C-Glycoside D-galacturonates suitable as glycosyl acceptors for the synthesis of allyl *C*-homo- and rhamno-galacturonan modules[1]

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Dedicated to Prof. Richard R. Schmidt on the occasion of his 78th anniversary

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Abstract

Methyl 2,3-di-*O*-benzyl-1-deoxy-1-(prop-2-enyl)-α-D-galactopyranuronate and benzyl 2,3-di-*O*-benzyl-1-deoxy-1-(prop-2-enyl)-α-D-galactopyranuronate were prepared as glycosyl acceptors. The glycosyl donors benzyl 4-*O*-acetyl-2,3-di-*O*-benzyl-1-(trichloroacetimidoyloxy)-α-D-galactopyranosyluronate and benzyl 4-*O*-acetyl-2,3-di-*O*-benzyl-1-(trichloroacetimidoyloxy)-β-D-galactopyranosyluronate were synthesized in 98% and 76% yields respectively. Disaccharides methyl (methyl 4-O-acetyl-2,3-di-O-benzyl-α/β-D-galactopyranosyluronate)-(1→4)-2,3-di-O-benzyl-1-deoxy-1-(prop-2-enyl)-α-D-galactopyranuronate and benzyl (benzyl 4-O-acetyl-2,3-di-O-benzyl-α/β-D-galactopyranosyluronate)-(1→4)-2,3-di-O-benzyl-1-deoxy-1-(prop-2-enyl)-α-D-galactopyranuronate were synthesized in 53% and 44% yields respectively and with moderate stereoselectivity. The synthesis of 1,2-*O*-acetyl-3,4-di-*O*-benzyl-L-rhamnopyranose (α/β) and 2-*O*-acetyl-1-bromo-3,4-di-*O*-benzyl-α-L-rhamnopyranosyl suitable as glycosyl donors is described. The disaccharide methyl (2-*O*-acetyl-3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→4)-2,3-di-*O*-benzyl-1-deoxy-1-(prop-2-enyl)-α-D-galactopyranuronate, and benzyl (2-*O*-acetyl-3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→4)-2,3-di-*O*-benzyl-1-deoxy-1-(prop-2-enyl)-α-D-galactopyranuronate were obtained in 54% and 56% yield respectively.

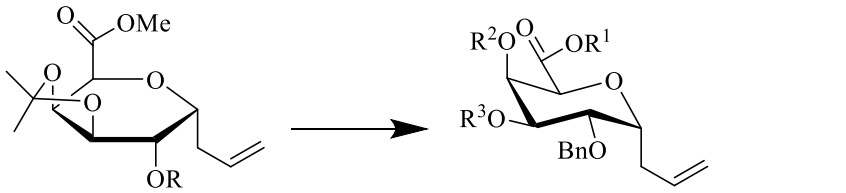
Keywords: C-glycoside, D-galacturonic acid**,** allyl *C*-homogalacturonan, allyl *C*-rhamnogalacturonan

Introduction

In order to develop a program directed at the synthesis of homo- and rhamnogalacturonan disaccharide mimics, we looked for an option to use α-*C*-galacturonate acceptors[1,2] in glycosidic reactions to form higher oligomers of defined structure in our ongoing program for the synthesis of pectin fragments by a modular design principle.[1-3]

Results and Discussion

In our previous paper[2] methyl (**4**) and benzyl (**5**) glycosyl acceptors were obtained by different routes starting from D-galactose and D-galacturonic acid respectively. Exploring several protecting group manipulations, an effective route was found for the preparation of the key intermediate **3** (Scheme 1) through the isopropylidene compound **1** and its benzylation under basic conditions, where no β-elimination was observed.[2,3] Selective benzylation via 3,4-*O*-benzylstannyl intermediates resulted in methyl (**4**) and benzyl (**5**) glycosyl acceptors, both suitable as acceptors in glycosylation reactions.

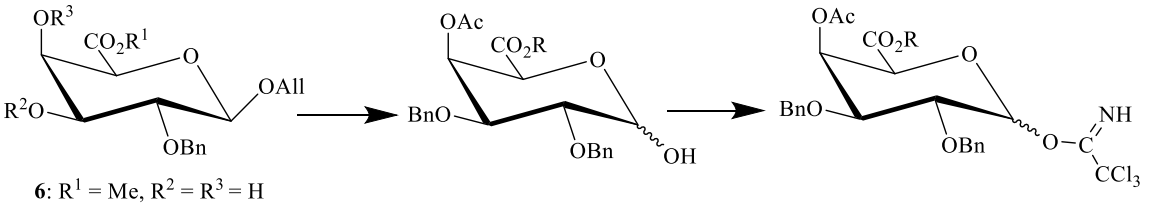


1: R = H, 85%
2: R = Bn 70%

3: R^1 = Me; R^2 = R^3 = H, 81%
4: R^1 = Me; R^2 = H; R^3 = Bn, 16%
5: R^1 = Bn; R^2 = H; R^3 = Bn, 37%

Scheme 1

For the preparation of the galacturonate trichloroacetimidate donors, the introduction of the trichloroacetimidate group at the anomeric centre of **11**[4,5] was re-examined (Scheme 2). In our investigations[1], the introduction of the trichloroacetimidate group at the anomeric center of **9** in the presence of DBU gave a 3:1 mixture of the α- and β-trichloroacetimidates (**11**α,β) in 98% total yield. After HPLC column chromatography the α-trichloroacetimidate (R_f 0.39, 73%) and the β-trichloroacetimidate (R_f 0.27, 25%) were characterized by NMR spectroscopy. For H-1, the smaller coupling constant ($J_{1,2}$ = 3.5 Hz) for compound **13**α and the larger ($J_{1,2}$ = 8.2 Hz) for the trichloroacetimidate **13**β match the observed results.



6: R^1 = Me, R^2 = R^3 = H
7: R^1 = Me, R^2 = Bn, R^3 = H
8: R^1 = Bn, R^2 = Bn, R^3 = H
9: R^1 = Me, R^2 = Bn, R^3 = Ac
10: R^1 = Bn, R^2 = Bn, R^3 = Ac, 98%

11: R = Me
12: R = Bn, 56%

13 (a:b, 3:1): R = Me, 98%
14 (a:b, 2:1): R = Bn, 76%

Scheme 2

In general, benzyl esters are less stable than the corresponding methyl esters. On the other hand, benzyl esters can be removed easily by hydrogenation. In order to get a defined pattern of protected and unprotected carboxylic esters in pectin fragments, both methyl and benzyl esters were prepared.[6,7] Thus, it was of interest to incorporate galacturonate **8**, protected as the benzyl ester, into our program for the synthesis of the glycosyl donors **14α/β**. Therefore, the 4-*O*-position was acetylated with acetic anhydride in dry pyridine to provide **10** in 98% yield. Deallylation with the aid of palladium(II) chloride[8] produced, surprisingly, only the α-product **12** in 56% yield (Scheme 2).

Regioselective benzylation of **6** via 3,4-*O*-butylstannyl intermediates gave galacturonates **7** and **8** in 80% overall yield (ratio 3:1). The galacturonate **7** was used as a glycosyl acceptor for the synthesis of homo- and rhamnogalacturonan oligosaccharides.[3, 9]

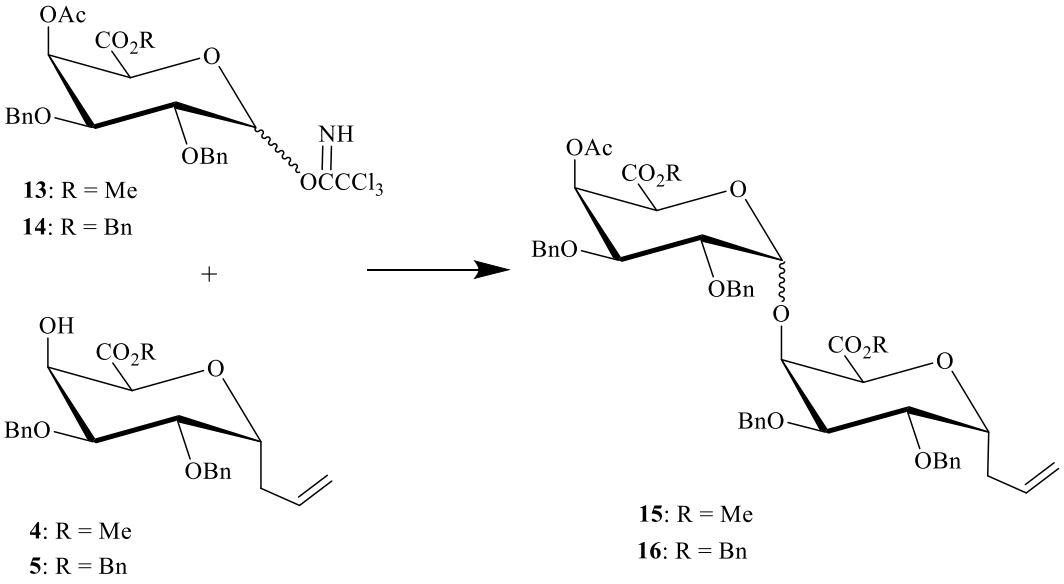
In the ^{1}H NMR (500 MHz) spectrum, the acetylation of **6** caused the expected downfield shift to the H-4 ring proton signal from δ 4.32 ppm (**8**) to 5.82 ppm (**10**). In the ^{13}C NMR spectrum, the signal at δ 20.53 ppm and 169.68 ppm confirmed the presence of the acetyl group at the 4-position. The deallylation was evidenced by the expected upfield shift of the H-1 ring proton signal from δ 4.48 ppm (**10**) to 5.40 ppm (**12**). The small coupling constant $J_{1,2}$ = 3.5 Hz of H-1 and the C-1 signal at δ 92.18 ppm are caused by the α-configuration of **8**.

