Synthesis of Hexasaccharide Fragments of Pectin

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Abstract: Short syntheses of partially methyl-esterified hexagalacturonates **1**–**5** are described as part of the development of strategies for the preparation of larger pectic oligosaccharides. The methodology is based on the repeated coupling of galactose mono- and disaccharide donors onto a galactose acceptor until a hexagalactan is obtained. All glycosylations are carried out with *n*-pentenyl glycosides to provide good yields of the desired α anomers. Pentenyl disaccharide donors are prepared by the coupling of two pentenyl galactosides controlled by either the armed–disarmed effect or by converting one pentenyl galactoside into the corresponding galactosyl bromide or fluoride. Two orthogonal protecting groups are employed at C6, which makes it possible to oxidize these positions to either the carboxylic acid or to the methyl ester. Each hexagalactan is therefore able to bifurcate into two different hexagalacturonates with a reverse methyl-esterification pattern. The methyl ester distribution in the hexagalacturonates is confirmed by tandem mass spectrometry.

Keywords: carbohydrates · glycosylation · oligosaccharides · pectin · synthetic methods

Introduction

Pectin is a complex polysaccharide, which is a major component of the primary cell walls in higher plants.[1] In the food industry pectin is used as a gelling and stabilizing agent.[2] The main structural feature in pectin is a linear $\alpha 1 \rightarrow$ 4-linked oligomer of D-galacturonic acid which is partially methyl-esterified. The functionality of pectin, both *in planta* and in commercial samples, is largely determined by the extent and pattern of methyl esterification. However, methyl esterification states are typically highly heterogeneous and present a considerable challenge for detailed analysis.[3] The development of molecular tools is important for the better understanding of the biological roles of pectin and to enhance its industrial applications.

Several pectin-degrading enzymes are essential for the elucidation of pectin structure because their activity is influenced by the extent and pattern of methyl esterification. These enzymes include pectin and pectate lyase as well as polygalacturonase, which all cleave the oligomer chain.[1, 4] Pectin and pectate lyase operate by a β-elimination mechanism, whilst polygalacturonase is a hydrolase. Another important enzyme is pectin methyl esterase, which hydrolyzes methyl esters.[1, 4] Chromatographic and mass spectrometric analyses of the degradation products have shown that polygalacturonases cleave preferentially between two uronic acids.[5] The structural requirements for lyases and methyl esterases are less certain, but it appears that they often prefer small sequences of acid or ester units.[5] A major problem in this regard is the lack of pectin fragments with a well-defined methyl ester pattern which could serve to elucidate the substrate specificity of these enzymes. With a better knowledge of their specificity, the utility of these enzymes for the analysis of pectin would be greatly enhanced.[6]

Monoclonal antibodies are also important for the molecular analysis of pectin. The binding of several antibodies is dependent on methyl esterification state although for most the detailed structure of the epitopes is not fully defined.[7] The availability of well-defined oligogalacturonates would be valuable for the elucidation of epitope structures.

We envisioned to make these pectin fragments available by chemical synthesis, which required synthetic methods tailored for this class of compounds. Although the common problems in complex oligosaccharide synthesis have been recognized,[8] a general solution to these challenges has not yet emerged and the synthesis of larger saccharides still requires strategies suited for the specifics of the target. We have recently developed a procedure for synthesis of smaller pectin fragments with a defined esterification pattern, which led to the preparation of three different monomethylated trigalacturonates.[9] While useful as reference compounds these trisaccharides are in general too short to give reasonable rates when employed as substrates for pectic enzymes.[10] In fact, recent studies of several polygalacturonases and pectate lyases have

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revealed that in most cases four to six galacturonic acids are accommodated in the active site.[11] As a result, substrates should be at least hexameric to provide meaningful information about the cleavage pattern of these enzymes. However, selectively methyl-esterified oligogalacturonates larger than trisaccharides have never previously been obtained pure on a preparative scale by synthesis or isolation from natural sources.[12, 13]

Herein, we report the synthesis of hexagalacturonates **1**–**5** (Figure 1). Compounds **1**–**4** all contain a block of three to four acid or ester residues. As many pectic enzymes appear to prefer small blocks of acids or esters these four molecules should provide valuable information about their substrate specificity. Compound **5** with an alternating acid–ester sequence serves as a reference, since it should not be cleaved readily by any of the pectic enzymes.

Results and Discussion

Retrosynthesis: In our earlier work, we assembled small oligogalacturonates by the coupling of galactose glycosyl donors and acceptors followed by oxidation at C6.[9] The glycosylations were carried out with *n*-pentenyl glycosyl donors[14] possessing two different protecting groups at C6.[9] Accordingly, hexagalacturonates **1**–**5** will be prepared from hexagalactans **6**–**8** in which an ester group and a *p*-methoxyphenyl (PMP) ether group serve as orthogonal C6 protecting groups (Figure 1). Hereby, C6 can be oxidized to either the carboxylic acid or to the corresponding methyl ester. By switching the order of these two oxidations hexagalacturonate **1** and **2** can arise from the same galactan **6**, while **3** and **4** can both originate from **7**. Hexagalactans **6** and **7** will be prepared from the same tetrasaccharide **11** by coupling with disaccharides **9** and **10**, respectively. This ability of the key intermediates to diverge into two products is an important feature, which reduces the number of steps for preparation of **1**–**4**.

Hexagalacturonate **5** will arise from hexagalactan **8** containing an alternating ether–ester protecting group sequence (Figure 1). The preparation of **8** will involve two consecutive couplings with pentenyl disaccharide **13**. An allyl group is used as a temporary protecting group at C4′ because this group is stable to pentenyl glycosylations and can be removed in the presence of ester and ether groups. We plan to assemble this disaccharide by controlled coupling of two pentenyl monosaccharides **15** and **16**. The donor pentenyl glycoside **15** is fully protected with ether protecting groups, while the acceptor pentenyl glycoside **16** has an ester group at C6 and ether groups at C2 and C3. Electron-withdrawing ester groups

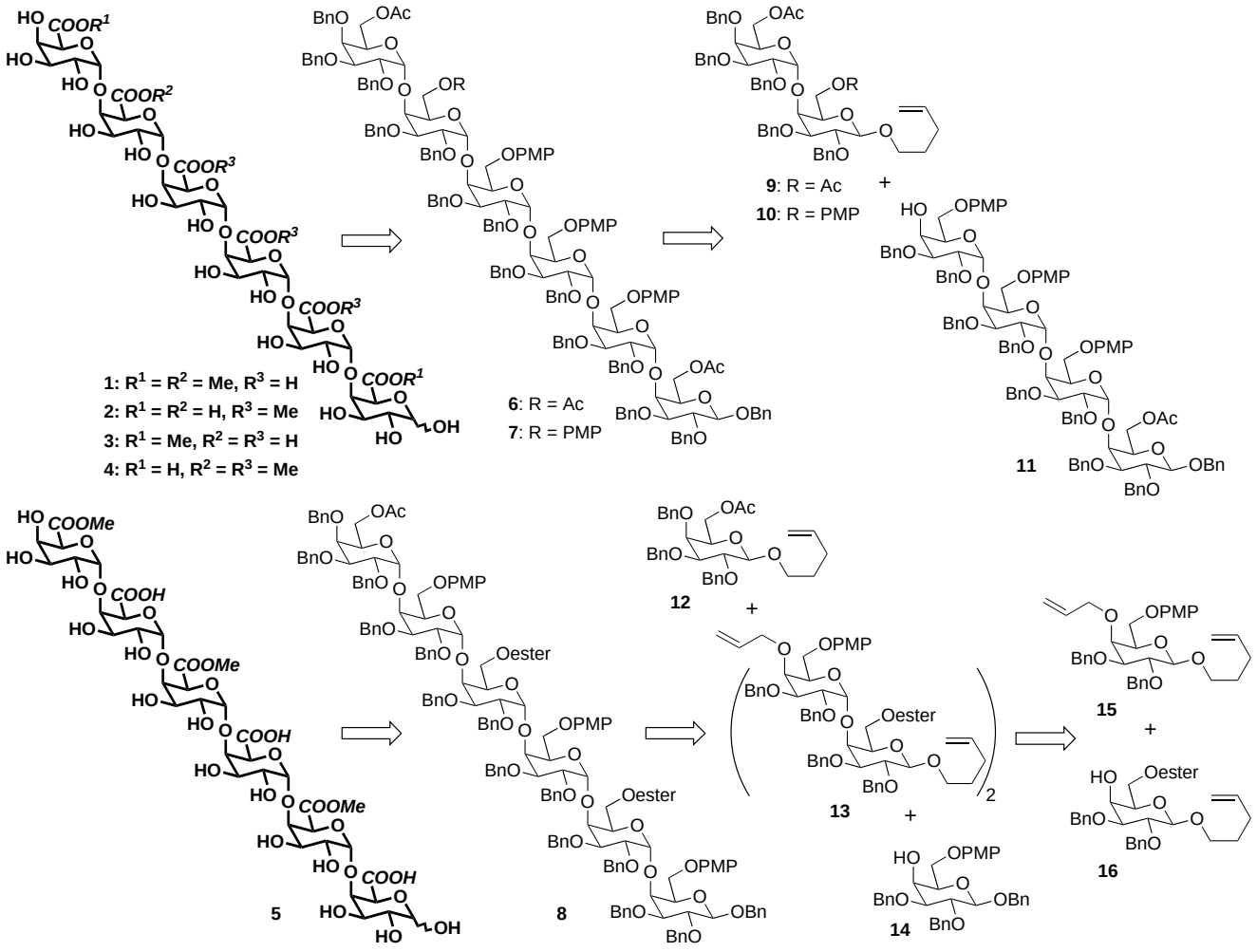
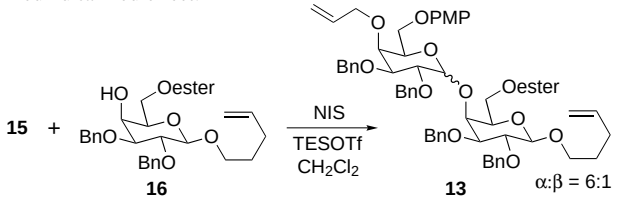


Figure 1. Retrosynthesis for partially methyl-esterified hexagalacturonates **1**–**5**.

are known to decrease the reactivity of glycosyl donors. It is also known that two pentenyl glycosides can be selectively coupled if the donor glycoside is fully protected with ether groups while the acceptor is protected with ester groups at all positions but one. This phenomenon has been termed the "armed–disarmed effect" where the donor is armed and the acceptor disarmed toward the coupling reaction.[15] However, this effect has never been extended to an acceptor which contains only one ester group at C6 and two ether groups at C2 and C3. The question is whether one ester group alone is sufficiently electron-withdrawing to allow this selective coupling to occur.

Pentenyl disaccharide 13: To probe this modification of the armed–disarmed coupling protocol we carried out a number of glycosylations between donor **15** and ester-protected acceptors **16**. All the glycosylations were performed with *N*-iodosuccinimide (NIS) and a catalytic amount of triethylsilyl trifluoromethanesulfonate (TESOTf) in CH_2Cl_2. The weaker promoter iodonium dicollidine perchlorate (IDCP)[14] was not reactive enough and led to incomplete conversion of the coupling partners. In the first reaction, acetate protected acceptor **16a** was employed giving rise to a 27% yield (based on **15**) of the desired disaccharide **13a** (Table 1, entry 1). Small

Table 1. Coupling of pentenyl galactosides **15** and **16** controlled by the armed–disarmed effect.

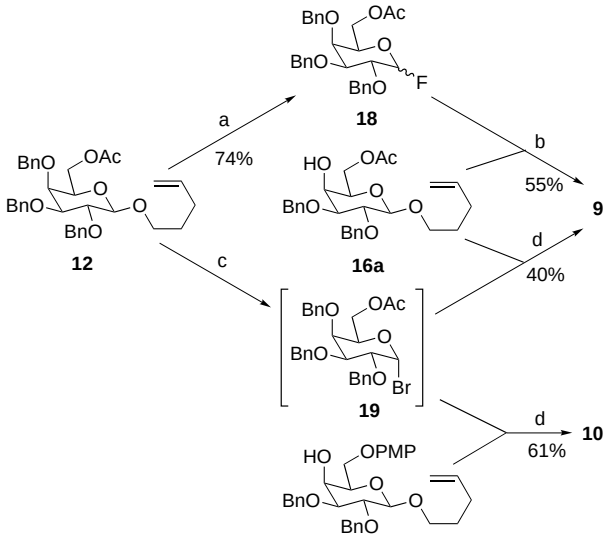


Entry	Acceptor	ester ($\delta_{C=O}$[ppm])	Product	Yield [%]
1	**16a**	Ac (170.9)	**13a**	27
2	**16b**	ClAc (167.1)	**13b**	33
3	**16c**	TCA (161.8)	**13c**	35
4	**16d**	4-NO_2Bz (164.6)	**13d**	42
5	**16e**	3,5-di-NO_2Bz (162.5)	**13e**	46
6	**16f**	PFBz (158.7)	**13f**	52

amounts of oligomers originating from the initial homocoupling of **16a** were also obtained, but were not further characterized. Disaccharide **13a** was obtained as a 6:1 α:β mixture, which could not be separated. After removing the acetate, the anomers were separated and fully characterized.

