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The Use of Selenophenyl Galactopyranosides for the Synthesis of α and β-(1→4)-*C*-Disaccharides

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Abstract: Methyl α-*C*-lactoside {β-D-Gal*p*-C-(1→4)-α-D-Glc*p*-OMe} and its α anomer were expeditiously synthesized by radical coupling of various selenophenyl galactopyranosides onto methyl 2,3-di-*O*-benzyl-4-deoxy-4-*C*-methylene-α-D-*xylo*-hexopyranoside, which are temporarily connected through a silaketal tether.

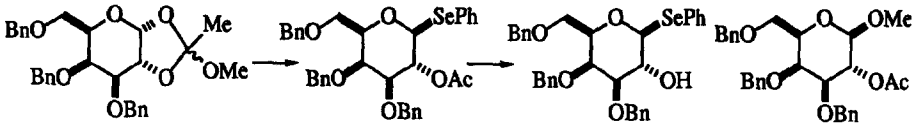
INTRODUCTION

C-Disaccharides are close analogues of disaccharides in which the interglycosidic oxygen atom has been replaced by a methylene group. These products are conformationally close to their natural counterparts[1], and cannot be chemically or biochemically hydrolyzed. They are thus potentially going to emerge as new tools in glycobiology. A decade ago, we reported[2] a synthesis of the first member of this challenging novel class of non natural analogues of disaccharides. Since then, several approaches to *C*-disaccharides have been reported[3]. An important distinction should be made between these strictly defined *C*-disaccharides and other types of synthetic carbon-linked disaccharides which have also started to appear on the scene[3]. We have recently outlined[4-6] an expeditious and potentially general synthetic entry into methyl α-*C*-maltoside {α-D-Glc*p*-C-(1→4)-α-D-Glc*p*-OMe}, based on an *endo-trig* radical cyclisation reaction from two tethered monosaccharides. The anomeric radical was generated either through reaction of tributyltin hydride with a selenophenyl glucoside[4,5], or through a one-electron reduction of an anomeric phenyl sulfone with a samarium (II) iodide solution[6]. We would like now to report on the successful application of this strategy to the synthesis of methylene bridged analogues of methyl 4-*O*-(α and β-D-galactopyranosyl)-α-D-glucopyranoside.

RESULTS AND DISCUSSION

Selenophenyl glycosides are well established derivatives[7] which have recently been used as glycosyl donors after activation either as oxycarbenium species[8,9] (*O*-glycosylation) or as anomeric radical[10] (*C*-glycosylation). Variously substituted selenophenyl galactosides have now been prepared in this work, the purpose being the generation of the corresponding anomeric radical as a reactive intermediate.

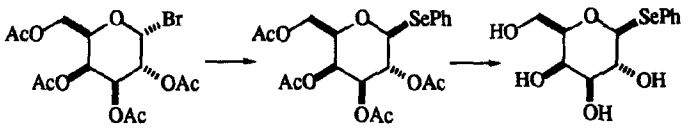
Crystalline phenyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-1-seleno-β-D-galactopyranoside (**2**) was prepared in 78% by reaction of the known[11] 3,4,6-tri-*O*-benzyl-1,2-*O*-(1-methoxyethylidene)-α-D-galactopyranose (**1**) with phenylselenol in the presence of mercury (II) bromide. An expected isolated by-product (17%) of this reaction was methyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl- β-D-galactopyranoside (**4**). Zemplén deacetylation of compound **2** afforded the crystalline selenophenyl galactoside **3** in quantitative yield (**Scheme 1**).



1 **2** **3** **4**

Scheme 1

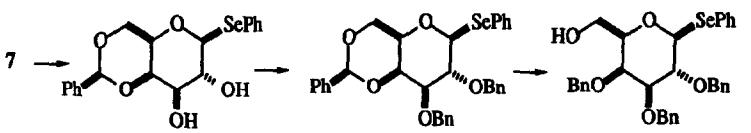
Phenyl 2,3,4,6-tetra-*O*-acetyl-1-seleno-β-D-galactopyranoside (**6**) has been prepared in 92% yield by Van Boom *et al.*[9] from the corresponding β-acetate with phenylselenol in the presence of boron trifluoride etherate. We rather prepared this compound in a similar yield by reaction of acetobromogalactose (**5**) with ethanolic phenylselenolate[12]. Subsequent Zemplén deacetylation gave crystalline phenyl 1-seleno-β-D galactopyranoside (**7**) in 96% yield (**Scheme 2**). This product has been prepared by Van Boom *et al.* [9] without characterization.



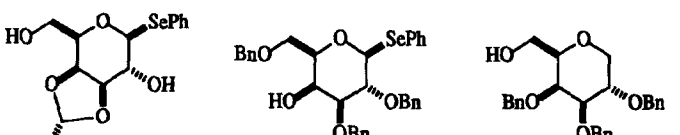
5 **6** **7**

Scheme 2

Compound **7** was benzylidenated with α,α-dimethoxytoluene in N,N-dimethylformamide (DMF) containing a trace of camphorsulfonic acid to give crystalline phenyl 4,6-*O*-benzylidene-1-seleno-β-D-galactopyranoside (**8**) in 77% yield (**Scheme 3**).



8 **10** **11**

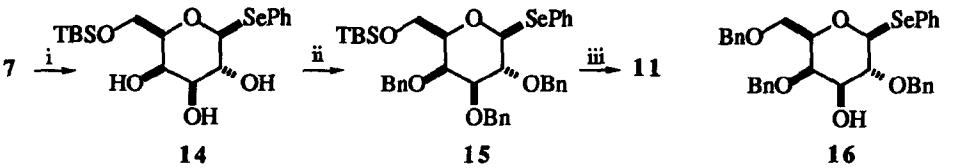


9 **12** **13**

Scheme 3

A by-product of this reaction was the 3,4-*O*-benzylidene isomer **9** which, on the basis[13] of the low field signal of the benzylic proton (δ 6.02), was considerated as the *exo*-phenyl-isomer **9**. Subsequent benzylation of **8** gave the crystalline derivative **10** (80%) which, upon reductive ring cleavage of the acetal ring with $LiAlH_4$-$AlCl_3$[14], selectively gave crystalline phenyl 2,3,4-tri-*O*-benzyl-1-seleno-β-D-galactopyranoside (**11**) in 69% yield. Isolated and identified by-products were phenyl 2,3,6-tri-*O*-benzyl-1-seleno-β-D-galactopyranoside (**12**) (10%) and 1,5-anhydro-2,3,4-tri-*O*-benzyl-D-galactitol (**13**) (3%) (**Scheme 3**). This well-established reductive methodology[14] is thus applicable to selenophenyl glycosides.

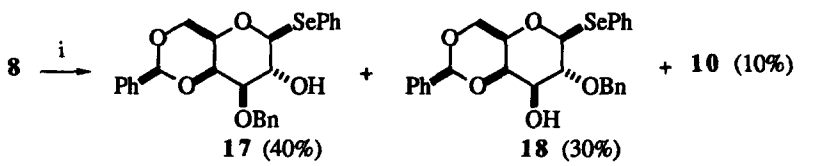
The primary alcohol **11** has alternatively been prepared has shown in **Scheme 4**. The silylated product **14** has previously[9] been synthesized from **7** in 65% yield. Two by-products probably originated from some migration of the *tert*-butyldimethylsilyl group during the benzylation: phenyl 2,3,6-tri-*O*-benzyl-1-seleno-β-D-galactopyranoside (**12**) (2%) (**Scheme 3**) and phenyl 2,4,6-tri-*O*-benzyl-1-seleno-β-D-galactopyranoside (**16**) (7%) have been identified.



Reagents:i)TBSCl, Et_3N, DMAP, DMF(87%); ii) BnBr, NaH, DMF; iii) 40% aq.HF, THF (70%, two steps)

Scheme 4

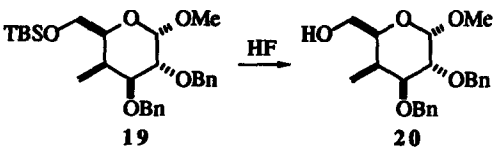
Finally, the two crystalline secondary alcohols, phenyl 3-*O*-benzyl-4,6-*O*-benzylidene-1-seleno-β-D-galactopyranoside (**17**) and phenyl 2-*O*-benzyl-4,6-*O*-benzylidene-1-seleno-β-D-galactopyranoside (**18**), have been prepared by selective benzylation of compound **8** by the phase transfer technique[15] (**Scheme 5**).



Reagent: i) BnBr, Bu_4NHSO_4, CH_2Cl_2, 50% aq. NaOH, 50°C, 40h.

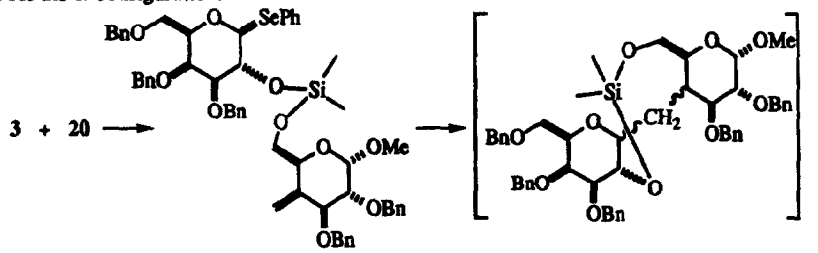
Scheme 5

It has previously been established by us[4-6] that methyl 2,3-di-*O*-benzyl-4-deoxy-4-*C*-methylene-α-D-*xylo*-hexopyranoside (**20**) is a suitable precursor for the stereoselective synthesis of methyl α-C-maltoside. It has been prepared in 86 % yield from the corresponding known[16] 6-*O*-*tert*-butyldimethylsilyl ether (**19**) by treatment with aqueous HF in acetonitrile (**Scheme 6**).



