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Synthesis of β-(1→2)-Linked Oligomannosides

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β-(1→2)-Linked oligomannosides constitute an important class of carbohydrate structures located on the cell surface of several *Candida* species, including *C. albicans*. As a result of the immunostimulating properties of such compounds, the upscaling of their synthesis is relevant. In this paper, a highly stereoselective synthesis of β-(1→2)-linked oligomannosides was performed by further development of and modifications to the methodologies described earlier in the literature. In addition to the synthesis of fully deprotected β-(1→2)-linked mannobiose and mannotriose, some preliminary modifications to the oligosaccharide core, resulting in close analogues with biological potential, are presented. The fully deprotected products form potential targets for screening against *C. albicans* and may also result in new model structures for vaccine development.

Introduction

In organic chemistry, the total synthesis of complex marine natural products is considered by many as the ultimate proving ground for methodology development.[1] In carbohydrate chemistry, a similar definition is often associated with the notoriously difficult, stereoselective construction of glycosidic bonds in β-mannosides and β-mannosamines and, in particular, the β-mannans (Figure 1).[2] The problems in constructing the β-mannosidic linkages arise from several intervening factors, including the greater thermodynamic and kinetic preference for the α-mannoside as a result of the anomeric effect.[2,3]

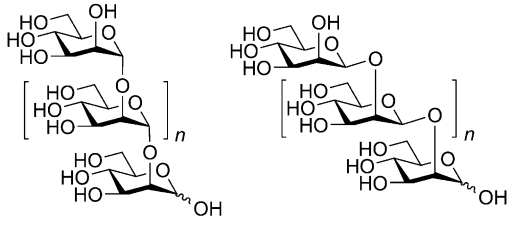

Figure 1. α-Linked mannan (left) and β-linked mannan (right).

In nature, β-(1→2)-linked mannans are produced by the genus *Candida* (e.g., *C. albicans*,[4] *C. glabrata*[5]) with the homopolymers of β-1,2-oligomannosides typically having an estimated degree of polymerization of 2 to 7[6] or 2 to 14.[7] The β-(1→2) mannans of *C. albicans* are immunogenic and elicit specific antibodies in humans and animals.[8] Branched α-(1→2) linked mannans in turn are promising targets for anti-HIV vaccines and related immunogen design.[9] Nevertheless, the natural sources seldom provide sufficient amounts of complex oligosaccharides for evaluating their full biological potential. Accordingly, efficient synthetic methodologies are required for producing enough material for biological studies.

As a result of the biological properties of mannoside oligomers and the associated synthetic challenges involved, the construction of β-linked mannosides has received considerable attention in recent years. Crich et al. developed direct protocols for highly stereoselective β-mannosylation, including the efficient construction of the β-(1→2)-,[10] β-(1→3)-,[11] and β-(1→4)-,[10] as well as the β-(1→3)-β-(1→4)-[12] linked mannopyranosides. In their work, the stereoselective β-mannosylation is based on the activation of the donor species (mannopyranosyl sulfoxides or thioglycosides) with Tf_2O, which at low temperature yields an α-D-mannopyranosyl triflate,[13] which in turn reacts with the D-mannose-derived acceptor in an S_N2 fashion to provide the desired β-mannopyranoside. In general, the structure of the donor significantly influences the outcome and stereoselectivity of the β-mannosylation reaction. The presence of a 4,6-*O*-benzylidene acetal in the donor provides sufficient torsional rigidity to the pyranose ring necessary for high selectivity of glycosylation.[13a,13b,14] The introduction of ether-type protecting groups at O-2 and O-3 has appeared to be important as well. A series of nonparticipating protecting groups including benzyl, *p*-methoxybenzyl, naphthylmethyl, and silyl (TBDMS) ether groups were investi-

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gated in order to improve the β-mannosylation selectivity.[11,15] Recently, a sterically minimal propargyl ether protecting group was introduced at the O-2 position of the donor unit.[11a] The use of propargyl protection at O-2, together with a benzyl ether at O-3 in the donor, resulted in a considerable increase in the β-mannosylation selectivity. This donor was successfully employed for efficient construction of β-1,3-mannan.[11b]

In more detail, the method developed by Crich for the synthesis of β-1,2-linked mannans is based on the triflate activation of a 4,6-*O*-benzylidene mannopyranosyl sulfoxide donor (bearing *p*-methoxybenzyl protection at O-2 and benzyl at O-3) in the presence of TTBP in CH_2Cl_2 at –60 °C, followed by coupling with the acceptor at –78 °C. Regioselective deprotection of the *p*-methoxybenzyl group provides a new acceptor. An octameric *cyclohexyl-capped* β-1,2-mannan was prepared by iteration of this procedure.[10] An analogous approach to the synthesis of β-1,2-linked oligomannans was reported by Mallet.[4d]

Another method for the construction of β-1,2-mannosidic linkages by employing anomeric sulfonium triflate as the glycosylation species was described by Seeberger.[16a] Activation of the free anomeric hydroxy group by Ph_2SO/Tf_2O provides an anomeric sulfonium triflate, which is more stable than the α-mannosyl triflate intermediate utilized by Crich. Glycosylation with these species requires higher reaction temperatures and longer reaction times. The sulfoxide/Tf_2O dehydrative coupling strategy provided β-1,2-disaccharides in high yields with moderate-to-very-good β-selectivities. Another one-pot glycosylation method using an anomeric hydroxy sugar as the donor and employing phthalic anhydride and triflic anhydride as activating agents was recently reported to proceed with perfect β-stereoselectivity.[16b]

Successful approach to β-1,2-mannosides was also achieved by utilization of a perbenzylated thioglycoside donor activated with dimethyl disulfide/triflic anhydride providing good selectivities (β:α > 9:1) in the construction of disaccharides. Importantly, in this case, highly selective glycosylation was observed without the use of 4,6-*O*-benzylidene protection, previously considered as crucial for obtaining highly stereoselective coupling reactions.[17]

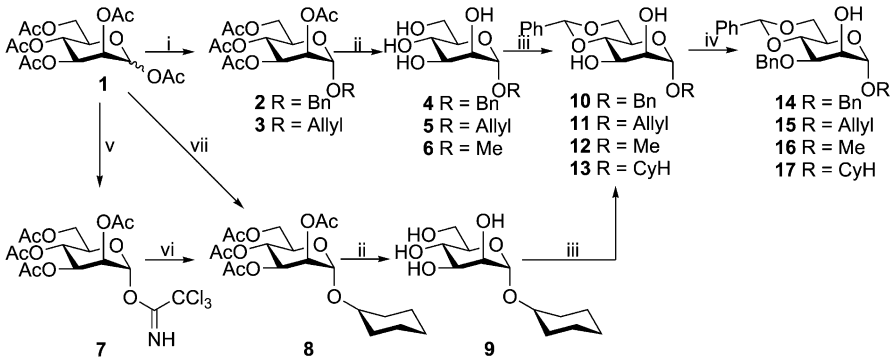
Yet, alternatively, β-1,2-linked mannans can be constructed by forming a β-glucopyranosyl linkage followed by epimerization at C-2 by an oxidation–reduction sequence. In the first reports, an ulosyl bromide was employed as a donor,[18] but this was later replaced by the more-stable glucopyranosyl trichloroacetimidate,[19a] which is particularly useful especially in scale-up reactions. With this indirect approach, excellent diastereoselectivity was observed in the reduction of β-ulopyranosides to β-mannopyranosides by using L-selectride in the key step.[19a,20] A series of glycoconjugates was prepared by this method.[19] By use of the same approach, β-1,2-linked di- and trimannosides with inter residues linked through the sulfur atom were likewise prepared. The introduction of sulfur to the molecule provides glycoconjugates with enhanced stabilities towards chemical and enzymatic hydrolysis.[21] An orthoester-based strategy, also involving a similar type of oxidation–reduction sequence, was presented by Fraser-Reid et al.[22]

In the present work, we further investigated the use of a mannosyl donor with propargyl ether protection at O-2 combined with benzyl ether protection at O-3 for construction of, specifically, β-1,2-linked di- and trimannosides and their glycosides and close analogues. The synthesis and characterization of these compounds together with the evaluation of the influence of protective group strategy on the glycosylation stereoselectivity is elucidated. Some of the compounds prepared here are analogous or closely related to those obtained by Crich and others. However, owing to the biological properties and potential of β-(1→2)-linked mannans in particular, we have specifically targeted the synthesis of *fully deprotected β-1,2-mannobiose and β-1,2-mannotriose*, which are reported here for the first time by utilization of this synthesis strategy. The synthetic strategies developed earlier by others have thus been adapted, modified, and further developed for this specific purpose and are discussed in detail in the present context. Furthermore, we carried out full ^1H and ^{13}C NMR spectroscopic analysis and signal assignments of the final products and building blocks thereof, including spectral simulations and accurate determinations of the coupling constants involved, which even for most of the compounds described earlier, are reported here for the first time.

Results and Discussion

Synthesis of Glycoside Donors and Acceptors

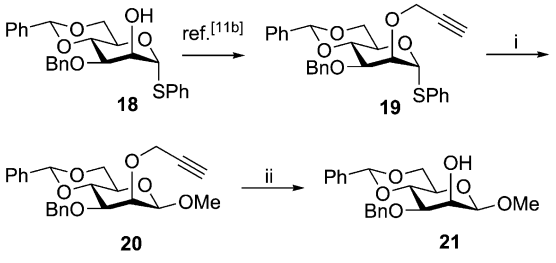
The oligosaccharide synthesis commenced by preparation of donor **19** according to a method described previously.[11b] Several acceptors were prepared by use of the stepwise, selective protecting group strategies illustrated in Scheme 1. The benzyl (**2**) and allyl (**3**)[23] tetra-*O*-acetyl α-D-mannopyranosides were easily obtained in high yields from the glycosylation reactions of the corresponding alcohols with peracetylated mannose (**1**) promoted by $BF_3{\cdot}OEt_2$. Our attempt to synthesize the analogous cyclohexyl tetra-*O*-acetyl α-D-mannopyranoside (**8**) by use of a similar strategy resulted in low yield. For synthesis of glycoside **8**, two alternative procedures were developed. The switch of the Lewis acid from $BF_3{\cdot}OEt_2$ to tin(IV) chloride[24] led to a moderate yield of desired mannoside **8** in one step. An alternative procedure consisting of a three-step sequence was also developed. Compound **8** was successfully prepared by reaction of imidate donor **7**[25,26] with cyclohexanol promoted by $BF_3{\cdot}OEt_2$. Zemplén deprotection of acetylated glycosides **2**, **3**, and **8**[26] then provided the corresponding benzyl (**4**),[27] allyl (**5**),[28] and cyclohexyl (**9**)[26] α-D-mannopyranosides. Interestingly, in the present study, a 92% yield of **4** was achieved over three steps, whereas by straightforward Fischer glycosylation, yields ranging from 35%[29] up to 87%[30] were reported. For further conversion to acceptors, glycosides **4**–**6** and **9** were transformed into their 4,6-*O*-benzylidene derivatives **10**,[26,31] **11**,[32] **12**,[31] and **13**.[26] Selective protection of the equatorial hydroxy



Scheme 1. Reagents and conditions: (i) $BF_3{\cdot}OEt_2$, BnOH/AllOH, CH_2Cl_2, room temp., 24 h, **2** (90%), **3** (82%); (ii) MeONa/MeOH, room temp., 3 h, **4** (95%), **5** (89%); (iii) $PhCH(OMe)_2$, *p*TosOH, DMF, 60 °C, 200 mbar, 2 h, **10** (50%), **11** (51%), **12** (52%), **13** (54%); (iv) 1. Bu_2SnO, toluene, 120 °C, 3 h, 2. BnBr, Bu_4NI, CsF, 120 °C, 3 h, **14** (88%), **15** (88%), **16** (89%), **17** (84%); (v) 1. NH_2NH_2.AcOH, DMF, 55 °C, 30 min, 2. Cl_3CCN, DBU, CH_2Cl_2, room temp., 1.5 h; (vi) $C_6H_{11}OH$, $BF_3{\cdot}OEt_2$, CH_2Cl_2, room temp., 22 h, ref.[26]; (vii) $SnCl_4$, CH_2Cl_2, room temp., 16 h, 64%.

group by treatment with Bu_2SnO in toluene and then alkylation of the 2,3-*O*-dibutylstannylene intermediate with BnBr gave 3-*O*-benzylated acceptors **14**,[26,31] **15**,[33] **16**,[31] **17**,[26] and **18**.[11b,26] Of these, cyclohexyl acceptor **17** is a new building block for oligosaccharide synthesis (Scheme 1). Another, however less effective, approach to such acceptors, for example, compound **16**, can be based on the ring opening of *endo* dibenzylidene derivatives, reportedly yielding only 10% of the desired compound (based on *endo* ylidene).[34]

The synthesis of β-D-mannopyranoside **21** was accomplished by a direct approach over three steps from **19** (Scheme 2). Reaction of activated donor **19** with methanol afforded exclusively corresponding β-glycoside **20**. Removal of the propargyl function gave desired acceptor **21** with β-configuration at the anomeric center. A strategy for the synthesis of **21** over four steps from methyl β-D-glucopyranoside by S_N2 epimerization to the corresponding β-mannopyranoside was reported recently.[35]



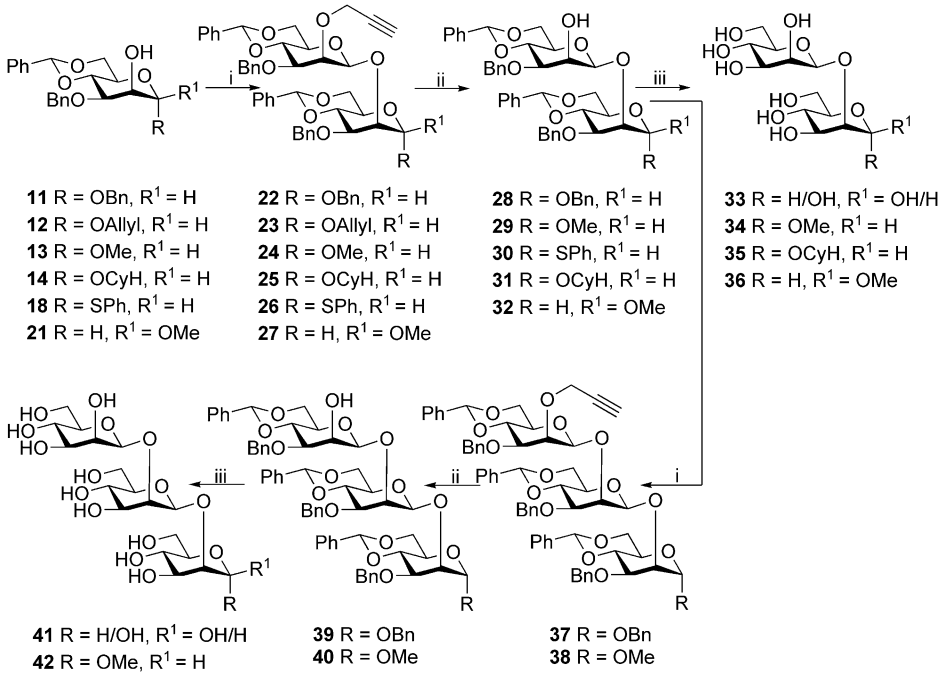
Scheme 2. Reagents and conditions: (i) 1. TTBP, BSP, Tf_2O, CH_2Cl_2, –60 °C, 30 min, 2. MeOH, –60 °C, 2 h, 70%; (ii) 1. *t*BuOK, THF, room temp., 5 h, 2. OsO_4, NMO, acetone/water, room temp., 4 h, 79%.

Synthesis of Mannobiose and Mannotriose

In the present glycosylation study, donor **19** was activated with Tf_2O in the presence of TTBP and BSP in CH_2Cl_2 at –60 °C to yield α-mannopyranosyl triflate. The activated species was then treated at –78 °C with various acceptors. The acceptors were added dropwise over 15 min and the reaction proceeded under continuous stirring at the same temperature over a period of 1.75 h. In total, six acceptors, **11**–**14**, **18**, and **21**, were tested for formation of the β-1,2-linkage (Scheme 3). The glycosylation reactions proved to be highly stereoselective and provided exclusively β-1,2-linked disaccharides **22**–**27** in 72–87% yield. In the ^1H and ^{13}C NMR spectra of these compounds, the characteristic signals for 5-H and C-5 in the β-mannosides were observed at approximately 3.3 and 68 ppm, respectively (for complete characterization see the Experimental Section).

Next, the propargyl ether group of selected disaccharides **22** and **24**–**27** was removed by using a two-step protocol. Isomerization of the propargyl functionality with *t*BuOK in dry THF for 5–6 h afforded the corresponding allenyl ethers. The reaction can be followed by ^1H NMR spectroscopy, which provides a simple and efficient method for the determination of the isomerization yield. The signal from the alkynyl proton (-CH_2–C≡C*H*) appears as a broad triplet (two almost identical coupling constants) with chemical shifts of δ = 2.4–2.5 ppm in all compounds studied. In the allenyl derivatives, this signal disappeared and a new signal for the allenyl proton (-C*H*=C=CH_2) appeared as a triplet at δ = 6.8–7.1 ppm (J = 5–6 Hz). In the second step, oxidative cleavage with NMO/OsO_4 in acetone/water[11b,36] provided disaccharides **28**–**32** with free hydroxy groups at O-2, suitable as acceptors for further oligosaccharide synthesis. In all cases, regioselective removal of the propargyl group proceeded in moderate-to-high yield. Final deprotection of compounds **29** and **32** by hydrogenolysis under 3.45 bar (50 psi) H_2 in methanol proceeded smoothly to provide the corresponding products **34** and **36**. This stereoselective synthesis and new efficient approach, improving the previously described nonselective ones for accessing compounds such as **34** and **21**, which are precursors to methyl β-D-mannopyranoside, is of importance, as such derivatives are of interest for enzyme immunoassays and competitive inhibitor studies.[37]

Slightly modified conditions for hydrogenolysis were also examined and applied for compound **31**. Thus, a mixture



Scheme 3. Reagents and conditions: (i) 1. **19**, TTBP, BSP, Tf_2O, CH_2Cl_2, –60 °C, 30 min. 2. corresponding acceptor, –78 °C, 3 h, **22** (82%), **23** (85%), **24** (87%), **25** (81%), **26** (72%), **27** (85%), **37** (72%), **38** (74%); (ii) 1. *t*BuOK, THF, room temp., 2. OsO_4, NMO, acetone/water, room temp., **28** (80%), **29** (85%), **30** (70%), **31** (85%), **32** (72%), **39** (83%), **40** (81%); (iii) H_2, Pd/C, MeOH, 3.45 bar, room temp., **33** (93%), **34** (93%), **35** (100%), **36** (94%), **41** (crude yield 96%), **42** (97%).

of solvents (MeOH/EtOAc, 9:1) and lower pressure of 2.75 bar (40 psi) H_2 for 18.5 h afforded a smooth deprotection as well.

Apart from the investigation of the glycosylation selectivity, a specific objective of the present study was to investigate feasible strategies for the synthesis of β-1,2-mannobiose (**33**) and β-1,2-mannotriose (**41**) and to provide their full characterization by NMR spectroscopy for reference purposes. The development of methods for accessing these fully deprotected compounds is motivated by the potential biological properties of naturally occurring β-1,2-mannans.

In the first approach, disaccharide **28** was treated under similar hydrogenolysis conditions as that employed for **29** and **32**. The benzyl protecting group at the anomeric position of starting acceptor **11** was selected due to the possibility of being removed simultaneously with the other protecting groups in a single hydrogenolysis reaction, which would thus save an extra deprotection step. Exposure of disaccharide **28** to hydrogenolysis for 19 h gave desired **33** as a 3:1 mixture of the α- and β-disaccharides, as verified by ^1H NMR spectroscopy, together with some amount of side products. As a result of decomposition, a small amount (≈5%) of D-mannose was detected as well together with an unexpected product with *m*/*z* = 461 $[M + Na]^+$ as $[M + 96 + Na]^+$ (for **33**, *m*/*z* = 342 $[M]^+$), which suggests reduction (instead of cleavage) of the anomeric benzyl group to thus yield cyclohexylmethylene β-1,2-mannobioside instead of desired **33**. A sample of pure **33** was finally obtained by graphite solid-phase extraction (for details, see the Experimental Section). Neither change of solvent to ethanol nor a modification of the debenzylation protocol (cyclohexene, Pd/C, EtOH) improved the initial purity of product **33** obtained and resulted only in either significantly slower or uncontrolled reactions.

A similar iterative protocol, coupling of donor **19** with disaccharide acceptors **28** and **29**, afforded protected trisaccharides **37** and **38** with 9.5:1 β/α-selectivities in 72 and 74% yield, respectively. Repeating the deprotection steps utilized earlier for the corresponding disaccharides (vide supra), isomerization of the 2-*O*-propargyl groups to allenyl, followed by oxidative cleavage and hydrogenolysis of precursors **39** and **40** under 3.45 bar H_2 over Pd/C in methanol for 21 h/24 h, provided trimers **41** and **42**. Also in this case, the course of hydrogenolysis was similar to that observed with the disaccharides, namely, formation of trimeric **41** along with a small amount of side product. In the trisaccharide case, however, no decomposition was observed. LC–MS analysis of the crude product mixture confirmed the presence of, except **41**, also cyclohexylmethylene β-1,2-mannotrioside with *m*/*z* = 623 $[M + Na]^+$ as $[M + 96 + Na]^+$ (for **41**, *m*/*z* = 504 $[M]^+$). Pure **41** was gained after chromatographic purification (for details, see the Experimental Section). Formation of the unexpected cyclohexylmethylene side products in the deprotection steps of both the disaccharide and trisaccharide synthesis was confirmed, in addition to mass spectra, by the presence of additional high-field ^1H NMR signals (1.1–1.9 ppm) and ^{13}C NMR signals (29–39 ppm) consistent with cyclohexyl resonances.

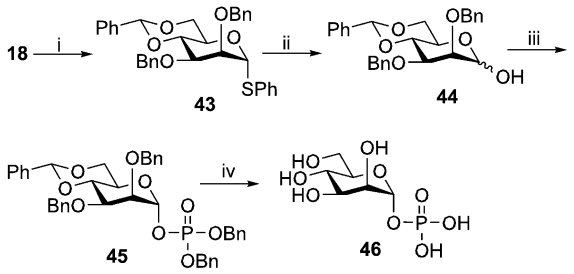
On the basis of the results above, even larger unprotected oligosaccharides from β-1,2-mannotetraose onwards should likewise be accessible by utilization of the methodology investigated here.

Generally, the introduction of nonparticipating groups to the donor molecule, in various combinations, has resulted in highly stereoselective mannosylations. In the present study, the use of donor **19** for stereoselective construction of β-1,2-mannosidic linkages was specifically addressed. In the coupling reactions of **19** with monosaccharide acceptors, exclusive β-selectivities were observed. When larger compounds, in this case trisaccharides, were constructed, the introduction of the third sugar unit decreased the yield to 70–75% together with a drop in stereoselectivity to a β/α ratio of 9.5:1. In light of earlier studies, this is, however, not unexpected, as similar results are often obtained when constructing larger oligomannosides. In the previously reported approach to β-1,2-mannooligosaccharides by utilizing sulfoxide donors (PMB at O-2/Bn at O-3),[10] similar selectivities were recorded: β-only in the disaccharide synthesis and 9.9:1 in the trisaccharide synthesis. The isolated yields for single synthesis steps were, however, higher than those gained by the method and reaction scale utilized in the present study. It is, nevertheless, demonstrated here that glycoside donor **19**, earlier reported to provide highly stereoselective β-1,3-mannosylations,[11b] is also well suited for stereoselective construction of β-1,2-mannosidic linkages and in this way serves as another option to access such compounds. The selectivity obtained by using **19** is in agreement with the earlier reports showing that the size of the substituent at O-3 of the glycoside donor critically influences the stereochemical outcome of the reaction. A benzyl group at O-3 appears to be an ideal choice.[11c] In this sense, donor **19** shows enhanced potential for use as a reagent in β-1,2-mannosylation.

Synthesis of Phosphorylated Mannose and Mannobiose

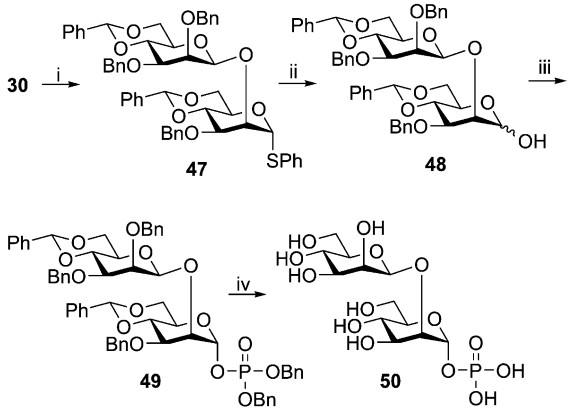
As a result of the biological importance of glycosyl 1-phosphates, the preparation of similar derivatives of mannose was also briefly addressed in the present study. In earlier reports, the analysis of fragments isolated from cell wall mannan of *Candida species* (e.g., *C. glabrata*[38] and *C. albicans*[39]) has confirmed the presence of β-1,2-linked mannobiosyl residues esterified with a phosphate group through C-1 having the α-configuration, as in Man-β-1,2-Man-α-1-HPO_3^-.[38]

In previous investigations, variously protected[40] as well as deprotected[41] mannopyranosyl-1-phosphate derivatives were prepared by chemical synthesis. By enzymatic transformations, mannose-6-phosphate was isomerized by phosphomannose mutase into mannose-1-phosphate.[42] The synthesis of phosphate **50** has not been disclosed earlier. In the present study, monosaccharide **18** and disaccharide **30** with a thiophenyl group at the anomeric position were selected as precursors for the preparation of phosphorylated units (Schemes 4 and 5). Various phosphorylation species,[43] including protected phosphoramidites in the presence of 1*H*-tetrazole, were used to form phosphites, which were subsequently transformed into phosphates with *m*-CPBA in one pot.[44] In analogy to the strategy applied earlier, by simultaneous removal of all protecting groups in one step, benzyl-protected phosphoramidite was here selected as the starting species for introducing the phosphate group to the saccharide molecule.



