Directed and Efficient Syntheses of β(1→4)-Linked Galacto-Oligosaccharides

Frieder W. Lichtenthaler,*[a] Markus Oberthür,[a] and Siegfried Peters[a]

Keywords: Carbohydrates / Glycosides / Glycosylations / Oligosaccharides / Thiogalatosides

Straightforward, preparatively efficient procedures are described for the construction of β(1→4)-intergalactosidic linkages up to the hexasaccharide level. Key elements were the use of phenylthio and/or phenyl sulfoxide functionalities for glycosylations and a judiciously designed blocking group pattern for donor and acceptor alike: pivaloyl protection at *O*-2 for securing β-selectivity, sterically undemanding allyl or benzyl groups at *O*-3 and *O*-6 to minimise the steric bulk around the unreactive galactosyl-4-OH, the *p*-methoxyphenyl moiety, readily replaceable by SPh, as an intermediate anomeric substituent, and an acetyl group for temporary protection of the terminal Gal-4-OH. This strategy lends itself to iterative block synthesis and interchange of donors and acceptors, thereby demonstrating the broad scope and generality of the overall approach. Although predicted by molecular modelling, inclinations towards starch-like coiling could not so far be verified in any of the galacto-tetra-, -penta-, or -hexaoses or their *p*-methoxyphenyl glycosides.

Introduction

The pectins found universally in the primary cell walls and intercellular layers of land plants constitute a highly complex assemblage of homo- and hetereopolysaccharides, of which arabans, galactans, arabinogalactans, and rhamnogalacturonans are the most prominent.[1,2] The constituent sugars vary widely not only in their proportions but also in their intersaccharidic link-up, so no complete structure[3] can currently be given for any individual pectin. Of the major carbohydrate components known, a significant one has emerged in the form of a neutral polysaccharide composed of linear chains of (1→4)-linked β-D-galactopyranose residues: i.e., a β(1→4)-D-galactan. This has been isolated from a large number of species, ranging from citrus fruits,[4] tomato,[5] lupins,[6,7] and tobacco[8,9] to flax,[10,11] willow bark,[12] and various kinds of wood.[13–16] The chain lengths obviously depended on the isolation procedure, as they varied between four,[4] 28 (aloe[17]), and 33 (citrus pectin,[4] garlic[18]) galactose units.

Clear experimental evidence concerning the folding patterns of β(1→4)-D-galactans is currently not available (the chiroptical data on a *Lupinus angustifolius*-derived preparation[19] that was not free from other sugars have little bearing in this context). On the other hand, the conformational similarity of a β(1→4)-D-galactan to its α(1→4)-D-glucan analogue amylose is striking (Figure 1): only the orientations of the intersaccharidic linkages are interchanged − axial at one side of the pyranoid ring and equatorial at the other − to give rise to kinks at every glycosidic bond in either case as well as 2-O···HO-3′ hydrogen bonds between contiguous residues. Thus, both have a pronounced predisposition towards coiling in a helical molecular geometry. This analogy, which has been alluded to previously and corroborated by simple calculations,[20–24] can be carried even

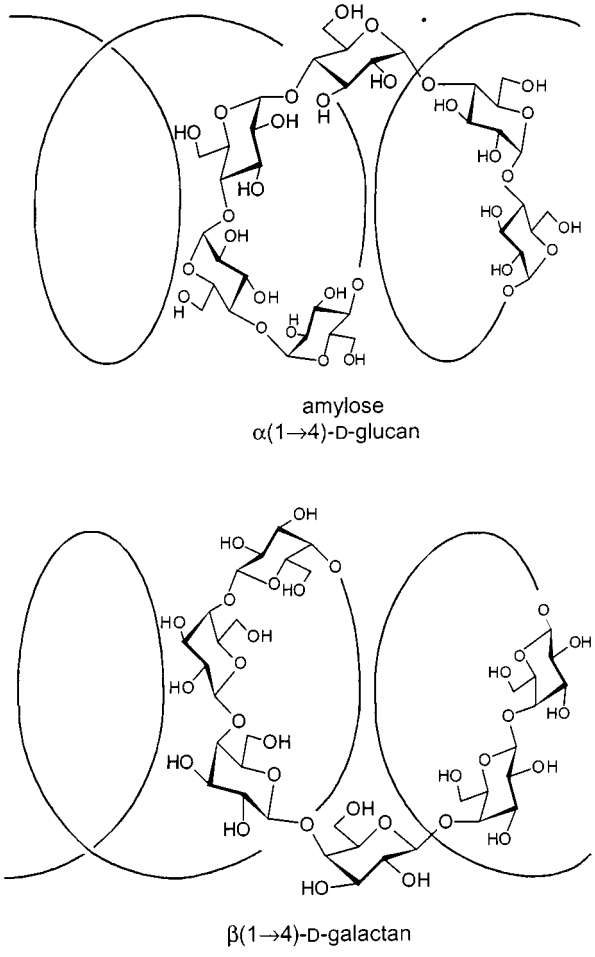


Figure 1. Sketched representation of a left-handed, single stranded helix of V_H-amylose *(top)* and a right-handed β (1→4)-D-galactan helix *(bottom)*, both free of steric constraints as predicted by early computational studies (see refs.[20–24])

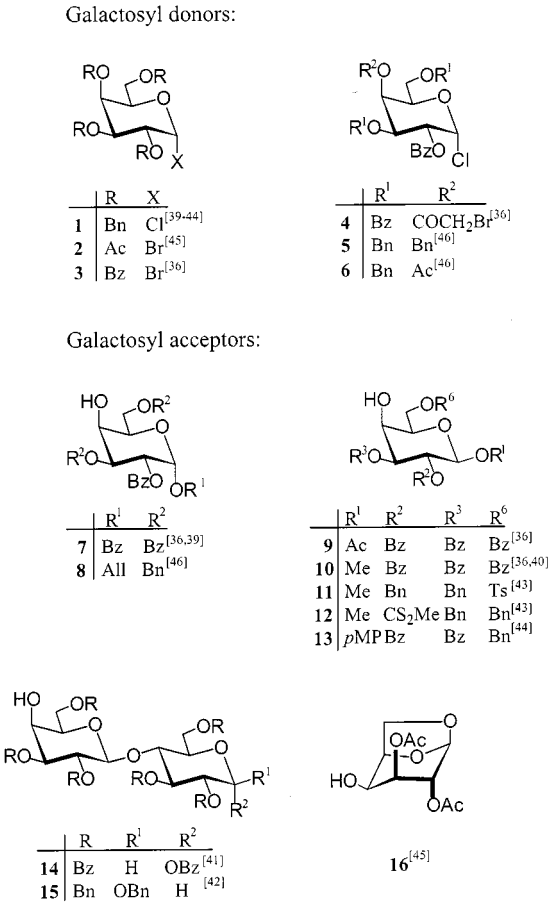
[a] Institut für Organische Chemie, Technische Universität Darmstadt
Petersenstraße 22, 64287 Darmstadt, Germany
Fax: (internat.) +49-(0)6151/166674
E-mail: fwlicht@sugar.oc.chemie.tu-darmstadt.de

  1434–193X/01/1020–3849 $ 17.50+.50/0

further. Amylose, because of its six glucose units per helix turn, elaborates a distinctly hydrophobic channel of about 5.4 Å in diameter[25] – dimensions similarly found in the cavity of α-cyclodextrin.[26–28] Elaborate molecular modelling on the hexameric β(1→4)-cyclogalactin revealed similar cavity dimensions,[29,30] so the existence of an amylose-type channel is to be inferred for a β(1→4)-galactan.

Aside from more sophisticated MD simulations[31] that will undoubtedly provide deeper insights into the molecular architecture of β(1→4)-D-galactans, further advancements are to be derived from the study of pure oligomers. However, their isolation from pectic cell wall material is exceedingly cumbersome and has rarely provided well defined products – exceptions being mg quantities of galactobiose,[13] -triose, and -tetraose.[12] Similarly, the generation of oligo-β(1→4)-galactosides by β-galactosidase-induced galactosyl transfer has, despite its simplicity, not passed the β(1→4)-galactobiose stage,[32,33] while their chemical synthesis has proven to be a particularly formidable task, since the axially disposed 4-OH of a galactosyl acceptor, necessarily carrying blocking groups at *O*-6 and *O*-3, is sterically less accessible for glycosylation than primary or equatorial OHs, aside from its being comparatively unreactive to begin with.

Thus, whilst syntheses of β(1→6)- and β(1→3)-D-galactooligosaccharides have been taken to the hexa-[34] and heptasaccharide[35] stages by application of standard glycosylation methodology, those of their β(1→4) analogues have barely reached the trisaccharide level. In fact, of the two cases reported, only mg amounts of methyl[36] and propyl[37] galactotriosides were obtained, as hygroscopic solids without full characterization. Thus, for effective installation of consecutive Gal-β(1→4)-Gal linkages to produce higher oligogalactosides, an improvement in methodology with concomitant development of more suitable donors and acceptors appeared warranted. Our studies in this area,[38] detailed here, first focused on the fine-tuning of galactosyl donor and acceptor reactivities and then on assembly of oligogalactosides up to the hexasaccharide level.



Scheme 1. Galactosyl donors and acceptors previously used for the generation of Gal-β(1→4)-Gal intersaccharidic linkages (see refs.[36, 39–46])

Results and Discussion

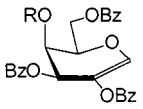
Donors and Acceptors Previously Used for the Generation of Gal-(1→4)-Gal Linkages

As the galactosyl donors and acceptors used up to now for the generation of β(1→4)-oligogalactosides have barely reached the trisaccharide level, the production of preparatively more efficient, and, for preference, iteratively usable galactosyl building blocks was required. Their design, in turn, had to be based on a detailed evaluation of previously used galactosyl donors and acceptors with respect to their anomeric and 4-OH reactivities as well as the β-selectivities attainable in the coupling reactions, of which a brief a priori explanation is given.

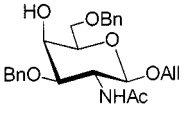
Surprisingly, up to now, only galactosyl halides **1**–**6** have been employed to glycosylate the crucially unreactive, axially disposed 4-OH of otherwise protected galactose derivatives **7**–**16** (cf. Scheme 1). From the respective glycosylations, the following picture emerges: the *O*-benzylated α-D-galactosyl chloride **1**, upon activation with silver triflate, is reactive enough to successfully glycosylate the galactose-4-OH of acceptors **7**[39] and **9**–**15**,[40–44] but because of the lack of an *O*-2 participating group in the donor, α(1→4)-linked galactobiosides products are invariably obtained in high yields.

Acetobromogalactose (**2**), however, despite possession of an *O*-2 ester function to promote β-selectivity, gave a galactobioside mixture[45] containing more α than β anomer on mercury cyanide-induced coupling with acceptor **16**. Similarly unsuited for straightforward generation of Gal-β(1→4)-Gal linkages were benzoylated donors of type **3** and **4** in combination with the equally benzoylated 4-OH-acceptors **7**, **9**, and **10**, since silver triflate-promoted couplings provided the β(1→4)-disaccharides in only modest to moderate yields, due to tedious separation from a host of side products: α anomers, orthoesters, Gal-β(1→1)-Gal derivatives, and, most notably, the hydroxygalactal esters **17**

or **18**.[36] Their partial formation through dehydrohalogenation of donors **3** and **4** under the glycosylation conditions (silver triflate/trimethylpyridine in dichloromethane, 2 h at 25 °C) appears to reflect the low reactivity and/or poor steric accessibility of the axial 4-OH of acceptors **7** and **10**, thereby siphoning the activated donors into alternative reaction channels.



17 R = Bz
18 R = $COCH_2Br$



19

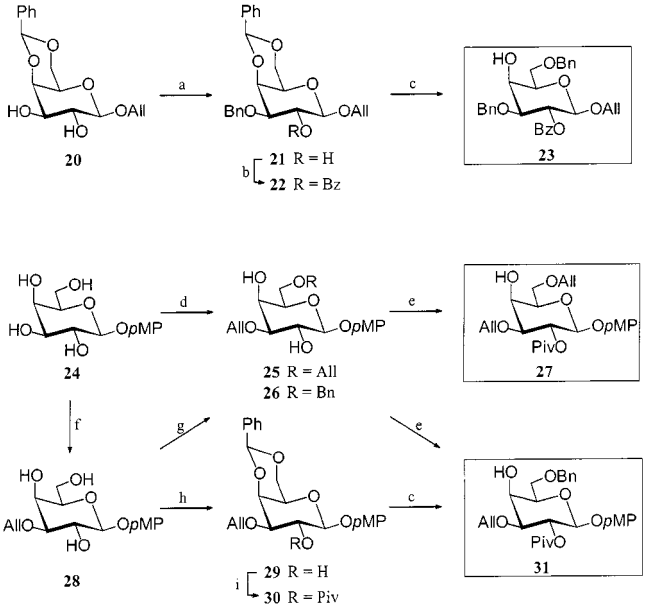
By contrast, donors bearing an ester group at *O*-2 for fostering β-selectivity, but with benzyl groups elsewhere, appear to be more propitious for clean galactosylations, particularly in combination with an acceptor of type **8**: thanks to the benzyl groups at *O*-3 and *O*-6, its 4-OH is sterically more accessible, so that silver trifluoroethylsulfonate-promoted couplings with donor **5** or **6** provide the respective β(1→4)-galactobiosides in yields of 65 and 62%.[46] Another example of the preparative favourability of slender *O*-protection in donor and acceptor, is documented in the excellent yield of a Gal-β(1→4)-GalNAc disaccharide (81%)[47] upon silver triflate-promoted coupling of **5** with the galactosamine derivative **19**, in which the reactivity of the 4-OH group is deemed even lower than in **8**.

This survey of the literature on the generation of Gal-β(1→4)-Gal linkages led us to recognize the necessity to develop new, versatile galactosyl building blocks with donor and acceptor qualities with the potential to be exploitable in iterative fashion for straightforward assembly of β(1→4)-*galacto*-oligosaccharides.

Galactosyl-4-OH Acceptors for Iterative Use

For suitable galactosyl-4-OH acceptors required towards this end, it was considered imperative to implement three factors: (i) use of slender, alkyl-type protecting groups at *O*-3 and *O*-6 to enhance steric accessibility as well as the reactivity of the axially disposed 4-OH, (ii) instalment of an anomeric substituent with inherent capacity to be grafted onto a donor function at a later stage, and (iii) an *O*-2-ester group for the utilisation of glycosylation products for further β-selective extensions. These requirements were met by acceptors **23**, **27**, and **31**, bearing allyl or *p*-methoxyphenyl residues at *O*-1, benzoyl or pivaloyl groups at *O*-2, and allyl or benzyl protection at *O*-3 and *O*-6. Their preparation was readily effected by employing standard procedures, as outlined in Scheme 2.

The 3,6-di-*O*-benzylated allyl galactoside **23** was readily obtained from the easily accessible[48] benzylidene-galactoside **20** in a single three-step sequence: dibutyltin oxide-mediated benzylation proceeded with high regioselectivity to give the 3-*O*-benzyl ether **21**, due to preferential reaction of the intermediate 2,3-*O*-stannylidene acetal at *O*-3;[49,50]



Scheme 2. Synthesis of suitably protected, iterative galactosyl acceptors. Reagents and conditions: a) Bu_2SnO, toluene, reflux, 16 h, then BnBr, 90 °C, 8 h; 91%. − b) BzCl, DMAP, pyridine/CH_2Cl_2, 25 °C, 24 h; 96%. − c) $NaBH_3CN$/HCl, Et_2O/THF, 0 °C, 20 min; 87% (**23**); 77% (**31**). − d) $(Bu_3Sn)_2O$, toluene, reflux, 16 h, then AllBr/Bu_4NI, 90 °C, 8 h; 76% (**25**). − e) PivCl, Et_3N, DMAP, pyridine, CH_2Cl_2, 25 °C, 12 h; 69% (**27**), 78% (**31**). − f) Bu_2SnO, toluene, reflux, 16 h, then AllBr/Bu_4NBr, THF, reflux, 8 h; 74%. − g) $(Bu_3Sn)_2O$, reflux, 16 h, then AllBr/Bu_4NI, 80 °C, 8 h; 96% (**25**); BnBr/Bu_4NI, 90 °C, 8 h; 92% (**26**). − h) $PhCH(OMe)_2$, TsOH, THF, 25 °C, 2 h; 91%. − i) PivCl, DMAP, Et_3N, CH_2Cl_2, reflux, 16 h; 96%. − Abbreviations used throughout: All = allyl, Bn = benzyl, Bz = benzoyl, *p*MP = *p*-methoxyphenyl, Ph = phenyl, Piv = pivaloyl

subsequent benzoylation (→ **22**) followed by reductive fission of the 4,6-*O*-benzylidene ring with $NaBH_3CN$/HCl[51] gave the suitably blocked model acceptor **23** in an overall yield of 78% for the three steps.

Access to the key galactosyl acceptors with 3,6-di-*O*-allyl and 3-*O*-allyl-6-*O*-benzyl blocking group patterns − i.e., **27** and **31** − was gained by starting from easily accessible[52] *p*-methoxyphenyl β-D-galactoside (**24**). Acquisition of the former target compound was particular straightforward, since allylation of the bis(tributylstannyl) ether of **24**, generated in situ,[53] proceeded at the *O*-3 and *O*-6 positions with high regioselectivity, to afford **25** in 76% yield. Subsequent acylation with pivaloyl chloride proved capricious, as it required meticulous adjustment of conditions (DMAP/Et_3N/pyridine in CH_2Cl_2, 12 h at 25 °C), high dilution and the presence of triethylamine, pyridine, and DMAP in order to obtain an approximate 8:1 mixture of the mono-2-*O*- (**27**) and the 2,4-di-*O*-pivaloate, from which **27** was isolable in 69% yield. − For generation of the 3-*O*-allyl-6-*O*-benzyl-protected acceptor **31** from **24**, two routes using conventional methodology were elaborated (cf. Scheme 2): a three-step sequence involving dibutyltin oxide-promoted 3-*O*-allylation[54] (**24** → **28**), followed by selective 6-*O*-benzylation (→ **26**) and 2-*O*-pivaloylation or, alternatively, a four-step approach comprising introduction of a 4,6-*O*-benzylidene group into the 3-*O*-allyl derivative (**24** → **28** → **29**), sub-

sequent pivaloylation (→ **30**) and reductive benzylidene ring-opening (**30** → **31**). Either way, the overall yields obtainable are in the 50% range, but the four step-sequence may be preferable, due to the high crystallinity of the two benzylidene intermediates **29** and **30**.

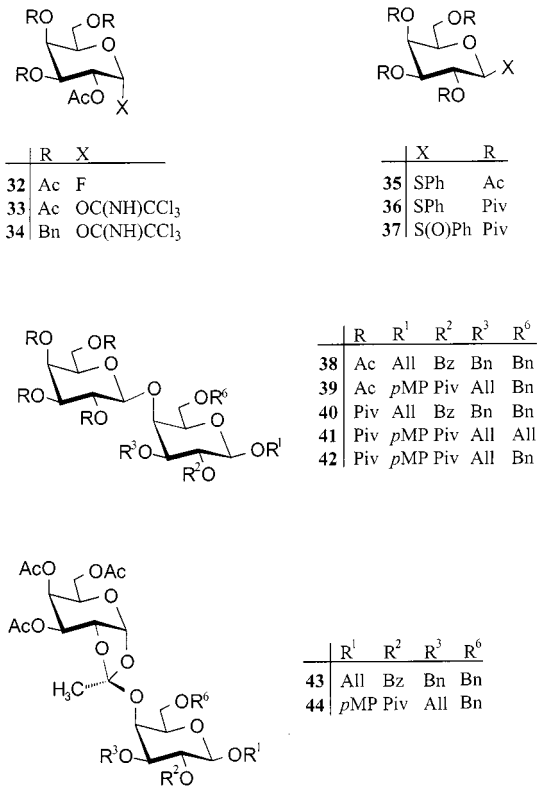
Assessment of Suitable Galactosyl Donors

It was deemed that donors suitable for iterative galactosylation for efficient generation of β(1→4)-oligogalactosides should contain (i) an ester function at *O*-2 for enhancement of β-selectivity in the glycosylation step by anchimeric assistance, (ii) slender alkyl-type protection at *O*-3 and *O*-6 for augmentation of anomeric reactivity, (iii) a temporary, selectively removable blocking group at *O*-4, and (iv) anomeric substituents more effective towards β-selective Gal-4-OH glycosylations than the halides **1**−**6** used previously.

Conditions i−iii were readily implemented by settling on pivaloyl protection at *O*-2, acetyl groups at *O*-4, since Zemplén conditions (NaOMe/MeOH) allow their removal without affecting pivaloyl ester groups, and allyl or benzyl protection at *O*-3 and *O*-6. Judicious selection of the anomeric substituent, however, entailed model studies geared towards evaluation of the most appropriate modern glycosylation methodology: i.e., whether galactosyl fluorides,[55] or their imidate analogues[56] had advantages over their bromide and chloride counterparts, or whether thiogalactosides[57] and/or the respective sulfoxides[58,59] were more suitable donors in this context.

Exploratory couplings of peracetylated α-D-galactosyl fluoride **32**[60] and its β anomer[61] with acceptor galactoside **23** showed these donors to be insufficiently reactive to glycosylate the crucial Gal-4-OH group adequately (Scheme 3). With all of the activators used (boron trifluoride·diethyl ether,[62] TMS triflate,[63] or hafnocene dichloride/silver triflate[55,64,65]), reactions (CH_2Cl_2, −20 → 25 °C, 5−16 h) were incomplete, even in the presence of a large excess of the fluoride donor. Galactosyl trichloroacetimidates proved to be similarly unsuited as donors: coupling of tetraacetate **33**, previously used for glycosylation of the 3-OH[66] and 4-OH[67] moieties of otherwise protected glucosamines, with acceptor **23** proceeded exceedingly sluggish, irrespective of solvent, temperature and activation (BF_3·Et_2O or TMS triflate), while the tri-*O*-benzyl analogue **34**[68] did display higher reactivity when coupled with **23**, but produced α/β-galactobioside mixtures in only moderate yields.

The per-*O*-acetylated phenylthio galactoside **35**,[69] upon methyl triflate-promoted coupling with acceptors **23** and **31**, gave the β(1→4)-galactobiosides **38** and **39**, but invariably in admixture with the respective 2,3-orthoesters **43** and **44**, the only clues to be gained from the isolated yields listed in Table 1 being that an allyl group at *O*-3 of the acceptor (as in **31**) is more propitious than benzyl protection (as in **23**) for obtainment of the desired galactobioside. In contrast, however, triflate-induced coupling of per-*O*-pivaloylated phenylthio galactoside **36**[58,59] with acceptors **23**, **27**, and **31** was entirely free of orthoester formation, providing the respective β(1→4)-galactobiosides **40**−**42** in reasonable



Scheme 3. Evaluation of galactosyl donors **32**−**37** for generation of β(1→4)-galactobiosides by coupling with acceptors **23**, **27**, and **31**. Only the pivaloylated donors **36** and **37** proved free of orthoester formation, yielding disaccharides **40**−**42** efficiently (cf. Table 1)

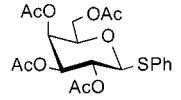
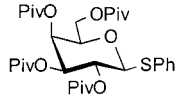
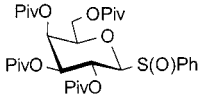
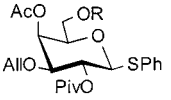
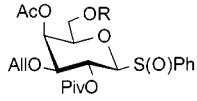
to satisfactory yields (48, 64, and 70%), the 3,6-bis-allylated acceptor performing best here too (Table 1). Preparatively useful results were also obtained with the phenylsulfoxido galactoside **37**,[59] which reacted with acceptors **27** and **31** through triflic anhydride activation under exceedingly mild conditions (1 h, −78 → 0 °C) to yield the respective β(1→4)-disaccharides **41** and **42** in the 70−80% yield range.

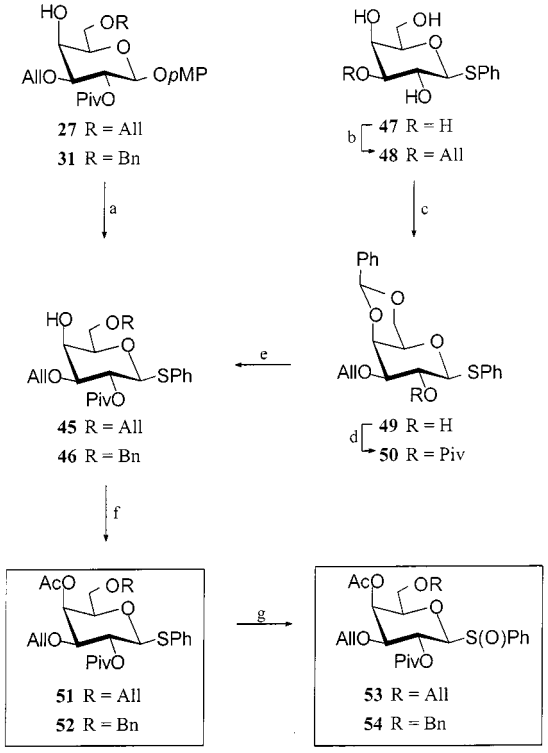
These results clearly pointed towards the use of phenylthio galactosides and/or their sulfoxide analogues with pivaloyl protection at *O*-2 for attainment of β-selective, orthoester-free galactosylation − a conclusion that, given the protective group pattern outlined above for iterative use, called for expedient generation of donors **51**−**54**, to be coupled subsequently with the equally well suited Gal-4-OH acceptors **27** and **31**.

