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Copper-catalyzed anomeric *O*-arylation of carbohydrate derivatives at room temperature

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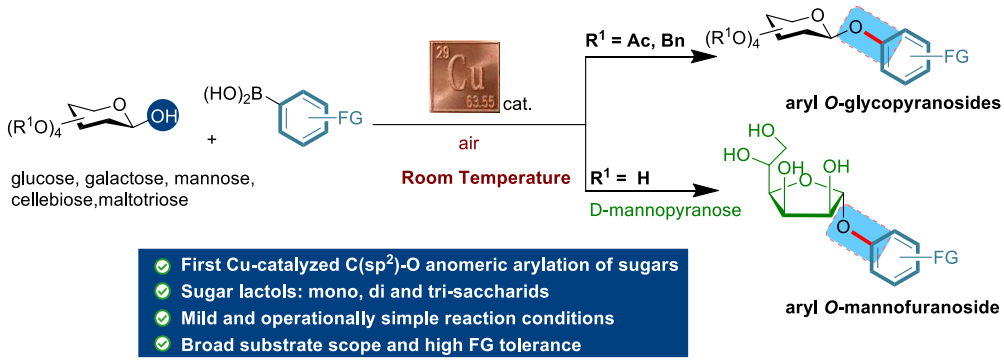
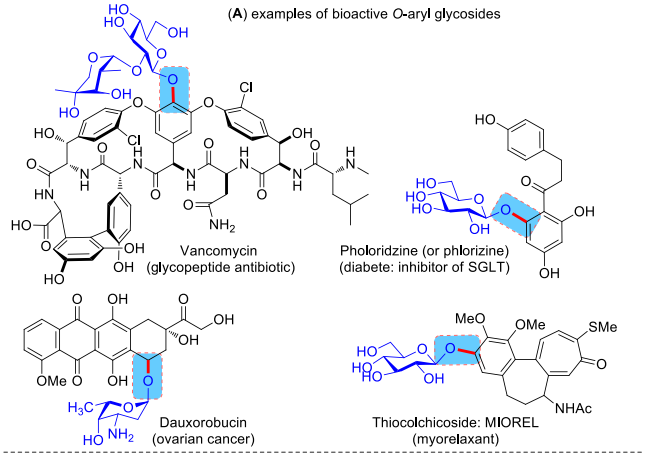
Supporting Information Placeholder



ABSTRACT: Direct and practical anomeric *O*-arylation of sugars lactols with substituted aryl boronic acids has been established. Using copper catalysis at room temperature under air atmosphere, the protocol proved to be general, and a variety of aryl *O*-glycosides have been prepared in good to excellent yields. Furthermore, this approach was extended successfully to unprotected carbohydrates including α-mannose, and demonstrated here how the interaction between carbohydrates and boronic acids can be combined with copper catalysis to achieve selective anomeric *O*-arylation.

INTRODUCTION

O-aryl glycosides are an important class of glycosides that exhibit promising biological activities, including antibiotic (*e.g.*, vancomycin and chromomycin), antiviral, and anticancer (*e.g.*, dauxorubucin) properties[1] (Figure 1-A). Usually, these derivatives are prepared by treating phenol derivatives with glycosyl donors through an S_N2 type mechanism under basic conditions or through an S_N1 reaction under acidic conditions (Figure 1-B, path 1).[2] Glycosyl acetates, halides, and trichloroacetimidates have been used as donors in the formation of β-*O*-aryl glycosides, these later, however, only work well with specific phenol nucleophiles. For instance, glycosyl acetates and trichloroacetimidates are preferred for electron-donating phenol substrates. Glycosyl acetates usually provide the β-*O*-aryl glycosides with lower yields than trichloroacetimidates due to anomerization of both the glycosyl donor and the coupling product.[2] Alternative routes to *O*-glycosidic bond formation consist on the use of phenols as partners in a Mitsunobu coupling glycosylation with sugar hemiacetal.[3] However, the yield is clearly dependent on the acidity of the phenols, that is, the least acidic phenols give usually low yields. Nucleophilic aromatic substitution (S_NAr) reactions have been also used to generate *O*-arylglycosides from protected carbohydrates and activated fluoroarenes[4] or electrophilic diaryliodonium salts[5] (Figure 1-B, path 2). Other anomeric arylation methods that have been applied to hydroxyl group in protected sugars include photoredox substitution of aryl bromides under iridium catalysis[6] (Figure 1-B, path 3). Although elegant, this method is restricted to aryl bromides bearing electron deficient groups. Besides, only per-*O*-benzylated sugar lactols were used as partners, thus limited the scope of the reaction. An



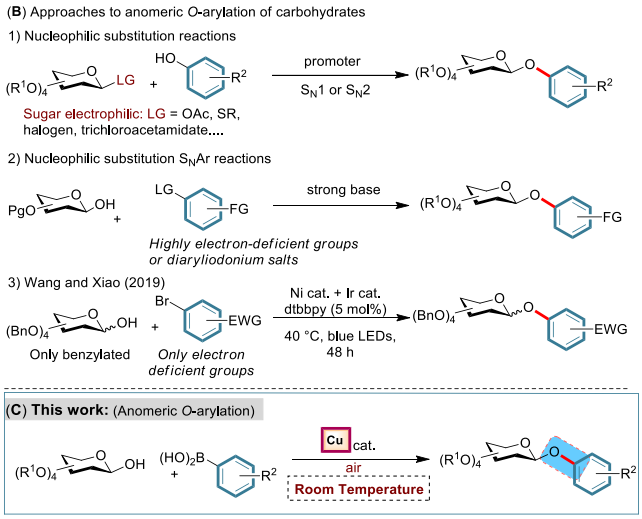


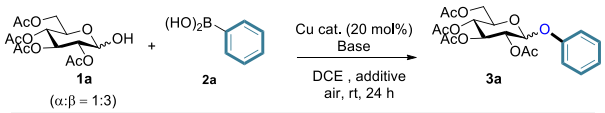
Figure 1. Example of bioactive *O*-aryl glycosides, and approaches to anomeric *O*-arylation of carbohydrates

appealing option to access aryl *O*-glycosides would be the use of carbohydrate hemiacetals as nucleophiles in transition metal-catalyzed reactions. Owing to the biological significance and existing restricted synthetic methodologies, there is an exigent need for a facile and efficient protocol to synthesize aryl *O*-glycosides. Since our initial reports on Chan-Lam-Evans cross coupling of 1-aminosugars with arylboronic acids under copper catalysis,[7] to the best of our knowledge, there is no report describing the formation of aryl *O*-glycosides from carbohydrates hemiacetal and arylboronic acids.[8] Consequently, in continuation of our interest in C-heteroatom bond formation,[9] we report herein that *O*-arylation of sugar hemiacetals can be realized efficiently using a catalytic amount of $Cu(OAc)_2$ at room temperature under air atmosphere (Figure 1-C).

RESULTS AND DISCUSSION

In the first set of experiments, we examined the coupling of 2,3,4,6-*tetra*-*O*-acetyl-D-glucopyranose **1a** (in a mixture of α/β = 1:3) with phenylboronic acid **2a** as a model study under various source of copper catalysts, bases and solvents. Representative results from this study are summarized in Table 1. The reaction of **1a** (1 equiv) with **2a** (3 equiv) was first investigated under our previously reported procedure [$Cu(OAc)_2.H_2O$ (20 mol%), pyridine, CH_2Cl_2, 24 h at 25 °C] (Table 1, entry 1). Unfortunately, this protocol afforded the desired aryl *O*-glycoside **3a** in a low 32% yield. Switching from CH_2Cl_2 as the solvent to the less volatile dichloroethane (DCE) furnished **3a** in a slightly increased yield (39%, entry 2). However in both cases, a significant erosion of the diastereomeric ratio (α/β ratio from 1:3 to 1:1.2) was observed. This result indicates clearly that the reactivity of hemiacetal carbohydrates is far to be similar to those of 1-aminosugars and are more prone to anomerization than their aminocongeners. To increase the yield of **3a** and reduce the erosion of the diastereomeric ratios, we examined the influence of other nitrogen bases under otherwise identical conditions. When DMAP, 2,6-lutidine or Et_3N were used instead pyridine, the yield has never exceed 15% demonstrating that pyridine is the best choice (compare entries 2 and 3-5). The optimization reaction conditions was continued with respect to copper catalyst, however, no significant improvement of the yield of **3a** was observed when $Cu(acac)_2$, $Cu(OTf)_2$ or CuO were used (entries 6-8). Extensive examinations of the other reaction parameters revealed that the use of molecular sieves plays a critical role in the outcome of the $C(Sp^2)$–O bond formation. Pleasingly, the yield of **3a** was improved up to 73% with complete retention of the anomeric ratio (α/β = 1:3) when the

Table 1 Survey of reaction conditions for the *O*-arylation of Glu-$(OAc)_4$ **1a** with phenylboronic acid **2a**[a]



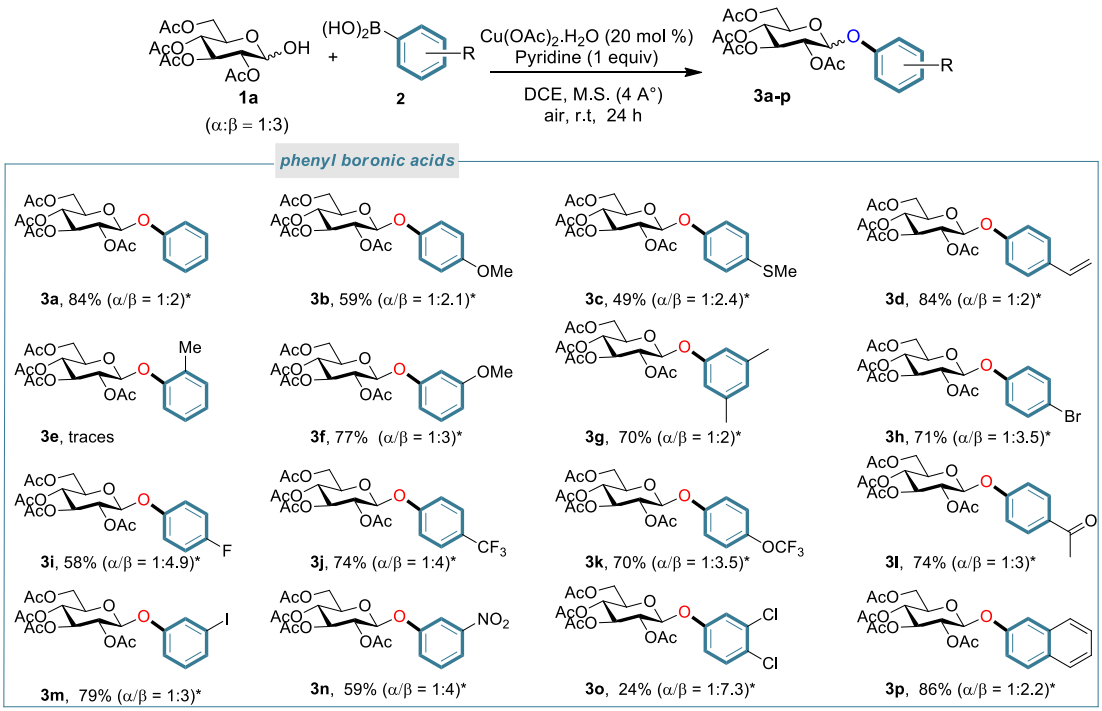
entry	[Cu]	Base	yield (%)[b]	Ratio α:β[c]
1	$Cu(OAc)_2.H_2O$	Pyridine	32	1:1.2
2	$Cu(OAc)_2.H_2O$	Pyridine	39	1:1.2
3	$Cu(OAc)_2.H_2O$	DMAP	15	1:2.8
4	$Cu(OAc)_2.H_2O$	2,6-lutidine	8	1:3
5	$Cu(OAc)_2.H_2O$	Et_3N	-	-
6	$Cu(acac)_2$	Pyridine	10	3:1
7	$Cu(OTf)_2$	Pyridine	11	β only
8	CuO	Pyridine	-	-
9	$Cu(OAc)_2.H_2O$	Pyridine	73	1:3[d]
10	$Cu(OAc)_2.H_2O$	**Pyridine**	**84**	**1:2**[d,e]
11	$Cu(OAc)_2$	**Pyridine**	**82**	**1:2**[d,e]

[a] **1a** (1 equiv), phenylboronic acid **2a** (3 equiv), [Cu] (20 mol %), base (1 equiv), 24 h, rt, [0.5M]. [b] Yield of isolated **3a** as a mixture of both anomers. [c] anomer ratio was measured by ^{1}H NMR of the crude mixture and found to be the same when calculated after purification of both α:β anomers [d] The reaction performed with molecular sieves as additive.[e] 30 mol% of $Cu(OAc)_2.H_2O$ was used and reaction concentration increased to [0.7M].

reaction was conducted in the presence of molecular sieves (entry 9). By increasing the amount of Cu-catalyst (from 20 mol% to 30 mol%) and the reaction concentration (from 0.5 M to 0.7 M), we managed to isolate 84 % of the desired product **3a** with a slight erosion of the anomeric purity (from α:β 1:3 to 1:2) (entry 10). One can be noted that the use of anhydrous $Cu(OAc)_2$ led to **3a** in the same yield and same α/β-ratio (1:2, entry 11). Importantly, the stability of **1a** (α/β =1:3) and both isolated pure anomeres α-**3a** and β-**3a** in deuterated dichloromethane (CD_2Cl_2) was measured by ^{1}HNMR after 19 h at room temperature. The results demonstrated that both anomeres α-**3a** and β-**3a** are completely stable in CD_2Cl_2 and no anomerization was detected by ^{1}HNMR. However, analysis of the ^{1}HNMR of the starting material **1a** revealed that the anomeric purity was lost and the ratio α/β is 1:1.1. This result demonstrate cclearly that the erosion observed during the reaction is due to the anomerization of the starting glycosyl lactol (see SI, p98).

