Shotgun Ion Mobility Mass Spectrometry Sequencing of Heparan Sulfate Saccharides

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Supplementary Information

Supplementary Table 8. CCS of B, Y, C, Z ions - hexasaccharide GlcNAc6S-[I-GlcNAc6S]$_2$-I-R$_2$.

Supplementary Table 9. CCS of B, Y, C, Z ions - octasaccharide GlcNAc6S-[I-GlcNAc6S]$_3$-I-R$_2$.

Supplementary Table 10. CCS of B, Y, C, Z ions - octasaccharide GlcNAc6S-[G-GlcNAc6S]$_3$-G-R$_2$.

Supplementary Table 11. CCS of B, Y, C, Z ions - octasaccharide GlcNAc6S-G-GlcNac6S-G-GlcNAc6S-I-GlcNAc6S-I-R$_2$.

Supplementary Table 12. CCS of B, Y, C, Z ions - octasaccharide GlcNAc6S-G-GlcNac6S-I-GlcNAc6S-I-GlcNAc6S-G-R$_2$.

Supplementary Table 13. CCS of B, Y, C, Z ions - octasaccharide GlcNAc6S-I-GlcNAc6S-G-GlcNAc6S-I-GlcNAc6S-G-R$_2$.

Supplementary Table 14. CCS of B, Y, C, Z ions - octasaccharide GlcNAc6S-G-GlcNAc6S-I-GlcNAc6S-G-GlcNAc6S-I-R$_2$.

Supplementary Table 15. CCS of B, Y, C, Z ions - nonasaccharide G-GlcNS-G-GlcNS-I-GlcNS-G-GlcNS-G-R$_3$.

Supplementary Table 16. CCS of B, Y, C, Z ions - nonasaccharide G-GlcNS-G-GlcNS-I2S-GlcNS-G-GlcNS-G-R$_3$.

Supplementary Table 17. CCS of B, Y, C, Z ions - decasaccharide GlcNAc6S-[I-GlcNAc6S]$_4$-I-R$_2$.

Supplementary Table 18. CCS of B, Y, C, Z ions - decasaccharide GlcNAc6S-[G-GlcNAc6S]$_4$-G-R$_2$.

Supplementary Table 19 CCS of B, Y, C, Z ions - disaccharide ΔUA2S-GlcNS3S6S

Supplementary Table 20 CCS of B, Y, C, Z ions - tetrasaccharide ΔUA-GlcNS-I2S-GlcNS3S

Supplementary Table 21 CCS of B, Y, C, Z ions - tetrasaccharide ΔUA-GlcNS6S-G-GlcNS3S6S

Supplementary Table 22 CCS of B, Y, C, Z ions - tetrasaccharide ΔUA-GlcNAc6S-G-GlcNS3S6S

Supplementary Table 23 CCS of B, Y, C, Z ions - G-GlcNS6S-G-GlcNS6S-I2S-GlcNS6S-R$_1$

Supplementary Table 24 CCS of B, Y, C, Z ions - G-GlcNS6S-G-GlcNS3S-I2S-GlcNS6S-R$_1$

Supplementary Table 25 CCS of B, Y, C, Z ions - G-GlcNS6S-G-GlcNS6S3S-I2S-GlcNS6S-R$_1$

Supplementary Table 26. CCS of B, Y, C, Z ions - septasaccharide ΔUA-GlcNS-I2S-GlcNS-G-GlcNS-G-R$_3$.

Supplementary Table 27 CCS of B, Y, C, Z -SO_3 ions - tetrasaccharides UA-GlcNAc6S-UA-GlcNAc6S-R$_1$

Supplementary Table 28. CCS of B, Y, C, Z -SO_3 ions - tetrasaccharides G-GlcNS6S-I-GlcNS6S-R$_1$

Supplementary Table 29. CCS of B, Y, C, Z -SO_3 ions – tetrasaccharides I-GlcNS6S-G-GlcNS6S-R$_1$

Supplementary Table 30. CCS of B, Y, C, Z -SO_3 ions - tetrasaccharide G-GlcNS6S-I2S-GlcNS6S-R$_1$

Supplementary Table 31. CCS of B, Y, C, Z -SO_3 ions - hexasaccharide G-GlcNS6S-I-GlcNS6S-G-GlcNS6S-R$_1$.

Supplementary Table 32. CCS of B, Y, C, Z -SO_3 ions - hexasaccharide GlcNAc6S-[G-GlcNAc6S]$_2$-G-R$_2$.

Supplementary Table 33. CCS of B, Y, C, Z -SO_3 ions - hexasaccharide GlcNAc6S-[I-GlcNAc6S]$_2$-I-R$_2$.

Supplementary Table 34 CCS of B, Y, C, Z -SO_3 ions - GlcNAc6S-[I-GlcNAc6S]$_3$-I-R$_2$

Supplementary Table 35. CCS of B, Y, C, Z -SO_3 ions - octasaccharide GlcNAc6S-[G-GlcNAc6S]$_3$-G-R$_2$.

Supplementary Table 36. CCS of B, Y, C, Z -SO_3 ions - octasaccharide GlcNAc6S-G-GlcNAc6S-G-GlcNAc6S-I-GlcNAc6S-I-R$_2$.

Supplementary Table 37. CCS of B, Y, C, Z -SO_3 ions - octasaccharide GlcNAc6S-G-GlcNAc6S-I-GlcNAc6S-I-GlcNAc6S-G-R$_2$.

Supplementary Table 38. CCS of B, Y, C, Z -SO_3 ions - octasaccharide GlcNAc6S-I-GlcNAc6S-G-GlcNAc6S-I-GlcNAc6S-G-R$_2$.

Supplementary Table 39. CCS of B, Y, C, Z -SO_3 ions - octasaccharide GlcNAc6S-G-GlcNAc6S-I-GlcNAc6S-G-GlcNAc6S-I-R$_2$.

Supplementary Table 40. CCS of B, Y, C, Z -SO_3 ions - nonasaccharide G-GlcNS-G-GlcNS-I-GlcNS-G-GlcNS-G-R$_3$.

Supplementary Table 41. CCS of B, Y, C, Z -SO_3 ions - nonasaccharide G-GlcNS-G-GlcNS-I2S-GlcNS-G-GlcNS-G-R$_3$.

Supplementary Table 42. CCS of B, Y, C, Z -SO_3 ions - decasaccharide GlcNAc6S-[I-GlcNAc6S]$_4$-I-R$_2$.

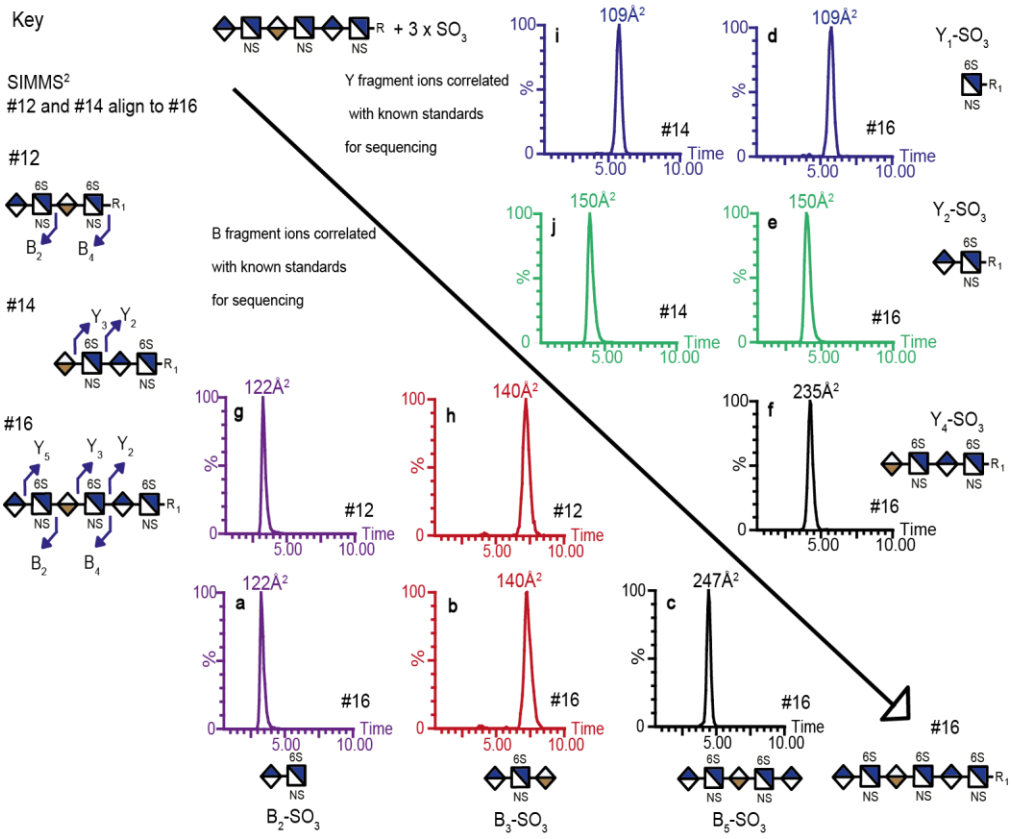
Supplementary Table 43. CCS of B, Y, C, Z -SO_3 ions - decasaccharide GlcNAc6S-[G-GlcNAc6S]$_4$-G-R$_2$.

Supplementary Table 44 CCS of B, Y, C, Z -SO_3 ions - disaccharide ΔUA2S-GlcNS3S6S

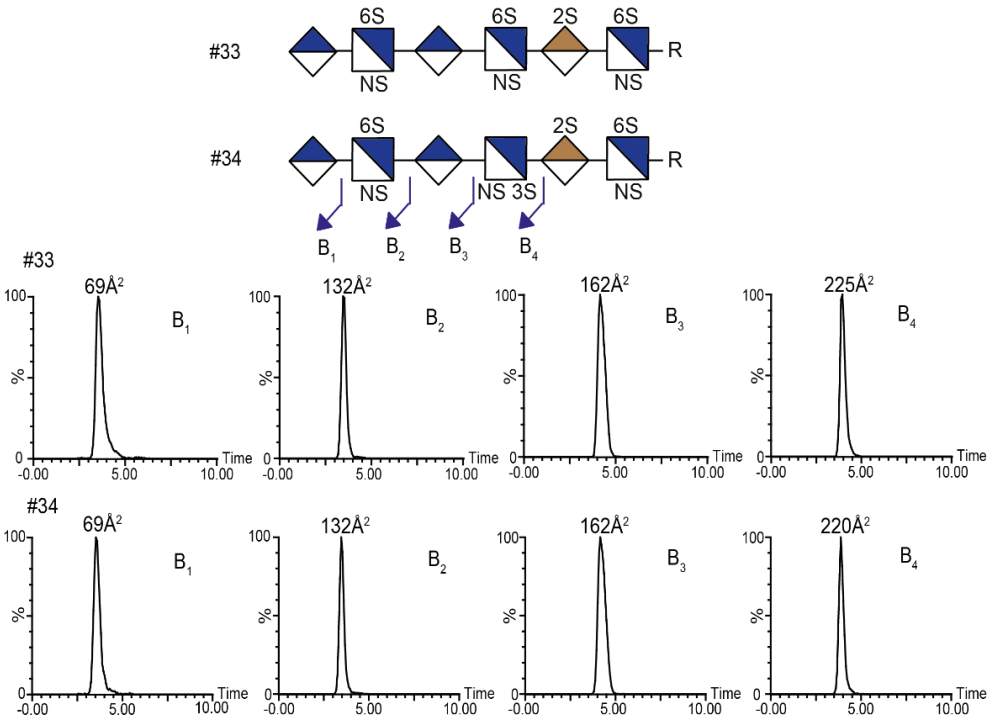
Supplementary Table 45 CCS of B, Y, C, Z -SO_3 ions - tetrasaccharide ΔUA-GlcNS-I2S-GlcNS3S

35

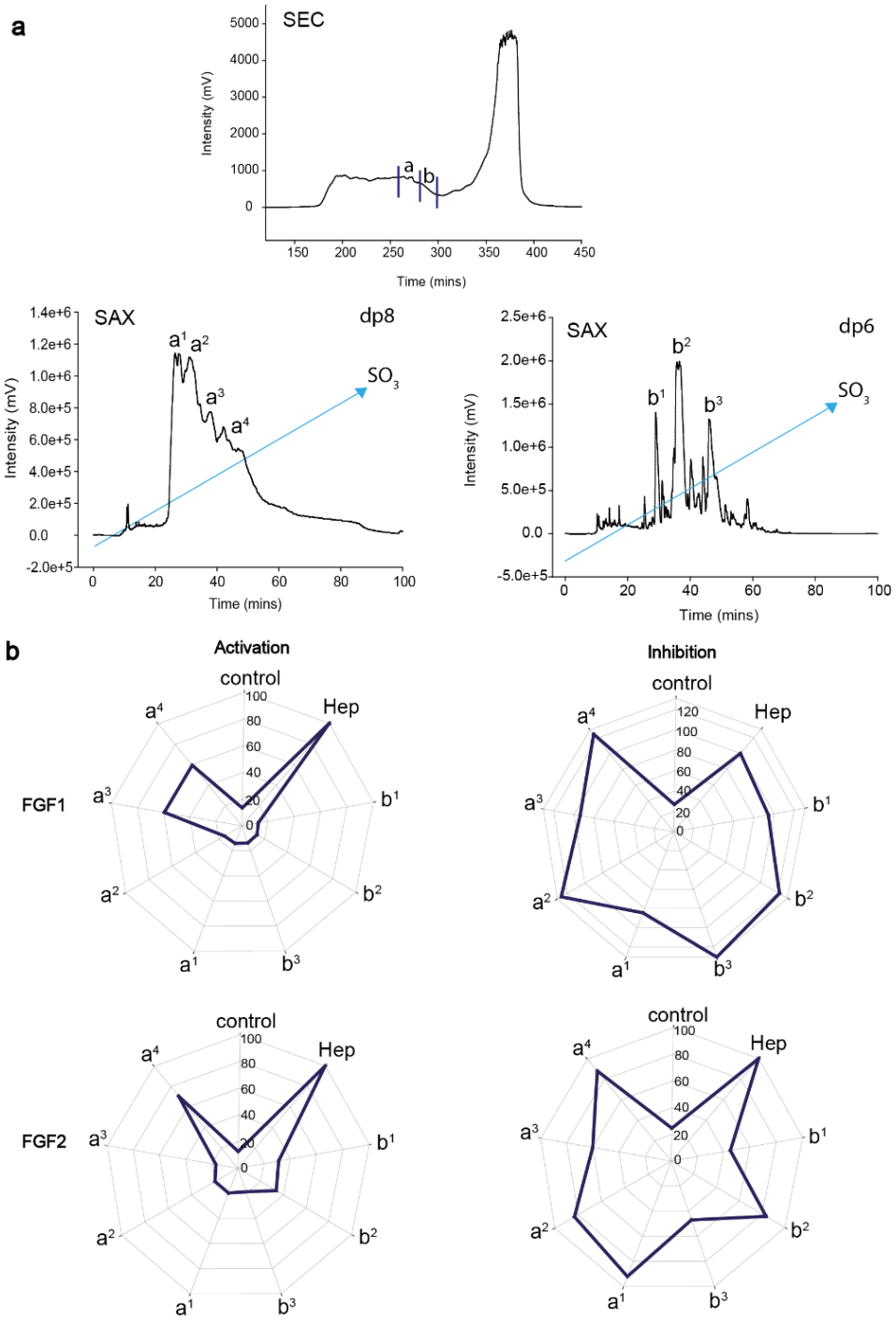
36



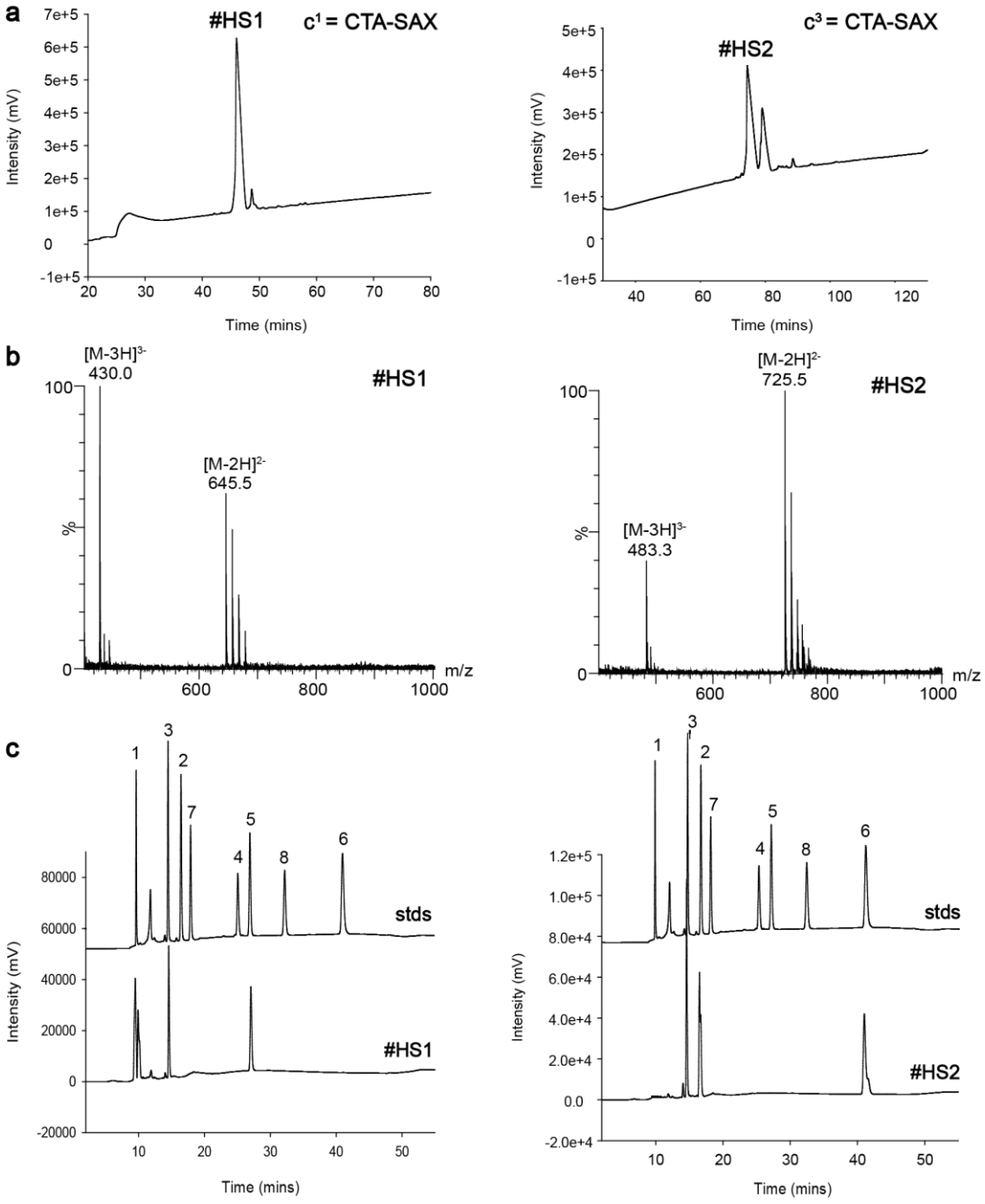
Supplementary Fig. 1. Using the SIMMS^2 method for sequencing a hexasaccharide. Overlaying two tetrasaccharide standard structures (#12 and #14) provides complete sequence coverage of the hexasaccharide (#16). Each structure was fragmented in the trap of the mass spectrometer and analysed using DTIMS, resulting in accurate CCS values. A comparison of overlapping fragment ions displayed the same CCS value between the two tetra- and hexasaccharides, providing a three-dimensional (MS, MS/MS and IMMS) sequencing method. **a-f**, The hexasaccharide #16 displays the DTIMS data to be determined. **g-h**, Tetrasaccharide #12 displayed CCS values from B -SO_3 ions; B_2-SO_3 – 122Å^2 and B_3-SO_3 – 140Å^2 matched CCS values observed in the hexasaccharide (a-c). **i-j**, Tetrasaccharide #14 displayed CCS values from Y ions; Y_1-SO_3 109Å^2 and Y_3-SO_3 150Å^2 matched the CCS values observed in the hexasaccharide **d-f**.