Galactosyl Donors for Iterative Use

Two routes were pursued for acquisition of galactosyl thio and sulfoxide donors bearing the desired *O*-protection: pivaloyl at *O*-2, allyl and/or benzyl at *O*-3 and *O*-6, and acetyl at *O*-4, as this can be selectively removed after glycosylation. Most straightforward proved to be the two/three-step sequences starting from acceptors **27** and **31**, since their anomeric *p*-methoxyphenyloxy groups had the inherent capacity to be directly replaced by thiophenyl residues.[70] Indeed, on exposure to thiophenol/BF_3 in dichloromethane, **27** and **31** smoothly (15 min, 25 °C) gave the re-

Table 1. Couplings of *O*-protected phenylthio galactosides and their sulfoxide analogues with the Gal-4-OH of acceptors **23**, **27**, and **31**. Coupling conditions used for phenylthio galactoside donors for **35**, **36**, **51**, and **52**: Components, 4-Å molecular sieves, and 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP) in CH_2Cl_2, then activation with methyl triflate, room temperature, 16 h. − Sulfoxides **37**, **53**, and **54**: Analogous reaction mixture, but activation by triflic anhydride at −78 °C, then −60 → 0 °C, 1 h

Donor		Acceptor	β(1→4)-Galactobioside (isol. yield)	Orthoester
	**35**	**23**	**38** (39%)	**43** (25%)
		31	**39** (43%)	**44** (29%)
	**36**	**23**	**40** (48%)	–
		27	**41** (70%)	–
		31	**42** (64%)	–
	**37**	**23**	**40** (56%)	–
		27	**41** (71%)	–
		31	**42** (77%)	–
	**51** R = All	**27**	**55** (80%)	–
	52 R = Bn	**31**	**56** (79%)	–
	**53** R = All	**27**	**55** (86%)	–
	54 R = Bn	**31**	**56** (81%)	–



Scheme 4. Generation of β-selective galactosyl donors with the selectively removable acetyl blocking group at *O*-4. Reagents and conditions: a) PhSH, $BF_3{\cdot}OEt_2$, CH_2Cl_2, 25 °C, 15 min; 79% (**45**), 82% (**46**). − b) Bu_2SnO, toluene, reflux, 16 h, then AllBr/Bu_4NBr, THF, reflux, 8 h; 68%. − c) $PhCH(OMe)_2$, TsOH, THF, 25 °C, 2 h; 94%. − d) PivCl, DMAP, Et_3N, CH_2Cl_2, reflux, 16 h; 93%. − e) $NaBH_3CN$/HCl, Et_2O/THF, 0 °C, 20 min; 82%. − f) Ac_2O, Et_3N, DMAP, CH_2Cl_2, 25 °C, 2 h; 94% (**51**), 93% (**52**). − g) *m*CPBA, CH_2Cl_2, -78 °C, 15 min; 84% (**53**), 92% (**54**). − *p*MP = *p*-methoxyphenyl

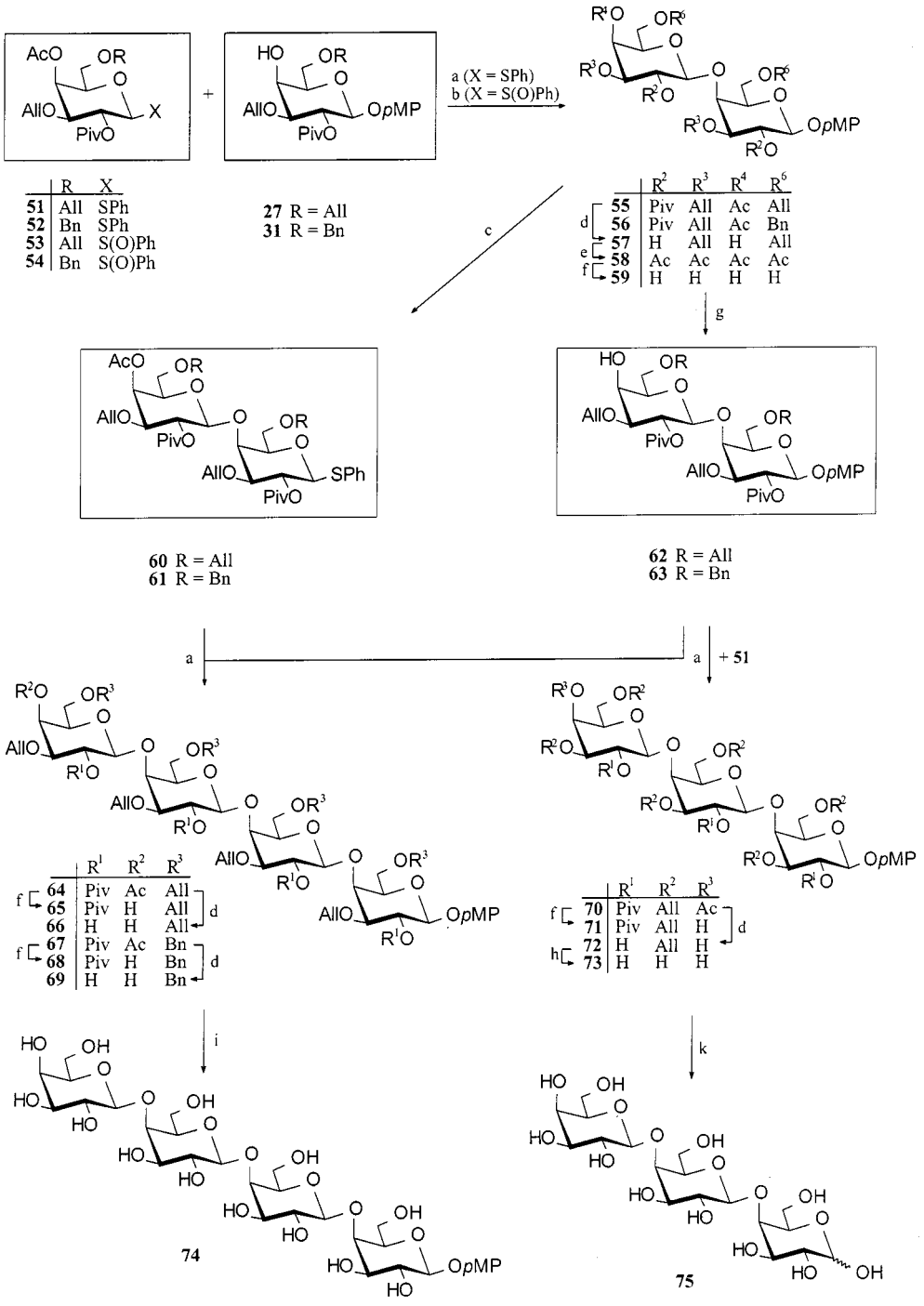
spective phenyl thiogalactosides **45** and **46** in high yields (cf. Scheme 4), their free 4-OH groups being unaffected when the reaction was terminated after 15 min by addition of triethylamine. Subsequent acetylation provided the donors **51** and **52**, respectively, and these were readily converted into the corresponding sulfoxide analogues **53** and **54** on oxidation with *m*-chloroperbenzoic acid.

As an alternate route to donors **52** and **54**, an approach based on the easily accessible[69] phenylthio galactoside **47** was examined, utilising the methodology developed for the acquisition of acceptors **27** and **31** from *p*-methoxyphenyl galactoside **24**. This approach could readily be accomplished for the 6-*O*-benzylated donor **52**: by dibutyltin-promoted allylation at *O*-3 (→ **48**), acid-catalysed 4,6-*O*-benzylidenation with benzaldehyde dimethylacetal (→ **49**), selective 2-*O*-pivaloylation (→ **50**), reductive opening of the cycloacetal (→ **46**), and acetylation. The yield of **52** over the five steps amounted to a respectable 45%, comparing favourably with its generation from *p*-methoxyphenyl galactoside **24** by way of **31**, which likewise required five steps, but gave an overall yield of only 30%.

Attempts to prepare the 3,6-di-*O*-allylated donor **51** similarly from phenyl thiogalactoside **47**, however, proved unavailing, since neither tributyltin-mediated bis-allylation nor mono-allylation of **49** proceeded with reasonable regioselectivities. Complex mixtures were invariably obtained, from which the desired 3,6-di-*O*-allyl derivative of **47** could only be isolated through extensive chromatography in yields of around 20%. This highly unselective course was unexpected, inasmuch as the respective *p*-methoxyphenyl galactoside **28** behaved distinctly differently under the same allylation conditions, providing the 3,6-di-*O*-allyl derivative **25** in 96% yield (Scheme 2).

Assembly of Di- and Oligo-β(1→4)-galactosides

With suitably blocked 4-OH-free acceptors and β-selective galactosyl donors now at hand, the stage was set for addressing the assembly of β(1→4)-linked galactooligosaccharides, using conventional combination strategies and blocking group manipulations. In an effort to demonstrate the repetitive and block-construction nature of the intended approach, the production of Gal-β(1→4)-Gal building blocks with donor and acceptor characteristics was targeted first. Thus, the galactobiosides **55** and **56** were obtained in high yields (> 80%) by glycosylation of acceptors **27** or **31** with phenylthio galactoside donors **51** and **52**, either through methyl triflate[71] activation, or, alternately, with the triflic anhydride-activated sulfoxide analogues **53** and **54** (Scheme 5). The two glycosylation methods proved equally effective in preparative terms, and both have been carried



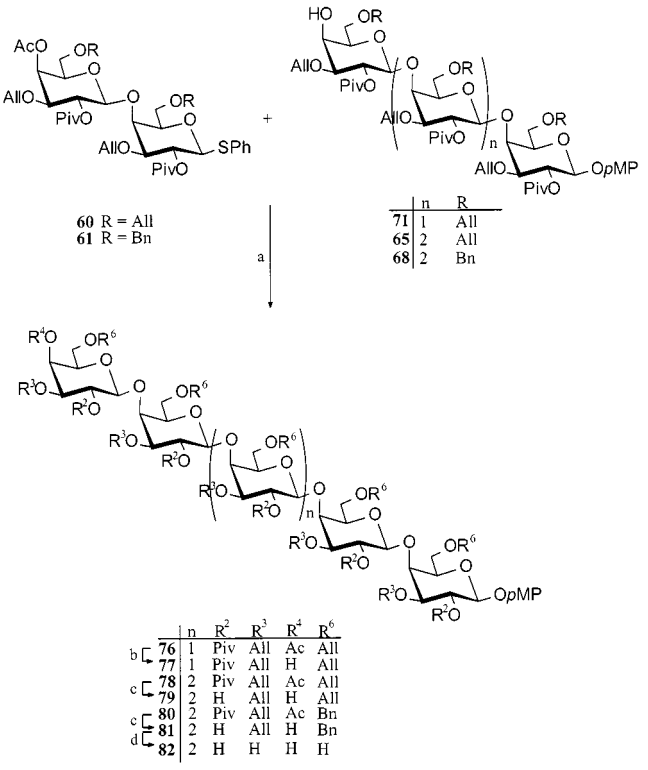
Scheme 5. Synthesis of β(1→4)-linked galactotri- and -tetraosides. Reagents and conditions: a) MeOTf, DTBMP, molecular sieves 4 Å, CH_2Cl_2, 25 °C, 16 h; 80% (**55**), 79% (**56**), 77% (**64**), 76% (**67**), 78% (**70**). − b) Tf_2O, DTBMP, CH_2Cl_2, −78 °C, then −60 → 0 °C, 1 h; 86% (**55**), 81% (**56**). − c) $PhSSiMe_3/BF_3{\cdot}OEt_2$, $ClCH_2CH_2Cl$, 40 °C, 2 h; 92% (**60**), 94% (**61**). − d) LiOH/MeOH, reflux, 12 h; 88% (**57**), 90% (**66**), (**69**), and (**72**). − e) DIBAL/[$NiCl_2$(dppp)], THF/Et_2O, 0 → 25 °C, 12 h → Ac_2O/DMAP/pyridine, 40 °C, 4 h; 78%. − f) NaOMe/MeOH, 25 °C, 16 h; 90% (**59**), 83% (**65**), 86% (**68**), 81% (**71**). − g) NaOMe/MeOH, CH_2Cl_2, 25 °C, 16 h; 84% (**62**), 85% (**63**). − h) $NaBH_4$/[$NiCl_2$(dppp)], THF/EtOH, 25 °C, 24 h → Ac_2O/ DMAP/pyridine, 25 °C, 6 h → NaOMe/MeOH, 25 °C, 16 h; 69%. − i) **67** → **74**: LiOH/MeOH, reflux, 12 h → DIBAL/[$NiCl_2$(dppp)], THF/Et_2O, 0 → 25 °C, 16 h → Ac_2O/DMAP/pyridine, 40 °C, 4 h → H_2, Pd/C, AcOH, 25 °C, 5 h → NaOMe/MeOH, 25 °C, 6 h; 67%. − k) **72**→**75**: $NaBH_4$/[$NiCl_2$(dppp)], THF/EtOH, 25 °C, 24 h → Ac_2O/ DMAP/pyridine, 25 °C, 6 h → CAN, CH_3CN/H_2O, 0 °C, 30 min → NaOMe/MeOH, 25 °C, 16 h; 70%. − *p*MP = *p*-methoxyphenyl

through to the hexasaccharide stage. Subsequently, however, only the use of the thioglycoside procedure is described for acquisition of the oligogalactosides as it required one fewer step for preparation of the respective donors − the oxidation to the corresponding sulfoxide is saved − although it entails the use of the comparatively toxic methyl triflate[71] as the only efficient promoter. Generation of the β(1→4)-galactotetra- and -hexaosides by

Kahne's[58] sulfoxide glycosylation method is described elsewhere.[72]

The preselected blocking group pattern in galactobiosides **55** and **56** allowed their ready conversion into Gal-β(1→4)-Gal building blocks with both donor and acceptor reactivity. Thus, replacement of the anomeric *p*MP substituent by an SPh moiety was readily accomplished with phenylthiotrimethylsilane/BF_3 (2 h, 40 °C) to provide the galactobiosyl donors **60** and **61** in yields over 90%; here the BF_3-mediated reaction with thiophenol, which had given useful results at the monosaccharide stage (**27** → **45** and **31** → **46**, for example), proved less advantageous as it resulted in partial decomposition of the products. For conversion of the disaccharide building blocks **55** and **56** into acceptors, the removal of the terminal acetate group was smoothly affected under Zemplén conditions (NaOMe/MeOH) to provide the 4′-OH-free galactobiosides **62** and **63** effectively (> 80% isol. yields). The further construction of the Gal-β(1→4)-trimers and tetramers followed obvious donor/acceptor combinations and proceeded in a most straightforward manner: methyl triflate-mediated coupling of **51** with digalactoside acceptor **62** gave trisaccharide **70** (78%). Correspondingly, coupling of the key disaccharide building blocks **60** with **62**, and **61** with **63**, uniformly provided the tetrasaccharides **64** and **67** with equal efficiencies, isolated yields surpassing 75%.

Reiteration of the process, coupling the requisite tri- and tetrasaccharide acceptors with free 4-OH groups in their terminal galactosyl residues with galactobiosyl donors **60** and **61**, smoothly afforded higher oligogalactosides. The galactopentaoside **76** thus resulted from treatment of galactotrioside acceptor **71** with donor **60** (67%), whereas the corresponding hexamers **78** and **80** were obtained by coupling of tetrasaccharide acceptor **65** with **60** (77%) and of **68** with **61** (78%), each glycosylation being effected by methyl triflate activation (Scheme 6).



	n	R			
71	1	All			
65	2	All			
68	2	Bn			

	n	R^2	R^3	R^4	R^6
76	1	Piv	All	Ac	All
77	1	Piv	All	H	All
78	2	Piv	All	Ac	All
79	2	H	All	H	All
80	2	Piv	All	Ac	Bn
81	2	H	All	H	Bn
82	2	H	H	H	H

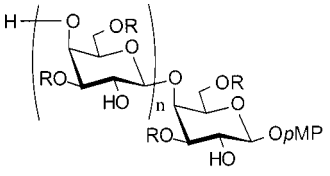
Scheme 6. Synthesis of β(1→4)-galactopenta- and -hexasaccharides. Reagents and conditions: a) MeOTf, DTBMP, 4 Å molecular sieves, CH_2Cl_2, 25 °C, 16 h; 67% (**76**), 77% (**78**), 78% (**80**). − b) NaOMe/ MeOH, 25 °C, 16 h; 88%. − c) LiOH/MeOH, reflux, 16 h; 89% (**79**), 86% (**81**). − d) DIBAL/[$NiCl_2$(dppp)], THF/Et_2O, 0 → 25 °C, 16 h → Ac_2O/DMAP/pyridine, 40 °C, 4 h → H_2, Pd/C, AcOH, 25 °C, 5 h → NaOMe/MeOH, 25 °C, 6 h; 64%

Deprotection of Blocked Di- and Oligogalactosides

The pattern of blocking groups having been judiciously chosen for selective sequential deprotection, their successive removal could indeed readily be accomplished either by direct use of conventional techniques or by adaptation of them. Thus, *selective de-O-acetylation* of the terminal Gal-4-OAc groups was smoothly effected under Zemplén conditions (NaOMe/MeOH, 25 °C, 16 h), with isolated yields uniformly in the 80−90% range, irrespective of whether the di- (**55** → **62**, **56** → **63**), tri- (**70** → **71**), tetra- (**64** → **65**, **67** → **68**) (cf. Scheme 5), or pentagalactoside levels (**76** → **77**, Scheme 6) were involved. These conditions were also effective for complete deesterification of peracetates (e.g., **58** → **59**, 90%).

De-O-pivaloylations required more strongly basic conditions, such as overnight exposure to lithium hydroxide in methanol either at room temperature[58,59] (e.g., **55** → **57**, 88%), or under reflux, which proved more suitable for the higher oligogalactosides [i.e., **70** → **72** (90%), **78** → **79** (89%) and **80** → **81** (86%)].

De-O-allylation: Removal of the allyl ether groups from *O*-3 and/or *O*-6 of otherwise unprotected galactosides proved to be intricate, as shown by model experiments with galactobioside **57**. Use of Wilkinson's catalyst $(Ph_3P)_3RhCl$ for isomerization to the enol ether and subsequent hydrolysis[73] gave the deallylated disaccharide **59** only in modest yields, due to the concomitant formation of side products, among which the 6-*O*-propyl ethers could be identified unequivocally (^{1}H NMR). The *tert*-butoxide-mediated isomerization/hydrolysis,[74] iodotrimethylsilane[75] and chlorotrimethylsilane/sodium iodide[76] procedures proved similarly unsuited. Of the various other deallylation techniques[77,78] evaluated for **57** → **59**, the action of *trans*-[$Pd(NH_3)Cl_2$] in refluxing *tert*-butyl alcohol[79] and exposure to DIBAL in the presence of a catalytic amount of a nickel(II) complex[80] proved promising. In particular, the



	n	R
57	1	All
59	1	H
72	2	All
73	2	H
66	3	All
74	3	H
79	5	All
82	5	H

Scheme 7. Removal of allyl ether functionalities by DIBAL in THF/ether or $NaBH_4$ in THF/EtOH in the presence of $NiCl_2$(dppp) (see ref. [81]) as catalyst

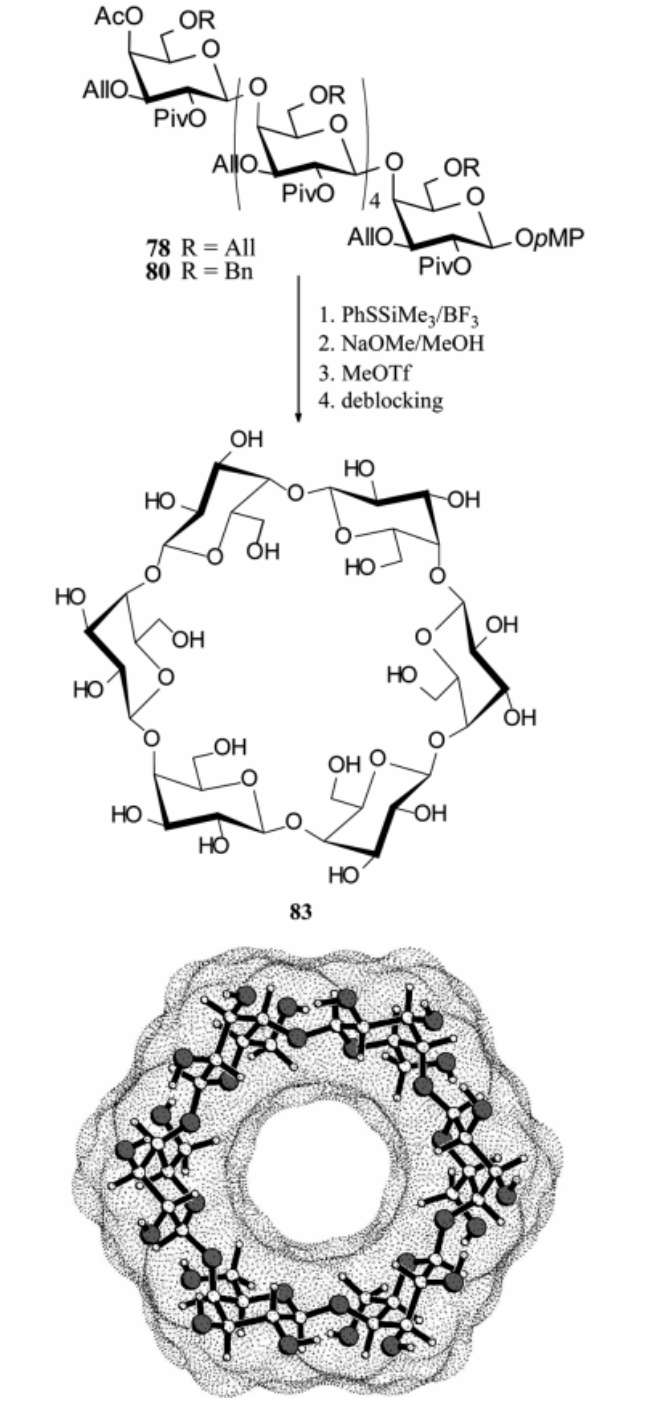
latter − exceedingly mild − procedure, comprising treatment with DIBAL/$NiCl_2$(dppp)[81] in THF/Et_2O for 12 h at ambient temperature[80] or $NaBH_4$/$NiCl_2$(dppp) in THF/EtOH, which we found as useful, effected clean removal of allyl groups in the di- (**57** → **59**) and trigalactosides (**72** → **73**), as evidenced by TLC (Scheme 7). For isolation of the highly hydrophilic products it was found advantageous to convert them first into their peracetates, as these are most readily separated from the aluminates or boronates generated on workup; subsequent release of the free *p*-methoxyphenyl oligogalactosides by Zemplén deacetylation then afforded the pure products in overall yields around 75%.

At the tetrasaccharide stage **66** → **74**, comprising the removal of a total of eight allyl ether functionalities, however, the DIBAL or $NaBH_4$/$NiCl_2$(dppp) procedure appeared to reach its limits, as the reaction proceeded sluggishly and resulted in the partial reduction of one or two of the allyl double bonds, the respective propyl ethers thus formed being removable only with difficulty. The same was observed for deallylation of the hexasaccharide **79** under these conditions, so the yields of the free *p*-methoxyphenyl oligogalactosides **74** and **82** did not exceed 30%. Sequential deprotection of tetragalactoside **68** with its four 3-*O*-allyl and four 6-*O*-benzyl groups proved considerably more effective, treatment with DIBAL/$NiCl_2$(dppp), followed by acetylation, hydrogenolysis, and de-*O*-acetylation, giving an acceptable overall yield (67%). The same procedure proceeded as efficiently (69%) when applied to deprotection at the hexasaccharide level (i.e., **81** → **82**; cf. Scheme 6).

The suitability of the *p*-methoxyphenyl group for anomeric protection is reflected − its convertibility into donor functionalities aside − in the mildness of its cleavage by cerium(IV) ammonium nitrate in aqueous acetonitrile,[82] 30 min at ambient temperature being sufficient for full removal. When applied to the peracetate of trisaccharide **73**, the fully deblocked galactotriose β-D-Gal*p*-(1→4)-β-D-Gal*p*-(1→4)-D-Gal*p* (**75**) was readily obtained as a 1:2 mixture of α and β anomers (70%). Its chemical shifts (^{1}H NMR) correlated well with those reported for a product isolated − albeit in undisclosed quantities − from a mixture of oligosaccharides generated by digestion of soy arabinogalactan with an *A. niger*-derived endogalactanase.[83]

Configurational Assignments

Structural and configurational assignments of each of the newly described β(1→4)-galactooligosaccharides, most notably their β-glycosidic linkages, were unequivocally secured from their ^{1}H and ^{13}C NMR spectroscopic data. In the galactobiosides **55**−**63**, the anomeric protons 1a-H and 1b-H are separated by 0.30−0.35 ppm and each exhibit large couplings of 7.8−8.1 Hz, clearly indicating axial dispositions for both, and hence β configurations. Similarly, for the galactotriosides **70**, **72**, and **73**, as well as for β(1→4)-galactotriose **75**, three anomeric signals with $J_{1,2}$ couplings of around 8 Hz were obtained in each case. Most notably, an arabinogalactan-derived product, isolated in undisclosed quantities from a complex oligosaccharide mixture[83] had ^{1}H chemical shifts (couplings not reported) identical with those obtained for synthetic **75**. In the oligosaccharides with four, five or six β(1→4)-linked galactose moieties, the individual anomeric protons appear within a very narrow shift range, only poorly resolved and hence not assignable to individual sugar protons. If an α(1→4)-linkage − i.e., an equatorially disposed anomeric proton − were present, it



Scheme 8. Conceptual approach to a hexameric β(1→4)-cyclogalactin **83**, an "inside-out" analogue of α-cyclodextrin, possessing a slightly wider, less hydrophobic cavity, based on calculations of its solvent-accessible surface (given in dotted form with a ball-and-stick model insert) and molecular lipophilicity distribution (see refs. [29, 30])

would have to appear as a 3−4 Hz doublet at substantially lower field (Δδ = 0.5 ppm); that signals of this type were not observed in any of the oligogalactosides provides indirect, but unequivocal, evidence of their continuous β-linkages.