Motivated by these results, we next explored the scope of the coupling reaction of glucopyranose **1a** (in a mixture of α/β = 1:3) with various arylboronic acids. Gratifyingly, all the arylations proceeded cleanly to give the substituted aryl *O*-glycosides **3a–p** as a mixture of β and α anomers in ratios ranging from 1:2 to 1:7.3 and yields up to 86%. As depicted in Scheme 1, **1a** was readily coupled with aryl boronic acids having *para*- and *meta*-electron-donating or electron-withdrawing substituents to give aryl *O*-glycosides **3b-d**, **3f-p** in good yields with a retention of the diastereomeric α/β ratio. Interestingly, this cross-coupling tolerated the presence of C–halogen bonds (*e.g.*, F, Cl, Br, I) which offers a platform for further metal-catalyzed cross coupling reactions (compounds **3h, 3i, 3m** and **3o**). It is well known that substitution *ortho* to boron had a dramatic influence on the reaction efficency. Thus, when 2-methylphenylboronic acid was used as the coupling partner, only traces of product **3e** were detected

Scheme 1 Scope of Arylboronic Acids **2** for Cu-Catalyzed *O*-Arylation of **1a**[a]

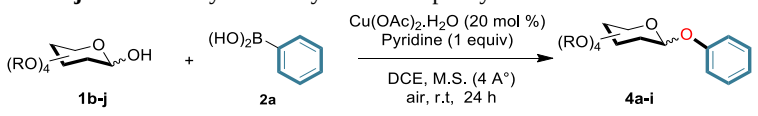


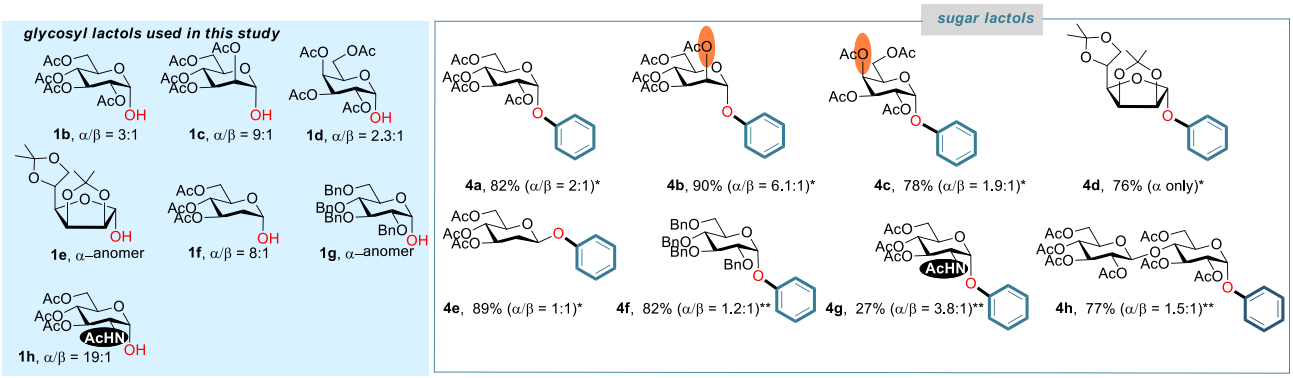
Reaction conditions: reaction of **1a** (1 equiv) with $ArB(OH)_2$ **2** (3 equiv) were performed in flask at r.t. in DCE by using $Cu(OAc)_2.H_2O$ (30 mol %), Pyridine (1 equiv) and molecular sieves. *anomer ratio was calculated after purification and isolation of both α- and β-products from the crude mixture.** anomer ratio was measured by ^1H NMR (and confirmed by HPLC) on the mixture of both anomers.

by LCMS analysis even when a stoichiometric amount of copper catalyst was used.

In a further set of experiments, we investigated the scope and generality of the method with respect to mono- di- and poly-saccharides. As depicted in Scheme 2, this coupling reaction tolerates a large variety of sugars **1b–h** and furnished the desired aryl *O*-glycosides in yields up to 90%. At first we investigated the influence of the stereochemistry of the anomeric hydroxyl group on the coupling reaction. Thus, when the α/β-ratio of *tetra*-acetoxy-D-glucopyranose was inversed from 1:3 to 3:1 in favour of the α-anomer **1b**, the coupling reaction with **2a** proceeded smoothly giving the desired product **4a** in 82% yield and 2:1 of anomeric purity. Moving from D-glucopyranose to *O*-acetylated α-D-mannose **1c** (α/β = 9:1), and *O*-acetylated D-galactopyranose **1d** (α/β = 1:2.3) resulted in the isolation of compound **4b** and **4c** in excellent yields and a slight loss of anomeric purity (<5%). The synthetic potential of this protocol was demonstrated by performing a gram scale process with **1c** (5.7 mmol). Delightedly, the reaction proceeded well to afford phenolic glycoside **4b** in 94% yield with the anomeric purity α/β = 6.1:1. Interestingly, joining of the phenylboronic acid moiety to α–D-mannofuranose **1e** was

Scheme 2 Scope of Sugar Lactols **1b-j** for Cu-Catalyzed *O*-Arylation with phenylboronic Acids **2a**[a]



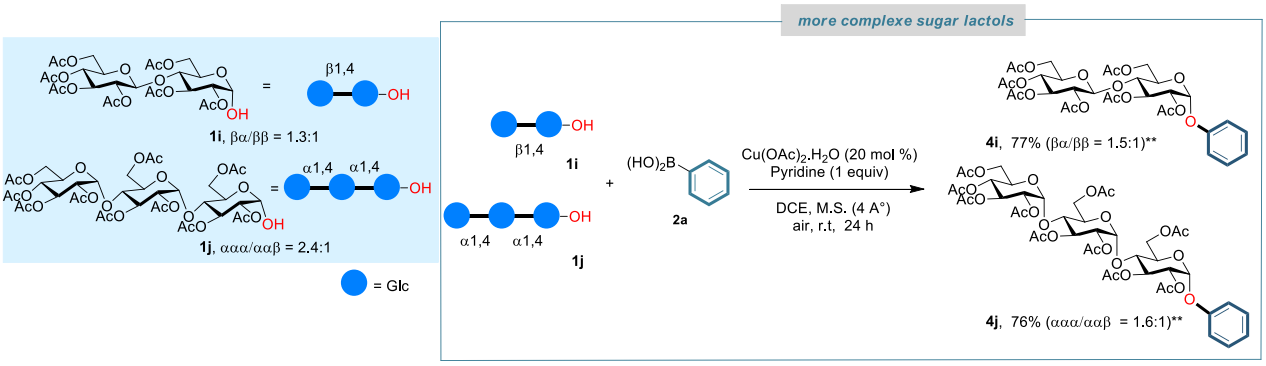


Reaction conditions: reaction of **1b-j** (1 equiv) with $PhB(OH)_2$ **2a** (3 equiv) were performed in flask at r.t. in DCE by using $Cu(OAc)_2.H_2O$ (30 mol %), Pyridine (1 equiv) and molecular sieves. *anomer ratio was calculated after purification and isolation of both α- and β-products from the crude mixture.** anomer ratio was measured by ^1H NMR (and confirmed by HPLC) on the mixture of both anomers.

effective and resulted in the formation of the desired product **4d** in 76% yield as the only α–anomer.

Next, the scope of the new reaction was investigated by using two glycosyl partners devoid from the C-2 ester neighboring participating group: the 2-deoxy glucose **1f** and **1g** bearing a benzyl group rather than the acetyl. As we can expect, when these two substrates where used, the coupling products **4e** and **4f** were isolated nicely in excellent 89% and 82% yields, respectively but the anomeric purity was completely lost in these cases. These results indicate that the acetyl group at the C2-position plays a pivotal role in maintaining the stability of the anomeric purity of glycosyl lactols **1f** and **1g** under the reaction conditions.

Scheme 3 Scope of the Cu-Catalyzed *O*-Arylation with more complex carbohydrates[a]



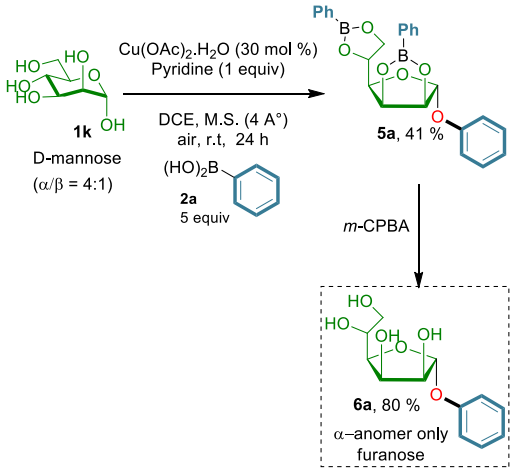
Reaction conditions: reaction of **1i-j** (1 equiv) with $PhB(OH)_2$ **2a** (3 equiv) were performed in flask at r.t. in DCE by using $Cu(OAc)_2.H_2O$ (30 mol %), Pyridine (1 equiv) and molecular sieves.** anomer ratio was measured by ^1H NMR (and confirmed by HPLC) on the mixture of both anomers.

Having demonstrated the efficacy of our method with various sugar lactols, we next turned our attention to the validation of the method with respect to more complex and biologically relevant saccharides (Scheme 3). We were delighted to find that di- and trisaccharide derivatives cellobiose **1i** (α/β = 1.2:1) and maltotriose **1j** (α/β = 3:1), readily undergo *O*-arylation coupling in this transformation. The desired *O*-aryl glycoside **4i** was isolated in 77% (α/β = 1.1:1). Moreover, the *O*-aryl trisaccharide **4j** which is commonly used in bacterial imaging[10] was isolated in 76% yield (α/β = 1.6:1). Importantly, the stereochemistry of the 1,4′-O-glycosidic bond in the disaccharides **4i** and the α-1,4′ in trisaccharide **4j** remained intact.

Of note in almost all cases, the β and α anomers were separated by SiO_2 flash chromatography or preparative HPLC and the NMR of pure single anomers has been reported (see SI).

It was well known that arylboronic acids react with non-protected sugars having erythro-configured OH groups at C-2 and C-3 (*e.g.*, mannose, allose)[11] to favor the formation of furanosides, with which they form particularly stable chelated complexes. Thus we were interesting whether this strategy may be applied to unprotected sugars to perform a selective *O*-arylation reaction of the anomeric OH group. In this context, we were pleased to observe that when the commercially available α-D-mannose **1k** (α/β = 4:1) and phenylboronic acid **2a** (5 equiv) were subjected to our conditions, phenyl *O*-furanoside **5a** was generated in moderate yield as a single α–anomer (Scheme 4). After reaction with *m*-CPBA to cleave boronic ester groups, **6a** could be isolated in a good 80% yield despite the fact that the conditions were not been optimized.

Based on previous works[12] on the mechanistic study of the Chan-Lam-Evans reaction, we proposed in Figure 2 a mechanistic description of the *O*-arylation of sugar lactols. At first, the complex (I) is formed through denucleation of the complex $[Cu(OAc)_2]_2.2H_2O$. Engagement of the arylboronic acid leads to transmetalation via 4-membered transition state (II) to



Scheme 4 Cu-catalyzed *O*-arylation of unprotected α–Man **1k** with phenylboronic acid **2a**[a]

deliver Cu(II) species (III). Oxidation to Cu(III) *via* disproportionation of $Cu^{II}(OAc)_2$ to $Cu^{I}(OAc)$ gives complex (IV). A selective C–O reductive elimination liberates the desired *O*-arylglycoside and a Cu(I)OAc species (**V**). Completion of the catalytic cycle is achieved *via* oxidation to Cu(II) in the presence of O_2 and AcOH.

CONCLUSION

In summary, we have succeeded in achieving the coupling of sugar lactols with functionalized arylboronic acid at room temperature to furnish aryl *O*-arylglycosides. To the best of our knowledge the $C(sp^2)$–O bond of aryl *O*-glycosides was formed, for the first time, directly by using anomeric hydroxyl group of sugars as nucleophile in the presence of $Cu(OAc)_2$ as the catalyst system. Because of the mildness of the reaction conditions, the protocol developed is stereoretentive, functional-group tolerant, and proceeds in good to excellent yields. Given its distinct convenience we expect this method to be widely adopted within the synthetic and medicinal chemistry community.