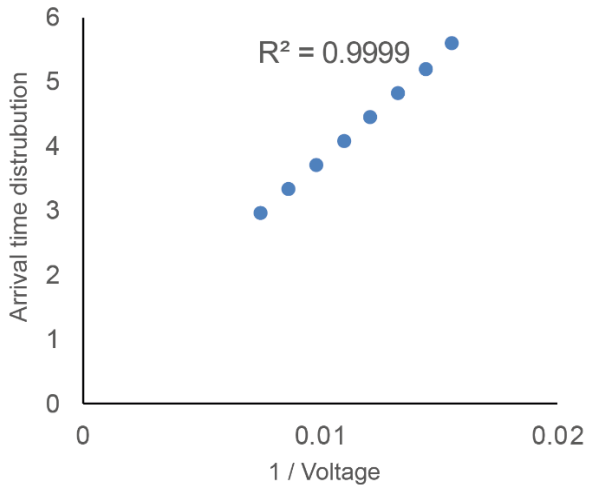
Supplementary Figure 2. SIMMS^2 sequencing of two hexasaccharides differing in a single 3*O*- and 6*O*-sulfation. HS structures #33 and #34 were fragmented in the trap and separated through IMMS to create a defined set of CCS values for each fragment. B ion fragments from #33 and #34 showed a difference at B_4 with the 6*O*-sulfated isomer (#33) showing a CCS value of 225 Å^2 and the B_4 fragment for 3*O*-sulfation (#34) demonstrating a CCS value of 220Å^2 respectively. Fragment ions from B/Y/C/Z are displayed in **Supplementary Tables 23 and 24.**



Supplementary Fig. 3. Purification of HS oligosaccharides with FGF1/2 bioactivity from porcine HS. a, Heparinase III digested porcine HS was separated by SEC and fractions a and b (corresponding to a dp8 and dp6, respectively) were further separated by SAX-HPLC to yield fractions $a^{1\text{-}4}$ and $b^{1\text{-}3}$. **b,** Radar charts illustrating BaF3 cell activation and inhibition of fractions $a^{1\text{-}4}$ and $b^{1\text{-}3}$. Activation assays were performed with FGF1 or FGF2 (1 ng/mL) and fractions as indicated. Heparin (3 μg/mL) was used as positive control, while FGF1 or FGF2 alone was used as negative. Inhibition assays were performed with the same fractions (3 μg/mL) in the presence of a sub-maximal dose of heparin (0.1 μg/mL). Cell proliferation results were expressed as a percentage of heparin activity set as 100%.



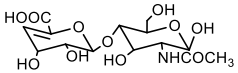
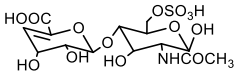
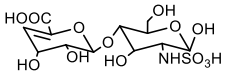
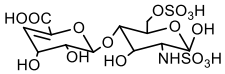
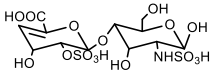
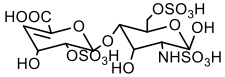
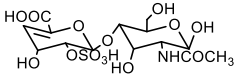
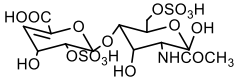
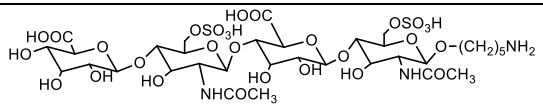
Supplementary Fig. 4. Isolation of pure hexasaccharides and their resulting disaccharide composition. a, Bioactive inhibitory hexasaccharides were purified further with CTA-SAX HPLC. **b,** Isolated CTA-SAX fractions #HS1 and #HS2 were subjected to mass spectrometry to confirm purity and mass. **c,** Disaccharide analysis of #HS1 and #HS2 through complete digestion to disaccharide products and separation on SAX ProPac PA1 (compared to authentic standards). Structure #HS1 contained ΔUA-GlcNAc, ΔUA-GlcNS and ΔUA2S-GlcNS, whereas structure #HS2 was composed of ΔUA-GlcNS, ΔUA-GlcNAc6S and ΔUA2S-GlcNS6S. Standards are 1- ΔUA-GlcNAc, 2 - ΔUA-GlcNAc6S, 3 - ΔUA-GlcNS, 4 - ΔUA-GlcNS6S, 5 – ΔUA2S-GlcNS, 6 – ΔUA2S-GlcNS6S, 7 – ΔUA2S-GlcNAc, 8 – ΔUA2S-GlcNAc6S.

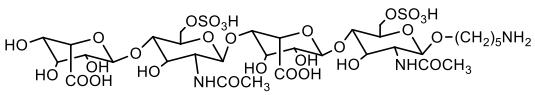
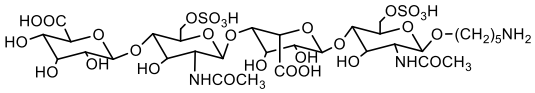
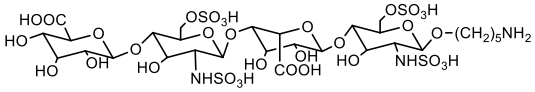
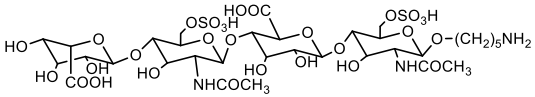
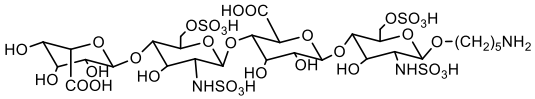
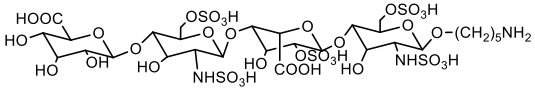
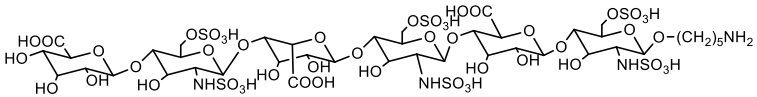
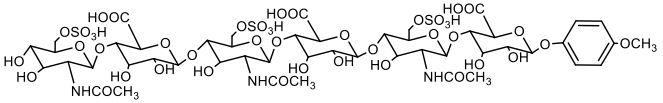
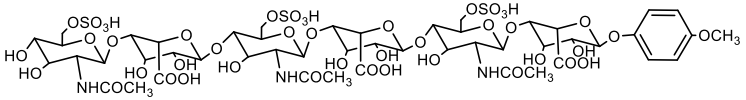
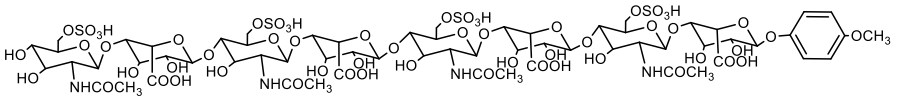
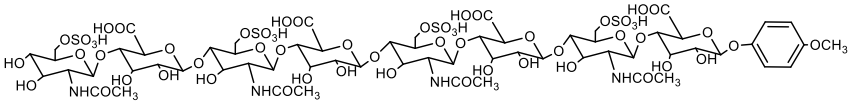


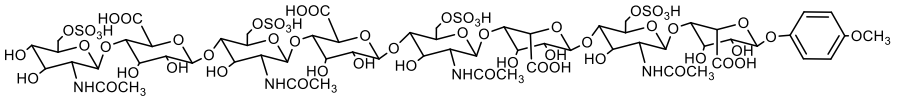
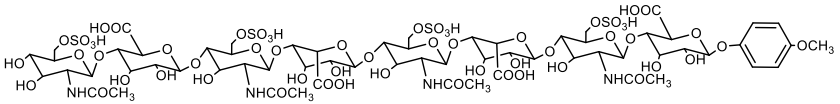
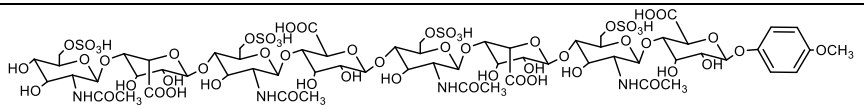
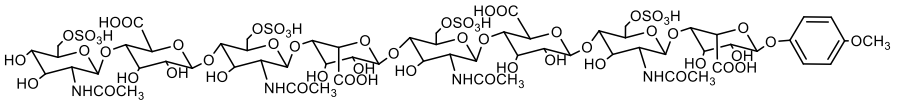
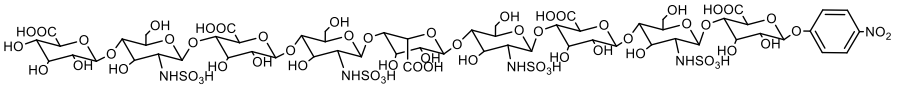
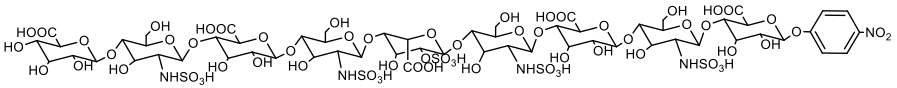
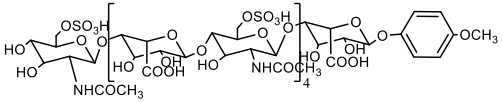
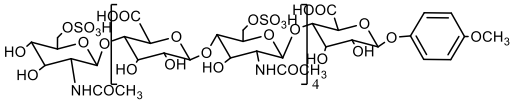
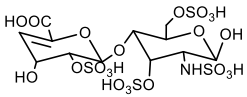
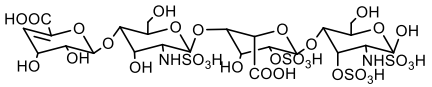
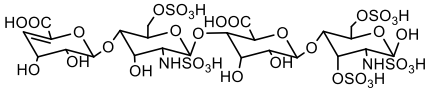
	Capillary - 0.6kV	Capillary - 0.8kV
Sample Cone - 2	210.33 (0.4)	210.60 (0.3)
Sample Cone - 20	210.70 (0.3)	210.38 (0.3)

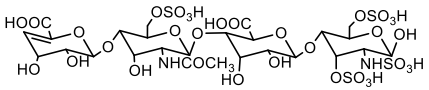
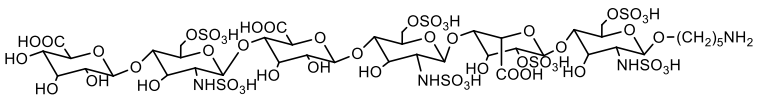
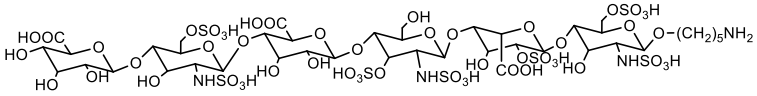
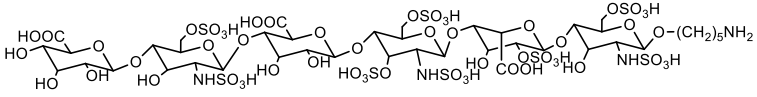
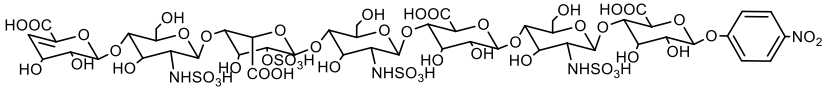
Supplementary Fig. 5. CCS of #10 using different DTIMS source conditions. Standard #10 was sprayed at a capillary voltage of 0.6 kV and 0.8 kV and a sample cone voltage or 2 and 20. The CCS value of #10 was determined from 8 DTIMS voltage measurements.

Supplementary Table 1. Summary of the used library of standards.

No.	Chemdraw Structure	Structure[1]
#1		ΔUA-GlcNAc
#2		ΔUA-GlcNAc6S
#3		ΔUA-GlcNS
#4		ΔUA-GlcNS6S
#5		ΔUA2S-GlcNS
#6		ΔUA2S-GlcNS6S
#7		ΔUA2S-GlcNAc
#8		ΔUA2S-GlcNAc6S
#9		G-GlcNAc6S-G-GlcNAc6S-R_1

#10		I-GlcNAc6S-I-GlcNAc6S-R_1
#11		G-GlcNAc6S-I-GlcNAc6S-R_1
#12		G-GlcNS6S-I-GlcNS6S-R_1
#13		I-GlcNAc6S-G-GlcNAc6S-R_1
#14		I-GlcNS6S-G-GlcNS6S-R_1
#15		G-GlcNS6S-I2S-GlcNS6S-R_1
#16		G-GlcNS6S-I-GlcNS6S-G-GlcNS6S-R_1
#17		GlcNAc6S-[G-GlcNAc6S]$_2$-G-R_2
#18		GlcNAc6S-[I-GlcNAc6S]$_2$-I-R_2
#19		GlcNAc6S-[I-GlcNAc6S]$_3$-I-R_2
#20		GlcNAc6S-[G-GlcNAc6S]$_3$-G-R_2

#21		GlcNAc6S-G-GlcNAc6S-G-GlcNAc6S-I-GlcNAc6S-I-R_2
#22		GlcNAc6S-G-GlcNAc6S-I-GlcNAc6S-I-GlcNAc6S-G-R_2
#23		GlcNAc6S-I-GlcNAc6S-G-GlcNAc6S-I-GlcNAc6S-G-R_2
#24		GlcNAc6S-G-GlcNAc6S-I-GlcNAc6S-G-GlcNAc6S-I-R_2
#25		G-GlcNS-G-GlcNS-I-GlcNS-G-GlcNS-G-R_3
#26		G-GlcNS-G-GlcNS-I2S-GlcNS-G-GlcNS-G-R_3
#27		GlcNAc6S-[I-GlcNAc6S]$_4$-I-R_2
#28		GlcNAc6S-[G-GlcNAc6S]$_4$-G-R_2
#29		ΔUA2S-GlcNS3S6S
#30		ΔUA-GlcNS-IdoA2S-GlcNS3S
#31		ΔUA-GlcNS6S-GlcA-GlcNS3S6S

#32		ΔUA-GlcNAc6S-GlcA-GlcNS3S6S
#33		G-GlcNS6S-G-GlcNS6S-I2S-GlcNS6S-R_1
#34		G-GlcNS6S-G-GlcNS3S-I2S-GlcNS6S-R_1
#35		G-GlcNS6S-G-GlcNS3S6S-I2S-GlcNS6S-R_1
#36		ΔUA-GlcNS-I2S-GlcNS-G-GlcNS-G-R_3

[1] The GlcA residues are represented by G and the IdoA residues represented by I. Tags R_1 is $(CH_2)_5NH_2$, R_2 is C_7H_7O and R_3 is $C_6H_4NO_2$.

[2] Standard #26 was digested with heparinase II and then separated using SAX, resulting in the purification of the dp7 + 2OS (#36) required.

Supplementary Table 2. Summary of CCS values obtained from the standard library.

	CCS (1-)[1]	CCS (2-)	CCS (3-)	CCS (4-)	CCS (5-)
#1	111.9 (0.3)[2]				
#2	121.0 (0.5)				
#3	112.4 (0.4)				
#4	123.5 (0.1)				
#5	124.3 (0.2)				
#6	137.4 (0.5)				
#7	123.6 (0.5)				
#8	134.2 (0.5)				
#9		206.2 (0.8)	214.2 (0.7)/247 (0.9)		
#10		210.1 (0.5)	242.0 (0.2)		
#11		206.8 (0.5)	232.4 (0.7)		
#12		200.1 (0.9)	236.2 (0.2)		
#13		208.7 (0.4)	245.5 (0.7)		
#14		201.5 (0.8)	234.0 (0.1)		
#15		203.9 (0.5)	238.8 (0.5)		
#16		255.6 (0.9)	258.8 (0.8)		
#17		266.8 (0.6)	296.5 (0.4)	347.4 (0.2)	
#18		265.8 (0.2)	292.4 (0.4)	342.2 (0.5)	
#19				379.8 (0.7)/416.0 (0.2)	433.8 (0.5)
#20				391.4 (0.8)	442.9 (0.2)
#21				379.2 (0.8)	438.5 (0.5)
#22				396.5 (0.7)	440.8 (0.5)
#23				400.8 (0.3)	435.6 (0.4)
#24				378.3 (0.5)	439.7 (0.4)
#25				437.4 (0.3)	438.4 (0.8)
#26				441.4 (0.3)	445.7 (0.5)
#27					499.8 (0.4)
#28					496.1 (0.7)
#29		149.7 (0.2)			
#30			228.0 (0.1)		
#31			228.9 (0.3)		
#32			234.5 (0.1)		
#33			280.5 (0.1)	339.5 (0.3)	
#34			282.4 (0.4)		
#35				328.3 (0.6)	
#36				363.2 (0.8)	

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 3. CCS of B, Y, C and Z ions identified in isomeric tetrasaccharide UA-GlcNAc6S-UA-GlcNAc6S-R_1 structures, where R_1 is $(CH_2)_5NH_2$.

			#9		**#10**		**#11**		**#13**	
			G-GlcNAc6S-G-GlcNAc6S-R_1		I-GlcNAc6S-I-GlcNAc6S-R_1		G-GlcNAc6S-I-GlcNAc6S-R_1		I-GlcNAc6S-G-GlcNAc6S-R_1	
$[M-2H]^{2-}$			509.61	206.2 (0.8)[2]	509.61	210.1 (0.5)	509.61	206.8 (0.5)	509.61	208.7 (0.4)
$[M-3H]^{3-}$			339.4	214.2 (0.7)/247 (0.9)	339.4	242.0 (0.2)	339.4	232.4 (0.7)	339.4	245.5 (0.7)
	(1-)[1]	(2-)	(1-)[1]	(2-)	(1-)	(2-)	(1-)	(2-)	(1-)	(2-)
B1	175.02	87.01	x	x	x	x	x	x	x	x
B2	458.06	228.53	120.9 (0.3)	x	121.5 (0.5)	x	121.5 (0.3)	x	120.8 (0.1)	x
B3	634.09	316.54	150.6 (0.1)	x	150.7 (0.5)	x	150.7 (0.5)	x	150.5 (0.11)	x
B4	917.13	458.06	x	x	x	x	x	x	x	x
Y0	102.09	50.54	x	x	x	x	x	x	x	x
Y1	385.13	192.06	120.1 (0.5)	x	119.7 (0.6)	x	119.8 (0.2)	x	120.2 (0.5)	x
Y2	561.16	280.08	x	x	145.27 (0.1)	161.5 (0.3)	145.9 (0.4)	161.9 (0.2)	x	x
Y3	844.20	421.59	x	188.9 (0.2)	x	187.5 (0.5)	x	186.2 (0.7)	x	188.6 (0.3)
C1	193.03	96.01	x	x	x	x	x	x	x	x
C2	476.07	237.53	122.5 (0.2)	x	122.3 (0.2)	x	122.6 (0.3)	x	122.2 (0.2)	x
C3	652.10	325.55	x	x	x	x	x	x	x	x
C4	935.14	467.07	x	x	x	x	x	x	x	x
Z0	84.08	41.54	x	x	x	x	x	x	x	x
Z1	367.12	183.05	116.7 (0.2)	x	117.4 (0.3)	x	117.3 (0.2)	x	116.9 (0.3)	x
Z2	543.15	271.07	x	x	x	x	x	x	x	x
Z3	826.19	412.59	x	x	x	x	x	x	x	x

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 4. CCS of B, Y, C and Z ions identified in isomeric tetra-saccharide UA-GlcNS6S-UA-GlcNS6S-R_1 structures, where R_1 is $(CH_2)_5NH_2$.

				#12			**#14**		
				G-GlcNS6S-I-GlcNS6S-R_1			I-GlcNS6S-G-GlcNS6S-R_1		
$[M-2H]^{2-}$				547.55	200.1 (0.9)[2]		547.55	201.5 (0.8)	
$[M-3H]^{3-}$				364.7	236.2 (0.2)		364.7	234.0 (0.1)	
	(1-)	(2-)	(3-)	(1-)[1]	(2-)	(3-)	(1-)	(2-)	(3-)
B1	175.02	87.01	57.67	68.9 (0.2)	x	x	69.0 (0.4)	x	x
B2	496.01	247.50	164.66	x	134.5 (0.6)	x	x	133.8 (0.3)	x
B3	672.04	335.52	223.34	x	160.2 (0.2)	x	x	165.5 (0.2)	x
B4	993.02	496.01	330.34	x	x	225.7 (0.2)	x	x	226.1 (0.2)
Y0	102.09	50.54	33.46	x	x	x	x	x	x
Y1	423.07	211.03	140.35	112.5 (0.3)	x	x	112.1 (0.1)	x	x
Y2	599.11	299.05	199.03	x	162.2 (0.5)	x	x	156.5 (0.5)	x
Y3	920.09	459.54	306.02	x	x	x	x	x	212.6 (0.6)
C1	193.03	96.01	63.67	x	x	x	x	x	x
C2	514.02	256.50	170.67	x	x	x	x	x	x
C3	690.05	344.52	229.34	x	x	x	x	165.6 (0.1)	x
C4	1011.03	505.01	336.34	x	x	x	x	x	x
Z0	84.08	41.54	27.36	x	x	x	x	x	x
Z1	405.06	202.03	134.35	x	x	x	x	x	x
Z2	581.10	290.04	193.03	x	x	x	x	x	x
Z3	902.08	450.54	300.02	x	x	x	x	x	x

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 5. CCS of B, Y, C and Z ions identified in a tetra-saccharide structure (R_1 is $(CH_2)_5NH_2$).