Although the yield of disaccharide **13a** was not synthetically useful it did provide some hope that the armed–disarmed coupling would indeed be feasible. Several more electron-withdrawing ester groups were therefore investigated. In fact, glycosylation with chloroacetate (ClAc) and trichloroacetate (TCA) protected acceptors **16b** and **16c** afforded a slightly higher yield of the corresponding disaccharides **13b** and **13c** (Table 1, entries 2 and 3). It was also attempted to prepare **16** with a trifluoroacetate at C6. Unfortunately, this group was very sensitive to hydrolysis upon purification by chromatography giving rise to low yields in the preparation of **16** and the coupling to **15**. Consequently, attention then shifted toward electron-withdrawing aromatic esters. Three acceptors containing benzoate groups at C6 were prepared and glycosylated with **15**: 4-nitrobenzoate **16d**, 3,5-dinitrobenzoate **16e**, and pentafluorobenzoate (PFBz) **16f** (Table 1, entries 4–6). Interestingly, these all gave rise to higher yields of disaccharide **13** and the best result was obtained with the pentafluorobenzoate at C6. The 52% yield of **13f** is an acceptable result for further synthetic applications. No other coupling products were observed by TLC, but some unreacted acceptor **16f** was recovered. The controlled coupling of **15** and **16f** represents a new application of the armed–disarmed effect in glycoside synthesis. The electronic properties of the different ester groups are evident from the chemical shift of the carbonyl group in the ^{13}C NMR spectra of **16a**–**16f**. The disaccharides **13a**–**13f** were in all cases obtained as a 6:1 mixture of α and β anomers, regardless of the ester protecting group. Unfortunately, the anomeric mixture could not be separated by silica gel chromatography in any of the six cases.

Pentenyl disaccharides 9 and 10: We would also like to prepare disaccharides **9** and **10** from the corresponding pentenyl monosaccharides **12**, **16a**, and **17** (Scheme 1). The



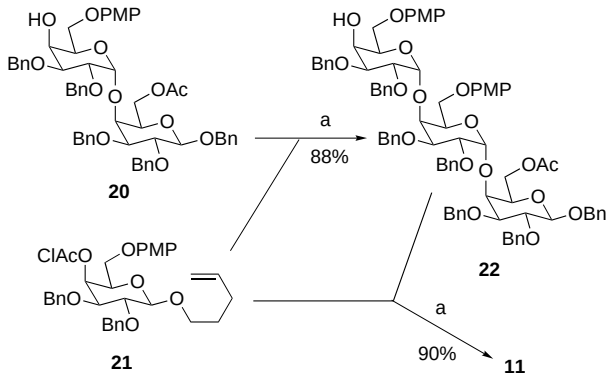
Scheme 1. a) NBS, DAST, CH_2Cl_2, 0 °C; b) $SnCl_2$, $AgClO_4$, 4 Å MS, CH_2Cl_2, −30 °C; c) Br_2, CH_2Cl_2, 0 °C; d) AgOTf, 4 Å MS, CH_2Cl_2, −50 °C.

armed–disarmed protocol cannot be employed in this case because donor **12** has an ester group at C6. Instead, **12** should be converted into another glycosyl donor that can be coupled under conditions not affecting a pentenyl moiety. Therefore, the transformation of **12** into the corresponding glycosyl fluoride and bromide was investigated. The conversion of pentenyl glycosides into glycosyl bromides is a well-known reaction,[16] while the conversion into glycosyl fluorides has not been achieved before. On the other hand, thioglycosides are known to undergo reaction into glycosyl fluorides in the presence of *N*-bromosuccinimide (NBS) and (diethylamino)-sulfur trifluoride (DAST).[17] In fact, subjecting pentenyl glycoside **12** to these conditions gave glycosyl fluoride **18** as a 3:1 α:β mixture which was purified by flash chromatography.

The anomeric configurations were assigned on the basis of ^{1}H NMR spectra. For the α anomer H1 appeared as a double doublet at $\delta = 5.60$ ppm with $J_{H1,F} = 54$ Hz and $J_{H1,H2} = 2.8$ Hz, while in the β anomer H1 was observed at $\delta = 5.19$ ppm with $J_{H1,F} = 53$ Hz and $J_{H1,H2} = 6.6$ Hz. Subsequent coupling of this anomeric mixture to acceptor **16a** was performed under Mukaiyama conditions[18] to afford α-linked disaccharide **9** in 55% yield and the corresponding β anomer in 18% yield. In this case, the anomeric configuration was determined from ^{13}C NMR spectra. For the α anomer, the C1′ signal appeared at $\delta = 100.5$ ppm with $J_{C1,H1} = 167.8$ Hz, while C1′ for the β anomer was observed at $\delta = 103.3$ ppm with $J_{C1,H1} = 159.6$ Hz.[19]

To explore the alternative method, pentenyl galactoside **12** was titrated with bromine, which formed glycosyl bromide **19** very cleanly as judged by ^{1}H NMR spectroscopy (Scheme 1). Only the α anomer of **19** was observed with H1 as a doublet at $\delta = 6.41$ ppm ($J_{H1,H2} = 2.0$ Hz). Bromide **19** was too unstable to be isolated and the crude reaction mixture was cannulated into a solution of AgOTf, 4 Å molecular sieves, and acceptor **16a**. Hereby, the α anomer of disaccharide **9** was obtained in 40% yield based on acceptor **16a** and only traces of the corresponding β anomer were observed. All in all, this latter synthesis of **9** is more convenient than the glycosyl fluoride route. It involves only one chromatographic purification and the overall yield from **12** is approximately the same in both cases. Thus, bromide **19** was also adopted for coupling to acceptor **17** to furnish α-linked disaccharide **10** in 61% yield.

Tetragalactan 11: The tetrasaccharide **11** was prepared by two consecutive couplings of monosaccharide donor **21** to disaccharide acceptor **20** (Scheme 2). Both **20** and **21** were



Scheme 2. a) NIS, TESOTf, CH_2Cl_2, $-20\,^\circ$C, then thiourea, $NaHCO_3$, Bu_4NI, THF, 55 °C.

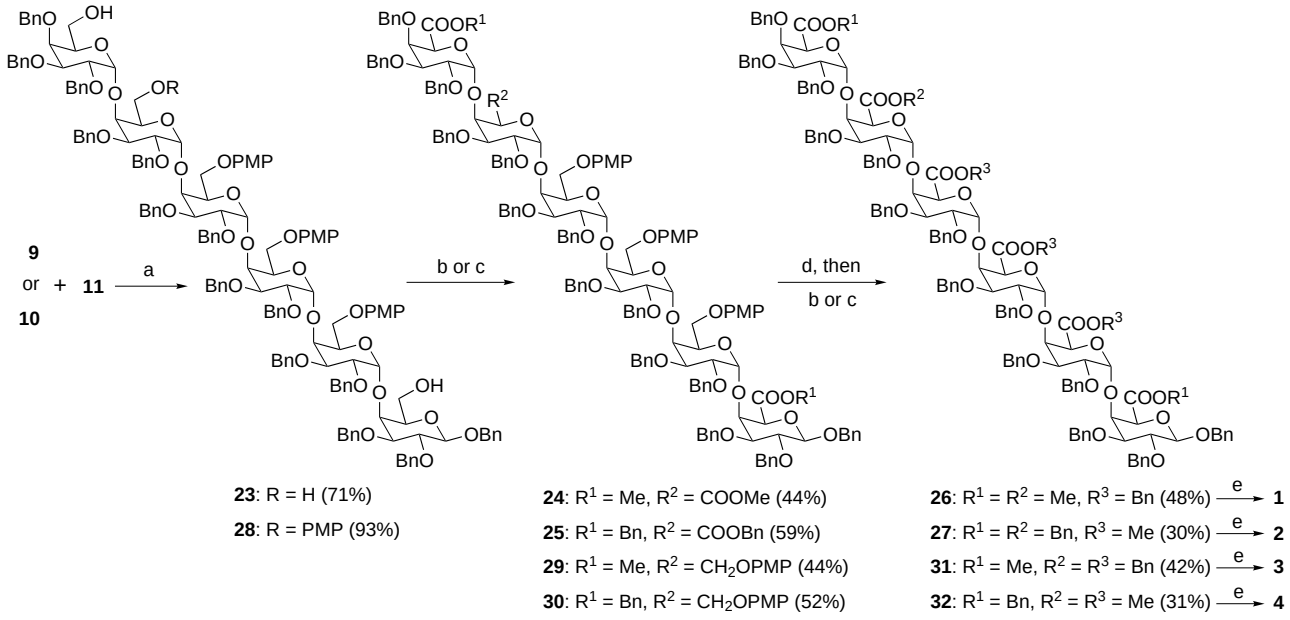
prepared in our earlier study.[9] In the donor **21** a chloroacetate at C4 serves as a temporary protecting group during the glycosylations. It is removed after the coupling with thiourea leaving the primary acetate unaffected. The glycosylation between **20** and **21** was performed with NIS and TESOTf to furnish the desired trisaccharide, which was subsequently treated with thiourea to afford alcohol **22** in 88% overall yield as a pure α anomer. Coupling again to donor **21** followed by chloroacetate removal gave tetrasaccharide **11** in 90% yield.

Hexagalacturonates 1–4: Having finished the preparation of the necessary building blocks, the stage was now set for synthesis of hexamers **1–4**. Compounds **1** and **2** were first prepared and the synthesis commenced with the coupling of **9** and **11** (Scheme 3). In the workup the three primary acetyl groups were removed by Zemplén deacetylation and hexasaccharide **23** was obtained in a satisfying 71% overall yield as the pure α anomer. Oxidation to uronic acid and esters was achieved by a one-pot procedure. The primary alcohols were oxidized by the Dess–Martin periodinane[20] and the crude trialdehyde further oxidized with sodium chlorite. The obtained triacid was then esterified with either $TMSCHN_2$[21] to give **24** (44% yield from **23**) or with $PhCHN_2$[22] to afford **25** (59% yield from **23**). The latter benzyl protection reaction should be noticed. It is a very mild and efficient method for masking the carboxylic acids until they will be liberated again after the final hydrogenolysis. Furthermore, the benzyl protection of the acids facilitates handling and purification of the intermediates.

To complete the syntheses the PMP ethers in **24** and **25** were removed and the obtained triols oxidized and esterified to the corresponding benzyl and methyl esters. In this way, **26** was obtained from **24** in 48% overall yield, while **27** was prepared from **25** in 30% yield. Deprotection of the benzyl ethers and esters in **26** and **27** then provided selectively trimethyl-esterified hexagalacturonates **1** and **2**. The structures of **1** and **2** were confirmed by tandem mass spectrometry using the electrospray ionization technique with an ion-trap mass spectrometer.[5a] Fragmentation of the molecular ion of **1** and **2** occurred in both cases from the reducing end liberating one galacturonic acid unit at the time, as shown with **2** in Figure 2. Hereby, the ions of the corresponding penta-, tetra-, tri-, and digalacturonates were observed which indicated the positions of the methyl ester groups in **1** and **2**. The ^{1}H and ^{13}C NMR spectra of **1** and **2** were more complex due to the similarity of the six galacturonic acid units and the anomeric mixture at the reducing end.

A similar series of reactions were employed for preparation of **3** and **4** (Scheme 3). Coupling of **10** and **11** followed by deacetylation gave hexasaccharide **28** in a very good 93% yield. Oxidation and esterification of the two primary alcohols was then carried out using the same one-pot procedure as described above. Hereby, dimethyl ester **29** was obtained in 44% yield from **28** while dibenzyl ester **30** was prepared in a slightly higher 52% yield. The four PMP groups between these two ester moieties were then removed followed by another round of oxidations and esterifications. This gave rise to tetrabenzyl ester **31** in 42% yield from **29**, while tetramethyl ester **32** was prepared in 31% yield from **30**. Finally, hydrogenolysis of **31** and **32** furnished the target hexagalacturonates **3** and **4**, respectively. Again, the analysis by tandem mass spectrometry verified the structures of these two hexagalacturonates.

Hexagalacturonate 5: The alternating acid–ester sequence in hexamer **5** required a different synthetic strategy than employed for hexamers **1–4**. Two consecutive couplings should now be performed with disaccharide **13f** to monosaccharide acceptor **14**. Unfortunately, it was impossible to



Scheme 3. a) NIS, TESOTf, CH_2Cl_2, $-20\,^{\circ}C$, then NaOMe, MeOH, THF; b) Dess–Martin periodinane, CH_2Cl_2, then $NaClO_2$, NaH_2PO_4, THF, *t*BuOH, H_2O, then $TMSCHN_2$, THF, MeOH; c) Dess–Martin periodinane, CH_2Cl_2, then $NaClO_2$, NaH_2PO_4, THF, *t*BuOH, H_2O, then $PhCHN_2$, EtOAc; d) CAN, MeCN, H_2O; e) H_2, Pd/C, THF, MeOH, H_2O.

