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Regiospecific Anomerisation of Acylated Glycosyl Azides and Benzoylated Disaccharides by Using $TiCl_4$

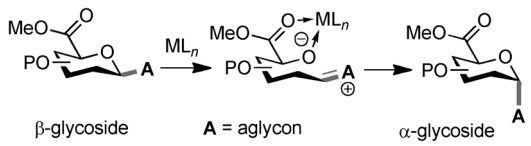
Mark Farrell, Jian Zhou, and Paul V. Murphy*[a]

Abstract: Chelation induced anomerisation is promoted when Lewis acids, such as $TiCl_4$ or $SnCl_4$, coordinate to the pyranose ring oxygen atom and another site, giving rise to endocyclic cleavage and isomerisation to the more stable anomer. In this research regiospecific site-directed anomerisation is demonstrated. $TiCl_4$ (2.5 equiv) was employed to induce anomerisation of 15 glycosyl azide and disaccharide substrates of low reactivity, and high yields (>75%) and stereoselectivies (α/β> 9:1) were achieved. The examples included glucopyranuronate, galactopyranuronate and mannopyranuronate as well as N-acetylated glucopyranuronate and galactopyranuronate derivatives. A disaccharide with the $\alpha1\rightarrow4$ linkage found in polygalacturonan was included. The use of benzoylated saccharides was found to be important in disaccharide anomerisation as attempts to isomerise related acetyl protected and 2,3-carbonate protected derivatives were not successful.

Keywords: anomerisation · glycuronic acid · Lewis acids · protecting groups · regioselectivity

Introduction

Glycosides are ubiquitous and important to life, health, food, materials, energy and the environment. Despite progress, it is still viewed as being important to improve the stereoselective synthesis of glycosides.[1,2] Previous studies from our laboratory have shown that the presence of a carboxylic acid or a derivative (e.g., ester or amide) at the C-5 of a saccharide, as found in glycuronic acids, leads to a significant increase in the rate of anomerisation promoted by Lewis acids, such as $TiCl_4$ or $SnCl_4$.[3] This is explained by chelation of the pyranose ring oxygen atom and C-6 carbonyl group to the Lewis acid facilitating endocyclic cleavage and consequent glycoside bond isomerisation to the thermodynamically more stable anomer (Scheme 1). A study of factors influencing anomerisation of glucose and galactose derivatives[4] has been carried out, with the impact of protecting group (e.g., benzoylation > acetylation) and promoter ($TiCl_4$ > $SnCl_4$) on the rate and stereoselectivity of the reaction being established.[5] In previous studies the presence of an azide or a saccharide residue at the anomeric carbon led to a significant reduction in reactivity of the linkage towards anomerisation. Herein we now report the generation of α-configured acylated glycosyl azides and benzoylated disaccharides using $TiCl_4$ promoted anomerisation of the corresponding β-linked precursors. This study shows that anomerisation is induced in a regiospecific manner at the glycuronic acid anomeric carbon, providing additional evidence for the significant rate enhancement for the Lewis acid in the presence of the C-6 carbonyl group. In the case of the disaccharides the use of benzoylated substrates was found to be important in achieving anomerisation.



Scheme 1. Lewis acid promoted anomerisation by endocyclic cleavage.

Results and Discussion

This study commenced with the synthesis of a variety of glycosyl azide and disaccharide substrates. The methyl ester **1** was prepared as previously reported.[6] Its analogous allyl ester **2** was generated via **1** by saponification, which was followed by the base-mediated allylation of the carboxylic acid and subsequent acetylation.[3] The bromide **3** was prepared from D-galacturonic acid through acetylation,[7] subsequent methyl ester formation and then treatment with HBr/AcOH (Scheme 2). Treatment of this bromide with sodium azide in DMF in an ultrasonic bath gave the azide **4**.[6] The β-mannopyranosyl azide **6** was prepared from **5** via a glycosyl iodide.[8] This azide **6** was then subjected to Zemplén deacetylation followed by one pot silylation–benzoylation to give the TBDPS derivative **7**. Removal of the the silyl protecting group, followed by oxidation and base-mediated esterification gave **8**.

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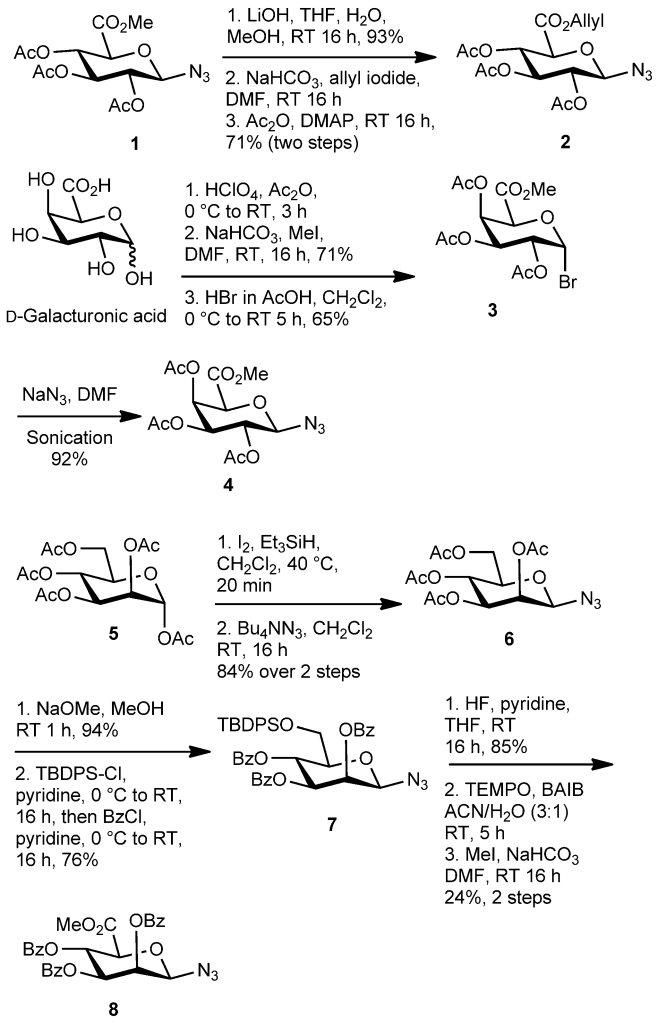
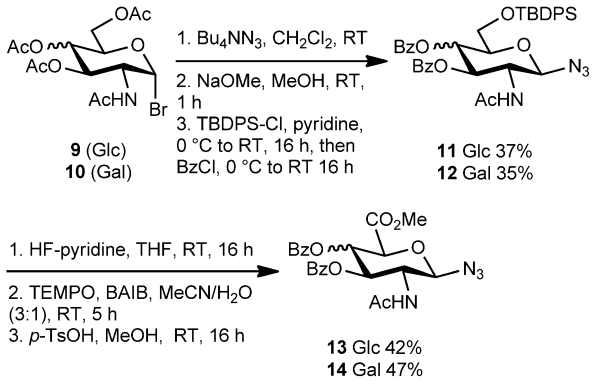


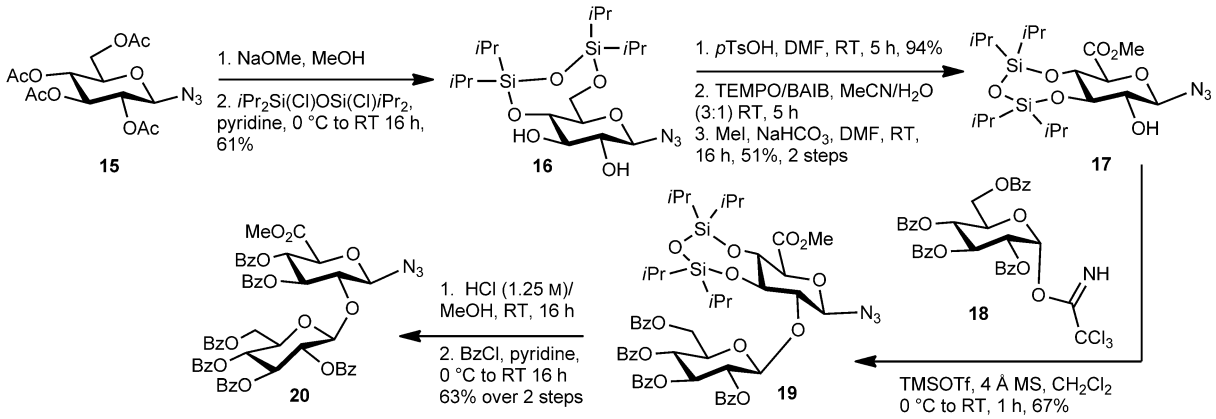
Scheme 2. Synthesis of β-azides **2**, **4** and **8**.

An approach similar to that used for the mannuronic acid derivative **8** was adopted for the preparation of the 2-deoxy-*N*-acetyl-glycuronides (Scheme 3). The α-glycosyl bromides **9** and **10** were converted to the corresponding β-azides using tetrabutylammonium azide in CH_2Cl_2.[9] These azides were then treated with sodium methoxide in methanol to bring about O-deacetylation and this was followed by one pot silylation–benzoylation to give **11** and **12**.[10] The TBDPS group was removed from **11** and **12** using HF/pyridine and the resulting primary alcohol was oxidised to the carboxylic acid using TEMPO/BAIB. Initial attempts to prepare the methyl ester by base-mediated esterification as described for other acids above gave low yields. However, the esterification with *p*-toluenesulfonic acid in MeOH gave the desired azides **13** and **14** in improved yields.

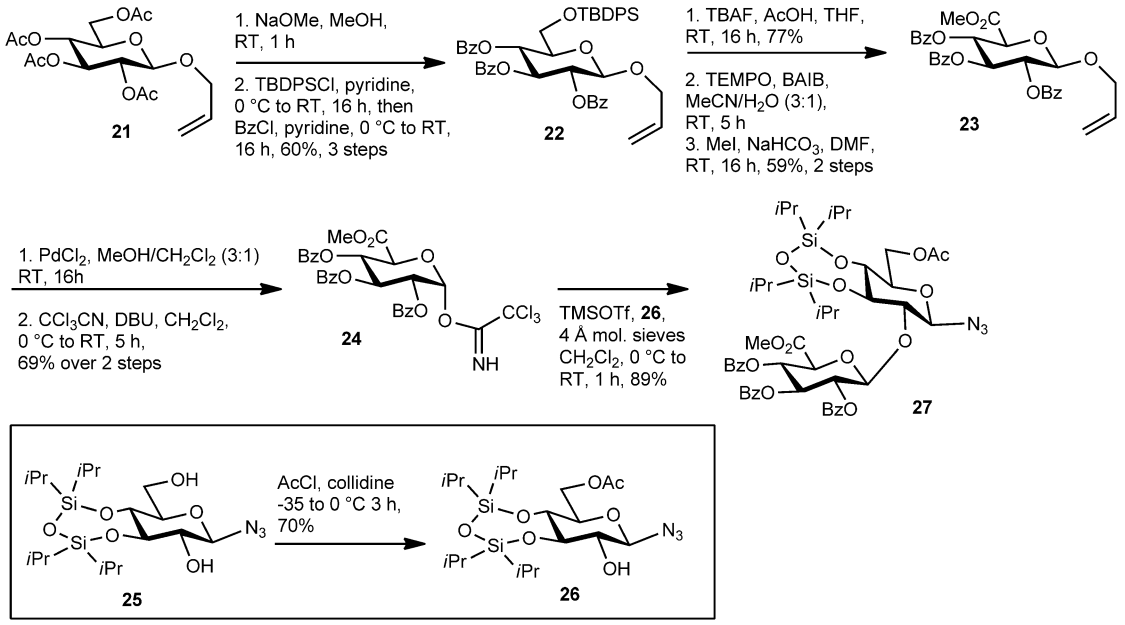


Scheme 3. Synthesis of β-azides **13** and **14**.

The preparation of the disaccharide **20** was carried out from azide **15**.[11] Deacetylation followed by treatment of 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane ($TIPDSCl_2$) in the presence of pyridine gave **16** in which both 4- and 6-OH groups are protected. The TIPDS group was then rearranged, using *p*-toluenesulfonic acid in DMF, so as to protect the 3- and 4-OH groups.[12] Then oxidation of the primary alcohol to the acid using TEMPO/BAIB followed by esterification gave **17**. Glycosidation using the trichloroacetimidate donor **18** gave **19**.[13] The TIPDS protecting group was removed using HCl/MeOH and subsequent treatment with benzoyl chloride and pyridine gave the disaccharide **20** (Scheme 4).



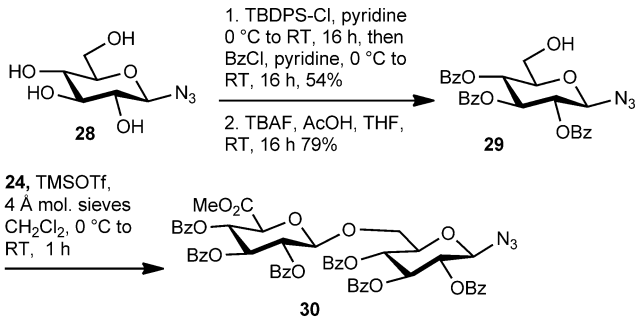
Scheme 4. Synthesis of **20**.



Scheme 5. Synthesis of **27**.

The synthesis of disaccharide **27** began from the allyl glycoside **21** (Scheme 5).[14] Deacetylation followed by treatment with TBDPSCl in the presence of pyridine and subsequent benzoylation gave **22**. Removal of the TBDPS group followed by oxidation and esterification gave **23**. The allyl group was removed using $PdCl_2$ to give a hemiacetal. Subsequent treatment of this hemiacetal with trichloroacetonitrile in the presence of DBU gave donor **24**.[15] The disilyloxy derivative **25**, prepared from **16** (Scheme 3), was used to give acceptor **26** through regioselective acetylation at the 6-OH. The glycoside bond forming reaction between **24** and **26** then gave the disaccharide **27**.

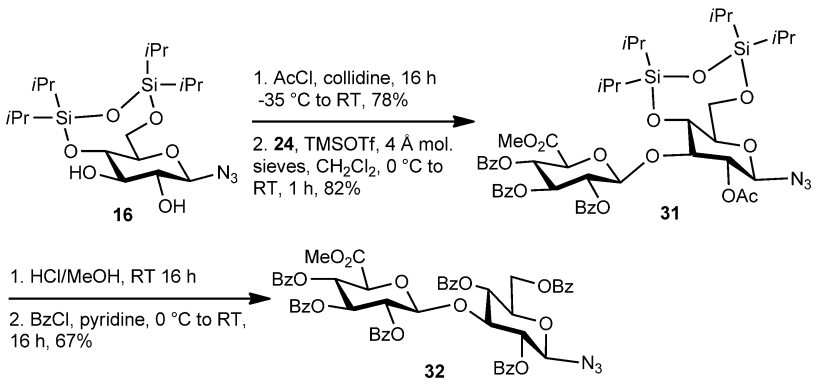
The glucosyl azide **28**, prepared by deacetylation of **15**, was next regioselectively silylated using TBDPSCl. The remaining hydroxyl groups were benzoylated and removal of the TBDPS group with TBAF gave acceptor **29**. The glycoside coupling reaction of **29** with **24** gave disaccharide **30** (Scheme 6).



Scheme 6. Synthesis of **30**.

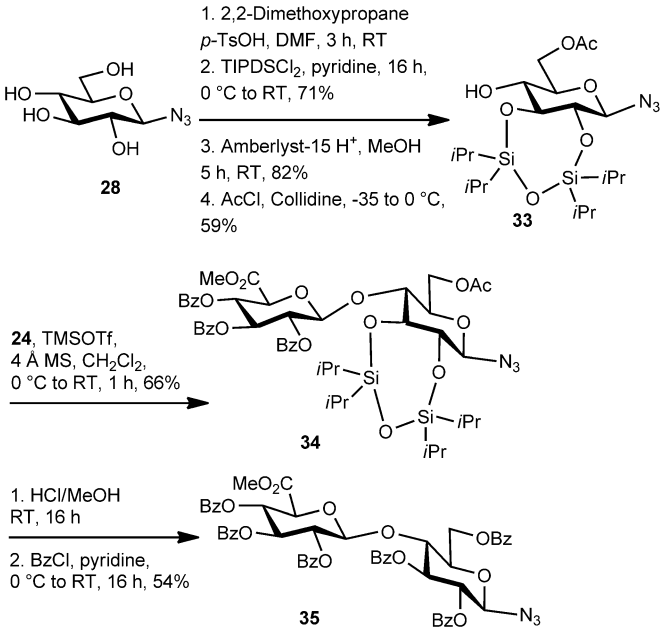
The diol **16** was used to prepare **31** and **32** (Scheme 7). Thus, the treatment of **16** with acetyl chloride in the presence of collidine led to the regioselective introduction of an acetyl group at the 2-OH.[16] Subsequent glycosidation of this acceptor with **24** gave **31**. Removal of the disilyloxy group using HCl/MeOH also led to the selective removal of the acetate from **31** but not the benzoate protecting groups. The subsequent benzoylation of the free OH groups in the aglycon of the intermediate gave **32**.

Azide **28** was used to prepare **34** and **35**. Treatment of **28** with dimethoxypropane under acidic conditions led to intro-



Scheme 7. Synthesis of **32**.

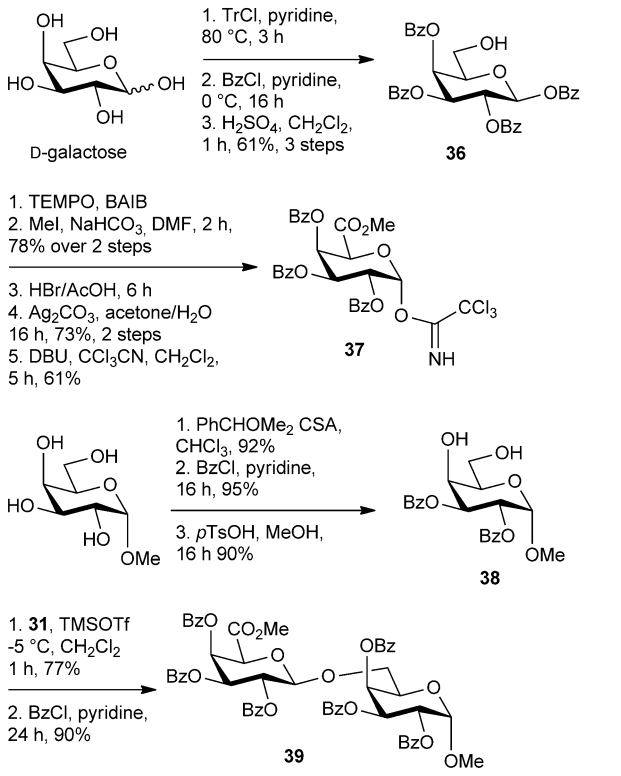
duction of an acetonide group at the 4- and 6-OH groups. Then treatment with $TIPDSCl_2$ in pyridine placed the TIPDS protecting group onto the 2- and 3-OH groups. Removal of the acetonide and regioselective acetylation gave **33**. The glycoside coupling treatment of **33** with **24** gave disaccharide **34**. Concomitant removal of the TIPDS protecting group and the acetate using Amberlyst-15 H^+ in methanol followed by benzoylation of the free OH groups gave **35** (Scheme 8).



Scheme 8. Synthesis of **35**.

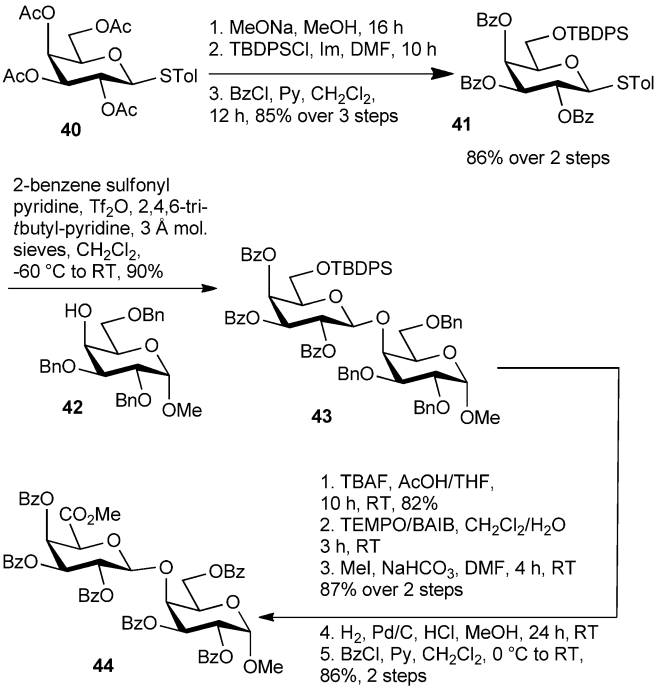
With a series of disaccharides based on glucuronic acid in hand, our attention next turned to preparation of disaccharides based on galacturonic acid. Hence, the donor **37** was required and its preparation was commenced from D-galactose which was first tritylated at the 6-OH group and then the remaining hydroxyl groups then benzoylated. Acid catalysed hydrolysis of the trityl group gave **36**. Subsequent oxidation of the primary alcohol and esterification followed by glycosyl bromide formation and silver ion promoted hydrolysis of the bromide gave a hemiacetal. Treatment of the hemiacetal with trichloroacetonitrile in the presence of DBU gave **37**. The acceptor **38** was prepared from methyl α-D-galactopyranoside by introduction of a benzylidene at the 4- and 6-OH groups, benzoylation of the 2- and 3-OH groups and then removal of the benzylidene. The glycoside coupling reaction of **37** and diol **38** was regioselective with bond formation occurring at the primary alcohol. Subsequent benzoylation of the initially formed glycoside gave 6-*O*-linked **39** (Scheme 9).

The 4-*O*-linked disaccharide **44** was prepared starting from thioglycoside **40**. Deacetylation of **40** followed by selective introduction of the TBDPS group at the primary alcohol and subsequent benzoylation gave **41**. The coupling of



Scheme 9. Synthesis of **39**.