Configurational assignments of the intersaccharidic linkages having readily been settled on the basis of ^{1}H NMR spectroscopic data (supporting information may be derived from the reported ^{13}C NMR spectroscopic data, which warrants little comment), confirmation of starch-like coiling within the linear oligogalactoside chains, strongly suggested both by analogy considerations (Figure 1) and by various molecular modelling approaches,[20−24] did not materialise. At present, none of the higher galactooligosaccharides has proved obtainable in crystalline form to allow X-ray structural investigations, either as a free sugar or as a *p*-methoxyphenyl derivative. Detailed analyses of their ^{1}H and ^{13}C NMR spectra, supported by COSY, TOCSY, and standard decoupling techniques, have also found no clear evidence of their overall conformations; i.e., whether [Gal*p*-β(1→4)]$_n$-Gal*p* oligosaccharides with n = 3−5 harbour any tendency towards coiling. Obviously, clarification of this issue must now await the synthesis of higher oligomers, acquisition of crystalline oligogalactosides suitable for X-ray structural analysis − inherently difficult in view of their polyhydroxylated surfaces − or the application of more sophisticated NMR techniques such as off-resonance ROESY experiments,[84] determination of proton-proton cross relaxation rates for calculation of interatomic distances,[85] or measurement of residual dipolar couplings.[86]

Conclusion

The methodology detailed here provides the first synthesis of β(1→4)-linked oligogalactosides beyond the trisaccharide level. It incorporates the use of activated phenylthio- and phenylsulfoxido galactosides for generation of the crucial β(1→4)-intersaccharidic linkages and a judiciously designed blocking group pattern for donors and acceptors alike: pivaloyl protection at *O*-2 for ensuring β-selectivity, sterically undemanding allyl and/or benzyl groups at *O*-3 and *O*-6 to enhance approachability of the notoriously unreactive galactosyl-4-OH, and the acetyl group for temporary protection at the terminal *O*-4. This strategy has allowed for iterative block syntheses and − by use of the *p*-methoxyphenyl moiety as an easily replaceable anomeric substituent − for interchange of donors and acceptors, thereby making the approach convergent and preparatively efficient. Accordingly, β(1→4)-galactooligosaccharides, hitherto obtained from various natural sources only in minimal amounts after extensive chromatography, are now readily accessible on a gram scale up to the hexasaccharide level. Moreover, the ready accessibility of two galactohexaosides, **78** and **80**, in suitably blocked form (Scheme 8) opens up the possibility of installing a donor functionality at one end, and a Gal-4-OH at the other. On anomeric activation this should result in intramolecular glycosylation and, after deblocking, in the hexameric cyclogalactin **83**. As this should, on the basis of calculations of its solvent-accessible surface and molecular lipophilicity distribution,[29,30] be an "inside-out" analogue of α-cyclodextrin, the obtainment of **83** and evaluation of its inclusion complexation behaviour is deemed to be of considerable interest.

Experimental Section

General Remarks: Reactions were carried out under Ar. − All solvents were of reagent grade and were also dried. All other reagents were used as received. − Melting points are uncorrected and were measured on a Büchi SMP-20. − Optical rotations were measured on a Perkin−Elmer 241 polarimeter at 20 °C using a cell of 1 dm path length. − Mass spectra were recorded on Varian MAT 311 and MAT 212 spectrometers. − Microanalyses were determined on a Perkin−Elmer 240 Elemental Analyzer. − Analytical thin-layer chromatography (TLC) was performed on precoated Merck plastic sheets (0.2 mm silica gel 60 F_{254}) with detection by UV (254 nm) and/or spraying with H_2SO_4 (50%) and heating. − Column chromatography was carried out on Fluka silica gel 60 (70−230 mesh); eluents are given in brackets. − ^{1}H and ^{13}C NMR spectra were recorded on Bruker WM 300, AC 300, and AVANCE 500 spectrometers. The structures of all new compounds were confirmed by COSY, TOCSY, selective TOCSY, and/or decoupling experiments. Chemical shifts are reported relative to sodium 2,2,3,3-tetradeutero-3-trimethylsilyl propionate (D_2O) or Me_4Si (all other solvents) as internal reference. Coupling constants are listed separately if an assignment was possible. *In the listings of ^{1}H and ^{13}C NMR spectroscopic data for the individual compounds, signals originating from blocking groups are omitted if well separated from the galactose-CH and CH_2 protons. This includes pivaloyl groups (9 H-singlets between δ = 1.18−1.26, carbon resonances at δ = 27−28 for CH_3, δ = 38−39 for CMe_3, δ = 176−178 ppm for CO), the aromatic protons and carbons of phenyl, p-methoxyphenyl, benzyl, and benzylidene moieties, and those allyl resonances that are distinctly separate. − Protons and carbons of the galactose moieties are designated alphabetically, starting from the reducing end: i.e., 1-Ha, 1-Hb,...up to 1-Hf for ^{1}H NMR, C-1a, C-1b, etc. for ^{13}C NMR spectroscopic data.*

1. Galactosyl Acceptors

Allyl 3-*O*-Benzyl-4,6-*O*-benzylidene-β-D-galactopyranoside (21): A suspension of allyl 4,6-*O*-benzylidene-β-D-galactopyranoside **20**[48] (8.02 g, 26 mmol) and Bu_2SnO (6.47 g, 26 mmol) in toluene (250 mL) was refluxed for 16 h with azeotropic removal of water. After reduction of the volume to approximately 20 mL, benzyl bromide (9.7 mL, 82 mmol) was added, and the mixture was stirred at 90 °C for 8 h. After concentration to dryness in vacuo, the residue was purified by elution from a silica gel column (eluent: toluene/EtOAc, 5:2) to give 9.47 g (91%) of **21**; m.p. 176−177 °C; R_f = 0.18 (toluene/EtOAc, 2:1); $[\alpha]_D^{20}$ = +31.3 (c = 1.0, $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.59 (d, 1 H, 2-OH), 3.32 (m, 1 H, 5-H), 3.48 (dd, 1 H, 3-H), 4.01 (m, 2 H, 2-H, 6-H), 4.04−4.16 (m, 2 H, 4-H, All-1-H), 4.28 (dd, 1 H, 6-H′), 4.34 (d, 1 H, 1-H), 4.42 (m, 1 H, All-1-H′), 4.74 (s, 2 H, CH_2Ph), 5.18−5.35 (m, 2 H, All-3-H_2), 5.45 (s, 1 H, CHPh); $J_{1,2}$ = 7.8, $J_{2,3}$ = 9.7, $J_{3,4}$ = 3.6, $J_{5,6'}$ = 1.3, $J_{6,6'}$ = −12.3 Hz. − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 66.8 (C-5), 69.4 (C-6), 70.1 (All-C-1), 70.2 (C-2), 71.6 (CH_2Ph), 73.2 (C-4), 79.3 (C-3), 101.2 (CHPh), 101.8 (C-1). − MS (FD): m/z = 398 [M^+]. − $C_{23}H_{26}O_6$ (398.45): calcd. C 69.33, H 6.58; found C 69.32, H 6.49.

Allyl 2-*O*-Benzoyl-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-galactopyranoside (22): Benzoyl chloride (2.8 mL, 24 mmol) was added to a solution of **21** (6.38 g, 16 mmol), pyridine (2.6 mL, 32 mmol), and DMAP (300 mg) in CH_2Cl_2 (45 mL). After this had been stirred for 24 h at room temperature, the solution was diluted with CH_2Cl_2 (200 mL) and washed successively with saturated aqueous $NaHCO_3$ (2 × 100 mL) and brine (100 mL). Drying ($MgSO_4$), removal of the solvent, and crystallization (CH_2Cl_2/cyclohexane) of the residue gave **22** (7.7 g, 96%) as colourless crystals of m.p. 174−175 °C; R_f = 0.43 (toluene/EtOAc, 2:1); $[\alpha]_D^{20}$ = +56.8 (*c* = 1.2, $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.43 (m, 1 H, 5-H), 3.79 (dd, 1 H, 3-H), 4.09 (dd, 1 H, 6-H), 4.13 (m, 1 H, All-1-H), 4.29 (d, 1 H, 4-H), 4.37 (m, 2 H, 6-H′, All-1-H′), 4.63, 4.74 (2 d, each 1 H, C*H*$_2$Ph), 4.64 (d, 1 H, 1-H), 5.06−5.26 (m, 2 H, All-3-H$_2$), 5.56 (s, 1 H, C*H*Ph), 5.72 (dd, 1 H, 2-H), 5.74−5.86 (m, 1 H, All-2-H); $J_{1,2}$ = 8.1, $J_{2,3}$ = 10.1, $J_{3,4}$ = 3.6, $J_{5,6}$ = 1.5, $J_{6,6'}$ = −12.2 Hz. − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 66.8 (C-5), 69.3 (All-C-1), 69.4 (C-6), 70.9 (C-2), 71.0 (*C*H$_2$Ph), 73.2 (C-4), 76.9 (C-3), 100.1 (C-1), 101.3 (*C*HPh). − MS (FD): *m*/*z* = 502 [M$^+$]. − $C_{30}H_{30}O_7$ (502.56): calcd. C 71.70, H 6.02; found C 71.73, H 6.00.

Allyl 2-*O*-Benzoyl-3,6-di-*O*-benzyl-β-D-galactopyranoside (23): $NaBH_3CN$ (6.91 g, 110 mmol) and freshly activated molecular sieves (3 Å, powdered, 10 g) were added with stirring, at room temperature, to a solution of **22** (5.53 g, 11 mmol) in THF (160 mL). After 10 min, the suspension was cooled (ice bath), and a saturated solution of HCl in Et_2O was added dropwise until the evolution of gas ceased. After another 20 min of stirring at 0 °C, the mixture was diluted with CH_2Cl_2 (400 mL) and filtered through a layer of Celite, which was washed thoroughly with CH_2Cl_2. The filtrates were washed successively with water (300 mL), saturated aqueous $NaHCO_3$ (2 × 200 mL) and brine (200 mL), dried ($MgSO_4$), and concentrated in vacuo. Coevaporation of the residue with MeOH (3 × 200 mL) and purification by elution from a silica gel column with 5:1 toluene/EtOAc afforded **23** (4.82 g, 87%) as a colourless syrup; R_f = 0.33 (toluene/EtOAc, 2:1); $[\alpha]_D^{20}$ = +26.4 (*c* = 1.6, $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.80 (br. s, 1 H, 4-OH), 3.63 (dd, 1 H, 3-H), 3.69 (m, 1 H, 5-H), 3.78, 3.86 (2 dd, each 1 H, 6-H$_2$), 4.08, 4.31 (2 m, each 1 H, All-1-H$_2$), 4.14 (d, 1 H, 4-H), 4.49, 4.66 (2 d, each 1 H, C*H*$_2$Ph), 4.54 (d, 1 H, 1-H), 4.60 (s, 2 H, C*H*$_2$Ph), 5.02−5.21 (m, 2 H, All-3-H$_2$), 5.50 (dd, 1 H, 2-H), 5.67−5.80 (m, 1 H, All-2-H); $J_{1,2}$ = 8.0, $J_{2,3}$ = 9.8, $J_{3,4}$ = 3.3, $J_{5,6}$ = 5.8, $J_{5,6'}$ = 6.1, $J_{6,6'}$ = −9.8 Hz. − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 66.0 (C-4), 69.0 (C-6), 69.4 (All-C-1), 71.1 (*C*H$_2$Ph), 71.2 (C-2), 73.5 (C-5), 73.7 (*C*H$_2$Ph), 78.3 (C-3), 99.9 (C-1). − MS (FD): *m*/*z* = 504 [M$^+$]. − $C_{30}H_{32}O_7$ (504.58): calcd. C 71.41, H 6.39; found C 71.31, H 6.34.

4-Methoxyphenyl 3,6-Di-*O*-allyl-β-D-galactopyranoside (25). − A. By Allylation of 4-Methoxyphenyl β-D-Galactoside (24) by Way of Tributylstannyl Ethers: A suspension of **24**[52] (13.2 g, 46 mmol) and $(Bu_3Sn)_2O$ (35 mL, 69 mmol) in toluene (200 mL) was refluxed for 16 h with azeotropic removal of water. The mixture was concentrated and redissolved in toluene (100 mL). Next, Bu_4NI (17.0 g, 46 mmol) and allyl bromide (46.5 mL, 0.55 mol) were added, and the mixture was stirred at 90 °C for 8 h. Evaporation of the solvent and purification of the residue by chromatography on silica gel (toluene/EtOAc, 2:1) gave **25** (12.8 g, 76%) as a syrup; R_f = 0.40 (CH_2Cl_2/MeOH, 20:1); $[\alpha]_D^{20}$ = −27.1 (*c* = 1.0, $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.68 (d, 1 H, 4-OH), 2.88 (d, 1 H, 2-OH), 3.45 (dd, 1 H, 3-H), 3.70 (m, 2 H, 5-H, 6-H), 3.76 (s, 3 H, OC*H*$_3$), 3.80 (m, 1 H, 6-H′), 3.97 (dt, 1 H, 2-H), 4.02−4.05 (m, 2 H, All-1-H$_2$), 4.08 (d, 1 H, 4-H), 4.16−4.28 (m, 2 H, All-1-H$_2$), 4.74 (d, 1 H, 1-H); $J_{1,2}$ = 7.9, $J_{2,3}$ = 9.5, $J_{2,OH}$ = 1.1, $J_{3,4}$ = 3.4, $J_{4,OH}$ = 2.4 Hz. − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 55.6 (O*C*H$_3$), 66.2 (C-4), 68.9 (C-6), 70.5 (C-2), 71.0, 72.6 (2 All-C-1), 73.8 (C-5), 80.1 (C-3), 102.4 (C-1). − MS (FD): *m*/*z* = 367 [M$^+$ + H]. − $C_{19}H_{26}O_7$ (366.41): calcd. C 62.28, H 7.15; found C 62.26, H 7.02.

B. By Tributyltin-Promoted Allylation of 4-Methoxyphenyl 3-*O*-Allyl-β-D-galactopyranoside (28): A suspension of **28** (0.98 g, 3 mmol) and $(Bu_3Sn)_2O$ (1.14 mL, 2.25 mmol) in toluene (40 mL) was refluxed for 16 h with azeotropic removal of water. The mixture was concentrated and redissolved in toluene (8 mL), after which Bu_4NI (1.10 g, 3 mmol) and allyl bromide (1.5 mL, 18 mmol) were added, and the mixture was stirred at 80 °C for 8 h. Evaporation of the solvent and purification of the residue by elution from a silica gel column (toluene/EtOAc, 2:1) gave 1.06 g (96%) of **25**, identical with the product described above.

4-Methoxyphenyl 3-*O*-Allyl-6-*O*-benzyl-β-D-galactopyranoside (26): A suspension of **28** (5.80 g, 17.8 mmol) and $(Bu_3Sn)_2O$ (6.8 mL, 13.3 mmol) in toluene (150 mL) was refluxed for 16 h with azeotropic removal of water. After addition of Bu_4NI (6.54 g, 17.7 mmol) and benzyl bromide (9.2 mL, 77 mmol), stirring was continued for 8 h at 90 °C. Evaporation of the solvent and column chromatography (toluene/EtOAc, 2:1) gave **26** (6.8 g, 92%) as a syrup; R_f = 0.40 (toluene/EtOAc, 1:1); $[\alpha]_D^{20}$ = +8.9 (*c* = 1.0, $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.60 (d, 1 H, 4-OH), 2.78 (d, 1 H, 2-OH), 3.42 (dd, 1 H, 3-H), 3.68 (t, 1 H, 5-H), 3.74 (s, 3 H, OC*H*$_3$), 3.80 (m, 2 H, 6-H$_2$), 3.99 (bt, 1 H, 2-H), 4.06 (br. s, 1 H, 4-H), 4.15−4.27 (m, 2 H, All-1-H$_2$), 4.56 (s, 2 H, C*H*$_2$Ph), 4.73 (d, 1 H, 1-H); $J_{1,2}$ = 7.8, $J_{2,3}$ = 9.4, $J_{2,OH}$ = 1.7, $J_{3,4}$ = 3.3, $J_{4,OH}$ = 1.8, $J_{5,6}$ = 5.7 Hz. − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 55.6 (O*C*H$_3$), 66.4 (C-4), 69.3 (C-6), 70.7 (C-2), 71.1 (All-C-1), 73.8 (*C*H$_2$Ph), 74.0 (C-5), 80.3 (C-3), 102.5 (C-1). − MS (FD): *m*/*z* = 416 [M$^+$]. − $C_{23}H_{28}O_7$ (416.47): calcd. C 66.33, H 6.78; found C 66.40, H 6.73.

4-Methoxyphenyl 3,6-Di-*O*-allyl-2-*O*-pivaloyl-β-D-galactopyranoside (27): Pivaloyl chloride (9.2 mL, 75 mmol) was added to a solution of **25** (11.0 g, 30 mmol), pyridine (4.8 mL, 60 mmol), Et_3N (8.4 mL, 60 mmol), and DMAP (730 mg, 6 mmol) in CH_2Cl_2 (280 mL). After stirring for 12 h at room temperature, the mixture was washed with 2 N HCl (2 × 250 mL) and saturated aqueous $NaHCO_3$ (2 × 250 mL) and dried ($MgSO_4$). Removal of the solvent in vacuo gave a liquid residue, which was subjected to chromatography on silica gel (toluene/EtOAc, 4:1). Eluted first (R_f = 0.60) was the minor product, which proved (^{1}H NMR) to be the 2,4-dipivaloate (2.2 g, 14%). Concentration of the fractions with R_f = 0.27 (toluene/EtOAc, 4:1) then gave the 2-pivaloate **27** (9.32 g, 69%) as a syrup; $[\alpha]_D^{20}$ = −11.0 (*c* = 1.0, $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.57 (br. s, 1 H, 4-OH), 3.55 (dd, 1 H, 3-H), 3.74 (m, 5 H, 5-H, 6-H, OC*H*$_3$), 3.82 (m, 1 H, 6-H′), 4.08 (m, 4 H, 2 All-1-H$_2$), 4.06 (m, 1 H, 4-H), 4.82 (d, 1 H, 1-H), 5.17−5.31 (m, 4 H, All-3-H$_2$), 5.39 (dd, 1 H, 2-H); $J_{1,2}$ = 8.1, $J_{2,3}$ = 9.8, $J_{3,4}$ = 3.3 Hz. − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 55.6 (O*C*H$_3$), 66.2 (C-4), 68.8 (C-6), 70.2 (C-2), 70.9, 72.6 (2 All-C-1), 73.9 (C-5), 78.9 (C-3), 100.9 (C-1). − MS (FD): *m*/*z* = 450 [M$^+$]. − $C_{24}H_{34}O_8$ (450.53): calcd. C 63.98, H 7.61; found C 64.10, H 7.67.

4-Methoxyphenyl 3-*O*-Allyl-β-D-galactopyranoside (28): A suspension of *p*-methoxyphenyl galactoside **24**[52] (6.87 g, 24 mmol) and Bu_2SnO (5.97 g, 24 mmol) in toluene (150 mL) was refluxed for 16 h with azeotropic removal of water. After evaporation of the solvent, the residue was dissolved in THF (90 mL), after which Bu_4NBr (7.74 g, 24 mmol) and allyl bromide (10.1 mL, 120 mmol) were added, and the mixture was refluxed for 8 h. After the solvent

was removed in vacuo, the residue was purified by column chromatography on silica gel (toluene/EtOAc, 1:1) to give, on evaporation of the appropriate fractions, a colourless solid residue that crystallised from EtOAc: 5.78 g (74%) of **28**; m.p. 138−139 °C (ref.:[54] 139−140 °C); R_f = 0.58 (CH_2Cl_2/MeOH, 5:1); $[\alpha]_D^{20}$ = −9.0 (*c* = 1.0, MeOH). − ^{1}H NMR (CD_3OD): δ = 3.41 (dd, 1 H, 3-H), 3.62 (m, 1 H, 5-H), 3.78 (m, 5 H, 6-H_2, OCH_3), 3.88 (dd, 1 H, 2-H), 4.09 (d, 1 H, 4-H), 4.14−4.32 (m, 2 H, All-1-H_2), 4.77 (d, 1 H, 1-H); $J_{1,2}$ = 7.8, $J_{2,3}$ = 9.7, $J_{3,4}$ = 3.2 Hz. − ^{13}C NMR (CD_3OD): δ = 56.2 (O*C*H$_3$), 62.6 (C-6), 67.1 (C-4), 71.6 (C-2), 72.0 (All-C-1), 76.9 (C-5), 82.3 (C-3), 104.2 (C-1). − MS (FD): *m*/*z* = 326 [M$^+$]. − $C_{16}H_{22}O_7$ (326.34): calcd. C 58.89, H 6.79; found C 58.91, H 6.92.

4-Methoxyphenyl 3-*O*-Allyl-4,6-*O*-benzylidene-β-D-galactopyranoside (29): $PhCH(OMe)_2$ (6.0 mL, 40 mmol) and $TsOH·H_2O$ (200 mg) were added to a solution of 3-*O*-allyl ether **28** (6.53 g, 20 mmol) in THF (70 mL). After stirring for 2 h at room temperature, the mixture was diluted with CH_2Cl_2 (200 mL), washed with saturated aqueous $NaHCO_3$ (200 mL) and saturated aqueous NaCl (200 mL), and dried ($MgSO_4$). Concentration gave a solid residue, which crystallised from CH_2Cl_2/cyclohexane as colourless needles: 7.54 g (91%) of **29**; m.p. 222−224 °C; R_f = 0.11 (toluene/EtOAc, 4:1); $[\alpha]_D^{20}$ = −20.8 (*c* = 0.5, $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.52 (br.s, 1 H, 2-OH), 3.49 (d, 1 H, 5-H), 3.53 (dd, 1 H, 3-H), 3.77 (s, 3 H, OCH_3), 4.08 (dd, 1 H, 6-H), 4.18 (dd, 1 H, 2-H), 4.23 (m, 2 H, All-1-H_2), 4.28 (dd, 1 H, 4-H), 4.35 (dd, 1 H, 6-H′), 4.82 (d, 1 H, 1-H), 5.20−5.37 (m, 2 H, All-3-H_2), 5.55 (s, 1 H, C*H*Ph); $J_{1,2}$ = 7.8, $J_{2,3}$ = 9.7, $J_{3,4}$ = 3.5, $J_{4,5}$ = 0.7, $J_{5,6}$ = 1.8, $J_{5,6'}$ = 1.5, $J_{6,6'}$ = −12.4 Hz. − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 55.7 (O*C*H$_3$), 66.9 (C-5), 69.3 (C-6), 69.7 (C-2), 70.8 (All-C-1), 73.0 (C-4), 79.0 (C-3), 101.2 (*C*HPh), 102.7 (C-1). − MS (FD): *m*/*z* = 414 [M$^+$]. − $C_{23}H_{26}O_7$ (414.45): calcd. C 66.66, H 6.32; found C 66.58, H 6.31.

4-Methoxyphenyl 3-*O*-Allyl-4,6-*O*-benzylidene-2-*O*-pivaloyl-β-D-galactopyranoside (30): A solution of **29** (6.63 g, 16 mmol), Et_3N (5.0 mL, 36 mmol), pivaloyl chloride (3.9 mL, 32 mmol), and DMAP (980 mg, 8 mmol) in CH_2Cl_2 (200 mL) was refluxed for 16 h. MeOH (20 mL) was added at room temperature, and stirring was continued for 10 min. After dilution with CH_2Cl_2 (300 mL), the mixture was washed with saturated aqueous $NaHCO_3$ (3 × 200 mL), dried ($MgSO_4$), and concentrated to give a solid residue, which crystallised on trituration with CH_2Cl_2/cyclohexane to give **30** (7.65 g, 96%) as colourless crystals, m.p. 152 °C; R_f = 0.53 (toluene/EtOAc, 4:1); $[\alpha]_D^{20}$ = +2.5 (*c* = 0.9, $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.50 (m, 1 H, 5-H), 3.67 (dd, 1 H, 3-H), 3.75 (s, 3 H, OCH_3), 4.05−4.20 (m, 2 H, All-1-H_2), 4.10 (dd, 1 H, 6-H), 4.31 (d, 1 H, 4-H), 4.35 (dd, 1 H, 6-H′), 4.91 (d, 1 H, 1-H), 5.15−5.31 (m, 2 H, All-3-H_2), 5.55 (dd, 1 H, 2-H), 5.56 (s, 1 H, C*H*Ph); $J_{1,2}$ = 8.1, $J_{2,3}$ = 10.2, $J_{3,4}$ = 3.5, $J_{4,5}$ = 0.8, $J_{5,6}$ = 1.8, $J_{5,6'}$ = 1.5, $J_{6,6'}$ = −12.4 Hz. − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 55.7 (O*C*H$_3$), 66.9 (C-5), 69.2 (C-6), 69.7 (C-2), 70.8 (All-C-1), 73.4 (C-4), 77.4 (C-3), 101.2 (*C*HPh), 101.3 (C-1). − MS (FD): *m*/*z* = 498 [M$^+$]. − $C_{28}H_{34}O_8$ (498.57): calcd. C 67.45, H 6.87; found C 67.40, H 6.86.

