{1,2}$=8.6 Hz, H-1); 3.68 (dd, 1H, $^3J_{4,5a}$=5.8 Hz, $^2J_{5a,5b}$=11.5 Hz, H-5a); 2.65 (t, 1H, $^3J_{4,5b}$=11.0 Hz, H-5b); 1.15, 1.11, 1.01 (3s, 27H, 3C(CH_3)$_3$). ^{13}C NMR (63 MHz, $CDCl_3$): δ=177.1, 177.0, 176.8 (3s, 3C=O); 153.2 (C-3-triazole); 144.0 (C-5-triazole); 86.3 (C-1); 71.4, 69.9, 68.1 (C-2, C-3, C-4); 65.6 (C-5); 38.8, 38.7 (3*C*(CH_3)$_3$); 27.1, 27.0, 26.8 (3C(*C*H_3)$_3$). Anal. Calcd for $C_{22}H_{34}ClN_3O_7$ (487.98): C, 54.15; H, 7.02; N, 8.61. Found: C, 54.30; H, 7.13; N, 8.66.

Compound **6**α: colorless crystals; mp 142–146 °C (heptane); $[\alpha]_D^{21}$ +96.71 (*c* 1.18, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ=8.06 (s, 1H, H-triazole); 6.16 (t, 1H, $^3J_{2,3}$=9.4 Hz, H-3); 5.97 (d, 1H, $^3J_{1,2}$=5.9 Hz, H-1); 5.17–5.03 (m, 2H, $^3J_{4,5a}$=5.8 Hz, $^3J_{1,2}$=6.0 Hz, $^3J_{4,5b}$=10.2 Hz, H-2, H-4); 4.00 (t, 1H, $^3J_{4,5b}$=10.7 Hz, H-5b); 3.90 (dd, 1H, $^3J_{4,5a}$=5.8 Hz, $^2J_{5a,5b}$=11.0 Hz, H-5a); 1.19, 1.15, 0.93 (3s, 27H, 3C(CH_3)$_3$). ^{13}C NMR (63 MHz, $CDCl_3$): δ=177.5, 176.6 (3s, 3C=O); 153.6 (C-3-triazole); 146.2 (C-5-triazole); 81.3 (C-1); 69.7, 68.8, 68.3 (C-2, C-3, C-4); 62.5 (C-5); 38.8, 38.7 (3*C*(CH_3)$_3$); 27.1, 27.0 (3C(*C*H_3)$_3$). Anal. Calcd for $C_{22}H_{34}ClN_3O_7$ (487.98): C, 54.15; H, 7.02; N, 8.61. Found: C, 54.37; H, 7.11; N, 8.26.

2.1.2. 3,5-Dichloro-1-(2,3,4-tri-*O*-pivaloyl-α-D-xylopyranosyl)-1,2,4-triazole (7α) and 3,5-dichloro-1-(2,3,4-tri-*O*-pivaloyl-β-D-xylopyranosyl)-1,2,4-triazole (7β). 1.0 g (2.05 mmol) of **1**, 0.57 g (4.1 mmol) of 3,5-dichloro-1,2,4-triazole (**3**)[15] and 3–5 equiv of $BF_3\cdot Et_2O$ dissolved in 50 mL of anhyd acetonitrile were reacted for about 3 days at room temperature (TLC control). The work-up procedure was analogous to that for **6**α/**6**β. After column chromatographic purification (eluent: heptane/ethyl acetate, v:v=20:1; **7**α: R_f=0.10, **7**β: R_f=0.07), 0.14 g (13%) of **7**α and 0.74 g (69%) of compound **7**β were isolated.

Compound **7**β: colorless crystals; mp 125–126 °C (heptane); $[\alpha]_D^{20}$ −33.10 (*c* 1.28, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ=5.65 (t, 1H, $^3J_{2,3}$=9.3 Hz, H-2); 5.52 (d, 1H, $^3J_{1,2}$=9.1 Hz, H-1); 5.48 (t, 1H, $^3J_{2,3}$=9.4 Hz, H-3); 5.23–5.10 (m, 1H, $^3J_{4,5a}$=5.8 Hz, $^3J_{3,4}$=9.3 Hz, $^3J_{4,5b}$=10.5 Hz, H-4); 4.30 (dd, 1H, $^3J_{4,5a}$=5.8 Hz, $^2J_{5a,5b}$=11.5 Hz, H-5a); 3.54 (t, 1H, $^3J_{4,5b}$=11.0 Hz, H-5b); 1.16, 1.14, 0.99 (3s, 27H, 3C(CH_3)$_3$). ^{13}C NMR (63 MHz, $CDCl_3$): δ=177.1, 177.0, 175.7, (3s, 3C=O); 153.0 (C-3-triazole); 143.1 (C-5-triazole); 84.2 (C-1); 71.7, 69.4, 68.1 (C-2, C-3, C-4); 65.6 (C-5); 38.8, 38.6 (3*C*(CH_3)$_3$); 27.1, 27.0, 26.7 (3C(*C*H_3)$_3$). Anal. Calcd for $C_{22}H_{33}Cl_2N_3O_7$ (522.42): C, 50.58; H, 6.37; N, 8.04. Found: C, 50.89; H, 6.46; N, 8.63.

