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Stereoselective syntheses of the *O*,*N*-protected subunits of the tunicamycins [1,2]

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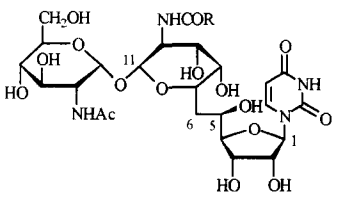
Abstract

The synthesis of the title compounds is described, i.e. coupling of the ylide, generated from the iodophosphonium salt of protected *N*-phthaloyl-D-galactosamine with 2,3-*O*-isopropylidene D-*ribo*-aldehyde afforded an undecose in high yield. Hydroboration–oxidation reaction of the olefinic linkage in the undecose led to the desired tunicamine, as the predominant product. After conversion of the latter to a glycosyl acceptor, this was assembled with the fully protected 2-oxyimino-2-deoxy-α-D-*arabino*-hexopyranosyl bromide, leading to a trehalose-type α,β-disaccharide. © 1997 Elsevier Science Ltd.

Keywords: Tunicamine; Wittig reaction; α,β-trehaloses

1. Introduction

Tunicamycins have been demonstrated [2] as potential inhibitors of glycosidase processing enzymes. Their structures are of particular interest, because they are composed of the eleven-carbon atoms tunicamine, connected by a trehalose-type linkage with *N*-acetyl-D-glucosamine, and by a nucleoside-type linkage with the uracil unit. Besides, tunicamine possesses the structure of a *C*-disaccharide owing to the C–C linkage between the terminal atoms of D-galactosamine and D-ribose. This structural complexity coupled with its biological properties has made tunicamycin an attractive target for a number of synthetic efforts [3]. Here we describe a novel synthetic approach to the tunicamycin subunits preceded by our model studies on the preparation of deaminotunicaminyl uracil [4], and α,β-nonreducing disaccharides related to tunicamycin [5].



R = -CH=CH-$(CH_2)_n$-CH-$(CH_3)_2$ n = 7-11
R = -CH=CH-$(CH_2)_n$-CH_3 n = 10-13

2. Results and discussion

In formulating a general strategy for the synthesis of tunicamine, being a central part of tunicamycins

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[1] Dedicated to Professor Hans Paulsen on the occasion of his 75th birthday.

[2] Preliminary communication – Ref. [1].

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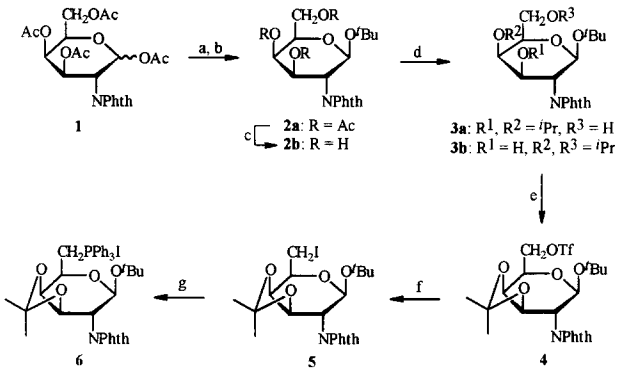
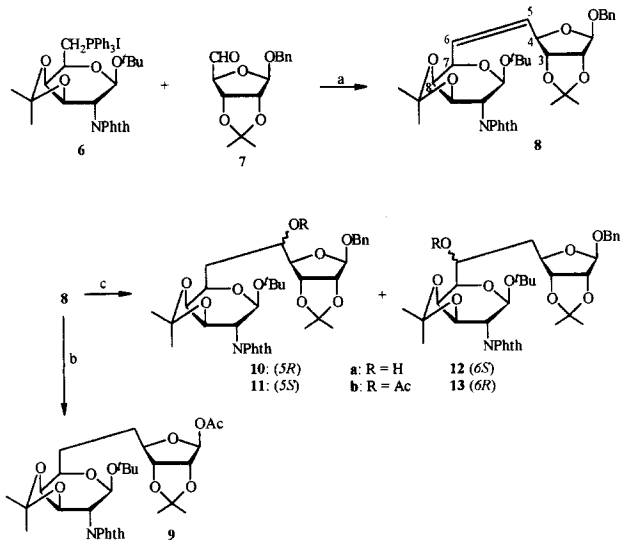


Scheme 1. (a) HBr, AcOH; (b) *t*-BuOH, AgOTf, sym.-collidine, CH_2Cl_2, −20 °C; (c) NaOMe, MeOH, 10 min; (d) acetone, $CuSO_4$, CSA; (e) Tf_2O, pyridine, CH_2Cl_2; (f) *n*-Bu_4NI, DMF; (g) PPh_3, sulfolane.

we recognized the potential of the Wittig reaction to generate the unsaturated aminoundecose from the terminal monosaccharide iodophosphonium ylide and the terminal sugar aldehyde [6]. In such an approach the synthesis of tunicamine could be simplified to the coupling of two sugar components, 'tail by tail', i.e. the 6-phosphonium iodide of *O,N*-protected D-galactosamine (Scheme 1) with an aldehyde derived from D-ribofuranoside, thus leading to the undecose **8** (Scheme 2), and subsequent hydration of its double bond in a stereo- and regio-selective manner [4].

Construction of the key compound, undecose **8** necessitated the preparation of the suitably protected Wittig partners. Assuming that tunicamine should be used further as a glycosylic acceptor in a condensation process with the glucosaminyl donor, the amino



Scheme 2. (a) HMDSLi, THF–HMPA; (b) H_2, Pd–C; (c) $BH_3 \cdot THF$; H_2O_2, OH^-.

group in the galactosamine was blocked with the phthaloyl residue. Its stereodirecting role in a creation of the desired β-glycosidic linkage from the side of the glycosylic acceptor, presumably because of steric interactions, was well documented in our previous studies on the synthesis of α,β-trehaloses [5].

For protection of the anomeric hydroxyl group in **1** the readily removable [7] *t*-butyl residue was used. As outlined in Scheme 1, the *t*-butyl glycoside **2** was obtained in 85% yield as the only isolated product. Sequential deacetylation–isopropylidenation of **2** afforded **3a** accompanied by its 4,6-di-*O*-isopropylidene derivative **3b** easily convertible (by treatment with catalytic amount of camphorosulfonic acid in acetone) to **3a**. Attempts at direct iodination [8] of **3a** to **5** either failed or gave the iodide **5** in a low yield. Therefore the 6-OH group in **3a** was converted to the *O*-triflate **4** (92% yield) which underwent reaction with *n*-Bu_4NI in DMF to afford **5** (82% yield) and subsequently was readily converted into the phosphonium iodide **6** (92%) by heating with triphenylphosphine in sulfolane.

