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# Improved synthesis of the Kijanimicin oligodeoxytetrasaccharide

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ABSTRACT

By sequential synthesis the four 2,6-dideoxy saccharide moieties of the kijanimicin tetrasaccharide could be stereoselectively assembled. For formation of all required 2-deoxy α-glycoside linkages various *S*-(hexopyranosyl)-phosphorodithioates as donor structures could be convincingly employed. The terminal 2-deoxy β-glycoside linkage was stereoselectively formed following the dibromomethyl methyl ether approach. The target octadeoxy-tetrasaccha-ride could be obtained via nine subsequent steps in 5% overall yield.

## 1. Introduction

From Kenian soil *Actinomadura kijanata* was isolated and shown to form the macrolide antibiotic Kijanimicin (**1**, Fig. 1) [1,2], the structure of which was nicely elucidated by Mallams et al. [3] In addition to antitumor activity **1** was observed to be effective against anaerobic bacteria as well as malaria [4,5]. The stereo-chemically rather complex macrolide is glycosylated at the 17-OH group with a methyl-branched dideoxy nitro-amino sugar E, named D-kijanose [6,7]. Further, at position 9 Kijanimicin is decorated with a tetrasaccharide moiety containing exclusively four L-digitoxose units A – D. The A, B, and C L-ribo moieties are interglycosidically linked via α,1–3 linkages, however, the 4-*O*-methylated terminal unit D is attached via a β,1–3 interglycosidic bond.

In previous studies the trisaccharide moity A-C could be nicely synthesized [8] employing the NIS reaction [9]. However, the attachment of the terminal D unit employing the approach reported by Wiesner et al. [10,11] could be just realized in moderate yields. Thus, substantial improvements toward formation of the decisive b,1–4 linkage and hence the tetrasaccharide would be desirable.

Earlier studies demonstrated the dibromomethyl methyl ether (DBE) [12] method to be efficiently employed for rather difficult β-glycosylations in the 2-deoxy sugar series [13,14]. Other accesses to α-glycosidically linked 2-deoxy sugars were developed by iodonium-promoted transformations employing *S*-(2-deoxy-glycosyl) phosphorodithioates obtained easily from glycals as donors [15].

## 2. Results and discussion

### 2.1. Synthesis of the B-A disaccharide precursor

Starting with L-rhamnal (**2**) [16] simple benzoylation using benzoylchloride at room temperature led to the mixture of 3-*O*– (**3**), 4-*O*– (**4**), and 3,4-di-*O*-benzoyl-L-rhamnal (**5**) in 95% yield and a ratio 19: 1: 3, which could be facile separated by chromatography. Thus, the desired compound **3** could be obtained in about 80% yield, which competes convincingly with previous more elaborate approaches for regioselective acylations of **2** employing dibutyl-stannylidene intermediates [17]. As reported before [15] treatment of **3** with *O*,*O*-diethyl *S*-hydrogen phosphorodithioate led to the raw *S*-(2-deoxy-α,β-L-arabino-hexopyranosyl)-phosphorodithioate (**6**), which could be directly used for glycosylation.

The acceptor formation started with 2-deoxy-L-rhamnose (**7**) [18] which gave both anomeric benzyl glycosides, from which the pure β-component **8** was separated. Inversion by Mitsunobu conditions [19,20] could be employed to give the monoinverted 3-*O*-benzoate **9**, and by alkaline treatment the L-ribo derivative **10** resulted in 75% yield via two steps. Benzylation with sodium hydride and benzylbromide in anhydrous dimethylformamide at room temperature gave 3-*O*– (**11**), 4-*O*– (**12**), and 3,4-di-*O*-benzyl-L-ribo-hexo-pyranoside (**13**) in 75% yield and a ratio of 4: 10: 1, which were separated by chromatography.

The rhamno-configured dithiophosphate **6** with its weakly nucleophilic ("disarmed") 4-OH group represents an ideal donor molecule.

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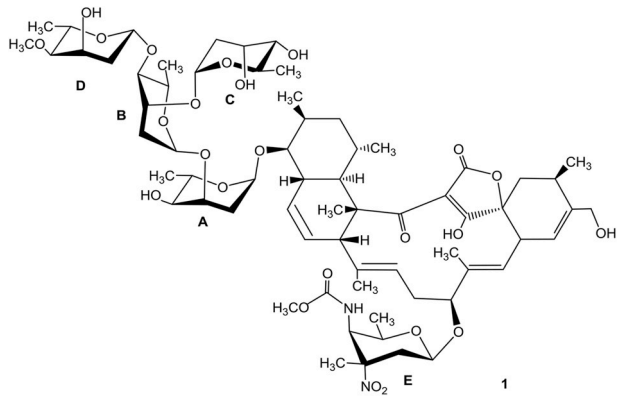
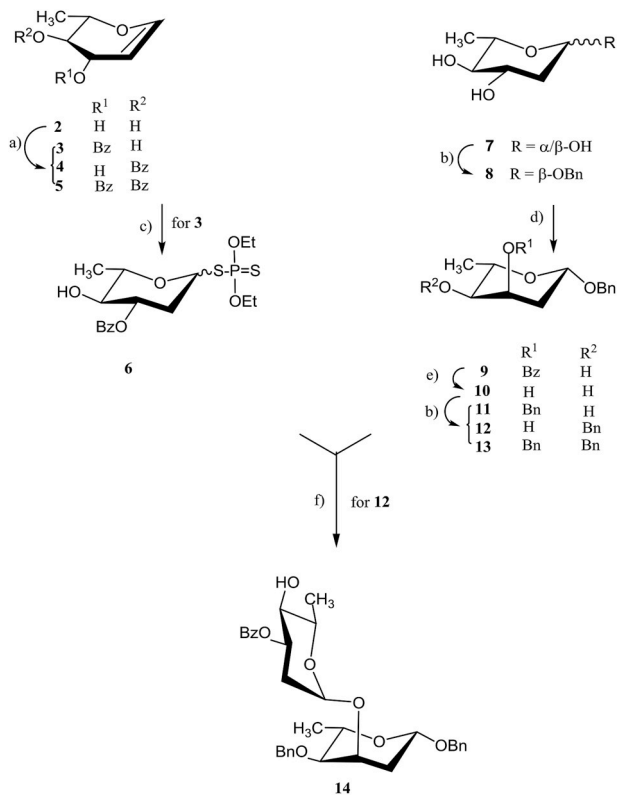


**Fig. 1.** Kijanimicin (**1**).

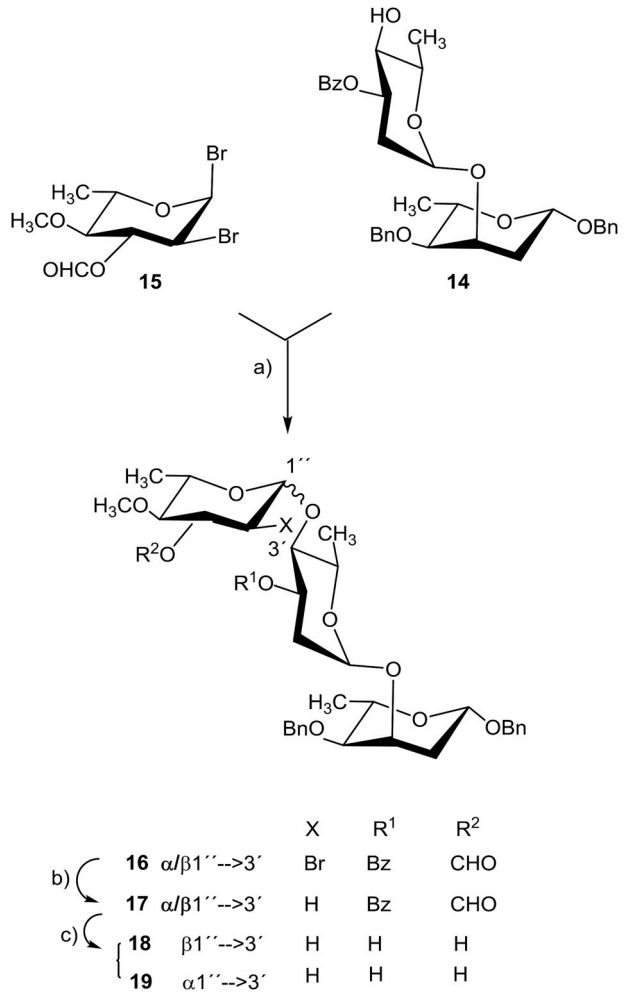


**Scheme 1.** *Synthesis of the A-B Disaccharide Precursor. Reaction conditions:(a)* Benzoyl chloride, pyridine; (b) benzyl bromide, NaH, DMF; (c) *O,O*-diethyl *S*-hydrogen phosphorodithioate; (d) $P(Ph)_3$, BzOH, diethylazodicarboxylate; e) NaOH, MeOH; f) $I(Coll)_2C1O_4$, MeCN.

Thus, for glycosylation the mixture of the crystalline acceptor **12** and the raw material **6** were treated with iodonium bis-collidine perchlorate $[I(Coll)_2ClO_4]$ as promotor at room temperature under exclusion of light in benzene/acetonitrile to give the α,1-3-glycosidically linked A-B disaccharide precursor **14** in 62% yield (Scheme 1).

### 2.2. Synthesis of the D-B-A trisaccharide precursor

En route to the trisaccharide precursor A-B—C the next stage was the introduction of the 4-*O*-methylated moiety C employing a stereoselective β-glycosylation with the glycosyl bromide precursor **15** [13]. As acceptor the above described disaccharide unit **14** with an unblocked 4′—OH position was employed. Indeed, the silver triflate mediated reaction resulted in formation of the trisaccharide **16** as anomeric mixture in 81% yield with a ratio α: β = 2: 13. Since

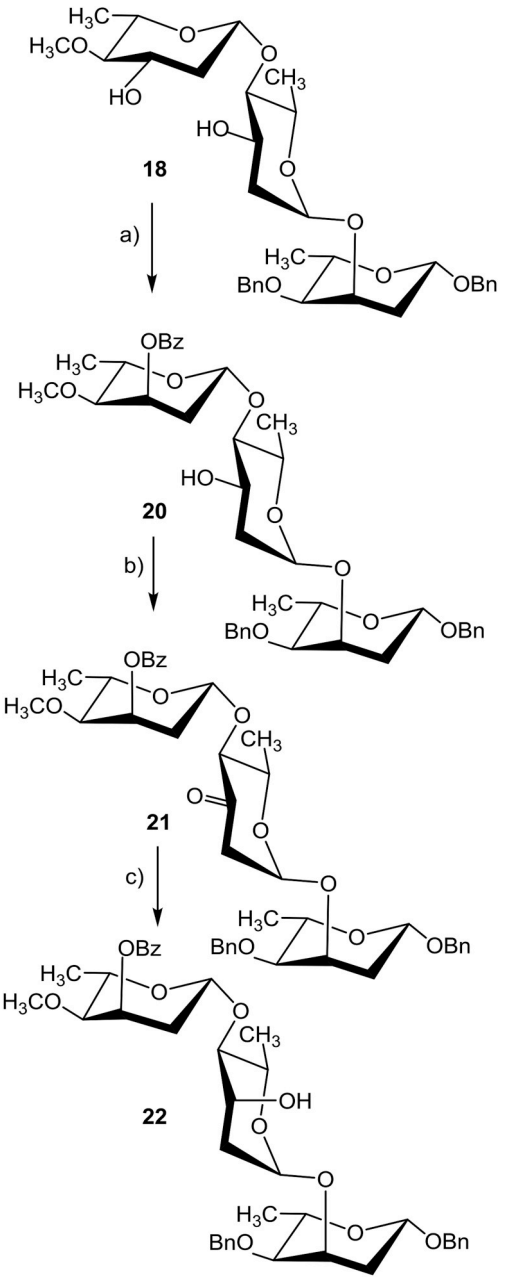


**Scheme 2.** *Synthesis of the A-B-D- Trisaccharide Precursor.* Reaction conditions: a) AgOTf, nitromethane/toluene; b) $nBu_3SnH$, AIBN, toluene, 70 °C; c) NaOH, MeOH.

separation of the anomers at this stage was inefficient, as next step the radical debromination with tri-*n*-butyl stannane was performed to give the anomeric mixture **17** in 95% yield, separation of which was not feasible as above. Thus, the alkaline deacylation was done with the anomeric mixture to give the trisaccharides **18** and **19** in 90% yield. These could be successfully separated resulting in the desired β,1′′-3′′-linked trisaccharide **18** (78%) and in addition 12% of the α,1′′-3′′-linked trisaccharide species **19** (Scheme 2).