#15						
G-GlcNS6S-I2S-GlcNS6S-R_1						
$[M-2H]^{2-}$	587.53	203.9 (0.5)[2]				
$[M-3H]^{3-}$	391.35	238.8 (0.5)				
	(1-)[1]	(2-)	(3-)	(1-)	(2-)	(3-)
B1	175.02	87.01	57.67	x	x	x
B2	496.01	247.50	164.66	x	135.2 (0.5)	x
B3	752.00	375.49	249.99	x	x	x
B4	1072.98	535.99	356.99	x	x	229.0 (0.4)
Y0	102.09	50.54	33.36	x	x	x
Y1	423.07	211.03	140.35	112.8 (0.3)	x	x
Y2	679.06	339.03	225.68	x	x	x
Y3	1000.05	499.52	332.68	x	x	x
C1	193.03	96.01	63.67	x	x	x
C2	514.02	256.50	170.67	x	x	x
C3	770.01	384.50	256.00	x	x	x
C4	1090.99	544.99	362.99	x	x	x
Z0	84.08	41.54	27.36	x	x	x
Z1	405.06	202.03	134.35	x	x	x
Z2	661.05	330.02	219.68	x	x	x
Z3	982.03	490.51	326.67	x	x	x

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 6. CCS of B, Y, C and Z ions identified in a hexa-saccharide structure (R_1 is $(CH_2)_5NH_2$).

#16								
G-GlcNS6S-I-GlcNS6S-G-GlcNS6S-R_1								
$[M-2H]^{2-}$	796.06	255.6 (0.9)[2]						
$[M-3H]^{3-}$	530.37	258.8 (0.8)						
	(1-)[1]	(2-)	(3-)	(4-)	(1-)	(2-)	(3-)	(4-)
B1	175.02	87.01	57.67	43.00	x	x	x	x
B2	496.01	247.50	164.66	123.25	x	134.6 (0.4)	x	x
B3	672.04	335.52	223.34	167.25	x	160.3 (0.2)	x	x
B4	993.02	496.01	330.34	247.50	x	x	226.1 (0.2)	x
B5	1169.05	584.02	389.01	291.51	x	x	249.4 (0.8)	275.9 (0.7)
B6	1490.04	744.51	496.01	371.75	x	x	x	x
Y0	102.09	50.54	33.36	24.77	x	x	x	x
Y1	423.07	211.03	140.35	105.01	x	130.0 (0.7)	x	x
Y2	599.11	299.05	199.03	149.02	x	156.4 (0.5)	x	x
Y3	920.09	459.54	306.02	229.27	x	x	213.1 (0.7)	x
Y4	1096.12	547.56	364.70	273.27	x	x	233.2 (0.6)	x
Y5	1417.10	708.05	471.70	353.52	x	x	x	324.5 (0.2)
C1	193.03	96.01	63.67	47.50	x	x	x	x
C2	514.02	256.50	170.67	127.75	x	x	x	x
C3	690.05	344.52	229.34	171.76	x	x	x	x
C4	1011.03	505.01	336.34	252.00	x	x	x	x
C5	1187.06	593.03	395.02	296.01	x	x	x	x
C6	1508.05	753.52	502.01	376.26	x	x	x	x
Z0	84.08	41.54	27.36	20.26	x	x	x	x
Z1	405.06	202.03	134.35	100.51	x	x	x	x
Z2	581.10	290.04	193.03	144.52	x	x	x	x
Z3	902.08	450.54	300.02	224.76	x	x	x	x

Z4	1078.11	538.55	358.70	268.77	x	x	x	x
Z5	1399.09	699.04	465.69	349.02	x	x	x	x

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 7. CCS of B, Y, C and Z ions identified in a hexa-saccharide GlcNAc6S-[G-GlcNAc6S]$_2$-G-R$_2$ structure, where R^2 is C_7H_7O.

#17						
GlcNAc6S-[G-GlcNAc6S]$_2$-G-R$_2$						
$[M-3H]^{3-}$	499.41	296.5 (0.4)[2]				
$[M-4H]^{4-}$	374.3	347.4 (0.2)				
	(1-)[1]	(2-)	(3-)	(1-)	(2-)	(3-)
B1	282.03	140.51	93.34	93.0 (0.2)	x	x
B2	458.06	228.53	152.01	120.8 (0.2)	135.1 (0.5)	x
B3	741.1	370.04	246.36	x	169.7 (0.6)	x
B4	917.13	458.06	305.04	x	x	225.6 (0.8)
B5	1200.16	599.58	399.38	x	x	270.4 (0.2)
B6	1376.2	687.59	458.06	x	x	291.3 (0.7)
Y0	122.04	60.51	40.01	x	x	x
Y1	299.08	149.03	99.02	105.4 (0.7)	x	x
Y2	582.11	290.55	193.37	154.4 (0.4)	166.0 (0.4)	x
Y3	758.14	378.57	252.04	x	x	x
Y4	1041.18	520.09	346.39	x	x	255.8 (0.5)
Y5	1217.21	608.1	405.07	x	x	x
C1	300.04	149.52	99.34	94.4 (0.2)	x	x
C2	476.07	237.53	158.02	122.3 (0.4)	x	x
C3	759.11	379.05	252.36	x	x	200.1 (0.9)
C4	935.14	467.07	311.04	x	185.2 (0.6)	x
C5	1218.18	608.58	405.39	x	x	273.9 (0.1)
C6	1394.21	696.6	464.06	x	x	x
Z0	105.03	52.01	34.34	x	x	x
Z1	281.07	140.03	93.02	x	x	x
Z2	564.1	281.55	187.36	x	x	x
Z3	740.13	369.56	246.04	x	x	x
Z4	1023.17	511.08	340.38	x	x	x
Z5	1199.2	599.1	399.06	x	x	x

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 8. CCS of B, Y, C and Z ions identified in a hexa-saccharide GlcNAc6S-[I-GlcNAc6S]$_2$-I-R$_2$ structure, where R$_2$ is C_7H_7O.

#18						
GlcNAc6S-[I-GlcNAc6S]$_2$-I-R$_2$						
$[M-3H]^{3-}$	499.41	291.8 (0.7)[2]				
$[M-4H]^{4-}$	374.3	342.2 (0.3)				
	(1-)[1]	(2-)	(3-)	(1-)[1]	(2-)	(3-)
B1	282.03	140.51	93.34	92.9 (0.2)	x	x
B2	458.06	228.53	152.01	122.6 (0.4)	x	x
B3	741.10	370.04	246.36	x	176.0 (0.8)	x
B4	917.13	458.06	305.04	x	197.1 (0.17)	x
B5	1200.16	599.58	399.38	x	x	269.2 (0.8)
B6	1376.20	687.59	458.06	x	x	294.1 (0.16)
Y0	122.04	60.51	40.01	x	x	x
Y1	299.08	149.03	99.02	103.7 (0.1)	x	x
Y2	582.11	290.55	193.37	153.9 (0.6)	166.3 (0.3)	x
Y3	758.14	378.57	252.04	x	x	x
Y4	1041.18	520.09	346.39	x	x	x
Y5	1217.21	608.10	405.07	x	229.9 (0.1)	x
C1	300.04	149.52	99.34	94.1 (0.2)	x	x
C2	476.07	237.53	158.02	122.6 (0.3)	x	x
C3	759.11	379.05	252.36	x	x	x
C4	935.14	467.07	311.04	x	x	x
C5	1218.18	608.58	405.39	x	x	x
C6	1394.21	696.60	464.06	x	x	x
Z0	105.03	52.01	34.34	x	x	x
Z1	281.07	140.03	93.02	x	x	x
Z2	564.10	281.55	187.36	x	x	x
Z3	740.13	369.56	246.04	x	x	x
Z4	1023.17	511.08	340.38	x	x	x
Z5	1199.20	599.10	399.06	x	x	x

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 9. CCS of B, Y, C and Z ions identified in an octa-saccharide GlcNAc6S-[I-GlcNAc6S]$_3$-I-R_2 structure, where R_2 is C_7H_7O.

#19								
GlcNAc6S-[I-GlcNAc6S]$_3$-I-R_2								
$[M-4H]^{4-}$	489.07	379.8 (0.7)[2]/416.0 (0.2)						
$[M-5H]^{5-}$	391.05	433.8 (0.5)						
$[M-6H]^{6-}$	325.7	449.4 (0.6)						
	(1-)[1]	(2-)	(3-)	(4-)	(1-)	(2-)	(3-)	(4-)
B1	282.03	140.51	93.34	69.75	93.3 (0.3)	x	x	x
B2	458.06	228.53	152.01	113.76	122.0 (0.6)	x	x	x
B3	741.10	370.04	246.36	184.52	x	176.3 (0.8)	x	x
B4	917.13	458.06	305.04	228.53	x	197.2 (0.7)	x	x
B5	1200.16	599.58	399.38	299.29	x	x	270.0 (0.3)	x
B6	1376.20	687.59	458.06	343.29	x	x	294.4 (0.7)	x
B7	1659.23	829.11	552.41	414.05	x	x	x	x
B8	1835.27	917.13	611.08	458.06	x	x	x	394.0 (0.6)
Y0	122.04	60.51	40.01	29.75	x	x	x	x
Y1	299.08	149.03	99.02	74.01	x	x	x	x
Y2	582.11	290.55	193.37	144.77	x	166.0 (0.6)	x	x
Y3	758.14	378.57	252.04	188.78	x	x	x	x
Y4	1041.18	520.09	346.39	259.54	x	x	x	x
Y5	1217.21	608.10	405.07	303.55	x	229.2 (0.2)	x	x
Y6	1500.25	749.62	499.41	374.31	x	290.5 (0.5)	x	x
Y7	1676.28	837.64	558.09	418.31	x	x	x	x
C1	300.04	149.52	99.34	74.25	94.0 (0.7)	x	x	x
C2	476.07	237.53	158.02	118.26	122.8 (0.5)	x	x	x
C3	759.11	379.05	252.36	189.02	x	x	x	x
C4	935.14	467.07	311.04	233.03	x	x	x	x

C5	1218.18	608.58	405.39	303.79	x	x	x	x
C6	1394.21	696.60	464.06	347.80	x	x	x	x
C7	1677.24	838.12	558.41	418.56	x	x	x	x
C8	1853.28	926.13	617.09	462.56	x	x	x	x
Z0	105.03	52.01	34.34	25.50	x	x	x	x
Z1	281.07	140.03	93.02	69.51	x	x	x	x
Z2	564.10	281.55	187.36	140.27	x	x	x	x
Z3	740.13	369.56	246.04	184.28	x	x	x	x
Z4	1023.17	511.08	340.38	255.04	x	x	x	x
Z5	1199.20	599.10	399.06	299.04	x	x	x	x
Z6	1482.24	740.62	493.41	369.80	x	x	x	x
Z7	1658.27	828.63	552.09	413.81	x	x	x	x

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 10. CCS of B, Y, C and Z ions identified in an octa-saccharide GlcNAc6S-[G-GlcNAc6S]$_3$-G-R_2 structure, where R_2 is C_7H_7O.

#20								
GlcNAc6S-[G-GlcNAc6S]$_3$-G-R_2								
$[M-4H]^{4-}$	489.07	391.4 (0.8)[2]						
$[M-5H]^{5-}$	391.05	442.9 (0.2)						
$[M-6H]^{6-}$	325.7	456.7 (0.8)						
	(1-)[1]	(2-)	(3-)	(4-)	(1-)[1]	(2-)	(3-)	(4-)
B1	282.03	140.51	93.34	69.75	93.4 (0.1)	x	x	x
B2	458.06	228.53	152.01	113.76	121.6 (0.5)	x	x	x
B3	741.10	370.04	246.36	184.52	x	169.9 (0.4)		x
B4	917.13	458.06	305.04	228.53	x	194.1 (0.3)	225.8 (0.8)	x
B5	1200.16	599.58	399.38	299.29	x	x	270.5 (0.2)	x
B6	1376.20	687.59	458.06	343.29	x	x	x	x
B7	1659.23	829.11	552.41	414.05	x	x	291.0 (0.1)	322.1 (0.2)
B8	1835.27	917.13	611.08	458.06	x	x	x	391.8 (0.1)
Y0	122.04	60.51	40.01	29.75	x	x	x	x
Y1	299.08	149.03	99.02	74.01	x	x	x	x
Y2	582.11	290.55	193.37	144.77	154.3 (0.5)	165.8 (0.7)	x	x
Y3	758.14	378.57	252.04	188.78	x	x	x	x
Y4	1041.18	520.09	346.39	259.54	x	x	255.1 (0.8)	x
Y5	1217.21	608.10	405.07	303.55	x	x	x	x
Y6	1500.25	749.62	499.41	374.31	x	x	x	x
Y7	1676.28	837.64	558.09	418.31	x	x	x	x
C1	300.04	149.52	99.34	74.25	94.6 (0.4)	x	x	x
C2	476.07	237.53	158.02	118.26	122.2 (0.4)	x	x	x
C3	759.11	379.05	252.36	189.02	x	167.5 (0.1)	x	x
C4	935.14	467.07	311.04	233.03	x	x	x	x
C5	1218.18	608.58	405.39	303.79	x	x	x	x

C6	1394.21	696.60	464.06	347.80	x	x	309.1 (0.87)	x
C7	1677.24	838.12	558.41	418.56	x	x	x	x
C8	1853.28	926.13	617.09	462.56	x	x	x	x
Z0	105.03	52.01	34.34	25.50	x	x	x	x
Z1	281.07	140.03	93.02	69.51	x	x	x	x
Z2	564.10	281.55	187.36	140.27	x	x	x	x
Z3	740.13	369.56	246.04	184.28	x	x	x	x
Z4	1023.17	511.08	340.38	255.04	x	x	x	x
Z5	1199.20	599.10	399.06	299.04	x	x	x	x
Z6	1482.24	740.62	493.41	369.80	x	x	x	x
Z7	1658.27	828.63	552.09	413.81	x	x	x	x

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 11. CCS of B, Y, C and Z ions identified in an octa-saccharide GlcNAc6S-G-GlcNac6S-G-GlcNAc6S-I-GlcNAc6S-I-R_2 structure, where R_2 is C_7H_7O.

#21								
GlcNAc6S-G-GlcNac6S-G-GlcNAc6S-I-GlcNAc6S-I-R_2								
$[M-4H]^{4-}$	489.07	379.2 (0.8)[2]						
$[M-5H]^{5-}$	391.05	438.5 (0.5)						
$[M-6H]^{6-}$	325.7	452.4 (0.8)						
	(1-)[1]	(2-)	(3-)	(4-)	(1-)	(2-)	(3-)	(4-)
B1	282.03	140.51	93.34	69.75	92.6 (0.5)	x	x	x
B2	458.06	228.53	152.01	113.76	121.4 (0.2)	x	x	x
B3	741.10	370.04	246.36	184.52	x	x	x	x
B4	917.13	458.06	305.04	228.53	x	x	224.8 (0.4)	x
B5	1200.16	599.58	399.38	299.29	x	x	270.1 (0.4)	x
B6	1376.20	687.59	458.06	343.29	x	x	x	322.3 (0.2)
B7	1659.23	829.11	552.41	414.05	x	x	x	367.3 (0.4)
B8	1835.27	917.13	611.08	458.06	x	x	x	x
Y0	122.04	60.51	40.01	29.75	x	x	x	x
Y1	299.08	149.03	99.02	74.01	103.4 (0.5)	x	x	x
Y2	582.11	290.55	193.37	144.77	153.8 (0.5)	x	x	x
Y3	758.14	378.57	252.04	188.78	x	x	x	x
Y4	1041.18	520.09	346.39	259.54	x	x	255.4 (0.6)	x
Y5	1217.21	608.10	405.07	303.55	x	x	x	x
Y6	1500.25	749.62	499.41	374.31	x	x	284.7 (0.6)	346.4 (0.7)
Y7	1676.28	837.64	558.09	418.31	x	x	x	x
C1	300.04	149.52	99.34	74.25	94.4 (0.3)	x	x	x
C2	476.07	237.53	158.02	118.26	122.4 (0.8)	x	x	x
C3	759.11	379.05	252.36	189.02	x	x	x	x
C4	935.14	467.07	311.04	233.03	x	x	x	x

C5	1218.18	608.58	405.39	303.79	x	x	x	x
C6	1394.21	696.60	464.06	347.80	x	x	x	x
C7	1677.24	838.12	558.41	418.56	x	x	x	x
C8	1853.28	926.13	617.09	462.56	x	x	x	x
Z0	105.03	52.01	34.34	25.50	x	x	x	x
Z1	281.07	140.03	93.02	69.51	x	x	x	x
Z2	564.10	281.55	187.36	140.27	x	x	x	x
Z3	740.13	369.56	246.04	184.28	x	x	x	x
Z4	1023.17	511.08	340.38	255.04	x	x	x	x
Z5	1199.20	599.10	399.06	299.04	x	x	x	x
Z6	1482.24	740.62	493.41	369.80	x	x	x	x
Z7	1658.27	828.63	552.09	413.81	x	x	x	x

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 12. CCS of B, Y, C and Z ions identified in an octa-saccharide GlcNAc6S-G- GlcNac6S-I-GlcNAc6S-I-GlcNAc6S-G-R_2 structure, where R_2 is C_7H_7O.

#22								
GlcNAc6S-G-GlcNac6S-I-GlcNAc6S-I-GlcNAc6S-G-R_2								
$[M-4H]^{4-}$	489.07	396.5 (0.7)[2]						
$[M-5H]^{5-}$	391.05	440.8 (0.5)						
$[M-6H]^{6-}$	325.7	461.3 (0.7)						
	(1-)[1]	(2-)	(3-)	(4-)	(1-)	(2-)	(3-)	(4-)
B1	282.03	140.51	93.34	69.75	93.0 (0.2)	x	x	x
B2	458.06	228.53	152.01	113.76	121.6 (0.3)	x	x	x
B3	741.10	370.04	246.36	184.52	x	x	x	x
B4	917.13	458.06	305.04	228.53	x	x	x	x
B5	1200.16	599.58	399.38	299.29	x	x	272.8 (0.6)	x
B6	1376.20	687.59	458.06	343.29	x	x	x	323.2 (0.2)
B7	1659.23	829.11	552.41	414.05	x	x	x	x
B8	1835.27	917.13	611.08	458.06	x	x	x	x
Y0	122.04	60.51	40.01	29.75	x	x	x	x
Y1	299.08	149.03	99.02	74.01	x	x	x	x
Y2	582.11	290.55	193.37	144.77	154.9 (0.3)	x	x	x
Y3	758.14	378.57	252.04	188.78	x	x	x	x
Y4	1041.18	520.09	346.39	259.54	x	x	254.1 (0.28)	x
Y5	1217.21	608.10	405.07	303.55	x	x	x	300.6 (0.2)
Y6	1500.25	749.62	499.41	374.31	x	x	289.1 (0.6)	x
Y7	1676.28	837.64	558.09	418.31	x	x	x	x
C1	300.04	149.52	99.34	74.25	94.1 (0.3)	x	x	x
C2	476.07	237.53	158.02	118.26	123.0 (0.4)	x	x	x
C3	759.11	379.05	252.36	189.02	x	x	x	x
C4	935.14	467.07	311.04	233.03	x	x	x	x

C5	1218.18	608.58	405.39	303.79	x	x	x	x
C6	1394.21	696.60	464.06	347.80	x	x	x	x
C7	1677.24	838.12	558.41	418.56	x	x	x	371.4 (0.5)
C8	1853.28	926.13	617.09	462.56	x	x	x	x
Z0	105.03	52.01	34.34	25.50	x	x	x	x
Z1	281.07	140.03	93.02	69.51	x	x	x	x
Z2	564.10	281.55	187.36	140.27	x	x	x	x
Z3	740.13	369.56	246.04	184.28	x	x	x	x
Z4	1023.17	511.08	340.38	255.04	x	x	x	x
Z5	1199.20	599.10	399.06	299.04	x	x	x	x
Z6	1482.24	740.62	493.41	369.80	x	x	x	x
Z7	1658.27	828.63	552.09	413.81	x	x	x	x

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 13. CCS of B, Y, C and Z ions identified in an octa-saccharide GlcNAc6S-I-GlcNAc6S-G-GlcNAc6S-I-GlcNAc6S-G-R_2 structure, where R_2 is C_7H_7O.