In keeping with earlier observations on the relative sensitivity of the phthalimido group towards bases, generation of the ylide from **6** required a milder base then *n*-BuLi, earlier used in the Wittig reaction of sugars [6,9,10]. Moreover, the ylide should be generated under modified conditions making possible its immediate trapping with the aldehyde **7**; as a consequence the well known β-elimination process, characteristic for compounds with the vicinal β-alkoxy substituent [11] should be avoided. With this in mind, the reaction was conducted by dropwise addition of HMDSLi (1 M solution in hexane) to a mixture of **6** and aldehyde **7** in HMPA–THF solvents at −70 °C (Scheme 2); as the result the desired undecose **8** was isolated in high yield (76%) after chromatography; no other reaction products were discernible. The configuration of the chiral centres C-5 (D-*galacto*) and C-4 (D-*ribo*) of the parent monosaccharides **6** and **7**, respectively, was preserved in product **8**, as indicated by its ^1H NMR data ($J_{3,4} < 0.5$; $J_{7,8}$ 2.3 Hz). The *Z*-configuration of the C-5–C-6 olefinic linkage was confirmed by coupling constants $J_{5,6}$ 11.2 Hz, this being in full agreement with that reported by Secrist for an analogous deaminoundecose [6].

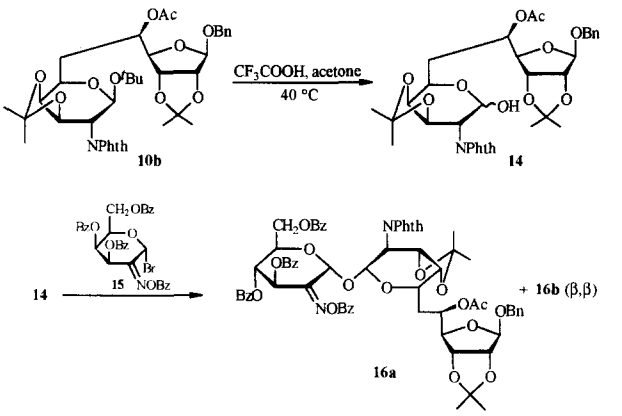
This high-yielding synthesis of the undecose **8**, employing 6-phosphonium iodide **6**, is the first example of a successful Wittig reaction in amino sugar chemistry. Previous attempts at such a condensation have been reported [10] but they failed. This repre-

sents a particularly attractive target for introduction of different functions across the double bond which could lead to a new class of the eleven-carbon amino sugars. The first one which we obtained was 5-deoxytunicamine **9**, simply formed by catalytic hydrogenation of **8**.

In order to prepare the desired tunicamine from **8**, the addition of one hydroxyl group at C-5 (5*R*) was necessary. For this purpose a hydroboration–oxidation procedure was applied (Scheme 2). Thus, undecose **8** was treated with $BH_3 \cdot THF$ complex at 0 °C for 1 h. Subsequently, careful oxidation of the reaction products with hydrogen peroxide under alkaline conditions at 0 °C led to the diastereomeric mixture of alcohols that, after acetylation, was separated by chromatography. All the stereoisomers **10a–13a** were formed in a ratio 61:10:21:8 (**10a**:**11a**:**12a**:**13a**, respectively). Their structure were deduced from ^1H NMR data, being for tunicamine derivative **10b** (5*R*) identical with those reported [3e], and for **11b–13b** comparable to those of analogous compounds [4,12]. Further evidence for the structure of **10b** was gained from a single crystal X-ray determination [13]. It is worth noting that the stereo- and regio-chemical outcome of the hydroboration–oxidation reaction of olefin **8** was unpredictable (lack of evident intra- or inter-molecular stereodirecting factors [14,15]). Nevertheless, the formation of the desired isomer **10a** (tunicamine) was highly favoured (61%). This may result from initial coordination of boron by the oxygen atom of the furanose ring.

Approaching the synthesis of a non-reducing disaccharide subunit composed of α-D-glucosamine and β-tunicamine we adopted the previously elaborated methodology [5]. We then established that α,β-configuration of the glycosylation reaction products is controlled by C-2 protecting groups both in the glycosyl donor and acceptor. Thus, the glycosyl donor with C-2 (benzoyloxy-imino) substituent (a precursor of the amino group) led to the α-linkage, whereas the glycosyl acceptor with C-2 phthalimido substituent formed the β glycosidic linkage. Hence, preparation of suitably protected glycosyl partners were required.

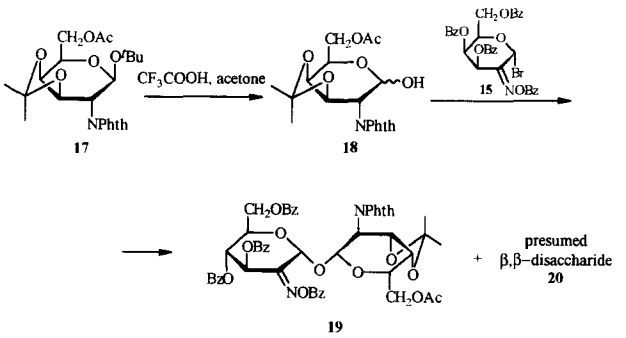
In the first stage, hydrolysis of the anomeric *t*-butyl group in tunicamine **10b** was attempted under the described condition [7] using CF_3COOH in dichloromethane at −10 °C → rt. This approach failed; instead the *O*-isopropylidene ring was cleaved. The hydrolysis was succeeded in a mixture of CF_3COOH and acetone (1:1) at 40 °C to give the glycosyl acceptor **14** (Scheme 3). Condensation of **14** with the bromide **15** [16] promoted by AgOTf and



Scheme 3.

sym.-collidine at −78 °C proceeded smoothly to furnish unexpectedly a mixture of two products which were separated by chromatography to give the desired α,β-disaccharide **16a** (Scheme 3), and its β,β-anomer **16b** in a ratio 2.5:1, respectively. Such a stereochemical outcome of glycosylation drastically differed from that of coupling of the analogues partners yielding α,β-glycosides exclusively [5]. To complete those experiments, the bromide **15** was coupled with **18**, to give rise to two products **19** and **20** in a ratio 3:1, respectively (Scheme 4). This revealed a conformational aspect of control on the stereochemistry of a trehalose linkage formation. Presumably, the rigid conformation of the galactopyranose ring in **14** and **17** owing to 3,4-*O*-isopropylidene protection, or the isopropylidene ring itself, causes a steric hindrance for the α-attack of the glycosylation agent. This observation corroborates previous data [5] on stereodirecting factors of α,β-linkage formation in nonreducing disaccharides related to tunicamycin.