Compound **7**α: colorless crystals; mp 120–124 °C (heptane); $[\alpha]_D^{21}$ +76.33 (*c* 0.96, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ=6.31–6.20 (m, 2H, $^3J_{1,2}$=6.0 Hz, $^3J_{2,3}$=9.9 Hz, H-3, H-1); 5.22–5.08 (m, 2H, $^3J_{4,5a}$=5.8 Hz, $^3J_{1,2}$=6.3 Hz, $^3J_{3,4}$=9.3 Hz, $^3J_{2,3}$=9.9 Hz, $^3J_{4,5b}$=10.5 Hz, H-2, H-4); 4.02 (t, 1H, $^3J_{4,5b}$=11.0 Hz, H-5b); 3.89 (dd, 1H, $^3J_{4,5a}$=5.8 Hz, $^2J_{5a,5b}$=11.0 Hz, H-5a); 1.19, 1.15, 0.96 (3s, 27H, 3C(CH_3)$_3$). ^{13}C NMR (63 MHz, $CDCl_3$): δ=177.5, 177.2, 176.7, (3s, 3C=O); 152.5 (C-3-triazole); 143.9 (C-5-triazole); 79.5 (C-1); 69.4, 68.5, 68.4 (C-2, C-3, C-4); 62.1 (C-5); 38.8, 38.7 (3*C*(CH_3)$_3$); 27.1, 27.0, 26.6 (3C(*C*H_3)$_3$). Anal. Calcd for $C_{22}H_{33}Cl_2N_3O_7$ (522.42): C, 50.58; H, 6.37; N, 8.04. Found: C, 50.79; H, 6.49; N, 7.78.

2.1.3. 3,5-Dibromo-1-(2,3,4-tri-*O*-pivaloyl-α-D-xylopyranosyl)-1,2,4-triazole (8α) and 3,5-dibromo-1-(2,3,4-tri-*O*-pivaloyl-β-D-xylopyranosyl)-1,2,4-triazole (8β). 2.0 g (4.1 mmol) of **1**, 1.85 g (8.2 mmol) of 3,5-dibromo-1,2,4-triazole (**4**)[16] and 3–5 equiv of $BF_3 \cdot Et_2O$ dissolved in 50 mL of anhyd acetonitrile were reacted for about 3–4 days at room temperature (TLC control). The work-up procedure was analogous to that for **6α/6**β. After column chromatographic separation (eluent: heptane/ethyl acetate, v:v=8:1; **8**α: R_f=0.21, **8**β: R_f=0.13), 0.38 g (15%) of **8**α and 1.79 g (71%) of **8**β were isolated.

Compound **8**β: colorless crystals; mp 142–145 °C (cyclohexane); $[\alpha]_D^{20}$ −30.51 (*c* 1.11, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ=5.70 (t, 1H, $^3J_{2,3}$=9.3 Hz, H-2); 5.55 (d, 1H, $^3J_{1,2}$=9.2 Hz, H-1); 5.49 (t, 1H, $^3J_{2,3}$=9.5 Hz, H-3); 5.17 (ddd, 1H, $^3J_{4,5a}$=5.8 Hz, $^3J_{3,4}$=9.5 Hz, $^3J_{4,5b}$=10.3 Hz, H-4); 4.30 (dd, 1H, $^3J_{4,5a}$=5.8 Hz, $^2J_{5a,5b}$=11.6 Hz, H-5a); 3.54 (dd, 1H, $^3J_{4,5b}$=10.3 Hz; $^2J_{5a,5b}$=11.6 Hz, H-5b); 1.16, 1.14, 0.98 (3s, 27H, 3C(CH_3)$_3$). ^{13}C NMR (63 MHz, $CDCl_3$): δ=177.3, 177.2, 175.7, (3s, 3C=O); 141.8 (C-3-triazole); 131.2 (C-5-triazole); 85.0 (C-1); 72.0, 69.6, 68.3 (C-2, C-3, C-4); 65.8 (C-5); 38.9, 38.8 (3*C*(CH_3)$_3$); 27.2, 26.9 (3C(*C*H_3)$_3$). Anal. Calcd for $C_{22}H_{33}Br_2N_3O_7$ (611.32): C, 43.22; H, 5.44; N, 6.87. Found: C, 43.51; H, 5.46; N, 6.77.

Compound **8**α: colorless crystals; mp 124–125 °C (heptane); $[\alpha]_D^{24}$ +59.23 (*c* 1.48, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ=6.28 (d, 1H, $^3J_{1,2}$=6.2 Hz, H-1); 6.25 (t, 1H, $^3J_{2,3}$=9.8 Hz, H-3); 5.20–5.02 (m, 2H, $^3J_{4,5a}$=6.0 Hz, $^3J_{1,2}$=6.4 Hz, $^3J_{2,3}$=9.8 Hz, H-2, H-4); 3.99 (t, 1H, $^3J_{4,5b}$=10.9 Hz, H-5b); 3.86 (dd, 1H, $^3J_{4,5a}$=6.0 Hz, $^2J_{5a,5b}$=11.1 Hz, H-5a); 1.17, 1.13, 0.93 (3s, 27H, 3C(CH_3)$_3$). ^{13}C NMR (63 MHz, $CDCl_3$): δ=177.6, 177.4, 176.8, (3s, 3C=O); 141.3 (C-3-triazole); 132.0 (C-5-triazole); 80.5 (C-1); 69.6, 68.7, 68.3 (C-2, C-3, C-4); 62.1 (C-5); 38.9, 38.8 (3*C*(CH_3)$_3$); 27.2, 26.7 (3C(*C*H_3)$_3$). Anal. Calcd for $C_{22}H_{33}Br_2N_3O_7$ (611.32): C, 43.22; H, 5.44; N, 6.87. Found: C, 43.86; H, 5.63; N, 6.55.

