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Homologation of Protected Hexoses with Grignard C_1 Reagents

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Abstract—Derivatives of three stereoisomeric hexodialdo-1,5-pyranosides were reacted with four Grignard C_1 reagents: methoxymethyl-, allyloxymethyl-, benzyloxymethyl, and dimethylphenylsilylmethyl-magnesium chlorides. Two stereoisomeric heptoses were obtained in each case in a good yield. The methyl alloside-derived heptosides were accompanied by C-5 inverted products. The addition of Grignard reagents to aldehydes **5**–**8** has been discussed in terms of parallel α- or β-chelated and Felkin–Anh transition states. It has been found that the silyl Grignard reagent **12** exhibits a strong preference for the formation of heptose derivatives of L-configuration at C-6.

Introduction

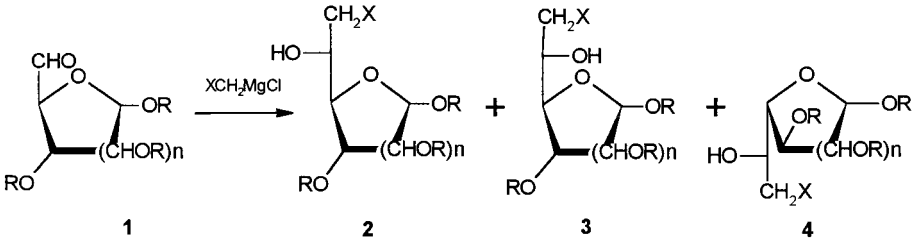
We recently performed a series of homologation reactions of pentofuranoses leading to hexofuranoses.[1] The reactions consisted of elongation of all stereoisomeric, protected pentofuranoses [pentodialdo-1,4-furanoses (1, n=1)] at the terminal C-atom (C-5) with Grignard C_1 reagents (Scheme 1). The following conclusions emerged from this study: (i) homologated products **2** and **3** were obtained in good to very good yields as mixtures of stereoisomers at C-5; their separation could be readily achieved by simple column chromatography, (ii) the stereoselectivity of the reactions depended on the possibility of forming α- or β-chelates in the transition state, this leading to a preference of L- or D-stereoisomers (α- or β-chelates, respectively), (iii) the silyl Grignard reagent (**12**) displayed a distinct preference for α-chelation which resulted in a dominating formation of L- hexoses, (iv) in some cases (substrates of the *ribo* and *xylo* configuration) side products **4**, with inverted configuration at C-4 were obtained.

For the present study four hexodialdo-1,5-pyranoses have been selected: methyl 2,3,4-tri-*O*-benzyl-β-D-*allo*-, -α-D-*gluco*, -*galacto*-dialdo-1,5-pyranosides (**5**–**7**), and 1,2:3,4-di-*O*-isopropylidene-α-D-*galacto*-dialdo-1,5-pyranose (**8**). Conversion of 2,3,4-protected alkyl mannopyranoside to the corresponding heptosides of D- and L-*glycero*-D-*manno* configuration according to the same protocol has been extensively described in literature.[2–11]

Results

Four aldehydes **5**–**8** (Fig. 1) were prepared by conventional methods (cf. Experimental). The aldehydes were reacted with four freshly prepared Grignard reagents **9**–**12**. The products were isolated by column chromatography. The results of reactions are presented in Tables 1–4.

It must be stressed again[1] that high yields of reactions are secured if the reaction conditions (cf. Experimental) are



Scheme 1.

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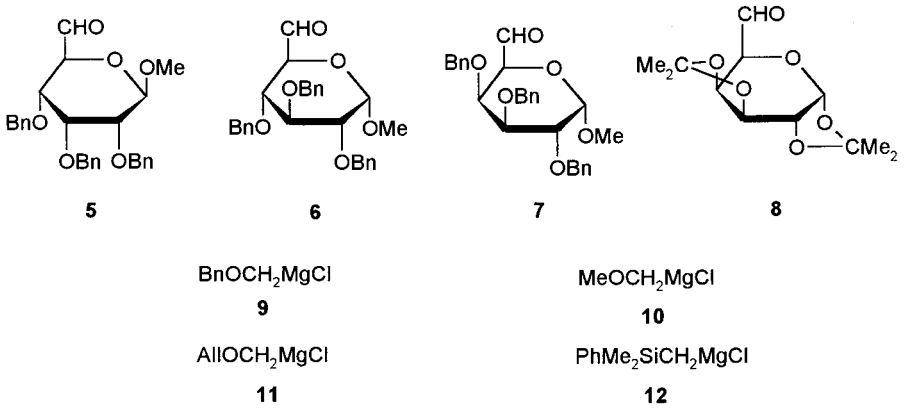


Figure 1.

Table 1. Chain-elongation reactions of protected hexose aldehydes **5**–**8** with Grignard reagents **9**–**12**. Methyl 2,3,4-tri-*O*-benzyl-β-D-*allo*-hexodialdo-1,5-pyranoside (**5**)

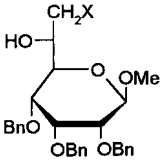
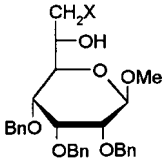
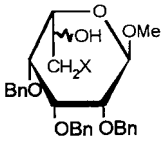
Entry No.	Reagent	Overall yield (%)	X	Compd No. (proportions, %)		
						
1	**9**	84.0	BnO	**13** (38)	**14** (51)	**15** (6) **16** (5)
2	**10**	90.2	MeO	**17** (31)	**18** (55)	**19** (10) **20** (4)
3	**11**	77.2	AllO	**21** (40)	**22** (48)	**23** (12)
4	**12**	70.2	$PhMe_2Si$	–	**24** (100)	-

Table 2. Chain-elongation reactions of protected hexose aldehydes **5**–**8** with Grignard reagents **9**–**12**. Methyl 2,3,4-tri-*O*-benzyl-α-D-*gluco*-hexodialdo-1,5-pyranoside (**6**)

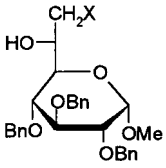
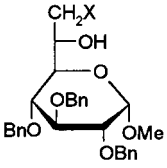
Entry No.	Reagent	Overall yield (%)	X	Compd No. (proportions, %)	
					
5	**9**	88.5	BnO	**25** (60)	**26** (40)
6	**10**	89.1	MeO	**27** (45)	**28** (55)
7	**11**	91.5	AllO	**29** (55)	**30** (45)
8	**12**	87.6	$PhMe_2Si$	–	**31** (100)

Table 3. Chain-elongation reactions of protected hexose aldehydes **5**–**8** with Grignard reagents **9**–**12**. Methyl 2,3,4-tri-*O*-benzyl-α-D-*galacto*-hexodialdo-1,5-pyranoside (**7**)

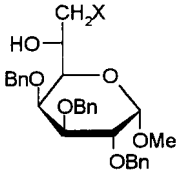
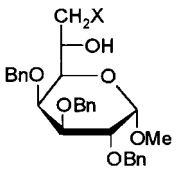
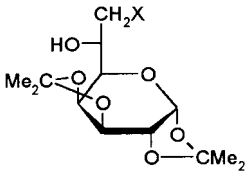
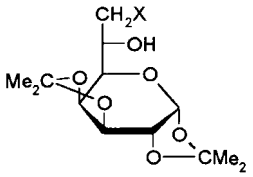
Entry No.	Reagent	Overall yield (%)	X	Compd No. (proportions, %)	
					
9	**9**	79.8	BnO	**32** (60)	**33** (40)
10	**10**	91.8	MeO	**34** (82)	**35** (18)
11	**11**	87.2	AllO	**36** (79)	**37** (21)
12	**12**	82.1	$PhMe_2Si$	**38** (2)	**39** (98)

Table 4. Chain-elongation reactions of protected hexose aldehydes **5**–**8** with Grignard reagents **9**–**12**. 1,2:3,4-Di-*O*-isopropylidene-α-D-*galacto*-hexodialdo-1,5-pyranose (**8**)

Entry No.	Reagent	Overall yield (%)	X	Compd No. (proportions, %)	
					
13	**9**	79.6	BnO	**40** (54)	**41** (46)
14	**10**	82.2	MeO	**42** (82)	**43** (18)
15	**11**	79.0	AllO	**44** (79)	**45** (21)
16	**12**	76.0	$PhMe_2Si$	**46** (52)	**47** (48)

strictly observed. The formation of Grignard reagents **9**–**11** is strongly dependent on the quality of the chloromethyl ethers used. We have constantly used freshly prepared and freshly distilled alkyl chloromethyl ethers. Grignard reagents prepared are rather unstable and should be kept below −20°C. Silyl reagent **12** is stable and the reactions can be performed under typical conditions. The overall yields of products were high. The products were separated by column chromatography, in some cases as 6-*O*-benzoates (cf. Experimental). Assignment of configuration to all stereoisomers is discussed in a separate section below.

As it can be seen from the Tables 1–4, there is a similarity in the stereochemical outcome of reactions for all reagents of the $ROCH_2MgCl$ type. The stereochemical results for Grignard **12** are different.

In the case of the *galacto* aldehydes (**7** and **8**) products of the D-*glycero* configuration (position C-6) dominated over the L-*glycero* partners (from 1.5:1 to 4:1, Tables 3 and 4). The *allo* aldehyde **5** yielded products where L-*glycero* stereoisomers slightly prevailed (1.3:1) over the D-*glycero* isomers (Table 1). The *gluco* aldehyde **6** led to both stereoisomeric heptosides with a slight prevalence of the D-*glycero* isomer (Table 2). The so-called 'inverted' products, i.e. methyl heptosides stemming from the aldehyde with inverted configuration at C-5, were obtained only in the case of methyl alloside elongated with alkoxymethyl Grignards **9**–**11**. Their yield remained within 10–14%. Although in two cases (Table 1, entries 1 and 2) the stereoisomeric products **15**, **16** and **19**, **20** could be obtained as individuals, their configuration at C-6 was not determined.

Discussion

Chain elongation of hexoses is of preparative value as the reactions may afford heptoses of any desired configuration. Several heptoses occur in nature, often as components of polysaccharides.[12] Synthetic access to these sugars using this homologation method may often be regarded as the 'method of choice'.

From the stereochemical point of view, the reactions present a contribution to the well-known problem of nucleophilic additions to α-oxyaldehydes. All four aldehydes **5**–**8** contain an α-oxygen atom (pyranose ring oxygen) and also a β-oxygen atom in a sterically defined position: *trans* (**5** and **6**) or *cis* (**7** and **8**) in relation to the carbonyl group. It is known that these atoms may influence the steric course of addition of nucleophiles due to the chance of forming α- or β-chelates.[13]

The question of α- and β-chelation in α- and β-alkoxyaldehydes and -ketones during nucleophilic additions has been studied experimentally[14–19] and theoretically.[20,21] Most relevant experimental investigations have been performed by E. L. Eliel[19,22,23] and theoretical calculations by E. Nakamura and K. Morokuma.[24] From the experiments it is known that α-chelation has a distinct influence on the

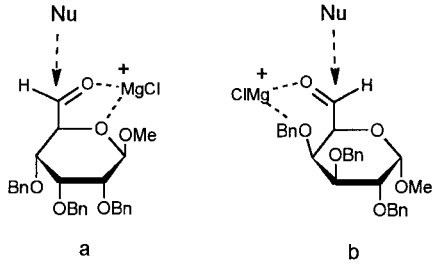


Figure 2. (a) α-chelation, (b) β-chelation.

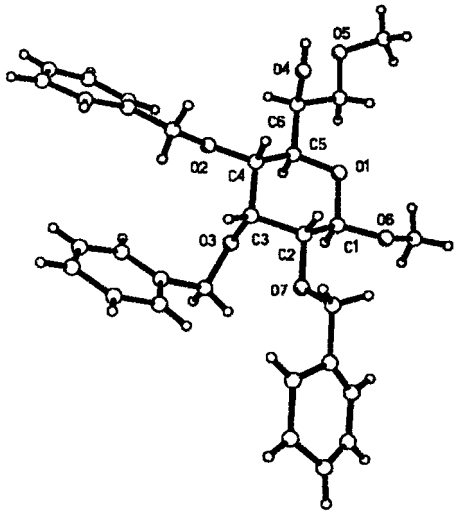
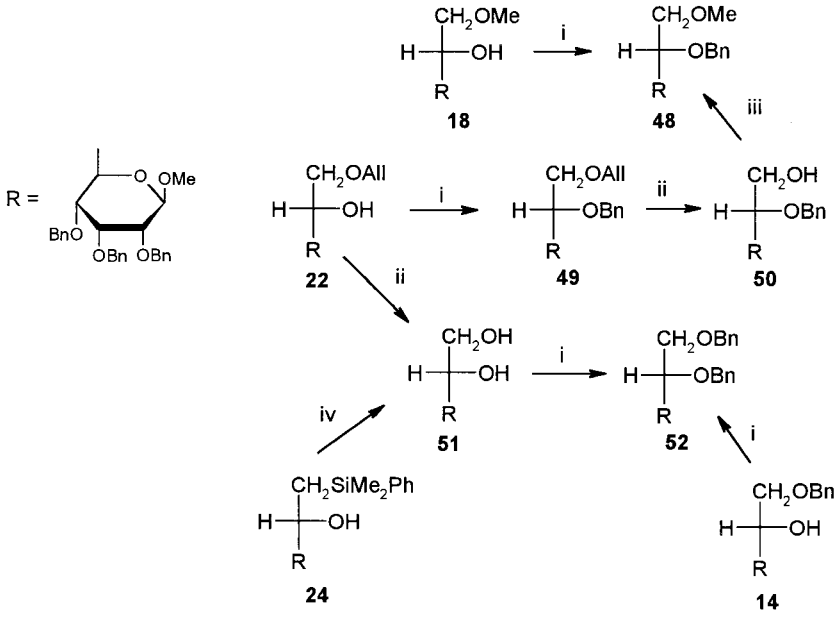


Figure 3. Methyl 2,3,4-tri-*O*-benzyl-7-*O*-methyl-L-*glycero*-β-D-*allo*-heptopyranoside (**18**).



Scheme 2. (i) $C_6H_5CH_2Br$, NaH, DMF, (ii) 1. $Rh(PPh_3)_3Cl$, DABCO, EtOH/benzene/H_2O (9:2:1), 2. HgO, $HgCl_2$, (iii) Mel, NaH, DMF, (iv) CH_3CO_3H, KBr, CH_3CO_2H, CH_3CO_2Na.

stereochemical result of reactions.[19] According to Eliel, β-chelation appears less important in steering the approach of nucleophiles to the carbonyl group.[19,25] However, ab initio calculations indicate that both types of chelation facilitate product formation through low-energy transition states (TS).[24]

From our results, discussed earlier,[1] and presented in this work, both types of chelation play an important role in determining the stereochemical outcome of reactions. At the same time we cannot exclude the participation of a non-chelated reaction pathway. Thus, the low stereoselectivity of addition of alkoxymethyl Grignards **9**–**11** to *allo* and *gluco* aldehydes (**5** and **6**, Tables 1 and 2) with only a slight preference for the L-*glycero* stereoisomers can be explained by an interplay of two reaction pathways: by the 'normal' Felkin–Anh (FA) transition state, competing with an α-chelated TS. It should be added that in this case α-chelation forces the approach of the nucleophile from 'below the ring' (Fig. 2a) this leading to L-configuration of the new CHOH grouping. Products of the D-configuration at C-6 are formed via the non-chelated FA TS. In the case of both *galacto* aldehydes, **7** and **8**, the FA transition state is additionally supported by β-chelation (Fig. 2b) this giving a clear preference of the D-*glycero* stereoisomers (Tables 3 and 4).

The stereochemical outcome of the reactions between hexose aldehydes **5** and **6** and the silyl Grignard is unidirectional: only products of L-*glycero* configuration were isolated. The alternative stereoisomers—if formed—were in negligible amounts (<1%). In the case of the aldehyde **7** the D-*glycero* stereoisomer **38** was obtained in 1.3% isolated yield, and in the case of the aldehyde **8** both C-6 stereoisomeric products were formed in approximately equal amounts. The rationalization is based in the assumption that for the silyl Grignard the α-chelation plays the decisive role. However, it appears that for the aldehyde **8** the 'normal' FA pathway is equally important as the α-chelation.

The 'inverted' products from the reactions of the *allo* aldehyde **5** were formed most probably[1] by epimerization of the aldehyde caused by the excessive Grignard reagent before reacting with it. Although this seems to be the most rational explanation, it must be added that our isomerization experiments with some isopropylidene-protected pentodialdo-1,4-furanosides with a strong base (lithium diisopropylamide) did not afford a conclusive evidence.[26]

Configuration of D- and L-*glycero*-D-*allo*-, *gluco*- and -*galacto*-heptopyranosides

Derivatives of the heptopyranosides obtained were, with a few exceptions, not described in literature, therefore their

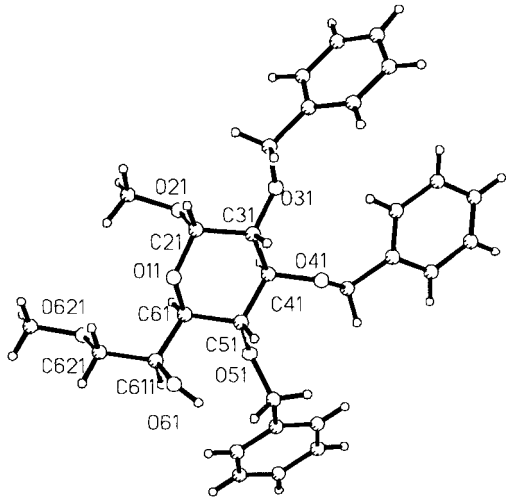
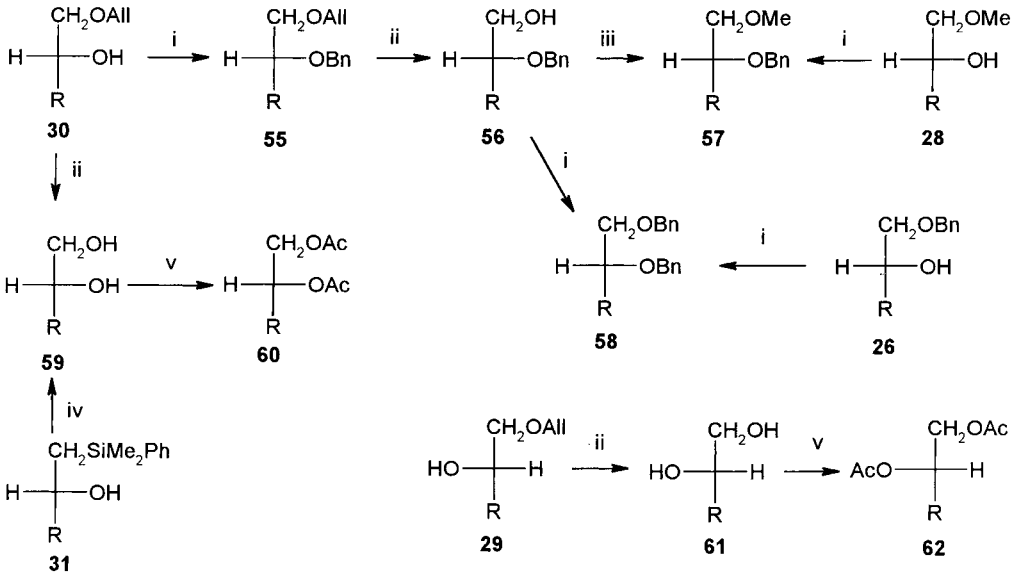
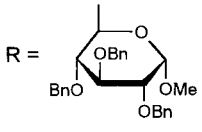


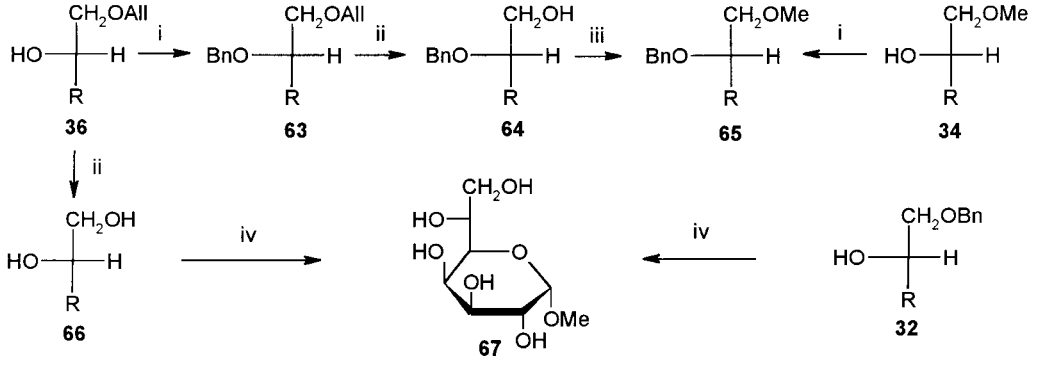
Figure 4. Methyl 2,3,4-tri-*O*-benzyl-7-*O*-methyl-L-*glycero*-α-D-*gluco*-heptopyranoside (**28**).

