Carbohydrate Research 343 (2008) 2545–2556

Contents lists available at ScienceDirect

Carbohydrate Research

journal homepage: www.elsevier.com/locate/carres

Stereoselective synthesis of a model α-glycoside of the β-D-ManNAc*p*-(1→4)-D-Glc disaccharide starting from lactose, avoiding the β-mannosaminylation step ☆

Emanuele Attolino[†], Filippo Bonaccorsi, Giorgio Catelani *, Felicia D'Andrea

Dipartimento di Chimica Bioorganica e Biofarmacia, Università di Pisa, Via Bonanno 33, I-56126 Pisa, Italy

ARTICLE INFO

Article history:
Received 17 May 2008
Received in revised form 8 July 2008
Accepted 11 July 2008
Available online 18 July 2008

Keywords:
β-Mannosamine
Epimerization
β-Talosamine
Lactose
β-D-ManNAc*p*-(1→4)-α-D-Glc*p* glycosides

ABSTRACT

A model isopropyl α-glycoside of the β-D-ManNAc-(1→4)-D-Glc disaccharide has been prepared from lactose, avoiding the β-mannosaminylation step. Three complementary approaches involving first the preparation and then the glycosidation of β-thiophenyl donors of the protected disaccharides, (a) β-D-ManNAc-(1→4)-D-Glc, (b) β-D-TalNAc-(1→4)-D-Glc and (c) lactose, were compared. The best results were obtained employing a suitably protected lactose donor, and submitting its α-isopropyl glycoside to an amination with inversion in position 2′ followed by an epimerization at C-4′.

1. Introduction

D-Mannosamine (2-amino-2-deoxy-D-mannose) was not mentioned amongst the most relevant naturally occurring hexosamines until thirty years ago.[1] However, more recently it has been the object of an increasing interest because of its presence in nature. Mannosamine is an important constituent of several complex biologically relevant oligosaccharides, mainly in the form of 2-acetamido-D-pyranose derivative (D-ManNAc*p*). Both α- and β-MaNAc*p* units are present in the capsular polysaccharide repeating units (CPS) of some pathogenic bacteria, as for instance, *Neisseria meningitidis*, *Haemophilus influenzae* and *Streptococcus pneumoniae* strains.[2] Furthermore, Kren and co-workers[3] demonstrated that ManNAc is a good agonist for rat Natural Killer activation receptor NKR-P1. Despite impressive developments in the stereoselective glycosidation methods,[4] the stereocontrolled synthesis of β-D-ManNAc glycosides represents until now one of the most challenging task for synthetic carbohydrate chemists.[5] In order to overcome these difficulties, we have recently developed a stereoselective methodology for the transformation of β-D-Gal*p* glycosides into β-D-ManNAc*p* ones,[6a] avoiding the β-mannosaminylation step.

In this context, the transformation of lactose into the β-D-ManNAc*p*-(1→4)-D-Glc disaccharide has been recently described.[6b,c] As a development of this method, we focused our attention to the stereoselective synthesis of α-glycosides of the above disaccharide that are present in some complex saccharides, as for instance, the trisaccharide repeating units of *S. pneumoniae 19A* and *19F* (*SP19A* and *SP19F*) CPS.[2] This idea has been developed exploring the three complementary approaches outlined in Figure 1, differing each other from the sequence in which the four key synthetic procedures (A. amination with inversion at C-2′; B. epimerization at C-4′; C. anomeric activation; D. glycosidation) can be performed. In order to simplify this study, we chose isopropyl alcohol as a simple model for a secondary alcoholic glycosyl acceptor. Herein, we report the results of this investigation.

2. Results and discussion

2.1. Synthesis of the glycosyl donors

The synthesis of β-D-ManNAc containing glycosyl donor **11**, characterized by the presence of an orthogonal protecting group on OH-4′ in view of a further use in the synthesis of oligomeric fragments of the *SP19A* or *SP19F* CPS, has been performed by allylation (AllBr, KOH, 18-crown-6/wet THF, 92%) of **1**,[6b,c] to give **3**. This has been converted into **5** (α/β ratio = 2:3) through complete deprotection of the *gluco* unit (80% aq AcOH, 80 °C) followed by

☆ Part 24 of the series 'Chemical Valorisation of Milk-Derived Carbohydrates'. For part 23, see Ref. 17.

* Corresponding author. Tel.: +39 0502219700; fax: +39 0502219660.
E-mail address: giocate@farm.unipi.it (G. Catelani).
† Present address: Dipharma S.p.A., Via Bissone 5, I-20021 Baranzate, Milano, Italy.

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doi:10.1016/j.carres.2008.07.006

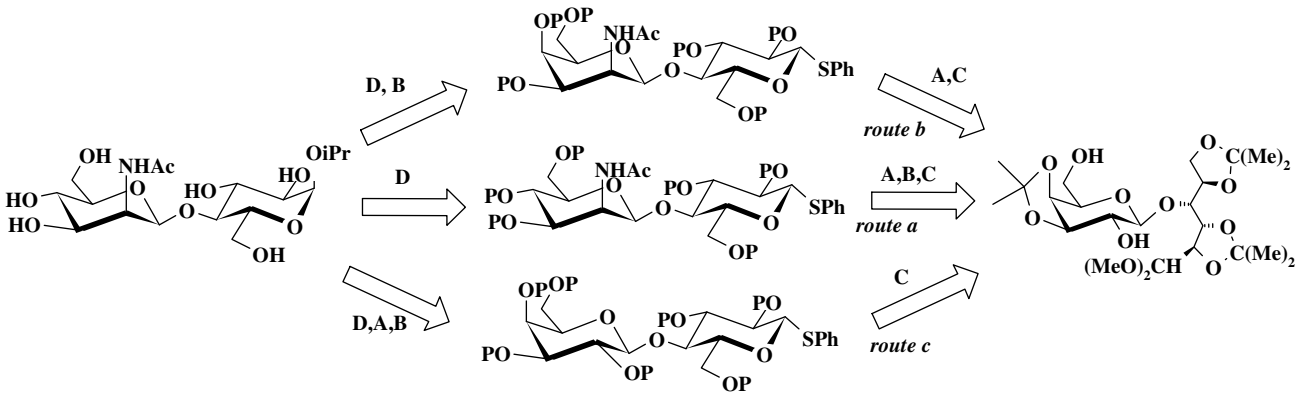
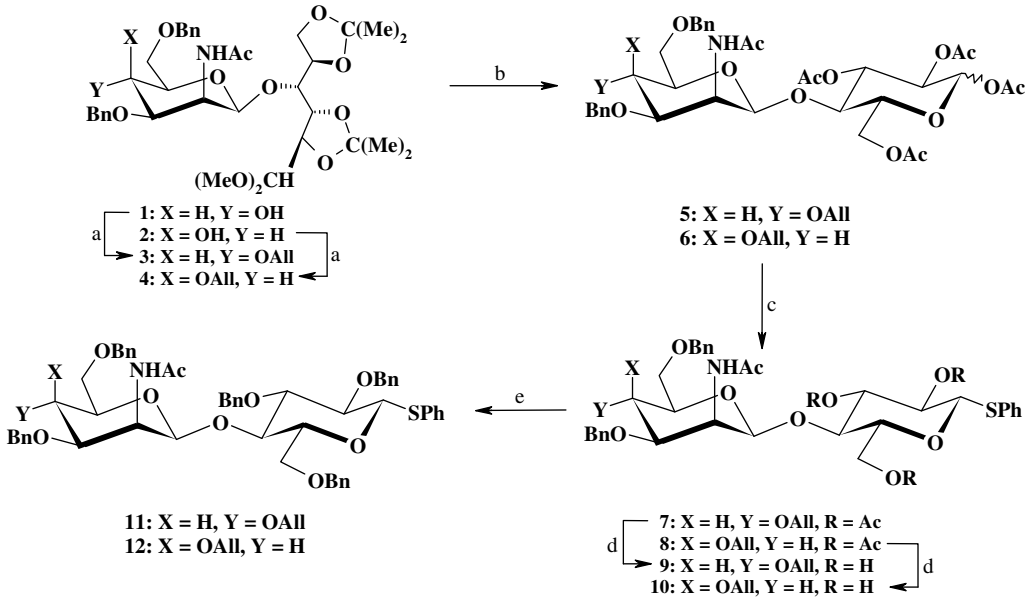


Figure 1. Three complementary approaches for the transformation of lactose into α-glycosides of the β-D-ManNAc*p*-(1→4)-D-Glc*p* disaccharide. (A) Amination with inversion at C-2′; (B) epimerization at C-4′; (C) anomeric activation; (D) glycosidation.



Scheme 1. Preparation of β-D-ManNAc- and β-D-TalNAc-(1→4)-β-D-Glc thiophenyl glycosyl donors. Reagents and conditions: (a) AllBr, KOH, 18-crown-6, wet THF, room temp (**3**: 82%, **4**: 96%); (b) (1) 80% aq AcOH, 80 °C; (2) Ac_2O, $AcONa·3H_2O$, reflux, 2 h (**5**: 82%, **6**: 90%); (c) TMSSPh, ZnI_2, 4 Å AWMS, room temp, 1 h (**7**: 82%, **8**: 76%); (d) KOH, EtOH, room temp, 1 h (**9**: 96%, **10**: 87%); (e) BnBr, KOH, 18-crown-6, wet THF, 0 °C (**11**: 95%, **12**: 95%).

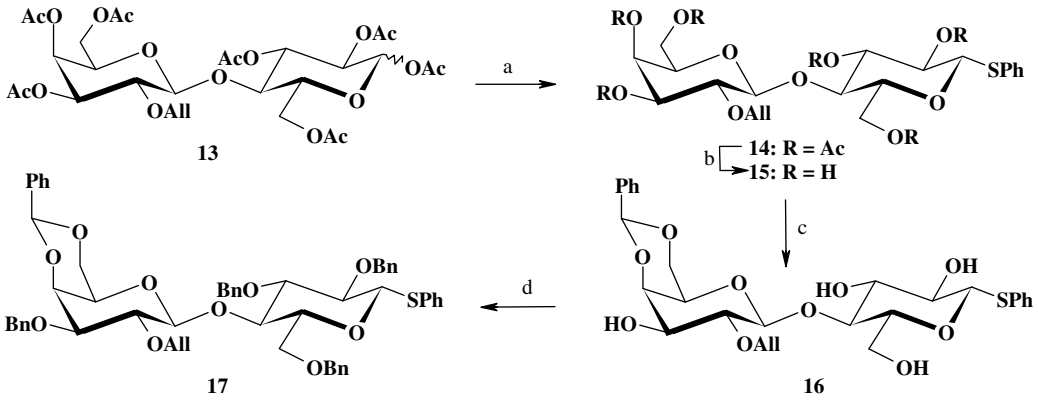
acetylation with acetic anhydride in the presence of sodium acetate trihydrate (see Scheme 1).

Attempts to convert **5** into the thioglycoside **7** with the most widely reported methods in the literature ($PhSH/BF_3·Et_2O$, or TMSSPh/MeOTf)[7] led to disappointing results, and the starting material was recovered in any case. Good results for the conversion of **5** into **7** (82% isolated yield) have been obtained treating **5** with TMSSPh in the presence of zinc iodide.[8] The exchange of the protection on **7** from acetate to benzyl groups for obtaining **11** has been carried out by saponification with potassium hydroxide in ethanol and benzylation of intermediate **9** (BnBr, KOH, 18-crown-6/wet THF, 91% from **7**). Following an identical sequence, the β-D-TalNAc containing thioglycoside **12** has been obtained starting from **2**,[6b,c] with minor changes in the yield of the single steps.

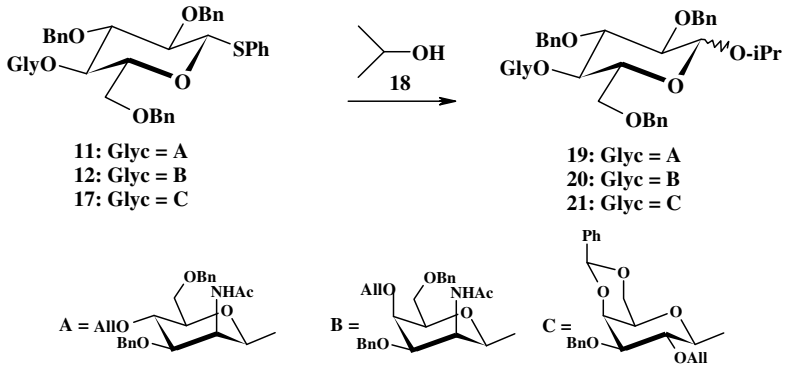
The preparation of the thiophenyl lactoside donor **17**, suitably protected for elaboration on C-2′ and C-4′ (Scheme 2), has been performed starting from the known[9] 2′-*O*-allyl-hepta-*O*-acetyllactose (**13**) through a first thiophenyl glycosidation with trimethylsylthiophenol and ZnI_2 as promoter. As for the above discussed thioglycosidations leading to **7** and **8**, the reaction was highly β-stereoselective, but the yield was sensibly higher reaching a fully satisfactory 90%. After O-deacetylation of **14**, the crude hexaol **15** was submitted to standard benzylidenation through acid-promoted (TsOH) transacetalation with α,α-dimethoxytoluene, giving **16**, and after a final benzylation (NaH, BnBr/DMF), the target glycosyl donor **17**, with an overall yield of 67% from **13**.

2.2. Glycosidation reactions

The glycosidation reactions (Scheme 3 and Table 1) have been carried out with the two most widely used promoters, MeOTf and NIS/TfOH,[7,10] that are classified between those of low and high reactivity, respectively. The NIS/TfOH promoted reactions of the three glycosyl donors **11, 12** and **17** were performed in dichloromethane (DCM) from −30 °C until room temperature with a slight excess of the acceptor isopropanol (**18**) and were left to react for 6 h. Whilst **12** and **17** gave an anomeric mixture of the expected glycosides in low yield and poor stereoselectivity (Table 1), the donor **11**, carrying a mannosamine unit at the non-reducing end, did not react under the same conditions and it was recovered



Scheme 2. Preparation of the lactose thiophenyl glycosyl donor **17**. Reagents and conditions: (a) TMSSPh, ZnI_2, 4 Å AW MS, room temp, 1 h (90%); (b) KOH, EtOH, room temp, 1 h (90%); (c) $C_6H_5C(OMe)_2$, TsOH, MeCN, room temp, 1 h (86%); (d) BnBr, NaH, DMF, room temp, 12 h (88%).



Scheme 3. Glycosidation with *i*-PrOH of disaccharide glycosyl donors **11**, **12** and **17**. Reagents and conditions: see Table 1.

Table 1
Glycosidation reactions of thiophenyl disaccharide glycosyl donors **11, 12** and **17**[a]

Entry	Donor	Activating system	*T* (°C)/*t* (h)	Solvent	Product	Yield (%)	α/β ratio
1	**11**	NIS (2 equiv)/TfOH (0.2 equiv)	−30 °C→rt/6	CH_2Cl_2	**19**	—[b]	—
2	**11**	MeTfO (5 equiv)/4 Å	rt/24	CH_2Cl_2	**19**	—[c]	—
3	**12**	NIS (2 equiv)/TfOH (0.2 equiv)	−30 °C→rt/6	CH_2Cl_2	**20**	50	2/3
4	**12**	MeOTf (5 equiv)/4 Å	rt/24	Et_2O	**20**	50	9/11
5	**17**	NIS (2 equiv)/TfOH (0.2 equiv)	−30 °C→rt/6	CH_2Cl_2	**21**	45	2/3
6	**17**	MeOTf (5 equiv)/4 Å	rt/24	1:4 CH_2Cl_2/Et_2O	**21**	78	39/11

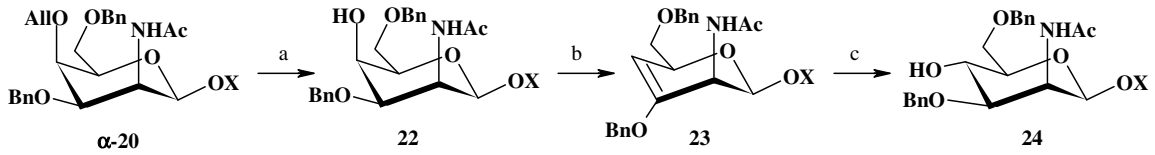
[a] All the reactions were conducted in the presence of a slight excess (1.2 equiv) of *i*-PrOH acceptor.
[b] Donor retrieved.
[c] Decomposition.

unchanged. When MeOTf was used as promoter (Table 1), similar results were obtained using donors **11** (almost complete decomposition) and **12** (moderate yields, poor selectivity), while pleasingly more satisfactory yield (78%) and stereoselectivity ($\alpha/\beta \approx 4/1$) were obtained using the lactoside donor **17**.