4-Methoxyphenyl 3-*O*-Allyl-6-*O*-benzyl-2-*O*-pivaloyl-β-D-galactopyranoside (31). − A. Selective Pivaloylation of 26: Pivaloyl chloride (7.4 mL, 60 mmol) was added to a solution of **26** (10.4 g, 25 mmol), pyridine (4.0 mL, 50 mmol), Et_3N (7.0 mL, 50 mmol), and DMAP (600 mg, 5 mmol) in CH_2Cl_2 (270 mL) . After stirring for 12 h at room temperature, the mixture was washed with 2 N HCl (2 × 250 mL) and saturated aqueous $NaHCO_3$ (2 × 250 mL), and dried ($MgSO_4$). Removal of the solvent in vacuo gave a liquid residue, which was subjected to chromatography on silica gel (toluene/EtOAc, 4:1), to afford, after evaporation of the appropriate fractions with R_f = 0.42 (toluene/EtOAc, 4:1), 9.76 g (78%) of **31** as a colourless syrup; $[\alpha]_D^{20}$ = −4.6 (*c* = 0.9, $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.60 (s, 1 H, 4-OH), 3.54 (dd, 1 H, 3-H), 3.76 (m, 4 H, 5-H, OCH_3), 3.81 (dd, 1 H, 6-H), 3.88 (dd, 1 H, 6-H′), 4.03 (m, 1 H, All-1-H), 4.12−4.24 (m, 2 H, 4-H, All-1-H′), 4.60 (s, 2 H, CH_2Ph), 4.82 (d, 1 H, 1-H), 5.19−5.31 (m, 2 H, All-3-H_2), 5.40 (dd, 1 H, 2-H); $J_{1,2}$ = 8.0, $J_{2,3}$ = 9.8, $J_{3,4}$ = 3.3, $J_{5,6}$ = 6.2, $J_{5,6'}$ = 5.7, $J_{6,6'}$ = −9.7 Hz. − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 55.7 (O*C*H$_3$), 66.4 (C-4), 69.2 (C-6), 70.2 (C-2), 71.0 (All-C-1), 73.9 (C-5), 74.0 (*C*H$_2$Ph), 78.9 (C-3), 101.0 (C-1). − MS (FD): *m*/*z* = 500 [M$^+$]. − $C_{28}H_{36}O_8$ (500.59): calcd. C 67.18, H 7.25; found C 67.17, H 7.27.

B. Reductive Opening of the Benzylidene Acetal in 30: $NaBH_3CN$ (9.4 g, 0.15 mol) and freshly activated, powdered molecular sieves (3 Å, 10 g) were added to a stirred solution of **30** (7.48 g, 15 mmol) in THF (200 mL), followed by cooling (ice bath) and dropwise addition of a saturated solution of HCl in Et_2O until the evolution of gas ceased. After another 20 min of stirring at 0 °C, the mixture was diluted with CH_2Cl_2 (400 mL) and filtered through a layer of Celite, which was washed thoroughly with CH_2Cl_2. The filtrates were washed successively with water (300 mL), saturated aqueous $NaHCO_3$ (2 × 200 mL) and brine (200 mL), dried ($MgSO_4$), and taken to dryness in vacuo. Purification of the residue by elution from a silica gel column (cyclohexane/EtOAc, 4:1) and removal of the solvents from the respective eluates gave 5.75 g (77%) of **31**, identical with the product described above.

2. Galactosyl Donors

Phenyl 3,6-Di-*O*-allyl-2-*O*-pivaloyl-1-thio-β-D-galactopyranoside (45): $BF_3·OEt_2$ (0.81 mL, 6.5 mmol) was added to a solution of *p*-methoxyphenyl galactoside **27** (5.85 g, 13 mmol) and PhSH (5.3 mL, 52 mmol) in CH_2Cl_2 (100 mL) . After stirring for 15 min at room temperature, the mixture was diluted with CH_2Cl_2 (100 mL), washed with saturated aqueous $NaHCO_3$ (2 × 200 mL), and dried ($MgSO_4$). Removal of the solvent in vacuo and subsequent column chromatography (toluene/EtOAc 6:1) gave thioglycoside **45** (4.47 g, 79%) as a colourless syrup; R_f = 0.38 (toluene/EtOAc, 4:1); $[\alpha]_D^{20}$ = +5.5 (*c* = 1.0, $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.56 (br. s, 1 H, 4-OH), 3.51 (dd, 1 H, 3-H), 3.66 (t, 1 H, 5-H), 3.68−3.82 (m, 2 H, 6-H_2), 3.96−4.17 (m, 5 H, 4-H, 2 All-1-H_2), 4.65 (d, 1 H, 1-H), 5.16−5.33 (m, 5 H, 2-H, 2 All-3-H_2); $J_{1,2}$ = 10.2, $J_{2,3}$ = 9.3, $J_{3,4}$ = 3.2, $J_{6,6'}$ = −6.0 Hz. − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 66.4 (C-4), 68.4 (C-2), 69.0 (C-6), 70.9, 72.6 (2 All-C-1), 77.3 (C-5), 79.8 (C-3), 87.1 (C-1). − MS (FD): *m*/*z* = 436 [M$^+$]. − $C_{23}H_{32}O_6S$ (436.57): calcd. C 63.28, H 7.39; found C 63.19, H 7.33.

Phenyl 3-*O*-Allyl-6-*O*-benzyl-2-*O*-pivaloyl-1-thio-β-D-galactopyranoside (46). A. By Replacement of Anomeric *Op*MP in 31 by SPh: Acceptor galactoside **31** (5.51 g, 11 mmol) was exposed to PhSH (4.5 mL, 44 mmol) in CH_2Cl_2 (80 mL) containing $BF_3·Et_2O$ (0.6 mL, 4.8 mmol) at ambient temperature for 15 min, followed by workup as described for **27** → **45**. Purification by column chromatography on silica gel (toluene/EtOAc, 7:1) gave thiogalactoside **46** (4.39 g, 82%) as a colourless syrup; R_f = 0.40 (toluene/EtOAc, 4:1); $[\alpha]_D^{20}$ = +3.4 (*c* = 1.03, $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.51 (br. s, 1 H, 4-OH), 3.64 (dd, 1 H, 3-H), 3.68 (t, 1 H, 5-H), 3.82 (m, 2 H, 6-H_2), 3.95−4.18 (m, 3 H, 4-H, All-1-H_2), 4.58 (s, 2 H, CH_2Ph), 4.65 (d, 1 H, 1-H), 5.15−5.29 (m, 3 H, 2-H, All-3-H_2); $J_{1,2}$ = 10.1, $J_{2,3}$ = 9.3, $J_{3,4}$ = 3.3, $J_{4,5}$ = 0.6, $J_{5,6}$ = 6.0 Hz. − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 66.5 (C-4), 68.4 (C-

2), 69.3 (C-6), 70.9 (All-C-1), 73.7 (CH_2Ph), 77.4 (C-5), 79.8 (C-3), 87.0 (C-1). − MS (FD): m/z = 486 [M^+]. − $C_{27}H_{34}O_6S$ (486.63): calcd. C 66.64, H 7.04; found C 66.56, H 7.11.

B. Reductive Opening of the Benzylidene Acetal in 50: $NaBH_3CN$ (9.4 g, 0.15 mol) and powdered molecular sieves (3 Å, 10 g) were added to a stirred solution of **50** (7.27 g, 15 mmol) in THF (200 mL), followed by cooling (ice bath) and dropwise addition of a saturated solution of HCl in Et_2O until the evolution of gas ceased. After another 20 min of stirring at 0 °C, the mixture was diluted with CH_2Cl_2 (400 mL) and filtered through a layer of Celite, which was washed thoroughly with CH_2Cl_2. The filtrates were washed successively with water (300 mL), saturated aqueous $NaHCO_3$ (2 × 200 mL) and brine (200 mL), dried ($MgSO_4$), and taken to dryness in vacuo. Purification of the residue by elution from a silica gel column (cyclohexane/EtOAc, 4:1) and removal of the solvents from the respective eluates gave 5.99 g (82%) of **46**, identical with the product described above.

Phenyl 3-*O*-Allyl-1-thio-β-D-galactopyranoside (48): A suspension of thiogalactoside **47**[69] (8.17 g, 30 mmol) and Bu_2SnO (7.47 g, 30 mmol) in toluene (150 mL) was refluxed for 16 h with azeotropic removal of water. After evaporation of the solvent, the residue was dissolved in THF (120 mL), after which Bu_4NBr (9.67 g, 30 mmol) and allyl bromide (12.7 mL, 150 mmol) were added and the mixture was refluxed for 8 h. After the solvent had been removed in vacuo, the residue was purified by column chromatography on silica gel (toluene/EtOAc, 1:1) to give **48** (6.37 g, 68%) upon evaporation of the appropriate fractions, as colourless crystals of m.p. 116−118 °C; R_f = 0.68 (CH_2Cl_2/MeOH, 5:1); $[\alpha]_D^{20}$ = −18.9 (c = 0.94, MeOH). − ^{1}H NMR (300 MHz, CD_3OD): δ = 3.34 (dd, 1 H, 3-H), 3.53 (dt 1 H, 5-H), 3.71 (t, 1 H, 2-H), 3.72 (dd, 1 H, 6-H), 3.77 (dd, 1 H, 6-H′), 4.07 (dd, 1 H, 4-H), 4.12−4.26 (m, 2 H, All-1-H_2), 4.60 (d, 1 H, 1-H); $J_{1,2}$ = 9.8, $J_{2,3}$ = 9.1, $J_{3,4}$ = 3.7, $J_{4,5}$ = 0.8, $J_{5,6}$ = 6.7, $J_{6,6'}$ = −11.4 Hz. − ^{13}C NMR (75.5 MHz, CD_3OD): δ = 63.1 (C-6), 67.9 (C-4), 70.5 (C-2), 72.3 (All-C-1), 80.5 (C-5), 84.0 (C-3), 90.7 (C-1). − MS (FD): m/z = 312 [M^+]. − $C_{15}H_{20}O_5S$ (312.39): calcd. C 57.67, H 6.45; found C 57.74, H 6.40.

Phenyl 3-*O*-Allyl-4,6-*O*-benzylidene-1-thio-β-D-galactopyranoside (49): $PhCH(OMe)_2$ (6.0 mL, 40 mmol) and $TsOH·H_2O$ (200 mg) were added to a solution of **48** (6.25 g, 20 mmol) in THF (70 mL). After stirring for 2 h at room temperature the mixture was diluted with CH_2Cl_2 (200 mL), washed with saturated aqueous $NaHCO_3$ (200 mL) and saturated aqueous NaCl (200 mL), and dried ($MgSO_4$). Concentration gave a solid residue, which crystallised from EtOH as colourless needles: 7.53 g (94%) of **49**; m.p. 161−162 °C; R_f = 0.25 (toluene/EtOAc, 4:1); $[\alpha]_D^{20}$ = +14.5 (c = 0.94, $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.52 (d, 1 H, 2-OH), 3.51 (m, 3 H, 5-H, 3-H), 3.90 (td, 1 H, 2-H), 4.03 (dd, 1 H, 6-H), 4.12−4.22 (m, 2 H, All-1-H_2), 4.25 (dd, 1 H, 4-H), 4.37 (dd, 1 H, 6-H′), 4.54 (d, 1 H, 1-H), 5.15−5.33 (m, 2 H, All-3-H_2), 5.51 (s, 1 H, C*H*Ph); $J_{1,2}$ = 9.5, $J_{2,3}$ = 9.5, $J_{3,4}$ = 3.2, $J_{4,5}$ = 0.6, $J_{5,6}$ = 1.6, $J_{6,6'}$ = −12.4 Hz. − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 67.1 (C-2), 69.4 (C-6), 70.1 (C-5), 70.9 (All-C-1), 73.3 (C-4), 80.0 (C-3), 87.1 (C-1), 101.1 (*C*HPh). − MS (FD): m/z = 400 [M^+]. − $C_{22}H_{24}O_5S$ (400.49): calcd. C 65.98, H 6.04; found C 66.15, H 5.97.

Phenyl 3-*O*-Allyl-4,6-*O*-benzylidene-2-*O*-pivaloyl-1-thio-β-D-galactopyranoside (50): A solution of **49** (7.21 g, 18 mmol), Et_3N (5.6 mL, 40 mmol), pivaloyl chloride (4.4 mL, 36 mmol), and DMAP (1.1 g, 9 mmol) in CH_2Cl_2 (200 mL) was refluxed for 16 h. MeOH (20 mL) was added at room temperature, and stirring was continued for 10 min. After dilution with CH_2Cl_2 (300 mL), the mixture was washed with saturated aqueous $NaHCO_3$ (3 × 200 mL), dried ($MgSO_4$), and concentrated to a solid residue, which crystallised on trituration with EtOH to give **50** (8.11 g, 96%) as colourless crystals, m.p. 131−133 °C; R_f = 0.55 (toluene/EtOAc, 4:1); $[\alpha]_D^{20}$ = −7.8 (c = 0.96, $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.48 (d, 1 H, 5-H), 3.64 (dd, 1 H, 3-H), 3.98−4.13 (m, 3 H, 6-H, All-1-H_2), 4.27 (d, 1 H, 4-H), 4.36 (dd, 1 H, 6-H′), 4.71 (d, 1 H, 1-H), 5.13−5.33 (m, 2 H, All-3-H_2, 2-H), 5.51 (s, 1 H, C*H*Ph); $J_{1,2}$ = 9.9, $J_{2,3}$ = 9.6, $J_{3,4}$ = 3.3, $J_{5,6}$ = 1.6, $J_{5,6'}$ = 1.5, $J_{6,6'}$ = −12.4 Hz. − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 67.9 (C-2), 69.4 (C-6), 70.0 (C-5), 70.7 (All-C-1), 73.5 (C-4), 78.6 (C-3), 85.8 (C-1), 101.2 (*C*HPh). − MS (FD): m/z = 484 [M^+]. − $C_{27}H_{32}O_6S$ (484.61): calcd. C 66.92, H 6.66; found C 66.90, H 6.72.

Phenyl 4-*O*-Acetyl-3,6-di-*O*-allyl-2-*O*-pivaloyl-1-thio-β-D-galactopyranoside (51): Ac_2O (1.4 mL, 15 mmol) was added to a stirred solution of thioglycoside **45** (4.36 g, 10 mmol), Et_3N (2.8 mL, 20 mmol), and DMAP (244 mg, 2 mmol) in CH_2Cl_2 (40 mL). After 2 h, MeOH (5 mL) was added, and stirring was continued for 10 min. The solution was diluted with CH_2Cl_2 (100 mL), washed with saturated aqueous $NaHCO_3$ (2 × 100 mL), dried ($MgSO_4$), and concentrated. Column chromatography (toluene/EtOAc, 9:1) gave acetate **51** (4.49 g, 94%) as a colourless syrup; R_f = 0.65 (toluene/EtOAc, 4:1); $[\alpha]_D^{20}$ = +8.1 (c = 1.0, $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.12 (s, 3 H, AcC*H*$_3$), 3.50 (dd, 1 H, 6-H), 3.56 (dd, 1 H, 3-H) 3.59 (dd, 1 H, 6-H′), 3.78 (t, 1 H, 5-H), 3.85−4.16 (m, 4 H, 2 All-1-H_2), 4.71 (d, 1 H, 1-H), 5.12−5.30 (m, 5 H, 2-H, 2 All-3-H_2), 5.52 (dd, 1 H, 4-H); $J_{1,2}$ = 10.2, $J_{2,3}$ = 9.7, $J_{3,4}$ = 3.2, $J_{4,5}$ = 0.8, $J_{5,6}$ = 6.2, $J_{6,6'}$ = −9.9 Hz. − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.8 (Ac*C*H$_3$), 66.6 (C-4), 68.3 (C-6), 68.4 (C-2), 70.7, 72.5 (2 All-C-1), 76.3 (C-5), 77.0 (C-3), 87.3 (C-1). − MS (FD): m/z = 478 [M^+]. − $C_{25}H_{34}O_7S$ (478.60): calcd. C 62.74, H 7.16; found C 62.75, H 7.28.

Phenyl 4-*O*-Acetyl-3-*O*-allyl-6-*O*-benzyl-2-*O*-pivaloyl-1-thio-β-D-galactopyranoside (52): Thioglycoside **46** (4.87 g, 10 mmol) was acetylated as in the preparation of **51**. Column chromatography (cyclohexane/EtOAc, 7:1) gave acetate **52** (4.92 g, 93%) as a colourless syrup; R_f = 0.47 (toluene/EtOAc, 9:1); $[\alpha]_D^{20}$ = −12.7 (c = 1.0, $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.06 (s, 3 H, AcC*H*$_3$), 3.54 (m, 2 H, 3-H, 6-H), 3.63 (dd, 1 H, 6-H′), 3.81 (dt, 1 H, 5-H), 3.88, 4.14 (2 m, each 1 H, All-1-H_2), 4.45, 4.58 (2 d, each 1 H, C*H*$_2$Ph), 4.71 (d, 1 H, 1-H), 5.11−5.24 (m, 3 H, 2-H, All-3-H_2), 5.54 (dd, 1 H, 4-H); $J_{1,2}$ = 10.2, $J_{3,4}$ = 3.3, $J_{4,5}$ = 0.7, $J_{5,6}$ = 6.2, $J_{6,6'}$ = −9.6 Hz. − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.8 (Ac*C*H$_3$), 66.5 (C-4), 68.2 (C-6), 68.4 (C-2), 70.7 (All-C-1), 73.7 (*C*H$_2$Ph), 76.2 (C-5), 80.0 (C-3), 87.4 (C-1). − MS (FD): m/z = 528 [M^+]. − $C_{29}H_{36}O_7S$ (528.66): calcd. C 65.89, H 6.86; found C 65.72, H 6.97.

Phenyl 4-*O*-Acetyl-3,6-di-*O*-allyl-2-*O*-pivaloyl-β-D-galactopyranosyl Sulfoxide (53): Thioglycoside **51** (4.31 g, 9 mmol) was dissolved in CH_2Cl_2 (70 mL), cooled to −78 °C and treated dropwise with a solution of 3-chloroperbenzoic acid (1.55 g, 9 mmol) in CH_2Cl_2 (30 mL). After 15 min at this temperature, the mixture was poured into saturated aqueous $NaHCO_3$ (200 mL). The organic layer was separated and washed with saturated aqueous $NaHCO_3$ (100 mL), dried ($MgSO_4$), and concentrated. The resulting syrup was purified by fast elution from a silica gel column (cyclohexane/EtOAc, 2:1) to give 3.74 g (84%) of sulfoxide **53** as a colourless powder, comprising (^{1}H NMR) a 1:1 mixture of the two diastereomers, which was used as such for all galactosylations.

Separation of the two sulfoxide diastereomers required further chromatography (cyclohexane/EtOAc, 2:1) and afforded both in crystalline form upon evaporation of the appropriate fractions.

Diastereomer 53A: Colourless crystals of m.p. 141−142 °C (cyclohexane/EtOAc); R_f = 0.24 (cyclohexane/EtOAc, 2:1); $[\alpha]_D^{20}$ = −82.4 (c = 1.0, $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.07 (s, 3 H, AcCH_3), 3.41 (dd, 1 H, 6-H), 3.45 (dd, 1 H, 6-H′), 3.63 (dd, 1 H, 3-H), 3.66 (t, 1 H, 5-H), 3.77 (m, 2 H, All-1-H_2), 3.83−4.00, 4.05−4.17 (2 m, each 1 H, All-1-H_2), 4.15 (d, 1 H, 1-H), 5.13−5.24 (m, 4 H, 2 All-3-H_2), 5.46 (dd, 1 H, 4-H), 5.49 (t, 1 H, 2-H); $J_{1,2}$ = 10.0, $J_{2,3}$ = 9.9, $J_{3,4}$ = 3.2, $J_{4,5}$ = 1.0, $J_{5,6}$ = 6.3, $J_{5,6'}$ = 5.8, $J_{6,6'}$ = −10.2 Hz. − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.8 (AcCH_3), 65.8 (C-4), 66.3 (C-2), 67.9 (C-6), 70.7, 72.3 (2 All-C-1), 77.5 (C-5), 78.0 (C-3), 91.3 (C-1).

Diastereomer 53B: Colourless crystals of m.p. 116−117 °C (cyclohexane/EtOAc); R_f = 0.18 (cyclohexane/EtOAc, 2:1); $[\alpha]_D^{20}$ = +4.3 (c = 1.0, $CHCl_3$). − ^{1}H NMR spectroscopic data (300 MHz, $CDCl_3$) differing from **53A**: δ = 1.81 (s, 3 H, AcCH_3), 3.20 (dd, 1 H, 6-H), 3.57 (dd, 1 H, 3-H), 3.74 (t, 1 H, 5-H), 3.84−4.15 (m, 4 H, 2 All-1-H_2), 4.49 (d, 1 H, 1-H), 5.05 (t, 1 H, 2-H), 5.39 (dd, 1 H, 4-H); $J_{1,2}$ = 10.3, $J_{2,3}$ = 9.4, $J_{3,4}$ = 3.0, $J_{5,6}$ = 7.0, $J_{5,6'}$ = 5.6, $J_{6,6'}$ = −9.8 Hz. − ^{13}C NMR spectroscopic data differing from **53A**: δ = 20.3 (AcCH_3), 67.1 (C-6), 76.1 (C-5), 77.7 (C-3), 92.4 (C-1). − MS (FD): m/z = 494 [M^+]. − $C_{25}H_{34}O_8S$ (494.60): calcd. C 60.71, H 6.93; found C 60.68, H 6.99.

Phenyl 4-*O*-Acetyl-3-*O*-allyl-6-*O*-benzyl-2-*O*-pivaloyl-β-D-galactopyranosyl Sulfoxide (54): The 3-chloroperbenzoic acid oxidation of thioglycoside **52** (4.76 g, 9 mmol) was carried out as described for sulfoxide **53**. Chromatographic separation of the residue (cyclohexane/EtOAc, 3:1) gave, after azeotropic drying, 4.51 g (92%) of sulfoxide **54** as a colourless powder, comprising (^{1}H NMR) a 1:1 mixture of the two diastereomers, which was used as such for the ensuing galactosylations.

Separation of the isomers could be effected by chromatography on silica gel (cyclohexane/EtOAc, 3:1) and evaporation of the appropriate fractions in vacuo.

Diastereomer 54A, eluted first: R_f = 0.20 (toluene/EtOAc, 4:1); $[\alpha]_D^{20}$ = −85.6 (c = 1.0, $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.00 (s, 3 H, AcCH_3), 3.46 (m, 2 H, 6-H_2), 3.62 (dd, 1 H, 3-H), 3.71 (t, 1 H, 5-H), 3.85, 4.14 (2 m, each 1 H, All-1-H_2), 4.16 (d, 1 H, 1-H), 4.34 (dd, 2 H, CH_2Ph), 5.12−5.24 (m, 2 H, All-3-H_2), 5.46 (t, 1 H, 2-H), 5.47 (dd, 1 H, 4-H); $J_{1,2}$ = 9.9, $J_{2,3}$ = 9.4, $J_{3,4}$ = 3.2, $J_{5,6}$ = 6.0 Hz. − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.8 (AcCH_3), 66.0 (C-4), 66.3 (C-2), 68.0 (C-6), 70.8 (All-C-1), 73.7 (CH_2Ph), 77.5 (C-5), 78.2 (C-3), 91.4 (C-1).

Diastereomer 54B, eluted next: R_f = 0.16 (toluene/EtOAc, 4:1); $[\alpha]_D^{20}$ = −1.5 (c = 0.72, $CHCl_3$). − ^{1}H NMR spectroscopic data (300 MHz, $CDCl_3$) differing from **54A**: δ = 1.76 (s, 3 H, AcCH_3), 3.23 (dd, 1 H, 6-H), 3.47 (dd, 1 H, 6-H′), 3.54 (dd, 1 H, 3-H), 3.75 (m, 1 H, 5-H), 4.40 (dd, 2 H, CH_2Ph), 4.47 (d, 1 H, 1-H), 5.06 (t, 1 H, 2-H), 5.41 (dd, 1 H, 4-H); $J_{1,2}$ = 10.2, $J_{2,3}$ = 9.4, $J_{3,4}$ = 3.1, $J_{4,5}$ = 0.8, $J_{5,6}$ = 7.2, $J_{5,6'}$ = 5.6, $J_{6,6'}$ = −9.7 Hz. − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.4 (AcCH_3), 67.4 (C-6), 76.4 (C-5), 92.7 (C-1). − MS (FD): m/z = 544 [M^+]. − $C_{29}H_{36}O_8S$ (544.66): calcd. C 63.95, H 6.66; found C 64.11, H 6.76.

3. General Coupling Procedures

General Procedure for Couplings with Phenylthio Galactoside Donors ("Coupling Procedure A"): 2,6-Di-*tert*-butyl-4-methylpyridine (DTBMP) (6 molar equiv.) and freshly dried molecular sieves (4 Å, 3 g/mmol of acceptor) were added to a solution of the appropriate thioglycoside (2 molar equiv.) and acceptor (1 molar equiv.) in CH_2Cl_2 (10 mL/mmol of acceptor). After this had been stirred for 10 min, methyl triflate[71] (3−4 molar equiv.) was added, and stirring was continued for 16 h at room temperature. After dilution with CH_2Cl_2, the mixture was filtered, washed with saturated aqueous $NaHCO_3$, dried ($MgSO_4$), and concentrated in vacuo. The syrupy residue was then subjected to purification by elution from a silica column.

For the coupling reactions providing di- and trigalactosides, 3 molar equiv. of methyl triflate were sufficient; for generation of the higher analogues, the tetra-, penta-, and hexagalactosides, 4 molar equiv. were required to ensure complete consumption of the acceptor within the time frame given.

General Glycosylation Procedure for Sulfoxide Donors ("Coupling Procedure B"): Tf_2O (0.6 molar equiv.) was added at −78 °C to a solution of the appropriate sulfoxide (2 molar equiv.) and 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP) (6 molar equiv.) in CH_2Cl_2 (20 mL/mmol of donor). After this had been stirred at −60 °C for 10 min, a solution of the acceptor (1 molar equiv.) in CH_2Cl_2 (10 mL/mmol of acceptor) was added dropwise by syringe. The mixture was then slowly warmed to 0 °C over 1 h and quenched by the addition of saturated aqueous $NaHCO_3$. The organic layer was washed with saturated aqueous $NaHCO_3$ (2 ×), dried ($MgSO_4$), and concentrated under reduced pressure to yield a residue, which was purified by silica gel chromatography.