#23								
GlcNAc6S-I-GlcNAc6S-G-GlcNAc6S-I-GlcNAc6S-G-R_2								
$[M-4H]^{4-}$	489.07	400.8 (0.3)[2]						
$[M-5H]^{5-}$	391.05	435.6 (0.4)						
$[M-6H]^{6-}$	325.7	453.4 (0.7)						
	(1-)[1]	(2-)	(3-)	(4-)	(1-)	(2-)	(3-)	(4-)
B1	282.03	140.51	93.34	69.75	93.3 (0.6)	x	x	x
B2	458.06	228.53	152.01	113.76	x	x	x	x
B3	741.10	370.04	246.36	184.52	x	x	x	x
B4	917.13	458.06	305.04	228.53	x	x	x	x
B5	1200.16	599.58	399.38	299.29	x	x	272.0 (0.1)	x
B6	1376.20	687.59	458.06	343.29	x	x	x	x
B7	1659.23	829.11	552.41	414.05	x	x	x	x
B8	1835.27	917.13	611.08	458.06	x	x	x	x
Y0	122.04	60.51	40.01	29.75	x	x	x	x
Y1	299.08	149.03	99.02	74.01	x	x	x	x
Y2	582.11	290.55	193.37	144.77	155.0 (0.2)	x	x	x
Y3	758.14	378.57	252.04	188.78	x	x	x	x
Y4	1041.18	520.09	346.39	259.54	x	x	x	x
Y5	1217.21	608.10	405.07	303.55	x	x	x	x
Y6	1500.25	749.62	499.41	374.31	x	x	x	339.5 (0.3)
Y7	1676.28	837.64	558.09	418.31	x	x	x	366.4 (0.3)
C1	300.04	149.52	99.34	74.25	93.2 (0.1)	x	x	x
C2	476.07	237.53	158.02	118.26	122.0 (0.2)	132.8 (0.4)	x	x
C3	759.11	379.05	252.36	189.02	x	x	x	x
C4	935.14	467.07	311.04	233.03	x	x	x	x

C5	1218.18	608.58	405.39	303.79	x	x	x	x
C6	1394.21	696.60	464.06	347.80	x	x	x	315.3 (0.3)
C7	1677.24	838.12	558.41	418.56	x	x	x	367.2 (0.5)
C8	1853.28	926.13	617.09	462.56	x	x	x	x
Z0	105.03	52.01	34.34	25.50	x	x	x	x
Z1	281.07	140.03	93.02	69.51	x	x	x	x
Z2	564.10	281.55	187.36	140.27	x	x	x	x
Z3	740.13	369.56	246.04	184.28	x	x	x	x
Z4	1023.17	511.08	340.38	255.04	x	x	x	x
Z5	1199.20	599.10	399.06	299.04	x	x	x	x
Z6	1482.24	740.62	493.41	369.80	x	x	x	x
Z7	1658.27	828.63	552.09	413.81	x	x	x	x

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 14. CCS of B, Y, C and Z ions identified in an octa-saccharide GlcNAc6S-G-GlcNAc6S-I-GlcNAc6S-G-GlcNAc6S-I-R_2 structure, where R_2 is C_7H_7O.

#24								
GlcNAc6S-G-GlcNac6S-I-GlcNAc6S-G-GlcNAc6S-I-R_2								
$[M-4H]^{4-}$	489.07	378.3 (0.5)[2]						
$[M-5H]^{5-}$	391.05	439.7 (0.4)						
$[M-6H]^{6-}$	325.7	451.4 (0.6)						
	(1-)[1]	(2-)	(3-)	(4-)	(1-)	(2-)	(3-)	(4-)
B1	282.03	140.51	93.34	69.75	93.1 (0.4)	x	x	x
B2	458.06	228.53	152.01	113.76	121.4 (0.6)	x	x	x
B3	741.10	370.04	246.36	184.52	x	170.5 (0.6)	x	x
B4	917.13	458.06	305.04	228.53	x	x	x	x
B5	1200.16	599.58	399.38	299.29	x	x	270.9 (0.8)	x
B6	1376.20	687.59	458.06	343.29	x	x	x	x
B7	1659.23	829.11	552.41	414.05	x	x	x	366.2 (0.5)
B8	1835.27	917.13	611.08	458.06	x	x	x	x
Y0	122.04	60.51	40.01	29.75	x	x	x	x
Y1	299.08	149.03	99.02	74.01	103.1 (0.4)	x	x	x
Y2	582.11	290.55	193.37	144.77	153.4 (0.3)	x	x	x
Y3	758.14	378.57	252.04	188.78	x	x	x	x
Y4	1041.18	520.09	346.39	259.54	x	x	x	x
Y5	1217.21	608.10	405.07	303.55	x	226.0 (0.5)	289.6 (0.6)	x
Y6	1500.25	749.62	499.41	374.31	x	288.4 (0.4)	x	x
Y7	1676.28	837.64	558.09	418.31	x	x	x	x
C1	300.04	149.52	99.34	74.25	94.1 (0.2)	x	x	x
C2	476.07	237.53	158.02	118.26	122.2 (0.2)	x	x	x
C3	759.11	379.05	252.36	189.02	x	x	x	x
C4	935.14	467.07	311.04	233.03	x	x	x	x

C5	1218.18	608.58	405.39	303.79	x	x	x	x
C6	1394.21	696.60	464.06	347.80	x	x	x	x
C7	1677.24	838.12	558.41	418.56	x	x	x	x
C8	1853.28	926.13	617.09	462.56	x	x	x	x
Z0	105.03	52.01	34.34	25.50	x	x	x	x
Z1	281.07	140.03	93.02	69.51	x	x	x	x
Z2	564.10	281.55	187.36	140.27	x	x	x	x
Z3	740.13	369.56	246.04	184.28	x	x	x	x
Z4	1023.17	511.08	340.38	255.04	x	x	x	x
Z5	1199.20	599.10	399.06	299.04	x	x	x	x
Z6	1482.24	740.62	493.41	369.80	x	x	x	x
Z7	1658.27	828.63	552.09	413.81	x	x	x	x

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 15. CCS of B, Y, C and Z ions identified in a 9mer, G-GlcNS-G-GlcNS-I-GlcNS-G-GlcNS-G-R_3 structure, where R_3 is $C_6H_4NO_2$.

#25								
G-GlcNS-G-GlcNS-I-GlcNS-G-GlcNS-G-R_3								
$[M-4H]^{4-}$	494.81	437.4 (0.3)[2]						
$[M-5H]^{5-}$	395.65	438.4 (0.8)						
	(1-)[1]	(2-)	(3-)	(4-)	(1-)	(2-)	(3-)	(4-)
B1	175.02	87.01	57.67	43.00	71.5 (0.3)	x	x	x
B2	416.05	207.52	138.01	103.26	112.4 (0.4)	x	x	x
B3	592.08	295.54	196.69	147.26	x	157.8 (0.4)	x	x
B4	833.11	416.05	277.03	207.52	x	197.4 (0.4)	x	x
B5	1009.14	504.07	335.71	251.53	x	235.2 (0.5)	x	x
B6	1250.17	624.58	416.05	311.79	x	x	x	x
B7	1426.20	712.59	474.73	355.79	x	x	321.4 (0.4)	x
B8	1667.22	833.11	555.07	416.05	x	x	x	x
B9	1843.25	921.12	613.75	460.06	x	x	x	407.6 (0.5)
Y0	138.02	68.51	45.33	33.75	x	x	x	x
Y1	314.05	156.52	104.01	77.76	x	x	x	x
Y2	555.08	277.03	184.35	138.01	x	x	x	x
Y3	731.11	365.05	243.03	182.02	x	x	x	x
Y4	972.13	485.56	323.37	242.28	x	x	x	x
Y5	1148.17	573.58	382.05	286.29	x	x	x	x
Y6	1389.19	694.09	462.39	346.54	x	x	x	x
Y7	1565.22	782.11	521.07	390.55	x	x	x	x
Y8	1806.25	902.62	601.41	450.81	x	x	x	x
C1	192.03	95.51	63.34	47.25	x	x	x	x
C2	433.05	216.02	143.68	107.51	x	x	x	x
C3	609.08	304.04	202.36	151.52	x	x	x	x
C4	850.11	424.55	282.70	211.77	x	x	x	x

C5	1026.14	512.57	341.38	255.78	x	x	x	x
C6	1267.17	633.08	421.72	316.04	x	x	x	x
C7	1443.20	721.10	480.39	360.04	x	x	x	x
C8	1684.23	841.61	560.74	420.30	x	x	x	x
C9	1860.26	929.62	619.41	464.31	x	x	x	x
Z0	120.01	59.50	39.33	29.25	x	x	x	x
Z1	296.04	147.52	98.01	73.25	x	x	x	x
Z2	537.07	268.03	178.35	133.51	x	x	x	x
Z3	713.10	356.05	237.03	177.52	x	x	x	x
Z4	954.12	476.56	317.37	237.78	x	x	x	x
Z5	1130.16	564.57	376.05	281.78	x	x	x	x
Z6	1371.18	685.09	456.39	342.04	x	x	x	x
Z7	1547.21	773.10	515.07	386.05	x	x	x	x
Z8	1788.24	893.62	595.41	446.30	x	x	x	x

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 16. CCS of B, Y, C and Z ions identified in a dp9 + 1x2*O*-sulfate, G-GlcNS-G-GlcNS-I2S-GlcNS-G-GlcNS-G-R_3 structure, where R_3 is $C_6H_4NO_2$.

#26								
G-GlcNS-G-GlcNS-I2S-GlcNS-G-GlcNS-G-R_3								
$[M-4H]^{4-}$	514.8	441.4 (0.3)[2]						
$[M-5H]^{5-}$	411.64	445.7 (0.5)						
	(1-)[1]	(2-)	(3-)	(4-)	(1-)	(2-)	(3-)	(4-)
B1	175.02	87.01	57.67	43.00	x	x	x	x
B2	416.05	207.52	138.01	103.26	112.2 (0.2)	x	x	x
B3	592.08	295.54	196.69	147.26	x	158.0 (0.2)	x	x
B4	833.11	416.05	277.03	207.52	x	197.3 (0.6)	x	x
B5	1089.10	544.04	362.36	271.52	x	x	249.6 (0.7)	x
B6	1330.12	664.56	442.70	331.77	x	x	x	x
B7	1506.15	752.57	501.38	375.78	x	x	330.0 (0.6)	x
B8	1747.18	873.09	581.72	436.04	x	x	x	379.0 (0.4)
B9	1923.21	961.10	640.40	480.05	x	x	x	405.5 (0.2)
Y0	138.02	68.51	45.33	33.75	x	x	x	x
Y1	314.05	156.52	104.01	77.76	x	x	x	x
Y2	555.08	277.03	184.35	138.01	x	x	x	x
Y3	731.11	365.05	243.03	182.02	x	x	x	x
Y4	972.13	485.56	323.37	242.28	x	x	x	x
Y5	1228.12	613.56	408.70	306.27	x	x	x	x
Y6	1469.15	734.07	489.04	366.53	x	x	x	x
Y7	1645.18	822.09	547.72	410.54	x	x	x	x
Y8	1886.21	942.60	628.06	470.80	x	x	x	x
C1	192.03	95.51	63.34	47.25	x	x	x	x
C2	433.05	216.02	143.68	107.51	x	x	x	x
C3	609.08	304.04	202.36	151.52	x	x	x	x

C4	850.11	424.55	282.70	211.77	x	x	x	x
C5	1106.10	552.55	368.03	275.77	x	x	x	x
C6	1347.12	673.06	448.37	336.03	x	x	x	x
C7	1523.16	761.07	507.05	380.03	x	x	x	x
C8	1764.18	881.59	587.39	440.29	x	x	x	x
C9	1940.21	969.60	646.07	484.30	x	x	x	x
Z0	120.01	59.50	39.33	29.25	x	x	x	x
Z1	296.04	147.52	98.01	73.25	x	x	x	x
Z2	537.07	268.03	178.35	133.51	x	x	x	x
Z3	713.10	356.05	237.03	177.52	x	x	x	x
Z4	954.12	476.56	317.37	237.78	x	x	x	x
Z5	1210.11	604.55	402.70	301.77	x	x	x	x
Z6	1451.14	725.07	483.04	362.03	x	x	x	x
Z7	1627.17	813.08	541.72	406.04	x	x	x	x
Z8	1868.20	933.59	622.06	466.29	x	x	x	x

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 17. CCS of B, Y, C and Z ions identified in a dp10 GlcNAc6S-[I-GlcNAc6S]$_4$-I-R_2 structure, where R_2 is C_7H_7O.

#27								
GlcNAc6S-[I-GlcNAc6S]$_4$-I-R_2								
$[M-5H]^{5-}$	482.87	499.8 (0.4)[2]						
$[M-6H]^{6-}$	402.22	536.4 (0.7)						
	(1-)[1]	(2-)	(3-)	(4-)	(1-)	(2-)	(3-)	(4-)
B1	282.03	140.51	93.34	69.75	92.9 (0.5)	x	x	x
B2	458.06	228.53	152.01	113.76	121.8 (0.6)	x	x	x
B3	741.10	370.04	246.36	184.52	x	176.0 (0.7)	x	x
B4	917.13	458.06	305.04	228.53	x	197.2 (0.5)	x	x
B5	1200.16	599.58	399.38	299.29	x	x	269.1 (0.3)	x
B6	1376.20	687.59	458.06	343.29	x	x	294.6 (0.2)	x
B7	1659.23	829.11	552.41	414.05	x	x	x	x
B8	1835.27	917.13	611.08	458.06	x	x	x	394.0 (0.6)
B9	2118.30	1058.65	705.43	528.82	x	x	x	x
B10	2294.33	1146.66	764.11	572.83	x	x	x	x
Y0	123.04	61.02	40.34	30.01	69.3 (0.1)	x	x	x
Y1	299.08	149.03	99.02	74.01	x	x	x	x
Y2	582.11	290.55	193.37	144.77	x	166.3 (0.8)	x	x
Y3	758.14	378.57	252.04	188.78	x	x	x	x
Y4	1041.18	520.09	346.39	259.54	x	x	x	x
Y5	1217.21	608.10	405.07	303.55	x	x	x	x
Y6	1500.25	749.62	499.41	374.31	x	x	x	x
Y7	1676.28	837.64	558.09	418.31	x	x	368.5 (0.9)	x
Y8	1959.32	979.15	652.43	489.07	x	x	x	x
Y9	2135.35	1067.17	711.11	533.08	x	x	x	x
C1	300.04	149.52	99.34	74.25	x	x	x	x
C2	476.07	237.53	158.02	118.26	x	x	x	x

C3	759.11	379.05	252.36	189.02	x	x	x	x
C4	935.14	467.07	311.04	233.03	x	x	x	x
C5	1218.18	608.58	405.39	303.79	x	x	x	x
C6	1394.21	696.60	464.06	347.80	x	x	x	x
C7	1677.24	838.12	558.41	418.56	x	x	x	x
C8	1853.28	926.13	617.09	462.56	x	x	x	x
C9	2136.31	1067.65	711.43	533.32	x	x	x	x
C10	2312.34	1155.67	770.11	577.33	x	x	x	x
Z0	105.03	52.01	34.34	25.50	x	x	x	x
Z1	281.07	140.03	93.02	69.51	x	x	x	x
Z2	564.10	281.55	187.36	140.27	x	x	x	x
Z3	740.13	369.56	246.04	184.28	x	x	x	x
Z4	1023.17	511.08	340.38	255.04	x	x	x	x
Z5	1199.20	599.10	399.06	299.04	x	x	x	x
Z6	1482.24	740.62	493.41	369.80	x	x	x	x
Z7	1658.27	828.63	552.09	413.81	x	x	x	x
Z8	1941.31	970.15	646.43	484.57	x	x	x	x
Z9	2117.34	1058.17	705.11	528.58	x	x	x	x

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

197 **Supplementary Table 18**. CCS of B, Y, C and Z ions identified in a dp10 GlcNAc6S-[G-GlcNAc6S]$_4$-G-R_2 structure, where R_2 is C_7H_7O.

#28								
GlcNAc6S-[G-GlcNAc6S]$_4$-G-R_2								
$[M-5H]^{5-}$	482.87	496.1 (0.7)[2]						
$[M-6H]^{6-}$	402.22	524.5 (0.2)						
	(1-)[1]	(2-)	(3-)	(4-)	(1-)	(2-)	(3-)	(4-)
B1	282.03	140.51	93.34	69.75	93.2 (0.2)	x	x	x
B2	458.06	228.53	152.01	113.76	121.3 (0.8)	x	x	x
B3	741.10	370.04	246.36	184.52	x	x	x	x
B4	917.13	458.06	305.04	228.53	x	194.2 (0.2)	225.5 (0.4)	x
B5	1200.16	599.58	399.38	299.29	x	x	x	x
B6	1376.20	687.59	458.06	343.29	x	x	291.6 (0.2)	x
B7	1659.23	829.11	552.41	414.05	x	x	x	x
B8	1835.27	917.13	611.08	458.06	x	x	x	390.9 (0.6)
B9	2118.30	1058.65	705.43	528.82	x	x	x	x
B10	2294.33	1146.66	764.11	572.83	x	x	x	x
Y0	123.04	61.02	40.34	30.01	69.0 (0.3)	x	x	x
Y1	299.08	149.03	99.02	74.01	x	x	x	x
Y2	582.11	290.55	193.37	144.77	x	x	x	x
Y3	758.14	378.57	252.04	188.78	x	x	x	x
Y4	1041.18	520.09	346.39	259.54	x	x	x	x
Y5	1217.21	608.10	405.07	303.55	x	x	281.0 (0.6)	x
Y6	1500.25	749.62	499.41	374.31	x	x	x	x
Y7	1676.28	837.64	558.09	418.31	x	x	x	x
Y8	1959.32	979.15	652.43	489.07	x	x	x	x
Y9	2135.35	1067.17	711.11	533.08	x	x	x	x
C1	300.04	149.52	99.34	74.25	x	x	x	x
C2	476.07	237.53	158.02	118.26	x	x	x	x

C3	759.11	379.05	252.36	189.02	x	x	x	x
C4	935.14	467.07	311.04	233.03	x	x	x	x
C5	1218.18	608.58	405.39	303.79	x	x	x	x
C6	1394.21	696.60	464.06	347.80	x	x	x	x
C7	1677.24	838.12	558.41	418.56	x	x	x	x
C8	1853.28	926.13	617.09	462.56	x	x	x	x
C9	2136.31	1067.65	711.43	533.32	x	x	x	x
C10	2312.34	1155.67	770.11	577.33	x	x	x	x
Z0	105.03	52.01	34.34	25.50	x	x	x	x
Z1	281.07	140.03	93.02	69.51	x	x	x	x
Z2	564.10	281.55	187.36	140.27	x	x	x	x
Z3	740.13	369.56	246.04	184.28	x	x	x	x
Z4	1023.17	511.08	340.38	255.04	x	x	x	x
Z5	1199.20	599.10	399.06	299.04	x	x	x	x
Z6	1482.24	740.62	493.41	369.80	x	x	x	x
Z7	1658.27	828.63	552.09	413.81	x	x	x	x
Z8	1941.31	970.15	646.43	484.57	x	x	x	x
Z9	2117.34	1058.17	705.11	528.58	x	x	x	x

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 19. CCS of B, Y, C and Z ions identified in disaccharide ΔUA2S-GlcNS3S6S structure. Error +/- values are donated in brackets.

#29				
ΔUA2S-GlcNS3S6S				
$[M-2H]^{2-}$	327.45	149.7 (0.2)		
	(1-)[1]	(2-)	(1-)	(2-)
B1	236.97	117.98	79.7 (0.3)	x
Y0	417.94	208.47	x	x
C1	254.98	126.99	138.6 (0.2)/162.2 (0.7)	x
Z0	399.93	199.46	x	x

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 20. CCS of B, Y, C and Z ions identified in tetrasaccharide ΔUA-GlcNS-IdoA2S-GlcNS3S structure. Error +/- values are donated in brackets.