2.1.4. 5-Bromo-3-chloro-1-(2,3,4-tri-*O*-pivaloyl-β-D-xylopyranosyl)-1,2,4-triazole (9β) and 3-bromo-5-chloro-1-(2,3,4-tri-*O*-pivaloyl-β-D-xylopyranosyl)-1,2,4-triazole (10β). 2.0 g (4.1 mmol) of **1**, 1.5 g (8.2 mmol) of 3-bromo-5-chloro-1,2,4-triazole (**5**)[16] and 3–5 equiv of $BF_3 \cdot Et_2O$ dissolved in 50 mL of anhyd acetonitrile were reacted for about 3–4 days at room temperature (TLC control). The work-up procedure was analogous to that for **6α/6**β. After column chromatographic separation (eluent: heptane/ethyl acetate, v:v=10:1), 0.98 g (42%) of **9**β and 0.91 g (39%) of **10**β were isolated; (eluent: heptane/ethyl acetate, v:v=2:1; **9**β: R_f=0.37, **10**β: R_f=0.32).

Compound **9**β: colorless crystals; mp 134–136 °C (cyclohexane); $[\alpha]_D^{22}$ −25.23 (*c* 1.20, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ=5.68 (t, 1H, $^3J_{2,3}$=9.3 Hz, H-2); 5.54 (d, 1H, $^3J_{1,2}$=9.0 Hz, H-1); 5.48 (t, 1H, $^3J_{2,3}$=9.4 Hz, H-3); 5.24–5.08 (m, 1H, $^3J_{4,5a}$=5.8 Hz, $^3J_{3,4}$=9.5 Hz, $^3J_{4,5b}$=10.4 Hz, H-4); 4.29 (dd, 1H, $^3J_{4,5a}$=5.8 Hz, $^2J_{5a,5b}$=11.6 Hz, H-5a); 3.54 (dd, 1H, $^3J_{4,5b}$=10.3 Hz, $^2J_{5a,5b}$=11.6 Hz, H-5b); 1.16, 1.13, 0.97 (3s, 27H, 3C(CH_3)$_3$). ^{13}C NMR (63 MHz, $CDCl_3$): δ=177.3, 177.2, 175.8, (3s, 3C=O); 154.4 (C-3-triazole); 131.0 (C-5-triazole); 85.1 (C-1); 72.0, 69.6, 68.3 (C-2, C-3, C-4); 65.8 (C-5); 38.9, 38.8 (3*C*(CH_3)$_3$); 27.3, 27.2, 26.9 (3C(*C*H_3)$_3$). Anal. Calcd for $C_{22}H_{33}BrClN_3O_7$ (566.87): C, 46.61; H, 5.87; N, 7.41. Found: C, 47.05; H, 5.94; N, 7.00.

Compound **10**β: colorless crystals; mp 128–131 °C (cyclohexane); $[\alpha]_D^{22}$ −21.08 (*c* 1.14, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ=5.65 (t, 1H, $^3J_{2,3}$=9.3 Hz, H-2); 5.51 (d, 1H, $^3J_{1,2}$=9.0 Hz, H-1); 5.46 (t, 1H, $^3J_{2,3}$=9.4 Hz, H-3); 5.22–5.06 (m, 1H, $^3J_{4,5a}$=5.7 Hz, $^3J_{3,4}$=9.4 Hz, $^3J_{4,5b}$=10.3 Hz, H-4); 4.28 (dd, 1H, $^3J_{4,5a}$=5.7 Hz, $^2J_{5a,5b}$=11.6 Hz, H-5a); 3.52 (dd, 1H, $^3J_{4,5b}$=10.4 Hz, $^2J_{5a,5b}$=11.6 Hz, H-5b); 1.14, 1.12, 0.97 (3s, 27H, 3C(CH_3)$_3$). ^{13}C NMR (63 MHz, $CDCl_3$): δ=177.3, 175.8, (3s, 3C=O); 140.5 (C-3 triazole); 143.5 (C-5 triazole); 84.4 (C-1); 71.9, 69.5, 68.3 (C-2, C-3, C-4); 65.8 (C-5); 38.9, 38.8 (3*C*(CH_3)$_3$); 27.2, 27.1, 26.9 (3C(*C*H_3)$_3$). Anal. Calcd for $C_{22}H_{33}BrClN_3O_7$ (566.87): C, 46.61; H, 5.87; N, 7.41. Found: C, 47.03; H, 6.00; N, 7.06.

