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# Sonication-Assisted Oligomannoside Synthesis

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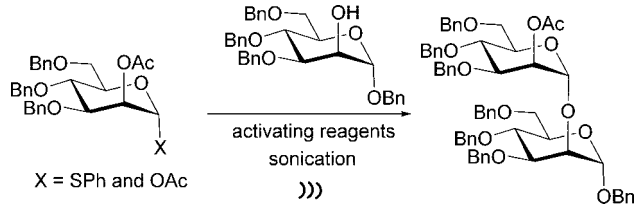


We have investigated the use of sonication for the synthesis of oligomannosides. A convenient sonication-mediated glycosylation protocol that is applicable to traditional glycosylation methods has been developed. This protocol can be applicable for activating glycosyl donors that are known to have low reactivity which enable the synthesis of oligomannosides of particular biological interest with the same efficiency.

## Introduction

Oligomannosides often possess important biological implications and applications, albeit they are rare on the surface of mammalian cells. For example, in addition to being utilized as tumor-associated antigens,[1] oligomannosides have been shown to regulate immune response,[2] mediate cellular interactions,[3] and be involved in the infection of fungal,[4] viral,[5] and bacterial[6] pathogens. Thus, the synthesis of structurally diverse natural and non-natural oligomannosides has been pursued by researchers in various fields.[7,8] Glycosylation is the essential step in the synthesis of complex oligomannosides. Numerous methods designed for activating various mannose-based donors have been reported.[9−11] Sophisticated methods, such as chemoenzymatic synthesis,[12] one-pot programmable glycosylation,[13,14] solid-phase oligosaccharide synthesis,[15,16] and iterative glycosylation,[17] have been developed with the goal of alleviating the challenges of oligosaccharide synthesis. Ironically, the diverse and complicated methods documented in the literature often bewilder researchers in selecting the appropriate mannose-based donors and optimal activating agents for synthesizing the desired oligomannosides, a common obstacle that could be both time- and resource-consuming.

Sonication has been employed to enhance the rate of many traditional chemical reactions[18] including carbohydrate synthesis.[19] Nevertheless, glycosylation using sonication has been reported in only a few examples that employ glycosyl donors, such as unprotected donors,[20] glycosyl halides,[21] and glycosyl

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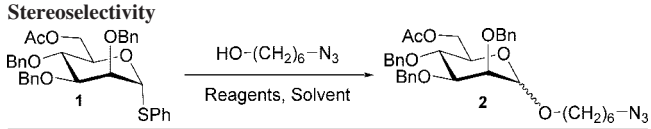
**TABLE 1. Effects of Solvent and Protecting Groups on Stereoselectivity**




| entry | solvent | reagents and condition | yield (%)[a] | α:β ratio |
|---|---|---|---|---|
| 1 | toluene | NIS, TMSOTf, −78 °C to rt, 5 h to overnight | no reaction | |
| 2 | $Et_2O$[b] | | no reaction | |
| 3 | $CH_2Cl_2$ | | 90 | 1:1 |
| 4 | $CH_3CN$ | | 98 | 3:2 |
| 5 | toluene | NIS, TMSOTf, sonication, ambient temp, 8 min | 80 | 2:1 |
| 6 | $Et_2O$ | | 40 | 1:1 |
| 7 | $CH_2Cl_2$ | | 92 | 3:2 |
| 8 | $CH_3CN$ | | 65 | 3:2 |
| 9 | $CH_2Cl_2$ | NIS, $BF_3-OEt_2$, sonication, ambient temp, 8 min | 80 | 3:1 |

[a] Isolated yield. [b] No reaction was noted even after heating (30−40 °C) for 5 h.

sulfones.[22] These glycosyl donors are either unsuitable or have not been applied for the synthesis of oligosaccharides. We have reported that sonication can also be applicable to glycosylation using glycosyl donors that are known to be less reactive.[23] Continuing from our prior work, we direct our effort on the development of general protocols of glycosylation using mannose-based donors including phenylthiomannosides and mannosyl acetate. These two donors are relatively stable and can be prepared in large quantity. However, their stability and low reactivity as compared to the other glycosyl donors, such as glycosyl trichloroacetimidate and glycosyl halide, especially with the acyl protecting groups attached, often result in the difficulty or unsatisfactory yields in glycosylation. As a result, diverse sulfur-philic reagents or Lewis acids have been developed for activating phenylthioglycosides and glycosyl acetate that have various degrees of relative reactivity, which lead to the need for optimizing criteria for achieving the desired synthetic goals.[9−11] In light of the significance and the synthetic deficiencies of oligomannosides, we wish to investigate the possibility of generalizing the glycosylation protocol by using sonication and NIS/TMSOTf or $BF_3-OEt_2$ for activating phenylthiomannosides or mannosyl acetate, respectively.

## Results and Discussion

The initial study was to determine the effects of solvent and protecting groups on the stereoselectivity of sonication-assisted glycosylation. Despite numerous studies, the solvent effect is still unclear. Both 2-*O*-acyl and 2-*O*-alkyl groups favor the formation of a α-glycosydic bond via neighboring group participation and anomeric effect, respectively. We chose **1**[24] and 6-azidohexanol[23] as the donor and acceptor, respectively. Among the solvents examined, there was no preference in the stereoselectivity under our sonication-assisted protocol (Table 1). Interestingly, as reported by Fraser-Reid, the similar donor 2,3,4,6-tetra-*O*-benzyl-1-thio-α-D-mannopyranoside activated using NIS/$BF_3-OEt_2$ in ether at −30 °C manifests excellent stereoselectivity in favoring the formation of an α-glycosidic bond.[25] Under our sonication-assisted protocol using the same activating agents, the selectivity was only slightly improved (Table 1, entry 9). Crich has proposed a general glycosylation mechanism using phenylthiomannosides as the donors and 1-benzenesulfinyl piperidine (BSP) and $Tf_2O$ as the activating agents.[26] In this mechanism, a α-mannosyl triflate intermediate converted from donor is in equilibrium with a β-selective contact ion pair (CIP) and sequentially an α-selective solvent separated ion pair (SSIP) (Figure 1). It is likely that sonication provides energy that facilitates an $S_N2$-like glycosylation via intermediate **A** or CIP, respectively, leading to the formation of β-mannosides. Under the condition reported by Fraser-Reid, the glycosylation is likely to occur via SSIP.

Despite the scramble in the stereoselectivity, it is evident that sonication can certainly enhance the efficiency of glycosylation (entries 5 −8, Table 1). For example, glycosylation under the traditional method (−78 °C to rt or heating) in relatively less polar solvents such as toluene and ether were unsuccessful, probably because of the difficulty in forming oxycarbenium or polar intermediates. In contrast, glycosylation can be accomplished in all of the examined solvents by using the same protocol with modest to excellent yields.

Several mannose donors, compounds **3**−**8**, were also examined including glycosyl acetate **3**,[27] which is known to have low reactivity (Scheme 1). As compared to **1**, glycosylation using **3** yielded better α-selectivity. It is possible that, unlike the phenylthio group, the acetate group is harder to activate by Lewis acid and hampers an $S_N2$-like glycosylation, leading to the formation of more α-selective product via SSIP.

As expected, glycosylation using **5** and **7** with *O*-2 acetyl participation offered only the α-anomer. Although the reason is still unclear, it has been noted that mannose donors bearing 3-*O*-carboxylated esters, such as a benzoyl group, provide predominantly α-mannosides.[28] Neighboring group participation via an intermediate in twist-boat conformation has been proposed to provide explanation in the observed α-selectivity.[29] Consistent with the reported observation, glycosylation using **4** and **6** both containing a 3-*O*-acetyl group gave only α-mannosides.

The presence of 4,6-*O*-benzylidene group has been utilized to favor the formation of β-glycosydic bond.[30] In contrast, the 4,6-*O*-benzylidene protected donors **8** provided α-anomers as the dominant products. It is likely that sonication provides enough energy to overcome the barrier in the conformation constraint imposed by the presence of the benzylidene group. In addition, the glycosylation method we used is different from what has been reported by Crich, which involves a prior activation of donor followed by addition of acceptor, whereas in our protocol, the donor and acceptor are mixed together followed by the addition of activating agent. The difference in

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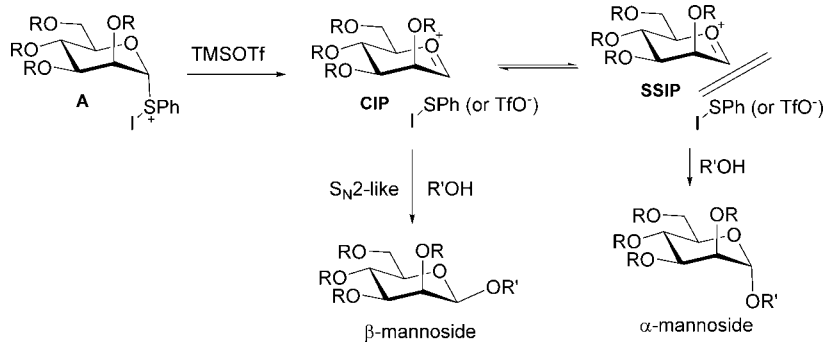
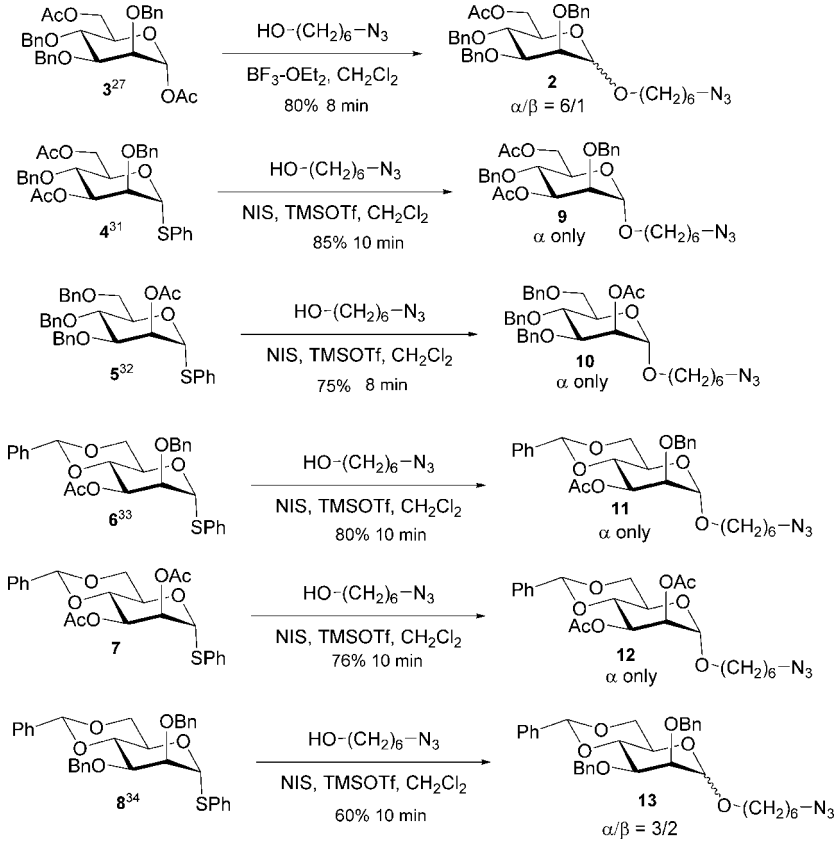



**FIGURE 1.** Proposed glycosylation mechanism.

**SCHEME 1. Investigation of Sonication-Assisted Glycosylation**



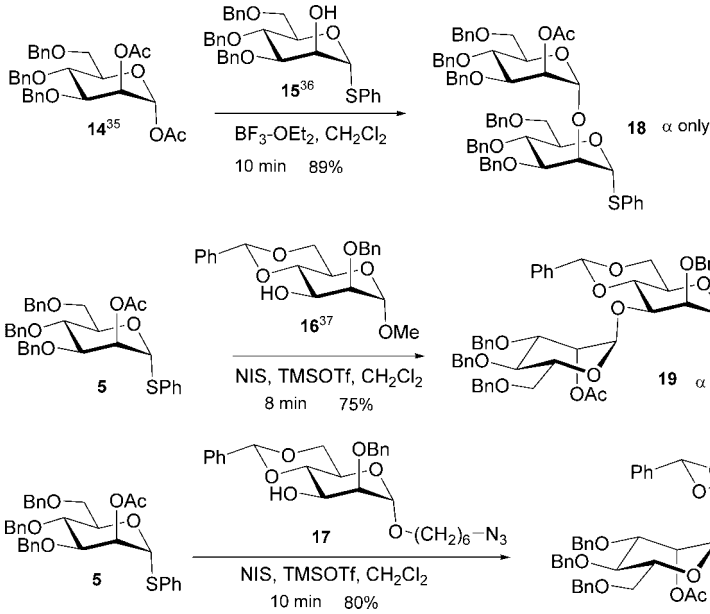

conducting glycosylation could lead to the decrease in $\beta$-selectivity that has also been noted by Crich.[30c] However, prior activation of donor **8** using sonication followed by addition of 6-azidohexanol did not generate any detectable product. Finally, although it has been reported in the literature that sonication may be used to cleave the glycosidic bond, the frequency for sonication is typically 500−800 kHz with power of 20−60 W.[19] The sonicator we used provides frequency of 40 kHz at 185 W. Under this condition, we did not observe any cleavage of the glycosidic bond even in acidic condition as we employed for glycosylation.

