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Synthesis of DTPA-conjugated (1,4)-linked 2-aminoglycosides varying in the anomeric configuration and their MRI contrast effect†

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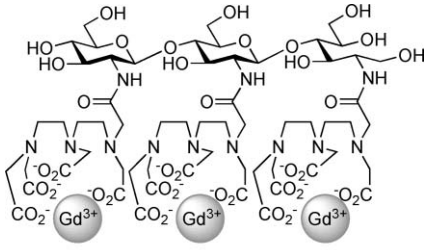
Received 3rd June 2005, Accepted 29th June 2005
First published as an Advance Article on the web 1st August 2005

We describe the efficient synthesis of DTPA-conjugated oligosaccharides composed of α- and/or β-linked tri to monoglucosamines. Gd(III) complex with DTPA-conjugated chitotriitol **1** has been reported to be an effective MRI contrast agent. In order to elucidate the structure–property relationships, we planned to synthesize the DTPA-conjugated 2-amino-tri-, di-, and monosaccharides varying in configuration at the anomeric positions and the C2 position on the reducing end. Our strategy for the synthesis of the DTPA-conjugated oligosaccharides involves *O*-perbenzyl protected 2-amino-tri-, di-, and monosaccharides as key intermediates. The 2-aminoglycosides were prepared by non-selective glycosidation of 2-azido-2-deoxyglycosyl donors, followed by separation of two anomeric isomers. Although the synthesis involves separation of the stereoisomers, it circumvents not only the careful tuning of reaction conditions, but also the time-consuming preparation of glycosyl donors attached to different protecting groups. The protected 2-aminoglycosides were converted to the fully deprotected DTPA-conjugated tri- to monosaccharides by the same operation. MRI phantom study using the Gd(III) complexes of DTPA-conjugated oligosaccharides indicates that the number of the monosaccharide units was critical for enhancing the relative signal intensity of water protons per Gd, and various stereoisomers would be candidate scaffolds for MRI contrast agents.

Introduction

Chitin is composed of poly-β(1,4) *N*-acetylglucosamine, and is a skeletal material in crustaceans. Hydrolysis of the acetamide groups in chitin under basic conditions provides chitosan, which possesses amino groups. Recently, chitosan has served as an effective biocompatible scaffold[1–3] amenable to conjugation with various functional devices *via* acylation of the C2 amino groups.[3] Acidic hydrolysis of the glycosidic bonds on chitosan, followed by reduction of the resulting hemiacetal to diol enables one to prepare oligo-β(1,4) *N*-acetylglucosamines as structurally-defined and water-soluble scaffolds. Additionally, the reduction is effective for improvement of their hydrophilicity. However, these degradation processes can unfortunately involve anomerization to the thermodynamically more stable α-glycosidic bond, and epimerization of the C2 amino group at the reducing end, thereby providing several stereoisomers, of which the purification and structure determination are difficult. Additionally, in most cases, there is limited information on their structure–property relationships because the stereoisomers of the chitosan derivatives are not available from natural sources.

Magnetic resonance imaging (MRI) is a powerful and non-invasive diagnostic technique based on the differences between relaxation rate of water protons, and provides important graphical images of the inside of the human body.[4] MRI contrast agents such as gadolinium–diethylenetriamine-*N*,*N*,*N*′,*N*″,*N*″-pentaacetic acid complexes (Gd–DTPA) assist improvement of the tissue discrimination in the MRI images. Recently, CH_3-DTPA–Gd (**1**) composed of a chitotriitol attached with three Gd–DTPA units on the amino groups, has been reported as an effective MRI contrast agent (Fig. 1).[5,6] The proton relaxivity per Gd of **1** is $R_1 = 8.3$ $(mMs)^{-1}$ at 37 °C in water at 1.5 T, which is twice as great as that of Gd–DTPA ($R_1 = 3.1$ $(mMs)^{-1}$). This result suggested us that linking multiple Gd–DTPA units with the various hydrophilic scaffolds such as the chitosan hydrolysates would be an effective way for the synthesis



CH3-DTPA-Gd (**1**)

Fig. 1 Structure of CH_3-DTPA–Gd (**1**).

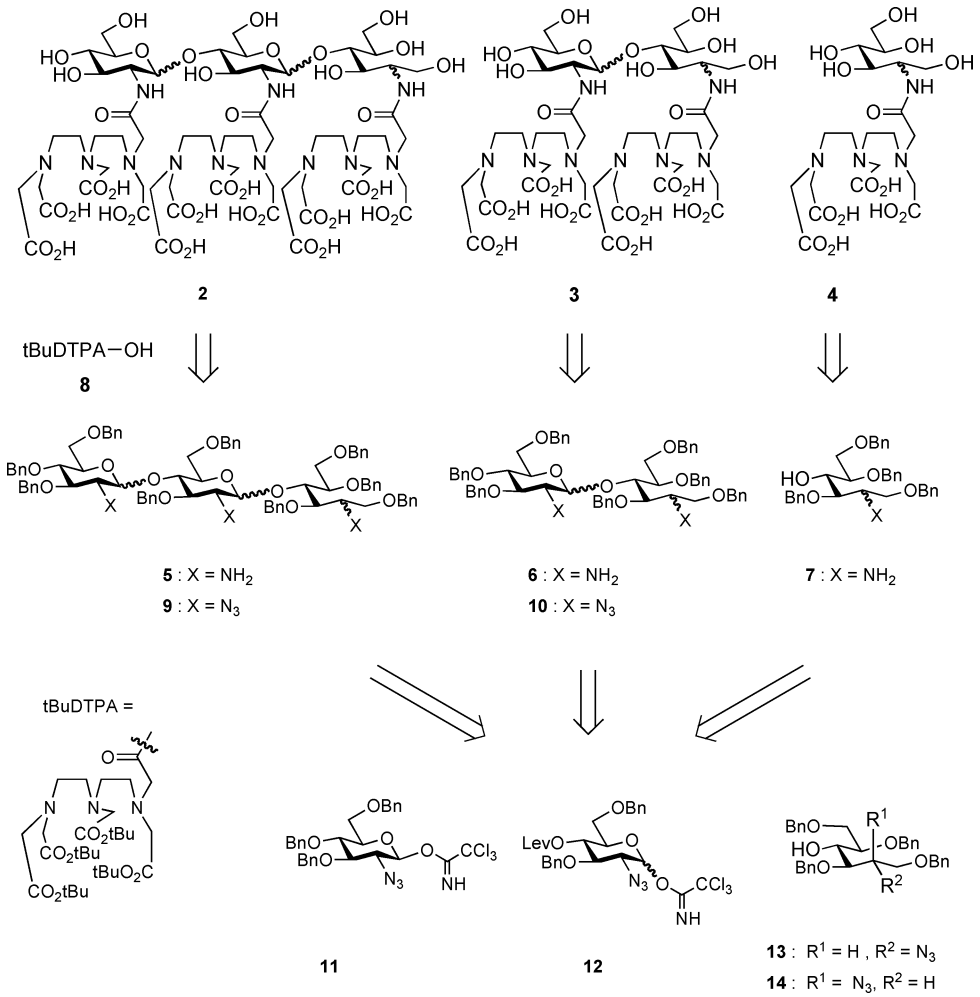
of effective MRI contrast agents. Additionally, in order to elucidate their structure–property relationships and confirm the purity of the final product, the total chemical synthesis of the 2-aminooligosaccharides varying in configuration at the anomeric position and the C2 position on the reducing end is required. Herein, we report an efficient synthesis of DTPA-conjugated oligosaccharides and their application as MRI contrast agents.

Results and discussion

We planned the synthesis of fourteen DTPA-conjugated oligosaccharides: eight trisaccharides **2**, four disaccharides **3** and two monosaccharides **4**, each varying in configuration at the anomeric positions and the C2 position at the reducing end (Scheme 1). Our strategy for the synthesis of the DTPA-conjugated oligosaccharides **2**, **3**, and **4** involves the perbenzyl protected amino glycosides **5**, **6**, and **7** as key intermediates. Acylation of the amines **5**, **6**, and **7** with the *tert*-butyl protected DTPA mono acid **8**,[7] followed by deprotection of all protecting groups provides the DTPA-conjugated oligosaccharides **2**, **3** and **4**. The intermediates **5**, **6**, and **7** would be prepared by non-stereoselective glycosylation of alditols **13** and **14** with the 2-azido glycosyl imidates **11** and **12**,[8] followed by chemoselective reduction of the azido groups. Although this methodology involves separation of the stereoisomers, it circumvents not only the careful tuning reaction conditions, but also time-consuming preparation of the glycosyl donors attached to

† Electronic supplementary information (ESI) available: NMR spectra. See http://dx.doi.org/10.1039/b507824e

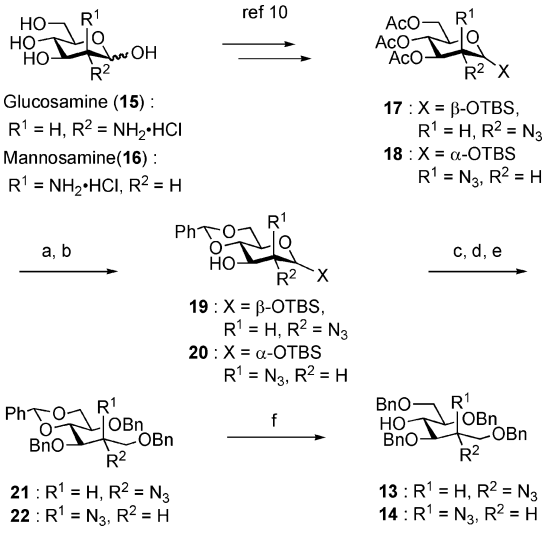
DOI: 10.1039/b507824e



Scheme 1 Strategy for the synthesis of the DTPA-conjugated amino glycosides **2**, **3**, and **4**.

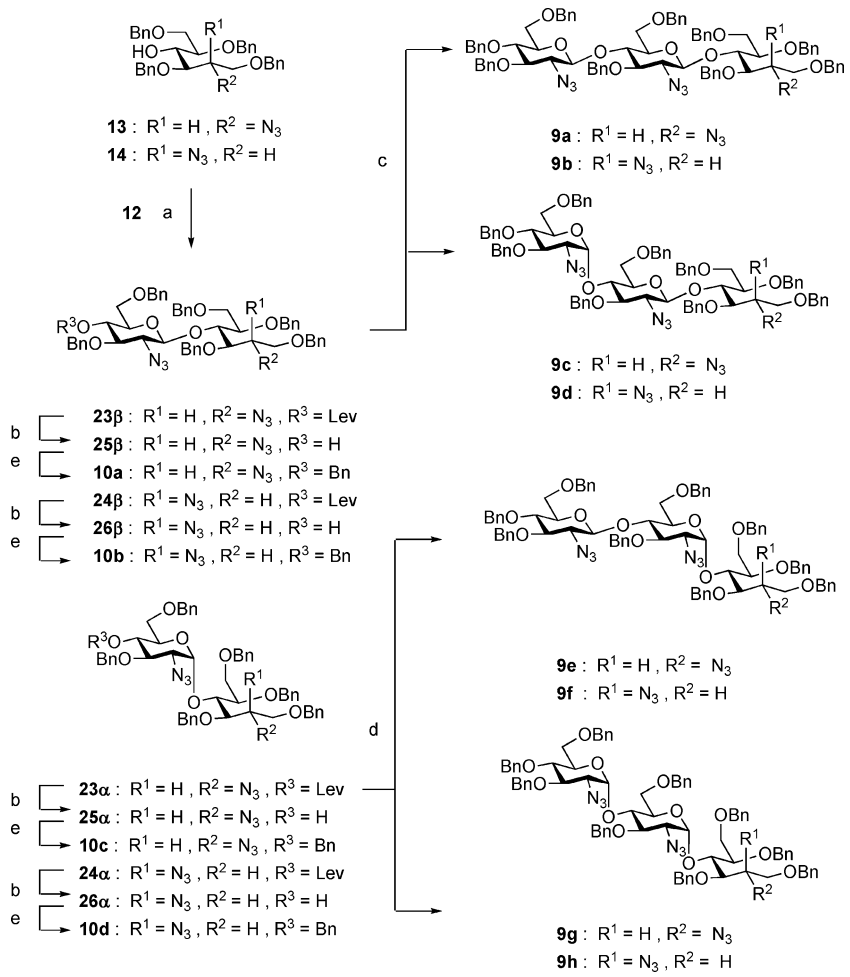
different protecting groups.[9] Furthermore, transformation of the resultant protected glycosides **9**, **10**, **13**, and **14** to the corresponding amino glycosides **5**, **6**, and **7** can be achieved by the same operation.

Preparation of the protected alditols **13** and **14** is shown in Scheme 2. The 2-azido glucoside **17** was prepared from glucosamine (**15**) by the established procedure.[10] Deacetylation of **17**, and formation of 4,6-benzyliden acetal provided acetal **19**. Selective removal of the silyl ether of **19**, followed by reduction of the anomeric position afforded triol. Protection of the resulting hydroxyl groups with benzyl ethers provided **21** in 91% yield from **17**. Regioselective reductive opening of the benzyliden acetal **21** provided acceptor **13** in 75% yield. The Manno derivative **14** was prepared from mannosamine (**16**)[10] by the same procedure.



Scheme 2 Reagents and conditions: (a) NaOMe, MeOH; (b) PhCH-(OMe)$_2$, *p*-TsOH, MeCN, 96% for **19**; (c) HF–Py., Py.; (d) $NaBH_4$, THF, EtOH; (e) BnBr, NaH, TBAI, DMF, 91% for **21**, 88% for **22**; (f) TFA, Et_3SiH, CH_2Cl_2, 75% for **13**, 89% for **14**.

The synthesis of amines **5**, **6**, and **7** was conducted as shown in Scheme 3. Glycosylation of **13** with imidate **12** using TMSOTf in several solvents (CH_2Cl_2, Et_2O, CH_3CN, and toluene) at −25 °C revealed that toluene was able to provide a mixture of disaccharides **23** in 68% yield (β : α = 47 : 53). Glycosylation of **14** with **12** under the same reaction conditions provided disaccharides **24** in 61% yield (β : α = 61 : 39), respectively. Deprotection of Lev group of **23** and **24**, followed by separation of the β- and α-isomers afforded the corresponding disaccharides **25β** and **25α**, and **26β** and **26α** in 43 and 48%, and 33 and 25% yields based on **23** and **24**, respectively. Glycosylation of the α-linked disaccharide **25α** and **26α** with donor **11** in toluene provided trisaccharides **9e** and **9g** in 80% yield (β : α = 50 : 50), and **9f** and **9h** in 90% (β : α = 42 : 58). Separation of the mixtures by column chromatography on silica gel provided trisaccharides **9e**, **9g**, **9f**, and **9h** in 31, 43, 34, and 47% yields, based on disaccharides **25α** and **26α**, respectively. Glycosylation of the β-linked disaccharide **25β** with donor **11** under the same reaction condition, unfortunately provided the β-isomer **9a** as the major product (81% yield, β : α = 79 : 21). After optimization of the reaction conditions, we found that diethylether was effective for the synthesis of a mixture of both isomers to provide trisaccharides **9a** and **9c** in 83% yield (β : α = 52 : 48) from **25β**, and **9b** and **9d** in 70% (β : α = 59 : 41) from **26β**. Separation of the β- and α-isomers by chromatography on silica gel provided



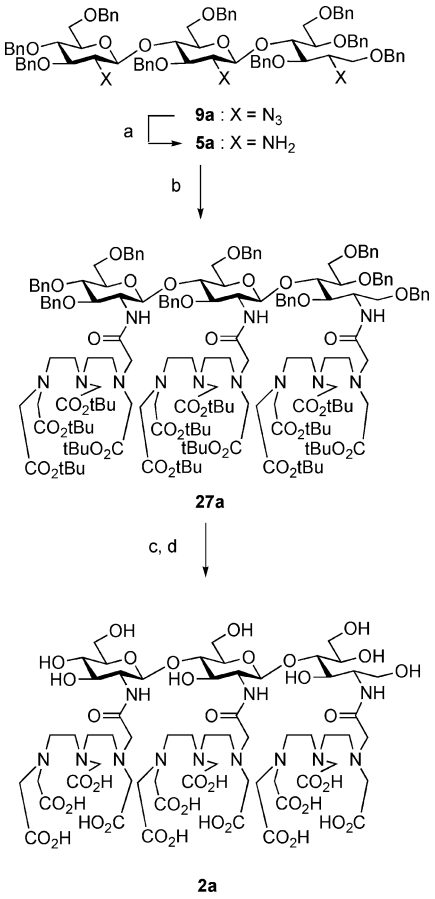
Scheme 3 Reagents and conditions: (a) TMSOTf, toluene, MS 4 Å, −25 °C, 68% (β : α = 47 : 53) for **25**, 61% (β : α = 61 : 39) for **26**; (b) H_2NNH_2–H_2O, AcOH, Py, rt, 43% for **25β**, 48% for **25α** from **23**, 33% for **26β**, 25% for **26α** from **24**; (c) TMSOTf, Et_2O, MS 4 Å −25 °C, 34% for **9a**, 40% for **9b**, 46% for **9c**, 28% for **9d**; (d) TMSOTf, toluene, MS 4 Å, −25 °C, 31% for **9e**, 34% for **9f**, 43% for **9g**, and 47% for **9h**; (e) BnBr, NaH, TBAI, DMF, 93% for **10a**, 71% for **10b**; 95% for **10c**, 83% for **10d**.

trisaccharides **9a**, **9c**, **9b**, and **9d** in 34, 46, 40, and 28% yields, respectively. The disaccharides **10a**–**d** bearing azido groups were prepared by benzylation of alcohols **25α**, **25β**, **26α**, and **26β** in excellent yields.

Next, we investigated the transformation of the protected oligosaccharides **9**, **10**, **13**, and **14** to DTPA-conjugates **2**, **3**, and **4** (Scheme 4, and Table 1). Treatment of the azido **9a** with trimethylphosphine[11] resulted in reduction to the corresponding amine **5a**. Tributyl- and triphenylphosphines were not effective for the reduction. Acylation of the crude **5a** with tBuDTPA-OH **8** using HATU smoothly proceeded to provide the corresponding DTPA conjugate **27a** in 58% yield in 2 steps. Finally, deprotection of the *tert*-butyl ester with TFA in the presence of Et_3SiH,[12] followed by hydrogenolysis in the presence of $Pd(OH)_2$ under H_2 afforded the fully deprotected product **2a**. It should be noted that the order of the removal of the protecting groups was critical for the success of the deprotection. Purification of the crude **2a** was achieved by reverse-phase HPLC to afford the fully deprotected DTPA-conjugated oligosaccharide **2a** in 23% yields. Transformation of azidos **9b**–**h**, **10a**–**d**, **13**, and **14** to the DTPA-conjugated oligosaccharides **2b**–**h**, **3a**–**d**, **4a**–**b** was achieved by the same procedure to provide the desired compounds **2b**–**h**, **3a**–**d**, and **4a**–**b** in moderate yields (Table 1 and Fig. 2).

Table 1 Yields of protected DTPA-conjugates **27**, **28**, and **29**, and DTPA-conjugates **2**, **3**, and **4**

Entry	Azido	Protected DTPA-conjugate	Yield of **27**, **28**, **29** (%)	DTPA-conjugate	Yield of **2**, **3**, **4** (%)
1	**9a**	**27a**	58%	**2a**	23%
2	**9b**	**27b**	71%	**2b**	36%
3	**9c**	**27c**	47%	**2c**	40%
4	**9d**	**27d**	46%	**2d**	33%
5	**9e**	**27e**	69%	**2e**	24%
6	**9f**	**27f**	81%	**2f**	30%
7	**9g**	**27g**	59%	**2g**	21%
8	**9h**	**27h**	78%	**2h**	36%
9	**10a**	**28a**	78%	**3a**	15%
10	**10b**	**28b**	80%	**3b**	28%
11	**10c**	**28c**	73%	**3c**	34%
12	**10d**	**28d**	77%	**3d**	20%
13	**13**	**29a**	73%	**4a**	38%
14	**14**	**29b**	74%	**4b**	43%



Scheme 4 Reagents and conditions: (a) PMe_3, toluene, 0.1 M NaOH aq.; (b) HATU, DIEA DMAP, CH_2Cl_2; (c) TFA, Et_3SiH, CH_2Cl_2; (d) $Pd(OH)_2$, H_2, EtOAc, MeOH, H_2O.

MRI examination

MRI phantom studies using the Gd(III) complexes with the DTPA-conjugated oligosaccharides **2a**–**h**, **3a**–**d** and **4a**–**b** were investigated. DTPA was used as a reference ligand for the MRI study. 0.46 mM aqueous solutions of $GdCl_3$ containing two equivalents of DTPA units on each oligosaccharides **2a**–**h**, **3a**–**d** and **4a**–**b** were prepared. Free gadolinium ions were not detected in these solutions. MRI images of each Gd complex solution with DTPA-conjugated oligosaccharides were obtained using spin echo (SE) sequence, where repetition time/echo time = 60 ms/10.3 ms, acquisition matrix = 256 × 256, number of excitations = 16, field of view = 40 mm × 40 mm, slice thickness = 5 mm, receiver band width = 50 kHz (Fig. 3 and Table 2). Table 3 summarizes the relative signal intensity per Gd in the regions of interest (ROI) based on Gd-DTPA. The relative signal intensities of the trisaccharides **2a**–**h** solution were larger than those of di- and mono-saccharides **3a**–**d** and **4a**–**b** solution. However, there were no significant differences between the stereoisomers **2a**–**h**. These results clearly indicate that the number of monosaccharide units is critical for the signal enhancement ability per Gd. However, the shape of the saccharide scaffolds did not largely influence this ability.

Conclusion

In summary we have demonstrated the efficient synthesis of triaminoglycosides **2a**–**h** attached with DTPA as MRI contrast agents. All possible anomeric isomers were prepared by non-stereoselective glycosidation of 2-azido glycosyl donors, followed by separation of the β- and α-isomers. MRI phantom studies to elucidate the signal enhancing ability of their Gd complexes, revealed that the number of the monosaccharide units was critical for enhancing the relative signal intensity per Gd, and various stereoisomers could be candidate scaffolds for MRI contrast agents. We plan to further study new biocompatible and functional materials using the aminoglycoside scaffolds for biomedical applications.