The introduction of the trichloroacetimidate group at the anomeric center of **11** in the presence of DBU produced the α-D-galactopyranosyl trichloroacetimidate **13**α (R_f 0.76) and the β-trichloroacetimidate **12**β (R_f 0.71). After HPLC chromatography compounds **13**α and **13**β were obtained in pure in 76% total yield (ratio 2:1). In the ^{1}H NMR (500 MHz) spectrum the small coupling constant $J_{1,2}$ = 3.5 Hz for compound **13**α, and the considerably larger coupling constant $J_{1,2}$ = 8.2 Hz for compound **13**β confirmed the proposed structure. Moreover, ^{13}C NMR signals at δ 94.54 ppm for compound **13**α, and at δ 97.78 ppm for compound **13**β assured the stereochemistry at the anomeric center of the glycosyl donor **13**α and **13**β respectively.

The coupling of galacturonate acceptor **4** with a slight excess of the α-configured donor **13**α was promoted by trimethylsilyl trifluoromethanesulfonate (TMSOTf).[3,11,12] Standard work-up of

the reaction mixture provided the (1→4)-linked disaccharides **16**α and **16**β in 53% total yield in a ratio 3:1 (Scheme 3). The same result was observed when **13**β was used as glycosyl donor.

Although the $R_{f.}$ values of the resulting diaccharides were so close together, the disaccharides **15**α and **15**β were successfully separated by using gradient HPLC. Still, both of the separated fractions **15**α and **15**β contained traces of the corresponding anomer. The ^{1}H NMR spectra of **15**α showed a doublet signal at δ 5.16 ppm with vicinal coupling constant $J_{1',2'}$ = 3.5 Hz for H-1′, and a triple doublet signal at δ 4.24 with vicinal coupling constants $J_{1,2}$ = 2.5 Hz, $J_{1,Ha}$ = 6.0 Hz, $J_{1,Hb}$ = 8.5 Hz for H-1. In addition, the ^{13}C NMR signal for C-1′ was found to fall within the expected range of δ 98.80 Hz with $J_{C\text{-}1,H\text{-}1'}$ = 171.0 Hz coupling constant for the α-coupled disaccharide **15**α. In the case of **15**β, the value of the C-1′ signal, which was determined at δ 102 Hz, matches the β-linked disaccharide. Subsequent experiments have shown that the α-or β-configured trichloroacetimidate group at the anomeric center of **13**α/β exerted no influence on the outcome of stereoselectivity of the glycosylations investigated here.[3,14] For that reason, in the subsequent experiments we used the α/β mixture of **13**α/β.

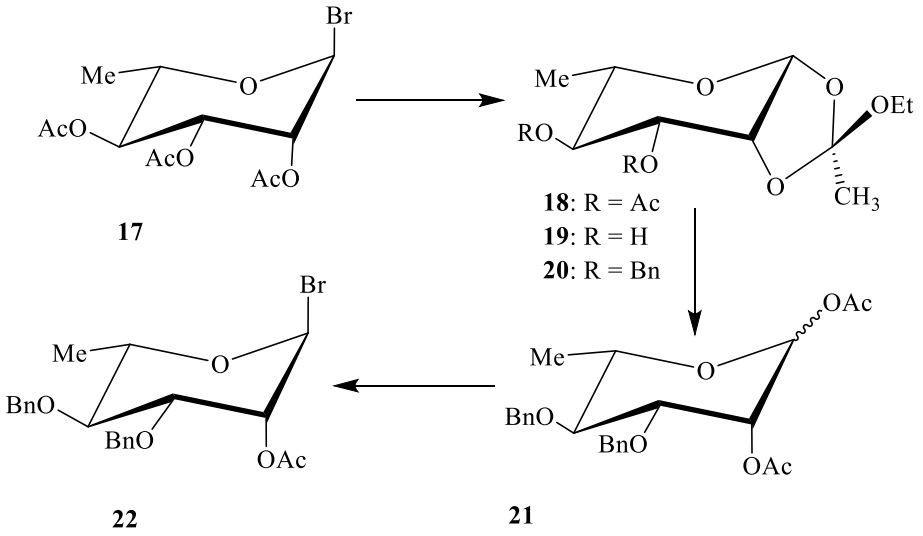


Scheme 3

The coupling of glycosyl acceptor **5** with a slight excess of the **14**α/β was initiated by TMSOTf as a glycosylation promoter.[3,11,12] Standard work-up of the reaction mixture provided the (1→4)-linked disaccharides **16**α and **16**β in 44% total yield in a ratio of 2:1 (Scheme 3). Unfortunately, the α- and β-coupled disaccharides **16**α and **16**β were difficult to separate this time. The ^{13}C NMR showed the signal for C-1′ has the expected range of δ 99.0 ppm for the α-coupled disaccharide **16**α, whereas the β-coupled disaccharide **16**β showed a signal at δ 102.3 ppm. The other ^{1}H and ^{13}C NMR data were also fully consistent with the assigned structures.

In connection with the synthesis of rhamnogalacturonan fragments type I, we required a simple approach to benzylated rhamnopyranosides with an *O*-acetyl group at 2-postion. To

achieve this, acetobromorhamnose **17** was prepared according to the literature.[14] Methyl orthoester **18** was prepared in 81% yield by the reaction of bromide **17** with dry EtOH in the presence of 2,4,6-collidine and tetrabutylammonium bromide (Scheme 4).[15,16] The structure of the obtained orthoester **18** was supported by the analytical data.[17] Compound **18** was then deacetylated by the Zemplén procedure to give **18**, but the subsequent neutralization decreased the yield of **20** dramatically. Therefore, deacetylation of orthoester **18** and the benzylation of the resulting compound **21** under basic conditions were carried out without further purification of **20**. Instead of using Zemplèn conditions, deacetylation was achieved by refluxing **18** with KOH in dry toluene.[18]



Scheme 4

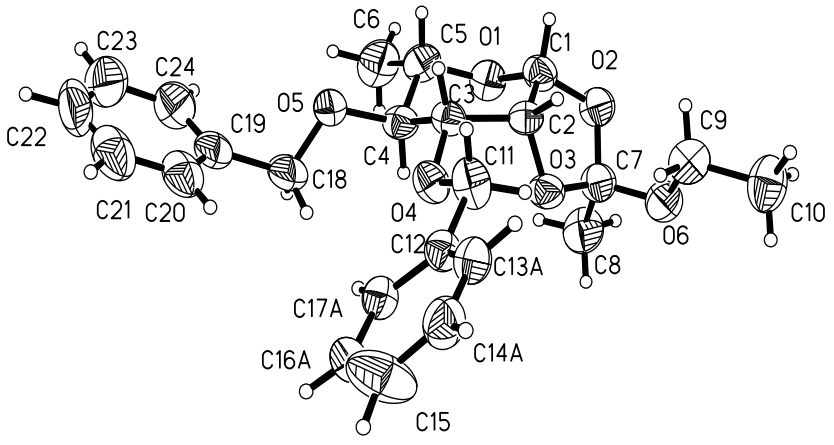


Figure 1. An ORTEP diagram of compound **20**, the aromatic ring of the benzyl group at O4 is disordered over two positions around the C11-C12 axis. Only one set of atoms is shown in Figure 1, the other is omitted for clarity.

After addition of benzyl chloride and classical work up orthoester **20** was obtained in 82% yield as colorless crystals suitable for X-ray investigation (Figure 1). NOESY studies (Figure 2) were employed to address the conformation and the absolute configuration of the orthoester **20**. In the ^{1}H-NMR spectrum of **20** the exchange of the acetyl groups at *O*-3 and *O*-4 positions by benzyl groups caused a significant upfield shift (*ca*. 1.5 ppm) of the geminal ring proton, with respect to the precursor **17**.[17] Furthermore, the H-1 signal of **20** appears at relatively high field δ 5.26 ppm with a coupling constant $J_{1,2}$ = 2.5 Hz. The NOESY spectrum (Figure 2) shows correlation between H1↔ H2, H1↔ H3, H1↔ H5, CCH_3 (orthoester) ↔ OCH_2CH_3 (orthoester), and H2 ↔ OCH_2CH_3 (orthoester). From these results, it could be concluded that the rhamnopyranose ring of **20** is in the $^1C_4$ chair conformation, and in the 1,2-*O*-(1-ethoxy-ethylidene) derivative **20** the ethoxy group exists in an *exo*-orientation (*S*-configuration). The distortion of the chair towards a half-chair conformation, as reported by Perlin,[19,20] which is to be expected from the fusion of the five-membered orthoester group at positions 1 and 2 of the sugar molecule, was not observed for **20**.

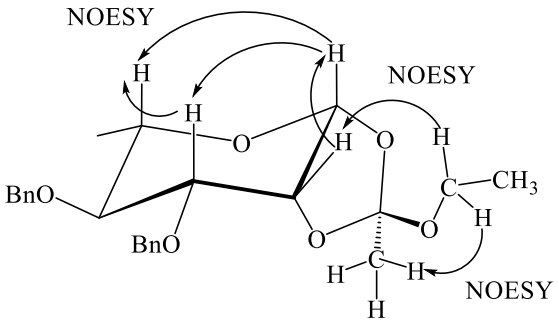


Figure 2. NOESY proton correlation of compound **20**.

The X-ray diffraction studies of **20** (Figure 1) established the configuration at C-1, C-2 and provided information on the conformation of the pyranose ring. The puckering parameters Q: 0.549 (5) Å, θ: 160.2 (5)º, ϕ: 114.8 (14)º of the sugar ring, show a nearly ideal $^1C_4$ chair conformation.

Hydrolysis of **20** in 70% AcOH solution followed by acetylation of the 1-position with acetic anhydride in presence of pyridine gave both α- and β-acetylated derivatives **21**α and **21**β in 66% and 14% yields, respectively. ^{1}H NMR and NOESY experiments (Figure 3) confirm the configuration at the 1-position in the diacetates **21**α and **21**β.