4. β(1→4)-Galactobiosides

Allyl 2-*O*-Benzoyl-3,6-di-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-β-D-galactopyranoside (38): Phenyl tetra-*O*-acetyl-1-thio-β-D-galactoside (**35**)[69] (350 mg, 0.8 mmol) and Gal-4-OH acceptor **23** (200 mg, 0.4 mmol) in 4 mL of CH_2Cl_2 were induced to react by addition of methyl triflate (0.18 mL, 1.6 mmol), following coupling procedure A, to yield a residue comprising (^{1}H NMR) an approximate 3:2 mixture of galactobioside **38** and the orthoester **43**. Partial separation was achieved by elution from a silica gel column (toluene/EtOAc, 6:1) to give, after removal of the solvent in vacuo, a syrup from which **38** crystallised on trituration with EtOAc/cyclohexane: 130 mg (39%, based on acceptor **23**) of colourless crystals; m.p. 129−130 °C; $[\alpha]_D^{20}$ = +11.0 (c = 0.7, $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.98, 2.00, 2.14, 2.15 (4 s, each 3 H, 4 AcCH_3), 3.63 (m, 2 H, 3a-H, 5a-H), 3.73 (m, 2 H, 5b-H, 6a-H), 3.82 (dd, 1 H, 6a-H′), 4.01−4.14 (m, 3 H, 6b-H_2, All-1-H), 4.20 (d, 1 H, 4a-H), 4.28 (m, 1 H, All-1-H′), 4.53 (d, 1 H, 1a-H), 4.55, 4.61 (2 d, each 1 H, CH_2Ph), 4.58 (s, 2 H, CH_2Ph), 4.90 (d, 1 H, 1b-H), 5.00 (dd, 1 H, 3b-H), 5.02−5.21 (m, 2 H, All-3-H_2), 5.24 (dd, 1 H, 2b-H), 5.36 (d, 1 H, 4b-H), 5.41 (dd, 1 H, 2a-H); $J_{1a,2a}$ = 7.9, $J_{2a,3a}$ = 10.0, $J_{3a,4a}$ = 2.6, $J_{5a,6a}$ = 5.8, $J_{5a,6'a}$ = 5.9, $J_{6,6'}$ = −10.0, $J_{1b,2b}$ = 7.9, $J_{2b,3b}$ = 10.6, $J_{3b,4b}$ = 3.1 Hz. − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.7, 20.8 (4 AcCH_3), 61.2 (C-6b), 67.1 (C-4b), 68.9 (C-2b), 69.0 (All-C-1), 69.5 (C-6a), 70.5 (C-3b), 70.9 (C-5b), 71.4 (C-2a), 72.3 (C-4a), 72.5, 73.7 (2 CH_2Ph), 73.8 (C-5a), 79.9 (C-3a), 100.1 (C-1a), 101.2 (C-1b); $J_{C\text{-}1a,H}$ = 158.9, $J_{C\text{-}1b,H}$ = 163.3 Hz. − MS (FD): m/z = 834 [M^+]. − $C_{44}H_{50}O_{16}$ (834.87): calcd. C 63.30, H 6.04; found C 63.24, H 5.92.

Isolation of the now enriched orthoester **43** from the mother liquor required further silica gel chromatography (toluene/EtOAc, 4:1), to yield 170 mg (25%, based on **23**) of a colourless syrup. Its ^{1}H NMR spectroscopic data exhibit the expected differences from **38**: 1b-H as a 4.9 Hz-d at δ = 5.90 (vs. 7.9 Hz-d at 4.90 for 1b-H of **38**), orthoester-CH_3 at 1.71, and a quaternary carbon at δ = 120.5.

4-Methoxyphenyl 3-*O*-Allyl-6-*O*-benzyl-2-*O*-pivaloyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-β-D-galactopyranoside (39) and 3,4,6-Tri-*O*-acetyl-α-D-galactopyranose-1,2-[4-methoxyphenyl

3-*O*-allyl-6-*O*-benzyl-2-*O*-pivaloyl-β-D-galactopyranoside-4-yl] Orthoacetate (44): Coupling of thioglycoside **35**[69] (530 mg, 1.2 mmol) and acceptor **31** (300 mg, 0.6 mmol) was carried out according to coupling procedure A, followed by elution of the residue obtained from a silica gel column (toluene/EtOAc, 6:1). Orthoester **44** was eluted first to give, upon removal of the eluents from the appropriate fractions, 144 mg (29%) of a colourless syrup; $[\alpha]_D^{20} = +34.9$ ($c = 0.94$, $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.71 (s, 3 H, orthoester-CH_3), 2.06, 2.14, (2 s, 6 H and 3 H, 3 AcCH_3), 3.42 (dd, 1 H, 3a-H), 3.65 (m, 2 H, 5a-H, 6a-H), 3.77 (m, 4 H, 6a-H′, OCH_3), 3.89 (m, 1 H, All-1-H), 4.12 (m, 2 H, 6b-H_2), 4.22 (m, 2 H, 4a-H, All-1-H′), 4.30 (dt, 1 H, 5b-H), 4.37 (dt, 1 H, 2b-H), 4.52 (m, 2 H, CH_2Ph), 4.82 (d, 1 H, 1a-H), 5.00 (dd, 1 H, 3b-H), 5.13−5.30 (m, 2 H, All-3-H_2), 5.39 (m, 2 H, 2a-H, 4b-H), 5.86 (m, 1 H, All-2-H), 5.94 (d, 1 H, 1b-H); $J_{1a,2a} = 7.9$, $J_{2a,3a} = 10.2$, $J_{3a,4a} = 2.7$, $J_{1b,2b} = 5.0$, $J_{2b,3b} = 6.8$, $J_{3b,4b} = 3.5$, $J_{6,6'} = -6.6$ Hz. − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.5, 20.7, 20.8 (3 AcCH_3), 24.0 (orthoester-CH_3), 55.6 (OCH_3), 61.5 (C-6b), 65.8 (C-4b), 67.2 (C-4a), 68.4 (C-6a), 68.8 (C-5b), 70.2 (C-2a), 71.3 (All-C-1), 71.6 (C-3b), 72.9 (C-2b), 73.4 (C-5a), 73.6 (CH_2Ph), 79.4 (C-3a), 97.9 (C-1b), 101.2 (C-1a), 117.0 (All-C-3), 134.4 (All-C-2), 120.9 (orthoester-*C*); $J_{C1a-H} = 160.5$, $J_{C1b-H} = 182.2$ Hz. − MS (FD): *m*/*z* = 830 [M$^+$]. − $C_{42}H_{54}O_{17}$ (830.88): calcd. C 60.71, H 6.55; found C 60.75, H 6.59.

Workup of the fractions with $R_f = 0.22$ (toluene/EtOAc, 4:1) afforded galactobioside **39** (214 mg, 43%); $[\alpha]_D^{20} = -5.0$ ($c = 1.1$, $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.99, 2.02, 2.14, 2.17 (4 s, each 3 H, 4 AcCH_3), 3.51 (dd, 1 H, 3a-H), 3.70−3.83 (m, 6 H, 5a-H, 6a-H_2, OCH_3), 3.86 (t, 1 H, 5b-H), 3.99−4.16 (m, 4 H, 6b-H_2, All-1-H_2), 4.23 (d, 1 H, 4a-H), 4.58 (m, 2 H, CH_2Ph), 4.79 (d, 1 H, 1a-H), 4.93 (d, 1 H, 1b-H), 5.03 (dd, 1 H, 3b-H), 5.19−5.35 (m, 4 H, 2a-H, 2b-H, All-3-H_2), 5.39 (d, 1 H, 4b-H); $J_{1a,2a} = 8.0$, $J_{2a,3a} = 10.1$, $J_{3a,4a} = 2.6$, $J_{1b,2b} = 7.9$, $J_{2b,3b} = 10.5$, $J_{3b,4b} = 3.4$, $J_{5b,6b} = 6.8$ Hz. − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.6 (4 AcCH_3), 55.6 (OCH_3), 61.3 (C-6b), 67.0 (C-4b), 68.7 (C-2b), 69.5 (C-6a), 70.3 (C-2a), 70.5 (C-5b), 70.9 (C-3b), 71.4 (All-C-1), 71.8 (C-4a), 73.7 (CH_2Ph), 74.0 (C-5a), 79.8 (C-3a), 101.0 (C-1a, C-1b); $J_{C1a-H} = 160.5$, $J_{C1b-H} = 165.5$ Hz. − MS (FD): *m*/*z* = 830 [M$^+$]. − $C_{42}H_{54}O_{17}$ (830.88): calcd. C 60.71, H 6.55; found C 60.72, H 6.53.

Allyl 2-*O*-Benzoyl-3,6-di-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-pivaloyl-β-D-galactopyranosyl)-β-D-galactopyranoside (40): Methyl triflate-promoted galactosylation of acceptor **23** (202 mg, 0.4 mmol) with thioglycoside **36**[58,59] (487 mg, 0.8 mmol) by coupling procedure A gave, after workup and chromatography on silica gel (toluene/EtOAc, 25:1), 192 mg (48%) of **40** as a colourless syrup. − Similar coupling of **23** (202 mg, 0.4 mmol) with sulfoxide donor **37**[58][59] (500 mg, 0.8 mmol) and analogous processing of the reaction mixture gave 225 mg (56%) of **40**, identical with the product obtained by procedure A; $R_f = 0.51$ (toluene/EtOAc, 4:1); $[\alpha]_D^{20} = +14.4$ ($c = 0.75$, $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.63−3.80 (m, 5 H, 3a-H, 5a-H, 5b-H, 6a-H_2), 3.93−4.08 (m, 3 H, 6b-H_2, All-1-H), 4.24−4.31 (m, 1 H, All-1-H′), 4.38 (d, 1 H, 4a-H), 4.50 (d, 1 H, 1a-H), 4.61 (m, 4 H, 2 CH_2Ph), 5.00−5.18 (m, 3 H, 3b-H, All-3-H_2), 5.10 (d, 1 H, 1b-H), 5.23 (dd, 1 H, 2b-H), 5.35 (d, 1 H, 4b-H), 5.42 (dd, 1 H, 2a-H); $J_{1a,2a} = 7.9$, $J_{2a,3a} = 10.1$, $J_{3a,4a} = 2.4$, $J_{1b,2b} = 7.8$, $J_{2b,3b} = 10.4$, $J_{3b,4b} = 2.8$ Hz. − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 60.8 (C-6b), 66.7 (C-4b), 69.2 (C-2b, All-C-1), 69.5 (C-6a), 69.6 (C-4a), 70.7 (C-5b), 71.2 (C-3b), 71.7 (C-2a), 72.3 (CH_2Ph), 73.9 (C-5a, CH_2Ph), 79.7 (C-3a), 99.8 (C-1b), 100.1 (C-1a); $J_{C-1a,H} = 158.9$, $J_{C-1b,H} = 165.8$ Hz. − MS (FD): *m*/*z* = 1003 [M$^+$]. − $C_{56}H_{74}O_{16}$ (1003.19): calcd. C 67.05, H 7.43; found C 66.95, H 7.39.

4-Methoxyphenyl 3,6-Di-*O*-allyl-2-*O*-pivaloyl-4-*O*-(2,3,4,6-tetra-*O*-pivaloyl-β-D-galactopyranosyl)-β-D-galactopyranoside (41): Thioglycoside **36**[58,59] (730 mg, 1.2 mmol) and acceptor **27** (270 mg, 0.6 mmol) were treated according to coupling procedure A, to give after column chromatography (toluene/EtOAc, 19:1) galactobioside **41** (397 mg, 70%) as a colourless foam; $R_f = 0.49$ (toluene/EtOAc, 4:1); $[\alpha]_D^{20} = -12.3$ ($c = 1.1$, $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.57 (dd, 1 H, 3a-H), 3.69 (m, 3 H, 5a-H, 6a-H_2), 3.75 (s, 3 H, OCH_3), 3.93 (m, 1 H, 5b-H), 3.96−4.07 (m, 4 H, 6b-H, All-1-H_2, All-1-H), 4.11−4.18 (m, 2 H, 6b-H′, All-1-H′), 4.35 (d, 1 H, 4a-H), 4.77 (d, 1 H, 1a-H), 5.08 (dd, 1 H, 3b-H), 5.11 (d, 1 H, 1b-H), 5.17−5.33 (m, 6 H, 2a-H, 2b-H, 2 All-3-H_2), 5.40 (d, 1 H, 4b-H); $J_{1a,2a} = 7.9$, $J_{2a,3a} = 10.2$, $J_{3a,4a} = 3.0$, $J_{1b,2b} = 7.7$, $J_{2b,3b} = 10.4$, $J_{3b,4b} = 3.0$ Hz. − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 55.6 (OCH_3), 61.1 (C-6b), 66.8 (C-4b), 69.1 (C-4a, C-6a), 69.3 (C-2b), 70.6 (C-2a), 70.8 (C-5b), 71.2 (C-3b), 71.4, 72.6 (2 All-C-1), 74.1 (C-5a), 79.7 (C-3a), 99.7 (C-1b), 101.1 (C-1a). − MS (FD): *m*/*z* = 949 [M$^+$]. − $C_{50}H_{76}O_{17}$ (949.14): calcd. C 63.27, H 8.07; found C 63.35, H 8.11.

Triflic anhydride-mediated galactosylation of **27** (270 mg, 0.6 mmol) with sulfoxide **37**[58,59] (750 mg, 1.2 mmol) by coupling procedure B afforded **41** (404 mg) in 71% yield.

4-Methoxyphenyl 3-*O*-Allyl-6-*O*-benzyl-2-*O*-pivaloyl-4-*O*-(2,3,4,6-tetra-*O*-pivaloyl-β-D-galactopyranosyl)-β-D-galactopyranoside (42): Acceptor **31** (300 mg, 0.6 mmol) was subjected to triflic anhydride-promoted galactosylation with sulfoxide **37**[58,59] (730 mg, 1.2 mmol) using general coupling procedure B. Column chromatography (toluene/EtOAc, 20:1) gave disaccharide **42** (460 mg, 77%) as a colourless foam; $R_f = 0.55$ (toluene/EtOAc, 4:1); $[\alpha]_D^{20} = -10.7$ ($c = 0.96$, $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.57 (dd, 1 H, 3a-H), 3.77 (m, 6 H, 5a-H, 6a-H_2, OCH_3), 3.92 (t, 1 H, 5b-H), 3.95−4.18 (m, 4 H, 6b-H_2, All-1-H_2), 4.37 (d, 1 H, 4a-H), 4.56 (s, 2 H, CH_2Ph), 4.78 (d, 1 H, 1a-H), 5.09 (dd, 1 H, 3b-H), 5.13 (d, 1 H, 1b-H), 5.19−5.35 (m, 4 H, 2a-H, 2b-H, All-3-H_2), 5.39 (d, 1 H, 4b-H); $J_{1a,2a} = 7.9$, $J_{2a,3a} = 10.2$, $J_{3a,4a} = 3.0$, $J_{1b,2b} = 7.8$, $J_{2b,3b} = 10.3$, $J_{3b,4b} = 3.3$ Hz. − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 55.6 (OCH_3), 61.1 (C-6b), 66.9 (C-4b), 69.2 (C-2b), 69.4 (C-4a), 69.7 (C-6a), 70.7 (C-2a), 70.9 (C-5b), 71.2 (C-3b), 71.5 (All-C-1), 73.9 (CH_2Ph), 74.2 (C-5a), 79.9 (C-3a), 99.8 (C-1b), 101.1 (C-1a); $J_{C1a-H} = 160.3$, $J_{C1b-H} = 165.0$ Hz. − MS (FD): *m*/*z* = 999 [M$^+$]. − $C_{54}H_{78}O_{17}$ (999.20): calcd. C 64.91, H 7.87; found C 65.04, H 7.97.

Methyl triflate-induced galactosylation of **31** with thiogalactoside **36** according to general procedure A and chromatography (toluene/EtOAc, 20:1) afforded 384 mg (64%) of galactobioside **42**.

4-Methoxyphenyl 4-*O*-(4-*O*-Acetyl-3,6-di-*O*-allyl-2-*O*-pivaloyl-β-D-galactopyranosyl)-3,6-di-*O*-allyl-2-*O*-pivaloyl-β-D-galactopyranoside (55): Methyl triflate-promoted glycosylation of acceptor **27** (2.70 g, 6 mmol) with thiogalactoside **51** (5.70 g, 12 mmol) was conducted according to general coupling procedure A. Column chromatography (toluene/EtOAc, 9:1) of the residue thus obtained gave **55** (3.95 g, 80%) as a colourless syrup; $R_f = 0.51$ (toluene/EtOAc, 4:1); $[\alpha]_D^{20} = -6.0$ ($c = 1$, $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.13 (s, 3 H, AcCH_3), 3.49 (m, 4 H, 3a-H, 3b-H, 6b-H_2), 3.69 (m, 4 H, 5a-H, 5b-H, 6a-H_2), 3.75 (s, 3 H, OCH_3), 3.82−4.23 (m, 8 H, 4 All-1-H_2), 4.44 (d, 1 H, 4a-H), 4.77 (d, 1 H, 1a-H), 5.04 (m, 1 H, 2b-H), 5.10 (d, 1 H, 1b-H), 5.12−5.37 (m, 8 H, 4 All-3-H_2), 5.33 (m, 1 H, 2a-H), 5.44 (d, 1 H, 4b-H); $J_{1a,2a} = 7.9$, $J_{3a,4a} = 2.4$, $J_{1b,2b} = 8.0$, $J_{3b,4b} = 2.7$ Hz. − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.9 (AcCH_3), 55.6 (OCH_3), 67.0 (C-4b), 67.8 (C-4a), 68.4 (C-6b), 69.1 (C-6a), 70.4 (C-2a), 70.7 (C-2b), 70.9, 71.1, 72.6 (4 All-C-1),

72.5 (C-5b), 74.2 (C-5a), 76.8 (C-3b), 80.2 (C-3a), 99.1 (C-1b), 101.2 (C-1a); J_{C1a-H} = 160, J_{C1b-H} = 159 Hz. − MS (FD): *m/z* = 819 [M^+ + H]. − $C_{43}H_{62}O_{15}$ (818.95): calcd. C 63.06, H 7.63; found C 62.86, H 7.66.

Coupling of acceptor **27** (270 mg, 0.6 mmol) with sulfoxide donor **53** (590 mg, 1.2 mmol) by general procedure B yielded, after chromatography (toluene/EtOAc, 9:1), 422 mg (86%) of **55**, identical with the product described above.

4-Methoxyphenyl 4-*O*-(4-*O*-Acetyl-3-*O*-allyl-6-*O*-benzyl-2-*O*-pivaloyl-β-D-galactopyranosyl)-3-*O*-allyl-6-*O*-benzyl-2-*O*-pivaloyl-β-D-galactopyranoside (56): Sulfoxide donor **54** (6.5 g, 12 mmol), upon triflic anhydride activation, was coupled with acceptor **31** (3.0 g, 6 mmol) using general procedure B. Purification of the resulting residue by elution from a silica gel column (toluene/EtOAc, 15:1) gave galactobioside **56** (4.46 g, 81%) as a colourless syrup; R_f = 0.31 (toluene/EtOAc, 9:1); $[\alpha]_D^{20}$ = −9.1 (*c* = 1.22, $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.01 (s, 3 H, Ac*CH*$_3$), 3.52 (m, 4 H, 3a-H, 3b-H, 6b-H_2), 3.66−3.82 (m, 7 H, 5a-H, 5b-H, 6a-H_2, O*CH*$_3$), 3.90, 4.13 (2 m, 4 H, 2 All-1-H_2), 4.45 (dd, 2 H, C*H*$_2$Ph), 4.46 (d, 1 H, 4a-H), 4.45 (s, 2 H, C*H*$_2$Ph), 4.78 (d, 1 H, 1a-H), 5.06 (t, 1 H, 2b-H), 5.09−5.22 (m, 4 H, 2 All-3-H_2), 5.12 (d, 1 H, 1b-H), 5.34 (dd, 1 H, 2a-H), 5.48 (d, 1 H, 4b-H); $J_{1a,2a}$ = 7.8, $J_{2a,3a}$ = 10.3, $J_{3a,4a}$ = 2.3, $J_{1b,2b}$ = 8.1, $J_{3b,4b}$ = 2.9 Hz. − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.8 (Ac*C*H$_3$), 55.6 (O*C*H$_3$), 67.0 (C-4b), 67.8 (C-4a), 68.4 (C-6b), 69.5 (C-6a), 70.4 (C-2a), 70.9 (C-2b), 71.0, 71.1 (2 All-C-1), 72.6 (C-5b), 73.7, 73.9 (2 *C*H$_2$Ph), 74.2 (C-5a), 76.9 (C-3b), 80.4 (C-3a), 99.2 (C-1b), 101.2 (C-1a); J_{C1a-H} = 156.9, J_{C1b-H} = 161.4 Hz. − MS (FD): *m/z* = 919 [M^+]. − $C_{51}H_{66}O_{15}$ (919.07): calcd. C 66.65, H 7.24; found C 66.64, H 7.16.

Methyl triflate-promoted glycosylation of acceptor **31** (300 mg, 0.6 mmol) with thioglycoside **52** (630 mg, 1.2 mmol) was conducted according to general coupling procedure A. Column chromatography (toluene/EtOAc, 15:1) of the resulting residue gave **56** (435 mg, 79%) as a colourless syrup.

4-Methoxyphenyl 3,6-Di-*O*-allyl-4-*O*-(3,6-di-*O*-allyl-β-D-galactopyranosyl)-β-D-galactopyranoside (57): LiOH·H_2O (630 mg, 15 mmol) was added to a solution of disaccharide **55** (410 mg, 0.5 mmol) in MeOH (15 mL) and the mixture was stirred at ambient temperature overnight. After filtration by suction, the mixture was neutralised with Amberlite IR 120 (H^+ form), filtered, and concentrated in vacuo to a syrup which was purified by elution from a silica gel column (toluene/EtOAc, 1:1): 270 mg (88%) of **57** as a colourless syrup; R_f = 0.13 (toluene/EtOAc, 2:1); $[\alpha]_D^{20}$ = −16.7 (*c* = 0.78, $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.50−3.00 (b, 3 H, 3 OH), 3.37 (dd, 1 H, 3b-H), 3.48 (dd, 1 H, 3a-H), 3.56 (m, 1 H, 5b-H), 3.64 (m, 3 H, 5a-H, 6a,b-H), 3.74 (m, 4 H, 6b-H′, O*CH*$_3$), 3.78 (dd, 1 H, 2b-H), 3.86 (m, 1 H, 6a-H′), 3.95−4.07 (m, 4 H, 2 All-1-H_2), 3.97 (m, 1 H, 4b-H), 4.06 (dd, 1 H, 2a-H), 4.13 (d, 1 H, 4a-H), 4.17−4.35 (m, 4 H, 2 All-1-H_2), 4.40 (d, 1 H, 1b-H), 4.70 (d, 1 H, 1a-H); $J_{1a,2a}$ = 7.8, $J_{2a,3a}$ = 9.7, $J_{3a,4a}$ = 3.1, $J_{1b,2b}$ = 7.7, $J_{2b,3b}$ = 9.4, $J_{3b,4b}$ = 3.5 Hz. − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 55.8 (O*C*H$_3$), 66.8 (C-4b), 69.0 (C-6a), 69.4 (C-6b), 71.2 (All-C-1), 71.6 (C-2a), 72.0 (C-2b), 72.4, 72.6, 72.7 (3 All-C-1), 74.0 (C-5a,b), 76.5 (C-4a), 80.4 (C-3a), 80.5 (C-3b), 102.8 (C-1a), 105.9 (C-1b). − MS (FD): *m/z* = 609 [(M + H)$^+$]. − $C_{31}H_{44}O_{12}$ (608.68): calcd. C 61.17, H 7.28; found C 60.99, H 7.32.

4-Methoxyphenyl 2,3,6-Tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-β-D-galactopyranoside (58): DIBAL (1 M in THF, 2.3 mL) and $NiCl_2$(dppp)[81] (2.5 mg, 4.6 μmol) were added to a stirred and cooled (0 °C) solution of disaccharide **57** (140 mg, 0.23 mmol) in Et_2O (1 mL), followed by continued stirring at 0 °C (8 h) and then at ambient temperature (8 h). The mixture was then diluted with Et_2O (20 mL) and hydrolysed with H_2O (2 mL) over 1 h, after which acetic acid (0.5 mL) was added and stirring was continued for 30 min. After concentration in vacuo, the residue was evaporated with toluene (3 × 20 mL), dissolved in pyridine (3 mL), Ac_2O (2 mL, 21 mmol), and DMAP (50 mg) and stirred for 4 h at 40 °C. MeOH (2 mL) was added and the mixture was stirred for 15 min, followed by dilution with CH_2Cl_2 (100 mL). The organic phase was washed with 2 N HCl (2 × 50 mL), saturated, aqueous $NaHCO_3$ (50 mL) and saturated, aqueous NaCl (50 mL), dried ($MgSO_4$), and concentrated. The residue was purified by elution from a silica gel column (toluene/EtOAc, 2:1) to give **58** (134 mg, 78%) as colourless needles, m.p. 148−149 °C; R_f = 0.15 (toluene/EtOAc, 2:1); $[\alpha]_D^{20}$ = +5.0 (*c* = 0.97, $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.00, 2.05, 2.06, 2.08, 2.13, 2.15, 2.20 (7 s, each 3 H, 7 Ac*CH*$_3$), 3.67 (m, 1 H, 5b-H), 3.77 (s, 3 H, O*CH*$_3$), 3.81 (m, 1 H, 5a-H), 3.86 (t, 1 H, 5b-H), 4.10 (d, 2 H, 6b-H_2), 4.16 (d, 1 H, 4a-H), 4.31 (dd, 1 H, 6b-H), 4.38 (dd, 1 H, 6b-H′), 4.48 (d, 1 H, 1b-H), 4.85 (d, 1 H, 1a-H), 4.95 (dd, 1 H, 3a-H), 5.02 (dd, 1 H, 3b-H), 5.25−5.35 (m, 2 H, 2a,b-H), 5.38 (d, 1 H, 4b-H); $J_{1a,2a}$ = 7.9, $J_{2a,3a}$ = 10.2, $J_{3a,4a}$ = 3.1, $J_{5a,6a}$ = 7.0, $J_{5a,6'a}$ = 4.9, $J_{6a,6'a}$ = −11.8, $J_{1b,2b}$ = 7.9, $J_{2b,3b}$ = 10.6, $J_{3b,4b}$ = 3.4 Hz. − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.6, 20.7, 20.8 (7 Ac*C*H$_3$), 55.6 (O*C*H$_3$), 61.3 (C-6b), 63.2 (C-6a), 66.8 (C-4b), 68.5 (C-2b), 69.0 (C-2a), 70.6 (C-3b, C-5b), 72.5 (C-5a), 73.1 (C-3a), 74.0 (C-4a), 100.3 (C-1a), 101.8 (C-1b). − MS (FD): *m/z* = 743 [(M + H)$^+$]. − $C_{33}H_{42}O_{19}$ (742.68): calcd. C 53.37, H 5.70; found C 53.26, H 5.72.