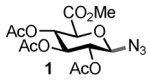
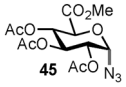
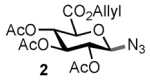
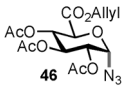
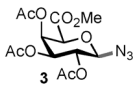
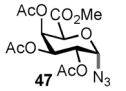
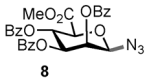
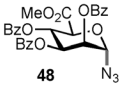
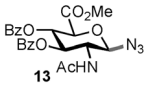
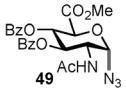
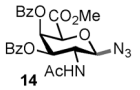
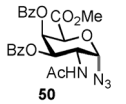
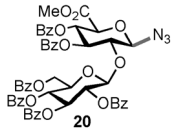
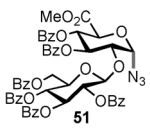
41 with the galactose acceptor **42** gave the disaccharide **43** in good yield.[17] Then the removal of the TBDPS, followed by oxidation, esterification, removal of the benzyl groups and finally benzoylation gave **44** (Scheme 10).



Scheme 10. Synthesis of **44**.

The anomerisation study commenced with a range of substrates in hand. This began with the azide **1** (Table 1, entry 1), which when subjected to treatment with $SnCl_4$ (0.5 equiv) was only partially converted (~5% conversion) to the α-anomer **45** after 24 h. This observation is indicative of a slow anomerisation reaction as reactions of simpler acetylated-*O*-glycosides were complete under these conditions.[5] However, when **1** was left to stand in the presence of $TiCl_4$ in 2.5-fold excess (entry 2) in a freezer at −15 to −18 °C for 48 h then **45** was isolated in high yield (94%) and with high stereoselectivity (ratio of **1**/**45** = 19:1). The use of $TiCl_4$ under these conditions was found to be successful for a range of the glycosyl azides (Table 1, entries 2–8). The yields of the products (>82%) and stereoselectivities (α/β > 9:1) were high. The glycosyl azides successfully anomerised included glucuronic acid, galacturonic acid, mannuronic acid and 2-deoxy-2-acetamido-D-glucuronic acid and 2-deoxy-2-acetamido-galacturonic acid derivatives. In the latter two examples the presence of the acetamido group in **13**/**14** did not impair the glycosyl azide isomerisation which gave **49**/**50** stereospecifically (entries 6 and 7). The regiospecific anomerisation of the glycosyl azide linkage in disaccharide **20** was also achieved (entry 8), which demonstrated clearly the rate enhancement brought about by the presence of the glucuronic acid carboxylate leading to the site-directed anomerisation. The excellent stereoselectivities observed are in part due to the use of 2.5-fold excess $TiCl_4$. In an earlier study on *O*- and *S*-glycosides the use of 2.5–3.0 equivalents of $TiCl_4$ was found to be optimum in terms of maximizing the α/β ratio. The impact of Lewis acid concentration on stereoselectivity of the glycosyl azides is explained by coordination of the Lewis acid at higher concentrations to the anomeric azide, which influences the anomer equilibrium. It is proposed that coordination at this site leads to enhancement of the anomeric effect. The use of $TiCl_4$ at lower or higher amounts gives rise to a reduction in stereoselectivity. The use of $TiCl_4$ at higher concentration than 0.5 equiv also enhances the rate, which is most likely important to induce isomerisation of the less reactive substrates as is the case with the glycosyl azides.

Table 1. Anomerisation of glycosyl azides.[a]

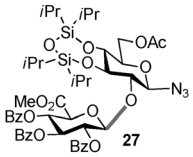
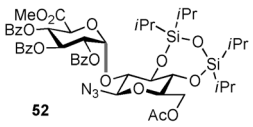
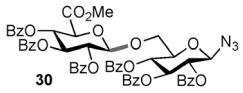
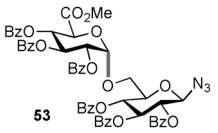
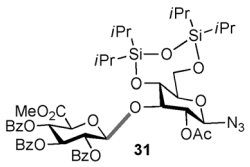
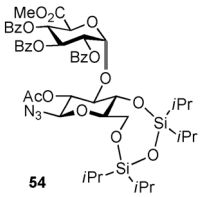
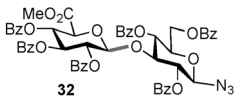
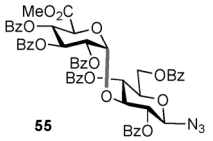
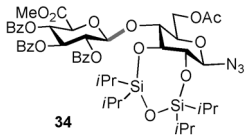
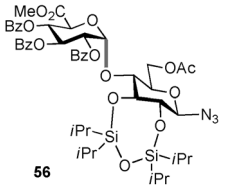
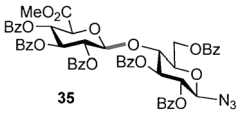
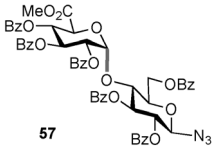
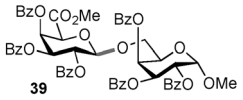
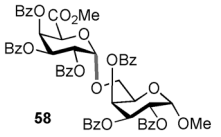
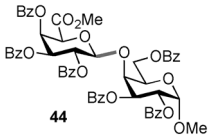
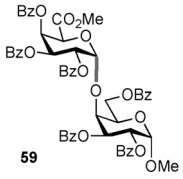
Entry	Substrate (β-anomer)	Product (α-anomer)	Reagents, conditions[b]	α/β ratio (yield [%])
1	 **1**	 **45**	A	5:95 (90)
2	**1**	**45**	B	95:5 (91)
3	 **2**	 **46**	B	94:6 (82)
4	 **3**	 **47**	B	>97:3 (93)
5	 **8**	 **48**	B	>95:5 (90)
6	 **13**	 **49**	B	>95:5 (90)
7	 **14**	 **50**	B	9:1 (87)
8	 **20**	 **51**	B	>90:10 (94)

[a] Experimental and analytical data of all compounds are available in the Supporting Information. [b] A: $SnCl_4$ (0.5 equiv) CH_2Cl_2, 20 °C, 24 h. B: $TiCl_4$ (2.5 equiv) CH_2Cl_2, −15 °C, 48 h.

Having successfully achieved the anomerisation of the glycosyl azides, we next turned our attention to disaccharide linkages. In previous research we observed the partial anomerisation (~33%) of an acetylated disaccharide using 0.5 equiv $TiCl_4$ after 24 h in nitromethane. Encouraged that use of 2.5 equivalents of $TiCl_4$ facilitated the rearrangement of glycosyl azides we explored these conditions with the series of disaccharides shown in Table 2 (entries 1–8). Gratifyingly, these disaccharides were all successfully isomerised to give the 1,2-*cis* glycosides **52**–**59**. The yields were > 75% and the stereoselectivity greater than 9:1. In a number of cases the selectivity was >95:5, with the β-configured starting disaccharide not being detected in the product mixture by ^{1}H NMR spectroscopy. In the case of the reaction of **44** conversion of its methyl glycoside to the corresponding glycosyl chloride occurred to a degree (~15%), explaining the lower yield of **56**. Anomerisation of disaccharides with a variety of glycosidic linkages (1→6, 1→4, 1→3 and 1→2) were all achieved and the successful examples included both glucuronic acid and galacturonic acid linkages. In contrast with the azides in Table 1, the glycosyl azide group in each disaccharide in Table 2 did not anomerise. Anomerisation occurred only at the site where efficient chelation to the C-6 carbonyl group could occur. The regiospecific nature of the reaction is worth noting and this provides additional convincing evidence for the rate enhancing effect of the C-6 carbonyl group. The TIPDS protecting group (Table 2, entries 6–8) was also highly compatible with the reaction conditions, especially when located on the aglycon. This contrasted with attempted anomerisation of the azides **17** and **19** (Scheme 4), which were not successful. The TIPDS group may hinder the approach of the Lewis acid in **17**/**19**. The disilyloxy group would be less likely to cause steric hindrance at the chelation site when placed on the aglycon.

The results described herein demonstrate a broader application of anomerisation for acylated substrates than hereto-

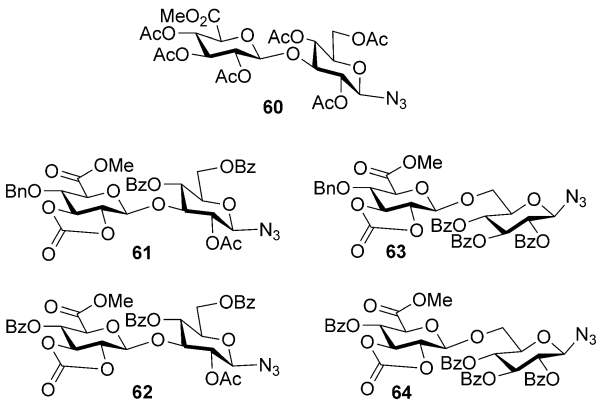
Table 2. Anomerisation of disaccharides.

Entry	Substrate (β-anomer)	Product (α-anomer)	Reagents, conditions[b]	α/β ratio (yield [%])
1	 **27**	 **52**	B	>90:10 (92)
2	 **30**	 **53**	B	95:5 (94)
3	 **31**	 **54**	B	95:5 (87)
4	 **32**	 **55**	B	>90:10 (92)
5	 **34**	 **56**	B	95:5 (94)
6	 **35**	 **57**	B	95:5 (90)
7	 **39**	 **58**	C	>95:5 (92)
8	 **44**	 **59**	C	>90:10 (75)

[b] B: $TiCl_4$ (2.5 equiv) CH_2Cl_2, −15 °C, 48 h; C: $TiCl_4$ (2.5 equiv), CH_2Cl_2, −20 °C, 36 h.

fore described. The presence of the benzoyl groups in the saccharides in which anomerisation takes place is important as the anomerisation reaction of **60** under the conditions described were not successful. Anomerisation with weaker Lewis acids and also $SnCl_4$ has been reported for pyranosides which have 2,3-*trans* carbamate or 2,3-*trans* carbonate groups, which demonstrate increased susceptibility to endocyclic cleavage and anomerisation due to inherent strain.[18,19] The disaccharides **61**–**65** were also investigated as part of this work as it had been anticipated that anomerisation would have been fast in these cases given that they contain both the 2,3-*trans* carbonate and C-6 carbonyl group, both of which promote endocyclic cleavage. However, the reaction of **61**–**65** led to intractable products when subjected to various Lewis acid promoters. Anomerisation of more reactive saccharides (e.g., benzyl protected saccharides) without the 2,3-*trans* carbamate or 2,3-*trans* carbonate, including that promoted by $TiCl_4$, have been carried out previously and this has included some examples of disaccharide anomerisation.[19,20] There are reports in which anomerisation with benzylated saccharides give high yields but in other cases they proceed with low yield (<50%). It is possible that $TiCl_4$ could cause the removal of benzyl groups, which would complicate the anomerisation of benzylated substrates. In our hands acetyl and benzoyl groups have been found to be stable to $TiCl_4$. Although benzoyl groups are more electron withdrawing than benzyl groups and acetate groups they still confer sufficient reactivity to enable the anomerisation and they are faster than for acetylated substrates. In a previous study the $SnCl_4$ promoted anomerisation of 2,3,4-tri-*O*-benzoylated glucuronides were 2–3-times faster than corresponding tri-*O*-acetylated analogues. This contrasts with impact of benzoate groups compared to acetate groups on reactivity in other carbohydrate-based model systems.[21] It is not clear yet why it is the case that anomerisation becomes possible for the benzoylated disaccharides compared to acetylated derivatives. Aside from our own investigations and that shown herein there has been limited investigation to date on anomerisation of acylated disaccharides.[22]

In terms of application there is potential for anomerisation of glycuronic acids and some applications have been recently described, such as the synthesis of *S*- and *O*-glycolipids.[23] Importantly, homogalacturonan is a major pectic



polymer of α-homogalacturonan and compounds related to **59** could be envisaged as building blocks for the synthesis of homogalacturonan fragments, which would be important for plant scientists.[24] The conditions described herein provide an alternative access to α-glycuronides.[25] α-Glycuronides are components of bacterial polysaccharides and hemicelluloses, providing a range of interesting target molecules. Although the presence of the uronate is necessary for the most efficient anomerisations,[26] it is possible to subsequently chemically transform the carboxylic acid group of the uronate (e.g., reduction) to increase the diversity of products that can be obtained. The azide group is the precursor to triazole-based conjugates prepared by metal catalysed alkyne–azide cycloaddition reactions.[27] Glycosyl triazoles have been prepared from the corresponding azide and α-glycosyl azides have also been used for the synthesis of α-glycosyl amides.[11b,28,29] The number of α-glycosyl azides is limited in the literature and, until now, these have usually been prepared by nucleophilic substitution of the β-glycosyl halide.[30]

In summary, we have described chelation-induced anomerisation of acylated glycosyl azides and disaccharide substrates. The work has included regiospecific or site-directed anomerisation. Further exploration of this reaction, in terms of understanding how the rates can be enhanced, including improving the activity of the promoter is under way. There are intriguing possibilities if regioselective or site-directed anomerisation of higher-order oligosaccharides or polysaccharides can ultimately be achieved. Understanding factors that influence rates of anomerisation will help chemists to achieve isomerisation of glycosidic linkages in increasingly complex substrates.

Experimental Section

Methyl 2,3,4-tri-*O*-acetyl-1-azido-1-deoxy-β-D-galactopyranuronate (4): The bromide **3**[31,32] (0.25 g, 0.63 mmol) and NaN_3 (0.41 g, 6.3 mmol) were placed in a Biotage microwave vial and then DMF (2.5 mL) was added and the vial was sealed and the resulting suspension was placed in an ultrasonic bath and then sonicated for 15–20 min. The vial was opened and the solution was poured on H_2O (15 mL) and extracted twice with EtOAc (15 mL). The combined organic extracts were washed with H_2O (40 mL), brine (40 mL), dried over Na_2SO_4, filtered and the solvent was removed under diminished pressure. Flash chromatography of the residue (petroleum ether/EtOAc 1:1) gave **4** (0.21 g, 92%) as a white solid; $[\alpha]_D = 16.3$ (c 0.6, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 5.74$ (dd, ^3J(H,H) = 3.5, 1.4 Hz, 1H; H-4), 5.19 (dd, ^3J(H,H) = 10.4, 8.8 Hz, 1H; H-2), 5.09 (dd, ^3J(H,H) = 10.4, 3.5 Hz, 1H; H-3), 4.67 (d, ^3J(H,H) = 8.8 Hz, 1H; H-1), 4.39 (d, ^3J(H,H) = 1.4 Hz, 1H; H-5), 3.78 (s, 3H; CO_2CH_3), 2.13 (s, 3H; $COCH_3$), 2.09 (s, 3H; $COCH_3$), 2.00 ppm (s, 3H; $COCH_3$); ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 170.1$ (CO_2CH_3), 169.8, 169.4, 165.9 (3× $COCH_3$), 88.6 (C-1), 74.2 (C-5), 70.5 (C-3), 68.1 (C-4), 67.8 (C-2), 53.1 (CO_2CH_3), 20.8, 20.7 ppm (2s) (3×$COCH_3$); IR (film): $\tilde{\nu} = 2980$, 2119, 1771, 1737, 1273, 1239, 1210, 1051 cm^{-1}; ESI-HRMS calcd for $C_{13}H_{17}O_9N_3Na$ 382.0862, found *m/z* (%) 382.0866 $[M+Na]^+$.

2,3,4,6-Tetra-*O*-acetyl-β-D-mannopyranosyl azide (6): Penta-*O*-acetyl-α-D-mannose **5** (3 g, 7.7 mmol) was dissolved in CH_2Cl_2 (80 mL), I_2 (2.74 g, 10.8 mmol) was added followed by the slow addition of Et_3SiH (1.72 mL, 10.8 mmol; **warning exothermic**). The reaction was heated at reflux for 20 min and was then cooled to room temperature, diluted with CH_2Cl_2 (80 mL) and washed with satd. aq. $NaHCO_3$ (150 mL) containing 10% $Na_2S_2O_3$. The aqueous phase was further extracted with CH_2Cl_2 (50 mL) and the combined organic extracts were dried over Na_2SO_4, filtered and the solvent was removed under diminished pressure. The residual glycosyl iodide was taken up in CH_2Cl_2 (60 mL) and tetrabutylammonium azide (3.3 g, 11.6 mmol) was added. The reaction mixture was stirred, overnight, before being diluted with CH_2Cl_2 (50 mL) and extracting with 1M HCl (100 mL). The aqueous phase was further washed with CH_2Cl_2 (30 mL) and the combined organic extracts were dried over Na_2SO_4, filtered and the solvent was removed under diminished pressure. Flash chromatography of the residue (petroleum ether/EtOAc 1:1) gave **6** (2.1 g, 64%) as a white solid; $[\alpha]_D = -70.6$ (*c* 0.3, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 5.44$ (dd, ^3J(H,H) = 3.3, 1.3 Hz, 1H; H-2), 5.26 (apt t, ^3J(H,H) = 10.0 Hz, 1H; H-4), 5.04 (dd, ^3J(H,H) = 10.1, 3.3 Hz, 1H; H-3), 4.73 (d, ^3J(H,H) = 1.3 Hz, 1H; H-1), 4.28 (dd, ^2J(H,H) = 12.4 Hz, ^3J-(H,H) = 5.7 Hz, 1H; H-6a), 4.20 (dd, ^2J(H, H) = 12.4 Hz, ^3J(H,H) = 2.5 Hz, 1H; H-6b), 3.76 (ddd, ^3J(H,H) = 10.0, 5.7, 2.5 Hz, 1H; H-5), 2.20 (s, 3H; $COCH_3$), 2.11 (s, 3H; $COCH_3$), 2.05 (s, 3H; $COCH_3$), 1.99 ppm (s, 3H; $COCH_3$); ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 170.6$, 169.9 (2s), 169.5 (each $COCH_3$), 85.1 (C-1), 74.6 (C-5), 70.9 (C-3), 69.2 (C-2), 65.3 (C-4), 62.3 (C-6), 20.7, 20.6, 20.5 ppm (each $COCH_3$); IR (film): $\tilde{\nu} = 2115$, 1744, 1366, 1238, 1209, 1038 cm^{-1}; ESI-HRMS calcd for $C_6H_{15}N_4O_5$ 391.1465, found *m/z* (%) 391.1469 $[M+NH_4]^+$.

6-*O*-*tert*-Butyldiphenylsilyl-2,3,4-tri-*O*-benzoyl-β-D-mannopyranosyl azide (7): Azide **6** (1.8 g, 4.8 mmol) was taken up in MeOH (20 mL) and NaOMe (0.05 g, 0.96 mmol) was added and the mixture was stirred for 1 h. Dowex 50WX8 H^+-resin (500 mg) was then added and the resulting suspension was stirred until the solution was neutral. This was then filtered and the solvent was removed to give the deprotected intermediate (0.93 g, 94%) as a white solid; $[\alpha]_D = -42.6$ (*c* 0.2, CH_3OH); ^{1}H NMR (500 MHz, D_2O): $\delta = 4.87$ (d, ^3J(H,H) = 1.1 Hz, 1H; H-1), 3.03 (dd, ^3J-(H,H) = 3.2, 1.1 Hz, 1H; H-2), 3.96 (dd, ^2J(H,H) = 12.3 Hz, ^3J(H,H) = 2.2 Hz, 1H; H-6a), 3.77 (dd, ^2J(H,H) = 12.3 Hz, ^3J(H,H) = 6.4 Hz, 1H; H-6b), 3.67 (dd, ^3J(H,H) = 9.7, 3.2 Hz, 1H; H-3), 3.61 (apt t, ^3J(H,H) = 9.6 Hz, 1H; H-4), 3.49 ppm (ddd, ^3J(H,H) = 9.5, 6.4, 2.2 Hz, 1H; H-5); ^{13}C NMR (126 MHz, D_2O): $\delta = 87.2$ (C-1), 78.3 (C-5), 72.7 (C-3), 71.0 (C-2), 66.4 (C-4), 60.9 ppm (C-6); IR (film): $\tilde{\nu} = 3332$, 2886, 2113, 1739, 1370, 1243, 1053, 1008 cm^{-1}; ESI-HRMS calcd for $C_8H_{13}N_3O_6Na$ 228.0596, found *m/z* (%) 228.0600 $[M+Na]^+$. This intermediate (0.9 g, 4.4 mmol) was dissolved in pyridine (50 mL) and the resulting solution was cooled over an ice-bath. TBDPSCl (1.36 mL, 5.3 mmol) was then added in a drop-wise manner and the reaction mixture was allowed to attain room temperature and was stirred, overnight. The resulting suspension was again cooled using an ice-bath and benzoyl chloride (1.12 mL, 9.7 mmol) was added slowly and the mixture was allowed to warm to room temperature and was stirred, overnight. Methanol (5 mL) was then added and the resulting slurry was diluted with EtOAc (50 mL), washed twice with 1M HCl (50 mL), satd aqueous $NaHCO_3$ (50 mL), brine (50 mL), dried over Na_2SO_4, filtered and the solvent was removed under diminished pressure. Flash chromatography of the residue (petroleum ether/EtOAc, 7:3) gave **7** (2.53 g, 76%) as a foam; $[\alpha]_D = -19.5$ (*c* 0.1, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 8.15$–7.13 (ms, 25H; Ar-H), 6.26 (apt t,

^3J(H,H) = 10.0 Hz, 1H; H-4), 5.96 (dd, ^3J(H,H) = 3.2, 1.3 Hz, 1H; H-2), 5.56 (dd, ^3J(H,H) = 10.3, 3.2 Hz, 1H; H-3), 5.00 (d, ^3J(H,H) = 1.3 Hz, 1H; H-1), 3.99–3.88 (m, 3H; H-6a, H-6b, H-5, overlapping peaks), 1.12 ppm (s, 9H; C(CH_3)$_3$); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 165.7, 165.4, 164.9 (each *C*OPh), 135.7, 135.5 (5 × Ar-CH, overlapping peaks), 133.5 133.3 (2s), 132.6 (5 × Ar-C), 130.2, 129.8, 129.7 (2s), 129.6, 129.3, 129.0, 128.8, 128.6, 128.5, 128.3, 127.8, 127.6 (20 × Ar-CH, overlapping peaks), 85.4 (C-1), 77.4 (C-5), 72.4 (C-3), 70.3 (C-2), 65.4 (C-4), 61.8 (C-6), 26.5 (C-(CH_3)$_3$, overlapping peaks), 19.2 ppm (C(CH$_3$)$_3$); IR (film): $\tilde{\nu}$ = 2931, 2119, 1729, 1452, 1259, 1092, 1025 cm^{-1}; ESI-HRMS calcd for $C_{43}H_{41}N_3O_8SiNa$ 778.2561, found *m/z* (%) 778.2553 [*M*+Na]$^+$.

