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Synthesis of new polyether glycodendrons as oligosaccharide mimetics

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Dedicated to Professor Dr. Joachim Thiem on the occasion of his 65th birthday

Abstract—Divalent and tetravalent glycomimetics based on polyether glycodendrons have been prepared. The branched scaffolds were decorated with galactose moieties on one hand and were elaborated into new glycodendrons of a 'mixed' type on the other, carrying both galactose and mannose moieties as biologically important sugar epitopes. All synthesized glycodendrons possess a focal point that can be employed for further derivatization and functionalization.

Keyword: Glycomimetics; Glycodendrimers; Mixed glycodendrons

1. Introduction

To mimic the complex and hyperbranched structure of oligosaccharides occurring on cell surfaces,[1] glycodendrimers and glycodendrons serve as valuable tools.[2] Their preparation is thought to be rather facile and highly flexible; however, the synthesis of such multivalent neoglycoconjugates does not always live up to expectations, as it can be laborious and limited to small scale synthesis.[3]

We have recently introduced a new class of aliphatic polyether glycodendrimers,[4] which can be easily prepared even in gram quantities. Our approach was based on chemistry reported by Fréchet and co-workers for the synthesis of aromatic polyether dendrimers.[5] This efficient strategy involves a sequence of repetitive Williamson etherifications with 3-chloro-2-chloromethyl-1-propene (methallyldichloride) and hydroboration–oxidation of the double bond with 9-BBN resulting in a convergent dendrimer synthesis.[6] Methallyldichloride serves as an activated alkenyl dihalogenide, possessing two leaving groups in allylic positions and yielding a single product no matter whether an S_N2 or S_N2' mechanism is operative. Polyether glycodendrimers are chemically robust, soluble in aqueous media and insensitive to pH changes. Furthermore, in case of possible enzymatic degradation in vivo, they lead only to nontoxic fragments.

This approach has allowed us the synthesis of glycodendrons containing two, four and eight α-mannosyl units, respectively. These compounds are of interest in a biological context and potentially also in material science. In our current studies, we are interested in further developing this chemistry regarding sugar decoration of the aliphatic polyether scaffold. We report here the extension of the polyether glycodendron chemistry to the incorporation of galactose moieties and to the synthesis of glycodendrons of a 'mixed' type, involving the scaffolding of both, mannosyl and galactose residues.

2. Results and discussion

Among many different protecting groups isopropylidene ketals have proved to be ideally compatible with the nec-

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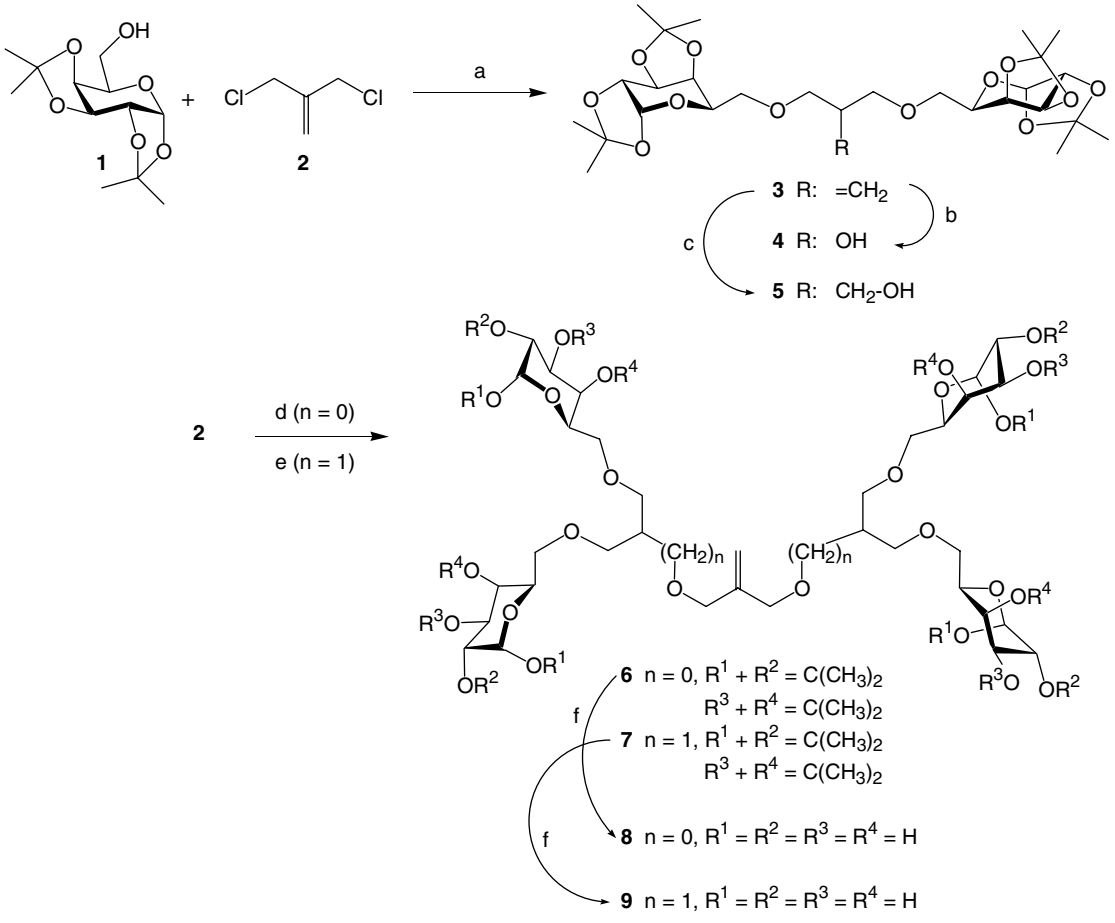
essary reaction steps involved in the dendron construction.[7] Therefore, to produce polyether glycodendrimers with galactose termini, 1,2:3,4-di-*O*-isopropylidene-galactose (**1**)[8] was employed. In the second part of this work, galactose derivative **1** was scaffolded, together with 2,3:4,6-di-*O*-isopropylidene-protected 2-hydroxyethyl mannoside **14**, to obtain polyether glycodendrons of a mixed type. This approach leads to glycomimetics in which mannose is attached to the scaffold molecule via its anomeric centre, whereas galactose is linked via its 6-position. It has to be kept in mind that the biological activity of 6-linked glycomimetics is not guaranteed and that 6-O-linked galactose does not necessarily mimic a galactose moiety, but might rather resemble another three-dimensional assembly of hydroxyl groups.

2.1. Synthesis of galactos-6-yl glycodendrons

1,2:3,4-Di-*O*-isopropylidene-galactose **1** was deprotonated with NaH in dry THF at the 6-OH group and then reacted with methallyldichloride (MDC, **2**) to give alkene **3** (Scheme 1) with two galactos-6-yl residues in 95% yield. There are two options for further derivatization of the double bond at the focal point of dimer **3**. Ozonolysis followed by reductive workup yields the secondary alcohol **4** with concomitant loss of one carbon, while submission to a hydroboration–oxidation protocol leads to primary alcohol **5**. Ozonolysis of **3** followed by reductive work-up with sodium borohydride proceeded with ease yielding the corresponding alcohol **4** in a quantitative reaction. Without any purification, this product was etherified with MDC, leading to the galactose-decorated polyether glycodendron of the next generation (**6**) as the single product in excellent yield. Deprotection of **6** employing TFA–water yielded the hydrophilic glycocluster **8**, after purification by GPC.

On the other hand, hydroboration of **3**, employing 9-BBN followed by oxidation and hydrolysis with NaOH and H_2O_2 led to **5** in 87% yield, which was in turn subjected to Williamson etherification using MDC (**2**) to yield glycodendron **7** as a more flexible analogue of tetramer **6**. Again, formation of by-products resulting from



Scheme 1. Synthesis of galactos-6-yl glycodendrons **8** and **9**. Reagents and conditions: (a) NaH, THF, 60 °C, 16 h, 95%; (b) (1) O_3; (2) $NaBH_4$, MeOH–CH_2Cl_2 (1:1), −60 °C to rt, 16 h, quant.; (c) 9-BBN, THF, 60 °C, 2 h, NaOH, H_2O_2, 0 °C→rt, 16 h, 87%; (d) **4**, NaH, THF, 60 °C, 16 h, 90%; (e) **5**, NaH, dry THF, 60 °C, 16 h, 54%; (f) TFA–water (9:1), 15 min, rt, 75%; (g) TFA–water (9:1), 15 min, rt, 73%.

partial etherification of MDC was not observed. Deprotection of the isopropylidene groups under acidic conditions led to the galactose-decorated glycodendron **9**.