After the investigation of stereoselectivity, attempts of using sonication for the synthesis of di- and trimannosides was engaged. We were pleased to notice that sonication exert similar efficacy in synthesizing the designed dimannosides (Scheme 2). Both mannose donors **5** and **14**[35] contain a 2-*O*-acetyl group, which will favor the formation of α-glycosidic bond, to minimize the complexity in characterizing the product.

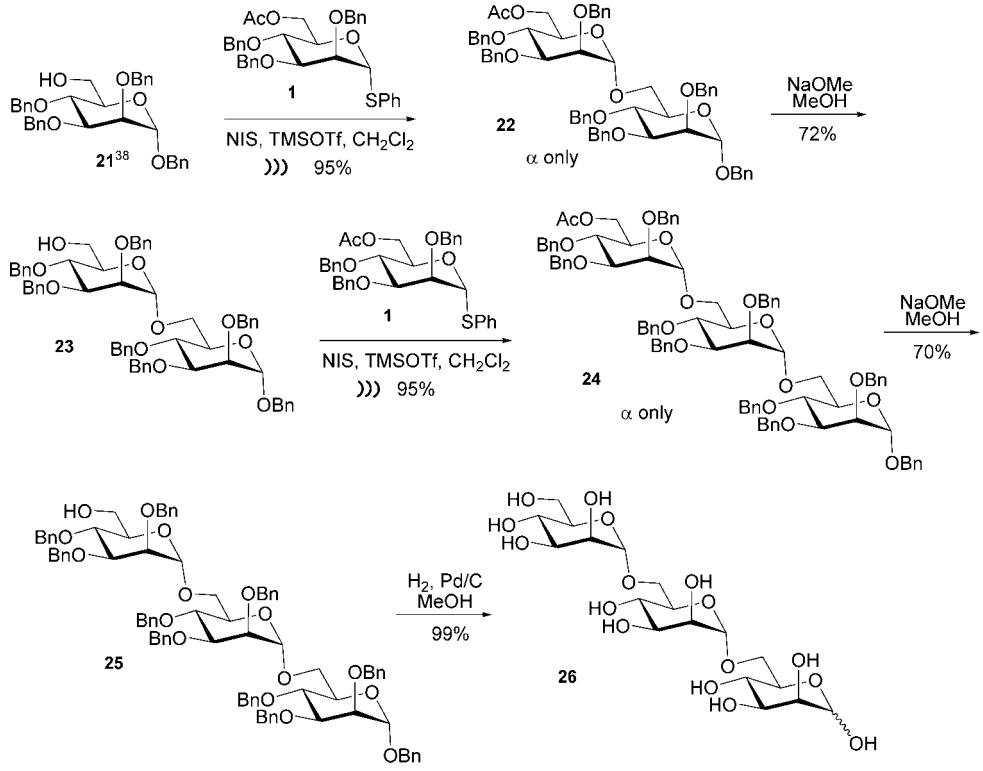
The synthesis of linear trimannosides with 1,2- and 1,6-linkages can be accomplished in similar efficiency using sonication (Schemes 3−6). The stereoselectivity was confirmed by $^1J_{CH}$ using HECTOR. The synthesis of 1,6-linked trimannoside can be accomplished by glycosylation of **21**[38] with donor **1** (Scheme 3). After deprotection of the *O*-6 acetyl group on **22** followed by another glycosylation, a trimannoside, **24**, can be obtained. The purity of desired trimannoside can be further enriched by additional column chromatography after the deprotection of the *O*-6 acetyl group on **24**. Global deprotection of the resulting trimannoside **25** using hydrogenation generates the designed trimannoside **26**.

Another 1,6-linked trimannoside, **32**, can be synthesized in similar fashion (Scheme 4). A different glycosyl donor, **5**, was employed for the second glycosylation. Interestingly, we did observe a small quantity of $\beta$-epimer from the second glycosylation despite the presence of an *O*-2 acetyl group on the employed glycosyl donor. Fortunately, the minor $\beta$-epimer **epi-**

**SCHEME 2. Synthesis of Dimannosides**




**SCHEME 3. Synthesis of 1,6-Linked Trimannosides**




**31** after deacetylation can be separated after column chromatography, allowing the preparation of pure final product.

The syntheses of 1,2-linked trimannosides were accomplished using compound **5** as the glycosyl donor in all glycosylations (Schemes 5 and 6). The synthesis of glycosyl acceptor **35**[40] can also be expedited by employing sonication using known compound **33**[32] as the starting material.

The stereoselectivity observed in the trimannoside synthesis is rather unique. Under our sonication protocol, the glycosyl donor **1** in previous examples in Table 1 exerts no obvious selectivity. However, when **1** was employed in the synthesis of trimannosides, excellent stereoselectivity favoring the formation

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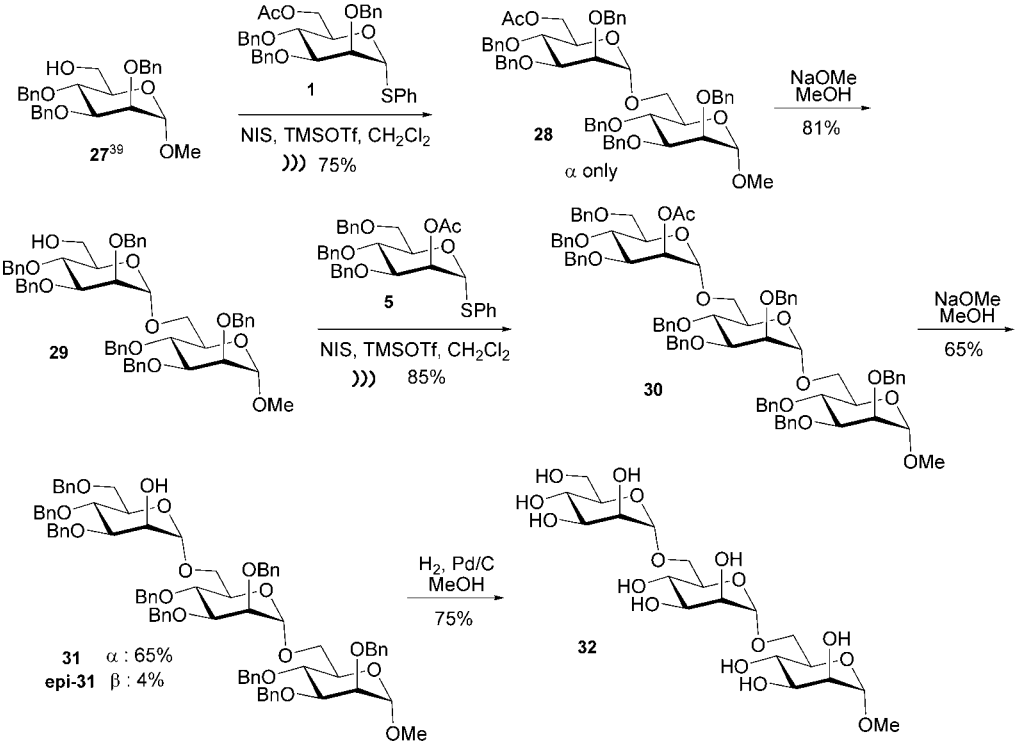
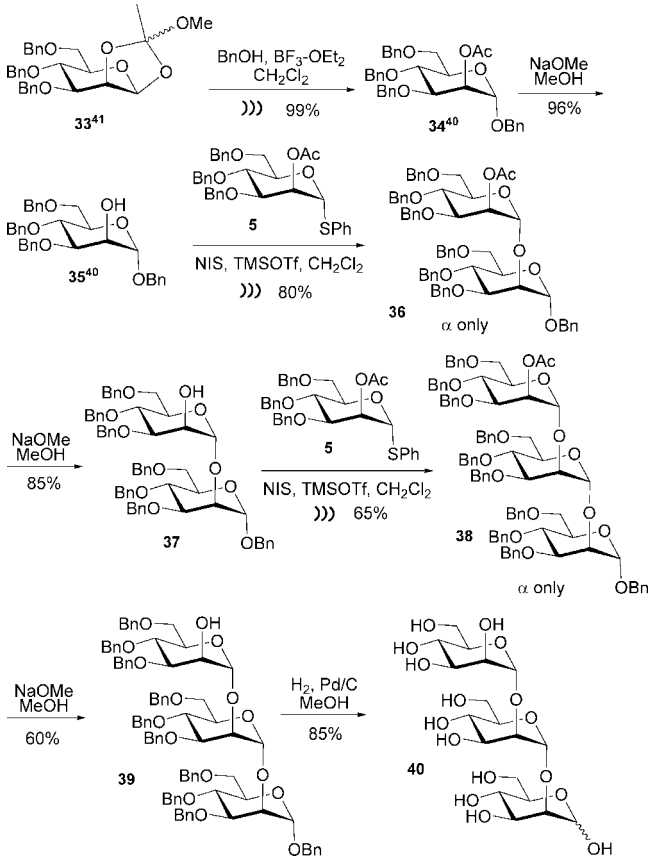
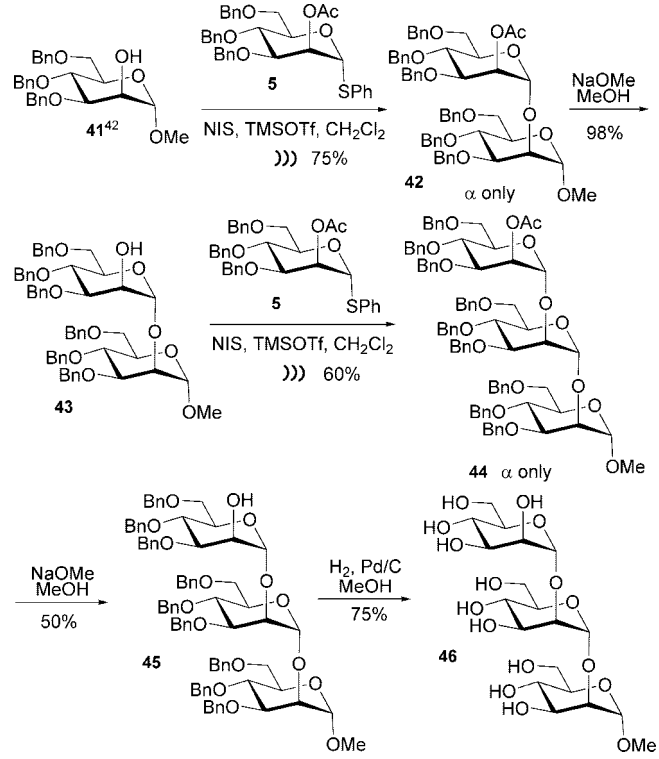
**SCHEME 4. Synthesis of 1,6-Linked Trimannosides**