2-Acetamido-6-*O*-*tert*-butyldiphenylsilyl-3,4-di-*O*-benzoyl-2-deoxy-β-D-glucopyranosyl azide (11): Pentaacetyl-D-glucosamine (3 g, 7.7 mmol) was suspended in CH_2Cl_2 (30 mL) and cooled to 0 °C. A 33% solution of HBr in AcOH (30 mL) was added and the reaction mixture was stirred for 5 h, keeping the reaction on ice. The reaction was then diluted with CH_2Cl_2 (50 mL) and poured onto ice (100 mL). The layers were separated and the aqueous layer was washed with a further portion of CH_2Cl_2 (30 mL). The combined organic extracts were washed with ice (100 mL), satd. aq. $NaHCO_3$ (100 mL), brine (100 mL), dried over Na_2SO_4, filtered and the solvent was removed under diminished pressure to give **9**. Freshly prepared **9** was dissolved in CH_2Cl_2 (30 mL) and tetrabutylammonium azide (4.38 g, 15.4 mmol) was added. The reaction mixture was stirred, overnight, and the solvent was removed under diminished pressure. Flash chromatography of the residue (EtOAc) gave the intermediate azide (1.55 g, 54%) as a white solid; $[\alpha]_D = -49.8$ (*c* 0.15, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.66 (d, ^3J(H,H) = 8.9 Hz, 1H; N*H*COCH$_3$), 5.24 (dd, ^3J(H,H) = 10.6, 9.4 Hz, 1H; H-3), 5.10 (dd, ^3J(H,H) = 10.1, 9.4 Hz, 1H; H-4), 4.76 (d, ^3J(H,H) = 9.2 Hz, 1H; H-1), 4.27 (dd, ^2J(H,H) = 12.4 Hz, ^3J(H,H) = 4.9 Hz, 1H; H-6a), 4.16 (dd, ^2J(H,H) = 12.4 Hz, ^3J-(H,H) = 2.3 Hz, 1H; H-6b), 3.91 (apt dt, ^3J(H,H) = 10.6, 9.2 Hz, 1H; H-2), 3.79 (ddd, ^3J(H,H) = 10.1, 4.9, 2.3 Hz, 1H; H-5), 2.10 (s, 3H; COCH_3), 2.04 (s, 3H; COCH_3), 2.03 (s, 3H; NHCOCH_3), 1.98 ppm (s, 3H; COCH_3); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 171.0, 170.6, 170.3 (each *C*OCH$_3$), 169.2 (NH*C*OCH$_3$), 88.4 (C-1), 74.0 (C-5), 72.1 (C-3), 68.0 (C-4), 61.8 (C-6), 54.2 (C-2), 23.2 (NHCOCH_3), 20.7, 20.6 ppm (2s) (3 × COCH_3); IR (film): $\tilde{\nu}$ = 3334, 2959, 2141, 2105, 1740, 1659, 1371, 1224, 1034 cm^{-1}; ESI-HRMS calcd for $C_{14}H_{20}N_4O_8Na$ 395.1179, found *m/z* (%) 395.1187 [*M*+Na]$^+$. This intermediate (1.5 g, 4.0 mmol) was dissolved in MeOH (20 mL) and NaOMe (0.04 g, 0.8 mmol) was added. The reaction was quenched after 1 h by the addition of Dowex 50WX8 H$^+$-resin (50 mg). The reaction was filtered and the solvent was removed to give the unprotected GlcNAc derivative (0.89 g, 91%) as a white solid; $[\alpha]_D = -21.9$ (*c* 0.07, CH_3OH); ^{1}H NMR (500 MHz, D_2O): δ = 4.78 (d, ^3J-(H,H) = 9.4 Hz, 1H; H-1), 3.95 (dd, ^2J(H, H) = 12.5 Hz, ^3J(H,H) = 2.2 Hz, 1H; H-6a), 3.79 (dd, ^2J(H,H) = 12.5 Hz, ^3J(H,H) = 5.5 Hz, 1H; H-6b), 3.73 (dd, ^3J(H,H) = 10.2, 9.4 Hz, 1H; H-2), 3.62–3.57 (m, 1H; H-3), 3.57–3.34 (m, 1H; H-5), 3.50 (dd, ^3J(H,H) = 9.8, 8.7 Hz, 1H; H-4), 2.08 ppm (s, 3H; NHCOCH_3); ^{13}C NMR (126 MHz, D_2O): δ = 174.7 (NH*C*OCH$_3$), 88.6 (C-1), 77.8 (C-5), 73.6 (C-3), 69.4 (C-4), 60.5 (C-6), 55.0 (C-2), 22.0 ppm (NHCOCH_3); IR (film): $\tilde{\nu}$ = 3266, 2920, 2112, 1737, 1544, 1373, 1235, 1034 cm^{-1}; ESI-HRMS calcd for $C_8H_{15}N_4O_5$ 233.1012, found *m/z* (%) 233.1019[*M*+H]$^+$. This polyhydroxylated intermediate (0.84 g, 3.4 mmol) was taken up in pyridine (15 mL) and the resulting solution was cooled and treated with TBDPSCl (1.1 mL, 4.1 mmol) followed by benzoyl chloride (0.87 mL, 7.5 mmol) as described above in formation of **7**. Flash chromatography (petroleum ether/EtOAc 6:4) gave **11** (1.8 g, 76%) as a white foam; $[\alpha]_D = -51.2$ (*c* 0.13, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.98–7.91 (m, 2H; Ar-H), 7.90–7.83 (m, 2H; Ar-H), 7.75–7.68 (m, 2H; Ar-H), 7.61–7.45 (m, 4H; Ar-H), 7.42–7.32 (m, 6H; Ar-H), 7.18 (dd, ^3J(H,H) = 8.1, 7.0 Hz, 2H; Ar-H), 5.82–5.70 (m, 2H; H-4, N*H*COCH$_3$, overlapping peaks), 5.59 (dd, ^3J(H,H) = 10.7, 9.6 Hz, 1H; H-3), 4.76 (d, ^3J(H,H) = 9.2 Hz, 1H; H-1), 4.25 (apt dt, ^3J-(H,H) = 10.7, 9.2 Hz, 1H; H-2), 3.91–3.78 (m, 3H; H-6a, H-6b, H-5, overlapping peaks), 1.91 (s, 3H; NHCOCH_3), 1.04 ppm (s, 9H; C(CH_3)$_3$); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 170.5 (NH*C*OCH$_3$), 167.1, 164.8 (2 × *C*OPh), 135.6, 135.5, 133.6, 133.5, 133.3 (6 × Ar-CH, overlapping peaks), 132.9, 132.8 (2 × Ar-C), 130.0, 129.7 (2s), 129.6, 128.5 (2s) (6 × Ar-CH, overlapping peaks) (Ar-C, 2 × Ar-CH, overlapping peaks), 128.4 (2s) (Ar-C, 2 × Ar-CH, overlapping peaks), 127.7, 127.6 (4 × Ar-CH, overlapping peaks), 88.6 (C-1), 77.1 (C-5), 73.2 (C-3), 68.3 (C-4), 62.2 (C-6), 54.6 (C-2), 26.6 (C(CH_3)$_3$, overlapping peaks), 23.3 (NHCOCH_3), 19.2 ppm (*C*-(CH$_3$)$_3$); IR (film): $\tilde{\nu}$ = 3268, 2931, 2113, 1725, 1657, 1548, 1240, 1061 cm^{-1}; ESI-HRMS calcd for $C_{38}H_{40}N_4O_7SiNa$ 701.2533, found *m/z* (%) 701.2540 [*M*+Na]$^+$.

2-Acetamido-6-*O*-*tert*-butyldiphenylsilyl-3,4-di-*O*-benzoyl-2-deoxy-β-D-galactopyranosyl azide (12): Treatment of pentaacetyl-D-galactosamine (3 g, 7.7 mmol) as described above for the glucosamine gave, via bromide **10**, the intermediate azide (1.7 g, 59%) as a white solid; $[\alpha]_D = -30.5$ (*c* 0.04, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.56 (d, ^3J(H,H) = 8.8 Hz, 1H; N*H*COCH$_3$), 5.38 (dd, ^3J(H,H) = 3.3, 1.1 Hz, 1H; H-4), 5.24 (dd, ^3J-(H,H) = 11.1, 3.3 Hz, 1H; H-3), 4.79 (d, ^3J(H,H) = 9.2 Hz, 1H; H-1), 4.19–4.13 (m, 2H; H-6a, H-6b, overlapping peaks), 4.07–3.97 (m, 2H; H-5, H-2, overlapping peaks), 2.16 (s, 3H; NHCOCH_3), 2.06 (s, 3H; COCH_3), 2.01 (s, 3H; COCH_3), 1.99 ppm (s, 3H; COCH_3); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 170.5, 170.4 (3 × *C*OCH$_3$), 170.1 (NH*C*OCH$_3$), 88.7 (C-1), 72.8 (C-5), 69.7 (C-3), 66.5 (C-4), 61.4 (C-6), 50.8 (C-2), 23.4 (NHCOCH_3), 20.7, 20.6 ppm (2s) (3 × COCH_3); IR (film): $\tilde{\nu}$ = 3267, 2932, 2113, 1723, 1549, 1315, 1240, 1061 cm^{-1}; ESI-HRMS calcd for $C_{14}H_{20}N_4O_8Na$ 395.1179, found *m/z* (%) 395.1184 [*M*+Na]$^+$. Treatment of this azide (1.65 g, 4.4 mmol) as described above for the corresponding GlcNAc derivative with MeOH (20 mL) and NaOMe (0.05 g, 0.9 mmol) gave the unprotected GalNAc azide (0.93 g, 86%) as a white solid; $[\alpha]_D = -145.2$ (*c* 0.04, CH_3OH); ^{1}H NMR (500 MHz, D_2O): δ = 4.68 (d, ^3J(H,H) = 9.3 Hz, 1H; H-1), 3.99 (dd, ^3J(H,H) = 3.1, 0.8 Hz, 1H; H-4), 3.94 (dd, ^3J(H,H) = 10.7, 9.3 Hz, 1H; H-2), 3.85–3.75 (m, 4H; H-6a, H-6b, H-5, H-3, overlapping peaks), 2.07 ppm (s, 3H; NHCOCH_3); ^{13}C NMR (126 MHz, D_2O): δ = 174.9 (NH*C*OCH$_3$), 89.0 (C-1), 77.2 (C-5), 70.7 (C-3), 67.6 (C-4), 60.9 (C-6), 51.7 (C-2), 22.1 ppm (NHCOCH_3); IR (film): $\tilde{\nu}$ = 3329, 2907, 2095, 1639, 1553, 1429, 1326, 1226, 1018 cm^{-1}; ESI-HRMS calcd for $C_8H_{14}N_4O_5Na$ 269.0862, found *m/z* (%) 269.0851 [*M*+Na]$^+$. This intermediate (0.9 g, 3.7 mmol) when treated with pyridine (15 mL) and TBDPSCl (1.14 mL, 4.4 mmol) and then benzoyl chloride (0.93 mL, 8.0 mmol) as described above in preparation of **7** gave after chromatography (petroleum ether/EtOAc, 6:4) the title compound **12** (1.79 g, 70%) as a white foam; $[\alpha]_D = +32.7$ (*c* 0.1, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.07–8.02 (m, 2H; Ar-H), 7.87–7.83 (m, 2H; Ar-H), 7.66–7.60 (m, 3H; Ar-H), 7.54–7.47 (m, 5H; Ar-H), 7.42–7.28 (m, 5H; Ar-H), 7.11 (t, ^3J(H,H) = 7.6 Hz, 2H; Ar-H), 6.00–5.94 (m, 1H; H-3), 5.64–5.57 (m, 2H; H-4, N*H*COCH$_3$, overlapping peaks), 4.80 (d, ^3J(H,H) = 9.2 Hz, 1H; H-1), 4.33 (apt dt, ^3J(H,H) = 11.1, 9.0 Hz, 1H; H-2), 4.06 (ddd, ^3J-(H,H) = 7.4, 6.1, 1.2 Hz, 1H; H-5), 3.86–3.75 (m, 2H; H-6a, H-6b, overlapping peaks), 1.89 (s, 3H; NHCOCH_3), 0.99 ppm (s, 9H; C(CH_3)$_3$); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 170.5 (NH*C*OCH$_3$), 166.4, 165.3 (2 × *C*OPh), 135.5, 135.4, 133.5 (2s), 133.4 (6 × Ar-CH, overlapping peaks), 132.7, 132.5 (2 × Ar-C), 129.9 (2s), 129.8, 129.7 (6 × Ar-CH, overlapping peaks), 129.4, 128.8 (2 × Ar-C), 128.6, 128.4, 127.8, 127.6 (8 × Ar-CH, overlapping peaks), 89.0 (C-1), 75.7 (C-5), 71.0 (C-4), 67.1 (C-3), 61.1 (C-6), 51.4 (C-2), 26.6 (C(CH_3)$_3$, overlapping peaks), 23.3 (NHCOCH_3), 19.0 ppm (C(CH$_3$)$_3$); IR (film): $\tilde{\nu}$ = 3994, 2860, 2115, 1722, 1657, 1272, 1106, 1068 cm^{-1}; ESI-HRMS calcd for $C_{38}H_{40}N_4O_7SiNa$ 701.2533, found *m/z* (%) 701.2525[*M*+Na]$^+$.

4,6-*O*-(1,1,3,3-Tetraisopropyl-1,3-disiloxanediyl)-β-D-glucopyranosyl azide (16): Sodium methoxide (0.2 g, 4.0 mmol) was added to the azide **15** (7.5 g, 20.1 mmol) in MeOH (50 mL) and the mixture was stirred for 1 h and then Dowex 50WX8 H$^+$-resin (500 mg) was added and the resulting suspension was stirred until the pH was 7. This mixture was then filtered and the solvent was removed under diminished pressure to give β-D-glucopyranosyl azide (3.92 g, 95%) as a white solid; $[\alpha]_D = -31.0$ (*c* 0.3, CH_3OH); ^{1}H NMR (500 MHz, D_2O): δ = 4.75 (d, ^3J(H,H) = 8.8 Hz, 1H; H-1), 3.93 (dd, ^2J(H,H) = 12.4 Hz, ^3J(H,H) = 2.2 Hz, 1H; H-6a), 3.75 (dd, ^2J(H,H) = 12.4 Hz, ^3J(H,H) = 5.7 Hz, 1H; H-6b), 3.57–3.49 (m, 2H; H-5, H-3, overlapping peaks), 3.41 (apt t, ^3J(H,H) = 9.0 Hz, 1H; H-4), 3.27 ppm (apt t, ^3J(H,H) = 9.0 Hz, 1H; H-2); ^{13}C NMR (126 MHz, D_2O): δ = 90.9 (C-1), 79.0 (C-5), 76.9 (C-3), 73.6 (C-2), 69.9 (C-4), 61.4 ppm (C-6); IR (film): $\tilde{\nu}$ = 3303, 2881, 2125, 1472, 1377, 1263, 1064 cm^{-1}; ESI-HRMS calcd for $C_6H_{12}N_3O_5$ 206.0777, found *m/z* (%) 206.0772 [*M*+H]$^+$. To this intermediate (3.5 g, 17.1 mmol) in pyridine (50 mL) at 0 °C was

added 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane (0.99 mL, 20.5 mmol) and the mixture was allowed to warm to room temperature and was then stirred for 5 h at which point MeOH (1 mL) was added and the solvent removed under diminished pressure. The resulting residue was taken up in EtOAc (50 mL) and washed with 1 M HCl (50 mL), $NaHCO_3$ (50 mL), brine (50 mL), then dried over Na_2SO_4, filtered and the solvent removed under diminished pressure. Flash chromatography of the residue (petroleum ether/EtOAc, 7:3) gave **16** (4.7 g, 61%) as a white solid; $[\alpha]_D = -80.7$ (*c* 0.20, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 4.58$ (d, ^3J(H,H) = 8.6 Hz, 1H; H-1), 4.09 (dd, ^2J(H,H) = 12.7 Hz, ^3J(H,H) = 2.1 Hz, 1H; H-6a), 4.00 (dd, ^2J(H,H) = 12.7 Hz, ^3J(H,H) = 1.5 Hz, 1H; H-6b), 3.83 (apt t, ^3J(H,H) = 9.1 Hz, 1H; H-4), 3.60 (apt t, ^3J(H,H) = 9.1 Hz, 1H; H-3), 3.34–3.26 (m, 2H; H-5, H-2, overlapping peaks), 2.56 (s, 2H; 2× OH), 1.25–0.89 ppm (m, 28H; 4×C*H*(C*H*$_3$)$_2$, overlapping peaks); ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 90.8$ (C-1), 78.7 (C-5), 76.5 (C-3), 73.5 (C-2), 68.8 (C-4), 60.6 (C-6), 17.4, 17.3, 17.2 (3s), 17.1 (2s) (8×CH(*C*H$_3$)$_2$, overlapping peaks), 13.6, 13.2, 12.5 ppm (2s) (4×*C*H(CH$_3$)$_2$, overlapping peaks); IR (film): $\tilde{\nu} = 3420$, 2868, 2115, 1465, 1248, 1025 cm^{-1}; ESI-HRMS calcd for $C_{18}H_{37}N_3O_6Si_2Na$ 442.2349, found *m/z* (%) 442.2352 $[M+Na]^+$.

Methyl 1-azido-1-deoxy-3,4-*O*-(1,1,3,3-tetraisopropyl-1,3-disiloxanediyl)-β-D-glucopyranuronate (17): *p*-TsOH.H$_2$O (0.17 g, 0.9 mmol) was added to diol **16** (2 g, 4.45 mmol), in DMF (25 mL) and the mixture was stirred at room temperature for 5 h and it was then diluted with EtOAc (50 mL), washed with H_2O (2×25 mL), satd. aq. $NaHCO_3$ (50 mL), brine (50 mL), dried over Na_2SO_4, filtered and the solvent was removed under diminished pressure. Flash chromatography of the residue (petroleum ether/EtOAc 8:2) gave the 3,4-protected intermediate (1.87 g, 94%) as a clear oil; $[\alpha]_D = -4.8$ (*c* 0.17, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta =$ 4.60 (d, ^3J(H,H) = 8.6 Hz, 1H; H-1), 3.93 (ddd, ^2J(H,H) = 12.0 Hz, ^3J(H,H) = 6.3, 2.2 Hz, 1H; H-6a), 3.77 (ddd, ^2J(H,H) = 12.0 Hz, ^3J(H,H) = 7.2, 4.9 Hz, 1H; H-6b), 3.73–3.64 (m, 2H; H-4, H-3, overlapping peaks), 3.45 (ddd, ^3J(H,H) = 8.9, 4.9, 2.8 Hz, 1H; H-5), 3.38 (apt td, ^3J(H,H) = 8.6, 2.2 Hz, 1H; H-2), 2.44 (d, ^3J(H,H) = 2.3 Hz, 1H; OH), 1.93 (apt t, ^3J(H,H) = 6.8 Hz, 1H; OH), 1.16–0.86 ppm (m, 28H; 4×C*H*(CH_3)$_2$, overlapping peaks); ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 89.5$ (C-1), 79.8 (C-3), 78.4 (C-5), 73.9 (C-2), 72.1 (C-4), 61.9 (C-6), 17.3 (3s), 17.2 (2s), 17.1 (8× CH(*C*H$_3$)$_2$, overlapping peaks), 12.9, 12.8, 12.1 ppm (2s) (4×*C*H(CH$_3$)$_2$, overlapping peaks); IR (film): $\tilde{\nu} = 3349$, 2868, 2114, 1464, 1248, 1052, 987 cm^{-1}; ESI-HRMS calcd for $C_{18}H_{37}N_3O_6Si_2Na$ 442.2349, found *m/z* (%) 442.2356 $[M+Na]^+$. This intermediate (1.8 g, 4.0 mmol) was dissolved in MeCN/H_2O (60 mL, 3:1) and treated with BAIB (3.24 g, 10.1 mmol) and TEMPO (0.06 g, 0.4 mmol) as described above to give the carboxylic acid, which when treated in DMF (25 mL) with $NaHCO_3$ (0.5 g, 6.0 mmol) and methyl iodide (0.37 mL, 6.0 mmol) gave **17** (0.97 g, 51%) as a clear oil after chromatography (petroleum ether/EtOAc 9:1); $[\alpha]_D$:−3.6° (*c* 0.06, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 4.61$ (d, ^3J(H,H) = 8.7 Hz, 1H; H-1), 3.96–3.90 (m, 2H; H-5, H-4, overlapping peaks), 3.78 (s, 3H; O*C*H$_3$), 3.68 (ddd, ^3J(H,H) = 8.5, 6.4, 1.9 Hz, 1H; H-3), 3.45 (td, ^3J(H,H) = 8.7, 1.9 Hz, 1H; H-2), 2.43 (d, ^3J(H,H) = 2.4 Hz, 1H; OH), 1.29–0.46 ppm (m, 28H; 4×C*H*(C*H*$_3$)$_2$, overlapping peaks); ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 168.2$ (*C*O$_2$CH$_3$), 89.9 (C-1), 79.3 (C-3), 77.4 (C-5), 73.7 (C-4), 73.4 (C-2), 52.4 (CO$_2$*C*H$_3$), 17.3, 17.2 (4s), 17.1, 17.0 (2s) (8×CH(*C*H$_3$)$_2$, overlapping peaks), 12.9, 12.8, 12.2, 12.1 ppm (4×*C*H(CH$_3$)$_2$, overlapping peaks); IR (film): $\tilde{\nu} = 3441$, 2867, 2125, 1785, 1736, 1464, 1251, 1081, 987 cm^{-1}; ESI-HRMS calcd for $C_{19}H_{37}N_3O_7Si_2Na$ 498.2068, found *m/z* (%) 498.2074 $[M+Na]^+$.

