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Construction of β-Mannosidic Bonds via Gold(I)-Catalyzed Glycosylations with Mannopyranosyl *ortho*-Hexynylbenzoates and Its Application in Synthesis of Acremomannolipin A

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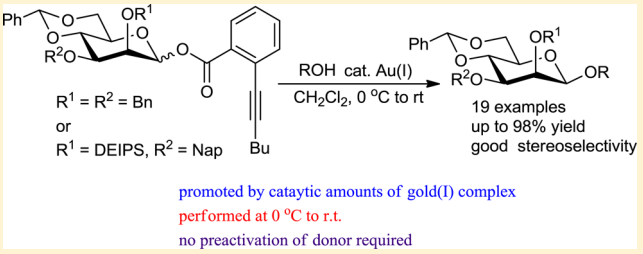
Supporting Information

ABSTRACT: A mild and convenient protocol for direct synthesis of β-mannosides has been developed. Glycosylation of 4,6-*O*-benzylidene-protected mannosyl *ortho*-hexynylbenzoates with various alcohol acceptors catalyzed by gold(I) complex proceeded smoothly at 0 °C to room temperature and afforded the corresponding β-mannoside in high yield and satisfactory stereoselectivity. This reaction was applied to the total synthesis of acremomannolipin A and its analogue.



β-Mannopyranosyl unit is an essential constituent of naturally occurring bioactive oligosaccharides and glycopeptides. Formation of β-mannosidic linkages has long been considered one of the most difficult and challenging targets in carbohydrate chemistry because of both anomeric effects and the axial C2−O2 substituent favoring α-mannosides when the mannosyl donors function as glycosylation reagents.[1] Among the methods reported, synthesis of β-mannoside using mannosyl sulfoxide and thioglycoside developed by Crich and co-workers are notable breakthroughs (Scheme 1, eqs 1a and 1b).[2,3] In these methods, preactivation and nonpreactivation protocols have been exploited to synthesize β-mannosides through activation of 4,6-*O*-benzylidene-protected mannosyl sulfoxide or thioglycoside with the 2-OH and 3-OH groups blocked with ether-type protective groups such as the benzyl group by stoichiometric amounts of the appropriate activators. The glycosylation generally proceeded with high yield and selectivity.

Thereafter, a wide array of 4,6-*O*-benzylidene-protected mannosyl donors including 2-(hydroxycarbonyl)benzyl ether,[4] 4-pentenoate,[5] diethyl phosphite,[6] hemiacetal,[7] trichloroacetimidate,[8] and *N*-phenyl trifluoroacetimide[9] were successfully utilized in the preparation of β-mannosides (Scheme 1, eqs 1c−1g). Mannosyl donors with replacement of benzylidene by 4,6-silylene and those without benzylidene have also been employed to construct β-mannosides.[10] In particular, the glycosylations with 4,6-silylene protected mannosyl thioglycoside were conducted at 0 °C or room temperature and requires no preactivation. Recently, a novel strategy involving hydrogen bond-mediated aglycone delivery with thioglycosides bearing either picolinyl or picoloyl group as donors has been used to construct challenging β-manno, β-rhamno, and α-glucosides with stereoselectivities.[11]

Gold(I)-catalyzed glycosylation of glycosyl *ortho*-alkynylbenzoate donors, introduced by Yu and co-workers,[12] is a mild and versatile method for the synthesis of various glycosides with a thoroughly studied mechanism. To extend the methodologies of formation of the challenging β-mannosidic bond, we herein disclose our results on direct construction of β-mannosidic bonds with mannosyl *ortho*-hexynylbenzoates as donors and its application toward the synthesis of acremomannolipin A. Our method prepares β-mannoside in high yield by mixing the mannosyl donor and glycosyl acceptor with the promotion of a catalytic amount of the gold(I) complex at 0 °C to room temperature (Scheme 1). Thus, this reaction constitutes an operationally simple approach to the formation of β-mannosidic linkages.

Guided by the discovery that the 4,6-*O*-benzylidene protective group facilitates the highly stereoselective β-mannopyranosylation, we initially prepared *ortho*-hexynylbenzoate **2** as a mixture (α/β = 3.5:1) in 82% yield. This could be readily separated by silica gel column chromatography (Table 1). We then used the glycosylation of **2α** with rhamnosyl thioglycoside **3a** as a model reaction to determine the optimal reaction conditions. After screenings of various combinations of gold(I) complex and silver salt as promoter (Table 1, Entry 1), $(p\text{-MeOPh})_3AuCl/Ag[B(C_6F_5)_4]$[9a] emerged as the catalyst of choice. The corresponding β-mannoside **4a** was attained in 76% yield with no α-isomer detected.

With the optimized conditions in hand, we then explored the scope of this reaction (Table 1). Although the sugar acceptors **3a**−**3e** reacted to afford the corresponding β-mannosides in high

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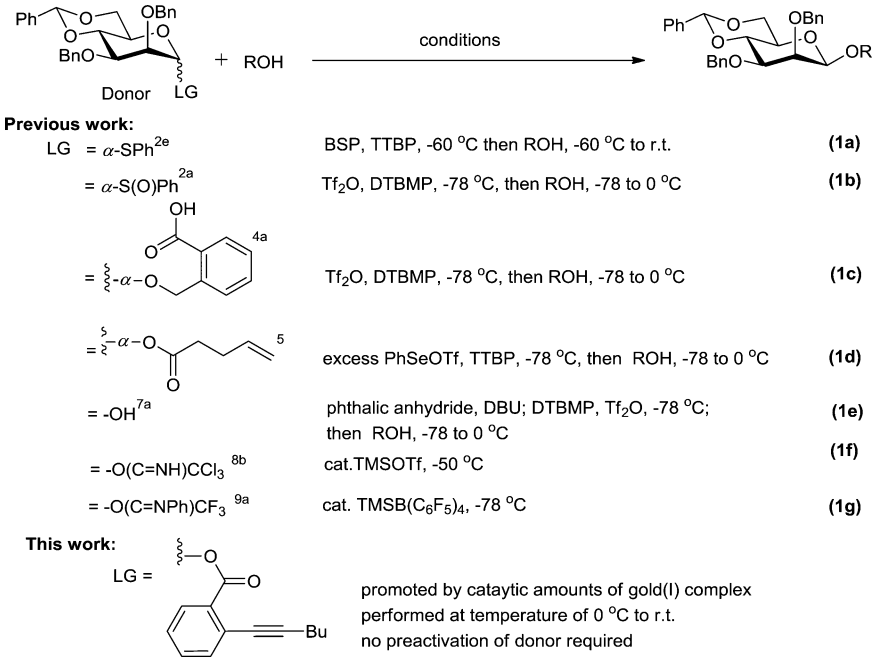
Scheme 1. Representative Protocols for Direct Synthesis of β-Mannoside and This Work



yields with exclusive stereoselectivities, some comments are required. Versus the exclusive formation of β-mannoside **4e** (Table 1, Entry 5), compound **4f** (Table 1, Entry 6) was obtained as a 5.6:1 β/α mixture in 78% yield. The reduction in stereoselectivity is attributed to reduced nucleophilicity of the 4-OH on acceptor **3f** because of the presence of adjacent electron-withdrawing benzoyl groups.[10b] β-Mannosylations of donor **2**$\boldsymbol{\beta}$ also performed well under the optimized conditions, and disaccharides **4e** (Table 1, Entry 9) and **4h** (Table 1, Entry 8) were both obtained in a stereocontrolled manner. Comparable outcomes for **4e** from **2**$\boldsymbol{\alpha}$ and **2**$\boldsymbol{\beta}$ (Table 1, Entries 5 and 9) suggest that a common active intermediate should be involved in their glycosylation process. On the basis of these observations together with Yu's,[3a] Crich's[12e] and Pedersen's[10b] elegant works on glycosylation mechanism, we speculate that it is an oxocarbenium ion occupying $^4H_3$ and $B_{2,5}$ conformations that equilibrates with a transient contact ion pair (CIP) and is responsible for stereoselective formation of the β-mannosidic bond. The preferable axial acttack on energically favorable $B_{2,5}$ conformations and/or S_N2-like displacement of CIP by the alcohol stereocontrol resulted in β-mannoside. However, for an acceptor with weak nucleophilicity such as **3f**, attack on $^4H_3$ conformation, which is less stable and therefore more reactive than $B_{2,5}$, occurred as a competing reaction to give α-mannoside. This diminished the β-selectivity of the glycosylation (Scheme 2).

Saponins are an especially important class of secondary metabolites exhibiting diverse bioactivities.[13] Recently, the indoditerpene saponin emindole β-mannoside has been isolated from marine-derived strain of *Dichotomomyces cejpii*.[14] Despite enormous progress in the synthesis of saponins[15] there are few methods[2c,d] for carrying out β-mannosylation at the 3-OH of sapogenins where a sugar chain is usually appended. Thus, we examined applications of the present glycosylation in the synthesis of such compounds. Couplings of typical sapogenins including glycyrrhetic acid **3i** (Table 1, Entry 10), oleanolic acid **3j** (Table 1, Entry 11), diosgenin **3k** (Table 1, Entry 12), and cholesterol **3l** (Table 1, Entry 13) with **2**$\boldsymbol{\alpha}$ or **2**$\boldsymbol{\beta}$ to generate β-mannosides **4i**−**4l** in excellent yields and stereoselectivities demonstrate the potential of this reaction for the synthesis of β-mannosyl saponins.

Inspired by Boon's related work[16] and to benefit late-stage modifications of β-mannosides, we also prepared orthogonally protected mannosyl benzoate **6** as a donor and tested its β-mannosylations (Table 2). Although **6**$\boldsymbol{\alpha}$ reacted with diosgenin **3k** to afford saponin **7a** smoothly (Table 2, Entry 1), its couplings with 4-OH sugar acceptors **3d** (Table 2, Entry 2) and **3f** (Table 2, Entry 3) showed decreased stereoselectivity; disaccharides **7b** and **7c** were obtained at β/α = 8.6:1 and 1.6:1, respectively. Galactosyl diacetonide **3g** (Table 2, Entry 4), which had shown decreased β-stereoselectivity relative to other acceptors in sulfoxide[2b] and trichloroacetimidate glycosylation,[8a] was treated with **6**$\boldsymbol{\alpha}$ to deliver 89% yield of **7d** in a ratio of β/α = 20:1. This is a big improvement in stereoselectivity by comparison with the generation of **4g** (64% yield, β/α = 10:1, Table 1, Entry 7) from **2**$\boldsymbol{\alpha}$.

The method was extended to such acceptors as **3m** and **3n** (Table 2, Entries 5 and 6) with the 6-OH free and disaccharides **7e** and **7f** readily obtained in 77% and 86% yields with excellent stereoselectivity, respectively. These results indicated that **6**$\boldsymbol{\alpha}$ might be an appropriate donor to construct β-mannosidic (1 → 6) linkages. Additionally, easy access to disaccharide thioglycosides **4a**, **4d**, **7b**, and **7e** opens up new prospects for the synthesis of β-mannosyl fragment-containing oligosaccharides because they could be immediately utilized as donors in their next coupling reaction.

The configuration of newly generated glycosidic bonds was unambiguously assigned by both chemical shift of H-5 and one-bond coupling constant ($^1J_{CH}$) of anomeric center derived from mannosyl units. The former appeared in a region ranging from 2.9 to 3.3 ppm as a multiplet,[2d] which is diagnostic for 4,6-*O*-benzylindene protected β-mannoside (see Section A in SI). The latter spanned from 154 to 158 Hz, further confirming the formation of β-mannosidic linkages (see Section A in SI).[17]

After establishing the protocol for direct β-mannosylation of glycosyl acceptors, we set out to synthesize acremomannolipin A, which is a novel glycolipid composed of mannitol and per-acylated mannopyranosyl moiety through a β-glycosidic linkage.

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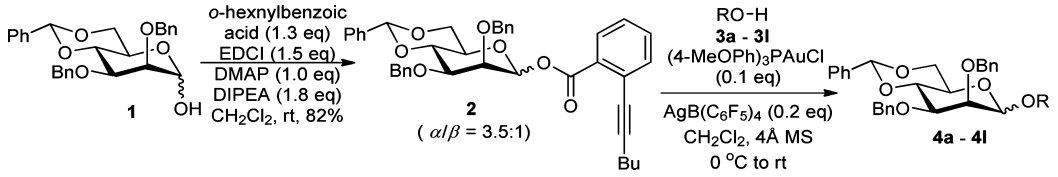
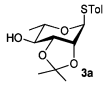
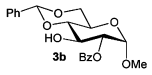
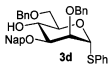
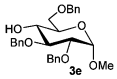
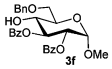
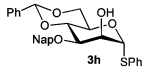
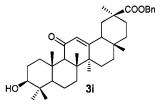
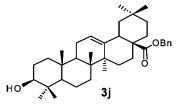
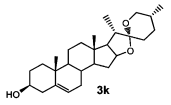
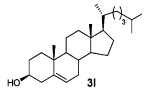
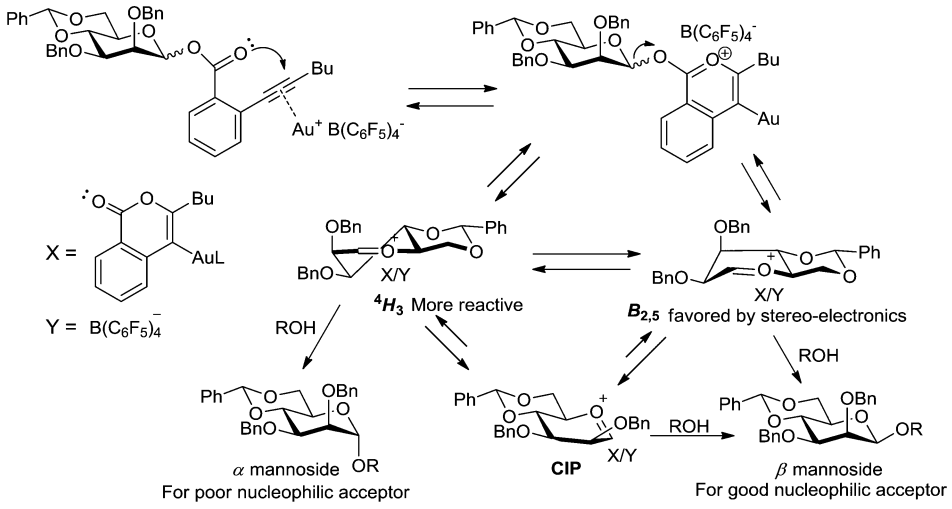
Table 1. Glycosylations of Donor 2 with Acceptors 3a−3l



Entry	Donor	Acceptor	Prod.	Yield[a]	β/α[b]
1	**2α**		**4a**	0%[c]	NR
				58%[d]	β only
				62%[e]	β only
				73%[f]	β only
2	**2α**		**4b**	76%	β only
3	**2α**		**4c**	88%	β only
4	**2α**		**4d**	82%	β only
5	**2α**		**4e**	90%	β only
6	**2α**		**4f**	78%	5.6/1
7	**2α**		**4g**	64%	10/1
8	**2β**		**4h**	78%	β only
9	**2β**	**3e**	**4e**	81%	β only
10	**2β**		**4i**	93%	β only
11	**2α**		**4j**	98%	β only
12	**2α**		**4k**	86%	β only
13	**2β**		**4l**	93%	11.4/1

[a]Isolated yield. [b]The ratios were determined by ^{1}H NMR spectroscopy of purified products by silica gel charomatography. [c]Catalyzed by $AgB(C_6F_5)_4$ (0.1 or 0.2 equiv). [d]Catalyzed by Ph_3PAuCl (0.1 equiv) and AgOTf (0.2 equiv). [e]Catalyzed by Ph_3PAuCl (0.1 equiv) and $AgB(C_6F_5)_4$ (0.2 equiv). [f]Catalyzed by Ph_3PAuCl (0.1 equiv) and $AgB(C_6F_5)_4$ (0.1 equiv).

