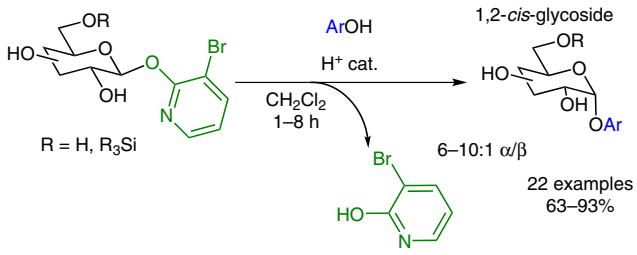
Synthesis G. St-Pierre et al. Paper

Stereocontrolled Synthesis of Phenolic α-D-Glycopyranosides

Gabrielle St-Pierre
Laila Dafik
Ellen Klegraf
Stephen Hanessian*

Department of Chemistry, Université de Montréal,
PO Box 6128, Succ., Centre-ville, Montréal, Québec,
H3C 3J7, Canada
stephen.hanessian@umontreal.ca

Dedicated to Professor Richard Schmidt for his seminal contributions to glycoside synthesis



Received: 04.04.2016
Accepted after revision: 25.04.2016
Published online: 14.06.2016
DOI: 10.1055/s-0035-1561461; Art ID: ss-2016-m0233-op

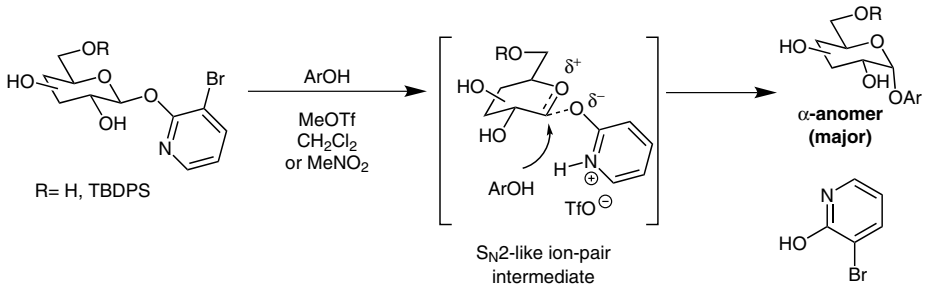
Abstract Adopting the 'remote activation concept' toward stereocontrolled glycoside synthesis with minimal use of protection groups, a general synthesis of phenolic 1,2-*cis* glycopyranosides is reported, as exemplified by aryl α-D-galacto-, α-D-gluco- and 2-azido α-D-glucopyranosides among others using glycosyl donors bearing an anomeric (3-bromo-2-pyridyloxy) group and catalyzed by methyl triflate.

Key words aryl glycoside, stereocontrolled glycosidation, minimal protection, 1,2-*cis* D-glycopyranoside, phenyl sialoside

Phenolic glycosides are widespread in the plant world and exhibit a variety of activities including their mobilization as host defensive agents against herbivores.[1] They are among the most common of all plant metabolites, occurring as simple monoglycosides or more complex congeners.[2] Salicin, (2-carboxyphenyl-β-D-glucopyranoside), is perhaps historically the most well studied phenolic glycoside since the realization even from millennia, that the extracts from the bark of the Salix plant and willow leaf had analgesic properties.[3] The synthesis of phenolic α-D-glycopyranosides is less well documented.[4] The first documented synthesis of phenyl D-glucopyranoside dates back to 1879 when A. Michael treated 2,3,4,6-*O*-acetyl-D-glucopyranosyl bromide with phenol and potassium carbonate in ethanol.[5] During the following half century, a number of methods were reported toward the preparation of α- and β-phenyl D-glucopyranosides by some of the most prodigious carbohydrate chemists of their time. In 1926, Fischer and Mechel[6] were the first to report the preparation of phenyl α-D-glucopyranoside acetate and its β-anomer in a ratio 2:3, from the reaction of tetra-*O*-acetyl-D-glucopyranosyl bromide with phenol in presence of quinoline. Helferich and co-workers[7] reported a practical method for the preparation of acetylated phenyl α- and β-D-glucopyranosides by heating β-D-glucose pentaacetate with phenol in the presence of catalysts such as $ZnCl_2$ or TsOH, respectively. Performing the reaction as a melt in the presence of $ZnCl_2$ with removal of acetic acid under vacuum, Montgomery, Richtmyer, and Hudson[8] obtained crystalline phenyl α-D-glucopyranoside tetraacetate in 64% yield. They also showed that phenyl β-D-glucopyranoside tetraacetate could be partially converted into the α-anomer by heating with phenol in the presence of $ZnCl_2$. The method was extended to *p*-nitrophenyl α- and β-D-glucopyranosides.[8]

Interest in the preparation of aryl α-D-glycopyranosides continues to flourish to this day. For example, Briner and Vasella[9] obtained 1,2-*cis*-*p*-substituted aryl glucopyranosides using an anomeric diazirine derivative of tetra-*O*-benzyl-D-glucopyranoside. Mahling and Schmidt[10] prepared phenyl α-D-glycopyranosides from the corresponding glycopyranosyl trichloroacetimidates in the presence of TMSOTf as catalyst. Using catalytic ytterbium(III) triflate with triaryloxyboranes as acceptors and anomerically acetylated donors, Yamanoi and co-workers[11] prepared the corresponding aryl α-D-glycopyranosides. Schmidt and co-workers[12] explored a 1,2-*cis*-conjugated addition of phenols, including *N*-Boc L-tyrosine methyl ester to tetra-*O*-benzyl-2-nitro-D-galactal. Sokolov and co-workers[13] used $BF_3{\cdot}OEt_2$ as catalyst to prepare aryl α- and β-D-glucopyranosides. Very recently, Ye and co-workers[14] used additives in the conversion of *O*-protected and functionalized thiocresyl 2-amino-2-deoxy β-D-glycopyranosides into the corresponding phenolic glycopyranosides with α/β ratios of >20:1, or mixtures thereof, depending on the nature of the additive and the promoter. In all of these reactions, care should be exercised to avoid the formation of aryl *C*-glycosides.[15]

Although meritorious in many ways, the above methods all rely on the use of *O*-protected glycopyranosyl donors.



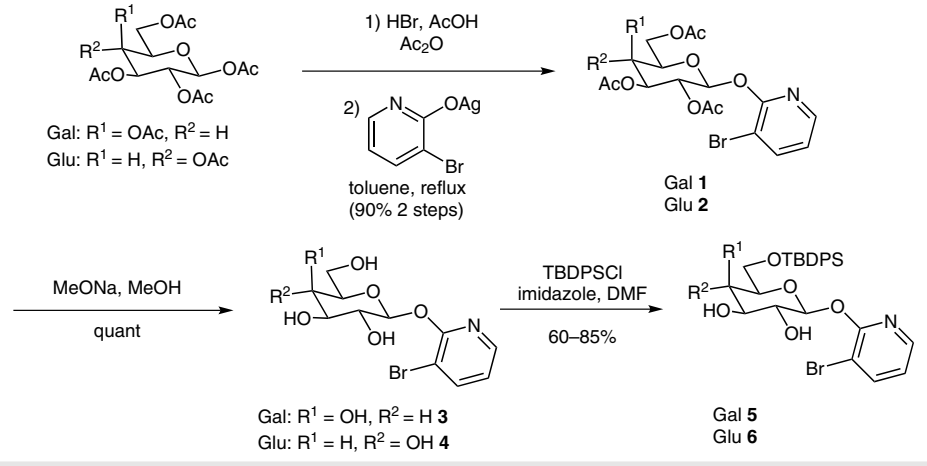
Scheme 1 Aryl glycosidation via the 'remote activation concept'

In 1980, we reported the use of 2-pyridylthio-β-D-glucopyranosides as unprotected glycopyranosyl donors toward the synthesis of glycosides.[16] Using a variety of alcohol acceptors including sugars, and activation with soft heavy metal salts such as mercuric nitrate led to alkyl α-D-glucopyranosides as major products.

The metal served to activate the heterocyclic moiety leading to an S_N2-like attack at the anomeric position. Further studies led to the anomeric (3-methoxy-2-pyridyloxy) (MOP) glycopyranosides which also led to smooth S_N2-like displacements when activated with sub-stoichiometric amounts of methyl triflate (Scheme 1).[17] Unprotected or minimally (*O*-6 TBDPS) protected MOP glycosides afforded alkyl α-D-glycopyranosides with excellent selectivity. The reactions were equally successful for the synthesis of 1,2-*cis*-glycopyranosyl esters[18] and phosphates.[19] We termed the process 'remote activation'.[17,20]

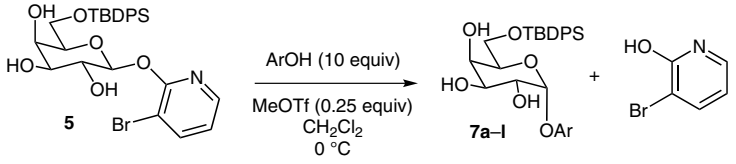
In this paper, we report on our efforts to synthesize a variety of phenyl, naphthyl, and related aryl glycopyranosides, predominantly as α-D-galacto-, α-D-gluco-, and 2-azido-2-deoxy-α-D-glucopyranosides as prototypes. We chose 6-*O*-TBDPS substituted (3-bromo-2-pyridyloxy) β-D-galacto and β-D-glucopyranosides as glycopyranosyl donors (Scheme 2). Typically, reactions were run in dichloromethane as solvent with 10 equivalents of the phenolic acceptor in the presence of 0.25 equivalents of MeOTf. The results are summarized in Table 1 and Table 2. In general, yields were above 75% with excellent α-selectivities for D-galacto- and D-glucopyranosides. The amount of the phenol could be reduced to 1.5 equivalents at the expense of some stereochemical erosion, but with only minor changes in yields. In most cases, the anomeric glycosides could be separated by column chromatography. A practical advantage is that the progress of the reaction could be easily monitored with the release of 2-hydroxy-3-bromopyridine.

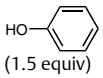
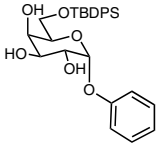
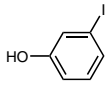
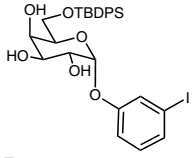
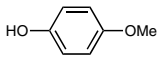
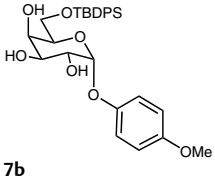
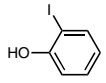
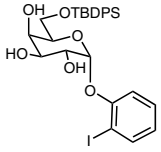
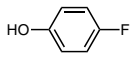
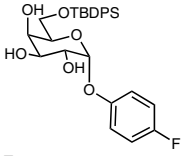
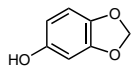
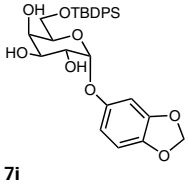
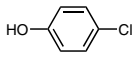
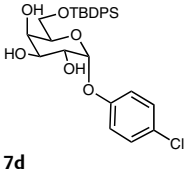
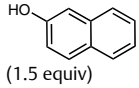
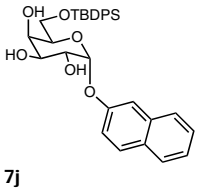
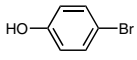
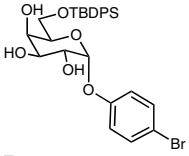
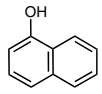
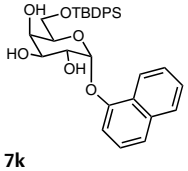
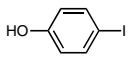
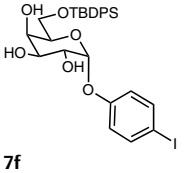
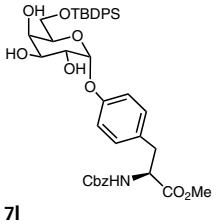
To totally avoid the use of the 6-*O*-TBDPS group, we turned to DMF as a solvent. However, this led to total recovery of starting material, presumably due to the consumption of MeOTf by reaction with the DMF. Successful glycosidation could be achieved using nitromethane as solvent with the unprotected D-galactopyranosyl donor **3**, albeit in dilute solution due to low solubility (Scheme 3).



Scheme 2 Synthesis of the (3-bromo-2-pyridyloxy) β-D-glycopyranosyl donors

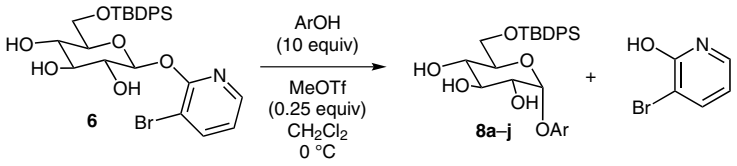
Table 1 Formation of Aryl 6-*O*-TBDPS-α-D-galactopyranosides



Entry	ArOH	Yield (%)[a]	Time (h)	α/β[b]	α-Anomer	Entry	ArOH	Yield (%)[a]	Time (h)	α/β[b]	α-Anomer
1	 (1.5 equiv)	88	3	10.0:1 (4.0:1)	 **7a**	7		65	8	6.5:1	 **7g**
2		84	2.5	9.0:1	 **7b**	8		63	8	6.0:1	 **7h**
3		82	2.5	6.6:1	 **7c**	9		93	3	7.0:1	 **7i**
4		83	2.5	7.2:1	 **7d**	10	 (1.5 equiv)	83	3	8.4:1 (4.4:1)	 **7j**
5		85	2.5	8.0:1	 **7e**	11	 (1.5 equiv)	83	3	8.2:1 (4.8:1)	 **7k**
6		80	2.5	8.8:1	 **7f**	12	Cbz-Tyr-OMe[c]	70	1	7.0:1	 **7l**

[a] Yields of α/β obtained from flash chromatography; α and β separable with a careful flash column chromatography; β-anomer was not isolated.
[b] Determined by ^{1}H NMR 400 MHz on the crude.
[c] 5 equiv of Cbz-Tyr-OMe were used.