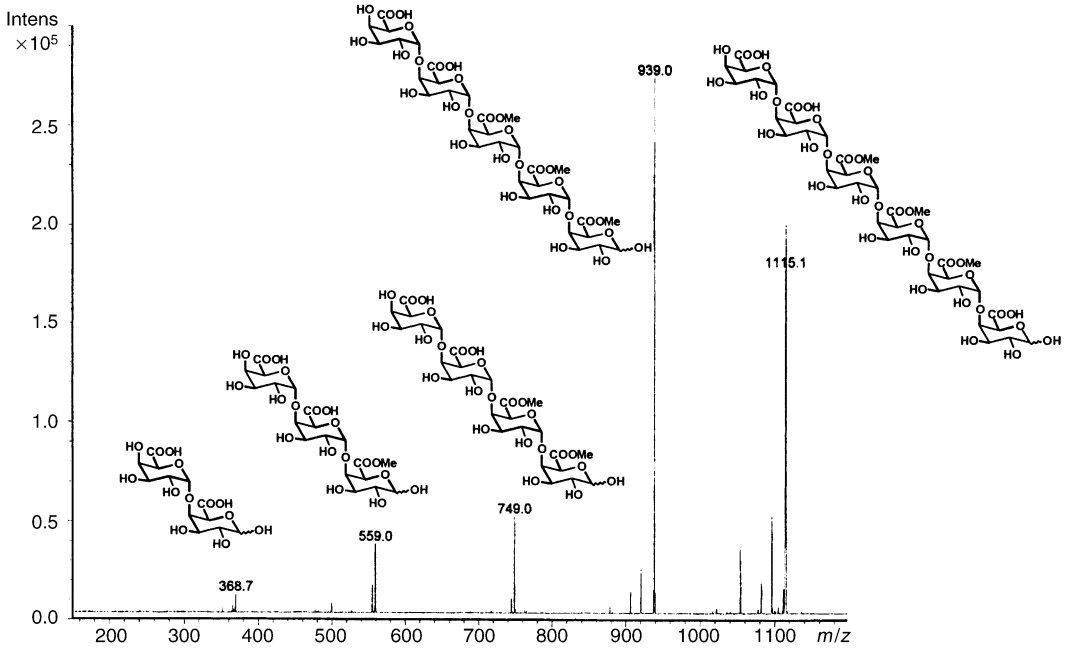
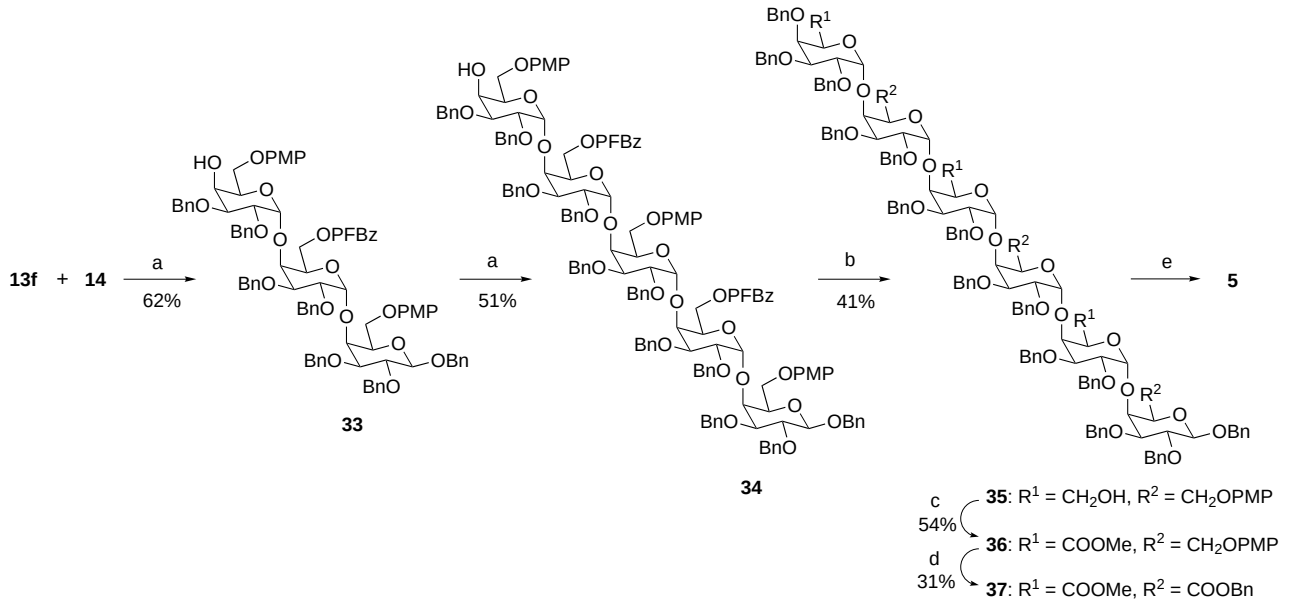


Figure 2. ESI MS/MS spectrum of hexagalacturonate **2**.

obtain **13f** anomerically pure. Coupling with an anomeric mixture of **13f** did cause some concern with regard to purification of the coupling products. However, all the previous pentenyl couplings in Scheme 2 and Scheme 3 proceeded with very high α-selectivity and separating the coupling products was not a problem. Consequently, acceptor **14** was glycosylated with the anomeric mixture of **13f** followed by removal of the allyl protecting group at C4″ (Scheme 4). Gratifyingly, it was possible to isolate a good yield of anomerically pure trisaccharide **33**. Initially, removal of the allyl group did create some problems. Excess $Pd(OAc)_2$ in aqueous acidic acid is often employed as a protocol for allyl group removal in carbohydrate chemistry.[23] Unfortunately, when these conditions were applied in our case a substantial amount of the propan-2-on-1-yl substituted trisaccharide was obtained as a by-product most likely arising from a competing Wacker oxidation. This prompted us to look for other methods. In this regard, several transition metal complexes are known to catalyze isomerization of allyl ethers to prop-2-en-1-yl ethers.[23] Wilkinson's catalyst $[ClRh(PPh_3)_3]$ is often used for this purpose, but in our case it reacted too slowly. Instead, we treated Wilkinson's catalyst with butyl lithium



Scheme 4. a) NIS, TESOTf, CH_2Cl_2, $-20\,^{\circ}C$, then $[ClRh(PPh_3)_3]$, *n*BuLi, THF, $67\,^{\circ}C$, then Amberlite IR-120 (H^+), MeOH, $50\,^{\circ}C$; b) NIS, TESOTf, CH_2Cl_2, $-20\,^{\circ}C$, then NaOMe, MeOH, THF; c) Dess–Martin periodinane, CH_2Cl_2, then $NaClO_2$, NaH_2PO_4, THF, *t*BuOH, H_2O, then $TMSCHN_2$, THF, MeOH; d) CAN, MeCN, H_2O, then Dess–Martin periodinane, CH_2Cl_2, then $NaClO_2$, NaH_2PO_4, THF, *t*BuOH, H_2O, then $PhCHN_2$, EtOAc; e) H_2, Pd/C, THF, MeOH, H_2O.

prior to the isomerization which is known to generate a more reactive catalyst in situ, presumably $[HRh(PPh_3)_3]$.[24] With this method the allyl group was isomerized completely in 1 h to provide a 2:1 mixture of (*Z*) and (*E*)-prop-2-enyl ethers as determined by ^1H NMR spectroscopy. These were then cleaved by addition of methanol and acidic ion-exchange resin followed by stirring for 24 h. Despite the long reaction time this procedure gave very clean removal of the allyl group without affecting the pentafluorobenzoyl group.

Trisaccharide **33** was then ready for another glycosylation with the anomeric mixture of disaccharide **13f**. Again, the coupling followed by allyl group removal generated a pure coupling product **34**. In this case, cleavage of the allyl ether by isomerization and methanolysis was slower than with the trisaccharide above, but the reaction still proceeded very cleanly. Pentasaccharide **34** was then coupled with monosaccharide donor **12**. The crude product was subjected to alkaline methanol solution to remove the acetyl group and the two pentafluorobenzoyl groups. Hereby, hexasaccharide **35** was isolated in 41% overall yield. The three primary hydroxy groups were then oxidized to methyl esters to give triester **36**. Oxidative cleavage of the PMP ethers followed by another round of alcohol oxidations then afforded protected hexagalacturonate **37**. Ultimately, hydrogenolysis gave the desired trimethyl esterified hexamer **5**. The alternating acid–ester sequence was confirmed by tandem mass spectrometry where fragmentation again occurred from the reducing end with one monosaccharide at the time. Finally, a general trend should be noticed about the ^{13}C NMR data for all the galactose and galacturonic acid containing compounds in this study. The anomeric carbon atom in an α-glycosidic linkage is always found in the $\delta = 98-101$ ppm range, while C1 for a β-linkage appears between $\delta = 102$ and 105 ppm. These values are in accordance with earlier observations.[9]

Preliminary experiments have revealed that hexagalacturonates **1** and **3** are cleaved by *endo*-polygalacturonase I and II from *Aspergillus niger* while hexamers **2**, **4**, and **5** are not substrates for these two enzymes.[25] These observations confirm that *endo*-polygalacturonase preferentially cleaves the oligomer chain between two galacturonic acid residues. The results are promising and show that the synthetic hexagalacturonates can be used as substrates for studying the cleavage pattern of pectic enzymes. Details of the enzymatic studies will be published elsewhere.

Conclusion

In conclusion, we have developed a general and divergent protocol for synthesis of selectively methyl-esterified oligomers of galacturonic acid. The syntheses feature several different aspects of pentenyl glycoside chemistry particularly coupling of two pentenyl glycosides controlled by either the armed–disarmed effect or by prior conversion of the donor glycoside into a glycosyl halide. This has resulted in the assembly of hexagalacturonates **1**–**5**, where about 100 mg has been obtained of each oligomer. These constitute the most complex oligogalacturonates with a well-defined esterification pattern prepared to date. Currently, hexamers **1**–**5** are being investigated as substrates for several pectic enzymes and as tools for the elucidation of the precise epitope structures of a number of monoclonal antibodies.

Experimental Section

General: Thin-layer chromatography was performed on aluminum plates precoated with silica gel. Compounds were visualized by heating after

dipping in a solution of $Ce(SO_4)_2$ (2.5 g) and $(NH_4)_6Mo_7O_{24}$ (6.25 g) in 10% aqueous H_2SO_4 (250 mL). Flash chromatography was performed using silica gel 60. Optical rotations were measured with a Perkin-Elmer 241 polarimeter. NMR spectra were recorded on a Varian Unity Inova 500 or a Varian Mercury 300 spectrometer. Unless otherwise stated ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution at 500 and 75 MHz, respectively. Mass spectrometry was carried out at the Department of Biochemistry and Molecular Biology, University of Southern Denmark. Tandem mass spectra were acquired on an Esquire-LC quadrupole ion-trap mass spectrometer (Bruker Daltonik) using electrospray ionization in the negative-ion mode. Microanalyses were conducted by the Department of Chemistry at the University of Copenhagen.

General procedure for acylations to prepare 16a–16f: Pent-4-enyl 2,3-di-*O*-benzyl-β-D-galactopyranoside[9] (4.28 g, 10.0 mmol) was dissolved in anhydrous CH_2Cl_2 (40 mL). The solution was cooled to 0 °C followed by addition of Et_3N (2.23 mL, 16.0 mmol) and the acyl anhydride or chloride (11 mmol). The mixture was stirred at 0 °C until TLC revealed full conversion (0.5–2 h). Silica gel (10 g) was added and the mixture was concentrated and purified by flash chromatography.

General procedure for armed–disarmed glycosylation reactions (Table 1): A mixture of **15** (1.0 mmol) and the acceptor (1.3 mmol) was dried azeotropically with toluene and subjected to high vacuum for 2 h. The mixture was dissolved in anhydrous CH_2Cl_2 (13 mL), cooled to −20 °C, followed by addition of NIS (293 mg, 1.3 mmol) and TESOTf (0.06 mL, 0.26 mmol). The reaction mixture was stirred at −20 °C for 30 min. The solution was diluted with CH_2Cl_2 and washed with 10% aqueous $Na_2S_2O_3$ and saturated aqueous $NaHCO_3$. The combined aqueous phases were extracted with CH_2Cl_2. The combined organic phases were dried, concentrated, and purified by flash chromatography.

General procedure for glycosylations via glycosyl bromides (Scheme 1): Pentenyl glycoside **12**[9] (9.0 mmol) was dissolved in anhydrous CH_2Cl_2 (30 mL), cooled to 0 °C, and titrated with a 1M solution of Br_2 in CH_2Cl_2 until a faint yellow color persisted. The solution was cannulated into a mixture of the acceptor (5.0 mmol), 4 Å MS (10 g), and AgOTf (3.47 g, 13.5 mmol) in anhydrous CH_2Cl_2 (15 mL) at −50 °C. The reaction was stirred at −50 °C and monitored by TLC (2–4 h). It was then quenched by addition of saturated aqueous $NaHCO_3$ (50 mL), allowed to reach room temperature and filtered through Celite. The pad was rinsed with CH_2Cl_2. The phases were separated and the aqueous phase extracted with CH_2Cl_2. The combined organic phases were dried, concentrated, and purified by flash chromatography.

General procedure for glycosylations via pentenyl glycosides (Schemes 2–4): A mixture of the donor (6.5 mmol) and the acceptor (5.0 mmol) was dried azeotropically with toluene and subjected to high vacuum for 2 h. The mixture was dissolved in anhydrous CH_2Cl_2 (60 mL), cooled to −20 °C, followed by addition of NIS (1.49 g, 6.63 mmol) and TESOTf (0.29 mL, 1.3 mmol). The reaction mixture was stirred at −20 °C until TLC revealed full conversion of the donor (15–45 min). Workup as described above.

General procedure for removal of chloroacetyl group (Scheme 2): The protected saccharide (5 mmol) was dissolved in THF (50 mL). Thiourea (1.14 g, 15 mmol), $NaHCO_3$ (1.39 g, 16.5 mmol), and Bu_4NI (369 mg, 1 mmol) were added and the suspension heated to 55 °C. The reaction was monitored by TLC until full conversion was observed (12–24 h). The mixture was cooled, filtered, concentrated, and purified by flash chromatography.

General procedure for removal of allyl group (Scheme 4): Wilkinson's catalyst $[ClRh(PPh_3)_3]$ (463 mg, 1.0 mmol, prepared from $RhCl_3 \cdot 3H_2O$[26]) was dissolved in anhydrous THF (27 mL) and the solution was degassed. *n*BuLi (0.75 mL, 1.6M in hexanes, 1.2 mmol) was added, and the mixture was stirred for 10 min. A degassed solution of the protected saccharide (5 mmol) in anhydrous THF (40 mL) was heated to reflux, and the solution of the catalyst was added. The reaction mixture was refluxed until ^1H NMR spectroscopy revealed full conversion into the vinyl ether (1–6 h). It was then cooled to 50 °C followed by addition of MeOH (140 mL) and Amberlite IR-120 (H^+) (15 mL). The resulting mixture was stirred at 50 °C until TLC revealed full conversion (24–36 h). The resin was filtered off, washed with CH_2Cl_2, and the filtrate was concentrated and purified by flash chromatography.

General procedure for removal of acyl groups (Scheme 3 and 4): The protected saccharide (1 mmol) was dissolved in THF (25 mL) and MeOH (50 mL). Sodium (12 mg, 0.5 mmol) was added followed by stirring at 20 °C until full conversion was observed by TLC (1–24 h). The reaction was quenched with Amberlite IR-120 (H^+) (5 mL) and stirred for an additional 30 min. The resin was filtered off, washed with CH_2Cl_2, and the filtrate was concentrated and purified by flash chromatography.