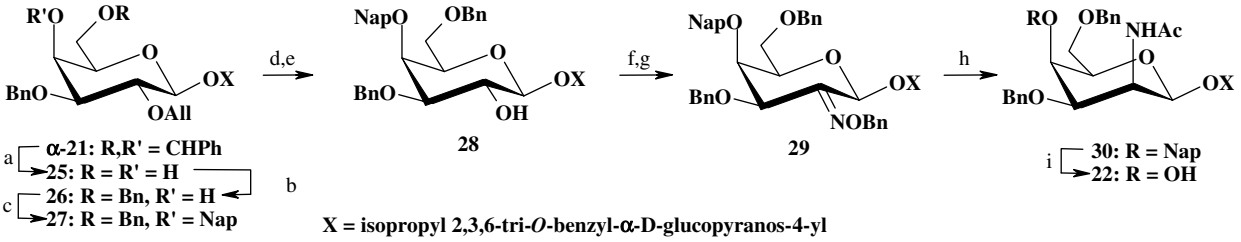
On the light of the general difficulties reported[11] for glycosidation reactions in the presence of acetamido groups on the glycosyl donor and/or acceptor, these results are not so much surprising. Although we have not find any literature report for glycosyl donor containing TalNAc residue, in order to explain the different reactivity between the two aminated donors **11** and **12**, it is reasonable to consider that in the case of the donor **12**, the steric access of reactants to the axial acetamido group is reduced because of the presence of the axial oxygenated substituent at C-4′, thus determining more clean reaction in glycosidation conditions. As a matter of fact, it appears possible to gain the targeted isopropyl β-D-ManNAc*p*-(1→4)-α-D-Glc*p* glycoside carrying out first the glycosidation of the β-D-TalNAc-(1→4)-D-Glc thiophenyl glycoside **12** or the thiophenyl lactoside **17**, and then submitting either isopropyl glycoside **α-20** or **α-21** to the stereoselective manipulations outlined in Figure 1 (route b, step B; and route c, steps A and B, respectively).

2.3. Stereoselective transformation of the protected *i*-PrOH glycosides α-20 and α-21 into the β-D-ManNAc*p*-(1→4)-α-D-Glc*p* one

The most direct route to reach the proposed goal was the epimerization at C-4′ of the derivative **α-20** easily separated from its β-anomer through chromatographic purification. After deprotection of the OH-4′ group by treatment with $PdCl_2$[12] in EtOH–MeOH solution (90% yield), the alcohol **22** was subjected to our two-step epimerization protocol,[6] based on a first regiospecific dehydration (Im_2SO_2/NaH in DMF) to give the enol ether **23**, followed by its regio- and stereoselective hydroboration-oxidation to give the hemiprotected target isopropyl β-D-ManNAc*p*-(1→4)-α-D-Glc*p* derivative **24** with an overall 57% yield from **22** (Scheme 4).



Scheme 4. Epimerization at C-4′ of the isopropyl β-D-TalNAc*p*-(1→4)-α-D-Glc*p* derivative **α-20**. Reagents and conditions: (a) $PdCl_2$, 1:1 EtOH–MeOH (90%); (b) Im_2SO_2, NaH, DMF, from −30 °C (30 min) to rt (98%); (c) $BH_3{\cdot}Me_2S$ (5 M Et_2O), THF, 40 °C, 40 min, then 35% aq H_2O_2, 10% aq NaOH, room temp, 30 min (60%).



Scheme 5. Amination with inversion at C-2′ of the isopropyl α-lactoside **α-21**. Reagents and conditions: (a) 80% aq AcOH, 80 °C, 1 h (95%); (b) Bu_2SnO, $C_6H_5CH_3$, reflux, 12 h, then BnBr, Bu_4NBr, reflux, 4 h (89%); (c) NapBr, NaH, DMF, 0 °C, 30 min (95%); (d) $(Ph_3P)_3RhCl$, DABCO, 9:1 EtOH–H_2O; (e) MCPBA, DCM then Et_3N (85% from **27**); (f) PCC, DCM, room temp, 8 h; (g) $NH_2OBn{\cdot}HCl$, Py, room temp, 6 h (70% from **28**); (h) (1) $LiAlH_4$, Et_2O, reflux, 1.5 h; (2) Ac_2O, MeOH, room temp, 1 h (83%); (i) DDQ, 9:1 CH_3CN–H_2O, room temp, 9 h (85%).

An identical overall result was obtained by transforming the α-isopropyl lactoside **α-21** into the above TalNAc intermediate **22** through the sequence outlined in Scheme 5.

A series of protecting group manipulations were preliminarily needed in order to orthogonally cap OH-2′ and OH-4′. The sequence was based on a first debenzylidenation (80% aq AcOH, 80 °C) followed by a stannylidene acetal-mediated OH-6 benzylation to give the alcohol **26**, that was finally alkylated with 2-naphthylmethyl bromide[13] (NapBr) and NaH in DMF, obtaining the desired orthogonally fully protected derivative **27** in a satisfactory 80% overall yield from **α-21**. The allyl group of **27** was removed by isomerization to vinyl ether with Wilkinson's catalyst and DABCO, followed by treatment with MCPBA and Et_3N[14] giving **28** in 85% isolated yield. Several attempts to oxidize the hydroxyl group at C-2 of **28** with the TPAP-NMO system or Swern's reagents gave unsatisfactory results. The oxidation at C-2′ was accomplished with PCC in anhydrous CH_2Cl_2, which yielded a crude uloside that was directly transformed into the oximino derivative **29** (*E*/*Z* mixture, 70% yield) with $BnONH_3Cl$ in pyridine. A completely stereoselective reduction of **29** was performed by treatment with $LiAlH_4$ in Et_2O at reflux, giving, after N-acetylation with Ac_2O in MeOH, the protected TalNAc-containing disaccharide **30**. It is worth of note that the outcome of the reduction of **29** is strongly dependent from the reaction time. Whilst quenching the reaction after a relatively short time (1.5 h), high yields of the expected disaccharide **30** were obtained, with prolonged reaction times (12 h), and about 1:1 mixture of **30** and the OH-4′ deprotected derivative **22** was obtained. The removal of a benzyl or benzyl-like group with $LiAlH_4$ is unusual, but it has been already reported.[15] In view of our scope, we considered the possibility of obtaining **22** directly from **29**. However, several attempts to push the reaction in this direction failed, giving always mixtures of **22** and **29**, along with some degradation by-products under forcing conditions. The selective removal of the Nap group was, finally, made by treatment with DDQ in 9:1 MeCN–water affording **22** in 85% yield.

In conclusion, the stereoselective synthesis of a model α-glycoside of the β-D-ManNAc*p*-(1→4)-α-D-Glc*p* from lactose avoiding the β-mannosaminylation step has been achieved using either the suitably protected thiophenyl lactosyl donor **17** or the β-D-TalNAc*p*-(1→4)-D-Glc*p* **12** as intermediate. Although the proposed overall procedures require several protecting group manipulations lowering the overall yields, the route starting with the glycosidation of the lactosyl donor **17** appears as a practicable method for obtaining α-glycosides of the D-MaNAc*p*-(1→4)-D-Glc*p* disaccharide avoiding the β-mannosaminylation step. Taking also into account that lactosides are easily available and cheap starting materials, this new method could be complementary to the existing procedures[5] for obtaining oligosaccharides containing the β-D-ManNAc*p*-(1→4)-α-D-Glc*p* framework.

3. Experimental

3.1. General methods

Melting points were determined with a Kofler hot-stage apparatus and are uncorrected. Optical rotations were measured on a Perkin–Elmer 241 polarimeter at 20 ± 2 °C. ^1H NMR spectra were recorded in appropriate solvents (internal standard Me_4Si) with a Bruker AC 200 instrument operating at 200.13 MHz (^1H) and 50 MHz (^{13}C), with a Bruker Avance II 250 spectrometer operating at 250.15 MHz (^1H) and 62.9 MHz (^{13}C) and with a Varian INOVA600 instrument operating at 600 MHz (^1H). Assignments were made, when possible, with the aid of DEPT, HETCOR, COSY experiments, and by comparison of values for known compounds and applying the additivity rules.[15] In the case of mixtures, assignments were made by referring to the differences in the peak intensities. All reactions were followed by TLC on Kieselgel 60 F_{254} with detection by UV light and/or with ethanolic 10% phosphomolybdic or sulfuric acid, and heating. Kieselgel 60 (E. Merck, 70–230 and 230–400 mesh, respectively) was used for column and flash chromatography. Solvents were dried and purified by distillation according to standard procedure,[16] and stored over 4 Å molecular sieves activated for at least 24 h at 200 °C. $MgSO_4$ was used as the drying agent for solutions. The preparation of the previously reported[6a] compound **1** was appreciably improved (from 64% to 71%), changing the solvent for the hydroboration–oxidation of the enol ether precursor[6a] from ether to tetrahydrofuran. Compounds **2** and **13** were prepared through literature methods.[6b,9]

3.2. 4-*O*-(2-Acetamido-4-*O*-allyl-3,6-di-*O*-benzyl-2-deoxy-β-D-mannopyranosyl)-2,3:5,6-di-*O*-isopropylidene-*aldehydo*-D-glucose dimethyl acetal (3)

To a soln of **1** (1.33 g, 1.92 mmol) in THF containing 0.5% of water (15 mL), 18-crown-6 (30 mg, 0.113 mmol) followed by powdered KOH (431 mg, 7.69 mmol) was added, and the suspension was stirred at room temp. After 30 min, the mixture was treated with allyl bromide (0.36 mL, 518 mg, 4.30 mmol) and was stirred at room temp. After 4 h, the TLC analysis (3:7 hexane–EtOAc) revealed the complete disappearance of the starting material (R_f 0.16) and the formation of a major faster-moving product (R_f 0.29). MeOH (5 mL) was added and the mixture was further stirred at room temp for 30 min, concentrated under diminished pressure and the residue was taken up with CH_2Cl_2 (100 mL) and washed with water (30 mL). The aq phase was extracted with CH_2Cl_2 (3 × 40 mL), and the combined organic phases were dried, filtered and concentrated under diminished pressure. The crude residue (1.80 g) was subjected to flash chromatography (2:3 hexane–EtOAc) to give pure **3** (1.29 g, 92% yield) as a syrup; $[\alpha]_D$ −26.4 (*c* 0.95, $CHCl_3$); R_f 0.23 (2:3 hexane–EtOAc); ^{1}H NMR (200 MHz, CD_3CN): δ 7.40–7.28 (m, 10H, Ar-H), 6.33 (d, 1H, $J_{2',NH}$ 10.0 Hz, NH), 5.87 (ddt, 1H, J_{trans} 17.3 Hz, J_{cis} 10.4 Hz, *J* 5.2 Hz, C*H*=), 5.17 (dq, 1H, J_{trans} 17.3 Hz, *J* 1.7 Hz, CH_2=), 5.08 (dq, 1H, J_{cis} 10.4 Hz, *J* 1.3 Hz, CH_2=), 4.85 (d, 1H, $J_{1',2'}$ 1.3 Hz, H-1′), 4.83 (ddd, 1H, $J_{2',3'}$ 4.1 Hz, H-2′), 4.58, 4.52 (AB system, 2H, $J_{A,B}$ 12.5 Hz, CH_2Ph), 4.73, 4.40 (AB system, 2H, $J_{A,B}$ 11.1 Hz, CH_2Ph), 4.32 (d, 1H, $J_{1,2}$ 6.2 Hz, H-1), 4.18 (dd, 1H, $J_{2,3}$ 7.0 Hz, H-2), 4.29–4.03 (m, 3H, H-5, CH_2O), 4.02 (dd, 1H, $J_{3,4}$ 1.3 Hz, H-3), 3.95 (m, 3H, H-4, H-6a, H-6b), 3.69 (m, 2H, H-6′a, H-6′b), 3.56 (dd, 1H, $J_{3',4'}$ 9.0 Hz, H-3′), 3.48–3.28 (m, 2H, H-4′, H-5′), 3.35, 3.33 (2s, each 3H, 2 × O*Me*), 1.87 (s, 3H, *Me*CO), 1.41, 1.33, 1.32, 1.31 (4s, each 3H, 2 × C*Me*$_2$); ^{13}C NMR (50 MHz, CD_3CN): δ 170.9 (Me*C*O), 139.7, 139.4 (Ar-C), 136.4 (*C*H=), 129.2–128.4 (Ar-CH), 116.6 (*C*H_2=), 111.0, 108.7 (2 × *C*Me$_2$), 106.2 (C-1), 100.5 (C-1′), 81.3 (C-3′), 78.4, 78.8 (C-2, C-5), 76.6, 76.3, 76.2, 75.4 (C-3, C-4, C-4′, C-5′), 74.4, 74.0, 71.3, 70.5 (C-6′, 2 × *C*H_2Ph, *C*H_2O), 66.0 (C-6), 55.8, 54.4 (2 × O*Me*), 50.0 (C-2′), 27.9, 27.0, 26.8, 25.6, (2 × C*Me*$_2$), 23.3 (*Me*CO). Anal. Calcd for $C_{39}H_{55}NO_{12}$: C, 64.18; H, 7.60; N, 1.92. Found: C, 64.15; H, 7.58; N, 1.88.

3.3. 4-*O*-(2-Acetamido-4-*O*-allyl-3,6-di-*O*-benzyl-2-deoxy-β-D-talopyranosyl)-2,3:5,6-di-*O*-isopropylidene-*aldehydo*-D-glucose dimethyl acetal (4)

A soln of **2**[6b] (3.56 g, 5.16 mmol) was allylated as described above for the preparation of **3** giving, after complete disappearance of the starting material (12 h), work-up and flash chromatography (1:1 hexane–EtOAc), pure **4** (3.22 g, 96% yield) as a colourless syrup; $[\alpha]_D$ −52.5 (*c* 1.60, $CHCl_3$); R_f 0.47 (1:4 hexane–EtOAc); ^{1}H NMR (250 MHz, CD_3CN): δ 7.40–7.25 (m, 10H, Ar-H), 6.70 (d, 1H, $J_{2',NH}$ 9.6 Hz, NH), 5.93 (ddt, 1H, J_{trans} 17.3 Hz, J_{cis} 10.4 Hz, *J* 5.6 Hz, C*H*=), 5.21 (dq, 1H, J_{trans} 17.3 Hz, *J* 1.6 Hz, CH_2=), 5.13 (dq, 1H, J_{cis} 10.4 Hz, *J* 1.3 Hz, CH_2=), 4.74 (m, 1H, H-2′), 4.70 (d, 1H, $J_{1',2'}$ 1.7 Hz, H-1′), 4.65, 4.46 (AB system, 2H, $J_{A,B}$ 11.7 Hz, CH_2Ph), 4.56, 4.48 (AB system, 2H, $J_{A,B}$ 11.9 Hz, CH_2Ph), 4.37 (dd, 1H, $J_{1,2}$ 6.1 Hz, $J_{2,3}$ 6.8 Hz, H-2), 4.34 (ddt, 1H, J_{gem} 12.4 Hz, *J* 5.6 Hz, *J* 1.5 Hz, CH_2O), 4.30 (d, 1H, H-1), 4.16 (dt, 1H, $J_{4,5}$ 3.9 Hz, $J_{5,6a} = J_{5,6b}$ 6.7 Hz, H-5), 4.04 (ddt, 1H, J_{gem} 12.4 Hz, *J* 5.6 Hz, *J* 1.5 Hz, CH_2O), 3.98 (dd, 1H, $J_{3,4}$ 1.5 Hz, H-3), 3.93 (m, 2H, H-6a, H-6b), 3.89 (dd, 1H, H-4), 3.75 (m, 1H, H-4′), 3.60 (m, 2H, H-5′, H-6′b), 3.59 (dd, 1H, $J_{2',3'}$ 3.5 Hz, $J_{3',4'}$ 1.4 Hz, H-3′), 3.54 (dd, 1H, $J_{5',6'a}$ 4.3 Hz, $J_{6'a,6'b}$ 10.1 Hz, H-6′a), 3.31, 3.30 (2s, each 3H, 2 × O*Me*), 1.80 (s, 3H, *Me*CO), 1.38, 1.30, 1.29, 1.28 (4s, each 3H, 2 × C*Me*$_2$); ^{13}C NMR (62.9 MHz, CD_3CN): δ 170.2 (Me*C*O), 139.4, 139.3 (2 × Ar-C), 136.3 (*C*H=), 129.3–128.4 (Ar-CH), 117.1 (*C*H_2=), 110.9, 108.7 (2 × *C*Me$_2$), 106.1 (C-1), 101.6 (C-1′), 78.8 (C-3), 78.5 (C-5), 76.9 (C-3′), 76.5, 76.4 (C-2, C-4), 75.7 (C-5′), 75.3 (C-4′), 74.4, 73.9 (2 × *C*H_2Ph), 70.7 (*C*H_2O), 69.2 (C-6′), 66.1 (C-6), 55.9, 54.1 (2 × O*Me*), 50.0 (C-2′), 27.7, 27.0, 26.7, 25.8 (2 × C*Me*$_2$), 23.8 (*Me*CO). Anal. Calcd for $C_{39}H_{55}NO_{12}$: C, 64.18; H, 7.60; N, 1.92. Found: C, 64.08; H, 7.55; N, 1.89.