Table 2 Formation of Aryl 6-*O*-TBDPS-α-D-glucopyranosides



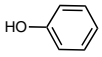
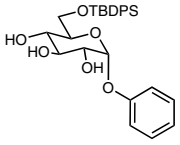
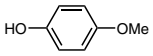
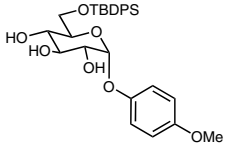
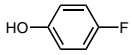
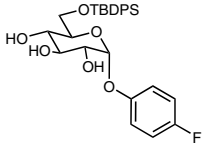
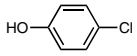
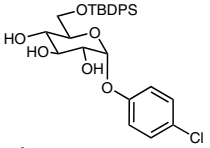
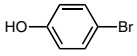
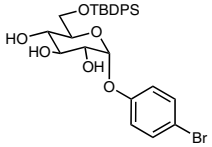
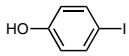
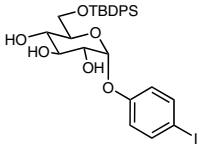
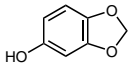
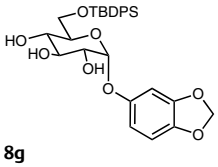
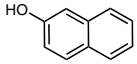
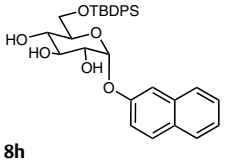
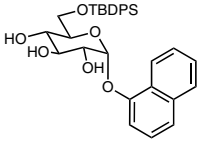
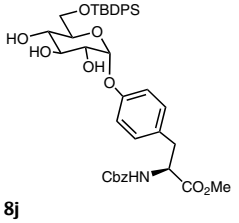
Entry	ArOH	Yield (%)[a]	Time (h)	α/β[b]	α-Anomer
1		80	3	9.2:1	 **8a**
2		80	3	6.6:1	 **8b**
3		76	3	5.1:1	 **8c**
4		76	3	6.8:1	 **8d**
5		75	3	7.2:1	 **8e**
6		79	3	8.3:1	 **8f**
7		93	4	6.0:1	 **8g**

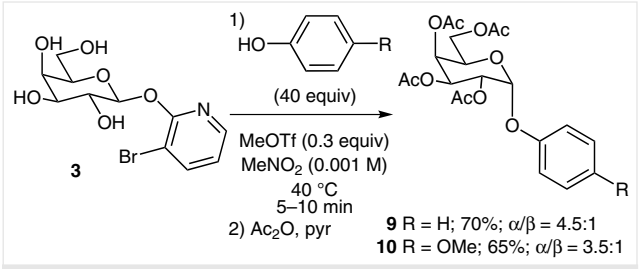
Table 2 (continued)

Entry	ArOH	Yield (%)[a]	Time (h)	α/β[b]	α-Anomer
8	 (1.5 equiv)	80	4	7.4:1 (4.0:1)	 **8h**
9	 (1.5 equiv)	80	4	7.3:1 (4.0:1)	 **8i**
10	Cbz-Tyr-OMe[c]	68	2	6.6:1	 **8j**

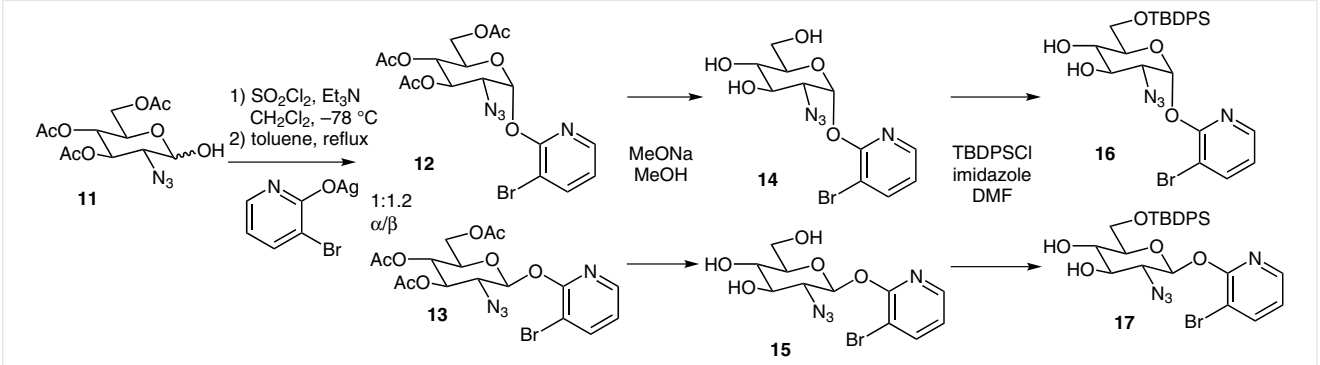
[a] Yields of α/β obtained from flash chromatography; α and β separable with a careful flash column chromatography; β-anomer was not isolated.
[b] Determined by ^{1}H NMR 400 MHz on the crude.
[c] 5 equiv of Cbz-Tyr-OMe were used.

Next, the formation of aryl α-D-glycopyranosides containing a masked amino group at C-2 in the form of an azide was explored. The synthesis of (3-bromo-2-pyridyloxy) 2-azido-2-deoxy α- and β-D-glucopyranosyl donors **16** and **17** is shown in Scheme 4. Starting from the known triacetate **11**,[21] it was possible to obtain the two donors **12** and **13** in a ratio 1:1.2, respectively. Deprotection of the esters and introduction of the 6-*O*-TBDPS group gave the (3-bromo-2-pyridyloxy) α- and β-glycopyranosyl donors **16** and **17**.

Application of the glycosidation reaction in this series led to the corresponding aryl 2-azido-2-deoxy D-glucopyranosides in a ratio favoring the α-anomer regardless of the anomeric configuration of the starting donor (Scheme 5). We attribute this to a stereoelectronic effect, wherein the oxocarbenium ion intermediate, now harboring the linear electron-withdrawing azide group at C-2, is attacked by the alcohol more favorably in an axial mode thereby restoring

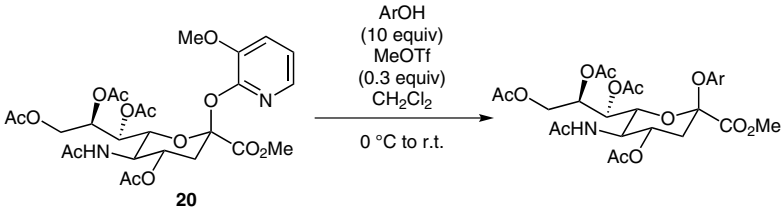


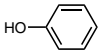
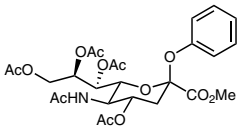
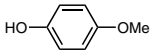
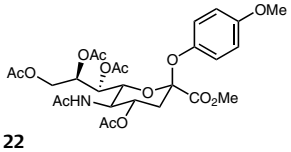
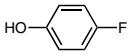
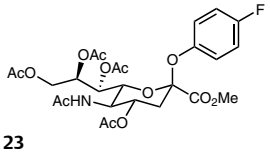
Scheme 3 Formation of aryl α-D-galactopyranosides in nitromethane



Scheme 4 Synthesis of the (3-bromo-2-pyridyloxy) 2-azido-2-deoxy α- and β-D-glucopyranosyl donors

Table 3 Formation of Aryl Sialosides



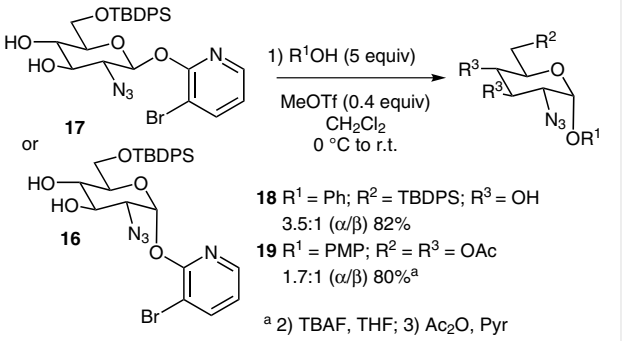
Entry	ArOH	Yield (%)[a]	Time (h)	α/β[b]	Product β-anomer
1		65	6	1:5	 **21**
2		73	6	1:5	 **22**
3		63	6	1:3.6	 **23**

[a] Yields of α/β obtained from preparative HPLC-MS; anomers are separable by preparative HPLC.
[b] Determined by ^{1}H NMR 400 MHz on the crude.

the charge. This is in line with the much longer reaction times compared to the 2-hydroxy counterparts. No anomerization of the donors was observed under the reaction conditions.

Finally, we were pleased that the remote activation glycosidation reaction was also applicable to sialic acid derivatives using (3-methoxy-2-pyridyloxy) sialyl donor **20** previously reported from our group,[18] giving separable mixtures of aryl *N*-acetylneuraminic acid methyl esters, in which the β-anomers predominated (Table 3). It is also interesting to note the formation of the glycal, which is often reported as a side-product in glycosidations with anomerically activated sialyl donors such as chloride or fluoride.[22,23]

In spite of numerous methods of anomeric activation, the synthesis of phenolic glycosides has invariably relied on the use of *O*-protected donors. The yields appear to vary with the nature of the anomeric substituent and the conditions. For example, peracetylated β-D-glucopyranose is converted into the α-anomer in the presence of excess $BF_3{\cdot}OEt_2$, which is inert to glycosidation.[24] Longer reaction times at higher temperatures in polar solvents are needed to increase the ratio of the phenyl α-D-glucopyranoside,[13] at the risk of forming *C*-glycosides.[10] The formation of *C*-glycosides, particularly in the case of electron-rich aromatic phenols, is common under acidic conditions with hard Lewis acid such as $BF_3{\cdot}OEt_2$ or TMSOTf.[10] The yields and reaction rates of aryl glycosides from peracetylated sugars depend on the nature of the substituent on the phenol. In general, the electron-donating groups such as alkoxy ethers give better yields compared to ones with electron-withdrawing groups.[4]



Scheme 5 Synthesis of the anomeric phenyl 2-azido-2-deoxy-D-glucopyranosides

As shown in Tables 1 and 2, the formation of aryl α-D-galactopyranosides and aryl α-D-glucopyranosides as the major products is independent of the electronic nature of the phenol (Table 1, entries 1–5; Table 2, entries 1–5). Reactions are completed within 3 hours under mild conditions, generally at 0 °C, and in the presence of 0.25 equivalent of MeOTf. The presence of the *O*-TBDPS group, as a minimal protection, aids in preforming the reactions in dichloromethane as solvent. A significant rate difference is observed between *ortho*-, *meta*-, and *para*-iodophenols. While 2- and 3-iodophenols required 8 hours for completion of reaction to afford the corresponding 2- and 3-iodophenyl glycopyranosides (Table 1, entries 7, 8; 65% and 63% yield; 5.8:1 and 6.5:1 α/β ratio, respectively), 4-iodophenol led to a 80% yield and 8.8:1 ratio in favor of the α-anomer (Table 1, entry 6). Sesamol, 1-, and 2-naphthols led to the corresponding aryl α-D-galacto- and α-glucopyranosides in excellent yields and good anomeric selectivities (Table 1, entries 9–11; Table 2, entries 7–9). The resulting 2-naphthyl 6-*O*-TBDPS-α-D-galactopyranoside was stable in the presence of 50 mol% of MeOTf and only a trace of anomerization was detected by NMR spectroscopy (~19:1 α/β) over 72 hours contrary to the case of the α- an β-D-phenyl glycopyranosides of peracetylated sugars which are converted into anomeric mixtures in the presence of Lewis acids to varying degrees.[13,25,26] Excellent yields and selectivities were observed in the case of *N*-Cbz-tyrosine methyl ester (Table 1, entry 12; Table 2, entry 10). This is a good example of direct and highly stereoselective α-glycosidation with tyrosine in the absence of protecting groups such as benzyl ethers.[12,27]

Adopting the 'remote anomeric activation' methodology, using (3-bromo-2-pyridyloxy) β-D-hexopyranosides as minimally protected glycopyranosyl donors in the D-gluco-, D-galacto-, and 2-azido-2-deoxy-D-glucopyranoside series, in conjunction with methyl triflate as a sub-stoichiometric Lewis acid promoter, we can achieve the synthesis of the arduously accessible aryl α-D-glycopyranosides in good to excellent α/β selectivities and preparatively useful yields. The facile synthesis of aryl 2-azido-2-deoxy-α-D-glucopyranosides is particularly interesting since it provides access to aryl 2-amino-2-deoxy-α-D-glucopyranosides that can be orthogonally functionalized.[28] The easily separated anomeric glycosides in their mostly unprotected form can find utility in the synthesis of libraries of phenolic glycopyranosides with a variety of applications as enzyme inhibitors[29,30] or substrates[31] and in carbohydrate mediated drug delivery.[32,33] Selected examples toward the synthesis of aryl β-D-hexopyranosides from acetylated 3-bromo-2-pyridyloxy β-glycopyranosyl donors by anchimeric assistance are shown in the Supporting Information.