In conclusion, a new synthesis of tunicamine is described in a straightforward procedure permitting preparation of various amino undecoses from readily available substrates in two steps. The stereoselective formation of the tunicamine-disaccharide subunit with



Scheme 4.

differently blocked amino functions is also noteworthy as it allows for introduction of the desired acyl residues. A stereospecific conversion of 2-benzoyloxyimno-2-deoxy-α-D-*arabino* unit in compound **16a** to the glucosamine is accessible by the previously elaborated method for the analogous disaccharides [5,17].

3. Experimental

General methods.—Optical rotations were determined with a JASCO DIP-360 digital polarimeter on solution in $CHCl_3$. ^1H NMR spectra were recorded with a Bruker AM-500 (500 MHz) for solution in $CDCl_3$ (internal Me_4Si). High resolution mass spectra (HRMS) were measured on a AMD-604 mass spectrometer. Melting points were measured on a Kofler hot-stage and are uncorrected. Reactions were monitored by TLC on Silica Gel 60 F_{254} plates (Merck), and column chromatography was performed on Silica Gel G (Merck 230–400 mesh).

t-*Butyl 3,4,6-tri*-O-*acetyl-2-deoxy-2*-N-*phthaloyl*-β-D-*galactopyranoside* (**2a**).—To a solution of **1** [16] (8.5 g, 17.8 mmol) in CH_2Cl_2 (250 mL) was added HBr (4.1 M solution in CH_3COOH, 6.5 mL, 26.6 mmol) at 0 °C. The ice bath was removed and the mixture was stirred for 4 h, whereupon dry toluene (ca. 10 mL) was added and solvents were removed under reduced pressure. The residue was filtered through alkaline Al_2O_3 in vacuo by the use of dry toluene as the eluant, to provide the crude bromide which was dissolved in CH_2Cl_2 (10 mL). This solution was added dropwise to a mixture of *t*-BuOH (2.8 g, 35 mmol), AgOTf (6.3 g, 24.5 mmol), and sym.-collidine (2.5 mL, 18.8 mmol) in CH_2Cl_2 (100 mL) at −20 °C. The mixture was stirred for 2 h at 0 °C, then quenched with saturated aq $Na_2S_2O_3$, and washed successively with H_2O, aq HCl (1 M), and H_2O. Isolation of the product by chromatography using hexane–EtOAc (3:1) as eluant gave the β-glycoside **2a** as an amorphous powder (7.4 g, 85%): $[\alpha]_D$ −15.5° (c 2.1, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ 1.10 (s, 9 H, *t*-Bu), 1.86, 2.05, 2.18 (3s, 3 × 3 H, 3 × Ac), 4.05–4.30 (m, 3 H, H-5, H-6a, H-6b), 4.53 (dd, 1 H, H-2), 5.40 (d, 1 H, H-1), 5.48 (bd, 1 H, H-4), 5.89 (dd, 1 H, H-3), 7.70–7.90 (m, 4 H, *N*-Phth); $J_{1,2}$ 8.4, $J_{2,3}$ 11.5, $J_{3,4}$ 3.5, $J_{4,5} < 0.8$ Hz. HRMS (EI) Calcd for $C_{21}H_{20}NO_9$ $(M-O-t\text{-}Bu)^+$: 418.1138. Found: 418.1140.

t-*Butyl 2-deoxy-2*-N-*phthaloyl*-β-D-*galactopyranoside* (**2b**).—To a solution of **2a** (7.2 g, 14.65 mmol) in abs MeOH (80 mL), cooled to 0 °C, was slowly added NaOMe (1 g, 18.5 mmol) while stirring. After 10 min solid NH_4Cl (~ 2.0 g) was added, and oxygen was bubbled during 1 h. Methanol was evaporated, and the residue redissolved in $CHCl_3$ (100 mL) was filtered through Celite. Removal of the solvent left the crude product **2b** (5.5 g) as an amorphous powder: $[\alpha]_D$ −16.2° (c 1.0, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$ with D_2O): δ 1.06 (s, 9 H, *t*-Bu), 3.75 (~ t, 1 H, H-5), 3.48 (~ d, 2 H, H-6a, H-6b), 4.14 (bd, 1 H, H-4), 4.26 (dd, 1 H, H-2), 4.50 (dd, 1 H, H-3), 5.26 (d, 1 H, H-1), 7.67–7.88 (m, 4 H, *N*-Phth); $J_{1,2}$ 8.3, $J_{2,3}$ 11.1, $J_{3,4}$ 3.4, $J_{5,6a} = J_{5,6b} \sim 6.0$ Hz.

t-*Butyl 2-deoxy-2*-N-*phthaloyl-3,4*-O-*isopropylidene- and 4,6*-O-*isopropylidene*-β-D-*galactopyranoside* (**3a** *and* **3b**), *respectively.*—Anhydrous $CuSO_4$ (16 g) and camphorosulfonic acid (200 mg) were added to a solution of **2b** (5.5 g) in acetone, and the mixture was stirred for 24 h at room temperature. After neutralisation with solid $NaHCO_3$, acetone was removed to give a syrup, composed of two products which were separated by chromatography (hexane–EtOAc, 2:1). Eluted first was **3a** (3.4 g, 57%): mp 202–203 °C; $[\alpha]_D$ +14.6° (c 1.7, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 1.10 (s, 9 H, *t*-Bu), 1.32, 1.63 (2s, 2 × 3 H, *i*-Pr), 2.08 (dd, 1 H, OH), 3.86 (~ ddd, 1 H, H-5), 3.97–4.14 (m, 2 H, H-6a, H-6b), 4.22 (dd, 1 H, H-4), 4.28 (t, 1 H, H-2), 4.91 (dd, 1 H, H-3), 5.22 (d, 1 H, H-1), 7.70–7.90 (m, 4 H, *N*-Phth); $J_{1,2}$ 8.7, $J_{2,3}$ 9.2, $J_{3,4}$ 5.1, $J_{4,5}$ 1.8, $J_{5,6a}$ 7.5, $J_{5,6b}$ 9.7 Hz. HRMS (EI) Calcd for $C_{17}H_{18}NO_6$ $(M-O-t\text{-}Bu)^+$: 332.1134. Found: 332.1135.

Eluted second was **3b** (1.5 g, 25%): amorphous powder; $[\alpha]_D$ −20.0° (c 1.7, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 1.09 (s, 9 H, *t*-Bu), 1.49, 1.53 (2s, 2 × 3 H, *i*-Pr), 2.51 (d, 1 H, OH), 3.48 (m, 1 H, H-5), 3.95 (dd, 1 H, H-6a), 4.13 (dd, 1 H, H-6b), 4.22 (dd, 1 H, H-4), 4.34 (dd, 1 H, H-2), 4.56 (ddd, 1 H, H-3), 5.24 (d, 1 H, H-1), 7.68–7.92 (m, 4 H, Ar); $J_{1,2}$ 8.2, $J_{2,3}$ 11.0, $J_{3,4}$ 4.1, $J_{4,5}$ 1.0, $J_{6a,5}$ 1.7, $J_{6b,5}$ 2.3, $J_{6a,6b}$ 12.7 Hz. HRMS (EI) Calcd for $C_{17}H_{18}NO_6$ $(M-O-t\text{-}Bu)^+$: 332.1134. Found: 332.1135.

