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Synthesis of the pentasaccharide related to the repeating unit of the antigen from *Shigella dysenteriae* type 4 in the form of its methyl ester 2-(trimethylsilyl)ethyl glycoside

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Abstract

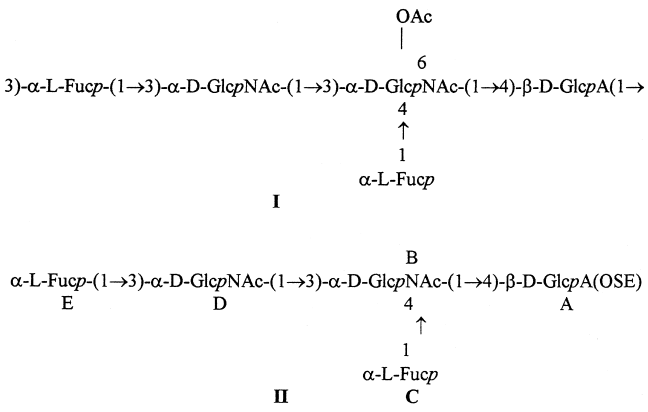
Starting from D-mannose, D-glucose and L-fucose, the pentasaccharide derivative methyl 2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1→3)-2-*O*-acetyl-4,6-*O*-benzylidene-α-D-mannopyranosyl-(1→3)-2-*O*-acetyl-6-*O*-benzyl-4-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-α-D-mannopyranosyl-(1→4)-[2-(trimethylsilyl)ethyl 2,3-di-*O*-benzyl-β-D-glucopyranosid]uronate was synthesized. This compound with two α-mannopyranosyl units was transformed, via Walden inversion and subsequent deprotection, into the α-D-glucosamine-type target compound, namely methyl α-L-fucopyranosyl-(1→3)-2-acetamido-2-deoxy-α-D-glucopyranosyl-(1→3)-2-acetamido-2-deoxy-4-*O*-(α-L-fucopyranosyl)-α-D-glucopyranosyl-(1→4)-[2-(trimethylsilyl)ethyl β-D-glucopyranosid]uronate which is related to the repeating unit of the *O*-antigen from *Shigella dysenteriae* type 4. © 2003 Elsevier Science Ltd. All rights reserved.

Keywords: Synthesis; Pentasaccharide repeating unit; *Shigella dysenteriae* type 4

1. Introduction

Shigella dysenteriae is the most virulent among the pathogenic bacilli of the genus *Shigella*.[1] They are responsible for many intestinal diseases including dysentery and have the potential for causing catastrophic public health problems in developing countries.[2] Their resistance to antimicrobial drugs necessitates the exploration of other medical approaches for controlling the diseases caused by this pathogen.[3] It has been suggested[4,5] that antibodies to the O-specific polysaccharide of *Shigella* may have the potential to protect the host from shigellosis, and that conjugate vaccines consisting of the O-specific polysaccharide (O-SP) of *Shigella* covalently attached to an immunogenic protein could, indeed, confer protective immunity to human against shigellosis. Much synthetic works on the oligosaccharides related to *Shigella flexneri* variant Y,[6] *S. flexneri* serotypes 5a[7] and 2a[8] and *S. dysenteriae* types 1,[9] 2[10] and 5[11] have been reported. Recently, a glycoconjugate vaccine against *S. dysenteriae* type 1 was synthesized[12] which was shown to have better antigenicity than the native antigen. It is, therefore, probable that the O-SP from *S. dysenteriae* type 4 may also play a protective role against bacillary dysentery and shigellosis in human.

We report herein the total synthesis of the pentasaccharide **II** related to the repeating unit **I**[13] of *S. dysenteriae* type 4. The reason for using the 2-(trimethylsilyl)-



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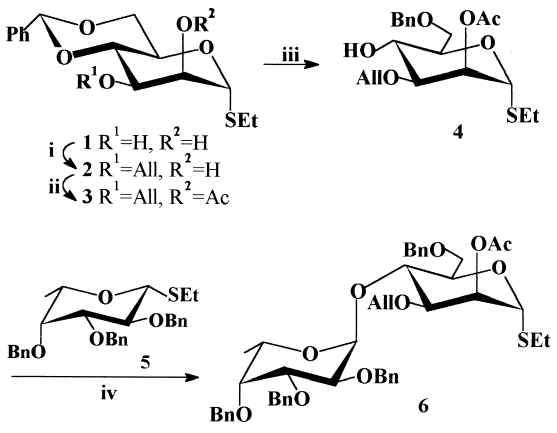
ethyl protecting group for the terminal sugar is the possibility of its easy removal from the oligosaccharide derivative and subsequent utilization of the product in making glycoconjugates. The synthetic oligosaccharide can also be utilized as a molecular probe for studying the immunochemical behavior of the antigen.

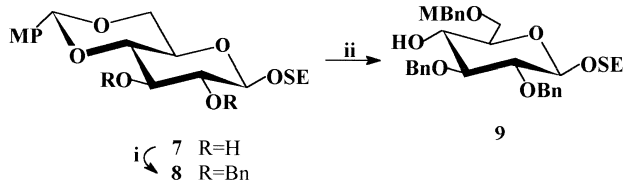
2. Results and discussion

Our strategy was to synthesise the blocks CBA and ED and attach the latter to the 3^{II} position of CBA, and finally convert the α-D-Man*p* residue to the α-D-Glc*p*-NAc component.

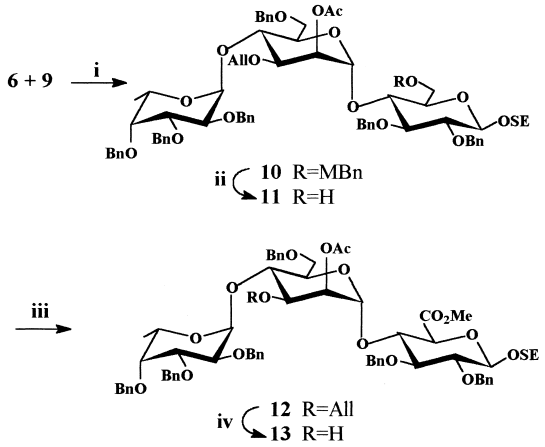
Starting from the known ethyl 4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside (**1**)[14], prepared from D-mannose, ethyl 3-*O*-allyl-4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside (**2**) was prepared in 83% yield by treatment of **1** with dibutyltin oxide in methanol[15] followed by reaction of the product with allyl bromide. Acetylation[16] of the monohydroxy compound (**2**) with acetic anhydride and pyridine afforded the monoacetate derivative **3**. Regioselective opening[17] of the benzylidene ring of **3** using sodium cyanoborohydride and hydrogen chloride-ether in tetrahydrofuran gave the thioglycoside acceptor **4** with a hydroxyl group in its 4-position in 82% yield (Scheme 1). The structure of **4** was confirmed by its ^{1}H NMR spectrum which showed



Scheme 1. (i) Bu_2SnO, MeOH, AllBr; (ii) Ac_2O, Py; (iii) $NaCNBH_3$, HCl–ether, THF; (iv) NIS–TfOH, CH_2Cl_2.