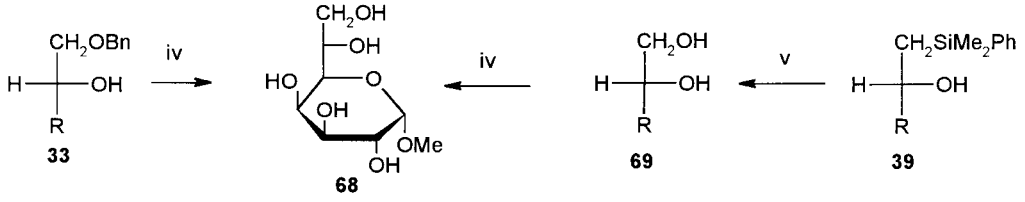


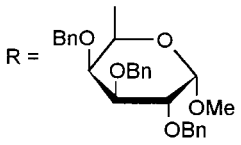


i. $PhCH_2Br$, NaH, DMF
ii. 1.$Rh(PPh_3)_3Cl$, DABCO, EtOH:benzene:H_2O (9:2:1)
2. HgO, $HgCl_2$
iii. MeI, NaH, DMF
iv. CH_3CO_3H, KBr, CH_3CO_2H, CH_3CO_2Na
v. Ac_2O, Py, DMAP

Scheme 3.

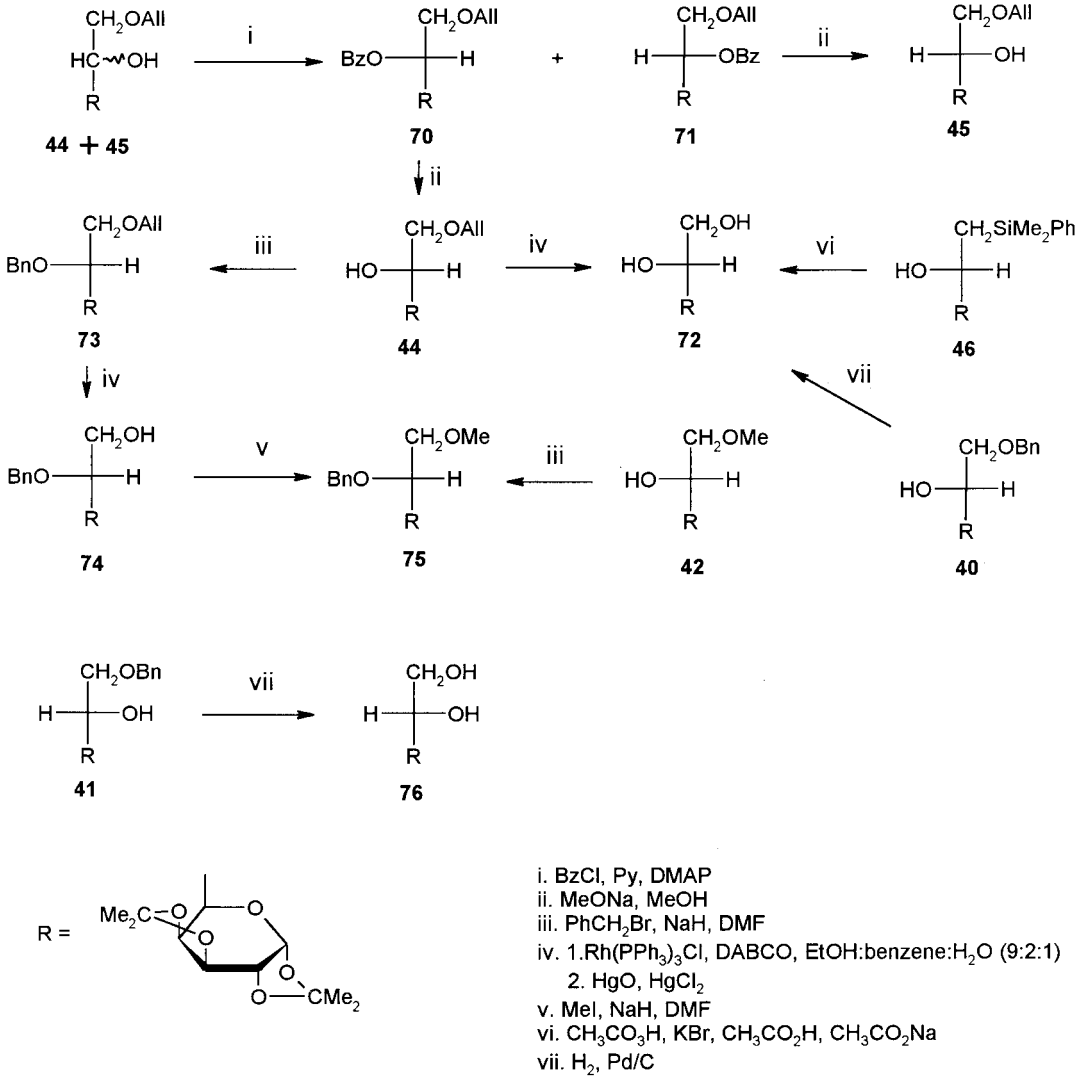






i. $PhCH_2Br$, NaH, DMF
ii. 1.$Rh(PPh_3)_3Cl$, DABCO, EtOH:benzene:H_2O (9:2:1)
2. HgO, $HgCl_2$
iii. MeI, NaH, DMF
iv. H_2, Pd/C
v. CH_3CO_3H, KBr, CH_3CO_2H, CH_3CO_2Na

Scheme 4.



Scheme 5.

identification was based on conversion to products configuration of which was determined by X-ray method.

From methyl 2,3,4,-tri-*O*-benzyl-7-*O*-methyl-L-*glycero*-β-D-*allo*-heptopyranoside (**18**, Table 1) crystals suitable for X-ray structural determination were obtained, what enabled to assign L configuration at C-6 (Fig. 3) The corelation of the spectral data of **18** with other products obtained: **14** (7-*O*-benzyl), **22** (7-*O*-allyl) and **24** [7-deoxy-7-(dimethylphenylsilyl)] is shown in Scheme 2. Heptoside **22** was benzylated at C-6 and the product **49** was de-allylated under typical conditions (Wilkinson's catalyst, DABCO, then hydrolysis) to yield **50** which was next methylated to yield 7-*O*-methyl derivative identical (TLC, NMR) with **18**. 7-*O*-Benzyl derivative **14** was benzylated at C-6 to yield pentabenzyl derivative **52**. Parallelly, **22** was de-allylated to 6,7-diol **51**. Oxidation of 7-deoxy-7-dimethylphenylsilyl derivative **24** led to the same diol **51**. And, finally, di-benzylation of the diol **51** furnished pentabenzyl heptoside identical in every respect with **52** (Scheme 2).

Both substituted methyl D- and L-*glycero*-β-D-*allo*-heptopyranosides (**13** and **14**) were fully deprotected to free heptoses by acetolysis followed by hydrogenolysis to yield free sugars **53** and **54**. The optical rotation and ^{13}C NMR data of D-*glycero*-α,β-D-*allo*-heptopyranose (**53**) were identical with the literature values.[27,28]

For the stereoisomeric methyl (DD- and LD-) *gluco* heptopyranosides the key compound, for which an X-ray structural determination was performed, was methyl 2,3,4-tri-*O*-benzyl-7-*O*-methyl-L-*glycero*-α-D-*gluco*-heptopyranoside (**28**, Fig. 4), leaving for **27** the D-*glycero*-D-*gluco* configuration. These assignments were further supported by comparison of the spectral and optical rotation data of 6,7-diols **59** and **61** with the literature values.[29,30] Structural correlation of other products: **26**, **29**, **30**, and **31** is shown in Scheme 3.

Configuration of derivatives of methyl galactoheptosides (Table 3) was determined by corelation with methyl D- and L-*glycero*-D-*galacto*-heptopyranosides **67** and **68**.[7] All reactions and products which were performed are collected in Scheme 4. A basically similar structural correlation was

made for derivatives of diisopropylidene-D-galactose (Scheme 5). Compounds **46**, **47** (cf. Table 4) and **72** are known from literature.[31]

Conclusion

Homologation reactions of hexodialdo-1,5-pyranoses **5**–**8** with C_1 Grignard reagents **9**–**12** opens a facile access to higher sugars. Heptoses which are otherwise difficult to obtain may be prepared readily. A several 7-O etherified heptoses become available. The reactions performed present a contribution to the problem of nucleophilic additions to aldehydes having α- and β-oxygen atoms in sterically defined positions. These results confirm our earlier observations[1] that the reactions proceed through formation of α- and β-chelates depending on the steric accessibility of oxygen atoms. It seems again that β-chelation to acetonide oxygen atoms (aldehyde **9**) is almost as effective as to ether oxygen atom (aldehyde **8**). It is remarkable that the silyl Grignard **12** exhibits a distinct preference for α-chelated forms in the transition state, this leading to L-configuration at the new CHOH grouping.

Experimental

General methods

Melting points were determined with a Kofler apparatus and are uncorrected. ^{1}H NMR spectra were recorded with a Varian AC-200 (200 MHz) or Bruker AM-500 (500 MHz) spectrometers. ^{13}C NMR were recorded in the DEPT mode. The assignments of signals for compounds **13**–**47** was based on ^{1}H-^{13}C COSY and ^{1}H–^{1}H COSY spectra. Mass spectra were recorded on an AMD-604 mass spectrometer (LSIMS, positive mode) and on an Per Septive Biosystems Mariner™ mass spectrometer (ESI/TOF, positive mode). Optical rotations were determined at 22±2°C with a Jasco DIP 360 automatic polarimeter and are given in 10^{-1} deg cm^2 g^{-1}. TLC was performed on Kieselgel 60 F_{254} ready plates and column chromatography on Silica Gel 230–400 or 70–230 mesh (Merck). High-performance liquid chromatography was carried out on a Shimadzu instrument: central unit C-R4A, pump unit LC-8A, UV detector SPD250-6A on a column SP250/21 Nucleosil 100-7 (Macherey-Nagel).

Aldehydes **6**, **7** and **8** were obtained from readily available methyl 2,3,4-tri-*O*-benzyl-α-D-*gluco*-,[32] and -α-D-*galacto*-pyranosides[33] and 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose,[34] respectively, by Swern oxidation. Methyl β-D-allopyranoside was obtained from the commercially available methyl β-D-*gluco*-pyranoside by Mitsunobu reaction in according to Weinges.[35,36]

Methyl 2,3,4-tri-*O*-benzyl-β-D-allopyranoside. To a suspension of methyl β-D-allopyranoside (4.47 g, 0.023 mol) in pyridine (80 ml) was added trityl chloride (7.80 g, 0.028 mol) and a catalytic amount of DMAP. The mixture was stirred overnight at 40°C. Then water (190 ml) was added and after 10 min the product was extracted with chloroform. The organic extract was dried and concentrated to dryness. To a cooled (0°C) solution of the residue in abs DMF (130 ml) was added sodium hydride (50% suspension in mineral oil, 3.64 g, 0.076 mol). The suspension was stirred for 30 min and benzyl bromide (9.0 ml, 0.076 mol) was added. Stirring was continued for 8 h whereupon the excess of the hydride was decomposed with MeOH and the mixture was poured into ice-water. The product was extracted with ether, and the organic extract was dried and concentrated to dryness. The residue was dissolved in a mixture of CH_3CN (80 ml) and ether (58 ml) and HBF_4 (50% in water, 5.8 ml) was added. After 2 h the solution was neutralized with Et_3N and washed twice with water. The organic layer was dried and evaporated to dryness under reduced pressure. The residue was chromatographed with hexane–ethyl acetate (10:1→3:2) to yield methyl 2,3,4-tri-*O*-benzyl-β-D-allopyranoside (6.74 g, 63.1%) as a colourless oil; $[\alpha]_D$= +17.0 (*c* 3.0, $CHCl_3$); ν_{max} (film) 3480 (br), 3063, 3030, 2890, 1497, 1454, 1206, 1127, 1091, 1045, 1028, 736, 698 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.46–7.22 (15H, m, 3Ph), 4.94–4.38 (3×2H, 3ABq, 3CH_2Ph), 4.85 (1H, d, *J*=8.0 Hz, H-1), 4.12 (1H, dd, *J*=2.4, 2.6 Hz, H-3), 3.96 (1H, ddd, *J*=3.0, 4.1, 9.5 Hz, H-5), 3.88 (1H, dd, *J*=3.0, 11.9 Hz, H-6a), 3.73 (1H, dd, *J*=4.1, 11.9 Hz, H-6b), 3.56 (3H, s, OCH_3), 3.42 (1H, dd, *J*=2.4, 9.5 Hz, H-4), 3.19 (1H, dd, *J*=2.6, 8.0 Hz, H-2). ^{13}C NMR (200 MHz, $CDCl_3$) δ: 138.8, 138.5, 137.6 and 128.4–127.4 (Ph), 102.0 (C-1), 79.0, 75.6, 74.5 and 72.4 (C-2,3,4,5), 74.4, 72.9 and 71.5 (3CH_2Ph), 62.3 (C-6), 57.1 (OCH_3). HR MS (LSIMS): $C_{28}H_{32}O_6$+Na^+ $[M+Na]^+$; Calcd: 487.20966. Found: 487.21035.

Methyl 2,3,4-tri-*O*-benzyl-β-D-*allo*-hexodialdo-1,5-pyranose (5). A solution of oxalyl chloride (1.56 ml, 18.1 mmol) in CH_2Cl_2 (44 ml) was cooled (−50 to −60°C) and a solution of Me_2SO (2.57 ml, 36.3 mmol) in CH_2Cl_2 (36 ml) was slowly added. After 5 min a solution of methyl 2,3,4-tri-*O*-benzyl-β-D-allopyranoside (6.74 g, 14.5 mmol) in CH_2Cl_2 (36 ml) was slowly added. Stirring at −60°C was continued for 1 h whereupon Et_3N (10.11 ml, 72.5 mmol) was added. After 5 min of stirring the reaction mixture was allowed to attain room temperature. To the solution was added water (45 ml), and the mixture was extracted with CH_2Cl_2. The organic extract was dried and concentrated. The residue was purified by chromatography with hexane–ethyl acetate (10:1→2:1) to give methyl 2,3,4-tri-*O*-benzyl-β-D-*allo*-hexodialdo-1,5-pyranose (**5**, 5.71 g, 85.3%) as a colourless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 9.70s, 1H, (C*H*O), 7.48–7.20 (15H, m, 3Ph), 4.92–4.36 (8H, m, H-1, H-5, 3CH_2Ph), 4.09 (1H, t, *J*=2.6 Hz, H-3), 3.60–3.53 (1H, m, H-4), 3.56 (3H, s, OCH_3), 3.25 (1H, dd, *J*=2.6, 7.5 Hz, H-2). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 198.9 (*C*HO), 138.5, 138.4, 137.0 and 128.5–127.5 (Ph), 78.0, 76.1, 75.5, 74.4 (C-2,3,4,5), 74.3, 73.1, 71.7 (3CH_2Ph), 57.2 (OCH_3).

The synthesis of protected derivatives of heptopyranosides

General method. To dry magnesium turnings (474 mg, 19.5 mmol) covered with freshly distilled THF (1 ml) under dry argon was added sublimed $HgCl_2$ (18 mg), and a few drops of neat, freshly distilled alkoxymethyl chloride were added while lowering the temperature to −15°C (for allyloxymethyl chloride), 0 to −5°C (for benzyloxymethyl chloride) or −20°C (for methyloxymethyl chloride). When

the formation of the Grignard reagent had started, the rest of the alkoxymethyl chloride (19.5 mmol) in THF (2 ml) was added at −20°C (for allyloxymethyl chloride), −10°C (for benzyloxymethyl chloride) or −25°C (for methoxymethyl chloride) and the stirring was continued for 2 h. The temperature was then lowered to −78°C and a solution of aldehyde (3.25 mmol) in abs THF (8 ml) was added dropwise. The mixture was stirred at this temperature for 2 h and was slowly brought to room temperature while stirring for another 12 h. Cold (0°C) aq NH_4Cl (82 ml) was added and the products were extracted with CH_2Cl_2. The extract was dried with $MgSO_4$ and concentrated, and the residue was chromatographed on a silica gel column. In case of difficult separable products HPLC was used.

Grignard reagent **12**, containing phenyldimethylsilyl group, was obtained according to Boons et al.[37] The reactions of **12** with hexodialdo-1,5-pyranoses (**5**–**8**) were performed in the same manner at −78°C.

Methyl 2,3,4,7-tetra-*O*-benzyl-D-*glycero*-β-D-*allo*-heptopyranoside (13). HPLC eluent: CH_2Cl_2–ether 8:1; yield: 33%; colourless needles, mp 72–73°C (from hexane–ether); $[\alpha]_D$=+12.7 (*c* 1.4, $CHCl_3$); ν_{max} (KBr) 3402 (br), 3031, 2881, 1497, 1454, 1209, 1134, 1091, 1060, 1026, 735, 697 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.39–7.20 (20H, m, 4Ph), 4.90–4.30 (4×2H, 4ABq, 4CH_2Ph), 4.78 (1H, d, *J*=7.9 Hz, H-1), 4.10 (1H, dd, *J*=2.4, 2.6 Hz, H-3), 4.08–4.01 (2H, m, H-5, H-6), 3.60 (1H, dd, *J*=6.1, 10.0 Hz, H-7a), 3.58 (1H, dd, *J*=3.7, 10.0 Hz, H-7b), 3.47 (1H, dd, *J*=2.4, 9.2 Hz, H-4), 3.47 (3H, s, OCH_3), 3.17 (1H, dd, *J*=2.6, 7.9 Hz, H-2). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 138.8, 138.6, 138.3, 137.1 and 128.5–127.4 (Ph), 102.1 (C-1), 78.9 (C-2), 77.9 (C-4), 74.4 (*C*H_2Ph), 74.1 (C-3), 73.3 (*C*H_2Ph), 72.9 (*C*H_2Ph), 72.4 (C-6), 71.6 (C-5), 71.0 (*C*H_2Ph), 70.9 (C-7), 56.8 (OCH_3). HR MS (ESI): $C_{36}H_{40}O_7$+Na^+ $[M+Na]^+$; Calcd: 607.2666. Found: 607.2663. Anal. Calcd for $C_{36}H_{40}O_7$: C, 73.95; H, 6.90. Found: C, 74.08; H, 7.04.

