Direct Synthesis of Pseudo-Disaccharides by Rearrangement of Unsaturated Disaccharides

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Keywords: Carbohydrates / 5′a-Carbadisaccharides / Cyclohexane / Triisobutylaluminium / Rearrangements

The series of unsaturated disaccharides **10–14** undergo stereoselective reductive rearrangement with TIBAL (triisobutylaluminium) to afford (1→4) and (1→6) ether-linked pseudo-disaccharides **2–9**.

Introduction

Carbadisaccharides are carbocyclic analogues of disaccharides in which one (or both) of the hexose residues is (are) replaced with a carba-sugar, that is, a cyclic monosaccharide in which the ring-oxygen atom is replaced by a methylene group. For example, there are three carbadisaccharide analogues of α-maltose, two monocarba-, and one dicarbadisaccharide, as shown in Figure 1.

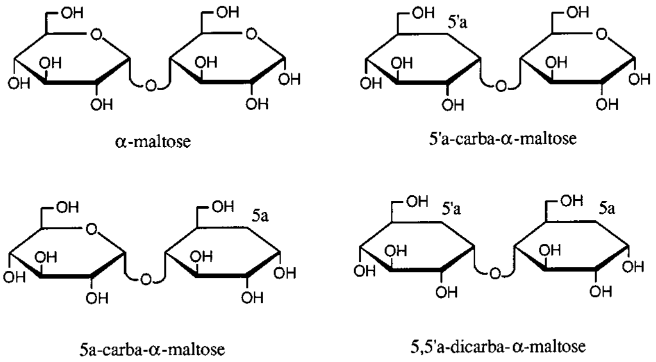

Figure 1. Maltose and its carbadisaccharide analogues

The 5′a-carbadisaccharides in which the two rings are connected through a stable ether linkage have received particular attention and have been shown to act as substrate analogues for glycosyltransferases,[1] and are building blocks for the preparation of biologically relevant carbaoligosaccharides.[2] 5′a-Carbadisaccharides are prepared by conventional assembly between the two rings.[3]

We recently reported[4] that perbenzylated α-methyl or benzyl 6-deoxyhex-5-enopyranosides undergo smooth reductive rearrangement with TIBAL (triisobutylaluminium) to afford substituted cyclohexane derivatives with retention of the anomeric information (Figure 2).

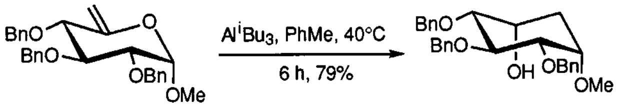

Figure 2. Typical example of TIBAL-promoted rearrangement

Likewise, we reported[5] the related carbocyclic ring closure of perbenzylated α-methyl or benzyl 6-deoxyhex-5-enopyranosides promoted by titanium(IV) (Figure 3). The use of the mild Lewis acid Ti(O*i*Pr)Cl$_3$ resulted in almost quantitative formation of the carbocycle **1** with retention of the keto function and the anomeric information. The analogous titanium(IV)-promoted pyranose-to-cyclohexane transformation of vinylic anomeric spiro-orthoesters has also been described.[6]

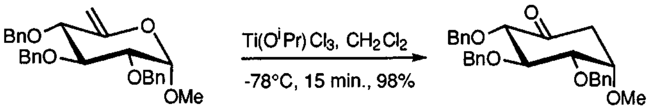

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Figure 3. Typical example of Ti^{IV}-promoted rearrangement

These novel reactions therefore complement the classical Ferrier-II[7] carbocyclisation reaction, which inherently requires *exo*-glycosidic cleavage to eject the aglycon. In contrast, the aglycon moiety is retained during the TIBAL- or Ti^{IV}-promoted rearrangements due to initial *endo*-glycosidic cleavage. We recognised that our conditions might be compatible with sugar aglycons allowing transformation of a pyranose ring at the nonreducing end of a disaccharide into a carbocycle, thereby providing a highly attractive synthesis of 5′a-carbadisaccharide precursors, which we will call pseudo-disaccharides. We now disclose the application of this methodology to the expedient and stereoselective synthesis of (1→4) and (1→6) ether-linked pseudo-disaccharides

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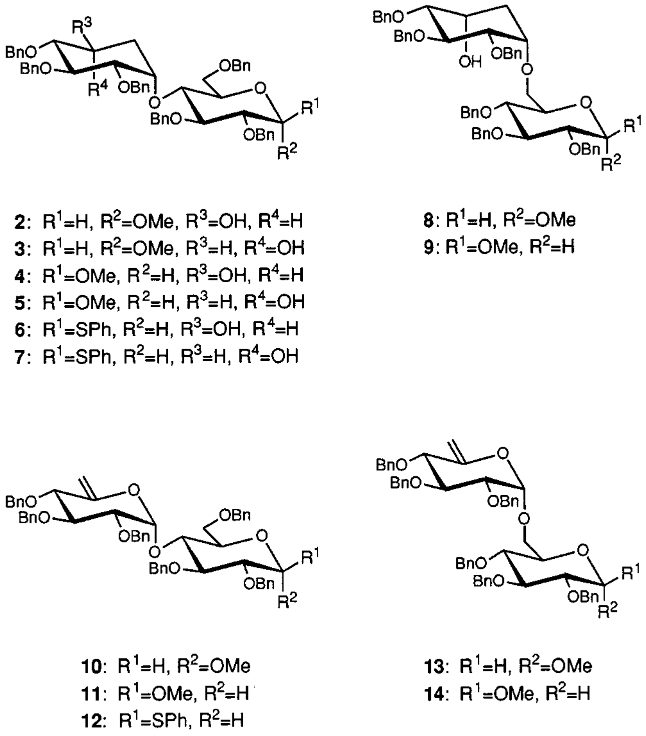
ides **2−9** from the readily prepared hex-5-enopyranosides **10−14** (Figure 4).



2: R^1=H, R^2=OMe, R^3=OH, R^4=H
3: R^1=H, R^2=OMe, R^3=H, R^4=OH
4: R^1=OMe, R^2=H, R^3=OH, R^4=H
5: R^1=OMe, R^2=H, R^3=H, R^4=OH
6: R^1=SPh, R^2=H, R^3=OH, R^4=H
7: R^1=SPh, R^2=H, R^3=H, R^4=OH

8: R^1=H, R^2=OMe
9: R^1=OMe, R^2=H

10: R^1=H, R^2=OMe
11: R^1=OMe, R^2=H
12: R^1=SPh, R^2=H

13: R^1=H, R^2=OMe
14: R^1=OMe, R^2=H

Figure 4. Pseudo-disaccharides and their unsaturated disaccharide precursors

Results and Discussion

TIBAL-Promoted Rearrangement

Synthesis of (1→4) Ether-Linked Pseudo-Disaccharides 2−7

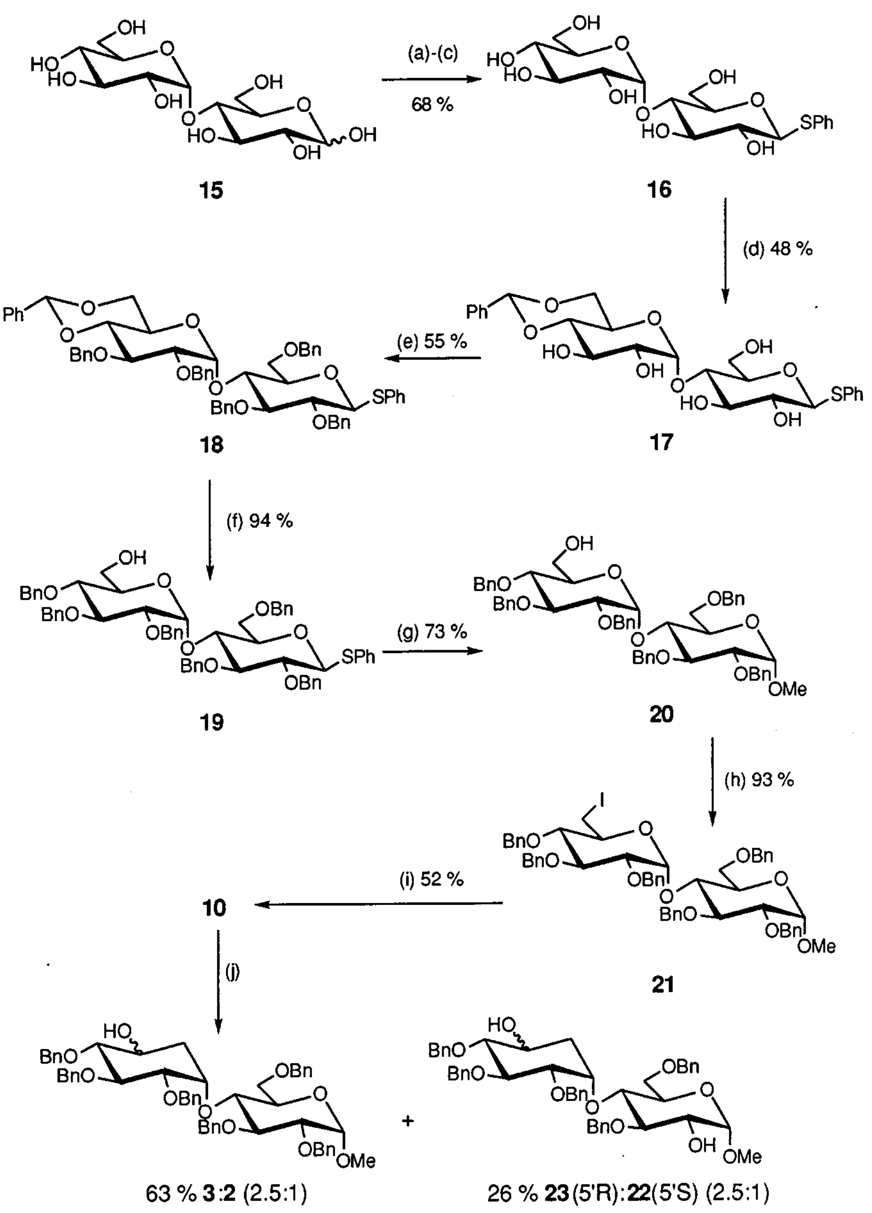
Construction of the α-methyl maltoside derived hex-5-enopyranoside **10** was readily achieved from D-maltose by a synthesis summarised in Scheme 1. Peracetylation of D-maltose (**15**) with refluxing acetic anhydride and sodium acetate[8] followed by glycosylation with thiophenol-promoted by boron trifluoride−diethyl ether and then deacetylation gave exclusively the phenyl 1-thio-β-maltoside (**16**)[9] (68% from **15**). Selective benzylidene protection of thioglycoside **16** was readily achieved by condensation with benzaldehyde dimethyl acetal in mildly acidic DMF, to afford the 4,6-*O*-benzylidene **17** (48% yield) and subsequent perbenzylation with benzylbromide and sodium hydride in DMF, to give the fully protected maltoside **18** (55%). Regioselective ring-opening of the benzylidene in **18** was achieved by the Lipták method[10] to give the 6′-OH alcohol **19** (94%). Glycosylation of the thioglycoside **19** in excess methanol with *N*-chlorosuccinimide as a promoter then gave the α-methyl maltoside **20** (68%) whose α-configuration was assigned by ^{1}H-NMR spectroscopy (δ = 4.65, $J_{1,2}$ 3.7 Hz). Iodination[11a] of the alcohol **20** under conditions developed by Garegg gave **21** (93%), which underwent slow (48 h) but smooth elimination[11b] with excess DBU in refluxing THF to give the desired hex-5′-enomaltoside **10** in 52% yield following recrystallisation. The structure of **10** was supported by ^{13}C-NMR spectroscopy which showed clear signals (δ = 154.1, s, C-5′) and (δ = 96.4, t, C-6′) due to the exocyclic double bond.

Reaction of hex-5′-enomaltoside **10** with excess TIBAL at 50°C resulted in the transposition of an oxygen on the ring with the exocyclic carbon atom as expected, to afford the (1→4) ether-linked pseudo-disaccharides **3** and **2** (63%) as a 2.5:1 mixture of diastereomers at C-5′ (by ^{1}H-NMR spectroscopy). Moderate diastereoselectivity observed is in favour of hydride delivery from the less hindered β-face of the keto intermediate;[12] however, it is noted that complete retention of stereochemical information at the anomeric centre (C-1′) is observed. Also isolated were the partially debenzylated pseudo-disaccharides **22** and **23** (26%) resulting from regioselective de-*O*-benzylation at the 2-O position. Similarly, we have recently shown[13] that perbenzylated α-methyl maltoside undergoes regioselective de-*O*-benzylation at the 2-O position with TIBAL, although after extended reaction times (3 days). In comparison, the TIBAL-mediated rearrangement of perbenzylated α-methylglucoside required only 6 hours[4] (Figure 2). We therefore propose that in general, successful TIBAL-mediated rearrangement of hex-5-enopyranosides is dependent on this differential rate difference.

Our detailed mechanistic studies[13] revealed that the TIBAL-promoted debenzylation: (i) required a *cis* 1,2-OR motif e.g. α-methylglycosides undergo debenzylation, whilst β-methyl- or thioglycosides do not; (ii) was relatively slower than the rate of reductive rearrangement of monosaccharide substrates. We therefore aimed to exploit these observations in order to minimise competitive de-*O*-benzylation during TIBAL-mediated reductive rearrangement.

Construction of the β-methyl maltoside derived hex-5-enopyranoside **11** was achieved from the readily available 4′,6′-*O*-benzylidene derivative **24**[14] as summarised in Scheme 2. Benzylidene hydrolysis of **24** and subsequent regioselective iodination of the primary alcohol of **25** gave **26**. Iodide **26** underwent one-pot benzylation−elimination with sodium hydride and benzyl bromide in DMF to give the desired hex-5′-enomaltoside **11** (81%), whose assignment was supported by ^{13}C-NMR spectroscopy, which showed clear signals (δ = 154.0, s, C-5′) and (δ = 96.6, t, C-6′) due to the exocyclic double bond. Reaction of hex-5′-enomaltoside **11** with excess TIBAL at 50°C resulted in smooth conversion into the (1→4) ether-linked pseudo-disaccharides **5** and **4** (65%) as a 4.7:1 mixture of diastereomers at C-5′ (by ^{1}H-NMR spectroscopy). Indeed, no products of debenzylation were observed, because as predicted the rate of reductive rearrangement was rapid relative to the rate of debenzylation of the β-OMe glycoside (vide supra).

β-Thioglycosides are resistant to TIBAL-mediated debenzylation even after extended reaction times; for example, perbenzylated β-thiophenyl maltoside remained intact after treatment with excess TIBAL for 8 days at 50°C. The thiog-



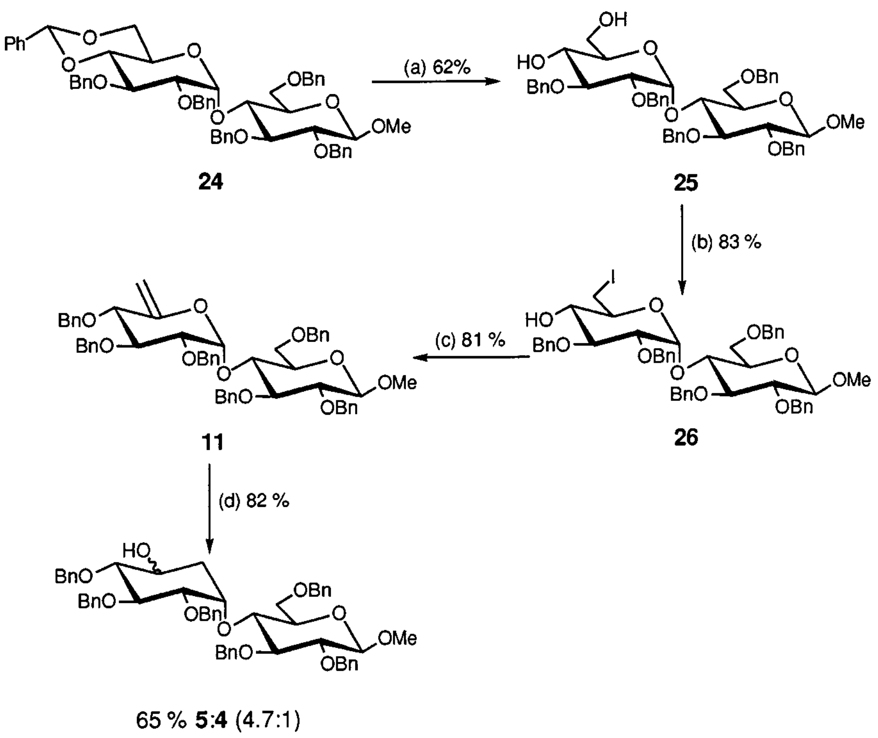
Reagents and Conditions: (a) Ac_2O, NaOAc, reflux; (b) PhSH; BF_3OEt_2, RT, 2h; (c) NaOMe, MeOH; (d) $PhC(OMe)_2$, DMF, 60 °C, 1 mmHg; (e) NaH, BnBr, DMF; (f) $LiAlH_4$, $AlCl_3$, DCM, Et_2O; (g) NCS, MeOH; (h) Ph_3P, I_2, Im, PhMe, 70 °C; (i) DBU, THF, reflux; (j) TIBAL, PhMe, 50 °C, 4 h

Scheme 1

lycoside hex-5′-enomaltoside **12** was therefore prepared from **19** by standard iodination−elimination. The intermediate iodide **27** was rather unstable and was therefore immediately subjected to elimination. As expected, **12** underwent TIBAL-promoted rearrangement to afford the desired thioglycoside pseudo-disaccharides **7** and **6** (60%) as a 2:1 mixture of diastereomers at C-5′ (by ^{1}H-NMR spectroscopy); no debenzylation products were detected. The success of the TIBAL-promoted rearrangement directly on thioglycoside substrates is advantageous providing direct access to selectively protected pseudo-disaccharide donors for further glycosylation.

