**Supporting Information.** Distributions of  $D_x A_y$  species for chito-oligomers from DP 3 to DP 7 as a function of the average DA, and MALDI-TOF mass spectrum assignments of the series of chito-oligomers.



**Figure 1.** Distributions of  $D_xA_y$  species for chito-oligomers of DP 3 as a function of the average DA (- $\blacktriangle$ - experimental distribution from MALDI-TOF MS analysis, - $\blacksquare$ - modelling distribution, D, for GlcN and A, for GlcNAc).



**Figure 2.** Distributions of  $D_x A_y$  species for chito-oligomers of DP 4 as a function of the average DA (- $\blacktriangle$ - experimental distribution from MALDI-TOF MS analysis, - $\blacksquare$ - modelling distribution, D, for GlcN and A, for GlcNAc).



Sample 5 (DA = 80 %)





Sample 3 (DA = 40 %)









**Figure 3.** Distributions of  $D_x A_y$  species for chito-oligomers of DP 5 as a function of the average DA (- $\blacktriangle$ - experimental distribution from MALDI-TOF MS analysis, - $\blacksquare$ - modelling distribution, D, for GlcN and A, for GlcNAc).



Sample 5 (DA = 80 %)









D2A4

D1A5

D0A6

D3A3







**Figure 4.** Distributions of  $D_x A_y$  species for chito-oligomers of DP 6 as a function of the average DA (- $\blacktriangle$ - experimental distribution from MALDI-TOF MS analysis, - $\blacksquare$ - modelling distribution, D, for GlcN and A, for GlcNAc).



Sample 5 (DA = 80 %)





Sample 3 (DA = 40 %)









**Figure 5.** Distributions of  $D_x A_y$  species for chito-oligomers of DP 7 as a function of the average DA (- $\blacktriangle$ - experimental distribution from MALDI-TOF MS analysis, - $\blacksquare$ - modelling distribution, D, for GlcN and A, for GlcNAc).

DP	Species <sup>a</sup>	$\mathrm{DA_{th}}\left(\% ight)^{\mathrm{b}}$	Peak assignment	theoretical mono- isotopic mass (m/z)		MALDI-TOF MS peak intensity <sup>c</sup>					
					Sample	2	3	4	5	6	
3	$D_3A_0$	0	$[D_3A_0 + H_2O + Na]^+$	524.2		1474	1562	1071	104	0	
	$D_2A_1$	33	$[D_2A_1 + H_2O + Na]^+$	566.2		3453	4762	2131	1275	655	
	$D_1A_2$	67	$[D_1A_2 + H_2O + Na]^+$	608.2		1049	3406	3236	7552	6535	
	$D_0A_3$	100	$[D_0A_3 + H_2O + Na]^+$	650.2		0	415	765	5232	9280	
4	$D_4A_0$	0	$[D_4A_0 + H_2O + Na]^+$	685.3		1714	970	0	0	0	
	$D_3A_1$	25	$[D_3A_1 + H_2O + Na]^+$	727.3		4317	5191	1504	0	0	
	$D_2A_2$	50	$[D_2A_2 + H_2O + Na]^+$	769.3		2332	6753	5123	3075	991	
	$D_1A_3$	75	$[D_1A_3 + H_2O + Na]^+$	811.3		452	2206	3693	8937	7035	
	$D_0A_4$	100	$[D_0A_4 + H_2O + Na]^+$	853.3		0	242	550	3996	10463	
5	$D_5A_0$	0	$[D_5A_0 + H_2O + Na]^+$	846.3		1496	425	0	0	0	
	$D_4A_1$	20	$[D_4A_1 + H_2O + Na]^+$	888.3		3491	4149	620	0	0	
	$D_3A_2$	40	$[D_3A_2 + H_2O + Na]^+$	930.4		3172	7947	3497	392	0	
	$D_2A_3$	60	$[D_2A_3 + H_2O + Na]^+$	972.4		1004	5357	6486	3841	1262	
	$D_1A_4$	80	$[D_1A_4 + H_2O + Na]^+$	1014.4		0	1245	3273	7028	7124	
	$D_0A_5$	100	$[D_0A_5 + H_2O + Na]^+$	1056.4		0	0	454	2551	9781	
6	$D_6A_0$	0	$[D_6A_0 + H_2O + Na]^+$	1007.4		729	0	0	0	0	
	$D_5A_1$	17	$[D_5A_1 + H_2O + Na]^+$	1049.4		2371	1757	0	0	0	
	$D_4A_2$	33	$[D_4A_2 + H_2O + Na]^+$	1091.4		2343	4716	1416	0	0	
	$D_3A_3$	50	$[D_3A_3 + H_2O + Na]^+$	1133.4		1293	5621	4470	751	0	
	$D_2A_4$	67	$[D_2A_4 + H_2O + Na]^+$	1175.4		305	2547	4736	3513	1209	
	$D_1A_5$	83	$[D_1A_5 + H_2O + Na]^+$	1217.5		0	420	2040	4569	5768	
	$D_0A_6$	100	$[D_0A_6 + H_2O + Na]^+$	1259.5		0	0	417	1589	5256	
7	$D_7A_0$	0	$[D_7A_0 + H_2O + Na]^+$	1168.5		276	0	0	0	0	
	$D_6A_1$	14	$[D_6A_1 + H_2O + Na]^+$	1210.5		1234	710	0	0	0	
	$D_5A_2$	29	$[D_5A_2 + H_2O + Na]^+$	1252.5		1065	1912	267	0	0	
	$D_4A_3$	43	$[D_4A_3 + H_2O + Na]^+$	1294.5		722	2470	1057	0	0	
	$D_3A_4$	57	$[D_3A_4 + H_2O + Na]^+$	1336.5		266	2059	2385	667	0	
	$D_2A_5$	71	$[D_2A_5 + H_2O + Na]^+$	1378.5		0	672	2184	1828	973	
	$D_1A_6$	86	$[D_1A_6 + H_2O + Na]^+$	1420.5		0	0	727	1848	2225	
	$D_0A_7$	100	$[D_0A_7 + H_2O + Na]^+$	1462.6		0	0	260	619	2202	

Table 1. Detailed MALDI-TOF mass spectrometry analyses of the series of chito-oligomers.

<sup>*a*</sup>D for GlcN, A for GlcNAc, <sup>*b*</sup> for each  $D_x A_y$  oligomer,  $DA_{th}(\%) = \frac{y}{x+y} \times 100$ ; <sup>*c*</sup> intensity value in arbitrary unit.