Methyl 2-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-1-azido-1-deoxy-3,4-*O*-(1,1,3,3-tetraisopropyl-1,3-disiloxanediyl)-β-D-glucopyranuronate (19): Compound **17** (0.25 g, 0.5 mmol), **18**[13] (0.58 g, 0.8 mmol) and CH_2Cl_2 (6 L) were added to a flame-dried flask containing freshly activated 4 Å molecular sieves (0.6 g). The resulting suspension was stirred at room temperature for 30 min before being cooled to 0 °C using an ice-bath. TMSOTf (0.029 mL, 0.16 mmol) was then added and the reaction mixture was allowed to attain room temperature over 1 h. Triethylamine (0.25 mL) was added, the mixture filtered and the solvent was removed under diminished pressure. Flash chromatography of the residue (petroleum ether/EtOAc 8:2) gave **19** (0.35 g, 67%) as a white foam; $[\alpha]_D = -22.6$ (*c* 0.07, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 8.06$–8.01 (m, 2H; Ar-H), 7.91 (ddd, ^3J(H,H) = 8.5, 4.0, 1.3 Hz, 4H; Ar-H), 7.82–7.71 (m, 2H; Ar-H), 7.57–7.52 (m, 1H; Ar-H), 7.50 (dd, ^3J(H,H) = 8.3, 6.7 Hz, 2H; Ar-H), 7.41 (apt q, ^3J(H,H) = 7.8 Hz, 3H; Ar-H), 7.35 (td, ^3J(H,H) = 7.7, 4.2 Hz, 4H; Ar-H), 7.28–7.22 (m, 1H; Ar-H), 5.85 (apt t, ^3J(H,H) = 9.5 Hz, 1H; H-3), 5.73 (apt t, ^3J(H,H) = 9.6 Hz, 1H; H-4), 5.58 (dd, ^3J-(H,H) = 9.6, 7.7 Hz, 1H; H-2), 5.35 (d, ^3J(H,H) = 7.7 Hz, 1H; H-1), 4.71 (dd, ^2J(H,H) = 12.1 Hz, ^3J(H,H) = 3.2 Hz, 1H; H-6a), 4.57–4.47 (m, 2H; H-1′, H6-b, overlapping peaks), 4.11 (ddd, ^3J(H,H) = 10.0, 5.2, 3.2 Hz, 1H; H-5), 3.93 (apt t, ^3J(H,H) = 8.5 Hz, 1H; H-2′), 3.89–3.79 (m, 3H; H-3′, H-4′, H-5′, overlapping peaks), 3.75 (s, 3H; OCH_3), 1.06–0.68 ppm (m, 28H; 4×C*H*(C*H*$_3$)$_2$, overlapping peaks); ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 168.1$ (*C*O$_2$CH$_3$), 166.1, 165.8, 165.1 (2s) (4×*C*OPh), 133.4, 133.2 (2s), 133.1, 129.9, 129.8, 129.7 (12×Ar-CH, overlapping peaks), 129.6, 129.2, 128.8, 128.0 (4×Ar-C), 128.4 (2s), 128.3, 128.2 (8×Ar-CH, overlapping peaks), 100.0 (C-1), 88.4 (C-1′), 79.7 (C-3′), 77.2 (C-5′), 76.4 (C-2′), 74.0 (C-4′), 73.1 (C-3), 72.5 (C-2), 72.3 (C-5), 69.6 (C-4), 62.9 (C-6), 52.4 (CO$_2$*C*H$_3$), 17.5, 17.4, 17.2 (2s), 17.1, 17.0 (2s) (8×CH(*C*H$_3$)$_2$, overlapping peaks), 12.8, 12.7, 12.3, 12.2 ppm (4×*C*H(CH$_3$)$_2$, overlapping peaks); IR (film): $\tilde{\nu} = 2946$, 2119, 1728, 1452, 1249, 1089, 986 cm^{-1}; ESI-HRMS calcd for $C_{53}H_{63}N_3O_{16}Si_2Na$ 1076.3645, found *m/z* (%) 1076.3652 $[M+Na]^+$.

Allyl 6-*O*-*tert*-butyldiphenylsilyl-2,3,4-tri-*O*-benzoyl-β-D-glucopyranoside (22): Deacetylation of **21** (9 g, 23.2 mmol) as described for **15** gave the intermediate (4.4 g, 87%) as a white solid; $[\alpha]_D = -35.0$ (*c* 0.24, CH_3OH); ^{1}H NMR (500 MHz, D_2O): $\delta = 5.99$ (dddd, *J* = 17.0, 10.5, 6.3, 5.5 Hz, 1H; $CH_2CH{=}CH_2$), 5.40 (dq, ^3J(H,H) = 17.0 Hz, ^2J(H,H) 1.5 Hz, 1H; $CH_2CH{=}CH_2$), 5.30 (dq, ^3J(H,H) = 10.5 Hz, ^2J(H,H) = 1.5 Hz, 1H; $CH_2CH{=}CH_2$), 4.51 (d, *J* = 8.0 Hz, 1H; H-1), 4.40 (ddt, ^2J(H,H) = 12.7, 1.4 Hz, ^3J(H,H) = 5.5 Hz, 1H; $CH_2CH{=}CH_2$), 4.24 (ddt, ^2J(H,H) = 12.7, 1.4 Hz, ^3J(H,H) = 6.3 Hz, 1H; CH_2CHCH_2), 3.93 (dd, ^2J(H,H) = 12.3 Hz, ^3J(H,H) = 2.2 Hz, 1H; H-6a), 3.73 (dd, ^2J(H,H) = 12.3 Hz, ^3J(H,H) = 6.0 Hz, 1H; H-6b), 3.50 (apt t, ^3J(H,H) = 9.2 Hz, 1H; H-3), 3.47–3.44 (m, 1H; H-5), 3.39 (dd, ^3J(H,H) = 9.9, 8.9 Hz, 1H; H-4), 3.30 ppm (dd, ^3J-(H,H) = 9.3, 8.0 Hz, 1H; H-2); ^{13}C NMR (126 MHz, D_2O): $\delta = 133.2$ (CH_2CHCH_2), 118.7 (CH_2CHCH_2), 101.1 (C-1), 75.8 (C-5), 75.7 (C-3), 73.0 (C-2), 70.5 (CH_2CHCH_2), 69.6 (C-4), 60.7 ppm (C-6); IR (film): $\tilde{\nu} =$ 3295, 2915, 1664, 1458, 1365, 1109, 1073, 1022 cm^{-1}; ESI-HRMS calcd for $C_9H_{16}O_6Na$ 243.0845, found *m/z* (%) 243.0852 $[M+Na]^+$. This intermediate (10 g, 45.4 mmol) was treated with pyridine (100 mL), TBDPSCl (14.1 mL, 54.5 mmol) and benzoyl chloride (34.82 mL, 299.7 mmol) as described previously to give **22** (27.3 g, 78%) as a foam; $[\alpha]_D = -21.1$ (*c* 0.1, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.99$–7.94 (m, 1H), 7.88–7.81 (m, 2H; Ar-H), 7.71–7.67 (m, 4H; Ar-H), 7.62–7.58 (m, 2H; Ar-H), 7.5–7.48 (m, 2H; Ar-H), 7.44–7.27 (m, 9H; Ar-H), 7.25–7.21 (m, 2H; Ar-H), 5.88–5.78 (m, 2H; CH_2CHCH_2, C-3, overlapping peaks), 5.62 (apt t, ^3J-(H,H) = 9.2 Hz, 1H; H-4), 5.53 (dd, ^3J(H,H) = 9.7, 7.9 Hz, 1H; H-2), 5.25 (dq, ^3J(H,H) = 17.3 Hz, ^2J(H,H) 1.7 Hz, 1H; CH_2CHCH_2), 5.15 (dq, ^3J-(H,H) = 10.5 Hz, ^2J(H,H) 1.4 Hz, 1H; $CH_2CH{=}CH_2$), 4.85 (d, ^3J(H,H) = 7.9 Hz, 1H; H-1), 4.38 (ddt, ^2J(H,H) = 13.3 Hz, ^3J(H,H) = 4.8, 1.7 Hz, 1H; $CH_2CH{=}CH_2$), 4.17 (ddt, ^2J(H,H) = 13.3 Hz, ^3J(H,H) = 6.3, 1.4 Hz, 1H; $CH_2CH{=}CH_2$), 3.90–3.82 (m, 2H; C-5, C-6a, C-6b, overlapping peaks), 1.04 ppm (s, 9H; C(*C*H$_3$)$_3$); ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 165.9$, 165.0 (3×*C*OPh, overlapping peaks), 135.6, 135.5 (4×Ar-CH, overlapping peaks), 133.6 ($CH_2CH{=}CH_2$), 133.2 (2×Ar-CH), 133.1 (2s) (Ar-C, 2×Ar-CH, overlapping peaks), 133.0 (Ar-C), 129.8 (2s), 129.7, 129.6 (2s) (6× Ar-CH, overlapping peaks), 129.5, 129.2, 129.0 (3×Ar-C),128.3 (2s), 128.2, 127.6 (2s) (11×Ar-CH, overlapping peaks), 117.6 (CH_2CHCH_2), 99.7 (C-1), 75.2 (C-5), 73.4 (C-3), 72.0 (C-2), 69.6 ($CH_2CH{=}CH_2$), 69.3 (C-4), 62.8 (C-6), 26.6 (C(*C*H$_3$)$_3$, overlapping peaks), 19.2 ppm (*C*-(CH$_3$)$_3$); IR (film): $\tilde{\nu} = 3071$, 2857, 1729, 1451, 1259, 1091, 1026 cm^{-1}; ESI-HRMS calcd for $C_{46}H_{46}O_9SiNa$ 793.2809, found *m/z* (%) 793.2798 $[M+Na]^+$.

1-*O*-Allyl-2,3,4-tri-*O*-benzoyl-β-D-glucopyranosiduronic acid, methyl ester (23): The TBDPS derivative **22** (27.0 g, 35.0 mmol) was dissolved in THF (250 mL) and the resulting solution was cooled using an ice-bath. AcOH (4 mL, 70.0 mmol) and 1 M TBAF in THF (70 mL, 70.0 mmol) were added to this. The mixture was allowed to attain room temperature and was stirred for 16 h and the product was adsorbed on silica gel. Flash chromatography (petroleum ether/EtOAc 3:2) gave the intermediate alcohol (14.4 g, 77%) as a white solid; $[\alpha]_D = -23.0$ (*c* 0.2, CH_2Cl_2);

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.95 (aptt, ^3J(H,H) = 7.3, 1.4 Hz, 4H; Ar-H), 7.89–7.81 (m, 2H; Ar-H), 7.59–7.47 (m, 2H; Ar-H), 7.46–7.35 (m, 5H; Ar-H), 7.31–7.26 (m, 2H; Ar-H), 5.93 (aptt, ^3J(H,H) = 9.7 Hz, 1H; H-3), 5.81 (dddd, ^3J(H,H) = 17.0, 10.7, 6.1, 5.0 Hz, 1H; CH_2CHCH_2), 5.60–5.39 (m, 2H; H-2, H-4, overlapping peaks), 5.26 (dq, ^3J(H,H) = 17.0 Hz, ^2J(H,H) = 1.4 Hz, 1H; CH_2CHCH_2), 5.15 (dq, ^3J(H,H) = 10.7 Hz, ^2J(H,H) = 1.4 Hz, 1H; CH_2CHCH_2), 4.89 (d, ^3J(H,H) = 7.9 Hz, 1H; H-1), 4.39 (ddt, ^2J(H,H) = 13.3 Hz, ^3J(H,H) = 5.0, 1.6 Hz, 1H; CH_2CHCH_2), 4.19 (ddt, ^2J(H,H) = 13.3 Hz, ^3J(H,H) = 6.1, 1.4 Hz, 1H; CH_2CHCH_2), 3.86 (ddd, ^2J(H,H) = 12.4 Hz, ^3J(H,H) = 8.8, 1.9 Hz, 1H; H-6a), 3.83–3.68 (m, 2H; H-6b, H-5), 2.55 ppm (dd, ^3J(H,H) = 8.8, 5.3 Hz, 1H; OH); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 166.0, 165.8, 165.0 (3×*C*OPh), 133.7 (Ar-CH, overlapping peaks), 133.4 (CH_2CHCH_2), 133.2 (2s) (2×Ar-CH), 129.9, 129.8, 129.7 (6×Ar-CH, overlapping peaks), 129.3, 128.8, 128.6 (3×Ar-C), 128.5, 128.3 (2s) (6×Ar-CH), 117.7 (CH_2CHCH_2), 100.0 (C-1), 74.6 (C-5), 72.8 (C-3), 71.8 (C-4), 70.2 (CH_2CHCH_2), 69.6 (C-2), 61.4 ppm (C-6); IR (film): $\tilde{\nu}$ = 3380, 2955, 1722, 1451, 1252, 1066, 1026 cm^{-1}; ESI-HRMS calcd for $C_{30}H_{28}O_9Na$ 555.1631, found *m/z* (%) 555.1637 $[M+Na]^+$. This intermediate (14 g, 26.3 mmol) in MeC/H_2O (100 mL, 3:1) was oxidised, using BAIB (21.17 g, 65.7 mmol) and TEMPO (0.4 g, 2.6 mmol), and the resulting acid was esterified in DMF (80 mL) using $NaHCO_3$ (3.3 g, 39.5 mmol) and methyl iodide (2.5 mL, 39.5 mmol) as described above to give **23** (8.7 g, 59%) as a foam; $[\alpha]_D$ = −40.0 (*c* 0.07, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.98–7.92 (m, 4H; Ar-H), 7.90–7.83 (m, 2H; Ar-H), 7.52 (dddd, ^3J(H,H) = 7.6, 4.9, 2.4, 1.3 Hz, 2H; Ar-H), 7.47–7.43 (m, 1H; Ar-H), 7.38 (dddd, ^3J(H,H) = 8.2, 6.2, 3.5, 1.7 Hz, 4H; Ar-H), 7.33–7.28 (m, 2H; Ar-H), 5.90 (aptt, ^3J(H,H) = 9.3 Hz, 1H; H-3), 5.80 (dddd, ^3J(H,H) = 17.0, 10.5, 6.4, 4.7 Hz, 1H; CH_2CHCH_2), 5.71 (aptt, ^3J(H,H) = 9.4 Hz, 1H; H-4), 5.57 (dd, ^3J(H,H) = 9.3, 7.3 Hz, 1H; H-2), 5.26 (dq, ^3J(H,H) = 17.0 Hz, ^2J(H,H) = 1.6 Hz, 1H; CH_2CHCH_2), 5.16 (dq, ^3J(H,H) = 10.5 Hz, ^3J(H,H) = 1.4 Hz, 1H; CH_2CHCH_2), 4.92 (d, ^3J(H,H) = 7.3 Hz, 1H; H-1), 4.42 (ddt, ^2J(H,H) = 13.2 Hz, ^3J(H,H) = 4.8, 1.6 Hz, 1H; $CH_2CH{=}CH_2$), 4.35 (d, ^3J(H,H) = 9.4 Hz, 1H), 4.17 (ddt, ^2J(H,H) = 13.2 Hz, ^3J(H,H) = 6.4, 1.4 Hz, 1H; $CH_2CH{=}CH_2$), 3.70 ppm (s, 3H; CO_2CH_3); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 167.4 (CO_2CH_3), 165.6, 165.2, 165.0 (3×*C*OPh), 133.4, 133.3, 133.2 (3×Ar-CH), 133.1 ($CH_2CH{=}CH_2$), 129.8 (3s) (6×Ar-CH, overlapping peaks), 129.2, 128.7, 128.5 (3×Ar-C), 128.4 (2s), 128.3 (6×Ar-CH, overlapping peaks), 118.0 ($CH_2CH{=}CH_2$), 99.6 (C-1), 72.9 (C-5), 72.0 (C-3), 71.5 (C-2), 70.2 (CH_2CHCH_2), 70.1 (C-4), 52.9 ppm (CO_2CH_3); IR (film): $\tilde{\nu}$ = 3068, 1761, 1726, 1451, 1250, 1088 cm^{-1}; ESI-HRMS calcd for $C_{31}H_{32}NO_{10}$ 578.2026, found *m/z* (%) 578.2031 $[M+NH_4]^+$.

2,3,4-Tri-*O*-benzoyl-1-deoxy-1-(2,2,2-trichloro-1-iminoethoxy)-D-glucopyranuronate, methyl ester (24): The allyl glycoside **23** (8.5 g, 15.1 mmol) was dissolved in MeOH/CH_2Cl_2 (60 mL, 3:1) and $PdCl_2$ (0.54 g, 3.0 mmol) was added and the mixture was stirred for 16 h at room temperature. The resulting suspension was filtered through Celite and the solvent was removed to give a foam. Flash chromatography (petroleum ether/EtOAc 6:4) gave the hemiacetal (5.6 g, 10.8 mmol). This intermediate was dissolved in CH_2Cl_2 (50 mL) and cooled on an ice-bath and trichloroacetonitrile (10.8 mL, 107.6 mmol) and DBU (0.5 mL) were added. The mixture was stirred for 5 h and was directly subjected to flash chromatography (petroleum ether/EtOAc 7:3, 0.1% Et_3N) to give **24** (6.95 g, 69%) as a white foam; $[\alpha]_D$ = +44.4 (*c* 0.18, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.68 (s, 1H; N*H*), 8.00–7.93 (m, 4H; Ar-H), 7.92–7.85 (m, 2H; Ar-H), 7.58–7.49 (m, 2H; Ar-H), 7.46 (ddt, ^3J(H,H) = 8.7, 7.2, 1.3 Hz, 1H; Ar-H), 7.42–7.30 (m, 5H; Ar-H), 6.91 (d, ^3J(H,H) = 3.6 Hz, 1H; H-1), 6.29 (aptt, ^3J(H,H) = 9.9 Hz, 1H; H-3), 5.76 (aptt, ^3J(H,H) = 9.9 Hz, 1H; H-4), 5.63 (dd, ^3J(H,H) = 10.1, 3.6 Hz, 1H; H-2), 4.77 (d, ^3J(H,H) = 10.5 Hz, 1H; H-5), 3.69 ppm (s, 3H; CO_2CH_3); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 167.2 (CO_2CH_3), 165.5, 165.2 (3×*C*OPh, overlapping peaks), 160.3 (O*C*(NH)CCl_3), 133.6 (2s), 133.4, 129.9 (2s), 129.7 (9×Ar-CH, overlapping peaks), 128.7, 128.6 (2×Ar-C), 128.5 (2×Ar-CH, overlapping peaks), 128.4 (2s) (4×Ar-CH, Ar-C, overlapping peaks), 92.9 (C-1), 70.9 (C-5), 70.2 (C-2), 69.6 (C-4), 69.3 (C-3), 53.0 ppm (CO_2CH_3); IR (film): $\tilde{\nu}$ = 3068, 1728, 1451, 1278, 1092, 1025 cm^{-1}.

6-*O*-Acetyl-3,4-*O*-(1,1,3,3-tetraisopropyl-1,3-disiloxanediyl)-β-D-glucopyranosyl azide (26): A solution of **25** (0.75 g, 1.7 mmol) in collidine (5 mL), prepared from **16** as described above was cooled to −35 °C. Freshly distilled AcCl (0.13 mL, 1.84 mmol) was added to this and the reaction mixture was allowed to attain room temperature. Methanol was added and the solvent was removed under diminished pressure. Flash chromatography of the residue (petroleum ether/EtOAc 9:1) gave **26** (0.58 g, 70%) as a white solid; $[\alpha]_D$ = −23.0 (*c* 0.18, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.56 (d, ^3J(H,H) = 8.7 Hz, 1H; H-1), 4.44 (dd, ^2J(H,H) = 12.0 Hz, ^3J(H,H) = 2.1 Hz, 1H; H-6a), 4.20 (dd, ^2J(H,H) = 12.0 Hz, ^3J(H,H) = 5.2 Hz, 1H; H-6b), 3.74–3.67 (m, 1H; H-4), 3.67–3.62 (m, 1H; H-3), 3.56 (ddd, ^3J(H,H) = 9.3, 5.3, 2.1 Hz, 1H; H-5), 3.40 (aptt, ^3J(H,H) = 8.7 Hz, 1H; H-2), 2.44 (d, ^3J(H,H) = 2.6 Hz, 1H; OH), 2.09 (s, 3H; CO*CH*$_3$), 1.12–0.93 ppm (m, 28H; 4×C*H*(*CH*$_3$)$_2$, overlapping peaks); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 170.7 (O*C*OCH$_3$), 89.6 (C-1), 79.7 (C-3), 76.1 (C-5), 73.7 (C-2), 72.2 (C-4), 62.9 (C-6), 20.9, 17.3 (3s), 17.2 (3s), 17.1 (8×CH(*CH*$_3$)$_2$, overlapping peaks), 12.8, 12.7, 12.1 ppm (2s) (4×*CH*(CH$_3$)$_2$, overlapping peaks); IR (film): $\tilde{\nu}$ = 3504, 2947, 2868, 2114, 1725, 1463, 1250, 1028, 980 cm^{-1}; ESI-HRMS calcd for $C_{20}H_{39}N_3O_7Si_2Na$ 512.224, found *m/z* (%) 512.2229 $[M+Na]^+$.