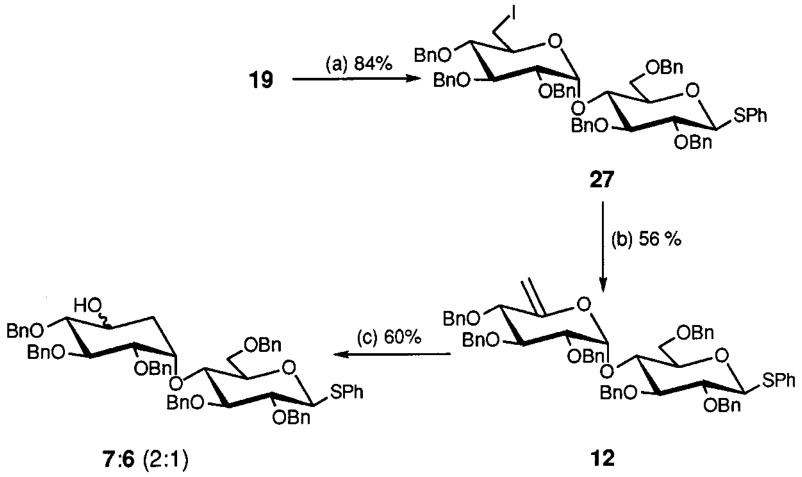
Synthesis of (1→6) Ether-Linked Pseudo-Disaccharides 8−9

Construction of the hex-5′-enoisomaltoside **13** was most readily achieved by standard iodination and elimination of the readily available α-methyl isomaltoside **28**[15] (Scheme 4). Reaction of hex-5′-enoisomaltoside **13** with excess TIBAL at 50°C gave the (1→6) ether-linked pseudo-disaccharide **8** (11%) as a single diastereomer at C-5′. Also isolated were the corresponding 2-*O*-debenzylated pseudo-disaccharide **29** (48%) together with the 2-*O*-debenzylated hex-5′-enoisomaltoside **30** (13%). This result was consistent



Reagents and Conditions: (a) 80 % AcOH; (b) Ph_3P, I_2, Im, PhMe, 80 °C; (c) NaH, BnBr, DMF, RT; (d) TIBAL, PhMe, 50 °C, 4 h

Scheme 2

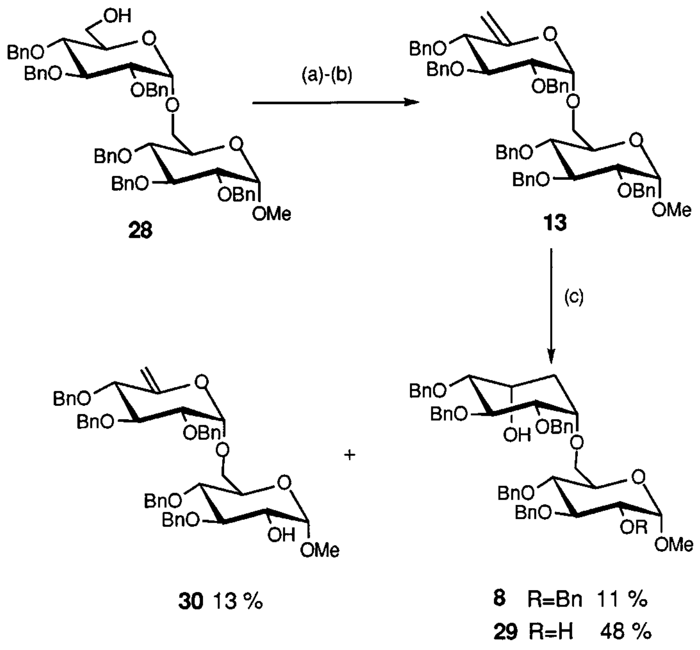


Reagents and Conditions: (a) Ph_3P, I_2, Im, PhMe, 70 °C; (b) DBU, THF, PhMe, 50 °C, 5 h; (c) TIBAL (10 eq.), PhMe, 50 °C, 4 h

Scheme 3

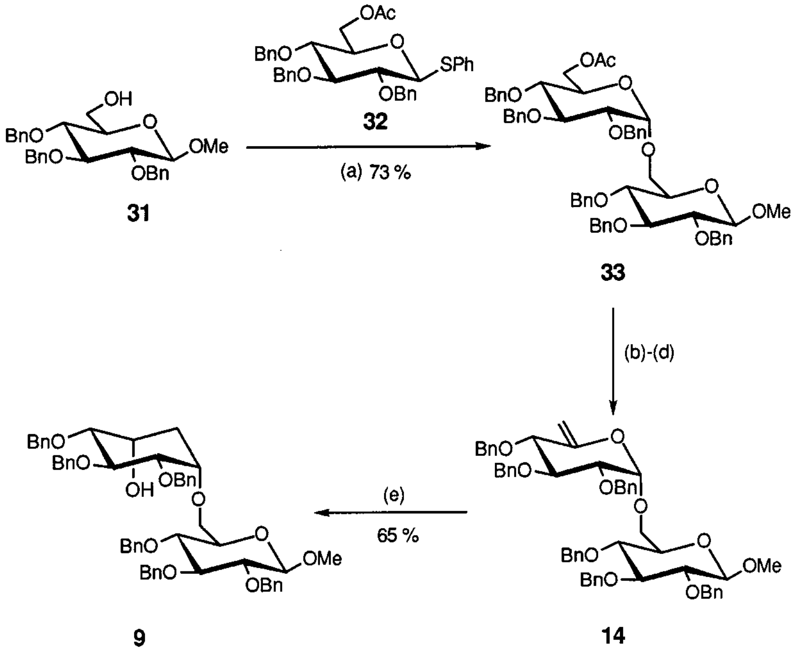
with our previous observations[13] that α-methyl glycosides of (1→6) linked disaccharides undergo more rapid regioselective debenzylation than (1→4) linked derivatives e.g. perbenzylated α-methyl gentiobioside underwent regioselective debenzylation at the 2-O position in 2 h, in contrast to 3 days for maltose.

Synthesis of the analogous β-methyl isomaltoside derived hex-5-enopyranosides **14** was similarly achieved by a con-



Reagents and Conditions: (a) Ph_3P, I_2, Im, PhMe, 70 °C, 83%; (b) DBU, THF, reflux, 46%; (c) TIBAL (10 eq.), PhMe, 50 °C, 3 h

Scheme 4



Reagents and Conditions: (a) NIS, TfOH, 4Å MS, Et_2O, DCM, -30 °C; (b) NaOMe, MeOH, 94%; (c) Ph_3P, I_2, Im, PhMe, 70 °C, 92%; (d) NaH, DMF, RT, 92%; (e) TIBAL (10 eq.), PhMe, 50 °C, 3 h

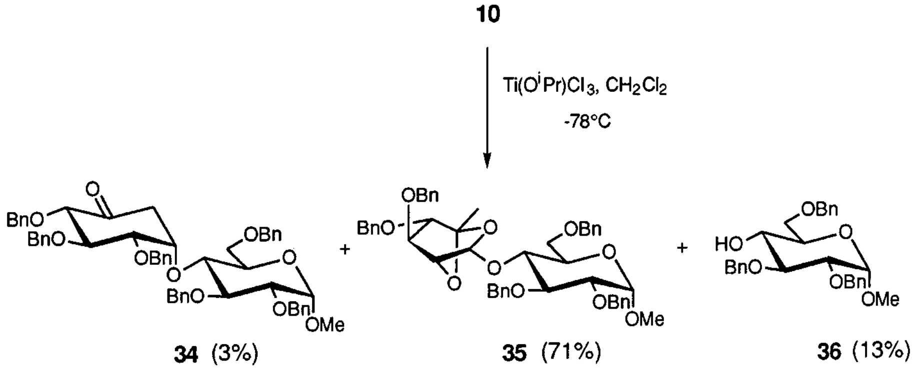
Scheme 5

vergent glycosylation strategy (Scheme 5). Glycosylation of methyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (**31**)[4] with the thioglycoside donor **32**[16] and NIS/TfOH promoter[17] gave the β-methyl isomaltoside **33** (73%). The α-configuration at C-1′ was confirmed by ^{1}H-NMR spectroscopy (δ = 5.08, $J_{1',2'}$ 3.5 Hz, H-1′). Deacetylation of **33** was followed by iodination and elimination to give the hex-5-enopyranoside **14** (80% from **33**). Reaction of hex-5′-enoisomaltoside **14** with excess TIBAL at 50°C gave the (1→6) ether-linked pseudo-disaccharide **9** (65%) as a single diastereomer; no products of debenzylation were observed.

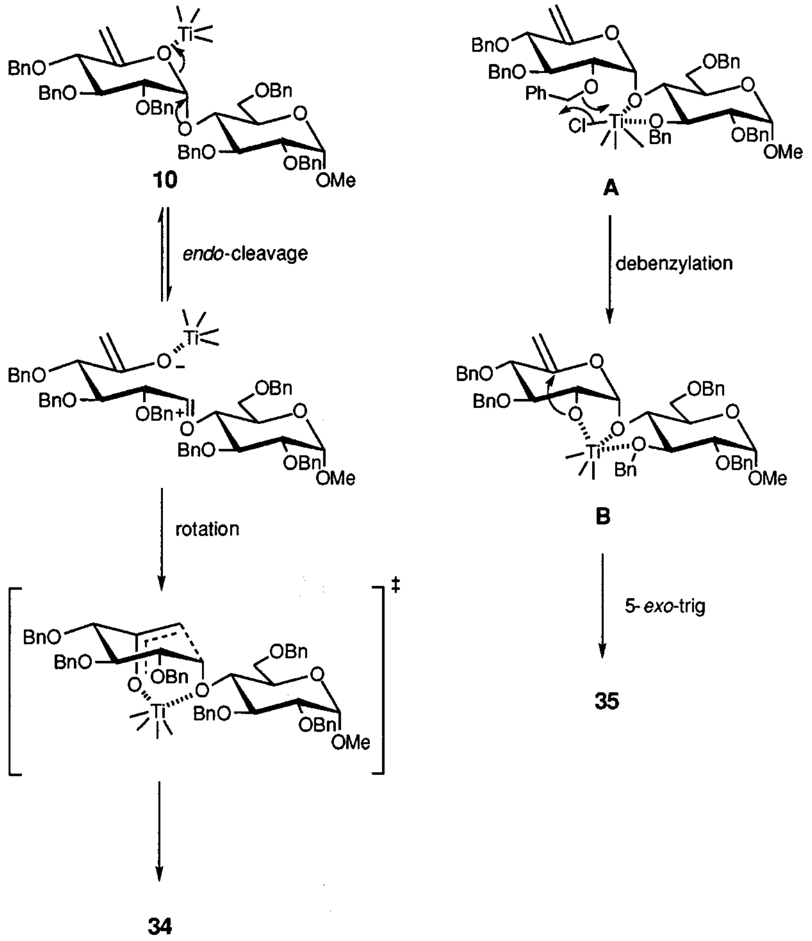
Titanium(IV)-Promoted Rearrangement

In the context of the synthesis of pseudo-disaccharides, the Ti^{IV}-promoted conditions were expected to be milder and also to allow retainment of the keto function subsequently of use for homologation to the carbadisaccharides. Reaction of 6′-deoxyhex-5′-enomaltoside **10** with Ti(O*i*Pr)Cl$_3$ under the standard reaction conditions[5] indeed afforded the desired ketone **34** (3%), together with the unusual bis-glycoside **35** (71%) and methyl 2,3,5-tri-*O*-benzyl-α-D-glucopyranoside (**36**)[18] (13%). The presence of the ketone **34** was confirmed by the characteristic absorption at 1737 cm^{-1} in the IR spectrum and by independent synthesis.[12] The structure of bis-glycoside **35** was supported by ^{1}H-NMR spectroscopy (δ = 5.47, $J_{1',2'}$ ca. 0 Hz, H-1′) and indicated a $B_{2,5}$ conformation[19] as illustrated.

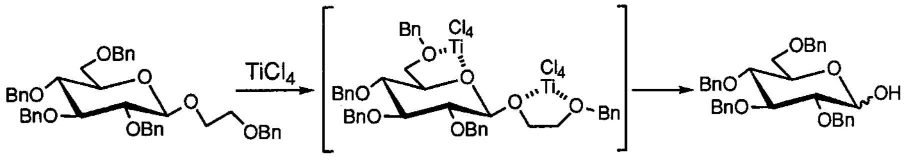
Reaction of **10** with Ti(O*i*Pr)Cl$_3$ is assumed to firstly involve *endo* cleavage[20] of the interglycosidic bond to give



Scheme 6



Scheme 7



37 **38**

Scheme 8

an acyclic oxycarbenium ion, which then undergoes intramolecular carbocyclisation to form the ketone **34**. A chair-like transition state has been invoked to explain the observed stereoselectivity.[21] It is possible that the *endo* cleavage is reversible and that the recyclisation step to give **34** may be retarded due to the increased steric demand of the aglycon monosaccharide (relative to simple methyl or benzyl glycosides studied previously[5]). The formation of the bis-glycoside **35** would also imply that debenzylation of the 2′-OBn occurs with a comparable rate to the desired rearrangement. Formation of an alternative complex **A** might therefore compete, leading to regioselective debenzylation with formation of the tridentate Ti^{IV} complex **B**. Similar regioselective debenzylation with titanium(IV) reagents have been reported.[22] Debenzylation at the 2′-O would then be followed by direct 5-*exo*-trig cyclisation of the intermediate **B** to the bis-glycoside **35** or *exo* cleavage resulting in formation of the aglycon alcohol **36** directly.

The Lewis acid mediated cleavage of simple glycosides may often represent a competition between both *exo* versus *endo* modes.[23] With more complex glycosides the availability of multiple coordination sites may, however, moderate reactivity. Koto[20a] reported that treatment of **37** with $TiCl_4$ led only to hydrolysis via a proposed complex **38** and demonstrated that the position of a benzyloxyl group in the agylcon was crucial to the desired anomerisation reaction (Scheme 8). Although this group also reported the interglycosidic anomerisation of two disaccharides, the product recovery was poor, presumably because of analogous direct hydrolysis. We may therefore propose that direct *exo* cleavage of **10** via complex **A** may also be occurring, leading to direct formation of the alcohol **36**.[24] Similarly, this may explain the observed reaction of the thioglycoside hex-5′-enomaltoside **12** and hex-5′-enoisomaltoside **13** with $Ti(OiPr)Cl_3$, which both led to rapid cleavage of the aglycon monosaccharides phenyl 2,3,5-tri-*O*-benzyl-1-thio-β-D-glucopyranoside and methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside respectively.

In summary, we have demonstrated that the triisobutylaluminium-assisted reductive rearrangement of (6-deoxyhex-5-enopyranosyl)glycosides provides direct and efficient access to highly functionalised cyclohexane derivatives at the disaccharide level. The success of the reaction is dependent on the rate of competitive de-*O*-benzylation mediated by TIBAL-a reaction which is now so well understood that a *judicious* choice of substrate is possible. The application of this methodology to pseudo-oligosaccharide synthesis is under investigation. In contrast, the carbocyclic ring closure of benzylated (6-deoxyhex-5-enopyranosyl)glycosides promoted by titanium(IV) is not practical at the disaccharide level due to competitive decomposition pathways.

Experimental Section

General: Melting points: Büchi 510 apparatus and were uncorrected. − IR: Nicolet Impact 400D. −Optical rotations: Perkin−Elmer 241 digital polarimeter. − Mass spectra: Nermag R10−10 spectrometer, C.I. (ammonia). − Elemental analyses: performed by Service d′Analyse de l′Université Pierre et Marie Curie, 75252 Paris Cedex 05, France. − NMR spectroscopy: Bruker AM-400 (400 MHz and 100.6 MHz, for ^1H and ^{13}C, respectively), TMS as internal standard. − TLC: silica gel 60 F_{254} (Merck) and detection by charring with conc. H_2SO_4. − Flash column chromatography: silica gel 60 (230−400 mesh, Merck).

Phenyl 2,3,6-Tri-*O*-benzyl-4-*O*-(2,3-di-*O*-benzyl-4,6-benzylidene-α-D-glucopyranosyl)-1-thio-β-D-glucopyranoside (18): Benzaldehyde dimethyl acetal (9.2 mL, 61.3 mmol) was added to a solution of phenyl 1-thio-β-D-maltoside (**16**)[9] (17.7 g, 40.8 mmol) in anhydrous DMF (350 mL) at room temp. under argon. Camphorsulfonic acid (600 mg, 2.6 mmol) was added and the solution was then heated at 60°C under 1 Torr pressure. After 1 h, TLC (MeOH/DCM, 1:4) indicated that no starting material (R_f = 0.3) and a major product (R_f = 0.7) was present. The mixture was neutralised with triethylamine, the solvent was removed in vacuo and the residue was purified by flash chromatography (DCM/acetone, 3:2) to afford phenyl 4-*O*-(4,6-benzylidene-α-D-glucopyranosyl)-1-thio-β-D-glucopyranoside (**17**) (10.2 g, 48%), as a colourless foam. Sodium hydride (6.25 g, 0.16 mol, 60% in mineral oil) was added portionwise over 1 h to a stirred solution of **17** in anhydrous DMF (250 mL) and benzyl bromide (27.9 mL, 0.23 mol) at room temp. After a further 1 h, methanol (15 mL) was added dropwise and the reaction mixture was partitioned between diethyl ether (400 mL) and water (400 mL). The aqueous layer was extracted with diethyl ether (2 × 400 mL) and combined extracts were dried ($MgSO_4$), filtered, and the solvent was removed in vacuo. The residue was purified by flash chromatography (eluent gradient, 2−10% EtOAc in cyclohexane) to afford **18** (10.5 g, 55%), as a colourless foam. − $[\alpha]_D^{21}$ +6.4 (c = 1.0 in $CHCl_3$). − ^1H NMR ($CDCl_3$): δ = 7.64−7.19 (m, 35 H, arom. H), 5.72 (d, $J_{1',2'}$ 3.8 Hz, 1 H, 1′-H), 5.59 (s, 1 H, PhC*H*O), 4.95 (d, *J* 11.8 Hz, 1 H, C*H*Ph), 4.94 (d, *J* 10.9 Hz, 1 H, C*H*Ph), 4.88 (d, *J* 9.9 Hz, 1 H, C*H*Ph), 4.87 (d, *J* 11.9 Hz, 1 H, C*H*Ph), 4.78 (d, *J* 11.1 Hz, 1 H, C*H*Ph), 4.74 (d, *J* 11.7 Hz, 1 H, C*H*Ph), 4.73 (d, *J* 12.0 Hz, 1 H, C*H*Ph), 4.72 (d, $J_{1,2}$ 9.7 Hz, 1 H, 1-H), 4.64 (d, *J* 12.0 Hz, 1 H, C*H*Ph), 4.60 (d, *J* 9.7 Hz, 1 H, C*H*Ph), 4.57 (d, *J* 11.5 Hz, 1 H, C*H*Ph), 4.21 (dd, $J_{6a,6b}$ 10.2, $J_{5,6a}$ 5.0 Hz, 1 H, 6-Ha), 4.20 (t, $J_{3,4}$ = $J_{4,5}$ 9.0 Hz, 1 H, 4-H), 4.05 (t, $J_{2',3'}$ = $J_{3',4'}$ 9.3 Hz, 1 H, 3′-H), 3.95 (dd, $J_{6'a,6'b}$ 11.0, $J_{5',6'a}$ 3.6 Hz, 1 H, 6′-Ha), 3.91 (m, 1 H, 5-H), 3.86 (t, $J_{2,3}$ = $J_{3,4}$ 9.0 Hz, 1 H, 3-H), 3.85 (dd, $J_{6'a,6'b}$ 11.0, $J_{5',6'b}$ 2.2 Hz, 1 H, 6′-Hb), 3.67 (dd, $J_{6a,6b}$ 10.2, $J_{5,6b}$ 7.4 Hz, 1 H, 6-Hb), 3.66 (t, $J_{3',4'}$ = $J_{4',5'}$ 9.3 Hz, 1 H, 4′-H), 3.65 (m, 1 H, 5′-H), 3.61 (dd, $J_{1,2}$ 9.7, $J_{2,3}$

9.0 Hz, 1 H, 2-H), 3.55 (dd, $J_{2',3'}$ 9.3, $J_{1',2'}$ 3.8 Hz, 1 H, 2′-H). − ^{13}C NMR ($CDCl_3$): δ = 138.6, 138.5, 138.3, 137.8, 137.5, 133.4, 132.1 (7 × s, C-arom. quat.), 128.9−126.0 (35 × d, Ph), 101.1 (d, Ph*C*HO), 97.5 (C-1′), 87.1, 86.8, 82.3, 80.9, 78.7, 78.4, 75.1, 74.1, 73.9, 73.4, 71.8, 68.9, 63.3. − MS (CI); *m/z* (%): 990 (80) [MNH_4^+], 541 (100). − $C_{60}H_{60}O_{10}S$ (973.2): calcd. C 74.05, H 6.21; found C 74.09, H 6.35.

