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NAP Ether Mediated Intramolecular Aglycon Delivery: A Unified Strategy for 1,2-*cis*-Glycosylation

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A methodology directed towards the stereoselective construction of 1,2-*cis*-glycosides through naphthylmethyl (NAP) ether mediated intramolecular aglycon derivery (IAD) has been developed. Stereospecific constructions of various 1,2-*cis* linkages, as in β-mannopyrano-, β-arabinofurano-, and α-glucopyranosides, were achieved through NAP-IAD. This methodology was successfully applied to the synthesis of Glcα(1→2)-Glcα(1→3)-Glcα(1→3)Man (Glc_3Man_1), the non-reducing terminal structure of the tetradecasaccharide $Glc_3Man_9GlcNAc_2$, a common precursor of all *N*-linked glycans.

Introduction

1,2-*cis* Glycoside linkages, as found in β-mannopyranoside, β-arabinofuranoside, and α-glucopyranoside, are prevalent in natural glycans, including glycoproteins,[1] glycolipids,[2] proteoglycans,[3] microbial polysaccharides,[4] and bioactive natural products.[5] Stereoselective synthesis of 1,2-*cis*-glycosides is potentially problematic.[6] Although the key factors that control the stereoselectivity of glycosylation have largely been elucidated, exclusive formation of the desired isomer is generally difficult. To achieve this, a number of strategies directed towards 1,2-*cis*-glycosides have been explored.[7] Among them, approaches based on intramolecular aglycon delivery (IAD) are of special promise, because they would be expected to ensure the exclusive formation of 1,2-*cis*-glycosides.[8]

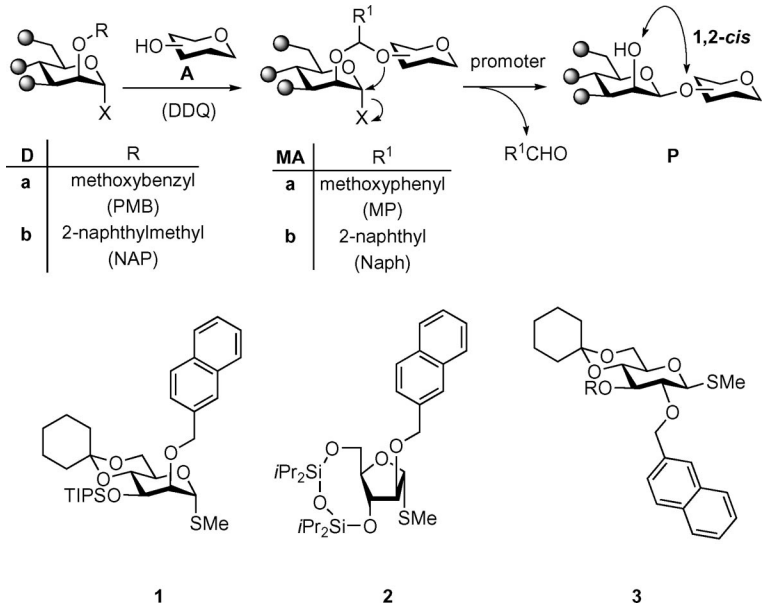

Figure 1. Intramolecular aglycon delivery using NAP ether protected glycosyl donors.

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The concept of IAD was first proposed by Baressi and Hindsgaul,[9] who employed an isopropylidene mixed acetal as a tether for β-mannopyranosylation. Subsequent work by Stork et al.[10] explored the use of silaketals[11,12] for similar purposes. Following these pioneering reports, newer versions of IAD using various types of tethers have been developed.[13] Our approach[14] took advantage of the special reactivity of *p*-methoxybenzyl (PMB) ethers (Figure 1).[15,16] Namely, a 2-*O*-PMB-protected mannosyl donor (**Da**) was cleanly converted into the mixed acetal (**MAa**) upon oxidative activation with DDQ. Subsequent activation of the thioglycosidic linkage initiated the rearrangement of an aglycon from the *p*-methoxybenzylidene acetal moiety to give a desired β-mannopyranoside (Man*p*, **P**). The practicality of this approach was shown in the syntheses of high-mannose-type[17] and complex-type[18] *N*-glycans.

Since the 2-naphthylmethyl (NAP) group[19] has properties similar to those of PMB,[20] being removable with DDQ,[21] it was expected that IAD with a 2-*O*-NAP-protected donor (**Db** → **MAb** → **P**) should be possible (Figure 1).[22] In fact, NAP-assisted IAD turned out to be highly versatile, giving various types of 1,2-*cis*-glycosides in high yields.

Results and Discussion

As we had already established the protocol for β-Man*p* formation through PMB-assisted IAD, we attempted a similar reaction with the 2-*O*-NAP-protected thiomannoside **1**.[23] As shown in Scheme 1, the formation of MA **5** proceeded quantitatively, and subsequent IAD (MeOTf–DTBMP[24]) cleanly gave β-Man*p* **6** after acetylation.

As in the case of the 2-*O*-PMB-substituted donor, the MA **5** was stereochemically homogeneous, most likely having the (*S*) configuration.[14b] Obviously, the efficiency of NAP-assisted IAD was even higher than that of its PMB-assisted counterpart, requiring only 1.05 equiv. of the donor **1** to give **6** in 90% yield.

Having observed the efficacy of NAP-IAD β-mannosylation, we turned our attention to β-arabinofuranoside (Ara*f*) formation.[16] β-Ara*f* has also been considered a difficult linkage in oligosaccharide synthesis.[25] In fact, during our synthetic studies directed towards mycobacterial arabinan,[26,27] we faced a difficulty in constructing the nonreducing terminal β-Ara*f*-(1,2)-Ara*f* linkage. Our former attempt to solve this problem had met with partial success through the choice of appropriate protecting groups,[26] especially 3,5-*O*-tetraisopropyldisiloxanylidene (TIPDS).[27] The stereoselectivity of the glycosylations was highly dependent upon the structure of the acceptor.

In the case of β-mannopyranosylation, the stereochemical outcome of IAD is obvious: the pathway directed towards the corresponding α-glycosides is essentially prohibited. Namely, the axial orientation of the NAP ether at the C-2 position (**MA1**) guarantees the formation of the β-glycoside (Figure 2). Although the pathway directed towards α-Ara*f* through IAD is also disfavored, because it requires the intermediacy of a *trans*-fused bicyclo[5.5.0] system (**MA2**), we employed the perdeuterated benzyl-protected ([D_7]Bn) Ara*f* derivative **7** as an acceptor to allow critical evaluation of the stereochemical homogeneity of the product (Scheme 2).[28,29]

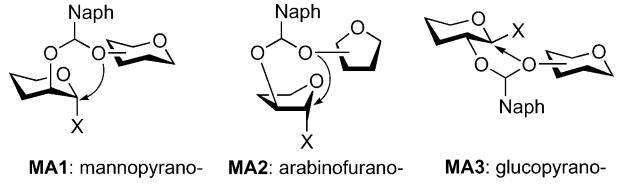
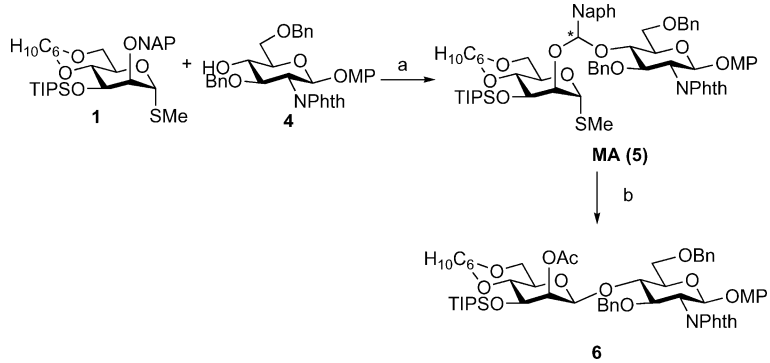


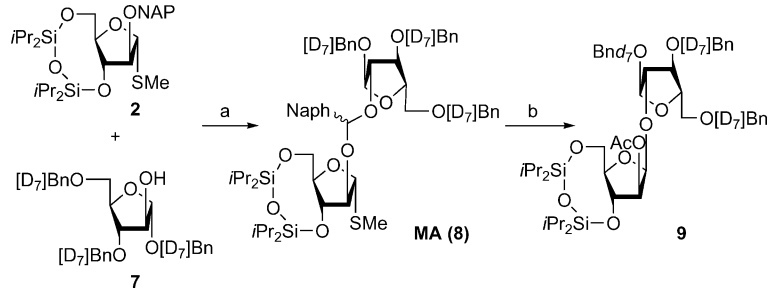
Figure 2. 1,2-*cis* induction via mixed acetals.

In fact, formation of the mixed acetal **8** from Ara*f* donor **2**[23] and acceptor **7**[23] proceeded cleanly to give **8** as a 3.4:1 mixture of diastereomers. Subsequent IAD provided **9** in satisfactory yield after acidic workup and acetylation. The anomeric configuration was assigned by ^{1}H NMR spectroscopy: The signal of 1-H of β-Ara*f* appeared as a singlet at δ = 4.93 ppm.

On the other hand, the stereochemical outcome of the α-glucopyranoside (α-Glc) formation is less obvious (Figure 2). In this case, the NAP ether at the C-2 position is equatorially oriented, and IAD directed towards 1,2-*trans*-β-Glc may not be completely prohibited (**MA3**). In order



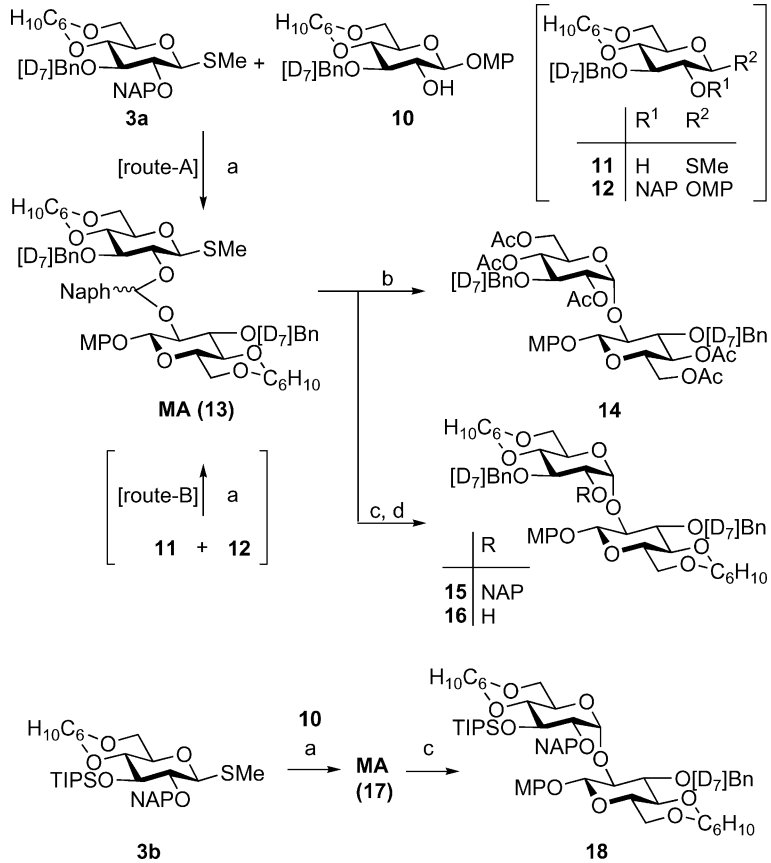
Scheme 1. NAP-IAD for β-mannopyranoside; reagents and conditions: (a) DDQ, MS (4 Å), $(CH_2Cl)_2$, room temp., quant. (single isomer); (b) (i) MeOTf, DTBMP, $(CH_2Cl)_2$, r.t.; (ii) Ac_2O, pyridine, 90% (only β-isomer).



Scheme 2. NAP-IAD for β-arabinofuranoside; reagents and conditions: (a) DDQ, MS (4 Å), $(CH_2Cl)_2$, quant. (3.40:1); (b) (i) MeOTf, DTBMP, $(CH_2Cl)_2$, r.t.; (ii) TFA; (iii) Ac_2O, pyridine, 77% (β-**9**).

to examine the stereospecificity of α-Glc formation through IAD, the mixed acetal **13** was prepared. As shown in Scheme 3, smooth formation of **13** from **3a**[23] and **10**[29] (route A) took place (diastereomers 3.18:1). The same **13** was also prepared from 2-*O*-unprotected donor **11**[23] and 2-*O*-NAP acceptor **12**[23] (route B). Interestingly, the diastereomeric composition according to route B (1:4.17) was the opposite of that according to route A. The subsequent intramolecular glycosylation of **13** afforded the desired 1,2-*cis*-glycoside in good yield as pentaacetate **14** after acidic treatment and acetylation.[30]

In our synthetic study on glucose-branched high-mannose-type *N*-glycans, the construction of α-Glc(1→2)-α-Glc(1→3)-α-Glc(1→3)Man (Figure 3) is problematic.[28,29] We thought that the 1,2-*cis*-α-glucosylation through NAP-mediated IAD could be applicable to the synthesis of structure **21**, with three continuous α-Glc units.[13d,13e,13h,31,32] For the synthesis of this structure, it would be necessary to retain cyclohexylidene acetals on the IAD product to afford **22**. We found that the addition of $(TMS)_3SiH$[33] was effective for the reductive in situ trapping of benzylic cation **20**, generated from an activated **19** at the last stage of IAD



Scheme 3. NAP-IAD for α-glucosides; reagents and conditions: (a) DDQ, MS (4 Å), CH_2Cl_2, room temp., 96% (3.18:1) from **3a** (route A); 93% (1:4.17) from **11** (route B); 84% (>10:1) from **3b**; (b) (i) MeOTf, DTBMP, $(CH_2Cl)_2$, r.t.; (ii) TFA; (iii) Ac_2O, pyridine, 72% (α-**14**); (c) MeOTf, DTBMP, $(TMS)_3SiH$, $(CH_2Cl)_2$, room temp., 73% (α-**15**) and 16% (α-**16**); 82% (α-**18**); (d) DDQ, 85% (**16**) in two steps from **13**.

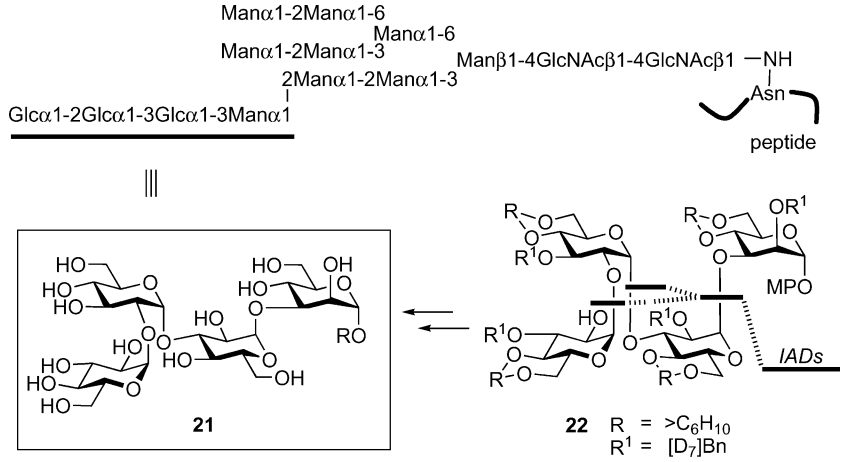
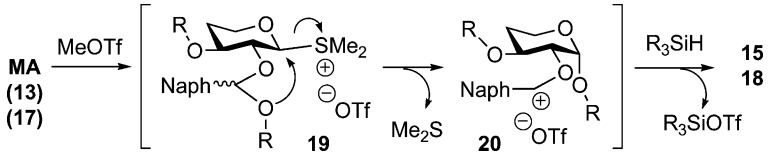


Figure 3. Triglucosylated high-mannose-type *N*-glycan.