Scheme 2. Plausible Mechanism of *β*-Mannosylation Reaction with *ortho*-Hexynylbenzoate 2 as the Donor



Acremomannolipin A was isolated from *Acremonium strictum* and is a potential calcium signal modulator.[18] Very recently, Muraoka and co-workers accomplished the first total synthesis of acremomannolipin A adopting Crich's glycosylation[2] and evaluated the effect of configuration of glycosidic bond and alditols on its bioactivities.[19] Herein, we describe our synthesis of acremomannolipin A and its analogue using **6α** as a glycosyl donor (Scheme 3).

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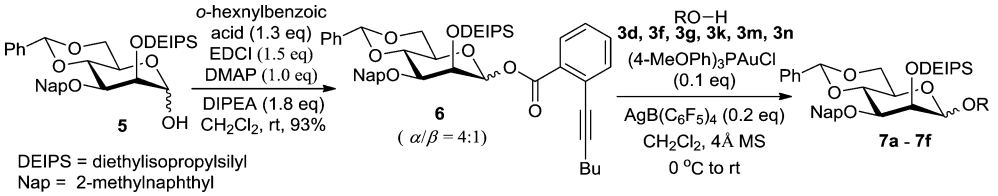
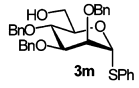
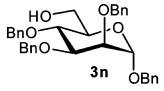
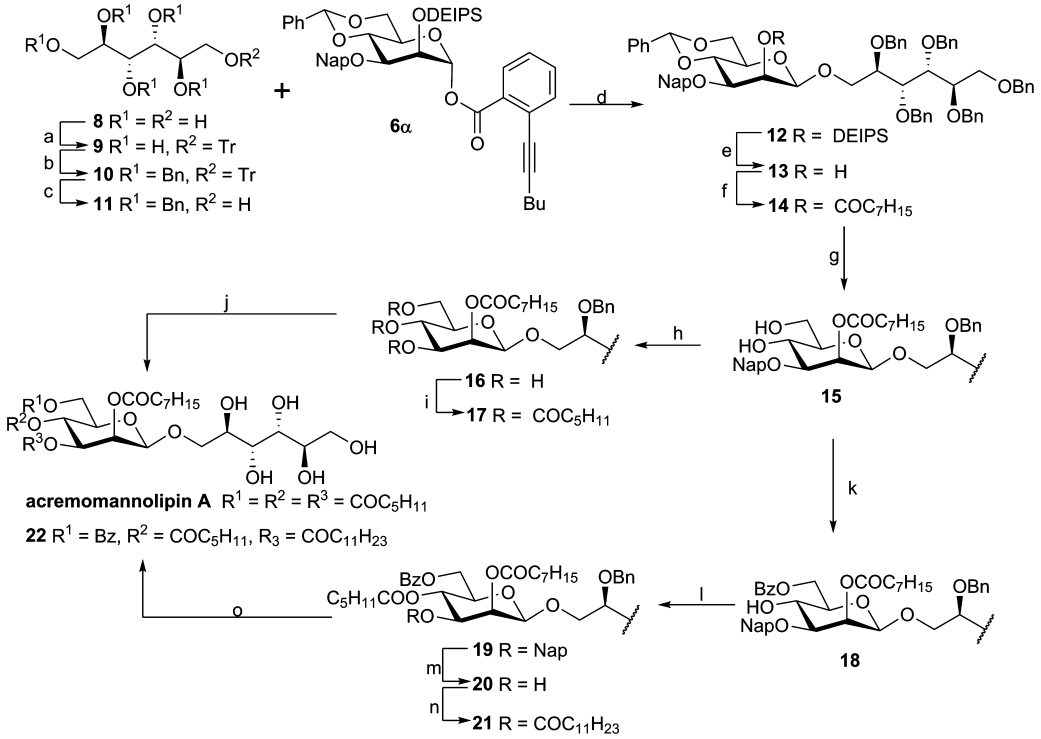
Table 2. Glycosylations of 6α with 3d, 3f, 3g, 3k, 3m, and 3n



Entry	Donor	Acceptor	Prod.	Yield[a]	β/α[b]
1	**6α**	**3k**	**7a**	93%	β only
2	**6α**	**3d**	**7b**	64%	8.6/1
3	**6α**	**3f**	**7c**	82%	1.6/1
4	**6α**	**3g**	**7d**	87%	20/1
5	**6α**	 **3m**	**7e**	77%	β only
6	**6α**	 **3n**	**7f**	86%	β only

[a]Isolated yields. [b]The ratios were determined by ^{1}H NMR spectroscopy of purified products by silica gel charomatography.

Scheme 3. Synthesis of Acremomannolipin A and Its Analogue (22)[a]



[a](a) TrCl, pyridine,75 °C for 12 h, then 45 °C for 24 h, then 25 °C for 36 h; (b) BnBr, NaH, DMF; (c) *p*-TsOH·H_2O, CH_2Cl_2/MeOH, 48% over three steps; (d) $(4\text{-MeOPh})_3PAuCl$, $AgB(C_6F_5)_4$, 4 Å MS, CH_2Cl_2, 85%, β/α = 13:1; (e) TBAF, THF, 25 °C, overnight, 93%; (f) *n*-$C_7H_{15}COOH$, CH_2Cl_2, DMAP, EDCI, DIPEA, overnight, 92%; (g) *p*-TsOH·H_2O, MeOH/CH_2Cl_2, 3 h, 95%; (h) DDQ, CH_2Cl_2/MeOH, 1 h, 57%; (i) CH_2Cl_2, pyridine, DMAP, *n*-$C_5H_{11}COCl$, 95%; (j) $Pd(OH)_2$/C, H_2, EtOH/MeOH, 48 h, 83%; (k) BzCl, collidine, CH_2Cl_2, 0 to 20 °C, 4 h, 83%; (l) CH_2Cl_2, pyridine, DMAP, $C_5H_{11}COCl$, 25 °C, overnight, 98%; (m) CAN, acetonitrile/H_2O (10/1), 30 °C, 5 h, 67%; (n) $C_{11}H_{23}COCl$, pyridine, CH_2Cl_2, DMAP, 15 °C, overnight, 92%; (o) $Pd(OH)_2$/C, H_2, MeOH/EtOH, 30 °C, 36 h, 88%.

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Our synthesis commenced with the preparation of the primary alcohol **11** in a three-step sequence composed of selective monotritylation of mannitol **8**, benzylation of **9**, and removal of the trityl group in **10**. Subjecting the benzoate **6α** and **11** to the optimal glycosylation conditions by stereocontrol led to β-mannoside **12** in 85% yield. Desilylation of **12** followed by acylation with octanoic acid furnished ester **14** in 86% yield over two steps. Removal of the benzylidene group in **14** with transacetalization followed by deprotection of 2-methylnaphthyl group (Nap) in **15** using 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) led to the formation of **16**. Condensation of **16** with *n*-hexanoyl chloride in pyridine installed three hexanoates simultaneously. Subsequent hydrogenolysis of benzyl ethers over $Pd(OH)_2/C$ gave acremomannolipin A in two steps in 79% yield. Thus, we accomplished the total synthesis of acremomannolipin A in 10 steps and a 15% overall yield with mannitol as starting material, and its ^1H and ^{13}C spectra as well as specific rotation were fully identical to those reported.[18,19a]

To demonstrate the versatility of our synthesis and facilitate investigation into structure−activity relationships, we intended to install different acyl groups onto the mannosyl unit of acremomannolipin A. Such compounds have not been documented in the literature.[19] Thus, selective benzoylation[20] of the primary 6′-OH in **15**, and hexanoylation of 4′-OH in **18** gave **19** in 81% yield in two steps. Attempting to cleave the naphthylmethyl group in **19** using DDQ led to a complicated reaction, and expected alcohol **20** was isolated in only 38% yield. However, to our delight, treatment of **19** with ceric ammonium nitrate (CAN) in acetonitrile led to **20** in 67% yield. Esterification of **20** with lauroyl chloride gave **21** in 50% yield over four steps. Final hydrogenolysis to remove the benzyl group furnished **22** in 88% yield.

In conclusion, a mild and convenient method for direct β-mannosylation of various alcohols based on gold(I)-catalyzed glycosylation with mannosyl *ortho*-hexynylbenzoates as donors has been developed. This reaction proceeded in high yield with satisfactory stereoselectivities, and its synthetic utility was demonstrated by the synthesis of acremomannolipin A and its analogue.

EXPERIMENTAL SECTION

General Information. All nonaqueous reactions were carried out under an atmosphere of argon in flame- or oven-dried glassware with magnetic stirring unless otherwise indicated. Dichloromethane for glycosylation reactions was distilled from calcium hydride. All other commercially obtained reagents were used as received, except where specified otherwise. Flash column chromatography was performed on Silica Gel H (300−400 mesh, Qingdao, China). Analytical thin layer chromatography was performed on Silicycle SiliaPlate glass-backed plates coated with silica gel (60 Å pore size, F-254 indicator) and visualized by exposure to ultraviolet light and/or staining with aqueous 5% sulfuric acid in methanol. Optical rotations were determined with a digital polarimeter. High-resolution mass spectral (HRMS) data were determined with a LTQ Orbitrap. ^1H and ^{13}C NMR spectra were recorded on a 500 or 600 MHz NMR spectrometer with Me_4Si as the internal standard. Chemical shifts are recorded in δ values and *J* values were given in Hz. Glycosyl acceptors **3c**, **3k**, and **3l** are commercially available. **3a**,[21] **3b**,[22] **3e**,[5] **3f**,[23] **3g**,[5] **3h**,[16a] **3i**,[24] **3j**,[24] **3m**,[25] **3n**,[26] and $Ag[B(C_6F_5)_4]$,[9a] $(p\text{-MeOPh})_3AuCl$,[27] and *ortho*-hexynylbenzoic acid[12b] were prepared according to the procedures in the corresponding literature.

4,6-O-Benzylidene-2,3-di-O-benzyl-1-(ortho-hexynyl-benzoate)-D-mannopyranoside (2). To a solution of hemiacetal **1**[7a] (1.9 g, 4.24 mmol, 1 equiv), *N*,*N*-diisopropylethylamine (DIPEA) (1.33 mL, 7.63 mmol, 1.8 equiv), *ortho*-hexynylbenzoic acid (1.11 g, 5.51 mmol, 1.3 equiv), and 4-dimethylaminopyridine (DMAP) (475 mg, 4.24 mmol, 1 equiv) in dry CH_2Cl_2 (20 mL) in the presence of 5 Å MS (500 mg) was added ethyldimethylaminopropylcarbodiimide (EDCI) (1.22 g, 6.35 mmol, 1.5 equiv). The resultant mixture was stirred at room temperature for 3 h, then diluted with CH_2Cl_2 and filtered through a pad of Celite. The filtrate was sequentially washed with saturated aqueous $NaHCO_3$ and brine. The collected organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 8:1) to afford **2α** (1.71 g, 2.70 mmol, 64%) and **2β** (0.49g, 0.77 mmol, 18%) as a colorless syrup, respectively. For **2α**: $[\alpha]_D^{26}$ = +45.9 (*c* 1.00, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.9 Hz, 1H), 7.56−7.41 (m, 6H), 7.39−7.25 (m, 12H), 6.43 (s, 1H), 5.68 (s, 1H), 4.86−4.80 (m, 3H), 4.64 (d, *J* = 12.0 Hz, 1H), 4.38 (t, *J* = 9.8 Hz, 1H), 4.31 (dd, *J* = 10.3, 4.8 Hz, 1H), 4.14 (dd, *J* = 10.1, 3.2 Hz, 1H), 4.12−4.07 (m, 1H), 3.95 (s, 1H), 3.89 (t, *J* = 10.3 Hz, 1H), 2.50−2.36 (m, 2H), 1.56−1.50 (m, 2H), 1.40−1.32 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.5, 138.4, 137.8, 137.6, 135.2, 132.4, 131.0, 130.3, 128.9, 128.6, 128.4, 128.3, 128.2, 128.0, 127.73, 127.72, 127.4, 126.1, 125.1, 101.5, 97.1, 93.5 ($^1J_{C-H}$ = 175.7 Hz, α-Man), 79.9, 78.7, 75.8, 75.5, 73.6, 73.2, 68.7, 66.9, 30.9, 22.1, 19.8, 13.8; MS-ESI *m/z*: 633.4 $[M + H]^+$, 655.4 $[M + Na]^+$, 671.3 $[M + K]^+$; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{40}H_{41}O_7$: 633.2847, Found: 633.2834. For **2β**: $[\alpha]_D^{26}$ = −25.0 (*c* 0.93, $CHCl_3$); ^1H NMR (500 MHz, CDCl3) δ 7.92 (d, *J* = 7.9 Hz, 1H), 7.56−7.45 (m, 4H), 7.43−7.22 (m, 14H), 5.93 (s, 1H), 5.66 (s, 1H), 4.96−4.89 (m, 2H), 4.82 (d, *J* = 12.3 Hz, 1H), 4.69 (d, *J* = 12.3 Hz, 1H), 4.36 (dd, *J* = 10.4, 4.9 Hz, 1H), 4.31 (t, *J* = 9.6 Hz, 1H), 4.12 (d, *J* = 2.1 Hz, 1H), 3.94 (t, *J* = 10.3 Hz, 1H), 3.80 (dd, *J* = 9.8, 2.9 Hz, 1H), 3.58−3.54 (m, 1H), 2.47 (t, *J* = 7.2 Hz, 2H), 1.65−1.58 (m, 2H), 1.51−1.45 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.7, 138.2, 138.1, 137.5, 134.7, 132.4, 130.7, 130.1, 129.1, 128.6, 128.5, 128.4, 128.3, 127.9, 127.8, 127.2, 126.2, 125.8, 101.7, 97.3, 94.0 ($^1J_{C-H}$ = 157.4 Hz, β-Man), 79.1, 78.5, 78.3, 75.9, 75.3, 73.0, 68.5, 68.4, 30.8, 22.2, 19.7, 13.8; MS-ESI *m/z*: 633.4 $[M + H]^+$, 655.4 $[M + Na]^+$, 671.4 $[M + K]^+$; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{40}H_{40}O_7Na$: 655.2666, Found: 655.2659.