Phenyl 2,3,6,2′,3′,4′-Hexa-*O*-benzyl-1-thio-β-D-maltoside (19): Lithium aluminium hydride (2.0 g, 0.05 mol) was added to a stirred solution of **18** (10.4 g, 10.7 mmol) in anhydrous DCM (100 mL) and diethyl ether (40 mL). Aluminium chloride (4.3 g, 0.03 mol) in anhydrous diethyl ether (60 mL) was added dropwise over 15 min and the resultant mixture was heated at 50°C. After 1 h, TLC (EtOAc/cyclohexane, 2:5) indicated that no starting material (R_f = 0.7) and a major product (R_f = 0.4) was present. The reaction mixture was cooled to 0°C and EtOAc (100 mL) was cautiously added dropwise, followed by water (100 mL) and 1 M HCl (150 mL). The aqueous layer was extracted with DCM (4 × 100 mL) and combined extracts were dried ($MgSO_4$), filtered, and the solvent was removed in vacuo. The residue was purified by flash chromatography (eluent gradient, 15−20% EtOAc in cyclohexane) to afford **19** (9.76 g, 94%), as a colourless oil. − $[\alpha]_D^{21}$ +24.5 (*c* = 0.8 in $CHCl_3$). − IR (KBr): ṽ = 3481 cm^{-1} (OH), 1079 (C−O). − ^{1}H NMR ($CDCl_3$): δ = 7.66−7.23 (m, 35 H, arom. H), 5.65 (d, $J_{1',2'}$ 3.6 Hz, 1 H, 1′-H), 4.97 (d, *J* 11.7 Hz, 1 H, C*H*Ph), 4.95−4.88 (m, 4 H, 4 × C*H*Ph), 4.85 (d, *J* 10.9 Hz, 1 H, C*H*Ph), 4.75 (d, $J_{1,2}$ 9.2 Hz, 1 H, 1-H), 4.71−4.61 (m, 5 H, 5 × C*H*Ph), 4.56 (d, *J* 12.0 Hz, 1 H, C*H*Ph), 4.16 (t, $J_{2,3}$ = $J_{3,4}$ 9.2 Hz, 1 H, 3-H), 4.00 (t, $J_{2',3'}$ = $J_{3',4'}$ 9.5 Hz, 1 H, 3′-H), 3.92 (dd, $J_{6a,6b}$ 11.2, $J_{5,6a}$ 3.8 Hz, 1 H, 6-Ha), 3.87 (t, $J_{3,4}$ = $J_{4,5}$ 9.2 Hz, 1 H, 4-H), 3.85 (dd, $J_{6a,6b}$ 11.2, $J_{5,6b}$ 2.1 Hz, 1 H, 6-Hb), 3.76 (dt, $J_{4',5'}$ 9.5, $J_{5',6'a}$ = $J_{5',6'b}$ 3.0 Hz, 1 H, 5′-H), 3.71 (ddd, $J_{6'a,6'b}$ 11.9, $J_{6'a,OH}$ 4.3, $J_{5',6'a}$ 3.0 Hz, 1 H, 6′-Ha), 3.66−3.59 (m, 2 H, 5-H, 6′-Hb), 3.63 (t, $J_{1,2}$ = $J_{2,3}$ 9.2 Hz, 1 H, 2-H), 3.56 (t, $J_{3',4'}$ = $J_{4',5'}$ 9.5 Hz, 1 H, 4′-H), 3.48 (dd, $J_{2',3'}$ 9.5, $J_{1',2'}$ 3.6 Hz, 1 H, 2′-H), 1.75 (dd, $J_{6'b,OH}$ 8.5, $J_{6'a,OH}$ 4.3 Hz, 1 H, 6′-OH). − ^{13}C NMR ($CDCl_3$): δ = 138.4, 138.0, 138.0, 137.4, 137.7, 133.5, 131.9 (7 × s, C-arom. quat.), 128.9−126.3 (35 × d, Ph), 96.4 (C-1′), 87.1, 86.6, 81.6, 80.8, 79.3, 78.6, 75.3, 75.1, 74.9, 74.1, 73.3, 72.4, 71.7, 68.6, 61.5. − MS (CI); *m/z* (%): 992 (100) [MNH_4^+]. − $C_{60}H_{62}O_{10}S$ (975.2): calcd. C 73.89, H 6.41; found C 73.79, H 6.48.

Methyl 2,3,6,2′,3′,4′-Hexa-*O*-benzyl-α-D-maltoside (20): *N*-Chlorosuccinimide (2.62 g, 0.02 mol) was added to a stirred solution of **19** (9.54 g, 0.01 mol) in anhydrous methanol (550 mL) at room temp. under argon. After 1 h, TLC (EtOAc/cyclohexane, 2:5) indicated that no starting material (R_f = 0.4) and a major product (R_f = 0.25) was present. Saturated sodium thiosulfate (100 mL) was added and after 15 min the methanol was removed in vacuo. The aqueous layer was extracted with DCM (3 × 150 mL) and combined extracts were dried ($MgSO_4$), filtered, and the solvent was removed in vacuo. The residue was recrystallised (methanol) to afford **20** (6.43 g, 73%), as a colourless crystalline solid, m.p. 112−114°C (methanol). − $[\alpha]_D^{21}$ +42.7 (*c* = 1.0 in $CHCl_3$). − IR (KBr): ṽ = 3492 cm^{-1} (OH), 1024 (C−O). − ^{1}H NMR ($CDCl_3$): δ = 7.35−7.24 (m, 30 H, arom. H), 5.67 (d, $J_{1',2'}$ 3.7 Hz, 1 H, 1′-H), 5.08 (d, *J* 11.6 Hz, 1 H, C*H*Ph), 4.93 (d, *J* 10.9 Hz, 1 H, C*H*Ph), 4.90 (d, *J* 11.1 Hz, 1 H, C*H*Ph), 4.83 (d, *J* 10.8 Hz, 1 H, C*H*Ph), 4.82 (d, *J* 11.6 Hz, 1 H, C*H*Ph), 4.75 (d, *J* 12.1 Hz, 1 H, C*H*Ph), 4.65 (d, *J* 11.6 Hz, 1 H, C*H*Ph), 4.65 (d, $J_{1,2}$ 3.7 Hz, 1 H, 1-H), 4.64 (d, *J* 10.6 Hz, 1 H, C*H*Ph), 4.62 (d, *J* 12.3 Hz, 1 H, C*H*Ph), 4.58 (d, *J* 11.4 Hz, 1 H, C*H*Ph), 4.57 (m, 2 H, C*H*Ph), 4.12 (t, $J_{2,3}$ =$J_{3,4}$ 9.0 Hz, 1 H, 3-H), 4.07 (t, $J_{3,4}$ =$J_{4,5}$ 9.0 Hz, 1 H, 4-H), 3.96 (t, $J_{2',3'}$ = $J_{3',4'}$ 9.3 Hz, 1 H, 3′-H), 3.89 (m, 1 H, 5-H), 3.86 (dd, $J_{6a,6b}$ 8.3, $J_{5,6a}$ 3.4 Hz, 1 H, 6-Ha), 3.70−3.66 (m, 3 H, 5′-H, 6′-Ha, 6-Hb), 3.63 (dd, $J_{2,3}$ 9.0, $J_{1,2}$ 3.7 Hz, 1 H, 2-H), 3.53 (m, 1 H, 6′-Hb), 3.53 (t, $J_{3',4'}$ = $J_{4',5'}$ 9.3 Hz, 1 H, 4′-H), 3.44 (dd, $J_{2',3'}$ 9.3, $J_{1',2'}$ 3.7 Hz, 1 H, 2′-H), 3.43 (s, 3 H, CH_3). − ^{13}C NMR ($CDCl_3$): δ = 139.0, 138.7, 138.3, 138.0 (6 × s, C-arom. quat.), 128.5−126.8 (30 × d, Ph), 97.8 (C-1), 96.4 (C-1′), 82.1, 81.8, 80.2, 79.6, 77.4, 73.4, 73.3, 72.2, 71.6, 69.6, 68.7, 61.6 (C-6′), 55.2 (CH_3). − MS (CI); *m/z* (%): 914.5 (100) [MNH_4^+]. − $C_{55}H_{60}O_{11}$ (897.1): calcd. C 73.63, H 6.74; found C 73.72, H 6.63.

Methyl 2,3,6,2′,3′,4′-Hexa-*O*-benzyl-6′-deoxy-6′-iodo-α-D-maltoside (21): Triphenylphosphane (2.77 g, 10.6 mmol), imidazole (1.44 g, 21.1 mmol), and iodine (3.57 g, 14.1 mmol) were added to a stirred solution of **20** (6.3 g, 7.0 mmol) in anhydrous toluene (65 mL) at room temp. under argon. The mixture was heated at 70°C for 1 h, when TLC (EtOAc/cyclohexane, 3:7) indicated that no starting material (R_f = 0.3) and a major product (R_f = 0.6) was present. The reaction mixture was cooled to room temp. and saturated sodium thiosulfate (50 mL) was added. After 5 min the aqueous layer was extracted with EtOAc (3 × 75 mL) and combined extracts were dried ($MgSO_4$), filtered, and the solvent was removed in vacuo. The residue was purified by flash chromatography (eluent gradient, 10−15% EtOAc in cyclohexane) to afford **21** (6.58 g, 93%), as a colourless oil. − $[\alpha]_D^{21}$ +50.3 (*c* = 1.6 in $CHCl_3$). − ^{1}H NMR ($CDCl_3$): δ = 7.37−7.25 (m, 30 H, arom. H), 5.66 (d, $J_{1',2'}$ 3.6 Hz, 1 H, 1′-H), 5.06 (d, *J* 11.7 Hz, 1 H, C*H*Ph), 4.98 (d, *J* 11.0 Hz, 1 H, C*H*Ph), 4.93 (d, *J* 10.8 Hz, 1 H, C*H*Ph), 4.82 (d, *J* 11.8 Hz, 1 H, C*H*Ph), 4.79 (d, *J* 10.8 Hz, 1 H, C*H*Ph), 4.74 (2 × d, *J* 11.8 Hz, 2 H, C*H*Ph), 4.65 (d, $J_{1,2}$ 3.6 Hz, 1 H, 1-H), 4.63 (d, *J* 10.9 Hz, 1 H, C*H*Ph), 4.62−4.56 (m, 4 H, C*H*Ph), 4.12 (t, $J_{2,3}$ =$J_{3,4}$ 8.7 Hz, 1 H, 3-H), 4.08 (t, $J_{3,4}$ =$J_{4,5}$ 8.7 Hz, 1 H, 4-H), 3.99 (dd, $J_{2',3'}$ 9.5, $J_{3',4'}$ 8.8 Hz, 1 H, 3′-H), 3.92 (dd, $J_{6a,6b}$ 8.1, $J_{5,6a}$ 4.0 Hz, 1 H, 6-Ha), 3.90 (m, 1 H, 5-H), 3.71 (dd, $J_{6a,6b}$ 8.1, $J_{5,6b}$ 3.1 Hz, 1 H, 6-Hb), 3.64 (dd, $J_{2,3}$ 8.7, $J_{1,2}$ 3.6 Hz, 1 H, 2-H), 3.48 (dd, $J_{2',3'}$ 9.5, $J_{1',2'}$ 3.6 Hz, 1 H, 2′-H), 3.43 (s, 3 H, CH_3), 3.42 (dd, $J_{4',5'}$ 9.5, $J_{3',4'}$ 8.8 Hz, 1 H, 4′-H), 3.33 (dt, $J_{4',5'}$ 9.5, $J_{5',6'a}$ = $J_{5',6'b}$ 3.1 Hz, 1 H, 5′-H), 3.29−3.22 (m, 2 H, 6′-Ha, 6′-Hb). − ^{13}C NMR ($CDCl_3$): δ = 138.9, 138.5, 138.2, 138.0, 137.9, 137.8 (6 × s, C-arom. quat.), 128.3−126.6 (30 × d, Ph), 97.7 (C-1), 96.1 (C-1′), 81.8, 81.6, 81.2, 80.1, 79.8, 75.4, 75.2, 74.1, 73.4, 73.2, 73.1, 72.7, 69.5, 69.2, 55.1 (CH_3), 9.1 (C-6′). − MS (CI); *m/z* (%): 1024.6 (100) [MNH_4^+]. − $C_{55}H_{59}IO_{10}$ (1006.9): calcd. C 65.60, H 5.91; found C 65.62, H 5.86.

Methyl 2,3,6-Tri-*O*-benzyl-4-*O*-(2,3,4-tri-*O*-benzyl-6-deoxy-α-D-*xylo*-hex-5-enopyranosyl)-α-D-glucopyranoside (10): DBU (5.87 mL, 0.04 mol) was added to a stirred solution of **21** (6.58 g, 6.54 mmol) in anhydrous THF (65 mL) at room temp. under argon. After heating at reflux for 42 h, the solvent was removed in vacuo. The residue was purified by flash chromatography (25% EtOAc in cyclohexane) to afford **10** (2.95 g, 52%), as a colourless crystalline solid, m.p. 78°C (diethyl ether/pentane). − $[\alpha]_D^{21}$ +4.1 (*c* = 1.1 in $CHCl_3$). − IR (KBr): ṽ = 1660 cm^{-1} (C=C), 1095 (C−O). − ^{1}H NMR ($CDCl_3$): δ = 7.39−7.23 (m, 30 H, arom. H), 5.81 (d, $J_{1',2'}$ 3.4 Hz, 1 H, 1′-H), 5.08 (d, *J* 11.7 Hz, 1 H, C*H*Ph), 4.90 (br s, 1 H, 6′-Ha), 4.79 (br s, 4 H, 4 × C*H*Ph), 4.75 (d, *J* 11.7 Hz, 1 H, C*H*Ph), 4.71 (d, *J* 12.1 Hz, 1 H, C*H*Ph), 4.70 (br s, 1 H, 6′-Hb), 4.67 (d, *J* 11.8 Hz, 1 H, C*H*Ph), 4.65 (d, $J_{1,2}$ 3.5 Hz, 1 H, 1-H), 4.62 (d, *J* 12.5 Hz, 2 H, CH_2Ph), 4.58 (d, *J* 11.8 Hz, 1 H, C*H*Ph), 4.50 (d, *J* 12.2 Hz, 1 H, C*H*Ph), 4.11 (m, 1 H, 3-H), 3.96−3.92 (m, 3 H, 4-H, 4′-H, 5-H), 3.90 (t, $J_{2',3'}$ =$J_{3',4'}$ 8.6 Hz, 1 H, 3′-H), 3.82 (dd, $J_{6a,6b}$ 11.0, $J_{5,6a}$ 1.2 Hz, 1 H, 6-Ha), 3.62 (dd, $J_{2,3}$ 9.7, $J_{1,2}$ 3.5 Hz, 1 H, 2-H), 3.58 (dd, $J_{6a,6b}$ 11.0, $J_{5,6b}$ 7.1 Hz, 1 H, 6-Hb), 3.57 (dd, $J_{2',3'}$ 8.6, $J_{1',2'}$ 3.4 Hz, 1 H, 2′-H), 3.44 (s, 3 H, CH_3). − ^{13}C NMR ($CDCl_3$): δ = 154.1 (s, C-5′), 138.8, 138.4, 138.3, 137.9, 137.8, 137.7 (6 × s, C-arom. quat.), 128.4−126.6 (30 × d, Ph), 97.4 (C-1), 97.0 (C-1′), 96.4 (C-6′), 81.9 (C-3), 80.3 (C-3′), 80.1 (C-2), 79.3 (C-4′), 78.5 (C-2′), 75.1, 74.4, 74.3, 73.4, 73.2, 73.2 (6 × t, CH_2Ph), 72.5 (C-4), 70.4 (C-6), 69.4 (C-5), 55.0 (CH_3). − MS (CI); *m/z* (%): 896.5 (100) [MNH_4^+], 806.5 (88) [MNH_4^+ − Bn], 482 (44). − $C_{55}H_{58}O_{10}$ (879.1): calcd. C 75.14, H 6.65; found C 74.99, H 6.75.

Methyl 2,3,6-Tri-*O*-benzyl-4-*O*-[1D-(1,2,4/3,5)-2,3,4-tri-*O*-benzyl-1,2,3,4,5-pentahydroxycyclohexyl]-α-D-glucopyranoside (2), Methyl 2,3,6-Tri-*O*-benzyl-4-*O*-[1D-(1,2,4,5/3)-2,3,4-tri-*O*-benzyl-1,2,3,4,5-pentahydroxycyclohexyl]-α-D-glucopyranoside (3), Methyl 3,6-Di-*O*-benzyl-4-*O*-[1D-(1,2,4/3,5)-2,3,4-tri-*O*-benzyl-1,2,3,4,5-pentahydroxycyclohexyl]-α-D-glucopyranoside (22), and Methyl 3,6-Di-*O*-benzyl-4-*O*-[1D-(1,2,4,5/3)-2,3,4-tri-*O*-benzyl-1,2,3,4,5-pentahydroxycyclohexyl]-α-D-glucopyranoside (23): TIBAL (11.85 mL, 11.9 mmol, 1 M in toluene) was added to a stirred solution of **10** (1.04 g, 1.18 mmol) in anhydrous toluene (10 mL) at room temp. under argon. The reaction mixture was heated at 50°C for 4 h, when TLC (EtOAc/cyclohexane, 3:7) indicated that no starting material (R_f = 0.7), and a major component (R_f = 0.4) and minor component (R_f = 0.1) was present. The mixture was cooled to 0°C and ice-water (20 mL) was added. The mixture was filtered into a separating funnel (washing with 20 mL of EtOAc) and the aqueous layer was extracted with EtOAc (2 × 100 mL). Combined extracts were dried ($MgSO_4$), filtered, and the solvent was removed in vacuo. The residue was purified by flash chromatography (eluent gradient, 30−50% EtOAc in cyclohexane) to afford **2**/**3** (660 mg, 63%, as a 2:5 mixture) and **22**/**23** (241 mg, 26%, as a 2:5 mixture). Further flash chromatography (eluent gradient, 20−40% EtOAc in cyclohexane) afforded **2** (189 mg, 18%), as a colourless oil. − $[\alpha]_D^{22}$ +35.5 (*c* = 1.0 in $CHCl_3$). − IR (film): ṽ = 3438 cm^{-1} (OH), 1063 (C−O). − ^1H NMR ($CDCl_3$): δ = 7.36−7.26 (m, 30 H, arom. H), 5.08 (d, *J* 11.8 Hz, 1 H, C*H*Ph), 4.99 (d, *J* 11.4 Hz, 1 H, C*H*Ph), 4.82 (d, *J* 10.7 Hz, 1 H, C*H*Ph), 4.76 (d, *J* 12.0 Hz, 1 H, C*H*Ph), 4.73 (d, *J* 12.1 Hz, 1 H, C*H*Ph), 4.69−4.58 (m, 9 H, 8 × C*H*Ph, 1-H), 4.50 (m, 1 H, 1′-H), 4.01 (t, $J_{2,3}$ =$J_{3,4}$ 9.0 Hz, 1 H, 3-H), 3.96 (t, $J_{3,4}$ = $J_{4,5}$ 9.0 Hz, 1 H, 4-H), 3.87 (dd, $J_{2',3'}$ 9.6, $J_{3',4'}$ 9.0 Hz, 1 H, 3′-H), 3.83−3.73 (m, 3 H, 5-H, 5′-H, 6-Ha), 3.70 (dd, $J_{6a,6b}$ 11.3, $J_{5,6b}$ 2.6 Hz, 1 H, 6-Hb), 3.61 (dd, $J_{2,3}$ 9.0, $J_{1,2}$ 3.5 Hz, 1 H, 2-H), 3.42 (s, 3 H, CH_3), 3.37 (dd, $J_{2',3'}$ 9.6, $J_{1',2'}$ 3.0 Hz, 1 H, 2′-H), 3.25 (t, $J_{3',4'}$ = $J_{4',5'}$ 9.0 Hz, 1 H, 4′-H), 2.42 (dt, J_{gem} 14.3, $J_{1',5'a(a)}$ = $J_{5',5'a(a)}$ 4.2 Hz, 1 H, 5′a-Ha), 2.01 (d, $J_{5',OH}$ 2.3 Hz, 1 H, OH), 1.13 (ddd, J_{gem} 14.3, $J_{5',5'a(b)}$ 12.0, $J_{1',5'a(b)}$ 1.9 Hz, 1 H, 5′a-Hb). − ^{13}C NMR ($CDCl_3$): δ = 139.1, 138.8, 138.7, 138.3, 138.3, 137.9 (6 × s, C-arom. quat.), 128.5−126.6 (30 × d, Ph), 97.8 (C-1), 86.3 (C-4′), 83.1 (C-2′), 82.0 (C-3), 81.5 (C-3′), 80.4 (C-2), 75.2, 75.2, 74.2, 73.4, 73.3, 72.7 (6 × t, CH_2Ph), 72.2 (C-1′), 71.9 (C-4), 69.6 (C-5), 69.0 (C-6), 68.0 (C-5′) 55.2 (CH_3), 31.2 (C-5′a). − MS (CI); *m/z* (%): 898.8 (25) [MNH_4^+], 808.6 (15) [MNH_4^+ − Bn], 212 (100). − $C_{55}H_{60}O_{10}$ (881.1): calcd. C 74.97, H 6.86; found C 74.94, H 6.97.