### 2.3. Synthesis of the D-B-A trisaccharide

Employing trisaccharide **18** in a Mitsunobu reaction was expected to result in inversion of both hydroxyl groups at 3′- as well as 3′′-positions. However, as a favorable outcome, apparently due to considerable steric shielding from the upper side of unit B, there was exclusively observed inversion at 3′′-position to give the crystalline component **20** in 85% yield. Thus, in deviation from the original planning, another method for inversion at 3′-position e.g. by an oxidation/reduction sequence had to be engaged. Use of pyridinium dichromate in dichloromethane with acetic acid catalysis [21] was the method of choice to result in formation of the crystalline 3′-ulose **21** in 90% yield. Indeed its reduction with sodium borohydride went extraordinarily well to give the desired trisaccharide **22** with an axial 3′-hydroxy group crystalline in 99% yield. As previously reported in other cases [22,23] axially glycosylated 3-keto derivatives allow an exclusive hydride attack from below. Since the A-B disaccharide moieties are α,1-3-glycosidically

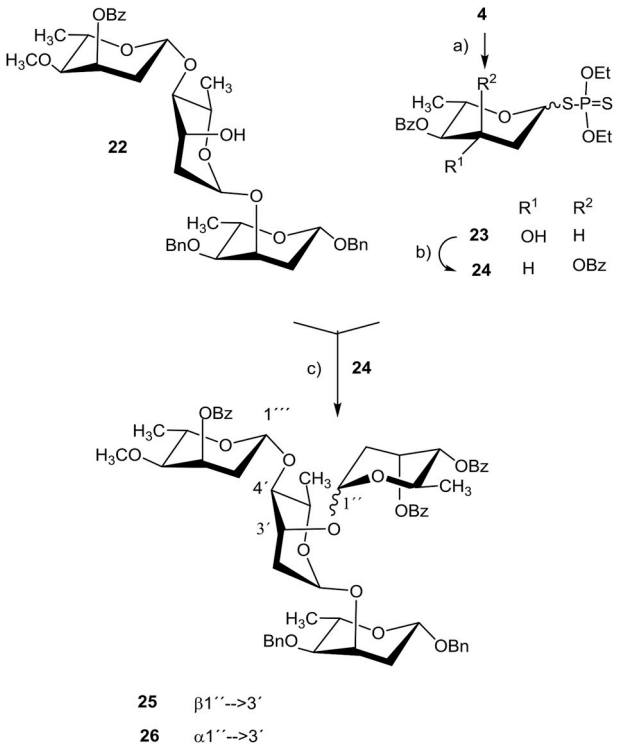



**Scheme 3.** *Synthesis of the D-B-A-Trisaccharide.* Reaction conditions: a) $P(Ph)_3$, BzOH, diethylazodicarboxylate; b) pyridinium dichromate, HOAc; c) $NaBH_4$, MeOH.

linked, this conception could be effectively employed here as well (Scheme 3).

### 2.4. Synthesis of the A-B—C-D tetrasaccharide precursor

Even though a stereoselective glycosylation was not necessarily to be expected employing an *S*-(2,6-dideoxy-α,β-L-ribo-hexopyranosyl)-phosphorodithioate [15] it was to be tested as expedient approach. Thus, 4-*O*-benzoyl-L-rhamnal (**4**) was reacted with *O,O*-diethyl *S*-hydrogen phosphorodithioate to give quantitatively the raw of *S*-(2,6-dideoxy-α,β-L-arabino-hexopyranosyl)-phosphorodithioate (**23**). Inversion of the 3-hydroxy group by Mitsunobu reaction led to the L-ribo derivative **24**, which could be directly used for glycosylation at 3′-position of the trisaccharide **22**. By catalysis with iodonium bis-collidine perchlorate $[I(Coll)_2ClO_4]$ as promotor at room temperature under




**Scheme 4.** *Synthesis of the A-B—C-D-Tetrasaccharide Precursor.* Reaction conditions: a) *O,O*-diethyl *S*-hydrogen phosphorodithioate; b) $P(Ph)_3$, BzOH, diethylazodicarboxylate; c) $l(Coll)_2ClO4$, MeCN.

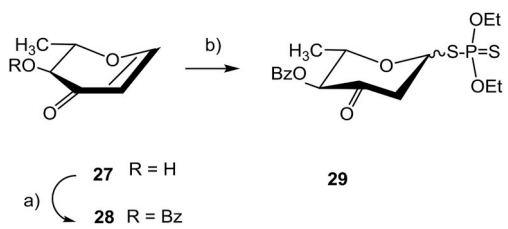
exclusion of light in acetonitrile the A-B—C-D tetrasaccharides **25** and **26** precursors were obtained in 20% yield with a ratio of **25**: **26** = 3: 1.$^1$H NMR clearly allowed to identify compound **25** having a β,1′′-3′-(H-1′′ with $J_{1'',2''ax}$ = 8.2, $J_{1'',2''eq}$ = 2.0 Hz) and the desired **26** an α,1′′-3′- interglycosidic linkage (H-1′′ with $J_{1'',2''ax}$ = 3.6, $J_{1'',2''eq}$ = 0.8 Hz). Even though the complete tetrasaccharide structure resulted, these yields in the range of previous approaches [8] were not convincing, which required an alternative approach (Scheme 4).

### 2.5. Synthesis of an alternative glycosylation precursor

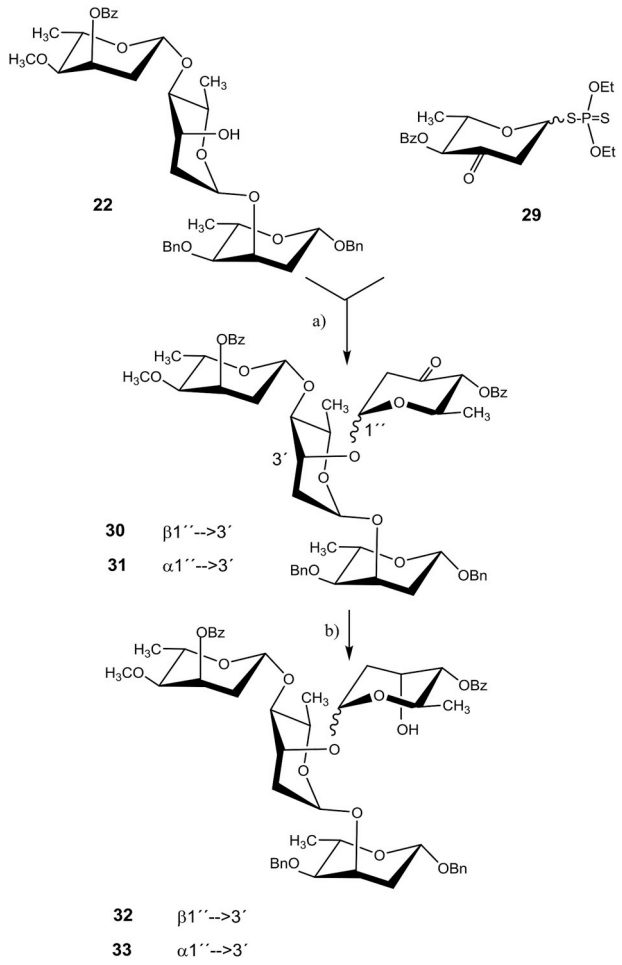
The results of the above findings clearly required a rather plain donor showing stereoselectivity for α-glycosylations. It seemed to be attractive to develop an ulose type hexopyranosyl-phosphorodithioate, even though it remains uncertain whether or not the keto function would survive the glycosylation conditions. Allylic oxidation of L-rhamnal (**2**) [16] with manganese oxide led to ulose **27** [24], which after benzoylation to **28** on treatment with *O,O*-diethyl *S*-hydrogen phosphoro-dithioate gave the glycosylation donor **29** (Scheme 5).

### 2.6. Final synthesis of the A-B—C-D-tetrasaccharide

Based on previous glycosylation approaches with corresponding




**Scheme 5.** *Synthesis of the Glycosylation Precursor.* Reaction conditions:.a) BzCl, pyridine; b) *O,O*-diethyl *S*-hydrogen phosphorodithioate.




**Scheme 6.** Synthesis of A-B-C-D- Tetrasaccharide.

donor components [15] compound **29** was used for glycosylation of the trisaccharide acceptor **22** under catalysis of iodonium bis-collidine perchlorate [I(Coll)$_2$ClO$_4$] as promotor, room temperature and exclusion of light. There was detected almost no solvent influence on the α: β ratio: in anhydrous dichloromethane the total yield amounted to 60% and a ratio α: β = 1.1: 2, whereas in anhydrous acetonitrile 55% were obtained with α: β = 1: 2.$^1$H NMR data clearly confirmed the anomeric assignment and also show a conservation of the keto unit C. Following this approach the desired tetrasaccharide **31** could be obtained in 33% and the anomeric counterpart **30** in 27% yield. The terminal step required a sodium borohydride reduction. As discussed above there is an exclusive hydride attack in both compounds at the 3´´-keto function from underneath to result in the required α-L-ribo-hexopyranosyl unit C. In addition to the syrupy isomer **32** (45%) the α,1´´-3′-anomer **33** was isolated as a crystalline material in 50% yield. This concluded the synthesis of the genuine kijanimicin tetrasaccharide, the correct interglycosidic linkages of which were clearly shown by extended NMR assignments (Scheme 6).

## 3. Conclusion

Essentially by use of the four monosaccharide building units **3**, **12**, **15**, and **28** the sequential synthesis of the kijanimicin octadeoxy-tetrasaccharide **33** could be achieved. This target compound having the required α,1′-3-, α,1´´-3´-, and β,1´´´-4′-interglycosidic linkages was obtained in nine steps and overall 5% yield.

## 4. Experimental

### 4.1. General methods

All reactions were monitored by thin layer chromatography on silica gel foils GF$_{254}$ (Merck). Detection was by UV or spraying with 10% ethanolic sulfuric acid and subsequent heating. Column chromatography was done on silica gel 60 (40–63 μm, Merck) by flash mode with the solvent mixture recorded. $^1$H NMR (250 or 400 MHz) and $^{13}$C NMR spectra (62.89 or 100.67 MHz) were done on Bruker AC-250 or AMX-400. Signal assignment was by $^1$H,$^1$H−COSY−, HSQC- and HMBC experiments. Melting points are uncorrected and were taken on a Reichert heating microscope. Optical rotations were measured with Perkin-Elmer polarimeter 243 using sodium D line (589 nm), cuvette length 10 cm, and temperature 20 °C.

### 4.2. General procedures

#### 4.2.1. DBE method (GP1)

The sugar (1.0 mmol) dissolved in dichloromethane (4 mL) was reacted with zinc bromide (45 mg) and dibromomethyl methyl ether (350 μL) at room temperature overnight. Following addition of dichloromethane (20 mL) the solution was washed twice with aqueous hydrochloric acid (4 M), the organic phase dried over MgSO$_4$, filtered and evaporated at room temperature. The raw material was directly used for glycosylation.

#### 4.2.2. Glycosylation employing silver triflate (GP2)

Under nitrogen cover a solution of the acceptor (1.0 mmol) in nitromethane (7 mL) and toluene (23 mL) was stirred with activated molecular sieves (4 A, small rods). Silver triflate (2.2 eq) and sym-collidine (5 drops) were added and the solution cooled to −78 °C. Then a pre-dried solution of the glycosyl bromide (GP1, 2.2 eq) in anhydrous toluene (2 mL) was added, and the reaction stirred under nitrogen and exclusion of light for 24–48 h, thereby gradually warming to room temperature. For work up the solution was diluted with ethyl acetate, washed with aqueous sodium thiosulfate and aqueous sodium hydrogen carbonate, filtered over celite, dried over MgSO$_4$ and evaporated. The raw material was purified by flash chromatography.

#### 4.2.3. Debromination with tri-n-butyl stannane (GP3)

Under nitrogen a solution of the bromo component (1.0 eq) in toluene (3 mL) was treated with tri-*n*-butyl stannic hydride (1.1 eq). Following addition of a catalytic amount of α,α′-azobis-isobutyronitrile as radical starter the mixture was heated to 70 °C and stirred for 3 h. The solvent was evaporated and the raw mixture directly purified by chromatography.

#### 4.2.4. Benzoylation (GP4)

The saccharide (1 eq) dissolved in anhydrous pyridine (4 mL) was cooled to 0 °C and treated dropwise with benzoyl chloride (1 eq per hydroxyl function). After 1–12 h the mixture was warmed to room temperature, evaporated and purified by chromatography.

#### 4.2.5. Benzylation (GP5)

The saccharide (1 mmol) dissolved in anhydrous *N*,*N*-dimethyl-formamide (DMF, 10 mL) was stirred with sodium hydride (1.2 eq per hydroxyl group) for 20 min. After cooling to 0 °C a solution of benzyl bromide (1 eq per hydroxyl group) in anhydrous DMF (2 mL) was added dropwise, and stirring continued for 2 h while gradually warming to room temperature. Then methanol (4 mL per mmol benzyl bromide) was added and stirred for another 20 min. The mixture was evaporated and the raw material purified by chromatography.

#### 4.2.6. Deacylation (GP6)

The acylated material (1 mmol) dissolved in methanol (20 mL) was

treated with sodium hydroxide (2 eq per acyl function) and stirred at room temperatures until complete saponification. The mixture was dissolved in water (20 mL) and neutralized with aqueous hydrochloric acid (4 M), then extracted with dichloromethane, dried over $MgSO_4$, filtered, evaporated and purified by chromatography.