Phenyl 2,6-Di-O-benzyl-3-O-(2-methylnaphthyl)-1-thio-α-D-mannopyranoside (3d). To a solution of phenyl 4,6-*O*-benzylidene-3-*O*-(2-methylnaphthyl)-2-*O*-benzyl-thio-α-D-mannopyranoside[28] (370 mg, 0.63 mmol, 1 equiv) and Et_3SiH (1.0 mL, 6.3 mmol, 10 equiv) in CH_2Cl_2 (4 mL) was dropwise added $BF_3{\cdot}OEt_2$ (0.16 mL, 1.25 mmol, 2 equiv) at 0 °C. The mixture was stirred for 1 h at 0 °C. The mixture was sequentially washed with saturated aqueous $NaHCO_3$ and brine. The collected organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated. The residual was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 6:1) to afford **3d** (315 mg, 0.53 mmol, 85%) as a colorless syrup. $[\alpha]_D^{26}$ = +15.3 (*c* 0.45, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.90−7.84 (m, 3H), 7.82 (s, 1H), 7.55−7.51 (m, 2H), 7.49 (dd, *J* = 4.5, 3.3 Hz, 3H), 7.38−7.33 (m, 6H), 7.32−7.29 (m, 4H), 7.28−7.25 (m, 3H), 5.66 (s, 1H), 4.78−4.70 (m, 3H), 4.72 (d, *J* = 11.9 Hz, 1H), 4.65 (d, *J* = 11.9 Hz, 1H), 4.58−4.56 (m, 2H), 4.35−4.31 (m, 1H), 4.21 (td, *J* = 9.5, 1.4 Hz, 1H), 4.09−4.06 (m, 1H), 3.89−3.84 (m, 2H), 3.80 (dd, *J* = 9.4, 3.0 Hz, 1H), 2.66 (d, *J* = 1.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.3, 137.8, 135.3, 134.2, 133.3, 133.1, 131.7, 129.1, 128.5, 128.4, 128.3, 127.9, 127.8, 127.8, 127.6, 127.5, 126.7, 126.3, 126.1, 125.8, 85.8, 79.7, 75.6, 73.4, 72.4, 71.94, 71.87, 70.1, 67.8; MS-ESI *m/z*: 615.2 $[M + Na]^+$; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{37}H_{37}O_5S$: 593.2356, Found: 593.2368.

General Procedure for Glycosylation. Glycosyl acceptor (0.10 mmol, 1.0 equiv) and *ortho*-hexynylbenzoate glycosyl donor (0.13 mmol, 1.3 equiv) were dissolved in anhydrous CH_2Cl_2 (2 mL); the mixture was stirred in the presence of flame activated 4 Å molecular sieves (200 mg) for 15 min at room temperature. The mixture was cooled to 0 °C, then $AgB(C_6F_5)_4$ (10 μmol, 0.1 equiv) was added in the dark under an atmosphere of argon. After stirring at 0 °C for 30 min, $AgB(C_6F_5)_4$ (10 μmol, 0.1 equiv) and $(4\text{-MeOPh})_3PAuCl$ (10 μmol, 0.1 equiv) was added sequentially. The resulting mixture was allowed to warm naturally up to room terperature. After complete consumption of starting material as assessed by TLC, the reaction was quenched with a few drops of triethylamine, then filtered through a pad of Celite.

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The filtrates were concentrated and the residue was purified by silica gel column chromatography to afford glycosylation product. In our cases, the desired glycoside could be readily isolated from the reaction mixture.

*p-Tolyl 2,3-Di-O-benzyl-4,6-O-benzylidene-β-D-mannopyranosyl-(1 → 4)-2,3-O-isopropylidene-1-thio-α-L-rhamnopyranoside (**4a**).* Compound **4a** was obtained in 76% yield (56 mg, β only) as a syrup by purification with silica gel column chromatography (petroleum ether/ethyl acetate 10:1) according to the general procedure. $[\alpha]_D^{20} = -114.9$ (*c* 5.20, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.50 (d, *J* = 6.6 Hz, 2H), 7.46 (d, *J* = 7.7 Hz, 2H), 7.40−7.29 (m, 13H), 7.13 (d, *J* = 7.7 Hz, 2H), 5.66 (s, 1H), 5.62 (s, 1H), 5.00 (s, 1H), 4.94 (d, *J* = 12.1 Hz, 1H), 4.83 (d, *J* = 12.1 Hz, 1H), 4.71 (d, *J* = 12.1 Hz, 1H), 4.61 (d, *J* = 12.1 Hz, 1H), 4.31 (d, *J* = 5.5 Hz, 1H), 4.26−4.24 (m, 1H), 4.20 (t, *J* = 9.9 Hz, 1H), 4.15−4.12 (m, 2H), 3.98 (d, *J* = 3.3 Hz, 1H), 3.97 (t, *J* = 9.9 Hz, 1H), 3.74 (dd, *J* = 9.9, 7.7 Hz, 1H), 3.65 (dd, *J* = 9.9, 3.2 Hz, 1H), 3.33−3.30 (m, 1H), 2.34 (s, 3H), 1.49 (s, 3H), 1.33 (s, 3H), 1.27 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.6, 138.4, 138.0, 137.6, 134.2, 134.1, 132.6, 132.0, 129.9, 129.5, 129.3, 129.2, 128.9, 128.5, 128.4, 128.20, 128.17, 127.60, 127.58, 127.5, 126.1, 109.6, 101.4, 100.0 ($^1J_{C-H}$ = 158.8 Hz, β-Man), 84.1($^1J_{C-H}$ = 168.8 Hz, α-Rha), 78.7, 78.1, 78.03, 77.96, 76.8, 76.4, 75.0, 72.2, 68.6, 67.7, 65.8, 27.9, 26.6, 21.2, 17.6; MS-ESI *m/z:* 763.4 $[M + Na]^+$; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{43}H_{49}O_9S$: 741.3092, Found: 741.3101.

*Methyl 2,3-Di-O-benzyl-4,6-O-benzylidene-β-D-mannopyranosyl-(1 → 3)-2-O-benzoyl-4,6-O-benzylidene-α-D-glucopyranoside (**4b**).* Compound **4b** was obtained in 88% yield (72 mg, β only) as a syrup by purification with silica gel column chromatography (petroleum ether/ethyl acetate 8:1) according to the general procedure. $[\alpha]_D^{20} = +11.9$ (*c* 7.78, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.1 Hz, 2H), 7.59 (t, *J* = 7.7 Hz, 1H), 7.53 (d, *J* = 7.1 Hz, 2H), 7.50−7.40 (m, 4H), 7.38−7.29 (m, 6H), 7.22−7.09 (m, 10H), 5.59 (s, 1H), 5.51 (s, 1H), 5.14 (dd, *J* = 9.4, 3.8 Hz, 1H), 5.07 (d, *J* = 3.8 Hz, 1H), 4.72 (d, *J* = 12.1 Hz, 1H), 4.69 (s, 1H), 4.53 (d, *J* = 12.1 Hz, 1H), 4.37 (t, *J* = 9.4 Hz, 1H), 4.33 (t, *J* = 5.5 Hz, 1H), 4.31 (d, *J* = 12.7 Hz, 1H), 4.25 (d, *J* = 12.1 Hz, 1H), 4.17 (dd, *J* = 10.4, 5.0 Hz, 1H), 4.09 (t, *J* = 9.3 Hz, 1H), 3.95−3.91 (m, 1H), 3.83 (t, *J* = 9.8 Hz, 2H), 3.76 (t, *J* = 9.4 Hz, 1H), 3.68 (d, *J* = 2.8 Hz, 1H), 3.39 (s, 3H), 3.38 (d, *J* = 3.2 Hz, 1H), 3.26−3.22 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.5, 138.3, 138.1, 137.5, 137.2, 133.7, 129.7, 129.3, 129.0, 128.8, 128.7, 128.19, 128.15, 128.11, 127.9, 127.4, 127.3, 126.1, 126.0, 103.4 ($^1J_{C-H}$ = 156.3 Hz, β-Man), 101.3, 101.2, 97.7 ($^1J_{C-H}$ = 176.2 Hz, α-Glu), 79.9, 78.2, 78.1, 77.9, 76.4, 74.9, 73.6, 71.6, 68.8, 68.6, 67.5, 62.7, 55.4; MS-ESI *m/z:* 839.4 $[M + Na]^+$; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{48}H_{48}O_{12}Na$: 839.3038, Found: 839.3067.

*Cyclohexyl 2,3-Di-O-benzyl-4,6-O-benzylidene-β-D-mannopyranoside (**4c**).*[6b] Compound **4c** was obtained in 88% yield (47 mg, β only) as a syrup by purification with silica gel column chromatography (petroleum ether/ethyl acetate 15:1) according to the general procedure. $[\alpha]_D^{24} = -57.2$ (*c* 0.96, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.52−7.48 (m, 4H), 7.40−7.27 (m, 11H), 5.62 (s, 1H), 5.02 (d, *J* = 12.5 Hz, 1H), 4.91 (d, *J* = 12.5 Hz, 1H), 4.66 (d, *J* = 12.5 Hz, 1H), 4.59 (d, *J* = 12.5 Hz, 1H), 4.58 (s, 1H), 4.30 (dd, *J* = 10.4, 4.9 Hz, 1H), 4.22 (t, *J* = 9.6 Hz, 1H), 3.95 (t, *J* = 10.3 Hz, 1H), 3.88 (d, *J* = 3.1 Hz, 1H), 3.74−3.66 (m, 1H), 3.58 (dd, *J* = 9.9, 3.2 Hz, 1H), 3.34−3.30 (m, 1H), 1.96−1.90 (m, 1H), 1.83−1.68 (m, 3H), 1.54−1.50 (m, 2H), 1.33−1.28 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.6, 138.5, 137.7, 128.9, 128.8, 128.3, 128.2, 128.1, 127.6, 127.5, 126.1, 101.4, 100.0 ($^1J_{C-H}$ = 153.9 Hz, β-Man), 78.7, 78.2, 76.8, 76.2, 74.6, 72.3, 68.7, 67.6, 33.4, 31.5, 25.7, 23.8, 23.7; MS-ESI *m/z:* 553.1 $[M + Na]^+$; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{33}H_{38}O_6Na$: 553.2561, Found: 553.2561.

*Phenyl 2,3-Di-O-benzyl-4,6-O-benzylidene-β-D-mannopyranosyl-(1 → 4)-2,6-di-O-benzyl-3-O-(2-methylnaphthyl)-1-thio-α-D-mannopyranoside (**4d**).* Compound **4d** was obtained in 82% yield (84 mg, β only) as a syrup by purification with silica gel column chromatography (petroleum ether/ethyl acetate 6:1) according to the general procedure. $[\alpha]_D^{24} = 22.9$ (*c* 1.01, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.85−7.75 (m, 4H), 7.48−7.20 (m, 33H), 5.58 (d, *J* = 2.2 Hz, 1H), 5.47 (s, 1H), 4.96 (d, *J* = 12.1 Hz, 1H), 4.83−4.78 (m, 2H), 4.74−4.66 (m, 3H), 4.65−4.62 (m, 2H), 4.58−4.52 (m, 2H), 4.36 (d, *J* = 11.9 Hz, 1H), 4.31 (t, *J* = 8.8 Hz, 1H), 4.22−4.18 (m, 1H), 4.10−4.05 (m, 2H), 3.96 (s, 1H), 3.92 (dd, *J* = 8.2, 2.8 Hz, 1H), 3.73 (d, *J* = 2.6 Hz, 1H), 3.68 (dd, *J* = 11.0, 4.2 Hz, 1H), 3.65−3.61 (m, 2H), 3.38 (dd, *J* = 9.8, 2.8 Hz, 1H), 3.07−3.02 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.7, 138.6, 138.2, 138.0, 137.7, 136.3, 134.5, 133.3, 133.0, 131.4, 129.1, 128.9, 128.44, 128.40, 128.38, 128.36, 128.20, 128.18, 128.1, 1278.0, 127.91, 127.88, 127.81, 127.79, 127.7, 127.61, 127.58, 127.5, 127.4, 126.21, 126.17, 125.9, 125.8, 101.9 ($^1J_{C-H}$ = 157.4 Hz, β-Man), 101.4, 85.9 ($^1J_{C-H}$ = 167.6 Hz, α-Man), 78.7, 78.5, 77.8, 77.1, 76.0, 75.1, 73.4, 72.8, 72.6, 72.3, 69.1, 68.6, 67.4; MS-ESI *m/z:* 1045.6 $[M + Na]^+$; HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{64}H_{62}O_{10}NaS$: 1045.3956, Found:1045.3992.

*Methyl 2,3-Di-O-benzyl-4,6-O-benzylidene-D-mannopyranosyl-(1 → 4)-2,3,6-tri-O-benzyl-α-D-glucopyranoside (**4e**).*[5] Compound **4e** was obtained in 81% yield (72 mg, β only) as a syrup by purification with silica gel column chromatography (petroleum ether/ethyl acetate 10:1) according to the general procedure. $[\alpha]_D^{24} = -21.2$ (*c* 1.06, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.49−7.47 (m, 2H), 7.41−7.20 (m, 28H), 5.52 (s, 1H), 5.05 (d, *J* = 10.6 Hz, 1H), 4.84−4.78 (m, 3H), 4.76−4.73 (m, 2H), 4.64 (d, *J* = 12.4 Hz, 2H), 4.60−4.57 (m, 2H), 4.36 (s, 1H), 4.28 (d, *J* = 12.1 Hz, 1H), 4.10−4.02 (m, 2H), 3.91−3.83 (m, 2H), 3.63 (d, *J* = 2.7 Hz, 1H), 3.61−3.59 (m, 1H), 3.55−3.50 (m, 3H), 3.46 (dd, *J* = 10.9, 3.0 Hz, 1H), 3.41 (s, 3H), 3.32 (dd, *J* = 9.9, 3.1 Hz, 1H), 3.07−3.03 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.5, 138.7, 138.6, 138.4, 137.7, 137.6, 128.9, 128.6, 128.48, 128.47, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.63, 127.57, 127.4, 127.3, 126.2, 101.6 ($^1J_{C-H}$ = 156.8 Hz, β-Man), 101.4, 98.5 ($^1J_{C-H}$ = 171.0 Hz, α-Glu), 80.4, 79.1, 78.8, 78.4, 77.8, 77.1, 75.4, 75.1, 73.73, 73.66, 72.6, 69.7, 68.7, 68.4, 67.3, 55.5; MS-ESI *m/z:* 917.1 $[M + Na]^+$; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{55}H_{58}O_{11}Na$: 917.3871, Found: 917.3893.