Scheme 4. Reagents and conditions: (i) BnBr, NaH, DMF, room temp., 2 h; (ii) NBS, acetone/water, room temp., 30 min, 62%; (iii) 1. 1*H*-tetrazole, $(OBn)_2PN(iPr)_2$, CH_2Cl_2, –40 °C, 1 h 45 min, 2. *m*-CPBA, –60 °C, 1 h 15 min, 82%; (iv) H_2, Pd/C, MeOH, 3.45 bar, room temp., 20 h, 95%.

First, derivative **18** was converted into di-*O*-benzylated product **43**,[14b,45] from which the thiophenyl group was released by treatment with NBS in acetone/water to give **44**[46] possessing a free anomeric functionality (Scheme 4). Subsequent derivatization of **44** with $(OBn)_2PN(iPr)_2$ and 1*H*-tetrazole in CH_2Cl_2 provided the corresponding phosphite (quantitative yield, monitored by TLC), which was immediately converted into phosphate **45** by in situ oxidation with *m*-CPBA in one pot. A similar strategy was applied to the synthesis of phosphate **50** (Scheme 5).



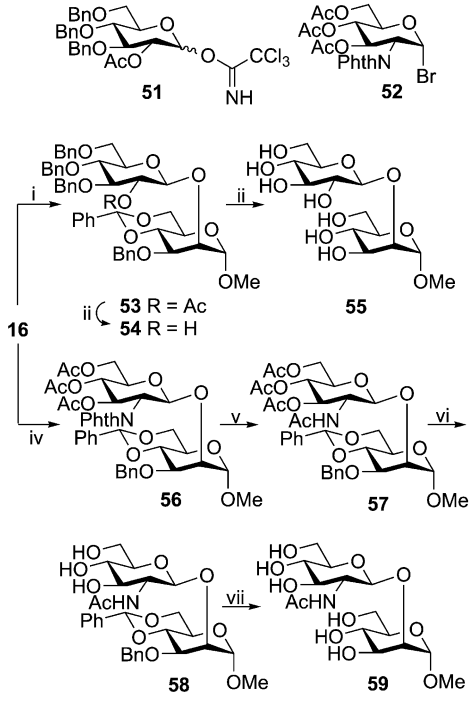
Scheme 5. Reagents and conditions: (i) BnBr, NaH, DMF, room temp., 1.5 h, 96%; (ii) NBS, acetone/water, room temp., 30 min, 62%; (iii) 1. 1*H*-tetrazole, $(OBn)_2PN(iPr)_2$, CH_2Cl_2, –40 °C, 1 h 45 min, 2. *m*-CPBA, –40 °C, 1 h 15 min, 75%; (iv) H_2, Pd/C, MeOH, 3.45 bar, room temp., 18 h, 70%.

In the corresponding monosaccharide synthesis, the conversion of intermediate phosphite to **45** by use of *m*-CPBA (2.5 equiv.) proceeded in quantitative yield. In the case of disaccharide **49**, however, a large excess of the oxidizing agent (5 equiv. of *m*-CPBA) was needed to achieve full conversion to the phosphate. The two-step phosphorylation protocol proved highly efficient. The isolated yield, however, was slightly reduced as a result of repeated purification (2 × column chromatography) required to obtain the prod-

uct with high purity for the final deprotection step. Compounds **45** and **49** were both found to exhibit only the α-configuration at the anomeric center. Next, removal of the benzyl and benzylidene protecting groups was achieved by catalytic hydrogenation to provide corresponding phosphorylated compounds **46**[47] and **50** in 95 and 70% yield, respectively. The structures of **46** and **50** were verified by both ^{1}H and ^{31}P NMR spectroscopic analyses. In the ^{31}P NMR spectrum, the phosphorus signals resonate at δ = –2.48 ppm for **46** and at δ = –2.45 ppm for **50**. Also, the ^{1}H–^{31}P HMBC spectrum clearly confirmed the presence of the phosphate group at the anomeric position.

Modifications to the Oligosaccharide Sugar Units

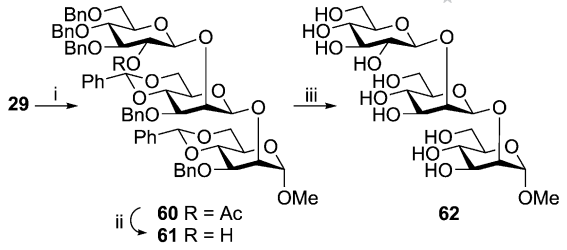
Preliminary modifications to the oligosaccharide structures were also carried out by replacing the nonreducing end mannose unit in the oligomannan structures by D-glucose and *N*-acetyl D-glucosamine (GlcNAc), as outlined in Schemes 6 and 7.



Scheme 6. Reagents and conditions: (i) **51**, TMSOTf (cat.), CH_2Cl_2, 0 °C, 30 min, 80%; (ii) MeONa, MeOH/THF, room temp., 18 h, 98%; (iii) H_2, Pd/C, MeOH, 3.45 bar, room temp., 19 h, 93%; (iv) **52**, AgOTf, CH_2Cl_2, –20 °C, 1 h, 78%; (v) 1. $NH_2NH_2{\cdot}H_2O$, EtOH, reflux, 15 h, 2. Ac_2O, py, room temp., 16 h, 90%; (vi) *t*BuOK, MeOH/THF, 15 h, room temp., 93%; (vii) H_2, Pd/C, MeOH, 3.45 bar, room temp., 6 h, 94%.

A TMSOTf-promoted glycosylation of earlier prepared acceptors **16** (Scheme 6) and **29** (Scheme 7) with glucopyranosyl trichloroacetimidate **51**[48] gave corresponding protected di- and trisaccharides **53** and **60** with full β-selectivity, as expected.

Removal of the acetyl group under Zemplén conditions to obtain desired compounds **54** and **61** was, however, not straightforward. In neither one of the cases was the use of a catalytic amount of MeONa (0.1 equiv. in MeOH[19] or 0.1 equiv. in MeOH/THF for 16 h) sufficient for complete deprotection. Instead, for removal of the 2-*O*-acetyl group in disaccharide **53**, 1.3 equiv. of MeONa in MeOH/THF (3:1) for 18 h was required. In the case of trisaccharide **60**, 1.6 equiv. of MeONa and a reaction time of 72 h was necessary to ensure quantitative yield.



Scheme 7. Reagents and conditions: (i) **51**, TMSOTf (cat.), CH_2Cl_2, 0 °C, 30 min, 78%; (ii) MeONa, MeOH/THF, room temp., 72 h, 98%; (iii) H_2, Pd/C, MeOH, 3.45 bar, room temp., 24 h, 92%.

Acceptor **16** was further glycosylated with protected glucosamine **52** to give disaccharide **56** (Scheme 6). Hydrazynolysis of **56** followed by *N*-acetylation afforded **57**, and then stepwise deprotection finally gave **59** in significantly improved overall yield.[49]

Conclusions

To summarize, donor **19** was shown to provide enhanced potential and was successfully applied for the highly stereoselective synthesis of various β-1,2-linked mannosides. The selection of suitably protected building blocks provided access to fully deprotected β-1,2-oligomannopyranoses (mannobiose and mannotriose). By simple modifications of the synthesis strategy, mannopyranosyl-α-1-phosphates can be obtained from similar building blocks as well. Finally, the synthesis of some modified β-1,2-linked mannoside oligosaccharide analogues having single mannose units replaced by D-glucose or GlcNAc was also presented. The full NMR spectroscopic characterization of the final products as well as their intermediates is enclosed with this paper (see Experimental Section), as for many of these compounds complete and fully resolved NMR spectroscopic data was not disclosed earlier and may be of use as reference data for other researchers in this field. The biological evaluation of the compounds prepared for immunostimulatory applications is currently in progress. Notably, as disclosed by us elsewhere,[26] some of the compounds prepared here may easily be applied as starting materials for further modifications towards multivalent structures by utilization of homodimerization/ruthenium-catalyzed olefin cross metathesis.

Experimental Section

Characterization of the Products and General Remarks: Reaction solvents were dried and distilled prior to use when necessary. All

reactions containing air- or moisture-sensitive reagents were carried out under an argon atmosphere.

All NMR spectra were recorded with Bruker Avance spectrometers operating at 500.13 or 600.13 MHz for ^{1}H, 125.77 or 150.90 MHz for ^{13}C, and 202.47 MHz for ^{31}P. All products were fully characterized with 1D ^{1}H, ^{13}C, and TOCSY in combination with the 2D NMR techniques COSY, TOCSY, HSQC, HMSC (heteronuclear multiple and single bond correlation), and HMBC by using pulse sequences provided by the instrument manufacturer. The probe temperature was for most measurements kept at 25 °C. All chemical shifts are quoted on the δ scale in parts per million (ppm). Chemical shifts are reported relative to internal Me_4Si in $CDCl_3$ and CD_3OD (δ_H = 0.0 ppm and δ_C = 0.0 ppm) and HOD for D_2O (δ_H = 4.79 ppm). ^{31}P chemical shifts are externally referenced to a solution of 0.0485 M triphenylphosphate (TPP) in [D_6]acetone (δ_P = –17.90 ppm). When the signals had very similar chemical shifts, additional decimals were used to show the order of the signals.

In the glycosidation steps, formation of the glycosidic linkage was confirmed by the heteronuclear one-bond coupling constants[50] from the anomeric proton (1-H) to the anomeric carbon atom (C-1). These coupling constants were measured by using HMBC or HMSC NMR spectroscopic techniques. A typical one-bond heteronuclear coupling constant for the β-anomer of D-mannose was around 160 Hz, whereas for the α-anomer it was approximately 170 Hz. Also, the characteristic chemical shift for the 5-H proton and C-5 carbon resonances were used for determining the anomeric configurations.

The ^{1}H and ^{13}C assignment was based on the ^{1}H-, ^{13}C-, COSY-, TOCSY-, HSQC-, HMBC-, and HMSC spectra, mainly recorded with a Bruker Avance 600 MHz spectrometer. The complete computational analysis of the ^{1}H NMR spectra was achieved by utilization of the PERCH NMR software[51] with the starting values and spectral parameters obtained from the various NMR techniques used and briefly described above. The ^{1}H NMR chemical shifts and coupling constants were accurately determined for all the described compounds and the carbon spectrum assignment was based on the HSQC spectrum. The signals of the anomeric protons are usually easily identified due to their characteristic chemical shifts between 4.5 and 5.4 ppm and each signal appears as a doublet (d) or as a broad singlet due to the small $^3J_{1,2}$ coupling for the β-anomer of D-mannopyranose. All other non-hydroxy sugar protons appear as doublets of doublets (dd), except 5-H, which has couplings to 4-H, 6a-H, and 6b-H (ddd), if not additional long-range coupling constants are visible to exchangeable protons in -NH or -OH or to another NMR active nucleus such as ^{31}P. The coupling constants are here reported only once for a proton, even though two protons share the same coupling constant.

As a result of the small couplings observed for mannose from 1-H to 2-H (varying between 0.7 Hz to 2 Hz for the two anomers) and further from 2-H to 3-H (approximately 3.3 Hz), the utilization of COSY and TOCSY correlation experiments for the well-resolved anomeric protons was problematic. Accordingly, in some cases it was easier to use instead the relatively well-separated low-field chemical shifts of 2-H or the high-field chemical shifts of 5-H, typical for the β-anomer, for the selective irradiation experiments. Long-range correlations between the rings as well as the positions of the different protective groups could then be determined by HMBC. By use of HMSC, the anomeric configurations could be unambiguously determined on the basis of the size of the $^1J_{C,H}$ coupling constant.

HRMS were recorded using either Bruker Micro Q-TOF with ESI (electrospray ionization) operated in positive mode or Fison ZabSpecOaTOF with EI (electron impact) ionization operated in positive mode. TLC was performed on aluminium sheets precoated with silica gel 60 F_{254} (Merck) and the spots were visualized by UV and charring with 1.5% (w/v) orcinol monohydrate in H_2SO_4/MeOH (1:10). Flash column chromatography was carried out with Silica Gel 60 (0.040–0.600 mm, Merck). Optical rotations were measured with a Perkin–Elmer 241 polarimeter equipped with a Na lamp (589 nm) at 23 °C. The LC–ESI-MS/MS analyses were performed with an Agilent 1100 Series LC/MSD Trap SL instrument (Agilent Technologies) equipped with an electrospray source and operated in the positive ion mode. HPLC purification was carried out with an Agilent 1100 Series liquid chromatographic system.

General Procedure for the Preparation of 2 and 3: To a mixture of 1,2,3,4,6-penta-*O*-acetyl-D-mannopyranose (3.0 g, 7.7 mmol, 1 equiv.) and 4 Å molecular sieves (3 g) in CH_2Cl_2 (20 mL) under an argon atmosphere was added the corresponding alcohol (5 equiv.). The reaction mixture was stirred for 20 min, cooled down with an ice bath, and $BF_3{\cdot}OEt_2$ (10 equiv.) was then added dropwise. The reaction mixture was brought to room temperature and stirring was continued for 24 h. The reaction mixture was diluted with CH_2Cl_2 (200 mL) and poured into ice water (200 mL) with stirring. After 30 min, the phases were separated, and the organic phase was washed with saturated $NaHCO_3$ (2 × 100 mL), water (2 × 100 mL), and brine (100 mL), dried, and concentrated. The crude products were purified by column chromatography (hexane/EtOAc, 3:1) to give compounds **2** (3.3 g, 90%) or **3** (2.4 g, 82%), respectively.

Benzyl 2,3,4,6-Tetra-*O*-acetyl-α-D-mannopyranoside (2): $[\alpha]_D$ = +58.3 (c = 1.0, $CHCl_3$). ^{1}H NMR (600.13 MHz, $CDCl_3$, 25 °C): δ = 7.35–7.23 (m, 5 H, arom. H), 5.38 (dd, $J_{3,4}$ = 10.1 Hz, 1 H, 3-H), 5.30 (dd, $J_{4,5}$ = 10.2 Hz, 1 H, 4-H), 5.29 (dd, $J_{2,3}$ = 3.5 Hz, 1 H, 2-H), 4.89 (d, $J_{1,2}$ = 1.8 Hz, 1 H, 1-H), 4.71 and 4.57 (each d, J = –11.9 Hz, each 1 H, 1-CH_2Ph), 4.28 (dd, 1 H, 6b-H), 4.04 (dd, $J_{6a,6b}$ = –12.3 Hz, 1 H, 6a-H), 4.01 (ddd, $J_{5,6a}$ = 2.4 Hz, $J_{5,6b}$ = 5.1 Hz, 1 H, 5-H), 2.14, 2.12, 2.04, 1.99 (each s, each 3 H, 4 × CH_3C=O) ppm. ^{13}C NMR (150.90 MHz, $CDCl_3$, 25 °C): δ = 170.6, 170.0, 169.9, 169.8 (4 × CH_3C=O), 136.2–128.2 (arom. C), 96.8 (C-1), 69.8 (1-CH$_2$Ph), 69.6 (C-2), 69.2 (C-3), 68.6 (C-5), 66.2 (C-4), 62.4 (C-6), 20.9 (2-CH$_3$C=O), 20.8 (6-CH$_3$C=O), 20.7 (3- and 4-CH$_3$C=O) ppm. HRMS: calcd. for $C_{17}H_{24}O_{10}Na$ $[M + Na]^+$ 411.1267; found 411.1262.

Allyl 2,3,4,6-Tetra-*O*-acetyl-α-D-mannopyranoside (3): $[\alpha]_D$ = +46.9 (c = 1.0, $CHCl_3$). ^{1}H NMR (600.13 MHz, $CDCl_3$, 25 °C): δ = 5.90 (dddd, $J_{CH,CH_{2cis}}$ = 10.4 Hz, $J_{CH,CH_{2trans}}$ = 17.2 Hz, 1 H, CH_2CH=CH_2), 5.38 (ddd, $J_{3,4}$ = 10.1 Hz, $J_{3,5}$ = –0.58 Hz, 1 H, 3-H), 5.32 (dddd, $J_{CH_{2trans},CH_{2cis}}$ = –1.4 Hz, 1 H, CH_2CH=CH_{2trans}), 5.29 (dd, $J_{4,5}$ = 10.1 Hz, 1 H, 4-H), 5.26 (dd, $J_{2,3}$ = 3.5 Hz, 1 H, 2-H), 5.25 (dddd, 1 H, CH_2CH=CH_{2cis}), 4.29 (dd, 1 H, 6b-H), 4.87 (d, $J_{1,2}$ = 1.8 Hz, 1 H, 1-H), 4.19 (dddd, $J_{CH_{2a},CH_{2b}}$ = –12.7 Hz, $J_{CH_{2a},CH}$ = 5.3 Hz, $J_{CH_{2a},CH_{2cis}}$ = –1.2 Hz, $J_{CH_{2a},CH_{2trans}}$ = –1.6 Hz, 1 H, CH_{2a}CH=CH), 4.11 (dd, $J_{6a,6b}$ = –12.2 Hz, 1 H, 6a-H), 4.04 (dddd, $J_{CH_{2b},CH}$ = 6.3 Hz, $J_{CH_{2b},CH_{2cis}}$ = –1.2 Hz, $J_{CH_{2b},CH_{2trans}}$ = –1.5 Hz, CH_{2b}CH=CH), 4.02 (dddd, $J_{5,6a}$ = 2.4 Hz, $J_{5,6b}$ = 5.3 Hz, 1 H, 5-H), 2.16 (s, 3 H, 2-CH_3C=O), 2.11 (s 3 H, 3-CH_3C=O), 2.04 (s, 3 H, 4-CH_3C=O), 2.00 (s, 3 H, 6-CH_3C=O) ppm. ^{13}C NMR (150.90 MHz, $CDCl_3$, 25 °C): δ = 170.7, 170.1, 169.9, 169.8 (4 × CH_3C=O), 132.9 (CH_2CH=CH_2), 118.5 (CH_2CH=CH_2), 96.6 (C-1), 69.7 (C-2), 69.1 (C-3), 68.7 (CH_2CH=CH_2), 68.6 (C-5), 66.2 (C-4), 62.5 (C-6), 20.9, 20.8, 20.7 (4 × CH$_3$C=O) ppm. HRMS: calcd. for $C_{17}H_{24}O_{10}Na$ $[M + Na]^+$ 411.1267; found 411.1262.

General Procedure for the Preparation of 4 and 5: To a solution of acetylated mannopyranoside **2** (3.3 g, 7.5 mmol) or **3** (2.4 g,

6.2 mmol) dissolved in dry MeOH (39 mL) was added 1 M NaOMe (1 mL). The reaction mixture was stirred under an argon atmosphere for 3 h, then neutralized with DOWEX 50 H^+-form, filtered, and concentrated. The crude product was purified by column chromatography (CH_2Cl_2/MeOH, 10:1→5:1) to give **4** (1.93 g, 95%) or **5** (1.21 g, 89%), respectively.

Benzyl α-D-Mannopyranoside (4) : $[\alpha]_D$ = +85.1 (*c* = 1.0, MeOH); ref.[27a] $[\alpha]_D^{26}$ = +74.0 (*c* = 1.3, H_2O). ^{1}H NMR (600.13 MHz, CD_3OD, 25 °C): δ = 7.38–7.26 (m, 5 H, arom. H), 4.75 and 4.52 (each d, *J* = –11.8 Hz, each 1 H, CH_2Ph), 4.83 (d, $J_{1,2}$ = 1.7 Hz, 1 H, 1-H), 3.84 (dd, $J_{6a,6b}$ = –11.8 Hz, 1 H, 6a-H), 3.82 (dd, $J_{2,3}$ = 3.4 Hz, 1 H, 2-H), 3.723 (dd, $J_{3,4}$ = 9.3 Hz, 1 H, 3-H), 3.715 (dd, 1 H, 6b-H), 3.62 (dd, $J_{4,5}$ = 9.9 Hz, 1 H, 4-H), 3.59 (ddd, $J_{5,6a}$ = 2.2 Hz, $J_{5,6b}$ = 6.0 Hz, 1 H, 5-H) ppm. ^{13}C NMR (150.90 MHz, CD_3OD, 25 °C): δ = 139.1–128.8 (arom. C), 100.7 (C-1), 75.0 (C-5), 72.7 (C-3), 72.3 (C-2), 69.9 (*C*H_2Ph), 68.7 (C-4), 63.0 (C-6) ppm. HRMS: calcd. for $C_{13}H_{18}O_6Na$ [M + Na]$^+$ 293.0996; found 293.0999.

Allyl α-D-Mannopyranoside (5): $[\alpha]_D$ = +73.6 (*c* = 1.0, MeOH); ref.[32] $[\alpha]_D^{26}$ = +51.6 (*c* = 0.23, H_2O). ^{1}H NMR (600.13 MHz, $CDCl_3$, 25 °C): δ = 5.93 (dddd, $J_{CH,CH_{2cis}}$ = 10.5 Hz, $J_{CH,CH_{2trans}}$ = 17.2 Hz, 1 H, CH_2CH=CH_2), 5.29 (dddd, $J_{CH_{2trans},CH_{2cis}}$ = –1.9 Hz, 1 H, CH_2CH=CH_{2trans}), 5.16 (dddd, 1 H, CH_2CH=CH_{2cis}), 4.79 (dd, $J_{1,2}$ = 1.7 Hz, $J_{1,5}$ = –0.61 Hz, 1 H, 1-H), 4.21 (dddd, $J_{CH_{2a},CH_{2b}}$ = –13.1 Hz, $J_{CH_{2a},CH}$ = 5.1 Hz, $J_{CH_{2a},CH_{2cis}}$ = –1.4 Hz, $J_{CH_{2a},CH_{2trans}}$ = –1.7 Hz, 1 H, CH_{2a}CH=CH), 4.00 (dddd, $J_{CH_{2b},CH}$ = 6.0 Hz, $J_{CH_{2b},CH_{2cis}}$ = –1.3 Hz, $J_{CH_{2b},CH_{2trans}}$ = –1.6 Hz, CH_{2b}CH=CH), 3.83 (dd, $J_{6a,6b}$ = –11.8 Hz, 1 H, 6a-H), 3.80 (dd, $J_{2,3}$ = 3.4 Hz, 1 H, 2-H), 3.700 (dd, $J_{3,4}$ = 9.5 Hz, 1 H, 3-H), 3.699 (dd, 1 H, 6b-H), 3.60 (dd, $J_{4,5}$ = 9.9 Hz, 1 H, 4-H), 3.53 (ddd, $J_{5,6a}$ = 2.3 Hz, $J_{5,6b}$ = 6.0 Hz, 1 H, 5-H) ppm. ^{13}C NMR (150.90 MHz, CD_3OD, 25 °C): δ = 135.5 (CH_2CH=CH_2), 117.3 (CH_2CH=CH_2), 100.8 (C-1), 74.8 (C-5), 72.7 (C-3), 72.2 (C-2), 68.9 (*C*H_2CH=CH_2), 68.7 (C-4), 63.0 (C-6) ppm. HRMS: calcd. for $C_9H_{16}O_6Na$ [M + Na]$^+$ 243.0839; found 243.0836.

Cyclohexyl 2,3,4,6-Tetra-*O*-acetyl-α-D-mannopyranoside (8): To a solution of 1,2,3,4,6-penta-*O*-acetyl-D-mannopyranose (2 g, 5.12 mmol, 1 equiv.) and cyclohexanol (0.62 g, 0.64 mL, 1.2 equiv.) in CH_2Cl_2 (30 mL) under an argon atmosphere was added tin(IV)-chloride (1 M in CH_2Cl_2, 0.26 g, 1.05 mL, 1 equiv.). The reaction mixture was stirred for 16 h, then diluted with CH_2Cl_2 (20 mL), and poured into saturated $NaHCO_3$ solution (50 mL). After being stirred for 20 min, the organic layer was separated, dried, and concentrated. The crude product was further purified by column chromatography (hexane/EtOAc, 3:1→2:1) to give **8** (1.41 g, 64%).

General Procedure for the Preparation of 10–13: The corresponding α-D-mannopyranoside **4**–**6** or **9** (1 equiv.), respectively, was dissolved in dry DMF (2.7 mL, 1 mmol) and treated with *p*TosOH (0.1 equiv.) and benzaldehyde dimethylacetal (1 equiv.) at room temperature. The reaction mixture was stirred for 2 h at 60 °C under reduced pressure (200 mbar) by using a rotary evaporator. The solvent was then evaporated, and the residue was diluted with EtOAc (100 mL). The organic phase was washed with saturated $NaHCO_3$ (50 mL), and the water phase was washed with EtOAc (3 × 50 mL). The combined organic phase was washed again with water (2 × 100 mL), dried, and concentrated. The crude product was purified by column chromatography ($CHCl_3$→$CHCl_3$/MeOH, 8:1) to give desired products **10** (50%), **11** (51%), **12** (52%), or **13** (54%), respectively.