Scheme 6

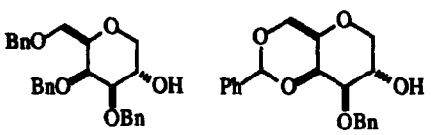
In a typical experiment, alcohols **3** and **20** were connected together through a silaketal tether as shown in **Scheme 7**. The tethered silaketal intermediate **21** can be isolated in pure form in 87% after silica gel chromatography, but was usually directly submitted to cyclisation reaction in refluxing toluene by slow syringe pump addition of a toluene solution of tributyltin hydride (2.2 eq) and azobisisobutyronitrile (0.1eq). The connector was then removed by aqueous HF. Silica gel flash chromatography of the reaction mixture gave the deoxy monosaccharide **22** (37%) (**Scheme 8**), the starting alcohol **20** (40%), and a mixture (60%) of the closely migrating isomeric *C*-disaccharides derivatives **23**, **24**, and **25** (ratio 6.5: 2.5: 1, according to ^{1}H NMR of the mixture). **22** was formed by a competing reduction of the anomeric radical. Upon careful rechromatography of the mixture of these *C*-disaccharides, the methyl α-*C*-lactoside derivative **24** and its α-isomer **23** have been isolated in pure form. The ^{1}H NMR spectrum (400MHz, C_6D_6) of **24** showed signals for H-2' (δ 4.05, $J_{1',2'}$ 9, $J_{2',3'}$ 9Hz) and H-3 (δ 3.77, $J_{2,3}$ 9, $J_{3,4}$ 9Hz) which confirm the assigned structure and call for an expected $^4C_1$ chair conformation of the two monosaccharide units. The ^{1}H NMR spectrum (400MHz, $CDCl_3$) of the diacetate **26** derived from **23** showed signals for H-2' (δ 4.91, $J_{1',2'}$ 2, $J_{2',3'}$ 4Hz) and H-3 (δ 3.77, $J_{2,3}$ 9, $J_{3,4}$ 9Hz) which again call for the assigned structure and for a conformation of the α-*C*-galactosyl moiety which largely deviated from the $^4C_1$ chair form. This deviation, when existing, is indeed diagnostic for the α-configuration.



23 α-D-Galp-C-(1→4)-α-D-Glcp-OMe
24 β-D-Galp-C-(1→4)-α-D-Glcp-OMe
25 α-D-Galp-C-(1→4)-α-D-Galp-OMe

26

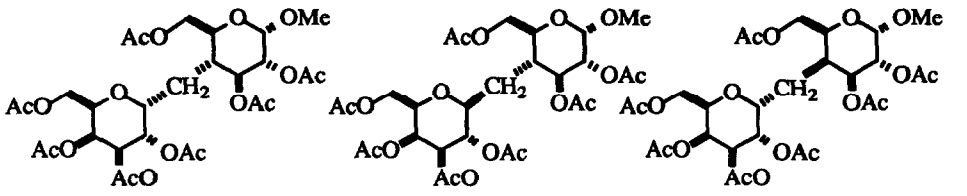
Scheme 7



22 **30**

Scheme 8

The two pure derivatives **23** and **24** have been easily transformed into the corresponding peracetates **27** and **28** (**Scheme 9**), the ^1H NMR spectra being in full agreement with the structure (see Experimental). Although the minor *C*-disaccharide derivative **25** could not be isolated in pure form, some relevant ^1H NMR data (400MHz, $CDCl_3$) of the corresponding peracetate **29** could be extracted from the spectrum of **29** (slightly contaminated with **28**): δ 5.26 ($J_{1',2'}$ 4.5, $J_{2',3'}$ 2Hz, H-2'); δ 2.46 (H-4). They are in agreement with the proposed structure.



27 α-D-Galp -C-(1→4)-α-D-Glcp-OMe

28 β-D-Galp -C-(1→4)-α-D-Glcp-OMe

29 α-D-Galp-C-(1→4)-α-D-Galp-OMe

Scheme 9

Similar results have been obtained when the selenophenyl galactopyranoside **17** was tethered with **20** (see **Table 1**). In agreement with our previous investigations[4-6] **entries 1** and **2** demonstrate that tethering of the exomethylene derivative **20** with the hydroxyl group at C-2 of a potential anomeric radical donor selectively provides a satisfactory amount of the *C*-disaccharide α-D-Gal*p*-C-(1→4)-α-D-Glc*p*OMe.

Table 1. Selectivity of the reaction of the exomethylene **20** (glycosyl acceptor) with various selenophenyl β-D-galactopyranosides (glycosyl donor).

Entry	Glycosyl donor	Overall Yield (%) [a]	Ratio[b] (%) 27	28	29
1	**3**	60	65	25	10
2	**17**	43	74	17	9
3	**11**	10	60	13	27
4	**18**	0	-	-	-

[a] Directly evaluated after treatment with HF.

[b] Evaluated by ^1H NMR spectroscopy on the crude mixture of peracetates **27, 28, 29.**

Tethering of **20** respectively with alcohols **11** and **18** gave a low yield (10%), or no cyclisation product. Tethering with poorly reactive hydroxyl group on position 4 of phenylseleno β-D-galactopyranoside has not been attempted in this work, a corresponding tethering in the gluco series having led to no cyclisation product[17].

The increased tendency for *endo* attack in ring systems incorporating silicon, as opposed to all carbon ring systems, has already been observed[18]. Glycosyl radicals are known to react in intermolecular manner to form axial bonds preferentially[10a,10b,19]; this α:β selectivity is also observed (α:β about 4:1, **entries 1** and **2**)

upon tethering between **20** and either **3** or **17**. The stereochemical outcome at C-4, on the other hand, was much less easily predictable. The stereoselectivity of free radical hydrogen donation from tributyltin hydride onto non-anomeric carbohydrate positions varies from small to very high[20]. The high diastereoselectivity observed in **entries 1** and **2** (gluco:galacto, 9:1) in the hydrogen donation from tributyltin hydride onto the C-4, incorporated in a 9-membered ring fused with two 6-membered rings, is noteworthy. It parallels previous results[4-6] and underlines an additional advantage of the silicon tether methodology, in terms of potential favourable conformational bias. The array of hydroxyl groups which is present in monosaccharides obviously provides a potentially flexible way of selecting beneficial connections in terms both of overall yield and of fine tuning of the stereoselectivity.

EXPERIMENTAL SECTION

General. Melting points (mp) were determined with a Büchi 510 apparatus and were uncorrected. Optical rotations were measured at 20± 2°C with a Perkin Elmer 241 digital polarimeter. C.i.(ammonia)-mass spectra were taken on a Nermag R10-10 spectrometer. Elemental analyses were performed by Service Central d'Analyse du CNRS, BP 22, 69390 Vernaison, France or Service d'Analyse de l'Université Pierre et Marie Curie, 75252 Paris cédex 05, France. ^{1}H NMR spectra were determined on Brüker AM 200, AM-250, and AM-400 spectrometers with Me_4Si as internal standard. ^{13}C NMR spectra were determined on Brüker AM-250 (62MHz) and AM-400 (100.57MHz) spectrometers with Me_4Si as reference (0 ppm). H-4α, H-4α', and C-4α relate to the interglycosidic methylene bridge. Reactions were monitored by tlc on silica gel 60 F_{254} (Merck) and detection by charring with sulfuric acid. Flash column chromatography was performed on silica gel 60 (230-400 mesh, Merck).

Phenyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-1-seleno-β-D-galactopyranoside (2)

A solution of **1**[11] (2.11g, 4.17mmol) in acetonitrile (15 mL) was treated with phenylselenol (1.5mL, 13.5mmol) and mercury (II) bromide (16mg, 0.042mmol) and heated at 50°C for 1 h. The reaction mixture was cooled at room temperature and aqueous 5% NaOH (5 mL) was added. The solution was concentrated to the half, diluted with dichloromethane, washed successively with water, aqueous NaOH, water, dried ($MgSO_4$), and concentrated. Flash column chromatography of the residue (cyclohexane-ethyl acetate 6:1 → 3:1) furnished first: **2** (2.05g, 78%), mp 97-98°C, $[\alpha]_D$ +9 (c 1.0, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$, δ): 7.64-7.15 (m, 20H, Ph); 5.49 (dd, 1H, $J_{1,2}=J_{2,3}$ 9.8 Hz, H-2); 4.96 and 4.57 (ABq, 2H, J 11.6 Hz, $PhCH_2$); 4.84 (d, 1H, H-1); 4.70 and 4.55 (ABq, 2H, J 12.0 Hz, $PhCH_2$); 4.50 and 4.42 (ABq, 2H, J 10.6 Hz, $PhCH_2$); 4.02 (d, 1H, $J_{3,4}$ 2.7 Hz, H-4); 3.70-3.60 (m, 3H, H-5, H-6a, H-6b); 3.56 (dd, 1H, H-3); 2.05 (s, 3H, Ac). ^{13}C NMR (62 MHz, $CDCl_3$, δ):169.5 (C=O); 138.4-127.4 (24C, Ph); 82.6 (C1); 81.3, 78.6, 74.3, 73.5, 72.9, 71.9, 70.5, 69.6 (C2-C6 and $PhCH_2$). MS (m/z): 649 (M^+18).

Anal. Calcd. for $C_{35}H_{36}O_6Se$: C, 66.55; H, 5.74. Found: C, 66.47; H,5.69.

Methyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-β-D-galactopyranoside (4) was then eluted (358mg, 17%), mp 72-73°C (cyclohexane-ethyl acetate), $[\alpha]_D$ +1 (c 0.75, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$, δ): 5.29 (dd, 1H, $J_{1,2}$ 8.0, $J_{2,3}$ 10.3 Hz, H-2); 4.87 and 4.42 (ABq, 2H, J 11.7 Hz, $PhCH_2$); 4.60 and 4.51 (ABq, 2H, J 12.7 Hz, $PhCH_2$); 4.39 and 4.13 (ABq, 2H, J 11.9 Hz, $PhCH_2$); 4.20 (d, 1H, H-1); 3.88 (d, 1H, $J_{3,4}$ 2.7, $J_{4,5}$ < 1 Hz, H-4); 3.60-3.44 (m, 4H, H-3, H-5, H-6a, H-6b); 3.38 (s, 3H, OMe); 1.95 (s, 3H, Ac). ^{13}C NMR (62 MHz,

$CDCl_3$, δ): 169.6 (C=O); 138.4-127.4 (18C, Ph); 102.0 (C1); 80.3, 74.3, 74.3, 73.5, 72.4, 71.9, 71.2, 68.6 (C2-C6 and 3 $PhCH_2$); 56.2 (O-CH_3); 21.0 (CH_3-C=O). MS (m/z): 524 (M^++18); 475 (M^+-OMe).