Scheme 2. (i) BnBR, NaH, DMF; (ii) $NaCNBH_3$, TFA, DMF MP = 4-methoxyphenyl, MBn = 4-methoxybenzyl.



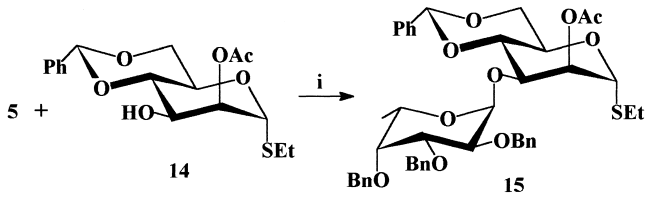
Scheme 3. (i) NIS–TfOH, CH_2Cl_2; (ii) 80% AcOH; (iii) a. CrO_3, H_2SO_4, H_2O, acetone; b. CH_2N_2, Et_2O; (iv) $PdCl_2$, MeOH.

characteristic NMR signals for allyl, acetyl and thioethyl groups.

In another experiment, ethyl 2,3,4-tri-*O*-benzyl-1-thio-β-L-fucopyranoside (**5**), was prepared from L-fucose as described by Lönn.[18] The thioglycoside acceptor **4** was allowed to react with the thioglycoside donor **5** in the presence of *N*-iodosuccinimide (NIS) and trifluoromethanesulfonic acid (TfOH) in dry dichloromethane at 0 °C[19] to afford the disaccharide ethyl 2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1→4)-2-*O*-acetyl-3-*O*-allyl-6-*O*-benzyl-1-thio-α-D-mannopyranoside (**6**) in 74% yield (Scheme 1). The lack of reactivity of **4** as a donor was ascribed to the deactivating effect of the *O*-acetyl group at C-2 which contrast with the activating benzyl group in the same position in **5**. The disaccharide **5** has the characteristic NMR signals for allyl, acetyl, thioethyl, 6-deoxy-sugar, anomeric protons and anomeric carbons.

In a separate experiment, 2-(trimethylsilyl)ethyl 4,6-*O*-(4-methoxybenzylidene)-β-D-glucopyranoside (**7**)[20] was benzylated[21] to give the di-O-benzyl derivative **8** in 89% yield. Regioselective opening of the 4-methoxybenzylidene ring of **8**, using sodium cyanoborohydride and trifluoroacetic acid in *N*,*N*-dimethylformamide,[22] afforded the 6-*O*-(4-methoxybenzyl) derivative **9** in 79% yield (Scheme 2). The structure of **9** was confirmed by its ^{1}H and ^{13}C NMR spectra.

The disaccharide donor **6** was then allowed to react with the acceptor **9** in the presence of NIS and TfOH in dry dichloromethane at 0 °C[19] to afford the trisaccharide, 2-(trimethylsilyl)ethyl 2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1→4)-2-*O*-acetyl-3-*O*-allyl-6-*O*-benzyl-α-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-(4-methoxybenzyl)-β-D-glucopyranoside (**10**) in 70% yield (Scheme 3). Compound **10** was characterized by its NMR signals for allyl, acetyl, one 6-deoxy sugar, one methoxy, trimethylsilyl and anomeric protons and car-

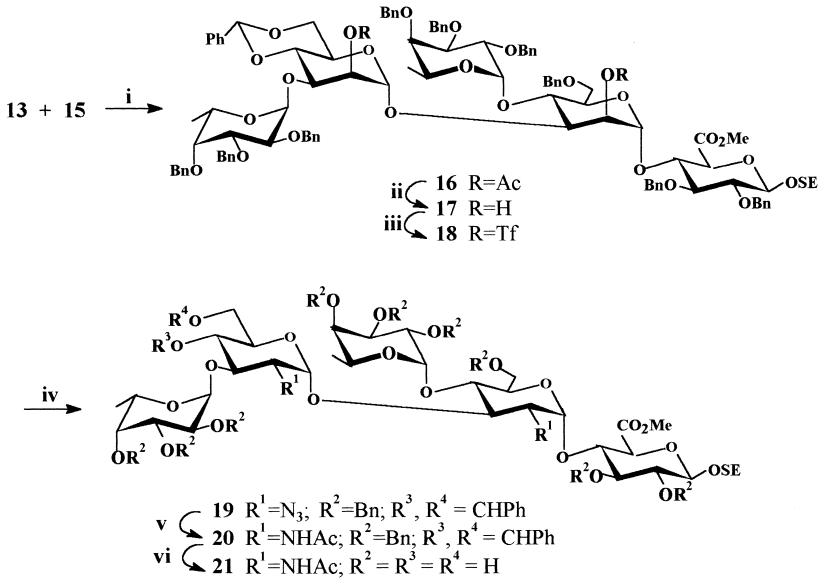


Scheme 4. (i) NIS–TfOH, CH_2Cl_2.

bons. The 6-O-(4-methoxybenzyl) group of **10** was removed by treatment with 80% aqueous acetic acid at 80 °C[23] to give 2-(trimethylsilyl)ethyl 2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1→4)-2-*O*-acetyl-3-*O*-allyl-6-*O*-benzyl-α-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-β-D-glucopyranoside (**11**) in 80% yield. The primary carbon atom of **11** was then oxidized with chromium[VI] oxide[24] and the resulting carboxylic acid group was esterified with diazomethane[25] to afford the methyl ester **12** in 63% overall yield. NMR spectral study of **12** revealed the disappearance of the 4-methoxybenzyl group at C-5^{I} position and the appearance of a COOMe group. The allyl group of **12** was removed with palladium chloride in methanol[26] to afford the trisaccharide acceptor (**13**). The structure of **13** was confirmed by the disappearance of the signals of the allyl group in the proton and carbon-13 NMR spectra.

In another experiment, ethyl 4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside (**1**) was treated with trimethyl orthoacetate and *p*-toluenesulfonic acid in dry acetonitrile[27] at room temperature to afford the 2,3-orthoester derivative which on treatment with 80% acetic acid at room temperature gave the 2-*O*-acetyl derivative **14** in 73% overall yield. The acceptor **14** was then allowed to react with the thioglycoside donor **5** in the presence of NIS and TfOH in dry dichloromethane to afford the disaccharide **15** in 75% yield (Scheme 4). The disaccharide **15** was characterized by its NMR signals for benzylidene, acetyl, one 6-deoxy sugar, thioethyl and anomeric protons and carbons.