2-*O*-(2,3,4-Tri-*O*-benzoyl-5-*S*-(methoxycarbonyl)-β-D-xylopyranosyl)-3,4-*O*-(1,1,3,3-tetraisopropyl-1,3-disiloxanediyl)-6-*O*-acetyl-β-D-glucopyranosyl azide (27): Glycosidation with acceptor 26 (0.5 g, 1.0 mmol) and donor 24 (0.91 g, 1.2 mmol) as described above gave **27** (0.88 g, 89%) as a foam; $[\alpha]_D$ = −4.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.91 (ddt, ^3J(H,H) = 17.1, 7.0, 1.4 Hz, 4H; Ar-H), 7.81 (dd, ^3J(H,H) = 8.4, 1.4 Hz, 2H; Ar-H), 7.54–7.48 (m, 2H; Ar-H), 7.44–7.33 (m, 5H; Ar-H), 7.28 (d, ^3J(H,H) = 7.8 Hz, 2H; Ar-H), 5.84 (aptt, ^3J(H,H) = 9.2 Hz, 1H; H-3′), 5.78 (aptt, ^3J(H,H) = 9.5 Hz, 1H; H-4′), 5.58 (dd, ^3J(H,H) = 9.0, 7.6 Hz, 1H; H-2′), 5.34 (d, ^3J(H,H) = 7.5 Hz, 1H; H-1′), 4.54 (d, ^3J(H,H) = 8.1 Hz, 1H; H-1), 4.44 (dd, ^2J(H,H) = 12.0 Hz, ^3J(H,H) = 2.2 Hz, 1H; H-6a), 4.33 (d, ^3J(H,H) = 9.6 Hz, 1H; H-5′), 4.14 (dd, ^3J(H,H) = 12.0 Hz, ^3J(H,H) = 5.1 Hz, 1H; H-6b), 3.87–3.82 (m, 1H; H-2), 3.79 (aptt, ^3J(H,H) = 8.5 Hz, 1H; H-3), 3.73 (s, 3H; CO_2CH_3), 3.71–3.63 (m, 1H; H-4), 3.49 (ddd, ^3J(H,H) = 9.5, 5.1, 2.1 H-z, 1H; H-5), 2.08 (s, 3H; CO*CH*$_3$), 1.08–0.72 ppm (m, 28H; 4×C*H*(CH$_3$)$_2$, overlapping peaks); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 170.7 (*C*OCH$_3$), 167.0 (*C*O$_2$CH$_3$), 165.7, 165.0 (2s), (3×*C*OPh), 133.4, 133.3 (2s)129.9, 129.8, 129.7 (9×Ar-CH, overlapping peaks), 129.2, 128.8, 128.6 (3×Ar-C), 128.4, 128.3, 128.2 (6×Ar-CH, overlapping peaks), 100.2 (C-1′), 88.4 (C-1), 79.8 (C-3), 78.0 (C-2), 75.6 (C-5), 73.1 (C-5′), 72.6 (C-3′), 72.5 (C-4), 72.1 (C-2′), 70.1 (C-4′), 62.8 (C-6), 53.0 (CO$_2$CH$_3$), 20.9 (CO*CH*$_3$), 17.5 (2s) 17.4, 17.3, 17.2 (3s)17.1 (8×CH(*CH*$_3$)$_2$, overlapping peaks), 12.8, 12.7, 12.3 ppm (2s) (4×*CH*(CH$_3$)$_2$, overlapping peaks); IR (film): $\tilde{\nu}$ = 3073, 2952, 2120, 1727, 1686, 1452, 1248, 1091, 1067, 1026 cm^{-1}; ESI-HRMS calcd for $C_{48}H_{61}O_{16}N_3Si_2Na$ 1014.3488, found *m/z* (%) 1014.3491 $[M+Na]^+$.

2,3,4-Tri-*O*-benzoyl-β-D-glucopyranosyl azide (29): Azide **28** (1 g, 4.87 mmol) prepared from **15** as described, was treated with TBDPSCl (1.5 mL, 5.85 mmol) in pyridine and then benzoyl chloride (3.73 mL, 32.14 mmol) as described above, to give the silylated intermediate (1.99 g, 54%) as a foam; $[\alpha]_D$ = −25.9 (*c* 0.41, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.99–7.94 (m, 2H; Ar-H), 7.91–7.86 (m, 2H; Ar-H), 7.86–7.81 (m, 2H; Ar-H), 7.74–7.69 (m, 2H; Ar-H), 7.61–7.56 (m, 2H; Ar-H), 7.56–7.50 (m, 2H; Ar-H), 7.45–7.34 (m, 7H; Ar-H), 7.34–7.27 (m, 3H; Ar-H), 7.23–7.18 (m, 2H; Ar-H), 5.86 (aptt, ^3J(H,H) = 9.7 Hz, 1H; H-3), 5.75 (aptt, ^3J(H,H) = 9.7 Hz, 1H; H-4), 5.47 (dd, ^3J(H,H) = 9.7, 8.8 Hz, 1H; H-2), 4.87 (d, ^3J(H,H) = 8.8 Hz, 1H; H-1), 3.96–3.84 (m, 3H; H-6a, H-6b, H-5, overlapping peaks), 1.06 ppm (s, 9H; C(*CH*$_3$)$_3$); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 165.8, 165.1, 164.8 (3×*C*OPh), 135.6, 135.5, 133.4, 133.3, 133.2 (7×Ar-CH, overlapping peaks), 132.9, 132.8 (2×Ar-C), 129.9, 129.8, 129.8, 129.7, 129.6 (8×Ar-CH, overlapping peaks), 129.0, 128.8, 128.7 (3×Ar-C), 128.4, 128.4, 128.3, 127.7, 127.6 (10×Ar-CH, overlapping peaks), 88.1 (C-1), 77.3 (C-5), 73.1 (C-3), 71.5 (C-2), 68.5 (C-4), 62.3 (C-6), 26.6 (C(*CH*$_3$)$_3$), 19.2 ppm (*C*(CH$_3$)$_3$); IR (film): $\tilde{\nu}$ = 3071, 2858, 2116, 1731, 1451, 1245, 1088, 1068 cm^{-1}; ESI-HRMS calcd for $C_{43}H_{42}N_3O_8Si$ 756.2736, found *m/z* (%) 756.2742 $[M+H]^+$. This intermediate in THF (50 mL) was cooled over ice and AcOH (0.29 mL, 5.03 mmol) and 1 M TBAF in THF (5.03 mL, 5.03 mmol) added and the mixture stirred for 16 h. The product was adsorbed onto silica gel and flash chromatography (petroleum ether/EtOAc 3:2) gave **29** (1.02 g, 79%) as a white solid; $[\alpha]_D$ = +88.1 (*c* 0.2, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.95 (td, ^3J(H,H) = 8.2, 1.4 Hz, 4H; Ar-H), 7.83 (dd, ^3J-

(H,H) = 8.3, 1.4 Hz, 2H; Ar-H), 7.54 (tdd, ^3J(H,H) = 6.7, 4.8, 1.3 Hz, 2H; Ar-H), 7.45–7.35 (m, 5H; Ar-H), 7.28 (t, ^3J(H,H) = 7.8 Hz, 2H; Ar-H), 5.96 (aptt, ^3J(H,H) = 9.8 Hz, 1H; H-3), 5.54 (aptt, ^3J(H,H) = 9.8 Hz, 1H; H-4), 5.47 (dd, ^3J(H,H) = 9.8, 8.8 Hz, 1H; H-2), 4.96 (d, ^3J(H,H) = 8.8 Hz, 1H; H-1), 3.96–3.86 (m, 2H; H-5, H-6a, overlapping peaks), 3.77 (dt, ^2J-(H,H) = 13.2 Hz, ^3J(H,H) = 4.8 Hz, 1H; H-6b), 2.60 ppm (dd, ^3J(H,H) = 8.8, 5.6 Hz, 1H; OH); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 166.0, 165.7, 165.0 (3×*C*OPh), 133.8, 133.5, 133.4, 130.0, 129.9, 129.7 (9×Ar-CH, overlapping peaks), 128.7, 128.6 (2×Ar-C), 128.5, 128.4 (4×Ar-CH, overlapping peaks), 128.3 (2s) (Ar-C, 2×Ar-CH, overlapping peaks), 88.4 (C-1), 77.0 (C-5), 72.6 (C-3), 71.2 (C-2), 69.0 (C-4), 61.1 ppm (C-6); IR (film): $\tilde{\nu}$ = 3491, 2122, 1723, 1450, 1244, 1088 cm^{-1}; ESI-HRMS calcd for $C_{27}H_{27}NO_8Na$ 399.0903, found *m/z* (%) 399.0887 $[M+Na]^+$.

2,3,4-Tri-*O*-benzoyl-6-*O*-(2,3,4-tri-*O*-benzoyl-5-*S*-(methoxycarbonyl)-β-D-xylopyranosyl)-β-D-glucopyranosyl azide (30): The glycosidation of acceptor **29** (0.2 g, 0.39 mmol) and donor **24** (0.43 g, 0.58 mmol) was carried out as previously described to give **30** (0.33 g, 84%) as a white solid; $[\alpha]_D = -10.1$ (*c* 0.75, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.06–7.97 (m, 2H), 7.98–7.90 (m, 4H), 7.90–7.85 (m, 4H), 7.79–7.74 (m, 2H), 7.52 (t, ^3J(H,H) = 7.5 Hz, 4H), 7.48–7.34 (m, 10H), 7.31 (t, ^3J(H,H) = 7.7 Hz, 2H), 7.29–7.24 (m, 3H), 5.91 (aptt, ^3J(H,H) = 9.2 Hz, 1H; H-3′), 5.79 (aptt, ^3J(H,H) = 9.6 Hz, 1H; H-3), 5.68 (aptt, ^3J(H,H) = 9.3 Hz, 1H; H-4′), 5.54 (dd, ^3J(H,H) = 9.3, 7.1 Hz, 1H; H-2′), 5.38 (aptt, ^3J(H,H) = 9.8 Hz, 1H; H-4), 5.35 (aptt, ^3J(H,H) = 9.3 Hz, 1H; H-2), 5.04 (d, ^3J-(H,H) = 7.3 Hz, 1H; H-1), 4.65 (d, ^3J(H,H) = 8.8 Hz, 1H; H-1′), 4.35 (d, ^3J(H,H) = 9.4 Hz, 1H; H-5′), 4.13 (dd, ^2J(H,H) = 12.0 Hz, ^3J(H,H) = 1.9 Hz, 1H; H-6a), 4.06 (ddd, ^3J(H,H) = 9.8, 7.4, 1.9 Hz, 1H; H-5), 3.90 (dd, ^2J(H,H) = 12.0 Hz, ^3J(H,H) = 7.4 Hz, 1H; H-6b), 3.66 ppm (s, 3H; CO_2CH_3); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 167.4 (*C*O_2CH$_3$), 165.7, 165.7, 165.4, 165.3, 165.2, 165.1 (6×*C*OPh), 133.8, 133.6, 133.6, 133.5, 130.0, 130.0, 130.0, 129.9 (18×Ar-CH, overlapping peaks), 129.3, 128.9, 128.9, 128.9, 128.7 (5×Ar-C), 128.6, 128.6 (8×Ar-CH, Ar-C, overlapping peaks), 128.5, 128.4 (4×Ar-CH, overlapping peaks), 101.6 (C-1), 88.0 (C-1′), 76.6 (C-5), 73.0 (C-5′), 72.8 (C-3), 72.0 (C-3′), 71.6 (C-2′), 71.4 (C-2), 70.1 (C-4′), 69.2 (C-4), 68.8 (C-6), 53.0 ppm (CO_2CH_3); IR (film): $\tilde{\nu}$ = 2956, 2120, 1727, 1452, 1245, 1087, 1067, 1026 cm^{-1}; ESI-HRMS calcd for $C_{55}H_{45}O_{17}N_3Na$ 1042.2647, found *m/z* (%) 1042.2656 $[M+Na]^+$.

2-*O*-Acetyl-3-*O*-(2,3,4-tri-*O*-benzoyl-5-*S*-(methoxycarbonyl)-β-D-xylopyranosyl)-4,6-*O*-(1,1,3,3-tetraisopropyl-1,3-disiloxanediyl)-β-D-glucopyranosyl azide (31): A solution of **16** (0.5 g, 1.1 mmol) in collidine (2.5 mL) was cooled to −35 °C. Freshly distilled AcCl (0.087 mL, 1.23 mmol) was added to this and the reaction mixture was allowed to attain room temperature and stirred for 16 h. MeOH was added and the solvent was removed and flash chromatography of the residue (petroleum ether/EtOAc 9:1) gave the 2-*O*-acetylated intermediate (0.42 g, 78%); $[\alpha]_D = -1.8$ (*c* 0.1, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.92–4.84 (m, 1H; H-2), 4.53 (d, ^3J(H,H) = 9.0 Hz, 1H; H-1), 3.99–3.91 (m, 1H; H-6a), 3.82–3.71 (m, 3H; H-6b, H-4, H-3, overlapping peaks), 3.45 (dddd, ^3J(H,H) = 7.9, 5.2, 2.8, 1.3 Hz, 1H; H-5), 2.09 (s, 3H; COCH_3), 1.98–1.91 (m, 1H; OH), 1.13–0.89 (m, 28H; 4×C*H*(CH_3)$_2$, overlapping peaks); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 169.2 (*C*OCH$_3$), 87.9 (C-1), 78.4 (C-5), 77.3 (C-4), 72.7 (C-3), 72.5 (C-2), 61.9 (C-6), 20.6 (CO*C*H$_3$), 17.2 (2s), 17.1 (4s) (8×CH*(C*H$_3$)$_2$, overlapping peaks), 12.8 (2s), 12.1, 12.0 ppm (4×*C*H(CH$_3$)$_2$, overlapping peaks); IR (film): $\tilde{\nu}$ = 3533, 2943, 2866, 2121, 1729, 1462, 1243, 980 cm^{-1}; ESI-HRMS calcd for $C_{20}H_{39}N_3O_7Si_2Na$ 512.224, found *m/z* (%) 512.2232 $[M+Na]^+$. Glycosidation of this intermediate (0.4 g, 0.8 mmol) with **24** (0.91 g, 1.2 mmol) gave **31** (0.65 g, 82%) after chromatography (petroleum ether/EtOAc 8:2) as a foam; $[\alpha]_D = -24.1$ (*c* 0.1, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.98 (dd, ^3J(H,H) = 8.3, 1.4 Hz, 2H; Ar-H), 7.93 (dd, ^3J(H,H) = 8.4, 1.4 Hz, 2H; Ar-H), 7.86 (dd, ^3J-(H,H) = 8.3, 1.4 Hz, 2H; Ar-H), 7.51 (dd, ^3J(H,H) = 7.5, 3.6 Hz, 2H; Ar-H), 7.47–7.42 (m, 1H), 7.38 (q, ^3J(H,H) = 7.9 Hz, 4H; Ar-H), 7.30 (t, ^3J-(H,H) = 7.8 Hz, 2H; Ar-H), 5.89 (aptt, ^3J(H,H) = 9.3 Hz, 1H; H-3′), 5.71 (aptt, ^3J(H,H) = 9.4 Hz, 1H; H-4′), 5.53 (dd, ^3J(H,H) = 9.3, 7.4 Hz, 1H; H-2′), 5.09 (d, ^3J(H,H) = 7.4 Hz, 1H; H-1′), 4.83 (t, ^3J(H,H) = 9.0 Hz, 1H; H-2), 4.36 (d, ^3J(H,H) = 9.5 Hz, 1H; H-5), 4.28–4.19 (m, 2H; H-6a, H-1, overlapping peaks), 3.85 (dd, ^2J(H,H) = 12.2 Hz, ^3J(H,H) = 7.3 Hz, 1H; H-6b), 3.70 (s, 3H; CO_2CH_3), 3.63 (dd, ^3J(H,H) = 9.1, 7.7 Hz, 1H; H-3), 3.59–3.49 (m, 2H; H-5, H-4, overlapping peaks), 2.06 (s, 3H; COCH_3), 1.09–0.94 ppm (m, 28H; 4×C*H*(CH_3)$_2$, overlapping peaks); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 169.3 (*C*OCH$_3$), 167.5 (*C*O_2CH$_3$), 165.7, 165.3, 165.2 (3×*C*OPh), 133.6, 133.4, 130.0, 129.9 (9×Ar-CH, overlapping peaks), 129.4, 129.0, 128.9 (3×Ar-C), 128.6 (2s), 128.5 (6×Ar-CH, overlapping peaks), 101.7 (C-1′), 87.6 (C-1), 79.0 (C-5), 77.4 (C-3), 73.3 (C-4), 73.0 (C-5′), 72.6 (C-2), 72.3 (C-3′), 71.8 (C-2′), 70.3 (C-4′), 69.0 (C-6), 53.0 (*C*O_2C*H*$_3$), 20.8 (CO*C*H$_3$), 17.6, 17.5, 17.3 (4s), 17.2 (8×CH*(C*H$_3$)$_2$, overlapping peaks), 12.9, 12.8, 12.3, 12.2 ppm (4×*C*H(CH$_3$)$_2$, overlapping peaks); IR (film): $\tilde{\nu}$ = 2948, 2868, 2118, 1732, 1452, 1248, 1223, 1092, 1068, 1041, 1027, 984 cm^{-1}; ESI-HRMS calcd for $C_{48}H_{61}O_{16}N_3Si_2Na$ 1014.3488, found *m/z* (%) 1014.3533 $[M+Na]^+$.

2,4,6-Tri-*O*-benzoyl-3-*O*-(2,3,4-tri-*O*-benzoyl-5-*S*-(methoxycarbonyl)-β-D-xylopyranosyl)-β-D-glucopyranosyl azide (32): Disaccharide **31** (0.25 g, 0.252 mmol) was added to 1.25 M HCl in methanol (10 mL) at 0 °C and the resulting solution was allowed to attain room temperature and stirred for 16 h. The reaction mixture was cooled over an ice-bath, diluted with MeOH (20 mL) and $NaHCO_3$ was added. The resulting slurry was concentrated to dryness and the residue suspended was in pyridine and cooled over an ice-bath. BzCl (0.18 mL, 1.5 mmol) was then added and the reaction mixture was allowed to warm to room temperature and was stirred, overnight. Methanol (0.5 mL) was added and the mixture was diluted with EtOAc (10 mL). This layer was washed with 1 M HCl (2×5 mL), satd. aq. $NaHCO_3$ (10 mL), brine (10 mL), dried over Na_2SO_4, filtered and the solvent was removed under diminished pressure. Flash chromatography of the residue (petroleum ether/EtOAc 6:4) gave **32** (0.15 g, 63%) as a glass; $[\alpha]_D = -15.6$ (*c* 1.25, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.00 (dd, ^3J(H,H) = 8.4, 1.4 Hz, 2H; Ar-H), 7.95–7.90 (m, 4H; Ar-H), 7.88 (ddd, ^3J(H,H) = 8.4, 3.0, 1.4 Hz, 4H; Ar-H), 7.79–7.75 (m, 2H; Ar-H), 7.55–7.50 (m, 4H; Ar-H), 7.48–7.27 (m, 14H; Ar-H), 5.91 (aptt, ^3J(H,H) = 9.3 Hz, 1H; H-3′), 5.79 (aptt, ^3J(H,H) = 9.6 Hz, 1H; H-3), 5.68 (aptt, ^3J(H,H) = 9.3 Hz, 1H; H-4′), 5.54 (dd, ^3J-(H,H) = 9.2, 7.3 Hz, 1H; H-2′), 5.38 (aptt, ^3J(H,H) = 9.8 Hz, 1H; H-2), 5.35 (dd, ^3J(H,H) = 9.7, 8.7 Hz, 1H; H-4), 5.04 (d, ^3J(H,H) = 7.3 Hz, 1H; H-1′), 4.65 (d, ^3J(H,H) = 8.8 Hz, 1H; H-1), 4.35 (d, ^3J(H,H) = 9.4 Hz, 1H; H-5′), 4.13 (dd, ^2J(H,H) = 12.0 Hz, ^3J(H,H) = 1.9 Hz, 1H; H-6a), 4.06 (ddd, ^3J(H,H) = 9.7, 7.6, 1.9 Hz, 1H; H-5), 3.90 (dd, ^2J(H,H) = 12.0 Hz, ^3J-(H,H) = 7.6 Hz, 1H; H-6b), 3.66 ppm (s, 3H; CO_2CH_3); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 167.2 (*C*O_2CH$_3$), 165.6, 165.5, 165.3, 165.2, 165.0, 164.9 (6×*C*OPh), 133.6, 133.5, 133.4, 133.3, 129.9 (2s), 129.8 (2s), 129.7 (18×Ar-CH, overlapping peaks), 129.1, 128.8, 128.7 (2s), 128.6 (5×Ar-C, overlapping peaks), 128.5, 128.4 (2s) (8×Ar-CH, Ar-C, overlapping peaks), 128.3 (2s) (4×Ar-CH, overlapping peaks), 101.5 (C-1′), 87.8 (C-1), 76.5 (C-5), 72.8 (C-5′), 72.6 (C-3), 71.8 (C-3′), 71.5 (C-2′), 71.2 (C-2), 70.0 (C-4′), 69.1 (C-4), 68.6 (C-6), 52.9 ppm (CO_2CH_3); IR (film): $\tilde{\nu}$ = 2956, 2120, 1714, 1451, 1247, 1088, 1068, 1026 cm^{-1}; ESI-HRMS calcd for $C_{55}H_{45}O_{17}N_3Na$ 1042.2647, found *m/z* (%) 1042.2646 $[M+Na]^+$.