Anhyd solvents such as CH_2Cl_2, toluene, nitromethane, and DMF were dried with molecular sieves. MeOH was distilled under a positive pressure of dry argon with CaH_2 before use. ^1H and ^{13}C NMR spectra were recorded on Bruker Avance III-400, AV-500, and AV-700 spectrometers. Reactions were performed under argon atmosphere. High-resolution mass spectra were recorded on LC-TOF Agilent Technologies 1260 Infinity spectrometer using electrospray technique (ESI). Low-resolution mass spectra of the reactions were recorded on Agilent Technologies 1200 Series spectrometer (ESI). Optical rotations were recorded on a PerkinElmer 343 polarimeter with wavelength of 589 nm in a 1 dm cell at 25 °C. The melting point was defined on Büchi B-540 apparatus. Analytical TLC was done using silica gel 0.25 mm glass sheets (Silicycle). Visualization was performed by UV light and/or by staining with ceric ammonium molybdate. Flash column chromatography was performed using (40–63 µM, Silicycle) silica gel at increased pressure.

(3-Bromo-2-pyridyloxy) 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside (1)

To a solution of β-D-galactose pentaacetate (7.80 g, 20.0 mmol) in AcOH (20.0 mL, 1.0 M) was added a solution of 30% HBr in AcOH (10.9 mL, 60.0 mmol, 3.00 equiv) and Ac_2O (0.47 mL, 5.00 mmol, 0.25 equiv). The solution was stirred at r.t. for 2 h, poured onto ice, and extracted with CH_2Cl_2 (2 × 150 mL). The separated and combined organic phases were washed with cold H_2O (100 mL), cold aq $NaHCO_3$ (100 mL), brine (150 mL), dried (Na_2SO_4), filtered, and concentrated in vacuo. The residue was co-evaporated with toluene and then dissolved in anhyd toluene (71.4 mL, 0.28 M). The (3-bromo-2-pyridyloxy) silver salt[34] (16.8 g, 60.0 mmol, 3.00 equiv) was added and the suspension was stirred at reflux for 3 h. The cooled mixture was filtered through Celite, washed with EtOAc, and then concentrated. The residue (1:13; α/β) was purified by flash column chromatography (40:60; EtOAc/hexanes). The major β-D-anomer was obtained as a white solid (8.07 g, 80%); mp 126.3–127.4 °C; $[\alpha]_D^{25}$ +13.0 (*c* 0.10, $CHCl_3$).

IR (neat): 3017, 2942, 1749, 1432, 1071 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.09 (dd, *J* = 4.8, 1.7 Hz, 1 H), 7.84 (dd, *J* = 7.7, 1.7 Hz, 1 H), 6.89 (dd, *J* = 7.7, 4.8 Hz, 1 H), 6.01 (d, *J* = 8.3 Hz, 1 H, H-1), 5.59 (dd, *J* = 10.4, 8.3 Hz, 1 H, H-2), 5.47 (d, *J* = 3.5 Hz, 1 H, H-4), 5.16 (dd, *J* = 10.4, 3.5 Hz, 1 H, H-3), 4.20–4.14 (m, 3 H, H-5, 2H-6), 2.18 (s, 3 H), 2.02 (s, 3 H), 2.01 (s, 3 H), 2.00 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.5, 170.4, 170.3, 169.4, 157.9, 145.5, 142.6, 120.0, 107.4, 95.1, 71.4, 71.1, 68.1, 67.1, 61.2, 20.84, 20.83, 20.80, 20.75.

HRMS-ESI: *m*/*z* $(M + Na)^+$ calcd for $C_{19}H_{22}BrNO_{10}Na$: 526.0319; found: 526.0328 (+1.62 ppm).

(3-Bromo-2-pyridyloxy) 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (2)

To a solution of β-D-glucose pentaacetate (7.80 g, 20.0 mmol) in anhyd CH_2Cl_2 (20.0 mL, 1.0 M) was added a solution of 30% HBr in AcOH (12.3 mL, 68.0 mmol, 2.5 equiv) and Ac_2O (0.47 mL, 5.00 mmol, 0.25 equiv). The solution was stirred at r.t. for 2 h, poured onto ice, and extracted with CH_2Cl_2 (2 × 150 mL). The separated and combined organic phase were washed with cold H_2O (100 mL), cold aq $NaHCO_3$ (100 mL), brine (150 mL), dried (Na_2SO_4), filtered, and concentrated in vacuo. The residue was co-evaporated with toluene and then dissolved in anhyd toluene (71.4 mL, 0.28 M). The (3-bromo-2-pyridyloxy) silver salt (16.8 g, 60.0 mmol, 3.00 equiv) was added and the suspension was stirred at reflux for 3 h. The cooled mixture was filtered through Celite, washed with EtOAc, and then concentrated. Purification by flash column chromatography (40:60; EtOAc/hexanes) provided the major β-D-anomer as a white solid (8.88 g, 88%); mp 123 °C; $[\alpha]_D^{25}$ +2.0 (*c* 0.10, $CHCl_3$).

IR (neat): 3118, 3066, 2981, 1754, 1439 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.09 (dd, *J* = 4.8, 1.6 Hz, 1 H), 7.85 (dd, *J* = 7.7, 1.6 Hz, 1 H), 6.90 (dd, *J* = 7.7, 4.8 Hz, 1 H), 6.07 (d, *J* = 7.7 Hz, 1 H, H-1), 5.47–5.19 (m, 3 H, H-2, H-3, H-4), 4.31 (dd, *J* = 12.4, 4.4 Hz, 1 H, H-6), 4.15 (dd, *J* = 12.4, 2.3 Hz, 1 H, H-6), 3.96 (ddd, *J* = 9.7, 4.4, 2.3 Hz, 1 H, H-5), 2.06 (s, 3 H), 2.05 (s, 3 H), 2.04 (s, 3 H), 2.02 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.8, 170.4, 169.5, 169.3, 157.8, 145.5, 142.6, 120.0, 107.4, 94.5, 73.0, 72.4, 70.6, 68.2, 61.8, 20.8, 20.8, 20.7 (2 C).

HRMS-ESI: *m*/*z* $(M + Na)^+$ calcd for $C_{19}H_{22}BrNO_{10}Na$: 526.0319; found: 526.0328 (+1.63 ppm).

(3-Bromo-2-pyridyloxy) β-D-galactopyranoside (3)

A freshly prepared solution of MeONa (8.0 mL, 0.25 equiv, 0.5 M in MeOH) was added to a solution of **1** (8.00 g, 15.9 mmol) in anhyd MeOH (53 mL, 0.3 M). The solution was stirred at r.t. for 1 h until a white solid appeared. The solid was filtered, washed with cold MeOH, and recrystallized from hot MeOH to give **3** as white needles (5.34 g, quant.); mp 173.4–175.2 °C; $[\alpha]_D^{25}$ –4.1 (*c* 0.06, $MeOH/H_2O$; 1:1).

IR (neat): 3346, 3060, 2968, 1439 cm^{-1}.

^1H NMR (500 MHz, CD_3OD): δ = 8.12 (dd, *J* = 4.8, 1.6 Hz, 1 H), 7.97 (dd, *J* = 7.7, 1.6 Hz, 1 H), 6.96 (dd, *J* = 7.7, 4.8 Hz, 1 H), 5.96 (d, *J* = 8.3 Hz, 1 H, H-1), 3.94 (d, *J* = 3.4 Hz, 1 H, H-4), 3.91 (dd, *J* = 9.6, 8.3 Hz, 1 H, H-2), 3.77–3.69 (m, 3 H, H-5, 2 × H-6), 3.62 (dd, *J* = 9.6, 3.4 Hz, 1 H, H-3).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 158.0, 145.7, 142.7, 119.6, 106.5, 96.7, 75.9, 73.6, 69.9, 68.1, 60.2.

HRMS-ESI: *m*/*z* $(M + Na)^+$ calcd for $C_{11}H_{14}BrNO_6Na$: 357.9897; found: 357.9880 (–4.61 ppm).

(3-Bromo-2-pyridyloxy) β-D-glucopyranoside (4)

A freshly prepared solution of MeONa (6.45 mL, 0.25 equiv, 0.5 M in MeOH) was added to a solution of **2** (6.50 g, 12.0 mmol) in anhyd MeOH (43 mL, 0.3 M). The solution was stirred at r.t. for 1 h, neutralized with Amberlite IRC-50S H^+ (4.38 g), filtered, concentrated in vacuo to give a white solid, which was recrystallized from hot EtOH to give **4** as white needles (4.25 g, 98%); mp 80 °C; $[\alpha]_D^{25}$ –12.8 (*c* 0.13, MeOH).

IR (neat): 3355, 3065, 2936, 1651, 1439, 1076 cm^{-1}.

^1H NMR (500 MHz, CD_3OD): δ = 8.13 (dd, *J* = 4.8, 1.6 Hz, 1 H), 7.97 (dd, *J* = 7.7, 1.6 Hz, 1 H), 6.96 (dd, *J* = 7.7, 4.8 Hz, 1 H), 6.00 (d, *J* = 8.0 Hz, 1 H, H-1), 3.83 (dd, *J* = 12.0, 0.8 Hz, 1 H, H-3), 3.70 (dd, *J* = 12.0, 4.1 Hz, 1 H, H-4), 3.57 (dd, *J* = 8.0, 0.8 Hz, 1 H, H-2), 3.53–3.48 (m, 1 H, H-5), 3.49–3.42 (m, 2 H, 2H-6).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 159.8, 146.6, 143.9, 120.6, 108.3, 97.7, 78.5, 78.4, 74.4, 71.1, 62.4.

HRMS-ESI: *m*/*z* $(M + Na)^+$ calcd for $C_{11}H_{14}BrNO_6Na$: 357.9897; found: 357.9903 (+1.61 ppm).

Protection of C-6 hydroxyl with TBDPS chloride: Glycosides 5, 6, 16, 17; General Procedure

To a solution of respective glycopyranosyl donor (2.53–1.75 mmol) and imidazole (10.1–7.00 mmol, 4.00 equiv) in anhyd DMF (0.5 M) was added *tert*-butyl(chloro)diphenylsilane (1.05 equiv). The solution was stirred at r.t. for 5 h, then concentrated in vacuo. The residue was dissolved in EtOAc, the organic layer was washed with aq $NaHCO_3$ and brine, dried (Na_2SO_4), filtered, and concentrated. Purification by flash column chromatography (40:60 to 80:20; EtOAc/hexanes) provided the 6-*O*-TBDPS-glycopyranosyl donor as a white foam (50–85%).

(3-Bromo-2-pyridyloxy) 6-*O*-*tert*-butyldiphenylsilyl-β-D-galactopyranoside (5)

White foam (1.06 g, 73%); $[\alpha]_D^{25}$ +8.7 (*c* 0.11, $CHCl_3$).

IR (neat): 3401, 3065, 3003, 2929, 2856, 1583, 1429, 1068 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.04 (dd, *J* = 4.8, 1.7 Hz, 1 H), 7.79 (dd, *J* = 7.7, 1.7 Hz, 1 H), 7.68–7.65 (m, 2 H), 7.64–7.60 (m, 2 H), 7.40–7.34 (m, 2 H), 7.33–7.27 (m, 4 H), 6.79 (dd, *J* = 7.7, 4.8 Hz, 1 H), 5.93 (d, *J* = 8.1 Hz, 1 H, H-1), 4.14–4.07 (m, 2 H, H-2, H-4), 3.90 (dd, *J* = 10.6, 6.0 Hz, 1 H, H-6), 3.86 (dd, *J* = 10.6, 5.5 Hz, 1 H, H-6), 3.79–3.75 (m, 2 H, H-3, H-5), 1.01 (s, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.4, 145.6, 142.4, 135.8, 135.7, 133.2 (2 C), 129.81, 129.79, 127.77, 127.76, 119.5, 107.8, 97.0, 75.3, 74.1, 71.2, 69.2, 63.2, 26.9, 19.3.

HRMS-ESI: *m*/*z* $(M + Na)^+$ calcd for $C_{27}H_{32}BrNO_6SiNa$: 596.1075; found: 596.1079 (+0.80 ppm).

(3-Bromo-2-pyridyloxy) 6-*O*-*tert*-butyldiphenylsilyl-β-D-glucopyranoside (6)

White foam (756 mg, 75%); $[\alpha]_D^{25}$ –8.7 (*c* 0.20, $CHCl_3$).

IR (neat): 3327, 3078, 2937, 2863, 1588, 1438, 1068 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.06 (dd, *J* = 4.8, 1.7 Hz, 1 H), 7.85 (dd, *J* = 7.7, 1.7 Hz, 1 H), 7.66–7.62 (m, 4 H), 7.42–7.28 (m, 6 H), 6.87–6.83 (m, 1 H), 5.93 (d, *J* = 7.6 Hz, 1 H, H-1), 3.92–3.89 (m, 2 H, H-2, H-3), 3.82–3.71 (m, 3 H, H-4, 2 × H-6), 3.68–3.63 (m, 1 H, H-5), 1.02 (s, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.3, 145.7, 142.6, 135.82, 135.76, 133.0, 132.9, 130.0 (2 C), 127.87, 127.85, 119.8, 107.7, 96.7, 76.7, 75.3, 73.2, 72.1, 64.8, 26.9, 19.3.

