Supporting Information

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1. Supporting Figures

26 steps
overall yields = 1.05 and 1.11%
scale = 268 mg or 440 mg
Dey *et al.*
Chem. Sci. **2018,** *9,* 6685.

23 steps
overall yield = 4.16 %
scale = 307 mg
Dey *et al.*
Chem. Sci. **2018**, *9*, 6685.

24 steps
overall yields = 2.11 and 3.06%
scale = 70 mg or 210 mg
Arungundram *et al.*
J. Am. Chem. Soc. **2009**, *131*, 17394.
Zong *et al. J. Am. Chem. Soc.* **2017**, *139*, 9534.

19 steps
overall yield = 1.89%
scale = 796 mg
Hansen *et al.*
J. Org. Chem. **2012**, *77*, 7823.

29 steps
overall yield = 5.09%
scale = 415 mg
Orgueira *et al.*
Chem. Eur. J. **2003**, *9*, 140.

21 steps
overall yield = 4.90%
scale = 35 mg
Codée *et al.*
J. Am. Chem. Soc. **2005**, *127*, 3767.

19 steps
overall yield = 0.67%
scale = 43 g
Dai *et al.*
J. Org. Chem. **2016**, *81*, 162.

21 steps + 2 (idose ox)
overall yield = 5.60%
scale = 2.8 mg
Hu *et al.*
Nat. Chem. **2011**, *3*, 557.

22 steps + 3 (idose ox)
overall yield = 3.10%
scale = 600 mg
Wang *et al.*
Chem. Eur. J. **2010**, *16*, 8365.

18 steps (intermediate)
overall yield = 3.20%
scale = 500 mg
Muñoz-García *et al.*
Chem. Eur. J. **2012**, *18*, 16319.
de Paz *et al. ChemBioChem* **2001**, *2*, 673.

17 steps (versatile intermediate)
overall yield = 2.41%
scale = 2.92 g
Hansen *et al.*
J. Org. Chem. **2015**, *80*, 3777.

10
9 steps (5 purifications) from heparin
(versatile intermediate)
overall yield = 9.19%
scale = 805 mg

Figure S1: Representative examples of HS disaccharides used for oligosaccharide assembly, with comparison to disaccharide **10**.[1] The total number of steps, overall yields, and scale of the isolated compounds starting from D-glucosamine, di-acetone-D-glucose, peracetylated-D-glucose, or glucuronic acid γ-lactone are provided in each case. Disaccharide **10** is a highly versatile intermediate that can be converted to numerous useful building blocks for HS oligosaccharide synthesis.

Figure S2. Controlled chemical digestion of *N*-Ac-heparin using 1M TfOH at 100 °C. (a) Reaction monitoring using ^{1}H NMR in D_2O (500 MHz) at various time points (1-9 h); (b) HILIC-FTMS/MS analysis of crude digest after 6h; (b1) Total ion chromatogram (TIC) of HILIC-MS analysis indicates the extent of digestion, predominantly gave disaccharide (dp2) as a major product ($[M-H]^+$=354); (b2) MS/MS analysis of $[M-H]^+$=354 showed further fragmentation patterns, suggesting possible formation of both disaccharides GlcN-UA ($[M-H]^+$=294) and UA-GlcN ($[M-H]^+$=295).

Figure S3. Controlled chemical digestion of heparin using 2M TfOH at 100 °C. (a) Reaction monitoring using ^{1}H NMR in D_2O (500 MHz) at various time points (2-8 h); (b) HILIC-FTMS/MS analysis of crude digest; (b1) TIC of HILIC-MS analysis indicates the extent of digestion, predominantly giving disaccharide (dp2) as a major product ($[M-H]^+$=354); (b2) MS/MS analysis of $[M-H]^+$=354 showed further fragmentation patterns, suggesting possible formation of both disaccharides GlcN-UA ($[M-H]^+$=294) and UA-GlcN ($[M-H]^+$=295).

Figure S4. Controlled chemical digestion of heparosan using 1M TfOH at 100 °C. (a) Reaction monitoring using ^{1}H NMR in D_2O (500 MHz) at various time points (1-9 h); (b) HILIC-FTMS/MS analysis of crude digest after 5h; (b1) TIC of HILIC-MS analysis indicates the extent of digestion, predominantly giving disaccharide (dp2) as a major product $[M-H]^+$=354 along with minor tetrasaccharide (dp4) $[M-H]^+$=691; (b2) MS/MS analysis of $[M-H]^+$=354 showed further fragmentation patterns, suggesting formation of only disaccharide UA-GlcN ($[M-H]^+$=295).

Figure S5. Chemical digestion of *N*-deacetylated heparosan using 1M TfOH at 100 °C. (a) Reaction monitoring using ^{1}H NMR in D_2O (500 MHz) at various time points (1-9h). No significant change in anomeric peaks of polysaccharide even after 9h; (b) HILIC-FTMS/MS analysis of crude digest; (b1) TIC of HILIC-MS analysis indicates the qualitative formation of disaccharide (dp2), tetrasaccharide (dp4), hexasaccharide (dp6), and octasaccharides (dp8); (b2) MS/MS analysis of $[M-H]^+$=354 showed further fragmentation patterns, suggesting possible formation of both disaccharides GlcN-UA ($[M-H]^+$=294) and UA-GlcN ($[M-H]^+$=295).

Figure S6. Proposed mechanisms for the selective hydrolysis of heparosan and heparin. (a) In the case of GlcN(α1-4)GlcA bond cleavage, **TS Ia** is expected to be favored due to anomeric hyperconjugation effects (per the anti-periplanar lone-pair hypothesis, ALPH),[2] leading to formation of the GlcA-GlcN disaccharide. Cleavage of the GlcA(β1-4)GlcN bond would require either an energetically demanding ring flip in the polymer backbone (**TS Ib**, **TS Ic)** to benefit from anomeric hyperconjugation or a less favorable syn-periplanar orientation between the lone pair and departing glycoside (syn-periplanar lone-pair hypothesis (SLPH)). (b) With heparin, both cleavage routes are supported by ALPH in their chair conformations (**TS IIa**, **TS IIb**). However, **TS IIa** is expected to be more favorable due to the unique conformational flexibility of IdoA,[3] which could assist in the transition to the half-chair oxocarbenium ion intermediate and lead to formation of the observed GlcN-IdoA disaccharide. Another possibility is that the IdoA linkage is more prone to hydrolysis because the IdoA units can readily adopt a more "axial-rich" $^{1}C_{4}$ conformation. As axial substituents are less electron withdrawing, the IdoA linkage should be more reactive. This conformational "arming" effect has been reported to significantly enhance glycoside hydrolysis rates.[4]

Scheme S1. Synthesis of Differentially Protected GlcN-IdoA Donor **19**

Scheme S2. Synthesis of Differentially Protected GlcN-IdoA Acceptor **20**

Scheme S3. Synthesis of Tetrasaccharide **S14** with β-selectivity

2. Supporting Tables

Table S1. Controlled hydrolysis of sodium heparinate

Entry	Reaction scale (g)	TfOH conc. (M)	Time (h)	% Yield[a] GlcNAc-IdoA[b]	% Yield[a] $GlcN_3$-IdoA[c]
1	10	2	8	17% (1.7 g)	-
2	20	2	8	18% (3.6 g)	-
3	25	2	8	18% (4.4 g)	-
4[d]	50	1	7	16% (7.9 g)	-
5	5	2	8	-	17% (0.83 g)
6	10	2	8	-	20% (1.9 g)
7	20	2	8	-	20% (3.9 g)
8	25	2	8	-	20% (4.8 g)

[a] Yields were calculated by comparing the weight of the isolated, pure disaccharide product to the weight of the polysaccharide starting material, correcting for minor differences in the relative molecular weights of the average disaccharide found in sodium heparinate (IdoA2S2Na-GlcNS6S2Na; MW 665.38) and the disaccharide product (**1**: 663.58 or **1b**: 647.54).
[b] Isolated yield for GlcNAc-IdoA (**1**) over four or six steps.
[c] Isolated yield for $GlcN_3$-IdoA (**1b**) over four steps.
[d] Reaction was performed on N-Ac heparin using 1M TfOH.

Table S2. Radical α-Dehalogenation of 5

entry	reducing reagent	radical initiator	temperature °C	IdoA:GlcA[a]
1	Ph_3SnH	AIBN	110	1:2.8
2	Ph_3SnH	AIBN	80	1:2.8
3	Ph_3SnH	Et_3B	20	1:1.7
4	Ph_3SnH	Et_3B	0	1:1.8
5	Bu_3SnH	AIBN	110	1:1.7
6	Bu_3SnH	AIBN	80	1:1.6
7	Bu_3SnH	Et_3B	20	2:1[b]
8	Bu_3SnH	Et_3B	0	1.5:1

[a] Diastereomeric ratio of IdoA-GlcN:GlcA-GlcN was evaluated by ^{1}H NMR analysis of the crude mixture. [b] Isolated yield for optimized reaction condition: IdoA-GlcN (63%), GlcA-GlcN (31%). Note: Bu_3SnH and Ph_3SnH are highly toxic. Obtain special instructions before use and do not handle until all safety precautions have been read and understood.

Table S3. Radical α-Dehalogenation of 6

entry	reducing reagent	radical initiator	temperature °C	GlcA:IdoA[a]
1	Ph_3SnH	AIBN	110	1:3.4
2	Ph_3SnH	Et_3B	20	1:2.8
3	Ph_3SnH	Et_3B	0	1:3
4	Bu_3SnH	AIBN	110	1:1.7 [b]
5	Bu_3SnH	Et_3B	20	1:2.4
6	Bu_3SnH	Et_3B	0	1:3.2
7	TTMSS	AIBN	110	1:1.5[c]
8	TTMSS	AIBN	80	sluggish

[a] Diastereomeric ratio of GlcN-GlcA:GlcN-IdoA was evaluated by ^{1}H NMR analysis of the crude mixture. [b] Isolated yield for optimized reaction condition: GlcN-GlcA(33%), GlcN-IdoA (62%). [c] The reaction gave complex mixtures. Note: Bu_3SnH and Ph_3SnH are highly toxic. Obtain special instructions before use and do not handle until all safety precautions have been read and understood.

Table S4. **Regioselective Protection of the 2-O or 3-O Positions of IdoA using Dibutyltin Oxide**

entry	reagent	temperature °C	time	2-O/3-O	isolated yield[a]
1	FmocCl	120	1 h	-	complex
2	FmocCl	90	1 h	2-O	85%
3	FmocCl	20	18 h	-	no reaction
4	TrocCl	70	1 h	2-O	73%
5	TrocCl	20	18 h	-	no reaction
6	BzCl	120	1 h	-	complex
7	BzCl	70	2 h	2-O	74%
8	BzCl	20	18 h	2-O	60%
9	MCACl	20	15 mins	3-O	65%
10	MCACl	0	15 mins	3-O	75%

[a] In addition to the isolated compound, 5-15% of the starting material **S2** was recovered. Note: Bu_2SnO is highly toxic. Obtain special instructions before use and do not handle until all safety precautions have been read and understood.

3. Synthetic procedures and characterization data

3-1. General Methods

Unless stated otherwise, reactions were performed in oven-dried glassware under an argon atmosphere using freshly dried solvents. Solvents were dried via passage through an activated alumina column under argon. All other commercially obtained reagents were used as received unless otherwise noted. Thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 pre-coated plates (0.25 mm). Visualization of the chromatogram was accomplished by UV, cerium ammonium molybdate, or ninhydrin staining as necessary. ICN silica gel (particle size 0.032–0.063 mm) was used for column chromatography. ^{1}H NMR (Varian Inova-500 MHz and Bruker-400 MHz), and ^{13}C NMR (Varian Inova-125 MHz and Bruker-100 MHz) spectra were recorded using $CDCl_3$, CD_3COCD_3, CD_3OD, or D_2O as solvent(s). Data for ^{1}H are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant in Hz, and integration. When necessary, proton and carbon assignments were made by means of ^{1}H-^{1}H gCOSY, ^{1}H-^{13}C gHSQCAD and ^{1}H-^{13}C gHMBCAD. Mass spectra were obtained using a Perkin Elmer/Sciex API 365 triple quadrupole/electrospray tandem mass spectrometer or a Waters LCT Premier XE high resolution mass spectrometer at the California Institute of Technology. Sodium heparinate was obtained from Celsus Laboratories and used as it is. Heparosan was produced by fermentation procedures from *Escherichia coli* K5.[5] Abbreviations: 9-fluorenylmethoxycarbonyl (Fmoc); monochloroacetyl (MCA); *tert*-butyldiphenylsilyl (TBDPS); benzoyl (Bz); benzyl (Bn); *p*-methoxyphenyl (PMP); 4-methylbenzenethiol (STol); levulinoyl (Lev); naphthyl (Naph); (2-naphthyl)methyl (Nap); 2,2,2-trichloroethoxycarbonyl (Troc); trifluoroacetic anhydride (TFAA); trifluoroacetyl (TFA); uronic acid (UA).

Characterization of anomeric center stereochemistry. The stereochemistry of the newly formed glycosidic linkages were determined by the $^{3}J_{H1,H1}$ coupling constants using ^{1}H NMR and/or the $^{1}J_{C1,H1}$ coupling constants using gHSQC 2-D NMR (without ^{1}H decoupling). In some cases, further support for the assignments was obtained using 1H,1H NOESY spectra. For the glucosamine and glucuronic acid linkages, smaller coupling constants of $^{3}J_{H1,H2}$ (~ 3 Hz) indicate α linkages and larger coupling constants $^{3}J_{H1,H2}$ (7.2 Hz or larger) indicate β linkages. For the idose and iduronic acid linkages, the small values (~ 3 Hz) of $^{3}J_{H2,H3}$ and $^{3}J_{H3,H4}$ indicate that the glycan ring is predominantly in the $^{1}C_{4}$ conformation.[6] The coupling constants of $^{1}J_{C1,H1}$ around 170 Hz are strongly suggestive of α linkages, while $^{1}J_{C1,H1}$ values around 160 Hz are strongly suggestive of β linkages.[7]

3-2. Synthesis of Compounds and Assignments

Methyl (2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-(1,2,3-tri-*O*-acetyl-α-L-idopyranosid)uronate (1). Sodium heparinate (25 g, Celsus Laboratories; commercial grade) was dissolved in 120 mL of 2 M trifluoromethanesulfonic acid (21 mL) in H_2O and refluxed at 100 °C for 8 h. The reaction progress was monitored by ^{1}H NMR on an hourly basis and quenched at the appropriate time to maximize the yield and minimize over-hydrolysis. The optimal conditions for quenching were reached when the NMR spectrum of the crude reaction resembled the spectrum shown after 8 h in **Figure S3a**. At this time, the oligosaccharide peak at 5.46 ppm was almost completely consumed and the height of the newly formed GlcN side product anomeric

peak at 5.42 matched the height of the newly formed (likely anomeric) peak of the desired product at 5.41 ppm. The crude products could also be analyzed by hydrophilic interaction chromatography-Fourier transform mass spectrometry (HILIC-FTMS; **Figure S3**). The mixture was cooled to room temperature (RT) and concentrated to dryness under reduced pressure. The crude mixture was then refluxed (75 °C) with 250 mL of 0.011 N HCl in MeOH (0.25 mL of acetyl chloride in 250 mL of MeOH) overnight. The mixture was cooled to RT and concentrated again to dryness. The resulting solid was dissolved in 200 mL of anhydrous acetic anhydride at –5 °C and was stirred for 10 h at RT. The solution was concentrated, dissolved in ethyl acetate (EtOAc), cooled to 0 °C, and saturated aqueous (aq.) $NaHCO_3$ solution was added. The organic layer was separated, dried over $MgSO_4$, and concentrated. The resulting crude mixture was further treated with 150 mL of 1:1 pyridine-acetic anhydride at 0 °C and stirred for 10 h at RT. The solution was concentrated, washed with 1 N aq. HCl, saturated aq. $NaHCO_3$ solution, and brine. The organic layer was dried over $MgSO_4$, concentrated, and purified by silica gel column chromatography (elution with 1:1 → 1:4 hexanes/EtOAc) to give peracetylated disaccharide **1**, along with peracetylated glucosamine (side product). The desired compound was further purified by silica gel column chromatography (elution with 1:9 → 2:8 acetone/DCM) to give peracetylated disaccharide **1** (4.4 g, 18%) as an off-white solid. Yields were calculated by comparing the weight of the isolated disaccharide product to the weight of the polysaccharide starting material, correcting for minor differences in the relative molecular weights of the average disaccharide found in heparin (IdoA2S2Na-GlcNS6S2Na; MW 665.38) and the disaccharide product (MW 663.58). R_f 0.6 (EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.37 (d, J = 4.1 Hz, 1H, H-1), 5.81 (d, J = 9.2 Hz, 1H, NH), 5.32 (t, J = 5.4 Hz, 1H, H-3), 5.12 (t, J = 9.6 Hz, 1H, H-4′), 5.07 (t, J = 9.6 Hz, 1H, H-3′), 5.00 (d, J = 3.5 Hz, 1H, H-1′), 4.91 (dd, J = 5.4, 4.3 Hz, 1H, H-2), 4.72 (d, J = 4.0 Hz, 1H, H-5), 4.30 (ddd, J = 9.6, 9.2, 3.5 Hz, 1H, H-2′), 4.19 (dd, J = 12.5, 4.0 Hz, 1H, H-6′), 4.15 (dd, J = 12.5,

2.5 Hz, 1H, H-6′), 4.13 (dd, J = 5.4, 4.0 Hz, 1H, H-4), 4.05 (ddd, J = 9.6, 4.0, 2.5 Hz, 1H, H-5′), 3.87 (s, 3H, OCH_3), 2.14 (s, 3H), 2.11 (s, 3H), 2.10 (s, 3H), 2.09 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.43 (C=O), 170.77 (C=O), 170.34 (C=O), 169.51 (C=O), 169.49 (C=O), 169.28 (C=O), 168.39 (2 x C=O), 98.67 (C-1′), 90.44 (C-1), 72.89 (C-4), 70.70 (C-5), 70.66 (C-4′), 69.03 (C-5′), 68.66 (C-3), 67.95 (C-2), 67.73 (C-3′), 61.75 (C-6′), 52.92 (OCH_3), 51.91 (C-2′), 21.18, 20.93, 20.85, 20.84, 20.78, 20.74, 20.70; HRMS (ESI-TOF) calcd for $C_{27}H_{37}NO_{18}$ Na $[M+Na]^+$: 686.1909; found: 686.1915. Notably, the HMBC spectrum showed cross peaks between H-4 (4.13 ppm) of IdoA and C-1 (98.7 ppm) of GlcN, indicative of a GlcN-IdoA linkage.

Methyl (3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-α-D-glucopyranosyl)-(1→4)-(1,2,3-tri-*O*-acetyl-α-L-idopyranosid)uronate (1b). Sodium heparinate (25 g) was dissolved in 120 mL of 2 M trifluoromethanesulfonic acid (21 mL) in H_2O and refluxed at 100 °C for 8 h. The progress of the reaction was monitored by ^1H NMR on an hourly basis and quenched at the appropriate time to maximize the yield and minimize over-hydrolysis. The optimal conditions for quenching were reached when the NMR spectrum of the crude reaction resembled the spectrum shown after 8 h in **Figure S3**. At this time, the oligosaccharide peak at 5.46 ppm was almost completely consumed and the height of the newly formed GlcN side product anomeric peak at 5.42 matched the height of the newly formed (likely anomeric) peak of the desired product at 5.41 ppm. The mixture was cooled to RT and concentrated to dryness under reduced pressure. The crude mixture was then refluxed (75 °C) with 250 mL of 0.011 N HCl in MeOH (0.25 mL of acetyl chloride in 250 mL of

MeOH) overnight. The mixture was cooled to RT, quenched with aq. $NaHCO_3$, filtered, and concentrated. The residue was again filtered through a silica bed (10 x 7 cm) and eluted with DCM (250 mL), followed by MeOH/DCM (1:4, 250 mL) and MeOH (1.5 L). The MeOH (1.5 L) fractions were concentrated. The crude product was dissolved in MeOH/water (4:1, 200 mL), and potassium carbonate (8.9 g, 64 mmol), $ZnCl_2$ (0.51 g, 3.7 mmol), and freshly prepared TfN_3 (0.15 mol) were added. [Preparation of TfN_3: To a solution of NaN_3 (49 g, 0.75 mol) in 2:1 DCM/H_2O (300 mL) was added Tf_2O (25 mL, 42 g, 0.15 mol) dropwise at 0 °C over 1 h. The reaction was stirred at 0 °C for an additional 2.5 h. The DCM layer was then extracted and used directly without concentration.] After stirring at RT overnight, the mixture was concentrated, dissolved in THF, filtered through Celite, and concentrated to dryness. The resulting solid was dissolved in 250 mL of anhydrous acetic anhydride at –5 °C, $HClO_4$ (25 mL, 0.44 mol) was added, and the reaction was stirred for 18 h at RT. The solution was concentrated, dissolved in EtOAc, and washed with saturated aq. $NaHCO_3$ solution and then brine. The organic layer was dried over $MgSO_4$, concentrated, and purified by silica gel column chromatography (elution with 2:1 → 1:1 hexanes/EtOAc) to give peracetylated azido disaccharide **1b** (4.8 g, 20%) as an off-white solid. Yields were calculated by comparing the weight of the isolated disaccharide product to the weight of the polysaccharide starting material, correcting for minor differences in the relative molecular weights of the average disaccharide found in heparin (IdoA2S2Na-GlcNS6S2Na; MW 665.38) and the disaccharide product (MW: 647.54). R_f 0.4 (2:3 hexanes/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.26 (d, J = 1.0 Hz, 1H, H-1), 5.38 (dd, J = 10.5, 9.3 Hz, 1H, H-3′), 5.26 (t, J = 2.5 Hz, 1H, H-3), 5.10 (d, J = 3.5 Hz, 1H, H-1′), 5.05 (dd, J = 10.2, 9.3 Hz, 1H, H-4′), 4.83 (dd, J = 2.5, 1.0 Hz, 1H, H-2), 4.77 (dd, J = 2.5 Hz, 1H, H-5), 4.23 (dd, J = 12.5, 3.4 Hz, 1H, H-6′), 4.16 (t, J = 2.5 Hz, 1H, H-4), 4.15 (dd, J = 12.5, 2.1 Hz, 1H, H-6′), 4.11–4.06 (m, 1H, H-5′), 3.85 (s, 3H, OCH_3), 3.47 (dd, J = 10.5, 3.5 Hz, 1H, H-2′), 2.19 (s, 3H), 2.14 (s, 3H), 2.12 (s, 3H), 2.08 (s, 3H),

2.07 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.5 (C=O), 169.8 (C=O), 169.7 (C=O), 169.6 (C=O), 168.8 (C=O), 168.4 (C=O), 167.9 (C=O), 98.4 (C-1′), 90.8 (C-1), 72.8 (C-4), 70.5 (C-3′), 68.9 (C-5), 68.6 (C-5′), 68.0 (C-4′), 66.7 (C-3), 66.0 (C-2), 61.2 (C-6′), 61.1 (C-2′), 52.7 (OCH_3), 20.79, 20.76, 20.7, 20.6, 20.53, 20.50; HRMS (ESI-TOF) calcd for $C_{25}H_{33}N_3O_{17}Na$ $[M+Na]^+$: 670.1708; found: 670.1707.

Methyl (3,4,6-tri-*O*-acetyl-2-((benzyloxy)carbonyl)amino-2-deoxy-α-D-glucopyranosyl)-(1→4)-(1,2,3-tri-*O*-acetyl-α-L-idopyranosid)uronate (1c). Sodium heparinate (2.0 g) was dissolved in 9.6 mL of 2 M trifluoromethanesulfonic acid in H_2O (1.7 mL trifluoromethanesulfonic acid) and refluxed at 100 °C for 8 h. The mixture was cooled to RT and concentrated to dryness under reduced pressure. The crude mixture was then refluxed (75 °C) with 20 mL of 0.011 N HCl in MeOH (20 μL of acetyl chloride in 20 mL of MeOH) overnight. The reaction was cooled to RT, quenched with aq. $NaHCO_3$, filtered, and concentrated. The residue was dissolved in water (10 mL), and $NaHCO_3$ (1.0 g, 12 mmol) and benzyl chloroformate (1.5 g, 9.1 mmol) were added. After stirring at RT overnight, the mixture was quenched with 1N aq. HCl and concentrated. The resulting solid was dissolved in 10 mL of anhydrous acetic anhydride at –5 °C, $HClO_4$ (1.2 mL) was added, and the reaction was stirred for 18 h at RT. The solution was concentrated, dissolved in EtOAc, washed with saturated aq. $NaHCO_3$ solution, and brine. The organic layer was dried over Na_2SO_4, concentrated and purified by silica gel column chromatography (elution with 2:1 → 1:1 hexanes/EtOAc) to give disaccharide **1c** (0.19 g, 8.5%) as an off-white solid. Yields were calculated by comparing the weight of the isolated disaccharide product to the weight of the

polysaccharide starting material, correcting for minor differences in the relative molecular weights of the average disaccharide found in heparin (IdoA2SNa-GlcNS6SNa; MW 665.38) and the disaccharide product (MW 755.68). R_f 0.4 (4:6 hexanes/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.31 (m, 5H, Ar), 6.24 (s, 1H, H-1), 5.22 (d, *J* = 9.9 Hz, 1H, NH), 5.17–5.08 (m, 5H, PhC*H*$_2$, H-4′, H-3′, H-3, H-1′), 5.01 (d, *J* = 12.1 Hz, 1H, PhC*H*$_2$), 4.82 (appt, *J* = 2.3 Hz, 1H, H-2), 4.79 (d, *J* = 2.6 Hz, 1H, H-5), 4.22 (dd, *J* = 12.6, 3.6 Hz, 1H, H-6′), 4.15–4.05 (m, 3H, H-6′, H-4, H-2′), 3.92–3.89 (m, 1H, H-5′), 3.86 (s, 3H, OCH_3), 2.13 (s, 3H, CH_3C=O), 2.11 (s, 6H, 2XCH_3C=O), 2.104 (s, 3H, CH_3C=O), 2.01 (s, 3H, CH_3C=O), 1.86 (s, 3H, CH_3C=O); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.73 (C=O), 170.70 (C=O), 169.4 (C=O), 169.3 (C=O), 168.9 (C=O), 168.4 (*C*=$OOCH_3$), 167.9 (C=O), 155.7 (PhCH_2O*C*=O), 135.9 (Ar), 128.6 (Ar), 128.44 (Ar), 128.41 (Ar), 97.9 (C-1′), 90.1 (C-1), 71.6 (C-4), 70.9 (C-3′), 69.0 (C-5), 68.8 (C-5′), 67.6 (C-4′), 67.3 (Ph*C*H_2O), 66.4 (C-3 and C-2), 61.4 (C-6′), 53.5 (C-2′), 52.9 (OCH_3), 20.82, 20.75, 20.72, 20.6, 20.5, 20.4; HRMS (FAB) calcd for $C_{33}H_{42}NO_{19}$ $[M+H]^+$: 756.2351; found: 756.2332.

Methyl (2,3,4-tri-*O*-acetyl-β-D-glucopyranosyluronate)-(1→4)-2-acetamido-1,3,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranoside (2). Heparosan (19 g) was heated at 100 °C in 120 mL of 1 M trifluoromethanesulfonic acid in H_2O (10.6 mL trifluoromethanesulfonic acid in total 120 mL H_2O) for 5 h. The hydrolysis reaction was monitored every hour by ^{1}H NMR and quenched at the appropriate time to maximize the yield and minimize over-hydrolysis. The optimal conditions for quenching were reached when the NMR spectrum of the crude reaction resembled the spectrum shown after 5-6 h in **Figure S4**. The resultant mixture was cooled to RT and concentrated to

dryness. The crude mixture was then dissolved in 200 mL of 0.01 N HCl in MeOH (200 μL of acetyl chloride in 200 mL of MeOH) and refluxed overnight. The mixture was then cooled to RT and concentrated again to dryness. The resulting solid was dissolved in 200 mL of anhydrous acetic anhydride at –5 °C. After stirring for 10 h at RT, the solution was concentrated, dissolved in EtOAc, cooled to 0 °C, and washed with saturated aq. $NaHCO_3$ solution. The organic layer was dried over $MgSO_4$ and concentrated, and the resulting crude mixture was further treated with 120 mL of 1:1 pyridine/acetic anhydride. After stirring at RT for 10 h, the solution was concentrated, washed with 1 N aq. HCl, saturated aq. $NaHCO_3$, and brine. The organic layer was dried over $MgSO_4$, concentrated, and purified by silica gel column chromatography (30 x 7 cm) using hexanes/EtOAc (1:1 → 1:4) to give peracetylated disaccharide **2** (4.9 g, 16%) as a colorless foam. Yields were calculated by comparing the weight of the isolated disaccharide product to the weight of the polysaccharide starting material, correcting for minor differences in the relative molecular weights of the average disaccharide found in heparosan (GlcANa-GlcN; MW 401.30) and the disaccharide product (MW 663.58). R_f 0.6 (EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.08 (d, *J* = 3.6 Hz, 1H, H-1), 5.57 (d, *J* = 9.0 Hz, 1H, NH), 5.27–5.19 (m, 2H, H-3′, H-3), 5.17 (t, *J* = 9.4 Hz, 1H, H-4′), 4.96 (dd, *J* = 9.4, 7.9 Hz, 1H, H-2′), 4.59 (d, *J* = 7.9 Hz, 1H, H-1′), 4.41 (dd, *J* = 12.0, 1.1 Hz, 1H, H-6), 4.36 (ddd, *J* = 11.0, 9.0, 3.6 Hz, 1H, H-2), 4.09 (dd, *J* = 12.0, 2.7 Hz, 1H, H-6), 3.98 (d, *J* = 9.4 Hz, 1H, H-5′), 3.89–3.84 (m, 2H, H-4, H-5), 3.75 (s, 3H, OCH_3), 2.19 (s, 3H), 2.13 (s, 3H), 2.09 (s, 3H), 2.05 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H), 1.93 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.7 (C=O), 170.4 (C=O), 170.2 (C=O), 170.1 (C=O), 169.4 (C=O), 169.3 (C=O), 168.9 (C=O), 166.8 (C=O), 101.0 (C-1′), 90.6 (C-1), 76.3 (C-4), 72.8 (C-5′), 72.1 (C-3′), 71.5 (C-2′), 70.6 (C-3), 70.4 (C-5), 69.4 (C-4′), 61.5 (C-6), 53.0 (OCH_3), 51.2 (C-2), 23.1, 21.1, 20.9, 20.8, 20.7, 20.6, 20.5; HRMS (ESI-TOF) calcd for $C_{27}H_{37}NO_{18}Na$ $[M+Na]^+$: 686.1909; found: 686.1918.

Methyl (2,3,4-tri-*O*-acetyl-α-L-idoopyranosyluronate)-(1→4)-2-acetamido-1,3,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranoside (4). A suspension of compound **2** (1.0 g, 1.6 mmol) and *N*-bromosuccinimide (0.97 g, 5.4 mmol) in carbon tetrachloride (90 mL) were refluxed under a UV lamp (254 nm). After 2.5 h, the mixture was cooled, and DCM (100 mL) was added. The organic layer was washed with H_2O, saturated aq. $Na_2S_2O_3$, and 10% aq. Na_2CO_3. The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by silica gel column chromatography using DCM/acetone (8.5:1.5) to afford the corresponding bromide **5** (0.86 g, 75% yield) and a mixture of epimers (0.05 g, 4.0%) as an off-white foam. R_f 0.5 (4:1 DCM/acetone); ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.07 (d, *J* = 3.6 Hz, 1H, H-1), 5.65 (d, *J* = 9.2 Hz, 1H, NH), 5.39 (t, *J* = 9.0 Hz, 1H, H-3′), 5.27 (d, *J* = 9.0 Hz, 1H, H-4′), 5.21 (dd, *J* = 10.9, 9.5 Hz, 1H, H-3), 5.13 (d, *J* = 9.0 Hz, 1H, H-1′), 5.06 (t, *J* = 9.0 Hz, 1H, H-2′), 4.45 (dd, *J* = 12.4, 1.8 Hz, 1H, H-6), 4.39 (ddd, *J* = 10.9, 9.3, 3.6 Hz, 1H, H-2), 4.08 (dd, *J* = 12.4, 3.3 Hz, 1H, H-6), 3.98 (t, *J* = 9.5 Hz, 1H, H-4), 3.88 (m, 1H, H-5), 3.82 (s, 3H, OCH_3), 2.17 (s, 3H), 2.14 (s, 3H), 2.08 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H), 1.98 (s, 3H), 1.93 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.9 (C=O), 170.3 (C=O), 170.2 (C=O), 169.7 (C=O), 169.2 (C=O), 169.0 (C=O), 168.8 (C=O), 164.2 (C=O), 100.4 (C-1′), 90.6 (C-1), 90.3 (C-5′), 76.0 (C-4), 71.1 (C-3′), 70.7 (C-2′), 70.3 (C-3), 70.2 (C-5), 69.9 (C-4′), 61.3 (C-6), 54.2 (OCH_3), 51.3 (C-2), 23.1, 21.1, 21.0, 20.9, 20.68, 20.67, 20.5; HRMS (ESI-TOF) calcd for $C_{27}H_{36}BrNO_{18}Na$ $[M+Na]^+$: 766.0993; found: 766.0999. Note: Carbon tetrachloride (CCl_4) is highly toxic. Obtain special instructions before use and do not handle until all safety precautions have been read and understood.