2,3-*O*-(1,1,3,3-Tetraisopropyl-1,3-disiloxanediyl)-6-*O*-acetyl-β-D-glucopyranosyl azide (33): Azide **28** (1.5 g, 7.3 mmol) was dissolved in DMF (15 mL) and 2,2-dimethoxypropane (1.78 mL, 14.6 mmol) and *p*-toluenesulfonic acid (0.14 g, 0.73 mmol) were added and the reaction mixture was stirred at room temperature for 3 h. Triethylamine (1 mL) was added and the solvent was removed and the residue was dissolved in pyridine (15 mL) and the mixture was cooled over ice. 1,3-Dichloro-1,1,3,3-tetraisopropyldisiloxane (2.88 g, 9.13 mmol) was added and the mixture stirred for 16 h at room temperature. Methanol (1 mL) was added followed by EtOAc (50 mL) and this layer was washed with 1 M HCl (2×50 mL), satd. aq. $NaHCO_3$ (50 mL), brine (50 mL), dried over Na_2SO_4, filtered and the solvent was removed under diminished pressure. Flash chromatography of the residue (petroleum ether/EtOAc 95:5) gave the protected intermediate (2.53 g, 71%) as a clear oil; $[\alpha]_D = +78.8$ (*c* 0.25, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.57 (d, ^3J(H,H) = 8.2 Hz, 1H; H-1), 3.95 (dd, ^2J(H,H) = 10.8 Hz, ^3J(H,H) = 5.3 Hz, 1H; H-6a), 3.75 (aptt, ^2J-(H,H) = 10.5 Hz, 1H; H-6b), 3.68 (dd, ^3J(H,H) = 8.9, 7.9 Hz, 1H; H-3), 3.55–3.49 (m, 2H; H-2, H-4, overlapping peaks), 3.32 (td, ^3J(H,H) = 10.0, 5.3 Hz, 1H; H-5), 1.47 (s, 3H; C*(C*H$_3$)$_2$), 1.38 (s, 3H; C*(C*H$_3$)$_2$), 1.13–0.99 ppm (m, 28H; 4×C*H*(CH_3)$_2$, overlapping peaks); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 99.5 (*C*(CH$_3$)$_2$), 91.3 (C-1), 78.1 (C-2), 76.6 (C-3), 72.7 (C-4), 69.5 (C-5), 62.0 (C-6), 28.9, 19.0 (C(*C*H$_3$)$_2$), 17.3, 17.2, 17.1 (2s), 17.0, 16.8 (8×CH*(C*H$_3$)$_2$, overlapping peaks), 12.9, 12.8, 12.2,

12.0 ppm ($4\times CH(CH_3)_2$, overlapping peaks); IR (film): $\tilde{\nu}=2945$, 2867, 2115, 1738, 1465, 1064, 983 cm^{-1}; ESI-HRMS calcd for $C_{21}H_{42}N_3O_6Si_2$ 488.7451, found *m/z* (%) 488.7458 $[M+H]^+$. This intermediate (2.5 g, 5.1 mmol) was dissolved in MeOH and Amberlyst 15 H^+ (3.0 g) was added and the mixture was stirred for 5 h. The resin was filtered off and the solvent was removed and flash chromatography of the residue (petroleum ether/EtOAc, 8:2) gave the required 2,3-*O*-silylated intermediate (1.88 g, 82%) as a wax; $[\alpha]_D=-18.0$ (*c* 0.11, CH_2Cl_2); ^1H NMR (500 MHz, $CDCl_3$): $\delta=4.61$ (d, $^3J(H,H)=8.1$ Hz, 1H; H-1), 3.95 (dd, $^2J(H,H)=12.1$ Hz, $^3J(H,H)=3.1$ Hz, 1H; H-6a), 3.81 (dd, $^2J(H,H)=12.1$ Hz, $^3J(H,H)=4.7$ Hz, 1H; H-6b), 3.66 (apt t, $^3J(H,H)=8.5$ Hz, 1H; H-3), 3.55 (apt td, $^3J(H,H)=9.2$, 8.6, 1.4 Hz, 1H; H-4), 3.51–3.45 (m, 2H; H-5, H-2, overlapping peaks), 2.45 (d, $^3J(H,H)=2.2$ Hz, 1H; OH), 2.04 (s, 1H; OH), 1.12–0.99 ppm (m, 28H; $4\times CH(CH_3)_2$, overlapping peaks); ^{13}C NMR (126 MHz, $CDCl_3$): $\delta=90.8$ (C-1), 80.1 (C-3), 76.9 (C-5) 76.5 (C-2), 70.6 (C-4), 62.3 (C-6), 17.4, 17.2 (3s) 17.1, 17.0 ($8\times CH(CH_3)_2$, overlapping peaks), 12.8 (2s), 12.1, 12.4 ppm ($4\times CH(CH_3)_2$, overlapping peaks); IR (film): $\tilde{\nu}=3372$, 2945, 2868, 2117, 1738, 1464, 1143, 1036, 986 cm^{-1}; ESI-HRMS calcd for $C_{18}H_{37}N_3O_6Si_2Na$ 442.2349, found *m/z* (%) 442.2354 $[M+Na]^+$. This intermediate (1.5 g, 3.35 mmol) was treated with freshly distilled AcCl (0.26 mL, 3.69 mmol) in collidine (7.5 mL) as previously described and gave **33** (0.97 g, 59%) after flash chromatography (petroleum ether/EtOAc 9:1); $[\alpha]_D=-25.6$ (*c* 0.25, CH_2Cl_2); ^1H NMR (500 MHz, $CDCl_3$): $\delta=4.57$ (d, $^3J(H,H)=8.2$ Hz, 1H; H-1), 4.42 (dd, $^2J(H,H)=12.2$ Hz, $^3J(H,H)=2.2$ Hz, 1H; H-6a), 4.30 (dd, $^2J(H,H)=12.2$ Hz, $^3J(H,H)=5.4$ Hz, 1H; H-6b), 3.64 (apt t, $^3J(H,H)=8.6$ Hz, 1H; H-3), 3.59 (ddd, $^3J(H,H)=9.7$, 5.4, 2.2 Hz, 1H; H-5), 3.49 (apt t, $^3J(H,H)=8.4$ Hz, 1H; H-2), 3.44 (ddd, $^3J(H,H)=9.7$, 8.6, 2.2 Hz, 1H; H-4), 2.48 (d, $^3J(H,H)=2.2$ Hz, 1H; OH), 2.11 (s, 3H; $CO(CH_3)$), 1.11–1.03 ppm (m, 28H; $4\times CH(CH_3)_2$, overlapping peaks); ^{13}C NMR (126 MHz, $CDCl_3$): $\delta=171.1$ ($COCH_3$), 90.8 (C-1), 80.0 (C-3), 76.4 (C-2), 75.1 (C-5), 70.2 (C-4), 63.1 (C-6), 20.9 ($CO(CH_3)$), 17.3, 17.2 (3s), 17.1, 17.0 ($8\times CH(CH_3)_2$, overlapping peaks), 12.8 (2s), 12.1 (2s), 12.1 ppm ($4\times CH(CH_3)_2$, overlapping peaks); IR (film): $\tilde{\nu}=3484$, 2946, 2869, 2116, 1736, 1464, 1245, 1149, 1039, 985 cm^{-1}; ESI-HRMS calcd for $C_{20}H_{39}N_3O_7Si_2Na$ 512.224, found *m/z* (%) 512.2219$[M+Na]^+$.

2,3-*O*-(1,1,3,3-Tetraisopropyl-1,3-disiloxanediyl)-4-*O*-(2,3,4-tri-*O*-benzoyl-5-*S*-(methoxycarbonyl)-β-D-xylopyranosyl)-6-*O*-acetyl-β-D-glucopyranosyl azide (34): Glycosidation of **33** (0.5 g, 1.02 mmol) with donor **24** (1.13 g, 1.53 mmol) as previously described gave **34** (0.67 g, 66%) after chromatography (petroleum ether/EtOAc 8:2) as a glass; $[\alpha]_D=-75.3$ (*c* 0.3, CH_2Cl_2); ^1H NMR (500 MHz, $CHCl_3$): $\delta=7.98$–7.90 (m, 4H; Ar-H), 7.86–7.81 (m, 2H; Ar-H), 7.58–7.51 (m, 2H; Ar-H), 7.48–7.36 (m, 6H; Ar-H), 7.30 (t, $^3J(H,H)=7.8$ Hz, 2H; Ar-H), 5.84 (apt t, $^3J(H,H)=9.5$ Hz, 1H; H-3′), 5.69 (apt t, $^3J(H,H)=9.6$ Hz, 1H; H-4′), 5.50 (dd, $^3J(H,H)=9.6$, 7.8 Hz, 1H; H-2′), 4.92 (d, $^3J(H,H)=7.8$ Hz, 1H; H-1′), 4.47 (d, $^3J(H,H)=8.3$ Hz, 1H; H-1), 4.35 (dd, $^2J(H,H)=12.2$ Hz, $^3J(H,H)=2.0$ Hz, 1H; H-6a), 4.28 (d, $^3J(H,H)=9.7$ Hz, 1H; H-5′), 4.14 (dd, $^3J(H,H)=12.2$ Hz, $^3J(H,H)=4.9$ Hz, 1H; H-6b), 3.80 (apt t, $^3J(H,H)=8.4$ Hz, 1H; H-3), 3.76–3.69 (m, 4H; CO_2CH_3, H-4, overlapping peaks), 3.49 (apt t, $^3J(H,H)=8.3$ Hz, 1H; H-2), 3.42 (ddd, $^3J(H,H)=10.0$, 4.9, 2.0 Hz, 1H; H-5), 2.03 (s, 3H; $COCH_3$), 1.23–1.04 ppm (m, 28H; $4\times CH(CH_3)_2$, overlapping peaks); ^{13}C NMR (126 MHz, $CDCl_3$): $\delta=170.3$ ($COCH_3$), 166.5 ($COCH_3$), 165.5, 164.9, 164.6 ($3\times COPh$), 133.5, 133.4, 133.3, 129.8 (2s) ($9\times$Ar-CH, overlapping peaks), 128.7, 128.6 ($3\times$Ar-C, overlapping peaks), 128.5, 128.4, 128.3 ($6\times$Ar-CH, overlapping peaks), 100.9 (C-1′), 90.5 (C-1), 77.8 (C-3), 77.1 (C-4), 74.6 (C-5), 73.7 (C-5′), 72.3 (C-3′), 71.8 (C-2′), 70.2 (C-4′), 61.9 (C-6), 52.8 (CO_2CH_3), 29.7, 20.8, 17.4, 17.3, 17.2 (2s), 17.1 (2s), 17.0 ($8\times CH(CH_3)_2$, overlapping peaks), 12.8 (2s), 12.1, 11.6 ppm ($4\times CH(CH_3)_2$, overlapping peaks); IR (film): $\tilde{\nu}=3072$, 2955, 2118, 1728, 1691, 1451, 1248, 1090, 1067, 1025 cm^{-1}; ESI-HRMS calcd for $C_{48}H_{61}O_{16}N_3Si_2Na$ 1014.3488, found *m/z* (%) 1014.3469 $[M+Na]^+$.

2,3,6-Tri-*O*-benzoyl-4-*O*-(2,3,4-tri-*O*-benzoyl-5-*S*-(methoxycarbonyl)-β-D-xylopyranosyl)-β-D-glucopyranosyl azide (35): Removal of the acetyl group and silyl protecting group from **34** (0.3 g, 0.3 mmol) as described above gave **35** (0.17 g, 54%) as a glass after chromatography (petroleum ether/EtOAc 6:4); $[\alpha]_D=-56.6$ (*c* 1.15, CH_2Cl_2); ^1H NMR (500 MHz, $CDCl_3$): $\delta=8.02$–7.98 (m, 2H; Ar-H), 7.89 (dd, $^3J(H,H)=8.3$, 1.4 Hz, 2H; Ar-H), 7.76–7.72 (m, 4H; Ar-H), 7.62 (dd, $^3J(H,H)=8.4$, 1.4 Hz, 2H; Ar-H), 7.58 (dd, $^3J(H,H)=8.3$, 1.4 Hz, 2H; Ar-H), 7.55–7.45 (m, 3H; Ar-H), 7.45–7.33 (m, 7H; Ar-H), 7.29–7.17 (m, 8H; Ar-H), 5.78–5.67 (m, 3H,H-3, H-4′, H-3′, overlapping peaks), 5.54–5.48 (m, 2H; H-2′, H4′, overlapping peaks), 5.07 (d, $^3J(H,H)=7.6$ Hz, 1H; H-1′), 4.87 (d, $^3J(H,H)=8.0$ Hz, 1H; H-1), 4.57 (dd, $^2J(H,H)=12.4$ Hz, $^3J(H,H)=3.0$ Hz, 1H; H-6a), 4.41 (dd, $^2J(H,H)=12.4$ Hz, $^3J(H,H)=5.1$ Hz, 1H; H-6b), 4.35 (d, $^3J(H,H)=9.1$ Hz, 1H; H-5′), 4.12–4.07 (m, 2H; H-5, H-2, overlapping peaks), 3.73 ppm (s, 3H; CO_2CH_3); ^{13}C NMR (126 MHz, $CDCl_3$): $\delta=166.7$ (CO_2CH_3), 166.0, 165.5, 165.1, 165.0, 164.9, 164.7 ($6\times COPh$), 133.4 (2s), 133.3, 133.1, 132.9, 129.8 (2s), 129.7 (3s), 129.6 ($18\times$Ar-CH, overlapping peaks), 129.5, 128.8, 128.7, 128.5 (3s) ($6\times$Ar-C), 128.4 (2s), 128.3 (2s), 128.2, 128.1 ($12\times$Ar-CH, overlapping peaks), 100.8 (C-1′), 88.8 (C-1), 77.7 (C-2), 73.9 (C-5 and C-3, overlapping peaks), 73.0 (C-5′), 72.2 (C-3′), 71.6 (C-2′), 70.0 (C-4′), 69.0 (C-4), 62.8 C-6), 53.0 ppm (CO_2CH_3); IR (film): $\tilde{\nu}=2945$, 2867, 2120, 1724, 1452, 1248, 1092, 1066, 1027, 986, 702 cm^{-1}; ESI-HRMS calcd for $C_{55}H_{45}O_{17}N_3Na$ 1042.2647, found *m/z* (%) 1042.2631 $[M+Na]^+$.

2,3,4-Tri-*O*-benzoyl-1-deoxy-1-(2,2,2-trichloro-1-iminoethoxy)-D-galacto-pyranuronate, methyl ester (37): The compound **36**[33] (10 g, 0.017 mol) in CH_2Cl_2 (100 mL) and H_2O (40 mL) was treated with TEMPO (0.5 g) and BAIB (16.2 g, 0.05 mol) as described above to give the galacturonic acid (9.5 g, 91%). Some of this acid (3 g, 4.9 mmol) was dissolved in DMF (40 mL) and treated with $NaHCO_3$ (0.8 g, 9.5 mmol) and MeI (0.50 mL, 7.2 mmol) as described above and gave after chromatography (petroleum ether/EtOAc 3:1) the methyl ester as a white solid (2.58 g, 86%, mixture of anomers, α/β = 3:1). Analytical data for the α anomer: ^1H NMR (500 MHz, $CDCl_3$): $\delta=8.10$–8.03 (m, 4H; Ar-H), 7.89 (d, $^3J(H,H)=7.8$ Hz, 2H; Ar-H), 7.83 (d, $^3J(H,H)=6.9$ Hz, 2H; Ar-H), 7.61 (t, $^3J(H,H)=7.3$ Hz, 1H; Ar-H), 7.59–7.51 (m, 1H; Ar-H), 7.51–7.40 (m, 6H; Ar-H), 7.30 (m, 4H; Ar-H), 6.27 (m, 2H; H_4 and H_1), 6.15–6.08 (m, 1H; H_2), 5.78 (dd, $^3J(H,H)=10.3$, 3.3 Hz, 1H; H_3), 4.84 (s, 1H; H_5), 3.71 ppm (s, 3H; CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=165.9$, 165.4, 165.2, 164.70 (each C=O), 133.9, 133.6, 133.5, 133.4 (each CH), 130.3, 130.1, 129.8, 129.7 (each CH), 128. 8, 128.7, (each C), 128.6, 128.5, 128.4, 128.3 (each CH), 92.6 (C-1), 73.7 (C-5), 71.2 (C-3), 69.0 (C-4), 68.2 (C-2), 52.9 ppm (CH_3); ESI-HRMS calcd for $C_{35}H_{28}O_{11}Na$ 647.1529, found *m/z* (%) 647.1533 $[M+Na]^+$. This intermediate (2 g, 3.2 mmol) was dissolved in CH_2Cl_2 (5 mL) and cooled to 0 °C and 33% HBr in AcOH (8 mL) was then added and the mixture was stirred at room temperature for 6 h. The mixture was then diluted with EtOAc, washed with water, satd. aq. $NaHCO_3$, water, brine, dried over Na_2SO_4, and the solvent was removed under diminished pressure to give the glycosyl bromide as a colourless oil. This was taken up in acetone (90 mL) and water (10 mL) and Ag_2CO_3 (530 mg, 1.9 mmol) were added and the mixture was stirred for 16 h at room temperature. The mixture was filtered through Celite, which was subsequently rinsed with CH_2Cl_2. The combined filtrate were dried over Na_2SO_4, and the solvent was removed under diminished pressure. Flash chromatography (petroleum ether/EtOAc 2:1) gave the hemiacetal as a white solid (1.21 g, 73% over 2 steps) and as mixture of anomers (α/β = 3:1). Analytical data for the α anomer: ^1H NMR (500 MHz, $CDCl_3$): $\delta=8.00$ (dd, $^3J(H,H)=17.5$, 7.8 Hz, 4H; Ar-H), 7.81 (d, $^3J(H,H)=7.7$ Hz, 2H; Ar-H), 7.59 (t, $^3J(H,H)=7.2$ Hz, 1H; Ar-H), 7.51 (t, $^3J(H,H)=7.3$ Hz, 1H; Ar-H), 7.45 (t, $^3J(H,H)=7.7$ Hz, 3H; Ar-H Ar-H), 7.37 (t, $^3J(H,H)=7.5$ Hz, 2H; Ar-H), 7.30–7.24 (m, 3H; Ar-H), 6.27 (s, 1H; H_1), 6.06 (dd, $^3J(H,H)=10.7$, 3.2 Hz, 1H; H_3), 5.96 (s, 1H; H_4), 5.69 (dd, $^3J(H,H)=10.8$, 3.0 Hz, 1H; H_2), 5.16 (s, 1H; H_5), 3.71 (s, 3H; CH_3), 3.55 ppm (s, 1H; OH); ^{13}C NMR (125 MHz, $CDCl_3$): $\alpha=167.8$, 165.9, 165.5, 165.2 (each C=O), 133.5 (2s), 133.2 (each CH), 129.9, 129.8, 129.7 (each C), 129.1, 129.0 (2s), 128.6, 128.5, 128.3 (each CH), 91.2 (C-1), 69.9 (C-4), 68.8 (2s) (C-5 and C-2), 67.6 (C-3), 52.8 ppm (CH_3); ESI-HRMS calcd for $C_{34}H_{28}O_{10}Na$ 619.1580, found *m/z* (%) 619.1591 $[M+Na]^+$. This hemiacetal (540 mg, 1.0 mmol) was dissolved in CH_2Cl_2 (20 mL) and cooled to 0 °C And Cl_3CCN (1.0 mL, 10.3 mmol) was added followed by DBU (6 drops). The mixture was stirred at 0 °C for 5 h, concentrated to 5 mL and subsequent chromatography of the residue (petroleum ether/EtOAc 2:1) gave the title compound **37** (425 mg, 61%) as a white solid; ^1H NMR (500 MHz, $CDCl_3$): $\delta=8.69$ (s, 1H; NH), 8.03 (d, $^3J(H,H)=7.7$ Hz, 2H; Ar-H), 7.94 (d, $^3J(H,H)=7.8$ Hz, 2H; Ar-H), 7.82 (d, $^3J(H,H)=7.8$ Hz, 2H; Ar-H), 7.61 (t, $^3J(H,H)=7.4$ Hz, 1H; Ar-H), 7.54–

7.43 (m, 4H; Ar-H), 7.35 (t, ^3J(H,H) = 7.7 Hz, 2H; Ar-H), 7.28 (t, ^3J-(H,H) = 7.8 Hz, 2H; Ar-H), 7.03 (d, ^3J(H,H) = 2.8 Hz, 1H; H-1), 6.34 (d, ^3J(H,H) = 1.4 Hz, 1H; H-4), 6.08 (dd, ^3J(H,H) = 10.7, 3.1 Hz, 1H; H-3), 5.96 (dd, ^3J(H,H) = 10.7, 3.2 Hz, 1H; H-2), 5.09 (s, 1H; H-5), 3.72 ppm (s, 3H; CH_3); ^{13}C (125 MHz, $CDCl_3$): δ = 166.4, 165.5, 165.4, 165.1, 160.2 (each C=O), 133.7, 133.6, 133.4 (each CH), 130.0, 129.8, 129.7 (each CH), 128.8, 128.7 (each C), 128.6 (CH), 128.6(C), 128.4, 128.3 (each CH), 93.6 (C-1), 90.6 (C=NH), 71.2 (C-5), 69.4 (C-4), 67.8 (C-3), 67.3 (C-2), 52.9 ppm (CH_3); HRMS calcd for $C_{28}H_{25}O_{10}$ 521.1448, found *m/z* (%) 521.1446 $[M+H]^+$.