2.1.5. 3-Chloro-5-phenyl-1-(2,3,4-tri-*O*-pivaloyl-β-D-xylopyranosyl)-1,2,4-triazole (11). 0.3 g (0.57 mmol) of the β-glycoside **7**β dissolved in 10 mL of anhyd DMF were placed in an ACS pressure tube. After pass through of argon (10–15 min), phenylboronic acid (210 mg, 1.52 mmol), potassium phosphate (240 mg, 1.14 mmol), 0.01 equiv of $Pd(OAc)_2$ and 0.01 equiv of $[(Ad)_2PHBu]^+I^-$ were added (argon atmosphere). The mixture was stirred at 100 °C for 20 h. For work-up the reaction mixture was diluted with ethyl acetate (50 mL), washed twice with 1 N aqueous solution of NaOH (30 mL), and water (30 mL) After separation and drying (Na_2SO_4), the organic phase was concentrated under reduced pressure. Compound **11** (0.2 g, 63%) was isolated via column chromatographic purification (eluent: heptane/ethyl acetate, v:v=10:1; R_f=0.21). Small amounts of starting material **7**β were recovered.

Compound **11**: colorless crystals; mp 124–126 °C (heptane/ethyl acetate); $[\alpha]_D^{22}$ −1.05 (*c* 2.63, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ=7.71–7.49 (m, 5H, Ph); 5.85 (t, 1H, $^3J_{2,3}$=9.3 Hz, H-2); 5.40 (d, 1H, $^3J_{1,2}$=9.2 Hz, H-1); 5.33 (t, 1H, $^3J_{2,3}$=9.5 Hz, H-3); 5.26–5.09 (m, 1H, $^3J_{4,5a}$=5.7 Hz, $^3J_{4,5b}$=10.3 Hz, H-4); 4.34 (dd, 1H, $^3J_{4,5a}$=5.8 Hz, $^2J_{5a,5b}$=11.5 Hz, H-5a); 3.47 (dd, 1H, $^3J_{4,5b}$=10.3 Hz, $^2J_{5a,5b}$=11.4 Hz, H-5b); 1.14, 1.12, 0.90 (3s, 27H, 3C(CH_3)$_3$). ^{13}C NMR (63 MHz, $CDCl_3$): δ=177.7, 177.4, 175.7, (3s, 3C=O); 158.9 (C-5 triazole); 153.4 (C-3 triazole); 132.0, 129.8, 129.2, 126.2 (Ph); 84.9 (C-1); 72.5, 69.9, 68.7 (C-2, C-3, C-4); 65.7 (C-5); 39.2, 39.0 (3*C*(CH_3)$_3$); 27.5, 27.4, 27.1 (3C(*C*H_3)$_3$). Anal. Calcd for $C_{28}H_{38}ClN_3O_7$ (564.07): C, 59.62; H, 6.79; N, 7.45. Found: C, 59.24; H, 6.84; N, 7.32.

2.1.6. 3-Chloro-5-(4-vinylphenyl)-1-(2,3,4-tri-*O*-pivaloyl-β-D-xylopyranosyl)-1,2,4-triazole (12). Glycoside **7**β (0.25 g, 0.48 mmol), 4-vinylphenylboronic acid (190 mg, 1.28 mmol), K_3PO_4 (204 mg, 0.96 mmol), 0.01 equiv of $Pd(OAc)_2$, and 0.01 equiv of $[(Ad)_2PHBu]^+I^-$ were reacted as described for compound **11**. After column chromatographic purification (eluent: heptane/ethyl acetate, v:v=5:1; R_f=0.18), 0.22 g (78%) of **12** were isolated.

Compound **12**: colorless crystals; mp 124–125 °C (cyclohexane); $[\alpha]_D^{21}$ −1.72 (*c* 1.04, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): δ=7.73–7.42 (m, 4H, Ph); 6.77 (dd, 1H, $^3J_{vinyl}$=11.0, 17.5 Hz, =CH); 5.90 (d, 1H, $^3J_{vinyl}$=17.5 Hz, =CH_2); 5.86 (t, 1H, $^3J_{2,3}$=9.3 Hz, H-3); 5.43 (d, 1H, $^3J_{vinyl}$=11.0 Hz, =CH_2); 5.41 (d, 1H, $^3J_{1,2}$=9.2 Hz, H-1); 5.33 (t, 1H, $^3J_{2,3}$=9.5 Hz, H-2); 5.26–5.12 (m, 1H, $^3J_{4,5a}$=5.7 Hz, $^3J_{4,5b}$=10.0 Hz, H-4); 4.35 (dd, 1H, $^3J_{4,5a}$=5.7 Hz, $^2J_{5a,5b}$=11.5 Hz, H-5a); 3.48 (dd, 1H, $^3J_{4,5b}$=10.3 Hz, $^2J_{5a,5b}$=11.5 Hz, H-5b); 1.14, 1.12, 0.90 (3s, 27H, 3C(CH_3)$_3$). ^{13}C NMR (63 MHz, $CDCl_3$): δ=177.4, 177.3, 175.4, (3s, 3C=O); 158.8 (C-5 triazole); 140.9 (C-3 triazole); 135.8 (=CH); 129.2, 127.2, 124.9 (Ph); 116.9 (=CH_2); 84.7 (C-1); 72.3, 69.6, 68.5 (C-2, C-3, C-4); 65.5 (C-5); 38.9, 38.7 (3*C*(CH_3)$_3$); 27.3, 27.2, 26.8 (3C(*C*H_3)$_3$). Anal. Calcd for $C_{30}H_{40}ClN_3O_7$ (590.11): C, 61.06; H, 6.83; N, 7.12. Found: C, 60.59; H, 6.90; N, 6.86.