Methyl 2,3,4,7-tetra-*O*-benzyl-L-*glycero*-β-D-*allo*-heptopyranoside (14). HPLC eluent: CH_2Cl_2–ether 8:1; yield 43%; colourless oil; $[\alpha]_D$=−8.7 (*c* 1.2, $CHCl_3$); ν_{max} (film) 3478 (br), 3063, 3030, 2901, 1497, 1454, 1362, 1206, 1096, 1048, 1028, 737, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.40–7.24 (20H, m, 4Ph), 4.87–4.51 (4×2H, 4ABq, 4CH_2Ph), 4.77 (1H, d, *J*=7.9 Hz, H-1), 4.14 (1H, ddd, *J*=1.4, 5.2, 7.7 Hz, H-6), 4.08 (1H, dd, *J*=2.2, 2.6 Hz, H-3), 3.93 (1H, dd, *J*=1.4, 9.7 Hz, H-5), 3.65 (1H, dd, *J*=7.7, 9.7 Hz, H-7a), 3.59 (1H, dd, *J*=2.2, 9.7 Hz, H-4), 3.59 (1H, dd, *J*=5.2, 9.7 Hz, H-7b), 3.44 (3H, s, OCH_3), 3.17 (1H, dd, *J*=2.6, 7.9 Hz, H-2). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 139.0, 138.6, 138.1, 137.9 and 128.4–127.3 (Ph), 102.0 (C-1), 78.8 (C-2), 75.3 (C-4), 75.0 (C-3), 74.4 (*C*H_2Ph), 73.3 (*C*H_2Ph), 72.8 (*C*H_2Ph), 71.9 (*C*H_2Ph), 71.7 (C-7), 71.7 (C-5), 68.2 (C-6), 56.7 (OCH_3). HR MS (ESI): $C_{36}H_{40}O_7$+Na^+ $[M+Na]^+$; Calcd: 607.2666. Found: 607.2696.

Methyl 2,3,4,7-tetra-*O*-benzyl-D(L)-*glycero*-α-L-*talo*-heptopyranoside (15). HPLC eluent: CH_2Cl_2–ether 8:1; yield 4%; colourless oil; $[\alpha]_D$=−6.4 (*c* 1.1, $CHCl_3$); ν_{max} (film) 3481 (br), 3064, 3031, 2907, 1497, 1454, 1359, 1206, 1131, 1053, 736, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.39–7.21 (20H, m, 4Ph), 5.07–4.40 (4×2H, 4ABq, 4CH_2Ph), 4.97 (1H, d, *J*=1.3 Hz, H-1), 4.16–4.13 (1H, m, H-6), 3.88–3.86 (1H, m, H-4), 3.83 (1H, dd, *J*=1.5, 4.9 Hz, H-5), 3.78–3.75 (1H, m, H-2), 3.74 (1H, dd, *J*=2.9, 3.1 Hz, H-3), 3.57 (1H, dd, *J*=5.7, 9.8 Hz, H-7a), 3.39 (1H, dd, *J*=4.6, 9.8 Hz, H-7b), 3.32 (3H, s, OCH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 138.5, 138.5, 138.1, 138.0 and 128.4–127.2 (Ph), 100.3 (C-1), 77.6 (C-3), 74.8 (C-4), 74.2 (C-2), 73.4 (*C*H_2Ph), 73.4 (*C*H_2Ph), 73.1 (*C*H_2Ph), 71.2 (*C*H_2Ph), 70.9 (C-6), 70.1 (C-5), 69.7 (C-7), 54.9 (OCH_3). HR MS (ESI): $C_{36}H_{40}O_7$+Na^+ $[M+Na]^+$; Calcd: 607.2666. Found: 607.2645.

Methyl 2,3,4,7-tetra-*O*-benzyl-D(L)-*glycero*-α-L-*talo*-heptopyranoside (16). HPLC eluent: CH_2Cl_2–ether 8:1; yield 5%; colourless oil; $[\alpha]_D$=−32.6 (*c* 2.1, $CHCl_3$); ν_{max} (film) 3480 (br), 3031, 2908, 1497, 1454, 1360, 1205, 1134, 1055, 973, 910, 736, 698 cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ: 7.53–7.06 (20H, m, 4Ph), 5.26–4.26 (4×2H, 4ABq, 4CH_2Ph), 4.86 (1H, d, *J*=1.1 Hz, H-1), 4.44 (1H, ddd, *J*=3.1, 4.9, 8.9 Hz, H-6), 4.24–4.22 (1H, m, H-4), 3.83–3.81 (1H, m, H-2), 3.80 (1H, dd, *J*=1.4, 8.9 Hz, H-5), 3.77 (1H, dd, *J*=3.1, 3.2 Hz, H-3), 3.72 (1H, dd, *J*=4.9, 9.5 Hz, H-7a), 3.65 (1H, dd, *J*=3.1, 9.5 Hz, H-7b), 3.07 (3H, s, OCH_3). ^{13}C NMR (125 MHz, C_6D_6) δ: 140.3, 139.6, 139.1, 138.7 and 128.6–127.2 (Ph), 100.8 (C-1), 77.9 (C-3), 75.4 (C-2), 74.6 (*C*H_2Ph), 73.5 (*C*H_2Ph), 73.5 (C-4), 73.3 (*C*H_2Ph), 71.8 (C-7), 71.2 (C-5), 70.9 (*C*H_2Ph), 68.7 (C-6), 54.4 (OCH_3). HR MS (ESI): $C_{36}H_{40}O_7$+Na^+ $[M+Na]^+$; Calcd: 607.2666. Found: 607.2662.

Methyl 2,3,4-tri-*O*-benzyl-7-*O*-methyl-D-*glycero*-β-D-*allo*-heptopyranoside (17). HPLC eluent: hexane–ethyl acetate 3:2; yield 28%; colourless needles, mp 92–93°C (from hexane–ethyl acetate); $[\alpha]_D$=+25.2 (*c* 1.1, $CHCl_3$); ν_{max} (KBr) 3401 (br), 3031, 2922, 2813, 1496, 1455, 1201, 1134, 1092, 1027, 745, 696 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.40–7.24 (15H, m, 3Ph), 4.91–4.34 (3×2H, 3ABq, 3CH_2Ph), 4.80 (1H, d, *J*=8.0 Hz, H-1), 4.12 (1H, dd, *J*=2.4, 2.6 Hz, H-3), 4.02–3.97 (2H, m, H-5, H-6), 3.52 (3H, s, OCH_3), 3.53–3.44 (3H, m, H-4, H-7a, H-7b), 3.34 (3H, s, OCH_3), 3.18 (1H, dd, *J*=2.6, 8.0 Hz, H-2). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 138.8, 138.6, 137.0 and 128.5–127.4 (Ph), 102.1 (C-1), 78.9 (C-2), 78.1 (C-4), 74.5 (*C*H_2Ph), 74.1 (C-3), 73.2 (C-7), 73.0 (*C*H_2Ph), 72.3, 71.5 (C-5, C-6), 70.9 (*C*H_2Ph), 59.1 (OCH_3), 56.8 (OCH_3). Anal. Calcd for $C_{30}H_{36}O_7$: C, 70.85; H, 7.13. Found: C, 70.66; H, 7.13.

Methyl 2,3,4-tri-*O*-benzyl-7-*O*-methyl-L-*glycero*-β-D-*allo*-heptopyranoside (18). HPLC eluent: hexane–ethyl acetate 3:2; yield 50%; colourless needles, mp 69–70°C (from hexane–ether); $[\alpha]_D$=−10.5 (*c* 1.0, $CHCl_3$); ν_{max} (KBr) 3421 (br), 3030, 2892, 1497, 1454, 1208, 1136, 1098, 1046, 1026, 970, 737, 697 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.41–7.24 (15H, m, 3Ph), 4.87–4.51 (3×2H, 3ABq, 3CH_2Ph), 4.80 (1H, d, *J*=7.9 Hz, H-1), 4.12–4.08 (1H, m, H-6), 4.10 (1H, dd, *J*=2.5, 2.6 Hz, H-3), 3.90 (1H, dd, *J*=1.4, 9.7 Hz, H-5), 3.59 (1H, dd, *J*=2.5, 9.7 Hz, H-4), 3.57 (1H, dd, *J*=7.9, 9.8 Hz, H-7a), 3.51 (3H, s, OCH_3), 3.49 (1H, dd, *J*=4.7, 9.8 Hz, H-7b), 3.38 (3H, s, OCH_3), 3.18 (1H, dd, *J*=2.6, 7.9 Hz, H-2). ^{13}C NMR (125 MHz,

$CDCl_3$) δ: 139.0, 138.6, 137.9 and 128.4–127.4 (Ph), 102.0 (C-1), 78.8 (C-2), 75.2 (C-4), 75.0 (C-3), 74.5 (CH_2Ph), 74.4 (C-7), 72.8 (CH_2Ph), 71.9 (CH_2Ph), 71.8 (C-5), 68.0 (C-6), 59.1 (OCH_3), 56.8 (OCH_3). Anal. Calcd for $C_{30}H_{36}O_7$: C, 70.85; H, 7.13. Found: C, 70.64; H, 7.07.

Methyl 2,3,4-tri-*O*-benzyl-7-*O*-methyl-D(L)-*glycero*-α-L-*talo*-heptopyranoside (19). HPLC eluent: hexane–ethyl acetate 3:2; yield 4%; colourless oil; $[\alpha]_D=-9.7$ (*c* 1.0, $CHCl_3$); ν_{max} (film) 3479 (br), 3064, 3031, 2902, 1497, 1454, 1360, 1200, 1129, 1053, 1029, 969, 766, 736, 698 cm^{-1};^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.39–7.21 (15H, m, 3Ph), 5.13–4.50 (3×2H, 3ABq, 3CH_2Ph), 4.98 (1H, d, *J*=1.2 Hz, H-1), 4.14–4.09 (1H, m, H-6), 3.94–3.91 (1H, m, H-4), 3.80–3.75 (3H, m, H-2, H-3, H-5), 3.44 (1H, dd, *J*=5.5, 9.8 Hz, H-7a), 3.34 (3H, s, OCH_3), 3.30 (3H, s, OCH_3), 3.29 (1H, dd, *J*=5.0, 9.8 Hz, H-7b). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 138.5, 138.4, 138.1 and 128.4–127.2 (Ph), 100.3 (C-1), 77.6 (C-3), 74.8 (C-4), 74.1 and 70.1 (C-2, 5), 73.4 (CH_2Ph), 73.1 (CH_2Ph), 72.3 (C-7), 71.3 (CH_2Ph), 70.7 (C-6), 59.1 (OCH_3), 54.9 (OCH_3). ^{1}H NMR (500 MHz, C_6D_6) δ: 7.37–7.03 (15H, m, 3Ph), 5.16–4.25 (3×2H, 3ABq, 3CH_2Ph), 4.98 (1H, d, *J*=1.7 Hz, H-1), 4.32–4.28 (1H, m, H-6), 3.99 (1H, dd, *J*=2.1, 3.7 Hz, H-5), 3.85–3.82 (1H, m, H-4), 3.74 (1H, dd, *J*=1.7, 3.3 Hz, H-2), 3.71 (1H, dd, *J*=3.0, 3.2 Hz, H-3), 3.69 (1H, dd, *J*=6.9, 9.6 Hz, H-7a), 3.54 (1H, dd, *J*=4.6, 9.6 Hz, H-7b), 3.15, 3.12 (2×3H, 2s, 2OCH_3). HR MS (ESI): $C_{30}H_{36}O_7+H^+$ $[M+H]^+$; Calcd: 509.2534. Found: 509.2553.

Methyl 2,3,4-tri-*O*-benzyl-7-*O*-methyl-L(D)-*glycero*-α-L-*talo*-heptopyranoside (20). HPLC eluent: hexane–ethyl acetate 3:2; yield 9%; colourless oil; $[\alpha]_D=-46.2$ (*c* 2.1, $CHCl_3$); ν_{max} (film) 3471 (br), 3031, 2907, 1497, 1454, 1360, 1198, 1134, 1055, 953, 907, 736, 698 cm^{-1}; ^{1}H NMR (500 MHz, C_6D_6) δ: 7.53–7.06 (15H, m, 3Ph), 5.27–4.32 (3×2H, 3ABq, 3CH_2Ph), 4.87 (1H, d, *J*=1.1 Hz, H-1), 4.40–4.36 (1H, m, H-6), 4.26–4.23 (1H, m, H-4), 3.83 (1H, dd, *J*=1.1, 3.4 Hz, H-2), 3.78 (1H, dd, *J*=3.1, 3.4 Hz, H-3), 3.76 (1H, dd, *J*=1.4, 8.9 Hz, H-5), 3.58 (1H, dd, *J*=4.9, 9.5 Hz, H-7a), 3.48 (1H, dd, *J*=3.0, 9.5 Hz, H-7b), 3.10, 3.04 (2×3H, 2s, 2OCH_3). ^{13}C NMR (125 MHz, C_6D_6) δ: 140.1, 139.4, 138.8 and 128.3–126.9 (Ph), 100.6 (C-1), 77.7 (C-3), 75.1 (C-2), 74.4 (CH_2Ph), 73.6 (C-7), 73.2 (C-4), 73.0 (CH_2Ph), 70.9 (C-5), 70.6 (CH_2Ph), 68.3 (C-6), 58.3 and 54.1 (2OCH_3). HR MS (LSIMS): $C_{30}H_{36}O_7+Na^+$ $[M+Na]^+$; Calcd: 531.23587. Found: 531.23506.

Methyl 7-*O*-allyl-2,3,4-tri-*O*-benzyl-D-*glycero*-β-D-*allo*-heptopyranoside (21). HPLC eluent: CH_2Cl_2–ether 8:1; yield: 31%; colourless needles, mp 80–81°C (from hexane–ether); $[\alpha]_D=+21.9$ (*c* 1.1, $CHCl_3$); ν_{max} (KBr) 3410 (br), 3033, 2921, 1497, 1455, 1204, 1134, 1067, 1025, 923, 739, 696 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.40–7.22 (15H, m, 3Ph), 5.93–5.84 (1H, m, OCH_2CHCH_2), 5.26–5.12 (2H, m, OCH_2CHCH_2), 4.91–4.34 (3×2H, 3ABq, 3CH_2Ph), 4.80 (1H, d, *J*=7.9 Hz, H-1), 4.12 (1H, dd, *J*=2.4, 2.6 Hz, H-3), 4.05–4.00 (2H, m, H-5, H-6), 4.00–3.94 (2H, m, OCH_2CHCH_2), 3.58–3.51 (2H, m, H-7a, H-7b), 3.52 (3H, s, OCH_3), 3.48 (1H, dd, *J*=2.4, 9.2 Hz, H-4), 3.18 (1H, dd, *J*=2.6, 7.9 Hz, H-2). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 138.8, 138.6 and 137.1 (Ph),134.8 (OCH_2CHCH_2), 128.5–127.4 (Ph), 117.0 (OCH_2CHCH_2), 102.1 (C-1), 78.9 (C-2), 78.0 (C-4), 74.4 (CH_2Ph), 74.1 (C-3), 73.0 (CH_2Ph), 72.5 and 71.6 (C-5, C-6), 72.3 (OCH_2CHCH_2), 71.0 (CH_2Ph), 70.8 (C-7), 56.8 (OCH_3). Anal. Calcd for $C_{32}H_{38}O_7$: C, 71.89; H, 7.16. Found: C, 71.88; H, 7.33.

Methyl 7-*O*-allyl-2,3,4-tri-*O*-benzyl-L-*glycero*-β-D-*allo*-heptopyranoside (22). HPLC eluent: CH_2Cl_2–ether 8:1; yield 37%; colourless oil; $[\alpha]_D=-9.2$ (*c* 1.4, $CHCl_3$); ν_{max} (film) 3480 (br), 3064, 3030, 2902, 1497, 1454, 1206, 1095, 1048, 1028, 926, 737, 698 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.45–7.22 (15H, m, 3Ph), 5.95–5.86 (1H, m, $OCH_2CH=CH_2$), 5.30–5.15 (2H, m, $OCH_2CH=CH_2$), 4.88–4.49 (3×2H, 3ABq, 3CH_2Ph), 4.79 (1H, d, *J*=7.9 Hz, H-1) 4.13–4.08 (1H, m, H-6), 4.09 (1H, dd, *J*=2.5, 2.6 Hz, H-3), 4.07–3.97 (2H, m, $OCH_2CH=CH_2$), 3.92 (1H, dd, *J*=1.4, 9.7 Hz, H-5), 3.62 (1H, dd, *J*=7.7, 9.8 Hz, H-7a), 3.60 (1H, dd, *J*=2.5, 9.7 Hz, H-4), 3.56 (1H, dd, *J*=4.8, 9.8 Hz, H-7b), 3.50 (3H, s, OCH_3), 3.18 (1H, dd, *J*=2.6, 7.9 Hz, H-2). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 139.0, 138.6 and 137.9 (Ph), 134.7 ($OCH_2CH=CH_2$), 128.4–127.3 (Ph), 117.1 ($OCH_2CH=CH_2$), 102.0 (C-1), 78.8 (C-2), 75.3 (C-4), 75.1 (C-3), 74.5 (CH_2Ph), 72.8 (CH_2Ph), 72.3 ($OCH_2CH=CH_2$), 71.9 (CH_2Ph), 71.8 (C-7), 71.7 (C-5), 68.2 (C-6), 56.7 (OCH_3). HR MS (ESI): $C_{32}H_{38}O_7+Na^+$ $[M+Na]^+$; Calcd: 557.2510. Found: 557.2499.