Phenyl 3,4,6-tri-*O*-benzyl-1-seleno-β-D-galactopyranoside (3)

2 (2.0g, 3.17mmol) was treated with a solution of MeONa (cat.) in methanol (40mL). The solution was neutralized with IR 120 (H^+), filtered, and concentrated. Flash column chromatography of the residue (cyclohexane-ethyl acetate 3:1) gave **3** (1.83g, 98%), mp 77-78°C (cyclohexane-ethyl acetate), $[\alpha]_D$ -11 (c 1.1, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$, δ): 7.70-7.13 (m, 20H, Ph); 4.92 and 4.57 (ABq, 2H, *J* 11.4 Hz, $PhCH_2$); 4.77 (d, 1H, $J_{1,2}$ 9.4 Hz, H-1); 4.76 and 4.68 (ABq, 2H, *J* 12.0 Hz, $PhCH_2$); 4.53 and 4.45 (ABq, 2H, *J* 11.7 Hz, $PhCH_2$); 4.04 (dd, 1H, $J_{2,3}$ 9.4 Hz, H-2); 4.00 (d, 1H, $J_{3,4}$ 2.5 Hz, H-4); 3.67 (s, 3H, H-5, H-6a, H-6b); 3.48 (dd, 1H, H-3); 2.45 (br. s, 1H, OH). ^1H NMR (250 MHz, C_6D_6, δ): 7.78-6.92 (m, 20H, Ph); 4.95 and 4.48 (ABq, 2H, *J* 11.6 Hz, $PhCH_2$); 4.62 (d, 1H, $J_{1,2}$ 9.7 Hz, H-1); 4.60 and 4.49 (ABq, 2H, *J* 11.7 Hz, $PhCH_2$); 4.27 and 4.20 (ABq, 2H, *J* 12 Hz, $PhCH_2$); 4.18 (dd, 1H, $J_{2,3}$ 9.3 Hz, H-2); 3.80 (d, 1H, $J_{3,4}$ 2.5 Hz, H-4); 3.64 (dd, 1H, $J_{5,6a}$ 7.5, $J_{6a,6b}$ 9.1 Hz, H-6a); 3.58 (dd, 1H, $J_{5,6b}$ 5.6 Hz, H-6b); 3.35 (dd, 1H, H-5); 3.20 (dd, 1H, H-3); 2.27 (br. s, 1H, OH).^{13}C NMR (62 MHz, $CDCl_3$, δ): 140.0-127.0 (24C, Ph); 85.2 (C1); 82.9, 78.6, 74.3, 73.5, 73.4, 72.3, 69.6, 67.8 (C2-C6 and 3 $PhCH_2$). MS (m/z) : 608 (M^++18).
Anal. Calcd. for $C_{33}H_{34}O_5Se$: C, 67.22; H, 5.81. Found: C, 67.36; H, 5.85.

Phenyl 2,3,4,6-tetra-*O*-acetyl-1-seleno-β-D-galactopyranoside (6)

$NaBH_4$ (1.43g, 38mmol) was added at 0°C under argon to a solution of diphenyldiselenide (5.9g, 19mmol) in dry ethanol (100 mL). The solution was stirred for 15min at 0°C then 20min at room temperature. This solution was added to a solution of acetobromogalactose (**5**) (12g, 29.19mmol) in anhydrous dichloromethane (20 mL) at 0°C under argon. The solution was stirred for 2h at room temperature under argon, then for 15min in air (in order to oxidize remaining PhSeNa in PhSeSePh), and concentrated. A solution of the residue in dichloromethane was washed succesively with water, aqueous 10% NaOH, water, dried ($MgSO_4$), and concentrated. Flash column chromatography of the residue (cyclohexane-ethyl acetate 6:1→ 2:1) gave **6** (13.22g, 93%) as a syrup. $[\alpha]_D$ -2 (c 0.8, $CHCl_3$); litt.[9] $[\alpha]_D$ +8 (c 1, $CHCl_3$). ^1H -NMR (200 MHz, $CDCl_3$, δ): 7.66-7.26 (m, 5H, Ph); 5.42 (d, $J_{3,4}$ 3.1 Hz, 1H, H-4); 5.28 (dd, 1H, $J_{1,2}$ 10.0, $J_{2,3}$ 9.8 Hz, H-2); 5.03 (dd, 1H, H-3); 4.93 (d, 1H, H-1); 4.18 (dd, 1H, $J_{5,6a}$ 7.2, $J_{6a,6b}$ 11.2 Hz, H-6a); 4.09 (dd, 1H, $J_{5,6b}$ 6.1 Hz, H-6b); 3.95-3.87 (m, 1H, H-5); 2.10, 2.09, 2.04 and 1.97 (4 Ac). ^{13}C NMR (62 MHz, $CDCl_3$, δ): 170.3-169.4 (4C, C=O); 134.8-127.6 (6C, Ph); 81.6 (C1); 75.4, 71.7, 67.9, 67.2, 61.5 (C2-6); 20.8-20.5 (4C, CH_3-C=O). MS (m/z): 507 (M^++18).

Phenyl 1-seleno-β-D-galactopyranoside (7)

6 (13g, 26.69mmol) was treated for 3h with a solution of MeONa (cat.) in methanol (60mL) for 3h. The solution was neutralized with IR 120 (H^+), filtered, and concentrated. Flash column chromatography of the residue (dichloromethane:MeOH 4:1→ 2:1) gave **7** (8.17g, 96%), mp 113-114°C(EtOH), $[\alpha]_D$ -45 (c 1 MeOH). ^1H NMR (250 MHz, CD_3OD, δ): 7.50-7.02 (m, 5H, Ph); 4.61 (d, 1H, $J_{1,2}$ 9.8 Hz, H-1); 3.70 (δ, 1H, $J_{3,4}$ 3.0 Hz, H-4); 3.51-3.32 (m, 3H, H-2, H-6a, H-6b); 3.23-1.36 (m, 2H, H-3, H-5). ^{13}C NMR (62 MHz, CD_3OD, δ): 132.0-126.0 (6C, Ph); 85.3 (C1); 79.9, 74.3, 69.7, 68.6, 60.7 (C2-6). MS (m/z): 321(M^+).
Anal. Calcd. for $C_{12}H_{16}O_5Se$: C, 45.15; H, 5.052. Found: C, 45.18; H, 5.17.

Phenyl 4,6-*O*-benzylidene-1-seleno-β-D-galactopyranoside (8) and Phenyl 3,4-*exo*-*O*-benzylidene-1-seleno-β-D-galactopyranoside (9)

A solution of **7** (6g, 18.88mmol), α,α-dimethoxytoluene (4.5mL), and camphorsulfonic acid (263 mg, 1.13mmol) in DMF (60 mL) was stirred for 3h under vaccum at 50°C, then neutralized with Et_3N, and concentrated. A solution of the residue in dichloromethane was washed with water, dried ($MgSO_4$), and concentrated. A solution of the residue in acetic acid (7 mL) was stirred at 20°C for 2h then concentrated. Flash column chromatography of the residue (cyclohexane-ethyl acetate 3:1→ 1:2 and NEt_3) gave first: **9** (0.65g, 8.4%), mp 95-96°C (cyclohexane-ethyl acetate), $[\alpha]_D$ +28 (c 1, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$, δ): 7.72-7.28 (m, 10H, Ph); 6.02 (s, 1H, CHPh); 4.78 (d, 1H, $J_{1,2}$ 10.0 Hz, H-1); 4.43 (dd, 1H, $J_{2,3}$ 7.0, $J_{3,4}$ 5.5 Hz, H-3); 4.17 (dd, 1H, $J_{4,5}$ 1.7 Hz, H-4); 3.98 (dd, 1H, $J_{5,6a}$ 8.6, $J_{6a,6b}$ 12.9 Hz, H-6a); 3.87-3.73 (m, 3H, H-2, H-5, H-6b). ^1H NMR (250 MHz, $CDCl_3$ + trichloroacetyl isocyanate, δ): 8.65 and 8.20 (2s, 2H, N-H); 7.68-7.25 (m, 10H, Ph); 6.20 (s, 1H, CHPh); 5.25 (dd, 1H, $J_{1,2}$ 9.5, $J_{2,3}$ 7.0 Hz, H-2); 5.02 (d, 1H, H-1); 4.65 (dd, 1H, $J_{3,4}$ 5.6 Hz, H-3); 4.57 and 4.58 (2s, 2H, H-6a, H-6b); 4.34 (dd, 1H, $J_{4,5}$ < 1 Hz, H-4); 4.10-4.20 (m, 1H, H-5). ^{13}C NMR (62 MHz, $CDCl_3$), δ): 138.2-126.1 (12C, Ph); 103.5 (CH-Ph); 84.2 (C1); 79.7, 78.3, 73.7, 69.4, (C2-5); 62.5 (C6). MS (m/z) : 426 (M^++18), 409 (M^++1), 303 (M^+-OCH_2Ph), 251 (M^+-SePh).
Anal. Calcd. for $C_{19}H_{20}O_5Se$: C, 56.02; H, 4.95. Found: C, 56.02; H, 5.03.
Next eluted was **8** (5.90g, 77%), mp 75-77° C (cyclohexane-ethyl acetate), $[\alpha]_D$ -39 (c 1.2, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$, δ): 7.80-7.20 (m, 10H Ph); 5.52 (s, 1H, CHPh); 4.75 (d, 1H, $J_{1,2}$ 9.3 Hz, H-1); 4.39 (dd, 1H, $J_{5,6a}$ 1.3, $J_{6a,6b}$ 12.5 Hz, H-6a); 4.22 (dd, 1H, $J_{3,4}$ 2.0, $J_{4,5}$ < 1 Hz, H-4); 4.03 (dd, 1H, $J_{5,6b}$ 1.5 Hz, H-6b); 3.74-3.64 (m, 2H, H-2, H-3); 3.54 (dd, 1H, H-5). ^{13}C NMR (62 MHz, $CDCl_3$, δ): 137.0-125.0 (12C, Ph); 101.3 (CH-Ph); 83.6 (C1); 75.4, 73.4, 70.9, 69.4, 69.2 (C2-6). MS (m/z) : 426 (M^++18), 409 (M^++1), 303 (M^+-$PhCH_2O$), 251 (M^+-SePh).
Anal. Calcd. for $C_{19}H_{20}O_5Se$: C, 56.02; H, 4.95. Found: C, 55.80; H, 5.09.
7 (0.30g, 5%) was finally eluted from the column.