**SCHEME 5. Synthesis of 1,2-Linked Trimannosides**

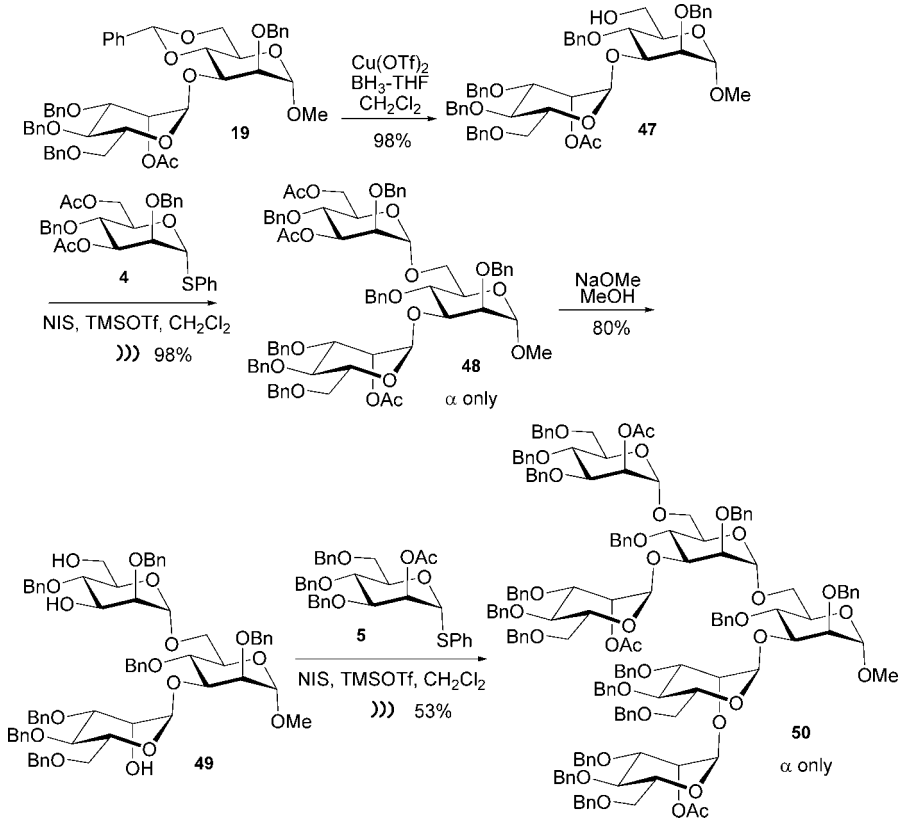



**SCHEME 6. Synthesis of 1,2-Linked Trimannosides**




of an α-glycosidic bond was obtained. One of the possible reasons is that the steric hindrance between the 2-*O*-benzyl group and the mannose acceptors in the trimannoside synthesis may prevent $S_N2$-like glycosylation via α-mannosyl intermediate or CIP. When a smaller nucleophile such as 6-azidohexanol was used for glycosylation, the steric factor was less significant, which resulted in the lack of stereoselectivity. Interestingly, one recent article by Huang reported an unusual stereoselectivity of glycosylation: when dimannose-based donor and mannose acceptor were used, a modest selectivity was observed in favoring the formation of $\beta$-glycosidic bond.[43] Considering all results, we agree with Huang's comment that "factors controlling

**SCHEME 7. Synthesis of Man6**



stereochemistry of glycosylation especially in the absence of neighboring group participation are still not well understood".

Following the synthesis of trimannosides, the focus was directed to the synthesis of more complex Man6,[44] which can be considered as the prelude to the synthesis of Man9 with potential of being used for HIV vaccine development (Scheme 7).[45] The synthesis began with a glycosylation using compounds **16** and **5** as the glycosyl acceptor and donor, respectively. A regioselective reductive ring opening of the 4,6-benzylidene group using $Cu(OTf)_2/BH_3$[46] yielded **47** with *O*-6 OH, which can be glycosylated using compound **4** as the donor. After the deprotection of acetyl groups, the triol **49** can be glycosylated using compound **5**. Once again, sonication enabled smooth glycosylation even for the last glycosylation step, which involved the incorporation of three glycosyl donors simultaneously. In addition, we did not observe cleavage of a glycosidic bond in any of the oligomannosides syntheses.

## Conclusion

We have reported a convenient sonication-mediated glycosylation protocol that is applicable to traditional glycosylation methods. This protocol can be applicable even for the glycosyl donors that are known to have low reactivity. We have also demonstrated that oligomannosides of particular biological interest can be prepared with the same efficiency.

## Experimental Section

Proton magnetic resonance spectra were recorded using 300 or 400 MHz spectrometers. Chemical shifts are reported as parts per million (ppm) downfield from tetramethylsilane in $\delta$ units, and coupling constants are given in cycles per second (Hz). Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. $^{13}C$ spectra were obtained using a Jeol 300 spectrometer at 75 Hz or Bruker 400 spectrometer at 100 Hz. Routine $^{13}C$ NMR spectra were fully decoupled by broadband waltz decoupling. All NMR spectra were recorded at ambient temperature unless otherwise noted. Sonication was conducted using Bransonic ultrasonic bath (model 5510) at 40 kHz with a power of 185 W.

**6′-Azidohexyl 6-*O*-Acetyl-2,3,4-tri-*O*-benzyl-α-D-mannopyranoside (2).** Please refer to the general procedure for sonication-assisted glycosylation using phenylthioglycosyl donor ($R_f$ = 0.5 eluted with hexane/EtOAc = 3/1). $^1H$ ($CDCl_3$, 300 MHz) $\delta$ 7.3−7.6 (m, 30H), 5.0−4.9 (m, 3H), 4.88 (d, $J$ = 1.7 Hz, 1H), 4.80 (d, $J$ = 12.4 Hz, 1H), 4.74 (d, $J$ = 12.4 Hz, 1H), 4.6−4.7 (m, 4H), 4.57 (d, $J$ = 11.7 Hz, 1H), 4.48 (d, $J$ = 11.7 Hz, 1H), 4.4 (m, 1H), 4.3−4.4 (m, 3H), 3.9−4.0 (m, 6H), 3.8−3.9 (m, 3H), 3.6 (m, 1H), 3.4−3.6 (m, 3H), 3.27 (t, $J$ = 6.9 Hz, 4H), 2.09 (s, 3H, $CH_3$), 2.07 (s, 3H, $CH_3$), 1.6 (m, 8H), 1.3 (m, 8H); $^{13}C$ NMR ($CDCl_3$, 75 MHz) $\delta$ 171.05 ($\beta$), 171.0 (α), 138.8, 138.5 (2 carbons), 138.4 (2 carbons), 138.29 (2 carbons), 138.28, 137.16, 128.6 (3 carbons), 128.5 (4 carbons), 128.47 (3 carbons), 128.33 (2 carbons), 128.28, 128.23,

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127.9 (2 carbons), 127.89 (3 carbons), 127.79 (5 carbons), 127.78 (2 carbons), 127.6, 101.9 ($\beta$), 98.0 ($\alpha$), 82.4, 80.3, 75.3, 74.8, 74.7, 74.68, 73.9, 73.8, 73.6, 72.7, 72.2, 71.5, 70.2, 69.9, 67.7, 63.9, 63.7, 51.4, 29.6, 29.4, 28.9, 28.87, 26.6, 25.9, 25.83, 21.06, 21.04; ESI/APCI calcd for $C_{35}H_{43}N_3O_7Na$ ([M + Na]$^+$) *m/e* 640.2999; measured *m/e* 640.2998.

**Phenyl 2,3-Di-*O*-acetyl-4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside (7).** To a solution of phenyl 4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside[29] (2.50 g, 6.94 mmol), $Et_3N$ (3.41 mL, 24.3 mmol), and a catalytic amount of DMAP in anhydrous $CH_2Cl_2$ (20 mL) was slowly added acetic anhydride (1.64 mL, 17.3 mmol). The reaction was stirred for 1 h and then quenched with saturated $NaHCO_{3(aq)}$. The mixture was diluted with ethyl acetate, washed with 1 N $HCl_{(aq)}$, water, saturated $NaHCO_{3(aq)}$, water, and brine, and then dried over anhydrous $Na_2SO_{4(s)}$. After removal of solvent and purification with column chromatography, the product was obtained as an oil (2.80 g, 6.31 mmol, 91%) ($R_f$ = 0.5 eluted with hexane/EtOAc = 3/1). $^1$H ($CDCl_3$, 400 MHz) $\delta$ 7.3 −7.5 (m, 10H), 5.63 (dd, $J$ = 1.3, 3.4 Hz, H-2, 1H,), 5.61(s, 1H, H-1′), 5.45 (d, $J$ = 0.8 Hz, H-1, 1H,), 5.43 (dd, $J$ = 3.4, 10.5 Hz, H-3, 1H), 4.5 (m, 1H, H-5), 4.27 (dd, $J$ = 4.9 Hz, 10.4 Hz, H-6, 1H,), 4.15 (t, $J$ = 9.7 Hz, H-4, 1H), 3.89 (t, $J$ = 10.3 Hz, H-6′, 1H), 2.18 (s, 3H, $CH_3$), 2.06 (s, 3H, $CH_3$); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 169.9, 169.8, 137.1, 132.2 (2 carbons), 129.3 (3 carbons), 128.4 (3 carbons), 128.2, 126.3 (2 carbons), 102.1, 86.9, 76.3, 71.6, 68.6, 68.5, 65.3, 21.0, 20.9; ESI/APCI calcd for $C_{23}H_{24}O_7SNa$ ([M + Na]$^+$) *m/e* 467.1140; measured *m/e* 467.1141.

**6′-Azidohexyl 3,6-Di-*O*-acetyl-2,4-di-*O*-benzyl-α-D-mannopyranoside (9).** Please refer to the general procedure for sonication-assisted glycosylation using phenylthioglycosyl donor ($R_f$ = 0.6 eluted with hexane/EtOAc = 3/1). $^1$H ($CDCl_3$, 400 MHz) $\delta$ 7.3 (m, 10H), 5.25 (dd, $J$ = 3.3, 9.1 Hz, 1H, H-3), 4.82 (s, 1H, H-1), 4.70 (d, $J$ = 11.2 Hz, 1H), 4.66 (d, $J$ = 12.3 Hz, 1H), 4.60 (s, 1H), 4.58 (d, $J$ = 11.1 Hz, 1H), 4.3 (m, 2H, H-6, H-6′), 3.9 (t, $J$ = 9.6 Hz, 1H, H-4), 3.9 (m, 2H, H-2, H-5), 3.7 (m, 1H), 3.4 (m, 1H), 3.27 (t, $J$ = 6.9 Hz, 2H), 2.08 (s, 3H, $CH_3$), 2.00 (s, 3H, $CH_3$), 1.6 (m, 4H), 1.4 (m, 4H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 171.0, 170.3, 138.1, 138.0, 128.7 (2 carbons), 128.6 (2 carbons), 128.1 (2 carbons), 128.0 (2 carbons), 127.9 (2 carbons), 97.9, 76.2, 75.0, 74.1, 73.6, 73.1, 69.9, 68.0, 63.6, 57.6, 29.4, 28.9, 26.7, 26.6, 21.3, 21.1; ESI/APCI calcd for $C_{30}H_{39}N_3O_8Na$ ([M + Na]$^+$) *m/e* 592.2635; measured *m/e* 592.2629.

**6′-Azidohexyl 2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (10).** Please refer to the general procedure for sonication-assisted glycosylation using phenylthioglycosyl donor ($R_f$ = 0.6 eluted with hexane/EtOAc = 3/1). $^1$H ($CDCl_3$, 270 MHz) $\delta$ 7.1−7.5 (m, 15H), 5.37 (dd, $J$ = 3.0, 1.6 Hz, 1H), 4.87 (d, $J$ = 12.2 Hz, 1H), 4.84 (d, $J$ = 1.6 Hz, 1H), 4.72 (d, $J$ = 11.2 Hz, 1H), 4.69 (d, $J$ = 12.2 Hz, 1H), 4.55 (d, $J$ = 10.7 Hz, 1H), 4.52 (d, $J$ = 11.2 Hz, 1H), 4.48 (d, $J$ = 10.7 Hz, 1H), 4.00 (dd, $J$ = 8.9, 3.0 Hz, 1H), 3.89 (dd, $J$ = 9.2, 9.2 Hz, 1H), 3.6−3.8 (m, 2H), 3.52 (dd, $J$ = 6.8, 6.8 Hz, 1H), 3.43 (dd, $J$ = 6.8, 6.3 Hz, 1H), 3.40 (dd, $J$ = 6.8, 6.3 Hz, 1H), 3.25 (t, $J$ = 6.8 Hz, 2H), 2.16 (s, 3H), 1.5−1.6 (m, 4H), 1.3−1.4 (m, 4H); $^{13}$C NMR ($CDCl_3$, 68 MHz) $\delta$ 170.6, 138.6, 138.49, 138.22, 128.7, 128.58 (2 carbons), 128.53 (3 carbons), 128.25 (2 carbons), 128.14 (2 carbons), 127.96 (2 carbons), 127.93, 127.85, 127.78, 97.9, 78.4, 75.3, 74.5, 73.5, 71.9, 71.5, 69.03, 68.97, 67.8, 51.5, 29.3, 28.8, 26.6, 25.8, 21.2; HRFAB calcd for $C_{35}H_{43}N_3O_7Na$ ([M + Na]$^+$) *m/e* 640.2999; measured *m/e* 640.2987.