#30						
ΔUA-GlcNS-IdoA2S-GlcNS3S						
$[M-3H]^{3-}$	330.33	228.0 (0.1)				
	(1-)[1]	(2-)	(3-)	(1-)	(2-)	(3-)
B1	157.01	78.00	51.67	70.7 (0.4)	x	x
B2	398.04	198.52	132.01	x	119.9 (0.5)	x
B3	654.03	326.51	217.34	x	162.4 (0.3)	x
B4	975.01	487.00	324.33	x	x	218.1 (0.7)
Y0	337.99	168.49	111.99	x	104.9 (0.1)	x
Y1	593.97	296.48	197.32	x	x	x
Y2	835.00	417.00	277.66	x	x	x
C1	175.02	87.01	57.67	71.5 (0.5)	x	x
C2	416.05	207.52	138.01	113.9 (0.1)	120.8 (0.5)	x
C3	672.04	335.52	223.34	147.16 (0.5)	x	x
Z0	319.97	159.48	105.99	x	x	x
Z1	575.96	287.48	191.32	x	x	x
Z2	816.99	407.99	271.66	x	x	x

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 21. CCS of B, Y, C and Z ions identified in tetrasaccharide ΔUA-GlcNS6S-GlcA-GlcNS3S6S structure. Error +/- values are donated in brackets.

#31				
ΔUA-GlcNS6S-G-GlcNS3S6S				
$[M-3H]^{3-}$	356.98	228.9 (0.3)		
	(1-)[1]	(2-)	(1-)	(2-)
B1	157.01	78.00	70.0 (0.5)	x
B2	478.00	238.49	118.0 (0.1)	128.5 (0.1)
B3	654.03	326.51	x	163.4 (0.1)
Y0	417.94	208.47	x	x
Y1	593.97	296.48	x	x
Y2	914.96	456.97	x	x
C1	175.02	87.01	71.6 (0.5)	x
C2	496.01	247.50	x	131.8 (0.4)
C3	672.04	335.52	x	164.7 (0.2)
Z0	399.93	199.46	x	x
Z1	575.96	287.48	x	x
Z2	896.95	447.97	x	x

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 22. CCS of B, Y, C and Z ions identified in tetrasaccharide ΔUA-GlcNAc6S-GlcA-GlcNS3S6S structure. Error +/- values are donated in brackets.

#32				
ΔUA-GlcNAc6S-GlcA-GlcNS3S6S				
$[M-3H]^{3-}$	344.33	234.5 (0.1)		
	(1-)[1]	(2-)	(1-)	(2-)
B1	157.01	78.00	69.7 (0.1)	x
B2	440.05	219.52	117.7 (0.1)	132.4 (0.8)
B3	616.08	307.54	151.7 (0.1)	x
Y0	417.94	208.47	x	x
Y1	593.97	296.48	x	x
Y2	877.01	438.00	x	x
C1	175.02	87.01	71.5 (0.5)	x
C2	458.06	228.53	120.6 (0.1)	131.5 (0.1)
C3	634.09	316.54	154.3 (0.2)	x
Z0	399.93	199.46	x	x
Z1	575.96	287.48	x	x
Z2	859.00	429.00	x	x

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 23. CCS of B, Y, C and Z ions identified in hexasaccharide G-GlcNS6S-G-GlcNS6S-I2S-GlcNS6S-R_1 structure, where R_1 is $(CH_2)_5NH_2$.

#33						
G-GlcNS6S-G-GlcNS6S-I2S-GlcNS6S-R_1						
$[M-3H]^{3-}$	557.06	280.5 (0.1)				
$[M-4H]^{4-}$	417.52	339.5 (0.3)				
	(1-)[1]	(2-)	(3-)	(1-)	(2-)	(3-)
B1	175.02	87.01	57.67	69.0 (0.4)	x	x
B2	496.01	247.50	164.66	x	132.5 (0.5)	x
B3	672.04	335.52	223.34	x	161.7 (0.5)	x
B4	993.02	496.01	330.34	x	x	225.1 (0.7)
B5	1249.01	624.00	415.66	x	x	x
B6	1569.99	784.49	522.66	x	x	x
Y0	102.09	50.54	33.36	x	x	x
Y1	423.07	211.03	140.35	x	128.8 (0.7)	x
Y2	679.06	339.03	225.68	x	x	x
Y3	1000.05	499.52	332.68	x	x	x
Y4	1176.08	587.53	391.35	x	x	x
Y5	1497.06	748.03	498.35	x	x	x
C1	193.03	96.01	63.67	74.2 (0.4)	x	x
C2	514.02	256.50	170.67	x	133.7 (0.5)	x
C3	690.05	344.52	229.34	x	x	x
C4	1011.03	505.01	336.34	x	x	x
C5	1267.02	633.01	421.67	x	x	x
C6	1588.00	793.50	528.66	x	x	x
Z0	84.08	41.54	27.36	x	x	x
Z1	405.06	202.03	134.35	x	x	x
Z2	661.05	330.02	219.68	x	x	x
Z3	982.03	490.51	326.67	x	x	x
Z4	1158.07	578.53	385.35	x	x	x
Z5	1479.05	739.02	492.34	x	x	x

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 24. CCS of B, Y, C and Z ions identified in hexasaccharide G-GlcNS6S-G-GlcNS3S-I2S-GlcNS6S-$(CH_2)_5NH_2$ structure, where R_1 is $(CH_2)_5NH_2$.

#34						
G-GlcNS6S-G-GlcNS3S-I2S-GlcNS6S-R_1						
$[M-3H]^{3-}$	557.06	282.4 (0.4)				
	(1-)[1]	(2-)	(3-)	(1-)	(2-)	(3-)
B1	175.02	87.01	57.67	68.8 (0.2)	x	x
B2	496.01	247.50	164.66	x	132.2 (0.5)	x
B3	672.04	335.52	223.34	x	162.1 (0.4)	x
B4	993.02	496.01	330.34	x	x	220.4 (0.5)
B5	1249.01	624.00	415.66	x	x	x
B6	1569.99	784.49	522.66	x	x	x
Y0	102.09	50.54	33.36	x	x	x
Y1	423.07	211.03	140.35	x	128.9 (0.5)	x
Y2	679.06	339.03	225.68	x	x	x
Y3	1000.05	499.52	332.68	x	x	x
Y4	1176.08	587.53	391.35	x	x	x
Y5	1497.06	748.03	498.35	x	x	x
C1	193.03	96.01	63.67	73.8 (0.4)	x	x
C2	514.02	256.50	170.67	x	133.9 (0.6)	x
C3	690.05	344.52	229.34	x	x	x
C4	1011.03	505.01	336.34	x	x	x
C5	1267.02	633.01	421.67	x	x	x
C6	1588.00	793.50	528.66	x	x	x
Z0	84.08	41.54	27.36	x	x	x
Z1	405.06	202.03	134.35	x	x	x
Z2	661.05	330.02	219.68	x	x	x
Z3	982.03	490.51	326.67	x	x	x
Z4	1158.07	578.53	385.35	x	x	x
Z5	1479.05	739.02	492.34	x	x	x

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 25. CCS of B, Y, C and Z ions identified in hexasaccharide G-GlcNS6S-G-GlcNS6S3S-I2S-GlcNS6S-R_1, where R_1 is $(CH_2)_5NH_2$.

#35						
G-GlcNS6S-G-GlcNS6S3S-I2S-GlcNS6S-R_1						
$[M-4H]^{4-}$	437.51	328.3 (0.6)				
	(1-)[1]	(2-)	(3-)	(1-)	(2-)	(3-)
B1	175.02	87.01	57.67	69.0 (0.2)	x	x
B2	496.01	247.50	164.66	x	132.8 (0.4)	x
B3	672.04	335.52	223.34	x	162.4 (0.4)	x
B4	1072.98	535.99	356.99	x	x	x
B5	1328.97	663.98	442.32	x	x	x
B6	1649.95	824.47	549.31	x	x	x
Y0	102.09	50.54	33.36	x	x	x
Y1	423.07	211.03	140.35	x	x	x
Y2	679.06	339.03	225.68	x	x	x
Y3	1080.00	539.50	359.33	x	x	x
Y4	1256.03	627.51	418.01	x	x	x
Y5	1577.02	788.00	525.00	x	x	x
C1	193.03	96.01	63.67	x	x	x
C2	514.02	256.50	170.67	x	x	x
C3	690.05	344.52	229.34	x	x	x
C4	1090.99	544.99	362.99	x	x	x
C5	1346.98	672.98	448.32	x	x	x
C6	1667.96	833.48	555.31	x	x	x
Z0	84.08	41.54	27.36	x	x	x
Z1	405.06	202.03	134.35	x	x	x
Z2	661.05	330.02	219.68	x	x	x
Z3	1061.99	530.49	353.33	x	x	x
Z4	1238.02	618.51	412.00	x	x	x
Z5	1559.01	779.00	519.00	x	x	x

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 26. CCS of B, Y, C and Z ions identified in a dp7 + 1x2*O*-sulfate, ΔUA-GlcNS-I2S-GlcNS-G-GlcNS-G-R_3 structure, where R_3 is $C_6H_4NO_2$.

#36								
ΔUA-GlcNS-I2S-GlcNS-G-GlcNS-G-R_3								
	(1-)[1]	(2-)	(3-)	(4-)	(1-)	(2-)	(3-)	(4-)
B1	157.01	78.00	51.67	38.50	70.5 (0.76)	x	x	x
B2	398.04	198.52	132.01	98.75	110.5 (0.8)	120.5 (0.5)	x	x
B3	654.03	326.51	217.34	162.75	x	162.6 (0.5)	x	x
B4	895.05	447.02	297.68	223.01	x	201.1 (0.5)	x	x
B5	1071.09	535.04	356.36	267.02	x	211.7 (0.3)	246.2 (0.8)	x
B6	1312.11	655.55	436.70	327.27	x	x	x	x
B7	1488.14	743.57	495.38	371.28	x	x	x	329.8 (0.1)
Y0	138.02	68.51	45.33	33.75	x	x	x	x
Y1	314.05	156.52	104.01	77.76	x	x	x	x
Y2	555.08	277.03	184.35	138.01	x	x	x	x
Y3	731.11	365.05	243.03	182.02	x	x	x	x
Y4	972.13	485.56	323.37	242.28	x	x	x	x
Y5	1228.12	613.56	408.70	306.27	x	x	x	x
Y6	1469.15	734.07	489.04	366.53	x	x	x	x
C1	174.02	86.50	57.33	42.75	x	x	x	x
C2	415.04	207.02	137.68	103.00	x	x	x	x
C3	671.03	335.01	223.01	167.00	x	x	x	x
C4	912.06	455.52	303.35	227.26	x	x	x	x
C5	1088.09	543.54	362.02	271.27	x	x	x	x
C6	1329.11	664.05	442.37	331.52	x	x	x	x
C7	1505.15	752.07	501.04	375.53	x	x	x	x
Z0	120.01	59.50	39.33	29.25	x	x	x	x

Z1	296.04	147.52	98.01	73.25	x	x	x	x
Z2	537.07	268.03	178.35	133.51	x	x	x	x
Z3	713.10	356.05	237.03	177.52	x	x	x	x
Z4	954.12	476.56	317.37	237.78	x	x	x	x
Z5	1210.11	604.55	402.70	301.77	x	x	x	x
Z6	1451.14	725.07	483.04	362.03	x	x	x	x

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 27. CCS of B, Y, C and Z (-SO_3) ions identified in isomeric tetrasaccharide UA-GlcNAc6S-UA-GlcNAc6S-R_1 structures, where R_1 is $(CH_2)_5NH_2$.

			#9		**#10**		**#11**		**#13**	
			G-GlcNAc6S-G-GlcNAc6S-R_1		I-GlcNAc6S-I-GlcNAc6S-R_1		G-GlcNAc6S-I-GlcNAc6S-R_1		I-GlcNAc6S-G-GlcNAc6S-R_1	
			- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $2SO_3$
			(1-)[1]	(2-)	(1-)	(2-)	(1-)	(2-)	(1-)	(2-)
B1	95.07	47.03	x	x	x	x	x	x	x	x
B2	378.10	188.55	112.04 (0.1)	x	112.5 (0.3)	x	112.41 (0.5)	x	112.02 (0.2)	x
B3	554.14	276.56	x	x	x	x	x	x	x	x
B4	837.17	418.08	x	x	x	x	x	x	x	x
Y0	22.14	10.56	x	x	x	x	x	x	x	x
Y1	305.17	152.08	x	x	x	x	x	x	x	x
Y2	481.20	240.10	139.34 (0.2)	x	137.09 (0.3)	x	137.38 (0.6)	x	139.3 (0.2)	x
Y3	764.24	381.62	x	x	x	x		x	x	x
C1	113.08	56.04	x	x	x	x	x	x	x	x
C2	396.11	197.55	115.2 (0.6)	x	115.7 (0.5)	x	114.85 (0.4)	x	114.88 (0.2)	x
C3	572.15	285.57	x	x	x	x	x	x	x	x
C4	855.18	427.09	x	x	x	x	x	x	x	x
Z0	4.12	1.56	x	x	x	x	x	x	x	x
Z1	287.16	143.08	x	x	x	x	x	x	x	x
Z2	463.19	231.09	x	x	x	x	x	x	x	x
Z3	746.23	372.61	x	x	x	x	x	x	x	x

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 28. CCS of B, Y, C and Z (-SO_3) ions identified in isomeric tetra-saccharide UA-GlcNS6S-UA-GlcNS6S-R_1 structures, where R_1 is $(CH_2)_5NH_2$.

#12						
G-GlcNS6S-I-GlcNS6S-R_1						
				- $1SO_3$	- $1SO_3$	- $1SO_3$
				(1-)[1]	(2-)	(3-)
B1	95.07	47.03	31.02	x	x	x
B2	416.05	207.52	138.01	x	122.4 (0.3)	x
B3	592.08	295.54	196.69	139.6 (0.3)	x	x
B4	913.06	456.03	303.68	x	x	214.9 (0.2)
Y0	22.14	10.56	6.71	x	x	x
Y1	343.12	171.05	113.70	x	x	x
Y2	519.15	259.07	172.38	x	x	x
Y3	840.13	419.56	279.37	x	x	x
C1	113.08	56.04	37.02	x	x	x
C2	434.06	216.53	144.01	x	x	x
C3	610.09	304.54	202.69	x	x	x
C4	931.07	465.03	309.69	x	x	x
Z0	4.12	1.56	0.70	x	x	x
Z1	325.11	162.05	107.70	x	x	x
Z2	501.14	250.07	166.37	x	x	x
Z3	822.12	410.56	273.37	x	x	x

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 29. CCS of B, Y, C and Z (-SO_3) ions identified in isomeric tetra-saccharide UA-GlcNS6S-UA-GlcNS6S-R_1 structures, where R_1 is $(CH_2)_5NH_2$.

#14				
I-GlcNS6S-G-GlcNS6S-R_1				
	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$
	(1-)	(2-)	(1-)	(2-)
B1	95.07	47.03	x	x
B2	416.05	207.52	x	x
B3	592.08	295.54	x	x
B4	913.06	456.03	x	x
Y0	22.14	10.56	x	x
Y1	343.12	171.05	108.9(0.1)[2]	x
Y2	519.15	259.07	133.7 (0.1)	149.8 (0.3)
Y3	840.13	419.56	x	175.7 (0.8)
C1	113.08	56.04	x	x
C2	434.06	216.53	x	x
C3	610.09	304.54	x	x
C4	931.07	465.03	x	x
Z0	4.12	1.56	x	x
Z1	325.11	162.05	x	x
Z2	501.14	250.07	x	x
Z3	822.12	410.56	x	x

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 30. CCS of B, Y, C and Z (-SO_3) ions identified in isomeric tetra-saccharide G-GlcNS6S-I2S-GlcNS6S-R_1 structures, where R_1 is $(CH_2)_5NH_2$.

#15						
G-GlcNS6S-I2S-GlcNS6S-R_1						
	- $1SO_3$	- $1SO_3$	- $1SO_3$			
	(1-)[1]	(2-)	(3-)			
B1	95.07	47.03	31.02	x	x	x
B2	416.05	207.52	138.01	x	122.4 (0.1)[2]	x
B3	672.04	335.52	223.34	x	167.1 (0.4)	x
B4	993.02	496.01	330.34	x	x	226.7 (0.2)
Y0	22.14	10.56	6.71	x	x	x
Y1	343.12	171.05	113.70	109.3 (0.6)	x	x
Y2	599.11	299.05	199.03	x	x	x
Y3	920.09	459.54	306.02	x	x	x
C1	113.08	56.04	37.02	x	x	x
C2	434.06	216.53	144.01	x	x	x
C3	690.05	344.52	229.34	x	x	x
C4	1011.03	505.01	336.34	x	x	x
Z0	4.12	1.56	0.70	x	x	x
Z1	325.11	162.05	107.70	x	x	x
Z2	581.10	290.04	193.03	x	x	x
Z3	902.08	450.54	300.02	x	x	x

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 31. CCS of B, Y, C and Z (-SO_3) ions identified in a hexa-saccharide structure (R_1 is $(CH_2)_5NH_2$).

#16						
G-GlcNS6S-I-GlcNS6S-G-GlcNS6S-R_1						
	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$
	(1-)[1]	(2-)	(3-)	(1-)	(2-)	(3-)
B1	95.07	47.03	31.02	x	x	x
B2	416.05	207.52	138.01	x	122.5 (0.2)[2]	x
B3	592.08	295.54	196.69	140.2 (0.7)	x	x
B4	913.06	456.03	303.68	x	x	214.8 (0.7)
B5	1089.10	544.04	362.36	x	x	247.4 (0.9)
B6	1410.08	704.54	469.35	x	x	x
Y0	22.14	10.56	6.71	x	x	x
Y1	343.12	171.05	113.70	109.1 (0.1)	x	x
Y2	519.15	259.07	172.38	x	150.0 (0.8)	x
Y3	840.13	419.56	279.37	x	x	x
Y4	1016.16	507.58	338.05	x	x	234.8 (0.2)
Y5	1337.15	668.07	445.04	x	x	x
C1	113.08	56.04	37.02	x	x	x
C2	434.06	216.53	144.01	114.8 (0.46)	x	x
C3	610.09	304.54	202.69	x	x	x
C4	931.07	465.03	309.69	x	x	x
C5	1107.11	553.05	368.36	x	x	x
C6	1428.09	713.54	475.36	x	x	x
Z0	4.12	1.56	0.70	x	x	x
Z1	325.11	162.05	107.70	x	x	x
Z2	501.14	250.07	166.37	x	x	x
Z3	822.12	410.56	273.37	x	x	x
Z4	998.15	498.57	332.05	x	x	x
Z5	1319.14	659.06	439.04	x	x	x

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 32. CCS of B, Y, C and Z (-SO_3) ions identified in a hexa-saccharide GlcNAc6S-[G-GlcNAc6S]$_2$-G-R_2 structure, where R_2 is C_7H_7O.

#17						
GlcNAc6S-[G-GlcNAc6S]$_2$-G-R_2						
	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$
	(1-)[1]	(2-)	(3-)	(1-)	(2-)	(3-)
B1	202.07	100.53	66.69	x	x	x
B2	378.10	188.55	125.36	111.4 (0.2)	x	x
B3	661.14	330.07	219.71	160.1 (0.7)	x	x
B4	837.17	418.08	278.39	x	x	x
B5	1120.21	559.60	372.73	x	214.1 (0.7)	x
B6	1296.24	647.62	431.41	x	234.0 (0.4)	x
Y0	42.08	20.54	13.35	x	x	x
Y1	219.12	109.06	72.37	x	x	x
Y2	502.16	250.57	166.71	x	x	x
Y3	678.19	338.59	225.39	x	x	x
Y4	961.22	480.11	319.74	x	x	x
Y5	1137.26	568.12	378.41	x	x	x
C1	220.08	109.54	72.69	x	x	x
C2	396.11	197.55	131.37	x	x	x
C3	679.15	339.07	225.71	x	x	x
C4	855.18	427.09	284.39	x	x	x
C5	1138.22	568.61	378.73	x	x	x
C6	1314.25	656.62	437.41	x	x	x
Z0	25.08	12.03	7.69	x	x	x
Z1	201.11	100.05	66.36	x	x	x
Z2	484.15	241.57	160.71	x	x	x
Z3	660.18	329.58	219.39	x	x	x
Z4	943.21	471.10	313.73	x	x	x
Z5	1119.25	559.12	372.41	x	x	X

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 33. CCS of B, Y, C and Z (-SO_3) ions identified in a hexa-saccharide GlcNAc6S-[I-GlcNAc6S]$_2$-I-R_2 structure, where R_2 is C_7H_7O.