A solution of bromide **5** (0.86 g, 1.2 mmol) in toluene (40 mL) was bubbled with argon for 10 min. Tributyltin hydride (0.68 g, 0.63 mL, 2.3 mmol) and Et_3B (23 mg, 0.23 mmol, 230 μL, 1 M solution

in hexanes) were added, and the reaction was stirred at RT. After 2 h, the mixture was concentrated, the resulting residue was dissolved in CH_3CN (100 mL), and the solution was washed three times with hexanes. The CH_3CN solution was concentrated under reduced pressure. Purification by silica gel column chromatography first using 2:3→1:4 toluene/EtOAc gave the GlcA-GlcN building block **2** (240 mg, 31% yield) as a white solid. R*f* 0.5 (1:9 toluene/EtOAc). Further elution with 1:4→1:9 toluene/EtOAc gave the IdoA-GlcN building block **4** (490 mg, 63% yield) as an off-white foam. R*f* 0.4 (1:9 toluene/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.09 (d, *J* = 3.7 Hz, 1H, H-1), 5.51 (d, *J* = 9.3 Hz, 1H, NH), 5.20 (dd, *J* = 10.9, 9.4 Hz, 1H, H-3), 5.14 (d, *J* = 2.7 Hz, 1H, H-1′), 5.10-5.06 (m, 2H, H-3′, H-4′), 4.83 (d, *J* = 2.4 Hz, 1H, H-5′), 4.68 (dd, *J* = 5.0, 2.7 Hz, 1H, H-2′), 4.40 (ddd, *J* = 10.9, 9.3, 3.7 Hz, 1H, H-2), 4.36 (dd, *J* = 12.4, 2.0 Hz, 1H, H-6), 4.19 (dd, *J* = 12.4, 3.5 Hz, 1H, H-6), 3.99 (t, *J* = 9.4 Hz, 1H, H-4), 3.90-3.85 (m, 1H, H-5), 3.78 (s, 3H, OCH_3), 2.19 (s, 3H), 2.12 (s, 3H), 2.10 (s, 3H), 2.09 (s, 3H), 2.08 (s, 3H), 2.07 (s, 3H), 1.92 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.2 (C=O), 170.7 (C=O), 170.2 (C=O), 169.7 (C=O), 169.6 (C=O), 169.0 (C=O), 168.8 (C=O), 168.2 (C=O), 98.6 (C-1′), 90.8 (C-1), 75.2 (C-4), 71.7 (C-3), 70.6 (C-5), 67.8 (C-5′), 67.7 (C-2′), 67.3 (C-4′), 67.2 (C-3′), 61.7 (C-6), 52.7 (OCH_3), 51.2 (C-2), 23.2, 21.2, 21.0, 20.93, 20.91, 20.8, 20.7; HRMS (ESI-TOF) calcd for $C_{27}H_{37}NO_{18}Na$ $[M+Na]^+$: 686.1908; found: 686.1922. Note: Tributyltin hydride (Bu_3SnH) is highly toxic. Obtain special instructions before use and do not handle until all safety precautions have been read and understood.

Methyl (2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-(1,2,3-tri-*O*-acetyl-β-D-glucopyranosid)uronate (3). A suspension of compound **1** (1.0 g, 1.5 mmol) and *N*-

bromosuccinimide (0.94 g, 5.3 mmol) in carbon tetrachloride (80 mL) was refluxed under a UV lamp (254 nm). After 2 h, the reaction was cooled, and DCM (80 mL) was added. The mixture was washed with H_2O, saturated aq. NaS_2O_3, and 10% aq. Na_2CO_3. The organic layer was dried over Na_2SO_4, filtered, and concentrated. The resulting residue was purified by silica gel column chromatography, eluting first with acetone in DCM (13→20%) to afford the corresponding bromide epimers **6** (0.89 g, 80% yield) as an off-white foam. R_f 0.5 (4:1 DCM/acetone); HRMS (ESI-TOF) calcd for $C_{27}H_{36}BrNO_{18}Na$ $[M+Na]^+$:766.0993; found: 766.0999. Note: Carbon tetrachloride (CCl_4) is highly toxic. Obtain special instructions before use and do not handle until all safety precautions have been read and understood.

A solution of bromide **6** (0.89 g, 1.2 mmol) in toluene (30 mL) was bubbled with argon for 10 min. Tributyltin hydride (0.70 g, 2.4 mmol) and AIBN (19 mg in 1 mL of toluene) were added, and the reaction was heated at 105 °C. After 30 min, the mixture was concentrated, the residue dissolved in CH_3CN (30 mL), and the resulting solution was washed three times with hexanes. The CH_3CN solution was then concentrated, and the residue was purified by silica gel column chromatography, eluting first with acetone in DCM (10→15%) to afford GlcN-GlcA building block **3** (0.26 g, 33% yield) as a white foam. R_f 0.6 (4:1 DCM/acetone); ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.79 (d, *J* = 7.5 Hz, 1H, H-1), 5.58 (d, *J* = 9.0 Hz, 1H, NH), 5.33 (t, *J* = 9.0 Hz, 1H, H-3), 5.17 (d, *J* = 3.8 Hz, 1H, H-1′), 5.10 (t, *J* = 10.0 Hz, 1H, H-4′), 5.06 (t, *J* = 10.0 Hz, 1H, H-3′), 5.02 (dd, *J* = 9.0, 7.5 Hz, 1H, H-2), 4.34 (t, *J* = 9.0 Hz, 1H, H-4), 4.30 (ddd, *J* = 10.0, 9.0, 3.8 Hz, 1H, H-2′), 4.21 (d, *J* = 9.0 Hz, 1H, H-5), 4.20 (dd, *J* = 12.4, 3.8 Hz, 1H, H-6′), 4.11 (dd, *J* = 12.4, 2.0 Hz, 1H, H-6′), 3.79 (s, 3H, OCH_3), 3.66–3.62 (m, 1H, H-5′), 2.12 (s, 3H), 2.11 (s, 3H), 2.03 (s, 3H), 2.02 (s, 6H), 2.01 (s, 3H), 1.94 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.6 (C=O), 170.9 (C=O), 170.5 (C=O), 170.4 (C=O), 169.4 (C=O), 169.2 (C=O), 168.8 (C=O), 167.9 (C=O), 97.7 (C-1′), 91.6 (C-1), 74.4 (C-5), 74.3 (C-3), 73.0 (C-4), 70.7 (C-2), 70.5 (C-3′), 68.8 (C-5′), 67.5 (C-4′), 61.4 (C-6′), 53.1

(OCH_3), 51.7 (C-2′), 23.1, 20.9, 20.86, 20.83, 20.82, 20.7, 20.6; HRMS (ESI-TOF) calcd for $C_{27}H_{37}NO_{18}Na$ $[M+Na]^+$: 686.1909; found: 686.1922. Further elution with acetone in DCM (15→25%) afforded GlcN-IdoA building block **1** (0.49 g, 62% yield). Note: Tributyltin hydride (Bu_3SnH) is highly toxic. Obtain special instructions before use and do not handle until all safety precautions have been read and understood.

Methyl (2-azido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-(2,3-di-*O*-acetyl-1-phenylthio-α-L-idopyranosid)uronate (7). To a solution of compound **1b** (3.9 g, 6.0 mmol) in anhydrous DCM (190 mL) were added trimethyl(phenylthio)silane (TMSSPh, 4.6 mL, 24 mmol) and ZnI_2 (5.8 g, 18 mmol). After stirring at RT overnight, the mixture was filtered, diluted with DCM (400 mL), and the organic layer was washed with saturated aq. $NaHCO_3$, dried over Na_2SO_4, and concentrated. The residue was purified by silica gel column chromatography (elution with 3:1 → 3:2 hexanes/EtOAc) to afford compound **7** (3.69 g, 88%) as a colorless foam. R_f 0.54 (1:1 hexanes/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54–7.50 (m, 2H, Ar), 7.35–7.29 (m, 3H, Ar), 5.66 (d, *J* = 1.0 Hz, 1H, H-1), 5.41 (dd, *J* = 10.6, 9.3 Hz, 1H, H-3′), 5.29 (td, *J* = 3.5, 1.0 Hz, 1H, H-3), 5.24 (d, *J* = 2.4 Hz, 1H, H-5), 5.13 (d, *J* = 3.5 Hz, 1H, H-1′), 5.09–5.04 (m, 2H, H-4′, H-2), 4.25 (dd, *J* = 4.2, 3.5 Hz, 1H, H-6′), 4.19–4.14 (m, 3H, H-5′, H-6′, H-4), 3.87 (s, 3H, OCH_3), 3.49 (dd, *J* = 10.6, 3.5 Hz, 1H, H-2′), 2.22 (s, 3H, CH_3C=O), 2.20 (s, 3H, CH_3C=O), 2.09 (s, 6H), 2.02 (s, 3H, CH_3C=O); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7 (C=O), 170.0 (C=O), 169.9 (C=O), 169.7 (C=O), 168.9 (C=O), 168.8 (C=O), 134.1 (Ar), 131.8 (Ar), 129.2 (Ar), 128.0 (Ar), 98.6 (C-1′),

86.3 (C-1), 73.6 (C-4), 70.6 (C-3′), 68.6 (C-5′, C-5), 68.5 (C-2), 68.1(C-4′), 67.2 (C-3), 61.3 (C-6′), 61.2 (C-2′), 52.7 (OCH_3), 20.9 (CH_3), 20.73 (CH_3), 20.68 (2XCH_3), 20.6 (CH_3); HRMS (FAB) calcd for $C_{29}H_{36}O_{15}SN_3$ $[M+H]^+$: 698.1867; found: 698.1869.

Methyl (2-azido-2-deoxy-4,6-*O*-2-naphthylidene-α-D-glucopyranosyl)-(1→4)-(1-phenylthio-α-L-idopyranosid)uronate (8). To a solution of disaccharide **7** (1.7 g, 2.4 mmol) in anhydrous MeOH (20 mL) was added a solution of NaOMe in MeOH (0.05M, 20 mL) at RT. After stirring for 3 h, the reaction was quenched with IR-120 resin. The solution was filtered and concentrated under reduced pressure to give the unprotected disaccharide. 2-(Dimethoxymethyl)naphthalene (0.97 g, 4.8 mmol) and *p*-toluenesulfonic acid (0. 12 g, 0.62 mmol) were subsequently added to a solution of this disaccharide in CH_3CN (85 mL) under argon. The reaction was heated at 50 °C for 3 h and then quenched by Et_3N (120 μL, 0.85 mmol). The reaction was concentrated, and the crude residue was purified by silica gel column chromatography (elution with 2:1 → 1:2 hexanes/EtOAc) to afford compound **8 (**1.25 g, 82%) as a colorless foam. R_f 0.43 (2:3 hexanes/EtOAc); ^{1}H NMR (400 MHz, CD_3COCD_3): δ 8.02 (s, 1H, Ar), 7.97–7.93 (m, 3H, Ar), 7.65–7.53 (m, 5H, Ar), 7.37–7.25 (m, 3H, Ar), 5.82 (s, 1H, $CH(O)_2$), 5.58 (d, J = 2.9 Hz, 1H, H-1), 5.37 (d, J = 3.9 Hz, 1H, H-1′), 5.36 (d, J = 4.5 Hz, 1H, OH), 5.25 (d, J = 2.7 Hz, 1H, H-5), 5.04 (d, J = 3.8 Hz, 1H, OH), 4.30 (dd, J = 9.9, 4.4 Hz, 1H, H-6′), 4.28–4.25 (m, 1H, H-3), 4.20 (t, J = 3.5 Hz, 1H, H-4), 4.02 (td, J = 9.4, 4.5 Hz, 1H, H-3′), 3.85 (t, J = 9.9 Hz, 1H, H-6′), 3.85 (s, 3H, OCH_3), 3.78–3.70 (m, 3H, H-2′, H-2, H-5′), 3.67 (t, J = 9.4 Hz, 1H, H-4′); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 169.5 (C=O), 136.7 (Ar), 135.5 (Ar), 133.7 (Ar), 132.9 (Ar), 130.3 (Ar), 128.9 (Ar), 128.2 (Ar), 127.8 (Ar),

127.6(Ar), 126.8 (Ar), 126.4 (Ar), 126.2 (Ar), 125.7 (Ar), 124.2 (Ar), 101.6 ($CH(O)_2$), 96.4 (C-1′), 88.6 (C-1), 81.4 (C-4′), 74.1 (C-4), 71.6 (C-2), 69.8 (C-3′), 68.5 (C-5), 68.1 (C-6′), 66.6 (C-3), 64.2 (C-2′), 63.5 (C-5′), 51.6 (OCH_3); HRMS (FAB) calcd for $C_{30}H_{32}O_{10}SN_3$ $[M+H]^+$: 626.1808; found: 626.1829.

Methyl (2-azido-2-deoxy-4,6-*O*-2-naphthylidene-α-D-glucopyranosyl)-(1→4)-(2-*O*-benzoyl-1-phenylthio-α-L-idopyranosid)uronate (9). To a solution of **8** (1.2 g, 2.0 mmol) in anhydrous toluene (0.40 L) were added *n*-Bu_2SnO (2.0 g, 8.0 mmol), BzCl (0.84 g, 6.0 mmol), TBAI (1.5 g, 4.6 mmol) and 4Å molecular sieves. The mixture was heated at 70 °C for 4 h, after which it was diluted with EtOAc (300 mL). The organic layer was washed with saturated aq. $NaHCO_3$ (300 mL), brine (300 mL), and dried over Na_2SO_4. The solution was concentrated under reduced pressure, and the crude residue was purified by silica gel column chromatography (elution with 3:1 → 2:1 hexanes/EtOAc) to afford compound **9** (1.4 g, 91%) as a colorless foam. R_f 0.56 (1:1 hexanes/EtOAc); ^{1}H NMR (400 MHz, CD_3COCD_3): δ 8.17–8.15 (m, 2H, Ar), 8.05 (s, 1H, Ar), 7.97–7.93 (m, 3H, Ar), 7.68–7.47 (m, 8H, Ar), 7.36–7.26 (m, 3H, Ar), 5.88 (d, *J* = 3.5 Hz, 1H, H-1), 5.82 (s, 1H, $CH(O)_2$), 5.39 (d, *J* = 4.3 Hz, 1H, OH), 5.31 (d, *J* = 3.5 Hz, 1H, H-5), 5.25 (t, *J* = 3.5 Hz, 1H, H-2), 5.24 (d, *J* = 3.5 Hz, 1H, H-1′), 5.08 (d, *J* = 4.4 Hz, 1H, OH), 4.28–4.25 (appt, *J* = 4.5 Hz, 1H, H-3), 4.38 (dd, *J* = 10.0, 4.9 Hz, 1H, H-6′), 4.26 (dd, *J* = 4.5, 3.5 Hz, 1H, H-4), 4.12–4.01 (m, 2H, H-3′, H-5′), 3.83 (s, 3H, OCH_3), 3.81 (t, *J* = 10.0 Hz, 1H, H-6′), 3.64 (t, *J* = 9.5 Hz, 1H, H-4′), 3.43 (dd, *J* = 10.0, 3.5 Hz, 1H, H-2′); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 169.2 (*C*=$OOCH_3$), 165.2 (*C*=OPh), 135.6 (Ar), 135.5 (Ar), 133.7 (Ar), 133.1 (Ar), 132.9 (Ar), 130.8

(Ar), 129.9 (Ar), 129.7 (Ar), 128.9 (Ar), 128.6 (Ar), 128.2 (Ar), 127.7 (Ar), 127.6(Ar), 127.2 (Ar), 126.4 (Ar), 126.2 (Ar), 125.7 (Ar), 124.3 (Ar), 101.6 ($CH(O)_2$), 99.6 (C-1′), 85.5 (C-1), 81.9 (C-4′), 76.5 (C-4), 72.1 (C-2), 69.3 (C-5), 68.8 (C-3′), 68.3 (C-6′), 67.7 (C-3), 63.9 (C-2′), 63.5 (C-5′), 51.6 (OCH_3); HRMS (FAB) calcd for $C_{37}H_{36}O_{11}SN_3$ $[M+H]^+$: 730.2071; found: 730.2058. Note: Dibutyltin oxide (*n*-Bu_2SnO) is highly toxic. Obtain special instructions before use and do not handle until all safety precautions have been read and understood.

Methyl (2-azido-3-*O*-benzyl-2-deoxy-4,6-*O*-2-naphthylidene-α-D-glucopyranosyl)-(1→4)-(2-*O*-benzoyl-3-*O*-benzyl-1-phenylthio-α-L-idopyranosid)uronate (10). To a solution of compound **9** (0.90 g, 1.2 mmol) in anhydrous DCM (35 mL) and DMF (35 mL) were added 4Å molecular sieves, BnBr (9.0 mL, 76 mmol) and freshly prepared Ag_2O (9.0 g, 38 mmol). After stirring at RT for 12 h, the reaction was filtered, concentrated, and the crude residue was purified by silica gel column chromatography (elution with 7:1 → 5:1 hexanes/EtOAc) to afford compound **10** (0.81 g, 72%) as a colorless foam. R_f 0.74 (2:1 hexanes/EtOAc); ^{1}H NMR (400 MHz, CD_3COCD_3): δ 8.20–8.18 (m, 2H, Ar), 8.07 (s, 1H, Ar), 8.00–7.95 (m, 3H, Ar), 7.70–7.55 (m, 7H, Ar), 7.46–7.18 (m, 14H, Ar), 5.97 (s, 1H, H-1), 5.87 (s, 1H, $CH(O)_2$), 5.44–5.43 (m, 1H, H-2), 5.37 (d, J = 2.0 Hz, 1H, H-5), 5.08 (d, J = 3.6 Hz, 1H, H-1′), 5.02 (d, J = 11.6 Hz, 1H, Bn), 4.92 (d, J = 11.6 Hz, 1H, Bn), 4.50 (d, J = 11.3 Hz, 1H, Bn), 4.40 (dd, J = 10.0, 5.0 Hz, 1H, H-6′), 4.37–4.33 (m, 2H, H-3, H-4), 4.10 (td, J = 10.0, 5.0 Hz, 1H, H-5′), 3.98 (d, J = 11.3 Hz, 1H, Bn), 3.82 (t, J = 10.0 Hz, 1H, H-6′), 3.81 (s, 3H, OCH_3), 3.80 (t, J = 10.0 Hz, 1H, H-4′), 3.67 (t, J = 10.0 Hz, 1H, H-3′), 3.50 (dd, J = 10.0, 3.6 Hz, 1H, H-2′); ^{13}C NMR (100 MHz, CD_3COCD_3): δ

168.7 (*C*=OOCH$_3$), 165.1 (*C*=OPh), 138.5 (Ar), 137.7 (Ar), 135.6 (Ar), 135.5 (Ar), 133.7 (Ar), 133.2 (Ar), 133.0 (Ar), 131.2 (Ar), 130.1 (Ar), 129.9 (Ar), 129.0 (Ar), 128.8 (Ar), 128.3 (Ar), 128.3 (Ar), 128.0 (Ar), 127.9 (Ar), 127.8 (Ar), 127.4 (Ar), 127.3 (Ar), 126.7 (Ar), 126.5 (Ar), 126.3 (Ar), 125.5 (Ar), 124.1 (Ar), 101.2 (CH(O)$_2$), 100.1 (C-1′), 86.6 (C-1), 82.3 (C-4′), 76.9 (C-3′), 76.1 (C-4), 74.1 (*C*H$_2$Ph), 73.2 (C-3), 72.5 (*C*H$_2$Ph), 69.2 (C-2), 68.3 (C-5), 68.2 (C-6′), 63.6 (C-5′), 63.3 (C-2′), 51.6 (OCH$_3$); HRMS (FAB) calcd for $C_{51}H_{48}O_{11}SN_3$ $[M+H]^+$: 910.3010; found: 910.3022.

Methyl (2-azido-3-*O*-benzyl-2-deoxy-4,6-*O*-2-naphthylidene-α-D-glucopyranosyl)-(1→4)-(3-*O*-benzyl-2-*O*-levulinoyl-1-phenylthio-α-L-idopyranosid)uronate (11). To a solution of disaccharide **10** (0.60 g, 0.66 mmol) in anhydrous DCM (12 mL) was added a solution of NaOMe in MeOH (0.05M, 24 mL) at RT. After stirring for 4 h, the reaction was quenched with 1M of aq. NH$_4$Cl (10 mL). DCM (120 mL) was then added, and the organic layer was washed with brine, dried over Na$_2$SO$_4$ and concentrated under reduced pressure to give the crude disaccharide intermediate. The intermediate was dissolved in DCM (6.0 mL), and EDC (1.3 g, 6.6 mmol), LevOH (0.78 g, 6.6 mmol), and DMAP (60 mg) were added at RT. The mixture was stirred at RT for 10 h. DCM (120 mL) was then added, and the organic layer was washed with brine, dried over Na$_2$SO$_4$, and concentrated. Purification by silica gel column chromatography (elution with 3:1 → 2:1 hexanes/EtOAc) afforded compound **11** (0.56 g, 91%) as a colorless foam. R_f 0.57 (2:1 hexanes/EtOAc); ^{1}H NMR (400 MHz, CD$_3$COCD$_3$): δ 8.05 (s, 1H, Ar), 7.97–7.92 (m, 3H, Ar), 7.66–7.50 (m, 7H, Ar), 7.43–7.27 (m, 11H, Ar), 5.90 (s, 1H, CH(O)$_2$), 5.66 (d, J = 2.2 Hz, 1H, H-

1), 5.26 (d, J = 2.4 Hz, 1H, H-5), 5.21 (d, J = 3.6 Hz, 1H, H-1′), 5.20–5.19 (m, 1H, H-2), 5.02 (d, J = 11.5 Hz, 1H, Bn), 4.91 (d, J = 11.6 Hz, 1H, Bn), 4.83 (d, J = 11.5 Hz, 1H, Bn), 4.82 (d, J = 11.6 Hz, 1H, Bn), 4.36 (dd, J = 10.0, 4.6 Hz, 1H, H-6′), 4.29 (t, J = 3.0 Hz, 1H, H-4), 4.15 (t, J = 3.0 Hz, 1H, H-3), 4.04–3.97 (m, 2H, H-3′, H-5′), 3.91 (t, J = 9.5 Hz, 1H, H-4′), 3.85 (t, J = 10.0 Hz, 1H, H-6′), 3.80 (s, 3H, OCH_3), 3.62 (dd, J = 9.8, 3.6 Hz, 1H, H-2′), 2.88–2.77 (m, 2H, CH_2), 2.70–2.66 (m, 2H, CH_2), 2.07 (s, 3H, $CH_3C{=}O$); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 205.5 (CH_3*C*=O), 171.7 (*C*=OCH_2), 168.8 (*C*=$OOCH_3$), 138.6 (Ar), 137.8 (Ar), 135.6 (Ar), 135.5 (Ar), 133.7 (Ar), 133.0 (Ar), 130.9 (Ar), 129.0 (Ar), 128.4 (Ar), 128.3 (Ar), 128.2 (Ar), 127.9 (Ar), 127.8 (Ar), 127.6 (Ar), 127.5 (Ar), 127.3 (Ar), 126.4 (Ar), 126.2 (Ar), 125.4 (Ar), 124.0 (Ar), 101.3 ($CH(O)_2$), 98.5 (C-1′), 85.9 (C-1), 82.4 (C-4′), 76.5 (C-3′), 74.3 (*C*H_2Ph), 73.7 (C-4), 72.9 (C-3), 72.6 (*C*H_2Ph), 68.9 (C-2), 68.6 (C-5), 68.3 (C-6′), 63.5 (C-5′), 63.1 (C-2′), 51.6 (OCH_3), 37.4 (CH_2), 28.8 (C=O*C*H_3), 27.8 (CH_2); HRMS (FAB) calcd for $C_{49}H_{50}O_{12}N_3S$ $[M+H]^+$: 904.3115; found: 904.3136.

Methyl (2-azido-3-*O*-benzyl-2-deoxy-6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranosyl)-(1→4)-(3-*O*-benzyl-2-*O*-levulinoyl-1-phenylthio-α-L-idopyranosid)uronate (12). To a solution of compound **11** (0.46 g, 0.51 mmol) in anhydrous MeOH (2.0 mL) and DCM (20 mL) was added *p*-toluenesulfonic acid (50 mg, 0.25 mmol) at RT. The reaction was stirred for 12 h, washed with water, and the organic phase was concentrated to give the crude diol product. To a solution of this diol in anhydrous DCM were added TBDPSCl (1.4 g, 5.1 mmol) and imidazole (0.52 g, 7.6 mmol). After stirring at RT for 12 h, the reaction was washed with brine, dried over H_2SO_4, and

concentrated. Purification by silica gel column chromatography (elution with 4:1 → 3:1 hexanes/EtOAc) afforded the 6-OTBDPS-protected disaccharide **12** (0.44 g, 85%) as a colorless foam. R_f 0.57 (2:1 hexanes/EtOAc); ^{1}H NMR (400 MHz, CD_3COCD_3): δ 7.81–7.78 (m, 4H, Ar), 7.55–7.53 (m, 2H, Ar), 7.47–7.41 (m, 10H, Ar), 7.38–7.29 (m, 9H, Ar), 5.66 (d, *J* = 3.6 Hz, 1H, H-1), 5.29 (d, *J* = 3.5 Hz, 1H, H-1′), 5.19 (d, *J* = 3.5 Hz, 1H, H-5), 5.16 (t, *J* = 3.6 Hz, 1H, H-2), 5.06 (d, *J* = 11.1 Hz, 1H, Bn), 4.87 (d, *J* = 11.5 Hz, 1H, Bn), 4.84 (d, *J* = 11.1 Hz, 1H, Bn), 4.78 (d, *J* = 11.5 Hz, 1H, Bn), 4.30 (t, *J* = 3.6 Hz, 1H, H-4), 4.22 (t, *J* = 4.1 Hz, 1H, H-3), 4.06–3.99 (m, 2H, H-6′), 3.93–3.80 (m, 3H, H-3′, H-4′, H-5′), 3.73 (s, 3H, OCH_3), 3.42 (dd, *J* = 10.0, 3.5 Hz, 1H, H-2′), 2.84–2.82 (m, 2H, CH_2), 2.74–2.65 (m, 2H, CH_2), 2.15 (s, 3H, $CH_3C{=}O$), 1.06 (s, 9H, *t*-Bu); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 206.6 (CH_3*C*=O), 171.8 (*C*=OCH_2), 168.9 (*C*=$OOCH_3$), 138.9 (Ar), 137.8 (Ar), 135.7 (Ar), 135.5 (Ar), 135.2 (Ar), 133.6 (Ar), 133.4 (Ar), 131.1 (Ar), 129.7 (Ar), 129.0 (Ar), 128.3 (Ar), 128.1 (Ar), 127.8 (Ar), 127.7 (Ar), 127.6 (Ar), 127.4 (Ar), 96.9 (C-1′), 85.1 (C-1), 79.9 (C-4′), 74.5 (*C*H_2Ph), 73.5 (C-3′), 72.9 (C-3, Bn), 71.8 (C-4), 70.5 (C-5′), 69.7 (C-5), 69.3 (C-2), 63.1 (C-6′), 63.0 (C-2′), 51.5 (OCH_3), 37.4 (CH_2), 28.8 (C=O*C*H_3), 27.7 (CH_2), 26.4 (C(*C*H_3)$_3$), 19.0 (*C*(CH_3)$_3$); HRMS (FAB) calcd for $C_{54}H_{62}SiO_{12}N_3S$ $[M+H]^+$: 1004.3823; found: 1004.3836.

Methyl (2-azido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranosyl)-(1→4)-(3-*O*-benzyl-2-*O*-levulinoyl-1-phenylthio-α-L-idopyranosid)uronate (13). To a solution of the 6-OTBDPS-protected disaccharide **12** (0.44 g, 0.43 mmol) in pyridine (10 mL) was added BzCl (1.5 g, 11 mmol) at RT. After stirring overnight, the mixture was

concentrated under reduced pressure, and the residue was dissolved in DCM (100 mL). The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. Purification by silica gel column chromatography (elution with 4:1 → 3:1 hexanes/EtOAc) gave compound **13** (0.45 g, 93%) as a colorless foam. R_f 0.58 (2:1 hexanes/EtOAc); ^{1}H NMR (400 MHz, CD_3COCD_3): δ 8.10–8.08 (m, 2H, Ar), 7.76–7.70 (m, 3H, Ar), 7.65–7.54 (m, 6H, Ar), 7.47–7.45 (m, 2H, Ar), 7.40–7.19 (m, 17H, Ar), 5.68 (d, *J* = 3.1 Hz, 1H, H-1), 5.63 (dd, *J* = 10.1, 9.3 Hz, 1H, H-4′), 5.40 (d, *J* = 3.5 Hz, 1H, H-1′), 5.24 (d, *J* = 3.0 Hz, 1H, H-5), 5.21 (t, *J* = 3.3 Hz, 1H, H-2), 4.90 (d, *J* = 11.5 Hz, 1H, Bn), 4.82 (d, *J* = 10.8 Hz, 1H, Bn), 4.81 (d, *J* = 11.5 Hz, 1H, Bn), 4.69 (d, *J* = 10.8 Hz, 1H, Bn), 4.34 (t, *J* = 3.4 Hz, 1H, H-4), 4.25 (t, *J* = 3.3 Hz, 1H, H-3), 4.19–4.14 (m, 1H, H-5′), 4.15 (dd, *J* = 10.3, 9.3 Hz, 1H, H-3′), 3.86 (dd, *J* = 11.5, 2.5 Hz, 1H, H-6′), 3.81 (dd, *J* = 11.5, 3.6 Hz, 1H, H-6′), 3.73 (s, 3H, OCH_3), 3.72 (dd, *J* = 10.3, 3.5 Hz, 1H, H-2′), 2.86–2.83 (m, 2H, CH_2), 2.77–2.73 (m, 2H, CH_2), 2.15 (s, 3H, $CH_3C{=}O$), 1.02 (s, 9H, *t*-Bu); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 205.6 (CH_3*C*=O), 171.8 (*C*=OCH_2), 168.9 (*C*=$OOCH_3$), 164.7 (*C*=OPh), 137.9 (Ar), 137.8 (Ar), 135.6 (Ar), 135.4 (Ar), 135.3 (Ar), 133.4 (Ar), 133.0 (Ar), 132.9 (Ar), 131.1 (Ar), 129.9 (Ar), 129.7 (Ar), 129.6 (Ar), 129.0 (Ar), 128.8 (Ar), 128.3 (Ar), 128.1 (Ar), 128.0 (Ar), 127.8 (Ar), 127.7 (Ar), 127.6 (Ar), 127.5 (Ar), 127.4 (Ar), 97.1 (C-1′), 85.4 (C-1), 77.9 (C-3′), 74.3 (*C*H_2Ph), 72.8 (*C*H_2Ph), 72.6 (C-3), 72.3 (C-4), 71.4 (C-5′), 70.6 (C-4′), 69.2 (C-5), 69.1 (C-2), 63.1 (C-2′), 62.4 (C-6′), 51.6 (OCH_3), 37.4 (CH_2), 28.8 (C=O*C*H_3), 27.7 (CH_2), 26.4 (C(*C*H_3)$_3$), 18.0 (*C*(CH_3)$_3$); HRMS (FAB) calcd for $C_{61}H_{66}SiO_{13}N_3S$ $[M+H]^+$: 1108.4086; found: 1108.4091.

Methyl (3-*O*-benzyl-2-deoxy-4,6-*O*-2-naphthylidene-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(2-*O*-benzoyl-3-*O*-benzyl-1-phenylthio-α-L-idopyranosid)uronate (14). Triethylamine (0.80 mL) and 1,3-propanedithiol (0.80 mL) were added to a solution of compound **10** (0.40 g, 0.44 mol) in 5:1 pyridine/water (24 mL) at RT. The reaction was stirred at 50 °C for 5 h, after which it was concentrated to give the crude disaccharide, which was used in the next step without purification. To the crude disaccharide in pyridine (8.0 mL) was added TFAA (1.6 mL) dropwise at 0 °C. After stirring for 2 h at RT, the mixture concentrated under reduced pressure and then dissolved in DCM (80 mL). The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. Purification by silica gel column chromatography (elution with 4:1 → 3:1 hexanes/EtOAc) gave compound **14** (0.35 g, 81%) as a colorless foam. R_f 0.63 (2:1 hexanes/EtOAc); ^{1}H NMR (400 MHz, CD_3COCD_3): δ 8.13–8.10 (m, 3H, Ar), 8.00–7.95 (m, 3H, Ar), 7.73–7.49 (m, 7H, Ar), 7.41–7.13 (m, 14H, Ar), 5.96 (s, 1H, $CH(O)_2$), 5.93 (s, 1H, H-1), 5.54–5.53 (m, 1H, H-2), 5.41 (d, J = 1.7 Hz, 1H, H-5), 5.25 (d, J = 3.5 Hz, 1H, H-1′), 4.97 (d, J = 12.0 Hz, 1H, Bn), 4.89 (d, J = 12.0 Hz, 1H, Bn), 4.67 (d, J = 11.7 Hz, 1H, Bn), 4.58 (t, J = 2.2 Hz, 1H, H-4), 4.52–4.45 (m, 2H, H-5′, H-6′), 4.38 (td, J = 3.2, 1.0 Hz, 1H, H-3), 4.28–4.22 (m, 1H, H-2′), 4.15 (d, J = 11.7 Hz, 1H, Bn), 4.02 (t, J = 9.5 Hz, 1H, H-3′), 3.99–3.87 (m, 2H, H-4′, H-6′), 3.82 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 168.7 (C=$OOCH_3$), 165.0 (C=OPh), 157.0 (q, $^2J_{C,F}$ = 37.1 Hz, CF_3C=O), 139.0 (Ar), 137.7 (Ar), 135.6 (Ar), 135.5 (Ar), 133.7 (Ar), 133.1 (Ar), 133.0 (Ar), 131.5 (Ar), 129.8 (Ar), 129.0 (Ar), 128.9 (Ar), 128.4 (Ar), 128.35 (Ar), 128.31 (Ar), 127.9 (Ar), 127.8 (Ar), 127.7 (Ar), 127.5 (Ar), 127.4 (Ar), 126.7 (Ar), 126.5 (Ar), 126.3 (Ar), 125.5 (Ar), 124.2 (Ar), 115.9 (q, $^1J_{C,F}$ = 286.5 Hz, CF_3), 101.4 ($CH(O)_2$), 99.3 (C-1′), 87.2 (C-1), 82.9 (C-4′), 75.8 (C-3′), 75.5 (C-4), 74.6 (C-3), 74.0 (CH_2Ph), 72.4 (CH_2Ph), 69.4 (C-2), 68.3 (C-6′), 68.0 (C-5), 63.8 (C-5′), 54.0 (C-2′), 51.5 (OCH_3); HRMS (FAB) calcd for $C_{53}H_{49}O_{12}SNF_3$ $[M+H]^+$: 980.2928; found: 980.3380.