Compound **3b** was transformed into **3a** by treatment with camphorosulfonic acid in acetone followed by isolation in the above described manner.

t-*Butyl 2-deoxy-2*-N-*phthaloyl-3,4*-O-*isopropylidene-6*-O-*(trifluorometanesulfonyl)*-β-D-*galactopyranoside* (**4**).—Freshly distilled Tf_2O (2.25 mL, 14.9 mmol) was slowly added to a solution of pyridine (1.2 mL, 14.9 mmol) in CH_2Cl_2 (80 mL) at −20 °C. Compound **3a** (2.8 g, 66.9 mmol) dissolved in CH_2Cl_2 was added and the mixture was allowed to attain

room temperature. After 2 h the solution was washed with aq HCl (0.1 M), aq $NaHCO_3$, H_2O, and dried. Removal of the solvent left a syrup, that was purified by filtration through silica gel (hexane–EtOAc, 3:1) to afford the crystalline **4** (3.4 g, 92%): mp – decomp > 105 °C; $[\alpha]_D$ +13.2° (c 1.7, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ 1.10 (s, 9 H, *t*-Bu), 1.31, 1.63 (2s, 2 × 3 H, *i*-Pr), 4.21 (dd, 1 H, H-4), 4.27 (t, 1 H, H-2), 4.31 (m, 1 H, H-5), 4.71–4.85 (m, 2 H, H-6a, H-6b), 4.92 (dd, 1 H, H-3), 5.24 (d, 1 H, H-1), 7.70–7.90 (m, 4 H, *N*-Phth); $J_{1,2}$ 8.7, $J_{3,2}$ 9.0, $J_{3,4}$ 5.1, $J_{4,5}$ 2.0 Hz. HRMS (LSIMS-NBA) Calcd for $C_{18}H_{17}F_3NO_8S$ $(M–O–t\text{-}Bu)^+$: 464.0627. Found: 464.0621.

t-*Butyl 2,6-dideoxy-2-*N*-phthaloyl-3,4-*O*-isopropylidene-6-iodo-β-*D*-galactopyranoside* (**5**).—After heating of **4** (3.3 g, 6.14 mmol) with $n\text{-}Bu_4NI$ (5.0 g, 13.5 mmol) in DMF (50 mL) for 1.5 h at 60 °C the mixture was poured into H_2O (500 mL), and the product was extracted with ether. The extract was washed with satd aq $Na_2S_2O_3$, H_2O, and concentrated to dryness. Chromatography (hexane–EtOAc, 4:1) gave the iodide **5** as a crystals (2.6 g, 82%): mp 137 °C; $[\alpha]_D$ +24.6° (c 1.9, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 1.18 (s, 9 H, *t*-Bu), 1.38, 1.68 (2s, 2 × 3 H, *i*-Pr), 3.44–3.59 (m, 2 H, H-6a, H-6b), 4.15 (ddd, 1 H, H-5), 4.31 (t, 1 H, H-2), 4.40 (dd, 1 H, H-4), 4.93 (dd, 1 H, H-3), 5.10 (d, 1 H, H-1), 7.75–7.94 (m, 4 H, *N*-Phth); $J_{1,2}$ 8.7, $J_{3,2}$ 9.2, $J_{3,4}$ 5.1, $J_{4,5}$ 2.0, $J_{5,6a}$ 5.9, $J_{5,6b}$ 7.9 Hz. HRMS (EI) Calcd for $C_{17}H_{17}INO_5$ $(M–O–t\text{-}Bu)^+$: 442.0151. Found: 442.0148.

t-*Butyl 2,6-dideoxy-2-*N*-phthaloyl-3,4-*O*-isopropylidene-6-(triphenylphosphonioiodo)-β-*D*-galactopyranoside* (**6**).—To a solution of **5** (0.96 g, 1.86 mmol) in sulfolane (10 mL) was added PPh_3 (2.5 g, 9.5 mmol) at 80 °C, then the temperature was raised to 110 °C. Heating was continued for 5 h. After cooling the reaction mixture was diluted with $CHCl_3$ (10 mL), and added dropwise to ether (2.5 L) with vigorous stirring, then left for 16 h; white precipitate was formed, separated by filtration. The mother liquor was concentrated and we proceeded as above; the title **6** was obtained in 92% yield altogether (1.33 g): mp 177–179 °C; $[\alpha]_D$ +30.3° (c 1.6, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ 0.58 (s, 9 H, *t*-Bu), 1.41, 1.61 (2s, 2 × 3 H, *i*-Pr), 3.80 (dt, 1 H, H-6a), 4.22 (t, 1 H, H-2), 4.60 (m, 1 H, H-5), 4.88 (d, 1 H, H-1), 4.89 (dd, 1 H, H-3), 5.06 (dd, 1 H, H-4), 5.20 (dt, 1 H, H-6b), 7.56–8.00 (m, 19 H, Ar); $J_{1,2}$ 9.5, $J_{3,2}$ 9.6, $J_{3,4}$ 4.9, $J_{4,5}$ 1.9, $J_{6a,5}$ 10.0, $J_{6a,6b}$ 16.0, $J_{6a,P}$ 10.0, $J_{6b,5}$ 2.6, $J_{6b,P}$ 15.6 Hz. HRMS (EI) Calcd for $C_{39}H_{41}NO_6P$ $(M + I)^+$: 650.2672. Found: 650.2673.