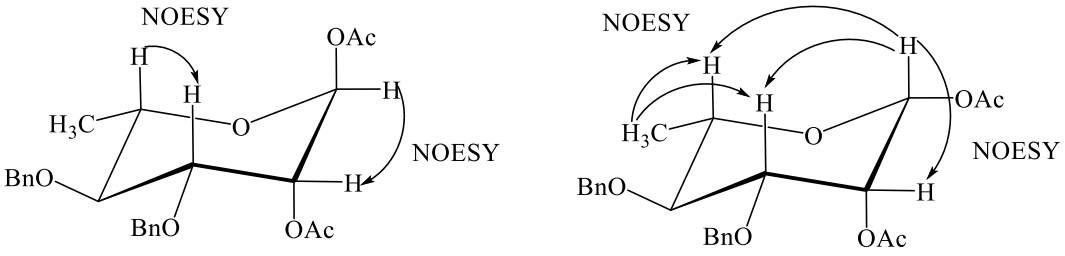
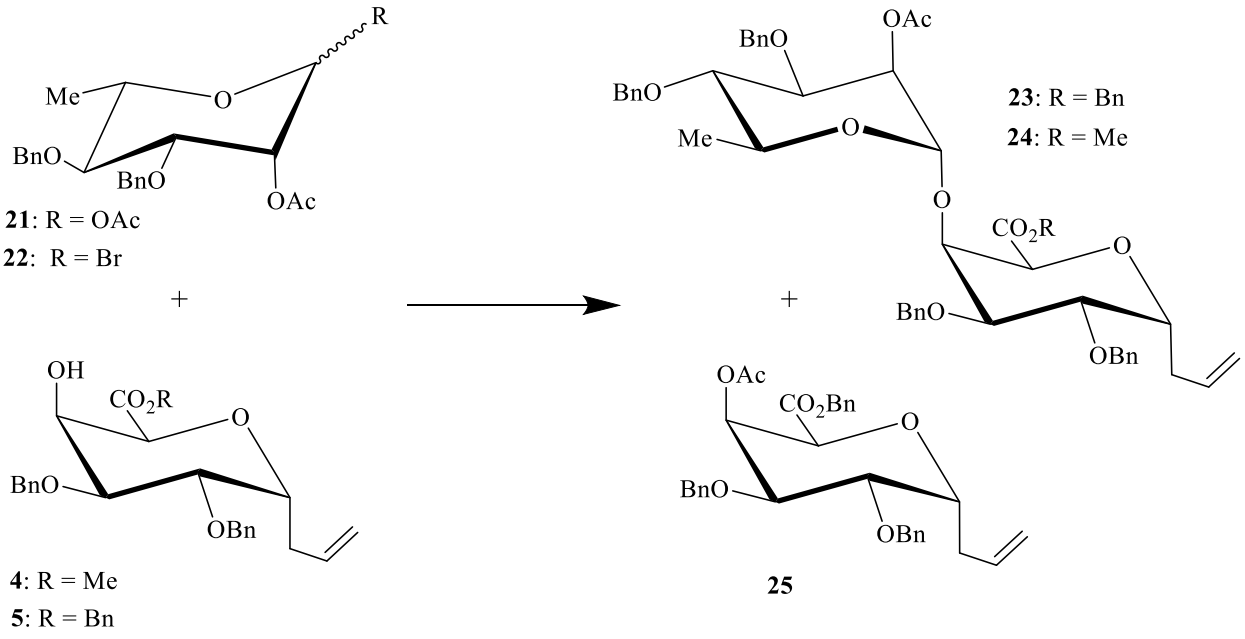


Figure 3. NOESY proton correlation of compounds **21**α and **21**β.

As shown in Scheme 5, the rhamnopyranose donors **21**αβ were coupled with the C-glycoside galacturonate acceptors **4** in a ratio of 1.1:1 in the presence of trimethylsilyl trifluoromethanesulfonate.[10-12] This coupling produced the desired α-(1→4)-coupled disaccharide **23** in 18% yield, **21**α/β (donors) in 26% yield, and the accompanying transesterfication[21,22] product of the acceptor **25** in 23% yield. To improve the yield of the disaccharide **23**, the bromide donor **22** was synthesized from compounds **21**α/β by the reaction with oxalyl bromide in dry dichloromethane to give the bromosugar **22** (Scheme 4) in 95% yield.[3,11] Compound **22** was unstable on storage and was used directly without further purification.



Scheme 5

The coupling of compounds **4** and **5** with **22** (Scheme 4) in the presence of 2,6-di-*tert*-butyl-4-methylpyridine and silver trifluoromethanesulfonate[3,11] for 2 h at –70 ºC gave the desired disaccharides **23** and **24** in 54% and 56% yields, respectively. The stereochemistry of the *O*-

glycosidic linkages were assigned based on the geminal coupling constants $J_{C\text{-}1,H\text{-}1}$ = 170.46 Hz for disaccharide **23** and $J_{C\text{-}1,H\text{-}1}$ = 171.5 Hz for disaccharide **24**.[3] In addition, all other analytical data of the disaccharides **23** and **24** supported the proposed structures.

Conclusions

Introduction of the trichloroacetimidate group at the anomeric center of **9**[23,24] was reexamined, and the resulting trichloroacetimidate derivatives **13** were obtained in 98% total yield (α/β, 3:1). Trichloroacetimidate derivatives **14** were synthesized in 76% total (α/β, 2:1) yield and incorporated in our program as glycosyl donors.

The (1→4)-linked disaccharide derivatives **15** were obtained in 53% total yield with low stereoselectivity[3,23,24] (α,β 3:1). The α-linked disaccharide **15** and its β-linked anomer were successfully separated, and characterized by the aid of NMR spectroscopy. The change of the methyl ester to a benzyl ester in both glycosyl acceptor and donor had no strong influence on the outcome of the glycosylation. Disaccharide derivatives **16** were obtained in 44% total yield (α/β, 2:1). Separation of **16**α and **16**β was cumbersome and NMR investigation could be done only with enriched fractions.

Glycosyl derivatives **21**α/β and the corresponding bromide[25,26] **22** were prepared as glycosyl donors in high yield from the orthoacetate **18**. Glycosylation reaction of C-allylated galacturonate **5** with rhamnose acetates **21**α,β gave only a moderate yield (18%) compared with results for the glycosylation of *O*-allylated galacturonates[3]. In order to improve the yield, the more reactive bromide **22** was used. Glycosylation of acceptors **4** and **5** with **22** gave the α-linked disaccharides **23** and **24** in 54% and 56% yields, respectively.

Experimental Section

General. Melting points were determined with a Boetius micro apparatus BHMK 05 (Rapido, Dresden) and are uncorrected. Optical rotations were measured for solutions in a 2-cm cell with an automatic polarimeter " Gyromat " (Dr. Kernchen Co.). Infrared analysis was recorded with an FT-IR spectrometer Nicolet (Protégé system 460). NMR spectra were recorded with Bruker Avance-500 spectrometers, (500.15 MHz for ^{1}H, and 125.7 MHz for ^{13}C). The calibration of spectra was carried out by means of solvent peaks ($CDCl_3$: δ ^{1}H 7.25 ppm, δ ^{13}C 77.00 ppm; CD_3OD: δ ^{1}H 2.65 ppm, δ ^{13}C 40.45 ppm). Chemical shifts are given relative to the signal of internal standard tetramethylsilane (δ = 0). First order chemical shifts and coupling constants were obtained from one-dimensional spectra, and assignment of proton resonance was based on COSY, COR, and NOSY experiments. For the determination of the molecular structure of compound **20** by X-ray diffraction, an X8Apex diffractometer system device was used with area detector and Mo-K_α radiation. A graphite monochromator system was used. The data collections

were performed in routine ω-scan at the Bruker P4 system, in ω/2θ–scans at the MACH3 and ϕ- and ω-scans at the area detector system. For the data collections on the four-circle diffractometer systems, suitable crystals were checked by rotational photos prior to the data collections. On the area detector system the crystal quality was evaluated by checking the reciprocal space plots after the collection of sixty frames. The structure solutions were obtained with the Bruker SHELXTL software. The refinement calculations were carried out by the full-matrix least-squares method of SHELXL-97 (G.M.Sheldrick, SHELXL-97. programs for Crystal Structure Determinations, University of Göttingen, 1997). The non-hydrogen atoms were refined anisotropically while the hydrogen atoms were refined using the riding model. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1RZ, UK (via e-mail: TUdeposit@ccdc.cam.ac.uk, or from the url address www.ccdc.cam.ac.uk/conts/retrieving.html)

Thin-layer chromatography (TLC) on pre-coated plates of silica gel (Merck Silica gel 60, FB254B, 0.25 mm) was performed with the following eluent systems (v/v): (A) 3:1, (B) 2:1, (C) 3:2, (D) 1:1, (E) 1:2 heptane-ethyl acetate, (F) 5:1, (G) 3:1 toluene-ethyl acetate, (H) 1:1:1:0.1 toluene-acetone-isopropanol-formic acid, (I) 4:2:2:1 toluene-ethyl acetate-ethanol-acetic acid, (J) 7:1, (K) 6:1 chloroform-methanol, (L) 1:1:0.05% toluene-ethyl acetate-pyridine. The spots were made visible by spraying with methanolic 10 % H_2SO_4 solution and charring them for 3-5 min with a heat gun. Detection of benzyl derivatives was achieved by UV illumination. Preparative flash chromatography, MPLC and HPLC chromatography were performed by elution from columns of slurry-packed Silica Gel 60 (Merck, 40-63 μm) and Nucleosil 100-7 (Knauer, 7.0 μm), respectively. All solvents and reagents were purified and dried according to standard procedures[26]. After classical work up of the reaction mixtures, the organic layers as a rule, were dried over $MgSO_4$, and then concentrated under reduced pressure (rotary evaporator).

