## 1 Shotgun Ion Mobility Mass Spectrometry Sequencing of Heparan Sulfate Saccharides

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Supplementary Table 13.	CCS of B, Y, C, Z ions - octasaccharide GlcNAc6S-I-GlcNAc6S-G-GlcNAc6S-I-
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Supplementary Table 33.	CCS of B, Y, C, Z -SO3 ions - hexasaccharide GlcNAc6S-[I-GlcNAc6S]2-I-R2.
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Supplementary Table 36.	CCS of B, Y, C, Z -SO3 ions - octasaccharide GlcNAc6S-G-GlcNAc6S-G-GlcNAc6S-
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Supplementary Table 38.	CCS of B, Y, C, Z -SO3 ions - octasaccharide GlcNAc6S-I-GlcNAc6S-G-GlcNAc6S-I-
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Supplementary Table 40.	CCS of B, Y, C, Z -SO3 ions - nonasaccharide G-GlcNS-G-GlcNS-I-GlcNS-G-GlcNS-
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Supplementary Table 42.	CCS of B, Y, C, Z -SO3 ions - decasaccharide GlcNAc6S-[I-GlcNAc6S] <sub>4</sub> -I-R <sub>2</sub> .
Supplementary Table 43.	CCS of B, Y, C, Z -SO3 ions - decasaccharide GlcNAc6S-[G-GlcNAc6S]4-G-R2.
Supplementary Table 44	CCS of B, Y, C, Z -SO <sub>3</sub> ions - disaccharide $\Delta$ UA2S-GlcNS3S6S
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Supplementary Table 48	CCS of B, Y, C, Z ions - G-GlcNS6S-G-GlcNS6S-I2S-GlcNS6S-R <sub>1</sub>
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Supplementary Table 50	CCS of B, Y, C, Z ions - G-GlcNS6S-G-GlcNS6S3S-I2S-GlcNS6S-R <sub>1</sub>
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Supplementary Table 52.	Theoretically ions - dp6+3SO <sub>3</sub> +1NAc, $\Delta$ UA-GlcNS-UA-GlcNAc-UA2S-GlcNS.
Supplementary Table 53	Theoretically ions - dp6+3SO <sub>3</sub> +1NAc, $\Delta$ UA-GlcNS-UA2S-GlcNS-UA-GlcNAc.
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Supplementary Table 56.	Theoretically ions - dp6+3SO <sub>3</sub> +1NAc, $\Delta$ UA2S-GlcNS-UA-GlcNS-UA-GlcNAc.
Supplementary Table 57.	Theoretically ions - dp6+3SO <sub>3</sub> +1NAc, $\Delta$ UA2S-GlcNS-UA-GlcNAc-UA-GlcNS.
Supplementary Table 58.	Summary overview of the B, Y, C and Z ions for dp6+3SO <sub>3</sub> +1NAc.
Supplementary Table 59.	CCS of B, Y, C and Z ions - $\Delta$ UA-GlcNS-I2S-GlcNS-G-GlcNAc.
Supplementary Table 60	CCS of B, Y, C and Z -SO <sub>3</sub> ions - $\Delta$ UA-GlcNS-I2S-GlcNS-G-GlcNAc
Supplementary Table 61.	Theoretically ions - dp6+5SO <sub>3</sub> +1NAc, $\Delta$ UA-GlcNS-UA-GlcNAc6S-UA2S-GlcNS6S.
Supplementary Table 62.	Theoretically ions - dp6+5SO <sub>3</sub> +1NAc, $\Delta$ UA-GlcNS-UA2S-GlcNS6S-UA-GlcNAc6S.
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Supplementary Table 67.	Summary overview of the B, Y, C and Z ions for dp6+5SO <sub>3</sub> +1NAc.
Supplementary Table 68.	CCS of B, Y, C and Z ions - ΔUA-GlcNS-I2S-GlcNS6S-UA-GlcNAc6S
Supplementary Table 69	CCS of B, Y, C and Z -SO <sub>3</sub> ions - $\Delta$ UA-GlcNS-I2S-GlcNS6S-UA-GlcNAc6S



Supplementary Fig. 1. Using the SIMMS<sup>2</sup> 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,

- 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<sub>3</sub> ions;  $B_2$ -SO<sub>3</sub> 122Å<sup>2</sup> and B<sub>3</sub>-
- 45  $SO_3 140 Å^2$  matched CCS values observed in the hexasaccharide (a-c). i-j, Tetrasaccharide #14
- displayed CCS values from Y ions;  $Y_1$ -SO<sub>3</sub> 109Å<sup>2</sup> and  $Y_3$ -SO<sub>3</sub> 150Å<sup>2</sup> matched the CCS values observed
- 47 in the hexasaccharide **d-f**.
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54 Supplementary Figure 2. SIMMS<sup>2</sup> sequencing of two hexasaccharides differing in a single 3*O*- and 55 6*O*-sulfation. HS structures #33 and #34 were fragmented in the trap and separated through IMMS to

56 create a defined set of CCS values for each fragment. B ion fragments from #33 and #34 showed a

difference at B<sub>4</sub> with the 6*O*-sulfated isomer (#33) showing a CCS value of 225 Å<sup>2</sup> and the B<sub>4</sub> fragment

for 3*O*-sulfation (#34) demonstrating a CCS value of 220Å<sup>2</sup> respectively. Fragment ions from B/Y/C/Z

59 are displayed in **Supplementary Tables 23 and 24.** 

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63 Supplementary Fig. 3. Purification of HS oligosaccharides with FGF1/2 bioactivity from porcine

64 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  $a^{1-4}$  and  $b^{1-3}$ . **b**,

- Radar charts illustrating BaF3 cell activation and inhibition of fractions  $a^{1-4}$  and  $b^{1-3}$ . Activation assays
- 67 were performed with FGF1 or FGF2 (1 ng/mL) and fractions as indicated. Heparin (3  $\mu$ g/mL) was used as
- positive control, while FGF1 or FGF2 alone was used as negative. Inhibition assays were performed with
- 69 the same fractions (3  $\mu$ g/mL) in the presence of a sub-maximal dose of heparin (0.1  $\mu$ g/mL). Cell
- proliferation results were expressed as a percentage of heparin activity set as 100%.





composition. a, Bioactive inhibitory hexasaccharides were purified further with CTA-SAX HPLC. b,

75 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-

78 GlcNAc,  $\Delta$ UA-GlcNS and  $\Delta$ UA2S-GlcNS, whereas structure #HS2 was composed of  $\Delta$ UA-GlcNS,

79  $\Delta$ UA-GlcNAc6S and  $\Delta$ UA2S-GlcNS6S. Standards are 1-  $\Delta$ UA-GlcNAc, 2 -  $\Delta$ UA-GlcNAc6S, 3 -  $\Delta$ UA-

 $\text{ GlcNS}, 4 - \Delta \text{UA-GlcNS6S}, 5 - \Delta \text{UA2S-GlcNS}, 6 - \Delta \text{UA2S-GlcNS6S}, 7 - \Delta \text{UA2S-GlcNAc}, 8 - \Delta \text{U$ 

81 GlcNAc6S.



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. 

No.	Chemdraw Structure	Structure <sup>1</sup>
#1	HOOC OH OH HO OH HO NHCOCH <sub>3</sub>	ΔUA-GlcNAc
#2	HOOC HOOT HOOT HOOT HOOT HOOT HOOT HOOT	ΔUA-GlcNAc6S
#3	HOOC HO OH HO NHSO <sub>3</sub> H	ΔUA-GlcNS
#4	$H_{OOC} OSO_{3H} OOH OOH OOH OOH OOH OOH OOH OOH OOH O$	ΔUA-GlcNS6S
#5	$H_{OOC} O O O O O O O O O O O O O O O O O O$	ΔUA2S-GlcNS
#6	HOOC O O O O O O O O O O O O O O O O O O	ΔUA2S-GlcNS6S
#7	HOOC HO OSO <sub>3</sub> H NHCOCH <sub>3</sub>	ΔUA2S-GlcNAc
#8	HOOC O O O O O O O O O O O O O O O O O O	ΔUA2S-GlcNAc6S
#9	$HOOC OSO_3H OO-(CH_2)_5NH_2 OO-(CH_2)_5NH_2 OO-(CH_2)_5NH_2 OO-(CH_2)_5NH_2 OO-(CH_3) OO-(CH_3$	G-GlcNAc6S-G-GlcNAc6S-R <sub>1</sub>

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

#10	HO T TO T	I-GlcNAc6S-I-GlcNAc6S-R <sub>1</sub>
#11	$HOOC OSO_3H OS$	G-GlcNAc6S-I-GlcNAc6S-R <sub>1</sub>
#12	$\begin{array}{c} HOOC \\ HO \\ HO \\ HO \\ HO \\ HO \\ HO \\ HO$	G-GlcNS6S-I-GlcNS6S-R <sub>1</sub>
#13	HO + O + O + O + O + O + O + O + O + O +	I-GlcNAc6S-G-GlcNAc6S-R1
#14	$HOOC OSO_3H OO-(CH_2)_8NH_2 OO-(CH_2) OO-(CH_2)_8NH_2 OO-(CH_2) $	I-GlcNS6S-G-GlcNS6S-R <sub>1</sub>
#15	$\begin{array}{c} HOOC \\ HO \\ HO \\ HO \\ HO \\ HO \\ HO \\ HO$	G-GlcNS6S-I2S-GlcNS6S-R <sub>1</sub>
#16	$\begin{array}{c} HOOC \\ HO \\ HO \\ HO \\ HO \\ HO \\ HO \\ HO$	G-GlcNS6S-I-GlcNS6S-G-GlcNS6S-R <sub>1</sub>
#17	$\begin{array}{c} HOOC \\ OSO_3H \\ HO \\ HO \\ HO \\ HO \\ HCCCH_3 \end{array} \xrightarrow{HOOC} OSO_3H \\ HO \\ HO \\ HCCCH_3 \\ HO \\ HCCCH_3 \\ HO \\ HO \\ HCCCH_3 \\ HO \\ HO \\ HCCCH_3 \\ HO \\ HO \\ HCCCH_3 \\ H$	GlcNAc6S-[G-GlcNAc6S]2-G-R2
#18	$HO \longrightarrow HO CCH_{3}COOH HO HO CCH_{3}COOH HO HO COCH_{3}COOH HO HO COCH_{3}COOH HO HO COCH_{3}COOH HO HO COCH_{3}COOH COCH_{$	GlcNAc6S-[I-GlcNAc6S] <sub>2</sub> -I-R <sub>2</sub>
#19	HO TO HO COL HO	GlcNAc6S-[I-GlcNAc6S] <sub>3</sub> -I-R <sub>2</sub>
#20	$\begin{array}{c} \begin{array}{c} \begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 $	GlcNAc6S-[G-GlcNAc6S] <sub>3</sub> -G-R <sub>2</sub>

#21	$\begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 $	GlcNAc6S-G-GlcNAc6S-G-GlcNAc6S-I-GlcNAc6S-I-R <sub>2</sub>
#22	$\begin{array}{c} \begin{array}{c} HOOC\\ OSO_3H\\ HO\\ HO\\ HO\\ HO\\ HO\\ HCOCH_3\end{array} \xrightarrow{OSO_3H} OSO_3H\\ OSO_3H\\ OSO_3H\\ HO\\ OSO_3H\\ O$	GlcNAc6S-G-GlcNAc6S-I-GlcNAc6S-I-GlcNAc6S-G-R <sub>2</sub>
#23	$\begin{array}{c} \begin{array}{c} 0 \\ 0 \\ H \\ H \\ H \\ H \\ 0 \\ H \\ 0 \\ H \\ 0 \\ 0$	GlcNAc6S-I-GlcNAc6S-G-GlcNAc6S-I-GlcNAc6S-G-R <sub>2</sub>
#24	$\begin{array}{c} 0 \\ 0 \\ H \\ H \\ H \\ H \\ 0 \\ H \\ 0 \\ H \\ 0 \\ 0$	GlcNAc6S-G-GlcNAc6S-I-GlcNAc6S-G-GlcNAc6S-I-R2
#25	HOOC OH HOOC O	G-GlcNS-G-GlcNS-I-GlcNS-G-GlcNS-G-R <sub>3</sub>
#26	HOOC OH HOOC OH OH OH OOC OH OH OH OOC OH OH OOC OH OH OOC OH	G-GlcNS-G-GlcNS-I2S-GlcNS-G-GlcNS-G-R <sub>3</sub>
#27	HO = OOH =	GlcNAc6S-[I-GlcNAc6S] <sub>4</sub> -I-R <sub>2</sub>
#28	$HO = OSO_{3}HOOC OSO_{3}HOOC OCH_{3}$ $HO = OH $	GlcNAc6S-[G-GlcNAc6S]4-G-R2
#29	$\begin{array}{c} HOOC & OSO_3H \\ HO & OSO_3H \\ HO & OSO_3H \\ HO_3SO \end{array} H \\ HO_3SO \end{array}$	ΔUA2S-GlcNS3S6S
#30	HOOC HO OH OH OH HO OH OH OH OH HO OH OH OH OH OH NHSO <sub>3</sub> HO COOH OSO <sub>3</sub> H NHSO <sub>3</sub> H	ΔUA-GlcNS-IdoA2S-GlcNS3S
#31	$\begin{array}{c} HOOC \\ HOOC \\ HO \\ HO \\ HO \\ HO \\ HO \\ $	ΔUA-GlcNS6S-GlcA-GlcNS3S6S

#32	$\begin{array}{c} HOOC \\ HOOC \\ HO \\ HO \\ HO \\ HO \\ HO \\ $	ΔUA-GlcNAc6S-GlcA-GlcNS3S6S
#33	$\begin{array}{c} HOOC \\ HO \\ HO \\ HO \\ HO \\ HO \\ HO \\ HO$	G-GlcNS6S-G-GlcNS6S-I2S-GlcNS6S-R <sub>1</sub>
#34	$\begin{array}{c} HOOC \\ HO \\ HO \\ HO \\ HO \\ HO \\ HO \\ HO$	G-GlcNS6S-G-GlcNS3S-I2S-GlcNS6S-R <sub>1</sub>
#35	$\begin{array}{c} HOOC \\ HO \\ HO \\ HO \\ HO \\ HO \\ HO \\ HO$	G-GlcNS6S-G-GlcNS3S6S-I2S-GlcNS6S-R <sub>1</sub>
#36	$\begin{array}{c} HOOC \\ HOOC \\ HO \\ OH \\ HO \\ OH \\ HO \\ HO$	$\Delta$ UA-GlcNS-I2S-GlcNS-G-GlcNS-G-R <sub>3</sub>

<sup>1</sup> The GlcA residues are represented by G and the IdoA residues represented by I. Tags  $R_1$  is (CH<sub>2</sub>)<sub>5</sub>NH<sub>2</sub>,  $R_2$  is C<sub>7</sub>H<sub>7</sub>O and  $R_3$  is C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>.

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

	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)	

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

97

98 <sup>1</sup> Columns represent different charge states.