Scheme 4.

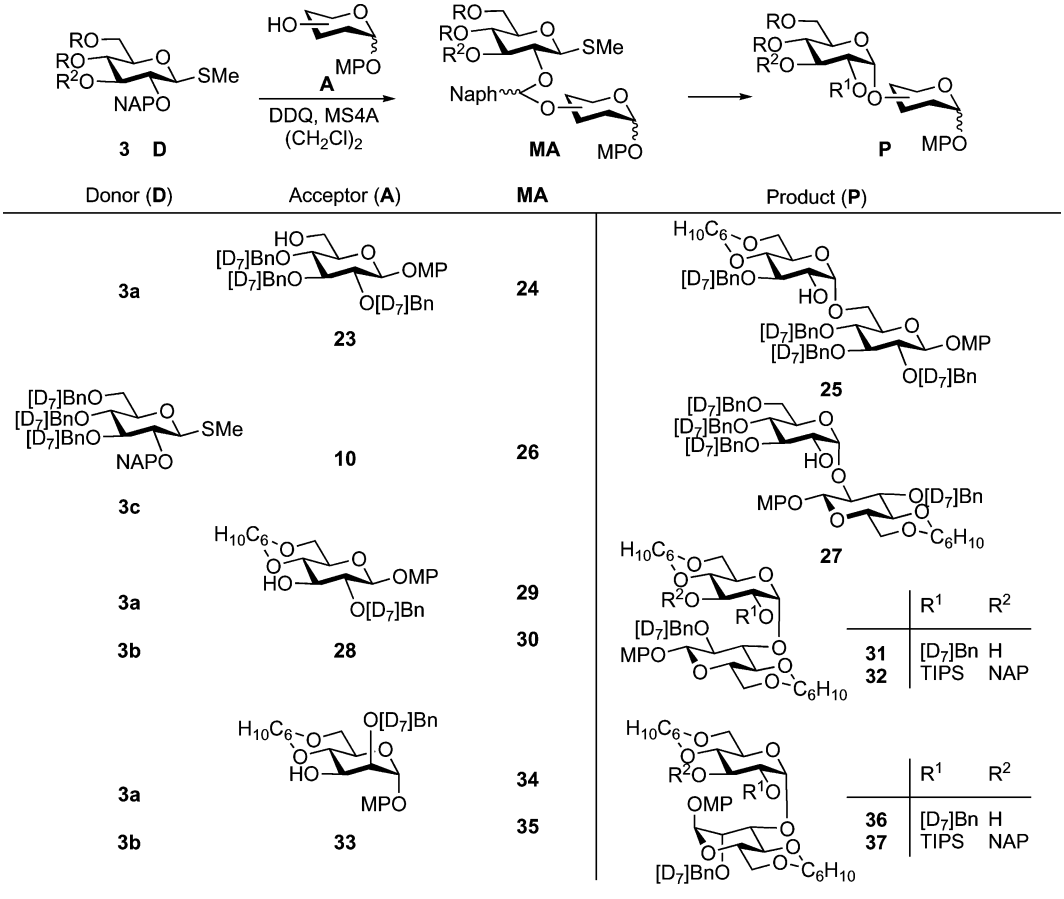


Figure 4. α-Glucosylation via NAP-IAD.

(Scheme 4). Interestingly, IAD of **3b**[23] with **10** gave NAP ether **18** (82%) as sole product. The advantage of IAD with the reducing additive is the regeneration of the NAP ether in the product; this can be used not only as the orthogonal protective group but also as the key functionality of a subsequent NAP-IAD for further elongation. IAD of **13** in the presence of $(TMS)_3SiH$ also afforded NAP ether **15** (73%), together with **16** (16%) (Scheme 3). The crude mixture (**15** and **16**) was immediately treated with DDQ to give the sole product **16**, with the desired α-stereochemistry.[34]

NAP-IAD of **3a** with **23**[23] as primary alcohol afforded the desired α-**25**[23] as a single isomer through **24** (Figure 4, Table 1, Entry 1). IAD of **3c**[23] with **10**, however, gave a mixture of anomers (Entry 2). It is therefore clear that the cyclic protection at the 4,6-positions[14g] of the donor seemed to be important for control of the 1,2-*cis* stereoselectivity.

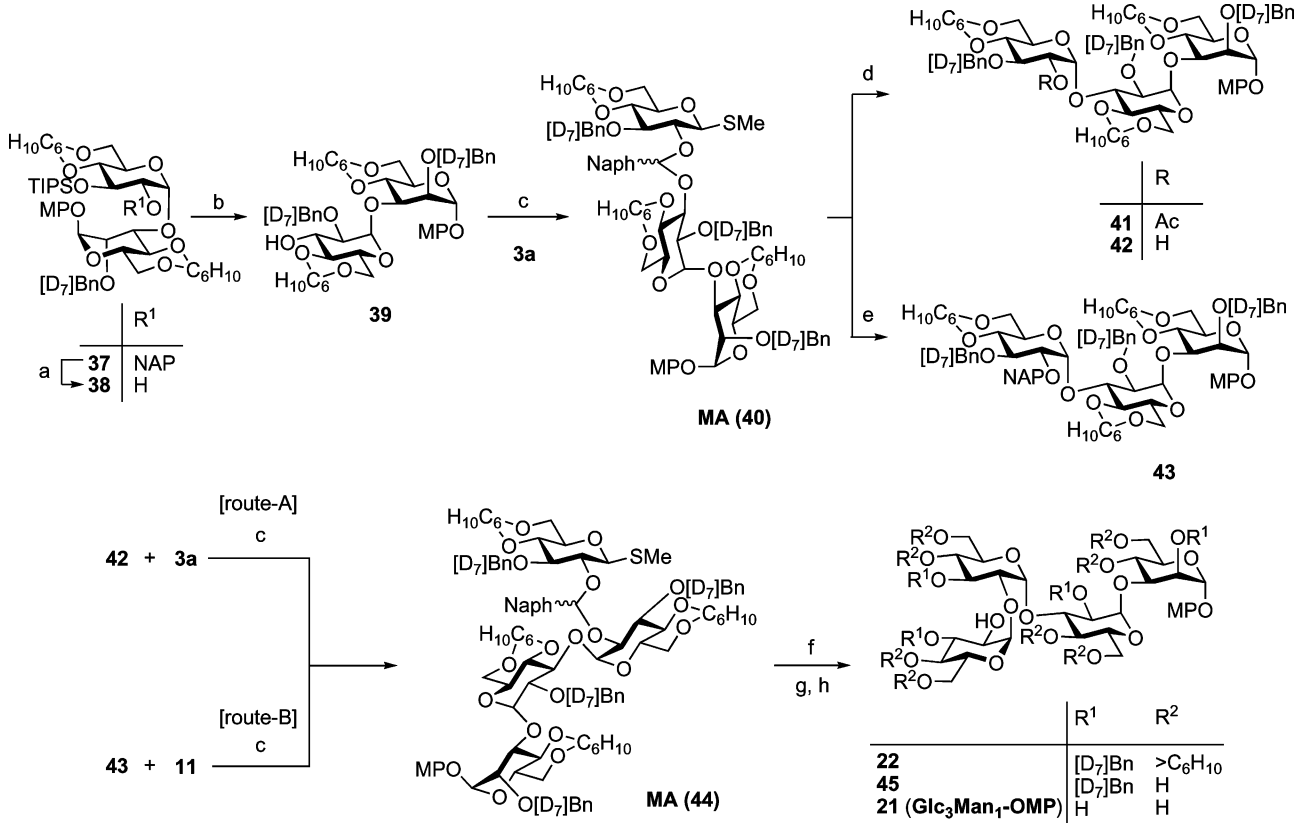
For the synthesis of **21**, NAP-IAD of glucose and mannose acceptors (**28**, **33**) with cyclohexylidene-protected donors (**3a**, **3b**) were examined through MAs (**29**, **30** and **34**, **35**) (Figure 4, Table 1, Entries 3–6). In all cases, the desired α-isomers (**31**, **32** and **36**, **37**) were obtained in high yields with complete stereoselectivity.

Finally, NAP-IAD was applied to the construction of **21** with the iterative α-glucosidic linkages (Scheme 5). Three-step conversion of **37**, obtained by NAP-IAD (Table 1), afforded acceptor **39** in good yield. In the second IAD of **39** with **3a**, formation of a MA **40** followed by intramolecular glycosylation resulted in a stereoselective formation of **42** via acetate **41** in good yield. In the third NAP-IAD, however, mixed acetalization between **42** with **3a** (route A) afforded **44** in low yield (50%). In route B, treatment of **11** with **43**, prepared from **40** (76%), resulted in almost quantitative conversion into MA **44**.[35] Intramolecular glycosylation of **44** gave **22** as sole product in 77% yield. After conventional deprotection, the synthesis of Glc_3Man_1-OMP (**21**) was accomplished in high yield and with complete stereoselectivity.

Table 1. NAP-IAD for various α-glucosides; yields for formation of MA and glycosylation.[a]

Entry	D	A	MA (%, *dr*[b])	Glucoside (%)
1	**3a**	**23**	**24** (91, 2.32:1)	**25**[c] (63, α)
2	**3c**	**10**	**26** (94, 3.11:1)	**27**[c] (77[d])
3	**3a**	**28**	**29** (97, 3.00:1)	**31**[c] (89, α)
4	**3b**	**28**	**30** (84, 11.1:1)	**32** (83, α)
5	**3a**	**33**	**34** (97, 3.11:1)	**36**[c] (74, α)
6	**3b**	**33**	**35** (84, 14.3:1)	**37** (86, α)

[a] MeOTf, DTBMP, and $(TMS)_3SiH$ were used for intramolecular glycosylation. [b] Diastereomer ratio. [c] DDQ workup. [d] α/β = 2.17:1.



Scheme 5. Synthesis of Glc_3Man_1-OMP **21**; reagents and conditions: (a) DDQ, $NaHCO_3$, $(CH_2Cl)_2$, 86%; (b) $[D_7]BnBr$, NaH, DMF; then TBAF, THF, 75% in two steps; (c) DDQ, MS (4 Å), CH_2Cl_2, 96% (2.72:1) (**40**), 47% (2.33:1) (**44**) from **42** (route A), 97% (3.43:1) (**44**) from **43** (route B); (d) (i) MeOTf, DTBMP, MS (4 Å), $(CH_2Cl)_2$; (ii) Ac_2O pyridine, 85% (**41**); (iii) NaOMe, MeOH, 88% (**42**); (e) MeOTf, DTBMP, $(TMS)_3SiH$, MS (4 Å), $(CH_2Cl)_2$, 76% (**43**) and 6% (**42**); (f) (i) MeOTf, DTBMP, $(TMS)_3SiH$, CH_2Cl_2; (ii) DDQ, $NaHCO_3$, $(CH_2Cl)_2$, 77%; (g) TFA; (h) $Pd(OH)_2$, H_2, MeOH/H_2O (2:1), quant. in two steps.

Conclusions

We have developed a methodology directed towards the stereoselective construction of 1,2-*cis*-glycosides through the use of NAP ether mediated IAD. It was applied with high generality to the construction of various 1,2-*cis* linkages, such as β-Man*p*, β-Ara*f*, and α-Glc*p*. The complete stereoselective synthesis of a Glc_3Man_1 derivative containing three continuous 1,2-*cis* linkages in a high-mannose-type *N*-glycan was successfully achieved. This clearly suggests that this novel stereospecific IAD methodology is highly efficient, useful, and practical.[36]

Experimental Section

General Methods: All reactions sensitive to air and/or moisture were carried out under nitrogen or argon in anhydrous solvents. Column chromatography was performed on silica gel 60N, 100–210 mesh (Kanto Kagaku Co., Ltd.). Preparative TLC was performed on silica gel 60 F_{254}, 0.5 mm (E. Merck). Gel filtration was performed on Sephadex LH-20 (Pharmacia). All other reagents were purchased from Wako Pure Chemical Industries Ltd., Kanto Chemicals Co. Inc., Tokyo Kasei Kogyo Co. and Aldrich Chemical Company. Optical rotations were measured with a JASCO DIP 370 polarimeter. ^{1}H NMR spectra were recorded at 400 MHz with a JEOL JNM-AL 400 or an ECX 400 spectrometer, and chemical shifts are referred to internal tetramethylsilane (δ = 0 ppm), $CDCl_3$ (δ = 7.24 ppm), or CD_3OD (δ = 3.30 ppm). ^{13}C NMR spectra were recorded at 100 MHz with the same instruments, and chemical shifts are referred to internal $CDCl_3$ (δ = 77.0 ppm), C_6D_6 (δ = 128.0 ppm), or CD_3OD (δ = 49.0 ppm). MALDI-TOF mass spectra were recorded with a Shimadzu Kompact MALDI AXIMA-CFR spectrometer with 2,5-dihydroxybenzoic acid as the matrix. ESI-TOF mass spectra were recorded with a JEOL AccuTOF JMS-T700LCK with CF_3CO_2Na as the internal standard.

Methoxyphenyl 2-*O*-Acetyl-4,6-*O*-cyclohexylidene-3-*O*-triisopropylsilyl-β-D-mannopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucose (6): DDQ (609 mg, 2.91 mmol) was added under Ar at room temperature to a mixture of acceptor **4**[37] (1.4476 g, 2.43 mmol), donor **1**[23] (1.5028 g, 2.56 mmol), and dried powdered MS (4 Å, 2.0 g) in dry CH_2Cl_2 (10 mL). The mixture was stirred at the same temperature for 2 h, quenched with aqueous ascorbate buffer [L-ascorbic acid (0.7 g), citric acid monohydrate (1.2 g), and NaOH (0.92 g) in H_2O (100 mL)], and filtered through Celite. The filtrate was extracted with $CHCl_3$ and washed with satd. aq. $NaHCO_3$ and brine. The combined organic layers were dried with Na_2SO_4, and the solvents were evaporated in vacuo. The crude mixed acetal **5** (one isomer) was used without further purification. DTBMP (2.10 g, 10.3 mmol) and MS (4 Å) in dry $(CH_2Cl)_2$ (200 mL) were added to **5** at room temperature under Ar. MeOTf (937 μL, 8.30 μmol) was then added to the mixture, which was stirred at 40 °C for 48 h. After cooling to room temperature, the reaction mixture was quenched with triethylamine, diluted with EtOAc, and filtered through Celite. Pyridine (20 mL), Ac_2O (3.0 mL), and a catalytic amount of DMAP were added to the filtrate. The mixture was stirred overnight at room temperature and concentrated in vacuo. The residue was diluted with EtOAc and washed with satd. aq. $NaHCO_3$ and brine. The washed organic layer was dried with Na_2SO_4, and the solvents were evaporated in vacuo. The crude product was purified by silica gel column chromatography (hexane/EtOAc, 50:1 to 1:1) to give the product (2.266 g, 90%, β) as the acetate.