2.1.7. 3-Chloro-5-(4-methoxyphenyl)-1-(2,3,4-tri-*O*-pivaloyl-β-D-xylopyranosyl)-1,2,4-triazole (13), 5-chloro-3-(4-methoxyphenyl)-1-(2,3,4-tri-*O*-pivaloyl-β-D-xylopyranosyl)-1,2,4-triazole (14), and 3,5-di-(4-methoxyphenyl)-1-(2,3,4-tri-*O*-pivaloyl-β-D-xylopyranosyl)-1,2,4-triazole (15). Glycoside **7**β (0.2 g, 0.38 mmol), 4-methoxyphenylboronic acid (150 mg, 1.01 mmol), K_3PO_4 (160 mg, 0.76 mmol), 0.01 equiv of $Pd(OAc)_2$, and 0.01 equiv of $[(Ad)_2PHBu]^+I^-$ were reacted as described for compound **11**. After column chromatographic purification (eluent: heptane/ethyl acetate, v:v=7:1), 0.1 g (44%) of **13**, 0.02 g (9%) of **14** and 0.03 g (12%) of **15**, were isolated (TLC: eluent: heptane/ethyl acetate, v:v=2:1; **15**: R_f=0.46, **13**: R_f=0.40, **14**: R_f=0.34).

Compound **13**: colorless crystals; mp 112–113 °C (heptane/ethyl acetate); $[\alpha]_D^{21}$ +5.29 (*c* 1.01, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): δ=7.64–7.56 (m, 2H, Ph); 7.11–702 (m, 2H, Ph); 5.85 (t, 1H, $^3J_{2,3}$=9.4 Hz, H-2); 5.40 (d, 1H, $^3J_{1,2}$=9.1 Hz, H-1); 5.35 (t, 1H, $^3J_{2,3}$=9.5 Hz, H-3); 5.26–5.12 (m, 1H, $^3J_{4,5a}$=5.7 Hz, $^3J_{4,5b}$=10.1 Hz, H-4); 4.35 (dd, 1H, $^3J_{4,5a}$=5.8 Hz, $^2J_{5a,5b}$=11.6 Hz, H-5a); 3.91 (s, 3H, OCH_3); 3.49 (dd, 1H, $^3J_{4,5b}$=10.4 Hz, $^2J_{5a,5b}$=11.4 Hz, H-5b); 1.16, 1.14, 0.91 (3s, 27H, 3C(CH_3)$_3$). ^{13}C NMR (63 MHz, $CDCl_3$): δ=177.5, 177.3, 175.4 (3s, 3C=O); 162.3 ($C_{quart.}$-Ph) 158.6 (C-5 triazole); 153.0 (C-3 triazole); 130.5, 118.1 ($C_{quart.}$-Ph), 114.9 (Ph); 84.7 (C-1); 72.3, 69.6, 68.5 (C-2, C-3, C-4); 65.5 (C-5); 55.6 (s, OCH_3); 38.9, 38.7 (3*C*(CH_3)$_3$); 27.3, 27.2, 26.8 (3C(*C*H_3)$_3$). Anal. Calcd for $C_{29}H_{40}ClN_3O_8$ (594.10): C, 58.63; H, 6.79; N, 7.07. Found: C, 58.53; H, 6.80; N, 6.93.

Compound **14**: colorless crystals; mp 172–173 °C (heptane/ethyl acetate); $[\alpha]_D^{22}$ −34.62 (*c* 2.81, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): δ=8.04–7.90 (m, 2H, Ph); 6.98–6.87 (m, 2H, Ph); 5.89 (t, 1H, $^3J_{2,3}$=9.4 Hz, H-2); 5.57 (d, 1H, $^3J_{1,2}$=9.1 Hz, H-1); 5.52 (t, 1H, $^3J_{2,3}$=9.6 Hz, H-3); 5.32–5.15 (m, 1H, H-4); 4.33 (dd, 1H, $^3J_{4,5a}$=5.8 Hz, $^2J_{5a,5b}$=11.6 Hz, H-5a); 3.85 (s, 3H, OCH_3); 3.49 (dd, 1H, $^3J_{4,5b}$=10.4 Hz, $^2J_{5a,5b}$=11.4 Hz, H-5b); 1.18, 1.17, 0.92 (3s, 27H, 3C(CH_3)$_3$). ^{13}C NMR (63 MHz, $CDCl_3$): δ=177.4, 177.3, 175.8 (3C=O); 162.8 ($C_{quart.}$-Ph), 162.4 (C-3 triazole); 143.2 (C-5 triazole); 121.1 ($C_{quart.}$-Ph), 128.1, 114.1 (Ph); 83.9 (C-1); 72.3, 69.4, 68.5 (C-2, C-3, C-4); 65.8 (C-5); 55.56 (s, OCH_3); 38.9, 38.7 (3*C*(CH_3)$_3$); 27.3, 27.2, 26.8 (3C(*C*H_3)$_3$). Anal. Calcd for $C_{29}H_{40}ClN_3O_8$ (594.10): C, 58.63; H, 6.79; N, 7.07. Found: C, 58.25; H, 6.59; N, 6.96.