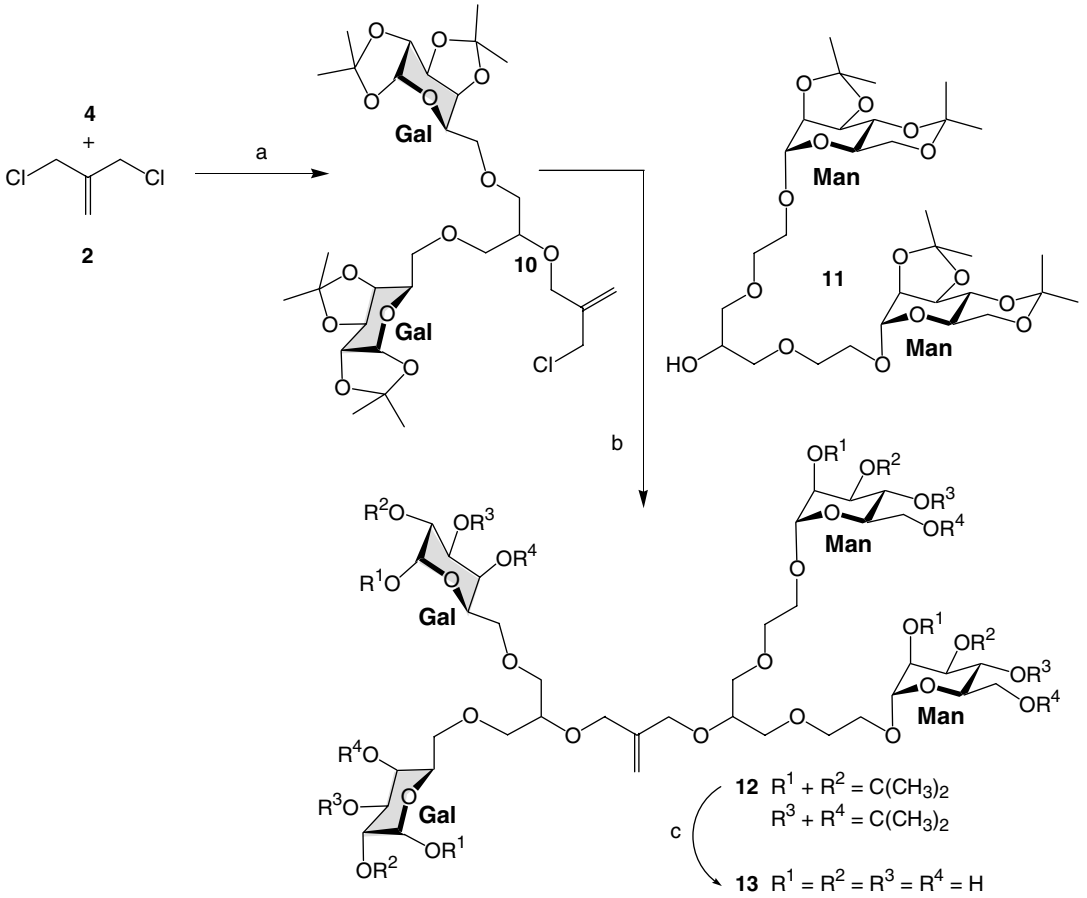
2.2. Synthesis of mixed glycodendrons

Considering the highly complex character of natural oligosaccharides, we envisaged the synthesis of polyether glycodendrons of a 'mixed' type, carrying carbohydrate moieties of different kinds. The synthetic strategy reported herein suggests two different routes for the preparation of the desired mixed glycodendrons. Starting from the bis-galactose-substituted alcohol **4** reaction with an equimolar amount of MDC (**2**) allowed the synthesis of glycodendron-functionalized allylchloride **10** (Scheme 2) in 67% yield. Etherification of **10** with the literature-known mannose-modified alcohol **11**[4] furnished **13** as a first example of a mixed type polyether glycodendron after mildly acidic deprotection.

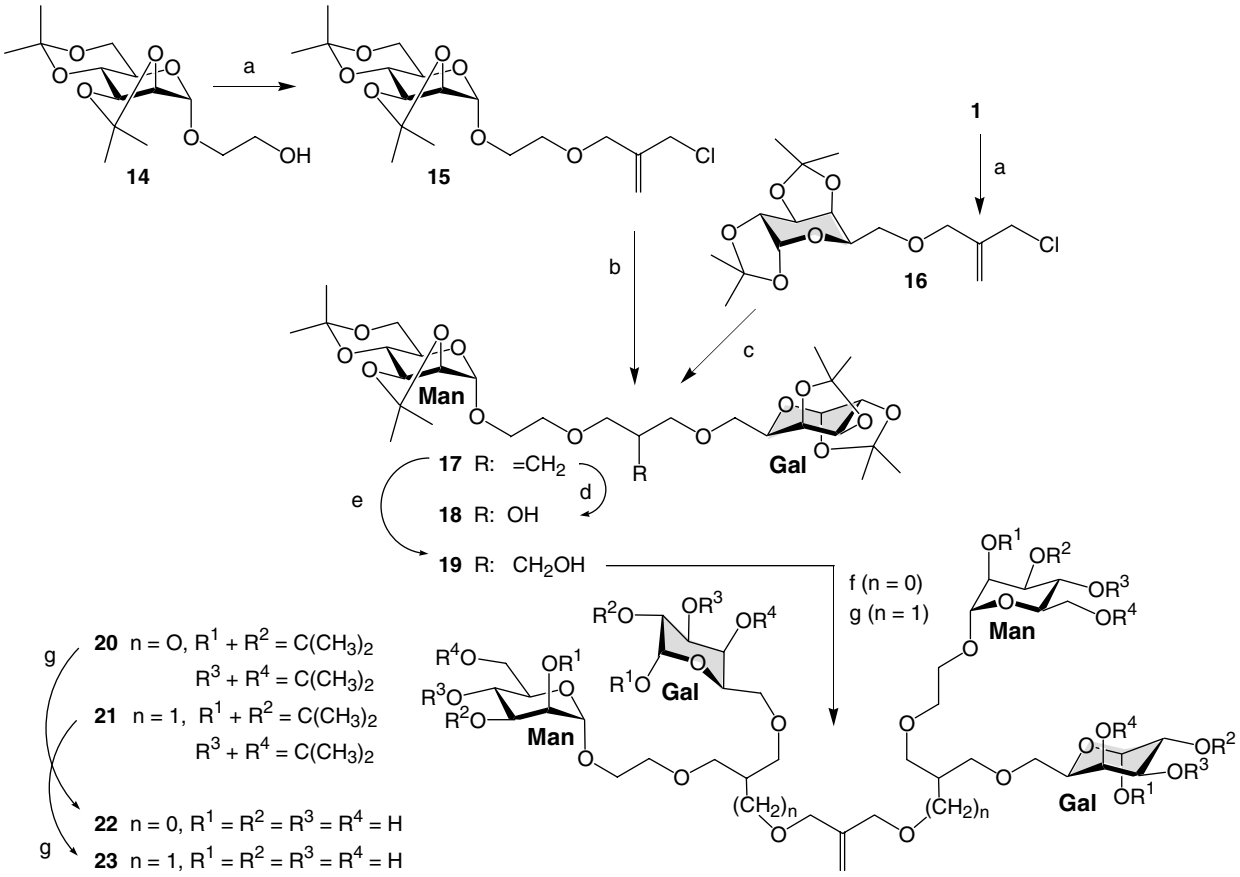
An alternative approach to mixed glycodendrons of a slightly different type started from the allylchloride-functionalized mannoside **15** or from the allylchloride-functionalized galactose derivative **16** (Scheme 3). In either case, the mixed dimer **17** could be obtained after etherification with the complementary sugar alcohol, **1** or **14**, respectively. By analogy to the procedures reported for **3**, alkene **17** could be transformed into alcohols **18** or **19**, which were used for subsequent etherification with dichloride **2** (MDC) yielding polyether glycodendrons of the second generation, **20** and **21**, respectively. Finally both tetramers were deprotected employing TFA–water mixture to yield the target compounds **22** and **23**.

3. Conclusions

We have demonstrated that the synthetic procedure for the preparation of mannose-coated polyether glycodendrons earlier reported by us could be successfully extended to allow the synthesis of galactose-decorated analogues such as **8** and **9**, as well as the preparation of the first glycodendrons of a mixed type, such as **13**, **22** and **23**. It should be kept in mind that in contrast to mannose, galactose has been linked to the branched scaffold via its 6-position. Unfortunately, we were not able to employ other protecting groups than isopropylidene ketals in this chemistry. Likewise, our attempts



Scheme 2. Preparation of the mixed glycodendron **13**. Reactions and conditions: (a) NaH, THF, 60 °C, 16 h, 67%; (b) NaH, THF, 59%; (c) TFA–water (9:1), 15 min, rt, 86%.



Scheme 3. Preparation of mixed glycodendrons **22** and **23**. Reactions and conditions: (a) NaH, MDC, THF, 60 °C, 16 h, 57% for **15**, 56% for **16**; (b) **1**, NaH, THF, 63%; (c) **14**, NaH, THF, 58%; (d) (1) O_3; (2) $NaBH_4$, MeOH–CH_2Cl_2 (1:1), −60 °C→rt, 16 h, 85%; (e) (1) 9-BBN, THF, reflux, 2 h; (2) NaOH, H_2O_2, 0 °C→rt, 16h, 90%; (f) NaH, MDC, THF, 76%; (g) NaH, MDC, THF, 75%; (h) TFA–water (9:1), 15 min, rt, 75%; (i) TFA–water (9:1), 15 min, rt, 85%.

to synthesize higher generation polyether glycodendrons did not lead to products in acceptable yields and purity. To use the di- and tetravalent glycomimetics reported herein for new biological applications, derivatization of the focal point of these compounds is necessary and currently in progress in our laboratory.

4. Experimental

4.1. General methods

All reactions requiring dry conditions were carried out under nitrogen as protective gas atmosphere (Schlenk conditions). THF was dried by distillation from sodium–potassium alloy under nitrogen atmosphere, methanol by distillation from magnesium turnings and dichloromethane by distillation from calcium hydride. Sodium hydride was used as a suspension in paraffin oil (content 60%). TLC was performed on Silica Gel 60 F_{254} plates (Merck). Detection was effected by charring with 10% sulfuric acid in ethanol, or staining with 10% phosphomolybdic acid in ethanol, both followed by heat treatment. Flash chromatography was performed on Silica Gel 60 (230–400 mesh, particle size 0.040–0.063 mm, Merck). Optical rotations were measured with a Perkin–Elmer 341 polarimeter (sodium-D-line: 589 nm, length of cell 1 dm) in the solvents mentioned for each individual experiment. NMR spectra were recorded with Bruker DRX 500 (500 MHz for ^1H, 125.47 MHz for ^{13}C), ARX 300 instruments (300 MHz for ^1H) and AV 600 (600 MHz for ^1H and 150.91 MHz for ^{13}C). Chemical shifts are given in ppm and the spectra were calibrated on respective solvent peak caused by residual proton content ($CDCl_3$, 7.24 ppm for ^1H and 77.0 ppm for ^{13}C and CD_3OD, 4.84 ppm for ^1H and 49.1 ppm for ^{13}C). Assignment of the peaks was achieved with aid of 2D NMR techniques (^1H–^1H-COSY and HSQC). Assignments that may be interchangeable are marked. ESIMS mass spectra were recorded on a Finnegan MAT 95 instrument and MALDI-TOF mass spectra were recorded on a Bruker Biflex III instrument with DHB (2,4-dihydroxy benzoic acid) in acetonitrile–water (2:1) with 0.1% TFA or CCA (α-cyano-4-hydroxycinnamic acid) in acetonitrile–water (2:1) as matrices. The mass peaks obtained for all the

samples were calibrated in reference to the $[M+H]^+$ peaks of angiotensin II (1046.54), angiotensin I (1296.69), bombesin (1619.82) and to the $[2M+H]^+$ peak of CCA (380.02). For sample preparation, a drop sample solution was first placed on the target and left to evaporate. Afterwards, the sample was covered by a drop of matrix solution for co-crystallization.

4.2. General procedures

4.2.1. Procedure A for reaction of alcohols and MDC under Williamson ether synthesis conditions. Under Schlenk conditions the alcohol component (3 equiv) was dissolved in dry THF. Sodium hydride suspension (3.1 equiv) was added and the mixture was stirred at room temperature for 5 min. Then MDC (1 equiv) was added, and the resulting mixture was heated to 60 °C for 16 h. Progress of the reaction was monitored by TLC. After completion, the reaction mixture was cooled to room temperature, quenched with water and saturated with solid potassium carbonate. The phases were separated, and the aqueous layer was extracted with five portions of EtOAc. The combined organic phases were dried over anhydrous magnesium sulfate and filtered and the solvent was removed under vacuum. The resulting crude product was purified by flash chromatography on silica gel with the solvent combinations given.