Table 2 Signal intensities of Gd containing DTPA-conjugated oligosaccharide solution using SE sequence

Compound	Signal intensity (×10⁶)	Standard division (×10⁶)
3a	7.92	0.52
3c	7.53	0.52
4a	6.82	0.52
Gd–DTPA	6.00	0.52
3b	7.97	0.52
3d	7.84	0.51
4b	6.69	0.53
Gd–DTPA	5.88	0.54
2a	8.79	0.53
2c	8.78	0.53
2e	8.17	0.53
2g	8.34	0.51
Gd–DTPA	6.06	0.51
2b	8.82	0.54
2d	8.50	0.53
2f	8.37	0.52
2h	8.78	0.53
Gd–DTPA	6.01	0.51

Experimental section

General

NMR spectra were recorded on a JEOL Model ECP-400 (400 MHz for ^1H, 100 MHz for ^{13}C) instrument in the indicated solvent. Chemical shifts are reported in units parts per million (ppm) relative to the signal (0 ppm) for internal tetramethylsilane for solutions in $CDCl_3$. ^1H NMR spectrum data are reported as follows: $CDCl_3$ (7.26 ppm) or D_2O (HOD (4.8654 ppm at 285 K, 4.7015 ppm at 303 K, 4.6201 ppm at 311 K, 4.3560 ppm at 339 K as internal standard using 3-(trimethylsilyl)-1-propanesulfonicacid sodium salt as external standard)). ^{13}C NMR spectrum data are reported as follows: $CDCl_3$ (77.0 ppm) or acetone-d_6 (30.3 ppm) as internal standard for D_2O. Multiplicities are reported by using the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad; *J*, coupling constants in Hertz. IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrophotometer. Only the strongest and/or structurally important peaks are reported as the IR data given in cm^{-1}. Optical rotations were measured on a JASCO model P-1020 polarimeter. All reactions were monitored by thin-layer chromatography carried out on 0.2 mm E. Merck silica gel plates (60F-254) with UV light, visualized by 10% ethanolic phosphomolybdic acid, *p*-anisaldehyde solution or 0.5% ninhydrin *n*-butanol solution. Kanto silica gel was used for column chromatography. Fuji silysia chemical NH–silica gel was used for column chromatography. Gel permeation chromatography (GPC) for qualitative analysis were performed on Japan Analytical Industry Model LC908 (recycling preparative HPLC), on a Japan Analytical Industry Model RI-5 refractive index detector and on a Japan Analytical Industry Model 310 ultra violet detector with a polystyrene gel column (JAIGEL-1H, 20mm × 600 mm), using chloroform as solvent (3.5 mL min^{-1}). High performance liquid chromatography (HPLC) was performed on a Waters apparatus using a Senshu Pak Silica 3301-N Column with a Waters 2996 photodiode array detector at 254 nm. ESI-TOF Mass spectra were measured with P. E. Biosystems TK-3500 Biospectrometry Workstation. High performance liquid chromatography

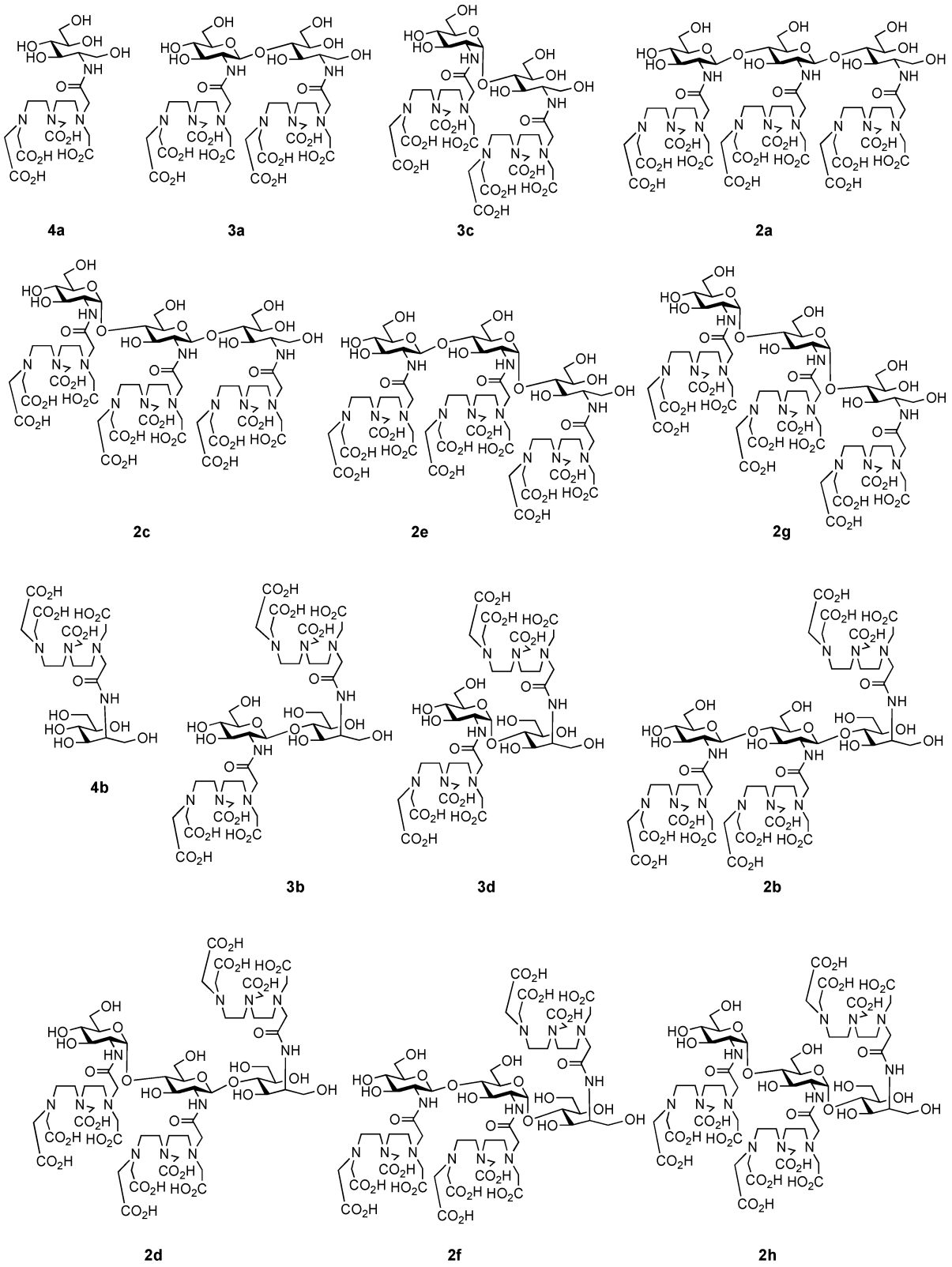


Fig. 2 Structure of the DTPA-conjugated oligosaccharides **2**, **3**, and **4**.

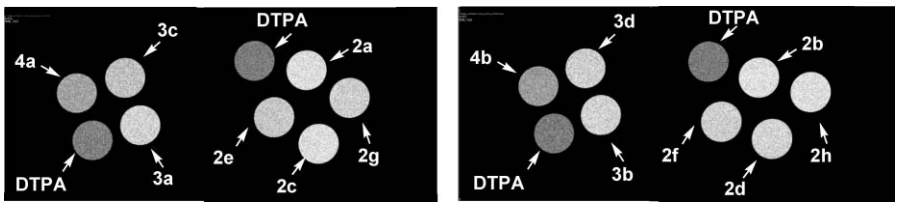


Fig. 3 MRI phantom images and signal intensities of Gd containing DTPA-conjugated oligosaccharide solution using SE sequence.

Table 3 Relative signal intensity per Gd based on Gd–DTPA

Entry	DTPA derivative	Relative signal intensity per Gd based on Gd–DTPA	Mean ± SD
1	**2a**	1.45	1.42 ± 0.04[a,d]
2	**2b**	1.47	—
3	**2c**	1.45	—
4	**2d**	1.41	—
5	**2e**	1.35	—
6	**2f**	1.39	—
7	**2g**	1.38	—
8	**2h**	1.46	—
9	**3a**	1.32	1.32 ± 0.04[b,e]
10	**3b**	1.36	—
11	**3c**	1.26	—
12	**3d**	1.33	—
13	**4a**	1.14	1.14[c]
14	**4b**	1.14	—
15	DTPA	1	1

[a] Trisaccharides **2a**–**h**. [b] Disaccharides **3a**–**d**. [c] Monosaccharides **4a**–**b**. [d] $p < 0.01$ *vs. b*. [e] $p < 0.005$ *vs c*.

(HPLC) for qualitative and quantitative analysis were performed on a Gilson 506C system using a Develosil® ODS-UG-5 column. Dry THF, dry hexane, and dry diethylether, were distilled from sodium were contained with a catalytic amount of benzophenone. Dry benzene, dry toluene, were distilled from a lump of sodium. Dry dichloromethane was distilled from P_2O_5. Dry DMF, dry triethylamine and dry pyridine were distilled from CaH_2. Dry methanol and dry ethanol were distilled from magnesium contained with a catalytic amount of iodine.

***tert*-Butyldimethylsilyl 2-azido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (19).** To a stirred solution of *tert*-butyldimethylsilyl 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-β-D-glucopyranoside (**17**) (20.0 g, 44.9 mmol) in MeOH (150 mL) was added sodium (50 mg) at room temperature. After being stirred at the same temperature for 3 h, the reaction mixture was concentrated *in vacuo* and azeotroped with toluene. The residue was used for the next reaction without further purification. To a stirred solution of the residue in dry CH_3CN (250 mL) was added benzaldehyde dimethyl acetal (10.1 mL, 67.4 mmol) and a catalytic amount of *p*-toluenesulfonic acid (200 mg) at room temperature. After being stirred at the same temperature for 2 h, the reaction mixture was neutralized with K_2CO_3 (18.7 g, 135 mmol) at the same temperature. After 30 min, the reaction mixture was filtered through a pad of celite and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel with hexane–ethyl acetate 80 : 20 to give *tert*-butyldimethylsilyl-2-azido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (**19**) (17.6 g, 43.2 mmol, 2 steps 96%) as a colorless oil. $[\alpha]_D^{27}$ −35.5 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.49 (m, 5H, aromatic), 5.52 (s, 1H, a), 4.63 (d, 1H, anomeric, $J = 7.2$ Hz), 4.28 (dd, 1H, $J = 4.8$ Hz, $J = 10.6$ Hz), 3.77 (dd, 1H, $J = 10.1$ Hz, $J = 10.1$ Hz), 3.61 (dd, 1H, $J = 9.2$ Hz, $J = 9.2$ Hz), 3.55 (dd, 1H, $J = 9.2$ Hz, $J = 9.2$ Hz), 3.39 (ddd, 1H, $J = 9.2$ Hz, $J = 9.7$ Hz), 3.32 (dd, 1H, $J = 7.7$ Hz, $J = 9.2$ Hz), 0.94 (s, 9H), 0.16, 0.17 (2s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.82, 129.35, 128.35, 126.26, 101.98, 97.52 (anomeric), 80.70, 71.72, 68.94, 68.51, 66.27, 25.23, 17.89, −4.38, −5.21; IR (KBr) 3403, 3038, 2930, 2860, 2109 (cm^{-1}).

***tert*-Butyldmethylsilyl 2-azido-4,6-*O*-benzylidene-2-deoxy-α-D-mannopyranoside (20).** According to the procedure for the synthesis of **19**, tetraacetate (**18**) (4.10 g, 9.20 mmol) was treated with NaOMe, which was prepared from sodium (10.0 mg) in MeOH (46 mL) to provide a tetraol. The tetraol was treated with benzaldehyde dimethyl acetal (2.07 mL, 13.8 mmol) in the presence of *p*-toluenesulfonic acid (40.0 mg) in CH_3CN (50 mL), followed by neutralization of the reaction mixture with K_2CO_3 (3.81 g, 27.6 mmol, 3.00 eq.) to provide acetal **20** (3.75 g, 9.20 mmol, quant in 2 steps.); $[\alpha]_D^{25}$ −101.4 (*c* 1.25, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.49 (m, 5H, aromatic), 5.52 (s, 1H), 4.96 (d, 1H, anomeric, $J = 1.4$ Hz), 4.27 (dd, 1H, $J = 4.8$ Hz, $J = 10.6$ Hz), 3.91 (dd, 1H, $J = 1.4$ Hz, $J = 3.9$ Hz), 3.84 (dd, 1H, $J = 3.9$ Hz, $J = 9.7$ Hz), 3.83 (dd, 1H, $J = 10.1$ Hz, $J = 10.6$ Hz), 3.70 (dd, 1H, $J = 9.7$ Hz, $J = 9.2$ Hz), 3.32 (ddd, 1H, $J = 9.2$ Hz, $J = 4.8$ Hz, $J = 10.1$ Hz), 0.94 (d, 9H), 0.16, 0.17 (2s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.97, 129.25, 128.30, 126.23, 102.11, 96.14 (anomeric), 78.40, 69.61, 68.32, 67.05, 66.33, 25.55, 17.90, −4.16, −5.46; IR (KBr) 3380, 3067, 2930, 2859, 2110 (cm^{-1}).

2-Azido-1,3,5-tri-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-D-glucitol (21). To a stirred solution of *tert*-butyldimethylsilyl 2-azido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (**19**) (1.39 g, 3.41 mmol) in dry pyridine (10 mL) was added hydrogen fluoride–pyridine (1.00 mL) at 0 °C. After being stirred at room temperature for 5 h, the reaction mixture was poured into ice-cooled saturated aq. $NaHCO_3$. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with saturated aq. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and evaporated *in vacuo*. The residue was used for the next reaction without further purification. To a stirred solution of $NaBH_4$ (155 mg, 4.09 mmol) in dry THF (15 mL) was added a solution of the residue in dry EtOH (15 mL) at 0 °C. After being stirred at room temperature for 3 h, the reaction mixture was poured into saturated aq. NH_4Cl. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with aq. NH_4Cl and brine, dried over $MgSO_4$, filtered and evaporated *in vacuo*. The residue was used for the next reaction without further purification. To a stirred 55% sodium hydride solution (367 mg, 15.3 mmol), which had been washed twice with dry hexane, was added a solution of the residue in dry *N*,*N*-dimethylformamide (5 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 30 min. Then benzyl bromide (1.46 mL, 12.3 mmol) and a catalytic amount of *n*-Bu_4NI were added to the reaction mixture at 0 °C. The reaction mixture was allowed to warm to room temperature. After being stirred at the same temperature for 3 h, the reaction mixture was poured into saturated aq. NH_4Cl. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with 1 M HCl, saturated aq. $NaHCO_3$ and brine, dried over $MgSO_4$. After removal of the solvent *in vacuo*, the residue was purified by column chromatography on silica gel with hexane–ethyl acetate 80 : 20 to give 2-azido-1,3,5-tri-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-D-glucitol (**21**) (1.88 g, 3.32 mmol, 3 steps 94%) as a colorless oil. $[\alpha]_D^{26}$ −9.6 (*c* 1.14, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26–7.39 (m, 20H, aromatic), 5.23 (s, 1H), 4.79 (d, 1H, $J = 11.6$ Hz), 4.59 (d, 1H, $J = 12.1$ Hz), 4.57 (d, 1H, $J = 11.1$ Hz), 4.48 (d, 1H, $J = 11.6$ Hz), 4.47 (d, 1H, $J = 12.1$ Hz),

4.40 (d, 1H, J = 11.6 Hz), 4.38 (dd, 1H, J = 4.8 Hz, J = 10.6 Hz), 3.98–4.03 (m, 2H), 3.87 (ddd, 1H, J = 5.3 Hz, J = 4.8 Hz, J = 9.7 Hz), 3.71–3.75 (m, 2H), 3.61–3.65 (m, 1H), 3.56 (dd, 1H, J = 9.7 Hz, J = 10.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.06, 137.74, 137.57, 137.38, 128.88, 128.49, 128.43, 128.35, 128.14, 128.00, 127.94, 127.80, 127.67, 127.63, 126.03, 101.10, 79.48, 76.47, 74.06, 73.28, 71.50, 69.43, 69.36, 68.35, 62.42; IR (KBr) 3089, 3065, 3033, 2865, 2097 (cm^{-1}).

2-Azido-1,3,5-tri-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-D-mannitol (22). According to the procedure for the synthesis of **21**, silyl glycoside **20** (3.75 g, 9.20 mmol) was treated with hydrogen fluoride–pyridine (4.0 mL) in dry (**18**) pyridine (40 mL) to provide an acetal. The acetal was treated with $NaBH_4$ (416 mg, 11.0 mmol) in THF (50 mL) and EtOH (50 mL) to provide a triol. The triol was reacted with benzyl bromide (3.94 mL, 33.1 mmol) in the presence of sodium hydride (994 mg, 41.4 mmol) in DMF (45 mL) to afforded tribenzyl ether **22** (4.60 g, 8.14 mmol, 3 steps 88%). $[\alpha]_d^{25}$ −27.7 (c 1.25, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21–7.48 (m, 20H, aromatic), 5.52 (s, 1H), 4.82 (d, 1H, J = 11.6 Hz), 4.53 (d, 1H, J = 11.6 Hz), 4.52 (m, 2H), 4.35 (d, 1H, J = 11.6 Hz), 4.47 (dd, 1H, J = 4.8 Hz, J = 10.6 Hz), 4.41 (d, 1H, J = 11.6 Hz), 3.95–4.02 (m, 3H), 3.90 (ddd, 1H, J = 4.8 Hz, J = 9.7 Hz), 3.83 (dd, 1H, J = 1.9 Hz, J = 10.6 Hz), 3.68 (dd, 1H, J = 9.7 Hz, J = 10.6 Hz), 3.67 (dd, 1H, J = 10.6 Hz, J = 5.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.90, 137.74, 137.72, 137.48, 128.88, 128.51, 128.41, 128.37, 128.15, 127.98, 127.71, 127.69, 127.64, 126.18, 101.33, 79.94, 75.50, 74.03, 73.33, 71.32, 69.80, 69.49, 68.40, 60.61; IR (KBr) 3064, 6033, 2866, 2097 (cm^{-1}).

2-Azido-1,3,5,6-tetra-*O*-benzyl-2-deoxy-D-glucitol (13). To a stirred solution of 2-azido-1,3,5-tri-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-D-glucitol (**21**) (4.00 g, 7.07 mmol) in dry CH_2Cl_2 (47 mL) was added triethylsilane (6.78 mL, 42.4 mmol) and TFA (3.27 mL, 42.4 mmol) at 0 °C. After being stirred at room temperature for 4 h, the reaction mixture was poured into ice-cooled saturated aq. $NaHCO_3$. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with saturated aq. $NaHCO_3$ and brine, dried over $MgSO_4$. After removal of the solvent *in vacuo*, the residue was purified by column chromatography on silica gel with hexane–ethyl acetate 75 : 25 to give 2-azido-1,3,5,6-tetra-*O*-benzyl-2-deoxy-D-glucitol (**13**) (3.00 g, 5.28 mmol, 75%) as a colorless oil. $[\alpha]_D^{24}$ −28.1 (c 1.10, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22–7.34 (m, 20H, aromatic), 4.72 (d, 1H, J = 12.1 Hz), 4.66 (d, 1H, J = 11.1 Hz), 4.55 (m, 2H), 4.52 (m, 2H), 4.40 (d, 1H, J = 12.1 Hz), 4.38 (d, 1H, J = 11.1 Hz), 3.90 (dd, 1H, J = 6.8 Hz, J = 1.4 Hz), 3.85 (dd, 1H, J = 2.9 Hz, J = 9.7 Hz), 3.84 (dd, 1H, J = 3.4 Hz, J = 10.6 Hz), 3.75 (ddd, 1H, J = 1.4 Hz, J = 7.7 Hz, J = 8.2 Hz), 3.69 (dd, 1H, J = 4.8 Hz, J = 10.6 Hz), 3.66 (ddd, 1H, J = 2.9 Hz, J = 3.9 Hz, J = 6.8 Hz), 3.63 (dd, 1H, J = 3.9 Hz, J = 9.7 Hz), 3.59 (ddd, 1H, J = 7.7 Hz, J = 3.4 Hz, J = 3.9 Hz), 2.56 (d, 1H, J = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.12, 138.05, 137.68, 137.63, 128.41, 128.38, 127.99, 127.89, 127.86, 127.70, 127.65, 77.79, 76.86, 74.38, 73.50, 73.37, 71.63, 70.46, 69.65, 63.14; IR (KBr) 3473, 3089, 3065, 3032, 2867, 2098 (cm^{-1}); HRMS (ESI) calcd. $[M + Na]^+$ 590.2625, found 590.2625.

2-Azido-1,3,5,6-tetra-*O*-benzyl-2-deoxy-D-mannitol (14). According to the procedure for the synthesis of **13**, acetal **22** (4.14 g, 7.32 mmol), with triethylsilane (7.01 mL, 43.9 mmol) and TFA (3.38 mL, 43.9 mmol) in dry CH_2Cl_2 (40 mL) to provide the secondary alcohol **14** (3.70 g, 6.52 mmol, 89%). $[\alpha]_D^{24}$ −22.1 (c 1.10, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12–7.35 (m, 20H, aromatic), 4.73 (d, 1H, J = 11.6 Hz), 4.57 (m, 2H), 4.55 (d, 1H, J = 11.6 Hz), 4.51 (d, 1H, J = 11.6 Hz), 4.48 (d, 1H, J = 11.1 Hz), 4.39 (d, 1H, J = 11.6 Hz), 4.30 (d, 1H, J = 11.1 Hz), 3.91 (dd, 1H, J = 1.9 Hz, J = 7.7 Hz), 3.88 (dd, 1H, J = 3.4 Hz, J = 10.1 Hz), 3.82 (dd, 1H, J = 7.7 Hz, J = 8.2 Hz, J = 8.7 Hz), 3.77–3.81 (m, 2H, H-1), 3.72 (dd, 1H, J = 4.8 Hz, J = 10.1 Hz), 3.66–3.71 (m, 1H, H-2), 3.59 (ddd, 1H, J = 8.2 Hz, J = 3.4 Hz, J = 4.8 Hz), 2.58 (d, 1H, J = 8.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.17, 138.10, 137.67, 137.62, 128.40, 128.38, 127.93, 127.86, 127.79, 127.70, 127.64, 127.63, 77.96, 75.91, 74.00, 73.51, 73.35, 71.63, 70.40, 69.94, 69.61, 62.05; IR (KBr) 3536, 3089, 3065, 3032, 2866, 2099 (cm^{-1}).

2-Azido-1,3,5,6-tetra-*O*-benzyl-2-deoxy-4-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-D-glucopyranosyl)-D-glucitol (25). A mixture of 2-azido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-levulinoyl-D-glucopyranosyl trichloroacetimidate (**12**) (70.0 mg, 111 mmol), 2-azido-1,3,5,6-tetra-*O*-benzyl-2-deoxy-D-glucitol (**13**) (52.5 mg, 92.5 mmol) and pulverized activated MS 4 Å in dry toluene (1.5 mL) was stirred at −25 °C for 30 min under argon to remove a trace amount of water. Trimethylsilyl trifluoromethanesulfonate (1.67 μL, 9.25 μmol) was added to the reaction mixture at the same temperature. After being stirred for 1 h, the reaction mixture was neutralized with triethylamine and filtered through a pad of celite. The filtrate was concentrated *in vacuo* and the residue was purified by column chromatography on silica gel with hexane–ethyl acetate 65 : 35, and further purified by gel permeation chromatography (GPC) to give 2-azido-1,3,5,6-tetra-*O*-benzyl-2-deoxy-4-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-levulinoyl-D-glucopyranosyl)-D-glucitol (**23**) (α : β = 53 : 47, 65.0 mg, 0.0629 mmol, 68%). The α : β ratio was determined by HPLC analysis (Senshu Pak Silica-3301-N, Eluent: hexane–2-propanol = 99 : 1, 3 mL min^{-1}; Retention time: α-isomer 18.9 min, β-isomer 22.7 min). To a stirred solution of 2-azido-1,3,5,6-tetra-*O*-benzyl-2-deoxy-4-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-levulinoyl-D-glucopyranosyl)-D-glucitol (**23**) (2.55 g, 2.47 mmol) in dry pyridine (12 mL) was added AcOH (18 mL) and hydrazine monohydrate (601 μL, 12.4 mmol) at 0 °C. After being stirred at room temperature for 1 h, the reaction mixture was poured into ice-cooled water. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with 1 M HCl, saturated aq. $NaHCO_3$ and brine, dried over $MgSO_4$. After removal of the solvent *in vacuo*, the residue was purified by chromatography on silica gel with toluene–ethyl acetate 90 : 10 to give 2-azido-1,3,5,6-tetra-*O*-benzyl-2-deoxy-4-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-D-glucitol (**25α**) (1.11 g, 1.19 mmol, 48%) and 2-azido-1,3,5,6-tetra-*O*-benzyl-2-deoxy-4-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-D-glucitol (**25β**) (995 mg, 1.06 mmol, 43%) as a colorless oil.

