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Stereocontrolled Synthesis of D- and L-β-Rhamnopyranosides with 4-*O*-6-*S*-α-Cyanobenzylidene-Protected 6-Thiorhamnopyranosyl Thioglycosides

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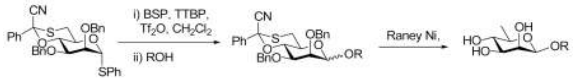
Abstract

The synthesis of both enantiomers of a 4-*O*-6-*S*-α-cyanobenzylidene-protected 6-thio-rhamnopyranosyl thioglycoside is described starting from D-mannnose and L-arabinose derivatives for the D- and L-series, respectively. This donor is effective in the preparation of the corresponding β-glycosides using the 1-benzenesulfinyl piperidine/trifluoromethanesulfonic anhydride protocol. Following desulfurization and concomitant debenzylation with Raney nickel the so-formed 6-thio-β-mannosides are converted in high yield to the β-rhamnopyranosides.



Introduction

The 4,6-*O*-benzylidene-directed β-mannosylation reaction has provided a practical, convenient solution to the long-standing problem of the sterecontrolled formation of the β-mannopyranosides.[1] The β-rhamnopyranosides, the 6-deoxy congeners of the β-mannopyranosides, remain problematic due to their 6-deoxy nature. Mechanistic considerations[2] led to the study of a series of L-rhamnopyranosyl donors carrying strongly electron-withdrawing groups on O2,[3] and also to the investigation of a series of 6-mono-, di-, and tri-fluororhamnopyranosyl donors, with good success for coupling to more reactive alcohols but only limited selectivity for the less reactive, carbohydrate-based acceptor alcohols.[4] In the L-series the Ito group recently has provided a practical solution to this problem through their adaptation[5] of the Hindsgaul intramolecular aglycone delivery method,[6] but the method is not readily extended to the D-series owing to the very limited availability of D-rhamnose other than through synthesis. Accordingly, in the D-series we have developed first and second generation methods based on the use of 4,6-*O*-acetal protected mannopyranosyl donors followed by reductive radical fragmentation reactions leading directly to the β-D-rhamnopyranosides.[7] Although we have successfully applied this type of methodology to the synthesis of a β-(1→3)-rhamnotetraose and other β-rhamnoside and 6-deoxy-β-mannoheptoside-containing oligosaccharides,[8] its reliance on a temperature sensitive radical fragmentation reaction is likely to preclude its widespread applicability. Here, we describe our investigations into the synthesis, glycosylation, and subsequent desulfurization of a set of 4-*O*-6-*S*-cyclic monothioacetals of 6-thiomannopyranose in both the D- and L-series.[9]

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Results and Discussion

In a seminal contribution[10] Bols and coworkers revealed the disarming effect of 4,6-*O*-benzylidene groups on glycosyl donors to be due to a combination of a torsional effect, as originally postulated by the Fraser-Reid group for the 4-pentenyl 4,6-*O*-benzylidene-glucopyranosides,[11] and, more importantly, the locking of the O5-C5-C6-O6 in the antiperiplanar conformation (*tg* conformation) thereby maximizing the electron-withdrawing effect of O6. In line with this rational a 4,7-*O*-alkylidene protected D-glycero-D-mannoheposyl donor studied in this laboratory was found to be lacking in selectivity owing to the greater conformational mobility of the 7-membered system which mitigates any effects based on changes in torsional strain and precluded the adoption of the *tg* conformation about O5-C5-C6-O6.[8c] On this basis, and taking into account the lower electronegativity of sulfur compared to oxygen and the greater C-S bond length it was by no means clear at the onset of this work that a 4-*O*-6-*S*-acetal protected 6-thiomannopyranosyl donor would exhibit the requisite β-selectivity. Furthermore, our ability to activate a thioglycoside selectively in the presence of an oxathiane ring was open to question.

We began with the synthesis of a simple benzylidene monothioacetal **3**, employing the thio-Mitsunobu reaction[12] to access the 6-thio system from a suitably protected D-mannopyranoside as set out in Scheme 1. In anticipation of the inadequacy of this simple system, a cyanoacetal **4** was also introduced through a two-step, orthoester exchange, cyanation protocol (Scheme 1). The cyano group in donor **4** was anticipated to improve selectivity on the basis of its electron-withdrawing ability which was predicated to counteract the expected detrimental effect of the replacement of O6 by a sulfur atom. In addition we anticipated that the electron-withdrawing cyano group would deactivate the oxathiane ring system toward the promoter employed to bring about glycosylation. The equatorial location of the phenyl substituent on the oxathiane ring in **3** was established by NOE correlations between the acetal hydrogen and H's 4 and 6_{ax} of the pyranose ring. The acetal hydrogen in **3** exhibits a chemical shift in $CDCl_3$ somewhat downfield from that found in the more common benzylidene acetals (dioxanes) but this is in keeping with other 1,3-oxathianes and is considered to be the result of the reduced reverse Perlin effect of the ring sulfur.[13] The stereochemistry of the cyanoacetal moiety in **4** is assigned based on analogy with earlier cyanoacetals prepared in this laboratory, which were assigned rigorously by X-ray crystallography,[7b] and is the result of the minimal steric bulk of the cyano group in combination with the role of the anomeric effect in the formation of this derivative.

Coupling reactions with **3**, carried by means of the 1-benzenesulfinylpiperidine (BSP)/trifluoromethanesulfonic anhydride preactivation protocol[1c] in the presence of the hindered base 2,4,6-tri-*tert*-butylpyrimidine (TTBP)[14] were both complex and difficult to reproduce owing to the apparent incompatibility of the oxathiane ring system with the activation conditions coupled with poor diastereoselectivity. Similar results were observed on activation with 4-nitrobenzenesulfenyl chloride[15] in combination with silver trifluoromethanesulfonate. Therefore, we rapidly moved to the cyanoacetal **4** and were fortunate to find both a high degree of chemo- and stereoselectivity in couplings conducted by the BSP/Tf_2O/TTBP method as set out for the examples in Table 1. With methyl 2,3-*O*-isopropylidene-α-L-rhamnopyranoside as acceptor inspection of the crude coupling reaction mixture by NMR spectroscopy revealed the formation of only a single glycoside, the β-product **5** in excellent yield (Table 1, entry 1). With the less reactive methyl 2,3,6-tri-*O*-acetyl-α-D-glucopyranoside as acceptor the β:α ratio was somewhat reduced but was still respectable at 4.9:1 (Table 1, entry 2). A primary carbohydrate acceptor, methyl 2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside gave only the desired β-glycoside (Table 1, entry 3). Finally, with 1-adamantanol the observed anomeric ratio was 10.5:1 in favor of the β-isomer (Table 1, entry 4). Desulfurization was affected by means of Raney Nickel in

methanol at reflux, and was complimented by the removal of all benzyl ether protecting groups, resulting in the formation of the β-D-rhamnosides presented in Table 1.

With a successful, practical entry to the β-D-rhamnopyranosides in hand, it was of interest to investigate its extrapolation to the L-series. In view of the cost of L-mannose this required a de novo synthesis of an appropriately functionalized 6-thio-L-mannose derivative. This was achieved as set out in Scheme 2 from allyl 3,4-*O*-isopropylidene-L-arabinopyranoside **13**,[16] which was converted conventionally to the 3,4-di-*O*-benzyl-2-*O*-naphthylmethyl hemiacetal **15** with palladium-mediated cleavage of the allyl glycoside.[17] Wittig olefination[18] afforded the alkene **16** that was subjected to dihydroxylation with the Sharpless $(DHQD)_2PYR$ catalyst[19] resulting in a mixture of diols that was converted directly to the acetonide derivative **17** in good overall yield. In this sequence the in-built selectivity of the allylic ether system[20] for the desired isomer is reinforced by the use of the chiral ligand, leading to the formation of a workable 6.5:1 selectivity for the mannitol isomer.[21] Swern oxidation of the primary alcohol was followed by release of the acetal, resulting in the formation of the L-mannopyranose derivative **18**, which was converted to the corresponding thioglycoside by acetylation and then exposure to thiophenol and BF_3 etherate.[22] After removal of the naphthylmethyl ether and the residual acetate group diol **20** was obtained, whose α-anomer was spectroscopically identical in all respects to compound **1**, thereby confirming the identity of the major isomer resulting from the osmoylation reaction. Thereafter the remaining steps of the synthesis of donor **22** mirrored exactly those of the enantiomer **4**, except that an anomeric mixture of thioglycosides was carried through the sequence.

Donor **22** was then coupled to three of the same alcohols as its enantiomer **4** leading to the results presented in Table 2. A fourth coupling involved the use of 1,2;5,6-di-*O*-isopropylidene-α-D-glucofuranose as acceptor. As with the D-series, Table 1, yields and selectivities in these coupling reactions were generally excellent. Raney-Nickel was again the reagent of choice for the final desulfurization step, with concomitant removal of any benzyl ethers.

The comparison of entry 2 in Table 1 and Table 2 reveals an obvious case of diastereomeric matching and mismatching[23] in glycosylation reactions. Such phenomena were alluded to several decades ago by Paulsen,[24] then were highlighted by van Boeckel and coworkers.[25] Other examples of the phenomenon have been established by Ziegler for intramolecular aglycone delivery,[26] and the phenomenon has been discussed more recently in the guise of reciprocal donor acceptor selectivity (RDAS) by Fraser-Reid and coworkers.[27,28] The striking difference in selectivities for the two couplings to methyl 2,3,6-tri-*O*-acetyl-α-D-glucopyranoside presented here highlight the difficulties faced by any attempt at the development of any truly general glycosylation methodology, and underline the need for considerable caution in and critical appraisal of the results from lengthy oligosaccharide synthesis conducted on polymeric supports in an automated manner.[29]

In our work on the use of 4,6-*O*-benzyldiene protected mannopyranosyl donors we have repeatedly emphasized the chemical shift of the mannose H5 proton as being a ready indicator of the stereochemistry at the anomeric center. Thus, in the β-series H5 typically resonates in an otherwise largely empty spectral window from δ3.0– δ3.4, whereas in the corresponding α-isomers the corresponding signal is to be found from δ3.6– δ3.9. This simple, completely reliable tool unfortunately does not extend to the acetal protected 6-thio series studied here for which H5 in the β-series is found to resonate at a more typical value of ~ δ3.4– δ3.5 for an axial proton on a cyclohexane chair. It is apparent from this change in chemical shift between the standard 4,6-*O*-benzylidene series and the oxathianes presented here that the unusual upfield in the former is due to the shielding of H5 by the axial lone pairs on O4 and O6 coupled with the absence any deshielding from the anomeric position (Fig. 1). In the oxathiane series the longer C-S bond coupled with the less tightly held, more diffuse S lone pair suffices to

return the H5 chemical shift to a more normal value. In the absence of this convenient indicator we fall back on the measurement of anomeric $^1J_{CH}$ anomeric coupling constants, which follow the well-established pattern, for the assignment of anomeric stereochemistry.

Conclusion

The stereocontrolled synthesis of β-rhamnopyranosides may be conveniently achieved through prior activation of a 4-*O*-6-*S*-cyclic cyanoacetal-protected 6-thio-rhamnopyranosyl thioglycoside followed by introduction of the acceptor alcohol and subsequent desulfurization with Raney nickel. The presence of the electron-withdrawing cyano group, which serves inter alia to protect the oxathiane ring from attack by the glycosylation promoter, is essential to the success of the coupling reaction.

Experimental Section

Phenyl 2,3-Di-*O*-benzyl-1,6-dithio-α-D-mannopyranoside (2)

To an ice-cooled solution of PPh_3 (1.22 g, 4.64 mmol) in THF (10 mL) was added DIAD (914 μL, 4.64 mmol) drop wise. The reaction mixture was stirred at 0 °C for 1 h, **1**[1d] (1.40 g, 3.09 mmol) in THF (5 mL) was then added followed by AcSH (442 μL, 6.18 mmol). The cooling bath was removed and the reaction mixture was stirred at room temperature for 12 h. After TLC showed no starting material remained, the reaction mixture was cooled to 0 °C, and $LiAlH_4$ (352 mg, 9.27 mmol) was added portion wise. After 15 min, the cooling bath was removed, and the reaction mixture was stirred at room temperature for 3 h. The reaction mixture was again cooled to 0 °C, before water was added drop wise to quench the reaction. The reaction mixture was then diluted with CH_2Cl_2 and washed with 1N HCl and brine. The organic layer was dried over Na_2SO_4 and concentrated. Chromatographic purification on silica gel (15% ethyl acetate in hexane) afforded **2** (1.23 g, 85%) as colorless oil: $[\alpha]^{16}_D$ +54.0 (*c*, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52−7.50 (m, 2H), 7.39−7.26 (m, 13H), 5.60 (s, 1H), 4.70 (d, *J* = 12.5 Hz, 1H), 4.58 (d, *J* = 11.5 Hz, 1H), 4.57 (d, *J* = 12.0 Hz, 1H), 4.45 (d, *J* = 12.0 Hz, 1H), 4.14 (t, *J* = 9.0 Hz, 1H), 4.04−4.00 (m, 2H), 3.67−3.65 (dd, *J* = 2.5, 9.5 Hz, 1H), 3.00−2.96 (dd, *J* = 9.5, 11.5 Hz, 1H), 2.83−2.77 (dt, *J* = 7.0, 14.0 Hz, 1H), 2.42 (d, *J* = 1.5 Hz, 1H), 1.59 (t, *J* = 8.5 Hz, 1H); ^{13}C NMR (125.9 MHz, $CDCl_3$) δ 137.7, 137.6 134.0, 132.0, 129.1, 128.7, 128.5, 128.1, 128.00, 127.96, 127.9, 127.7, 86.0, 79.6, 75.4, 74.2, 72.1, 71.6, 69.1, 26.5; HRESIMScalcd for $C_{26}H_{28}O_4S_2Na$ $[M + Na]^+$, 491.1322; found, 491.1328.