General procedure for removal of the 4-methoxyphenyl group (Scheme 3 and 4): The protected saccharide (0.5 mmol) was dissolved in MeCN (20 mL) and cooled to 0 °C. A solution of cerium ammonium nitrate (CAN; 5 equiv/PMP group) in water (5 mL) was added. The reaction mixture was stirred for 15 min, then diluted with $CHCl_3$ and washed twice with H_2O. The combined aqueous phases were extracted with $CHCl_3$. The combined organic phases were dried, concentrated, and purified by flash chromatography.

General procedure for oxidation to uronic acid (Scheme 3 and 4): To a suspension of the Dess–Martin periodinane (1.5 equiv/alcohol) in anhydrous CH_2Cl_2 (36 mL) was added a solution of the hexasaccharide (0.5 mmol) in CH_2Cl_2 (24 mL). The reaction was stirred for 45–60 min, then diluted with Et_2O (120 mL), quenched with 10% aqueous $Na_2S_2O_3$ (120 mL), and stirred for an additional 30 min. The organic phase was separated and washed with saturated aqueous $NaHCO_3$. The combined aqueous phases were extracted with Et_2O (100 mL). The combined organic phases were dried and concentrated. The crude aldehyde was taken up in THF (11 mL) followed by addition of *t*BuOH (26 mL), 2-methylbut-2-ene (50 equiv/aldehyde), and a solution of $NaClO_2$ (10 equiv/aldehyde) and $NaH_2PO_4 \cdot H_2O$ (7.5 equiv/aldehyde) in H_2O (11 mL). The reaction was stirred at 20 °C until full conversion was observed by TLC (1–2 h). The mixture was concentrated to half the volume and acidified with 1M aqueous HCl. The aqueous phase was extracted three times with EtOAc. The combined organic phases were dried and concentrated to afford the crude acid.

General procedure for methyl esterification (Scheme 3 and 4): The crude product from the oxidation was taken up in THF (2.8 mL) and MeOH (25 mL) followed by addition of $TMSCHN_2$ (2M solution in hexanes, 6 equiv/acid). The reaction was stirred for 12–24 h and monitored by TLC (more $TMSCHN_2$ added if necessary). When full conversion was observed, the reaction mixture was concentrated and purified by flash chromatography.

General procedure for benzyl esterification (Scheme 3 and 4): The crude product from the oxidations was taken up in EtOAc (30 mL) and titrated with $PhCHN_2$[22] (0.5M solution in Et_2O, 1.5–2 equiv/acid) until full conversion was observed by TLC (1–2 h). The reaction mixture was concentrated and purified by flash chromatography. Note: $PhCHN_2$ is potentially explosive and may burn violently when exposed to air. Can be redistilled under high vacuum at room temperature and should not be subjected to temperatures above 30 °C. Obtained as a red liquid, which solidifies at temperatures below −30 °C.

General procedure for hydrogenolysis (Scheme 3 and 4): The protected hexagalacturonate (0.1 mmol) was dissolved in THF (5 mL) and MeOH (15 mL). Then 10% Pd/C (125 mg) was added and an atmosphere of H_2 (1 atm) was installed. The reaction mixture was stirred for 2–3 h followed by addition of H_2O (5 mL). The stirring under the H_2 atmosphere was then continued until TLC revealed only one spot (12–30 h). The mixture was filtered through Celite, and lyophilized yielding a white solid.

Pent-4-enyl 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-acetyl-2,3-di-*O*-benzyl-β-D-galactopyranoside (9): $[\alpha]_D^{20} = +38.3$ (c = 0.5, $CHCl_3$); ^1H NMR: δ = 7.46–7.18 (m, 25H), 5.82 (m, 1H), 5.03 (dq, J = 16.8, 1.5 Hz, 1H), 4.99–4.66 (m, 11H), 4.59 (d, J = 11.2 Hz, 1H), 4.44–4.29 (m, 4H), 4.13–4.02 (m, 3H), 3.98–3.86 (m, 4H), 3.64 (dd, J = 9.7, 7.6 Hz, 1H), 3.55 (dt, J = 9.7, 7.1 Hz, 1H), 3.49 (t, J = 6.6 Hz, 1H), 3.38 (dd, J = 10.2, 3.1 Hz, 1H), 2.17 (m, 2H), 2.01 (s, 3H), 1.81 (s, 3H), 1.77 ppm (m, 2H); ^{13}C NMR: δ = 170.59, 170.22, 138.83, 138.79, 138.60, 138.54, 138.43, 138.17, 115.03, 104.07, 100.46, 80.23, 79.14, 79.05, 76.54, 75.57, 75.15, 74.71, 74.60, 73.99, 73.10, 72.78, 72.41, 69.69, 69.01, 62.70, 62.65, 30.37, 29.14, 21.02, 20.89 ppm; ESI MS (944.4): m/z 967.5 [M + Na].

Pent-4-enyl 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-α-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-(4-methoxyphenyl)-β-D-galactopyranoside (10): $[\alpha]_D^{20} = +33.0$ (c = 1.2, $CHCl_3$); ^1H NMR: δ = 7.40–7.21 (m, 25H), 6.73–6.64 (m, 4H), 5.84 (m, 1H), 5.04 (dq, J = 17.1, 1.7 Hz, 1H), 5.03 (d, J = 3.4 Hz, 1H), 4.98 (bd, J = 10.2 Hz, 1H), 4.94 (d, J = 11.1 Hz, 1H), 4.93 (d, J = 11.1 Hz, 1H), 4.82 (d, J = 11.9 Hz, 1H), 4.81 (d, J = 12.4 Hz, 1H), 4.80

(d, $J = 11.1$ Hz, 1H), 4.79 (d, $J = 11.9$ Hz, 1H), 4.73 (d, $J = 12.6$ Hz, 1H), 4.71 (d, $J = 12.6$ Hz, 1H), 4.58 (d, $J = 12.4$ Hz, 1H), 4.57 (d, $J = 11.1$ Hz, 1H), 4.43–4.35 (m, 3H), 4.13 (d, $J = 3.0$ Hz, 1H), 4.09 (dd, $J = 10.2$, 7.7 Hz, 1H), 4.08–3.89 (m, 6H), 3.74 (s, 3H), 3.69 (dd, $J = 9.8$, 7.7 Hz, 1H), 3.63 (dd, $J = 7.7$, 6.0 Hz, 1H), 3.58 (dt, $J = 9.4$, 6.8 Hz, 1H), 3.46 (dd, $J = 9.8$, 3.0 Hz, 1H), 2.19 (m, 2H), 1.80 (s, 3H), 1.79 ppm (m, 2H); ^{13}C NMR: $\delta =$ 170.19, 153.87, 152.29, 138.71, 138.52, 138.43, 138.36, 138.32, 137.94, 115.36 (2C), 114.87, 114.54 (2C), 103.89, 99.92, 80.24, 78.89, 78.74, 76.29, 74.84, 74.47, 74.38, 74.33, 73.30, 72.87, 72.73, 72.39, 69.21, 68.61, 65.87, 62.47, 55.52, 30.18, 28.99, 20.63 ppm; ESI MS (1008.5): m/z 1031.6 [M + Na].

Benzyl 2,3-di-*O*-benzyl-6-*O*-(4-methoxyphenyl)-α-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-(4-methoxyphenyl)-α-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-(4-methoxyphenyl)-α-D-galactopyranosyl-(1→4)-6-*O*-acetyl-2,3-di-*O*-benzyl-β-D-galactopyranoside (11): ^{1}H NMR: $\delta = 7.76-7.08$ (m, 45H), 6.75–6.42 (m, 12H), 5.12 (d, $J = 3.0$ Hz, 1H), 5.09 (d, $J = 3.4$ Hz, 1H), 5.04 (d, $J = 3.8$ Hz, 1H), 5.00 (d, $J = 11.5$ Hz, 1H), 4.97 (d, $J = 11.5$ Hz, 1H), 4.93 (d, $J = 11.9$ Hz, 1H), 4.90 (d, $J = 11.9$ Hz, 1H), 4.88–4.23 (m, 25H), 4.10 (dd, $J = 10.7$, 2.1 Hz, 1H), 4.01 (dd, $J = 10.7$, 3.4 Hz, 1H), 3.98 (d, $J = 2.6$ Hz, 1H), 3.95–3.87 (m, 3H), 3.84–3.68 (m, 4H), 3.76 (s, 3H), 3.71 (s, 3H), 3.69 (s, 3H), 3.65 (dd, $J = 8.1$, 5.1 Hz, 1H), 3.58 (t, $J = 6.8$ Hz, 1H), 3.50 (dd, $J = 8.5$, 4.3 Hz, 1H), 3.44 (dd, $J = 9.8$, 2.6 Hz, 1H), 2.49 (s, 1H), 2.12 ppm (s, 3H); ^{13}C NMR: $\delta = 170.55$, 153.81, 153.76 (2C), 152.67, 152.53, 152.33, 115.34 (4C), 115.29 (2C), 114.68 (2C), 114.58 (2C), 114.46 (2C), 102.81, 100.91, 100.28, 100.00, 80.75, 79.12, 78.70, 78.35, 78.28, 75.79 (2C), 75.42, 75.38, 75.07, 74.66, 73.97, 73.58, 73.30, 73.05, 72.90, 72.76, 72.67, 72.38, 72.08, 71.09, 69.67, 69.44, 67.94, 66.62, 66.12, 64.43, 64.25, 62.44, 55.80, 55.75 (2C), 21.05 ppm; ESI MS (1837.8): m/z 1860.8 [M + Na]; elemental analysis calcd (%) for $C_{110}H_{116}O_{25}$: C 71.88, H 6.36; found: C 71.64, H 6.41.

Pent-4-enyl 4-*O*-allyl-2,3-di-*O*-benzyl-6-*O*-(4-methoxyphenyl)-α-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-pentafluorobenzoyl-β-D-galactopyranoside (13f): $[\alpha]_D^{20} = +32.5$ ($c = 1.7$, $CHCl_3$); IR(KBr): $\tilde{\nu} = 1742$ cm^{-1}; ^{1}H NMR: $\delta = 7.44-7.17$ (m, 20H), 6.76–6.63 (m, 4H), 5.87–5.77 (m, 2H), 5.13 (dq, $J = 17.1$, 1.7 Hz, 1H), 5.06–4.99 (m, 3H), 4.96 (bd, $J = 10.2$ Hz, 1H), 4.88 (d, $J = 11.5$ Hz, 1H), 4.86 (d, $J = 11.5$ Hz, 1H), 4.82 (d, $J = 11.9$ Hz, 1H), 4.82 (d, $J = 11.9$ Hz, 1H), 4.78–4.62 (m, 6H), 4.43 (dd, $J = 9.0$, 4.7 Hz, 1H), 4.36–4.31 (m, 2H), 4.12–4.02 (m, 4H), 3.97–3.89 (m, 3H), 3.72 (s, 3H), 3.69 (dd, $J = 8.1$, 4.7 Hz, 1H), 3.66 (dd, $J = 10.8$, 8.3 Hz, 1H), 3.60 (t, $J = 6.4$ Hz, 1H), 3.54 (dt, $J = 9.4$, 6.8 Hz, 1H), 3.41 (dd, $J = 9.8$, 2.6 Hz, 1H), 2.17 (m, 2H), 1.77 ppm (m, 2H); ^{13}C NMR: $\delta = 158.36$, 153.86, 152.66, 145.40 (bd, $J_{C,F} = 263$ Hz, 2C), 143.20 (bd, $J_{C,F} = 253$ Hz, 1C), 138.70, 138.57, 138.50, 138.26, 137.98, 137.59 (bd, $J_{C,F} = 242$ Hz, 2C), 135.43, 116.97, 115.31 (2C), 114.87, 114.53 (2C), 107.91 (m, 1C), 103.99, 101.17, 80.67, 79.07, 78.76, 76.98, 76.51, 75.18, 74.39, 74.21, 73.99, 73.16, 72.58, 72.31, 69.67, 69.46, 65.79, 64.79, 55.57, 30.23, 28.95 ppm; ESI MS (1110.4): m/z 1133.2 [M + Na]; elemental analysis calcd (%) for $C_{62}H_{63}F_5O_{13}$: C 67.02, H 5.71; found: C 66.68, H 5.58.

Pent-4-enyl 4-*O*-allyl-2,3-di-*O*-benzyl-6-*O*-(4-methoxyphenyl)-α-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzyl-β-D-galactopyranoside: $[\alpha]_D^{20} = +32.7$ ($c = 0.7$, $CHCl_3$); ^{1}H NMR: $\delta = 7.44-7.13$ (m, 20H), 6.78–6.69 (m, 4H), 5.89–5.76 (m, 2H), 5.16 (dq, $J = 17.1$, 1.7 Hz, 1H), 5.09–5.04 (m, 2H), 5.01 (dq, $J = 17.1$, 1.7 Hz, 1H), 4.96 (bd, $J = 10.2$ Hz, 1H), 4.91 (d, $J = 11.5$ Hz, 1H), 4.82 (d, $J = 11.1$ Hz, 1H), 4.81 (d, $J = 11.5$ Hz, 1H), 4.76 (d, $J = 11.5$ Hz, 1H), 4.69 (d, $J = 11.9$ Hz, 1H), 4.68 (d, $J = 11.5$ Hz, 1H), 4.67 (d, $J = 11.1$ Hz, 1H), 4.64 (d, $J = 11.9$ Hz, 1H), 4.38 (dd, $J = 8.5$, 5.1 Hz, 1H), 4.34 (ddq, $J = 12.8$, 6.8, 1.3 Hz, 1H), 4.31 (d, $J = 7.3$ Hz, 1H), 4.10 (bdd, $J = 12.4$, 6.0 Hz, 1H), 4.08–4.02 (m, 4H), 3.96 (t, $J = 8.7$ Hz, 1H), 3.91 (dt, $J = 9.8$, 6.4 Hz, 1H), 3.79–3.72 (m, 2H), 3.72 (s, 3H), 3.64 (m, 1H), 3.62 (dd, $J = 9.8$, 7.3 Hz, 1H), 3.51 (dt, $J = 9.8$, 6.8 Hz, 1H), 3.47 (bt, $J = 7.0$ Hz, 1H), 3.42 (dd, $J = 9.8$, 2.6 Hz, 1H), 3.27 (bs, 1H), 2.15 (m, 2H), 1.74 ppm (m, 2H); ^{13}C NMR: $\delta = 153.88$, 152.72, 138.60, 138.46, 138.41, 138.02, 137.58, 135.30, 117.14, 115.45 (2C), 114.90, 114.58 (2C), 104.05 ($J_{C,H} = 156.7$ Hz), 100.39 ($J_{C,H} = 168.1$ Hz), 81.23, 79.08, 78.69, 77.54, 75.83, 75.02, 74.84, 74.13, 74.07, 73.97, 72.96, 72.31, 69.59, 69.57, 66.18, 60.18, 55.66, 30.21, 28.98 ppm; elemental analysis calcd (%) for $C_{55}H_{64}O_{12}$: C 72.03, H 7.03; found: C 71.69, H 7.10.