Benzyl 4-*O*-acetyl-1-*O*-allyl-2,3-di-*O*-benzyl-β-D-galactopyranuronate (**10**). To a stirred solution of compound **8** (850 mg, 1.68 mmol) in pyridine (16.85 mL) was added acetic anhydride (8.42 mL) at 0 ºC. After 3 h at ambient temperature (TLC eluent D, R_f 0.67), the mixture was poured into ice-water (100 mL). The aqueous layer was extracted with chloroform (2 × 45 mL). The combined organic extracts were washed with cold aqueous 1 % hydrochloric acid (35 mL), ice-water (35 mL), and cold saturated aqueous $NaHCO_3$ (35 mL), then dried and concentrated. The residue was purified by MPLC (eluent A) to give **10** (830 mg, 98%) as colorless syrup: $[\alpha]_D^{21}$ + 21.7 (*c* 1.0, chloroform); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.97 (OCOC*H*$_3$), 3.63 (dd, 1H, $J_{3,4}$ 3.5 Hz, H-3), 3.70 (dd, 1H, $J_{2,3}$ 9.8 Hz, H-2), 4.18 (d, 1H, $J_{4,5}$ 1.2 Hz, H-5), 4.17 – 4.21 (m, 2H, OC*H*$_2$CHCH$_2$), 4.48 (d, 1H, $J_{1,2}$ 7.8 Hz, H-1), 4.55 (d, 1H, *J* 11.5 Hz, OC*H*$_2$C$_6$H$_5$), 4.74 (d, 1H, *J* 11.0 Hz, OC*H*$_2$C$_6$H$_5$), 4.78 (d, 1H, *J* 11.5 Hz, OC*H*$_2$C$_6$H$_5$), 4.92 (d, 1H, *J* 11.0 Hz, OC*H*$_2$C$_6$H$_5$), 5.17 (d, 1H, *J* 12.0 Hz, OC*H*$_2$C$_6$H$_5$), 5.24 (d, 1H, *J* 12.0 Hz, OC*H*$_2$C$_6$H$_5$), 5.21 - 5.25 (m, 1H, OCH$_2$CHC*H*$_2$), 5.34 - 5.39 (m, 1H, OCH$_2$CHC*H*$_2$), 5.82 (dd, 1H, $J_{4,5}$ 1.2 Hz, H-4), 5.98 (m, 1H, OCH$_2$C*H*CH$_2$), 7.25 – 7.44 (m, 15H, OCH$_2$C$_6$H$_5$); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 20.53 (CO*C*H$_3$), 67.39 (*C*H$_2$C$_6$H$_5$), 67.58 (C-4), 70.39 (*C*H$_2$C$_6$H$_5$), 72.23 (*C*H$_2$C$_6$H$_5$), 72.31 (C-

5), 75.32 (O*C*H$_2$CHCH$_2$), 78.17 (C-2), 78.69 (C-3), 102.19 (C-1), 117.44 (OCH$_2$*C*H=CH$_2$), 127.53, 127.65, 127.93, 128.00, 128.15, 128.32, 128.51, 128.54, 128.92, 134.89, 137.72, 138.34 (3 × *C*H$_2$C$_6$H$_5$ six signals are isochronous), 133.69 (OCH$_2$CH=*C*H$_2$), 166.53 (*C*O$_2$C$_6$H$_5$), 169.81 (*C*OCH$_3$). Anal. Calcd for C$_{32}$H$_{34}$O$_8$ (546.61): C, 70.31, H, 6.27. Found: C, 69.54, H, 6.26.

Deallylation of compound 10. Benzyl 4-*O*-acetyl-2,3-di-*O*-benzyl-α-D-galactopyranuronate (**12**). To a stirred solution of **10** (1.10 g, 1.9 mmol) in a mixture of acetic acid and water (20:1 v/v, 58.50 mL), anhydrous sodium acetate (1.6 g, 1.95 mmol) and palladium(II) chloride (1.38 g, 7.77 mmol) were added. After stirring for 4 h at 40 – 45 ºC (TLC eluent F, R$_f$ 0.48), the reaction mixture was filtered, and the solids were washed with chloroform. The combined filtrate and washings were washed with sat aq NaHCO$_3$ (3 × 50 mL), and water (2 × 50 mL), and were dried and concentrated. The residue was purified by flash chromatography (eluent F) to provide **12** (610 mg, 56%) as an amorphous yellow solid: [α]$_D^{21}$ + 29.7 (*c* 1.0, chloroform); ^{1}H NMR (500 MHz, CDCl$_3$): δ 1.89 (s, 3H, COC*H$_3$*), 3.12 (br., 1H, OH), 3.79 (dd, 1H *J*$_{2,3}$ 9.8 Hz, H-2), 3.98 (dd, 1H, *J*$_{3,4}$ 3.5 Hz, H-3), 4.53 (d, 1H, *J* 11.0 Hz, C*H$_2$*C$_6$H$_5$), 4.64 (d, 1H, *J* 11.7 Hz, C*H$_2$*C$_6$H$_5$), 4.77 (d, 1H, *J* 11.0 Hz, C*H$_2$*C$_6$H$_5$), 4.78 (d, 1H, *J* 1.5 Hz, H-5), 4.81 (d, 1H, *J* 11.7 Hz, C*H$_2$*C$_6$H$_5$), 5.20 (center of AB, 2H, *J* 12.0 Hz, C*H$_2$*C$_6$H$_5$), 5.40(d, 1H, *J*$_{1,2}$ 3.5 Hz, H-1), 5.90 (dd, 1H, *J*$_{4,5}$ 1.5 Hz, H-4), 7.40 – 7.25 (m, 15H, C$_6$*H$_5$*); ^{13}C NMR (125.7 MHz, CDCl$_3$): δ 20.54 (OCO*C*H$_3$), 67.49 (O*C*H$_2$C$_6$H$_5$), 68.43 (C-4), 69.02 (C-5), 72.17 (O*C*H$_2$C$_6$H$_5$), 73.89 (O*C*H$_2$C$_6$H$_5$), 74.94 (C-2), 75.40 (C-3), 92.14 (C-1), 127.75, 127.95, 127.98, 128.03, 128.37, 128.64, 129.10, 134.96, 137.73, 137.91 (OCH$_2$*C$_6$*H$_5$ eight signals are isochronous), 167.69 (*C*O$_2$CH$_2$C$_6$H$_5$), 169.76 (O*C*OCH$_3$). Anal. Calcd for C$_{29}$H$_{30}$O$_8$ (506.54): C, 68.76, H, 5.97. Found: C, 68.82, H, 6.03.

Introduction of the trichloroacetamidate group at the anomeric center of 11. To a solution of compound **11** (330 mg, 0.77 mmol) in dry dichloromethane (5 mL), trichloroacetonitrile (2.84 mL, 28.4 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 23 μL, 0.15 mmol) were added under argon at –20 ºC. The reaction mixture was stirred at that temperature for one hour, and then for an additional hour at room temperature (TLC eluent B; R$_{f.}$ 0.39, R$_{f.}$ 0.27). Finally, the mixture was concentrated. The residue was suspended in ethyl acetate (30 mL) and filtered over a layer of silica gel. The remaining solids were washed with ethyl acetate (3 × 8 mL); the combined filtrate and washings were dried and concentrated. The residue was purified by HPLC (eluent ethyl acetate gradient 0% → 50% in petrol ether v/v) to provide the product.

Methyl 4-*O*-acetyl-2,3-di-*O*-benzyl-1-(trichloroacetimidoyloxy)-α-D-galactopyranosyl-uronate (**13**α) (320 mg, 73%, R$_f$ 0.39), yellow syrup; [α]$_D^{22}$ + 88.9 (*c* 1.4, chloroform); ^{1}H NMR (500 MHz, CDCl$_3$) δ 2.09 (s, 3H, COC*H$_3$*), 3.74 (s, 3H, CO$_2$C*H$_3$*), 4.04 (dd, 1H, *J*$_{2,3}$ 10.0 Hz, H-2), 4.09 (dd, *J*$_{3,4}$ 3.5 Hz, H-3), 4.61 (d, 1H, *J* 11.8 Hz, C*H$_2$*C$_6$H$_5$), 4.71 (d, 1H, *J* 1.5 Hz, H-5), 4.74 (center of AB, 2H, C*H$_2$*C$_6$H$_5$), 4.78 (d, 2H, *J* 10.8 Hz, C*H$_2$*C$_6$H$_5$), 5.90 (dd, 1H, *J*$_{4,5}$ 1.5 Hz, H-4), 6.69 (d, 1H, *J*$_{1,2}$ 3.5 Hz, H-1), 7.22 – 7.35 (m, 15H, C$_6$*H$_5$*), 8.66 [s, 1H, O(C=N*H*)CCl$_3$]; ^{13}C NMR (125.7 MHz, CDCl$_3$) δ 20.55 (OCO*C*H$_3$), 52.54 (*C*O$_2$CH$_3$), 68.23 (C-4), 71.12 (C-5), 72.02 (O*C*H$_2$C$_6$H$_5$), 73.14 (O*C*H$_2$C$_6$H$_5$), 74.19 (C-2), 74.38 (C-3), 90.91 [OC(=NH)CCl$_3$], 94.38

(C-1), 127.33, 127.51, 127.95, 128.15, 128.21, 137.42, 137.92 (2 × $OCH_2C_6H_5$ five signals are isochronous), 160.43 [O*C*(=NH)CCl_3], 167.17 (*C*O_2Me), 169.89 (O*C*OCH_3).