### 4.3. Syntheses

#### 4.3.1. 3-O-Benzoyl-L-rhamnal (3), 4-O-Benzoyl-L-rhamnal (4) and 3,4-Di-O-benzoyl-L-rhamnal (5)

L-Rhamnal (**2**, 900 mg, 6.92 mmol) [16] was treated with benzoyl chloride (1eq/OH) according to GP4. The raw material was separated by column chroma-tography (toluene/ethyl acetate 8: 1) to give compounds **3** (1.27 g, 78%), **4** (67 mg, 4.1%), and **5**290 mg, 12.3%) as colourless solids. $^1$H-NMR-data, melting points and optical rotations were in accord with the literature data [17].

#### 4.3.2. Benzyl 2,6-dideoxy-β-L-arabino-hexopyranoside (8)

According to GP5 2-deoxy-L-rhamnose [18] (**7**, 1.2 g, 8.1 mmol) was treated with benzyl bromide (1 eq). The raw material was purified by flash chromatography (toluene/ethyl acetate 2: 1) to give 1.35 g (70%) yellow syrup (anomeric mixture α: β = 1:4). Further separation gave the pure β-anomer **8**, the $^1$H NMR data of which are in accord with those of the D-isomer [25].

#### 4.3.3. Benzyl 3-O-benzoyl-2,6-dideoxy-β-L-ribo-hexopyranoside (9)

A solution of compound **8** (7.7 g, 32.0 mmol) and triphenylphosphine (11.0 g, 48.0 mmol) in tetrahydrofuran (100 mL) were stirred for 20 min. Then benzoic acid (5.0 g, 48 mmol) and a solution of diethylazodicarboxylate (6.4 mL, 48 mmol) in tetra-hydrofuran (60 mL) were added and stirring continued for another 30 min. The mixture was evaporated and the raw material purified by column chroma-tography (toluene/ethyl acetate 15: 1) to give **9** (8.2 g, 75%) as amorphous solid. $^1$H NMR (250 MHz, $CDCl_3$): δ = 4.94 (dd, 1H, $J_{1,2ax}$ 9.6, $J_{1,2eq}$ 2.4 Hz,H-1), 1.95 (dd, 1H, $J_{1,2ax}$ 9.6, $J_{2ax,2eq}$ 14.0, $J_{2ax,3}$ 2.8 Hz, H-2ax), 2.26 (dd, 1H, $J_{1,2eq}$ 2.4, $J_{2ax,2eq}$ 14.0, $J_{2eq,3}$ 3.6 Hz, H-2eq), 5.52 (m, 1H, H-3), 3.54 (dd, 1H, $J_{3,4}$ 3.2, $J_{4,5}$ 9.6 Hz, H-4), 3.88 (dq, 1H, $J_{4,5}$ 9.6, $J_{5,6}$ 6.4 Hz, H-5), 1.36 (d, 3H, $J_{5,6}$ 6.4 Hz, $CH_3$-6), 4.60 and 4.93 (each d, each 1H, $J_{CH2Bn}$ 12.0 Hz, $CH_2$Bn), 7.40–8.10 (m, 5-H, aryl-H).

#### 4.3.4. Benzyl 2,6-dideoxy-β-L-ribo-hexopyranoside (10)

According to GP6 compound **9** (8.2 g, 24.0 mmol) were saponified for 30 min. After filtration over silica gel (toluene/ethyl acetate 1: 1) the pure product **10** (5.7 g, quantitative yield) was obtained as colourless syrup, $[\alpha]_D^{20}$ = + 32.1 (*c* = 1.0, $CH_2Cl_2$). $^1$H NMR (250 MHz, $CDCl_3$): δ = 4.90 (dd, 1H, $J_{1,2ax}$ 9.6, $J_{1,2eq}$ 2.4 Hz, H-1), 1.75 (dd, 1H, $J_{1,2ax}$ 9.6, $J_{2ax,2eq}$ 14.0, $J_{2ax,3}$ 2.8 Hz, H-2ax), 2.12 (dd, 1H, $J_{1,2eq}$ 2.4, $J_{2ax,2eq}$ 14.0, $J_{2eq,3}$ 3.6 Hz, H-2eq), 4.06 (m, 1H, H-3), 3.30 (dd, 1H, $J_{3,4}$ 3.2, $J_{4,5}$ 9.6 Hz, H-4), 3.72 (dq, 1H, $J_{4,5}$ 9.6, $J_{5,6}$ 6.4 Hz, H-5), 1.34 (d, 3H, $J_{5,6}$ 6.4 Hz, $CH_3$-6), 4.58 and 4.82 (each d, each 1H, $J_{CH2Bn}$ 12.0 Hz, $CH_2$Bn), 7.40–7.60 (m, 5-H, aryl-H). Calcd. for $C_{13}H_{18}O_4$ (238.2): C, 65.52; H, 7.61. Found: C, 65.34; H, 7.59.

#### 4.3.5. Benzyl 3-O-benzyl-2,6-dideoxy-β-L-ribo-hexopyranoside (11), Benzyl 4-O-benzyl-2,6-dideoxy-β-L-ribo-hexopyranoside (12) and Benzyl 3,4-di-O-benzyl-2,6-dideoxy-β-L-ribo-hexopyranoside (13)

According to GP5 compound **10** (7.44 g, 31.0 mmol) was benzylated regioselectively. After workup chromatographic separation (petroleum ether/ether 3:1) gave 640 mg (5%) of **13,** 5.1 g (50%) of **12,** and 2.08 g (20%) of **11**. Compound **11**: colourless syrup, $[\alpha]_D^{20}$ = + 24.3 (*c* = 1.0, $CH_2Cl_2$); $^1$H NMR (250 MHz, $CDCl_3$): δ = 4.94 (dd, 1H, $J_{1,2ax}$ 9.6, $J_{1,2eq}$ 2.4 Hz, H-1), 1.60 (dd, 1H, $J_{1,2ax}$ 9.6, $J_{2ax,2eq}$ 14.0, $J_{2ax,3}$ 2.8 Hz, H-2ax), 2.20 (dd, 1H, $J_{1,2eq}$ 2.4, $J_{2ax,2eq}$ 14.0, $J_{2eq,3}$ 3.6 Hz, H-2eq), 3.98 (m, 1H, H-3), 3.28 (dd, 1H, $J_{3,4}$ 3.2, $J_{4,5}$ 9.6 Hz, H-4), 3.72 (dq, 1H, $J_{4,5}$ 9.6, $J_{5,6}$ 6.4 Hz, H-5), 1.32 (d, 3H, $J_{5,6}$ 6.4 Hz, $CH_3$-6), 4.42, 4.52, 4.64 and 4.88 (each d, each 1H, $J_{CH2Bn}$ 12.0 Hz, $CH_2$Bn), 7.40–7.60 (m, 5-H, aryl-H). Compound **12**: colourless solid, mp 53 °C, $[\alpha]_D^{20}$ = + 16.4 (*c* = 1.0, $CH_2Cl_2$); $^1$H NMR (250 MHz, $CDCl_3$): δ = 4.92 (dd, 1H, $J_{1,2ax}$ 9.6, $J_{1,2eq}$ 2.4 Hz, H-1), 1.70 (dd, 1H, $J_{1,2ax}$ 9.6, $J_{2ax,2eq}$ 14.0, $J_{2ax,3}$ 2.8 Hz, H-2ax), 2.20 (dd, 1H, $J_{1,2eq}$ 2.4, $J_{2ax,2eq}$ 14.0, $J_{2eq,3}$ 3.6 Hz, H-2eq), 4.20 (m, 1H, H-3), 3.16 (dd, 1H, $J_{3,4}$ 3.2, $J_{4,5}$ 9.6 Hz, H-4), 3.82 (dq, 1H, $J_{4,5}$ 9.6, $J_{5,6}$ 6.4 Hz, H-5), 1.32 (d, 3H, $J_{5,6}$ 6.4 Hz, $CH_3$-6), 4.52, 4.54, 4.62 and 4.86 (each d, each 1H, $J_{CH2Bn}$ 12.0 Hz, $CH_2$Bn), 7.40–7.60 (m, 5-H, aryl-H). Calcd. for $C_{20}H_{24}O_4$ (328.3): C, 73.14; H, 7.36. Found: C, 73.20; H, 7.36. Compound **13**: colourless syrup, $[\alpha]_D^{20}$ = - 18.4 (*c* = 1.0, $CH_2Cl_2$); $^1$H NMR (250 MHz, $CDCl_3$): δ = 4.94 (dd, 1H, $J_{1,2ax}$ 9.6, $J_{1,2eq}$ 2.4 Hz, H-1), 1.60 (dd, 1H, $J_{1,2ax}$ 9.6, $J_{2ax,2eq}$ 14.0, $J_{2ax,3}$ 2.8 Hz, H-2ax), 2.22 (dd, 1H, $J_{1,2eq}$ 2.4, $J_{2ax,2eq}$ 14.0, $J_{2eq,3}$ 3.6 Hz, H-2eq), 3.92 (m, 1H, H-3), 3.16 (dd, 1H, $J_{3,4}$ 3.2, $J_{4,5}$ 9.6 Hz, H-4), 4.04 (dq, 1H, $J_{4,5}$ 9.6, $J_{5,6}$ 6.4 Hz, H-5), 1.32 (d, 3H, $J_{5,6}$ 6.4 Hz, $CH_3$-6), 4.42, 4.52, 4.56, 4.62, 4.64 and 4.82 (each d, each 1H, $J_{CH2Bn}$ 12.0 Hz, $CH_2$Bn), 7.40–7.60 (m, 5-H, aryl-H).

#### 4.3.6. Benzyl 3-O-(3-O-benzoyl-2,6-dideoxy-α-L-arabino-hexopyranosyl)-4-O-benzyl-2,6-dideoxy-β-L-ribo-hexopyranoside (14)

A solution of compound **3** (1.1 g, 4.7 mmol) in benzene (15 mL) was stirred with an equimolar amount of *O*,*O*-diethyl *S*-hydrogen phosphoro-dithioate (800 μL) for 12 h at room temperature. The solvent was evaporated and the raw of *S*-(2-deoxy-α,β-L-arabino-hexo-pyranosyl)-phosphorodithioate (**6**) used directly for glycosylation with compound **12** (4.0 g, 12.1 mmol, 2.5 eq) dissolved in anhydrous acetonitrile (20 mL). After stirring with molecular sieves (3A) for 20 min as promotor iodonium bis-collidine perchlorate [$I(Coll)_2ClO_4$, 3.0 g, 1.5 eq] was added and stirring continued at room temperature under exclusion of light for another hour. The mixture was dissolved with dichloromethane (100 mL), washed with sodium thiosulfate (10% aqueous solution), dried over $MgSO_4$, filtered and evaporated. By chromatographic purification (petroleum ether/ether 7: 2) 1.58 g (62%) of compound **14** resulted as colourless syrup; $[\alpha]_D^{20}$ = - 95.2 (*c* = 1.0, $CH_2Cl_2$). $^1$H NMR (250 MHz, $CDCl_3$): δ = 4.92 (dd, 1H, $J_{1,2ax}$ 9.6, $J_{1,2eq}$ 2.0 Hz, H-1), 1.62 (dd, 1H, $J_{1,2ax}$ 9.6, $J_{2ax,2eq}$ 14.0, $J_{2ax,3}$ 2.4 Hz, H-2ax), 2.12 (dd, 1H, $J_{1,2eq}$ 2.0, $J_{2ax,2eq}$ 14.0, $J_{2eq,3}$ 4.0 Hz, H-2eq), 4.31 (m, 1H, H-3), 3.16 (dd, 1H, $J_{3,4}$ 2.8, $J_{4,5}$ 9.2 Hz, H-4), 4.06 (dq, 1H, $J_{4,5}$ 9.2, $J_{5,6}$ 6.4 Hz, H-5), 1.32 (d, 3H, $J_{5,6}$ 6.4 Hz, $CH_3$-6), 5.03 (dd, 1H, $J_{1',2'ax}$ 3.6, $J_{1',2'eq}$ 0.4 Hz, H-1′), 1.91 (dt, 1H, $J_{1',2'ax}$ 3.6, $J_{2'ax,2'eq}$ 12.4, $J_{2'ax,3'}$ 12.0 Hz, H-2′ax), 2.22 (dd, 1H, $J_{1',2'eq}$ 0.4, $J_{2'ax,2'eq}$ 12.4, $J_{2'eq,3'}$ 5.2 Hz, H-2′eq), 5.38 (m, 1H, H-3′), 3.34 (t, 1H, $J_{3',4'}$ 9.2, $J_{4',5'}$ 9.2 Hz, H-4′), 4.06 (dq, 1H, $J_{4',5'}$ 9.2, $J_{5',6'}$ 6.2 Hz, H-5′), 1.18 (d, 3H, $J_{5',6'}$ 6.2 Hz, $CH_3$-6′), 4.50, 4.53, 4.71 and 4.91 (each d, each 1H, $J_{CH2Bn}$ 12.0 Hz, $CH_2$Bn), 7.40–7.80 (m, 15-H, aryl-H). Calcd. for $C_{33}H_{37}O_8$ (561.6): C, 70.44; H, 6.80. Found: C, 69.98; H, 6.80.