2-Azido-1,3,5,6-tetra-*O*-benzyl-2-deoxy-4-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-D-glucitol (25α). $[\alpha]_D^{29}$ +60.2 (c 1.35, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21–7.42 (m, 30H, aromatic), 5.34 (d, 1H, anomeric, J = 3.4 Hz), 4.91 (d, 1H, J = 11.1 Hz), 4.87 (m, 2H), 4.58 (m, 2H), 4.52 (d, 1H, J = 11.1 Hz), 4.52 (d, 2H, J = 11.1 Hz), 4.41 (d, 1H, J = 11.1 Hz), 4.40 (m, 2H), 4.30 (br-dd, 1H, J = 8.2 Hz), 4.28 (d, 1H, J = 11.1 Hz), 4.11 (br-ddd, 1H, J = 9.2 Hz, J = 3.4 Hz, J = 4.3 Hz), 3.91 (br-dd, 1H, J = 8.2 Hz), 3.73–3.81 (m, 4H), 3.67 (dd, 1H, J = 4.8 Hz, J = 8.7 Hz), 3.62 (dd, 1H, J = 7.7 Hz, J = 7.2 Hz), 3.55–3.53 (m, 1H), 3.52 (dd, 1H, J = 4.8 Hz, J = 7.2 Hz), 3.41 (dd, 1H, J = 3.4 Hz, J = 10.1 Hz), 3.30 (dd, 1H, J = 4.3 Hz, J = 10.1 Hz), 3.21 (dd, 1H, J = 3.4 Hz, J = 9.7 Hz), 2.57 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.15, 138.05, 137.99, 137.89, 137.47, 128.51, 128.42, 128.35, 128.03, 127.88, 127.79, 127.70, 127.66, 127.54, 127.31, 97.99 (anomeric), 79.63, 79.36, 74.85, 74.38, 73.48, 73.41, 73.22, 72.59, 72.02, 69.73, 69.48, 69.30, 69.01, 62.81, 61.13; IR (KBr) 3486, 3089, 3022, 2919, 2868, 2108 (cm^{-1}); HRMS (ESI) calcd. $[M + Na]^+$ 957.4157, found 957.4157.

2-Azido-1,3,5,6-tetra-*O*-benzyl-2-deoxy-4-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-D-glucitol (25b). $[\alpha]_D^{26}$

−21.9 (*c* 1.10, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23–7.40 (m, 30H, aromatic), 4.88 (d, 1H, J = 11.1 Hz), 4.78 (d, 1H, J = 11.1 Hz), 4.70 (d,1H, J = 11.6 Hz), 4.60 (d, 2H, J = 11.6 Hz), 4.58 (d, 1H, anomeric, J = 8.2 Hz), 4.52 (d, 1H, J = 11.6 Hz), 4.30 (d, 1H, J = 11.6 Hz), 4.44 (m, 2H), 4.43 (d, 1H, J = 12.1 Hz), 4.41 (d, 1H, J = 11.6 Hz), 4.35 (d, 1H, J = 12.1 Hz), 4.21 (dd, 1H, J = 3.9 Hz, J = 4.8 Hz), 3.91 (ddd, 1H, J = 6.3 Hz, J = 3.4 Hz, J = 2.9 Hz), 3.84–3.89 (m, 3H), 3.78–3.81 (m, 1H), 3.64 (dd, 1H, J = 6.3 Hz, J = 10.1 Hz), 3.60 (dd, 1H, J = 4.8 Hz), 3.57 (ddd, 1H, J = 9.7 Hz, J = 9.7 Hz, J = 1.9 Hz), 3.53 (dd, 1H, J = 4.8 Hz, J = 10.1 Hz), 3.48 (dd, 1H, J = 3.4 Hz, J = 10.1 Hz), 3.32 (dd, 1H, J = 8.2 Hz, J = 10.1 Hz), 3.20 (ddd, 1H, J = 9.7 Hz, J = 4.8 Hz, J = 4.8 Hz), 3.17 (dd, 1H, J = 10.1 Hz, J = 9.7 Hz), 2.70 (d, 1H, J = 1.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.41, 138.17, 138.11, 138.02, 137.86, 137.53, 128.55, 128.47, 128.41, 128.35, 128.19, 128.04, 127.96, 127.91, 127.85, 127.73, 127.66, 127.63, 127.58, 127.55, 127.47, 127.40, 100.67 (anomeric), 82.63, 78.11, 77.62, 75.00, 74.66, 73.63, 73.42, 73.29, 73.16, 72.49, 71.49, 70.40, 69.81, 67.61, 66.02, 62.21; IR (KBr) 3473, 3089, 3065, 3032, 2868, 2110 (cm^{-1}); HRMS (ESI) calcd. $[M + Na]^+$ 957.4157, found 957.4157.

2-Azido-1,3,5,6-tetra-*O*-benzyl-2-deoxy-4-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-D-glucopyranosyl)-D-mannitol (26). According to the procedure for the synthesis of **13**, alcohol **14** (62.2 mg, 0.110 mmol) was treated with imidate **12** (82.9 mg, 0.132 mmol) in the presence of trimethylsilyl trifluoromethanesulfonate (1.99 µL, 11.0 µmol) in toluene (1.5 mL) to provide levulinoyl disaccharide (α : β = 39 : 61, 69.0 mg, 0.0668 mmol, 61%, HPLC retention time: α-isomer 17.6 min, β-isomer 19.6 min). The levulinoyl disaccharide was treated with AcOH (21.6 mL) and hydrazine monohydrate (737 µL, 15.2 mmol) in dry pyridine (14.4 mL) to provide an α-glycoside (**26α**) (701 mg, 0.750 mmol, 25%) and b-glycoside (**26β**) (942 mg, 1.01 mmol, 33%).

2-Azido-1,3,5,6-tetra-*O*-benzyl-2-deoxy-4-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-D-mannitol (26α). $[\alpha]_D^{23}$ +59.4 (*c* 1.11, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21–7.42 (m, 30H, aromatic), 5.33 (d, 1H, anomeric, J = 3.9 Hz), 4.88 (d, 1H, J = 11.1 Hz), 4.85 (d, 1H, J = 11.1 Hz), 4.74 (d, 1H, J = 10.6 Hz), 4.70 (d, 1H, J = 10.6 Hz), 4.52 (d, 1H, J = 11.6 Hz), 4.51 (m, 2H), 4.47 (m, 2H), 4.45 (d, 1H, J = 10.6 Hz), 4.40 (d, 1H, J = 12.1 Hz), 4.28 (d, 1H, J = 12.1 Hz), 4.13 (dd, 1H, J = 1.9 Hz, J = 6.8 Hz), 4.05 (ddd, 1H, J = 8.7 Hz, J = 3.4 Hz, J = 4.3 Hz), 3.94–3.88 (m, 2H), 3.81–3.84 (m, 2H), 3.79 (dd, 1H, J = 9.7 Hz, J = 9.7 Hz), 3.71–3.75 (m, 2H), 3.66–3.70 (m, 2H), 3.38 (dd, 1H, J = 3.4 Hz, J = 10.1 Hz), 3.28 (dd, 1H, J = 4.3 Hz, J = 10.1 Hz), 3.20 (dd, 1H, J = 3.9 Hz, J = 9.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.16, 138.10, 137.99, 137.72, 137.61, 128.53, 128.44, 128.40, 128.36, 128.31, 128.27, 128.05, 127.90, 127.79, 127.73, 127.69, 127.61, 127.53, 127.50, 98.15 (anomeric), 80.19, 79.27, 77.90, 76.51, 74.84, 74.30, 73.48, 73.39, 72.41, 71.95, 69.83, 69.39, 69.24, 69.16, 62.87, 62.39; IR (KBr) 3481, 3089, 3065, 3032, 2917, 2868, 2107 (cm^{-1}).

2-Azido-1,3,5,6-tetra-*O*-benzyl-2-deoxy-4-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-D-mannitol (26β). $[\alpha]_D^{23}$ −40.5 (*c* 1.28, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18–7.41 (m, 30H, aromatic), 4.87 (d, 1H, J = 11.0 Hz), 4.82 (d, 1H, J = 11.0 Hz), 4.57 (d, 1H, J = 12.1 Hz), 4.56 (d, 2H, J = 12.1 Hz, J = 11.6 Hz), 4.52 (d, 1H, J = 11.6 Hz), 4.51 (d, 1H, J = 11.6 Hz), 4.49 (d, 1H, J = 10.1 Hz), 4.47 (d, 1H, anomeric, J = 8.2 Hz), 4.46 (d, 1H, J = 10.1 Hz), 4.45 (d, 1H, J = 11.6 Hz), 4.42 (d, 1H, J = 12.1 Hz), 4.29 (d, 1H, J = 12.1 Hz), 4.23 (dd, 1H, J = 1.9 Hz, J = 7.7 Hz), 4.02 (ddd, 1H, J = 2.4 Hz, J = 6.8 Hz, J = 7.2 Hz), 3.89 (dd, 1H, J = 2.4 Hz, J = 10.6 Hz), 3.87 (dd, 1H, J = 2.4 Hz, J = 10.1 Hz), 3.86 (dd, 1H, J = 7.2 Hz, J = 1.9 Hz), 3.82 (dd, 1H, J = 3.4 Hz, J = 10.6 Hz), 3.78 (ddd, 1H, J = 7.7 Hz, J = 2.4 Hz, J = 3.4 Hz), 3.75 (dd, 1H, J = 4.3 Hz, J = 10.1 Hz), 3.67 (dd, 1H, J = 6.8 Hz, J = 10.1 Hz), 3.65 (dd, 1H, J = 4.8 Hz, J = 10.1 Hz), 3.63 (dd, 1H, J = 9.2 Hz, J = 9.7 Hz), 3.43 (dd, 1H, J = 8.2 Hz, J = 9.7 Hz), 3.25 (dd, 1H, J = 4.3 Hz, J = 4.8 Hz, J = 9.7 Hz), 3.16 (dd, 1H, J = 9.7 Hz, J = 9.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.23, 138.19, 138.16, 138.02, 137.97, 137.56, 128.50, 128.44, 128.36, 128.31, 128.25, 128.02, 127.89, 127.79, 127.78, 127.73, 127.60, 127.54, 127.49, 127.44, 127.42, 100.84 (anomeric), 82.75, 77.81, 75.00, 74.22, 73.71, 73.24, 73.19, 73.15, 73.00, 70.98, 70.66, 70.27, 66.80, 65.74, 61.46; IR (KBr) 3474, 3089, 3065, 3032, 2868, 2110 (cm^{-1}).

2-Azido-1,3,5,6-tetra-*O*-benzyl-2-deoxy-4-*O*-(2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-D-glucitol (10a). To a stirred 55% sodium hydride (4.87 mg, 0.203 mmol, 1.20 eq.), washed twice with dry hexane, was added a solution of the 2-azido-1,3,5,6-tetra-*O*-benzyl-2-deoxy-4-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-D-glucitol (**25β**) (158 mg, 0.169 mmol) in dry *N*,*N*-dimethylformamide (0.800 mL) at 0 °C. The reaction mixture was stirred at the same temperature for 30 min. Then, benzyl bromide (21.1 µL, 0.177 mmol) and a catalytic amount of *n*-Bu_4NI were added to the reaction mixture at the same temperature. After being stirred at room temperature for 3 h, the reaction mixture was poured into saturated aq. NH_4Cl. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with 1 M HCl, saturated aq. $NaHCO_3$ and brine, and dried over $MgSO_4$. After removal of the solvent *in vacuo*, the residue was used for the next reaction without further purification. The residue was purified by chromatography on silica gel with hexane–ethyl acetate 70 : 30 to give 2-azido-1,3,5,6-tetra-*O*-benzyl-2-deoxy-4-*O*-(2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-D-glucitol (**10b**) (173 mg, 0.168 mmol, 93%) as a colorless oil. $[\alpha]_D^{23}$ −15.7 (*c* 1.10, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16–7.35 (m, 35H, aromtic), 4.86 (d, 1H, J = 11.1 Hz), 4.79 (d, 1H, J = 11.1 Hz), 4.77 (d, 1H, J = 11.1 Hz), 4.74 (d, 1H, J = 11.6 Hz), 4.61 (d, 1H, J = 11.6 Hz), 4.59 (d, 1H, J = 12.1 Hz), 4.56 (d, 1H, anomeric, J = 7.7 Hz), 4.54 (d, 1H, J = 11.1 Hz), 4.51 (m, 2H), 4.45 (d, 1H, J = 12.1 Hz), 4.44 (d, 1H, J = 12.1 Hz), 4.39 (d, 2H, J = 12.1 Hz), 4.35 (d, 1H, J = 12.1 Hz), 4.22 (dd, 1H, J = 3.4 Hz, J = 5.3 Hz), 3.98 (ddd, 1H, J = 5.8 Hz, J = 3.4 Hz, J = 6.8 Hz), 3.94 (dd, 1H, J = 6.8 Hz, J = 3.4 Hz), 3.86–3.90 (m, 2H), 3.74 (dd, 1H, J = 4.8 Hz, J = 11.6 Hz), 3.68 (dd, 1H, J = 5.8 Hz, J = 10.6 Hz), 3.58 (dd, 1H, J = 2.9 Hz, J = 11.1 Hz), 3.57 (dd, 1H, J = 8.2 Hz, J = 4.3 Hz), 3.51 (dd, 1H, J = 1.4 Hz, J = 11.1 Hz), 3.48 (dd, 1H, J = 3.4 Hz, J = 10.6 Hz), 3.38 (dd, J = 7.7 Hz, J = 10.1 Hz), 3.32 (dd, 1H, J = 10.1 Hz, J = 8.2 Hz), 3.22 (ddd, 1H, J = 4.3 Hz, J = 2.9 Hz, J = 1.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.47, 138.23, 138.07, 138.01, 137.93, 137.90, 128.42, 128.40, 128.36, 128.34, 128.31, 128.21, 127.94, 127.87, 127.85, 127.83, 127.67, 127.58, 127.50, 127.45, 127.39, 100.70 (anomeric), 83.23, 78.19, 77.71, 73.19, 71.46, 69.79, 68.50, 67.63, 66.67, 62.31; IR (KBr) 3089, 3064, 3031, 2867, 2110 (cm^{-1}).

2-Azido-1,3,5,6-tetra-*O*-benzyl-2-deoxy-4-*O*-(2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-D-glucitol (10c). According to the procedure for the synthesis of **10a**, alcohol **25a** (149 mg, 0.159 mmol) was treated with sodium hydride (4.59 mg, 0.191 mmol) and benzyl bromide (19.9 µL, 0.167 mmol) in, dry *N*,*N*-dimethylformamide (0.800 mL) to provide disaccahride **10c** (155 mg, 0.151 mmol, 95%); $[\alpha]_D^{24}$ +66.0 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09–7.36 (m, 35H, aromatic), 5.39 (d, 1H, anomeric, J = 3.9 Hz), 4.91 (d, 1H, J = 11.1 Hz), 4.89 (d, 1H, J = 11.1 Hz), 4.86 (d, 1H, J = 11.1 Hz), 4.71 (d, 1H, J = 11.1 Hz), 4.59 (m, 2H), 4.52 (d, 1H, J = 12.1 Hz), 4.50 (d, 1H, J = 12.1), 4.48 (d, 2H, J = 11.1 Hz), 4.43 (d, 1H, J = 11.1 Hz), 4.41 (s, 2H), 4.33 (d, 1H, J = 8.2 Hz), 4.25 (br-d, 1H, J = 12.1 Hz), 4.11 (br-d, 1H, J = 9.7 Hz), 3.91 (dd, 1H, J = 8.7 Hz, J = 1.4 Hz), 3.89 (dd, 1H, J = 10.1 Hz, J = 9.7

Hz), 3.75–3.80 (m, 2H), 3.72 (dd, 1H, $J = 9.7$ Hz, $J = 9.7$ Hz), 3.64–3.69 (m 1H), 3.63 (br-dd, 1H, $J = 1.4$ Hz, $J = 7.7$ Hz), 3.57 (ddd, 1H, $J = 1.4$ Hz, $J = 4.8$ Hz, $J = 8.7$ Hz), 3.53 (dd, 1H, $J = 4.8$ Hz, $J = 7.7$ Hz), 3.39 (dd, 1H, $J = 1.9$ Hz, $J = 10.6$ Hz), 3.26 (dd, 1H, $J = 3.9$ Hz, $J = 10.1$ Hz), 3.20 (dd, 1H, $J = 1.4$ Hz, $J = 10.6$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.16, 138.07, 138.05, 137.92, 137.81, 137.50, 128.42, 128.41, 128.32, 128.26, 127.96, 127.91, 127.85, 127.78, 127.74, 127.68, 127.66, 127.60, 127.51, 127.24, 98.00 (anomeric), 79.91, 79.81, 78.21, 75.17, 74.84, 74.39, 73.40, 73.22, 72.11, 70.64, 64.33, 68.95, 67.67, 63.48, 61.08; IR (KBr) 3089, 3065, 3032, 2916, 2867, 2107 (cm^{-1}).

2-Azido-1,3,5,6-tetra-*O*-benzyl-2-deoxy-4-*O*-(2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-D-mannitol (10d). According to the procedure for the synthesis of **10a**, alcohol **26α** (134 mg, 0.143 mmol) was treated with sodium hydride (4.13 mg, 0.172mmol) and benzyl bromide (17.8 μL, 0.150 mmol) in dry *N*,*N*-dimethylformamide (0.800 mL) to provide disaccahride **10c** (122 mg, 0.119 mmol, 83%); $[\alpha]_D^{23}$ +60.4 (*c* 0.87, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09–7.37 (m, 35H, aromatic), 5.38 (d, 1H, anomeric, $J = 3.4$ Hz), 4.87 (d, 1H, $J = 11.1$ Hz), 4.83 (d, 1H, $J = 11.1$ Hz), 4.75 (d, 1H, $J = 11.1$ Hz), 4.71 (d, 2H, $J = 10.6$ Hz), 4.53 (d, 1H, $J = 12.1$ Hz), 4.51 (m, 2H), 4.49 (d, 2H, $J = 12.1$ Hz), 4.48 (d, 1H, $J = 8.7$ Hz), 4.43 (d, 1H, $J = 12.1$ Hz), 4.43 (d, 1H, $J = 10.6$ Hz), 4.24 (d, 1H, $J = 12.1$ Hz), 4.14 (dd, 1H, $J = 1.9$ Hz, $J = 6.3$ Hz), 4.07 (br-d, 1H, $J = 9.2$ Hz), 3.91–3.93 (m, 2H), 3.90 (dd, 1H, $J = 10.1$ Hz, $J = 8.7$ Hz), 3.82 (dd, 1H, $J = 5.3$ Hz, $J = 9.2$ Hz), 3.73 (ddd, 1H, $J = 6.3$ Hz, $J = 5.3$ Hz, $J = 4.8$ Hz), 3.70 (dd, 1H, $J = 8.7$ Hz, $J = 9.2$ Hz), 3.68 (br-d, 2H), 3.67 (dd, 1H, $J = 4.8$ Hz, $J = 9.2$ Hz), 3.37 (dd, 1H, $J = 1.9$ Hz, $J = 10.6$ Hz), 3.24 (dd, 1H, $J = 3.4$ Hz, $J = 10.1$ Hz), 3.17 (dd, 1H, $J = 1.4$ Hz, $J = 10.6$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.21, 138.16, 138.14, 138.07, 138.00, 137.81, 137.66, 128.44, 128.40, 128.30, 128.28, 128.27, 127.96, 127.92, 127.79, 127.72, 127.67, 127.62, 127.56, 127.50, 127.46, 98.14 (anomeric), 80.37, 79.81, 78.22, 77.94, 76.54, 75.15, 74.81, 74.35, 73.41, 72.01, 70.65, 69.25, 69.17, 67.73, 63.54, 62.47; IR (KBr) 3066, 3031, 2867, 2105 (cm^{-1}).

2-Azido-1,3,5,6-tetra-*O*-benzyl-2-deoxy-4-*O*-(2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-D-mannitol (10b). According to the procedure for the synthesis of **10a**, alcohol **26b** (153 mg, 0.164 mmol) was treated with sodium (4.73 mg, 0.197 mmol) and benzyl bromide (20.5 μL, 0.172 mmol)in dry *N*,*N*-dimethylformamide (0.800 mL) to provide disaccharide **10b** (119 mg, 0.116 mmol, 71%); $[\alpha]_D^{24}$ −27.6 (*c* 1.12, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16–7.35 (m, 35H, aromatic), 4.85 (d, 1H, $J = 10.6$ Hz), 4.79 (d, 1H, $J = 10.6$ Hz), 4.76 (d, 1H, $J = 10.6$ Hz), 4.58 (d, 1H, $J = 11.6$ Hz), 4.57 (d, 1H, $J = 12.1$ Hz), 4.55 (d, 1H, $J = 10.6$ Hz), 4.53 (d, 1H, $J = 11.6$ Hz), 4.53 (m, 2H), 4.50 (m, 2H), 4.47 (d, 1H, anomeric, $J = 7.7$ Hz), 4.44 (d, 2H, $J = 11.6$ Hz), 4.30 (d, 1H, $J = 11.6$ Hz), 4.27 (dd, 1H, $J = 1.4$ Hz, $J = 7.2$ Hz), 4.13 (ddd, 1H, $J = 2.4$ Hz, $J = 3.4$ Hz, $J = 7.7$ Hz), 3.89 (dd, 1H, $J = 7.7$ Hz, $J = 1.4$ Hz), 3.88–3.90 (m, 1H), 3.85 (br-d, 1H, $J = 8.7$ Hz), 3.38 (br-d, 1H), 3.80 (br-dd, 1H, $J = 9.2$ Hz), 3.68 (m, 1H), 3.71 (br-d, 2H), 3.63 (dd, 1H, $J = 9.2$ Hz, $J = 9.2$ Hz), 3.38 (dd, 1H, $J = 7.7$ Hz, $J = 9.7$ Hz), 3.31 (dd, 1H, $J = 9.7$ Hz, $J = 9.2$ Hz), 3.28 (br-dd, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) d 138.28, 138.25, 138.08, 138.02, 128.41, 128.38, 128.34, 128.28, 128.26, 128.24, 127.93, 127.79, 127.74, 127.72, 127.65, 127.56, 127.45, 127.40, 100.95 (anomeric), 83.31, 77.91, 77.72, 77.39, 76.80, 75.39, 74.92, 74.87, 74.25, 73.39, 73.21, 73.16, 71.03, 70.19, 68.44, 66.98, 66.50, 61.26; IR (KBr) 3089, 3064, 3031, 2867, 2110 (cm^{-1}).