(**3**) (471 mg, 45%): as a colourless oil. − $[\alpha]_D^{22}$ +30.2 (*c* = 1.3 in $CHCl_3$). − IR (film): ṽ = 3449 cm^{-1} (OH), 1069 (C−O). − ^1H NMR ($CDCl_3$): δ = 7.39−7.22 (m, 30 H, arom. H), 5.02 (d, *J* 11.3 Hz, 1 H, C*H*Ph), 4.82 (d, *J* 11.3 Hz, 1 H, C*H*Ph), 4.75 (2 × d, *J* 12.2 Hz, 2 H, 2 × C*H*Ph), 4.66 (d, *J* 12.2 Hz, 1 H, C*H*Ph), 4.66−4.60 (m, 4 H, 3 × C*H*Ph, 1-H), 4.57 (d, *J* 11.9 Hz, 1 H, C*H*Ph), 4.52 (d, *J* 11.7 Hz, 1 H, C*H*Ph), 4.30 (d, *J* 11.8 Hz, 1 H, C*H*Ph), 4.27 (d, *J* 10.0 Hz, 1 H, C*H*Ph), 4.24 (dt, $J_{1',5'a(a)}$ 8.6, $J_{1',2'}$ = $J_{1',5'a(b)}$ 3.4 Hz, 1 H, 1′-H), 3.92 (dd, $J_{2,3}$ 9.5, $J_{3,4}$ 9.0 Hz, 1 H, 3-H), 3.90−3.85 (m, 2 H, 3′-H, 5′-H), 3.85−3.80 (m, 1 H, 4-H), 3.77−3.72 (m, 3 H, 5-H, 6-Ha, 6-Hb), 3.64−3.59 (m, 1 H, 2′-H), 3.59 (dd, $J_{2,3}$ 9.5, $J_{1,2}$ 3.6 Hz, 1 H, 2-H), 3.45 (s, 3 H, CH_3), 3.45 (m, 1 H, 4′-H), 2.80 (br s, 1 H, OH), 2.42 (dt, J_{gem} 12.8, $J_{1',5'a(a)}$ = $J_{5',5'a(a)}$ 8.6 Hz, 1 H, 5′a-Ha), 1.82−1.75 (m, 1 H, 5′a-Hb). − ^{13}C NMR ($CDCl_3$): δ = 138.9, 138.8, 138.8, 138.1, 138.0, 137.7 (6 × s, C-arom. quat.), 128.3−127.1 (30 × d, Ph), 97.9 (C-1), 81.9 (C-3), 79.9 (C-2), 76.1 (C-1′), 75.1 (C-4), 75.0, 73.5, 73.4, 73.2, 73.2, 73.1 (6 × t, CH_2Ph), 70.0 (C-5), 68.7 (C-6), 67.3 (C-5′) 55.2 (CH_3), 30.6 (C-5′a). − MS (CI); *m/z* (%): 898.8 (100) [MNH_4^+], 808.6 (10) [MNH_4^+ − Bn]. − $C_{55}H_{60}O_{10}$ (881.1): calcd. C 74.97, H 6.86; found C 74.96, H 6.83.

Further elution (45−50% EtOAc in cyclohexane) afforded **22** (69 mg, 7%), as a colourless oil. − $[\alpha]_D^{22}$ +61.1 (*c* = 0.7 in $CHCl_3$). − IR (film): ṽ = 3443 cm^{-1} (OH), 1056 (C−O). − ^1H NMR ($CDCl_3$): δ = 7.38−7.26 (m, 25 H, arom. H), 4.99 (2 × d, *J* 11.5 Hz, 2 H, 2 × C*H*Ph), 4.82 (d, *J* 10.7 Hz, 1 H, C*H*Ph), 4.82 (d, $J_{1,2}$ 3.4 Hz, 1 H, 1-H), 4.78 (d, *J* 11.8 Hz, 1 H, C*H*Ph), 4.67 (d, *J* 11.6 Hz, 1 H, C*H*Ph), 4.67 (d, *J* 11.7 Hz, 1 H, C*H*Ph), 4.64 (2 × d, *J* 10.4 Hz, 2 H, 2 × C*H*Ph), 4.63 (d, *J* 11.9 Hz, 1 H, C*H*Ph), 4.60 (d, *J* 12.0 Hz, 1 H, C*H*Ph), 4.47 (m, 1 H, 1′-H), 3.97 (dd, *J* 9.2, *J* 8.4 Hz, 1 H, 4-H), 3.87 (t, $J_{2',3'}$ = $J_{3',4'}$ 9.3 Hz, 1 H, 3′-H), 3.84−3.75 (m, 5 H, 2-H, 3-H, 5-H, 5′-H, 6-Ha), 3.72 (dd, $J_{6a,6b}$ 11.9, $J_{5,6b}$ 2.3 Hz, 1 H, 6-Hb), 3.47 (s, 3 H, CH_3), 3.36 (dd, $J_{2',3'}$ 9.3, $J_{1',2'}$ 3.0 Hz, 1 H, 2′-H), 3.24 (t, $J_{3',4'}$ = $J_{4',5'}$ 9.3 Hz, 1 H, 4′-H), 2.34 (dt, J_{gem} 14.0, $J_{1',5'a(a)}$ = $J_{5',5'a(a)}$ 4.3 Hz, 1 H, 5′a-Ha), 2.16 (d, $J_{2,OH}$ 8.0 Hz, 1 H, 2-OH), 2.07 (br s, 1 H, 5′-OH), 1.12 (ddd, J_{gem} 14.0, $J_{5',5'a(b)}$ 12.0, $J_{1',5'a(b)}$ 2.1 Hz, 1 H, 5′a-Hb). − ^{13}C NMR ($CDCl_3$): δ = 138.8, 138.7, 138.7, 138.3, 137.9 (5 × s, C-arom. quat.), 128.5−126.9 (25 × d, Ph), 99.1 (C-1), 86.3 (C-4′), 83.7 (C-2′), 82.6 (C-3), 81.6 (C-3′), 75.3, 75.3, 73.8, 73.5 (4 × t, CH_2Ph), 73.1 (C-2), 72.6 (t, CH_2Ph), 72.3 (C-1′), 72.2 (C-4), 70.0 (C-5), 69.0 (C-6), 68.1 (C-5′), 55.2 (CH_3), 31.6 (C-5′a). − MS (CI); *m/z* (%): 808.6 (100) [MNH_4^+]. − $C_{48}H_{54}O_{10}$ (791.0): calcd. C 72.89, H 6.88; found C 72.81, H 7.13.

(**23**) (172 mg, 19%): as a colourless oil. − $[\alpha]_D^{22}$ +68.3 (*c* = 1.3 in $CHCl_3$). − IR (film): ṽ = 3443 cm^{-1} (OH), 1057 (C−O). − ^1H NMR ($CDCl_3$): δ = 7.39−7.24 (m, 25 H, arom. H), 4.88 (s, 2 H, CH_2Ph), 4.83 (d, $J_{1,2}$ 3.3 Hz, 1 H, 1-H), 4.75 (d, *J* 12.0 Hz, 1 H, C*H*Ph), 4.68 (2 × d, *J* 11.8 Hz, 2 H, 2 × C*H*Ph), 4.66 (d, *J* 12.0 Hz, 1 H, C*H*Ph), 4.58 (d, *J* 11.9 Hz, 1 H, C*H*Ph), 4.57 (d, *J* 12.8 Hz, 1 H, C*H*Ph), 4.37 (s, 2 H, CH_2Ph), 4.21 (dt, $J_{1',5'a(a)}$ 8.0, $J_{1',2'}$ = $J_{1',5'a(b)}$ 3.4 Hz, 1 H, 1′-H), 3.99−3.90 (m, 2 H, 3′-H, 5′-H), 3.86−3.83 (m, 1 H, 4-H), 3.81−3.74 (m, 4 H, 2-H, 5-H, 6-Ha, 6-Hb), 3.72 (t, $J_{2,3}$ =$J_{3,4}$ 9.2 Hz, 1 H, 3-H), 3.57 (m, 1 H, 2′-H), 3.49 (s, 3 H, CH_3), 3.45 (br t, $J_{3',4'}$ = $J_{4',5'}$ 3.0 Hz, 1 H, 4′-H), 2.90 (br s, 1 H, 5′-OH), 2.26 (d, $J_{2,OH}$ 6.5 Hz, 1 H, 2-OH), 2.05 (dt, J_{gem} 12.7, $J_{1',5'a(a)}$ = $J_{5',5'a(a)}$ 8.0 Hz, 1 H, 5′a-Ha), 1.70 (m, 1 H, 5′a-Hb). − ^{13}C NMR ($CDCl_3$): δ = 138.8, 138.6, 138.2, 138.1, 137.7 (5 × s, C-arom. quat.), 128.5−127.3 (25 × d, Ph), 99.0 (C-1), 83.1 (C-3), 76.0 (C-1′), 75.2 (C-4), 74.6, 73.6, 73.6, 73.1 (4 × t, CH_2Ph), 72.6 (C-2), 72.2 (t, CH_2Ph), 70.5 (C-5), 68.7 (C-6), 67.4 (C-5′), 55.2 (CH_3), 30.8 (C-5′a). − MS (CI); *m/z* (%): 808.7 (60) [MNH_4^+], 213.3 (100). − $C_{48}H_{54}O_{10}$ (791.0): calcd. C 72.89, H 6.88; found C 72.81, H 7.00.

Methyl 2,3,6,2′,3′-Penta-*O*-benzyl-β-D-maltoside (25): A solution of methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3-di-*O*-benzyl-4,6-benzylidene-α-D-glucopyranosyl)-β-D-glucopyranoside (**24**)[14] (13.0 g, 14.5 mmol) in glacial acetic acid (160 mL) and water (40 mL) was stirred at 80°C. After 2 h, TLC (EtOAc/cyclohexane, 3:7) indicated that no starting material (R_f = 0.6) and a major product (R_f = 0.05) was present. The solvent was removed in vacuo and the residue was purified by flash chromatography (eluent gradient, 40−50% EtOAc in cyclohexane) to afford **25** (7.29 g, 62%), as a colourless crystalline solid, m.p. 111−112°C. − $[\alpha]_D^{22}$ +23.3 (*c* = 1.0 in $CHCl_3$). −

IR (KBr): $\tilde{\nu}$ = 3345 cm^{-1} (O−H), 1063 (C−O). − ^1H NMR ($CDCl_3$): δ = 7.42−7.24 (m, 25 H, arom. H), 5.73 (d, $J_{1',2'}$ 3.6 Hz, 1 H, 1′-H), 5.06 (d, *J* 11.7 Hz, 1 H, C*H*Ph), 4.98 (d, *J* 11.4 Hz, 1 H, C*H*Ph), 4.97 (d, *J* 11.0 Hz, 1 H, C*H*Ph), 4.80 (d, *J* 11.7 Hz, 1 H, C*H*Ph), 4.73−4.65 (m, 4 H, 4 × C*H*Ph), 4.59 (m, 2 H, CH_2Ph), 4.42 (d, $J_{1,2}$ 7.8 Hz, 1 H, 1-H), 4.14 (t, $J_{3,4}$ =$J_{4,5}$ 9.0 Hz, 1 H, 4-H), 3.89 (dd, $J_{6a,6b}$ 11.5, $J_{5,6a}$ 4.3 Hz, 1 H, 6-Ha), 3.88 (t, $J_{2,3}$ =$J_{3,4}$ 9.0 Hz, 1 H, 3-H), 3.84 (dd, $J_{6a,6b}$ 11.5, $J_{5,6b}$ 1.9 Hz, 1 H, 6-Hb), 3.78 (t, $J_{2',3'}$ = $J_{3',4'}$ 9.4 Hz, 1 H, 3′-H), 3.76−3.70 (m, 3 H, 5′-H, 6′-Ha, 6′-Hb), 3.65 (s, 3 H, CH_3), 3.58 (dd, $J_{2,3}$ 9.0, $J_{1,2}$ 7.8 Hz, 1 H, 2-H), 3.56 (m, 1 H, 4′-H), 3.46 (dd, $J_{2',3'}$ 9.4, $J_{1',2'}$ 3.7 Hz, 1 H, 2′-H), 2.61 (m, 1 H, 4′-OH), 2.12 (m, 1 H, 6′-OH). − ^{13}C NMR ($CDCl_3$): δ = 138.6, 138.5, 138.2, 138.0, 137.6 (5 × s, C-arom. quat.), 128.5−126.5 (25 × d, Ph), 104.4 (C-1), 96.3 (C-1′), 84.7 (C-3), 82.1 (C-2), 81.1 (C-3′), 79.2 (C-2′), 75.1, 74.5 (2 × t, CH_2Ph), 74.4 (C-5), 73.8, 73.4, 72.9 (3 × t, CH_2Ph), 72.1 (C-4), 71.8 (C-5′), 70.3 (C-4′), 68.5 (C-6), 62.1 (C-6′), 56.9 (CH_3). − MS (CI); *m/z* (%): 824.0 (100) [MNH_4^+]. − $C_{48}H_{54}O_{11}$ (806.9): calcd. C 71.44, H 6.74; found C 71.54, H 6.78.

Methyl 2,3,6,2′,3′-Penta-*O*-benzyl-6′-deoxy-6′-iodo-β-D-maltoside (26): Triphenylphosphane (4.52 g, 17.2 mmol), imidazole (1.47 g, 21.6 mmol) and iodine (2.62 g, 10.32 mmol) were added to a stirred solution of **25** (6.94 g, 8.61 mmol) in anhydrous toluene (100 mL) at room temp. under argon. The mixture was heated at 80°C for 45 min, when TLC (EtOAc/cyclohexane, 2:3) indicated that no starting material (R_f = 0.3) and a major product (R_f = 0.6) was present. The reaction mixture was cooled to room temp. and saturated sodium thiosulfate (50 mL) was added. After 5 min the aqueous layer was extracted with EtOAc (3 × 75 mL) and combined extracts were dried ($MgSO_4$), filtered, and the solvent was removed in vacuo. The residue was purified by flash chromatography (eluent gradient, 17−22% EtOAc in cyclohexane) to afford **26** (6.52 g, 83%), as a colourless oil. − $[\alpha]_D^{22}$ +26.0 (*c* = 1.0 in $CHCl_3$). − IR (film): $\tilde{\nu}$ = 3449 cm^{-1} (O−H), 1058 (C−O). − ^1H NMR ($CDCl_3$): δ = 7.42−7.28 (m, 25 H, arom. H), 5.73 (d, $J_{1',2'}$ 3.6 Hz, 1 H, 1′-H), 5.03 (d, *J* 11.7 Hz, 1 H, C*H*Ph), 4.98 (d, *J* 11.3 Hz, 1 H, C*H*Ph), 4.96 (d, *J* 10.9 Hz, 1 H, C*H*Ph), 4.79 (d, *J* 11.7 Hz, 1 H, C*H*Ph), 4.71 (d, *J* 12.1 Hz, 1 H, C*H*Ph), 4.68 (d, *J* 10.7 Hz, 1 H, C*H*Ph), 4.67 (d, *J* 12.1 Hz, 1 H, C*H*Ph), 4.65 (d, *J* 10.9 Hz, 1 H, C*H*Ph), 4.61 (d, *J* 11.9 Hz, 1 H, C*H*Ph), 4.56 (d, *J* 11.9 Hz, 1 H, C*H*Ph), 4.43 (d, $J_{1,2}$ 7.8 Hz, 1 H, 1-H), 4.15 (t, $J_{3,4}$ =$J_{4,5}$ 8.9 Hz, 1 H, 4-H), 3.95 (dd, $J_{6a,6b}$ 11.1, $J_{5,6a}$ 4.8 Hz, 1 H, 6-Ha), 3.87 (t, $J_{2,3}$ =$J_{3,4}$ 8.9 Hz, 1 H, 3-H), 3.87 (m, 1 H, 6-Hb), 3.78 (dd, $J_{2',3'}$ 9.6, $J_{3',4'}$ 8.2 Hz, 1 H, 3′-H), 3.68 (ddd, $J_{4,5}$ 8.9, $J_{5,6a}$ 4.8, $J_{5,6b}$ 2.2 Hz, 1 H, 5-H), 3.66 (s, 3 H, CH_3), 3.59 (dd, $J_{2,3}$ 8.9, $J_{1,2}$ 7.8 Hz, 1 H, 2-H), 3.47 (dd, $J_{2',3'}$ 9.6, $J_{1',2'}$ 3.6 Hz, 1 H, 2′-H), 3.43−3.34 (m, 3 H, 4′-H, 5′-H, 6′-Ha), 3.27 (dd, $J_{6a',6b'}$ 10.7, $J_{5',6'b}$ 5.1 Hz, 1 H, 6′-Hb), 2.25 (d, $J_{4',OH}$ 2.7 Hz, 1 H, 4′-OH). − ^{13}C NMR ($CDCl_3$): δ = 138.6, 138.4, 138.2, 138.1, 137.6 (5 × s, C-arom. quat.), 128.6−126.6 (25 × d, Ph), 104.5 (C-1), 96.0 (C-1′), 84.5 (C-3), 81.9 (C-2), 80.4 (C-3′), 79.2 (C-2′), 75.2, 74.5 (2 × t, CH_2Ph), 74.4 (C-4), 73.6 (C-5), 73.5, 73.4, 72.8 (3 × t, CH_2Ph), 72.4 (C-4′), 70.0 (C-5′), 69.3 (C-6), 57.0 (CH_3), 8.1 (C-6′). − MS (CI); *m/z* (%): 934.3 (30) [MNH_4^+], 808.4 (100). − $C_{48}H_{53}IO_{10}$ (916.9): calcd. C 62.88, H 5.83; found C 62.80, H 5.89.