The trisaccharide acceptor **13** was allowed to react with the disaccharide donor **15** in the presence of NIS and TfOH in dry dichloromethane at 0 °C to afford the pentasaccharide methyl 2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1→3)-2-*O*-acetyl-4,6-*O*-benzylidene-α-D-mannopyranosyl-(1→3)-2-*O*-acetyl-6-*O*-benzyl-4-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-α-D-mannopyranosyl-(1→4)-[2-(trimethylsilyl)ethyl 2,3-di-*O*-benzyl-β-D-glucopyranosid]uronate (**16**) in 70% yield (Scheme 5). The pentasaccharide **16** showed NMR signals for benzylidene, methyl ester, two acetyl groups, two 6-deoxy sugars, trimethylsilyl and anomeric protons and carbons. The two acetyl groups of **16** were removed in the usual way to yield **17**. Compound **17** was converted to the di-*O*-triflyl derivative **18** with trifluoromethanesulfonic anhydride and pyridine and further treatment with sodium azide in *N*,*N*-dimethylformamide[9a] gave the diazido compound, methyl 2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1→3)-2-azido-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranosyl-(1→3)-2-azido-6-*O*-benzyl-2-deoxy-4-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-α-D-glucopyranosyl-(1→4)-[2-(trimethylsilyl)ethyl-2,3-di-*O*-benzyl-β-D-glucopyranosid]uronate (**19**), with inversion of configuration at the 2^{II} and 2^{IV} positions in 60% overall yield. The structure of **19** was confirmed by its characteristic IR signal at 2125 cm^{-1}. The ^{13}C NMR spectrum of **19** showed signals for *C*OOMe, *C*HPh, anomeric carbons, peaks for C-2^{II}, C-2^{IV} at 63.8 and 63.5, $COOCH_3$, CH_2SiMe_3 2 $CHCH_3$ and $Si(CH_3)_3$.



Scheme 5. (i) NIS, TfOH; (ii) 0.05 M NaOMe, MeOH; (iii) Tf_2O, Pyr; (iv) NaN_3, DMF; (v) thioacetic acid, Pyr; (vi) Pd–C, H_2, AcOH.

Compound **19** was treated with thioacetic acid and pyridine[28] to afford methyl 2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1→3)-2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranosyl-(1→3)-2-acetamido-6-*O*-benzyl-2-deoxy-4-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-α-D-glucopyranosyl-(1→4)-[2-(trimethylsilyl)ethyl 2,3-di-*O*-benzyl-β-D-glucopyranosid]uronate (**20**) in 60% overall yield (Scheme 5). The NMR spectra of **20** had signals for CHPh, anomeric carbons, *C*OOMe, 2 NH*C*OCH$_3$, COO*C*H$_3$, C-2^{II} and C-2^{IV} (at 53.9, 53.3), 2 NHCO*C*H$_3$ and 2 CH*C*H$_3$. Hydrogenolysis of **20** with Pd–C and H_2 in AcOH[29] afforded the target pentasaccharide, methyl α-L-fucopyranosyl-(1→3)-2-acetamido-2-deoxy-α-D-glucopyranosyl-(1→3)-2-acetamido-2-deoxy-4-*O*-(α-L-fucopyranosyl)-α-D-glucopyranosyl-(1→4)-[2-(trimethylsilyl)ethyl β-D-glucopyranosid]uronate (**21**) in 80% yield (Scheme 5). The structure of **21** was confirmed by its ^{1}H and ^{13}C NMR spectra. The peak for the azide was absent in the IR spectrum.

3. Experimental

3.1. General

All the reactions were monitored by TLC on Silica Gel G (E. Merck). Column chromatography were performed on 100–200 mesh Silica Gel (SRL, India). The organic extracts were dried over anhyd Na_2SO_4. All solvents were distilled and/or dried before use and all evaporations were conducted at or below 50 °C under reduced pressure unless stated otherwise. Optical rotations were measured at 25 °C with a Perkin–Elmer 241 MC polarimeter. The ^{1}H and ^{13}C NMR spectra were recorded with a Bruker DPX 300 spectrometer using $CDCl_3$ as solvent and Me_4Si as internal standard unless otherwise stated. Melting points were determined in a paraffin oil bath and are uncorrected.

3.2. Ethyl 2-*O*-acetyl-3-*O*-allyl-4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside (3)

Ethyl 4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside (**1**)[14] (3.5 g, 11.3 mmol) was dissolved in MeOH (30 mL) and Bu_2SnO (2.8 g, 11.3 mmol) was added. The soln was refluxed for 2 h until a clear soln was obtained. The solvent was evaporated and the residue was dried under diminished pressure for 2 h. The product was dissolved in allyl bromide and the soln was stirred at 63 °C for 10 h. Excess reagent was evaporated and the residue was chromatographed using 5:1 benzene–EtOAc as eluent to afford pure ethyl 3-*O*-allyl-4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside (**2**) (3.3 g, 83%) as a syrup. To a soln of **2** (3 g, 8.5 mmol) in pyridine (15 mL) was added Ac_2O (10 mL) and the soln was stirred at rt for 2 h. The solvents were evaporated and the residue was chromatographed using 6:1 benzene–EtOAc to afford ethyl 2-*O*-acetyl-3-*O*-allyl-4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside (**3**) (3.4 g, quantitative) as a syrup; $[\alpha]_D$ +131.1° (*c* 1.2, $CHCl_3$); ^{1}H NMR: δ 7.43–7.19 (m, 5 H, aromatic protons), 5.80 (m, 1 H, CH_2–*C*H=CH_2), 5.54 (s, 1 H, C*H*Ph), 5.33 (bs, 1 H, H-2), 5.25 (s, 1 H, H-1), 5.23–5.09 (m, 2 H, CH_2–CH=C*H*$_2$), 2.57 (m, 2 H, S–C*H*$_2$CH$_3$), 2.10 (s, 3 H, COC*H*$_3$), 1.22 (t, 3 H, *J* 7.2 Hz, S–CH$_2$C*H*$_3$). Anal. Calcd for $C_{20}H_{26}O_6S$: C, 60.89; H, 6.64. Found: C, 60.72; H, 6.85.

