Identification of differential N-glycans in the serum and tissue of colon cancer patients by mass spectrometry

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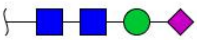
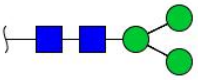
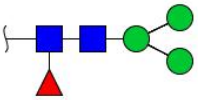
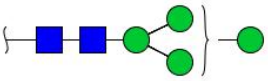
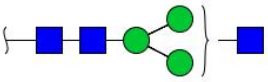
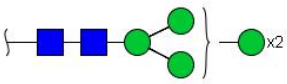
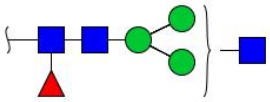
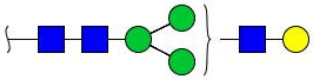
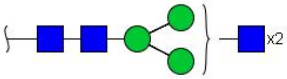
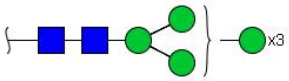
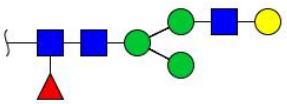
Supplemental material 1

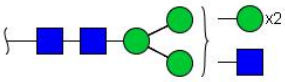
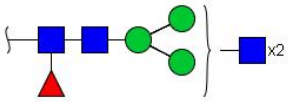
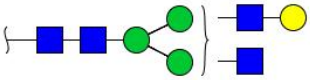
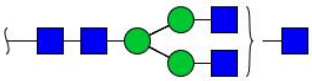
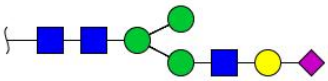
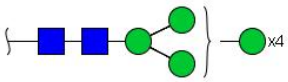
Table S1. Clinicodemographic characteristics of healthy individuals (control group) (n=11)

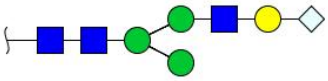
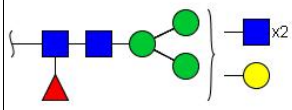
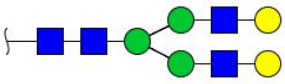
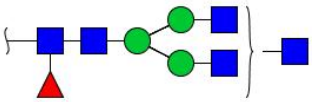
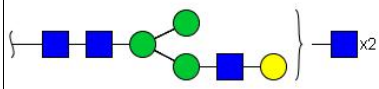
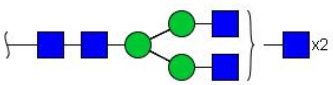
Individuals	Genre	Age (years)	Indication	Colonoscopy
1	F	67	SCREENING	Normal
2	F	68	SCREENING	Diverticular disease
3	F	53	SCREENING	Normal
4	F	50	SCREENING	Normal
5	M	58	SCREENING	Diverticular disease
6	M	55	SCREENING	Normal
7	M	56	SCREENING	Normal
8	M	57	SCREENING	Normal
9	M	61	SCREENING	Diverticular disease
10	M	61	SCREENING	Normal
11	F	52	SCREENING	Normal

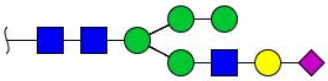
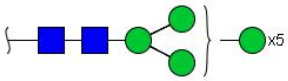
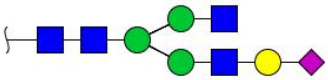
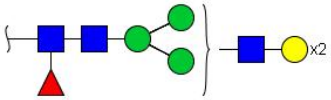
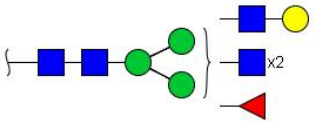
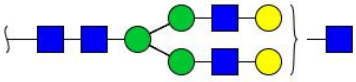
Table S2. N-glycan number, structure, accurate mass, mass used for quantification, corresponding adduct and the heavy reference number used for LC-MS and MALDI MS quantification methods.