Methyl 7-*O*-allyl-2,3,4-tri-*O*-benzyl-D(L)-*glycero*-α-L-*talo*-heptopyranoside (23). HPLC eluent: CH_2Cl_2–ether 8:1; yield 9%; colourless oil; $[\alpha]_D=-43.5$ (*c* 1.8, $CHCl_3$); ν_{max} (film) 3471 (br), 3064, 3031, 2910, 2867, 1497, 1454, 1359, 1202, 1135, 1055, 1028, 736, 698 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.42–7.20 (15H, m, 3Ph), 5.92–5.84 (1H, m, $OCH_2CH=CH_2$), 5.27–5.14 (2H, m, $OCH_2CH=CH_2$), 5.06–4.50 (3×2H, 3ABq, 3CH_2Ph), 4.83 (1H, d, *J*=1.1 Hz, H-1), 4.22 (1H, ddd, *J*=3.5, 4.7, 9.0 Hz, H-6), 4.15–4.12 (1H, m, H-4), 4.03–3.95 (2H, m, $OCH_2CH=CH_2$), 3.76 (1H, dd, *J*=1.1, 3.3 Hz, H-2), 3.71 (1H, dd, *J*=3.1, 3.3 Hz, H-3), 3.66 (1H, dd, *J*=1.3, 9.0 Hz, H-5), 3.65 (1H, dd, *J*=3.5, 9.8 Hz, H-7a), 3.62 (1H, dd, *J*=4.7, 9.8 Hz, H-7b), 3.28 (3H, s, OCH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 139.2, 138.7 and 138.3 (Ph), 134.5 ($OCH_2CH=CH_2$), 128.3–127.1 (Ph), 117.1 ($OCH_2CH=CH_2$), 100.6 (C-1), 77.4 (C-3), 74.0 (CH_2Ph), 74.0 (C-2), 73.2 (CH_2Ph), 72.3 (C-4), 72.2 ($OCH_2CH=CH_2$), 70.9 (C-7), 70.8 (CH_2Ph), 70.4 (C-5), 68.0 (C-6), 54.7 (OCH_3). HR MS (ESI): $C_{36}H_{40}O_7+H^+$ $[M+H]^+$; Calcd: 535.2690. Found: 535.2672. Anal. Calcd for $C_{32}H_{38}O_7$: C, 71.89; H, 7.16. Found: C, 71.68; H, 7.02.

Methyl 7-deoxy-2,3,4-tri-*O*-benzyl-7-(phenyldimethylsilyl)-L-*glycero*-β-D-*allo*-heptopyranoside (24). Column chromatography, eluent hexane–ethyl acetate 6:1; yield 70%; colourless oil; $[\alpha]_D=-20.2$ (*c* 1.4, $CHCl_3$); ν_{max} (film) 3517 (br), 3066, 3031, 2897, 1497, 1454, 1250, 1205, 1126, 1087, 838, 735, 699 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.55–7.19 (20H, m, 4Ph), 4.85–4.42 (3×2H, 3ABq, 3CH_2Ph), 4.67 (1H, d, *J*=7.9 Hz, H-1), 4.07 (1H, dd, *J*=2.4, 2.6 Hz, H-3), 4.08–4.03 (1H, m, H-6), 3.68 (1H, dd, *J*=1.2, 9.6 Hz, H-5), 3.49 (3H, s, OCH_3), 3.46 (1H, dd, *J*=2.4, 9.6 Hz, H-4), 3.12 (1H, dd, *J*=2.6, 7.9 Hz, H-2), 1.32 (1H, dd, *J*=9.3, 14.6 Hz, H-7a),

1.12 (1H, dd, J=5.9, 14.6 Hz, H-7b), 0.34, 0.33 (2×3H, 2s, $(CH_3)_2Si$). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 139.2, 139.1, 138.6, 138.0, 133.6 and 128.8–127.3 (Ph), 102.0 (C-1), 78.9 (C-2), 76.0 (C-4), 75.1 (C-5), 75.0 (C-3), 74.3 (CH_2Ph), 72.8 (CH_2Ph), 71.8 (CH_2Ph), 67.3 (C-6), 56.9 (OCH_3), 21.9 (C-7), −2.1 and −2.6 [$(CH_3)_2Si$]. HR MS (ESI): $C_{37}H_{44}O_6Si+Na^+$ $[M+Na]^+$; Calcd: 635.2804. Found: 635.2799. Anal. Calcd for $C_{37}H_{44}O_6Si$: C, 72.52; H, 7.24. Found: C, 72.44; H, 7.41.

Methyl 2,3,4,7-tetra-*O*-benzyl-D-*glycero*-α-D-*gluco*-heptopyranoside (25). Column chromatography, eluent hexane–ethyl acetate 3:1; yield 53%; colourless oil; $[\alpha]_D$=+19.7 (c 1.7, $CHCl_3$); ν_{max} (film) 3481 (br), 3089, 3064, 3031, 2917, 2870, 1497, 1454, 1361, 1209, 1195, 1160, 1072, 1030, 738, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.38–7.15 (20H, m, 4Ph), 5.02–4.42 (4×2H, 4ABq, 4CH_2Ph), 4.56 (1H, d, J=3.6 Hz, H-1), 4.07–4.03 (1H, m, H-6), 4.00 (1H, dd, J=9.6, 10.0 Hz, H-3), 3.76 (1H, dd, J=3.7, 10.0 Hz, H-5), 3.55 (1H, dd, J=10.0, 10.0 Hz, H-4), 3.54–3.47 (2H, m, H-7a, H-7b), 3.49 (1H, dd, J=3.6, 9.6 Hz, H-2), 3.35 (3H, s, OCH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 138.6, 138.1, 138.0, 137.9 and 128.4–127.6 (Ph), 97.8 (C-1), 82.4 (C-3), 80.0 (C-2), 78.7 (C-4), 75.7 (CH_2Ph), 74.7 (CH_2Ph), 73.4 (CH_2Ph), 73.3 (CH_2Ph), 71.7 (C-6), 70.9 (C-7), 70.1 (C-5), 55.2 (OCH_3). ^1H NMR (500 MHz, C_6D_6) δ: 7.35–7.05 (20H, m, 4Ph), 5.04–4.33 (4×2H, 4ABq, 4CH_2Ph), 4.59 (1H, d, J=3.5 Hz, H-1), 4.27–4.22 (1H, m, H-6), 4.23 (1H, dd, J=9.0, 9.6 Hz, H-3), 4.03 (1H, dd, J=3.4, 10.0 Hz, H-5), 3.72 (1H, dd, J=9.0, 10.0 Hz, H-4), 3.68 (1H, dd, J=6.9, 9.8 Hz, H-7a), 3.59 (1H, dd, J=3.8, 9.8 Hz, H-7b), 3.49 (1H, dd, J=3.5, 9.6 Hz, H-2), 3.16 (3H, s, OCH_3). HR MS (LSIMS): $C_{36}H_{40}O_7+Na^+$ $[M+Na]^+$; Calcd: 607.26717. Found: 607.26958. Anal. Calcd for $C_{36}H_{40}O_7$: C, 73.95; H, 6.90. Found: C, 73.69; H, 6.82.

Methyl 2,3,4,7-tetra-*O*-benzyl-L-*glycero*-α-D-*gluco*-heptopyranoside (26). Column chromatography, eluent hexane–ethyl acetate 3:1; yield 35%; colourless needles, mp 58–59°C (from hexane–ether), $[\alpha]_D$=+4.9 (c 1.6, $CHCl_3$); ν_{max} (film) 3481 (br), 3089, 3064, 3031, 2929, 2865, 1497, 1454, 1361, 1165, 1136, 1102, 1053, 737, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.40–7.20 (20H, m, 4Ph), 5.02–4.51 (4×2H, 4ABq, 4CH_2Ph), 4.58 (1H, d, J=3.6 Hz, H-1), 4.19–4.12 (1H, m, H-6), 4.01 (1H, dd, J=9.2, 9.5 Hz, H-3), 3.75 (1H, dd, J=9.2, 10.00 Hz, H-4), 3.67 (1H, dd, J<1, 10.00 Hz, H-5), 3.64 (1H, dd, J=8.1, 9.5 Hz, H-7a), 3.54 (1H, dd, J=5.3, 9.5 Hz, H-7b), 3.53 (1H, dd, J=3.6, 9.5 Hz, H-2), 3.31 (3H, s, OCH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 138.8, 138.3, 138.1, 137.9 and 128.4–127.5 (Ph), 98.3 (C-1), 82.1 (C-3), 79.7 (C-2), 77.2 (C-4), 75.7 (CH_2Ph), 75.1 (CH_2Ph), 73.4 (CH_2Ph), 73.4 (CH_2Ph), 71.6 (C-7), 69.6 (C-5), 67.6 (C-6), 55.1 (OCH_3). HR MS (LSIMS): $C_{36}H_{40}O_7+Na^+$ $[M+Na]^+$; Calcd: 607.26715. Found: 607.26970. Anal. Calcd for $C_{36}H_{40}O_7$: C, 73.95; H, 6.90. Found: C, 73.65; H, 6.67.

Methyl 2,3,4-tri-*O*-benzyl-7-*O*-methyl-D-*glycero*-α-D-*gluco*-heptopyranoside (27). HPLC eluent: hexane–ethyl acetate 2:1; yield 40%; colourless oil; $[\alpha]_D$=+26.6 (c 1.6, $CHCl_3$); ν_{max} (film) 3479 (br), 3064, 3031, 2924, 1454, 1360, 1195, 1159, 1072, 1030, 738, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.38–7.25 (15H, m, 3Ph), 5.04–4.64 (3×2H, 3ABq, 3CH_2Ph), 4.58 (1H, d, J=3.6 Hz, H-1), 4.02 (1H, dd, J=9.1, 9.6 Hz, H-3), 4.02–3.97 (1H, m, H-6), 3.77 (1H, dd, J=4.2, 10.0 Hz, H-5), 3.58 (1H, dd, J=9.1, 10.0 Hz, H-4), 3.51 (1H, dd, J=3.6, 9.6 Hz, H-2), 3.45 (1H, dd, J=6.9, 9.9 Hz, H-7a), 3.41 (1H, dd, J=3.5, 9.9 Hz, H-7b), 3.39, 3.31 (2×3H, 2s, 2OCH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 138.6, 138.1, 137.8 and 128.5–127.6 (Ph), 97.8 (C-1), 82.4 (C-3), 80.1 (C-2), 79.0 (C-4), 75.7 (CH_2Ph), 74.7 (CH_2Ph), 73.3 (CH_2Ph), 73.2 (C-7), 71.6 (C-6), 69.8 (C-5), 59.0 and 55.2 (2OCH_3). HR MS (LSIMS): $C_{30}H_{36}O_7+Na^+$ $[M+Na]^+$; Calcd: 531.23587. Found: 531.23574.

Methyl 2,3,4-tri-*O*-benzyl-7-*O*-methyl-L-*glycero*-α-D-*gluco*-heptopyranoside (28). HPLC, eluent hexane–ethyl acetate 2:1; yield 35%; colourless needles, mp 83–84°C (from hexane–ether); $[\alpha]_D$=+16.0 (c 1.4, $CHCl_3$); ν_{max} (KBr) 3488 (br), 3063, 3029, 3002, 2938, 2897, 2866, 1498, 1455, 1360, 1117, 1072, 1056, 1029, 964, 740, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.37–7.24 (15H, m, 3Ph), 5.00–4.62 (3×2H, 3ABq, 3CH_2Ph), 4.57 (1H, d, J=3.6 Hz, H-1), 4.11–4.05 (1H, m, H-6), 3.98 (1H, dd, J=9.0, 9.6 Hz, H-3), 3.71 (1H, dd, J=9.0, 10.00 Hz, H-4), 3.62 (1H, dd, J=1.0, 10.00 Hz, H-5), 3.51 (1H, dd, J=8.1, 9.5 Hz, H-7a), 3.51 (1H, dd, J=3.6, 9.6 Hz, H-2), 3.41 (1H, dd, J=4.9, 9.5 Hz, H-7b), 3.35, 3.33 (2×3H, 2s, 2OCH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 138.8, 138.3, 138.1 and 128.4–127.5 (Ph), 98.3 (C-1), 82.1 (C-3), 79.7 (C-2), 77.1 (C-4), 75.7 (CH_2Ph), 75.1 (CH_2Ph), 74.0 (C-7), 73.4 (CH_2Ph), 69.6 (C-5), 67.4 (C-6), 59.0, 55.0 (2OCH_3). HR MS (LSIMS): $C_{30}H_{36}O_7+Na^+$ $[M+Na]^+$; Calcd: 531.23590. Found: 531.23458.

Methyl 7-*O*-allyl-2,3,4-tri-*O*-benzyl-D-*glycero*-α-D-*gluco*-heptopyranoside (29). Column chromatography, eluent hexane–ethyl acetate 3:1; yield 50%; colourless oil; $[\alpha]_D$=+23.5 (c 2.3, $CHCl_3$); ν_{max} (film) 3482 (br), 3031, 2914, 1454, 1360, 1159, 1139, 1072, 1030, 738, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.37–7.24 (15H, m, 3Ph), 5.90–5.81 (1H, m, OCH_2CH=CH_2), 5.23–5.11 (2H, m, OCH_2CH=CH_2), 5.02–4.63 (3×2H, 3ABq, 3CH_2Ph), 4.57 (1H, d, J=3.6 Hz, H-1), 4.04–3.99 (1H, m, H-6), 4.01 (1H, dd, J=9.0, 10.0 Hz, H-3), 3.94–3.91 (2H, m, OCH_2CH=CH_2), 3.77 (1H, dd, J=3.9, 9.8 Hz, H-5), 3.58 (1H, dd, J=9.0, 9.8 Hz, H-4), 3.50 (1H, dd, J=3.6, 10.0 Hz, H-2), 3.50–3.45 (2H, m, H-7a, H-7b), 3.38 (3H, s, OCH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 138.6, 138.0 and 137.9 (Ph), 134.5 (OCH_2CH=CH_2), 128.4–127.6 (Ph), 117.2 (OCH_2CH=CH_2), 97.8 (C-1), 82.3 (C-3), 80.0 (C-2), 78.8 (C-4), 75.6 (CH_2Ph), 74.7 (CH_2Ph), 73.2 (CH_2Ph), 72.3 (OCH_2CH=CH_2), 71.7 (C-6), 70.8 (C-7), 69.9 (C-5), 55.2 (OCH_3). HR MS (LSIMS): $C_{32}H_{38}O_7+Na^+$ $[M+Na]^+$; Calcd: 557.25152. Found: 557.25135.

Methyl 7-*O*-allyl-2,3,4-tri-*O*-benzyl-L-*glycero*-α-D-*gluco*-heptopyranoside (30). Column chromatography, eluent hexane–ethyl acetate 3:1; yield 41%; colourless needles, mp 80–81°C (from hexane–ethyl acetate), $[\alpha]_D$=+9.6 (c 1.0, $CHCl_3$); ν_{max} (KBr) 3489 (br), 3063, 3034, 2937, 2869, 1455, 1361, 1167, 1139, 1104, 1058, 1003, 948, 922, 739, 699 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.42–7.20 (15H,

m, 3Ph), 5.93–5.83 (1H, m, $OCH_2CH{=}CH_2$), 5.28–5.14 (2H, m, $OCH_2CH{=}CH_2$), 4.99–4.62 (3×2H, 3ABq, $3CH_2Ph$), 4.57 (1H, d, J=3.6 Hz, H-1), 4.14–4.07 (1H, m, H-6), 4.03–3.95 (3H, m, H-3, $OCH_2CH{=}CH_2$), 3.72 (1H, dd, J=8.9, 10.0 Hz, H-4), 3.64 (1H, dd, J=0.9, 10.0 Hz, H-5), 3.56 (1H, dd, J=8.0, 9.5 Hz, H-7a), 3.51 (1H, dd, J=3.6, 9.7 Hz, H-2), 3.47 (1H, dd, J=5.0, 9.5 Hz, H-7b), 3.32 (3H, s, OCH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 138.8, 138.3 and 138.1 (Ph), 134.4 ($OCH_2CH{=}CH_2$), 128.4–127.5 (Ph), 117.2 ($OCH_2CH{=}CH_2$), 98.3 (C-1), 82.1 (C-3), 79.7 (C-2), 77.2 (C-4), 75.7 (CH_2Ph), 75.1 (CH_2Ph), 73.4 (CH_2Ph), 72.3 ($OCH_2CH{=}CH_2$), 71.4 (C-7), 69.6 (C-5), 67.5 (C-6), 55.1 (OCH_3). HR MS (LSIMS): $C_{32}H_{38}O_7+Na^+$ $[M+Na]^+$; Calcd: 557.25153. Found: 557.25514. Anal. Calcd for $C_{32}H_{38}O_7$: C, 71.89; H, 7.16. Found: C, 71.77; H, 7.13.

Methyl 7-deoxy-2,3,4-tri-*O*-benzyl-7-(phenyldimethylsilyl)-L-*glycero*-α-D-*gluco*-heptopyranoside (31). Column chromatography, eluent hexane–ethyl acetate 8:1; yield 50%; colourless oil; $[\alpha]_D$=+5.8 (c 0.8, $CHCl_3$); ν_{max} (film) 3513 (br), 3067, 3031, 2929, 1454, 1361, 1250, 1160, 1111, 1088, 1072, 1052, 1029, 914, 837, 734, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 7.55–7.17 (20H, m, 4Ph), 5.00–4.58 (3×2H, 3ABq, $3CH_2Ph$), 4.59 (1H, d, J=3.6 Hz, H-1), 4.04 (1H, ddd, J=0.7, 3.9, 10.8 Hz, H-6), 3.97 (1H, dd, J=9.2, 9.6 Hz, H-3), 3.57 (1H, dd, J=9.6, 9.6 Hz, H-4), 3.48 (1H, dd, J=3.6, 9.6 Hz, H-2), 3.39 (1H, dd, J=0.7, 9.6 Hz, H-5), 3.34 (3H, s, OCH_3), 1.34 (1H, dd, J=10.8, 14.9 Hz, H-7a), 0.90 (1H, dd, J=3.9, 14.9 Hz, H-7b), 0.34, 0.33 (2×3H, 2s, $(CH_3)_2Si$). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 139.1, 138.8, 138.2, 138.1, 133.6 and 128.9–127.6 (Ph), 98.2 (C-1), 82.1 (C-3), 80.0 (C-2), 77.8 (C-4), 75.7 (CH_2Ph), 75.2 (CH_2Ph), 74.1 (C-5), 73.4 (CH_2Ph), 66.7 (C-6), 55.2 (OCH_3), 21.6 (C-7), −2.1 and −2.4 [$(CH_3)_2Si$]. HR MS (LSIMS): $C_{37}H_{44}O_6Si+Na^+$ $[M+Na]^+$; Calcd: 635.28049. Found: 635.28177.

Methyl 2,3,4,7-tetra-*O*-benzyl-D-*glycero*-α-D-*galacto*-heptopyranoside (32). Column chromatography, eluent hexane–ethyl acetate 7:2; yield 48%; colourless oil; $[\alpha]_D$=+32.0 (c 1.64, $CHCl_3$); ν_{max} (film) 3487 (br), 3031, 2912, 2865, 1497, 1454, 1353, 1196, 1105, 1054, 1028, 906, 737, 698 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.40–7.20 (20H, m, 4Ph), 5.01–4.46 (4×2H, 4ABq, $4CH_2Ph$), 4.63 (1H, d, J=3.6 Hz, H-1), 4.18–4.16 (1H, m, H-4), 4.03 (1H, dd, J=3.6, 10.1 Hz, H-2), 3.99–3.92 (1H, m, H-6), 3.92 (1H, dd, J=2.8, 10.1 Hz, H-3), 3.67 (1H, dd, J<1, 8.8 Hz, H-5), 3.65 (1H, dd, J=3.1, 9.5 Hz, H-7a), 3.58 (1H, dd, J=5.2, 9.5 Hz, H-7b), 3.28 (3H, s, OCH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 138.8, 138.8, 138.5, 137.8 and 128.4–127.5 (Ph), 98.9 (C-1), 79.2 (C-3), 76.2 (C-2), 74.8 (CH_2Ph), 74.5 (C-4), 73.5 (CH_2Ph), 73.4 (CH_2Ph), 73.1 (CH_2Ph), 71.1 (C-7), 69.7 (C-5), 68.1 (C-6), 55.2 (OCH_3). HR MS (LSIMS): $C_{36}H_{40}O_7+Na^+$ $[M+Na]^+$; Calcd: 607.26717. Found: 607.26607. Anal. Calcd for $C_{36}H_{40}O_7$: C, 73.95; H, 6.90. Found: C, 74.00; H, 6.85.