#18						
GlcNAc6S-[I-GlcNAc6S]$_2$-I-R_2						
	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$
	(1-)[1]	(2-)	(3-)	(1-)	(2-)	(3-)
B1	202.07	100.53	66.69	x	x	x
B2	378.10	188.55	125.36	112.5 (0.1)	x	x
B3	661.14	330.07	219.71	157.7 (0.3)	x	x
B4	837.17	418.08	278.39	x	179.8 (0.9)	x
B5	1120.21	559.60	372.73	x	215.6 (0.2)	x
B6	1296.24	647.62	431.41	x	237.8 (0.4)	x
Y0	42.08	20.54	13.35	x	x	x
Y1	219.12	109.06	72.37	x	x	x
Y2	502.16	250.57	166.71	x	x	x
Y3	678.19	338.59	225.39	x	x	x
Y4	961.22	480.11	319.74	x	x	x
Y5	1137.26	568.12	378.41	x	x	x
C1	220.08	109.54	72.69	x	x	x
C2	396.11	197.55	131.37	x	x	x
C3	679.15	339.07	225.71	x	x	x
C4	855.18	427.09	284.39	x	x	x
C5	1138.22	568.61	378.73	x	x	x
C6	1314.25	656.62	437.41	x	x	x
Z0	25.08	12.03	7.69	x	x	x
Z1	201.11	100.05	66.36	x	x	x
Z2	484.15	241.57	160.71	x	x	x
Z3	660.18	329.58	219.39	x	x	x
Z4	943.21	471.10	313.73	x	x	x
Z5	1119.25	559.12	372.41	x	x	x

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 34. CCS of B, Y, C and Z (-SO_3) ions identified in an octa-saccharide GlcNAc6S-[I-GlcNAc6S]$_3$-I-R_2 structure, where R_2 is C_7H_7O.

#19						
GlcNAc6S-[I-GlcNAc6S]$_3$-I-R_2						
	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$
	(1-)[1]	(2-)	(3-)	(1-)	(2-)	(3-)
B1	202.07	100.53	66.69	x	x	x
B2	378.10	188.55	125.36	112.0 (0.3)[2]	x	x
B3	661.14	330.07	219.71	158.2 (0.2)	x	x
B4	837.17	418.08	278.39	x	x	x
B5	1120.21	559.60	372.73	x	216.3 (0.7)	x
B6	1296.24	647.62	431.41	x	x	x
B7	1579.28	789.13	525.75	x	x	x
B8	1755.31	877.15	584.43	x	x	
Y0	42.08	20.54	13.35	x	x	x
Y1	219.12	109.06	72.37	x	x	x
Y2	502.16	250.57	166.71	x	x	x
Y3	678.19	338.59	225.39	x	x	x
Y4	961.22	480.11	319.74	x	x	x
Y5	1137.26	568.12	378.41	x	x	x
Y6	1420.29	709.64	472.76	x	x	x
Y7	1596.32	797.66	531.44	x	x	x
C1	220.08	109.54	72.69	x	x	x
C2	396.11	197.55	131.37	x	x	x
C3	679.15	339.07	225.71	x	x	x
C4	855.18	427.09	284.39	x	x	x
C5	1138.22	568.61	378.73	x	x	x
C6	1314.25	656.62	437.41	x	x	x
C7	1597.29	798.14	531.76	x	x	x
C8	1773.32	886.16	590.43	x	x	x
Z0	25.08	12.03	7.69	x	x	x
Z1	201.11	100.05	66.36	x	x	x
Z2	484.15	241.57	160.71	x	x	x
Z3	660.18	329.58	219.39	x	x	x
Z4	943.21	471.10	313.73	x	x	x
Z5	1119.25	559.12	372.41	x	x	x
Z6	1402.28	700.64	466.76	x	x	x
Z7	1578.31	788.65	525.43	x	x	x

[1] Columns represent different charge states. [2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 35. CCS of B, Y, C and Z (-SO_3) ions identified in an octa-saccharide GlcNAc6S-[G-GlcNAc6S]$_3$-G-R_2 structure, where R_2 is C_7H_7O.

#20						
GlcNAc6S-[G-GlcNAc6S]$_3$-G-R_2						
	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$
	(1-)[1]	(2-)	(3-)	(1-)	(2-)	(3-)
B1	202.07	100.53	66.69	x	x	x
B2	378.10	188.55	125.36	111.5 (0.1)[2]	x	x
B3	661.14	330.07	219.71	160.4 (0.2)	x	x
B4	837.17	418.08	278.39	x	185.4 (0.4)	x
B5	1120.21	559.60	372.73	x	214.9 (0.8)	x
B6	1296.24	647.62	431.41	x	x	x
B7	1579.28	789.13	525.75	x	x	x
B8	1755.31	877.15	584.43	x	x	x
Y0	42.08	20.54	13.35	x	x	x
Y1	219.12	109.06	72.37	x	x	x
Y2	502.16	250.57	166.71	x	x	x
Y3	678.19	338.59	225.39	x	x	x
Y4	961.22	480.11	319.74	x	199.7 (0.18)	x
Y5	1137.26	568.12	378.41	x	216.2 (0.1)	x
Y6	1420.29	709.64	472.76	x	x	x
Y7	1596.32	797.66	531.44	x	x	x
C1	220.08	109.54	72.69	x	x	x
C2	396.11	197.55	131.37	x	x	x
C3	679.15	339.07	225.71	x	x	x
C4	855.18	427.09	284.39	x	x	x
C5	1138.22	568.61	378.73	x	x	x
C6	1314.25	656.62	437.41	x	x	x
C7	1597.29	798.14	531.76	x	x	x
C8	1773.32	886.16	590.43	x	x	x
Z0	25.08	12.03	7.69	x	x	x
Z1	201.11	100.05	66.36	x	x	x
Z2	484.15	241.57	160.71	x	x	x
Z3	660.18	329.58	219.39	x	x	x
Z4	943.21	471.10	313.73	x	x	x
Z5	1119.25	559.12	372.41	x	x	x
Z6	1402.28	700.64	466.76	x	x	x
Z7	1578.31	788.65	525.43	x	x	x

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 36. CCS of B, Y, C and Z (-SO_3) ions identified in an octa-saccharide GlcNAc6S-G-GlcNac6S-G-GlcNAc6S-I-GlcNAc6S-I-R_2 structure, where R_2 is C_7H_7O.

#21						
GlcNAc6S-G-GlcNac6S-G-GlcNAc6S-I-GlcNAc6S-I-R_2						
	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$
	(1-)[1]	(2-)	(3-)	(1-)[1]	(2-)	(3-)
B1	202.07	100.53	66.69	x	x	x
B2	378.10	188.55	125.36	112.3 (0.3)[2]	x	x
B3	661.14	330.07	219.71	x	x	x
B4	837.17	418.08	278.39	x	x	x
B5	1120.21	559.60	372.73	x	213.8 (0.1)	x
B6	1296.24	647.62	431.41	x	x	x
B7	1579.28	789.13	525.75	x	x	x
B8	1755.31	877.15	584.43	x	x	x
Y0	42.08	20.54	13.35	x	x	x
Y1	219.12	109.06	72.37	x	x	x
Y2	502.16	250.57	166.71	x	x	x
Y3	678.19	338.59	225.39	x	x	x
Y4	961.22	480.11	319.74	x	x	x
Y5	1137.26	568.12	378.41	x	x	x
Y6	1420.29	709.64	472.76	x	x	x
Y7	1596.32	797.66	531.44	x	x	x
C1	220.08	109.54	72.69	x	x	x
C2	396.11	197.55	131.37	x	x	x
C3	679.15	339.07	225.71	x	x	x
C4	855.18	427.09	284.39	x	x	x
C5	1138.22	568.61	378.73	x	x	x
C6	1314.25	656.62	437.41	x	x	x
C7	1597.29	798.14	531.76	x	x	x
C8	1773.32	886.16	590.43	x	x	x
Z0	25.08	12.03	7.69	x	x	x
Z1	201.11	100.05	66.36	x	x	x
Z2	484.15	241.57	160.71	x	x	x
Z3	660.18	329.58	219.39	x	x	x
Z4	943.21	471.10	313.73	x	x	x
Z5	1119.25	559.12	372.41	x	x	x
Z6	1402.28	700.64	466.76	x	x	x
Z7	1578.31	788.65	525.43	x	x	x

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 37. CCS of B, Y, C and Z (-SO_3) ions identified in an octa-saccharide GlcNAc6S-G-GlcNac6S-I-GlcNAc6S-I-GlcNAc6S-G-R_2 structure, where R_2 is C_7H_7O.

#22						
GlcNAc6S-G-GlcNac6S-I-GlcNAc6S-I-GlcNAc6S-G-R_2						
	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$
	(1-)[1]	(2-)	(3-)	(1-)[1]	(2-)	(3-)
B1	202.07	100.53	66.69	x	x	x
B2	378.10	188.55	125.36	112.9 (0.6)[2]	x	x
B3	661.14	330.07	219.71	159.6 (0.5)	x	x
B4	837.17	418.08	278.39	x	x	x
B5	1120.21	559.60	372.73	x	216.3 (0.33)	x
B6	1296.24	647.62	431.41	x	x	x
B7	1579.28	789.13	525.75	x	x	x
B8	1755.31	877.15	584.43	x	x	308.6 (0.5)
Y0	42.08	20.54	13.35	x	x	x
Y1	219.12	109.06	72.37	x	x	x
Y2	502.16	250.57	166.71	x	x	x
Y3	678.19	338.59	225.39	x	x	x
Y4	961.22	480.11	319.74	x	x	x
Y5	1137.26	568.12	378.41	x	x	x
Y6	1420.29	709.64	472.76	x	x	x
Y7	1596.32	797.66	531.44	x	x	x
C1	220.08	109.54	72.69	x	x	x
C2	396.11	197.55	131.37	x	x	x
C3	679.15	339.07	225.71	x	x	x
C4	855.18	427.09	284.39	x	x	x
C5	1138.22	568.61	378.73	x	x	x
C6	1314.25	656.62	437.41	x	x	x
C7	1597.29	798.14	531.76	x	x	x
C8	1773.32	886.16	590.43	x	x	x
Z0	25.08	12.03	7.69	x	x	x
Z1	201.11	100.05	66.36	x	x	x
Z2	484.15	241.57	160.71	x	x	x
Z3	660.18	329.58	219.39	x	x	x
Z4	943.21	471.10	313.73	x	x	x
Z5	1119.25	559.12	372.41	x	x	x
Z6	1402.28	700.64	466.76	x	x	x
Z7	1578.31	788.65	525.43	x	x	x

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 38. CCS of B, Y, C and Z (-SO_3) ions identified in an octa-saccharide GlcNAc6S-I-GlcNAc6S-G-GlcNAc6S-I-GlcNAc6S-G-R_2 structure, where R_2 is C_7H_7O.

#23						
GlcNAc6S-I-GlcNAc6S-G-GlcNAc6S-I-GlcNAc6S-G-R_2						
	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$
	(1-)[1]	(2-)	(3-)	(1-)[1]	(2-)	(3-)
B1	202.07	100.53	66.69	x	x	x
B2	378.10	188.55	125.36	112.1 (0.3)[2]	x	x
B3	661.14	330.07	219.71	157.8 (0.2)	x	x
B4	837.17	418.08	278.39	x	x	x
B5	1120.21	559.60	372.73	x	215.1 (0.11)	x
B6	1296.24	647.62	431.41	x	x	x
B7	1579.28	789.13	525.75	x	x	x
B8	1755.31	877.15	584.43	x	x	x
Y0	42.08	20.54	13.35	x	x	x
Y1	219.12	109.06	72.37	x	x	x
Y2	502.16	250.57	166.71	x	x	x
Y3	678.19	338.59	225.39	x	x	x
Y4	961.22	480.11	319.74	x	x	x
Y5	1137.26	568.12	378.41	x	x	x
Y6	1420.29	709.64	472.76	x	x	x
Y7	1596.32	797.66	531.44	x	x	x
C1	220.08	109.54	72.69	x	x	x
C2	396.11	197.55	131.37	x	x	x
C3	679.15	339.07	225.71	x	x	x
C4	855.18	427.09	284.39	x	x	x
C5	1138.22	568.61	378.73	x	x	x
C6	1314.25	656.62	437.41	x	x	x
C7	1597.29	798.14	531.76	x	x	x
C8	1773.32	886.16	590.43	x	x	x
Z0	25.08	12.03	7.69	x	x	x
Z1	201.11	100.05	66.36	x	x	x
Z2	484.15	241.57	160.71	x	x	x
Z3	660.18	329.58	219.39	x	x	x
Z4	943.21	471.10	313.73	x	x	x
Z5	1119.25	559.12	372.41	x	x	x
Z6	1402.28	700.64	466.76	x	x	x
Z7	1578.31	788.65	525.43	x	x	x

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 39. CCS of B, Y, C and Z (-SO_3) ions identified in an octa-saccharide GlcNAc6S-G-GlcNAc6S-I-GlcNAc6S-G-GlcNAc6S-I-R_2 structure, where R_2 is C_7H_7O.

#24						
GlcNAc6S-G-GlcNAc6S-I-GlcNAc6S-G-GlcNAc6S-I-R_2						
	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$
	(1-)[1]	(2-)	(3-)	(1-)	(2-)	(3-)
B1	202.07	100.53	66.69	x	x	x
B2	378.10	188.55	125.36	111.64 (0.2)	x	x
B3	661.14	330.07	219.71	x	x	x
B4	837.17	418.08	278.39	x	x	x
B5	1120.21	559.60	372.73	x	215.7 (0.6)	x
B6	1296.24	647.62	431.41	x	x	x
B7	1579.28	789.13	525.75	x	x	x
B8	1755.31	877.15	584.43	x	x	x
Y0	42.08	20.54	13.35	x	x	x
Y1	219.12	109.06	72.37	x	x	x
Y2	502.16	250.57	166.71	x	x	x
Y3	678.19	338.59	225.39	x	x	x
Y4	961.22	480.11	319.74	x	x	x
Y5	1137.26	568.12	378.41	x	x	x
Y6	1420.29	709.64	472.76	x	x	x
Y7	1596.32	797.66	531.44	x	x	x
C1	220.08	109.54	72.69	x	x	x
C2	396.11	197.55	131.37	x	x	x
C3	679.15	339.07	225.71	x	x	x
C4	855.18	427.09	284.39	x	x	x
C5	1138.22	568.61	378.73	x	x	x
C6	1314.25	656.62	437.41	x	x	x
C7	1597.29	798.14	531.76	x	x	x
C8	1773.32	886.16	590.43	x	x	x
Z0	25.08	12.03	7.69	x	x	x
Z1	201.11	100.05	66.36	x	x	x
Z2	484.15	241.57	160.71	x	x	x
Z3	660.18	329.58	219.39	x	x	x
Z4	943.21	471.10	313.73	x	x	x
Z5	1119.25	559.12	372.41	x	x	x
Z6	1402.28	700.64	466.76	x	x	x
Z7	1578.31	788.65	525.43	x	x	x

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 40. CCS of B, Y, C and Z (-SO_3) ions identified in a 9mer, G-GlcNS-G-GlcNS-I-GlcNS-G-GlcNS-G-R_3 structure, where R_3 is $C_6H_4NO_2$.

#25						
G-GlcNS-G-GlcNS-I-GlcNS-G-GlcNS-G-R_3						
	- $1SO_3$	- $1SO_3$	- $1SO_3$			
	(1-)[1]	(2-)	(3-)	(1-)	(2-)	(3-)
B1	95.07	47.03	31.02	x	x	x
B2	336.09	167.54	111.36	x	x	x
B3	512.13	255.56	170.04	132.30 (0.5)[2]	x	x
B4	753.15	376.07	250.38	x	x	x
B5	929.18	464.09	309.06	x	x	x
B6	1170.21	584.60	389.40	x	227.58 (0.2)	x
B7	1346.24	672.62	448.07	x	x	x
B8	1587.27	793.13	528.42	x	x	x
B9	1763.30	881.15	587.09	x	x	x
Y0	58.06	28.53	18.68	x	x	x
Y1	234.09	116.54	77.36	x	x	x
Y2	475.12	237.06	157.70	x	x	x
Y3	651.15	325.07	216.38	x	x	x
Y4	892.18	445.58	296.72	x	x	x
Y5	1068.21	533.60	355.40	x	x	x
Y6	1309.24	654.11	435.74	x	x	x
Y7	1485.27	742.13	494.42	x	x	x
Y8	1726.29	862.64	574.76	x	x	x
C1	112.07	55.53	36.68	x	x	x
C2	353.10	176.04	117.03	x	x	x
C3	529.13	264.06	175.70	x	x	x
C4	770.15	384.57	256.05	x	x	x
C5	946.19	472.59	314.72	x	x	x
C6	1187.21	593.10	395.07	x	x	x
C7	1363.24	681.12	453.74	x	x	x
C8	1604.27	801.63	534.08	x	x	x
C9	1780.30	889.65	592.76	x	x	x
Z0	40.05	19.52	12.68	x	x	x
Z1	216.08	107.54	71.36	x	x	x
Z2	457.11	228.05	151.70	x	x	x
Z3	633.14	316.07	210.38	x	x	x
Z4	874.17	436.58	290.72	x	x	x
Z5	1050.20	524.60	349.39	x	x	x
Z6	1291.22	645.11	429.74	x	x	x
Z7	1467.26	733.12	488.41	x	x	x

Z8	1708.28	853.64	568.76	x	x	x

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 41. CCS of B, Y, C and Z (-SO_3) ions identified in a dp9 + 1x2*O*-sulfate, G-GlcNS-G-GlcNS-I2S-GlcNS-G-GlcNS-G-R_3 structure, where R_3 is $C_6H_4NO_2$.

#26						
G-GlcNS-G-GlcNS-I2S-GlcNS-G-GlcNS-G-R_3						
	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$
	(1-)[1]	(2-)	(3-)	(1-)	(2-)	(3-)
B1	95.07	47.03	31.02	x	x	x
B2	336.09	167.54	111.36	x	x	x
B3	512.13	255.56	170.04	131.6 (0.5)[2]	x	x
B4	753.15	376.07	250.38	x	x	x
B5	1009.14	504.07	335.71	x	234.21 (0.2)	x
B6	1250.17	624.58	416.05	x	x	x
B7	1426.20	712.59	474.73	x	x	x
B8	1667.22	833.11	555.07	x	x	x
B9	1843.25	921.12	613.75	x	x	x
Y0	58.06	28.53	18.68	x	x	x
Y1	234.09	116.54	77.36	x	x	x
Y2	475.12	237.06	157.70	x	x	x
Y3	651.15	325.07	216.38	x	x	x
Y4	892.18	445.58	296.72	x	x	x
Y5	1148.17	573.58	382.05	x	x	x
Y6	1389.19	694.09	462.39	x	x	x
Y7	1565.22	782.11	521.07	x	x	x
Y8	1806.25	902.62	601.41	x	x	x
C1	112.07	55.53	36.68	x	x	x
C2	353.10	176.04	117.03	x	x	x
C3	529.13	264.06	175.70	x	x	x
C4	770.15	384.57	256.05	x	x	x
C5	1026.14	512.57	341.38	x	x	x
C6	1267.17	633.08	421.72	x	x	x
C7	1443.20	721.10	480.39	x	x	x
C8	1684.23	841.61	560.74	x	x	x
C9	1860.26	929.62	619.41	x	x	x
Z0	40.05	19.52	12.68	x	x	x
Z1	216.08	107.54	71.36	x	x	x
Z2	457.11	228.05	151.70	x	x	x
Z3	633.14	316.07	210.38	x	x	x
Z4	874.17	436.58	290.72	x	x	x
Z5	1130.16	564.57	376.05	x	x	x
Z6	1371.18	685.09	456.39	x	x	x
Z7	1547.21	773.10	515.07	x	x	x

Z8	1788.24	893.62	595.41	x	x	x

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 42. CCS of B, Y, C and Z (-SO_3) ions identified in a dp10 GlcNAc6S-[I-GlcNAc6S]$_4$-I-R_2 structure, where R_2 is C_7H_7O.