Methyl 2,3,6-Tri-*O*-benzyl-4-*O*-(2,3,4-tri-*O*-benzyl-6-deoxy-α-D-xylohex-5-enopyranosyl)-β-D-glucopyranoside (11): Benzylbromide (0.54 mL, 4.54 mmol) and then sodium hydride (1.39 g, 34.8 mmol, 60% in mineral oil) were added to a vigorously stirred solution of **26** (3.18 g, 3.47 mmol) in anhydrous DMF (100 mL) at room temp. After 24 h, TLC (EtOAc/cyclohexane, 1:4) indicated that no starting material (R_f = 0.3) and a product (R_f = 0.4) was present. Methanol (15 mL) was added dropwise and the solvent was removed in vacuo. The residue was partitioned between DCM (100 mL) and water (100 mL) and the aqueous layer was extracted with DCM (2 × 100 mL). Combined extracts were washed with brine (50 mL), dried (Na_2SO_4), filtered, and the solvent was removed in vacuo. The residue was purified by flash chromatography (eluent gradient, 10−15% EtOAc in cyclohexane) to afford **11** (2.46 g, 81%), as a colourless oil. − $[\alpha]_D^{21}$ −7.5 (*c* = 1.0 in $CHCl_3$). − IR (film): $\tilde{\nu}$ = 1660 cm^{-1} (C=C), 1042 (C−O). − ^1H NMR ($CDCl_3$): δ = 7.43−7.23 (m, 30 H, arom. H), 5.83 (d, $J_{1',2'}$ 3.4 Hz, 1 H, 1′-H), 5.06 (d, *J* 11.7 Hz, 1 H, C*H*Ph), 4.98 (d, *J* 11.0 Hz, 1 H, C*H*Ph), 4.88 (br s, 1 H, 6′-Ha), 4.85 (d, *J* 11.3 Hz, 1 H, C*H*Ph), 4.85 (br s, 2 H, CH_2Ph), 4.82 (d, *J* 11.3 Hz, 1 H, C*H*Ph), 4.75 (d, *J* 11.7 Hz, 1 H, C*H*Ph), 4.75 (br s, 1 H, 6′-Hb), 4.71−4.66 (m, 3 H, 3 × C*H*Ph), 4.61 (d, *J* 11.9 Hz, 1 H, C*H*Ph), 4.59 (d, *J* 12.2 Hz, 1 H, C*H*Ph), 4.44 (d, $J_{1,2}$ 7.8 Hz, 1 H, 1-H), 4.00−3.96 (m, 2 H, 4′-H, 6-Ha), 3.98 (t, $J_{3,4}$ =$J_{4,5}$ 9.0 Hz, 1 H, 4-H), 3.94 (t, $J_{2',3'}$ =$J_{3',4'}$ 8.9 Hz, 1 H, 3′-H), 3.85 (t, $J_{2,3}$ =$J_{3,4}$ 9.0 Hz, 1 H, 3-H), 3.71 (m, 1 H, 5-H), 3.68 (s, 3 H, CH_3), 3.64−3.58 (m, 2 H, 2′-H, 6-Hb), 3.56 (dd, $J_{2,3}$ 9.0, $J_{1,2}$ 7.8 Hz, 1 H, 2-H). − ^{13}C NMR ($CDCl_3$): δ = 154.0 (s, C-5′), 138.5, 138.4, 138.4, 138.2, 137.8, 137.6 (6 × s, C-arom. quat.), 128.5−126.5 (30 × d, Ph), 104.3 (C-1), 96.7 (C-1′), 96.6 (C-6′), 84.7 (C-3), 82.3 (C-2), 80.2 (C-3′), 79.3 (C-4′), 78.4 (C-2′), 75.2, 74.6, 74.5 (3 × t, CH_2Ph), 74.4 (C-5), 73.8, 73.4, 73.3 (3 × t, CH_2Ph), 72.2 (C-4), 70.9 (C-6), 57.0 (CH_3). − MS (CI); *m/z* (%): 896.6 (100) [MNH_4^+], 806.4 (10) [MNH_4^+ − Bn]. − $C_{55}H_{58}O_{10}$ (879.1): calcd. C 75.14, H 6.65; found C 75.01, H 6.75.

Methyl 2,3,6-Tri-*O*-benzyl-4-*O*-[1D-(1,2,4/3,5)-2,3,4-tri-*O*-benzyl-1,2,3,4,5-pentahydroxycyclohexyl]-β-D-glucopyranoside (4) and Methyl 2,3,6-Tri-*O*-benzyl-4-*O*-[1D-(1,2,4,5/3)-2,3,4-tri-*O*-benzyl-1,2,3,4,5-pentahydroxycyclohexyl]-β-D-glucopyranoside (5): TIBAL (11.85 mL, 11.9 mmol, 1 M in toluene) was added to a stirred solution of **11** (1.0 g, 1.14 mmol) in anhydrous toluene (10 mL) at room temp. under argon. The reaction mixture was heated at 50°C for 4 h, when TLC (EtOAc/cyclohexane, 3:7) indicated that no starting material (R_f = 0.7) and a major component (R_f = 0.4) was present. The mixture was cooled to 0°C and ice-water (20 mL) was added. The mixture was filtered into a separating funnel (washing with 20 mL of EtOAc) and the aqueous layer was extracted with EtOAc (2 × 100 mL). Combined extracts were dried (Na_2SO_4), filtered, and the solvent was removed in vacuo. The residue was purified by flash chromatography (eluent gradient, 25−30% EtOAc in cyclohexane) to afford **4/5** (649 mg, 65%, as a 1:4.7 mixture). Further flash chromatography gave **4** (114 mg, 11%), as a colourless oil. − $[\alpha]_D^{22}$ +16.3 (*c* = 1.0 in $CHCl_3$). − IR (film): $\tilde{\nu}$ = 3454 cm^{-1} (OH), 1068 (C−O). − ^1H NMR ($CDCl_3$): δ = 7.37−7.27 (m, 30 H, arom. H), 4.99 (2 × d, *J* 11.5 Hz, 2 H, 2 × C*H*Ph), 4.93 (d, *J* 11.0 Hz, 1 H, C*H*Ph), 4.81 (d, *J* 10.8 Hz, 1 H, C*H*Ph), 4.73 (d, *J* 11.8 Hz, 1 H, C*H*Ph), 4.68 (d, *J* 11.4 Hz, 1 H, C*H*Ph), 4.67−4.62 (m, 6 H, 6 × C*H*Ph), 4.51 (m, 1 H, 1′-H), 4.38 (d, $J_{1,2}$ 8.0 Hz, 1 H, 1-H), 3.98 (dd, $J_{4,5}$ 9.5, $J_{3,4}$ 8.5 Hz, 1 H, 4-H), 3.87 (t, *J* 9.3 Hz, 1 H, 3′-H), 3.84−3.80 (m, 3 H, 5′-H, 6-Ha, 6-Hb), 3.74 (t, $J_{2,3}$ =$J_{3,4}$ 8.5 Hz, 1 H, 3-H), 3.62 (s, 3 H, CH_3), 3.54 (dt, $J_{4,5}$ 9.4, $J_{5,6a}$ = $J_{5,6b}$ 3.0 Hz, 1 H, 5-H), 3.51 (dd, $J_{2,3}$ 8.5, $J_{1,2}$ 8.0 Hz, 1 H, 2-H), 3.37 (dd, $J_{2',3'}$ 9.7, $J_{1',2'}$ 3.0 Hz, 1 H, 2′-H), 3.25 (t, *J* 9.1 Hz, 1 H, 4′-H), 2.38 (dt, J_{gem} 14.2, $J_{1',5'a(a)}$ = $J_{5',5'a(a)}$ 4.3 Hz, 1 H, 5′a-Ha), 2.06 (d, $J_{5',OH}$ 2.5 Hz, 1 H, OH), 1.15 (ddd, J_{gem} 14.2, $J_{5',5'a(b)}$ 12.1, $J_{1',5'a(b)}$ 2.0 Hz, 1 H, 5′a-Hb). − ^{13}C NMR ($CDCl_3$): δ = 138.9, 138.7, 138.6, 138.3, 138.3, 138.0 (6 × s, C-arom. quat.), 128.5−126.6 (30 × d, Ph), 104.5 (C-1), 86.3 (C-4′), 84.7 (C-3), 82.5 (C-2), 82.4 (C-2′), 81.5 (C-3′), 75.3, 75.2 (2 × t, CH_2Ph), 74.7 (C-5), 74.4, 73.7, 73.4, 72.7 (4 × t, CH_2Ph), 72.5 (C-4), 72.2 (C-1′), 69.1 (C-6), 68.1 (C-5′), 57.0 (CH_3), 31.4 (C-5′a). − MS (CI); *m/z*

(%): 898.8 (100) [MNH$_4^+$]. − $C_{55}H_{60}O_{10}$ (881.1): calcd. C 74.97, H 6.86; found C 74.81, H 6.89.

(**5**) (535 mg, 54%): as a colourless oil. − $[\alpha]_D^{22}$ +20.1 (*c* = 1.0 in $CHCl_3$). − IR (film): $\tilde{\nu}$ = 3470 cm^{-1} (OH), 1069 (C−O). − ^{1}H NMR ($CDCl_3$): δ = 7.39−7.21 (m, 30 H, arom. H), 4.92 (d, *J* 11.4 Hz, 1 H, C*H*Ph), 4.92 (d, *J* 10.9 Hz, 1 H, C*H*Ph), 4.74 (d, *J* 12.0 Hz, 1 H, C*H*Ph), 4.70 (d, *J* 12.4 Hz, 1 H, C*H*Ph), 4.68−4.61 (m, 5 H, 5 × C*H*Ph), 4.54 (d, *J* 11.9 Hz, 1 H, C*H*Ph), 4.40 (d, $J_{1,2}$ 7.6 Hz, 1 H, 1-H), 4.37−4.31 (m, 2 H, CH_2Ph), 4.27 (dt, $J_{1',5'a(a)}$ 8.1, $J_{1',2'}$ = $J_{1',5'a(b)}$ 2.9 Hz, 1 H, 1′-H), 3.93−3.90 (m, 2 H, 3′-H, 5′-H), 3.89 (dd, $J_{6a,6b}$ 10.8, $J_{5,6a}$ 2.1 Hz, 1 H, 6-Ha), 3.86−3.81 (m, 1 H, 4-H), 3.76 (dd, $J_{6a,6b}$ 10.8, $J_{5,6b}$ 5.0 Hz, 1 H, 6-Hb), 3.64 (s, 3 H, CH_3), 3.62 (t, $J_{2,3}$ = $J_{3,4}$ 8.5 Hz, 1 H, 3-H), 3.57 (br t, $J_{1',2'}$ = $J_{2',3'}$ 2.9 Hz, 1 H, 2′-H), 3.52 (ddd, $J_{4,5}$ 9.1, $J_{5,6b}$ 5.0, $J_{5,6a}$ 2.1 Hz, 1 H, 5-H), 3.49 (dd, $J_{2,3}$ 8.5, $J_{1,2}$ 7.6 Hz, 1 H, 2-H), 3.45 (m, 1 H, 4′-H), 2.90 (br s, 1 H, OH), 2.09 (dt, J_{gem} 13.2, $J_{1',5'a(a)}$ = $J_{5',5'a(a)}$ 8.1 Hz, 1 H, 5′a-Ha), 1.72 (m, 1 H, 5′a-Hb). − ^{13}C NMR ($CDCl_3$): δ = 138.8, 138.6, 138.3, 138.2, 138.1, 137.0 (6 × s, C-arom. quat.), 128.3−127.1 (30 × d, Ph), 104.5 (C-1), 84.3 (C-3), 82.1 (C-2), 75.9 (C-1′), 75.2 (C-4), 75.1 (C-5), 74.6, 74.5, 73.5, 73.4, 73.1, 72.1 (6 × t, *C*H$_2$Ph), 69.3 (C-6), 67.3 (C-5′), 57.0 (CH_3), 30.7 (C-5′a). − MS (CI); *m/z* (%): 898.9 (100) [MNH$_4^+$]. − $C_{55}H_{60}O_{10}$ (881.1): calcd. C 74.97, H 6.86; found C 74.90, H 6.93.

Phenyl 2,3,6,2′,3′,4′-Hexa-*O*-benzyl-6′-deoxy-6′-iodo-1-thio-β-D-maltoside (27): Triphenylphosphane (3.0 g, 11.4 mmol), imidazole (1.6 g, 23.5 mmol) and iodine (2.7 g, 10.6 mmol) were added to a stirred solution of **19** (7.5 g, 7.7 mmol) in anhydrous toluene (200 mL) at room temp. under argon. The mixture was heated at 70°C for 1 h, when TLC (EtOAc/cyclohexane, 1:2) indicated that no starting material (R_f = 0.6) and product (R_f = 0.8) was present. The reaction mixture was cooled to room temp. and saturated sodium thiosulfate (50 mL) was added. After 15 min the aqueous layer was extracted with EtOAc (3 × 50 mL) and combined extracts were dried ($MgSO_4$), filtered, and the solvent was removed in vacuo. The residue was purified by flash chromatography (eluent gradient, 2−10% EtOAc in cyclohexane) to afford **27** (7.0 g, 84%), as a colourless oil, used immediately without further purification.

Phenyl 2,3,6-Tri-*O*-benzyl-4-*O*-(2,3,4-tri-*O*-benzyl-6-deoxy-α-D-xylohex-5-enopyranosyl)-1-thio-β-D-glucopyranoside (12): DBU (6.0 mL, 40.1 mmol) was added to a stirred solution of **27** (7.0 g, 6.46 mmol) in anhydrous THF (200 mL) at room temp. under argon. After heating at reflux for 48 h, the solvent was removed in vacuo. The residue was purified by flash chromatography (5% EtOAc in toluene) to afford **12** (3.5 g, 56%), as a colourless oil. − $[\alpha]_D^{22}$ +11.0 (*c* = 2.2 in $CHCl_3$). − ^{1}H NMR ($CDCl_3$): δ = 7.60−7.55 (m, 5 H, arom. H), 7.45−7.15 (m, 30 H, arom. H), 5.74 (d, $J_{1',2'}$ 3.4 Hz, 1 H, 1′-H), 4.96 (d, *J* 11.9 Hz, 1 H, C*H*Ph), 4.92 (d, *J* 10.2 Hz, 1 H, C*H*Ph), 4.84 (s, 1 H, 6′-Ha), 4.81 (d, *J* 11.7 Hz, 1 H, C*H*Ph), 4.80 (br s, 4 H, 4 × C*H*Ph), 4.77 (d, $J_{1,2}$ 9.8 Hz, 1 H, 1-H), 4.74 (s, 1 H, 6′-Hb), 4.68 (d, *J* 11.8 Hz, 1 H, C*H*Ph), 4.64 (d, *J* 10.0 Hz, 1 H, C*H*Ph), 4.58 (d, *J* 11.6 Hz, 1 H, C*H*Ph), 4.55 (d, *J* 12.0 Hz, 1 H, C*H*Ph), 4.54 (d, *J* 11.9 Hz, 1 H, C*H*Ph), 4.00 (t, $J_{3,4}$ = $J_{4,5}$ 9.0 Hz, 1 H, 4-H), 3.96 (d, $J_{6a,6b}$ 9.3 Hz, 1 H, 6-Ha), 3.95 (s, 1 H, 4′-H), 3.94 (d, $J_{2',3'}$ 6.2 Hz, 1 H, 3′-H), 3.83 (t, $J_{2,3}$ = $J_{3,4}$ 8.7 Hz, 1 H, 3-H), 3.70 (td, $J_{3,5}$ = $J_{5,6b}$ 9.1, $J_{5,6a}$ 1.2 Hz, 1 H, 5-H), 3.65 (t, $J_{5,6b}$ = $J_{6a,6b}$ 9.7 Hz, 1 H, 6-Hb), 3.60 (t, $J_{1,2}$ = $J_{2,3}$ 9.5 Hz, 1 H, 2-H), 3.56 (t, $J_{1',2'}$ 3.4, $J_{2',3'}$ 6.3 Hz, 1 H, 2′-H). − ^{13}C NMR ($CDCl_3$): δ = 153.9 (s, C-5′), 138.4, 138.3, 138.2, 137.6, 137.5, 137.4, 133.9 (7 × s, C-arom. quat.), 131.2−126.2 (35 × d, Ph), 97.1 (C-1′), 96.5 (C-6′), 87.2 (C-1), 86.6 (C-3), 81.1 (C-2), 80.1 (C-3′), 79.2 (C-4′), 78.5 (C-5), 78.2 (C-2′), 75.1, 75.0, 74.3, 74.0, 73.4, 73.1 (6 × t, *C*H$_2$Ph), 72.4 (C-4), 70.6 (C-6). − MS (CI); *m/z* (%): 974 (100) [MNH$_4^+$]. − $C_{60}H_{60}O_9S$ (957.2): calcd. C 75.28, H 6.32; found C 75.13, H 6.76.