*Methyl 2,3-Di-O-benzyl-4,6-O-benzylidene-D-mannopyranosyl-(1 → 4)-2,3-di-O-benzoyl-6-O-benzyl-α-D-glucopyranoside (**4f**).* Compound **4f** was obtained in 78% yield (72 mg, β/α = 5.6/1) as a syrup by purification with silica gel column chromatography (petroleum ether/ethyl acetate 6:1) according to the general procedure. For **4α**: $[\alpha]_D^{24} = 29.8$ (*c* 0.45, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 8.01−7.96 (d, *J* = 7.9 Hz, 2H), 7.95 (d, *J* = 7.7 Hz, 2H), 7.50−7.15 (m, 24H), 6.97 (d, *J* = 6.3 Hz, 2H), 6.03 (t, *J* = 9.1 Hz, 1H), 5.58 (s, 1H), 5.18−5.11 (m, 3H), 4.68 (d, *J* = 12.5 Hz, 2H), 4.61 (d, *J* = 11.9 Hz, 1H), 4.48 (d, *J* = 12.1 Hz, 1H), 4.27 (d, *J* = 11.6 Hz, 1H), 4.21 (t, *J* = 9.5 Hz, 1H), 4.18−4.11 (m, 2H), 3.97−3.92 (m, 2H), 3.90−3.83 (m, 3H), 3.81−3.75 (m, 2H), 3.66 (s, 1H), 3.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.0, 165.7, 138.7, 138.0, 137.9, 137.7, 133.7, 133.4, 130.0, 129.9, 129.4, 129.2, 128.94, 128.85, 128.6, 128.5, 128.4, 128.3, 128.2, 127.9, 127.8, 127.7, 127.6, 127.5, 126.2, 101.6 ($^1J_{C-H}$ = 165.5 Hz, α-Man), 101.1, 97.0 ($^1J_{C-H}$ = 177.3 Hz, α-Glu), 78.8, 77.4, 76.3, 75.7, 73.9, 73.6, 73.1, 72.7, 72.2, 69.8, 68.72, 68.68, 65.5, 55.6; MS-ESI *m/z:* 923.5 $[M + H]^+$; 945.5 $[M + Na]^+$; HRMS (ESI) *m/z*: $[M + NH_4]^+$ Calcd for $C_{55}H_{58}O_{13}N$: 940.3903, Found: 940.3906. For **4β**: $[\alpha]_D^{20} = +23.6$ (*c* 2.94, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.99−7.96 (m, 4H), 7.52−7.48 (m, 2H), 7.45−7.20 (m, 24H), 5.95 (t, *J* = 9.4 Hz, 1H), 5.32 (s, 1H), 5.19−5.16 (m, 2H), 4.83 (d, *J* = 12.1 Hz, 1H), 4.70−4.68 (m, 3H), 4.54 (d, *J* = 12.1 Hz, 1H), 4.39 (d, *J* = 12.1 Hz, 1H), 4.29 (s, 1H), 4.11 (t, *J* = 9.9 Hz, 1H), 3.86−3.82 (m, 2H), 3.62−3.54 (m, 4H), 3.43 (s, 3H), 3.30 (dd, *J* = 9.9, 3.3 Hz, 1H), 2.99 (t, *J* = 9.9 Hz, 1H), 2.98−2.94 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.0, 165.4, 138.7, 138.6, 137.54, 137.45, 133.3, 132.8, 130.5, 129.9, 129.7, 129.2, 128.8, 128.6, 128.5, 128.4, 128.3, 128.17, 128.15, 128.0, 127.5, 127.4, 127.3, 126.0, 102.0 ($^1J_{C-H}$ = 154.6 Hz, β-Man), 101.1, 97.1 ($^1J_{C-H}$ = 174.0 Hz, α-Glu), 78.3, 77.9, 76.3, 76.1, 74.6, 73.7, 72.3, 72.1, 70.7, 69.6, 68.0, 67.9, 67.2, 55.5; MS-ESI *m/z:* 945.2 $[M + Na]^+$; HRMS (ESI) *m/z*: $[M + NH_4]^+$ Calcd for $C_{55}H_{58}O_{13}N$: 940.3903, Found: 940.3940.

*2,3-Di-O-benzyl-4,6-O-benzylidene-β-D-mannopyranosyl-(1 → 6)-1,2:3,4-di-O-isopropylidene-α-D-galactopyranoside (**4g**).*[5] Compound **4g** was obtained in 64% yield (44 mg, β/α = 10/1) as a syrup by purification with silica gel column chromatography (petroleum ether/ethyl acetate 7:1) according to the general procedure. $[\alpha]_D^{24} = -96.2$ (*c* 1.17, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.52−7.49 (m, 4H), 7.41−7.22 (m, 11H), 5.62 (s, 1H), 5.60 (d, *J* = 5.0 Hz, 1H), 5.03 (d, *J* = 12.2 Hz, 1H), 4.92 (d, *J* = 12.3 Hz, 1H), 4.63 (dd, *J* = 7.9, 2.5 Hz, 1H), 4.60−4.52 (m, 3H), 4.35 (dd, *J* = 5.0, 2.5 Hz, 1H), 4.30 (dd, *J* = 10.4,

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4.9 Hz, 1H), 4.23 (dd, J = 7.9, 1.9 Hz, 1H), 4.20−4.17 (m, 2H), 4.12−4.00 (m, 1H), 4.03 (d, J = 3.0 Hz, 1H), 3.94 (t, J = 10.3 Hz, 1H), 3.64 (dd, J = 10.8, 8.4 Hz,1H), 3.55 (dd, J = 10.0, 3.2 Hz, 1H), 3.34−3.30 (m, 1H), 1.51 (s, 3H), 1.46 (s, 3H), 1.35 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.4, 138.3, 137.7, 128.9, 128.4, 128.29, 128.26, 127.6, 126.1, 109.6, 108.9, 103.0 ($^1J_{C-H}$ = 157.9 Hz, β-Man), 101.5, 96.5 ($^1J_{C-H}$ = 175.8 Hz, α-Gal), 78.6, 77.5, 74.9, 74.6, 72.2, 71.7, 70.9, 70.5, 70.2, 68.7, 68.1, 67.6, 26.2, 26.1, 25.2, 24.5; MS-ESI m/z: 713.3 $[M + Na]^+$; HRMS (ESI) m/z: $[M + NH_4]^+$ Calcd for $C_{39}H_{50}O_{11}N$: 708.3378, Found: 708.3398.

*Phenyl 2,3-Di-O-benzyl-4,6-O-benzylidene-β-D-mannopyranosyl-(1 → 2)-3-O-(2-methylnaphthyl)-4,6-O-benzylidene-1-thio-α-D-mannopyranoside (**4h**).* Compound **4h** was obtained in 78% yield (73 mg, β only) as a syrup by purification with silica gel column chromatography (petroleum ether/ethyl acetate 12:1) according to the general procedure. $[\alpha]_D^{20}$ = −2.8 (c 1.83, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (brs, 1H), 7.85−7.82 (m, 1H), 7.80 (d, J = 8.2 Hz, 1H), 7.75−7.73 (m, 1H), 7.66−7.20 (m, 28H), 5.57 (s, 1H), 5.55(s, 1H), 5.52 (s, 1H), 5.08 (d, J = 12.7 Hz, 1H), 5.01 (d, J = 12.1 Hz, 1H), 4.98 (d, J = 12.7 Hz, 1H), 4.88 (d, J = 12.7 Hz, 1H), 4.69 (d, J = 12.7 Hz, 1H), 4.66 (s, 1H), 4.65 (d, J = 12.1 Hz, 1H), 4.57 (d, J = 1.7 Hz, 1H), 4.35−4.32 (m, 1H), 4.30−4.20 (m, 4H), 4.06 (dd, J = 9.9, 2.8 Hz, 1H), 4.01 (d, J = 2.8 Hz, 1H), 3.84−3.80 (m, 2H), 3.61 (dd, J = 9.8, 2.7 Hz, 1H), 3.35−3.32 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.5, 138.3, 137.49, 137.45, 135.9, 133.6, 133.3, 133.0, 131.9, 129.3, 129.0, 128.9, 128.6, 128.4, 128.3, 128.2, 128.0, 127.9, 127.7, 127.60, 127.56, 126.4, 126.2, 126.1, 126.0, 125.9, 125.7, 101.8, 101.4, 99.7 ($^1J_{C-H}$ = 151.8 Hz, β-Man), 86.3 ($^1J_{C-H}$ = 167.0 Hz, α-Man), 78.6, 78.4, 77.5, 76.0, 75.8, 74.7, 74.3, 72.2, 71.3, 68.6, 68.5, 67.8, 65.5; MS-ESI m/z: 953.5 $[M + Na]^+$; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{57}H_{55}O_{10}S$: 931.3510, Found: 931.3531.

*Benzyl 3-O-(2,3-Di-O-benzyl-4,6-O-benzylidene-β-D-mannopyranosyl)-glycyrrhetinate (**4i**).* Compound **4i** was obtained in 93% yield (92 mg, β only) as a foam by purification with silica gel column chromatography (petroleum ether/ethyl acetate 15:1) according to the general procedure. $[\alpha]_D^{20}$ = +25.3 (c 2.24, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52−7.46 (m, 4H), 7.40−7.28 (m, 16H), 5.61 (s, 1H), 5.55 (s, 1H), 5.20 (d, J = 12.2 Hz, 1H), 5.09 (d, J = 12.2 Hz, 1H), 5.03 (d, J = 12.4 Hz, 1H), 4.86 (d, J = 12.5 Hz, 1H), 4.65 (d, J = 12.5 Hz, 1H), 4.56 (d, J = 12.5 Hz, 1H), 4.50 (s, 1H), 4.28 (dd, J = 10.2, 4.3 Hz, 1H), 4.21 (t, J = 9.4 Hz, 1H), 3.99−3.91 (m, 2H), 3.58 (d, J = 9.6 Hz, 1H), 3.34−3.28 (m, 1H), 3.12 (t, J = 8.0 Hz, 1H), 2.79 (d, J = 13.3 Hz, 1H), 2.30 (s, 1H), 1.33 (s, 3H), 1.15 (s, 6H), 1.11 (s, 3H), 0.96 (s, 3H), 0.90 (s, 3H), 0.73 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.0, 176.2, 168.9, 138.6, 138.4, 137.6, 136.1, 128.8, 128.6, 128.5, 128.32, 128.26, 128.2, 128.1, 127.5, 126.0, 104.9 ($^1J_{C-H}$ = 155.6 Hz, β-Man), 101.3, 90.7, 78.5, 78.2, 76.2, 74.7, 72.2, 68.7, 67.6, 66.2, 61.8, 55.2, 48.2, 45.3, 44.0, 43.1, 41.0, 39.3, 39.2, 37.6, 36.8, 32.7, 31.8, 31.2, 28.44, 28.41, 28.3, 26.5, 26.4, 25.9, 23.3, 18.7, 17.5, 16.7, 16.4; MS-ESI m/z: 991.7 $[M + H]^+$; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{64}H_{78}O_9Na$: 1013.5538, Found: 1013.5540.

*Benzyl 3-O-(2,3-Di-O-benzyl-4,6-O-benzylidene-β-D-mannopyranosyl)-oleanate (**4j**).* Compound **4j** was obtained in 98% yield (95 mg, β only) as a foam by purification with silica gel column chromatography (petroleum ether/ethyl acetate 20:1) according to the general procedure. $[\alpha]_D^{20}$ = −9.27 (c 2.06, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51−7.46 (m, 4H), 7.38−7.26 (m, 16H), 5.60 (s, 1H), 5.28 (t, J = 3.3 Hz, 1H), 5.08 (d, J = 12.6 Hz, 1H), 5.04 (d, J = 12.7 Hz, 1H), 5.02 (d, J = 12.7 Hz, 1H), 4.83 (d, J = 12.1 Hz, 1H), 4.63 (d, J = 12.7 Hz, 1H), 4.56 (d, J = 12.7 Hz, 1H), 4.49 (s, 1H), 4.26 (dd, J = 10.5, 5.0 Hz, 1H), 4.20 (t, J = 9.9 Hz, 1H), 3.97 (d, J = 2.8 Hz, 1H), 3.93 (t, J = 10.4 Hz, 1H), 3.58 (dd, J = 9.9, 3.3 Hz, 1H), 3.33−3.30 (m, 1H), 3.10 (dd, J = 11.6, 4.4 Hz, 1H), 2.89 (dd, J = 13.2, 3.8 Hz, 1H), 1.11 (s, 3H), 0.94 (s, 3H), 0.91 (s, 3H), 0.90 (s, 3H), 0.89 (s, 3H), 0.87 (s, 3H), 0.60 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 177.4, 143.6, 138.6, 138.4, 137.6, 136.4, 128.8, 128.5, 128.4, 128.3, 128.18, 128.15, 128.0, 127.9, 127.5, 126.1, 122.6, 110.0, 105.0 ($^1J_{C-H}$ = 154.2 Hz, β-Man), 101.3, 91.0, 78.5, 78.2, 76.1, 74.7, 72.2, 68.7, 67.5, 65.9, 55.5, 47.6, 46.7, 45.9, 41.6, 41.4, 39.3, 39.0, 38.5, 36.7, 33.9, 33.1, 32.7, 32.4, 30.7, 29.7, 28.5, 27.6, 25.9, 23.7, 23.4, 23.0, 18.3, 16.9, 16.7, 15.4; MS-ESI m/z: 999.6 $[M + Na]^+$; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{64}H_{80}O_8Na$:999.5745, Found: 999.5735.

*Diosgenyl 2,3-Di-O-benzyl-4,6-O-benzylidene-β-D-mannopyranoside (**4k**).* Compound **4k** was obtained in 86% yield (73 mg, β only) as a foam by purification with silica gel column chromatography (petroleum ether/ethyl acetate 18:1) according to the general procedure. $[\alpha]_D^{18}$ = −69.4 (c 1.58, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52−7.48 (m, 4H), 7.39−7.27 (m, 11H), 5.61 (s, 1H), 5.33 (m, 1H), 4.98 (d, J = 12.6 Hz, 1H), 4.88 (d, J = 12.7 Hz, 1H), 4.68 (d, J = 12.7 Hz, 1H), 4.58 (d, J = 11.0 Hz, 2H), 4.41 (q, J = 7.7 Hz, 1H), 4.29 (dd, J = 10.4, 4.9 Hz, 1H), 4.20 (t, J = 9.4 Hz, 1H), 3.93 (t, J = 10.4 Hz, 1H), 3.86 (d, J = 2.8 Hz, 1H), 3.58 (dd, J = 9.9, 3.3 Hz, 1H), 3.56−3.52 (m, 1H), 3.48−3.42 (m, 1H), 3.37 (t, J = 11.0 Hz, 1H), 3.33−3.29 (m, 1H), 2.30 (m, 1H), 2.20 (m, 1H), 1.04 (s, 3H), 0.97 (d, J = 7.1 Hz, 3H), 0.78 (d, 5.5 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 140.5, 138.5, 138.4, 137.6, 128.8, 128.3, 128.2, 128.1, 127.5, 126.0, 121.7, 109.3, 101.4, 100.0 ($^1J_{C-H}$ = 153.9 Hz, β-Man), 80.8, 78.6, 78.0, 76.1, 74.7, 72.3, 68.7, 67.5, 66.8, 62.1, 56.5, 50.1, 41.6, 40.3, 39.8, 38.8, 37.2, 36.9, 32.1, 31.9, 31.41, 31.38, 30.3, 29.7, 29.6, 28.80, 20.83, 19.4, 17.2, 16.3, 14.6; MS-ESI m/z: 867.5 $[M + Na]^+$; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{54}H_{68}O_8Na$: 867.4806, Found: 867.4794.

*Cholesteryl 2,3-Di-O-benzyl-4,6-O-benzylidene-β-D-mannopyranoside (**4l**).*[6a] Compound **4l** was obtained in 93% yield (76 mg, β/α = 11.4/1) as a foam by purification with silica gel column chromatography (petroleum ether/ethyl acetate 20:1) according to the general procedure. $[\alpha]_D^{24}$ = −43.1 (c 1.08, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52−7.48 (m, 4H), 7.41−7.26 (m, 11H), 5.62 (s, 1H), 5.35 (d, J = 4.6 Hz, 1H), 5.00 (d, J = 12.4 Hz, 1H), 4.91 (d, J = 12.4 Hz, 1H), 4.68 (d, J = 12.5 Hz, 1H), 4.60 (d, J = 11.6 Hz, 2H), 4.29 (dd, J = 10.4, 4.8 Hz, 1H), 4.21 (t, J = 9.5 Hz, 1H), 3.94 (t, J = 10.3 Hz, 1H), 3.88 (d, J = 2.8 Hz, 1H), 3.65−3.51 (m, 2H), 3.34−3.30 (m, 1H), 2.33−2.27 (m, 1H), 2.24−2.19 (m, 1H), 2.05−1.93 (m, 3H), 1.89−1.81 (m, 2H), 0.92 (d, J = 6.4 Hz, 3H), 0.87 (d, J = 2.4 Hz, 3H), 0.86 (d, J = 2.4 Hz, 3H), 0.69 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 140.5, 138.6, 138.5, 137.7, 128.9, 128.4, 128.2, 128.1, 127.58, 127.56, 126.1, 122.1, 101.4, 100.1 ($^1J_{C-H}$ = 153.9 Hz, β-Man), 78.71, 78.69, 78.1, 76.2, 74.7, 72.4, 68.8, 67.6, 56.8, 56.2, 50.2, 42.4, 39.8, 39.6, 38.9, 37.3, 36.8, 36.3, 35.9, 32.0, 31.9, 29.7, 28.3, 28.1, 24.4, 23.9, 22.9, 22.7, 21.1, 19.5, 18.8, 12.0; MS-ESI m/z: 839.5 $[M + Na]^+$; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{54}H_{72}O_6Na$: 839.5221, Found: 839.5225.