			#9		#10		#11		#13	
			G-GlcNAc65	S-G-GlcNAc6S-	I-GlcNAc6S-I-GlcNAc6S-		G-GlcNAc6S-I-GlcNAc6S-		I-GlcNAc6S-G-GlcNAc6S-	
				R <sub>1</sub>	$R_1$		$\mathbf{R}_1$		$\mathbf{R}_1$	
[M-2H] <sup>2-</sup>			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] <sup>3-</sup>			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	Х	Х	Х	Х	Х	Х	Х	х
B2	458.06	228.53	120.9 (0.3)	Х	121.5 (0.5)	Х	121.5 (0.3)	Х	120.8 (0.1)	Х
B3	634.09	316.54	150.6 (0.1)	Х	150.7 (0.5)	Х	150.7 (0.5)	Х	150.5 (0.11)	Х
B4	917.13	458.06	Х	X	Х	Х	Х	Х	Х	Х
Y0	102.09	50.54	Х	x	х	Х	Х	Х	х	х
Y1	385.13	192.06	120.1 (0.5)	Х	119.7 (0.6)	Х	119.8 (0.2)	Х	120.2 (0.5)	х
Y2	561.16	280.08	Х	Х	145.27 (0.1)	161.5 (0.3)	145.9 (0.4)	161.9 (0.2)	Х	х
Y3	844.20	421.59	Х	188.9 (0.2)	х	187.5 (0.5)	Х	186.2 (0.7)	х	188.6 (0.3)
C1	193.03	96.01	X	X	Х	X	X	Х	X	Х
C2	476.07	237.53	122.5 (0.2)	X	122.3 (0.2)	Х	122.6 (0.3)	Х	122.2 (0.2)	Х
C3	652.10	325.55	х	Х	Х	х	х	Х	х	х
C4	935.14	467.07	Х	x	Х	Х	Х	Х	х	Х
Z0	84.08	41.54	X	X	Х	Х	X	Х	X	X
Z1	367.12	183.05	116.7 (0.2)	х	117.4 (0.3)	Х	117.3 (0.2)	Х	116.9 (0.3)	х
Z2	543.15	271.07	x	х	X	х	x	Х	x	х
Z3	826.19	412.59	х	х	Х	Х	х	Х	Х	Х

100 **Supplementary Table 3.** CCS of B, Y, C and Z ions identified in isomeric tetrasaccharide UA-GlcNAc6S-UA-GlcNAc6S- $R_{+}$  structures, where  $R_{1}$  is 101 (CH<sub>2</sub>)<sub>5</sub>NH<sub>2</sub>.

102 <sup>1</sup> Columns represent different charge states.

				#12			#14		
				G-GlcNS6S-	G-GlcNS6S-I-GlcNS6S-R <sub>1</sub>			G-GlcNS6S-R1	
[M-2H] <sup>2-</sup>				547.55	$200.1 (0.9)^2$		547.55	201.5 (0.8)	
[M-3H] <sup>3-</sup>				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)	Х	х	69.0 (0.4)	х	Х
B2	496.01	247.50	164.66	х	134.5 (0.6)	х	х	133.8 (0.3)	х
B3	672.04	335.52	223.34	х	160.2 (0.2)	х	х	165.5 (0.2)	х
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)	х	х	112.1 (0.1)	X	Х
Y2	599.11	299.05	199.03	X	162.2 (0.5)	х	х	156.5 (0.5)	х
Y3	920.09	459.54	306.02	Х	x	Х	Х	Х	212.6 (0.6)
C1	193.03	96.01	63.67	X	X	X	X	X	X
C2	514.02	256.50	170.67	х	х	х	х	х	х
C3	690.05	344.52	229.34	х	Х	х	х	165.6 (0.1)	Х
C4	1011.03	505.01	336.34	x	x	x	x	x	Х
70	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
72	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

Supplementary Table 4. CCS of B, Y, C and Z ions identified in isomeric tetra-saccharide UA-GlcNS6S-UA-GlcNS6S-R<sub>1</sub> structures, where R<sub>1</sub> is
 (CH<sub>2</sub>)<sub>5</sub>NH<sub>2</sub>.

<sup>1</sup>Columns represent different charge states.

#15						
G	-GlcNS6S-I	2S-GlcNS6S-R	1			
[M-2H] <sup>2-</sup>	587.53	$203.9 (0.5)^2$				
[M-3H] <sup>3-</sup>	391.35	238.8 (0.5)				
	$(1-)^1$	(2-)	(3-)	(1-)	(2-)	(3-)
B1	175.02	87.01	57.67	Х	Х	Х
B2	496.01	247.50	164.66	Х	135.2 (0.5)	Х
B3	752.00	375.49	249.99	Х	Х	Х
B4	1072.98	535.99	356.99	Х	Х	229.0 (0.4)
YO	102.09	50.54	33.36	X	X	Х
Y1	423.07	211.03	140.35	112.8 (0.3)	Х	Х
Y2	679.06	339.03	225.68	X	Х	х
Y3	1000.05	499.52	332.68	Х	Х	Х
C1	193.03	96.01	63.67	X	X	X
C2	514.02	256.50	170.67	х	Х	х
C3	770.01	384.50	256.00	Х	Х	х
C4	1090.99	544.99	362.99	Х	Х	х
70	8/1 08	41.54	27.36	x	x	x
Z0	405.06	202.03	134 35	X	X	x
72	661.05	330.02	219.68	x	x	x
Z3	982.03	490.51	326.67	X	X	X

108 **Supplementary Table 5.** CCS of B, Y, C and Z ions identified in a tetra-saccharide structure ( $R_1$  is 109 ( $CH_2$ )<sub>5</sub>NH<sub>2</sub>).

<sup>1</sup>Columns represent different charge states.

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<sup>&</sup>lt;sup>2</sup> Each CCS is an average of independent measurements with the corresponding standard deviation

#16								
G-G	lcNS6S-I-Glc	NS6S-G-GlcNS	6S-R <sub>1</sub>					
[M-2H] <sup>2-</sup>	796.06	$255.6 (0.9)^2$						
[M-3H] <sup>3-</sup>	530.37	258.8 (0.8)						
	$(1-)^1$	(2-)	(3-)	(4-)	(1-)	(2-)	(3-)	(4-)
B1	175.02	87.01	57.67	43.00	Х	Х	Х	Х
B2	496.01	247.50	164.66	123.25	Х	134.6 (0.4)	Х	Х
B3	672.04	335.52	223.34	167.25	Х	160.3 (0.2)	Х	Х
B4	993.02	496.01	330.34	247.50	Х	х	226.1 (0.2)	Х
B5	1169.05	584.02	389.01	291.51	Х	Х	249.4 (0.8)	275.9 (0.7)
B6	1490.04	744.51	496.01	371.75	Х	Х	Х	Х
Y0	102.09	50.54	33.36	24.77	X	Х	Х	Х
Y1	423.07	211.03	140.35	105.01	Х	130.0 (0.7)	X	х
Y2	599.11	299.05	199.03	149.02	Х	156.4 (0.5)	х	х
Y3	920.09	459.54	306.02	229.27	Х	Х	213.1 (0.7)	Х
Y4	1096.12	547.56	364.70	273.27	Х	Х	233.2 (0.6)	Х
Y5	1417.10	708.05	471.70	353.52	Х	Х	X	324.5 (0.2)
C1	193.03	96.01	63.67	47.50	Х	X	X	Х
C2	514.02	256.50	170.67	127.75	Х	X	X	х
C3	690.05	344.52	229.34	171.76	Х	х	х	х
C4	1011.03	505.01	336.34	252.00	Х	Х	Х	Х
C5	1187.06	593.03	395.02	296.01	Х	Х	Х	Х
C6	1508.05	753.52	502.01	376.26	Х	X	X	Х
Z0	84.08	41.54	27.36	20.26	Х	X	X	Х
Z1	405.06	202.03	134.35	100.51	Х	X	X	х
Z2	581.10	290.04	193.03	144.52	Х	х	X	х
Z3	902.08	450.54	300.02	224.76	X	X	X	X

**Supplementary Table 6.** CCS of B, Y, C and Z ions identified in a hexa-saccharide structure (R<sub>1</sub> is (CH<sub>2</sub>)<sub>5</sub>NH<sub>2</sub>).

Z4	1078.11	538.55	358.70	268.77	Х	Х	Х	х
Z5	1399.09	699.04	465.69	349.02	Х	Х	Х	Х

<sup>1</sup>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]<sub>2</sub>-G-R<sub>2</sub> structure, where  $R^2$  is  $C_7H_7O$ . 

#17						
GlcNAc6S-	[G-GlcNA	$c6S]_2-G-R_2$				
[M-3H] <sup>3-</sup>	499.41	$296.5 (0.4)^2$				
[M-4H] <sup>4-</sup>	374.3	347.4 (0.2)				
	$(1-)^1$	(2-)	(3-)	(1-)	(2-)	(3-)
B1	282.03	140.51	93.34	93.0 (0.2)	Х	Х
B2	458.06	228.53	152.01	120.8 (0.2)	135.1 (0.5)	Х
B3	741.1	370.04	246.36	Х	169.7 (0.6)	Х
B4	917.13	458.06	305.04	Х	Х	225.6 (0.8)
B5	1200.16	599.58	399.38	Х	Х	270.4 (0.2)
B6	1376.2	687.59	458.06	Х	Х	291.3 (0.7)
Y0	122.04	60.51	40.01	Х	X	X
Y1	299.08	149.03	99.02	105.4 (0.7)	Х	Х
Y2	582.11	290.55	193.37	154.4 (0.4)	166.0 (0.4)	Х
Y3	758.14	378.57	252.04	Х	х	х
Y4	1041.18	520.09	346.39	Х	Х	255.8 (0.5)
Y5	1217.21	608.1	405.07	Х	Х	Х
C1	300.04	149.52	99.34	94.4 (0.2)	Х	Х
C2	476.07	237.53	158.02	122.3 (0.4)	Х	Х
C3	759.11	379.05	252.36	Х	Х	200.1 (0.9)
C4	935.14	467.07	311.04	Х	185.2 (0.6)	Х
C5	1218.18	608.58	405.39	Х	Х	273.9 (0.1)
C6	1394.21	696.6	464.06	Х	Х	Х
Z0	105.03	52.01	34.34	Х	Х	Х
Z1	281.07	140.03	93.02	х	х	Х
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

<sup>1</sup> Columns represent different charge states. 

<sup>2</sup> 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]<sub>2</sub>-I-R<sub>2</sub> structure, where  $R_2$  is  $C_7H_7O$ . 

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

<sup>1</sup> Columns represent different charge states. 

<sup>2</sup> Each CCS is an average of independent measurements with the corresponding standard deviation 

#19								
G	lcNAc6S-[I-Gl	cNAc6S] <sub>3</sub> -I-R <sub>2</sub>						
[M-4H] <sup>4-</sup>	489.07	379.8 (0.7)	<sup>2</sup> /416.0 (0.2)					
[M-5H] <sup>5-</sup>	391.05	433.8 (0.5)						
[M-6H] <sup>6-</sup>	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)	Х	Х	Х
B2	458.06	228.53	152.01	113.76	122.0 (0.6)	Х	х	х
B3	741.10	370.04	246.36	184.52	X	176.3 (0.8)	х	Х
B4	917.13	458.06	305.04	228.53	X	197.2 (0.7)	Х	Х
B5	1200.16	599.58	399.38	299.29	X	Х	270.0 (0.3)	Х
B6	1376.20	687.59	458.06	343.29	х	Х	294.4 (0.7)	Х
B7	1659.23	829.11	552.41	414.05	х	Х	Х	Х
B8	1835.27	917.13	611.08	458.06	X	Х	Х	394.0 (0.6)
Y0	122.04	60.51	40.01	29.75	X	Х	Х	Х
Y1	299.08	149.03	99.02	74.01	X	х	Х	х
Y2	582.11	290.55	193.37	144.77	X	166.0 (0.6)	х	х
Y3	758.14	378.57	252.04	188.78	X	Х	Х	х
Y4	1041.18	520.09	346.39	259.54	X	Х	Х	Х
Y5	1217.21	608.10	405.07	303.55	X	229.2 (0.2)	Х	Х
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	Х	Х	Х	Х
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)	х	х	х
C3	759.11	379.05	252.36	189.02	x	х	х	х
C4	935.14	467.07	311.04	233.03	X	Х	Х	Х

Supplementary Table 9. CCS of B, Y, C and Z ions identified in an octa-saccharide GlcNAc6S-[I-GlcNAc6S]<sub>3</sub>-I-R<sub>2</sub> structure, where R<sub>2</sub> is C<sub>7</sub>H<sub>7</sub>O.

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

<sup>1</sup>Columns represent different charge states.

141 <sup>2</sup> Each CCS is an average of independent measurements with the corresponding standard deviation