3.4. 4-*O*-(2-Acetamido-4-*O*-allyl-3,6-di-*O*-benzyl-2-deoxy-β-D-mannopyranosyl)-1,2,3,6-tetra-*O*-acetyl-α,β-D-glucopyranose (5)

A soln of **3** (3.00 g, 4.11 mmol) in 80% aq AcOH (80 mL) was heated to 80 °C until the TLC analysis (9:1 $CHCl_3$–MeOH) revealed the disappearance of the starting material (3 h, R_f 0.66) and the formation of a slower-moving product (R_f 0.18). The soln was then cooled to room temp, concentrated and co-evaporated with toluene (5 × 40 mL) under diminished pressure to give a white solid (2.60 g) constituted exclusively (NMR) of the 4-*O*-(2-acetamido-4-*O*-allyl-3,6-di-*O*-benzyl-2-deoxy-β-D-mannopyranosyl)-D-glucopyranose (**31**, not shown) as a mixture of α and β anomers in 2:3 ratio calculated on the basis of the relative intensities of C-1 signals (δ 92.8 and 97.1, respectively); R_f 0.18 (9:1 $CHCl_3$–MeOH); $[\alpha]_D$ −4.8 (*c* 1.0, H_2O); selected ^{13}C NMR (50 MHz, CD_3CN-D_2O) signals of **α-anomer**: δ 100.5 (C-1′), 92.8 (C-1), 80.9 (C-4), 80.7 (C-3′), 70.5 (C-5), 69.3 (C-6′), 61.4 (C-6), 50.3 (C-2′), **β-anomer**: δ 100.5 (C-1′), 97.1 (C-1), 80.9 (C-4), 80.3 (C-3′), 69.3 (C-6′), 61.4 (C-6), 50.3 (C-2′); cluster of signals for both anomers: δ 173.5 (Me*C*O), 139.1–138.4 (Ar-C); 135.9 (CH=), 129.4–128.6 (Ar-CH), 117.3 (CH_2=), 75.5, 75.2, 75.1, 74.6 (C-4′, C-5′), 74.5, 73.8, 71.7 (*C*H_2Ph, *C*H_2O), 22.9 (*Me*CO).

Crude tetraol **31** (2.60 g) was added to a soln obtained by refluxing AcONa·3H_2O (1.30 g, 9.46 mmol) in Ac_2O (21 mL). The resulting mixture was heated to 110 °C for 2 h when the TLC analysis (1:4 hexane–EtOAc) revealed the complete disappearance of tetraol **31**. The soln was co-evaporated with toluene (5 × 40 mL), and the residue was taken up in CH_2Cl_2 (100 mL) and washed with water (50 mL). The aq phase was extracted with CH_2Cl_2 (3 × 40 mL), and the combined organic layers were dried, filtered and concentrated under diminished pressure. The residue (2.80 g) was purified by flash chromatography (3:7 hexane–EtOAc) and gave **5** (2.60 g, 82% yield calculated from **3**) as a mixture of α and β anomers in 1:4 ratio calculated on the basis of the relative intensities of H-1 signals (δ 6.27 and 5.66, respectively). Selected ^{1}H NMR (200 MHz, $CDCl_3$) data of **α-5**: δ 6.27 (d, 1H, $J_{1,2}$ 3.8 Hz, H-1), 2.15, 2.08, 2.05, 2.03, 1.99, (5s, each 3H, *Me*CO); **β-5**: δ 5.66 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 2.34, 2.07, 2.06, 2.02, 2.01 (5s, each 3H, *Me*CO); ^{13}C NMR data (50 MHz, $CDCl_3$): **α-5**: δ 171.4, 170.4, 170.2, 169.5, 168.7 (Me*C*O), 137.2 (2 × Ar-C), 98.8 (C-1′), 88.6 (C-1), 80.7 (C-3′), 74.0, 73.0, 71.0 (2 × *C*H_2Ph, *C*H_2O), 72.5, 72.4, 72.3, 70.4, 70.3, 68.8 (C-2, C-3, C-4, C-5, C-4′, C-5′), 68.2 (C-6′), 61.6 (C-6), 49.5 (C-2′), 23.0 (*Me*-CONH), 20.3 (3 × *Me*CO), 21.1 (*Me*CO); **β-5**: δ 171.2, 170.2, 170.1, 169.1, 168.6 (Me*C*O), 137.5 (2 × Ar-C), 98.6 (C-1′), 91.4 (C-1), 80.1 (C-3′), 74.9, 74.4, 73.7, 73.3, 73.2, 73.0 (C-2, C-3, C-4, C-5, C-4′, C-5′), 73.7, 73.0, 70.9 (2 × *C*H_2Ph, *C*H_2O), 68.2 (C-6′), 61.6 (C-6), 49.3 (C-2′), 23.1 (*Me*CONH), 21.8, 21.7, 20.5, 20.4 (4 × *C*H_3CO); cluster of signals for both anomers: δ 134.5 (*C*H=), 128.7–125.0 (Ar-CH), 116.4 (*C*H_2=). Anal. Calcd for $C_{39}H_{49}NO_{15}$: C, 60.69; H, 6.40; N, 1.81. Found: C, 60.65; H, 6.35; N, 1.78.

3.5. 4-*O*-(2-Acetamido-4-*O*-allyl-3,6-di-*O*-benzyl-2-deoxy-β-D-talopyranosyl)-1,2,3,6-tetra-*O*-acetyl-α,β-D-glucopyranose (6)

A soln of **4** (3.05 g, 4.18 mmol) in 80% aq AcOH was hydrolyzed as reported above for the preparation of **5** giving, after complete disappearance of the starting material (3 h) and elimination of solvents, a white solid (2.45 g) constituted exclusively (NMR) of a 1:1 α/β anomeric mixture of 4-*O*-(2-acetamido-4-*O*-allyl-3,6-di-*O*-

benzyl-2-deoxy-β-D-talopyranosyl)-D-glucopyranose (**32**, not shown) having R_f 0.15 (9:1 $CHCl_3$–MeOH); selected ^{13}C NMR (50 MHz, $CDCl_3$) signals of **α-anomer**: δ 171.1 (Me*C*O), 100.8 (C-1′), 92.0 (C-1), 81.3 (C-4), 72.2, 71.9 (C-2, C-3), 69.6 (C-5), 68.0 (C-6′), 61.1 (C-6), 49.0 (C-2′), **β-anomer**: δ 171.3 (Me*C*O), 100.8 (C-1′), 96.5 (C-1), 80.5 (C-4), 77.2 (C-3, C-5), 68.1 (C-6′), 60.7 (C-6), 48.9 (C-2′); cluster of signals for both anomers: δ 137.8–137.4 (Ar-C); 134.5 (CH=), 128.3–127.3 (Ar-CH), 117.2 (CH_2=), 75.2, 74.3, 74.1 (C-3′, C-4′, C-5′), 73.8–73.4 (*C*H_2Ph), 69.8 *C*H_2O), 23.4 (*Me*CO).

The crude tetraol **32** was acetylated as reported above for the preparation of **5** giving, after completion of the reaction (2 h), work-up and flash chromatography (1:1 hexane–EtOAc), **6** (3.21 g, 90% yield calculated from **4**) as a mixture of α and β anomers in 1:4 ratio measured on the basis of the relative intensities of H-1 signals (δ 6.22 and 5.66, respectively); white solid foam; R_f 0.43 (1:4 hexane–EtOAc); Selected ^1H NMR (200 MHz, $CDCl_3$) data of **α-6**: δ 6.67 (d, 1H, $J_{2',NH}$ 9.8 Hz, NH), 6.22 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1), 5.42 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 9.2 Hz, H-3), 4.99 (dd, 1H, H-2), 2.15, 2.04, 2.03, 2.00, 1.98 (5s, each 3H, *Me*CO); **β-6**: δ 6.65 (d, 1H, $J_{2',NH}$ 9.8 Hz, NH), 5.66 (d, 1H, $J_{1,2}$ 8.2 Hz, H-1), 5.04 (dd, 1H, $J_{2,3}$ 9.7 Hz, H-2), 2.08, 2.05, 2.02, 2.01, 1.97 (5s, each 3H, *Me*CO); ^{13}C NMR data (50 MHz, $CDCl_3$): **α-6**: δ 99.5 (C-1′), 88.8 (C-1), 77.6 (C-3′), 76.4 (C-4), 74.6 (C-4′), 73.9 (C-5′), 70.5 (C-5), 69.3, 69.1 (C-2, C-3), 67.8 (C-6′), 61.9 (C-6), 48.3 (C-2′); **β-6**: 99.3 (C-1′), 91.4 (C-1), 77.6 (C-3′), 77.0 (C-4′), 75.0 (C-3), 73.9 (C-5, C-5′), 72.3 (C-4), 70.1 (C-2), 67.7 (C-6′), 61.8 (C-6), 48.3 (C-2′); cluster of signals for both anomers: δ 170.8–168.6 (Me*C*O), 137.4 (Ar-C), 134.5 (*C*H=), 128.3–127.3 (Ar-CH), 116.5 (CH_2=), 73.5–73.3 (*C*H_2Ph), 69.5 (*C*H_2O), 23.2 (*Me*CONH), 21.9–20.4 (*Me*CO). Anal. Calcd for $C_{39}H_{49}NO_{15}$: C, 60.69; H, 6.40; N, 1.81. Found: C, 60.61; H, 6.34; N, 1.79.

3.6. Phenyl 4-*O*-(2-acetamido-4-*O*-allyl-3,6-di-*O*-benzyl-2-deoxy-β-D-mannopyranosyl)-2,3,6-tri-*O*-acetyl-1-thio-β-D-glucopyranoside (7)

To a soln of **5** (1.23 g, 1.59 mmol) in dry $(CH_2)_2Cl_2$ (20 mL), anhyd ZnI_2 (862 mg, 2.70 mmol) and powdered 4 Å MS AW 300 (4.20 g) were added under argon atmosphere. The resulting mixture was stirred for 30 min in the dark and TMSSPh (1.2 mL, 1.16 g, 6.36 mmol) was added. The suspension was stirred until the TLC analysis (3:7 hexane–EtOAc) showed the disappearance of the starting material (24 h, R_f 0.33) and the formation of a major faster-moving product (R_f 0.41). The reaction mixture was filtered through a Celite pad, and the filter was washed with CH_2Cl_2 (60 mL). Satd aq $NaHCO_3$ (40 mL) was added, the aq phase was extracted with CH_2Cl_2 (4 × 20 mL), and the combined organic layers were dried, filtered and concentrated under diminished pressure. The crude residue (3.50 g) was purified by flash chromatography (1:1 hexane–EtOAc then 45:55 hexane–EtOAc) to give pure **7** (1.07 g, 82% yield) as a white solid; mp 195–200 °C (dec.); $[\alpha]_D$ −22.4 (*c* 0.92, EtOAc); R_f 0.41 (3:7 hexane–EtOAc); ^1H NMR (600 MHz, $CDCl_3$): δ 7.46 (m, 2H, ArS-H), 7.36–7.24 (m, 13H, Ar-H, ArS-H), 5.79 (ddt, 1H, J_{trans} 17.1 Hz, J_{cis} 10.2 Hz, C*H*=), 5.61 (d, 1H, $J_{2',NH}$ 9.5 Hz, NH), 5.14 (dd, 1H, $J_{2,3}$ 9.3 Hz, $J_{3,4}$ 8.9 Hz, H-3), 5.15 (dq, 1H, J_{trans} 17.1 Hz, *J* 1.7 Hz, C*H*$_2$=), 5.13 (dq, 1H, J_{cis} 10.2 Hz, *J* 1.4 Hz, C*H*$_2$=), 4.92 (dd, 1H, $J_{1,2}$ 9.9 Hz, H-2), 4.83, 4.44 (AB system, 2H, $J_{A,B}$ 10.9 Hz, C*H*$_2$Ph), 4.68 (ddd, 1H, $J_{1',2'}$ 1.4 Hz, $J_{2',3'}$ 4.1 Hz, H-2′), 4.63 (d, 1H, H-1), 4.50, 4.43 (AB system, 2H, $J_{A,B}$ 11.7 Hz, C*H*$_2$Ph), 4.39 (dd, 1H, $J_{6a,6b}$ 12.3 Hz, $J_{5,6b}$ 2.1 Hz, H-6b), 4.38 (d, 1H, H-1′), 4.32 (ddt, 1H, J_{gem} 12.3 Hz, *J* 5.8 Hz, *J* 1.4 Hz, C*H*$_2$O), 4.21 (dd, 1H, $J_{5,6a}$ 4.8 Hz, H-6a), 3.94 (ddt, 1H, J_{gem} 12.3 Hz, *J* 5.8 Hz, *J* 1.4 Hz, C*H*$_2$O), 3.70 (m, 3H, H-6′a, H-6′b, H-4), 3.66 (ddd, 1H, $J_{4,5}$ 9.9 Hz, H-5), 3.53 (dd, 1H, $J_{3',4'}$ 9.2 Hz, H-3′), 3.48 (t, 1H, $J_{4',5'}$ 9.2 Hz, H-4′), 3.27 (dt, 1H, $J_{5',6'a} = J_{5',6'b}$ 2.7 Hz, H-5′), 2.08, 2.07, 2.02, 1.97 (4s, each 3H, *Me*CO); ^{13}C NMR (50 MHz, $CDCl_3$): see Table 2 and δ 173.1, 172.4, 172.0, 170.4 (Me*C*O); 137.3, 136.9 (Ar-C), 134.2 (*C*H=), 132.2–126.1 (Ar-CH, ArS-CH), 131.6 (ArS-C), 117.1 (CH_2=), 73.9, 73.3 (2 × *C*H_2Ph), 73.3 (C-4′, C-3), 71.7 (*C*H_2O), 69.6 (C-2), 68.1 (C-6′), 60.9 (C-6), 51.3 (C-2′), 24.1 (*Me*CONH), 21.6, 21.2, 20.8 (3 × *Me*CO). Anal. Calcd for $C_{43}H_{51}NO_{13}S$: C, 62.84; H, 6.25; N, 1.70; S, 3.90. Found: C, 62.86; H, 6.24; N, 1.64; S, 3.75.

3.7. Phenyl 4-*O*-(2-acetamido-4-*O*-allyl-3,6-di-*O*-benzyl-2-deoxy-β-D-talopyranosyl)-2,3,6-tri-*O*-acetyl-1-thio-β-D-glucopyranoside (8)

A soln of **6** (3.4 g, 4.40 mmol) in dry $(CH_2)_2Cl_2$ was thioglycosylated as reported above for the preparation of **7** giving, after completion of the reaction (24 h), work-up and flash chromatography (7:3 hexane–EtOAc then 2:3 hexane–EtOAc), pure **8** (2.75 g, 76% yield) as a white foam; $[\alpha]_D$ −59.5 (*c* 1.02, $CHCl_3$); R_f 0.38 (7:3

Table 2
Selected ^{13}C NMR signals (δ, ppm) of disaccharide derivatives **7–12, 14–17, α,β-20, α,β-20–21** and **25–28**

Compound	Solvent	C-1	C-2	C-3	C-4	C-5	C-6	C-1′	C-2′	C-3′	C-4′	C-5′	C-6′
7	$CDCl_3$	84.8	69.6	73.3	74.4	75.6	60.9	98.6	51.3	79.0	73.3	74.8	68.1
9	CD_3CN–D_2O	88.0	72.9	79.6[a]	79.7[a]	77.0[a]	61.5	100.4	50.2	80.9	74.8[a]	75.3[a]	69.5
11	$CDCl_3$	86.7	79.7	84.6	77.8	75.7[a]	67.7[a]	99.3	48.9	79.9	72.8	75.6[a]	68.0[a]
24	CD_3CN	95.5	81.1[a]	81.0[a]	77.4[a]	77.2[a]	70.8[a]	99.9	49.7	80.4[a]	67.9	75.4	69.8[a]
8	$CDCl_3$	85.7	70.8	74.1	75.2	75.3	63.4	100.3	49.8	77.4	76.8	74.2	69.4
10	CD_3CN	87.9	72.9	76.4	79.6	77.2	61.7	101.3	50.4	81.0	75.0[a]	75.1[a]	69.7
12	CD_3CN	87.6	81.4	85.4	76.1	79.5	69.2	100.2	50.1	75.2	75.4	77.1	70.2
α-20	CD_3CN	95.7	80.4	80.8	76.7	76.5	69.8	100.2	50.1	75.1	75.4	77.1	69.1
β-20	CD_3CN	102.5	82.7	83.6	76.4	75.0	69.7	100.1	50.0	74.9	72.5	77.0	69.0
22	CD_3CN	94.1	79.5	80.5	76.6[a]	74.0	69.7[a]	100.5	48.4	76.5[a]	67.5	69.3	68.5[a]
30	CD_3CN	95.8	80.5	81.0	76.1[a]	72.2	69.2	100.1	50.0	77.2	75.9[a]	70.5	69.9
14	$CDCl_3$	85.2	73.5	72.2	75.8[a]	75.7[a]	60.8	102.9	76.9	70.3	66.9	69.8	61.8
15	CD_3CN–D_2O	88.1	72.7	76.2	79.8[a]	79.7[a]	60.9	103.7	79.0[a]	73.5	69.7	76.2	61.9
16	CD_3CN–D_2O	87.9	72.4	76.7	79.7[a]	79.3[a]	60.9	103.8	80.0[a]	76.7	73.9	67.5	69.6
17	CD_3CN	87.5	81.2	85.5	77.8	79.6	69.3	103.7	80.2	79.1	73.9	67.3	69.7
α-21	CD_3CN	95.4	79.1	80.8	78.5	74.0	69.2	103.7	80.2	80.1	71.2	67.2	69.8
β-21	CD_3CN	103.6	82.5	83.8	78.2	75.3	69.2	102.5	80.2	79.1	73.9	67.3	69.7
25	CD_3CN–D_2O	95.4	80.5[a]	81.9	77.7	75.5	69.2	103.5	79.6[a]	80.3[a]	66.4	71.2	61.9
26	CD_3CN	95.6	80.6[a]	81.9	77.6	74.3	69.2[a]	103.6	79.7	80.2[a]	66.8	71.3	69.9[a]
27	CD_3CN	95.6	80.6[a]	82.9	77.5	74.2	69.3[a]	103.6	80.3[a]	80.4[a]	75.1	71.3	70.1[a]
28	CD_3CN	95.5	80.5[a]	83.1	77.5	74.3	69.4	103.9	72.6	80.8[a]	74.7	71.5	69.6