Compound 5: For analytical measurements, the residue was separated by gel filtration (SX-3, toluene/EtOAc, 1:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.87–1.13 (m, 21 H, TIPS), 1.48–1.75 (m, 9 H, cyclohexyl), 2.15 (s, 3 H, SMe), 2.42–2.50 (m, 1 H, cyclohexyl), 3.68 (s, 3 H, OMe), 3.68–3.75 (m, 1 H, C5-H$^{GlcN\,p}$), 3.81 (d, J = 11.2 Hz, 1 H, C6-H$^{GlcN\,p}$), 3.90–3.96 (m, 2 H, C6-H$^{GlcN\,p}$, C2-H$^{Man\,p}$), 4.00 (dd, J = 10.0, 4.8 Hz, 1 H, C6-H$^{Man\,p}$), 4.05–4.12 (m, 1 H, C5-H$^{Man\,p}$), 4.19 (dd, J = 9.6, 2.4 Hz, 1 H, C3-H$^{Man\,p}$), 4.25 (t, J = 10.0 Hz, 1 H, C6-H$^{Man\,p}$), 4.37 (t, J = 10.0 Hz, 1 H, C3-H$^{GlcN\,p}$), 4.47–4.53 (m, 2 H, C2-H$^{GlcN\,p}$, C4-H$^{GlcN\,p}$), 4.58 (t, J = 9.2 Hz, 1 H, C4-H$^{Man\,p}$), 4.68 (d, J = 12.4 Hz, 1 H, Bn), 4.85 (d, J = 12.4 Hz, 1 H, Bn), 4.90 (d, J = 12.8 Hz, 1 H, Bn), 5.18 (d, J = 12.8 Hz, 1 H, Bn), 5.71 (d, J = 8.8 Hz, 1 H, C1-H$^{GlcN\,p}$), 5.89 (s, 1 H, C1-H$^{Man\,p}$), 5.99 (s, 1 H, CH Naph), 6.69–7.86 (m, 21 H, MP, Naph, Bn ×2) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 12.3, 13.6, 17.8, 17.9, 22.5, 22.6, 25.8, 27.9, 38.0, 43.4, 55.4, 55.7, 61.7, 66.5, 67.7, 70.4, 70.6, 73.8, 74.5, 75.2, 76.2, 76.6, 78.7, 82.8, 97.7, 99.8, 101.6, 114.1, 118.6, 123.0, 124.3, 125.9, 126.1, 126.2, 127.0, 127.5, 127.67, 127.73, 127.88, 127.92, 128.1, 128.2, 128.4, 131.6, 132.6, 133.5, 133.6, 135.6, 137.5, 138.3, 150.6, 155.1, 167.1, 167.5 ppm. MALDI TOF MS: calcd. for $C_{68}H_{81}NNaO_{13}SSi$ $[M + Na]^+$ 1202.5; found 1202.5.

Compound 6: $[\alpha]_D^{29}$ = 24.8 (c = 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.96–1.10 (m, 21 H, TIPS), 1.48–1.75 (m, 9 H, cyclohexyl), 2.12 (s, 3 H, Ac), 2.28–2.35 (m, 1 H, cyclohexyl), 2.97 (ddd, J = 10.8, 9.2, 5.6 Hz, 1 H, C5-H$^{Man\,p}$), 3.50 (t, J = 10.8 Hz, 1 H, C6-H$^{Man\,p}$), 3.60–3.80 (m, 5 H, C5-H$^{GlcN\,p}$, C6-H$^{GlcN\,p}$, C3-H$^{Man\,p}$, C4-H$^{Man\,p}$, C6-H$^{Man\,p}$), 3.84 (dd, J = 11.2, 3.2 Hz, 1 H, C6-H$^{GlcN\,p}$), 4.16 (dd, J = 10.0, 8.4 Hz, 1 H, C4-H$^{GlcN\,p}$), 4.27 (dd, J = 10.8, 8.4 Hz, 1 H, C3-H$^{GlcN\,p}$), 4.37 (dd, J = 10.8, 8.4 Hz, 1 H, C2-H$^{GlcN\,p}$), 4.39 (d, J = 12.4 Hz, 1 H, Bn), 4.51 (d, J = 12.4 Hz, 1 H, Bn), 5.68 (d, J = 0.8 Hz, 1 H, C1-H$^{Man\,p}$), 4.73 (d, 1 H, Bn), 4.82 (d, J = 12.4 Hz, 1 H, Bn), 5.32 (dd, J = 2.8, 0.8 Hz, 1 H, C2-H$^{Man\,p}$), 5.56 (d, J = 8.0 Hz, 1 H, C1-H$^{GlcN\,p}$), 6.65–7.65 (m, 18 H, MP, NPhth, Bn ×2) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 12.3, 14.1, 17.9, 21.0, 22.2, 22.4, 25.5, 27.7, 37.8, 55.3, 55.4, 60.2, 60.9, 67.9, 68.2, 70.3, 71.1, 72.3, 73.2, 74.4, 74.6, 76.9, 78.9, 97.4 (J_{C-H} = 163.4 Hz, C1$^{\beta\text{-}GlcN\,p}$), 99.5 (J_{C-H} = 161.7 Hz, C1$^{\beta\text{-}Man\,p}$), 99.6, 114.1, 118.3, 123.0, 126.9, 127.4, 127.5, 127.7, 128.2, 131.3, 137.7, 138.3, 150.5, 155.0, 167.2, 167.9, 169.7 ppm. MALDI TOF MS: calcd. for $C_{58}H_{73}NNaO_{14}Si$ $[M + Na]^+$ 1058.5; found 1058.7. HRMS ESI-TOF: calcd. for $C_{58}H_{73}NNaO_{14}Si$ $[M + Na]^+$ 1058.4698; found 1058.4702.

2-Naphthaldehyde ([D$_7$]Benzyl 3,5-*O*-bis[D$_7$]benzyl-α-D-arabinofuranosid-2-yl) [Methyl 3,5-*O*-(tetraisopropylsiloxane-1,3-diyl)-1-thio-α-D-arabinofuranosid-2-yl] Acetal (8): DDQ (10.3 mg, 49.7 μmol) was added under Ar at room temperature to a mixture of acceptor **7**[23] (21.0 mg, 47.6 μmol), donor **2**[23] (29.5 mg, 52.4 μmol), and dried powdered MS (4 Å, 250 mg) in dry CH_2Cl_2 (2.0 mL). The mixture was stirred at the same temperature for 48 h, and further DDQ (10.3 mg) was added. The mixture was stirred for 24 h, quenched with aqueous ascorbate buffer, and filtered through Celite. The filtrate was extracted with $CHCl_3$ and washed with satd. aq. $NaHCO_3$ and brine. The combined organic layers were dried with Na_2SO_4, and the solvents were evaporated in vacuo. The crude product was purified by gel filtration chromatography (SX-3; EtOAc/toluene, 1:1) to give the mixed acetal (49.2 mg, quant., 3.44:1). ^{1}H NMR ($CDCl_3$, 400 MHz) of the major isomer: δ = 0.87–1.17 (m, 28 H, TIPDS), 2.08 (s, 3 H, SMe), 3.58 (dd, J = 10.8, 5.6 Hz, 1 H, C5-H$^{Ara\,f2}$), 3.63 (dd, J = 10.8, 3.2 Hz, 1 H, C5-H$^{Ara\,f2}$), 3.85–4.20 (m, 4 H, C2-H$^{Ara\,f1}$, C3-H$^{Ara\,f2}$, C5-H$^{Ara\,f1}$), 4.18–4.26 (m, 1 H, C4-H$^{Ara\,f2}$), 4.32–4.36 (m, 2 H, C3-H$^{Ara\,f1}$, C4-H$^{Ara\,f1}$), 4.48 (d, J = 3.2 Hz, 1 H, C2-H$^{Ara\,f2}$), 5.12 (s, 1 H, C1-H$^{Ara\,f2}$), 5.28 (d, J =

4.0 Hz, 1 H, C1-H^{Araf1}), 5.80 (s, 1 H, CH Naph), 7.18–7.84 (m, 7 H, Naph) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 12.6, 12.9, 13.1, 13.5, 14.3, 17.0, 17.1, 17.3, 17.3, 17.5, 61.1, 69.8, 75.4, 79.8, 80.7, 83.7, 84.4, 86.9, 88.1, 102.5, 105.6, 124.3, 126.2, 126.4, 126.7, 127.0, 127.5, 127.6, 128.2, 128.3, 132.7, 133.7, 134.7, 126–137 ([D_7]Bn) ppm. MALDI TOF MS: calcd. for $C_{55}H_{51}D_{21}NaO_{10}SSi$ [M + Na]$^+$ 1024.6; found 1024.9.

[D_7]Benzyl 2-*O*-Acetyl-3,5-*O*-(tetraisopropylsiloxane-1,3-diyl)-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-[D_7]benzyl-α-D-arabinofuranoside (9): DTBMP (19.8 mg, 96.4 μmol) and MS (4 Å) in dry $(CH_2Cl)_2$ (2.41 mL) were added at room temperature under Ar to the mixed acetal **8** (24.2 mg, 24.1 μmol). MeOTf (9.3 μL, 81.9 μmol) was then added to the mixture, which was stirred at the same temperature for 48 h. The reaction mixture was quenched with triethylamine, diluted with EtOAc, and filtered through Celite. The filtrate was washed with satd. aq. $NaHCO_3$ and brine. The washed organic layer was dried with Na_2SO_4, and the solvents were evaporated in vacuo. TFA (200 μL) was added at 0 °C to the mixture in CH_2Cl_2 (2.0 mL), which was stirred at the same temperature for 30 min. Pyridine (2.0 mL) and Ac_2O (200 μL) were added, and the mixture was stirred at room temperature for 12 h. After concentration, the residue was diluted with EtOAc and washed with satd. aq. $NaHCO_3$ and brine. The washed organic layer was dried with Na_2SO_4, and the solvents were evaporated in vacuo. The crude product was purified by PTLC (hexane/EtOAc, 3:1) to give the product (15.9 mg, 77%, β) as the acetate. $[\alpha]_D^{29}$ = –42.5 (c = 0.40, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.87–1.25 (m, 28 H, TIPDS), 1.97 (s, 3 H, Ac), 3.52–3.61 (m, 2 H, C5-H^{Araf1}), 3.75–3.92 (m, 4 H, C3-H^{Araf1}, C4-H^{Araf2}, C5-H^{Araf2}), 4.23 (dt, J = 5.2, 4.0 Hz, 1 H, C4-H^{Araf1}), 4.27 (d, J = 2.4 Hz, 1 H, C2-H^{Araf1}), 4.27 (d, J = 8.4, 6.0 Hz, 1 H, C3-H^{Araf2}), 4.74 (d, J = 8.4, 4.8 Hz, 1 H, C2-H^{Araf2}), 4.93 (s, 1 H, C1-H^{Araf1}), 5.25 (d, J = 4.8 Hz, 1 H, C1-H^{Araf2}) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 12.5, 12.8, 13.3, 13.4, 16.95, 16.97, 16.99, 17.40, 17.48, 17.52, 17.60, 20.5, 65.5, 69.8, 75.2, 76.7, 79.1, 80.6, 81.2, 84.0, 86.3, 98.6 (J_{C-H} = 174.0 Hz, C1$^{\beta\text{-}Araf}$), 105.4 (J_{C-H} = 170.8 Hz, C1$^{\alpha\text{-}Araf}$), 126–137 ([D_7]Bn), 170.4 ppm. MALDI TOF MS: calcd. for $C_{45}H_{43}D_{21}NaO_{11}Si_2$ [M + Na]$^+$ 880.5; found 880.4. HRMS ESI-TOF: calcd. for $C_{45}H_{43}D_{21}NaO_{11}Si_2$ [M + Na]$^+$ 880.5203; found 880.5243.

2-Naphthaldehyde (4-Methoxyphenyl 3-*O*-[D_7]benzyl-4,6-*O*-cyclohexylidene-β-D-glucopyranosid-2-yl) (Methyl 3-*O*-[D_7]benzyl-4,6-*O*-cyclohexylidene-1-thio-β-D-glucopyranosid-2-yl) Acetal (13); 3a + 10 → 13 (Route A): DDQ (32.4 mg, 0.143 mmol) was added under Ar at room temperature to a mixture of acceptor **10**[29] (38.9 mg, 0.0840 mmol), **3a**[23] (57.6 mg, 0.109 mmol), and dried powdered MS (4 Å, 1.0 g) in dry CH_2Cl_2 (5.0 mL). The mixture was stirred at the same temperature for 17 h, quenched with aqueous ascorbate buffer, and filtered through Celite. The filtrate was extracted with EtOAc and washed with satd. aq. $NaHCO_3$ and brine and dried with Na_2SO_4, and the solvents were evaporated in vacuo. The crude product was purified by gel filtration chromatography (SX-3; EtOAc/toluene, 1:1) to give the mixed acetal **13** (80.0 mg, 96%, 3.18:1). ^{1}H NMR ($CDCl_3$, 400 MHz) of the major isomer: δ = 1.32–1.62 (m, 28 H, cyclohexyl), 2.35 (s, 3 H, SMe), 3.31–3.87 (m, 18 H, C2-H^{Glcp2}, C3-H^{Glcp2}, C4-H^{Glcp2}, C5-H^{Glcp2}, C6-H^{Glcp2}, C2-H^{Glcp1}, C3-H^{Glcp1}, C4-H^{Glcp1}, C5-H^{Glcp1}, C6-H^{Glcp1}), 4.42 (d, J = 9.6 Hz, 1 H, C1-H^{Glcp2}), 4.88 (d, J = 7.6 Hz, 1 H, C1-H^{Glcp1}), 6.14 [s, 0.35 H, CH Naph (minor)], 6.34 (s, 1 H, CH Naph), 6.37–7.72 (m, 20 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 13.5, 13.7, 21.5, 22.4, 22.5, 22.9, 25.6, 27.7, 38.0, 55.5, 61.4, 61.5, 66.3, 66.7, 71.2, 72.9, 73.4, 76.3, 78.9, 79.9, 80.6, 81.7, 83.0, 86.3, 86.7, 99.3, 99.5, 100.5, 101.3, 106.0, 107.3, 113.9, 114.2, 117.4, 117.9, 124.3, 124.6, 125.2, 125.6, 125.9, 126.2, 127.4, 127.9, 128.08, 128.12, 128.9, 132.7, 133.5, 136.9, 150.2, 154.7 ppm. MALDI-TOF MS: calcd. for $C_{57}H_{52}D_{14}NaO_{12}S$ [M + Na]$^+$ 1011.5; found 1011.7. HRMS ESI-TOF: calcd. for $C_{57}H_{52}D_{14}NaO_{12}S$ [M + Na]$^+$ 1011.5051; found 1011.5050.

2-Naphthaldehyde (4-Methoxyphenyl 3-*O*-[D_7]benzyl-4,6-*O*-cyclohexylidene-β-D-glucopyranosid-2-yl) (Methyl 3-*O*-[D_7]benzyl-4,6-*O*-cyclohexylidene-1-thio-β-D-glucopyranosid-2-yl) Acetal (13); 11 + 12 → 13 (Route B): Compound **13** was synthesized from **11**[23] and **12**[23] by the procedure used for the synthesis of **13** from **3a** and **10** (93%, 1:4.17). ^{1}H NMR ($CDCl_3$, 400 MHz) of the major isomer: δ = 1.30–1.61 (m, 20 H, cyclohexyl), 2.04 (m, 3 H, SMe), 2.20 [s, 1 H, SMe (minor)], 2.92 (m, 2 H, C5-H^{Glcp1}, C4-H^{Glcp2}), 3.16–4.03 (m, 18 H, C2-H^{Glcp1}, C3-H^{Glcp1}, C4-H^{Glcp1}, C6-H^{Glcp1}, C2-H^{Glcp2}, C3-H^{Glcp2}, C5-H^{Glcp2}, C6-H^{Glcp2}), 4.22 (d, J = 10.4 Hz, 1 H, C1-H^{Glcp2}), 4.99 (d, J = 8.0 Hz, 1 H, C1-H^{Glcp1}), 6.13 (s, 1 H, CH Naph), 6.33 (s, 0.3 H, CH Naph), 6.84 (d, J = 9.2 Hz, 2 H, Ar), 6.99 (d, J = 8.8 Hz, 2 H, Ar), 7.43–7.86 (m, 7 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 13.6, 22.4, 22.5, 22.9, 25.5, 25.6, 27.6, 37.96, 38.01, 55.5, 61.4, 61.5, 66.3, 71.3, 72.9, 73.5, 78.3, 79.9, 80.6, 81.7, 86.7, 99.3, 100.5, 107.3, 113.9, 114.2, 117.4, 117.9, 124.3, 125.2, 125.8, 125.9, 127.7, 128.1, 128.3, 129.0, 132.9, 133.6, 137.3, 149.9, 154.8 ppm. MALDI-TOF MS: calcd. for $C_{57}H_{52}D_{14}NaO_{12}S$ [M + Na]$^+$ 1011.5; found 1011.7. HRMS ESI-TOF: calcd. for $C_{57}H_{52}D_{14}NaO_{12}S$ [M + Na]$^+$ 1011.5051; found 1011.5035.