Phenyl 2,3-Di-*O*-benzyl-4-*O*,6-*S*-benzylidene-1,6-dithio-α-D-mannopyranoside (3)

2 (178 mg, 0.380 mmol), CSA (8.8 mg, 38.0 μmol) and benzaldehyde dimethyl acetal (114 μL, 0.760 mmol) were dissolved in DMF (5 mL) and heated on a rotary evaporator at 50 °C for 4 h. The reaction mixture was cooled to room temperature and neutralized by the addition of triethylamine. DMF was removed under vacuum, and the reaction residue was diluted with EtOAc, washed with saturated $NaHCO_3$. The aqueous phase was extracted with EtOAc, and the combined organic phase was washed with water and brine, dried and concentrated. Chromatographic purification (5% ethyl acetate in hexane) afforded **3** (181 mg, 85%) as a colorless oil: $[\alpha]^{12}_D$ +139.6 (*c*, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52−7.41 (m, 2H), 7.39−7.26 (m, 18H), 5.98 (s, 1H), 5.52 (s, 1H), 4.76−4.70 (m, 3H), 4.64 (d, *J* = 12.0 Hz, 1H), 4.43−4.38 (dt, *J* = 3.5, 10.0 Hz, 1H), 4.13 (t, *J* = 9.5 Hz, 1H), 4.02 (d, *J* = 1.5 Hz, 1H), 3.96 −3.94 (dd, *J* = 3.0, 10.0 Hz, 1H), 3.32−3.27 (dd, *J* = 11.0, 13.0 Hz, 1H), 2.85−2.81 (dd, *J* = 4.0, 13.0 Hz, 1H); ^{13}C NMR (125.9 MHz, $CDCl_3$) δ 138.3, 138.1, 137.7, 134.0, 131.4, 129.2, 128.6, 128.5, 128.4, 128.2, 127.9, 127.8, 127.7, 127.6, 126.1, 86.4, 83.9, 81.2, 77.7, 76.3, 73.3, 72.8, 68.0, 32.2; HRESIMS calcd for $C_{33}H_{32}O_4S_2Na$ $[M + Na]^+$, 579.1635; found, 579.1636.

Phenyl 2,3-di-*O*-Benzyl-4-*O*,6-*S*-(1-cyano)benzylidene-1,6-dithio-α-D-mannopyranoside (4)

To a stirred solution of **2** (181 mg, 386 μmol) and CSA (17.9 mg, 77.2 μmol) in CH_2Cl_2 (800 μL) was add trimethyl orthobenzoate (663 μL, 3.86 mmol) at room temperature. After 4 h, the reaction mixture was diluted with CH_2Cl_2, washed with aqueous $NaHCO_3$ and brine, and dried over Na_2SO_4. The organic layer was concentrated, and subjected to chromatographic purification on silica gel (5% ethyl acetate in hexane) to give the orthoester. To an ice-cooled solution of this orthoester and TMSCN (193 μL, 1.54 mmol) in CH_2Cl_2 (1.7 mL) was added $BF_3{\cdot}Et_2O$ (19 μL, 154 μmol) drop wise. The reaction mixture was stirred at 0 °C for 1h and another 2 h at room temperature, before saturated $NaHCO_3$ was added and stirring continued for ~10 min. The reaction mixture was then diluted with CH_2Cl_2 and washed with saturated $NaHCO_3$ and brine. The organic layer was dried over Na_2SO_4 and concentrated. Chromatographic purification on silica gel (5% ethyl acetate in hexane) afforded **4** (166 mg, 74%) as a colorless oil: $[\alpha]^{23}_D$ +130.0 (*c*, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72−7.70 (m, 2H), 7.47−7.45 (m, 3H), 7.38−7.26 (m, 15H), 5.50 (s, 1H), 4.78 (d, *J* = 12.0 Hz, 1H), 4.73 (d, *J* = 12.0 Hz, 1H), 4.69 (t, *J* = 10.0 Hz, 1H), 4.67 (d, *J* = 12.5 Hz, 1H), 4.61 (d, *J* = 12.5 Hz, 1H), 4.44−4.39 (dt, *J* = 3.5, 10.0 Hz, 1H), 4.03 (d, *J* = 2.0 Hz, 1H), 3.94−3.92 (dd, *J* = 3.0, 9.5 Hz, 1H), 3.63−3.58 (dd, *J* = 11.0, 13.0 Hz, 1H), 2.90−2.87 (dd, *J* = 4.0, 13.0 Hz, 1H); ^{13}C NMR (125.9 MHz, $CDCl_3$) δ 138.1, 137.7, 135.4, 133.7, 131.2, 130.2, 129.3, 128.8, 128.5, 128.4, 128.2, 127.9, 127.8, 127.7, 125.5, 115.9, 86.7, 78.7, 78.2, 77.5, 75.9, 73.1, 72.9, 67.2, 31.4; HRESIMS calcd for $C_{34}H_{31}NO_4S_2Na$ $[M + Na]^+$, 604.1587; found, 604.1575.

General Glycosylation Procedure Using the BSP/TTBP/Tf_2O System

To a stirred solution of donor (1 equiv.), BSP (1.2 equiv.), TTBP (1.5 equiv.), and 4 Å molecular sieves in CH_2Cl_2 (0.05 M in donor) at −60 °C, was added Tf_2O (1.2 equiv.). After 30 min of stirring at −60 °C, a 0.15 M solution of the glycosyl acceptor (1.5 equiv.) in CH_2Cl_2 was slowly added. The reaction mixture was stirred for a further 2 h at −60 °C, before saturated $NaHCO_3$ was added to quench the reaction. The reaction mixture was allowed to reach room temperature and then filtered through a pad of Celite and washed with CH_2Cl_2, after which the filtrate was washed with saturated $NaHCO_3$ and brine. The organic layer was separated, dried over Na_2SO_4, and concentrated. Purification by column chromatography on silica gel, eluting with hexane/ethyl acetate mixtures, afforded the corresponding coupled products.

General Procedure for Raney Nickel Desulfurization

To a stirred solution of β-mannoside in MeOH: CH_2Cl_2 (6:1, 0.02 M) was added a solid portion (~30.0 g/mmol) of wet Raney Nickel slurry (W.R. Grace and Co. Raney®2800, Aldrich). The reaction mixture was heated to reflux with stirring under hydrogen (1 atm) until TLC showed that all the starting material was consumed. The mixture was filtered through a pad of Celite and washed with MeOH, the filtrate was concentrated. Chromatographic purification on silica gel (~10% MeOH in CH_2Cl_2) afforded the corresponding β-rhamnoside.

Methyl 2,3-Di-*O*-benzyl-4-*O*,6-*S*-[(1-cyano)benzylidene]-β-D-mannopyranosyl-(1→4)-2,3-*O*-isopropylidene-α-L-rhamnopyranoside (5)

Prepared by the general glycosylation procedure with a yield of 97.4 mg (89%). Colorless oil; $[\alpha]^{19}_D$ −36.0 (*c*, 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68−7.66 (m, 2H), 7.46−7.43 (m, 5H), 7.33−7.21 (m, 8H), 4.95 (s, 1H), 4.91 (d, *J* = 12.5 Hz, 1H), 4.87 (s, 1H), 4.83 (d, *J* = 12.0 Hz, 1H), 4.55 (t, *J* = 9.5 Hz, 1H), 4.53 (d, *J* = 13.0 Hz, 1H), 4.48 (d, *J* = 13.0 Hz, 1H), 4.12−4.09 (m, 2H), 3.96 (d, *J* = 3.0 Hz, 1H), 3.69−3.65 (m, 3H), 3.61−3.58 (dd, *J* = 3.0, 9.5 Hz, 1H), 3.51−3.46 (dt, *J* = 3.0, 9.5 Hz, 1H), 3.41 (s, 3H), 2.95−2.91 (dd, *J* = 3.5, 13.0 Hz, 1H), 1.49 (s, 3H), 1.36 (d, *J* = 5.5 Hz, 3H), 1.34 (s, 3H); ^{13}C NMR (125.9 MHz, $CDCl_3$) δ 138.5, 138.1, 135.4, 130.2, 128.8, 128.4, 128.3, 128.1, 127.6, 127.54, 127.50, 115.9, 109.3, 99.5 ($^1J_{CH}$ = 158.6 Hz), 97.9 ($^1J_{CH}$ = 168.7 Hz), 78.8, 78.3, 78.0, 77.9, 77.8, 76.1, 75.6, 74.6,

71.8, 69.5, 64.1, 55.0, 31.5, 28.0, 26.4, 17.7; HRESIMS calcd for $C_{38}H_{43}NO_9SNa$ [M + Na]$^+$, 712.2551; found, 712.2551.

Methyl β-D-rhamnopyranosyl-(1→4)-2,3-*O*-isopropylidene-α-L-rhamnopyranoside (6)

Prepared by the general desulfurization procedure with a yield of 22.1 mg (79%). Colorless oil; $[\alpha]^{12}_D$: −61.9 (*c*, 1.0, CH_3Cl); ^{1}H NMR (500 MHz, CD_3OD) δ 4.87 (s, 1H), 4.81 (s, 1H), 4.13 (t, *J* = 6.0 Hz, 1H), 4.09 (d, *J* = 5.5 Hz, 1H), 3.86 (d, *J* = 3.0 Hz, 1H), 3.63−3.60 (m, 2H), 3.39−3.36 (dd, *J* = 3.5, 9.5 Hz, 1H), 3.36 (s, 3H), 3.33−3.29 (m, 1H), 3.33−3.29 (m, 1H), 3.20 −3.13 (m, 1H), 1.49 (s, 3H), 1.33 (s, 3H), 1.31 (d, *J* = 6.0 Hz, 3H), 1.27 (d, *J* = 5.5 Hz, 3H); ^{13}C NMR (125.9 MHz, CD_3OD) δ 109.1, 98.6 ($^1J_{CH}$ = 159.9 Hz), 97.9 ($^1J_{CH}$ = 172.5 Hz), 78.4, 77.8, 76.0, 73.8, 72.6, 72.4, 71.3, 64.0, 53.8, 26.8, 25.3, 16.66, 16.62; HRESIMS calcd for $C_{16}H_{28}O_9Na$ [M + Na]$^+$, 387.1626; found, 387.1626.

Methyl 2,3-di-*O*-benzyl-4-*O*,6-*S*-(1-cyano)benzylidene-β-D-mannopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-α-D-glucopyranoside (7β) and Methyl 2,3-di-*O*-benzyl-4-*O*,6-*S*-(1-cyano) benzylidene-α-D-mannopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-α-D-glucopyranoside (7α)

Prepared by the general glycosylation procedure with a combined yield of 132.2 mg (67%, α/β = 1:4.9). **7β:** Colorless oil; $[\alpha]^{22}_D$ +20.0 (*c*, 1.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 −7.65 (m, 2H), 7.46−7.27 (m, 13H), 5.52 (t, *J* = 9.5 Hz, 1H), 4.89−4.82 (m, 2H), 4.81 (d, *J* = 12.5 Hz, 1H), 4.78 (d, *J* = 12.5 Hz, 1H), 4.57 (s, 2H), 4.51 (t, *J* = 9.5 Hz, 1H), 4.37 (s, 1H), 4.24−4.22 (dd, *J* = 1.5, 12.0 Hz, 1H), 4.16−4.12 (dd, *J* = 4.0, 12.0 Hz, 1H), 3.84 (d, *J* = 2.5 Hz, 1H), 3.82−3.78 (ddd, *J* = 2.5, 3.5, 10.0 Hz, 1H), 3.74 (t, *J* = 9.5 Hz, 1H), 3.58−3.53 (m, 2H), 3.48−3.45 (dd, *J* = 3.5, 9.5 Hz, 1H), 3.43 (s, 3H), 3.02−2.99 (dd, *J* = 3.5, 13.0 Hz, 1H), 2.11 (s, 3H), 2.09 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (125.6 MHz, $CDCl_3$) δ 170.8, 170.7, 169.9, 138.6, 138.2, 135.4, 130.5, 129.0, 128.9, 128.6, 128.3, 127.8, 127.7, 125.7, 115.9, 101.1 ($^1J_{CH}$ = 153.1 Hz), 97.0 ($^1J_{CH}$ = 177.7 Hz), 79.0, 78.1, 77.8, 76.2, 75.6, 74.7, 72.4, 71.2, 69.9, 68.4, 62.5, 55.7, 31.8, 21.4, 21.1, 21.0; HRESIMS calcd for $C_{41}H_{45}NO_{13}SNa$ [M + Na]$^+$, 814.2509; found, 814.2485. **7α:** Colorless oil; $[\alpha]^{22}_D$ +67.2 (*c*, 0.29, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67−7.65 (m, 2H), 7.45−7.27 (m, 13H), 5.47 (t, *J* = 9.5 Hz, 1H), 4.93−4.81 (m, 4H), 4.68−4.60 (m, 4H), 4.41−4.38 (dd, *J* = 1.5, 12.5 Hz, 1H), 4.18−4.15 (dd, *J* = 5.0, 12.5 Hz, 1H), 3.98−3.93 (dt, *J* = 3.5, 10.0 Hz, 1H), 3.92−3.88 (m, 2H), 3.78 (t, *J* = 9.5 Hz, 1H), 3.71−3.69 (m, 1H), 3.53 −3.48 (dd, *J* = 11.0, 13.0 Hz, 1H), 3.41 (s, 3H), 3.00−2.97 (dd, *J* = 3.5, 13.0 Hz, 1H), 2.11 (s, 3H), 2.08 (s, 3H), 1.82 (s, 3H); ^{13}C NMR (125.6 MHz, $CDCl_3$) δ 170.9, 170.5, 169.9, 138.4, 138.2, 135.6, 130.3, 129.0, 128.8, 128.6, 128.1, 127.9, 127.8, 125.7, 116.1, 102.3 ($^1J_{CH}$ = 172.2 Hz), 96.9 ($^1J_{CH}$ = 174.5 Hz), 79.0, 78.1, 77.9, 76.7, 76.2, 73.8, 73.3, 72.0, 71.1, 68.1, 67.7, 63.1, 55.7, 31.4, 21.1, 21.0, 20.8; HRESIMS calcd for $C_{41}H_{45}NO_{13}SNa$ [M + Na]$^+$, 814.2509; found, 814.2467.