Methyl (3-*O*-benzyl-2-deoxy-4,6-*O*-2-naphthylidene-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(2-*O*-benzoyl-3-*O*-benzyl-1-*O*-2-((*tert*-butoxy)-2-oxoacetyl)-α-L-idopyranosid)uronate (15). A mixture of donor **14** (0.20 g, 0.20 mmol), *t*-butyl 2-hydroxyacetate (0.11 g, 0.80 mmol), and powdered 4 Å molecular sieves was suspended in anhydrous DCM (12 mL) and stirred at RT. After 10 min, NIS (0.11 g, 0.50 mmol) and AgOTf (26 mg, 0.10 mmol) were added. The solution was stirred for 8 h before Et_3N (50 μL) was added and the mixture was filtered. The filtrate was concentrated, and the resulting residue was purified by silica gel column chromatography (elution with 5:1 → 4:1 hexanes/EtOAc) to afford compound **15** (0.16 g, 82%) as a colorless foam. R_f 0.49 (2:1 hexanes/EtOAc); ^{1}H NMR (400 MHz, CD_3COCD_3): δ 8.43 (d, J = 8.8 Hz, 1H, NH), 8.14–8.12 (m, 3H, Ar), 8.01–7.96 (m, 3H, Ar), 7.76–7.74 (m, 1H, Ar), 7.60–7.55 (m, 2H, Ar), 7.46–7.27 (m, 8H, Ar), 7.26–7.20 (m, 3H, Ar), 7.15–7.13 (m, 2H, Ar), 5.98 (s, 1H, NapCH), 5.38–5.37 (m, 1H, H-2), 5.30 (s, 1H, H-1), 5.21–5.20 (m, 2H, H-1′, H-5), 4.93 (d, J = 12.0 Hz, 1H, Bn), 4.81 (d, J = 12.0 Hz, 1H, Bn), 4.70 (d, J = 11.7 Hz, 1H, Bn), 4.53–4.45 (m, 3H, H-4, H-6′, H-5′), 4.33 (d, J = 16.5 Hz, 1H, CH_2CO$_2$*t*-Bu), 4.29–4.28 (m, 1H, H-3), 4.26–4.17 (m, 3H, Bn, H-2′, CH_2CO$_2$*t*-Bu), 4.04 (t, J = 9.2 Hz, 1H, H-3′), 3.99–3.89 (m, 2H, H-4′, H-6′), 3.79 (s, 3H, OCH_3), 1.46 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 169.1 (*C*=$OOCH_3$), 168.7 (*C*O$_2$*t*-Bu), 164.8 (*C*=OPh), 157.0 (q, $^2J_{C,F}$ = 37.0 Hz, CF_3*C*=O), 139.0 (Ar), 138.1 (Ar), 135.6 (Ar), 133.7 (Ar), 133.2 (Ar), 133.0 (Ar), 129.8 (Ar), 129.7 (Ar), 128.9 (Ar), 128.31 (Ar), 128.27 (Ar), 127.94 (Ar), 127.88 (Ar), 127.7 (Ar), 127.6 (Ar), 127.4 (Ar), 127.1 (Ar), 126.7 (Ar), 126.5 (Ar), 126.3 (Ar), 125.6 (Ar), 124.2 (Ar), 116.1 (q, $^1J_{C,F}$ = 286.0 Hz, CF_3), 101.5 (Nap*C*H), 100.0

(C-1), 98.7 (C-1′), 83.0 (C-4′), 80.9 (O*C*(CH_3)$_3$), 75.8 (C-3′), 75.2 (C-3), 75.0 (C-4), 74.0 (*C*H_2Ph), 71.8 (*C*H_2Ph), 68.3 (C-6′), 67.8 (C-2), 67.3 (C-5), 65.5 (O*C*H_2CO_2*t*-Bu), 63.8 (C-5′), 54.1 (C-2′), 51.3 (OCH_3), 27.3 (OC(*C*H_3)$_3$); HRMS (ESI) calcd for $C_{53}H_{54}F_3NO_{15}Na$ $[M+Na]^+$: 1024.3343; found: 1024.3318.

Methyl (3-*O*-benzyl-2-deoxy-4,6-*O*-2-naphthylidene-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(3-*O*-benzyl-1-*O*-2-((*tert*-butoxy)-2-oxoacetyl)-α-L-idopyranosid)uronate (16). To a solution of disaccharide **15** (0.15 g, 0.15 mmol) in anhydrous DCM (42 mL) was added the solution of NaOMe in MeOH (0.05M, 0.70 mL) at RT. After stirring for 6 h, additional NaOMe (0.05M in MeOH, 0.30 mL) was added at RT. The reaction was stirred for another 2 h and then quenched with saturated aq. NH_4Cl. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. Purification by silica gel column chromatography (elution with 4:1 → 2:1 hexanes/EtOAc) afforded compound **16** (0.12 g, 89%) as a colorless foam. R_f 0.31 (2:1 hexanes/EtOAc); ^{1}H NMR (400 MHz, CD_3COCD_3): δ 8.55 (d, *J* = 8.9 Hz, 1H, NH), 8.06–7.93 (m, 4H, Ar), 7.67–7.65 (m, 1H, Ar), 7.56–7.54 (m, 2H, Ar), 7.46–7.22 (m, 10H, Ar), 5.91 (s, 1H, NapCH), 5.26 (d, *J* = 3.6 Hz, 1H, H-1′), 5.09 (d, *J* = 2.0 Hz, 1H, H-5), 5.03 (s, 1H, H-1), 5.00–4.98 (m, 1H, OH), 4.91 (d, *J* = 11.6 Hz, 1H, Bn), 4.83 (d, *J* = 11.6 Hz, 1H, Bn), 4.68 (d, *J* = 11.6 Hz, 1H, Bn), 4.67 (d, *J* = 11.6 Hz, 1H, Bn), 4.34–4.29 (m, 2H, H-2′, H-6′), 4.27–4.25 (m, 1H, H-4), 4.24 (d, *J* = 16.5 Hz, 1H, C*H*$_2CO_2$*t*-Bu), 4.09 (d, *J* = 16.5 Hz, 1H, C*H*$_2CO_2$*t*-Bu), 4.04–3.99 (m, 2H, H-2, H-3), 3.95–3.89 (m, 3H, H-3′, H-4′, H-6′), 3.85 (s, 3H, OCH_3), 3.83–3.78 (m, 1H, H-5′), 1.47 (s, 9H, C(CH_3)$_3$); ^{13}C NMR (100 MHz, CD_3COCD_3): δ

169.7 (*C*=OOCH$_3$), 169.0 (*C*O$_2$*t*-Bu), 157.1 (q, $^2J_{C,F}$ = 38.0 Hz, CF$_3$*C*=O), 138.9 (Ar), 138.4 (Ar), 135.5 (Ar), 133.7 (Ar), 133.0 (Ar), 128.3 (Ar), 128.2 (Ar), 128.0 (Ar), 127.9 (Ar), 127.7 (Ar), 127.5 (Ar), 127.4 (Ar), 127.2 (Ar), 127.1 (Ar), 126.4 (Ar), 126.2 (Ar), 125.5 (Ar), 124.0 (Ar), 116.1 (q, $^1J_{C,F}$ = 286.0 Hz, CF$_3$), 101.8 (C-1), 101.3 (NapCH), 96.3 (C-1′), 82.2 (C-4′), 80.9 (O*C*(CH$_3$)$_3$), 76.9 (C-3′), 74.1 (*C*H$_2$Ph), 73.5 (C-3), 72.6 (C-4), 71.5 (*C*H$_2$Ph), 68.3 (C-6′), 67.4 (C-5), 66.1 (C-2), 65.5 (O*C*H$_2$CO$_2$*t*-Bu), 63.5 (C-5′), 53.3 (C-2′), 51.6 (OCH$_3$), 27.3 (OC(*C*H$_3$)$_3$); HRMS (ESI-TOF) calcd for $C_{46}H_{50}F_3NO_{14}Na$ $[M+Na]^+$: 920.3081; found: 920.3084.

Methyl (3-*O*-benzyl-2-deoxy-4,6-*O*-2-naphthylidene-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(3-*O*-benzyl-1-*O*-2-((*tert*-butoxy)-2-oxoacetyl)-2-*O*-((9*H*-fluoren-9-yl)methoxycarbonyl)-α-L-idopyranosid)uronate (17). To a mixture of disaccharide **16** (0.12 g, 0.13 mmol) in pyridine (4.0 mL) at RT was added FmocCl (0.66 g, 2.6 mmol) portion-wise (0.22 g X 3). The reaction was stirred for 2 h, concentrated under reduced pressure, and the resulting residue was dissolved in DCM. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. Purification by silica gel column chromatography (elution with 6:1 → 4:1 hexanes/EtOAc) afforded compound **17** (0.13 g, 90%) as a colorless foam. R_f 0.47 (2:1 hexanes/EtOAc); ^{1}H NMR (400 MHz, CD$_3$COCD$_3$): δ 8.26 (d, *J* = 9.3 Hz, 1H, NH), 8.05–7.91 (m, 4H, Ar), 7.85–7.83 (m, 2H, Ar), 7.67–7.62 (m, 3H, Ar), 7.55–7.53 (m, 2H, Ar), 7.42–7.25 (m, 9H, Ar), 7.21–7.16 (m, 5H, Ar), 5.93 (s, 1H, NapCH), 5.30 (d, *J* = 3.7 Hz, 1H, H-1′), 5.22 (d, *J* = 2.8 Hz, 1H, H-1), 5.14 (d, *J* = 2.8 Hz, 1H, H-5), 4.99 (dd, *J* = 4.4, 2.8 Hz, 1H, H-2), 4.90 (d, *J* = 11.6 Hz, 1H, Bn), 4.82 (d, *J* = 11.6 Hz, 1H, Bn), 4.71 (d, *J* = 11.6 Hz, 1H, Bn), 4.68 (d, *J* = 11.6

Hz, 1H, Bn), 4.59–4.53 (m, 1H, OCO_2CH_2-Fluoren), 4.44–4.41 (m, 2H, H-4, H-6′), 4.38–4.33 (m, 1H, H-2′), 4.30–4.24 (m, 3H, OCO_2CH_2-Fluoren, OCO_2CH_2CH, CH_2CO_2t-Bu), 4.15 (t, J = 4.4 Hz, 1H, H-3), 4.14 (d, J = 16.4 Hz, 1H, CH_2CO_2t-Bu), 4.11–4.03 (m, 2H, H-3′, H-5′), 4.00–3.90 (m, 2H, H-4′, H-6′), 3.84 (s, 3H, OCH_3), 1.46 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 168.8 (C=$OOCH_3$), 168.5 (CO_2t-Bu), 157.0 (q, $^2J_{C,F}$ = 37.0 Hz, CF_3C=O), 154.0 (Fluoren-CH_2OC=O), 143.4 (Ar), 143.3 (Ar), 141.1 (Ar), 138.9 (Ar), 138.8 (Ar), 135.5 (Ar), 133.0 (Ar), 128.31 (Ar), 128.29 (Ar), 127.95 (Ar), 127.85 (Ar), 127.82 (Ar), 127.7 (Ar), 127.6 (Ar), 127.3 (Ar), 127.2 (Ar), 127.0 (Ar), 126.4 (Ar), 126.2 (Ar), 125.4 (Ar), 125.3 (Ar), 125.1 (Ar), 124.0 (Ar), 120.0 (Ar), 118.7 (q, $^1J_{C,F}$ = 286.0 Hz, CF_3), 101.3 (NapCH), 98.9 (C-1), 97.4 (C-1′), 82.4 (C-4′), 81.0 ($OC(CH_3)_3$), 76.4 (C-3′), 74.7 (C-3), 74.2 (CH_2Ph), 73.5 (C-4), 72.5 (C-2), 72.3 (CH_2Ph), 70.1 (Fluoren-CH_2O), 68.6 (C-5), 68.3 (C-6′), 65.7 (OCH_2CO_2t-Bu), 63.7 (C-5′), 53.5 (C-2′), 51.6 (OCH_3), 46.5 ($CHCH_2$), 27.3 ($OC(CH_3)_3$); HRMS (ESI-TOF) calcd for $C_{61}H_{60}F_3NO_{16}Na$ $[M+Na]^+$: 1142.3762; found: 1142.3735.

Methyl (3-*O*-benzyl-2-deoxy-6-*O*-2-naphthylmethyl-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(3-*O*-benzyl-1-*O*-2-((*tert*-butoxy)-2-oxoacetyl)-2-*O*-((9*H*-fluoren-9-yl)methoxycarbonyl)-α-L-idopyranosid)uronate (18). To a suspension of compound **17** (0.12 g, 0.11 mmol) and 4 Å activated molecular sieves in DCM (20 mL) were added triethylsilane (2.6 mL, 16 mmol) and TFA (0.82 mL, 10 mmol) at 0 °C. The reaction was stirred at RT for 1 h and then quenched with saturated aq. $NaHCO_3$. The resulting mixture was filtered, diluted with DCM (20 mL), and the organic layer was washed with brine, dried over Na_2SO_4, and concentrated.

Purification by silica gel column chromatography (elution with 3:1 → 2:1 hexanes/EtOAc) afforded compound **18** (86 mg, 72%) as a colorless foam. R_f 0.21 (2:1 hexanes/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86–7.75 (m, 6H, Ar), 7.54–7.47 (m, 5H, Ar), 7.42–7.39 (m, 2H, Ar), 7.34–7.29 (m, 7H, Ar), 7.25–7.17 (m, 3H, Ar), 7.14–7.12 (m, 2H, Ar), 6.86 (d, *J* = 9.4 Hz, 1H, NH), 5.21 (s, 1H, H-1), 5.12 (d, *J* = 1.8 Hz, 1H, H-5), 4.97–4.96 (m, 1H, H-2), 4.83 (d, *J* = 3.4 Hz, 1H, H-1′), 4.81 (d, *J* = 12.1 Hz, 1H, NapC*H*$_2$), 4.80 (d, *J* = 11.9 Hz, 1H, 3-OC*H*$_2$Ph), 4.75 (d, *J* = 12.1 Hz, 1H, NapC*H*$_2$), 4.62 (s, 2H, 3′-OC*H*$_2$Ph), 4.58 (d, *J* = 11.9 Hz, 1H, 3-OC*H*$_2$Ph), 4.51 (dd, *J* = 9.9, 6.8 Hz, 1H, OCO$_2$C*H*$_2$-Fluoren), 4.28 (d, *J* = 16.4 Hz, 1H, C*H*$_2$CO$_2$*t*-Bu), 4.30–4.14 (m, 4H, OCO$_2$C*H*$_2$-Fluoren, H-2′, H-4, OCO$_2$CH$_2$C*H*), 4.11 (d, *J* = 16.4 Hz, 1H, C*H*$_2$CO$_2$*t*-Bu), 3.85–3.79 (m, 3H, H-3, H-4′, H-6′), 3.76–3.69 (m, 2H, H-5′, H-6′), 3.72 (s, 3H, OCH$_3$), 3.61 (dd, *J* = 10.5, 8.7 Hz, 1H, H-3′), 1.47 (s, 9H, C(CH$_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.3 (*C*=OOCH$_3$), 168.5 (*C*O$_2$*t*-Bu), 157.1 (q, $^2J_{C,F}$ = 37.0 Hz, CF$_3$*C*=O), 153.9 (Fluoren-CH$_2$O*C*=O), 143.0 (Ar), 142.9 (Ar), 141.23 (Ar), 141.21 (Ar), 137.8 (Ar), 136.6 (Ar), 135.1 (Ar), 133.2 (Ar), 133.1 (Ar), 128.6 (Ar), 128.5 (Ar), 128.4 (Ar), 128.3 (Ar), 128.0 (Ar), 127.9 (Ar), 127.8 (Ar), 127.7 (Ar), 127.5 (Ar), 127.32 (Ar), 127.30 (Ar), 126.7 (Ar), 126.3 (Ar), 126.1 (Ar), 125.6 (Ar), 125.1 (Ar), 125.0 (Ar), 120.1 (Ar), 115.8 (q, $^1J_{C,F}$ = 286.0 Hz, CF$_3$), 98.7 (C-1), 96.2 (C-1′), 82.1 (O*C*(CH$_3$)$_3$), 79.3 (C-3′), 74.7 (3′-O*C*H$_2$Ph), 73.8 (Nap*C*H$_2$), 72.3 (3-O*C*H$_2$Ph), 71.7 (C-4), 81.6 (C-4′), 71.1 (C-5′), 70.9 (Fluoren-*C*H$_2$O), 70.7 (C-3), 70.6 (C-2), 69.5 (C-6′), 67.5 (C-5), 65.9 (O*C*H$_2$CO$_2$*t*-Bu), 52.7 (C-2′), 52.3 (OCH$_3$), 46.5 (*C*HCH$_2$), 28.0 (OC(*C*H$_3$)$_3$); HRMS (ESI-TOF) calcd for $C_{61}H_{62}F_3NO_{16}Na$ $[M+Na]^+$: 1144.3918; found: 1144.3893.

Methyl (2-azido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-levulinoyl-α-L-idopyranoosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-2-naphthylmethyl-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(3-*O*-benzyl-1-*O*-3-((*tert*-butoxy)-2-oxoacetyl)-2-*O*-((9*H*-fluoren-9-yl)methoxycarbonyl)-α-L-idopyranosid)uronate (21). A mixture of donor **13** (0.11 g, 0.10 mmol), acceptor **18** (46 mg, 0.041 mmol) and powdered 4 Å molecular sieves was suspended in anhydrous DCM (4.0 mL) and stirred at RT. After 10 min, NIS (46 mg, 0.20 mmol) and AgOTf (catalytic amount) were added. The solution was stirred for another 12 h before Et_3N (0.10 mL) was added. The mixture was filtered, and the residue was purified by silica gel column chromatography, eluting first with 4:1 → 2:1 hexanes/EtOAc to afford compound **21** (52 mg, 60%) as a colorless foam. R_f 0.21 (2:1 hexanes/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95–7.81 (m, 6H, Ar), 7.75–7.73 (m, 2H, Ar), 7.64–7.57 (m, 4H, Ar), 7.53–7.42 (m, 9H, Ar), 7.40–7.27 (m, 17H, Ar), 7.18–7.11 (m, 8H, Ar), 6.99–6.91 (m, 4H, Ar), 6.86 (d, *J* = 9.6 Hz, 1H, NH), 5.58 (t, *J* = 9.6 Hz, 1H, H-4‴), 5.38 (d, *J* = 3.5 Hz, 1H, H-1″), 5.20 (s, 1H, H-1), 5.08–5.07 (m, 2H, H-5, H-1‴), 4.96–4.94 (m, 2H, H-2, H-2″), 4.83 (d, *J* = 3.8 Hz, 1H, H-1′), 4.81–4.62 (m, 8H, OCH_2Ph, OCH_2Nap, H-5″), 4.55 (d, *J* = 11.0 Hz, 1H, Bn), 4.55 (d, *J* = 11.5 Hz, 1H, Bn), 4.46–4.41 (m, 2H, OCH_2Ph, OCH_2-Fluoren), 4.35 (apptd, *J* = 10.5, 3.5 Hz, 1H, H-2′), 4.26 (d, *J* = 16.3 Hz, 1H, CH_2CO_2t-Bu), 4.19–4.07 (m, 5H), 4.01–3.94 (m, 3H), 3.86–3.70 (m, 5H), 3.68–3.61 (m, 3H), 3.58 (s, 3H, OCH_3), 3.45 (dd, *J* = 10.3, 3.5 Hz, 1H, H-2‴), 3.26 (s, 3H, OCH_3), 2.61–2.58 (m, 2H, CH_2), 2.44–2.40 (m, 2H, CH_2), 2.11 (s, 3H, $C{=}OCH_3$), 1.46 (s, 9H, $OC(CH_3)_3$), 0.97 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.9 ($CH_3C{=}OCH_2$), 172.0 ($CH_2C{=}O$), 169.3 ($C{=}OOCH_3$), 169.0 ($C{=}OOCH_3$), 168.5 (CO_2t-Bu), 164.8 ($C{=}OPh$), 157.0 (q, $^2J_{C,F}$ = 37.0 Hz, $CF_3C{=}O$), 153.9 (Fluoren-$CH_2OC{=}O$), 143.1 (Ar), 142.9 (Ar), 141.20 (Ar), 141.16 (Ar), 137.6 (Ar), 137.4 (Ar), 137.1 (Ar), 136.6 (Ar), 135.7 (Ar), 135.5 (Ar), 135.4 (Ar), 133.32 (Ar), 133.28 (Ar), 133.0 (Ar),

132.9 (Ar), 129.7 (Ar), 129.6 (Ar), 129.5 (Ar), 128.6 (Ar), 128.5 (Ar), 128.31 (Ar), 128.26 (Ar), 128.20 (Ar), 128.05 (Ar), 128.00 (Ar), 127.95 (Ar), 127.91 (Ar), 127.8 (Ar), 127.7 (Ar), 127.6 (Ar), 127.5 (Ar), 127.3 (Ar), 126.9 (Ar), 126.8 (Ar), 126.6 (Ar), 126.2 (Ar), 126.1 (Ar), 125.9 (Ar), 125.1 (Ar), 125.0 (Ar), 120.0 (Ar), 115.7 (q, $^{1}J_{C,F}$ = 286 Hz, CF_3), 98.7 (C-1), 97.9 (C-1″), 97.2 (C-1‴), 96.0 (C-1′), 82.0 (O*C*(CH_3)$_3$), 78.1, 77.2, 75.1, 74.5, 74.1, 73.6, 73.5, 73.3, 72.4, 72.0, 71.9, 71.6, 71.2, 70.9, 70.8, 70.1 (C-4‴), 69.5, 69.2, 67.7 (C-5), 67.5, 65.8 (O*C*H_2CO_2*t*-Bu), 62.9, 61.9, 52.8 (C-2′), 52.2 (OCH_3), 51.6 (OCH_3), 46.4 (*C*HCH_2), 37.7 (CH_2C=O), 29.7 (CH_3C=O), 28.0 (CO_2C(*C*H_3)$_3$), 27.6 (CH_2C=O), 26.6 (SiC(*C*H_3)$_3$), 19.1 (Si*C*(CH_3)$_3$); HRMS (ESI-TOF) calcd for $C_{116}H_{121}F_3N_4O_{29}SiNa$ $[M+Na]^+$: 2141.7736; found: 2141.7729; gHSQC 2-D NMR (without ^{1}H decoupling): $^{1}J_{C1,H1}$ = 174.5 Hz, $^{1}J_{C1',H1'}$ = 173.1 Hz, $^{1}J_{C1'',H1''}$ = 174.3 Hz, $^{1}J_{C1''',H1'''}$ = 175.1 Hz. As the H-2 and H-2" peaks overlap, we cannot identify the exact coupling constants between H-2" and H-3". However, the peaks of H-2 and H-2" showed that the coupling constants of $^{3}J_{H2''-H3''}$ and $^{3}J_{H2-H3}$ are both less than 3.5 Hz, which indicates that both IdoA residues adopt primarily the $^{1}C_4$ conformation.[6] The coupling constants of $^{1}J_{C1,H1}$ (174.5 Hz) and $^{1}J_{C1'',H1''}$ (174.3) Hz are above 170 Hz, which confirms the α configuration of the two IdoA-GlcN linkages.[7] In addition, the coupling constants of $^{1}J_{C1',H1'}$ (173.1 Hz) and $^{1}J_{C1''',H1'''}$ (175.1) Hz are greater than 170 Hz, which is indicative of the α configuration for the two GlcN-IdoA linkages. Further elution with 2:1 → 1:1 hexanes/EtOAc afforded unreacted acceptor **18** (8.3 mg, 18%) and hydrolyzed donor (35 mg,), which could be potentially recycled.

Methyl (2-azido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-levulinoyl-α-L-idopyranoosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-2-naphthylmethyl-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(3-*O*-benzyl-1-*O*-3-((*tert*-butoxy)-2-oxoacetyl)-2-*O*-((9*H*-fluoren-9-yl)methoxycarbonyl)-α-L-idopyranosid)urinate (22). To a solution of tetrasaccharide **21** (20 mg, 9.4 μmol) in pyridine (3.0 mL) was added hydrogen fluoride pyridine (0.80 ml) at 0 °C. After stirring at RT for 2 h, the reaction was quenched with saturated aq. $NaHCO_3$. The mixture was then extracted with DCM, and the organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated. The resulting residue was purified by silica gel column chromatography (elution with 2:1 → 1:1 hexanes/EtOAc) to afford compound **22** (16 mg, 91%) as a white foam. R_f 0.20 (3:2 hexanes/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95–7.72 (m, 8H, Ar), 7.62–7.29 (m, 21H, Ar), 7.14–7.05 (m, 9H, Ar), 6.92–6.89 (m, 2H, Ar), 6.81 (d, *J* = 9.6 Hz, 1H, NH), 5.32 (d, *J* = 2.2 Hz, 1H, H-1″), 5.18 (s, 1H, H-1), 5.17 (dd, *J* = 10.1, 9.2 Hz, 1H, H-4‴), 5.07 (d, *J* = 1.8 Hz, 1H, H-5), 4.96 (d, *J* = 3.5 Hz, 1H, H-1‴), 4.93 (s, 1H, H-2), 4.92 (s, 1H, H-2″), 4.82 (d, *J* = 12.4 Hz, 1H, Bn), 4.78 (d, *J* = 3.6 Hz, 1H, H-1′), 4.77–4.61 (m, 8H, OCH_2Ph, OCH_2Nap, H-5″), 4.53 (d, *J* = 11.9 Hz, 1H, Bn), 4.45–4.39 (m, 2H, OCH_2Ph, OCH_2-Fluoren), 4.35 (apptd, *J* = 10.0, 3.4 Hz, 1H, H-2′), 4.24 (d, *J* = 16.4 Hz, 1H, CH_2CO_2t-Bu), 4.18–4.05 (m, 5H), 4.02 (t, *J* = 9.9 Hz, 1H, H-3‴), 3.93 (s, 1H, H-3″), 3.93 (s, 1H, H-4″), 3.84 (dd, *J* = 10.8, 2.8 Hz, 1H), 3.78–3.58 (m, 6H), 3.55 (s, 3H, OCH_3), 3.49–3.46 (m, 1H), 3.39 (dd, *J* = 10.2, 3.5 Hz, 1H, H-2‴), 3.32 (s, 3H, OCH_3), 2.65 (br, 1H), 2.63–2.57 (m, 2H, CH_2), 2.49–2.41 (m, 2H, CH_2), 2.09 (s, 3H, $C{=}OCH_3$), 1.44 (s, 9H, $OC(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.8 ($CH_3C{=}OCH_2$), 172.0 ($CH_2C{=}O$), 169.3 ($C{=}OOCH_3$), 169.1 ($C{=}OOCH_3$), 168.5 (CO_2t-Bu), 166.4 ($C{=}OPh$), 153.9 (Fluoren-$CH_2OC{=}O$), 143.1 (Ar), 142.8 (Ar), 141.2 (Ar), 137.5 (Ar), 137.20 (Ar), 137.16 (Ar), 136.5 (Ar), 135.4 (Ar), 133.9 (Ar), 133.1 (Ar), 133.0 (Ar), 129.9 (Ar), 128.74 (Ar), 128.69 (Ar), 128.61 (Ar), 128.58 (Ar), 128.3 (Ar), 128.2 (Ar), 128.0 (Ar), 127.96 (Ar), 127.86

(Ar), 127.7 (Ar), 127.3 (Ar), 127.0 (Ar), 126.6 (Ar), 126.1 (Ar), 126.0 (Ar), 125.9 (Ar), 125.1 (Ar), 125.0 (Ar), 120.1 (Ar), 98.7 (C-1), 98.0 (C-1″), 97.6 (C-1‴), 96.5 (C-1′), 82.0 (O*C*$(CH_3)_3$), 78.3, 77.3 (C-3‴), 74.9, 74.5, 74.1, 73.3, 73.2, 73.13, 73.08, 72.3, 72.2, 71.9 (C-4‴), 71.3, 71.0, 70.90, 70.86, 70.7, 68.8, 68.3 (C-5″), 67.5, 65.9 (O*C*H_2CO_2*t*-Bu), 63.1 (C-2‴), 60.7, 52.9 (C-2′), 52.1 (OCH_3), 51.9 (OCH_3), 46.4 (*C*HCH_2), 37.7 (CH_2C=O), 29.7 (CH_3C=O), 28.0 (CO_2C(*C*H_3)$_3$), 27.7 (CH_2C=O); HRMS (ESI-TOF) calcd for $C_{100}H_{102}F_3N_4O_{29}$ $[M-H]^-$: 1879.6582; found: 1879.6582.

Methyl (2-azido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-levulinoyl-α-L-idopyranoosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(3-*O*-benzyl-1-*O*-3-((*tert*-butoxy)-2-oxoacetyl)-2-*O*-((9*H*-fluoren-9-yl)methoxycarbonyl)-α-L-idopyranosid)urinate (23). To a solution of tetrasaccharide **21** (5.0 mg, 2.4 μmol) in 10:1 CH_2Cl_2/H_2O (2.0 mL) was added DDQ (0.044 mmol). The mixture was stirred at RT for 6 h, then diluted with DCM, and the organic layer was washed with saturated aq. $NaHCO_3$, dried over anhydrous Na_2SO_4, filtered, and concentrated. The resulting residue was purified by silica gel column chromatography (elution with 2:1 → 1:1 hexanes/EtOAc) to afford compound **23** (3.3 mg, 71%) as a colorless foam. R_f 0.12 (3:2 hexanes/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95–7.93 (m, 2H, Ar), 7.76–7.73 (m, 2H, Ar), 7.64–7.60 (m, 3H, Ar), 7.53–7.30 (m, 23H, Ar), 7.18–7.12 (m, 8H, Ar), 7.10–6.98 (m, 3H, Ar), 6.92–6.89 (m, 2H, Ar), 6.82 (d, *J* = 9.5 Hz, 1H, NH), 5.55 (t, *J* = 9.7 Hz, 1H, H-4‴), 5.34 (d, *J* = 3.3 Hz, 1H, H-1″), 5.20 (s, 1H, H-1), 5.11 (d, *J* = 2.0 Hz, 1H, H-5), 5.07 (d, *J* = 3.5 Hz, 1H, H-1‴), 4.98 (d, *J* = 3.3 Hz, 1H, H-2″), 4.96 (s, 1H, H-2), 4.82 (d, *J* =

11.0 Hz, 1H, Bn), 4.79 (d, J = 3.6 Hz, 1H, H-1′), 4.79 (d, J = 10.5 Hz, 1H, Bn), 4.72–4.68 (m, 4H, OCH_2Ph, H-5″), 4.58 (d, J = 11.5 Hz, 1H, Bn), 4.56 (d, J = 10.5 Hz, 1H, Bn), 4.49–4.41 (m, 2H, OCH_2Ph, OCH_2-Fluoren), 4.29 (apptd, J = 10.5, 3.5 Hz, 1H, H-2′), 4.28 (d, J = 16.3 Hz, 1H, CH_2CO_2t-Bu), 4.17–4.04 (m, 6H), 4.02–3.92 (m, 2H), 3.88–3.78 (m, 4H), 3.79 (s, 3H, OCH_3), 3.70–3.64 (m, 4H), 3.47 (dd, J = 10.3, 3.5 Hz, 1H, H-2‴), 3.27 (s, 3H, OCH_3), 2.82–2.75 (m, 2H, CH_2), 2.63–2.60 (m, 2H, CH_2), 2.37 (br, 1H), 2.21 (s, 3H, $C{=}OCH_3$), 1.47 (s, 9H, $OC(CH_3)_3$), 0.98 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.9 ($CH_3C{=}OCH_2$), 172.0 ($CH_2C{=}O$), 169.3 ($C{=}OOCH_3$), 169.1 ($C{=}OOCH_3$), 168.5 (CO_2t-Bu), 164.8 ($C{=}OPh$), 153.9 (Fluoren-$CH_2OC{=}O$), 143.1 (Ar), 142.9 (Ar), 141.2 (Ar), 137.6 (Ar), 137.2 (Ar), 137.1 (Ar), 136.5 (Ar), 135.7 (Ar), 135.3 (Ar), 133.3 (Ar), 133.0 (Ar), 129.71 (Ar), 129.68 (Ar), 129.60 (Ar), 128.9.54 (Ar), 128.7 (Ar), 128.5 (Ar), 128.4 (Ar), 128.3 (Ar), 128.1 (Ar), 128.0 (Ar), 127.9 (Ar), 127.8 (Ar), 127.6 (Ar), 127.5 (Ar), 127.3 (Ar), 126.9 (Ar), 126.6 (Ar), 125.1 (Ar), 125.0 (Ar), 120.0 (Ar), 98.8 (C-1), 98.1 (C-1″), 96.6 (C-1‴), 96.4 (C-1′), 82.1 ($OC(CH_3)_3$), 77.9, 74.8, 74.6, 74.2, 72.95, 72.88, 72.4, 72.2, 71.6, 71.3, 71.0, 70.9, 70.8, 70.2 (C-4‴), 69.4 (C-2″), 69.2 (C-5 ″), 67.6 (C-5), 65.9 (OCH_2CO_2t-Bu), 63.1 (C-2‴), 62.0, 60.8, 53.0 (C-2′), 52.5 (OCH_3), 51.7 (OCH_3), 46.4 ($CHCH_2$), 38.0 ($CH_2C{=}O$), 29.7 ($CH_3C{=}O$), 28.0 ($CO_2C(CH_3)_3$), 27.8 ($CH_2C{=}O$), 26.6 ($SiC(CH_3)_3$), 19.1 ($SiC(CH_3)_3$); HRMS (ESI-TOF) calcd for $C_{105}H_{112}F_3N_4O_{29}Si$ $[M-H]^-$: 1977.7134; found: 1977.7155.