4-Methoxyphenyl 3-*O*-[D_7]Benzyl-4,6-di-*O*-acetyl-α-D-glucopyranosyl-(1→2)-3-*O*-[D_7]benzyl-2,4,6-tri-*O*-acetyl-β-D-glucopyranoside (14): MeOTf (16.7 μL, 148 μmol), diluted with dry 1,2-dichloroethane (1.0 mL), was added under Ar at room temperature to a solution of mixed acetal **13** (41.7 mg, 42.2 μmol), DTBMP (34.6 mg, 169 μmol), and dried powdered MS (4 Å, 1.0 g) in dry 1,2-dichloroethane (6.0 mL). The mixture was stirred at room temperature for 21 h and then quenched with triethylamine, diluted with EtOAc, and filtered through Celite. The filtrate was washed with satd. aq. $NaHCO_3$ and brine and dried with Na_2SO_4, and the solvents were evaporated in vacuo. TFA (200 μL) was added at 0 °C to the mixture in CH_2Cl_2 (2.0 mL), which was stirred at the same temperature for 3 h. Pyridine (5.0 mL), Ac_2O (500 μL), and a catalytic amount of DMAP were added. The mixture was stirred at room temperature for 12 h and then concentrated in vacuo. The residue was diluted with EtOAc, washed with satd. aq. $NaHCO_3$ and brine and dried with Na_2SO_4, and the solvents were evaporated in vacuo. The crude product was purified by gel filtration chromatography (SX-3; EtOAc/toluene, 1:1) to give product **14** (72%, 25.8 mg) as the pentaacetate. $[\alpha]_D^{26}$ = +11.2 (c = 0.50, $CHCl_3$). ^{1}H NMR (C_6D_6, 400 MHz): δ = 1.55 (s, 3 H, Ac), 1.85 (s, 3 H, Ac), 1.97 (s, 3 H, Ac), 1.99 (s, 3 H, Ac), 2.06 (s, 3 H, Ac), 3.59 (dd, J = 12.4, 3.6 Hz, 1 H, C6-H^{Glcp1}), 3.67 (dd, J = 12.4, 2.0 Hz, 1 H, C6-H^{Glcp1}), 3.70–3.78 (m, 2 H, C5-H^{Glcp2}, C3-H^{Glcp2}), 3.74 (s, 3 H, OMe), 3.90 (t, J = 10.4 Hz, 1 H, C3-H^{Glcp1}), 3.93 (dd, J = 10.4, 8.0 Hz, 1 H, C2-H^{Glcp2}), 4.05 (ddd, J = 10.4, 3.6, 2.0 Hz, 1 H, C5-H^{Glcp1}), 4.12 (dd, J = 12.8, 2.0 Hz, 1 H, C6-H^{Glcp2}), 4.22 (dd, J = 12.4, 6.0 Hz, 1 H, C6-H^{Glcp1}), 4.94 (d, J = 10.4 Hz, 1 H, C1-H^{Glcp2}), 4.98 (dd, J = 10.0, 3.6 Hz, 1 H, C2-H^{Glcp1}), 5.02 (t, J = 8.8 Hz, 1 H, C4-H^{Glcp1}), 5.02 (t, J = 10.0 Hz, 1 H, C4-H), 5.69 (d, J = 3.6 Hz, 1 H, C1-H^{Glcp1}), 6.80 (d, J = 8.8 Hz, 2 H, Ar), 7.87 (d, J = 8.8 Hz, 2 H, Ar) ppm. ^{13}C NMR (C_6D_6, 100 MHz): δ = 20.3, 20.7, 20.74 (×2), 20.8, 22.7, 59.2, 61.1, 62.3, 67.9, 69.0, 70.5, 72.0, 72.2, 75.3, 80.5, 95.3 (C1^{Glcp2}), 101.3 (C1^{Glcp1}), 114.6, 117.0, 150.5, 155.3, 169.1, 169.5, 169.6, 170.70 (×2). MALDI-TOF MS: calcd. for $C_{43}H_{36}D_{14}NaO_{17}$ [M + Na]$^+$ 875.4; found 875.7. HRMS ESI-TOF: calcd. for $C_{43}H_{36}D_{14}NaO_{17}$ [M + Na]$^+$ 875.3824; found 875.3831.

4-Methoxyphenyl 3-*O*-[D_7]Benzyl-4,6-*O*-cyclohexylidene-2-*O*-(2-naphthylmethyl)-α-D-glucopyranosyl-(1→2)-3-*O*-[D_7]benzyl-4,6-*O*-

cyclohexylidene-β-D-glucopyranoside (15) and 4-Methoxyphenyl 3-*O*-[D_7]Benzyl-4,6-*O*-cyclohexylidene-α-D-glucopyranosyl-(1→2)-3-*O*-[D_7]benzyl-4,6-*O*-cyclohexylidene-β-D-glucopyranoside (16): MeOTf (12.7 μL, 112 μmol) was added under Ar at room temperature to a solution of mixed acetal **13** (31.7 mg, 32.0 μmol), DTBMP (26.3 mg, 128 μmol), tris(trimethylsilyl)silane (49.4 μL, 160 μmol), and dried powdered MS (4 Å, 1.0 g) in dry 1,2-dichloroethane (8.0 mL). The mixture was stirred at room temperature for 17 h and then quenched with triethylamine, diluted with EtOAc, and filtered through Celite. The filtrate was diluted with EtOAc, washed with satd. aq. $NaHCO_3$ and brine and dried with Na_2SO_4, and the solvents were evaporated in vacuo. The crude product was purified by gel filtration chromatography (SX-3; EtOAc/toluene, 1:1) and by PTLC (EtOAc/hexane, 1:6) to give product **15** (73%, 22.0 mg) as the NAP ether and **16** (4.7 mg, 16%). DDQ treatment of the crude mixture without any purification was carried out to give **16** (85%) as described for the synthesis of **11** from **3a**.

Compound 15: $[\alpha]_D^{26}$ = +29.8 (*c* = 0.92, $CHCl_3$). ^1H NMR (C_6D_6, 400 MHz): δ = 1.27–1.76 (m, 20 H, cyclohexyl), 2.98 (td, *J* = 10.0, 5.6 Hz, 1 H, C5-H^{Glcp2}), 3.22 (s, 3 H, OMe), 3.55 (t, *J* = 10.8 Hz, 1 H, C6-H^{Glc2}), 3.64–3.90 (m, 7 H, C3-H^{Glc2}, C4-H^{Glc2}, C6-H^{Glc2}, C2-H^{Glc1}, C4-H^{Glc1}, C6-H^{Glcp1}), 4.06 (dd, *J* = 10.4, 5.2 Hz, 1 H, C6-H^{Glcp1}), 4.19 (t, *J* = 8.0 Hz, 1 H, C2-H^{Glcp2}), 4.31 (t, *J* = 9.2 Hz, 1 H, C3-H^{Glcp1}), 4.70 (d, *J* = 11.6 Hz, 1 H, NAP), 4.80 (m, 2 H, C5-H^{Glcp1}, NAP), 4.93 (d, *J* = 8.0 Hz, 1 H, C1-H^{Glcp2}), 5.96 (d, *J* = 3.6 Hz, 1 H, C1-H^{Glcp1}), 6.58 (d, *J* = 8.8 Hz, 2 H, Ar), 6.91 (d, *J* = 8.8 Hz, 2 H, Ar), 7.22–7.62 (m, 7 H, NAP) ppm. ^{13}C NMR (C_6D_6, 100 MHz): δ = 22.8, 23.0, 23.4, 23.5, 25.9, 26.2, 27.9, 28.2, 38.6, 38.7, 55.2, 61.6, 62.4, 64.1, 67.1, 73.5, 75.0, 75.2, 76.6, 77.9, 78.9, 80.5, 97.4 (C1^{Glcp2}), 99.6, 99.7, 102.6 (C1^{Glcp1}), 114.9, 118.6, 125.9, 126.1, 126.1, 126.4, 133.4, 133.8, 136.6, 151.1, 155.9 ppm. MALDI-TOF MS: calcd. for $C_{56}H_{50}D_{14}NaO_{12}$ [M + Na]$^+$ 965.5; found 966.1. HRMS ESI-TOF: calcd. for $C_{56}H_{50}D_{14}NaO_{12}$ [M + Na]$^+$ 965.5174; found 965.5205.

Compound 16: $[\alpha]_D^{26}$ = +39.1 (*c* = 0.43, $CHCl_3$). ^1H NMR (C_6D_6, 400 MHz): δ = 1.21–1.89 (m, 20 H, cyclohexyl), 2.11 (br. s, 1 H, OH), 3.05 (td, *J* = 10.0, 5.6 Hz, 1 H, C5-H^{Glcp2}), 3.28 (s, 3 H, OMe), 3.50 (t, *J* = 9.2 Hz, 1 H, C3-H^{Glcp2}), 3.60–3.88 (m, 7 H, C2-H^{Glcp2}, C4-H^{Glcp2}, C6-H^{Glcp2}, C6-H^{Glcp2}, C3-H^{Glcp1}, C4-H^{Glcp1}, C6-H^{Glcp1}), 3.93 (dd, *J* = 10.4, 5.6 Hz, 1 H, C6-H^{Glcp1}), 4.00 (t, *J* = 9.2 Hz, 1 H, C2-H^{Glcp1}), 4.51 (td, *J* = 10.4, 5.2 Hz, 1 H, C5-H^{Glcp1}), 4.61 (d, *J* = 8.0 Hz, 1 H, C1-H^{Glcp2}), 5.71 (d, *J* = 3.2 Hz, 1 H, C1-H^{Glcp1}), 6.73 (d, *J* = 8.8 Hz, 2 H, Ar), 7.03 (d, *J* = 8.8 Hz, 2 H, Ar) ppm. ^{13}C NMR (C_6D_6, 100 MHz): δ = 21.5, 22.8, 23.0, 23.4, 23.5, 25.9, 26.1, 27.9, 28.1, 38.6, 38.7, 55.2, 61.7, 62.1, 64.4, 67.4, 73.5, 74.5, 74.9, 77.9, 78.1, 79.8, 99.6 (C1^{Glcp2}), 99.7 (×2), 104.0 (C1^{Glcp1}), 114.8, 120.3, 125.7, 151.6, 156.5 ppm. MALDI-TOF MS: calcd. for $C_{45}H_{42}D_{14}NaO_{12}$ [M + Na]$^+$ 825.5; found 825.6. HRMS ESI-TOF: calcd. for $C_{45}H_{42}D_{14}NaO_{12}$ [M + Na]$^+$ 825.4548; found 825.4536.

2-Naphthaldehyde (4-Methoxyphenyl 3-*O*-[D_7]benzyl-4,6-*O*-cyclohexylidene-β-D-glucopyranosid-2-yl) (Methyl 3-*O*-triisopropylsilyl-4,6-*O*-cyclohexylidene-1-thio-β-D-glucopyranosid-2-yl) Acetal (17); 3b + 10 → 17: The title compound was synthesized from **3b**[23] and **10** by the procedure used for the synthesis of **13** (84%, >10.0:1). ^1H NMR ($CDCl_3$, 400 MHz) of the major isomer: δ = 0.94–1.58 (m, 41 H, cyclohexyl, TIPS), 2.21 (s, 3 H, SMe), 3.13 (td, *J* = 10.4, 5.2 Hz, 1 H, C5-H^{Glcp2}), 3.22 (t, *J* = 9.6 Hz, 1 H, C6-H^{Glcp1}), 3.28–3.37 (m, 2 H, C4-H^{Glcp1}, C5-H^{Glcp1}), 3.58 (s, 3 H, OMe), 3.67–3.84 (m, 6 H, C3-H^{Glcp2}, C6-H^{Glcp1}, C4-H^{Glcp2}, C6-H^{Glcp2}), 3.89 (t, *J* = 8.0 Hz, 1 H, C2-H^{Glcp1}), 3.98 (t, *J* = 8.8 Hz, 1 H, C3-H^{Glcp1}), 4.28 (t, *J* = 8.8 Hz, 1 H, C2-H^{Glcp2}), 4.48 (d, *J* = 8.8 Hz, 1 H, C1-H^{Glcp2}), 4.81 (d, *J* = 8.4 Hz, 1 H, C1-H^{Glcp1}), 6.09 (s, 1 H, CH Naph), 6.10 (d, *J* = 8.8 Hz, 2 H, Ar), 6.32 (d, *J* = 9.2 Hz, 2 H, Ar), 7.37–7.71 (m, 7 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 13.6, 14.4, 18.4, 22.3, 22.4, 22.7, 22.8, 25.5, 25.7, 27.6, 37.8, 37.9, 55.5, 61.2, 61.4, 66.5, 71.2, 72.8, 74.2, 77.7, 80.3, 80.7, 86.7, 99.4, 99.4, 101.0, 106.8, 113.6, 117.1, 124.6, 125.5, 125.7, 126.2, 127.4, 127.8, 128.0, 132.7, 133.4, 137.3, 139.4, 149.8, 154.5 ppm. MALDI-TOF MS: calcd. for $C_{59}H_{73}D_7NaO_{12}SSi$ [M + Na]$^+$ 1070.5; found 1070.7. HRMS ESI-TOF: calcd. for $C_{59}H_{73}D_7NaO_{12}SSi$ [M + Na]$^+$ 1070.5477; found 1070.5516.

4-Methoxyphenyl 4,6-*O*-Cyclohexylidene-2-*O*-(2-naphthylmethyl)-3-*O*-triisopropylsilyl-α-D-glucopyranosyl-(1→2)-3-*O*-[D_7]benzyl-4,6-*O*-cyclohexylidene-β-D-glucopyranoside (18): DTBMP (33.5 mg, 163 μmol), MS (4 Å, 1.0 g), and tris(trimethylsilyl)silane (63.0 μL, 204 μmol) in dry 1,2-dichloroethane (10 mL) were added under Ar at room temperature to mixed acetal **17** (42.8 mg, 40.8 μmol). MeOTf (16.2 μL, 143 μmol) was then added to the mixture, which was stirred at room temperature. for 14 h The reaction mixture was quenched with TEA, diluted with EtOAc, and filtered through Celite. The filtrate was extracted with EtOAc and washed with satd. aq. $NaHCO_3$ and brine. The combined organic layers were dried with Na_2SO_4. After filtration and concentration, the crude product was purified by gel filtration chromatography (SX-3; EtOAc/toluene, 1:1) and by PTLC (EtOAc/hexane, 1:6) to give the product as NAP ether **18** (33.2 mg, 82%). $[\alpha]_D^{27}$ = +24.3 (*c* = 2.76, $CHCl_3$). ^1H NMR (C_6D_6, 400 MHz): δ = 1.28–1.72 (m, 41 H, cyclohexyl, TIPS), 2.92 (td, *J* = 10.0, 5.2 Hz, 1 H, C5-H^{Glcp2}), 3.15 (s, 3 H, OMe), 3.49–3.75 (m, 7 H, C2-H^{Glcp1}, C4-H^{Glcp1}, C6-H^{Glcp1}, C3-H^{Glcp2}, C4-H^{Glcp2}, C6-H^{Glcp2}), 4.03 (dd, *J* = 10.4 Hz, 1 H, C6-H^{Glcp1}), 3.64 (d, *J* = 8.4 Hz, 1 H, C2-H^{Glcp2}), 4.56–4.73 (m, 4 H, C3-H^{Glcp1}, C5-H^{Glcp1}, NAP), 4.93 (d, *J* = 7.6 Hz, 1 H, C1H^{Glcp2}), 6.01 (d, *J* = 3.6 Hz, 1 H, C1-H^{Glcp1}), 6.45 (d, *J* = 8.8 Hz, 2 H, Ar), 6.76 (d, *J* = 8.8 Hz, 2 H, Ar), 7.23–7.71 (m, 7 H, NAP) ppm. ^{13}C NMR (C_6D_6, 100 MHz): δ = 13.7, 18.8, 18.9, 22.8, 22.9, 23.2, 23.4, 25.9, 26.3, 27.9, 28.2, 38.6, 55.1, 61.6, 62.0, 64.2, 67.1, 72.1, 72.8, 74.55, 74.64, 76.4, 78.9, 81.7, 96.5 (C-1^{Glcp2}), 99.6 (×2), 102.2 (C-1^{Glcp1}), 114.8, 117.9, 125.4, 125.6, 125.8, 126.2, 133.3, 133.8, 136.4, 138.4, 150.7, 155.6 ppm. MALDI-TOF MS: calcd. for $C_{58}H_{71}D_7NaO_{12}Si$ [M + Na]$^+$ 1024.6; found 1025.1. HRMS ESI-TOF: calcd. for $C_{58}H_{71}D_7NaO_{12}Si$ [M + Na]$^+$ 1024.5600; found 1024.5578.