Pent-4-enyl 4-*O*-allyl-2,3-di-*O*-benzyl-6-*O*-(4-methoxyphenyl)-β-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzyl-β-D-galactopyranoside: $[\alpha]_D^{20} = +10.1$ ($c = 1.1$, $CHCl_3$); ^{1}H NMR: $\delta = 7.46-7.13$ (m, 20H), 6.81–6.67 (m, 4H), 5.91–5.76 (m, 2H), 5.23 (d, $J = 11.1$ Hz, 1H), 5.22 (dq, $J = 17.1$, 1.7 Hz, 1H), 5.14 (bd, $J = 10.2$ Hz, 1H), 5.00 (dq, $J = 17.1$, 1.7 Hz, 1H), 4.95 (bd, $J =$ 10.2 Hz, 1H), 4.83–4.68 (m, 7H), 4.44 (d, $J = 11.1$ Hz, 1H), 4.43 (ddt, $J = 12.8$, 5.1, 1.3 Hz, 1H), 4.35 (d, $J = 7.3$ Hz, 1H), 4.22 (d, $J = 2.6$ Hz, 1H), 4.13 (dd, $J = 9.4$, 7.7 Hz, 1H), 4.07 (bdd, $J = 12.8$, 6.4 Hz, 1H), 4.01 (dd, $J =$ 9.8, 5.1 Hz, 1H), 3.97 (m, 1H), 3.94 (dt, $J = 9.4$, 6.6 Hz, 1H), 3.92 (dd, $J =$ 9.8, 7.7 Hz, 1H), 3.77 (s, 3H), 3.74 (d, $J = 3.0$ Hz, 1H), 3.73–3.67 (m, 2H), 3.62 (m, 1H), 3.56 (dd, $J = 9.8$, 3.0 Hz, 1H), 3.52 (dt, $J = 9.4$, 6.8 Hz, 1H), 3.50–3.44 (m, 2H), 3.41 (bs, 1H), 2.15 (m, 2H), 1.76 ppm (m, 2H); ^{13}C NMR: $\delta = 154.53$, 152.30, 139.29, 138.86, 138.73, 138.63, 138.23, 135.21, 117.17, 115.97 (2C), 114.94, 114.91 (2C), 104.90 ($J_{C,H} = 161.9$ Hz), 104.05 ($J_{C,H} = 161.3$ Hz), 81.66, 81.29, 80.34, 79.53, 75.42, 75.12, 73.99, 73.85, 73.81, 73.59, 73.31, 73.14, 72.83, 69.55, 67.96, 59.79, 55.88, 30.36, 29.11 ppm; elemental analysis calcd (%) for $C_{55}H_{64}O_{12}$: C 72.03, H 7.03; found: C 71.81, H 7.20.

Pent-4-enyl 4-*O*-allyl-2,3-di-*O*-benzyl-6-*O*-(4-methoxyphenyl)-β-D-galactopyranoside (15): Alcohol **17** (5.35 g, 10 mmol) was dissolved in anhydrous THF (30 mL). NaH (720 mg, 30 mmol) was added and the resulting suspension stirred for 2 h before addition of allyl bromide (1.3 mL, 15 mmol). The mixture was stirred 24 h, then diluted with Et_2O and washed twice with H_2O. The combined aqueous phases were extracted with Et_2O, and the combined organic phases were dried, concentrated, and purified by flash chromatography to afford a white solid (6.32 g, 91%). $[\alpha]_D^{20} = -36.3$ ($c = 0.9$, $CHCl_3$); m.p. 52.5–53 °C; ^{1}H NMR: $\delta = 7.40-7.26$ (m, 10H), 6.91–6.81 (m, 4H), 5.90–5.78 (m, 2H), 5.17 (bd, $J = 17.5$ Hz, 1H), 5.07 (bd, $J = 10.2$ Hz, 1H), 5.02 (dq, $J = 17.1$, 2.1 Hz, 1H), 4.99 (bd, $J =$ 10.2 Hz, 1H), 4.94 (d, $J = 11.1$ Hz, 1H), 4.79 (d, $J = 12.2$ Hz, 1H), 4.78 (d, $J = 11.1$ Hz, 1H), 4.77 (d, $J = 12.2$ Hz, 1H), 4.39 (d, $J = 7.7$ Hz, 1H), 4.37 (dd, $J = 12.4$, 5.6 Hz, 1H), 4.16 (t, $J = 8.3$ Hz, 1H), 4.14 (dd, $J = 12.8$, 6.8 Hz, 1H), 4.07 (dd, $J = 9.0$, 5.1 Hz, 1H), 3.99–3.92 (m, 2H), 3.80 (dd, $J = 9.8$, 7.7 Hz, 1H), 3.78 (s, 3H), 3.70 (dd, $J = 7.3$, 5.6 Hz, 1H), 3.58–3.51 (m, 2H), 2.17 (m, 2H), 1.76 ppm (m, 2H); ^{13}C NMR: $\delta = 154.14$, 152.63, 138.86, 138.52, 138.18, 135.43, 128.39, 128.29 (3C), 128.10 (3C), 127.60 (2C), 127.55, 117.22, 115.61 (2C), 114.85, 114.74 (2C), 104.05, 81.96, 79.68, 75.29, 73.97, 73.08, 73.00, 72.76, 69.37, 66.67, 55.74, 30.32, 29.06 ppm; elemental analysis calcd (%) for $C_{35}H_{42}O_7$: C 73.15, H 7.37; found: C 73.12, H 7.37.

Pent-4-enyl 6-*O*-acetyl-2,3-di-*O*-benzyl-β-D-galactopyranoside (16a): $[\alpha]_D^{20} = +2.0$ ($c = 2.8$, $CHCl_3$); IR(KBr): $\tilde{\nu} = 1723$ cm^{-1}; ^{1}H NMR: $\delta =$ 7.40–7.26 (m, 10H), 6.83 (m, 1H), 5.03 (dq, $J = 17.1$, 1.7 Hz, 1H), 4.98 (bd, $J = 10.2$ Hz, 1H), 4.93 (d, $J = 11.1$ Hz, 1H), 4.76 (d, $J = 11.7$ Hz, 1H), 4.75 (d, $J = 11.1$ Hz, 1H), 4.72 (d, $J = 11.7$ Hz, 1H), 4.39–4.31 (m, 3H), 3.96 (dt, $J = 9.4$, 6.4 Hz, 1H), 3.93 (bs, 1H), 3.65 (dd, $J = 9.4$, 7.7 Hz, 1H), 3.61–3.54 (m, 2H), 3.51 (dd, $J = 9.4$, 3.4 Hz, 1H), 2.49 (bs, 1H), 2.18 (m, 2H), 2.08 (s, 3H), 1.77 ppm (m, 2H); ^{13}C NMR: $\delta = 170.88$, 138.66, 138.18, 137.92, 128.62 (2C), 128.44 (2C), 128.22, 128.08 (2C), 127.96 (2C), 127.77, 115.01, 103.80, 80.56, 78.96, 75.33, 72.80, 71.88, 69.46, 66.85, 63.17, 30.36, 29.13, 21.02 ppm; elemental analysis calcd (%) for $C_{27}H_{34}O_7$: C 68.92, H 7.27; found: C 68.84, H 7.30.

Pent-4-enyl 2,3-di-*O*-benzyl-6-*O*-chloroacetyl-β-D-galactopyranoside (16b): $[\alpha]_D^{20} = +0.7$ ($c = 0.9$, $CHCl_3$); m.p. 62–63.5 °C; IR (KBr): $\tilde{\nu} =$ 1745 cm^{-1}; ^{1}H NMR: $\delta = 7.39-7.26$ (m, 10H), 5.83 (m, 1H), 5.03 (dq, $J =$ 17.1, 1.7 Hz, 1H), 4.98 (bd, $J = 10.2$ Hz, 1H), 4.92 (d, $J = 11.1$ Hz, 1H), 4.76 (d, $J = 11.7$ Hz, 1H), 4.76 (d, $J = 11.1$ Hz, 1H), 4.71 (d, $J = 11.7$ Hz, 1H), 4.49 (dd, $J = 11.1$, 6.8 Hz, 1H), 4.42 (dd, $J = 11.5$, 5.1 Hz, 1H), 4.34 (d, $J =$ 8.1 Hz, 1H), 4.08 (s, 2H), 3.94 (dt, $J = 9.8$, 6.6 Hz, 1H), 3.92 (m, 1H), 3.66–3.61 (m, 2H), 3.56 (dt, $J = 9.4$, 6.8 Hz, 1H), 3.51 (dd, $J = 9.4$, 3.4 Hz, 1H), 2.46 (bs, 1H), 2.17 (m, 2H), 1.76 ppm (m, 2H); ^{13}C NMR: $\delta = 167.12$, 138.56, 138.08, 137.78, 128.56, 128.37 (2C), 128.12 (3C), 128.06, 127.90 (2C), 127.71, 114.98, 103.72, 80.34, 78.80, 75.24, 72.82, 71.61, 69.44, 66.81, 64.82, 40.81, 30.29, 29.05 ppm; elemental analysis calcd (%) for $C_{27}H_{33}ClO_7$: C 64.22, H 6.59; found: C 64.14, H 6.53.

Pent-4-enyl 2,3-di-*O*-benzyl-6-*O*-trichloroacetyl-β-D-galactopyranoside (16c): $[\alpha]_D^{20} = +0.2$ ($c = 1.0$, $CHCl_3$); m.p. 52.5–54.5 °C; IR (KBr): $\tilde{\nu} =$ 1757 cm^{-1}; ^{1}H NMR: $\delta = 7.39-7.27$ (m, 10H), 5.81 (m, 1H), 5.01 (dd, $J =$ 17.1, 1.7 Hz, 1H), 4.97 (bd, $J = 10.2$ Hz, 1H), 4.93 (d, $J = 11.1$ Hz, 1H), 4.78 (d, $J = 11.5$ Hz, 1H), 4.74 (d, $J = 11.1$ Hz, 1H), 4.70 (d, $J = 11.5$ Hz, 1H), 4.68 (dd, $J = 11.5$, 7.7 Hz, 1H), 4.54 (dd, $J = 11.5$, 5.1 Hz, 1H), 4.36 (d, $J =$ 8.1 Hz, 1H), 3.93 (dt, $J = 9.8$, 6.4 Hz, 1H), 3.91 (m, 1H), 3.71 (dd, $J = 7.7$, 5.1 Hz, 1H), 3.64 (dd, $J = 9.4$, 8.1 Hz, 1H), 3.54–3.50 (m, 2H), 2.48 (bs, 1H), 2.15 (m, 2H), 1.74 ppm (m, 2H); ^{13}C NMR: $\delta = 161.77$, 138.57, 138.05, 137.76, 128.65, 128.43 (3C), 128.17 (2C), 127.97 (3C), 127.78, 115.07, 103.73, 80.24, 78.77, 75.27, 73.09, 71.40, 69.44, 67.63, 66.91, 53.55, 30.33, 29.01 ppm;

elemental analysis calcd (%) for $C_{27}H_{31}Cl_3O_7$: C 56.51, H 5.44, Cl 18.53; found: C 56.65, H 5.54, Cl 18.48.

Pent-4-enyl 2,3-di-*O*-benzyl-6-*O*-(4-nitrobenzoyl)-β-D-galactopyranoside (16d): $[\alpha]_D^{20} = -5.4$ ($c = 0.9$, $CHCl_3$); m.p. 97–98.5 °C; IR (KBr): $\tilde{\nu} =$ 1718, 1527, 1296 cm^{-1}; ^1H NMR: $\delta = 8.30$ (m, 2H), 8.21 (m, 2H), 7.39–7.26 (m, 10H), 5.80 (m, 1H), 5.01 (dq, $J = 17.1$, 1.7 Hz, 1H), 4.95 (bd, $J =$ 10.2 Hz, 1H), 4.94 (d, $J = 11.1$ Hz, 1H), 4.78 (d, $J = 11.7$ Hz, 1H), 4.75 (d, $J = 11.1$ Hz, 1H), 4.72 (d, $J = 11.7$ Hz, 1H), 4.66–4.63 (m, 2H), 4.38 (d, $J =$ 8.1 Hz, 1H), 3.97 (m, 1H), 3.93 (dt, $J = 9.4$, 6.4 Hz, 1H), 3.75 (t, $J = 6.2$ Hz, 1H), 3.67 (dd, $J = 9.4$, 8.1 Hz, 1H), 3.58–3.52 (m, 2H), 2.52 (bs, 1H), 2.16 (m, 2H), 1.76 ppm (m, 2H); ^{13}C NMR: $\delta = 164.55$, 150.79, 138.57, 138.05, 137.85, 135.43, 130.92 (2C), 128.65 (2C), 128.47, 128.21 (3C), 128.15, 127.97 (2C), 127.82, 123.68 (2C), 115.06, 103.88, 80.48, 78.88, 75.35, 73.04, 71.87, 69.51, 67.10, 64.62, 30.34, 29.11 ppm; elemental analysis calcd (%) for $C_{32}H_{35}NO_9$: C 66.54, H 6.11, N 2.42; found: C 66.31, H 6.05, N 2.45.