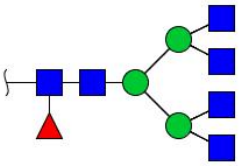
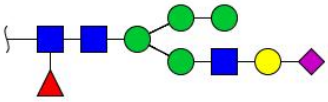
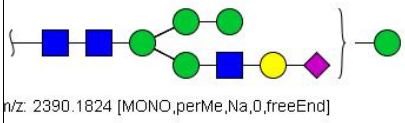
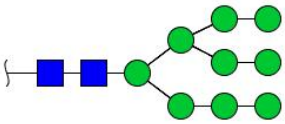
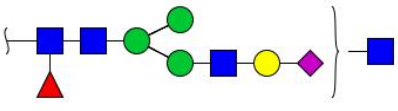
Number	Proposed structure, theoretical mass and composition	Mass used for LCMS based quantification [a]	Adduct	Serum Heavy reference [b]		Structure confirmed by MS/MS data [c]
				LC-MS	MALDI	
1	 m/z: 1124.5572 [MONO,perMe,Na,0,freeEnd] HexNAc2Hex1NeuAc1	1124.5572	$[M+Na]^+$	13	-	-
2	 m/z: 1171.5831 [MONO,perMe,Na,0,freeEnd] HexNAc2Hex3	1171.5831	$[M+Na]^+$	13	-	-
3	 m/z: 1345.6723 [MONO,perMe,Na,0,freeEnd] HexNAc2Hex3Fuc1	1345.6723	$[M+Na]^+$	13	-	-
4*	 m/z: 1375.6828 [MONO,perMe,Na,0,freeEnd] HexNAc2Hex4	1375.6828*	$[M+Na]^+$	13	-	-
5	 m/z: 1416.7094 [MONO,perMe,Na,0,freeEnd] HexNAc3Hex3	1416.7094	$[M+Na]^+$	13	-	✓✓

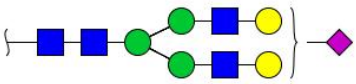
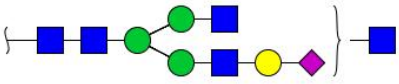
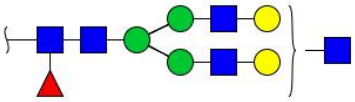
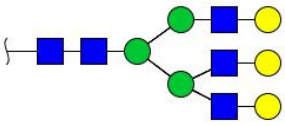
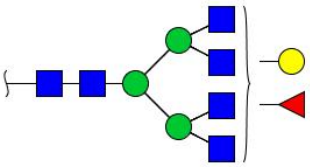
6	 m/z: 1579.7826 [MONO,perMe,Na,0,freeEnd] HexNAc2Hex5	1579.7826	$[M+Na]^+$	52	6	✓
7	 m/z: 1590.7986 [MONO,perMe,Na,0,freeEnd] HexNAc3Hex3Fuc1	1590.7986	$[M+Na]^+$	27	-	-
8	 m/z: 1620.8091 [MONO,perMe,Na,0,freeEnd] HexNAc3Hex4	1620.8090	$[M+Na]^+$	19	-	*
9	 m/z: 1661.8357 [MONO,perMe,Na,0,freeEnd] HexNAc4Hex3	842.4125*	$[M+2Na]^+$	13	-	✓✓
10	 m/z: 1783.8824 [MONO,perMe,Na,0,freeEnd] HexNAc2Hex6	903.4358	$[M+2Na]^{2+}$	52	6	✓✓
11	 m/z: 1794.8984 [MONO,perMe,Na,0,freeEnd] HexNAc3Hex4Fuc1	908.9438	$[M+2Na]^{2+}$	27	-	-