**6′-Azidohexyl 3-*O*-Acetyl-2-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (11).** Please refer to the general procedure for sonication-assisted glycosylation using phenylthioglycosyl donor ($R_f$ = 0.7 eluted with hexane/EtOAc = 3/1). $^1$H ($CDCl_3$, 400 MHz) $\delta$ 7.4−7.5 (m, 2H), 7.3−7.4 (m, 8H), 5.59 (s, 1H, H-1′), 5.31 (dd, $J$ = 3.4, 10.4 Hz, 1H, H-3), 4.81 (s, 1H, H-1), 4.68 (d, $J$ = 11.9 Hz, 1H), 4.64 (d, $J$ = 11.9 Hz, 1H), 4.26 (d, $J$ = 5.6 Hz, 1H), 4.2 (m, 1H, H-5), 3.96 (s, 1H), 3.9 (m, 2H), 3.7 (m, 1H), 3.4 (m, 1H), 3.29 (t, $J$ = 6.8 Hz, 2H), 2.05 (s, 3H, $CH_3$), 1.6 (m, 4H), 1.4 (m, 4H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 170.4, 137.8, 137.5, 129.2, 128.7 (2 carbons), 128.4 (2 carbons), 128.2 (2 carbons), 126.4 (2 carbons), 101.9, 99.0, 77.4, 76.6, 76.5, 73.9, 70.8, 69.0, 68.0, 64.2, 51.6, 29.4, 28.9, 26.7, 25.9, 21.3; HRFAB calcd for $C_{28}H_{35}N_3O_7Na$ ([M + Na]$^+$) *m/e* 548.2373; measured *m/e* 548.2371.

**6′-Azidohexyl 2,3-Di-*O*-acetyl-4,6-*O*-benzylidene-α-D-mannopyranoside (12).** Please refer to the general procedure for sonication-assisted glycosylation using phenylthioglycosyl donor ($R_f$ = 0.5 eluted with hexane/EtOAc = 3/1). $^1$H ($CDCl_3$, 300 MHz) $\delta$ 7.4−7.5 (m, 2H), 7.3−7.4 (m, 3H), 5.58 (s, 1H), 5.40 (dd, $J$ = 3.6, 9.6 Hz, 1H, H-3), 5.33 (dd, $J$ = 1.7, 3.6 Hz, 1H, H-2), 4.75 (d, $J$ = 1.3 Hz, 1H, H-1), 4.27 (dd, $J$ = 4.1, 9.9 Hz, 1H), 4.03 (t, $J$ = 9.3 Hz, 1H), 3.9 (m, 1H, H-5), 3.85 (t, $J$ = 9.9 Hz, 1H), 3.7 (m, 1H), 3.4 (m, 1H), 3.28 (t, $J$ = 6.9 Hz, 2H), 2.17 (s, 3H, $CH_3$), 2.02 (s, 3H, $CH_3$), 1.6 (m, 4H), 1.4 (m, 4H); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 170.0, 169.9, 137.2, 129.2, 128.4 (2 carbons), 126.2 (2 carbons), 101.9, 98.7, 77.3, 76.3, 70.3, 68.8, 68.2, 63.9, 51.5, 29.3, 28.8, 26.6, 25.8, 21.0, 20.9; HRFAB calcd for $C_{23}H_{31}N_3O_8Na$ ([M + Na]$^+$) *m/e* 500.2009; measured *m/e* 500.2008.

**6′-Azidohexyl 2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (13).** Please refer to the general procedure for sonication-assisted glycosylation using phenylthioglycosyl donor ($R_f$ = 0.7 eluted with hexane/EtOAc = 3/1). $^1$H ($CDCl_3$, 300 MHz) $\delta$ 7.5−7.6 (m, 4H), 7.2−7.5 (m, 26H), 5.68 (s, 1H), 5.66 (s, 1H), 5.03 (d, $J$ = 12.4 Hz, 1H), 4.8−5.0 (m, 3H), 4.82 (d, $J$ = 1.4 Hz, 1H, H-1), 4.79 (s, 1H), 4.6−4.7 (m, 4H), 4.47 (s, 1H), 4.2−4.4 (m, 3H), 4.10 (t, $J$ = 6.9 Hz, 1H), 3.9−4.1 (m, 3H), 3.8−3.9 (m, 3H), 3.6 (m, 1H), 3.5 (m, 1H), 3.4 (m, 1H), 3.3 (m, 4H), 1.6 (m, 8H), 1.4 (m, 8H); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 138.9, 138.6, 138.5, 138.3, 137.85, 137.83, 128.9, 128.8, 128.51 (3 carbons), 128.50 (3 carbons), 128.42 (4 carbons), 128.3, (5 carbons), 128.29 (2 carbons), 128.2 (3 carbons), 127.9 (2 carbons), 127.7, 127.6 (3 carbons), 127.2 (3 carbons), 126.2 (2 carbons), 102.4, 101.5, 99.5, 79.4, 78.8, 78.1, 76.7 (2 carbons), 75.9, 74.8, 73.7, 73.3, 72.5, 70.1, 69.0, 68.7, 67.7 (2 carbons), 64.3, 51.5 (2 carbons), 29.7, 29.3, 28.9 (2 carbons), 26.6 (2 carbons), 25.8; HRFAB calcd for $C_{33}H_{39}N_3O_6Na$ ([M + Na]$^+$) *m/e* 596.2737; measured *m/e* 596.2731.

**6′-Azidohexyl 2-*O*-Benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (17).** To a solution of 6′-azidohexyl-4,6-*O*-benzylidene-α-D-mannopyranoside (1.35 g, 3.43 mmol), tetrabutylammonium hydrogen sulfate (0.35 g, 1.03 mmol), and BnBr (0.45 mL, 3.77 mmol) in $CH_2Cl_2$ (15 mL) was added aqueous NaOH (1 N, 6 mL). The mixture was refluxed for 15 h and then diluted with $CH_2Cl_2$. The organic layer was washed with water and brine and then dried over anhydrous $Na_2SO_{4(s)}$ After removal of solvent and purification with column chromatography, the product was obtained as an oil (0.71 g, 1.99 mmol, 58%) ($R_f$ = 0.7 eluted with hexane/EtOAc = 65/35). $^1$H ($CDCl_3$, 300 MHz) $\delta$ 7.5−7.6 (m, 2H), 7.3−7.4 (m, 8H), 5.59 (s, 1H, H-1′), 4.84 (d, $J$ = 1.2 Hz, H-1, 1H,), 4.76 (d, $J$ = 11.8 Hz, 1H), 4.72 (d, $J$ = 11.8 Hz, 1H), 4.26 (dd, $J$ = 3.7, 9.1 Hz, H-6, 1H), 4.10 (m, 1H, H-5), 3.93 (t, $J$ = 9.0 Hz, H-4, 1H), 3.8−3.7 (m, 3H), 3.6 (m, 1H), 3.3 (m, 1H), 3.28 (t, $J$ = 6.9 Hz. 2H), 2.38 (d, 1H, OH), 1.61 (m, 4H), 1.39 (m, 4H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 137.9, 137.5, 129.3, 128.8 (2 carbons), 128.5 (2 carbons), 128.3, 128.2 (2 carbons), 126.4 (2 carbons), 102.3, 98.5, 79.8, 78.9, 73.9, 69.0, 68.9, 67.9, 63.7, 51.6, 29.4, 28.9, 26.7, 25.9; ESI/APCI calcd for $C_{26}H_{33}N_3O_6Na$ ([M + Na]$^+$) *m/e* 506.2267; measured *m/e* 506.2281.

**Phenyl 2-*O*-(2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-3,4,6-tri-*O*-benzyl-1-thio-α-D-mannopyranoside (18).** Please refer to the general procedure for sonication-assisted glycosylation using glycosyl acetate as the donor ($R_f$ = 0.5 eluted with hexane/EtOAc = 3/1). $^1$H ($CDCl_3$, 400 MHz) $\delta$ 7.4 (m, 2H), 7.1−7.4 (m, 33H), 5.67 (d, $J$ = 1.6 Hz, 1H, H-1), 5.54 (dd, $J$ = 1.8, 3.1 Hz, 1H, H-2′), 5.09 (d, $J$ = 1.5 Hz, 1H, H-1′), 4.91 (d, $J$ = 10.8 Hz, 1H), 4.84 (d, $J$ = 10.9 Hz, 1H), 4.75 (d, $J$ = 11.7 Hz, 1H), 4.71 (d, $J$ = 11.7 Hz, 1H), 4.68 (d, $J$ = 10.8 Hz, 1H), 4.62 (d, $J$ = 11.0 Hz, 1H), 4.56 (d, $J$ = 12.3 Hz, 1H), 4.49 (d, $J$ = 12.6 Hz, 2H), 4.4 (m, 2H), 4.3 (m, 1H), 4.25 (t, $J$ = 2.1 Hz, 1H), 3.9−4.0

(m, 5H), 3.8−3.9 (m, 2H), 3.7−3.8 (m, 2H), 3.60 (dd, $J$ = 1.7, 10.6 Hz, 1H), 2.15 (s, 3H, $CH_3$); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 170.4, 138.7, 138.6 (2 carbons), 138.4, 138.3, 138.2, 134.4, 131.9 (2 carbons), 129.2 (2 carbons), 128.7 (2 carbons), 128.6 (2 carbons), 128.55 (6 carbons), 128.50 (4 carbons), 128.4 (4 carbons), 128.3 (2 carbons), 128.2 (2 carbons), 128.0 (2 carbons), 127.9 (4 carbons), 127.8 (2 carbons), 127.7 (3 carbons), 127.6 (2 carbons), 99.9, 87.4, 80.2, 78.3, 77.0, 75.4, 75.3, 75.0, 74.6, 73.4 (2 carbons), 73.1, 72.4, 72.2, 72.1, 69.4, 69.0, 68.9, 21.3; ESI/APCI calcd for $C_{62}H_{64}O_{11}SNa$ ([M + Na]$^+$) *m/e* 1039.4067; measured *m/e* 1039.4082.

**Methyl 3-*O*-(2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-2-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (19).** Please refer to the general procedure for sonication-assisted glycosylation using phenylthioglycosyl donor ($R_f$ = 0.7 eluted with hexane/EtOAc = 65/35). $^1$H ($CDCl_3$, 400 MHz) $\delta$ 7.2−7.5 (m, 25H), 5.64 (s, 2H, H-1′, H-2), 5.33 (s, 1H, H-1), 4.90 (d, $J$ = 10.8 Hz, 2H), 4.74 (d, $J$ = 12.2 Hz), 4.72 (s, 1H, H-1), 4.6−4.7 (m, 5H), 4.4−4.5 (m, 4H), 4.2−4.3 (m, 4H), 4.00 (dd, $J$ = 3.2, 12.1 Hz, 2H), 3.6−3.9 (m, 9H), 3.31 (s, 3H, OMe). 2.11 (s, 3H, $CH_3$); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 170.2, 138.8, 138.6, 138.1, 138.0, 137.6, 128.9128.7, 128.5, 128.4 (3 carbons), 128.30 (2 carbons), 128.28 (2 carbons), 128.0 (4 carbons), 127.9 (4 carbons), 127.7 (2 carbons), 126.2 (2 carbons), 101.4, 100.5, 99.0, 79.3, 78.1, 77.4 (4 carbons), 75.2, 74.5, 73.8, 73.6, 73.4, 72.4, 71.7, 68.9, 68.4, 64.1, 60.6, 55.0, 21.2; ESI/APCI calcd for $C_{50}H_{54}O_{12}Na$ ([M + Na]$^+$) *m/e* 869.3513; measured *m/e* 869.3507.