(Z)-*1-(Benzyl 2,3-*O*-isopropylidene-β-*D*-ribo-tetrafuranosid-4-yl)-2-(*t*-butyl 2-deoxy-2-*N*-phthaloyl-3,4-*O*-isopropylidene-α-*D*-galacto-pentopyranos-5-yl)ethylene* (**8**).—To a solution of **6** (0.8 g, 1.05 mmol) and the aldehyde **7** [4] (0.43 g, 1.55 mmol) in a mixture of THF-HMPA (5:1, 24 mL) cooled to −78 °C lithium bis(trimethylsilyl)amide (1.0 mL, 1 M solution in hexane) was added dropwise under Ar. The temperature was allowed to rise to −10 °C during 1 h period, whereupon satd aq NH_4Cl was added, and stirring was continued for 1 h at rt. Extraction with ether and subsequent chromatography (hexane–EtOAc, 4:1) gave the olefin **8** (0.52 g, 76%) as an amorphous powder: $[\alpha]_D$ −32.0° (c 1.4, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 1.09 (s, 9 H, *t*-Bu), 1.27, 1.31, 1.52, 1.62 (4s, 4 × 3 H, 2 × *i*-Pr), 4.30 (t, 1 H, H-10), 4.33 (dd, 1 H, H-8), 4.37 and 4.68 (ABq, 2 H, CH_2Ph, *J* 11.2 Hz), 4.70, 4.76 (2d, 2 H, H-2, H-3), 4.83 (m, 1 H, H-7), 4.92 (dd, 1 H, H-9), 5.03 (bd, 1 H, H-4), 5.19 (s, 1 H, H-1), 5.27 (d, 1 H, H-11), 5.80 (ddd, 1 H, H-5), 5.97 (ddd, 1 H, H-6), 7.28–7.38 (m, 5 H, Ph), 7.69–7.89 (m, 4 H, *N*-Phth); $J_{2,3}$ 5.9, $J_{5,4}$ 9.1, $J_{5,6}$ 11.1 (*Z*), $J_{5,7}$ 1.1, $J_{6,4}$ 1.1, $J_{6,7}$ 8.2, $J_{8,7}$ 2.3, $J_{8,9}$ 5.1, $J_{9,10}$ 9.3, $J_{11,10}$ 8.7 Hz. HRMS (EI) Calcd for $C_{35}H_{40}NO_{10}$ $(M–CH_3)^+$: 634.2652. Found: 634.2657.

*1-*O*-Acetyl-5-*C*-(t-butyl 2,6-dideoxy-2-*N*-phthaloyl-3,4-*O*-isopropylidene-β-*D*-galactopyranosid-6-yl)-5-deoxy-2,3-*O*-isopropylidene-β-*D*-ribofuranose* (**9**).—A solution of olefin **8** (60 mg, 0.119 mmol) in EtOH (10 mL) was hydrogenated with H_2 in presence of Pd–C (10%, 30 mg) for 24 h. After filtration and evaporation to dryness, the residue was treated with a mixture of pyridine and Ac_2O. Usual work-up followed by chromatography (hexane–EtOAc, 3:1) gave **9** (35 mg, 58%) as an oil: $[\alpha]_D$ −12.9° (c 0.7, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 1.07 (s, 9 H, *t*-Bu), 1.31, 1.33, 1.50, 1.62 (4s, 4 × 3 H, 2 × *i*-Pr), 1.64–1.87 (m, 3 H, H-5a, H-5b, H-6), 2.07 (s, 3 H, Ac), 3.87 (ddd, 1 H, H-7), 4.08 (dd, 1 H, H-8), 4.22 (t, 1 H, H-10), 4.33 (dd, 1 H, H-4), 4.59 (dd, 1 H, H-3), 4.73 (d, 1 H, H-2), 4.82 (dd, 1 H, H-9), 5.15 (d, 1 H, H-10), 6.21 (s, 1 H, H-1), 7.68–7.89 (2m, 2 × 2 H, *N*-Phth); $J_{2,3}$ 5.9, $J_{3,4}$ 0.5, $J_{4,5a}$ 6.1, $J_{4,5b}$ 9.5, $J_{7,6a}$ 3.4, $J_{7,6b}$ 10.2, $J_{7,8}$ 1.9, $J_{8,9}$ 5.1, $J_{9,10}$ 9.2, $J_{11,10}$ 8.7 Hz. HRMS (EI) Calcd for $C_{30}H_{38}NO_{11}$ $(M–CH_3)^+$: 588.2444. Found: 588.2439.

*Hydroboration-oxidation of (Z)-1-(benzyl 2,3-*O*-isopropylidene-β-*D*-ribo-tetrafuranosid-4-yl-2-(t-butyl 2-deoxy-2-*N*-phthaloyl-3,4-*O*-isopropylidene-α-*D*-*

galacto-pentopyranos-5-yl)ethylene (**8**).—To a solution of **8** (0.43 g, 0.66 mmol) in abs THF (20 mL) was added dropwise B_2H_6 (6 mL, 1.2 M in THF) at −20 °C, and the mixture was stirred for 0.5 h at 0 °C. Then MeOH (20 mL) was slowly added, followed by aq NaOH (2 mL, 25%) and H_2O_2 (2 mL, 40%). After keeping the reaction for 1 h at 0 °C it was poured into satd aq NH_4Cl. Extraction with ether, and chromatography (hexane–EtOAc, 2:1) of the extract gave three fractions: (1) a mixture of two isomers **11a** and **12a**; (2) isomer **10a** (0.16 g, 34%); (3) isomer **13a** (23 mg, 4.5%).

Characteristic data for *benzyl-5*-C-(t-*butyl 2,6-dideoxy-2*-N-*phthaloyl-3,4*-O-*isopropylidene*-β-D-*galactopyranosid-6-yl*)-*2,3*-O-*isopropylidene*-β-D-allo-*pentofuranoside* (**10a**): crystals; mp 207–208 °C; $[\alpha]_D$ −17.3° (c 1.2, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 1.07 (s, 9 H, *t*-Bu), 1.31, 1.33, 1.48, 1.63 (4s, 4 × 3 H, 2 × *i*-Pr), 1.72 (ddd, 1 H, H-6a), 2.19 (m, 1 H, H-6b), 4.03 (m, 1 H, H-5), 4.09 (dd, 1 H, H-8), 4.20 (dt, 1 H, H-7), 4.26 (t, 1 H, H-10), 4.32 (d, 1 H, H-4), 4.56 and 4.76 (ABq, 2 H, CH_2Ph, *J* 11.5 Hz), 4.67 (d, 1 H, H-3), 4.86 (dd, 1 H, H-9), 4.89 (d, 1 H, H-2), 5.18 (s, 1 H, H-1), 5.18 (d, 1 H, H-11), 7.28–7.37 (m, 5 H, Ph), 7.68–7.89 (m, 4 H, *N*-Phth); $J_{2,3}$ 6.0, $J_{4,5}$ 1.4, $J_{6a,5}$ 2.2, $J_{6a,6b}$ 14.2, $J_{6a,7}$ 11.1, $J_{7,6b}$ 1.7, $J_{8,7}$ 1.9, $J_{8,9}$ 5.1, $J_{9,10}$ 9.2, $J_{11,10}$ 8.7 Hz. HRMS (EI) Calcd for $C_{35}H_{42}NO_{11}$ $(M-CH_3)^+$: 652.2758. Found: 652.2760.