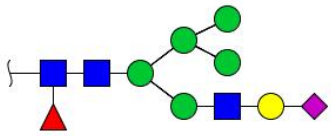
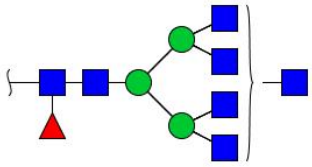
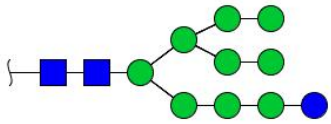
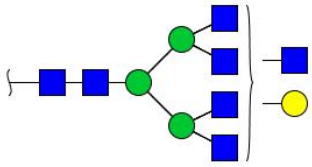
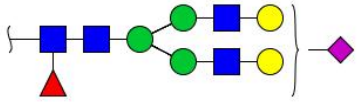
12	 m/z: 1824.9089 [MONO,perMe,Na,0,freeEnd] HexNAc3Hex5	1824.9089	$[M+Na]^+$	52	-	-
13	 m/z: 1835.9249 [MONO,perMe,Na,0,freeEnd] HexNAc4Hex3Fuc1	929.4571	$[M+2Na]^{2+}$	13	13	✓✓
14	 m/z: 1865.9355 [MONO,perMe,Na,0,freeEnd] HexNAc4Hex4	1865.9355	$[M+Na]^+$	19	**19**	✓✓
15	 m/z: 1906.9620 [MONO,perMe,Na,0,freeEnd] HexNAc5Hex3	964.9756	$[M+2Na]^{2+}$	13	-	-
16	 m/z: 1981.9828 [MONO,perMe,Na,0,freeEnd] HexNAc3Hex4NeuAc1	1002.4860	$[M+2Na]^{2+}$	16	-	✓✓
17	 m/z: 1987.9821 [MONO,perMe,Na,0,freeEnd] HexNAc2Hex7	1005.4857*	$[M+2Na]^{2+}$	52	6	✓✓

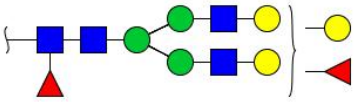
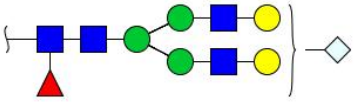
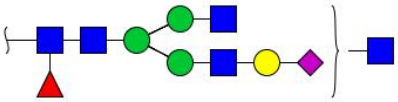
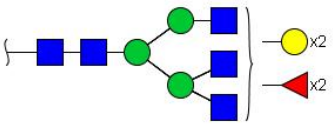
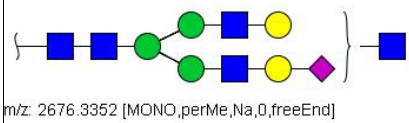
18	 m/z: 2011.9934 [MONO,perMe,Na,0,freeEnd] HexNAc3Hex4NeuGc1	1017.4913	$[M+2Na]^{2+}$	35	-	-
19	 m/z: 2040.0247 [MONO,perMe,Na,0,freeEnd] HexNAc4Hex4Fuc1	1031.5070	$[M+2Na]^{2+}$	19	19	✓✓
20	 m/z: 2070.0352 [MONO,perMe,Na,0,freeEnd] HexNAc4Hex5	1046.5122	$[M+2Na]^{2+}$	52	27	✓✓
21	 m/z: 2081.0512 [MONO,perMe,Na,0,freeEnd] HexNAc5Hex3Fuc1	1052.0202	$[M+2Na]^{2+}$	13	13	-
22	 m/z: 2111.0618 [MONO,perMe,Na,0,freeEnd] HexNAc5Hex4	1067.0255	$[M+2Na]^{2+}$	19	-	*
23	 m/z: 2152.0883 [MONO,perMe,Na,0,freeEnd] HexNAc6Hex3	1087.5388*	$[M+2Na]^{2+}$	13	-	✓