#### 4.3.7. Benzyl 3-O-[3-O-benzoyl-4-O-(2-bromo-2,6-dideoxy-3-O-formyl-4-O-methyl-α/β-L-glucopyranosyl)-2,6-dideoxy-α-L-arabino-hexopyranosyl]-4-O-benzyl-2,6-dideoxy-β-L-ribo-hexopyranoside (16)

The raw material **15** [13] obtained from methyl 6-deoxy-2,3-*O*-isopropylidene-4-*O*-methyl-α-L-mannopyranoside (300 mg, 1.29 mmol) following GP1 and the disaccharide **14** (195 mg, 0.34 mmol) were reacted for 12 h and worked up according to GP2. By chromatographic purification (petroleum ether/ether 5: 1) 224 mg (81%) of compound **16** resulted as colourless syrup. Anomeric mixture α: β = 2: 13.**16β:** $^1$H NMR (400 MHz, $CDCl_3$): δ = 4.94 (dd, 1H, $J_{1,2ax}$ 9.6, $J_{1,2eq}$ 2.0 Hz, H-1), 1.58 (dd, 1H, $J_{1,2ax}$ 9.6, $J_{2ax,2eq}$ 13.6, $J_{2ax,3}$ 2.4 Hz, H-2ax), 2.10 (dd, 1H, $J_{1,2eq}$ 2.0, $J_{2ax,2eq}$ 13.6, $J_{2eq,3}$ 3.6 Hz, H-2eq), 4.30 (m, 1H, H-3), 3.14 (dd, 1H, $J_{3,4}$ 2.8, $J_{4,5}$ 9.6 Hz, H-4), 4.23 (dq, 1H, $J_{4,5}$ 9.6, $J_{5,6}$ 6.4 Hz, H-5), 1.20 (d, 3H, $J_{5,6}$ 6.4 Hz, $CH_3$-6), 4.99 (dd, 1H, $J_{1',2'ax}$ 2.8, $J_{1',2'eq}$ 0.8 Hz, H-1′), 1.84 (dd, 1H, $J_{1',2'ax}$ 2.8, $J_{2'ax,2'eq}$ 12.4, $J_{2'ax,3'}$ 11.2 Hz, H-2′ax), 2.24 (dd, 1H, $J_{1',2'eq}$ 0.8, $J_{2'ax,2'eq}$ 12.4, $J_{2'eq,3'}$ 5.6 Hz, H-2′eq), 5.57 (dd, 1H, $J_{2'ax,3'}$ 11.2, $J_{2'eq,3'}$ 5.6, $J_{3',4'}$ 9.2 Hz, H-3′), 3.58 (t, 1H, $J_{3',4'}$ 9.2, $J_{4',5'}$ 9.2 Hz, H-4′), 4.08 (dq, 1H, $J_{4',5'}$ 9.2, $J_{5',6'}$ 6.4 Hz, H-5′), 0.92 (d, 3H, $J_{5',6'}$ 6.4 Hz, $CH_3$-6′), 4.64 (d, 1H, $J_{1'',2''}$ 8.4 Hz, H-1′′), 3.64 (dd, 1H, $J_{1'',2''}$ 8.4, $J_{2'',3''}$ 10.8 Hz, H-2′′), 5.09 (t, 1H, $J_{2'',3''}$ 10.8.

$J_{3'',4''}$ 9.6, H-3´´), 2.74 (t, 1H, $J_{3'',4''}$ 9.6, $J_{4'',5''}$ 9.6 Hz, H-4´´), 3.01 (dq, 1H, $J_{4'',5''}$ 9.6, $J_{5'',6''}$ 6.4 Hz, H-5´´), 1.32 (d, 3H, $J_{5'',6''}$ 6.4 Hz, $CH_3$-6´´), 3.32 (s, 3H, $OCH_3$), 4.46, 4.51, 4.71 and 4.91 (each d, each 1H, $J_{CH2Bn}$ 12.0 Hz, $CH_2$Bn), 8.18 (s, 1H, OC*H*O), 7.20–8.00 (m, 15-H, aryl-H). Calcd. for $C_{41}H_{48}BrO_{12}$(812.6): C, 60.51; H, 6.06; Br, 9.82. Found: C, 59.95; H, 6.07; Br, 9.70.

#### *4.3.8. Benzyl 3-O-[3-O-benzoyl-4-O-(2,6-dideoxy-3-O-formyl-4-O-methyl-α/β-L-arabino-hexopyranosyl)-2,6-dideoxy-α-L-arabino-hexopyranosyl]-4-O-benzyl-2,6-dideoxy-β-L-ribo-hexopyranoside (17)*

The trisaccharide **16** (1.0 g, 1.23 mmol) was reacted according to GP3. Chromatographic purification (petroleum ether/ether 2: 1) gave 885 mg (95%) of the anomeric mixture **17** as amorphous solid. **17β:** $^1$H NMR (400 MHz, $CDCl_3$): δ = 4.93 (dd, 1H, $J_{1,2ax}$ 9.6, $J_{1,2eq}$ 2.0 Hz, H-1), 1.50 (dd, 1H, $J_{1,2ax}$ 9.6, $J_{2ax,2eq}$ 13.6, $J_{2ax,3}$ 2.4 Hz, H-2ax), 1.95 (dd, 1H, $J_{1,2eq}$ 2.0, $J_{2ax,2eq}$ 13.6, $J_{2eq,3}$ 3.6 Hz, H-2eq), 4.28 (m, 1H, H-3), 3.12 (dd, 1H, $J_{3,4}$ 2.8, $J_{4,5}$ 9.6 Hz, H-4), 4.16 (dq, 1H, $J_{4,5}$ 9.6, $J_{5,6}$ 6.4 Hz, H-5), 1.05 (d, 3H, $J_{5,6}$ 6.4 Hz, $CH_3$-6), 4.98 (dd, 1H, $J_{1',2'ax}$ 3.2, $J_{1',2'eq}$ 0.8 Hz, H-1′), 1.91 (dd, 1H, $J_{1',2'ax}$ 3.2, $J_{2'ax,2'eq}$ 12.4, $J_{2'ax,3'}$ 11.2 Hz, H-2′ax), 2.30 (dd, 1H, $J_{1',2'eq}$ 0.8, $J_{2'ax,2'eq}$ 12.4, $J_{2'eq,3'}$ 5.2 Hz, H-2′eq), 5.53 (dd, 1H, $J_{2'ax,3'}$ 11.2, $J_{2'eq,3'}$ 5.2, $J_{3',4'}$ 9.2 Hz, H-3′), 3.43 (t, 1H, $J_{3',4'}$ 9.2, $J_{4',5'}$ 9.2 Hz, H-4′), 4.05 (dq, 1H, $J_{4',5'}$ 9.2, $J_{5',6'}$ 6.4 Hz, H-5′), 0.90 (d, 3H, $J_{5',6'}$ 6.4 Hz, $CH_3$-6′), 4.50 (dd, 1H, $J_{1'',2''ax}$ 9.6, $J_{1'',2''eq}$ 2.0 Hz, H-1´´), 1.50 (dd, 1H, $J_{1'',2''ax}$ 9.6, $J_{2''ax,2''eq}$ 12.4, $J_{2''ax,3''}$ 12.0 Hz, H-2´´ax), 2.18 (dd, 1H, $J_{1',2''eq}$ 2.0, $J_{2''ax,2''eq}$ 12.4, $J_{2''eq,3''}$ 5.2 Hz, H-2´´eq), 4.85 (dd, 1H, $J_{2''ax,3''}$ 12.0, $J_{2''eq,3''}$ 5.2, $J_{3'',4''}$ 9.2 Hz, H-3´´), 2.72 (t, 1H, $J_{3'',4''}$ 9.2, $J_{4'',5''}$ 9.2 Hz, H-4´´), 3.03 (dq, 1H, $J_{4'',5''}$ 9.2, $J_{5'',6''}$ 6.4 Hz, H-5´´), 1.30 (d, 3H, $J_{5'',6''}$ 6.2 Hz, $CH_3$-6´´), 3.38 (s, 3H, $OCH_3$), 4.48, 4.52, 4.69 and 4.91 (each d, each 1H, $J_{CH2Bn}$ 12.0 Hz, $CH_2$Bn), 8.12 (s, 1H, OC*H*O), 7.20–8.00 (m, 15-H, aryl-H).

#### *4.3.9. Benzyl 3-O-[4-O-(2,6-dideoxy-4-O-methyl-β-L-arabino-hexopyranosyl)-2,6-dideoxy-α-L-arabino-hexopyranosyl]-4-O-benzyl-2,6-dideoxy-β-L-ribo-hexopyranoside (18) and Benzyl 3-O-[4-O-(2,6-dideoxy-4-O-methyl-α-L-arabino-hexopyranosyl)-2,6-dideoxy-α-L-arabino-hexopyranosyl]-4-O-benzyl-2,6-dideoxy-β-L-ribo-hexopyranoside (19)*

The anomeric mixture **17** (800 mg, 1.09 mmol) was completely deacylated according to GP6. By chromatographic separation (toluene/ethyl acetate 2: 1) 510 mg (78%) of **18** were obtained as colourless crystals, mp 103–105 °C, $[\alpha]_D^{20}$ = - 56.6 (*c* = 1.0, $CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$): δ = 4.87 (dd, 1H, $J_{1,2ax}$ 9.6, $J_{1,2eq}$ 2.0 Hz, H-1), 1.60 (dd, 1H, $J_{1,2ax}$ 9.6, $J_{2ax,2eq}$ 12.0, $J_{2ax,3}$ 2.4 Hz, H-2ax), 2.11 (dd, 1H, $J_{1,2eq}$ 2.0, $J_{2ax,2eq}$ 12.0, $J_{2eq,3}$ 3.6 Hz, H-2eq), 4.26 (m, 1H, H-3), 3.12 (dd, 1H, $J_{3,4}$ 2.8, $J_{4,5}$ 9.2 Hz, H-4), 3.98 (dq, 1H, $J_{4,5}$ 9.2, $J_{5,6}$ 6.4 Hz, H-5), 1.28 (d, 3H, $J_{5,6}$ 6.4 Hz, $CH_3$-6), 4.95 (dd, 1H, $J_{1',2'ax}$ 3.2, $J_{1',2'eq}$ 0.8 Hz, H-1′), 1.60 (dd, 1H, $J_{1',2'ax}$ 3.2, $J_{2'ax,2'eq}$ 12.4, $J_{2'ax,3'}$ 11.2 Hz, H-2′ax), 2.11 (dd, 1H, $J_{1',2'eq}$ 0.8, $J_{2'ax,2'eq}$ = 12.4, $J_{2'eq,3'}$ 5.2 Hz, H-2′eq), 3.97 (m, 1H, H-3′), 2.91 (t, 1H, $J_{3',4'}$ 9.2, $J_{4',5'}$ 9.2 Hz, H-4′), 3.96 (dq, 1H, $J_{4',5'}$ 9.2, $J_{5',6'}$ 6.4 Hz, H-5′), 1.02 (d, 3H, $J_{5',6'}$ 6.4 Hz, $CH_3$-6′), 4.44 (dd, 1H, $J_{1'',2''ax}$ 9.6, $J_{1'',2''eq}$ 2.0 Hz, H-1´´), 1.67 (dd, 1H, $J_{1'',2''ax}$ 9.6, $J_{2''ax,2''eq}$ 12.4, $J_{2''ax,3''}$ 12.0 Hz, H-2´´ax), 2.18 (dd, 1H, $J_{1'',2''eq}$ 2.0, $J_{2''ax,2''eq}$ 12.8, $J_{2''eq,3''}$ 5.2 Hz, H-2´´eq), 3.63 (m, 1H, H-3´´), 2.74 (t, 1H, $J_{3'',4''}$ 9.2, $J_{4'',5''}$ 9.2 Hz, H-4´´), 3.34 (dq, 1H, $J_{4'',5''}$ 9.2, $J_{5'',6''}$ = 6.4 Hz, H-5´´), 1.37 (d, 3H, $J_{5'',6''}$ 6.4 Hz, $CH_3$-6´´), 3.58 (s, 3H, $OCH_3$), 4.46, 4.52, 4.68 and 4.89 (each d, each 1H, $J_{CH2Bn}$ 12.0 Hz, $CH_2$Bn), 7.20 (m, 10-H, aryl-H). Calcd. for $C_{33}H_{46}O_{10}$(602.7): C, 65.75; H, 7.96. Found: C, 65.81; H, 7.69.