Phenyl 4,6-*O*-benzylidene-2,3-di-*O*-benzyl-1-seleno-β-D-galactopyranoside (10)

Sodium hydride (60% in oil, 1.2g, 29.4mmol, defatted with cyclohexane prior to use) was portionwise added at 0°C to a solution of **8** (5g, 12.28mmol) and benzyl bromide (4.5mL, 18.42mmol) in DMF (100 mL). After stirring at room temperature for 2.5h the reaction mixture was cooled at 0°C. Methanol (20mL) was added, and the solution was stirred at room temperature for 20min, then concentrated. A solution of the residue in dichloromethane was washed with water, dried ($MgSO_4$) and concentrated. Flash column chromatography of the residue (cyclohexane-ethyl acetate 8:1→ 3:1 with NEt_3) gave **10** (5.8g, 80.5%), mp 123-125 °C (hexane-ethyl acetate), $[\alpha]_D$ -48 (c 1.5, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$, δ): 7.84-7.10 (m, 20H, Ph); 5.50 (d, 1H, CHPh); 4.83 (d, 1H, $J_{1,2}$ 9.4 Hz, H-1); 4.73 (s, 4H, 2 $PhCH_2$); 4.28 (dd, 1H, $J_{5,6a}$ 2.1, $J_{6a,6b}$ 11.5 Hz, H-6a); 4.19 (d, 1H, $J_{3,4}$ 3.4, $J_{4,5}$ < 1 Hz, H-4); 3.99 (dd, 1H, $J_{5,6b}$ 1.4 Hz, H-6b); 3.92 (dd, 1H, $J_{2,3}$ 9.4 Hz, H-2); 3.67 (dd, 1H, H-3); 3.52 (s, 1H, H-5). ^{13}C NMR (62 MHz, $CDCl_3$, δ): 138.0-126.0 (24 C, Ph); 101.2 (CH-Ph); 82.41 (C1); 81.3, 76.0, 75.3, 73.7, 71.7, 70.6, 69.3 (C2-6 and 2 $PhCH_2$). MS (m/z) : 606 (M^++18).
Anal. Calcd. for $C_{33}H_{32}O_5Se$: C, 67.45; H, 5.49. Found: C, 67.55; H, 5.49.

Phenyl 2,3,4-tri-*O*-benzyl-1-seleno-β-D-galactopyranoside (11) from (10)

An ice-cooled solution of $AlCl_3$ (2.5g, 18.75mmol) in dry ether (15 mL), was dropwise added to an ice cooled solution of **10** (1.96g, 3.34mmol) and $LiAlH_4$ (0.38g, 10.02mmol) in dichloromethane:ether 1:1 (30 mL). The solution was then refluxed for 2h, and cooled to 0°C. Ethyl acetate (5 mL) then water (10 mL) were carefully added, and the solution was concentrated. A solution of the residue in ether was washed with water, dried ($MgSO_4$), and concentrated. Flash column chromatography of the residue (cyclohexane-ethyl acetate 4:1→2:1) gave first **Phenyl 2,3,6-tri-*O*-benzyl-1-seleno-β-D-galactopyranoside (12)** (196.6mg, 10%), mp 84-86°C (n-hexane-ethyl acetate), $[\alpha]_D$ -17 (c 0.9, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$, δ): 7.74-7.20 (m, 20H, Ph); 4.87 (d, 1H, $J_{1,2}$ 8.5 Hz, H-1); 4.82 and 4.77 (ABq, 2H, J 10.5 Hz, $PhCH_2$); 4.77 and 4.69 (ABq, 2H, J 11.7 Hz, $PhCH_2$); 4.60 (s, 2H, $PhCH_2$); 4.15 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4); 3.86-3.74 (m, 3H, H-2, H-5, H-6a); 3.64-3.56 (m, 2H, H-3, H-6b). ^{13}C NMR (62 MHz, $CDCl_3$, δ): 138.1-127.6 (24C, Ph); 83.4 (C1); 82.6, 77.6, 76.0, 75.5, 73.6, 71.9, 69.3, 66.8 (C2-C6 and 3 $PhCH_2$). MS (m/z) 608 (M^++18), 483 (M^+-$PhCH_2O$), 450 (M^++18- SePh), 433 (M^+-SePh)

Anal. Calcd. for $C_{33}H_{34}O_5Se$: C, 67.22; H, 5.81. Found: C, 67.09; H, 5.90.

Next eluted was **Phenyl 2,3,4-tri-*O*-benzyl-1-seleno-β-D-galactopyranoside (11)** (1.35g, 69%), mp 75-76°C (n-hexane-ethyl acetate), $[\alpha]_D$ -18 (c 0.9, $CHCl_3$).^1H NMR (250 MHz, $CDCl_3$, δ): 7.73-7.13 (m, 20H, Ph); 5.00 and 4.64 (ABq, 2H, J 11.7 Hz, $PhCH_2$); 4.87 (d, 1H, $J_{1,2}$ 9.7 Hz, H-1); 4.81 (s, 2H, $PhCH_2$); 4.78 (s, 2H, $PhCH_2$); 4.02 (dd, 1H, $J_{2,3}$ 9.2 Hz, H-2); 3.88 (d, 1H, $J_{3,4}$ 2.7 Hz, H-4); 3.93-3.80 (m, 1H, H-6a); 3.63 (dd, 1H, H-3); 3.57-3.51 (m, 1H, H-5); 3.45 (dd, 1H, $J_{5,6b}$ 5.3, $J_{6b,6a}$ 10 Hz, H-6b); 1.72 (dd, 1H, OH). MS (m/z) : 608 (M^++18), 483 (M^+-$PhCH_2O$), 450 (M^++18-SePh), 433 (M^+-SePh).

Anal. Calcd. for $C_{33}H_{34}O_5Se.H_2O$: C, 65.23; H, 5.97. Found: C, 65.40; H, 5.94.

Finally eluted was **1,5-Anhydro-2,3,4-tri-*O*-benzyl-D-galactitol (13)** (43mg, 3%), syrup, $[\alpha]_D$ -8 (c 1, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$, δ): 7.48-7.24 (m, 15H, Ph); 4.78 and 4.67 (ABq, 2H, J 11.7 Hz, $PhCH_2$); 4.86 and 4.78 (ABq, 2H, J 12.0 Hz, $PhCH_2$); 4.81 and 4.78 (ABq, 2H, J 10.6 Hz, $PhCH_2$); 4.16-4.0 (m, 2H, H-1a, H-2); 3.88 (d, 1H, $J_{3,4}$ 3.1Hz, H-4); 3.78-3.68 (m, 1H, H-6a); 3.55 (dd, 1H, $J_{2,3}$ 9.2 Hz, H-3); 3.45-3.38 (m, 1H, H-6b); 3.25 (dd, 1H, $J_{5,6a}$ 8.2, $J_{5,6b}$ 5.5 Hz); 3.27-3.13 (m, 1H, H-1b). MS (m/z): 452 (M^++18).

Anal. Calcd. for $C_{27}H_{30}O_5$: C, 74.63; H, 6.96. Found: C, 74.42; H, 7.19.

Phenyl 6-*O*-tert-butyldimethylsilyl-1-seleno-β-D-galactopyranoside (14)

A solution of **7** (2g, 6.27mmol) in DMF (30 mL was treated at -30°C with triethylamine (1.04mL, 7.52mmol), *tert*-butyldimethylsilyl chloride (1.23g 8.15mmol), and *N,N*-dimethylaminopyridine (35mg, 0.31mmol). The reaction mixture was stirred for 1h at -30°C then 5h at room temperature. Methanol (15 mL) was added, and the solution was concentrated. Flash column chromatography of the residue (cyclohexane-ethyl acetate 4:1 → 1:2) gave **14** (2.348g, 86%) as a colorless syrup, $[\alpha]_D$ -18 (c 1.3, $CHCl_3$); litt.[9] -21 (c 1.0, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$, δ): 7.62-7.12 (m, 5H, Ph); 4.67 (d, 1H, $J_{1,2}$ 9.6 Hz, H-1); 3.98 (d, 1H, $J_{3,4}$ 3.2, $J_{4,5}$ <1 Hz, H-4); 3.85 (dd, 1H, $J_{6a,6b}$ 10.7, $J_{5,6a}$ 5.5 Hz, H-6a); 3.77 (dd, 1H, $J_{5,6b}$ 4.8 Hz, H-6b); 3.67 (dd, 1H, $J_{2,3}$ 9.2 Hz, H-2); 3.46 (dd, 1H, H-3); 3.39 (dd, 1H, H-5); 0.82 (s, 9H, $(C\underline{H}_3)_3$-C); 0.02 (s, 6H, $(C\underline{H}_3)_2$-Si). ^{13}C NMR (62 MHz, $CDCl_3$, δ): 134.4 (2C, C Ph ortho); 129.0 (3C, 2C Ph meta + 1C Ph para); 127.9 (C PhSe); 85.5 (C1); 79.3, 74.7, 70.5, 69.5, 63.1 (5C, C2-C6); 25.8 (3C, 3 CH_3-C); 18.2 (1C, $\underline{C}$-(CH_3));-5.4 (2 CH_3Si).