Allyl 4,6-*O*-Benzylidene-α-D-mannopyranoside (11): $[\alpha]_D$ = +71.4 (*c* = 1.0, $CHCl_3$); ref.[32] $[\alpha]_D^{26}$ = +68.6 (*c* = 0.26, $CHCl_3$). ^{1}H NMR (600.13 MHz, CD_3OD, 25 °C): δ = 7.50–7.37 (m, 5 H, arom. H), 5.91 (dddd, $J_{CH,CH_{2cis}}$ = 10.4 Hz, $J_{CH,CH_{2trans}}$ = 17.2 Hz, 1 H, CH_2CH=CH_2), 5.31 (dddd, $J_{CH_{2trans},CH_{2cis}}$ = –1.6 Hz, 1 H, CH_2CH=CH_{2trans}), 5.58 (s 1 H, C*H*Ph), 5.23 (dddd, 1 H, CH_2CH=CH_{2cis}), 4.93 (d, $J_{1,2}$ = 1.5 Hz, 1 H, 1-H), 4.28 (dd, $J_{6a,6b}$ = –10.3 Hz, 1 H, 6a-H), 4.21 (dddd, $J_{CH_{2a},CH_{2b}}$ = –12.9 Hz, $J_{CH_{2a},CH}$ = 5.2 Hz, $J_{CH_{2a},CH_{2cis}}$ = –1.3 Hz, $J_{CH_{2a},CH_{2trans}}$ = –1.7 Hz, 1 H, CH_{2a}CH=CH), 4.12 (dd, $J_{3,4}$ = 9.7 Hz, 1 H, 3-H), 4.08 (dd, $J_{2,3}$ = 3.5 Hz, 1 H, 2-H), 4.02 (dddd, $J_{CH_{2b},CH}$ = 6.1 Hz, $J_{CH_{2b},CH_{2cis}}$ = –1.2 Hz, $J_{CH_{2b},CH_{2trans}}$ = –1.5 Hz, CH_{2b}CH=CH), 3.94 (dd, $J_{4,5}$ = 9.4 Hz, 1 H, 4-H), 3.87 (ddd, $J_{5,6a}$ = 5.0 Hz, $J_{5,6b}$ = 10.3 Hz, 1 H, 5-H), 3.83 (dd, 1 H, 6b-H) ppm. ^{13}C NMR (150.90 MHz, $CDCl_3$, 25 °C): δ = 137.2–126.2 (arom. C), 133.4 (CH_2CH=CH_2), 117.8 (CH_2CH=CH_2), 102.3 (*C*HPh), 99.3 (C-1), 78.9 (C-4), 71.0 (C-2), 68.8 (C-6), 68.7 (C-3), 68.3 (*C*H_2CH=CH_2), 63.1 (C-5) ppm. HRMS: calcd. for $C_{16}H_{20}O_6Na$ [M + Na]$^+$ 331.1152; found 331.1164.

Methyl 4,6-*O*-Benzylidene-α-D-mannopyranoside (12): $[\alpha]_D$ = +64.7 (*c* = 1.0, $CHCl_3$); ref.[31b] $[\alpha]_D^{23}$ = +70.1 (*c* = 1.07, $CHCl_3$). ^{1}H NMR (600.13 MHz, $CDCl_3$, 25 °C): δ = 7.50–7.36 (m, 5 H, arom. H), 5.58 (s, 1 H, C*H*Ph), 4.78 (d, $J_{1,2}$ = 1.4 Hz, 1 H, 1-H), 4.29 (dd, $J_{5,6a}$ = 4.9 Hz, $J_{6a,6b}$ = –10.3 Hz, 1 H, 6a-H), 4.08 (ddd, $J_{3,3\text{-OH}}$ = 1.4 Hz, $J_{2,3}$ = 3.7 Hz, $J_{3,4}$ = 9.6 Hz, 1 H, 3-H), 4.06 (ddd, $J_{2,2\text{-OH}}$ = 1.1 Hz, 1 H, 2-H), 3.93 (dd, $J_{4,5}$ = 9.3 Hz, 1 H, 4-H), 3.84 (dd, $J_{5,6b}$ = 10.4 Hz, 1 H, 6b-H), 3.82 (ddd, 1 H, 5-H), 3.41 (s 3 H, OCH_3), 2.59 (d, 1 H, 3-O*H*), 2.56 (d, 1 H, 2-O*H*) ppm. ^{13}C NMR (150.90 MHz, $CDCl_3$, 25 °C): δ = 137.2–126.3 (arom. C), 102.3 (*C*HPh), 101.2 (C-1), 78.9 (C-4), 70.9 (C-2), 68.9 (C-6), 68.7 (C-3), 62.8 (C-5), 55.1 (OCH_3) ppm.

General Procedure for the Preparation of Acceptors 14–17: To a solution containing the corresponding α-D-mannopyranoside **10**–**13** (1 equiv.) in dry toluene (7 mL, 1 mmol) was added Bu_2SnO (1.02 equiv.). The reaction mixture was stirred under reflux at 120 °C under an argon atmosphere for 3 h, cooled down to room temperature, followed by the addition of Bu_4NBr (1.06 equiv.), CsF (1.02 equiv.), and BnBr (1.05 equiv.). The reaction mixture was stirred at 120 °C for 3 h, cooled down to room temperature, and diluted with EtOAc (40 mL) and saturated $NaHCO_3$ (30 mL). The organic phase was separated, and the water phase was extracted with EtOAc (3 × 40 mL). The combined organic phase was washed with water (30 mL) and brine (30 mL), dried, and concentrated. The crude product was purified by column chromatography (hexane/EtOAc, 4:1) to give 3-*O*-benzylated products **14** (88%), **15** (88%), **16** (89%), or **17** (84%), respectively.

Allyl 3-*O*-Benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (15): $[\alpha]_D$ = +52.8 (*c* = 1.0, $CHCl_3$); ref.[33] $[\alpha]_D^{24}$ = +41.0 (*c* = 5.5, $CHCl_3$). ^{1}H NMR (600.13 MHz, $CDCl_3$, 25 °C): δ = 7.52–7.28 (m, 10 H, arom. H), 5.90 (dddd, $J_{CH,CH_{2cis}}$ = 10.4 Hz, $J_{CH,CH_{2trans}}$ = 17.2 Hz, 1 H, CH_2CH=CH_2), 5.62 (s, 1 H, C*H*Ph), 5.29 (dddd, $J_{CH_{2trans},CH_{2cis}}$ = –1.6 Hz, 1 H, CH_2CH=CH_{2trans}), 5.22 (dddd, 1 H, CH_2CH=CH_{2cis}), 4.93 (d, $J_{1,2}$ = 1.5 Hz, 1 H, 1-H), 4.87 and 4.73 (each d, *J* = –11.8 Hz, each 1 H, CH_2Ph), 4.27 (dd, $J_{6a,6b}$ = –10.5 Hz, 1 H, 6a-H), 4.19 (dddd, $J_{CH_{2a},CH_{2b}}$ = –12.9 Hz, $J_{CH_{2a},CH}$ = 5.2 Hz, $J_{CH_{2a},CH_{2cis}}$ = –1.3 Hz, $J_{CH_{2a},CH_{2trans}}$ = –1.7 Hz, 1 H, CH_{2a}CH=CH), 4.11 (dd, $J_{4,5}$ = 9.3 Hz, 1 H, 4-H), 4.09 (ddd, $J_{2,3}$ = 3.5 Hz, $J_{2,2\text{-OH}}$ = 1.4 Hz, 1 H, 2-H), 4.00 (dddd, $J_{CH_{2b},CH}$ = 6.2 Hz, $J_{CH_{2b},CH_{2cis}}$ = –1.2 Hz, $J_{CH_{2b},CH_{2trans}}$ = –1.5 Hz, CH_{2b}CH=CH), 3.96 (dd, $J_{3,4}$ = 9.6 Hz, 1 H, 3-H), 3.87 (ddd, $J_{5,6a}$ = 5.1 Hz, $J_{5,6b}$ = 10.3 Hz, 1 H, 5-H), 3.86 (dd, 1 H, 6b-H) 2.64 (d, 1 H, 2-OH) ppm. ^{13}C NMR (150.90 MHz, $CDCl_3$, 25 °C): δ = 138.0–126.1 (arom. C), 133.5 (CH_2CH=CH_2), 117.9 (CH_2CH=CH_2), 101.6 (*C*HPh), 99.1 (C-1), 78.9 (C-4), 75.7 (C-3), 73.1 (*C*H_2Ph), 70.0 (C-2), 68.9 (C-6), 68.2 (*C*H_2CH=CH_2), 63.4 (C-5) ppm. HRMS: calcd. for $C_{23}H_{26}O_6$ [M]$^+$ 398.1729; found 398.1733.

Methyl 3-*O*-Benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (16): $[a]_D$ = +34.2 (*c* = 0.5, EtOH); ref.[34] $[a]_D^{24}$ = +30.0 (*c* = 0.4, EtOH). ^{1}H NMR (600.13 MHz, $CDCl_3$, 25 °C): δ = 7.50–7.28 (m, 10 H, arom. H), 5.61 (s, 1 H, C*H*Ph), 4.85 and 4.71 (each d, *J* = –11.8 Hz, each 1 H, 3-CH_2Ph), 4.77 (d, $J_{1,2}$ = 1.4 Hz, 1 H, 1-H), 4.28 (dd, $J_{6a,6b}$ = –9.9 Hz, 1 H, 6a-H), 4.12 (dd, $J_{4,5}$ = 9.6 Hz, 1 H, 4-H), 4.05 (ddd, $J_{2,3}$ = 3.3 Hz, $J_{2,2\text{-OH}}$ = 1.2 Hz, 1 H, 2-H), 3.90 (dd, $J_{3,4}$ = 9.6 Hz, 1 H, 3-H), 3.86 (dd, 1 H, 6b-H), 3.81 (ddd, $J_{5,6a}$ = 4.9 Hz, $J_{5,6b}$ = 10.2 Hz, 1 H, 5-H), 3.38 (s, 3 H, OCH_3) ppm. 2.65 (d, 1 H, 2-OH). ^{13}C NMR (150.90 MHz, $CDCl_3$, 25 °C): δ = 138.1–125.8 (arom. C), 101.2 (*C*HPh), 100.5 (C-1), 78.4 (C-4), 75.2 (C-3), 72.5 (3-*C*H_2Ph), 69.4 (C-2), 68.6 (C-6), 62.6 (C-5), 54.7 (OCH_3) ppm.

Methyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-β-D-mannopyranoside (20): Donor **19** (0.31 g, 0.63 mmol, 1 equiv.), TTBP (0.24 g, 0.95 mmol, 1.5 equiv.), 4 Å molecular sieves (0.5 g) were stirred in dry CH_2Cl_2 (6 mL) under an argon atmosphere. The temperature was reduced to –40 °C. 1-Benzenesulfinylpiperidine (BSP; 0.16 g, 0.76 mmol, 1.2 equiv.) was then added, and the temperature was lowered to –60 °C. Tf_2O (0.23 g, 0.14 mL, 0.82 mmol, 1.3 equiv.) was added into the solution followed by the addition of dry MeOH (61 mg, 77 μL, 1.9 mmol, 3 equiv.) after stirring for 20 min. The reaction mixture was stirred for 2 h at –60 °C, then warmed up to room temperature and diluted with CH_2Cl_2 (40 mL). The organic phase was washed with saturated $NaHCO_3$ (2 × 20 mL) and water (20 mL), dried, and concentrated. Purification by column chromatography (hexane/EtOAc, 8:1→5:1) afforded the title compound (0.18 g, 70%). $[a]_D$ = –80.0 (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (600.13 MHz, $CDCl_3$, 25 °C): δ = 7.51–7.27 (m, 10 H, arom. H), 5.60 (s, 1 H, C*H*Ph), 4.84 and 4.81 (each d, *J* = –12.5 Hz, each 1 H, 3-CH_2Ph), 4.60 (dd, $J_{CH_{2a},CH}$ = 2.4 Hz, $J_{CH_{2a},CH_{2b}}$ = –16.1 Hz, 1 H, CH_{2a}C≡CH), 4.56 (dd, $J_{CH_{2b},CH}$ = 2.4 Hz, 1 H, CH_{2b}C≡CH), 4.40 (d, $J_{1,2}$ = 0.95 Hz, 1 H, 1-H), 4.32 (dd, $J_{6a,6b}$ = –10.4 Hz, 1 H, 6a-H), 4.18 (dd, $J_{2,3}$ = 3.1 Hz, 1 H, 2-H), 4.12 (dd, $J_{4,5}$ = 9.3 Hz, 1 H, 4-H), 3.91 (dd, 1 H, 6b-H), 3.63 (dd, $J_{3,4}$ = 9.9 Hz, 1 H, 3-H), 3.52 (s, 3 H, OCH_3), 3.32 (ddd, $J_{5,6a}$ = 4.9 Hz, $J_{5,6b}$ = 10.1 Hz, 1 H, 5-H), 2.48 (dd, 1 H, CH_2C≡C*H*) ppm. ^{13}C NMR (150.90 MHz, $CDCl_3$, 25 °C): δ = 138.2–126.2 (arom. C), 102.9 (C-1), 101.4 (*C*HPh), 80.2 (CH_2*C*≡CH), 78.5 (C-4), 77.0 (C-3), 75.1 (C-2), 74.9 (CH_2C≡*C*H), 72.5 (3-*C*H_2Ph), 68.6 (C-6), 67.5 (C-5), 60.0 (*C*H_2C≡CH), 57.5 (OCH_3) ppm. HRMS: calcd. for $C_{24}H_{26}O_6$ $[M]^+$ 410.1729; found 410.1728.

Methyl 3-*O*-Benzyl-4,6-*O*-benzylidene-β-D-mannopyranoside (21): Compound **20** (0.18 g, 0.44 mmol) was dissolved in dry THF (5 mL) and treated with *t*BuOK (52 mg, 0.47 mmol, 1.2 equiv.). After being stirred for 5 h, the mixture was diluted with CH_2Cl_2 (30 mL) and washed with water (2 × 15 mL). The organic phase was dried and concentrated to give the isomerized product (2-*O*-allenyl ether), which was analyzed by NMR spectroscopy and used directly in the next step. 2-*O*-Allenyl ether (0.18 g, 0.044 mmol) was dissolved in acetone/water (4:1, 5 mL) and treated with OsO_4 (13 mg, 0.052 mmol, 0.12 equiv.) and NMO (0.10 g, 0.87 mmol, 2 equiv.). The mixture was stirred for 4 h at room temperature. The solvent was evaporated, and the residue was dissolved in CH_2Cl_2 (20 mL). The organic phase was washed with brine (20 mL) and brine washed with dichloromethane (20 mL). The combined organic phase was again washed with brine (2 × 10 mL) and water (20 mL), dried, and concentrated. The residue was purified by column chromatography (hexane/EtOAc, 2:1→1.5:1), and desired product **21** was obtained (0.13 g, 79%). Analytical data for compound **21** are in excellent agreement with those previously reported.[35a]

Phenyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-1-thio-α-D-mannopyranoside (19): $[a]_D$ = +143.9 (*c* = 1.0, $CHCl_3$); ref.[11b] $[a]_D^{26}$ = +167.5 (*c* = 2.0, $CHCl_3$). ^{1}H NMR (600.13 MHz, $CDCl_3$, 25 °C): δ = 7.52–7.28 (m, 15 H, arom. H), 5.63 (s, 1 H, C*H*Ph), 5.62 (d, $J_{1,2}$ = 1.5 Hz, 1 H, 1-H), 4.88 and 4.76 (each d, *J* = –12.1 Hz, each 1 H, 3-CH_2Ph), 4.43 (dd, $J_{CH_{2a},CH}$ = 2.3 Hz, $J_{CH_{2a},CH_{2b}}$ = –16.2 Hz, 1 H, CH_{2a}C≡CH), 4.41 (dd, $J_{CH_{2b},CH}$ = 2.4 Hz, 1 H, CH_{2b}C≡CH), 4.29 (ddd, $J_{5,6a}$ = 4.8 Hz, $J_{5,6b}$ = 10.2 Hz, 1 H, 5-H), 4.27 (dd, $J_{2,3}$ = 3.2 Hz, 1 H, 2-H), 4.23 (dd, $J_{4,5}$ = 9.4 Hz, 1 H, 4-H), 4.22 (dd, $J_{6a,6b}$ = –10.3 Hz, 1 H, 6a-H), 4.00 (dd, $J_{3,4}$ = 10.0 Hz, 1 H, 3-H), 3.87 (dd, 1 H, 6b-H), 2.44 (dd, 1 H, CH_2C≡C*H*) ppm. ^{13}C NMR (150.90 MHz, $CDCl_3$, 25 °C): δ = 138.2–126.1 (arom. C), 101.5 (*C*HPh), 87.4 (C-1), 79.5 (CH_2*C*≡CH), 79.4 (C-4), 77.7 (C-2), 76.1 (C-3), 75.2 (CH_2C≡*C*H), 73.3 (3-*C*H_2Ph), 68.5 (C-6), 65.3 (C-5), 58.8 (*C*H_2C≡CH) ppm.

General Procedure for the Coupling Reaction: To donor **19** (1 equiv.) in dry CH_2Cl_2 (4 mL/0.5 mmol of donor) under an argon atmosphere was added TTBP (1.5 equiv.) and 4 Å molecular sieves, and the temperature was reduced to –40 °C. BSP (1.2 equiv.) was then added, and the temperature was brought to –60 °C. The mixture was stirred for 10 min, and Tf_2O (1.3 equiv.) was added into solution; stirring was continued for 30 min. The temperature was reduced to –78 °C, and the acceptor (1.15 equiv.) in dry CH_2Cl_2 (2.4 mL/0.056 mmol of acceptor) was added dropwise over a period of 15 min. Stirring was continued for 2 h at –78 °C, and the reaction was quenched by the addition of $(EtO)_3P$ (3 equiv.) at the same temperature. Stirring was continued for an additional 1 h at –78 °C, and the reaction mixture was then brought to room temperature. The reaction mixture was diluted with CH_2Cl_2 (20 mL), and the molecular sieves were filtered off. The organic phase was washed with saturated $NaHCO_3$ (3 × 20 mL), brine (20 mL), and water (20 mL), dried, and concentrated. Column chromatography (hexane/EtOAc, 8:1→4:1) gave the desired disaccharides or trisaccharides, respectively.

General Procedure for Propargyl Deprotection

Step 1: To a solution of the corresponding 2-*O*-propargylated compound (**22**, **24**, **25**, **26**, **27**, **37**, or **38**, respectively) dissolved in dry THF (1 mL, 50 mg of compound) was added *t*BuOK (1.2 equiv.). The mixture was stirred at room temperature and then diluted with CH_2Cl_2 (20 mL), and washed with water (2 × 10 mL). The organic phase was dried and concentrated. Products were analyzed by NMR spectroscopy and directly used in the next step.

Step 2: The isomerized 2-*O*-allenyl sugar (1 equiv.) was dissolved in acetone/water (4:1, 3 mL) and treated with OsO_4 (1.1 equiv.) followed by NMO (2 equiv.). The mixture was stirred at room temperature. The solvent was evaporated, and the residue was dissolved in CH_2Cl_2 (20 mL). The organic phase was washed with brine (10 mL) and brine washed with CH_2Cl_2 (10 mL). The combined organic phase was again washed with brine (2 × 10 mL) and water (10 mL), dried, and concentrated. The residue was purified by column chromatography (hexane/EtOAc, 3:1→2.5:1) to give the 2-*O*-deprotected product.

Benzyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (22): The coupling reaction was carried out starting from donor **19** (0.32 g, 0.66 mmol). Yield: 0.44 g (82%). $[a]_D$ = –37.0 (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (600.13 MHz, $CDCl_3$, 25 °C): δ = 7.51–7.28 (m, 25 H, arom. H), 5.60 (s, 1 H, C*H*Ph), 5.57 (s, 1 H, C*H*′Ph), 4.96 (d, $J_{1,2}$ = 1.6 Hz, 1 H, 1-H), 4.80 (s, 2 H, 3′-CH_2Ph), 4.73 and 4.50 (each d, *J* = –11.9 Hz, each 1 H, 1-CH_2Ph), 4.72 (s, 2 H, 3-CH_2Ph), 4.70 (dd, $J_{CH_{2a},CH}$ = 2.4 Hz, $J_{CH_{2a},CH_{2b}}$ = –16.1 Hz, 1 H, CH_{2a}C≡CH), 4.63 (d, $J_{1',2'}$ = 0.84 Hz, 1 H, 1′-H), 4.61 (dd, $J_{CH_{2b},CH}$ = 2.4 Hz, 1 H, CH_{2b}C≡CH), 4.27 (dd, $J_{2,3}$ = 3.4 Hz, 1 H, 2-H), 4.239 (dd, $J_{6'a,6'b}$ = –10.4 Hz, 1 H, 6′a-H), 4.239 (dd, $J_{2',3'}$ =

3.1 Hz, 1 H, 2′-H), 4.231 (dd, $J_{6a,6b}$ = –10.2 Hz, 1 H, 6a-H), 4.16 (dd, $J_{4',5'}$ = 9.4 Hz, 1 H, 4′-H), 4.12 (dd, $J_{4,5}$ = 9.5 Hz, 1 H, 4-H), 4.02 (dd, $J_{3,4}$ = 10.0 Hz, 1 H, 3-H), 3.87 (ddd, $J_{5,6a}$ = 4.9 Hz, $J_{5,6b}$ = 10.4 Hz, 1 H, 5-H), 3.84 (dd, 1 H, 6′b-H), 3.82 (dd, 1 H, 6b-H), 3.60 (dd, $J_{3',4'}$ = 9.9 Hz, 1 H, 3′-H), 3.26 (ddd, $J_{5',6'a}$ = 4.8 Hz, $J_{5',6'b}$ = 10.1 Hz, 1 H, 5′-H), 2.44 (dd, 1 H, $CH_2C{\equiv}CH$) ppm. ^{13}C NMR (150.90 MHz, $CDCl_3$, 25 °C): δ = 138.7–126.0 (arom. C), 101.6 (*C*HPh), 101.4 (*C*′HPh), 100.2 (C-1′), 97.3 (C-1), 80.4 ($CH_2C{\equiv}CH$), 78.6 (C-4), 78.3 (C-4′), 76.9 (C-3′), 75.0 ($CH_2C{\equiv}CH$), 74.5 (C-2′), 74.4 (C-2), 74.4 (C-3), 72.2 (3′-*C*H_2Ph), 71.7 (3-*C*H_2Ph), 69.4 (1-*C*H_2Ph(, 68.9 (C-6), 68.5 (C-6′), 67.8 (C-5′), 64.4 (C-5), 59.8 ($CH_2C{\equiv}CH$) ppm. HRMS: calcd. for $C_{50}H_{50}O_{11}$ $[M]^+$ 826.3353; found 826.3325.

Allyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (23): The coupling reaction was carried out by starting from donor **19** (0.16 g, 0.33 mmol). Yield: 0.22 g (85%). $[\alpha]_D$ = –49.0 (*c* = 1.0, CH_2Cl_2). ^1H NMR (600.13 MHz, $CDCl_3$, 25 °C): δ = 7.52–7.26 (m, 20 H, arom. H), 5.89 (dddd, J_{CH,CH_2cis} = 10.4, J_{CH,CH_2trans} = 17.2 Hz, 1 H, $CH_2CH{=}CH_2$), 5.60 (s, 1 H, C*H*Ph), 5.59 (s, 1 H, C*H*′Ph), 5.27 (dddd, J_{CH_2trans,CH_2cis} = –1.6 Hz, 1 H, $CH_2CH{=}CH_{2trans}$), 5.22 (dddd, 1 H, $CH_2CH{=}CH_{2cis}$), 4.91 (d, $J_{1,2}$ = 1.6 Hz, 1 H, 1-H), 4.82 (s, 2 H, 3′-CH_2Ph), 4.74 and 4.712 (each d, *J* = –12.1 Hz, each 1 H, 3-CH_2Ph), 4.713 (dd, $J_{CH_{2a},CH}$ = 2.4 Hz, $J_{CH_{2a},CH_{2b}}$ = –16.2 Hz, 1 H, CH_{2a}C≡CH), 4.67 (d, $J_{1',2'}$ = 0.44 Hz, 1 H, 1′-H), 4.62 (dd, $J_{CH_{2b},CH}$ = 2.4 Hz, 1 H, CH_{2b}C≡CH), 4.28 (dd, $J_{6'a,6'b'}$ = –10.4 Hz, 1 H, 6′a-H), 4.27 (dd, $J_{2,3}$ = 3.4 Hz, 1 H, 2-H), 4.26 (dd, $J_{2',3'}$ = 3.2 Hz, 1 H, 2′-H), 4.25 (dd, $J_{6a,6b}$ = –10.1 Hz, 1 H, 6a-H), 4.19 (dddd, $J_{CH_{2a},CH_{2b}}$ = –13.0 Hz, $J_{CH_{2a},CH}$ = 5.1 Hz, $J_{CH_{2a},CH_{2cis}}$ = –1.4 Hz, $J_{CH_{2a},CH_{2trans}}$ = –1.7 Hz, 1 H, CH_{2a}CH=CH_2), 4.18 (dd, $J_{4',5'}$ = 9.3 Hz, 1 H, 4′-H), 4.10 (dd, $J_{4,5}$ = 9.2 Hz, 1 H, 4-H), 3.983 (dd, $J_{3,4}$ = 10.0 Hz, 1 H, 3-H), 3.977 (dddd, $J_{CH_{2b},CH}$ = 6.2 Hz, $J_{CH_{2b},CH_{2cis}}$ = –1.2 Hz, $J_{CH_{2b},CH_{2trans}}$ = –1.6 Hz, 1 H, CH_{2b}CH=CH_2), 3.86 (dd, 1 H, 6′b-H), 3.83 (ddd, $J_{5,6a}$ = 4.8 Hz, $J_{5,6b}$ = 10.4 Hz, 1 H, 5-H), 3.81 (dd, 1 H, 6b-H), 3.63 (dd, $J_{3',4'}$ = 9.9 Hz, 1 H, 3′-H), 3.31 (ddd, $J_{5',6'a}$ = 4.8 Hz, $J_{5',6'b}$ = 10.1 Hz, 1 H, 5′-H), 2.50 (dd, 1 H, $CH_2C{\equiv}CH$) ppm. ^{13}C NMR (150.90 MHz, $CDCl_3$, 25 °C): δ = 138.7–126.0 (arom. C), 133.3 ($CH_2CH{=}CH_2$), 117.8 ($CH_2CH{=}CH_2$), 101.6 (*C*HPh), 101.4 (*C*′HPh), 100.3 (C-1′), 97.3 (C-1), 80.4 ($CH_2C{\equiv}CH$), 78.5 (C-4), 78.3 (C-4′), 76.9 (C-3′), 75.0 ($CH_2C{\equiv}CH$), 74.5 (C-2′), 74.30 (C-2), 74.26 (C-3), 72.2 (3′-*C*H_2Ph), 71.5 (3-*C*H_2Ph), 68.8 (C-6), 68.5 (C-6′), 68.2 (*C*H_2CH=CH_2), 67.8 (C-5′), 64.2 (C-5), 59.8 (*C*H_2C≡CH) ppm. HRMS: calcd. for $C_{46}H_{48}O_{11}$ $[M]^+$ 776.3197; found 776.3217.

Methyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (24): The coupling reaction was carried out as outlined in the general procedure by starting from donor **19** (0.27 g, 0.55 mmol). Yield: 0.35 g (87%). $[\alpha]_D$ = –56.5 (*c* = 1.0, CH_2Cl_2). ^1H NMR (600.13 MHz, $CDCl_3$, 25 °C): δ = 7.50–7.23 (m, 20 H, arom. H), 5.60 (s, 1 H, C*H*′Ph), 5.59 (s, 1 H, C*H*Ph), 4.82 (s, 2 H, 3′-CH_2Ph), 4.76 (d, $J_{1,2}$ = 1.6 Hz, 1 H, 1-H), 4.73 and 4.70 (each d, *J* = –12.1 Hz, each 1 H, 3-CH_2Ph), 4.72 (dd, $J_{CH_{2a},CH}$ = 2.4 Hz, $J_{CH_{2a},CH_{2b}}$ = –16.2 Hz, 1 H, CH_{2a}C≡CH), 4.68 (dd, $J_{1',2'}$ = 0.92 Hz, 1 H, 1′-H) 4.63 (dd, $J_{CH_{2b},CH}$ = 2.4 Hz, 1 H, CH_{2b}C≡CH), 4.28 (dd, $J_{6'a,6'b}$ = –10.3 Hz, 1 H, 6′a-H), 4.27 (dd, $J_{2',3'}$ = 3.1 Hz, 1 H, 2′-H), 4.26 (dd, $J_{6a,6b}$ = –10.3 Hz, 1 H, 6a-H), 4.23 (dd, $J_{2,3}$ = 3.4 Hz, 1 H, 2-H), 4.18 (dd, $J_{4',5'}$ = 9.3 Hz, 1 H, 4′-H), 4.09 (dd, $J_{4,5}$ = 9.4 Hz, 1 H, 4-H), 3.93 (dd, $J_{3,4}$ = 10.0 Hz, 1 H, 3-H), 3.87 (dd, 1 H, 6′b-H), 3.82 (dd, 1 H, 6b-H), 3.78 (ddd, $J_{5,6a}$ = 4.7 Hz, $J_{5,6b}$ = 10.4 Hz, 1 H, 5-H), 3.63 (dd, $J_{3',4'}$ = 9.9 Hz, 1 H, 3′-H), 3.37 (s, 3 H, OCH_3), 3.32 (ddd, $J_{5',6'a}$ = 4.9 Hz, $J_{5',6'b}$ = 10.1 Hz, 1 H, 5′-H), 2.51 (dd, 1 H, $CH_2C{\equiv}CH$) ppm. ^{13}C NMR (150.90 MHz, $CDCl_3$, 25 °C): δ = 138.7–126.0 (arom. C), 101.6 (*C*′HPh), 101.4 (*C*HPh), 100.3 (C-1′), 99.2 (C-1), 80.4 ($CH_2C{\equiv}CH$), 78.5 (C-4), 78.3 (C-4′), 77.0 (C-3′), 75.0 ($CH_2C{\equiv}CH$), 74.6 (C-2′), 74.3 (C-2), 74.1 (C-3), 72.2 (3′-*C*H_2Ph), 71.5 (3-*C*H_2Ph), 68.9 (C-6′), 68.5 (C-6), 67.8 (C-5′), 64.0 (C-5), 59.8 (*C*H_2C≡CH), 54.9 (OCH_3) ppm. HRMS: calcd. for $C_{44}H_{46}O_{11}$ $[M]^+$ 750.3040; found 750.3056.

Cyclohexyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-β-D-mannopyrano-syl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (25): The coupling reaction was carried out by starting from donor **19** (90 mg, 0.18 mmol). Yield: 0.12 g (81%). $[\alpha]_D$ = –39.0 (*c* = 1.0, CH_2Cl_2). ^1H NMR (600.13 MHz, $CDCl_3$, 25 °C): δ = 7.50–7.25 (m, 20 H, arom. H), 5.60 (s, 1 H, C*H*Ph), 5.58 (s, 1 H, C*H*′Ph), 5.00 (d, $J_{1,2}$ = 1.7 Hz, 1 H, 1-H), 4.82 (s, 2 H, 3′-CH_2Ph), 4.73 (s, 2 H, 3-CH_2Ph), 4.72 (dd, $J_{CH_{2a},CH}$ = 2.3 Hz, $J_{CH_{2a},CH_{2b}}$ = –16.1 Hz, 1 H, CH_{2a}C≡CH), 4.68 (d, $J_{1',2'}$ = 0.73 Hz, 1 H, 1′-H), 4.62 (dd, $J_{CH_{2b},CH}$ = 2.4 Hz, 1 H, CH_{2b}C≡CH), 4.27 (dd, $J_{6'a,6'b}$ = –10.4 Hz, 1 H, 6′a-H), 4.26 (dd, $J_{2',3'}$ = 3.1 Hz, 1 H, 2′-H), 4.24 (dd, $J_{6a,6b}$ = –10.2 Hz, 1 H, 6a-H), 4.18 (dd, $J_{2,3}$ = 3.3 Hz, 1 H, 2-H), 4.17 (dd, $J_{4',5'}$ = 9.3 Hz, 1 H, 4′-H), 4.10 (dd, $J_{4,5}$ = 9.5 Hz, 1 H, 4-H), 3.99 (dd, $J_{3,4}$ = 10.0 Hz, 1 H, 3-H), 3.89 (ddd, $J_{5,6a}$ = 4.7 Hz, $J_{5,6b}$ = 10.4 Hz, 1 H, 5-H), 3.86 (dd, 1 H, 6′b-H), 3.80 (dd, 1 H, 6b-H), 3.63 (dd, $J_{3',4'}$ = 9.9 Hz, 1 H, 3′-H), 3.58 (m, 1 H, OC*H*C_5H_{10}), 3.32 (ddd, $J_{5',6'a}$ = 4.8 Hz, $J_{5',6'b}$ = 10.0 Hz, 1 H, 5′-H), 2.50 (dd, 1 H, $CH_2C{\equiv}CH$), 1.86–1.18 (m, 10 H, $OCHC_5H_{10}$) ppm. ^{13}C NMR (150.90 MHz, $CDCl_3$, 25 °C): δ = 138.9–125.9 (arom. C), 101.5 (*C*HPh), 101.4 (*C*′HPh), 100.4 (C-1′), 96.1 (C-1), 81.0 ($CH_2C{\equiv}CH$), 79.0 (C-4), 78.2 (C-2), 76.9 (C-3′), 75.7 (O*C*HC_5H_{10}), 75.4 (C-2′), 75.0 ($CH_2C{\equiv}CH$), 74.8 (C-4′), 74.5 (C-3), 72.2 (3-*C*H_2Ph), 71.6 (3′-*C*H_2Ph), 69.0 (C-6′), 68.7 (C-6), 67.8 (C-5′), 64.3 (C-5), 59.8 (*C*H_2C≡CH), 33.3, 31.3, 25.6, 23.8, 23.5 ($OCH{C_5}H_{10}$) ppm. HRMS: calcd. for $C_{49}H_{54}O_{11}$ $[M]^+$ 818.3666; found 818.3730.

Phenyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside (26): The coupling reaction was carried out by starting from donor **19** (0.23 g, 0.48 mmol). Yield: 0.28 g (72%). $[\alpha]_D$ = +9.0 (*c* = 1.0, CH_2Cl_2). ^1H NMR (600.13 MHz, $CDCl_3$, 25 °C): δ = 7.57–7.28 (m, 25 H, arom. H), 5.61 (s, 1 H, C*H*Ph), 5.58 (s, 1 H, C*H*′Ph), 5.54 (d, $J_{1,2}$ = 1.5 Hz, 1 H, 1-H), 4.80 (s, 2 H, 3′-CH_2Ph), 4.76 and 4.73 (each d, *J* = –12.0 Hz, each 1 H, 3-CH_2Ph), 4.71 (dd, $J_{CH_{2a},CH}$ = 2.4 Hz, $J_{CH_{2a},CH_{2b}}$ = –16.2 Hz, 1 H, CH_{2a}C≡CH), 4.66 (d, $J_{1',2'}$ = 0.84 Hz, 1 H, 1′-H), 4.61 (dd, $J_{CH_{2b},CH}$ = 2.4 Hz, 1 H, CH_{2b}C≡CH), 4.50 (dd, $J_{2,3}$ = 3.3 Hz, 1 H, 2-H), 4.32 (ddd, $J_{5,6a}$ = 4.8 Hz, $J_{5,6b}$ = 10.2 Hz, 1 H, 5-H), 4.26 (dd, $J_{6'a,6'b}$ = –10.3 Hz, 1 H, 6′a-H), 4.25 (dd, $J_{2',3'}$ = 3.1 Hz, 1 H, 2′-H), 4.23 (dd, $J_{6a,6b}$ = –10.2 Hz, 1 H, 6a-H), 4.18 (dd, $J_{4,5}$ = 9.5 Hz, 1 H, 4-H), 4.17 (dd, $J_{4',5'}$ = 9.3 Hz, 1 H, 4′-H), 3.96 (dd, $J_{3,4}$ = 10.0 Hz, 1 H, 3-H), 3.85 (dd, 1 H, 6′b-H), 3.84 (dd, 1 H, 6b-H), 3.62 (dd, $J_{3',4'}$ = 9.9 Hz, 1 H, 3′-H), 3.30 (dd, $J_{5',6'a}$ = 4.8 Hz, $J_{5',6'b}$ = 10.1 Hz, 1 H, 5′-H), 2.46 (dd, 1 H, $CH_2C{\equiv}CH$) ppm. ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = 137.4–126.0 (arom. C), 102.0 (*C*HPh), 101.8 (*C*′HPh), 99.3 (C-1′), 86.0 (C-1), 80.3 ($CH_2C{\equiv}CH$), 78.5 (C-4), 78.2 (C-4′), 76.9 (C-3′), 75.4 ($CH_2C{\equiv}CH$), 75.1 (C-2′), 74.5 (C-2), 74.2 (C-3), 72.1 (3′-*C*H_2Ph), 71.4 (3-*C*H_2Ph), 68.5, 68.4 (C-6, C-6′), 67.7 (C-5′), 65.4 (C-5), 59.7 (*C*H_2C≡CH) ppm. HRMS: calcd. for $C_{49}H_{49}O_{10}S$ $[M + H]^+$ 829.3046; found 829.3103.

Methyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranoside (27): The coupling reaction was carried out by starting from donor **19** (0.11 g, 0.23 mmol). Yield: 0.17 g (85%). $[\alpha]_D$ =

–122.5 (c = 1.0, CH_2Cl_2). ^{1}H NMR (600.13 MHz, $CDCl_3$, 25 °C): δ = 7.50–7.24 (m, 20 H, arom. H), 5.59 (s, 1 H, C*H*Ph), 5.57 (s, 1 H, C*H*′Ph), 4.85 (d, $J_{1',2'}$ = 0.86 Hz, 1 H, 1′-H), 4.84 and 4.82 (each d, J = –12.9 Hz, each 1 H, 3′-CH_2Ph), 4.76 and 4.72 (each d, J = –12.3 Hz, each 1 H, CH_2Ph), 4.72 (dd, $J_{CH_{2a},CH}$ = 2.3 Hz, $J_{CH_{2a},CH_{2b}}$ = –16.0 Hz, 1 H, CH_{2a}C≡CH), 4.62 (dd, $J_{CH_{2b},CH}$ = 2.4 Hz, 1 H, CH_{2b}C≡CH), 4.38 (d, $J_{1,2}$ = 0.76 Hz, 1 H, 1-H), 4.34 (dd, $J_{6a,6b}$ = –10.4 Hz, 1 H, 6a-H), 4.33 (dd, $J_{2',3'}$ = 3.3 Hz, 1 H, 2′-H), 4.30 (dd, $J_{6'a,6'b}$ = –10.4 Hz, 1 H, 6′a-H), 4.28 (dd, $J_{2,3}$ = 3.3 Hz, 1 H, 2-H), 4.17 (dd, $J_{4',5'}$ = 9.3 Hz, 1 H, 4′-H), 4.04 (dd, $J_{4,5}$ = 9.3 Hz, 1 H, 4-H), 3.89 (dd, 1 H, 6′b-H), 3.84 (dd, 1 H, 6b-H), 3.62 (dd, $J_{3,4}$ = 9.9 Hz, 1 H, 3-H), 3.61 (dd, $J_{3',4'}$ = 9.9 Hz, 1 H, 3′-H), 3.50 (s, 3 H, OCH_3), 3.34 (ddd, $J_{5,6a}$ = 4.8 Hz, $J_{5,6b}$ = 10.1 Hz, 1 H, 5-H), 3.33 (ddd, $J_{5',6'a}$ = 4.8 Hz, $J_{5',6'b}$ = 10.1 Hz, 1 H, 5′-H), 2.47 (dd, 1 H, $CH_2C{\equiv}CH$) ppm. ^{13}C NMR (150.90 MHz, $CDCl_3$, 25 °C): δ = 138.5–126.1 (arom. C), 102.9 (C-1′), 102.8 (C-1), 101.6 (*C*′HPh), 101.4 (*C*HPh), 81.0 ($CH_2C{\equiv}CH$), 78.2 (C-4 and C-4′), 76.8 (C-3), 76.0 (C-3′), 75.3 (C-2), 75.1 (C-2′), 74.4 ($CH_2C{\equiv}CH$), 71.9 (3′-*C*H_2Ph), 71.0 (3-*C*H_2Ph), 68.72 (C-6), 68.68 (C-6′), 67.6 (C-5), 67.5, (C-5′), 60.0 (*C*H_2C≡CH), 57.4 (OCH_3) ppm. HRMS: calcd. for $C_{44}H_{47}O_{11}$ $[M + H]^+$ 751.3118; found 751.3115.

Benzyl 3-*O*-Benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (28): The propargyl deprotection was carried out by starting from disaccharide **22** (0.4 g, 0.48 mmol). Reaction time for 1st step 6 h, for 2nd step 2.5 h. Yield: 0.30 g (80%). $[\alpha]_D$ = –15.0 (c = 1.0, CH_2Cl_2). ^{1}H NMR (600.13 MHz, $CDCl_3$, 25 °C): δ = 7.49–7.25 (m, 25 H, arom. H), 5.56 (s, 1 H, C*H*Ph), 5.47 (s, 1 H, C*H*′Ph), 4.90 (d, $J_{1,2}$ = 1.6 Hz, 1 H, 1-H), 4.82 and 4.75 (each d, J = –12.3 Hz, each 1 H, 3-CH_2Ph), 4.80 and 4.75 (each d, J = –11.8 Hz, each 1 H, 3′-CH_2Ph), 4.71 and 4.49 (each d, J = –11.9 Hz, each 1 H, 1-CH_2Ph), 4.67 (d, $J_{1',2'}$ = 1.3 Hz, 1 H, 1′-H), 4.43 (dd, $J_{2,3}$ = 3.5 Hz, 1 H, 2-H), 4.24 (dd, $J_{3',4'}$ = 9.1 Hz, 1 H, 4′-H), 4.210 (dd, $J_{6a,6b}$ = –10.3 Hz, 1 H, 6a-H), 4.207 (dd, $J_{6'a,6'b}$ = –10.4 Hz, 1 H, 6′a-H), 4.140 (dd, $J_{4,5}$ = 9.4 Hz, 1 H, 4-H), 4.139 (dd, $J_{2',3'}$ = 3.7 Hz, 1 H, 2′-H), 4.04 (dd, $J_{3,4}$ = 9.9 Hz, 1 H, 3-H), 3.85 (ddd, $J_{5,6a}$ = 4.8 Hz, $J_{5,6b}$ = 10.4 Hz, 1 H, 5-H), 3.78 (dd, 1 H, 6b-H), 3.73 (dd, 1 H, 6′b-H), 3.64 (dd, $J_{3',4'}$ = 9.1 Hz, 1 H, 3′-H), 3.34 (ddd, $J_{5',6'a}$ = 4.9 Hz, $J_{5',6'b}$ = 10.0 Hz, 1 H, 5′-H), 3.22 (br. s, 1 H, 2′-OH) ppm. ^{13}C NMR (150.90 MHz, $CDCl_3$, 25 °C): δ = 138.7–126.0 (arom. C), 101.4 (*C*HPh), 101.3 (*C*′HPh), 98.2 (C-1′), 97.9 (C-1), 78.8 (C-4), 78.4 (C-4′), 76.0 (C-3′), 74.2 (C-3), 72.8 (C-2), 72.6 (3′-*C*H_2Ph), 72.4 (3-*C*H_2Ph), 69.4 (C-2′), 69.1 (1-*C*H_2Ph), 68.4, (C-6), 68.3 (C-6′), 66.8 (C-5′), 63.9 (C-5) ppm. HRMS: calcd. for $C_{47}H_{48}O_{11}$ $[M]^+$ 788.3197; found 788.3211.

Methyl 3-*O*-Benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (29): The propargyl deprotection was carried out as outlined in the general procedure by starting from disaccharide **24** (0.20 g, 0.26 mmol). Reaction time for 1st step 5 h, for 2nd step 2 h. Yield: 0.16 g (85%). $[\alpha]_D$ = –48.5 (c = 1.0, CH_2Cl_2). ^{1}H NMR (600.13 MHz, $CDCl_3$, 25 °C): δ = 7.49–7.24 (m, 20 H, arom. H), 5.56 (s, 1 H, C*H*Ph), 5.50 (s, 1 H, C*H*′Ph), 4.84 and 4.77 (each d, J = –12.3 Hz, each 1 H, 3-CH_2Ph) 4.77 and 4.74 (each d, J = –12.0 Hz, each 1 H, 3′-CH_2Ph), 4.72 (d, $J_{1',2'}$ = 1.2 Hz, 1 H, 1′-H), 4.71 (d, $J_{1,2}$ = 1.6 Hz, 1 H, 1-H), 4.38 (dd, $J_{2,3}$ = 3.5 Hz, 1 H, 2-H), 4.28 (dd, $J_{6'a,6'b}$ = –10.4 Hz, 1 H, 6′a-H), 4.27 (dd, $J_{4',5'}$ = 9.4 Hz, 1 H, 4′-H), 4.23 (dd, $J_{6a,6b}$ = –10.3 Hz, 1 H, 6a-H), 4.17 (ddd, $J_{2',3'}$ = 3.8 Hz, $J_{2',2'\text{-OH}}$ = 0.79 Hz, 1 H, 2′-H), 4.11 (dd, $J_{4,5}$ = 9.3 Hz, 1 H, 4-H), 3.95 (dd, $J_{3,4}$ = 10.0 Hz, 1 H, 3-H), 3.781 (dd, 1 H, 6′b-H), 3.779 (dd, 1 H, 6b-H), 3.76 (ddd, $J_{5,6a}$ = 5.0 Hz, $J_{5,6b}$ = 10.4 Hz, 1 H, 5-H), 3.67 (dd, $J_{3',4'}$ = 9.1 Hz, 1 H, 3′-H), 3.39 (ddd, $J_{5',6'a}$ = 4.8 Hz, $J_{5',6'b}$ = 10.1 Hz, 1 H, 5′-H), 3.36 (s, 3 H, OCH_3), 3.17 (d, 1 H, 2′-OH) ppm. ^{13}C NMR (150.90 MHz, $CDCl_3$, 25 °C): δ = 138.3–126.0 (arom. C), 101.5 (*C*HPh), 101.4 (*C*′HPh), 99.6 (C-1), 98.2 (C-1′), 78.6 (C-4), 78.5 (C-4′), 76.3 (C-3′), 74.3 (C-3), 72.9 (C-2), 72.4 (3-*C*H_2Ph), 72.3 (3′-*C*H_2Ph), 69.6 (C-2′), 68.7 (C-6), 68.7 (C-6′), 67.0 (C-5′), 63.8 (C-5), 54.9 (OCH_3) ppm. HRMS: calcd. for $C_{41}H_{44}O_{11}$ $[M]^+$ 712.2884; found 712.2885.

Phenyl 3-*O*-Benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-α-D-manno-pyranoside (30): The propargyl deprotection was carried out by starting from disaccharide **26** (0.25 g, 0.30 mmol). Reaction time for 1st step 5 h, for 2nd step 2.5 h. Yield: 0.16 g (70%). $[\alpha]_D$ = +11.0 (c = 1.0, CH_2Cl_2). ^{1}H NMR (600.13 MHz, $CDCl_3$, 25 °C): δ = 7.51–7.26 (m, 25 H, arom. H), 5.54 (s, 1 H, C*H*Ph), 5.49 (d, $J_{1,2}$ = 1.4 Hz, 1 H, 1-H), 5.46 (s, 1 H, C*H*′Ph), 4.84 and 4.76 (each d, J = –12.2 Hz, each 1 H, 3-CH_2Ph), 4.81 and 4.78 (each d, J = –11.8 Hz, each 1 H, 3′-CH_2Ph), 4.73 (d, $J_{1',2'}$ = 1.3 Hz, 1 H, 1′-H), 4.61 (dd, $J_{2,3}$ = 3.4 Hz, 1 H, 2-H), 4.283 (dd, $J_{4',5'}$ = 9.5 Hz, 1 H, 4′-H), 4.281 (ddd, $J_{5,6a}$ = 4.8 Hz, $J_{5,6b}$ = 10.2 Hz, 1 H, 5-H), 4.25 (dd, $J_{6'a,6'b}$ = –10.3 Hz, 1 H, 6′a-H), 4.194 (dd, $J_{6a,6b}$ = –10.3 Hz, 1 H, 6a-H), 4.188 (dd, $J_{4,5}$ = 9.5 Hz, 1 H, 4-H), 4.15 (dd, $J_{2',3'}$ = 3.9 Hz, 1 H, 2′-H), 3.98 (dd, $J_{3,4}$ = 9.9 Hz, 1 H, 3-H), 3.77 (dd, 1 H, 6b-H), 3.74 (dd, 1 H, 6′b-H), 3.68 (dd, $J_{3',4'}$ = 8.9 Hz, 1 H, 3′-H), 3.39 (ddd, $J_{5',6'a}$ = 4.9 Hz, $J_{5',6'b}$ = 10.0 Hz, 1 H, 5′-H), 3.09 (s, 1 H, 2′-OH) ppm. ^{13}C NMR (150.90 MHz, $CDCl_3$, 25 °C): δ = 138.1–126.0 (arom. C), 100.4 (*C*HPh), 100.3 (*C*′HPh), 97.6 (C-1′), 86.7 (C-1), 78.7 (C-4), 78.6 (C-4′), 75.1 (C-3′), 73.5 (C-3), 73.4 (C-2), 71.5 (3-*C*H_2Ph), 71.4 (3′-*C*H_2Ph), 68.5 (C-2′), 67.6 (C-6′), 67.4 (C-6), 65.8 (C-5′), 64.2 (C-5) ppm. HRMS: calcd. for $C_{46}H_{46}O_{10}S$ $[M]^+$ 790.2812; found 790.2826.