HRMS-ESI: *m*/*z* $(M + H)^+$ calcd for $C_{27}H_{33}BrNO_6Si$: 574.12550; found: 574.12553 (+0.04 ppm).

Glycosides 7a–l, 8a–j; General Procedure

To a solution of (3-bromo-2-pyridyloxy) 6-*O*-TBDSPS-β-D-glycosyl donor **5** or **6** and the acceptor ArOH (10.0 equiv) in anhyd CH_2Cl_2 (0.1 M) was added a solution of MeOTf (0.25 equiv, 1 M in anhyd CH_2Cl_2) at 0 °C. The solution was stirred at 0 °C and the progress of the reaction was followed by TLC (70:30; EtOAc/hexanes) or by MS ESI(+). The mixture was neutralized with a drop of Et_3N, then concentrated in vacuo. The α/β ratio was measured by ^1H NMR on the crude. Quick flash column chromatography (50:50 to 80:20; EtOAc/hexanes) removed excess of acceptor. The α/β anomers were separated by careful flash column chromatography (70:30; EtOAc/hexanes) (Tables 1 and 2).

Phenyl 6-*O*-*tert*-butyldiphenylsilyl-α-D-galactopyranoside (7a)

White foam (20.0 mg, 88%, 10.0:1, α/β); $[\alpha]_D^{25}$ +53.3 (*c* 0.04, $CHCl_3$).

IR (neat): 3344, 3078, 2938, 2865, 1595, 1497, 1115, 1079 cm^{-1}.

^1H NMR (500 MHz, CD_3OD): δ = 7.64–7.58 (m, 4 H), 7.43–7.22 (m, 8 H), 7.17–7.13 (m, 2 H), 7.02–6.98 (m, 1 H), 5.47 (d, *J* = 2.7 Hz, 1 H, H-1), 4.01 (t, *J* = 6.3 Hz, 1 H, H-4), 3.97–3.91 (m, 3 H, H-2, H-3, H-5), 3.85 (dd, *J* = 10.6, 5.3 Hz, 1 H, H-6), 3.78 (dd, *J* = 10.6, 6.8 Hz, 1 H, H-6), 0.96 (s, 9 H).

^{13}C NMR (125 MHz, CD_3OD): δ = 158.8, 136.8 (2 C), 134.6, 134.5, 130.9 (2 C), 130.5, 128.8 (2 C), 123.4, 118.5, 99.7, 73.4, 71.5, 70.9, 70.1, 64.7, 27.3, 19.9.

HRMS-ESI: *m*/*z* $(M + Na)^+$ calcd for $C_{28}H_{34}O_6SiNa$: 517.2017; found: 517.1993 (–4.60 ppm).

4-Methoxyphenyl 6-*O*-*tert*-butyldiphenylsilyl-α-D-galactopyranoside (7b)

White foam (15.6 mg, 84%, 9.0:1, α/β); $[\alpha]_D^{25}$ +63.9 (*c* 0.05, $CHCl_3$).

IR (neat): 3384, 3065, 3010, 2930, 2857, 1506, 1464, 1428, 1213, 1111, 1033 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.70–7.62 (m, 4 H), 7.46–7.33 (m, 6 H), 6.99 (d, *J* = 9.1 Hz, 2 H), 6.78 (d, *J* = 9.1 Hz, 2 H), 5.46 (d, *J* = 3.7 Hz, 1 H, H-1), 4.21–4.18 (m, 1 H, H-4), 4.02–3.92 (m, 3 H, H-2, 2 × H-6), 3.92–3.89 (m, 2 H, H-3, H-5), 3.76 (s, 3 H), 1.05 (s, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.5, 150.8, 135.8, 135.7, 133.1, 132.9, 130.1, 130.0, 128.0, 127.9, 118.5, 114.8, 98.8, 71.5, 70.6, 69.9, 69.8, 63.9, 55.8, 26.9, 19.3.

HRMS-ESI: *m*/*z* (M + Na)$^+$ calcd for $C_{29}H_{36}O_7SiNa$: 547.2122; found: 547.2133 (+1.90 ppm).

4-Fluorophenyl 6-*O*-*tert*-butyldiphenylsilyl-α-D-galactopyranoside (7c)

White foam (15.7 mg, 82%, 6.6:1, α/β); $[\alpha]_D^{25}$ +49.3 (*c* 0.03, $CHCl_3$).

IR (neat): 3374, 3072, 3010, 2932, 2853, 1504, 1428, 1203, 1112, 1076 cm^{-1}.

^1H NMR (700 MHz, $CDCl_3$): δ = 7.66 (d, *J* = 6.8 Hz, 2 H), 7.63 (d, *J* = 6.8 Hz, 2 H), 7.46–7.33 (m, 6 H), 7.02–6.98 (m, 2 H), 6.95–6.90 (m, 2 H), 5.48 (d, *J* = 3.7 Hz, 1 H, H-1), 4.19 (d, *J* = 2.4 Hz, 1 H, H-4), 4.01 (dd, *J* = 9.2, 2.4 Hz, 1 H, H-3), 3.96–3.88 (m, 4 H, H-2, H-5, 2H-6), 1.04 (s, 9 H).

^{13}C NMR (175 MHz, $CDCl_3$): δ = 158.6 (d, *J* = 240.8 Hz), 152.89 (d, *J* = 2.3 Hz), 135.8, 135.7, 133.0, 132.8, 130.10, 130.07, 128.0, 127.9, 118.48 (d, *J* = 8.1 Hz), 116.17 (d, *J* = 23.1 Hz), 98.5, 71.4, 70.8, 69.82, 69.74, 64.0, 26.9, 19.3.

HRMS-ESI: *m*/*z* (M + Na)$^+$ calcd for $C_{28}H_{33}FO_6SiNa$: 535.1923; found: 535.1933 (+1.81 ppm).

4-Chlorophenyl 6-*O*-*tert*-butyldiphenylsilyl-α-D-galactopyranoside (7d)

White foam (17.3 mg, 83%, 7.2:1, α/β); $[\alpha]_D^{25}$ +66.3 (*c* 0.05, $CHCl_3$).

IR (neat): 3373, 3058, 3010, 2928, 2856, 1490, 1428, 1230, 1112, 1033, 824 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.67–7.60 (m, 4 H), 7.44–7.32 (m, 6 H), 7.19 (d, *J* = 8.8 Hz, 2 H), 6.98 (d, *J* = 8.8 Hz, 2 H), 5.52 (d, *J* = 3.7 Hz, 1 H, H-1), 4.18 (d, *J* = 3.0 Hz, 1 H, H-4), 4.03 (dd, *J* = 9.8, 3.7 Hz, 1 H, H-2), 3.94 (dd, *J* = 9.8, 3.0 Hz, 1 H, H-3), 3.90–3.85 (m, 3 H, H-5, 2 × H-6), 1.03 (s, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.3, 135.8, 135.7, 132.9, 132.8, 130.12, 130.09, 129.7, 128.0, 127.9, 118.3, 97.9, 71.4, 70.8, 69.8, 69.7, 63.9, 26.9, 19.3.

HRMS-ESI: *m*/*z* (M + Na)$^+$ calcd for $C_{28}H_{33}ClO_6SiNa$: 551.1627; found: 551.1638 (+1.92 ppm).

4-Bromophenyl 6-*O*-*tert*-butyldiphenylsilyl-α-D-galactopyranoside (7e)

White foam (16.9 mg, 85%, 8.0:1, α/β); $[\alpha]_D^{25}$ +74.7 (*c* 0.08, $CHCl_3$).

IR (neat): 3376, 3017, 2930, 2857, 1486, 1219, 1112, 1073, 630 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.67–7.60 (m, 4 H), 7.47–7.33 (m, 8 H), 6.95–6.92 (m, 2 H), 5.54 (d, *J* = 3.7 Hz, 1 H, H-1), 4.21–4.17 (m, 1 H, H-4), 4.02 (dd, *J* = 8.8, 3.7 Hz, 1 H, H-2), 3.97–3.91 (m, 1 H, H-3), 3.90–3.84 (m, 3 H, H-5, 2 × H-6), 1.03 (s, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.8, 135.8, 135.7, 132.9, 132.8, 132.6, 130.12, 130.10, 128.0, 127.9, 118.8, 115.3, 97.8, 71.3, 70.8, 69.8, 69.7, 63.9, 26.9, 19.3.

HRMS-ESI: *m*/*z* (M + Na)$^+$ calcd for $C_{28}H_{33}BrO_6SiNa$: 595.1122; found: 595.1126 (+0.61 ppm).

4-Iodophenyl 6-*O*-*tert*-butyldiphenylsilyl-α-D-galactopyranoside (7f)

White foam (14.5 mg, 80%, 8.8:1, α/β); $[\alpha]_D^{25}$ +24.7 (*c* 0.11, $CHCl_3$).

IR (neat): 3397, 3071, 2931, 2893, 2857, 1483, 1427, 1229, 1111, 1078 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.68–7.60 (m, 4 H), 7.54 (d, *J* = 9.0 Hz, 2 H), 7.48–7.33 (m, 6 H), 6.83 (d, *J* = 9.0 Hz, 2 H), 5.54 (d, *J* = 3.5 Hz, 1 H, H-1), 4.19 (d, *J* = 3.0 Hz, 1 H, H-4), 4.02 (dd, *J* = 9.0, 3.5 Hz, 1 H, H-2), 3.93 (dd, *J* = 9.0, 3.0 Hz, 1 H, H-3), 3.89 (d, *J* = 2.8 Hz, 1 H, H-6), 3.88 (d, *J* = 1.1 Hz, 1 H, H-6), 3.86–3.83 (m, 1 H, H-5), 1.03 (s, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.6, 138.6, 135.8, 135.7, 132.9, 132.8, 130.13, 130.11, 127.97, 127.95, 119.2, 97.7, 85.6, 71.4, 70.8, 69.74, 69.72, 63.9, 26.9, 19.3.

HRMS-ESI: *m*/*z* (M + Na)$^+$ calcd for $C_{28}H_{33}IO_6SiNa$: 643.0983; found: 643.0988 (+0.69 ppm).

3-Iodophenyl 6-*O*-*tert*-butyldiphenylsilyl-α-D-galactopyranoside (7g)

White foam (9.7 mg, 65%, 6.5:1, α/β); $[\alpha]_D^{25}$ +45.7 (*c* 0.05, $CHCl_3$).

IR (neat): 3070, 2928, 2856, 1583, 1471, 1218, 1077 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.76–7.60 (m, 4 H), 7.53–7.32 (m, 7 H), 7.35–7.27 (m, 1 H), 7.04 (d, *J* = 9.9 Hz, 1 H), 6.97 (t, *J* = 8.0 Hz, 1 H), 5.57 (d, *J* = 3.7 Hz, 1 H, H-1), 4.20 (d, *J* = 2.8 Hz, 1 H, H-4), 4.03 (dd, *J* = 9.7, 3.7 Hz, 1 H, H-2), 3.98–3.83 (m, 4 H, H-3, H-5, 2 × H-6), 1.04 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.2, 149.8, 135.8, 135.6, 132.9, 132.8, 132.0, 131.1, 130.11, 130.10, 128.0 (2 C), 126.2, 116.1, 97.7, 71.3, 70.8, 69.8, 69.7, 64.0, 26.9, 19.3.

HRMS-ESI: *m*/*z* (M + Na)$^+$ calcd for $C_{28}H_{33}IO_6SiNa$: 643.0983; found: 643.0988 (+0.71 ppm).

2-Iodophenyl 6-*O*-*tert*-butyldiphenylsilyl-α-D-galactopyranoside (7h)

White foam (10.4 mg, 63%, 5.8:1, α/β); $[\alpha]_D^{25}$ +64.8 (*c* 0.02, $CHCl_3$).

IR (neat): 3343, 3004, 2858, 1584, 1471, 1219 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.76 (dd, *J* = 7.9, 1.4 Hz, 1 H), 7.68–7.61 (m, 4 H), 7.45–7.32 (m, 6 H), 7.24–7.15 (m, 2 H), 6.80 (ddd, *J* = 7.9, 6.9, 1.9 Hz, 1 H), 5.58 (d, *J* = 3.7 Hz, 1 H, H-1), 4.21 (d, *J* = 3.2 Hz, 1 H, H-4), 4.05 (dd, *J* = 9.7, 3.2 Hz, 1 H, H-2), 4.01–3.96 (m, 1 H, H-3), 3.94–3.89 (m, 3 H, H-5, 2 × H-6), 1.04 (s, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.3, 139.2, 135.8, 135.7, 133.0, 132.9, 130.2, 130.1 (2 C), 128.0, 127.9, 124.7, 115.8, 99.4, 87.6, 71.8, 71.3, 69.9, 69.5, 63.8, 26.9, 19.3.

HRMS-ESI: *m*/*z* (M + Na)$^+$ calcd for $C_{28}H_{33}IO_6SiNa$: 643.0983; found: 643.0982 (–0.21 ppm).