Pent-4-enyl 2,3-di-*O*-benzyl-6-*O*-(3,5-dinitrobenzoyl)-β-D-galactopyranoside (16e): $[\alpha]_D^{20} = +2.5$ ($c = 1.0$, $CHCl_3$); m.p. 119–121 °C; IR (KBr): $\tilde{\nu} =$ 1736, 1545, 1345 cm^{-1}; ^1H NMR: $\delta = 9.24$ (t, $J = 2.1$ Hz, 1H), 9.16 (d, $J =$ 2.1 Hz, 2H), 7.39–7.28 (m, 10H), 5.80 (m, 1H), 5.00 (dq, $J = 17.1$, 1.7 Hz, 1H), 4.94 (d, $J = 11.1$ Hz, 1H), 4.93 (bd, $J = 10.2$ Hz, 1H), 4.81–4.68 (m, 5H), 4.41 (d, $J = 7.7$ Hz, 1H), 4.00–3.94 (m, 2H), 3.79 (t, $J = 6.2$ Hz, 1H), 3.68 (dd, $J = 9.4$, 7.7 Hz, 1H), 3.61–3.55 (m, 2H), 2.56 (bs, 1H), 2.17 (m, 2H), 1.77 ppm (m, 2H); ^{13}C NMR: $\delta = 162.48$, 148.92, 138.62, 138.14, 137.83, 133.89, 129.67 (2C), 128.76 (2C), 128.55 (2C), 128.29 (2C), 128.22, 128.15 (2C), 128.06, 127.92, 122.69, 115.10, 103.95, 80.38, 78.91, 75.45, 73.16, 71.87, 69.69, 67.25, 65.81, 30.39, 29.19 ppm; elemental analysis calcd (%) for $C_{32}H_{34}N_2O_{11}$: C 61.73, H 5.50, N 4.50; found: C 61.58, H 5.48, N 4.50.

Pent-4-enyl 2,3-di-*O*-benzyl-6-*O*-pentafluorobenzoyl-β-D-galactopyranoside (16f): $[\alpha]_D^{20} = -2.3$ ($c = 0.9$, $CHCl_3$); m.p. 94–95 °C; IR (KBr): $\tilde{\nu} =$ 1729 cm^{-1}; ^1H NMR: $\delta = 7.39–7.27$ (m, 10H), 5.81 (m, 1H), 5.01 (dq, $J =$ 17.1, 1.7 Hz, 1H), 4.96 (m, 1H), 4.94 (d, $J = 11.1$ Hz, 1H), 4.77 (d, $J =$ 11.7 Hz, 1H), 4.74 (d, $J = 11.1$ Hz, 1H), 4.72 (d, $J = 11.7$ Hz, 1H), 4.69 (dd, $J = 11.5$, 7.3 Hz, 1H), 4.59 (dd, $J = 11.5$, 5.1 Hz, 1H), 4.36 (d, $J = 7.7$ Hz, 1H), 3.98–3.92 (m, 2H), 3.71 (t, $J = 6.2$ Hz, 1H), 3.65 (dd, $J = 9.2$, 7.9 Hz, 1H), 3.55 (dt, $J = 9.4$, 6.4 Hz, 1H), 3.53 (dd, $J = 9.4$, 3.4 Hz, 1H), 2.48 (bs, 1H), 2.17 (m, 2H), 1.76 ppm (m, 2H); ^{13}C NMR: $\delta = 158.73$, 145.68 (bd, $J_{C,F} = 258$ Hz, 2C), 143.27 (bd, $J_{C,F} = 259$ Hz, 1C), 138.62, 138.07, 138.02 (bd, $J_{C,F} = 251$ Hz, 2C), 137.81, 128.58 (2C), 128.39 (2C), 128.14 (2C), 128.07, 127.91 (2C), 127.73, 114.91, 108.06 (dt, $J_{C,F} = 11$, 4 Hz, 1C), 103.76, 80.34, 78.84, 75.26, 72.89, 71.72, 69.34, 66.91, 65.40, 30.30, 29.02 ppm; elemental analysis calcd (%) for $C_{32}H_{31}F_5O_7$: C 61.73, H 5.02; found: C 61.71, H 4.91.

Pent-4-enyl 2,3-di-*O*-benzyl-6-*O*-(4-methoxyphenyl)-β-D-galactopyranoside (17): Prepared from pent-4-enyl 2,3-di-*O*-benzyl-β-D-galactopyranoside according to our previous procedure.[9] $[\alpha]_D^{20} = +9.7$ ($c = 2.7$, $CHCl_3$); ^1H NMR: $\delta = 7.42–7.26$ (m, 10H), 6.92–6.83 (m, 4H), 5.85 (m, 1H), 5.05 (dq, $J = 17.1$, 1.7 Hz, 1H), 4.99 (bd, $J = 10.2$ Hz, 1H), 4.95 (d, $J = 11.1$ Hz, 1H), 4.78 (d, $J = 11.1$ Hz, 1H), 4.76 (s, 2H), 4.42 (d, $J = 7.7$ Hz, 1H), 4.27 (dd, $J = 9.8$, 6.4 Hz, 1H), 4.18 (dd, $J = 9.8$, 6.0 Hz, 1H), 4.12 (d, $J = 3.1$ Hz, 1H), 3.98 (dt, $J = 9.4$, 6.4 Hz, 1H), 3.78 (s, 3H), 3.74 (t, $J = 6.0$ Hz, 1H), 3.70 (dd, $J = 9.4$, 7.7 Hz, 1H), 3.61–3.56 (m, 2H), 2.63 (bs, 1H), 2.19 (m, 2H), 1.78 ppm (m, 2H); ^{13}C NMR: $\delta = 154.18$, 152.85, 138.70, 138.15, 137.94, 128.54 (3C), 128.37, 128.14 (3C), 127.97, 127.89, 127.67, 115.90 (2C), 114.92, 114.73 (2C), 103.81, 80.70, 79.05, 75.27, 72.74, 72.63, 69.37, 67.57, 66.69, 55.78, 30.33, 29.09 ppm; elemental analysis calcd (%) for $C_{32}H_{38}O_7$: C 71.89, H 7.16; found: C 71.62, H 6.96.

Benzyl 2,3-di-*O*-benzyl-6-*O*-(4-methoxyphenyl)-α-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-(4-methoxyphenyl)-α-D-galactopyranosyl-(1→4)-6-*O*-acetyl-2,3-di-*O*-benzyl-β-D-galactopyranoside (22): ^1H NMR: $\delta = 7.50–7.16$ (m, 35H), 6.79–6.54 (m, 8H), 5.15 (d, $J = 3.0$ Hz, 1H), 5.08 (d, $J = 3.4$ Hz, 1H), 5.02 (d, $J = 11.9$ Hz, 1H), 4.98 (d, $J = 11.9$ Hz, 1H), 4.94–4.84 (m, 4H), 4.80–4.55 (m, 11H), 4.52 (d, $J = 7.3$ Hz, 1H), 4.47 (dd, $J = 9.4$, 5.1 Hz, 1H), 4.38–4.32 (m, 3H), 4.13 (dd, $J = 10.7$, 2.6 Hz, 1H), 4.08 (dd, $J = 10.7$, 3.4 Hz, 1H), 4.04 (t, $J = 8.5$ Hz, 1H), 4.01 (d, $J = 3.0$ Hz, 1H), 3.91 (dd, $J = 9.8$, 2.6 Hz, 1H), 3.90 (dd, $J = 9.8$, 3.0 Hz, 1H), 3.77 (s, 3H), 3.76–3.67 (m, 3H), 3.69 (s, 3H), 3.62 (t, $J = 6.4$ Hz, 1H), 3.47 (dd, $J = 10.2$, 3.0 Hz, 1H), 2.60 (s, 1H), 2.15 ppm (s, 3H); ^{13}C NMR: $\delta = 170.50$, 153.87, 153.78, 152.71, 152.41, 138.62, 138.52, 138.45 (2C), 138.31, 138.26, 137.53, 115.42 (2C), 115.39 (2C), 114.52 (2C), 114.47 (2C), 102.75, 100.88, 99.91, 80.81, 78.66, 78.39, 78.02, 75.91, 75.80, 75.60, 75.02, 74.74, 73.62, 73.26, 72.87, 72.74, 72.41, 72.02, 71.05, 69.59, 68.06, 66.70, 66.37, 64.69, 62.55, 55.64 (2C), 21.00 ppm; elemental analysis calcd (%) for $C_{83}H_{88}O_{19}$: C 71.74, H 6.38; found: C 71.59, H 6.36.

Benzyl 2,3,4-tri-*O*-benzyl-α-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-(4-methoxyphenyl)-α-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-(4-methoxyphenyl)-α-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-(4-methoxyphenyl)-α-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzyl-β-D-galactopyranoside (23): ^1H NMR: $\delta = 7.40–7.05$ (m, 70H), 6.70–6.32 (m, 12H), 5.11 (d, $J =$ 3.4 Hz, 1H), 5.07 (d, $J = 3.0$ Hz, 1H), 5.06 (d, $J = 3.0$ Hz, 1H), 5.01 (d, $J = 3.0$ Hz, 1H), 4.95–4.28 (m, 38H), 4.21 (m, 1H), 4.14 (dd, $J = 9.8$, 8.5 Hz, 1H), 4.09–4.00 (m, 4H), 3.97–3.88 (m, 3H), 3.85–3.61 (m, 13H), 3.68 (s, 3H), 3.67 (s, 3H), 3.66 (s, 3H), 3.50–3.39 (m, 5H), 3.29–3.11 ppm (m, 4H); ^{13}C NMR: $\delta = 153.85$, 153.81, 153.63, 152.59, 152.39, 152.19, 115.29 (2C), 115.25 (2C), 115.23 (2C), 114.69 (2C), 114.62 (2C), 114.47 (2C), 103.02, 100.80, 100.31 (2C), 100.02, 99.37, 55.74 ppm (3C); ESI MS (2571.1): m/z 2593.9 [M + Na]; elemental analysis calcd (%) for $C_{155}H_{164}O_{34}$: C 72.41, H 6.43; found: C 72.06, H 6.44.

(Methyl 2,3,4-tri-*O*-benzyl-α-D-galactopyranosyluronate)-(1→4)-(methyl 2,3-di-*O*-benzyl-α-D-galactopyranosyluronate)-(1→4)-2,3-di-*O*-benzyl-6-*O*-(4-methoxyphenyl)-α-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-(4-methoxyphenyl)-α-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-(4-methoxyphenyl)-α-D-galactopyranosyl-(1→4)-(methyl (benzyl 2,3-di-*O*-benzyl-β-D-galactopyranosid)uronate) (24): ^1H NMR: $\delta = 7.41–6.88$ (m, 70H), 6.79–6.41 (m, 12H), 5.16 (d, $J = 3.5$ Hz, 1H), 5.09 (d, $J = 3.4$ Hz, 1H), 5.07–5.01 (m, 2H), 5.01 (d, $J = 3.4$ Hz, 1H), 4.94–4.15 (m, 42H), 4.10–4.05 (m, 2H), 4.01 (dd, $J = 10.2$, 2.6 Hz, 1H), 3.99 (bs, 1H), 3.91 (dd, $J = 7.3$, 3.4 Hz, 1H), 3.89 (dd, $J = 7.3$, 3.4 Hz, 1H), 3.79–3.62 (m, 6H), 3.72 (s, 3H), 3.70 (s, 3H), 3.66 (s, 3H), 3.63 (s, 3H), 3.61–3.49 (m, 4H), 3.47 (dd, $J = 9.8$, 3.0 Hz, 1H), 3.17 (s, 3H), 3.04 ppm (s, 3H); ^{13}C NMR: $\delta = 169.07$, 168.54, 168.39, 153.69 (3C), 152.45, 152.24, 151.97, 115.14 (4C), 115.02 (2C), 114.57 (4C), 114.50 (2C), 102.71, 99.92, 99.72, 99.58, 99.47, 98.93, 55.69 (2C), 55.62, 52.26, 51.57, 51.49 ppm; ESI MS (2655.1): m/z: 2678.0 [M + Na].

(Benzyl 2,3,4-tri-*O*-benzyl-α-D-galactopyranosyluronate)-(1→4)-(benzyl 2,3-di-*O*-benzyl-α-D-galactopyranosyluronate)-(1→4)-2,3-di-*O*-benzyl-6-*O*-(4-methoxyphenyl)-α-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-(4-methoxyphenyl)-α-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-(4-methoxyphenyl)-α-D-galactopyranosyl-(1→4)-(benzyl (benzyl 2,3-di-*O*-benzyl-β-D-galactopyranosid)uronate) (25): ^1H NMR: $\delta = 7.41–6.81$ (m, 85H), 6.70–6.43 (m, 12H), 5.18 (d, $J = 3.4$ Hz, 1H), 5.10–4.98 (m, 4H), 5.09 (d, $J = 3.4$ Hz, 1H), 4.94–4.84 (m, 4H), 4.81–4.13 (m, 42H), 4.07–3.99 (m, 4H), 3.97 (dd, $J = 10.2$, 3.4 Hz, 1H), 3.89 (dd, $J = 10.2$, 3.4 Hz, 1H), 3.82–3.62 (m, 7H), 3.72 (s, 3H), 3.69 (s, 3H), 3.68 (s, 3H), 3.57–3.46 ppm (m, 5H); ^{13}C NMR: $\delta = 168.43$, 167.77, 167.62, 153.82 (2C), 153.77, 152.56, 152.34, 152.09, 115.25 (4C), 115.10 (2C), 114.66 (2C), 114.59 (2C), 114.58 (2C), 102.73, 99.94, 99.78 (2C), 99.11, 98.93, 55.81 (2C), 55.75 ppm; ESI MS (2883.2): m/z: 2905.9 [M + Na].