Methyl 2,3,4,7-tetra-*O*-benzyl-L-*glycero*-α-D-*galacto*-heptopyranoside (33). Column chromatography, eluent hexane–ethyl acetate 7:2; yield 32%; colourless oil; $[\alpha]_D$=+11.2 (c 2.41, $CHCl_3$); ν_{max} (film) 3494 (br), 3031, 2908, 1497, 1454, 1351, 1195, 1130, 1099, 1049, 782, 737, 698 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.40–7.22 (20H, m, 4Ph), 5.04–4.39 (4×2H, 4ABq, $4CH_2Ph$), 4.74 (1H, d, J=3.6 Hz, H-1), 4.05 (1H, dd, J=3.6, 10.0 Hz, H-2), 3.98–3.90 (1H, m, H-6), 3.94 (1H, dd, J=2.7, 10.0 Hz, H-3), 3.92–3.90 (1H, m, H-4), 3.81 (1H, dd, J<1, 4.4 Hz, H-5), 3.46 (1H, dd, J=6.1, 9.6 Hz, H-7a), 3.34 (3H, s, OCH_3), 3.32 (1H, dd, J=4.7, 9.6 Hz, H-7b). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 138.6, 138.4, 137.9, 137.9 and 128.4–127.5 (Ph), 98.8 (C-1), 79.3 (C-3), 77.3 (C-4), 76.1 (C-2), 74.4 (CH_2Ph), 73.7 (CH_2Ph), 73.5 (CH_2Ph), 73.4 (CH_2Ph), 71.0 (C-6), 69.8 (C-7), 68.9 (C-5), 55.3 (OCH_3). HR MS (LSIMS): $C_{36}H_{40}O_7+Na^+$ $[M+Na]^+$; Calcd: 607.26715. Found: 607.26602. Anal. Calcd for $C_{36}H_{40}O_7$: C, 73.95; H, 6.90. Found: C, 73.79; H, 6.99.

Methyl 2,3,4-tri-*O*-benzyl-7-*O*-methyl-D-*glycero*-α-D-*galacto*-heptopyranoside (34). Column chromatography, eluent hexane–ethyl acetate 3:1; yield 75%; colourless oil; $[\alpha]_D$=+40.5 (c 2.41, $CHCl_3$); ν_{max} (film) 3479 (br), 3031, 2923, 1497, 1454, 1351, 1194, 1116, 1055, 1028, 904, 783, 737, 698 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.40–7.23 (15H, m, 3Ph), 5.01–4.67 (3×2H, 3ABq, $3CH_2Ph$), 4.65 (1H, d, J=3.7 Hz, H-1), 4.18–4.16 (1H, m, H-4), 4.04 (1H, dd, J=3.7, 10.1 Hz, H-2), 3.93 (1H, dd, J=2.8, 10.1 Hz, H-3), 3.94–3.89 (1H, m, H-6), 3.63 (1H, dd, J<1, 9.1 Hz, H-5), 3.52 (1H, dd, J=3.0, 9.6 Hz, H-7a), 3.46 (1H, dd, J=5.2, 9.6 Hz, H-7b), 3.34, 3.32 (2×3H, 2s, $2OCH_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 138.8, 138.7, 138.5 and 128.3–127.4 (Ph), 98.8 (C-1), 79.1 (C-3), 76.2 (C-2), 74.8 (CH_2Ph), 74.4 (C-4), 73.5 (CH_2Ph), 73.3 (C-7), 73.1 (CH_2Ph), 69.6 (C-5), 67.8 (C-6), 58.9 (OCH_3), 55.0 (OCH_3). HR MS (LSIMS): $C_{30}H_{36}O_7+Na^+$ $[M+Na]^+$; Calcd: 531.23590. Found: 531.23702.

Methyl 2,3,4-tri-*O*-benzyl-7-*O*-methyl-L-*glycero*-α-D-*galacto*-heptopyranoside (35). Column chromatography, eluent hexane–ethyl acetate 3:1; yield 17%; colourless oil; $[\alpha]_D$=+15.1 (c 0.84, $CHCl_3$); ν_{max} (film) 3493 (br), 3031, 2900, 1497, 1455, 1351, 1196, 1128, 1099, 1048, 970, 782, 737, 698 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.41–7.25 (15H, m, 3Ph), 5.10–4.64 (3×2H, 3ABq, $3CH_2Ph$), 4.75 (1H, d, J=3.6 Hz, H-1), 4.06 (1H, dd, J=3.6, 10.8 Hz, H-2), 3.96 (1H, dd, J=2.8, 10.8 Hz, H-3), 3.97–3.96 (1H, m, H-4), 3.95–3.90 (1H, m, H-6) 3.75 (1H, dd, J<1, 4.1 Hz, H-5), 3.36 (3H, s, OCH_3), 3.34 (1H, dd, J=6.0, 9.6 Hz, H-7a), 3.29 (3H, s, OCH_3), 3.23 (1H, dd, J=5.0, 9.6 Hz, H-7b). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 138.6, 138.3, 137.8 and 128.4–127.5 (Ph), 98.7 (C-1), 79.3 (C-3), 77.4 (C-4), 76.1 (C-2), 74.4 (CH_2Ph), 73.7 (CH_2Ph), 73.5 (CH_2Ph), 72.5 (C-7), 70.8 (C-6), 68.8 (C-5), 59.0 (OCH_3), 55.2 (OCH_3). HR MS (LSIMS): $C_{30}H_{36}O_7+Na^+$ $[M+Na]^+$; Calcd: 531.23590. Found: 531.23608.

Methyl 7-*O*-allyl-2,3,4-tri-*O*-benzyl-D-*glycero*-α-D-*galacto*-heptopyranoside (36). Column chromatography, eluent hexane–ethyl acetate 7:2; yield 69%; colourless oil; $[\alpha]_D$=+35.7 (c 1.81, $CHCl_3$); ν_{max} (film) 3481 (br), 3064, 3031, 2914, 1497, 1454, 1351, 1195, 1105, 1055, 1028, 934, 904, 784, 737, 698 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.40–7.23 (15H, m, 3Ph), 5.91–5.82 (1H, m, OCH_2CHCH_2), 5.27–5.15 (2H, m, OCH_2CHCH_2), 5.02–4.66 (3×2H, 3ABq, $3CH_2Ph$), 4.64 (1H, d, J=3.6 Hz, H-1), 4.19–4.17 (1H, m, H-4), 4.04 (1H, dd, J=3.6,

10.1 Hz, H-2), 4.02–3.91 (3H, m, H-6, OCH_2CHCH$_2$), 3.93 (1H, dd, J=2.8, 10.1 Hz, H-3), 3.65 (1H, dd, J<1, 9.0 Hz, H-5), 3.59 (1H, dd, J=3.1, 9.6 Hz, H-7a), 3.52 (1H, dd, J=5.2, 9.6 Hz, H-7b), 3.32 (3H, s, OCH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 138.8, 138.8 and 138.5 (Ph), 134.4 (OCH$_2$*C*HCH$_2$), 128.3–127.4 (Ph), 117.2 (OCH$_2$CH*C*H$_2$), 98.8 (C-1), 79.2 (C-3), 76.2 (C-2), 74.8 (*C*H$_2$Ph), 74.5 (C-4), 73.5 (*C*H$_2$Ph), 73.1 (*C*H$_2$Ph), 72.2 (O*C*H$_2$CHCH$_2$), 70.9 (C-7), 69.7 (C-5), 68.0 (C-6), 55.1 (OCH_3). HR MS (LSIMS): $C_{32}H_{38}O_7$+Na$^+$ [M+Na]$^+$; Calcd: 557.25152. Found: 557.25052.

Methyl 7-*O*-allyl-2,3,4-tri-*O*-benzyl-L-*glycero*-α-D-*galacto*-heptopyranoside (37). Column chromatography, eluent hexane–ethyl acetate 7:2; yield 18%; colourless oil; $[\alpha]_D$=+16.2 (c 1.39, $CHCl_3$); ν_{max} (film) 3492 (br), 3064, 3031, 2909, 1497, 1454, 1350, 1195, 1131, 1099, 1049, 929, 782, 737, 698 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.41–7.24 (15H, m, 3Ph), 5.89–5.80 (1H, m, OCH$_2$C*H*CH$_2$), 5.25–5.14 (2H, m, OCH$_2$CHC*H*$_2$), 5.09–4.64 (3×2H, 3ABq, 3C*H*$_2$Ph), 4.75 (1H, d, J=3.6 Hz, H-1), 4.06 (1H, dd, J=3.6, 10.0 Hz, H-2), 4.00–3.98 (1H, m, H-4), 3.96 (1H, dd, J=2.7, 10.0 Hz, H-3), 3.98–3.89 (3H, m, H-6, OC*H*$_2$CHCH$_2$), 3.79 (1H, dd, J<1, 3.7 Hz, H-5), 3.41 (1H, dd, J=6.3, 9.6 Hz, H-7a), 3.36 (3H, s, OCH_3), 3.31 (1H, dd, J=5.0, 9.6 Hz, H-7b). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 138.6, 138.3 and 137.9 (Ph), 134.4 (OCH$_2$*C*HCH$_2$), 128.4–127.5 (Ph), 117.3 (OCH$_2$CH*C*H$_2$), 98.8 (C-1), 79.3 (C-3), 77.5 (C-4), 76.1 (C-2), 74.4 (*C*H$_2$Ph), 73.7 (*C*H$_2$Ph), 73.5 (*C*H$_2$Ph), 72.3 (O*C*H$_2$CHCH$_2$), 71.0 (C-6), 69.9 (C-7), 68.7 (C-5), 55.2 (OCH_3). HR MS (LSIMS): $C_{32}H_{38}O_7$+Na$^+$ [M+Na]$^+$; Calcd: 557.25152. Found: 557.25110.

Methyl 7-deoxy-2,3,4-tri-*O*-benzyl-7-(phenyldimethylsilyl)-D-*glycero*-α-D-*galacto*-heptopyranoside (38). HPLC eluent: hexane–CH_2Cl_2–ether 10:20:1; yield: 1.3%; colourless oil; $[\alpha]_D$=+10.5 (c 0.43, $CHCl_3$); ν_{max} (film) 3579, 3491 (br), 3066, 3031, 2911, 1454, 1351, 1248, 1196, 1112, 1053, 1029, 835, 779, 735, 699 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.51–7.24 (20H, m, 4Ph), 4.95–4.64 (3×2H, 3ABq, 3C*H*$_2$Ph), 4.66 (1H, d, J=3.7 Hz, H-1), 4.03 (1H, dd, J=3.7, 10.1 Hz, H-2), 4.03–4.00 (1H, m, H-4), 3.81 (1H, dd, J=2.7, 10.1 Hz, H-3), 3.81–3.74 (1H, m, H-6), 3.32 (3H, s, OCH_3), 3.22 (1H, dd, J<1, 7.6 Hz, H-5), 1.22 (1H, dd, J=3.6, 14.8 Hz, H-7a), 0.81 (1H, dd, J=10.9, 14.8 Hz, H-7b), 0.27, 0.26 (2×3H, 2s, $(CH_3)_2$Si). ^{13}C NMR ($CDCl_3$) δ: 139.3, 138.8, 138.5, 138.4, 133.6 and 129.0–127.6 (Ph), 98.8 (C-1), 79.6 (C-3), 76.6 (C-2), 74.4 (C-5), 74.1 (*C*H$_2$Ph), 73.6 (*C*H$_2$Ph), 73.5 (*C*H$_2$Ph), 73.1 (C-4), 67.8 (C-6), 55.2 (OCH_3), 21.5 (C-7), −2.0 and −2.5 [$(CH_3)_2$Si]. HR MS (ESI): $C_{37}H_{44}O_6Si$+Na$^+$ [M+Na]$^+$; Calcd: 635.2799. Found: 635.2774.

Methyl 7-deoxy-2,3,4-tri-*O*-benzyl-7-(phenyldimethylsilyl)-L-*glycero*-α-D-*galacto*-heptopyranoside (39). HPLC eluent: hexane–CH_2Cl_2–ether 10:20:1; yield: 81%; colourless oil; $[\alpha]_D$=−7.5 (c 1.2, $CHCl_3$); ν_{max} (film) 3576, 3510 (br), 3066, 3031, 2907, 1454, 1350, 1248, 1198, 1132, 1112, 1049, 1029, 945, 834, 783, 735, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 7.51–7.18 (20H, m, 4Ph), 4.99–4.53 (3×2H, 3ABq, 3C*H*$_2$Ph), 4.70 (1H, d, J=3.7 Hz, H-1), 4.02 (1H, dd, J=3.7, 10.1 Hz, H-2), 3.96 (1H, ddd, J=3.3, 6.4, 10.8 Hz, H-6), 3.91–3.89 (1H, m, H-4), 3.85 (1H, dd, J=2.6, 10.1 Hz, H-3), 3.36–3.34 (1H, m, H-5), 3.35 (3H, s, OCH_3), 0.92 (1H, dd, J=10.8, 14.4 Hz, H-7a), 0.73–0.67 (1H, m, H-7b), 0.32, 0.31 (2×3H, 2s, $(CH_3)_2$Si). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 139.5, 138.7, 138.3, 138.0, 133.6 and 128.8–127.4 (Ph), 98.7 (C-1), 79.6 (C-3), 76.2 (C-2), 75.8 (C-4),75.3 (C-5), 74.4 (*C*H$_2$Ph), 73.7 (*C*H$_2$Ph), 73.5 (*C*H$_2$Ph), 68.9 (C-6), 55.4 (OCH_3), 19.8 (C-7), −1.7 and −2.4 [$(CH_3)_2$Si]. HR MS (LSIMS): $C_{37}H_{44}O_6Si$+Na$^+$ [M+Na]$^+$; Calcd: 635.28052. Found: 635.27944. Anal. Calcd for $C_{37}H_{44}O_6Si$: C, 72.52; H, 7.24. Found: C, 72.34; H, 7.21.

7-*O*-Benzyl-1,2:3,4-di-*O*-isopropylidene-D-*glycero*-α-D-*galacto*-heptopyranose (40). HPLC eluent: hexane–ethyl acetate 5:2; yield: 43%; colourless oil; $[\alpha]_D$=−50.6 (c 1.3, $CHCl_3$); ν_{max} (film) 3496 (br), 2988, 2937, 1497, 1455, 1382, 1256, 1170, 1104, 1001, 898, 805, 739, 699 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.35–7.20 (5H, m, Ph), 5.51 (1H, d, J=5.0 Hz, H-1), 4.62 (1H, dd, J=2.4, 8.0 Hz, H-3), 4.58 (2H, s, C*H*$_2$Ph), 4.47 (1H, dd, J=1.9, 8.0 Hz, H-4), 4.31 (1H, dd, J=2.4, 5.0 Hz, H-2), 4.02–3.95 (1H, m, H-6), 3.83 (1H, dd, J=1.9, 8.7 Hz, H-5), 3.74 (1H, dd, J=3.3, 9.8 Hz, H-7a), 3.65 (1H, dd, J=5.3, 9.8 Hz, H-7b), 1.49, 1.46, 1.37, 1.32 (4×3H, 4s, 2×$(CH_3)_2$C). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 138.1, 128.3, 127.6 and 127.6 (Ph), 109.2 and 108.7 (2×$(CH_3)_2$*C*), 96.3 (C-1), 73.4 (*C*H$_2$Ph), 71.2 (C-7), 70.8 (C-4), 70.7 (C-2), 70.6 (C-3), 68.9 (C-6), 67.0 (C-5), 26.0, 25.9, 25.0 and 24.4 (2×(*C*H$_3$)$_2$C). HR MS (LSIMS): $C_{20}H_{28}O_7$+Na$^+$ [M+Na]$^+$; Calcd: 403.17327. Found: 403.17489. Anal. Calcd for $C_{20}H_{28}O_7$: C, 63.14; H, 7.42. Found: C, 62.89; H, 7.61.

7-*O*-Benzyl-1,2:3,4-di-*O*-isopropylidene-L-*glycero*-α-D-*galacto*-heptopyranose (41). HPLC eluent: hexane–ethyl acetate 5:2; yield: 37%; colourless oil; $[\alpha]_D$=−44.6 (c 2.22, $CHCl_3$); ν_{max} (film) 3523 (br), 2988, 2936, 1497, 1455, 1383, 1256, 1213, 1169, 1114, 1070, 1004, 901, 835, 738, 699 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.35–7.20 (5H, m, Ph), 5.60 (1H, d, J=5.0 Hz, H-1), 4.63 (1H, d, J=11.9 Hz, C*H*HPh), 4.58 (1H, dd, J=2.4, 8.0 Hz, H-3), 4.53 (1H, d, J=11.9 Hz, CH*H*Ph), 4.32 (1H, dd, J=2.4, 5.0 Hz, H-2), 4.26 (1H, dd, J=1.8, 8.0 Hz, H-4), 4.08–4.04 (1H, m, H-6), 3.96 (1H, dd, J=1.8, 5.1 Hz, H-5), 3.69 (1H, dd, J=5.5, 9.9 Hz, H-7a), 3.63 (1H, dd, J=4.5, 9.9 Hz, H-7b), 1.49, 1.46, 1.33, 1.31 (4×3H, 4s, 2×$(CH_3)_2$C). ^{13}C NMR ($CDCl_3$) δ: 138.2, 128.3, 127.7 and 127.5 (Ph), 109.5 and 108.8 (2×$(CH_3)_2$*C*), 96.5 (C-1), 73.5 (*C*H$_2$Ph), 72.6 (C-4), 70.9 (C-3), 70.7 (C-6), 70.7 (C-2), 69.9 (C-7), 66.9 (C-5), 25.9, 25.8, 25.0 and 24.1 (2×(*C*H$_3$)$_2$C). HR MS (LSIMS): $C_{20}H_{28}O_7$+Na$^+$ [M+Na]$^+$; Calcd: 403.17327. Found: 403.17498. Anal. Calcd for $C_{20}H_{28}O_7$: C, 63.14; H, 7.42. Found: C, 63.15; H, 7.35.