Methyl 4-*O*-acetyl-2,3-di-*O*-benzyl-1-(trichloroacetimidoyloxy)-β-D-galactopyranosyl-uronate (**13**β) (110 mg, 25%, R_f 0.27), yellow color syrup; [α] $_D^{22}$ + 67.1(*c* 1.05, chloroform); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.14 (s, COC*H*$_3$), 3.75 (dd, 1H, $J_{3,4}$ 3.5 Hz, H-3), 3.75 (s, 3H, CO_2CH_3), 3.91(dd, 1H, $J_{1,2}$ 8.2 Hz, H-2), 4.35 (d, 1H, $J_{4,5}$ 1.5 Hz, H-5), 4.55 (d, 1H, *J* 11.5 Hz, O*CH*$_2$$C_6H_5$), 4.78 (d, 2H, *J* 11.5 Hz, O*CH*$_2$$C_6H_5$), 4.79 (d, 2H, *J* 10.8 Hz, O*CH*$_2$$C_6H_5$), 4.88 (d, 1H, *J* 10.8 Hz, O*CH*$_2$$C_6H_5$), 5.79 (d, 1H, $J_{1,2}$ 8.2 Hz, H-1), 5.84 (dd, 1H, $J_{3,4}$ 3.5 Hz, $J_{4,5}$ 1.5 Hz, H-4), 7.24 – 7.34 (m, 15H, C_6H_5), 8.73 [s, 1H, (C=N*H*)CCl_3]. ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 20.55 (OCO*C*H_3), 52.50 (CO_2CH_3), 67.25 (C-4), 72.10 (O*C*$H_2$$C_6H_5$), 73.00 (C-5), 75.15 (O*C*$H_2$$C_6H_5$), 76.61 (C-2), 78.62 (C-3), 91.92 [OC(=NH)*C*Cl_3], 97.52 (C-1), 127.55, 127.77, 128.18, 128.22, 137.26, 137.67 (2 × $OCH_2C_6H_5$ six signals are isochronous), 163.41 [O*C*(=NH)CCl_3], 168.26 (*C*O_2CH_3), 169.83 (O*C*OCH_3).

Introduction of the trichloroacetimidate group at the anomeric center of 12. To a solution of compound **12** (510 mg, 1.0 mmol) in dry dichloromethane (7 ml), trichloroacetonitrile (3.7 mL, 37 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU 30 μl, 0.20 mmol) were added under argon at -20 ºC. The reaction mixture was stirred at that temperature for one hour, and then for an additional hour at room temperature (TLC eluent F; $R_{f.}$ 0.77, $R_{f.}$ 0.73). Finally, the mixture was concentrated; the residue was suspended in ethyl acetate (30 mL) and filtered over a layer of silica gel. The remaining solids were washed with ethyl acetate (3 × 8 mL), the combined filtrate and washings were dried and concentrated. The residue was purified by HPLC (eluent ethyl acetate gradient 0% → 50% in petrol ether v/v) to provide **14**α (R_f 0.77, 210 mg, 40%), **14**β (R_f 0.73, 100 mg, 19%), and α/β mixture (90 mg, 17%).

Benzyl 4-*O*-acetyl-2,3-di-*O*-benzyl-1-(trichloroacetimidoyloxy)-α-D-galactopyranosyl-uronate (**14**α): [α]$_D^{21}$ + 70.0 (*c* 1.0, chloroform); 1H NMR (500 MHz, $CDCl_3$) δ 1.87 (s, 3H, COC*H*$_3$), 3.97 (dd, 1H, $J_{2,3}$ 10.0 Hz, H-2), 4.03 (dd, 1H, $J_{3,4}$ 2.1 Hz, H-3), 4.54 (d, 1H, *J* 11.5 Hz, C*H*$_2$$C_6H_5$), 4.69 (center of AB, 2H, $J_{A,B}$ 11.8 Hz, C*H*$_2$$C_6H_5$), 4.70 (d, 1H, $J_{4,5}$ 1.5 Hz, H-5), 4.72 (d, 1H, *J* 11.5 Hz, C*H*$_2$$C_6H_5$), 5.12 (center of AB, 2H, $J_{A,B}$ 11.8 Hz, C*H*$_2$$C_6H_5$), 5.87 (dd, 1H, $J_{4,5}$ 1.5 Hz, H-4), 6.65 (d, 1H, $J_{1,2}$ 3.5 Hz, H-1), 7.21 - 7.36 (m, 15H, C_6H_5), 8.60 [s, 1H, (C=N*H*)CCl_3], ^{13}C NMR (500 MHz, $CDCl_3$) δ 20.46 (CO*C*H_3), 67.72 (*C*$H_2$$C_6H_5$), 68.23 (C-4), 71.20 (C-5), 72.13 (*C*$H_2$$C_6H_5$), 73.23 (*C*$H_2$$C_6H_5$), 74.27 (C-2), 74.53 (C-3), 91.01 [O(C=NH)*C*Cl_3], 94.54 (C-1), 127.41, 127.57, 127.69, 128.06, 128.22, 128.27, 128.64, 128.72, 129.16, 134.75, 137.53, 138.03 (3 × $OCH_2C_6H_5$ six signals are isochronous), 160.59 [O(*C*=NH)CCl_3], 166.69 (*C*$O_2CH_2C_6H_5$), 169.62 (O*C*OCH_3); FAB [M+Na]+: *m/z* 674. Anal.Calcd for $C_{29}H_{30}O_8$ (650.93): C, 57.20, H, 4.65, N, 2.15 Found: C, 57.64, H, 4.69, N, 2.10;

Benzyl 4-*O*-acetyl-2,3-di-*O*-benzyl-1-(trichloroacetimidoyloxy)-β-D-galactopyranosyl-uronate (**14**β): [α]$_D^{21}$ + 44.6 (*c* 1.0, chloroform); 1H NMR (500 MHz, $CDCl_3$) δ 1.95 (s, 3H, COC*H*$_3$), 3.73 (dd, 1H, $J_{3,4}$ 3.5 Hz, H-3), 3.88 (dd, 1H, $J_{2,3}$ 9.8 Hz, H-2), 4.37 (d, 1H, *J* 1.5 Hz, H-5), 4.52 (d, 1H, *J* 11.5 Hz, C*H*$_2$$C_6H_5$), 4.76 (d, 1H, *J* 10.7 Hz, C*H*$_2$$C_6H_5$), 4.77 (d, 1H, *J* 11.5 Hz, C*H*$_2$$C_6H_5$), 4.87 (d, 1H, *J* 10.7 Hz, C*H*$_2$$C_6H_5$), 5.16 (center of AB, 2H, $J_{A,B}$ 12.0 Hz,

$CH_2C_6H_5$), 5.79 (d, 1H, $J_{1,2}$ 8.2 Hz, H-1), 5.85 (dd, 1H, $J_{3,4}$ 3.5 Hz, $J_{4,5}$ 1.5 Hz, H-4), 7.24 – 7.40 (m, 15H, C_6H_5), 8.72 [s, 1H, (C=N*H*)CCl_3], ^{13}C NMR (500 MHz, $CDCl_3$) δ 20.59 ($COCH_3$), 67.40 (C-4), 72.48 ($CH_2C_6H_5$), 73.17 (C-5), 75.41 ($CH_2C_6H_5$), 76.88 (C-2), 79.03 (C-3), 90.73 [(C=NH)CCl_3], 97.78 (C-1), 127.71, 127.87, 127.90, 128.11, 128.25, 128.38, 128.60, 128.64, 129.04, 134.89, 137.34, 137.92 (3 × $CH_2C_6H_5$ three signals are isochronous), 161.27 [(*C*=NH)CCl_3], 165.83 ($CO_2CH_2C_6H_5$), 169.80 ($OCOCH_3$).

Glycosylation reactions of D-galacturonate acceptors with D-galacturonate donors. A mixture of glycosyl acceptor **4** (170 mg, 0.4 mmol), glycosyl donors **12**α/β (290 mg, 0.5 mmol), and powdered activated molecular sieves (4Å, 4.0 g) was dried azeotropically with toluene, and then subjected to high vacuum for 2h. The mixture was dissolved in dry dichloromethane (8 mL), and stirred for 2 h under argon at room temperature. After cooling to -70 ºC, TMSOTf (83 μL, 0.5 mmol) was added, and stirring was continued for 3 h at that temperature. The reaction mixture was then allowed to warm-up to room temperature and stirring was continued for an additional 18 h (TLC eluent D; $R_{f.}$ 0.35, $R_{f.}$ 0.33). The reaction mixture was passed through a layer of alkaline alumina by elution with chloroform. The eluate was concentrated to (30 mL) then was washed with cold aq sat $NaHCO_3$ (2 × 15 mL), and ice-water (2 × 15 mL), dried and concentrated. The crude disaccharides were purified by HPLC (eluent ethyl acetate gradient 0% → 25% in petrol ether v/v) to yield **15**α/β (180 mg, 53%) in the ratio 3:1.

Methyl (methyl 4-*O*-acetyl-2,3-di-*O*-benzyl-α-D-galactopyranosyluronate)-(1→4)-2,3-di-*O*-benzyl-1-deoxy-1-(prop-2-enyl)-α-D-galactopyranuronate (**15**α). (120 mg, 35%) ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.02 (s, 3H, $OCOCH_3$), 2.27-2.48 (m, 2H, -CH_2CHCH_2), 3.47, 3.51 (2 × s, 6H, CO_2CH_3), 3.58-3.62 (m, 1H, H-2), 3.79-3.85 (m, 3H, H-2′, H-3′, H-3), 3.97 (dd, 1H, $J_{3,4}$ 10.5 Hz, $J_{4,5}$ 3.5 Hz, H-4), 4.24 (ddd, 1H, $J_{1,2}$ 2.5 Hz, $J_{1,Ha}$ 6.0 Hz, $J_{1,Hb}$ 8.5 Hz, H-1), 4.52-4.76 (m, 9H, H-4′, $CH_2C_6H_5$), 4.83 (d, 1H, H-5′), 5.04-5.14 (4 × m, 2H, -CH_2CHCH_2), 5.16 (d, 1H, $J_{1',2'}$ 3.5 Hz, H-1′), 5.75-5.85 (m, 1H, -CH_2CHCH_2), 7.20-7.36 (m, 20H, -$CH_2C_6H_5$); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 20.64 ($OCOCH_3$), 31.98 (-CH_2CHCH_2), 51.9, 52.2 (2 × CO_2CH_3), 68.86, 69.79, 70.89, 71.30, 71.40, 72.99, 73.16, 73.22, 73.41, 75.27, 75.30, 75.5, 76.28 [(4 × $CH_2C_6H_5$), (C2′-C5′), (C1-C5)], 98.80 (C-1′), 117.00 (-$CH_2CH=CH_2$), 134.5 (-CH_2CHCH_2), 137.68-128.45 ($CH_2C_6H_5$), 169.70, 169.80, 171.90 (3 × $COCH_3$); FAB $[M+Na]^+$: *m/z* 847.