Compound **15**: colorless crystals; mp 89–90 °C (ethyl acetate); $[\alpha]_D^{22}$ −23.95 (*c* 0.89, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): δ=8.11–8.01 (m, 2H, Ph); 7.71–7.60 (m, 2H, Ph); 7.12–7.01 (m, 2H, Ph); 6.98–6.87 (m, 2H, Ph); 6.10 (t, 1H, $^3J_{2,3}$=9.4 Hz, H-2); 5.42–5.18 (m, 3H, $^3J_{4,5a}$=5.7 Hz, $^3J_{1,2}$=9.2 Hz, $^3J_{2,3}$=9.6 Hz, H-1, H-3, H-4); 4.37 (dd, 1H, $^3J_{4,5a}$=5.6 Hz, $^2J_{5a,5b}$=11.5 Hz, H-5a); 3.91, 3.84 (2s, 6H, 2OCH_3); 3.48 (dd, 1H, $^3J_{4,5b}$=10.3 Hz, $^2J_{5a,5b}$=11.3 Hz, H-5b); 1.16, 1.14, 0.81 (3s, 27H, 3C(CH_3)$_3$). ^{13}C NMR (63 MHz, $CDCl_3$): δ=177.4, 177.3, 175.6 (3s, 3C=O); 161.9, 161.8 (2$C_{quart.}$-Ph) 160.9 (C-3 triazole); 157.9 (C-5 triazole); 130.5, 128.4, 114.8, 114.0 (Ph); 123.2, 119.5 (2$C_{quart.}$-Ph); 84.6 (C-1); 72.6, 69.5, 68.6 (C-2, C-3, C-4); 65.4 (C-5); 55.6, 55.4 (2OCH_3); 38.9, 38.6 (3*C*(CH_3)$_3$); 27.3, 27.2, 26.7 (3C(*C*H_3)$_3$). Anal. Calcd for $C_{26}H_{47}N_3O_9$ (665.78): C, 64.95; H, 7.12; N, 6.31. Found: C, 64.71; H, 7.10; N, 6.27.

2.1.8. 3-Bromo-5-(4-vinylphenyl)-1-(2,3,4-tri-*O*-pivaloyl-β-D-xylopyranosyl)-1,2,4-triazole (16). Glycoside **8**β (1.0 g, 1.6 mmol), 4-vinylphenylboronic acid (630 mg, 4.26 mmol), K_3PO_4 (680 mg, 3.2 mmol), 0.01 equiv of $Pd(OAc)_2$, and 0.01 equiv of $[(Ad)_2PHBu]^+I^-$ were reacted as described for compound **11**. After column chromatographic purification (eluent: heptane/diethyl ether, v:v=5:1; R_f=0.22), 0.7 g (67%) of **16** were isolated.

Compound **16**: colorless crystals; mp 94–95 °C (heptane); $[\alpha]_D^{21}$ +3.98 (*c* 1.09, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): δ=7.73–7.42 (m, 4H, Ph); 6.77 (dd, 1H, $^3J_{vinyl}$=11.0, 17.5 Hz, =CH); 5.90 (d, 1H, $^3J_{vinyl}$=17.5 Hz, =CH_2); 5.86 (t, 1H, $^3J_{2,3}$=9.3 Hz, H-3); 5.43 (d, 1H, $^3J_{vinyl}$=11.0 Hz, =CH_2); 5.41 (d, 1H, $^3J_{1,2}$=9.2 Hz, H-1); 5.33 (t, 1H, $^3J_{2,3}$=9.5 Hz, H-2); 5.26–5.12 (m, 1H, $^3J_{4,5a}$=5.7 Hz, $^3J_{4,5b}$=10.0 Hz, H-4); 4.35 (dd, 1H, $^3J_{4,5a}$=5.7 Hz, $^2J_{5a,5b}$=11.5 Hz, H-5a); 3.48 (dd, 1H, $^3J_{4,5b}$=10.3 Hz, $^2J_{5a,5b}$=11.5 Hz, H-5b); 1.14, 1.12, 0.90 (3s, 27H, 3C(CH_3)$_3$). ^{13}C NMR (63 MHz, $CDCl_3$): δ=177.4, 177.3, 175.4, (3s, 3C=O); 158.8 (C-5 triazole); 140.9 (C-3 triazole); 135.8 (=CH); 129.2, 127.2, 124.9 (Ph); 116.9 (=CH_2); 84.7 (C-1); 72.3, 69.6, 68.5 (C-2, C-3, C-4); 65.5 (C-5); 38.9, 38.7 (3*C*(CH_3)$_3$); 27.3, 27.2, 26.8 (3C(*C*H_3)$_3$). Anal. Calcd for $C_{30}H_{40}BrN_3O_7$ (634.56): C, 56.78; H, 6.35; N, 6.62. Found: C, 56.66; H, 6.30; N, 6.31.