4-Methoxyphenyl 4-*O*-(β-D-Galactopyranosyl)-β-D-galactopyranoside (59): A solution of galactobioside **57** (275 mg, 0.45 mmol) in ether (2 mL) was de-*O*-allylated by exposure to DIBAL (1 M in THF, 4.5 ml) and a catalytic amount (5 mg) of [$NiCl_2$(dppp)],[81] first at 0 °C (8 h) and then at room temperature (8 h). The mixture was neutralised with an acidic ion-exchange resin (Amberlite IR 120, H^+ form), filtered, and concentrated. Purification of the residue by chromatography on silica gel (CH_2Cl_2/MeOH, 3:1) gave **59** (175 mg, 82%) as an amorphous solid; R_f = 0.14 (CH_2Cl_2/MeOH, 3:1); $[\alpha]_D^{20}$ = −34.7 (*c* = 0.97, H_2O). − ^{1}H NMR (300 MHz, D_2O): δ = 3.64 (m, 2 H, 2b-H, 3b-H), 3.71 (m, 1 H, 5b-H), 3.75−3.81 (m, 3 H, 6a-H, 6b-H_2), 3.82 (s, 3 H, O*CH*$_3$), 3.87 (m, 4 H, 2a-H, 3a-H, 5a-H, 6a-H′), 3.92 (dd, 1 H, 4b-H), 4.24 (bd, 1 H, 4a-H), 4.64 (d, 1 H, 1b-H), 4.98 (m, 1 H,[87] 1a-H); $J_{1b,2b}$ = 7.4, $J_{3b,4b}$ = 3.3, $J_{4b,5b}$ = 0.6 Hz. − ^{13}C NMR (75.5 MHz, D_2O): δ = 58.7 (O*C*H$_3$), 63.2 (C-6a), 63.8 (C-6b), 71.5 (C-4b), 73.9 (C-2a), 74.3 (C-2b), 75.6 (C-3b), 75.9 (C-3a), 77.3 (C-5a), 78.0 (C-5b), 79.8 (C-4a), 104.6 (C-1a), 107.1 (C-1b). − MS (ESI): *m/z* = 471.2 [(M + Na)$^+$].

De-*O*-acetylation of crystalline heptaacetate **58** by exposure to NaOMe/MeOH under standard Zemplén conditions and workup as described above afforded **59** in 90% yield.

Phenyl 4-*O*-(4-*O*-Acetyl-3,6-di-*O*-allyl-2-*O*-pivaloyl-β-D-galactopyranosyl)-3,6-di-*O*-allyl-2-*O*-pivaloyl-1-thio-β-D-galactopyranoside (60): BF_3·OEt_2 (0.26 mL, 2.1 mmol) was added to a solution of *p*MP-galactobioside **55** (2.46 g, 3 mmol) and $PhSSiMe_3$ (2.3 mL, 12 mmol) in $ClCH_2CH_2Cl$ (30 mL). After 2 h of stirring at 40 °C, the solution was diluted with CH_2Cl_2 (100 mL) and washed with saturated, aqueous $NaHCO_3$ (2 × 100 mL). Drying ($MgSO_4$) and concentration in vacuo gave a liquid residue, which was subjected to column chromatography (toluene/EtOAc, 10:1), to give 2.22 g (92%) of syrupy **60** after removal of the solvents from the appropriate fractions; R_f = 0.56 (toluene/EtOAc, 4:1); $[\alpha]_D^{20}$ = −5.3 (*c* = 1.1, $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.12 (s, 3 H, Ac*CH*$_3$), 3.44 (dd, 1 H, 6b-H), 3.50 (m, 3 H, 3a-H, 3b-H, 6b-H′), 3.60 (t, 1 H, 5a-H), 3.66 (m, 2 H, 5b-H, 6a-H), 3.73 (dd, 1 H, 6a-

H′), 3.83−4.18 (m, 8 H, 4 All-1-H_2), 4.41 (d, 1 H, 4a-H), 4.62 (d, 1 H, 1a-H), 5.02 (m, 2 H, 1b-H, 2b-H), 5.11−5.30 (m, 9 H, 2a-H, 4 All-3-H_2), 5.42 (d, 1 H, 4b-H); $J_{1a,2a}$ = 10.0, $J_{3a,4a}$ = 2.3, $J_{5a,6a}$ = 5.9, $J_{3b,4b}$ = 2.7, $J_{5b,6b}$ = 6.2, $J_{6b,6'b}$ = −9.4 Hz. − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 21.0 (Ac*C*H_3), 67.0 (C-4b), 68.5 (C-6b), 68.6 (C-4a), 69.1 (C-2a), 69.4 (C-6a), 70.7 (C-2b), 70.9, 71.2 (2 All-C-1), 72.6 (C-5b, 2 All-C-1), 77.0 (C-3b), 77.9 (C-5a), 81.3 (C-3a), 87.9 (C-1a), 99.5 (C-1b); J_{C1a-H} = 157.2, J_{C1b-H} = 163.8 Hz. − MS (FD): *m*/*z* = 805 [M^+]. − $C_{42}H_{60}O_{13}S$ (804.99): calcd. C 62.67, H 7.51; found C 62.63, H 7.38.

Phenyl 4-*O*-(4-*O*-Acetyl-3-*O*-allyl-6-*O*-benzyl-2-*O*-pivaloyl-β-D-galactopyranosyl)-3-*O*-allyl-6-*O*-benzyl-2-*O*-pivaloyl-1-thio-β-D-galactopyranoside (61): The *p*MP galactobioside **56** (2.3 g, 2.5 mmol) was thiated as described above for **55** → **60**. Column chromatography of the resulting residue (toluene/EtOAc, 17:1) yielded thiogalactobioside **61** (2.13 g, 94%) as a syrup; R_f = 0.60 (toluene/EtOAc, 4:1); $[\alpha]_D^{20}$ = −8.3 (*c* = 1.0, $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.00 (s, 3 H, AcCH_3), 3.44−3.55 (m, 4 H, 3a-H, 3b-H, 6b-H_2), 3.66 (t, 1 H, 5a-H), 3.71 (t, 1 H, 5b-H), 3.76 (m, 2 H, 6a-H_2), 3.83−3.96, 4.09−4.15 (2 m, 4 H, 2 All-1-H_2), 4.45 (dd, 2 H, CH_2Ph), 4.46 (d, 1 H, 4a-H), 4.56 (s, 2 H, CH_2Ph), 4.65 (d, 1 H, 1a-H), 5.05 (m, 2 H, 1b-H, 2b-H), 5.10−5.25 (m, 5 H, 2a-H, 2 All-3-H_2), 5.48 (d, 1 H, 4b-H); $J_{1a,2a}$ = 10.0, $J_{3a,4a}$ = 2.2, $J_{5,6}$ = 6.0, $J_{1b,2b}$ = 8.0, $J_{3b,4b}$ =2.8, $J_{5,6}$ = 6.5 Hz. − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.8 (Ac*C*H_3), 66.8 (C-4b), 68.2 (C-6b), 68.4 (C-4a), 69.0 (C-2a), 69.7 (C-6a), 70.7 (C-2b), 70.8, 71.1 (2 All-C-1), 72.4 (C-5b), 73.7, 73.8 (2 *C*H_2Ph), 76.9 (C-3b), 77.7 (C-5a), 81.3 (C-3a), 87.8 (C-1a), 99.4 (C-1b). − MS (FD): *m*/*z* = 927 [(M + Na)$^+$]. − $C_{50}H_{64}O_{13}S$ (905.11): calcd. C 66.35, H 7.13; found C 66.22, H 7.09.

4-Methoxyphenyl 3,6-Di-*O*-allyl-4-*O*-(3,6-di-*O*-allyl-2-*O*-pivaloyl-β-D-galactopyranosyl)-2-*O*-pivaloyl-β-D-galactopyranoside (62): Galactobioside **55** (2.30 g, 2.8 mmol) was dissolved in CH_2Cl_2 (4 mL) and MeOH (16 mL) and treated with NaOMe (0.5 M in MeOH, 1.4 mL, 0.7 mmol). After stirring for 15 h at room temperature, the solution was neutralized with acidic ion-exchange resin (Amberlite IR 120) and concentrated. The residue was subjected to column chromatography (toluene/EtOAc, 4:1) to yield 1.83 g (84%) of galactobioside acceptor **62** as a colourless syrup; R_f = 0.51 (toluene/EtOAc, 4:1); $[\alpha]_D^{20}$ = −15.5 (*c* = 1.0, $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.35 (br. s, 1 H, 4b-OH), 3.50 (m, 2 H, 3a-H, 3b-H), 3.58 (m, 1 H, 5a-H), 3.65−3.78 (m, 5 H, 5b-H, 6a-H_2, 6b-H_2), 3.75 (s, 3 H, OCH_3), 3.94−4.25 (m, 8 H, 4 All-1-H_2), 4.03 (m, 1 H, 4b-H), 4.44 (d, 1 H, 4a-H), 4.77 (d, 1 H, 1a-H), 5.08 (m, 2 H, 1b-H, 2b-H), 5.13−5.32 (m, 8 H, 4 All-3-H_2), 5.34 (dd, 1 H, 2a-H); $J_{1a,2a}$ = 7.9, $J_{2a,3a}$ = 10.3, $J_{3a,4a}$ = 2.5 Hz. − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 55.6 (O*C*H_3), 66.4 (C-4b), 67.6 (C-4a), 68.9, 69.4 (C-6a, C-6b), 70.3 (C-2a),70.6 (C-2b), 70.9, 71.0, 72.5, 72.6 (4 All-C-1), 73.5 (C-5b), 74.4 (C-5a), 78.6 (C-3b), 80.3 (C-3a), 99.8 (C-1b), 101.1 (C-1a). − MS (FD): *m*/*z* = 777 [(M + H)$^+$]. − $C_{41}H_{60}O_{14}$ (776.92): calcd. C 63.38, H 7.78; found C 63.09, H 7.65.

4-Methoxyphenyl 3-*O*-Allyl-4-*O*-(3-*O*-allyl-6-*O*-benzyl-2-*O*-pivaloyl-β-D-galactopyranosyl)-6-*O*-benzyl-2-*O*-pivaloyl-β-D-galactopyranoside (63): Galactobioside **56** (2.30 g, 2.5 mmol) was de-*O*-acetylated with NaOMe/MeOH as described above for **55** → **62**. Column chromatography (toluene/EtOAc, 6:1) of the residue gave the 4-OH free analogue **63** (1.86 g, 85%) as a yellow syrup; R_f = 0.44 (toluene/EtOAc, 4:1); $[\alpha]_D^{20}$ = −17.4 (*c* = 1.0, $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.49 (m, 2 H, 3a-H, 3b-H), 3.60 (m, 1 H, 5a-H) 3.67−3.83 (m, 8 H, 5b-H, 6a-H_2, 6b-H_2, OCH_3), 3.87−4.19 (m, 4 H, 2 All-1-H_2), 4.04 (br. s, 1 H, 4b-H), 4.46 (d, 1 H, 4a-H), 4.49 (m, 4 H, 2 CH_2Ph), 4.77 (d, 1 H, 1a-H), 5.08−5.29 (m, 6 H, 1b-H, 2b-H, 2 All-3-H_2), 5.35 (dd, 1 H, 2a-H); $J_{1a,2a}$ = 7.9, $J_{2a,3a}$ = 10.2, $J_{3a,4a}$ =2.3 Hz. − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 55.6 (O*C*H_3), 66.6 (C-4b), 67.5 (C-4a), 69.1, 69.8 (C-6a, C-6b), 70.3 (C-2a), 70.7 (C-2b), 70.9, 71.1 (2 All-C-1), 73.6 (C-5b), 73.8 (2 *C*H_2Ph), 74.4 (C-5a), 78.6 (C-3b), 80.4 (C-3a), 98.8 (C-1b), 101.1 (C-1a). − MS (FD): *m*/*z* = 877 [M^+]. − $C_{49}H_{64}O_{14}$ (877.04): calcd. C 67.10, H 7.35; found C 67.01, H 7.24.

5. β(1→4)-Galactotriosides

4-Methoxyphenyl (4-*O*-Acetyl-3,6-di-*O*-allyl-2-*O*-pivaloyl-β-D-galactopyranosyl)-(1→4)-(3,6-di-*O*-allyl-2-*O*-pivaloyl-β-D-galactopyranosyl)-(1→4)-3,6-di-*O*-allyl-2-*O*-pivaloyl-β-D-galactopyranoside (70): Thiogalactoside **51** (760 mg, 1.6 mmol) and 4-OH-free galactobioside **62** (620 mg, 0.8 mmol) were coupled according to general procedure A. Column chromatography (toluene/EtOAc, 6:1) afforded trisaccharide **70** (715 mg, 78%) as a syrup; R_f = 0.41 (toluene/EtOAc, 4:1); $[\alpha]_D^{20}$ = −4.8 (*c* = 1.0, $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.12 (s, 3 H, AcCH_3), 3.47 (m, 5 H, 3-H (a−c), 6c-H_2], 3.54 (t, $J_{5,6}$ = 6.2 Hz, 1-H, 5-H) 3.58−3.72 (m, 5 H, two 5-H, 6a,b-H_2), 3.75 (s, 3 H, OCH_3), 3.83−4.20 (m, 12 H, 6 All-1-H_2), 4.33 (d, 1 H, 4a-H), 4.39 (d, 1 H, 4b-H), 4.75 (d, 1 H, 1a-H), 4.98 (d, 1 H, 1b-H), 5.01 (dd, 1 H, 2b-H), 5.04 (dd, 1 H, 2c-H), 5.07 (d, 1 H, 1c-H), 5.12−5.35 (m, 12 H, 6 All-3-H_2), 5.33 (m, 1 H, 2a-H), 5.42 (d, 1 H, 4c-H); $J_{1a,2a}$ = 7.8, $J_{3a,4a}$ = 2.5, $J_{1b,2b}$ = 7.8, $J_{2b,3b}$ = 9.4, $J_{3b,4b}$ = 2.6, $J_{1c,2c}$ = 7.9, $J_{2c,3c}$ = 9.8, $J_{3c,4c}$ = 3.0 Hz. − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.8 (Ac*C*H_3), 55.6 (O*C*H_3), 66.9 (C-4c), 67.9 (C-4b), 68.3 (C-4a), 68.4 (C-6c), 69.1 (C-6a), 69.8 (C-6b), 70.4, 70.6, 70.8 [C-2 (a−c)], 70.9, 71.0, 71.1, 72.5 (6 All-C-1), 72.4 (C-5c), 73.7 (C-5b), 74.6 (C-5a), 76.9 (C-3c), 80.1, 80.3 (C-3a,b), 99.2 (C-1c), 99.5 (C-1b), 101.1 (C-1a); $J_{C-1a,H}$ = 160.2, $J_{C-1b,H}$ = 165.4, $J_{C-1c,H}$ = 166.6 Hz. − MS (FD): *m*/*z* = 1145 [M^+]. − $C_{60}H_{88}O_{21}$ (1145.34): calcd. C 62.92, H 7.74; found C 62.83, H 7.77.

4-Methoxyphenyl (3,6-Di-*O*-allyl-2-*O*-pivaloyl-β-D-galactopyranosyl)-(1→4)-(3,6-di-*O*-allyl-2-*O*-pivaloyl-β-D-galactopyranosyl)-(1→4)-3,6-di-*O*-allyl-2-*O*-pivaloyl-β-D-galactopyranoside (71): A solution of galactotrioside **70** (420 mg, 0.37 mmol) and NaOMe (0.15 mL, 0.5 M in MeOH) in MeOH (3 mL) was stirred at room temperature for 16 h, followed by neutralisation with Amberlite IR 120 (H^+ form) and removal of the solvent in vacuo. Purification of the residue by elution from a silica gel column (toluene/EtOAc, 4:1) afforded **71** (330 mg, 81%) as a colourless syrup; R_f = 0.48 (toluene/EtOAc, 2:1); $[\alpha]_D^{20}$= −17.0 (*c* = 1.0, $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.10−2.40 (b, 1 H, 4c-OH), 3.42−3.48 [m, 3 H, 3-H (a−c)], 3.49−3.77 [m, 9 H, 5-H (a−c), 6-H_2 (a−c)], 3.74 (s, 3 H, OCH_3), 3.92−4.21 (m, 12 H, 6 All-1-H_2), 4.02 (m, 1 H, 4c-H), 4.34 (d, 1 H, 4a-H), 4.38 (bd, 1 H, 4b-H), 4.74 (d, 1 H, 1a-H), 4.96−5.09 (m, 4 H, 1b,c-H, 2b,c-H), 5.12−5.34 (m, 12 H, 6 All-3-H_2), 5.29 (m, 1 H, 2a-H); $J_{1a,2a}$ = 7.9, $J_{3a,4a}$ = 2.6, $J_{3b,4b}$ = 2.1 Hz. − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 55.8 (O*C*H_3), 66.7, 68.2, 68.6 [C-4 (a−c)], 69.2, 69.8, 70.1 [C-6 (a−c)], 70.6, 70.7, 71.1 [C-2 (a−c)], 71.2, 71.2, 71.3, 72.7 (6 All-C-1), 73.7, 74.2, 74.8 [C-5 (a−c)], 79.1, 80.4, 80.6 [C-3 (a−c)], 99.3, 99.7 (C-1b,c), 101.3 (C-1a). − MS (ESI): *m*/*z* = 1125.8 [(M + Na)$^+$]. − $C_{58}H_{86}O_{20}$ (1103.31): calcd. C 63.14, H 7.86; found C 62.98, H 7.99.

4-Methoxyphenyl (3,6-Di-*O*-allyl-β-D-galactopyranosyl)-(1→4)-(3,6-di-*O*-allyl-β-D-galactopyranosyl)-(1→4)-3,6-di-*O*-allyl-β-D-galactopyranoside (72): LiOH·H_2O (570 mg, 13.6 mmol) was added to a solution of trisaccharide **70** (390 mg, 0.34 mmol) in MeOH (15 mL). After refluxing for 16 h, the mixture was filtered, the filtrate was neutralised with an acidic ion-exchange resin (Amberlite IR 120), and taken to dryness in vacuo. Chromatography (toluene/

EtOAc, 1:1) of the residue gave **72** (260 mg, 90%) as a yellow syrup; R_f = 0.21 (toluene/EtOAc, 1:1); $[\alpha]_D^{20}$ = −11.5 (*c* = 1.0, $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.70−3.30 (b, 4 H, 4 OH), 3.36 (dd, 1 H, 3c-H), 3.39 (dd, 1 H, 3b-H), 3.47 (dd, 1 H, 3a-H), 3.48−3.63 [m, 3 H, 5-H (a−c)], 3.54−3.88 [6-H_2 (a−c)], 3.73 (m, 1 H, 2c-H), 3.75 (s, 3 H, OCH_3), 3.82−4.40 (m, 12 H, 6 All-1-H_2), 3.87 (m, 1 H, 2b-H), 3.96 (m, 1 H, 4c-H), 4.01 (m, 1 H, 4b-H), 4.03 (m, 1 H, 2a-H), 4.10 (d, 1 H, 4a-H), 4.34 (d, 1 H, 1c-H), 4.37 (d, 1 H, 1b-H), 4.68 (d, 1 H, 1a-H); $J_{1a,2a}$ = 7.8, $J_{2a,3a}$ = 9.0, $J_{3a,4a}$ = 2.9, $J_{1b,2b}$ = 8.0, $J_{2b,3b}$ = 8.9, $J_{3b,4b}$ = 3.2, $J_{1c,2c}$ = 7.9, $J_{2c,3c}$ = 9.4, $J_{3c,4c}$ = 3.2 Hz. − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 55.6 (O*C*H_3), 66.7 (C-4c), 68.8, 69.0, 69.2 [C-6 (a−c)], 70.1 (C-2c), 71.1, 72.1, 72.4, 72.5 (6 All-C-1), 71.9 (C-2b), 73.3, 73.6, 73.8 [C-5 (a−c)], 76.0 (C-4a), 77.3 (C-4b), 80.2, 80.3, 80.5 [C-3 (a−c)], 102.6 (C-1a), 105.6 (C-1b), 106.1 (C-1c). − MS (FD): *m*/*z* = 851 [M^+]. − $C_{43}H_{62}O_{17}$ (850.95): calcd. C 60.69, H 7.34; found C 60.53, H 7.24.

4-Methoxyphenyl β-D-Galactopyranosyl-(1→4)-β-D-galactopyranosyl-(1→4)-β-D-galactopyranoside (73): $[NiCl_2(dppp)]$[81] (2.2 mg, 4 μmol) and $NaBH_4$ (90 mg, 2.4 mmol) were added to a stirred and cooled (0 °C) solution of trisaccharide **72** (170 mg, 0.2 mmol) in THF/EtOH (4:1, 5 mL). After 24 h at room temperature, the mixture was diluted with Et_2O (10 mL) and hydrolysed with H_2O (2 mL) for 1 h, followed by stirring with acetic acid (0.5 mL) for 30 min. After concentration in vacuo, the residue, syrupy **73**, was purified by conversion into its peracetate and subsequent de-*O*-acetylation: i.e., it was first exposed to pyridine/Ac_2O (4 mL each) for 6 h at ambient temperature, followed by quenching with ice, extraction with CH_2Cl_2 (3 × 20 mL), and washing of the combined organic phases with 2 N HCl (50 mL) and saturated aqueous $NaHCO_3$ (50 mL). Drying ($MgSO_4$) and removal of the solvent gave a residue, which was chromatographed on silica gel (toluene/EtOAc, 1:1) to give the uniform peracetate of **73** (R_f = 0.24, toluene/EtOAc, 1:1). This was dissolved in MeOH (4 mL), NaOMe (0.5 M in MeOH, 20 μL, 10 μmol) was added, and the mixture was stirred for 16 h at room temperature. Neutralisation with Amberlite IR 120 (H^+ form), evaporation to dryness and chromatography of the resulting syrup on silica gel (CH_2Cl_2/MeOH, 1:1) gave **73** (84 mg, 69%) as a colourless solid; R_f = 0.51 (CH_2Cl_2/MeOH, 1:1); $[\alpha]_D^{20}$ = −5.9 (*c* = 0.5, H_2O). − ^{1}H NMR (300 MHz, D_2O): δ = 3.58−3.72 (m, 3 H, 2b,c-H, 3c-H), 3.73−3.88 [m, 12 H, 2a-H, 3a,b-H, 5-H (a−c), 6-H_2 (a−c)], 3.82 (s, 3 H, OCH_3), 3.92 (d, 1 H, 4c-H), 4.19 (d, 1 H, 4b-H), 4.24 (m, 1 H, 4a-H), 4.61 (d, 1 H, 1c-H), 4.69 (d, 1 H, 1b-H), 4.99 (m, 1 H,[87] 1a-H); $J_{1b,2b}$ = 7.8, $J_{3b,4b}$ = 3.0, $J_{1c,2c}$ = 7.5, $J_{3c,4c}$ = 2.9 Hz. − ^{13}C NMR (75.5 MHz, D_2O): δ = 55.6 (O*C*H_3), 63.3, 63.4, 63.9 [C-6 (a−c)], 71.5 (C-4c), 73.9, 74.2, 74.7, 75.6, 76.0, 76.1, 77.3, 77.4, 78.0 [C-2 (a−c), C-3 (a−c), C-5 (a−c)], 80.0 (C-4b), 80.3 (C-4a), 104.5 (C-1a), 107.2, 107.3 (C-1b,c). − MS (FD): *m*/*z* = 633 [(M + Na)$^+$]. − $C_{25}H_{38}O_{17}$ (610.56): calcd. C 49.18, H 6.27; found C 49.12, H 6.21.