3.3. Ethyl 2-*O*-acetyl-3-*O*-allyl-6-*O*-benzyl-1-thio-α-D-mannopyranoside (4)

To a soln of **3** (3 g, 7.6 mmol) in THF (25 mL) at 0 °C, $NaCNBH_3$ (4.3 g, 68.4 mmol) was added and the soln was stirred for 15 min. A saturated soln of HCl in ether was then added dropwise to the soln until effervescence was ceased. The soln was stirred for 10 min and was poured into a cold satd $NaHCO_3$ solution. The mixture was extracted with diethyl ether (30 mL × 3) and the organic layer was successively washed with aq satd $NaHCO_3$ and water. The soln was collected, dried (Na_2SO_4), filtered and evaporated to give a syrupy product. Column chromatography using 5:1 benzene–EtOAc afforded **4** (2.4 g, 82%) as a syrup; $[\alpha]_D$ +103.5° (*c* 1.2, $CHCl_3$); ^{1}H NMR: δ 7.34–7.26 (m, 5 H, aromatic protons), 5.88 (m, 1 H, CH_2–*C*H=CH_2), 5.35 (d, 1 H, *J* 2.4 Hz, H-2), 5.32 (s, 1 H, H-1), 5.31–5.19 (m, 2 H, CH_2–CH=C*H*$_2$), 4.68–4.54 (m, 2 H, C*H*$_2$Ph), 4.55, 4.75 (2d, 2 H, *J* 11.5 Hz, S–C*H*$_2$CH$_3$), 2.11 (s, 3 H, COC*H*$_3$), 1.28 (t, 3 H, *J* 7.5 Hz, S–CH$_2$C*H*$_3$). ^{13}C NMR: δ 170.6 (*C*OCH$_3$), 134.4 (CH_2–*C*H=CH_2), 118.5 (CH_2–CH=*C*H$_2$), 82.9 (C-1), 77.5, 74.0, 71.1, 70.0, 67.5, 21.3 (CO*C*H$_3$), 15.2 (SCH$_2$*C*H$_3$). Anal. Calcd for $C_{20}H_{28}O_6S$: C, 60.58; H, 7.12. Found: C, 60.42; H, 7.38.

3.4. Ethyl 2,3,4-tri-*O*-benzyl-1-thio-α-L-fucopyranosyl-(1→4)-2-*O*-acetyl-3-*O*-allyl-6-*O*-benzyl-1-thio-α-D-mannopyranoside (6)

A soln of donor **5** (2.2 g, 4.6 mmol), acceptor **4** (1.4 g, 3.5 mmol) and 4 Å MS (1.5 g) in dry CH_2Cl_2 (25 mL) was stirred under nitrogen for 8 h. The soln was cooled to −10 °C and NIS (1.3 g, 6 mmol) and TfOH (53 μL, 0.6 mmol) were added. The mixture was stirred for 45 min when TLC showed optimum reaction. The mixture was then diluted with CH_2Cl_2 (25 mL) and filtered through Celite. The filtrate was successively washed with 10% aq $Na_2S_2O_7$ and a saturated aq $NaHCO_3$ soln. The organic layer was collected, dried (Na_2SO_4) and evaporated to a syrup. Column chromatography with 6:1 benzene–EtOAc gave **8** (2 g, 74%) as a syrup;

$[\alpha]_D$ +21.3°; ^{1}H NMR: 7.97–7.17 (m, 20 H, aromatic protons), 5.96 (m, 1 H, CH_2–C*H*–CH_2), 5.54 (m, 2 H, CH_2–CH–CH_2), 5.36 (bs, 1 H, H-2^I), 5.32 (s, 1 H, H-1^I), 4.98 (d, 1 H, *J* 3.0 Hz, H-1^{II}), 4.87–4.45 (m, 8 H, 4 CH_2Ph), 2.66 (m, 2 H, S–CH_2–CH_3), 2.11 (s, 3 H, COCH_3), 1.29 (t, 3 H, *J* 9.9 Hz, S–CH_2–CH_3), 0.7 (d, 3 H, *J* 6.0 Hz, C–CH_3). ^{13}C NMR ($CDCl_3$): 169.9 (*C*OCH_3), 133.1 (CH_2–*C*H=CH_2), 117.2 (CH_2–CH=*C*H_2), 99.6 (*C*-1^{II}), 81.7 (*C*-1^I), 77.9, 77.8, 74.5, 73.3, 72.8, 71.5, 71.0, 69.5, 69.4, 67.5, 66.4, 25.2 (S–*C*H_2–CH_3), 20.9 (CO*C*H_3), 16.2 (S–CH_2–*C*H_3), 14.7 (C–*C*H_3). Anal. Calcd for $C_{47}H_{56}O_{10}S$: C, 69.43; H, 6.94. Found: C, 69.22; H, 7.16.

3.5. 2-(Trimethylsilyl)ethyl 2,3-di-*O*-benzyl-4,6-*O*-(4-methoxybenzylidene)-β-D-glucopyrano-side (8)

2-(Trimethylsilyl)ethyl 4,6-*O*-(4-methoxybenzylidene)-β-D-glucopyranoside (**7**)[21] (5 g, 12.5 mmol) was dissolved in DMF (30 mL).The soln was cooled to 0 °C and NaH (3 g, 62.5 mmol, 50% dispersion in mineral oil) was introduced followed by the addition of BnBr (3.6 mL, 30 mmol) and the mixture was allowed to stir at rt for 6 h when TLC showed complete conversion. Methanol (5 mL) was added to decompose the excess NaH and the soln was diluted with ethyl ether and washed with cold water (50 mL × 3). The organic layer was collected, dried (Na_2SO_4) and solvents were evaporated. The residue was chromatographed with 2:1 petroleum ether (bp 40–60 °C)–ether to afford **8** as a syrup (6.6 g, 90%); $[\alpha]_D$ +9.8° (*c* 1.3, $CHCl_3$); ^{1}H NMR: δ 7.81–6.84 (m, 14 H, aromatic protons), 5.53 (s, 1 H, C*H*$C_6H_4OCH_3$), 4.90 (m, 4 H, 2 CH_2Ph), 4.52 (d, 1 H, *J* 9.3 Hz, H-1), 3.82 (s, 3 H, $C_6H_4OCH_3$), 3.68 (m, 2 H, OCH_2CH_2Si), 1.05 (t, 2 H, *J* 6.0, OCH_2CH_2Si), −0.14 [s, 9 H, Si(CH_3)$_3$]. Anal. Calcd for $C_{33}H_{42}O_7Si$: C, 68.48; H, 7.31. Found: C, 68.73; H, 7.48.