Methyl 6-*O*-(2,3,4-tri-*O*-benzoyl-5-*S*-(methoxycarbonyl)-α-L-arabinopyranosyl)-2,3,4-tri-*O*-benzoyl-α-D-galactopyranose (39): Regioselective glycosidation of **38**[34,35] (150 mg, 0.22 mmol) and **37** (100 mg, 0.22 mmol) as described above gave the intermediate alcohol (165 mg, 77%) as a colorless foam; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.02–7.92 (m, 8H; Ar-H), 7.80 (d, ^3J(H,H) = 7.3 Hz, 2H; Ar-H), 7.56 (t, ^3J(H,H) = 7.5 Hz, 1H; Ar-H), 7.52–7.41 (m, 6H; Ar-H), 7.39–7.32 (m, 6H; Ar-H), 7.26 (dd, ^3J-(H,H) = 9.1, 6.5 Hz, 2H; Ar-H), 6.17 (d, ^3J(H,H) = 3.3 Hz, 1H; H-4′), 5.78 (dd, ^3J(H,H) = 10.4, 7.9 Hz, 1H; H-2′), 5.69 (dd, ^3J(H,H) = 10.7, 3.5 Hz, 1H; H-2), 5.62 (ddd, ^3J(H,H) = 10.5, 7.3, 3.5 Hz, 2H; H-3 and H-3′), 5.01 (d, ^3J(H,H) = 3.5 Hz, 1H; H-1), 4.97 (d, ^3J(H,H) = 7.9 Hz, 1H; H-1′), 4.61 (s, 1H; H-5′), 4.54 (s, 1H; H-4), 4.26 (dd, ^2J(H,H) = 10.2 Hz, ^3J(H,H) = 6.4 Hz, 1H; H-6a), 4.18 (t, ^3J(H,H) = 6.3 Hz, 1H; H-5), 4.00 (dd, ^2J(H,H) = 10.2 Hz, ^3J(H,H) = 6.4 Hz, 1H; H-6b), 3.61 (s, 3H; CH_3), 3.42(d, ^3J(H,H) = 5.0 Hz, 1H; OH), 3.17 ppm (s, 3H; CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.8, 166.1, 165.8, 165.6, 165.2, 165.1 (each C=O), 133.6, 133.4 (×2), 133.2, 133.1 (each CH), 130.0, 129.8 (×2), 129.7 (each CH), 129.5, 129.2, 128.8, 128.7 (each C), 128.6, 128.4 (2s), 128.3 (each CH), 101.4 (C-1′), 97.3 (C-1), 72.6 (C-5′), 71.3 (C-3′), 70.9 (C-2), 69.3 (C-3 and C-2′), 68.9 (C-4′), 68.7 (C-6), 68.5 (C-5), 67.3 (C-4), 55.1 (CH_3), 52.9 ppm (CH_3); ESI-HRMS calcd for $C_{49}H_{45}O_{17}$ 905.2657, found *m/z* (%) 905.2655 $[M+H]^+$. This intermediate (125 mg, 0.132 mmol) was benzoylated using pyridine (4 mL) and benzoyl chloride (30 μL, 0.263 mmol) as described above to give **39** (118 mg, 90%) as a white solid after chromatography (petroleum ether/EtOAc 2:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.11–8.05 (m, 2H; Ar-H), 8.05– 8.00(m, 2H; Ar-H), 7.93 (m, 4H; Ar-H), 7.81–7.78 (m, 2H; Ar-H), 7.76–7.72 (m, 2H; Ar-H), 7.60 (m, 2H; Ar-H), 7.53–7.30 (m, 12H; Ar-H), 7.29–7.17 (m, 4H; Ar-H), 6.21–6.12 (m, 1H; H-4′), 5.90 (m, 2H; H-4, H-3), 5.83 (dd, ^3J-(H,H) = 10.4, 7.9 Hz, 1H; H-2′), 5.61 (dd, ^3J(H,H) = 10.4, 3.5 Hz, 1H; H-3′), 5.56 (dd, ^3J(H,H) = 10.2, 3.6 Hz, 1H; H-2), 4.99 (d, ^3J(H,H) = 3.6 Hz, 1H; H-1), 4.89 (d, ^3J(H,H) = 7.9 Hz, 1H; H-1′), 4.58 (m, 1H; H-5′), 4.49 (m, 1H; H-5), 4.21 (dd, ^2J(H,H) = 11.0 Hz, ^3J(H,H) = 2.3 Hz, 1H; H-6a), 3.82 (dd, ^2J(H,H) = 11.0 Hz, ^3J(H,H) = 8.6 Hz, 1H; H-6b), 3.69 (s, 3H; CH_3), 3.10 ppm (s, 3H; CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.3, 166.1, 165.5 (2s) 165.3, 165.2 (2s) (each C=O), 133. (2s), 133.3 (2s), 133.0 (each CH), 130.0, 129.9, 129.8 (2s), 129.7, 129.6 (each CH), 129.3, 129.2 (2s), 128.9, 128.7 (each C), 128.6 (2s), 128.4 (2s), 128.4, 128.3, 128.2 (each CH), 101.9 (C-1′), 97.0 (C-1), 72.9 (C-5′), 71.2 (C-3′), 70.2 (C-6), 70.0 (C-4), 69.4 (C-2), 69.2 (C-2′), 69.1 (C-4′), 68.4 (C-5), 68.9 (C-3), 55.0 (CH_3), 52.8 ppm (CH_3); ESI-HRMS calcd for $C_{56}H_{49}O_{18}$ 1009.2919, found *m/z* (%) 1009.2924 $[M+H]^+$.

Methyl 4-*O*-(6-*O*-*tert*-butyldiphenylsilyl-2,3,4-tri-*O*-benzoyl-β-D-galactopyranosyl)-2,3,6-tri-*O*-benzyl-α-D-galactopyranose (43): Tf_2O (0.080 mL, 0.48 mmol) was added to a stirred solution of the thioglycoside **41**[36,37] (370 mg, 0.44 mmol), benzene sulfonyl pyridine (92 mg, 0.44 mmol), 2,4,6-tri-*tert*-butylpyrimidine (220 mg, 0.89 mmol), and activated 3 Å powdered sieves in CH_2Cl_2 (5 mL), at −60 °C, under argon. After 5 min, a solution of the glycosyl acceptor **42** (286 mg, 0.60 mmol) in dichloromethane (4 mL) was added. The mixture was allowed to attain room temperature, filtered, washed with satd. aq. $NaHCO_3$, brine, dried (Na_2SO_4), and the solvent was then removed under diminished pressure. Chromatography of the residue (petroleum ether/EtOAc, 3:1) gave the title compound **43** (466 mg, 90%) as a white foam; ^{1}H NMR (500 Hz, $CDCl_3$): δ = 8.04 (d, *J* = 7.4 Hz, 2H; Ar-H), 7.91 (d, *J* = 7.5 Hz, 2H; Ar-H), 7.82 (d, *J* = 7.4 Hz, 2H; Ar-H), 7.64 (dd, ^3J(H,H) = 13.1, 7.0 Hz, 3H; Ar-H), 7.49 (t, ^3J(H,H) = 7.7 Hz, 2H; Ar-H), 7.46–7.31 (m, 12H; Ar-H), 7.29–7.00 (m, 15H; Ar-H), 6.95 (d, ^3J(H,H) = 3.8 Hz, 2H; Ar-H), 6.07 (d, ^3J(H,H) = 2.2 Hz, 1H; Ar-H), 5.74–5.63 (m, 1H; Ar-H), 5.54 (dd, ^2J(H,H) = 10.4, 3.2 Hz, 1H; Ar-H), 5.12 (d, ^2J(H,H) = 7.9 Hz, 1H; Ar-H), 4.69 (d, ^2J-(H,H) = 11.7 Hz, 1H; 1×PhC*H*H), 4.62 (d, ^2J(H,H) = 11.7 Hz, 1H; 1×PhC*H*H), 4.47–4.38 (m, 2H; 1×PhC*H*H and H-1), 4.34 (d, ^2J(H,H) = 11.9 Hz, 1H; 1×PhC*H*H), 4.12–4.04 (m, 2H; 1×PhC*H*H and H-4), 3.92 (t, ^3J(H,H) = 7.2 Hz, 1H; H-5′), 3.81 (m, 3H; 1×PhC*H*H and H-5 and H-3), 3.71 (m, 2H; H-6a' and H-6b′), 3.67–3.50 (m, 3H; H-6a and H-6b and H-2), 3.28 (s, 3H; CH_3), 0.99 (s, 9H; C*(CH$_3$)$_3$)*; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.2, 165.6, 165.3, 165.1 (each C=O), 138.8, 138.4, 138.1 (each C), 135.5, 135.4 (each CH), 133.3, 133.0, 132.9 (each CH), 132.8, 132.4 (each C), 130.0, 129.9, 129.8, 129.7 (2s), (each CH), 129.6, 129.1 (each C), 128.6, 128.5, 128.2 (2s), 128.1, 127.8 (2s) 127.8, 127.7, 127.6 (2s), 127.5 (2s) (each CH), 101.6 (C-1′), 98.5 (C-1), 78.1 (C-3), 77.4 (C-2), 75.1 (C-4), 73.8 (Ph*C*H$_2$), 73.5 (Ph*C*H$_2$), 73.4 (Ph*C*H$_2$), 73.2 (C-5′), 72.2 (C-3′), 70.3 (C-2′), 69.7 (C-6), 69.1 (C-5), 67.6 (C-4′), 60.8 (C-6), 55.3 (OCH_3), 26.6 (C*(CH$_3$)$_3$)*, 18.9 ppm (*C*(CH$_3$)$_3$); ESI-HRMS calcd for $C_{71}H_{73}O_{14}Si$ 1177.4770, found *m/z* (%) 1177.4762 $[M+H]^+$.

Methyl 4-*O*-(2,3,4-tri-*O*-benzoyl-5-*S*-(methoxycarbonyl)-α-L-arabinopyranosyl)-2,3,6-tri-*O*-benzoyl-α-D-galactopyranoside (44): Acetic acid (13 μL, 1 equiv) was added to a solution of **43** (263 mg, 0.22 mmol) in THF (6 mL), and the mixture was cooled to 0 °C. After addition of TBAF (1 M in THF, 0.25 mL, 0.25 mmol), the mixture was stirred at 0 °C for 2 h, then diluted with diethyl ether and washed with brine (×2). The aqueous phase was reextracted with diethyl ether, and the combined organic phases were dried with Na_2SO_4, filtered, and the solvent was removed under diminished pressure. Flash chromatography furnished the desilylated intermediate (172 mg, 82%) as a white foam; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.10 (d, ^3J(H,H) = 7.3 Hz, 2H; Ar-H), 7.93 (d, ^3J-(H,H) = 7.4 Hz, 2H; Ar-H), 7.82 (d, ^3J(H,H) = 7.3 Hz, 2H; Ar-H), 7.64 (t, ^3J(H,H) = 7.4 Hz, 1H; Ar-H), 7.51 (t, ^3J(H,H) = 7.7 Hz, 2H; Ar-H), 7.48–7.33 (m, 7H; Ar-H), 7.33–7.20 (m, 10H; Ar-H), 7.17 (t, ^3J(H,H) = 7.8 Hz, 2H; Ar-H), 6.97 (dd, ^3J(H,H) = 6.5, 2.7 Hz, 2H; Ar-H), 5.84 (dd, ^3J-(H,H) = 10.3, 8.0 Hz, 1H; H-2′), 5.79 (d, ^3J(H,H) = 3.4 Hz, 1H; H-4′), 5.52 (dd, ^3J(H,H) = 10.3, 3.4 Hz, 1H; H-3′), 5.04 (d, ^3J(H,H) = 8.0 Hz, 1H; H-1′), 4.70–4.59 (ABq, ^2J(H,H) = 16.8, 11.7 Hz, 2H; PhCH$_2$), 4.58–4.49 (ABq, ^2J(H,H) = 15.9, 12.2 Hz, 2H; PhCH$_2$), 4.44 (d, ^3J(H,H) = 3.6 Hz, 1H; H-1), 4.18 (d, ^2J(H,H) = 11.8 Hz, 1H; 1×PhCH$_2$), 4.14 (d, ^3J-(H,H) = 2.4 Hz, 1H; H-4), 4.05 (dd, ^2J(H,H) = 10.6 Hz, ^3J(H,H) = 8.1 Hz, 1H; H-6a), 3.95 (dd, ^3J(H,H) = 7.9, 5.2 Hz, 1H; H-5), 3.89 (d, ^2J(H,H) = 11.8 Hz, 1H; 1×PhCH$_2$), 3.75 (m, 2H; H-5 and H-3), 3.72–3.65 (m, 1H; H-6a′), 3.65–3.54 (m, 2H; H-6b and H-2), 3.45 (dd, ^3J(H,H) = 10.6, 5.0 Hz, 1H; H-6b), 3.32–3.27 (m, 1H; OH), 3.26 (s, 3H; CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.3, 165.6, 165.3 (each C=O), 138.7, 138.4, 137.8 (each C), 133.7, 133.3, 133.0 (each CH), 130.0 (2s), 129.8 (each CH), 129.5, 128.9, 128.8 (each C), 128.7, 128.6, 128.5, 128.3, 128.2, 128.1, 128.0, 127.9 (2 s), 127.8 (3s) (each CH), 102.3 (C-1′), 98.8 (C-1), 77.9 (C-3), 77.1 (C-2), 76.0 (C-4), 74.0 (C-5′), 73.7 (2×Ph*C*H$_2$), 73.5 (Ph*C*H$_2$), 72.2 (C-3′), 70.1 (C-2′), 68.8 (C-4′), 68.3 (C-6), 67.6 (C-5), 61.0 (C-6′), 55.3 ppm (CH_3); ESI-HRMS calcd for $C_{55}H_{54}NaO_{14}$ 961.3411, found *m/z* (%) 961.3407 $[M+Na]^+$. This intermediate (326 mg, 0.35 mmol) was added to CH_2Cl_2 (10 mL) and H_2O (5 mL) and treated with TEMPO (10 mg, 0.065 mmol) and BAIB (336 mg, 1.043 mmol) to give the acid. This was esterified in DMF (10 mL) using $NaHCO_3$ (220 mg, 2.6 mmol) and MeI (0.055 mL, 0.87 mmol) to give the ester (290 mg, 87%) after chromatography (petroleum ether/EtOAc 2:1) as a white foam; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.02 (dd, ^3J(H,H) = 8.2, 1.1 Hz, 2H; Ar-H), 7.96 (dd, ^3J(H,H) = 8.3, 1.1 Hz, 2H; Ar-H), 7.83 (dd, ^3J(H,H) = 8.3, 1.2 Hz, 2H; Ar-H), 7.63–7.57 (m, 1H; Ar-H), 7.51–7.16 (m, 21H; Ar-H), 7.01 (dd, ^3J(H,H) = 6.8, 2.6 Hz, 2H; Ar-H), 6.14 (dd, ^3J(H,H) = 3.4, 1.1 Hz, 1H; H-4′), 5.80 (dd, ^3J(H,H) = 10.4, 7.9 Hz, 1H; H-2′), 5.53 (dd, ^3J-(H,H) = 10.4, 3.4 Hz, 1H; H-3′), 5.18 (d, ^3J(H,H) = 7.9 Hz, 1H; H-1′), 4.71 (dd, ^2J(H,H) = 11.8, 8.0 Hz, 2H; PhCH$_2$), 4.64 (dd, ^2J(H,H) = 11.8, 4.3 Hz, 2H; PhCH$_2$), 4.50 (d, ^3J(H,H) = 3.6 Hz, 1H; H-1), 4.43 (d, ^3J-(H,H) = 1.2 Hz, 1H; H-5′), 4.26 (d, ^3J(H,H) = 2.4 Hz, 1H; H-4), 4.15 (d, ^2J(H,H) = 11.7 Hz, 1H; PhC*H*H), 4.01 (dd, ^2J(H,H) = 9.9 Hz, ^3J(H,H) = 6.0 Hz, 1H; H-6a), 3.96 (t, ^3J(H,H) = 6.0 Hz, 1H; H-5), 3.91 (d, ^2J(H,H) = 11.7 Hz, 1H; PhC*H*H), 3.86 (dd, ^3J(H,H) = 10.0, 2.4 Hz, 1H; H-3), 3.79 (dd, ^2J(H,H) = 9.9 Hz, ^3J(H,H) = 6.0 Hz, 1H; H-6b), 3.65–3.59 (m, 4H; CH_3 and H-2), 3.32 ppm (s, 3H; CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.2, 165.6, 165.2, 165.1 (each C=O), 138.8 (2s), 138.4 (each C), 133.5,

133.3, 133.1 (each CH), 130.0, 129.9, 129.8 (each CH), 129.5, 129.1, 128.8 (each C), 128.6 (2s), 128.3 (3s), 128.2, 127.9, 127.7 (3s), 127.6, 127.5, 127.4 (each CH), 101.6 (C-1′), 98.5 (C-1), 78.2 (C-3), 77.4 (C-2), 76.1 (C-4), 73.9 (PhCH_2), 73.5 (PhCH_2), 73.4 (PhCH_2), 72.5 (C-5′), 71.6 (C-3′), 70.0 (C-6), 69.5 (C-2′), 69.3 (C-5), 69.1 (C-4′), 55.3 (CH_3), 52.5 ppm (CH_3); ESI-HRMS calcd for $C_{56}H_{54}NaO_{15}$ 989.3360, found *m/z* (%) 989.3355 $[M+Na]^+$. To this intermediate (155 mg, 0.160 mmol) in MeOH (5 mL), Pd/C (30 mg) was added and the mixture was stirred under hydrogen for 24 h. The mixture was filtered through Celite and the filtrate concentrated to dryness. The residue was taken up in pyridine (4 mL) and cooled to 0 °C and benzoyl chloride (100 μL, 0.80 mmol) was added and the reaction allowed to attain room temperature for 24 h. Work up as described previously and chromatography (petroleum ether/EtOAc 1:1) gave **44** (138 mg, 86 %) as a white solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.12 (d, ^3J(H,H) = 7.2 Hz, 2H; Ar-H), 8.05 (d, ^3J(H,H) = 7.2 Hz, 2H; Ar-H), 7.95 (d, ^3J(H,H) = 7.3 Hz, 2H; Ar-H), 7.91 (d, ^3J(H,H) = 7.3 Hz, 2H; Ar-H), 7.83 (m, 4H; Ar-H), 7.63–7.53 (m, 3H, Ar-H), 7.53–7.42 (m, 6H; Ar-H), 7.39–7.24 (m, 7H; Ar-H), 7.16 (t, ^3J(H,H) = 7.8 Hz, 2H; Ar-H), 6.12 (d, ^3J(H,H) = 2.5 Hz, 1H; $H_{4'}$), 5.89–5.82 (m, 2H; H-2' and H-3), 5.57 (dd, ^3J-(H,H) = 10.5, 2.5 Hz, 1H; H-3′), 5.37 (dd, ^3J(H,H) = 10.8, 3.5 Hz, 1H; H-2), 5.24 (d, ^3J(H,H) = 3.5 Hz, 1H; H-1), 5.02 (d, ^3J(H,H) = 7.9 Hz, 1H; H-1′), 4.96 (dd, ^2J(H,H) = 12.1 Hz, ^3J(H,H), 3.9 Hz, 1H; H-6a), 4.80 (dd, ^2J-(H,H) = 12.1 Hz, ^3J(H,H) = 7.9 Hz, 1H; H-6b), 4.72 (d, ^3J(H,H) = 1.9 Hz, 1H; H-4), 4.48–4.39 (m, 2H; H-5 and H-5′), 3.61 (s, 3H; CH_3), 3.39 ppm (s, 3H; CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.2, 166.0, 165.9, 165.6, 165.4, 165.2 (s), (each C=O), 133.6 (2s), 133.4, 133.1, 132.9 (2s), 132.9 (each CH), 130.3 (C), 130.1, 129.8 (2s), 129.8, 129.7 (2s) (each CH), 129.4, 129.3, 129.0, 128.9 (each C), 128.7 (2s, CH), 128.7 (C), 128.4, 128.3, 128.2 (2s) (each CH), 101.0 (C-1), 97.3 (C-1), 74.7 (C-4), 72.7 (C-5), 71.2 (C-3′), 70.6 (C-3), 69.7 (C-2′), 69.4 (C-2), 69.0 (C-4), 68.1 (C-5), 64.5 (C-6), 55.3 (CH_3), 52.7 ppm (CH_3). ESI-HRMS calcd for $C_{56}H_{49}O_{18}$ 1009.2919, found *m/z* (%) 1009.2922 $[M+H]^+$.

General procedure for the anomerisation reaction (conditions B; see Tables 1 and 2): The β-anomer (1 equiv) was added to a flame-dried round bottomed flask and anhydrous CH_2Cl_2 (10 mL per g of substrate) was added. The flask was then cooled on an ice-bath and 2.5 equiv $TiCl_4$ (1 M in CH_2Cl_2) was added dropwise. The flask was then left to stand in a freezer (−15 to −18 °C) for 48–72 h. The mixture was diluted with CH_2Cl_2 and washed with NH_4Cl (1.0 M, 10 mL). The aqeous layer was extracted with CH_2Cl_2 and the combined organic layers were washed with satd. aq. $NaHCO_3$ and brine. The organic layer was dried over Na_2SO_4, filtered through silica gel and the solvent removed to give the products.

2-*O*-(2,3,4-Tri-*O*-benzoyl-5-*S*-(methoxycarbonyl)-α-D-xylopyranosyl)-3,4-*O*-(1,1,3,3-tetraisopropyl-1,3-disiloxanediyl)-6-*O*-acetyl-β-D-glucopyranosyl azide (52): $[\alpha]_D$ = 48.0 (*c* 0.35, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.00 (dd, ^3J(H,H) = 8.3, 1.5 Hz, 2H; Ar-H), 7.96–7.91 (m, 2H; Ar-H), 7.88 (dd, ^3J(H,H) = 8.3, 1.5 Hz, 2H; Ar-H), 7.57–7.49 (m, 1H; Ar-H), 7.46–7.37 (m, 5H; Ar-H), 7.30 (t, ^3J(H,H) = 7.7 Hz, 2H; Ar-H), 6.21 (aptt, ^3J(H,H) = 10.1 Hz, 1H; H-3′), 6.08 (d, ^3J(H,H) = 3.7 Hz, 1H; H-1′), 5.65 (aptt, ^3J(H,H) = 10.0 Hz, 1H; H-4′), 5.35 (dd, ^3J(H,H) = 10.4, 3.7 Hz, 1H; H-2′), 4.94 (d, ^3J(H,H) = 10.3 Hz, 1H; H-5′), 4.49 (d, ^3J(H,H) = 8.7 Hz, 1H; H-1), 4.40 (dd, ^2J(H,H) = 12.0 Hz, ^3J(H,H) = 2.2 Hz, 1H; H-6a), 4.15 (dd, ^2J(H,H) = 12.0 Hz, ^3J(H,H) = 5.0 Hz, 1H; H-6b), 3.87 (aptt, ^3J(H,H) = 8.7 Hz, 1H; H-3), 3.73 (aptt, ^3J(H,H) = 8.9 Hz, 1H; H-4), 3.64 (s, 3H; CO_2CH_3), 3.56 (aptt, ^3J(H,H) = 8.8 Hz, 1H; H-2), 3.51 (dq, ^3J-(H,H) = 7.3, 3.0, 2.5 Hz, 1H; H-5), 2.05 (s, 3H; $COCH_3$), 1.45–0.75 ppm (m, 28H; 4×C*H*(CH_3)$_2$, overlapping peaks); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 170.7 ($COCH_3$), 168.2 (CO_2CH_3), 165.6, 165.4, 165.3 (3×*C*OPh), 133.4 (2s), 133.2, 129.8, 129.7 (9×Ar-CH, overlapping peaks),129.1, 129.0, 128.9 (3×Ar-C) 128.5, 128.4, 128.3 (6×Ar-CH, overlapping peaks), 94.9 (C-1′), 89.7 (C-1), 78.0 (C-3), 76.9 (C-2), 75.7 (C-5), 72.7 (C-4), 71.0 (C-2′), 70.0 (C-4′), 69.0 (C-3′), 68.6 (C-5′), 62.7 (C-6), 52.7 (CO_2CH_3), 29.7 ($COCH_3$), 20.8, 17.5 (2s), 17.4, 17.3, 17.2 (2s), 17.1 (2s) (8×CH(CH_3)$_2$, overlapping peaks), 12.9, 12.7, 12.2, 11.4 ppm (4×*C*H-(CH_3)$_2$, overlapping peaks); IR (film): $\tilde{\nu}$ = 3072, 2953, 2120, 1727, 1452, 1248, 1091, 1067, 1026 cm^{-1}; ESI-HRMS calcd for $C_{48}H_{61}O_{16}N_3Si_2Na$ 1014.3488, found *m/z* (%) 1014.3494 $[M+Na]^+$.