#20								
GlcNAc6S-[G-C	GlcNAc6S]3-G-F	R <sub>2</sub>						
[M-4H] <sup>4-</sup>	489.07	$391.4(0.8)^2$						
[M-5H] <sup>5-</sup>	391.05	442.9 (0.2)						
[M-6H] <sup>6-</sup>	325.7	456.7 (0.8)						
	$(1-)^1$	(2-)	(3-)	(4-)	(1-) <sup>1</sup>	(2-)	(3-)	(4-)
B1	282.03	140.51	93.34	69.75	93.4 (0.1)	х	Х	Х
B2	458.06	228.53	152.01	113.76	121.6 (0.5)	Х	Х	x
B3	741.10	370.04	246.36	184.52	Х	169.9 (0.4)		x
B4	917.13	458.06	305.04	228.53	Х	194.1 (0.3)	225.8 (0.8)	x
B5	1200.16	599.58	399.38	299.29	Х	Х	270.5 (0.2)	x
B6	1376.20	687.59	458.06	343.29	Х	х	Х	x
B7	1659.23	829.11	552.41	414.05	Х	Х	291.0 (0.1)	322.1 (0.2)
B8	1835.27	917.13	611.08	458.06	х	Х	Х	391.8 (0.1)
Y0	122.04	60.51	40.01	29.75	x	x	x	x
Y0 Y1	122.04 299.08	60.51 149.03	40.01	29.75 74.01	X	X	X	x
Y0 Y1 Y2	122.04 299.08 582.11	60.51 149.03 290.55	40.01 99.02 193.37	29.75 74.01 144.77	x x 154.3 (0.5)	x x 165.8 (0.7)	X X X	X X X X
Y0 Y1 Y2 Y3	122.04 299.08 582.11 758.14	60.51 149.03 290.55 378.57	40.01 99.02 193.37 252.04	29.75 74.01 144.77 188.78	x x 154.3 (0.5) x	x x 165.8 (0.7) x	X X X X	x x x x x
Y0 Y1 Y2 Y3 Y4	122.04 299.08 582.11 758.14 1041.18	60.51 149.03 290.55 378.57 520.09	40.01 99.02 193.37 252.04 346.39	29.75 74.01 144.77 188.78 259.54	x x 154.3 (0.5) x x	x x 165.8 (0.7) x x	x x x x 255.1 (0.8)	x x x x x x x
Y0 Y1 Y2 Y3 Y4 Y5	122.04 299.08 582.11 758.14 1041.18 1217.21	60.51 149.03 290.55 378.57 520.09 608.10	40.01 99.02 193.37 252.04 346.39 405.07	29.75 74.01 144.77 188.78 259.54 303.55	x x 154.3 (0.5) x x x x	x x 165.8 (0.7) x x x x	x x x x 255.1 (0.8) x	X X X X X X X
Y0 Y1 Y2 Y3 Y4 Y5 Y6	122.04 299.08 582.11 758.14 1041.18 1217.21 1500.25	60.51 149.03 290.55 378.57 520.09 608.10 749.62	40.01 99.02 193.37 252.04 346.39 405.07 499.41	29.75 74.01 144.77 188.78 259.54 303.55 374.31	x x 154.3 (0.5) x x x x x x	x x 165.8 (0.7) x x x x x x	x x x x 255.1 (0.8) x x x	x x x x x x x x x x x x
Y0 Y1 Y2 Y3 Y4 Y5 Y6 Y7	122.04 299.08 582.11 758.14 1041.18 1217.21 1500.25 1676.28	60.51 149.03 290.55 378.57 520.09 608.10 749.62 837.64	40.01 99.02 193.37 252.04 346.39 405.07 499.41 558.09	29.75 74.01 144.77 188.78 259.54 303.55 374.31 418.31	x x 154.3 (0.5) x x x x x x x x x	x x 165.8 (0.7) x x x x x x x x x	x x x x 255.1 (0.8) x x x x x	X X X X X X X X X X X
Y0 Y1 Y2 Y3 Y4 Y5 Y6 Y7 C1	122.04 299.08 582.11 758.14 1041.18 1217.21 1500.25 1676.28 300.04	60.51 149.03 290.55 378.57 520.09 608.10 749.62 837.64	40.01 99.02 193.37 252.04 346.39 405.07 499.41 558.09	29.75 74.01 144.77 188.78 259.54 303.55 374.31 418.31 74.25	x x 154.3 (0.5) x x x x x x y 4.6 (0.4)	x x 165.8 (0.7) x x x x x x x	x x x x 255.1 (0.8) x x x x x	X X X X X X X X X X
Y0 Y1 Y2 Y3 Y4 Y5 Y6 Y7 C1 C1 C2	122.04 299.08 582.11 758.14 1041.18 1217.21 1500.25 1676.28 300.04 476.07	60.51 149.03 290.55 378.57 520.09 608.10 749.62 837.64 149.52 237.53	40.01 99.02 193.37 252.04 346.39 405.07 499.41 558.09 99.34 158.02	29.75 74.01 144.77 188.78 259.54 303.55 374.31 418.31 74.25 118.26	x x 154.3 (0.5) x x x x x 94.6 (0.4) 122.2 (0.4)	x x 165.8 (0.7) x x x x x x x x x x	x x x x 255.1 (0.8) x x x x x x x	X X X X X X X X X X X
Y0 Y1 Y2 Y3 Y4 Y5 Y6 Y7 C1 C2 C2 C3	122.04 299.08 582.11 758.14 1041.18 1217.21 1500.25 1676.28 300.04 476.07 759.11	60.51           149.03           290.55           378.57           520.09           608.10           749.62           837.64           149.52           237.53           379.05	40.01 99.02 193.37 252.04 346.39 405.07 499.41 558.09 99.34 158.02 252.36	29.75 74.01 144.77 188.78 259.54 303.55 374.31 418.31 74.25 118.26 189.02	x x 154.3 (0.5) x x x x y 94.6 (0.4) 122.2 (0.4) x	x x 165.8 (0.7) x x x x x x x x x x 167 5 (0 1)	x x x x 255.1 (0.8) x x x x x x x x x	x x x x x x x x x x x x x x x x x x x
Y0 Y1 Y2 Y3 Y4 Y5 Y6 Y7 C1 C2 C2 C3 C4	122.04 299.08 582.11 758.14 1041.18 1217.21 1500.25 1676.28 300.04 476.07 759.11 935.14	60.51           149.03           290.55           378.57           520.09           608.10           749.62           837.64           149.52           237.53           379.05	40.01 99.02 193.37 252.04 346.39 405.07 499.41 558.09 99.34 158.02 252.36 311.04	29.75 74.01 144.77 188.78 259.54 303.55 374.31 418.31 74.25 118.26 189.02 233.03	x x 154.3 (0.5) x x x x x y 94.6 (0.4) 122.2 (0.4) x x	x x 165.8 (0.7) x x x x x x x 167.5 (0.1) x	x x x x 255.1 (0.8) x x x x x x x x x x x x x x x x x x x	X X X X X X X X X X X X X X X X X X X
Y0 Y1 Y2 Y3 Y4 Y5 Y6 Y7 C1 C2 C2 C3 C4	122.04 299.08 582.11 758.14 1041.18 1217.21 1500.25 1676.28 300.04 476.07 759.11 935.14	60.51           149.03           290.55           378.57           520.09           608.10           749.62           837.64           149.52           237.53           379.05           467.07	40.01 99.02 193.37 252.04 346.39 405.07 499.41 558.09 99.34 158.02 252.36 311.04	29.75 74.01 144.77 188.78 259.54 303.55 374.31 418.31 74.25 118.26 189.02 233.03	x x 154.3 (0.5) x x x x x y 4.6 (0.4) 122.2 (0.4) x x	x x 165.8 (0.7) x x x x x x x 167.5 (0.1) x	x x x x 255.1 (0.8) x x x x x x x x x x x x x x x x x	X X X X X X X X X X X X X X X X X X X

**Supplementary Table 10.** CCS of B, Y, C and Z ions identified in an octa-saccharide GlcNAc6S-[G-GlcNAc6S]<sub>3</sub>-G-R<sub>2</sub> structure, where R<sub>2</sub> is C<sub>7</sub>H<sub>7</sub>O.

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

146 <sup>1</sup> Columns represent different charge states.

<sup>2</sup> Each CCS is an average of independent measurements with the corresponding standard deviation

#21								
GlcN	Ac6S-G-GlcNac6	5S-G-GlcNAc6S	-I-GlcNAc6S-I-	<b>R</b> <sub>2</sub>				
[M-4H] <sup>4-</sup>	489.07	$379.2 (0.8)^2$						
[M-5H] <sup>5-</sup>	391.05	438.5 (0.5)						
[M-6H] <sup>6-</sup>	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)	Х	Х	Х
B2	458.06	228.53	152.01	113.76	121.4 (0.2)	Х	Х	Х
B3	741.10	370.04	246.36	184.52	x	X	Х	x
B4	917.13	458.06	305.04	228.53	х	Х	224.8 (0.4)	х
B5	1200.16	599.58	399.38	299.29	х	Х	270.1 (0.4)	Х
B6	1376.20	687.59	458.06	343.29	х	Х	Х	322.3 (0.2)
B7	1659.23	829.11	552.41	414.05	X	Х	Х	367.3 (0.4)
B8	1835.27	917.13	611.08	458.06	x	Х	х	x
Y0	122.04	60.51	40.01	29.75	X	Х	x	X
Y1	299.08	149.03	99.02	74.01	103.4 (0.5)	Х	Х	х
Y2	582.11	290.55	193.37	144.77	153.8 (0.5)	Х	х	х
Y3	758.14	378.57	252.04	188.78	Х	Х	Х	Х
Y4	1041.18	520.09	346.39	259.54	Х	Х	255.4 (0.6)	Х
Y5	1217.21	608.10	405.07	303.55	Х	Х	Х	Х
Y6	1500.25	749.62	499.41	374.31	X	Х	284.7 (0.6)	346.4 (0.7)
Y7	1676.28	837.64	558.09	418.31	x	X	Х	x
C1	300.04	1/10.52	00 3/	74.25	94 4 (0 3)	v	v	v
C1 C2	476.07	237 53	158.02	118.26	122 4 (0.8)	<u>л</u> х	x	x
C2	759.11	379.05	252.36	189.02	т22.ч (0.0) х	x	x	x
C4	935.14	467.07	311.04	233.03	x	x	x	x

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<sub>2</sub> structure,
 where R<sub>2</sub> is C<sub>7</sub>H<sub>7</sub>O.

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

153 <sup>1</sup> Columns represent different charge states.

 $^{2}$  Each CCS is an average of independent measurements with the corresponding standard deviation

#22								
GlcN	Ac6S-G-GlcNa	c6S-I-GlcNAce	6S-I-GlcNAc6S	-G-R <sub>2</sub>				
[M-4H] <sup>4-</sup>	489.07	$396.5 (0.7)^2$						
[M-5H] <sup>5-</sup>	391.05	440.8 (0.5)						
[M-6H] <sup>6-</sup>	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)	Х	Х	Х
B2	458.06	228.53	152.01	113.76	121.6 (0.3)	Х	Х	Х
B3	741.10	370.04	246.36	184.52	Х	Х	Х	Х
B4	917.13	458.06	305.04	228.53	х	Х	х	х
B5	1200.16	599.58	399.38	299.29	Х	Х	272.8 (0.6)	Х
B6	1376.20	687.59	458.06	343.29	Х	Х	х	323.2 (0.2)
B7	1659.23	829.11	552.41	414.05	Х	Х	Х	Х
B8	1835.27	917.13	611.08	458.06	Х	Х	Х	Х
Y0	122.04	60.51	40.01	29.75	Х	Х	x	Х
Y1	299.08	149.03	99.02	74.01	Х	Х	Х	Х
Y2	582.11	290.55	193.37	144.77	154.9 (0.3)	Х	Х	Х
Y3	758.14	378.57	252.04	188.78	Х	Х	Х	Х
Y4	1041.18	520.09	346.39	259.54	Х	Х	254.1 (0.28)	Х
Y5	1217.21	608.10	405.07	303.55	Х	Х	Х	300.6 (0.2)
Y6	1500.25	749.62	499.41	374.31	Х	Х	289.1 (0.6)	Х
Y7	1676.28	837.64	558.09	418.31	Х	Х	X	Х
C1	300.04	149.52	99.34	74.25	94.1 (0.3)	Х	X	Х
C2	476.07	237.53	158.02	118.26	123.0 (0.4)	Х	Х	Х
C3	759.11	379.05	252.36	189.02	X	Х	X	X
C4	935.14	467.07	311.04	233.03	X	Х	X	Х

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<sub>2</sub> structure,
 where R<sub>2</sub> is C<sub>7</sub>H<sub>7</sub>O.

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

160 <sup>1</sup> Columns represent different charge states.

<sup>2</sup> Each CCS is an average of independent measurements with the corresponding standard deviation

#23								
GlcNAc6S-I-	GlcNAc6S-G-G	lcNAc6S-I-Glo	NAc6S-G-R <sub>2</sub>					
$[M-4H]^{4-}$	489.07	$400.8 (0.3)^2$						
[M-5H] <sup>5-</sup>	391.05	435.6 (0.4)						
[M-6H] <sup>6-</sup>	325.7	453.4 (0.7)						
	(1-) <sup>1</sup>	(2-)	(3-)	(4-)	(1-)	(2-)	(3-)	(4-)
B1	282.03	140.51	93.34	69.75	93.3 (0.6)	Х	Х	X
B2	458.06	228.53	152.01	113.76	х	х	Х	х
B3	741.10	370.04	246.36	184.52	х	х	х	х
B4	917.13	458.06	305.04	228.53	Х	Х	Х	х
B5	1200.16	599.58	399.38	299.29	х	х	272.0 (0.1)	х
B6	1376.20	687.59	458.06	343.29	х	х	х	х
B7	1659.23	829.11	552.41	414.05	x	х	х	х
B8	1835.27	917.13	611.08	458.06	Х	Х	х	Х
Y0	122.04	60.51	40.01	29.75	X	Х	x	X
Y1	299.08	149.03	99.02	74.01	X	х	х	x
Y2	582.11	290.55	193.37	144.77	155.0 (0.2)	х	х	X
Y3	758.14	378.57	252.04	188.78	х	Х	Х	Х
Y4	1041.18	520.09	346.39	259.54	X	X	X	X
Y5	1217.21	608.10	405.07	303.55	x	х	Х	х
Y6	1500.25	749.62	499.41	374.31	х	х	х	339.5 (0.3)
Y7	1676.28	837.64	558.09	418.31	Х	Х	Х	366.4 (0.3)
C1	300.04	149.52	99.34	74.25	93.2 (0.1)	Х	Х	X
C2	476.07	237.53	158.02	118.26	122.0 (0.2)	132.8 (0.4)	Х	X
C3	759.11	379.05	252.36	189.02	X	х	х	X
C4	935.14	467.07	311.04	233.03	x	Х	x	Х

**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<sub>2</sub> structure, 168 where  $R_2$  is  $C_7H_7O$ .

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

170 <sup>1</sup> Columns represent different charge states.

 $^{2}$  Each CCS is an average of independent measurements with the corresponding standard deviation

#24								
Glc	NAc6S-G-GlcN	ac6S-I-GlcNAc6S	S-G-GlcNAc6S-I-	$\mathbf{R}_2$				
[M-4H] <sup>4-</sup>	489.07	$378.3 (0.5)^2$						
[M-5H] <sup>5-</sup>	391.05	439.7 (0.4)						
[M-6H] <sup>6-</sup>	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	х	х
B2	458.06	228.53	152.01	113.76	121.4 (0.6)	Х	Х	Х
B3	741.10	370.04	246.36	184.52	X	170.5 (0.6)	Х	Х
B4	917.13	458.06	305.04	228.53	х	х	х	х
B5	1200.16	599.58	399.38	299.29	Х	Х	270.9 (0.8)	Х
B6	1376.20	687.59	458.06	343.29	Х	Х	Х	Х
B7	1659.23	829.11	552.41	414.05	Х	х	Х	366.2 (0.5)
B8	1835.27	917.13	611.08	458.06	х	x	х	X
Y0	122.04	60.51	40.01	29.75	Х	Х	Х	Х
Y1	299.08	149.03	99.02	74.01	103.1 (0.4)	X	Х	х
Y2	582.11	290.55	193.37	144.77	153.4 (0.3)	Х	х	х
Y3	758.14	378.57	252.04	188.78	Х	Х	Х	Х
Y4	1041.18	520.09	346.39	259.54	Х	Х	Х	Х
Y5	1217.21	608.10	405.07	303.55	Х	226.0 (0.5)	289.6 (0.6)	Х
Y6	1500.25	749.62	499.41	374.31	Х	288.4 (0.4)	Х	Х
Y7	1676.28	837.64	558.09	418.31	Х	x	х	Х
C1	300.04	149.52	00.34	74.25	94.1 (0.2)	v	v	v
	476.07	237 53	158.02	118.26	122.2 (0.2)	x	x	x
$C_2$	750.11	237.33	252.26	110.20	122.2 (0.2) v	A v	A v	A v
	025.14	319.03	232.30	107.02	A v	A v	A v	A v
C4	933.14	407.07	311.04	233.03	Х	Х	Х	Х

**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<sub>2</sub> structure, 177 where  $R_2$  is  $C_7H_7O$ .

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

179 <sup>1</sup> Columns represent different charge states.

 $^{2}$  Each CCS is an average of independent measurements with the corresponding standard deviation

#25								
G-	GlcNS-G-G	lcNS-I-GlcNS-C	G-GlcNS-G-	·R <sub>3</sub>				
[M-4H] <sup>4-</sup>	494.81	$437.4 (0.3)^2$						
[M-5H] <sup>5-</sup>	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)	Х	Х	Х
B2	416.05	207.52	138.01	103.26	112.4 (0.4)	Х	Х	Х
B3	592.08	295.54	196.69	147.26	Х	157.8 (0.4)	Х	Х
B4	833.11	416.05	277.03	207.52	Х	197.4 (0.4)	Х	Х
B5	1009.14	504.07	335.71	251.53	Х	235.2 (0.5)	X	X
B6	1250.17	624.58	416.05	311.79	Х	Х	Х	Х
B7	1426.20	712.59	474.73	355.79	Х	Х	321.4 (0.4)	X
B8	1667.22	833.11	555.07	416.05	Х	Х	Х	Х
B9	1843.25	921.12	613.75	460.06	Х	Х	X	407.6 (0.5)
Y0	138.02	68.51	45.33	33.75	Х	X	X	X
Y1	314.05	156.52	104.01	77.76	Х	Х	Х	Х
Y2	555.08	277.03	184.35	138.01	Х	Х	Х	Х
Y3	731.11	365.05	243.03	182.02	х	Х	Х	Х
Y4	972.13	485.56	323.37	242.28	Х	Х	Х	Х
Y5	1148.17	573.58	382.05	286.29	Х	Х	Х	Х
Y6	1389.19	694.09	462.39	346.54	х	Х	Х	Х
Y7	1565.22	782.11	521.07	390.55	Х	Х	Х	Х
Y8	1806.25	902.62	601.41	450.81	Х	Х	Х	Х
C1	192.03	95.51	63.34	47.25	х	x	х	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	Х	X	Х	X

182 Supplementary Table 15. CCS of B, Y, C and Z ions identified in a 9mer, G-GlcNS-G-GlcNS-G-GlcNS-G-GlcNS-G-R<sub>3</sub> structure, where R<sub>3</sub> is C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>.

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

<sup>1</sup>Columns represent different charge states.