Methyl (2-azido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-α-L-idopyranoosyluronate)-(1→4)-(3-*O*-benzyl-

2-deoxy-6-*O*-2-naphthylmethyl-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(3-*O*-benzyl-1-*O*-3-((*tert*-butoxy)-2-oxoacetyl)-2-*O*-((9*H*-fluoren-9-yl)methoxycarbonyl)-α-L-idopyranosid)urinate (24). A solution of tetrasaccharide **21** (5.0 mg, 2.4 μmol) and hydrazine acetate (20 mg, 0.22 mmol) in 9:1 CH_2Cl_2/CH_3OH (3.0 mL) was stirred at RT for 3 h. The solution was then concentrated, and the resulting residue was purified by silica gel column chromatography (elution with 4:1 → 2:1 hexanes/EtOAc) to afford compound **24** (4.3 mg, 90%) as a colorless foam. R_f 0.62 (3:2 hexanes/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96–7.83 (m, 6H, Ar), 7.75–7.73 (m, 2H, Ar), 7.66–7.56 (m, 4H, Ar), 7.53–7.43 (m, 8H, Ar), 7.40–7.27 (m, 18H, Ar), 7.16–7.12 (m, 8H, Ar), 7.01–6.96 (m, 2H, Ar), 6.86–6.84 (m, 2H, Ar), 6.78 (d, *J* = 9.6 Hz, 1H, NH), 5.55 (t, *J* = 9.7 Hz, 1H, H-4‴), 5.37 (s, 1H, H-1″), 5.19 (s, 1H, H-1), 5.08 (d, *J* = 1.5 Hz, 1H, H-5), 5.01 (d, *J* = 3.7 Hz, 1H, H-1‴), 4.96 (s, 1H, H-2), 4.91 (d, *J* = 11.5 Hz, 1H, Bn), 4.84 (d, *J* = 1.2 Hz, 1H, H-5″), 4.79 (d, *J* = 3.3 Hz, 1H, H-1′), 4.79–4.63 (m, 6H, OCH_2Ph, OCH_2Nap,), 4.54 (d, *J* = 11.0 Hz, 1H, Bn), 4.51 (d, *J* = 10.2 Hz, 1H, Bn), 4.46 (d, *J* = 11.8 Hz, 1H, Bn), 4.43–4.36 (m, 2H, OCH_2-Fluoren, H-2′), 4.26 (d, *J* = 16.3 Hz, 1H, CH_2CO_2t-Bu), 4.19–4.02 (m, 6H), 3.94 (t, *J* = 9.5 Hz, 1H), 3.90 (t, *J* = 3.5 Hz, 1H), 3.82–3.60 (m, 10H), 3.51 (s, 3H, OCH_3), 3.05 (s, 3H, OCH_3), 2.35 (br, 1H), 1.45 (s, 9H, $OC(CH_3)_3$), 0.99 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.25 (*C*=$OOCH_3$), 169.19 (*C*=$OOCH_3$), 168.5 (CO_2t-Bu), 164.7 (*C*=OPh), 153.9 (Fluoren-CH_2OC=O), 143.2 (Ar), 142.8 (Ar), 141.2 (Ar), 137.5 (Ar), 137.3 (Ar), 136.9 (Ar), 136.5 (Ar), 135.7 (Ar), 135.5 (Ar), 133.3 (Ar), 133.1 (Ar), 132.9 (Ar), 129.7 (Ar), 129.6 (Ar), 129.5 (Ar), 128.6 (Ar), 128.55 (Ar), 128.47 (Ar), 128.4 (Ar), 128.3 (Ar), 128.0 (Ar), 127.96 (Ar), 127.89 (Ar), 127.7 (Ar), 127.57 (Ar), 127.53 (Ar), 127.30 (Ar), 127.27 (Ar), 127.0 (Ar), 126.8 (Ar), 126.15 (Ar), 126.1 (Ar), 125.9 (Ar), 125.0 (Ar), 120.0 (Ar), 101.3 (C-1″), 98.8 (C-1), 96.9 (C-1′), 95.4 (C-1‴), 82.0 ($OC(CH_3)_3$), 78.7, 78.3, 75.5, 74.8, 73.7, 73.5, 72.7, 72.5, 72.3, 71.2 ($CHCH_2$), 70.9 (C-2), 70.0 (C-4‴), 67.9, 67.6 (C-5″), 67.4 (C-5), 65.9 (OCH_2CO_2t-Bu), 63.4, 61.7, 52.8 (C-2′), 52.0 (OCH_3),

51.6 (OCH_3), 46.1 ($CHCH_2$), 28.0 ($CO_2C(CH_3)_3$), 26.6 ($SiC(CH_3)_3$), 19.1 ($SiC(CH_3)_3$); HRMS (ESI-TOF) calcd for $C_{111}H_{114}F_3N_4O_{27}Si$ $[M-H]^-$: 2019.7391; found: 2019.7411.

Methyl (2-azido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-levulinoyl-α-L-idopyranoosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-2-naphthylmethyl-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(3-*O*-benzyl-1-*O*-3-((*tert*-butoxy)-2-oxoacetyl))-α-L-idopyranosid)urinate (25). Piperidine (100 mg, 1.2 mmol) was added to a solution of tetrasaccharide **21** (25 mg, 0.012 mmol) in DCM (10 mL) at RT. After stirring for 3 h, the mixture was concentrated and the resulting residue purified by silica gel column chromatography (elution with 3:1 → 2:1 hexanes/EtOAc) to afford compound **25** (22 mg, 88%) as a white foam. R_f 0.38 (3:2 hexanes/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03–7.71 (m, 8H, Ar), 7.65–7.45 (m, 10H, Ar), 7.39–7.23 (m, 12H, Ar), 7.24 (d, J = 9.1 Hz, 1H, NH), 7.18–7.09 (m, 12H, Ar), 5.58 (t, J = 9.7 Hz, 1H, H-4‴), 5.40 (d, J = 3.6 Hz, 1H, H-1″), 5.13 (d, J = 3.4 Hz, 1H, H-1), 5.07 (s, 1H, H-1‴), 4.97 (d, J = 2.0 Hz, 1H, H-5), 4.93 (t, J = 4.1 Hz, 1H, H-2″), 4.88 (d, J = 3.4 Hz, 1H, H-1′), 4.78–4.68 (m, 7H, OCH_2Ph, OCH_2Nap, H-5″), 4.61 (d, J = 11.5 Hz, 1H, Bn), 4.57 (d, J = 10.6 Hz, 1H, Bn), 4.54 (d, J = 11.6 Hz, 1H, Bn), 4.43 (d, J = 11.6 Hz, 1H, Bn), 4.30-4.24 (m, 1H, H-2′), 4.25 (d, J = 16.6 Hz, 1H, CH_2CO_2t-Bu), 4.13–3.95 (m, 7H), 3.91–3.87 (m, 1H), 3.84–3.81 (m, 1H), 3.71–3.57 (m, 6H), 3.60 (s, 3H, OCH_3), 3.45 (dd, J = 10.3, 3.5 Hz, 1H, H-2‴), 3.28 (s, 3H, OCH_3), 2.75 (br, 1H), 2.61–2.58 (m, 2H, CH_2), 2.44–2.38 (m, 2H, CH_2), 2.09 (s, 3H, $C{=}OCH_3$), 1.48 (s, 9H, $OC(CH_3)_3$), 0.98 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.3 ($CH_3C{=}OCH_2$),

172.2 (CH_2C=O), 170.1 (C=$OOCH_3$), 169.50 (C=$OOCH_3$), 169.48 (CO_2t-Bu), 165.1 (C=OPh), 157.6 (q, $^2J_{C,F}$ = 37.3 Hz, CF_3C=O), 141.3 (Ar), 138.1 (Ar), 137.7 (Ar), 137.4 (Ar), 137.3 (Ar), 136.0 (Ar), 135.8 (Ar), 135.7 (Ar), 133.64 (Ar), 133.32 (Ar), 133.27 (Ar), 130.0 (Ar), 129.93 (Ar), 129.87 (Ar), 128.9 (Ar), 128.8 (Ar), 128.6 (Ar), 128.5 (Ar), 128.4 (Ar), 128.3 (Ar), 128.2 (Ar), 128.0 (Ar), 127.9 (Ar), 127.86 (Ar), 127.80 (Ar), 127.6 (Ar), 127.1 (Ar), 126.5 (Ar), 126.4 (Ar), 126.2 (Ar), 125.8 (Ar), 120.0 (Ar), 116.1 (q, $^1J_{C,F}$ = 288 Hz, CF_3), 101.8 (C-1‴), 98.1 (C-1″), 97.5 (C-1), 96.5 (C-1′), 82.5 (O$C(CH_3)_3$), 77.8, 77.6, 75.6, 74.8, 74.7, 74.1, 73.8, 73.7, 72.7, 72.5, 72.4, 72.1, 71.6, 70.5 (C-4‴), 70.0 (C-2″), 69.7 (C-5″), 68.3 (C-5), 67.9, 67.4, 65.8 (OCH_2CO_2t-Bu), 63.2 (C-2‴), 62.3, 53.2 (C-2′), 52.6 (OCH_3), 52.1 (OCH_3), 38.0 (CH_2C=O), 30.0 (CH_3C=O), 28.4 ($CO_2C(CH_3)_3$), 27.9 (CH_2C=O), 26.9 ($SiC(CH_3)_3$), 19.4 ($SiC(CH_3)_3$); HRMS (ESI-TOF) calcd for $C_{101}H_{110}F_3N_4O_{27}Si$ $[M-H]^-$: 1895.7079; found: 1895.7070.

Methyl (2-azido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-levulinoyl-α-L-idopyranoosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-2-naphthylmethyl-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(3-*O*-benzyl-1-*O*-3-(2-carboxylacetyl)-2-*O*-((9*H*-fluoren-9-yl)methoxycarbonyl)-α-L-idopyranosid)urinate (26). To a solution of tetrasaccharide **21** (5.0 mg, 2.4 μmol) in anhydrous DCM (2.0 mL) was added 60 μL of TFA at 0 °C. The reaction was stirred at RT under argon for 12 h. The mixture was then diluted with DCM, and the organic layer was washed with saturated aq. $NaHCO_3$, dried over anhydrous Na_2SO_4, filtered, and concentrated. The resulting residue was purified by silica gel column chromatography (elution with 40:1 → 20:1

DCM/MeOH) to give compound **26** (4.0 mg, 82%) as a colorless foam. R_f 0.20 (15:1 DCM/MeOH); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96–7.82 (m, 6H, Ar), 7.75–7.73 (m, 2H, Ar), 7.66–7.58 (m, 5H, Ar), 7.53–7.29 (m, 24H, Ar), 7.19–7.12 (m, 9H, Ar), 7.02–6.95 (m, 4H, Ar), 6.67 (d, *J* = 9.5 Hz, 1H, NH), 5.57 (t, *J* = 9.5 Hz, 1H, H-4‴), 5.40 (d, *J* = 3.9 Hz, 1H, H-1″), 5.19 (d, *J* = 2.1 Hz, 1H, H-1), 5.11 (d, *J* = 3.3 Hz, 1H, H-1‴), 4.96–4.93 (m, 2H, H-5, H-2″), 4.91 (d, *J* = 3.6 Hz, 1H, H-1′), 4.87 (t, *J* = 2.6 Hz, 1H, H-2), 4.81–4.65 (m, 7H, OCH_2Ph, OCH_2Nap, H-5″), 4.61 (d, *J* = 11.5 Hz, 1H, Bn), 4.56 (d, *J* = 10.8 Hz, 1H, Bn), 4.55 (d, *J* = 11.7 Hz, 1H, Bn), 4.47–4.41 (m, 2H, OCH_2Ph, OCH_2-Fluoren), 4.36–4.26 (m, 3H, H-2′, C*H*$_2$CO$_2$*t*-Bu), 4.22–4.11 (m, 4H), 4.04–3.94 (m, 3H), 3.89–3.70 (m, 5H), 3.72–3.57 (m, 3H), 3.61 (s, 3H, OCH_3), 3.45 (dd, *J* = 10.3, 3.5 Hz, 1H, H-2‴), 3.32 (s, 3H, OCH_3), 2.63–2.54 (m, 2H, CH_2), 2.41–2.32 (m, 2H, CH_2), 2.11 (s, 3H, C=OCH_3), 0.97 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.1 (CH_3*C*=OCH_2), 171.9 (CH_2*C*=O), 171.3 (*C*=$OOCH_3$), 169.1 (*C*=$OOCH_3$), 169.0 (*C*O_2H), 164.7 (*C*=OPh), 156.9 (q, $^2J_{C,F}$ = 37.0 Hz, CF_3*C*=O), 154.0 (Fluoren-CH_2O*C*=O), 143.0 (Ar), 142.9 (Ar), 141.23 (Ar), 141.19 (Ar), 137.6 (Ar), 137.4 (Ar), 137.1 (Ar), 136.4 (Ar), 135.6 (Ar), 135.3 (Ar), 133.3 (Ar), 133.0 (Ar), 132.9 (Ar), 129.74 (Ar), 129.70 (Ar), 129.6 (Ar), 129.5 (Ar), 128.6 (Ar), 128.52 (Ar), 128.47 (Ar), 128.36 (Ar), 128.31 (Ar), 128.2 (Ar), 128.04 (Ar), 127.99 (Ar), 127.86 (Ar), 127.82 (Ar), 127.72 (Ar), 127.69 (Ar), 127.6 (Ar), 127.5 (Ar), 127.31 (Ar), 127.26 (Ar), 126.92 (Ar), 126.86 (Ar), 126.2 (Ar), 126.1 (Ar), 125.9 (Ar), 125.1 (Ar), 125.0 (Ar), 120.0 (Ar), 115.7 (q, $^1J_{C,F}$ = 286 Hz, CF_3), 98.5 (C-1), 98.0 (C-1″), 97.3 (C-1‴), 95.9 (C-1′), 77.8, 77.4, 75.2, 74.5, 74.2, 74.1, 73.5, 72.8, 72.3, 72.0, 71.7, 71.5, 71.3, 70.9 (Fluoren-*C*H$_2$), 70.1(C-4‴), 70.0 (C-2″), 69.6, 68.5, 67.5, 65.0 (O*C*H$_2$CO$_2$H), 62.9 (C-2‴), 61.9, 52.7 (C-2′), 52.3 (OCH_3), 51.7 (OCH_3), 46.4 (*C*HCH_2), 37.7 (CH_2C=O), 29.7 (CH_3C=O), 27.2 (CH_2C=O), 26.6 (SiC(*C*H$_3$)$_3$), 19.1 (Si*C*$(CH_3)_3$); HRMS (ESI-TOF) calcd for $C_{112}H_{112}F_3N_4O_{29}Si$ $[M-H]^-$: 2061.7134; found: 2061.7124.

Methyl (2-azido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-sulfonato-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-levulinoyl-α-L-idopyranoosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-2-naphthylmethyl-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(3-*O*-benzyl-2-*O*-((9*H*-fluoren-9-yl)methoxycarbonyl)-1-*O*-3-((*tert*-butoxy)-2-oxoacetyl))-α-L-idopyranosid)uronate mono sodium salt (27). A solution of the tetrasaccharide **22** (16 mg, 8.5 μmol) and SO_3Et_3N (15 mg, 85 μmol) in DMF (2.0 mL) was stirred at RT under N_2 atmosphere. After stirring for 12 h, a solution of saturated aq. $NaHCO_3$ was added to the mixture, and the resulting solution was stirred for 1 h. The mixture was extracted with DCM, and the organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated. The resulting residue was purified by silica gel column chromatography (elution with 20:1 → 10:1 DCM/MeOH) and then incubated with Dowex 50WX4Na+ resin to obtain the *O*-sulfated compound **27** (14 mg, 85%). R_f 0.37 (9:1 DCM/MeOH); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94–7.81 (m, 5H, Ar), 7.75–7.73 (m, 2H, Ar), 7.56–7.33 (m, 13H, Ar), 7.30–7.25 (m, 11H, Ar), 7.12–6.95 (m, 10H, Ar, NH), 5.40–5.35 (m, 1H, H-4'''), 5.29 (s, 1H, H-1''), 5.21 (s, 1H, H-1), 5.08 (d, J = 1.5 Hz, 1H), 5.04 (s, 1H, H-1′′′), 4.94 (s, 1H, H-2 or H-2′′), 4.93 (s, 1H, H-2 or H-2′′), 4.87 (d, J = 3.5 Hz, 1H, H-1′), 4.83–4.62 (m, 7H, OCH_2Ph, OCH_2Nap, H-5′′), 4.55–4.37 (m, 5H, OCH_2Ph, H-2′), 4.31–4.06 (m, 8H), 4.01–3.85 (m, 5H), 3.83–3.63 (m, 5H), 3.56 (s, 3H, OCH_3), 3.51–3.48 (m, 1H), 3.35 (s, 3H, OCH_3), 2.60–2.57 (m, 2H, CH_2), 2.48–2.46 (m, 2H, CH_2), 2.07 (s, 3H, C=OCH_3), 1.45 (s, 9H, $OC(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.5 (CH_3*C*=OCH_2), 171.1 (*C*=O), 168.4 (*C*=O), 167.5 (*C*=O), 164.7 (*C*=O), 156.0 (q, $^2J_{C,F}$ = 37.6 Hz, CF_3*C*=O), 152.9 (Fluoren-CH_2O*C*=O), 142.1 (Ar), 141.9 (Ar), 140.2 (Ar), 140.1 (Ar), 136.4 (Ar), 135.6 (Ar), 134.5 (Ar), 132.5 (Ar), 132.3 (Ar), 132.0 (Ar),

128.8 (Ar), 127.5 (Ar), 127.2 (Ar), 127.13 (Ar), 127.10 (Ar), 127.05 (Ar), 127.02 (Ar), 126.98 (Ar), 126.8 (Ar), 126.7 (Ar), 126.6 (Ar), 126.2 (Ar), 125.73 (Ar), 125.68 (Ar), 125.06 (Ar), 125.02 (Ar), 124.8 (Ar), 124.1 (Ar), 124.0 (Ar), 119.0 (Ar), 114.7 (q, $^{1}J_{C,F}$ = 288 Hz, CF_3), 97.7 (C-1), 97.2 (C-1″), 96.5 (C-1‴), 94.8 (C-1′), 81.0 (O*C*$(CH_3)_3$), 76.9, 73.6, 73.4, 72.2, 71.9, 71.3, 70.9, 70.5, 70.3, 69.9, 69.8, 69.4, 68.9, 68.8, 68.4, 68.3, 68.2, 68.1, 66.7, 66.5, 64.9, 61.6, 52.4 (C-2′), 51.2 (OCH_3), 51.1 (OCH_3), 45.4 (*C*HCH_2), 36.7 (CH_2C=O), 28.7 (CH_3C=O), 27.0 (CO_2C(*C*$H_3)_3$), 26.6 (CH_2C=O); HRMS (ESI-TOF) calcd for $C_{100}H_{102}F_3N_4O_{32}S$ $[M-Na]^-$: 1959.6150; found: 1959.6136.

Methyl (2-azido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-levulinoyl-α-L-idopyranoosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-2-naphthylmethyl-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(3-*O*-benzyl-2-*O*-sulfonato-1-*O*-3-((*tert*-butoxy)-2-oxoacetyl))-α-L-idopyranosid)urinate mono sodium salt (28). A solution of the tetrasaccharide **25** (22 mg, 0.011 mmol) and SO_3Et_3N (21 mg, 0.11 mmol) in DMF (3.0 mL) was stirred at 60 °C for 36 h under N_2 atmosphere. After cooling to RT, a solution of saturated aq. $NaHCO_3$ was added to the mixture, and the resulting solution was stirred for 1 h. The mixture was extracted with DCM, and the organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated. The resulting residue was purified by Sephadex LH-20 (elution with 1:1 DCM/MeOH) and then incubated with Dowex 50WX4Na+ resin to obtain the *O*-sulfated compound **28** (17 mg, 72%). R_f 0.13 (15:1 DCM/MeOH); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96–7.94 (m, 2H, Ar), 7.83–7.76 (m, 4H, Ar, NH),

7.65–7.41 (m, 11H, Ar), 7.37–7.23 (m, 12H, Ar), 7.18–7.06 (m, 14H, Ar), 5.58 (t, J = 9.6 Hz, 1H, H-4'''), 5.42 (d, J = 4.3 Hz, 1H, H-1''), 5.18 (d, J = 3.4 Hz, 1H, H-1'''), 5.12 (d, J = 2.8 Hz, 1H, H-1'), 5.07 (s, 1H, H-1), 5.00 (d, J = 2.8 Hz, 1H, H-5), 4.96 (d, J = 10.4 Hz, 1H, OCH_2Ph), 4.91 (t, J = 4.9 Hz, 1H, H-2''), 4.73–4.65 (m, 6H, OCH_2Ph, OCH_2Nap, H-5''), 4.58–4.54 (m, 3H, OCH_2Ph), 4.45 (d, J = 11.3 Hz, 1H, OCH_2Ph), 4.28 (d, J = 15.5 Hz, 1H, CH_2CO_2t-Bu), 4.23-4.07 (m, 5H), 4.06–3.94 (m, 4H), 3.89–3.75 (m, 4H), 3.71–3.59 (m, 4H), 3.64 (s, 3H, OCH_3), 3.46 (dd, J = 10.3, 3.3 Hz, 1H, H-2'''), 3.43 (s, 3H, OCH_3), 2.56–2.51 (m, 2H, CH_2), 2.36–2.26 (m, 2H, CH_2), 2.08 (s, 3H, $C{=}OCH_3$), 1.46 (s, 9H, $OC(CH_3)_3$), 0.98 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.6 ($CH_3C{=}OCH_2$), 172.0 ($CH_2C{=}O$), 169.9 (CO_2t-Bu), 169.3 ($C{=}OOCH_3$), 168.6 ($C{=}OOCH_3$), 164.8 ($C{=}OPh$), 137.9 (Ar), 137.3 (Ar), 137.1 (Ar), 135.6 (Ar), 135.5 (Ar), 135.2 (Ar), 133.3 (Ar), 133.2 (Ar), 130.0 (Ar), 132.9 (Ar), 129.7 (Ar), 129.65 (Ar), 128.6 (Ar), 128.56 (Ar), 128.53 (Ar), 128.3 (Ar), 128.2 (Ar), 128.1 (Ar), 128.06 (Ar), 128.0 (Ar), 127.9 (Ar), 127.7 (Ar), 127.63 (Ar), 127.56 (Ar), 127.4 (Ar), 127.3 (Ar), 115.6 (q, $^1J_{C,F}$ = 288 Hz, CF_3), 100.4 (C-1'), 97.7 (C-1''), 97.1 (C-1'''), 83.0 ($OC(CH_3)_3$), 77.5, 77.2, 76.8, 75.3, 74.5, 73.7, 73.5, 72.1, 71.4, 71.2, 70.3 (C-2''), 70.2 (C-4'''), 70.0 (C-5''), 67.6, 66.0 (OCH_2CO_2t-Bu), 62.9 (C-2'''), 62.0, 53.0 (C-2'), 52.3 (OCH_3), 51.8 (OCH_3), 37.6 ($CH_2C{=}O$), 29.7 ($CH_3C{=}O$), 27.9 ($CO_2C(CH_3)_3$), 27.6 ($CH_2C{=}O$), 26.6 ($SiC(CH_3)_3$), 19.1 ($SiC(CH_3)_3$); HRMS (ESI-TOF) calcd for $C_{101}H_{110}F_3N_4O_{30}SSi$ $[M-Na]^-$: 1975.6647; found: 1975.6633.

Methyl (2-azido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-levulinoyl-α-L-idopyranoosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-2-

naphthylmethyl-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(3-*O*-benzyl-2-*O*-sulfonato-1-*O*-3-((*tert*-butoxy)-2-oxoacetyl))-α-L-idopyranosid)urinate mono sodium salt (28a). To a solution of O-sulfated tetrasaccharide **28** (17 mg, 8.5 μmol) in pyridine (2.0 mL) was added hydrogen fluoride pyridine (0.40 ml) at 0 °C. After stirring at RT for 3 h, the reaction was quenched with saturated aq. $NaHCO_3$. The mixture was extracted by DCM, and the organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated. The resulting residue was purified by Sephadex LH-20 (elution with 1:1 DCM/MeOH) and then incubated with Dowex 50WX4Na+ resin to afford tetrasaccharide **28a** (14 mg, 91%) as colorless foam. R_f 0.10 (15:1 DCM/MeOH); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99–7.97 (m, 2H, Ar), 7.85–7.78 (m, 4H, Ar), 7.65–7.62 (m, 1H, Ar), 7.53–7.42 (m, 5H, Ar), 7.39–7.30 (m, 7H, Ar), 7.26–7.14 (m, 13H, Ar), 5.39 (d, *J* = 3.5 Hz, 1H, H-1''), 5.21 (t, *J* = 9.6 Hz, 1H, H-4'''), 5.17 (s, 1H, H-1'), 5.13 (d, *J* = 3.1 Hz, 1H, H-1'''), 4.98–4.89 (m, 4H, H-1, H-5, OCH_2Ph, H-2''), 4.83–4.54 (m, 10H, OCH_2Ph, OCH_2Nap, H-5''), 4.45 (d, *J* = 11.3 Hz, 1H, OCH_2Ph), 4.30–4.26 (m, 1H, H-2'), 4.20–3.97 (m, 8H), 3.84–3.57 (m, 7H), 3.61 (s, 3H, OCH_3), 3.53 (s, 3H, OCH_3), 3.53–3.49 (m, 1H), 3.38 (dd, *J* = 9.7, 3.0 Hz, 1H, H-2'''), 2.55–2.49 (m, 2H, CH_2), 2.37–2.28 (m, 2H, CH_2), 2.09 (s, 3H, C=OCH_3), 2.01 (Br, 1H), 1.43 (s, 9H, $OC(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.9 (CH_3*C*=OCH_2), 172.0 (CH_2*C*=O), 169.8 (*C*=$OOCH_3$), 169.6 (*C*=$OOCH_3$), 169.5 (*C*O_2*t*-Bu), 166.1 (*C*=OPh), 157.6 (q, $^2J_{C,F}$ = 37.3 Hz, CF_3*C*=O), 137.8 (Ar), 137.4 (Ar), 137.1 (Ar), 135.3 (Ar), 133.9 (Ar), 133.2 (Ar), 133.0 (Ar), 129.8 (Ar), 128.9 (Ar), 128.8 (Ar), 128.7 (Ar), 128.5 (Ar), 128.34 (Ar), 128.25 (Ar), 128.16 (Ar), 128.0 (Ar), 127.97 (Ar), 127.9 (Ar), 127.8 (Ar), 127.64 (Ar), 127.59 (Ar), 127.4 (Ar), 126.8 (Ar), 126.2 (Ar), 126.1 (Ar), 125.9 (Ar), 115.7 (q, $^1J_{C,F}$ = 288 Hz, CF_3), 100.0 (C-1'), 98.3 (C-1''), 97.9 (C-1'''), 83.0 (O*C*$(CH_3)_3$), 76.9, 76.7, 74.9, 74.7, 73.7, 73.5, 72.8, 71.3, 71.1, 71.1 (C-4'''), 71.07 (C-2''), 70.1 (C-5''), 67.4, 66.0 (O*C*H_2CO_2*t*-Bu), 62.8 (C-2'''), 60.7, 52.8 (C-2'), 52.2 (OCH_3), 52.1

(OCH_3), 37.6 ($CH_2C{=}O$), 29.7 ($CH_3C{=}O$), 27.9 ($CO_2C(CH_3)_3$), 27.7 ($CH_2C{=}O$); HRMS (ESI-TOF) calcd for $C_{85}H_{92}F_3N_4O_{30}S$ $[M-Na]^-$: 1737.5469; found: 1737.5461.

Carboxylmethyl 2-azido-3-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-3-*O*-benzyl-α-L-idopyranosyluronate)-(1→4)-3-*O*-benzyl-2-deoxy-6-*O*-2-naphthylmethyl-2-acetamido-α-D-glucopyranosyl-(1→4)-3-*O*-benzyl-2-*O*-sulfonato-α-L-idopyranoside uronate tetra sodium salt (29). Compound **28a** (13 mg, 7.3 μmol) was dissolved in MeOH (1.0 mL), and 1.0 M aq. LiOH (2 mL) was added dropwise at 0 °C. The reaction mixture was stirred at RT for 36 h, then brought to pH 8-8.5 by the addition of IR 120 H^+ resin to give the intermediate with a free amine group. The intermediate was dissolved in a mixture of anhydrous MeOH (3.0 mL) and Et_3N (15 mg, 0.15 mmol), to which was added acetic anhydride (7.5 mg, 73 μmol). The reaction mixture was stirred for 4 h at RT and concentrated under reduced pressure. The resulting residue was purified by Sephadex LH-20 (elution with MeOH) and then incubated with Dowex 50WX4Na+ resin to obtain compound **29** (9.3 mg, 85%) as a colorless foam. ^{1}H NMR (400 MHz, CD_3OD): δ 7.97–7.94 (m, 1H, Ar), 7.88–7.82 (m, 3H, Ar, NH), 7.57–7.55 (m, 1H, Ar), 7.46–7.21 (m, 22H, Ar), 5.36 (d, J = 2.3 Hz, 1H, H-1''), 5.31 (s, 1H, H-1), 5.13 (d, J = 3.6 Hz, 1H, H-1'''), 5.05 (d, J = 10.8 Hz, 1H, OCH_2Ph), 4.82–4.70 (m, 8H, H-5'', OCH_2Ph, OCH_2Nap), 4.62 (d, J = 11.7 Hz, 1H, OCH_2Ph), 4.61 (d, J = 11.1 Hz, 1H, OCH_2Ph), 4.58 (d, J = 1.6 Hz, 1H, H-5), 4.54 (s, 1H, H-2), 4.50 (d, J = 3.2 Hz, 1H, H-1'), 4.33 (s, 1H, H-4''), 4.26–4.23 (m, 1H, H-5'), 4.21 (d, J = 15.6 Hz, 1H, CH_2CO_2), 4.16–4.13 (m, 1H, H-2'), 4.10 (s, 1H, H-4), 4.05–3.99 (m, 3H, H-3', H-4', CH_2CO_2),

3.94–3.80 (m, 8H, H-2'', H-3, H-3''', H-3'', H-5''', H-6a', H-6b', H-6a'''), 3.73 (dd, J = 11.9, 4.6 Hz, 1H, H-6b'''), 3.56 (t, J = 9.3 Hz, 1H, H-4'''), 3.52 (dd, J = 10.2, 3.6 Hz, 1H, H-2'''), 1.93 (s, 3H, C=OCH_3); ^{13}C NMR (100 MHz, CD_3OD): δ 175.1 (CH_2CO_2), 174.6 (CO_2), 174.2 (CO_2), 172.6 (C=ONH), 138.56 (Ar), 138.54 (Ar), 138.2 (Ar), 136.6 (Ar), 135.8 (Ar), 133.4 (Ar), 133.1 (Ar), 129.8 (Ar), 128.8 (Ar), 128.5 (Ar), 128.3 (Ar), 128.0 (Ar), 127.9 (Ar), 127.8 (Ar), 127.77 (Ar), 127.72 (Ar), 127.64 (Ar), 127.56 (Ar), 127.52 (Ar), 127.30 (Ar), 127.27 (Ar), 127.24 (Ar), 127.2 (Ar), 127.0 (Ar), 126.4 (Ar), 125.8 (Ar), 125.6 (Ar), 125.5 (Ar), 98.9 (C-1''), 98.4 (C-1), 96.4 (C-1'''), 94.5 (C-1'), 80.9 (C-3'''), 77.4 (C-3'), 75.9 (C-4'), 74.9 (OCH_2Ph), 74.3 (C-3''), 73.9 (OCH_2Ph), 73.4 (OCH_2Nap), 72.8 (C-4''), 72.4 (C-5'''), 71.59 (OCH_2Ph), 71.57 (OCH_2Ph), 71.3 (C-2), 71.0 (C-3, C-4'''), 70.9 (C-4), 70.4 (C-5'), 70.1 (C-5''), 68.8 (C-6'), 68.5 (C-2''), 67.5 (C-5, CH_2CO_2), 63.6 (C-2'''), 60.6 (C-6'''), 52.8 (C-2'), 21.9 (CH_3C=O); HRMS (ESI-TOF) calcd for $C_{67}H_{70}N_4O_{27}SNa_3$ $[M-Na]^-$: 1463.3641; found: 1463.3641.