1,2:3,4-Di-*O*-isopropylidene-7-*O*-methyl-D-*glycero*-α-D-*galacto*-heptopyranose (42). HPLC eluent: hexane–ethyl acetate 2:1; yield: 67%; colourless oil; $[\alpha]_D$=−51.9 (c 1.59, $CHCl_3$); ν_{max} (film) 3493 (br), 2987, 2937, 1457, 1382, 1256, 1213, 1170, 1109, 1067, 1002, 898, 776 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.50 (1H, d,

J=4.9 Hz, H-1), 4.63 (1H, dd, J=2.4, 8.0 Hz, H-3), 4.48 (1H, dd, J=1.8, 8.0 Hz, H-4), 4.31 (1H, dd, J=2.4, 4.9 Hz, H-2), 3.97–3.90 (1H, m, H-6), 3.78 (1H, dd, J=1.8, 8.8 Hz, H-5), 3.64 (1H, dd, J=3.0, 9.8 Hz, H-7a), 3.50 (1H, dd, J=5.7, 9.8 Hz, H-7b), 3.40 (3H, s, OCH_3), 1.53, 1.46, 1.37, 1.33 (4×3H, 4s, 2×$(CH_3)_2C$). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 109.2 and 108.7 (2×$(CH_3)_2C$), 96.3 (C-1), 73.4 (C-7), 70.7 (C-2), 70.7 (C-4), 70.6 (C-3), 68.7 (C-6), 67.0 (C-5), 59.0 (OCH_3), 25.9, 25.9, 25.0, 24.4 (2×$(CH_3)_2C$). HR MS (LSIMS): $C_{14}H_{24}O_7+Na^+$ $[M+Na]^+$; Calcd: 327.14197. Found: 327.14115. Anal. Calcd for $C_{14}H_{24}O_7$: C, 55.25; H, 7.95. Found: C, 54.93; H, 8.01.

1,2:3,4-Di-*O*-isopropylidene-7-*O*-methyl-L-*glycero*-α-D-*galacto*-heptopyranose (43). HPLC eluent: hexane–ethyl acetate 2:1; yield: 15%; colourless oil; $[\alpha]_D=-52.6$ (c 1.82, $CHCl_3$); ν_{max} (film) 3519 (br), 2988, 2936, 1458, 1383, 1256, 1213, 1170, 1070, 1003, 901, 778 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 5.60 (1H, d, J=5.0 Hz, H-1), 4.62 (1H, dd, J=2.4, 8.0 Hz, H-3), 4.34 (1H, dd, J=2.4, 5.0 Hz, H-2), 4.33 (1H, dd, J=1.7, 8.0 Hz, H-4), 4.05–4.00 (1H, m, H-6), 3.89 (1H, dd, J=1.7, 4.9 Hz, H-5), 3.57 (1H, dd, J=5.3, 9.8 Hz, H-7a), 3.55 (1H, dd, J=5.0, 9.8 Hz, H-7b), 3.40 (3H, s, OCH_3), 1.54, 1.48, 1.35, 1.34 (4×3H, 4s, 2×$(CH_3)_2C$). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 109.6 and 108.8 (2×$(CH_3)_2C$), 96.4 (C-1), 72.7 (C-4), 72.3 (C-7), 70.9 (C-3), 70.6 (C-2), 70.6 (C-6), 66.7 (C-5), 59.2 (OCH_3), 25.9, 25.8, 25.0 and 24.2 (2×$(CH_3)_2C$). HR MS (LSIMS): $C_{14}H_{24}O_7+Na^+$ $[M+Na]^+$; Calcd: 327.14197. Found: 327.14176. Anal. Calcd for $C_{14}H_{24}O_7$: C, 55.25; H, 7.95. Found: C, 54.96; H, 7.88.

7-*O*-Allyl-1,2:3,4-di-*O*-isopropylidene-D-*glycero*-α-D-*galacto*-heptopyranose (44). (**44**+**45** formed an inseparable mixture which was separated after conversion to 6-*O*-benzoates **71** and **72** respectively; separation by HPLC with hexane–ethyl acetate 6:1, then hydrolysis with MeONa in methanol); yield: 62%; colourless oil; $[\alpha]_D=-51.6$ (c 1.23, $CHCl_3$); ν_{max} (film) 3496 (br), 2988, 2938, 1457, 1382, 1256, 1213, 1170, 1069, 1002, 929, 898, 777 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 5.97–5.88 (1H, m, OCH_2CHCH_2), 5.52 (1H, d, J=5.0 Hz, H-1), 5.32–5.16 (2H, m, OCH_2CHCH_2), 4.65 (1H, dd, J=2.4, 8.0 Hz, H-3), 4.51 (1H, dd, J=1.8, 8.0 Hz, H-4), 4.33 (1H, dd, J=2.4, 5.0 Hz, H-2), 4.10–4.03 (2H, m, OCH_2CHCH_2), 3.97 (1H, ddd, J=3.2, 5.3, 8.8 Hz, H-6), 3.83 (1H, dd, J=1.8, 8.8 Hz, H-5), 3.70 (1H, dd, J=3.2, 9.8 Hz, H-7a), 3.60 (1H, dd, J=5.3, 9.8 Hz, H-7b), 1.54, 1.48, 1.39, 1.35 (4×3H, 4s, 2×$(CH_3)_2C$). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 134.6 (OCH_2CHCH_2), 116.9 (OCH_2CHCH_2), 109.2 and 108.7 (2×$(CH_3)_2C$), 96.3 (C-1), 72.2 (OCH_2CHCH_2), 70.8 (C-7), 70.7 and 70.7 (C-4, C-2), 70.6 (C-3), 68.8 (C-6), 66.9 (C-5), 26.0, 26.0, 25.0 and 24.4 (2×$(CH_3)_2C$). HR MS (LSIMS): $C_{16}H_{26}O_7+Na^+$ $[M+Na]^+$; Calcd: 353.15762. Found: 353.15629. Anal. Calcd for $C_{16}H_{26}O_7$: C, 58.17; H, 7.93. Found: C, 58.07; H, 8.09.

7-*O*-Allyl-1,2:3,4-di-*O*-isopropylidene-L-*glycero*-α-D-*galacto*-heptopyranose (45). (Second component of the mixture **44**+**45**, separated as 6-*O*-benzoate **72** by HPLC with hexane–ethyl acetate 6:1, then Zemplen hydrolysis); yield: 17%; colourless oil; $[\alpha]_D=-46.4$ (c 1.58, $CHCl_3$); ν_{max} (film) 3525 (br), 2988, 2937, 1383, 1255, 1213, 1169, 1070, 1003, 901 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 5.97–5.88 (1H, m, OCH_2CHCH_2), 5.63 (1H, d, J=5.0 Hz, H-1), 5.32–5.16 (2H, m, OCH_2CHCH_2), 4.64 (1H, dd, J=2.4, 8.0 Hz, H-3), 4.37 (1H, dd, J=1.8, 8.0 Hz, H-4), 4.36 (1H, dd, J=2.4, 5.0 Hz, H-2), 4.12–4.01 (3H, m, H-6, OCH_2CHCH_2), 3.95 (1H, dd, J=1.8, 4.6 Hz, H-5), 3.65 (1H, dd, J=5.8, 9.8 Hz, H-7a), 3.61 (1H, dd, J=4.7, 9.8 Hz, H-7b), 1.55, 1.50, 1.37, 1.36 (4×3H, 4s, 2×$(CH_3)_2C$). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 134.5 (OCH_2CHCH_2), 116.9 (OCH_2CHCH_2), 109.5, 108.8 (2×$(CH_3)_2C$), 96.5 (C-1), 72.9 (C-4), 72.4 (OCH_2CHCH_2), 71.0 (C-3), 70.7 (C-6), 70.6 (C-2), 69.7 (C-7), 66.6 (C-5), 25.9, 25.8, 25.0 and 24.2 (2×$(CH_3)_2C$). HR MS (LSIMS): $C_{16}H_{26}O_7+Na^+$ $[M+Na]^+$; Calcd: 353.15762. Found: 353.15932. Anal. Calcd for $C_{16}H_{26}O_7$: C, 58.17; H, 7.93. Found: C, 58.01; H, 8.10.

7-Deoxy-1,2:3,4-di-*O*-isopropylidene-7-(phenyldimethylsilyl)-D-*glycero*-α-D-*galacto*-heptopyranose (46). Column chromatography, eluent hexane–ethyl acetate 8:1; yield 40%; colourless oil; $[\alpha]_D=-52.3$ (c 1.09, $CHCl_3$); lit.[31]: $[\alpha]_D=-52.9$ (c 1, $CHCl_3$); ν_{max} (film) 3504 (br), 2989, 2937, 1428, 1382, 1255, 1212, 1113, 1071, 1001, 900, 831, 730, 701 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.62–7.35 (5H, m, Ph), 5.58 (1H, d, J=5.1 Hz, H-1), 4.61 (1H, dd, J=2.4, 8.0 Hz, H-3), 4.48 (1H, dd, J=2.0, 8.0 Hz, H-4), 4.33 (1H, dd, J=2.4, 5.1 Hz, H-2), 4.04–3.95 (1H, m, H-6), 3.51 (1H, dd, J=2.0, 7.2 Hz, H-5), 1.54, 1.47 (2×3H, 2s, $(CH_3)_2C$), 1.40 (1H, dd, J=3.3, 14.9 Hz, H-7a), 1.37, 1.35 (2×3H, 2s, $(CH_3)_2C$), 1.06 (1H, dd, J=10.9, 14.9 Hz, H-7b), 0.41, 0.39 (2×3H, 2s, $(CH_3)_2Si$). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 139.3, 133.6, 128.8 and 127.7 (Ph), 109.3 and 108.5 (2×$(CH_3)_2C$), 96.5 (C-1), 72.0 (C-5), 70.9 (C-4), 70.8 (C-3), 70.4 (C-2), 69.0 (C-6), 26.1, 25.9, 25.0 and 24.5 (2×$(CH_3)_2C$), 21.9 (C-7), −2.1, −2.2 [$(CH_3)_2Si$]. HR MS (LSIMS): $C_{21}H_{32}O_6Si+Na^+$ $[M+Na]^+$; Calcd: 431.18658. Found: 431.18901. Anal. Calcd for $C_{21}H_{32}O_6Si$: C, 61.73; H, 7.90. Found: C, 61.76; H, 7.95.

7-Deoxy-1,2:3,4-di-*O*-isopropylidene-7-(phenyldimethylsilyl)-L-*glycero*-α-D-*galacto*-heptopyranose (47). Column chromatography, eluent hexane–ethyl acetate 8:1; yield 36%; colourless oil; $[\alpha]_D=-68.2$ (c 1.62, $CHCl_3$); lit.[31]: $[\alpha]_D=-68.2$ (c 1, $CHCl_3$); ν_{max} (film) 3510 (br), 2989, 2934, 1381, 1254, 1213, 1111, 1074, 999, 901, 830, 729, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.64–7.36 (5H, m, Ph), 5.62 (1H, d, J=5.0 Hz, H-1), 4.59 (1H, dd, J=2.3, 8.0 Hz, H-3), 4.34 (1H, dd, J=2.3, 5.0 Hz, H-2), 4.32 (1H, dd, J=1.8, 8.0 Hz, H-4), 4.05 (1H, ddd, J=2.9, 6.0, 11.1 Hz, H-6), 3.51 (1H, dd, J=1.8, 6.0 Hz, H-5), 1.54, 1.46, 1.36, 1.35 (4×3H, 4s, 2×$(CH_3)_2C$), 1.17 (1H, dd, J=11.1, 14.4 Hz, H-7a), 1.05 (1H, dd, J=2.9, 14.4 Hz, H-7b), 0.43, 0.40 (2×3H, 2s, $(CH_3)_2Si$). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 139.8, 133.6, 128.7 and 127.6 (Ph), 109.3 and 108.5 (2×$(CH_3)_2C$), 96.4 (C-1), 72.9 (C-5), 71.8 (C-4), 70.9 (C-3), 70.6 (C-2), 68.8 (C-6), 26.1, 25.9, 24.9 and 24.2 (2×$(CH_3)_2C$), 19.5 (C-7), −1.3, −2.5 [$(CH_3)_2Si$]. HR MS (LSIMS): $C_{21}H_{32}O_6Si+Na^+$ $[M+Na]^+$; Calcd: 431.18658. Found: 431.18714. Anal. Calcd for $C_{21}H_{32}O_6Si$: C, 61.73; H, 7.90. Found: C, 61.72; H, 8.13.

Determination of configuration of heptoses

Methyl 2,3,4,6-tetra-*O*-benzyl-7-*O*-methyl-L-*glycero*-β-D-*allo*-heptopyranoside (48). To a cooled (0°C) solution of **18** (100 mg, 0.20 mmol) in abs DMF (1 ml) was added NaH (suspension in mineral oil, 5 mg, 0.22 mmol). The suspension was stirred for 10 min and a solution of benzyl bromide (37 mg, 0.22 mmol) was added. Stirring was continued for 8 h whereupon the excess of the hydride was decomposed with MeOH and the mixture was poured into ice-water. The product was extracted with ether, and the organic extract was dried and concentrated to dryness. The residue was purified by chromatography in 6:1 hexane–EtOAc to yield **48** (100 mg, 85%) as a colourless oil; $[\alpha]_D$=+13.2 (*c* 1.1, $CHCl_3$); ν_{max} (film) 3064, 3031, 2893, 1497, 1454, 1349, 1308, 1206, 1128, 1094, 1029, 737, 698 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ: 7.41–7.14 (20H, m, 4Ph), 4.92–4.14 (4×2H, 4ABq, 4CH_2Ph), 4.78 (1H, d, *J*=7.8 Hz, H-1), 4.20–4.14 (1H, m, H-3), 4.08–3.98 (2H, m, H-5, H-6), 3.77–3.60 (3H, m, H-4, H-7a, H-7b), 3.53, 3.36 (2×3H, 2s, 2OCH_3), 3.28 (1H, dd, *J*=2.4, 7.8 Hz, H-2). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 139.0, 138.8, 138.8, 138.0 and 128.2–127.3 (Ph), 102.2 (C-1), 78.9, 75.5, 75.5, 74.6 and 73.1 (C-2,3,4,5,6), 74.4, 73.2, 73.1, 72.9 and 70.8 (C-7, 4CH_2Ph), 59.1 and 56.6 (2OCH_3). HR MS (LSIMS): $C_{37}H_{42}O_7$+Na^+ $[M+Na]^+$; Calcd: 621.28282. Found: 621.28272. Anal. Calcd for $C_{37}H_{42}O_7$: C, 74.22; H, 7.07. Found: C, 74.20; H, 6.88.

Methylation of **50** was carried out in similar manner as benzylation using MeI instead of BnBr to afford a compound (84%) displaying the same optical rotation, IR and NMR spectra as **48**.

Methyl 7-*O*-allyl-2,3,4,6-tetra-*O*-benzyl-L-*glycero*-β-D-*allo*-heptopyranoside (49). Benzylation of **22** to **49** was carried out in the same way as benzylation of **18**. Colourless oil; yield 82%, $[\alpha]_D$=+10.1 (*c* 1.1, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$) δ: 7.40–7.15 (20H, m, 4Ph), 6.00–5.80 (1H, m, OCH_2CHCH_2), 5.33–5.12 (2H, m, OCH_2CHCH_2), 4.92–4.15 (4×2H, 4ABq, 4CH_2Ph), 4.77 (1H, d, *J*=7.9 Hz, H-1), 4.18 (1H, dd, *J*=2.5, 2.6 Hz, H-3), 4.10–3.97 (4H, m, H-5, H-6, OCH_2CHCH_2), 3.81–3.65 (2H, m, H-7a, H-7b), 3.67 (1H, dd, *J*=2.5, 9.7 Hz, H-4), 3.52 (3H, s, OCH_3), 3.28 (1H, dd, *J*=2.6, 7.9 Hz, H-2). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 139.0, 138.8, 138.8 and 138.0 (Ph), 134.7 (OCH_2CHCH_2), 128.2–127.3 (Ph), 116.8 (OCH_2CHCH_2), 102.2 (C-1), 79.0, 75.7, 75.6, 74.6 and 72.5 (C-2,3,4,5,6), 74.4, 73.2, 72.9, 72.3, 70.8 and 70.7 (C-7, 4CH_2Ph, OCH_2CHCH_2), 56.6 (OCH_3). HR MS (LSIMS): $C_{39}H_{44}O_7$+Na^+ $[M+Na]^+$; Calcd: 647.29847. Found: 647.29817.

Methyl 2,3,4,6-tetra-*O*-benzyl-L-*glycero*-β-D-*allo*-heptopyranoside (50). Obtained by de-allylation of **49** in 70%. De-allylation protocol is described below for **22** (affording **51**). Colourless oil; $[\alpha]_D$=+18.1 (*c* 1.3, $CHCl_3$); ν_{max} (film) 3493 (br), 3064, 3031, 2888, 1497, 1454, 1350, 1207, 1132, 1093, 1048, 737, 698 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ: 7.42–7.15 (20H, m, 4Ph), 4.95–4.23 (4×2H, 4ABq,4CH_2Ph), 4.84 (1H, d, *J*=7.9 Hz, H-1), 4.19 (1H, dd, *J*=2.4, 2.5 Hz, H-3), 4.11 (1H, dd, *J*=1.5, 9.6 Hz, H-5), 4.03–3.80 (3H, m, H-6, H-7a, H-7b), 3.70 (1H, dd, *J*=2.4, 9.6 Hz, H-4), 3.53 (3H, s, OCH_3), 3.30 (1H, dd, *J*=2.5, 7.9 Hz, H-2). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 138.8, 138.6, 138.3, 137.7 and 128.3–127.4 (Ph), 102.5 (C-1), 78.7, 75.8, 75.4, 74.8 and 74.4 (C-2,3,4,5,6), 74.5, 73.0, 72.1, 70.9 and 62.7 (C-7, 4CH_2Ph), 56.9 (OCH_3). HR MS (LSIMS): $C_{36}H_{40}O_7$+Na^+ $[M+Na]^+$; Calcd: 607.26717. Found: 607.26760.

Methyl 2,3,4-tri-*O*-benzyl-L-*glycero*-β-D-*allo*-heptopyranoside (51). To a solution of **22** (300 mg, 0.56 mmol) in a mixture of EtOH (9 ml), benzene (2 ml) and water (1 ml) was added 1,4-diazabicyclo[2.2.2]octane (DABCO, 18 mg), and the solution was heated to 80°C. Wilkinson's catalyst (37 mg) was added and the mixture was refluxed for 3 h and left at room temperature overnight. The mixture was filtered and the filtrate was concentrated under lowered pressure. The remaining oil was dissolved in 10:1 acetone–water, and HgO (153 mg) and $HgCl_2$ (187 mg) were added. The suspension was stirred (0.5 h) at room temperature, then filtered, the filtrate was concentrated, and the residue was dissolved in ether. The ether solution was washed with aq 50% KI, aq 10% $NaHSO_3$, and aq 1% $NaHCO_3$, dried, and concentrated. The residue was chromatographed with 1:2 hexane–EtOAc to yield **51** (196 mg, 71%) as an amorphous solid; $[\alpha]_D$=+1.0 (*c* 1.0, $CHCl_3$); ν_{max} (film) 3385 (br), 3308 (br), 3032, 2965, 2915, 1454, 1206, 1134, 1096, 1047, 1026, 741, 697 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ: 7.42–7.25 (15H, m, 3Ph), 4.93–4.45 (3×2H, 3ABq, 3CH_2Ph), 4.85 (1H, d, *J*=7.9 Hz, H-1), 4.12 (1H, dd, *J*=2.4, 2.6 Hz, H-3), 4.00–3.92 (2H, m, H-6, H-5), 3.82 (1H, dd, *J*=5.9, 11.4 Hz, H-7a), 3.71 (1H, dd, *J*=4.4, 11.4 Hz, H-7b), 3.58 (1H, dd, *J*=2.4, 9.7 Hz, H-4), 3.51 (3H, s, OCH_3), 3.19 (1H, dd, *J*=2.6, 7.9 Hz, H-2). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 138.8, 138.4, 137.6 and 128.4–127.4 (Ph), 102.1 (C-1), 78.6, 75.2, 74.7, 73.6 and 69.1 (C-2,3,4,5,6), 74.5, 72.9, 71.8 and 65.2 (C-7, 3CH_2Ph), 57.1 (OCH_3). HR MS (LSIMS): $C_{29}H_{34}O_7$+Na^+ $[M+Na]^+$; Calcd: 517.22022. Found: 517.22081.