**6′-Azidohexyl 3-*O*-(2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-2-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (20).** Please refer to the general procedure for sonication-assisted glycosylation using phenylthioglycosyl donor ($R_f$ = 0.5 eluted with hexane/EtOAc = 3/1). $^1$H ($CDCl_3$, 400 MHz) $\delta$ 7.4−7.6 (m, 3H,), 7.1−7.3 (m, 22H), 5.65 (s, 1H), 5.63 (d, $J$ = 1.9 Hz, 1H), 5.34 (s, 1H), 4.90 (d, $J$ = 10.9 Hz, 2H), 4.77 (s, 2H), 4.73 (d, $J$ = 5.4 Hz, 1H), 4.6 (m, 3H), 4.4−4.5 (m, 4H), 4.2 (m, 2H), 4.00 (dd, $J$ = 3.3 hz, 1H), 3.7−3.9 (m, 3H), 3,5−3.6 (m, 2H), 3.3 (m, 1H), 3.24 (t, $J$ = 6.9 Hz, 2H), 2.11 (s, 3H, $CH_3$), 1.5 (m, 4H), 1.4 (m, 4H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 170.2, 138.8, 138.5, 138.1 (2 carbons), 137.6, 128.9, 128.7 (2 carbons), 128.6 (3 carbons), 128.5 (4 carbons), 128.4 (3 carbons), 128.3 (2 carbons), 128.3 (3 carbons), 128.0 (4 carbons), 127.9 (3 carbons), 127.7 (2 carbons), 126.2 (2 carbons), 101.4, 99.4, 99.1, 79.3, 78.1, 77.8 (2 carbons), 77.4 (2 carbons), 75.2, 74.4, 73.8, 73.7, 73.5 (2 carbons), 72.4, 71.7, 69.1, 68.9, 68.4, 67.8, 64.3, 51.6, 29.4, 28.9, 26.7, 25.9, 21.2; ESI/APCI calcd for $C_{55}H_{67}N_4O_{12}$ ([M + $NH_4$]$^+$) *m/e* 975.4755; measured *m/e* 975.4774.

**Benzyl 6-*O*-(6-*O*-Acetyl-2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-mannopyranoside (22).** Please refer to the general procedure for sonication-assisted glycosylation using phenylthioglycosyl donor ($R_f$ = 0.6 eluted with hexane/EtOAc = 3/1). $^1$H ($CDCl_3$, 300 MHz) $\delta$ 7.2−7.4 (m, 35H), 5.13, (s, 1H, H-1), 4.97 (d, $J$ = 10.6 Hz, 1H), 4.94 (d, $J$ = 11.0 Hz, 1H), 4.90 (d, $J$ = 1.7 Hz, 1H, H-1′), 4.4−4.7 (m, 11H), 4.41 (d, $J$ = 12.0 Hz, 1H), 4.2−4.4 (m, 2H), 3.8−3.9 (m, 6H), 3.84 (m, 2H), 3.7−3.8 (m, 2H) 2.03 (s, 3H, $CH_3$); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 171.1, 138.7, 138.5 (3 carbons), 138.29, 138.24, 137.2, 128.56, 128.53 (8 carbons), 128.3, 128.2, 128.0 (4 carbons), 127.9 (4 carbons), 127.85, 127.80 (3 carbons), 127.7, 127.65 (2 carbons), 127.6, 98.1, 97.0, 80.4, 79.5, 75.2 (2 carbons), 74.9, 74.7 (2 carbons), 74.4, 72.9, 72.5, 72.3, 72.0, 71.6, 70.2, 68.9, 66.3, 63.6, 21.0; ESI/APCI calcd for $C_{63}H_{66}O_{12}Na$ ([M + Na]$^+$) *m/e* 1037.4446; measured *m/e* 1037.4445.

**Benzyl 2,3,4-Tri-*O*-benzyl-6-*O*-(2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl)-α-D-mannopyranoside (23).** To a solution of compound **22** (0.80 g, 0.79 mmol) in anhydrous $CH_2Cl_2$ (1 mL) and MeOH (8 mL) was added 5 drops of NaOMe solution (1 M in methanol), and the reaction mixture was stirred at room temperature for 1 h. After completion of the reaction, Amberlite IR-120 resin ($H^+$) was added, and the mixture was filtered through Celite. After removal of solvents and purification with gradient column chromatography, the product was obtained as an oil (0.55 g,, 0.57 mmol, 72%) ($R_f$ = 0.4 eluted with hexane/EtOAc = 3/1). $^1$H ($CDCl_3$, 300 MHz) $\delta$ 7.2−7.4 (m, 35H), 5.10 (d, $J$ = 1.4 Hz, 1H), 5.00 (d, $J$ = 11.0 Hz, 1H), 4.92 (d, $J$ = 1.7 Hz, 1H, H-1), 4.6−4.8 (m, 9H), 4.61 (d, $J$ = 12.0 Hz, 1H), 4.55 (d, $J$ = 12.0 Hz, 1H), 4.53 (d, $J$ = 14.0 Hz, 1H), 4.43 (d, $J$ = 11.7 Hz, 1H), 3.7−4.0 (m, 12H) 1.98 (s, 1H, OH); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 138.72, 138.70, 138.5 (2 carbons), 138.4, 138.2, 137.2, 128.6, 128.5 (10 carbons), 128.4 (2 carbons), 128.1, 128.0 (5 carbons), 127.9 (2 carbons), 127.8 (2 carbons), 127.7 (3 carbons), 127.6 (2 carbons), 98.4, 97.1, 80.4, 79.5, 75.3, 75.1, 74.90, 74.86, 74.7, 72.9, 72.8, 72.3 (2 carbons), 71.9, 71.7, 69.0, 66.3, 62.4; ESI/APCI calcd for $C_{61}H_{64}O_{11}Na$ ([M + Na]$^+$) *m/e* 995.4346; measured *m/e* 995.4340.

**Benzyl 6-*O*-(6-*O*-(6-*O*-Acetyl-2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-mannopyranoside (24).** Please refer to the general procedure for sonication-assisted glycosylation using phenylthioglycosyl donor ($R_f$ = 0.7 eluted with hexane/EtOAc = 65/35). $^1$H ($CDCl_3$, 400 MHz) $\delta$ 7.2−7.4 (m, 65H), 5.15 (s, 1H), 5.07 (s, 1H), 4.8−5.0 (m, 4H), 4.4−4.7 (m, 20H), 4.23 (m, 1H), 3.8−4.0 (m, 10H), 3.7 (m, 2H), 3.6 (m, 1H), 2.01 (s, 3H, $CH_3$), 1.99 (s, 3H, $CH_3$); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 171.0 (2 carbons), 138.8 (2 carbons), 138.6 (2 carbons),, 138.5 (3 carbons),, 138.3, 138.2 (3 carbons), 137.2, 128.5 (2 carbons), 128.4 (8 carbons),, 128.31 (2 carbons), 128.30 (2 carbons), 128.1, 127.9 (8 carbons), 127.82 (2 carbons), 127.8 (2 carbons), 127.7 (3 carbons), 127.66 (3 carbons), 127.60, 102.4 ($\beta$), 98.3 ($\alpha$), 98.1 (2 carbons, $\alpha/\beta$), 97.0 (2 carbons, $\alpha/\beta$), 81.9, 80.4, 79.6 (2 carbons), 79.3, 77.9, 77.3 (4 carbons), 75.2 (5 carbons), 74.8 (2 carbons), 74.7 (3 carbons), 74.5, 74.3 (2 carbons), 72.9, 72.8, 72.3, 72.2, 71.9, 71.8, 71.6, 71.3, 71.2, 70.1, 68.9 (2 carbons), 66.2, 65.9, 63.3, 20.9; ESI/APCI calcd for $C_{90}H_{98}NO_{17}$ ([M + $NH_4$]$^+$) *m/e* 1464.6835; measured *m/e* 1464.6818.

**Benzyl 2,3,4-Tri-*O*-benzyl-6-*O*-(6-*O*-(2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl)-α-D-mannopyranoside (25).** Please refer to the procedure for the synthesis of compound **23** ($R_f$ = 0.5 eluted with hexane/EtOAc = 65/35). $^1$H ($CDCl_3$, 400 MHz) $\delta$ 7.2−7.4 (m, 50H), 5.10 (d, $J$ = 1.0 Hz, 1H), 5.08 (s, 1H), 4.94 (d, $J$ = 11.0 Hz, 1H), 4.93 (d, $J$ = 10.9 Hz, 1H), 4.90 (d, $J$ = 1.6 Hz, 1H), 4.6 (m, 11H), 4.6 (m, 2H), 4.5 (m, 4H), 4.42 (d, $J$ = 11.9 Hz, 1H), 3.9 (m, 10H), 3.8 (m, 2H), 3.6 (m, 7H); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 138.8 (2 carbons), 138.7, 138.6, 138.5 (2 carbons), 138.4, 138.3, 138.2, 137.2, 128.5 (2 carbons), 128.45 (6 carbons), 128.40 (4 carbons), 128.3 (4 carbons), 128.1 (2 carbons), 127.95 (4 carbons), 127.92 (4 carbons), 127.82 (2 carbons), 127.78 (2 carbons), 127.71 (4 carbons), 127.64 (4 carbons), 127.58 (2 carbons), 127.54 (2 carbons), 98.4, 98.3, 97.1, 80.4, 79.6, 79.4, 77.3 (2 carbons), 75.2 (5 carbons), 75.1 (3 carbons), 74.8 (2 carbons), 74.7 (2 carbons), 74.67, 74.4, 72.9, 72.8, 72.7, 72.3 (4 carbons), 71.9, 71.7, 71.7, 71.6 (2 carbons), 71.5 (2 carbons); ESI/APCI calcd for $C_{88}H_{92}O_{16}Na$ ([M + Na]$^+$) *m/e* 1427.6283; measured *m/e* 1427.6259.

**6-*O*-(6-*O*-(α-D-Mannopyranosyl)-α-D-mannopyranosyl)-D-mannopyranose (26).** A solution of compound **25** (0.15 g, 0.11 mmol) and catalytic amount of Pd/C in degassed methanol was stirred at room temperature under atmospheric hydrogen overnight. The reaction mixture was filtered through Celite, and the residue was washed with distilled water. After removal of solvents, the product (0.060 g, 0.11 mmol, 99%) ($R_f$ = 0.1 eluted with EtOAc). $^1$H ($D_2O$, 400 MHz) $\delta$ 5.06 (s, 1H), 4.8 (m, 3H), 4.71 (s, 1H), 3.8 (m, 11H), 3.5−3.7 (m, 16H); $^{13}$C NMR ($D_2O$, 75 MHz) $\delta$ 102.2 ($\beta$), 102.1, 101.9, 96.8, 96.4 ($\beta$), 84.3, 76.7 ($\beta$), 75.8 ($\beta$), 75.3 (2 carbons), 73.7 ($\beta$), 73.3 (3 carbons), 73.1 (4 carbons), 72.5 (2 carbons), 72.4, 69.3 (2 carbons), 69.2 (2 carbons), 69.1 (2 carbons), 69.0 ($\beta$), 68.3 ($\beta$), 68.2 (2 carbons), 63.5; ESI/APCI calcd for $C_{18}H_{32}O_{16}Na$ ([M + Na]$^+$) *m/e* 527.1588; measured *m/e* 527.1581.

**Methyl 6-*O*-(6-*O*-Acetyl-2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-mannopyranoside (28).** Please refer to the general procedure for sonication-assisted glycosylation using phenylthioglycosyl donor ($R_f$ = 0.5 eluted with hexane/EtOAc =

65/35). $^1$H ($CDCl_3$, 300 MHz) $\delta$ 7.2−7.4 (m, 30H), 5.10 (s, 1H), 4.92 (d, $J$ = 10.9 Hz, 1H), 4.90 (d, $J$ = 10.9 Hz, 1H), 4.4−4.7 (m, 11H), 4.2 (m, 2H), 3.86 −3.94 (m, 6H), 3.8 (m, 2H), 3.7 (m, 2H), 3.24 (s, 3H, OMe), 1.99 (s, 3H, $CH_3$); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 171.04, 138.6, 138.5 (2 carbons), 138.47, 138.3, 138.27, 128.5 (5 carbons), 128.4 (4 carbons), 128.3 (2 carbons), 128.1 (2 carbons), 127.9 (3 carbons), 127.8, 127.7 (4 carbons), 127.68 (2 carbons), 127.64 (2 carbons), 127.56, 99.02, 98.04, 80.4 (2 carbons), 79.3, 77.3, 75.1 (2 carbons), 74.8, 74.7, 74.6, 74.4, 72.9, 72.4, 72.2, 71.5 (4 carbons), 70.2, 66.2, 63.6, 54.8, 20.9; ESI/APCI calcd for $C_{57}H_{62}O_{12}Na$ ([M + Na]$^+$) *m/e* 961.4139; measured *m/e* 961.4135.

**Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-(2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl)-α-D-mannopyranoside (29).** Please refer to the procedure for the synthesis of compound **23** ($R_f$ = 0.3 eluted with hexane/EtOAc = 65/35). $^1$H ($CDCl_3$, 300 MHz) $\delta$ 7.2−7.4 (m, 30H), 5.06 (d, $J$ = 1.3 Hz, 1H), 4.95 (d, $J$ = 10.7 Hz, 1H), 4.91 (d, $J$ = 10.7 Hz, 1H), 4.7 (m, 4H), 4.6−4.7 (m, 5H), 4.54 (d, $J$ = 12.0 Hz, 1H), 4.49 (d, $J$ = 11.0 Hz, 1H), 3.8−4.0 (m, 7H), 3.8 (m, 1H), 3.8−3.6 (m, 4H), 3.25 (s, 3H, OMe), 1.92 (s, 1H, OH); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 138.7 (2 carbons), 138.6, 138.5, 138.4, 138.3, 128.5 (4 carbons), 128.4 (5 carbons), 128.4 (2 carbons), 128.1 (2 carbons), 127.9 (2 carbons), 127.9 (2 carbons), 127.84, 127.80 (3 carbons), 127.7 (4 carbons), 127.6 (2 carbons), 99.0, 98.3, 80.3, 79.4, 75.2, 75.1, 75.0, 74.8, 74.7, 74.6, 72.9, 72.8, 72.3, 72.2, 71.7, 71.4, 66.2 (2 carbons), 62.4 (2 carbons), 54.8; ESI/APCI calcd for $C_{55}H_{60}O_{11}Na$ ([M + Na]$^+$) *m/e* 919.4033; measured *m/e* 919.4027.

**Methyl 6-*O*-(6-*O*-(2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-mannopyranoside (30).** Please refer to the general procedure for sonication-assisted glycosylation using phenylthioglycosyl donor ($R_f$ = 0.5 eluted with hexane/EtOAc = 65/35). $^1$H ($CDCl_3$, 400 MHz) $\delta$ 7.4−7.10 (m, 45H), 5.51 (dd, $J$ = 2.7, 4.8 Hz, 1H, H-2″), 5.10 (s, 1H, H-1″), 4.96 (s, 1H, H-1′), 4.95 (d, $J$ = 10.9 Hz, 1H), 4.90 (d, $J$ = 10.6 Hz, 1H), 4.83 (d, $J$ = 10.9 Hz, 1H), 4.6−4.7 (m, 13H), 4.3−4.5 (m, 8H), 3.8−3.9 (m, 14H), 3.5−3.7 (m, 8H), 3.23 (s, 3H, OMe), 2.15 (s, 3H, $CH_3$); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 170.3, 138.97, 138.91, 138.8, 138.7, 138.54, 138.50, 138.47, 138.1, 128.6 (6 carbons), 128.48 (5 carbons), 128.41 (4 carbons), 128.1 (2 carbons), 128.08 (2 carbons), 128.00 (3 carbons), 127.9 (4 carbons), 127.87 (4 carbons), 127.85 (4 carbons), 127.81 (4 carbons), 127.7 (2 carbons), 127.67 (4 carbons), 127.60, 127.5, 99.1, 98.3, 98.1, 80.5, 79.5, 77.9, 75.2 (2 carbons), 75.1, 75.02, 74.9, 74.7, 74.6, 74.3, 73.5, 73.04, 72.6, 72.3, 71.7, 71.6, 71.5 (2 carbons), 71.3, 68.9, 68.6, 66.7, 66.2, 21.4; ESI/APCI calcd for $C_{84}H_{94}NO_{17}$ ([M + $NH_4$]$^+$) *m/e* 1388.6522; measured *m/e* 1388.6500.

**Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-(6-*O*-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl)-α-D-mannopyranoside (31).** Please refer to the procedure for the synthesis of compound **23** ($R_f$ = 0.5 eluted with hexane/EtOAc = 1/1). $^1$H ($CDCl_3$, 400 MHz) $\delta$ 7.1−7.4 (m, 45H), 5.1 (m, 2H, H-1′, H-1″), 4.9 (m, 3H), 4.8 (m, 2H), 4.4−4.7 (m, 27H), 4.1 (m, 1H), 3.8−3.9 (m, 17H), 3.6−3.7 (m, 11H), 3.3 (m, 3H, OMe); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 138.93, 138.88, 138.78, 138.71, 138.6, 138.56, 138.51, 138.4, 138.1, 128.66 (3 carbons), 128.60 (5 carbons), 128.54 (4 carbons), 128.50 (5 carbons), 128.45 (3 carbons), 128.15 (2 carbons), 128.11 (5 carbons), 128.08 (5 carbons), 127.9 (2 carbons), 127.86 (3 carbons), 127.81 (5 carbons), 127.7 (2 carbons), 127.6, 99.9, 99.2, 98.1, 80.5, 79.8, 79.4, 77.4, 75.2 (3 carbons), 74.9, 74.7, 74.6, 74.4, 73.6, 73.1, 72.7, 72.3, 71.7 (2 carbons), 71.6 (2 carbons), 71.3, 69.0, 68.1, 66.3, 66.1, 54.9; ESI/APCI calcd for $C_{82}H_{92}O_{16}N$ ([M + $NH_4$]$^+$) *m/e* 1346.6416; measured *m/e* 1346.6383.

**Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-(6-*O*-(3,4,6-tri-*O*-benzyl-β-D-mannopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl)-α-D-mannopyranoside (epi-31).** Please refer to the procedure for the synthesis of compound **23** ($R_f$ = 0.6 eluted with hexane/EtOAc = 1/1). $^1$H ($CDCl_3$, 400 MHz) $\delta$ 7.5 (m, 2H), 7.2−7.4 (m, 41H), 7.1 (m, 2H), 5.31 (s, 1H), 5.07 (s, 1H), 4.99 (d, $J$ = 12.2 Hz, 1H), 4.9 (d, $J$ = 11.0 Hz, 1H), 4.89 (d, $J$ = 11.4 Hz, 1H), 4.8 (m, 2H), 4.6−4.7 (m, 4H) 4.68 (m, 4H), 4.4−4.6 (m, 13H), 4.1−4.2 (m, 3H), 3.9−3.7 (m, 14H), 3.7 (m, 1H), 3.6 (m, 2H), 3.5 (m, 1H), 3.3 (m, 1H), 3.2 (m, 3H, OMe); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 138.9, 138.7, 138.6 (2 carbons), 138.5, 138.4, 138.2 (2 carbons), 138.0, 128.7 (2 carbons), 128.5 (2 carbons), 128.4 (8 carbons), 128.34 (2 carbons), 128.31 (2 carbons), 128.2 (2 carbons), 128.1 (2 carbons), 128.0 (2 carbons), 127.9 (2 carbons), 127.8 (4 carbons), 127.7 (4 carbons), 127.6 (4 carbons), 127.5, (2carbons), 102.2, 100.3, 98.9, 82.2, 80.4, 79.4, 77.9, 77.3 (2 carbons), 75.3, 75.1, 75.0 (3 carbons), 74.8, 74.4 (2 carbons), 74.3, 73.8, 73.4 (3 carbons), 72.7, 72.0, 71.4 2 (carbons) 71.3 (2 carbons), 69.0, 68.9, 67.8, 66.8, 54.7; ESI/APCI calcd for $C_{82}H_{92}O_{16}N$ ([M + $NH_4$]$^+$) *m/e* 1346.6416; measured *m/e* 1346.6401.

**Methyl 6-*O*-(6-*O*-(α-D-Mannopyranosyl)-α-D-mannopyranosyl)-α-D-mannopyranoside (32).** Please refer to the procedure for the synthesis of compound **26** ($R_f$ = 0.1 eluted EtOAc). $^1$H ($D_2O$, 400 MHz) $\delta$ 4.80 (s, 1H), 4.78 (s, 1H), 4.70 (s, 2H), 4.64 (s, 1H), 3.8 (m, 7H), 3.7 (m, 6H), 3.6 (m, 10H), 3.29 (s, 3H, OMe), 3.23 (d, $J$ = 2.2 Hz, 1H), 2.90 (s, 1H), 2.74 (s, 1H); $^{13}$C NMR ($D_2O$, 100 MHz) $\delta$ 101.2, 99.6, 99.4, 72.9, 70.9 (2 carbons), 70.8, 70.7 (2 carbons), 70.1 (3 carbons), 66.9, 66.7, 66.6, 65.7, 65.6, 61.1, 54.9; ESI/APCI calcd for $C_{19}H_{34}O_{16}Na$ ([M + Na]$^+$) *m/e* 541.1745; measured *m/e* 541.1736.

**Benzyl 2-*O*-(2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (36).** Please refer to the general procedure for sonication-assisted glycosylation using phenylthioglycosyl donor ($R_f$ = 0.5 eluted with hexane/EtOAc = 3/1). $^1$H ($CDCl_3$, 400 MHz) $\delta$ 7.1−7.4 (m, 35H), 5.59 (d, $J$ = 0.9 Hz, 1H, H-2), 5.11 (s, broad, 1H, H-1′), 5.00 (d, $J$ = 0.9 Hz, 1H, H-1), 4.90 (d, $J$ = 10.7 Hz, 1H), 4.88 (d, $J$ = 10.8 Hz, 1H), 4.6−4.7 (m, 6H), 4.5−4.6 (m, 2H), 4.3 −4.5 (m, 4H), 4.08 (broad, 1H), 3.9−4.0 (m, 2H), 3.7−3.9 (m, 7H), 3.59 (d, $J$ = 10.1 Hz, 1H), 2.16 (s, 3H, $CH_3$); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 170.4, 138.75, 138.71, 138.6 (2 carbons), 138.4, 138.2, 137.5, 128.6 (4 carbons), 128.55 (5 carbons), 128.5 (4 carbons), 128.41 (2 carbons), 128.3 (2 carbons), 128.1 (2 carbons), 128.06 (2 carbons), 128.02 (3 carbons), 127.9 (2 carbons), 127.8, 127.76 (4 carbons), 127.71 (2 carbons), 127.6, 99.9, 98.2, 79.9, 78.4, 75.4, 75.3, 75.1, 74.9, 74.5, 73.6, 73.5, 72.3, 72.2, 72.0, 69.4, 69.2, 69.0, 68.9 (2 carbons), 21.4; ESI/APCI calcd for $C_{63}H_{70}NO_{12}$ ([M + $NH_4$]$^+$) *m/e* 1032.4898; measured *m/e* 1032.4892.

**Benzyl 3,4,6-Tri-*O*-benzyl-2-*O*-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-α-D-mannopyranoside (37).** Please refer to the procedure for the synthesis of compound **23** ($R_f$ = 0.2 eluted with hexane/EtOAc = 3/1). $^1$H ($CDCl_3$, 300 MHz) $\delta$ 7.1−7.4 (m, 35H), 5.16 (s, 1H), 5.02 (s, 1H), 4.8−4.9 (m, 2H), 4.6−4.7 (m, 4H), 4.6 (m, 1H), 4.4−4.6 (m, 6H), 4.36 (d, $J$ = 12.0 Hz, 1H), 4.15 (s, 1H), 4.09 (s, 1H), 3.9 (m, 1H), 3.7−3.9 (m, 6H), 3.6−3.7 (m, 2H), 3.58 (d, $J$ = 10.7 Hz, 1H), 2.42 (d, $J$ = 2.1 Hz, 1H, OH); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 138.7, 138.5 (2 carbons), 138.3 (2 carbons), 138.1, 137.4, 128.7, 128.6 (3 carbons), 128.5 (5 carbons), 128.4 (5 carbons), 128.1, 128.09 (3 carbons), 127.9, 127.86 (3 carbons), 127.82 (3 carbons), 127.7 (4 carbons), 127.6 (2 carbons), 127.5, 101, 98.3, 80.1, 79.8, 75.3, 75.07, 75.0, 74.9, 74.4 (2 carbons), 73.5, 73.4, 72.4, 72.3, 72.2, 71.6, 69.4, 69.1 (2 carbons), 69.0, 68.6 (2 carbons); ESI/APCI calcd for $C_{61}H_{64}O_{11}Na$ ([M + $NH_4$]$^+$) *m/e* 995.4346; measured *m/e* 995.4354.