Carboxylmethyl 2-deoxy-2-sulfamino-α-D-glucopyranosyl-(1→4)-α-L-idopyranosyluronate)-(1→4)-2-deoxy-2-acetamido-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranoside uronate penta sodium salt (30). To a solution of compound **29** (5.7 mg, 0.0038 mmol) in 1:1 *tert*-butanol/water (2.0 mL) was added palladium hydroxide on carbon (30 mg). The reaction mixture was stirred under hydrogen atmosphere for 36 h. After completion of the reaction, the mixture was filtered, and the residue was washed with a mixture of 1:1 *tert*-butanol/H_2O (2.0 mL). The combined solvents were concentrated under reduced pressure, and the residue was dissolved in distilled water (0.5 mL), $NaHCO_3$ (5.0 mg, 0.060 mmol) and

pyridine sulfur trioxide complex (5.0 mg, 0.030 mmol) was added with vigorous stirring. This procedure was repeated after 2 h and 4 h. The reaction mixture was stirred for 12 h at RT and then purified by Sephadex G15 (elution with H_2O) to give sulfated compound **30** (3.5 mg, 86%). ^{1}H NMR (400 MHz, D_2O): δ 5.28 (d, *J* = 3.5 Hz, 1H, H-1'''), 5.01 (s, 1H, H-1), 5.00 (d, *J* = 3.5 Hz, 1H, H-1'), 4.81 (d, *J* = 2.3 Hz, 1H, H-1''), 4.64 (s, 1H, H-5''), 4.46 (s, 1H, H-5), 4.24 (s, 1H, H-3), 4.21 (s, 1H, H-2), 4.02 (d, *J* = 15.7 Hz, 1H, C*H*$_2$CO$_2$), 3.98–3.88 (m, 5H, H-3'', H-4'', H-4, H-2', C*H*$_2$CO$_2$), 3.79–3.57 (m, 9H, H-2'', H-3', H-4', H-5', H-5'', H-6a', H-6b', H-6a''', H-6b'''), 3.51 (t, *J* = 9.8 Hz, 1H, H-3'''), 3.34 (t, *J* = 9.5 Hz, 1H, H-4'''), 3.09 (dd, *J* = 10.2, 3.2 Hz, 1H, H-2'''), 1.93 (s, 3H, C=OCH$_3$); ^{13}C NMR (100 MHz, D_2O): δ 177.1 (CH$_2$*C*O$_2$), 175.24 (*C*O$_2$), 175.17 (*C*O$_2$), 174.3 (*C*=ONH), 101.6 (C-1''), 98.2 (C-1), 95.3 (C-1'''), 93.2 (C-1'), 76.7 (C-4'), 74.8 (C-4''), 72.8 (C-3), 71.6 (C-5'''), 71.2 (C-3'''), 71.1 (C-5'), 70.1 (C-4), 69.9 (C-3'), 69.7 (C-4'''), 69.4 (C-5''), 69.3 (C-2''), 68.9 (C-3''), 66.7 (*C*H$_2$CO$_2$), 66.6 (C-5), 62.9 (C-2), 60.1 (C-6'''), 59.6 (C-6'), 57.8 (C-2'''), 53.5 (C-2'), 22.2 (CH$_3$C=O); HRMS (ESI-TOF) calcd for $C_{28}H_{39}N_2O_{30}S_2Na_4$ [M-Na]$^-$: 1039.0620; found: 1039.0638.

Methyl (2-acetamido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-sulfonato-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-levulinoyl-α-L-idopyranoosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-2-naphthylmethyl-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(3-*O*-benzyl-2-*O*-((9*H*-fluoren-9-yl)methoxycarbonyl)-1-*O*-3-((*tert*-butoxy)-2-oxoacetyl))-α-L-idopyranosid)uronate mono sodium salt (31). To a solution of compound **27** (13 mg, 6.5 μmol)

in DCM (0.30 mL) was added pyridine (0.50 mL) followed by thioacetic acid (0.50 mL) at RT. After stirring for 18 h, the mixture was diluted with DCM and washed with saturated aq. $NaHCO_3$ and then brine. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated. The resulting residue was purified by silica gel column chromatography (elution with 20:1 → 10:1 DCM/MeOH) and then incubated with Dowex 50WX4Na+ resin to obtain the *O*-sulfated compound **31** (11 mg, 82%). R_f 0.34 (9:1 DCM/MeOH); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92–7.72 (m, 8H, Ar), 7.52–7.29 (m, 18H, Ar), 7.27–6.82 (m, 16H, Ar, NH), 5.64 (br, 1H, H-4'''), 5.24 (s, 1H, H-1''), 5.20 (s, 1H, H-1), 5.07 (s, 1H, H-5 or H-5″), 5.01 (s, 1H, H-1‴), 4.96 (s, 1H, H-2 or H-2″), 4.94 (s, 1H, H-2 or H-2″), 4.88 (s, 1H, H-5 or H-5″), 4.82 (s, 1H, H-1′), 4.79–4.52 (m, 7H, OCH_2Ph, OCH_2Nap), 4.46–4.32 (m, 5H, OCH_2Ph, OCH_2-Fluoren, H-2′), 4.29–3.96 (m, 10H), 3.89–3.62 (m, 8H), 3.56 (s, 3H, OCH_3), 3.28 (s, 3H, OCH_3), 2.66–2.56 (m, 2H, CH_2), 2.48–2.40 (m, 2H, CH_2), 2.03 (s, 3H, C=OCH_3), 1.70 (s, 3H, C=OCH_3), 1.45 (s, 9H, $OC(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.2 (CH_3*C*=OCH_2), 172.0 (*C*=O), 171.9 (*C*=O), 169.2 (*C*=O), 168.5 (*C*=O), 165.6 (*C*=O), 165.5 (*C*=O), 157.0 (q, $^2J_{C,F}$ = 37.6 Hz, CF_3*C*=O), 153.9 (Fluoren-CH_2O*C*=O), 143.1 (Ar), 142.8 (Ar), 141.2 (Ar), 137.6 (Ar), 136.6 (Ar), 135.5 (Ar), 133.5 (Ar), 133.3 (Ar), 132.9 (Ar), 129.9 (Ar), 129.2 (Ar), 128.6 (Ar), 128.3 (Ar), 128.2 (Ar), 128.0 (Ar), 127.9 (Ar), 127.7 (Ar), 127.5 (Ar), 127.3 (Ar), 127.0 (Ar), 126.5 (Ar), 126.4 (Ar), 126.1 (Ar), 125.9 (Ar), 125.8 (Ar), 125.0 (Ar), 124.9 (Ar), 120.0 (Ar), 115.7 (q, $^1J_{C,F}$ = 288 Hz, CF_3), 98.7 (C-1), 97.9 (C-1″), 96.2 (C-1′), 82.0 (O*C*$(CH_3)_3$), 78.3, 74.3, 74.1, 73.1, 72.7, 72.3, 72.1, 71.8, 71.4, 71.0, 70.8, 70.1, 69.7, 69.6, 69.5, 69.3, 68.6, 67.6, 67.5, 65.9, 64.5, 53.1 (C-2′), 52.1 (OCH_3), 51.8 (OCH_3), 46.4 (*C*HCH_2), 37.7 (CH_2C=O), 29.7 (CH_3C=O), 28.0 ($CO_2C(CH_3)_3$), 27.6 (CH_2C=O), 22.7 (CH_3C=O); HRMS (ESI-TOF) calcd for $C_{102}H_{106}F_3N_2O_{33}S$ $[M-Na]^-$: 1975.6351; found: 1975.6366.

Carboxylmethyl 2-deoxy-2-acetamido-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-α-L-idopyranosyluronate)-(1→4)-2-deoxy-2-sulfamino-α-D-glucopyranosyl-(1→4)-α-L-idopyranoside uronate penta sodium salt (32). Compound **31** (9.0 mg, 4.5 μmol) was dissolved in MeOH (0.3 mL), and 1.0 M aq. LiOH (1.0 mL) was added dropwise at 0 °C. The reaction mixture was stirred at RT for 12 h, then brought to pH 8-8.5 by the addition of IR 120 H^+ resin. After filtration and concentration, the crude intermediate was obtained. This intermediate was dissolved in 1:1 *tert*-butanol/water (4.0 mL) and palladium hydroxide on carbon (30 mg) was added. The reaction mixture was stirred under a H_2 atmosphere for 36 h. After completion of the reaction, the mixture was filtered, and the residue was washed with a mixture of 1:1 *tert*-butanol/H_2O (4.0 mL). The combined solvents were concentrated under reduced pressure, and the resulting residue was dissolved in distilled water (0.5 mL). $NaHCO_3$ (5.0 mg, 0.060 mmol) and sulfur trioxide pyridine complex (5.0 mg, 0.030 mmol) were then added with vigorous stirring. This procedure was repeated after 2 h and 4 h. The reaction mixture was stirred for 12 h at RT and then purified by Sephadex G15 (elution with H_2O) to give sulfated compound **32** (3.4 mg, 71%). ^{1}H NMR (400 MHz, D_2O): δ 5.27 (d, *J* = 3.5 Hz, 1H, H-1'), 5.15 (d, *J* = 3.5 Hz, 1H, H-1'''), 4.87 (s, 1H, H-1 or H-1''), 4.86 (s, 1H, H-1 or H-1''), 4.72 (s, 1H, H-5'' or H-5), 4.46 (d, *J* = 1.8 Hz, 1H, H-5'' or H-5), 4.31 (dd, *J* = 11.2, 2.5 Hz, 1H, H-6'''), 4.15 (dd, *J* = 11.2, 1.0 Hz, 1H, H-6'''), 4.12–4.04 (m, 3H), 3.98–3.92 (m, 3H), 3.90 (dd, *J* = 10.0, 3.5 Hz, 1H, H-2'''), 3.83–3.74 (m, 5H), 3.70–3.64 (m, 3H), 3.61 (t, *J* = 9.2 Hz, 1H, H-3'), 3.52 (t, *J* = 9.6 Hz, 1H, H-4'''), 3.09 (dd, *J* = 10.0, 3.5 Hz, 1H, H-2'), 1.97 (s, 3H, C=OCH_3); ^{13}C NMR (100 MHz, D_2O): δ 177.5 (C=O), 175.4 (C=O), 174.9 (C=O), 174.3 (*C*=O), 101.4 (C-1 or C-1''), 100.4 (C-1 or C-1''), 95.7 (C-1'), 94.3 (C-1'''),

76.8, 74.4 (2 x C), 70.95, 70.86, 70.1, 69.8 (2 x C), 69.65, 69.61, 69.0 (C-4'''), 67.9, 67.7, 67.2, 66.5 (CH_2CO_2), 66.3 (C-6'''), 59.6 (C-6'), 57.9 (C-2'), 53.2 (C-2'''), 21.9 (CH_3C=O); HRMS (ESI-TOF) calcd for $C_{28}H_{39}N_2O_{30}S_2Na_4$ $[M-Na]^-$: 1039.0620; found: 1039.0621.

Methyl (2-azido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-(2,3-di-*O*-acetyl-1-*p*-tolylthio-α-L-idopyranosid)uronate (S1). To a solution of compound **1b** (2.0 g, 3.1 mmol) in anhydrous DCM (20 mL) were added trimethyl(*p*-tolylthio)silane (TMSSTol, 1.8 g, 9.3 mmol) and ZnI_2 (3.9 g, 12 mmol). After stirring at RT overnight, the reaction was diluted with DCM (80 mL), and the organic layer was washed with saturated aq. $NaHCO_3$, dried over anhydrous $MgSO_4$, filtered, and concentrated. Purification of the residue via silica gel column chromatography (20 x 3 cm; elution using 2:1 hexanes/EtOAc) gave compound **S1** (1.9 g, 89%) as an off-white foam. R_f 0.5 (1:1 hexanes/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 (d, *J* = 8.1 Hz, 2H, Ar), 7.10 (d, *J* = 8.1 Hz, 2H, Ar), 5.55 (d, *J* = 1.9 Hz, 1H, H-1), 5.38 (dd, *J* = 10.6, 9.3 Hz, 1H, H-3′), 5.26 (t, *J* = 3.4 Hz, 1H, H-3), 5.21 (d, *J* = 2.5 Hz, 1H, H-5), 5.10 (d, *J* = 3.5 Hz, 1H, H-1′), 5.04 (dd, *J* = 10.0, 9.3 Hz, 1H, H-4′), 5.00 (dd, *J* = 3.4, 1.9 Hz, 1H, H-2), 4.22 (dd, *J* = 12.5, 3.5 Hz, 1H, H-6′), 4.16–4.09 (m, 3H, H-4, H-5′, H-6′), 3.85 (s, 3H, OCH_3), 3.45 (dd, *J* = 10.6, 3.5 Hz, 1H, H-2′), 2.32 (s, 3H), 2.18 (s, 3H), 2.16 (s, 3H), 2.06 (s, 6H), 1.99 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.7 (C=O), 170.1 (C=O), 169.9 (C=O), 169.8 (C=O), 169.1 (C=O), 168.9 (C=O), 138.3, 132.5, 130.3, 130.0, 98.7 (C-1′), 86.6 (C-1), 73.7 (C-4), 70.7 (C-3′), 68.7 (C-5′), 68.6 (C-2, C-5), 68.2 (C-4′), 67.4 (C-3), 61.4 (C-6′), 61.3 (C-2′), 52.75 (OCH_3), 21.26, 21.01, 20.84, 20.79, 20.78, 20.69; HRMS (ESI-TOF) calcd for $C_{30}H_{37}N_3O_{15}SNa$ $[M+Na]^+$: 734.1843; found: 734.1839.

Methyl (2-azido-2-deoxy-4,6-*O*-*p*-methoxybenzylidene-α-D-glucopyranosyl)-(1→4)-(1-*p*-tolylthio-α-L-idopyranosid)uronate (S2). To a solution of disaccharide **S1** (1.9 g, 3.8 mmol) in anhydrous MeOH (40 mL) was added 25 wt% of NaOMe in MeOH (0.40 mL, 1.8 mmol) at 0 °C. The reaction was stirred at RT under argon for 2 h, quenched with IR-120 resin, and stirred for an additional 15 min. The solution was filtered and concentrated under reduced pressure to give the unprotected disaccharide. To a solution of the unprotected disaccharide in anhydrous CH_3CN (30 mL) were added *p*-methoxybenzaldehyde dimethylacetal (1.4 mg, 7.8 mmol) and *p*TsOH (49 mg, 0.26 mmol). After stirring at 45 °C for 1 h, the reaction was quenched with Et_3N (35 μL, 0.26 mmol) and concentrated. Purification by silica gel column chromatography (elution with 2:1 → 1:1 hexanes/EtOAc) gave compound **S2** (1.4 g, 84%) as a colorless foam. R_f 0.6 (1:4 hexanes/EtOAc); ^{1}H NMR (500 MHz, CD_3COCD_3): δ 7.42– 7.37 (m, 4H, Ar), 7.15 (d, *J* = 7.8 Hz, 2H, Ar), 6.92 (d, *J* = 8.8 Hz, 2H, Ar), 5.56 (s, 1H), 5.47 (d, *J* = 2.8 Hz, 1H, H-1), 5.32 (d, *J* = 3.8 Hz, 1H, H-1′), 5.26 (d, *J* = 4.6 Hz, 1H, OH-3′), 5.22 (d, *J* = 2.8 Hz, 1H, H-5), 4.95 (d, *J* = 3.9 Hz, 1H, OH-3), 4.25– 4.20 (m, 2H, H-3, OH-2), 4.19 (dd, *J* = 10.0, 4.7 Hz, 1H, H-6′), 4.15 (t, *J* = 2.8 Hz, 1H, H-4), 3.98– 3.91 (m, 1H, H-3′), 3.81 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 3.73 (t, *J* = 10.0 Hz, 1H, H-6′), 3.71–3.69 (m, 1H, H-2), 3.67 (dd, *J* = 9.9, 3.8 Hz, 1H, H-2′), 3.63 (td, *J* = 10.0, 4.7 Hz, 1H, H-5′), 3.55 (t, *J* = 10.0 Hz, 1H, H-4′), 2.30 (s, 3H); ^{13}C NMR (125 MHz, CD_3COCD_3): δ 170.3 (C=O), 161.1, 137.7, 133.7, 131.9, 131.3, 130.4, 128.6, 114.1, 102.4, 97.2 (C-1′), 89.9 (C-1), 82.1 (C-4′), 74.9 (C-4), 72.3 (C-2), 70.6 (C-3′), 69.4 (C-5), 68.9 (C-6′), 67.4 (C-3), 65.1 (C-2′),

64.3 (C-5′) 55.56 (OCH_3), 52.46 (OCH_3), 21.00; HRMS (ESI-TOF) calcd for $C_{28}H_{33}N_3O_{11}SNa$ $[M+Na]^+$: 642.1733; found: 642.1749.

Methyl (2-azido-2-deoxy-4,6-*O*-*p*-methoxybenzylidene-α-D-glucopyranosyl)-(1→4)-2-*O*-((9*H*-fluoren-9-yl)methylcarbonyl)-1-*p*-tolylthio-α-L-idopyranosid)uronate (S3). To a solution of **S2** (0.60 g, 0.97 mmol) in anhydrous toluene (40 mL) were added dibutyltin oxide (0.48 g, 1.9 mmol) and TBAI (0.71 g, 1.9 mmol). The mixture was refluxed for 1 h, then allowed to cool to 90 °C, and fluorenylmethyloxycarbonyl chloride (FmocCl) (0.75 g, 2.9 mmol) was added. After stirring at 90 °C for an additional 1 h, the reaction was quenched using saturated aq. $NaHCO_3$ (50 mL) and extracted with EtOAc (100 mL x 3). The organic layer was washed with water (50 mL), dried over Na_2SO_4, and concentrated. Purification by silica gel column chromatography (elution with 3:2 hexanes/EtOAc) afforded **S3** (0.69 g, 85%) as a white foam. R_f 0.5 (1:1 hexanes/EtOAc); ^{1}H NMR (500 MHz, CD_3COCD_3): δ 7.85 (d, *J* = 7.5 Hz, 2H, Ar), 7.73 (d, *J* = 7.5 Hz, 1H, Ar), 7.70 (d, *J* = 7.5 Hz, 1H, Ar), 7.43– 7.25 (m, 8H, Ar), 7.15 (d, *J* = 7.9 Hz, 2H, Ar), 6.83 (d, *J* = 8.7 Hz, 2H, Ar), 5.68 (d, *J* = 4.1 Hz, 1H, H-1), 5.53 (s, 1H), 5.28 (d, *J* = 4.5 Hz, 1H, OH-3), 5.21 (d, *J* = 3.5 Hz, 1H, H-1′), 5.18 (d, *J* = 3.3 Hz, 1H, H-5), 5.05 (d, *J* = 4.4 Hz, 1H, OH-3′), 4.80 (t, *J* = 4.1 Hz, 1H, H-2), 4.46–4.39 (m, 3H, H-3, Fmoc-CH_2), 4.33 (t, *J* = 7.4 Hz, 1H), 4.26 (dd, *J* = 10.0, 4.9 Hz, 1H, H-6′), 4.21–4.15 (m, 2H, H-3′, H-4), 3.94 (td, *J* = 10.0, 4.9 Hz, 1H, H-5′), 3.79 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3), 3.69 (t, *J* = 10.0 Hz, 1H, H-6′), 3.52 (t, *J* = 10.0 Hz, 1H, H-4′), 3.40 (dd, *J* = 10.0, 3.5 Hz, 1H, H-2′), 2.31 (s, 3H); ^{13}C NMR (125 MHz, CD_3COCD_3): δ 170.0 (C=O), 160.9, 155.2 (C=O), 144.7, 144.3, 142.1, 141.9, 138.3, 132.4, 132.4,

131.3, 130.5, 128.7, 128.6, 128.6, 128.2, 128.1, 126.3, 126.2, 120.82, 120.80, 114.0, 102.4, 100.4 (C-1′), 86.2 (C-1), 82.7 (C-4′), 77.04 (C-4), 76.04 (C-2), 70.7, 70.4 (C-5), 69.4 (C-3′), 69.0 (C-6′), 68.2 (C-3), 64.82 (C-2′), 64.3 (C-5′), 55.5 (OCH_3), 52.4 (OCH_3), 47.5, 21.0; HRMS (ESI-TOF) calcd for $C_{43}H_{43}N_3O_{13}SNa$ $[M+Na]^+$: 864.2415; found: 864.2440. Note: Dibutyltin oxide (*n*-Bu_2SnO) is highly toxic. Obtain special instructions before use and do not handle until all safety precautions have been read and understood.

Methyl (2-azido-2-deoxy-4,6-*O*-*p*-methoxybenzylidene-α-D-glucopyranosyl)-(1→4)-(1-*p*-tolylthio-2-*O*-((2,2,2-trichloroethoxy)carbonyl)-α-L-idopyranosid)uronate (S4). To a solution of **S2** (0.11 g, 0.18 mmol) in anhydrous toluene (10 mL) were added dibutyltin oxide (92 mg, 0.37 mmol) and TBAI (0.14 g, 0.37 mmol). The mixture was refluxed for 1 h, then allowed to cool to 70 °C, and 2,2,2-trichloroethyl chloroformate (78 mg, 0.37 mmol) was added. After stirring at 70 °C for an additional 1 h, the reaction was quenched using saturated aq. $NaHCO_3$ (25 mL) and extracted with EtOAc (40 mL x 3). The organic layer was washed with water (50 mL), dried over Na_2SO_4, and concentrated. Purification by silica gel column chromatography (eluted with 3:2 hexanes/EtOAc) afforded **S4** (0.11 g, 73%) as an off-white foam. R_f 0.5 (6:4 hexanes/EtOAc); ^{1}H NMR (500 MHz, CD_3COCD_3): δ 7.43– 7.36 (m, 4H, Ar), 7.15 (d, *J* = 7.9 Hz, 2H, Ar), 6.90 (d, *J* = 8.8 Hz, 2H, Ar), 5.67 (d, *J* = 4.5 Hz, 1H, H-1), 5.54 (s, 1H), 5.32 (d, *J* = 4.7 Hz, 1H, OH-3), 5.21 (d, *J* = 3.6 Hz, 1H, H-1′), 5.14 (d, *J* = 3.7 Hz, 1H, H-5), 5.04 (d, *J* = 4.4 Hz, 1H, OH-3′), 5.00 (d, *J* = 12.0 Hz, 1H, CCl_3CH_2), 4.85 (d, *J* = 12.0 Hz, 1H, CCl_3CH_2), 4.81 (t, *J* = 4.5 Hz, 1H, H-2), 4.42–4.37 (m, 1H, H-3), 4.24 (dd, *J* = 10.1, 4.8 Hz, 1H, H-6′), 4.15 (dd, *J* = 5.0, 3.7 Hz, 1H,

H-4), 4.10–4.04 (m, 1H, H-3′), 3.88–3.80 (m, 1H, H-5′), 3.79 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 3.69 (t, J = 10.1 Hz, 1H, H-6′), 3.51 (t, J = 9.4 Hz, 1H, H-4′), 3.35 (dd, J = 10.0, 3.6 Hz, 1H, H-2′), 2.31 (s, 3H); ^{13}C NMR (125 MHz, CD_3COCD_3): δ 169.9 (C=O), 161.0, 154.1 (C=O), 138.4, 132.5, 132.0, 131.3, 130.5, 128.6, 114.1, 102.4, 100.2 (C-1′), 95.5, 85.72 (C-1), 82.61 (C-4′), 77.6, 76.9 (C-2), 76.5 (C-4), 70.8 (C-5), 69.2 (C-3′), 69.0 (C-6′), 68.1 (C-3), 64.7 (C-2′), 64.3 (C-5′), 55.5 (OCH_3), 52.4 (OCH_3), 21.0; HRMS (ESI-TOF) calcd for $C_{31}H_{34}Cl_3N_3O_{13}SNa$ $[M+Na]^+$: 816.0776; found: 816.0759. Note: Dibutyltin oxide (n-Bu_2SnO) is highly toxic. Obtain special instructions before use and do not handle until all safety precautions have been read and understood.

Methyl (2-azido-2-deoxy-4,6-*O*-*p*-methoxybenzylidene-α-D-glucopyranosyl)-(1→4)-(2-*O*-benzoyl-1-*p*-tolylthio-α-L-idopyranosid)uronate (S5). To a solution of **S2** (50 mg, 0.080 mmol) in anhydrous toluene (6 mL) were added dibutyltin oxide (40 mg, 0.16 mmol) and TBAI (59 mg, 0.16 mmol). The mixture was refluxed for 1 h, then allowed to cool to 70 °C, and benzoyl chloride (23 mg, 0.16 mmol) was added. After stirring for an additional 2 h at 70 °C, the reaction was quenched using saturated aq. $NaHCO_3$ (20 mL) and extracted with EtOAc (30 mL x 3). The organic layer was washed with water (30 mL), dried over Na_2SO_4, and concentrated. Purification by silica gel column chromatography (elution with 1:1 hexanes/EtOAc) afforded **S5** (43 mg, 74%) as an off-white solid. R_f 0.6 (2:3 hexanes/EtOAc); ^{1}H NMR (500 MHz, CD_3COCD_3): δ 8.12 (d, J = 8.4 Hz, 2H, Ar), 7.55 (t, J = 8.0 Hz, 1H, Ar), 7.45– 7.36 (m, 6H, Ar), 7.10 (d, J = 7.8 Hz, 2H, Ar), 6.91 (d, J = 8.8 Hz, 2H, Ar), 5.75 (d, J = 6.4 Hz, 1H, H-1), 5.46 (s, 1H), 5.11 (t, J = 6.4 Hz, 1H, H-2), 5.04 (d, J = 3.8 Hz, 1H, H-1′), 5.00 (d, J = 4.7 Hz, 1H, H-5), 4.45 (bt, J = 6.4 Hz, 1H, H-3), 4.28

(dd, J = 10.1, 4.9 Hz, 1H, H-6′), 3.99 (dd, J = 6.4, 4.7 Hz, 1H, H-4), 3.94 (t, J = 9.7 Hz, 1H, H-3′), 3.93–3.88 (m, 1H, H-5′), 3.83 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 3.67 (t, J = 10.1 Hz, 1H, H-6′), 3.43 (t, J = 9.7 Hz, 1H, H-4′), 3.38 (dd, J = 9.7, 3.8 Hz, 1H, H-2′), 3.24 (bs, 1H, OH), 2.45 (bs, 1H, OH), 2.33 (s, 3H); ^{13}C NMR (125 MHz, CD_3COCD_3): δ 169.5 (C=O), 165.9 (C=O), 160.5, 138.4, 133.5, 133.1, 130.2, 129.9, 129.6, 129.5, 129.1, 128.6, 127.7, 113.9, 102.2, 100.6 (C-1′), 84.4 (C-1), 81.4 (C-4′), 78.7 (C-4), 72.1 (C-2), 71.6 (C-5), 70.0 (C-3′), 69.9 (C-3), 68.6 (C-6′), 63.8 (C-2′), 63.43 (C-5′), 55.5 (OCH_3), 52.4 (OCH_3), 21.3; HRMS (ESI-TOF) calcd for $C_{35}H_{37}N_3O_{12}SNa$ $[M+Na]^+$: 746.1996; found: 746.1999. Note: Dibutyltin oxide (n-Bu_2SnO) is highly toxic. Obtain special instructions before use and do not handle until all safety precautions have been read and understood.

Methyl (2-azido-2-deoxy-4,6-*O*-*p*-methoxybenzylidene-α-D-glucopyranosyl)-(1→4)-(3-*O*-chloroacetyl-1-*p*-tolylthio-α-L-idopyranosid)uronate (S6). To a solution of **S2** (50 mg, 0.080 mmol) in anhydrous toluene (6 mL) were added dibutyltin oxide (40 mg, 0.16 mmol) and TBAI (59 mg, 0.16 mmol). The mixture was refluxed for 1 h, then cooled to 0 °C, and chloroacetyl chloride (11 mg, 0.090 mmol) was added. After stirring for an additional 15 min at 0 °C, the reaction was quenched using saturated aq. $NaHCO_3$ (20 mL) and extracted with EtOAc (30 mL x 3). The organic layer was washed with water (30 mL), dried over Na_2SO_4, and concentrated. Purification by silica gel column chromatography (eluted with 1:1 hexanes/EtOAc) gave **S6** (44 mg, 75%) as an off-white foam. R_f 0.5 (1:1 hexanes/EtOAc); ^{1}H NMR (500 MHz, CD_3COCD_3): δ 7.44– 7.37 (m, 4H, Ar), 7.16 (d, J = 7.9 Hz, 2H, Ar), 6.91 (d, J = 8.8 Hz, 2H, Ar), 5.55 (s, 1H),

5.50 (d, J = 5.8 Hz, 1H, H-1), 5.49 (t, J = 6.1 Hz, 1H, H-3), 5.25 (d, J = 4.6 Hz, 1H, OH-3′), 5.22 (d, J = 3.9 Hz, 1H, H-1′), 5.00 (d, J = 4.5 Hz, 1H, H-5), 4.63 (d, J = 8.1 Hz, 1H, OH-2), 4.44 (d, J = 15.5 Hz, 1H, $ClCH_2$), 4.36 (d, J = 15.5 Hz, 1H, $ClCH_2$), 4.21–4.18 (m, 1H, H-6′), 4.15 (dd, J = 6.1, 4.5 Hz, 1H, H-4), 3.95–3.90 (m, 1H, H-3′), 3.81 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 3.75–3.69 (m, 2H, H-5′, H-6′), 3.68–3.64 (m, 1H, H-2), 3.61 (dd, J = 9.9, 3.9 Hz, 1H, H-2′), 3.57–3.52 (m, 1H, H-4′), 2.32 (s, 3H); ^{13}C NMR (125 MHz, CD_3COCD_3): δ 168.9 (C=O), 165.9 (C=O), 160.1, 137.5, 132.0, 130.3, 130.0, 129.5, 127.6, 113.1, 101.4, 98.3 (C-1′), 86.9 (C-1), 81.1 (C-4′), 73.0 (C-4), 71.6 (C-3), 71.1 (C-5), 69.2 (C-3′), 69.0 (C-2), 67.9 (C-6′), 63.7 (C-2′), 63.6 (C-5′), 54.56 (OCH_3), 51.64 (OCH_3), 40.87, 20.04; HRMS (ESI-TOF) calcd for $C_{30}H_{34}ClN_3O_{12}SNa$ $[M+Na]^+$: 718.1449; found: 718.1452. Note: Dibutyltin oxide (n-Bu_2SnO) is highly toxic. Obtain special instructions before use and do not handle until all safety precautions have been read and understood.

Methyl (3,4-*O*-di-acetyl-2-azido-2-deoxy-6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranosyl)-(1→4)-(3-*O*-acetyl-2-*O*-((9*H*-fluoren-9-yl)methoxycarbonyl)-1-*p*-tolylthio-α-L-idopyranosid)uronate (19) To a solution of compound **S3** (0.10 g, 0.12 mmol) in anhydrous MeOH (5.0 mL) was added *p*-toluenesulfonic acid (5.0 mg, 0.026 mmol) at RT. The reaction was and stirred for 3 h, concentrated under pressure, and the resultant residue was triturated with 2% EtOAc in hexanes (5 mL x 3). The crude mixture was dissolved in anhydrous THF (5 mL), and TBDPSCl (0.13 g, 0.60 mmol) and imidazole (66 mg, 0.97 mmol) were added at 0 °C. After stirring at RT for 3 h, the reaction was diluted with EtOAc, washed with saturated aq. NH_4Cl and brine.