4.2.2. Procedure B for ozonolysis of the olefinic double bond and reductive work-up. A solution of the unsaturated compound in dry methanol–dichloromethane (1:1) was cooled to −60 °C and a stream of oxygen enriched with ozone was bubbled through the solution until the mixture turned blue. Completion of the reaction was verified by TLC as well. After the removal of excess ozone by bubbling first O_2 and then N_2 through the solution for 5 min each, sodium borohydride (6 equiv) was added. While stirring for 16 h the mixture was allowed to warm to room temperature. Completion of the reaction was checked by TLC. The reaction mixture was quenched by the addition of saturated ammonium chloride solution followed by stirring for 30 min. The phases were separated and the aqueous layer was extracted with five portions of EtOAc. The combined organic phases were washed with water, dried over anhydrous magnesium sulfate and filtered and the solvent removed under vacuum. The target compound was purified by flash chromatography on silica gel with the solvent combinations given.

4.2.3. Procedure C for hydroboration of the olefinic double bond. Under Schlenk conditions 9-BBN as a solution in THF ($c = 0.5$ M, 1.5 equiv) was added to a solution of the olefinic compound in dry THF. The mixture was heated to 60 °C, and progress of the reaction was monitored by TLC. After completion, the reaction mixture was cooled to 0 °C, and excess of 9-BBN was destroyed by addition of a portion of water. Afterwards, sodium hydroxide (12.5 equiv, $c = 3.0$ M) and hydrogen peroxide solution (30% in water, 49 equiv) were added and the mixture was stirred for 16 h while it was allowed to warm to room temperature. Completion of the reaction was checked by TLC (charring with 10% phosphomolybdic acid hydrate in ethanol followed by heat treatment). The mixture was saturated with solid potassium carbonate, the phases were separated, and the aqueous layer was extracted with five portions of EtOAc. The combined organic phases were dried over anhydrous magnesium sulfate and filtered, and the solvent was removed under vacuum. The resulting crude product was purified by flash chromatography on silica gel with the solvent combinations given.

4.2.4. Procedure D for deprotection of isopropylidene-protected derivatives. TFA–H_2O (9:1) was added to the isopropylidene-protected compound and the resulting mixture stirred for 15 min at room temperature. The solvent was then removed and the residue co-evaporated with toluene to remove the last of the acid and subsequently purified by GPC on Sephadex gel (H_2O).

4.3. Synthesis of galactos-6-yl glycodendrons

4.3.1. Di-(ipr-gal)-C=C (3). Reaction conditions and workup were as described in Procedure A, with isopropylidene-protected galactose **1** (3.836 g, 14.73 mmol), sodium hydride (60%) (609 mg, 15.22 mmol), MDC (0.57 mL, 4.91 mmol), dry THF (40 mL), TLC (cyclohexane–EtOAc, 1:1). Purification was achieved by flash chromatography on silica gel (cyclohexane–EtOAc, 1:1). The desired compound **3** (2.675 mg, 4.674 mmol, 95%) was obtained as colourless oil; $R_f = 0.52$ (cyclohexane–EtOAc, 1:1); $[\alpha]_D^{20}$ −62.4 (c 1.1, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ 5.53 (d, $^3J_{1,2} = 5.0$ Hz, 2H, H-1), 5.19 (s, 2H, C=CH_2), 4.60 (dd, $^3J_{2,3} = 2.4$, $^3J_{3,4} = 8.0$ Hz, 2H, H-3), 4.30 (dd, $^3J_{2,3} = 2.4$, $^3J_{1,2} = 5.0$ Hz, 2H, H-2), 4.23 (dd, $^3J_{4,5} = 1.8$, $^3J_{3,4} = 8.0$ Hz, 2H, H-4), 4.07 (d, $^2J_{CH_2,CH_2} = 13.3$ Hz, 2H, (CH_2)$_2$C=CH_2), 4.02 (d, $^2J_{CH_2,CH_2} = 13.3$ Hz, 2H, (CH_2)$_2$C=CH_2), 3.97 (ddd ≈ dt, $^3J_{4,5} = 1.8$, $^3J_{5,6} = 6.3$ Hz, 2H, H-5), 3.64 (dd, $^3J_{5,6} = 6.1$, $^2J_{6,6'} = 9.9$ Hz, 2H, H-6), 3.56 (dd, $^3J_{5,6} = 6.6$, $^2J_{6,6'} = 9.9$ Hz, 2H, H-6′), 1.54 (s, 6H, CH_3), 1.44 (s, 6H, CH_3), 1.34 (s, 6H, CH_3), 1.33 (s, 6H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$, TMS): δ 142.4 (C=CH_2), 114.0 (C=CH$_2$), 109.2 (Me–C–Me), 108.5 (Me–C–Me), 96.3 (C-1), 71.9 ((CH$_2$)$_2$C=CH_2), 71.1 (C-4), 70.6 (C-2, C-3), 68.7 (C-6), 66.7 (C-5), 26.1 (CH_3), 26.0 (CH_3), 25.0 (CH_3), 24.4 (CH_3). ESIMS: m/z: $[M+Na]^+$ calcd for $C_{28}H_{44}O_{12}$, 572.2833; found, 595.2709.

4.3.2. Di-(ipr-gal)-OH (4). Reaction conditions and workup were as described in Procedure B, with Di-(ipr-gal)-C=C **3** (300 mg, 0.524 mmol), sodium borohydride (120 mg, 3.15 mmol), dry methanol–CH_2Cl_2 (1:1, 40 mL), TLC (cyclohexane–EtOAc, 1:1). The desired compound **4** (302 mg, 0.524 mmol, quant.) was obtained as colourless oil; $R_f = 0.22$ (cyclohexane–EtOAc, 1:1); $[\alpha]_D^{20}$ −61.6 (*c* 1.3, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ 5.53 (d, $^3J_{1,2} = 5.0$ Hz, 2H, H-1), 4.61 (dt ≈ dd, $^3J_{2,3} = 2.1$, $^3J_{3,4} = 7.9$ Hz, 2H, H-3), 4.32 (dd, $^3J_{2,3} = 2.4$, $^3J_{1,2} = 5.0$ Hz, 2H, H-2), 4.26 (dt ≈ dd, $^3J_{4,5} = 1.9$, $^3J_{3,4} = 8.0$ Hz, 2H, H-4), 4.01–3.96 (m, 3H, $(CH_2)_2CH$, H-5), 3.69 (dd, $^3J_{5,6} = 6.2$, $^2J_{6,6'} = 10.0$ Hz, 2H, H-6), 3.67–3.61 (m, 3H, 1H of $(CH_2)_2CH$, H-6′), 3.58 (dd, $^3J_{CH_2,CH} = 4.5$, $^2J_{CH_2,CH_2} = 10.3$ Hz, 1H, $(CH_2)_2CH$), 3.55 (dd, $^3J_{CH_2,CH} = 6.3$, $^2J_{CH_2,CH_2} = 10.3$ Hz, 1H, $(CH_2)_2CH$), 3.50 (dd, $^3J_{CH_2,CH} = 6.6$, $^2J_{CH_2,CH_2} = 10.2$ Hz, 1H, $(CH_2)_2CH$), 1.54 (s, 6H, CH_3), 1.45 (s, 6H, CH_3), 1.35 (s, 6H, CH_3), 1.33 (s, 6H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$, TMS): δ 109.3 (Me–*C*–Me), 108.6 (Me–*C*–Me), 96.3 (C-1), 72.7 ($(CH_2)_2CH$), 72.4 ($(CH_2)_2CH$), 71.1 (C-4), 70.6 (C-3), 70.5 (C-2), 69.7 (C-6), 69.0 ($(CH_2)_2CH$), 66.6 (C-5), 26.1 (CH_3), 26.0 (CH_3), 24.9 (CH_3), 24.4 (CH_3). ESIMS *m*/*z*: $[M+Na]^+$ calcd for $C_{27}H_{44}O_{13}$, 576.2782; found, 599.2700.

4.3.3. Di-(ipr-gal)-CH_2OH (5). Reaction conditions and workup were as described in Procedure C, with Di-(ipr-gal)-C=C **3** (500 mg, 0.873 mmol), 9-BBN (*c* = 0.5 M in THF) (2.62 mL, 1.31 mmol), dry THF (10 mL), H_2O_2 (30% in water) (1.31 mL, 0.39 mmol), NaOH (*c* = 3.0 M) (1.31 mL, 3.92 mmol), TLC (cyclohexane–EtOAc, 1:2). Purification was performed by flash chromatography on silica gel (cyclohexane–EtOAc, 1:2). The desired compound **5** (447 mg, 0.757 mmol, 87%) was obtained as colourless oil; $R_f = 0.34$ (cyclohexane–EtOAc, 1:2); $[\alpha]_D^{20}$ −64.3 (*c* 0.9, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ 5.53 (d, $^3J_{1,2} = 5.0$ Hz, 2H, H-1), 4.60 (dd, $^3J_{2,3} = 2.4$, $^3J_{3,4} = 7.9$ Hz, 2H, H-3), 4.31 (dd, $^3J_{2,3} = 2.4$, $^3J_{1,2} = 5.0$ Hz, 2H, H-2), 4.23 (dd, $^3J_{4,5} = 1.9$, $^3J_{3,4} = 7.9$ Hz, 2H, H-4), 3.96 (m, 2H, H-5), 3.76 (dd, $^3J_{CH_2,CH} = 5.1$, $^2J_{CH_2,CH_2} = 11.3$ Hz, 1H, CH_2OH), 3.73 (dd, $^3J_{CH_2,CH} = 4.8$, $^2J_{CH_2,CH_2} = 11.3$ Hz, 1H, CH_2OH), 3.65–3.58 (m, 7H, 3H of $(CH_2)_2CH$, H-6, H-6′), 3.53 (dd, $^3J_{CH_2,CH} = 7.0$, $^2J_{CH_2,CH_2} = 9.3$ Hz, 1H, $(CH_2)_2$-CH), 2.12 (m_c, 1H, C*H*CH_2OH), 1.54 (s, 6H, CH_3), 1.44 (s, 6H, CH_3), 1.34 (s, 6H, CH_3), 1.33 (s, 6H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$, TMS): δ 109.3 (Me–*C*–Me), 108.6 (Me–*C*–Me), 96.3 (C-1), 71.2 (C-4), 71.0 ($(CH_2)_2CH$), 70.6 (C-3), 70.5 (C-2), 68.9 (C-6), 66.6 (C-5), 63.2 (CH_2OH), 41.2 (*C*HCH_2OH), 26.0 (CH_3), 26.0 (CH_3), 24.9 (CH_3), 24.4 (CH_3). ESIMS *m*/*z*: $[M+Na]^+$ calcd for $C_{28}H_{46}O_{13}$, 590.2939; found, 613.2868.