Characteristic data for (**10b**): crystals; mp 190–191 °C; $[\alpha]_D$ −27.8° (c 1.1, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 1.06 (s, 9 H, *t*-Bu), 1.31, 1.33, 1.48, 1.62 (4s, 4 × 3 H, 2 × *i*-Pr), 1.87 (ddd, 1 H, H-6a), 2.02 (s, 3 H, Ac), 2.45 (ddd, 1 H, H-6b), 3.86 (dt, 1 H, H-7), 4.04 (dd, 1 H, H-8), 4.24 (t, 1 H, H-10), 4.25 (dd, 1 H, H-4), 4.47 and 4.73 (ABq, 2 H, CH_2Ph, *J* 12.2 Hz), 4.67 (d, 1 H, H-3), 4.77 (dd, 1 H, H-3), 4.85 (dd, 1 H, H-9), 5.13 (d, 1 H, H-11), 5.14 (s, 1 H, H-1), 5.35 (ddd, 1 H, H-5), 7.28–7.40 (m, 5 H, Ph), 7.65–7.90 (m, 4 H, *N*-Phth); $J_{2,3}$ 6.0, $J_{3,4}$ 1.2, $J_{5,4}$ 6.2, $J_{5,6a}$ 10.0, $J_{5,6b}$ 2.0, $J_{6a,6b}$ 15.2, $J_{6a,7}$ 2.1, $J_{6b,7}$ 10.4, $J_{8,7}$ 2.0, $J_{8,9}$ 5.1, $J_{9,10}$ 9.3, $J_{11,10}$ 8.7 Hz. HRMS (EI) Calcd for $C_{37}H_{44}NO_{12}$ $(M-CH_3)^+$: 694.2864. Found: 694.2867.

Characteristic data for *benzyl-5*-C-(t-*butyl 2-dideoxy-2*-N-*phthaloyl-3,4*-O-*isopropylidene*-D-*glycero*-β-D-*galactopyranosid-6-yl*)-*5-deoxy-2,3*-O-*isopropylidene*-β-D-*ribofuranoside* (**13a**): crystals; mp 202–203 °C; $[\alpha]_D$ −15.3° (c 1.2, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$ with D_2O): δ 1.03 (s, 9 H, *t*-Bu), 1.32, 1.33, 1.49, 1.59 (4s, 4 × 3 H, 2 × *i*-Pr), 1.79 (ddd, 1 H, H-5a), 2.21 (ddd, 1 H, H-5b), 3.71 (dd, 1 H, H-7), 4.26 (t, 1 H, H-10), 4.30 (dt, 1 H, H-6), 4.44 (dd, 1 H, H-8), 4.48 and 4.77 (ABq, 2 H, CH_2Ph), 4.55 (dd, 1 H, H-4), 4.71 (d, 1 H, H-2), 4.73 (dd, 1 H, H-3), 4.88 (dd, 1 H, H-9), 5.14 (d, 1 H, H-11), 5.18 (s, 1 H, H-1), 7.28–7.38 (m, 5 H, Ph), 7.69–7.90 (m, 4 H, *N*-Phth); $J_{2,3}$ 6.0, $J_{3,4} < 0.3$, $J_{4,5a}$ 5.3, $J_{4,5b}$ 9.6, $J_{5a,6}$ 9.5, $J_{5a,5b}$ 14.4, $J_{5b,6}$ 2.5, $J_{7,6}$ 8.3, $J_{7,8}$ 2.2, $J_{8,9}$ 5.2, $J_{9,10}$ 9.3, $J_{11,10}$ 8.7 Hz. HRMS (EI) Calcd for $C_{35}H_{42}NO_{11}$ $(M-CH_3)^+$: 652.2758. Found: 652.2759.

Characteristic data for (**13b**): amorphous powder; $[\alpha]_D$ −11.0° (c 0.7, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 1.05 (s, 9 H, *t*-Bu), 1.19, 1.32, 1.48, 1.54 (4s, 4 × 3 H, 2 × *i*-Pr), 2.05 (ddd, 1 H, H-5a), 2.11 (s, 3 H, Ac), 2.39 (ddd, 1 H, H-5b), 3.99 (dd, 1 H, H-7), 4.23 (t, 1 H, H-10), 4.24 (dd, 1 H, H-8), 4.34 (dd, 1 H, H-4), 4.51 and 4.78 (ABq, 2 H, CH_2Ph, *J* 12.2 Hz), 4.66 (dd, 1 H, H-3), 4.72 (d, 1 H, H-2), 4.82 (dd, 1 H, H-9), 5.13 (s, 1 H, H-1), 5.15 (d, 1 H, H-11), 5.45 (ddd, 1 H, H-6), 7.28–7.40 (m, 5 H, Ph), 7.69–7.89 (m, 4 H, *N*-Phth); $J_{2,3}$ 5.9, $J_{3,4} < 0.4$, $J_{4,5a}$ 4.8, $J_{4,5b}$ 10.1, $J_{5a,6}$ 8.2, $J_{5a,5b}$ 14.5, $J_{5b,6}$ 3.0, $J_{6,7}$ 5.2, $J_{7,8}$ 2.0, $J_{9,8}$ 5.0, $J_{9,10}$ 9.2, $J_{11,10}$ 8.7 Hz.

A mixture of isomers **11a** and **12a** was acetylated, and the products were separated by chromatography (hexane–EtOAc, 3:1). Eluted first was *benzyl 5*-O-*acetyl-5*-C-(t-*butyl 2,6-dideoxy-2*-N-*phthaloyl-3,4*-O-*isopropylidene*-β-D-*galactopyranosid-6-yl*)-*2,3*-O-*isopropylidene*-α-L-talo-*pentofuranoside* (**11b**): (25 mg, 5%); amorphous powder; $[\alpha]_D$ −34.6° (c 0.7, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 1.08 (s, 9 H, *t*-Bu), 1.28, 1.31, 1.49, 1.62 (4s, 4 × 3 H, 2 × *i*-Pr), 2.07 (s, 3 H, Ac), 2.11–2.20 (m, 1 H, H-6a), 2.28 (ddd, 1 H, H-6b), 3.96 (dt, 1 H, H-7), 4.23 (dd, 1 H, H-8), 4.24 (t, 1 H, H-10), 4.34 (dd, 1 H, H-4), 4.43 and 4.71 (ABq, 2 H, CH_2Ph), 4.61 (d, 1 H, H-2), 4.74 (dd, 1 H, H-3), 4.83 (dd, 1 H, H-9), 5.17 (d, 1 H, H-11), 5.20 (s, 1 H, H-1), 5.19–5.23 (m, 1 H, H-5), 7.28–7.36 (m, 5 H, Ph), 7.66–7.90 (m, 4 H, *N*-Phth); $J_{2,3}$ 6.0, $J_{3,4}$ 1.8, $J_{4,5}$ 6.3, $J_{6b,5}$ 4.7, $J_{6b,7}$ 7.1, $J_{6b,6a}$ 14.2, $J_{7,6a}$ 7.1, $J_{7,8}$ 2.0, $J_{9,8}$ 5.1, $J_{9,10}$ 9.3, $J_{11,10}$ 8.7 Hz. HRMS (EI) Calcd for $C_{37}H_{44}NO_{12}$ $(M-CH_3)^+$: 694.2860. Found: 694.2860.