β-D-Galactopyranosyl-(1→4)-β-D-galactopyranosyl-(1→4)-α/β-D-galactopyranose (75): Trisaccharide **72** (170 mg, 0.2 mmol) was de-*O*-allylated and subsequently *O*-acetylated as described for **72** → **73**. The resulting peracetate of **73** was exposed to ceric ammonium nitrate (0.55 g, 1 mmol) treatment in a cooled (0 °C) solution of acetonitrile/water (2:1, 5 mL), and the mixture was stirred for 30 min, followed by dilution with water (20 mL) and extraction with CH_2Cl_2 (3 × 25 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ (30 mL) and saturated aqueous Na_2SO_3 (2 × 30 mL), and subsequently evaporated to dryness in vacuo. The resulting syrup was de-*O*-acetylated in methanol solution (4 mL) with NaOMe (0.5 M in MeOH, 20 μL) for 16 h at ambient temperature. Neutralisation with Amberlite IR 120 (H^+ form), evaporation to dryness and elution of the resulting syrup from a Sephadex column with water/ethanol and removal of the solvents in vacuo afforded 71 mg (70%) of galactotriose **75** as a colourless syrup, comprising a 1:2 α/β mixture of anomers (^{1}H NMR); $[\alpha]_D^{20}$ = +53.0 (*c* = 0.95, H_2O); ref.:[14] $[\alpha]_D^{25}$ = +58.0 (*c* = 1.5, H_2O) for an amorphous product isolated from spruce wood. − ^{1}H NMR (500 MHz, D_2O): δ = 3.57 (dd, 0.7 H, 2a$_\beta$-H), 3.61 (m, 1 H, 2c-H), 3.68 (m, 2 H, 2b-H, 3c-H,), 3.73 (m, 0.3 H, 6a$_\alpha$-H), 3.75 (m, 0.7 H, 3a$_\beta$-H), 3.79 (m, 1 H, 3b-H), 3.82 (m, 0.3 H, 6a$_\alpha$ -H′), 3.66−3.88 (m, 8.1 H, 5a$_\beta$-H, 5b,c-H, 6a$_\beta$-H_2, 6b,c-H_2), 3.91 (m, 0.3 H, 2a$_\alpha$-H), 3.92 (d, 1 H, 4c-H), 3.96 (dd, 0.3 H, 3a$_\alpha$-H), 4.13 (bt, 0.3 H, 5a$_\alpha$-H), 4.17 (m, 0.7 H, 4a$_\beta$-H), 4.18 (m, 1 H, 4b-H), 4.23 (d, 0.3 H, 4a$_\alpha$-H), 4.60 (d, 1 H, 1c-H), 4.62 (m, 0.7 H, 1a$_\beta$-H), 4.63 (m, 1 H, 1b-H), 5.28 (d, 0.3 H, 1a$_\alpha$-H); the chemical shift data compare favourably with those reported[83] for a soy arabinogalactan-derived sample; $J_{1a,2a\alpha}$ = 3.8, $J_{2a,3a\alpha}$ = 10.5, $J_{3a,4a\alpha}$ = 2.5, $J_{5a,6a\alpha}$ = 6.5, $J_{1a,2a\beta}$ = 7.9, $J_{2a,3a\beta}$ = 9.8, $J_{1c,2c\alpha/\beta}$ = 7.8, $J_{3c,4c\alpha/\beta}$ = 3.2 Hz. − ^{13}C NMR (125 MHz, D_2O): δ = 61.1, 61.3, 61.4, 61.5 (C-6), 69.2 (C-4c), 69.4 (C-2a$_\alpha$), 70.3 (C-3a$_\alpha$), 70.4 (C-5a$_\alpha$), 72.0 (C-2c), 72.4, 72.5, 72.8, 73.3, 73.8, 73.9, 74.9, 75.0 (C-2a$_\beta$, C-2c, C-3b, C-3c, C-3a$_\beta$, C-5a$_\beta$, C-5b,c), 77.7 (C-4b), 78.4 (C-4a$_\beta$), 79.3 (C-4a$_\alpha$), 92.9 (C-1a$_\alpha$), 97.0 (C-1a$_\beta$), 104.8, 104.9, 105.0 (C-1b,c). − MS (ESI): *m*/*z* = 527.4 [(M + Na)$^+$].

6. β(1→4)-Galactotetraosides

4-Methoxyphenyl (4-*O*-Acetyl-3,6-di-*O*-allyl-2-*O*-pivaloyl-β-D-galactopyranosyl)-(1→4)-[(3,6-di-*O*-allyl-2-*O*-pivaloyl-β-D-galactopyranosyl)-(1→4)-]$_2$-3,6-di-*O*-allyl-2-*O*-pivaloyl-β-D-galactopyranoside (64): Methyl triflate-promoted treatment of phenylthio galactobioside **60** (2.25 g, 2.8 mmol) with acceptor **62** (1.09 g, 1.4 mmol) was effected using general coupling procedure A, followed by column chromatography of the residue (toluene/EtOAc, 7:1) to provide 1.59 g (77%) of tetrasaccharide **64** as a syrup; R_f = 0.41 (toluene/EtOAc, 4:1); $[\alpha]_D^{20}$ = −5.9 (*c* = 0.9, $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.12 (s, 3 H, AcCH_3), 3.39−3.53 [m, 8 H, 3-H (a−d), two 5-H, 6d-H_2], 3.59−3.71 (m, 8 H, two 5-H, 6-H_2 (a−c)], 3.75 (s, 3 H, OCH_3), 3.83−4.19 (m, 16 H, 8 All-1-H_2), 4.33 [m, 3 H, 4-H (a−c)], 4.74 (d, 1 H, 1a-H), 4.93−5.04 [m, 6 H, 1-H (b−d), 2-H (b−d)], 5.10−5.35 (m, 17 H, 2a-H, 8 All-3-H_2), 5.43 (d, 1 H, 4d-H); $J_{1a,2a}$ = 7.9, $J_{3d,4d}$ = 2.8 Hz. − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.8 (Ac*C*H_3), 55.5 (O*C*H_3), 66.8 (C-4d), 68.0, 68.5 [C-4 (a−c)], 68.3 (C-6d), 69.3, 69.5, 69.6 [C-6 (a−c)], 70.3 (C-2a), 70.7, 70.8 [C-2 (b−d)], 70.8, 70.9, 71.1, 72.4 (8 All-C-1), 72.3 (C-5d), 73.6, 74.0 (C-5b,c), 74.7 (C-5a), 76.9 (C-3d), 79.9, 80.1 [C-3 (a−c)], 99.4, 99.5 [C-1 (b−d)], 101.1 (C-1a). − MS (ESI): *m*/*z* = 1494.6 [(M + Na)$^+$]. − $C_{77}H_{114}O_{27}$ (1471.73): calcd. C 62.84, H 7.81; found C 62.51, H 7.75.

4-Methoxyphenyl [(3,6-Di-*O*-allyl-2-*O*-pivaloyl-β-D-galactopyranosyl)-(1→4)-]$_3$-3,6-di-*O*-allyl-2-*O*-pivaloyl-β-D-galactopyranoside (65): Tetrasaccharide **64** (1.77 g, 1.2 mmol) was deacetylated as described above for **55** → **62**. Column chromatography (toluene/EtOAc, 3:1) of the residue gave galactotetraoside acceptor **65** (1.42 g, 83%) as a yellow syrup; R_f = 0.23 (toluene/EtOAc, 4:1); $[\alpha]_D^{20}$ = −14.8 (*c* = 0.84, $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.36 (br. s, 1 H, 4d-OH), 3.43 [m, 4 H, 3-H (a−d)], 3.51 (m, 3 H, three 5-H), 3.55−3.68 (m, 9 H, 5-H, 6-H_2 (a−d)], 3.75 (s, 3 H, OCH_3), 3.90−4.20 (m, 16 H, 8 All-1-H_2), 4.01 (m, 1 H, 4d-H), 4.33 [m, 3 H, 4-H (a−c)], 4.73 (d, 1 H, 1a-H), 4.92−5.04 (m, 5 H, 1-H (b−d), 2b,c-H], 5.06 (dd, 1 H, 2d-H), 5.11−5.34 (m, 16 H, 8 All-3-H_2), 5.30 (m, 1 H, 2a-H); $J_{1a,2a}$ = 7.9, $J_{1d,2d}$ = 8.0, $J_{2d,3d}$ = 9.9 Hz. − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 55.8 (O*C*H_3), 66.5 (C-4d), 68.3, 68.6, 68.8 [C-4 (a−c)], 69.1, 69.9, 70.2 [C-6 (a−d)], 70.3, 70.6, 71.0 [C-2 (a−d)], 71.1, 71.4, 72.6, 72.7 (8 All-C-1), 73.5

(C-5d), 74.2, 74.4 (C-5b,c), 74.9 (C-5a), 79.0 (C-3d), 80.1, 80.3, 80.4 [C-3 (a−c)], 99.5, 99.7 [C-1 (b−d)], 101.3 (C-1a). − MS (ESI): m/z = 1452.5 [(M + Na)$^+$]. − $C_{75}H_{112}O_{26}$ (1429.69): calcd. C 63.01, H 7.90; found C 62.78, H 7.98.

4-Methoxyphenyl [(3,6-Di-*O*-allyl-β-D-galactopyranosyl)-(1→4)]$_3$-3,6-di-*O*-allyl-β-D-galactopyranoside (66): LiOH·H_2O (630 mg, 15 mmol) was added to a methanolic solution of tetrasaccharide **64** (440 mg, 0.3 mmol, in 15 mL) and the mixture was refluxed for 12 h. After suction filtration, the filtrate was neutralised with Amberlite IR 120 (H^+ form), and taken to dryness in vacuo. Purification of the residue by elution from a silica gel column (toluene/EtOAc, 1:2) afforded **66** (295 mg, 90%) as a yellow syrup; R_f = 0.26 (toluene/EtOAc, 1:2); $[\alpha]_D^{20}$ = +3.4 (c = 0.98, $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.80−3.15 (b, 5 H, 5 OH), 3.36 [m, 3 H, 3-H (b−d)], 3.48 (m, 3 H, 3a-H, two 5-H), 3.54−3.69 [m, 6 H, two 5-H, 6-H (a−d)], 3.72−3.85 [m, 10 H, 2-H (b−d), 6-H′ (a−d), OCH_3], 3.92−4.08 [m, 12 H, 2a-H, 4-H (b−d), 4 All-1-H_2], 4.10 (d, 1 H, 4a-H), 4.17−4.42 (m, 9 H, 1-H, 4 All-1-H_2), 4.32 (d, 1 H, $J_{1,2}$ = 7.8 Hz, 1-H), 4.37 (d, 1 H, $J_{1,2}$ = 7.6 Hz, 1-H), 4.68 (d, 1 H, 1a-H); $J_{1a,2a}$ = 7.8, $J_{3a,4a}$ = 3.0 Hz. − MS (ESI): m/z = 1116.5 [(M + Na)$^+$].

4-Methoxyphenyl (4-*O*-Acetyl-3-*O*-allyl-6-*O*-benzyl-2-*O*-pivaloyl-β-D-galactopyranosyl)-(1→4)-[(3-*O*-allyl-6-*O*-benzyl-2-*O*-pivaloyl-β-D-galactopyranosyl)-(1→4)-]$_2$-3-*O*-allyl-6-*O*-benzyl-2-*O*-pivaloyl-β-D-galactopyranoside (67): Methyl triflate-promoted glycosylation of galactobioside acceptor **63** (530 mg, 0.6 mmol) with thiogalactobioside **61** (1.09 g, 1.2 mmol) by general coupling procedure A and subsequent column chromatography of the residue (toluene/EtOAc, 11:1) afforded tetrasaccharide **67** (760 mg, 76%) as a syrup; R_f = 0.52 (toluene/EtOAc, 4:1); $[\alpha]_D^{20}$ = −10.0 (c = 0.98, $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.00 (s, 3 H, AcCH_3), 3.38−3.49 (m, 6 H, four 3-H, 6d-H_2), 3.55 (m, 3 H, two 5-H, 6-H), 3.61−3.79 (m, 10 H, two 5-H, two 6-H_2, 6-H′, OCH_3), 3.80−4.15 (m, 8 H, 4 All-1-H_2), 4.29, 4.32, 4.34 [3 d, $J_{3,4}$ = 2.3, 2.7, 3.0 Hz, each 1 H, 4-H (a−c)], 4.41−4.64 (m, 8 H, 4 CH_2Ph), 4.74 (d, 1 H, 1a-H), 4.91−5.05 [m, 6 H, 1-H (b−d), 2-H (b−d)], 5.06−5.26 (m, 8 H, 4 All-3-H_2), 5.29 (dd, 1 H, 2a-H), 5.48 (d, 1 H, 4d-H); $J_{1a,2a}$ = 7.9, $J_{2a,3a}$ = 9.8 Hz. − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.8 (AcCH_3), 55.6 (OCH_3), 66.7 (C-4d), 67.7 (C-4), 68.2 (C-6d), 68.9, 69.0 (2 C-4), 69.5 (C-6a), 70.0 (C-6b,c), 70.4, 70.5 [C-2 (a−d)], 70.6, 70.9 (4 All-C-1), 72.3 (C-5d), 73.6, 73.7 (4 CH$_2$Ph), 73.8, 73.9 (C-5b,c), 74.9 (C-5a), 76.7 (C-3d), 80.1, 80.4 [C-3 (a−c)], 99.5, 99.7, 99.9 [C-1 (b−d)], 101.1 (C-1a). − MS (ESI): m/z = 1694.2 [(M + Na)$^+$]. − $C_{93}H_{122}O_{27}$ (1671.97): calcd. C 66.81, H 7.35; found C 66.65 H 7.11.

4-Methoxyphenyl [(3-*O*-Allyl-6-*O*-benzyl-2-*O*-pivaloyl-β-D-galactopyranosyl)-(1→4)-]$_3$-3-*O*-allyl-6-*O*-benzyl-2-*O*-pivaloyl-β-D-galactopyranoside (68): Tetrasaccharide **67** (750 mg, 0.45 mmol) was deacetylated as described for the conversion **64** → **65**. Column chromatography (toluene/EtOAc, 6:1) gave **68** (630 mg, 86%) as a colourless foam; R_f = 0.29 (toluene/EtOAc, 4:1); $[\alpha]_D^{20}$ = −18.3 (c = 0.92, $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.49 (br. s, 1 H, 4d-OH), 3.43 [m, 4 H, 3-H (a−d)], 3.55 (m, 4 H, three 5-H, 6-H), 3.61−3.81 (m, 11 H, 5-H, three 6-H_2, 6-H′, OCH_3), 3.84−4.15 (m, 8 H, 4 All-1-H_2), 4.04 (br. s, 1 H, 4d-H), 4.30, 4.32, 4.35 [3 d, $J_{3,4}$ = 2.0, 2.6, 3.4 Hz, each 1 H, 4-H (a−c)], 4.42 (s, 2 H, CH_2Ph), 4.46−4.64 (m, 6 H, 3 CH_2Ph), 4.74 (d, 1 H, 1a-H), 4.95 [m, 3 H, 1-H (b−d)], 5.01−5.27 [m, 11 H, 2-H (b−d), 4 All-3-H_2], 5.28 (dd, 1 H, 2a-H); $J_{1a,2a}$ = 7.9, $J_{2a,3a}$ = 9.9 Hz. − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 55.5 (OCH_3), 66.3 (C-4d), 67.7, 68.8 [C-4 (a−c)], 69.0, 69.8, 70.0 [C-6 (a−d)], 70.4, 70.5, 70.9 [C-2 (a−d)], 70.8, 71.0, 71.2 (4 All-C-1), 73.3 (C-5d), 73.5, 73.6 (4 CH$_2$Ph), 73.9 (C-5b,c), 74.8 (C-5a), 78.8 (C-3d), 79.9, 80.0, 80.2 [C-3 (a−c)], 99.4, 99.5, 99.6 [C-1 (b−d)], 101.1 (C-1a). − MS (ESI): m/z = 1652.6 [(M + Na)$^+$], 837.9 [(M + 2 Na)$^{2+}$]. − $C_{91}H_{120}O_{26}$ (1629.93): calcd. C 67.06, H 7.42; found C 66.79 H 7.36.

4-Methoxyphenyl [(β-D-Galactopyranosyl)-(1→4)-]$_3$-β-D-galactopyranoside (74): Tetrasaccharide **67** (500 mg, 0.3 mmol) was de-*O*-acylated by refluxing for 12 h in methanolic LiOH·H_2O (500 mg, 12 mmol, in 15 mL). Neutralisation by stirring with Amberlite IR 120 (H^+ form), filtration, and removal of the solvent in vacuo left a syrup that was purified by elution from a silica gel column (CH_2Cl_2/MeOH, 40:1) to give 355 mg (90%) of the 3-*O*-allyl-6-*O*-benzylgalactotetraoside **69** as a colourless foam after evaporation of the fractions with R_f = 0.45 (CH_2Cl_2/MeOH, 10:1). Subsequent de-*O*-allylation was by dissolution in ether (2 mL), cooling (0 °C), addition of [$NiCl_2$(dppp)][81] (3.5 mg) and DIBAL (1 M in THF, 2.7 mL, 10 molar excess), stirring for 8 h at 0 °C and for another 8 h at ambient temperature, followed by dilution with ether (30 mL), addition of water (4 mL), stirring for 1 h to hydrolyse excess DIBAL, dissolution of the aluminate precipitate by addition of acetic acid (2 mL), evaporation to dryness in vacuo, and co-evaporation with toluene (2 × 20 mL). The resulting solid was acetylated with pyridine/Ac_2O (5 mL each) in the presence of DMAP (100 mg) for 4 h at 40 °C. MeOH (5 mL) was added to destroy excess Ac_2O (15 min, 40 °C), followed by CH_2Cl_2 (100 mL), washings with 2 N HCl (2 × 50 mL) and saturated aqueous $NaHCO_3$ (50 mL), drying ($MgSO_4$), and removal of the solvent in vacuo. Elution of the residue from a silica gel column (toluene/EtOAc, 2:1) afforded the syrupy 6-*O*-benzyl-peracetate of **74**, which was dissolved in acetic acid (3 mL) and hydrogenated over 10% Pd/C (120 mg) for 5 h. Filtration through Kieselguhr, evaporation to dryness in vacuo and exposure of the residue to NaOMe/MeOH (0.2 mL of 0.5 M methanolic solution in 4 mL) for 6 h at 25 °C, neutralisation (Amberlite IR 120, H^+ form), and removal of the solvent in vacuo gave pure **74** (155 mg, 67% based on **67**) as a colourless solid; R_f = 0.18 (CH_2Cl_2/MeOH/H_2O, 12:6:1). − ^{1}H NMR (300 MHz, D_2O): δ = 3.58−3.80 [m, 13 H, 2-H (b−d), 3-H (b−d), 5-H (b−d), two 6-H_2], 3.82 (s, 3 H, OCH_3), 3.86 (m, 7 H, 2a-H, 3a-H, 5a-H, two 6-H_2), 3.91 (d, 1 H, 4d-H), 4.17 (m, 2 H, 4b,c-H), 4.24 (br. s, 1 H, 4a-H), 4.60 (d, 1 H, 1d-H), 4.65, 4.67 (2 d, each 1 H, 1b,c-H), 4.97 (m, 1 H,[87] 1a-H); $J_{1b,2b}$ = $J_{1c,2c}$ = 8.0, $J_{1d,2d}$ = 7.3, $J_{3d,4d}$ = 2.6 Hz. − ^{13}C NMR (75.5 MHz, D_2O): δ = 58.6 (OCH_3), 63.2, 63.3, 63.5, 63.8 [C-6 (a−d)], 71.4 (C-4d), 73.8 (C-2a), 74.2 (C-2d), 74.6, 74.7 (C-2b,c), 75.6 (C-3d), 75.9 (C-3a), 76.0, 76.1 (C-3b,c), 77.2, 77.3, 77.9 [C-5 (a−d)], 80.0, 80.2, 80.4 [C-4 (a−c)], 104.8 (C-1a), 107.2 [C-1 (b−d)]. − MS (ESI): m/z = 795.3 [(M + Na)$^+$]. − $C_{31}H_{48}O_{22}$(772.87): calcd. C 48.18, H 6.28; found C 48.10, H 6.19.

Attempts to effect removal of the eight allyl groups from 3,6-di-*O*-allylated tetrasaccharide **66** with DIBAL/$NiCl_2$(dppp), in a manner analogous to the respective trisaccharide conversion **72**→**73**, resulted in product mixtures of **74** and substantial amounts of propyl ethers (^{1}H NMR) formed by reduction of one or more of the allyl double bonds. After purification by peracetylation, extensive chromatography, and subsequent de-*O*-acetylation, **74** was obtained in only 27% yield.

7. β(1→4)-Galactopenta- and Hexaosides

4-Methoxyphenyl (4-*O*-Acetyl-3,6-di-*O*-allyl-2-*O*-pivaloyl-β-D-galactopyranosyl)-(1→4)-[(3,6-di-*O*-allyl-2-*O*-pivaloyl-β-D-galactopyranosyl)-(1→4)-]$_3$-3,6-di-*O*-allyl-2-*O*-pivaloyl-β-D-galactopyranoside (76): Galactotrioside acceptor **71** (330 mg, 0.3 mmol), disaccharide donor **60** (480 mg, 0.6 mmol), and DTBMP (308 mg, 1.5 mmol) in

CH_2Cl_2 (7 mL) were treated and processed according to general procedure A and the resulting syrup was purified by elution from a silica gel column (toluene/EtOAc, 6:1): 360 mg (67%) of galactopentaoside **76** as a colourless syrup; R_f = 0.33 (toluene/EtOAc, 4:1); $[\alpha]_D^{20}$= −7.4 (*c* = 1.0, $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.11 (s, 3 H, Ac*CH*$_3$), 3.37−3.72 [m, 20 H, 3-H (a−e), 5-H (a−e), 6-H$_2$ (a−e)], 3.74 (s, 3 H, O*CH*$_3$), 3.83−4.20 (m, 20 H, 10 All-1-H$_2$), 4.28 (bd, 2 H, two 4-H), 4.33 (bd, 2 H, two 4-H), 4.74 (d, 1 H, 1a-H), 4.87−5.03 [m, 8 H, 1-H (b−e), 2-H (b−e)], 5.10−5.35 (m, 21 H, 10 All-3-H$_2$, 2a-H), 5.42 (d, 1 H, 4e-H); $J_{1a,2a}$ = 7.9, $J_{3e,4e}$ = 2.9 Hz. − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.9 (Ac*CH*$_3$), 55.8 (O*CH*$_3$), 67.1 (C-4e), 68.5, 68.7 [C-4 (a−d)], 68.6, 69.4, 70.1, 70.3, 70.5 [C-6 (a−e)], 70.7, 70.8, 71.0 [C-2 (a−e)], 71.1, 71.2, 71.3, 72.4, 72.5, 72.7 (10 All-C-1), 73.9, 74.2, 74.5, 75.0, 77.3, 80.2, 80.4 [C-3 (a−e), C-5 (a−e)], 99.7, 100.0 [C-1 (b−e)], 101.3 (C-1a). − MS (ESI): *m*/*z* = 1821.3 [(M + Na)$^+$]. − $C_{94}H_{140}O_{33}$ (1798.12): calcd. C 62.79, H 7.85; found C 62.56, H 7.99.

4-Methoxyphenyl [(3,6-Di-*O*-allyl-2-*O*-pivaloyl-β-D-galactopyranosyl)-(1→4)-]$_4$-3,6-di-*O*-allyl-2-*O*-pivaloyl-β-D-galactopyranoside (77): As solution of **76** (360 mg, 0.2 mmol) in MeOH (4 mL) and 80 μL of 0.5 M NaOMe/MeOH was stirred at room temperature for 16 h, followed by neutralisation with Amberlite IR 120 (H^+ form), filtration, and evaporation to dryness in vacuo. Purification of the residue by elution from a silica gel column (toluene/EtOAc, 4:1) afforded **77** (310 mg, 88%) as a colourless syrup; R_f = 0.56 (toluene/EtOAc, 2:1); $[\alpha]_D^{20}$= −13.2 (*c* = 1.0, $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.10−2.40 (b, 1 H, 4e-OH), 3.37−3.78 [m, 20 H, 3-H (a−e), 5-H (a−e), 6-H$_2$ (a−e)], 3.74 (s, 3 H, O*CH*$_3$) 3.89−4.21 (m, 20 H, 10 All-1-H$_2$), 4.08 (m, 1 H, 4e-H), 4.28 (bd, 2 H, two 4-H), 4.33 (m, 2 H, two 4-H), 4.74 (d, 1 H, 1a-H), 4.86−5.08 [m, 8 H, 1-H (b−e), 2-H (b−e)], 5.09−5.34 (m, 20 H, 10 All-3-H$_2$), 5.31 (m, 1 H, 2a-H), 5.75−5.97 (m, 10 H, 10 All-2-H); $J_{1a,2a}$ = 7.9 Hz. − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 55.5 (O*CH*$_3$), 66.3 (C-4e), 68.5 [C-4 (a−d)], 68.8, 69.6, 69.9, 70.0, 70.3 [C-6 (a−e)], 70.4, 70.8 [C-2 (a−e)], 70.9, 71.1, 72.3, 72.4 (10 All-C-1), 73.4, 73.9, 74.0, 74.2, 74.8 [C-5 (a−e)], 78.9, 80.0, 80.1, 80.3 [C-3 (a−e)], 99.3, 99.5, 99.6, 99.7 [C-1 (b−e)], 101.1 (C-1a). − MS (ESI): *m*/*z* = 1779.2 [(M + Na)$^+$]. − $C_{92}H_{138}O_{32}$ (1756.08): calcd. C 62.92, H 7.92; found C 62.65, H 8.05.

4-Methoxyphenyl (4-*O*-Acetyl-3,6-di-*O*-allyl-2-*O*-pivaloyl-β-D-galactopyranosyl)-(1→4)-[(3,6-di-*O*-allyl-2-*O*-pivaloyl-β-D-galactopyranosyl)-(1→4)-]$_4$-3,6-di-*O*-allyl-2-*O*-pivaloyl-β-D-galactopyranoside (78): Methyl triflate-promoted treatment of phenyl thiogalactobioside **60** (1.61 g, 2 mmol) with tetrasaccharide acceptor **65** (1.63 g, 1 mmol) was effected using general coupling procedure A, followed by column chromatography of the residue (toluene/EtOAc, 5:1), providing 1.63 g (77%) of hexasaccharide **78** as a syrup; R_f = 0.29 (toluene/EtOAc, 4:1); $[\alpha]_D^{20}$ = −3.6 (*c* = 1.1, $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.12 (s, 3 H, Ac*CH*$_3$), 3.36−3.54 [m, 12 H, 3-H (a−f), four 5-H, 6f-H$_2$], 3.56−3.70 [m, 12 H, two 5-H, 6-H$_2$ (a−e)], 3.75 (s, 3 H, O*CH*$_3$), 3.83−4.20 (m, 24 H, 12 All-1-H$_2$), 4.31 [m, 5 H, 4-H (a−e)], 4.74 (d, 1 H, 1a-H), 4.84 (d, 1 H, 1-H), 4.87 (d, 1 H, 1-H), 4.96 [m, 8 H, three 1-H, 2-H (b−f)], 5.10−5.35 (m, 24 H, 12 All-3-H$_2$), 5.33 (m, 1 H, 2a-H), 5.43 (d, 1 H, 4f-H); $J_{1a,2a}$ = 7.9, $J_{1,2}$ = 8.0, 7.9, $J_{3f,4f}$ = 2.9 Hz. − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.8 (Ac*CH*$_3$), 55.6 (O*CH*$_3$), 66.8 (C-4f), 68.1, 68.3, 68.8 [C-4 (a−e)], 68.4 (C-6f), 69.0 (C-6a), 70.1, 70.3 [C-6 (b−e)], 70.5, 70.8 [C-2 (a−f)], 70.9, 71.1, 72.4, 72.5 (12 All-C-1), 72.4 (C-5f), 73.7, 74.3 [C-5 (b−e)], 74.8 (C-5a), 77.0 (C-3f), 80.0, 80.2 [C-3 (a−e)], 99.4, 99.9 [C-1 (b−f)], 101.1 (C-1a). − MS (ESI): *m*/*z* = 2146.9 [(M + Na)$^+$]. − $C_{111}H_{166}O_{39}$ (2124.51): calcd. C 62.75, H 7.88; found C 62.88, H 8.13.