2-Naphthaldehyde (4-Methoxyphenyl 2,3,4-tri-*O*-[D_7]benzyl-β-D-glucopyranosid-6-yl) (Methyl 3-*O*-[D_7]benzyl-4,6-*O*-cyclohexylidene-1-thio-β-D-glucopyranosid-2-yl) Acetal (24); 3a + 23 → 24: The title compound was synthesized from **3a** and **23**[23] by the procedure used for the synthesis of **16** (91%, 2.32:1). ^1H NMR ($CDCl_3$, 400 MHz) of the major isomer: δ = 1.24–1.64 (m, cyclohexyl, 10 H), 2.29 (s, 3 H, SMe), 3.25–4.04 (m, 15 H, C2-H^{Glcp2}, C3-H^{Glcp2}, C4-H^{Glcp2}, C5-H^{Glcp2}, C6-H^{Glcp2}, C6-H^{Glcp2}, C2-H^{Glcp1}, C3-H^{Glcp1}, C4-H^{Glcp1}, C5-H^{Glcp1}, C6-H^{Glcp1}, C6-H^{Glcp1}, OMe), 4.49 (d, *J* = 9.2 Hz, 1 H, C1-H^{Glcp2}), 4.85 (d, *J* = 8.0 Hz, 1 H, C1-H^{Glcp1}), 6.16 [s, 1 H, CH Naph (major)], 6.22 [s, 0.43 H, CH Naph (minor)], 6.67–7.41 (m, 11 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 12.1, 21.5, 22.5, 23.0, 25.6, 27.7, 27.8, 38.0, 55.6, 61.4, 64.2, 71.4, 73.9, 74.8, 76.1, 77.6, 81.9, 83.5, 84.5, 85.1, 99.5, 102.3, 103.6, 114.6, 118.0, 124.8, 125.2, 125.9, 126.0, 126.1, 126.3, 127.6, 128.0, 128.1, 128.2, 128.9, 132.8, 133.4, 136.0, 151.4, 154.9 ppm. MALDI-TOF MS: calcd. for $C_{65}H_{42}D_{28}NaO_{12}S$ [M + Na]$^+$ 1125.6; found 1125.3.

4-Methoxyphenyl 4,6-*O*-Cyclohexylidene-3-*O*-[D_7]benzyl-α-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-[D_7]benzyl-β-D-glucopyranoside (25): Compound **25** was synthesized from **24** by the procedure used for

the synthesis of **16** (12.4 mg, 63%). $[\alpha]_D^{27}$ = 50.0 (c = 0.06, $CHCl_3$). ^1H NMR (C_6D_6, 400 MHz): δ = 1.34–1.68 (m, 10 H, cyclohexyl), 2.32 (br. s, 1 H, OH), 3.26–3.33 (m, 4 H, C5-H^{Glcp1}, OMe), 3.55–3.97 (m, 11 H, C2-H^{Glcp1}, C3-H^{Glcp1}, C4-H^{Glcp1}, C6-H^{Glcp1}, C6-H^{Glc1}, C2-H^{Glcp2}, C3-H^{Glcp2}, C4-H^{Glcp2}, C5-H^{Glcp2}, C6-H^{Glcp2}, C6-H^{Glcp2}), 4.84 (d, J = 7.6 Hz, 1 H, C1-H^{Glcp2}), 4.87 (d, J = 3.6 Hz, 1 H, C1-H^{Glcp1}), 6.85 (d, J = 8.8 Hz, 2 H, Ar), 7.19 (d, J = 8.8 Hz, 2 H, Ar) ppm. ^{13}C NMR (C_6D_6, 100 MHz): δ = 22.9, 23.4, 26.1, 28.1, 38.5, 55.2, 62.2, 64.6, 67.1, 73.4, 74.4, 74.5, 77.7, 82.5, 84.9, 99.7 (C1^{Glcp2}), 99.9, 103.8 (C1^{Glcp1}), 115.1, 119.7, 152.0, 156.2 ppm. MALDI-TOF MS: calcd. for $C_{53}H_{32}D_{28}NaO_{12}$ $[M + Na]^+$ 939.6; found 940.0. HRMS ESI-TOF: calcd. for $C_{53}H_{32}D_{28}NaO_{12}$ $[M + Na]^+$ 939.5740; found 939.5749.

2-Naphthaldehyde (4-Methoxyphenyl 3-*O*-[D_7]benzyl-4,6-cyclohexylidene-β-D-glucopyranosid-2-yl) (Methyl 3,4,6-tri-*O*-[D_7]benzyl-1-thio-β-D-glucopyranosid-2-yl) Acetal (26); 3c + 10 → 26: The title compound was synthesized from **3c**[23] and **10** by the procedure used for the synthesis of **13** (94%, 3.11:1). ^1H NMR ($CDCl_3$, 400 MHz) of the major isomer: δ = 1.20–1.75 (m, 9 H, cyclohexyl), 2.04–2.12 (m, 1 H, cyclohexyl), 2.26 (s, 3 H, SMe), 3.19 (d, J = 9.6 Hz, 1 H, C4-H^{Glcp1}), 3.33–4.02 (m, 14 H, C2-H^{Glcp1}, C3-H^{Glcp1}, C5-H^{Glcp1}, C6-H^{Glcp1}, C6-H^{Glcp1}, C2-H^{Glcp2}, C3-H^{Glcp2}, C4-H^{Glcp2}, C5-H^{Glcp2}, C6-H^{Glcp2}, C6-H^{Glcp2}, OMe), 4.42 (d, J = 9.6 Hz, 1 H, C1-H^{Glcp1}), 4.92 (d, J = 7.6 Hz, 1 H, C1-H^{Glcp1}), 6.19 [s, 0.44 H, CH Naph (minor)], 6.27 [s, 1 H, CH Naph (major)], 6.75–8.01 (m, 11 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 13.4, 22.3, 22.8, 25.5, 27.5, 37.9, 55.5, 61.4, 66.6, 68.9, 72.4, 73.8, 76.8, 78.1, 79.1, 81.0, 85.6, 86.4, 99.5, 100.9, 106.4, 113.9, 117.3, 124.6, 125.6, 125.9, 127.0, 127.5, 128.0, 128.2, 129.0, 134.5, 136.4, 150.4, 154.7 ppm. MALDI-TOF MS: calcd. for $C_{65}H_{42}D_{28}NaO_{12}S$ $[M + Na]^+$ 1125.6; found 1125.4.

4-Methoxyphenyl 3,4,6-Tri-*O*-[D_7]benzyl-α-D-glucopyranosyl-(1→2)-2-*O*-[D_7]benzyl-4,6-*O*-cyclohexylidene-β-D-glucopyranoside (27): Compound **27** was synthesized from **26** by the procedure used for the synthesis of **16** (77%, 2.17:1). Major isomer: $[\alpha]_D^{27}$ = 42.0 (c = 1.0, $CHCl_3$). ^1H NMR (C_6D_6, 400 MHz): δ = 1.10–1.95 (m, 10 H, cyclohexyl), 2.11 (d, J = 8.8 Hz, 1 H, OH), 3.12 (td, J = 10.0, 5.6 Hz, 1 H, C5-H^{Glcp1}), 3.28 (s, 3 H, OMe), 3.48–3.54 (m, 2 H, C3-H^{Glcp1}, C6-H^{Glcp2}), 3.58 (dd, J = 9.2, 2.8 Hz, 1 H, C6-H^{Glcp2}), 3.62–3.74 (m, 2 H, C4-H^{Glcp1}, C6-H^{Glcp2}), 3.78–3.95 (m, 2 H, C5-H^{Glcp1}, C6-H^{Glcp1}), 3.94 (t, J = 10.4 Hz, 1 H, C4-H^{Glcp1}), 4.02 (t, J = 8.8 Hz, 1 H, C3-H^{Glcp1}), 4.10 (t, J = 8.0 Hz, 1 H, C2-H^{Glcp2}), 4.48 (br. d, J = 10.0 Hz, 1 H, C5-H^{Glcp1}), 4.73 (d, J = 8.0 Hz, 1 H, C1-H^{Glcp2}), 5.78 (d, J = 4.0 Hz, 1 H, C1-H^{Glcp1}), 6.70–7.36 (m, 4 H, Ar) ppm. ^{13}C NMR (C_6D_6, 100 MHz): δ = 22.5, 23.0, 25.5, 27.6, 38.2, 54.8, 61.4, 67.2, 68.7, 71.3, 73.7, 74.3, 77.0, 77.8, 79.3, 83.4, 98.8 (C1^{Glcp2}), 99.4, 103.8 (C1^{Glcp1}), 114.8, 119.7, 126.0–129.0 (overlapped with C_6D_6 signal), 151.4, 156.2 ppm. MALDI-TOF MS: calcd. for $C_{53}H_{32}D_{28}NaO_{12}$ $[M + Na]^+$ 939.6; found 940.0. HRMS ESI-TOF: calcd. for $C_{53}H_{32}D_{28}NaO_{12}$ $[M + Na]^+$ 939.5740; found 939.5713.

2-Naphthaldehyde (4-Methoxyphenyl 2-*O*-[D_7]benzyl-4,6-*O*-cyclohexylidene-β-D-glucopyranosid-3-yl) (Methyl 3-*O*-[D_7]benzyl-4,6-*O*-cyclohexylidene-1-thio-β-D-glucopyranosid-2-yl) Acetal (29); 3a + 28 →29: The title compound was synthesized from **3a** and **28**[28] by the procedure used for the synthesis of **13** (97%, 3.00:1). ^1H NMR ($CDCl_3$, 400 MHz) of the major isomer: δ = 1.22–1.81 (m, 20 H, cyclohexyl), 2.34 (s, 3 H, SMe), 3.22–4.38 (m, 25 H, C2-H^{Glcp1}, C3-H^{Glcp1}, C4-H^{Glcp1}, C5-H^{Glcp1}, C6-H^{Glcp1}, C2-H^{Glcp2}, C3-H^{Glcp2}, C4-H^{Glcp2}, C5-H^{Glcp2}, C6-H^{Glcp2}, OMe), 4.44 (d, J = 9.6 Hz, 1 H, C1-H^{Glcp2}), 4.95 (d, J = 7.2 Hz, 1 H, C1-H^{Glcp1}), 6.31 [s, 0.31 H, CH Naph (minor)], 6.38 (s, 1 H, CH Naph), 6.38–8.33 (m, 25 H, Ar) ppm. ^{13}C NMR (C_6D_6, 100 MHz): δ = 13.6, 21.5, 22.5, 22.8, 23.2, 23.4, 25.9, 25.9, 26.1, 26.4, 27.2, 28.0, 28.1, 30.6, 38.3, 38.5, 55.2, 61.8, 67.3, 71.6, 71.8, 73.7, 74.7, 75.6, 79.1, 80.2, 81.7, 82.3, 83.9, 87.0, 99.5, 99.6, 100.1, 103.9, 105.5, 106.4, 107.2, 114.8, 114.9, 119.2, 125.6, 126.1, 126.6, 126.9, 133.4, 134.0, 137.8, 139.5, 151.9, 155.9 ppm. MALDI-TOF MS: calcd. for $C_{57}H_{52}D_{14}NaO_{12}S$ $[M + Na]^+$ 1011.5; found 1011.7. HRMS ESI-TOF: calcd. for $C_{57}H_{52}D_{14}NaO_{12}S$ $[M + Na]^+$ 1011.5051; found 1011.5050.

4-Methoxyphenyl 4,6-*O*-Cyclohexylidene-3-*O*-[D_7]benzyl-α-D-glucopyranosyl-(1→3)-2-*O*-[D_7]benzyl-4,6-*O*-cyclohexylidene-α-D-glucopyranoside (31): Compound **31** was synthesized from **29** by the procedure used for the synthesis of **16** (89%). $[\alpha]_D^{27}$ = +47.9 (c = 1.59, $CHCl_3$). ^1H NMR (C_6D_6, 400 MHz): δ = 1.28–1.90 (m, 20 H, cyclohexyl), 2.71 (br. s, 1 H, OH), 3.05 (td, J = 10.0, 5.6 Hz, 1 H, C5-H ^{Glcp2}), 3.28 (s, 3 H, OMe), 3.51–3.74 (m, 7 H, C2-H^{Glcp2}, C4-H^{Glcp2}, C6-H^{Glcp2}, C6-H^{Glcp2}, C3-H^{Glcp1}, C4-H^{Glcp1}, C6-H^{Glcp1}), 3.82–3.87 (m, 3 H, C2-H^{Glcp1}, C6-H^{Glcp1}, C3-H^{Glcp2}), 4.35 (td, J = 10.0, 5.2 Hz, 1 H, C5-H^{Glcp1}), 4.79 (d, J = 7.6 Hz, 1 H, C1-H^{Glcp2}), 5.51 (d, J = 2.8 Hz, 1 H, C1-H ^{Glcp1}), 6.71 (d, J = 8.8 Hz, 2 H, Ar), 7.01 (d, J = 8.8 Hz, 2 H, Ar) ppm. ^{13}C NMR (C_6D_6, 100 MHz): δ = 22.7, 22.9, 23.2, 23.5, 25.9, 26.1, 28.0, 28.11, 38.3, 38.7, 55.2, 61.6, 62.2, 64.7, 67.1, 73.4, 74.0, 74.3, 79.2, 80.2, 80.4, 99.7, 100.1, 101.0 (C1^{Glcp2}), 104.1 (C1^{Glcp1}), 115.0, 151.7, 156.1 ppm. MALDI-TOF MS: calcd. for $C_{45}H_{42}D_{14}NaO_{12}$ $[M + Na]^+$ 825.5; found 825.5. HRMS ESI-TOF: calcd. for $C_{45}H_{42}D_{14}NaO_{12}$ $[M + Na]^+$ 825.4548; found 825.4586.