3.6. 2-(Trimethylsilyl)ethyl 2,3-di-*O*-benzyl-6-*O*-(4-methoxybenzyl)-β-D-glucopyranoside (9)

A soln of **8** (6 g, 10.3 mmol) in DMF (30 mL) was cooled to 0 °C and $NaCNBH_3$ (5.8 g, 93 mmol) was added. A soln of TFA (7.9 mL) in DMF (20 mL) was then added dropwise and the mixture was allowed to stir at rt for 7 h. The reaction mixture was poured into cold saturated aq $NaHCO_3$ and extracted with diethylether. The organic layer was collected, dried (Na_2SO_4) and evaporated to give a syrupy liquid which was chromatographed using 5:1 benzene–EtOAc to give **9** (4.7 g, 79%); $[\alpha]_D$ −14.1° (*c* 1.5, $CHCl_3$); ^{1}H NMR: δ 7.34, 6.81 (m, 14 H, aromatic protons), 4.91 (d, 1 H, *J* 10.8 Hz, H-3), 4.68 (dd, 1 H, $J_{3,4}$ 3.6 Hz, $J_{4,5}$ 7.5 Hz, H-4), 4.40 (d, 1 H, *J* 7.2 Hz, H-1), 3.77 (s, 3 H, $C_6H_4OCH_3$), 3.59 (m, 2 H, OCH_2CH_2Si), 1.01 (m, 2 H, OCH_2CH_2Si), −0.14 [s, 9 H, Si(CH_3)$_3$]. ^{13}C NMR: δ 140.08–129.04 (aromatic carbons), 103.1 (C-1), 84.2, 80.5, 75.7, 75.2, 70.4, 96.0, 66.5, 55.6 ($C_6H_4OCH_3$), 18.1 (OCH_2CH_2Si), −1.5 [Si(CH_3)$_3$]. Anal. Calcd for $C_{33}H_{44}O_7Si$: C, 68.25; H, 7.63. Found: C, 67.96; H, 7.88.

3.7. 2-(Trimethylsilyl)ethyl 2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1→4)-2-*O*-acetyl-3-*O*-allyl-6-*O*-benzyl-α-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-(4-methoxybenzyl)-β-D-glucopyranoside (10)

A soln of the disaccharide donor **6** (1.2 g, 1.4 mmol), acceptor **9** (830 mg, 1.4 mmol) and MS 4 Å (1 g) in dry CH_2Cl_2 (10 mL) was stirred for 8 h. The mixture was cooled to −10 °C and NIS (400 mg, 1.85 mmol) and TfOH (16 μL, 0.18 mmol) were added. Stirring was continued for 45 min when TLC showed a major spot for the desired product in between the spots for the trace amounts of donor and acceptor together with a minor spot at the starting point. The mixture was then diluted with CH_2Cl_2 (20 mL) and filtered through Celite. The filtrate was washed successively with saturated aq $NaHCO_3$ and water. The organic layer was dried (Na_2SO_4) and evaporated and the resulting syrupy product was chromatographed using 10:1 benzene–EtOAc yielding **10** as syrup (1.35 g, 70%); $[\alpha]_D$ +3.9° (*c* 1.2, $CHCl_3$); ^{1}H NMR: δ 7.41–6.75 (m, 34 H, aromatic protons), 5.74 (m, 1 H, CH_2–C*H*=CH_2), 5.32–5.26 (m, 2 H, CH_2–CH=CH_2), 5.18 (d, 1 H, *J* 3.9 Hz, H-2^{II}), 5.1 (s, 1 H, H-1^{II}), 5.04 (d, 1 H, *J* 3.3 Hz, H-1^{III}), 4.62 (d, 1 H, *J* 11.4 Hz, H-1^I), 3.73 (s, 3 H, $C_6H_4OCH_3$), 3.42 (m, 2 H, C$H_2CH_2SiMe_3$), 1.99 (s, 3 H, COCH_3), 1.02 (m, 2 H, $CH_2CH_2SiMe_3$), 0.97 (d, 3 H, *J* 6.6 Hz, C–CH_3), −0.14 [s, 9 H, Si(CH_3)$_3$], ^{13}C NMR: 170.2 (*C*OCH_3), 135.1 (CH_2–*C*H=CH_2), 114.0 (CH_2–CH=*C*H_2), 138.5–127.5 (aromatic carbons), 102.9 (C-1^I), 99.4 (C-1^{II}), 98.8 (C-1^{III}), 84.3, 82.2, 79.3, 77.3, 77.2, 76.9, 74.8, 74.7, 74.4, 73.9, 73.2, 73.1, 73.0, 72.7, 72.1, 70.7, 69.8, 69.5, 68.7, 67.3, 66.9, 55.1 ($C_6H_4OCH_3$), 20.6 (*C*OCH_3), 18.4 (*C*H_2SiMe$_3$), 16.5 (C–*C*H_3), −1.5 [Si (*C*H_3)$_3$]. Anal. Calcd for $C_{78}H_{94}O_{17}Si$: C, 70.35; H, 7.11. Found: C, 70.64; H, 6.90.

3.8. Methyl 2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1→4)-2-*O*-acetyl-3-*O*-allyl-6-*O*-benzyl-α-D-mannopyranosyl-(1→4)-[2-(trimethylsilyl)ethyl 2,3-di-*O*-benzyl-β-D-glucopyranosid] uronate (12)

Compound **10** (2.35 g, 1.73 mmol) was dissolved in 80% AcOH (15 mL) and the soln was stirred at 80 °C for 4 h. The soln was concentrated to dryness and the crude material was chromatographed with 5:1 benzene–EtOAc to give pure **11** (1.75 g, 80%). A soln of **11** (1.75 g, 1.4 mmol) in 3:2 acetone–CH_2Cl_2 (32 mL) was