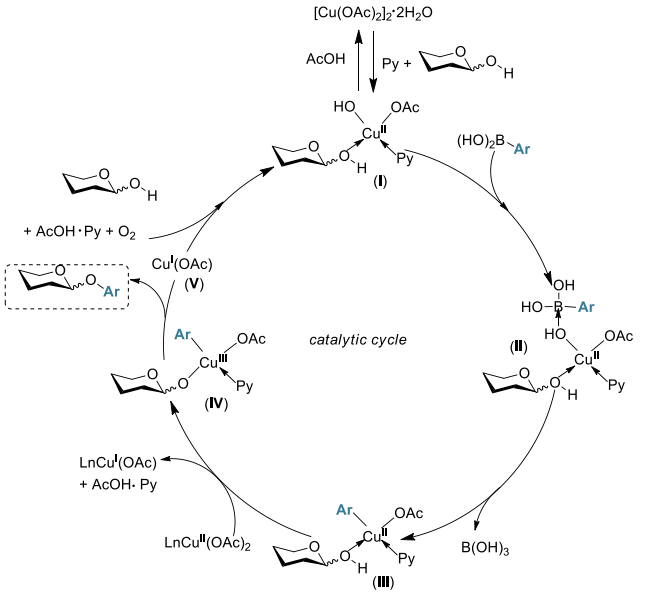


Figure 2. A proposed mechanism to anomeric *O*-arylation of carbohydrates

EXPERIMENTAL SECTION

General Procedure. Unknown compounds were all identified by usual physical methods, e.g., ^{1}H NMR, ^{13}C NMR, IR, MS (ESI). ^{1}H and ^{13}C NMR spectra were measured in deuterated solvents with a Bruker Avance-300. ^{1}H chemical shifts are reported in ppm from an internal standard TMS or of residual solvent peak. ^{13}C chemical shifts are reported in ppm from the residual solvent peak. IR spectra were measured on a Bruker Vector 22 spectrophotometer. Analytical TLC was performed on Merck precoated silica gel 60F plates. Merck silica gel 60 (0.015–0.040 mm) was used for column chromatography. High pressure liquid chromatography was recorded with a Waters Alliance 2695 device using a DAD 2996 as UV detector. High resolution mass spectra (HR-MS) were recorded on a Bruker MicroTOF spectrometer, using ESI with methanol as the carrier solvent. Nominal and exact m/z values are reported in Daltons. 2,3,4,6-Tetra-O-acetyl-β-D-glucopyranose **1a** (α:β = 1:3), β-D-glucose pentacetate, β-D-galactose pentacetate, D-mannose, D-glucosamine, 2,3,4,6-Tetra-O-benzyl-α-D-glucopyranose **1g**, maltotriose, α-D-cellobiose octaacetate, tri-O-acetyl-D-glucal, 2,3,5,6-di-O-isopropylidene-α-D-mannofuranose **1e** and all boronic acids were bought from available commercial sources.

General procedure for copper-catalyzed anomeric *O*-arylation of carbohydrate derivatives.

In a 50 mL round bottom flask, monohydrated copper (II) acetate (30 mg, 0.15 mmol) and pyridine (40 µL, 0.50 mmol) were added on activated 4 Å molecular sieves (200 mg). Dichloroethane (700 µL, c = 0.7 M) was added and the resulting suspension was stirred for 5 minutes. The boronic acid (1.50 mmol) was then introduced and the reaction media was stirred again for 5 minutes. Finally, the carbohydrate (0.50 mmol) was added and the resulting mixture was stirred at room temperature and under air atmosphere for 24 hours (the round bottom flask was capped to prevent the evaporation of dichloromethane). The media was then diluted with dichloromethane and filtered over celite. Purification by silica gel chromatography (cyclohexane/EtOAc) afforded the desired compound. Unless other specified indications, α and β anomers were isolated separately.

Description of coupling products 3a-d, 3f-p and 4a-i

1-Phenyl-2,3,4,6-tetra-O-acetyl-D-glucopyranoside 3a.

The title compound was prepared according to the general procedure from commercially available 2,3,4,6-tetra-O-acetyl-D-glucopyranose (174 mg, 0.5 mmol, α:β = 1:3) and phenylboronic acid (183 mg) and was purified on silica gel chromatography (cyclohexane/EtOAc, from 90/10 to 70/30) to afford 59 mg of the α anomer and 115 mg of the β anomer as amorphous white solids. Global yield: 84 % (0.42 mmol, 178 mg).

1-Phenyl-2,3,4,6-tetra-O-acetyl-α-D-glucopyranoside.[13]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35-7.28 (m, 2 H), 7.12-7.05 (m, 3 H), 5.75 (d, *J* = 3.3 Hz, 1 H), 5.72 (app t, *J* = 9.8 Hz, 1 H), 5.17 (app t, *J* = 9.8 Hz, 1 H), 5.06 (dd, *J* = 10.2, 3.7 Hz, 1 H), 4.27 (dd, *J* = 12.2, 4.5 Hz, 1 H), 4.15 (ddd, *J* = 10.2, 4.5, 2.1 Hz, 1 H), 4.07 (dd, *J* = 12.2, 2.2 Hz, 1 H), 2.08 (s, 3 H), 2.07 (s, 3 H), 2.06 (s, 3 H), 2.05 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.6, 170.2, 169.6, 156.1, 129.7 (2 C), 123.0, 116.6 (2 C), 94.2, 70.5, 70.1, 68.3, 68.0, 61.6, 20.6 (4 C).

1-Phenyl 2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside.[14]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34-7.28 (m, 2 H), 7.11-7.07 (m, 1 H), 7.02-6.99 (m, 2 H), 5.35-5.26 (m, 2 H), 5.22-5.17 (m, 1 H), 5.12-5.09 (m, 1 H), 4.31 (dd, *J* = 12.2, 5.3 Hz, 1 H), 4.18 (dd, *J* = 12.3, 2.5 Hz, 1 H), 3.88 (ddd, *J* = 9.9, 5.3, 2.5 Hz, 1 H), 2.09 (s, 3 H), 2.08 (s, 3H), 2.06 (s, 3 H), 2.05 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.6, 170.2, 169.4, 169.3, 156.8, 129.6 (2 C), 123.4, 117.0 (2 C), 99.1, 72.7, 72.0, 71.2, 68.3, 62.0, 20.7, 20.6 (3 C).

1-(4'-Methoxy)-2,3,4,6-tetra-O-acetyl-D-glucopyranoside 3b.

The title compound was prepared according to the general procedure from commercially available 2,3,4,6-tetra-O-acetyl-D-glucopyranose (174 mg, 0.5 mmol, α:β = 1:3) and 4-methoxyphenylboronic acid (228 mg) and was purified on silica gel chromatography (cyclohexane/EtOAc, from 90/10 to 70/30) to afford 43 mg of the α anomer and 90 mg of the β anomer as amorphous white solids. Global yield: 59 % (0.29 mmol, 134 mg).

1-(4'-Methoxy)-2,3,4,6-tetra-O-acetyl-α-D-glucopyranoside.[15]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.04-7.01 (m, 2 H), 6.86-6.83 (m, 2 H), 5.70 (app t, *J* = 9.8 Hz, 1 H), 5.63 (d, *J* = 3.7 Hz, 1 H), 5.16 (app t, *J* = 9.8 Hz, 1 H), 5.03 (dd, *J* = 10.3, 3.7 Hz, 1 H), 4.27 (dd, *J* = 12.1, 4.6 Hz, 1 H), 4.18 (ddd, J = 12.0, 4.7, 2.1 Hz, 1 H), 4.09 (dd, *J* = 12.1, 2.1 Hz, 1 H), 3.79 (s, 3 H), 2.09-2.06 (m, 12 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 170.1 (2 C), 169.6, 155.5, 150.2, 117.9 (2 C), 114.7 (2 C), 95.1, 70.6, 70.1, 68.4, 67.9, 61.7, 55.7, 20.7, 20.6 (3 C).

1-(4'-Methoxy)-2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside.[16]

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.98-6.95 (m, 2 H), 6.85-6.82 (m, 2 H), 5.93-5.22 (m, 1 H), 5.17 (t, *J* = 9.1 Hz, 1 H), 4.97 (d, *J* = 7.1 Hz, 1 H), 4.31 (dd, *J* = 12.3, 5.2 Hz, 1 H), 4.18 (dd, *J* = 12.3, 2.5 Hz, 1 H), 3.85-3.79 (m, 1 H), 3.79 (s, 3 H), 2.10 (s, 3 H), 2.09 (s, 3 H), 2.06 (s, 3 H), 2.05 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.6, 170.2, 169.4, 169.3, 155.8, 150.9, 118.7 (2 C), 114.6 (2 C), 100.3, 72.8, 72.0, 71.3, 68.3, 62.0, 55.6, 20.7 (2 C), 20.6 (2 C).

1-(4'-Thiomethyl)-2,3,4,6-tetra-O-acetyl-α-D-glucopyranoside 3c.

The title compound was prepared according to the general procedure from commercially available 2,3,4,6-tetra-O-acetyl-D-glucopyranose (174 mg, α:β = 1:3) and 4-thiomethylphenylboronic acid (250 mg) and was purified on silica gel chromatography (cyclohexane/EtOAc, from 90/10 to 70/30) to afford 34 mg of the α anomer and 82 mg of the β anomer as amorphous white solids. Global yield: 49 % (0.24 mmol, 115 mg).

1-(4'-Thiomethyl)-2,3,4,6-tetra-O-acetyl-α-D-glucopyranoside.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27-7.24 (m, 2 H), 7.05-7.03 (m, 2 H), 5.73-5.66 (m, 2 H), 5.16 (t, *J* = 9.7 Hz, 1 H), 5.04 (dd, *J* = 10.2, 3.7 Hz, 1 H), 4.26 (dd, *J* = 11.9, 4.2 Hz, 1 H), 4.12 (ddd, *J* = 10.3, 4.4, 2.2 Hz, 1 H), 4.07 (dd, *J* = 12.3, 2.3 Hz, 1 H), 2.47 (s, 3 H), 2.07-2.05 (m, 12 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 170.1 (2 C), 169.5, 154.3, 132.1, 129.3 (2 C), 117.3 (2 C), 94.4, 70.4, 70.0, 68.3, 68.0, 61.6, 20.7, 20.6 (3 C), 17.3. HRMS (ESI) calculated for $C_{21}H_{26}O_{10}NaS$ $[M + Na]^+$ 493.1144, found 493.1136. $[\alpha]_D^{13}$ +160.7° (*c* 0.28, MeOH). FT-IR ν_{max}/cm^{-1} : 1733, 1493, 1368, 1222, 1034, 816, 604, 559.

1-(4'-Thiomethyl)-2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26-7.23 (m, 2 H), 6.97-6.94 (m, 2 H), 5.36-5.22 (m, 1 H), 5.17 (app t, *J* = 9.2 Hz, 1 H), 5.05 (d, *J* = 7.3 Hz, 1 H), 4.30 (dd, *J* = 12.3, 5.3 Hz, 1 H), 4.18 (dd, *J* = 12.3, 2.5 Hz, 1 H), 3.86 (ddd, *J* = 9.8, 5.3, 2.5 Hz, 1 H), 2.46 (s, 3 H), 2.09 (s, 3 H), 2.07 (s, 3 H), 2.06 (s, 3 H), 2.05 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 170.2, 169.3, 169.2, 155.0, 132.5, 129.2 (2 C), 117.8 (2 C), 99.3, 72.7, 72.1, 71.2, 68.3, 61.9, 20.7, 20.6 (3 C), 17.2. HRMS (ESI) calculated for $C_{21}H_{26}O_{10}NaS$ $[M + Na]^+$ 493.1144, found 493.1138. $[\alpha]_D^{13}$ -21.6° (*c* 0.37, MeOH). FT-IR ν_{max}/cm^{-1}: 1740, 1493, 1366, 1218, 1059, 1033, 818, 699, 642.

1-(4'-vinyl)-phenyl-2,3,4,6-tetra-O-acetyl-D-glucopyranoside 3d.

The title compound was prepared according to the general procedure from commercially available 2,3,4,6-tetra-O-acetyl-D-glucopyranose (174 mg, α:β = 1:3) and 4-vinylphenylboronic acid (222 mg) and was purified on silica gel chromatography (cyclohexane/EtOAc, from 90/10 to 70/50) to afford 62 mg of the α anomer and 126 mg of the β anomer as amorphous white solids. Global yield: 84 % (0.42 mmol, 189 mg).

1-(4'-vinyl)-phenyl-2,3,4,6-tetra-O-acetyl-α-D-glucopyranoside.[17]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35-7.32 (m, 2 H), 7.04-7.02 (m, 2 H), 6.65 (dd, *J* = 17.6, 10.9 Hz, 1 H), 5.73-5.60 (m, 3 H), 5.18-5.11 (m, 2 H), 5.03 (dd, *J* = 10.2, 3.7 Hz, 1 H), 4.13-4.01 (m, 2 H), 4.23 (dd, *J* = 12.1, 4.4 Hz, 1 H), 2.05 (s, 3 H), 2.04 (s, 3 H), 2.03 (s, 3 H), 2.02 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 170.1 (2 C), 169.5, 155.7, 135.8, 132.7, 127.4 (2 C), 116.6 (2 C), 112.9, 94.2, 70.4, 70.0, 68.3, 68.1, 61.6, 20.7, 20.6 (3 C).

1-(4'-vinyl)-phenyl-2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside.[17]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34-7.31 (m, 2 H), 6.95-6.92 (m, 2 H), 6.65 (dd, *J* = 17.6, 10.9 Hz, 1 H), 5.63 (d, *J* = 17.6 Hz, 1 H), 5.32-5.22 (m, 2 H), 5.22-5.12 (m, 2 H), 5.08-5.06 (m, 1 H), 4.28 (dd, *J* = 12.3, 5.3 Hz, 1 H), 4.16 (dd, *J* = 12.3, 2.5 Hz, 1 H), 3.91-3.78 (m, 1 H), 2.06 (s, 3 H), 2.04 (s, 3 H), 2.03 (s, 3 H), 2.02 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 170.2, 169.3, 169.2, 156.5, 135.8, 133.1, 127.4 (2 C), 117.0 (2 C), 113.0, 99.1, 72.7, 72.1, 71.2, 68.3, 61.9, 20.7, 20.6 (3 C).