Methyl (methyl 4-*O*-acetyl-2,3-di-*O*-benzyl-β-D-galactopyranosyluronate)-(1→4)-2,3-di-*O*-benzyl-1-deoxy-1-(prop-2-enyl)-α-D-galactopyranuronate (**15**β). (60 mg, 18%) ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.07 (s, 3H, $OCOCH_3$), 2.39 (m, 2H, -CH_2CHCH_2), 3.51-3.64 (m, 3H, H-2′, H-3′, H-4′), 3.74, 3.78 (2 × s, 6H, CO_2CH_3), 3.73-3.85 (m, 2H, H-2, H-3), 4.41 (m, 1H, H-1), 4.36 (d, 1H, *J* 11.7 Hz, $CH_2C_6H_5$), 4.44 (d, 1H, *J* 11.7 Hz, $CH_2C_6H_5$), 4.46 (d, 1H, $J_{4,5}$ 3.5 Hz, H-5), 4.52 (d, 1H, *J* 11.7 Hz, $CH_2C_6H_5$), 4.36 (center of AB, 2H, $J_{A,B}$ 12 Hz, $CH_2C_6H_5$), 4.66-4.73 (m, 2H, H-1′, H-4), 4.73 (d, 1H, *J* 11.7 Hz, $CH_2C_6H_5$), 4.77 (d, 1H, *J* 11.5 Hz, $CH_2C_6H_5$), 4.97 (d, 1H, *J* 11.5 Hz, $CH_2C_6H_5$), 5.04-5.12 (4 × m, 2H, -CH_2CHCH_2), 5.70 (d, 1H, H-5′), 5.81 (m, 1H, -CH_2CHCH_2), 7.16-7.35 (m, 20H, -$CH_2C_6H_5$); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 20.72 ($OCOCH_3$), 32.04 (-CH_2CHCH_2), 52.09, 52.41 (2 × CO_2CH_3), 67.63, 69.21, 72.09, 72.21, 72.31, 72.65, 73.50, 73.52, 74.94, 77.24, 78.32, 78.35, [(4 × $CH_2C_6H_5$), (C2′-C5′), (C1-C5)], 102.02 (C-

1′), 116.95 (-$CH_2CH=CH_2$), 134.63 (-CH_2CHCH_2), 127.09-138.20 ($CH_2C_6H_5$), 168.98, 169.95, 171.00 (3 × C=O); FAB $[M+Na]^+$: *m/z* 847.

Glycosylation reactions of D-galacturonate acceptor (5) with D-galacuronates donors (14α/β)

A mixture of glycosyl acceptor **5** (195 mg, 0.4 mmol), glycosyl donors **14**α/β (270 mg, 0.5 mmol), and powdered activated molecular sieves (4Å, 4.0 g) were dried azeotropically with toluene, and then subjected to high vacuum for 2h. The mixture was dissolved in dry dichloromethane (8 ml), and stirred for 2 h under argon at room temperature. After cooling to -70 ºC, TMSOTf (83 μL, 0.5 mmol) was added, and stirring was continued for 3 h at that temperature. The reaction mixture was then allowed to warm-up to room temperature and stirring was continued for an additional 18 h (TLC eluent F, $R_{f.}$ 0.68). The reaction mixture was passed through a layer of alkaline alumina by elution with chloroform. The eluate was concentrated to (30 mL) then was washed with cold aq sat $NaHCO_3$ (2 × 15 mL), and ice-water (2 × 15 mL), dried and concentrated. The crude disaccharides were purified by HPLC (eluent ethyl acetate gradient 0% → 25% in petrol ether v/v) to yield a mixture of **16**α/β (175 mg, 44%) in the ratio 3:1.

Benzyl (benzyl 4-*O*-acetyl-2,3-di-*O*-benzyl-α/β-D-galactopyranosyluronate)-(1→4)-2,3-di-*O*-benzyl-1-deoxy-1-(prop-2-enyl)-α-D-galactopyranuronate (**16**α/β). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.83, 1.85 [2 × s, 6H, $OCOCH_3$ (α,β)], 2.29-2.35, 2.42-2.49 [2 × m, 4H, -CH_2CHCH$_2$ (α,β)], 3.52-5.27 (m, 54H), 4.74 (d, 1H, $J_{1′,2′}$ 6.5 Hz, H-1′β), 5.01 (d, 1H, $J_{1′,2′}$ 3.2 Hz, H-1′α), 7.08-7.39 [m, 60H, -$OCH_2C_6H_5$ (α,β)]; ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 20.44, 20.47 [2 × OCOCH_3 (α,β)], 32.77, 33.33 [2 × -CH_2CHCH$_2$ (α,β)], 60.27, 66.46, 66.79, 67.23, 67.38, 71.77, 72.12, 72.53, 72.81, 73.49, 73.59, 75.05 [12 × -O$CH_2C_6H_5$ (α,β)], 67.45, 68.56, 69.77, 71.37, 72.33, 72.65, 74.34, 74.43, 75.20, 75.55, 75.84, 77.18, 78.37, 78.49 [(C-1)-(C-5) (α,β), (C-2′)-(C-5′) (α,β), 4 signals are isochronous], 99.02 (C-1′α), 102.31(C-1′β),116.80, 116.95 [2 × -CH_2CHCH_2 (α,β)], 126.86, 127.06, 127.36, 127.41, 127.63, 127.67, 127.73, 127.83, 127.88, 128.09, 128.25, 128.39, 128.48, 128.72, 128.84, 129.21, 134.53, 134.65, 134.71, 134.97, 135.25, 135.90, 137.52, 137.60, 137.91, 137.93, 138.07, 138.29, 138.55 [-CH_2CHCH_2 (α,β), -$OCH_2C_6H_5$ (α,β), 23 signals are isochronous], 166.11, 166.80, 169.59, 169.79, 169.82, 171.01 [6 × C=O (α,β)]; FAB $[M+Li]^+$: *m/z* 983. Anal.calcd for $C_{59}H_{60}O_{13}$ (977.10): C, 72.52; H, 6.19. Found: C, 72.25; H, 6.15.

2,3-Di-*O*-acetyl-1,2- *O*-(1-ethoxyethylidene)-β-L-rhamnopyranose (**18**). To a mixture of 2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl bromide[14] 17 (6.0 g, 18.9 mmol), 2,4,6-collidine (2.9 mL, 163.7 mmol), and tetrabutylammonium bromide (2.4 g, 2.4 mmol) in CH_2Cl_2 (45 mL), EtOH (anhydrous, 2.1 mL, 24 mmol) was added. The reaction mixture was stirred under argon for 9 h at room temperature (TLC eluent L, $R_{f.}$ 0.64). Chloroform (100 mL) was added; the organic solution was washed with ice-water, dried and concentrated. The excess of collidine was removed under vacuum, and the resulting syrup was purified by flash chromatography (eluent ethyl acetate gradient 0% → 25% in petrol ether - pyridine 0.05% v/v/v) to give 18 (4.4 g, 81 %): mp 86-88 ºC; $[\alpha]_D^{22}$ + 32.7 (*c* 1.0, chloroform). Lit.[82]; mp 87-88 ºC; $[\alpha]_D^{22}$ + 35.1 (*c* 0.82, chloroform).

2,3-Di-*O*-benzyl-1,2-*O*-(1-ethoxyethylidene)-β-L-rhamnopyranose (**20**). Compound **19** (4.40 g, 13.8 mmol) was dissolved in dry toluene (20 mL) and potassium hydroxide (9.60 g, powder) was added. The mixture was heated to reflux, and benzyl chloride (14.5 mL) was added dropwise. The reaction mixture was heated under reflux for 2.5 h and cooled to room temperature, and ice-water was added. The organic phase was diluted with toluene and washed with ice-water until neutral. The toluene solution was concentrated to an oil, which was then shifted to flash chromatography (eluent G, R_f 0.61) to give a syrupy product, which crystallized from petrol ether-ethyl acetate to give **20** (4.7 g, 82%) as colorless crystals: mp 76-78 ºC; $[\alpha]_D^{22}$ + 2.9 (*c* 1.0 chloroform); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.21 [t, 3H, *J* 6.9 Hz, C(OCH$_2$C*H*$_3$)CH$_3$], 1.31 (d, 3H, *J* 6.3 Hz, C*H*$_3$-5), 1.73 [s, 3H, C(OCH$_2$CH$_3$)C*H*$_3$], 3.31 (m, 1H, H-5), 3.48 (t, 1H, $J_{4,5}$ 18.29 Hz, H-4), 3.55 [m, 2H, C(OC*H*$_2$CH$_3$)CH$_3$], 3.67 (dd, 1H, $J_{3,4}$ 9.15 Hz, H-3), 4.36 (dd, 1H, $J_{2,3}$ = 4.1 Hz, H-2), 4.67 (d, 1H, *J* 11.03 Hz, C*H*$_2$C$_6$H$_5$), 4.76 (s, 2H, C*H*$_2$C$_6$H$_5$), 4.95 (d, 1H, *J* 11.04 Hz, C*H*$_2$C$_6$H$_5$), 5.26 (d, 1H, $J_{1,2}$ 2.52 Hz, H-1), 7.29 – 7.39 (m, 10H, C$_6$*H*$_5$); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 15.30 [C(OCH$_2$*C*H$_3$)CH$_3$], 18.00 (*C*H$_3$-5), 24.70 [C(OCH$_2$CH$_3$)*C*H$_3$], 58.00 [C(O*C*H$_2$CH$_3$)CH$_3$], 70.30 (C-5), 72.30 (*C*H$_2$C$_6$H$_5$), 75.50 (*C*H$_2$C$_6$H$_5$), 77.03 (C-2), 79.10 (C-3), 79.60 (C-4), 97.30 (C-1), 123.60 [*C*(OEt)CH$_3$], 127.80, 127.90, 128.00, 128.10, 128.40, 128.50, 137.90, 138.30 (C$_6$H$_5$ four signals are isochronous). Anal.Calcd for $C_{24}H_{30}O_6$ (414.49): C, 69.54; H, 7.30. Found: C, 69.17; H, 7.33.