The organic layer was dried over Na_2SO_4 and concentrated using reduced pressure. The resulting crude mixture was further treated with 3.0 mL of 2:1 pyridine/acetic anhydride at 0 °C. After stirring at RT for 0.5 h, the solution was concentrated, re-dissolved in EtOAc, washed with saturated aq. $NaHCO_3$, and brine. The organic layer was dried over Na_2SO_4, concentrated, and purified by silica gel column chromatography (elution with 5:1 → 4:1 hexanes/EtOAc) to give compound **19** (0.10 g, 78%, over three steps) as a colorless foam. R_f 0.6 (2:1 hexanes/EtOAc); ^{1}H NMR (500 MHz, C_6D_6): δ 7.89–7.84 (m, 2H, Ar), 7.83–7.77 (m, 2H, Ar), 7.66–7.59 (m, 2H, Ar), 7.60–7.53 (m, 4H, Ar), 7.35–7.18 (m, 10H, Ar), 6.85 (d, *J* = 7.9 Hz, 2H, Ar), 6.09 (d, *J* = 5.5 Hz, 1H, H-1), 5.94 (t, *J* = 5.5 Hz, 1H, H-3), 5.72 (dd, *J* = 10.5, 9.5 Hz, 1H, H-3′), 5.50 (t, *J* = 9.5 Hz, 1H, H-4′), 5.17 (d, *J* = 4.3 Hz, 1H, H-5), 5.14 (t, *J* = 5.5 Hz, 1H, H-2), 4.92 (d, *J* = 3.5 Hz, 1H, H-1′), 4.38 (dd, *J* = 8.5, 5.7 Hz, 1H, OCO_2CH_{2a}-Fluoren), 4.35-4.31 (m, 1H, H-5′), 4.30-4.23 (m, 2H, OCO_2CH_{2b}-Fluoren, OCO_2CH_2-C*H*), 4.14 (dd, *J* = 5.5, 4.4 Hz, 1H, H-4), 3.96 (dd, *J* = 11.5, 1.5 Hz, 1H, H-6a′), 3.83 (dd, *J* = 11.5, 3.9 Hz, 1H, H-6b′), 3.48 (s, 3H, OCH_3), 3.08 (dd, *J* = 10.5, 3.5 Hz, 1H, H-2′), 1.98 (s, 3H, CH_3), 1.73 (s, 3H, CH_3), 1.72 (s, 3H, CH_3), 1.58 (s, 3H, CH_3), 1.25 (s, 9H, *t*-Bu); ^{13}C NMR (125 MHz, C_6D_6): δ 169.4 (*C*=O), 168.84 (*C*=O), 168.81 (*C*=O), 168.2 (*C*=O), 154.4 (*C*=O), 143.7 (Ar), 143.5 (Ar), 141.4 (Ar), 141.3 (Ar), 137.9 (Ar), 135.82 (2C, Ar), 135.79 (2C, Ar), 133.24 (Ar), 133.18 (Ar), 133.0 (2C, Ar), 129.80 (2C, Ar), 129.78 (Ar), 129.74 (Ar), 128.0 (Ar), 127.82 (Ar), 127.81 (Ar), 127.78 (Ar), 127.73 (Ar), 127.6 (Ar), 127.3 (Ar), 127.24 (Ar), 127.19 (Ar), 125.5 (Ar), 125.4 (Ar), 119.9 (2C, Ar), 98.1 (C-1′), 84.8 (C-1), 73.1 (C-2), 72.3 (C-4), 71.2 (C-5′), 71.1 (C-5), 70.6 (OCO_2CH_2-Fluoren), 70.5 (C-3′), 68.5 (C-4′), 68.2 (C-3), 62.1 (C-6′), 60.8 (C-2′), 51.8 (OCH_3), 46.6 (OCO_2CH_2-*C*H), 26.7 ($C(CH_3)_3$), 20.6 (CH_3), 20.0 (CH_3), 19.91 (CH_3), 19.86 (CH_3), 19.1 ($C(CH_3)_3$); HRMS (ESI-TOF) calcd for $C_{57}H_{61}N_3O_{15}SSiNa$ $[M+Na]^+$: 1110.3490; found: 1110.3462.

Methyl (2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-(2,3-di-*O*-acetyl-1-*p*-tolylthio-α-L-idopyranosid)uronate (S7). To a solution of compound **1** (2.6 g, 3.8 mmol) in anhydrous DCM (100 mL) were added trimethyl(*p*-tolylthio)silane (TMSSTol, 2.8 g, 15 mmol) and ZnI_2 (4.8 g, 15 mmol). After stirring at RT overnight, the mixture was filtered and diluted with DCM (100 mL). The organic layer was washed with saturated aq. $NaHCO_3$, dried over Na_2SO_4, and concentrated. Purification by silica gel column chromatography (elution with 3:1 → 3:2 hexanes/EtOAc) gave compound **S7** (2.5 g, 88%) as an off-white solid. R_f 0.18 (1:2 hexanes/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40–7.38 (m, 2H, Ar), 7.16–7.14 (m, 2H, Ar), 5.82 (d, *J* = 9.4 Hz, 1H, NH), 5.62 (d, *J* = 4.6 Hz, 1H, H-1), 5.31 (t, *J* = 5.3 Hz, 1H, H-3), 5.16 (t, *J* = 9.5 Hz, 1H, H-4′), 5.09 (t, *J* = 9.5 Hz, 1H, H-3′), 5.07 (d, *J* = 3.9 Hz, 1H, H-5), 5.02 (d, *J* = 3.5 Hz, 1H, H-1′), 4.98 (t, *J* = 5.0 Hz, 1H, H-2), 4.34 (ddd, *J* = 10.3, 9.3, 3.5 Hz, 1H, H-2′), 4.22 (dd, *J* = 12.6, 3.8 Hz, 1H, H-6′), 4.18 (dd, *J* = 12.6, 2.3 Hz, 1H, H-6′), 4.12–4.09 (m, 2H, H-4, H-5′), 3.90 (s, 3H, OCH_3), 2.37 (s, 3H, CH_3Ph), 2.18 (s, 3H, C=OCH_3), 2.15 (s, 3H, C=OCH_3), 2.12 (s, 3H, C=OCH_3), 2.05 (s, 3H, C=OCH_3), 2.04 (s, 3H, C=OCH_3), 2.00 (s, 3H, C=OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.3 (C=O), 170.7 (C=O), 170.2 (C=O), 169.5 (C=O), 169.4 (C=O), 169.1 (C=O), 168.8 (C=O), 138.8 (Ar), 132.9 (Ar), 129.9 (Ar), 129.8 (Ar), 98.7 (C-1′), 85.1 (C-1), 73.3 (C-4), 70.7 (C-3′), 70.1 (C-5), 69.0 (C-2), 68.8 (C-3, C-5′), 67.5 (C-4′), 61.5 (C-6′), 52.6 (OCH_3), 51.8 (C-2′), 21.2, 20.82, 20.80, 20.73, 20.69, 20.6; HRMS (ESI-TOF) calcd for $C_{32}H_{41}NO_{16}NaSNa$ $[M+Na]^+$: 750.2044; found: 750.2026.

Methyl (2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-2-*N*-(1,1-dimethylethoxy)carbonyl-α-D-glucopyranosyl)-(1→4)-(2,3-di-*O*-acetyl-1-*p*-tolylthio-α-L-idopyranosid)uronate (S8). To a solution of **S7** (2.5 g, 3.5 mmol) in 25 mL of anhydrous THF were added di-*tert*-butyl dicarbonate (11 g, 52 mmol) and DMAP (0.21 g, 0.50 mmol) at RT. The reaction was refluxed for 3 h under argon and then cooled to RT. The mixture was concentrated under reduced pressure and purified by silica gel column chromatography (elution with 3:1 → 1:1 hexanes/EtOAc) to give **S8** (2.3g, 80%) as a colorless foam. R_f 0.75 (1:2 hexanes/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40–7.38 (m, 2H, Ar), 7.15–7.13 (m, 2H, Ar), 6.13 (dd, *J* = 11.0, 9.0 Hz, 1H, H-3′), 5.61 (d, *J* = 4.3 Hz, 1H, H-1), 5.21 (t, *J* = 5.0 Hz, 1H, H-3), 5.02–4.93 (m, 4H, H-1′, H-5, H-4′, H-2), 4.63 (d, *J* = 11.3, 1H, H-2′), 4.31–4.28 (m, 2H, H-5′, H-6′), 4.22–4.19 (m, 1H, H-6′), 4.08 (t, *J* = 4.7 Hz, 1H, H-4), 3.88 (s, 3H, OCH_3), 2.41 (s, 3H, C=OCH_3), 2.25 (s, 3H, CH_3Ph), 2.21 (s, 3H, C=OCH_3), 2.11 (s, 3H, C=OCH_3), 2.10 (s, 3H, C=OCH_3), 2.01 (s, 3H, C=OCH_3), 1.96 (s, 3H, C=OCH_3), 1.53 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.5 (C=O), 170.7 (C=O), 170.2 (C=O), 170.0 (C=O), 169.4 (C=O), 169.0 (C=O), 168.9 (C=O), 138.3, 132.9, 129.8, 129.3, 99.4 (C-1′), 85.4 (C-1), 84.6 ($(CH_3)_3$*C*O), 73.9 (C-4), 70.0 (C-4′), 69.8 (C-5), 69.5 (C-3), 69.3 (C-3′), 68.9 (C-2), 68.6(C-5′), 61.6 (C-6′), 56.9 (C-2′), 52.6 (OCH_3), 27.8 ($(CH_3)_3$C), 21.1, 21.0, 20.81, 20.80, 20.76, 20.7; HRMS (ESI-TOF) calcd for $C_{37}H_{49}NO_{18}NaSNa$ $[M+Na]^+$: 850.2568; found: 850.2565.

Methyl (2-amino-2-deoxy-α-D-glucopyranosyl)-(1→4)-(1-*p*-tolylthio-α-L-idopyranosid)uronate (S9). To a solution of **S8** (2.0 g, 2.4 mmol) in 30 mL of anhydrous MeOH was added 20 mL of 0.05 M NaOMe in MeOH at RT. After stirring for 2 h, the reaction was quenched with IR-120 resin. The solution was filtered and concentrated under reduced pressure to give the deacetylated disaccharide. To a solution of the disaccharide in anhydrous DCM (50 mL) was added 5 mL of TFA at 0 °C. The reaction was stirred at RT under argon for 2 h and then concentrated under reduced pressure. This crude intermediate was dissolved in MeOH, CF_3CO_2Me (3 mL) and Et_3N (3 mL) were added, and the reaction was stirred at RT for 6 h. After the reaction was complete, the mixture was concentrated, and the resulting residue was purified by silica gel column chromatography (elution with 10:1 → 5:1 DCM/MeOH) to give compound **S9** (1.2 g, 91% yield) as a colorless foam. R_f 0.4 (6:1 DCM/MeOH); ^{1}H NMR (500 MHz, CD_3OD): δ 7.42–7.39 (m, 2H, Ar), 7.17–7.15 (m, 2H, Ar), 5.39 (d, J = 2.5 Hz, 1H, H-1), 5.27 (d, J = 2.6 Hz, 1H, H-5), 5.13 (d, J = 3.5 Hz, 1H, H-1′), 4.07 (t, J = 3.0 Hz, 1H, H-4), 4.03 (t, J = 3.8 Hz, 1H, H-3), 4.02 (dd, J = 10.6, 3.5 Hz, 1H, H-2′), 3.83 (s, 3H, OCH_3), 3.83–3.76 (m, 3H, H-6′, H-2), 3.67 (dd, J = 10.6, 8.4 Hz, 1H, H-3′), 3.52–3.44 (m, 2H, H-5′, H-4′), 2.35 (s, 3H, CH_3Ph); ^{13}C NMR (100 MHz, CD_3OD): δ 170.3 (CO$_2$Me), 158.1 (q, $^2J_{C,F}$ = 37.1 Hz, CF_3C=O), 135.5 (Ar), 131.3 (Ar), 129.3 (Ar), 128.4 (Ar), 116.3 (q, $^1J_{C,F}$ = 286.4 Hz, CF_3), 95.7 (C-1′), 89.2 (C-1), 73.7 (C-4), 73.1 (C-5′), 71.2 (C-3′), 70.9 (C-2), 70.1 (C-4′), 68.2 (C-5), 66.2 (C-3), 60.8 (C-6′), 54.3 (C-2′), 51.6 (OCH_3), 19.7 (CH$_3$Ph); HRMS (ESI-TOF) calcd for $C_{22}H_{28}NO_{11}F_3SNa$ $[M+Na]^+$: 594.1233; found: 594.1227.

Methyl (2-deoxy-4,6-*O*-2-naphthylidene-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(1-tolylthio-α-L-idopyranosid)uronate (S10). To a solution of disaccharide **S9** (1.1 g, 1.9 mmol) in CH_3CN (25 mL) were added $NapCH(OMe)_2$ (0.78 g, 3.9 mmol) and *p*-toluenesulfonic acid (70 mg, 0.37 mmol) under argon. The reaction was heated at 50 °C for 3 h, then quenched with Et_3N (69 μL, 0.49 mmol), and concentrated. Purification by silica gel column chromatography (elution with 2:1 → 1:2 hexanes/EtOAc) gave compound **S10** (1.2 g, 87%) as a colorless foam. R_f 0.37 (1:1 hexanes/EtOAc); ^{1}H NMR (500 MHz, CD_3COCD_3): δ 8.49 (d, *J* = 8.8 Hz, 1H, NH), 8.04 (s, 1H, Ar), 7.98–7.94 (m, 3H, Ar), 7.67–7.65 (m, 1H, Ar), 7.58–7.55 (m, 2H, Ar), 7.45–7.42 (m, 2H, Ar), 7.20–7.18 (m, 2H, Ar), 5.84 (s, 1H, $CH(O)_2$), 5.55 (d, *J* = 2.3 Hz, 1H, H-1), 5.31–5.29 (m, 2H, H-1′, H-5), 4.97–4.93 (m, 2H, OH), 4.82 (d, *J* = 4.9 Hz, 1H, OH), 4.31 (dd, *J* = 9.9, 4.6 Hz, 1H, H-6′), 4.25–4.21 (m, 2H, H-2′, H-3), 4.18 (t, *J* = 3.0 Hz, 1H, H-4), 4.04–3.95 (m, 2H, H-3′, H-2), 3.91 (t, *J* = 9.9 Hz, 1H, H-6′), 3.89 (s, 3H, OCH_3), 3.81 (td, *J* = 9.6, 4.6 Hz, 1H, H-5′), 3.73 (t, *J* = 9.4 Hz, 1H, H-4′), 2.34 (s, 3H, CH_3Ph); ^{13}C NMR (125 MHz, CD_3COCD_3): δ 169.5 (CO_2Me), 157.2 (q, $^2J_{C,F}$ = 36.2 Hz, CF_3C=O), 136.9 (Ar), 135.6 (Ar), 133.6 (Ar), 133.0 (Ar), 132.9 (Ar), 131.0 (Ar), 129.6 (Ar), 128.2 (Ar), 127.7 (Ar), 127.6(Ar), 126.4 (Ar), 126.2 (Ar), 125.7 (Ar), 124.2 (Ar), 116.3 (q, $^1J_{C,F}$ = 286.3 Hz, CF_3), 101.7 ($CH(O)_2$), 96.8 (C-1′), 88.8 (C-1), 81.8 (C-4′), 74.8 (C-4), 71.2 (C-2), 68.7 (C-3′), 68.4 (C-5), 68.3 (C-6′), 66.7 (C-3), 63.7 (C-5′), 54.8 (C-2′), 51.6 (OCH_3), 21.2 (CH_3Ph); HRMS (ESI-TOF) calcd for $C_{33}H_{34}NO_{11}F_3SNa$ $[M+Na]^+$: 732.1702; found: 732.1686.

Methyl (2-deoxy-4,6-*O*-2-naphthylidene-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(1-*p*-tolylthio-2-*O*-((2,2,2-trichloroethoxy)carbonyl)-α-L-idopyranosid)uronate (S11). To a solution of **S10** (0.21 g, 0.29 mmol) in anhydrous toluene (18 mL) were added *n*-Bu_2SnO (0.15 g, 0.58 mmol), TrocCl (0.19 g, 0.88 mmol) and TBAI (0.11 g, 0.29 mmol). The reaction was stirred at 65 °C for 1 h. The mixture was then diluted with EtOAc (300 mL), and the organic layer was washed with saturated aq. $NaHCO_3$ (300 mL) and brine (300 mL), and dried over Na_2SO_4. The solution was concentrated, and the crude residue was purified by silica gel column chromatography (elution with 3:1 → 2:1 hexanes/EtOAc) to give compound **S11 (**0.16 g, 64%) as a colorless foam. ^{1}H NMR (500 MHz, CD_3COCD_3): δ 8.14 (d, *J* = 8.8 Hz, 1H, NH), 8.05 (s, 1H, Ar), 7.98–7.94 (m, 3H, Ar), 7.68–7.66 (m, 1H, Ar), 7.58–7.55 (m, 2H, Ar), 7.45–7.43 (m, 2H, Ar), 7.22–7.20 (m, 2H, Ar), 5.85 (s, 1H, $CH(O)_2$), 5.58 (d, *J* = 7.4 Hz, 1H, H-1), 5.33 (d, *J* = 3.7 Hz, 1H, H-1′), 5.27 (d, *J* = 5.4 Hz, 1H, OH), 5.06 (d, *J* = 12.1 Hz, 1H, CCl_3CH_2O), 5.04 (d, *J* = 5.0 Hz, 1H, H-5), 4.93 (d, *J* = 12.1 Hz, 1H, CCl_3CH_2O), 4.87 (d, *J* = 4.4 Hz, 1H, OH), 4.80 (t, *J* = 7.4 Hz, 1H, H-2), 4.43–4.39 (m, 1H, H-3), 4.36 (dd, *J* = 9.9, 4.8 Hz, 1H, H-6′), 4.23–4.19 (m, 1H, H-2′), 4.15 (dd, *J* = 7.5, 5.1 Hz, 1H, H-4), 4.09–4.04 (m, 1H, H-3′), 4.02–3.97 (m, 1H, H-5′), 3.89 (t, *J* = 9.9 Hz, 1H, H-6′), 3.86 (s, 3H, OCH_3), 3.74 (t, *J* = 9.3 Hz, 1H, H-4′), 2.36 (s, 3H, CH_3Ph); ^{13}C NMR (125 MHz, CD_3COCD_3): δ 169.1 (*C*=$OOCH_3$), 156.9 (q, $^2J_{C,F}$ = 37.5 Hz, CF_3*C*=O), 153.2 (O*C*=$OOCH_2$), 137.9 (Ar), 135.5 (Ar), 133.7 (Ar), 132.9 (Ar), 132.2 (Ar), 129.7 (Ar), 128.2 (Ar), 127.7 (Ar), 127.6(Ar), 126.4 (Ar), 126.2 (Ar), 125.7 (Ar), 124.2 (Ar), 116.1 (q, $^1J_{C,F}$ = 285 Hz, CF_3), 101.6 ($CH(O)_2$), 99.8 (C-1′), 94.6 (CCl_3), 83.8 (C-1), 82.0 (C-4′), 77.9 (C-4), 76.8 (C-2), 76.7 (CCl_3*C*H_2O), 72.3 (C-5), 69.3 (C-3), 68.3 (C-6′), 68.0 (C-3′), 63.9 (C-5′), 55.1 (C-2′), 51.7 (OCH_3), 20.2 (*C*H_3Ph); HRMS (ESI-TOF) calcd for $C_{36}H_{35}NO_{13}Cl_3F_3SNa$ $[M+Na]^+$: 906.0744; found: 906.0750. Note: Dibutyltin oxide (*n*-Bu_2SnO) is highly toxic. Obtain special instructions before use or do not handle until all safety precautions have been read and understood.

Methyl (3-*O*-acetyl-2-deoxy-4,6-*O*-2-naphthylidene-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(3-*O*-acetyl-1-*p*-tolylthio-2-*O*-((2,2,2-trichloroethoxy)carbonyl)-α-L-idopyranosid)uronate (S12). To a solution of **S11**(0.25 g, 0.28 mmol) in pyridine (3.0 mL) was added acetic anhydride (0.80 mL) dropwise at 0 °C. After stirring at RT for 2 h, the mixture was concentrated, and the residue was dissolved in DCM (20 mL). The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. Purification by silica gel column chromatography (elution with 4:1 → 3:1 hexanes/EtOAc) gave compound **S12** (0.25 g, 91%) as a colorless foam. R_f 0.53 (2:1 hexanes/EtOAc); ^{1}H NMR (500 MHz, CD_3COCD_3): δ 8.00 (s, 1H, Ar), 7.96–7.90 (m, 4H, Ar, NH), 7.63–7.61 (m, 1H, Ar), 7.58–7.54 (m, 2H, Ar), 7.48–7.45 (m, 2H, Ar), 7.24–7.21 (m, 2H, Ar), 5.86 (s, 1H, $CH(O)_2$), 5.78 (d, J = 5.8 Hz, 1H, H-1), 5.60 (t, J = 6.2 Hz, 1H, H-3), 5.43 (dd, J = 10.5, 9.5 Hz, 1H, H-3′), 5.33 (d, J = 3.7 Hz, 1H, H-1′), 5.18 (d, J = 4.4 Hz, 1H, H-5), 5.08 (d, J = 12.1 Hz, 1H, CCl_3CH_2O), 4.99 (d, J = 12.1 Hz, 1H, CCl_3CH_2O), 4.92 (t, J = 6.0 Hz, 1H, H-2), 4.46–4.41 (m, 3H, H-4, H-2′, H-6′), 4.15 (td, J = 9.9, 4.8 Hz, 1H, H-5′), 4.01 (t, J = 9.6 Hz, 1H, H-4′), 3.93 (t, J = 10.2 Hz, 1H, H-6′), 3.90 (s, 3H, OCH_3), 2.36 (s, 3H, CH_3Ph), 2.12 (s, 3H, CH_3C=O), 2.00 (s, 3H, CH_3C=O); ^{13}C NMR (125 MHz, CD_3COCD_3): δ 169.7 (3′-O*C*=OCH_3), 168.8 (3-O*C*=OCH_3), 168.7 (*C*=$OOCH_3$), 157.0 (q, $^2J_{C,F}$ = 37.5 Hz, CF_3*C*=O), 153.0 (O*C*=$OOCH_2$), 138.3 (Ar), 135.2 (Ar), 133.7 (Ar), 132.9 (Ar), 132.5 (Ar), 129.8 (Ar), 129.3 (Ar), 128.2 (Ar), 127.8 (Ar), 127.6(Ar), 126.4 (Ar), 126.2 (Ar), 125.6 (Ar), 124.0 (Ar), 115.8 (q, $^1J_{C,F}$ = 287 Hz, CF_3), 101.4 ($CH(O)_2$), 98.6 (C-1′), 94.6 (CCl_3), 84.1 (C-1), 78.8 (C-4′), 76.8 (CCl_3*C*H_2O), 73.9 (C-2),73.3 (C-4), 71.0 (C-5), 69.1 (C-3), 69.0 (C-3′), 68.0 (C-6′), 64.1 (C-5′), 52.8 (C-2′),

51.9 (OCH_3), 20.2 (CH_3Ph), 19.9 ($CH_3C{=}O$), 19.7 ($CH_3C{=}O$); HRMS (ESI-TOF) calcd for $C_{40}H_{39}NO_{15}F_3SCl_3Na$ $[M+Na]^+$: 990.0956; found: 990.0967.

S13

S13-α–isomer

Methyl (3-*O*-acetyl-2-deoxy-4,6-*O*-2-naphthylidene-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(3-*O*-acetyl-1-O-allyl-2-*O*-((2,2,2-trichloroethoxy)carbonyl)-α-L-idopyranosid)uronate (S13). A mixture of donor **S12** (50 mg, 51 μmol), AgOTf (40 mg, 0.15 mmol), and 4 Å molecular sieves (0.10 g) in Et_2O (4.0 mL) was stirred at – 78 ºC. After 30 min, *p*-toluenesulfonyl chloride (*p*-TolSCl) (10 μL, 72 μmol) was added via a micro-syringe. After five minutes when TLC indicated that the donor was completely activated, a solution of allyl alcohol (4.5 mg, 77 μmol) and 2,4,6-tri-*tert*-butylpyrimidine (TTBP) (26 mg, 0.10 mmol) in Et_2O (1.0 mL) was added. The reaction was stirred for an additional 1 h, then quenched with Et_3N (0.050 mL), and concentrated. Purification by silica gel column chromatography (elution first with 5:1 → 4:1 hexanes/EtOAc) gave the α–isomer of **S13** (9.0 mg, 20% yield) as an off-white foam. R_f 0.41 (2:1 hexanes/EtOAc); ^{1}H NMR (500 MHz, CD_3COCD_3): δ 8.03–7.93 (m, 5H, Ar, NH), 7.67–7.64 (m, 1H, Ar), 7.61–7.57 (m, 2H, Ar), 5.97 (dddd, J = 17.2, 10.5, 5.7, 4.9 Hz, 1H, $CH_2{=}CH$), 5.90 (s, 1H, $CH(O)_2$), 5.58 (t, J = 6.4 Hz, 1H, H-3), 5.45 (dd, J = 10.6, 9.6 Hz, 1H, H-3′), 5.38 (d, J = 4.8 Hz, 1H, H-1), 5.37 (dt, J = 17.2, 1.7 Hz, 1H, $CH_2{=}CH$), 5.34 (d, J = 3.7 Hz, 1H, H-1′), 5.23 (dt, J = 10.5, 1.5 Hz, 1H, $CH_2{=}CH$), 5.02 (d, J = 12.1 Hz, 1H, CCl_3CH_2O), 5.00 (d, J = 12.1 Hz, 1H, CCl_3CH_2O), 4.98 (d, J = 4.5 Hz, 1H, H-5), 4.86 (dd, J = 6.5, 4.8 Hz, 1H, H-2), 4.49–4.44 (m, 3H, H-4, H-2′, H-6′), 4.36 (ddt, J = 13.3, 4.9, 1.7 Hz, 1H, $CH_2CH_2{=}CH$), 4.18 (ddt, J = 13.3, 5.7, 1.5

Hz, 1H, C*H*$_2$CH$_2$=CH), 4.18–4.15 (m, 1H, H-5′), 4.05 (t, *J* = 9.5 Hz, 1H, H-4′), 3.97 (t, *J* = 10.0 Hz, 1H, H-6′), 3.93 (s, 3H, OCH$_3$), 2.10 (C*H*$_3$C=O), 2.03 (C*H*$_3$C=O); ^{13}C NMR (125 MHz, CD$_3$COCD$_3$): δ 169.8 (C=O), 169.1 (C=O), 168.9 (C=O), 153.1 (O*C*=OOCH$_2$), 135.2 (Ar), 133.9 (Ar), 133.7 (CH$_2$=*C*H), 132.9 (Ar), 128.3 (Ar), 127.8 (Ar), 127.6 (Ar), 126.5 (Ar), 126.2 (Ar), 125.7 (Ar), 124.1 (Ar), 116.4 (*C*H$_2$=CH), 101.5 (CH(O)$_2$), 98.3 (C-1′), 96.8 (C-1), 94.6 (CCl$_3$), 78.8 (C-4′), 76.7 (CCl$_3$*C*H$_2$O), 74.2 (C-2), 73.2 (C-4), 70.0 (C-5), 69.11 (C-3), 69.07 (*C*H$_2$CH$_2$=CH, C-3′), 68.0 (C-6′), 64.0 (C-5′), 52.8 (C-2′), 51.9 (OCH$_3$), 19.9 (*C*H$_3$C=O), 19.7 (*C*H$_3$C=O); HRMS (FAB) calcd for $C_{36}H_{38}NO_{16}F_3Cl_3$ $[M+H]^+$: 902.1208; found: 902.1198. Further elution with 4:1 → 3:1 hexanes/EtOAc gave the β-isomer of **S13** (32 mg, 71%) as a white foam. R_f 0.25 (2:1 hexanes/EtOAc); ^{1}H NMR (500 MHz, CD$_3$COCD$_3$): δ 8.03–7.94 (m, 5H, Ar, NH), 7.65–7.63 (m, 1H, Ar), 7.60–7.57 (m, 2H, Ar), 5.94 (dddd, *J* = 17.1, 10.6, 6.0, 4.9 Hz, 1H, CH$_2$=C*H*), 5.89 (s, 1H, CH(O)$_2$), 5.76 (t, *J* = 6.0 Hz, 1H, H-3), 5.42 (dd, *J* = 10.5, 9.5 Hz, 1H, H-3′), 5.41 (d, *J* = 4.0 Hz, 1H, H-1′), 5.38 (dt, *J* = 17.1, 1.6 Hz, 1H, C*H*$_2$=CH), 5.23 (d, *J* = 2.8 Hz, 1H, H-1), 5.23 (dt, *J* = 10.4, 1.4 Hz, 1H, C*H*$_2$=CH), 5.07 (d, *J* = 12.1 Hz, 1H, CCl$_3$CH$_2$O), 4.92 (dd, *J* = 6.0, 2.8 Hz, 1H, H-2), 4.90 (d, *J* = 12.1 Hz, 1H, CCl$_3$CH$_2$O), 4.84 (d, *J* = 3.6 Hz, 1H, H-5), 4.47 (dd, *J* = 10.5, 4.0 Hz, 1H, H-2′), 4.43 (ddt, *J* = 13.3, 4.9, 1.5 Hz, 1H, C*H*$_2$CH$_2$=CH), 4.36 (dd, *J* = 9.3, 3.8 Hz, 1H, H-6′), 4.34 (dd, *J* = 5.5, 3.6 Hz, 1H, H-4), 4.21 (ddt, *J* = 13.3, 6.0, 1.4 Hz, 1H, C*H*$_2$CH$_2$=CH), 4.05 (t, *J* = 9.4 Hz, 1H, H-4′), 3.99 (td, *J* = 9.5, 4.2 Hz, 1H, H-5′), 3.95 (t, *J* = 9.3 Hz, 1H, H-6′), 3.89 (s, 3H, OCH$_3$), 2.16 (C*H*$_3$C=O), 2.03 (C*H*$_3$C=O); ^{13}C NMR (125 MHz, CD$_3$COCD$_3$): δ 170.0 (3′-O*C*=OCH$_3$), 169.1 (3-O*C*=OCH$_3$), 168.4 (*C*=OOCH$_3$), 153.3 (O*C*=OOCH$_2$), 135.1 (Ar), 133.7 (CH$_2$=*C*H), 133.6 (Ar), 132.9 (Ar), 128.3 (Ar), 127.8 (Ar), 127.6 (Ar), 126.5 (Ar), 126.2 (Ar), 125.7 (Ar), 124.1 (Ar), 117.1 (*C*H$_2$=CH), 101.5 (CH(O)$_2$), 98.0 (C-1′), 96.0 (C-1), 94.6 (CCl$_3$), 78.5 (C-4′), 76.7 (CCl$_3$*C*H$_2$O), 74.3 (C-4), 73.3 (C-2), 71.9 (C-5), 69.5 (*C*H$_2$CH$_2$=CH, C-3′), 68.1 (C-3), 68.0 (C-6′), 64.0 (C-5′), 52.9 (C-2′), 51.8 (OCH$_3$), 19.9

(CH_3C=O), 19.7 (CH_3C=O); HRMS calcd for $C_{36}H_{38}NO_{16}F_3Cl_3$ $[M+H]^+$: 902.1208; found: 902.1213.

Methyl (3-*O*-acetyl-2-deoxy-6-*O*-2-naphthylmethyl-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(3-*O*-acetyl-1-O-allyl-2-*O*-(2,2,2-trichloroethoxy)carbonyl-β-L-idopyranosid)uronate (20). To a suspension of compound **S13** (70 mg, 0.08 mmol) in DCM (5.0 mL) were added triethylsilane (45 mg, 0.38 mmol) and BF_3•Et_2O (15 mg, 0.11 mmol) at 0 °C. After stirring for 1 h at 0 °C, the reaction was diluted with DCM (20 mL) and washed with saturated aq. $NaHCO_3$, and brine. The organic layer was dried over Na_2SO_4, concentrated, and the residue was purified by silica gel column chromatography (elution with 3:1 → 3:2 hexanes/EtOAc) to give compound **20** (56 mg, 80%) as a colorless foam. R_f 0.3 (1:1 hexanes/EtOAc); ^{1}H NMR (500 MHz, CD_3COCD_3, mixture of rotamers): δ 7.94–7.86 (m, 4H, Ar), 7.55–7.45 (m, 3H, Ar), 7.43 (d, *J* = 9.0 Hz, 1H, NH), 5.90–5.80 (m, 2H, H-3, Allyl-C*H*), 5.33–5.27 (m, 1H, Allyl-C*H*), 5.25 (d, *J* = 3.7 Hz, 1H, H-1′), 5.19–5.15 (m, 2H, H-1, Allyl-C*H*), 5.10 (dd, *J* = 10.8, 8.6 Hz, 1H, H-3′), 4.96 (d, *J* = 12.1 Hz, 1H, CCl_3C*HA*), 4.91–4.84 (m, 3H, H-2, CCl_3C*HB*, OH), 4.83 (d, *J* = 4.6 Hz, 1H, H-5), 4.76 (ABq, *J* = 12.4 Hz, 2H, CH_2Nap), 4.32–4.27 (m, 1H, Allyl-C*H*), 4.24–4.18 (m, 2H, H-2′, H-4), 4.12–4.06 (m, 1H, Allyl-C*H*), 3.85 (dd, *J* = 10.0, 1.2 Hz, 1H, H-6a′), 3.82–3.75 (m, 3H, H-4′, H-5′, H-6b′), 3.75 (s, 3H, OCH_3), 2.04 (s, 3H, CH_3), 1.97 (s, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, mixture of rotamers): δ 171.5 (C=OCH_3), 170.1 (C=OCH_3), 169.4 (C=$OOCH_3$), 157.7 (q, $^2J_{C,F}$ = 37.5 Hz, CF_3C=O, rotamer-1), 157.6 (q, $^2J_{C,F}$ = 36.2 Hz, CF_3C=O, rotamer-2), 154.2 (CCl_3CH_2OC=O), 137.2 (Ar), 134.4 (Ar), 134.3 (-CH_2CH=CH_2), 133.9 (Ar), 128.7 (2C-Ar), 128.5

(Ar), 126.9 (Ar), 126.7 (Ar), 126.6 (Ar), 126.5 (Ar), 118.1 (-CH_2CH=CH_2), 116.7 (q, $^1J_{C,F}$ = 285.0 Hz, CF_3), 98.6 (C-1′), 96.6 (C-1), 95.5 (CCl_3), 77.5 CCl_3*C*HOC=O), 75.3 (C-2), 75.2 (C-4), 74.2 (C-3′), 73.9 (Nap*C*H_2), 73.75 (C-5′, rotamer-1), 73.72 (C-5′, rotamer-2), 72.1 (C-5), 70.4 (*C*H_2-CH=CH2), 70.0 (C-6′), 69.0 (C-4′, rotamer-1), 68.9 (C-4′, rotamer-2), 68.6 (C-3), 53.5 (C-2′, rotamer-1), 53.4 (C-2′, rotamer-2), 52.52 (OCH_3, rotamer-1), 52.51 (OCH_3, rotamer-2), 20.8 (*C*H_3), 20.7 (*C*H_3); HRMS (ESI-TOF) calcd for $C_{36}H_{39}Cl_3F_3NO_{16}Na$ $[M+Na]^+$: 926.1184; found: 926.1188.