4-Methoxyphenyl [(3,6-Di-*O*-allyl-β-D-galactopyranosyl)-(1→4)]$_5$-3,6-di-*O*-allyl-β-D-galactopyranoside (79): Hexasaccharide **78** (1.0 g, 0.47 mmol) was de-*O*-acylated with LiOH·H_2O (1.38 g, 33 mmol) as described above for **64** → **66**. Column chromatography (CH_2Cl_2/MeOH, 20:1) of the residue gave galactohexaoside **79** (660 mg, 89%) as a colourless foam; R_f = 0.21 (CH_2Cl_2/MeOH, 20:1); $[\alpha]_D^{20}$ = +10.8 (*c* = 0.72, $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.80−3.15 (b, 7 H, 7 OH), 3.31 [m, 5 H, 3-H (b−f)], 3.38−3.60 [m, 13 H, 3a-H, 5-H (a−f), 6-H (a−f)], 3.63−3.80 [m, 14 H, 2-H (b−f), 6-H′ (a−f), O*CH*$_3$], 3.84−4.01 [m, 18 H, 2a-H, 4-H (b−f), 6 All-1-H$_2$], 4.06 (d, 1 H, 4a-H), 4.10−4.23 (m, 8 H, 4 All-1-H$_2$), 4.29 [m, 9 H, 1-H (b−f), 2 All-1-H$_2$], 4.62 (d, 1 H, 1a-H); $J_{1a,2a}$ = 7.7, $J_{3a,4a}$ = 3.0 Hz. − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 55.6 (O*CH*$_3$), 66.7 (C-4f), 68.7, 68.9, 69.0, 69.2 [C-6 (a−f)], 71.1, 72.0, 72.3, 72.4, 72.5, 72.7, 72.8 (12 All-C-1), 71.4, 71.9, 72.7, 72.8, 72.9 [C-2 (a−f)], 73.4, 73.6, 73.7, 73.8 [C-5 (a−f)], 75.4, 76.0, 76.5, 77.2, 77.9 [C-4 (a−e)], 80.2, 80.3, 80.5 [C-3 (a−f)], 102.6 (C-1a), 105.2, 105.4, 105.6, 106.0, 106.4 [C-1 (b−f)]. − MS (ESI): *m*/*z* = 1600.4 [(M + Na)$^+$]. − $C_{79}H_{116}O_{32}$ (1577.77): calcd. C 60.14, H 7.41; found C 59.79, H 7.21.

4-Methoxyphenyl (4-*O*-Acetyl-3-*O*-allyl-6-*O*-benzyl-2-*O*-pivaloyl-β-D-galactopyranosyl)-(1→4)-[(3-*O*-allyl-6-*O*-benzyl-2-*O*-pivaloyl-β-D-galactopyranosyl)-(1→4)-]$_4$-3-*O*-allyl-6-*O*-benzyl-2-*O*-pivaloyl-β-D-galactopyranoside (80): Thiogalactoside **61** (400 mg, 0.44 mmol) and 4d-OH-free tetragalactoside **68** (360 mg, 0.22 mmol) were coupled according to general procedure A. Column chromatography (toluene/EtOAc, 11:1) of the residue afforded hexasaccharide **80** (415 mg, 78%) as a syrup; R_f = 0.49 (toluene/EtOAc, 4:1); $[\alpha]_D^{20}$ = −4.8 (*c* = 1.0, $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.00 (s, 3 H, Ac*CH*$_3$), 3.32−3.45 (m, 5 H, five 3-H), 3.47−3.60 [m, 10 H, 3-H, 5-H (a−e), two 6-H$_2$], 3.61−3.78 (m, 12 H, 5f-H, four 6-H$_2$, O*CH*$_3$), 3.80−4.10 (m, 12 H, 6 All-1-H$_2$), 4.25, 4.30, 4.33 [m, 5 H, 4-H (a−e)], 4.36−4.62 (m, 12 H, 6 C*H*$_2$Ph), 4.72 (d, 1 H, 1a-H), 4.84 (d, 1 H, 1-H), 4.90−5.25 [m, 21 H, four 1-H, 2-H (b−f), 6 All-3-H$_2$], 5.28 (dd, 1 H, 2a-H), 5.48 (d, 1 H, 4f-H); $J_{1a,2a}$ = 7.9, $J_{2a,3a}$ = 10.1, $J_{3f,4f}$ = 3.2 Hz. − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.8 (Ac*CH*$_3$), 55.6 (O*CH*$_3$), 66.7 (C-4f), 68.0, 68.5, 68.8, 68.9 [C-4 (a−e)], 68.1 (C-6f), 69.4 (C-6a), 69.8 [C-6 (b−e)], 70.5, 70.8 (6 C-2), 70.6, 71.1, 71.2, 71.3 (6 All-C-1), 72.3 (C-5f), 73.4, 73.6 (6 *C*H$_2$Ph), 74.0, 74.4 [C-5 (b−e)], 74.9 (C-5a), 76.0 (C-3f), 80.0, 80.3 [C-3 (a−e)], 99.5, 99.8 [C-1 (b−e)], 101.1 (C-1a). − MS (ESI): *m*/*z* = 2447.0 [(M + Na)$^+$], 1234.9 [(M + 2 Na)$^{2+}$]. − $C_{135}H_{178}O_{39}$ (2424.87): calcd. C 66.87, H 7.40; found C 66.88, H 7.61.

4-Methoxyphenyl [(3-*O*-Allyl-6-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-]$_5$-3-*O*-allyl-6-*O*-benzyl-β-D-galactopyranoside (81): Hexasaccharide **80** (1.72 g, 0.71 mmol) was de-*O*-acylated by refluxing in a methanolic suspension of LiOH·H_2O (2.08 g, 50 mmol, in 30 mL) for 16 h, followed by workup as described for **64** → **66**. Chromatography of the resulting residue on silica gel (toluene/EtOAc, 1:1) gave **81** (1.14 g, 86%) as a colourless foam; R_f = 0.19 (toluene/EtOAc, 1:1); $[\alpha]_D^{20}$ = +10.8 (*c* = 0.9, $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.37 [m, 5 H, 3-H (a−f)], 3.42−3.80 [m, 13 H, 3a-H, 5-H (a−f), 6-H (a−f)], 3.74 (s, 3 H, O*CH*$_3$), 3.76−3.94 [m, 12 H, 2-H (a−f), 6-H′ (a−f)], 3.99 [m, 5 H, 4-H (b−f)], 4.14 (d, 1 H, 4a-H), 4.18−4.50 [m, 29 H, 1-H (b−f), 6 C*H*$_2$Ph, 6 All-1-H$_2$], 4.69 (d, 1 H, 1a-H); $J_{1a,2a}$ = 7.7, $J_{3a,4a}$ = 2.9 Hz. − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 55.6 (O*CH*$_3$), 66.7 (C-4f), 68.8, 69.0, 69.3 [C-6 (a−f)], 71.2, 71.4, 72.0, 72.1, 72.2, 72.5, 72.6, 72.8, 73.0, 73.1, 73.2, 73.4, 73.7 [C-2 (a−f), C-5 (a−f), 6 *C*H$_2$Ph, 6 All-C-1], 75.4, 76.1, 76.6, 77.4, 78.3 [C-4 (a−e)], 80.1, 80.2, 80.4, 80.8 [C-3 (a−f)], 102.6 (C-1a), 105.2, 105.5, 105.8, 106.2, 106.6 [C-1 (b−f)]. − MS (ESI): *m*/*z* = 1889.3 [(M + Na)$^+$].

4-Methoxyphenyl [β-D-Galactopyranosyl-(1→4)-]$_5$-β-D-galactopyranoside (82): De-*O*-allylation of hexasaccharide **81** (620 mg, 0.33 mmol) was effected with DIBAL (1 M in THF, 6.0 mL, 6.0 mmol) and [$NiCl_2$(dppp)][81] (4 mg, 7 μmol) as described for the respective galactobioside (**57** → **58**), and the resulting residue was acetylated (pyridine/Ac_2O/DMAP) and subsequently subjected to column chromatography (toluene/EtOAc, 2:1). The fractions with R_f = 0.15 (toluene/EtOAc, 2:1) were combined and concentrated. Next, the residue was dissolved in AcOH (10 mL), Pd/C (10%, 400 mg) was added, and the mixture was hydrogenated (5 h). Filtration through Celite and evaporation of the solvent gave a residue, which was dissolved in MeOH (5 mL) and NaOMe (0.5 M in MeOH, 0.2 mL). After stirring for 6 h, the solution was neutralised with Amberlite IR 120 (H^+ form). Evaporation of the solvent and column chromatography (CH_2Cl_2/MeOH/water, 6:6:1) of the residue gave the free galactohexaoside **82** (230 mg, 64%) as a colourless solid; R_f = 0.31 (CH_2Cl_2/MeOH/water, 6:6:1). – ^{1}H NMR (300 MHz, D_2O): δ = 3.56–3.80 (m, 23 H, 2-H (b–f), 3-H (b–f), 5-H (b–f), four 6-H_2], 3.81 (s, 3 H, OCH_3), 3.86 (m, 7 H, 2a-H, 3a-H, 5a-H, two 6-H_2), 3.90 (d, 1 H, 4f-H), 4.16 [bs, 4 H, 4-H (b–e)], 4.23 (br. s, 1 H, 4a-H), 4.59 (d, 1 H, 1f-H), 4.64 [d, 4 H, 1-H (b–e)], 4.97 (m, 1 H,[87] 1a-H); $J_{1f,2f}$ = 7.4, $J_{3f,4f}$ = 2.9 Hz. – ^{13}C NMR (75.5 MHz, D_2O): δ = 58.7 (O*C*H_3), 63.3, 63.4, 63.6, 63.8 [C-6 (a–f)], 71.4 (C-4f), 73.9 (C-2a), 74.2, 74.6 [C-2 (b–f)], 75.6, 76.0, 76.1 [C-3 (a–f)], 77.3, 77.4, 78.0 [C-5 (a–f)], 80.0, 80.2, 80.4 [C-4 (a–e)], 104.5 (C-1a), 107.1 [C-1 (b–f)]. – MS (ESI): *m*/*z* = 1119.6 [(M + Na)$^+$].

Acknowledgments

We wish to thank the Fonds der Chemischen Industrie, Frankfurt and the Südzucker AG, Mannheim/Ochsenfurt for supporting of this work.

[1] G. O. Aspinall, in: *The Biochemistry of Plants, Vol. 3. Chemistry of Cell Wall Polysaccharides* (Ed.: J. Preiss), Acad. Press, New York, **1980**, pp. 473–500.
[2] A. M. Stephen, in: *The Polysaccharides, Vol. 2* (Ed.: G. O. Aspinall), Acad. Press, New York, **1983**, 122–193.
[3] For a resourceful attempt to assemble the various polysaccharide components of sycamore cell walls into a tentative model, see: K. Keegstra, K. W. Talmadge, W. D. Bauer, P. Albersheim, *Plant Physiol.* **1973**, *51*, 188–196; P. Albersheim, *Scient. American* **1975**, *232*, 81–95.
[4] J. M. Labavitch, L. E. Freeman, P. Albersheim, *J. Biol. Chem.* **1976**, *251*, 5904–5910.
[5] R. Pressey, D. S. Himmelsbach, *Carbohydr. Res.* **1984**, *127*, 356–359.
[6] E. L. Hirst, J. K. N. Jones, W. O. Walder, *J. Chem. Soc.* **1947**, 1225–1230.
[7] M. T. Al-Kaisey, K. C. B. Wilkie, *Carbohydr. Res.* **1992**, *227*, 147–161.
[8] S. Eda, K. Kato, *Agric. Biol. Chem.* **1978**, *42*, 2253–2257.
[9] S. Eda, K. Miyabe, Y. Akiyama, A. Ohnishi, K. Kato, *Carbohydr. Res.* **1986**, *158*, 205–216.
[10] E. A. Davies, C. Derouet, C. Hervé du Penhoat, C. Morvan, *Carbohydr. Res.* **1990**, *197*, 205–215; F. Goubet, C. Morvan, *Plant Cell Physiol.* **1993**, *34*, 1297–1303.
[11] R. Girault, F. Bert, C. Rihouey, A. Jauneau, C. Morvan, M. Jarvis, *Int. J. Biol. Macromol.* **1997**, *21*, 179–188.
[12] R. Toman, S. Karácsonyi, M. Kubacková, *Carbohydr. Res.* **1975**, *43*, 111–116.
[13] J. K. Gillham, A. S. Perlin, T. E. Timell, *Can. J. Chem.* **1958**, *36*, 1741–1743.
[14] H. O. Bouveng, H. Meier, *Acta Chem. Scand.* **1959**, *13*, 1884–1889.
[15] H. Meier, *Acta Chem. Scand.* **1962**, *16*, 2275–2283.
[16] H. R. Scheuder, W. A. Côté, T. E. Timell, *Svensk Papperstidn.* **1966**, *69*, 641–647.
[17] G. Mandal, A. Das, *Carbohydr. Res.* **1980**, *86*, 247–257.
[18] N. N. Das, A. Das, A. K. Mukherjee, *Carbohydr. Res.* **1977**, *56*, 337–349.
[19] C. A. Duda, E. S. Stevens, J. S. G. Reid, *Macromolecules* **1991**, *24*, 431–435.
[20] P. R. Sundararajan, V. S. R. Rao, *Biopolymers* **1970**, *9*, 1239–1247.
[21] D. A. Rees, W. E. Scott, *J. Chem. Soc. B* **1971**, 469–479.
[22] D. A. Brant, in: *The Biochemistry of Plants, Vol. 3. Structure and Function of Carbohydrates* (Ed.: J. Preiss), Acad. Press, New York, **1980**, pp. 425–472.
[23] B. A. Burton, D. A. Brant, *Biopolymers* **1983**, *22*, 1784–1786.
[24] F. Tanaka, Y. Mizoguchi, Y. Shuto, K. Okamura, K. Ogawa, T. Koshijima, *Mokuzai Kenkyu Shiryo (Wood Res. Notes)* **1986**, *22*, 37–45 [*Chem. Abstr.* **1987**, *107*, 35367e].
[25] S. Immel, F. W. Lichtenthaler, *Starch/Stärke* **2000**, *52*, 1–8, and literature cited there.
[26] J. Szejtli, *Chem. Rev.* **1998**, *98*, 1743–1753.
[27] K. B. Lipkowitz, *Chem. Rev.* **1998**, *98*, 1829–1873.
[28] S. Immel, F. W. Lichtenthaler, *Liebigs Ann.* **1996**, 27–37.
[29] F. W. Lichtenthaler, S. Immel, *Tetrahedron: Asymmetry* **1994**, *5*, 2045–2060.
[30] F. W. Lichtenthaler, S. Immel, *J. Inclusion Phenom. Mol. Recogn. Chem.* **1996**, *25*, 3–16.
[31] S. Immel, S. Peters, Techn. Univ. Darmstadt, to be published.
[32] E. Farkas, J. Thiem, *Eur. J. Org. Chem.* **1999**, 3073–3077.
[33] J. Hart, A. Falshaw, E. Farkas, J. Thiem, *Synlet* **2001**, 329–332.
[34] P. Kovác, *Carbohydr. Res.* **1986**, *153*, 237–251.
[35] P. Kovác, R. B. Taylor, C. P. J. Glaudemans, *J. Org. Chem.* **1985**, *50*, 5323–5333.
[36] P. Kovác, R. B. Taylor, *Carbohydr. Res.* **1987**, *167*, 153–157.
[37] H. A. El-Shenawy, C. Schuerch, *Carbohydr. Res.* **1984**, *131*, 239–246.
[38] M. Oberthür, S. Peters, F. W. Lichtenthaler, *Oral and Poster Presentation at the 20th Int. Carbohydr. Symp.*, Hamburg, August **2000**; Abstract B-029.
[39] P. J. Garegg, H. Hultberg, *Carbohydr. Res.* **1982**, *110*, 261–266.
[40] P. J. Garegg, S. Oscarson, *Carbohydr. Res.* **1985**, *137*, 270–275.
[41] J.-C. Jacquinet, P. Sinaÿ, *Carbohydr. Res.* **1985**, *143*, 143–149.
[42] K. Koike, M. Sugimoto, S. Sato, Y. Ito, Y. Nakahara, T. Ogawa, *Carbohydr. Res.* **1987**, *163*, 189–208.
[43] J. Kihlberg, T. Frejd, K. Jansson, A. Sundin, G. Magnusson, *Carbohydr. Res.* **1988**, *176*, 271–286.
[44] Z. Zhang, G. Magnusson, *J. Org. Chem.* **1996**, *61*, 2383–2393.
[45] M. E. Chacón-Fuertes, M. Martín-Lomas, *Carbohydr. Res.* **1975**, *43*, 51–56.
[46] H. A. El-Shenawy, C. Schuerch, *Carbohydr. Res.* **1984**, *131*, 227–238.
[47] M. A. Nashed, L. Anderson, *Carbohydr. Res.* **1983**, *114*, 53–61.
[48] J. C. Jacquinet, P. Sinaÿ, *Tetrahedron* **1979**, *35*, 365–371.
[49] S. David, A. Thiéffry, A. Veyrières, *J. Chem. Soc. Perkin Trans. 1* **1981**, 1796–1801.
[50] H. Qin, T. B. Grindley, *J. Carbohydr. Chem.* **1996**, *15*, 95–108.
[51] P. J. Garegg, H. Hultberg, S. Wallin, *Carbohydr. Res.* **1982**, *108*, 97–101.
[52] C. Murakata, T. Ogawa, *Carbohydr. Res.* **1992**, *235*, 95–114.
[53] [53a] This regioselectivity for *O*-3 and *O*-6 has previously been observed in the bis(tributyltin) oxide-promoted allylation of methyl β-D-galactopyranoside (refs. [53b–53d]), obviously caused by the intermediate generation of the 3,6-di-*O*-tributyltin ether. – [53b] T. Ogawa, M. Matsui, *Tetrahedron* **1981**, *37*, 2363–2369. – [53c] S. David, A. Fernandez-Mayoralas, *Carbohydr. Res.* **1987**, *165*, C11–C13. – [53d] Y.-M. Zhang, J.-M. Mallet, P. Sinaÿ, *Carbohydr. Res.* **1992**, *236*, 73–88.
[54] F. Goto, T. Ogawa, *Tetrahedron Lett.* **1992**, *33*, 5099–5102.

[55] K. C. Nicolaou, H. Ueno, *Preparative Carbohydrate Chemistry*, M. Dekker, New York, **1996**, pp. 317−338.
[56] R. R. Schmidt, W. Kinzy, *Adv. Carbohydr. Chem. Biochem.* **1994**, *50*, 49 ff.
[57] P. J. Garegg, *Adv. Carbohydr. Chem. Biochem.* **1997**, *52*, 179−205.
[58] D. Kahne, S. Walker, Y. Cheng, D. van Engen, *J. Am. Chem. Soc.* **1989**, *111*, 6881−6882.
[59] L. Yan, D. Kahne, *J. Am. Chem. Soc.* **1996**, *118*, 9239−9248.
[60] W. A. Szarek, G. Grynkiewicz, B. Doboszewski, G. W. Hay, *Chem. Lett.* **1984**, 1751−1754.
[61] F. Micheel, A. Klemer, G. Baum, *Chem. Ber.* **1955**, *88*, 475−479.
[62] H. Kunz, W. Sager, *Helv. Chim. Acta* **1985**, *68*, 283−287.
[63] S. Hashimoto, M. Hayashi, R. Noyori, *Tetrahedron Lett.* **1984**, *25*, 1379−1382.
[64] K. Suzuki, H. Maeta, T. Matsumoto, G. Tsuchihashu, *Tetrahedron Lett.* **1988**, *29*, 3571−3574.
[65] K. C. Nicolaou, C. W. Hummel, Y. Iwabuchi, *J. Am. Chem. Soc.* **1992**, *114*, 3126−3128.
[66] P.-H. Amvam-Zolle, P. Sinaÿ, *Carbohydr. Res.* **1986**, *150*, 199−212.
[67] S. Sato, Y. Ito, T. Nukada, T. Nakahara, T. Ogawa, *Carbohydr. Res.* **1987**, *167*, 197−210.
[68] K. Sakai, Y. Nakahara, T. Ogawa, *Tetrahedron Lett.* **1990**, *31*, 3035−3038.
[69] N. Khiar, M. Martín-Lomas, *J. Org. Chem.* **1995**, *60*, 7017−7021.
[70] Z. Zhang, G. Magnusson, *Carbohydr. Res.* **1996**, *295*, 41−55.
[71] Replacement of the comparatively toxic methyl triflate (ref.[71a]) by other promoters, such as NIS-TfOH (ref.[71b]) and tris(4-bromophenyl)ammonium hexachloroantimonate (ref.[71c]) resulted in sluggish reactions that could only partially be forced to completion by further addition (up to 10 molar equiv.) of the promoter and grossly extended reaction times. Only dimethyl(methylthio)sulfonium triflate (ref.[71d]) proved to be a methyl triflate-equivalent activator, but was not employed as it is prepared (ref.[71e]) by thiolysis of methyl triflate. − [71a] H. Lönn, *Carbohydr. Res.* **1985**, *139*, 105−113; H. Lönn, *Carbohydr. Res.* **1985**, *139*, 115−121. − [71b] G. H. Veeneman, S. H. van Leeuwen, J. H. van Boom, *Tetrahedron Lett.* **1990**, *31*, 1331−1334. − P. Konradsson, U. E. Udodong, B. Fraser-Reid, *Tetrahedron Lett.* **1990**, *31*, 4313−4316. − [71c] A. Marra, J. M. Mallet, C. Amatore, P. Sinaÿ, *Synlett* **1990**, 572−574. − [71d] P. Fügedi, P. J. Garegg, *Carbohydr. Res.* **1986**, *149*, C9−C12. − [71e] M. Ravenscoft, R. M. G. Roberts, J. G. Gillet, *J. Chem. Soc. Perkin Trans. 2* **1982**, 1569−1572.
[72] The assembly of oligo-β(1→4)-galactosides **64**, **67**, **78**, and **80** by the sulfoxide glycosylation procedure, employing the respective galactobiosyl sulfoxides prepared by 3-chloroperbenzoic acid oxidation of **60** and **61**, is described in: M. Oberthür, Dissertation, Techn. Univ. Darmstadt, **1999**.
[73] E. J. Corey, W. Suggs, *J. Org. Chem.* **1973**, *38*, 3224.
[74] J. Gigg, R. Gigg, *J. Chem. Soc. C* **1966**, 82−86.
[75] G. A. Olah, S. C. Narang, B. G. B. Gupta, R. Malhotra, *J. Org. Chem.* **1979**, *44*, 1247−1251.
[76] A. Kamal, E. Laxman, N. V. Rao, *Tetrahedron Lett.* **1999**, *40*, 371−372.
[77] T. W. Greene, P. G. M. Wuts, *Protective Groups in Organic Synthesis*, 2nd ed., John Wiley & Sons, New York, **1991**.
[78] F. Guibe, *Tetrahedron* **1997**, *53*, 13509−13556.
[79] T. Bieg, W. Szeja, *J. Carbohydr. Chem.* **1985**, *4*, 441−446.
[80] T. Taniguchi, K. Ogasawara, *Angew. Chem.* **1998**, *110*, 1137−1139; *Angew. Chem. Int. Ed.* **1998**, *37*, 1136−1137.
[81] $NiCl_2$(dppp) refers to (1,3-bis{diphenylphosphanyl}propane)-dichloronickel(II), commercially available from Aldrich Chem. Co.
[82] T. Fukuyama, A. A. Laird, L. M. Hotchkiss, *Tetrahedron Lett.* **1985**, *26*, 6291−6292.
[83] C. T. M. Fransen, K. M. J. Van Laere, A. A. V. van Wijk, L. P. Brüll, M. Dignum, J. E. Thomas-Oates, J. Haverkamp, H. A. Schols, A. G. J. Voragen, J. P. Kamerling, J. F. G. Vliegenthart, *Carbohydr. Res.* **1998**, *314*, 101−114.
[84] P. Berthault, N. Birlirakis, G. Rubinstein, P. Sinaÿ, H. Desvaux, *J. Biomol. NMR* **1996**, *8*, 23−35.
[85] T. Rundlöf, C. Landersjö, K. Lycknert, A. Maliniak, G. Widmalm, *Magn. Reson. Chem.* **1998**, *36*, 773−776.
[86] T. Rundlöf, L. Erikson, G. Widmalm, *Chem. Eur. J.* **2001**, 1750−1758.
[87] X-Part of the 1a-H/2a-H/3a-H ABX-system, appearing as an approximate equal-intensity 1:2:1 triplet; see, for example: H. Günther, *NMR-Spektroskopie*, 3. Aufl., Thieme-Verlag, Stuttgart, **1992**, pp. 166−167.

Received May 3, 2001
[O01216]