Sesamyl 6-*O*-*tert*-butyldiphenylsilyl-α-D-galactopyranoside (7i)

White foam (17.8 mg, 93%, 7.0:1, α/β); $[\alpha]_D^{25}$ +63.7 (*c* 0.5, $CHCl_3$).

IR (neat): 3353, 3014, 2956, 2922, 1599, 1483, 1297, 1246, 766 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.67–7.61 (m, 4 H), 7.44–7.32 (m, 6 H), 6.73 (d, *J* = 2.1 Hz, 1 H), 6.66–6.60 (m, 2 H), 5.88 (dd, *J* = 8.8, 1.1 Hz, 2 H), 5.33 (d, *J* = 1.4 Hz, 1 H, H-1), 4.02 (t, *J* = 5.9 Hz, 1 H, H-4), 3.94 (d, *J* = 1.4 Hz, 1 H, H-2), 3.89–3.87 (m, 2 H, H-3, H-5), 3.85 (dd, *J* = 10.6, 5.0 Hz, 1 H, H-6), 3.80 (dd, *J* = 10.6, 7.0 Hz, 1 H, H-6), 0.99 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.0, 148.3, 143.32, 135.8, 135.7, 133.0, 132.8, 130.08, 130.05, 128.0, 127.9, 109.4, 108.3, 101.5, 100.2, 98.9, 77.4, 71.4, 70.67, 69.8, 63.9, 26.9, 19.3.

HRMS-ESI: *m*/*z* (M + Na)$^+$ calcd for $C_{29}H_{34}O_8SiNa$: 561.1915; found: 561.1910 (–0.84 ppm).

2-Naphthyl 6-*O*-*tert*-butyldiphenylsilyl-α-D-galactopyranoside (7j)

White foam (20.4 mg, 83%, 8.4:1, α/β); $[\alpha]_D^{25}$ +100.2 (*c* 0.06, $CHCl_3$).

IR (neat): 3360, 3052, 3013, 2930, 2891, 2856, 1600, 1511, 1467, 1427, 1106 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.76 (dd, *J* = 16.0, 8.5 Hz, 2 H), 7.69–7.59 (m, 6 H), 7.47–7.27 (m, 8 H), 7.22 (dd, *J* = 8.9, 2.5 Hz, 1 H), 5.74 (d, *J* = 3.7 Hz, 1 H, H-1), 4.23 (d, *J* = 3.2 Hz, 1 H, H-4), 4.10 (dd, *J* = 9.8, 3.7 Hz, 1 H, H-2), 4.03 (dd, *J* = 9.8, 3.2 Hz, 1 H, H-3), 3.98–3.87 (m, 3 H, H-5, 2 × H-6), 1.00 (s, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.5, 135.8, 135.6, 134.4, 132.94, 132.85, 130.03, 130.00, 129.7, 128.0, 127.91, 127.90, 127.8, 127.4, 126.6, 124.6, 118.9, 111.4, 97.8, 71.5, 70.8, 69.9, 69.8, 64.0, 26.9, 19.2.

HRMS-ESI: *m*/*z* (M + Na)$^+$ calcd for $C_{32}H_{36}O_6SiNa$: 567.2173; found: 567.2166 (–1.31 ppm).

1-Naphthyl 6-*O*-*tert*-butyldiphenylsilyl-α-D-galactopyranoside (7k)

White foam (21.3 mg, 83%, 8.2:1, α/β); $[\alpha]_D^{25}$ +59.3 (*c* 0.06, $CHCl_3$).

IR (neat): 3420, 3050, 2940, 2867, 1429, 1273, 1083 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21–8.13 (m, 1 H), 7.87–7.81 (m, 1 H), 7.67–7.56 (m, 4 H), 7.55–7.27 (m, 10 H), 7.16 (d, *J* = 7.7 Hz, 1 H), 5.81 (d, *J* = 1.2 Hz, 1 H, H-1), 4.27–4.22 (m, 1 H, H-4), 4.18–4.15 (m, 2 H, H-2, H-3), 3.98–3.86 (m, 3 H, H-5, 2 × H-6), 1.01 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.1, 135.8, 135.6, 134.5, 133.0, 132.8, 130.03, 130.00, 128.0, 127.90, 127.88, 126.6, 126.1, 125.9, 125.8, 122.23, 121.4, 109.1, 97.6, 71.6, 70.8, 70.00, 69.95, 63.9, 26.9, 19.2.

HRMS-ESI: *m*/*z* (M + Na)$^+$ calcd for $C_{32}H_{36}O_6SiNa$: 567.2173; found: 567.2176 (+0.49 ppm).

Methyl *N*-(benzyloxycarbonyl)-*O*-(6-*O*-*tert*-butyldiphenylsilyl-α-D-galactopyranosyl)-L-tyrosinate (7l)

White foam (18.6 mg, 70%, 7.3:1, α/β); $[\alpha]_D^{25}$ +68.2 (*c* 0.1, $CHCl_3$).

IR (neat): 3389, 3017, 2931, 2858, 1723, 1510, 1428, 1218, 1112, 1077 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69–7.61 (m, 4 H), 7.46–7.29 (m, 11 H), 6.99–6.95 (m, 4 H), 5.53 (d, *J* = 3.7 Hz, 1 H, H-1), 5.20 (d, *J* = 8.1 Hz, 1 H, NH), 5.09 (s, 2 H), 4.62 (dt, *J* = 8.1, 5.9 Hz, 1 H), 4.20 (d, *J* = 2.9 Hz, 1 H, H-4), 4.01 (dd, *J* = 9.0, 3.7 Hz, 1 H, H-2), 3.97–3.87 (m, 4 H, H-3, H-5, 2 × H-6), 3.70 (s, 3 H), 3.11–2.98 (m, 2 H), 1.03 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.1, 156.2, 155.8, 135.81, 135.77, 135.70, 135.65, 133.0, 132.8, 130.5, 130.1, 130.0, 128.7, 128.4, 128.2, 127.94, 127.90, 117.2, 98.0, 71.4, 70.6, 69.8, 69.7, 67.1, 63.9, 55.0, 52.5, 37.5, 26.9, 19.2.

HRMS-ESI: *m*/*z* (M + Na)$^+$ calcd for $C_{40}H_{47}NO_{10}SiNa$: 752.2861; found: 752.2873 (+1.55 ppm).

Phenyl 6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranoside (8a)

White foam (18.7 mg, 80%, 9.2:1, α/β); $[\alpha]_D^{25}$ +48.9 (*c* 0.08, $CHCl_3$).

IR (neat): 3345, 3065, 3010, 2926, 2856, 1495, 1428, 1112, 1075 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69–7.62 (m, 4 H), 7.45–7.27 (m, 8 H), 7.08–7.00 (m, 3 H), 5.51 (d, *J* = 3.8 Hz, 1 H, H-1), 3.96 (dt, *J* = 12.4, 6.2 Hz, 1 H, H-4), 3.89–3.85 (m, 2 H, 2 × H-6), 3.82–3.77 (m, 1 H, H-5), 3.75–3.67 (m, 2 H, H-2, H-3), 1.04 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.6, 135.8, 135.7, 133.1, 133.0, 130.02, 130.00, 129.8, 127.94, 127.89, 123.0, 117.1, 97.3, 74.8, 72.3, 71.8, 71.6, 64.3, 27.0, 19.4.

HRMS-ESI: *m*/*z* (M + Na)$^+$ calcd for $C_{28}H_{34}O_6SiNa$: 517.2017; found: 517.2024 (+1.30 ppm).

4-Methoxyphenyl 6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranoside (8b)

White foam (17.6 mg, 80%, 6.6:1, α/β); $[\alpha]_D^{25}$ +32.0 (*c* 0.05, $CHCl_3$).

IR (neat): 3374, 3058, 2929, 2853, 1508, 1464, 1428, 1216, 1113, 1039 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.68–7.64 (m, 4 H), 7.46–7.32 (m, 6 H), 6.98 (d, *J* = 9.1 Hz, 2 H), 6.77 (d, *J* = 9.1 Hz, 2 H), 5.38 (d, *J* = 3.8 Hz, 1 H, H-1), 3.94 (t, *J* = 8.7 Hz, 1 H, H-4), 3.89–3.87 (m, 2 H, 2 × H-6), 3.86–3.82 (m, 1 H, H-5), 3.76 (s, 3 H), 3.69 (dd, *J* = 9.4, 1.7 Hz, 1 H, H-3), 3.64 (dd, *J* = 9.4, 3.8 Hz, 1 H, H-2), 1.05 (s, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.5, 150.6, 135.8, 135.7, 133.13, 133.05, 130.01, 130.00, 127.94, 127.90, 118.6, 114.8, 98.4, 74.8, 72.3, 71.8, 71.6, 64.4, 55.8, 27.0, 19.4.

HRMS-ESI: *m*/*z* (M + Na)$^+$ calcd for $C_{29}H_{36}O_7SiNa$: 547.2122; found: 547.2134 (+2.10 ppm).

4-Fluorophenyl 6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranoside (8c)

White foam (15.4 mg, 76%, 5.1:1, α/β), $[\alpha]_D^{25}$ +11.4 (*c* 0.06, $CHCl_3$).

IR (neat): 3394, 3078, 3010, 2930, 2860, 1504, 1428, 1202, 1112, 1075 cm^{-1}.

^{1}H NMR (700 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 7.1 Hz, 4 H), 7.46–7.31 (m, 6 H), 7.02–6.98 (m, 2 H), 6.95–6.91 (m, 2 H), 5.41 (d, *J* = 3.7 Hz, 1 H, H-1), 3.94 (t, *J* = 9.4 Hz, 1 H, H-4), 3.87 (d, *J* = 4.5 Hz, 2 H, 2 × H-6), 3.78 (dt, *J* = 9.4, 4.5 Hz, 1 H, H-3), 3.71–3.65 (m, 2 H, H-2, H-5), 1.05 (s, 9 H).

^{13}C NMR (175 MHz, $CDCl_3$): δ = 158.7 (d, *J* = 240.9 Hz), 152.7 (d, *J* = 2.4 Hz), 135.81, 135.71, 133.1, 133.00, 130.1, 130.0, 128.0, 127.9, 118.6 (d, *J* = 8.1 Hz), 116.2 (d, *J* = 23.2 Hz), 98.1, 74.7, 72.2, 71.8, 71.7, 64.3, 27.0, 19.4.

HRMS-ESI: *m*/*z* (M + Na)$^+$ calcd for $C_{28}H_{33}FO_6SiNa$: 535.1923; found: 535.1937 (+2.69 ppm).

4-Chlorophenyl 6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranoside (8d)

White foam (12.4 mg, 76%, 6.8:1, α/β); $[\alpha]_D^{25}$ +46.6 (*c* 0.07, $CHCl_3$).

IR (neat): 3355, 3072, 3010, 2928, 2856, 1489, 1428, 1228, 1113, 1034, 824 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.66–7.62 (m, 4 H), 7.46–7.33 (m, 6 H), 7.20 (d, *J* = 9.0 Hz, 2 H), 6.97 (d, *J* = 9.0 Hz, 2 H), 5.45 (d, *J* = 3.8 Hz, 1 H, H-1), 3.95 (t, *J* = 8.9 Hz, 1 H, H-4), 3.86 (dd, *J* = 3.9, 1.9 Hz, 2 H, 2 × H-6), 3.75–3.66 (m, 3 H, H-2, H-3, H-5), 1.04 (s, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.1, 135.8, 135.7, 133.1, 133.00, 130.07, 130.05, 129.8, 128.00, 127.95, 127.9, 118.4, 97.5, 74.6, 72.1, 71.79, 71.7, 64.2, 27.0, 19.4.

HRMS-ESI: *m*/*z* (M + Na)$^+$ calcd for $C_{28}H_{33}ClO_6SiNa$: 551.1627; found: 551.1638 (+1.93 ppm).

4-Bromophenyl 6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranoside (8e)

White foam (16.3 mg, 75%, 7.2:1, α/β); $[\alpha]_D^{25}$ +56.5 (*c* 0.03, $CHCl_3$).

IR (neat): 3350, 3072, 3017, 2928, 2856, 1486, 1228, 1112, 630 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.66–7.62 (m, 4 H), 7.46–7.28 (m, 8 H), 6.92 (d, *J* = 9.0 Hz, 2 H), 5.46 (d, *J* = 3.8 Hz, 1 H, H-1), 3.97–3.92 (m, 1 H, H-4), 3.85 (t, *J* = 3.1 Hz, 2 H, 2 × H-6), 3.73–3.66 (m, 3 H, H-2, H-3, H-5), 1.04 (s, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 149.9, 135.8, 135.7, 133.04, 132.99, 132.6, 130.08, 130.06, 128.0, 127.9, 118.8, 115.4, 97.4, 74.6, 72.1, 71.8, 71.7, 64.2, 27.0, 19.4.

HRMS-ESI: *m*/*z* (M + Na)$^+$ calcd for $C_{28}H_{33}BrO_6SiNa$: 595.1122; found: 595.1118 (–0.71 ppm).

4-Iodophenyl 6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranoside (8f)

White foam (14.7 mg, 79%, 8.3:1, α/β); $[\alpha]_D^{25}$ +65.8 (*c* 0.09, $CHCl_3$).