*4,6-O-Benzylidene-2-O-(diethylisopropylsilyl)-3-O-(2-methylnaphthyl)-D-mannopyranose (**5**).* Phenyl 4,6-benzylidene-2-*O*-(diethylisopropylsilyl)-3-*O*-(2-methylnaphthyl)-1-thio-α-D-mannopyranoside[16a] (1.31 g, 2.09 mmol, 1 equiv) was dissolved in acetone (15 mL). Then, H_2O (0.75 mL, 20 mmol, 10 equiv), pyridine (504 μL, 6.26 mmol, 3 equiv), and NBS (2.6 g, 14.60 mmol, 7 equiv) were added at 0 °C. After the resulting mixture was stirred at 0 °C for 3 h and TLC monitoring showed complete consumption of starting material, the reaction was quenched with saturated aqueous $Na_2S_2O_3$ and washed with saturated aqueous $NaHCO_3$ and brine. The collected organic phase was dried over Na_2SO_4, filtered, and concentrated in vacuum. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 12:1 to 8:1) to provide lactol **5** (927 mg, 1.77 mmol, 85%) as a colorless syrup, which was directly took up next step. MS-ESI m/z: 537.1 $[M + H]^+$, 559.1 $[M + Na]^+$, 575.1 $[M + K]^+$.

*4,6-O-Benzylidene-2-O-(diethylisopropylsilyl)-3-O-(2-methylnaphthyl)-1-(ortho-hexynylbenzoate)-D-mannopyranoside (**6**).* Following the procedure for the preparation of **2** from **1**, treatment of **5** (1.05 g, 1.96 mmol, 1 equiv) with DIPEA (615 μL, 3.53 mmol, 1.8 equiv), *ortho*-hexynylbenzoic acid (516 mg, 2.55 mmol, 1.3 equiv), DMAP (240 mg, 1.96 mmol, 1 equiv), and EDCI (564 mg, 2.94 mmol, 1.5 equiv) in dry CH_2Cl_2 (15 mL) furnished **6α** (1.06 g, 1.46 mmol, 75%) and **6β** (0.26 g, 0.37 mmol, 18%) as a colorless syrup, respectively, by flash chromatography (petroleum ether/ethyl acetate 30:1 to 20:1) as a colorless syrup. For **6α**: $[\alpha]_D^{26}$ = +26.6 (c 1.06, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83−7.77 (m, 4H), 7.68 (d, J = 8.2 Hz, 1H), 7.53−7.35 (m, 10H), 7.20 (t, J = 7.7 Hz, 1H), 6.23 (s, 1H), 5.69 (s, 1H), 5.00 (d, J = 12.3 Hz, 1H), 4.91 (d, J = 12.3 Hz, 1H), 4.35 (t, J = 9.7 Hz, 1H), 4.30 (dd, J = 10.2, 4.7 Hz, 1H), 4.26 (s, 1H), 4.13−4.06 (m, 2H), 3.87 (t, J = 10.3 Hz, 1H), 2.48−2.41 (m, 1H), 2.34−2.27 (m, 1H),

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1.50−1.48(m, 2H), 1.36−1.26 (m, 3H), 1.08−1.00 (m, 12H), 0.83 (t, J = 7.3 Hz, 3H), 0.79−0.69 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.6, 137.8, 136.1, 135.1, 133.4, 133.1, 132.2, 130.9, 130.5, 128.9, 128.3, 128.0, 127.8, 127.4, 126.7, 126.2, 126.1, 126.0, 125.9, 125.0, 101.7, 97.1, 96.1 ($^1J_{C-H}$ = 176.8 Hz, α-Man), 80.0, 78.9, 77.4, 77.2, 76.9, 75.5, 73.2, 70.6, 68.9, 67.1, 30.9, 22.1, 19.8, 17.5, 13.8, 13.2, 7.2, 4.0, 3.8; MS-ESI *m/z:* 721.2 $[M + H]^+$, 743.1 $[M + Na]^+$; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{44}H_{53}O_7Si$: 721.3555, Found: 721.3549, $[M + NH_4]^+$ Calcd for $C_{44}H_{56}O_7NSi$: 738.3821, Found: 738.3820. For **6*β***: $[\alpha]_D^{26}$ = −27.6 (*c* 0.97, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, J = 7.8 Hz, 1H), 7.89−7.66 (m, 4H), 7.60−7.32 (m, 10H), 7.28 (t, J = 7.6 Hz, 1H), 5.88 (s, 1H), 5.66 (s, 1H), 5.00 (d, J = 12.3 Hz, 1H), 4.93 (d, J = 12.3 Hz, 1H), 4.4−4.33 (m, 2H), 4.24 (t, J = 9.5 Hz, 1H), 3.91 (t, J = 10.2 Hz, 1H), 3.75 (dd, J = 9.6, 2.5 Hz, 1H), 3.56−3.52 (m, 1H), 2.46 (t, J = 7.1 Hz, 2H), 1.65−1.58 (m, 2H), 1.52−1.49 (m, 2H), 1.00−0.90 (m, 16H), 0.72−0.58 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.2, 137.7, 135.8, 134.4, 133.4, 133.1, 132.2, 130.8, 130.5, 129.1, 128.4, 128.10, 128.05, 127.8, 127.0, 126.8, 126.3, 126.14, 126.09, 126.81, 125.5, 101.8, 97.0, 94.4 ($^1J_{C-H}$ = 160.7 Hz, β-Man), 78.91, 78.86, 77.8, 77.4, 77.2, 76.9, 73.2, 71.3, 68.8, 68.4, 30.8, 22.2, 19.7, 17.60, 17.57, 13.8, 13.4, 7.3, 4.21, 4.15; MS-ESI *m/z:* 721.2 $[M + H]^+$, 743.1 $[M + Na]^+$; HRMS (ESI) *m/z*: $[M + NH_4]^+$ Calcd for $C_{44}H_{56}O_7NSi$: 738.3821, Found: 738.3830, $[M + Na]^+$ Calcd for $C_{44}H_{52}O_7NaSi$: 743.3375, Found: 743.3374.

*Diosgenyl 4,6-Di-O-benzylidene-2-O-(diethylisopropylsilyl)-3-O-(2-methylnaphthyl)-β-D-mannopyranoside (**7a**).* Compound **7a** was obtained in 93% yield (86 mg, β only) as a foam by purification with silica gel column chromatography (petroleum ether/ethyl acetate/CH_2Cl_2 20:1:1) according to the general procedure. $[\alpha]_D^{21}$ = −66.4 (*c* 1.03, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86−7.78 (m, 3H), 7.74−7.68 (m, 1H), 7.63−7.30 (m, 8H), 5.62 (s, 1H), 5.32 (d, J = 4.0 Hz, 1H), 4.96−4.88 (m, 2H), 4.46 (s, 1H), 4.43−4.37 (m, 1H), 4.27 (dd, J = 10.4, 4.7 Hz, 1H), 4.16−4.09 (m, 2H), 3.88 (t, J = 10.2 Hz, 1H), 3.58−3.45 (m, 3H), 3.37 (t, J = 10.9 Hz, 1H), 3.32−3.26 (m, 1H), 2.33−2.28 (m, 1H), 2.23−2.16 (m, 1H), 1.05 (s, 3H), 1.02 (s, 3H), 1.01 (s, 3H), 0.97 (d, J = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.8, 137.9, 136.2, 133.4, 133.0, 128.9, 128.3, 128.0, 127.8, 126.5, 126.3, 126.1, 126.0, 125.9, 121.7, 109.4, 101.7, 99.6 ($^1J_{C-H}$ = 153.0 Hz, β-Man), 81.0, 79.0, 78.4, 78.0, 72.3, 69.1, 67.6, 67.0, 62.2, 56.7, 50.3, 41.8, 40.4, 39.9, 38.9, 37.4, 37.0, 32.2, 32.0, 31.6, 31.5, 30.5, 29.6, 29.0, 21.0, 19.5, 17.7, 17.3, 16.4, 14.7, 13.5, 7.4, 4.3, 4.0; MS-ESI *m/z:* 933.8 $[M + H]^+$, 955.8 $[M + Na]^+$; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{58}H_{81}O_8Si$: 933.5695, Found: 933.5683, $[M + NH_4]^+$ Calcd for $C_{58}H_{84}O_8NSi$: 950.5961, Found: 950.5953.

*Phenyl 4,6-Di-O-benzylidene-2-O-(diethylisopropylsilyl)-3-O-(2-methylnaphthyl)-β-D-manno-pyranosyl-(1 → 4)-2,6-di-O-benzyl-3-O-(2-methylnaphthyl)-1-thio-α-D-mannopyranoside (**7b**).* Compound **7b** was obtained in 64% yield (71 mg, β/α = 8.6/1) as a syrup by purification with silica gel column chromatography (petroleum ether/ethyl acetate 13:1 to 8:1) according to the general procedure. $[\alpha]_D^{18}$ = +17.11 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85−7.76 (m, 6H), 7.72−7.67 (m, 1H), 7.52−7.22 (m, 27H), 5.59 (d, J = 2.6 Hz, 1H), 5.50 (s, 1H), 5.05 (d, J = 12.0 Hz, 1H), 4.89 (d, J = 12.5 Hz, 1H), 4.82 (d, J = 12.5 Hz, 1H), 4.72−4.62 (m, 4H), 4.39−4.32 (m, 2H), 4.32−4.27 (m, 1H), 4.24 (s, 1H), 4.10 (dd, J = 10.1, 4.7 Hz, 1H), 4.04 (t, J = 9.5 Hz, 1H), 3.98 (brs, 2H), 3.91 (d, J = 5.4 Hz, 1H), 3.74 (dd, J = 10.8, 4.4 Hz, 1H), 3.67 (d, J = 9.5 Hz, 1H), 3.56 (t, J = 10.3 Hz, 1H), 3.31 (dd, J = 9.6, 2.3 Hz, 1H), 3.10−3.04 (m, 1H), 1.03−0.95 (m, 13H), 0.74−0.64 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.2, 138.1, 137.9, 136.7, 136.3, 134.7, 133.42, 133.37, 133.03, 132.99, 131.4, 129.1, 129.0, 128.5, 128.4, 128.3, 128.02, 127.97, 127.91, 127.86, 127.8, 127.7, 127.4, 126.4, 126.3, 126.2, 126.13, 126.07, 125.96, 125.90, 125.87, 125.8, 101.8 ($^1J_{C-H}$ = 155.9 Hz, β-Man), 101.6, 86.1 ($^1J_{C-H}$ = 166.6 Hz, α-Man), 79.0, 78.2, 77.7, 77.6, 77.0, 73.5, 73.2, 72.8, 72.5, 72.4, 72.2, 69.4, 68.9, 67.4, 29.8, 17.7, 13.5, 7.5, 7.4, 4.4, 4.2; MS-ESI *m/z:* 1111.7 $[M + H]^+$, 1133.7 $[M + Na]^+$, 1149.7 $[M + K]^+$; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{68}H_{75}O_{10}SSi$: 1111.4845, Found: 1111.4844, $[M + NH_4]^+$ Calcd for $C_{68}H_{78}O_{10}NSSi$: 1128.5110, Found: 1128.5123.

*Methyl 4,6-Di-O-benzylidene-2-O-(diethylisopropylsilyl)-3-O-(2-methylnaphthyl)-D-manno-pyranosyl-(1 → 4)-2,3-di-O-benzoyl-6-O-benzyl-α-D-glucopyranoside (**7c**).* Compounds **7cα** (32 mg, 32%) and **7cβ** (51 mg, 50%) as a syrup, respectively, were obtained by purification with silica gel column chromatography (petroleum ether/ethyl acetate 7:1) according to the general procedure. For **7cα**: $[\alpha]_D^{18}$ = +9.38 (*c* 0.85, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, J = 8.0 Hz, 2H), 7.93 (d, J = 8.0 Hz, 2H), 7.88−7.74 (m, 3H), 7.70 (d, J = 7.3 Hz, 1H), 7.63−7.22 (m, 19H), 6.01 (t, J = 9.6 Hz, 1H), 5.60 (s, 1H), 5.20−5.13 (m, 2H), 4.90 (s, 1H), 4.79 (d, J = 12.3 Hz, 1H), 4.72−4.63 (m, 2H), 4.57 (d, J = 11.7 Hz, 1H), 4.22 (t, J = 9.4 Hz, 1H), 4.17−4.11 (m, 2H), 3.99−3.82 (m, 5H), 3.82−3.73(m, 2H), 3.40 (s, 3H), 0.89−0.63 (m, 13H), 0.40−0.19 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.0, 165.7, 138.0, 137.9, 136.3, 133.5, 133.4, 132.97, 130.00, 129.97, 129.4, 129.2, 128.9, 128.6, 128.5, 128.3, 128.1, 128.0, 127.8, 127.7, 126.38, 126.36, 126.1, 125.9, 125.7, 103.6 ($^1J_{C-H}$ = 169.2 Hz, α-Man), 101.8, 97.0 ($^1J_{C-H}$ = 171.0 Hz, α-Glu), 78.8, 76.1, 75.8, 73.7, 72.73, 72.65, 72.26, 71.31, 70.0, 69.0, 68.5, 65.7, 55.5, 29.9, 17.32, 17.30, 13.0, 7.09, 7.07, 3.6, 3.4; MS-ESI *m/z:* 1011.51 $[M + H]^+$, 1033.5 $[M + Na]^+$, 1049.5 $[M + K]^+$; HRMS (ESI) *m/z*: $[M + NH_4]^+$ Calcd for $C_{59}H_{70}O_{13}NSi$: 1028.4611, Found: 1028.4628, $[M + Na]^+$ Calcd for $C_{59}H_{66}O_{13}NaSi$: 1033.4165, Found: 1033.4174. For **7*β***: $[\alpha]_D^{18}$ = +45.51 (*c* 1.125, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, J = 7.4 Hz, 4H), 7.88−7.75 (m, 3H), 7.69 (d, J = 6.6 Hz, 1H), 7.61−7.07 (m, 19H), 5.91 (t, J = 9.3, 1H), 5.42 (s, 1H), 5.22−5.12 (m, 2H), 4.90−4.82 (m, 2H), 4.65 (d, J = 12.0 Hz, 1H), 4.38 (d, J = 12.0 Hz, 1H), 4.30 (s, 1H), 4.15 (t, J = 9.5 Hz, 1H), 3.95−3.88 (m, 3H), 3.73−3.68 (m, 3H), 3.43 (s, 3H), 3.31 (d, J = 9.5 Hz, 1H), 3.14 (t, J = 10.0 Hz, 1H), 3.08−3.04 (m, 1H), 1.09−0.84 (m, 13H), 0.72−0.57 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.1, 165.3, 137.8, 137.6, 136.3, 133.38, 133.35, 133.0, 132.9, 130.6, 130.1, 129.9, 129.3, 129.0, 128.7, 128.5, 128.3, 128.2, 128.1, 128.0, 127.8, 126.3, 126.2, 126.1, 125.9, 125.7, 101.5 ($^1J_{C-H}$ = 156.3 Hz, β-Man), 101.4, 97.2 ($^1J_{C-H}$ = 171.3 Hz, α-Glu), 78.7, 78.2, 76.5, 73.9, 72.5, 72.4, 71.7, 70.3, 69.9, 68.4, 68.3, 67.4, 55.7, 17.6, 17.5, 13.3, 7.4, 7.3, 4.2, 4.1; MS-ESI *m/z:* 1011.52 $[M + H]^+$, 1033.5 $[M + Na]^+$, 1049.5 $[M + K]^+$; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{59}H_{67}O_{13}Si$: 1011.4345, Found: 1011.4348, $[M + NH_4]^+$ Calcd for $C_{59}H_{70}O_{13}NSi$: 1028.4611, Found: 1028.4619.