Cyclohexyl 3-*O*-Benzyl-4,6-*O*-benzylidene-β-D-manno-pyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-manno-pyranoside (31): Propargyl deprotection was carried out by starting from disaccharide **25** (92 mg, 0.11 mmol). Reaction time for 1st step 5.5 h, for 2nd step 3 h. Yield: 74 mg (85%). $[\alpha]_D$ = –15.1 (c = 0.1, $CHCl_3$). ^{1}H NMR (600.13 MHz, $CDCl_3$, 25 °C): δ = 7.50–7.28 (m, 20 H, arom. H), 5.55 (s, 1 H, C*H*Ph), 5.48 (s, 1 H, C*H*′Ph), 4.95 (d, $J_{1,2}$ = 1.7 Hz, 1 H, 1-H), 4.83 and 4.76 (each d, J = –12.3 Hz, each 1 H, 3-CH_2Ph), 4.81 and 4.76 (each d, J = –11.7 Hz, each 1 H, 3′-CH_2Ph), 4.74 (d, $J_{1',2'}$ = 1.3 Hz, 1 H, 1′-H), 4.34 (dd, $J_{2,3}$ = 3.4 Hz, 1 H, 2-H), 4.27 (dd, $J_{4',5'}$ = 9.5 Hz, 1 H, 4′-H), 4.26 (dd, $J_{6'a,6'b}$ = –10.3 Hz, 1 H, 6′a-H), 4.21 (dd, $J_{6a,6b}$ = –10.3 Hz, 1 H, 6a-H), 4.16 (ddd, $J_{2',3'}$ = 3.8 Hz, $J_{2',2'\text{-OH}}$ = 3.1 Hz, 1 H, 2′-H), 4.11 (dd, $J_{4,5}$ = 9.2 Hz, 1 H, 4-H), 4.02 (dd, $J_{3,4}$ = 9.9 Hz, 1 H, 3-H), 3.87 (ddd, $J_{5,6a}$ = 4.8 Hz, $J_{5,6b}$ = 10.4 Hz, 1 H, 5-H), 3.76 (dd, 1 H, 6b-H), 3.76 (dd, 1 H, 6′b-H), 3.67 (dd, $J_{3',4'}$ = 9.0 Hz, 1 H, 3′-H), 3.57 (m, 1 H, OC*H*C_5H_{10}), 3.40 (ddd, $J_{5',6'a}$ = 4.9 Hz, $J_{5',6'b}$ = 10.0 Hz, 1 H, 5′-H), 3.22 (d, 1 H, 2′-OH), 1.80–1.65 (m, 4 H, OCHC$_5H_{10}$), 1.55–1.15 (m, 6 H, OCHC$_5H_{10}$) ppm. ^{13}C NMR (150.90 MHz, $CDCl_3$, 25 °C): δ = 139.4–126.0 (arom. C), 101.4 (*C*HPh and *C*′HPh), 98.3 (C-1′), 96.7 (C-1), 79.0 (C-4), 78.5 (C-4′), 76.3 (C-3′), 75.5 (O*C*HC$_5H_{10}$), 74.8 (C-3), 73.9 (C-2), 72.6 (3-*C*H_2Ph and 3′-*C*H_2Ph), 68.8 (C-2′), 68.7 (C-6 and C-6′), 66.9 (C-5′), 64.0 (C-5), 33.3, 31.3, 25.5, 24.0 (OCH*C*$_5H_{10}$) ppm. HRMS: calcd. for $C_{46}H_{52}O_{11}Na$ $[M + Na]^+$ 803.3402; found 803.3380. HRMS: calcd. for $C_{46}H_{52}O_{11}K$ $[M + K]^+$ 819.3141; found 819.3105.

Methyl 3-*O*-Benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranoside (32): The propargyl deprotection was carried out by starting from disaccharide **27** (0.1 g, 0.13 mmol). Reaction time for 1st step 5 h, for 2nd step 3 h. Yield: 68 mg (72%). $[\alpha]_D$ = –108.0 (c = 1.0, CH_2Cl_2). ^{1}H NMR (600.13 MHz, $CDCl_3$, 25 °C): δ = 7.53–7.28 (m, 20 H, arom. H),

5.584 (s, 1 H, C*H*Ph), 5.579 (s, 1 H, C*H*′Ph), 4.91 (d, $J_{1',2'}$ = 1.1 Hz, 1′-H), 4.85 and 4.83 (each d, J = –12.6 Hz, each 1 H, 3-CH_2Ph), 4.754 and 4.746 (each d, J = –12.3 Hz, each 1 H, 3′-CH_2Ph), 4.39 (d, $J_{1,2}$ = 0.95 Hz, 1 H, 1-H), 4.34 (dd, $J_{2,3}$ = 3.4 Hz, 1 H, 2-H), 4.33 (dd, $J_{6'a,6'b}$ = –10.3 Hz, 1 H, 6′a-H), 3.32 (dd, $J_{6a,6b}$ = –10.4 Hz, 1 H, 6a-H) 4.27 (dd, $J_{2',3'}$ = 3.3 Hz, 1 H, 2′-H), 4.26 (dd, $J_{4',5'}$ = 9.4 Hz, 1 H, 4′-H), 4.09 (dd, $J_{4,5}$ = 9.3 Hz, 1 H, 4-H), 3.87 (dd, 1 H, 6b-H), 3.85 (dd, 1 H, 6′b-H), 3.64 (dd, $J_{3',4'}$ = 9.5 Hz, 1 H, 3′-H), 3.63 (dd, $J_{3,4}$ = 9.9 Hz, 1 H, 3-H), 3.51 (s, 3 H, OCH_3), 3.38 (ddd, $J_{5',6'a}$ = 4.9 Hz, $J_{5',6'b}$ = 10.1 Hz, 1 H, 5′-H), 3.33 (ddd, $J_{5,6a}$ = 4.8 Hz, $J_{5,6b}$ = 10.1 Hz, 1 H, 5-H), 3.03 (br. s, 1 H, 2′-OH) ppm. ^{13}C NMR (150.90 MHz, $CDCl_3$, 25 °C): δ = 138.3–125.8 (arom. C), 102.3 (C-1), 101.45 (*C*′HPh) 101.49 (*C*HPh), 100.3 (C-1′), 78.4 (C-4′), 78.0 (C-4), 76.2 (C-3 and C-3′), 72.8 (C-2), 72.1 (3-*C*H_2Ph), 71.6 (3′-*C*H_2Ph), 69.1 (C-2′), 68.6 (C-6′), 68.4 (C-6), 67.3 (C-5′), 67.0 (C-5), 57.4 (OCH_3) ppm. HRMS: calcd. for $C_{41}H_{44}O_{11}$ $[M]^+$ 712.2883; found 712.2875.

Benzyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (37): The coupling reaction was carried out by starting from donor **19** (0.15 mg, 0.30 mmol). Yield: 0.26 g (72%). $[\alpha]_D$ = –63.8 (c = 0.66, CH_2Cl_2). ^{1}H NMR (600.13 MHz, $CDCl_3$, 25 °C): δ = 7.52–7.11 (m, 35 H, arom. H), 5.592 (s, 1 H, C*H*′Ph), 5.588 (s, 1 H, C*H*′′Ph), 5.57 (s, 1 H, C*H*Ph), 5.14 (dd, $J_{1'',2''}$ = 0.93 Hz, 1 H, 1′′-H), 4.90 (dd, $J_{1,2}$ = 1.5 Hz, 1 H, 1-H), 4.80 and 4.75 (each d, J = –12.5 Hz, each 1 H, 3′-CH_2Ph), 4.74 and 4.69 (each d, J = –12.8 Hz, each 1 H, 3-CH_2Ph), 4.71 and 4.49 (each d, J = –11.9 Hz, each 1 H, 1-CH_2Ph), 4.63 and 4.49 (each d, J = –12.2 Hz, each 1 H, 3′′-CH_2Ph), 4.56 (dd, $J_{1',2'}$ = 0.87 Hz, 1 H, 1′-H), 4.50 (dd, $J_{CH_{2a},CH}$ = 2.4 Hz, $J_{CH_{2a},CH_{2b}}$ = –16.0 Hz, 1 H, CH_{2a}C≡CH), 4.49 (dd, $J_{2'',3''}$ = 3.2 Hz, 2′′-H), 4.47 (dd, $J_{CH_{2b},CH}$ = 2.3 Hz, 1 H, CH_{2b}C≡CH), 4.35 (dd, $J_{2',3'}$ = 3.0 Hz, 2′-H), 4.34 (dd, $J_{6''a,6''b}$ = –10.3 Hz, 1 H, 6′′a-H), 4.33 (dd, $J_{6'a,6'b}$ = –10.2 Hz, 1 H, 6′a-H), 4.30 (dd, $J_{2,3}$ = 3.5 Hz, 2-H), 4.22 (dd, $J_{6a,6b}$ = –10.3 Hz, 1 H, 6a-H), 4.17 (dd, $J_{4',5'}$ = 9.3 Hz, 1 H, 4′-H), 4.15 (dd, $J_{4'',5''}$ = 9.2 Hz, 1 H, 4′′-H), 4.01 (dd, $J_{3,4}$ = 10.0 Hz, 1 H, 3-H), 3.96 (dd, 1 H, 6′′b-H), 3.92 (dd, $J_{4,5}$ = 9.4 Hz, 1 H, 4-H), 3.89 (dd, 1 H, 6′b-H), 3.86 (ddd, $J_{5,6a}$ = 4.8, $J_{5,6b}$ = 10.3 Hz, 1 H, 5-H), 3.75 (dd, 1 H, 6b-H), 3.61 (dd, $J_{3',4'}$ = 9.8 Hz, 1 H, 3′-H), 3.52 (dd, $J_{3'',4''}$ = 9.9 Hz, 1 H, 3′′-H), 3.41 (ddd, $J_{5'',6''a}$ = 4.7 Hz, $J_{5'',6''b}$ = 10.2 Hz, 1 H, 5′′-H), 3.32 (ddd, $J_{5',6'a}$ = 4.7 Hz, $J_{5',6'b}$ = 10.1 Hz, 1 H, 5′-H), 2.31 (dd, 1 H, $CH_2C{\equiv}CH$) ppm. ^{13}C NMR (150.90 MHz, $CDCl_3$, 25 °C): δ = 138.4–126.0 (arom. C), 102.4 (C-1′′), 101.9 (*C*HPh), 101.6 (*C*′HPh), 101.3 (*C*′′HPh), 99.4 (C-1′), 96.9 (C-1), 81.2 ($CH_2C{\equiv}CH$), 78.9 (C-4), 78.4 (C-3′′), 78.2 (C-4′), 77.9 (C-4′′), 75.6 (C-3′), 75.4 (C-2′), 75.3 (C-2′′), 74.3 (C-3), 74.2 ($CH_2C{\equiv}CH$), 73.8 (C-2), 72.0 (3′′-*C*H_2Ph), 71.9 (3-*C*H_2Ph), 71.1 (3′-*C*H_2Ph), 69.6 (1-*C*H_2Ph), 68.8 (C-6), 68.7 (C-6′′), 68.6 (C-6′), 67.8 (C-5′), 67.8 (C-5′′), 64.2 (C-5), 60.2 (*C*H_2C≡CH) ppm. HRMS: calcd. for $C_{70}H_{71}O_{16}$ $[M + H]^+$ 1167.4742; found 1167.4723.

Methyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (38): The coupling reaction was carried out by starting from donor **19** (64 mg, 0.13 mmol). Yield: 0.103 g (74%). $[\alpha]_D$ = –97.0 (c = 1.0, CH_2Cl_2). ^{1}H NMR (600.13 MHz, $CDCl_3$, 25 °C): δ = 7.52–7.12 (m, 30 H, arom. H), 5.61 (s, 1 H, C*H*′Ph), 5.60 (s, 1 H, C*H*′′Ph), 5.56 (s, 1 H, C*H*Ph), 5.15 (d, $J_{1',2'}$ = 0.81 Hz, 1 H, 1′-H), 4.81 and 4.76 (each d, J = –12.6 Hz, each 1 H, 3′-CH_2Ph), 4.74 and 4.68 (each d, J = –12.5 Hz, each 1 H, 3-CH_2Ph), 4.71 (d, $J_{1,2}$ = 1.5 Hz, 1 H, 1-H), 4.65 and 4.50 (each d, J = –11.8 Hz, each 1 H, 3′′-CH_2Ph), 4.64 (d, $J_{1'',2''}$ = 0.84 Hz, 1 H, 1-H′′), 4.53 (dd, $J_{2'',3''}$ = 3.2 Hz, 1 H, 2′′-H), 4.52 (dd, $J_{CH_{2a},CH}$ = 2.4 Hz, $J_{CH_{2a},CH_{2b}}$ = –15.9 Hz, 1 H, CH_{2a}C≡CH), 4.49 (dd, $J_{CH_{2b},CH}$ = 2.4 Hz, 1 H, CH_{2b}C≡CH), 4.38 (dd, $J_{2',3'}$ = 3.1 Hz, 1 H, 2′-H), 4.37 (dd, $J_{6'a,6'b}$ = –10.4 Hz, 1 H, 6′a-H), 4.35 (dd, $J_{6''a,6''b}$ = –10.5 Hz, 1 H, 6′′a-H), 4.29 (dd, $J_{2,3}$ = 3.5 Hz, 1 H, 2-H), 4.26 (dd, $J_{6a,6b}$ = –10.3 Hz, 1 H, 6a-H), 4.20 (dd, $J_{4',5'}$ = 9.3 Hz, 1 H, 4′-H), 4.16 (dd, $J_{4'',5''}$ = 9.3 Hz, 1 H, 4′′-H), 3.97 (dd, 1 H, 6′′b-H), 3.94 (dd, $J_{3,4}$ = 10.0 Hz, 1 H, 3-H), 3.91 (dd, 1 H, 6′b-H), 3.88 (dd, $J_{4,5}$ = 9.3 Hz, 1 H, 4-H), 3.78 (ddd, $J_{5,6a}$ = 4.8 Hz, $J_{5,6b}$ = 10.4 Hz, 1 H, 5-H), 3.75 (dd, 1 H, 6b-H), 3.64 (dd, $J_{3',4'}$ = 9.8 Hz, 1 H, 3′-H), 3.54 (dd, $J_{3'',4''}$ = 9.9 Hz, 1 H, 3′′-H), 3.43 (ddd, $J_{5'',6''a}$ = 4.8 Hz, $J_{5'',6''b}$ = 10.1 Hz, 1 H, 5′′-H), 3.38 (ddd, $J_{5',6'a}$ = 4.7 Hz, $J_{5',6'b}$ = 9.9 Hz, 1 H, 5′-H), 3.36 (s, 3 H, OCH_3), 2.31 (dd, 1 H, $CH_2C{\equiv}CH$) ppm. ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = 137.6–126.0 (arom. C), 102.4 (C-1′), 102.0 (*C*HPh), 101.7 (*C*′HPh), 101.3 (*C*′′HPh), 99.4 (C-1′′), 98.7 (C-1), 81.2 ($CH_2C{\equiv}CH$), 78.9 (C-4), 78.5 (C-3′′), 78.3 (C-4′), 77.9 (C-4′′), 75.7 (C-3′), 75.5 (C-2′), 75.3 (C-2′′), 74.2 ($CH_2C{\equiv}CH$), 74.0 (C-3), 73.6 (C-2), 72.1 (3′′-*C*H_2Ph), 71.7 (3-*C*H_2Ph), 71.1 (3′-*C*H_2Ph), 68.9 (C-6), 68.7 (C-6′′), 68.7 (C-6′), 67.9 (C-5′), 67.8 (C-5′′), 63.8 (C-5), 60.2 (*C*H_2C≡CH), 55.1 (OCH_3) ppm. HRMS: calcd. for $C_{64}H_{66}O_{16}Na$ $[M + Na]^+$ 1113.4248; found 1113.4347.

Benzyl 3-*O*-Benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (39): The propargyl deprotection was carried out by starting from trisaccharide **37** (0.24 g, 0.21 mmol). Reaction time for 1st step 6.5 h, for 2nd step 3 h. Yield: 0.19 g (83%). $[\alpha]_D$ = –39.0 (c = 0.66, CH_2Cl_2). ^{1}H NMR (600.13 MHz, $CDCl_3$, 25 °C): δ = 7.50–7.16 (m, 35 H, arom. H), 5.582 (s, 1 H, C*H*Ph), 5.577 (s, 1 H, C*H*′′Ph), 5.52 (s, 1 H, C*H*′Ph), 5.08 (d, $J_{1',2'}$ = 0.91 Hz, 1 H, 1′-H), 4.90 (d, $J_{1,2}$ = 1.6 Hz, 1 H, 1-H), 4.77 (s, 2 H, 3′-CH_2Ph) 4.72 and 4.49 (each d, J = –11.9 Hz, each 1 H, 1-CH_2Ph), 4.71 and 4.65 (each d, J = –11.9 Hz, each 1 H, 3-CH_2Ph), 4.60 and 4.58 (each d, J = –12.0 Hz, each 1 H, 3′′-CH_2Ph), 4.58 (d, $J_{1'',2''}$ = 0.81 Hz, 1 H, 1-H), 4.37 (dd, $J_{2',3'}$ = 3.3 Hz, 1 H, 2′-H), 4.354 (dd, $J_{2'',3''}$ = 3.3 Hz, 1 H, 2′′-H), 4.349 (dd, $J_{6''a,6''b}$ = –10.4 Hz, 1 H, 6′′a-H), 4.31 (dd, $J_{2,3}$ = 3.5 Hz, 1 H, 2-H), 4.26 (dd, $J_{6'a,6'b}$ = –10.3 Hz, 1 H, 6′a-H), 4.24 (dd, $J_{4'',5''}$ = 9.4 Hz, 1 H, 4′′-H), 4.20 (dd, $J_{6a,6b}$ = –10.3 Hz, 1 H, 6a-H), 4.18 (dd, $J_{4',5'}$ = 9.4 Hz, 1 H, 4′-H), 4.00 (dd, $J_{3,4}$ = 10.0 Hz, 1 H, 3-H), 3.96 (dd, $J_{4,5}$ = 9.5 Hz, 1 H, 4-H), 3.90 (dd, 1 H, 6′′b-H), 3.86 (ddd, $J_{5,6a}$ = 4.7 Hz, $J_{5,6b}$ = 10.3 Hz, 1 H, 5-H), 3.85 (dd, 6′b-H), 3.71 (dd, 1 H, 6b-H), 3.63 (dd, $J_{3',4'}$ = 9.8 Hz, 1 H, 3′-H), 3.52 (dd, $J_{3'',4''}$ = 9.5 Hz, 1 H, 3′′-H), 3.40 (ddd, $J_{5'',6''a}$ = 4.8 Hz, $J_{5'',6''b}$ = 10.1 Hz, 1 H, 5′′-H), 3.29 (ddd, $J_{5',6'a}$ = 4.8 Hz, $J_{5',6'b}$ = 10.0 Hz, 1 H, 5′-H) ppm. ^{13}C NMR (150.90 MHz, $CDCl_3$, 25 °C): δ = 138.4–126.0 (arom. C), 101.7 (*C*′HPh), 101.5 (*C*HPh), 101.4 (*C*′′HPh), 100.8 (C-1′), 99.2 (C-1′′), 96.9 (C-1), 78.7 (C-4), 78.3 (C-4′′), 78.1 (C-4′), 77.5 (C-3′′), 76.2 (C-3′), 74.0 (C-3), 73.9 (C-2), 73.9 (C-2′), 72.1, 71.7, 71.6, 69.5 (4× *C*H_2Ph), 68.9 (C-2′′), 68.8 (C-6), 68.8 (C-6′′), 68.4 (C-6′), 67.7 (C-5′′), 67.3 (C-5′), 64.1 (C-5) ppm. HRMS: calcd. for $C_{67}H_{68}O_{16}Na$ $[M + Na]^+$ 1151.4405; found 1151.4433.

Methyl 3-*O*-Benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (40): The propargyl deprotection was carried out as outlined in the general procedure by starting from trisaccharide **38** (33.5 mg, 0.031 mmol). Reaction time for 1st step 7 h, for 2nd step 3 h. Yield: 26 mg (81%). $[\alpha]_D$ = –72.0 (c = 1.0, CH_2Cl_2). ^{1}H NMR (600.13 MHz, $CDCl_3$, 25 °C): δ = 7.50–7.14 (m, 30 H, arom. H.), 5.60 (s, 1 H, C*H*′Ph), 5.58 (s, 1 H, C*H*′′Ph), 5.51 (s, 1 H, C*H*Ph), 5.10 (d, $J_{1',2'}$ = 1.1 Hz, 1 H, 1′-H), 4.79 (s, 2 H, 3′′-CH_2Ph), 4.71 (d, $J_{1,2}$ = 1.5 Hz, 1 H, 1-H), 4.71 and 4.63 (each d, J = –12.0 Hz, each 1 H, 3′-CH_2Ph), 4.65 (d,

$J_{1'',2''}$ = 0.61 Hz, 1 H, 1''-H), 4.62 and 4.60 (each d, J = –12.0 Hz, each 1 H, 3-CH_2Ph), 4.39 (dd, $J_{2'',3''}$ = 3.3 Hz, 1 H, 2''-H), 4.374 (dd, $J_{2',3'}$ = 3.2 Hz, 1 H, 2'-H), 4.366 (dd, $J_{6'a,6'b}$ = –10.4 Hz, 1 H, 6'a-H), 4.31 (dd, $J_{6a,6b}$ = –10.4 Hz, 1 H, 6a-H), 4.28 (dd, $J_{2,3}$ = 3.3 Hz, 1 H, 2-H), 4.25 (dd, $J_{4',5'}$ = 9.3 Hz, 1 H, 4'-H), 4.24 (dd, $J_{6''a,6''b}$ = –9.9 Hz, 1 H, 6''a-H), 4.20 (dd, $J_{4'',5''}$ = 9.5 Hz, 1 H, 4''-H), 3.93 (dd, $J_{4,5}$ = 9.2 Hz, 1 H, 4-H), 3.92 (dd, $J_{3,4}$ = 10.0 Hz, 1 H, 3-H), 3.91 (dd, 1 H, 6'b-H), 3.89 (dd, 1 H, 6b-H), 3.77 (ddd, $J_{5,6a}$ = 4.9 Hz, $J_{5,6b}$ = 10.1 Hz, 1 H, 5-H), 3.71 (dd, 1 H, 6''b-H), 3.67 (dd, $J_{3',4'}$ = 9.7 Hz, 1 H, 3'-H), 3.55 (dd, $J_{3'',4''}$ = 9.5 Hz, 1 H, 3''-H), 3.42 (ddd, $J_{5'',6''a}$ = 4.6 Hz, $J_{5'',6''b}$ = 10.2 Hz, 1 H, 5''-H), 3.363 (s, 3 H, OCH_3), 3.362 (ddd, $J_{5',6'a}$ = 4.9 Hz, $J_{5',6'b}$ = 10.0 Hz, 1 H, 5'-H) ppm. ^{13}C NMR (150.90 MHz, $CDCl_3$, 25 °C): δ = 138.5–126.0 (arom. C), 101.8 (*C*HPh), 101.5 (*C*'HPh), 101.4 (*C*''HPh), 100.9 (C-1'), 99.3 (C-1''), 98.8 (C-1), 78.7 (C-4), 78.3 (C-4'), 78.1 (C-4''), 77.5 (C-3''), 76.2 (C-3'), 74.0 (C-2''), 73.8 (C-2), 73.8 (C-3), 72.2 (3-*C*H_2Ph), 71.7 (3''-*C*H_2Ph), 71.5 (3'-*C*H_2Ph), 68.9 (C-2), 68.9 (C-6''), 68.8 (C-6'), 68.4 (C-6) 67.7 (C-5'), 67.3 (C-5''), 63.7 (C-5), 55.0 (OCH_3) ppm. HRMS: calcd. for $C_{61}H_{64}O_{16}Na$ [M + Na]$^+$ 1075.2589; found 1075.2575.

2,3-Di-*O*-Benzyl-4,6-*O*-benzylidene-D-mannopyranose (44): To a solution of **43** (0.16 g, 0.3 mmol, 1 equiv.) dissolved in acetone/water (50:1, 5 mL:0.1 mL) and cooled to 0 °C was added NBS (0.11 g, 0.62 mmol, 2.1 equiv.) in one portion. The mixture was warmed up to room temperature and after 30 min the reaction was quenched by the addition of solid $Na_2S_2O_3$ (23 mg, 0.13 mmol, 0.5 equiv.). The solvent was evaporated, and the residue was diluted with CH_2Cl_2 (20 mL) and washed with water (2 × 15 mL), dried, and concentrated. Chromatography (hexane/EtOAc, 6:1→2:1) gave the desired product (55 mg, 62%). α/β, >10:1. Data for the α-anomer: ^{1}H NMR (600.13 MHz, $CDCl_3$, 25 °C): δ = 7.53–7.26 (m, 15 H, arom. H.), 5.65 (s, 1 H, C*H*Ph), 5.51 (d, $J_{1,2}$ = 1.4 Hz, 1 H, 1-H), 4.82 and 4.66 (each d, J = –12.2 Hz, each 1 H, 3-CH_2Ph), 4.76 (s, 2 H, 2-CH_2Ph), 4.32 (dd, $J_{4,5}$ = 9.4 Hz, 1 H, 4-H), 4.28 (ddd, $J_{5,6a}$ = 4.8 Hz, $J_{5,6b}$ = 10.2 Hz, 1 H, 5-H), 4.22 (dd, $J_{6a,6b}$ = –10.3 Hz, 1 H, 6a-H), 4.04 (dd, $J_{2,3}$ = 3.2 Hz, 1 H, 2-H), 3.97 (dd, $J_{3,4}$ = 9.4 Hz, 1 H, 3-H), 3.89 (dd, 1 H, 6b-H) ppm. ^{13}C NMR (150.90 MHz, $CDCl_3$, 25 °C): δ = 138.4–126.1 (arom C), 101.5 (*C*HPh), 87.1 (C-1), 79.1 (C-4), 78.1 (C-2), 76.2 (C-3), 73.1 (3-*C*H_2Ph), 73.0 (2-*C*H_2Ph), 68.5 (C-6), 65.4 (C-5) ppm. Data for the β-anomer: ^{1}H NMR (600.13 MHz, $CDCl_3$, 25 °C): δ = 7.53–7.26 (m, 15 H, arom. H.), 5.64 (s, 1 H, C*H*Ph), 4.81 (d, $J_{1,2}$ = 1.2 Hz, 1 H, 1-H), 5.11 and 4.86 (each d, J = –11.1 Hz, each 1 H, 3-CH_2Ph), 4.86 and 4.74 (each d, J = –11.1 Hz, each 1 H, 2-CH_2Ph), 4.31 (dd, $J_{4,5}$ = 9.4 Hz, 1 H, 4-H), 4.29 (dd, $J_{6a,6b}$ = –10.5 Hz, 1 H, 6a-H), 4.18 (dd, $J_{2,3}$ = 3.1 Hz, 1 H, 2-H), 3.95 (dd, 1 H, 6b-H), 3.74 (dd, $J_{3,4}$ = 9.7 Hz, 1 H, 3-H), 3.42 (ddd, $J_{5,6a}$ = 4.9 Hz, $J_{5,6b}$ = 9.8 Hz, 1 H, 5-H) ppm. HRMS: calcd. for $C_{27}H_{28}O_6$ [M + Na]$^+$ 449.1964; found 449.1964.