[a] Assignments may have to be interchanged.

hexane–EtOAc); ^{1}H NMR (250 MHz, CD_3CN): δ 7.45 (m, 2H, ArS-H), 7.38–7.28 (m, 13H, Ar-H, ArS-H), 6.56 (d, 1H, $J_{2',NH}$ 9.9 Hz, NH), 5.90 (ddt, 1H, J_{trans} 17.3 Hz, J_{cis} 10.4 Hz, J 5.4 Hz, C*H*=), 5.19 (dd, 1H, $J_{2,3}$ 8.9 Hz, $J_{3,4}$ 9.10 Hz, H-3), 5.20 (dq, 1H, J_{trans} 17.3 Hz, J 1.7 Hz, CH_2=), 5.13 (dq, 1H, J_{cis} 10.4 Hz, J 1.3 Hz, CH_2=), 4.90 (d, 1H, $J_{1,2}$ 9.9 Hz, H-1), 4.81 (dd, 1H, H-2), 4.63, 4.43 (AB system, 2H, $J_{A,B}$ 11.6 Hz, CH_2Ph), 4.60 (m, 1H, H-2′), 4.57, 4.53 (AB system, 2H, $J_{A,B}$ 12.0 Hz, CH_2Ph), 4.45 (d, 1H, $J_{1',2'}$ 1.7 Hz, H-1′), 4.39 (dd, 1H, $J_{6a,6b}$ 12.1 Hz, $J_{5,6b}$ 2.3 Hz, H-6b), 4.34 (ddt, 1H, J_{gem} 12.7 Hz, J 5.4 Hz, J 1.5 Hz, CH_2O), 4.26 (dd, 1H, $J_{5,6a}$ 5.2 Hz, H-6a), 4.01 (ddt, 1H, J_{gem} 12.7 Hz, J 5.4 Hz, J 1.5 Hz, CH_2O), 3.88 (dd, 1H, $J_{4,5}$ 10.1 Hz, H-4), 3.73 (dd, 1H, $J_{3',4'}$ 2.8 Hz, $J_{4',5'}$ 3.9 Hz, H-4′), 3.70 (m, 1H, H-5), 3.62 (m, 3H, H-5′, H-6′a, H-6′b), 3.60 (dd, 1H, $J_{2',3'}$ 4.2 Hz, H-3′), 2.02, 2.01, 1.97 (3s, each 3H, *Me*CO); 1.84 (s, 3H, *Me*CONH). ^{13}C NMR (62.9 MHz, $CDCl_3$): see Table 2 and δ 171.2, 170.7, 170.5, 170.4 (Me*C*O); 139.4, 139.3 (Ar-C), 136.2 (*C*H=), 133.6 (ArS-C), 132.4–128.4 (Ar-CH, ArS-CH), 116.7 (*C*H_2=), 73.8 (*C*H_2O), 70.8, 70.7 (2 × *C*H_2Ph), 23.6 (*Me*CONH), 21.3, 21.0, 20.9 (3 × *Me*CO). Anal. Calcd for $C_{43}H_{51}NO_{13}S$: C, 62.84; H, 6.25; N, 1.70; S, 3.90. Found: C, 62.79; H, 6.21; N, 1.65; S, 3.85.

3.8. Phenyl 4-*O*-(2-acetamido-4-*O*-allyl-3,6-di-*O*-benzyl-2-deoxy-β-D-mannopyranosyl)-1-thio-β-D-glucopyranoside (9)

To a soln of **7** (876 mg, 1.07 mmol) in EtOH (5 mL) was slowly added a soln of KOH in EtOH (1 M, 10 mL), and the mixture was stirred at room temp until the TLC analysis (EtOAc) showed the complete disappearance of the starting material (1 h, R_f 0.53) and the formation of a spot at R_f 0.25. The soln was treated with an excess of Et_3N·HCl and stirred at room temp for 1 h, then the solvents were removed under diminished pressure, and the residue was dissolved in EtOAc (50 mL) and washed with water (30 ml). The aq phase was extracted with EtOAc (3 × 20 mL), and the combined organic layers were dried, filtered and evaporated under diminished pressure. Flash chromatography purification (EtOAc + 0.1% *i-PrOH)* of the residue (903 mg) afforded pure **9** (715 mg, 96% yield) as a white solid; mp 77–80 °C (chrom); $[\alpha]_D$ −59.4 (*c* 1.0, MeOH); R_f 0.25 (EtOAc); ^{1}H NMR (250 MHz, CD_3CN-D_2O): δ 7.56 (m, 2H, ArS-H), 7.48–7.20 (m, 13H, Ar-H, ArS-H), 5.76 (ddt, 1H, J_{trans} 17.3 Hz, J_{cis} 10.6 Hz, C*H*=), 5.08 (m, 2H, CH_2=), 4.75 (dd, 1H, $J_{1',2'}$ 1.6 Hz, $J_{2',3'}$ 4.2 Hz, H-2′), 4.69 (d, 1H, H-1′), 4.65, 4.39 (AB system, 2H, $J_{A,B}$ 11.1 Hz, CH_2Ph), 4.63 (d, 1H, $J_{1,2}$ 9.8 Hz, H-1), 4.56, 4.48 (AB system, 2H, $J_{A,B}$ 12.1 Hz, CH_2Ph), 4.18 (ddt, 1H, J_{gem} 12.4 Hz, J 6.1 Hz, J 1.3 Hz, CH_2O), 3.88 (ddt, 1H, J_{gem} 12.4 Hz, J 1.3 Hz, J 5.8 Hz, CH_2O), 3.72 (dd, 1H, $J_{6'a,6'b}$ 12.2 Hz, $J_{5',6b'}$ 2.3 Hz, H-6′b), 370–3.53 (m, 4H, H-3′, H-6′a, H-4, H-5), 3.50–3.32 (m, 5H, H-4′, H-5′, H-3, H-6a, H-6b), 3.35 (m, 1H, H-2), 1.88 (s, 3H, *Me*CO); ^{13}C NMR (62.9 MHz, CD_3CN-D_2O): see Table 2 and δ 173.5 (Me*C*O); 139.2, 138.5 (Ar-C), 135.9 (*C*H=), 134.2 (ArS-C), 130.0–128.4 (Ar-CH, ArS-CH), 117.3 (*C*H_2=), 74.5 (*C*H_2O), 73.9, 71.8 (2 × *C*H_2Ph), 22.9 (*Me*CO). Anal. Calcd for $C_{37}H_{45}NO_{10}S$: C, 63.87; H, 6.52; N, 2.01; S, 4.61. Found: C, 63.84; H, 6.49; N, 1.99.; S, 4.58.

3.9. Phenyl 4-*O*-(2-acetamido-4-*O*-allyl-3,6-di-*O*-benzyl-2-deoxy-β-D-talopyranosyl)-1-thio-β-D-glucopyranoside (10)

A soln of **8** (871 mg, 1.06 mmol) in absolute EtOH (5.0 mL) was O-deacetylated as described above for the preparation of **9** giving, after flash chromatographic purification (3:7 hexane–EtOAc + 0.1% *i-PrOH),* pure **10** (640 mg, 87% yield) as a colourless syrup; $[\alpha]_D$ −61.1 (*c* 1.0, $CHCl_3$); R_f 0.30 (EtOAc); ^{1}H NMR (250 MHz, CD_3CN): δ 7.48 (m, 2H, ArS-H), 7.38–7.23 (m, 13H, Ar-H, ArS-H), 6.99 (d, 1H, $J_{2',NH}$ 9.8 Hz, NH), 5.86 (ddt, 1H, J_{trans} 17.2 Hz, J_{cis} 10.6 Hz, J 5.6 Hz, C*H*=), 5.19 (dq, 1H, J_{trans} 17.2 Hz, J 1.6 Hz, CH_2=), 5.11 (dq, 1H, J_{cis} 10.6 Hz, J 1.3 Hz, CH_2=), 4.66 (m, 1H, H-2′), 4.64 (d, 1H, $J_{1,2}$ 9.9 Hz, H-1), 4.61 (d, 1H, $J_{1',2'}$ 1.8 Hz, H-1′), 4.60, 4.47 (AB system, 2H, $J_{A,B}$ 11.6 Hz, CH_2Ph), 4.54, 4.49 (AB system, 2H, $J_{A,B}$ 12.1 Hz, CH_2Ph), 4.27 (ddt, 1H, J_{gem} 12.5 Hz, J 5.6 Hz, J 1.5 Hz, CH_2O), 3.99 (ddt, 1H, J_{gem} 12.5 Hz, J 1.5 Hz, J 5.6 Hz, CH_2O), 3.80–3.58 (m, 5H, H-3′, H-4′, H-5′, H-6′a, H-6′b), 3.50 (m, 2H, H-3, H-4), 3.38 (m, 1H, H-5), 3.25 (m, 3H, H-2, H-6a, H-6b), 1.88 (s, 3H, *Me*CO); ^{13}C NMR (62.9 MHz, CD_3CN): see Table 2 and δ 172.6 (Me*C*O); 139.2, 138.9 (Ar-C), 135.9 (*C*H=), 134.4 (ArS-C), 132.1–128.3 (Ar-CH, ArS-CH), 117.6 (*C*H_2=), 74.4 (*C*H_2O), 73.8, 71.0 (2 × *C*H_2Ph), 23.6 (*Me*CO). Anal. Calcd for $C_{37}H_{45}NO_{10}S$: C, 63.87; H, 6.52; N, 2.01; S, 4.61. Found: C, 63.80; H, 6.49; N, 1.99; S, 4.57.

3.10. Phenyl 4-*O*-(2-acetamido-4-*O*-allyl-3,6-di-*O*-benzyl-2-deoxy-β-D-mannopyranosyl)-2,3,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (11)

To a soln of triol **9** (494 mg, 0.71 mmol) in THF containing 0.5% of water (7 mL) cooled to 0 °C, 18-crown-6 (10 mg, 0.036 mmol) followed by powdered KOH (476 mg, 8.51 mmol) was added and the mixture was stirred for 30 min. Benzyl bromide (505 μL, 4.26 mmol) was added and the soln was stirred at 0 °C until the TLC analysis (1:4 hexane–EtOAc) revealed the disappearance of the starting material (1 h, R_f 0.12) and the formation of a major faster-moving product (R_f 0.61). MeOH (5 mL) was added and the reaction mixture was further stirred at room temp for 30 min. Solvents were removed under diminished pressure, and the residue was taken up in CH_2Cl_2 (30 mL) and washed with water (10 mL). The aq phase was extracted with CH_2Cl_2 (3 × 10 mL), and the combined organic phases were dried, filtered and evaporated under diminished pressure. The crude residue (943 mg) was subjected to flash chromatography (1:1 hexane–EtOAc) to give pure **11** (650 mg, 95% yield) as a colourless syrup; $[\alpha]_D$ −30.3 (*c* 1.3, $CHCl_3$); R_f 0.18 (1:1 hexane–EtOAc); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.55 (m, 2H, ArS-H), 7.35–7.18 (m, 28H, Ar-H, ArS-H), 5.79 (ddt, 1H, J_{trans} 17.1 Hz, J_{cis} 10.3 Hz, C*H*=), 5.74 (d, 1H, $J_{2',NH}$ 9.9 Hz, NH), 5.15 (dq, 1H, J_{trans} 17.1 Hz, J 1.7 Hz, CH_2=), 5.10 (dq, 1H, J_{cis} 10.3 Hz, J 1.4 Hz, CH_2=), 4.98, 4.81 (AB system, 2H, $J_{A,B}$ 11.6 Hz, CH_2Ph), 4.80, 4.63 (AB system, 2H, $J_{A,B}$ 10.4 Hz, CH_2Ph), 4.71, 4.31 (AB system, 2H, $J_{A,B}$ 11.3 Hz, CH_2Ph), 4.66, 4.58 (AB system, 2H, $J_{A,B}$ 11.9 Hz, CH_2Ph), 4.48, 4.38 (AB system, 2H, $J_{A,B}$ 12.0 Hz, CH_2Ph), 4.38 (br s, 1H, H-1′), 4.63 (d, 1H, $J_{1,2}$ 9.9 Hz, H-1), 4.62 (m, 1H, H-2′), 4.28 (ddt, 1H, J_{gem} 12.3 Hz, J 5.8 Hz, J 1.3 Hz, CH_2O), 4.02 (dd, 1H, $J_{3,4}$ 9.3 Hz, $J_{4,5}$ 9.5 Hz, H-4), 3.92 (ddt, 1H, J_{gem} 12.3 Hz, J 5.5 Hz, J 1.3 Hz, CH_2O), 3.76 (m, 2H, H-6a, H-6b), 3.63 (dd, 1H, $J_{2,3}$ 9.0 Hz, H-3), 3.54 (dd, 1H, $J_{6'a,6'b}$ 10.6 Hz, $J_{5',6'b}$ 3.1 Hz, H-6′b), 3.48 (m, 2H, H-2, H-6′a), 3.45 (dd, 1H, $J_{3',4'}$ 9.2 Hz, $J_{4',5'}$ 9.9 Hz, H-4′), 3.43 (dt, 1H, $J_{5,6a} = J_{5,6b}$ 2.7 Hz, H-5), 3.36 (dd, 1H, H-3′), 3.12 (ddd, 1H, $J_{5',6'a}$ 2.0 Hz, H-5′); 1.77 (s, 3H, *Me*CO); ^{13}C NMR (50 MHz, $CDCl_3$): see Table 2 and δ 169.9 (Me*C*O); 138.4, 137.4, 137.2, 137.1, 137.0 (5 × Ar-C), 134.1 (CH=), 132.8 (ArS-C), 131.4–125.9 (Ar-CH, ArS-CH), 115.8 (*C*H_2=), 74.6, 74.4, 73.2, 72.6, 72.5, 70.3 (5 × *C*H_2Ph, *C*H_2O), 22.5 (*Me*CONH). Anal. Calcd for $C_{58}H_{63}NO_{10}S$: C, 72.10; H, 6.57; N, 1.45; S, 3.32. Found: C, 72.05; H, 6.56; N, 1.40; S, 3.25.