Methyl β-D-rhamnopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-α-D-glucopyranoside (8)

Prepared by the general desulfurization procedure with a yield of 21.8 mg (69%). Colorless gel; $[\alpha]^{23}_D$ +78.0 (*c*, 0.15, $CHCl_3$); ^{1}H NMR (500 MHz, CD_3OD) δ 5.41 (t, *J* = 9.5 Hz, 1H), 4.82−4.79 (*dd, J* = 3.0, 10.0 Hz, 1H), 4.48 (s, 1H), 4.41−4.38 (dd, *J* = 1.5, 12.0 Hz, 1H), 4.31 −4.28 (dd, *J* = 5.0, 12.5 Hz, 1H), 3.96−3.93 (ddd, *J* = 1.5, 4.5, 10.0 Hz, 1H), 3.87 (d, *J* = 9.5 Hz, 1H), 3.83 (d, *J* = 3.0 Hz, 1H), 3.41 (s, 3H), 3.31−3.27 (m, 1H), 3.22−3.16 (m, 1H), 2.10 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H), 1.31 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (125.6 MHz, CD_3OD) δ 171.3, 171.4, 170.6, 100.5, 96.9, 76.2, 73.7, 72.6, 72.4, 71.4, 71.2, 70.5, 68.5, 62.6, 54.5, 20.2, 19.5, 19.3, 17.1; HRESIMS calcd for $C_{19}H_{30}O_{13}Na$ [M + Na]$^+$, 489.1584; found, 489.1570.

Methyl 2,3-di-*O*-benzyl-4-*O*,6-*S*-(1-cyano)benzylidene-β-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (9)

Prepared by the general glycosylation procedure with a yield of 154.9 mg (82%). Colorless gel; $[\alpha]^{24}_{D}$ +10.8 (*c*, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03−7.88 (m, 6H), 7.69 −7.22 (m, 24H), 6.21 (t, *J* = 9.5 Hz, 1H), 5.52 (t, *J* = 9.5 Hz, 1H), 5.31−5.27 (m, 2H), 5.04 (d, *J* = 12.5 Hz, 1H), 4.97 (d, *J* = 12.5 Hz, 1H), 4.58 (t, *J* = 9.5 Hz, 1H), 4.53 (s, 2H), 4.50 (s, 1H), 4.35−4.32 (m, 1H), 4.21−4.18 (dd, *J* = 1.5, 10.5 Hz, 1H), 4.09 (d, *J* = 3.0 Hz, 1H), 3.71−3.67 (dd, *J* = 6.5, 11.0 Hz, 1H), 3.61−3.56 (m, 2H), 3.51−3.46 (m, 1H), 3.48 (s, 3H), 2.89−2.86 (dd, *J* = 3.5, 13.0 Hz, 1H); ^{13}C NMR (125.6 MHz, $CDCl_3$) δ 166.1, 166.0, 165.8, 138.5, 138.3, 135.6, 133.9, 133.7, 133.4, 130.4, 130.2, 130.1, 129.9, 129.5, 129.3, 129.0, 128.8, 128.7, 128.6, 128.5, 127.87, 127.85, 125.4, 115.9, 102.2 ($^1J_{CH}$ = 155.7 Hz), 97.1 ($^1J_{CH}$ = 177.6 Hz), 79.1, 77.8, 75.6, 75.0, 72.4, 72.2, 70.7, 69.8, 69.7, 69.1, 68.9, 55.8, 31.5; HRESIMS calcd for $C_{56}H_{51}NO_{13}SNa$ $[M + Na]^+$, 1000.2979; found, 1000.3001.

Methyl β-D-rhamnopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (10)

Prepared by the general desulfurization procedure with a yield of 34.0 mg (73%). Colorless gel; $[\alpha]^{22}_{D}$ +35.2 (*c*, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99−7.85 (m, 6H), 7.53 −7.26 (m, 9H), 6.16 (t, *J* = 10.0 Hz, 1H), 5.63 (t, *J* = 10.0 Hz, 1H), 5.30−5.27 (dd, *J* = 3.5, 10.0 Hz, 1H), 5.24 (d, *J* = 3.5 Hz, 1H), 4.48 (s, 1H), 4.28−4.25 (ddd, *J* = 1.5, 5.0, 10.0 Hz, 1H), 4.16 −4.12 (m, 2H), 3.75−3.71 (dd, *J* = 5.5, 13.0 Hz, 1H), 3.51−3.43 (m, 2H), 3.47 (s, 3H), 3.27 −3.23 (m, 1H), 3.10 (s, 1H), 2.95 (s, 1H), 1.90 (s, 1H), 1.34 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (125.6 MHz, $CDCl_3$) δ 166.1, 166.0, 165.8, 133.8, 133.6, 133.4, 130.2, 130.1, 129.9, 129.4, 129.3, 129.0, 128.8, 128.7, 128.5, 100.6, 97.2, 74.4, 73.4, 72.3, 72.1, 70.73, 70.65, 69.4, 69.0, 68.0, 55.9, 17.7; HRESIMS calcd for $C_{34}H_{36}O_{13}Na$ $[M + Na]^+$, 675.2054; found, 675.2020.

1-Adamantanyl 2,3-di-*O*-benzyl-4-*O*,6-*S*-(1-cyano)benzylidene-β-D-mannopyranoside (11β) and 1-Adamantanyl 2,3-di-*O*-benzyl-4-*O*,6-*S*-(1-cyano)benzylidene-α-D-mannopyranoside (11α)

Prepared by the general glycosylation procedure with a combined yield of 112.4 mg (87%, α/β = 1:10.5). **11β**: White solid; mp 182 °C; $[\alpha]^{15}_{D}$ +9.5 (*c*, 0.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68−7.66 (m, 2H), 7.50−7.44 (m, 5H), 7.37−7.22 (m, 8H), 5.01 (d, *J* = 12.5 Hz, 1H), 4.95 (d, *J* = 12.5 Hz, 1H), 4.73 (s, 1H), 4.58 (t, *J* = 9.5 Hz, 1H), 4.51 (d, *J* = 13.0 Hz, 1H), 4.48 (d, *J* = 12.5 Hz, 1H), 3.77 (d, *J* = 2.5 Hz, 1H), 3.69−3.64 (dd, *J* = 10.5, 13.0 Hz, 1H), 3.58 −3.56 (dd, *J* = 3.0, 9.5 Hz, 1H), 3.53−3.48 (dt, *J* = 3.0, 10.0 Hz, 1H), 2.97−2.93 (dd, *J* = 3.5, 13.5 Hz, 1H), 2.17 (s, 3H), 1.86 (d, *J* = 11.0 Hz, 3H), 1.76 (d, *J* = 11.5 Hz, 3H), 1.66 (d, *J* = 12.0 Hz, 3H), 1.61 (d, *J* = 12.0 Hz, 3H); ^{13}C NMR (125.9 MHz, $CDCl_3$) δ 138.5, 138.2 135.5, 130.1, 128.9, 128.8, 128.3, 128.1, 127.55, 127.51, 127.47, 125.5, 115.8, 94.3 ($^1J_{CH}$ = 152.3 Hz), 78.8, 78.3, 77.8, 76.1, 75.4, 74.3, 72.0, 69.0, 42.5, 36.2, 31.6, 30.6; HRESIMS calcd for $C_{38}H_{41}NO_5SNa$ $[M + Na]^+$, 646.2603; found, 646.2589. **11α**: Colorless oil; $[\alpha]^{22}_{D}$ +67.2 (*c*, 0.29, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72−7.66 (m, 3H), 7.54−7.22 (m, 12H), 5.01 (d, *J* = 1.0 Hz, 1H), 4.88 (d, *J* = 12.5 Hz, 1H), 4.72−4.57 (m, 4H), 4.11−4.08 (dt, *J* = 3.5, 10.0 Hz, 1H), 4.01−3.98 (dd, *J* = 3.0, 10.0 Hz, 1H), 3.64−3.63 (m, 1H), 3.57−3.52 (dd, *J* = 11.5, 13.0 Hz, 1H), 2.87−2.84 (dd, *J* = 4.0, 13.5 Hz, 1H), 2.12 (s, 3H), 1.68−1.54 (m, 12H); ^{13}C NMR (125.6 MHz, $CDCl_3$) δ 138.9, 138.6 135.6, 130.5, 129.2, 129.0, 128.6, 128.5, 127.9, 127.7, 125.7, 124.6, 116.2, 92.5 ($^1J_{CH}$ = 168.4 Hz), 78.9, 78.8, 77.7, 76.6, 75.1, 73.7, 73.3, 65.8, 42.4, 36.4, 31.8, 30.8; HRESIMS calcd for $C_{38}H_{41}NO_5SNa$ $[M + Na]^+$, 646.2603; found, 646.2617.

1-Adamantanyl β-D-rhamnopyranoside (12)

Prepared by the general desulfurization procedure with a yield of 25.6 mg (74%). White solid; mp 156 °C; $[\alpha]^{24}_{D}$ −5.8 (*c*, 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.78 (s, 1H), 3.83 (s,

1H), 3.46−3.40 (m, 2H), 3.29−3.21 (m, 1H), 2.77−2.43 (br s, 3H), 2.16 (s, 3H), 1.84 (d, *J* = 11.6 Hz, 3H), 1.78 (d, *J* = 11.2 Hz, 3H), 1.65 (d, *J* = 12.8 Hz, 3H), 1.60 (d, *J* = 12.4 Hz, 3H), 1.33 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 92.5, 74.9, 73.6, 72.6, 71.4, 42.6, 36.4, 30.9, 18.0; HRESIMS calcd for $C_{16}H_{26}O_5Na$ $[M + Na]^+$, 321.1678; found, 321.1694.

Allyl 3,4-*O*-isopropylidene-α-L-arabinopyranoside (13α) and Allyl 3,4-*O*-isopropylidene-β-L-arabinopyranoside (13β)

13 was prepared from L-arabinose in two steps according to literature precedrue[16] (75%, α/β = 1.9:1). Analytically pure samples of the two anomers were obtained by further purification of a portion of the product by radial chromatography (20% ethyl acetate in hexane). **13α:** white solid; mp 71–72 °C; $[\alpha]^{22}_D$: +225.6 (*c*, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.96−5.88 (m, 1H), 5.33−5.28 (dd, *J* = 1.5, 17.5 Hz, 1H), 5.24−5.21 (dd, *J* = 1.5, 10.5 Hz, 1H), 4.87 (d, *J* = 3.5 Hz, 1H), 4.27−4.18 (m, 3H), 4.07−4.02 (dd, *J* = 6.0, 13.0 Hz, 1H), 3.99−3.95 (dd, *J* = 3.0, 13.0 Hz, 1H), 3.92− 3.89 (dd, *J* = 1.5, 13.0 Hz, 1H), 3.80−3.77 (dt, *J* = 3.5, 7.0 Hz, 1H), 2.30 (d, *J* = 10.5 Hz, 1H), 1.52 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (125.6 MHz, $CDCl_3$) δ 133.8, 118.1, 109.4, 97.0 ($^1J_{CH}$ = 170.9 Hz), 76.2, 73.2, 70.3, 68.9, 59.9, 28.2, 26.2; HRESIMS calcd for $C_{11}H_{18}O_5Na$ $[M + Na]^+$, 253.1052; found, 253.1065. **13β:** colorless oil; $[\alpha]^{22}$D : +25.8 (*c*, 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.97−5.88 (m, 1H), 5.33−5.29 (dd, *J* = 1.5, 17.5 Hz, 1H), 5.23−5.20 (dd, *J* = 1.5, 10.5 Hz, 1H), 4.36−4.31 (ddt, *J* = 1.5, 5.5, 12.5 Hz, 1H), 4.25−4.21 (m, 2H), 4.19−4.15 (dd, *J* = 3.5, 13.0 Hz, 1H), 4.11−4.06 (m, 2H), 3.79−3.75 (dd, *J* = 3.5, 13.0 Hz, 1H), 3.66−3.62 (dt, *J* = 3.0, 7.5 Hz, 1H), 2.64 (d, *J* = 2.5 Hz, 1H), 1.53 (s, 3H), 1.36 (s, 3H); ^{13}C NMR (125.6 MHz, $CDCl_3$) δ 134.0, 118.2, 110.4, 101.3 ($^1J_{CH}$ = 163.4 Hz), 78.3, 73.8, 73.2, 69.9, 63.3, 28.2, 26.3; HRESIMS calcd for $C_{11}H_{18}O_5Na$ $[M + Na]^+$, 253.1052; found, 253.1050.