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

**Supplementary Table 16.** CCS of B, Y, C and Z ions identified in a dp9 + 1x2O-sulfate, G-GlcNS-G-GlcNS-G-GlcNS-G-GlcNS-G-R<sub>3</sub> structure, where R<sub>3</sub> is C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>.

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

188 <sup>1</sup> Columns represent different charge states.

 $^{2}$  Each CCS is an average of independent measurements with the corresponding standard deviation
#27								
	(	GlcNAc6S-[I-Gle	cNAc6S] <sub>4</sub> -I-R <sub>2</sub>					
[M-5H] <sup>5-</sup>	482.87	$499.8 (0.4)^2$						
[M-6H] <sup>6-</sup>	402.22	536.4 (0.7)						
	(1-) <sup>1</sup>	(2-)	(3-)	(4-)	(1-)	(2-)	(3-)	(4-)
B1	282.03	140.51	93.34	69.75	92.9 (0.5)	Х	Х	Х
B2	458.06	228.53	152.01	113.76	121.8 (0.6)	Х	Х	Х
B3	741.10	370.04	246.36	184.52	х	176.0 (0.7)	Х	х
B4	917.13	458.06	305.04	228.53	х	197.2 (0.5)	Х	х
B5	1200.16	599.58	399.38	299.29	х	Х	269.1 (0.3)	х
B6	1376.20	687.59	458.06	343.29	х	х	294.6 (0.2)	х
B7	1659.23	829.11	552.41	414.05	x	Х	Х	х
B8	1835.27	917.13	611.08	458.06	x	Х	Х	394.0 (0.6)
B9	2118.30	1058.65	705.43	528.82	x	x	Х	X
B10	2294.33	1146.66	764.11	572.83	х	Х	Х	Х
Y0	123.04	61.02	40.34	30.01	69.3 (0.1)	X	Х	X
Y1	299.08	149.03	99.02	74.01	X	Х	Х	Х
Y2	582.11	290.55	193.37	144.77	х	166.3 (0.8)	Х	Х
Y3	758.14	378.57	252.04	188.78	х	Х	Х	Х
Y4	1041.18	520.09	346.39	259.54	х	Х	Х	Х
Y5	1217.21	608.10	405.07	303.55	X	Х	Х	Х
Y6	1500.25	749.62	499.41	374.31	X	Х	Х	Х
Y7	1676.28	837.64	558.09	418.31	x	Х	368.5 (0.9)	Х
Y8	1959.32	979.15	652.43	489.07	x	X	Х	Х
Y9	2135.35	1067.17	711.11	533.08	x	X	Х	Х
C1	300.04	149.52	99.34	74.25	X	X	Х	X
C2	476.07	237.53	158.02	118.26	X	X	Х	Х

**Supplementary Table 17**. CCS of B, Y, C and Z ions identified in a dp10 GlcNAc6S-[I-GlcNAc6S]<sub>4</sub>-I-R<sub>2</sub> structure, where R<sub>2</sub> is C<sub>7</sub>H<sub>7</sub>O.

C3	759.11	379.05	252.36	189.02	х	х	Х	х
C4	935.14	467.07	311.04	233.03	х	Х	Х	Х
C5	1218.18	608.58	405.39	303.79	х	Х	Х	Х
C6	1394.21	696.60	464.06	347.80	х	Х	Х	х
C7	1677.24	838.12	558.41	418.56	х	х	х	х
C8	1853.28	926.13	617.09	462.56	х	Х	Х	х
C9	2136.31	1067.65	711.43	533.32	х	х	х	х
C10	2312.34	1155.67	770.11	577.33	Х	Х	Х	Х
70	105.02	52.01	24.24	25.50	v	v	v	v
20	105.05	32.01	34.34	23.30	Λ	Λ	Λ	Λ
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	х	x
Z4	1023.17	511.08	340.38	255.04	х	х	х	х
Z5	1199.20	599.10	399.06	299.04	х	Х	х	х
Z6	1482.24	740.62	493.41	369.80	х	Х	Х	Х
Z7	1658.27	828.63	552.09	413.81	X	X	X	X
Z8	1941.31	970.15	646.43	484.57	X	Х	Х	х
Z9	2117.34	1058.17	705.11	528.58	X	Х	Х	х

<sup>1</sup> Columns represent different charge states.

 $^{2}$  Each CCS is an average of independent measurements with the corresponding standard deviation

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

**Supplementary Table 18**. CCS of B, Y, C and Z ions identified in a dp10 GlcNAc6S-[G-GlcNAc6S]<sub>4</sub>-G-R<sub>2</sub> structure, where R<sub>2</sub> is C<sub>7</sub>H<sub>7</sub>O.

C3	759.11	379.05	252.36	189.02	Х	Х	х	Х
C4	935.14	467.07	311.04	233.03	Х	Х	Х	Х
C5	1218.18	608.58	405.39	303.79	Х	Х	х	Х
C6	1394.21	696.60	464.06	347.80	Х	Х	х	Х
C7	1677.24	838.12	558.41	418.56	Х	Х	x	Х
C8	1853.28	926.13	617.09	462.56	Х	Х	х	Х
C9	2136.31	1067.65	711.43	533.32	Х	Х	х	Х
C10	2312.34	1155.67	770.11	577.33	Х	Х	x	Х
ZO	105.03	52.01	34.34	25.50	Х	Х	Х	X
Z1	281.07	140.03	93.02	69.51	Х	Х	х	Х
Z2	564.10	281.55	187.36	140.27	Х	Х	х	Х
Z3	740.13	369.56	246.04	184.28	Х	Х	Х	Х
Z4	1023.17	511.08	340.38	255.04	Х	Х	Х	Х
Z5	1199.20	599.10	399.06	299.04	Х	Х	Х	Х
Z6	1482.24	740.62	493.41	369.80	Х	Х	х	х
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

<sup>1</sup>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				
ΔUA	A2S-GlcNS3S6	S		
[M-2H] <sup>2-</sup>	327.45	149.7 (0.2)		
	$(1-)^1$	(2-)	(1-)	(2-)
B1	236.97	117.98	79.7 (0.3)	Х
Y0	417.94	208.47	Х	Х
C1	254.98	126.99	138.6 (0.2)/162.2 (0.7)	X
ZO	399.93	199.46	Х	X

210 <sup>1</sup> Columns represent different charge states.

<sup>2</sup> Each CCS is an average of independent measurements with the corresponding standard deviation

#30						
Δ١	JA-GlcNS-I	doA2S-GlcNS3	S			
[M-3H] <sup>3-</sup>	330.33	228.0 (0.1)				
	(1-) <sup>1</sup>	(2-)	(3-)	(1-)	(2-)	(3-)
B1	157.01	78.00	51.67	70.7 (0.4)	х	х
B2	398.04	198.52	132.01	x	119.9 (0.5)	х
B3	654.03	326.51	217.34	x	162.4 (0.3)	х
B4	975.01	487.00	324.33	x	х	218.1 (0.7)
YO	337.99	168.49	111.99	x	104.9 (0.1)	х
Y1	593.97	296.48	197.32	x	х	х
Y2	835.00	417.00	277.66	х	х	х
C1	175.02	87.01	57.67	71.5 (0.5)	х	х
C2	416.05	207.52	138.01	113.9 (0.1)	120.8 (0.5)	х
C3	672.04	335.52	223.34	147.16 (0.5)	х	х
Z0	319.97	159.48	105.99	x	х	х
Z1	575.96	287.48	191.32	x	x	x
Z2	816.99	407.99	271.66	x	x	x

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

<sup>1</sup> Columns represent different charge states.

<sup>2</sup> Each CCS is an average of independent measurements with the corresponding standard deviation

220

**Supplementary Table 21**. CCS of B, Y, C and Z ions identified in tetrasaccharide  $\Delta$ UA-GlcNS6S-

#31				
∆UA-Glo	NS6S-G-C	GlcNS3S6S		
[M-3H] <sup>3-</sup>	356.98	228.9 (0.3)		
	$(1-)^1$	(2-)	(1-)	(2-)
B1	157.01	78.00	70.0 (0.5)	Х
B2	478.00	238.49	118.0 (0.1)	128.5 (0.1)
B3	654.03	326.51	Х	163.4 (0.1)
Y0	417.94	208.47	Х	Х
Y1	593.97	296.48	Х	Х
Y2	914.96	456.97	х	х
C1	175.02	87.01	71.6 (0.5)	Х
C2	496.01	247.50	х	131.8 (0.4)
C3	672.04	335.52	Х	164.7 (0.2)
Z0	399.93	199.46	х	х
Z1	575.96	287.48	Х	Х
Z2	896.95	447.97	Х	Х

224

<sup>225</sup> <sup>1</sup> Columns represent different charge states.

<sup>2</sup>Each CCS is an average of independent measurements with the corresponding standard deviation

227

#32				
ΔU	NS3S6S			
[M-3H] <sup>3-</sup>	344.33	234.5 (0.1)		
	$(1-)^1$	(2-)	(1-)	(2-)
B1	157.01	78.00	69.7 (0.1)	Х
B2	440.05	219.52	117.7 (0.1)	132.4 (0.8)
B3	616.08	307.54	151.7 (0.1)	Х
Y0	417.94	208.47	Х	Х
Y1	593.97	296.48	Х	Х
Y2	877.01	438.00	Х	Х
C1	175.02	87.01	71.5 (0.5)	Х
C2	458.06	228.53	120.6 (0.1)	131.5 (0.1)
C3	634.09	316.54	154.3 (0.2)	Х
ZO	399.93	199.46	Х	Х
Z1	575.96	287.48	X	х
Z2	859.00	429.00	Х	Х

229 Supplementary Table 22. CCS of B, Y, C and Z ions identified in tetrasaccharide ΔUA-GlcNAc6S-

230 GlcA-GlcNS3S6S structure. Error +/- values are donated in brackets.

231

<sup>1</sup>Columns represent different charge states.

<sup>2</sup> Each CCS is an average of independent measurements with the corresponding standard deviation

234

#33						
	G-Glc	NS6S-G-GlcN	S6S-I2S-G	lcNS6S-R <sub>1</sub>		
[M-3H] <sup>3-</sup>	557.06	280.5 (0.1)				
[M-4H] <sup>4-</sup>	417.52	339.5 (0.3)				
	$(1-)^1$	(2-)	(3-)	(1-)	(2-)	(3-)
B1	175.02	87.01	57.67	69.0 (0.4)	х	Х
B2	496.01	247.50	164.66	х	132.5 (0.5)	х
B3	672.04	335.52	223.34	Х	161.7 (0.5)	Х
B4	993.02	496.01	330.34	х	х	225.1 (0.7)
B5	1249.01	624.00	415.66	х	х	х
B6	1569.99	784.49	522.66	Х	x	Х
YO	102.09	50.54	33.36	x	x	X
Y1	423.07	211.03	140.35	х	128.8 (0.7)	х
Y2	679.06	339.03	225.68	х	x	х
Y3	1000.05	499.52	332.68	х	x	х
Y4	1176.08	587.53	391.35	х	x	х
Y5	1497.06	748.03	498.35	Х	Х	Х
C1	193.03	96.01	63.67	74.2 (0.4)	X	Х
C2	514.02	256.50	170.67	х	133.7 (0.5)	х
C3	690.05	344.52	229.34	х	х	х
C4	1011.03	505.01	336.34	х	х	х
C5	1267.02	633.01	421.67	Х	х	Х
C6	1588.00	793.50	528.66	Х	X	Х
ZO	84.08	41.54	27.36	X	X	Х
Z1	405.06	202.03	134.35	х	X	х
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

Supplementary Table 23. CCS of B, Y, C and Z ions identified in hexasaccharide G-GlcNS6S-G GlcNS6S-I2S-GlcNS6S-R<sub>1</sub> structure, where R<sub>1</sub> is (CH<sub>2</sub>)<sub>5</sub>NH<sub>2</sub>.

239 <sup>1</sup> Columns represent different charge states.

<sup>2</sup> Each CCS is an average of independent measurements with the corresponding standard deviation

#34						
	G-GlcNS6	S-G-GlcNS3S-	I2S-GlcNS6S-F	<b>R</b> <sub>1</sub>		
[M-3H] <sup>3-</sup>	557.06	282.4 (0.4)				
	$(1-)^1$	(2-)	(3-)	(1-)	(2-)	(3-)
B1	175.02	87.01	57.67	68.8 (0.2)	х	Х
B2	496.01	247.50	164.66	х	132.2 (0.5)	Х
B3	672.04	335.52	223.34	х	162.1 (0.4)	Х
B4	993.02	496.01	330.34	х	х	220.4 (0.5)
B5	1249.01	624.00	415.66	х	х	Х
B6	1569.99	784.49	522.66	х	х	Х
V0	102.00	50.54	33.36	v	v	v
10 V1	102.09	211.03	140.35	X	$\frac{\lambda}{1280(0.5)}$	X
11 V2	679.06	339.03	225.68	X v	128.9 (0.3) v	X V
12 V2	1000.05	400.52	223.08	A V	A V	A V
13 V/	1176.08	499.32 587.53	301 35	x x	x	A V
14 V5	1407.06	748.03	408.35	A V	A V	A V
15	1497.00	748.03	498.33	Λ	λ	Λ
C1	193.03	96.01	63.67	73.8 (0.4)	x	Х
C2	514.02	256.50	170.67	Х	133.9 (0.6)	Х
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	Х	x	Х
70	84.08	41 54	27.36	x	x	x
<u>Z</u> 0	405.06	202.03	134.35	x	x	x
72	661.05	330.02	219.68	x	x	x
73	982.03	490 51	326.67	x	x	x
74	1158.07	578.53	385.35	x	x	x
Z5	1479.05	739.02	492.34	X	X	X
	-					

Supplementary Table 24. CCS of B, Y, C and Z ions identified in hexasaccharide G-GlcNS6S-G GlcNS3S-I2S-GlcNS6S-(CH<sub>2</sub>)<sub>5</sub>NH<sub>2</sub> structure, where R<sub>1</sub> is (CH<sub>2</sub>)<sub>5</sub>NH<sub>2</sub>.

248

249 <sup>1</sup> Columns represent different charge states.

<sup>2</sup> Each CCS is an average of independent measurements with the corresponding standard deviation

251

#35						
	G-GlcN	IS6S-G-GlcNS	6S3S-I2S-(	GlcNS6S-R1		
[M-4H] <sup>4-</sup>	437.51	328.3 (0.6)				
	$(1-)^1$	(2-)	(3-)	(1-)	(2-)	(3-)
B1	175.02	87.01	57.67	69.0 (0.2)	Х	Х
B2	496.01	247.50	164.66	Х	132.8 (0.4)	Х
B3	672.04	335.52	223.34	Х	162.4 (0.4)	Х
B4	1072.98	535.99	356.99	Х	Х	Х
B5	1328.97	663.98	442.32	Х	Х	Х
B6	1649.95	824.47	549.31	Х	Х	Х
<b>V</b> 0	102.09	50.54	33.36	v	v	v
Y1	423.07	211.03	140 35	x	x	x
Y2.	679.06	339.03	225.68	x	x	x
¥3	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	Х	Х	Х
C1	193.03	96.01	63.67	X	X	X
C2	514.02	256.50	170.67	Х	Х	Х
C3	690.05	344.52	229.34	Х	Х	Х
C4	1090.99	544.99	362.99	X	X	X
C5	1346.98	672.98	448.32	Х	Х	Х
C6	1667.96	833.48	555.31	Х	Х	х
Z0	84.08	41.54	27.36	Х	X	Х
Z1	405.06	202.03	134.35	х	х	х
Z2	661.05	330.02	219.68	х	х	х
Z3	1061.99	530.49	353.33	х	x	х
Z4	1238.02	618.51	412.00	х	x	х
Z5	1559.01	779.00	519.00	Х	х	х

Supplementary Table 25. CCS of B, Y, C and Z ions identified in hexasaccharide G-GlcNS6S-G GlcNS6S3S-I2S-GlcNS6S-R<sub>1</sub>, where R<sub>1</sub> is (CH<sub>2</sub>)<sub>5</sub>NH<sub>2</sub>.