3.11. Phenyl 4-*O*-(2-acetamido-4-*O*-allyl-3,6-di-*O*-benzyl-2-deoxy-β-D-talopyranosyl)-2,3,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (12)

A soln of triol **10** (438 mg, 0.63 mmol) in THF containing 0.5% of water was benzylated in the same conditions used for the preparation of **11**. After completion of the reaction (7 h), work-up and flash chromatography (55:45 hexane–EtOAc), pure **12** (578 mg, 95% yield) was obtained as a colourless syrup; $[\alpha]_D$ −46.2 (*c* 1.1, $CHCl_3$); R_f 0.60 (3:7 hexane–EtOAc); ^{1}H NMR (250 MHz, CD_3CN): δ 7.47 (m, 2H, ArS-H), 7.38–7.12 (m, 28H, Ar-H, ArS-H), 6.80 (d, 1H, $J_{2',NH}$ 9.7 Hz, NH), 5.89 (ddt, 1H, J_{trans} 17.2 Hz, J_{cis} 10.6 Hz, J 5.5 Hz,

CH=), 5.17 (dq, 1H, J_{trans} 17.2 Hz, J 1.6 Hz, CH_2=), 5.07 (dq, 1H, J_{cis} 10.6 Hz, J 1.3 Hz, CH_2=), 5.08, 4.66 (AB system, 2H, $J_{A,B}$ 10.5 Hz, CH_2Ph), 4.77 (d, 1H, $J_{1,2}$ 9.8 Hz, H-1), 4.73, 4.69 (AB system, 2H, $J_{A,B}$ 10.7 Hz, CH_2Ph), 4.65 (m, 1H, H-2′), 4.63, 4.42 (AB system, 2H, $J_{A,B}$ 11.6 Hz, CH_2Ph), 4.62, 4.53 (AB system, 2H, $J_{A,B}$ 11.8 Hz, CH_2Ph), 4.58 (d, 1H, $J_{1',2'}$ 1.6 Hz, H-1′), 4.51, 4.36 (AB system, 2H, $J_{A,B}$ 11.9 Hz, CH_2Ph), 4.33 (ddt, 1H, J_{gem} 12.5 Hz, J 5.5 Hz, J 1.6 Hz, CH_2O), 4.03 (dd, 1H, $J_{3,4}$ 8.9 Hz, $J_{4,5}$ 9.5 Hz, H-4), 4.02 (ddt, 1H, J_{gem} 12.5 Hz, J 5.5 Hz, J 1.6 Hz, CH_2O), 3.78 (m, 2H, H-6a, H-6b), 3.73 (m, 1H, H-4′), 3.64 (dd, 1H, $J_{6'a,6'b}$ 9.2 Hz, $J_{5',6'b}$ 2.6 Hz, H-6′b), 3.59 (dd, 1H, $J_{2,3}$ 8.7 Hz, H-3), 3.50 (m, 4H, H-3′, H-5′, H-6′a, H-5), 3.30 (dd, 1H, H-2), 1.70 (s, 3H, *Me*CO); ^{13}C NMR (62.9 MHz, CD_3CN): δ 170.4 (Me*C*O); 140.1–139.5 (5 × Ar-C), 136.2 (*C*H=), 135.2 (ArS-C), 131.7–128.1 (Ar-CH, ArS-CH), 116.9 (CH_2=), 76.0, 75.9, 74.5, 73.9, 68.8 (5 × CH_2Ph), 73.9 (CH_2O), 23.6 (*Me*CO). Anal. Calcd for $C_{58}H_{63}NO_{10}S$: C, 72.10; H, 6.57; N, 1.45; S, 3.32. Found: C, 72.07; H, 6.54; N, 1.41; S, 3.28.

When a crude sample of **10** obtained from **8** (2.57 g, 3.35 mmol) was directly benzylated, pure **12** (2.78 g, 2.88 mmol) was obtained, after flash chromatography in 86% yield over two steps.

3.12. Phenyl 4-*O*-(2-*O*-allyl-3,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-2,3,6-tri-*O*-acetyl-1-thio-β-D-glucopyranoside (14)

A soln of **13**[9] (6.74 g, 9.96 mmol) in dry $(CH_2)_2Cl_2$ was thiophenyl glycosidated as described above for the preparation of **7**. After completion of the reaction (24 h), work-up and flash chromatography (7:3 hexane–EtOAc then 3:2 hexane–EtOAc), pure **14** (6.48 g, 90% yield) was obtained as a white solid foam; mp 62–65 °C (chrom); $[\alpha]_D$ −5.8 (*c* 0.95, $CHCl_3$); R_f 0.43 (2:3 hexane–EtOAc); ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.48, (m, 2H, ArS-H), 7.30 (m, 3H, ArS-H), 5.79 (ddt, 1H, J_{trans} 17.4 Hz, J_{cis} 10.3 Hz, J 5.5 Hz, CH=), 5.25, 5.15 (2 m, each 1H, CH_2=), 5.20 (m, 2H, H-4′, H-3); 4.92 (dd, 1H, $J_{1,2}$ 10.0 Hz, $J_{2,3}$ 9.5 Hz, H-2), 4.86 (dd, 1H, $J_{2',3'}$ 10.2 Hz, $J_{3',4'}$ 3.4 Hz, H-3′), 4.67 (d, 1H, H-1), 4.65 (dd, 1H, $J_{6a,6b}$ 12.3 Hz, $J_{5,6b}$ 1.7 Hz, H-6b), 4.32 (d, 1H, $J_{1',2'}$ 7.7 Hz, H-1′), 4.22 (dd, 1H, $J_{5,6a}$ 5.2 Hz, H-6a), 4.15 (m, 2H, CH_2O), 4.10 (m, 3H, H-4, H-6′a, H-6′b), 3.85 (m, 2H, H-5, H-5′), 3.40 (dd, 1H, H-2′), 2.12, 2.10, 2.09, 2.03, 2.02, 2.00 (6s, each 3H, *Me*CO). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 170.2, 170.1, 170.0, 169.9, 169.8, 169.3 (6 × Me*C*O); 134.1 (*C*H=), 133.0–128.1 (ArS-CH), 131.5 (ArS-C), 116.6 (CH_2=), 73.7 (CH_2O), 20.6–20.4 (*Me*CO). Anal. Calcd for $C_{33}H_{42}O_{16}S$ (726.74): C, 54.54; H, 5.83; S, 4.41. Found: C, 54.50; H, 5.80; S, 4.37.

3.13. Phenyl 4-*O*-(2-*O*-allyl-β-D-galactopyranosyl)-1-thio-β-D-glucopyranoside (15)

The O-deacetylation of **14** (6.48 g, 11.5 mmol) as reported above for the preparation of **9** gave crude **15** (5.50 g, 98% yield), almost pure by NMR. An analytical sample was obtained by flash chromatography (4:1 $CHCl_3$–MeOH). **15** was a white solid; mp 206–208 °C (MeOH); $[\alpha]_D$ −34.0 (*c* 0.94, MeOH); R_f 0.15 (4:1 $CHCl_3$–MeOH); ^{1}H NMR (200 MHz, CD_3CN-D_2O): δ 7.53 (m, 2H, ArS-H), 7.20 (m, 3H, ArS-H), 5.89 (ddt, 1H, J_{trans} 17.3 Hz, J_{cis} 10.3 Hz, J 5.9 Hz, CH=), 5.23 (dq, 1H, J_{trans} 17.3 Hz, J 1.6 Hz, CH_2=), 5.13 (dq, 1H, J_{cis} 10.3 Hz, J 1.2 Hz, CH_2=), 4.67 (d, 1H, $J_{1,2}$ 9.8 Hz, H-1), 4.36 (d, 1H, $J_{1',2'}$ 7.7 Hz, H-1′), 4.20 (m, 2H, CH_2O), 3.81–3.40 (m, 10H, H-3, H-4, H-5, H-6a, H-6b, H-3′, H-4′, H-5′, H-6′a, H-6′b), 3.26 (dd, 1H, $J_{2',3'}$ 9.7 Hz, H-2′), 3.25 (dd, 1H, $J_{2,3}$ 8.6 Hz, H-2). ^{13}C NMR (50 MHz, CD_3CN-D_2O): see Table 2 and δ 135.8 (CH=), 134.4 (ArS-C), 132.0–128.2 (ArS-CH), 117.9 (CH_2=), 74.7 (CH_2O). Anal. Calcd for $C_{28}H_{34}O_{10}S$: C, 59.77; H, 6.09; S, 5.70. Found: C, 59.73; H, 6.05; S, 5.74.

3.14. Phenyl 4-*O*-(2-*O*-allyl-4,6-*O*-benzylidene-β-D-galctopyranosyl)-1-thio-β-D-glucopyranoside (16)

A soln of crude **15** (5.50 g, 11.3 mmol) in dry MeCN (30 mL) was cooled to 0 °C and treated under argon atmosphere with α,α-dimethoxytoluene (2.4 mL, 16.0 mmol) and TsOH (214 mg, 1.13 mmol), and the soln was stirred at room temp. After 1 h, the TLC analysis (4:1 $CHCl_3$–MeOH) showed the disappearance of the starting material (R_f 0.15) and the formation of a major faster-moving compound (R_f 0.53). The reaction mixture was neutralized by addition of Et_3N (5 mL) and further stirred for 15 min, and finally solvents were removed under diminished pressure. The residue (6.75 g) was purified by flash chromatography (9:1 $CHCl_3$–MeOH) to give pure **5** (5.56 g, 86% yield) as a white solid; mp 107–110 °C (MeOH); $[\alpha]_D$ −44.1 (*c* 0.97, MeOH); R_f 0.22 (9:1 $CHCl_3$–MeOH); ^{1}H NMR (200 MHz, CD_3CN–D_2O): δ *7.53–7.23* (m, 10H, ArS-H, Ar-H), 5.90 (ddt, 1H, J_{trans} 17.3 Hz, J_{cis} 10.4 Hz, J 5.8 Hz, CH=), 5.58 (s, 1H, Ph*C*H), 5.24 (dq, 1H, J_{trans} 17.3 Hz, J 1.6 Hz, CH_2=), 5.02 (dq, 1H, J_{cis} 10.4 Hz, J 1.2 Hz, CH_2=), 4.66 (d, 1H, $J_{1,2}$ 9.8 Hz, H-1), 4.43 (d, 1H, $J_{1',2'}$ 7.8 Hz, H-1′), 4.20 (m, 3H, H-4′, CH_2O), 4.10 (m, 2H, H-6a, H-6b), 3.81–3.41 (m, 7H, H-3, H-4, H-5, H-3′, H-5′, H-6′a, H-6′b), 3.34 (dd, 1H, $J_{2',3'}$ 9.8 Hz, H-2′), 3.24 (dd, 1H, $J_{2,3}$ 8.9 Hz, H-2). ^{13}C NMR (50 MHz, CD_3CN-D_2O): see Table 2 and δ 139.0 (Ar-C), 136.1 (CH=), 132.0 (ArS-C), 132.1–127.1 (ArS-CH, Ar-CH), 117.6 (CH_2=), 101.5 (Ph*C*H), 74.7 (CH_2O). Anal. Calcd for $C_{28}H_{34}O_{10}S$: C, 59.77; H, 6.09; S, 5.70. Found: C, 59.84; H, 6.08; S, 5.65.

3.15. Phenyl 4-*O*-(2-*O*-allyl-4,6-*O*-benzylidene-β-D-galactopyranosyl)-2,3,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (17)

NaH (64.4 mmol) obtained from 2.57 g of an 60% dispersion in mineral oil after washing with hexane (3 × 30 mL) was suspended in dry DMF (40 mL) and treated at 0 °C with a soln of **16** (3.02 g, 5.37 mmol) in dry DMF (30 mL). The mixture was stirred for 30 min at 0 °C, then benzyl bromide (5.00 mL, 43.0 mmol) was added and the reaction mixture was further stirred overnight at room temp. The TLC analysis (3:2 hexane–EtOAc) showed the disappearance of starting material (R_f 0) and the formation of a major faster-moving product (R_f 0.60). Excess of NaH was destroyed with MeOH under stirring for 30 min, and then the solvents were evaporated under diminished pressure. The residue was taken up with CH_2Cl_2 (300 mL) and washed with water (150 mL). The aq phase was further extracted with CH_2Cl_2 (3 × 50 mL), and the combined organic phases were dried, filtered and concentrated under diminished pressure. The crude product (5.10 g) was subjected to flash chromatography (75:25 hexane–EtOAc) to give pure **17** (4.36 g, 88%) as white solid, mp 160–162 °C (MeOH); $[\alpha]_D$ −49.8 (*c* 1.0, $CHCl_3$); R_f 0.22 (4:1 hexane–EtOAc); ^{1}H NMR (250 MHz, CD_3CN): δ *7.65–7.16* (m, 30H, ArS-H, 5 × Ar-H,), 5.94 (ddt, 1H, J_{trans} 17.3 Hz, J_{cis} 10.5 Hz, J 5.5 Hz, CH=), 5.56 (s, 1H, Ph*C*H), 5.28 (dq, 1H, J_{trans} 17.3 Hz, J 1.7 Hz, CH_2=), 5.13 (dq, 1H, J_{cis} 10.5 Hz, J 1.3 Hz, CH_2=), 5.26, 4.63 (AB system, 2H, $J_{A,B}$ 10.8 Hz, CH_2Ph), 4.81 (d, 1H, $J_{1,2}$ 9.8 Hz, H-1), 4.74 (s, 2H, CH_2Ph), 4.71, 4.46 (AB system, 2H, $J_{A,B}$ 11.1 Hz, CH_2Ph), 4.61, 4.48 (AB system, 2H, $J_{A,B}$ 11.8 Hz, CH_2Ph), 4.55 (d, 1H, $J_{1',2'}$ 8.0 Hz, H-1′), 4.27 (m, 3H, H-4′, CH_2O), 4.09 (dd, 1H, $J_{6'a,6'b}$ 12.4 Hz, $J_{5',6'b}$ 1.4 Hz, H-6′b), 3.96 (dd, 1H, $J_{5',6'a}$ 1.7 Hz, H-6′a), 3.94 (dd, 1H, $J_{3,4}$ 8.9 Hz, $J_{4,5}$ 9.8 Hz, H-4), 3.92 (m, 1H, H-6b), 3.83 (dd, 1H, $J_{6a,6b}$ 10.0 Hz, $J_{5,6a}$ 1.6 Hz, H-6a), 3.71 (dd, 1H, $J_{2,3}$ 8.7 Hz, H-3), 3.61 (m, 1H, H-5), 3.48 (m, 2H, H-2′, H-3′), 3.41 (dd, 1H, H-2), 3.21 (m, 1H, H-5′), ^{13}C NMR (62.9 MHz, CD_3CN): δ see Table 2.and 140.3, 139.7, 139.6, 139.5, 139.4 (5 × Ar-C), 136.5 (CH=), 135.4 (ArS-C), 131.6–127.3 (Ar-CH, ArS-CH), 116.5 (CH_2=), 101.6 (Ph*C*H), 76.0, 75.7, 73.6, 72.0 (4 × CH_2Ph), 74.4 (CH_2O). Anal. Calcd for $C_{56}H_{58}O_{10}S$: C, 72.86; H, 6.33; S, 3.47. Found: C, 72.96; H, 6.30; S, 3.40.

3.16. General procedures for glycosidation reactions

(A) With NIS/TfOH. A soln of donor (1 equiv) and acceptor (1.2 equiv) in CH_2Cl_2 and 4 Å activated molecular sieves under inert atmosphere was stirred for 30 min at room temp and then cooled at −30 °C. NIS (2 equiv) was first added followed by TfOH (0.2 equiv). The temperature was slowly (6 h) raised up to room temp and the mixture was filtered trough a Celite short pad and washed with 10% aq Na_2SO_3 and satd aq $NaHCO_3$. The aq phases were extracted with CH_2Cl_2 and the collected organic layers were combined, dried over $MgSO_4$, concentrated under diminished pressure and subjected to chromatographic purification.

(B) With MeOTf. A soln of donor (1 equiv) and acceptor (1.2 equiv) in the opportune solvent (Table 1) was dried as stated under (A). After cooling to 0 °C, MeOTf (5 equiv) was added and the mixture was allowed to warm to room temp and further stirred for 24 h. The soln was cooled to 0 °C and an excess of Et_3N was added, after 20 min stirring, warming to room temp, the soln was filtered through a short pad of Celite, concentrated under diminished pressure, dried ($MgSO_4$) and purified through chromatography.

3.16.1. Isopropyl 4-*O*-(2-acetamido-4-*O*-allyl-3,6-di-*O*-benzyl-2-deoxy-β-D-talopyranosyl)-2,3,6-tri-*O*-benzyl-α- (α-20) and -β-D-glucopyranoside (β-20)

The glycosidation of **12** (150 mg, 0.155 mmol) by method A led, after flash chromatography (65:35 hexane–EtOAc), to pure samples of **α-20** (31 mg, 22% yield) and **β-20** (33 mg, 23% yield).