(Methyl 2,3,4-tri-*O*-benzyl-α-D-galactopyranosyluronate)-(1→4)-(methyl 2,3-di-*O*-benzyl-α-D-galactopyranosyluronate)-(1→4)-(benzyl 2,3-di-*O*-benzyl-α-D-galactopyranosyluronate)-(1→4)-(benzyl 2,3-di-*O*-benzyl-α-D-galactopyranosyluronate)-(1→4)-(benzyl 2,3-di-*O*-benzyl-α-D-galactopyranosyluronate)-(1→4)-(methyl (benzyl 2,3-di-*O*-benzyl-β-D-galactopyranosid)uronate) (26): ^1H NMR: $\delta = 7.41–6.98$ (m, 85H), 5.22 (d, $J =$ 3.4 Hz, 1H), 5.11 (d, $J = 3.1$ Hz, 2H), 5.07–4.98 (m, 4H), 4.90 (d, $J =$ 11.9 Hz, 1H), 4.86 (d, $J = 11.9$ Hz, 1H), 4.84–4.21 (m, 41H), 4.16 (m, 1H), 3.98 (dd, $J = 10.3$, 3.4 Hz, 1H), 3.89–3.82 (m, 4H), 3.81–3.76 (m, 2H), 3.68 (dd, $J = 10.2$, 2.6 Hz, 1H), 3.65–3.51 (m, 4H), 3.64 (s, 3H), 3.30 (dd, $J = 9.8$, 2.6 Hz, 1H), 3.24 (s, 3H), 3.11 ppm (s, 3H); ^{13}C NMR: $\delta =$ 169.12, 168.28, 168.19, 168.06, 167.88, 167.70, 102.66, 99.32, 98.68, 98.55 (2C), 98.54, 52.21, 51.66, 51.51 ppm.

(Benzyl 2,3,4-tri-*O*-benzyl-α-D-galactopyranosyluronate)-(1→4)-(benzyl 2,3-di-*O*-benzyl-α-D-galactopyranosyluronate)-(1→4)-(methyl 2,3-di-*O*-benzyl-α-D-galactopyranosyluronate)-(1→4)-(methyl 2,3-di-*O*-benzyl-α-D-galactopyranosyluronate)-(1→4)-(methyl 2,3-di-*O*-benzyl-α-D-galactopyranosyluronate)-(1→4)-(benzyl (benzyl 2,3-di-*O*-benzyl-β-D-galactopyranosid)uronate) (27): ^1H NMR: $\delta = 7.41–6.95$ (m, 85H), 5.20 (d, $J =$ 3.4 Hz, 1H), 5.12–4.98 (m, 7H), 4.88, (d, $J = 11.3$ Hz, 1H), 4.86 (d, $J =$ 11.3 Hz, 1H), 4.82–4.28 (m, 38H), 4.23 (d, $J = 12.4$ Hz, 1H), 4.20 (d, $J =$ 13.2 Hz, 1H), 4.06 (m, 1H), 4.00 (dd, $J = 10.2$, 3.5 Hz, 1H), 3.93 (bs, 1H), 3.91 (dd, $J = 10.7$, 2.6 Hz, 1H), 3.84 (dd, $J = 10.2$, 3.4 Hz, 1H), 3.79–3.72 (m, 3H), 3.66–3.47 (m, 5H), 3.39 (s, 3H), 3.38 (m, 1H), 3.36 (s, 3H), 3.29 ppm

(s, 3H); ^{13}C NMR: δ = 168.81, 168.76, 168.62, 168.43, 167.51, 167.41, 102.67, 99.65, 98.67, 98.62, 98.40, 98.34, 51.78 (2C), 51.70 ppm; ESI MS (2649.0): *m*/*z* 2671.9 [*M* + Na].

Benzyl 2,3,4-tri-*O*-benzyl-α-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-(4-methoxyphenyl)-α-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-(4-methoxyphenyl)-α-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-(4-methoxyphenyl)-α-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzyl-β-D-galactopyranoside (28): ^{1}H NMR: δ = 7.40–6.97 (m, 70H), 6.69–6.29 (m, 16H), 5.10 (d, *J* = 3.2 Hz, 1H), 5.08 (d, *J* = 3.7 Hz, 1H), 5.04 (d, *J* = 3.7 Hz, 1H), 5.03 (d, *J* = 3.7 Hz, 1H), 4.96–4.79 (m, 8H), 4.77–4.27 (m, 31H), 4.21 (d, *J* = 9.0 Hz, 1H), 4.19 (d, *J* = 9.0 Hz, 1H), 4.10–4.03 (m, 3H), 3.97–3.61 (m, 15H), 3.69 (s, 3H), 3.68 (s, 3H), 3.67 (s, 3H), 3.66 (s, 3H), 3.55–3.40 (m, 4H), 3.26–3.10 (m, 3H), 2.66 (bs, 1H), 2.49 ppm (bs, 1H); ^{13}C NMR: δ = 154.05 (2C), 153.91, 153.87, 152.79, 152.60, 152.53, 152.35, 115.50 (2C), 115.41 (4C), 115.38 (2C), 114.90 (4C), 114.79 (2C), 114.69 (2C), 103.22, 100.53 (3C), 100.06, 99.63, 56.02, 55.99 (2C), 55.95 ppm; ESI MS (2677.2): *m*/*z* 2700.2 [M + Na]; elemental analysis calcd (%) for $C_{162}H_{170}O_{35}$: C 72.68, H 6.40; found: C 72.47, H 6.46.

(Methyl 2,3,4-tri-*O*-benzyl-α-D-galactopyranosyluronate)-(1→4)-2,3-di-*O*-benzyl-6-*O*-(4-methoxyphenyl)-α-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-(4-methoxyphenyl)-α-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-(4-methoxyphenyl)-α-D-galactopyranosyl-(1→4)-(methyl (benzyl 2,3-di-*O*-benzyl-β-D-galactopyranosid)uronate) (29): ^{1}H NMR: δ = 7.41–6.88 (m, 70H), 6.69–6.26 (m, 16H), 5.16 (d, *J* = 3.4 Hz, 1H), 5.08 (d, *J* = 3.4 Hz, 1H), 5.06 (d, *J* = 12.0 Hz, 1H), 5.03 (d, *J* = 2.6 Hz, 1H), 4.99 (d, *J* = 3.4 Hz, 1H), 4.96 (d, *J* = 3.4 Hz, 1H), 4.94–4.12 (m, 42H), 4.03–3.96 (m, 3H), 3.90 (dd, *J* = 10.2, 3.0 Hz, 1H), 3.86 (dd, *J* = 10.2, 3.4 Hz, 1H), 3.84–3.62 (m, 7H), 3.80 (s, 3H), 3.79 (s, 3H), 3.78 (s, 3H), 3.66 (s, 3H), 3.63 (s, 3H), 3.61–3.54 (m, 3H), 3.50–3.42 (m, 2H), 3.40 (dd, *J* = 7.7, 5.1 Hz, 1H), 3.09 ppm (s, 3H); ^{13}C NMR: δ = 169.38, 168.52, 153.81, 153.76, 153.73, 153.70, 152.60, 152.46, 152.34, 152.00, 115.27 (2C), 115.23 (2C), 115.11 (4C), 114.67 (4C), 114.60 (2C), 114.50 (2C), 102.82, 100.08, 100.12, 100.00, 99.55, 99.32, 55.83, 56.82, 55.77, 55.74, 52.39, 51.67 ppm; ESI MS (2733.1): *m*/*z* 2756.1 [*M* + Na]; elemental analysis calcd (%) for $C_{164}H_{170}O_{37}$: C 72.07, H 6.27; found: C 71.85, H 6.27.

(Benzyl 2,3,4-tri-*O*-benzyl-α-D-galactopyranosyluronate)-(1→4)-2,3-di-*O*-benzyl-6-*O*-(4-methoxyphenyl)-α-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-(4-methoxyphenyl)-α-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-(4-methoxyphenyl)-α-D-galactopyranosyl-(1→4)-(benzyl (benzyl 2,3-di-*O*-benzyl-β-D-galactopyranosid)uronate) (30): ^{1}H NMR: δ = 7.41–6.89 (m, 80H), 6.69–6.27 (m, 16H), 5.18 (d, *J* = 3.0 Hz, 1H), 5.09 (d, *J* = 3.4 Hz, 1H), 5.08–5.02 (m, 2H), 5.00 (d, *J* = 3.4 Hz, 1H), 4.93 (d, *J* = 3.4 Hz, 1H), 4.90 (d, *J* = 3.4 Hz, 1H), 4.88–4.16 (m, 43H), 4.08 (t, *J* = 2.1 Hz, 1H), 4.03 (dd, *J* = 10.2, 2.1 Hz, 1H), 4.01–3.96 (m, 2H), 3.90 (dd, *J* = 10.7, 3.4 Hz, 1H), 3.86 (dd, *J* = 10.2, 3.4 Hz, 1H), 3.83–3.64 (m, 8H), 3.70 (s, 3H), 3.69 (s, 3H), 3.68 (s, 3H), 3.66 (s, 3H), 3.61–3.56 (m, 2H), 3.54 (dd, *J* = 10.7, 3.0 Hz, 1H), 3.48 (dd, *J* = 9.8, 3.0 Hz, 1H), 3.46 (m, 1H), 3.41 ppm (dd, *J* = 8.1, 5.1 Hz, 1H); ^{13}C NMR: δ = 168.63, 167.75, 153.78, 153.73, 153.69, 153.66, 152.55, 152.33, 152.30, 151.97, 115.23 (4C), 115.07 (4C), 114.62 (4C), 114.55 (2C), 114.46 (2C), 102.69, 100.14, 100.03 (2C), 99.94, 99.14, 55.78, 55.77, 55.73, 55.70 ppm; ESI MS (2885.2): *m*/*z*: 2908.3 [*M* + Na]; elemental analysis calcd (%) for $C_{176}H_{178}O_{37}$: C 73.26, H 6.22; found: C 72.98, H 6.14.

(Methyl 2,3,4-tri-*O*-benzyl-α-D-galactopyranosyluronate)-(1→4)-(benzyl 2,3-di-*O*-benzyl-α-D-galactopyranosyluronate)-(1→4)-(benzyl 2,3-di-*O*-benzyl-α-D-galactopyranosyluronate)-(1→4)-(benzyl 2,3-di-*O*-benzyl-α-D-galactopyranosyluronate)-(1→4)-(benzyl 2,3-di-*O*-benzyl-α-D-galactopyranosyluronate)-(1→4)-(methyl (benzyl 2,3-di-*O*-benzyl-β-D-galactopyranosid)uronate) (31): ^{1}H NMR: δ = 7.41–6.92 (m, 90H), 5.21 (d, *J* = 3.7 Hz, 1H), 5.12 (d, *J* = 3.1 Hz, 1H), 5.09 (d, *J* = 3.7 Hz, 1H), 5.07 (d, *J* = 3.1 Hz, 1H), 5.04 (d, *J* = 12.1 Hz, 1H), 5.02 (d, *J* = 3.2 Hz, 1H), 4.99 (d, *J* = 12.1 Hz, 1H), 4.92 (d, *J* = 12.1 Hz, 1H), 4.86–4.28 (m, 42H), 4.23–4.18 (m, 2H), 4.14 (m, 1H), 4.02 (dd, *J* = 10.0, 3.2 Hz, 1H), 3.87–3.76 (m, 6H), 3.68 (dd, *J* = 10.0, 2.6 Hz, 1H), 3.64 (s, 3H), 3.60–3.61 (m, 4H), 3.30 (dd, *J* = 10.0, 3.1 Hz, 1H), 3.21 ppm (s, 3H); ^{13}C NMR: δ = 168.99, 168.13, 167.99, 167.85, 167.67, 167.37, 102.60, 99.45, 98.63, 98.46 (2C), 98.40, 52.15, 51.57 ppm; ESI MS (2725.1): *m*/*z*: 2748.1 [*M* + Na]; elemental analysis calcd (%) for $C_{164}H_{162}O_{37}$: C 72.28, H 5.99; found: C 71.97, H 5.91.

(Benzyl 2,3,4-tri-*O*-benzyl-α-D-galactopyranosyluronate)-(1→4)-(methyl 2,3-di-*O*-benzyl-α-D-galactopyranosyluronate)-(1→4)-(methyl 2,3-di-*O*-benzyl-α-D-galactopyranosyluronate)-(1→4)-(methyl 2,3-di-*O*-benzyl-α-D-galactopyranosyluronate)-(1→4)-(benzyl (benzyl 2,3-di-*O*-benzyl-β-D-galactopyranosid)uronate) (32): ^{1}H NMR: δ = 7.41–7.01 (m, 80H), 5.29 (d, *J* = 3.2 Hz, 1H), 5.13–4.96 (m, 7H), 4.89–4.27 (m, 40H), 4.07 (bs, 1H), 3.97–3.90 (m, 3H), 3.85 (dd, *J* = 10.5, 3.2 Hz, 1H), 3.81–3.74 (m, 3H), 3.67–3.61 (m, 2H), 3.59–3.52 (m, 3H), 3.41 (s, 3H), 3.38 (m, 1H), 3.37 (s, 3H), 3.29 (s, 3H), 3.12 ppm (s, 3H); ^{13}C NMR: δ = 168.74, 168.69, 168.54, 168.39, 168.36, 167.32, 102.58, 99.39, 98.60, 98.52, 98.48, 98.25, 51.71, 51.69, 51.62, 51.51 ppm; ESI MS (2573.0): *m*/*z*: 2595.9 [*M* + Na]; elemental analysis calcd for $C_{152}H_{154}O_{37}$: C 70.96, H 6.03; found: C 70.67, H 6.13.