2-Naphthaldehyde (4-Methoxyphenyl 2-*O*-[D_7]benzyl-4,6-*O*-cyclohexylidene-β-D-glucopyranosid-3-yl) (Methyl 3-*O*-triisopropylsilyl-4,6-*O*-cyclohexylidene-1-thio-β-D-glucopyranosid-2-yl) Acetal (30); 3b + 28 → 30: The title compound was synthesized from **3b** and **28** by the procedure used for the synthesis of **13** (84%, 11.1:1). ^1H NMR ($CDCl_3$, 400 MHz) of the major isomer: δ = 0.98–1.59 (m, 41 H, cyclohexyl, TIPS), 2.23 (s, 3 H, SMe), 3.25–3.89 (m, 13 H, C2-H^{Glcp2}, C4-H^{Glcp2}, C5-H^{Glcp2}, C6-H^{Glcp2}, C2-H^{Glcp1}, C4-H^{Glcp1}, C5-H^{Glcp1}, C6-H^{Glcp1}, OMe), 4.08 (t, J = 8.4 Hz, 1 H, C3-H^{Glcp1}), 4.27 (t, J = 8.0 Hz, 1 H, C3-H^{Glcp2}), 4.57 (d, J = 8.0 Hz, 1 H, C1-H^{Glcp2}), 4.98 (d, J = 8.8 Hz, 1 H, C1-H^{Glcp1}), 6.14 (s, 1 H, CH Naph), 6.78 (d, J = 9.2 Hz, 2 H, Ar), 6.91 (d, J = 9.2 Hz, 2 H, Ar), 7.44–7.84 (m, 7 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 13.6, 14.6, 18.5, 18.5, 21.5, 22.0, 22.4, 22.7, 25.2, 25.7, 26.4, 27.5, 37.4, 37.8, 55.6, 61.3, 61.4, 66.9, 70.5, 72.8, 75.7, 80.9, 86.1, 99.4, 103.7, 104.8, 114.4, 118.4, 124.8, 125.2, 125.8, 125.8, 126.2, 127.6, 128.1, 132.7, 133.5, 137.8, 138.3, 138.9, 151.1, 155.3 ppm. MALDI-TOF MS: calcd. for $C_{59}H_{73}D_7NaO_{12}SSi$ $[M + Na]^+$ 1070.54; found 1070.69. HRMS ESI-TOF: calcd. for $C_{59}H_{73}D_7NaO_{12}SSi$ $[M + Na]^+$ 1070.5477; found 1070.5518.

4-Methoxyphenyl 4,6-*O*-Cyclohexylidene-2-*O*-(2-naphthylmethyl)-3-*O*-triisopropylsilyl-α-D-glucopyranosyl-(1→3)-2-*O*-[D_7]benzyl-4,6-*O*-cyclohexylidene-α-D-glucopyranoside (32): Compound **32** was synthesized from **30** by the procedure used for the synthesis of **18** (83%). $[\alpha]_D^{27}$ = +45.5 (c = 0.95, $CHCl_3$). ^1H NMR (C_6D_6, 400 MHz): δ = 1.23–1.76 (m, 41 H, cyclohexyl, TIPS), 3.12 (td, J = 10.0, 5.6 Hz, 1 H, C5-H^{Glcp2}), 3.27 (s, 3 H, OMe), 3.55 (t, J = 10.4 Hz, 1 H, C6-H^{Glcp2}), 3.58 (dd, J = 10.4, 5.2 Hz, 1 H, C2-H^{Glcp1}), 3.64 (dd, J = 10.0, 5.6 Hz, 1 H, C6-H^{Glcp2}), 3.70–3.84 (m, 4 H, C4-H^{Glcp1}, C6-H^{Glcp1}, C2-H^{Glcp2}, C4-H^{Glpc2}), 4.11 (dd, J = 10.0, 5.6 Hz, 1 H, C6-H^{Glcp1}), 4.15 (t, J = 5.2 Hz, 1 H, C3-H^{Glcp2}), 4.70 (d, J = 11.6 Hz, 1 H, NAP), 4.80 (d, J = 7.6 Hz, 1 H, C1-H^{Glcp2}), 5.12 (d, J = 11.2 Hz, 1 H, NAP), 5.98 (d, J = 3.6 Hz, 1 H, C1-H^{Glcp1}), 6.58 (d, J = 8.8 Hz, 2 H, Ar), 6.91 (d, J = 8.8 Hz, 2 H, Ar), 7.22–7.62 (m, 7 H, NAP) ppm. ^{13}C NMR (C_6D_6, 100 MHz): δ = 13.6, 18.8, 18.8, 22.9, 23.2, 23.2, 25.8, 27.6, 28.2, 38.4, 55.2,

61.3, 62.1, 64.2, 67.1, 71.9, 72.5, 74.3, 74.6, 75.9, 80.6, 81.7, 96.9 ($C1^{Glcp2}$), 99.6 (×2), 103.8 ($C1^{Glcp1}$), 114.9, 119.1, 125.3, 125.7, 126.0, 133.9, 136.6, 151.7, 156.0 ppm. MALDI-TOF MS: calcd. for $C_{58}H_{71}D_7NaO_{12}Si$ $[M + Na]^+$ 1024.6; found 1024.9. HRMS ESI-TOF: calcd. for $C_{58}H_{71}D_7NaO_{12}Si$ $[M + Na]^+$ 1024.5600; found 1024.5549.

2-Naphthaldehyde (4-Methoxyphenyl 2-*O*-[D_7]benzyl-4,6-*O*-cyclohexylidene-α-D-mannopyranosid-3-yl) (Methyl 3-*O*-[D_7]benzyl-4,6-*O*-cyclohexylidene-1-thio-β-D-glucopyranosid-2-yl) Acetal (34); 3a + 33 →34: The title compound was synthesized from **3a** and **33**[29] by the procedure used for the synthesis of **13** (101.3 mg, 97%, 3.11:1). ^1H NMR ($CDCl_3$, 400 MHz) of the major isomer: δ = 1.22–1.81 (m, 20 H, cyclohexyl), 2.23 (s, 3 H, SMe), 3.34–3.38 (m, 1 H, C5-H^{Glcp}), 3.64–4.41 (m, 11 H, C2-H^{Glcp}, C3-H^{Glcp}, C4-H^{Glcp}, C6-H^{Glcp}, C2-H^{Manp}, C4-H^{Manp}, C5-H^{Manp}, C6-H^{Manp}, OMe), 4.55 (d, J = 9.6 Hz, 1 H, C1-H^{Glcp}), 4.63 (dd, J = 10.0, 9.6 Hz, 1 H, C3-H^{Manp}), 5.31 (d, J = 1.6 Hz, 1 H, C1-H^{Manp}), 6.24 [s, 0.22 H, CH Naph (minor)], 6.43 (s, 1 H, CH Naph), 6.47–6.88 (m, 5 H, Ar), 7.44–7.86 (m, 11 H, Ar) ppm. ^{13}C NMR (C_6D_6, 100 MHz): δ = 13.0, 22.1, 22.4, 22.7, 22.9, 25.4, 25.5, 27.5, 27.7, 37.9, 37.9, 55.6, 61.4, 61.5, 65.4, 71.1, 74.3, 75.0, 83.0, 85.5, 98.5, 99.5, 99.8, 104.4, 114.4, 114.5, 117.6, 117.9, 124.7, 125.4, 125.7, 125.8, 127.5, 127.6, 128.1, 132.8, 133.3, 138.0, 149.9, 154.7 ppm. MALDI-TOF MS: calcd. for $C_{57}H_{52}D_{14}NaO_{12}S$ $[M + Na]^+$ 1011.5; found 1011.3. HRMS ESI-TOF: calcd. for $C_{57}H_{52}D_{14}NaO_{12}S$ $[M + Na]^+$ 1011.5051; found 1011.5050.

4-Methoxyphenyl 4,6-*O*-Cyclohexylidene-3-*O*-[D_7]benzyl-α-D-glucopyranosyl-(1→3)-2-*O*-[D_7]benzyl-4,6-*O*-cyclohexylidene-α-D-mannopyranoside (36): Compound **36** was synthesized from **34** by the procedure used for the synthesis of **16** (74%). $[\alpha]_D^{27}$ = +101.3 (c = 1.67, $CHCl_3$). ^1H NMR (C_6D_6, 400 MHz): δ = 1.23–1.86 (m, 20 H, cyclohexyl), 3.00 (br. s, 1 H, OH), 3.29 (s, 3 H, OMe), 3.63–4.18 (m, 10 H, C2-H^{Glcp}, C4-H^{Glcp}, C5-H^{Glcp}, C6-H^{Glcp}, C6-H^{Glcp}, C3-H^{Manp}, C4-H^{Manp}, C5-H^{Manp}, C6-H^{Manp}, C6-H^{Manp}), 4.54 (t, J = 9.2 Hz, 1 H, C3-H^{Glcp}), 4.42 (dd, J = 10.0, 3.6 Hz, 1 H, C2-H^{Manp}), 5.31 (d, J = 3.6 Hz, 1 H, C1-H^{Glcp}), 5.47 (d, J = 1.2 Hz, 1 H, C1-H^{Manp}), 6.70 (d, J = 8.8 Hz, 2 H, Ar), 6.89 (d, J = 8.8 Hz, 2 H, Ar) ppm. ^{13}C NMR (C_6D_6, 100 MHz): δ = 22.9, 23.2, 23.4, 25.9, 26.1, 28.1, 28.2, 38.5, 38.7, 55.20, 61.7, 62.3, 65.3, 66.5, 70.7, 74.0, 74.1, 77.2, 78.9, 80.3, 98.2 ($C1^{Manp}$), 99.8, 100.6, 102.1 ($C1^{Glcp}$), 115.0, 118.2, 150.3, 155.8 ppm. MALDI-TOF MS: calcd. for $C_{45}H_{42}D_{14}NaO_{12}$ $[M + Na]^+$ 825.5; found 825.8. HRMS ESI-TOF: calcd. for $C_{45}H_{42}D_{14}NaO_{12}$ $[M + Na]^+$ 825.4548; found 825.4534.

2-Naphthaldehyde (4-Methoxyphenyl 2-*O*-[D_7]benzyl-4,6-*O*-cyclohexylidene-α-D-mannopyranosid-3-yl) (Methyl 3-*O*-triisopropylsilyl-4,6-*O*-cyclohexylidene-1-thio-β-D-glucopyranosid-2-yl) Acetal (35); 3b + 33 → 35: The title compound was synthesized from **3b** and **33** by the procedure used for the synthesis of **13** (90%, 14.3:1). ^1H NMR ($CDCl_3$, 400 MHz) of the major isomer: δ = 1.00–1.57 (m, 41 H, cyclohexyl, TIPS), 2.19 (s, 3 H, SMe), 3.25 (td, J = 10.0, 5.6 Hz, 1 H, C5-H^{Glcp}), 3.64–3.90 (m, 13 H, C2-H^{Glcp}, C3-H^{Glcp}, C4-H^{Glcp}, C6-H^{Glcp}, C5-H^{Manp}, C6-H^{Manp}, OMe), 4.02–4.32 (m, 2 H, C4-H^{Manp}, C6-H^{Manp}), 4.23 (d, J = 2.0 Hz, 1 H, C2-H^{Manp}), 4.48 (dd, J = 10.0, 9.6 Hz, 1 H, C3-H^{Manp}), 4.57 (d, J = 8.4 Hz, 1 H, C1-H^{Glcp}), 5.37 (d, J = 2.0 Hz, 1 H, C1-H^{Manp}), 6.36 (s, 1 H, CH Naph), 6.79 (d, J = 9.2 Hz, 2 H, Ar), 6.89 (d, J = 9.2 Hz, 2 H, Ar), 7.34–7.94 (m, 7 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 13.9, 14.1, 14.3, 18.3, 18.7, 22.0, 22.6, 22.7, 25.5, 25.8, 27.3, 37.8, 37.9, 55.7, 61.2, 61.6, 65.6, 70.7, 70.9, 73.1, 77.9, 78.1, 86.0, 98.3, 99.8, 103.7, 114.6, 117.6, 124.9, 125.8, 125.9, 126.2, 127.6, 127.8, 128.1, 132.8, 133.5, 137.8, 149.9, 154.9 ppm. MALDI-TOF MS: calcd. for $C_{59}H_{73}D_7NaO_{12}SSi$ $[M + Na]^+$ 1070.6; found 1070.7. HRMS ESI-TOF: calcd. for $C_{59}H_{73}D_7NaO_{12}SSi$ $[M + Na]^+$ 1070.5477; found 1070.5481.

4-Methoxyphenyl 4,6-*O*-Cyclohexylidene-2-*O*-(2-naphthylmethyl)-3-*O*-triisopropylsilyl-α-D-glucopyranosyl-(1→3)-2-*O*-[D_7]benzyl-4,6-*O*-cyclohexylidene-α-D-mannopyranoside (37): Compound **37** was synthesized from **35** by the procedure used for the synthesis of **18** (86%). $[\alpha]_D^{26}$ = +104.8 (c = 0.92, $CHCl_3$). ^1H NMR (C_6D_6, 400 MHz): δ = 1.21–1.78 (m, 41 H, cyclohexyl, TIPS), 3.29 (s, 3 H, OMe), 3.58–4.18 (m, 9 H, C2-H^{Glcp}, C4-H^{Glcp}, C5-H^{Glcp}, C6-H^{Glcp}, C2-H^{Manp}, C5-H^{Manp}, C6-H^{Manp}), 4.54 (t, J = 9.2 Hz, 1 H, C3-H^{Glcp}), 4.65–4.75 (m, 3 H, C3-H^{Manp}, C4-H^{Manp}, NAP), 5.13 (d, J = 11.6 Hz, 1 H, NAP), 5.52 (s, 1 H, C-1H^{Manp}), 5.90 (d, J = 3.6 Hz, 1 H, C1-H^{Glcp}), 6.68 (d, J = 9.2 Hz, 2 H, Ar), 6.87 (d, J = 8.8 Hz, 2 H, Ar), 7.24–8.03 (m, 7 H, Ar) ppm. ^{13}C NMR (C_6D_6, 100 MHz): δ = 13.5, 18.8, 22.6, 22.9, 23.2, 23.2, 25.8, 26.2, 27.8, 28.2, 38.8, 55.2, 61.5, 62.2, 64.8, 66.7, 71.3, 71.7, 72.6, 73.5, 74.6, 79.3, 81.2, 97.9 ($C1^{Glcp}$), 99.0 ($C1^{Manp}$), 100.06 (×2), 115.0, 118.2, 125.8, 126.1, 126.4, 133.4, 133.9, 136.6, 138.6, 150.3, 155.6 ppm. MALDI-TOF MS: calcd. for $C_{58}H_{71}D_7NaO_{12}Si$ $[M + Na]^+$ 1024.6; found 1025.0. HRMS ESI-TOF: calcd. for $C_{58}H_{71}D_7NaO_{12}Si$ $[M + Na]^+$ 1024.5600; found 1024.5601.