256 <sup>1</sup> Columns represent different charge states.

<sup>2</sup> Each CCS is an average of independent measurements with the corresponding standard deviation

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261	Supplementary Table 26. CCS of B, Y, C and Z ions identified in a dp7 + 1x2O-sulfate, $\Delta$ UA-GlcNS-I2S-GlcNS-G-GlcNS-G-R <sub>3</sub> structure,
262	where $R_3$ is $C_6H_4NO_2$ .

#36								
∆UA-Glc	NS-I2S-Glc	NS-G-GlcNS-G	-R3					
	$(1-)^1$	(2-)	(3-)	(4-)	(1-)	(2-)	(3-)	(4-)
B1	157.01	78.00	51.67	38.50	70.5 (0.76)	Х	х	х
B2	398.04	198.52	132.01	98.75	110.5 (0.8)	120.5 (0.5)	Х	х
B3	654.03	326.51	217.34	162.75	х	162.6 (0.5)	Х	х
B4	895.05	447.02	297.68	223.01	х	201.1 (0.5)	Х	х
B5	1071.09	535.04	356.36	267.02	х	211.7 (0.3)	246.2 (0.8)	х
B6	1312.11	655.55	436.70	327.27	x	Х	Х	Х
B7	1488.14	743.57	495.38	371.28	x	X	х	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	Х	X	х
Y2	555.08	277.03	184.35	138.01	х	Х	Х	х
Y3	731.11	365.05	243.03	182.02	х	Х	Х	Х
Y4	972.13	485.56	323.37	242.28	х	Х	Х	х
Y5	1228.12	613.56	408.70	306.27	х	Х	Х	х
Y6	1469.15	734.07	489.04	366.53	X	Х	X	x
C1	174.02	86.50	57.33	42.75	X	x	x	x
C2	415.04	207.02	137.68	103.00	х	Х	х	х
C3	671.03	335.01	223.01	167.00	х	Х	х	х
C4	912.06	455.52	303.35	227.26	x	Х	X	X
C5	1088.09	543.54	362.02	271.27	X	Х	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	Х	X

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

264 <sup>1</sup> Columns represent different charge states.

<sup>2</sup> Each CCS is an average of independent measurements with the corresponding standard deviation

			#9		#10		#11		#13	
			G-GlcNAc6S GlcNAc6S-R	- <b>G</b> -	I-GlcNAc6S-I- GlcNAc6S-R <sub>1</sub>		G-GlcNAc6S-I GlcNAc6S-R <sub>1</sub>	[-	I-GlcNAc6S-C GlcNAc6S-R <sub>1</sub>	j-
			- 1SO <sub>3</sub>	- 1SO <sub>3</sub>	- 1SO3	- 1SO <sub>3</sub>	- 1SO3	- 1SO3	- 1SO <sub>3</sub>	- 2SO3
			$(1-)^1$	(2-)	(1-)	(2-)	(1-)	(2-)	(1-)	(2-)
B1	95.07	47.03	Х	Х	Х	Х	Х	Х	Х	Х
B2	378.10	188.55	112.04 (0.1)	Х	112.5 (0.3)	Х	112.41 (0.5)	Х	112.02 (0.2)	Х
B3	554.14	276.56	Х	Х	Х	Х	х	Х	х	х
B4	837.17	418.08	х	х	х	Х	х	Х	х	Х
Y0	22.14	10.56	х	х	Х	Х	х	Х	х	Х
Y1	305.17	152.08	Х	Х	Х	Х	X	Х	Х	Х
Y2	481.20	240.10	139.34 (0.2)	Х	137.09 (0.3)	Х	137.38 (0.6)	Х	139.3 (0.2)	Х
Y3	764.24	381.62	Х	Х	X	Х		Х	Х	Х
C1	113.08	56.04	X	X	X	Х	x	Х	x	Х
C2	396.11	197.55	115.2 (0.6)	X	115.7 (0.5)	Х	114.85 (0.4)	Х	114.88 (0.2)	Х
C3	572.15	285.57	Х	Х	Х	Х	Х	Х	Х	Х
C4	855.18	427.09	Х	Х	Х	Х	Х	Х	Х	Х
Z0	4.12	1.56	Х	Х	X	Х	X	Х	X	Х
Z1	287.16	143.08	Х	Х	X	Х	X	Х	X	Х
Z2	463.19	231.09	Х	Х	X	Х	X	Х	X	Х
Z3	746.23	372.61	Х	Х	Х	Х	Х	Х	Х	Х

267 **Supplementary Table 27.** CCS of B, Y, C and Z (-SO<sub>3</sub>) ions identified in isomeric tetrasaccharide UA-GlcNAc6S-UA-GlcNAc6S-R<sub> $\pm$ </sub> structures, 268 where R<sub>1</sub> is (CH<sub>2</sub>)<sub>5</sub>NH<sub>2</sub>.

269 <sup>1</sup> Columns represent different charge states.

<sup>2</sup> Each CCS is an average of independent measurements with the corresponding standard deviation

#12						
G-Gl	cNS6S-I-	GlcNS6S-F	R <sub>1</sub>			
				- 1 <b>SO</b> 3	- 1 <b>SO</b> 3	- 1 <b>SO</b> <sub>3</sub>
				$(1-)^1$	(2-)	(3-)
B1	95.07	47.03	31.02	Х	Х	Х
B2	416.05	207.52	138.01	Х	122.4 (0.3)	Х
B3	592.08	295.54	196.69	139.6 (0.3)	Х	Х
B4	913.06	456.03	303.68	Х	Х	214.9 (0.2)
YO	22.14	10 56	671	X	X	X
Y1	343.12	171.05	113.70	X	X	X
Y2	519.15	259.07	172.38	Х	Х	Х
Y3	840.13	419.56	279.37	Х	Х	Х
C1	113.08	56.04	37.02	Х	Х	X
C2	434.06	216.53	144.01	Х	Х	Х
C3	610.09	304.54	202.69	х	Х	Х
C4	931.07	465.03	309.69	Х	Х	Х
Z0	4.12	1.56	0.70	Х	Х	Х
Z1	325.11	162.05	107.70	Х	Х	Х
Z2	501.14	250.07	166.37	Х	Х	Х
Z3	822.12	410.56	273.37	Х	Х	Х

**Supplementary Table 28.** CCS of B, Y, C and Z (-SO<sub>3</sub>) ions identified in isomeric tetra-saccharide UA-

273 GlcNS6S-UA-GlcNS6S- $R_1$  structures, where  $R_1$  is (CH<sub>2</sub>)<sub>5</sub>NH<sub>2</sub>.

<sup>275</sup> <sup>1</sup> Columns represent different charge states.

 $^{2}$  Each CCS is an average of independent measurements with the corresponding standard deviation

#14				
	I-GlcNS65	S-G-GlcNS	$5S-R_1$	
	- 1SO <sub>3</sub>	- 1SO <sub>3</sub>	- 1SO <sub>3</sub>	- 1SO <sub>3</sub>
	(1-)	(2-)	(1-)	(2-)
B1	95.07	47.03	Х	x
B2	416.05	207.52	Х	x
B3	592.08	295.54	Х	х
B4	913.06	456.03	х	Х
Y0	22.14	10.56	Х	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	х	х
C3	610.09	304.54	Х	х
C4	931.07	465.03	Х	х
70	4.10	1.50		
20	4.12	1.56	X	X
Z1	325.11	162.05	Х	Х
Z2	501.14	250.07	Х	X
Z3	822.12	410.56	X	х

279 Supplementary Table 29. CCS of B, Y, C and Z (-SO<sub>3</sub>) ions identified in isomeric tetra-saccharide UA-

280 GlcNS6S-UA-GlcNS6S- $R_1$  structures, where  $R_1$  is (CH<sub>2</sub>)<sub>5</sub>NH<sub>2</sub>.

281

<sup>1</sup>Columns represent different charge states.

 $^{2}$  Each CCS is an average of independent measurements with the corresponding standard deviation

#15						
G-0	GlcNS6S-I2	S-GlcNS6S	$-R_1$			
	- 1SO <sub>3</sub>	- 1SO <sub>3</sub>	- 1SO <sub>3</sub>			
	$(1-)^1$	(2-)	(3-)			
B1	95.07	47.03	31.02	Х	Х	Х
B2	416.05	207.52	138.01	Х	$122.4 (0.1)^2$	Х
B3	672.04	335.52	223.34	X	167.1 (0.4)	х
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)	х	Х
Y2	599.11	299.05	199.03	х	Х	Х
Y3	920.09	459.54	306.02	Х	Х	Х
C1	113.08	56.04	37.02	X	X	X
C2	434.06	216.53	144.01	Х	Х	Х
C3	690.05	344.52	229.34	х	х	х
C4	1011.03	505.01	336.34	x	X	х
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

Supplementary Table 30. CCS of B, Y, C and Z (-SO<sub>3</sub>) ions identified in isomeric tetra-saccharide G GlcNS6S-I2S-GlcNS6S-R<sub>1</sub> structures, where R<sub>1</sub> is (CH<sub>2</sub>)<sub>5</sub>NH<sub>2</sub>.

287

288 <sup>1</sup> Columns represent different charge states.

 $^{2}$  Each CCS is an average of independent measurements with the corresponding standard deviation

#16						
G-Glc	NS6S-I-GlcNS	6S-G-GlcNS	6S-R <sub>1</sub>			
	- 1SO3	- 1SO3	- 1SO <sub>3</sub>	- 1SO3	- 1SO3	- 1SO3
	$(1-)^1$	(2-)	(3-)	(1-)	(2-)	(3-)
B1	95.07	47.03	31.02	Х	Х	Х
B2	416.05	207.52	138.01	х	$122.5 (0.2)^2$	Х
B3	592.08	295.54	196.69	140.2 (0.7)	Х	Х
B4	913.06	456.03	303.68	х	Х	214.8 (0.7)
B5	1089.10	544.04	362.36	Х	Х	247.4 (0.9)
B6	1410.08	704.54	469.35	Х	Х	х
Y0	22.14	10.56	6.71	X	X	Х
Y1	343.12	171.05	113.70	109.1 (0.1)	х	х
Y2	519.15	259.07	172.38	х	150.0 (0.8)	х
Y3	840.13	419.56	279.37	х	х	Х
Y4	1016.16	507.58	338.05	Х	Х	234.8 (0.2)
Y5	1337.15	668.07	445.04	Х	Х	X
C1	113.08	56.04	37.02	X	X	х
C2	434.06	216.53	144.01	114.8 (0.46)	х	х
C3	610.09	304.54	202.69	Х	х	х
C4	931.07	465.03	309.69	Х	Х	Х
C5	1107.11	553.05	368.36	Х	Х	Х
C6	1428.09	713.54	475.36	Х	Х	x
Z0	4.12	1.56	0.70	X	X	х
Z1	325.11	162.05	107.70	х	Х	Х
Z2	501.14	250.07	166.37	х	Х	Х
Z3	822.12	410.56	273.37	х	Х	Х
Z4	998.15	498.57	332.05	X	Х	X
Z5	1319.14	659.06	439.04	X	X	X

**Supplementary Table 31**. CCS of B, Y, C and Z (-SO<sub>3</sub>) ions identified in a hexa-saccharide structure ( $R_1$ 292 is (CH<sub>2</sub>)<sub>5</sub>NH<sub>2</sub>).

<sup>1</sup>Columns represent different charge states.

<sup>2</sup> Each CCS is an average of independent measurements with the corresponding standard deviation

#17						
	GlcNAc68	S-[G-GlcNA	$(6S]_2-G-R_2$	2		
	- 1 <b>SO</b> <sub>3</sub>	- 1 <b>SO</b> <sub>3</sub>	- 1 <b>SO</b> <sub>3</sub>	- 1SO <sub>3</sub>	- 1SO <sub>3</sub>	- 1SO <sub>3</sub>
	$(1-)^1$	(2-)	(3-)	(1-)	(2-)	(3-)
B1	202.07	100.53	66.69	Х	Х	Х
B2	378.10	188.55	125.36	111.4 (0.2)	Х	Х
B3	661.14	330.07	219.71	160.1 (0.7)	Х	Х
B4	837.17	418.08	278.39	Х	Х	Х
B5	1120.21	559.60	372.73	Х	214.1 (0.7)	Х
B6	1296.24	647.62	431.41	Х	234.0 (0.4)	Х
Y0	42.08	20.54	13.35	X	Х	Х
Y1	219.12	109.06	72.37	Х	Х	Х
Y2	502.16	250.57	166.71	Х	Х	Х
Y3	678.19	338.59	225.39	Х	Х	Х
Y4	961.22	480.11	319.74	Х	Х	Х
Y5	1137.26	568.12	378.41	Х	Х	Х
C1	220.08	109.54	72.69	Х	Х	Х
C2	396.11	197.55	131.37	х	х	Х
C3	679.15	339.07	225.71	Х	х	Х
C4	855.18	427.09	284.39	Х	Х	Х
C5	1138.22	568.61	378.73	Х	Х	Х
C6	1314.25	656.62	437.41	Х	Х	Х
Z0	25.08	12.03	7.69	Х	Х	Х
Z1	201.11	100.05	66.36	Х	х	Х
Z2	484.15	241.57	160.71	X	X	X
Z3	660.18	329.58	219.39	х	Х	Х
Z4	943.21	471.10	313.73	х	Х	Х
Z5	1119.25	559.12	372.41	X	X	X

Supplementary Table 32. CCS of B, Y, C and Z (-SO<sub>3</sub>) ions identified in a hexa-saccharide GlcNAc6S [G-GlcNAc6S]<sub>2</sub>-G-R<sub>2</sub> structure, where R<sub>2</sub> is C<sub>7</sub>H<sub>7</sub>O.

300

301 <sup>1</sup> Columns represent different charge states.

 $^{2}$  Each CCS is an average of independent measurements with the corresponding standard deviation

303

#18						
GlcNAc6S-[	I-GlcNAc6S]	2 <b>-I-R</b> 2				
	- 1SO <sub>3</sub>	- 1 <b>SO</b> <sub>3</sub>	- 1SO <sub>3</sub>	- 1SO <sub>3</sub>	- 1SO <sub>3</sub>	- 1SO3
	$(1-)^1$	(2-)	(3-)	(1-)	(2-)	(3-)
B1	202.07	100.53	66.69	х	Х	Х
B2	378.10	188.55	125.36	112.5 (0.1)	Х	х
B3	661.14	330.07	219.71	157.7 (0.3)	х	х
B4	837.17	418.08	278.39	х	179.8 (0.9)	х
B5	1120.21	559.60	372.73	х	215.6 (0.2)	х
B6	1296.24	647.62	431.41	Х	237.8 (0.4)	Х
Y0	42.08	20.54	13.35	X	X	X
Y1	219.12	109.06	72.37	х	х	х
Y2	502.16	250.57	166.71	х	х	х
Y3	678.19	338.59	225.39	х	х	х
Y4	961.22	480.11	319.74	х	х	х
Y5	1137.26	568.12	378.41	х	Х	Х
C1	220.08	109.54	72.69	X	Х	X
C2	396.11	197.55	131.37	Х	Х	х
C3	679.15	339.07	225.71	х	х	х
C4	855.18	427.09	284.39	х	х	х
C5	1138.22	568.61	378.73	Х	Х	х
C6	1314.25	656.62	437.41	х	Х	Х
Z0	25.08	12.03	7.69	X	Х	Х
Z1	201.11	100.05	66.36	х	Х	Х
Z2	484.15	241.57	160.71	X	X	X
Z3	660.18	329.58	219.39	X	X	Х
Z4	943.21	471.10	313.73	X	X	Х
Z5	1119.25	559.12	372.41	x	X	x

Supplementary Table 33. CCS of B, Y, C and Z (-SO<sub>3</sub>) ions identified in a hexa-saccharide GlcNAc6S [I-GlcNAc6S]<sub>2</sub>-I-R<sub>2</sub> structure, where R<sub>2</sub> is C<sub>7</sub>H<sub>7</sub>O.