Benzyl 2,3-di-*O*-benzyl-6-*O*-(4-methoxyphenyl)-α-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-pentafluorobenzoyl-α-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-(4-methoxyphenyl)-β-D-galactopyranoside (33): $[\alpha]_D^{20}$ = +25.6 (*c* = 1.7, $CHCl_3$); ^{1}H NMR: δ = 7.42–7.14 (m, 35H), 6.81–6.58 (m, 8H), 5.06 (d, *J* = 3.4 Hz, 1H), 4.99 (d, *J* = 3.4 Hz, 1H), 4.97 (d, *J* = 12.0 Hz, 1H), 4.90–4.63 (m, 15H), 4.54–4.42 (m, 5H), 4.28 (d, *J* = 1.8 Hz, 1H), 4.16 (d, *J* = 2.6 Hz, 1H), 4.10–4.07 (m, 2H), 4.01 (t, *J* = 8.5 Hz, 1H), 3.92 (dd, *J* = 9.9, 3.4 Hz, 1H), 3.90 (dd, *J* = 9.4, 3.1 Hz, 1H), 3.81 (dd, *J* = 9.9, 3.1 Hz, 1H), 3.76 (s, 3H), 3.74 (s, 3H), 3.73–3.65 (m, 3H), 3.44 (dd, *J* = 9.9, 2.9 Hz, 1H), 2.50 ppm (bs, 1H); ^{13}C NMR: δ = 157.90, 154.06, 153.91, 152.73, 152.47, 145.39 (bd, $J_{C,F}$ = 257 Hz, 2C), 143.15 (bd, $J_{C,F}$ = 260 Hz, 1C), 138.66, 138.57, 138.51, 138.29, 138.19, 138.15, 137.80, 137.61 (bd, $J_{C,F}$ = 257 Hz, 2C), 115.45 (2C), 115.43 (2C), 114.75 (2C), 114.53 (2C), 107.78 (dt, $J_{C,F}$ = 15, 3.5 Hz, 1C), 102.91, 100.42, 100.20, 79.84, 79.25, 78.46, 77.35, 76.86, 75.90, 75.08, 74.98, 74.59, 74.31, 73.02, 72.96, 72.77, 72.43, 72.12, 71.09, 69.00, 68.38, 66.66, 66.43, 65.65, 63.77, 55.72, 55.69 ppm; ESI MS (1540.6): *m*/*z*: 1563.7 [*M* + Na].

Benzyl 2,3-di-*O*-benzyl-6-*O*-(4-methoxyphenyl)-α-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-pentafluorobenzoyl-α-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-(4-methoxyphenyl)-α-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-pentafluorobenzoyl-α-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-(4-methoxyphenyl)-β-D-galactopyranoside (34): ^{1}H NMR: δ = 7.41–7.02 (m, 55H), 6.77–6.45 (12H), 5.06 (d, *J* = 1.7 Hz, 1H), 5.02 (d, *J* = 3.4 Hz, 1H), 4.96 (d, *J* = 3.7 Hz, 1H), 4.95 (d, *J* = 11.4 Hz, 1H), 4.93 (d, *J* = 3.4 Hz, 1H), 4.88–4.01 (m, 40H), 3.93–3.88 (m, 2H), 3.86 (dd, *J* = 9.9, 3.4 Hz, 1H), 3.83–3.76 (m, 4H), 3.74 (s, 6H), 3.71–3.62 (m, 3H), 3.69 (s, 3H), 3.51 (dd, *J* = 8.2, 4.5 Hz, 1H), 3.42 (dd, *J* = 9.9, 2.8 Hz, 1H), 2.45 ppm (bs, 1H); ^{13}C NMR: δ = 157.99, 157.66, 154.09, 153.91, 153.89, 152.68, 152.48, 152.35, 145.45 (bd, $J_{C,F}$ = 257 Hz, 4C), 143.22 (bd, $J_{C,F}$ = 260 Hz, 2C), 137.69 (bd, $J_{C,F}$ = 257 Hz, 4C), 115.47 (2C), 115.38 (2C), 115.27 (2C), 114.79 (2C), 114.71 (2C), 114.54 (2C), 107.56 (m, 2C), 102.94, 100.59, 100.43, 100.15, 99.79, 55.80 ppm (3C); elemental analysis calcd (%) for $C_{142}H_{134}F_{10}O_{31}$: C 67.50, H 5.35; found: C 67.17, H 5.15.

Benzyl 2,3,4-tri-*O*-benzyl-α-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-(4-methoxyphenyl)-α-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-(4-methoxyphenyl)-α-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-(4-methoxyphenyl)-β-D-galactopyranoside (35): ^{1}H NMR: δ = 7.42–6.97 (m, 70H), 6.73–6.34 (m, 12H), 5.01 (d, *J* = 4.0 Hz, 1H), 5.00 (d, *J* = 3.6 Hz, 1H), 4.99–4.94 (m, 4H), 4.91 (d, *J* = 11.0 Hz, 1H), 4.89 (d, *J* = 11.0 Hz, 1H), 4.83–4.43 (m, 28H), 4.27–3.99 (m, 14H), 3.95–3.74 (m, 10H), 3.72 (s, 3H), 3.71–3.52 (m, 6H), 3.69 (s, 3H), 3.67 (s, 3H), 3.43 (dd, *J* = 10.0, 2.9 Hz, 1H), 3.40 (m, 1H), 3.32–3.24 (m, 3H), 3.08 (bs, 1H), 2.81 ppm (m, 1H); ^{13}C NMR: δ = 153.97, 153.74, 153.72, 152.46, 152.33, 152.29, 115.43 (2C), 115.20 (4C), 114.70 (2C), 114.59 (2C), 114.52 (2C), 102.99, 100.34, 100.26, 100.19, 99.84, 99.77, 55.74 (2C), 53.52 ppm; ESI MS (2571.1): *m*/*z*: 2593.7 [*M* + Na]; elemental analysis calcd (%) for $C_{155}H_{164}O_{34}$: C 72.41, H 6.43; found: C 72.16, H 6.31.

Benzyl (methyl 2,3,4-tri-*O*-benzyl-α-D-galactopyranosyluronate)-(1→4)-2,3-di-*O*-benzyl-6-*O*-(4-methoxyphenyl)-α-D-galactopyranosyl-(1→4)-(methyl 2,3-di-*O*-benzyl-α-D-galactopyranosyluronate)-(1→4)-2,3-di-*O*-benzyl-6-*O*-(4-methoxyphenyl)-α-D-galactopyranosyl-(1→4)-(methyl 2,3-di-*O*-benzyl-α-D-galactopyranosyluronate)-(1→4)-2,3-di-*O*-benzyl-6-*O*-(4-methoxyphenyl)-β-D-galactopyranoside (36): ^{1}H NMR: δ = 7.42–6.86 (m, 70H), 6.80–6.28 (m, 12H), 5.15 (d, *J* = 3.1 Hz, 1H), 5.10 (d, *J* = 3.3 Hz, 1H), 5.06 (d, *J* = 3.1 Hz, 1H), 5.02 (d, *J* = 3.1 Hz, 1H), 5.00–4.03 (m, 46H), 3.99 (t, *J* = 9.0 Hz, 1H), 3.88 (dd, *J* = 10.5, 3.3 Hz, 1H), 3.85 (dd, *J* = 10.5, 3.3 Hz, 1H), 3.81–3.58 (m, 9H), 3.75 (s, 3H), 3.70 (s, 3H), 3.69 (s, 3H),

3.45–3.35 (m, 2H), 3.33 (s, 3H), 3.14 (s, 3H), 3.12 ppm (s, 3H); ^{13}C NMR: δ = 169.62, 169.60, 169.39, 154.38, 154.09, 153.99, 152.46, 152.40, 152.29, 115.63 (2C), 115.50 (2C), 115.46 (2C), 115.05 (2C), 114.91 (2C), 114.75 (2C), 103.27, 100.25, 100.11, 100.09, 99.57 (2C), 56.02 (2C), 53.80, 52.17, 52.05, 51.92 ppm; elemental analysis calcd (%) for $C_{158}H_{164}O_{37}$: C 71.48, H 6.23; found: C 71.26, H 6.47.

(Methyl 2,3,4-tri-*O*-benzyl-α-D-galactopyranosyluronate)-(1→4)-(benzyl 2,3-di-*O*-benzyl-α-D-galactopyranosyluronate)-(1→4)-(methyl 2,3-di-*O*-benzyl-α-D-galactopyranosyluronate)-(1→4)-(benzyl 2,3-di-*O*-benzyl-α-D-galactopyranosyluronate)-(1→4)-(methyl 2,3-di-*O*-benzyl-α-D-galactopyranosyluronate)-(1→4)-(benzyl (benzyl 2,3-di-*O*-benzyl-β-D-galactopyranosid)uronate) (37): ^{1}H NMR: δ = 7.42–6.95 (m, 85H), 5.25 (d, J = 3.2 Hz, 1H), 5.14 (d, J = 12.4 Hz, 1H), 5.09–4.94 (m, 7H), 4.87–4.28 (m, 42H), 4.22 (d, J = 12.7 Hz, 1H), 4.12 (m, 1H), 4.00 (dd, J = 10.2, 3.2 Hz, 1H), 3.92 (bs, 1H), 3.87 (dd, J = 10.2, 2.2 Hz, 1H), 3.82–3.75 (m, 3H), 3.63 (dd, J = 10.2, 2.6 Hz, 1H), 3.61–3.52 (m, 3H), 3.38 (s, 3H), 3.36 (dd, J = 10.2, 2.9 Hz, 1H), 3.27 (s, 3H), 3.21 ppm (s, 3H); ^{13}C NMR: δ = 169.14, 168.80, 168.53, 168.02, 167.52, 167.41, 102.64, 99.66, 98.65, 98.52 (2C), 98.40, 51.74, 51.68, 51.65 ppm; ESI MS (2649.0): m/z: 2671.7 [M + Na]; elemental analysis calcd (%) for $C_{158}H_{158}O_{37}$: C 71.64, H 6.01; found: C 71.27, H 5.88.

(Methyl α-D-galactopyranosyluronate)-(1→4)-(methyl α-D-galactopyranosyluronate)-(1→4)-(α-D-galactopyranosyluronic acid)-(1→4)-(α-D-galactopyranosyluronic acid)-(1→4)-(α-D-galactopyranosyluronic acid)-(1→4)-(methyl D-galactopyranuronate) (1): ^{13}C NMR (D_2O): δ = 171.62, 170.94, 170.08, 100.67, 99.95, 99.85, 96.08, 92.76, 79.12, 78.87, 78.30, 78.19, 73.47, 71.69, 71.50, 71.32, 70.77, 70.22, 68.84, 68.64, 68.27, 68.17, 68.05, 67.99, 53.22, 53.14, 53.04 ppm; ESI MS/MS: m/z: 1114.6, 925.1, 749.0, 572.8; ESI HRMS calcd for $C_{39}H_{56}O_{37}Na$: m/z: 1139.2398; found: m/z: 1139.2382 [M + Na]$^+$.

(α-D-Galactopyranosyluronic acid)-(1→4)-(α-D-galactopyranosyluronic acid)-(1→4)-(methyl α-D-galactopyranosyluronate)-(1→4)-(methyl α-D-galactopyranosyluronate)-(1→4)-(methyl α-D-galactopyranosyluronate)-(1→4)-D-galactopyranuronic acid (2): ^{13}C NMR (D_2O): δ = 171.48, 171.38, 101.08, 100.30, 96.90, 82.49, 79.67, 79.52, 79.21, 78.75, 78.70, 72.79, 72.72, 72.02, 71.28, 71.23, 69.97, 69.31, 69.07, 68.87, 68.73, 68.67, 68.51, 53.60 ppm; ESI MS/MS: m/z: 1115.1, 939.0, 749.0, 559.0, 368.7; ESI HRMS calcd for $C_{39}H_{56}O_{37}Na$: m/z: 1139.2398; found: m/z: 1139.2406 [M + Na]$^+$.

(Methyl α-D-galactopyranosyluronate)-(1→4)-(α-D-galactopyranosyluronic acid)-(1→4)-(α-D-galactopyranosyluronic acid)-(1→4)-(α-D-galactopyranosyluronic acid)-(1→4)-(methyl D-galactopyranuronate) (3): ^{13}C NMR (D_2O): δ = 171.67, 170.93, 170.05, 99.93, 96.59, 92.63, 78.83, 78.41, 78.12, 73.45, 71.66, 71.44, 71.30, 70.25, 70.06, 68.90, 68.74, 68.16, 68.03, 53.19, 53.14, 53.03 ppm; ESI MS/MS: m/z: 1100.9, 910.9, 734.9, 558.9, 382.8; ESI HRMS calcd for $C_{38}H_{54}O_{37}Na$: m/z: 1125.2242; found: m/z: 1125.2218 [M + Na]$^+$.

(α-D-Galactopyranosyluronic acid)-(1→4)-(methyl α-D-galactopyranosyluronate)-(1→4)-(methyl α-D-galactopyranosyluronate)-(1→4)-(methyl α-D-galactopyranosyluronate)-(1→4)-(methyl α-D-galactopyranosyluronate)-(1→4)-D-galactopyranuronic acid (4): ^{13}C NMR (D_2O): δ = 170.96, 170.86, 100.60, 99.90, 96.40, 79.22, 78.90, 78.24, 72.18, 71.54, 70.81, 70.61, 69.31, 68.04, 53.14 ppm; ESI MS/MS: m/z: 1128.9, 952.9, 762.9, 572.8, 382.8 ppm; ESI HRMS calcd for $C_{40}H_{58}O_{37}Na$: m/z: 1153.2555; found: m/z: 1153.2551 [M + Na]$^+$.

(Methyl α-D-galactopyranosyluronate)-(1→4)-(α-D-galactopyranosyluronic acid)-(1→4)-(methyl α-D-galactopyranosyluronate)-(1→4)-(α-D-galactopyranosyluronic acid)-(1→4)-(methyl α-D-galactopyranosyluronate)-(1→4)-D-galactopyranuronic acid (5): ^{13}C NMR (D_2O): δ = 171.67, 171.02, 99.90, 94.45, 92.61, 82.00, 78.77, 78.68, 78.16, 72.14, 71.45, 70.77, 70.25, 68.92, 68.59, 68.53, 68.22, 53.13, 53.05 ppm; ESI MS/MS: m/z: 1115.1, 939.1, 749.0, 572.9, 382.9; ESI HRMS calcd for $C_{39}H_{56}O_{37}Na$: m/z: 1139.2398; found: m/z: 1139.2435 [M + Na]$^+$.

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