Further 80 mg (12%) of **19** were isolated, colourless syrup, $[\alpha]_D^{20}$ = - 96.4 (*c* = 1.0, $CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$): δ = 4.85 (dd, 1H, $J_{1,2ax}$ 9.6, $J_{1,2eq}$ 2.0 Hz, H-1), 1.59 (dd, 1H, $J_{1,2ax}$ 9.6, $J_{2ax,2eq}$ 13.2, $J_{2ax,3}$ 2.4 Hz, H-2ax), 2.12 (dd, 1H, $J_{1,2eq}$ 2.0, $J_{2ax,2eq}$ 12.0, $J_{2eq,3}$ 3.6 Hz, H-2eq), 4.28 (m, 1H, H-3), 3.14 (dd, 1H, $J_{3,4}$ 2.8, $J_{4,5}$ 9.2 Hz, H-4), 3.87 (dq, 1H, $J_{4,5}$ 9.2, $J_{5,6}$ 6.4 Hz, H-5), 1.30 (d, 3H, $J_{5,6}$ 6.4 Hz, $CH_3$-6), 4.94 (dd, 1H, $J_{1',2'ax}$ 3.2, $J_{1',2'eq}$ 0.8 Hz, H-1′), 1.65 (dd, 1H, $J_{1',2'ax}$ 3.2, $J_{2'ax,2'eq}$ 12.4, $J_{2'ax,3'}$ 11.2 Hz, H-2′ax), 1.97 (dd, 1H, $J_{1',2'eq}$ 0.8, $J_{2'ax,2'eq}$ 12.4, $J_{2'eq,3'}$ 5.2 Hz, H-2′eq), 4.07 (m, 1H, H-3′), 3.11 (t, 1H, $J_{3',4'}$ 9.2, $J_{4',5'}$ 9.2 Hz, H-4′), 3.96 (dq, 1H, $J_{4',5'}$ 9.2, $J_{5',6'}$ 6.4 Hz, H-5′), 1.10 (d, 3H, $J_{5',6'}$ 6.4 Hz, $CH_3$-6′), 5.29 (dd, 1H, $J_{1'',2''ax}$4.0, $J_{1'',2''eq}$ 1.2 Hz, H-1´´), 1.68 (dd, 1H, $J_{1'',2''ax}$ 4.0, $J_{2''ax,2''eq}$ 12.4, $J_{2''ax,3''}$ 11.2 Hz, H-2´´ax), 2.08 (dd, 1H, $J_{1'',2''eq}$ 1.2, $J_{2''ax,2''eq}$ 12.4, $J_{2''eq,3''}$ 5.2 Hz, H-2´´eq), 3.88 (m, 1H, H-3´´), 2.68 (t, 1H, $J_{3'',4''}$ 9.2, $J_{4'',5''}$ 9.2 Hz, H-4´´), 3.65 (dq, 1H, $J_{4'',5''}$ 9.2, $J_{5'',6''}$ 6.4 Hz, H-5´´), 1.28 (d, 3H, $J_{5'',6''}$ 6.4 Hz, $CH_3$-6´´), 3.56 (s, 3H, $OCH_3$), 4.45, 4.52, 4.66 and 4.89 (each d, each 1H, $J_{CH2Bn}$ 12.0 Hz, $CH_2$Bn), 7.20 (m, 10-H, aryl-H).

#### *4.3.10. Benzyl 3-O-[4-O-(3-O-benzoyl-2,6-dideoxy-4-O-methyl-β-L-ribo-hexopyran-osyl)-2,6-dideoxy-α-L-arabino-hexopyranosyl]-4-O-benzyl-2,6-dideoxy-β-L-ribo-hexopyranoside (20)*

A solution of trisaccharide **18** (580 mg, 0.96 mmol) in anhydrous tetrahydrofuran (30 mL) was stirred with triphenylphosphine (3.1 g, 13.64 mmol) for 30 min and cooled to 0 °C. Then a solution of benzoic acid (1.56 g, 12.8 mmol) and diethylazodicarboxylate (1.8 mL, 11.5 mmol) in anhydrous tetrahydrofuran (15 mL) was added and stirring continued for 1 h at room temperature. The solvent was evaporated and the residue purified by column chromatography (petroleum ether/ether 7: 2) to give 595 mg (85%) of **20** as colourless crystals; mp 65–66 °C, $[\alpha]_D^{20}$ = - 73.7 (*c* = 1.0, $CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$): δ = 4.88 (dd, 1H, $J_{1,2ax}$ 9.2, $J_{1,2eq}$ 2.0 Hz, H-1), 1.59 (dd, 1H, $J_{1,2ax}$ 9.2, $J_{2ax,2eq}$ 13.2, $J_{2ax,3}$ 2.4 Hz, H-2ax), 2.11 (dd, 1H, $J_{1,2eq}$ 2.0, $J_{2ax,2eq}$ 13.2, $J_{2eq,3}$ 3.6 Hz, H-2eq), 4.26 (m, 1H, H-3), 3.11 (dd, 1H, $J_{3,4}$ 2.8, $J_{4,5}$ 9.2 Hz, H-4), 3.97 (dq, 1H, $J_{4,5}$ 9.2, $J_{5,6}$ 6.4 Hz, H-5), 1.28 (d, 3H, $J_{5,6}$ 6.4 Hz, $CH_3$-6), 4.96 (dd, 1H, $J_{1',2'ax}$ 3.2, $J_{1',2'eq}$ 0.8 Hz, H-1′), 1.66 (dd, 1H, $J_{1',2'ax}$ 3.2, $J_{2'ax,2'eq}$ 13.2, $J_{2'ax,3'}$ 11.6 Hz, H-2′ax), 2.11 (dd, 1H, $J_{1',2'eq}$ 0.8, $J_{2'ax,2'eq}$ 13.2, $J_{2'eq,3'}$ 5.2 Hz, H-2′eq), 3.97 (m, 1H, H-3′), 2.98 (t, 1H, $J_{3',4'}$ 9.2, $J_{4',5'}$ 9.2 Hz, H-4′), 4.04 (dq, 1H, $J_{4',5'}$ 9.2, $J_{5',6'}$ 6.4 Hz, H-5′), 0.98 (d, 3H, $J_{5',6'}$ 6.4 Hz, $CH_3$-6′), 4.84 (dd, 1H, $J_{1'',2''ax}$ 9.6, $J_{1'',2''eq}$ 2.0 Hz, H-1´´), 1.90 (dd, 1H, $J_{1'',2''ax}$ 9.6, $J_{2''ax,2''eq}$ 14.4, $J_{2''ax,3''}$ = 2.8 Hz, H-2´´ax), 2.20 (dd, 1H, $J_{1'',2''eq}$ = 2.0, $J_{2''ax,2''eq}$ = 14.4, $J_{2''eq,3''}$ = 3.6 Hz, H-2´´eq), 5.80 (q, 1H, $J_{2''ax,3''}$ 2.8, $J_{2''eq,3''}$ 3.6, $J_{3'',4''}$ 2.8 H, H-3´´), 3.05 (dd, 1H, $J_{3'',4''}$ 2.8, $J_{4'',5''}$ 9.6 Hz, H-4´´), 3.07 (dq, 1H, $J_{4'',5''}$ = 9.6, $J_{5'',6''}$ 6.4 Hz, H-5´´), 1.32 (d, 3H, $J_{5'',6''}$ 6.4 Hz, $CH_3$-6´´), 3.38 (s, 3H, $OCH_3$), 4.45, 4.52, 4.67 and 4.89 (each d, each 1H, $J_{CH2Bn}$ 12.0 Hz, $CH_2$Bn), 7.30–8.00 (m, 15-H, aryl-H). Calcd. for $C_{40}H_{50}O_{11}$(706.8): C, 67.96; H, 7.13. Found: C, 67.36; H, 7.15.

#### *4.3.11. Benzyl 3-O-[4-O-(3-O-benzoyl-2,6-dideoxy-4-O-methyl-β-L-ribo-hexopyranosyl)-2,6-dideoxy-3-ulose-α-L-erythro-hexopyranosyl]-4-O-benzyl-2,6-dideoxy-β-L-ribo-hexopyranoside (21)*

A solution of trisaccharide **20** (300 mg, 0.42 mmol) in anhydrous dichloromethane (12 mL) was stirred with molecular sieves (4 A), a drop of acetic acid and pyridinium dichromate (376 mg, 1.0 mmol) for 4 h at room temperature. The solvent was evaporated and the residue purified by column chromatography (toluene/ethyl acetate 2: 1) to give 270 mg (90%) of **21** as colourless crystals; mp 70–72 °C, $[\alpha]_D^{20}$ = - 117.6 (*c* = 1.0, $CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$): δ = 4.86 (dd, 1H, $J_{1,2ax}$ 9.6, $J_{1,2eq}$ 2.0 Hz, H-1), 1.60 (dd, 1H, $J_{1,2ax}$ 9.6, $J_{2ax,2eq}$ 13.6, $J_{2ax,3}$ 2.4 Hz, H-2ax), 2.05 (dd, 1H, $J_{1,2eq}$ 2.0, $J_{2ax,2eq}$ 13.6, $J_{2eq,3}$ 4.0 Hz, H-2eq), 4.26 (m, 1H, H-3), 3.08 (dd, 1H, $J_{3,4}$ 2.8, $J_{4,5}$ 9.2 Hz, H-4), 3.92 (dq, 1H, $J_{4,5}$ 9.2, $J_{5,6}$ 6.4 Hz, H-5), 1.22 (d, 3H, $J_{5,6}$ 6.4 Hz, $CH_3$-6), 5.24 (dd, 1H, $J_{1',2'ax}$ 4.0, $J_{1',2'eq}$ 0.8 Hz, H-1′), 2.77 (dd, 1H, $J_{1',2'ax}$ 4.0, $J_{2'ax,2'eq}$ 13.6, $J_{2'ax,4'}$ 0.8 Hz, H-2′ax), 2.56 (dd, 1H, $J_{1',2'eq}$ 0.8, $J_{2'ax,2'eq}$ 13.6 Hz, H-2′eq), 3.90 (dd, 1H, $J_{2'ax,4'}$ 0.8, $J_{4',5'}$ 9.6 Hz, H-4′), 4.43 (dq, 1H, $J_{4',5'}$ 9.6, $J_{5',6'}$ 6.4 Hz, H-5′), 1.10 (d, 3H, $J_{5',6'}$ 6.4 Hz, $CH_3$-6′), 4.90 (dd, 1H, $J_{1'',2''ax}$ 9.6, $J_{1'',2''eq}$ 2.0 Hz, H-1´´), 1.96 (dd, 1H, $J_{1'',2''ax}$ 9.6, $J_{2''ax,2''eq}$ 14.4, $J_{2''ax,3''}$ 2.8 Hz, H-2´´ax), 2.25 (dd, 1H, $J_{1'',2''eq}$ 2.0, $J_{2''ax,2''eq}$ 14.4, $J_{2''eq,3''}$ 3.6 Hz, H-2´´eq), 5.79 (q, 1H, $J_{2''ax,3''}$ 2.8, $J_{2''eq,3''}$ 3.6, $J_{3'',4''}$ 2.8 Hz, H-3´´), 3.05 (dd, 1H, $J_{3'',4''}$ 2.8, $J_{4'',5''}$ 9.6 Hz, H-4´´), 3.87 (dq, 1H, $J_{4'',5''}$ = 9.6, $J_{5'',6''}$ 6.4 Hz, H-5´´), 1.28 (d, 3H, $J_{5'',6''}$ 6.4 Hz, $CH_3$-6´´), 3.32 (s, 3H, $OCH_3$), 4.45, 4.49, 4.64 and 4.88 (each d, each 1H, $J_{CH2Bn}$ 12.0 Hz, $CH_2$Bn), 7.30–8.00 (m, 15-H, aryl-H). Calcd. for $C_{40}H_{48}O_{11}$(704.7): C, 68.16; H, 6.86. Found: C,

67.55; H, 6.97.