α-20: colourless syrup; $[\alpha]_D$ −17.5 (*c* 1.1 $CHCl_3$); R_f 0.37 (1:1 hexane–EtOAc); ^{1}H NMR (250 MHz, CD_3CN): δ 7.50–7.24 (m, 15H, Ar-H), 6.77 (d, 1H, $J_{2',NH}$ 9.9 Hz, NH), 5.90 (ddt, 1H, J_{trans} 17.3 Hz, J_{cis} 10.4 Hz, *J* 5.5 Hz, C*H*=), 5.18 (dq, 1H, J_{trans} 17.3 Hz, *J* 1.7 Hz, CH_2=), 5.09 (dq, 1H, J_{cis} 10.3 Hz, *J* 1.4 Hz, CH_2=), 4.93, 4.66 (AB system, 2H, $J_{A,B}$ 10.8 Hz, CH_2Ph), 4.63, 4.42 (AB system, 2H, $J_{A,B}$ 11.5 Hz, CH_2Ph), 4.62, 4.57 (AB system, 2H, $J_{A,B}$ 12.1 Hz, CH_2Ph), 4.60 (s, 2H, CH_2Ph), 4.49, 4.34 (AB system, 2H, $J_{A,B}$ 12.0 Hz, CH_2Ph), 4.61 (m, 1H, H-2′), 4.51 (d, 1H, $J_{1',2'}$ 1.8 Hz, H-1′), 4.99 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1), 4.34 (ddt, 1H, J_{gem} 12.3 Hz, *J* 5.5 Hz, *J* 1.5 Hz, CH_2O), 4.03 (ddt, 1H, J_{gem} 12.3 Hz, *J* 5.5 Hz, *J* 1.5 Hz, CH_2O), 3.73 (m, 1H, H-4′), 3.95 (m, 1H, H-4), 3.90 (m, 1H, H-5), 3.89 (m, 1H, Me$_2$*CH*), 3.75 (m, 2H, H-6a, H-6b), 3.65 (m, 1H, H-5′), 3.64 (dd, 1H, $J_{2,3}$ 9.7 Hz, $J_{3,4}$ 10.8 Hz, H-3), 3.52–3.44 (m, 2H, H-6′a, H-6′b), 3.48 (dd, 1H, $J_{2',3'}$ 4.0 Hz, $J_{3',4'}$ 1.4 Hz, H-3′), 3.33 (dd, 1H, H-2), 1.71 (s, 3H, *Me*CO), 1.21, 1.15 (2 d, each 3H, *J* 6.2 Hz, *Me*$_2$CH); ^{13}C NMR (62.9 MHz, CD_3CN): see Table 2 and δ 170.3 (Me*CO*); 140.6–139.5 (5 × Ar-C), 136.2 (*C*H=), 129.3–128.1 (Ar-CH), 116.9 (*C*H$_2$=), 75.7, 74.2, 73.8, 73.5, 73.2 (5 × *C*H$_2$Ph), 70.6 (Me$_2$*CH*O), 70.7 (*C*H$_2$O), 23.6 (*Me*$_2$CHO), 21.8 (*Me*CO). Anal. Calcd for $C_{55}H_{65}NO_{11}$: C, 72.11; H, 7.15; N, 1.53. Found: C, 72.10; H, 7.18; N, 1.52.

β-20: colourless syrup; $[\alpha]_D$ −24.5 (*c* 1.0, $CHCl_3$); R_f 0.30 (1:1 hexane–EtOAc); ^{1}H NMR (250 MHz, CD_3CN): δ 7.44–7.26 (m, 15H, Ar-H), 6.78 (d, 1H, $J_{2',NH}$ 9.7 Hz, NH), 5.90 (ddt, 1H, J_{trans} 17.3 Hz, J_{cis} 10.4 Hz, *J* 5.5 Hz, C*H*=), 5.18 (dq, 1H, J_{trans} 17.3 Hz, *J* 1.6 Hz, CH_2=), 5.09 (dq, 1H, J_{cis} 10.3 Hz, *J* 1.3 Hz, CH_2=), 4.96, 4.67 (AB system, 2H, $J_{A,B}$ 10.6 Hz, CH_2Ph), 4.85, 4.66 (AB system, 2H, $J_{A,B}$ 11.3 Hz, CH_2Ph), 4.52, 4.43 (AB system, 2H, $J_{A,B}$ 11.9 Hz, CH_2Ph), 4.49, 4.35 (AB system, 2H, $J_{A,B}$ 11.9 Hz, CH_2Ph), 4.51, 4.49 (AB system, 2H, $J_{A,B}$ 12.0 Hz, CH_2Ph), 4.63 (m, 1H, H-2′), 4.55 (d, 1H, $J_{1',2'}$ 1.4 Hz, H-1′), 4.48 (d, 1H, $J_{1,2}$ 7.8 Hz, H-1), 4.34 (ddt, 1H, J_{gem} 12.5 Hz, *J* 5.7 Hz, *J* 1.4 Hz, CH_2O), 4.04 (ddt, 1H, J_{gem} 12.5 Hz, *J* 5.7 Hz, *J* 1.4 Hz, CH_2O), 3.96 (dd, 1H, $J_{3',4'}$ 2.6 Hz, $J_{4',5'}$ 3.7 Hz, H-4′), 3.95 (dd, 1H, $J_{3,4}$ 9.1 Hz, $J_{4,5}$ 9.8 Hz, H-4), 3.74 (m, 3H, H-6a, H-6b, Me$_2$*CH*), 3.64 (dd, 1H, $J_{6'a,6'b}$ 11.9 Hz, $J_{5',6'b}$ 2.3 Hz, H-6′b), 3.48 (m, 1H, H-5′), 3.46 (t, 1H, $J_{2,3}$ 9.1 Hz, H-3), 3.42 (m, 3H, H-3′, H-6′a, H-5), 3.14 (dd, 1H, H-2), 1.70 (s, 3H, *Me*CO), 1.23, 1.16 (2 d, each 3H, *J* 6.2 Hz, *Me*$_2$CH); ^{13}C NMR (62.9 MHz, CD_3CN): see Table 2 and δ 170.2 (Me*CO*); 140.3, 140.0, 139.5, 139.4, 139.3 (5 × Ar-C), 136.2 (*C*H=), 129.2–128.1 (Ar-CH), 116.8 (*C*H$_2$=), 75.8, 75.2, 74.4, 73.4, 70.7 (5 × *C*H$_2$Ph), 75.3 (Me$_2$*CH*O), 73.8 (*C*H$_2$O), (C-2′), 23.9, 23.5 (*Me*$_2$CHO), 22.3 (*Me*CO). Anal. Calcd for $C_{55}H_{65}NO_{11}$: C, 72.11; H, 7.15; N, 1.53. Found: C, 72.13; H, 7.16; N, 1.51.

3.16.2. Isopropyl 4-*O*-(2-*O*-allyl-4,6-*O*-benzylidene-3-*O*-benzyl-β-D-galactopyranosyl)-2,3,6-tri-*O*-benzyl-α- (α-21) and -β-D-glucopyranoside (β-21)

The glycosidation of **17** (1.52 g, 1.62 mmol) by method B led, after flash chromatography (99:1 CH_2Cl_2–Me_2CO), to pure samples of **α-21** (0.79 g, 56% yield) and **β-21** (0.27 g, 19% yield).

α-21: colourless syrup; $[\alpha]_D$ +34.6 (*c* 1.0, $CHCl_3$); R_f 0.44 (98:2 CH_2Cl_2–Me_2CO); ^{1}H NMR (250 MHz, CD_3CN): δ 7.50–7.17 (m, 25H, 5 × Ar-H), 5.94 (ddt, 1H, J_{trans} 17.4 Hz, J_{cis} 10.6 Hz, *J* 5.3 Hz, C*H*=), 5.56 (s, 1H, Ph*CH*), 5.25 (dq, 1H, J_{trans} 17.4 Hz, *J* 1.8 Hz, CH_2=), 5.10 (dq, 1H, J_{cis} 10.6 Hz, *J* 1.4 Hz, CH_2=), 5.10, 4.62 (AB system, 2H, $J_{A,B}$ 10.8 Hz, CH_2Ph), 5.02 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1), 4.71, 4.61 (AB system, 2H, $J_{A,B}$ 12.3 Hz, CH_2Ph), 4.63 (s 2H, CH_2Ph), 4.59, 4.44 (AB system, 2H, $J_{A,B}$ 11.9 Hz, CH_2Ph), 4.44 (d, 1H, $J_{1',2'}$ 7.7 Hz, H-1′), 4.18 (m, 3H, H-4′, CH_2O), 4.01 (dd, 1H, $J_{6'a,6'b}$ 12.3 Hz, $J_{5',6'b}$ 1.5 Hz, H-6′b), 3.97 (dd, 1H, $J_{6a,6b}$ 10.7 Hz, $J_{5,6b}$ 2.7 Hz, H-6b), 3.95 (dd, 1H, $J_{5',6'a}$ 1.7 Hz, H-6′a), 3.90–3.70 (m, 4H, H-3, H-4, H-5, Me$_2$*CH*O), 3.65 (dd, 1H, $J_{5,6a}$ 1.1 Hz, H-6a), 3.45 (m, 2H, H-2′, H-3′), 3.40 (dd, 1H, $J_{2,3}$ 9.7 Hz, H-2), 3.18 (m, 1H, H-5′), 1.19 (d, 3H, *J* 6.3 Hz, *Me*$_2$CH), 1.16 (d, 3H, *J* 6.1 Hz, *Me*$_2$CH); ^{13}C NMR (62.9 MHz, CD_3CN): see Table 2 and δ *140.7–139.7* (5 × Ar-C), 136.7 (*C*H=), 129.7–127.3 (Ar-CH), 116.3 (*C*H$_2$=), 101.6 (Ph*CH*), 75.6, 74.4, 73.1, 71.9 (4 × *C*H$_2$Ph), 73.7 (*C*H$_2$O), 70.3 (Me$_2$*CH*O), 23.6, 21.8 (*Me*$_2$CH). Anal. Calcd for $C_{53}H_{60}O_{11}$: C, 72.91; H, 6.93. Found: C, 72.89; H, 6.90.

β-21: white solid; mp 105–108 °C (MeOH)); $[\alpha]_D$ +24.0 (*c* 1.25, $CHCl_3$); R_f 0.27 (98:2 CH_2Cl_2–Me_2CO); ^{1}H NMR (250 MHz, CD_3CN): δ 7.46–7.17 (m, 25H, 5 × Ar-H), 6.00 (ddt, 1H, J_{trans} 17.3 Hz, J_{cis} 10.5 Hz, *J* 5.3 Hz, C*H*=), 5.56 (s, 1H, Ph*CH*), 5.26 (dq, 1H, J_{trans} 17.34 Hz, *J* 1.8 Hz, CH_2=), 5.12, 4.69 (AB system, 2H, $J_{A,B}$ 10.8 Hz, CH_2Ph), 5.11 (dq, 1H, J_{cis} 10.5 Hz, *J* 1.4 Hz, CH_2=), 4.87, 4.61 (AB system, 2H, $J_{A,B}$ 11.0 Hz, CH_2Ph), 4.70, 4.46 (AB system, 2H, $J_{A,B}$ 12.1 Hz, CH_2Ph), 4.64, 4.55 (AB system, 2H, $J_{A,B}$ 11.4 Hz, CH_2Ph), 4.50 (d, 1H, $J_{1,2}$ 7.8 Hz, H-1), 4.48 (d, 1H, $J_{1',2'}$ 8.6 Hz, H-1′), 4.25 (m, 3H, H-4′, CH_2O), 3.99 (dd, 1H, $J_{6'a,6'b}$ 12.3 Hz, $J_{5',6'b}$ 1.5 Hz, H-6′b), 3.95 (dd, 1H, $J_{5',6'a}$ 1.7 Hz, H-6′a), 3.92 (m, 2H, H-6b, Me$_2$*CH*O), 3.86 (dd, 1H, $J_{3,4}$ 8.9 Hz, $J_{4,5}$ 9.7 Hz, H-4), 3.79 (dd, 1H, $J_{6a,6b}$ 10.9 Hz, $J_{5,6a}$ 1.7 Hz, H-6a), 3.55 (dd, 1H, $J_{2,3}$ 9.1 Hz, H-3), 3.50 (m, 1H, H-5), 3.44 (m, 2H, H-2′, H-3′), 3.21 (dd, 1H, H-2), 3.15 (m, 1H, H-5′), 1.23 (d, 3H, *J* 6.2 Hz, *Me*$_2$CH), 1.19 (d, 3H, *J* 6.31 Hz, *Me*$_2$CH); ^{13}C NMR (62.9 MHz, CD_3CN): see Table 2 and δ 140.5–139.6 (5 × Ar-*C*), 136.6 (*C*H=), 129.7–127.3 (Ar-CH), 116.4 (*C*H$_2$=), 101.6 (Ph*CH*), 75.6, 75.2, 73.6, 71.9 (4 × *C*H$_2$Ph), 74.3 (*C*H$_2$O), 72.5 (Me$_2$*CH*O), 23.9, 22.3 (*Me*$_2$CH). Anal. Calcd for $C_{53}H_{60}O_{11}$: C, 72.91; H, 6.93. Found: C, 72.88; H, 6.91.

3.17. Isopropyl 4-*O*-[2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-talopyranosyl)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (22)

(A) From **α-*20***: To a soln of **α-20** (139 mg, 0.152 mmol) in 1:1 EtOH–MeOH (30 mL) $PdCl_2$ was added (5 equiv), and the soln was stirred until the TLC analysis (1:1 hexane–EtOAc) showed the disappearance of the starting material and the formation of a single spot at R_f 0.28. The suspension was filtered through a Celite short pad, and solvents were removed under diminished pressure. The crude was purified by flash chromatography (1:1 hexane–EtOAc) to give **22** (120 mg, 90%) as a colourless syrup.

*(B) From **30***: A soln of **30** (217 mg, 0.214 mmol) in 9:1 MeCN–water (4.0 mL) was treated at 0 °C with DDQ (236 mg, 1.07 mmol) and the mixture was stirred at room temp. After 9 h the TLC analysis (1:1 hexane–EtOAc) revealed the disappearance of the starting

material (R_f 0.46) and the formation a single spot at R_f 0.28. The mixture was cooled to 0 °C, Et_3N (3 mL) was added, diluted with CH_2Cl_2 (20 mL) and washed with satd aq $NaHCO_3$ (10 mL). The aq phase was extracted with CH_2Cl_2 (3 × 10 mL), and the combined organic layers were dried, filtered and concentrated under diminished pressure. The residue (500 mg) was subjected to flash chromatographic purification (3:2 hexane–EtOAc) and gave pure **22** (160 mg, 85% yield) as a colourless syrup $[\alpha]_D$ −15.2 (*c* 1.3, $CHCl_3$); R_f 0.28 (1:1 hexane–EtOAc); ^{1}H NMR (200 MHz, CD_3CN): δ 7.42–7.17 (m, 25H, Ar-H), 6.53 (d, 1H, $J_{2',NH}$ 10.0 Hz, NH), 4.92 (s, 2H, CH_2Ph), 4.73, 4.50 (AB system, 2H, $J_{A,B}$ 12.0 Hz, CH_2Ph), 4.82 (d, 1H, $J_{1,2}$ 3.8 Hz, H-1), 4.69, 4.56 (AB system, 2H, $J_{A,B}$ 12.1 Hz, CH_2Ph), 4.66, 4.33 (AB system, 2H, $J_{A,B}$ 11.8 Hz, CH_2Ph), 4.45, 4.36 (AB system, 2H, $J_{A,B}$ 11.9 Hz, CH_2Ph), 4.58 (m, 1H, H-2′), 4.42 (br s, 1H, H-1′), 4.00–3.78 (m, 6H, H-4′, H-6′b, H-3, H-4, H-5, Me_2CHO), 3.48 (dd, 1H, $J_{2,3}$ 8.9 Hz, H-2), 3.67 (dd, 1H, $J_{5,6b}$ 6.7 Hz, $J_{6a,6b}$ 9.8 Hz, H-6b), 3.62 (dd, 1H, $J_{5',6'a}$ 1.7 Hz, $J_{6'a,6'b}$ 9.2 Hz, H-6′a), 3.44 (dd, 1H, $J_{5,6a}$ 5.0 Hz, H-6a), 3.22 (m, 1H, H-5′), 3.09 (dd, 1H, $J_{2',3'}$ 4.1 Hz, $J_{3',4'}$ 3.1 Hz, H-3′), 2.81 (br s, 1H, OH), 1.85 (s, 3H, *Me*CO), 1.22 (d, 3H, *J* 6.3 Hz, Me_2CH), 1.17 (d, 3H, *J* 6.1 Hz, Me_2CH). ^{13}C NMR (50 MHz, CD_3CN): see Table 2 and δ 170.4 (Me*CO*), 139.6, 138.2, 138.1, 137.8, 137.4 (5 × Ar-C), 128.5–126.3 (Ar-CH), 74.8, 73.5, 73.4, 73.2, 73.1 (5 × CH_2Ph), 69.1 (Me_2CHO), 23.5, 23.2, 21.2 (*Me*CO, Me_2CH). Anal. Calcd for $C_{52}H_{61}NO_{11}$: C, 71.29; H, 7.02; N, 1.60. Found: C, 71.26; H, 7.00; N, 1.58.