308 <sup>1</sup> Columns represent different charge states.

 $^{2}$  Each CCS is an average of independent measurements with the corresponding standard deviation

313	Supplementary Table 34.	CCS of B, Y, C and Z (-SO <sub>3</sub> ) ions identified in an octa-saccharide Gl	cNAc6S-

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#19						
Gle	cNAc6S-[I-G	lcNAc6S] <sub>3</sub> -I	- <b>R</b> <sub>2</sub>			
	- 1SO <sub>3</sub>	- 1SO <sub>3</sub>	- 1SO <sub>3</sub>	- 1SO <sub>3</sub>	- 1SO <sub>3</sub>	- 1SO <sub>3</sub>
	$(1-)^1$	(2-)	(3-)	(1-)	(2-)	(3-)
B1	202.07	100.53	66.69	Х	Х	Х
B2	378.10	188.55	125.36	$112.0 (0.3)^2$	Х	Х
B3	661.14	330.07	219.71	158.2 (0.2)	Х	Х
B4	837.17	418.08	278.39	Х	Х	Х
B5	1120.21	559.60	372.73	Х	216.3 (0.7)	Х
B6	1296.24	647.62	431.41	Х	Х	Х
B7	1579.28	789.13	525.75	Х	Х	Х
B8	1755.31	877.15	584.43	Х	Х	
Y0	42.08	20.54	13.35	Х	Х	Х
Y1	219.12	109.06	72.37	Х	Х	Х
Y2	502.16	250.57	166.71	Х	Х	Х
Y3	678.19	338.59	225.39	Х	Х	Х
Y4	961.22	480.11	319.74	Х	Х	Х
Y5	1137.26	568.12	378.41	Х	Х	Х
Y6	1420.29	709.64	472.76	Х	Х	Х
Y7	1596.32	797.66	531.44	Х	Х	Х
C1	220.08	109.54	72.69	Х	Х	Х
C2	396.11	197.55	131.37	Х	Х	Х
C3	679.15	339.07	225.71	Х	Х	Х
C4	855.18	427.09	284.39	Х	Х	Х
C5	1138.22	568.61	378.73	Х	Х	Х
C6	1314.25	656.62	437.41	Х	Х	Х
C7	1597.29	798.14	531.76	Х	Х	Х
C8	1773.32	886.16	590.43	Х	Х	Х
ZO	25.08	12.03	7.69	X	х	Х
Z1	201.11	100.05	66.36	X	Х	Х
Z2	484.15	241.57	160.71	Х	Х	Х
Z3	660.18	329.58	219.39	Х	Х	Х
Z4	943.21	471.10	313.73	Х	Х	Х
Z5	1119.25	559.12	372.41	Х	Х	Х
Z6	1402.28	700.64	466.76	Х	Х	Х
Z7	1578.31	788.65	525.43	Х	Х	Х

<sup>1</sup> Columns represent different charge states. <sup>2</sup> Each CCS is an average of independent measurements with the corresponding standard deviation 

#20						
Gl	cNAc6S-[G-0	GlcNAc6S]3-	G-R <sub>2</sub>			
	- 1SO <sub>3</sub>	- 1 <b>SO</b> <sub>3</sub>	- 1 <b>SO</b> <sub>3</sub>	- 1SO <sub>3</sub>	- 1SO <sub>3</sub>	- 1SO <sub>3</sub>
	$(1-)^1$	(2-)	(3-)	(1-)	(2-)	(3-)
B1	202.07	100.53	66.69	х	Х	Х
B2	378.10	188.55	125.36	$111.5(0.1)^2$	х	Х
B3	661.14	330.07	219.71	160.4 (0.2)	Х	Х
B4	837.17	418.08	278.39	Х	185.4 (0.4)	Х
B5	1120.21	559.60	372.73	Х	214.9 (0.8)	Х
B6	1296.24	647.62	431.41	Х	Х	Х
B7	1579.28	789.13	525.75	Х	Х	Х
B8	1755.31	877.15	584.43	Х	Х	Х
Y0	42.08	20.54	13.35	X	Х	Х
Y1	219.12	109.06	72.37	Х	Х	X
Y2	502.16	250.57	166.71	Х	X	Х
Y3	678.19	338.59	225.39	Х	Х	Х
Y4	961.22	480.11	319.74	Х	199.7 (0.18)	Х
Y5	1137.26	568.12	378.41	Х	216.2 (0.1)	Х
Y6	1420.29	709.64	472.76	Х	Х	Х
Y7	1596.32	797.66	531.44	X	Х	Х
C1	220.08	109.54	72.69	X	Х	X
C2	396.11	197.55	131.37	Х	Х	Х
C3	679.15	339.07	225.71	х	Х	Х
C4	855.18	427.09	284.39	Х	Х	Х
C5	1138.22	568.61	378.73	Х	Х	Х
C6	1314.25	656.62	437.41	Х	Х	Х
C7	1597.29	798.14	531.76	Х	Х	Х
C8	1773.32	886.16	590.43	Х	Х	Х
Z0	25.08	12.03	7.69	X	Х	Х
Z1	201.11	100.05	66.36	Х	Х	Х
Z2	484.15	241.57	160.71	Х	Х	Х
Z3	660.18	329.58	219.39	X	X	Х
Z4	943.21	471.10	313.73	X	X	Х
Z5	1119.25	559.12	372.41	Х	Х	Х
Z6	1402.28	700.64	466.76	Х	Х	Х
Z7	1578.31	788.65	525.43	х	X	x

**Supplementary Table 35**. CCS of B, Y, C and Z (-SO<sub>3</sub>) ions identified in an octa-saccharide GlcNAc6S-

318  $[G-GlcNAc6S]_3$ -G-R<sub>2</sub> structure, where R<sub>2</sub> is C<sub>7</sub>H<sub>7</sub>O.

<sup>1</sup> Columns represent different charge states.

#21						
(	GlcNAc6S-G-	-GlcNac6S-C	G-GlcNAc6S	I-GlcNAc6S-I	-R <sub>2</sub>	
	- 1SO <sub>3</sub>	- 1SO3				
	$(1-)^1$	(2-)	(3-)	$(1-)^1$	(2-)	(3-)
B1	202.07	100.53	66.69	69 X X		Х
B2	378.10	188.55	125.36	$112.3 (0.3)^2$	Х	Х
B3	661.14	330.07	219.71	х	Х	Х
B4	837.17	418.08	278.39	х	Х	Х
B5	1120.21	559.60	372.73	х	213.8 (0.1)	Х
B6	1296.24	647.62	431.41	х	Х	Х
B7	1579.28	789.13	525.75	Х	Х	Х
B8	1755.31	877.15	584.43	Х	Х	Х
Y0	42.08 20.54		13.35	Х	Х	Х
Y1	219.12	109.06	72.37	х	Х	Х
Y2	502.16 250.57		166.71	Х	Х	Х
Y3	678.19	338.59	225.39	Х	Х	Х
Y4	961.22	480.11	319.74	Х	Х	Х
Y5	1137.26	568.12	378.41	Х	Х	Х
Y6	1420.29	709.64	472.76	Х	Х	Х
Y7	1596.32	797.66	531.44	Х	X X	
C1	220.08	109.54	72.69	Х	Х	Х
C2	396.11	197.55	131.37	х	Х	Х
C3	679.15	339.07	225.71	Х	Х	Х
C4	855.18	427.09	284.39	х	Х	х
C5	1138.22	568.61	378.73	х	Х	х
C6	1314.25	656.62	437.41	Х	Х	Х
C7	1597.29	798.14	531.76	Х	Х	Х
C8	1773.32	886.16	590.43	Х	Х	Х
Z0	25.08	12.03	7.69	X	Х	X
Z1	201.11	100.05	66.36	х	Х	Х
Z2	484.15	241.57	160.71	х	Х	х
Z3	660.18	329.58	219.39	х	Х	Х
Z4	943.21	471.10	313.73	X	X	Х
Z5	1119.25	559.12	372.41	Х	Х	Х
Z6	1402.28	700.64	466.76	X	Х	X
Z7	1578.31	788.65	525.43	X	Х	Х

Supplementary Table 36. CCS of B, Y, C and Z (-SO<sub>3</sub>) ions identified in an octa-saccharide GlcNAc6S G-GlcNac6S-G-GlcNAc6S-I-GlcNAc6S-I-R<sub>2</sub> structure, where R<sub>2</sub> is C<sub>7</sub>H<sub>7</sub>O.

<sup>1</sup> Columns represent different charge states.

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

Supplementary Table 37. CCS of B, Y, C and Z (-SO<sub>3</sub>) ions identified in an octa-saccharide GlcNAc6S G-GlcNac6S-I-GlcNAc6S-G-R<sub>2</sub> structure, where R<sub>2</sub> is C<sub>7</sub>H<sub>7</sub>O.

<sup>1</sup> Columns represent different charge states.

#23						
	GlcNAc6S-I	-GlcNAc6S-	G-GlcNAc6S	-I-GlcNAc6S-	G-R <sub>2</sub>	
	- 1 <b>SO</b> <sub>3</sub>	- 1 <b>SO</b> <sub>3</sub>	- 1 <b>SO</b> <sub>3</sub>	- 1SO <sub>3</sub>	- 1SO3	- 1SO <sub>3</sub>
	$(1-)^1$	(2-)	(3-)	(1-) <sup>1</sup>	(2-)	(3-)
B1	202.07	100.53	66.69	Х	Х	Х
B2	378.10	188.55	125.36	$112.1 (0.3)^2$	Х	Х
B3	661.14	330.07	219.71	157.8 (0.2)	Х	Х
B4	837.17	418.08	278.39	Х	Х	Х
B5	1120.21	559.60	372.73	Х	215.1 (0.11)	Х
B6	1296.24	647.62	431.41	Х	Х	Х
B7	1579.28	789.13	525.75	Х	Х	Х
B8	1755.31	877.15	584.43	Х	Х	Х
Y0	42.08	20.54	13.35	X	Х	х
Y1	219.12	109.06	72.37	х	Х	Х
Y2	502.16	250.57	166.71	х	Х	Х
Y3	678.19	338.59	225.39	х	Х	Х
Y4	961.22	480.11	319.74	х	Х	Х
Y5	1137.26	568.12	378.41	Х	Х	Х
Y6	1420.29	709.64	472.76	Х	Х	Х
Y7	1596.32	797.66	531.44	Х	Х	Х
C1	220.08	109.54	72.69	X	Х	Х
C2	396.11	197.55	131.37	х	Х	Х
C3	679.15	339.07	225.71	х	Х	Х
C4	855.18	427.09	284.39	х	Х	Х
C5	1138.22	568.61	378.73	х	Х	Х
C6	1314.25	656.62	437.41	Х	Х	Х
C7	1597.29	798.14	531.76	X	X	X
C8	1773.32	886.16	590.43	X	Х	X
Z0	25.08	12.03	7.69	X	X	Х
Z1	201.11	100.05	66.36	х	X	Х
Z2	484.15	241.57	160.71	х	Х	Х
Z3	660.18	329.58	219.39	х	Х	Х
Z4	943.21	471.10	313.73	Х	Х	Х
Z5	1119.25	559.12	372.41	х	Х	Х
Z6	1402.28	700.64	466.76	Х	Х	Х
Z7	1578.31	788.65	525.43	X	X	Х

Supplementary Table 38. CCS of B, Y, C and Z (-SO<sub>3</sub>) ions identified in an octa-saccharide GlcNAc6S I-GlcNAc6S-G-GlcNAc6S-I-GlcNAc6S-G-R<sub>2</sub> structure, where R<sub>2</sub> is C<sub>7</sub>H<sub>7</sub>O.

<sup>1</sup> Columns represent different charge states.

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

Supplementary Table 39. CCS of B, Y, C and Z (-SO<sub>3</sub>) ions identified in an octa-saccharide GlcNAc6S G-GlcNAc6S-I-GlcNAc6S-G-GlcNAc6S-I-R<sub>2</sub> structure, where R<sub>2</sub> is C<sub>7</sub>H<sub>7</sub>O.

<sup>1</sup> Columns represent different charge states.

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

**Supplementary Table 40**. CCS of B, Y, C and Z (-SO<sub>3</sub>) ions identified in a 9mer, G-GlcNS-G-GlcNS-I-GlcNS-G-GlcNS-G-R<sub>3</sub> structure, where  $R_3$  is  $C_6H_4NO_2$ .

	Z8	1708.28	853.64	568.76	Х	Х	х			
339				· · · · · · · · · · · · · · · · · · ·						
340	<sup>1</sup> Columns represent different charge states.									
341	<sup>2</sup> Each CCS is an average of independent measurements with the corresponding standard deviation									
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351	Supplementary Table 41. CCS of B, Y, C and Z (-SO <sub>3</sub> ) ions identified in a dp9 + 1x2O-sulfate, G-
352	GlcNS-G-GlcNS-I2S-GlcNS-G-GlcNS-G-R <sub>3</sub> structure, where R <sub>3</sub> is C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> .

#26						
G-GlcNS	-G-GlcNS-I2	S-GlcNS-G-G	lcNS-G-R <sub>3</sub>			
	- 1 <b>SO</b> <sub>3</sub>	- 1 <b>SO</b> <sub>3</sub>	- 1SO3	- 1SO3	- 1SO <sub>3</sub>	- 1SO3
	$(1-)^1$	(2-)	(3-)	(1-)	(2-)	(3-)
B1	95.07 47.03		31.02	X	Х	Х
B2	336.09	167.54	111.36	X	Х	Х
B3	512.13	255.56	170.04	$131.6 (0.5)^2$	Х	Х
B4	753.15	376.07	250.38	Х	Х	Х
B5	1009.14	504.07	335.71	х	234.21 (0.2)	Х
B6	1250.17	624.58	416.05	х	Х	Х
B7	1426.20	712.59	474.73	Х	Х	Х
B8	1667.22	833.11	555.07	х	Х	Х
B9	1843.25	921.12	613.75	X	Х	Х
Y0	58.06	28.53	18.68	Х	Х	x
Y1	234.09	116.54	77.36	X	Х	х
Y2	475.12	237.06	157.70	X	Х	Х
Y3	651.15	325.07	216.38	Х	Х	х
Y4	892.18	445.58	296.72	X	Х	Х
Y5	1148.17	573.58	382.05	х	Х	Х
Y6	1389.19	694.09	462.39	x	Х	Х
Y7	1565.22	782.11	521.07	x	Х	Х
Y8	1806.25	902.62	601.41	x	Х	Х
C1	112.07	55.53	36.68	X	Х	Х
C2	353.10	176.04	117.03	x	Х	Х
C3	529.13	264.06	175.70	x	Х	Х
C4	770.15	384.57	256.05	x	Х	Х
C5	1026.14	512.57	341.38	x	Х	Х
C6	1267.17	633.08	421.72	X	Х	x
C7	1443.20	721.10	480.39	X	Х	x
C8	1684.23	841.61	560.74	X	Х	x
C9	1860.26	929.62	619.41	Х	Х	Х
Z0	40.05	19.52	12.68	x	Х	Х
Z1	216.08	107.54	71.36	x	Х	Х
Z2	457.11	228.05	151.70	x	X	х
Z3	633.14	316.07	210.38	x	Х	х
Z4	874.17	436.58	290.72	x	Х	х
Z5	1130.16	564.57	376.05	x	Х	х
Z6	1371.18	685.09	456.39	x	Х	х
Z7	1547.21	773.10	515.07	х	Х	Х

	Z8	1788.24	893.62	595.41	Х	х	х
353							

- 354 <sup>1</sup> Columns represent different charge states.
- $^{2}$  Each CCS is an average of independent measurements with the corresponding standard deviation