#### 4.3.12. Benzyl 3-O-[4-O-(3-O-benzoyl-2,6-dideoxy-4-O-methyl-β-L-ribo-hexopyranosyl)-2,6-dideoxy-α-L-ribo-hexopyranosyl]-4-O-benzyl-2,6-dideoxy-β-L-ribo-hexopyranoside (22)

A solution of trisaccharide **21** (230 mg, 0.32 mmol) in anhydrous methanol (5 mL) was cooled to 0 °C and treated with sodium borohydride (50 mg, 1.32 mmol). After stirring for 10 min at room temperature the mixture was neutralized with hydrochloric acid (4 M), diluted with water, extracted with dichloromethane, the organic phase dried ($MgSO_4$), filtered, evaporated and the raw material purified by column chromatography (toluene/ethyl acetate 10: 1) to give 230 mg (99%) of **22** as colourless crystals; mp 63–65 °C, $[\alpha]_D^{20}$ = - 103.5 (*c* = 1.0, $CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$): δ = 4.86 (dd, 1H, $J_{1,2ax}$ 9.6, $J_{1,2eq}$ 2.0 Hz, H-1), 1.57 (dd, 1H, $J_{1,2ax}$ 9.6, $J_{2ax,2eq}$ 13.6, $J_{2ax,3}$ 2.8 Hz, H-2ax), 2.17 (dd, 1H, $J_{1,2eq}$ 2.0, $J_{2ax,2eq}$ 13.6, $J_{2eq,3}$ 3.6 Hz, H-2eq), 4.29 (m, 1H, H-3), 3.13 (dd, 1H, $J_{3,4}$ 2.8, $J_{4,5}$ 9.2 Hz, H-4), 3.91 (dq, 1H, $J_{4,5}$ 9.2, $J_{5,6}$ 6.4 Hz, H-5), 1.24 (d, 3H, $J_{5,6}$ 6.4 Hz, $CH_3$-6), 5.00 (dd, 1H, $J_{1',2'ax}$ 3.2, $J_{1',2'eq}$ 0.8 Hz, H-1′), 1.94 (dt, 1H, $J_{1',2'ax}$ 3.2, $J_{2'ax,2'eq}$ 13.6, $J_{2'ax,3'}$ = 3.2 Hz, H-2′ax), 2.08 (dd, 1H, $J_{1',2'eq}$ 0.8, $J_{2'ax,2'eq}$ 13.6, $J_{2'eq,3'}$ 3.6 Hz, H-2′eq), 4.23 (m, 1H, H-3′), 3.24 (dd, 1H, $J_{3',4'}$ 2.8, $J_{4',5'}$ 10.0 Hz, H-4′), 4.23 (dq, 1H, $J_{4',5'}$ 10.0, $J_{5',6'}$ 6.4 Hz, H-5′), 1.08 (d, 3H, $J_{5',6'}$ 6.4 Hz, $CH_3$-6′), 4.91 (dd, 1H, $J_{1'',2''ax}$ 9.6, $J_{1'',2''eq}$ 2.0 Hz, H-1′′), 1.99 (dd, 1H, $J_{1'',2''ax}$ 9.6, $J_{2''ax,2''eq}$ 13.2, $J_{2''ax,3''}$ 2.8 Hz, H-2′′ax), 2.15 (dd, 1H, $J_{1'',2''eq}$ 2.0, $J_{2''ax,2''eq}$ 13.2, $J_{2''eq,3''}$ 3.6 Hz, H-2′′eq), 5.78 (q, 1H, $J_{2''ax,3''}$ 2.8, $J_{2''eq,3''}$ 3.6, $J_{3'',4''}$ 2.8 Hz H-3′′), 3.03 (dd, 1H, $J_{3'',4''}$ 2.8, $J_{4'',5''}$ 9.2 Hz, H-4′′), 3.91 (dq, 1H, $J_{4'',5''}$ 9.2, $J_{5'',6''}$ 6.4 Hz, H-5′′), 1.28 (d, 3H, $J_{5'',6''}$ 6.4 Hz, $CH_3$-6′′), 3.32 (s, 3H, $OCH_3$), 4.49, 4.50, 4.69 and 4.88 (each d, each 1H, $J_{CH2Bn}$ 12.0 Hz, $CH_2$Bn), 7.30–8.00 (m, 15-H, aryl-H). Calcd. for $C_{40}H_{50}O_{11}$(706.8): C, 67.96; H, 7.13. Found: C, 67.92; H, 7.35.

#### 4.3.13. S-[O,O-Diethyl-(4-O-benzoyl-2,6-dideoxy-α/β-L-arabino-hexopyranosyl)]-dithiophosphate (23)

A solution of 4-*O*-benzoyl-L-rhamnal (**4**, 100 mg, 0.42 mmol) in anhydrous benzene (2 mL) was stirred with *O,O*-diethyl *S*-hydrogen phosphorodithioate (70 μL, 1.42 mmol) for 16 h at room temperature. Following evaporation the remaining syrup was purified by column chromatography (petroleum ether/ether 1: 1) to give 175 mg (quant.) of **23** as greenish syrup; α: β ratio = 11: 1. α-anomer: $^1$H NMR (250 MHz, $CDCl_3$): δ = 5.90 (dd, 1H, $J_{1,2ax}$ 5.0, $J_{1,2eq}$ 1.0, $J_{1,P}$ 10.0 Hz, H-1), 2.20–2.60 (m, 2H, H-2ax,-2eq), 4.20 (m, 1H, H-3), 4.80 (dd, 1H, $J_{3,4}$ 9.2, $J_{4,5}$ 9.6 Hz, H-4), 4.20 (m, 1H, H-5), 1.25 (d, 3H, $J_{5,6}$ 6.4 Hz, $CH_3$-6), 7.40–8.00 (m, 5H, aryl-H), 4.20 (m, 4H, 2x $CH_2$), 1.22 (m, 6H, 2x $CH_3$). β-anomer: $^1$H NMR (250 MHz, $CDCl_3$): δ = 5.00 (t, 1H, $J_{1,2ax}$ 9.6, $J_{1,P}$ 10.0 Hz, H-1), 2.20–2.60 (m, 2H, H-2ax,-2eq), 4.20 (m, 1H, H-3), 4.75 (t, 1H, $J_{3,4}$ 9.2, $J_{4,5}$ 9.6 Hz, H-4), 4.20 (m, 1H, H-5), 1.28 (d, 3H, $J_{5,6}$ 6.4 Hz, $CH_3$-6), 7.40–8.00 (m, 5H, aryl-H), 4.20 (m, 4H, 2x $CH_2$), 1.22 (m, 6H, 2x $CH_3$).

#### 4.3.14. S-[O,O-Diethyl-(3,4-di-O-benzoyl-2,6-dideoxy-α/β-L-ribo-hexopyranosyl)]-dithiophosphate (24)

A solution of **23** (150 mg, 0.35 mmol) in anhydrous tetrahydrofuran (2 mL) was stirred with triphenylphosphine (130 mg, 0.82 mmol) for 30 min and cooled to 0 °C. Then a solution of benzoic acid (130 mg, 1.1 mmol) and diethyl azodicarboxylate (150 μL, 0.96 mmol) in anhydrous tetrahydrofuran (2 mL) was added and stirring continued for 1 h at room temperature. The solvent was evaporated and the residue purified by column chromatography (petroleum ether/ether 8: 1) to give 75 mg (40%) of **24** as light green syrup; α: β ratio = 1: 9. β-anomer: $^1$H NMR (250 MHz, $CDCl_3$): δ = 5.50 (dt, 1H, $J_{1,2ax}$ 9.6, $J_{1,2eq}$ 2.2, $J_{1,P}$ 9.6 Hz, H-1), 2.40 (m, 2H, H-2ax,-2eq), 5.80 (m, 1H, H-3), 4.95 (dd, 1H, $J_{3,4}$ 3.6, $J_{4,5}$ 9.6 Hz, H-4), 4.20 (m, 1H, H-5), 1.30 (d, 3H, $J_{5,6}$ 6.2 Hz, $CH_3$-6), 7.40–8.00 (m, 10H, aryl-H), 4.20 (m, 4H, 2x $CH_2$), 1.40 (m, 6H, 2x $CH_3$).

#### 4.3.15. Benzyl 3-O-[4-O-(3-O-benzoyl-2,6-dideoxy-4-O-methyl-β-L-ribo-hexopyranosyl)-3-O-(3,4-di-O-benzoyl-2,6-dideoxy-β-L-ribo-hexopyranosyl)-2,6-dideoxy-α-L-ribo-hexopyranosyl]-4-O-benzyl-2,6-dideoxy-β-L-ribo-hexopyranoside (25) and Benzyl 3-O-[4-O-(3-O-benzoyl-2,6-dideoxy-4-O-methyl-β-L-ribo-hexopyranosyl)-3-O-(3,4-di-O-benzoyl-2,6-dideoxy-α-L-ribo-hexopyranosyl)-2,6-dideoxy-α-L-ribo-hexopyranosyl]-4-O-benzyl-2,6-dideoxy-β-L-ribo-hexopyranoside (26)

A solution of compound **24** (75 mg, 0.14 mmol) and the acceptor **22** (20 mg, 0.028 mmol) in anhydrous acetonitrile (0.2 mL) were stirred with activated molecular sieves (3 A) for 20 min. Then under light exclusion as promotor iodonium bis-collidine perchlorate (100 mg, 0.21 mmol) was added and stirred for 30 min at room temperature. The mixture was diluted with dichloro-methane (10 mL) washed with aqueous sodium thiosulfate(10%, 20 mL), dried over $MgSO_4$,filtered, evaporated and purified by chromatography (toluene/ethyl acetate 10: 1) to give 6 mg (20%) of the anomeric mixture **25** + **26**; anomeric ratio β: α = 3: 1. β-anomer **25**: $^1$H NMR (400 MHz, $CDCl_3$): δ = 4.99 (dd, 1H, $J_{1,2ax}$ 9.6, $J_{1,2eq}$ 2.0 Hz, H-1), 1.58 (dd, 1H, $J_{1,2ax}$ 9.6, $J_{2ax,2eq}$ = 13.6, $J_{2ax,3}$ = 2.8 Hz, H-2ax), 2.16 (dd, 1H, $J_{1,2eq}$ 2.0, $J_{2ax,2eq}$ 13.6, $J_{2eq,3}$ 3.6 Hz, H-2eq), 4.38 (m, 1H, H-3), 3.24 (dd, 1H, $J_{3,4}$ 2.8, $J_{4,5}$ 9.6 Hz, H-4), 4.35 (dq, 1H, $J_{4,5}$ 9.6, $J_{5,6}$ 6.4 Hz, H-5), 0.92 (d, 3H, $J_{5,6}$ 6.4 Hz, $CH_3$-6), 4.87 (dd, 1H, $J_{1',2'ax}$ 3.6, $J_{1',2'eq}$ 0.8 Hz, H-1′), 1.35 (dt, 1H, $J_{1',2'ax}$ 3.6, $J_{2'ax,2'eq}$ 13.6, $J_{2'ax,3'}$ 3.2 Hz, H-2′ax), 1.96 (dd, 1H, $J_{1',2'eq}$ 0.8, $J_{2'ax,2'eq}$ 13.6, $J_{2'eq,3'}$ 3.6 Hz, H-2′eq), 4.26 (m, 1H, H-3′), 3.12 (dd, 1H, $J_{3',4'}$ 2.8, $J_{4',5'}$ 8.8 Hz, H-4′), 4.13 (dq, 1H, $J_{4',5'}$ 8.8, $J_{5',6'}$ 6.4 Hz, H-5′), 1.32 (d, 3H, $J_{5',6'}$ 6.4 Hz, $CH_3$-6′), 5.38 (dd, 1H, $J_{1'',2''ax}$ 8.2, $J_{1'',2''eq}$ 2.0 Hz, H-1′′), 1.93 (dd, 1H, $J_{1'',2''ax}$ 8.2, $J_{2''ax,2''eq}$ 14.0, $J_{2''ax,3''}$ 2.8 Hz, H-2′′ax), 2.38 (dd, 1H, $J_{1'',2''eq}$ 2.0, $J_{2''ax,2''eq}$ 14.0, $J_{2''eq,3''}$ 3.6 Hz, H-2′′eq), 5.71 (m, 1H, H-3′′), 5.01 (dd, 1H, $J_{3'',4''}$ 2.8, $J_{4'',5''}$ 9.2 Hz, H-4′′), 4.23 (dq, 1H, $J_{4'',5''}$ 9.2, $J_{5'',6''}$ 6.4 Hz, H-5′′), 1.34 (d, 3H, $J_{5'',6''}$ 6.4 Hz, $CH_3$-6′′), 4.82 (dd, 1H, $J_{1''',2'''ax}$ 10.0, $J_{1''',2'''eq}$ 2.0 Hz, H-1′′′), 1.45 (dd, 1H, $J_{1''',2'''ax}$ 10.0, $J_{2'''ax,2'''eq}$ 13.2, $J_{2'''ax,3'''}$ 2.8 Hz, H-2′′′ax), 1.98 (dd, 1H, $J_{1''',2'''eq}$ 2.0, $J_{2'''ax,2'''eq}$ 13.2, $J_{2'''eq,3'''}$ 3.6 Hz, H-2′′′eq), 5.43 (m, 1H, H-3′′′), 2.65 (dd, 1H, $J_{3''',4'''}$ 2.8, $J_{4''',5'''}$ 9.2 Hz, H-4′′′), 3.83 (dq, 1H, $J_{4''',5'''}$ 9.2, $J_{5''',6'''}$ 6.4 Hz, H-5′′′), 1.24 (d, 3H, $J_{5''',6'''}$ 6.4 Hz, $CH_3$-6′′′), 3.28 (s, 3H, $OCH_3$), 4.48, 4.56, 4.74 and 4.94 (each d, each 1H, $J_{CH2Bn}$ = 12.0 Hz, $CH_2$Bn), 7.40–8.00 (m, 25-H, aryl-H). α-anomer **26**: $^1$H NMR (400 MHz, $CDCl_3$): δ = 4.99 (dd, 1H, $J_{1,2ax}$ 9.6, $J_{1,2eq}$ 2.0 Hz, H-1), 1.48 (dd, 1H, $J_{1,2ax}$ 9.6, $J_{2ax,2eq}$ 13.6, $J_{2ax,3}$ 2.8 Hz, H-2ax), 2.24 (dd, 1H, $J_{1,2eq}$ 2.0, $J_{2ax,2eq}$ 13.6, $J_{2eq,3}$ 3.6 Hz, H-2eq), 4.40 (m, 1H, H-3), 3.35 (dd, 1H, $J_{3,4}$ 2.8, $J_{4,5}$ 9.6 Hz, H-4), 4.40 (dq, 1H, $J_{4,5}$ 9.6, $J_{5,6}$ 6.4 Hz, H-5), 1.10 (d, 3H, $J_{5,6}$ 6.4 Hz, $CH_3$-6), 4.87 (dd, 1H, $J_{1',2'ax}$ 3.6, $J_{1',2'eq}$ 0.8 Hz, H-1′), 1.78 (dt, 1H, $J_{1',2'ax}$ 3.6, $J_{2'ax,2'eq}$ 13.6, $J_{2'ax,3'}$ = 3.2 Hz, H-2′ax), 2.00 (dd, 1H, $J_{1',2'eq}$ = 0.8, $J_{2'ax,2'eq}$ = 13.6, $J_{2'eq,3'}$ = 3.6 Hz, H-2′eq), 4.09 (m, 1H, H-3′), 2.86 (dd, 1H, $J_{3',4'}$ = 2.8, $J_{4',5'}$ = 8.8 Hz, H-4′), 3.74 (dq, 1H, $J_{4',5'}$ 8.8, $J_{5',6'}$ 6.4 Hz, H-5′), 1.10 (d, 3H, $J_{5',6'}$ 6.4 Hz, $CH_3$-6′), 5.71 (dd, 1H, $J_{1'',2''ax}$ 3.6, $J_{1'',2''eq}$ 0.8 Hz, H-1′′), 2.08 (dd, 1H, $J_{1'',2''ax}$ 3.6, $J_{2''ax,2''eq}$ 14.0, $J_{2''ax,3''}$ 2.8 Hz, H-2′′ax), 2.34 (dd, 1H, $J_{1'',2''eq}$ 0.8, $J_{2''ax,2''eq}$ 14.0, $J_{2''eq,3''}$ 3.6 Hz, H-2′′eq), 5.71 (m, 1H, H-3′′), 5.06 (dd, 1H, $J_{3'',4''}$ 2.8, $J_{4'',5''}$ 9.2 Hz, H-4′′), 4.23 (dq, 1H, $J_{4'',5''}$ 9.2, $J_{5'',6''}$ 6.4 Hz, H-5′′), 1.30 (d, 3H, $J_{5'',6''}$ 6.4 Hz, $CH_3$-6′′), 5.05 (dd, 1H, $J_{1''',2'''ax}$ 10.6, $J_{1''',2'''eq}$ 2.0 Hz, H-1′′′), 1.84 (dd, 1H, $J_{1''',2'''ax}$ 10.6, $J_{2'''ax,2'''eq}$ 13.2, $J_{2'''ax,3'''}$ 2.8 Hz, H-2′′′ax), 2.27 (dd, 1H, $J_{1''',2'''eq}$ 2.0, $J_{2'''ax,2'''eq}$ 13.2, $J_{2'''eq,3'''}$ 3.6 Hz, H-2′′′eq), 5.77 (m, 1H, H-3′′′), 2.90 (dd, 1H, $J_{3''',4'''}$ 2.8, $J_{4''',5'''}$ 9.2 Hz, H-4′′′), 3.94 (dq, 1H, $J_{4''',5'''}$ 9.2, $J_{5''',6'''}$ 6.4 Hz, H-5′′′), 1.30 (d, 3H, $J_{5''',6'''}$ 6.4 Hz, $CH_3$-6′′′), 3.32 (s, 3H, $OCH_3$), 4.48, 4.56, 4.74 and 4.94 (each d, each 1H, $J_{CH2Bn}$ 12.0 Hz, $CH_2$Bn), 7.40–8.00 (m, 25-H, aryl-H).