*4,6-Di-O-benzylidene-2-O-(diethylisopropylsilyl)-3-O-(2-methylnaphthyl)-β-D-mannopyranosyl-(1 → 6)-1,2:3,4-di-O-isopropylidene-α-D-galactopyranoside (**7d**).* Compound **7d** was obtained in 87% yield (68 mg, β/α = 20/1) as a syrup by purification with silica gel column chromatography (petroleum ether/ethyl acetate 7:1) according to the general procedure. $[\alpha]_D^{18}$ = −69.39 (*c* 1.12, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85−7.77 (m, 3H), 7.74−7.69 (m, 1H), 7.54−7.49 (m, 2H), 7.80−7.44 (m, 3H), 7.40−7.35 (m, 3H), 5.63 (s, 1H), 5.54 (d, J = 5.1 Hz, 1H), 4.90 (d, J = 12.3 Hz, 2H), 4.59 (dd, J = 7.9, 2.1 Hz, 1H), 4.42 (s, 1H), 4.32−4.26 (m, 3H), 4.20 (d, J = 7.9 Hz, 1H), 4.15 (t, J = 9.5 Hz, 1H), 4.05 (dd, J = 11.3, 2.6 Hz, 1H), 3.98 (d, J = 7.9 Hz, 1H), 3.87 (t, J = 10.2 Hz, 1H), 3.67−3.63 (m, 1H), 3.56 (dd, J = 9.7, 2.5 Hz, 1H), 3.33−3.28 (m, 1H), 1.52 (s, 3H), 1.44 (s, 3H), 1.33 (s, 3H), 1.32 (s, 3H), 1.05−1.00 (m, 13H), 0.77−0.69 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.8, 136.1, 133.4, 133.0, 129.0, 128.3, 128.0, 127.8, 126.5, 126.3, 126.1, 125.9, 125.8, 109.4, 108.5, 102.5 ($^1J_{C-H}$ = 155.7 Hz, β-Man), 101.7, 96.4 ($^1J_{C-H}$ = 176.3 Hz, α-Gal), 78.9, 77.8, 72.2, 71.5, 71.3, 70.8, 70.4, 69.8, 69.0, 67.7, 67.6, 26.1, 25.0, 24.4, 17.71, 17.66, 13.4, 7.43, 7.40, 4.2, 4.0; MS-ESI *m/z:* 779.5 $[M + H]^+$, 801.4 $[M + Na]^+$, 817.4 $[M + K]^+$; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{43}H_{59}O_{11}Si$: 779.3821, Found: 779.3830, $[M + NH_4]^+$ Calcd for $C_{43}H_{62}O_{11}NSi$: 796.4087, Found: 796.4095.

*Phenyl 4,6-Di-O-benzylidene-2-O-(diethylisopropylsilyl)-3-O-(2-methylnaphthyl)-β-D-manno-pyranosyl-(1 → 6)-2,3,4-tri-O-benzyl-1-thio-α-D-mannopyranoside (**7e**).* Compound **7e** was obtained in 77% yield (82 mg, β only) as a syrup by purification with silica gel column chromatography (petroleum ether/ethyl acetate 15:1 to 12:1) according to the general procedure. $[\alpha]_D^{18}$ = +2.24 (*c* 1.03, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87−7.80 (m, 3H), 7.76−7.69 (m, 1H), 7.55−7.43 (m, 5H), 7.42−7.07 (m, 23H), 5.61 (s, 1H), 5.55 (s, 1H), 4.96−4.86 (m, 3H), 4.72 (d, J = 12.4 Hz, 1H), 4.65−4.52 (m, 4H), 4.32−4.25 (m, 2H), 4.25−4.19 (t, J = 8.4, 1H), 4.15−4.08 (m, 2H), 4.01 (d, J = 2.3 Hz, 1H), 3.98 (brs, 1H), 3.86−3.82 (m, 2H), 3.81−3.73 (m, 2H), 3.44 (dd, J = 9.6, 2.4 Hz, 1H), 3.25−3.21 (m, 1H), 1.04−0.86 (m, 13H), 0.67−0.60 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.3,

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138.2, 137.90, 137.88, 136.3, 135.1, 133.4, 133.0, 130.4, 129.1, 129.0, 128.6, 128.54, 128.53, 128.3, 128.2, 128.03, 128.00, 127.98, 127.91, 127.88, 127.78, 127.0, 126.3, 126.1, 125.9, 125.8, 101.8 ($^1J_{C-H}$ = 157.8 Hz, β-Man), 101.6, 85.5 ($^1J_{C-H}$ = 166.3 Hz, α-Man), 80.2, 79.1, 78.1, 76.3, 75.3, 75.2, 73.8, 72.31, 72.26, 71.4, 69.0, 68.3, 67.5, 17.7, 17.6, 13.4, 7.4, 4.2, 4.0; MS-ESI *m/z:* 1083.7 $[M + Na]^+$, 1099.7 $[M + K]^+$; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{64}H_{73}O_{10}SSi$: 1061.4688, Found: 1061.4684, $[M + NH_4]^+$ Calcd for $C_{64}H_{76}O_{10}NSSi$: 1078.4954, Found: 1078.4965.

*Benzyl 4,6-Di-O-benzylidene-2-O-(diethylisopropylsilyl)-3-O-(2-methylnaphthyl)-β-D-manno-pyranosyl-(1 → 6)-2,3,4-tri-O-benzyl-α-D-mannopyranoside (**7f**).* Compound **7f** was obtained in 86% yield (91 mg, β only) as a syrup by purification with silica gel column chromatography (petroleum ether/ethyl acetate 12:1) according to the general procedure. $[\alpha]_D^{18}$ = +3.04 (*c* 1.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85−7.75 (m, 3H), 7.72−7.68 (m, 1H), 7.53 (dd, *J* = 7.3, 2.2 Hz, 2H), 7.48−7.17 (m, 26H), 5.63 (s, 1H), 4.95−4.88 (m, 3H), 4.84 (d, *J* = 1.5 Hz, 1H), 4.72−4.65 (m, 3H), 4.60 (s, 2H), 4.57 (d, *J* = 11.1 Hz, 1H), 4.41−4.35 (m, 2H), 4.28 (dd, *J* = 10.3, 4.8 Hz, 1H), 4.20−4.13 (m, 3H), 3.97 (dd, *J* = 9.3, 3.0 Hz, 1H), 3.95−3.85 (m, 2H), 3.78 (dd, *J* = 2.8, 2.0 Hz, 1H), 3.75−3.66 (m, 2H), 3.54 (dd, *J* = 9.6, 2.7 Hz, 1H), 3.32−3.27 (m, 1H), 1.02−0.94 (m, 13H), 0.72−0.66 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.5, 138.4, 138.3, 137.9, 137.3, 136.2, 133.4, 133.0, 129.0, 128.6, 128.50, 128.46, 128.3, 128.10, 128.07, 128.02, 127.9, 127.81, 127.76, 127.73, 126.4, 126.3, 126.1, 125.89, 125.86, 102.4 ($^1J_{C-H}$ = 157.1 Hz, β-Man), 101.7, 97.0 ($^1J_{C-H}$ = 170.0 Hz, α-Man), 80.4, 79.1, 78.0, 75.5, 75.3, 74.6, 72.9, 72.5, 72.3, 71.6, 69.6, 69.0, 68.7, 67.7, 17.7, 17.6, 13.5, 7.4, 4.3, 4.1; MS-ESI *m/z*: 1081.7 $[M + Na]^+$, 1097.7 $[M + K]^+$; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{65}H_{75}O_{11}Si$: 1059.5073, Found: 1059.5066; $[M + NH_4]^+$ Calcd for $C_{65}H_{78}O_{11}NSi$: 1076.5339, Found: 1076.5355; $[M + Na]^+$ Calcd for $C_{65}H_{74}O_{11}NaSi$: 1081.4893, Found: 1081.4901.

*1,2,3,4,5-Penta-O-benzyl-D-mannitol (**11**).* To a solution of D-mannitol (5 g, 27.45 mmol, 2 equiv) in anhydrous pyridine (50 mL) was added triphenylmethyl chloride (1.91 g, 6.86 mmol, 0.5 equiv). After the mixture was stirred at 75 °C for 12 h, another portion of triphenylmethyl chloride (950 mg, 3.43 mmol, 0.25 equiv) was added, and stirring was continued at 45 °C for 24 h. Then the reaction was cooled to room termperature, and more triphenylmethyl chloride (950 mg, 3.43 mmol, 0.25 equiv) was added, followed by stirring at room temperature for another 36 h. At this stage the solution was concentrated in vacuo, and the remaining solid was diluted with water (30 mL). The aqueous layer was extracted with CH_2Cl_2 (5 × 40 mL). The combined organic layers were dried over Na_2SO_4, filtered, and then concentrated to give crude 1-*O*-triphenylmethy-D-mannitol (**9**) as a syrup. MS-ESI *m/z:* 447.3 $[M + Na]^+$.

Trityl ether **9** was dissolved in anhydrous DMF (70 mL), BnBr (12.3 mL, 102.94 mmol, 7.5 equiv), and TBAI (507 mg, 1.37 mmol, 0.1 equiv) were added. After the mixture was stirred for 10 min, NaH (2.47 g, 102.94 mmol, 7.5 equiv) was added at 0 °C. Then the resulting mixture was stirred at room temperature for 4 h followed by addition of MeOH to quench the reaction. The volatile was removed in vacuum, and the remain syrup was diluted with CH_2Cl_2. The solution was sequentially washed with saturated aqueous $NaHCO_3$ and brine. The collected organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated to give crude **10** as a yellow syrup, which was dissolved in MeOH:CH_2Cl_2 (2/1, 150 mL), and *p*-TsOH monohydrate (3.92 g, 20.59 mmol, 1.5 equiv) was added. The reaction mixture was stirred under an atmosphere of argon at room temperature for 3 h. Afterward, the reaction was neutralized with Et_3N, concentrated, and then diluted with CH_2Cl_2 (30 mL) and sequentially washed with water and brine. The collected organic phase was dried over Na_2SO_4, filtered, and concentrated. The crude was purified by flash column chromatography (petroleum ether/ethyl acetate 6:1) to give **11** (4.17 g, 6.59 mmol, 48% over 3 steps) as a colorless syrup. $[\alpha]_D^{19}$ = −2.52 (*c* 0.71, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38−7.20 (m, 25H), 4.76−4.67 (m, 3H), 4.66−4.57 (m, 2H), 4.56−4.42 (m, 4H), 4.39 (d, *J* = 11.6 Hz, 1H), 4.01 (brs, 1H), 3.95 (brs, 1H), 3.92−3.83 (m, 3H), 3.83−3.76 (m, 1H), 3.76−3.70 (m, 1H), 3.67 (s, 1H), 2.15 (s, 1H, OH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.6, 138.5, 138.3, 138.2, 128.54, 128.47, 128.44, 128.41, 128.39, 128.00, 127.9, 127.83, 127.81, 127.76, 127.73, 127.68, 127.6, 79.8, 79.1, 79.0, 78.9, 74.7, 74.2, 73.5, 71.9, 71.4, 69.2, 60.6; MS-ESI *m/z:* 655.3 $[M + Na]^+$, 671.3 $[M + K]^+$; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{41}H_{45}O_6$: 633.3211, Found: 633.3221; $[M + Na]^+$ Calcd for $C_{41}H_{44}O_6Na$: 655.3030, Found: 655.3031.

*2,3,4,5,6-Penta-O-benzyl-D-mannitol-1-yl 4,6-di-O-benzylidene-2-O-(diethylisopropylsilyl)-3-O-(2-methylnaphthyl)-D-mannopyranoside (**12**).* Adopting the general procedure for glycosylation, **11** (69 mg, 0.11 mmol, 1 equiv) reacted with *ortho*-hexynylbenzoate glycosyl donor **6α** (118 mg, 0.16 mmol, 1.5 equiv) in anhydrous CH_2Cl_2 (2 mL) to afford **12β** (100 mg, 86.9 μmol, 79%) and **12α** (8 mg, 7.0 μmol, 6%) as a colorless syrup, respectively, by purification by silica gel column chromatography (petroleum ether/ethyl acetate 13:1). For **12β**: $[\alpha]_D^{26}$ = −13.4 (*c* 1.08, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81−7.79 (m, 3H), 7.74−7.70 (m, 1H), 7.52 (dd, *J* = 6.6, 2.9 Hz, 2H), 7.49−7.19 (m, 31H), 5.61 (s, 1H), 4.90 (d, *J* = 12.7 Hz, 2H), 4.71 (d, *J* = 11.5 Hz, 1H), 4.69−4.62 (m, 4H), 4.59 (d, *J* = 11.6 Hz, 1H), 4.52−4.44 (m, 4H), 4.36−4.26 (m, 2H), 4.19 (dd, *J* = 10.3, 4.7 Hz, 1H), 4.16−4.09 (m, 2H), 4.04 (t, *J* = 4.1 Hz, 1H), 3.96−3.90 (m, 2H), 3.87−3.82 (m, 2H), 3.76−3.72(m, 3H), 3.47 (dd, *J* = 9.6, 2.6 Hz, 1H), 3.24−3.18 (m, 1H), 1.06−0.96 (m, 13H), 0.76−0.67 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.9, 138.8, 138.7, 138.6, 138.4, 137.9, 136.2, 133.4, 133.1, 129.0, 128.5, 128.42, 128.35, 128.3, 128.1, 128.0, 127.93, 127.88, 127.8, 127.7, 127.6, 127.5, 127.4, 126.5, 126.3, 126.1, 125.93, 125.86, 102.4 ($^1J_{C-H}$ = 154.6 Hz, β-Man), 101.7, 80.8, 79.9, 79.3, 79.12, 79.05, 78.0, 74.6, 74.4, 73.5, 72.4, 72.2, 72.1, 71.6, 70.4, 69.2, 69.0, 67.6, 17.7, 13.5, 7.5, 7.4, 4.3, 4.2; MS-ESI *m/z:* 1174.0 $[M + Na]^+$, 1190.0 $[M + K]^+$; HRMS (ESI) *m/z*: $[M + NH_4]^+$ Calcd for $C_{72}H_{86}O_{11}NSi$: 1168.5965, Found: 1168.5995; $[M + Na]^+$ Calcd for $C_{72}H_{82}O_{11}NaSi$: 1173.5519, Found: 1173.5539. For **12α**: $[\alpha]_D^{26}$ = +13.7 (*c* 0.70, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78−7.68 (m, 4H), 7.62−7.03 (m, 33H), 5.67 (s, 1H), 4.93 (dd, *J* = 12.2, 6.3 Hz, 1H), 4.86 (dd, *J* = 12.2, 6.3 Hz, 1H), 4.81−4.45 (m, 11H), 4.33 (dd, *J* = 11.3, 5.6 Hz, 1H), 4.25−4.15 (m, 3H), 4.00−3.81 (m, 9H), 3.76−3.72 (m, 1H), 1.06−0.89 (m, 13H), 0.72−0.63 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.7, 138.6, 138.4, 138.3, 138.1, 136.3, 133.4, 133.0, 128.9, 128.5, 128.43, 128.36, 128.2, 128.0, 127.9, 127.8, 127.7, 127.6, 126.5, 126.0, 125.7, 101.9 ($^1J_{C-H}$ = 169.9 Hz, α-Man), 101.8, 79.31, 79.27, 79.2, 79.1, 75.7, 74.4, 74.2, 73.5, 72.9, 72.3, 72.0, 71.5, 69.6, 69.1, 66.9, 64.7, 17.5, 13.2, 7.2, 4.0, 3.8; MS-ESI *m/z:* 1174.1 $[M + Na]^+$, 1190.0 $[M + K]^+$; HRMS (ESI) *m/z*: $[M + NH_4]^+$ Calcd for $C_{72}H_{86}O_{11}NSi$: 1168.5965, Found: 1168.5992; $[M + Na]^+$ Calcd for $C_{72}H_{82}O_{11}NaSi$: 1173.5519, Found: 1173.5537.