2,3,4-Tri-*O*-benzoyl-6-*O*-(2,3,4-tri-*O*-benzoyl-5-*S*-(methoxycarbonyl)-α-D-xylopyranosyl)-β-D-glucopyranosyl azide (53): $[\alpha]_D$ = 44.9 (*c* 1.1, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.13–8.02 (m, 2H; Ar-H), 8.00 (dd, ^3J-(H,H) = 8.5, 1.5 Hz, 2H; Ar-H), 7.96 (d, ^3J(H,H) = 6.9 Hz, 2H; Ar-H), 7.91 (ddd, ^3J(H,H) = 8.2, 3.7, 1.4 Hz, 4H; Ar-H), 7.81 (dd, ^3J(H,H) = 8.3, 1.5 Hz, 2H; Ar-H), 7.55–7.27 (m, 17H; Ar-H), 6.29 (aptt, ^3J(H,H) = 9.8 Hz, 1H; H-3′), 5.88 (aptt, ^3J(H,H) = 9.7 Hz, 1H; H-3), 5.68 (aptt, ^3J-(H,H) = 9.8 Hz, 1H; H-4′), 5.60 (aptt, ^3J(H,H) = 9.8 Hz, 1H; H-4), 5.51 (d, ^3J(H,H) = 3.6 Hz, 1H; H-1′), 5.40–5.31 (m, 2H; H-2, H-2′, overlapping peaks), 4.90 (d, ^3J(H,H) = 8.8 Hz, 1H; H-1), 4.74 (d, ^3J(H,H) = 10.1 Hz, 1H; H-5′), 4.16–4.02 (m, 2H; H-5, H-6a, overlapping peaks), 3.80 (dd, ^2J-(H,H) = 11.5 Hz, ^3J(H,H) = 1.9 Hz, 1H; H-6b), 3.60 (s, 3H; CO_2CH_3); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 168.3 (CO_2CH_3), 165.9, 165.8, 165.7, 165.5, 165.2, 165.0 (6×*C*OPh), 133.7 (2s), 133.6, 133.5, 133.3, 130.1 (2s), 130.0, 129.9 (2s) (18×Ar-CH, overlapping peaks), 129.2, 129.1, 129.0, 128.9 (4×Ar-C), 128.7 (2s) (2×Ar-CH, Ar-C, overlapping peaks), 128.6 (2s) (4×Ar-CH, Ar-C, overlapping peaks), 128.5 (2s), 128.4 (6×Ar-CH, overlapping peaks), 96.4 (C-1′), 88.2 (C-1), 75.5 (C-5), 72.9 (C-3), 71.5 (C-2), 71.3 (C-2′), 70.2 (C-4′) 69.9 (C-3′), 68.9 (C-4), 68.6 (C-5′), 67.0 (C-6), 52.9 ppm (CO_2CH_3); IR (film): $\tilde{\nu}$ = 2955, 2924, 2118, 1726, 1451, 1248, 1090, 1067, 1025 cm^{-1}; ESI-HRMS calcd for $C_{55}H_{45}O_{17}N_3Na$ 1042.2647, found *m/z* (%) 1042.2649 $[M+Na]^+$.

2-*O*-Acetyl-3-*O*-(2,3,4-tri-*O*-benzoyl-5-*S*-(methoxycarbonyl)-α-D-xylopyranosyl)-4,6-*O*-(1,1,3,3-tetraisopropyl-1,3-disiloxanediyl)-β-D-glucopyranosyl azide (54): $[\alpha]_D$ = −9.7 (*c* 0.35, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.00 (dd, ^3J(H,H) = 8.2, 1.4 Hz, 2H; Ar-H), 7.95 (dd, ^3J(H,H) = 8.3, 1.4 Hz, 2H; Ar-H), 7.90 (dd, ^3J(H,H) = 8.3, 1.4 Hz, 2H; Ar-H), 7.54–7.49 (m, 2H; Ar-H), 7.46–7.36 (m, 5H; Ar-H), 7.31 (t, ^3J(H,H) = 7.7 Hz, 2H; Ar-H), 6.19 (aptt, ^3J(H,H) = 9.9 Hz, 1H; H-3′), 5.68–5.62 (m, 2H; H-1′, H-4′, overlapping peaks), 5.32 (dd, ^3J(H,H) = 10.1, 3.7 Hz, 1H; H-2), 4.68 (d, ^3J(H,H) = 10.1 Hz, 1H; H-5′), 4.56 (aptt, ^3J(H,H) = 8.8 Hz, 1H; H-2), 4.43 (d, ^3J(H,H) = 9.0 Hz, 1H; H-1), 4.01–3.98 (m, 2H; H-6a, H-6b, overlapping peaks), 3.71–3.63 (m, 5H; CO_2CH_3, H-3, H-4, overlapping peaks), 3.53–3.46 (m, 1H; H-5) 2.05 (s, 3H; $COCH_3$), 1.22–0.94 (m, 28H; 4×C*H*(CH_3)$_2$, overlapping peaks); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 168.9 ($COCH_3$), 168.4 (CO_2CH_3), 165.7 (2s), 165.5 (3×*C*OPh), 133.6, 133.5, 133.3, 130.0, 129.9 (9×Ar-CH, overlapping peaks), 129.2, 129.0, 128.9 (3×Ar-C), 128.7, 128.5 (2s) (6×Ar-CH, overlapping peaks), 96.6 (C-1′), 87.9 (C-1), 77.9 (C-5), 77.6 (C-4), 72.5 (C-2), 72.4 (C-3), 71.6 (C-2′), 70.3 (C-4), 69.8 (C-3′), 68.7 (C-5), 65.9 (C-6), 53.0 (CO_2CH_3), 20.8 ($COCH_3$), 17.4 (4s), 17.3 (2s) (8×CH(CH_3)$_2$, overlapping peaks), 12.9, 12.8, 12.3, 12.2 ppm (4×*C*H(CH_3)$_2$, overlapping peaks); IR (film): $\tilde{\nu}$ = 2925, 2867, 2117, 1731, 1452, 1260, 1095, 1067, 1041, 983 cm^{-1}; ESI-HRMS calcd for $C_{48}H_{61}O_{16}N_3Si_2Na$ 1014.3488, found *m/z* (%) 1014.3492 $[M+Na]^+$.

2,4,6-Tri-*O*-benzoyl-3-*O*-(2,3,4-tri-*O*-benzoyl-5-*S*-(methoxycarbonyl)-α-D-xylopyranosyl)-β-D-glucopyranosyl azide (55): $[\alpha]_D$ = 40.2 (*c* 0.95, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.15–8.10 (m, 2H; Ar-H), 8.08–8.03 (m, 2H; Ar-H), 8.02–7.98 (m, 2H; Ar-H), 7.97–7.94 (m, 2H; Ar-H), 7.94–7.89 (m, 3H Ar-H), 7.83–7.77 (m, 2H; Ar-H), 7.64–7.60 (m, 1H; Ar-H), 7.56–7.27 (m, 19H; Ar-H), 6.29 (aptt, ^3J(H,H) = 9.8 Hz, 1H; H-3′), 5.88 (aptt, ^3J(H,H) = 9.7 Hz, 1H; H-3), 5.68 (aptt, ^3J(H,H) = 9.8 Hz, 1H; H-4′), 5.59 (aptt, ^3J(H,H) = 9.8 Hz, 1H; H-4), 5.51 (d, ^3J-(H,H) = 3.7 Hz, 1H; H-1′), 5.40–5.30 (m, 2H; H-2, H-2′, overlapping peaks), 4.90 (d, ^3J(H,H) = 8.8 Hz, 1H; H-1), 4.74 (d, ^3J(H,H) = 10.1 Hz, 1H; H-5′), 4.11 (ddd, ^3J(H,H) = 9.6, 6.4, 1.7 Hz, 1H; H-5), 4.05 (dd, ^2J-(H,H) = 11.3 Hz, ^3J(H,H) = 6.4 Hz, 1H; H-6a), 3.79 (d, ^2J(H,H) = 11.3 Hz, ^3J(H,H) = 1.7 Hz, 1H; H-6b), 3.60 ppm (s, 3H; CO_2CH_3); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 168.1 (CO_2CH_3), 165.7 (2s), 165.6, 165.4, 165.0, 164.8 (6×*C*OPh), 133.7, 133.6, 133.5 (2s), 133.3, 133.2, 130.2, 130.0 (2s), 129.9, 129.8 (2s) (18×Ar-CH, overlapping peaks), 129.1, 128.9, 128.8 (2s), 128.6 (5×Ar-C), 128.5 (3s) (4×Ar-CH, Ar-C, overlapping peaks), 128.4 (2s), 128.3 (2s) (8×Ar-CH, overlapping peaks), 96.3 (C-1′), 88.1 (C-1), 75.4 (C-5), 72.8 (C-3), 71.3 (C-3′), 71.2 (C-4′), 70.0 (C-2′), 69.8 (C-2), 68.8 (C-4), 68.4 (C-5′), 66.8 (C-6), 52.8 ppm (CO_2CH_3); IR (film): $\tilde{\nu}$ = 2957, 2924, 2119, 1724, 1452, 1248, 1090, 1067, 1025 cm^{-1}; ESI-HRMS calcd for $C_{55}H_{45}O_{17}N_3Na$ 1042.2647, found *m/z* (%) 1042.2653 $[M+Na]^+$.

2,3-*O*-(1,1,3,3-Tetraisopropyl-1,3-disiloxanediyl)-4-*O*-(2,3,4-tri-*O*-benzoyl-5-*S*-(methoxycarbonyl)-α-D-xylopyranosyl)-6-*O*-acetyl-β-D-glucopyranosyl azide (56): $[\alpha]_D = +29.0$ (*c* 0.2, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 8.05$ (dd, $^3J(H,H) = 8.2$, 1.4 Hz, 2H; Ar-H), 7.94–7.89 (m, 4H; Ar-H), 7.58–7.53 (m, 2H; Ar-H), 7.51–7.46 (m, 1H; Ar-H), 7.43–7.36 (m, 4H; Ar-H), 7.26 (m, 2H; Ar-H), 5.99 (d, $^3J(H,H) = 2.4$ Hz, 1H; H-1′), 5.81 (aptt, $^3J(H,H) = 5.5$ Hz, 1H; H-3′), 5.65 (aptt, $^3J(H,H) = 4.9$ Hz, 1H; H-4′), 5.46 (dd, $^3J(H,H) = 5.9$, 2.4 Hz, 1H; H-2′), 4.77 (d, $^3J(H,H) = 4.7$ Hz, 1H; H-5′), 4.60 (dd, $^2J(H,H) = 12.2$ Hz, $^3J(H,H) = 2.3$ Hz, 1H; H-6a), 4.53 (d, $^3J(H,H) = 8.2$ Hz, 1H; H-1), 4.40 (dd, $^2J(H,H) = 12.2$ Hz, $^3J(H,H) = 5.0$ Hz, 1H; H-6b), 4.04 (dd, $^3J(H,H) = 9.9$, 8.6 Hz, 1H; H-4), 3.87 (aptt, $^3J(H,H) = 8.6$ Hz, 1H; H-3), 3.65–3.59 (m, 4H; CO_2CH_3, H-5, overlapping peaks), 3.53 (aptt, $^3J(H,H) = 8.4$ Hz, 1H; H-2), 2.06 (s, 3H; $COCH_3$), 1.17–0.83 ppm (m, 28H; 4×$CH(CH_3)_2$, overlapping peaks); ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 170.7$ ($COCH_3$), 168.4 ($COCH_3$), 165.4, 165.2 (3×*C*OPh, overlapping peaks), 133.7, 133.4, 130.1, 130.0, 129.8 (9×Ar-CH, overlapping peaks), 199.3 128.8, 128.6 (3×Ar-C) 128.4, 128.4, 128.3 (6×Ar-CH, overlapping peaks), 94.6 (C-1′), 90.5 (C-1), 80.3 (C-3), 76.7 (C-2), 74.4 (C-5), 74.2 (C-4) 72.3 (C-5′), 68.6 (H-3′), 68.2 (H-4′), 67.4 (H-2′) 63.0 (C-6), 52.6 (CO_2CH_3), 20.8 ($COCH_3$), 17.3 (2s), 17.2 (2s), 17.1, 16.9 (8×$CH(CH_3)_2$, overlapping peaks), 12.9, 12.7, 12.1, 12.0 ppm (4×$CH(CH_3)_2$, overlapping peaks); IR (film): $\tilde{\nu} = 2927$, 2868, 2118, 1729, 1452, 1246, 1091, 1068, 1026, 988 cm^{-1}; ESI-HRMS calcd for $C_{48}H_{61}O_{16}N_3Si_2Na$ 1014.3488, found *m/z* (%) 1014.3467 $[M+Na]^+$.

2,3,6-Tri-*O*-benzoyl-4-*O*-(2,3,4-tri-*O*-benzoyl-5-*S*-(methoxycarbonyl)-α-D-xylopyranosyl)-β-D-glucopyranosyl azide (57): $[\alpha]_D = +65.3$ (*c* 0.15, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 8.07$–8.02 (m, 2H; Ar-H), 8.01–7.98 (m, 2H; Ar-H), 7.97–7.94 (m, 2H; Ar-H), 7.91 (ddd, $^3J(H,H) = 8.5$, 3.9, 1.4 Hz, 4H; Ar-H), 7.83–7.79 (m, 2H; Ar-H), 7.55–7.27 (m, 17H; Ar-H), 6.28 (aptt, $^3J(H,H) = 9.8$ Hz, 1H; H-3′), 5.87 (aptt, $^3J(H,H) = 9.7$ Hz, 1H; H-3), 5.67 (aptt, $^3J(H,H) = 9.8$ Hz, 1H; H-4′), 5.59 (aptt, $^3J(H,H) = 9.7$ Hz, 1H; H-4), 5.50 (d, $^3J(H,H) = 3.7$ Hz, 1H; H-1′), 5.38–5.32 (m, 2H; H-2, H-2′, overlapping peaks), 4.89 (d, $^3J(H,H) = 8.8$ Hz, 1H; H-1), 4.73 (d, $^3J(H,H) = 10.1$ Hz, 1H; H-5′), 4.10 (ddd, $^3J(H,H) = 9.8$, 6.3, 1.7 Hz, 1H; H-5), 4.05 (dd, $^2J(H,H) = 11.3$ Hz, $^3J(H,H) = 6.4$ Hz, 1H; H-6a), 3.79 (dd, $^2J(H,H) = 11.3$ Hz, $^3J(H,H) = 1.7$ Hz, 1H; H-6b), 3.60 ppm (s, 3H; CO_2CH_3); ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 168.1$ (CO_2CH_3), 165.7 (2s), 165.6, 165.4, 165.0, 164.8 (6×*C*OPh), 133.6, 133.5 (2s), 133.3, 133.2, 130.0, 129.9 (2s), 129.8 (2s) (18×Ar-CH, overlapping peaks), 129.1, 128.9, 128.8 (2s), 128.6 (5×Ar-C), 128.5 (2s) (2×Ar-CH, Ar-C, overlapping peaks), 128.4(2s), 128.3 (2s) (10×Ar-CH, overlapping peaks), 96.3 (C-1′), 88.1 (C-1), 75.4 (C-5), 72.8 (C-3), 71.3 (C-2), 71.2 (C-2′), 70.0 (C4′), 69.8 (C-3′), 68.8 (C-4), 68.4 (C-5′), 66.8 (C-6), 52.8 ppm (CO_2CH_3); IR (film): $\tilde{\nu} = 2952$, 2119, 1725, 1452, 1247, 1091, 1067, 1026, 704 cm^{-1}; ESI-HRMS calcd for $C_{55}H_{45}O_{17}N_3Na$ 1042.2647, found *m/z* (%) 1042.2665 $[M+Na]^+$.

Methyl 6-*O*-(2,3,4-tri-*O*-benzoyl-5-*S*-(methoxycarbonyl)-β-L-arabinopyranosyl)-2,3,4-tri-*O*-benzoyl-α-D-galactopyranose (58): ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 8.08$–7.93 (m, 8H; Ar-H), 7.83–7.78 (m, 2H; Ar-H), 7.76–7.73 (m, 2H; Ar-H), 7.64–7.56 (m, 2H; Ar-H), 7.55–7.32 (m, 12H; Ar-H), 7.24 (m, 4H; Ar-H), 6.23 (dd, $^3J(H,H) = 3.4$, 1.5 Hz, 1H; H-4′), 5.99–5.93 (m, 2H; H-3’ and H-3), 5.87 (d, $^3J(H,H) = 3.2$ Hz, 1H; H-4), 5.72 (dd, $^3J(H,H) = 10.7$, 3.5 Hz, 1H; H-2), 5.66 (dd, $^3J(H,H) = 10.7$, 3.5 Hz, 1H; H-2′), 5.48 (d, $^3J(H,H) = 3.5$ Hz, 1H; H-1′), 5.30 (d, $^3J(H,H) = 3.5$ Hz, 1H; H-1), 5.08 (d, $^3J(H,H) = 1.5$ Hz, 1H; H-5′), 4.51 (dd, $^3J(H,H) = 7.9$, 3.6 Hz, 1H; H-5), 4.00 (dd, $^2J(H,H) = 10.5$ Hz, $^3J(H,H) = 7.9$ Hz, 1H; H-6a), 3.77 (dd, $^2J(H,H) = 10.5$ Hz, $^3J(H,H) = 3.6$ Hz, 1H; H-6b), 3.72 (s, 3H; CH_3), 3.54 ppm (s, 3H; CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta =$ 167.3, 166.1, 165.8, 165.5 (2s), 165.4, 165.2 (each C=O), 133.6, 133.5, 133.4, 133.2, 133.1 (each CH), 129.9 (3s), 129.8, 129.7, 129.6 (each CH), 129.2, 129.1, 129.0 (4s) (each C), 128.6 (2s), 128.4, 128.3, 128.2 (each CH), 97.6 (C-1), 96.9 (C-1′), 70.0 (C-4), 69.6 (C-4), 69.4 (C-2′), 69.2 (C-5′), 68.3 (C-3′), 68.3 (C_2), 68.0 (C-5), 67.9 (C-3′), 67.7 (C-6), 55.7 (CH_3), 52.8 ppm (CH_3); ESI-HRMS calcd for $C_{56}H_{48}NaO_{18}$ 1031.2738, found *m/z* (%) 1031.2745 $[M+Na]^+$.

Methyl 4-*O*-(2,3,4-tri-*O*-benzoyl-5-*S*-(methoxycarbonyl)-β-L-arabinopyranosyl)-2,3,6-tri-*O*-benzoyl-α-D-galactopyranose (59): ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 8.06$–8.03 (m, 2H; Ar-H), 7.97–7.90 (m, 8H; Ar-H), 7.83–7.79 (m, 2H; Ar-H), 7.64–7.23 (m, 18H; Ar-H), 6.27 (dd, $^3J(H,H) = 3.4$, 1.9 Hz, 1H; H-4′), 6.18 (dd, $^3J(H,H) = 11.0$, 3.4 Hz, 1H; H-3′), 5.89–5.80 (m, 2H; H-2’ and H-2), 5.63 (d, $^3J(H,H) = 3.6$ Hz, 1H; H-1′), 5.59 (dd, $^3J(H,H) = 11.0$, 2.6 Hz, 1H; H-3), 5.30 (d, $^3J(H,H) = 1.5$ Hz, 1H; H-5′), 5.26 (d, $^3J(H,H) = 3.6$ Hz, 1H; H-1), 4.67 (d, $^3J(H,H) = 2.6$ Hz, 1H; H-4), 4.50 (dd, $^2J(H,H) = 10.3$ Hz, $^3J(H,H) = 5.9$ Hz, 1H; H-6a), 4.38–4.32 (m, 1H; H-5), 4.28 (dd, $^2J(H,H) = 10.3$ Hz, $^3J(H,H) = 8.3$ Hz, 1H; H-6b), 3.45 (s, 3H; OCH_3), 3.08 ppm (s, 3H; $COOCH_3$); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 166.6$, 166.3, 166.0, 165.8, 165.6, 165.5, 165.0 (each C=O), 133.5, 133.4, 133.3, 133.2 (2s), 129.8 (2s), 129.7 (2s) (each CH), 129.3 (2s) 129.1, 129.0, 128.9, 128.6 (each C), 128.5 (2s) 128.4 (2s), 128.3, 128.2 (each CH), 99.5 (C-1′), 97.7 (C-1), 77.1 (C-4), 71.0 (C-3), 70.2 (C-4′), 70.0 (C-5′), 68.5 (C-2’ and C-2), 67.5 (C-3′), 67.2 (C-5), 60.8 (C-6), 55.7 (CH_3), 52.1 ppm (CH_3). ESI-HRMS calcd for $C_{56}H_{48}NaO_{18}$ 1031.2738, found *m/z* (%) 1031.2742 $[M+Na]^+$.

Supporting information: Additional experimental prodedures and NMR spectra can be found in the Supporting Information.

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