IR (neat): 3373, 3065, 2932, 2856, 1485, 1428, 1219, 1113, 1034 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.66–7.61 (m, 4 H), 7.52 (d, *J* = 8.9 Hz, 2 H), 7.45–7.33 (m, 6 H), 6.81 (d, *J* = 8.9 Hz, 2 H), 5.46 (d, *J* = 3.7 Hz, 1 H, H-1), 3.98–3.91 (m, 1 H, H-4), 3.87–3.82 (m, 2 H, 2 × H-6), 3.73–3.64 (m, 3 H, H-2, H-3, H-5), 1.04 (s, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.4, 138.6, 135.8, 135.7, 133.03, 132.99, 130.1, 130.0, 128.0, 127.9, 119.3, 97.2, 85.7, 74.6, 72.1, 71.8, 71.7, 64.2, 27.0, 19.4.

HRMS-ESI: *m*/*z* (M + Na)$^+$ calcd for $C_{28}H_{33}IO_6SiNa$: 643.0983; found: 643.0970 (–2.08 ppm).

Sesamyl 6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranoside (8g)

White foam (16.6 mg, 93%, 6.0:1, α/β); $[\alpha]_D^{25}$ +59.4 (*c* 0.12, $CHCl_3$).

IR (neat): 3353, 3014, 2929, 2857, 1485, 1428, 1181, 1112, 1036 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.70–7.67 (m, 4 H), 7.47–7.36 (m, 6 H), 6.67 (d, *J* = 8.5 Hz, 1 H), 6.64 (d, *J* = 2.4 Hz, 1 H), 6.53 (dd, *J* = 8.5, 2.4 Hz, 1 H), 5.94 (d, *J* = 1.3 Hz, 1 H), 5.93 (d, *J* = 1.3 Hz, 1 H), 5.38 (d, *J* = 3.7 Hz, 1 H, H-1), 3.95 (t, *J* = 9.1 Hz, 1 H, H-4), 3.90 (d, *J* = 4.5 Hz, 2 H, 2 × H-6), 3.85–3.80 (m, 1 H, H-5), 3.73–3.65 (m, 1 H, H-3), 3.67 (dd, *J* = 5.8, 3.7 Hz, 1 H, H-2), 1.07 (s, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 151.7, 148.1, 143.2, 135.7, 135.6, 133.0, 132.9, 129.88, 129.87, 127.80, 127.76, 109.5, 108.1, 101.4, 100.2, 98.34, 74.5, 72.1, 71.60, 71.58, 64.12, 26.8, 19.2.

HRMS-ESI: *m*/*z* (M + Na)$^+$ calcd for $C_{29}H_{34}O_8SiNa$: 561.1915; found: 561.1922 (+1.30 ppm).

2-Naphthyl 6-*O*-*tert*-Butyldiphenylsilyl-α-D-glucopyranoside (8h)

White foam (19.8 mg, 80%, 7.4:1, α/β); $[\alpha]_D^{25}$ +43.3 (*c* 0.11, $CHCl_3$).

IR (neat): 3408, 3071, 2940, 2860, 1603, 1471, 1431, 1115 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.78–7.69 (m, 2 H), 7.68–7.61 (m, 6 H), 7.45–7.27 (m, 8 H), 7.22 (dd, *J* = 8.9, 2.5 Hz, 1 H), 5.66 (d, *J* = 3.7 Hz, 1 H, H-1), 4.06 (t, *J* = 9.2 Hz, 1 H, H-4), 3.90–3.80 (m, 3 H, H-5, 2 × H-6), 3.78–3.74 (m, 2 H, H-2, H-3), 1.01 (s, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.3, 135.8, 135.7, 135.8, 134.4, 133.1, 130.02, 129.98 (2 C), 129.7, 127.90, 127.86, 127.8, 127.4, 126.6, 124.6, 118.9, 111.4, 97.4, 74.7, 72.3, 71.8, 71.8, 64.3, 26.9, 19.4.

HRMS-ESI: *m*/*z* (M + Na)$^+$ calcd for $C_{32}H_{36}O_6SiNa$: 567.2173; found: 567.2169 (–0.84 ppm).

1-Naphthyl 6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranoside (8i)

White foam (17.7 mg, 80%, 7.3:1, α/β); $[\alpha]_D^{25}$ +38.8 (*c* 0.08, $CHCl_3$).

IR (neat): 3389, 3071, 2937, 2866, 1602, 1467, 1266, 1116 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.21–8.15 (m, 1 H), 7.86–7.82 (m, 1 H), 7.65–7.60 (m, 4 H), 7.54–7.49 (m, 3 H), 7.45–7.39 (m, 1 H), 7.37–7.28 (m, 6 H), 7.13 (d, *J* = 7.6 Hz, 1 H), 5.74 (d, *J* = 3.7 Hz, 1 H, H-1), 4.18 (dd, *J* = 9.3, 8.6 Hz, 1 H, H-4), 3.88 (d, *J* = 4.3 Hz, 1 H, H-6), 3.90–3.86 (m, 1 H, H-6), 3.83–3.77 (m, 3 H, H-2, H-3, H-5), 1.03 (s, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 151.9, 135.8, 135.7, 134.70, 134.70, 132.97, 130.01, 130.01, 128.0, 127.92, 127.88, 126.6, 126.0, 125.9, 125.8, 122.5, 121.5, 109.1, 97.2, 74.9, 72.5, 72.0, 71.7, 64.4, 27.0, 19.3.

HRMS-ESI: *m*/*z* (M + Na)$^+$ calcd for $C_{32}H_{36}O_6SiNa$: 567.2173; found: 567.2172 (–0.17 ppm).

Methyl *N*-(benzyloxycarbonyl)-*O*-(6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranosyl)-L-tyrosinate (8j)

White foam (14.5 mg, 68%, 6.6:1, α/β); $[\alpha]_D^{25}$ +57.6 (*c* 0.05, $CHCl_3$).

IR (neat): 3437, 3072, 3031, 2933, 2853, 1723, 1520, 1428, 1218 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 6.7 Hz, 4 H), 7.49–7.21 (m, 11 H), 6.99–6.94 (m, 4 H), 5.46 (d, *J* = 3.6 Hz, 1 H, H-1), 5.20 (d, *J* = 8.0 Hz, 1 H, NH), 5.09 (s, 2 H), 4.66–4.57 (m, 1 H), 3.98–3.82 (m, 3 H, H-4, 2 × H-6), 3.80–3.71 (m, 2 H, H-3, H-5), 3.70 (s, 3 H), 3.66 (dd, *J* = 9.6, 3.7 Hz, 1 H, H-2), 3.12–2.97 (m, 2 H), 1.04 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.1, 155.9, 155.8, 135.82, 135.79, 135.7(2 C), 133.12, 133.05, 130.6, 130.1, 130.01, 129.99, 128.7, 128.4, 128.3, 127.92, 127.87, 97.5, 74.6, 72.2, 71.7, 71.5, 67.2, 64.2, 55.0, 52.5, 37.5, 27.0, 19.4.

HRMS-ESI: *m*/*z* (M + Na)$^+$ calcd for $C_{40}H_{47}NO_{10}SiNa$: 752.2861; found: 752.2850 (–1.50 ppm).

Glycosides 9, 10; General Procedure

To a solution of (3-bromo-2-pyridyloxy) β-D-glycosyl donor **3** (0.045–0.043 mmol) and the acceptor ArOH (1.82–1.71 mmol, 40 equiv) in anhyd nitromethane (0.001 M), was added a solution of MeOTf (0.014–0.013 mmol, 0.30 equiv, 1 M in nitromethane) at 40 °C. The mixture was stirred and the progress of the reaction was followed by MS ESI(+). Pyridine (2.27–2.14 mmol, 50 equiv) and Ac_2O (1.82–1.71 mmol, 40 equiv) were added. The solution was stirred for 2 h, treated with aq $NaHCO_3$, and extracted with EtOAc. The organic layer was washed with aq 1 M HCl, aq $NaHCO_3$ and brine, dried (Na_2SO_4), filtered, and concentrated in vacuo. The α/β ratio was measured by ^{1}H NMR analysis of the crude. Purification by a careful flash column chromatography (30:70; EtOAc/hexanes) led to the α-D-anomer.

Phenyl 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranoside (9)[7a]

White needles (12.7 mg, 70%, 4.5:1, α/β); mp 129–130 °C (Lit.[7a] mp 131–132 °C); $[\alpha]_D^{25}$ +57.6 (*c* 0.05, $CHCl_3$).

IR (neat): 3437, 3072, 3031, 2933, 2853, 1723, 1520, 1428, 1218 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.33–7.28 (m, 2 H), 7.08–7.04 (m, 3 H), 5.78 (d, *J* = 3.6 Hz, 1 H, H-1), 5.58 (dd, *J* = 10.8, 3.4 Hz, 1 H, H-3), 5.53 (dd, *J* = 3.4, 1.2 Hz, 1 H, H-4), 5.29 (dd, *J* = 10.8, 3.6 Hz, 1 H, H-2), 4.36

(t, *J* = 7.1 Hz, 1 H, H-5), 4.12 (dd, *J* = 11.3, 7.1 Hz, 1 H, H-6), 4.06 (dd, *J* = 11.3, 7.1 Hz, 1 H, H-6), 2.17 (s, 3 H), 2.08 (s, 3 H), 2.03 (s, 3 H), 1.94 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.6, 170.5, 170.4, 170.2, 156.5, 129.9, 123.2, 116.9, 95.0, 68.1, 68.0, 67.7, 67.3, 61.6, 20.9, 20.84, 20.80, 20.7.

4-Methoxyphenyl 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranoside (10)

White foam (13.4 mg, 65%, 3.5:1, α/β); $[\alpha]_D^{25}$ +61.7 (*c* 0.05, $CHCl_3$).

IR (neat): 3044, 2921, 2860, 1744, 1507, 1205, 1033 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.00–6.96 (m, 2 H), 6.85–6.81 (m, 2 H), 5.65 (d, *J* = 3.6 Hz, 1 H, H-1), 5.56 (dd, *J* = 10.8, 3.4 Hz, 1 H, H-3), 5.53 (dd, *J* = 3.4, 1.1 Hz, 1 H, H-4), 5.26 (dd, *J* = 10.8, 3.6 Hz, 1 H, H-2), 4.39 (t, *J* = 7.1 Hz, 1 H, H-5), 4.15–4.05 (m, 2 H, 2 × H-6), 3.77 (s, 3 H), 2.17 (s, 3 H), 2.09 (s, 3 H), 2.03 (s, 3 H), 1.97 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.6, 170.5, 170.4, 170.2, 155.6, 150.5, 118.3, 114.8, 96.0, 68.13, 68.06, 67.7, 67.2, 61.7, 55.8, 29.9, 20.9, 20.84, 20.80, 20.77.

HRMS-ESI: *m*/*z* (M + NH_4)$^+$ calcd for $C_{21}H_{30}NO_{11}$: 472.1813; found: 472.1834 (+4.4 ppm).

(3-Bromo-2-pyridyloxy) 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-β-D-glucopyranoside (13)

To a solution of **11** (3.20 g, 9.66 mmol) in CH_2Cl_2 (190 mL, 0.05 M) was added Et_3N (4.0 mL, 28.9 mmol, 3.00 equiv). The solution was stirred for 15 min at –78 °C, then SO_2Cl_2 (0.94 mL, 11.6 mmol, 1.20 equiv) was added. The solution was stirred at –78 °C for 2 h, then treated with aq $NaHCO_3$. The separated organic layer was washed with brine (150 mL), dried (Na_2SO_4), filtered, and concentrated in vacuo. The (3-bromo-2-pyridyloxy) silver salt (3.20 g, 11.6 mmol, 1.20 equiv) was added to the chloride in anhyd toluene (97 mL, 0.1 M). The suspension was stirred at reflux for 2 h and the cooled mixture was filtered through Celite, washed with EtOAc and concentrated. The mixture of α/β-D-anomers (1:1.2; **13**/**14**) was separated by careful flash column chromatography (30:70; EtOAc/hexanes); white foam (1.95 g, 42%); $[\alpha]_D^{25}$ –43.4 (*c* 0.13, $CHCl_3$).

IR (neat): 3014, 2970, 2119, 1748, 1437, 1238, 908 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.08 (dd, *J* = 4.8, 1.7 Hz, 1 H), 7.86 (dd, *J* = 7.7, 1.7 Hz, 1 H), 6.91 (dd, *J* = 7.7, 4.8 Hz, 1 H), 5.99 (d, *J* = 8.5 Hz, 1 H, H-1), 5.15–5.09 (m, 2 H, 2 × H-6), 4.31 (dd, *J* = 12.5, 4.5 Hz, 1 H, H-3), 4.09 (dd, *J* = 12.5, 2.3 Hz, 1 H, H-4), 3.94–3.87 (m, 2 H, H-2, H-5), 2.10 (s, 3 H), 2.04 (s, 3 H), 2.02 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.7, 170.0, 169.7, 157.4, 145.4, 142.8, 120.2, 107.4, 95.2, 72.8, 72.4, 68.2, 63.4, 61.7, 20.8 (2 C), 20.7.

HRMS-ESI: *m*/*z* (M + Na)$^+$ calcd for $C_{17}H_{19}BrN_4O_8Na$: 511.0261; found: 511.0262 (–0.31 ppm).

(3-Bromo-2-pyridyloxy) 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-α-D-glucopyranoside (12)

White foam (1.63 g, 35%); $[\alpha]_D^{25}$ +141 (*c* 0.17, $CHCl_3$).