#27								
GlcNAc6S-[I-GlcNAc6S]$_4$-I-R_2								
	- 1SO_3	- 1SO_3	- 1SO_3	- 1SO_3	- 1SO_3	- 1SO_3	- 1SO_3	- 1SO_3
	(1-)[1]	(2-)	(3-)	(4-)	(1-)	(2-)	(3-)	(4-)
B1	202.07	100.53	66.69	49.76	x	x	x	x
B2	378.10	188.55	125.36	93.77	112.38 (0.2)[2]	x	x	x
B3	661.14	330.07	219.71	164.53	x	167.6 (0.5)	x	x
B4	837.17	418.08	278.39	208.54	x	x	x	x
B5	1120.21	559.60	372.73	279.30	x	215.7 (0.2)	255.5 (0.4)	x
B6	1296.24	647.62	431.41	323.30	x	x	283.0 (0.5)	x
B7	1579.28	789.13	525.75	394.06	x	x	x	x
B8	1755.31	877.15	584.43	438.07	x	x	x	x
B9	2038.34	1018.67	678.78	508.83	x	x	x	x
B10	2214.38	1106.68	737.45	552.84	x	x	x	x
Y0	43.09	21.04	13.69	10.02	x	x	x	x
Y1	219.12	109.06	72.37	54.02	x	x	x	x
Y2	502.16	250.57	166.71	124.78	x	x	x	x
Y3	678.19	338.59	225.39	168.79	x	x	x	x
Y4	961.22	480.11	319.74	239.55	x	x	x	x
Y5	1137.26	568.12	378.41	283.56	x	x	x	x
Y6	1420.29	709.64	472.76	354.32	x	x	x	x
Y7	1596.32	797.66	531.44	398.33	x	x	x	x
Y8	1879.36	939.18	625.78	469.08	x	x	x	x
Y9	2055.39	1027.19	684.46	513.09	x	x	x	x
C1	220.08	109.54	72.69	54.26	x	x	x	x
C2	396.11	197.55	131.37	98.27	x	x	x	x
C3	679.15	339.07	225.71	169.03	x	x	x	x
C4	855.18	427.09	284.39	213.04	x	x	x	x
C5	1138.22	568.61	378.73	283.80	x	x	x	x

C6	1314.25	656.62	437.41	327.81	x	x	x	x
C7	1597.29	798.14	531.76	398.57	x	x	x	x
C8	1773.32	886.16	590.43	442.57	x	x	x	x
C9	2056.35	1027.67	684.78	513.33	x	x	x	x
C10	2232.39	1115.69	743.46	557.34	x	x	x	x
Z0	25.08	12.03	7.69	5.51	x	x	x	x
Z1	201.11	100.05	66.36	49.52	x	x	x	x
Z2	484.15	241.57	160.71	120.28	x	x	x	x
Z3	660.18	329.58	219.39	164.29	x	x	x	x
Z4	943.21	471.10	313.73	235.05	x	x	x	x
Z5	1119.25	559.12	372.41	279.06	x	x	x	x
Z6	1402.28	700.64	466.76	349.81	x	x	x	x
Z7	1578.31	788.65	525.43	393.82	x	x	x	x
Z8	1861.35	930.17	619.78	464.58	x	x	x	x
Z9	2037.38	1018.19	678.46	508.59	x	x	x	x

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 43. CCS of B, Y, C and Z (-SO_3) ions identified in a dp10 GlcNAc6S-[G-GlcNAc6S]$_4$-G-R_2 structure, where R_2 is C_7H_7O.

#28								
GlcNAc6S-[G-GlcNAc6S]4-G-R_2								
	(1-)[1]	(2-)	(3-)	(4-)	(1-)	(2-)	(3-)	(4-)
B1	202.07	100.53	66.69	49.76	x	x	x	x
B2	378.10	188.55	125.36	93.77	111.3 (0.2)[2]	x	x	x
B3	661.14	330.07	219.71	164.53	159.9 (0.2)	x	x	x
B4	837.17	418.08	278.39	208.54	x	x	x	x
B5	1120.21	559.60	372.73	279.30	x	214.4 (0.8)	x	x
B6	1296.24	647.62	431.41	323.30	x	x	x	x
B7	1579.28	789.13	525.75	394.06	x	x	300.8 (0.5)	x
B8	1755.31	877.15	584.43	438.07	x	x	x	x
B9	2038.34	1018.67	678.78	508.83	x	x	x	x
B10	2214.38	1106.68	737.45	552.84	x	x	x	x
Y0	43.09	21.04	13.69	10.02	x	x	x	x
Y1	219.12	109.06	72.37	54.02	x	x	x	x
Y2	502.16	250.57	166.71	124.78	x	x	x	x
Y3	678.19	338.59	225.39	168.79	x	x	x	x
Y4	961.22	480.11	319.74	239.55	x	x	x	x
Y5	1137.26	568.12	378.41	283.56	x	x	x	x
Y6	1420.29	709.64	472.76	354.32	x	x	x	x
Y7	1596.32	797.66	531.44	398.33	x	x	x	x
Y8	1879.36	939.18	625.78	469.08	x	x	x	x
Y9	2055.39	1027.19	684.46	513.09	x	x	x	x
C1	220.08	109.54	72.69	54.26	x	x	x	x
C2	396.11	197.55	131.37	98.27	x	x	x	x
C3	679.15	339.07	225.71	169.03	x	x	x	x
C4	855.18	427.09	284.39	213.04	x	x	x	x
C5	1138.22	568.61	378.73	283.80	x	x	x	x

C6	1314.25	656.62	437.41	327.81	x	x	x	x
C7	1597.29	798.14	531.76	398.57	x	x	x	x
C8	1773.32	886.16	590.43	442.57	x	x	x	x
C9	2056.35	1027.67	684.78	513.33	x	x	x	x
C10	2232.39	1115.69	743.46	557.34	x	x	x	x
Z0	25.08	12.03	7.69	5.51	x	x	x	x
Z1	201.11	100.05	66.36	49.52	x	x	x	x
Z2	484.15	241.57	160.71	120.28	x	x	x	x
Z3	660.18	329.58	219.39	164.29	x	x	x	x
Z4	943.21	471.10	313.73	235.05	x	x	x	x
Z5	1119.25	559.12	372.41	279.06	x	x	x	x
Z6	1402.28	700.64	466.76	349.81	x	x	x	x
Z7	1578.31	788.65	525.43	393.82	x	x	x	x
Z8	1861.35	930.17	619.78	464.58	x	x	x	x
Z9	2037.38	1018.19	678.46	508.59	x	x	x	x

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 44. CCS of B, Y, C and Z -SO_3 ions identified in disaccharide ΔUA2S-GlcNS3S6S structure.

#29				
ΔUA2S-GlcNS3S6S				
	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$
	(1-)[1]	(2-)	(1-)	(2-)
B1	157.01	78.00	69.4 (0.1)[2]	x
Y0	337.99	168.49	x	106 (0.5)
C1	175.02	87.01	x	x
Z0	319.97	159.48	x	x

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 45. CCS of B, Y, C and Z -SO_3 ions identified in tetraaccharide ΔUA-GlcNS-IdoA2S-GlcNS3S structure.

#30				
ΔUA-GlcNS-IdoA2S-GlcNS3S				
	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$
	(1-)[1]	(2-)	(1-)	(2-)
B1	77.06	38.02	x	x
B2	318.08	158.54	99.5 (0.5)[2]	x
B3	574.07	286.53	141.4 (0.1)	150.5 (0.1)
Y0	258.03	128.51	85.3 (0.1)	x
Y1	514.02	256.50	x	133.0 (0.5)
Y2	755.04	377.02	x	172.8 (0.1)
C1	95.07	47.03	x	x
C2	336.09	167.54	x	x
C3	592.08	295.54	x	148.5 (0.4)

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 46. CCS of B, Y, C and Z -SO_3 ions identified in tetrasaccharide ΔUA-GlcNS6S-GlcA-GlcNS3S6S structure.

#31				
UA-GlcNS6S-G-GlcNS3S6S				
	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$
	(1-)[1]	(2-)	(1-)	(2-)
B1	77.06	38.02	x	x
B2	398.04	198.52	x	x
B3	574.07	286.53	140.9 (0.5)[2]	151.1 (0.3)
Y0	337.99	168.49	x	105.8 (0.3)
Y1	514.02	256.50	x	133.5 (0.5)
Y2	835.00	417.00	x	x
C1	95.07	47.03	x	x
C2	416.05	207.52	x	x
C3	592.08	295.54	133.5 (0.5)	x
Z0	319.97	159.48	x	x
Z1	496.01	247.50	x	x
Z2	816.99	407.99	x	x

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 47. CCS of B, Y, C and Z -SO_3 ions identified in tetrasaccharide ΔUA-GlcNAc6S-GlcA-GlcNS3S6S structure.

#32				
ΔUA-GlcNAc6S-GlcA-GlcNS3S6S				
	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$
	(1-)[1]	(2-)	(1-)	(2-)
B1	77.06	38.02	x	x
B2	360.09	179.54	x	x
B3	536.13	267.56	136.7 (0.2)[2]	x
Y0	337.99	168.49	x	x
Y1	514.02	256.50	x	x
Y2	797.05	398.02	x	x
C1	95.07	47.03	x	x
C2	378.10	188.55	x	x
C3	554.14	276.56	138.13 (0.2)	x
Z0	319.97	159.48	x	x
Z1	496.01	247.50	x	x
Z2	779.04	389.02	x	x

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 48. CCS of B, Y, C and Z (-SO_3) ions identified in a hexasaccharide G-GlcNS6S-G-GlcNS6S-I2S-GlcNS6S-R_1 structure, where R_1 is $(CH_2)_5NH_2$.

#33						
G-GlcNS6S-G-GlcNS6S-I2S-GlcNS6S-R_1						
	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$
	(1-)[1]	(2-)	(3-)	(1-)	(2-)	(3-)
B1	95.07	47.03	31.02	x	x	x
B2	416.05	207.52	138.01	x	122.2 (0.6)[2]	x
B3	592.08	295.54	196.69	x	152.5 (0.2)	x
B4	913.06	456.03	303.68	x	x	216.5 (0.3)
B5	1169.05	584.02	389.01	x	x	x
B6	1490.04	744.51	496.01	x	x	x
Y0	22.14	10.56	6.71	x	x	x
Y1	343.12	171.05	113.70	109.1 (0.3)	x	x
Y2	599.11	299.05	199.03	x	157.0 (0.2)	x
Y3	920.09	459.54	306.02	x	x	x
Y4	1096.12	547.56	364.70	x	x	246.3 (0.6)
Y5	1417.10	708.05	471.70	x	x	x
C1	113.08	56.04	37.02	x	x	x
C2	434.06	216.53	144.01	x	x	x
C3	610.09	304.54	202.69	x	x	x
C4	931.07	465.03	309.69	x	x	x
C5	1187.06	593.03	395.02	x	x	x
C6	1508.05	753.52	502.01	x	x	x
Z0	4.12	1.56	0.70	x	x	x
Z1	325.11	162.05	107.70	x	x	x
Z2	581.10	290.04	193.03	x	x	x
Z3	902.08	450.54	300.02	x	x	x
Z4	1078.11	538.55	358.70	x	x	x
Z5	1399.09	699.04	465.69	x	x	x

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 49. CCS of B, Y, C and Z (-SO_3) ions identified in a hexasaccharide G-GlcNS6S-G-GlcNS3S-I2S-GlcNS6S-R_1 structure, where R_1 is $(CH_2)_5NH_2$.

#34						
G-GlcNS6S-G-GlcNS3S-I2S-GlcNS6S-R_1						
	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$
	(1-)[1]	(2-)	(3-)	(1-)	(2-)	(3-)
B1	95.07	47.03	31.02	x	x	x
B2	416.05	207.52	138.01	x	121.8 (0.4)[2]	x
B3	592.08	295.54	196.69	139.1 (0.3)	X	x
B4	913.06	456.03	303.68	x	x	x
B5	1169.05	584.02	389.01	x	x	x
B6	1490.04	744.51	496.01	x	x	x
Y0	22.14	10.56	6.71	x	x	x
Y1	343.12	171.05	113.70	109.5 (0.3)	x	x
Y2	599.11	299.05	199.03	x	156.4 (0.1)	x
Y3	920.09	459.54	306.02	x	x	x
Y4	1096.12	547.56	364.70	x	209.9 (0.5)	x
Y5	1417.10	708.05	471.70	x	x	x
C1	113.08	56.04	37.02	x	x	x
C2	434.06	216.53	144.01	x	x	x
C3	610.09	304.54	202.69	x	x	x
C4	931.07	465.03	309.69	x	x	x
C5	1187.06	593.03	395.02	x	x	x
C6	1508.05	753.52	502.01	x	x	x
Z0	4.12	1.56	0.70	x	x	x
Z1	325.11	162.05	107.70	x	x	x
Z2	581.10	290.04	193.03	x	x	x
Z3	902.08	450.54	300.02	x	x	x
Z4	1078.11	538.55	358.70	x	x	x
Z5	1399.09	699.04	465.69	x	x	x

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 50. CCS of B, Y, C and Z (-SO_3) ions identified in a hexasaccharide G-GlcNS6S-G-GlcNS6S3S-I2S-GlcNS6S-R_1 structure, where R_1 is $(CH_2)_5NH_2$.

#35						
G-GlcNS6S-G-GlcNS6S3S-I2S-GlcNS6S-R_1						
	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$
	(1-)[1]	(2-)	(3-)	(1-)	(2-)	(3-)
B1	95.07	47.03	31.02	x	x	x
B2	416.05	207.52	138.01	x	122.4 (0.2)	x
B3	592.08	295.54	196.69	139.3 (0.3)	x	x
B4	993.02	496.01	330.34	x	x	x
B5	1249.01	624.00	415.66	x	x	x
B6	1569.99	784.49	522.66	x	x	x
Y0	22.14	10.56	6.71	x	x	x
Y1	343.12	171.05	113.70	109.8 (0.2)	x	x
Y2	599.11	299.05	199.03	x	x	x
Y3	1000.05	499.52	332.68	x	x	x
Y4	1176.08	587.53	391.35	x	x	242.3 (0.5)
Y5	1497.06	748.03	498.35	x	x	x
C1	113.08	56.04	37.02	x	x	x
C2	434.06	216.53	144.01	x	x	x
C3	610.09	304.54	202.69	x	x	x
C4	1011.03	505.01	336.34	x	x	x
C5	1267.02	633.01	421.67	x	x	x
C6	1588.00	793.50	528.66	x	x	x
Z0	4.12	1.56	0.70	x	x	x
Z1	325.11	162.05	107.70	x	x	x
Z2	581.10	290.04	193.03	x	x	x
Z3	982.03	490.51	326.67	x	x	x
Z4	1158.07	578.53	385.35	x	x	x
Z5	1479.05	739.02	492.34	x	x	x

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 51. CCS of B, Y, C and Z (-SO_3) ions identified in a septa-saccharide G-GlcNS-G-GlcNS-I2S-GlcNS-G-GlcNS-G-R_3 structure.

#36						
G-GlcNS-G-GlcNS-I2S-GlcNS-G-GlcNS-G-R_3						
	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$
	(1-)[1]	(2-)	(3-)	(1-)	(2-)	(3-)
B1	77.06	38.02	25.01	x	x	x
B2	318.08	158.54	105.36	x	x	x
B3	574.07	286.53	190.69	x	x	x
B4	815.10	407.04	271.03	x	x	x
B5	991.13	495.06	329.70	x	x	x
B6	1232.15	615.57	410.05	x	x	x
B7	1408.19	703.59	468.72	x	x	x
B8	1546.21	772.60	514.73	x	x	x
Y0	58.06	28.53	18.68	x	x	x
Y1	234.09	116.54	77.36	x	x	x
Y2	475.12	237.06	157.70	x	x	x
Y3	651.15	325.07	216.38	x	x	x
Y4	892.18	445.58	296.72	x	x	x
Y5	1148.17	573.58	382.05	x	x	x
Y6	1389.19	694.09	462.39	x	x	x
Y7	1547.21	773.10	515.07	x	x	x
C1	94.06	46.53	30.68	x	x	x
C2	335.09	167.04	111.02	x	x	x
C3	591.07	295.03	196.35	x	x	x
C4	832.10	415.55	276.69	x	x	x
C5	1008.13	503.56	335.37	x	x	x
C6	1249.16	624.07	415.71	x	x	x
C7	1425.19	712.09	474.39	x	x	x
C8	1563.21	781.10	520.40	x	x	x
Z0	40.05	19.52	12.68	x	x	x
Z1	216.08	107.54	71.36	x	x	x
Z2	457.11	228.05	151.70	x	x	x
Z3	633.14	316.07	210.38	x	x	x
Z4	874.17	436.58	290.72	x	x	x
Z5	1130.16	564.57	376.05	x	x	x
Z6	1371.18	685.09	456.39	x	x	x
Z7	1546.21	772.60	514.73	x	x	x

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 52. Summary of B, Y, C and Z ions theoretically identified from one of the six possible hexasaccharide sequences (dp6 + $3SO_3$ + 1NAc) as a result of one glycosidic bond cleavage in the structure ΔUA-GlcNS-UA-GlcNAc-UA2S-GlcNS.

ΔUA-GlcNS-UA-GlcNAc-UA2S-GlcNS				
	(1-)	(2-)	(1-)	(2-)
B1	157.014	78.003	✓	x
B2	398.039	198.516	x	✓
B3	574.071	286.532	✓	✓
B4	777.151	388.071	x	x
B5	1033.140	516.066	x	x
Y0	258.028	128.510	x	x
Y1	514.017	256.505	x	x
Y2	717.097	358.044	x	x
Y3	893.129	446.060	x	x
Y4	1134.154	566.573	x	x
C1	175.024	87.008	✓	x
C2	416.050	207.521	✓	✓
C3	592.082	295.537	✓	✓
C4	795.161	397.077	x	x
C5	1051.150	525.071	x	x
Z0	240.018	119.505	✓	x
Z1	496.007	247.499	x	✓
Z2	699.086	349.039	x	x
Z3	875.118	437.055	x	x
Z4	1116.144	557.568	x	x
			Total	8

Supplementary Table 53. Summary of B, Y, C and Z ions theoretically identified from one of the six possible hexasaccharide sequences (dp6 + $3SO_3$ + 1NAc) as a result of one glycosidic bond cleavage in the structure ΔUA-GlcNS-UA2S-GlcNS-UA-GlcNAc.

ΔUA-GlcNS-UA2S-GlcNS-UA-GlcNAc				
	(1-)	(2-)	(1-)	(2-)
B1	157.014	78.003	✓	x
B2	398.039	198.516	✓	✓
B3	654.028	326.510	x	✓
B4	895.054	447.023	x	x
B5	1071.086	535.039	x	✓
Y0	220.082	109.537	x	x
Y1	396.114	197.553	✓	x
Y2	637.140	318.066	✓	x
Y3	893.129	446.060	x	✓
Y4	1134.154	566.573	x	x
C1	175.024	87.008	✓	x
C2	416.050	207.521	✓	✓
C3	672.039	335.515	x	x
C4	913.064	456.028	x	x
C5	1089.096	544.044	x	x
Z0	202.072	100.532	x	x
Z1	378.104	188.548	✓	x
Z2	619.129	309.061	✓	x
Z3	875.118	437.055	x	x
Z4	1116.144	557.568	x	x
			Total	11

Supplementary Table 54. Summary of B, Y, C and Z ions theoretically identified from one of the six possible hexasaccharide sequences (dp6 + $3SO_3$ + 1NAc) as a result of one glycosidic bond cleavage in the structure ΔUA-GlcNAc-UA-GlcNS-UA2S-GlcNS

ΔUA-GlcNAc-UA-GlcNS-UA2S-GlcNS				
	(1-)	(2-)	(1-)	(2-)
B1	157.014	78.003	✓	x
B2	360.093	179.543	x	x
B3	536.125	267.559	✓	x
B4	777.151	388.071	x	x
B5	1033.140	516.066	x	x
Y0	258.028	128.510	x	x
Y1	514.017	256.505	x	x
Y2	755.043	377.017	x	x
Y3	931.075	465.034	x	x
Y4	1134.154	566.573	x	x
C1	175.024	87.008	✓	x
C2	378.104	188.548	✓	x
C3	554.136	276.564	x	x
C4	795.161	397.077	x	x
C5	1051.150	525.071	x	x
Z0	240.018	119.505	✓	x
Z1	496.007	247.499	x	✓
Z2	737.032	368.012	x	x
Z3	913.064	456.028	x	x
Z4	1116.144	557.568	x	x
			Total	6

Supplementary Table 55. Summary of B, Y, C and Z ions theoretically identified from one of the six possible hexasaccharide sequences (dp6 + $3SO_3$ + 1NAc) as a result of one glycosidic bond cleavage in the structure ΔUA-GlcNAc-UA2S-GlcNS-UA-GlcNS.