cooled to 0 °C and a freshly prepared chromium(VI) trioxide soln, prepared by dissolving 1.2 g of CrO_3 in 3.5 M H_2SO_4 (6 mL), was added dropwise with stirring. After 15 min, the reaction mixture was allowed to attain rt and stirring was continued for another 9 h. The reaction was quenched with EtOH and the solid precipitates were filtered off. The filtrate was concentrated at 20 °C under diminished pressure to a small vol and the remaining aq phase was extracted with CH_2Cl_2 (25 mL × 3). The combined extract was washed with water and a saturated NaCl solution, dried (Na_2SO_4) and evaporated to a small vol (30 mL). To this soln, a freshly prepared ethereal diazomethane soln was added dropwise until persistence of the yellow colour. Excess diazomethane was destroyed by adding ethereal AcOH solution. The solution was concentrated to a syrupy product which was chromatographed with 7:1 benzene–EtOAc to afford pure **12** (1.13 g, 63%); $[\alpha]_D$ + 8.4° (*c* 1.2, $CHCl_3$); ^{1}H NMR: δ 7.43–7.16 (m, 30 H, aromatic protons), 5.75 (m, 1 H, CH_2–CH=CH_2), 5.32–5.25 (m, 2 H, CH_2–CH=CH_2), 5.03 (s, 1 H, H-1^{II}), 4.95 (d, 1 H, *J* 3.3 Hz, H-1^{III}), 4.76 (d, 1 H, *J* 11.7 Hz, H-1^{I}), 3.89 (s, 3 H, $COOCH_3$), 3.50 (m, 2 H, $CH_2CH_2SiMe_3$), 1.96 (s, 3 H, $COCH_3$), 1.21 (m, 2 H, $CH_2CH_2SiMe_3$), 1.08 (d, 3 H, *J* 6.3 Hz, C–CH_3), −0.15 [s, 9 H, $Si(CH_3)_3$]. ^{13}C NMR: δ 173.4 ($COOCH_3$), 170.1 ($COCH_3$), 134.3 (CH_2–CH=CH_2), 140.4–128.9 (aromatic carbons), 117.1 (CH_2–CH=CH_2), 103.0 (C-1^{I}), 99.3 (C-1^{II}), 99.0 (C-1^{III}), 84.1, 82.3, 79.3, 77.3, 77.2, 76.7, 74.7, 74.6, 74.3, 73.8, 73.4, 73.2, 72.7, 72.1, 70.5, 69.7, 69.6, 68.6, 67.1, 56.3 ($COOCH_3$), 20.5 ($COCH_3$), 18.5 (CH_2SiMe_3), 16.2 (C–CH_3), −1.5 [$Si(CH_3)_3$]. Anal. Calcd for $C_{71}H_{86}O_{17}Si$: C, 68.80; H, 6.99. Found: C, 70.01; H, 6.73.

3.9. Methyl 2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1 → 4)-2-*O*-acetyl-6-*O*-benzyl-α-D-mannopyranosyl-(1 → 4)-[2-(trimethylsilyl)ethyl 2,3-di-*O*-benzyl-β-D-glucopyranosid]uronate (13)

To a mixture of **12** (1.3 g, 1 mmol) in MeOH (20 mL) $PdCl_2$ (90 mg, 0.5 mmol) was added and the solution was stirred at rt for 3 h. The solvent was removed and the crude product was immediately charged into a column of silica gel and eluted with 7:1 benzene–EtOAc to afford pure **13** (1.0 g, 80%); $[\alpha]_D$ + 10.2° (*c* 1.3, $CHCl_3$); ^{1}H NMR: δ 7.41–7.25 (m, 30 H, aromatic protons), 5.01 (s, 1 H, H-1^{II}), 4.98 (d, 1 H, *J* 3.3 Hz, H-1^{III}), 4.75 (d, 1 H, *J* 11.7 Hz, H-1^{I}), 3.87 (s, 3 H, $COOCH_3$), 3.46 (m, 2 H, $CH_2CH_2SiMe_3$), 2.01 (s, 3 H, $COCH_3$), 1.14 (m, 2 H, $CH_2CH_2SiMe_3$), 1.06 (d, 3 H, *J* 6.3 Hz, CCH_3), −0.14 [s, 9 H, $Si(CH_3)_3$]. ^{13}C NMR: δ 172.4 ($COOCH_3$), 169.1 ($COCH_3$), 140.4–128.9 (aromatic carbons), 102.9 (C-1^{I}), 99.2 (C-1^{II}), 98.7 (C-1^{III}), 84.2, 81.5, 78.1, 77.0, 75.2, 74.7, 74.2, 73.4, 73.0, 72.5, 72.0, 70.7, 69.7, 68.5, 67.0, 57.3 ($COOCH_3$), 20.3 ($COCH_3$), 18.4 (CH_2SiMe_3), 15.7 (C–CH_3), −1.5 [$Si(CH_3)_3$]. Anal. Calcd for $C_{68}H_{82}O_{17}Si$: C, 68.09; H, 6.89. Found: C, 67.91; H, 7.12.

3.10. Ethyl 2-*O*-acetyl-4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside (14)

To a soln of **1** (2 g, 6.4 mmol) in CH_3CN (15 mL), trimethylorthoacetate (1.2 mL, 9.6 mmol) and *p*-TsOH (200 mg) were added and the mixture was allowed to stir at rt for 45 min after complete conversion (TLC), the soln was neutralized with Et_3N and the solvents were evaporated. The residue was dissolved in 15 mL 80% AcOH and stirred for 30 min at rt when TLC showed complete conversion. The solvents were evaporated and the crude product was chromatographed using 5:1 benzene–EtOAc to afford **14** (1.7 g, 74%); $[\alpha]_D$ + 125.4°; ^{1}H NMR: 7.55–7.25 (m, 4 H, aromatic protons), 5.56 (s, 1 H, C*H*Ph), 5.27 (d, 1 H, *J* 3.6 Hz, H-2), 5.26 (s, 1 H, H-1), 2.65 (m, 2 H, S–CH_2–CH_3), 2.12 (s, 3 H, $COCH_3$), 1.26 (t, 3 H, *J* 7.5 Hz, S–CH_2–CH_3). ^{13}C NMR: 170.9 ($COCH_3$), 128.74–126.6 (aromatic carbons), 102.6 (*C*HPh), 83.7 (*C*-1), 78.5, 74.0, 68.9, 68.1, 64.0, 26.0 (S–CH_2–CH_3), 21.4 ($COCH_3$), 15.3 (S–CH_2–CH_3).

3.11. Ethyl 2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1 → 3)-2-*O*-acetyl-4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside (15)

A mixture of donor **7** (2.3 g, 4.74 mmol), acceptor **14** (1.3 g, 3.65 mmol) and 4 Å MS (2 g) in CH_2Cl_2 (25 mL) was stirred at rt for 12 h and then cooled to 0 °C. NIS (1.3 g, 6.2 mmol) and TfOH (54 μL, 0.6 mmol) were added and the soln was stirred for 45 min when TLC showed complete conversion. The mixture was diluted with CH_2Cl_2 (25 mL) and filtered through Celite. The filtrate was washed successively with aq $Na_2S_2O_3$, saturated aq $NaHCO_3$ and water. The organic layer was dried (Na_2SO_4) and concentrated to a syrup. Column chromatography of the material with 8:1 benzene–EtOAc afforded **15** (2.3 g, 75%) also as syrup; $[\alpha]_D$ + 59.1°. ^{1}H NMR: 7.36–7.12 (m, 20 H, aromatic protons), 5.6 (s, 1 H, C*H*Ph), 5.54 (bs, 1 H, H-2^{I}), 5.38 (s, 1 H, H-1^{I}), 5.01 (d, 1 H, J 3.5 Hz, H-1^{II}), 2.65 (m, 2 H, S–CH_2–CH_3), 1.87 (s, 3 H, $COCH_3$), 1.26 (t, 3 H, *J* 7.5 Hz, S–CH_2–CH_3), 1.02 (d, 3 H, *J* 6.5 Hz, C–CH_3). ^{13}C NMR: 169.9 ($COCH_3$), 135.1–127.2 (aromatic carbons), 102.0 (CHC_6H_5), 94.6 (*C*-1^{II}), 83.9 (*C*-1^{I}), 24.7 (S–CH_2–CH_3), 20.6 ($COCH_3$), 16.7 (S–CH_2–CH_3), 15.1 (C–CH_3). Anal. Calcd for $C_{44}H_{50}O_{10}S$: C, 68.55; H, 6.54. Found: C, 68.68; H, 6.66.