Eluted second was *benzyl-5*-C-(t-*butyl 6*-O-*acetyl-2-deoxy-2*-N-*phthaloyl-3,4*-O-*isopropylidene*-L-*glycero*-β-D-*galactopyranosid-6-yl*)-*5-deoxy-2,3*-O-*isopropylidene*-β-D-ribo-*furanoside* (**12b**): (53 mg, 11%); crystals; mp 178 °C; $[\alpha]_D$ −34.0° (c 1.5, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 1.07 (s, 9 H, *t*-Bu), 1.19, 1.32, 1.48, 1.60 (4s, 4 × 3 H, 2 × *i*-Pr), 2.00–2.07 (m, 1 H, H-5a), 2.06 (s, 3 H, Ac), 2.14 (ddd, 1 H, H-5b), 3.97 (dd, 1 H, H-7), 4.14 (dd, 1 H,

H-8), 4.24 (t, 1 H, H-10), 4.33 (bt, 1 H, H-4), 4.50 and 4.75 (ABq, 2 H, CH_2Ph), 4.65 (dd, 1 H, H-3), 4.70 (d, 1 H, H-2), 4.80 (dd, 1 H, H-9), 5.14 (d, 1 H, H-11), 5.17 (s, 1 H, H-1), 5.49 (ddd, 1 H, H-6), 7.28–7.36 (m, 5 H, Ph), 7.67–7.88 (m, 4 H, *N*-Phth); $J_{2,3}$ 6.0, $J_{3,4} < 0.5$, $J_{4,5a}$ 7.3, $J_{5b,4}$ 7.0, $J_{5b,6}$ 4.7, $J_{5b,5a}$ 14.2, $J_{6,5a}$ 8.0, $J_{6,7}$ 6.8 $J_{8,7}$ 1.9, $J_{8,9}$ 5.0, $J_{9,10}$ 9.2, $J_{11,10}$ 8.7 Hz. HRMS (EI) Calcd for $C_{37}H_{44}NO_{12}$ $(M-CH_3)^+$: 694.2864. Found: 694.2867.

Benzyl 5-O-acetyl-5-C-(2,6-dideoxy-2-N-phthaloyl-3,4-O-isopropylidene-β-D-galactopyranos-6-yl)-2,3-O-isopropylidene-β-D-allo-pentofuranoside (**14**).—A solution of **10b** (0.12 g, 0.169 mmol) and CF_3COOH (2 mL) in acetone (2 mL) was kept at 40 °C for 1.5 h, then neutralized with solid $NaHCO_3$, and filtered through Celite. Evaporation to dryness, followed by chromatography yielded **14** (65 mg, 59%) as an amorphous powder: $[\alpha]_D$ +12.5° (c 0.6, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$ with D_2O): δ 1.32, 1.33, 1.50, 1.63 (4s, 4 × 3 H, 2 × *i*-Pr), 1.84 (ddd, 1 H, H-6a), 2.02 (s, 3 H, Ac), 2.51 (ddd, 1 H, H-6b), 3.80 (dt, 1 H, H-7), 4.05 (dd, 1 H, H-8), 4.17 (t, 1 H, H-10), 4.24 (dd, 1 H, H-4), 4.44 and 4.76 (ABq, 2 H, CH_2Ph, *J* 11.7 Hz), 4.69 (d, 1 H, H-2), 4.73 (dd, 1 H, H-3), 4.80 (dd, 1 H, H-9), 5.14 (d, 1 H, H-11), 5.19 (s, 1 H, H-1), 5.43 (ddd, 1 H, H-5), 7.28-7.41 (m, 5 H, Ph), 7.69–7.88 (m, 4 H, *N*-Phth); $J_{2,3}$ 6.0, $J_{3,4}$ 0.7, $J_{4,5}$ 6.9, $J_{5,6a}$ 10.5, $J_{5,6b}$ 2.2, $J_{6a,6b}$ 15.0, $J_{6a,7}$ 2.1, $J_{6b,7}$ 10.9, $J_{8,7}$ 2.0, $J_{8,9}$ 5.0, $J_{9,10}$ 9.1, $J_{10,11}$ 8.7 Hz (β). HRMS (EI) Calcd for $C_{33}H_{36}NO_{12}$ $(M-CH_3)^+$: 638.2237. Found: 638.2236.

Benzyl 5-O-acetyl-5-C-[3′,4′,6′-tri-O-benzoyl-2′-(benzoyloxyimino)-2′-deoxy-α-D-arabino-hexopyranosyl 2,6-dideoxy-2-N-phthaloyl-3,4-O-isopropylidene-β-D-galactopyranosid-6-yl]-2,3-O-isopropylidene-β-D-allo-pentofuranoside (**16a**) *and benzyl 5-O-acetyl-5-C-[3′,4′,6′-tri-O-benzoyl-2′-(benzoyloxyimino)-2′-deoxy-β-D-arabino-hexopyranosyl 2,6-dideoxy-2-N-phthaloyl-3,4-O-iso-propylidene-β-D-galactopyranosid-6-yl]-2,3-O-isopropylidene-β-D-allo-pentofuranoside* (**16b**).—A solution of **14** (30 mg, 45.9 mmol), AgOTf (30 mg, 0.117 mmol), and sym. collidine (7 μL) in dry CH_2Cl_2 (2 mL) containing 3 A molecular sieves (~ 50 mg), was stirred at rt for 1.5 h under Ar in a light-protected flask, whereupon the mixture was cooled to −78 °C and the solution of bromide **15** [16] (50 mg, 74.3 μmol) in CH_2Cl_2 (1 mL) was added dropwise. Stirring at −78 °C was continued for 1.5 h, then the mixture was diluted with CH_2Cl_2 and filtered through Celite. The filtrate was successively washed with H_2O, aq $Na_2S_2O_3$, 0.1 M HCl, and aq $NaHCO_3$. Evaporation of the solvent, followed by chromatography of the residue (hexane–EtOAc, 2:1) afforded β,β-disaccharide **16b** (11 mg, 19%) in the first fraction and the desired α,β-disaccharide (26 mg, 46%) **16a** in the second fraction; characteristic data for **16a**: amorphous powder; $[\alpha]_D$ +30.5° (c 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 1.36, 1.38, 1.48, 1.72 (4s, 4 × 3 H, 2 × *i*-Pr), 1.84 (s, 3 H, Ac), 1.90 (ddd, 1 H, H-6a), 2.73 (ddd, 1 H, H-6b), 3.95 (dt, 1 H, H-7), 4.12 (dd, 1 H, H-8), 4.16–4.23 (m, 3 H, H-6′a, H-6′b, H-4), 4.48 (1/2 ABq, 1 H, 1/2 CH_2Ph, J_{AB} 12.3 Hz), 4.52 (t, 1 H, H-10), 4.79–4.85 (m, 4 H, H-2, H-9, H-5′, 1/2 CH_2Ph), 4.95 (d, 1 H, H-3), 5.21 (s, 1 H, H-1), 5.34 (ddd, 1 H, H-5), 5.44 (d, 1 H, H-11), 5.89 (t, 1 H, H-4′), 6.09 (d, 1 H, H-3′), 6.39 (s, 1 H, H-1′), 7.28–8.03 (m, 24 H, Ph); $J_{3,2}$ 5.9, $J_{3,4}$ 0.8, $J_{5,4}$ 1.1, $J_{5,6a}$ 9.0, $J_{5,6b}$ 1.1, $J_{6a,6b}$ 12.8, $J_{6a,7}$ 2.3, $J_{6b,7}$ 10.8, $J_{8,7}$ 1.9, $J_{8,9}$ 4.9, $J_{11,10}$ 8.8 (β), $J_{3',4'}$ 10.3, $J_{4',5'}$ 10.2 Hz. HRMS (LSIMS) Calcd for $C_{68}H_{64}N_2O_{21}$ $(M + Na)^+$: 1267.3901. Found: 1267.3899.