ΔUA-GlcNAc-UA2S-GlcNS-UA-GlcNS				
	(1-)	(2-)	(1-)	(2-)
B1	157.014	78.003	✓	x
B2	360.093	179.543	x	x
B3	616.082	307.537	x	✓
B4	857.107	428.050	x	x
B5	1033.140	516.066	x	x
Y0	258.028	128.510	x	x
Y1	434.060	216.526	x	x
Y2	675.086	337.039	x	x
Y3	931.075	465.034	x	x
Y4	1134.154	566.573	x	x
C1	175.024	87.008	✓	x
C2	378.104	188.548	✓	x
C3	634.092	316.542	x	x
C4	875.118	437.055	x	x
C5	1051.150	525.071	x	x
Z0	240.018	119.505	✓	x
Z1	416.050	207.521	✓	✓
Z2	657.075	328.034	✓	✓
Z3	913.064	456.028	x	x
Z4	1116.144	557.568	x	x
			Total	7

Supplementary Table 56. Summary of B, Y, C and Z ions theoretically identified from one of the six possible hexasaccharide sequences (dp6 + $3SO_3$ + 1NAc) as a result of one glycosidic bond cleavage in the structure ΔUA2S-GlcNS-UA-GlcNS-UA-GlcNAc.

ΔUA2S-GlcNS-UA-GlcNS-UA-GlcNAc				
	(1-)	(2-)	(1-)	(2-)
B1	236.970	117.981	x	x
B2	477.996	238.494	x	x
B3	654.028	326.510	x	✓
B4	895.054	447.023	x	x
B5	1071.086	535.039	x	x
Y0	220.082	109.537	x	x
Y1	396.114	197.553	✓	x
Y2	637.140	318.066	✓	x
Y3	813.172	406.082	x	✓
Y4	1054.197	526.595	x	✓
C1	254.981	126.987	x	x
C2	496.007	247.499	x	✓
C3	672.039	335.515	x	x
C4	913.064	456.028	x	x
C5	1089.096	544.044	x	x
Z0	202.072	100.532	x	x
Z1	378.104	188.548	✓	x
Z2	619.129	309.061	✓	x
Z3	795.161	397.077	x	x
Z4	1036.187	517.590	x	x
			Total	8

Supplementary Table 57. Summary of B, Y, C and Z ions theoretically identified from one of the six possible hexasaccharide sequences (dp6 + $3SO_3$ + 1NAc) as a result of one glycosidic bond cleavage in the structure ΔUA2S-GlcNS-UA-GlcNAc-UA-GlcNS.

ΔUA2S-GlcNS-UA-GlcNAc-UA-GlcNS				
	(1-)	(2-)	(1-)	(2-)
B1	236.970	117.981	x	x
B2	477.996	238.494	x	x
B3	654.028	326.510	x	✓
B4	857.107	428.050	x	x
B5	1033.140	516.066	x	x
Y0	258.028	128.510	x	x
Y1	434.060	216.526	x	x
Y2	637.140	318.066	✓	x
Y3	813.172	406.082	x	✓
Y4	1054.197	526.595	x	✓
C1	254.981	126.987	x	x
C2	496.007	247.499	x	✓
C3	672.039	335.515	x	x
C4	875.118	437.055	x	x
C5	1051.150	525.071	x	x
Z0	240.018	119.505	✓	x
Z1	416.050	207.521	✓	✓
Z2	619.129	309.061	✓	x
Z3	795.161	397.077	x	x
Z4	1036.187	517.590	x	x
			Total	9

Supplementary Table 58. Summary overview of the B, Y, C and Z ions theoretically identified from one glycosidic bond cleavage in the purified hexasaccharide.

Possible structures	B/C/Y/Z ions
ΔUA-GlcNS-UA-GlcNAc-UA2S-GlcNS	8
ΔUA-GlcNS-UA2S-GlcNS-UA-GlcNAc	11
ΔUA-GlcNAc-UA-GlcNS-UA2S-GlcNS	6
ΔUA-GlcNAc-UA2S-GlcNS-UA-GlcNS	7
ΔUA2S-GlcNS-UA-GlcNS-UA-GlcNAc	8
ΔUA2S-GlcNS-UA-GlcNAc-UA-GlcNS	9

Supplementary Table 59. CCS of B, Y, C and Z ions identified in a ΔUA-GlcNS-I2S-GlcNS-G-GlcNAc structure.

#HS1				
ΔUA-GlcNS-I2S-GlcNS-G-GlcNAc				
$[M-3H]^{3-}$	430.05	274.0 (0.6)		
	(1-)[1]	(2-)	(1-)	(2-)
B1	157.014	78.003	70.5 (0.9)	x
B2	398.039	198.516	110.1 (0.8)	119.6 (0.4)
B3	654.028	326.510	x	162.0 (0.7)
B4	895.054	447.023	x	201.0 (0.7)
B5	1071.086	535.039	x	x
Y0	220.082	109.537	x	x
Y1	396.114	197.553	116.1 (0.5)	x
Y2	637.140	318.066	151.8 (0.5)	x
Y3	893.129	446.060	x	x
Y4	1134.154	566.573	x	x
C1	175.024	87.008	71.0 (0.6)	x
C2	416.050	207.521	113.6 (0.4)	x
C3	672.039	335.515	x	164.0 (0.8)
C4	913.064	456.028	x	x
C5	1089.096	544.044	x	x
Z0	202.072	100.532	x	x
Z1	378.104	188.548	113.8 (0.6)	x
Z2	619.129	309.061	149.2 (0.2)	x
Z3	875.118	437.055	x	156.2 (0.6)
Z4	1116.144	557.568	x	x

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 60. CCS of B, Y, C and Z (-SO_3) ions identified in a hexasaccharide ΔUA-GlcNS-I2S-GlcNS-G-GlcNAc structure.

#HS1				
ΔUA-GlcNS-I2S-GlcNS-G-GlcNAc				
$[M-2H]^{2-}$	605.6	225.05 (0.4)		
$[M-3H]^{3-}$	403.4	255.39 (0.1)		
	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$
	(1-)[1]	(2-)	(1-)	(2-)
B1	77.06	38.02	x	x
B2	318.08	158.54	x	x
B3	574.07	286.53	x	150.3 (0.8)[2]
B4	815.10	407.04	x	x
B5	991.13	495.06	x	200.1 (0.6)
Y0	140.13	69.56	x	x
Y1	316.16	157.57	x	x
Y2	557.18	278.09	x	x
Y3	813.17	406.08	x	181.47 (0.5)
Y4	1054.20	526.59	x	x
C1	95.07	47.03	x	x
C2	336.09	167.54	x	x
C3	592.08	295.54	x	x
C4	833.11	416.05	x	179.5 (0.5)
C5	1009.14	504.07	x	x
Z0	122.12	60.55	x	x
Z1	298.15	148.57	x	x
Z2	539.17	269.08	x	x
Z3	795.16	397.08	x	x
Z4	1036.19	517.59	x	x

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 61. Summary of B, Y, C and Z ions theoretically identified from one of the six possible hexasaccharide sequences (dp6 + $5SO_3$ + 1NAc) as a result of one glycosidic bond cleavage in the structure ΔUA-GlcNS-UA-GlcNAc6S-UA2S-GlcNS6S.

ΔUA-GlcNS-UA-GlcNAc6S-UA2S-GlcNS6S						
	(1-)	(2-)	(3-)	(1-)	(2-)	(3-)
B1	157.014	78.003	51.666	✓	x	x
B2	398.039	198.516	132.008	✓	✓	x
B3	574.071	286.532	190.685	✓	✓	x
B4	857.107	428.050	285.031	x	x	x
B5	1113.096	556.044	370.360	x	x	x
Y0	337.985	168.489	111.990	x	x	x
Y1	593.974	296.483	197.319	x	x	x
Y2	877.010	438.001	291.665	x	x	✓
Y3	1053.042	526.017	350.342	x	x	✓
Y4	1294.068	646.530	430.684	x	x	✓
C1	175.024	87.008	57.670	✓	x	x
C2	416.050	207.521	138.011	✓	x	x
C3	592.082	295.537	196.689	x	x	x
C4	875.118	437.055	291.034	x	x	x
C5	1131.107	565.050	376.364	x	x	x
Z0	319.974	159.483	105.986	x	x	x
Z1	575.963	287.478	191.316	x	x	x
Z2	858.999	428.996	285.661	x	x	x
Z3	1035.031	517.012	344.339	x	x	x
Z4	1276.057	637.525	424.680	x	x	
				Total	9	

Supplementary Table 62. Summary of B, Y, C and Z ions theoretically identified from one of the six possible hexasaccharide sequences (dp6 + $5SO_3$ + 1NAc) as a result of one glycosidic bond cleavage in the structure ΔUA-GlcNS-UA2S-GlcNS6S-UA-GlcNAc6S.

ΔUA-GlcNS-UA2S-GlcNS6S-UA-GlcNAc6S						
	(1-)	(2-)	(3-)	(1-)	(2-)	(3-)
B1	157.014	78.003	51.666	✓	x	x
B2	398.039	198.516	132.008	✓	✓	x
B3	654.028	326.510	217.338	✓	✓	x
B4	975.011	487.001	324.332	x	✓	x
B5	1151.043	575.017	383.009	x	x	✓
Y0	300.039	149.516	99.341	✓	x	x
Y1	476.071	237.532	158.018	✓	✓	x
Y2	797.053	398.023	265.013	x	x	✓
Y3	1053.042	526.017	350.342	x	x	✓
Y4	1294.068	646.530	430.684	x	x	✓
C1	175.024	87.008	57.670	✓	x	x
C2	416.050	207.521	138.011	✓	x	x
C3	672.039	335.515	223.341	✓	x	x
C4	993.021	496.007	330.335	x	x	x
C5	1169.053	584.023	389.013	x	✓	x
Z0	282.028	140.510	93.338	✓	x	x
Z1	458.060	228.526	152.015	✓	✓	x
Z2	779.043	389.018	259.009	x	x	✓
Z3	1035.032	517.012	344.339	x	x	x
Z4	1276.057	637.525	424.681	x	x	✓
				Total	18	

Supplementary Table 63. Summary of B, Y, C and Z ions theoretically identified from one of the six possible hexasaccharide sequences (dp6 + $5SO_3$ + 1NAc) as a result of one glycosidic bond cleavage in the structure ΔUA-GlcNAc6S-UA-GlcNS-UA2S-GlcNS6S

ΔUA-GlcNAc6S-UA-GlcNS-UA2S-GlcNS6S						
	(1-)	(2-)	(3-)	(1-)	(2-)	(3-)
B1	157.014	78.003	51.666	✓	x	x
B2	440.050	219.521	146.011	x	x	x
B3	616.082	307.537	204.689	x	✓	x
B4	857.107	428.050	285.031	x	✓	x
B5	1113.096	556.044	370.360	x	x	x
Y0	337.985	168.489	111.990	x	x	x
Y1	593.974	296.483	197.319	x	x	x
Y2	835.000	416.996	277.661	x	x	x
Y3	1011.032	505.012	336.339	x	x	x
Y4	1294.068	646.530	430.684	x	x	x
C1	175.024	87.008	57.670	✓	x	x
C2	458.060	228.526	152.015	✓	✓	x
C3	634.092	316.542	210.692	x	x	x
C4	875.118	437.055	291.034	x	x	x
C5	1131.107	565.050	376.364	x	x	x
Z0	319.975	159.483	105.986	x	x	x
Z1	575.963	287.478	191.316	x	x	x
Z2	816.989	407.991	271.658	x	x	x
Z3	993.021	496.007	330.335	x	x	x
Z4	1276.057	637.525	424.681	x	x	x
				Total	5	

Supplementary Table 64. Summary of B, Y, C and Z ions theoretically identified from one of the six possible hexasaccharide sequences (dp6 + $5SO_3$ + 1NAc) as a result of one glycosidic bond cleavage in the structure ΔUA-GlcNAc6S-UA2S-GlcNS6S-UA-GlcNS

ΔUA-GlcNAc6S-UA2S-GlcNS6S-UA-GlcNS						
	(1-)	(2-)	(3-)	(1-)	(2-)	(3-)
B1	157.014	78.003	51.666	✓	x	x
B2	440.050	219.521	146.011	x	x	x
B3	696.039	347.515	231.341	x	x	x
B4	1017.021	508.007	338.335	x	x	x
B5	1193.053	596.023	397.013	x	x	x
Y0	258.028	128.510	85.338	x	x	x
Y1	434.060	216.526	144.015	✓	✓	x
Y2	755.043	377.018	251.009	x	x	x
Y3	1011.032	505.012	336.339	x	x	x
Y4	1294.068	646.530	430.684	x	x	x
C1	175.024	87.008	57.670	✓	x	x
C2	458.060	228.526	152.015	✓	✓	x
C3	714.049	356.521	237.345	x	x	x
C4	1035.032	517.012	344.339	x	✓	x
C5	1211.064	605.028	403.016	x	x	x
Z0	240.018	119.505	79.334	✓	x	x
Z1	416.050	207.521	138.011	✓	✓	x
Z2	737.032	368.012	245.006	x	x	✓
Z3	993.021	496.007	330.335	x	x	x
Z4	1276.057	637.525	424.681	x	x	x
				Total	8	

Supplementary Table 65. Summary of B, Y, C and Z ions theoretically identified from one of the six possible hexasaccharide sequences (dp6 + $5SO_3$ + 1NAc) as a result of one glycosidic bond cleavage in the structure ΔUA2S-GlcNS6S-UA-GlcNS-UA-GlcNAc6S

ΔUA2S-GlcNS6S-UA-GlcNS-UA-GlcNAc6S						
	(1-)	(2-)	(3-)	(1-)	(2-)	(3-)
B1	236.970	117.981	78.318	x	x	x
B2	557.953	278.473	185.312	x	x	x
B3	733.985	366.489	243.990	x	x	x
B4	975.011	487.001	324.332	x	x	x
B5	1151.043	575.017	383.009	x	✓	x
Y0	300.039	149.516	99.341	✓	x	x
Y1	476.071	237.532	158.018	✓	✓	x
Y2	717.097	358.044	238.360	✓	✓	x
Y3	893.129	446.060	297.038	x	✓	x
Y4	1214.111	606.552	404.032	x	x	x
C1	254.981	126.987	84.322	✓	x	x
C2	575.963	287.478	191.316	x	x	x
C3	751.996	375.494	249.993	x	x	x
C4	993.021	496.007	330.335	x	✓	x
C5	1169.053	584.023	389.013	x	✓	✓
Z0	282.028	140.510	93.338	✓	x	x
Z1	458.060	228.526	152.015	✓	✓	x
Z2	699.086	349.039	232.357	x	✓	x
Z3	875.118	437.055	291.034	x	x	x
Z4	1196.101	597.546	398.028	x	x	x
				Total	11	

Supplementary Table 66. Summary of B, Y, C and Z ions theoretically identified from one of the six possible hexasaccharide sequences (dp6 + $5SO_3$ + 1NAc) as a result of one glycosidic bond cleavage in the structure ΔUA2S-GlcNS6S-UA-GlcNAc6S-UA-GlcNS

ΔUA2S-GlcNS6S-UA-GlcNAc6S-UA-GlcNS						
	(1-)	(2-)	(3-)	(1-)	(2-)	(3-)
B1	236.970	117.981	78.318	x	x	x
B2	557.953	278.473	185.312	x	x	x
B3	733.985	366.489	243.990	x	x	x
B4	1017.021	508.007	338.335	x	x	x
B5	1193.053	596.023	397.013	x	x	x
Y0	258.028	128.510	85.338	x	x	x
Y1	434.060	216.526	144.015	✓	✓	x
Y2	717.097	358.044	238.360	✓	✓	x
Y3	893.129	446.060	297.038	x	✓	x
Y4	1214.111	606.552	404.032	x	x	x
C1	254.981	126.987	84.322	x	x	x
C2	575.963	287.478	191.316	x	x	x
C3	751.996	375.494	249.993	x	x	x
C4	1035.032	517.012	344.339	x	✓	x
C5	1211.064	605.028	403.016	x	x	x
Z0	240.018	119.505	79.334	✓	x	x
Z1	416.050	207.521	138.011	✓	✓	x
Z2	699.086	349.039	232.357	x	✓	x
Z3	875.118	437.055	291.034	x	x	x
Z4	1196.101	597.546	398.028	x	x	x
				Total	7	

Supplementary Table 67. Summary overview of the B, Y, C and Z ions theoretically identified from one glycosidic bond cleavage in the purified oligosaccharide.

Possible structures	B/Y/C/Z ions
ΔUA-GlcNS-UA-GlcNAc6S-UA2S-GlcNS6S	9
ΔUA-GlcNS-UA2S-GlcNS6S-UA-GlcNAc6S	18
ΔUA-GlcNAc6S-UA-GlcNS-UA2S-GlcNS6S	5
ΔUA-GlcNAc6S-UA2S-GlcNS6S-UA-GlcNS	8
ΔUA2S-GlcNS6S-UA-GlcNS-UA-GlcNAc6S	11
ΔUA2S-GlcNS6S-UA-GlcNAc6S-UA-GlcNS	7

Supplementary Table 68. CCS of B, Y, C and Z ions identified in a ΔUA-GlcNS-I2S-GlcNS6S-UA-GlcNAc6S structure.

#HS2						
ΔUA-GlcNS-I2S-GlcNS6S-G-GlcNAc6S						
$[M-2H]^{2-}$	362.26	331.0 (0.2)[2]				
$[M-3H]^{3-}$	483.35	265.7 (0.4)				
	(1-)[1]	(2-)	(3-)	(1-)	(2-)	(3-)
B1	157.014	78.003	51.666	70.4 (0.8)	x	x
B2	398.039	198.516	132.008	110.3 (0.5)	x	x
B3	654.028	326.510	217.338	x	162.4 (0.2)	x
B4	975.011	487.001	324.332	x	225.3 (0.5)	x
B5	1151.043	575.017	383.009	x	x	272.9 (0.4)
Y0	300.039	149.516	99.341	94.7 (0.3)	x	x
Y1	476.071	237.532	158.018	123.2 (0.5)	134.1 (0.5)	x
Y2	797.053	398.023	265.013	x	x	199.6 (0.6)
Y3	1053.042	526.017	350.342	x	x	250.4 (0.5)
Y4	1294.068	646.530	430.684	x	x	276.9 (0.4)
C1	175.024	87.008	57.670	70.4 (0.6)	x	x
C2	416.050	207.521	138.011	x	x	x
C3	672.039	335.515	223.341	146.9 (0.7)	x	x
C4	993.021	496.007	330.335	x	x	x
C5	1169.053	584.023	389.013	x	x	x
Z0	282.028	140.510	93.338	93.2 (0.5)	x	x
Z1	458.060	228.526	152.015	120.5 (0.3)	x	x
Z2	779.043	389.018	259.009	X	x	x
Z3	1035.032	517.012	344.339	x	x	x
Z4	1276.057	637.525	424.681	x	x	x

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation

Supplementary Table 69. CCS of B, Y, C and Z (-SO_3) ions identified in a hexasaccharide ΔUA-GlcNS-I2S-GlcNS6S-G-GlcNAc6S structure.

#HS2				
ΔUA-GlcNS-I2S-GlcNS6S-G-GlcNAc6S				
$[M-3H]^{3-}$	342.27	318.8 (0.5)		
	- $1SO_3$	- $1SO_3$	- $1SO_3$	- $1SO_3$
	(1-)[1]	(2-)	(1-)	(2-)
B1	77.06	38.02	x	x
B2	318.08	158.54	x	x
B3	574.07	286.53	x	x
B4	895.05	447.02	x	x
B5	1071.09	535.04	x	x
Y0	220.08	109.54	x	x
Y1	396.11	197.55	x	x
Y2	717.10	358.04	x	x
Y3	973.09	486.04	x	x
Y4	1214.11	606.55	x	x
C1	95.07	47.03	x	x
C2	336.09	167.54	x	x
C3	592.08	295.54	145.7 (0.6)[2]	x
C4	913.06	456.03	x	x
C5	1089.10	544.04	x	x
Z0	202.07	100.53	x	x
Z1	378.10	188.55	x	x
Z2	699.09	349.04	x	x
Z3	955.08	477.03	x	x
Z4	1196.10	597.55	x	x

[1] Columns represent different charge states.

[2] Each CCS is an average of independent measurements with the corresponding standard deviation