*4.3.16. Benzyl 3-O-[4-O-(3-O-benzoyl-2,6-dideoxy-4-O-methyl-β-L-ribo-hexopyranosyl)-3-O-(4-O-benzoyl-2,6-dideoxy-3-ulose-β-L-erythro-hexo-pyranosyl)-2,6-dideoxy-α-L-ribo-hexopyranosyl]-4-O-benzyl-2,6-dideoxy-β-L-ribo-hexopyranoside (**30**) and Benzyl 3-O-[4-O-(3-O-benzoyl-2,6-dideoxy-4-O-methyl-β-L-ribo-hexopyrano-syl)-3-O-(4-O-benzoyl-2,6-dideoxy-3-ulose-α-L-erythro-hexopyranosyl)-2,6-dideoxy-α-L-ribo-hexopyranosyl]-4-O-benzyl-2,6-dideoxy-β-L-ribo-hexopyranoside (**31**)*

**a)** Compound **28** (65 mg, 0.28 mmol) and *O*,*O*-diethyl *S*-hydrogen phosphorodithioate (70 μL, 1.01 mmol) dissolved in benzene (1 mL) were stirred overnight at room temperature. The solvent was evaporated and the raw anomeric material **29** directly used for glycosylation. Dissolved in anhydrous dichloromethane (1.5 mL) it was mixed with the acceptor **22** (90 mg, 0.12 mmol) and stirred with molecular sieves (3 A) for 20 min. Then the promotor iodine bis-collidinium perchlorate (195 mg, 0.41 mmol) was added under light exclusion and stirred for 1 h at room temperature. The mixture was diluted with dichloromethane (20 mL), washed with aqueous sodium thiosulfate(10%, 40 mL), dried over $MgSO_4$, filtered, evaporated and purified by chromatography (petroleum ether/ether 2: 1) to give 71 mg (60%) of the anomeric mixture **30** + **31**; anomeric ratio α: β = 1.1: 1.

b) Compound **28** (22 mg, 0.09 mmol) and *O*,*O*-diethyl *S*-hydrogen phosphorodithioate (25 μL, 0.34 mmol) dissolved in benzene (1 mL) were stirred overnight at room temperature. The solvent was evaporated and the raw anomeric material **29** directly used for glycosylation. Dissolved in anhydrous acetonitrile (0.5 mL) it was mixed with the acceptor **22** (30 mg, 0.04 mmol) and stirred with molecular sieves (3 A) for 20 min. Then the promotor iodonium bis-collidine perchlorate (195 mg, 0.41 mmol) was added under light exclusion and stirred for 1 h at room temperature. The mixture was diluted with dichloromethane (10 mL) washed with aqueous sodium thiosulfate(10%, 20 mL), dried over $MgSO_4$,filtered, evaporated and purified by chromatography (petroleum ether/ether 2: 1) to give 22 mg (55%) of the anomeric mixture **30** + **31**; anomeric ratio α: β = 1: 2. Part of the β-anomer **30** was obtained as colourless crystals, mp 163–165 °C; $[\alpha]_D^{20}$ = - 73.4 (*c* = 1.0, $CH_2Cl_2$); β-anomer **30**: $^1$H NMR (400 MHz, $CDCl_3$): δ = 4.99 (dd, 1H, $J_{1,2ax}$ 9.2, $J_{1,2eq}$ 2.0 Hz, H-1), 1.60 (dd, 1H, $J_{1,2ax}$ 9.2, $J_{2ax,2eq}$ 13.2, $J_{2ax,3}$ 2.8 Hz, H-2ax), 2.13 (dd, 1H, $J_{1,2eq}$ 2.0, $J_{2ax,2eq}$ 13.2, $J_{2eq,3}$ 3.6 Hz, H-2eq), 4.27 (m, 1H, H-3), 3.13 (dd, 1H, $J_{3,4}$ 2.4, $J_{4,5}$ 8.4 Hz, H-4), 4.09 (dq, 1H, $J_{4,5}$ 8.4, $J_{5,6}$ 6.4 Hz, H-5), 1.32 (d, 3H, $J_{5,6}$ 6.4 Hz, $CH_3$-6), 4.90 (dd, 1H, $J_{1',2'ax}$ 4.0, $J_{1',2'eq}$ = 0.8 Hz, H-1′), 1.97 (dt, 1H, $J_{1',2'ax}$ 4.0, $J_{2'ax,2'eq}$ 14.4, $J_{2'ax,3'}$ 4.0 Hz, H-2′ax), 2.27 (dd, 1H, $J_{1',2'eq}$ 0.8, $J_{2'ax,2'eq}$ 14.4, $J_{2'eq,3'}$ 3.6 Hz, H-2′eq), 4.42 (m, 1H, H-3′), 3.26 (dd, 1H, $J_{3',4'}$ 2.8, $J_{4',5'}$ 9.6 Hz, H-4′), 4.35 (dq, 1H, $J_{4',5'}$ 9.6, $J_{5',6'}$ 6.4 Hz, H-5′), 0.96 (d, 3H, $J_{5',6'}$ 6.4 Hz, $CH_3$-6′), 5.22 (dd, 1H, $J_{1'',2''ax}$ 9.2, $J_{1'',2''eq}$ 2.4 Hz, H-1′′), 2.67 (dd, 1H, $J_{1'',2''ax}$ 9.2, $J_{2''ax,2''eq}$ 14.4 Hz, H-2′′ax), 2.86 (dd, 1H, $J_{1'',2''eq}$ 2.4, $J_{2''ax,2''eq}$ 14.4 Hz, H-2′′eq), 5.12 (d, 1H, $J_{4'',5''}$ 10.0 Hz, H-4′′), 3.80 (dq, 1H, $J_{4'',5''}$ 10.0, $J_{5'',6''}$ 6.4 Hz, H-5′′), 1.44 (d, 3H, $J_{5'',6''}$ 6.4 Hz, $CH_3$-6′′), 4.88 (dd, 1H, $J_{1''',2'''ax}$ 9.6, $J_{1''',2'''eq}$ 2.0 Hz, H-1′′′), 1.77 (dd, 1H, $J_{1''',2'''ax}$ 9.6, $J_{2'''ax,2'''eq}$ 14.0, $J_{2'''ax,3'''}$ 2.8 Hz, H-2′′′ax), 2.14 (dd, 1H, $J_{1''',2'''eq}$ 2.0, $J_{2'''ax,2'''eq}$ 14.0, $J_{2'''eq,3'''}$ 3.6 Hz, H-2′′′eq), 5.78 (m, 1H, H-3′′′), 2.99 (dd, 1H, $J_{3''',4'''}$ 2.8, $J_{4''',5'''}$ 9.2 Hz, H-4′′′), 3.92 (dq, 1H, $J_{4''',5'''}$ 9.2, $J_{5''',6'''}$ 6.4 Hz, H-5′′′), 1.30 (d, 3H, $J_{5''',6'''}$ 6.4 Hz, $CH_3$-6′′′), 3.38 (s, 3H, $OCH_3$), 4.48, 4.55, 4.74 and 4.93 (each d, each 1H, $J_{CH2Bn}$ 12.0 Hz, $CH_2$Bn), 7.40–8.00 (m, 25-H, aryl-H). α-anomer **31**: $^1$H NMR (400 MHz, $CDCl_3$): δ = 4.76 (dd, 1H, $J_{1,2ax}$ 9.6, $J_{1,2eq}$ 2.0 Hz, H-1), 1.75 (dd, 1H, $J_{1,2ax}$ 9.6, $J_{2ax,2eq}$ 13.6, $J_{2ax,3}$ 2.8 Hz, H-2ax), 2.09 (dd, 1H, $J_{1,2eq}$ 2.0, $J_{2ax,2eq}$ 13.6, $J_{2eq,3}$ 3.6 Hz, H-2eq), 4.25 (m, 1H, H-3), 3.06 (dd, 1H, $J_{3,4}$ 2.8, $J_{4,5}$ 9.2 Hz, H-4), 3.90 (dq, 1H, $J_{4,5}$ 9.2, $J_{5,6}$ 6.4 Hz, H-5), 1.30 (d, 3H, $J_{5,6}$ 6.4 Hz, $CH_3$-6), 4.87 (dd, 1H, $J_{1',2'ax}$ 4.4, $J_{1',2'eq}$ 0.8 Hz, H-1′), 1.78 (dd, 1H, $J_{1',2'ax}$ 4.4, $J_{2'ax,2'eq}$ 13.6, $J_{2'ax,3'}$ 3.2 Hz, H-2′ax), 2.09 (dd, 1H, $J_{1',2'eq}$ 0.8, $J_{2'ax,2'eq}$ 13.6, $J_{2'eq,3'}$ 3.6 Hz, H-2′eq), 4.25 (m, 1H, H-3′), 3.28 (dd, 1H, $J_{3',4'}$ 3.2, $J_{4',5'}$ 10.0 Hz, H-4′), 4.33 (dq, 1H, $J_{4',5'}$ 10.0, $J_{5',6'}$ 6.4 Hz, H-5′), 0.94 (d, 3H, $J_{5',6'}$ 6.4 Hz, $CH_3$-6′), 5.34 (dd, 1H, $J_{1'',2''ax}$ 4.0, $J_{1'',2''eq}$ 0.8 Hz, H-1′′), 2.72 (dd, 1H, $J_{1'',2''ax}$ 4.0, $J_{2''ax,2''eq}$ 14.0 Hz, H-2′′ax), 2.80 (dd, 1H, $J_{1'',2''eq}$ 0.8, $J_{2''ax,2''eq}$ 14.0 Hz, H-2′′eq), 5.20 (d, 1H, $J_{4'',5''}$ 10.0 Hz, H-4′′), 4.74 (dq, 1H, $J_{4'',5''}$ 10.0, $J_{5'',6''}$ 6.4 Hz, H-5′′), 1.40 (d, 3H, $J_{5'',6''}$ 6.4 Hz, $CH_3$-6′′), 4.90 (dd, 1H, $J_{1''',2'''ax}$ 0.6, $J_{1''',2'''eq}$ 2.0 Hz, H-1′′′), 1.84 (dd, 1H, $J_{1''',2'''ax}$ 9.6, $J_{2'''ax,2'''eq}$ 13.2, $J_{2'''ax,3'''}$ 2.8 Hz, H-2′′′ax), 2.21 (dd, 1H, $J_{1''',2'''eq}$ 2.0, $J_{2'''ax,2'''eq}$ 13.2, $J_{2'''eq,3'''}$ 3.6 Hz, H-2′′′eq), 5.79 (dt, 1H, $J_{2'''\ ax,3'''}$ 2.8, $J_{2'''\ eq,3'''}$ 3.6, $J_{3''',4'''}$ 2.8 Hz, H-3′′′), 2.90 (dd, 1H, $J_{3''',4'''}$ 2.8, $J_{4''',5'''}$ 9.2 Hz, H-4′′′), 3.86 (dq, 1H, $J_{4''',5'''}$ 9.2, $J_{5''',6'''}$ 6.4 Hz, H-5′′′), 1.30 (d, 3H, $J_{5''',6'''}$ 6.4 Hz, $CH_3$-6′′′), 3.34 (s, 3H, $OCH_3$), 4.45, 4.54, 4.72 and 4.87 (each d, each 1H, $J_{CH2Bn}$ 12.0 Hz, $CH_2$Bn), 7.40–8.00 (m, 25-H, aryl-H). Calcd. for $C_{53}H_{62}O_{15}$(939.0): C, 67.78; H, 6.65. Found: C, 67.71; H, 6.70.