Allyl 2-*O*-(2-naphthylmethyl)-α-L-arabinopyranoside (14α) and Allyl 2-*O*-(2-naphthylmethyl)-β-L-arabinopyranoside (14β)

To a ice-cooled solution of **13αβ** (9.21 g, 40.0 mmol) and tetrabutylammonium iodide (1.48 g, 4.00 mmol) in DMF (50 mL) was added sodium hydride (60% in mineral oil, 2.40 g, 60.0 mmol) under stirring. After 10 min, 2-(bromomethyl)naphthalene (10.6 g, 48.0 mmol) was added and stirring was continued for 4 h at room temperature. The reaction mixture was concentrated. The resulting residue was dissolved in AcOH: H_2O (4:1, 100 mL), and stirred at 80 °C for 3 h. The reaction mixture was concentrated, dissolved in ethyl acetate, and washed with saturated $NaHCO_3$. The aqueous phase was extracted with EtOAc three times, and the combined organic phase was washed with water and brine, dried and concentrated. Chromatographic purification (20% ethyl acetate in hexane to ethyl acetate) on silica gel afforded **14** (11.8 g, α/β = 1.9:1, 89%). Analytically pure samples of the two anomers were obtained by further purification of a portion of the product by radial chromatography (60% ethyl acetate). **14α**: white solid; mp 86–87 °C; $[\alpha]^{25}_D$: +108.5 (*c*, 0.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84−7.78 (m, 4H), 7.50−7.47 (m, 3H), 5.96−5.87 (m, 1H), 5.35−5.31 (dd, *J* = 1.5, 17.0 Hz, 1H), 5.21−5.19 (dd, *J* = 1.5, 10.5 Hz, 1H), 4.90 (d, *J* = 3.5 Hz, 1H), 4.79 (s, 2H), 4.17−4.13 (ddt, *J* = 12.5, 5.0, 1.5 Hz, 1H), 4.07−4.06 (dd, *J* = 3.0, 10.0 Hz, 1H), 3.95 −3.90 (m, 2H), 3.81−3.76 (m, 2H), 3.67−3.64 (dd, *J* = 2.0, 12.5 Hz, 1H), 3.03 (s, 1H), 2.99 (s, 1H); ^{13}C NMR (125.6 MHz, $CDCl_3$) δ 135.7, 134.1, 133.5, 133.3, 128.6, 128.2, 128.0, 127.1, 126.5, 126.4, 126.1, 118.0, 96.1 ($^1J_{CH}$ = 174.7 Hz), 77.1, 73.0, 69.3, 68.8, 68.6, 62.3; HRESIMS calcd for $C_{19}H_{22}O_9Na$ $[M + Na]^+$, 353.1365; found, 353.1377. **14β**: white solid; mp 103 °C; $[\alpha]^{25}_D$: +5.4 (*c*, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86−7.80 (m, 4H), 7.51−7.47 (m, 3H), 5.96−5.88 (m, 1H), 5.34−5.30 (dd, *J* = 1.5, 17.5 Hz, 1H), 5.23−5.21 (dd, *J* = 1.5, 10.5 Hz, 1H), 4.97 (d, *J* = 12.0 Hz, 1H), 4.83 (d, *J* = 12.0 Hz, 1H), 4.58 (d, *J* = 4.5 Hz, 1H), 4.36−4.32 (dd, *J* = 5.0, 13.0 Hz, 1H), 4.10−4.05 (dd, *J* = 6.0, 13.0 Hz, 1H), 3.98− 3.92 (m, 1H), 3.84−3.77 (m, 2H), 3.68−3.65 (dd, *J* = 5.0, 6.5 Hz, 1H), 3.57−3.54 (dd, *J* = 3.0, 12.0 Hz, 1H), 3.12 (d, *J* = 7.0 Hz, 1H), 2.74 (d, *J* = 6.5 Hz, 1H); ^{13}C NMR (125.6 MHz, $CDCl_3$) δ

135.6, 133.8, 133.5, 133.3, 128.6, 128.2, 128.0, 127.1, 126.5, 126.3, 126.1, 118.1, 100.5 ($^1J_{CH}$ = 163.4 Hz), 77.7, 74.0, 71.2, 69.6, 66.6, 63.0; HRESIMS calcd for $C_{19}H_{22}O_9Na$ [M + Na]$^+$, 353.1365; found, 353.1380.

3,4-Di-*O*-benzyl-2-*O*-(2-naphthylmethyl)-L-arabinopyranose (15)

To a ice-cooled solution of **14αβ** (12.1 g, 36.6 mmol) and tetrabutylammonium iodide (1.35 g, 3.66 mmol) in DMF (54 mL) was added sodium hydride (60% in mineral oil, 3.67 g, 91.6 mmol) under stirring. After 15 min, benzyl bromide (10.9 mL, 91.6 mmol) was added and stirring was continued for 6 h at room temperature. The reaction mixture was concentrated, dissolved in ethyl acetate, and washed with brine. The organic layer was concentrated and the resulting residue was dissolved in AcOH (135 mL) and water (15 mL). AcONa (9.01 g, 109.8 mmol) and $PdCl_2$ (2.60 g, 14.6 mmol) were added and the reaction mixture was stirred at room temperature for 20 h. The reaction mixture was concentrated, dissolved in CH_2Cl_2 and filtered through Celite. The filtrate was washed with saturated $NaHCO_3$ and brine. The organic layer was separated, dried over Na_2SO_4 and concentrated. Chromatographic purification on silica gel (20% ethyl acetate in hexane) afforded **15** (13.4 g, 78%) as colorless oil, which was used for the next step without further purification. HRESIMS calcd for $C_{30}H_{30}O_5Na$ [M + Na]$^+$, 493.1991; found, 493.2004. The sugar proton signals for the two α/β anomers are difficult to distinguish, only assignable peaks from the NMR spectra are listed. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87−7.71 (m), 7.53−7.23 (m), 5.96−5.87 (m, 1H), 5.20 (s), 4.93−4.55 (m), 4.08 −4.04 (dd, *J* = 9.0, 11.5 Hz), 3.95−3.66 (m), 3.13 (d, *J* = 5.0 Hz); ^{13}C NMR (125.6 MHz, $CDCl_3$) δ 138.6, 138.4, 138.3, 137.6, 135.6, 133.4, 133.3, 128.74, 128.71, 128.6, 128.3, 128.2, 128.1, 128.04, 128.97, 127.9, 127.1, 127.0, 126.5, 126.3, 126.1, 126.0, 94.0, 92.4, 76.4, 76.3, 75.7, 74.0, 73.2, 72.9, 72.3, 71.8, 61.2, 58.6.

3,4-Di-*O*-benzyl-2-*O*-(2-naphthylmethyl)-L-*arabino*-hex-1-enitol (16)

To a stirred suspension of methyltriphenylphosphonium bromide (9.58 g, 26.8 mmol) in THF (35 mL) was added potassium *tert*-butoxide (2.88 g, 25.7 mmol) after which the reaction mixture was stirred at room temperature for 1 h, then cooled to −40 °C. A solution of **15** (5.05 g, 10.7 mmol) in THF (18.5 mL) was added drop wise to the above suspension and the resulting mixture was warm up to 0 °C over 1 h and stirred at 0 °C overnight. Acetone (25 mL) was added to quench the reaction and the reaction mixture was stirred at room temperature for ~15 min. The reaction mixture was filtered through Celite and concentrated. The residue was purified by column chromatography on silica gel to afford **16** (3.60 g, 72%). Colorless oil; $[\alpha]^{24}_D$: +19.3 (*c*, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81−7.76 (m, 2H), 7.47−7.11 (m, 15H), 5.98−5.91 (m, 1H), 5.41−5.33 (m, 2H), 4.82 (d, *J* = 12.0 Hz, 1H), 4.77 (d, *J* = 11.5 Hz, 1H), 4.74 (d, *J* = 11.5 Hz, 1H), 4.51 (d, *J* = 12.0 Hz, 1H), 4.46 (d, *J* = 11.5 Hz, 1H), 4.32 (d, *J* = 11.5 Hz, 1H), 4.11−4.08 (dd, *J* = 4.5, 7.5 Hz, 1H), 3.84−3.80 (m, 2H), 3.77−3.11 (m, 2H), 2.18 (t, *J* = 6.5 Hz, 1H); ^{13}C NMR (125.6 MHz, $CDCl_3$) δ 138.4, 138.2, 136.1, 135.9, 133.5, 133.2, 128.60, 128.57, 128.5, 128.4, 128.1, 128.0, 127.93, 127.89, 127.0, 126.4, 126.3, 126.1, 119.2, 81.8, 80.8, 79.1, 75.4, 71.9, 70.8, 61.1; HRESIMS calcd for $C_{31}H_{32}O_4Na$ [M + Na]$^+$, 491.2198; found, 491.2184.

2,3-Di-*O*-benzyl-5,6-*O*-isopropylidene-4-*O*-(2-naphthylmethyl)-L-mannitol (17)

To a well stirred suspension of $(DHQD)_2PYR$ (58.6 mg, 6.65 μmol), $K_3Fe(CN)_6$ (3.28 g, 9.99 mmol), K_2CO_3 (1.38 g, 9.99 mmol), and OsO_4 (834 μL, 2.5% in *tert*-BuOH, 6.65 μmol) in *tert*-BuOH (9 mL) and water (15 mL) at 0 °C was added **16** (3.12 g, 6.65 mmol) in *tert*-BuOH (6 mL). The reaction mixture was stirred at 0 °C for 24 h before saturated Na_2SO_3 was added and stirring continued for ~30 min at room temperature. The reaction mixture was extracted with EtOAc, washed with saturated $NaHCO_3$. The aqueous phase was extracted with EtOAc, and the combined organic phase was washed with water and brine, dried and concentrated to

give a white solid. To a stirred solution of this preparation in CH_3CN (10 mL) was added 2,2-dimethoxypropane (3.40 mL, 26.6 mmol) and CSA (309 mg, 1.33 mmol). The reaction mixture was stirred at room temperature for 4 h before triethylamine was added to quench to reaction. The reaction mixture was concentrated and radial chromatographic purification (15% ethyl acetate in hexane) afforded **17** (2.64 g, mannitol/gulitol = 6.5:1, 73%). Colorless oil; $[\alpha]^{22}_D$: 3.2 (*c*, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82−7.70 (m, 3H), 7.47−7.25 (m, 12H), 4.88 (d, *J* = 12.0 Hz, 1H), 4.79−4.70 (m, 3H), 4.59 (d, *J* = 11.5 Hz, 1H), 4.40 (d, *J* = 11.5 Hz, 1H), 4.30−4.26 (m, 1H), 4.03−3.76 (m, 7H), 2.08−2.05 (m, 1H), 1.45 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (125.6 MHz, $CDCl_3$) δ 138.3, 138.2, 136.0, 133.5, 133.2, 128.8, 128.7, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 126.6, 126.3, 126.11, 126.07, 108.8, 79.6, 79.2, 77.4, 76.8, 74.8, 74.6, 71.7, 66.9, 60.2, 26.8, 25.4; HRESIMS calcd for $C_{34}H_{38}O_6Na$ $[M + Na]^+$, 565.2566; found, 565.2564.