Desilylation of 24

To a solution of **24** (600 mg, 0.98 mmol) in CH_3COOH (8 ml) were added KBr (139 mg, 1.17 mmol) and CH_3COONa (1 g). The mixture was cooled to 0°C and stirred with exclusion of light. CH_3CO_3H (5 ml, 30% solution in acetic acid) was added to the mixture. After stirring for 2 h at 0°C mixture was brought to room temperature. Aq 15% $Na_2S_2O_5$ was added to reduce the remaining peroxyacetic acid. The product was extracted with CH_2Cl_2 and the organic extract was washed with water, aq 10% $NaHCO_3$ and water again, dried and concentrated. The residue was purified on a silica gel column with 1:2 hexane–EtOAc to yield 6,7-diol (377 mg, 78%) identical after IR and NMR spectra with **51**.

Methyl 2,3,4,6,7-penta-*O*-benzyl-L-*glycero*-β-D-*allo*-heptopyranoside (52). Benzylation of **14** and **51** leading to **52** was carried out as for **18**. Both benzylation products (83 and 81%, respectively) displayed identical IR and NMR spectra. Colourless oil; $[\alpha]_D$=+11.7 (*c* 1.2, $CHCl_3$); ν_{max} (film) 3064, 3031, 2908, 1497, 1454, 1351, 1206, 1095, 1028, 912, 737, 698 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ: 7.42–7.15 (25H, m, 5Ph), 4.92–4.15 (5×2H, 5ABq,

5CH_2Ph), 4.75 (1H, d, J=8.0 Hz, H-1), 4.20–4.15 (1H, m, H-3), 4.13–4.03 (2H, m, H-5, H-6), 3.81 (1H, dd, J=5.8, 9.9 Hz, H-7a), 3.76 (1H, dd, J=5.9, 9.9 Hz, H-7b), 3.67 (1H, dd, J=2.4, 9.5 Hz, H-4), 3.46 (3H, s, OCH_3), 3.27 (1H, dd, J=2.6, 8.0 Hz, H-2). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 139.0, 138.7, 138,7, 138.2, 137.9 and 128.3–127.3 (Ph), 102.2 (C-1), 78.9, 75.7, 75.6, 74.5 and 72.4 (C-2,3,4,5,6), 74.4, 73.4, 73.2, 72.9, 70.9 and 70.7 (C-7, 5CH$_2$Ph), 56.6 (OCH_3). HR MS (LSIMS): $C_{43}H_{46}O_7$+Na^+ $[M+Na]^+$; Calcd: 697.31412. Found: 697.31737.

D-*glycero*-αβ-D-*allo*-heptose (53). To a cooled (10°C) solution of **13** (104 mg, 0.18 mmol) in EtOAc (1.11 ml) was added a solution of H_2SO_4 in Ac_2O (1:300 v/v, 2.23 ml) and was stirred 50 min (TLC) at room temperature. Then an excess of $NaHCO_3$ was added to neutralize the reaction mixture, $NaHCO_3$ was filtered off and washed with toluene twice. The combined organic layers were evaporated to dryness. The crude product was dissolved in MeOH (1 ml), and 0.1N MeONa in MeOH (0.01 ml) was added. The mixture was stirred 30 min and then neutralized with Amberlite IR 120 (H^+) ion exchange resin. After filtration, the resin was washed several times with aq methanol, and filtrate was evaporated to dryness under lowered pressure. The residue was chromatographed with 1:2 hexane–EtOAc. The dry product was dissolved in MeOH (3 ml) and 10% Pd–C catalyst (100 mg) was added. Suspension was hydrogenated (Pd/C) overnight. Filtration through a Celite pad and concentration of the filtrate left a foam which was washed by decantation with ether, then the rest of ether was evaporated to dryness giving **53** as a foam. Yield 20 mg, 79%, $[\alpha]_D$=+10.7 (24 h) (c 1.6, H_2O). Lit.[27]: $[\alpha]_D$=+7.2 (3 min)→+12.7 (24 h) (c 4.6, H_2O). ^{13}C NMR (50 MHz, D_2O) δ: major: 93.8 (C-1), 73.8, 72.1, 71.3, 71.2, 67.7, 61.8; minor: 92.7 (C-1), 72.0, 71.7, 67.6, 67.1, 66.9, 62.1. These data are identical with the literature[28] values for β- and α-pyranose forms.

The same protocol was used for deprotection of **14**. L-*glycero*-D-*allo*-heptose (**54**) obtained was characterized only by optical rotation $[\alpha]_D$=+8.9 (c 1.77, H_2O), and ^{13}C NMR data of the major component [β-pyranose (?)] (50 MHz, D_2O) δ 93.7 (C-1), 72.2, 71.4, 71.3, 69.0, 66.2, 62.8.

Methyl 7-*O*-allyl-2,3,4,6-tetra-*O*-benzyl-L-*glycero*-α-D-*gluco*-heptopyranoside (55). Obtained by benzylation of **30** (carried out in the same manner as benzylation of **18**). Colourless oil; yield 86%, $[\alpha]_D$=+36.8 (c 1.1, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.40–7.17 (20H, m, 4Ph), 6.00–5.80 (1H, m, OCH_2CHCH_2), 5.34–5.14 (2H, m, OCH_2CHCH_2), 5.04–4.31 (4×2H, 4ABq, 4CH_2Ph), 4.63 (1H, d, J=3.6 Hz, H-1), 4.11–3.96 (4H, m, H-3, H-6, OCH_2CHCH$_2$), 3.87–3.54 (5H, m, H-2, H-4, H-5, H-7a, H-7b), 3.36 (3H, s, OCH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 138.5, 138.5, 138.5 and 138.1 (Ph), 134.4 (OCH_2CHCH_2), 128.4–127.3 (Ph), 117.0 (OCH_2CHCH_2), 98.1 (C-1), 82.5, 79.8, 77.2, 74.7 and 69.9 (C-2,3,4,5,6), 75.8, 74.5, 73.4, 73.0, 72.3 and 69.9 (C-7, 4CH$_2$Ph, OCH_2CHCH$_2$), 55.1 (OCH_3). Anal. Calcd for $C_{39}H_{44}O_7$: C, 74.98; H, 7.10. Found: C, 74.77; H, 7.06.

Methyl 2,3,4,6-tetra-*O*-benzyl-L-*glycero*-α-D-*gluco*-heptopyranoside (56). Obtained (83%) by de-allylation of **55** (carried out as de-allylation of **22**). Colourless needles, mp 88–89°C (from hexane–ethanol); $[\alpha]_D$=+40.3 (c 1.0, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.40–7.15 (20H, m, 4Ph), 5.50–4.36 (4×2H, 4ABq, 4CH_2Ph), 4.63 (1H, d, J=3.6 Hz, H-1), 4.02 (1H, dd, J=8.4, 9.6 Hz, H-3), 4.00–3.72 (5H, m, H-4, H-5, H-6, H-7a, H-7b), 3.58 (1H, dd, J=3.6, 9.6 Hz, H-2), 3.40 (3H, s, OCH_3). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 138.5, 138.3, 138.0, 137.8 and 128.4–127.4 (Ph), 98.3 (C-1), 82.3, 79.6, 77.2, 75.1 and 72.4, (C-2,3,4,5,6), 75.8, 74.6, 73.5, 72.0 and 62.5 (C-7, 4CH$_2$Ph), 55.4 (OCH_3). HR MS (LSIMS): $C_{36}H_{40}O_7$+Na^+ $[M+Na]^+$; Calcd: 607.26715. Found: 607.27034. Anal. Calcd for $C_{36}H_{40}O_7$: C, 73.95; H, 6.90. Found: C, 73.76; H, 7.00.

Methyl 2,3,4,6-tetra-*O*-benzyl-7-*O*-methyl-L-*glycero*-α-D-*gluco*-heptopyranoside (57). Obtained (94%):by methylation of **56** (carried out as methylation of **50**). Colourless oil; $[\alpha]_D$=+38.4 (c 4.9, $CHCl_3$); ν_{max} (film) 3064, 3031, 2924, 1497, 1454, 1360, 1196, 1158, 1141, 1095, 1069, 1030, 739, 698 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.42–7.18 (20H, m, 4Ph), 5.04–4.30 (4×2H, 4ABq, 4CH_2Ph), 4.64 (1H, d, J=3.6 Hz, H-1), 4.09–3.98 (2H, m, H-3, H-6), 3.85–3.55 (4H, m, H-4, H-5, H-7a, H-7b), 3.58 (1H, dd, J=3.6, 9.6 Hz, H-2), 3.37, 3.36 (2×3H, 2s, 2OCH_3). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 138.5, 138.5, 138.0, 138.0 and 128.4–127.3 (Ph), 98.1 (C-1), 82.5, 79.8, 77.2, 74.5 and 69.9 (C-2,3,4,5,6), 75.8, 74.5, 73.4, 72.9 and 72.4 (C-7, 4CH$_2$Ph), 58.9 and 55.0 (2OCH_3). HR MS (LSIMS): $C_{37}H_{42}O_7$+Na^+ $[M+Na]^+$; Calcd: 621.28284. Found: 621.28135.

Benzylation of **28** (carried out as benzylation of **18**) gave a compound (78.9%) with the same optical rotation, and identical IR and NMR spectra as 57.

Methyl 2,3,4,6,7-penta-*O*-benzyl-L-*glycero*-α-D-*gluco*-heptopyranoside (58). Benzylation of **56** was carried out as benzylation of **18**. Colourless oil; yield 87%, $[\alpha]_D$=+27.1 (c 3.8, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.42–7.20 (25H, m, 5Ph), 5.05–4.31 (5×2H, 5ABq, 5CH_2Ph), 4.63 (1H, d, J=3.6 Hz, H-1), 4.15–4.06 (1H, m, H-6), 4.04 (1H, dd, J=8.6, 9.5 Hz, H-3), 3.89–3.67 (4H, m, H-4, H-5, H-7a, H-7b), 3.58 (1H, dd, J=3.6, 9.6 Hz, H-2), 3.32 (3H, s, OCH_3). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 138.5, 138.5, 138.1, 138.1, 137.9 and 128.4–127.3 (Ph), 98.1 (C-1), 82.5, 79.8, 77.2, 74.8 and 70.0 (C-2,3,4,5,6), 75.8, 74.5, 73.4, 73.4, 73.0 and 70.2 (C-7, 5CH$_2$Ph), 55.1 (OCH_3). HR MS (LSIMS): $C_{43}H_{46}O_7$+Na^+ $[M+Na]^+$; Calcd: 697.31415. Found: 697.31273.

Benzylation of **26** (carried out as benzylation of **18**) gave a compound (89.6%) with the same optical rotation and identical NMR spectra as **58**.

Methyl 2,3,4-tri-*O*-benzyl-L-*glycero*-α-D-*gluco*-heptopyranoside (59). De-allylation of **30** (carried out as de-allylation of **22**) gave **59** (77%): Colourless needles, mp 105–106°C (from hexane–methanol); $[\alpha]_D$=+18.2 (c 1.0, $CHCl_3$); ν_{max} (KBr) 3354 (br), 3062, 3031, 2921, 1498, 1455, 1360, 1163, 1095, 1052, 1025, 732, 695 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.42–7.24 (15H, m, 3Ph), 5.04–4.61 (3×2H, 3ABq, 3CH_2Ph), 4.55 (1H, d, J=3.6 Hz, H-1), 4.05–3.88 (2H, m, H-3, H-6), 3.82–3.60

(4H, m, H-4, H-5, H-7a, H-7b), 3.50 (1H, dd, J=3.6, 9.7 Hz, H-2), 3.34 (3H, s, OCH_3). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 138.6, 138.0, 138.0 and 128.5–127.6 (Ph), 98.4 (C-1), 81.9, 79.6, 77.1, 71.3 and 68.8 (C-2,3,4,5,6), 75.7, 75.1, 73.5 and 64.9 (C-7, 3CH_2Ph), 55.2 (OCH_3). Anal. Calcd for $C_{29}H_{34}O_7$: C, 70.43; H, 6.93. Found: C, 70.27; H, 6.91.

Oxidative removal of the phenyldimethylsilyl group in **31** was carried out in the same manner as in the case of **24** to give a compound (78.2%) having the same melting point, the same optical rotation and identical IR and NMR spectra as **59**.

Methyl 6,7-di-*O*-acetyl-2,3,4-tetra-*O*-benzyl-7-*O*-methyl-L-*glycero*-α-D-*gluco*-heptopyranoside (60). Acetylation of **59** under standard condition gave **60** (90%). Colourless oil; $[\alpha]_D$=−9.9 (*c* 2.3, $CHCl_3$); lit.[29,30]: $[\alpha]_D$=−10.6 (*c* 1.1, $CHCl_3$).

Methyl 2,3,4-tri-*O*-benzyl-D-*glycero*-α-D-*gluco*-heptopyranoside (61). De-allylation of **29** (carried out as de-allylation of **22**) gave **61** (61%). Amorphous solid; $[\alpha]_D$=+34.2 (*c* 2.4, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$) δ: 7.40–7.20 (15H, m, 3Ph), 5.08–4.61 (3×2H, 3ABq, 3CH_2Ph), 4.54 (1H, d, J=3.7 Hz, H-1), 4.03 (1H, dd, J=9.0, 9.3 Hz, H-3), 3.84–3.46 (6H, m, H-2, H-4, H-5, H-6, H-7a, H-7b), 3.39 (3H, s, OCH_3). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 138.4, 137.9, 137.3 and 128.6–127.7 (Ph), 97.7 (C-1), 82.2, 80.0, 79.8, 72.5 and 69.7 (C-2,3,4,5,6), 75.7, 74.9, 73.3 and 62.8 (C-7, 3CH_2Ph), 55.4 (OCH_3). HR MS (LSIMS): $C_{29}H_{34}O_7$+Na^+ $[M+Na]^+$; Calcd: 517.22022. Found: 517.22034. Anal. Calcd for $C_{29}H_{34}O_7$: C, 70.43; H, 6.93. Found: C, 70.18; H, 6.91.

Methyl 6,7-di-*O*-acetyl-2,3,4-tetra-*O*-benzyl-7-*O*-methyl-D-*glycero*-α-D-*gluco*-heptopyranoside (62). Acetylation of **61** under standard condition gave **62** (92%). Colourless oil; $[\alpha]_D$=+23.5 (*c* 1.8, $CHCl_3$); lit.[29,30]: $[\alpha]_D$=+21.8 (*c* 0.9, $CHCl_3$).

Methyl 7-*O*-allyl-2,3,4,6-tetra-*O*-benzyl-D-*glycero*-α-D-*galacto*-heptopyranoside (63). Benzylation of **36** (carried out as benzylation of **18**) gave **63** (85%). Colourless oil; $[\alpha]_D$=+16.7 (*c* 1.1, $CHCl_3$); ν_{max} (film) 3064, 3031, 2907, 2865, 1497, 1454, 1350, 1196, 1103, 1059, 1028, 929, 784, 737, 698 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ: 7.42–7.20 (20H, m, 4Ph), 6.00–5.79 (1H, m, OCH_2CHCH_2), 5.32–5.12 (2H, m, OCH_2CHCH_2), 5.11–4.30 (4×2H, 4ABq, 4CH_2Ph), 4.68 (1H, d, J=3.4 Hz, H-1), 4.21–4.17 (1H, m, H-4), 4.06 (1H, dd, J=3.4, 10.0 Hz, H-2), 4.02–3.92 (3H, m, H-3, OCH_2CHCH_2), 3.90–3.83 (2H, m, H-5, H-6), 3.78 (1H, dd, J=1.4, 10.6 Hz, H-7a), 3.59 (1H, dd, J=3.4, 10.6 Hz, H-7b), 3.37 (3H, s, OCH_3). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 139.0, 138.9, 138.5 and 138.4 (Ph), 134.7 (OCH_2CHCH_2), 128.3–127.3 (Ph), 116.9 (OCH_2CHCH_2), 98.8 (C-1), 79.6, 76.3, 76.0, 75.0 and 68.5 (C-2,3,4,5,6), 74.5, 73.5, 73.3, 72.3, 71.8 and 68.3 (C-7, 4CH_2Ph, OCH_2CHCH_2), 55.2 (OCH_3). HR MS (LSIMS): $C_{39}H_{44}O_7$+Na^+ $[M+Na]^+$; Calcd: 647.29847. Found: 647.29792.

Methyl 2,3,4,6-tetra-*O*-benzyl-D-*glycero*-α-D-*galacto*-heptopyranoside (64). De-allylation of **63** (carried out as de-allylation of **22**) gave **64** (77%). Colourless oil; $[\alpha]_D$=+4.4 (*c* 1.96, $CHCl_3$); ν_{max} (film) 3493 (br), 3031, 2923, 1497, 1454, 1350, 1197, 1138, 1102, 1057, 784, 737, 698 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ: 7.45–7.20 (20H, m, 4Ph), 5.14–4.22 (4×2H, 4ABq, 4CH_2Ph), 4.69 (1H, d, J=3.3 Hz, H-1), 4.14–4.10 (1H,m, H-4), 4.07 (1H, dd, J=3.3, 10.1 Hz, H-2), 3.98 (1H, dd, J=2.2, 10.1 Hz, H-3), 3.90–3.68 (4H, m, H-5, H-6, H-7a, H-7b), 3.40 (3H, s, OCH_3). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 138.8, 138.8, 138.4, 137.8 and 128.5–127.4 (Ph), 98.8 (C-1), 79.5, 76.7, 76.2, 74.9 and 69.1 (C-2,3,4,5,6), 74.5, 73.5, 73.4, 71.7 and 60.2 (C-7, 4CH_2Ph), 55.3 (OCH_3). HR MS (LSIMS): $C_{36}H_{40}O_7$+Na^+ $[M+Na]^+$; Calcd: 607.26717. Found: 607.26805.

Methyl 2,3,4,6-tetra-*O*-benzyl-7-*O*-methyl-D-*glycero*-α-D-*galacto*-heptopyranoside (65). Methylation of **64** (carried out as methylation of **50**) gave **65** (90%). Colourless oil; $[\alpha]_D$=+12.7 (*c* 1.73, $CHCl_3$); ν_{max} (film) 3031, 2922, 1497, 1454, 1349, 1195, 1103, 1060, 1028, 784, 737, 698 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ: 7.43–7.21 (20H, m, 4Ph), 5.09–4.28 (4×2H, 4ABq, 4CH_2Ph), 4.67 (1H, d, J=3.4 Hz, H-1), 4.19–4.15 (1H,m, H-4), 4.06 (1H, dd, J=3.4, 10.1 Hz, H-2), 3.96 (1H, dd, J=2.6, 10.1 Hz, H-3), 3.89 (1H, dd, J<1, 9.5 Hz, H-5), 3.80 (1H, ddd, J=1.8, 3.2, 9.5 Hz, H-6), 3.70 (1H, dd, J=1.8, 10.6 Hz, H-7a), 3.55 (1H, dd, J=3.2, 10.6 Hz, H-7b), 3.36, 3.34 (2×3H, 2s, 2OCH_3). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 139.0, 138.8, 138.5, 138.3 and 128.3–127.3 (Ph), 98.8 (C-1), 79.5, 76.3, 75.9, 75.0 and 68.3 (C-2,3,4,5,6), 74.6, 73.5, 73.3, 71.7 and 70.5 (C-7, 4CH_2Ph), 59.1 and 55.0 (2OCH_3). HR MS (LSIMS): $C_{37}H_{42}O_7$+Na^+ $[M+Na]^+$; Calcd: 621.28282. Found: 621.28401.