4.3.4. Tetra-(ipr-gal)-C=C (6). Reaction conditions and workup were as described in Procedure A, with Di-(ipr-gal)-OH **4** (1.38 g, 2.40 mmol), sodium hydride (60%) (100 mg, 2.48 mmol), MDC (93 μL, 800 μmol), dry THF (20 mL), TLC (cyclohexane–EtOAc, 1:1). Purification was performed by flash chromatography on silica gel (cyclohexane–EtOAc, 1:1). The desired compound **6** (864 mg, 717 μmol, 90%) was obtained as colourless oil; $R_f = 0.45$ (cyclohexane–EtOAc, 1:1); $[\alpha]_D^{20}$ −61.6 (*c* 1.3, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ 5.52 (d, $^3J_{1,2} = 5.0$ Hz, 4H, H-1), 5.20 (s, 2H, C=CH_2), 4.59 (dd, $^3J_{2,3} = 2.2$, $^3J_{3,4} = 7.9$ Hz, 4H, H-3), 4.29 (dd, $^3J_{2,3} = 2.3$, $^3J_{1,2} = 5.1$ Hz, 4H, H-2), 4.25 (m_c, 4H, H-4), 4.14 (s, 4H, $(CH_2)_2C{=}CH_2$), 3.95 (m_c, 4H, H-5), 3.69–3.63 (m, 8H, $(CH_2)_2CHO$, 2H of $(CH_2)_2CH$, H-6), 3.61–3.55 (m, 9H, 5H of $(CH_2)_2CH$, H-6′), 3.53 (dd, $^3J_{CH_2,CH} = 5.5$, $^2J_{CH_2,CH_2} = 10.19$ Hz, 1H, 1H of $(CH_2)_2CH$), 1.54 (s, 6H, CH_3), 1.53 (s, 6H, CH_3), 1.46 (s, 6H, CH_3), 1.44 (s, 6H, CH_3), 1.34 (s, 6H, CH_3), 1.33 (s, 9H, CH_3), 1.32 (s, 9H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$, TMS): δ 143.3 (*C*=CH_2), 114.1 (C=*C*H_2), 109.5 (Me–*C*–Me), 109.2 (Me–*C*–Me), 108.7 (Me–*C*–Me), 108.5 (Me–*C*–Me), 96.3 (C-1), 76.8 ($(CH_2)_2CH$), 71.6 ($(CH_2)_2CH$), 71.3 ($(CH_2)_2CH$), 71.1 (C-4), 70.7 ($(CH_2)_2C{=}CH_2$), 70.6 (C-2, C-3), 70.0 (C-6), 66.7 (C-5), 26.1 (CH_3), 26.0 (CH_3), 25.9 (CH_3), 25.0 (CH_3), 24.4 (CH_3), 24.3 (CH_3). ESIMS *m*/*z*: $[M+2Na]^{2+}$ calcd for $C_{58}H_{92}O_{26}$, 1204.5878; found, 625.2812.

4.3.5. M-Tetra-(ipr-gal)-C=C (7). Reaction conditions and workup were as described in Procedure A, with Di-(ipr-gal)-CH_2OH **5** (1.29 g, 2.19 mmol), sodium hydride (60%) (91 mg, 2.26 mmol), MDC (84 μL, 0.73 mmol), dry THF (10 mL), TLC (cyclohexane–EtOAc, 1:1). Purification was performed by flash chromatography on silica gel (cyclohexane–EtOAc, 1:1). The desired compound **7** (486 mg, 394 μmol, 54%) was obtained as colourless oil; $R_f = 0.47$ (cyclohexane–EtOAc, 1:1); $[\alpha]_D^{20}$ −63.8 (*c* 0.8, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ 5.51 (d, $^3J_{1,2} = 5.0$ Hz, 4H, H-1), 5.11 (s, 2H, C=CH_2), 4.58 (dd, $^3J_{2,3} = 2.3$, $^3J_{3,4} = 8.0$ Hz, 4H, H-3), 4.28 (dd, $^3J_{2,3} = 2.3$, $^3J_{1,2} = 5.0$ Hz, 4H, H-2), 4.24 (m, 4H, H-4), 3.93 (ddd ≈ t, $^3J_{5,6} = 6.1$, $^3J_{5,6'} = 6.5$ Hz, 4H, H-5), 3.91 (s, 4H, $(CH_2)_2C{=}CH_2$), 3.61 (dd, $^3J_{5,6'} = 6.3$, $^2J_{6,6'} = 10.1$ Hz, 4H, H-6′), 3.57–3.53 (m, 8H, $(CH_2)_2CH$), 3.50 (dd, $^3J_{5,6} = 6.1$, $^2J_{6,6'} = 9.5$ Hz, 4H, H-6), 3.44 (d, $^3J_{CH_2,CH} = 5.9$ Hz, 4H, CHCH_2O), 2.19 (quin., $^3J_{CH_2,CH} = 5.9$ Hz, 2H, C*H*CH_2O), 1.53 (s, 12H, CH_3), 1.43 (s, 12H, CH_3), 1.33 (s, 12H, CH_3), 1.32 (s, 12H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$, TMS): δ 143.1 (*C*=CH_2), 112.9 (C=*C*H_2), 109.1 (Me–*C*–Me), 108.4 (Me–*C*–Me), 96.3 (C-1), 71.8 ($(CH_2)_2C{=}CH_2$), 71.1 (C-4), 70.6 (C-2, C-3), 69.7 (C-6), 69.6 ($(CH_2)_2CH$), 68.6 (CH*C*H_2O), 66.5 (C-5), 40.1 (*C*HCH_2O), 26.1 (CH_3), 26.0 (CH_3), 24.9 (CH_3), 24.4

(CH_3). ESIMS *m/z*: calcd for $C_{60}H_{96}O_{26}$: 1232.6190; $[M+Na]^+$ found, 1255.6367 and $[M+2Na]^{2+}$ 639.3100.

4.3.6. Tetra-(gal)-C=C (8). Reaction conditions and workup were as described in Procedure D, with Tetra-(ipr-gal)-C=C **6** (40 mg, 33 μmol), 5 ml TFA–H_2O (9:1). Purification was performed on a Sephadex LH 20 column with H_2O as eluant. The desired compound **8** (22 mg, 25 μmol, 75%) was obtained as colourless oil (α:β ratio 0.46:1); $[\alpha]_D^{20}$ +43.5 (*c* 1.8, CH_3OH–H_2O 1:1); ^{1}H NMR (500 MHz, D_2O): δ 5.22 (s, 4H, C=C*H*$_2$), 5.13 (d, $^3J_{1,2} = 3.6$ Hz, 4H, α-H-1), 4.46 (d, $^3J_{1,2} = 7.9$ Hz, 4H, β-H-1), 4.11–4.07 (m, 12H, (C*H*$_2$)$_2$C=CH$_2$, α-H-5), 3.85 (m, 4H, α-H-4), 3.79 (m, 4H, β-H-4), 3.73 (dd, $^3J_{2,3} = 10.4$, $^3J_{3,4} = 3.3$ Hz, 4H, α-H-3), 3.72–3.68 (m, 12H, (CH$_2$)$_2$C*H*, α-H-2, β-H-5), 3.68 (dd, $^3J_{1,2} = 3.8$, $^3J_{2,3} = 10.3$ Hz, 4H, α-H-2), 3.64–3.50 (m, 24H, (C*H*$_2$)$_2$CH, H-6, H-6′), 3.52 (dd, $^3J_{2,3} = 9.7$, $^3J_{3,4} = 3.3$ Hz, 4H, β-H-3), 3.36 (dd, $^3J_{1,2} = 8.0$, $^3J_{2,3} = 9.8$ Hz, 4H, β-H-2); ^{13}C NMR (125 MHz, D_2O): δ 143.4 (*C*=CH$_2$), 119.2 (C=*C*H$_2$), 98.4 (β-C-1), 94.3 (α-C-1), 78.5 ((CH$_2$)$_2$*C*H), 75.3 (β-C-5), 74.7 (β-C-3), 73.8 (β-C-2), 72.6 (CH$_2$), 72.5 (CH$_2$), 72.3 (CH$_2$), 72.2 (CH$_2$), 71.9 ((*C*H$_2$)$_2$C=CH$_2$), 71.5 (α-C-4), 71.1 (α-C-3), 71.0 (β-C-4), 70.7 (α-C-5), 70.3 (α-C-2). ESIMS *m/z*: $[M+Na]^+$ calcd for $C_{34}H_{60}O_{26}$, 884.3373; found, 907.3268.

4.3.7. M-Tetra-(gal)-C=C (9). Reaction conditions and workup were as described in Procedure D, with M-Tetra-(ipr-gal)-C=C **7** (80 mg, 65 μmol), 10 mL TFA–H_2O (9:1). Purification was performed on a Sephadex LH 20 column with H_2O as eluant. The desired compound **9** (43 mg, 47 μmol, 73%) was obtained as colourless oil (α:β ratio 0.49:1); $[\alpha]_D^{20}$ +47.7 (*c* 1.1, $CHCl_3$); ^{1}H NMR (600 MHz, D_2O–CD_3OD): δ 5.23 (s, 2H, α-anomer C=C*H*$_2$), 5.18 (s, 2H, β-anomer C=C*H*$_2$), 5.14 (m, 4H, α-H-1), 4.45 (dd, $^3J = 3.9$, $^3J_{1,2} = 7.9$ Hz, 4H, β-H-1), 4.10 (s, 12H, (C*H*$_2$)$_2$-CH=CH$_2$, α-H-5), 3.94 (s, 4H, CH$_2$), 3.85 (m, 4H, α-H-4), 3.79 (m, 4H, β-H-4), 3.73 (m, 4H, α-H-3), 3.72–3.68 (m, 4H, β-H-5), 3.68 (dd, $^3J_{1,2} = 3.85$, $^3J = 10.4$ Hz, 4H, α-H-2), 3.64–3.47 (m, 32H, $14 \times CH_2$, β-H-3), 3.44 (d, $^3J_{CH_2,CH} = 5.8$ Hz, 8H, (CH$_2$)$_2$CHC*H*$_2$O), 3.37 (dd, $^3J_{1,2} = 7.9$, $^3J_{2,3} = 9.8$ Hz, 4H, β-H-2), 2.13 (quin., 4H, (CH$_2$)$_2$C*H*); ^{13}C NMR (150 MHz, D_2O–CD_3OD): δ 144.9 (*C*=CH$_2$), 144.6 (*C*=CH$_2$), 120.1 (α-anomer C=*C*H$_2$), 119.2 (β-anomer C=*C*H$_2$), 99.7 (β-C-1), 95.5 (α-C-1), 76.5 (β-C-5), 75.9 (β-C-3), 75.0 (β-C-2), 74.3 (CH$_2$), 73.6 (CH$_2$), 73.5 (CH$_2$), 73.4 (CH$_2$), 73.3 (CH$_2$), 73.1 (CH$_2$), 72.7 (α-C-4), 72.5 (CH$_2$), 72.4 (CH$_2$), 72.3 (α-C-3), 72.1 (β-C-4), 71.7 (α-C-5), 71.5 (α-C-2), 71.3 ((CH$_2$)$_2$CH*C*H$_2$), 42.2 ((CH$_2$)$_2$*C*H). ESIMS *m/z*: $[M+Na]^+$ calcd for $C_{36}H_{64}O_{26}$, 912.3686; found, 935.3560.