2,3-Di-*O*-benzyl-4-*O*-(2-naphthylmethyl)-L-mannopyranose (18)

To a stirred solution of DMSO (750 μL, 10.6 mmol) in CH_2Cl_2 (8.4 mL) at −78 °C, was added oxalyl chloride (714 μL, 8.44 mmol) drop wise. The reaction mixture was stirred at −78 °C for 30 min and the solution of **17** (2.29 g, 4.21 mmol) in CH_2Cl_2 (4.2 mL) was added slowly. The reaction mixture was stirred for 45 min at −78 °C. Triethylamine (2.93 mL, 21.1 mmol) was added drop wise and the reaction mixture was stirred for 30 min at −78 °C and then allowed to warm up to 0 °C over 1 h, before water was added to quench the reaction. The reaction mixture was then diluted with CH_2Cl_2 and washed with water and brine. The organic layer was dried over Na_2SO_4 and concentrated. The resulting residue was dissolved in THF:trifluoroacetic acid (4:1, 10 mL). The reaction mixture was stirred at room temperature for 2 h before solid $NaHCO_3$ was added and stirring continued for ~10 min. The reaction mixture was concentrated, dissolved in ethyl acetate, and washed with saturated $NaHCO_3$. The aqueous phase was extracted with EtOAc, and the combined organic phase was washed with water and brine, dried and concentrated to give crude **18** (1.90 g, 90%) as colorless oil, which was used for the next step without further purification. HRESIMS calcd for $C_{31}H_{32}O_6Na$ $[M + Na]^+$, 523.2097; found, 523.2136. The sugar proton signals for the two α/β anomers are difficult to distinguish, only assignable peaks from the NMR spectra are listed. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84−7.78 (m), 7.55−7.27 (m), 5.20 (s), 5.18−5.14 (m), 4.75−4.42 (m), 4.17 (t, *J* = 8.0 Hz), 4.03−3.81 (m), 3.66−3.46 (m), 2.95 (d, *J* = 6.0 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 138.4, 138.2, 138.0, 135.1, 133.4, 133.3, 128.8, 128.73, 128.69, 128.6, 128.5, 128.4, 128.2, 128.1, 128.04, 128.00, 127.97, 127.9, 127.3, 127.2, 126.7, 126.6, 126.5, 126.07, 126.01, 94.9, 93.0, 78.0, 75.5, 75.2, 74.6, 74.4, 74.1, 73.5, 73.3, 73.0, 72.7, 72.2, 71.1, 66.4, 62.7, 62.6.

Phenyl 6-*O*-acetyl-2,3-di-*O*-benzyl-4-*O*-(2-naphthylmethyl)-1-thio-α-L-mannopyranoside (19α) and Phenyl 6-*O*-acetyl-2,3-di-*O*-benzyl-4-*O*-(2-naphthylmethyl)-1-thio-β-L-mannopyranoside (19β)

To a stirred solution of **18αβ** (1.12 g, 2.24 mmol) and DMAP (27.4 mg, 0.224 mmol) in CH_2Cl_2 (11 mL) was added Ac_2O (1.27 mL, 13.4 mmol) and triethylamine (2.50 mL, 17.9 mmol) at room temperature. After 6 h, the mixture was concentrated, dissolved in CH_2Cl_2, and washed with saturated $NaHCO_3$ and brine. The organic layer was dried over Na_2SO_4 and concentrated. To the stirred solution of the resulting crude in CH_2Cl_2 (5.5 mL) at 0 °C, was added PhSH (253 μL, 2.64 mmol), followed by $BF_3{\cdot}Et_2O$ (553 μL, 4.48 mmol). The solution was stirred at 0 °C for 4 h, before saturated $NaHCO_3$ was added and stirring continued for ~10 min at room temperature. The reaction mixture was then diluted with CH_2Cl_2 and washed with saturated $NaHCO_3$ and brine. The organic layer was dried over Na_2SO_4 and concentrated. Column chromatography on silica gel (15% ethyl acetate in hexane) provided **19** (1.11 g, α/β = 1:3.5, 78%). Analytically pure samples of the two anomers were obtained by further purification of a portion of the product by radial chromatography (15% ethyl acetate in hexane) on silica gel. **19α:** Colorless oil; $[\alpha]^{22}_D$: −70.0 (*c*, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$)

δ 7.83−7.75 (m, 3H), 7.48−7.25 (m, 19H), 5.58 (d, *J* = 1.5 Hz, 1H), 5.10 (d, *J* = 11.0 Hz, 1H), 4.78 (d, *J* = 11.0 Hz, 1H), 4.73 (d, *J* = 12.5 Hz, 1H), 4.65 (d, *J* = 12.5 Hz, 1H), 4.64 (s, 2H), 4.37−4.32 (m, 3H), 4.05−4.01 (m, 2H), 3.94−3.91 (dd, *J* = 3.0, 9.5 Hz, 1H), 1.93 (s, 3H); ^{13}C NMR (125.6 MHz, $CDCl_3$) δ 171.1, 138.2, 138.1, 135.8, 134.3, 133.5, 133.3, 131.9, 129.3, 128.73, 128.66, 128.5, 128.2, 128.13, 128.11, 128.08, 128.05, 127.9, 127.8, 127.2, 126.4, 126.3, 126.2, 85.8 ($^1J_{CH}$ = 168.9 Hz), 80.5, 76.3, 75.5, 74.7, 72.3, 72.2, 71.2, 63.7, 21.0; HRESIMS calcd for $C_{39}H_{38}O_6SNa$ $[M + Na]^+$, 657.2287; found, 657.2246. **19β:** Colorless oil; $[\alpha]^{22}_D$: +45.2 (*c*, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83−7.71 (m, 3H), 7.51 −7.23 (m, 19H), 5.07 (d, *J* = 11.0 Hz, 1H), 5.06 (d, *J* = 12.0 Hz, 1H), 4.88 (d, *J* = 12.0 Hz, 1H), 4.80−4.76 (m, 3H), 4.71 (d, *J* = 12.0 Hz, 1H), 4.48−4.45 (dd, *J* = 2.0, 11.5 Hz, 1H), 4.27−4.23 (dd, *J* = 7.0, 12.0 Hz, 1H), 4.18 (d, *J* = 2.0 Hz, 1H), 4.00 (t, *J* = 9.5 Hz, 1H), 3.69−3.66 (dd, *J* = 2.5, 9.0 Hz, 1H), 3.59−3.55 (dt, *J* = 2.0, 9.0 Hz, 1H), 1.99 (s, 3H); ^{13}C NMR (125.6 MHz, $CDCl_3$) δ 171.1, 138.4, 138.1, 135.7, 135.5, 133.5, 133.3, 131.1, 129.1, 128.8, 128.5, 128.2, 128.1, 127.94, 127.91, 127.5, 127.2, 126.4, 126.3, 126.2, 88.0 ($^1J_{CH}$ = 153.0 Hz), 84.6, 77.9, 77.5, 75.5, 75.3, 74.9, 72.8, 64.2, 21.0; HRESIMS calcd for $C_{39}H_{38}O_6SNa$ $[M + Na]^+$, 657.2287; found, 657.2291.

Phenyl 2,3-di-*O*-benzyl-1-thio-α-L-mannopyranoside (20α) and Phenyl 2,3-di-*O*-benzyl-1-thio-β-L-mannopyranoside (20β)

To a stirred solution of **19αβ** (1.10 g, 1.73 mmol) in CH_2Cl_2:H_2O (10:1, 5.5 mL) was added DDQ (787 mg, 3.46 mmol) at room temperature. After 2 h, the reaction mixture was diluted with CH_2Cl_2, and washed with saturated $NaHCO_3$ and brine. The organic layer was dried over Na_2SO_4 and concentrated. A stirred solution of the resulting crude in MeOH:CH_2Cl_2 (20:1, 10.5 mL) was treated with K_2CO_3 (718 mg, 5.19 mmol) and stirred at room temperature for 3 h. The reaction mixture was concentrated, dissolved in CH_2Cl_2 and washed with water and brine. The organic layer was dried over Na_2SO_4 and concentrated. Chromatographic purification (35% ethyl acetate in hexane) afforded **20** (634 mg, α/β = 1:3.5, 81%). Analytically pure samples of the two anomers were obtained by further purification of a portion of the product by radial chromatography (35% ethyl acetate in hexane). **20α:** white solid; mp 94–95 °C; $[\alpha]^{22}_D$: −39.1 (*c*, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46−7.27 (m, 15H), 5.58 (d, *J* = 1.0 Hz, 1H), 4.69 (d, *J* = 12.5 Hz, 1H), 4.60 (d, *J* = 12.0 Hz, 1H), 4.59 (d, *J* = 12.0 Hz, 1H), 4.53 (d, *J* = 11.5 Hz, 1H), 4.18−4.11 (m, 2H), 4.03−4.02 (dd, *J* = 1.5, 3.0 Hz, 1H), 3.91 −3.82 (m, 2H), 3.74−3.71 (dd, *J* = 3.0, 9.5 Hz, 1H), 2.85 (d, *J* = 1.5 Hz, 1H), 2.26 (t, *J* = 5.0 Hz, 1H); ^{13}C NMR (125.6 MHz, $CDCl_3$) δ 138.0, 137.9, 134.2, 132.1, 129.4, 128.9, 128.7, 128.3, 128.24, 128.15, 128.0, 86.3 ($^1J_{CH}$ = 167.9 Hz), 79.9, 75.9, 73.6, 72.5, 72.1, 67.5, 62.8; HRESIMS calcd for $C_{26}H_{28}O_5SNa$ $[M + Na]^+$, 475.1555; found, 475.1532. **20β:** colorless oil; $[\alpha]^{22}_D$: +50.5 (*c*, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48−7.26 (m, 15H), 4.98 (d, *J* = 11.5 Hz, 1H), 4.86 (s, 1H), 4.85 (d, *J* = 11.0 Hz, 1H), 4.76 (d, *J* = 11.5 Hz, 1H), 4.20 (d, *J* = 2.0 Hz, 1H), 4.10−4.05 (dt, *J* = 2.0, 9.5 Hz, 1H), 3.95−3.91 (m, 1H), 3.86−3.22 (m, 1H), 3.48−3.45 (dd, *J* = 3.0, 9.5 Hz, 1H), 3.40−3.36 (m, 1H), 2.49 (d, *J* = 2.5 Hz, 1H), 2.28 (t, *J* = 6.5 Hz, 1H); ^{13}C NMR (125.6 MHz, $CDCl_3$) δ 138.1, 137.7, 135.3, 130.9, 129.3, 129.0, 128.6, 128.5, 128.4, 128.1, 128.0, 127.6, 88.1 ($^1J_{CH}$ = 154.5 Hz), 83.8, 80.3, 76.8, 75.5, 72.4, 67.7, 63.3; HRESIMS calcd for $C_{26}H_{28}O_5SNa$ $[M + Na]^+$, 475.1555; found, 475.1566.

Phenyl 2,3-di-*O*-benzyl-1,6-dithio-α-L-mannopyranoside (21α) and Phenyl 2,3-di-*O*-benzyl-1,6-dithio-β-L-mannopyranoside (21β)

Following the general procedure for making **2**, **20αβ** was converted to **21** (α/β = 1:3.5, 87%). Analytically pure samples of the two anomers were obtained by further purification of a portion of the product by radial chromatography (10% ethyl acetate in hexane). **21α**: colorless oil: $[\alpha]^{23}_D$ −53.5 (*c*, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52−7.50 (m, 2H), 7.39−7.26 (m, 13H), 5.60 (s, 1H), 4.70 (d, *J* = 12.5 Hz, 1H), 4.58 (d, *J* = 11.5 Hz, 1H), 4.57 (d, *J* = 12.0 Hz, 1H), 4.45 (d, *J* = 12.0 Hz, 1H), 4.14 (t, *J* = 9.0 Hz, 1H), 4.04−4.00 (m, 2H), 3.67−3.65 (dd,

J = 2.5, 9.5 Hz, 1H), 3.00−2.96 (dd, *J* = 9.5, 11.5 Hz, 1H), 2.83−2.77 (dt, *J* = 7.0, 14.0 Hz, 1H), 2.42 (d, *J* = 1.5 Hz, 1H), 1.59 (t, *J* = 8.5 Hz, 1H); ^{13}C NMR (125.6 MHz, $CDCl_3$) δ 137.9, 137.8 134.2, 132.2, 129.4, 128.9, 128.7, 128.4, 128.25, 128.20, 128.1, 127.9, 86.2 ($^1J_{CH}$ = 167.4 Hz), 79.8, 75.6, 74.4, 72.3, 71.8, 69.3, 26.7; HRESIMS calcd for $C_{26}H_{28}O_4S_2Na$ [M + Na]$^+$, 491.1327; found, 491.1342. **21β:** white solid; mp 99 °C; $[\alpha]^{22}_D$ +81.4 (*c*, 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58−7.47 (m, 4H), 7.38−7.25 (m, 11H), 4.97 (d, *J* = 11.5 Hz, 1H), 4.88 (d, *J* = 11.5 Hz, 1H), 4.84 (s, 1H), 4.74 (d, *J* = 12.0 Hz, 1H), 4.49 (d, *J* = 11.5 Hz, 1H), 4.21 (d, *J* = 2.0 Hz, 1H), 3.95−3.90 (dt, *J* = 3.0, 9.5 Hz, 1H), 3.43−3.40 (dd, *J* = 3.0, 9.5 Hz, 1H), 3.34−3.30 (dt, *J* = 1.5, 9.0 Hz, 1H), 2.98−2.92 (dt, *J* = 2.5, 12.5 Hz, 1H), 2.86 −2.79 (m, 1H), 2.32 (d, *J* = 1.5 Hz, 1H), 1.84−1.80 (dd, *J* = 6.0, 11.0 Hz, 1H); ^{13}C NMR (125.6 MHz, $CDCl_3$) δ 138.1, 137.6, 135.3, 131.1, 129.2, 129.0, 128.6, 128.5, 128.1, 127.6, 88.0 ($^1J_{CH}$ = 154.0 Hz), 83.8, 82.1, 76.4, 75.4, 72.2, 69.7, 27.0. HRESIMS calcd for $C_{26}H_{28}O_4S_2Na$ [M + Na]$^+$, 491.1327; found, 491.1353.