**Benzyl 2-*O*-(2-*O*-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (38).** Please refer to the general procedure for sonication-assisted glycosylation using phenylthioglycosyl donor ($R_f$ = 0.5 eluted with hexane/EtOAc = 3/1). $^1$H ($CDCl_3$, 400 MHz) $\delta$ 7.1−7.4 (m, 50H), 5.55 (dd, $J$ = 1.8, 3.2 Hz, 1H, H-2″), 5.19 (d, $J$ = 1.6 Hz, 1H, H-1″), 5.06 (d, $J$ = 1.6 Hz, H-1′), 5.02 (d, $J$ = 1.7 Hz, 1H, H-1), 4.8−4.9 (m, 3H), 4.71 (d, $J$ = 11.6 Hz, 2H), 4.5−4.7 (m, 9H), 4.5 (m, 1H), 4.41 (d, $J$ = 10.9 Hz, 1H), 4.33 (d, $J$ = 11.7 Hz, 1H), 4.30 (d, $J$ = 12.0 Hz, 1H), 4.1 (m, 1H), 4.03 (m, 2H), 3.8−3.9 (m, 6H), 3.7−3.8 (m, 5H), 3.6−3.7 (m, 5H), 3.52 (d, $J$ = 10.5 Hz, 1H), 2.14 (s, 3H, $CH_3$); $^{13}$C NMR

($CDCl_3$, 100 MHz) $\delta$ 170.3, 138.8 (2 carbons), 138.7 (2 carbons), 138.6 (2 carbons), 138.5, 138.4, 138.2, 137.6, 128.6 (3 carbons), 128.5 (6 carbons), 128.4 (3 carbons), 128.4 (2 carbons), 128.2 (4 carbons), 128.0 (4 carbons), 127.9 (4 carbons), 127.8 (3 carbons), 127.7 (5 carbons), 127.7 (6 carbons), 100.9, 99.6, 98.4, 79.7 (2 carbons), 79.5, 78.4 (2 carbons), 77.5 (3 carbons), 75.3 (4 carbons), 75.2 (2 carbons), 75.1, 74.9, 74.4, 73.5, (5 carbons) 72.3, (2 carbons), 72.2, 72.1, (3 carbons), 69.5 (2 carbons), 69.3, 68.9 (3 carbons), 21.9; ESI/APCI calcd for $C_{90}H_{98}NO_{17}$ ($[M + NH_4]^+$) *m/e* 1464.6835; measured *m/e* 1464.6838.

**Benzyl 3,4,6-Tri-*O*-benzyl-2-*O*-(2-*O*-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-α-D-mannopyranoside (39).** Please refer to the procedure for the synthesis of compound **23** ($R_f$ = 0.7 eluted with hexane/EtOAc = 65/35). $^1H$ ($CDCl_3$, 300 MHz) $\delta$ 7.1−7.4 (m, 50H), 5.21 (d, $J$ = 1.7 Hz, 1H, H-1″), 5.13 (d, $J$ = 1.4 Hz, 1H, H-1′), 5.03 (d, $J$ = 1.7 Hz, 1H, H-1), 4.82 (d, $J$ = 11.0 Hz, 1H), 4.80 (d, $J$ = 10.7 Hz, 1H), 4.7−4.4 (m, 16H), 4.34 (d, $J$ = 11.7 Hz, 1H), 4.31 (d, $J$ = 12.0 Hz, 1H), 4.12 (s, 2H), 4.02 (s, 1H), 3.8−3.9 (m, 7H), 3.5−3.8 (m, 8H), 2.36 (d, $J$ = 2.4 Hz, 1H, OH); $^{13}C$ NMR ($CDCl_3$, 75 MHz) $\delta$ 138.7 (2 carbons), 138.6 (2 carbons), 138.5, 138.4 (2 carbons), 138.3, 138.1, 137.5, 128.55 (3 carbons), 128.5 (2 carbons), 128.4 (9 carbons), 128.1 (2 carbons), 127.9 (8 carbons), 127.86 (3 carbons), 127.79 (4 carbons), 127.72 (5 carbons), 127.6 (5 carbons), 127.5 (2 carbons), 101.1, 101.0, 98.3, 80.1, 79.5, 77.3 (2 carbons), 75.4, 75.2 (2 carbons), 75.1, 75.0, 74.9 (2 carbons), 74.4, 73.4 (2 carbons), 73.3 (3 carbons), 72.4 (2 carbons), 72.3, 72.2 (2 carbons), 72.1, 71.96, 71.67, 69.5, 69.4, 69.16 (2 carbons), 69.03, 68.63 (2 carbons); ESI/APCI calcd for $C_{88}H_{96}NO_{16}$ ($[M + NH_4]^+$) *m/e* 1422.6729; measured *m/e* 1422.6729.

**2-*O*-(2-*O*-(α-D-Mannopyranosyl)-α-D-mannopyranosyl)-D-mannopyranose (40).** Please refer to the procedure for the synthesis of compound **26** ($R_f$ = 0.2 eluted with EtOAc/MeOH = 9/1). $^1H$ ($D_2O$, 400 MHz) $\delta$ 5.26 (s, 1H), 5.19 (s, 1H), 4.93 (s, 2H), 3.5−4.0 (m, 28H); $^{13}C$ NMR ($D_2O$, 100 MHz) $\delta$ 102.4, 100.7, 92.6, 79.5, 78.7, 73.4 (2 carbons), 72.6, 70.5, 70.1 (3 carbons), 67.2 (2 carbons), 66.9, 61.2 (2 carbons), 61.1; ESI/APCI calcd for ESI/APCI calcd for $C_{18}H_{32}O_{16}Na$ ($[M + Na]^+$) *m/e* 527.1588; measured *m/e* 527.1577.

**Methyl 2-*O*-(2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (42).** Please refer to the general procedure for sonication-assisted glycosylation using phenylthioglycosyl donor ($R_f$ = 0.7 eluted with hexane/EtOAc = 65/35). $^1H$ ($CDCl_3$, 300 MHz) $\delta$ 7.1−7.5 (m, 30H), 5.53 (dd, $J$ = 3.1, 1.8 Hz, 1H), 5.07 (d, $J$ = 1.8 Hz, 1H), 4.84 (d, $J$ = 10.9 Hz, 1H), 4.83 (d, $J$ = 10.9 Hz, 1H), 4.76 (d, $J$ = 2.0 Hz, 1H), 4.6−4.7 (m, 4H), 4.4−4.6 (m, 5H), 4.39 (d, $J$ = 10.9 Hz, 1H), 3.7−4.0 (m, 11H), 3.24 (s, 3H), 2.10 (m, 3H); $^{13}C$ NMR ($CDCl_3$, 75 MHz) $\delta$ 170.2, 138.61, 138.58, 138.55, 138.46, 138.29, 138.09, 128.48 (3 carbons), 128.40 (5 carbons), 128.28 (2 carbons), 128.15 (2 carbons), 127.97 (3 carbons0, 127.8, 127.68 (3 carbons), 127.61 (3 carbons), 127.5 (3 carbons), 99.8, 99.6, 79.8, 78.2, 77.3, 75.2 (2 carbons), 74.7 (3 carbons), 74.4, 73.5 (2 carbons), 73.4 (2 carbons), 72.1 (2 carbons), 72.0 (2 carbons), 71.9 (2 carbons), 71.7 (2 carbons), 54.8, 21.2; HRFAB calcd for $C_{57}H_{62}O_{12}Na$ ($[M + Na]^+$) *m/e* 961.4133; measured *m/e* 961.4148.

**Methyl 3,4,6-Tri-*O*-benzyl-2-*O*-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-α-D-mannopyranoside (43).** Please refer to the procedure for the synthesis of compound **23** ($R_f$ = 0.4 eluted with hexane/EtOAc = 65/35). $^1H$ ($CDCl_3$, 300 MHz) $\delta$ 7.4 (m, 30H), 5.16 (s, 1H, H-1′), 4.8−4.9 (m, 3H), 4.7 (m, 1H), 4.6−4.7 (m, 4H), 4.5−4.6 (m, 5H), 4.1 (m, 1H), 4.0 (m, 1H), 3.7−4.0 (m, 11H), 3.25 (s, 3H, O Me), 2.44 (d, $J$ = 1.7 Hz, 1H, OH); $^{13}C$ NMR ($CDCl_3$, 75 MHz) $\delta$ 138.7, 138.6, 138.5, 138.4, 138.3, 138.1, 128.6 (3 carbons), 128.4 (7 carbons), 127.99 (5 carbons), 127.96 (6 carbons), 127.8 (3 carbons), 127.7 (2 carbons), 127.6, 127.56 (2 carbons), 127.50, 101.2, 99.9, 80.1, 79.9, 75.2, 75.1, 74.9, 74.8, 74.5, 73.5, 73.4, 72.3, 72.2, 71.8, 71.7, 69.4, 69.3, 68.6, 54.8; ESI/APCI calcd for $C_{55}H_{60}O_{11}Na$ ($[M + Na]^+$) *m/e* 919.4033; measured *m/e* 919.4030.

**Methyl 2-*O*-(2-*O*-(2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (44).** Please refer to the general procedure for sonication-assisted glycosylation using phenylthioglycosyl donor ($R_f$ = 0.4 eluted with hexane/EtOAc = 3/1). $^1H$ ($CDCl_3$, 300 MHz) $\delta$ 7.1 −7.4 (m, 45H), 5.52 (d, $J$ = 2.1 Hz, 1H), 5.18 (s, 1H), 5.04 (d, $J$ = 1.7 Hz, 1H), 4.8 (m, 4H), 4.6−4.7 (m, 3H), 4.61 (m, 1H), 4.5 (m, 4H), 4.5 (m, 2H), 4.4−4.5 (m, 3H), 4.30 (d, $J$ = 12.0 Hz, 1H), 4.1 (m, 1H), 3.8−4.0 (m, 6H), 3.6−3.8 (m, 10H), 3.51 (d, $J$ = 10.3 Hz, 1H), 3.22 (s, 3H, OMe), 2.12 (s, 3H, $CH_3$); $^{13}C$ NMR ($CDCl_3$, 100 MHz) $\delta$ 170.1, 138.65 (2 carbons), 137.54 (3 carbons), 138.4 (2 carbons), 138.25, 138.1, 128.5 (8 carbons), 128.4 (3 carbons), 128.36 (3 carbons), 128.2 (3 carbons),128.10 (3 carbons), 127.97 (3 carbons), 127.96 (3 carbons), 127.90 (3 carbons), 127.88 (3 carbons), 127.7 (5 carbons), 127.68 (4 carbons), 127.5 (3 carbons), 100.8, 99.9, 99.8, 79.9, 78.3 (2 carbons), 77.4 (4 carbons), 75.3 (2 carbons), 75.2, 74.95, 74.94, 73.56 (3 carbons), 72.3, 72.29, 72.25, 72.1 (2 carbons), 71.8, 69.5 (2 carbons), 68.9 (2 carbons), 54.8, 21.4; ESI/APCI calcd for $C_{84}H_{94}NO_{17}$ ($[M + NH_4]^+$) *m/e* 1388.6522; measured *m/e* 1388.6519.