4-Methoxyphenyl 2-*O*-[D_7]Benzyl-4,6-*O*-cyclohexylidene-α-D-glucopyranosyl-(1→3)-2-*O*-[D_7]benzyl-4,6-*O*-cyclohexylidene-α-D-mannopyranoside (39): DDQ (22.3 mg, 98.5 μmol) was added at room temperature to a solution of NAP ether **37** (32.9 mg, 32.8 μmol) and $NaHCO_3$ (27.6 mg, 328 μmol) in dry 1,2-dichloroethane (3.0 mL). The mixture was stirred at room temperature for 14 h. After addition of aqueous ascorbate buffer solution, the product was extracted with EtOAc. The combined extracts were washed with satd. aq. $NaHCO_3$ and brine. The washed organic layer was dried with Na_2SO_4. After filtration and concentration, the residue was purified by PTLC (hexane/EtOAc, 5:1) to give **38** (24.2 mg, 86%). NaH (16.0 mg, 40.0 μmol) and then [D_7]BnBr (4.0 μL, 32.0 μmol) were added at 0 °C to a solution of alcohol **38** (23.0 mg, 26.7 μmol) in dry DMF (2.0 mL), and the mixture was stirred for 3 h, during which the temperature was allowed to rise to room temperature. After addition of triethylamine and brine to the mixture, the product was extracted with EtOAc. The combined extracts were washed with brine and dried with Na_2SO_4. After filtration and concentration, the residue was used for the next reaction without further purification. A TBAF solution in THF (1 M, 80.0 μL, 80.0 μmol) was added at room temperature to a solution of the mixture in dry THF (2.0 mL), and the mixture was stirred for 16 h. After concentration, the residue was purified by PTLC (hexane/EtOAc, 4:1) to give the title compound **39**[29] (16.1 mg, 75% in two steps). $[\alpha]_D^{28}$ = –125.2 (c = 1.00, $CHCl_3$). ^1H NMR (C_6D_6, 400 MHz): δ = 1.00–2.10 (m, 20 H, cyclohexyl ×2), 2.48 (br. s, 1 H, OH), 3.29 (s, 3 H, OMe), 3.59 (dd, J = 9.2, 4.0 Hz, 1 H, C2-H^{Glcp}), 3.69 (t, J = 9.2 Hz, 1 H, C4-H^{Glcp}), 3.73–3.79 (m, 2 H, C6-H^{Manp}), 3.80 (t, J = 10.4 Hz, 1 H, C6-H^{Glcp}), 3.98 (t, J = 1.2 Hz, 1 H, C2-H^{Manp}), 4.02 (dd, J = 10.4, 5.6 Hz, 1 H, C6-H^{Glcp}), 4.04–4.18 (m, 2 H, C5-H^{Manp}, C5-H^{Glcp}), 4.39 (t, J = 9.2 Hz, 1 H, C3-H^{Glcp}), 4.65–4.73 (m, 2 H, C3-H^{Manp}, C4-H^{Manp}), 5.53 (d, J = 1.2 Hz, 1 H, C1-H^{Man}), 5.82 (d, J = 4.0 Hz, 1 H, C1-H^{Glcp}), 6.68–6.90 (m, 4 H, Ar) ppm. ^{13}C NMR (C_6D_6, 100 MHz): δ = 22.4, 22.5, 22.85, 22.92, 25.6, 25.7, 27.7, 38.3, 38.4, 54.8, 61.3, 61.9, 64.3, 66.2, 70.8, 71.3, 73.3, 73.5, 78.8, 79.5, 97.9 ($C1^{Glcp}$), 98.5 ($C1^{Manp}$), 99.7, 99.8, 114.7, 118.0, 126.9–128.7 (overlapped with C_6D_6 signal), 138.2, 138.5, 150.1, 155.4 ppm. MALDI-TOF MS: calcd. for $C_{45}H_{42}D_{14}NaO_{12}$ $[M + Na]^+$ 825.45; found 825.50. HRMS ESI-TOF: calcd. for $C_{45}H_{42}D_{14}NaO_{12}$ $[M + Na]^+$ 825.4548; found 825.4565.

2-Naphthaldehyde (4-Methoxyphenyl 2-*O*-[D_7]benzyl-4,6-*O*-cyclohexylidene-α-D-glucopyranosyl-(1→3′)-2′-*O*-[D_7]benzyl-4′,6′-*O*-cyclohexylidene-α-D-mannopyranosid-3-yl) (Methyl 3-*O*-[D_7]benzyl-4,6-*O*-cyclohexylidene-1-thio-β-D-glucopyranosid-2-yl) Acetal (40): DDQ (26.7 mg, 117 μmol) was added under Ar at room temperature to a mixture of acceptor **39** (55.5 mg, 69.1 μmol), donor **3a** (47.4 mg, 89.8 μmol), and dried powdered MS (4 Å, 500 mg) in dry CH_2Cl_2 (3.0 mL). The mixture was stirred at same temperature for 23 h, quenched with aqueous ascorbate buffer (3.0 mL), and filtered through Celite. The filtrate was extracted with EtOAc and then washed with satd. aq. $NaHCO_3$ and brine. The combined organic layers were dried with Na_2SO_4, and the solvents were evaporated in vacuo. The crude product was purified by gel filtration chromatography (SX-3; EtOAc/toluene, 1:1) to give mixed acetal **40** (88.0 mg, 96%). ^{1}H NMR ($CDCl_3$, 400 MHz) of the major isomer: δ = 1.27–1.59 (m, 30 H, cyclohexyl), 2.18 (s, 3 H, SMe), 2.90 (td, J = 10.0, 5.2 Hz, 1 H, C5-H^{Glcp1}), 3.20 (t, J = 9.6 Hz, 1 H, C6-H^{Glcp2}), 3.37–4.43 (m, 17 H, C2-H^{Glcp1}, C3-H^{Glcp1}, C4-H^{Glcp1}, C6-H^{Glcp1}, C2-H^{Glcp2}, C3-H^{Glcp2}, C4-H^{Glcp2}, C5-H^{Glcp2}, C6-H^{Glcp2}, C2-H^{Manp}, C3-H^{Manp}, C4-H^{Manp}, C5-H^{Manp}, C6-H^{Manp}, OMe), 5.30 (s, 1 H, C1-H^{Manp}), 5.64 (d, J = 3.6 Hz, 1 H, C1-H^{Glcp2}), 6.34 (s, 1 H, CH Naph), 6.39 [s, 0.4 H, CH Naph (minor)], 6.75–7.76 (m, 11 H, Ar, NAP) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 12.9, 21.5, 22.2, 22.5, 22.7, 22.9, 25.5, 27.3, 27.6, 27.8, 37.7, 38.0, 55.7, 60.5, 61.3, 61.4, 62.0, 63.8, 64.0, 65.6, 71.1, 71.4, 72.0, 73.5, 73.7, 82.6, 85.7, 97.4, 98.7, 99.2, 99.5, 99.8, 105.2, 114.2, 114.5, 117.8, 125.0, 125.2, 125.6, 125.8, 126.4, 127.6, 127.8, 128.0, 128.2, 129.0, 132.6, 133.6, 137.2, 149.8, 154.9, 177.7 ppm. MALDI-TOF MS: calcd. for $C_{76}H_{69}D_{21}NaO_{17}$ [M + Na]$^+$ 1350.7; found 1350.8. HRMS ESI-TOF: calcd. for $C_{76}H_{69}D_{21}NaO_{17}$ [M + Na]$^+$ 1350.7115; found 1350.7110.

4-Methoxyphenyl 2-*O*-Acetyl-3-*O*-[D_7]benzyl-4,6-*O*-cyclohexylidene-α-D-glucopyranosyl-(1→3)-2-*O*-[D_7]benzyl-4,6-*O*-cyclohexylidene-α-D-glucopyranosyl-(1→3)-2-*O*-[D_7]benzyl-4,6-*O*-cyclohexylidene-α-D-mannopyranoside (41): DTBMP (21.1 mg, 103 μmol) and MS (4 Å, 1.0 g) in dry 1,2-dichloroethane (5.0 mL) were added under Ar at room temperature to mixed acetal **40** (34.2 mg, 25.7 μmol). MeOTf (10.2 μL, 0.0901 mmol), diluted in dry 1,2-dichloroethane (1.0 mL), was then added to the mixture, which was stirred at room temperature for 7 h. The reaction mixture was quenched with triethylamine, diluted with EtOAc, and filtered through Celite. Pyridine (4.0 mL), Ac_2O (300 μL), and a catalytic amount of DMAP were added to the filtrate. The mixture was stirred at room temperature for 14 h and concentrated in vacuo. The residue was diluted with EtOAc, washed with satd. aq. $NaHCO_3$ and brine and dried with Na_2SO_4, and the solvents were evaporated in vacuo. The crude product was purified by gel filtration chromatography (SX-3; EtOAc/toluene, 1:1) to give the product (25.8 mg, 85%) as an acetate. $[a]_D^{26}$ = +125.9 (c = 1.69, $CHCl_3$). ^{1}H NMR (C_6D_6, 400 MHz): δ = 1.22–1.87 (m, 33 H, cyclohexyl, Ac), 3.29 (s, 3 H, OMe), 3.64–3.96 (m, 13 H, C4-H^{Glcp1}, C5-H^{Glcp1}, C6-H^{Glcp1}, C2-H^{Glcp2}, C3-H^{Glcp2}, C4-H^{Glcp2}, C5-H^{Glcp2}, C6-H^{Glcp2}, C5-H^{Manp}, C6-H^{Manp}), 4.21–4.71 (m, 4 H, C3-H^{Glcp1}, C2-H^{Manp}, C3-H^{Manp}, C4-H^{Manp}), 5.35 (dd, J = 3.6, 4.0 Hz, 1 H, C2-H^{Glcp1}), 5.53 (s, 1 H, C1-H^{Manp}), 5.87 (d, J = 3.6 Hz, 1 H, C1-H^{Glcp2}), 6.06 (d, J = 4.0 Hz, 1 H, C1-H^{Glcp1}), 6.69 (d, J = 8.8 Hz, 2 H, Ar), 6.86 (d, J = 9.6 Hz, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 12.9, 21.5, 22.2, 22.5, 22.7, 22.9, 25.5, 27.3, 27.6, 27.8, 37.7, 38.0, 55.7, 60.5, 61.3, 61.4, 62.0, 63.8, 64.0, 65.6, 71.1, 71.4, 72.0, 73.5, 73.7, 82.6, 85.7, 97.4 (C1^{Glcp2}), 98.7 (C1^{Manp}), 99.2, 99.5, 99.8, 105.2 (C1^{Glcp1}), 114.2, 114.5, 117.8, 125.0, 125.2, 125.6, 125.8, 126.4, 127.6, 127.8, 128.0, 128.2, 129.0, 132.6, 133.6, 137.2, 149.8, 154.9, 177.7 ppm. MALDI-TOF MS: calcd. for $C_{66}H_{61}D_{21}NaO_{18}$ [M + Na]$^+$ 1206.7; found 1207.1. HRMS ESI-TOF: calcd. for $C_{66}H_{61}D_{21}NaO_{18}$ [M + Na]$^+$ 1206.6717; found 1206.6736.

4-Methoxyphenyl 3-*O*-[D_7]Benzyl-4,6-*O*-cyclohexylidene-α-D-glucopyranoside-(1→3)-2-*O*-[D_7]benzyl-4,6-*O*-cyclohexylidene-α-D-glucopyranoside-(1→3)-2-*O*-[D_7]benzyl-4,6-*O*-cyclohexylidene-α-D-mannopyranoside (42): NaOMe (30.0 mg) was added to the solution of the resulting acetate **41** (above, 28.4 mg, 24.0 μmol) in methanol/THF (5:1) until the mixture was alkaline, as indicated by phenolphthalein, and the mixture was stirred at 50 °C for 20 h. Amberlyst 15H$^+$ was added to the mixture to quench excess NaOMe. The resin was filtered off and concentrated. The residue was purified by PTLC (SiO_2; hexane/EtOAc, 5:1) to give title compound **42**[29] (20.0 mg, 88%). $[a]_D^{27}$ = +126.0 (c = 0.47, $CHCl_3$). ^{1}H NMR (C_6D_6, 400 MHz): δ = 1.22–1.90 (m, 30 H, cyclohexyl), 2.64 (d, J = 10.4 Hz, 1 H, OH), 3.29 (s, 3 H, OMe), 3.54 (dd, J = 9.2, 4.0 Hz, 1 H, C2-H^{Glcp1}), 3.60–4.11 (m, 13 H, C4-H^{Glcp1}, C5-H^{Glcp1}, C6-H^{Glcp1}, C6-H^{Glcp1}, C2-H^{Glcp2}, C4-H ^{Glcp2}, C5-H^{Glcp2}, C6-H^{Glcp2}, C6-H^{Glcp2}, C2-H^{Manp}, C5-H^{Manp}, C6-H^{Manp}, C6-H^{Manp}), 4.41–4.46 (m, 2 H, C3-H^{Glcp1}, C3-H^{Glcp2}), 4.68–4.95 (m, 2 H, C3-H^{Manp}, C4-H^{Manp}), 5.53–5.55 (m, 2 H, C1-H^{Glcp2}, C1-H^{Manp}), 5.84 (d, J = 3.6 Hz, 1 H, C1-H^{Glcp1}), 6.69 (d, J = 8.8 Hz, 2 H, Ar), 6.86 (d, J = 9.6 Hz, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 22.8, 22.9, 23.2, 23.3, 23.5, 26.0, 26.1, 28.1, 28.2, 38.5, 38.7, 38.8, 55.2, 61.6, 62.1, 62.2, 64.3, 64.6, 66.6, 71.6, 73.6, 74.0, 74.4, 74.4, 76.3, 77.5, 79.0, 80.2, 97.9 (C1^{Glcp2}), 98.6 (C1^{Manp}), 99.6, 100.2, 100.4, 100.9 (C1^{Glcp1}), 115.0, 118.3, 138.1, 138.2, 139.2, 150.3, 155.7 ppm. MALDI-TOF MS: calcd. for $C_{64}H_{59}D_{21}NaO_{17}$ [M + Na]$^+$ 1164.7; found 1165.2. HRMS ESI-TOF: calcd. for $C_{64}H_{59}D_{21}NaO_{17}$ [M + Na]$^+$ 1164.6611; found 1164.6655.

2-Naphthaldehyde (4-Methoxyphenyl 3-*O*-[D_7]benzyl-4,6-*O*-cyclohexylidene-α-D-glucopyranosyl-(1→3′)-2′-*O*-[D_7]benzyl-4′,6′-*O*-cyclohexylidene-α-D-glucopyranosyl-(1′→3′′)-2′′-*O*-[D_7]benzyl-4′′,6′′-*O*-cyclohexylidene-α-D-mannopyranosid-2-yl) (Methyl 3-*O*-[D_7]benzyl-4,6-*O*-cyclohexylidene-1-thio-α-D-glucopyranosid-2-yl) Acetal (44) (Route A): DDQ (15.8 mg, 70.0 μmol) was added under Ar at room temperature to a mixture of acceptor **42** (18.0 mg, 15.8 μmol), donor **3a** (10.8 mg, 20.5 μmol), and dried powdered MS (4 Å, 800 mg) in dry CH_2Cl_2 (4.0 mL). The mixture was stirred at same temperature for 20 h, quenched with aqueous ascorbate buffer (1.0 mL), and filtered through Celite. The filtrate was extracted with EtOAc and then washed with satd. aq. $NaHCO_3$ and brine and dried with Na_2SO_4, and the solvents were evaporated in vacuo. The crude product was purified by gel filtration chromatography (SX-3; EtOAc/toluene, 1:1) to give mixed acetal **44** (13.2 mg, 50%, 2.33:1). ^{1}H NMR ($CDCl_3$, 400 MHz) of the major isomer: δ = 1.25–2.00 (m, 40 H, cyclohexyl), 2.35 (s, 3 H, SMe), 3.32–4.52 (m, 28 H, C1-H^{Glcp1}, C2-H^{Glcp1}, C3-H^{Glcp1}, C4-H^{Glcp1}, C5-H^{Glcp1}, C6-H^{Glcp1}, C6-H^{Glcp1}, C2-H^{Glcp2}, C3-H^{Glcp2}, C4-H^{Glcp2}, C5-H^{Glcp2}, C6-H^{Glcp2}, C6-H^{Glcp2}, C2-H^{Glcp3}, C3-H^{Glcp3}, C4-H^{Glcp3}, C5-H^{Glcp3}, C6-H^{Glcp3}, C6-H^{Glcp3}, C2-H^{Manp}, C3-H^{Manp}, C4-H^{Manp}, C5-H^{Manp}, C6-H^{Manp}, C6-H^{Manp}, OMe), 5.36 (d, J = 1.6 Hz, 1 H, C1-H^{Manp}), 5.61 (d, J = 3.6 Hz, 1 H, C1-H^{Glcp3}), 5.69 (d, J = 3.2 Hz, 1 H, C1-H^{Glcp2}), 6.25 (s, 1 H, CH Naph), 6.30 [s, 0.4 H, CH Naph (minor)], 6.80–7.77 (m, 16 H, Ar, NAP) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 10.5, 22.3, 22.4, 22.6, 22.9, 23.0, 25.5, 25.7, 27.6, 27.9, 37.9, 38.3, 55.7, 61.3, 63.7, 65.7, 70.9, 71.3, 71.8, 72.1, 74.2, 74.4, 74.7, 75.1, 83.6, 84.5, 97.0, 98.6, 98.7, 99.1, 99.4, 99.6, 99.8, 114.5, 117.8, 125.2, 125.7, 125.9, 126.0, 127.2, 127.6, 128.1, 128.1, 129.0, 133.7, 136.0, 137.5, 149.8, 154.9 ppm. MALDI-TOF MS: calcd. for $C_{95}H_{86}D_{28}NaO_{22}S$ [M + Na]$^+$ 1689.9; found 1690.5. HRMS ESI-TOF: calcd. for $C_{95}H_{86}D_{28}NaO_{22}S$ [M + Na]$^+$ 1689.9178; found 1689.9170.