Phenyl 2,3,4-tri-O-benzyl-6-*O*-tert-butyldimethylsilyl-1-seleno-β-D-galactopyranoside (15)

Sodium hydride (60% in oil, 764mg, 19.1mmol, defatted with cyclohexane prior to use) was protionwise added at 0°C to a solution of **14** (2.3g, 5.31mmol) and benzyl bromide (2.9mL, 23.9mmol) in DMF (30 mL). The suspension was stirred at room temperature for 4h then cooled at 0°C. Methanol (10mL) was added. The solution was stirred at room temperature for 20min, then concentrated. A solution of the residue in dichloromethane was washed with water, dried ($MgSO_4$), and concentrated. The residue was used in the next step without further purification. Flash column chromatography (cyclohexane-ethyl acetate 12:1 → 5:1) of a portion gave **15** as a pure syrup studied by NMR : ^1H NMR (250 MHz, $CDCl_3$, δ): 7.73-7.12 (m, 20H, Ph); 5.02 and 4.64 (ABq, 2H, *J* 11.7 Hz, $PhCH_2$); 4.87 (d, 1H, $J_{1,2}$ 9.8 Hz, H-1); 4.79 and 4.78 (2s, 4H, 2 $PhCH_2$); 3.98 (dd, 1H, $J_{2,3}$ 9.2 Hz, H-2); 4.02 (d, 1H, $J_{3,4}$ 2.7, $J_{4,5}$<1 Hz, H-4); 3.78 (d, 2H, $J_{5,6a} = J_{5,6b}$ =7.0 Hz, H-6a, H-6b); 3.55 (dd, 1H, H-3); 3.48 (dd, 1H, H-5); 0.92 (s, 9H, $(\underline{C}H_3)_3C$); 0.04 (s, 6H, 2 CH_3-Si). ^{13}C NMR (62 MHz, $CDCl_3$, δ): 138.9-127.2 (24C, Ph); 84.2 (C1); 83.7, 79.8, 77.8, 75.4, 74.4, 73.5, 72.6, 72.0 (C2-C6 and 3 $PhCH_2$); 25.8 ($(CH_3)_3\text{-}\underline{C}$); 16.1 $(\underline{C}H_3)_3$-C); -5.3 and -5.4 (2s, 2 CH_3-Si).

Phenyl 2,3,4-tri-*O*-benzyl-1-seleno-β-D-galactopyranoside (11) (from 15)

A solution of **15** (2.30g, 5.31mmol) and aqueous 40% HF (2 mL) in THF (15 mL) was stirred overnight, neutralized with saturated aqueous $NaHCO_3$, diluted with dichloromethane and water. The organic layer was dried ($MgSO_4$) and concentrated. Flash column chromatography (cyclohexane-ethyl acetate 3:1→1:1) of the residue gave first a mixture of previously reported **12** and **16** (**16**:**12** ratio 4:1 from ^1H NMR) (280mg, 0.509mmol, 9% overall yield). **16** has not been purified. Nmr data for **phenyl 2,4,6-tri-*O*-benzyl-1-seleno-β-D-galactopyranoside (16)**: ^1H NMR (250 MHz, $CDCl_3$, δ): 7.74-7.17 (m, 20H, Ph); 4.87 and 4.63 (ABq, 2H, *J* 10.8 Hz, $PhCH_2$); 4.52 (d, 1H, $J_{1,2}$ 10.5 Hz, H-1); 4.77 and 4.63 (ABq, 2H, *J* 11.5 Hz, $PhCH_2$); 4.57 and 4.48 (ABq, 2H, *J* 11.7 Hz, $PhCH_2$); 3.95 (d, 1H, $J_{3,4}$ 2.2 Hz, H-4); 3.85-3.55 (m, 5H, H-2, H-3, H-5, H-6a, H-6b); 2.20-3.56 (br. d, OH). ^1H NMR (250 MHz, $CDCl_3$, + trichloroacetyl isocyanate, δ): 8.05 (s, 1H, NH); 7.68-7.13 (m, 20H, Ph); 4.88 (d, 1H, $J_{1,2}$ 9.7 Hz, H-1); 4.82 (dd, 1H, $J_{2,3}$ 9.7, $J_{3,4}$ 3.0 Hz, H-3); 4.86 and 4.76 (ABq, 2H, *J* 10 Hz, $PhCH_2$); 4.60- 4.43 (m, 4H, $PhCH_2$); 4.15 (d, 1H, H-4); 3.97 (dd, 1H, H-2); 3.78-3.52 (m, 3H, H-5, H-6a, H-6b).

Next eluted was **phenyl 2,3,4-tri-*O*-benzyl-1-seleno-β-D-galactopyranoside (11)** (2.2g, 70% from **14**), identical with the compound prepared from **10**.

Benzylation of 8 under phase transfer catalysis

A mixture of **8** (1.7g, 4.17mmol), tetrabutylammonium hydrogenosulfate (288mg, 0.83mmol), benzyl bromide (750 µL, 6.26mmol), 10% aqueous NaOH (6 mL), and dichloromethane (100 mL) was stirred at 50°C for 40h. Methanol (4 mL) was added and the solution was diluted with dichloromethane then water. The organic layer was dried ($MgSO_4$) and concentrated. Flash column chromatography of the residue (cyclohexane-ethyl acetate 3:1→ 1:1 with NEt_3) gave first previously reported **Phenyl 4,6-*O*-benzylidene-2,3-di-*O*-benzyl-1-seleno-β-D-galactopyranoside (10)** (367mg, 15%), then: **Phenyl 3-*O*-benzyl-4,6-*O*-benzylidene-1-seleno-β-D-galactopyranoside (17)** (829.6mg, 40%), mp 143-145°C (n-hexane-ethyl acetate), $[\alpha]_D$ -13 (c 0.9, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$, δ): 7.80-7.15 (m, 15H Ph); 5.44 (s, 1H, C<u>H</u>-Ph); 4.97 (d, 1H, $J_{1,2}$ 9.5 Hz, H-1); 4.73 (s, 2H, $PhCH_2$); 4.37 (dd, 1H, $J_{5,6a}$ 1.3, $J_{6a,6b}$ 12.3 Hz, H-6a); 4.17 (d, 1H, $J_{3,4}$

3.0, $J_{4,5}$ < 1 Hz, H-4); 3.99 (dd, 1H, $J_{5,6b}$ 1.8 Hz, H-6b); 3.98 (dd, 1H, $J_{2,3}$ 9.4 Hz, H-2); 3.51 (dd, 1H, H-3); 3.45 (d, 1H, H-5); 2.5 (broad s, 1H, OH).^{13}C NMR (62 MHz, $CDCl_3$, δ): 137.0-126.0 (18C Ph); 101.3 (CHPh); 83.8 (C1); 79.9, 73.4, 71.6, 70.9, 69.3, 67.9 (C2-6 + $PhCH_2$). MS (m/z) : 515 (M^++18), 498 (M^++1).
Anal. Calcd. for $C_{26}H_{26}O_5Se$: C, 62.77; H, 5.27. Found: C, 62.61; H, 5.24.
Next eluted was **Phenyl 2-*O*-benzyl-4,6-*O*-benzylidene-1-seleno-β-D-galactopyranoside (18)** (643mg, 30%), mp 65-68°C (hexane-ethyl acetate), $[\alpha]_D$ -54 (c 0.8, $CHCl_3$).^{1}H NMR (250 MHz, $CDCl_3$, δ): 7.85-7.18 (m, 15H, Ph); 5.58 (d, 1H, C<u>H</u>-Ph); 4.84 (d, 1H, $J_{1,2}$ 9.5 Hz, H-1); 4.79 and 4.70 (ABq, 2H, *J* 10.4 Hz, $PhCH_2$); 4.42 (dd, 1H, $J_{5,6a}$ 1.1, $J_{6a,6b}$ 12.3 Hz, H-6a); 4.26 (d, 1H, $J_{3,4}$ 3.5, $J_{4,5}$ < 1 Hz, H-4); 4.05 (dd, 1H, $J_{5,6b}$ 1.6 Hz, H-6b); 3.87-3.74 (m, 1H, H-3); 3.67 (dd, 1H, $J_{2,3}$ 9.5 Hz, H-2); 3.52 (d, 1H, H-5); 2.47 (broad d, 1H, OH).^{13}C NMR (62 MHz, $CDCl_3$, δ): 138.1-126.4 (18C, Ph); 101.3 (CHPh); 81.9 (C1); 77.8, 75.6, 75.1, 74.3, 70.2, 69.2 (C2-6 + $PhCH_2$). MS (m/z) 515 (M^++18), 498 (M^++1).
Anal. Calcd. for $C_{26}H_{26}O_5Se$: C, 62.77; H, 5.27. Found: C, 62.93; H, 5.38.
Some starting material **8** (238mg, 14%) was recovered.

Methyl 2,3-di-*O*-benzyl-4-deoxy-4-*C*-methylene-α-D-*xylo*-hexopyranoside (20)

A solution of **19**[16] (4g, 8.26mmol) and aqueous 40% HF (5 mL) in THF (10mL) was stirred at room temperature for 30 min, diluted with water, and extracted with dichloromethane. The organic layer was dried ($MgSO_4$) and concentrated. Flash column chromatography (cyclohexane-ethyl acetate 3:1→1:1) of the residue gave **20** (2.63g, 86 %) as a syrup, $[\alpha]_D$ + 76 (c 1.0, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$, δ): 7.45-7.25 (m, 10H, Ph); 5.40 (s, 1H, C<u>H</u>=); 4.95 (s, 1H, C<u>H</u>=); 4.89-4.68 (m, 4H, $PhCH_2$); 4.72 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1); 4.39 (d, 1H, $J_{2,3}$ 9.7 Hz, H-3); 4.20 (dd, 1H, $J_{5,6a}$ 6.3, $J_{5,6b}$ 4.0 Hz, H-5); 4.00-3.80 (m, 2H, H-6a, 6b); 3.52 (dd, 1H, H-2); 3.46 (s, 3H, OCH_3); 1.98 (dd, 1H, $J_{OH,6a}$ 4.6, $J_{OH,6b}$ 7.9 Hz, O<u>H</u>). ^{13}C NMR (62 MHz, $CDCl_3$, δ): 142.24 (C4); 138.4, 138.3 (2 $PhCH_2$); 128.4-127.6 (12C, Ph); 107.74 (CH_2=); 98.74 (C1); 81.5, 78.9, 74.0, 73.6, 69.2 (C2,3,5 and 2 $PhCH_2$); 62.4 (C-6), 55.36 (O<u>C</u>H$_3$). MS (m/z): 388 (M^++18), 356 (M^+-$HOCH_3$).
Anal. Calcd. for $C_{22}H_{26}O_5$: C, 71.33; H 7.07. Found: C, 71.20; H 7.12.