1-(3'-Methoxy)-phenyl-2,3,4,6-tetra-O-acetyl-D-glucopyranoside 3f.

The title compound was prepared according to the general procedure from commercially available 2,3,4,6-tetra-O-acetyl-D-glucopyranose (174 mg, α:β = 1:3) and 3-methoxyphenylboronic acid (227 mg) and was purified on silica gel chromatography (cyclohexane/EtOAc, from 90/10 to 70/30) to afford 42 mg of the α anomer and 134 mg of the β anomer as amorphous white solids. Global yield: 77 % (0.38 mmol, 175 mg).

1-(3'-Methoxy)-phenyl-2,3,4,6-tetra-O-acetyl-α-D-glucopyranoside.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19 (app t, *J* = 8.1 Hz, 1 H), 6.69-6.60 (m, 3 H), 5.79-5.60 (m, 2 H), 5.14 (app t, *J* = 9.7 Hz, 1 H), 5.03 (dd, *J* = 10.3, 3.6 Hz, 1 H), 4.25 (dd, *J* = 12.1, 4.5 Hz, 1 H), 4.16-4.08 (m, 1 H), 4.05 (dd, *J* = 12.1, 2.2 Hz, 1 H), 3.79 (s, 3 H), 2.06 (m, 6 H), 2.05 (s, 3 H), 2.04 (s, 5 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 170.1 (2 C), 169.6, 160.8, 157.2, 130.1, 108.7, 108.5, 103.0, 94.2, 70.4, 70.1, 68.4, 68.0, 61.6, 55.4, 20.7, 20.6 (3 C). HRMS (ESI) calculated for $C_{21}H_{26}O_{11}Na$ $[M+Na]^+$ 477.1373, found 477.1378. $[\alpha]_D^{14}$ +146.3° (*c* 0.21, MeOH). FT-IR ν_{max}/cm^{-1} : 1739, 1593, 1493, 1368, 1223, 1033, 787, 691, 603.

1-(3'-Methoxy)-phenyl-2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside.[15]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18 (app t, *J* = 8.2 Hz, 1 H), 6.67-6.52 (m, 2 H), 5.35-5.21 (m, 2 H), 5.19-5.11 (m, 1 H), 5.07 (app d, *J* = 7.3 Hz, 1 H), 4.27 (dd, *J* = 12.3, 5.4 Hz, 1 H), 4.16 (dd, *J* = 12.3, 2.5 Hz, 1 H), 3.85 (ddd, *J* = 9.8, 5.4, 2.5 Hz, 1 H), 3.78 (s, 3 H), 2.07 (s, 3 H), 2.05 (s, 3 H), 2.04 (s, 3 H), 2.03 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.6, 170.2, 169.4, 169.3, 160.8, 158.0, 130.0, 110.0, 108.9, 108.6, 103.6, 99.0, 72.8, 72.1, 71.2, 68.4, 62.0, 55.4, 20.6 (4 C).

1-(3',5'-dimethyl)-phenyl-2,3,4,6-tetra-O-acetyl-D-glucopyranoside 3g.

The title compound was prepared according to the general procedure from commercially available 2,3,4,6-tetra-O-acetyl-D-glucopyranose (174 mg, α:β = 1:3) and 3,5-dimethylphenylboronic acid (225 mg) and was purified on silica gel chromatography (cyclohexane/EtOAc, from 90/10 to 70/30) to afford 52 mg of the α anomer and 106 mg of the β anomer as amorphous white solids. Global yield: 70 % (0.35 mmol, 158 mg).

1-(3',5'-dimethyl)-phenyl-2,3,4,6-tetra-O-acetyl-α-D-glucopyranoside.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.70 (m, 3 H), 5.69 (app t, *J* = 9.7 Hz, 1 H), 5.70 (d, *J* = 3.7 Hz, 1 H), 5.15 (app t, *J* = 9.8 Hz, 1H), 5.02 (dd, *J* = 10.2, 3.7 Hz, 1 H), 4.26 (dd, *J* = 12.2, 4.5 Hz, 1 H), 4.13 (ddd, *J* = 10.1, 4.5, 2.1 Hz, 1 H), 4.05 (dd, *J* = 12.2, 2.3 Hz, 1 H), 2.29 (s, 6 H), 2.05-2.03 (m, 12 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 170.1 (2 C), 169.6, 156.1, 139.5, 124.7, 114.2 (2 C), 94.1, 70.5, 70.1, 68.4, 67.9, 61.7, 21.4 (2 C), 20.7, 20.6 (3 C). HRMS (ESI) calculated for $C_{22}H_{28}O_{10}Na$ $[M+Na]^+$ 475.1580, found 475.1574. $[\alpha]_D^{14}$ +160.9° (*c* 0.23, MeOH). FT-IR ν_{max}/cm^{-1} : 1743, 1593, 1367, 1214, 1172, 1155, 1033, 839, 600.

1-(3',5'-dimethyl)-phenyl-2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.71 (m, 1 H), 6.61 (m, 2 H), 5.32-5.21 (m, 2 H), 5.14 (app t, *J* = 9.4 Hz, 1 H), 5.05 (app d, *J* = 7.1 Hz, 1 H), 4.26 (dd, *J* = 12.2, 5.5 Hz, 1 H), 4.18 (dd, *J* = 12.2, 2.6 Hz, 1 H), 3.87 (ddd, *J* = 9.9, 5.5, 2.5 Hz, 1 H), 2.28 (s, 6 H), 2.08 (s, 3 H), 2.05 (s, 3 H), 2.04 (s, 3 H), 2.03 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 170.2, 169.4, 169.3, 156.9, 139.4, 125.0, 114.6 (2 C), 99.0, 72.8, 72.0, 71.2, 68.4, 62.2, 21.4 (2 C), 20.7, 20.6 (3 C). HRMS (ESI) calculated for $C_{22}H_{28}O_{10}Na$ $[M+Na]^+$ 475.1580, found 475.1579. $[\alpha]_D^{14}$ -25.3° (*c* 0.48, MeOH). FT-IR ν_{max}/cm^{-1} : 1751, 1595, 1367, 1214, 1136, 1036, 954, 906, 846, 599.

1-(4'-Bromo)-phenyl-2,3,4,6-tetra-O-acetyl-D-glucopyranoside 3h.

The title compound was prepared according to the general procedure from commercially available 2,3,4,6-tetra-O-acetyl-D-glucopyranose (174 mg, α:β = 1:3) and 4-bromophenylboronic acid (301 mg) and was purified on silica gel chromatography (cyclohexane/EtOAc, from 90/10 to 70/30) to afford 40 mg of the α anomer and 139 mg of the β anomer as amorphous white solids. Global yield: 71 % (0.35 mmol, 178 mg).

1-(4'-Bromophenyl)-2,3,4,6-tetra-O-acetyl-α-D-glucopyranoside.[16]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42-7.39 (m, 2 H), 6.99-6.96 (m, 2 H), 5.73-5.59 (m, 1 H), 5.14 (app t, *J* = 9.9 Hz, 1 H), 5.02 (dd, *J* = 10.3, 3.7 Hz, 1 H), 4.23 (dd, *J* = 12.3, 4.7 Hz, 1 H), 4.12-3.99 (m, 1 H), 2.06 (s, 3 H), 2.04 (s, 3 H), 2.03 (s, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 170.1 (2 C), 169.5, 155.1, 132.6 (2 C), 118.4 (2 C), 115.6, 94.4, 70.4, 69.9, 68.2, 61.6, 20.7, 20.6 (3 C).

1-(4'-Bromophenyl)-2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside.[18]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40-7.37 (m, 2 H), 6.89-6.86 (m, 2 H), 5.34-5.19 (m, 2 H), 5.15 (app t, *J* = 9.2 Hz, 1 H), 5.03 (d, *J* = 7.3 Hz, 1 H), 4.27 (dd, *J* = 12.3, 5.3 Hz, 1 H), 4.15 (dd, *J* = 12.3, 2.5 Hz, 1 H), 3.84 (ddd, *J* = 10.0, 5.4, 2.5 Hz, 1 H), 2.07 (s, 3 H), 2.05 (s, 3 H), 2.04 (s, 3 H), 2.02 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 170.2, 169.3, 169.2, 155.9, 132.5 (2 C), 118.9 (2 C), 115.9, 99.1, 72.6, 72.1, 71.1, 68.2, 61.9, 20.7 (2 C), 20.6 (2 C).

1-(4'-Fluorophenyl)-2,3,4,6-tetra-O-acetyl-D-glucopyranoside 3i.

The title compound was prepared according to the general procedure from commercially available 2,3,4,6-tetra-O-acetyl-D-glucopyranose (174 mg, α:β = 1:3) and 4-fluorophenylboronic acid (210 mg) and was purified on silica gel chromatography (cyclohexane/EtOAc, from 90/10 to 70/30) to afford 22 mg of the α anomer and 105 mg of the β anomer as amorphous white solids. Global yield: 58 % (0.29 mmol, 128 mg).

1-(4'-Fluorophenyl)-2,3,4,6-tetra-O-acetyl-α-D-glucopyranoside.[16]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.06-6.95 (m, 4 H), 5.74-5.57 (m, 2 H), 5.13 (app t, *J* = 9.6 Hz, 1 H), 5.01 (dd, *J* = 10.3, 3.7 Hz, 1 H), 4.23 (dd, *J* = 11.8, 4.4 Hz, 1 H), 4.16-3.99 (m, 2 H), 2.06-2.03 (m, 12 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 170.1 (2 C), 169.6, 158.6 ($J_{13C\{F\}}$ = 241.4 Hz), 152.2, 118.0 ($J_{13C\{F\}}$ = 7.9 Hz, 2 C), 116.1 ($J_{13C\{F\}}$ = 23.1 Hz, 2 C), 94.9, 70.5, 70.0, 68.3, 68.1, 61.6, 20.7, 20.6 (3 C). ^{19}F (188 MHz, $CDCl_3$) δ -120.6.

1-(4'-Fluorophenyl)-2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside.[15]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.00-6.95 (m, 4 H), 5.31-5.20 (m, 2 H), 5.15 (app t, *J* = 9.2 Hz, 1 H), 4.98 (d, *J* = 7.0 Hz, 1 H), 4.28 (dd, *J* = 12.3, 5.3 Hz, 1 H), 4.16 (dd, *J* = 12.3, 2.5 Hz, 1 H), 3.81 (ddd, *J* = 10.0, 5.3, 2.5 Hz, 1 H), 2.07 (s, 3 H), 2.06 (s, 3 H), 2.03 (s, 3 H), 2.02 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 170.2, 169.3, 169.2, 158.8 ($J_{13C\{F\}}$ = 241.5 Hz), 152.9, 118.8 ($J_{13C\{F\}}$ = 8.5 Hz, 2 C), 116.0 ($J_{13C\{F\}}$ = 23.2 Hz, 2 C), 99.9, 72.7, 72.1, 71.2, 68.3, 61.9, 20.7, 20.6 (3 C). ^{19}F (188 MHz, $CDCl_3$) δ -120.1.

1-(4'-Trifluoromethyl)-phenyl-2,3,4,6-tetra-O-acetyl-D-glucopyranoside 3j.

The title compound was prepared according to the general procedure from commercially available 2,3,4,6-tetra-O-acetyl-D-glucopyranose (174 mg, α:β = 1:3) and 4-trifluoromethylphenylboronic acid (286 mg) and was purified on silica gel chromatography (cyclohexane/EtOAc, from 90/10 to 70/30) to afford 36 mg of the α anomer and 145 mg of the β anomer as amorphous white solids. Global yield: 74 % (0.29 mmol, 182 mg).

1-(4'-Trifluoromethyl)-phenyl-2,3,4,6-tetra-O-acetyl-α-D-glucopyranoside.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59-7.56 (m, 2 H), 7.19-7.17 (m, 2 H), 5.80 (d, *J* = 3.7 Hz, 1 H), 5.69 (app t, *J* = 9.8 Hz, 1 H), 5.15 (app t, *J* = 9.7 Hz, 1 H), 5.05 (dd, *J* = 10.3, 3.7 Hz, 1 H), 4.23 (dd, *J* = 12.8, 5.1 Hz, 1 H), 4.06-4.03 (m, 2 H), 2.06 (s, 3 H), 2.05 (s, 3 H), 2.04 (s, 3H), 2,02 (s, 3 H). ^{13}C NMR

(75 MHz, $CDCl_3$) δ 170.4, 170.1 (2 C), 169.5, 158.3, 127.1, 127.0, 125.3 (q, $J_{13C\{F\}}$ = 33 Hz), 124.0 (q, $J_{13C\{F\}}$ = 270 Hz), 116.5 (2 C), 94.0, 70.3, 69.9, 68.4, 68.2, 61.5, 20.6, 20.5 (3 C). ^{19}F (188 MHz, $CDCl_3$) δ -61.9. HRMS (ESI) calculated for $C_{21}H_{23}O_{10}NaF_3$ $[M + Na]^+$ 515.1141, found 515.1143. $[\alpha]_D^{13}$ +137.0° (*c* 0.27, MeOH). FT-IR ν_{max}/cm^{-1} : 1742, 1330, 1224, 1123, 1032, 844, 687, 608.