*2,3,4,5,6-Penta-O-benzyl-D-mannitol-1-yl-4,6-di-O-benzylidene-3-O-(2-methylnaphthyl)-β-D-mannopyranoside (**13**).* To a solution of **12β** (191 mg, 0.17 mmol, 1 equiv) in THF (1.5 mL) was added TBAF (1 M in THF, 1.67 mL, 1.67 mmol, 10 equiv). The resulting mixture was stirred at room temperature overnight, then diluted with CH_2Cl_2 (30 mL). The mixture was washed with water and brine and then the organic phase was collected, dried over Na_2SO_4, filtered, and concentrated. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 4:1) to provide **13** (157 mg, 0.153 mmol, 93%) as a colorless syrup. $[\alpha]_D^{26}$ = +13.7 (*c* 1.03, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88−7.71 (m, 4H), 7.66−7.38 (m, 9H), 7.34−7.20 (m, 24H), 5.61 (s, 1H), 5.00−4.90 (m, 2H), 4.72−4.60 (m, 5H), 4.59−4.43 (m, 5H), 4.36 (s, 1H), 4.27 (d, *J* = 10.6 Hz, 1H), 4.23 (dd, *J* = 7.9, 2.3 Hz, 1H), 4.17 (t, *J* = 9.5 Hz, 1H), 4.04 (s, 1H), 4.00 (s, 1H), 3.92 (t, *J* = 4.7 Hz, 1H), 3.89−3.82 (m, 3H), 3.82−3.73 (m, 2H), 3.73−3.68 (m, 1H), 3.58 (dd, *J* = 9.5, 2.5 Hz, 1H), 3.27−3.20 (m, 1H), 2.61 (brs, 1H, OH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.7, 138.63, 138.59, 138.57, 138.3, 137.7, 135.6, 133.4, 133.2, 129.1, 128.5, 128.5, 128.42, 128.38, 128.35, 128.3, 128.1, 128.0, 127.92, 127.90, 127.80, 127.77, 127.73, 127.67, 127.65, 127.6, 126.9, 126.2, 126.1, 125.9, 101.7, 101.0, 79.9, 79.4, 79.3, 79.0, 78.5, 76.6, 74.42, 74.38, 73.5, 72.5, 72.3, 72.0, 70.1, 70.0, 69.2, 68.7, 66.9; MS-ESI *m/z:* 1045.8 $[M + Na]^+$, 1061.9 $[M + K]^+$; HRMS (ESI) *m/z*: $[M + NH_4]^+$ Calcd for $C_{65}H_{70}O_{11}N$: 1040.4943, Found: 1040.4969.

*2,3,4,5,6-Penta-O-benzyl-D-mannitol-1-yl 4,6-di-O-benzylidene-2-O-octanoyl-3-O-(2-methyl-naphthyl)-β-D-mannopyranoside (**14**).* To a solution of **13** (151 mg, 0.15 mmol, 1 equiv), DIPEA (52 μL, 0.30 mmol, 2 equiv), *n*-octanoic acid (94 μL, 0.59 mmol, 4 equiv), and

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DMAP (18 mg, 0.15 mmol, 1 equiv) in dry CH_2Cl_2 (3 mL) was added EDCI (113 mg, 0.59 mmol, 4 equiv). The resultant mixture was stirred at room temperature overnight, then diluted with CH_2Cl_2 (30 mL). The resulting mixture was sequentially washed with 1 M aqueous HCl, saturated aqueous $NaHCO_3$ and brine. The collected organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate 7:1) to provide **14** (156 mg, 0.14 mmol, 92%) as a colorless syrup. $[\alpha]_D^{26} = -9.7$ (*c* 0.46, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81−7.78 (m, 3H), 7.67 (d, *J* = 7.3 Hz, 1H), 7.54−7.23 (m, 33H), 5.65 (d, *J* = 3.1 Hz, 1H), 5.61 (s, 1H), 4.83 (d, *J* = 12.8 Hz, 1H), 4.72−4.67 (m, 2H), 4.67−4.59 (m, 5H), 4.52−4.42 (m, 5H), 4.27 (d, *J* = 9.8 Hz, 1H), 4.23 (dd, *J* = 10.4, 4.9 Hz, 1H), 3.99 (t, *J* = 9.5 Hz, 1H), 3.94 (t, *J* = 4.0 Hz, 1H), 3.88 (d, *J* = 4.0 Hz, 2H), 3.84−3.74 (m, 4H), 3.70 (dd, *J* = 10.4, 4.6 Hz, 1H), 3.63 (dd, *J* = 9.8, 3.3 Hz, 1H), 3.30−3.21 (m, 1H), 2.48−2.38 (m, 2H), 1.67−1.62 (m, 2H), 1.27−1.17 (m, 8H), 0.82 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.3, 138.9, 138.8, 138.7, 138.6, 138.4, 137.6, 135.4, 133.4, 133.1, 129.1, 128.5, 128.47, 128.42, 128.36, 128.2, 128.1, 127.91, 127.87, 127.78, 127.75, 127.7, 127.64, 127.61, 127.58, 127.51, 126.48, 126.3, 126.1, 125.9, 125.7, 101.8, 100.4, 80.1, 79.7, 79.4, 79.0, 78.1, 75.8, 74.4, 73.5, 72.6, 72.0, 71.6, 71.4, 69.3, 68.7, 68.6, 67.3, 34.4, 31.8, 29.2, 29.1, 25.2, 22.7, 14.2; MS-ESI *m/z:* 1172.0 $[M + Na]^+$, 1188.0 $[M + K]^+$; HRMS (ESI) *m/z*: $[M + NH_4]^+$ Calcd for $C_{73}H_{84}O_{12}N$: 1166.5988, Found: 1166.5999; $[M + Na]^+$ Calcd for $C_{73}H_{80}O_{12}Na$: 1171.5542, Found: 1171.5544.

*2,3,4,5,6-Penta-O-benzyl-D-mannitol-1-yl 2-O-octanoyl-3-O-(2-methylnaphthyl)-β-D-mannopyranoside (**15**).* To a solution of **14** (128 mg, 0.11 mmol, 1 equiv) in MeOH:CH_2Cl_2(4/1, 2 mL) was added *p*-TsOH monohydrate (21 mg, 0.11 mmol, 1 equiv). The reaction mixture was stirred under an atmosphere of argon at room temperature for 3 h, then neutralized with Et_3N and concentrated. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate 2:1) to give **15** (112 mg, 0.11 mmol, 95%) as a colorless syrup. $[\alpha]_D^{25} = -34.58$ (*c* 0.70, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83−7.72 (m, 4H), 7.48−7.40 (m, 3H), 7.34−7.19 (m, 25H), 5.61 (d, *J* = 2.8 Hz, 1H), 4.85 (d, *J* = 11.3 Hz, 1H), 4.72−4.59 (m, 6H), 4.53−4.41 (m, 6H), 4.23 (d, *J* = 11.0 Hz, 1H), 3.95 (t, *J* = 4.1 Hz, 1H), 3.93−3.87 (m, 2H), 3.87−3.76 (m, 5H), 3.72−3.69 (m, 2H), 3.35 (dd, *J* = 9.4, 3.0 Hz, 1H), 3.25−3.21 (m, 1H), 2.41−2.30 (m, 3H), 2.16 (s, 1H), 1.65−1.60 (m, 2H), 1.26−1.12 (m, 8H), 0.81 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.4, 138.9, 138.8, 138.62, 138.59, 138.3, 134.8, 133.4, 133.3, 128.6, 128.48, 128.45, 128.39, 128.37, 128.1, 128.0, 127.93, 127.92, 127.84, 127.80, 127.75, 127.63, 127.60, 127.55, 127.3, 126.4, 126.3, 126.0, 100.0, 80.1, 79.8, 79.7, 79.3, 78.9, 75.7, 74.42, 74.39, 73.5, 72.6, 71.9, 71.4, 71.3, 69.2, 67.3, 67.2, 62.7, 34.4, 31.7, 29.2, 29.1, 25.3, 22.7, 14.2; MS-ESI *m/z:* 1084.0 $[M + Na]^+$; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{66}H_{77}O_{12}$: 1061.5410, Found: 1061.5418; $[M + NH_4]^+$ Calcd for $C_{66}H_{80}O_{12}N$: 1078.5675, Found: 1078.5699.

*2,3,4,5,6-Penta-O-benzyl-D-mannitol-1-yl 2-O-octanoyl-β-D-mannopyranoside (**16**).* **15** (121 mg, 114 μmol, 1 equiv) was dissolved in CH_2Cl_2/MeOH/H_2O (10/10/1, 4 mL), followed by the dropwise addition of a solution of DDQ (60 mg, 0.26 mmol, 2.3 equiv) in MeOH (1 mL) over 60 min. After the mixture was stirred for another1 h at room temperature with the exclusion of light, it was diluted with CH_2Cl_2 and then washed with saturated aqueous $NaHCO_3$ and brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated. The resultant residue was purified by silica gel column chromatography (CH_2Cl_2/ethyl acetate 2:1 to 1:1) to provide **16** (60 mg, 65 μmol, 57%) as a colorless syrup along with recovery of starting material **15** (35 mg, 34.0 μmol, 29%). $[\alpha]_D^{25} = -5.9$ (*c* 1.00, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35−7.15 (m, 25H), 5.32 (d, *J* = 3.1 Hz, 1H), 4.68−4.59 (m, 5H), 4.54−4.43 (m, 5H), 4.21 (d, *J* = 10.8 Hz, 1H), 3.95−3.87 (m, 3H), 3.85−3.78 (m, 4H), 3.77−3.67 (m, 4H), 3.56 (d, *J* = 9.0 Hz, 1H), 3.21−3.16 (m, 1H), 2.39−2.28 (m, 3H), 1.63−1.55 (m, 2H), 1.28−1.18 (m, 8H), 0.84 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.2, 138.8, 138.7, 138.6, 138.3, 128.49, 128.45, 128.43, 128.39, 128.37, 128.05, 127.95, 127.9, 127.80, 127.76, 127.70, 127.65, 127.6, 99.6, 79.9, 79.6, 79.2, 78.9, 75.7, 74.40, 74.37, 73.5, 73.1, 72.5, 71.9, 71.1, 71.0, 69.2, 68.7, 62.5, 34.4, 31.8, 29.2, 29.0, 25.1, 22.7, 14.2; MS-ESI *m/z:* 943.7 $[M + Na]^+$, 959.8 $[M + K]^+$; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{55}H_{68}O_{12}Na$: 943.4603, Found: 943.4626.

*2,3,4,5,6-Penta-O-benzyl-D-mannitol-1-yl 2-O-octanoyl-3,4,6-tri-O-hexanoyl-β-D-mannopyranoside (**17**).* To a solution of **16** (78 mg, 84.7 μmol, 1 equiv), pyridine (41 μL, 0.51 mmol, 6 equiv) in dry CH_2Cl_2 (3 mL) was added *n*-hexanoyl chloride (71 μL, 0.51 mmol, 6 equiv) at 0 °C. The mixture was stirred at room temperature overnight with the temperature lifting naturally to rt. Then the reaction was diluted with CH_2Cl_2 (30 mL) and washed sequentially with saturated aqueous $NaHCO_3$ and brine. The collected organic layer was dried over Na_2SO_4, filtered, and concentrated. The resultant residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate 10:1) to provide **17** (98 mg, 80.62 mol, 95%) as a colorless syrup. $[\alpha]_D^{26} = -7.7$ (*c* 0.56, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56−7.25 (m, 25H), 5.48 (d, *J* = 2.6 Hz, 1H), 5.28 (t, *J* = 10.0 Hz, 1H), 4.99 (dd, *J* = 10.0, 2.7 Hz, 1H), 4.70−4.54 (m, 6H), 4.53−4.43 (m, 4H), 4.40 (d, *J* = 11.6 Hz, 1H), 4.27 (d, *J* = 10.7 Hz, 1H), 4.19 (dd, *J* = 12.2, 5.0 Hz, 1H), 4.11 (d, *J* = 11.7 Hz, 1H), 3.91 (m, 1H), 3.88 (m, 1H), 3.85−3.78 (m, 3H), 3.76−3.72 (m, 1H), 3.71−3.67 (m, 1H), 3.54−3.49 (m, 1H), 2.41−2.34 (m, 2H), 2.31−2.16 (m, 6H), 1.65−1.53 (m, 8H), 1.41−1.14 (m, 20H), 1.00−0.76 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.6, 173.0, 172.7, 172.4, 138.8, 138.7, 138.63, 138.58, 138.4, 128.5, 128.43, 128.42, 128.35, 128.1, 128.0, 127.87, 127.86, 127.78, 127.72, 127.6, 99.3, 79.7, 79.6, 79.2, 78.9, 74.4, 74.3, 73.4, 72.5, 72.4, 71.9, 71.1, 70.8, 69.4, 68.7, 65.9, 62.4, 34.3, 34.2, 34.1, 34.0, 31.8, 31.4, 31.3, 29.2, 29.1, 25.2, 24.6, 24.50, 24.45, 22.7, 22.41, 22.39, 14.2, 14.03, 13.98, 13.96; MS-ESI *m/z:* 1215.7 $[M + H]^+$, 1237.8 $[M + Na]^+$; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{73}H_{99}O_{15}$: 1215.6978, Found: 1215.7012.