Phenyl 2,3-di-*O*-benzyl-4-*O*,6-*S*-(1-cyano)benzylidene-1,6-dithio-α-L-mannopyranoside (22α) and Phenyl 2,3-di-*O*-benzyl-4-*O*,6-*S*-(1-cyano)benzylidene-1,6-dithio-β-L-mannopyranoside (22β)

Following the general procedure for making **4**, **21αβ** was converted to **22** (α/β = 1:3.5, 75%). Analytically pure samples of the two anomers were obtained by further purification of a portion of the product by radial chromatography (5% ethyl acetate in hexane). **22α**: colorless oil: $[\alpha]^{22}_D$ −129.8 (*c*, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73−7.71 (m, 2H), 7.48−7.26 (m, 18H), 5.51 (s, 1H), 4.78 (d, *J* = 12.0 Hz, 1H), 4.74 (d, *J* = 12.0 Hz, 1H), 4.69 (t, *J* = 9.5 Hz, 1H), 4.67 (d, *J* = 12.5 Hz, 1H), 4.61 (d, *J* = 12.5 Hz, 1H), 4.44−4.39 (dt, *J* = 3.5, 9.5 Hz, 1H), 4.04−4.03 (dd, *J* = 1.0, 3.0 Hz, 1H), 3.95−3.92 (dd, *J* = 3.0, 9.5 Hz, 1H), 3.63−3.58 (dd, *J* = 11.0, 13.0 Hz, 1H), 2.91−2.87 (dd, *J* = 4.0, 13.0 Hz, 1H); ^{13}C NMR (125.6 MHz, $CDCl_3$) δ 138.3, 137.9, 135.6, 133.9, 131.4, 130.4, 129.5, 129.0, 128.7, 128.6, 128.4, 128.1, 128.0, 127.9, 125.8, 116.1, 86.9 ($^1J_{CH}$ = 169.8 Hz), 79.0, 78.4, 77.7, 76.1, 73.3, 73.1, 67.4, 31.6; HRESIMS calcd for $C_{34}H_{31}NO_4S_2Na$ [M + Na]$^+$, 604.1592; found, 604.1576. **22β:** white solid; mp 152–153 °C; $[\alpha]^{22}_D$ −6.3 (*c*, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70−7.67 (m, 2H), 7.52−7.27 (m, 18H), 5.13 (d, *J* = 11.5 Hz, 1H), 4.88 (d, *J* = 11.0 Hz, 1H), 4.82 (d, *J* = 1.0 Hz, 1H), 4.75 (d, *J* = 13.0 Hz, 1H), 4.70 (t, *J* = 9.5 Hz, 1H), 4.68 (d, *J* = 12.5 Hz, 1H), 4.20 (d, *J* = 2.5 Hz, 1H), 3.74−3.67 (m, 2H), 3.62−3.57 (dt, *J* = 4.0, 9.5 Hz, 1H), 3.04−3.00 (dd, *J* = 3.5, 13.0 Hz, 1H); ^{13}C NMR (125.6 MHz, $CDCl_3$) δ 138.1, 138.0, 135.5, 135.0, 131.7, 130.5, 129.2, 129.1, 129.0, 128.7, 128.5, 128.1, 128.0, 127.9, 125.7, 116.0, 88.8 ($^1J_{CH}$ = 153.5 Hz), 79.9, 79.0, 78.4, 78.1, 75.9, 73.5, 73.3, 31.6; HRESIMS calcd for $C_{34}H_{31}NO_4S_2Na$ [M + Na]$^+$, 604.1592; found, 604.1608.

Methyl 2,3-di-*O*-benzyl-4-*O*,6-*S*-(1-cyano)benzylidene-β-L-mannopyranosyl-(1→4)-2,3-*O*-isopropylidene-α-L-rhamnopyranoside (23)

Prepared by the general glycosylation procedure with a yield of 96.4 mg (85%). Colorless oil; $[\alpha]^{23}_D$ −3.4 (*c*, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70−7.68 (m, 2H), 7.46−7.44 (m, 5H), 7.34−7.21 (m, 8H), 4.96 (d, *J* = 12.5 Hz, 1H), 4.87 (d, *J* = 12.5 Hz, 1H), 4.85 (s, 1H), 4.65 (s, 1H), 4.59 (t, *J* = 9.5 Hz, 1H), 4.54 (s, 2H), 4.43 (t, *J* = 6.5 Hz, 1H), 4.12 (d, *J* = 6.0 Hz, 1H), 3.96 (d, *J* = 3.0 Hz, 1H), 3.72−3.66 (m, 2H), 3.61−3.58 (dd, *J* = 3.0, 9.5 Hz, 1H), 3.55−3.50 (dt, *J* = 3.5, 10.0 Hz, 1H), 3.42−3.36 (m, 1H), 3.39 (s, 3H), 2.99−2.96 (dd, *J* = 3.5, 13.0 Hz, 1H), 1.49 (s, 3H), 1.36 (d, *J* = 5.5 Hz, 3H), 1.34 (s, 3H); ^{13}C NMR (125.6 MHz, $CDCl_3$) δ 138.5, 138.3, 135.6 130.4, 129.0, 128.8, 128.5, 128.4, 127.80, 127.77, 125.7, 116.0, 109.1, 101.5 ($^1J_{CH}$ = 156.4 Hz), 98.5 ($^1J_{CH}$ = 172.1 Hz), 83.5, 79.1, 78.5, 78.0, 76.9, 75.9, 75.7, 74.7, 72.4, 69.6, 64.2, 55.1, 31.6, 28.4, 26.5, 18.1; HRESIMS calcd for $C_{38}H_{43}NO_9SNa$ [M + Na]$^+$, 712.2556; found, 712.2563.

Methyl β-L-rhamnopyranosyl-(1→4)-2,3-*O*-isopropylidene-α-L-rhamnopyranoside (24)

Prepared by the general desulfurization procedure with a yield of 28.8 mg (76%). Colorless oil; $[\alpha]^{23}_{D}$: +14.0 (*c*, 0.4, CH_3Cl); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.85 (s, 1H), 4.65 (s, 1H), 4.25 (t, *J* = 7.5 Hz, 1H), 4.13 (d, *J* = 5.5 Hz, 1H), 4.01 (s, 1H), 3.72−3.68 (m, 1H), 3.56−3.53 (dd, *J* = 7.0, 9.5 Hz, 1H), 3.49−3.40 (m, 2H), 3.37 (s, 3H), 3.31−3.28 (m, 1H), 2.87 (br s, 1H), 2.78 (br s, 1H), 2.67 (br s, 1H), 1.54 (s, 3H), 1.37 (d, *J* = 6.5 Hz, 3H), 1.36 (s, 3H), 1.29 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (125.6 MHz, $CDCl_3$) δ 109.5, 99.7, 98.3; 81.0, 76.7, 76.3, 74.8, 73.5, 72.3, 71.1, 64.8, 55.1, 28.2, 26.4, 17.9, 17.6; HRESIMS calcd for $C_{16}H_{28}O_9Na$ $[M + Na]^+$, 387.1631; found, 387.1640.

Methyl 2,3-di-*O*-benzyl-4-*O*,6-*S*-(1-cyano)benzylidene-β-L-mannopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-α-D-glucopyranoside (25β) and Methyl 2,3-di-*O*-benzyl-4-*O*,6-*S*-(1-cyano) benzylidene-α-L-mannopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-α-D-glucopyranoside (25α)

Prepared by the general glycosylation procedure with a combined yield of 98.7 mg (63%, α/β = 1:9.6). **25β:** Colorless oil; $[\alpha]^{23}_{D}$ +67.2 (*c*, 2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 −7.65 (m, 2H), 7.45−7.13 (m, 13H), 5.48 (t, *J* = 9.0 Hz, 1H), 4.87−4.74 (m, 4H), 4.49−4.40 (m, 5H), 4.36−4.31 (dd, *J* = 7.0, 15.0 Hz, 1H), 3.86−3.81 (m, 1H), 3.73−3.9 (m, 2H), 3.61−3.55 (dd, *J* = 13.0, 16.0 Hz, 1H), 3.47−3.40 (m, 2H), 3.42 (s, 3H), 2.95− 2.91 (dd, *J* = 4.0, 16.5 Hz, 1H), 2.08 (s, 6H), 1.90 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 170.7, 170.6, 169.6, 138.5, 138.1, 135.5, 130.4, 129.0, 128.7, 128.6, 128.4, 127.9, 127.7, 125.7, 115.8, 102.5 ($^1J_{CH}$ = 162.0 Hz), 96.9 ($^1J_{CH}$ = 172.3 Hz), 79.0, 77.5, 76.5, 76.4, 75.2, 72.4, 72.1, 71.1, 69.8, 68.1, 63.2, 55.6, 31.5, 21.1, 21.0; HRESIMS calcd for $C_{41}H_{45}NO_{13}SNa$ $[M + Na]^+$, 814.2509; found, 814.2465. **25α:** Colorless oil; $[\alpha]^{22}_{D}$ −15.2 (*c*, 0.25, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69−7.67 (m, 2H), 7.46−7.27 (m, 13H), 5.41 (t, *J* = 9.5 Hz, 1H), 4.89 (d, *J* = 12.5 Hz, 1H), 4.86 (d, *J* = 4.0 Hz, 1H), 4.78−4.75 (ddd, *J* = 1.0, 4.0, 10.0 Hz, 1H),4.73 (s, 1H), 4.69 (d, *J* = 12.5 Hz, 1H), 4.68 (d, *J* = 12.5 Hz, 1H), 4.62−4.56 (m, 2H), 4.17−4.14 (dd, *J* = 1.5, 12.5 Hz, 1H), 4.04−4.00 (dd, *J* = 4.0, 12.0 Hz, 1H), 3.94−3.89 (dt, *J* = 3.5, 10.0 Hz, 1H), 3.84−3.81 (dd, *J* = 3.0, 10.0 Hz, 1H), 3.77 (d, *J* = 10.0 Hz, 1H), 3.71 (s, 1H), 3.57 (t, *J* = 10.0 Hz, 1H), 3.48 −3.43 (dd, *J* = 11.0, 12.5 Hz, 1H), 3.40 (s, 3H), 2.97−2.93 (dd, *J* = 3.5, 13.0 Hz, 1H), 2.10 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (125.6 MHz, $CDCl_3$) δ 170.6, 170.5, 138.5, 138.2, 135.7, 130.3, 129.0, 128.7, 128.6, 128.3, 128.0, 127.9, 125.7, 116.1, 101.0 ($^1J_{CH}$ = 172.6 Hz), 97.1 ($^1J_{CH}$ = 174.0 Hz), 78.9, 78.1, 77.9, 76.6, 76.4, 75.2, 73.9, 73.1, 71.5, 71.2, 68.1, 67.3, 62.1, 55.7, 31.1, 21.5, 21.02, 20.95; HRESIMS calcd for $C_{41}H_{45}NO_{13}SNa$ $[M + Na]^+$, 814.2509; found, 814.2485.

Methyl β-L-rhamnopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-α-D-glucopyranoside (26)

Prepared by the general desulfurization procedure with a yield of 14.5 mg (72%). Colorless gel; $[\alpha]^{23}_{D}$ +137.5 (*c*, 0.2, CH_3OH); ^{1}H NMR (500 MHz, CD_3OD) δ 5.45 (t, *J* = 10.0 Hz, 1H), 4.80−4.78 (dd, *J* = 3.5, 10.5 Hz, 1H), 4.54 (s, 1H), 4.48−4.45 (dd, *J* = 1.5, 12.0 Hz, 1H), 4.35 −4.31 (dd, *J* = 5.0, 12.0 Hz, 1H), 3.93− 3.90 (ddd, *J* = 1.5, 5.5, 10.0 Hz, 1H), 3.86 (t, *J* = 9.5 Hz, 1H), 3.72 (d, *J* = 2.5 Hz, 1H), 3.40 (s, 3H), 3.38−3.27 (m, 1H), 3.22−3.17 (m, 1H), 2.08 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H), 1.29 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (125.6 MHz, CD_3OD) δ 171.5, 170.6, 101.2, 96.9, 75.4, 73.8, 72.6, 72.4, 72.3, 71.5, 71.2, 68.3, 63.4, 54.5, 19.7, 19.3, 16.7; HRESIMS calcd for $C_{19}H_{30}O_{13}Na$ $[M + Na]^+$, 489.1584; found, 489.1557.