1-(4'-Trifluoromethyl)-phenyl-2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside.[16]

^1H NMR (300 MHz, $CDCl_3$) δ 7.57-7.55 (m, 2 H), 7.07-7.05 (m, 2 H), 5.34-5.25 (m, 2 H), 5.20-5.14 (m, 2 H), 4.28 (dd, *J* = 12.3, 5.4 Hz, 1 H), 4.17 (dd, *J* = 12.3, 2.5 Hz, 1 H), 3.89 (ddd, *J* = 9.9, 5.4, 2.5 Hz, 1 H), 2.06 (s, 3 H), 2.05 (s, 6 H), 2.03 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.4, 170.1, 169.3, 169.2, 159.0, 127.0 (2 C), 125.4 (q, $J_{13C\{F\}}$ = 33 Hz), 124.0 (q, $J_{13C\{F\}}$ = 270 Hz), 116.8 (2 C), 98.4, 72.5, 72.2, 71.0, 68.2, 61.9, 20.6 (2 C), 20.5 (2 C). ^{19}F (188 MHz, $CDCl_3$) δ -61.9.

1-(4'-trifluoromethoxy)-phenyl-2,3,4,6-tetra-O-acetyl-D-glucopyranoside 3k.

The title compound was prepared according to the general procedure from commercially available 2,3,4,6-tetra-O-acetyl-D-glucopyranose (174 mg, α:β = 1:3) and 4-(trifluoromethoxy)phenylboronic acid (310 mg) and was purified on silica gel chromatography (cyclohexane/EtOAc, from 90/10 to 60/40) to afford 39 mg of the α anomer and 139 mg of the β-anomer as amorphous white solids. Global yield: 70 % (0.35 mmol, 178 mg).

1-(4'-trifluoromethoxy)-phenyl-2,3,4,6-tetra-O-acetyl-α-D-glucopyranoside.

^1H NMR (300 MHz, $CDCl_3$) δ 7.24-6.98 (m, 4 H), 5.71-5.64 (m, 2 H), 5.14 (app t, *J* = 9.9 Hz, 1 H), 5.03 (dd, *J* = 10.3, 3.7 Hz, 1 H), 4.23 (dd, *J* = 12.3, 4.8 Hz, 1 H), 4.11-4.05 (m, 2 H), 2.06 (s, 3 H), 2.05 (s, 3 H), 2.03 (s, 3 H), 2.02 (s, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.4, 170.1 (2 C), 169.5, 154.4, 144.5, 122.5, 122.2 (2 C), 120.5 (q, $J_{13C\{F\}}$ = 252 Hz), 117.6 (2 C), 94.5, 70.4, 69.9, 68.3, 68.2, 61.6, 20.5 (4 C). ^{19}F (188 MHz, $CDCl_3$) δ -58.4. HRMS (ESI) calculated for $C_{21}H_{23}O_{11}F_3Na$ $[M+Na]^+$ 531.1090, found 531.1082. $[\alpha]_D^{14}$ +128.6° (*c* 0.21, MeOH). FT-IR ν_{max}/cm^{-1} : 1745, 1505, 1368, 1213, 1192, 1161, 1033, 918, 801, 601.

1-(4'-trifluoromethoxy)-phenyl-2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside.[16]

^1H NMR (300 MHz, $CDCl_3$) δ 7.17-7.14 (m, 2 H), 7.01-6.98 (m, 2 H), 5.33-5.23 (m, 2 H), 5.16 (app t, *J* = 9.4 Hz, 1 H), 5.06 (d, *J* = 7.2 Hz, 1 H), 4.28 (dd, *J* = 12.3, 5.3 Hz, 1 H), 4.17 (dd, *J* = 12.3, 2.5 Hz, 1 H), 3.85 (ddd, *J* = 10.0, 5.4, 2.6 Hz, 1 H), 2.06 (m, 6 H), 2.05 (s, 3 H), 2.03 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.4, 170.1, 169.3, 169.2, 155.1, 144.7, 122.4 (2 C), 120.4 (J_{C-F} = 255 Hz), 118.1 (2 C), 99.2, 72.6, 72.2, 71.1, 68.3, 61.9, 20.5 (4 C). ^{19}F (188 MHz, $CDCl_3$) δ -58.3.

1-(4'-acetyl)-phenyl-2,3,4,6-tetra-O-acetyl-D-glucopyranoside 3l.

The title compound was prepared according to the general procedure from commercially available 2,3,4,6-tetra-O-acetyl-D-glucopyranose (174 mg, α:β = 1:3) and 4-acetylphenylboronic acid (245 mg) and was purified on silica gel chromatography (cyclohexane/EtOAc, from 90/10 to 50/50) to afford 32 mg of the α anomer and 95 mg of the β anomer as amorphous white solids. Global yield: 74 % (0.37 mmol, 172 mg).

1-(4'-acetyl)-phenyl-2,3,4,6-tetra-O-acetyl-α-D-glucopyranoside.

^1H NMR (300 MHz, $CDCl_3$) δ 7.95-7.93 (m, 2 H), 7.16-7.13 (m, 2 H), 5.82 (d, *J* = 3.6 Hz, 1 H), 5.70 (app t, *J* = 9.8 Hz, 1 H), 5.16 (app t, *J* = 9.9 Hz, 1 H), 5.06 (dd, *J* = 10.2, 3.6 Hz, 1 H), 4.24 (dd, *J* = 12.3, 4.5 Hz, 1 H), 4.09-4.02 (m, 2 H), 2.57 (s, 3 H), 2,06-2.03 (m, 12 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.6, 170.4, 170.1 (2 C), 169.5, 159.6, 132.3, 130.5 (2 C), 116.2 (2 C), 93.9, 70.3, 69.9, 68.4, 68.2, 61.5, 26.4, 20.7, 20.6 (2 C). HRMS (ESI) calculated for $C_{22}H_{26}O_{11}Na$ $[M+Na]^+$ 489.1373, found 489.1365. $[\alpha]_D^{13}$ +177.8° (*c* 0.23, MeOH). FT-IR ν_{max}/cm^{-1} : 1736, 1677, 1600, 1360, 1223, 1033, 829, 761, 590.

1-(4'-acetyl)-phenyl-2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside.[19]

^1H NMR (300 MHz, $CDCl_3$) δ 7.96-7.93 (m, 2 H), 7.06-7.03 (m, 2 H), 5.37-5.28 (m, 2 H), 5.22-5.16 (m, 2 H), 4.30 (dd, *J* = 12.3, 5.4 Hz, 1 H), 4.19 (dd, *J* = 12.3, 2.5 Hz, 1 H), 3.96-3.91 (m, 1 H), 2.58 (s, 3H), 2.09-2.05 (m, 12 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.6, 170.5, 170.1, 169.3, 169.2, 160.2, 132.4, 130.5 (2 C), 116.3 (2 C), 98.2, 72.6, 72.3, 71.1, 68.2, 61.9, 26.4, 20.7, 20.6 (2 C).

1-(3'-Iodo)-phenyl-2,3,4,6-tetra-O-acetyl-D-glucopyranoside 3m.

The title compound was prepared according to the general procedure from commercially available 2,3,4,6-tetra-O-acetyl-D-glucopyranose (174 mg, α:β = 1:3) and 3-iodophenylboronic acid (373 mg) and was purified on silica gel chromatography (cyclohexane/EtOAc, from 90/10 to 70/30) to afford 54 mg of the α anomer and 164 mg of the β anomer as amorphous white solids. Global yield: 79 % (0.4 mmol, 217 mg).

1-(3'-Iodo)-phenyl-2,3,4,6-tetra-O-acetyl-α-D-glucopyranoside.[20]

^1H NMR (300 MHz, $CDCl_3$) δ 7.47 (m, 1 H), 7.42-7.39 (m, 1 H), 7.07-6.99 (m, 2 H), 5.69 (d, *J* = 3.4 Hz, 1 H), 5.66 (app t, *J* = 9.9 Hz, 1 H), 5.13 (app t, *J* = 9.9 Hz, 1 H), 5.02 (dd, *J* = 10.2, 3.7 Hz, 1 H), 4.24 (dd, *J* = 12.5, 5.1 Hz, 1 H), 4.14-3.88 (m, 2 H), 2.06 (m, 6 H), 2.04 (s, 3 H), 2.03 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 170.1 (2 C), 169.5, 156.4, 132.3, 131.0, 125.8, 116.0, 94.3, 94.2, 70.3, 69.9, 68.3, 68.2, 61.6, 20.7 (2 C), 20.6 (2 C).

1-(3'-Iodo)-phenyl-2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside.[18]

^1H NMR (300 MHz, $CDCl_3$) δ 7.45-7.32 (m, 2 H), 7.04-6.93 (m, 2 H), 5.32-5.21 (m, 2 H), 5.12 (app t, *J* = 9.3 Hz, 1 H), 5.05 (app d, *J* = 7.1 Hz, 1 H), 4.32-4.13 (m, 2 H), 3.88 (ddd, *J* = 10.2, 5.8, 2.7 Hz, 1 H), 2.11 (s, 3 H), 2.05 (s, 3 H), 2.04 (s, 3 H), 2.02 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.6, 170.1,

169.4, 169.2, 157.1, 132.5, 130.9, 125.9, 116.6, 98.8, 94.0, 72.6, 72.2, 71.1, 68.3, 62.1, 20.8, 20.6 (3 C).

1-(3'-Nitro)-phenyl-2,3,4,6-tetra-O-acetyl-D-glucopyranoside 3n.

The title compound was prepared according to the general procedure from commercially available 2,3,4,6-tetra-O-acetyl-D-glucopyranose (174 mg, α:β = 1:3) and 3-nitrophenylboronic acid (250 mg) and was purified on silica gel chromatography (cyclohexane/EtOAc, from 90/10 to 50/50) to afford 28 mg of the α anomer and 111 mg of the β anomer as amorphous solids. Global yield: 59 % (0.29 mmol, 138 mg).

1-(3'-Nitro)-phenyl-2,3,4,6-tetra-O-acetyl-α-D-glucopyranoside.[20]

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04-7.86 (m, 2 H), 7.56-7.34 (m, 2 H), 5.80 (d, *J* = 3.6 Hz, 1 H), 5.68 (app t, *J* = 9.8 Hz, 1 H), 5.15 (app t, *J* = 9.9 Hz, 1 H), 5.06 (dd, *J* = 10.3, 3.6 Hz, 1 H), 4.24 (dd, *J* = 12.6, 5.2 Hz, 1 H), 4.14-3.97 (m, 2 H), 2.07 (s, 3 H), 2.05 (s, 3 H), 2.03 (s, 3 H), 2.02 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 170.4, 170.0 (2 C), 169.4, 156.5, 149.2, 130.3, 122.9, 118.0, 111.9, 94.7, 70.2, 69.7, 68.6, 68.2, 61.6, 20.6, 20.5 (3 C).

1-(3'-Nitro)-phenyl-2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside.[21]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (ddd, *J* = 8.2, 2.1, 1.0 Hz, 1 H), 7.86 (app t, *J* = 2.3 Hz, 1 H), 7.47 (app t, *J* = 8.2 Hz, 1 H), 7.31 (ddd, *J* = 8.3, 2.4, 1.1 Hz, 1 H), 5.40-5.25 (m, 2 H), 5.24-5.06 (m, 2 H), 4.22 (d, *J* = 4.2 Hz, 2 H), 4.01-3.88 (m, 1 H), 2.09 (s, 3 H), 2.07 (s, 3 H), 2.06 (s, 3 H), 2.04 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.6, 170.1, 169.4, 169.2, 157.0, 149.1, 130.2, 123.7, 118.2, 111.3, 98.6, 72.5 (2 C), 71.0, 68.2, 62.0, 20.6 (4 C).

1-(3',4'-dichloro)-phenyl-2,3,4,6-tetra-O-acetyl-D-glucopyranoside 3o.

The title compound was prepared according to the general procedure from commercially available 2,3,4,6-tetra-O-acetyl-D-glucopyranose (174 mg, α:β = 1:3) and 3,4-dichlorophenylboronic acid (288 mg) and was purified on silica gel chromatography (cyclohexane/EtOAc, from 90/10 to 70/30) to afford 7 mg of the α anomer and 53 mg of the β anomer as amorphous white solids. Global yield: 24 % (0.12 mmol, 59 mg).

1-(3',5'-dichloro)-phenyl-2,3,4,6-tetra-O-acetyl-α-D-glucopyranoside.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.9 Hz, 1 H), 7.28 (s, 1 H), 6.98 (dd, *J* = 8.9, 2.9 Hz, 1 H), 5.70 (d, *J* = 3.3 Hz, 1 H), 5.67 (app t, *J* = 9.8 Hz, 1 H), 5.15 (app t, *J* = 9.7 Hz, 1 H), 5.05 (dd, *J* = 10.3, 3.7 Hz, 1 H), 4.26 (dd, *J* = 12.9, 5.6 Hz, 1 H), 4.17-3.97 (m, 2H), 2.09-2.06 (m, 12 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 170.1 (2 C), 169.5, 154.9, 133.2, 130.9, 126.7, 118.8, 116.3, 94.6, 70.3, 69.8, 68.4, 68.2, 61.6, 20.7, 20.6 (3 C). HRMS (ESI) calculated for $C_{20}H_{22}O_{10}NaCl_2$ $[M+Na]^+$ 515.0488, found 515.0483. $[\alpha]_D^{14}$ +186.7° (*c* 0.08, Me0H). FT-IR ν_{max}/cm^{-1} : 1739, 1474, 1383, 1224, 1033, 932, 826, 776, 687, 608.