Benzylation of **34** (carried out as benzylation of **18**) afforded (81%) a compound identical (optical rotation, IR and NMR spectra) with **65**.

Methyl 2,3,4-tri-*O*-benzyl-D-*glycero*-α-D-*galacto*-heptopyranoside (66). De-allylation of **36** (carried out as de-allylation of **22**) gave **66** (90%). Colourless oil; $[\alpha]_D$=+13.6 (*c* 1.22, $CHCl_3$); ν_{max} (film) 3446 (br), 3031, 2928, 1497, 1455, 1352, 1195, 1147, 1101, 1049, 901, 783, 738, 697 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ: 7.45–7.22 (15H, m, 3Ph), 5.05–4.65 (3×2H, 3ABq, 3CH_2Ph), 4.65 (1H, d, J=3.6 Hz, H-1), 4.10–4.06 (1H, m, H-4), 4.05 (1H, dd, J=3.6, 10.1 Hz, H-2), 3.94 (1H, dd, J=2.8, 10.1 Hz, H-3), 3.80–3.52 (4H, m, H-5, H-6, H-7a, H-7b), 3.33 (3H, s, OCH_3). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 138.7, 138.5, 138.4 and 128.7–127.5 (Ph), 98.8 (C-1), 79.2, 76.4, 73.4, 69.8 and 69.2 (C-2,3,4,5,6), 74.3, 73.6, 73.5 and 63.9 (C-7, 3CH_2Ph), 55.3 (OCH_3). HR MS (LSIMS): $C_{29}H_{34}O_7$+Na^+ $[M+Na]^+$; Calcd: 517.22022. Found: 517.22085.

Methyl D-*glycero*-α-D-*galacto*-heptopyranoside (67). To a solution of **66** (300 mg, 0.51 mmol) in EtOH (5 ml) was added 10% Pd–C (300 mg), and the suspension was hydrogenated overnight. Filtration through a Celite pad and concentration of the filtrate left a foam which was washed by decantation with ether, then the rest of ether was evaporate and the product was recrystallized from ethanol as

colourless solid. Yield 84 mg, 85%, mp 140–142°C, $[\alpha]_D$=+158.9 (*c* 1.1, H_2O). Lit.[7]: $[\alpha]_D$=+165 (*c* 0.9, H_2O). The ^{13}C NMR data of **67** (in D_2O) are the same as in literature.[7]

Hydrogenation of **32** was carried out in the same manner to give a compound (89.3%) having identical data (melting point, optical rotation and the NMR spectra) as **67**.

Methyl L-*glycero*-α-D-*galacto*-heptopyranoside (68). Hydrogenation of **33** (carried out as hydrogenation of **66**) gave **68** (87%). Yield 80.2%, colourless solid, mp 129–130°C (from ethanol); $[\alpha]_D$=+154.6 (*c* 1.0, H_2O); ^{13}C NMR (50 MHz, D_2O) δ: 99.4 (C-1), 71.3, 70.5, 69.6, 69.4 and 68.1 (C-2,3,4,5,6), 61.9 (C-7), 55.1 (OCH_3). HR MS (LSIMS): $C_8H_{16}O_7+Na^+$ $[M+Na]^+$; Calcd: 247.07937. Found: 247.07919.

Hydrogenation of **69** (carried out as hydrogenation of **66**) gave a compound (80%) identical (melting point, optical rotation and NMR spectra) with **68**.

Methyl 2,3,4-tri-*O*-benzyl-L-glycero-α-D-*galacto*-heptopyranoside (69). Oxidative removal of phenyldimethylsilyl group in **39** (carried out as for **24**) led to **69** (84%). Colourless oil; $[\alpha]_D$=+16.6 (*c* 1.7, $CHCl_3$); ν_{max} (film) 3468 (br), 3031, 2908, 1497, 1454, 1351, 1196, 1132, 1095, 1048, 782, 738, 698 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ: 7.46–7.24 (15H, m, 3Ph), 5.12–4.62 (3×2H, 3ABq, 3CH_2Ph), 4.74 (1H, d, *J*=3.5 Hz, H-1), 4.08 (1H, dd, *J*=3.5, 10.6 Hz, H-2), 4.01–3.95 (1H,m, H-4), 3.96 (1H, dd, *J*=2.3, 10.6 Hz, H-3), 3.92–3.82 (1H, m, H-6), 3.73 (1H, dd, *J*<1, 5.7 Hz, H-5), 3.49 (1H, dd, *J*=3.8, 11.5 Hz, H-7a), 3.37 (3H, s, OCH_3), 3.34 (1H, dd, *J*=5.0, 11.5 Hz, H-7b). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 138.5, 138.2, 137.7 and 128.5–127.5 (Ph), 98.7 (C-1), 79.2, 76.2, 76.1, 71.5 and 69.2 (C-2,3,4,5,6), 74.5, 73.8, 73.6 and 62.8 (C-7, 3CH_2Ph), 55.4 (OCH_3). HR MS (LSIMS): $C_{29}H_{34}O_7+Na^+$ $[M+Na]^+$; Calcd: 517.22022. Found: 517.22006.

The mixture of **44** and **45** was benzoylated under standard condition to give a mixture of 6-*O*-benzoyl derivatives (overall yield 92%), which was separated by HPLC (eluent: hexane–ethyl acetate 6:1) to afford **70** (71%) and **71** (17%).

7-*O*-Allyl-6-*O*-benzoyl-1,2:3,4-di-*O*-isopropylidene-D-*glycero*-α-D-*galacto*-heptopyranose (70). Colourless oil; $[\alpha]_D$=−47.5 (*c* 2.2, $CHCl_3$); ν_{max} (film) 2988, 2937, 1724 (C=O), 1383, 1272, 1213, 1169, 1071, 1005, 898, 713 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ: 8.11–7.40 (Ph), 5.97–5.76 (1H, m, OCH_2CHCH_2), 5.54 (1H, d, *J*=5.0 Hz, H-1), 5.30 (1H, ddd, *J*=2.3, 3.6, 8.9 Hz, H-6), 5.29–5.06 (2H, m, OCH_2CHCH_2), 4.64 (1H, dd, *J*=2.4, 7.9 Hz, H-3), 4.42–4.31 (2H, m, H-4, H-5), 4.33 (1H, dd, *J*=2.4, 5.0 Hz, H-2), 4.05–3.99 (2H, m, OCH_2CHCH_2), 3.89 (1H, dd, *J*=2.3, 11.3 Hz, H-7a), 3.80 (1H, dd, *J*=3.6, 11.3 Hz, H-7b), 1.57, 1.43, 1.35, 1.25 (4×3H, 4s, 2×$(CH_3)_2C$). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 165.5 (C=O), 134.9, 132.9, 130.3, 129.7 and 128.3 (Ph, OCH_2CHCH_2), 116.7 (OCH_2CHCH_2), 109.4 and 109.0 (2×$(CH_3)_2C$), 96.3 (C-1), 72.4 (OCH_2CHCH_2), 71.9, 70.9, 70.6, 70.6 and 65.4 (C-2,3,4,5,6), 67.7 (C-7), 26.1, 25.9, 25.1 and 24.4 (2×$(CH_3)_2C$). HR MS (LSIMS): $C_{23}H_{30}O_8+Na^+$ $[M+Na]^+$; Calcd: 457.18384. Found: 457.18425.

7-*O*-Allyl-6-*O*-benzoyl-1,2:3,4-di-*O*-isopropylidene-L-*glycero*-α-D-*galacto*-heptopyranose (71). Amorphous solid; $[\alpha]_D$=−48.9 (*c* 1.6, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$) δ: 8.11–7.35 (Ph), 5.98–5.77 (1H, m, OCH_2CHCH_2), 5.53 (1H, d, *J*=5.0 Hz, H-1), 5.43 (1H, ddd, *J*=3.1, 3.7, 7.7 Hz, H-6), 5.32–5.08 (2H, m, OCH_2CHCH_2), 4.64 (1H, dd, *J*=2.5, 7.9 Hz, H-3), 4.37 (1H, dd, *J*=1.8, 7.9 Hz, H-4), 4.33 (1H, dd, *J*=2.5, 5.0 Hz, H-2), 4.27 (1H, dd, *J*=1.8, 7.7 Hz, H-5), 4.15–3.92 (2H, m, OCH_2CHCH_2), 3.90 (1H, dd, *J*=3.7, 11.4 Hz, H-7a), 3.80 (1H, dd, *J*=3.1, 11.4 Hz, H-7b), 1.60, 1.42, 1.34, 1.32 (4×3H, 4s, 2 $(CH_3)_2C$). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 166.2 (C=O), 134.4, 132.7, 130.5, 129.7 and 128.2 (Ph, $OCH_2CH=CH_2$), 116.8 ($OCH_2CH=CH_2$), 109.6 and 108.7 (2×$(CH_3)_2C$), 96.4 (C-1), 73.3, 71.2, 71.0, 70.6 and 67.0 (C-2,3,4,5,6), 72.3 ($OCH_2CH=CH_2$), 68.5 (C-7), 26.0, 26.0, 25.1 and 24.5 (2×$(CH_3)_2C$). HR MS (LSIMS): $C_{23}H_{30}O_8+Na^+$ $[M+Na]^+$; Calcd: 457.18384. Found: 457.18429.

1,2:3,4-Di-*O*-isopropylidene-D-*glycero*-α-D-*galacto*-heptopyranose (72). De-allylation of **44** (carried out as de-allylation of **22**) gave **72** (89%). Colourless oil; $[\alpha]_D$=−48.5 (*c* 1.1, $CHCl_3$); lit.[31]: $[\alpha]_D$=−51.7 (*c* 2.1, $CHCl_3$); ν_{max} (film) 3445 (br), 2988, 2938, 1458, 1382, 1256, 1213, 1170, 1068, 1001, 899, 776 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ: 5.52 (1H, d, *J*=5.1 Hz, H-1), 4.65 (1H, dd, *J*=2.4, 7.9 Hz, H-3), 4.45 (1H, dd, *J*=1.7, 7.9 Hz, H-4), 4.33 (1H, dd, *J*=2.4, 5.1 Hz, H-2), 4.00–3.70 (4H, m, H-5, H-6, H-7a, H-7b), 1.53, 1.46, 1.37, 1.33 (4×3H, 4s, 2×$(CH_3)_2C$). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 109.4 and 108.8 (2×$(CH_3)_2C$), 96.3 (C-1), 70.9, 70.7, 70.6, 70.3 and 67.4 (C-2,3,4,5,6), 63.9 (C-7), 25.9, 25.9, 25.0 and 24.4 (2×$(CH_3)_2C$). HR MS (LSIMS): $C_{13}H_{22}O_7+Na^+$ $[M+Na]^+$; Calcd: 313.12632. Found: 313.12677.

Oxidative removal of phenyldimethylsilyl group in **46** (carried out as for **24**) afforded a compound (78%) with the same optical rotation and the same IR and NMR spectra as **72**.

Hydrogenation of **40** (carried out as hydrogenation of **66**) gave a compound (83%) having the same optical rotation and NMR spectra as **72**.

7-*O*-Allyl-6-*O*-benzyl-1,2:3,4-di-*O*-isopropylidene-D-*glycero*-α-D-*galacto*-heptopyranose (73). Benzylation of **44** (carried out as benzylation of **18**) gave **73** (82%). Colourless oil; $[\alpha]_D$=−53.8 (*c* 1.3, $CHCl_3$); ν_{max} (film) 2988, 2903, 1455, 1382, 1256, 1213, 1108, 1069, 1003, 921, 899, 747, 699 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ: 7.43–7.22 (5H, m, Ph), 6.05–5.83 (1H, m, $OCH_2CH=CH_2$), 5.49 (1H, d, *J*=4.9 Hz, H-1), 5.35–5.10 (2H, m, $OCH_2CH=CH_2$), 4.79 (1H, d, *J*=11.2 Hz, CHHPh), 4.64 (1H, d, *J*=11.2 Hz, CHHPh), 4.61 (1H, dd, *J*=2.2, 8.0 Hz, H-3), 4.49 (1H, dd, *J*=1.7, 8.0 Hz, H-4), 4.27 (1H, dd, *J*=2.2, 4.9 Hz, H-2), 4.07–4.02 (2H, m, OCH_2CHCH_2), 3.93 (1H, dd, *J*=1.7, 9.3 Hz, H-5), 3.81–3.72 (2H, m, H-6, H-7a), 3.57 (1H, dd, *J*=5.1, 10.8 Hz, H-7b), 1.50, 1.45, 1.37, 1.31 (4×3H, 4s, 2×$(CH_3)_2C$). ^{13}C

NMR (50 MHz, $CDCl_3$) δ: 138.6 (Ph), 135.1 ($OCH_2CH{=}CH_2$), 128.2, 128.1 and 127.5 (Ph), 116.5 ($OCH_2CH{=}CH_2$), 108.8 and 108.6 ($2{\times}(CH_3)_2C$), 96.3 (C-1), 76.7, 71.0, 70.6, 70.4 and 66.1 (C-2,3,4,5,6), 73.2, 72.5 and 69.7 (C-7, $OCH_2CH{=}CH_2$, CH_2Ph), 26.1, 26.1, 25.1 and 24.4 ($2{\times}(CH_3)_2C$). HR MS (LSIMS): $C_{23}H_{32}O_7{+}Na^+$ $[M{+}Na]^+$; Calcd: 443.20457. Found: 443.20380.

6-*O*-Benzyl-1,2:3,4-di-*O*-isopropylidene-D-*glycero*-α-D-*galacto*-heptopyranose (74). De-allylation of **73** (carried out as de-allylation of **22**) gave **74** (85%). Colourless oil; $[\alpha]_D{=}-55.5$ (*c* 1.7, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$) δ: 7.40–7.25 (5H, m, Ph), 5.50 (1H, d, *J*=4.9 Hz, H-1), 4.67 (2H, s, CH_2Ph), 4.62 (1H, dd, *J*=2.4, 8.1 Hz, H-3), 4.45 (1H, dd, *J*=1.7, 8.1 Hz, H-4), 4.30 (1H, dd, *J*=2.4, 4.9 Hz, H-2), 4.01–3.68 (4H, m, H-5, H-6, H-7a, H-7b), 1.53, 1.46, 1.37, 1.32 ($4{\times}3H$, 4s, $2{\times}(CH_3)_2C$). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 138.3, 128.3, 128.0 and 127.8 (Ph), 109.0 and 108.8 ($2{\times}(CH_3)_2C$), 96.3 (C-1), 77.1, 70.9, 70.6, 70.4 and 66.7 (C-2,3,4,5,6), 72.8 and 61.7 (C-7, CH_2Ph), 26.0, 26.0, 25.0 and 24.4 ($2{\times}(CH_3)_2C$). HR MS (LSIMS): $C_{20}H_{28}O_7{+}Na^+$ $[M{+}Na]^+$; Calcd: 403.17327. Found: 403.17518.

6-*O*-Benzyl-1,2:3,4-di-*O*-isopropylidene-7-*O*-methyl-D-*glycero*-α-D-*galacto*-heptopyranose (75). Methylation of **74** (carried out as methylation of **50**) gave **75** (96%). Colourless oil; $[\alpha]_D{=}-52.3$ (*c* 1.6, $CHCl_3$); ν_{max} (film) 2987, 2936, 1455, 1382, 1255, 1213, 1170, 1110, 1069, 1003, 897, 747, 699 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ: 7.43–7.25 (5H, m, Ph), 5.49 (1H, d, *J*=4.9 Hz, H-1), 4.77 (1H, d, *J*=11.3 Hz, C*H*HPh), 4.64 (1H, d, *J*=11.3 Hz, CH*H*Ph), 4.61 (1H, dd, *J*=2.2, 8.1 Hz, H-3), 4.49 (1H, dd, *J*=1.6, 8.1 Hz, H-4), 4.27 (1H, dd, *J*=2.2, 4.9 Hz, H-2), 3.94 (1H, dd, *J*=1.6, 9.5 Hz, H-5), 3.78–3.67 (2H, m, H-6, H-7a), 3.52 (1H, dd, *J*=4.8, 10.7 Hz, H-7b), 3.40 (3H, s, OCH_3), 1.52, 1.45, 1.37, 1.31 ($4{\times}3H$, 4s, $2{\times}(CH_3)_2C$). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 138.6, 128.2 and 127.5 (Ph), 108.8 and 108.7 ($2{\times}(CH_3)_2C$), 96.3 (C-1), 76.6, 71.0, 70.6, 70.4 and 66.0 (C-2,3,4,5,6), 73.1 and 72.1 (C-7, CH_2Ph), 59.4 (OCH_3), 26.0, 25.9, 25.1 and 24.4 ($2(CH_3)_2C$). HR MS (LSIMS): $C_{21}H_{30}O_7{+}H^+$ $[M{+}H]^+$; Calcd: 395.20698. Found: 395.20881.

Benzylation of **42** (carried out as benzylation of **18**) led to a compound (89%) having the same IR and NMR spectra as **75**.

1,2:3,4-Di-*O*-isopropylidene-L-*glycero*-α-D-*galacto*-heptopyranose (76). Hydrogenation of **41** (carried out as hydrogenation of **66**) gave **76** (76%). Colourless needles, mp 101–102°C (from ether), $[\alpha]_D{=}-56.1$ (*c* 2.0, $CHCl_3$); ν_{max} (KBr) 3411 (br), 2993, 2935, 1456, 1386, 1258, 1212, 1111, 1070, 1004, 893 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ: 5.58 (1H, d, *J*=5.0 Hz, H-1), 4.61 (1H, dd, *J*=2.4, 8.0 Hz, H-3), 4.34 (1H, dd, *J*=1.6, 8.0 Hz, H-4), 4.33 (1H, dd, *J*=2.4, 5.0 Hz, H-2), 3.99–3.89 (1H, m, H-6), 3.86 (1H, dd, *J*=1.6, 6.2 Hz, H-5), 3.79 (1H, dd, *J*=3.8, 11.8 Hz, H-7a), 3.71 (1H, dd, *J*=4.3, 11.8 Hz, H-7b), 1.52, 1.46, 1.33, 1.33 ($4{\times}3H$, 4s, $2{\times}(CH_3)_2C$). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 109.5 and 108.8 ($2{\times}(CH_3)_2C$), 96.4 (C-1), 71.6, 71.2, 70.8, 70.6 and 67.5 (C-2,3,4,5,6), 62.4 (C-7), 26.0, 25.9, 25.0 and 24.2 ($2{\times}(CH_3)_2C$). HR MS (LSIMS): $C_{13}H_{22}O_7{+}Na^+$ $[M{+}Na]^+$; Calcd: 313.12632. Found: 313.12775. Anal. Calcd for $C_{13}H_{22}O_7$: C, 53.58; H, 7.64. Found: C, 53.75; H, 7.79.

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