#27								
	GlcNAd	c6S-[I-GlcNAc	:6S] <sub>4</sub> -I-R <sub>2</sub>					
	- 1 <b>SO</b> <sub>3</sub>	- 1 <b>SO</b> <sub>3</sub>	- 1SO <sub>3</sub>	- 1SO <sub>3</sub>	- 1 <b>SO</b> <sub>3</sub>	- 1SO <sub>3</sub>	- 1SO <sub>3</sub>	- 1SO <sub>3</sub>
	$(1-)^1$	(2-)	(3-)	(4-)	(1-)	(2-)	(3-)	(4-)
B1	202.07	100.53	66.69	49.76	Х	Х	Х	Х
B2	378.10	188.55	125.36	93.77	$112.38(0.2)^2$	Х	Х	Х
B3	661.14	330.07	219.71	164.53	Х	167.6 (0.5)	Х	Х
B4	837.17	418.08	278.39	208.54	Х	Х	Х	Х
B5	1120.21	559.60	372.73	279.30	Х	215.7 (0.2)	255.5 (0.4)	Х
B6	1296.24	647.62	431.41	323.30	Х	Х	283.0 (0.5)	Х
B7	1579.28	789.13	525.75	394.06	Х	Х	Х	Х
B8	1755.31	877.15	584.43	438.07	Х	Х	Х	Х
B9	2038.34	1018.67	678.78	508.83	Х	Х	Х	Х
B10	2214.38	1106.68	737.45	552.84	Х	Х	Х	Х
Y0	43.09	21.04	13.69	10.02	x	X	Х	X
Y1	219.12	109.06	72.37	54.02	Х	Х	Х	Х
Y2	502.16	250.57	166.71	124.78	Х	Х	Х	Х
Y3	678.19	338.59	225.39	168.79	Х	Х	Х	Х
Y4	961.22	480.11	319.74	239.55	Х	Х	Х	Х
Y5	1137.26	568.12	378.41	283.56	Х	Х	Х	Х
Y6	1420.29	709.64	472.76	354.32	Х	Х	Х	Х
Y7	1596.32	797.66	531.44	398.33	Х	Х	Х	Х
Y8	1879.36	939.18	625.78	469.08	Х	Х	Х	Х
Y9	2055.39	1027.19	684.46	513.09	Х	Х	Х	X
C1	220.08	109.54	72.69	54.26	Х	Х	Х	Х
C2	396.11	197.55	131.37	98.27	Х	Х	Х	Х
C3	679.15	339.07	225.71	169.03	Х	Х	Х	Х
C4	855.18	427.09	284.39	213.04	Х	Х	Х	Х
C5	1138.22	568.61	378.73	283.80	X	X	X	Х

**Supplementary Table 42**. CCS of B, Y, C and Z (-SO<sub>3</sub>) ions identified in a dp10 GlcNAc6S-[I-GlcNAc6S]<sub>4</sub>-I-R<sub>2</sub> structure, where R<sub>2</sub> is C<sub>7</sub>H<sub>7</sub>O.

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

<sup>1</sup> Columns represent different charge states.

#28								
	GlcNAc6S	G-[G-GlcNAc6S]	]4-G-R <sub>2</sub>					
	$(1-)^1$	(2-)	(3-)	(4-)	(1-)	(2-)	(3-)	(4-)
B1	202.07	100.53	66.69	49.76	х	Х	Х	Х
B2	378.10	188.55	125.36	93.77	$111.3 (0.2)^2$	Х	Х	Х
B3	661.14	330.07	219.71	164.53	159.9 (0.2)	Х	Х	Х
B4	837.17	418.08	278.39	208.54	Х	Х	Х	Х
B5	1120.21	559.60	372.73	279.30	Х	214.4 (0.8)	Х	Х
B6	1296.24	647.62	431.41	323.30	Х	Х	Х	Х
B7	1579.28	789.13	525.75	394.06	Х	Х	300.8 (0.5)	Х
B8	1755.31	877.15	584.43	438.07	X	х	x	х
B9	2038.34	1018.67	678.78	508.83	Х	Х	Х	Х
B10	2214.38	1106.68	737.45	552.84	Х	Х	X	Х
Y0	43.09	21.04	13.69	10.02	X	X	X	Х
Y1	219.12	109.06	72.37	54.02	х	х	х	х
Y2	502.16	250.57	166.71	124.78	Х	Х	X	Х
Y3	678.19	338.59	225.39	168.79	Х	Х	Х	Х
Y4	961.22	480.11	319.74	239.55	Х	Х	Х	Х
Y5	1137.26	568.12	378.41	283.56	Х	Х	Х	Х
Y6	1420.29	709.64	472.76	354.32	Х	Х	Х	Х
Y7	1596.32	797.66	531.44	398.33	Х	х	х	х
Y8	1879.36	939.18	625.78	469.08	Х	Х	Х	Х
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	Х	X	Х
C5	1138.22	568.61	378.73	283.80	х	Х	x	Х

**Supplementary Table 43**. CCS of B, Y, C and Z (-SO<sub>3</sub>) ions identified in a dp10 GlcNAc6S-[G-GlcNAc6S]<sub>4</sub>-G-R<sub>2</sub> structure, where R<sub>2</sub> is C<sub>7</sub>H<sub>7</sub>O.

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

362 <sup>1</sup> 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<sub>3</sub> ions identified in disaccharide  $\Delta$ UA2S-
- 370 GlcNS3S6S structure.

#29				
ΔUA	A2S-GlcNS3S6	S		
	- 1 <b>SO</b> <sub>3</sub>	- 1SO <sub>3</sub>	- 1SO <sub>3</sub>	- 1 <b>SO</b> <sub>3</sub>
	$(1-)^1$	(2-)	(1-)	(2-)
B1	157.01	78.00	$69.4 (0.1)^2$	Х
Y0	337.99	168.49	Х	106 (0.5)
C1	175.02	87.01	Х	Х
Z0	319.97	159.48	х	х

- <sup>1</sup> Columns represent different charge states.
- <sup>2</sup> Each CCS is an average of independent measurements with the corresponding standard deviation

374

**Supplementary Table 45**. CCS of B, Y, C and Z -SO<sub>3</sub> ions identified in tetraaccharide  $\Delta$ UA-GlcNS-

377 IdoA2S-GlcNS3S structure.

#30				
ΔUA-				
	- 1SO <sub>3</sub>	- 1SO <sub>3</sub>	- 1SO <sub>3</sub>	- 1SO <sub>3</sub>
	$(1-)^1$	(2-)	(1-)	(2-)
B1	77.06	38.02	Х	Х
B2	318.08	158.54	99.5 $(0.5)^2$	Х
B3	574.07	286.53	141.4 (0.1)	150.5 (0.1)
Y0	258.03	128.51	85.3 (0.1)	Х
Y1	514.02	256.50	Х	133.0 (0.5)
Y2	755.04	377.02	Х	172.8 (0.1)
C1	95.07	47.03	Х	Х
C2	336.09	167.54	X	X
C3	592.08	295.54	X	148.5 (0.4)

378

<sup>1</sup> Columns represent different charge states.

 $^{2}$  Each CCS is an average of independent measurements with the corresponding standard deviation

381
**Supplementary Table 46**. CCS of B, Y, C and Z -SO<sub>3</sub> ions identified in tetrasaccharide  $\Delta$ UA-GlcNS6S-

384 GlcA-GlcNS3S6S structure.

#31				
UA-GlcNS6	5S-G-GlcN	S3S6S		
	- 1SO <sub>3</sub>	- 1 <b>SO</b> <sub>3</sub>	- 1SO <sub>3</sub>	- 1SO <sub>3</sub>
	$(1-)^1$	(2-)	(1-)	(2-)
B1	77.06	38.02	Х	Х
B2	398.04	198.52	Х	Х
B3	574.07	286.53	$140.9 (0.5)^2$	151.1 (0.3)
YO	337.99	168.49	X	105.8 (0.3)
Y1	514.02	256.50	Х	133.5 (0.5)
Y2	835.00	417.00	Х	Х
C1	95.07	47.03	X	X
C2	416.05	207.52	Х	Х
C3	592.08	295.54	133.5 (0.5)	Х
Z0	319.97	159.48	X	X
Z1	496.01	247.50	Х	Х
Z2	816.99	407.99	Х	Х

385

386 <sup>1</sup> Columns represent different charge states.

 $^{2}$  Each CCS is an average of independent measurements with the corresponding standard deviation

388

**Supplementary Table 47**. CCS of B, Y, C and Z -SO<sub>3</sub> ions identified in tetrasaccharide  $\Delta$ UA-

391 GlcNAc6S-GlcA-GlcNS3S6S structure.

#32				
ΔUA- <b>(</b>				
	- 1SO <sub>3</sub>	- 1 <b>SO</b> <sub>3</sub>	- 1SO <sub>3</sub>	- 1SO <sub>3</sub>
	$(1-)^1$	(2-)	(1-)	(2-)
B1	77.06	38.02	Х	х
B2	360.09	179.54	Х	х
B3	536.13	267.56	$136.7 (0.2)^2$	х
Y0	337.99	168.49	X	X
Y1	514.02	256.50	х	х
Y2	797.05	398.02	Х	Х
C1	05.07	47.02		
CI	95.07	47.03	X	X
C2	378.10	188.55	X	Х
C3	554.14	276.56	138.13 (0.2)	Х
ZO	319.97	159.48	Х	Х
Z1	496.01	247.50	Х	х
Z2	779.04	389.02	Х	х

392

<sup>1</sup>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<sub>3</sub>) ions identified in a hexasaccharide G-GlcNS6S-G-GlcNS6S-I2S-GlcNS6S-R<sub>1</sub> structure, where  $R_1$  is (CH<sub>2</sub>)<sub>5</sub>NH<sub>2</sub>. 

#33						
G-GlcNS6	S-G-GlcNS	6S-I2S-Glo	NS6S-R <sub>1</sub>			
	- 1SO3	- 1SO3	- 1SO3	- 1SO3	- 1SO3	- 1 <b>SO</b> <sub>3</sub>
	$(1-)^1$	(2-)	(3-)	(1-)	(2-)	(3-)
B1	95.07	47.03	31.02	Х	Х	х
B2	416.05	207.52	138.01	х	$122.2 (0.6)^2$	х
B3	592.08	295.54	196.69	Х	152.5 (0.2)	Х
B4	913.06	456.03	303.68	Х	Х	216.5 (0.3)
B5	1169.05	584.02	389.01	Х	Х	Х
B6	1490.04	744.51	496.01	х	Х	х
YO	22.14	10.56	671	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	Х	X	Х
Y4	1096.12	547.56	364.70	х	Х	246.3 (0.6)
Y5	1417.10	708.05	471.70	Х	Х	Х
C1	112.08	56.04	37.02	v	v	v
$C^2$	134.06	216.53	144.01	X	X	X
C2	610.00	304 54	202.69	x	X V	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
	1000.00	100102	002.01			
ZO	4.12	1.56	0.70	X	Х	X
Z1	325.11	162.05	107.70	Х	Х	Х
Z2	581.10	290.04	193.03	Х	Х	Х
Z3	902.08	450.54	300.02	х	Х	х
Z4	1078.11	538.55	358.70	x	X	x
Z5	1399.09	699.04	465.69	Х	Х	х

<sup>1</sup> Columns represent different charge states. 

<sup>2</sup> Each CCS is an average of independent measurements with the corresponding standard deviation 

**Supplementary Table 49**. CCS of B, Y, C and Z (-SO<sub>3</sub>) ions identified in a hexasaccharide G-GlcNS6S-G-GlcNS3S-I2S-GlcNS6S-R<sub>1</sub> structure, where  $R_1$  is (CH<sub>2</sub>)<sub>5</sub>NH<sub>2</sub>. 

#34						
G-GlcNS6S	-G-GlcNS3S-	I2S-GlcNS6S	-R <sub>1</sub>			
	- 1SO3	- 1SO <sub>3</sub>	- 1SO3	- 1SO3	- 1 <b>SO</b> <sub>3</sub>	- 1 <b>SO</b> 3
	$(1-)^1$	(2-)	(3-)	(1-)	(2-)	(3-)
B1	95.07	47.03	31.02	Х	х	Х
B2	416.05	207.52	138.01	х	$121.8 (0.4)^2$	Х
B3	592.08	295.54	196.69	139.1 (0.3)	Х	Х
B4	913.06	456.03	303.68	Х	Х	Х
B5	1169.05	584.02	389.01	Х	Х	Х
B6	1490.04	744.51	496.01	х	х	Х
YO	22.14	10.56	671	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
¥3	920.09	459.54	306.02	х	X	Х
Y4	1096.12	547.56	364.70	Х	209.9 (0.5)	Х
Y5	1417.10	708.05	471.70	Х	Х	Х
C1	113.08	56.04	37.02	X	Х	Х
C2	434.06	216.53	144.01	Х	Х	Х
C3	610.09	304.54	202.69	х	х	Х
C4	931.07	465.03	309.69	х	х	Х
C5	1187.06	593.03	395.02	х	х	Х
C6	1508.05	753.52	502.01	Х	Х	Х
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	х	х	Х
Z5	1399.09	699.04	465.69	Х	Х	Х

<sup>1</sup> Columns represent different charge states. 

<sup>2</sup> Each CCS is an average of independent measurements with the corresponding standard deviation 

**Supplementary Table 50**. CCS of B, Y, C and Z (-SO<sub>3</sub>) ions identified in a hexasaccharide G-GlcNS6S-G-GlcNS6S3S-I2S-GlcNS6S-R<sub>1</sub> structure, where  $R_1$  is  $(CH_2)_5NH_2$ . 

#35						
(	G-GlcNS6S-G-					
	- 1SO <sub>3</sub>	- 1SO <sub>3</sub>	- 1SO <sub>3</sub>	- 1SO <sub>3</sub>	- 1 <b>SO</b> <sub>3</sub>	- 1SO <sub>3</sub>
	$(1-)^1$	(2-)	(3-)	(1-)	(2-)	(3-)
B1	95.07	47.03	31.02	Х	Х	х
B2	416.05	207.52	138.01	Х	122.4 (0.2)	х
B3	592.08	295.54	196.69	139.3 (0.3)	Х	х
B4	993.02	496.01	330.34	Х	Х	х
B5	1249.01	624.00	415.66	Х	Х	х
B6	1569.99	784.49	522.66	Х	Х	Х
Y0	22.14	10.56	6.71	X	X	X
Y1	343.12	171.05	113.70	109.8 (0.2)	Х	х
Y2	599.11	299.05	199.03	X	х	х
Y3	1000.05	499.52	332.68	x	х	x
Y4	1176.08	587.53	391.35	х	х	242.3 (0.5)
Y5	1497.06	748.03	498.35	Х	Х	Х
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	Х	Х	х
C4	1011.03	505.01	336.34	x	х	x
C5	1267.02	633.01	421.67	x	х	x
C6	1588.00	793.50	528.66	Х	Х	Х
70	4.12	1.56	0.70	x	x	x
<u>Z1</u>	325.11	162.05	107.70	x	x	x
72	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	Х	Х

<sup>1</sup> Columns represent different charge states. 

<sup>2</sup> Each CCS is an average of independent measurements with the corresponding standard deviation 

**Supplementary Table 51**. CCS of B, Y, C and Z (-SO<sub>3</sub>) ions identified in a septa-saccharide G-GlcNS-G-GlcNS-I2S-GlcNS-G-GlcNS-G-R<sub>3</sub> structure. 