1-(3',5'-dichloro)-phenyl-2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.8 Hz, 1 H), 7.12 (d, *J* = 2.8 Hz, 1 H), 6.84 (dd, *J* = 8.9, 2.8 Hz, 1 H) 5.31-5.20 (m, 2 H), 5.12 (app t, *J* = 9.3 Hz, 1 H), 5.03 (d, *J* = 7.1 Hz, 1 H), 4.33-4.07 (m, 2 H), 3.87 (ddd, *J* = 9.5, 5.8, 2.6 Hz, 1 H), 2.09 (s, 3 H), 2.05 (s, 3 H), 2.04 (s, 3 H), 2.02 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 170.1, 169.3, 169.2, 155.5, 133.0, 130.8, 126.9, 118.9, 117.0, 99.0, 72.5, 72.3, 71.0, 68.2, 62.0, 20.7, 20.6 (3 C). HRMS (ESI) calculated for $C_{20}H_{22}O_{10}NaCl_2$ $[M+Na]^+$ 515.0488, found 515.0495. $[\alpha]_D^{14}$ -22.2° (*c* 0.23, Me0H). FT-IR ν_{max}/cm^{-1} : 1749, 1477, 1367, 1211, 913, 873, 825, 711, 600.

1-(2'-naphthyl)-2,3,4,6-tetra-O-acetyl-D-glucopyranoside 3p.

The title compound was prepared according to the general procedure from commercially available 2,3,4,6-tetra-O-acetyl-D-glucopyranose (174 mg, α:β = 1:3) and naphthalen-2-ylboronic acid (258 mg) and was purified on silica gel chromatography (cyclohexane/EtOAc, from 90/10 to 70/30) to afford 64 mg of the α anomer and 141 mg of the β anomer as yellowish solids. Global yield: 86 % (0.43 mmol, 203 mg).

1-(2'-naphthyl)-2,3,4,6-tetra-O-acetyl-α-D-glucopyranoside.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83-7.75 (m, 3 H), 7.50-7.38 (m, 3 H), 7.31-7.28 (m, 1 H), 5.91 (d, *J* = 3.6 Hz, 1 H), 5.79 (app t, *J* = 9.8 Hz, 1 H), 5.21 (app t, *J* = 9.8 Hz, 1 H), 5.13 (dd, *J* = 10.2, 3.6 Hz, 1 H), 4.29 (dd, *J* = 12.2, 4.7 Hz, 1 H), 4.19 (ddd, *J* = 10.3, 4.8, 2.1 Hz, 1 H), 4.08 (dd, *J* = 12.2, 2.1 Hz, 1 H), 2.09 (m, 6 H), 2.07 (s, 3 H), 2.00 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 170.2 (2 C), 169.6, 153.7, 134.2, 129.9, 129.7, 127.7, 127.1, 126.7, 124.7, 118.5, 110.9, 94.3, 70.5, 70.1, 68.4, 68.1, 61.6, 20.7, 20.6 (3 C). HRMS (ESI) calculated for $C_{24}H_{26}O_{10}Na$ $[M+Na]^+$ 497.1424, found 497.1428. $[\alpha]_D^{14}$ +184.3° (*c* 0.26, MeOH). FT-IR ν_{max}/cm^{-1} : 1739, 1227, 1213, 1180, 1032, 973, 839, 751, 662, 609.

1-(2'-naphthyl)-2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside.[22]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86-7.66 (m, 3 H), 7.52-7.35 (m, 2 H), 7.34 (d, *J* = 2.5 Hz, 1 H), 7.19 (dd, *J* = 8.9, 2.5 Hz, 1 H), 5.43-5.28 (m, 2 H), 5.27-5.06 (m, 2 H), 4.31 (dd, *J* = 12.2, 5.5 Hz, 1 H), 4.21 (dd, *J* = 12.3, 2.5 Hz, 1 H), 3.94 (ddd, *J* = 9.9, 5.6, 2.5 Hz, 1 H), 2.08 (m, 6H), 2.06 (s, 3 H), 2.05 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 170.2, 169.4, 169.3, 154.6, 134.1, 130.2, 129.7, 127.7, 127.1, 126.6, 124.7, 118.8, 111.5, 99.2, 72.8, 72.1, 71.3, 68.4, 62.1, 20.7, 20.6 (3 C).

1-Phenyl-2,3,4,6-tetra-O-acetyl-D-mannopyranoside 4b.

The title compound was prepared according to the general procedure from 2,3,4,6-tetra-O-acetyl-α-D-mannopyranose **1c** (175 mg, α:β = 9:1) and phenylboronic acid (185 mg) and was purified on silica gel chromatography (cyclohexane/EtOAc, from 90/10 to 70/30) to afford 165 mg of the α anomer and 27 mg of the β anomer as amorphous white solids. Global yield: 90 % (0.45 mmol, 191 mg).

1-Phenyl-2,3,4,6-tetra-O-acetyl-α-D-mannopyranoside.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33-7.28 (m, 2 H), 7.11-7.04 (m, 3 H), 5.57 (dd, *J* = 10.0, 3.5 Hz, 1 H), 5.53 (d, *J* = 1.8 Hz, 1 H), 5.45 (dd, *J* = 3.6, 1.8 Hz, 1 H), 5.37 (app t, *J* = 10.2 Hz, 1 H), 4.28 (dd, *J* = 12.4, 5.5 Hz, 1 H), 4.19-4.02 (m, 2 H), 2.20 (s, 3 H), 2.06 (s, 3 H), 2.04 (s, 3 H), 2.02 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 169.9, 169.9, 169.7, 155.6, 129.6 (2 C), 123.0, 116.5 (2 C), 95.8, 69.4, 69.1, 68.9, 66.0, 62.1, 20.8, 20.7, 20.6 (2 C). HRMS (ESI) calculated for $C_{20}H_{24}O_{10}Na$ $[M+Na]^+$ 447.1267, found 447.1271. $[\alpha]_D^{14}$ +79.1° (*c* 0.22, MeOH). FT-IR ν_{max}/cm^{-1} : 1743, 1489, 1366, 1213, 1124, 1036, 975, 915, 757, 692;

1-Phenyl-2,3,4,6-tetra-O-acetyl-β-D-mannopyranoside.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32-7.27 (m, 2 H), 7.17-6.78 (m, 3 H), 5.69 (d, *J* = 3.3 Hz, 1 H), 5.33 (app t, *J* = 9.8 Hz, 1 H), 5.24 (s, 1 H), 5.16 (dd, *J* = 9.9, 3.3 Hz, 1 H), 4.35 (dd, *J* = 12.1, 6.2 Hz, 1 H), 4.22 (dd, *J* = 12.1, 2.8 Hz, 1 H), 3.85 (ddd, *J* = 9.4, 6.2, 2.8 Hz, 1 H), 2.26 (s, 3 H), 2.10 (s, 3 H), 2.09 (s, 3 H), 2.04 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 170.3, 169.9, 169.6, 156.6, 129.5 (2 C), 123.2, 116.8 (2 C), 96.9, 72.5, 70.9, 68.8, 66.1, 62.6, 20.8, 20.7 (2 C), 20.6. HRMS (ESI) calculated for $C_{20}H_{24}O_{10}Na$ $[M+Na]^+$ 447.1267, found 447.1264. $[\alpha]_D^{14}$ -63.6° (*c* 0.44, MeOH). FT-IR ν_{max}/cm^{-1} : 1735, 1492, 1369, 1214, 1053, 913, 844, 769, 694, 599.

1-Phenyl-2,3,4,6-tetra-O-acetyl-D-galactopyranoside 4c.
The title compound was prepared according to the general procedure from 2,3,4,6-tetra-O-acetyl-α-D-galactopyranose **1d** (175 mg, α:β = 2.3:1) and phenylboronic acid (185 mg) and was purified on silica gel chromatography (cyclohexane/EtOAc, from 90/10 to 70/30) to afford 108 mg of the α anomer and 57 mg of the β anomer as amorphous white solids. Global yield: 78 % (0.39 mmol, 165 mg).

1-Phenyl-2,3,4,6-tetra-O-acetyl-α-D-galactopyranoside.[23]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40-7.22 (m, 2 H), 7.09-7.04 (m, 3 H), 5.79 (d, *J* = 3.6 Hz, 1 H), 5.59 (dd, *J* = 10.7, 3.4 Hz, 1 H), 5.56-5.51 (m, 1 H), 5.30 (dd, *J* = 10.7, 3.6 Hz, 1 H), 4.37 (app t, *J* = 6.6 Hz, 1 H), 4.17-4.04 (m, 2 H), 2.18 (s, 3 H), 2.08 (s, 3 H), 2.04 (s, 3 H), 1.94 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.3, 170.2, 170.1, 170.0, 156.3, 129.6 (2 C), 123.0, 116.8 (2 C), 94.9, 67.9, 67.8, 67.5, 67.1, 61.5, 20.7, 20.6 (2 C), 20.5.

1-Phenyl-2,3,4,6-tetra-O-acetyl-β-D-galactopyranoside.[22]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36-7.26 (m, 2 H), 7.13-7.04 (m, 1 H), 7.03-7.00 (m, 2 H), 5.50 (dd, *J* = 10.5, 8.0 Hz, 1 H), 5.45 (d, *J* = 3.2 Hz, 1 H), 5.13 (dd, *J* = 10.3, 3.6 Hz, 1 H), 5.06 (d, *J* = 7.9 Hz, 1 H), 4.34-3.96 (m, 4 H), 2.19 (s, 3 H), 2.07 (s, 3 H), 2.06 (S, 3 H), 2.02 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.3, 170.2, 170.1, 169.3, 156.9, 129.5 (2 C), 123.3, 116.9 (2 C), 99.7, 71.0, 70.8, 68.7, 66.9, 61.3, 20.7, 20.6 (3 C).

1-Phenyl-2,3,5,6-di-O-isopropylidene-α-D-mannofuranose 4d.[24]
The title compound was prepared according to the general procedure from commercially available 2,3,5,6-di-O-isopropylidene-α-D-mannofuranose (132 mg) and phenylboronic acid (185 mg) and was purified on silica gel chromatography (cyclohexane/EtOAc, from 100/0 to 80/20) to afford 128 mg (76%) of α anomer only as a white amorphous solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44-7.22 (m, 2 H), 7.06-7.01 (m, 3 H), 5.66 (s, 1 H), 4.94 (dd, *J* = 5.9, 3.4 Hz, 1 H), 4.89 (d, *J* = 5.9 Hz, 1 H), 4.45 (ddd, *J* = 7.9, 6.2, 4.2 Hz, 1 H), 4.21-4.06 (m, 2 H), 4.01 (dd, *J* = 8.7, 4.2 Hz, 1 H), 1.54 (s, 3 H), 1.45 (s, 3 H), 1.40 (s, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.3, 129.5 (2 C), 122.2, 116.6 (2 C), 113.0, 109.4, 104.9, 85.5, 81.2, 79.6, 73.0, 66.9, 26.9, 26.0, 25.2, 24.6.

1-Phenyl-2-deoxy-,3,4,6-tri-O-acetyl-D-glucopyranoside 4e.

The title compound was prepared according to the general procedure from 2-deoxy-3,4,6-tri-O-acetyl-α-D-glucopyranose **1f** (145 mg, α:β = 8:1) and phenylboronic acid (185 mg) and was purified on silica gel chromatography (cyclohexane/EtOAc, from 90/10 to 50/50) to afford 78 mg of the α anomer and 78 mg of the β anomer as white amorphous solids. Global yield: 89 % (0.44 mmol, 163 mg).

1-Phenyl-2-deoxy-,3,4,6-tri-O-acetyl-α-D-glucopyranoside.[25]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40-7.23 (m, 2 H), 7.19-6.91 (m, 3 H), 5.70 (d, *J* = 3.5 Hz, 1 H), 5.55 (ddd, *J* = 11.5, 9.4, 5.4 Hz, 1 H), 5.11 (app t, *J* = 9.8 Hz, 1 H), 4.31 (dd, *J* = 12.1, 4.7 Hz, 1 H), 4.08 (ddd, *J* = 10.1, 4.7, 2.2 Hz, 1 H), 4.01 (dd, *J* = 12.2, 2.3 Hz, 1 H), 2.49 (dd, *J* = 13.1, 5.4 Hz, 1 H), 2.07 (s, 3 H), 2.06 (s, 3 H), 2.03 (s, 3 H), 2.07-1.97 (m, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.6, 170.2, 169.9, 156.1, 129.5 (2 C), 122.4, 116.4 (2 C), 95.2, 69.1, 68.9, 68.6, 62.1, 35.1, 21.0, 20.7 (2 C).