3.12. Methyl 2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1 → 3)-2-*O*-acetyl-4,6-*O*-benzylidene-α-D-mannopyranosyl-(1 → 3)-2-acetyl-6-*O*-benzyl-4-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-α-D-mannopyranosyl-(1 → 4)-[2-(trimethylsilyl)ethyl 2,3-di-*O*-benzyl-β-D-glucopyranosid]uronate (16)

A mixture of trisaccharide acceptor **13** (717 mg, 0.6 mmol), disaccharide donor **15** (714 mg, 0.9 mmol) and 4 Å MS (1 g) in CH_2Cl_2 (15 mL) was allowed to stir at rt for 12 h. The mixture was then cooled to 0 °C and NIS (240 mg, 1.1 mmol) and TfOH (10 μL, 0.1 mmol) were added. After stirring for 45 min (TLC optimum conversion), the soln was diluted with CH_2Cl_2 (25 mL) and filtered through Celite. The filtrate was washed successively with aq $Na_2S_2O_3$, saturated aq $NaHCO_3$ and water. The organic layer was dried (Na_2SO_4) and evaporated to a syrup. Column chromatography with 8:1 benzene–EtOAc gave **16** (850 mg, 70%) as glassy syrup; $[\alpha]_D$ +37.5° (*c* 1.1, $CHCl_3$); ^1H NMR: δ 7.39–7.17 (m, 50 H, aromatic protons), 5.50 (s, 1 H, C*H*Ph), 5.42, 5.26 (2 bs, 2 H, H-1^{II}, H-1^{IV}), 4.96 (d, 1 H, *J* 3.6 Hz, H-1^{III}), 4.85 (d, 1 H, *J* 3.3 Hz, H-1^{V}), 4.75 (d, 1 H, *J* 11.4 Hz, H-1^{I}), 3.95 (s, 3 H, COOC*H*$_3$), 2.57 (m, 2 H, C*H*$_2$CH$_2$SiMe$_3$), 2.18, 2.05 (2 OCOCH$_3$), 1.26 (m, 2 H, CH$_2$C*H*$_2$SiMe$_3$), 1.13 (d, 3 H, *J* 6.6 Hz, C–C*H*$_3$), 1.09 (d, 3 H, *J* 6.3 Hz, C–C*H*$_3$), −0.14 [s, 9 H, Si(C*H*$_3$)$_3$]. ^{13}C NMR: δ 171.3 (*C*OOMe), 168.4, 167.3 (2 *C*OCH$_3$), 103.3 (C-1^{I}), 102.2 (*C*HPh), 100.2, 99.9 (C-1^{II}, C-1^{IV}), 98.5, 96.3 (C-1^{III}, C-1^{V}), 84.5, 81.8, 79.8, 78.0, 77.9, 77.7, 77.0, 76.8, 76.7, 75.8, 75.2, 74.8, 74.6, 74.2, 73.7, 73.5, 73.1, 73.0, 72.6, 72.2, 69.8, 69.5, 68.7, 68.6, 67.1, 66.5, 63.3 (C*H*$_2$CH$_2$SiMe$_3$), 55.1 (COOMe), 20.9, 20.7 (2 CO*C*H$_3$), 18.7 (*C*H$_2$SiMe$_3$), 16.3, 16.1 (2 C–*C*H$_3$), −1.5 [Si(*C*H$_3$)$_3$]. Anal. Calcd for $C_{110}H_{126}O_{27}Si$: C, 69.24; H, 6.66. Found: C, 68.96; H, 6.82.

3.13. Methyl 2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1 → 3)-2-azido-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranosyl-(1 → 3)-2-azido-6-*O*-benzyl-2-deoxy-4-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-α-D-glucopyranosyl-(1 → 4)-[2-(trimethylsilyl)ethyl 2,3-di-*O*-benzyl-β-D-glucopyranosid] uronate (19)

To a soln of compound **16** (650 mg, 0.32 mmol) in MeOH (15 mL), 0.05 M NaOMe (1 mL) was added and the soln was stirred at rt for 3 h. Then the soln was neutralized with a Dowex 50W H^+ resin, filtered and evaporated. Column chromatography of the material with 5:1 benzene–EtOAc gave **17** (623 mg, quantitative). Compound **17** (550 mg, 0.27 mmol) was dissolved in CH_2Cl_2 (10 mL) and pyridine (500 μL) and the soln was cooled to −35 °C. Triflic anhydride (135 μL, 0.8 mmol) was added and the soln was stirred for 3 h. The reagents were then evaporated, the residue (**18**) was dried under diminished pressure for 1 h, then dissolved in DMF (5 mL) and NaN_3 (100 mg, 0.54 mmol) was added. The soln was stirred for 4 h at rt and then diluted with CH_2Cl_2 and washed with cold water. The organic layer was dried (Na_2SO_4) and evaporated to a syrup. Column chromatography of the crude material with 6:1 benzene–EtOAc afforded **19** (321 mg, 60% overall); $[\alpha]_D$ +31.4 (*c* 1.2, $CHCl_3$). The IR spectrum ($CHCl_3$) of **19** showed a strong band at 2125 cm^{-1} for the N_3 stretching vibration; ^1H NMR: δ 7.65–7.20 (m, 50 H, aromatic protons), 5.54 (s, 1 H, C*H*Ph), 5.04, 4.96 (m, 2 H, H-1^{II}, H-1^{IV}), 4.91 (d, 1 H, *J* 3.6 Hz, H-1^{III}), 4.80 (d, 1 H, *J* 3.2 Hz, H-1^{V}), 4.72 (d, 1 H, *J* 10.8 Hz, H-1^{I}), 3.72 (s, 3H, COOC*H*$_3$), 1.02, 0.98 (2s, 6H, 2 C–C*H*$_3$), −0.14 [Si(C*H*$_3$)$_3$]. ^{13}C NMR: δ 168.4 (*C*OOMe), 126.3–138.8 (aromatic carbons), 103.2 (C-1^{I}), 102.2 (*C*HPh), 99.4, 99.2, 99.0, 97.1 (C-1^{II}, C-1^{III}, C-1^{IV}, C-1^{V}), 83.4, 81.7, 79.8, 79.2, 79.1, 78.0, 77.6, 76.8, 76.1, 75.9, 75.2, 74.9, 74.8, 74.4, 73.4, 73.3, 73.2, 73.1, 73.0, 72.0, 71.8, 69.5, 68.5, 67.7, 67.4, 66.5, 64.3, 63.6, 63.1 (C-2^{II}, C-2^{IV}), 61.3 (*C*H$_2$CH$_2$SiMe$_3$), 52.3 (COO*C*H$_3$), 18.4 (*C*H$_2$SiMe$_3$), 16.7, 16.1 (2 C–*C*H$_3$), −1.5 [Si(*C*H$_3$)$_3$]. Anal. Calcd for $C_{106}H_{120}O_{23}N_6Si$: C, 67.93; H, 6.45; N, 4.48. Found: C, 67.70; H, 6.66; N, 4.69.