*4.3.17. Benzyl 3-O-[4-O-(3-O-benzoyl-2,6-dideoxy-4-O-methyl-β-L-ribo-hexopy-ranosyl)-3-O-(4-O-benzoyl-2,6-dideoxy-β-L-ribo-hexopyranosyl)-2,6-dideoxy-α-L-ribo-hexopyranosyl]-4-O-benzyl-2,6-dideoxy-β-L-ribo-hexopyranoside (**32**) and Benzyl 3-O-[4-O-(3-O-benzoyl-2,6-dideoxy-4-O-methyl-β-L-ribo-hexopyranosyl)-3-O-(4-O-benzoyl-2,6-dideoxy-α-L-ribo-hexopyranosyl)-2,6-dideoxy-α-L-ribo-hexopyranosyl]-4-O-benzyl-2,6-dideoxy-β-L-ribo-hexopyranoside (**33**)*

A solution of the anomeric mixture of tetrasaccharides **30** + **31** (40 mg, 0.043 mmol) in anhydrous methanol (2 mL) was cooled to 0 °C and treated with sodium borohydride (20 mg, 0.52 mmol). After stirring for 10 min at room temperature the mixture was neutralized with hydrochloric acid (4 M), diluted with water, extracted with dichloromethane (10 mL), the organic phase dried ($MgSO_4$), filtered, evaporated and the raw material purified and separated by column chromatography (toluene/ethyl acetate 6: 1) to give 38 mg (95%) of **32** + **33.**

β-anomer **32**: 18 mg (45%) as colourless syrup; $[\alpha]_D^{20}$ = - 84.2 (*c* = 1.0, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$): δ = 5.01 (dd, 1H, $J_{1,2ax}$ 8.8, $J_{1,2eq}$ 2.0 Hz, H-1), 1.58 (dd, 1H, $J_{1,2ax}$ 8.8, $J_{2ax,2eq}$ 13.6, $J_{2ax,3}$ 2.8 Hz, H-2ax), 2.13 (dd, 1H, $J_{1,2eq}$ 2.0, $J_{2ax,2eq}$ 13.6, $J_{2eq,3}$ 3.6 Hz, H-2eq), 4.27 (m, 1H, H-3), 3.12 (dd, 1H, $J_{3,4}$ 2.8, $J_{4,5}$ 8.8 Hz, H-4), 4.14 (dq, 1H, $J_{4,5}$ 8.8, $J_{5,6}$ 6.4 Hz, H-5), 1.28 (d, 3H, $J_{5,6}$ 6.4 Hz, $CH_3$-6), 4.89 (dd, 1H, $J_{1',2'ax}$ 4.0, $J_{1',2'eq}$ 0.8 Hz, H-1′), 1.95 (dd, 1H, $J_{1',2'ax}$ 4.0, $J_{2'ax,2'eq}$ 14.4, $J_{2'ax,3'}$ 4.4 Hz, H-2′ax), 2.21 (dd, 1H, $J_{1',2'eq}$ 0.8, $J_{2'ax,2'eq}$ 14.4, $J_{2'eq,3'}$ 3.6 Hz, H-2′eq), 4.34 (m, 1H, H-3′), 3.29 (dd, 1H, $J_{3',4'}$ 2.8, $J_{4',5'}$ 9.6 Hz, H-4′), 4.36 (dq, 1H, $J_{4',5'}$ 9.6, $J_{5',6'}$ 6.4 Hz, H-5′), 1.00 (d, 3H, $J_{5',6'}$ 6.4 Hz, $CH_3$-6′), 5.04 (dd, 1H, $J_{1'',2''ax}$ 8.4, $J_{1'',2''eq}$ 2.0 Hz, H-1′′), 1.76 (dd, 1H, $J_{1'',2''ax}$ 8.4, $J_{2''ax,2''eq}$ 12.8, $J_{2''ax,3''}$ 9.6 Hz, H-2′′ax), 2.36 (dd, 1H, $J_{1'',2''eq}$ 2.0, $J_{2''ax,2''eq}$ 12.8, $J_{2''eq,3''}$ 5.6 Hz, H-2′′eq), 3.89 (m, 1H, H-3′′), 4.84 (t, 1H, $J_{3'',4''}$ 8.8, $J_{4'',5''}$ 8.8 Hz, H-4′′), 3.58 (dq, 1H, $J_{4'',5''}$ 8.8, $J_{5'',6''}$ 6.4 Hz, H-5′′), 1.30 (d, 3H, $J_{5'',6''}$ 6.4 Hz, $CH_3$-6′′), 4.90 (dd, 1H, $J_{1''',2'''ax}$ 9.6, $J_{1''',2'''eq}$ 2.0 Hz, H-1′′′), 1.82 (dd, 1H, $J_{1''',2'''ax}$ 9.6, $J_{2'''ax,2'''eq}$ 13.2, $J_{2'''ax,3'''}$ 2.8 Hz, H-2′′′ax), 2.24 (dd, 1H, $J_{1''',2'''eq}$ 2.0, $J_{2'''ax,2'''eq}$ 14.4, $J_{2'''eq,3'''}$3.6 Hz, H-2′′′eq), 5.80 (dt, 1H, $J_{2'''\ ax,3'''}$ 2.8, $J_{2'''\ eq,3'''}$ 3.6, $J_{3''',4'''}$ 2.8 Hz, H-3′′′), 3.00 (dd, 1H, $J_{3''',4'''}$ 2.8, $J_{4''',5'''}$ 9.2 Hz, H-4′′′), 3.93 (dq, 1H, $J_{4''',5'''}$ 9.2, $J_{5''',6'''}$ 6.4 Hz, H-5′′′), 1.30 (d, 3H, $J_{5''',6'''}$ 6.4 Hz, $CH_3$-6′′′), 3.38 (s, 3H, $OCH_3$), 4.40, 4.57, 4.75 and 4.93 (each d, each 1H, $J_{CH2Bn}$ 12.0 Hz, $CH_2$Bn), 7.40–8.00 (m, 25-H, aryl-H).

α-anomer **33**: 20 mg (50%) as colourless crystals; mp 78–80 °C, $[\alpha]_D^{20}$ = - 131.2 (*c* = 1.0, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$): δ = 4.78 (dd, 1H, $J_{1,2ax}$ 9.6, $J_{1,2eq}$ 2.0 Hz, H-1), 1.57 (dd, 1H, $J_{1,2ax}$ 9.6, $J_{2ax,2eq}$ 13.6, $J_{2ax,3}$ 2.8 Hz, H-2ax), 2.10 (dd, 1H, $J_{1,2eq}$ 2.0, $J_{2ax,2eq}$ 13.6, $J_{2eq,3}$ 3.6 Hz, H-2eq), 4.28 (m, 1H, H-3), 3.10 (dd, 1H, $J_{3,4}$ 2.8, $J_{4,5}$ 9.2 Hz, H-4), 3.85 (dq, 1H, $J_{4,5}$ 9.2, $J_{5,6}$ 6.4 Hz, H-5), 1.26 (d, 3H, $J_{5,6}$ 6.4 Hz, $CH_3$-6), 4.87 (dd, 1H, $J_{1',2'ax}$ 4.0, $J_{1',2'eq}$ 0.8 Hz, H-1′), 1.76 (dd, 1H, $J_{1',2'ax}$ 4.0, $J_{2'ax,2'eq}$ 14.8, $J_{2'ax,3'}$ 3.2 Hz, H-2′ax), 2.20 (dd, 1H, $J_{1',2'eq}$ 0.8, $J_{2'ax,2'eq}$ 14.8, $J_{2'eq,3'}$ 3.6 Hz, H-2′eq), 4.32 (m, 1H, H-3′), 3.35 (dd, 1H, $J_{3',4'}$ 3.2, $J_{4',5'}$ 9.6 Hz, H-4′), 4.33 (dq, 1H, $J_{4',5'}$ 9.6, $J_{5',6'}$ 6.4 Hz, H-5′), 0.94 (d, 3H, $J_{5',6'}$ 6.4 Hz, $CH_3$-6′), 5.23 (dd, 1H, $J_{1'',2''ax}$ 2.8, $J_{1'',2''eq}$ 0.4 Hz, H-1′′), 1.93 (dt, 1H, $J_{1'',2''ax}$ = 2.8, $J_{2''ax,2''eq}$ 14.4, $J_{2''ax,3''}$ 3.2 Hz, H-2′′ax), 2.22 (dd, 1H, $J_{1'',2''eq}$ 0.4, $J_{2''ax,2''eq}$ 14.4, $J_{2''eq,3''}$ 3.6 Hz, H-2′′eq), 4.23 (m, 1H, H-3′′), 4.78 (dd, 1H, $J_{3'',4''}$ 3.2, $J_{4'',5''}$ 10.4 Hz, H-4′′), 4.57 (dq, 1H, $J_{4'',5''}$ 10.4, $J_{5'',6''}$ 6.4 Hz, H-5′′),

1.29 (d, 3H, $J_{5''',6'''}$ 6.4 Hz, $CH_3$-6´´´), 4.96 (dd, 1H, $J_{1''',2'''ax}$ 9.6, $J_{1''',2'''eq}$ 2.0 Hz, H-1´´´), 2.07 (dd, 1H, $J_{1''',2'''ax}$ 9.6, $J_{2'''ax,2'''eq}$ 13.2, $J_{2'''ax,3'''}$ 2.8 Hz, H-2´´´ax), 2.24 (dd, 1H, $J_{1''',2'''eq}$ 2.0, $J_{2'''ax,2'''eq}$ 13.2, $J_{2'''eq,3'''}$ 3.6 Hz, H-2´´´eq), 5.82 (dt, 1H, $J_{2''' ax,3'''}$ 2.8, $J_{2''' eq,3'''}$ = 3.6, $J_{3''',4'''}$ 2.8 Hz, H-3´´´), 2.99 (dd, 1H, $J_{3''',4'''}$ 2.8, $J_{4''',5'''}$ 9.2 Hz, H-4´´´), 3.95 (dq, 1H, $J_{4''',5'''}$ 9.2, $J_{5''',6'''}$ 6.4 Hz, H-5´´´),1.33 (d, 3H, $J_{5''',6'''}$ 6.4 Hz, $CH_3$-6´´´), 3.32 (s, 3H, $OCH_3$), 4.46, 4.52, 4.71 and 4.89 (each d, each 1H, $J_{CH2Bn}$ 12.0 Hz, $CH_2$Bn), 7.40–8.00 (m, 25-H, aryl-H). Calcd. for $C_{53}H_{64}O_{15}$(941.0): C, 67.64; H, 6.85. Found: C, 67.54; H, 6.90.

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