1-Phenyl-2-deoxy-,3,4,6-tri-O-acetyl-β-D-glucopyranoside.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41-7.24 (m, 2 H), 7.09-7.01 (m, 3 H), 5.22 (dd, *J* = 9.6, 2.2 Hz, 1 H), 5.19-5.02 (m, 2 H), 4.34 (dd, *J* = 12.1, 5.6 Hz, 1 H), 4.17 (dd, *J* = 12.2, 2.6 Hz, 1 H), 3.80 (ddd, *J* = 8.6, 5.6, 2.5 Hz, 1 H), 2.54 (ddd, *J* = 13.0, 4.8, 2.2 Hz, 1 H), 2.13-2.02 (m, 10 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.6, 170.2, 169.7, 156.7, 129.5 (2 C), 122.8, 116.7 (2 C), 97.4, 72.2, 70.3, 68.9, 62.5, 35.9, 20.9, 20.7 (2 C). HRMS (ESI) calculated for $C_{18}H_{22}O_8Na$ $[M+Na]^+$ 389.1212, found 389.1205. $[\alpha]_D^{14}$ -30.3° (*c* 0.17, MeOH). FT-IR ν_{max}/cm^{-1} : 1735, 1494, 1364, 1228, 1115, 1050, 993, 914, 762, 695, 593.

1-Phenyl-2,3,4,6-tetra-O-benzyl-D-glucopyranoside 4f.[26]
The title compound was prepared according to the general procedure from commercially available 2,3,4,6-tetra-O-benzyl-α-D-glucopyranoside (270 mg) and phenylboronic acid (185 mg) and was purified on silica gel chromatography (cyclohexane/EtOAc, from 100/0 to 90/10) to afford 252 mg of an inseparable mixture of α and β anomers as an amorphous white solid (82%, α:β = 1.2:1 in NMR, 1.4:1 in HPLC).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37-7.06 (m, 25 Hα, 25 Hβ), 5.55 (d, *J* = 3.5 Hz, 1 Hα), 5.14-5.07 (m, 1 Hα, 2 Hβ), 5.04-4.84 (m, 3 Hα, 4 Hβ), 4.74 (app d, *J* = 12.0 Hz, 1 Hα), 4.68-4.55 (m, 2 Hα, 3 Hβ), 4.47 (app d, *J* = 12.0 Hz, 1 Hα), 4.28 (app t, *J* = 9.2 Hz, 1 Hα), 3.98-3.62 (m, 5 Hα, 6 Hβ). ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.4, 156.8, 138.9, 138.6, 138.3, 138.2, 138.1, 137.9, 129.6, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9,

127.7, 127.6, 122.7, 122.4, 117.0, 116.9, 101.7, 95.5, 84.7, 82.1, 79.8, 77.8, 77.5, 75.8, 75.2, 75.1, 73.5, 73.3, 70.9, 68.9, 68.3. HRMS (ESI) calculated for $C_{40}H_{40}O_6Na$ $[M+Na]^+$ 639.2723, found 639.2737.

1-Phenyl-2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranose 4g.

The title compound was prepared according to the general procedure from 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranose **1h** (172 mg, α:β = 19:1) and phenylboronic acid (185 mg) and was purified on silica gel chromatography (cyclohexane/EtOAc, from 90/10 to 40/60) to afford 45 mg of the α anomer and 12 mg of the β anomer as amorphous white solids. Global yield: 27 % (0.135 mmol, 57 mg).

1-Phenyl-2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-α-D-glucopyranose.[27]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28-7.20 (m, 2 H), 7.03-6.98 (m, 3 H), 5.81 (d, *J* = 9.4 Hz, 1 H), 5.50 (d, *J* = 3.6 Hz, 1 H), 5.37 (dd, *J* = 10.8, 9.4 Hz, 1 H), 5.14 (app t, *J* = 9.7 Hz, 1 H), 4.45 (ddd, *J* = 10.8, 9.4, 3.6 Hz, 1 H), 4.14 (dd, *J* = 12.8, 5.2 Hz, 1 H), 4.00-3.96 (m, 2 H), 2.00 (s, 3 H), 1.97 (s, 3 H), 1.95 (s, 3 H), 1.89 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.5, 170.6, 170.0, 169.3, 155.8, 129.7 (2 C), 123.1, 116.4 (2 C), 95.6, 71.1, 68.4, 67.9, 61.7, 51.9, 23.1, 20.7, 20.6 (2 C).

1-Phenyl-2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranose.[28]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32-7.13 (m, 2 H), 7.04-6.79 (m, 3 H), 5.61 (d, *J* = 8.7 Hz, 1 H), 5.34 (dd, *J* = 10.5, 9.2 Hz, 1 H), 5.20 (d, *J* = 8.2 Hz, 1 H), 5.07 (app t, *J* = 9.5 Hz, 1 H), 4.22 (dd, *J* = 12.2, 5.4 Hz, 1 H), 4.16-3.99 (m, 2 H), 3.90-3.70 (m, 1 H), 2.00 (s, 3 H), 1.99 (s, 3 H), 1.97 (s, 3 H), 1.88 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.8, 170.6, 170.3, 169.4, 157.0, 129.5 (2 C), 123.2, 116.9 (2 C), 99.0, 72.1, 72.0, 68.6, 62.2, 54.8, 23.3, 20.7 (2 C), 20.6.

1-phenyl-2,3,6,2',3',4',6'-Hepta-O-acetylcellobiose 4i.

The title compound was prepared according to the general procedure from **1i** (320 mg) and phenylboronic acid (185 mg) and was purified on silica gel chromatography (cyclohexane/EtOAc, (50/50) to afford 274 mg of an inseparable mixture of α and β anomers as an amorphous white solid (77%, α:β = 1.5:1 in NMR, 1.2:1 in HPLC).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26-7.20 (m, 2 Hα, 2 Hβ), 7.02-6.96 (m, 3 Hα, 1 Hβ), 6.91-6.88 (m, 2 Hβ), 5.63 (app t, *J* = 9.7 Hz, 1 Hα), 5.57 (d, *J* = 3.5 Hz, 1 H α), 5.23-4.96 (m, 2 Hα, 5 Hβ), 4.92-4.84 (m, 2 Hα, 1 Hβ), 4.48-4.29 (m, 3 Hα, 3 Hβ), 4.11-3.94 (m, 3 Hα, 2 Hβ), 3.83-3.71 (m, 1 Hα, 2 Hβ), 3.62-3.59 (m, 1 Hα, 1 Hβ), 2.02-1.91 (m, 21 Hα, 21 Hβ). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 170.4, 170.2, 169.6, 169.3, 169.0, 156.8, 156.2, 129.6, 129.5, 123.3, 122.9, 116.9, 116.6, 100.8, 98.9, 94.1, 76.5, 76.4, 73.0, 72.9, 72.5, 72.0, 71.6, 71.4, 70.6, 69.5, 68.9, 67.8, 61.9, 61.6, 20.6, 20.5. HRMS (ESI) calculated for $C_{32}H_{40}O_{18}Na$ $[M+Na]^+$ 735.2112, found 735.2112. $[\alpha]_D^{14}$ +38.0° (*c* 0.40, DCM). FT-IR ν_{max}/cm^{-1} : 1742, 1368, 1218, 1038, 908, 762, 693, 598.

1-Phenyl-(4-*O*-(4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl))-2,3,6-tri-*O*-acetyl-D-glucopyranose 4j.

The title compound was prepared according to the general procedure from **1j** (462 mg) and phenylboronic acid (185 mg) and was purified on silica gel chromatography (cyclohexane/EtOAc, (50/50) to afford 379 mg of an inseparable mixture of α and β anomers as a white solid (76%, α:β = 1.6:1 in NMR, 1.6:1 in HPLC).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30-7.18 (m, 2 Hα, 2 Hβ), 7.06-6.98 (m, 3 Hα, 1 Hβ), 6.93-6.90 (2 Hβ), 5.68 (app t, *J* = 9.5 Hz, 1 Hα), 5.55 (d, *J* = 3.6 Hz, 1 Hα), 5.37-5.22 (m, 4 Hα, 4 Hβ), 5.08-5.95 (m, 1 Hα, 3 Hβ), 4.87-4.75 (m, 2 Hα, 1 Hβ), 4.71-4.67 (m, 1 Hα, 1 Hβ), 4.42-3.83 (m, 11 Hα, 12 Hβ), 2.08-1.91 (m, 30 Hα, 30 Hβ). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.7, 170.6, 170.5, 170.4, 170.3, 170.0, 169.7, 169.6, 169.4, 156.7, 156.2, 129.6, 123.3, 123.0, 117.0, 116.9, 98.5, 95.9, 95.7, 95.6, 94.3, 75.2, 73.9, 72.7, 72.5, 72.4, 72.2, 72.0, 71.7, 71.0, 70.5, 70.0, 69.4, 69.0, 68.6, 68.5, 68.0, 63.0, 62.6, 62.3, 61.4, 20.8, 20.7, 20.6, 20.5. HRMS (ESI) calculated for $C_{44}H_{56}O_{26}Na$ $[M+Na]^+$ 1023.2958, found 1023.2950. $[\alpha]_D^{14}$ +130.5° (*c* 0.48, MeOH). FT-IR ν_{max}/cm^{-1} : 1742, 1368, 1213, 1029, 897, 761, 693, 600.

(3aS,4R,6R,6aR)-4-phenoxy-2-phenyl-6-(2-phenyl-1,3,2-dioxaborolan-4-yl)tetrahydrofuro[3,4-d][1,3,2]dioxaborole 5a.

Phenylboronic acid (245 mg, 2 mmol) and $MgSO_4$ (2.0 g, 16.6 mmol) were added to a suspension of α-mannose (180 mg, 1.0 mmol) in dioxane (20 mL). The reaction media was then stirred for three hours at room temperature, filtrated and the solvent was evaporated. The resulting diboronate was used without further purification. In a 100 mL round bottom flask, molecular sieves (350 mg), $Cu(OAc)_2{*}H_2O$ (60.0 mg, 0.30 mmol), pyridine (80.0 µL, 1.0 mmol) and dichloroethane (3.0 mL) were introduced successively. The suspension was stirred 5 minutes and phenylboronic acid (365 mg, 3 mmol) was added, followed by the previous diboronate. This mixture was stirred under air atmosphere at room temperature for 24 hours. The media was diluted DCM and filtrated over celite. The solvent was removed by evaporation and the crude residue was purified by silica gel chromatographie (DCM) to afford 172 mg (40%) of the title compound as a single α anomer.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79-7.73 (m, 4 H), 7.49-7.36 (m, 2 H), 7.36-7.26 (m, 4 H), 7.24-7.16 (m, 2 H), 7.01-6.89 (m, 3 H), 5.72 (s, 1 H), 5.24 (dd, *J* = 6.2, 3.9 Hz, 1 H), 5.14 (d, *J* = 6.1 Hz, 1 H), 4.93 (app dt, *J* = 8.1, 6.4 Hz, 1 H), 4.41-4.31 (m, 1 H), 4.21 (dd, *J* = 9.4, 6.6 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 135.1 (2 C), 135.0 (2 C), 132.1, 131.6, 129.6 (2 C), 128.0 (2 C), 127.8 (2 C), 122.6, 116.7 (2 C), 105.2, 86.0, 82.3, 80.6, 74.3, 68.0.[29] ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.2. $[\alpha]_D^{14}$ +106.4° (*c* 0.24, MeOH). FT-IR ν_{max}/cm^{-1} : 1601, 1369, 1297, 1223, 1097, 982, 754, 692, 634.

1-Phenyl-α-D-mannofuranose 6a.

In a round bottom flask, **5a** (693 mg, 1.62 mmol) was suspended in a mixture of EtOH (9.1 mL) and water (4.9 mL). *m*-CPBA[30] (800 mg, 3.24 mmol) was added and the resulting mixture was stirred at room temperature for 4 hours. The solvent was evaporated on a rotavapor and the crude residue was purified by silica gel chromatography (DCM/MeOH, from 100/0 to 90/10) to afford 334 mg (80%) of the titled compound as a colorless oil that solidified over time.

^{1}H NMR (300 MHz, CD_3OD) δ 7.37-7.18 (m, 2 H), 7.04-6.96 (m, 3 H), 5.56 (d, *J* = 3.3 Hz, 1 H),4.39-4.33 (m, 2 H), 4.11 (dd, *J* = 8.1, 3.1 Hz, 1 H), 4.03-3.97 (m, 1 H), 3.78 (dd, *J* = 11.5, 3.1 Hz, 1 H), 3.61 (dd, *J* = 11.5, 6.0 Hz, 1 H). ^{13}C NMR (75 MHz, CD_3OD) δ 158.8, 130.4 (2 C), 123.0, 117.7 (2 C), 107.7, 81.6, 78.9, 72.6, 71.4, 64.7. HRMS (ESI) calculated for $C_{12}H_{16}O_6Na$ $[M+Na]^+$ 279.0845, found 279.0850. $[\alpha]_D^{14}$ +171.4° (*c* 0.32, MeOH). FT-IR ν_{max}/cm^{-1} : 3332, 1599, 1494, 1222, 1007, 885, 823, 752, 690.

Synthesis of starting material 1b, 1d, 1f, 1h, 1i and 1j.