Phenyl 2,3,6-Tri-*O*-benzyl-4-*O*-[1D-(1,2,4/3,5)-2,3,4-tri-*O*-benzyl-1,2,3,4,5-pentahydroxycyclohexyl]-1-thio-β-D-glucopyranoside (6) and Phenyl 2,3,6-Tri-*O*-benzyl-4-*O*-[1D-(1,2,4,5/3)-2,3,4-tri-*O*-benzyl-1,2,3,4,5-pentahydroxycyclohexyl]-1-thio-β-D-glucopyranoside (7): TIBAL (4.2 mL, 4.2 mmol, 1 M in toluene) was added to a stirred solution of **12** (400 mg, 0.42 mmol) in anhydrous toluene (5 mL) at room temp. under argon. The reaction mixture was heated at 50°C for 5 h, when TLC (EtOAc/cyclohexane, 3:7) indicated that no starting material (R_f = 0.7), and a major component (R_f = 0.4) was present. The mixture was cooled to 0°C and ice-water (20 mL) was added. The mixture was filtered into a separating funnel (washing with 20 mL of EtOAc) and the aqueous layer was extracted with EtOAc (2 × 100 mL). Combined extracts were dried ($MgSO_4$), filtered, and the solvent was removed in vacuo. The residue was purified by flash chromatography (20% EtOAc in cyclohexane) to afford **6**/**7** (240 mg, 60%, as a 1:2 mixture). Flash chromatography (eluent gradient, 5−10% EtOAc in toluene) of the acetylated mixture and deacetylation afforded **6** (80 mg, 20%), as a colourless oil. − $[\alpha]_D^{22}$ +10.0 (*c* = 0.8 in $CHCl_3$). − ^{1}H NMR ($CDCl_3$): δ = 7.64−7.20 (m, 35 H, arom. H), 4.98 (d, *J* 11.4 Hz, 1 H, C*H*Ph), 4.95 (d, *J* 12.0 Hz, 1 H, C*H*Ph), 4.87 (d, *J* 10.1 Hz, 1 H, C*H*Ph), 4.82 (d, *J* 12.0 Hz, 1 H, C*H*Ph), 4.76 (d, *J* 10.8 Hz, 1 H, C*H*Ph), 4.73 (d, $J_{1,2}$ 9.7 Hz, 1 H, 1-H), 4.68 (d, *J* 11.3 Hz, 1 H, C*H*Ph), 4.67 (d, *J* 11.9 Hz, 1 H, C*H*Ph), 4.66 (d, *J* 12.3 Hz, 1 H, C*H*Ph), 4.64 (d, *J* 10.9 Hz, 1 H, C*H*Ph), 4.61 (d, *J* 12.0 Hz, 1 H, C*H*Ph), 4.59 (d, *J* 10.1 Hz, 1 H, C*H*Ph), 4.57 (d, *J* 10.8 Hz, 1 H, C*H*Ph), 4.50−4.48 (m, 1 H, 1′-H), 4.03 (t, $J_{4,5}$ = $J_{3,4}$ 9.0 Hz, 1 H, 4-H), 3.87 (t, *J* 9.3 Hz, 1 H, 3′-H), 3.88−3.81 (m, 3 H, 5′-H, 6-Ha, 6-Hb), 3.75 (dd, $J_{3,4}$ 9.0, $J_{2,3}$ 8.5 Hz, 1 H, 3-H), 3.58 (dd, $J_{1,2}$ 9.7, $J_{2,3}$ 8.5 Hz, 1 H, 2-H), 3.59−3.53 (m, 1 H, 5-H), 3.37 (dd, $J_{2',3'}$ 9.3, $J_{1',2'}$ 3.0 Hz, 1 H, 2′-H), 3.26 (dd, $J_{3',4'}$ 9.3, $J_{4',5'}$ 9.0 Hz, 1 H, 4′-H), 2.38 (dt, J_{gem} 14.0, $J_{1',5'a(a)}$ = $J_{5',5'a(a)}$ 4.2 Hz, 1 H, 5′a-Ha), 2.12 (d, $J_{5',OH}$ 2.1 Hz, 1 H, OH), 1.21 (ddd, J_{gem} 14.0, $J_{5',5'a(b)}$ 12.1, $J_{1',5'a(b)}$ 2.0 Hz, 1 H, 5′a-Hb). − ^{13}C NMR ($CDCl_3$): δ = 138.7, 138.7, 138.6, 138.3, 138.2, 137.8, 133.7 (7 × s, C-arom. quat.), 131.8−126.3 (35 × d, Ph), 87.1 (C-1), 86.5 (C-3), 86.2 (C-4′), 82.5 (C-2′), 81.5 (C-3′), 81.0 (C-2), 78.8 (C-5), 75.3, 75.2, 75.1, 74.0, 73.4, 72.8 (6 × t, *C*H$_2$Ph), 72.6 (C-4), 69.1 (C-6), 68.1 (2 × d, C-5′, C-1′), 31.6 (C-5′a). − MS (CI); *m/z* (%): 976.2 (100) [MNH$_4^+$]. − $C_{60}H_{62}O_9S$ (959.2): calcd. C 75.13, H 6.52; found C 75.29, H 6.65.

(**7**) (160 mg, 40%): as a colourless oil. − $[\alpha]_D^{22}$ +12.8 (*c* = 1.2 in $CHCl_3$). − ^{1}H NMR ($CDCl_3$): δ = 7.63−7.19 (m, 35 H, arom. H), 4.86 (2 × d, *J* 11.6 Hz, 2 H, 2 × C*H*Ph), 4.77 (d, *J* 11.6 Hz, 1 H, C*H*Ph), 4.74 (d, $J_{1,2}$ 8.5 Hz, 1 H, 1-H), 4.68 (d, *J* 12.2 Hz, 1 H, C*H*Ph), 4.68−4.59 (m, 4 H, 4 × C*H*Ph), 4.59 (d, *J* 11.8 Hz, 1 H, C*H*Ph), 4.51 (d, *J* 11.7 Hz, 1 H, C*H*Ph), 4.31−4.21 (m, 3 H, CH_2Ph, 1′-H), 3.93−3.85 (m, 2 H, 3′-H, 5′-H), 3.90 (dd, $J_{6a,6b}$ 10.8, $J_{5,6a}$ 2.1 Hz, 1 H, 6-Ha), 3.86−3.81 (m, 1 H, 4-H), 3.78 (dd, $J_{6a,6b}$ 10.8, $J_{5,6b}$ 5.1 Hz, 1 H, 6-Hb), 3.64 (t, $J_{2,3}$ = $J_{3,4}$ 8.5 Hz, 1 H, 3-H), 3.60−3.51 (m, 2 H, 2′-H, 5-H), 3.53 (t, $J_{2,3}$ = $J_{1,2}$ 8.5 Hz, 1 H, 2-H), 3.46 (m, 1 H, 4′-H), 2.90 (br s, 1 H, OH), 2.09 (dt, J_{gem} 12.9, $J_{1',5'a(a)}$ = $J_{5',5'a(a)}$ 8.6 Hz, 1 H, 5′a-Ha), 1.79 (m, 1 H, 5′a-Hb). − ^{13}C NMR ($CDCl_3$): δ = 138.7, 138.7, 138.3, 138.1, 138.0, 137.8, 133.8 (7 × s, C-arom. quat.), 128.9−127.1 (35 × d, Ph), 87.2 (C-1), 86.4 (C-3), 80.8 (C-2), 79.2 (C-5), 76.2 (C-1′), 75.2 (t, *C*H$_2$Ph), 75.0 (C-4), 74.9, 74.9, 73.5, 73.1, 72.2 (5 × t, *C*H$_2$Ph), 69.3 (C-6), 67.3 (C-5′), 30.8 (C-5′a). − MS (CI); *m/z* (%): 976.2 (100) [MNH$_4^+$]. − $C_{60}H_{62}O_9S$ (959.2): calcd. C 75.13, H 6.52; found C 74.62, H 6.81.

Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-(2,3,4-tri-*O*-benzyl-6-deoxy-6-iodo-α-D-glucopyranosyl)-α-D-glucopyranoside: Triphenylphosphane (283 mg, 1.08 mmol), imidazole (147 mg, 2.16 mmol) and iodine (365 mg, 10.32 mmol) were added to a stirred solution of methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl)-α-D-glucopyranoside (**28**)[15] (645 mg, 8.61 mmol) in anhydrous toluene (10 mL) at room temp. under argon. The mixture was heated at 70°C for 30 min, when TLC (EtOAc/cyclohexane, 1:2) indicated that no starting material ($R_f = 0.1$) and product ($R_f = 0.5$) was present. The reaction mixture was cooled to room temp. and saturated sodium thiosulfate (20 mL) was added. After 15 min the aqueous layer was extracted with EtOAc (3 × 20 mL) and combined extracts were dried ($MgSO_4$), filtered, and the solvent was removed in vacuo. The residue was purified by flash chromatography (eluent gradient, 10−20% EtOAc in cyclohexane) to afford *the title compound* (602 mg, 83%), as a colourless foam. − $[\alpha]_D^{21}$ +62.5 ($c = 1.0$ in $CHCl_3$). − ^{1}H NMR ($CDCl_3$): δ = 7.39−7.28 (m, 30 H, arom. H), 5.05 (d, $J_{1',2'}$ 3.5 Hz, 1 H, 1′-H), 5.02 (d, *J* 10.9 Hz, 1 H, C*H*Ph), 5.00 (d, *J* 10.8 Hz, 1 H, C*H*Ph), 4.99 (d, *J* 12.0 Hz, 1 H, C*H*Ph), 4.98 (d, *J* 11.1 Hz, 1 H, C*H*Ph), 4.87 (d, *J* 10.8 Hz, 1 H, C*H*Ph), 4.81 (d, *J* 10.8 Hz, 1 H, C*H*Ph), 4.76 (d, *J* 12.0 Hz, 1 H, C*H*Ph), 4.74−4.67 (m, 4 H, 4 × C*H*Ph), 4.62 (d, *J* 12.4 Hz, 1 H, C*H*Ph), 4.60 (d, $J_{1,2}$ 3.5 Hz, 1 H, 1-H), 4.04 (2 × t, $J_{2,3} = J_{3,4} = J_{2',3'} = J_{3',4'}$ 9.5 Hz, 1 H, 3-H, 3′-H), 3.91 (dd, $J_{6a,6b}$ 11.6, $J_{5,6a}$ 4.0 Hz, 1 H, 6-Ha), 3.82 (m, 1 H, 5-H), 3.79 (dd, $J_{6a,6b}$ 11.6, $J_{5,6b}$ 1.4 Hz, 1 H, 6-Hb), 3.72 (t, $J_{3,4} = J_{4,5}$ 9.5 Hz, 1 H, 4-H), 3.57 (dd, $J_{2',3'}$ 9.5, $J_{1',2'}$ 3.5 Hz, 1 H, 2′-H), 3.49 (dd, $J_{2,3}$ 9.5, $J_{1,2}$ 3.5 Hz, 1 H, 2-H), 3.46 (m, 1 H, 5′-H), 3.42 (m, 1 H, 6′-Ha), 3.40 (s, 3 H, CH_3), 3.39 (t, $J_{3',4'} = J_{4',5'}$ 9.5 Hz, 1 H, 4′-H), 3.32 (dd, $J_{6a',6b'}$ 10.6, $J_{5',6'b}$ 5.5 Hz, 1 H, 6′-Hb). − ^{13}C NMR ($CDCl_3$): δ = 138.8, 138.5, 138.3, 138.2, 138.2, 138.1 (6 × s, C-arom. quat.), 128.4−127.5 (30 × d, Ph), 98.0 (C-1), 97.0 (C-1′), 82.1 (C-3), 81.4 (C-4′), 81.1 (C-3′), 80.1 (2 × d, C-2, C-2′), 77.7 (C-4), 75.7, 75.5, 75.2, 75.0, 73.4, 73.2 (6 × t, *C*H$_2$Ph), 70.3 (C-5), 69.1 (C-5′), 66.1 (C-6), 55.2 (CH_3), 8.3 (C-6′). − MS (CI); *m/z* (%): 1024.6 (75) $[MNH_4^+]$, 510.2 (100). − $C_{55}H_{59}IO_{10}$ (1006.9): calcd. C 65.60, H 5.91; found C 65.49, H 5.83.

Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-(2,3,4-tri-*O*-benzyl-6-deoxy-α-D-xylohex-5-enopyranosyl)-α-D-glucopyranoside (13): DBU (0.96 mL, 6.42 mmol) was added to a stirred solution of methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,4-tri-*O*-benzyl-6-deoxy-6-iodo-α-D-glucopyranosyl)-α-D-glucopyranoside (535 mg, 0.53 mmol) in anhydrous THF (5 mL) at room temp. under argon. After heating at reflux for 24 h, the solvent was removed in vacuo. The residue was purified by flash chromatography (17% EtOAc in cyclohexane) to afford **13** (216 g, 46%), as a colourless amorphous solid, m.p. 118−119°C. − $[\alpha]_D^{21}$ +18.9 ($c = 1.0$ in $CHCl_3$). − IR (KBr): $\tilde{\nu}$ = 1668 cm^{-1} (C=C), 1079 (C−O). − ^{1}H NMR ($CDCl_3$): δ = 7.39−7.29 (m, 30 H, arom. H), 5.15 (d, $J_{1',2'}$ 3.4 Hz, 1 H, 1′-H), 5.00 (d, *J* 10.8 Hz, 1 H, C*H*Ph), 4.92 (d, *J* 10.8 Hz, 1 H, C*H*Ph), 4.90 (d, *J* 11.0 Hz, 1 H, C*H*Ph), 4.87 (d, *J* 10.4 Hz, 1 H, C*H*Ph), 4.87 (br s, 1 H, 6′-Ha), 4.87 (d, *J* 11.0 Hz, 1 H, C*H*Ph), 4.82 (m, 2 H, C*H*$_2$Ph), 4.77 (d, *J* 12.1 Hz, 1 H, C*H*Ph), 4.74 (d, *J* 12.1 Hz, 1 H, C*H*Ph), 4.72 (br s, 1 H, 6′-Hb), 4.72 (m, 2 H, C*H*$_2$Ph), 4.61 (d, *J* 12.1 Hz, 1 H, C*H*Ph), 4.61 (d, $J_{1,2}$ 3.6 Hz, 1 H, 1-H), 4.07−4.00 (m, 2 H, 3-H, 6-Ha), 4.01 (t, $J_{2',3'} = J_{3',4'}$ 9.0 Hz, 1 H, 3′-H), 3.96 (dt, $J_{3',4'}$ 9.0, $J_{4',6'a} = J_{4',6'b}$ 1.8 Hz, 1 H, 4′-H), 3.81 (d, $J_{6a,6b}$ 12.4 Hz, 1 H, 6-Hb), 3.80 (t, $J_{3,4} = J_{4,5}$ 9.8 Hz, 1 H, 4-H), 3.78 (m, 1 H, 5-H), 3.67 (dd, $J_{2',3'}$ 9.0, $J_{1',2'}$ 3.4 Hz, 1 H, 2′-H), 3.47 (dd, $J_{2,3}$ 9.6, $J_{1,2}$ 3.6 Hz, 1 H, 2-H), 3.40 (s, 3 H, CH_3). − ^{13}C NMR ($CDCl_3$): δ = 153.9 (s, C-5′), 138.8, 138.6, 138.4, 138.3, 138.2, 138.1 (6 × s, C-arom. quat.), 128.4−127.5 (30 × d, Ph), 98.3 (C-1), 98.1 (C-1′), 96.9 (C-6′), 82.0 (C-3), 80.7 (C-3′), 80.1 (C-2), 79.3 (2 × d, C-2′, C-4′), 77.4 (C-4), 75.7, 75.5, 75.0, 74.3, 73.4, 72.3 (6 × t, *C*H$_2$Ph), 70.4 (C-5), 65.8 (C-6), 55.1 (CH_3). − MS (CI); *m/z* (%): 898.5 (100) $[MNH_4^+]$. − $C_{55}H_{58}O_{10}$ (879.1): calcd. C 75.14, H 6.65; found C 75.10, H 6.53.

Methyl 3,4-Di-*O*-benzyl-6-*O*-(2,3,4-tri-*O*-benzyl-6-deoxy-α-D-xylohex-5-enopyranosyl)-α-D-glucopyranoside (30), Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-[1D-(1,2,4,5/3)-2,3,4-tri-*O*-benzyl-1,2,3,4,5-pentahydroxycyclohexyl]-α-D-glucopyranoside (8), and Methyl 3,4-Di-*O*-benzyl-6-*O*-[1D-(1,2,4,5/3)-2,3,4-tri-*O*-benzyl-1,2,3,4,5-pentahydroxycyclohexyl]-α-D-glucopyranoside (29): TIBAL (2.62 mL, 2.6 mmol, 1 M in toluene) was added to a stirred solution of **13** (216 mg, 0.25 mmol) in anhydrous toluene (3 mL) at room temp. under argon. The reaction mixture was heated at 50°C for 3 h, when TLC (EtOAc/cyclohexane, 3:7) indicated that no starting material ($R_f = 0.6$), minor products ($R_f = 0.4$ and 0.2) and a major component ($R_f = 0.05$) was present. The mixture was cooled to 0°C and ice-water (5 mL) was added. The mixture was filtered into a separating funnel (washing with 5 mL of EtOAc) and the aqueous layer was extracted with EtOAc (3 × 10 mL). Combined extracts were dried ($MgSO_4$), filtered, and the solvent was removed in vacuo. The residue was purified by flash chromatography (eluent gradient, 30−80% EtOAc in cyclohexane) to afford **30** (26 mg, 13%), as a colourless crystalline solid, m.p. 149−150°C (ether/pentane). − $[\alpha]_D^{21}$ +47.2 ($c = 0.9$ in $CHCl_3$). − IR (KBr): $\tilde{\nu}$ = 3400 cm^{-1} (O−H), 1665 (C=C), 1090 (C−O). − ^{1}H NMR ($CDCl_3$): δ = 7.40−7.30 (m, 25 H, arom. H), 5.19 (d, $J_{1',2'}$ 3.4 Hz, 1 H, 1′-H), 4.93 (d, *J* 13.0 Hz, 1 H, C*H*Ph), 4.92 (d, *J* 11.0 Hz, 1 H, C*H*Ph), 4.88 (d, *J* 11.0 Hz, 1 H, C*H*Ph), 4.88 (br s, 1 H, 6′-Ha), 4.87−4.84 (m, 2 H, 2 × C*H*Ph), 4.83 (m, 2 H, C*H*$_2$Ph), 4.78 (s, 2 H, C*H*$_2$Ph), 4.77 (d, $J_{1,2}$ 3.7 Hz, 1 H, 1-H), 4.75 (d, *J* 11.1 Hz, 1 H, C*H*Ph), 4.73 (br s, 1 H, 6′-Hb), 4.07 (dd, $J_{6a,6b}$ 12.4, $J_{5,6a}$ 2.2 Hz, 1 H, 6-Ha), 4.02 (t, $J_{2',3'} = J_{3',4'}$ 8.7 Hz, 1 H, 3′-H), 3.98 (dt, $J_{3',4'}$ 8.7, $J_{4',6'a} = J_{4',6'b}$ 1.9 Hz, 1 H, 4′-H), 3.85 (br d, $J_{6a,6b}$ 12.4 Hz, 1 H, 6-Hb), 3.82−3.75 (m, 3 H, 3-H, 4-H, 5-H), 3.70 (dd, $J_{2',3'}$ 8.7, $J_{1',2'}$ 3.4 Hz, 1 H, 2′-H), 3.61 (td, $J_{2,3} = J_{2,OH}$ 8.0, $J_{1,2}$ 3.7 Hz, 1 H, 2-H), 3.44 (s, 3 H, CH_3), 2.17 (d, $J_{2,OH}$ 8.0 Hz, 1 H, OH). − ^{13}C NMR ($CDCl_3$): δ = 153.9 (s, C-5′), 138.7, 138.5, 138.3, 138.2, 138.0 (5 × s, C-arom. quat.), 128.4−127.5 (25 × d, Ph), 99.2 (C-1), 98.3 (C-1′), 96.9 (C-6′), 83.0 (C-3), 80.7 (C-3′), 79.5 (C-2′), 79.4 (C-4′), 77.2 (C-4), 75.5, 75.3, 74.9, 74.3 (4 × t, *C*H$_2$Ph), 72.9 (C-2), 72.5 (t, *C*H$_2$Ph), 70.8 (C-5), 65.7 (C-6), 55.2 (CH_3). − MS (CI); *m/z* (%): 806.4 (100) $[MNH_4^+]$. − $C_{48}H_{52}O_{10}$ (788.9): calcd. C 73.07, H 6.64; found C 72.98, H 6.59.