2-Azido-1,3,5,6-tetra-*O*-benzyl-2-deoxy-4-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-(2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranosyl)-β-D-glucopyranosyl)-D-glucitol (9a) and (9c). A mixture of 2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranosyl trichloroacetimidate (**11**) (632 mg, 1.02 mmol), 2-azido-1,3,5,6-tetra-*O*-benzyl-2-deoxy-4-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-D-glucitol (**25β**) (632 mg, 0.512 mmol) and pulverized activated MS 4 Å in dry Et_2O (12 mL) was stirred at −25 °C for 1 h under argon to remove a trace amount of water. Trimethylsilyl trifluoromethanesulfonate (9.25 μL, 51.2 μmol) was added to the reaction mixture at the same temperature. After being stirred for 1.5 h, the reaction mixture was neutralized with triethylamine and filtered through a pad of celite. The filtrate was concentrated *in vacuo*. Then, the residue was purified by column chromatography on silica gel with hexane–ethyl acetate 70 : 30, and gel permeation chromatography (GPC) to give 2-azido-1,3,5,6-tetra-*O*-benzyl-2-deoxy-4-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-(2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranosyl)-β-D-glucopyranosyl)-D-glucitol (**9a**) and (**9c**) (β : α = 52 : 48, 590 mg, 0.424 mmol, 83%). The β : α ratio was determined by 1H NMR analysis. The β/α-isomers were separated by column chromatography on silica gel with toluene–ethyl acetate 94 : 6 to give 2-azido-1,3,5,6-tetra-*O*-benzyl-2-deoxy-4-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-(2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-β-D-glucopyranosyl)-D-glucitol (**9a**) (242 mg, 0.174 mmol, 34%) and 2-azido-1,3,5,6-tetra-*O*-benzyl-2-deoxy-4-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-(2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-a-D-glucopyranosyl)-β-D-glucopyranosyl)-D-glucitol (**9c**) (326 mg, 0.236 mmol, 46%) as a colorless oil.

2-Azido-1,3,5,6-tetra-*O*-benzyl-2-deoxy-4-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-(2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-β-D-glucopyranosyl)-D-glucitol (9a). $[\alpha]_D^{24}$ −26.5 (*c* 1.20, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15–7.38 (m, 45H, aromatic), 5.01 (d, 1H, anomeric, $J = 11.6$ Hz), 4.84 (d, 1H, $J = 10.4$ Hz), 4.79 (d, 1H, $J = 10.4$ Hz), 4.77 (d, 1H, $J = 11.1$ Hz), 4.71 (d, 1H, $J = 11.6$ Hz), 4.70 (d, 1H, $J = 11.6$ Hz), 4.61 (d, 1H, $J = 11.6$ Hz), 4.60 (d, 1H, $J = 12.1$ Hz), 4.54 (d, 1H, $J = 11.1$ Hz), 4.52 (d, 1H, $J = 11.6$ Hz), 4.50 (d, 1H, $J = 10.6$ Hz), 4.48 (d, 1H, anomeric, $J = 10.1$ Hz), 4.47 (m, 2H), 4.40 (d, 1H, $J = 12.1$ Hz), 4.36 (d, 2H, $J = 10.6$ Hz), 4.35 (m, 2H), 4.33 (d, 1H, anomeric, $J = 8.2$ Hz), 4.16 (dd, 1H, $J = 3.4$ Hz, $J = 4.8$ Hz), 3.99 (dd, 1H, $J = 9.7$ Hz, $J = 7.7$ Hz), 3.97 (ddd, 1H, $J = 5.8$ Hz, $J = 3.4$ Hz, $J = 6.8$ Hz), 3.93 (dd, 1H, $J = 6.8$ Hz, $J = 3.4$ Hz), 3.88 (dd, 1H, $J = 3.4$ Hz, $J = 11.6$ Hz), 3.85 (ddd, 1H, $J = 4.8$ Hz, $J = 3.4$ Hz, $J = 3.4$ Hz), 3.80 (dd, 1H, $J = 3.4$ Hz, $J = 11.6$ Hz), 3.75 (dd, 1H, $J = 3.4$ Hz, $J = 11.1$ Hz), 3.65 (dd, 1H, $J = 5.8$ Hz, $J = 10.1$ Hz), 3.63 (dd, 1H, $J = 9.7$ Hz, $J = 7.7$ Hz), 3.62 (dd, 1H, $J = 1.4$ Hz, $J = 9.7$ Hz), 3.51 (dd, 1H, $J = 1.9$ Hz, $J = 9.7$ Hz), 3.51 (dd, 1H, $J = 1.4$ Hz, $J = 11.1$ Hz), 3.45 (dd, 1H, $J = 3.4$ Hz, $J = 10.1$ Hz), 3.34 (dd, 1H, $J = 8.2$ Hz, $J = 9.7$ Hz), 3.30 (dd, 1H, $J = 10.1$ Hz, $J = 7.7$ Hz), 3.27 (dd, 1H, $J = 9.7$ Hz, $J = 9.7$ Hz), 3.26 (dd, 1H, $J = 7.7$ Hz, $J = 9.7$ Hz), 3.21 (ddd, 1H, $J = 7.7$ Hz, $J = 1.4$ Hz, $J = 1.9$ Hz), 3.14 (ddd, 1H, $J = 7.7$ Hz, $J = 3.4$ Hz, $J = 1.4$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.47, 138.44, 138.25, 138.18, 138.03, 137.93, 137.86, 137.79, 128.46, 128.38, 128.31, 128.25, 128.21, 128.10, 127.98, 127.95, 127.83, 127.70, 127.62, 127.52, 127.44, 100.91 (anomeric), 100.60 (anomeric), 83.16, 81.19, 78.10, 77.79, 77.64, 75.97, 75.50, 75.16, 74.88, 74.82, 74.63, 73.32, 73.25, 71.41, 69.74, 68.49, 67.76, 67.47, 66.92, 66.15, 62.33; IR (KBr) 3090, 3065, 3032, 2869, 2110 (cm^{-1}); HRMS (ESI) calcd. $[M + Na]^+$ 1414.6159, found 1414.6155.

2-Azido-1,3,5,6-tetra-*O*-benzyl-2-deoxy-4-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-(2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-β-D-glucopyranosyl)-D-glucitol (9c). $[\alpha]_D^{24}$ +14.5 (*c* 1.20, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10–7.36 (m, 45H, aromatic), 5.64 (d, 1H, anomeric, $J = 3.9$ Hz), 5.01 (d, 1H, $J = 10.1$ Hz), 4.87 (d, 1H, $J = 10.6$ Hz), 4.83 (d, 1H, $J = 10.6$ Hz), 4.81 (d, 1H, $J = 10.1$ Hz), 4.73 (d, 1H, $J = 10.6$ Hz), 4.72 (d, 1H, $J = 11.6$ Hz), 4.64 (d, 1H, anomeric, $J = 7.7$ Hz), 4.61 (d, 1H, $J = 11.6$ Hz), 4.60 (d, 1H, $J = 11.6$ Hz), 4.53 (d, 1H, $J = 14.0$ Hz), 4.51 (d, 1H, $J = 14.0$ Hz), 4.49 (d,

1H, J = 12.1 Hz), 4.45 (d, 1H, J = 10.6 Hz), 4.42 (d, 2H, J = 11.6 Hz), 4.39 (m, 2H), 4.33 (d, 1H, J = 12.1 Hz), 4.25–4.26 (m, 1H), 4.24 (d, 1H, J = 12.1 Hz), 3.92 (br-s, 2H), 3.88 (dd, 1H, J = 9.7 Hz, J = 9.7 Hz), 3.86–3.90 (m, 2H), 3.83 (dd, 1H, J = 10.1 Hz, J = 8.7 Hz), 3.79 (dd, 1H, J = 5.3 Hz, J = 11.6 Hz), 3.69 (dd, 1H, J = 8.7 Hz, J = 9.7 Hz), 3.63 (ddd, 1H, J = 9.7 Hz, J = 2.4 Hz, J = 4.3 Hz), 3.64–3.67 (m, 1H), 3.63 (dd, 1H, J = 4.3 Hz, J = 11.1 Hz), 3.52 (dd, 1H, J = 2.4 Hz, J = 10.6 Hz), 3.51 (dd, 1H, J = 2.4 Hz, J = 11.1 Hz), 3.43 (dd, 1H, J = 6.3 Hz, J = 9.7 Hz), 3.43 (dd, 1H, J = 2.4 Hz, J = 10.1 Hz), 3.39 (dd, 1H, J = 7.7 Hz, J = 10.1 Hz), 3.29 (br-d, 1H, J = 10.6 Hz), 3.24 (ddd, 1H, J = 9.7 Hz, J = 4.3 Hz, J = 2.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.43, 138.17, 138.05, 137.97, 137.93, 137.83, 137.76, 137.68, 128.46, 128.44, 128.35, 128.20, 127.97, 127.96, 127.92, 127.85, 127.80, 127.77, 127.74, 127.71, 127.57, 127.44, 127.41, 127.38, 100.65 (anomeric), 97.52 (anomeric), 83.65, 80.00, 78.17, 77.99, 77.76, 75.30, 74.97, 74.63, 74.59, 74.35, 73.49, 73.43, 73.38, 73.20, 72.58, 71.55, 71.39, 69.76, 68.89, 67.70, 67.66, 67.15, 63.20, 62.20; IR (KBr) 3089, 3065, 3031, 2867, 2110 (cm^{-1}); HRMS (ESI) calcd. [M + Na]$^+$ 1414.6159, found 1414.6159.

2-Azido-1,3,5,6-tetra-*O*-benzyl-2-deoxy-4-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-(2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranosyl)-α-D-glucopyranosyl)-D-mannitol (9b) and (9d). According to the method for the synthesis of **9a** and **9c**, disaccharide **26β** (942 mg, 1.01 mmol) was treated with donor **11** (1.25 g, 2.02 mmol) in the presence of trimethylsilyl trifluoromethanesulfonate (18.3 μL, 0.101 mmol) in Et_2O (30 mL) to provide the mixture of **9b** and **9d** (β : α = 59 : 41, 983 mg, 0.706 mmol, 70%). Further purification of the mixture afforded β-isomer **9d** (570 mg, 0.409 mmol, 40%) and α-isomer (**9d**) (390 mg, 0.280 mmol, 28%).

2-Azido-1,3,5,6-tetra-*O*-benzyl-2-deoxy-4-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-(2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-β-D-glucopyranosyl)-D-mannitol (9b). $[\alpha]_D^{26}$ −32.1 (c 1.10, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16–7.40 (m, 45H, aromatic), 5.03 (d, 1H, J = 11.1 Hz), 4.83 (d, 1H, J = 10.6 Hz), 4.78 (d, 1H, J = 10.6 Hz), 4.77 (d, 1H, J = 11.1Hz), 4.69 (d, 1H, J = 11.1 Hz), 4.61 (d, 1H, J = 12.1 Hz), 4.59 (d, 1H, J = 11.6 Hz), 4.56 (d, 1H, J = 10.6 Hz), 4.54 (d, 2H, J = 11.1 Hz), 4.50 (m, 2H), 4.48 (d, 1H, J = 10.6 Hz), 4.40 (d, 1H, J = 12.1 Hz), 4.39 (d, 1H, anomeric, J = 8.7 Hz), 4.38 (d, 1H, anomeric, J = 8.2 Hz), 4.35 (m, 2H), 4.29 (d, 1H, J = 11.6 Hz), 4.22 (br-d, 1H, J = 7.7 Hz), 4.11 (ddd, 1H, J = 2.4 Hz, J = 6.8 Hz, J = 8.7 Hz), 4.05 (dd, 1H, J = 9.2 Hz, J = 9.7 Hz), 3.83–3.89 (m, 4H), 3.83 (dd, 1H, J = 2.4 Hz, J = 10.1 Hz), 3.77–3.79 (m, 2H)3.69 (dd, 1H, J = 6.8 Hz, J = 10.1 Hz), 3.63 (dd, 1H, J = 9.7 Hz, J = 8.7 Hz), 3.63 (dd, 1H, J = 2.9 Hz, J = 10.6 Hz), 3.50 (dd, 1H, J = 3.9 Hz, J = 10.6 Hz), 3.34 (dd, 1H, J = 8.2 Hz, J = 10.1 Hz), 3.33 (dd, 1H, J = 8.7 Hz, J = 9.7 Hz), 3.26 (dd, 1H, J = 10.1 Hz, J = 9.7 Hz), 3.23 (dd, 1H, J = 9.7 Hz, J = 9.2 Hz), 3.19 (br-dd, 1H, J = 8.7 Hz, J = 2.9 Hz, J = 3.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.51, 138.25, 138.21, 138.18, 138.01, 137.99, 137.96, 137.86, 128.44, 128.38, 128.37, 128.31, 128.28, 128.24, 128.11, 128.01, 128.04, 127.96, 127.86, 127.80, 127.73, 127.67, 127.63, 127.54, 127.50, 127.44, 127.41, 127.37, 100.81 (anomeric), 100.76 (anomeric), 83.11, 81.24, 77.79, 77.63, 77.20, 77.08, 76.62, 75.72, 75.49, 75.12, 74.82, 74.78, 74.68, 74.22, 73.38, 73.22, 73.15, 70.85, 70.15, 68.48, 67.79, 66.92, 66.58, 65.88, 60.95; IR (KBr) 3089, 3065, 3032, 2868, 2110 (cm^{-1}).

2-Azido-1,3,5,6-tetra-*O*-benzyl-2-deoxy-4-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-(2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-β-D-glucopyranosyl)-D-mannitol (9d). $[\alpha]_D^{25}$ +7.8 (c 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09–7.37 (m, 45H, aromatic), 5.66 (d, 1H, anomeric, J = 3.9 Hz), 4.99 (d, 1H, J = 10.1 Hz), 4.87 (d, 1H, J = 10.6 Hz), 4.82 (d, 2H, J = 10.1 Hz), 4.72 (d, 1H, J = 11.6 Hz), 4.58 (d, 2H, J = 11.1 Hz), 4.57 (d, 1H, J = 12.1 Hz), 4.53 (d, 1H, J = 11.1 Hz), 4.52 (d, 1H, J = 12.1 Hz), 4.51 (d, 1H, J = 6.8 Hz), 4.49 (d, 1H, J = 9.7 Hz), 4.48 (d, 1H, J = 12.1 Hz), 4.46 (d, 1H, J = 9.7 Hz), 4.43 (d, 1H, J = 11.6 Hz), 4.42 (d, 2H, J = 12.1 Hz), 4.29 (d, 1H, J = 11.6 Hz), 4.28 (br-dd, 1H, J = 1.0 Hz, J = 5.3 Hz), 4.18 (d, 1H, J = 12.1 Hz), 4.04 (ddd, 1H, J = 2.4 Hz, J = 4.3 Hz, J = 6.3 Hz), 3.93 (dd, 1H, J = 8.7 Hz, J = 6.3 Hz), 3.92 (br-d, 1H, J = 6.3 Hz, J = 1.0 Hz), 3.90 (dd, 1H, J = 3.4 Hz, J = 11.1 Hz), 3.84 (dd, 1H, J = 10.6 Hz, J = 11.1 Hz), 3.79–3.85 (m, 3H), 3.75 (dd, 1H, J = 3.4 Hz, J = 11.1 Hz), 3.70 (dd, 1H, J = 11.1 Hz, J = 11.1 Hz), 3.69 (dd, 1H, J = 4.3 Hz, J = 11.1 Hz), 3.64–3.67 (m, 2H), 3.48 (dd, 1H, J = 1.9 Hz, J = 10.6 Hz), 3.35–3.43 (m, 2H), 3.30 (dd, 1H, J = 3.9 Hz, J = 10.6 Hz), 3.30 (br-d, 1H, J = 6.3 Hz, J = 3.4 Hz, J = 4.3 Hz), 3.23 (br-d, 1H, J = 10.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.31, 138.17, 137.92, 137.86, 137.84, 137.75, 137.67, 128.48, 128.44, 128.41, 128.33, 128.31, 128.29, 128.23, 128.18, 128.07, 127.96, 127.92, 127.84, 127.80, 127.76, 127.73, 127.66, 127.59, 127.47, 127.44, 127.41, 127.37, 127.35, 127.29, 100.91 (anomeric), 97.41 (anomeric), 83.76, 79.97, 77.95, 77.76, 77.24, 77.20, 75.29, 74.87, 74.56, 74.42, 74.26, 73.53, 73.41, 73.26, 73.20, 72.32, 71.26, 70.98, 70.04, 68.93, 67.60, 66.84, 66.71, 63.22, 61.15; IR (KBr) 3090, 3065, 3032, 2867, 2110 (cm^{-1}).

2-Azido-1,3,5,6-tetra-*O*-benzyl-2-deoxy-4-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-(2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranosyl)-α-D-glucopyranosyl)-D-glucitol (9e) and (9g). According to the method for the synthesis of **9a** and **9c**, disaccharide **25α** (575 mg, 0.615 mmol) was treated with donor **11** (763 mg, 1.23 mmol) in the presence of trimethylsilyl trifluoromethanesulfonate (11.1 μL, 61.5 μmol) in toluene (30 mL) to provide the mixture of **9e** and **9g** (β : α = 50 : 50, 685 mg, 0.492 mmol, 80%). Further purification of the mixture afforded β-isomer **9e** (265 mg, 0.190 mmol, 31%) and α-isomer **9g** (368 mg, 0.264 mmol, 43%).

2-Azido-1,3,5,6-tetra-*O*-benzyl-2-deoxy-4-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-(2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-α-D-glucopyranosyl)-D-glucitol (9e). $[\alpha]_D^{24}$ +25.7 (c 1.10, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16–7.39 (m, 45H, aromatic), 5.32 (d, 1H, anomeric, J = 3.4 Hz), 5.09 (d, 1H, J = 11.1Hz), 4.90 (d, 1H, J = 11.1 Hz), 4.82 (d, 1H, J = 10.6 Hz), 4.77 (d, 2H, J = 10.6 Hz), 4.67 (d, 1H, J = 11.1 Hz), 4.66 (m, 2H), 4.54 (d, 1H, J = 11.1 Hz), 4.54 (d, 2H, J = 10.6 Hz), 4.49 (d, 1H, J = 10.6 Hz), 4.47 (d, 1H, J = 11.1 Hz), 4.41 (m, 2H), 4.35 (d, 1H, J = 12.1 Hz), 4.31 (dd, 1H, J = 1.4 Hz, J = 5.8 Hz), 4.30 (d, 1H, J = 12.1 Hz), 4.15 (d, 1H, J = 12.1 Hz), 4.15 (br-dd, 1H, J = 10.1 Hz, J = 2.9 Hz), 4.12 (d, 1H, anomeric, J = 8.2 Hz), 4.01 (dd, 1H, J = 8.7 Hz, J = 10.1 Hz), 3.89 (dd, 1H, J = 8.7 Hz, J = 1.4 Hz), 3.80 (dd, 1H, J = 8.7 Hz, J = 10.1 Hz), 3.80 (dd, 1H, J = 5.3 Hz, J = 8.7 Hz), 3.74 (br-dd, 1H, J = 5.8 Hz, J = 5.6 Hz), 3.68 (dd, 1H, J = 5.3 Hz, J = 8.7 Hz), 3.64 (br-dd, 1H, J = 1.4 Hz, J = 7.7 Hz), 3.62 (dd, 1H, J = 3.4 Hz, J = 11.1 Hz), 3.57 (br-dd, 1H, J = 1.4 Hz, J = 8.7 Hz), 3.55 (dd, 1H, J = 9.2 Hz, J = 9.2 Hz), 3.52 (dd, 1H, J = 7.7 Hz), 3.52 (dd, 1H, J = 2.9 Hz, J = 9.7 Hz), 3.43 (dd, 1H, J = 4.8 Hz, J = 11.1 Hz), 3.32 (dd, 1H, J = 8.2 Hz, J = 9.7 Hz), 3.16 (br-d, 1H, J = 9.7 Hz), 3.13 (dd, J = 3.4 Hz, J = 8.7 Hz), 3.13 (ddd, 1H, J = 9.2 Hz, J = 3.4 Hz, J = 4.8 Hz), 3.12 (dd, 1H, J = 9.7 Hz, J = 9.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.55, 138.32, 138.13, 138.04, 137.92, 137.88, 137.66, 137.47, 128.49, 128.45, 128.42, 128.35, 128.30, 128.27, 128.21, 128.14, 128.09, 127.99, 127.88, 127.86, 127.79, 127.71, 127.69, 127.66, 127.60, 127.57, 127.49, 127.36, 127.31, 127.27, 100.64 (anomeric), 97.82 (anomeric), 82.99, 79.88, 77.92, 77.70, 77.56, 77.20, 77.11, 76.17, 75.42, 75.13, 74.78, 74.68, 74.39, 73.48, 73.27, 73.22, 72.31, 70.30, 69.32, 68.94, 68.60, 67.40, 66.71, 62.78, 61.08; IR (KBr) 3089, 3065, 3032, 2919, 2868, 2109 (cm^{-1}); HRMS (ESI) calcd. [M + Na]$^+$ 1414.6159, found 1414.6161.

2-Azido-1,3,5,6-tetra-*O*-benzyl-2-deoxy-4-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-(2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-α-D-glucopyranosyl)-D-glucitol (9g). $[\alpha]_D^{28}$ +90.6 (*c* 1.16, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.12–7.41 (m, 45H, aromatic), 5,69 (d, 1H, anomeric, $J = 3.4$ Hz), 5.39 (d, 1H, anomeric, $J = 3.4$ Hz), 4.96 (d, 1H, $J = 10.1$ Hz), 4.93 (d, 1H, $J = 11.6$ Hz), 4.91 (d, 1H, $J = 10.6$ Hz), 4.89 (d, 1H, $J = 10.1$ Hz), 4.87 (d, 1H, $J = 10.6$ Hz), 4.76 (d, 1H, $J = 11.1$ Hz), 4.60 (d, 1H, $J = 12.1$ Hz), 4.55 (d, 1H, $J = 12.1$ Hz), 4.54 (d, 1H, $J = 12.1$ Hz), 4.51 (d, 1H, $J = 11.6$ Hz), 4.50 (d, 1H, $J = 12.1$ Hz), 4.45 (d, 1H, $J = 12.1$ Hz), 4.45 (d, 1H, $J = 11.1$ Hz), 4.41 (m, 2H), 4.37 (d, 1H, $J = 12.6$ Hz), 4.30 (br-dd, 1H, $J = 2.9$ Hz, $J = 5.8$ Hz), 4.28 (d, 1H, $J = 12.6$ Hz), 4.15 (br-dd, 1H, $J = 8.7$ Hz, $J = 2.4$ Hz), 4.15 (d, 1H, $J = 12.1$ Hz), 4.05 (dd, 1H, $J = 9.2$ Hz, $J = 8.7$ Hz), 4.03 (dd, 1H, $J = 9.2$ Hz, $J = 9.2$ Hz), 3.93 (dd, 1H, $J = 10.6$ Hz, $J = 9.7$ Hz), 3.92 (dd, 1H, $J = 9.7$ Hz, $J = 2.9$ Hz), 3.83 (dd, 1H, $J = 5.3$ Hz, $J = 8.7$ Hz), 3.73 (dd, 1H, $J = 9.7$ Hz, $J = 8.7$ Hz), 3.73 (br-ddd, 1H, $J = 5.8$ Hz, $J = 5.3$ Hz, $J = 5.3$ Hz), 3.70 (dd, 1H, $J = 5.3$ Hz, $J = 8.7$ Hz), 3.64 (br-d, 1H, $J = 8.2$ Hz), 3.61 (br-ddd, 1H, $J = 8.7$ Hz, $J = 2.4$ Hz, $J = 4.8$ Hz), 3.57 (br-dd, 1H, $J = 1.4$ Hz, $J = 4.8$ Hz, $J = 9.7$ Hz), 3.52 (dd, 1H, $J = 4.8$ Hz, $J = 8.7$ Hz), 3.48 (dd, 1H, $J = 2.4$ Hz, $J = 11.1$ Hz), 3.38 (dd, 1H, $J = 2.4$ Hz, $J = 11.6$ Hz), 3.30 (dd, 1H, $J = 3.4$ Hz, $J = 9.2$ Hz), 3.24 (br-dd, 1H, $J = 4.8$ Hz, $J = 11.1$ Hz), 3.23 (br-dd, 1H, $J = 11.6$ Hz), 3.21 (dd, 1H, $J = 3.4$ Hz, $J = 10.6$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.26, 138.16, 138.10, 137.99, 137.93, 137.89, 137.63, 137.54, 137.45, 128.42, 128.37, 128.30, 128.26, 128.16, 127.96, 127.89, 127.85, 127.81, 127.68, 127.64, 127.54, 127.31, 127.20, 127.13, 97.79 (anomeric), 96.07 (anomeric), 80.98, 79.65, 79.59, 77.86, 75.17, 74.76, 74.42, 74.23, 73.43, 73.22, 72.50, 72.12, 71.17, 70.19, 69.35, 68.98, 68.36, 67.62, 64.00, 62.96, 61.13; IR (KBr) 3089, 3065, 3032, 2922, 2867, 2107 (cm^{-1}); HRMS (ESI) calcd. $[M + Na]^+$ 1414.6159, found 1414.6159.