2,3,4,6-tetra-α-O-acetyl-D-glucopyranose 1b.
β-D-glucose pentacetate (3.9 g, 10.0 mmol) was introduced in THF (50.0 mL) and benzylamine (1.2 mL, 11.0 mmol) was added. The resulting solution was stirred at room temperature for 18 hours. The media was diluted with Et_2O and washed with a solution of HCl (1 M) and brine, dried over sodium sulfate and concentrated on a rotavapor. The crude residue was purified on silica gel chromatography (cyclohexahe/EtOAc, from 70/30 to 60/40) to afford the desired product as an inseparable mixture of two anomers. White foam, 2.9 g (82%, α:β = 3:1). NMR data were in good agreement with the literature.[31]

^{1}H NMR (300 MHz, $CDCl_3$) δ (α anomer) 5.54 (app t, *J* = 9.8 Hz, 1 H), 5.47 (app t, *J* = 3.7 Hz, 1 H), 5.09 (app t, *J* = 9.8 Hz, 1 H), 4.93-4.87 (m, 1 H), 4.29-4.22 (m, 2 H), 4.17-4.12 (m, 1 H), 3.52 (d, *J* = 3.9 Hz, 1H), 2.11-2.03 (m, 12 H), (β anomer) 5.26 (app t, *J* = 9.5 Hz, 1 H), 5.13-5.06 (m, 1 H), 4.93-4.87 (m, 1 H), 4.75 (app t, *J* = 8.3 Hz, 1 H), 4.29-4.22 (m, 1 H), 4.17-4.12 (m, 1 H), 3.85 (d, *J* = 8.7 Hz, 1H), 3.77 (ddd, *J* = 10.0, 4.8, 2.4 Hz, 1 H), 2.11-2.03 (m, 12 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.8, 170.7 (β), 170.2, 169.6, 169.5 (β), 95.5 (β), 90.1(α), 73.2(β), 72.3(β), 72.1(β), 71.1, 69.9(α), 68.5(α), 68.5(β), 67.2(α), 62.0(α), 20.7, 20.6.

2,3,4,6-Tetra-O-acetyl-α-D-mannopyranose 1c.
In a round bottom flask, D-mannose (3.06 g, 17 mmol) was dissolved in pyridine (15.0 mL, 186 mmol). Then, acetic anhydride (16.0 mL, 170 mmol) was carefully added. The resulting mixture was stirred overnight at room temperature. The media was poured into water and the aqueous layer was extracted three times with EtOAc. The combined organic layer was then successively washed with $NaHCO_3$ (sat), water and brine, dried over sodium sulfate and concentrated under reduced pressure to afford a brown foam. This intermediate was introduced in Et_2O (85.0 mL) and benzylamine (2.05 mL, 18.7 mmol) was added. The resulting solution was stirred at room temperature for 5 hours. The media was then washed with NH4Cl (sat) and brine, dried over sodium sulfate and concentrated on a rotavapor. The crude residue was purified on silica gel chromatography (cyclohexahe/EtOAc, from 80/20 to 50/50) to afford the desired product as an inseparable mixture of two anomers. White foam, 4.1 g (70%, α:β = 9:1). NMR data were in good agreement with the literature.[32]

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.41 (dd, *J* = 10.1, 3.2 Hz, 1 H), 5.32-5.22 (m, 3 H), 4.27-4.19 (m, 2 H), 4.16-4.11 (m, 1 H), 3.75 (d, *J* = 4.1 Hz, 1 H), 2.15 (s, 3 H), 2.09 (s, 3 H), 2.04 (s, 3 H), 1.99 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.9, 170.2, 170.1, 169.8, 92.1, 70.1, 68.8, 68.5, 66.2, 62.6, 20.9 (2 C), 20.7 (2 C).

2,3,4,6-Tetra-O-acetyl-D-galactopyranose 1d.
In a round bottom flask, hydrazine acetate (0.26 g, 2.82 mmol) was added to a solution of β-D-galactose pentaacetate (1.00 g, 2.56 mmol) in DMF (30 mL). The resulting mixture was stirred at 55 °C for 2 hours. The media was allowed to cool down at room temperature and was diluted with EtOAc and a saturated solution of $NaHCO_3$. The aqueous layer was extracted with EtOAc and the combined organic layer was washed with brine. The solvent was dried over $MgSO_4$, filtrated and evaporated. The resulting oil was diluted with toluene and the volatiles were evaporated on a rotavapor. This procedure was performed until most of the DMF was eliminated. The crude residue was then purified by silica gel flash chromatography (cyclohexane/EtOAc, from 80/20 to 40/60) to afford the title compound as a mixture of two anomers. Amorphous white solid, 400 mg (45%, α:β = 2.3:1). The NMR data were in good agreement with the literature.[33]

^{1}H NMR (300 MHz, $CDCl_3$) δ (α anomer) 5.44 (app t, *J* = 3.6 Hz, 1 H), 5-41-5.40 (m, 1 H), 5.33-5.32 (m, 1 H), 5.07 (dd, *J* = 10.8, 3.5 Hz, 1 H), 4.41 (app t, *J* = 6.6 Hz, 1 H), 4.10-4.02 (m, 2 H), 3.93-3.90 (m, 1H), 2.08 (s, 3 H), 2.03 (s, 3 H), 1.99 (s, 3 H), 1.93 (s, 3 H), (β anomer) 5.36 (d, *J* = 3.4 Hz, 1 H),5.02-5.00 (m, 2 H), 4.65 (app t, *J* = 7.5 Hz, 1 H), 4.14 (d, *J* = 8.5 Hz, 1 H), 4.10-4.02 (m, 2 H), 3.93-3.90 (m, 1 H), 2.10 (s, 3 H), 2.03 (s, 3 H), 1.99 (s, 3 H), 1.93 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (α anomer) 170.6, 170.5, 170.3, 170.2, 170.1, 90.6, 68.4, 68.2, 67.3, 66.1, 61.8, 20.8, 20.7, 20.6, 20.5, (β anomer) 170.9, 170.6, 170.2, 170.1, 95.9, 70.9 (2 C), 70.5, 67.2, 61.5, 20.8, 20.7, 20.6, 20.5.

2-Deoxy-3,4,6-tri-O-acetyl-α-D-glucopyranose 1f.
In a round bottom flask and under inert atmosphere, LiBr (1.00 g, 11.52 mmol), amberlite IR120 (1.00 g) and water (1.2 ml) were added to a solution of tri-O-acetyl-D-glucal (1.00 g, 3.67 mmol) in MeCN (30 mL). The solution was stirred at room temperature for 5 h, filtered and neutralized with triethylamine. The volatiles were removed by evaporation on a rotavapor . The residue was dissolved in DCM and water. The organic phase was washed with an ice cold solution of HCl (1M) and $NaHCO_3$ (sat), dried over Na_2SO_4, filtered and evaporated to dryness. Purification by flash column chromatography on silica gel (cyclohexane/EtOAc, 60/40) afforded the desired product as a mixture of two anomers. White amorphous solid, 390 mg (37%, α:β = 8:1). NMR data were in good agreement with the literature.[34]

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.43-5.34 (m, 2 H), 5.01 (app t, *J* = 9.5 Hz, 1 H), 4.30-4.19 (m, 2 H), 4.11-4.07 (m, 1 H), 2.82-2.80 (m, 1 H), 2.28 (dd, *J* = 13.3, 5.6 Hz, 1 H), 2.09 (s, 3 H), 2.04 (s, 3 H), 2.01 (s, 3 H), 1.86-1.77 (m, 1 H). ^{1}H NMR (300 MHz, $CDCl_3$) δ 170.8, 170.2, 169.9, 91.6, 69.5, 68.7, 68.0, 62.5, 35.1, 20.9, 20.7(2 C).

2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranose 1h.
In a round bottom flask, glucosamine hydrochloride (2.0 g, 9.3 mmol) was introduced in pyridine (26.0 mL, 322 mmol). Then, acetic anhydride (13.0 mL, 138 mmol) was carefully added. The resulting mixture was stirred overnight at room temperature. The media was poured into water and the aqueous layer was extracted three times with EtOAc. The combined organic layer was then successively washed with $NaHCO_3$ (sat), water and brine, dried over sodium sulfate and

concentrated under reduced pressure. This intermediate was dissolved in Et_2O (40 mL) and 4.6 mL of a 2 M solution of methylamine in MeOH (9.2 mmol) was then added. The resulting solution was stirred at room temperature for 4 hours. The media was then washed with NH4Cl (sat) and brine, dried over sodium sulfate and concentrated on a rotavapor. The crude residue was purified on silica gel chromatography (DCM/MeOH, from 100/0 to 95/5) to afford the desired product as a mixture of two anomers. White amorphous solid, 2.4 g (73%, α:β = 19:1). NMR data were in good agreement with the literature.[35]

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.00 (d, *J* = 9.3 Hz, 1 H), 5.31-5.22 (m, 2 H), 5.11 (app t, *J* = 9.5 Hz, 1 H), 4.67-4.66 (m, 1 H), 4.30-4.07 (m, 4 H), 2.07 (s, 3H), 2.01 (s, 4H), 2.01 (s, 4H), 1.95 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.4, 171.0, 170.6, 169.4, 91.5, 71.0, 68.3, 67.5, 62.1, 52.4, 23.1, 20.7 (2 C), 20.6.

2,3,6,2',3',4',6'-Hepta-O-acetylcellobiose 1i.
In a round bottom flask, α-D-cellobiose octaacetate (1.36 g, 2.00 mmol) was dissolved in a mixture of THF (15.0 mL) and acetone (2.0 mL). To this solution was added benzylamine (660 µL, 6.0 mmol) and the resulting mixture was heated at 50 °C overnight. After cooling, the volatiles were evaporated and the residue was dissolved in DCM. The organic layer was successively washed with a solution of HCl(1 M), $NaHCO_3$ (sat) and brine, dried over magnesium sulfate, filtrated and evaporated to dryness. Purification by flash column chromatography on silica gel (cyclohexane/EtOAc, 60/40) afforded the desired product as a mixture of two anomers. White amorphous solid, 710 mg (56%, α:β = 1.3:1). NMR data were in good agreement with the literature.[36]

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.48 (app t, *J* = 9.7 Hz, 1 Hα), 5.34 (app t, *J* = 3.7 Hz, 1 Hα), 5.22-5.01 (m, 2 Hα, 3 Hβ), 4.93-4.87 (m, 1 Hα, 1 Hβ), 4.82-4.68 (m, 1 Hα, 2 Hβ), 4.53-4.47 (m, 2 Hα, 2 Hβ), 4.37-4.32 (m, 1 Hα, 1 Hβ), 4.17-3.92 (m, 3 Hα, 3 Hβ), 3.79-3.62 (m, 3 Hα, 3 Hβ), 2.11-1.96 (m, 21 Hα, 21 Hβ). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.6, 170.4, 170.3, 169.7, 169.3, 169.0, 100.8, 100.6, 95.2, 90.0, 76.5, 73.3, 73.0, 72.9, 71.9, 71.6, 71.3, 69.3, 68.2, 67.9, 67.8, 61.9, 61.8, 61.6, 20.9, 20.7, 20.6, 20.5. HRMS (ESI) calculated for $C_{26}H_{36}O_{18}Na$ $[M+Na]^+$ 654.2245, found 654.2251.

4-*O*-(4-*O*-(2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl)-2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl)-2,3,6-tri-*O*-acetyl-D-glucopyranose 1j.
In a round bottom flask, sodium acetate (0.70 g, 8.30 mmol) and maltotriose (3.00 g, 6.00 mmol) were added in acetic anhydride (50 mL). The reaction media was then refluxed under stirring for 2 hours. The mixture was allowed to cool down at room temperature and was diluted with DCM (50 mL). Water (100 mL) was carefully added and the media was stirred at room temperature for 10 minutes. The aqueous layer was extracted twice with DCM. The combined organic layers were washed twice with a solution of $NaHCO_3$ (sat) and with brine, dried over magnesium sulfate and the solvent was evaporated to afford a yellow oil that was directly engaged in the next step. This crude product was dissolved in THF (20 mL) and benzylamine (0.98 mL, 9.00 mmol) was added. The reaction mixture was stirred at room temperature overnight. Volatiles were evaporated, and the resulting residue was dissolved in DCM (50 mL) and successively washed with a solution of HCl (1 M), $NaHCO_3$ (sat) and brine. The organic layer was dried over magnesium sulfate, filtrated and the solvent was evaporated. Purification by silica gel chromatography (cyclohexane/EtOAc : 60/40) afforded the desired compound as a mixture of two anomers. White amorphous solid, 3.05 g (55%, α:β = 1.6:1). NMR data were in good agreement with the literature.[37]

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.56 (app t, *J* = 9.4 Hz, 1 H), 5.42-5.24 (m, 5 Hα, 5 Hβ), 5.08-5.01 (m, 1 Hα, 1 Hβ), 4.85-4.81 (m, 1 Hα, 1 Hβ), 4.77-4.70 (m, 2 Hα, 2 Hβ), 4.48-4.44 (m, 2 Hα, 2 Hβ), 4.30-3.89 (m, 9 Hα, 10 Hβ), 3.78-3.74 (m, 1 Hα, 1 Hβ), 2.15-1.97 (m, 30 Hα, 30 Hβ). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.7, 170.6, 170.5, 170.4, 170.2, 169.9, 169.8, 169.7, 169.4, 95.8, 95.6, 94.9, 90.0, 74.7, 73.8, 73.7, 72.6, 72.5, 72.4, 72.3, 71.8, 71.7, 71.6, 70.4, 70.1, 69.4, 69.0, 68.9, 68.5, 68.0, 67.7, 63.0, 62.4, 62.3, 61.4, 20.9, 20.8, 20.6, 20.5. HRMS (ESI) calculated for $C_{38}H_{52}O_{26}Na$ $[M+Na]^+$ 947.2645, found 947.2674.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.
Full optimization table, NMR spectra of all synthesized compounds and HPLC chromatograms.

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Author Contributions

The manuscript was written through contributions of all authors. / All authors have given approval to the final version of the manuscript.

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