(2,3-Di-*O*-Benzyl-4,6-*O*-benzylidene-α-D-mannopyranosyl) Dibenzyl Phosphate (45): To a solution of compound **44** (80 mg, 0.18 mmol, 1 equiv.) in dry CH_2Cl_2 (4 mL) was added 1*H*-tetrazole (0.45 M in acetonitrile, 47 mg, 1.8 mL, 0.67 mmol, 3.75 equiv.). After cooling the reaction mixture to –40 °C, dibenzyl(*N*,*N*-diisopropyl)phosphoramidite (0.15 g, 0.15 mL, 0.45 mmol, 2.5 equiv.) was added dropwise, and the mixture was slowly warmed up to room temperature (45 min) followed by stirring for 1 h. Next, the reaction was cooled to –60 °C and *m*-CPBA (77%, 0.1 mg, 0.45 mmol, 2.5 equiv.) was added. The mixture was stirred for 30 min at 0 °C and then for 45 min with slow warming to room temperature. The reaction mixture was diluted with CH_2Cl_2 (40 mL), washed with 10% solution $Na_2S_2O_3$ (2 × 15 mL), saturated $NaHCO_3$ (2 × 15 mL), and water (2 × 10 mL), dried, and concentrated. The crude product was purified by column chromatography (hexane/EtOAc, 8:1→3.5:1). The isolated product was repurified by column chromatography (hexane/EtOAc, 1:1) to afford the title compound. Yield: 0.103 g (82%). $[\alpha]_D$ = +5.5 (c = 1.0, CH_2Cl_2). ^{1}H NMR (500.13 MHz, $CDCl_3$, 30 °C): δ = 7.52–7.28 (m, 25 H, arom. H.), 5.65 (dd, $J_{1,2}$ = 1.8 Hz, $^3J_{P,1\text{-}H}$ = 6.2 Hz, 1 H, 1-H), 5.58 (s, 1 H, C*H*Ph), 5.08 and 5.03 [each d, J = –11.9 Hz, $J_{P,CH_{2a}}$ = 9.9 Hz, $J_{P,CH_{2b}}$ = 9.3 Hz, each 1 H, PO(OCH_2Ph)], 5.04 and 5.01 [each d, J = –11.8 Hz, $J_{P,CH_{2a}}$ = 8.8 Hz, $J_{P,CH_{2b}}$ = 8.4 Hz, each 1 H, PO(OCH_2Ph)], 4.75 and 4.57 (each d, J = –12.2 Hz, each 1 H, 3-CH_2Ph), 4.71 and 4.64 (each d, J = –12.0 Hz, each 1 H, 2-CH_2Ph), 4.21 (dd, $J_{4,5}$ = 9.6 Hz, 1 H, 4-H), 4.04 (dd, $J_{6a,6b}$ = –10.3 Hz, 1 H, 6a-H), 3.855 (ddd, $J_{5,6a}$ = 4.9 Hz, $J_{5,6b}$ = 10.3 Hz, 1 H, 5-H), 3.846 (dd, $J_{3,4}$ = 10.1 Hz, 1 H, 3-H), 3.76 (dd, 1 H, 6b-H), 3.73 (dd, $J_{2,3}$ = 3.2 Hz, 1 H, 2-H) ppm. ^{13}C NMR (125.77 MHz, $CDCl_3$, 30 °C): δ = 138.4–126.2 (arom. C), 101.6 (*C*HPh), 97.0 ($^2J_{P,C\text{-}1}$ = 6.0 Hz, C-1), 78.4 (C-4), 76.2 ($^3J_{P,C\text{-}2}$ = 9.6 Hz, C-2), 75.2 (C-3), 73.7 (2-*C*H_2Ph), 73.1 (3-*C*H_2Ph), 69.6 [$^2J_{P,C}$ = 5.5 Hz, PO(O*C*H_2Ph)], 68.3 (C-6), 67.3 [$^2J_{P,C}$ = 5.7 Hz, PO(O*C*H_2Ph)], 65.8 (C-5) ppm. ^{31}P NMR (202.47 MHz, $CDCl_3$, 30 °C): δ = –3.17 ppm. HRMS: calcd. for $C_{41}H_{42}O_9P$ [M + H]$^+$ 709.2566; found 709.2522.

Phenyl 2,3-di-*O*-Benzyl-4,6-*O*-benzylidene-β-D-manno-pyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside (47): Disaccharide **30** (0.15 g, 0.19 mmol, 1 equiv.) was dissolved in dry DMF (1.5 mL) and the solution was then cooled to 0 °C. Sodium hydride (60% in oil, 10 mg, 0.25 mmol, 1.3 equiv.) was added. After stirring for 30 min, benzyl bromide (39 mg, 27 μL, 0.22 mmol, 1.2 equiv.) was added, and the mixture was warmed up to room temperature. After 1.5 h, the reaction was quenched by the addition of methanol. The solvent was evaporated, and the residue was diluted with EtOAc (20 mL) and washed with water (3 × 20 mL) and brine (1 × 20 mL), dried, and concentrated. Chromatography (hexane/EtOAc, 8:1) gave the title compound. Yield: 0.16 g (96%). $[\alpha]_D$ = –3.5 (c = 0.166, CH_2Cl_2). ^{1}H NMR (600.13 MHz, $CDCl_3$, 25 °C): δ = 7.51–7.25 (m, 30 H, arom. H), 5.60 (s, 1 H, C*H*Ph), 5.51 (s, 1 H, C*H*'Ph), 5.49 (d, $J_{1,2}$ = 1.5 Hz, 1 H, 1-H), 5.04 and 4.96 (each d, J = –12.3 Hz, each 1 H, 3'-CH_2Ph), 4.80 and 4.76 (each d, J = –12.1 Hz, each 1 H, 3-CH_2Ph), 4.69 and 4.61 (each d, J = –12.5 Hz, each 1 H, 2'-CH_2Ph), 4.62 (d, $J_{1',2'}$ = 0.93 Hz, 1 H, 1'-H), 4.51 (dd, $J_{2,3}$ = 3.2 Hz, 1 H, 2-H), 4.33 (ddd, $J_{5,6a}$ = 4.8 Hz, $J_{5,6b}$ = 10.2 Hz, 1 H, 5-H), 4.25 (dd, $J_{4',5'}$ = 9.3 Hz, 1 H, 4'-H), 4.25 (dd, $J_{6'a,6'b}$ = –10.4 Hz, 1 H, 6'a-H), 4.23 (dd, $J_{6a,6b}$ = –10.2 Hz, 1 H, 6a-H), 4.17 (dd, $J_{4,5}$ = 9.5 Hz, 1 H, 4-H), 3.98 (dd, $J_{3,4}$ = 10.0 Hz, 1 H, 3-H), 3.97 (dd, $J_{2',3'}$ = 3.2 Hz, 1 H, 2'-H), 3.87 (dd, 1 H, 6'b-H), 3.79 (dd, 1 H, 6b-H), 3.59 (dd, $J_{3',4'}$ = 9.9 Hz, 1 H, 3'-H), 3.31 (ddd, $J_{5',6'a}$ = 4.8 Hz, $J_{5',6'b}$ = 10.1 Hz, 1 H, 5'-H) ppm. ^{13}C NMR (150.90 MHz, $CDCl_3$, 25 °C): δ = 138.5–126 (arom. C), 101.7 (*C*'HPh), 101.4 (*C*HPh), 99.8 (C-1'), 86.4 (C-1), 78.7 (C-4), 78.4 (C-4'), 77.5 (C-3'), 76.2 (C-2), 76.0 (C-2'), 74.6 (3'-*C*H_2Ph), 74.3 (C-3), 72.3 (2'-*C*H_2Ph), 71.5 (3-*C*H_2Ph), 68.6 (C-6), 68.5 (C-6'), 67.8 (C-5'), 65.4 (C-5) ppm. HRMS: calcd. for $C_{55}H_{51}O_{10}S$ [M – H]$^-$ 903.3203; found 903.3810.

2,3-Di-*O*-Benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-D-mannopyranose (48): Compound **47** (0.10 g, 0.11 mmol, 1 equiv.) was dissolved in acetone/water (33:1, 5 mL:0.15 mL). The solution was cooled to 0 °C and NBS (24 mg, 0.14 mmol, 1.2 equiv.) was added in one portion. The mixture was warmed up to room temperature and after 30 min the reaction was quenched by the addition of solid $Na_2S_2O_3$ (13 mg, 0.09 mmol, 0.75 equiv.). The solvent was evaporated, and the residue was diluted with CH_2Cl_2 (20 mL) and washed with water (2 × 15 mL), dried, and concentrated. Chromatography (hexane/EtOAc,

6:1→2:1) gave the desired product (55 mg, 62%). The product obtained was used in the next step without detailed NMR spectroscopic characterization as a result of the complexity of both the ^1H and ^{13}C NMR spectra of the anomeric disaccharide mixture. HRMS: calcd. for $C_{47}H_{48}O_{11}Na$ [M + Na]$^+$ 811.3089; found 811.3070. HRMS: calcd. for $C_{47}H_{48}O_{11}K$ [M + K]$^+$ 827.2828; found 827.2861.

[2,3-Di-*O*-Benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranosyl] Dibenzyl Phosphate (49): To a solution of compound **48** (46 mg, 0.058 mmol, 1 equiv.) in dry CH_2Cl_2 (3 mL) was added 1*H*-tetrazole (0.45 M in acetonitrile, 15.3 mg, 0.6 mL, 0.22 mmol, 3.75 equiv.). After cooling the reaction mixture to –40 °C, dibenzyl(*N*,*N*-diisopropyl)phosphoramidite (50 mg, 49 μL, 0.15 mmol, 2.5 equiv.) was added dropwise, and the reaction mixture was slowly warmed up to room temperature (45 min) followed by stirring for 1 h. Next, the reaction mixture was cooled to –60 °C and *m*-CPBA (77%, 66 mg, 0.30 mmol, 5.0 equiv.) was added. The reaction mixture was stirred for 30 min at 0 °C and then for 45 min with slow warming to room temperature. The mixture was diluted with CH_2Cl_2 (50 mL), washed with 10% solution $Na_2S_2O_3$ (2×20 mL), saturated $NaHCO_3$ (2×20 mL), and water (2×20 mL), dried, and concentrated. The crude product was purified by column chromatography (hexane/EtOAc, 8:1→3.5:1). The product was repurified by column chromatography (hexane/EtOAc, 1:1) to afford the title compound. Yield: 45.5 mg (75%). $[\alpha]_D$ = –25.0 (*c* = 1.0, MeOH). ^1H NMR (500.13 MHz, $CDCl_3$, 25 °C): δ = 7.52–7.24 (m, 35 H, arom. H.), 5.580 (s, 1 H, C*H*Ph), 5.579 (dd, $J_{1,2}$ = 1.9 Hz, $^3J_{P,1\text{-}H}$ = 6.2 Hz, 1 H, 1-H), 5.42 (s, 1 H, C*H*′Ph), 5.08 and 5.03 [each d, *J* = –11.7 Hz, $J_{P,CH_{2a}}$ = 8.8 Hz, $J_{P,CH_{2b}}$ = 8.4 Hz, each 1 H, PO(OCH_2Ph)$_a$], 5.00 and 4.98 [each d, *J* = –11.7 Hz, $J_{P,CH_{2a}}$ = 9.6 Hz, $J_{P,CH_{2b}}$ = 8.4 Hz, each 1 H, PO(OCH_2Ph)$_b$], 4.99 and 4.91 (each d, *J* = –12.2 Hz, each 1 H, CH_2Ph), 4.69 and 4.68 (each d, *J* = –12.4 Hz, each 1 H, CH_2Ph), 4.68 and 4.62 (each d, *J* = –12.3 Hz, each 1 H, CH_2Ph), 4.44 (d, $J_{1',2'}$ = 0.97 Hz, 1 H, 1′-H), 4.22 (dd, $J_{6'a,6'b}$ = –10.1 Hz, 1 H, 6′a-H), 4.21 (dd, $J_{4',5'}$ = 9.3 Hz, 1 H 4′-H), 4.06 (dd, $J_{4,5}$ = 9.6 Hz, 1 H, 4-H), 4.05 (dd, $J_{2,3}$ = 3.4 Hz, 1 H, 2-H), 4.04 (dd, $J_{6a,6b}$ = –10.3 Hz, 1 H, 6a-H), 3.91 (dd, $J_{2',3'}$ = 3.2 Hz, 1 H, 2′-H), 3.85 (ddd, $J_{5,6a}$ = 4.8 Hz, $J_{5,6b}$ = 10.2 Hz, 1 H, 5-H), 3.84 (dd, $J_{3,4}$ = 10.1 Hz, 1 H, 3-H), 3.83 (dd, 1 H, 6′b-H), 3.65 (dd, 1 H, 6b-H), 3.55 (dd, $J_{3',4'}$ = 9.9 Hz, 1 H, 3′-H), 3.23 (ddd, $J_{5',6'a}$ = 4.8 Hz, $J_{5',6'b}$ = 10.1 Hz, 1 H, 5′-H) ppm. ^{13}C NMR (150.90 MHz, $CDCl_3$, 25 °C): δ = 138.6–126.1 (arom. C), 101.6 (*C*′HPh), 101.4 (*C*HPh), 101.0 (C-1′), 96.3 ($^2J_{P,C\text{-}1}$ = 5.4 Hz, C-1), 78.3 (C-4′), 77.9 (C-4), 77.4 (C-3′), 76.0 (C-2′), 75.4 ($^3J_{P,C\text{-}2}$ = 9.9 Hz, C-2), 74.7 (*C*H_2Ph), 73.1 (C-3), 72.3 (*C*H_2Ph), 71.6 (*C*H_2Ph), 69.8 and 69.7 [$^2J_{P,C}$= 5.5 Hz, PO(O*C*H_2Ph)], 68.4 (C-6′), 68.3 (C-6), 67.6 (C-5′), 65.8 (C-5) ppm. ^{31}P NMR (242.94 MHz, $CDCl_3$, 25 °C): δ = –2.95 ppm. HRMS: calcd. for $C_{61}H_{61}O_{14}PNa$ [M + Na]$^+$ 1071.3696; found 1071.3743.

General Procedure for the Coupling of the Acceptor with the Glucopyranosyl Imidate Donor: A mixture of trichloroacetimidate **51** (1.2 equiv.), acceptor **16** or **29** (1 equiv.), and 4 Å molecular sieves (0.3 g) was dried under reduced pressure for 2 h. Dry CH_2Cl_2 (10 mL) was added, and the solution was stirred for 30 min at room temperature under an argon atmosphere. The mixture was then cooled to –10 °C and TMSOTf (0.05 equiv.) was added; stirring was continued for a further 30 min, after which the temperature was brought up to room temperature. The reaction mixture was neutralized by the addition of Et_3N and concentrated. The residue was purified by column chromatography (hexane/EtOAc, 6:1→4:1) to give the title compound.

Methyl 2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (53): The coupling was carried out as outlined in the general procedure by starting from donor **51** (0.36 g, 0.56 mmol). Yield: 0.32 g (80%). $[\alpha]_D$ = –10.0 (*c* = 1.0, CH_2Cl_2). ^1H NMR (600.13 MHz, $CDCl_3$, 25 °C): δ = 7.51–7.18 (m, 25 H, arom. H), 5.60 (s, 1 H, C*H*Ph), 5.12 (dd, $J_{2',3'}$ = 9.6 Hz, 1 H, 2′-H), 4.80 and 4.56 (each d, *J* = –10.8 Hz, each 1 H, CH_2Ph), 4.80 and 4.69 (each d, *J* = –11.5 Hz, each 1 H, CH_2Ph), 4.78 and 4.68 (each d, *J* = –12.5 Hz, each 1 H, CH_2Ph), 4.62 (d, $J_{1,2}$ = 1.7 Hz, 1 H, 1-H), 4.53 and 4.51 (each d, *J* = –12.1 Hz, each 1 H, CH_2Ph), 4.41 (d, $J_{1',2'}$ = 7.9 Hz, 1 H, 1′-H), 4.19 (dd, $J_{6a,6b}$ = –10.1 Hz, 1 H, 6a-H), 4.11 (dd, $J_{2,3}$ = 3.2 Hz, 1 H, 2-H), 4.09 (dd, $J_{4,5}$ = 9.5 Hz, 1 H, 4-H), 3.87 (dd, $J_{3,4}$ = 10.0 Hz, 1 H, 3-H), 3.77 (dd, 1 H, 6b-H), 3.75 (dd, $J_{6'a,6'b}$ = –10.9 Hz, 1 H, 6′a-H), 3.69 (ddd, $J_{5,6a}$ = 4.7 Hz, $J_{5,6b}$ = 10.3 Hz, 1 H, 5-H), 3.674 (dd, $J_{3',4'}$ = 8.9 Hz, 1 H, 3′-H), 3.672 (dd, 1 H, 6′b-H), 3.64 (dd, $J_{4',5'}$ = 9.9 Hz, 1 H, 4′-H), 3.53 (ddd, $J_{5',6'a}$ = 1.8 Hz, $J_{5',6'b}$ = 5.7 Hz, 1 H, 5′-H), 3.33 (s, 3 H, OCH_3), 2.04 (s, 3 H, CH_3C=O) ppm. ^{13}C NMR (150.90 MHz, $CDCl_3$, 25 °C): δ = 169.5 (CH_3C=O), 138.7–126.1 (arom. C), 101.5 (*C*HPh), 100.2 (C-1′), 99.5 (C-1), 82.8 (C-3′), 78.1 (C-4), 78.0 (C-4′), 75.5 (C-2 and C-5′), 75.2 (*C*H_2Ph), 74.9 (*C*H_2Ph), 73.7 (*C*H_2Ph, and C-3), 72.9 (C-2′), 71.2 (*C*H_2Ph), 69.4 (C-6′), 68.8 (C-6), 64.1 (C-5), 54.9 (OCH_3), 21.0 (*C*H_3C=O) ppm. HRMS: calcd. for $C_{50}H_{54}O_{12}$ 846.3615 [M]$^+$; found 846.3594.

Methyl 2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (60): The coupling was carried out as outlined in the general procedure by starting from donor **51** (0.12 g, 0.18 mmol). Yield: 0.14 g (78%). $[\alpha]_D$ = –60.0 (*c* = 1.0, CH_2Cl_2). ^1H NMR (600.13 MHz, $CDCl_3$, 25 °C): δ = 7.50–7.12 (m, 35 h, arom. H), 5.58 (s, 1 H, C*H*′Ph), 5.56 (s, 1 H, C*H*Ph), 5.21 (dd, $J_{2'',3''}$ = 9.5 Hz, 1 H, 2′′-H), 4.96 (dd, $J_{1'',2''}$ = 7.9 Hz, 1 H, 1′′-H), 4.88 and 4.67 (each d, *J* = –13.0 Hz, each 1 H, 3′-CH_2Ph), 4.80 and 4.53 (each d, *J* = –10.8 Hz, each 1 H, 4′′-CH_2Ph), 4.78 and 4.68 (each d, *J* = –11.5 Hz, each 1 H, 3′′-CH_2Ph), 4.69 and 4.62 (each d, *J* = –12.1 Hz, each 1 H, 3-CH_2Ph), 4.52 and 4.48 (each d, *J* = –12.0 Hz, each 1 H, 6′′-CH_2Ph), 4.67 (d, $J_{1,2}$ = 1.8 Hz, 1 H, 1-H), 4.50 (dd, $J_{1',2'}$ = 0.84 Hz, 1 H, 1′-H), 4.30 (dd, $J_{6a,6b}$ = –10.2 Hz, 1 H, 6a-H), 4.28 (dd, $J_{2',3'}$ = 3.2 Hz, 1 H, 2′-H), 4.26 (dd, $J_{4,5}$ = 9.4 Hz, 1 H, 4-H), 4.16 (dd, $J_{6'a,6'b}$ = –10.3 Hz, 1 H, 6′a-H), 4.09 (dd, $J_{2,3}$ = 3.1 Hz, 1 H, 2-H), 4.06 (dd, $J_{4',5'}$ = 9.3 Hz, 1 H, 4′-H), 3.91 (dd, $J_{3,4}$ = 10.0 Hz, 1 H, 3-H), 3.79 (ddd, $J_{5,6a}$ = 4.7 Hz, $J_{5,6b}$ = 10.3 Hz, 1 H, 5-H), 3.77 (dd, $J_{6''a,6''b}$ = –10.6 Hz, 1 H, 6′′a-H), 3.76 (dd, 1 H, 6b-H), 3.75 (dd, 1 H, 6′b-H), 3.70 (dd, $J_{3'',4''}$ = 8.8 Hz, 1 H, 3′′-H), 3.64 (dd, 1 H, 6′′b-H), 3.63 (dd, $J_{4'',5''}$ = 9.8 Hz, 1 H, 4′′-H), 3.62 (ddd, $J_{5'',6''a}$ = 1.7 Hz, $J_{4'',6''b}$ = 6.2 Hz, 1 H, 5′′-H), 3.55 (dd, $J_{3',4'}$ = 9.9 Hz, 1 H, 3′-H), 3.37 (s, 3 H, OCH_3), 3.25 (ddd, $J_{5',6'a}$ = 4.8 Hz, $J_{5',6b}$ = 10.1 Hz, 1 H, 5′-H), 1.91 (s, 3 H, 2′′-CH_3C=O) ppm. ^{13}C NMR (150.90 MHz, $CDCl_3$, 25 °C): δ = 170.2 (2′′-CH_3C=O), 138.7–125.9 (arom. C), 101.7 (*C*H′Ph), 101.3 (*C*HPh), 101.1 (C-1′′), 101.0 (C-1′), 100.0 (C-1), 83.3 (C-3′′), 78.5 (C-4), 78.2 (C-5′′), 77.2 (C-4′), 76.9 (C-2), 75.7 (C-3′), 75.1 (4′′-*C*H_2Ph), 75.0 (C-4′′ and 3′′-*C*H_2Ph), 74.5 (C-3), 74.3 (C-2′), 73.6 (6′′-*C*H_2Ph), 73.2 (C-2′′), 71.5 (3-*C*H_2Ph), 70.4 (3′-*C*H_2Ph), 69.9 (C-6′′), 69.3 (C-6), 68.6 (C-6′), 67.7 (C-5′), 64.3 (C-5), 55.0 (OCH_3), 21.1 (2′′-*C*H_3C=O) ppm. HRMS: calcd. for $C_{70}H_{74}O_{17}Na$ [M + Na]$^+$ 1209.4824; found 1209.4978.

Methyl 3,4,6-Tri-*O*-benzyl-β-D-glucopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (54): To a solution of disaccharide **53** (0.24 g, 0.28 mmol) in dry MeOH/THF (3:1, 12 mL) was added 2% MeONa (8.5 mg, 0.4 mL, 0.37 mmol, 1.3 equiv.),

and the mixture was stirred for 18 h at room temperature. The solvent was evaporated, and the residue was dissolved in EtOAc (40 mL) and washed with saturated $NaHCO_3$ (2 × 10 mL) and water (10 mL), dried, and concentrated. The crude product was purified by column chromatography (hexane/EtOAc, 3:1) to give the desired product. Yield: 0.22 g (98%). $[\alpha]_D$ = +9.5 (c = 1.0, CH_2Cl_2). ^{1}H NMR (600.13 MHz, $CDCl_3$, 25 °C): δ = 7.54–7.12 (m, 25 H, arom. H), 5.65 (s, 1 H, C*H*Ph), 4.93 and 4.71 (each d, J = –11.2 Hz, each 1 H, 3′-CH_2Ph), 4.91 and 4.74 (each d, J = –11.4 Hz, each 1 H, 6′-CH_2Ph), 4.87 and 4.57 (each d, J = –10.8 Hz, each 1 H, 4′-CH_2Ph), 4.77 (d, $J_{1,2}$ = 1.7 Hz, 1 H, 1-H), 4.55 and 4.49 (each d, J = –12.1 Hz, each 1 H, 3-CH_2Ph), 4.51 (d, $J_{1',2'}$ = 8.4 Hz, 1 H, 1′-H), 4.28 (dd, $J_{6a,6b}$ = –10.4 Hz, 1 H, 6a-H), 4.21 (ddd, $J_{2,3}$ = 3.4 Hz, $J_{2,2\text{-OH}}$ = 2.5 Hz, 1 H, 2-H), 4.19 (dd, $J_{4,5}$ = 9.5 Hz, 1 H, 4-H), 3.99 (dd, $J_{3,4}$ = 9.9 Hz, 1 H, 3-H), 3.88 (dd, 1 H, 6b-H), 3.83 (d, 1 H, 2-OH), 3.79 (ddd, $J_{5,6a}$ = 4.8 Hz, $J_{5,6b}$ = 10.4 Hz, 1 H, 5-H), 3.72 (dd, 1 H, 6′b-H), 3.6872 (dd, $J_{6'a,6'b}$ = –11.2 Hz, 1 H, 6′a-H), 3.6871 (dd, $J_{2',3'}$ = 9.1 Hz, 1 H, 2′-H), 3.59 (dd, $J_{4',5'}$ = 9.8 Hz, 1 H, 4′-H), 3.58 (dd, $J_{3',4'}$ = 8.9 Hz, 1 H, 3′-H), 3.48 (ddd, $J_{5',6'a}$ = 2.0 Hz, $J_{5',6'b}$ = 4.2 Hz, 1 H, 5′-H), 3.32 (s, 3 H, OCH_3) ppm. ^{13}C NMR (150.90 MHz, $CDCl_3$, 25 °C): δ = 138.9–126.0 (arom. C), 101.64 (C-1), 101.62 (*C*HPh) 101.5 (C-1′), 83.9 (C-3′), 79.6 (C-4), 77.0 (C-4′), 75.9 (C-5′), 74.9 (4′-CH_2Ph), 74.5 (3′-*C*H_2Ph), 74.5 (C-3), 74.2 (6′-*C*H_2Ph), 73.5 (3-*C*H_2Ph), 71.6 (C-2), 71.5 (C-2′), 69.0 (C-6′), 68.9 (C-6), 63.6 (C-5), 55.0 (OCH_3) ppm. HRMS: calcd. for $C_{48}H_{52}O_{11}$ $[M]^+$ 804.3509; found 804.3487.