2.1.9. 3-Bromo-5-(4-hexyloxyphenyl)-1-(2,3,4-tri-*O*-pivaloyl-β-D-xylopyranosyl)-1,2,4-triazole (17). Glycoside **8**β (0.47 g, 0.77 mmol), 4-hexyloxyphenylboronic acid (454 mg, 2.05 mmol), K_3PO_4 (330 mg, 1.54 mmol), 0.01 equiv of $Pd(OAc)_2$, and 0.01 equiv of $[(Ad)_2PHBu]^+I^-$ were reacted as described for compound **11**. After column chromatographic purification (eluent: heptane/ethyl acetate, v:v=10:1), 0.29 g (53%) of **17** were isolated (eluent: heptane/ethyl acetate, v:v=2:1; R_f=0.64) beside traces of the 3,5-diarylated product.

Compound **17**: colorless crystals; mp 113–115 °C (heptane/ethyl acetate); $[\alpha]_D^{21}$ +12.34 (*c* 0.50, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): δ=7.64–7.50 (m, 2H, Ph); 7.10–6.96 (m, 2H, Ph); 5.85 (t, 1H, $^3J_{2,3}$=9.2 Hz, H-2); 5.39 (d, 1H,

$^3J_{1,2}$=9.1 Hz, H-1); 5.33 (t, 1H, $^3J_{2,3}$=9.5 Hz, H-3); 5.25–5.12 (m, 1H, $^3J_{4,5a}$=5.7 Hz, $^3J_{4,5b}$=10.1 Hz, H-4); 4.34 (dd, 1H, $^3J_{4,5a}$=5.8 Hz, $^2J_{5a,5b}$=11.4 Hz, H-5a); 4.04 (t, 2H, OCH_2); 3.47 (t, 1H, $^3J_{4,5b}$=10.8 Hz, H-5b); 1.91–1.74 (m, 2H, OCH_2CH_2); 1.57–1.29 (m, 6H, $3CH_2$); 1.15, 1.12, 0.90 (3s, 27H, $3C(CH_3)_3$); 0.89 (t, 3H, CH_3). ^{13}C NMR (63 MHz, $CDCl_3$): δ=177.5, 177.2, 175.4 (3C=O); 161.8 ($C_{quart.}$-Ph); 159.0 (C-5 triazole); 140.9 (C-3 triazole); 130.4, 115.3 (Ph); 117.6 ($C_{quart.}$-Ph); 84.6 (C-1); 72.5, 69.6, 68.7 (C-2, C-3, C-4); 67.5 (s, OCH_2); 65.4 (C-5); 38.9, 38.7 ($3C(CH_3)_3$); 31.7, 29.1, 25.7, 22.7 ($4CH_2$); 27.3, 27.2, 26.8 ($3C(CH_3)_3$); 14.2 (CH_3). Anal. Calcd for $C_{34}H_{50}BrN_3O_8$ (708.69): C, 57.62; H, 7.11; N, 5.93. Found: C, 57.22; H, 7.15; N, 5.68.

2.1.10. 3-Perfluorohexyl-1-(2,3,4-tri-*O*-pivaloyl-β-D-xylopyranosyl)-1,2,4-triazole (18). To a suspension of copper powder (0.75 g, 11.8 mmol) in 10 mL anhyd DMSO, 50 mg of iodine were added under Argon. After the mixture was sonicated by ultrasound for 5 min, 1-iodo-perfluorohexane (1.30 mL, 6.0 mmol) was dropwise added with stirring. Stirring was continued for 30–40 min at 110 °C before the glycoside **8**β (0.45 g, 0.74 mmol) was added. Then stirring was continued at this temperature for 15–20 h. Finally, the mixture was diluted with ethyl acetate (20 mL), filtered through Celite, and concentrated under reduced pressure. The residue was column chromatographically purified (eluent: heptane/ethyl acetate, v:v=10:1; R_f=0.21) yielding 0.21 g (37%) of product **18**.

Compound **18**: colorless crystals; mp 130–133 °C (heptane/ethyl acetate); $[\alpha]_D^{21}$ −17.43 (*c* 0.95, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ=8.44 (s, 1H, H-5 triazole); 5.66–5.43 (m, 3H, H-1, H-2, H-3); 5.28–5.12 (m, 1H, $^3J_{4,5a}$=5.8 Hz, $^3J_{3,4}$=9.4 Hz, $^3J_{4,5b}$=10.4 Hz, H-4); 4.32 (dd, 1H, $^3J_{4,5a}$=5.8 Hz, $^2J_{5a,5b}$=11.5 Hz, H-5a); 3.55 (dd, 1H, $^3J_{4,5b}$=10.6 Hz, $^2J_{5a,5b}$=11.5 Hz, H-5b); 1.18, 1.14, 0.97 (3s, 27H, $3C(CH_3)_3$). ^{13}C NMR (63 MHz, $CDCl_3$): δ=177.3, 177.1, 176.3 (3s, 3C=O); 155.6 (C-3 triazole); 144.7 (C-5 triazole); 87.0 (C-1); 71.6, 70.1, 68.3 (C-2, C-3, C-4); 65.9 (C-5); 39.0, 38.9, 38.8 ($3C(CH_3)_3$); 27.2, 26.8 ($3C(CH_3)_3$). ^{19}F NMR (235 MHz, $CDCl_3$): δ=−80.5 (s, CF_3); −112.0, −121.3, −121.8, 122.5, −125.8 (5s, $5CF_2$). Anal. Calcd for $C_{28}H_{34}F_{13}N_3O_7$ (771.57): C, 43.59; H, 4.44; N, 5.45. Found: C, 43.81; H, 4.38; N, 5.35.