Tethering of 20 with a phenylseleno-β-D-galactopyranoside

For a typical example, the following procedure corresponding to **entry 1** in **Table 1** is described as follows: A 1.6 M solution of BuLi in hexane (2.34mL, 3.74mmol) was added with stirring under argon at -78°C to a solution of **3** (1.7g, 2.88mmol) in dry THF (6 mL) in a dry Schlenk tube. After 15 min, dichlorodimethylsilane (2.22mL, 10.1mmol) was added and stirring was continued for 30 min at -78°C, then for 3h at room temperature. After removal of the solvents from the Schlenk tube under high vaccum, the residue was dissolved in THF (2 mL). A solution of **20** (1.077g, 2.9mmol) and imidazole (0.30g, 4.35mmol) in THF (6 ml) was added at room temperature with stirring. Stirring was continued for 1h, then dichloromethane and water were added. The organic layer was dried ($MgSO_4$) and concentrated to give **21** which was immediately used in the cyclisation step. In another experiment starting from 0.78mmol of **3**, **21** was flash chromatographed (cyclohexane-ethyl acetate 6:1 →4:1 in the presence of Et_3N) to give pure silaketal **21** (690mg, 87%) as a syrup. ^{1}H -NMR (400 MHz, C_6D_6, δ): 7.96-7.07 (m, 30 H, Ph); 5.65 (s, 1H, <u>H</u>C=); 5.22 (s, 1H, <u>H</u>C=); 4.98 (d, 1H, $J_{1'2'}$ 9.5 Hz, H-1'); 4.95 and 4.57 (ABq, 2H, J 11.5 Hz, $PhCH_2$); 4.86 (d, 1H, $J_{1,2}$ 3.3 Hz, H-1); 4.81 and 4.71 (ABq, 2H, J 11.7 Hz, $PhCH_2$); 4.73 and 4.55 (ABq, 2H, J 12.0 Hz,

$PhCH_2$); 4.65 (dd, 1H, $J_{2',3'}$ 9.5 Hz, H-2'); 4.61 (d, 1H, $J_{3,4}$ 9.0 Hz, H-3); 4.52-4.45 (m, 3H, H-5 and $PhCH_2$); 4.53 (dd, 1H, $J_{5,6a}$ 5.7, $J_{6a,6b}$ 10.5 Hz, H-6a); 4.35 and 4.28 (ABq, 2H, J 11.8 Hz, $PhCH_2$); 4.33 (dd, 1H, $J_{5,6b}$ 5.6 Hz, H-6b); 3.94 (d, 1H, $J_{3',4'}$ 2.5Hz, H-4'); 3.78 (dd, 1H, $J_{5',6'a}$ 7.5, $J_{6'a,6'b}$ 8.5 Hz, H-6'a); 3.70 (dd, 1H, $J_{5,6'b}$ 6.5 Hz, H-6'b); 3.69 (dd, 1H, $J_{2,3}$ 9.0 Hz, H-2); 3.51 (dd, 1H, H-5'); 3.34 (s, 3H, OCH_3); 3.30 (dd, 1H, H-3'); 0.35 and 0.40 (2s, 6H, Me-Si). Prime refers to the selenophenyl unit. MS (m/z): 1034 (M+18).

Formation of C-(1→4) disaccharides

For a typical example, the following procedure corresponding to **entry 1** in **Table 1** is describes as follows: A solution of Bu_3SnH (403μL, 1.5mmol) and AIBN (11.2mg) in toluene (8.0mL) was added during 15 h,using a syringe pump to a refluxing solution of **21** (0.68mmol) in dry and oxygen free toluene (34mL). The solution was then cooled and concentrated. A solution of the residue in THF (10mL) and 40% aqueous HF (1.5mL) was stirred for 2h, neutralised with aqueous saturated $NaHCO_3$, diluted with water, and extracted with dichloromethane (3x50mL). The organic solution was dried ($MgSO_4$) and concentrated. The residue was flash chromatographed (cyclohexane-ethyl acetate 1:1→ethyl acetate) to afford first: **1,5-Anhydro-3,4,6-tri-*O*-benzyl-D-galactitol 22** (111mg, 37%) as a syrup, $[\alpha]_D$ +49 (c 1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$, δ): 7.43-7.30 (m, 15H, Ph); 4.92 and 4,64 (ABq, 2H, J 11.5 Hz, $PhCH_2$); 4.80 and 4,59 (ABq, 2H, J 12 Hz, $PhCH_2$); 4.57 and 4,49 (ABq, 2H, J 12 Hz, $PhCH_2$); 4.27-4.18 (m, 1H, H-2); 4.14 (dd, 1H, $J_{1a,1b}$ 10.5 Hz $J_{1a,2}$ 5 Hz, H-1a); 4,05 (d, 1H, $J_{3,4}$ 4 Hz, H-4);3,65 (dd, 1H, $J_{5,6a}$ 6, J $_{5,6b}$ 3.5 Hz, H-5); 3.63-3.55 (m, 2H, H-6a, H-6b); 3.41 (dd, 1H, $J_{2,3}$ 9 Hz, H-3); 3.25 (dd, 1H, $J_{1b,2}$ 10,5Hz, H-1b). ^{13}C NMR (62 MHz, $CDCl_3$, δ): 138.4-127.7 (24C, Ph); 84.4, 77.95, 74.6, 73.6, 73.0, 71.8, 69.9, 69.0, 66.7 (C1-C6 and 3 $PhCH_2$). MS (m/z) : 452 (M^++18).

Anal. Cald. for $C_{27}H_{30}O_5$: C, 74.63; H, 6.96. Found: C, 74.50; H, 7.01.

Next eluted was **20** (76.5mg, 40%) then a co-eluting mixture of 3 *C*-disaccharides **23, 24, 25** (328mg, 60%), the ratio evaluated by NMR being **23:24:25**, 65:25:10. After another chromatography using the same system, **23** and **24** could be obtained as pure fractions:

Methyl 2,3-di-*O*-benzyl-4-deoxy-4-*C*-(2,6-anhydro-4,5,7-tri-*O*-benzyl-1-deoxy-D-*glycero*-L-*gluco*-heptit-1-yl)-α-D-glucopyranoside (23)

Syrup, $[\alpha]_D$ +55 (c 1.0, $CHCl_3$). ^1H NMR (400 MHz, C_6D_6, δ): 7.41-7.23 (25H, Ph); 5.10 and 4.71 (ABq, 2H, J 11.5 Hz, $PhCH_2$); 4.77 and 4.68 (ABq, 2H, J 12.0 Hz, $PhCH_2$); 4.75 (d, 1H, $J_{1,2}$ 3.5 Hz, H-1); 4.67 and 4.57 (ABq, J 11.5Hz, $PhCH_2$); 4.615 and 4.575 (ABq, 2H, J 12.5 Hz, $PhCH_2$); 4.58 and 4.51 (ABq, 2H, J 12.0 Hz, $PhCH_2$); 4.23 (ddd, 1H, $J_{4',5'}$ 5.5, $J_{5',6'a}$ 10.0, $J_{5',6b'}$ 3.0 Hz, H-5'); 4.155 (d, 1H, $J_{6'a,6'b}$ 10 Hz, H-6'a); 4.125-4.06 (m, 1H, H-1'); 3.95 (dd, 1H, $J_{3',4'}$ 3.0 Hz, H-4'); 3.92-3.85 (m, 1H, H-6a); 3.75 (dd, 1H, $J_{2',3'}$ 5.0 Hz, H-3'); 3.72-3.66 (m, 3H, H-2', H-3, H-6b); 3.60 (dd, 1H, $J_{2,3}$ 9.0 Hz, H-2); 3.575 (dd, 1H, H-6'b); 3.49-3.43 (m, 1H, H-5); 3.42 (s, 3H, CH_3O); 3.33-3.25 (m, 1H, OH-6); 2.0-1.9 (m, 1H, H-4); 1.58-1.43 (m, 2H, H-4α, H-4α', methylene bridge). ^{13}C NMR (400 MHz, $CDCl_3$, δ): 138.7-127.3 (30 C Ph); 98.3 (OCH_3), 81.4, 80.7, 76.6, 73.7, 72.8, 72.6, 70.1, 69.9 (8C); 75.3, 73.1, 72.8, 72.6, 71.7 (5 $PhCH_2$); 65.3, 61.9 (C6, C6'); 55.1 (OMe); 39.6 (C4); 28.6 (C4α, methylene bridge). MS: (m/z) 822 (M^++18), 773 (M^+-OCH_3).

Anal. Calcd. for $C_{49}H_{56}O_{10}$. H_2O : C, 71.51; H, 7.10. Found: C, 71.53; H, 7.10.