3.18. Isopropyl 4-*O*-[2-acetamido-3,6-di-*O*-benzyl-2,4-dideoxy-β-D-*threo*-hex-3-enopyranosyl)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (23)

NaH (50 mg of 60% dispersion in mineral oil, 1.25 mmol) was washed with dry hexane (4 × 2 mL) and suspended in dry DMF (1.5 mL). The mixture was treated with a soln of **22** (124 mg, 0.137 mmol) in dry DMF (2.0 mL) at room temp under Ar atmosphere. The resulting mixture was stirred at room temp for 1 h and then cooled to −30 °C. Solid Im_2SO_2 (42 mg, 0.212 mmol) was added and the resulting mixture was stirred for 30 min at −30 °C. The mixture was allowed to warm to room temp and further stirred until TLC analysis (1:1 hexane–EtOAc) revealed the complete formation of a faster-moving product (R_f 0.35). The reaction was cooled to –30 °C and quenched by addition of MeOH (2 mL). The resulting soln was diluted with CH_2Cl_2 (10 mL), washed with water (10 mL) and further extracted with CH_2Cl_2 (3 × 5 mL), and the combined organic layers were dried, filtered and concentrated under diminished pressure. Flash chromatography (3:2 hexane–EtOAc) of the crude residue (126 mg) gave pure **23** (115 mg, 98% yield), as a colourless syrup: $[\alpha]_D$ +38.8 (*c* 1.0, $CHCl_3$); R_f 0.28 (3:2 hexane–EtOAc); ^{1}H NMR (200 MHz, CD_3CN): δ 7.44–7.23 (m, 25H, Ar-H), 6.32 (d, 1H, $J_{2',NH}$ 9.7 Hz, NH), 5.02, 4.80 (AB system, 2H, $J_{A,B}$ 11.7 Hz, CH_2Ph), 5.00 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1), 4.83 (d, 1H, $J_{1',2'}$ 1.8 Hz, H-1′), 4.78 (d, 1H, $J_{4',5'}$ 1.5 Hz, H-4′), 4.71, 4.52 (AB system, 2H, $J_{A,B}$ 11.5 Hz, CH_2Ph), 4.70, 4.41 (AB system, 2H, $J_{A,B}$ 12.0 Hz, CH_2Ph), 4.59 (s, 2H, CH_2Ph), 4.58, 4.46 (AB system, 2H, $J_{A,B}$ 11.6 Hz, CH_2Ph), 4.48 (dt, 1H, $J_{2',5'}$ 1.5 Hz, H-2′), 4.21 (tt, 1H, $J_{5',6'a} = J_{5',6'b}$ 5.3 Hz, H-5′), 3.88 (m, 1H, Me_2CHO), 3.79 (m, 2H, H-5, H-6b), 3.76 (dd, 1H, $J_{2,3}$ 9.3 Hz, $J_{3,4}$ 8.4 Hz, H-3), 3.67 (dd, 1H, $J_{4,5}$ 9.4 Hz, H-4), 3.62 (dd, 1H, $J_{5,6a}$ 3.2 Hz, $J_{6a,6b}$ 12.3 Hz, H-6a), 3.48 (dd, 1H, $J_{6'a,6'b}$ 10.0 Hz, H-6′b), 3.43 (dd, 1H, H-6′a), 3.39 (dd, 1H, H-2), 1.76 (s, 3H, *Me*CO), 1.20 (d, 3H, *J* 6.2 Hz, Me_2CH), 1.15 (d, 3H, *J* 6.1 Hz, Me_2CH). ^{13}C NMR (50 MHz, CD_3CN): δ 170.4 (Me*CO*), 153.4 (C-3′), 140.8, 139.6, 139.5, 139.3, 137.8 (5 × Ar-C), 129.4–127.9 (Ar-CH), 99.4 (C-1′), 98.5 (C-4′), 95.5 (C-1), 80.5, 81.0 (C-2, C-3), 77.5 (C-4), 75.5, 73.8, 73.7, 73.6, 73.2 (5 × CH_2Ph), 73.0 (C-5), 70.7, 70.6 (C-5′, Me_2CHO), 70.1, 69.6 (C-6, C-6′), 49.5 (C-2′), 23.6, 23.0, 21.8 (*Me*CO, Me_2CH). Anal. Calcd for $C_{52}H_{59}NO_{10}$: C, 72.79; H, 6.93; N, 1.63. Found: C, 72.56; H, 7.01; N, 1.65.

3.19. Isopropyl 4-*O*-[2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-mannopyranosyl)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (24)

A soln of **23** (113 mg, 0.132 mmol) in dry THF (5 mL) was treated at 0 °C with a soln of $BH_3{\cdot}Me_2S$ (0.023 mL, 0.198 mmol) in Et_2O (5 M), and the resulting soln was warmed up to 40 °C and stirred until the starting material (R_f 0.53) had completely reacted (TLC, 2:3 hexane–EtOAc, 40 min). The mixture was cooled to 0 °C, and water (0.129 mL), 10% aq NaOH (0.397 mL) and finally 35% aq H_2O_2 (1.05 mL) were sequentially added. The mixture was stirred at room temp until the TLC analysis (2:3 hexane–EtOAc) revealed the disappearance of the borane intermediate (30 min) and the formation of a single spot (R_f 0.35). Water (5 mL) was added and the aq soln was extracted with CH_2Cl_2 (3 × 10 mL). The collected organic phases were dried, filtered and concentrated under diminished pressure. The crude residue was subjected to a flash chromatographic purification (55:45 hexane–EtOAc, then 2:3 hexane–EtOAc) to give pure **24** (70 mg, 60% yield) as a colourless syrup; $[\alpha]_D$ −13.0 (*c* 0.9, $CHCl_3$); R_f 0.35 (2:3 hexane–EtOAc), ^{1}H NMR (200 MHz, CD_3CN–D_2O): δ 7.46–7.22 (m, 25H, Ar-H), 6.26 (d, 1H, $J_{2',NH}$ 10.2 Hz, NH), 5.02, 4.72 (AB system, 2H, $J_{A,B}$ 12.3 Hz, CH_2Ph), 4.94 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1), 4.72 (m, 1H, H-2′), 4.70 (br s, 1H, H-1′), 4.70, 4.32 (AB system, 2H, $J_{A,B}$ 10.9 Hz, CH_2Ph), 4.60, 4.45 (AB system, 2H, $J_{A,B}$ 12.2 Hz, CH_2Ph), 4.58 (s, 2H, CH_2Ph), 4.58, 4.52 (AB system, 2H, $J_{A,B}$ 11.8 Hz, CH_2Ph), 3.90–3.65 (m, 3H, H-4, H-5, H-6b), 3.86 (m, 1H, Me_2CHO), 3.67 (dd, 1H, $J_{2,3}$ 9.2 Hz, $J_{3,4}$ 8.7 Hz, H-3), 3.57 (dd, 1H, $J_{5,6a}$ 6.1 Hz, $J_{6a,6b}$ 10.9 Hz, H-6a), 3.52 (m, 2H, H-6′a, H-6′b), 3.44 (dd, 1H, $J_{4',5'}$ 9.8 Hz, $J_{3',4'}$ 9.5 Hz, H-4′), 3.34 (dd, 1H, H-2), 3.24 (dd, 1H, $J_{2',3'}$ 4.1 Hz, H-3′), 3.10 (dt, 1H, $J_{5',6'a} = J_{5',6'b}$ 3.6 Hz, H-5′), 1.83 (s, 3H, *Me*CO), 1.20 (d, 3H, *J* 6.2 Hz, Me_2CH), 1.14 (d, 3H, *J* 6.1 Hz, Me_2CH); ^{13}C NMR (50 MHz, CD_3CN–D_2O): see Table 2 and δ 171.0 (Me*CO*), 140.8, 140.7, 139.8, 139.5, 139.4 (5 × Ar-C), 129.3–128.0 (Ar-CH), 75.6, 73.8, 73.6, 73.2, 71.3 (5 × CH_2Ph), 70.5 (Me_2CHO), 23.6, 23.2, 21.8 (*Me*CO, Me_2CH). Anal. Calcd for $C_{52}H_{61}NO_{11}$: C, 71.29; H, 7.02; N, 1.60. Found: C, 71.27; H, 6.99; N, 1.61.

3.20. Isopropyl 4-*O*-(2-*O*-allyl-3-*O*-benzyl-β-D-galactopyranosyl)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (25)

A soln of **α-21** (1.90 g, 2.17 mmol) in 80% aq AcOH (50 mL) was stirred at 80 °C until the TLC analysis (1:1 hexane–EtOAc) showed the disappearance of the starting material (1 h, R_f 0.55) and the formation of a slower-moving product (R_f 0.31). The soln was concentrated and co-evaporated with toluene (5 × 30 mL) under diminished pressure. The residue (1.85 g) was subjected to flash chromatographic purification (1:1 hexane–EtOAc) to give pure **25** (1.62 g, 95% yield) as a white solid; mp 98–100 °C (chrom); $[\alpha]_D$ +49 (*c* 1.0, $CHCl_3$); R_f 0.31 (1:1 hexane–EtOAc); ^{1}H NMR (200 MHz, CD_3CN-D_2O): δ *7.49–7.25* (m, 20H, 4 × Ar-H,), 5.95 (ddt, 1H, J_{trans} 17.3 Hz, J_{cis} 10.6 Hz, *J* 5.4 Hz, C*H*=), 5.26 (dq, 1H, J_{trans} 17.3 Hz, *J* 1.7 Hz, CH_2=), 5.11 (dq, 1H, J_{cis} 10.6 Hz, *J* 1.4 Hz, CH_2=), 4.97 (d, 1H, $J_{1,2}$ 3.9 Hz, H-1), 4.96, 4.67 (AB system, 2H, $J_{A,B}$ 10.9 Hz, CH_2Ph), 4.70, 4.54 (AB system, 2H, $J_{A,B}$ 12.0 Hz, CH_2Ph), 4.63, 4.56 (AB system, 2H, $J_{A,B}$ 11.7 Hz, CH_2Ph), 4.55, 4.40 (AB system, 2H, $J_{A,B}$ 11.9 Hz, CH_2Ph), 4.28 (d, 1H, $J_{1',2'}$ 7.6 Hz, H-1′), 4.18 (m, 2H, CH_2O), 3.95 (m, 1H, H-4′), 3.90–3.65 (m, 6H, H-3, H-4, H-5, H-6′a, H-6′b, Me_2CHO), 3.68 (dd, 1H, $J_{6a,6b}$ 11.7 Hz, $J_{5,6b}$ 7.3 Hz, H-6b), 3.55 (dd, 1H, $J_{5,6a}$ 4.3 Hz, H-6a), 3.42 (dd, 1H, $J_{2,3}$ 9.3 Hz, H-2), 3.39 (dd, 1H, $J_{2',3'}$ 9.6 Hz, H-2′), 3.23 (dd, 1H, $J_{3',4'}$ 3.2 Hz, H-3′), 3.21 (m, 1H, H-5′), 1.16 (d, 3H, *J* 6.3 Hz, Me_2CH), 1.12 (d, 3H, *J* 6.1 Hz, Me_2CH). ^{13}C NMR (50 MHz, CD_3CN-D_2O): see Table 2 and δ 140.4, 139.7, 139.6, 139.4 (4 × Ar-C), 136.6 (*C*H=), 129.3–128.1 (Ar-CH), 116.2 (CH_2=), 75.6, 74.4, 73.6, 73.1, 72.0 (4 × CH_2Ph, CH_2O), 70.4 (Me_2CHO), 23.6, 21.8 (Me_2CH). Anal. Calcd for $C_{46}H_{56}O_{11}$: C, 70.39; H, 7.19. Found: C, 70.45; H, 7.25.

3.21. Isopropyl 4-*O*-(2-*O*-allyl-3,6-di-*O*-benzyl-β-D-galactopyranosyl)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (26)

A mixture of **25** (1.57 g, 2.00 mmol) and dibutyltin oxide (589 mg, 2.07 mmol) in toluene (65 mL) was heated to reflux with a Dean–Stark apparatus overnight. Tetrabutylammonium bromide (1.00 g, 3.10 mmol) and benzyl bromide (0.62 mL, 5.57 mmol) were added, and the reaction mixture was stirred at reflux. After 4 h, the TLC analysis (1:1 hexane–EtOAc) revealed the complete disappearance of the starting material (R_f 0.31). The soln was cooled to room temp, concentrated to dryness and the resulting residue (3.02 g) was purified by flash chromatography, (4:1 hexane–EtOAc) to give pure **26** (1.45 g, 89% yield) as a colourless syrup; $[\alpha]_D$ +35.8 (*c* 0.81, $CHCl_3$); ^1H NMR (200 MHz, CD_3CN): δ 7.50–7.24 (m, 25H, 5 × Ar-H,), 5.96 (ddt, 1H, J_{trans} 17.3 Hz, J_{cis} 10.5 Hz, *J* 5.4 Hz, C*H*=), 5.29 (dq, 1H, J_{trans} 17.3 Hz, *J* 1.7 Hz, CH_2=), 5.19 (dq, 1H, J_{cis} 10.5 Hz, *J* 1.4 Hz, CH_2=), 5.01, 4.71 (AB system, 2H, $J_{A,B}$ 10.9 Hz, CH_2Ph), 5.02 (d, 1H, $J_{1,2}$ 3.8 Hz, H-1), 4.74, 4.59 (AB system, 2H, $J_{A,B}$ 11.9 Hz, CH_2Ph), 4.67, 4.60 (AB system, 2H, $J_{A,B}$ 11.7 Hz, CH_2Ph), 4.58, 4.38 (AB system, 2H, $J_{A,B}$ 12.2 Hz, CH_2Ph), 4.53, 4.46 (AB system, 2H, $J_{A,B}$ 11.8 Hz, CH_2Ph), 4.47 (d, 1H, $J_{1',2'}$ 7.8 Hz, H-1′), 4.25 (m, 2H, CH_2O), 3.97 (m, 1H, H-4′), 3.92 (m, 1H, Me$_2$*CH*O), 3.95–3.64 (m, 5H, H-3, H-4, H-5, H-6′a, H-6′b), 3.68 (dd, 1H, $J_{6a,6b}$ 9.9 Hz, $J_{5,6b}$ 5.8 Hz, H-6b), 3.52 (dd, 1H, $J_{5,6a}$ 6.0 Hz, H-6a), 3.46 (dd, 1H, $J_{2',3'}$ 9.6 Hz, H-2′), 3.41 (dd, 1H, $J_{2,3}$ 9.4 Hz, H-2), 3.38 (m, 1H, H-5′), 3.33 (dd, 1H, $J_{3',4'}$ 3.2 Hz, H-3′), 3.08 (dd, 1H, $J_{4',OH}$ 3.5 Hz, OH), 1.19 (d, 3H, *J* 6.2 Hz, *Me*$_2$CH), 1.14 (d, 3H, *J* 6.1 Hz, *Me*$_2$CH); ^{13}C NMR (50 MHz, CD_3CN): see Table 2 and δ 140.6–139.5 (5 × Ar-C), 136.7 (*C*H=), 129.3–128.0 (Ar-CH), 116.2 (*C*H$_2$=), 75.4, 74.3, 73.8, 73.6, 73.2, 72.2 (5 × *C*H$_2$Ph, *C*H$_2$O), 70.4 (Me$_2$*CH*O), 23.6, 21.8 (*Me*$_2$CH). Anal. Calcd for $C_{53}H_{62}O_{11}$: C, 72.75; H, 7.14. Found: C, 72.81; H, 7.20.

3.22. Isopropyl 4-*O*-[2-*O*-allyl-3,6-di-*O*-benzyl-4-*O*-(2-*O*-naphthylmethyl)-β-D-galactopyranosyl]-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (27)

NaH (2.42 mmol) obtained from 100 mg of 60% dispersion in mineral oil after washing with hexane (3 × 10 mL) was suspended in dry DMF (10 mL) and treated at 0 °C with a soln of **26** (524 mg, 0.604 mmol) in dry DMF (50 mL). The mixture was stirred for 30 min at 0 °C, treated with 2-methylnaphthyl bromide (534 mg, 2.42 mmol) and the reaction mixture was stirred at room temp. After 12 h, the TLC analysis (3:2 hexane–EtOAc) showed the disappearance of starting material (R_f 0.46) and the formation of a single spot at R_f 0.63. Excess of NaH was destroyed with MeOH under stirring for 30 min, first at 0 °C and then at room temp. The soln was concentrated to dryness under diminished pressure and the resulting residue CH_2Cl_2 (50 mL) was taken up and washed with water (30 mL). The aq phase was extracted with CH_2Cl_2 (3 × 20 mL), and the combined organic phases were dried, filtered and concentrated under diminished pressure. The crude product (1.10 g) was subjected to flash chromatography (4:1 hexane–EtOAc) to give pure **27** (580 mg, 95% yield) as a colourless syrup; $[\alpha]_D$ +12.5 (*c* 0.73, $CHCl_3$); R_f 0.63 (3:2 hexane–EtOAc); ^1H NMR (200 MHz, CD_3CN): δ 7.78 (m, 4H, Ar-H), 749–7.23 (m, 25H, Ar-H), 7.10 (m, 3H, Ar-H), 5.97 (ddt, 1H, J_{trans} 17.3 Hz, J_{cis} 10.4 Hz, *J* 5.3 Hz, C*H*=), 5.29 (dq, 1H, J_{trans} 17.3 Hz, *J* 1.7 Hz, CH_2=), 5.13 (dq, 1H, J_{cis} 10.3 Hz, *J* 1.3 Hz, CH_2=), 5.03, 4.64 (AB system, 2H, $J_{A,B}$ 12.2 Hz, CH_2Ph), 5.00 (d, 1H, $J_{1,2}$ 3.5 Hz, H-1), 4.94, 4.70 (AB system, 2H, $J_{A,B}$ 10.8 Hz, CH_2NAP), 4.73, 4.69 (AB system, 2H, $J_{A,B}$ 11.9 Hz, CH_2Ph), 4.71, 4.59 (AB system, 2H, $J_{A,B}$ 12.0 Hz, CH_2Ph), 4.65, 4.46 (AB system, 2H, $J_{A,B}$ 11.8 Hz, CH_2Ph), 4.47 (d, 1H, $J_{1',2'}$ 7.5 Hz, H-1′), 4.45, 4.27 (AB system, 2H, $J_{A,B}$ 12.0 Hz, CH_2Ph), 4.21 (m, 2H, CH_2O), 4.01–3.55 (m, 8H, H-4, H-5, H-6a, H-6b, H-4′, H-6′a, H-6′b, Me$_2$*CH*O), 3.66 (dd, 1H, $J_{2,3}$ 9.5 Hz, $J_{3,4}$ 9.0 Hz, H-3), 3.56 (dd, 1H, $J_{2',3'}$ 9.7 Hz, H-2′), 3.45 (dd, 1H, $J_{3',4'}$ 3.5 Hz, H-3′), 3.40 (m, 1H, H-5′), 3.38 (dd, 1H, H-2), 1.21 (d, 3H, *J* 6.2 Hz, *Me*$_2$CH), 1.16 (d, 3H, *J* 6.1 Hz, *Me*$_2$CH); ^{13}C NMR (50 MHz, CD_3CN): see Table 2 and δ 140.5, 139.9, 139.8, 139.5, 137.7, 134.1 (6 × Ar-C), 136.7 (*C*H=), 129.2–126.8 (Ar-CH), 116.3 (*C*H$_2$=), 75.5, 75.4, 74.5, 73.8, 73.6, 73.2, 73.1 (5 × *C*H$_2$Ph, *C*H$_2$Nap, *C*H$_2$O), 70.5 (Me$_2$*CH*O), 23.6, 21.9 (*Me*$_2$CH). Anal. Calcd for $C_{64}H_{70}O_{11}$: C, 75.72; H, 6.95. Found: C, 75.68; H, 7.05.