2-Azido-1,3,5,6-tetra-*O*-benzyl-2-deoxy-4-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-(2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranosyl)-α-D-glucopyranosyl)-D-mannitol (9f) and (9h). According to the method for the synthesis of **9a** and **9c**, disaccharide **26α** (701 mg, 0.750 mmol) was treated with donor **11** (930 mg, 1.50 mmol) in the presence of trimethylsilyl trifluoromethanesulfonate (13.6 μL, 75.0 μmol) in toluene (30 mL) to provide the mixture of **9e** and **9g** (β : α = 42 : 58, 933 mg, 0.670 mmol, 90%). Further purification of the mixture afforded β-isomer **9e** (357 mg, 0.256 mmol, 34%) and α-isomer **9g** (485 mg, 0.348 mmol, 47%).

2-Azido-1,3,5,6-tetra-*O*-benzyl-2-deoxy-4-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-(2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-α-D-glucopyranosyl)-D-mannitol (9f). $[\alpha]_D^{21}$ +42.3 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.17–7.40 (m, 45H, aromatic), 5.32 (d, 1H, anomeric, $J = 3.9$ Hz), 5.09 (d, 1H, $J = 11.1$ Hz), 4.81 (d, 1H, $J = 10.6$ Hz), 4.77 (d, 2H, $J = 10.6$ Hz), 4.74 (d, 1H, $J = 9.7$ Hz), 4.71 (d, 1H, $J = 9.7$ Hz), 4.68 (d, 1H, $J = 11.1$ Hz), 4.54 (d, 1H, $J = 11.6$ Hz), 4.54 (d, 2H, $J = 11.1$ Hz), 4.52 (m, 2H), 4.51 (d, 1H, $J = 10.1$ Hz), 4.47 (d,1H, $J = 10.1$ Hz), 4.45 (d, 1H, $J = 11.6$ Hz), 4.35 (d, 1H, $J = 12.1$ Hz), 4.30 (d, 1H, $J = 12.1$ Hz), 4.15 (d, 1H, $J = 12.1$ Hz), 4.10 (d, 1H, anomeric, $J = 8.2$ Hz), 4.09–4.13 (m, 2H), 4.00 (dd, 1H, $J = 10.1$ Hz, $J = 8.7$ Hz), 3.89–3.93 (m, 2H), 3.85 (dd, 1H, $J = 5.3$ Hz, $J = 9.7$ Hz), 3.81 (dd, 1H, $J = 8.7$ Hz, $J = 10.1$ Hz), 3.73 (ddd, 1H, $J = 5.3$ Hz, $J = 3.9$ Hz), 3.66–3.70 (m, 3H), 3.63 (br-d, 1H, $J = 10.6$ Hz), 3.56 (dd, 1H, $J = 9.2$ Hz, $J = 9.7$ Hz), 3.52 (br-d, 1H, $J = 12.6$ Hz), 3.43 (dd, 1H, $J = 4.3$ Hz, $J = 10.6$ Hz), 3.31 (dd, 1H, $J = 8.2$ Hz, $J = 8.7$ Hz), 3.13 (dd, 1H, $J = 3.9$ Hz, $J = 8.7$ Hz), 3.11 (dd, 1H, $J = 8.7$ Hz, $J = 9.2$ Hz), 3.09–3.13 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.56, 138.33, 138.18, 138.05, 138.04, 137.87, 137.62, 137.60, 128.51, 128.45, 128.38, 128.36, 128.31, 128.28, 128.22, 128.13, 128.09, 127.98, 127.89, 127.88, 127.80, 127.76, 127.73, 127.70, 127.66, 127.62, 127.57, 127.52, 127.44, 127.35, 127.31, 127.28, 100.65 (anomeric), 97.97 (anomeric), 83.00, 80.52, 78.12, 77.92, 77.57, 76.19, 75.41, 75.16, 74.78, 74.69, 74.35, 73.44, 73.38, 73.27, 73.23, 72.20, 70.30, 69.33, 69.05, 68.61, 67.39, 66.70, 62.80, 62.34; IR (KBr) 3089, 3065, 3032, 2913, 2868, 2110 (cm^{-1}).

2-Azido-1,3,5,6-tetra-*O*-benzyl-2-deoxy-4-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-(2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-α-D-glucopyranosyl)-D-mannitol (9h). $[\alpha]_D^{25}$ +102.0 (*c* 1.13, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.12–7.42 (m, 45H, aromatic), 5.69 (d, 1H, anomeric, $J = 3.9$ Hz), 5.38 (d, 1H, anomeric, $J = 3.4$ Hz), 4.97 (d, 1H, $J = 10.1$ Hz), 4.90 (d, 1H, $J = 10.6$ Hz), 4.90 (d, 1H, $J = 10.1$ Hz), 4.86 (d, 1H, $J = 10.6$ Hz), 4.76 (d, 2H, $J = 11.1$ Hz), 4.72 (d, 1H, $J = 11.1$ Hz), 4.55 (d, 1H, $J = 11.6$ Hz), 4.55 (d, 1H, $J = 11.6$ Hz), 4.51 (d, 1H, $J = 11.6$ Hz), 4.49 (d, 1H, $J = 11.6$ Hz), 4.48 (d, 1H, $J = 11.1$ Hz), 4.48 (d, 1H, $J = 11.6$ Hz), 4.45 (d, 1H, $J = 12.6$ Hz), 4.42 (d, 1H, $J = 11.6$ Hz), 4.35 (d, 1H, $J = 12.1$ Hz), 4.27 (d, 1H, $J = 12.1$ Hz), 4.15 (d, 1H, $J = 12.6$ Hz), 4.12–4.14 (m, 2H), 4.03–4.07 (m, 2H), 3.91 (dd, 1H, $J = 9.7$ Hz, $J = 8.7$ Hz), 3.90–3.96 (m, 2H), 3.87 (dd, 1H, $J = 3.4$ Hz, $J = 8.2$ Hz), 3.74 (dd, 1H, $J = 8.7$ Hz, $J = 10.1$ Hz), 3.67–3.70 (m, 4H), 3.60 (br-d, 1H, $J = 10.1$ Hz), 3.48 (dd, 1H, $J = 1.9$ Hz, $J = 10.6$ Hz), 3.36 (dd, 1H, $J = 1.9$ Hz, $J = 11.1$ Hz), 3.28 (dd, 1H, $J = 3.4$ Hz, $J = 9.7$ Hz), 3.24 (dd, 1H, $J = 1.0$ Hz, $J = 10.6$ Hz), 3.21 (dd, 1H, $J = 3.9$ Hz, $J = 9.7$ Hz), 3.20 (br-d, 1H, $J = 11.1$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.23, 138.18, 138.14, 138.10, 138.05, 137.92, 137.69, 137.60, 128.44, 128.39, 128.35, 128.30, 128.28, 128.18, 127.96, 127.90, 127.83, 127.79, 127.70, 127.67, 127.65, 127.48, 127.34, 127.12, 97.92 (anomeric), 97.80 (anomeric), 80.80, 80.22, 79.68, 77.93, 77.87, 75.17, 74.77, 74.35, 74.20, 73.41, 73.39, 73.19, 72.59, 72.02, 71.21, 70.13, 69.29, 69.18, 68.41, 67.65, 63.97, 62.99, 62.48; IR (KBr) 3090, 3065, 3032, 2921, 2867, 2106 (cm^{-1}).

1,3,5,6-Tetra-*O*-benzyl-2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetrakis-(*tert*-butyloxycarbonylmethyl)-*N*″-acetylamino)-4-*O*-(3,6-di-*O*-benzyl-2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetrakis-(*tert*-butyloxycarbonylmethyl)-*N*″-acetylamino)-4-*O*-(3,4,6-tri-*O*-benzyl-2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetrakis-(*tert*-butyloxycarbonylmethyl)-*N*″-acetylamino)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-D-glucitol (27a). To a solution of 2-azido-1,3,5,6-tetra-*O*-benzyl-2-deoxy-4-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-(2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-β-D-glucopyranosyl)-D-glucitol (**9a**) (97.1 mg, 69.7 mmol) in toluene (1.30 mL) was added 0.1 M NaOH aq. (23.0 μL) and 1 M trimethyl phosphine in toluene solution (0.230 mL, 0.230 mmol) at room temperature. After being stirred at 110 °C for 1 h, the reaction mixture was concentrated *in vacuo*. The residue was purified by chromatography on NH–silica gel with $CHCl_3$ to remove the NaOH. The residue was used without further purification. To a solution of the residue and diethylenetriamine-*N*,*N*,*N*′,*N*″-tetrakis-(*tert*-butyloxycarbonylmethyl)-*N*″-acetic acid (**8**) (646 mg, 1.05 mmol) in CH_2Cl_2 (0.730 mL) was added DIEA (0.182 mL, 1.05 mmol), DMAP (128 mg, 1.05 mmol) and HATU (399 mg, 1.05 mmol, 15.0 eq.) at room temperature. After being stirred at the same temperature for 15 h, the reaction mixture was concentrated *in vacuo*. The residue was chromatographed on NH-silica gel with $CHCl_3$ and gel permeation chromatography (GPC) to give 1,3,5,6-tetra-*O*-benzyl-2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetrakis-(*tert*-butyloxycarbonylmethyl)-*N*″-acetylamino)-4-*O*-(3,6-di-*O*-benzyl-2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetrakis-(*tert*-butyloxycarbonylmethyl)-*N*″-acetylamino)-4-*O*-(3,4,6-tri-*O*-benzyl-2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetrakis-(*tert*-butyloxycarbonylmethyl)-*N*″-acetylamino)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-D-glucitol (**27a**) (126 mg, 40.5 μmol, 2 steps 58%); $[\alpha]_D^{26}$ +5.3 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, 1H, $J = 8.2$ Hz), 7.88 (d, 1H, $J = 8.7$ Hz), 7.58 (d, 1H, $J = 9.7$ Hz), 7.09–7.28 (m, 45H, aromatic), 5.06 (d, 1H, $J = 11.6$ Hz), 4.94 (d, 1H, anomeric, $J = 7.7$ Hz),

4.87 (d, 1H, anomeric, J = 8.2 Hz), 4.80 (d, 1H, J = 11.6 Hz), 4.79 (d, 1H, J = 11.6 Hz), 4.67 (d, 1H, J = 10.1 Hz), 4.64 (d, 1H, J = 11.6 Hz), 4.58 (d, 1H, J = 12.1 Hz), 4.56 (d, 1H, J = 11.6 Hz), 4.53 (d, 2H, J = 11.6 Hz), 4.51 (d, 1H, J = 10.1 Hz), 4.50–4.55 (m, 1H), 4.50 (m, 2H), 4.44 (m, 2H), 4.32 (d, 1H, J = 11.6 Hz), 4.28 (m, 2H), 4.26 (d, 1H, J = 11.6 Hz), 4.21 (dd, 1H, J = 1.9 Hz, J = 5.8 Hz), 4.00–4.05 (m, 4H), 3.91 (dd, 1H, J = 8.7 Hz, J = 9.7 Hz), 3.83 (dd, 1H, J = 7.7 Hz, J = 8.7 Hz), 3.71 (dd, 1H, J = 3.4 Hz, J = 10.6 Hz), 3.60–3.65 (m, 3H), 3.56 (br-d, 1H, J = 10.6 Hz), 3.46 (dd, 1H, J = 3.9 Hz, J = 10.1 Hz), 3.44–3.45 (m, 3H), 3.29–3.33 (m, 2H), 3.30 (br-d, 1H, J = 10.1 Hz), 3.04–3.37 (m, 30H), 2.48–2.73 (m, 24H), 1.36–1.43 (m, 108H, *t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.62, 171.23, 171.17, 171.11, 170.58, 170.53, 170.48, 170.43, 170.21, 139.58, 138.95, 138.86, 138.60, 138.52, 138.41, 138.35, 138.24, 128.22, 128.19, 128.15, 128.09, 128.02, 127.88, 127.62, 127.60, 127.47, 127.44, 127.34, 127.17, 127.08, 127.02, 126.67, 100.88 (anomeric), 99.30 (anomeric), 81.44, 81.28, 80.92, 80.71, 80.66, 80.50, 80.44, 80.20, 79.27, 78.44, 77.20, 76.87, 75.26, 74.95, 74.74, 74.22, 74.19, 73.50, 73.12, 72.77, 72.64, 72.32, 71.87, 70.16, 70.13, 68.78, 59.31, 59.06, 58.80, 56.89, 56.47, 56.24, 56.17, 55.89, 53.25, 52.77, 52.63, 52.50, 52.39, 52.28, 51.96, 47.33, 28.09; IR (KBr) 3338, 3090, 3065, 3032, 3979, 3933, 3870, 1733, 1674 (cm^{-1}); MS(ESI-TOF) $[M + H]^+$ calcd. 3114.80, found 3115.38, $[M + 2H]^{2+}$ calcd. 1557.90, found 1558.12, $[M + 3H]^{3+}$ calcd. 1038.93, found 1039.06.

1,3,5,6-Tetra-*O*-benzyl-2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetrakis-(*tert*-butyloxycarbonylmethyl)-*N*″-acetylamino)-4-*O*-(3,6-di-*O*-benzyl-2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetrakis-(*tert*-butyloxycarbonylmethyl)-*N*″-acetylamino)-4-*O*-(3,4,6-tri-*O*-benzyl-2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetrakis-(*tert*-butyloxycarbonylmethyl)-*N*″-acetylamino)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-D-mannitol (27b). According to the method for the synthesis of **27a**, triazido **9b** (129 mg, 92.7 mmol) was treated with 1 M trimethyl phosphine in toluene solution (0.306 mL, 0.306 mmol) in toluene (1.30 mL) and 0.1 M NaOH aq. (28.6 µL) to provide a triamine. The triamine was reacted with *t*-BuDTPAOH (**8**) (859 mg, 1.39 mmol) by DMAP (170 mg, 1.39 mmol), HATU (528 mg, 1.39 mmol) in CH_2Cl_2 (0.904 mL) and DIEA (0.242 mL, 1.39 mmol, 15.0 eq.) to provide triamide **27b** (205 mg, 65.8 µmol, 2 steps 71%); $[\alpha]_D^{25}$ +2.6 (*c* 1.22, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, 1H, J = 8.7 Hz), 7.79 (d, 1H, J = 9.2 Hz), 7.60 (d, 1H, J = 8.7 Hz), 7.09–7.30 (m, 45H, aromatic), 5.12 (d, 1H, J = 11.6 Hz), 4.95 (d, 1H, J = 12.1 Hz), 4.92 (d, 1H, anomeric, J = 8.2 Hz), 4.81 (d, 1H, anomeric, J = 7.2 Hz), 4.78 (d, 1H, J = 11.1H,), 4.66 (d, 1H, J = 10.6 Hz), 4.64 (d, 1H, J = 11.1 Hz), 4.54 (d, 3H, J = 11.6 Hz), 4.51 (d, 1H, J = 10.6 Hz), 4.50 (d, 1H, J = 10.6 Hz), 4.47 (d, 2H, J = 10.6 Hz), 4.45–4.51 (m, 1H), 4.40 (d, 1H, J = 11.6 Hz), 4.39 (d, 1H, J = 12.1 Hz), 4.36 (dd, 1H, J = 2.9 Hz, J = 8.7 Hz), 4.31 (d, 1H, J = 11.6 Hz), 4.24 (1H, J = 11.6 Hz), 4.22 (m, 2H), 4.02 (dd, 1H, J = 9.2 Hz, J = 8.7 Hz), 3.89–3.98 (m, 2H), 3.82 (br-dd, 1H, J = 8.7 Hz, J = 2.9 Hz), 3.81 (dd, 1H, J = 2.9 Hz, J = 10.1 Hz), 3.79 (dd, 1H, J = 6.8 Hz, J = 2.9 Hz), 3.75–3.80 (m, 2H), 3.71 (m, 1H), 3.64 (dd, 1H, J = 9.7 Hz, J = 8.7 Hz), 3.58–3.66 (m, 3H), 3.53–3.56 (m, 2H), 3.44 (dd, 1H, J = 3.9 Hz, J = 10.6 Hz), 3.28–3.39 (m, 2H), 3.01–3.39 (m, 30H), 2.47–2.73 (m, 24H), 1.37–1.43 (m, 108H, *t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.65, 171.44, 171.10, 170.62, 170.58, 170.52, 170.49, 170.46, 170.34, 139.69, 139.38, 138.73, 138.70, 138.61, 138.56, 138.38, 138.31, 138.26, 128.24, 128.17, 128.09, 127.99, 127.89, 127.66, 127.56, 127.54, 127.46, 127.38, 127.29, 127.20, 127.15, 126.93, 126.89, 126.64, 100.72 (anomeric), 99.74 (anomeric), 81.77, 81.29, 81.01, 80.84, 80.74, 80.70, 80.54, 79.94, 78.80, 78.35, 75.56, 75.38, 74.72, 74.25, 74.15, 73.32, 73.08, 72.98, 72.93, 72.62, 71.66, 69.33, 68.84, 68.54, 68.48, 59.35, 59.16, 58.30, 56.55, 56.34, 56.18, 55.96, 55.91, 55.79, 55.51, 53.15, 52.92, 52.67, 52.54, 52.44, 52.34, 52.02, 49.22, 28.43, 28.11; IR (KBr) 3361, 3064, 3032, 2978, 2933, 2870, 1733, 1674 (cm^{-1}); MS(ESI-TOF) $[M + 2H]^{2+}$ calcd. 1557.90, found, 1558.03, $[M + 3H]^{3+}$ calcd. 1038.93, found 1039.00.

1,3,5,6-Tetra-*O*-benzyl-2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetrakis-(*tert*-butyloxycarbonylmethyl)-*N*″-acetylamino)-4-*O*-(3,6-di-*O*-benzyl-2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetrakis-(*tert*-butyloxycarbonylmethyl)-*N*″-acetylamino)-4-*O*-(3,4,6-tri-*O*-benzyl-2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetrakis-(*tert*-butyloxycarbonylmethyl)-*N*″-acetylamino)-α-D-glucopyranosyl)-β-D-glucopyranosyl)-D-glucitol (27c). According to the method for the synthesis of **27a**, triazido **9c** (96.4 mg, 69.2 mmol) was treated with 1 M trimethyl phosphine in toluene solution (0.228 mL, 0.228 mmol) in toluene (1.30 mL) and 0.1 M NaOH aq. (22.8 µL) to provide a triamine. The triamine was reacted with *t*-BuDTPAOH (**8**) (642 mg, 1.04 mmol) by DMAP (127 mg, 1.04 mmol) and HATU (395 mg, 1.04 mmol) in CH_2Cl_2 (0.732 mL) and DIEA (0.181 mL, 1.04 mmol) to provide triamide **27c** (100 mg, 32.1 µmol, 2 steps 47%); $[\alpha]_D^{25}$ +18.2 (*c* 1.30, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, 1H, J = 8.7 Hz), 7.63 (d, 1H, J = 9.7 Hz), 7.58 (d, 1H, J = 9.7 Hz), 7.11–7.29 (m, 45H, aromatic), 5.51 (d, 1H, anomeric, J = 3.4 Hz), 4.99 (d, 1H, anomeric, J = 6.3 Hz), 4.80 (d, 1H, J = 11.6 Hz), 4.74 (d, 1H, J = 11.6 Hz), 4.68 (d, 1H, J = 11.1 Hz), 4.65 (d, 1H, J = 11.6 Hz), 4.60 (d, 2H, J = 11.6 Hz), 4.57 (d, 1H, J = 11.6 Hz), 4,54 (d, 1H, J = 11.6 Hz), 4.51–4.58 (m, 1H), 4.50 (d, 2H, J = 11.6 Hz), 4.47 (d, 1H, J = 11.1 Hz), 4.45 (d, 1H, J = 12.1 Hz), 4.45 (m, 2H), 4.41 (d, 1H, J = 12.1 Hz), 4.37 (ddd, 1H, J = 3.4 Hz, J = 8.7 Hz, J = 9.7 Hz), 4.34 (d, 1H, J = 12.1 Hz), 4.30, (d, 1H, J = 12.1 Hz), 4.29 (d, 1H, J = 12.1 Hz), 4.25 (dd, 1H, J = 2.4 Hz, J = 5.3 Hz), 4.14 (m, 1H), 4.05 (br-d, 1H, J = 5.6 Hz,), 4.02 (m, 1H), 4.01 (m, 1H), 3.91 (m, 1H), 3.65–3.83 (m, 5H), 3.58 (dd, 1H, J = 6.3 Hz, J = 10.6 Hz), 3.48–3.53 (m, 3H), 3.32–3.41 (m, 2H), 3.05–3.37 (m, 30H), 2.52–2.77 (m, 24H)1.33–1.43 (m, 108H, *t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.48, 171.13, 170.94, 170.81, 170.61, 170.49, 170.46, 170.24, 138.94, 138.86, 138.60, 138.57, 138.44, 138.43, 138.27, 138.12, 137.74, 128.31, 128.18, 128.13, 128.05, 127.81, 127.60, 127.54, 127.48, 127.45, 127.40, 127.25, 127.21, 126.98, 100.68 (anomeric), 96.42 (anomeric), 81.27, 80.94, 80.83, 80.75, 80.69, 80.56, 80.52, 80.47, 79.04, 78.51, 74.36, 74.21, 73.53, 73.48, 73.29, 73.09, 72.64, 72.40, 71.92, 71.69, 70.22, 69.40, 68.28, 59.19, 58.84, 58.54, 56.43, 56.31, 55.90, 53.30, 52.84, 52.63, 52.49, 52.37, 52.24, 51.86, 47.39, 28.41, 28.10, 27.99; IR (KBr) 3351, 3065, 3032, 2979, 2933, 2869, 1733, 1682 (cm^{-1}); MS(ESI-TOF) $[M + H]^+$ calcd. 3114.80, found 3115.33, $[M + 2H]^{2+}$ calcd. 1557.90, found 1558.12, $[M + 3H]^{3+}$ calcd. 1038.93, found 1039.06.