Crystal data. Mol. formula $C_{24}H_{30}O_6$; Formula weight: 414.48; temperature: 173(2) K; wavelength: 0.71073 Å; crystal system: Orthorhombic; space group (H.-M.): $P2_12_12_1$; space group (Hall): P 2ac 2ab; Unit cell dimensions:a = 10.4095(9) Å, α = 90°, b = 11.4518(11) Å, β= 90°, c = 18.9505(13) Å, γ = 90°; volume: 2259.0(3) Å^3; Z = 4; density (calculated): 1.219 Mg/m^3; absorption coefficient : 0.087 mm^{-1} ; F(000): 888; crystal size: 0.60 × 0.40 × 0.15 mm^3; Θ range for data collection: 2.91 to 22.49°; index ranges: -11 ≤ h ≤ 11, -12≤ k ≤ 12, -18≤ l ≤ 20; reflections collected: 13542; independent reflections: 2935 [R(int) = 0.0303]; completeness to Θ = 22.49° : 98.8 %; absorption correction: none; max. and min. transmission: 0.9871 and 0.9498; refinement method: full-matrix least-squares on F2; data / restraints / parameters: 2935 / 6 / 312; goodness-of-fit on F2: 1.113; final R indices: [I>2σ(I)]; R1 = 0.0622, wR2 = 0.1695; R indices (all data): R1 = 0.0658, wR2 = 0.1717; absolute structure parameter: 0(2); extinction coefficient : 0.020(3) ; largest diff. peak and hole: 0.183 and -0.195 e.Å^{-3}.

Hydrolysis of compound 20. 2,3-Di-*O*-benzyl-1,2-*O*-(1-ethoxyethylidene)-β-L-rhamno-pyranose. Compound **20** (4.4 g, 10.61 mmol) was hydrolysed by sequential treatment with 70% aqueous acetic acid (28 mL) at room temperature for 7 min (TLC eluent K, R_f 0.52). The solution was then concentrated and acetic acid in the syrupy residue was removed by co-evaporation with toluene. The ^{1}H NMR spectrum indicated the product to be essentially pure. Without further purification, the crude syrupy residue was dissolved in dry pyridine (106.5 mL). Acetic anhydride (53 mL) was added at 0 ºC and the reaction mixture stirred at room temperature for 1h (TLC eluent I, R_f 0.71). The mixture was poured into ice-water and the aqueous layer extracted with chloroform. The combined organic extracts was washed with cold 1% HCl, ice-water, cold

sat aq $NaHCO_3$, then again with ice-water, dried and concentrated. The syrupy residue was purified by flash chromatography (eluent A).

1,2-Di-*O*-acetyl-3,4-di-*O*-benzyl-α-L-rhamnopyranose (**21**α). Colourless amorphous solid (3.01 g, 66%): $[\alpha]_D^{21}$ – 20.8 (*c* 1.0, chloroform); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.34 (d, 3H, *J* 6.31 Hz, C*H*$_3$-5), 2.08, 2.17 (2s, 6H, OCOC*H*$_3$), 3.49 (t, 1H, $J_{4,5}$ 9.5 Hz, H-4), 3.81 (m, 1H, H-5), 3.94 (dd, 1H, $J_{3,4}$ 9.46 Hz, H-3), 4.55 (d, 1H, *J* 11.04, C*H*$_2$C$_6$H$_5$), 4.65 (d, 1H, *J* 10.92, C*H*$_2$C$_6$H$_5$), 4.75 (d, 1H, *J* 11.04, C*H*$_2$C$_6$H$_5$), 4.93 (d, 1H, *J* 10.73, C*H*$_2$C$_6$H$_5$), 5.36 (dd, 1H, $J_{2,3}$ 2.84, H-2), 6.01 (d, 1H, $J_{1,2}$ 1.89 Hz, H-1), 7.29 – 7.37 (m, 10H, CH$_2$C$_6$*H*$_5$); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 17.95 (*C*H$_3$-5), 20.81, 20.87 (2 × CO*C*H$_3$), 67.80 (C-2), 70.00 (C-5), 71.90, 75.50 (2 × CH$_2$C$_6$H$_5$), 77.60 (C-3), 79.50 (C-4), 91.11 (C-1), 127.76, 127.89, 127.90, 128.00, 128.40, 137.70, 138.20 (CH$_2$*C*$_6$H$_5$ seven signals are isochronous), 168.40, 169.90 (2 × *C*OCH$_3$). Anal. calcd. for $C_{24}H_{28}O_7$ (428.47): C, 67.28; H, 6.59. Found: C, 67.29; H, 6.59.

1,2-Di-*O*-acetyl-3,4-di-*O*-benzyl-β-L-rhamnopyranose (**21**β). Colorless syrup (0.62 g, 14%): $[\alpha]_D^{21}$ + 29.2 (*c* 1, chloroform); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.38 (d, 3H, *J* = 5.99 Hz, C*H*$_3$-5), 2.09, 2.22 (2s, 6H, OCOC*H*$_3$), 3.44 (t, 1H, $J_{4,5}$ 9.5 Hz, H-4), 3.48 – 3.55 (m, 1H, H-5), 3.70 (dd, 1H, $J_{3,4}$ 9.15 Hz, H-3), 4.50 (d, 1H, *J* 11.04, C*H*$_2$C$_6$H$_5$), 4.62 (d, 1H, *J* 11.03, CH$_2$C$_6$H$_5$), 4.72 (d, 1H, *J* 11.03, C*H*$_2$C$_6$H$_5$), 4.92 (d, 1H, *J* 11.04, C*H*$_2$C$_6$H$_5$), 5.61 (dd, 1H, $J_{2,3}$ 3.47, H-2), 5.73 (d, 1H, $J_{1,2}$ 1.27 Hz, H-1), 7.27 – 7.37 (m, 10H, C$_6$*H*$_5$); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 17.80 (*C*H$_3$-5), 20.70, 20.90 (2 × CO*C*H$_3$), 67.50 (C-2), 71.50, 75.40 (2 × *C*H$_2$C$_6$H$_5$), 72.70 (C-5), 79.20 (C-3), 79.60 (C-4), 91.10 (C-1), 127.70, 127.80, 127.90, 128.00, 128.30, 128.40, 137.40, 138.10 (CH$_2$*C*$_6$H$_5$ six signals are isochronous), 168.60, 170.50 (2 × *C*OCH$_3$).

2-*O*-Acetyl-1-bromo-3,4-di-*O*-benzyl-α-L-rhamnopyranose (**22**). To a solution of 21α/β (500 mg, 1.17 mmol) in dry dichloromethane (7 mL), was added oxalyl bromide[70,78] (162 μl) was added under argon at -40 ºC. After an additional one hour at that temperature, the reaction mixture was kept at room temperature for one hour (TLC eluent F, R_f 0.75). The mixture was concentrated and repeatedly co-evaporated with toluene to give crude product of 20 (500 mg, 96 %). The compound 20 was unstable for storage and was used directly without further purification.

Benzyl (2-*O*-acetyl-3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→4)-2,3-di-*O*-benzyl-1-deoxy-1-(prop-2-enyl)-α-D-galactopyranuronate (**23**). *(a) Via* **21**. Glycosyl acceptor 5 (0.4 mmol), glycosyl donor **19** (α/β) (0.5 mmol), and powdered activated molecular sieves (4Å, 4.0 g) were dried azeotropically with toluene, and then subjected to high vacuum for 2h. The mixture was dissolved in dry dichloromethane (8 mL), and the reaction mixture was stirred for 2 h under argon at room temperature in the dark. After cooling to -70 ºC, TMSOTf (83 μl, 0.5 mmol) was added, and stirring was continued for 3 h at that temperature. The reaction mixture was then allowed to warmup to room temperature and stirring was continued for an additional 18 h (TLC eluent F). The reaction mixture was passed through a layer of alkaline alumina by elution with chloroform. The eluate was concentrated to 30 mL and then washed with cold aq sat $NaHCO_3$ (2 × 15 mL), ice-water (2 × 15 mL), dried and concentrated. The crude residue was purified by HPLC (eluent ethyl acetate gradient 0% → 25% in petrol ether v/v) to give disaccharide **23** (R_f

0.55, 18%), donor 21 (R_f 0.48, 26%), and accompanying transesterification product of the acceptor **5** (R_f 0.68, 23%). The NMR data of **25** supported the chemical structure shown in Scheme 4.