Methyl 2,3-di-*O*-benzyl-4-*O*,6-*S*-(1-cyano)benzylidene-β-L-mannopyranosyl-(1→4)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (27)

Prepared by the general glycosylation procedure with a yield of 134.0 mg (81%). Colorless gel; $[\alpha]^{22}_{D}$ +61.4 (*c*, 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03−7.90 (m, 6H), 7.69 −7.22 (m, 24H), 6.21 (t, *J* = 9.5 Hz, 1H), 5.64 (t, *J* = 9.5 Hz, 1H), 5.29−5.26 (dd, *J* = 4.0, 10.0 Hz, 1H), 5.24 (d, *J* = 3.5 Hz, 1H), 4.84 (d, *J* = 12.5 Hz, 1H), 4.75 (d, *J* = 12.5 Hz, 1H), 4.56

(t, J = 9.5 Hz, 1H), 4.52 (s, 1H), 4.51 (d, J = 12.5 Hz, 1H), 4.46 (d, J = 12.5 Hz, 1H), 4.29−4.25 (dt, J = 4.0, 10.0 Hz, 1H), 4.22−4.19 (dd, J = 4.0, 11.0 Hz, 1H), 3.83 (d, J = 2.5 Hz, 1H), 3.81 −3.78 (dd, J = 3.5, 11.0 Hz, 1H), 3.64−3.59 (dd, J = 11.0, 13.0 Hz, 1H), 3.57−3.51 (m, 2H), 3.50−3.45 (m, 1H), 3.49 (s, 3H), 2.95−2.91 (dd, J = 3.5, 13.0 Hz, 1H); ^{13}C NMR (125.6 MHz, $CDCl_3$) δ 166.14, 166.08, 165.5, 138.6, 138.3, 135.6, 133.73, 133.68, 133.4, 130.4, 130.2, 130.1, 129.9, 129.5, 129.4, 129.3, 129.0, 128.8, 128.7, 128.6, 128.4, 127.84, 127.76, 1277.7, 125.4, 116.0, 102.0 ($^1J_{CH}$ = 157.3 Hz), 97.2 ($^1J_{CH}$ = 178.6 Hz), 79.1, 77.9, 77.8, 75.5, 74.8, 72.4, 72.1, 70.61, 70.56, 69.7, 68.9, 68.8, 56.0, 31.5; HRESIMS calcd for $C_{56}H_{51}NO_{13}SNa$ $[M + Na]^+$, 1000.2979; found, 1000.2957.

Methyl β-L-rhamnopyranosyl-(1→4)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (28)

Prepared by the general desulfurization procedure with a yield of 33.2 mg (76%). White solid; mp 156−157 °C; $[\alpha]^{23}_D$ +91.2 (*c*, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00−7.87 (m, 6H), 7.53−7.26 (m, 9H), 6.14 (t, J = 9.5 Hz, 1H), 5.78 (t, J = 10.0 Hz, 1H), 5.29−5.26 (m, 2H), 4.54 (s, 1H), 4.27 (d, J = 10.0 Hz, 1H), 4.18−4.15 (dd, J = 4.0, 11.0 Hz, 1H), 4.00 (s, 1H), 4.04 (d, J = 10.0 Hz, 1H), 3.80−3.78 (dd, J = 2.0, 11.0 Hz, 1H), 3.47 (s, 3H), 3.43−3.36 (m, 2H), 3.21−3.15 (m, 1H), 3.05−2.90 (br, 1H), 2.90−2.74 (br, 1H), 2.04−1.84 (br, 1H), 1.05 (d, J = 6.0 Hz, 3H); ^{13}C NMR (125.6 MHz, $CDCl_3$) δ 166.1, 165.9, 133.7, 133.6, 133.4, 130.2, 130.1, 129.9, 129.44, 129.40, 129.3, 128.7, 128.5, 99.2, 97.5, 74.7, 73.7, 72.5, 71.9, 70.8, 70.7, 69.2, 68.6, 66.3, 56.0, 17.3; HRESIMS calcd for $C_{34}H_{36}O_{13}Na$ $[M + Na]^+$, 675.2054; found, 675.2016.

2,3-Di-*O*-benzyl-4-*O*,6-*S*-(1-cyano)benzylidene-β-D-mannopyranosyl-(1→3)-1,2:5,6-di-isopropylidene-α-D-glucofuranose (29)

Prepared by the general glycosylation procedure with a yield of 95.5 mg (84%). Colorless oil; $[\alpha]^{23}_D$ −12.3 (*c*, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70−7.68 (m, 2H), 7.47−7.43 (m, 5H), 7.35−7.23 (m, 8H), 5.92 (d, J = 3.5 Hz, 1H), 4.90 (s, 2H), 4.79 (d, J = 3.0 Hz, 1H), 4.63−4.58 (m, 4H), 4.18 (d, J = 2.5 Hz, 1H), 4.07−4.02 (m, 2H), 3.94−3.90 (m, 2H), 3.85−3.82 (m, 1H), 3.70−3.66 (dd, J = 4.0, 13.5 Hz, 1H), 3.60−3.56 (m, 2H), 3.07−3.04 (dd, J = 3.5, 13.0 Hz, 1H), 1.50 (s, 3H), 1.34 (s, 3H), 1.33 (s, 3H), 1.19 (s, 3H); ^{13}C NMR (125.6 MHz, $CDCl_3$) δ 138.2, 135.5, 130.5, 129.05,128.98, 128.6, 128.5, 128.0, 127.92, 127.87, 125.7, 115.9, 112.3, 109.3, 105.7 ($^1J_{CH}$ = 184.1 Hz), 102.8 ($^1J_{CH}$ = 159.0 Hz), 84.4, 83.4, 81.3, 79.1, 78.12, 78.09, 74.9, 74.7, 72.7, 72.6, 69.7, 68.2, 31.6, 27.1, 26.5, 25.6; HRESIMS calcd for $C_{40}H_{45}NO_{10}SNa$ $[M + Na]^+$, 754.2662; found, 754.2661.

β-L-rhamnopyranosyl-(1→3)-1,2:5,6-di-isopropylidene-α-D-glucofuranose (30)

Prepared by the general desulfurization procedure with a yield of 23.7 mg (77%). Colorless oil; $[\alpha]^{12}_D$: −8.7 (*c*, 0.15, CH_3Cl); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.93 (d, J = 4.0 Hz, 1H), 4.74 (d, J = 3.5 Hz, 1H), 4.66 (s, 1H), 4.31−4.27 (m, 1H), 4.22 (d, J = 3.0 Hz, 1H), 4.16−4.13 (dd, J = 6.5, 9.0 Hz, 1H), 4.11−4.08 (dd, J = 3.0, 9.0 Hz, 1H), 4.07 (s, 1H), 4.04−4.01 (dd, J = 5.0, 9.0 Hz, 1H), 3.48−3.42 (m, 2H), 3.36−3.30 (m, 1H), 1.52 (s, 3H), 1.44 (s, 3H), 1.41 (d, J = 6.0 Hz, 3H), 1.35 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (125.6 MHz, CD_3OD) δ 111.8, 109.6, 105.6, 101.7, 84.3, 82.4, 81.1, 73.8, 72.9, 72.7, 72.6, 71.0, 67.1, 26.0, 25.9, 25.3, 24.4, 16.9; HRESIMS calcd for $C_{18}H_{30}O_{10}Na$ $[M + Na]^+$, 429.1737; found, 429.1715.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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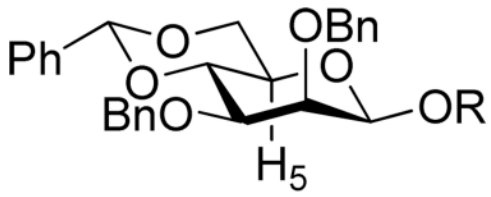
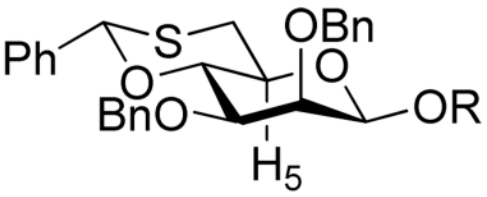
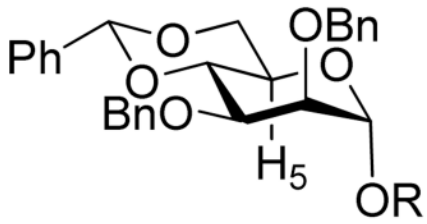


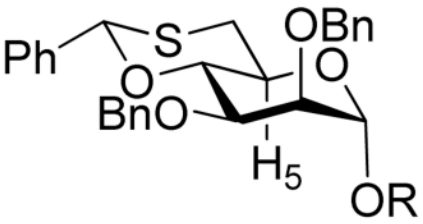
dH5: 3.0-3.4



dH5: 3.4-3.5

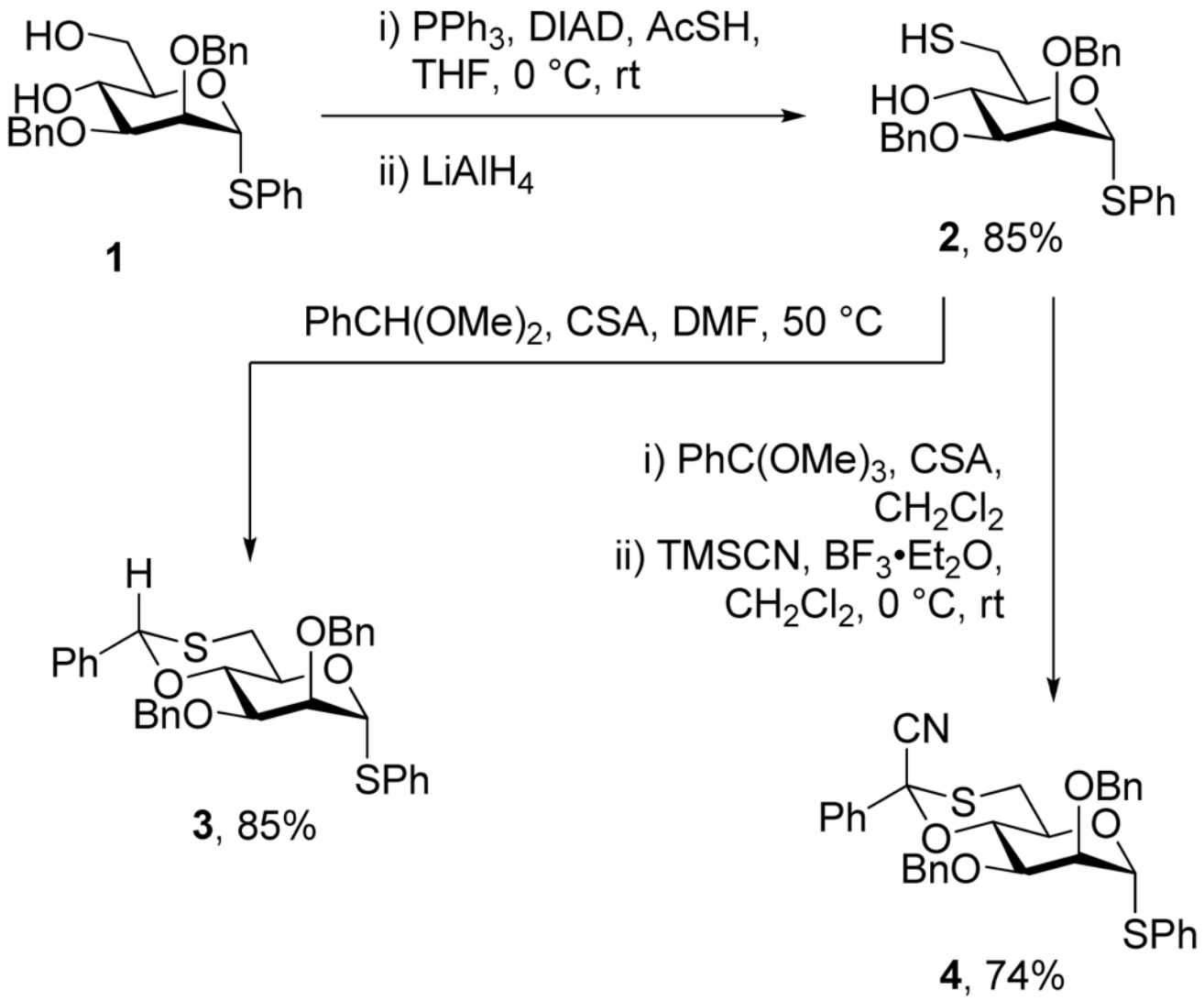


dH5: 3.6-3.9

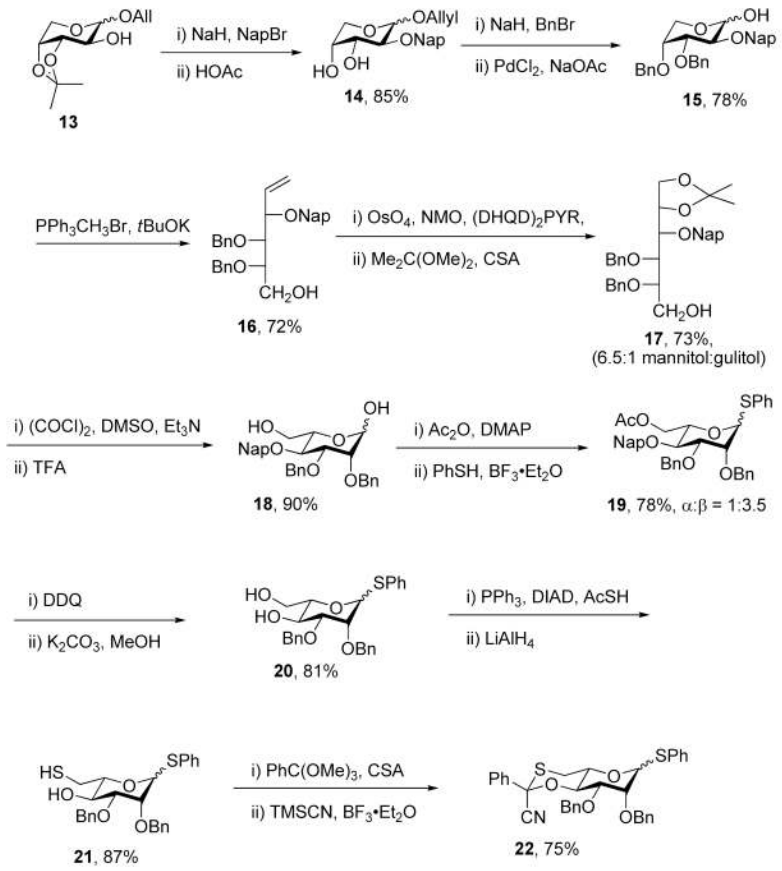


dH5: 3.9-4.1

Figure 1.
Diagnostic Chemical Shifts.