3.14. Methyl 2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1 → 3)-2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranosyl-(1 → 3)-2-acetamido-6-*O*-benzyl-2-deoxy-4-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-α-D-glucopyranosyl-(1 → 4)-[2-(trimethylsilyl)ethyl 2,3-di-*O*-benzyl-β-D-glucopyranosid]uronate (20)

A soln of compound **19** (400 mg, 0.21 mmol) in thioacetic acid (5 mL) and pyridine (2.5 mL) was allowed to stir at rt for 24 h. The solvents were carefully removed and the residue was chromatographed with 5:1 benzene–EtOAc to afford **20** (240 mg, 60%); $[\alpha]_D$ +27.6° (*c* 1.2, $CHCl_3$). ^1H NMR: δ 7.65–7.20 (m, 50 H, aromatic protons), 5.51 (s, 1 H, C*H*Ph), 5.02 (d, 1 H, *J* 3.2 Hz, H-1^{II}), 4.93, 4.90 (2 bs, 2 H, H-1^{III}, H-1^{IV}), 4.80 (d, 1 H, *J* 3.4 Hz, H-1^{V}), 4.70 (d, 1 H, *J* 11.0 Hz, H-1^{I}), 3.71 (s, 3H, COOC*H*$_3$), 1.04, 0.99 (2s, 6H, 2 C–C*H*$_3$), −0.14 [Si(*C*H$_3$)$_3$]. ^{13}C NMR: δ 171.4 (*C*OOMe), 168.6, 168.1 (2 NH*C*OCH$_3$), 130.7–127.8 (aromatic carbons), 103.6 (C-1^{I}), 102.2 (*C*HPh), 99.2, 98.9, 98.7, 96.9 (C-1^{II}, C-1^{III}, C-1^{IV}, C-1^{V}), 84.3, 81.4, 79.8, 78.2, 77.9, 77.5, 77.1, 76.8, 76.6, 75.4, 75.2, 74.6, 74.3, 74.2, 73.8, 73.3, 73.1, 72.8, 72.4, 72.2, 69.7, 69.1, 68.3, 68.2, 64.8, 63.9, 62.5, 54.4 (COO*C*H$_3$), 53.9, 53.3 (C-2^{II}, C-2^{IV}), 22.4, 22.9 (2 NHCO*C*H$_3$), 18.7 (*C*H$_2$SiMe$_3$), 16.9, 16.3 (2 C–*C*H$_3$), −1.5 [Si(*C*H$_3$)$_3$]. Anal. Calcd for $C_{110}H_{128}O_{25}N_2Si$: C, 69.31; H, 6.77; N, 1.47. Found: C, 68.98; H, 6.92; N, 1.64.

3.15. Methyl α-L-fucopyranosyl-(1 → 3)-2-acetamido-2-deoxy-α-D-glucopyranosyl-(1 → 3)-2-acetamido-2-deoxy-4-*O*-(α-L-fucopyranosyl)-α-D-glucopyranosyl-(1 → 4)-[2-(trimethylsilyl) ethyl-β-D-glucopyranosid]uronate (21)

Compound **20** (200 mg, 0.1 mmol) and 10% Pd–C (300 mg) in AcOH (15 mL) were stirred under hydrogen for 48 h at rt. The mixture was filtered through a Celite bed and and the filtrate was concentrated to dryness. The crude product was chromatographed with 10:5:1 $CHCl_3$–CH_3OH–H_2O and then filtered through a 0.45 μm Millipore membrane to afford pure **21** (81 mg, 80%); $[\alpha]_D$ +68.5° (*c* 0.5, $CHCl_3$). ^1H NMR (D_2O): δ 5.28 (bs, 2 H, H-1^{III}, H-1^{V}), 5.10, 5.03 (2 d, 2 H, *J* 3.8 Hz, H-1^{II}, H-1^{IV}), 4.81 (d, 1H, *J* 10.5 Hz, H-1^{I}), 3.70 (s, 3H, $COOCH_3$), 2.04, 1.90 (2s, 6H, 2 $NHCOCH_3$), 3.29 (m, 2H, $CH_2CH_2SiMe_3$), 1.16, 1.14 (2d, 6H, *J* 6.6 Hz, 2 C–CH_3), 1.10 (t, 2H, $CH_2CH_2SiMe_3$), −0.14 [$Si(CH_3)_3$]. ^{13}C NMR (D_2O): δ 175.4, 175.0 (2 $NHCOCH_3$), 171.6 (*C*OOMe), 102.7 (C-1^{I}), 101.8, 100.4, 100.1, 97.3 (C-1^{II}, C-1^{III}, C-1^{IV}, C-1^{V}), 78.7, 76.9, 74.8, 73.9, 73.8, 73.7, 73.6, 72.9, 72.8, 70.6, 70.5, 69.7, 69.2, 69.0, 68.9, 68.1, 67.9, 61.4, 61.1 (CH_2 CH_2SiMe_3), 54.5, 54.1 (C-2^{II}, C-2^{IV}), 49.5 ($COOCH_3$), 23.2, 22.9 (2 $NHCOCH_3$), 18.5 ($CH_2CH_2SiMe_3$), 16.6, 16.3 (2 C–CH_3), −1.5 [$Si(CH_3)_3$]. Anal. Calcd for $C_{40}H_{70}O_{25}N_2Si$: C, 47.71; H, 7.01; N, 2.79. Found: C, 47.56; H, 6.72; N, 2.95.

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