2.1.11. 3-Perfluorohexyl-1-(β-D-xylopyranosyl)-1,2,4-triazole (19). A solution of **18** (0.2 g, 0.26 mmol) in 1% methanolic KOBu^t was stirred for 4–5 days at room temperature (TLC-control). For work-up, the mixture was neutralized with cation exchange resin (IR 120), filtered, and the solvent removed under reduced pressure. The residue was purified by column chromatography (eluent: toluene/ethyl acetate/ethanol, v:v:v=7:2:1; R_f=0.16). Yield of **19**: 0.10 g (75%).

Compound **19**: colorless crystals; mp 126–131 °C (toluene/ethanol); $[\alpha]_D^{22}$ −18.81 (*c* 0.95, MeOH). ^{1}H NMR (250 MHz, CD_3OD): δ=8.87 (s, 1H, H-5 triazole); 5.43 (d, 1H, $^3J_{1,2}$=9.1 Hz, H-1); 4.03 (dd, 1H, $^3J_{4,5a}$=5.3 Hz, $^2J_{5a,5b}$=11.2 Hz, H-5a); 3.93 (t, 1H, $^3J_{2,3}$=9.1 Hz, H-2); 3.69 (ddd, 1H, $^3J_{4,5a}$=5.2 Hz, $^3J_{3,4}$=9.0 Hz, $^3J_{4,5b}$=10.4 Hz, H-4); 3.48 (t, 1H, $^3J_{3,4}$=9.0 Hz, H-3); 3.46 (t, 1H, $^2J_{5a,5b}$=10.9 Hz, H-5b). ^{13}C NMR (63 MHz, CD_3OD): δ=154.4 (C-3 triazole); 148.0 (C-5 triazole); 89.9 (C-1); 78.7, 73.3, 70.6 (C-2, C-3, C-4); 69.9 (C-5). ^{19}F NMR (235 MHz, CD_3OD): δ=−78.8 (s, CF_3); −109.8, −119.1, −119.9, 120.3, −123.7 (5s, $5CF_2$). Anal. Calcd for $C_{13}H_{10}F_{13}N_3O_4$ (519.21): C, 30.07; H, 1.94; N, 8.09. Found: C, 30.26; H, 2.01; N, 7.62.

2.1.12. Bis (3-bromo-1-(2,3,4-tri-*O*-pivaloyl-β-D-xylopyrano-syl)-1,2,4-triazol-5-yl) (20). To a solution of glycoside **8**β (0.25 g, 0.41 mmol) in anhyd DMF (argon atmosphere), CuI (0.16 g, 0.84 mmol), KF (60 mg, 1.0 mmol), and $CF_3Si(CH_3)_3$ (0.15 mL, 1.0 mmol) were added. The mixture was stirred at 80 °C for 24 h. For work-up, the mixture was diluted with 50 mL of ethyl acetate and washed three times with 20 mL of water. After drying (Na_2SO_4), filtration and concentration of the organic layer under reduced pressure, the residue was purified by column chromatography (eluent: heptane/ethyl acetate, v:v=8:1; R_f=0.26) yielding 0.11 g (51%) of compound **20**.

Compound **20**: colorless crystals; mp 166–171 °C (heptane); $[\alpha]_D^{23}$ +0.75 (*c* 1.20, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ=6.70 (d, 1H, $^3J_{1,2}$=9.2 Hz, H-1); 5.88 (t, 1H, $^3J_{1,2}$=9.3 Hz, H-2); 5.51 (t, 1H, $^3J_{3,4}$=9.5 Hz, H-3); 5.18 (sym. M, 1H, $^3J_{4,5a}$=5.8 Hz, $^3J_{3,4}$=9.9 Hz, H-4); 4.22 (dd, 1H, $^3J_{4,5a}$=5.8 Hz, $^2J_{5a,5b}$=11.5 Hz, H-5a); 3.55 (dd, 1H, $^3J_{4,5b}$=10.3 Hz, $^2J_{5a,5b}$=11.5 Hz, H-5b); 1.16, 1.15, 0.90 (3s, 27H, $3C(CH_3)_3$). ^{13}C NMR (63 MHz, $CDCl_3$): δ=177.4, 177.3, 175.6 (3s, 3C=O); 144.1 (C-5 triazole); 140.6 (C-3 triazole); 84.9 (C-1); 72.4, 69.7, 68.5 (C-2, C-3, C-4); 65.7 (C-5); 38.9, 38.9, 38.7 ($3C(CH_3)_3$); 27.3, 27.2, 26.8 ($3C(CH_3)_3$). MS-FAB (pos. NBA): *m/z*=1066 $[M+2H]^{2+}$. MS-EI: *m/z*=677 $[M-385]^+$, 385 [2,3,4-tri-*O*-pivaloyl-D-xylopyranosyl $(C_{20}H_{33}O_7)]^+$. Anal. Calcd for $C_{44}H_{66}Br_2N_6O_{14}$ (1062.84): C, 49.72; H, 6.26; N, 7.91. Found: C, 49.64; H, 6.07; N, 7.66.

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