4-Methoxyphenyl 3-*O*-[D_7]Benzyl-4,6-*O*-cyclohexylidene-2-*O*-(2-naphthylmethyl)-α-D-glucopyranosyl-(1→3)-2-*O*-[D_7]benzyl-4,6-*O*-cyclohexylidene-α-D-glucopyranosyl-(1→3)-2-*O*-[D_7]benzyl-4,6-*O*-cyclohexylidene-α-D-mannopyranoside (43): MeOTf (20.0 μL, 0.174 mmol) was added at room temperature under Ar to mixed acetal **40** (66.0 mg, 0.0500 mmol), DTBMP (40.8 mg, 0.199 mmol), MS (4 Å, 2.0 g), and tris(trimethylsilyl)silane (76.6 μL, 0.248 mmol) in dry 1,2-dichloroethane (12.0 mL). The mixture was stirred at room temperature for 14 h, quenched with triethylamine, diluted with EtOAc, and filtered through Celite. The filtrate was extracted with EtOAc, washed with satd. aq. $NaHCO_3$ and brine, and dried with Na_2SO_4. After filtration and concentration, the residue was purified by PTLC (EtOAc/hexane, 1:7) to give product **43** (48.0 mg, 76%) as the NAP ether, together with **42** (3.0 mg, 6%). NAP ether **43**: $[\alpha]_D^{27}$ = +103.0 (*c* = 0.47, $CHCl_3$). ^1H NMR (C_6D_6, 400 MHz): δ = 1.25–1.86 (m, 30 H, cyclohexyl), 3.28 (s, 3 H, OMe), 3.54 (dd, *J* = 9.2, 4.0 Hz, 1 H, C2-H^{Glcp1}), 3.67–4.10 (m, 13 H, C4-H^{Glcp1}, C5-H^{Glcp1}, C6-H^{Glcp1}, C2-H^{Glcp2}, C4-H^{Glcp2}, C5-H^{Glcp2}, C6-H^{Glcp2}, C2-H^{Manp}, C5-H^{Manp}, C6-H^{Manp}), 4.36 (t, *J* = 9.2 Hz, 1 H, C3-H^{Glcp2}), 4.63–4.81 (m, 4 H, C3-H^{Glcp1}, C5-H^{Glcp2}, C3-H^{Manp}, C4-H^{Manp}), 5.00 (s, 2 H, NAP), 5.30 (d, *J* = 1.6 Hz, 1 H, C1-H^{Manp}), 5.90 (d, *J* = 4.0 Hz, 1 H, C1-H^{Glcp2}), 5.95 (d, *J* = 3.6 Hz, 1 H, C1-H^{Glcp1}), 6.68 (d, *J* = 8.8 Hz, 2 H, Ar), 6.86 (d, *J* = 9.6 Hz, 2 H, Ar), 7.25–7.95 (m, 7 H, Ar) ppm. ^{13}C NMR (C_6D_6, 100 MHz): δ = 22.8, 22.8, 23.0, 23.3, 23.4, 23.5, 25.95, 26.03, 26.2, 27.9, 28.0, 28.3, 38.6, 38.75, 38.82, 55.2, 61.6, 62.0, 62.5, 63.9, 64.3, 66.6, 71.8, 73.2, 73.4, 75.2, 75.4, 77.2, 78.9, 80.4, 97.6 ($C1^{Glcp2}$), 97.9 ($C1^{Glcp1}$), 98.8 ($C1^{Manp}$), 99.5, 99.9, 100.1, 118.2, 125.7, 126.0, 126.1, 126.3, 133.4, 133.9, 136.9, 138.4, 139.7, 150.3, 155.6 ppm. MALDI-TOF MS: calcd. for $C_{75}H_{67}D_{21}NaO_{17}$ $[M + Na]^+$ 1304.7; found 1305.4. HRMS ESI-TOF: calcd. for $C_{75}H_{67}D_{21}NaO_{17}$ $[M + Na]^+$ 1304.7237; found 1304.7255.

2-Naphthaldehyde (4-Methoxyphenyl 3-*O*-[D_7]benzyl-4,6-*O*-cyclohexylidene-α-D-glucopyranosyl-(1→3′)-2′-*O*-[D_7]benzyl-4′,6′-*O*-cyclohexylidene-α-D-glucopyranosyl-(1′→3′′)-2′′-*O*-[D_7]benzyl-4′′,6′′-*O*-cyclohexylidene-α-D-mannopyranosid-2-yl) (Methyl 3-*O*-[D_7]benzyl-4,6-*O*-cyclohexylidene-1-thio-α-D-glucopyranosid-2-yl) Acetal (44) (Route B): DDQ (7.5 mg, 33.0 μmol) was added under Ar at room temperature to a mixture of **43** (33.4 mg, 25.2 μmol), **11** (7.5 mg, 1.94 μmol), and dried powdered MS (4 Å, 800 mg) in dry CH_2Cl_2 (3.0 mL). The mixture was stirred at the same temperature for 15 h, quenched with aqueous ascorbate buffer (2.0 mL), and filtered through Celite. The filtrate was extracted with EtOAc, washed with satd. aq. $NaHCO_3$ and brine and dried with Na_2SO_4, and the solvents were evaporated in vacuo. The crude product was purified by gel filtration chromatography (SX-3; EtOAc/toluene, 1:1) to give mixed acetal **35** (31.4 mg, 97%, 3.43:1). ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.25–2.00 (m, 40 H, cyclohexyl), 2.35 (s, 3 H, SMe), 3.32–4.52 (m, 28 H, C1-H^{Glcp1}, C2-H^{Glcp1}, C3-H^{Glcp1}, C4-H^{Glcp1}, C5-H^{Glcp1}, C6-H^{Glcp1}, C6-H^{Glcp1}, C2-H^{Glcp2}, C3-H^{Glcp2}, C4-H^{Glcp2}, C5-H^{Glcp2}, C6-H^{Glcp2}, C6-H^{Glcp2}, C2-H^{Glcp3}, C3-H^{Glcp3}, C4-H^{Glcp3}, C5-H^{Glcp3}, C6-H^{Glcp3}, C6-H^{Glcp3}, C2-H^{Manp}, C3-H^{Manp}, C4-H^{Manp}, C5-H^{Manp}, C6-H^{Manp}, C6-H^{Manp}, OMe), 5.36 (d, *J* = 1.6 Hz, 1 H, C1-H^{Manp}), 5.61 (d, *J* = 3.6 Hz, 1 H, C1-H^{Glcp3}), 5.69 (d, *J* = 3.2 Hz, 1 H, C1-H^{Glcp2}), 6.25 (s, 1 H, CH Naph), 6.30 [s, 0.4 H, CH Naph (minor)], 6.80–7.77 (m, 11 H, Ar, NAP) ppm.

4-Methoxyphenyl 3-*O*-[D_7]Benzyl-4,6-*O*-cyclohexylidene-α-D-glucopyranosyl-(1→2)-3-*O*-[D_7]benzyl-4,6-*O*-cyclohexylidene-α-D-glucopyranosyl-(1→3)-2-*O*-[D_7]benzyl-4,6-*O*-cyclohexylidene-α-D-glucopyranosyl-(1→3)-2-*O*-[D_7]benzyl-4,6-*O*-cyclohexylidene-α-D-mannopyranoside (22): MeOTf (5.6 μL, 49.7 μmol) was added under Ar at room temperature to mixed acetal **44** (23.7 mg, 14.2 μmol), DTBMP (11.7 mg, 56.8 μmol), MS (4 Å, 1.0 g), and tris(trimethylsilyl)silane (22.0 μL, 71.0 μmol) in dry 1,2-dichloroethane (3.6 mL). The mixture was stirred at room temperature for 14 h, quenched with triethylamine, diluted with EtOAc, and filtered through Celite. The filtrate was extracted with EtOAc, washed with satd. aq. $NaHCO_3$ and brine and dried with Na_2SO_4, and the solvents were evaporated in vacuo. The residue was used for the next reaction without further purification. It was dissolved in dry 1,2-dichloroethane (1.0 mL), and $NaHCO_3$ (12.0 mg, 142 μmol) and DDQ (9.6 mg, 42.6 μmol) were added at room temperature. The residue was stirred at room temperature for 5 h. After addition of aqueous ascorbate buffer solution (2.0 mL), the product was extracted with EtOAc. The combined extracts were washed with satd. aq. $NaHCO_3$ and brine and dried with Na_2SO_4. After filtration and concentration, the residue was purified by gel filtration chromatography (SX-3; EtOAc/toluene, 1:1) to give product **22** (17.7 mg, 77%). $[\alpha]_D^{25}$ = +143.6 (*c* = 1.54, $CHCl_3$). ^1H NMR (C_6D_6, 400 MHz): δ = 0.90–2.00 (m, 40 H, cyclohexyl), 3.30 (s, 3 H, OMe), 3.45 (br d, *J* = 10.8 Hz, 1 H, C2-OH^{Glcp3}), 3.59 (dd, *J* = 9.6, 3.6 Hz, 1 H, C2-H^{Glcp1}), 3.63–3.76 (m, 7 H, C6-H^{Glcp1}, C6-H^{Glcp2}, C2-H^{Glcp3}, C3-H^{Glcp3}, C6-H^{Glcp3}, C6-H^{Manp}, C6-H^{Manp}), 3.81 (t, *J* = 10.8 Hz, 1 H, C4-H^{Glcp2}), 3.80–4.10 (m, 9 H, C4-H^{Glcp1}, C6-H^{Glcp1}, C2-H^{Glcp2}, C3-H^{Glcp2}, C6-H^{Glcp2}, C4-H^{Glcp3}, C6-H^{Glcp3}, C2-H^{Manp}, C5-H^{Manp}), 4.15 (td, *J* = 10.0, 5.2 Hz, 1 H, C5-H^{Glcp2}), 4.36 (td, *J* = 10.8, 5.6 Hz, 1 H, C5-H^{Glcp1}), 4.46 (td, *J* = 10.8, 5.6 Hz, 1 H, C5-H^{Glcp3}), 4.60 (t, *J* = 9.6 Hz, 1 H, C3-H^{Glcp2}), 4.65–4.74 (m, 2 H, C3-H^{Manp}, C4-H^{Manp}), 4.81 (br. s, 1 H, C1-H^{Glcp3}), 5.50 (d, *J* = 1.6 Hz, 1 H, C1-H^{Manp}), 5.79 (d, *J* = 3.2 Hz, 1 H, C1-H^{Glcp2}), 5.84 (d, *J* = 3.6 Hz, 1 H, C1-H^{Glcp1}), 6.70 (d, *J* = 9.2 Hz, 2 H, Ar), 6.88 (d, *J* = 9.2 Hz, 2 H, Ar) ppm. ^{13}C NMR (C_6D_6, 100 MHz): δ = 22.77 (×4), 23.2, 23.31 (×3), 25.92 (×4), 27.97 (×3), 28.2, 38.3, 38.47 (×2), 38.7, 55.1, 61.5, 61.9, 62.2, 64.0, 64.4, 66.4, 71.6, 73.3, 73.5, 74.4, 74.8, 75.3, 76.7, 79.1, 79.2, 80.9, 96.5 ($C1^{Glcp2}$), 96.6 ($C1^{Glcp3}$), 97.7 ($C1^{Glcp1}$), 98.7 ($C1^{Manp}$), 99.5, 99.7, 100.0, 100.2, 114.9, 118.2, 138.8, 138.9, 139.7, 150.3, 155.6 ppm. MALDI-TOF MS: calcd. for $C_{83}H_{76}D_{28}NaO_{22}$ $[M + Na]^+$ 1503.9; found 1504.4. HRMS ESI-TOF: calcd. for $C_{83}H_{76}D_{28}NaO_{22}$ $[M + Na]^+$ 1503.8674; found 1503.8626.

4-Methoxyphenyl α-D-Glucopyranosyl-(1→2)-α-D-glucopyranosyl-(1→3)-α-D-glucopyranosyl-(1→3)-α-D-mannopyranoside (21): TFA (200 μL) was added to a solution of compound **22** (6.8 mg, 4.59 μmol) in CH_2Cl_2 (2.0 mL), and the mixture was stirred at room temperature for 2 h and then concentrated in vacuo, followed by azetropic removal of TFA with toluene. Hydrogenolysis of the resulting residue **45** was carried out in the presence of $Pd(OH)_2$ (28.0 mg) in MeOH/H_2O (1:1, 2.0 mL) at room temperature over 5 h. The mixture was filtered through Celite, and the filtrate was concentrated in vacuo. The residue was purified by gel filtration (Sephadex LH-20; MeOH/H_2O, 1:1) to give title compound **21** (3.5 mg, 100%). ^1H NMR (CD_3OD, 400 MHz): δ = 3.33–4.12 (m, 23 H, C2-H^{Glcp1}, C3-H^{Glcp1}, C4-H^{Glcp1}, C5-H^{Glcp1}, C6-H^{Glcp1}, C6-H^{Glcp1}, C2-H^{Glcp2}, C3-H^{Glcp2}, C4-H^{Glcp2}, C5-H^{Glcp2}, C6-H^{Glcp2}, C6-H^{Glcp2}, C2-H^{Glcp3}, C3-H^{Glcp3}, C4-H^{Glcp3}, C5-H^{Glcp3}, C6-H^{Glcp3}, C6-H^{Glcp3}, C2-H^{Manp}, C3-H^{Manp}, C4-H^{Manp}, C6-H^{Manp}, C6-H^{Manp}), 4.24–4.26 (m, 1 H, C2-H^{Manp}), 5.04 (d, *J* = 3.6 Hz, 1 H, C1-H^{Glcp3}), 5.19 (d, *J* = 4.0 Hz, 1 H, C1-H^{Glcp2}), 5.32 (d, *J* = 2.0 Hz, 1 H, C1-H^{Manp}), 5.42 (d, *J* = 3.6 Hz, 1 H, C1-H^{Glcp1}), 6.82 (d, *J* = 9.2 Hz, 2 H, Ar), 7.03 (d, *J* = 9.2 Hz, 2 H, Ar) ppm. ^{13}C NMR (CD_3OD, 100 MHz): δ = 56.0, 62.5, 62.6, 67.2, 71.3, 71.6, 71.7, 72.7, 73.1, 73.3, 73.5, 73.6, 73.7, 73.8, 74.8, 75.2, 78.7, 81.8, 82.9, 98.4 ($C1^{Glcp3}$), 98.7 ($C1^{Glcp1}$), 101.2 ($C1^{Manp2}$), 102.4 ($C1^{Glcp2}$), 115.5, 119.2, 151.8, 156.5 ppm. MALDI-TOF MS: calcd. for $C_{31}H_{48}NaO_{22}$ $[M + Na]^+$ 795.3; found 795.9. HRMS ESI-TOF MS: calcd. for $C_{31}H_{48}NaO_{22}$ $[M + Na]^+$ 795.2535; found 795.2507.

Supporting Information (see footnote on the first page of this article): Experimental procedure and characterization data for ref.[23]; ^{1}H and ^{13}C NMR spectra of synthesized compounds including the final products **21**.

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