1,3,5,6-Tetra-*O*-benzyl-2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetrakis-(*tert*-butyloxycarbonylmethyl)-*N*″-acetylamino)-4-*O*-(3,6-di-*O*-benzyl-2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetrakis-(*tert*-butyloxycarbonylmethyl)-*N*″-acetylamino)-4-*O*-(3,4,6-tri-*O*-benzyl-2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetrakis-(*tert*-butyloxycarbonylmethyl)-*N*″-acetylamino)-α-D-glucopyranosyl)-β-D-glucopyranosyl)-D-mannitol (27d). According to the method for the synthesis of **27a**, triazido **9d** (111 mg, 79.6 mmol) was treated with 1 M trimethyl phosphine in toluene (0.263 mL, 0.263 mmol), in toluene (1.30 mL) and 0.1 M NaOH aq. (22.8 µL) to provide a triamine. The triamine was reacted with *t*-BuDTPAOH **8** (735 mg, 1.19 mmol) by DMAP (145 mg, 1.19 mmol) and HATU (452 mg, 1.19 mmol) in CH_2Cl_2 (0.732 mL) and DIEA (0.207 mL, 1.19 mmol) to provide triamide **27d** (114 mg, 36.6 µmol, 2 steps 46%); $[\alpha]_D^{24}$ +17.8 (*c* 0.96, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, 1H, J = 8.7 Hz), 7.63 (d, 1H, J = 8.7 Hz), 7.62 (d, 1H, J = 9.7 Hz), 7.14–7.33 (m, 45H, aromatic), 5.54 (d, 1H, anomeric, J = 3.4 Hz), 4.98 (d, 1H, anomeric, J = 7.2 Hz), 4.91 (d, 1H, J = 12.1 Hz), 4.76 (d, 1H, J = 11.1 Hz), 4.68 (d, 1H, J = 11.1 Hz), 4.65 (d, 1H, J = 13.0 Hz), 4.61 (d, 1H, J = 11.1 Hz), 4.59 (d, 1H, J = 11.1 Hz), 4.52 (d, 1H, J = 12.1 Hz), 4.50 (m,

2H), 4.49 (d, 3H, J = 11.1 Hz), 4.45–4.50 (m, 1H), 4.43 (d, 1H, J = 11.1 Hz), 4.42 (d, 1H, J = 12.1 Hz), 4.40 (d, 1H, J = 11.1 Hz), 4.38 (d, 1H, J = 12.1 Hz), 4.35–4.42 (m, 2H), 4.30 (d, 1H, J = 12.1 Hz), 4.29 (d, 1H, J = 12.6 Hz), 3.87–4.07 (m, 4H), 3.77–3.87 (m, 5H), 3.79 (dd, 1H, J = 9.7 Hz, J = 8.2 Hz), 3.71 (dd, 1H, J = 8.7 Hz, J = 9.7 Hz), 3.60–3.66 (m, 2H), 3.61 (dd, 1H, J = 6.3 Hz, J = 9.7 Hz), 3.53 (dd, 1H, J = 1.9 Hz, J = 8.7 Hz), 3.37–3.51 (m, 2H), 3.07–3.39 (m, 30H), 2.57–2.74 (m, 24H), 1.34–1.44 (m, 108H, *t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.30, 171.03, 170.90, 170.84, 170.64, 170.61, 170.58, 170.51, 170.48, 170.45, 170.36, 139.30, 138.67, 138.57, 138.56, 138.54, 138.44, 138.30, 138.15, 137.75, 128.28, 128.17, 128.12, 128.05, 127.98, 127.87, 127.77, 127.57, 127.53, 127.50, 127.44, 127.34, 127.30, 127.23, 127.05, 126.95, 100.43 (anomeric), 96.18 (anomeric), 81.58, 80.97, 80.85, 80.70, 80.67, 80.56, 80.52, 80.46, 79.55, 78.93, 77.98, 74.56, 74.52, 74.31, 73.50, 73.35, 73.25, 72.88, 72.69, 71.60, 69.39, 69.13, 68.63, 68.30, 59.22, 58.60, 58.35, 56.43, 56.34, 56.13, 55.95, 55.89, 53.11, 52.90, 52.73, 52.65, 52.61, 52.46, 52.41, 52.31, 51.88, 49.50, 28.09, 27.98; IR (KBr) 3663, 2978, 1733, 1683 (cm^{-1}); MS(ESI-TOF) $[M + H]^+$ calcd. 3114.80, found 3115.20, $[M + 2H]^{2+}$ calcd. 1557.90, found 1558.03, $[M + 3H]^{3+}$ calcd. 1038.93, found 1038.99.

1,3,5,6-Tetra-*O*-benzyl-2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetrakis-(*tert*-butyloxycarbonylmethyl)-*N*″-acetylamino)-4-*O*-(3,6-di-*O*-benzyl-2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetrakis-(*tert*-butyloxycarbonylmethyl)-*N*″-acetylamino)-4-*O*-(3,4,6-tri-*O*-benzyl-2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetrakis-(*tert*-butyloxycarbonylmethyl)-*N*″-acetylamino)-β-D-glucopyranosyl)-α-D-glucopyranosyl)-D-glucitol (27e). According to the method for the synthesis of **27a**, triazido **9e** (94.1 mg, 67.6 mmol) was treated with 1 M trimethyl phosphine in toluene (0.263 mL, 0.263 mmol), in toluene (1.30 mL) and 0.1 M NaOH aq. (22.3 μL) to provide a triamine. The triamine was reacted with *t*-BuDTPAOH **8** (624 mg, 1.01 mmol) by DMAP (123 mg, 1.01 mmol) and HATU (384 mg, 1.01 mmol) in CH_2Cl_2 (0.732 mL) and DIEA (0.176 mL, 1.01 mmol) to provide triamide **27e** (145 mg, 46.6 μmol, 2 steps 69%); $[\alpha]_D^{24}$ +23.9 (c 1.30, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, 1H, J = 8.0 Hz), 7.78 (d, 1H, J = 9.2 Hz), 7.69 (d, 1H, J = 9.7 Hz), 7.08–7.36 (m, 45H, aromatic), 5.34 (d, 1H, anomeric, J = 3.9 Hz), 5.13 (d, 1H, J = 12.1 Hz), 4.81 (d, 1H, anomeric, J = 7.7 Hz), 4.75 (d, 1H, J = 11.1 Hz), 4.74 (d, 1H, J = 11.6 Hz), 4.62 (d, 1H, J = 11.1Hz), 4.55 (m, 2H), 4.60 (m, 2H), 4.54 (d, 1H, J = 12.1 Hz), 4.52 (d, 1H, J = 12.1 Hz), 4.48 (d, 1H, J = 12.1 Hz), 4.47 (d, 1H, J = 12.1 Hz), 4.46 (br-dd, 1H, J = 3.9 Hz, J = 9.2 Hz), 4.37 (d, 1H, J = 11.6 Hz), 4.24–4.31 (m, 1H), 4.27 (d, 1H, J = 12.1 Hz), 4.20–4.24 (m, 1H), 4.20 (d, 1H, J = 12.1 Hz), 4.19 (d, 1H, J = 12.1 Hz), 4.17 (d, 1H, J = 12.1 Hz), 4.15–4.20 (m, 1H), 4.09 (m, 1H), 3.95 (m, 1H), 3.88 (m, 2H), 3.83 (br-dd, 1H, J = 1.9 Hz, J = 6.8 Hz), 3.77 (dd, 1H, J = 6.8 Hz, J = 9.7 Hz), 3.73–3.75 (m, 1H), 3.73 (dd, 1H, J = 8.7 Hz, J = 9.7 Hz), 3.68 (dd, 1H, J = 4.3 Hz, J = 9.7 Hz), 3.61 (dd, 1H, J = 9.2 Hz, J = 8.7 Hz), 3.57 (br-d, 1H, J = 9.7 Hz), 3.51 (br-d, 1H, J = 9.2 Hz), 3.40 (dd, 1H, J = 3.9 Hz, J = 9.2 Hz), 3.27 (dd, 1H, J = 5.8 Hz, J = 9.2 Hz), 3.17–3.27 (m, 2H), 2.95–3.38 (m, 30H), 2.41–2.83 (m, 24H), 1.37–1.44 (m, 108H, *t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.45, 171.33, 171.13, 171.09, 170.97, 170.55, 170.47, 170.42, 170.29, 139.77, 138.70, 138.59, 138.56, 138.46, 138.30, 137.98, 137.91, 128.32, 128.20, 128.15, 128.11, 128.02, 127.81, 127.70, 127.58, 127.43, 127.36, 127.31, 127.23, 127.14, 127.01, 126.66, 126.47, 99.43 (anomeric), 96.34 (anomeric), 81.69, 81.18, 80.82, 80.72, 80.68, 80.49, 80.46, 78.83, 78.22, 78.08, 75.78, 74.79, 74.59, 74.09, 74.06, 73.93, 73.71, 73.02, 72.76, 72.67, 72.38, 72.27, 71.19, 70.93, 70.62, 69.00, 68.70, 68.28, 59.39, 59.15, 58.66, 56.61, 56.55, 56.40, 55.99, 55.90, 55.85, 55.82, 55.75, 55.62, 53.16, 52.88, 52.65, 52.53, 52.29, 52.08, 51.77, 51.70, 48.25, 28.41, 28.09; IR (KBr) 3343, 3090, 3065, 3031, 2979, 2934, 2871, 1733, 1675 (cm^{-1}); MS(ESI-TOF) $[M + H]^+$ calcd. 3114.80, found 3115.38, $[M + 2H]^{2+}$ calcd. 1557.90, found 1558.11, $[M + 3H]^{3+}$ calcd. 1038.93, found 1039.06.

1,3,5,6-Tetra-*O*-benzyl-2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetrakis-(*tert*-butyloxycarbonylmethyl)-*N*″-acetylamino)-4-*O*-(3,6-di-*O*-benzyl-2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetrakis-(*tert*-butyloxycarbonylmethyl)-*N*″-acetylamino)-4-*O*-(3,4,6-tri-*O*-benzyl-2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetrakis-(*tert*-butyloxycarbonylmethyl)-*N*″-acetylamino)-β-D-glucopyranosyl)-α-D-glucopyranosyl)-D-mannitol (27f). According to the method for the synthesis of **27a**, triazido **9f** (115 mg, 82.9 mmol) was treated with 1 M trimethyl phosphine in toluene (0.273 mL, 0.273 mmol) in toluene (1.30 mL) and 0.1 M NaOH aq. (27.3 μL), to provide a triamine. The triamine was reacted with *t*-BuDTPAOH **8** (766 mg, 1.24 mmol) by DMAP (151 mg, 1.24 mmol) and HATU (471 mg, 1.24 mmol) in CH_2Cl_2 (0.732 mL) and DIEA (0.216 mL, 1.24 mmol) to provide triamide **27f** (208 mg, 66.8 μmol, 2 steps 81%); $[\alpha]_D^{25}$ +23.2 (c 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, 1H, J = 8.7 Hz), 7.59 (d, 1H, J = 8.7 Hz), 7.54 (d, 1H, J = 9.7 Hz), 7.07–7.35 (m, 45H, aromatic), 5.34 (d, 1H, anomeric, J = 3.4 Hz), 5.05 (d, 1H, J = 11.6 Hz), 4.84 (d, 1H, anomeric, J = 7.7 Hz), 4.76 (d, 1H, J = 11.6 Hz), 4.70 (d, 1H, J = 11.1 Hz), 4.63 (d, 1H, J = 10.6 Hz), 4.62 (d, 1H, J = 11.6 Hz), 4.61 (m, 2H), 4.59 (d, 1H, J = 11.6 Hz), 4.55 (d, 1H, J = 10.6 Hz), 4.54 (d, 1H, J = 11.6 Hz), 4.52 (d, 1H, J = 10.6 Hz), 4.51–4.58 (m, 1H), 4.47 (d, 1H, J = 10.6 Hz), 4.45 (d, 1H, J = 11.1 Hz), 4.43 (d, 1H, J = 11.6 Hz), 4.32 (d, 1H, J = 11.6 Hz), 4.23 (m, 2H), 4.18 (dd, 1H, J = 9.6 Hz, J = 9.2 Hz), 4.15–4.21 (m, 2H), 4.08 (br-d, 1H, J = 9.2 Hz), 3.97 (m, 1H), 3.89 (dd, 1H, J = 3.4 Hz, J = 9.7 Hz), 3.88 (dd, 1H, J = 8.2 Hz, J = 6.3 Hz), 3.82 (br-dd, 1H, J = 7.7 Hz, J = 8.7 Hz), 3.80–3.87 (m, 2H), 3.78 (dd, 1H, J = 10.1 Hz, J = 9.6 Hz), 3.74 (dd, 1H, J = 2.9 Hz, J = 8.2 Hz), 3.71 (dd, 1H, J = 3.9 Hz, J = 10.6 Hz), 3.65 (br-d, 1H, J = 8.2 Hz), 3.65 (br-d, 1H, J = 8.2 Hz), 3.59 (dd, 1H, J = 4.8 Hz, J = 10.6 Hz), 3.50 (br-d, 1H, J = 9.2 Hz), 3.39–3.41 (m, 1H), 3.18–3.22 (m, 1H), 3.00–3.04 (m, 30H), 2.43–2.89 (m, 24H), 1.38–1.44 (m, 108H, *t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.49, 170.94, 170.72, 170.60, 170.57, 170.49, 170.42, 170.37, 139.64, 138.57, 138.41, 138.38, 138.27, 138.08, 128.36, 128.27, 128.19, 128.15, 128.12, 128.05, 127.86, 127.82, 127.71, 127.60, 127.47, 127.43, 127.38, 127.21, 127.10, 127.07, 126.60, 126.49, 99.84 (anomeric), 98.25 (anomeric), 81.24, 80.89, 80.69, 80.63, 50.59, 50.52, 50.40, 78.89, 78.59, 78.08, 77.63, 75.10, 74.97, 74.74, 74.32, 74.09, 73.90, 73.03, 72.93, 72.84, 72.72, 72.17, 71.58, 69.63, 68.69, 68.41, 68.31, 59.38, 58.66, 58.22, 56.60, 56.26, 56.21, 56.14, 55.92, 55.87, 55.75, 55.65, 53.05, 52.84, 52.59, 52.54, 52.52, 52.35, 52.30, 52.12, 52.09, 51.76, 70.75, 28.09; IR (KBr) 3335, 3064, 3032, 2978, 2932, 1733, 1682 (cm^{-1}); MS(ESI-TOF) $[M + H]^+$ calcd. 3114.80, found 3115.19, $[M + 2H]^{2+}$ calcd. 1557.90, found 1558.03, $[M + 3H]^{3+}$ calcd. 1038.93, found 1038.99.

1,3,5,6-Tetra-*O*-benzyl-2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetrakis-(*tert*-butyloxycarbonylmethyl)-*N*″-acetylamino)-4-*O*-(3,6-di-*O*-benzyl-2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetrakis-(*tert*-butyloxycarbonylmethyl)-*N*″-acetylamino)-4-*O*-(3,4,6-tri-*O*-benzyl-2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetrakis-(*tert*-butyloxycarbonylmethyl)-*N*″-acetylamino)-α-D-glucopyranosyl)-α-D-glucopyranosyl)-D-glucitol (27g). According to the method for the synthesis of **27g**, triazido **9g** (101 mg, 72.4 mmol) was treated with 1 M trimethyl phosphine in toluene (0.239 mL, 0.239 mmol) in toluene (1.30 mL) and 0.1 M NaOH aq. (21.9 μL) to provide a triamine. The triamine was reacted with *t*-BuDTPAOH **8** (673 mg, 1.09 mmol) by DMAP (133 mg, 1.09 mmol) and HATU (414 mg, 1.09 mmol) in CH_2Cl_2 (0.732 mL) and DIEA (0.190 mL, 1.09 mmol) to provide triamide **27g** (133 mg, 42.7 μmol, 2 steps 59%); $[\alpha]_D^{24}$ +38.4 (c 1.30, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) d 7.95 (d, 1H, J = 10.1 Hz), 7.74 (d, 1H, J = 9.7 Hz), 7.14–7.35 (m, 45H,

aromatic), 7.06 (d, 1H, $J = 9.7$ Hz), 5.34 (d, 1H, anomeric, $J = 2.9$ Hz), 5.30 (d, 1H, anomeric, $J = 2.9$ Hz), 4.75 (d, 1H, $J = 9.2$ Hz), 4.72 (d, 1H, $J = 11.6$ Hz), 4.62 (m, 2H), 4.60 (d, 1H, $J = 9.2$ Hz), 4.58–4.62 (m, 1H), 4.57 (d, 1H, $J = 11.6$ Hz), 4.51 (m, 2H), 4.48 (d, 1H, $J = 11.6$ Hz), 4.45 (d, 1H, $J = 13.0$ Hz), 4.43 (m, 2H), 4.37 (d, 1H, $J = 11.6$ Hz), 4.33 (ddd, 1H, $J = 2.9$ Hz, $J = 8.2$ Hz, $J = 9.7$ Hz), 4.29 (d, 2H, $J = 11.6$ Hz), 4.22–4.31 (m, 1H), 4.19 (d, 1H, $J = 11.6$ Hz), 4.18–4.21 (m, 1H), 4.10–4.12 (m, 2H), 4.00 (m, 1H), 3.93 (dd, 1H, $J = 2.9$ Hz, $J = 9.7$ Hz), 3.84–3.92 (m, 3H), 3.82 (dd, 1H, $J = 2.9$ Hz, $J = 9.7$ Hz), 3.76 (dd, 1H, $J = 9.2$ Hz, $J = 8.7$ Hz), 3.71 (dd, 1H, $J = 8.2$ Hz, $J = 9.2$ Hz), 3.72 (dd, 1H, $J = 3.4$ Hz, $J = 9.7$ Hz), 3.49 (dd, 1H, $J = 2.4$ Hz, $J = 9.7$ Hz), 3.49 (dd, 1H, $J = 2.4$ Hz, $J = 10.1$ Hz), 3.46 (dd, 1H, $J = 6.3$ Hz, $J = 9.7$ Hz), 3.33 (br-d, 1H, $J = 10.1$ Hz), 3.18–3.30 (m, 2H), 2.80–3.41 (m, 30H), 2.44–2.73 (m, 24H), 1.35–1.45 (m, 108H, *t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.28, 170.95, 170.84, 170.71, 170.58, 170.52, 170.48, 170.44, 170.32, 138.61, 138.57, 138.52, 138.44, 138.19, 137.92, 137.79, 128.38, 128.25, 128.18, 128.14, 127.84, 127.79, 127.69, 127.63, 127.57, 127.47, 127.42, 127.37, 127.29, 127.26, 127.21, 127.07, 97.63 (anomeric), 96.07 (anomeric), 80.86, 80.69, 80.67, 80.61, 80.57, 80.51, 80.47, 80.36, 80.06, 77.97, 75.64, 74.45, 74.07, 73.80, 73.15, 73.03, 72.96, 72.77, 72.43, 71.69, 71.44, 71.05, 70.61, 70.52, 68.81, 68.57, 68.35, 59.19, 58.79, 57.55, 56.66, 56.00, 55.91, 55.86, 55.70, 68.35, 59.19, 58.79, 57.55, 56.66, 56.00, 55.91, 55.86, 55.70, 55.56, 53.12, 52.99, 52.66, 52.57, 52.48, 52.45, 52.21, 51.56, 50.79, 48.25, 28.09; IR (KBr) 3327, 3090, 3065, 3032, 2979, 2934, 2872, 1733, 1682 (cm^{-1}); MS(ESI-TOF) $[M + H]^+$ calcd. 3114.80, found 3115.37, $[M + 2H]^{2+}$ calcd. 1557.90, found 1558.11, $[M + 3H]^{3+}$ calcd. 1038.93, found 1039.06.

1,3,5,6-Tetra-*O*-benzyl-2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetrakis-(*tert*-butyloxycarbonylmethyl)-*N*″-acetylamino)-4-*O*-(3,6-di-*O*-benzyl-2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetrakis-(*tert*-butyloxycarbonylmethyl)-*N*″-acetylamino)-4-*O*-(3,4,6-tri-*O*-benzyl-2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetrakis-(*tert*-butyloxycarbonylmethyl)-*N*″-acetylamino)-α-D-glucopyranosyl)-α-D-glucopyranosyl)-D-mannitol (27h). According to the method for the synthesis of **27g**, triazido **9h** (115 mg, 82.9 mmol) was treated with 1 M trimethyl phosphine in toluene (0.239 mL, 0.239 mmol) in toluene (1.30 mL) and 0.1 M NaOH aq. (27.4 μL) to provide a triamine. The triamine was reacted with *t*-BuDTPAOH **8** (766 mg, 1.24 mmol) by DMAP (151 mg, 1.24 mmol) and HATU (471 mg, 1.24 mmol) in CH_2Cl_2 (0.732 mL) and DIEA (0.216 mL, 1.24 mmol) to provide triamide **27h** (205 mg, 65.8 μmol, 2 steps 79%); $[\alpha]_D^{24}$ +34.6 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) d 7.72 (d, 1H, $J = 9.7$ Hz), 7.67 (d, 1H, $J = 8.7$ Hz), 7.11–7.33 (m, 45H, aromatic), 7.11–7.13 (m, 1H), 5.36 (d, 1H, anomeric, $J = 3.4$ Hz), 5.33 (d, 1H, anomeric, $J = 2.9$ Hz), 4.70 (d, 2H, $J = 11.1$ Hz, $J = 11.1$ Hz), 4.68 (d, 2H, $J = 11.6$ Hz, $J = 12.1$ Hz), 4.61 (d, 1H, $J = 12.1$ Hz), 4.58 (d, 1H, $J = 11.6$ Hz), 4.57 (d, 1H, $J = 12.1$ Hz), 4.57–4.62 (m, 1H), 4.56 (m, 2H), 4.54 (d, 1H, $J = 11.1$ Hz), 4.48 (d, 2H, $J = 11.1$ Hz), 4.48 (d, 1H, $J = 12.1$ Hz), 4.45 (d, 2H, $J = 12.1$ Hz), 4.45 (d, 1H, $J = 12.1$ Hz), 4.36 (d, 1H, $J = 12.1$ Hz), 4.32–4.38 (m, 1H), 4.29 (d, 1H, $J = 12.1$ Hz), 4.20–4.21 (m, 2H), 4.12–4.13 (m, 1H), 3.99–4.01 (m, 1H), 3.92–3.95 (m, 2H), 3.90 (dd, 1H, $J = 11.6$ Hz, $J = 9.2$ Hz), 3.82–3.89 (m, 3H), 3.76 (dd, 1H, $J = 8.7$ Hz, $J = 9.2$ Hz), 3.73 (m, 1H), 3.70 (dd, 1H, $J = 9.7$ Hz, $J = 8.7$ Hz), 3.69 (m, 1H), 3.62 (dd, 1H, $J = 4.3$ Hz, $J = 9.7$ Hz), 3.49–3.55 (m, 2H), 3.37–3.39 (m, 1H), 2.81–3.39 (m, 30H), 2.46–2.74 (m, 24H), 1.37–1.44 (m, 108H, *t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.05, 170.77, 170.67, 170.52, 170.49, 170.45, 170.39, 138.47, 138.41, 138.35, 138.23, 138.15, 138.00, 137.92, 137.69, 128.38, 128.33, 128.22, 128.15, 128.12, 128.09, 127.75, 127.70, 127.63, 127.48, 127.41, 127.35, 127.29, 127.24, 127.18, 127.01, 98.09 (anomeric), 97.47 (anomeric), 80.93, 80.69, 80.63, 80.59, 80.55, 80.43, 80.34, 80.10, 78.76, 78.62, 74.72, 74.34, 73.69, 73.15, 72.86, 72.78, 72.42, 72.20, 71.78, 71.28, 71.06, 69.75, 68.56, 68.37, 68.28, 58.70, 58.35, 57.60, 56.31, 55.91, 55.85, 55.66, 55.59, 52.99, 52.88, 52.57, 52.53, 52.45, 52.41, 52.30, 52.21, 51.97, 51.11, 50.72, 28.07; IR (KBr) 3339, 3065, 3032, 3979, 2931, 2870, 1733, 1682 (cm^{-1}); MS(ESI-TOF) $[M + H]^+$ calcd. 3114.80, found 3115.24, $[M + 2H]^{2+}$ calcd. 1557.90, found 1558.01, $[M + 3H]^{3+}$ calcd. 1038.93, found 1039.00.