(b) Via **22**. Glycosyl acceptor **5** (0.4 mmol), glycosyl donor **22** (0.5 mmol), powdered activated molecular sieves (4Å, 4.0 g), and 2,6-di-*tert*-butyl-4-methylpyridine (0.6 mmol) were dried under high vacuum at ambient temperature for 2h. The solids were then suspended in dry dichloromethane (8 mL), and the reaction mixture was stirred for 2 h under argon at room temperature in the dark. Subsequently, after chilling to -70 ºC, silver trifluoromethanesulfonate (141 mg, 0.55 mmol) was added. After stirring for 2h at that temperature, the chilling was terminated and the mixture was stirred for 18h at ambient temperature (TLC eluent B, R_f 0.54). The reaction mixture was then passed through a layer of alkaline alumina by elution with chloroform. The eluate was concentrated to (30 mL) and then washed with cold aq sat $NaHCO_3$ (2 × 15 mL), ice-water (2 × 15 mL), dried and concentrated. The residue was purified by HPLC (eluent ethyl acetate gradient 0% → 25% in petrol ether v/v) to give the desired disaccharide **23** in 54% yield as a colourless syrup, ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.28 [d, 3H, *J* 6.4 Hz, C*H*$_3$ (Rha)], 2.13 [s, 3H, OCOC*H*$_3$ (Rha)], 2.41 (m, 1H, C*H*$_2$CHCH$_2$), 3.40 [t, 1H, $J_{2,3}$ = $J_{3,4}$ = 9.5 Hz, H-4 (Rha)], 3.64 [s, 3H, CO_2CH_3 (GalA)], 3.71 - 3.78 [m, 2H, H-3 (GalA), H-5 (Rha)], 3.83 [dd, 1H, $J_{1,2}$ 4.5 Hz, $J_{2,3}$ 7.3 Hz, H-2 (GalA)], 3.88 [dd, 1H, $J_{2,3}$ 3.3 Hz, $J_{3,4}$ 9.5 Hz, H-3 (Rha)], 4.28 [d, 1H, $J_{4,5}$ 3.5 Hz, H-5 (GalA)], 4.37 - 4.41 [m, 1H, H-1 (GalA)], 4.45 [dd, 1H, $J_{3,4}$ 2.5 Hz, H-4 (GalA)], 4.47 (d, 1H, *J* 11.6 Hz, OC*H*$_2$C$_6$H$_5$), 4.57 - 4.68 (m, 5H, OC*H*$_2$C$_6$H$_5$), 4.73 (d, 1H, *J* 12.0 Hz, OC*H*$_2$C$_6$H$_5$), 4.91 (d, 1H, *J* 11.3 Hz, OC*H*$_2$C$_6$H$_5$), 5.05 [d, 1H, $J_{1,2}$ 1.5 Hz, H-1 (Rha)], 5.05 - 5.14 (4m, 2H, CH$_2$CH=C*H*$_2$), 5.45 [dd, 1H, $J_{1,2}$ 1.8 Hz, $J_{2,3}$ 3.3 Hz, H-2 (Rha)], 5.83 (m, 1H, CH$_2$C*H*=CH$_2$), 7.23 - 7.36 (m, 20H, OCH$_2$C$_6$*H*$_5$); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 17.95 [*C*H$_3$ (Rha)], 21.06 [OCO*C*H$_3$ (Rha)], 31.61 (*C*H$_2$CH=CH$_2$), 51.96 (CO_2CH_3), 68.43 [C-5 (Rha)], 69.02 [C-2 (Rha)], 71.67 [C-5 (GalA)], 71.70 (O*C*H$_2$C$_6$H$_5$), 72.89 (O*C*H$_2$C$_6$H$_5$), 72.97 [C-1 (GalA)], 73.38 (O*C*H$_2$C$_6$H$_5$), 73.70 [C-4 (GalA)], 74.93 (O*C*H$_2$C$_6$H$_5$), 76.01 [C-2 (GalA)], 76.55 [C-3 (GalA)], 77.63 [C-3 (Rha)], 79.69 [C-4 (Rha)], 98.26 [C-1 (Rha], 116.93 (CH$_2$CH=*C*H$_2$), 127.42, 127.54, 127.59, 127.66, 127.82, 127.91, 128.00, 128.05, 128.08, 128.19, 128.29, 128.38, 128.43, 137.95, 138.05, 138.08, 138.76 (OCH$_2$*C*$_6$H$_5$ seven signals are isochronous), 134.62 (CH$_2$*C*H=CH$_2$), 169.07 [*C*O$_2$CH$_3$(GalA)], 170.06 [O*C*O$_3$CH$_3$(Rha)]; m/z 879.37216 [M+Na]$^+$. Calc. For $C_{52}H_{56}O_{11}$ M+Na: m/z, 879.37201. Anal.calcd for $C_{52}H_{56}O_{11}$ (856.99): C, 72.88; H, 6.59. Found: C, 72.70; H, 6.54.

Methyl (2-*O*-acetyl-3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→4)-2,3-di-*O*-benzyl-1-deoxy-1-(prop-2-enyl)-α-D-galactopyranuronate (**24**)

Glycosyl acceptor **4** (0.4 mmol), glycosyl donor **22** (0.5 mmol), powdered activated molecular sieves (4 Å, 4.0 g), and 2,6-di-*tert*-butyl-4-methylpyridine (0.6 mmol) were dried under high vacuum at ambient temperature for 2h . The solids were then suspended in dry dichloromethane (8 mL), and the reaction mixture was stirred for 2 h under argon at room temperature in the dark. Subsequently, after chilling to -70 ºC, silver trifluoromethanesulfonate (141 mg, 0.55 mmol) was added. After stirring for 2h at that temperature, the chilling was terminated and the mixture was

stirred for 18h at ambient temperature (TLC eluent F, R_f 0.77). The reaction mixture was then passed through a layer of alkaline alumina by elution with chloroform. The eluate was concentrated to (30 mL) and then washed with cold aq sat $NaHCO_3$ (2 × 15 mL), ice-water (2 × 15 mL), dried and concentrated. After HPLC chromatography (eluent ethyl acetate gradient 0% → 25% in petrol ether v/v) the desired disaccharide **24** was obtained in 57% yield as a colorless syrup; $[\alpha]_D^{21}$ + 29.6 (*c* 1.0, in chloroform); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.28 [d, 3H, *J* 6.4 Hz, C*H*$_3$ (Rha)], 2.13 [s, 3H, OCOC*H*$_3$ (Rha)], 2.41 (m, 1H, C*H*$_2$CH=CH$_2$), 3.40 [t, 1H, $J_{2,3}$ = $J_{3,4}$ = 9.5 Hz, H-4 (Rha)], 3.64 [s, 3H, CO_2CH_3 (GalA)], 3.71 - 3.78 [m, 2H, H-3 (GalA), H-5 (Rha)], 3.83 [dd, 1H, $J_{1,2}$ 4.5 Hz, $J_{2,3}$ 7.3 Hz, H-2 (GalA)], 3.88 [dd, 1H, $J_{2,3}$ 3.3 Hz, $J_{3,4}$ 9.5 Hz, H-3 (Rha)], 4.28 [d, 1H, $J_{4,5}$ 3.5 Hz, H-5 (GalA)], 4.37-4.41 [m, 1H, H-1 (GalA)], 4.45 [dd, 1H, $J_{3,4}$ 2.5 Hz, H-4 (GalA)], 4.47 (d, 1H, *J* 11.6 Hz, OC*H*$_2$C$_6$H$_5$), 4.57-4.68 (m, 5H, OC*H*$_2$C$_6$H$_5$), 4.73 (d, 1H, *J* 12.0 Hz, OC*H*$_2$C$_6$H$_5$), 4.91 (d, 1H, *J* 11.3 Hz, OC*H*$_2$C$_6$H$_5$), 5.05 [d, 1H, $J_{1,2}$ 1.5 Hz, H-1 (Rha)], 5.05 - 5.14 (4m, 2H, CH$_2$CH=C*H*$_2$), 5.45 [dd, 1H, $J_{1,2}$ 1.8 Hz, $J_{2,3}$ 3.3 Hz, H-2 (Rha)], 5.83 (m, 1H, C*H*$_2$CH=CH$_2$), 7.23 - 7.36 (m, 20H, OCH$_2$C$_6$*H*$_5$); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 17.95 [*C*H$_3$ (Rha)], 21.06 [OCO*C*H$_3$ (Rha)], 31.61 (*C*H$_2$CH=CH$_2$), 51.96 (CO_2*C*H$_3$), 68.43 [C-5 (Rha)], 69.02 [C-2 (Rha)], 71.67 [C-5 (GalA)], 71.70 (O*C*H$_2$C$_6$H$_5$), 72.89 (O*C*H$_2$C$_6$H$_5$), 72.97 [C-1 (GalA)], 73.38 (OCH$_2$C$_6$H$_5$), 73.70 [C-4 (GalA)], 74.93 (O*C*H$_2$C$_6$H$_5$), 76.01 [C-2 (GalA)], 76.55 [C-3 (GalA)], 77.63 [C-3 (Rha)], 79.69 [C-4 (Rha)], 98.26 [C-1 (Rha], 116.93 (CH$_2$CH=*C*H$_2$), 127.42, 127.54, 127.59, 127.66, 127.82, 127.91, 128.00, 128.05, 128.08, 128.19, 128.29, 128.38, 128.43, 137.95, 138.05, 138.08, 138.76 (OCH$_2$*C*$_6$H$_5$ seven signals are isochronous), 134.62 (CH$_2$*C*H=CH$_2$), 169.07 [*C*O$_2$CH$_3$(GalA)], 170.06 [O*C*OCH$_3$(Rha)]; m/z 803.34023 $[M+Na]^+$. Calc. for $C_{46}H_{52}O_{11}Na$: *m/z*, 803.34076. Anal.calcd for $C_{46}H_{52}O_{11}$ (780.90): C, 70.75; H, 6.71. Found: C, 70.50; H, 6.54.

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7657 Graphical Abstract

_C_-Glycoside D-galacturonates suitable as glycosyl acceptors for the synthesis of allyl _C_-homo- and rhamno-galacturonan modules *Mahmoud Farouk, Dirk Michalik, Alexander Villinger, and Christian Vogel*