Methyl 2,3-di-*O*-benzyl-4-deoxy-4-*C*-(2,6-anhydro-4,5,7-tri-*O*-benzyl-1-deoxy-D-*glycero*-L-*manno*-heptit-1-yl)-α-D-glucopyranoside (methyl α-C-lactoside derivative) **(24)**

Syrup, $[\alpha]_D$ +25 (c 1.6, $CHCl_3$). ^1H NMR (400 MHz, C_6D_6, δ): 7.27-7.47 (m, 25 H, Ph); 5.17 and 4.70 (ABq, 2H, J 11.0 Hz, $PhCH_2$); 4.92 and 4.65 (ABq, 2H, J 12.0 Hz, $PhCH_2$); 4.81 and 4.71 (ABq, 2H, J 12.0 Hz, $PhCH_2$); 4.74 (d, 1H, $J_{1,2}$ 3.5 Hz, H-1); 4.73 and 4.64 (ABq, 2H, J 11.0 Hz, $PhCH_2$); 4.43 and 4.36 (ABq, 2H, J 11.5 Hz, $PhCH_2$); 4.05 (ddd, 1H, $J_{1',2'}=J_{2',3'}$ 9.0, $J_{2',OH}$ 3.0 Hz, H-2'); 3.91 (d, 1H, $J_{3',4'}$ 2.7, $J_{4',5'}$<1Hz, H-4'); 3.88-3.84 (m, 1H, H-6a); 3.77 (dd, 1H, $J_{2,3}=J_{3,4}$ 9.0 Hz, H-3); 3.75-3.70 (m, 1H, H-6b); 3.67 (dd, 1H, H-2); 3.59-3.48 (m, 3H, H-5, H-5', H-6'a); 3.44-3.35 (m, 3H, H-1, H-3', H-6'b); 3.40 (s, 3H, CH_3O); 3.27-3.21 (m, 1H, OH-6); 2.92 (d, 1H, OH-2'); 2.075 (dddd, 1H, $J_{4,5}$ 9.0, $J_{4,4\alpha}=J_{4,4\alpha'}$ 3.5 Hz, H-4); 1.89-1.84 (m, 2H, H-4α and H-4α', methylene bridge). ^{13}C NMR (400 MHz, $CDCl_3$, δ): 138.3-127.5 (30C, Ph); 98.2 (C1); 82.9, 81.6, 79.3, 78.8, 77.3, 73.2, 72.9, 68.9 (8C, rings); 75.8, 74.1, 73.3, 72.7, 72.4 (5 $PhCH_2$); 72.4, 68.9 (C6); 55.0 (O-$\underline{C}H_3$); 36.7 (C4), 28.2 (C4α, methylene bridge). MS (m/z): 822 (M^++18), 773 (M^+-OCH_3).

Anal. Cald. for $C_{49}H_{56}O_{10}$. H_2O: C, 71.51; H, 7.10. Found C, 71.58; H, 7.18.

Methyl 6-*O*-acetyl-2,3-di-*O*-benzyl-4-deoxy-4-*C*-(3-*O*-acetyl-2,6-anhydro-4,5,7-tri-*O*-benzyl-1-deoxy-D-*glycero*-L-*gluco*-heptit-1-yl)-α-D-glucopyranoside (26)

Compound **23** (30mg, 0.037mmol) was acetylated (Ac_2O, pyridine) to give **26** (32mg, 97%) as a syrup, $[\alpha]_D$ +53 (c 1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$, δ): 7.40-7.15 (25H Ph); 5.02 and 4.70 (ABq, 2H, J 11.0 Hz, $PhCH_2$); 4.91 (dd, 1H, $J_{1',2'}$ 2.0, $J_{2',3'}$ 4.0 Hz, H-2'); 4.74 and 4.60 (ABq, 2H, J 12.0 Hz, $PhCH_2$); 4.66 (d, 1H, $J_{1,2}$ 3.5 Hz, H-1); 4.65 and 4.61 (ABq, 2H, J 12.0 Hz, $PhCH_2$); 4.57 and 4.48 (ABq, 2H, J 12.0 Hz, $PhCH_2$); 4.53 (s, 2H, $PhCH_2$); 4.41 (dd, 1H, $J_{5,6a}$ 2.0, $J_{6a,6b}$ 12.0 Hz, H-6a); 4.31-4.24 (m, 2H, H-1', H-5'); 4.11 (dd, 1H, $J_{5,6b}$ 6.0 Hz, H-6b); 4.09 (dd, 1H, $J_{5',6a'}=J_{6a',6b'}$ 10 Hz, H-6'a); 3.88 (dd, 1H, J $_{3',4'}$ 3.0, $J_{4',5'}$ 6.0 Hz, H-4'); 3.795 (dd, 1H, $J_{5',6'b}$ 3.0 Hz, H-6'b); 3.77 (dd, 1H, $J_{3,4}=J_{2,3}$ 9.0 Hz, H-3); 3.74 (dd, 1H, $J_{2',3'}$ 4.0 Hz, H-3'); 3.71 (ddd, 1H, $J_{4,5}$ 10.0 Hz, H-5); 3.48 (dd, 1H, H-2); 3.38 (s, 3H, MeO); 1.95-1.85 (m, 1H, H-4); 1.61 (ddd, $J_{4\alpha,4\alpha'}$ 14, $J_{4\alpha,1'}$ 10, $J_{4\alpha,4}$ 2.5 Hz, H-4α, methylene bridge); 1.35 (ddd, $J_{4\alpha',1'}$ 2.5, $J_{4\alpha',4}$ 5.0 Hz, H-4α', methylene bridge). ^{13}C NMR (62 MHz, $CDCl_3$, δ): 171.2 and 170.3 (2 Me-$\underline{C}$=O); 138.7-127.3 (30C, Ph); 98.2 (C1), 81.6, 80.3, 75.3, 74.2, 73.3, 73.1, 72.9, 72.7, 71.8, 71.7, 70.0, 66.3, 64.7, (10C rings+ 5C $PhCH_2$); 55.0 (OMe); 39.8 (C4); 29.2 (C4α, methylene bridge), 20.8 ($\underline{C}H_3$-C=O). MS (m/z): 906 (M^++18).

Anal. Cald. for $C_{53}H_{60}O_{12}$. H_2O: C, 70.18; H, 6.89. Found C, 70.19; H, 6.95.

Methyl 2,3,6-tri-*O*-acetyl-4-deoxy-4-C-(3,4,5,7-tetra-*O*-acetyl-2,6-anhydro-1-deoxy-D-glycero-L-gluco-heptit-1-yl)-α-D-glucopyranoside (27)

A solution of **23** (80mg, 0.1mmol) in MeOH (5mL) was stirred with a catalytic amount of 10% Pd/C under hydrogen for 5h, filtered, and concentrated. The residue was acetylated (Ac_2O, pyridine) and flash chromatographed (cyclohexane-ethyl acetate 2:1→1:1) to afford **27** (57mg, 87%) as a syrup. $[\alpha]_D$ +124 (c 1 $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$:C_6D_6 1:1, δ): 5.40 (dd, 1H, $J_{2,3}=J_{3,4}$ 10.0Hz, H-3); 5.41 (d, 1H, $J_{3',4'}$ 3.0 Hz, H-4'); 5.19 (dd, 1H, $J_{1',2'}$ 5.0, $J_{2',3'}$ 9.0 Hz, H-2'); 5.13 (dd, 1H, H-3'); 4.91 (d, 1H, $J_{1,2}$ 3.5Hz, H-1); 4.82 (dd, 1H, H-2); 4.38 (dd, 1H, $J_{5,6a}$ 2.5, $J_{6a,6b}$ 12 Hz, H-6a); 4.30-4.25 (m, 1H, H-1'); 4.26 (dd, 1H, $J_{5',6'a}$ 7.0, $J_{6'a,6'b}$ 11.0 Hz, H-6'a); 4.15 (dd, 1H, $J_{5,6b}$ 6.0Hz, H-6b); 4.16-4.10 (m, 1H, H-6'b); 4.10-4.04 (m, 1H, H-5'); 3.82 (ddd, 1H, $J_{4,5}$ 10Hz, H-5); 3.41 (s, 3H, MeO); 2.1-2.05 (m, 1H, H-4); 2.20-2.05 (7s, 21H, OAc); 1.78 (ddd, 1H, $J_{4\alpha,1'}$ 2.5, $J_{4\alpha,4}$ 11, $J_{4\alpha,4\alpha'}$ 16 Hz, H-4α); 1.60 (ddd, 1H, $J_{4\alpha',1'}$ 7.0, $J_{4\alpha',4}$ 2.5 Hz, H-4α'). ^{13}C NMR

(62 MHz, $CDCl_3$, δ): 170.4-169.6 (7 C=O); 96.9 (C1); 72.5, 72.1, 70.6, 69.1, 68.4, 68.1, 67.3, 67.2, 64.2, 61.1 (10C, rings); 55.1 (OMe); 38.4 (C4); 25.4 (C4α), 20.8-20.6 (7 Ac). MS (m/z): 906 (M^++18).

Anal. Cald. for $C_{28}H_{40}O_{17}$. H_2O: C, 50.45; H, 6.351 Found C, 50.49; H, 6.41.

Methyl 2,3,6-tri-*O*-acetyl-4-deoxy-4-C-(3,4,5,7-tetra-*O*-acetyl-2,6-anhydro-1-deoxy-D-*glycero*-L-*manno*-heptit-1-yl)-α-D-glucopyranoside (peracetylated methyl α-C-lactoside) **(28)**

A solution of **24** (70mg, 0.087mmol) in MeOH (5mL) was stirred with a catalytic amount of 10% Pd/C under hydrogen for 5h, filtered, and concentrated. The residue was acetylated (Ac_2O, pyridine) and flash chromatographed to afford **28** (48mg, 85%) as a syrup. $[\alpha]_D$ +53 (c 1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$-C_6D_6 1:1, δ): 5.44 (d, 1H, $J_{3',4'}$ 2.5, $J_{4',5'}$<1 Hz, H-4'); 5.42 (dd, 1H, $J_{2,3}$ 10, $J_{3,4}$ 11 Hz, H-3); 5.04-4.96 (m, 2H, H-2', H-3'); 4.945 (d, 1H, $J_{1,2}$ 3.5 Hz, H-1); 4.87 (dd, 1H, H-2); 4.37 (dd, 1H, $J_{5,6a}$ 2.0, $J_{6a,6b}$ 12.0 Hz, H-6a); 4.28 (dd, 1H, $J_{5,6b}$ 5.0 Hz, H-6b); 4.12 (ddd, 1H, $J_{4,5}$ 10.0 Hz, H-5); 4.09 (dd, 1H, $J_{5',6'a}$ 6.0, $J_{6'a,6'b}$ 11.0 Hz, H-6'a); 4.01 (dd, 1H, $J_{5',6'b}$ 6.5 Hz, H-6'b); 3.89 (dd, 1H, H-5'); 3.62-3.55 (m, 1H, H-1'); 3.43 (s, 3H, CH_3O); 2.20-2.12 (m, 1H, H-4); 2.18, 2.14, 2.10, 2.09, 2.05, 2.05, 1.99 (7s, 21H, OAc); 1.73-1.63 (m, 2H, H-4α, H-4α'). ^{13}C NMR (400 MHz, $CDCl_3$, δ): 170.8-169.8 (7 C=O); 97.1 (C1); 75.2, 74.0, 72.7, 71.9, 69.2, 68.6, 68.3, 67.5 (8C, rings); 63.9, 61.8 (C6, C6'); 55.3 (OCH_3); 39.5(C4); 27.6 (C4α, methylene bridge), 20.8-20.5 (7 Ac). MS (m/z): 906 (M^++18).