1,3,5,6-Tetra-*O*-benzyl-2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetrakis-(*tert*-butyloxycarbonylmethyl)-*N*″-acetylamino)-4-*O*-(3,4,6-tri-*O*-benzyl-2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetrakis-(*tert*-butyloxycarbonylmethyl)-*N*″-acetylamino))-β-D-glucopyranosyl)-D-glucitol (28a). According to the method for the synthesis of **27a**, diazido **10a** (118 mg, 0.115 mmol) was treated with 1 M trimethyl phosphine in toluene (0.253 mL, 0.253 mmol) in toluene (1.30 mL) and 0.1 M NaOH aq. (25.3 μL) to provide a diamine. The diamine was reacted with *t*-BuDTPAOH **8** (710 mg, 1.15 mmol) by DMAP (140 mg, 1.15 mmol) and HATU (473 mg, 1.15 mmol) in CH_2Cl_2 (0.732 mL) and DIEA (0.200 mL, 1.15 mmol) to provide diamide **28a** (187 mg, 86.1 μmol, 2 steps 75%); $[\alpha]^{22}{}_D$ +4.0 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, 1H, $J = 8.7$ Hz), 7.61 (d, 1H, $J = 9.7$ Hz), 7.12–7.30 (m, 35H, aromatic), 4.95 (d, 1H, anomeric, $J = 7.7$ Hz), 4.89 (d, 1H, $J = 11.6$ Hz), 4.76 (d, 1H, $J = 11.1$ Hz), 4.71 (d, 1H, $J = 11.1$ Hz), 4.67 (d, 1H, $J = 11.1$ Hz), 4.60 (d, 1H, $J = 12.1$ Hz), 4.55 (d, 1H, $J = 11.6$ Hz), 4.54 (d, 1H, $J = 12.1$ Hz), 4.50 (d, 1H, $J = 11.1$ Hz), 4.49–4.53 (m, 1H), 4.46 (d, 1H, $J = 11.6$ Hz), 4.46 (m, 2H), 4.38 (d, 1H, $J = 11.6$ Hz), 4.35 (d, 1H, $J = 12.1$ Hz), 4.30 (d, 1H, $J = 12.1$ Hz), 4.24 (dd, 1H, $J = 1.9$ Hz, $J = 5.8$ Hz), 4.01 (m, 2H), 3.94 (dd, 1H, $J = 8.7$ Hz, $J = 9.7$ Hz), 3.87 (ddd, 1H, $J = 7.7$ Hz, $J = 8.7$ Hz, $J = 8.7$ Hz), 3.73 (dd, 1H, $J = 3.4$ Hz, $J = 10.6$ Hz), 3.60 (dd, 1H, $J = 9.7$ Hz, $J = 8.2$ Hz), 3.57–3.62 (m, 3H), 3.44–3.50 (m, 2H), 3.33–3.36 (m, 1H), 3.11–3.38 (m, 20H), 2.49–2.73 (m, 16H), 1.37–1.43 (m, 72H, *t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.42, 171.10, 170.70, 170.65, 170.58, 170.52, 170.49, 170.27, 139.16, 138.84, 138.64, 138.57, 138.50, 138.34, 138.24, 128.22, 128.15, 128.05, 127.79, 127.71, 127.57, 127.49, 127.32, 127.24, 127.18, 127.09, 100.99 (anomeric), 82.19, 81.07, 80.82, 80.71, 80.60, 80.51, 79.39, 78.61, 78.19, 74.67, 74.42, 73.90, 73.06, 72.72, 72.40, 72.02, 69.99, 69.80, 69.28, 59.23, 58.72, 56.44, 56.34, 55.95, 55.80, 53.25, 52.93, 52.70, 52.60, 52.55, 52.38, 25.21, 47.70, 28.12; IR (KBr) 3355, 3065, 3031, 2979, 2933, 2869, 1733, 1675 (cm^{-1}); MS(ESI-TOF) $[M + H]^+$ calcd. 2173.25, found 2173.67, $[M + 2H]^{2+}$ calcd. 1087.13, found 1087.30, $[M + 3H]^{3+}$ calcd. 725.09, found 725.21.

1,3,5,6-Tetra-*O*-benzyl-2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetrakis-(*tert*-butyloxycarbonylmethyl)-*N*″-acetylamino)-4-*O*-(3,4,6-tri-*O*-benzyl-2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetrakis-(*tert*-butyloxycarbonylmethyl)-*N*″-acetylamino))-β-D-glucopyranosyl)-D-mannitol (28b). According to the method for the synthesis of **27a**, diazido **10b** (95.0 mg, 92.7 μmol) was treated with 1 M trimethyl phosphine in toluene (0.204 mL, 0.204 mmol) in toluene (1.30 mL) and 0.1 M NaOH aq. (20.4 μL) to provide a diamine. The diamine was reacted with *t*-BuDTPAOH **8** (573 mg, 0.927 mmol) by DMAP (113 mg, 0.927 mmol) and HATU (352 mg, 0.927 mmol) in CH_2Cl_2 (0.800 mL) and DIEA (0.161 mL, 0.927 mmol) to provide diamide **28b** (161 mg, 74.1 μmol, 2 steps 80%); $[\alpha]_D^{25}$ −0.3 (*c* 1.14, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, 1H $J = 8.2$), 7.66 (d, 1H, $J = 9.2$ Hz), 7.13–7.33 (m, 35H, aromatic), 4.96 (d, 1H, anomeric, $J = 7.7$ Hz), 4.86 (d, 1H, $J = 11.1$ Hz), 4.78 (d, 1H, $J = 11.6$ Hz), 4.72 (d, 1H, $J = 10.6$ Hz), 4.66 (d, 1H, $J = 11.6$ Hz), 4.56 (d, 1H, $J = 11.1$ Hz), 4.50 (d, 1H, $J = 10.6$ Hz), 4.49–4.58 (m, 1H), 4.47 (d, 1H, $J = 12.1$ Hz), 4.44 (d, 1H, $J = 11.6$ Hz), 4.42 (m, 2H), 4.38–4.45 (m, 1H), 4.37 (d, 1H, $J = 12.1$ Hz), 4.35 (d, 1H, $J = 11.6$ Hz), 4.33 (d, 1H, $J = 12.1$ Hz), 3.82–3.89 (m, 4H), 3.70 (dd, 1H, $J = 6.5$ Hz,

J = 9.2 Hz), 3.59–3.68 (m, 5H), 3.59 (dd, 1H, J = 6.3 Hz, J = 9.2 Hz), 3.44–3.45 (m, 1H), 3.11–3.39 (m, 20H), 2.54–2.80 (m, 16H), 1.37–1.45 (m, 72H, *t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.33, 171.08, 170.69, 170.63, 170.56, 170.53, 170.47, 170.39, 139.18, 138.68, 138.61, 138.57, 138.39, 138.31, 138.21, 128.19, 128.02, 127.76, 127.70, 127.62, 127.55, 127.43, 127.40, 127.33, 127.27, 4127.22, 127.11, 127.03, 100.59 (anomeric), 82.28, 81.14, 80.72, 80.59, 80.52, 79.00, 78.23, 77.56, 74.91, 74.44, 74.15, 73.98, 73.27, 72.84, 72.76, 71.61, 69.16, 69.01, 68.60, 59.21, 58.29, 56.43, 56.39, 55.95, 55.89, 55.75, 53.13, 52.88, 52.70, 52.67, 52.57, 52.46, 52.39, 52.20, 48.94, 28.10, 28.05; IR (KBr) 3366, 3065, 3031, 2978, 2932, 2867, 1732, 1674 (cm^{-1}); MS(ESI-TOF) $[M + H]^+$ calcd. 2173.25, found 2173.70, $[M + 2H]^{2+}$ calcd. 1087.13, found 1087.30, $[M + 3H]^{3+}$ calcd. 725.09, found 725.21.

1,3,5,6-Tetra-*O*-benzyl-2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetrakis-(*tert*-butyloxycarbonylmethyl)-*N*″-acetylamino)-4-*O*-(3,4,6-tri-*O*-benzyl-2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetrakis-(*tert*-butyloxycarbonylmethyl)-*N*″-acetylamino))-α-D-glucopyranosyl)-D-glucitol (28c). According to the method for the synthesis of **27a**, diazido **10c** (109 mg, 0.106 mmol) was treated with 1 M trimethyl phosphine in toluene (0.233 mL, 0.233 mmol) in toluene (1.30 mL) and 0.1 M NaOH aq. (23.3 μL) to provide a diamine. The diamine was reacted with *t*-BuDTPAOH **8** (655 mg, 1.06 mmol) by DMAP (130 mg, 1.06 mmol) and HATU (403 mg, 1.06 mmol) in CH_2Cl_2 (0.800 mL) and DIEA (0.185 mL, 1.06 mmol) to provide diamide **28c** (171 mg, 78.7 μmol, 2 steps 73%); $[\alpha]_D^{25}$ +39.1 (*c* 1.10, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, 1H, J = 9.7 Hz), 7.76 (d, 1H, J = 10.1 Hz), 7.06–7.32 (m, 35H, aromatic), 5.34 (d, 1H, anomeric, J = 3.4 Hz), 4.83 (d, 1H, J = 11.6 Hz), 4.75 (d, 1H, J = 11.6 Hz), 4.64 (d, 2H, J = 10.6 Hz), 4.61 (d, 1H, J = 11.1 Hz), 4.60 (d, 1H, J = 11.6 Hz), 4.52 (d, 1H, J = 12.1 Hz), 4.52 (m, 2H), 4.45 (ddd, 1H, J = 3.4 Hz, J = 10.1Hz, J = 9.7 Hz), 4.43 (d, 1H, J = 10.6 Hz), 4.40 (d, 1H, J = 11.6 Hz), 4.33 (d, 1H, J = 12.1 Hz), 4.32–4.39 (m, 1H), 4.26 (d, 1H, J = 12.1 Hz), 4.25 (d, 1H, J = 12.1 Hz), 4.22–4.25 (m, 1H), 4.16 (br-d, 1H), 4.01 (br-d, 1H), 3.90–3.94 (m, 2H), 3.82 (dd, 1H, J = 9.2 Hz, J = 9.2 Hz), 3.80–3.83 (m, 1H), 3.76 (dd, 1H, J = 10.1 Hz, J = 9.2 Hz), 3.43 (m, 1H), 3.26–3.33 (m, 3H), 2.92–3.40 (m, 20H), 2.50–2.74 (m, 16H), 1.38–1.44 (m, 72H, *t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.20, 171.08, 171.01, 170.64, 170.59, 170.52, 170.48, 170.39, 138.82, 138.77, 138.67, 138.51, 138.14, 137.99, 137.88, 128.42, 128.29, 128.18, 128.15, 128.11, 128.04, 127.88, 127.79, 127.73, 127.66, 127.47, 127.37, 127.21, 127.11, 126.75, 96.23 (anomeric), 80.86, 80.70, 80.68, 80.52, 78.48, 77.85, 75.98, 74.30, 74.16, 73.56, 73.37, 73.20, 72.89, 72.54, 71.79, 70.74, 70.51, 68.90, 68.23, 59.13, 58.98, 56.68, 56.17, 56.13, 56.06, 55.96, 55.91, 55.66, 53.23, 53.05, 52.75, 52.58, 52.03, 48.29, 28.12; IR (KBr) 3348, 3065, 3032, 2978, 2932, 2869, 1733, 1679 (cm^{-1}); MS(ESI-TOF) $[M + H]^+$ calcd. 2173.25, found 2173.68, $[M + 2H]^{2+}$ calcd. 1087.13, found 1087.30, $[M + 3H]^{3+}$ calcd. 725.09, found 725.21.

1,3,5,6-Tetra-*O*-benzyl-2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetrakis-(*tert*-butyloxycarbonylmethyl)-*N*″-acetylamino)-4-*O*-(3,4,6-tri-*O*-benzyl-2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetrakis-(*tert*-butyloxycarbonylmethyl)-*N*″-acetylamino))-α-D-glucopyranosyl)-D-mannitol (28d). According to the method for the synthesis of **27a**, diazido **10d** (101 mg, 98.5 mmol) was treated with 1 M trimethyl phosphine in toluene (0.216 mL, 0.216 mmol) in toluene (1.30 mL) and 0.1 M NaOH aq. (21.6 μL) to provide a diamine. The diamine was reacted with *t*-BuDTPAOH **8** (609 mg, 0.985 mmol) by DMAP (120 mg, 0.985 mmol) and HATU (374 mg, 0.985 mmol) in CH_2Cl_2 (0.800 mL) and DIEA (0.185 mL, 1.06 mmol, 10.0 eq.) to provide diamide **28c** (164 mg, 75.5 μmol, 2 steps 77%); $[\alpha]_D^{25}$ +30.0 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, 2H, J = 9.7 Hz), 7.07–7.33 (m, 35H, aromatic), 5.38 (d, 1H, anomeric, J = 3.9 Hz), 4.77 (d, 1H, J = 11.6 Hz), 4.71 (d, 1H, J = 11.6 Hz), 4.66 (d, 1H, J = 11.1 Hz), 4.64 (d, 1H, J = 11.6 Hz), 4.56 (m, 2H), 4.55 (d, 1H, J = 11.6 Hz), 4.53 (d, 1H, J = 12.1 Hz), 4.52 (d, 1H, J = 11.6 Hz), 4.49 (d, 2H, J = 11.6 Hz), 4.45 (d, 1H, J = 11.1 Hz), 4.41 (d, 1H, J = 12.1 Hz), 4.39–4.45 (m, 1H), 4.31 (d, 1H, J = 12.1 Hz), 4.25–4.30 (m, 1H), 4.20 (dd, 1H, J = 2.4 Hz, J = 9.2 Hz), 4.12 (br-d, 1H, J = 8.2 Hz), 3.99 (dd, 1H, J = 6.3 Hz, J = 2.4 Hz), 3.95 (dd, 1H, J = 2.4 Hz, J = 10.1 Hz), 3.83–3.89 (m, 2H), 3.80 (dd, 1H, J = 10.1 Hz, J = 8.2 Hz), 3.75 (dd, 1H, J = 9.7 Hz, J = 10.1 Hz), 3.64–3.72 (m, 2H), 3.45 (dd, 1H, J = 2.9 Hz, J = 8.2 Hz), 3.36–3.39 (m, 1H), 2.85–3.44 (m, 20H), 2.47–2.75 (m, 16H), 1.28–1.44 (m, 72H, *t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.95, 170.81, 170.61, 170.58, 170.51, 170.44, 138.77, 138.58, 138.54, 138.48, 138.24, 138.13, 128.41, 128.29, 128.16, 128.09, 127.83, 127.74, 127.69, 127.55, 127.43, 127.34, 127.24, 127.10, 126.88, 97.96 (anomeric), 80.99, 80.81, 80.73, 80.71, 80.68, 80.59, 80.49, 79.01, 78.97, 77.70, 74.58, 74.42, 74.29, 73.35, 73.31, 72.99, 72.87, 72.34, 71.14, 70.00, 68.43, 58.76, 58.63, 56.44, 56.00, 55.95, 55.71, 53.10, 53.02, 52.69, 52.57, 52.51, 52.44, 52.21, 52.05, 50.85, 28.13; IR (KBr) 3338, 3090, 3065, 3031, 2979, 2934, 2870, 1733, 1679 (cm^{-1}); MS(ESI-TOF) $[M + H]^+$ calcd. 2173.25, found 2173.70, $[M + 2H]^{2+}$ calcd. 1087.13, found 1086.79, $[M + 3H]^{3+}$ calcd. 725.09, found 725.21.

1,3,5,6-Tetra-*O*-benzyl-2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetrakis-(*tert*-butyloxycarbonylmethyl)-*N*″-acetylamino)-D-glucitol (29a). According to the method for the synthesis of **27a**, azido **13** (27.3 mg, 48.1 mmol) was treated with 1 M trimethyl phosphine in toluene (52.9 mL, 52.9 mmol) in toluene (1.30 mL) and 0.1 M NaOH aq. (5.29 μL) to provide an amine. The amine was reacted with *t*-BuDTPAOH **8** (29.7 mg, 48.1 μmol) by DMAP (5.88 mg, 48.1 mmol) and HATU (18.3 mg, 48.1 μmol) in CH_2Cl_2 (0.481 mL) and DIEA (0.185 mL, 1.06 μmol) to provide amide **29a** (40.1 mg, 35.1 μmol, 2 steps 73%); $[\alpha]_D^{24}$ −7.0 (*c* 1.09, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, 1H, J = 8.7 Hz), 7.25–7.32 (m, 20H, aromatic), 4.68 (d, 1H, J = 11.6 Hz), 4.60 (d, 1H, J = 11.0 Hz), 4.54 (d, 1H, J = 11.0 Hz), 4.53 (m, 2H), 4.50 (d, 1H, J = 12.1 Hz), 4.46 (d, 1H, J = 12.1 Hz), 4.42 (dddd, 1H, J = 5.3 Hz, J = 6.8 Hz, J = 5.8 Hz, J = 8.7 Hz), 4.36 (d, 1H, J = 11.6 Hz), 4.08 (dd, 1H, J = 5.8 Hz, J = 2.9 Hz), 3.86 (dd, 1H, J = 2.9 Hz, J = 10.1 Hz), 3.72 (br-s, 1H), 3.66 (dd, 1H, J = 5.8 Hz, J = 10.1 Hz), 3.60–3.64 (m, 1H), 3.60 (dd, 1H, J = 5.3 Hz, J = 9.2 Hz), 3.52 (dd, 1H, J = 6.8 Hz, J = 9.2 Hz), 3.15–3.40 (m, 10H), 2.67–2.76 (m, 8H), 1.40–1.44 (m, 36H, *t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.31, 170.68, 170.55, 138.55, 138.39, 138.01, 128.31, 128.27, 128.25, 128.22, 127.89, 127.83, 127.63, 127.60, 127.53, 127.43, 127.38, 81.14, 80.81, 80.72, 78.44, 75.56, 73.93, 73.32, 72.91, 71.94, 71.53, 70.47, 68.98, 58.84, 56.89, 55.97, 55.88, 53.22, 52.79, 52.61, 52.24, 50.30, 28.14, 28.08; IR (KBr) 3357, 3065, 3032, 2979, 2932, 2867, 1733, 1674 (cm^{-1}); MS(ESI-TOF) $[M + H]^+$ calcd. 1141.66, found 1141.83.

1,3,5,6-Tetra-*O*-benzyl-2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetrakis-(*tert*-butyloxycarbonylmethyl)-*N*″-acetylamino)-D-mannitol (29b). According to the method for the synthesis of **27a**, azido **14** (31.2 mg, 55.0 mmol) was treated with 1 M trimethyl phosphine in toluene (60.5 mL, 60.5 mmol) in toluene (1.30 mL) and 0.1 M NaOH aq. (6.05 μL) to provide an amine. The amine was reacted with *t*-BuDTPAOH **8** (34.0 mg, 55.0 μmol) by DMAP 6.72 mg, 55.0 μmol) and HATU (20.9 mg, 55.0 μmol) in CH_2Cl_2 (0.550 mL) and DIEA (0.185 mL, 1.06 μmol) to provide amide **29b** (46.4 mg, 40.7 μmol, 2 steps 74%); $[\alpha]_D^{21}$ −12.7 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, 1H, J = 8.7 Hz), 7.17–7.34 (m, 20 H, aromatic), 4.80 (d, 1H, J = 11.6 Hz), 4.56 (d, 1H, J = 11.6 Hz), 4.56 (m, 2H), 4.50 (d, 1H, J = 11.6 Hz), 4.47 (d, 1H, J = 11.6 Hz), 4.45–4.55 (m, 1H), 4,42 (d, 1H, J = 11.6 Hz), 4.41 (d, 1H, J = 11.6 Hz), 3.97–4.01 (m, 1H), 3.98 (dd, 1H, J = 1.4 Hz, J = 9.7 Hz), 3.80–3.84 (m, 1H), 3.79 (dd, 1H, J = 3.9 Hz, J = 9.7 Hz), 3.73–3.77 (m, 2H), 3.57 (dd, 1H, J = 5.3 Hz, J = 9.7 Hz), 3.20–3.40 (m, 10H),

2.72–2.77 (m, 8H), 1.39–1.44 (m, 36H, *t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.49, 170.60, 170.51, 170.40, 138.72, 138.55, 138.32, 137.98, 128.30, 128.22, 128.15, 127.66, 127.63, 127.55, 127.51, 127.36, 127.25, 81.24, 80.78, 77.89, 75.68, 73.26, 72.98, 72.75, 71.56, 70.58, 69.64, 69.03, 58.74, 56.82, 55.98, 55.81, 53.12, 52.88, 52.55, 52.11, 49.01, 28.11, 28.03; IR (KBr) 3350, 3032, 2978, 2932, 2868, 1733, 1653 (cm^{-1}); MS(ESI-TOF) $[M + H]^+$ calcd. 1141.66, found 1141.85.