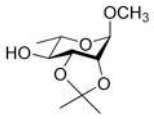
Scheme 1.
Synthesis of Two D-Rhamnopyranosyl Donors.

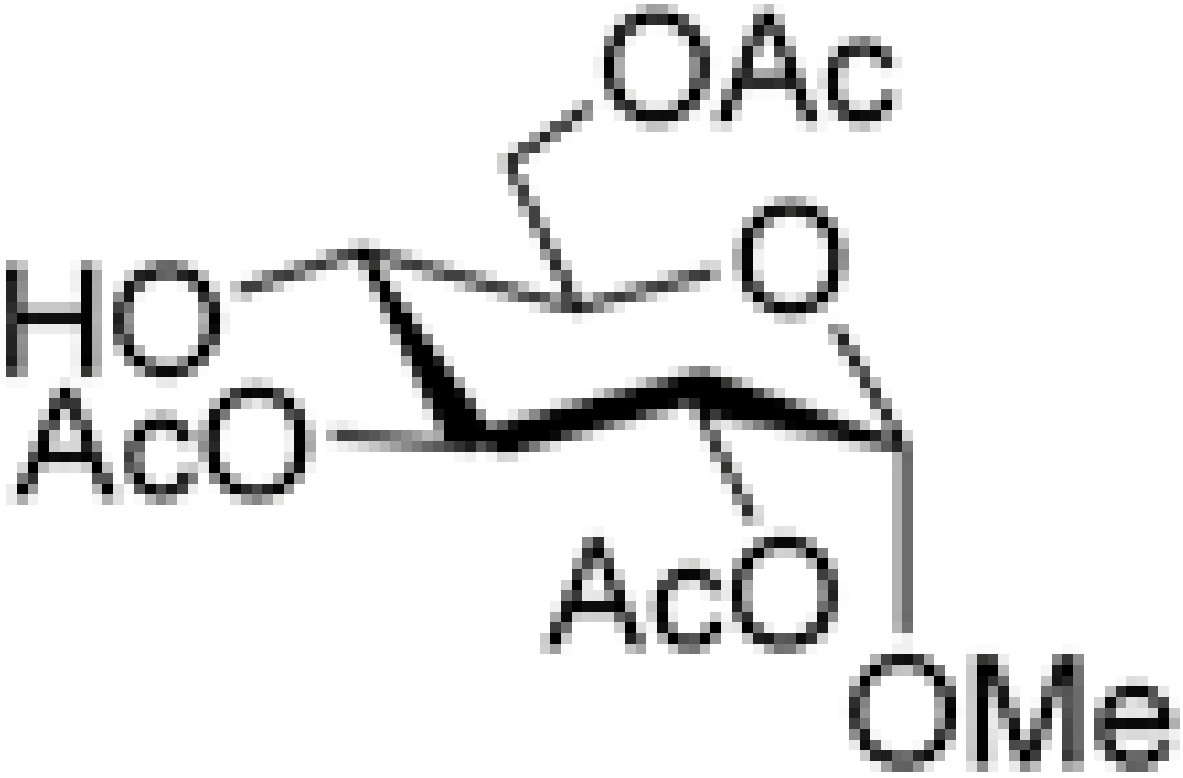


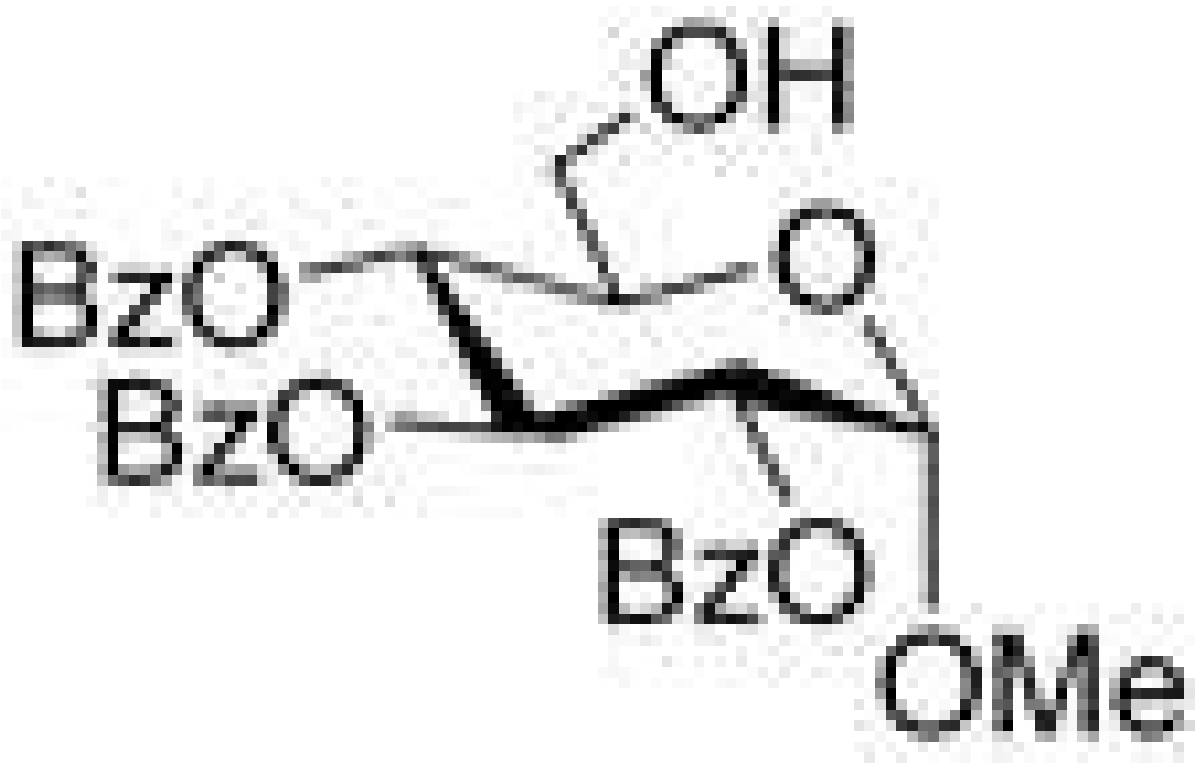
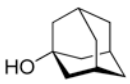
Scheme 2.
Synthesis of the Enantiomeric Donor **22**.

Table 1

Formation of β-D-Rhamnopyranosides by Means of Donor **4**.

Entry	Acceptor
1	

Entry	Acceptor
2	

Entry	Acceptor
3	
4	

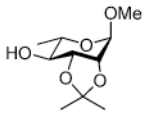
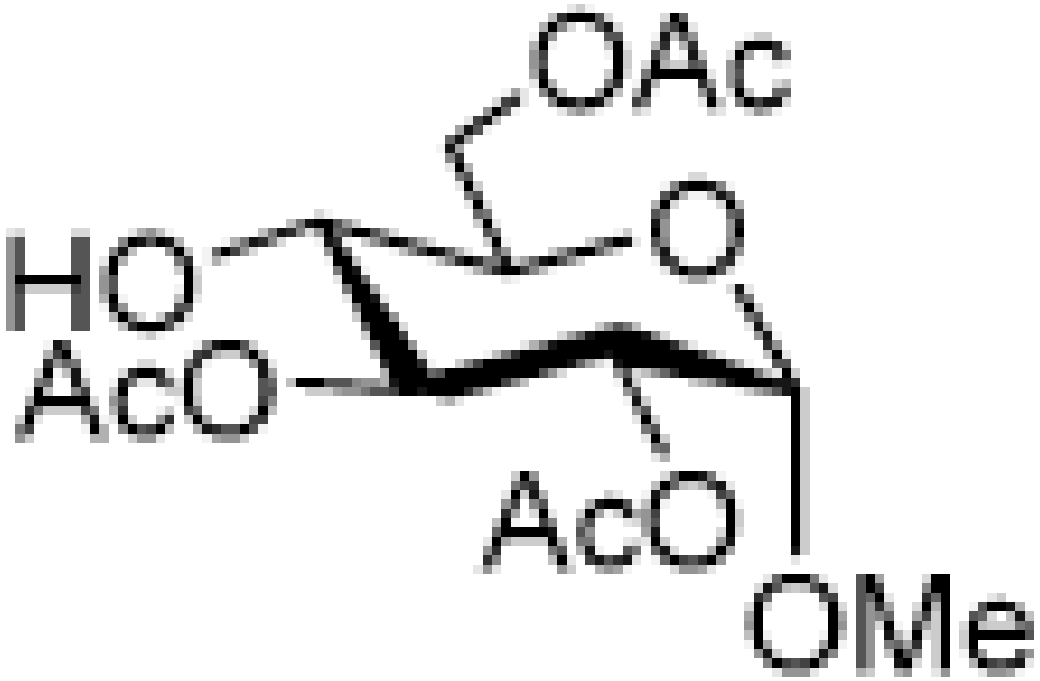
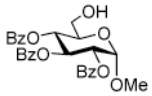
[a] determined by ^{1}H-NMR spectroscopy on the crude reaction mixture.

[b] ratio determined after chromatographic purification.

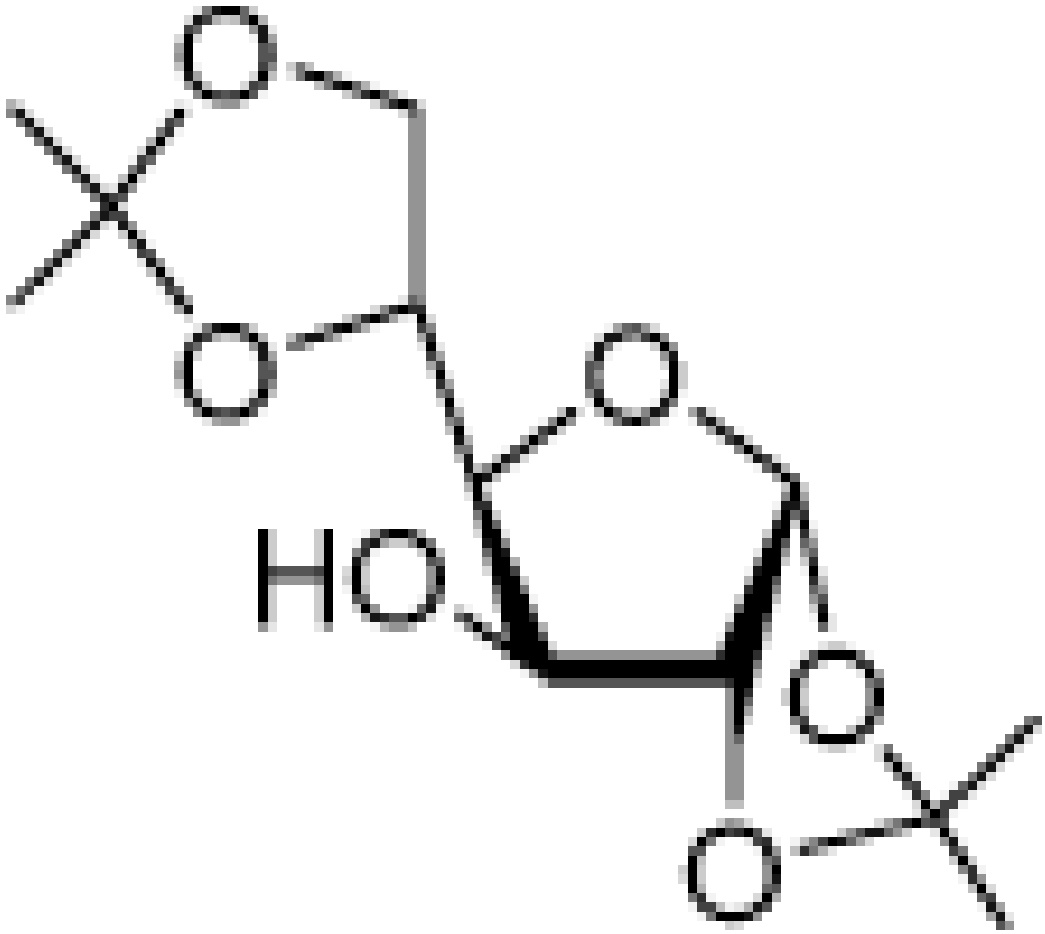
[c] Desulfurization was conducted with anomerically pure β-mannosides.

Table 2

Formation of β-L-Rhamnopyranosides by Means of Donor **22**.

Entry	Acceptor
1	
2	
3	

Ph

Entry	Acceptor
4	

[a] determined by ^{1}H-NMR spectroscopy on the crude reaction mixture.

[b] ratio determined after chromatographic purification.

[c] Desulfurization was conducted with anomerically pure β-mannosides