IR (neat): 3014, 2969, 2115, 1749, 1433, 1223, 1032 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.14 (dd, *J* = 4.8, 1.7 Hz, 1 H), 7.89 (dd, *J* = 7.7, 1.7 Hz, 1 H), 6.93 (dd, *J* = 7.7, 4.8 Hz, 1 H), 6.74 (d, *J* = 3.5 Hz, 1 H, H-1), 5.70 (dd, *J* = 10.5, 9.5 Hz, 1 H, H-3), 5.19 (t, *J* = 9.5 Hz, 1 H, H-4), 4.26 (dd, *J* = 12.3, 4.0 Hz, 1 H, H-6), 4.24–4.18 (m, 1 H, H-5), 4.01 (dd, *J* = 12.3, 2.0 Hz, 1 H, H-6), 3.70 (dd, *J* = 10.5, 3.5 Hz, 1 H, H-2), 2.11 (s, 3 H), 2.06 (s, 3 H), 2.01 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.6, 170.0, 169.8, 157.2, 145.8, 142.8, 120.3, 107.9, 92.6, 70.9, 69.5, 68.3, 61.6, 60.9, 20.84, 20.76 (2 C).

HRMS-ESI: *m*/*z* (M + Na)$^+$ calcd for $C_{17}H_{19}BrN_4O_8Na$: 511.0261; found: 511.0263 (–0.30 ppm).

(3-Bromo-2-pyridyloxy) 2-azido-2-deoxy-β-D-glucopyranoside (15)

A freshly prepared solution of MeONa (0.58 mL, 0.25 equiv, 0.35 M in MeOH) was added to a solution of **13** (391 mg, 0.813 mmol) in anhyd MeOH (8.1 mL, 0.1 M). The solution was stirred at r.t. for 1 h until a white solid appeared. The solid was filtered, washed with cold MOH, and recrystallized from hot MeOH; white needles (294 mg, quant.); mp 114–116 °C; $[\alpha]_D^{25}$ –23 (*c* 0.13, MeOH).

IR (neat): 3427, 3065, 2969, 2114, 1432 cm^{-1}.

^{1}H NMR (500 MHz, CD_3OD): δ = 8.13 (dd, *J* = 4.8, 1.7 Hz, 1 H), 8.00 (dd, *J* = 7.7, 1.7 Hz, 1 H), 7.00 (dd, *J* = 7.7, 4.8 Hz, 1 H), 5.95 (d, *J* = 8.4 Hz, 1 H, H-1), 3.83 (dd, *J* = 12.2, 2.1 Hz, 1 H, H-6), 3.71 (dd, *J* = 12.2, 4.7 Hz, 1 H, H-6), 3.53 (dd, *J* = 9.6, 8.4 Hz, 1 H, H-2), 3.50–3.45 (m, 2 H, H-3, H-4), 3.44–3.42 (m, 1 H, H-5).

^{13}C NMR (125 MHz, CD_3OD): δ = 159.1, 146.7, 144.0, 121.1, 108.0, 96.5, 78.6, 76.6, 71.1, 67.7, 62.1.

HRMS-ESI: *m*/*z* (M + Na)$^+$ calcd for $C_{11}H_{13}BrN_4O_5Na$: 382.9962; found: 382.9966 (–1.2 ppm).

(3-Bromo-2-pyridyloxy) 2-azido-2-deoxy-α-D-glucopyranoside (14)

Prepared from **12** by hydrolysis with MeONa following the same procedure as for **15**; white amorphous solid (610 mg, quant.); $[\alpha]_D^{25}$ +68 (*c* 0.12, MeOH).

IR (neat): 3290, 3065, 2982, 2114, 1432 cm^{-1}.

^{1}H NMR (500 MHz, CD_3OD): δ = 8.13 (dd, *J* = 4.8, 1.7 Hz, 1 H), 7.99 (dd, *J* = 7.7, 1.7 Hz, 1 H), 6.98 (dd, *J* = 7.7, 4.8 Hz, 1 H), 6.65 (d, *J* = 3.5 Hz, 1 H, H-1), 4.13 (dd, *J* = 10.4, 8.9 Hz, 1 H, H-3), 3.76 (ddd, *J* = 9.9, 3.6, 3.0 Hz, 1 H, H-5), 3.72–3.70 (m, 2 H, 2H-6), 3.54 (dd, *J* = 9.9, 8.9 Hz, 1 H, H-4), 3.45 (dd, *J* = 10.4, 3.5 Hz, 1 H, H-2).

^{13}C NMR (125 MHz, CD_3OD): δ = 159.1, 146.8, 144.0, 120.9, 108.6, 94.6, 76.0, 73.0, 71.5, 64.3, 62.1.

HRMS-ESI: *m*/*z* (M + Na)$^+$ calcd for $C_{11}H_{13}BrN_4O_5Na$: 382.9962; found: 382.9956 (–1.3 ppm).

(3-Bromo-2-pyridyloxy) 2-azido-6-*O*-*tert*-butyldiphenylsilyl-2-deoxy-α-D-glucopyranoside (16)

Prepared from **14**, following the same general procedure used for the protection of C-6 hydroxyl in **5** and **6** with TBDPS chloride (vide supra); white foam (253 mg, 73%); $[\alpha]_D^{25}$ –165 (*c* 0.15, $CHCl_3$).

IR (neat): 3442, 3044, 2928, 2852, 2110, 1583, 1431, 1220, 776 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.14 (dd, *J* = 4.8, 1.7 Hz, 1 H), 7.88 (dd, *J* = 7.7, 1.7 Hz, 1 H), 7.68–7.63 (m, 4 H), 7.48–7.36 (m, 6 H), 6.90 (dd, *J* = 7.7, 4.8 Hz, 1 H), 6.67 (d, *J* = 3.5 Hz, 1 H, H-1), 4.33 (t, *J* = 9.8 Hz, 1 H, H-3), 3.93–3.78 (m, 4 H, H-4, H-5, 2 × H-6), 3.53 (dd, *J* = 9.8, 3.5 Hz, 1 H, H-2), 1.05 (s, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.6, 145.8, 142.5, 135.7, 135.7, 132.8, 132.7, 130.2, 130.1, 128.01, 127.99, 119.8, 108.0, 92.8, 73.3, 72.0, 64.8, 62.4, 26.9, 19.3.

HRMS-ESI: *m*/*z* (M +H)$^+$ calcd for $C_{27}H_{32}BrN_4O_5Si$: 599.1320; found: 599.1323 (–0.57 ppm).

(3-Bromo-2-pyridyloxy) 2-azido-6-*O*-*tert*-butyldiphenylsilyl-2-deoxy-β-D-glucopyranoside (17)

Prepared from **15**, following the same general procedure used for the protection of C-6 hydroxyl in **5** and **6** with TBDPS chloride (vide supra); white foam (355 mg, 68%); $[\alpha]_D^{25}$ –67.7 (*c* 0.26, $CHCl_3$).

IR (neat): 3339, 3015, 2915, 2116, 1434, 1253, 1076 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.06 (dd, *J* = 4.8, 1.7 Hz, 1 H), 7.87 (dd, *J* = 7.7, 1.7 Hz, 1 H), 7.66–7.62 (m, 4 H), 7.44–7.37 (m, 2 H), 7.36–7.29 (m, 4 H), 6.88 (dd, *J* = 7.7, 4.8 Hz, 1 H), 5.97 (d, *J* = 8.3 Hz, 1 H, H-1), 3.93 (dd, *J* = 10.8, 4.9 Hz, 1 H, H-6), 3.89 (dd, *J* = 10.8, 5.3 Hz, 1 H, H-6), 3.76 (t, *J* = 9.1 Hz, 1 H, H-4), 3.69 (dd, *J* = 10.0, 8.3 Hz, 1 H, H-2), 3.64 (t, *J* = 4.9 Hz, 1 H, H-5), 3.62–3.57 (m, 1 H, H-3), 1.03 (s, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.7, 145.5, 142.6, 135.8, 135.7, 132.8, 132.7, 130.1, 127.93, 127.90, 119.9, 107.5, 95.2, 75.2, 74.8, 72.5, 65.3, 64.9, 26.9, 19.3.

HRMS-ESI: *m*/*z* (M + Na)$^+$ calcd for $C_{27}H_{31}BrN_4O_5SiNa$: 621.1139; found: 621.1154 (–2.4 ppm).

Phenyl 6-*O*-*tert*-butyldiphenylsilyl-2-azido-2-deoxy-α-D-glucopyranoside (18)

To a solution of **17** (16.0 mg, 0.0267 mmol) and phenol (12. 6 mg, 0.133 mmol, 5.00 equiv) in anhyd CH_2Cl_2 (0.27 mL, 0.1 M), was added a freshly prepared solution of MeOTf (10.7 µL, 0.40 equiv, 1 M in anhyd CH_2Cl_2) at 0 °C. The solution was stirred at 0 °C to r.t. over 16 h, neutralized with a drop of Et_3N, and concentrated in vacuo. The α/β ratio (3.5:1) was measured by ^1H NMR on the crude. Quick flash column chromatography (30:70 to 80:20; EtOAc/hexanes) removed excess of acceptor and provided a mixture α/β (8.9 mg, 82%). The α/β anomers were separated by a careful flash column chromatography (30:70; EtOAc/hexanes); white foam; $[\alpha]_D^{25}$ +23.4 (*c* 0.07, $CHCl_3$).

IR (neat): 3400, 3060, 2960, 2114, 1508, 1431, 1220, 1072 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.67–7.63 (m, 4 H), 7.46–7.34 (m, 6 H), 7.29–7.25 (m, 3 H), 7.07–7.03 (m, 3 H), 5.50 (d, *J* = 3.5 Hz, 1 H, H-1), 4.25 (dd, *J* = 10.4, 8.5 Hz, 1 H, H-3), 3.93–3.78 (m, 3 H, H-5, 2 × H-6), 3.78–3.71 (m, 1 H, H-4), 3.31 (dd, *J* = 10.4, 3.5 Hz, 1 H, H-2), 1.05 (s, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.6, 135.8, 135.7, 132.88, 132.85, 130.14, 130.11, 129.8, 128.01, 127.96, 123.1, 117.0, 97.1, 72.9, 71.6, 71.2, 64.4, 62.6, 27.0, 19.4.

HRMS-ESI: *m*/*z* (M + Na)$^+$ calcd for $C_{28}H_{33}N_3O_5SiNa$: 542.2082; found: 542.2086 (–0.73 ppm).

4-Methoxyphenyl 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-α-D-glucopyranoside (19)

To a solution of **16** (14.8 mg, 0.0247 mmol) and 4-methoxyphenol (15.3 mg, 0.247 mmol, 5.00 equiv) in anhyd CH_2Cl_2 (0.25 mL, 0.1 M), was added a freshly prepared solution of MeOTf (9.9 µL, 0.40 equiv, 1 M in anhyd CH_2Cl_2) at 0 °C. The solution was stirred at 0 °C to r.t. over 36 h, neutralized with a drop of Et_3N, and concentrated in vacuo. The α/β ratio (1.7:1) was measured by ^1H NMR on the crude. Quick flash column chromatography (30:70; EtOAc/hexanes) removed excess of 4-methoxyphenol and provided a α/β mixture (16.7 mg, 80%). The product was treated with TBAF (49.4 µL, 0.0494 mmol, 2.00 equiv, 1 M in THF) in anhyd THF (0.25 mL, 0.1 M) for 3 h, acetylated with excess of Ac_2O in pyridine for 16 h. The mxture was worked up by adding aq $NaHCO_3$ and extracting with EtOAc (5 mL). The separated organic phase was washed with aq 1 M HCl (5 mL), aq $NaHCO_3$ (5 mL), brine (5 mL), dried (Na_2SO_4), filtered, and concentrated. Purification by careful flash column chromatography (20:80; EtOAc/hexanes) gave the α-anomer as a white foam; $[\alpha]_D^{25}$ +24.7 (*c* 0.10, $CHCl_3$).

IR (neat): 3065, 2967, 2109, 1754, 1508, 1431, 1220, 1033, 769 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.06 (d, *J* = 9.1 Hz, 2 H), 6.85 (d, *J* = 9.1 Hz, 2 H), 5.69 (dd, *J* = 10.6, 9.2 Hz, 1 H, H-3), 5.51 (d, *J* = 3.5 Hz, 1 H, H-1), 5.14 (dd, *J* = 10.2, 9.2 Hz, 1 H, H-4), 4.29 (dd, *J* = 12.4, 4.7 Hz, 1 H, H-6), 4.20 (ddd, *J* = 10.2, 4.7, 2.2 Hz, 1 H, H-5), 4.07 (dd, *J* = 12.4, 2.2 Hz, 1 H, H-6), 3.78 (s, 3 H), 3.45 (dd, *J* = 10.6, 3.5 Hz, 1 H, H-2), 2.13 (s, 3 H), 2.06 (s, 3 H), 2.05 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.7, 170.2, 169.8, 155.8, 150.2, 118.1, 114.9, 97.6, 70.5, 68.5, 68.4, 61.8, 60.9, 55.8, 20.9, 20.84, 20.76.

HRMS-ESI: *m*/*z* (M + Na)$^+$ calcd for $C_{19}H_{23}N_3O_9SiNa$: 460.1327; found: 460.1321 (–1.29 ppm).