3.23. Isopropyl 4-*O*-[3,6-di-*O*-benzyl-4-*O*-(2-*O*-naphthylmethyl)-β-D-galactopyranosyl]-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (28)

A soln of **27** (359 mg, 0.354 mmol) in 9:1 EtOH-water (8 mL) was treated with DABCO (18 mg, 0.156 mmol) and heated at reflux. $(Ph_3P)_3RhCl$ (16 mg, 0.0178 mmol) was added, and the mixture was stirred at reflux until TLC analysis (2:1 $PhCH_3$–Et_2O) showed the disappearance of the starting material (R_f 0.76) and the formation of a single spot at R_f 0.80. The soln was concentrated under diminished pressure and the residue was taken up with CH_2Cl_2 (10 mL), washed with brine (5 mL) and the aq phase was extracted with CH_2Cl_2 (3 × 5 mL) The organic phases were dried, filtered and concentrated under diminished pressure, and the crude residue was constituted exclusively (^1H, ^{13}C NMR) of a diastereoisomeric mixture of 2-*O*-(1-propenyl) derivative (**33**, not shown, 350 mg, 97% yield) in a 4:1 (*E*)/(*Z*) ratio, measured on the basis of the relative intensities of *Me*CH= signals at δ 1.59 and 1.50, respectively. ^1H NMR (200 MHz, $CDCl_3$) analysis led to a partial assignment of the signals. (***E***)-**33**: δ 6.15 (d, 1H, *J* 16.5 Hz, OCH=), 5.05 (m, 1H, Me*CH*=), 1.59 (d, 1H, *J* 6.7 Hz, *Me*CH=); (***Z***)-**33**: δ 6.17 (d, 1H, *J* 10.3 Hz, OCH=), 5.05 (m, 1H, Me*CH*=), 1.50 (d, 1H, *J* 6.7 Hz, *Me*CH=); ^{13}C NMR (50 MHz, $CDCl_3$): (E)-33: δ 147.4 (OCH=), 97.8 (CH=), 101.8 (C-1′), 94.7 (C-1), 81.9, 80.9, 80.1, 79.0, (C-3′, C-4′, C-2, C-3), 77.4 (C-4), 68.1, 67.7 (C-6, C-6′), 9.3 (*Me*CH=); (Z)-33: δ 148.3 (OCH=), 99.0 (CH=), 102.0 (C-1′), 94.8 (C-1), 81.3, 81.4, 80.1, 79.0, (C-3′, C-4′, C-2, C-3), 77.6 (C-4), 68.3, 67.8 (C-6, C-6′), 12.1 (*Me*CH=); clusters of signals for both diastereomeric forms δ *139.4–133.1* (6 × Ar-C), 129.9–125.6 (Ar-CH), 75.1–73.0 (CH$_2$Ph, CH$_2$Nap), 72.7, 72.8 (C-2′, C-5), 69.7, 68.9 (C-5′. Me$_2$*CH*O), 23.0, 21.1 (*Me*$_2$CH). This crude product (350 mg) was employed without any further purification, so this was dissolved in CH_2Cl_2 (6 mL) and treated with 70% commercial MCPBA (96 mg, 0.390 mmol) at 0 °C, and the reaction was stirred for 1 h at room temp until TLC analysis (7:3 hexane–EtOAc) showed the complete disappearance of the starting material (R_f 0.46) and the formation of two spots at R_f 0.37 and 0.27. Et_3N (0.5 mL) was added and the soln was stirred overnight until TLC analysis (7:3 hexane–EtOAc) revealed the formation of a single spot at R_f 0.37. The reaction mixture was concentrated under diminished pressure and the residue (380 mg) was subjected to flash chromatography (75:25 hexane–EtOAc) to give pure **28** (295 mg, 85% yield calculated from **27**); as a colourless syrup; $[\alpha]_D$ +24.4 (*c* 0.9, $CHCl_3$); R_f 0.35 (7:3 hexane–EtOAc); ^1H NMR (250 MHz, CD_3CN): δ 7.78 (m, 4H, Ar-H), 7.47–7.23 (m, 25H, Ar-H), 7.11 (m, 3H, Ar-H), 4.99, 4.70 (AB system, 2H, $J_{A,B}$ 11.3 Hz, CH_2Ph), 5.00 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1), 4.91, 4.66 (AB system, 2H, $J_{A,B}$ 10.9 Hz, CH_2Nap), 4.77, 4.67 (AB system, 2H, $J_{A,B}$ 11.7 Hz, CH_2Ph), 4.61 (s, 2H, CH_2Ph), 4.58, 4.47 (AB system, 2H, $J_{A,B}$ 11.8 Hz, CH_2Ph), 4.42, 4.26 (AB system, 2H, $J_{A,B}$ 11.9 Hz, CH_2Ph), 4.41 (d, 1H, $J_{1',2'}$ 7.8 Hz, H-1′), 3.96 (m, 2H, H-4′, H-4), 3.95–3.80 (m, 2H, H-5′, Me$_2$*CH*O), 3.77–3.65 (m, 3H, H-2′, H-6′a, H-6′b), 3.60 (dd, 1H, $J_{2,3}$ 8.8 Hz, $J_{3,4}$ 7.8 Hz, H-3), 3.51–3.34 (m, 5H, H-2, H-5, H-6a, H-6b, H-3′), 2.21 (br s, 1H, OH), 1.20 (d, 3H, *J* 6.1 Hz, *Me*$_2$CH), 1.15 (d, 3H, *J* 6.2 Hz, *Me*$_2$CH). ^{13}C NMR (62.9 MHz, CD_3CN): see Table 2 and δ 140.6, 139.9, 139.8, 139.6, 137.8, 134.1 (6 × Ar-C), 129.2–126.8 (Ar-CH), 75.5, 75.4, 73.8, 73.7, 73.2, 73.0 (5 × *C*H$_2$Ph, *C*H$_2$Nap), 70.4 (Me$_2$-*CH*O), 23.6, 21.8 (*Me*$_2$CH). Anal. Calcd for $C_{61}H_{66}O_{11}$: C, 75.13; H, 6.82. Found: C, 75.10; H, 6.78.

3.24. Isopropyl 4-*O*-[3,6-di-*O*-benzyl-2-*O*-benzyloximino-2-deoxy-4-*O*-(2-*O*-naphthylmethyl)-β-D-*lyxo*-hexopyranosyl]-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (29)

A soln of **28** (944 mg, 0.968 mmol) in dry CH_2Cl_2 (60 mL) and powdered 3 Å molecular sieves (4.30 g) was stirred under Ar atmosphere. After 30 min, the suspension was treated with pyridinium chlorochromate (PCC, 965 mg, 4.47 mmol) and stirred at room temp until TLC analysis (99:1 CH_2Cl_2–Me_2CO) showed the complete disappearance of starting material (8 h, R_f 0.31). The reaction mixture was filtered through a Celite–silica gel–Celite triple alternate pad, the filtered mixture was washed with CH_2Cl_2 (30 mL) and the organic phase was concentrated under diminished pressure. The crude residue, constituted exclusively (^{13}C NMR) of 2-keto derivative (940 mg, quantitative yield), was directly employed in the next reaction without any further purification. ^{13}C NMR (50 MHz, $CDCl_3$) data: δ 199.1 (C-2′), 139.2, 138.1, 138.0, 137.5, 137.3, 132.9 (6 × Ar-C), 129.7–125.5 (Ar-CH), 100.6 (C-1′), 94.6 (C-1), 83.0, 80.2 (C-2, C-3′), 79.3, 78.3 (C-3, C-4), 74.9, 74.3, 73.3, 73.1, 73.0, 72.1 (5 × CH_2Ph, CH_2Nap), 73.7, 73.3 (C-4′, C-5), 69.3, 69.2 (C-5′, Me_2CHO), 68.4, 67.4 (C-6, C-6′), 22.9, 21.0 (Me_2CH). A soln of crude 2-keto derivative (940 mg) in dry pyridine (50 mL) was treated under Ar atmosphere with O-benzylhydroxylamine hydrochloride (485 mg, 3.03 mmol). The mixture was stirred at room temp until the starting material (R_f 030) was completely reacted [6 h, TLC (99:1 CH_2Cl_2–Me_2CO)]. The reaction mixture was concentrated and co-evaporated with toluene (4 × 20 mL) under diminished pressure and the crude product (1.60 g) was purified by flash chromatography (4:1 hexane–EtOAc) to give a diastereoisomeric mixture of **29** (712 mg, 70% yield) in a 75:25 (*Z*)/(*E*) ratio, measured on the basis of the relative intensities of H-1′ signals (δ 6.04 and 5.40, respectively); as a yellow pale syrup; R_f 0.35 (4:1 hexane–EtOAc); ^1H NMR (250 MHz, CD_3CN) analysis led to a partial assignment of the signals. **(*Z*)-29**: δ 6.04 (s, 1H, H-1′), 5.04 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1), 5.03 (m, 2H, PhCH_2ON=), 4.64 (d, 1H, $J_{3',4'}$ 7.2 Hz, H-3′), 3.41 (dd, 1H, $J_{2,3}$ 9.6 Hz, H-2), 4.12 (dd, 1H, $J_{3,4}$ 8.3 Hz, H-3). **(*E*)-29**: δ 5.40 (s, 1H, H-1′), 5.20 (d, 1H, $J_{1,2}$ 3.5 Hz, H-1), 5.06 (d, 1H, $J_{3',4'}$ 7.1 Hz, H-3′), 5.03 (m, 2H, PhCH_2ON=), 3.43 (dd, 1H, $J_{2,3}$ 9.5 Hz, H-2); ^{13}C NMR (63 MHz, CD_3CN): **(*Z*)-29**: δ 151.9 (C-2′), 95.4 (C-1), 93.3 (C-1′), 81.8, 81.1, 79.9 (C-4′, C-2, C-3), 77.4 (PhCH_2ON=), 76.6, 75.6 (C-4, C-5), 75.1, 74.1, 73.7, 72.9, 72.0, 71.6 (5 × CH_2Ph, CH_2Nap), 74.2 (C-3′), 70.8 (C-5′); **(*E*)-29**: δ 152.9 (C-2′), 100.2 (C-1′), 95.3 (C-1), 81.7, 81.0, 79.5 (C-4′, C-2, C-3), 77.2 (PhCH_2ON=), 76.5, 75.7 (C-4, C-5), 75.4, 73.9, 73.7, 72.9, 72.8, 72.3 (5 × CH_2Ph, CH_2Nap), 70.9 (C-5′), 67.3 (C-3′). Clusters of signals for both diastereomeric forms: δ *140.8–133.9* (6 × Ar-C), 130.5–126.8 (Ar-CH), 70.5 (Me_2CHO), 70.4–70.0 (C-6, C-6′), 23.8, 22.0 (Me_2CH). Anal. Calcd for $C_{68}H_{71}NO_{11}$: C, 75.74; H, 6.64; N, 1.30; Found: C, 75.70; H, 6.61; N, 1.28.

3.25. Isopropyl 4-*O*-[2-acetamido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-(2-*O*-naphthylmethyl)-β-D-talopyranosyl]-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (30)

A soln of a diastereoisomeric mixture of **29** (292 mg, 0.271 mmol) in dry Et_2O (20 mL) was slowly added (15 min) at 0 °C and under Ar atmosphere to a stirred suspension of $LiAlH_4$ (112 mg, 2.95 mmol) in dry Et_2O (10 mL). The mixture was then gently heated to reflux and after 1.5 h the TLC analysis (1:4 hexane–EtOAc) revealed the disappearance of the starting material (R_f 0.69) and the formation of a spot at R_f 0.31. Excess of hydride was decomposed by addition, in the order, of water (0.12 mL), 10% aq NaOH (0.16 mL) and water (0.12 mL), the white granular precipitate was filtered and repeatedly washed with Et_2O (5 × 10 mL), and the collected ethereal extracts were concentrated at diminished pressure. The crude residue (295 mg) was dissolved in MeOH (36 mL), treated with Ac_2O (18 mL) and stirred at room temp until N-acetylation was complete (1 h). The reaction mixture was co-evaporated with toluene (4 × 10 mL) under diminished pressure and the crude residue (325 mg) was subjected to flash chromatographic purification (3:2 hexane–EtOAc) to obtained pure 30 (227 mg, 83% yield) as a colourless syrup $[\alpha]_D$ −6.25 (*c* 0.96, $CHCl_3$); R_f 0.46 (1:1 hexane–EtOAc); ^1H NMR (250 MHz, CD_3CN): δ 7.79 (m, 4H, Ar-H), 7.53–7.21 (m, 25H, Ar-H), 6.96 (m, 3H, Ar-H), 6.69 (d, 1H, $J_{2',NH}$ 9.9 Hz, NH), 4.97 (d, 1H, $J_{1,2}$ 3.8 Hz, H-1), 4.96, 4.65 (AB system, 2H, $J_{A,B}$ 10.4 Hz, CH_2Ph), 4.81, 4.59 (AB system, 2H, $J_{A,B}$ 10.79 Hz, CH_2Nap), 4.69, 4.49 (AB system, 2H, $J_{A,B}$ 11.4 Hz, CH_2Ph), 4.65 (m, 1H, H-2′), 4.59, 4.51 (AB system, 2H, $J_{A,B}$ 12.4 Hz, CH_2Ph), 4.58 (br s, 1H, H-1′), 4.55, 4.53 (AB system, 2H, $J_{A,B}$ 11.8 Hz, CH_2Ph), 4.50, 4.37 (AB system, 2H, $J_{A,B}$ 11.9 Hz, CH_2Ph), 3.93 (m, 2H, H-4′, H-4), 3.86 (m, 1H, Me_2CHO), 3.76 (dd, 1H, $J_{5,6b}$ 5.6 Hz, $J_{6a,6b}$ 9.1 Hz, H-6b), 3.68 (m, 3H, H-5′, H-6′a, H-6′b), 3.59 (dd, 1H, $J_{2,3}$ 9.8 Hz, $J_{3,4}$ 8.9 Hz, H-3), 3.57 (dd, 1H, $J_{2',3'}$ 2.9 Hz, $J_{3',4'}$ 4.0 Hz, H-3′), 3.50 (m, 2H, H-5, H-6a), 3.31 (dd, 1H, H-2), 1.43 (s, 3H, *Me*CO), 1.19 (d, 3H, *J* 6.2 Hz, Me_2CH), 1.14 (d, 3H, *J* 6.1 Hz, Me_2CH). ^{13}C NMR (62.9 MHz, CD_3CN): see Table 2 and δ 170.2 (CO), 140.5, 139.8, 139.6, 139.5, 137.2, 134.2 (6 × Ar-C), 129.42–127.0 (Ar-CH), 76.2, 75.9, 74.0, 73.5, 73.3, 70.9 (5 × CH_2Ph, CH_2Nap), 70.5 (Me_2CHO), 23.6, 21.9 (Me_2CH), 23.4 (*Me*CO). Anal. Calcd for $C_{63}H_{69}NO_{11}$: C, 74.46; H, 6.84; N, 1.38. Found: C, 74.43; H, 6.81; N, 1.34.

Acknowledgement

This work was supported by Ministero dell'Università e della Ricerca (MIUR, Rome, Italy) in the frame of the COFIN national programme.

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