*D-Mannitol-1-yl 2-O-octanoyl-3,4,6-tri-O-hexanoyl-β-D-mannopyranoside (**acremomannolipin A**).* **17** (78 mg, 64 μmol, 1 equiv) was dissolved in MeOH/EtOH (v/v = 1/1, 4 mL), and then 20% of $Pd(OH)_2$/C (100 mg) was added to the mixture. The reaction vessel was evacuated and backfilled with nitrogen (three times), then backfilled with hydrogen (1 atm). The mixture was stirred at room temperature for 48 h. The mixture was filtered through a pad of Celite. The filtrate was concentrated and the residue was purified by silica gel column chromatography (CH_2Cl_2/MeOH 15:1) to afford **acremomannolipin A** (41 mg, 53.6 μmol, 83%) as a colorless syrup. $[\alpha]_D^{23} = -29.5$ (*c* 0.96, MeOH); ^{1}H NMR (500 MHz, CD_3OD) δ 5.52 (d, *J* = 2.8 Hz, 1H), 5.31 (t, *J* = 10.0 Hz, 1H), 5.17 (dd, *J* = 10.1, 3.1 Hz, 1H), 4.93 (s, 1H), 4.29 (dd, *J* = 12.3, 4.1 Hz, 1H), 4.18−4.12 (m, 2H), 3.86−3.66 (m, 7H), 3.63−3.61 (m, 1H), 2.50−2.28 (m, 6H), 2.21 (t, *J* = 7.4 Hz, 2H), 1.72−1.63 (m, 4H), 1.60−1.54 (m, 4H), 1.43−1.25 (m, 20H), 0.99−0.85 (m, 12H); ^{13}C NMR (125 MHz, CD_3OD) δ 175.0, 174.8, 173.9, 173.8, 100.5, 73.7, 73.4, 72.9, 72.7, 71.7, 71.1, 71.0, 70.5, 66.8, 65.2, 63.0, 35.2, 35.0, 34.9, 34.8, 33.0, 32.44, 32.35, 32.3, 30.3, 30.2, 26.4, 25.61, 25.58, 25.45, 23.8, 23.41, 23.38, 23.36, 14.5, 14.3, 14.2; MS-ESI *m/z:* 787.6 $[M + Na]^+$; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{38}H_{68}O_{15}Na$: 787.4450, Found: 787.4468.

*2,3,4,5,6-Penta-O-benzyl-D-mannitol-1-yl 2-O-octanoyl-3-O-(2-methylnaphthyl)-6-O-benzoyl-β-D-mannopyranoside (**18**).* Benzoyl chloride (91 μL, 0.78 mmol, 6 equiv) was added dropwise to a solution of **15** (138 mg, 0.13 mmol, 1 equiv) in dry collidine/CH_2Cl_2 (v/v = 1/2, 3 mL) at −20 °C. The reaction mixture was allowed to warm to room temperature and stirred for 4 h and then diluted with CH_2Cl_2 (30 mL). The mixture was sequentially washed with 1 M aqueous HCl, saturated aqueous $NaHCO_3$, and brine. The collected organic phase was dried over Na_2SO_4, filtered, and concentrated. The resultant residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate 4:1 to 3:1) to provide **18** (125 mg, 0.11 mmol, 83%) as a colorless syrup. $[\alpha]_D^{24} = -27.82$ (*c* 1.02, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.2 Hz, 2H), 7.82−2.78 (m, 4H), 7.53−7.41 (m, 4H), 7.36−7.18 (m, 27H), 5.62 (s, 1H), 4.86 (d, *J* = 11.3 Hz, 1H), 4.71 (d, *J* = 11.7 Hz, 1H), 4.68−4.56 (m, 7H), 4.54−4.42 (m, 6H), 4.31 (d, *J* = 10.6 Hz, 1H), 3.94 (s, 1H), 3.90−3.77 (m, 6H), 3.72−3.67 (m, 1H), 3.48−3.45 (m, 1H), 3.39−3.37 (m, 1H), 2.38−2.32 (m, 3H), 1.60−1.58 (m, 2H), 1.26−1.11 (m, 8H), 0.81 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.3, 166.8, 139.0, 138.9, 138.7, 138.6, 138.4, 134.8, 133.4, 133.2, 133.1, 130.0, 129.9, 128.5, 128.44, 128.41, 128.39, 128.37, 128.3, 128.1, 128.0, 127.9, 127.84, 127.82, 127.76, 127.66, 127.60,

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127.55, 127.5, 127.4, 127.3, 126.3, 126.2, 126.13, 126.05, 99.9, 79.9, 79.8, 79.5, 79.3, 79.0, 74.4, 74.3, 74.2, 73.4, 72.4, 71.9, 71.5, 70.8, 69.5, 67.2, 66.8, 63.9, 34.4, 31.7, 29.1, 29.0, 25.2, 22.7, 14.2; MS-ESI *m/z:* 1165.9 $[M + H]^+$, 1187.9 $[M + Na]^+$, 1204.9 $[M + K]^+$; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{73}H_{81}O_{13}$: 1165.5672, Found: 1165.5704, $[M + Na]^+$ Calcd for $C_{73}H_{80}O_{13}Na$: 1187.5491, Found: 1187.5524.

*2,3,4,5,6-Penta-O-benzyl-D-mannitol-1-yl 2-O-octanoyl-3-O-(2-methylnaphthyl)-4-O-hexanoyl-6-O-benzoyl-β-D-mannopyranoside (**19**).* According to the protocol for the conversion of **15** into **18**, **18** (100 mg, 85.8 μmol, 1 equiv) was treated with *n*-hexanoyl chloride (72 μL, 0.52 mmol, 6 equiv) to provide **19** (106 mg, 83.9 μmol, 98%) as a colorless syrup after separation on silica gel column chromatography (petroleum ether/ethyl acetate 8:1). $[\alpha]_D^{22} = -14.9$ (*c* 0.95, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.4 Hz, 2H), 7.83−7.78 (m, 3H), 7.69 (s, 1H), 7.52−7.42 (m, 3H), 7.38−7.09 (m, 28H), 5.63 (d, *J* = 2.6 Hz, 1H), 5.35 (t, *J* = 9.8 Hz, 1H), 4.79 (d, *J* = 12.3 Hz, 1H), 4.70−4.57 (m, 6H), 4.51−4.40 (m, 7H), 4.29 (d, *J* = 10.9 Hz, 1H), 4.24 (dd, *J* = 12.0, 5.3 Hz, 1H), 3.92 (t, *J* = 4.1 Hz, 1H), 3.86−3.75 (m, 5H), 3.70−3.66 (m, 1H), 3.57−3.53 (m, 1H), 3.50 (dd, *J* = 9.7, 3.1 Hz, 1H), 2.42−2.34 (m, 2H), 2.23 (t, *J* = 7.6 Hz, 2H), 1.63−1.55 (m, 4H), 1.27−1.13 (m, 12H), 0.81 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.4, 172.6, 166.3, 139.0, 138.6, 135.0, 133.1, 130.1, 129.9, 128.5, 128.44, 128.41, 128.34, 128.25, 128.1, 128.0, 127.9, 127.82, 127.79, 127.69, 127.66, 127.59, 127.53, 127.48, 126.7, 126.3, 126.1, 125.8, 99.8, 79.9, 79.8, 79.3, 79.0, 74.4, 73.5, 72.5, 72.0, 71.1, 71.0, 69.5, 67.7, 67.3, 63.5, 34.4, 34.3, 31.8, 31.4, 29.2, 29.1, 25.2, 24.6, 22.7, 22.4, 14.2, 14.0; MS-ESI *m/z:* 1264.0 $[M + H]^+$, 1286.0 $[M + Na]^+$, 1302.0 $[M + K]^+$; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{79}H_{91}O_{14}$: 1263.6403, Found: 1263.6432, $[M + NH_4]^+$ Calcd for $C_{79}H_{94}O_{14}N$: 1280.6669, Found: 1280.6703.

*2,3,4,5,6-Penta-O-benzyl-D-mannitol-1-yl 2-O-octanoyl-4-O-hexanoyl-6-O-benzoyl-β-D-manno-pyranoside (**20**).* To a solution of **19** (220 mg, 0.17 mmol, 1 equiv) in acetonitrile/H_2O (9/1, 15 mL) was added CAN (500 mg, 2.27 mmol, 13 equiv). The resulting mixture was stirred at 30 °C and the progress of reaction was monitored by TLC. After 5 h, the mixture was diluted with CH_2Cl_2 and sequentially washed with saturated aqueous $NaHCO_3$ and brine. The collected organic layer was dried over Na_2SO_4, filtered, and concentrated. The resultant residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 6:1 to 4:1) to provide **20** (131 mg, 0.12 mmol, 67%) as a colorless syrup. $[\alpha]_D^{16} = -10.43$ (*c* 0.83, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.5 Hz, 2H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.29−7.20 (m, 25H), 5.38 (d, *J* = 2.6 Hz, 1H), 5.15 (t, *J* = 9.6 Hz, 1H), 4.72−4.55 (m, 6H), 4.56−4.44 (m, 5H), 4.39 (d, *J* = 11.7 Hz, 1H), 4.34 (dd, *J* = 11.9, 5.0 Hz, 1H), 4.28 (d, *J* = 10.9 Hz, 1H), 3.91 (t, *J* = 4.1 Hz, 1H), 3.89−3.87 (m, 1H), 3.85−3.66 (m, 6H), 3.65−3.62 (m, 1H), 2.38−2.31 (m, 4H), 1.65−1.57 (m, 4H), 1.28−1.22 (m, 12H), 0.89−0.84 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.3, 173.4, 166.2, 138.94, 138.90, 138.7, 138.6, 138.4, 133.2, 129.8, 128.49, 128.46, 128.42, 128.38, 128.34, 128.1, 127.88, 127.85, 127.78, 127.73, 127.67, 127.57, 127.52, 127.49, 99.6, 79.73, 79.69, 79.3, 79.0, 74.4, 74.3, 73.5, 72.3, 72.2, 71.9, 71.6, 71.0, 70.5, 69.8, 69.5, 63.4, 34.4, 34.3, 31.8, 31.3, 29.2, 29.0, 25.1, 24.6, 22.7, 22.4, 14.2, 14.0; MS-ESI *m/z:* 1123.9 $[M + H]^+$, 1145.9 $[M + Na]^+$, 1161.9 $[M + K]^+$; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{68}H_{83}O_{14}$: 1123.5777, Found: 1123.5803, $[M + Na]^+$ Calcd for $C_{68}H_{82}O_{14}Na$: 1145.5597, Found: 1145.5630.

*2,3,4,5,6-Penta-O-benzyl-D-mannitol-1-yl 2-O-octanoyl-3-O-lauroyl-4-O-hexanoyl-6-O-benzoyl-β-D-mannopyranoside (**21**).* According to the protocol for the conversion of **15** into **18**, **20** (60 mg, 53.4 μmol, 1 equiv) was esterified with lauroyl chloride (47 μL, 0.214 mmol, 4 equiv) to provide **21** (64 mg, 49.0 μmol, 92%) as a colorless syrup which was eluted with petroleum ether/ethyl acetate 8:1 when purified by silica gel column chromatography. $[\alpha]_D^{15} = -4.6$ (*c* 0.5, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.3 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.32−7.20 (m, 25H), 5.49 (d, *J* = 3.1 Hz, 1H), 5.41 (t, *J* = 10.0 Hz, 1H), 5.03 (dd, *J* = 10.1, 3.2 Hz, 1H), 4.68−4.56 (m, 6H), 4.54 (s, 1H), 4.50−4.43 (m, 4H), 4.38 (d, *J* = 11.6 Hz, 1H), 4.32−4.25 (m, 2H), 3.91 (t, *J* = 4.2 Hz, 1H), 3.88−3.85 (m, 1H), 3.85−3.78 (m, 3H), 3.75 (t, *J* = 5.4 Hz, 1H), 3.71−3.67 (m, 1H), 3.66−3.62 (m, 1H), 2.38−2.33 (m, 2H), 2.27−2.17 (m, 4H), 1.66−1.53 (m, 6H), 1.32−1.19 (m, 28H), 0.90−0.86 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.0, 172.7, 172.5, 166.2, 138.8, 138.74, 138.69, 138.61, 138.4, 133.2, 130.0, 129.9, 128.5, 128.43, 128.40, 128.36, 128.34, 128.1, 128.0, 127.9, 127.81, 127.78, 127.7, 127.6, 127.5, 99.3, 79.7, 79.3, 79.0, 74.43, 74.35, 73.4, 72.42, 72.37, 71.9, 71.1, 70.7, 69.5, 68.8, 66.3, 63.2, 34.3, 34.2, 32.1, 31.9, 31.3, 29.78, 29.76, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 25.2, 24.8, 24.7, 22.82, 22.75, 22.4, 14.3, 14.2, 14.0; MS-ESI *m/z:* 1306.1 $[M + H]^+$, 1328.0 $[M + Na]^+$, 1344.0 $[M + K]^+$; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{80}H_{105}O_{15}$: 1305.7448, Found: 1305.7476, $[M + NH_4]^+$ Calcd for $C_{80}H_{108}O_{15}N$: 1322.7713, Found: 1322.7745.

*D-Mannitol-1-yl 2-O-octanoyl-3-O-lauroyl-4-O-hexanoyl-6-O-benzoyl-β-D-mannopyranoside (**22**).* According to the protocol for the conversion of **17** into **acremomannolipin A**, **21** (92 mg, 70.5 μmol, 1 equiv) was globally debenzylated by hydrogenolysis to afford **22** (53 mg, 62.0 μmol, 88%) by flash chromatography (CH_2Cl_2/MeOH 14:1) as a colorless syrup. $[\alpha]_D^{19} = -14.64$ (*c* 1.25, MeOH); ^1H NMR (500 MHz, CD_3OD) δ 8.06 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 2H), 5.54 (d, *J* = 2.8 Hz, 1H), 5.48 (t, *J* = 10.1 Hz, 1H), 5.21 (dd, *J* = 10.1, 3.2 Hz, 1H), 4.99 (s, 1H), 4.56 (dd, *J* = 12.3, 2.2 Hz, 1H), 4.40 (dd, *J* = 12.3, 4.0 Hz, 1H), 4.16 (dd, *J* = 10.7, 2.5 Hz, 1H), 4.00−3.97 (m, 1H), 3.82−3.68 (m, 5H), 3.68−3.64 (m, 1H), 3.62−3.58 (m, 1H), 2.47−2.27 (m, 4H), 2.25−2.19 (m, 2H), 1.70−1.63 (m, 2H), 1.58−1.52 (m, 4H), 1.40−1.23 (m, 28H), 0.95−0.83 (m, 9H); ^{13}C NMR (125 MHz, CD_3OD) δ 174.7, 173.83, 173.79, 167.5, 134.4, 131.2, 130.8, 129.6, 100.5, 73.7, 73.5, 73.0, 72.8, 71.7, 71.2, 71.0, 70.5, 67.0, 65.2, 63.7, 35.3, 35.0, 34.9, 33.1, 33.0, 32.3, 30.8, 30.74, 30.73, 30.63, 30.59, 30.5, 30.4, 30.24, 30.20, 26.4, 25.8, 25.7, 23.8, 23.7, 23.4, 14.50, 14.45, 14.2; MS-ESI *m/z:* 877.7 $[M + Na]^+$, 893.8 $[M + K]^+$; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{45}H_{75}O_{15}$: 855.5100, Found: 855.5114, $[M + NH_4]^+$ Calcd for $C_{45}H_{78}O_{15}N$: 872.5366, Found: 872.5385.

■ ASSOCIATED CONTENT

Supporting Information

^1H and ^{13}C NMR spectra for all compounds; NMR data for the chemical shift of H5 and the $^1J_{C,H}$ coupling to assign anomeric stereochemistry in the mannose system. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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