Methyl 3,4,6-Tri-*O*-benzyl-β-D-glucopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (61): To a solution of trisaccharide **60** (0.1 g, 0.084 mmol) in dry MeOH/THF (3:1, 12 mL) was added 1% MeONa (3.1 mg, 0.31 mL, 0.13 mmol, 1.6 equiv.), and the mixture was stirred for 72 h at room temperature. The solvent was evaporated, and the residue was dissolved in EtOAc (40 mL) and washed with saturated $NaHCO_3$ (2 × 10 mL) and water (10 mL), dried, and concentrated. Purification by column chromatography (hexane/EtOAc, 3:1) gave the desired product. Yield: 94 mg (98%). $[\alpha]_D$ = –73.5 (c = 1.0, CH_2Cl_2). ^{1}H NMR (600.13 MHz, $CDCl_3$, 25 °C): δ = 7.53–7.12 (m, 35 H, arom. H), 5.66 (s, 1 H, C*H*Ph), 5.56 (s, 1 H, C*H*′Ph), 5.06 and 4.65 (each d, J = –11.1 Hz, each 1 H, 3′′-CH_2Ph), 4.92 and 4.67 (each d, J = –13.6 Hz, each 1 H, 3′-CH_2Ph), 4.84 and 4.49 (each d, J = –10.7 Hz, each 1 H, 4′′-CH_2Ph), 4.76 and 4.70 (each d, J = –12.5 Hz, each 1 H, 3-CH_2Ph), 4.69 (d, $J_{1,2}$ = 1.6 Hz, 1 H, 1-H), 4.64 (d, $J_{1'',2''}$ = 7.8 Hz, 1 H, 1′′-H), 4.59 (d, $J_{1',2'}$ = 0.82 Hz, 1 H, 1′-H), 4.48 and 4.44 (each d, J = –12.0 Hz, each 1 H, 6′′-CH_2Ph), 4.40 (dd, $J_{4,5}$ = 9.6 Hz, 1 H, 4-H), 4.30 (dd, $J_{2',3'}$ = 3.2 Hz, 1 H, 2′-H), 4.29 (dd, $J_{6a,6b}$ = –10.3 Hz, 1 H, 6a-H), 4.26 (dd, $J_{6'a,6'b}$ = –10.2 Hz, 1 H, 6′a-H), 4.22 (dd, $J_{2,3}$ = 3.5 Hz, 1 H, 2-H), 4.12 (dd, $J_{4',5'}$ = 9.4 Hz, 1 H, 4′-H), 3.89 (dd, $J_{3,4}$ = 10.1 Hz, 1 H, 3-H), 3.81 (dd, 1 H, 6b-H), 3.789 (dd, 1 H, 6′b-H), 3.786 (ddd, $J_{2'',3''}$ = 8.8 Hz, $J_{2'',5''}$ = 1.3 Hz, 1 H, 2′′-H), 3.76 (ddd, $J_{5,6a}$ = 4.8 Hz, $J_{5,6b}$ = 10.5 Hz, 1 H, 5-H), 3.75 (dd, $J_{6''a,6''b}$ = –10.2 Hz, 1 H, 6′′a-H), 3.64 (dddd, $J_{5'',6''a}$ = 1.8 Hz, $J_{5'',6''b}$ = 6.6 Hz, 1 H, 5′′-H), 3.63 (dd, $J_{3'',4''}$ = 8.8 Hz, 1 H, 3′′-H), 3.61 (dd, 1 H, 6′′b-H), 3.57 (dd, $J_{3',4'}$ = 10.0 Hz, 1 H, 3′-H), 3.46 (dd, $J_{4'',5''}$ = 9.9 Hz, 1 H, 4′′-H), 3.36 (s, 3 H, OCH_3), 3.30 (ddd, $J_{5',6'a}$ = 4.8 Hz, $J_{5',6'b}$ = 9.9 Hz, 1 H, 5′-H) ppm. ^{13}C NMR (150.90 MHz, $CDCl_3$, 25 °C): δ = 138.9–125.9 (arom. C), 105.6 (C-1′′), 101.7 (*C*HPh), 101.3 (*C*′HPh), 99.4 (C-1), 98.8 (C-1′), 86.5 (C-3′′), 78.3 (C-4), 77.4 (C-4′), 77.1 (C-4′′), 76.8 (C-2′), 75.42 (C-3′), 75.35 (C-2′′), 75.3 (3′′-*C*H_2Ph), 75.22 (6′′-*C*H_2Ph), 75.18 (C-3′′), 73.9 (C-3), 73.6 (C-2), 73.4 (3-*C*H_2Ph), 71.7 (4′′-*C*H_2Ph), 70.4 (3′-*C*H_2Ph), 69.9 (C-6′′), 69.1 (C-6), 68.3 (C-6′), 67.5 (C-5′), 63.8 (C-5), 54.9 (OCH_3) ppm. HRMS: calcd. for $C_{68}H_{72}O_{16}Na$ $[M + Na]^+$ 1167.4713; found 1167.4691. HRMS: calcd. for $C_{68}H_{72}O_{16}K$ $[M + K]^+$ 1183.4453; found 1183.4452.

Methyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-gluco-pyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-manno-pyranoside (56): A suspension of 4 Å molecular sieves (0.3 g), collidine (42 mg, 46 μL, 0.35 mmol, 1.3 equiv.), AgOTf (83 mg, 0.32 mmol, 1.2 equiv.), and acceptor **16** (0.1 g, 0.27 mmol) in dry CH_2Cl_2 (3 mL) was stirred under an argon atmosphere for 2 h. The reaction mixture was cooled to –20 °C, and a solution of **52** (0.15 g, 0.29 mmol, 1.1 equiv.) in dry CH_2Cl_2 (1 mL) was added dropwise. The mixture was stirred at –20 °C for 40 min, then warmed up slowly to room temperature, and filtered through a pad of Celite. The filtrate was diluted with CH_2Cl_2 (25 mL), washed with saturated $NaHCO_3$ (2 × 20 mL), brine (20 mL), and water (20 mL), dried, and concentrated. Purification of the residue by column chromatography (hexane/EtOAc, 4:1→1:1) gave the title disaccharide. Yield: 0.17 g (78%). $[\alpha]_D$ = –21.5 (c = 1.0, CH_2Cl_2). ^{1}H NMR (600.13 MHz, $CDCl_3$, 25 °C): δ = 7.88 (m, 2 H, phth. H), 7.75 (m, 2 H, phth. H), 7.44–7.23 (m, 10 H, arom. H), 5.88 (dd, $J_{3',4'}$ = 9.1 Hz, 1 H, 3′-H), 5.45 (s, 1 H, C*H*Ph), 5.45 (d, $J_{1',2'}$ = 8.5 Hz, 1 H, 1′-H), 5.20 (dd, $J_{4',5'}$ = 10.1 Hz, 1 H, 4′-H), 4.71 and 4.65 (each d, J = –12.3 Hz, each 1 H, CH_2Ph), 4.50 (dd, $J_{2',3'}$ = 10.8 Hz, 1 H, 2′-H), 4.39 (d, $J_{1,2}$ = 1.8 Hz, 1 H, 1-H), 4.31 (dd, 1 H, 6′b-H), 4.23 (dd, $J_{6'a,6'b}$ = –12.2 Hz, 1 H, 6′a-H), 4.11 (dd, $J_{2,3}$ = 3.2 Hz, 1 H, 2-H), 3.88 (dd, $J_{4,5}$ = 9.6 Hz, 1 H, 4-H), 3.88 (ddd, $J_{5',6'a}$ = 2.4 Hz, $J_{5',6'b}$ = 4.9 Hz, 1 H, 5′-H), 3.82 (dd, $J_{3,4}$ = 10.0 Hz, 1 H, 3-H), 3.75 (dd, $J_{6a,6b}$ =–10.2 Hz, 1 H, 6a-H), 3.49 (ddd, $J_{5,6a}$ = 4.7 Hz, $J_{5,6b}$ = 10.2 Hz, 1 H, 5-H), 3.17 (s, 3 H, OMe), 3.16 (dd, 1 H, 6b-H), 2.06, 2.05, 1.90 (each s, each 3 H, 3 × CH_3C=O) ppm. ^{13}C NMR (150.90 MHz, $CDCl_3$, 25 °C): δ = 170.7, 170.2, 169.4 (3 × CH_3*C*=O), 138.4–123.4 (arom. C), 101.5 (*C*HPh), 99.0 (C-1), 96.7 (C-1′), 78.1 (C-4), 75.2 (C-2), 73.8 (C-3), 72.1 (C-5′), 71.5 (*C*H_2Ph), 70.4 (C-3′), 69.1 (C-4′), 68.4 (C-6), 63.7 (C-5), 62.2 (C-6′), 54.9 (OCH_3), 54.5 (C-2′), 20.8, 20.7, 20.6 (3 × *C*H_3C=O) ppm. HRMS: calcd. for $C_{41}H_{44}NO_{15}$ $[M]^+$ 790.2711; found 790.2691.

Methyl 2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-gluco-pyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-manno-pyranoside (57): A mixture of disaccharide **56** (65 mg, 0.08 mmol) and hydrazine hydrate (0.15 g, 0.15 mL, 3.16 mmol, 40 equiv.) in EtOH (4 mL, 96%) was heated at reflux overnight (15 h). The reaction mixture was cooled to room temperature and the solvent was evaporated. The residue was dissolved in pyridine (4 mL) into which acetic anhydride (2 mL) was added. The mixture was stirred overnight (15 h) at room temperature, after which it was concentrated. The residue was diluted with CH_2Cl_2 (20 mL), washed with saturated $NaHCO_3$ (2 × 10 mL), dried, and concentrated. Column chromatography gave the title compound. Yield: 50 mg (90%). $[\alpha]_D$ = –12.0 (c = 0.33, CH_2Cl_2). ^{1}H NMR (600.13 MHz, $CDCl_3$, 25 °C): δ = 7.40–7.26 (m, 10 H, arom. H), 5.68 (dd, $J_{3',4'}$ = 9.2 Hz, 1 H, 3′-H), 5.63 (d, $J_{NHAc,2'}$ = 7.4 Hz, 1 H, N*H*Ac), 5.62 (s, 1 H, C*H*Ph), 5.15 (d, $J_{1',2'}$ = 8.4 Hz, 1 H, 1′-H), 5.02 (dd, $J_{4',5'}$ = 10.1 Hz, 1 H, 4′-H), 4.77 and 4.71 (each d, J = –11.6 Hz, each 1 H, CH_2Ph), 4.64 (d, $J_{1,2}$ = 1.7 Hz, 1 H, 1-H), 4.24 (dd, $J_{6a,6b}$ = –10.3 Hz, 1 H, 6a-H), 4.23 (dd, 1 H, 6′b-H), 4.19 (dd, $J_{6'a,6'b}$ = –12.3 Hz, 1 H, 6′a-H), 4.16 (dd, $J_{2,3}$ = 3.4 Hz, 1 H, 2-H), 4.09 (dd, $J_{4,5}$ = 9.4 Hz, 1 H, 4-H), 3.95 (dd, $J_{3,4}$ = 10.0 Hz, 1 H, 3-H), 3.80 (dd, 1 H, 6b-H), 3.763 (ddd, $J_{5',6'a}$ = 2.4 Hz, $J_{5',6'b}$ = 4.9 Hz, 1 H, 5′-H), 3.758 (ddd, $J_{5,6a}$ = 4.8 Hz, $J_{5,6b}$ = 10.4 Hz, 1 H, 5-H), 3.50 (ddd, $J_{2',3'}$ = 10.7 Hz, 2′-H), 3.36 (s, 3 H, OCH_3), 2.04, 2.03 2.02, 1.80 (each s, each 3 H, NHC=O*C*H_3 and 3 × CH_3C=O) ppm. ^{13}C NMR (150.90 MHz, $CDCl_3$, 25 °C): δ = 170.7, 170.6, 170.3, 169.6 (NH*C*=OCH_3 and 3 × CH_3*C*=O), 138.2–126.0 (arom. C), 101.5 (*C*HPh), 100.2 (C-1), 98.4 (C-1′), 78.7 (C-4), 74.4 (C-2), 74.4 (C-3), 72.6 (*C*H_2Ph), 71.9

(C-5), 71.2 (C-3′), 69.0 (C-4′), 68.9 (C-6), 63.9 (C-5′), 62.2 (C-6′), 55.4 (C-2′), 55.0 (OCH_3), 23.4, 20.7 (NHC=OCH_3 and 3 × CH_3C=O) ppm. HRMS: calcd. for $C_{35}H_{44}NO_{15}$ $[M + H]^+$ 701.2684; found 701.2706.

Methyl 2-Acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (58): Compound **57** (50 mg, 0.076 mmol) was taken up to dry MeOH/THF (3:1, 4 mL) and treated with *t*BuOK (16 mg, 0.015 mmol, 2 equiv.). After stirring at room temperature for 15 h, the solvent was evaporated, and the crude product was purified by column chromatography ($CHCl_3$/MeOH, 5:1) to yield the deacetylated compound. Yield: 37 mg (93%). $[\alpha]_D$ = –57.8 (*c* = 0.66, CH_2Cl_2). ^{1}H NMR (600.13 MHz, CD_3OD, 25 °C): δ = 7.49–7.23 (m, 10 H, arom. H), 5.63 (s, 1 H, C*H*Ph), 4.78 and 4.63 (each d, *J* = –12.1 Hz, each 1 H, CH_2Ph), 4.76 (d, $J_{1,2}$ = 1.7 Hz, 1 H, 1-H), 4.57 (d, $J_{1',2'}$ = 8.4 Hz, 1 H, 1′-H), 4.24 (dd, $J_{2,3}$ = 3.3 Hz, 1 H, 2-H), 4.17 (dd, $J_{6a,6b}$ = –10.1 Hz, 1 H, 6a-H), 4.09 (dd, $J_{4,5}$ = 9.4 Hz, 1 H, 4-H), 3.91 (dd, $J_{6'a,6'b}$ = –11.7 Hz, 1 H, 6′a-H), 3.86 (dd, $J_{3,4}$ = 10.1 Hz, 1 H, 3-H), 3.80 (dd, 1 H, 6b-H), 3.71 (dd, 1 H, 6′b-H), 3.69 (dd, $J_{2',3'}$ = 10.5 Hz, 1 H, 2′-H), 3.67 (ddd, $J_{5,6a}$ = 4.8 Hz, $J_{5,6b}$ = 10.4 Hz, 1 H, 5-H), 3.53 (dd, $J_{3',4'}$ = 8.9 Hz, 1 H, 3′-H), 3.37 (s, 3 H, O CH_3), 3.36 (dd, $J_{4',5'}$ = 9.8 Hz, 1 H 4′-H), 3.32 (ddd, $J_{5',6'a}$ = 2.3 Hz, $J_{5',6'b}$ = 5.8 Hz, 1 H, 5′-H), 1.98 (s, 3 H, NHC=OCH_3) ppm. ^{13}C NMR (150.90 MHz, CD_3OD, 25 °C): δ = 173.9 (NH*C*=OCH_3), 139.6–127.4 (arom. C), 103.0 (*C*HPh), 101.5 (C-1′), 100.8 (C-1), 79.3 (C-4), 78.2 (C-5′), 75.9 (C-2), 75.5 (C-3), 75.4 (C-3′), 72.1 (C-4′), 72.0 (*C*H_2Ph), 69.9 (C-6), 65.4 (C-5), 63.0 (C-6′), 57.6 (C-2′), 55.5 (OCH_3), 23.4 (NHC=OCH_3) ppm. HRMS: calcd. for $C_{29}H_{38}NO_{11}$ $[M + Na]^+$ 576.2444; found 576.2422.

General Procedure for Hydrogenolysis: Benzyl/benzylidene-protected di- or trisaccharide (1 wt.equiv.), Pd/C (wet, contains 50% water; 2.5 wt.equiv.) in dry MeOH was stirred at 3.45 bar of H_2 at room temperature. The mixture was filtered through a pad of Celite. Evaporation of the solvent provided the crude product.

β-D-Mannopyranosyl-(1→2)-D-mannopyranose (33): The reaction was carried out with compound **28** (25 mg, 0.032 mmol) and Pd/C (62.5 mg) in MeOH (3 mL) for 16 h. Crude product **33** (10 mg, 93%) was obtained and purified further by graphite solid-phase extraction as follows: A sample of mannobiose (1 mg) was dissolved in water (100 μL) and applied to a column of graphitized carbon (150 mg, Carbograph Extract-clean column, Alltech) conditioned with ethanol and water. The column was washed with water (8 mL), and the disaccharide was eluted with 20% aqueous acetonitrile (4 mL) and finally dried in a vacuum centrifuge. The α/β ratio of **33** in CD_3OD was approximately 3:1 at 20 °C. ^{1}H NMR (600.13 MHz, CD_3OD, 20 °C): δ = 5.19 (d, $J_{1,2}$ = 1.8 Hz, 1 H, 1-H), 4.64 (d, $J_{1',2'}$ = 1.0 Hz, 1 H, 1′-H), 4.01 (dd, $J_{2,3}$ = 3.3 Hz, 1 H, 2-H), 3.90 (dd, $J_{2',3'}$ = 3.2 Hz, 1 H, 2′-H), 3.87 (dd, $J_{6'a,6'b}$ = –12.1 Hz, 1 H, 6′a-H), 3.79 (dd, $J_{6a,6b}$ = –11.7 Hz, 1 H, 6a-H), 3.77 (dd, $J_{3,4}$ = 9.6 Hz, 1 H, 3-H), 3.73 (ddd, $J_{5,6a}$ = 2.4 Hz, $J_{5,6b}$ = 5.3 Hz, 1 H, 5-H), 3.72 (dd, 1 H, 6b-H), 3.68 (dd, 1 H, 6′b-H), 3.64 (dd, $J_{4,5}$ = 9.6 Hz, 1 H, 4-H), 3.53 (dd, $J_{4',5'}$ = 9.7 Hz, 1 H, 4′-H), 3.46 (dd, $J_{3',4'}$ = 9.5 Hz, 1 H, 3′-H), 3.23 (ddd, $J_{5',6'a}$ = 2.3 Hz, $J_{5',6'b}$ = 6.5 Hz, 1 H, 5′-H) ppm. ^{13}C NMR (150.90 MHz, CD_3OD, 20 °C): δ = 100.0 (C-1′), 93.3 (C-1), 79.5 (C-2), 78.6 (C-5′), 75.1 (C-3′), 74.1 (C-5), 72.6 (C-2′), 71.7 (C-3), 69.1 (C-4), 68.5 (C-4′), 62.9 (C-6′), 62.7 (C-6) ppm. HRMS (ESI-TOF): calcd. for $C_{36}H_{66}O_{33}Na$ $[3M + Na]^+$ 1049.3384; found 1049.3357.

Methyl β-D-Mannopyranosyl-(1→2)-α-D-mannopyranoside (34): The reaction was carried out with **29** (60 mg, 0.084 mmol) and Pd/C (150 mg) in MeOH (6 mL) for 19 h. Yield: 28 mg (93%). The ^{13}C NMR spectroscopic data for **34** in D_2O was reported earlier.[37] $[\alpha]_D$ = –30.0 (*c* = 1.0, MeOH). ^{1}H NMR (600.13 MHz, CD_3OD, 25 °C): δ = 4.78 (d, $J_{1,2}$ = 1.7 Hz, 1 H, 1-H), 4.65 (d, $J_{1',2'}$ = 1.0 Hz, 1 H, 1′-H), 4.03 (dd, $J_{2,3}$ = 3.5 Hz, 1 H, 2-H), 3.89 (dd, $J_{2',3'}$ = 3.2 Hz, 1 H, 2′-H), 3.87 (dd, $J_{6'a,6'b}$ = –12.0 Hz, 1 H, 6′a-H), 3.83 (dd, $J_{6a,6b}$ = –11.8 Hz, 1 H, 6a-H), 3.70 (dd, 1 H, 6b-H), 3.68 (dd, 1 H, 6′b-H), 3.67 (dd, $J_{3,4}$ = 9.6 Hz, 1 H, 3-H), 3.61 (dd, $J_{4,5}$ = 9.8 Hz, 1 H, 4-H), 3.53 (dd, $J_{4',5'}$ = 9.7 Hz, 1 H, 4′-H), 3.48 (ddd, $J_{5,6a}$ = 2.3 Hz, $J_{5,6b}$ = 5.8 Hz, 1 H, 5-H), 3.45 (dd, $J_{3',4'}$ = 9.4 Hz, 1 H, 3′-H), 3.39 (s, 3 H, OCH_3), 3.23 (ddd, $J_{5',6'a}$ = 2.3 Hz, $J_{5',6'b}$ = 6.6 Hz, 1 H, 5′-H) ppm. ^{13}C NMR (150.90 MHz, CD_3OD, 25 °C): δ = 98.7 (C-1), 98.5 (C-1′), 77.2 (C-5′), 77.0 (C-2′), 73.7 (C-3′), 73.2 (C-5), 71.2 (C-2′), 70.7 (C-3), 67.6 (C-4), 67.1 (C-4′), 61.5 (C-6′), 61.2 (C-6), 53.8 (OCH_3) ppm. HRMS: calcd. for $C_{39}H_{72}O_{33}Na$ $[3M + Na]^+$ 1091.3854; found 1091.3820.

Cyclohexyl β-D-Mannopyranosyl-(1→2)-α-D-mannopyranoside (35): The reaction was carried out with **31** (22.2 mg, 0.029 mmol) and Pd/C (43 mg) in MeOH/EtOAc (9:1, 2.2 mL) for 18.5 h. Yield: 12.1 mg (100%). $[\alpha]_D$ = +0.5 (*c* = 1.0, MeOH). ^{1}H NMR (600.13 MHz, CD_3OD, 25 °C): δ = 5.04 (d, $J_{1,2}$ = 1.8 Hz, 1 H, 1-H), 4.66 (d, $J_{1',2'}$ = 1.0 Hz, 1 H, 1′-H), 3.98 (dd, $J_{2,3}$ = 3.4 Hz, 1 H, 2-H), 3.90 (dd, $J_{2',3'}$ = 3.2 Hz, 1 H, 2′-H), 3.87 (dd, $J_{6'a,6'b}$ = –12.0 Hz, 1 H, 6′a-H), 3.80 (dd, $J_{6a,6b}$ = –11.8 Hz, 1 H, 6a-H), 3.73 (dd, $J_{3,4}$ = 9.6 Hz, 1 H, 3-H), 3.70 (dd, 1 H, 6b-H), 3.68 (dd, 1 H, 6′b-H), 3.67 (m, 1 H, OC*H*C_5H_{10}), 3.63 (dd, $J_{4,5}$ = 9.8 Hz, 1 H, 4-H), 3.60 (ddd, $J_{5,6a}$ = 2.4 Hz, $J_{5,6b}$ = 5.8 Hz, 1 H, 5-H), 3.54 (dd, $J_{4',5'}$ = 9.7 Hz, 1 H, 4′-H), 3.47 (dd, $J_{3',4'}$ = 9.4 Hz, 1 H, 3′-H), 3.24 (ddd, $J_{5',6'a}$ = 2.3 Hz, $J_{5',6'b}$ = 6.4 Hz, 1 H, 5′-H), 1.98–1.82 (m, 2 H, OCHC$_5H_{10}$), 1.80–1.70 (m, 2 H, OCHC$_5H_{10}$), 1.55–1.20 (m, 6 H, OCHC$_5H_{10}$) ppm. ^{13}C NMR (150.90 MHz, CD_3OD, 25 °C): δ = 100.0 (C-1′), 97.1 (C-1), 79.2 (C-2), 78.6 (C-5′), 76.4 (O*C*HC$_5H_{10}$), 75.1 (C-3′), 74.8 (C-5), 72.6 (C-2′), 72.1 (C-3), 69.1 (C-4), 68.5 (C-4′), 62.9 (C-6′), 62.7 (C-6), 34.5, 32.6, 26.8, 25.2, 25.0 (OCH*C*$_5H_{10}$) ppm. HRMS: calcd. for $C_{18}H_{32}O_{11}Na$ $[M + Na]^+$ 447.1837; found 447.1843.