4.3.8. Di-(ipr-gal)-Cl (10). Under Schlenk conditions Di-(ipr-gal)-OH **4** (198 mg, 0.344 mmol), was dissolved in 10 mL dry THF. Sodium hydride suspension (60%) (14 mg, 0.344 mmol) was added and the mixture stirred at rt for 5 min. Then MDC (40.0 μL, 0.344 mmol) was added, and the resulting mixture was refluxed for 16 h. Progress of the reaction was monitored by TLC. After completion, the reaction mixture was cooled to room temperature, quenched with water and saturated with solid potassium carbonate. The phases were separated, and the aqueous layer was extracted with five portions of EtOAc. The combined organic phases were dried over anhydrous magnesium sulfate and filtered, and the solvent was removed under vacuum. The resulting crude product was purified by flash chromatography on silica gel (cyclohexane–EtOAc, 1:1). The desired compound **10** (152 mg, 0.229 mmol, 67%) was obtained as colourless oil; $R_f = 0.51$ (cyclohexane–EtOAc, 1:1); $[\alpha]_D^{20}$ −96.3 (*c* 0.4, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 5.54 (dd, $^3J_{1,2} = 5.0$ Hz, 2H, H-1), 5.25 (m, 2H, CH=C*H*$_2$), 4.60 (dd, $^3J_{2,3} = 2.19$, $^3J_{3,4} = 7.91$ Hz, 2H, H-3), 4.30 (dd, $^3J_{2,3} = 2.3$, $^3J_{1,2} = 5.0$ Hz, 2H, H-2), 4.25 (m, 4H, H-4, C*H*$_2$C=CH$_2$), 4.17 (d, $^2J_{CH_2,CH_2} = 11.9$ Hz, 1H, C*H*$_2$Cl), 4.14 (d, $^2J_{CH_2,CH_2} = 11.9$ Hz, 1H, C*H*$_2$Cl), 3.96 (ddd ≈ dq, $^3J_{4,5} = 1.7$, $^3J_{5,6} = 6.9$ Hz, 2H, H-5), 3.72 (m, 1H, (CH$_2$)$_2$C*H*), 3.70–3.52 (m, 8H, (C*H*$_2$)$_2$CH, H-6, H-6′), 1.54 (s, 6H, CH$_3$), 1.44 (s, 6H, CH$_3$), 1.34 (s, 6H, CH$_3$), 1.33 (s, 6H, CH$_3$); ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ = 142.6 (*C*=CH$_2$), 116.8 (C=*C*H$_2$), 109.2 (Me–*C*–Me), 108.6 (Me–*C*–Me), 96.4 (C-1), 77.0 ((CH$_2$)$_2$C*H*), 71.9 (CH$_2$), 71.6 (CH$_2$), 71.1 (C-4), 70.7 (C-3), 70.6 (C-2), 70.3 (*C*H$_2$C=CH$_2$), 70.2 (CH$_2$), 70.1 (CH$_2$), 66.8 (C-5), 45.3 (CH$_2$Cl), 26.1 (CH$_3$), 26.0 (CH$_3$), 25.0 (CH$_3$), 24.5 (CH$_3$). ESIMS *m/z*: $[M+Na]^+$ calcd for $C_{31}H_{49}ClO_{13}$, 664.2862; found, 687.2795.

4.3.9. Di-(ipr-manno)-di-(ipr-gal)-C=C (12). Under Schlenk conditions Di-(ipr-manno)-OH **11**[4] (303 mg, 0.456 mmol) was dissolved in 10 mL dry THF. Sodium hydride suspension (60%) (20 mg, 0.502 mmol) was added and the mixture stirred at rt for 5 min. Afterwards Di-(ipr-gal)-Cl **10** (303, 0.456 mmol) was added, and the resulting mixture was headed under reflux for 16 h. Progress of the reaction was monitored by TLC. After completion, the reaction mixture was cooled to room temperature, quenched with water and saturated with solid potassium carbonate. The phases were separated, and the aqueous layer was extracted with five portions of EtOAc. The combined organic phases were dried over anhydrous magnesium sulfate and filtered, and the solvent was removed under vacuum. The resulting crude product was purified by flash chromatography on silica gel (cyclohexane–EtOAc, 1:1). The desired compound **12** (347 mg, 269 μmol, 59%) was obtained as a white foam; $R_f = 0.30$ (cyclohexane–EtOAc, 1:1);

$[\alpha]_D^{20}$ −26.7 (*c* 0.9, CH_2Cl_2); ^1H NMR (600 MHz, $CDCl_3$, TMS): $\delta = 5.52$ (d, $^3J_{1,2} = 5.0$ Hz, 2H, H-1 Gal), 5.21 (m, 2H, CH=CH_2), 5.06 (d ≈ s, 2H, H-1 Man), 4.59 (dd, $^3J_{2,3} = 2.2$, $^3J_{3,4} = 7.9$ Hz, H-3 Gal), 4.30 (dd, $^3J_{2,3} = 2.2$, $^3J_{1,2} = 4.9$ Hz, 2H, H-2 Gal), 4.24 (dd ≈ ddd, $^3J_{4,5} = 1.8$, $^3J_{3,4} = 6.4$ Hz, 2H, H-4 Gal), 4.20 (d, $^3J_{1,2} = 5.6$ Hz, 2H, H-2 Man), 4.15 (m, 6H, CH_2, H-3 Man), 3.95 (m, 2H, H-5 Gal), 3.86 (dd, $^3J_{5,6} = 5.5$ Hz, $^2J_{6,6'} = 10.7$ Hz, 2H, H-6 Man), 3.80–3.71 (m, 6H, 1H of CH_{ab}, H-4 Man, H-6′ Man), 3.68–3.52 (m, 22H, 1H of CH_{ab}, $(CH_2)_2CH$, $6 \times CH_2$, H-6 Gal, H-6′ Gal, H-5 Man), 1.55 (s, 6H, CH_3), 1.53 (s, 6H, CH_3), 1.52 (s, 6H, CH_3), 1.44 (s, 6H, CH_3), 1.42 (s, 6H, CH_3), 1.35 (s, 6H, CH_3), 1.33 (s, 6H, CH_3), 1.32 (s, 6H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$, TMS): $\delta = 143.2$ (*C*=CH_2), 114.2 (C=*C*H_2), 109.4 (Me–*C*–Me), 109.2 (Me–*C*–Me), 108.5 (Me–*C*–Me), 99.7 (Me–*C*–Me), 97.9 (C-1 Man), 96.3 (C-1 Gal), 77.1 ((CH)$_2$*C*H), 76.8 ((CH)$_2$*C*H), 76.0 (C-2 Man), 74.8 (C-3 Man), 72.8 (C-4 Man), 71.6 (CH_2), 71.4 (CH_2), 71.1 ($2 \times CH_2$), 71.0 (C-4 Gal), 70.7 ($2 \times CH_2$), 70.6 (C-2, C-3 Gal), 70.4 ($2 \times CH_2$), 70.1 (C-6 Gal), 66.7 (C-5 Gal), 66.6 (C_{ab}), 62.1 (C-6 Man), 61.3 (C-5 Man), 29.1 (CH_3), 28.2 (CH_3), 26.2 (CH_3), 26.1 (CH_3), 26.0 (CH_3), 25.0 (CH_3), 24.5 (CH_3), 18.8 (CH_3). ESIMS *m*/*z*: $[M+Na]^+$ calcd for $C_{62}H_{100}O_{28}$, 1292.6401; found, 1315.6265.

4.3.10. Di-(manno)-di-(gal)-C=C (13). Reaction conditions and workup were as described in Procedure D, with Di-(ipr-manno)-di-(ipr-gal)-C=C **12** (34 mg, 26 μmol), 5 mL TFA–H_2O (9:1). Purification was achieved on a Sephadex LH 20 column with H_2O as eluant. The desired compound **13** (22 mg, 23 μmol, 86%) was obtained as colourless oil (α:β ratio 0.33:1); $[\alpha]_D^{20}$ +30.0 (*c* 1.1, CH_3OH); ^1H NMR (600 MHz, CD_3OD): δ 5.26 (m_c, 4H, C=CH_2), 5.19 (d, $^3J_{1,2} = 3.6$ Hz, 2H, α-H-1 Gal), 4.85 (s, 4H, H-1 Man), 4.49 (d, $^3J_{1,2} = 6.9$ Hz, 2H, β-H-1 Gal), 4.23 (m_c, 8H, (CH_2)$_2$C=CH_2), 4.19 (dd ≈ t, 2H, α-H-5 Gal), 3.90–3.86 (m, 14H, 1H of CH_{ab}, β-H-4 Gal, H-2 Man, H-6 Man), 3.82 (dd, $^3J_{3,4} = 3.1$, $^3J_{2,3} = 10.0$ Hz, 2H, α-H-3 Gal), 3.79–3.60 (m, 60H, (CH)$_2$C*H*, (CH_2)$_2$CH, CH_{cd}, 1H of CH_{ab}, α-H-2 Gal, α-H-6 Gal, α-H-6′ Gal, β-H-5 Gal, β-H-6 Gal, β-H-6′ Gal, H-3 Man, H-4 Man, H-5 Man, H-6′ Man), 3.51 (m, 4H, β-H-2 Gal, β-H-3 Gal); ^{13}C NMR (150 MHz, CD_3OD): δ 145.0 (*C*=CH_2), 115.2 (C=*C*H_2), 101.7 (C-1 Man), 98.7 (β-C-1 Gal), 94.3 (α-C-1 Gal), 78.5 ((CH)$_2$*C*H), 78.3 ((CH)$_2$*C*H), 75.0 (β-C-3 Gal), 74.8 (CH), 74.6 (CH), 73.8 (β-C-2 Gal), 72.6 (CH), 72.2 (CH_2), 72.1 ($2 \times CH_2$, C-2 Man), 71.9 (CH_2), 71.7 ($4 \times CH_2$), 71.6 ((*C*H_2)$_2$C=CH_2), 71.2 (α-C-3 Gal, α-C-4 Gal), 70.5 (CH, β-C-4 Gal), 69.9 (α-C-5 Gal), 68.7 (CH), 67.8 (C_{ab}), 63.0 (C-6 Man). ESIMS *m*/*z*: $[M+Na]^+$ calcd for $C_{38}H_{68}O_{28}$, 972.3897; found, 995.3766.