Methyl (2,3-*O*-acetyl-2-azido-2-deoxy-6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-acetyl-2-*O*-((9*H*-fluoren-9-yl)methoxycarbonyl)-β-L-idopyranoosyluronate)-(1→4)-(3-*O*-acetyl-2-deoxy-6-*O*-2-naphthylmethyl-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(3-*O*-acetyl-1-*O*-allyl-2-*O*-(2,2,2-trichloroethoxy)carbonyl-β-L-idopyranosid)uronate (S14). A mixture of donor **19** (20 mg, 18 μmol), AgOTf (14 mg, 55 μmol), and 4 Å molecular sieves (0.10 g) in Et_2O (2.0 mL) was stirred at – 78 ºC. After 30 min, *p*-toluenesulfonyl chloride (*p*-TolSCl) (5.0 mg, 27 μmol, 3.5 μL) was added via a micro-syringe. After 5 min when TLC indicated that the donor was completely activated, a solution of the acceptor **20** (16 mg, 18 μmol) in Et_2O and 2,4,6-tri-*tert*-butylpyrimidine (TTBP) (9.1 mg, 36 μmol) was added. The reaction was stirred for an additional 15 min, then warmed up to – 20 ºC, and stirred for 6 h. The reaction was then diluted with DCM and quenched

by the addition of Et_3N (0.050 mL) and filtered. The residue was purified by silica gel column chromatography (elution with 3:1 → 3:2 hexanes/EtOAc) to give compound **S14** (13 mg, 40%) as a colorless foam. R_f 0.4 (3:2 hexanes/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86–7.57 (m, 12H, Ar), 7.47–7.30 (m, 12H, Ar), 7.26–7.20 (m, 1H, Ar), 7.08 (d, *J* = 9.2 Hz, 1H, NH), 5.84–5,72 (m, 1H, C*H*=CH_2), 5.58 (dd, *J* = 8.4, 7.1 Hz, 1H, H-3), 5.53 (t, *J* = 3.6 Hz, 1H, H-3″), 5.38 (dd, *J* = 10.6, 9.3 Hz, 2H, H-3′, H-3‴), 5.35–5.13 (m, 6H, H-1′, H-1‴, H-4′, H-4‴, CH_2=CH), 5.07 (d, *J* = 3.3 Hz, 1H, H-1), 4.99 (d, *J* = 1.6 Hz, 1H, H-1″), 4.80 (dd, *J* = 7.1, 3.3 Hz, 1H, H-2), 4.78 (d, *J* = 11.9 Hz, 1H, C$H_{2A}$$CCl_3$), 4.76–4.71 (m, 3H, C$H_{2B}$$CCl_3$, OC$H_2$Nap), 4.68 (dd, *J* = 3.6, 1.6 Hz, 1H, H-2″), 4.51 (d, *J* = 3.9 Hz, 1H, H-5), 4.83 (dd, *J* = 10.4, 7.5 Hz, 1H, CH_{2a}- Fluoren), 4.44–4.38 (m, 2H, H-5″, CH_{2b}- Fluoren), 4.34–4.23 (m, 3H, H-2′, CH_{2a}CH=CH_2, OCO_2CH_2-C*H*), 4.08–4.00 (m, 3H, H-4, H-6a′, CH_{2b}CH=CH_2), 3.98 (dd, *J* = 3.6, 2.8 Hz, 1H, H-4″), 3.87 (dd, *J* = 10.8, 1.1 Hz, 1H, H-6b′), 3.85-3.68 (m, 4H, H-5′, H-5‴, H-6‴), 3.67 (s, 3H, OCH_3), 3.62 (s, 3H, OCH_3), 3.31 (dd, *J* = 10.6, 3.5 Hz, 1H, H-2‴), 2.03 (s, 3H, CH_3), 2.02 (s, 3H, CH_3), 2.01 (s, 3H, CH_3), 2.00 (s, 3H, CH_3), 1.82 (s, 3H, CH_3), 1.02 (s, 9H, $OC(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5 (C=O), 170.1 (C=O), 169.6 (C=O), 169.3 (C=O), 168.4 (C=O), 168.3 (C=O), 168.2 (C=O), 154.8 (C=O), 153.6 (C=O), 143.6 (Ar), 141.39 (Ar), 141.37 (Ar), 136.1 (Ar), 135.9 (Ar), 135.7 (Ar), 133.5 (Ar), 133.1 (Ar), 133.02 (Ar), 133.00 (Ar), 132.9 (*C*H=CH_2), 130.2 (Ar), 129.88 (Ar), 129.87 (Ar), 129.8 (Ar), 128.1 (Ar), 128.05 (Ar), 127.97 (Ar), 127.9 (Ar), 127.84 (Ar), 127.82 (Ar), 127.81 (Ar), 127.78 (Ar), 127.4 (Ar), 127.34 (Ar), 127.29 (Ar), 126.11 (Ar), 126.08 (Ar), 125.8 (Ar), 125.7 (Ar), 125.5 (Ar), 125.44 (Ar), 125.43 (Ar), 120.1 (Ar), 120.0 (Ar), 118.9 (*C*H_2=CH), 98.5 (C-1″), 96.9 (C-1′/(C-1‴), 96.2 (C-1′/(C-1‴), 94.9 (C-1), 94.3 (*C*Cl_3), 77.4 (*C*H_2CCl_3), 74.0 (C-5″), 73.7 (C-2), 73.4 (*C*H_2Nap), 73.0 (C-4), 72.1 (C-4′/C-4‴), 71.6 (C-5), 71.39 (C-5‴), 71.00 (C-5′), 70.8 (*C*H_2-Fluoren), 70.4 (4C, C-2″, C-3′, C-3‴, C-4″), 69.8 (*C*H_2CH=CH_2), 68.4 (2C, C-4′/C-4‴, C-6′), 67.9 (C-3), 66.3 (C-3″), 61.9 (C-6‴), 60.8 (C-2‴),

52.8 (2C, C-2′. O*C*H_3), 52.6 (O*C*H_3), 46.8 (OCO_2CH_2-*C*H), 26.8 (C(*C*H_3)$_3$), 20.9 (*C*H_3), 20.8 (*C*H_3), 20.7 (*C*H_3), 20.64 (*C*H_3), 20.56 (*C*H_3), 19.3 (*C*(CH_3)$_3$); HRMS (ESI-TOF) calcd for $C_{86}H_{92}Cl_3F_3N_4O_{31}SiNa$ $[M+Na]^+$: 1889.4430; found: 1889.4426; gHSQC 2-D NMR (without ^{1}H decoupling): $^1J_{C1,H1}$ = 170.7 Hz, $^1J_{C1',H1'}$ = $^1J_{C1''',H1'''}$ = 174.6 Hz, and $^1J_{C1'',H1''}$ = 161.1 Hz. The peaks of H-2, H-3, and H-4 showed large coupling constant values ($^1J_{H2\text{-}H3}$ = 7.1 Hz and $^1J_{H3\text{-}H4}$ = 8.4) for terminal IdoA, which indicates that the terminal IdoA residues adopt primarily the $^4C_1$ conformation. This is further supported by the large gHSQC $^1J_{C1,H1}$ coupling constant (170.7 Hz) value. In contrast, the coupling constants of $^3J_{H2''\text{-}H3''}$, and $^3J_{H3''\text{-}H4''}$ are 3.6 Hz, which indicates that these IdoA residues are primarily in the $^1C_4$ conformation.[6] The coupling constants of $^1J_{C1'',H1''}$ (161.1 Hz) are below 170 Hz, which confirms the β configuration of the newly formed IdoA stereocenters.[7]

4. General Methods for HILIC MS and MS/MS

4-1. Methods

1. LC conditions. Column: Luna HILIC column (2.0×50 mm^2, 200 Å, Phenomenex, Torrance, CA). Mobile phase A: 5 mM ammonium acetate prepared with HPLC grade water. Mobile phase B: 5 mM ammonium acetate prepared in 98% HPLC grade CH_3CN with 2% of HPLC grade water. The gradient was used from 5% A to 70% A in 7 min then reset to 5% A at a flow rate of 250 μL/min. See Reference 8 for details.

2. MS conditions. The optimized parameters included a spray voltage of 4.2 kV, a capillary voltage of -40 V, a tube lens voltage of -50 V, a capillary temperature of 275 ℃, a sheath flow rate of 30, and an auxiliary gas flow rate of 6. All mass spectra were acquired at a resolution 60000 with 200-2000 Da mass range.

3. Data process. Charge deconvolution was autoprocessed by DeconTools software, structural assignment was done by automatic processing using GlycReSoft 1.0 software. Results was presented as [ΔHexA, HexA, GlcN, Ac, SO_3]

4-2. Conclusions

Only $^{0,2}A_2$ of HexA-GlcN (295.1 *m/z*) was found without $^{0,2}A_2$ of GlcN-HexA (294.1 *m/z*) in the heparosan sample. Both $^{0,2}A_2$ of HexA-GlcN and $^{0,2}A_2$ of GlcN-HexA were found in the *N*-de-acetylated heparosan, heparin, and *N*-acetylated heparin samples. There was only HexA-GlcN existing on heparosan samples; both HexA-GlcN and GlcN-HexA were existing on *N*-de-acetylated heparosan, heparin and *N*-acetylated heparin samples.

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6. Nuclear Magnetic Resonance (NMR) Spectra

GlcN-IdoA peracetate_1H

GlcN-IdoA peracetate_13C
171.43
170.77
170.34
169.51
169.49
169.28
168.39
98.67
90.44
77.42 cdcl3
77.16 cdcl3
76.91 cdcl3
72.89
70.70
70.66
69.03
68.66
67.95
67.73
61.75
52.92
51.91
23.18
20.93
20.85
20.84
20.78
20.74
20.70
f1 (ppm)
1
AcO
AcO
AcHN
OAc
MeO2C
OAc
AcO
OAc

GlcN-IdoA peracetate_COSY
1
AcO
AcO
AcHN
OAc
O
MeO2C
O
AcO
O
OAc
OAc
f1 (ppm)
f2 (ppm)

GlcN-IdoA peracetate_HSQC
1
C-1-H-1
C-1'-H-1'
f1 (ppm)
f2 (ppm)

GlcN-IdoA peracetate_HMBC
C-4-H-1'
C-1'-H-4
1
f1 (ppm)
f2 (ppm)

PROTON01
NP_1_147_Pure1
1b
f1 (ppm)
0.97
1.04
1.00
1.00
1.11
0.99
1.00
1.07
1.99
1.02
3.04
1.01
2.86
2.85
2.90
2.93
2.85
2.83

CARBON01
NP_1_147_Pure1
170.55
169.77
169.69
169.61
168.81
168.40
167.95
98.39
90.81
77.23 cdcl3
76.98 cdcl3
76.72 cdcl3
72.84
70.48
68.92
68.56
67.96
66.69
66.04
61.21
61.07
52.75
20.79
20.76
20.68
20.60
20.53
20.50
1b
f1 (ppm)

gCOSY01
NP_1_147_Pure1
1b
f1 (ppm)
f2 (ppm)

HSQCAD01
NP_1_147_Pure1
1b
GlcN-IdoA
C-1-H-1
C-1'-H-1'
f2 (ppm)
f1 (ppm)

gHMBCAD01
NP_1_147_Pure1
C-4-H-1'
C-1'-H-4
1b
f1 (ppm)
f2 (ppm)

WL-1-141-NCbz-OAc-H.1.1.1r

1c

WL-1-141-NCbz-OAc-OAc
1c
170.73
170.71
169.44
169.25
168.91
168.42
167.90
155.67
135.89
128.59
128.44
128.41
97.93
90.14
77.38
77.26
77.06
76.74
71.56
70.87
69.00
68.78
67.59
67.26
66.41
61.42
53.53
52.86
29.72
20.82
20.75
20.72
20.59
20.51
20.44
f1 (ppm)

WL-1-141-NCbz-OAc-COSY.1.1.2rr
1c
f1 (ppm)
f2 (ppm)

WL-1-141-NCbz-OAc-HSQC.1.1.2rr
AcO
AcO
CbzHN
OAc
O
MeO2C
O
OAc
AcO
O
OAc
1c
f2 (ppm)
f1 (ppm)

WL-1-141-NCbz-OAc-HMBC.1.1.2rr
1c
f1 (ppm)
f2 (ppm)

PROTON04
NP_1_69_Pure
MeO2C
AcO
AcO
O
OAc
O
AcO
AcHN
OAc
O
OAc
2
0.96
1.01
2.96
0.99
1.00
2.01
1.03
1.03
1.98
2.97
2.84
2.82
2.75
2.89
5.41
2.82
f1 (ppm)

CARBON01
NP_1_69_P
171.75
170.42
170.22
170.10
169.40
169.29
168.91
166.79
100.99
90.56
77.42 cdcl3
77.16 cdcl3
76.91 cdcl3
76.28
72.83
72.15
71.47
70.64
70.39
69.36
61.51
52.97
51.18
23.13
21.09
20.93
20.78
20.67
20.64
20.54
f1 (ppm)
2

gCOSY03
NP_1_69_Pure
MeO2C
AcO
AcO
O
OAc
O
AcO
AcHN
OAc
O
OAc
2
f1 (ppm)
f2 (ppm)

HSQCAD01
NP_1_69_P
MeO2C
AcO
AcO
O
OAc
O
AcO
AcHN
OAc
OAc
O
2
C-1-H-1
C-1'-H-1'
f2 (ppm)
f1 (ppm)

gHMBCAD01
NP_1_69_P
C-4-H-1'
C-1'-H-4
2
f1 (ppm)
f2 (ppm)

PROTON01
NP_1_76

CARBON01
NP_1_76

5

PROTON02
NP_1_77_L3
MeO2C
OAc
AcO
AcO
O
O
O
AcO
AcHN
OAc
O
OAc
4
0.97
1.00
1.08
0.97
1.97
0.96
1.00
2.09
1.09
1.02
1.15
3.04
3.06
3.04
11.42
2.93
f1 (ppm)

CARBON01
NP_1_77_L3
4
172.16
170.67
170.07
169.63
169.60
169.00
168.82
168.16
98.60
90.79
77.41 cdcl3
77.16 cdcl3
76.91 cdcl3
75.21
74.66
70.65
67.86
67.79
67.27
67.21
61.69
52.70
51.24
23.23
21.17
21.04
20.93
20.91
20.82
20.76
f1 (ppm)

gCOSY01
NP_1_77_L3
4
f1 (ppm)
f2 (ppm)

HSQCAD01
NP_1_77_L3
MeO2C
OAc
AcO
AcO
O
O
O
AcO
AcHN
OAc
OAc
O
4
f2 (ppm)
f1 (ppm)

PROTON01
TH01-084-1a
3
f1 (ppm)
0.95
0.96
1.00
1.00
2.03
1.10
1.97
1.99
1.10
2.79
1.19
3.05
2.84
11.15
2.73

CARBON01
TH01-084-1a
171.58
170.95
170.48
170.39
169.43
169.23
168.85
167.87
97.75
91.58
77.41 cdcl3
77.16 cdcl3
76.91 cdcl3
74.42
74.36
73.01
70.69
70.51
68.85
67.53
61.37
53.11
51.74
23.14
20.88
20.86
20.83
20.82
20.71
20.64
AcO
AcO
AcHN
O
OAc
O
AcO
CO2Me
O
OAc
OAc
3
f1 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200

gCOSY01
TH01-084-1a
3
f1 (ppm)
f2 (ppm)

HSQCAD01
TH01-084-1a
3
f1 (ppm)
f2 (ppm)

WI-1-116-prod-H.1.1r
OAc
AcO
AcO
O
MeO2C
N3
O
7
AcO
O
OAc
SPh
2.13
3.20
1.00
1.06
1.01
1.00
1.00
2.05
1.06
3.05
3.05
1.00
6.16
6.40
3.09
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

WI-1-116-prod-C.1.1.1r
170.67
170.01
169.68
168.96
168.82
134.10
131.84
129.17
127.97
98.59
86.25
73.61
70.60
68.59
68.53
68.06
67.16
61.20
52.68
20.91
20.73
20.68
20.58
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
7
AcO
AcO
OAc
O
N3
O
MeO2C
AcO
O
OAc
SPh

WI-1-116-prod-COSY.1.1.2rr
7
AcO
AcO
OAc
O
MeO2C
N3
O
AcO
O
OAc
SPh
f1 (ppm)
f2 (ppm)

WI-1-116-prod-HSQC.1.1.2rr
7
f1 (ppm)
f2 (ppm)

WI-1-116-prod-HMBC.1.1.2rr
OAc
AcO
AcO
O
MeO2C
OAc
N3
O
O
SPh
AcO
7
f2 (ppm)
f1 (ppm)

WL-1-118-prod-H.1.1.1r
Naph
O
O
HO
O
N3
O
MeO2C
OH
HO
O
SPh
8
0.99
3.04
1.00
4.01
2.99
1.00
0.96
1.00
0.95
0.51
2.50
1.00
1.03
3.96
3.98
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

WL-1-118-prod-C11.1.1r
169.49
136.67
135.51
133.69
132.93
130.33
128.91
128.22
127.77
127.65
126.80
126.44
126.23
125.72
124.17
101.63
96.43
88.62
81.38
81.36
74.11
74.08
69.85
69.74
68.56
68.14
66.65
64.27
64.22
63.52
51.65
8
Naph
O
O
HO
O
N3
O
MeO2C
OH
HO
O
SPh
f1 (ppm)
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20

WL-1-118-prod-COSY.1.1.2rr
Naph
O
O
HO
O
N3
O
MeO2C
OH
HO
O
SPh
8
f1 (ppm)
f2 (ppm)

WL-1-118-prod-HSQC.1.1.2rr
Naph
O
O
HO
O
MeO2C
N3
O
OH
HO
O
SPh
8
f1 (ppm)
f2 (ppm)

WL-1-118-prod-HMBC.1.1.2rr
Naph
O
O
HO
O
MeO2C
N3
O
OH
HO
O
SPh
8
f2 (ppm)
f1 (ppm)

WL-1-119-Prod-H.1.fid
Naph
O
O
HO
O
N3
O
MeO2C
OH
BzO
O
SPh
9
2.06
1.12
3.18
1.12
7.62
3.13
1.00
1.03
0.63
1.01
2.03
0.60
1.03
1.03
1.04
2.44
4.12
1.06
1.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)

WL-1-119-prod-C.1.fid
169.19
165.17
135.60
135.55
133.68
133.12
132.93
130.81
129.95
129.73
128.97
128.56
128.21
127.72
127.66
127.20
126.42
126.23
125.73
124.26
101.63
99.60
85.54
81.92
81.90
76.47
72.10
72.07
69.29
68.77
68.26
67.73
63.96
63.53
51.55
Naph
HO
O
O
O
N3
O
MeO2C
OH
BzO
O
SPh
9
f1 (ppm)

WL-1-119-Prod-COSY.1.1.2rr
Naph
O
O
HO
O
MeO2C
N3
O
OH
BzO
O
SPh
9
f1 (ppm)
f2 (ppm)

WL-1-119-Prod-HSQC.1.1.2rr
Naph
O
O
HO
O
MeO2C
N3
O
OH
BzO
O
SPh
9
f1 (ppm)
f2 (ppm)

WL-1-119-prod-HMBC.2.1.2rr
f2 (ppm)
f1 (ppm)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
180
170
160
150
140
130
120
110
100
90
80
70
60
Naph
O
O
HO
O
MeO2C
N3
O
OH
BzO
O
SPh
9

PROTON01
wl-1-108-run6-column3

10

wl-1-108-fu02-pure-C01.1.18
168.71
165.01
138.51
137.70
135.71
135.51
133.61
133.19
133.08
131.20
130.06
129.85
129.03
128.79
128.35
128.30
128.05
128.02
127.93
127.83
127.70
127.45
127.41
127.32
126.67
126.46
126.29
125.46
124.07
101.23
100.09
86.56
82.26
76.87
76.09
74.10
73.20
72.52
69.56
68.31
68.23
63.62
63.24
51.56
Naph
BnO
O
O
O
N3
O
MeO2C
OBn
BzO
O
SPh
10
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

wl-1-108-run2-pure-COSY.1.1.2rr
Naph
BnO
O
O
O
MeO2C
OBn
N3
O
BzO
O
SPh
10
f1 (ppm)
f2 (ppm)

wl-1-108-run2-pure-HSQC.1.1.2rr
Naph
BnO
MeO2C
OBn
N3
BzO
SPh
10
f2 (ppm)
f1 (ppm)

wl-1-108-run2-pure-HMBC.1.1.2rr
Naph
BnO
O
O
O
MeO2C
OBn
N3
O
BzO
O
SPh
10
f2 (ppm)
f1 (ppm)

wl-1-122-prod-H.1.1.1r

11

wl-1-122-prod-C.1.1.1
205.55
171.75
168.77
138.61
137.79
135.64
135.46
133.65
132.99
130.95
129.02
128.35
128.32
128.16
127.85
127.83
127.78
127.76
127.64
127.48
127.34
126.43
126.22
125.42
124.04
101.27
98.46
85.89
82.36
76.47
74.27
73.73
72.87
72.55
68.86
68.62
68.26
63.51
63.12
51.57
37.38
11
Naph
BnO
N3
MeO2C
OBn
LevO
SPh
f1 (ppm)

wl-1-122-prod-COSY.1.1.2rr
Naph
BnO
O
O
O
MeO2C
N3
O
OBn
LevO
O
SPh
11
f1 (ppm)
f2 (ppm)

wl-1-122-prod-HSQC.1.1.2rr
Naph
O
O
BnO
O
MeO2C
N3
O
OBn
LevO
O
SPh
11
f1 (ppm)
f2 (ppm)

wl-1-122-prod-HMBC.1.1.2rr
Naph
BnO
MeO2C
OBn
N3
LevO
SPh
11
f2 (ppm)
f1 (ppm)

wl-2-13-prod-H.1.1.1r

12

wl-2-13prod-C.1.1.1r
205.67
171.82
168.88
138.92
137.86
135.66
135.55
135.19
133.59
133.42
131.12
129.74
129.72
128.98
128.26
128.10
127.75
127.72
127.65
127.37
96.94
85.09
79.89
79.87
74.48
73.53
73.51
72.96
71.75
70.56
70.46
69.70
69.28
63.08
62.99
51.50
37.38
27.74
26.36
19.01
HO
BnO
OTBDPS
O
MeO2C
N3
O
OBn
LevO
O
SPh
12
f1 (ppm)

wl-2-13-prod-COSY.1.1.2rr
OTBDPS
HO
BnO
O
MeO2C
N3
O
OBn
LevO
O
SPh
12
f1 (ppm)
f2 (ppm)

wl-2-13-prod-HSQC.1.1.2rr
OTBDPS
HO
BnO
O
MeO2C
N3
O
OBn
LevO
O
SPh
12
f1 (ppm)
f2 (ppm)

wl-2-13-prod-HMBC.1.1.2rr
OTBDPS
HO
BnO
O
MeO2C
N3
O
OBn
LevO
O
SPh
12
f2 (ppm)
f1 (ppm)

wl-2-014-prod-H.1.fid

wl-2-014-prod-C1fid
205.65
171.83
168.95
164.71
137.86
137.78
135.58
135.43
135.34
133.44
133.03
132.93
131.13
129.87
129.70
129.65
129.62
129.00
128.75
128.29
128.07
127.97
127.73
127.70
127.69
127.64
127.57
127.39
97.05
85.39
77.89
74.29
72.83
72.61
72.27
71.38
70.58
69.24
69.08
63.08
62.40
51.57
37.35
27.75
26.24
18.84
13
BzO
BnO
OTBDPS
O
MeO2C
OBn
N3
O
LevO
O
SPh
f1 (ppm)

wl-2-014-prod-COSY.3.1.2rr
OTBDPS
BzO
BnO
O
MeO2C
N3
O
OBn
13
LevO
O
SPh
f1 (ppm)
f2 (ppm)

wl-2-014-prod-HSQC.1.1.2rr
OTBDPS
BzO
BnO
O
MeO2C
N3
O
OBn
LevO
O
SPh
13
f2 (ppm)
f1 (ppm)

wl-2-014-prod-HMBC.1.1.2rr
OTBDPS
BzO
BnO
O
MeO2C
N3
O
OBn
LevO
O
SPh
13
f2 (ppm)
f1 (ppm)

wl-2-05-prod-H.1.fid

wl-2-05-prod-C13.jid
168.70
165.03
164.99
157.22
156.85
138.98
137.72
135.56
135.49
133.69
133.07
132.99
131.51
129.77
129.02
128.87
128.39
128.31
127.94
127.83
127.76
127.70
127.54
127.46
127.08
126.70
126.47
126.28
125.53
124.17
120.32
117.47
114.61
111.72
101.38
99.31
87.23
82.95
75.76
75.74
75.49
74.62
74.00
72.46
69.41
68.28
68.00
63.83
54.09
54.00
51.52
Naph
BnO
TFAHN
MeO2C
OBn
BzO
SPh
14
f1 (ppm)

wl-2-05-prod-COSY.1.1.2rr
Naph
O
O
BnO
TFAHN
O
MeO2C
OBn
BzO
O
SPh
14
f1 (ppm)
f2 (ppm)

WL-2-05-prod-HSQC.1.1.2rr
Naph
O
O
BnO
O
MeO2C
TFAHN
O
OBn
BzO
O
SPh
14
f1 (ppm)
f2 (ppm)

wl-2-05-prod-HMBC.1.1.2rr
Naph
O
O
BnO
TFAHN
O
MeO2C
OBn
BzO
O
SPh
14
f1 (ppm)
f2 (ppm)

WL-2-016-prod-H.1.1.1r

15

WI-2-016-prod-C.1.1.1
169.07
168.69
164.84
157.23
156.86
139.01
138.09
135.65
133.72
133.16
133.01
129.77
129.74
128.90
128.31
128.27
127.94
127.88
127.73
127.57
127.43
127.08
126.72
126.50
126.32
125.57
124.16
120.33
117.48
114.62
101.46
99.97
98.75
82.99
80.96
75.78
75.76
75.20
75.01
74.04
71.84
68.34
67.82
67.27
65.47
63.82
54.08
53.99
51.34
29.72
27.33
Naph
O
O
BnO
TFAHN
O
O
MeO2C
OBn
BzO
O
OCH2CO2t-Bu
15
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

WL-2-016-prod-COSY.1.1.2rr
Naph
O
O
BnO
O
TFAHN
O
MeO2C
OBn
15
BzO
O
OCH2CO2t-Bu
f1 (ppm)
f2 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5

WL-2-016-prod-HSQC.1.1.2rr
Naph
O
O
BnO
TFAHN
O
MeO2C
OBn
BzO
O
OCH2CO2t-Bu
15
f2 (ppm)
f1 (ppm)

WL-2-016-prod-HMBC-Acetone.2.1.2rr
Naph
BnO
TFAHN
MeO2C
OBn
BzO
OCH2CO2t-Bu
15
f1 (ppm)
f2 (ppm)

WL-2-017-prod-H.1.1.1r
Naph
O
O
BnO
TFAHN
O
MeO2C
OBn
HO
O
OCH2CO2t-Bu
16
0.64
1.22
3.27
1.21
2.39
1.76
2.20
6.80
1.00
1.01
1.05
1.16
1.04
1.01
2.06
2.07
2.32
1.09
2.03
3.16
3.19
0.98
9.09
f1 (ppm)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

WL-2-017-13C-C-01
169.68
169.03
157.25
156.81
138.91
138.38
135.51
133.67
132.99
128.31
128.21
128.05
128.01
127.85
127.65
127.51
127.42
127.21
127.15
126.43
126.23
125.46
124.03
117.59
114.73
101.78
101.28
96.28
82.25
80.87
76.88
76.85
74.09
73.55
73.52
72.56
71.53
68.31
67.43
66.09
65.48
63.62
53.30
51.56
Naph
BnO
TFAHN
MeO2C
OBn
HO
OCH2CO2t-Bu
16
f1 (ppm)

WL-2-017-prod-COSY.1.1.2rr
Naph
O
O
BnO
TFAHN
O
MeO2C
OBn
HO
O
OCH2CO2t-Bu
16
f1 (ppm)
f2 (ppm)

WL-2-017-prod-HSQC.1.1.2rr
Naph
O
O
BnO
TFAHN
O
MeO2C
OBn
O
HO
OCH2CO2t-Bu
16
f2 (ppm)
f1 (ppm)

WL-2-017-prod-HMBC.1.1.2rr
Naph
BnO
TFAHN
MeO2C
OBn
HO
OCH2CO2t-Bu
16
f1 (ppm)
f2 (ppm)

WL-2-018-prod-H.1.1.1r
Naph
BnO
TFAHN
MeO2C
OBn
FmocO
OCH2CO2t-Bu
17
0.65
1.04
3.14
2.15
3.16
2.15
10.03
5.16
1.00
1.01
1.04
1.01
1.03
1.03
2.08
1.07
2.03
1.14
3.18
4.26
2.25
3.12
9.47
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

WL-2-018-prod-C.1.1.1r
168.79
168.55
157.17
156.80
154.01
143.35
143.30
141.14
138.86
137.82
135.50
132.97
128.31
128.29
127.95
127.85
127.82
127.69
127.63
127.27
127.16
127.05
126.41
126.21
125.43
125.26
125.10
124.04
120.03
119.70
117.61
114.75
101.25
98.86
97.40
82.35
80.99
76.40
74.66
74.16
73.51
72.46
72.32
70.06
68.63
68.29
65.67
63.68
53.55
51.57
46.50
27.33
Naph
BnO
TFAHN
MeO2C
OBn
FmocO
OCH2CO2t-Bu
17
f1 (ppm)

WL-2-018-prod-COSY.1.1.2rr
Naph
BnO
TFAHN
MeO2C
OBn
FmocO
OCH2CO2t-Bu
17
f1 (ppm)
f2 (ppm)

WL-2-018-prod-HSQC.1.1.2rr
Naph
BnO
TFAHN
FmocO
MeO2C
OBn
OCH2CO2t-Bu
17
f1 (ppm)
f2 (ppm)

WL-2-018-prod-HMBC.1.1.2rr
Naph
BnO
TFAHN
MeO2C
OBn
FmocO
OCH2CO2t-Bu
17
f2 (ppm)
f1 (ppm)

WL-2-019-run2-prod-H.1.1.1r

18

WL-2-019-run2-prod-C-1511
169.44
168.59
157.77
157.32
156.95
156.58
153.96
143.04
142.92
141.23
141.21
137.80
136.58
135.08
133.23
133.06
128.61
128.49
128.38
128.30
127.97
127.92
127.79
127.75
127.46
127.32
127.30
126.67
126.26
126.06
125.61
125.12
125.02
120.10
117.22
114.36
98.67
96.24
82.07
79.67
77.37
77.25
77.05
76.74
74.67
73.83
72.29
71.72
71.57
71.13
70.90
70.67
70.59
69.50
67.53
65.86
52.73
52.34
46.46
28.05
ONap
HO
BnO
O
MeO2C
OBn
TFAHN
O
O
OCH2CO2t-Bu
FmocO
18
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

WL-2-019-run2-prod-COSY.1.1.2rr
18
ONap
HO
BnO
TFAHN
O
MeO2C
OBn
FmocO
OCH2CO2t-Bu
f1 (ppm)
f2 (ppm)

WL-2-019-run2-prod-HSQC.1.1.2rr
ONap
HO
BnO
O
MeO2C
OBn
TFAHN
O
O
OCH2CO2t-Bu
FmocO
18
f2 (ppm)
f1 (ppm)

WL-2-019-run2-prod-HMBC.1.1.2rr
ONap
HO
BnO
O
MeO2C
TFAHN
O
OBn
18
FmocO
O
OCH2CO2t-Bu
f1 (ppm)
f2 (ppm)

WL-2-020-prod-H.1.1.1r

WL-2-020-prod-C 111
171.91
169.24
168.40
153.99
142.99
141.21
141.16
137.64
137.37
137.10
136.58
135.66
135.53
135.39
133.32
133.28
133.02
132.95
129.70
129.61
129.54
128.58
128.53
128.31
128.26
128.20
128.05
128.00
127.95
127.91
127.82
127.67
127.59
127.53
127.29
126.83
126.65
126.18
126.10
125.91
125.12
125.03
82.04
74.50
73.46
73.32
72.35
71.88
71.64
71.24
70.93
70.81
70.12
69.20
67.68
65.84
62.95
52.19
51.62
46.40
37.69
29.73
29.69
28.03
27.62
26.62
19.10
OTBDPS
BzO
BnO
O
MeO2C
OBn
N3
O
LevO
O
O
ONap
BnO
TFAHN
O
MeO2C
OBn
O
OCH2CO2t-Bu
FmocO
21
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