Characteristic data for **16b**: amorphous powder; $[\alpha]_D$ −24.9° (c 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 1.26, 1.41, 1.43, 1.61 (4s, 4 × 3 H, 2 × *i*-Pr), 1.84 (s, 3 H, Ac), 1.90–1.97 (m, 1 H, H-6a), 2.33–2.40 (m, 1 H, H-6b), 3.95 (dt, 1 H, H-7), 4.02 (dd, 1 H, H-4), 4.13 (dd, 1 H, H-8), 4.29 and 4.46 (ABq, 2 H, CH_2Ph, J_{AB} 11.4 Hz), 4.43 (t, 1 H, H-10), 4.51 (d, 1 H, H-3), 4.59 (dd, 1 H, H-6′a), 4.61 (dd, 1 H, H-2), 4.79–4.85 (m, 2 H, H-5′, H-9), 5.04 (s, 1 H, H-1), 5.49 (dt, 1 H, H-5), 5.65 (d, 1 H, H-11), 5.68 (dd, 1 H, H-4′), 6.10 (d, 1 H, H-3′), 6.59 (s, 1 H, H-1′), 7.28–8.03 (m, 24 H, Ph); $J_{2,3}$ 6.0, $J_{3,4}$ 1.3, $J_{4,5}$ 3.8, $J_{5,6a,b}$ 3.2 and 10.2, $J_{7,6a,b}$ 9.8 and 1.8, $J_{8,7}$ 1.7, $J_{8,9}$ 5.1, $J_{10,9}$ 8.8, $J_{11,10}$ 8.8, $J_{3',4'}$ 3.4, $J_{4',5'}$ 6.3, $J_{6'b,5}$ 5.4, $J_{6'b,6'a}$ 11.5 Hz.

6-O-Acetyl-2-N-phthaloyl-3,4-O-isopropylidene-β-D-galactopyranose (**18**).—Hydrolysis of the anomeric *t*-butyl residue in **17** was performed according to procedure described for **14**, to give the product **18** in 62% yield: $[\alpha]_D$ +55.6° (c 1.3, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ 1.33, 1.63, (2s, 2 × 3 H, *i*-Pr), 2.12 (s, 3 H, Ac), 4.14–4.27 (m, 3 H, H-2, H-4, H-5), 4.35–4.46 (m, 2 H, H-6a, H-6b), 4.76 (bs, 1 H, OH), 4.88 (dd, 1 H, H-3), 5.30 (d, 1 H, H-1), 7.68–7.91 (m, 4 H, *N*-Phth); $J_{1,2}$ 8.8, $J_{3,2}$ 9.2, $J_{3,4}$ 5.0 Hz. HRMS (EI) Calcd for $C_{18}H_{18}NO_8$ $(M-CH_3)^+$: 376.1032. Found: 376.1032.

6-O-Acetyl-2-deoxy-2-N-phthaloyl-3,4-O-isopropylidene-β-D-galactopyranosyl 3,4,6 tri-O-benzoyl-2-(benzoyloxyimino)-2-deoxy-α-D-arabino-hexopyranoside (**19**).—A solution of **18** (15 mg, 38.3 μmol), AgOTf (20 mg, 77.8 μmol), and sym.-col-

lidine (4.6 mg) in dry CH_2Cl_2 containing 3 A molecular sieves (~ 30 mg), was treated with bromide **15** (39 mg, 58 μmol) according to the procedure described for **16**. The reaction products were isolated by chromatography (hexane–EtOAc, 2:1). Eluted first was β,β-disaccharide **20** (4 mg, 10%, not characterised), then **19** (20 mg, 53%): amorphous powder; $[\alpha]_D$ +48.3° (c 1.8, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 1.35, 1.73 (2 s, 2 × 3 H, *i*-Pr), 2.18 (s, 3 H, Ac), 4.26 (dd, 1 H, H-4), 4.47–4.35 (m, 2H, H-5, H-6 a), 4.37 (dd, 1 H, H-6'a), 4.46 (t, 1 H, H-2), 4.63 (dd, 1 H, H-6b), 4.73 (dd, 1 H, H-3), 4.83 (dd, 1 H, H-6'b), 4.92 (dt, 1 H, H-5'), 5.66 (d, 1 H, H-1), 6.02 (t, 1 H, H-4'), 6.36 (d, 1 H, H-3'), 6.43 (s, 1 H, H-1'), 7.3–8.1 (m, 24 H, Ph); $J_{1,2}$ 8.9, $J_{2,3}$ 9.1, $J_{3,4}$ 4.9, $J_{4,5}$ 1.9, $J_{6b,5}$ 1.7, $J_{6a,6b}$ 11.1, $J_{3',4'}$ 9.9, $J_{4',5'}$ 10.2, $J_{6'a,5'}$ 2.2, $J_{6'b,5'}$ 2.5, $J_{6'a,6'b}$ 12.5 Hz. HRMS (LSIMS) Calcd for $C_{53}H_{46}N_2Na$ $(M + Na)^+$: 1005.2694. Found: 1005.2704.

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