4.3.11. Mono-(ipr-manno)-Cl (15). Under Schlenk conditions Mono-(ipr-manno)-OH **14** (1.801 g, 5.924 mmol) was dissolved in 20 mL dry THF. Sodium hydride suspension (60%) (261 mg, 6.516 mmol) was added and the mixture stirred at rt for 5 min. Afterwards MDC (685 μL, 5.92 mmol) was added, and the resulting mixture was refluxed for 16 h. Progress of the reaction was monitored by TLC. After completion, the reaction mixture was cooled to room temperature, quenched with water and saturated with solid potassium carbonate. The phases were separated, and the aqueous layer was extracted with five portions of EtOAc. The combined organic phases were dried over anhydrous magnesium sulfate and filtered, and the solvent was removed under vacuum. The resulting crude product was purified by flash chromatography on silica gel (cyclohexane–EtOAc, 1:1). The desired compound **15** (1.312 g, 3.345 mmol, 57%) was obtained as colourless oil; $R_f = 0.55$ (cyclohexane–EtOAc, 1:1); $[\alpha]_D^{20}$ +4.0 (*c* 1.0, CH_2Cl_2), ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 5.32 (m, 1H, C=CH_2), 5.22 (m, 1H, C=CH_2), 5.07 (d ≈ s, 1H, H-1), 4.22 (d, $^3J_{2,3} = 5.66$ Hz, 1H, H-2), 4.15 (dd, $^3J_{2,3} = 5.7$, $^3J_{3,4} = 7.9$ Hz, 1H, H-3), 4.11 (m, 4H, (CH_2)$_2$C=CH_2), 3.87 (dd, $^3J_{5,6} = 5.62$, $^2J_{6,6'} = 10.8$ Hz, 1H, H-6), 3.85–3.80 (m, 1H, 1H of CH_{ab}), 3.78–3.72 (m, 2H, H-4, H-6′), 3.66–3.59 (m, 4H, 1H of CH_{ab}, CH_{cd}, H-5), 1.55 (s, 3H, CH_3), 1.53 (s, 3H, CH_3), 1.43 (s, 3H, CH_3), 1.35 (s, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 141.8 (*C*=CH_2), 117.0 (C=*C*H_2), 109.4 (Me–*C*–Me), 99.6 (Me–*C*–Me), 97.9 (C-1), 77.9 ((CH)$_2$CH), 76.0 (C-2), 74.8 (C-3), 72.7 (C-4), 71.3 (CH_2), 69.1 (CH_2), 66.7 (C_{ab}), 62.1 (C-6), 61.4 (C-5), 45.1 (CH_2Cl), 29.1 (CH_3), 28.2 (CH_3), 26.1 (CH_3), 18.8 (CH_3). ESIMS *m*/*z*: $[M+Na]^+$ calcd for $C_{18}H_{29}ClO_7$, 392.1602; found, 415.1461.

4.3.12. Mono-(ipr-gal)-Cl (16). Under Schlenk conditions Mono-(ipr-gal)-OH **1** (2.00 g, 7.69 mmol) was dissolved in 20 mL dry THF. Sodium hydride suspension (60%) (338 mg, 8.46 mmol) was added and the mixture stirred at rt for 5 min. Then MDC (890 μL, 7.69 mmol) was added, and the resulting mixture was refluxed for 16 h. Progress of the reaction was monitored by TLC. After completion, the reaction mixture was cooled to room temperature, quenched with water and saturated with solid potassium carbonate. The phases were separated, and the aqueous layer was extracted with five portions of EtOAc. The combined organic phases were dried over anhydrous magnesium sulfate and filtered, and the solvent was removed under vacuum. The resulting crude product was purified by flash chromatography on silica gel (cyclohexane–EtOAc, 1:1). The desired compound **16** (1.499 g, 4.306 mmol, 56%) was obtained as colourless oil; $R_f = 0.58$ (cyclohexane–EtOAc, 1:1); $[\alpha]_D^{20}$ −58.6 (*c* 1.35, CH_2Cl_2), ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 5.54 (d, $^3J_{1,2} = 5.0$ Hz, 1H, H-1), 5.30

(m, 1H, C=CH_2), 5.24 (m, 1H, C=CH_2), 4.61 (dd, $^3J_{2,3} = 2.4$, $^3J_{3,4} = 7.9$ Hz, 1H, H-3), 4.32 (dd, $^3J_{2,3} = 2.4$, $^3J_{1,2} = 5.0$ Hz, 1H, H-2), 4.27 (dd, $^3J_{4,5} = 1.9$, $^3J_{3,4} = 7.9$ Hz, 1H, H-4), 4.17 (d, $^2J_{CH_2,CH_2} = 12.9$ Hz, 1H, (CH_2)$_2$C=CH$_2$), 4.12 (m, 2H, (CH_2)$_2$C=CH$_2$), 4.10 (d, $^2J_{CH_2,CH_2} = 12.7$ Hz, 1H, (CH_2)$_2$C=CH$_2$), 3.98 (ddd ≈ dt, $^3J_{4,5} = 1.8$, $^3J_{5,6} = 6.4$ Hz, 1H, H-5), 3.65 (dd, $^3J_{5,6} = 5.9$, $^2J_{6,6'} = 10.0$ Hz, 1H, H-6), 3.57 (dd, $^3J_{5,6} = 6.8$, $^2J_{6,6'} = 10.0$ Hz, 1H, H-6′), 1.55 (s, 3H, CH$_3$), 1.45 (s, 3H, CH$_3$), 1.35 (s, 3H, CH$_3$), 1.34 (s, 3H, CH$_3$); ^{13}C NMR (125 MHz, CDCl$_3$, TMS): δ 141.9 (*C*=CH$_2$), 116.9 (C=*C*H$_2$), 109.3 (Me–*C*–Me), 108.6 (Me–*C*–Me), 96.3 (C-1), 71.4 (*C*H$_2$C=CH$_2$), 71.1 (C-4), 70.6 (C-2, C-3), 68.9 (C-6), 66.7 (C-5), 45.1 (CH$_2$Cl), 26.1 (CH$_3$), 26.0 (CH$_3$), 25.0 (CH$_3$), 24.4 (CH$_3$). ESIMS *m*/*z*: [M+Na]$^+$ calcd for $C_{16}H_{25}ClO_6$, 348.1340; found, 371.0987.

4.3.13. (Ipr-gal)-(ipr-manno)-C=C (17). Under Schlenk conditions Mono-(ipr-gal)-OH **1** (861mg, 3.312 mmol) was dissolved in 20 mL dry THF. Sodium hydride suspension (60%) (146 mg, 3.643 mmol) was added and the mixture stirred at rt for 5 min. Afterwards Mono-(ipr-manno)-Cl **15** (1.299 g, 3.312 mmol) was added, and the resulting mixture was headed at reflux for 16 h. Progress of the reaction was monitored by TLC. After completion, the reaction mixture was cooled to room temperature, quenched with water and saturated with solid potassium carbonate. The phases were separated, and the aqueous layer was extracted with five portions of EtOAc. The combined organic phases were dried over anhydrous magnesium sulfate and filtered, and the solvent was removed under vacuum. The resulting crude product was purified by flash chromatography on silica gel (cyclohexane–EtOAc, 1:1). Title compound **17** (1.282 g, 2.08 mmol, 63%) was obtained as colourless oil; $R_f = 0.44$ (cyclohexane–EtOAc, 1:1); $[\alpha]_D^{20}$ −28.6 (*c* 0.9, CH_2Cl_2); ^{1}H NMR (500 MHz, CDCl$_3$, TMS): δ 5.54 (d, $^3J_{1,2} = 5.1$ Hz, 1H, H-1 Gal), 5.20 (m, 1H, C=CH_2), 5.07 (d ≈ s, 1H, H-1 Man), 4.61 (dd, $^3J_{2,3} = 2.3$, $^3J_{3,4} = 7.9$ Hz, 1H, H-3 Gal), 4.31 (dd, $^3J_{2,3} = 2.4$, $^3J_{1,2} = 5.0$ Hz, 1H, H-2 Gal), 4.26 (dd, $^3J_{4,5} = 1.8$, $^3J_{3,4} = 7.9$ Hz, 1H, H-4 Gal), 4.23 (d, $^3J_{2,3} = 5.6$ Hz, 1H, H-2 Man), 4.16 (dd, $^3J_{2,3} = 5.7$, $^3J_{3,4} = 7.9$ Hz, 1H, H-3 Man), 4.09–4.01 (m, 4H, (CH_2)$_2$C=CH$_2$), 3.98 (dd, $^3J_{4,5} = 1.7$, $^3J_{5,6} = 6.3$ Hz, 1H, H-5 Gal), 3.87 (dd, $^3J_{CH_2,CH} = 5.6$, $^2J_{CH_2,CH_2} = 10.7$ Hz, 1H, 1H of CH$_{ab}$), 3.80 (ddd ≈ dt, $^3J_{5,6} = 4.3$, $^2J_{6,6'} = 10.8$ Hz, 1H, H-6 Man), 3.77–3.71 (m, 2H, H-4 Man, H-6′ Man), 3.66–3.50 (m, 6H, 1H of CH$_{ab}$, CH$_2$, H-5 Man, H-6 Gal, H-6′ Gal), 1.55 (s, 3H, CH$_3$), 1.54 (s, 3H, CH$_3$), 1.52 (s, 3H, CH$_3$), 1.45 (s, 3H, CH$_3$), 1.42 (s, 3H, CH$_3$), 1.35 (s, 3H, CH$_3$), 1.34 (s, 3H, CH$_3$), 1.33 (s, 3H, CH$_3$); ^{13}C NMR (125 MHz, CDCl$_3$, TMS): δ 142.2 (*C*=CH$_2$), 114.3 (C=*C*H$_2$), 109.5 (Me–*C*–Me), 109.4 (Me–*C*–Me), 108.6 (Me–*C*–Me), 99.7 (Me–*C*–Me), 97.9 (C-1 Man), 96.3 (C-1 Gal), 76.0 (C-2 Man), 74.8 (C-3 Man), 72.7 (C-4 Man), 71.8 ((*C*H$_2$)$_2$C=CH$_2$), 71.1 (C-4 Gal), 70.6 (C-2 Gal, C-3 Gal), 69.0 (CH$_2$), 68.9 (CH$_2$), 66.7 (C-5 Gal), 66.6 (C$_{ab}$), 62.0 (C-6 Man), 61.2 (C-5 Man), 26.1 (CH$_3$), 28.2 (CH$_3$), 26.2 (CH$_3$), 26.1 (CH$_3$), 26.0 (CH$_3$), 25.0 (CH$_3$), 24.4 (CH$_3$), 18.8 (CH$_3$). ESIMS *m*/*z*: [M+Na]$^+$ calcd for $C_{30}H_{48}O_{13}$, 616.3095; found, 639.2970.