2-Deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetraacetic acid-*N*″-acetylamino)-4-*O*-(2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetraacetic acid-*N*″-acetylamino)-4-*O*-(2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetraacetic acid-*N*″-acetylamino)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-D-glucitol (2a). To a stirred solution of 1,3,5,6-tetra-*O*-benzyl-2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetrakis-(*tert*-butyloxycarbonylmethyl)-*N*″-acetylamino)-4-*O*-(3,6-di-*O*-benzyl-2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetrakis-(*tert*-butyloxycarbonylmethyl)-*N*″-acetylamino)-4-*O*-(3,4,6-tri-*O*-benzyl-2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetrakis-(*tert*-butyloxycarbonylmethyl)-*N*″-acetylamino)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-D-glucitol (**27a**) (83.0 mg, 34.0 μmol, 1.00 eq.) in dry CH_2Cl_2 (0.90 mL) was added triethylsilane (0.18 mL) and TFA (0.45 mL) at room temperature. After being stirred at the same temperature for 15 h, the reaction mixture was concentrated *in vacuo* and azeotroped with toluene. The residue was used for the next reaction without further purification. To a solution of the residue in MeOH (3.60 mL), ethyl acetate (0.60 mL) and water (1.20 mL) was added $Pd(OH)_2$ (80 mg). The reaction mixture was hydolyzed for 12 h under H_2 gas atmosphere. The reaction mixture was filtered through a pad of celite and the filtrate was concentrated *in vacuo*. The residue was purified by reversed phase HPLC (Develosil® ODS-UG-5 column, Eluent: 0.1% TFA in H_2O–0.1% TFA in aq. 10% CH_3CN, Gradient: 0.00 min. [0.1% TFA in H_2O] : [0.1% TFA in aq. 10% CH_3CN] = 100 : 0, 30.0 min [0.1% TFA in H_2O] : [0.1% TFA in aq. 10% CH_3CN] = 75 : 25, 10 mL min^{-1}; Retention time: 14.9 min) to give 2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetraacetic acid-*N*″-acetylamino)-4-*O*-(2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetraacetic acid-*N*″-acetylamino)-4-*O*-(2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetraacetic acid-*N*″-acetylamino)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-D-glucitol (**2a**) (10.7 mg, 6.57 μmol, 2 steps 23%); $[\alpha]_D^{20}$ −4.2 (*c* 0.63, H_2O); ^{1}H NMR (400 MHz, D_2O, 303K) δ 4.65 (d, 2H, anomeric x2, J = 8.3 Hz), 4.32 (br-s, 1H), 3.25–4.05 (m, 73H); IR (solid) 3332, 3019, 1723, 1632 (cm^{-1}); MS(ESI-TOF) $[M–2H]^{2-}$ calcd. 813.30, found 813.56, $[M–3H]^{3-}$ calcd. 541.86, found 542.05.

2-Deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetraacetic acid-*N*′-acetylamino)-4-*O*-(2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetraacetic acid-*N*′-acetylamino)-4-*O*-(2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetraacetic acid-*N*′-acetylamino)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-D-mannitol (2b). According to the method for the synthesis of **2a**, *tert*-butyl ester **27b** (89.7 mg, 28.8 μmol) was treated with triethylsilane (0.18 mL) and TFA (0.45 mL) in dry CH_2Cl_2 (0.90 mL) to provide a carboxylic acid. The residue was hydrolyzed with a palladium catalyst under H_2, followed by purification by reversed phase HPLC (HPLC retention time: 16.1 min) to provide DTPA-conjugated trisaccharide **2b** (16.7 mg, 10.2 μmol, 2 steps 36%); $[\alpha]_D^{26}$ −6.6 (*c* 0.84, H_2O);^{1}H NMR (400 MHz, D_2O, 303K) δ 4.66 (d, 1H, anomeric, J = 7.7 Hz), 4.64 (d, 1H, anomeric, J = 8.7 Hz), 4.18 (m, 1H), 3.23–4.04 (m, 73H); IR (solid) 3316, 3014, 2966, 1723, 1673, 1630 (cm^{-1}); MS(ESI-TOF) $[M–2H]^{2-}$ calcd. 813.30, found 813.56, $[M–3H]^{3-}$ calcd. 541.86, found 542.05.

2-Deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetraacetic acid-*N*′-acetylamino)-4-*O*-(2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetraacetic acid-*N*′-acetylamino)-4-*O*-(2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetraacetic acid-*N*′-acetylamino)-α-D-glucopyranosyl)-β-D-glucopyranosyl)-D-glucitol (2c). According to the method for the synthesis of **2a**, *tert*-butyl ester **27c** (70.3 mg, 22.6 μmol) was treated with triethylsilane (0.18 mL) and TFA (0.45 mL) in dry CH_2Cl_2 (0.90 mL) to provide a carboxylic acid. The residue was hydrolyzed with a palladium catalyst under H_2, followed by purification by reversed phase HPLC (HPLC retention time: 14.9 min) to provide DTPA-conjugated trisaccharide **2c** (14.6 mg, 8.96 μmol, 2 steps 40%); $[\alpha]_D^{24}$ +9.4 (*c* 0.73, H_2O); ^{1}H NMR (400 MHz, D_2O, 303K) δ 5.39 (d, 1H, anomeric, J = 3.4 Hz), 4.65 (d, 1H, anomeric, J = 7.7 Hz), 4.31 (dd, 1H, J = 6.8 Hz, J = 11.1 Hz), 3.62–4.11 (m, 47H), 3.31–3.55 (m, 14 H), 3.20–3.29 (m,12H); IR (solid) 3325, 1636 1394, 1231 (cm^{-1}); MS(ESI-TOF) $[M–2H]^{2-}$ calcd. 813.30, found 813.56, $[M–3H]^{3-}$ calcd. 541.86, found 542.05.

2-Deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetraacetic acid-*N*′-acetylamino)-4-*O*-(2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetraacetic acid-*N*′-acetylamino)-4-*O*-(2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetraacetic acid-*N*′-acetylamino)-α-D-glucopyranosyl)-β-D-glucopyranosyl)-D-mannitol (2d). According to the method for the synthesis of **2a**, *tert*-butyl ester **27d** (97.0 mg, 31.2 μmol) was treated with triethylsilane (0.18 mL) and TFA (0.45 mL) in dry CH_2Cl_2 (0.90 mL) to provide a carboxylic acid. The residue was hydrolyzed with a palladium catalyst under H_2, followed by purification by reversed phase HPLC (HPLC retention time: 16.0 min) to provide DTPA-conjugated trisaccharide **2d** (16.7 mg, 10.2 μmol, 2 steps 36%); $[\alpha]_D^{24}$ +17.9 (*c* 0.84, H_2O); ^{1}H NMR (400 MHz, D_2O, 303 K) δ 5.39 (d, 1H, anomeric, J = 3.9 Hz), 4.67 (d, 1H, anomeric, J = 7.7 Hz), 4.22 (m, 1H), 3.44–4.12 (m, 61H), 3.21–3.28 (m, 12H); IR (solid) 3341, 3017, 1720, 1619 (cm^{-1}); MS(ESI-TOF) $[M–2H]^{2-}$ calcd. 813.30, found 813.56, $[M–3H]^{3-}$ calcd. 541.86, found 542.05.

2-Deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetraacetic acid-*N*″-acetylamino)-4-*O*-(2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetraacetic acid-*N*″-acetylamino)-4-*O*-(2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetraacetic acid-*N*″-acetylamino)-β-D-glucopyranosyl)-α-D-glucopyranosyl)-D-glucitol (2e). According to the method for the synthesis of **2a**, *tert*-butyl ester **27e** (99.3 mg, 31.9 μmol) was treated with triethylsilane (0.18 mL) and TFA (0.45 mL) in dry CH_2Cl_2 (0.90 mL) to provide a carboxylic acid. The residue was hydrolyzed with a palladium catalyst under H_2, followed by purification by reversed phase HPLC (HPLC retention time: 13.9 min) to provide DTPA-conjugated trisaccharide **2e** (12.7 mg, 7.79 μmol, 2 steps 24%); $[\alpha]_D^{24}$ +8.9 (*c* 0.64, H_2O); ^{1}H NMR (400 MHz, D_2O, 303 K) δ 5.11 (d, 1H, anomeric, J = 2.9 Hz), 4.67 (d, 1H, anomeric, J = 9.2 Hz), 3.79 (dd, 1H, J = 9.2 Hz, J = 9.7 Hz), 3.60 (dd, 1H, J = 9.7 Hz, J = 8.2 Hz), 3.58–4.25 (m, 48H), 3.20–3.55 (m, 28H); IR (solid) 3248, 2950, 1724, 1672, 1631 (cm^{-1}); MS(ESI-TOF) $[M–2H]^{2-}$ calcd. 813.30, found 813.56, $[M–3H]^{3-}$ calcd. 541.86, found 542.04.

2-Deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetraacetic acid-*N*″-acetylamino)-4-*O*-(2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetraacetic acid-*N*″-acetylamino)-4-*O*-(2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetraacetic acid-*N*″-acetylamino)-β-D-glucopyranosyl)-α-D-glucopyranosyl)-D-mannitol (2f). According to the method for the synthesis of **2a**, *tert*-butyl ester **27f** (91.8 mg, 29.5 μmol) was treated with triethylsilane (0.18 mL) and TFA (0.45 mL) in dry CH_2Cl_2 (0.90 mL) to provide a carboxylic acid. The residue was hydrolyzed with a palladium catalyst under H_2, followed by purification by reversed phase HPLC (HPLC retention time: 15.9 min) to provide DTPA-conjugated trisaccharide **2e** (14.3 mg, 8.78 μmol, 2 steps 30%); $[\alpha]_D^{25}$ +6.3 (*c* 0.72, H_2O); ^{1}H NMR (400 MHz, D_2O, 303 K) δ 4.87 (d, 1H, anomeric, J = 3.9 Hz), 4.67 (d, 1H, anomeric, J = 8.2 Hz), 4.08 (dd, 1H, J = 3.9 Hz, J = 11.1 Hz), 3.78 (dd, 1H, J = 8.2 Hz, J = 10.6 Hz), 3.57–4.13 (m, 46H), 3.39–3.50 (m, 14H), 3.23–3.30 (m, 12H); IR (solid) 3263, 2881, 1671, 1624 (cm^{-1}); MS(ESI-TOF) $[M–2H]^{2-}$ calcd. 813.30, found 813.56, $[M–3H]^{3-}$ calcd. 541.86, found 542.05.

2-Deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetraacetic acid-*N*″-acetylamino)-4-*O*-(2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetraacetic acid-*N*″-acetylamino)-4-*O*-(2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetraacetic acid-*N*″-acetylamino)-α-D-glucopyranosyl)-α-D-glucopyranosyl)-D-glucitol (2g). According to the method for the synthesis of **2a**, *tert*-butyl ester **27g** (91.7 mg, 29.4 μmol) was treated with triethylsilane (0.18 mL) and TFA (0.45 mL) in dry CH_2Cl_2 (0.90 mL) to provide a carboxylic acid. The residue was hydrolyzed with a palladium catalyst under H_2, followed by purification by reversed phase HPLC (HPLC retention time: 14.7 min) to provide DTPA-conjugated trisaccharide **2g** (10.1 mg, 6.20 μmol, 2 steps 21%); $[\alpha]_D^{24}$ +25.7 (*c* 0.51, H_2O); ^{1}H NMR (400 MHz, D_2O, 303 K) δ 5.42 (d, 1H, anomeric, $J = 3.4$ Hz), 5.11 (d, 1H, anomeric, $J = 3.4$ Hz), 4.21 (m, 1H), 3.45–4.14 (m, 61H), 3.20–3.27 (m, 12H); IR (solid) 3288, 3007, 1728, 1673, 1636 (cm^{-1}); MS(ESI-TOF) $[M–2H]^{2-}$ calcd. 813.30, found 813.56, $[M–3H]^{3-}$ calcd. 541.86, found 542.05.

2-Deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetraacetic acid-*N*″-acetylamino)-4-*O*-(2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetraacetic acid-*N*″-acetylamino)-4-*O*-(2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetraacetic acid-*N*″-acetylamino)-α-D-glucopyranosyl)-α-D-glucopyranosyl)-D-mannitol (2h). According to the method for the synthesis of **2a**, *tert*-butyl ester **27h** (94.5 mg, 30.3 μmol) was treated with triethylsilane (0.18 mL) and TFA (0.45 mL) in dry CH_2Cl_2 (0.90 mL) to provide a carboxylic acid. The residue was hydrolyzed with a palladium catalyst under H_2, followed by purification by reversed phase HPLC (HPLC retention time: 16.0 min) to provide DTPA-conjugated trisaccharide **2h** (17.6 mg, 10.8 μmol, 2 steps 36%); $[\alpha]_D^{26}$ +24.7 (*c* 0.88, H_2O); ^{1}H NMR (400 MHz, D_2O, 303 K) δ 5.42 (d, 1H, anomeric, $J = 3.4$ Hz), 4.86 (d, 1H, anomeric, $J = 3.4$ Hz), 3.58–4.24 (m, 49H), 3.42–3.52 (m, 13H), 3.20–3.27 (m, 12H); IR (solid) 3268, 3966, 1677, 1630 (cm^{-1}); MS(ESI-TOF) $[M–2H]^{2-}$ calcd. 813.30, found 813.56, $[M–3H]^{3-}$ calcd. 541.86, found 542.05.

2-Deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetraacetic acid-*N*″-acetylamino)-4-*O*-(2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetraacetic acid-*N*″-acetylamino)-β-D-glucopyranosyl)-D-glucitol (3a). According to the method for the synthesis of **2a**, *tert*-butyl ester **28a** (101 mg, 46.5 μmol) was treated with triethylsilane (0.18 mL) and TFA (0.45 mL) in dry CH_2Cl_2 (0.90 mL) to provide a carboxylic acid. The residue was hydrolyzed with a palladium catalyst under H_2, followed by purification by reversed phase HPLC (HPLC retention time: 11.4 min) to provide DTPA-conjugated trisaccharide **3a** (7.6 mg, 6.95 μmol, 2 steps 15%); $[\alpha]_D^{19}$ −3.4 (*c* 0.38, H_2O); ^{1}H NMR (400 MHz, D_2O, 303 K) δ 4.66 (d, 1H, anomeric, $J = 8.2$ Hz), 4.32 (ddd, 1H), 3.61 (dd, 1H, $J = 10.6$ Hz, $J = 8.7$ Hz), 3.42–4.20 (m, 40H), 3.23–3.41 (m, 8H); ^{13}C NMR (100 MHz, D_2O, acetone-d_6) δ 173.81, 173.45, 173.35, 171.36, 171.34, 169.65, 168.43, 101.52 (anomeric), 79.54, 76.55, 74.19, 71.84, 70.50, 68.95, 62.75, 61.73, 61.39, 57.55, 57.36, 57.19, 56.74, 55.18, 55.05, 53.95, 53.11, 53.01, 52.78, 52.74, 51.80, 51.18, 50.99, 50.96, 50.75; IR (solid) 3275, 1623, 1391, 1202, 1071 (cm^{-1}); MS(ESI-TOF) $[M–H]^-$ calcd. 1091.41, found 1091.73, $[M–2H]^{2-}$ calcd. 545.20, found 545.37.

2-Deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetraacetic acid-*N*″-acetylamino)-4-*O*-(2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetra-acdticacid-*N*″-acetylamino)-β-D-glucopyranosyl)-D-mannitol (3b). According to the method for the synthesis of **2a**, *tert*-butyl ester **28b** (101 mg, 46.5 μmol) was treated with triethylsilane (0.18 mL) and TFA (0.45 mL) in dry CH_2Cl_2 (0.90 mL) to provide a carboxylic acid. The residue was hydrolyzed with a palladium catalyst under H_2, followed by purification by reversed phase HPLC (HPLC retention time: 17.7 min) to provide DTPA-conjugated trisaccharide **3b** (14.3 mg, 13.1 μmol, 2 steps 28%); $[\alpha]_D^{24}$ −2.9 (*c* 0.72, H_2O); ^{1}H NMR (400 MHz, D_2O, 303 K) δ 4.67 (d, 1H, anomeric, $J = 7.7$ Hz), 4.21 (m, 1H), 3.69–4.05 (m, 19H), 3.60 (br-dd, 1H), 3.41–3.54 (m, 11H), 3.24–3.29 (m, 8H); ^{13}C NMR (100 MHz, D_2O, acetone-d_6) δ 173.77, 173.39, 171.98, 171.47, 171.33, 171.13, 169.49, 168.04, 101.47 (anomeric), 78.42, 76.37, 74.15, 72.10, 70.48, 68.86, 62.91, 61.25, 61.19, 57.46, 57.32, 57.11, 56.89, 56.70, 55.10, 54.99, 54.93, 53.27, 53.11, 52.84, 51.04, 50.74; IR (solid) 3301, 1614, 1170, 1012 (cm^{-1}); MS(ESI-TOF) $[M–H]^-$ calcd. 1091.42, found 1091.73, $[M–2H]^{2-}$ calcd. 545.20, found 545.37.

2-Deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetraacetic acid-*N*′-acetylamino)-4-*O*-(2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetraacetic acid-*N*′-acetylamino)-α-D-glucopyranosyl)-D-glucitol (3c). According to the method for the synthesis of **2a**, *tert*-butyl ester **28c** (116 mg, 53.4 μmol) was treated with triethylsilane (0.18 mL) and TFA (0.45 mL) in dry CH_2Cl_2 (0.90 mL) to provide a carboxylic acid. The residue was hydrolyzed with a palladium catalyst under H_2, followed by purification by reversed phase HPLC (HPLC retention time: 20.5 min) to provide DTPA-conjugated trisaccharide **3c** (19.7 mg, 18.0 μmol, 2 steps 34%); $[\alpha]_D^{20}$ +25.8 (*c* 0.99, H_2O); ^{1}H NMR (400 MHz, D_2O, 303 K) δ 5.11 (d, 1H, anomeric, $J = 3.4$ Hz), 3.20–4.28 (m, 50H); ^{13}C NMR (100 MHz, D_2O, acetone-d_6) δ 174.04, 173.68, 171.60, 171.21, 170.91, 168.30, 167.98, 99.28 (anomeric), 79.92, 73.45, 73.24, 71.58, 70.58, 70.53, 62.88, 61.77, 61.08, 57.10, 55.19, 54.91, 53.75, 53.63, 53.40, 53.29, 52.99, 51.26, 50.94, 50.84, 50.49; IR (solid) 3292, 2940, 1721, 1623 (cm^{-1}); MS(ESI-TOF) $[M–H]^-$ calcd. 1091.41, found 1091.70, $[M–2H]^{2-}$ calcd. 545.20, found 545.37.

2-Deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetraacetic acid-*N*″-acetylamino)-4-*O*-(2-deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetraacetic acid-*N*″-acetylamino)-α-D-glucopyranosyl)-D-mannitol (3d). According to the method for the synthesis of **2a**, *tert*-butyl ester **28d** (101 mg, 46.5 μmol) was treated with triethylsilane (0.18 mL) and TFA (0.45 mL) in dry CH_2Cl_2 (0.90 mL) to provide a carboxylic acid. The residue was hydrolyzed with a palladium catalyst under H_2, followed by purification by reversed phase HPLC (HPLC retention time: 11.5 min) to provide DTPA-conjugated trisaccharide **3d** (10.4 mg, 9.52 μmol, 2 steps 20%); $[\alpha]_D^{21}$ +13.0 (*c* 0.52, H_2O); ^{1}H NMR (400 MHz, D_2O, 303 K) δ 4.89 (d, 1H, anomeric, $J = 3.4$ Hz), 3.42–4.21 (m, 42H), 3.21–3.29 (m, 8H); ^{13}C NMR (100 MHz, D_2O, acetone-d_6) δ 174.01, 173.57, 171.32, 171.19, 171.08, 171.01, 168.07, 167.78, 100.52 (anomeric), 78.86, 74.63, 73.36, 71.59, 70.62, 70.12, 63.17, 61.34, 61.19, 57.53, 57.25, 56.99, 56.88, 55.11, 54.95, 54.56, 53.28, 53.30, 53.26, 53.14, 52.95, 52.84, 52.55, 51.15, 51.01, 50.92, 50.55; IR (solid) 3281, 2936, 1630, 1394, 1213 (cm^{-1}); MS(ESI-TOF) $[M–H]^-$ calcd. 1091.42, found 1091.72, $[M–2H]^{2-}$ calcd. 545.20, found 545.37.

2-Deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetraacetic acid-*N*″-acetylamino)-D-glucitol (4a). According to the method for the synthesis of **2a**, *tert*-butyl ester **29a** (95.0 mg, 83.2 μmol) was treated with triethylsilane (0.18 mL) and TFA (0.45 mL) in dry CH_2Cl_2 (0.90 mL) to provide a carboxylic acid. The residue was hydrolyzed with a palladium catalyst under H_2, followed by purification by reversed phase HPLC (HPLC retention time: 14.8 min) to provide DTPA-conjugated trisaccharide **4a** (17.6 mg, 31.6 μmol, 2 steps 38%); $[\alpha]_D^{25}$ −5.0 (*c* 0.85, H_2O); ^{1}H NMR (400 MHz, D_2O, 303 K) d 4.14 (br-dd, 1H, $J = 4.3$ Hz, $J = 5.8$ Hz), 4.04 (s, 2H), 3.97 (s, 4H), 3.95–3.97 (m, 1H), 3.91 (s, 2H), 3.80 (dd, 1H, $J = 2.4$ Hz, $J = 11.6$ Hz), 3.73 (dd, 1H, $J = 4.3$ Hz, $J = 11.6$ Hz), 3.71–3.74 (m, 1H), 3.68 (s, 2H), 3.62 (dd, 1H, $J = 5.8$ Hz, $J = 11.6$ Hz), 3.62 (dd, 1H, $J = 4.3$ Hz, $J = 11.6$ Hz), 3.57 (dd, 1H, $J = 1.4$ Hz, $J = 8.2$ Hz), 3.22–3.49 (m, 8H); ^{13}C NMR (100 MHz, D_2O, acetone-d_6) δ 173.88, 171.64, 171.17, 168.30, 71.83, 71.71, 68.95, 63.57, 61.56, 57.33, 57.20, 57.04, 54.94, 53.19, 53.15, 51.13, 50.69; IR (solid) 3338, 1627,

1394, 1205, 1085 (cm^{-1}); MS(ESI-TOF) $[M–H]^-$ calcd. 555.21, found 555.39.

2-Deoxy-2-(diethylenetriamine-*N*,*N*,*N*′,*N*″-tetraacetic acid-*N*″-acetylamino)-D-mannitol (4b). According to the method for the synthesis of **2a**, *tert*-butyl ester **29b** (97.7 mg, 85.6 μmol) was treated with triethylsilane (0.18 mL) and TFA (0.45 mL) in dry CH_2Cl_2 (0.90 mL) to provide a carboxylic acid. The residue was hydrolyzed with a palladium catalyst under H_2, followed by purification by reversed phase HPLC (HPLC retention time: 15.3 min) to provide DTPA-conjugated trisaccharide **4b** (20.6 mg, 37.0 μmol, 2 steps 43%); $[\alpha]_D^{26}$ −0.9 (*c* 1.00, H_2O); ^1H NMR (400 MHz, D_2O, 303 K) δ 4.13 (ddd, 1H, $J = 3.4$ Hz, $J = 6.3$ Hz, $J = 9.2$ Hz), 4.04 (s, 2H), 3.97 (s, 4H), 3.90 (s, 2H), 3.88–3.90 (m, 1H), 3.85 (dd, 1H, $J = 3.4$ Hz, $J = 12.1$ Hz), 3.80 (dd, 1H, $J = 1.9$ Hz, $J = 11.6$ Hz), 3.74 (dd, 1H, $J = 6.3$ Hz, $J = 12.1$ Hz), 3.71 (ddd, 1H, $J = 8.2$ Hz, $J = 1.9$ Hz, $J = 5.8$ Hz), 3.69 (s, 2H), 3.63 (dd, 1H, $J = 5.8$ Hz, $J = 11.6$ Hz), 3.41 (m, 5H), 3.22–3.26 (m, 4H); ^{13}C NMR (100 MHz, D_2O, acetone-d_6) δ 173.68, 171.66, 171.21, 168.41, 71.45, 70.20, 68.76, 63.87, 61.65, 57.31, 57.10, 54.98, 53.34, 53.20, 53.05, 51.24, 50.80; IR (solid) 3276, 2955, 1629, 1399, 1202 (cm^{-1}); MS(ESI-TOF) $[M–H]^-$ calcd. 555.21, found 555.40.

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