11 <b>0</b> 4						
#36						
G-GlcNS-G-	GlcNS-I2S-G	lcNS-G-GlcNS-				
	$G-R_3$	100	100	100	100	100
	- 1SO <sub>3</sub>					
	$(1-)^1$	(2-)	(3-)	(1-)	(2-)	(3-)
B1	77.06	38.02	25.01	Х	Х	Х
B2	318.08	158.54	105.36	Х	Х	Х
B3	574.07	286.53	190.69	Х	Х	Х
B4	815.10	407.04	271.03	Х	Х	Х
B5	991.13	495.06	329.70	Х	Х	Х
B6	1232.15	615.57	410.05	Х	Х	Х
B7	1408.19	703.59	468.72	Х	Х	Х
B8	1546.21	772.60	514.73	Х	Х	Х
Y0	58.06	28.53	18.68	Х	Х	Х
Y1	234.09	116.54	77.36	Х	Х	Х
Y2	475.12	237.06	157.70	Х	Х	Х
Y3	651.15	325.07	216.38	Х	Х	Х
Y4	892.18	445.58	296.72	Х	Х	Х
Y5	1148.17	573.58	382.05	Х	Х	Х
Y6	1389.19	694.09	462.39	Х	Х	Х
Y7	1547.21	773.10	515.07	Х	Х	Х
C1	94.06	46.53	30.68	Х	Х	X
C2	335.09	167.04	111.02	Х	Х	х
C3	591.07	295.03	196.35	Х	Х	Х
C4	832.10	415.55	276.69	Х	Х	х
C5	1008.13	503.56	335.37	Х	Х	Х
C6	1249.16	624.07	415.71	Х	Х	Х
C7	1425.19	712.09	474.39	Х	Х	Х
C8	1563.21	781.10	520.40	Х	Х	Х
Z0	40.05	19.52	12.68	Х	Х	X
Z1	216.08	107.54	71.36	Х	Х	Х
Z2	457.11	228.05	151.70	Х	Х	Х
Z3	633.14	316.07	210.38	Х	Х	Х
Z4	874.17	436.58	290.72	Х	Х	Х
Z5	1130.16	564.57	376.05	Х	Х	Х
Z6	1371.18	685.09	456.39	Х	Х	Х
Z7	1546.21	772.60	514.73	х	Х	Х

<sup>1</sup> Columns represent different charge states. 

<sup>2</sup> 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

428 possible hexasaccharide sequences ( $dp6 + 3SO_3 + 1NAc$ ) as a result of one glycosidic bond cleavage in 429 the structure  $\Delta UA$ -GlcNS-UA-GlcNAc-UA2S-GlcNS.

∆UA-GlcN	IS-UA-GlcNA	Ac-UA2S-Glo	cNS	
	(1-)	(2-)	(1-)	(2-)
B1	157.014	78.003	$\checkmark$	Х
B2	398.039	198.516	Х	$\checkmark$
B3	574.071	286.532	$\checkmark$	$\checkmark$
B4	777.151	388.071	Х	Х
B5	1033.140	516.066	Х	Х
Y0	258.028	128.510	x	X
Y1	514.017	256.505	Х	Х
Y2	717.097	358.044	Х	Х
Y3	893.129	446.060	Х	х
Y4	1134.154	566.573	х	Х
C1	175.024	87.008	✓	X
C2	416.050	207.521	~	✓
C3	592.082	295.537	~	✓
C4	795.161	397.077	Х	Х
C5	1051.150	525.071	х	Х
Z0	240.018	119.505	✓	Х
Z1	496.007	247.499	Х	✓
Z2	699.086	349.039	Х	Х
Z3	875.118	437.055	Х	Х
Z4	1116.144	557.568	Х	Х
			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  $\Delta UA$ -GlcNS-UA2S-GlcNS-UA-GlcNAc. 

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

ALLA CLON	A a U.A. ClaN		NIC	
DUA-GICNA	AC-UA-GICN	5-UA25-GIC	ND	
	(1-)	(2-)	(1-)	(2-)
B1	157.014	78.003	✓	Х
B2	360.093	179.543	Х	Х
B3	536.125	267.559	$\checkmark$	Х
B4	777.151	388.071	Х	Х
B5	1033.140	516.066	х	Х
Y0	258.028	128.510	X	Х
Y1	514.017	256.505	Х	Х
Y2	755.043	377.017	Х	Х
Y3	931.075	465.034	Х	Х
Y4	1134.154	566.573	X	Х
C1	175.024	87.008	✓	Х
C2	378.104	188.548	$\checkmark$	Х
C3	554.136	276.564	Х	Х
C4	795.161	397.077	Х	Х
C5	1051.150	525.071	Х	Х
Z0	240.018	119.505	✓	X
Z1	496.007	247.499	Х	✓
Z2	737.032	368.012	Х	Х
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  $\Delta UA$ -GlcNAc-UA2S-GlcNS-UA-GlcNS. 

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

ΔUA2S-GlcNS-UA-GlcNS-UA-GlcNAc					
	(1-)	(2-)	(1-)	(2-)	
B1	236.970	117.981	Х	Х	
B2	477.996	238.494	Х	Х	
B3	654.028	326.510	Х	$\checkmark$	
B4	895.054	447.023	Х	Х	
B5	1071.086	535.039	Х	Х	
Y0	220.082	109.537	Х	Х	
Y1	396.114	197.553	$\checkmark$	Х	
Y2	637.140	318.066	$\checkmark$	Х	
Y3	813.172	406.082	Х	$\checkmark$	
Y4	1054.197	526.595	Х	$\checkmark$	
C1	254.981	126.987	Х	X	
C2	496.007	247.499	Х	✓	
C3	672.039	335.515	Х	Х	
C4	913.064	456.028	Х	Х	
C5	1089.096	544.044	Х	Х	
Z0	202.072	100.532	Х	X	
Z1	378.104	188.548	$\checkmark$	Х	
Z2	619.129	309.061	$\checkmark$	Х	
Z3	795.161	397.077	Х	Х	
Z4	1036.187	517.590	Х	Х	
			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  $\Delta UA2S$ -GlcNS-UA-GlcNAc-UA-GlcNS. 

∆UA2S-Glc	NS-UA-GlcN	Ac-UA-GlcNS	5	
	(1-)	(2-)	(1-)	(2-)
B1	236.970	117.981	Х	Х
B2	477.996	238.494	Х	Х
B3	654.028	326.510	Х	✓
B4	857.107	428.050	Х	Х
B5	1033.140	516.066	Х	Х
Y0	258.028	128.510	Х	X
Y1	434.060	216.526	Х	Х
Y2	637.140	318.066	$\checkmark$	Х
Y3	813.172	406.082	Х	✓
Y4	1054.197	526.595	Х	✓
C1	254.981	126.987	X	X
C2	496.007	247.499	Х	✓
C3	672.039	335.515	Х	Х
C4	875.118	437.055	Х	Х
C5	1051.150	525.071	Х	Х
Z0	240.018	119.505	✓	X
Z1	416.050	207.521	✓	✓
Z2	619.129	309.061	✓	Х
Z3	795.161	397.077	Х	Х
Z4	1036.187	517.590	Х	Х
			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. 

	B/C/Y/Z
Possible structures	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

#HS1				
ΔUA-GlcNS-I2S	S-GlcNS-G-GlcN	Ac		
[M-3H] <sup>3-</sup>	430.05	274.0 (0.6)		
	$(1-)^1$	(2-)	(1-)	(2-)
B1	157.014	78.003	70.5 (0.9)	Х
B2	398.039	198.516	110.1 (0.8)	119.6 (0.4)
B3	654.028	326.510	Х	162.0 (0.7)
B4	895.054	447.023	Х	201.0 (0.7)
B5	1071.086	535.039	Х	Х
Y0	220.082	109.537	Х	Х
Y1	396.114	197.553	116.1 (0.5)	х
Y2	637.140	318.066	151.8 (0.5)	Х
Y3	893.129	446.060	Х	х
Y4	1134.154	566.573	Х	X
C1	175.024	87.008	71.0 (0.6)	Х
C2	416.050	207.521	113.6 (0.4)	х
C3	672.039	335.515	Х	164.0 (0.8)
C4	913.064	456.028	Х	х
C5	1089.096	544.044	Х	Х
Z0	202.072	100.532	Х	Х
Z1	378.104	188.548	113.8 (0.6)	х
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	Х	Х

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

486 <sup>1</sup> Columns represent different charge states.

 $^{2}$  Each CCS is an average of independent measurements with the corresponding standard deviation

489	Supplementary Table 60	CCS of B, Y, C and Z	(-SO <sub>3</sub> ) ions identified in a	hexasaccharide ∆UA-GlcNS-
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490 I2S-GlcNS-G-GlcNAc structure.

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

492 <sup>1</sup> Columns represent different charge states.

<sup>2</sup> 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 498 possible hexasaccharide sequences ( $dp6 + 5SO_3 + 1NAc$ ) as a result of one glycosidic bond cleavage in

499 the structure  $\Delta$ UA-GlcNS-UA-GlcNAc6S-UA2S-GlcNS6S.

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

**Supplementary Table 62.** Summary of B, Y, C and Z ions theoretically identified from one of the six 504 possible hexasaccharide sequences ( $dp6 + 5SO_3 + 1NAc$ ) as a result of one glycosidic bond cleavage in 505 the structure  $\Delta UA$ -GlcNS-UA2S-GlcNS6S-UA-GlcNAc6S.

ΔUA	A-GlcNS-UA28	5				
	(1-)	(2-)	(3-)	(1-)	(2-)	(3-)
B1	157.014	78.003	51.666	✓	Х	х
B2	398.039	198.516	132.008	✓	$\checkmark$	х
B3	654.028	326.510	217.338	$\checkmark$	$\checkmark$	х
B4	975.011	487.001	324.332	х	$\checkmark$	Х
B5	1151.043	575.017	383.009	Х	Х	✓
Y0	300.039	149.516	99.341	✓	Х	x
Y1	476.071	237.532	158.018	~	$\checkmark$	х
Y2	797.053	398.023	265.013	х	Х	$\checkmark$
Y3	1053.042	526.017	350.342	х	Х	$\checkmark$
Y4	1294.068	646.530	430.684	Х	Х	$\checkmark$
C1	175.024	87.008	57.670	✓	Х	х
C2	416.050	207.521	138.011	✓	Х	х
C3	672.039	335.515	223.341	✓	Х	х
C4	993.021	496.007	330.335	х	Х	х
C5	1169.053	584.023	389.013	Х	$\checkmark$	Х
Z0	282.028	140.510	93.338	✓	Х	х
Z1	458.060	228.526	152.015	✓	$\checkmark$	Х
Z2	779.043	389.018	259.009	х	Х	$\checkmark$
Z3	1035.032	517.012	344.339	х	Х	х
Z4	1276.057	637.525	424.681	х	Х	$\checkmark$
				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  $\Delta UA$ -GlcNAc6S-UA-GlcNS-UA2S-GlcNS6S 

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

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

ΔUA2S-GlcNS6S-UA-GlcNS-UA-GlcNAc6S						
	(1-)	(2-)	(3-)	(1-)	(2-)	(3-)
B1	236.970	117.981	78.318	Х	Х	Х
B2	557.953	278.473	185.312	Х	Х	Х
B3	733.985	366.489	243.990	Х	Х	Х
B4	975.011	487.001	324.332	Х	Х	Х
B5	1151.043	575.017	383.009	Х	$\checkmark$	Х
Y0	300.039	149.516	99.341	✓	Х	Х
Y1	476.071	237.532	158.018	✓	$\checkmark$	Х
Y2	717.097	358.044	238.360	✓	$\checkmark$	Х
Y3	893.129	446.060	297.038	Х	~	Х
Y4	1214.111	606.552	404.032	Х	Х	Х
C1	254.981	126.987	84.322	✓	Х	Х
C2	575.963	287.478	191.316	х	Х	Х
C3	751.996	375.494	249.993	х	Х	Х
C4	993.021	496.007	330.335	х	$\checkmark$	Х
C5	1169.053	584.023	389.013	х	$\checkmark$	$\checkmark$
Z0	282.028	140.510	93.338	~	X	X
Z1	458.060	228.526	152.015	✓	✓	Х
Z2	699.086	349.039	232.357	х	✓	Х
Z3	875.118	437.055	291.034	х	х	х
Z4	1196.101	597.546	398.028	Х	Х	Х
				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  $\Delta UA2S$ -GlcNS6S-UA-GlcNAc6S-UA-GlcNS 

ΔUA	A2S-GlcNS6S-	5				
	(1-)	(2-)	(3-)	(1-)	(2-)	(3-)
B1	236.970	117.981	78.318	х	Х	х
B2	557.953	278.473	185.312	х	Х	Х
B3	733.985	366.489	243.990	х	Х	х
B4	1017.021	508.007	338.335	х	х	Х
B5	1193.053	596.023	397.013	Х	Х	Х
Y0	258.028	128.510	85.338	х	х	X
Y1	434.060	216.526	144.015	$\checkmark$	$\checkmark$	Х
Y2	717.097	358.044	238.360	~	✓	Х
Y3	893.129	446.060	297.038	х	~	Х
Y4	1214.111	606.552	404.032	Х	Х	Х
C1	254.981	126.987	84.322	Х	х	X
C2	575.963	287.478	191.316	х	Х	Х
C3	751.996	375.494	249.993	х	х	Х
C4	1035.032	517.012	344.339	х	✓	Х
C5	1211.064	605.028	403.016	Х	х	Х
Z0	240.018	119.505	79.334	✓	х	X
Z1	416.050	207.521	138.011	~	✓	Х
Z2	699.086	349.039	232.357	х	✓	Х
Z3	875.118	437.055	291.034	х	X	X
Z4	1196.101	597.546	398.028	х	Х	Х
				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
∆UA2S-GlcNS6S-UA-GlcNS-UA-GlcNAc6S	11
ΔUA2S-GlcNS6S-UA-GlcNAc6S-UA-GlcNS	7

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

541 GlcNAc6S structure.

#HS2						
ΔUA-GlcNS	S-I2S-GlcNS6	S-G-GlcNAc6S				
[M-2H] <sup>2-</sup>	362.26	$331.0(0.2)^2$				
[M-3H] <sup>3-</sup>	483.35	265.7 (0.4)				
	$(1-)^1$	(2-)	(3-)	(1-)	(2-)	(3-)
B1	157.014	78.003	51.666	70.4 (0.8)	Х	x
B2	398.039	198.516	132.008	110.3 (0.5)	Х	Х
B3	654.028	326.510	217.338	х	162.4 (0.2)	х
B4	975.011	487.001	324.332	X	225.3 (0.5)	X
B5	1151.043	575.017	383.009	x	Х	272.9 (0.4)
Y0	300.039	149.516	99.341	94.7 (0.3)	Х	X
Y1	476.071	237.532	158.018	123.2 (0.5)	134.1 (0.5)	Х
Y2	797.053	398.023	265.013	Х	Х	199.6 (0.6)
Y3	1053.042	526.017	350.342	Х	Х	250.4 (0.5)
Y4	1294.068	646.530	430.684	X	Х	276.9 (0.4)
C1	175.024	87.008	57 670	70.4 (0.6)	v	v
C2	416.050	207 521	138.011	70.4 (0.0) 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	Х	Х	Х
Z0	282.028	140.510	93.338	93.2 (0.5)	Х	X
Z1	458.060	228.526	152.015	120.5 (0.3)	X	X
Z2	779.043	389.018	259.009	X	Х	Х
Z3	1035.032	517.012	344.339	X	Х	X
Z4	1276.057	637.525	424.681	х	Х	х

<sup>1</sup> Columns represent different charge states.

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<sup>&</sup>lt;sup>2</sup> Each CCS is an average of independent measurements with the corresponding standard deviation

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

Supplementary Table 69. CCS of B, Y, C and Z (-SO<sub>3</sub>) ions identified in a hexasaccharide  $\Delta$ UA-GlcNS-I2S-GlcNS6S-G-GlcNAc6S structure.

<sup>1</sup> Columns represent different charge states.

<sup>2</sup> Each CCS is an average of independent measurements with the corresponding standard deviation