4.3.14. (Ipr-gal)-(ipr-manno)-OH (18). Reaction conditions and workup were as described in Procedure B, with (ipr-gal)-(ipr-manno)-C=C **17** (370 mg, 0.600 mmol), sodium borohydride (136 mg, 3.6 mmol), dry methanol–CH_2Cl_2 (1:1, 30 mL), TLC (cyclohexane–EtOAc, 1:2). Purification was achieved by flash chromatography on silica gel (cyclohexane–EtOAc, 1:2). The desired compound **18** (313 mg, 0.505 mmol, 85%) was obtained as colourless oil; $R_f = 0.21$ (cyclohexane–EtOAc, 1:2); $[\alpha]_D^{20}$ −29.2 (*c* 1.3, CH_2Cl_2); ^{1}H NMR (600 MHz, CDCl$_3$, TMS): δ 5.53 (d, $^3J_{1,2} = 5.0$ Hz, 1H, H-1 Gal), 5.06 (d ≈ s, 1H, H-1 Man), 4.61 (dd, $^3J_{2,3} = 2.4$, $^3J_{3,4} = 7.9$ Hz, 1H, H-3 Gal), 4.32 (dd, $^3J_{2,3} = 2.4$, $^3J_{1,2} = 5.0$ Hz, 1H, H-2 Gal), 4.26 (dd, $^3J_{4,5} = 2.0$, $^3J_{3,4} = 8.0$ Hz, 1H, H-4 Gal), 4.21 (dd ≈ d, $^3J_{2,3} = 5.7$ Hz, 1H, H-2 Man), 4.15 (dd, $^3J_{2,3} = 5.7$, $^3J_{3,4} = 7.8$ Hz, 1H, H-3 Man), 3.96 (m, 2H, (CH$_2$)$_2$C*H*, H-5 Gal), 3.87 (dd, $^3J_{5,6} = 5.6$, $^2J_{6,6'} = 10.6$ Hz, 1H, H-6 Man), 3.80 (m, 1H, 1H of CH$_{ab}$), 3.77–3.72 (m, 2H, H-4 Man, H-6′ Man), 3.72–3.58 (m, 10H, 1H of CH$_{ab}$, CH$_{cd}$, (CH$_2$)$_2$CH, H-5 Man, H-6 Gal, H-6′ Gal), 2.45 (s (br), 1H, OH), 1.53 (m, 9H, CH$_3$), 1.45 (s, 3H, CH$_3$), 1.43 (s, 3H, CH$_3$), 1.34 (m, 9H, CH$_3$); ^{13}C NMR (150 MHz, CDCl$_3$, TMS): δ 109.5 (Me–*C*–Me), 109.4 (Me–*C*–Me), 108.7 (Me–*C*–Me), 99.7 (Me–*C*–Me), 97.9 (C-1 Man), 96.3 (C-1 Gal), 76.0 (C-2 Man), 74.8 (C-3 Man), 72.8 (C-4 Man), 72.5 (CH$_2$), 72.4 (CH$_2$), 71.2 (C-4 Gal), 70.6 (C-2 Gal, C-3 Gal), 70.4 (CH$_2$), 69.8 (C-6 Gal), 69.5 ((CH$_2$)$_2$*C*H), 66.8 (C-5 Gal), 66.6 (CH$_{ab}$), 62.1 (C-6 Man), 61.4 (C-5 Man), 29.0 (CH$_3$), 28.2 (CH$_3$), 26.2 (CH$_3$), 26.1 (CH$_3$), 26.0 (CH$_3$), 24.9 (CH$_3$), 24.5 (CH$_3$), 18.8 (CH$_3$). ESIMS *m*/*z*: [M+Na]$^+$ calcd for $C_{29}H_{48}O_{14}$, 620.3044; found, 643.2973.

4.3.15. (Ipr-gal)-(ipr-manno)-CH$_2$OH (19). Reaction conditions and workup were as described in Procedure C, with (ipr-gal)-(ipr-manno)-C=C**17** (1.178 mg, 1.911 mmol), 9-BBN ($c = 0.5$ M in THF) (5.73 mL, 2.86 mmol), dry THF (10 mL), H_2O_2 (30% in water) 2.9 mL, NaOH ($c = 3.0$ M) 2.9 mL. TLC (cyclohexane–EtOAc, 1:2) staining with phosphomolybdic acid, followed by heat treatment. Purification was performed by flash chromatography on silica gel (cyclohexane–EtOAc, 1:2). The desired compound **19** (1.086 g, 1.713 mmol, 90%) was obtained as colourless oil; $R_f = 0.34$ (1:2 cyclohexane–EtOAc); $[\alpha]_D^{20}$ −28.8 (*c* 0.7,

CH_2Cl_2); ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 5.54 (d, $^3J_{1,2} = 5.0$ Hz, 1H, H-1 Gal), 5.05 (d ≈ s, 1H, H-1 Man), 4.60 (dd, $^3J_{2,3} = 2.3$, $^3J_{3,4} = 7.9$ Hz, 1H, H-3 Gal), 4.31 (dd, $^3J_{2,3} = 2.4$, $^3J_{1,2} = 5.0$ Hz, 1H, H-2 Gal), 4.22 (ddd ≈ td, $^3J_{4,5} = 16$, $^3J_{3,4} = 7.9$ Hz, 1H, H-4 Gal), 4.20 (dd ≈ d, $^3J_{2,3} = 5.7$ Hz, 1H, H-2 Man), 4.15 (dd, $^3J_{2,3} = 5.7$, $^3J_{3,4} = 7.8$ Hz, 1H, H-3 Man), 3.96 (m, 1H, H-5 Gal), 3.86 (dd, $^3J_{5,6} = 5.6$, $^2J_{6,6'} = 10.8$ Hz, 1H, H-6 Man), 3.80–3.71 (m, 5H, 1H of CH_{ab}, CH_2, H-4 Man, H-6′ Man), 3.66–3.51 (m, 10H, 1H of CH_{ab}, $(CH_2)_2CH$, CH_2OH, H-5 Man, H-6 Gal, H-6′ Gal), 2.13 (m, 1H, $(CH_2)_2CH$), 1.54 (s, 3H, CH_3), 1.52 (s, 3H, CH_3), 1.51 (s, 3H, CH_3), 1.44 (s, 3H, CH_3), 1.42 (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 1.33 (s, 3H, CH_3), 1.32 (s, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 109.5 (Me–*C*–Me), 109.4 (Me–*C*–Me), 108.6 (Me–*C*–Me), 99.7 (Me–*C*–Me), 97.9 (C-1 Man), 96.3 (C-1 Gal), 76.0 (C-2 Man), 74.8 (C-3 Man), 72.8 (C-4 Man), 71.2 (C-4 Gal), 70.9 ($(CH_2)_2CH$), 70.8 ($(CH_2)_2CH$), 70.7 (C-3 Gal), 70.5 (C-2 Gal), 70.1 (CH_{cd}), 69.9 (C-6 Gal), 66.8 (C-5 Gal), 66.7 (C_{ab}), 63.2 (CH_2OH), 62.1 (C-6 Man), 61.3 (C-5 Man), 41.3 ($(CH_2)_2CH$), 29.1 (CH_3), 28.2 (CH_3), 26.2 (CH_3), 26.0 (CH_3), 25.9 (CH_3), 24.9 (CH_3), 24.4 (CH_3), 18.8 (CH_3). ESIMS *m*/*z*: $[M+Na]^+$ calcd for $C_{30}H_{50}O_{14}$, 634.3201; found, 657.3074.

4.3.16. Di-((ipr-gal)-(ipr-manno))-C═C (20). Reaction conditions and workup were as described in Procedure A, with (ipr-gal)-(ipr-manno)-OH **18** (272 mg, 438 μmol), sodium hydride (60%) (18 mg, 453 μmol), MDC (17 μL, 146 μmol), dry THF (7 mL), TLC (cyclohexane–EtOAc, 1:1). Purification was achieved by flash chromatography on silica gel (cyclohexane–EtOAc, 1:1). The desired compound **20** (143 mg, 111 μmol, 76%) was obtained as colourless oil; $R_f = 0.38$ (cyclohexane–EtOAc 1:1); $[\alpha]_D^{20}$ −29.7 (*c* 0.8, CH_2Cl_2); ^1H NMR (600 MHz, $CDCl_3$, TMS): δ 5.52 (d, $^3J_{1,2} = 5.0$ Hz, 2H, H-1 Gal), 5.20 (s, 2H, C═CH_2), 5.05 (d ≈ s, 2H, H-1 Man), 4.60 (dd, $^3J_{2,3} = 2.3$, $^3J_{3,4} = 7.9$ Hz, 2H, H-3 Gal), 4.30 (dd, $^3J_{2,3} = 2.3$, $^3J_{1,2} = 5.0$ Hz, 2H, H-2 Gal), 4.24 (dd, $^3J_{4,5} = 1.9$, $^3J_{3,4} = 7.9$ Hz, 2H, H-4 Gal), 4.20 (dd ≈ d, $^3J_{2,3} = 5.6$ Hz, 2H, H-2 Man), 4.15 (m, 6H, $(CH_2)_2C{=}CH_2$, H-3 Man), 3.95 (m, 2H, H-5 Gal), 3.87 (m, 2H, H-6 Man), 3.79–3.82 (m, 6H, 1H of CH_{ab}, H-4 Man, H-6′ Man), 3.70–3.52 (m, 22H, 1H of CH_{ab}, H-5 Man, H-6 Gal, H-6′ Gal, $6 \times CH_2$, $(CH_2)_2CH$), 1.55 (s, 6H, CH_3), 1.54 (s, 6H, CH_3), 1.52 (s, 6H, CH_3), 1.44 (s, 6H, CH_3), 1.42 (s, 6H, CH_3), 1.35 (s, 6H, CH_3), 1.34 (s, 6H, CH_3) 1.33 (s, 6H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$, TMS): δ 143.2 (*C*═CH_2), 114.2 (C═*C*H_2), 109.5 (Me–C–Me), 109.4 (Me–C–Me), 109.2 (Me–C–Me), 109.1 (Me–C–Me), 108.7 (Me–C–Me), 108.5 (Me–C–Me), 105.0 (Me–C–Me), 99.7 (Me–C–Me), 97.9 (C-1 Man), 96.3 (C-1 Gal), 76.9 ($(CH_2)_2CH$), 76.0 (C-2 Man), 74.8 (C-3 Man), 72.8 (C-4 Man), 71.3 (CH_2), 71.2 (CH_2), 71.0 (C-4 Gal), 70.7 ($(CH_2)_2C{=}CH_2$), 70.6 (C-2 Gal, C-3 Gal), 70.4 (CH_2), 70.3 (CH_2), 70.2 (CH_2), 70.1 (CH_2), 66.8 (C-5 Gal), 66.6 (C_{ab}), 62.0 (C-6 Man), 61.3 (C-5 Man), 29.0 (CH_3), 28.2 (CH_3), 26.2 (CH_3), 26.1 (CH_3), 26.0 (CH_3), 24.9 (CH_3), 24.4 (CH_3), 18.8 (CH_3). ESIMS *m*/*z*: $[M+Na]^+$ calcd for $C_{62}H_{100}O_{28}$, 1292.6401; found, 1315.6239.