WL-2-020-prod-COSY.1.1.2rr
21
OTBDPS
BzO
BnO
MeO2C
OBn
N3
LevO
BnO
ONap
TFAHN
MeO2C
OBn
FmocO
OCH2CO2t-Bu
f1 (ppm)
f2 (ppm)

WL-2-020-prod-HSQC.1.1.2rr
21
OTBDPS
BzO
BnO
MeO2C
OBn
N3
LevO
BnO
ONap
TFAHN
MeO2C
OBn
FmocO
OCH2CO2t-Bu
f1 (ppm)
f2 (ppm)

WL-2-020-1-CH-HSQC.1.1.2rr
21
OTBDPS
BzO
BnO
MeO2C
OBn
N3
LevO
ONap
BnO
TFAHN
MeO2C
OBn
FmocO
OCH2CO2t-Bu
{5.60,97.92}
{5.42,98.71}
{5.30,97.19}
{5.17,97.92}
{5.05,95.99}
{4.98,98.75}
{4.86,97.19}
{4.62,96.05}
f2 (ppm)
f1 (ppm)

WL-2-020-Prod-HMBC.1.1.2rr
21
f1 (ppm)
f2 (ppm)

WL-2-031-De-TBDPS-H.2.1.1r

22

Wt-2-031-De-TBDPS-C.1.1.1r
205.55
168.42
166.31
153.93
143.12
142.82
141.17
137.48
137.26
137.16
136.55
135.44
133.88
133.31
132.99
129.86
128.74
128.69
128.61
128.58
128.33
128.17
128.02
127.96
127.86
127.67
127.29
127.04
126.68
126.57
126.11
126.01
125.90
125.08
125.01
120.06
98.74
97.60
82.05
74.91
74.53
73.34
73.13
73.08
72.32
72.20
71.94
71.28
71.02
70.90
70.86
68.76
68.27
67.54
63.06
52.88
52.14
51.85
46.43
37.71
31.95
29.73
29.69
29.39
28.03
27.69
22.72
14.16
OH
BzO
BnO
O
MeO2C
OBn
N3
O
LevO
O
O
BnO
TFAHN
ONap
O
MeO2C
OBn
O
OCH2CO2t-Bu
O
FmocO
22
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

WL-2-031-DeTBDPS-COSY.2.1.2rr
22
f1 (ppm)
f2 (ppm)

WL-2-031-De-TBDPS-HSQC.3.1.2rr
OH
BzO
BnO
O
N3
O
MeO2C
OBn
O
LevO
O
BnO
ONap
O
TFAHN
O
MeO2C
OBn
O
OCH2CO2t-Bu
FmocO
22
f2 (ppm)
f1 (ppm)

WL-2-040-D-Nap-H.1.1.1r

Wt-2-040-De-Nap-C11r
206.97
172.11
169.10
168.40
164.77
153.99
142.81
141.19
137.51
137.21
137.05
136.51
135.66
135.53
133.29
132.97
129.71
129.68
129.60
129.54
128.66
128.55
128.52
128.39
128.31
128.09
127.97
127.93
127.83
127.58
127.53
127.29
126.96
126.63
125.12
125.02
120.04
98.76
98.07
96.65
82.08
77.92
74.57
72.95
72.88
72.45
72.19
71.59
71.29
70.77
70.19
67.61
65.91
63.08
52.98
52.46
51.70
46.40
37.96
31.95
29.81
29.73
29.39
28.04
26.64
22.72
19.11
14.16
OTBDPS
BzO
BnO
O
MeO2C
OBn
N3
O
LevO
O
O
OH
BnO
TFAHN
O
MeO2C
OBn
O
OCH2CO2t-Bu
FmocO
23
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

WL-2-040-D-Nap-COSY.2.1.2rr
23
f1 (ppm)
f2 (ppm)

Wl-2-040-DeNap-HSQC-run2.2.1.2rr
23
OTBDPS
BzO
BnO
MeO2C
OBn
N3
LevO
BnO
TFAHN
OH
MeO2C
OBn
FmocO
OCH2CO2t-Bu
f1 (ppm)
f2 (ppm)

WL-2-039-De-Lev-H.3.1.1r

24

24
169.21
169.12
168.49
164.63
153.86
143.18
141.17
137.49
137.28
136.87
136.46
135.68
135.55
135.05
133.30
133.07
132.91
129.71
129.60
129.56
128.68
128.63
128.55
128.47
128.37
128.29
128.26
128.00
127.96
127.89
127.69
127.57
127.53
127.30
127.27
126.99
126.15
126.08
125.96
125.04
120.03
101.29
98.77
96.92
95.44
82.06
78.30
75.51
73.71
72.49
72.32
71.21
67.58
67.40
65.89
63.37
52.03
51.62
46.41
31.95
29.73
29.68
29.39
28.03
26.63
22.72
19.16
14.16
f1 (ppm)

WL-2-039-De-Lev-COSY-New.5.1.2rr
24
f1 (ppm)
f2 (ppm)

WL-2-039-De-Lev-HSQC-New.7.1.2rr
24
OTBDPS
BzO
BnO
MeO2C
OBn
N3
O
HO
BnO
TFAHN
ONap
MeO2C
OBn
FmocO
OCH2CO2t-Bu
f1 (ppm)
f2 (ppm)

WL-2-032-De-Fmoc.1.fid

WL-2-032-De-FMOC-CNMR-111r
206.27
172.26
170.10
169.52
165.03
138.06
137.71
137.44
137.30
135.97
135.87
135.75
133.65
133.61
133.37
133.27
130.02
129.93
129.87
128.88
128.83
128.63
128.48
128.40
128.27
128.16
127.98
127.92
127.86
127.80
127.58
127.06
126.46
126.38
126.19
125.76
101.75
82.55
77.80
77.68
77.56
77.36
77.16
77.04
74.81
74.73
73.83
73.71
72.73
72.54
72.41
71.61
68.28
65.80
63.23
55.25
52.64
52.06
37.99
32.27
30.04
29.71
28.38
27.92
26.96
23.04
19.43
14.48
OTBDPS
BzO
BnO
O
MeO2C
OBn
N3
O
LevO
O
O
BnO
TFAHN
ONap
O
MeO2C
OBn
O
O
OCH2CO2t-Bu
HO
25
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

WL-2-032-DeFmoc-COSY.2.1.2rr
25
BzO
BnO
OTBDPS
MeO2C
OBn
N3
O
LevO
BnO
TFAHN
ONap
MeO2C
OBn
HO
OCH2CO2t-Bu
f1 (ppm)
f2 (ppm)

WL-2-032-De-FMoc-HSQC.2.1.2rr
25
OTBDPS
BzO
BnO
MeO2C
OBn
N3
LevO
ONap
BnO
TFAHN
MeO2C
OBn
HO
OCH2CO2t-Bu
f1 (ppm)
f2 (ppm)

WL-2-041-de-TBu-Acid-H2.2.1.1r

26

WL-2-041-de-TBu-Acid-C11-1r
26
206.17
171.92
171.27
169.12
168.99
164.75
157.12
156.74
153.97
98.47
98.00
97.34
95.96
75.21
74.48
74.21
74.09
73.50
72.84
72.31
71.98
71.68
71.55
71.30
71.24
70.89
70.14
69.99
69.65
68.47
67.48
65.05
62.92
61.93
52.69
52.30
51.70
46.43
37.67
f1 (ppm)

WL-2-041-de-TBu-Acid-COSY.4.1.2rr
26
OTBDPS
BzO
BnO
MeO2C
OBn
N3
O
LevO
ONap
BnO
TFAHN
MeO2C
OBn
FmocO
OCH2CO2H
f1 (ppm)
f2 (ppm)

WL-2-041-De-tBu-HSQC.4.1.2rr
26
OTBDPS
BzO
BnO
MeO2C
OBn
N3
O
LevO
ONap
BnO
TFAHN
MeO2C
OBn
FmocO
OCH2CO2H
f1 (ppm)
f2 (ppm)

WL-2-042-pure-H.1.1.1r

WL-2-042-6-OSO3-C.1.1.1e
27
205.47
171.06
168.38
167.53
164.68
152.92
142.10
141.86
140.15
140.12
136.32
135.60
134.46
132.27
131.96
128.84
127.50
127.18
127.13
127.10
127.05
127.02
126.98
126.91
126.84
126.72
126.64
126.24
125.73
125.68
125.06
125.02
124.84
124.06
123.98
119.01
97.71
80.99
73.36
72.25
71.94
71.30
70.93
70.45
69.90
68.19
68.10
66.72
64.89
54.97
52.42
51.18
51.07
45.40
f1 (ppm)

WL-2-033-2-OSO3-H.3.1.1r

WL-2-033-2-OSO3-C-111r
206.68
172.02
169.99
169.37
164.77
137.87
137.35
137.06
135.65
135.52
135.23
133.33
133.25
132.99
132.91
129.68
129.65
129.59
128.56
128.53
128.33
128.19
128.14
128.06
127.99
127.88
127.73
127.63
127.56
127.37
127.33
126.91
126.34
126.00
125.85
97.70
97.15
83.04
75.32
74.47
73.70
73.49
72.06
71.36
71.21
70.34
70.17
69.95
67.58
65.99
62.86
61.99
53.46
53.01
52.32
51.82
50.87
37.61
29.73
29.65
27.96
27.57
26.63
22.72
19.11
OTBDPS
BzO
BnO
O
MeO2C
OBn
N3
O
LevO
O
O
ONap
BnO
TFAHN
O
MeO2C
OBn
O
OCH2CO2t-Bu
−O3SO
28
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

WL-2-033-2-OSO3-COSY.4.1.2rr
28
OTBDPS
BzO
BnO
O
MeO2C
N3
O
OBn
LevO
O
O
BnO
ONap
O
MeO2C
TFAHN
O
OBn
-O3SO
O
OCH2CO2t-Bu
f1 (ppm)
f2 (ppm)

WL-2-033-2-OSO3-HSQC.5.1.2rr
OTBDPS
BzO
BnO
O
MeO2C
N3
O
OBn
LevO
O
O
28
BnO
TFAHN
O
ONap
O
MeO2C
−O3SO
O
OBn
OCH2CO2t-Bu
f2 (ppm)
f1 (ppm)

WL-2-034-2-OSO3-De-TBDPS-HSQC.4.1.1r

WL-2-034-2-OSO3-De-TBDPS-C11r
206.9
172.12
169.75
169.66
166.15
137.84
137.46
137.11
135.38
133.86
133.22
132.99
129.85
128.85
128.77
128.69
128.55
128.34
128.25
128.16
128.01
127.97
127.90
127.78
127.64
127.59
127.41
126.85
126.25
126.07
125.88
117.19
114.33
100.04
98.26
97.93
82.72
74.88
74.70
73.71
73.46
72.79
71.31
71.12
71.07
70.06
70.01
67.44
66.01
62.78
60.70
53.46
52.81
52.24
52.06
37.58
31.95
29.73
29.39
27.95
27.65
22.72
14.16
OH
BzO
BnO
O
N3
O
MeO2C
OBn
O
LevO
O
ONap
BnO
TFAHN
O
O
MeO2C
OBn
O
OCH2CO2t-Bu
−O3SO
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

WL-2-036-NAc-pure-HSQC.1.fid
29
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.62
3.32
0.79
21.58
2.00
0.92
0.98
7.45
2.84
1.74
0.86
1.90
2.18
3.04
7.60
1.16
2.18
3.01

Vil_2036-NAc-Pro-C 1 1H
179.01
175.19
174.56
174.21
172.55
138.54
138.54
138.15
136.51
135.72
133.43
133.11
129.84
128.84
128.53
128.30
127.99
127.95
127.84
127.77
127.72
127.64
127.56
127.52
127.30
127.27
127.24
127.19
127.03
126.42
125.83
125.64
125.46
98.91
98.40
96.38
94.53
80.86
77.44
76.85
75.96
74.86
74.35
73.88
73.42
72.77
72.44
72.40
71.59
71.57
71.31
71.01
70.88
70.38
70.13
68.82
68.53
67.50
63.58
62.96
60.64
54.88
52.79
29
f1 (ppm)

WL-2-036-NAc-Pure-COSY.3.1.2rr
29
f1 (ppm)
f2 (ppm)

WL-2-036-NAc-pure-HSQC.2.1.2rr
29
f2 (ppm)
f1 (ppm)

WL-2-038-N-Sulfation-pure-H.2.1.1r

30

WL-2-038-N-Sulfation-Pure-C.1.1.1r —

WL-2-038-N-Sulfation-pure-COSY.5.1.2rr
30
f1 (ppm)
f2 (ppm)

WL-2-038-N-Sulfation-pure-HSQC.3.1.2rr
30
f2 (ppm)
f1 (ppm)

WL-2-044-D-6-OSO3-D-NAc-H.5.fid
31
f1 (ppm)
8.04
17.75
15.40
0.98
0.94
1.00
0.94
1.96
0.96
1.36
1.28
1.22
3.92
1.41
5.07
11.81
10.39
2.93
3.05
2.07
2.51
3.60
3.25
9.63

WL-2-044-D6-OSO3-D2-NAc-C11r
171.91
169.24
168.46
157.21
153.92
143.09
142.81
141.16
137.66
137.25
136.55
135.50
133.31
132.99
129.94
128.55
128.27
128.15
128.08
127.99
127.93
127.66
127.53
127.26
127.03
126.56
126.45
126.10
125.83
125.02
124.97
120.06
117.12
114.26
98.74
97.90
96.19
82.04
78.29
74.31
74.11
73.08
72.72
72.32
72.09
71.80
71.37
71.01
70.75
70.06
69.78
69.71
69.62
69.46
69.25
67.55
65.86
53.46
53.07
52.12
51.84
46.45
37.69
29.73
29.38
28.03
27.59
22.71
OSO3−
BzO
BnO
AcHN
O
MeO2C
OBn
O
LevO
O
ONap
BnO
TFAHN
O
MeO2C
OBn
O
OCH2CO2t-Bu
HO
31
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

WL-2-047-D-6-SO3-D-2-NAc-B-2-NSO3-H.5.fid

32

WL-2-047-D-6-SO3-D-2-NAc-B-2-NSO3-C.6.fid

32

WL-2-047-D-6-SO3-D-2-NAc-B-2-NSO3-COSY.8.1.2rr
32
f1 (ppm)
f2 (ppm)

WL-2-047-D-6-SO3-D-2-NAc-B-2-NOS3-HSQC.2.1.2rr
32
f2 (ppm)
f1 (ppm)

PROTON01
NP_1_148
S1
AcO
AcO
OAc
O
N3
O
MeO2C
OAc
AcO
O
STol
1.80
1.85
0.90
1.00
0.92
0.90
0.92
1.88
1.06
2.87
2.62
0.93
3.14
5.40
5.57
2.62
f1 (ppm)

CARBON01
NP_1_148
S1
170.75
170.07
169.95
169.76
169.10
168.93
138.35
132.52
130.34
130.00
98.69
86.65
77.41 cdcl3
77.16 cdcl3
76.91 cdcl3
73.74
70.68
68.68
68.63
68.17
67.41
61.41
61.28
52.75
21.26
21.01
20.84
20.79
20.78
20.69
f1 (ppm)

PROTON02
NP_1_149

S2

CARBON01
NP_1_149
S2
PMP
O
O
HO
O
N3
O
MeO2C
OH
HO
O
STol
170.35
161.06
137.75
133.68
131.92
131.28
130.45
128.59
114.13
102.41
97.21
89.89
82.10
74.91
72.33
70.58
69.39
68.88
67.45
65.11
64.34
55.56
52.46
30.30 acetone
30.15 acetone
29.99 acetone
29.84 acetone
29.69 acetone
29.53 acetone
29.38 acetone
21.00
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

PROTON01
NP_1_152
PMP
O
O
HO
O
N3
O
MeO2C
OH
FmocO
O
STol
S3
2.03
2.03
8.01
2.02
1.98
1.01
1.08
0.47
1.03
1.01
0.54
1.00
2.99
1.05
1.03
2.01
1.12
2.94
2.89
1.12
1.08
1.09
3.10
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

CARBON01
NP_1_152

gCOSY01
NP_1_152
PMP
O
O
HO
O
N3
O
MeO2C
OH
FmocO
O
STol
S3
f1 (ppm)
f2 (ppm)

HSQCAD01
NP_1_152
S3
PMP
HO
MeO2C
OH
N3
FmocO
STol
f1 (ppm)
f2 (ppm)

gHMBCAD01
NP_1_152
PMP
O
O
HO
O
N3
O
MeO2C
OH
FmocO
O
STol
S3
f1 (ppm)
f2 (ppm)

PROTON01
NP_1_124_P
PMP
O
O
HO
O
N3
MeO2C
O
TrocO
O
OH
STol
S4
4.07
2.01
2.02
0.91
1.05
0.53
1.07
1.01
0.46
1.03
1.97
0.97
1.00
1.03
0.99
7.19
1.13
1.04
1.00
3.01
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

CARBON01
NP_1_124_P
169.93
161.00
154.11
138.45
132.54
131.98
131.35
130.55
128.60
114.07
102.36
100.23
95.51
85.72
82.61
77.60
76.94
76.52
70.76
69.17
68.98
68.09
64.67
64.29
55.55
52.40
30.30 acetone
30.15 acetone
29.99 acetone
29.84 acetone
29.68 acetone
29.53 acetone
29.38 acetone
21.03
PMP
O
O
O
HO
N3
O
MeO2C
OH
O
STol
TrocO
S4
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

gCOSY01
NP_1_124_P
PMP
O
O
HO
O
N3
O
MeO2C
OH
TrocO
O
STol
S4
f1 (ppm)
f2 (ppm)

HSQCAD01
NP_1_124_P
PMP
O
O
HO
O
N3
O
MeO2C
OH
TrocO
O
STol
S4
f1 (ppm)
f2 (ppm)

gHMBCAD01
NP_1_124_P
PMP
O
O
HO
O
N3
O
MeO2C
OH
TrocO
O
STol
S4
f1 (ppm)
f2 (ppm)

PROTON02
NP_1_83_U
PMP
O
O
HO
O
N3
O
MeO2C
OH
BzO
O
O
STol
S5
1.97
0.97
5.96
2.00
2.00
1.01
1.09
1.07
0.99
1.00
1.04
1.06
0.99
2.21
6.00
1.39
0.99
1.01
1.00
2.96
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

CARBON01
NP_1_83_U
S5
PMP
O
O
HO
O
N3
O
MeO2C
BzO
O
OH
STol
169.52
165.89
160.51
138.40
133.53
133.08
130.18
129.90
129.65
129.51
129.09
128.61
127.75
113.90
102.25
100.59
84.43
81.39
78.74
77.41 cdcl3
77.16 cdcl3
76.91 cdcl3
72.07
71.58
69.97
69.91
68.64
63.83
63.43
55.49
52.42
21.30
f1 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200

gCOSY01
NP_1_83_U
PMP
O
O
HO
O
MeO2C
N3
OH
O
S5
BzO
O
STol
f1 (ppm)
f2 (ppm)

HSQCAD01
NP_1_83_U
PMP
O
O
HO
O
MeO2C
N3
O
OH
S5
BzO
O
STol
f2 (ppm)
f1 (ppm)

gHMBCAD01
NP_1_83_U
PMP
O
O
HO
O
N3
O
MeO2C
OH
BzO
O
STol
S5
f1 (ppm)
f2 (ppm)

PROTON02
NP_1_87_MCA3
PMP
O
O
HO
O
N3
O
MeO2C
OMCA
S6
HO
O
STol
1.03
1.95
0.30
1.00
0.97
0.31
1.01
1.10
0.89
1.01
1.04
2.81
2.90
1.94
1.09
1.07
1.04
4.06
1.99
2.03
1.03
1.95
0.30
1.00
0.97
0.31
1.01
1.10
0.89
1.01
1.04
2.81
2.90
1.94
1.09
1.07
1.04
2.81
f1 (ppm)

CARBON01
NP_1_87_MCA3
PMP
O
O
HO
O
N3
O
MeO2C
OMCA
S6
HO
O
STol
168.86
165.91
160.07
137.52
132.02
130.28
130.04
129.53
127.59
113.13
101.39
98.33
86.89
81.12
73.00
71.65
71.13
69.17
69.00
67.86
63.74
63.60
54.56
51.64
40.87
29.30 acetone
29.15 acetone
28.99 acetone
28.84 acetone
28.69 acetone
28.53 acetone
28.38 acetone
20.04
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

gCOSY02
NP_1_87_MCA3
PMP
O
O
HO
O
N3
O
MeO2C
OMCA
S6
HO
O
STol
f2 (ppm)
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
f1 (ppm)
5.5
5.0
4.5
4.0
3.5

HSQCAD01
NP_1_87_MCA3
PMP
O
O
HO
O
N3
O
MeO2C
OMCA
HO
O
STol
S6
f2 (ppm)
f1 (ppm)

gHMBCAD01
NP_1_87_MCA3
PMP
O
O
HO
O
N3
O
MeO2C
OMCA
S6
HO
O
STol
f1 (ppm)
f2 (ppm)

PROTON01
NP_1_131P_Benzene
OTBDPS
AcO
AcO
O
N3
O
MeO2C
OAc
FmocO
O
STol
19
1.93
2.02
1.96
3.81
9.59
2.11
1.06
1.07
1.06
1.20
2.05
1.16
3.96
1.09
1.19
1.18
3.00
1.19
2.92
5.77
3.31
9.74
f1 (ppm)

CARBON01
NP_1_131P_Benzene
169.41
168.84
168.81
168.24
154.44
143.66
143.49
141.38
141.33
137.90
135.82
135.79
133.24
133.18
132.97
129.80
129.78
129.74
127.97
127.87 c6d6
127.82
127.81
127.78
127.73
127.68 c6d6
127.59
127.49 c6d6
127.34
127.24
127.19
125.52
125.44
119.86
98.10
84.80
73.07
72.26
71.21
71.08
70.56
70.47
68.53
68.16
62.14
60.85
51.84
46.60
26.73
20.60
19.98
19.91
19.86
19.14
OTBDPS
AcO
AcO
O
MeO2C
OAc
N3
O
O
STol
FmocO
19
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

PROTON01
WL-1-040-prod
S7
AcO
AcO
AcHN
OAc
O
MeO2C
O
AcO
OAc
O
STol
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
2.04
2.32
1.05
1.00
0.99
2.17
0.99
0.94
0.95
1.13
2.25
1.97
2.77
3.10
2.87
2.79
3.35
5.56
2.63

CARBON02
NP_1_29
171.31
170.23
169.49
169.39
169.14
168.82
138.51
132.85
129.87
129.77
98.73
85.06
77.27
77.22
77.01
76.76
73.35
70.67
70.10
69.01
68.79
67.53
61.53
52.64
51.82
21.16
20.82
20.80
20.73
20.69
20.58
S7
AcO
AcO
AcHN
OAc
O
MeO2C
OAc
AcO
O
STol
f1 (ppm)

gCOSY01
NP_1_29
S7
AcO
AcO
AcHN
OAc
O
MeO2C
O
AcO
OAc
O
STol
f1 (ppm)
f2 (ppm)

HSQCAD01
NP_1_29
S7
AcO
AcO
AcHN
OAc
O
MeO2C
O
AcO
O
OAc
STol
f2 (ppm)
f1 (ppm)

PROTON01
wl-1-041-prod

S8

CARBON01
NP_1_30

S8

PROTON01
wl-1-076-1

WL-1-075-prod-C.1.1.1r
S9
163.48
135.53
131.30
129.30
128.45
127.86
127.59
127.28
125.96
125.84
125.74
125.58
123.97
103.47
95.67
89.23
73.69
73.10
71.16
70.88
70.14
68.23
66.24
60.81
54.27
51.97
51.59
48.25
48.04
47.83
47.74
47.61
47.53
47.40
47.32
47.18
46.97
46.48
35.57
30.26
19.69
7.82
f1 (ppm)

WL-1-075-prod-COSY.1.1.2rr
S9
f1 (ppm)
f2 (ppm)

WL-1-075-prod-HSQC.1.1.2rr
S9
f1 (ppm)
f2 (ppm)

PROTON01
WL-1-079-prod-acetone

S10

CARBON01
WL-1-079-crud-acetone
S10
Naph
O
O
HO
TFAHN
O
O
MeO2C
OH
HO
O
STol
169.54
155.32
155.03
136.89
135.57
133.65
132.96
132.90
130.98
129.57
128.20
127.72
127.62
126.39
126.19
125.72
124.19
119.54
117.33
115.04
112.74
101.66
96.78
96.76
88.81
88.80
81.85
81.83
74.85
74.82
71.25
68.74
68.36
68.34
68.31
66.67
63.75
54.85
54.09
51.64
20.12
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

gCOSY01
WL-1-079-prod-acetone
Naph
O
O
HO
TFAHN
O
MeO2C
OH
O
HO
O
STol
S10
f1 (ppm)
f2 (ppm)

HSQCAD01
WL-1-079-prod-acetone
Nap
O
O
HO
TFAHN
O
MeO2C
OH
O
HO
O
STol
S10
f2 (ppm)
f1 (ppm)

gHMBCAD01
WL-1-079-prod-acetone
S10
Naph
O
O
HO
TFAHN
O
O
MeO2C
OH
HO
O
STol
f1 (ppm)
f2 (ppm)

PROTON01
wl-1-081-prod
Naph
O
O
HO
TFAHN
O
MeO2C
OH
O
TrocO
O
STol
S11
0.56
1.02
3.26
1.04
2.13
2.09
2.18
1.12
1.00
1.02
0.74
1.96
1.08
0.71
1.03
1.13
1.09
1.03
1.15
1.14
1.16
1.28
3.11
1.09
3.21
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

CARBON01
wl-1-081-prod
169.10
157.08
156.78
153.21
137.95
135.57
133.66
132.90
132.24
129.77
129.74
129.68
128.19
127.70
127.63
126.40
126.19
125.71
124.23
117.24
114.96
101.63
99.79
94.64
83.83
82.02
77.90
76.84
76.73
72.28
69.35
68.28
68.02
63.92
55.06
51.69
20.17
Naph
O
O
HO
TFAHN
O
O
MeO2C
OH
O
STol
TrocO
S11
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

PROTON01
WI-1-086-prod

S12

CARBON01
WI-1-086-prod

S12

gCOSY01
WI-1-086-prod
Naph
O
O
AcO
TFAHN
O
MeO2C
OAc
TrocO
O
O
STol
S12
f1 (ppm)
f2 (ppm)

HSQCAD01
Wl-1-086-prod
Naph
O
O
O
AcO
TFAHN
O
MeO2C
OAc
O
STol
TrocO
S12
f2 (ppm)
f1 (ppm)

gHMBCAD01
WI-1-086-prod
Naph
O
O
AcO
TFAHN
O
MeO2C
OAc
O
TrocO
O
STol
S12
f1 (ppm)
f2 (ppm)

PROTON01
NP_1_135_4P

S13

CARBON01
NP_1_135_4P

S13

gCOSY01
NP_1_135_4P
S13
Naph
AcO
TFAHN
MeO2C
OAc
TrocO
f1 (ppm)
f2 (ppm)

HSQCAD01
NP_1_135_4P
Naph
O
O
AcO
TFAHN
O
MeO2C
OAc
O
TrocO
O
O
S13
f2 (ppm)
f1 (ppm)

HSQCAD01
wl-1-093-HSQC-CH
Naph
O
O
O
AcO
TFAHN
O
MeO2C
OAc
O
TrocO
O
S13
{5.40,96.02}
{5.06,96.08}
{5.58,98.11}
{5.23,98.09}
{6.05,101.59}
{5.72,101.54}
92
93
94
95
96
97
98
99
100
101
102
103
104
105
f1 (ppm)
6.5
6.4
6.3
6.2
6.1
6.0
5.9
5.8
5.7
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
f2 (ppm)

gHMBCAD01
NP_1_135_4P
Naph
O
O
AcO
TFAHN
O
MeO2C
OAc
O
TrocO
O
O
S13
f2 (ppm)
f1 (ppm)

PROTON01
WL-1-093-up-prod

S13-α

CARBON01
WL-1-093-up-prod
169.75
169.06
168.86
153.15
135.22
133.86
133.70
132.89
128.26
127.80
127.64
126.46
126.22
125.68
124.06
116.44
101.47
98.22
96.83
94.64
78.82
76.72
74.24
73.16
70.05
69.11
69.07
68.03
64.05
52.84
52.75
51.90
29.44
29.29
29.23
29.13
28.98
28.82
28.67
28.52
19.85
19.72
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
Naph
AcO
TFAHN
MeO2C
OAc
TrocO
S13-α

gCOSY01
WL-1-093-up-prod
Naph
AcO
TFAHN
MeO2C
OAc
TrocO
S13-α
f2 (ppm)
f1 (ppm)

HSQCAD01
WL-1-093-up-prod
Naph
O
O
AcO
TFAHN
O
O
MeO2C
OAc
O
O
TrocO
S13-α
f2 (ppm)
f1 (ppm)

HSQCAD02
WL-1-093-up-prod
Naph
O
O
AcO
TFAHN
O
MeO2C
OAc
TrocO
O
O
O
S13-α
{6.06,101.46}
{5.73,101.47}
{5.55,96.85}
{5.52,98.21}
{5.20,96.81}
{5.17,98.21}
f2 (ppm)
6.15
6.05
5.95
5.85
5.75
5.65
5.55
5.45
5.35
5.25
5.15
5.05
f1 (ppm)
104
103
102
101
100
99
98
97
96
95

PROTON01
NP_1_136B
20
ONap
HO
AcO
TFAHN
O
MeO2C
OAc
TrocO
O
O
O
4.09
3.16
0.64
1.91
1.01
1.00
1.93
1.18
1.05
2.66
0.96
2.23
1.04
2.08
1.10
1.22
3.02
2.98
2.78
2.95
f1 (ppm)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.

CARBON01
NP_1_136B
20
171.53
170.12
169.37
158.17
158.09
157.88
157.79
157.58
157.50
157.28
157.20
154.18
137.22
134.43
134.33
133.87
128.72
128.72
128.47
126.87
126.71
126.59
126.45
120.11
118.11
117.83
115.55
113.25
98.65
96.63
95.50
77.53
75.24
75.19
74.19
73.90
73.75
73.72
72.09
70.44
70.05
68.99
68.88
68.59
53.48
53.39
52.52
52.51
20.76
20.71
f1 (ppm)

gCOSY01
NP_1_136B
20
ONap
HO
AcO
TFAHN
O
MeO2C
OAc
TrocO
O
O
O
f1 (ppm)
f2 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0

HSQCAD01
NP_1_136B
20
ONap
HO
AcO
TFAHN
O
MeO2C
OAc
TrocO
O
O
O
f1 (ppm)
f2 (ppm)

gHMBCAD01
NP_1_136B
20
ONap
HO
AcO
TFAHN
O
MeO2C
OAc
TrocO
O
O
f1 (ppm)
f2 (ppm)

NP_1_140_R2_P.5.fid
S14
OTBDPS
AcO
AcO
O
MeO2C
N3
O
FmocO
OAc
O
O
AcO
TFAHN
ONap
O
MeO2C
TrocO
O
OAc
O
OAll
11.90
12.03
1.16
0.80
1.00
2.12
7.86
1.00
0.90
4.56
1.01
3.77
3.00
4.00
5.17
3.00
2.71
0.80
12.02
3.04
9.31
f1 (ppm)

NP_1_140_R2_P.12.fid
S14
OTBDPS
AcO
AcO
N3
O
MeO2C
FmocO
OAc
O
AcO
TFAHN
ONap
MeO2C
TrocO
OAc
OAll
170.51
170.05
169.57
169.30
168.42
168.27
168.20
154.80
153.58
132.88
118.91
98.46
96.89
96.21
94.93
94.31
77.36
74.01
73.67
73.42
73.03
72.14
71.60
71.39
71.00
70.81
70.44
69.84
68.40
67.92
66.33
61.88
60.84
52.78
52.57
46.79
26.83
20.92
20.78
20.72
20.64
20.56
19.32
f1 (ppm)

NP_1_140_R2_P.6.ser
S14
OTBDPS
AcO
AcO
O
MeO2C
N3
O
FmocO
OAc
O
O
AcO
TFAHN
ONap
O
MeO2C
O
TrocO
OAc
O
OAll
f1 (ppm)
f2 (ppm)

NP_1_140_R2_P.8.ser
S14
OTBDPS
AcO
AcO
O
MeO2C
N3
O
FmocO
O
OAc
O
AcO
TFAHN
O
ONap
MeO2C
O
TrocO
O
OAc
OAll
f2 (ppm)
f1 (ppm)

NP_1_140_R2_P.4.ser
{5.43,96.40}
{5.30,94.88}
{5.22,98.49}
{4.99,96.42}
{4.87,94.85}
{4.81,98.41}
OTBDPS
AcO
AcO
O
MeO2C
OAc
N3
O
O
FmocO
ONap
O
O
MeO2C
OAc
AcO
TFAHN
O
O
TrocO
OAll
S14
f2 (ppm)
f1 (ppm)