Methyl β-D-Mannopyranosyl-(1→2)-β-D-mannopyranoside (36): The reaction was carried out with **32** (30 mg, 0.042 mmol) and Pd/C (75 mg) in MeOH (3 mL) for 19 h. Yield: 14 mg (94%). $[\alpha]_D$ = –70.0 (*c* = 1.0, MeOH). ^{1}H NMR (600.13 MHz, CD_3OD, 25 °C): δ = 4.73 (d, $J_{1',2'}$ = 0.86 Hz, 1 H, 1′-H), 4.48 (d, $J_{1,2}$ = 0.80 Hz, 1 H, 1′-H), 4.12 (dd, $J_{2,3}$ = 3.4 Hz, 1 H, 2-H), 3.96 (dd, $J_{2',3'}$ = 3.2 Hz, 1 H, 2′-H), 3.89 (dd, $J_{6a,6b}$ = –11.8 Hz, 1 H, 6a-H), 3.86 (dd, $J_{6'a,6'b}$ = –12.0 Hz, 1 H, 6′a-H), 3.71 (dd, 1 H, 6b-H), 3.67 (dd, 1 H, 6′b-H), 3.52 (dd, $J_{4,5}$ = 9.7 Hz, 1 H, 4-H), 3.50 (dd, $J_{4',5'}$ = 9.7 Hz, 1 H, 4′-H), 3.46 (dd, $J_{3,4}$ = 9.6 Hz, 1 H, 3-H), 3.40 (dd, $J_{3',4'}$ = 9.4 Hz, 1 H, 3′-H), 3.52 (s, 3 H, OCH_3), 3.21 (ddd, $J_{5,6a}$ = 2.3 Hz, $J_{5,6b}$ = 6.0 Hz, 5-H), 3.18 (ddd, $J_{5',6'a}$ = 2.3 Hz, $J_{5',6'b}$ = 6.6 Hz, 5′-H) ppm. ^{13}C NMR (150.90 MHz, CD_3OD, 25 °C): δ = 103.3 (C-1), 102.1 (C-1′), 78.8 (C-2), 78.62, (C-5′), 78.60 (C-5), 75.2 (C-3′), 74.7 (C-3), 72.1 (C-2′), 69.1 (C-4), 68.6 (C-4′), 63.0 (C-6′), 62.8 (C-6), 57.6 (OCH_3) ppm. HRMS: calcd. for $C_{39}H_{72}O_{33}Na$ $[3M + Na]^+$ 1091.3853; found 1091.3825.

β-D-Mannopyranosyl-(1→2)-β-D-mannopyranosyl-(1→2)-D-mannopyranose (41): The reaction was carried out with **39** (40 mg, 0.035 mmol) and Pd/C (100 mg) in MeOH (2.5 mL) for 21 h. Crude yield: 17 mg (96%). Compound **41** was further purified by HPLC (Hypercarb 5 μm, 4×125-mm). The column was eluted isocratically with 5% acetonitrile in water for 1 min and with a gradient from 5 to 60% acetonitrile over the course of 19 min at a flow rate of 0.7 mL min^{-1}. The α/β ratio of **41** in CD_3OD was approximately 3:1 at 20 °C. Data for the α-anomer: ^{1}H NMR (600.13 MHz, CD_3OD, 20 °C): δ = 5.18 (d, $J_{1,2}$ = 1.9 Hz, 1 H, 1-H), 4.86 (d, $J_{1'',2''}$ = 1.1 Hz, 1 H, 1′′-H), 4.72 (d, $J_{1',2'}$ = 0.80 Hz,

1 H, 1′-H), 4.13 (dd, $J_{2',3'}$ = 3.6 Hz, 1 H, 2′-H), 4.07 (dd, $J_{2'',3''}$ = 2.78 Hz, 1 H, 2′′-H), 3.97 (dd, $J_{2,3}$ = 3.2 Hz, 1 H, 2-H), 3.87 (dd, $J_{6'a,6'b}$ = –11.8 Hz, 1 H, 6′a-H), 3.86 (dd, $J_{6''a,6''b}$ = –12.0 Hz, 1 H, 6′′a-H), 3.81 (dd, $J_{3,4}$ = 9.6 Hz, 1 H, 3-H), 3.78 (dd, $J_{6a,6b}$ = –11.6 Hz, 1 H, 6a-H), 3.73 (dd, 1 H, 6b-H), 3.71 (dd, 1 H, 6′b-H), 3.70 (ddd, $J_{5,6a}$ = 2.3 Hz, $J_{5,6b}$ = 4.7 Hz, 5-H), 3.66 (dd, 1 H, 6′′b-H), 3.57 (dd, $J_{4,5}$ = 9.9 Hz, 1 H, 4-H), 3.56 (dd, $J_{4',5'}$ = 9.5 Hz, 1 H, 4′-H), 3.50 (dd, $J_{4'',5''}$ = 9.5 Hz, 1 H, 4′′-H), 3.49 (dd, $J_{3'',4''}$ = 9.6 Hz, 1 H, 3′′-H), 3.48 (dd, $J_{3',4'}$ = 9.7 Hz, 1 H, 3′-H), 3.236 (ddd, $J_{5',6'a}$ = 2.3 Hz, $J_{5',6'b}$ = 5.8 Hz, 5′-H), 3.235 (ddd, $J_{5'',6''a}$ = 2.3 Hz, $J_{5'',6''b}$ = 6.5 Hz, 5′′-H) ppm. ^{13}C NMR (150.90 MHz, CD_3OD, 20 °C): δ = 102.2 (C-1′′), 100.8 (C-1′), 93.7 (C-1), 80.8 (C-2), 79.3 (C-2′), 78.44, (C-5′′), 78.40 (C-5′), 75.0 (C-3′′), 74.4 (C-3′), 74.1 (C-5), 72.1 (C-2′′), 71.3 (C-3), 69.5 (C-4), 68.66 (C-4′′), 68.62 (C-4′), 63.1 (C-6′′), 62.6 (C-6), 62.4 (C-6′) ppm. Data for the β-anomer: ^{1}H NMR (600.13 MHz, CD_3OD, 20 °C): δ = 4.94 (d, $J_{1'',2''}$ = 0.96 Hz, 1 H, 1′′-H), 4.83 (d, $J_{1,2}$ = 0.87 Hz, 1 H, 1-H), 4.80 (d, $J_{1',2'}$ = 0.85 Hz, 1 H, 1′-H), 4.33 (dd, $J_{2',3'}$ = 3.4 Hz, 1 H, 2′-H), 4.05 (dd, $J_{2'',3''}$ = 3.2 Hz, 1 H, 2′′-H), 4.02 (dd, $J_{2,3}$ = 3.5 Hz, 1 H, 2-H), 3.863 (dd, $J_{6'a,6'b}$ = –11.7 Hz, 1 H, 6′a-H), 3.861 (dd, $J_{6''a,6''b}$ = –12.0 Hz, 1 H, 6′′a-H), 3.85 (dd, $J_{6a,6b}$ = –12.2 Hz, 1 H, 6a-H), 3.71 (dd, 1 H, 6′b-H), 3.67 (dd, 1 H, 6b-H), 3.66 (dd, 1 H, 6′′b-H), 3.54 (dd, $J_{4',5'}$ = 9.7 Hz, 1 H, 4′-H), 3.488 (dd, $J_{3'',4''}$ = 9.5 Hz, 1 H, 3′′-H), 3.487 (dd, $J_{4'',5''}$ = 9.5 Hz, 1 H, 4′′-H), 3.48 (dd, $J_{3,4}$ = 9.4 Hz, 1 H, 3-H), 3.45 (dd, $J_{3',4'}$ = 9.6 Hz, 1 H, 3′-H), 3.43 (dd, $J_{4,5}$ = 9.4 Hz, 1 H, 4-H), 3.27 (ddd, $J_{5'',6''a}$ = 2.4 Hz, $J_{5'',6''b}$ = 6.4 Hz, 1 H, 5′′-H), 3.21 (ddd, $J_{5',6'a}$ = 2.4 Hz, $J_{5',6'b}$ = 6.0 Hz, 1 H, 5′-H), 3.20 (ddd, $J_{5,6a}$ = 2.1 Hz, $J_{5,6b}$ = 5.1 Hz, 1 H, 5-H) ppm. ^{13}C NMR (150.90 MHz, CD_3OD, 20 °C): δ = 102.8 (C-1′), 102.2 (C-1′′), 95.6 (C-1), 81.4 (C-2), 78.9 (C-2′), 78.5 (C-5), 78.3 (C-5′ and C-5′′), 75.1 (C-3′), 74.5 (C-3′′), 74.4 (C-3), 72.2 (C-2′′), 69.2 (C-4), 68.7 (C-4′ and C-4′′), 63.1 (C-6′′), 62.8 (C-6), 62.5 (C-6′) ppm. HRMS: calcd. for $C_{18}H_{32}O_{16}Na$ [M + Na]$^+$ 527.1583; found 527.1581. HRMS: calcd. for $C_{18}H_{32}O_{16}K$ [M + K]$^+$ 543.1322; found 543.1317.

Methyl β-D-Mannopyranosyl-(1→2)-β-D-mannopyranosyl-(1→2)-α-D-mannopyranoside (42): The reaction was carried out with compound **40** (25 mg, 0.024 mmol) and Pd/C (63 mg) in MeOH (2.5 mL) for 24 h. Yield: 12 mg (97%). $[\alpha]_D$ = –25.0 (c = 1.0, MeOH). ^{1}H NMR (600.13 MHz, CD_3OD, 25 °C): δ = 4.85 (d, $J_{1'',2''}$ = 0.95 Hz, 1 H, 1′′-H), 4.77 (d, $J_{1,2}$ = 1.8 Hz, 1 H, 1-H), 4.72 (d, $J_{1',2'}$ = 0.90 Hz, 1 H, 1′-H), 4.13 (dd, $J_{2',3'}$ = 3.5 Hz, 1 H, 2′-H), 4.07 (dd, $J_{2'',3''}$ = 2.9 Hz, 1 H, 2′′-H), 3.98 (dd, $J_{2,3}$ = 3.2 Hz, 1 H, 2-H), 3.87 (dd, $J_{6'a,6'b}$ = –11.8 Hz, 1 H, 6′a-H), 3.86 (dd, $J_{6''a,6''b}$ = –12.0 Hz, 1 H, 6′′a-H), 3.82 (dd, $J_{6a,6b}$ = –11.9 Hz, 1 H, 6a-H), 3.718 (dd, 1 H, 6b-H), 3.715 (dd, 1 H, 6′b-H), 3.70 (dd, $J_{3,4}$ = 9.5 Hz, 1 H, 3-H), 3.68 (dd, 1 H, 6′′b-H), 3.56 (dd, $J_{4'',5''}$ = 9.6 Hz, 1 H, 4′′-H), 3.55 (dd, $J_{4',5'}$ = 9.6 Hz, 1 H, 4′-H), 3.51 (dd, $J_{4,5}$ = 9.1 Hz, 1 H, 4-H), 3.49 (dd, $J_{3'',4''}$ = 9.6 Hz, 1 H, 3′′-H), 3.48 (dd, $J_{3',4'}$ = 9.8 Hz, 1 H, 3′-H), 3.46 (ddd, $J_{5,6a}$ = 2.3 Hz, $J_{5,6b}$ = 5.0 Hz, 1 H, 5-H), 3.39 (s, 3 H, OCH_3), 3.24 (ddd, $J_{5',6'a}$ = 2.3 Hz, $J_{5',6'b}$ = 5.8 Hz, 1 H, 5′-H), 3.23 (ddd, $J_{5'',6''a}$ = 2.3 Hz, $J_{5'',6''b}$ = 6.5 Hz, 1 H, 5′′-H) ppm. ^{13}C NMR (150.90 MHz, CD_3OD, 25 °C): δ = 102.2 (C-1′′), 100.8 (C-1′), 100.5 (C-1), 79.8 (C-2), 79.3 (C-2′), 78.4 (C-5′ and C-5′′), 75.1 (C-3′′), 74.6 (C-5), 74.4 (C-3′), 72.1 (C-2′′), 71.6 (C-3), 69.2 (C-4′), 68.6 (C-4), 68.6 (C-4′′), 63.1 (C-6′′), 62.5 (C-6), 62.4 (C-6′), 55.3 (OCH_3) ppm. HRMS: calcd. for $C_{19}H_{34}O_{16}Na$ [M + Na]$^+$ 541.1745; found 541.1789.

α-D-Mannopyranosyl Phosphate (46): The reaction was carried out as outlined in the general procedure for hydrogenolysis. Compound **45** (30 mg, 0.042 mmol) and Pd/C (75 mg) in MeOH (3 mL) for 20 h. Yield: 10.4 mg (95%). $[\alpha]_D$ = +39.0 (c = 1.0, H_2O). ^{1}H NMR (500.13 MHz, D_2O 25 °C): δ = 5.32 (dd, $J_{1,2}$ = 2.0 Hz, $^3J_{P,1\text{-}H}$ = 7.7 Hz, 1 H, 1-H), 3.87 (dd, $J_{2,3}$ = 3.4 Hz, $^4J_{P,2\text{-}H}$ = 0.51 Hz, 1 H, 2-H), 3.80 (dd, $J_{3,4}$ = 9.9 Hz, 1 H, 3-H), 3.77 (dd, $J_{6a,6b}$ = –12.3 Hz, 1 H, 6a-H), 3.72 (ddd, $J_{5,6a}$ = 2.3 Hz, $J_{5,6b}$ = 5.8 Hz, 1 H, 5-H), 3.66 (dd, 1 H, 6b-H), 3.57 (dd, $J_{4,5}$ = 9.9 Hz, 1 H, 4-H) ppm. ^{13}C NMR (125.77 MHz, D_2O, 30 °C): δ = 96.6 ($^2J_{P,C\text{-}1}$ = 5.5 Hz, C-1), 74.1 (C-5), 71.0 ($^3J_{P,C\text{-}2}$ = 8.9 Hz, C-2), 70.4 (C-3), 67.0 (C-4), 61.4 (C-6) ppm. ^{31}P NMR (202.47 MHz, D_2O, 30 °C): δ = –2.4 ppm. HRMS: calcd. for $C_6H_{13}O_9P$ [M]$^+$ 260.0297; found 260.0289.

β-D-Mannopyranosyl-(1→2)-α-D-mannopyranosyl Phosphate (50): The reaction was carried out as outlined in the general procedure for hydrogenolysis. Compound **49** (35 mg, 0.033 mmol) and Pd/C (87.5 mg) in MeOH (3.5 mL) for 18 h. Yield: 14 mg (70%). $[\alpha]_D$ = +30.0 (c = 0.5, H_2O). ^{1}H NMR (600.13 MHz, D_2O, 25 °C): δ = 5.41 (dd, $J_{1,2}$ = 2.0 Hz, $^3J_{P,1\text{-}H}$ = 7.7 Hz, 1 H, 1-H), 4.70 (d, $J_{1',2'}$ = 0.98 Hz, 1 H, 1′-H), 4.06 (dd, $J_{2,3}$ = 3.4 Hz, 1 H, 2-H), 3.93 (dd, $J_{2',3'}$ = 3.3 Hz, 1 H, 2′-H), 3.793 (dd, $J_{3,4}$ = 9.9 Hz, 1 H, 3-H), 3.790 (dd, $J_{6'a,6'b}$ = –12.3 Hz, 1 H, 6′a-H), 3.73 (dd, $J_{6a,6b}$ = –12.4 Hz, 1 H, 6a-H), 3.69 (ddd, $J_{5,6a}$ = 2.3 Hz, $J_{5,6b}$ = 5.1 Hz, 1 H, 5-H), 3.67 (dd, 1 H, 6b-H), 3.61 (dd, $J_{4,5}$ = 10.0 Hz, 1 H, 4-H), 3.60 (dd, 1 H, 6′b-H), 3.53 (dd, $J_{3',4'}$ = 9.6 Hz, 1 H, 3′-H), 3.44 (dd, $J_{4',5'}$ = 10.0 Hz, 1 H, 4′-H), 3.27 (ddd, $J_{5',6'a}$ = 2.3 Hz, $J_{5',6'b}$ = 6.6 Hz, 1 H, 5′-H) ppm. ^{13}C NMR (150.90 MHz, D_2O, 25 °C): δ = 98.6 (C-1′), 93.8 ($^2J_{P,C\text{-}1}$ = 5.2 Hz, C-1), 77.6 ($^3J_{P,C\text{-}2}$ = 8.9 Hz, C-2), 76.3 (C-5′), 73.6 (C-5), 72.7 (C-3′), 70.7 (C-2′), 69.3 (C-3), 66.6 (C-4 and C-4′), 60.9 (C-6′), 60.4 (C-6) ppm. ^{31}P NMR (242.94 MHz, D_2O, 25 °C): δ = –2.45 ppm. HRMS: calcd. for $C_{12}H_{23}NaO_{14}P$ [M + Na]$^+$ 445.0718; found 445.0712.

Methyl β-D-Glucopyranosyl-(1→2)-α-D-mannopyranoside (55): The reaction was carried out as outlined in the general procedure for hydrogenolysis. Compound **54** (40 mg, 0.05 mmol) and Pd/C (100 mg) in MeOH (4 mL) for 19 h. Yield: 16.5 mg (93%). $[\alpha]_D$ = +8.5 (c = 1.0, MeOH). ^{1}H NMR (600.13 MHz, CD_3OD, 25 °C): δ = 4.77 (d, $J_{1,2}$ = 1.7 Hz, 1 H, 1-H), 4.32 (d, $J_{1',2'}$ = 8.0 Hz, 1 H, 1′-H), 3.94 (dd, $J_{2,3}$ = 3.4 Hz, 1 H, 2-H), 3.85 (dd, $J_{6'a,6'b}$ = –11.8 Hz, 1 H, 6′a-H), 3.79 (dd, $J_{6a,6b}$ = –11.9 Hz, 1 H, 6a-H), 3.78 (dd, 1 H, 6b-H), 3.69 (dd, $J_{3,4}$ = 9.7 Hz, 1 H, 3-H), 3.652 (dd, 1 H, 6′b-H), 3.651 (dd, $J_{4,5}$ = 9.6 Hz, 1 H, 4-H), 3.47 (ddd, $J_{5,6a}$ = 2.5 Hz, $J_{5,6b}$ = 4.7 Hz, 1 H, 5-H), 3.38 (s, 3 H, OCH_3), 3.36 (dd, $J_{3',4'}$ = 9.5 Hz, 1 H, 3′-H), 3.30 (dd, $J_{4',5'}$ = 9.0 Hz, 1 H, 4′-H), 3.29 (ddd, $J_{5',6'a}$ = 2.1 Hz, $J_{5',6'b}$ = 5.4 Hz, 1 H, 5′-H), 3.25 (dd, $J_{2',3'}$ = 9.4 Hz, 1 H, 2′-H) ppm. ^{13}C NMR (150.90 MHz, CD_3OD, 25 °C): δ = 104.1 (C-1′), 100.9 (C-1), 79.5 (C-2), 78.2 (C-5′), 77.6 (C-3′), 74.37 (C-5), 74.35 (C-2′), 71.8 (C-3), 71.4 (C-4′), 68.6 (C-4), 62.5 (C-6′), 62.1 (C-6), 55.2 (OCH_3) ppm. HRMS: calcd. for $C_{39}H_{72}O_{33}Na$ [3M + Na]$^+$ 1091.3854; found 1091.3861.

Methyl β-D-Glucopyranosyl-(1→2)-β-D-mannopyranosyl-(1→2)-α-D-mannopyranoside (62): The reaction was carried out as outlined in the general procedure for hydrogenolysis. Compound **61** (50 mg, 0.044 mmol) and Pd/C (125 mg) in MeOH (5 mL) for 24 h. Yield: 21 mg (92%). $[\alpha]_D$ = –32.0 (c = 1.0, MeOH). ^{1}H NMR (600.13 MHz, CD_3OD, 25 °C): δ = 4.78 (d, $J_{1,2}$ = 1.7 Hz, 1 H, 1-H), 4.77 (d, $J_{1',2'}$ = 0.71 Hz, 1 H, 1′-H), 4.63 (d, $J_{1'',2''}$ = 7.7 Hz, 1 H, 1′′-H), 4.10 (dd, $J_{2',3'}$ = 3.3 Hz, 1 H, 2′-H), 4.00 (dd, $J_{2,3}$ = 3.2 Hz, 1 H, 2-H), 3.85 (dd, $J_{6''a,6''b}$ = –11.9 Hz, 1 H, 6′′a-H), 3.824 (dd, $J_{6a,6b}$ = –11.8 Hz, 1 H, 6a-H), 3.824 (dd, $J_{6'a,6'b}$ = –11.7 Hz, 1 H, 6′a-H), 3.80 (dd, 1 H, 6′b-H), 3.76 (dd, $J_{4,5}$ = 9.9 Hz, 1 H, 4-H), 3.73 (dd, 1 H, 6b-H), 3.67 (dd, $J_{3,4}$ = 9.6 Hz, 1 H, 3-H), 3.66 (dd, 1 H, 6′′b-H), 3.62 (dd, $J_{4',5'}$ = 9.5 Hz, 1 H, 4′-H), 3.51 (dd, $J_{3',4'}$ = 9.6 Hz, 1 H, 3′-H), 3.46 (ddd, $J_{5,6a}$ = 2.3 Hz, $J_{5,6b}$ = 5.1 Hz, 1 H, 5-H), 3.41 (dd, $J_{3'',4''}$ = 9.9 Hz, 1 H, 3′′-H), 3.39 (s, 3 H, OCH_3), 3.295 (dd, $J_{4'',5''}$ = 9.4 Hz, 1 H, 4′′-H), 3.288 (ddd, $J_{5'',6''a}$

= 2.0 Hz, $J_{5'',6''a}$ = 5.4 Hz, 1 H, 5″-H), 3.28 (dd, $J_{2'',3'}$ = 9.3 Hz, 1 H, 2″-H), 3.22 (ddd, $J_{5',6'a}$ = 2.2 Hz, $J_{5',6'b}$ = 4.5 Hz, 1 H, 5′-H) ppm. ^{13}C NMR (150.90 MHz, CD_3OD, 25 °C): δ = 104.8 (C-1″), 99.8 (C-1), 99.7 (C-1′), 79.3 (C-2′), 78.1 (C-2 and C-5′), 78.0 (C-5″), 77.7 (C-3″), 75.1 (C-2″), 74.5 (C-5), 74.0 (C-3′), 71.8 (C-3), 71.5 (C-4″), 68.7 (C-4), 68.0 (C-4′), 62.6 (C-6), 62.5 (C-6″), 61.6 (C-6′), 55.3 (OCH_3) ppm. HRMS: calcd. for $C_{19}H_{34}O_{16}Na$ [M + Na]$^+$ 541.1744; found 541.1715.

Methyl 2-Acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-α-D-mannopyranoside (59):[49] The reaction was carried out as outlined in the general procedure for hydrogenolysis. Compound **58** (36 mg, 0.064 mmol) and Pd/C (72 mg, 2 wt. equiv.) in MeOH (3 mL) for 6 h. Yield: 24 mg (94%). $[\alpha]_D$ = –4.6 (c = 0.77, MeOH); ref.[49] $[\alpha]_D^{20}$ = +2.2 (c = 1.63, H_2O). ^{1}H NMR (600.13 MHz, CD_3OD, 25 °C): δ = 4.67 (d, $J_{1,2}$ = 1.7 Hz, 1 H, 1-H), 4.44 (d, $J_{1',2'}$ = 8.4 Hz, 1 H, 1′-H), 3.90 (dd, $J_{2,3}$ = 3.4 Hz, 1 H, 2-H), 3.85 (dd, $J_{6'a,6'b}$ = –12.0 Hz, 1 H, 6′a-H), 3.83 (dd, $J_{6a,6b}$ = –11.8 Hz, 6a-H), 3.67 (dd, 1 H, 6′b-H), 3.65 (dd, $J_{3,4}$ = 9.6 Hz, 1 H, 3-H), 3.63 (dd, $J_{2',3'}$ = 10.1 Hz, 1 H, 2′-H), 3.62 (dd, 1 H, 6b-H), 3.50 (dd, $J_{4,5}$ = 9.8 Hz, 1 H, 4-H), 3.46 (dd, $J_{4',5'}$ = 10.4 Hz, 1 H, 4′-H), 3.45 (ddd, $J_{5,6a}$ = 2.3 Hz, $J_{5,6b}$ = 6.6 Hz, 1 H, 5-H), 3.38 (s, 3 H, OCH_3), 3.32 (dd, $J_{3',4'}$ = 8.7 Hz, 1 H, 3′-H), 3.27 (ddd, $J_{5',6'a}$ = 2.3 Hz, $J_{5',6'b}$ = 5.7 Hz, 1 H, 5′-H), 2.00 (s, 3 H, NHC=OCH_3) ppm. ^{13}C NMR (150.90 MHz, CD_3OD, 25 °C): δ = 174.4 (NHC=OCH_3), 101.7 (C-1′), 99.9 (C-1), 78.8 (C-2), 78.1 (C-5′), 75.4 (C-4′), 74.8 (C-5), 72.0 (C-3′), 71.7 (C-3), 69.1 (C-4), 63.4 (C-6), 62.6 (C-6′), 57.3 (C-2′), 55.3 (OCH_3), 23.3 (NHC=OCH_3) ppm. HRMS: calcd. for $C_{15}H_{27}NO_{11}Na$ [M + Na]$^+$ 420.1476; found 420.1456.

Supporting Information (see footnote on the first page of this article): Copies of ^{1}H, ^{13}C, and/or ^{31}P NMR spectra of selected, deprotected final products (**33**–**36**, **41**, **42**, **46**, **50**, **55**, **59**, and **62**).

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