4.3.17. Di-((ipr-gal)-(ipr-manno)-CH_2O)-C═C (21). Reaction conditions and workup were as described in Procedure A, with (ipr-gal)-(ipr-manno)-CH_2OH **18** (645, 1.02 mmol), sodium hydride (60%) (43 mg, 1.05 mmol), MDC (39 μL, 339 μmol), dry THF (10 mL), TLC (cyclohexane–EtOAc, 1:1). Purification was by flash chromatography on silica gel (cyclohexane–EtOAc, 1:1). The desired compound **21** (335 mg, 254 μmol, 75%) was obtained as colourless oil; $R_f = 0.57$ (cyclohexane–EtOAc, 1:1); $[\alpha]_D^{20}$ −26.0 (*c* 1.0, CH_2Cl_2); ^1H NMR (600 MHz, $CDCl_3$, TMS): δ 5.52 (d, $^3J_{1,2} = 5.0$ Hz, 2H, H-1 Gal), 5.21 (m, 2H, C═CH_2), 5.06 (d ≈ s, 2H, H-1 Man), 4.60 (dd, $^3J_{2,3} = 2.4$, $^3J_{3,4} = 7.9$ Hz, 2H, H-3 Gal), 4.30 (dd, $^3J_{2,3} = 2.4$, $^3J_{1,2} = 5.0$ Hz, 2H, H-2 Gal), 4.24 (dd, $^3J_{4,5} = 1.9$, $^3J_{3,4} = 7.9$ Hz, 2H, H-4 Gal), 4.21 (dd ≈ d, $^3J_{2,3} = 5.7$ Hz, 2H, H-2 Man), 4.15 (dd, $^3J_{2,3} = 5.7$, $^3J_{3,4} = 7.9$ Hz, 2H, H-3 Man), 4.05 (s, 4H, $(CH_2)_2$-C═CH_2), 3.95 (dt, $^3J_{4,5} = 1.8$, $^3J_{5,6} = 6.3$ Hz, 2H, H-5 Gal), 3.86 (dd, $^3J_{5,6} = 5.6$, $^2J_{6,6'} = 10.9$ Hz, 2H, H-6 Man), 3.79–3.72 (m, 6H, 1H of CH_{ab}, H-4 Man, H-6′ Man), 3.65–3.53 (m, 12H, 1H of CH_{ab}, CH_{cd}, H-6 Gal, H-6′ Gal, H-5 Man), 3.52 (m, 4H, $(CH_2)_2CH$), 3.48 (m, 4H, $(CH_2)_2CH$), 2.21 (quin., $^3J_{CH_2,CH} = 6.0$ Hz, 2H, $(CH_2)_2CH$), 1.55 (s, 6H, CH_3), 1.54 (s, 6H, CH_3), 1.52 (s, 6H, CH_3), 1.44 (s, 6H, CH_3), 1.42 (s,6H, CH_3), 1.35 (s, 6H, CH_3), 1.34 (s, 6H, CH_3), 1.33 (s, 6H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$, TMS): δ 142.3 (*C*═CH_2), 116.4 (C═*C*H_2), 109.4 (Me–*C*–Me), 109.2 (Me–*C*–Me), 108.5 (Me–*C*–Me), 99.7 (Me–*C*–Me), 97.9 (C-1 Man), 96.4 (C-1 Gal), 76.0 (C-2 Man), 74.8 (C-3 Man), 72.8 (C-4 Man), 71.2 ($(CH_2)_2C{=}CH_2$), 71.1 (C-4 Gal), 70.6 (C-2 Gal, C-3 Gal), 70.1 (CH_2), 69.8 (CH_2), 69.6 ($(CH_2)_2CH$), 68.6 ($(CH_2)_2CH$), 66.6 (C_{ab}), 66.5 (C-5 Gal), 62.1 (C-6 Man), 61.3 (C-5 Man), 40.2 ($(CH_2)_2CH$), 29.1 (CH_3), 28.2 (CH_3), 26.2 (CH_3), 26.1 (CH_3), 26.0 (CH_3), 24.5 (CH_3), 22.7 (CH_3), 14.1 (CH_3). ESIMS *m*/*z*: $[M+Na]^+$ calcd for $C_{64}H_{104}O_{28}$, 1320.6714; found, 1343.6650.

4.3.18. Di-((gal)-(manno))-C═C (22). Reaction conditions and workup were as described in Procedure D, with Di-((ipr-gal)-(ipr-manno)-C═C **20** (40 mg, 31 μmol), 5 mL TFA–H_2O (9:1). Purification was achieved on a Sephadex LH 20 column with H_2O as eluant. The desired compound **22** (23 mg, 23 μmol, 75%) was obtained as colourless oil (α:β ratio 0.71:1); $[\alpha]_D^{20}$

+38.2 (*c* 1.0, CH_3OH); ^1H NMR (500 MHz, CD_3OD): δ 5.28 (m_c, 4H, C=CH_2), 5.20 (d, $^3J_{1,2} = 3.6$ Hz, 2H, α-H-1 Gal), 4.86 (d ≈ s, 4H, H-1 Man), 4.50 (d, $^3J_{1,2} = 7.3$ Hz, 2H, β-H-1 Gal), 4.25 (m_c, 8H, (CH_2)$_2$C=CH_2), 4.20 (ddd ≈ t, 2H, α-H-5 Gal), 3.94 (m, 2H, α-H-4 Gal), 3.90–3.86 (m, 14H, 1H of CH_{ab}, β-H-4 Gal, H-2 Man, H-6 Man), 3.82 (dd, $^3J_{3,4} = 3.1$, $^3J_{2,3} = 10.1$ Hz, 2H, α-H-3 Gal), 3.80–3.60 (m, 60H, (CH_2)$_2$C*H*, (CH_2)$_2$CH, CH_{cd}, 1H of CH_{ab}, α-H-2 Gal, α-H-6 Gal, α-H-6′ Gal, β-H-5 Gal, β-H-6 Gal, β-H-6′ Gal, H-3 Man, H-4 Man, H-5 Man, H-6′ Man), 3.54 (m, 2H, β-H-3 Gal), 3.51 (dd, $^3J_{3,4} = 7.4$, $^3J_{2,3} = 9.5$ Hz, 2H, β-H-2 Gal); ^{13}C NMR (150 MHz, CD_3OD): δ 144.7 (*C*=CH_2), 115.6 (C=*C*H_2), 101.6 (C-1 Man), 98.6 (β-C-1 Gal), 94.2 (α-C-1 Gal), 78.3 ((CH_2)$_2$C*H*), 78.2 ((CH_2)$_2$C*H*), 74.9 (β-C-3 Gal), 74.8 (CH), 74.5 (CH), 73.7 (β-C-2 Gal), 72.5 (CH), 72.1 (CH_2), 72.0 (CH_2, C-2 Man), 71.9 (CH_2), 71.7 (4 × CH_2), 71.6 (*C*H_2)$_2$C=CH_2), 71.1 (α-C-3 Gal, α-C-4 Gal), 70.5 (β-C-4 Gal), 70.3 (CH), 69.9 (α-C-5 Gal), 68.5 (CH), 67.8 (CH_{ab}), 62.8 (C-6 Man). ESIMS *m*/*z*: $[M+Na]^+$ calcd for $C_{38}H_{68}O_{28}$, 972.3897; found, 995.3754.

4.3.19. Di-((gal)-(manno)-CH_2O)-C=C (23). Reaction conditions and workup were as described in Procedure D, with Di-((ipr-gal)-(ipr-manno)-CH_2O)–C=C **21** (34 mg, 26 μmol), 5 mL TFA–H_2O (9:1). Purification was achieved on a Sephadex LH 20 column with H_2O as eluant. The desired compound **23** (22 mg, 22 μmol, 85%) was obtained as colourless oil (α:β ratio 0.66:1); $[\alpha]_D^{20}$ +43.5 (*c* 1.0, CH_3OH); ^1H NMR (500 MHz, CD_3OD): δ 5.21 (s, 4H, C=CH_2), 5.18 (d, $^3J_{1,2} = 3.6$ Hz, 2H, α-H-1 Gal), 4.85 (d ≈ s, 4H, H-1 Man), 4.48 (d, $^3J_{1,2} = 6.2$ Hz, 2H, β-H-1 Gal), 4.19 (ddd ≈ t, 2H, α-H-5 Gal), 4.02 (s, 8H, (CH_2)$_2$=CH_2), 3.93 (m, 2H, α-H-4 Gal), 3.89–3.85 (m, 14H, 1H of CH_{ab}, β-H-4 Gal, H-2 Man, H-6 Man), 3.82–3.74 (m, 10H, α-H-3 Gal, CH Man, H-6′ Man), 3.72–3.57 (m, 48H, 1H of CH_{ab}, (CH_2)$_2$CH, CH_{cd}, α-H-2 Gal, α-H-6 Gal, α-H-6′ Gal, β-H-5 Gal, β-H-6 Gal, β-H-6′ Gal, CH Man, CH Man), 3.52 (m, 12H, CHCH_2O, β-H-2 Gal, β-H-3 Gal), 2.19 (quin., $^3J_{CH_2,CH} = 5.9$ Hz, 4H, (CH_2)$_2$C*H*); ^{13}C NMR (150 MHz, CD_3OD): δ 114.5 (*C*H_2=C), 101.7 (C-1 Man), 98.7 (C-1 Gal), 75.0 (2 × CH), 74.6 (2 × CH), 73.8 (2 × CH), 72.8 (*C*H_2C=CH_2), 72.6 (2 × CH), 72.1 (H-2 Man), 71.7 (CH_2), 71.5 (2 × CH_2), 71.4 (2 × CH_2), 70.9 (2 × CH_2), 70.8 (2 × CH_2), 70.6 (2 × CH), 70.4 (2 × CH), 69.7 (CH_2), 68.6 (2 × CH), 67.7 (CH_{ab}), 62.9 (C-6 Man), 41.6 (2 × Cx). ESIMS *m*/*z*: $[M+Na]^+$ calcd for $C_{38}H_{64}O_{30}$, 1000.3483; found, 1023.3334.

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