**Methyl 3,4,6-Tri-*O*-benzyl-2-*O*-(2-*O*-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-α-D-mannopyranoside (45).** Please refer to the procedure for the synthesis of compound **23** ($R_f$ = 0.6 eluted with hexane/EtOAc = 65/35). $^1H$ ($CDCl_3$, 400 MHz) $\delta$ 7.2−7.4 (m, 45H), 5.25 (d, $J$ = 1.6 Hz, 1H), 5.15 (d, $J$ = 1.5 Hz, 1H), 4.8 (m, 4H), 4.70 (d, $J$ = 12.1 Hz, 1H), 4.68 (d, $J$ = 12.3 Hz, 1H), 4.6 (m, 4H), 4.5 (m, 6H), 4.49 (d, $J$ = 10.7 Hz, 1H), 4.47 (d, $J$ = 11.6 Hz, 1H), 4.36 (d, $J$ = 12.2 Hz, 1H), 4.14 (s, 2H), 4.00 (t, $J$ = 2.4 Hz, 1H), 3.9 (m, 5H), 3.8 (m, 2H), 3.8 (m, 4H), 3.7 (m, 2H), 3.6 (m, 1H), 3.6 (m, 1H), 3.25 (s, 3H, OMe), 2.46 (s, 1H, OH); $^{13}C$ NMR ($CDCl_3$, 100 MHz) $\delta$ 138.8 (2 carbons), 138.7 (3 carbons), 138.6, 138.5, 138.4, 138.3, 128.7 (4 carbons), 128.6 (2 carbons), 128.5 (8 carbons), 128.1 (8 carbons), 128.0 (5 carbons), 127.9 (2 carbons), 127.81 (2 carbons), 127.8 (2 carbons), 127.7 (5 carbons), 127.6 (2 carbons), 101.2, 101.0, 99.9, 80.2, 79.6 (2 carbons), 77.46, 75.3, 75.2 (3 carbons), 75.2 (3 carbons), 74.9, 74.5, 73.55 (2 carbons), 73.50 (3 carbons), 72.54, 72.5, 72.3, 71.9, 71.8, 71.7, 69.8, 69.6, 69.1, 68.7, 54.7; ESI/APCI calcd for $C_{82}H_{92}NO_{16}$ ($[M + NH_4]^+$) *m/e* 1346.6391; measured *m/e* 1346.6397.

**Methyl 2-*O*-(2-*O*-(α-D-Mannopyranosyl)-α-D-mannopyranosyl)-α-D-mannopyranoside (46).** Please refer to the procedure for the synthesis of compound **26** ($R_f$ = 0.1 eluted EtOAc). $^1H$ ($D_2O$, 400 MHz) $\delta$ 5.15 (d, $J$ = 1.0 Hz, 1H), 4.90 (d, $J$ = 1.4 Hz, 1H), 4.85 (d, $J$ = 1.0 Hz, 1H), 4.68 (s, 2H), 3.93 (s, 1H), 3.92 (s, 1H), 3.4−3.8 (m, 22H), 3.26 (s, 3H, OMe); $^{13}C$ NMR ($D_2O$, 100 MHz) $\delta$ 102.4, 100.8, 99.4, 78.9, 78.7, 73.4 (2 carbons), 72.7, 70.5, 70.3, 70.1 (2 carbons), 67.2, 67.1, 66.9, 61.3, 61.2, 61.1, 55.0; ESI/APCI calcd for $C_{19}H_{34}O_{16}Na$ ($[M + Na]^+$) *m/e* 541.1745; measured *m/e* 541.1733.

**Methyl 3-*O*-(2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-2,4-di-*O*-benzyl-α-D-mannopyranoside (47).** To a solution of compound **19** (0.27 g, 0.32 mmol) and $Cu(OTf)_2$ (0.017 g, 0.048 mmol) in anhydrous $CH_2Cl_2$ (10 mL), borane complex (0.6 mL) was added and the mixture was stirred for 2 h at room temperature. After completion of the reaction, the reaction was quenched with MeOH, diluted with EtOAc, and washed with saturated $NaHCO_{3(aq)}$, water, and brine. After removal of solvents and purification with gradient column chromatography, the product was obtained as an oil (0.27 g,, 0.31 mmol, 98%) ($R_f$ = 0.3 eluted with hexane/EtOAc = 65/35). $^1H$ ($CDCl_3$, 400 MHz) $\delta$ 7.2−7.4 (m, 25H), 5.52 (d, $J$ = 1.7 Hz, 1H, H-2), 5.23 (s, 1H, H-1), 4.90 (d, $J$ = 11.2 Hz, 1H), 4.81 (d, $J$ = 10.9 Hz, 1H), 4.6−4.7 (m, 8H), 4.4−4.5 (m, 4H), 4.1−4.2 (m, 3H), 3.6−4.0 (m); 3.28 (s, 3H, OMe), 2.11 (s, 3H, $CH_3$); $^{13}C$ NMR ($CDCl_3$, 100 MHz) $\delta$ 170.3, 138.8, 138.5, 138.3, 138.1, 138.0, 128.7 (5 carbons), 128.6 (2 carbons), 128.4 (5 carbons), 128.3 (2 carbons), 128.2 (3 carbons), 128.0, 127.9 (2

carbons), 127.88 (4 carbons), 127.74 (2 carbons), 127.71, 99.8, 98.9, 78.26, 78.1, 77.4, 75.4, 75.2, 75.14, 74.6, 73.7, 72.7, 72.4, 72.3, 71.9, 69.4, 68.9, 62.3, 55.04, 21.2; ESI/APCI calcd for $C_{50}H_{56}O_{12}Na$ ($[M + Na]^+$) *m/e* 871.3664; measured *m/e* 871.3650.

**Methyl 3-*O*-(2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-6-*O*-(3,6-di-*O*-acetyl-2,4-di-*O*-benzyl-α-D-mannopyranosyl)-2,4-di-*O*-benzyl-α-D-mannopyranoside (48).** Please refer to the general procedure for sonication-assisted glycosylation using phenylthioglycosyl donor ($R_f$ = 0.5 eluted with hexane/EtOAc = 65/35). $^1H$ ($CDCl_3$, 400 MHz) $\delta$ 7.1−7.3 (m, 35H), 5.51 (s, 1H, H-2″), 5.31 (s, 1H, H-1″), 5.21 (s, 1H, H-3‴), 5.11 (d, $J$ = 1.8 Hz, 1H, H-1″), 4.88 (d, $J$ = 10.9 Hz, 1H), 4.83 (d, $J$ = 11.1 Hz, 1H), 4.5−4.7 (m, 9H), 4.4−4.5 (m, 3H), 4.39 (d, $J$ = 12.2 Hz, 1H), 4.1 (m, 1H), 3.6−4.0 (m, 15H), 3.25 (s, 3H, OMe), 2.08 (s, 3H, $CH_3$), 2.05 (s, 3H, $CH_3$), 1.98 (s, 3H, $CH_3$); $^{13}C$ NMR ($CDCl_3$, 75 MHz) $\delta$ 170.9, 170.1 (2 carbons), 138.7, 138.4, 138.3, 138.2, 138.1, 138.07, 137.9, 128.5 (7 carbons), 128.4 (2 carbons), 128.3 (6 carbons), 127.9 (4 carbons), 127.8 (3 carbons), 127.7 (2 carbons), 127.65 (3 carbons), 127.6 (3 carbons), 99.8, 98.6, 97.7, 78.1 (2 carbons), 77.9, 77.3 (6 carbons), 76.3, 75.2 (2 carbons), 74.9, 74.8, 74.4, 73.8, 73.5, 73.3, 72.7, 72.6, 72.3, 71.9 (2 carbons), 69.8, 69.2, 68.8, 63.4, 54.8, 21.2, 21.1, 20.9; ESI/APCI calcd for $C_{74}H_{82}O_{19}Na$ ($[M + Na]^+$) *m/e* 1297.5348; measured *m/e* 1297.5328.

**Methyl 6-*O*-(2,4-Di-*O*-benzyl-α-D-mannopyranosyl)-3-*O*-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-2,4-di-*O*-benzyl-α-D-mannopyranoside (49).** Please refer to the procedure for the synthesis of compound **23** ($R_f$ = 0.1 eluted with hexane/EtOAc = 65/35). $^1H$ ($CDCl_3$, 400 MHz) $\delta$ 7.2−7.4 (m, 35H), 5,26 (s, 1H), 5.15 (s, 1H), 4.94 (d, $J$ = 11.1 Hz, 1H), 4.86 (d, $J$ = 11.1 Hz, 1H), 4.77 (d, $J$ = 11.0 Hz, 1H), 4.5−4.7 (m, 11H), 4.42 (d, $J$ = 11.8 Hz, 1H), 4.1 (m, 1H), 3.6−4.0 (m, 18H), 3.27 (s, 3H, OMe), 2.39 (s, 1H, OH), 2.33 (d, $J$ = 9.4 Hz, 1H, OH); $^{13}C$ NMR ($CDCl_3$, 100 MHz) $\delta$ 138.7, 138.6, 138.5, 138.4, 138.2, 138.0 (2 carbons), 128.7 (5 carbons), 128. Six (4 carbons), 128.4 (4 carbons), 128.1 (2 carbons), 128.0 (2 carbons), 127.97 (3 carbons), 127.9 (4 carbons), 127.79 (4 carbons), 127.76 (3 carbons), 127.6 (2 carbons), 127.56, 101.5, 98.7, 97.5, 80.2, 78.9, 77.7, 76.7, 75.2 (4 carbons), 75.0, 74.6, 73.7 (2 carbons), 72.9, 72.7, 72.3, 72.2, 71.9 (2 carbons), 71.6, 69.5, 68.9, 66.2, 62.4, 55.0; ESI/APCI calcd for $C_{68}H_{76}O_{16}Na$ ($[M + Na]^+$) *m/e* 1171.5031; measured *m/e* 1171.5005.

**Methyl 3-*O*-(2-*O*-(2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-6-*O*-(3,6-di-*O*-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-2,4-di-*O*-benzyl-α-D-mannopyranosyl)-2,4-di-*O*-benzyl-α-D-mannopyranoside (50).** Please refer to the general procedure for sonication-assisted glycosylation using phenylthioglycosyl donor ($R_f$ = 0.5 eluted with hexane/EtOAc = 1/1). $^1H$ ($CDCl_3$, 300 MHz) $\delta$ 7.4−7.1 (m, 80H), 5.51 (s, broad, 3H), 5.21 (s, 2H), 5.01 (s, 1H), 4.98 (s, 1H), 4.96 (s, 1H), 4.7−4.9 (m, 5H), 4.72 (d, $J$ = 11.3 Hz, 2H), 4.3−4.7 (m, 28H), 4.30 (d, $J$ = 12.0 Hz, 2H), 4.25 (d, $J$ = 12.0 Hz, 1H), 4.0−4.2 (m, 3H), 3.4−4.0 (m, 28H), 3.35 (d, $J$ = 10.3 Hz, 1H), 3.17 (s, 3H, OMe), 2.14 (s, 3H, $CH_3$), 2.10 (s, 3H, $CH_3$), 2.06(s, 3H, $CH_3$); $^{13}C$ NMR ($CDCl_3$, 75 MHz) $\delta$ 170.3, 170.2 (2 carbons), 138.8 (2 carbons), 138.7, 138.6 (2 carbons), 138.5 (2 carbons), 138.3 (4 carbons), 138.18 (2 carbons), 138.16, 137.96, 137.89, 128.6 (2 carbons), 128.47 (8 carbons), 128.40 (8 carbons), 128.3 (6 carbons), 128.29 (10 carbons), 128.16 (3 carbons), 127.89 (8 carbons), 127.86 (6 carbons), 127.78 (3 carbons), 127.67 (4 carbons), 127.56 (4 carbons), 127.55 (5 carbons), 127.48 (4 carbons), 127.29 (2 carbons), 101.2, 99.8, 99.5, 98.4, 98.1, 97.0, 79.8, 78.3 (2 carbons), 78.2 (2 carbons), 77.8 (2 carbons), 77.3 (3 carbons), 75.09 (2 carbons), 74.98 (3 carbons), 74.8 (2 carbons), 74.76, 74.74, 74.16 (4 carbons), 73.46 (2 carbons), 73.44 (3 carbons), 73.25 (2 carbons), 72.8, 72.25 (4 carbons), 72.12 (3 carbons), 71.92 (2 carbons), 72.90 (2 carbons), 71.63 (2carbons), 71.5, 71.3 (2 carbons), 71.0, 68.8 (3 carbons), 68.4 (2 carbons), 54.8, 21.26 (2 carbons), 21.2; ESI/APCI calcd for $C_{155}H_{170}O_{34}N$ ($[M + NH_4]^+$) *m/e* 2589.1599; measured *m/e* 2589.1604.

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**Supporting Information Available:** $^1H$ and $^{13}C$ spectra of the synthesized compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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