Sialosides 21–23; General Procedure

To a solution of (3-methoxy-2-pyridyloxy)-β-D-sialyl donor **20** and the acceptor ArOH (10.0 equiv) in anhyd CH_2Cl_2 (0.1 M) was added a freshly prepared solution of MeOTf (0.30 equiv, 1 M in anhyd CH_2Cl_2) at 0 °C. The solution was stirred at 0 to 25 °C and the progress of the reaction was followed by TLC (EtOAc) or by MS ESI(+). The mixture was neutralized with a drop of Et_3N and concentrated in vacuo. The α/β ratio was measured by ^1H NMR on the crude. Purification by preparative HPLC-MS in reverse phase (Synergi 4µ Polar-RP 80 Å, 100 × 21.20 mm). The β-D-anomer was obtained as a white foam.

Methyl [phenyl-5-acetamido-4,7,8-tri-*O*-acetyl-9-(4-biphenylcarboxamido)-3,5-dideoxy-β-D-glycero-D-galacto-2-nonulopyranosid]onate (21)

White foam (t_R = 6.02 min) (9.8 mg, 65%; 1:5, α/β).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.24–7.19 (m, 2 H), 7.02 (t, *J* = 7.3 Hz, 1 H), 6.95 (d, *J* = 8.4 Hz, 2 H), 5.49 (td, *J* = 10.9, 4.9 Hz, 1 H, H-4), 5.37 (dd, *J* = 5.3, 2.0 Hz, 1 H, H-7), 5.23 (d, *J* = 10.3 Hz, 1 H, NH), 4.97–4.90 (m, 1 H, H-8), 4.64 (dd, *J* = 12.5, 2.3 Hz, 1 H, H-9), 4.27–4.12 (m, 2 H, H-5, H-9), 4.08 (dd, *J* = 10.7, 2.2 Hz, 1 H, H-6), 3.70 (s, 3 H), 2.65 (dd, *J* = 12.8, 4.9 Hz, 1 H, H-3*eq*), 2.16 (s, 3 H), 2.05 (s, 6 H), 2.03–1.93 (m, 1 H, H-3*ax*), 1.89 (s, 3 H), 1.69 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.2, 170.7, 170.5, 170.4, 170.2, 167.6, 154.0, 130.0, 123.2, 116.7, 99.1, 72.3, 71.6, 68.7, 67.9, 62.0, 53.3, 49.4, 38.7, 23.4, 21.1, 20.95, 20.94, 20.8.

Gated ^{13}C-^1H NMR (decoupled with 3.70 ppm) (100 MHz, $CDCl_3$): δ = 167.55 (d, $J_{C1\text{-}H3ax}$ = 0.8 Hz).

Methyl [4-methoxyphenyl 5-acetamido-4,7,8-tri-*O*-acetyl-9-(4-biphenylcarboxamido)-3,5-dideoxy-β-D-glycero-D-galacto-2-nonulopyranosid]onate (22)

White foam (t_R = 6.07 min) (18.7 mg, 73%, 1:5, α/β); $[\alpha]_D^{25}$ –80.7 (*c* 0.01, $CHCl_3$).

IR (neat): 3254, 3077, 2960, 1741, 1656, 1505, 1215 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 6.91–6.88 (m, 2 H), 6.77–6.74 (m, 2 H), 5.47 (ddd, *J* = 11.6, 10.2, 4.9 Hz, 1 H, H-4), 5.39 (dd, *J* = 4.9, 2.2 Hz, 1 H, H-7), 5.29 (d, *J* = 9.9 Hz, 1 H, NH), 4.98 (ddd, *J* = 7.2, 4.9, 2.5 Hz, 1 H, H-8), 4.65 (dd, *J* = 12.6, 2.5 Hz, 1 H, H-9), 4.25–4.09 (m, 3 H, H-5, H-6, H-9), 3.75 (s, 3 H), 3.69 (s, 3 H), 2.64 (dd, *J* = 12.9, 4.9 Hz, 1 H, H-3*eq*), 2.15 (s, 3 H), 2.06–2.03 (m, 6 H), 1.97 (dd, *J* = 12.9, 11.6 Hz, 1 H, H-3*ax*), 1.88 (s, 3 H), 1.79 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.2, 170.64, 170.60, 170.4, 170.2, 167.5, 155.5, 147.8, 118.2, 114.9, 99.5, 72.3, 71.9, 68.8, 68.1, 62.2, 55.7, 53.2, 49.4, 23.3, 21.1, 20.94, 20.93 (3 C).

Gated ^{13}C-^{1}H NMR (decoupled with 3.75 ppm) (100 MHz, $CDCl_3$): δ = 167.38 (d, $J_{C1\text{-}H3ax}$ = 0.7 Hz).

HRMS-ESI: *m*/*z* (M + Na)$^+$ calcd for $C_{27}H_{35}NO_{14}Na$: 620.1950; found: 620.1965 (+2.4 ppm).

Methyl [4-fluorophenyl 5-acetamido-4,7,8-tri-*O*-acetyl-9-(4-biphenylcarboxamido)-3,5-dideoxy-β-D-glycero-D-galacto-2-nonulopyranosid]onate (23)

White foam (t_R = 6.04 min) (16.9 mg, 63%, 1:3.6, α/β); $[\alpha]_D^{25}$ –42.0 (*c* 0.01, $CHCl_3$).

IR (neat): 3257, 3077, 3026, 2958, 1742, 1659, 1503, 1034 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.96–6.91 (m, 4 H), 5.47 (td, *J* = 11.6, 4.9 Hz, 1 H, H-4), 5.37 (dd, *J* = 4.9, 2.3 Hz, 1 H, H-7), 5.28 (d, *J* = 9.8 Hz, 1 H, NH), 5.01–4.92 (m, 1 H, H-8), 4.65 (dd, *J* = 12.6, 2.3 Hz, 1 H, H-9), 4.25–4.07 (m, 3 H, H-5, H-6, H-9), 3.70 (s, 3 H), 2.65 (dd, *J* = 12.9, 4.9 Hz, 1 H, H-3*eq*), 2.16 (s, 3 H), 2.05 (s, 3 H), 2.05 (s, 3 H), 1.98 (dd, *J* = 12.9, 11.6 Hz, 1 H, H-3*ax*), 1.88 (s, 3 H), 1.79 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.2, 170.64, 170.59, 170.4, 170.2, 167.2, 158.6 (d, *J* = 241.7 Hz), 150.1 (d, *J* = 2.5 Hz), 118.3 (d, *J* = 8.1 Hz), 116.4 (d, *J* = 23.2 Hz), 99.6, 72.5, 71.8, 68.6, 68.1, 62.1, 53.3, 49.4, 23.3, 21.0, 20.93, 20.92, 20.86.

Gated ^{13}C-^{1}H NMR (decoupled with 3.70 ppm) (100 MHz, $CDCl_3$): δ = 167.1 (d, $J_{C1\text{-}H3ax}$ = 0.8 Hz).

HRMS-ESI: *m*/*z* (M + Na)$^+$ calcd for $C_{26}H_{32}FNO_{13}Na$: 608.1755; found: 608.1763 (+2.2 ppm).

Acknowledgment

We thank NSERC for financial assistance.

Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0035-1561461.

References

(1) (a) Hopkinson, S. M. *Q. Rev. Chem. Soc.* **1969**, *23*, 98. (b) Grynkiewicz, G.; Szeja, A. W. W.; Boryski, J. *Acta Pol. Pharm.* **2008**, *65*, 655.
(2) Quideau, S.; Deffieux, D.; Douat-Casassus, C.; Pouységu, L. *Angew. Chem. Int. Ed.* **2011**, *50*, 586.
(3) Vane, J. R.; Botting, R. M. *Aspirin and Other Salicylates*; Chapman and Hall: London, **1992**.
(4) Jacobsson, M.; Malmberg, J.; Ellervik, U. *Carbohydr. Res.* **2006**, *341*, 1266.
(5) Michael, A. *Am. Chem. J.* **1879**, *1*, 305.
(6) Fischer, E.; Mechel, L. V. *Ber. Dtsch. Chem. Ges.* **1926**, *59*, 2813.
(7) (a) Helferich, B.; Bredereck, H. *Justus Liebigs Ann. Chem.* **1928**, *465*, 166. (b) Helferich, B.; Schmitz-Hillebrecht, E. *Ber. Dtsch. Chem. Ges.* **1933**, *66B*, 378. (c) Helferich, B.; Demant, S.; Goerdeler, J.; Bosse, R. *Hoppe-Seyler's Z. Physiol. Chem.* **1948**, *283*, 179.
(8) (a) Montgomery, E. M.; Richtmyer, N. K.; Hudson, C. S. *J. Am. Chem. Soc.* **1942**, *64*, 690. (b) See also: Sisido, K. *J. Soc. Chem. Ind. Jpn* **1936**, *39*, 217. (c) See also: Pacsu, E. *J. Am. Chem. Soc.* **1930**, *52*, 2519.
(9) Briner, K.; Vasella, A. *Helv. Chim. Acta* **1990**, *73*, 1764.
(10) Mahling, J.-A.; Schmidt, R. R. *Synthesis* **1993**, 325.
(11) (a) Yamanoi, T.; Iwai, Y.; Inazu, T. *J. Carbohydr. Chem.* **1998**, *17*, 819. (b) Yamanoi, T.; Yamazaki, I. *Tetrahedron Lett.* **2001**, *42*, 4009.
(12) Khodair, A. I.; Winterfeld, G. A.; Schmidt, R. R. *Eur. J. Org. Chem.* **2003**, 1847.
(13) Sokolov, V. M.; Zakharov, V. I.; Studentsov, E. P. *Russ. J. Gen. Chem.* **2002**, *72*, 806.
(14) Qin, Q.; Xiong, D-C.; Ye, X-S. *Carbohydr. Res.* **2015**, *403*, 104.
(15) Suzuki, K.; Matsumoto, T. In *Preparative Carbohydrate Chemistry*; Hanessian, S., Ed.; Dekker: New York, **1997**, Chap. 24, 527.
(16) Hanessian, S.; Bacquet, C.; Lehong, N. *Carbohydr. Res.* **1980**, *80*, C17.
(17) Lou, B.; Reddy, G. V.; Wang, H.; Hanessian, S. In *Preparative Carbohydrate Chemistry*; Hanessian, S., Ed.; Dekker: New York, **1997**, Chap. 17, 389.
(18) Hanessian, S.; Mascitti, V.; Lu, P-P.; Ishida, H. *Synthesis* **2002**, 1959.
(19) Hanessian, S.; Lu, P.; Ishida, H. *J. Am. Chem. Soc.* **1998**, *120*, 13296.
(20) Hanessian, S.; Lou, B. *Chem. Rev.* **2000**, *100*, 4443.
(21) (a) Alper, P. B.; Hung, S.-C.; Wong, C.-H. *Tetrahedron Lett.* **1996**, *37*, 6029. (b) Koeller, K. M.; Smith, M. E. B.; Wong, C-H. *Bioorg. Med. Chem.* **2000**, *8*, 1017.
(22) (a) Sharma, M. N.; Eby, R. *Carbohydr. Res.* **1984**, *127*, 201. (b) Rothermel, J.; Faillard, H. *Carbohydr. Res.* **1990**, *196*, 29. (c) Gan, Z.; Roy, R. *Tetrahedron* **2000**, *56*, 1423.
(23) Dookhun, V.; Bennet, A. J. *J. Am. Chem. Soc.* **2005**, *127*, 7458.
(24) Ellervik, U.; Jansson, K.; Magnusson, G. *J. Carbohydr. Chem.* **1998**, *17*, 777.
(25) Hurd, C. D.; Bonner, W. A. *J. Org. Chem.* **1946**, *11*, 50.
(26) Malik, S.; Shah, K. J.; Kartha, K. P. R. *Carbohydr. Res.* **2010**, *345*, 867.
(27) Jensen, K. J.; Meldal, M.; Bock, K. *J. Chem. Soc., Perkin Trans. 1* **1993**, 2119.
(28) Mukherjee, C.; Misra, A. K. *Tetrahedron: Asymmetry* **2008**, *19*, 2746.
(29) Park, S.; Hyun, S.; Yu, J. *Bioorg. Med. Chem. Lett.* **2011**, *21*, 2441.
(30) Han, Z.; Pinkner, J. S.; Ford, B.; Obermann, R.; Nolan, W.; Wildman, S. A.; Hobbs, D.; Ellenberge, T.; Cusumano, C. K.; Hultgren, S. J.; Janetka, J. W. *J. Med. Chem.* **2010**, *53*, 4779.
(31) Viana, P. A.; de Rezende, S. T.; de A. Alves, A.; Manfrini, R. M.; Alves, R. J.; Bemquerer, A. P.; Santoro, M. M.; Guimaraes, V. M. *Carbohydr. Res.* **2011**, *346*, 602.
(32) Ahmad, M. U.; Ali, S. M.; Ahmad, A.; Sheikh, S.; Chen, P.; Ahmad, I. *Chem. Phys.* **2015**, *186*, 30.
(33) Prakash, T. P.; Wan, W. B.; Low, A.; Yu, J.; Chappell, A. E.; Gaus, H.; Kinberger, G. A.; Østergaard, M. E.; Migawa, M. T.; Swayze, E. E.; Seth, P. P. *Bioorg. Med. Chem. Lett.* **2015**, *25*, 4127.
(34) See the Supporting Information.