Anal. Cald. for $C_{28}H_{40}O_{17}$. H_2O: C, 50.45; H, 6.35. Found C, 50.51; H, 6.39.

Methyl 2,3,6-tri-*O*-acetyl-4-deoxy-4-C-(3,4,5,7-tetra-*O*-acetyl-2,6-anhydro-1-deoxy-D-*glycero*-L-*gluco*-heptit-1-yl)-α-D-galactopyranoside (29)

A solution of a mixture of **24** and **25** (70mg, 0.087mmol) in methanol (5mL),was stirred with a catalytic amount of 10% Pd/C under H_2 for 5h, filtered and concentrated The residue was acetylated (Ac_2O, pyridine) and chromatographed (cyclohexane-ethyl acetate 2:1→ 1:1) to afford the methyl *C*-lactoside derivative **28** (30mg, 0.0462mmol) then **29** (10mg, 0.154mmol) ^1H NMR (400 MHz, $CDCl_3$, δ): 5.46-5.40 (m, 2H, H-3, H-4'); 5.26 (dd, 1H, $J_{1',2'}$ 4.5, $J_{2',3'}$ 9.0 Hz, H-2'); 5.22 (dd, 1H, $J_{3'4'}$ 3.0 Hz, H-3'); 4.97 (d, 1H, $J_{1,2}$ 4.0 Hz, H-1); 4.87 (d, 1H, $J_{2,3}$ 11.0 Hz, H-2); 4.32-4.01 (m, 7H, H-1', H-5, H-5', H-6a, H-6b, H-6'a, H-6'b); 3.41 (s, 3H, OMe); 2.47 (dd, J=J 6.0 Hz, H-4); 2.19-2.05 (7s, 21 H, AcO-); 1.90 (ddd, 1H, J 12.0, J 14.0, J <2.0 Hz, H-4α); 1.85-1.77 (m, 1H, H-4α').^1H NMR (400 MHz, C_6H_6:$CDCl_3$ 1:1, δ): 5.53-5.475 (m, 2H, H-3, H-4'); 5.34-5.30 (m, 2H, H-2', H-3'); 4.97-4.91 (m, 2H, H-1, H-2); 4.43-3.90 (m, 7H, H-1', H-5, H-5', H-6a, H-6b, H-6'a, H-6'b); 3.20 (s, 3H, OMe); 2.465 (dd, 1H, J=J 6.0 Hz, H-4); 1.975-1.875 (m, 2H, H-4α, H-4α'); 1.975-1.84 (7s, 21 H, Ac). ^{13}C NMR (400 MHz, $CDCl_3$, δ): 170.62-169.5 (7 C=O); 96.97 (C1); 77.3, 76.6, 72.5, 70.6, 69.4, 69.2, 68.9, 67.6 (8C, C1', C2,3,5, C2'-5'); 64.3 and 63.1 (C6, C6'); 55.1 (OCH_3); 38.4(C4); 25.4 (C4α); 20.9-18.5 (7 $\underline{C}H_3$-CO).

1,5-Anhydro-4,6-*O*-benzylidene-3-*O*-benzyl-D-galactitol (30)

White crystals, mp 93-95°C (cyclohexane-ethyl acetate), $[\alpha]_D$ +144 (c 1, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$, δ): 7.60-7.25 (m, 10H, Ph); 5.50 (s, 1H, $C\underline{H}$-Ph); 4.80 and 4.67 (ABq, 2H, J 12.0 Hz, $PhCH_2$); 4.30 (dd, 1H, $J_{5,6a}$ 1.3, $J_{6a,6b}$ 12.5 Hz, H-6a); 4.30-4.18 (m, 2H, H-1a, H-2); 4.26 (d, 1H, $J_{3,4}$ 3.0 Hz, H-4); 4.02 (dd, $J_{5,6b}$ 1.7 Hz, H-6b); 3.44 (dd, 1H, $J_{2,3}$ 9.1 Hz, H-3); 3.34 (d, 1H, H-5); 3.34-3.23 (m, 1H, H-1b); 2.3 (br. s, 1H, OH).^{13}C NMR (62 MHz, $CDCl_3$, δ): 137.9, 137.7 (2C, Ph); 128.8-126.2 (10C, Ph); 101.0 ($\underline{C}$H-Ph); 81.7 (C3); 72.9, 70.8, 70.3, 69.8, 69.4, 65.7 (C1-C6, $PhCH_2$). MS (m/z) 360 : (M^++18), 343 (M^++1).

Anal. Cald. for $C_{20}H_{22}O_5$: C, 70.15; H 6.48. Found C, 69.97; H 6.39.

This compound was isolated in 29% after the cyclisation of tethered sugars **20** and **17**.

Methyl 4-*C*-(2,6-anhydro-5,7-*O*-benzylidene-4-*O*-benzyl-1-deoxy-D-*glycero*-L-*gluco*-heptit-1-yl)-2,3-di-*O*-benzyl-4-deoxy-D-glucopyranoside (31)

Syrup, $[\alpha]_D$ +32 (c 6, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$-C_6D_6 1:1, δ): 7.75-7.18 (m, 20H, Ph); 5.30 (s, 1H, CHPh); 5.245 and 4.85 (ABq, 2H, J 12.0 Hz, $PhCH_2$); 4.74-4.68 (m, 1H, H-1'); 4.71 (d, 1H, $J_{1,2}$ 3.5 Hz, H-1); 4.64 and 4.53 (ABq, 2H, J 12.0 Hz, $PhCH_2$); 4.62 and 4.54 (ABq, 2H, J 12.0 Hz, $PhCH_2$); 4.43-4.37 (m, 1H, H-2'); 4.17 (d, $J_{6'a,6'b}$ 12.0, $J_{5',6'a}$<1Hz, H-6'a); 4.10 (dd, 1H, $J_{2,3}$ 9.0, $J_{3,4}$ 10.0 Hz, H-3); 3.87 (d, 1H, $J_{3',4'}$ 2.7 Hz, H-4'); 3.86 (m, 1H, H-6a); 3.78-3.67 (m, 2H, H-5, H-6b); 3.61 (dd, 1H, H-2); 3.56 (d, 1H, H-6'b); 3.42 (dd, 1H, $J_{2',3'}$ 9.0 Hz, H-3'); 3.28 (s, 3H, OMe); 3.14 (s, 1H, H-5'); 2.18-2.10 (m, 1H, H-4); 1.93 (ddd, 1H, $J_{4\alpha,4}$ 4.0, $J_{4\alpha,1'}$ 4.0, $J_{4\alpha,4\alpha'}$ 14.0 Hz, H-4α); 1.78-1.71 (m, 1H, H-4α'). ^{13}C NMR (400 MHz, $CDCl_3$-C_6D_6 1:1, δ): 139.3, 138.5, 138.4, 138.3 (4C, Ph); 128.5-126.1 (20C, Ph); 100.4 (CH-Ph); 98.2 (C1); 82.1, 79.1, 77.8, 72.7, 72.2, 71.3, 68.0, 63.7 (C2, C3, C5, C'1-C'5); 72.2, 70.4, 70.3, 70.1 (2C 6,6' and 3 $PhCH_2$); 54.6 (OCH_3), 39.6 (C-4), 22.7 (C4α, methylene bridge). MS (m/z) : 730 (M^++18), 681 (M^+-OMe).

Anal.cald. for $C_{42}H_{48}O_{10}$. $0.5H_2O$: C, 69.89; H 6.84. Found C, 69.98; H 6.89.

Methyl 4-*C*-(2,6-anhydro-5,7-*O*-benzylidene-4-*O*-benzyl-1-deoxy-D-glycero-L-gluco-heptit-1-yl)-2,3-di-*O*-benzyl-4-deoxy-D-galactopyranoside (32)

Selected data: ^1H NMR of **32** (400 MHz, $CDCl_3$-C_6H_6 1:1, δ): 5.26 (s, 1H, CHPh); 4.82-4.58 (m, 6H, 3 $PhCH_2$); 4.57-4.53 (m, 1H, H-2'); 4.25 (ddd, $J_{1',2'}$ 2.5, $J_{1',4\alpha}$ 12.0, $J_{1',4\alpha'}$ 5.5 Hz, H-1'); 4.10 (dd, $J_{2,3}$ 9.0, $J_{3,4}$ 2.0 Hz, H-3); 4.04-3.98 (m, 2H, H-6'a, H-5'); 3.87-3.85 (m, 1H, H-6'b); 3.55 (dd, 1H, $J_{2',3'}$=$J_{3',4'}$ 9.5 Hz, H-3'); 3.33 (s, 3H, O-CH_3); 2.53 (ddd, $J_{4,4\alpha}$ 6.0, $J_{4,4\alpha'}$ 7.0 Hz, H-4); 2.27-2.18 (m, 1H, H-4α); 2.06-1.97 (m, 1H, H-4α').

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