(**8**) (23 mg, 11%): as a colourless solid, m.p. 74−75°C. − $[\alpha]_D^{21}$ +32.4 ($c = 0.8$ in $CHCl_3$). − IR (film): $\tilde{\nu}$ = 3468 cm^{-1} (O−H), 1067 (C−O). − ^{1}H NMR ($CDCl_3$): δ = 7.39−7.30 (m, 30 H, arom. H), 5.03 (d, *J* 10.8 Hz, 1 H, C*H*Ph), 4.93 (d, *J* 10.7 Hz, 1 H, C*H*Ph), 4.92 (d, *J* 11.2 Hz, 1 H, C*H*Ph), 4.88 (d, *J* 10.5 Hz, 1 H, C*H*Ph), 4.84 (d, *J* 10.7 Hz, 1 H, C*H*Ph), 4.80 (d, *J* 12.1 Hz, 1 H, C*H*Ph), 4.79 (s, 2 H, C*H*$_2$Ph), 4.76 (d, *J* 12.0 Hz, 1 H, C*H*Ph), 4.68 (d, *J* 12.0 Hz, 1 H, C*H*Ph), 4.67 (d, *J* 12.1 Hz, 1 H, C*H*Ph), 4.64 (d, $J_{1,2}$ 3.5 Hz, 1 H, 1-H), 4.57 (d, *J* 11.2 Hz, 1 H, C*H*Ph), 4.14 (t, $J_{2',3'} = J_{3',4'}$ 9.2 Hz, 1 H, 3′-H), 4.06−4.01 (m, 3 H, 3-H, 5′-H, 6-Ha), 3.89 (br s, 1 H, OH), 3.86 (ddd, $J_{4,5}$ 9.8, $J_{5,6b}$ 6.4, $J_{5,6a}$ 1.9 Hz, 1 H, 5-H), 3.76 (m, 1 H, 1′-H), 3.60 (dd, $J_{6a,6b}$ 10.3, $J_{5,6b}$ 6.4 Hz, 1 H, 6-Hb), 3.53 (dd, $J_{2,3}$ 9.6, $J_{1,2}$ 3.5 Hz, 1 H, 2-H), 3.45−3.39 (m, 2 H, 2′-H, 4-H), 3.43 (s, 3 H, CH_3), 3.35 (dd, $J_{3',4'}$ 9.2, $J_{4',5'}$ 3.2 Hz, 1 H, 4′-H), 2.20 (dt, J_{gem} 15.0, $J_{1',5'a(a)} = J_{5',5'a(a)}$ 3.8 Hz, 1 H, 5′a-Ha), 1.35 (m, 1 H, 5′a-Hb). − ^{13}C NMR ($CDCl_3$): δ = 138.8, 138.7, 138.5, 138.5, 138.2, 138.1 (6 × s, C-arom. quat.), 128.4−127.5 (30 × d, Ph), 97.8 (C-1), 82.4 (C-4′), 82.0 (C-3), 80.0 (C-2), 78.7 (C-3′), 78.0 (C-4), 77.7 (C-1′), 75.7, 75.7, 74.9, 73.3, 73.0, 72.2 (6 × t, *C*H$_2$Ph), 70.2 (C-6), 69.9 (C-5), 68.1 (C-5′), 55.4 (CH_3), 30.4 (C-5′a). − MS (CI); *m/z* (%): 898.6 (100) $[MNH_4^+]$, 808.6 (40) [MNH$_4^+$ − Bn]. − $C_{55}H_{60}O_{10}$ (881.1): calcd. C 74.97, H 6.86; found C 74.90, H 6.92.

(**29**) (100 mg, 48%): as a colourless amorphous solid, m.p. 108−110°C. − $[\alpha]_D^{21}$ +64.5 (*c* = 1.0 in $CHCl_3$). − IR (film): $\tilde{\nu}$ = 3464 cm^{-1} (O−H), 1074 (C−O). − ^{1}H NMR ($CDCl_3$): δ = 7.40−7.30 (m, 25 H, arom. H), 4.96 (d, *J* 11.1 Hz, 1 H, C*H*Ph), 4.95 (d, *J* 10.7 Hz, 1 H, C*H*Ph), 4.91 (d, *J* 11.1 Hz, 1 H, C*H*Ph), 4.89 (d, *J* 10.2 Hz, 1 H, C*H*Ph), 4.87 (d, *J* 11.4 Hz, 1 H, C*H*Ph), 4.79 (d, *J* 12.2 Hz, 1 H, C*H*Ph), 4.79 (d, $J_{1,2}$ 3.9 Hz, 1 H, 1-H), 4.77 (s, 2 H, CH_2Ph), 4.71 (d, *J* 11.9 Hz, 1 H, C*H*Ph), 4.59 (d, *J* 11.2 Hz, 1 H, C*H*Ph), 4.17 (t, $J_{2',3'} = J_{3',4'}$ 9.1 Hz, 1 H, 3′-H), 4.10 (br d, $J_{6a,6b}$ 10.1 Hz, 1 H, 6-Ha), 4.07 (m, 1 H, 5′-H), 3.89−3.84 (m, 3 H, 1′-H, 5′-OH, 5-H), 3.81 (t, $J_{2,3} = J_{3,4}$ 9.0 Hz, 1 H, 3-H), 3.69 (td, $J_{2,3} = J_{2,OH}$ 9.0, $J_{1,2}$ 3.9 Hz, 1 H, 2-H), 3.64 (dd, $J_{6a,6b}$ 10.1, $J_{5,6b}$ 6.4 Hz, 1 H, 6-Hb), 3.47 (s, 3 H, CH_3), 3.45−3.41 (m, 2 H, 2′-H, 4-H), 3.38 (dd, $J_{3',4'}$ 9.1, $J_{4',5'}$ 3.3 Hz, 1 H, 4′-H), 2.25 (dt, J_{gem} 15.0, $J_{1',5'a(a)} = J_{5',5'a(a)}$ 4.0 Hz, 1 H, 5′a-Ha), 2.19 (d, $J_{2,OH}$ 9.0 Hz, 1 H, 2-OH), 1.38 (m, 1 H, 5′a-Hb). − ^{13}C NMR ($CDCl_3$): δ = 138.8, 138.5, 138.5, 138.4, 138.1 (5 × s, C-arom. quat.), 128.4−127.5 (25 × d, Ph), 99.0 (C-1), 83.2 (C-3), 82.4 (C-4′), 78.7 (C-3′), 77.8 (C-1′), 77.7 (C-4), 75.8, 75.4, 74.8, 73.1 (4 × t, *C*H_2Ph), 73.0 (C-2), 72.2 (t, *C*H_2Ph), 70.3 (C-6), 70.2 (C-5), 68.1 (C-5′), 55.4 (CH_3), 30.5 (C-5′a). − MS (CI); *m/z* (%): 808.2 (100) [MNH$_4^+$]. − $C_{48}H_{54}O_{10}$ (791.0): calcd. C 72.89, H 6.88; found C 72.89, H 7.01.

Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-(6-*O*-acetyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl)-β-D-glucopyranoside (33): A mixture of methyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (**31**)[4] (1.62 g, 3.49 mmol), phenyl 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (**32**)[16] (2.04 g, 3.49 mmol) and powdered 4 Å molecular sieves (3.5 g) was stirred at room temp. under argon. After 30 min, *N*-iodosuccinimide (1.57 g, 6.98 mmol) was added and the mixture was cooled to −30°C. Triflic acid (93 μL, 1.05 mmol) was added dropwise over 5 min and after 15 min saturated $NaHCO_3$ (0.1 mL) was added. After 5 min, the reaction mixture was warmed to room temp., diluted with DCM (50 mL) and filtered (Celite®). The organic phase was washed with water (50 mL), saturated sodium thiosulfate (50 mL), brine (50 mL), dried ($MgSO_4$), filtered, and the solvent was removed in vacuo. The residue was purified by flash chromatography (eluent gradient, 20−25% EtOAc in cyclohexane) to afford **33** (2.42 g, 73%), as a colourless solid, m.p. 90−91°C. − $[\alpha]_D^{21}$ +48.0 (*c* = 1.0 in $CHCl_3$). − IR (KBr): $\tilde{\nu}$ = 1745 cm^{-1} (C=O). − ^{1}H NMR ($CDCl_3$): δ = 7.38−7.30 (m, 30 H, arom. H), 5.08 (d, $J_{1',2'}$ 3.5 Hz, 1 H, 1′-H), 5.06 (d, *J* 11.0 Hz, 1 H, C*H*Ph), 4.96 (d, *J* 11.2 Hz, 1 H, C*H*Ph), 4.95 (d, *J* 11.1 Hz, 1 H, C*H*Ph), 4.93 (d, *J* 11.5 Hz, 1 H, C*H*Ph), 4.90 (d, *J* 11.1 Hz, 1 H, C*H*Ph), 4.85 (d, *J* 10.8 Hz, 1 H, C*H*Ph), 4.83 (d, *J* 12.4 Hz, 1 H, C*H*Ph), 4.83 (d, *J* 10.2 Hz, 1 H, C*H*Ph), 4.77 (d, *J* 12.1 Hz, 1 H, C*H*Ph), 4.71 (d, *J* 11.1 Hz, 1 H, C*H*Ph), 4.66 (d, *J* 11.0 Hz, 1 H, C*H*Ph), 4.61 (d, *J* 11.0 Hz, 1 H, C*H*Ph), 4.35 (d, $J_{1,2}$ 7.8 Hz, 1 H, 1-H), 4.32 (dd, $J_{6a',6b'}$ 12.0, $J_{5',6'a}$ 3.7 Hz, 1 H, 6′-Ha), 4.27 (dd, $J_{6a',6b'}$ 12.0, $J_{5',6'a}$ 2.3 Hz, 1 H, 6′-Hb), 4.06 (t, $J_{2',3'} = J_{3',4'}$ 9.2 Hz, 1 H, 3′-H), 3.90 (ddd, $J_{4',5'}$ 10.1, $J_{5',6'a}$ 3.7, $J_{5',6'b}$ 2.3 Hz, 1 H, 5′-H), 3.90−3.83 (m, 2 H, 6-Ha, 6-Hb), 3.73 (dd, $J_{4,5}$ 9.3, $J_{3,4}$ 9.0 Hz, 1 H, 4-H), 3.69 (dd, $J_{3,4}$ 9.0, $J_{2,3}$ 8.6 Hz, 1 H, 3-H), 3.60 (dd, $J_{2',3'}$ 9.6, $J_{1',2'}$ 3.5 Hz, 1 H, 2′-H), 3.58 (s, 3 H, OCH_3), 3.57−3.50 (m, 2 H, 4′-H, 5-H), 3.36 (dd, $J_{2,3}$ 8.6, $J_{1,2}$ 7.8 Hz, 1 H, 2-H), 2.06 (s, 3 H, CH_3). − ^{13}C NMR ($CDCl_3$): δ = 170.7 (s, C=O), 138.6, 138.6, 138.5, 138.2, 138.2, 138.0 (6 × s, C-arom. quat.), 128.4−127.5 (30 × d, Ph), 104.5 (C-1), 96.9 (C-1′), 84.5 (C-3), 82.3 (C-2), 81.6 (C-3′), 79.9 (C-2′), 77.6 (C-4), 77.0 (C-4′), 75.6 (2 × t, 2 × *C*H_2Ph), 75.0, 74.8, 74.7 (3 × t, *C*H_2Ph), 74.6 (C-5), 72.4 (t, *C*H_2Ph), 68.6 (C-5′), 65.7 (C-6), 63.0 (C-6′), 57.0 (OCH_3), 20.9 (CH_3). − MS (CI); *m/z* (%): 956.6 (30) [MNH$_4^+$], 91.0 (100). − $C_{57}H_{62}O_{12}$ (939.1): calcd. C 72.90, H 6.65; found C 72.80, H 6.70.

Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-(2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl)-β-D-glucopyranoside: A solution of 1 M sodium methoxide in methanol (4 mL, 4.0 mmol) was added to a stirred solution of **33** (2.03 g, 2.16 mmol) in anhydrous toluene (10 mL) and methanol (40 mL) at room temp. After 30 min, TLC (EtOAc/cyclohexane, 1:2) indicated that no starting material (R_f = 0.6) and product (R_f = 0.3) was present. The reaction mixture was neutralised with Amberlite IR-120 (H$^+$ resin), filtered and the solvent was removed in vacuo. The residue was recrystallised (methanol) to afford the *title compound* (1.82 g, 94%), as a colourless crystalline solid, m.p. 149−150°C. − $[\alpha]_D^{22}$ +50.5 (*c* = 1.0 in $CHCl_3$). − ^{1}H NMR ($CDCl_3$): δ = 7.39−7.30 (m, 30 H, arom. H), 5.06 (d, $J_{1',2'}$ 3.2 Hz, 1 H, 1′-H), 5.05 (d, *J* 11.7 Hz, 1 H, C*H*Ph), 4.97 (d, *J* 10.9 Hz, 1 H, C*H*Ph), 4.95 (d, *J* 11.3 Hz, 1 H, C*H*Ph), 4.94 (d, *J* 11.0 Hz, 1 H, C*H*Ph), 4.91 (d, *J* 11.1 Hz, 1 H, C*H*Ph), 4.86 (d, *J* 10.9 Hz, 1 H, C*H*Ph), 4.84 (d, *J* 10.9 Hz, 1 H, C*H*Ph), 4.84 (d, *J* 12.1 Hz, 1 H, C*H*Ph), 4.78 (d, *J* 12.0 Hz, 1 H, C*H*Ph), 4.71 (d, *J* 11.1 Hz, 1 H, C*H*Ph), 4.70 (d, *J* 11.2 Hz, 1 H, C*H*Ph), 4.67 (d, *J* 11.0 Hz, 1 H, C*H*Ph), 4.36 (d, $J_{1,2}$ 7.8 Hz, 1 H, 1-H), 4.06 (t, $J_{2',3'} = J_{3',4'}$ 9.3 Hz, 1 H, 3′-H), 3.89−3.86 (m, 2 H, 6-Ha, 6-Hb), 3.83−3.80 (m, 2 H, 5′-H, 6′-Ha), 3.74 (dd, $J_{4,5}$ 9.4, $J_{3,4}$ 9.0 Hz, 1 H, 4-H), 3.70 (dd, $J_{3,4}$ 9.0, $J_{2,3}$ 8.3 Hz, 1 H, 3-H), 3.60 (s, 3 H, OCH_3), 3.62−3.52 (m, 4 H, 2′-H, 4′-H, 5-H, 6′-Hb), 3.38 (dd, $J_{2,3}$ 8.3, $J_{1,2}$ 7.8 Hz, 1 H, 2-H), 1.67 (m, 1 H, OH). − ^{13}C NMR ($CDCl_3$): δ = 138.7, 138.6, 138.4, 138.3, 138.3, 138.2 (6 × s, C-arom. quat.), 128.4−127.5 (30 × d, Ph), 104.5 (C-1), 97.0 (C-1′), 84.5 (C-3), 82.3 (C-2), 81.5 (C-3′), 80.0 (C-2′), 77.7 (C-4), 77.2 (C-4′), 75.6, 75.5, 75.0, 74.9, 74.7 (5 × t, 5 × *C*H_2Ph), 74.6 (C-5), 72.4 (t, *C*H_2Ph), 70.7 (C-5′), 65.7 (C-6), 61.8 (C-6′), 57.0 (OCH_3). − MS (CI); *m/z* (%): 914.3 (100) [MNH$_4^+$]. − $C_{55}H_{60}O_{11}$ (897.1): calcd. C 73.63, H 6.74; found C 73.62, H 6.79.

Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-(2,3,4-tri-*O*-benzyl-6-deoxy-6-iodo-α-D-glucopyranosyl)-β-D-glucopyranoside: Triphenylphosphane (457 mg, 1.74 mmol), imidazole (240 mg, 21.1 mmol) and iodine (3.57 g, 14.1 mmol) were added to a stirred solution of methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl)-β-D-glucopyranoside (6.3 g, 3.53 mmol) in anhydrous toluene (15 mL) at room temp. under argon. The mixture was heated at 70°C for 15 min, when TLC (EtOAc/cyclohexane, 1:2) indicated that no starting material (R_f = 0.3) and a major product (R_f = 0.7) was present. The reaction mixture was cooled to room temp. and saturated sodium thiosulfate (15 mL) was added. After 10 min the aqueous layer was extracted with EtOAc (3 × 25 mL) and combined extracts were dried ($MgSO_4$), filtered, and the solvent was removed in vacuo. The residue was purified by flash chromatography (15% EtOAc in cyclohexane) to afford the *title compound* (1.08 g, 92%), as a colourless crystalline solid, m.p. 118−120°C. − $[\alpha]_D^{21}$ +44.5 (*c* = 1.0 in $CHCl_3$). − ^{1}H NMR ($CDCl_3$): δ = 7.46−7.30 (m, 30 H, arom. H), 5.12 (d, $J_{1',2'}$ 3.5 Hz, 1 H, 1′-H), 5.06 (d, *J* 10.8 Hz, 1 H, C*H*Ph), 5.03 (d, *J* 11.1 Hz, 1 H, C*H*Ph), 4.98 (d, *J* 10.9 Hz, 1 H, C*H*Ph), 4.97 (d, *J* 11.1 Hz, 1 H, C*H*Ph), 4.92 (d, *J* 11.0 Hz, 1 H, C*H*Ph), 4.86 (d, *J* 12.0 Hz, 1 H, C*H*Ph), 4.85 (d, *J* 10.8 Hz, 1 H, C*H*Ph), 4.84 (d, *J* 10.8 Hz, 1 H, C*H*Ph), 4.78 (d, *J* 12.0 Hz, 1 H, C*H*Ph), 4.77 (d, *J* 11.1 Hz, 1 H, C*H*Ph), 4.73 (d, *J* 11.1 Hz, 1 H, C*H*Ph), 4.68 (d, *J* 11.1 Hz, 1 H, C*H*Ph), 4.38 (d, $J_{1,2}$ 7.8 Hz, 1 H, 1-H), 4.09 (t, $J_{2',3'} = J_{3',4'}$ 9.0 Hz, 1 H, 3′-H), 3.93 (m, 2 H, 6-Ha, 6-Hb), 3.76 (t, $J_{3,4} = J_{4,5}$ 9.0 Hz, 1 H, 4-H), 3.71 (t, $J_{2,3} = J_{3,4}$ 9.0 Hz, 1 H, 3-H), 3.63 (dd, $J_{2',3'}$ 9.0, $J_{1',2'}$ 3.5 Hz, 1 H, 2′-H), 3.61 (s, 3 H, CH_3), 3.59−3.55 (m, 2 H, 5-H, 5′-H), 3.51 (dd, $J_{6a',6b'}$ 10.7, $J_{5',6'a}$ 2.6 Hz, 1 H, 6′-Ha), 3.45 (t, $J_{3',4'} = J_{4',5'}$ 9.0 Hz, 1 H, 4′-H), 3.40 (m, 1 H, 6′-Hb), 3.38 (dd, $J_{2,3}$

9.0, $J_{1,2}$ 7.8 Hz, 1 H, 2-H). − ^{13}C NMR ($CDCl_3$): δ = 138.6, 138.5, 138.5, 138.2, 138.2, 138.1 (6 × s, C-arom. quat.), 128.4−127.5 (30 × d, Ph), 104.5 (C-1), 96.9 (C-1′), 84.5 (C-3), 82.3 (C-2), 81.4 (C-4′), 81.1 (C-3′), 80.0 (C-2′), 77.7 (C-4), 75.6 (2 × t, 2 × *C*H$_2$Ph), 75.2, 75.0, 74.7 (3 × t, *C*H$_2$Ph), 74.6 (C-5), 72.3 (t, *C*H$_2$Ph), 68.9 (C-5′), 65.9 (C-6), 57.0 (CH_3), 8.5 (C-6′). − MS (CI); *m/z* (%): 1024 (40) [MNH_4^+], 808.2 (100). − $C_{55}H_{59}IO_{10}$ (1006.9): calcd. C 65.60, H 5.91; found C 65.48, H 5.97.

Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-(2,3,4-tri-*O*-benzyl-6-deoxy-α-D-xylohex-5-enopyranosyl)-β-D-glucopyranoside (14): Sodium hydride (500 mg, 12.5 mmol, 60% in mineral oil) was added to a vigorously stirred solution of methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,4-tri-*O*-benzyl-6-deoxy-6-iodo-α-D-glucopyranosyl)-β-D-glucopyranoside (700 mg, 0.7 mmol) in anhydrous DMF (20 mL) at room temp. After 2 h the reaction mixture was cooled to 0°C and methanol (30 mL) was added dropwise. The solvent was removed in vacuo and the residue was partitioned between DCM (50 mL) and water (50 mL). The aqueous layer was extracted with DCM (2 × 50 mL) and combined extracts were washed with brine (50 mL), dried ($MgSO_4$), filtered, and the solvent was removed in vacuo. The residue was purified by flash chromatography (20% EtOAc in cyclohexane) to afford **14** (562 mg, 92%), as a colourless foam, m.p. 117−118°C. − $[\alpha]_D^{22}$ +4.5 (c = 1.0 in $CHCl_3$). − IR (KBr): $\tilde{\nu}$ = 1668 cm^{-1} (C=C), 1079 (C−O). − ^{1}H NMR ($CDCl_3$): δ = 7.41−7.30 (m, 30 H, arom. H), 5.26 (d, $J_{1',2'}$ 3.4 Hz, 1 H, 1′-H), 4.97 (d, *J* 10.8 Hz, 1 H, C*H*Ph), 4.95 (d, *J* 10.9 Hz, 1 H, C*H*Ph), 4.92 (br s, 1 H, 6′-Ha), 4.91 (d, *J* 10.9 Hz, 1 H, C*H*Ph), 4.89 (d, *J* 10.8 Hz, 1 H, C*H*Ph), 4.88 (d, *J* 11.0 Hz, 1 H, C*H*Ph), 4.87 (d, *J* 11.8 Hz, 1 H, C*H*Ph), 4.86 (d, *J* 11.1 Hz, 1 H, C*H*Ph), 4.85 (d, *J* 11.2 Hz, 1 H, C*H*Ph), 4.82 (d, *J* 11.4 Hz, 1 H, C*H*Ph), 4.78 (d, *J* 12.3 Hz, 1 H, C*H*Ph), 4.76 (br s, 1 H, 6′-Hb), 4.75 (d, *J* 11.0 Hz, 1 H, C*H*Ph), 4.68 (d, *J* 11.0 Hz, 1 H, C*H*Ph), 4.36 (d, $J_{1,2}$ 7.8 Hz, 1 H, 1-H), 4.06 (dd, $J_{6a,6b}$ 12.5, $J_{5,6a}$ 4.0 Hz, 1 H, 6-Ha), 4.11 (t, $J_{2',3'}$ =$J_{3',4'}$ 8.6 Hz, 1 H, 3′-H), 4.00 (m, 1 H, 4′-H), 3.96 (d, $J_{6a,6b}$ 12.5, $J_{5,6b}$ 1.5 Hz, 1 H, 6-Hb), 3.87 (t, $J_{3,4}$ =$J_{4,5}$ 9.1 Hz, 1 H, 4-H), 3.71 (dd, $J_{2',3'}$ 8.6, $J_{1',2'}$ 3.4 Hz, 1 H, 2′-H), 3.68 (dd, $J_{2,3}$ = $J_{3,4}$ 9.1 Hz, 1 H, 3-H), 3.62 (s, 3 H, CH_3), 3.47 (ddd, $J_{4,5}$ 9.1, $J_{5,6a}$ 4.0, $J_{5,6b}$ 1.5 Hz, 1 H, 5-H), 3.37 (dd, $J_{2,3}$ 9.1, $J_{1,2}$ 7.8 Hz, 1 H, 2-H). − ^{13}C NMR ($CDCl_3$): δ = 153.9 (s, C-5′), 138.7, 138.6, 138.5, 138.4, 138.3, 138.1 (6 × s, C-arom. quat.), 128.4−127.5 (30 × d, Ph), 104.6 (C-1), 98.3 (C-1′), 96.9 (C-6′), 84.4 (C-3), 82.3 (C-2), 80.7 (C-3′), 79.4 (C-2′), 79.3 (C-4′), 77.2 (C-4), 75.6 (2 × t, 2 × *C*H$_2$Ph), 75.0 (t, *C*H$_2$Ph), 74.9 (C-5), 74.8, 74.3, 72.3 (3 × t, *C*H$_2$Ph), 65.6 (C-6), 55.9 (CH_3). − MS (CI); *m/z* (%): 896.2 (100) [MNH_4^+]. − $C_{55}H_{58}O_{10}$ (879.1): calcd. C 75.14, H 6.65; found C 75.04, H 6.67.

Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-[1D-(1,2,4,5/3)-2,3,4-tri-*O*-benzyl-1,2,3,4,5-pentahydroxycyclohexyl]-β-D-glucopyranoside (9): TIBAL (3.64 mL, 3.6 mmol, 1 M in toluene) was added to a stirred solution of **14** (320 mg, 0.36 mmol) in anhydrous toluene (3 mL) at room temp. under argon. The reaction mixture was heated at 50°C for 3 h, when TLC (EtOAc/cyclohexane, 3:7) indicated that no starting material (R_f = 0.6) and a major product (R_f = 0.2) was present. The mixture was cooled to 0°C and ice-water (6 mL) was added. The mixture was filtered into a separating funnel (washing with 10 mL of EtOAc) and the aqueous layer was extracted with EtOAc (3 × 10 mL). Combined extracts were dried ($MgSO_4$), filtered, and the solvent was removed in vacuo. The residue was purified by flash chromatography (eluent gradient, 40−80% EtOAc in cyclohexane) to afford **9** (208 mg, 65%), as a colourless solid, m.p. 92−93°C. − $[\alpha]_D^{22}$ +24.5 (c = 1.0 in $CHCl_3$). − IR (KBr): $\tilde{\nu}$ = 3494 cm^{-1} (O−H), 1070 (C−O). − ^{1}H NMR ($CDCl_3$): δ = 7.40−7.30 (m, 30 H, arom. H), 4.99 (d, *J* 10.6 Hz, 1 H, C*H*Ph), 4.98 (d, *J* 10.6 Hz, 1 H, C*H*Ph), 4.95 (d, *J* 12.0 Hz, 1 H, C*H*Ph), 4.85 (d, *J* 10.5 Hz, 1 H, C*H*Ph), 4.90 (d, *J* 11.0 Hz, 1 H, C*H*Ph), 4.83 (2 × d, *J* 10.6 Hz, 2 H, 2 × C*H*Ph), 4.80 (d, *J* 10.8 Hz, 1 H, C*H*Ph), 4.78 (d, *J* 11.8 Hz, 1 H, C*H*Ph), 4.77 (d, *J* 10.5 Hz, 1 H, C*H*Ph), 4.86 (d, *J* 11.0 Hz, 1 H, C*H*Ph), 4.59 (d, *J* 11.1 Hz, 1 H, C*H*Ph), 4.36 (d, $J_{1,2}$ 7.8 Hz, 1 H, 1-H), 4.21 (t, $J_{2',3'}$ =$J_{3',4'}$ 9.2 Hz, 1 H, 3′-H), 4.15 (br d, $J_{6a,6b}$ 9.2 Hz, 1 H, 6-Ha), 4.13 (m, 1 H, 5′-H), 3.94 (m, 1 H, 1′-H), 3.86 (br d, $J_{4',OH}$ 7.3 Hz, OH), 3.71 (t, $J_{2,3}$ = $J_{3,4}$ 9.2 Hz, 1 H, 3-H), 3.65 (dd, $J_{6a,6b}$ 9.2, $J_{5,6b}$ 2.5 Hz, 1 H, 6-Hb), 3.64 (s, 3 H, CH_3), 3.60 (m, 1 H, 5-H), 3.44 (dd, $J_{2,3}$ 9.2, $J_{1,2}$ 7.8 Hz, 1 H, 2-H), 3.44 (t, $J_{3,4}$ = $J_{4,5}$ 9.2 Hz, 1 H, 4-H), 3.42 (dd, $J_{2',3'}$ 9.2, $J_{1',2'}$ 2.6 Hz, 1 H, 2′-H), 3.40 (dd, $J_{3',4'}$ 9.2, $J_{4',5'}$ 3.4 Hz, 1 H, 4′-H), 2.32 (dt, J_{gem} 15.0, $J_{1',5'a(a)}$ = $J_{5',5'a(a)}$ 3.8 Hz, 1 H, 5′a-Ha), 1.42 (m, 1 H, 5′a-Hb). − ^{13}C NMR ($CDCl_3$): δ = 138.9, 138.5, 138.5, 138.4, 138.4, 137.9 (6 × s, C-arom. quat.), 128.4−127.5 (30 × d, Ph), 104.5 (C-1), 84.5 (C-3), 82.5 (C-4′), 82.2 (C-2), 78.9 (C-3′), 78.1 (2 × d, C-2′, C-4), 78.0 (C-1′), 75.8, 75.7, 74.9, 74.7 (4 × t, *C*H$_2$Ph), 74.4 (C-5), 73.0, 72.1 (2 × t, *C*H$_2$Ph), 71.0 (C-6), 67.9 (C-5′), 57.3 (CH_3), 30.5 (C-5′a). − MS (CI); *m/z* (%): 898.2 (3) [MNH_4^+], 482.1 (100). − $C_{55}H_{60}O_{10}$ (881.1): calcd. C 74.97, H 6.86; found C 74.82, H 6.93.

Methyl 2,3,6-Tri-*O*-benzyl-4-*O*-[1D-(1,2,4/3)-2,3,4-tri-*O*-benzyl-1,2,3,4-tetrahydroxycyclohex-5-onyl]-α-D-glucopyranoside (34) and Methyl 2,3,6-Tri-*O*-benzyl-4-*O*-(2,5-anhydro-3,4-di-*O*-benzyl-6-deoxy-α-D-glucohex-5-ulopyranosyl)-α-D-glucopyranoside (35): A solution of **10** (440 mg, 0.5 mmol) in anhydrous DCM (5 mL) was added dropwise over 35 min to freshly prepared[5] Ti(O*i*Pr)Cl_3 (15 mL, 1.5 mmol, 0.1 M in DCM) at −78°C under argon. After stirring for 1 h, TLC (EtOAc/cyclohexane, 1:9) indicated that no starting material (R_f = 0.4) and products (R_f = 0.3, 0.2, and 0.15) was present. The reaction mixture was poured into ice-cooled saturated aqueous $NaHCO_3$ (50 mL) and stirred vigorously for 15 min. The mixture was then extracted with DCM (3 × 30 mL) and combined extracts were dried ($MgSO_4$), filtered, and the solvent was removed in vacuo. The residue was purified by flash chromatography (eluent gradient, 10−20% EtOAc in cyclohexane) to afford **34** (12 mg, 3%), as a colourless oil. − $[\alpha]_D^{22}$ −3.0 (c = 1.0 in $CHCl_3$). − IR (film): $\tilde{\nu}$ = 1737 cm^{-1} (C=O). − ^{1}H NMR ($CDCl_3$): δ = 7.41−7.21 (m, 30 H, arom. H), 5.04 (d, *J* 11.7 Hz, 1 H, C*H*Ph), 4.96 (d, *J* 11.6 Hz, 1 H, C*H*Ph), 4.76 (d, *J* 11.7 Hz, 1 H, C*H*Ph), 4.75 (d, *J* 12.0 Hz, 1 H, C*H*Ph), 4.71 (d, *J* 12.1 Hz, 1 H, C*H*Ph), 4.70 (m, 1 H, 1′-H), 4.69−4.65 (m, 4 H, 4 × C*H*Ph), 4.65 (d, $J_{1,2}$ 3.0 Hz, 1 H, 1-H), 4.61 (d, *J* 12.0 Hz, 1 H, C*H*Ph), 4.60 (d, *J* 12.0 Hz, 1 H, C*H*Ph), 4.56 (d, *J* 11.6 Hz, 1 H, C*H*Ph), 4.03 (t, $J_{2',3'}$ =$J_{3',4'}$ 8.3 Hz, 1 H, 3′-H), 4.00 (dd, $J_{3,4}$ 9.4, $J_{2,3}$ 8.3 Hz, 1 H, 3-H), 3.96 (d, $J_{3',4'}$ 8.3 Hz, 1 H, 4′-H), 3.78 (dd, $J_{4,5}$ 9.8, $J_{3,4}$ 9.4 Hz, 1 H, 4-H), 3.77 (dd, $J_{2',3'}$ 8.3, $J_{1',2'}$ 2.5 Hz, 1 H, 2′-H), 3.73 (ddd, $J_{4,5}$ 9.8, $J_{5,6a}$ 3.6, $J_{5,6b}$ 2.0 Hz, 1 H, 5-H), 3.67 (dd, $J_{6a,6b}$ 10.6, $J_{5,6a}$ 3.6 Hz, 1 H, 6-Ha), 3.60 (dd, $J_{6a,6b}$ 10.6, $J_{5,6b}$ 2.0 Hz, 1 H, 6-Hb), 3.59 (dd, $J_{2,3}$ 8.3, $J_{1,2}$ 3.0 Hz, 1 H, 2-H), 3.42 (s, 3 H, CH_3), 2.83 (dd, J_{gem} 15.4, $J_{1',5'a(a)}$ 5.2 Hz, 1 H, 5′a-Ha), 2.30 (dd, J_{gem} 15.4, $J_{1',5'a(b)}$ 3.7 Hz, 1 H, 5′a-Hb). − ^{13}C NMR ($CDCl_3$): δ = 204.6 (s, C-5′), 138.9, 138.3, 138.2, 138.2, 137.8, 137.7 (6 × s, C-arom. quat.), 129.0−126.7 (30 × d, Ph), 97.6 (C-1), 85.5 (C-4′), 81.7 (C-3), 81.3 (C-3′), 80.5 (C-2′), 80.4 (C-2), 74.7, 74.2 (2 × t, 2 × *C*H$_2$Ph), 73.9 (C-1′), 73.7 (C-4), 73.3, 73.2, 73.2, 72.9 (4 × t, 4 × *C*H$_2$Ph), 69.5 (C-5), 68.7 (C-6), 55.2 (CH_3), 40.8 (C-5′a). − MS (CI); *m/z* (%): 896.5 (5) [MNH_4^+], 482.2 (100). − $C_{55}H_{58}O_{10}$ (879.1): calcd. C 75.14, H 6.65; found C 75.06, H 6.71.

(**35**) (281 mg, 71%): as a colourless oil. − $[\alpha]_D^{22}$ +47.5 (c = 1.0 in $CHCl_3$). − ^{1}H NMR ($CDCl_3$): δ = 7.37−7.24 (m, 25 H, arom. H), 5.47 (s, 1 H, 1′-H), 5.02 (d, *J* 11.2 Hz, 1 H, C*H*Ph), 4.82 (d, *J* 11.2 Hz, 1 H, C*H*Ph), 4.78 (d, *J* 12.1 Hz, 1 H, C*H*Ph), 4.68−4.62 (m, 2 H, 2 × C*H*Ph), 4.65 (d, $J_{1,2}$ 3.6 Hz, 1 H, 1-H), 4.56 (d, *J*

11.9 Hz, 1 H, C*H*Ph), 4.47 (d, $J_{2',3'}$ 5.0 Hz, 1 H, 2′-H), 4.44 (s, 2 H, CH_2Ph), 4.30 (d, *J* 12.0 Hz, 1 H, C*H*Ph), 4.18 (d, *J* 12.0 Hz, 1 H, C*H*Ph), 3.96 (t, *J* 9.4 Hz, 1 H, 3-H), 3.85−3.80 (m, 3 H, 5-H, 6-Ha, 6-Hb), 3.78 (dd, $J_{2',3'}$ 5.0, $J_{3',4'}$ 1.5 Hz, 1 H, 3′-H), 3.70 (t, *J* 9.3 Hz, 1 H, 4-H), 3.56 (dd, $J_{2,3}$ 9.7, $J_{1,2}$ 3.6 Hz, 1 H, 2-H), 3.41 (s, 3 H, OCH_3), 3.40 (d, $J_{3',4'}$ 1.5 Hz, 1 H, 4′-H), 1.59 (s, 3 H, CH_3). − ^{13}C NMR ($CDCl_3$): $\delta = 138.7$, 138.3, 138.0, 137.5, 137.2 (5 × s, C-arom. quat.), 128.5−126.8 (25 × d, Ph), 110.8 (s, C-5′), 100.8 (C-1′), 97.8 (C-1), 84.8 (C-4′), 82.4 (C-3′), 80.9 (C-3), 79.9 (C-2), 79.7 (C-2′), 77.3 (C-4), 75.6, 73.4, 73.3, 72.3, 71.5 (5 × t, 5 × CH_2Ph), 69.5 (C-5), 68.8 (C-6), 55.0 (OCH_3), 15.4 (C-6′). − MS (CI); *m/z* (%): 806.7 (100) [MNH_4^+]. − $C_{48}H_{52}O_{10}$ (788.9): calcd. C 73.07, H 6.64; found C 72.97, H 6.73. Methyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (**36**)[18] (30 mg, 13%).

Methyl 2,3,6-Tri-*O*-benzyl-4-*O*-[1D-(1,2,4/3)-2,3,4-tri-*O*-benzyl-1,2,3,4-tetrahydroxycyclohex-5-onyl]-α-D-glucopyranoside (34): Powdered 4-Å molecular sieves (450 g) and then PCC (230 mg, 1.07 mmol) were added to a stirred solution of **2**/**3** (233 mg, 0.26 mmol, 2.5:1) in anhydrous DCM (20 mL) at room temp. under argon. After 15 min, TLC (EtOAc/cyclohexane, 1:9) indicated that no starting material ($R_f = 0.1$) and product ($R_f = 0.4$) was present. The reaction volume was reduced in vacuo (to 10 mL) and diethyl ether (10 mL) was added. The mixture was directly applied to a silica gel column (eluent: diethyl ether/DCM, 1:1) to afford **34** (159 mg, 68%). For characterisation see above.

Acknowledgments

We wish to thank Aventis Research & Technologies GmbH & Co KG for financial support.

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Received May 10, 1998
[O99141]