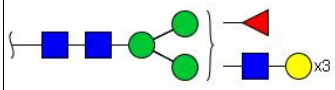
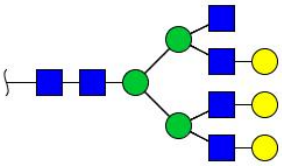
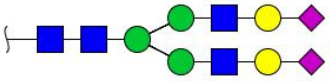
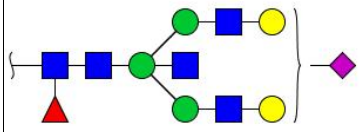
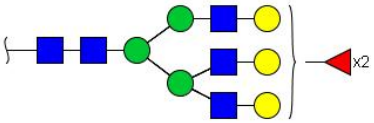
24	 m/z: 2186.0826 [MONO,perMe,Na,0,freeEnd] HexNAc3Hex5NeuAc1	1104.5359*	$[M+2Na]^{2+}$	52	35	✓✓
25	 m/z: 2192.0819 [MONO,perMe,Na,0,freeEnd] HexNAc2Hex8	1107.5356	$[M+2Na]^{2+}$	52	6	✓✓
26	 m/z: 2227.1091 [MONO,perMe,Na,0,freeEnd] HexNAc4Hex4NeuAc1	1125.0492	$[M+2Na]^{2+}$	26	35	✓✓
27	 m/z: 2244.1245 [MONO,perMe,Na,0,freeEnd] HexNAc4Hex5Fuc1	1133.5568	$[M+2Na]^{2+}$	27	27	✓✓
28	 m/z: 2285.1510 [MONO,perMe,Na,0,freeEnd] HexNAc5Hex4Fuc1	1154.0701	$[M+2Na]^{2+}$	19	19	✓
29	 m/z: 2315.1616 [MONO,perMe,Na,0,freeEnd] HexNAc5Hex5	1169.0754	$[M+2Na]^{2+}$	27	-	-

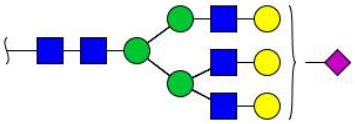
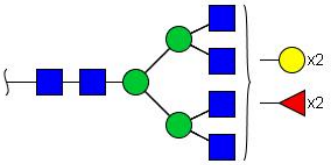
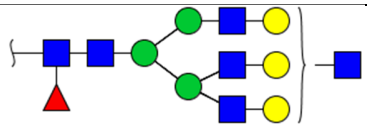
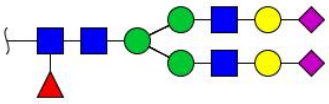
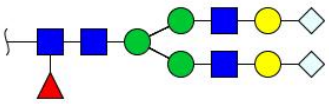
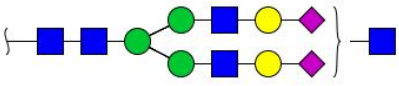
30	 m/z: 2326.1776 [MONO,perMe,Na,0,freeEnd] HexNAc6Hex3Fuc1	1174.5834	$[M+2Na]^{2+}$	13	-	-
31	 m/z: 2360.1718 [MONO,perMe,Na,0,freeEnd] HexNAc3Hex5Fuc1NeuAc1	1191.5805	$[M+2Na]^{2+}$	27	-	✓✓
32	 m/z: 2390.1824 [MONO,perMe,Na,0,freeEnd] HexNAc3Hex6NeuAc1	1206.5858	$[M+2Na]^{2+}$	52	35	✓✓
33	 m/z: 2396.1817 [MONO,perMe,Na,0,freeEnd] HexNAc2Hex9	1209.5855	$[M+2Na]^{2+}$	52	6	✓✓
34	 m/z: 2401.1983 [MONO,perMe,Na,0,freeEnd] HexNAc4Hex74Fuc1NeuAc1	1220.0808	$[M+Na+K]^{2+}$	34	-	✓✓

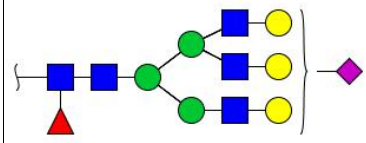
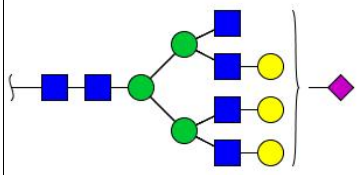
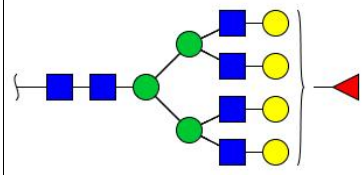
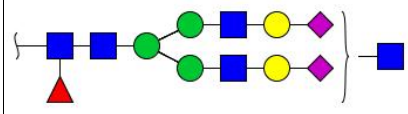
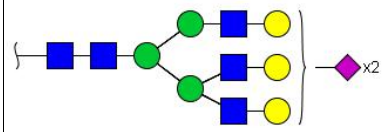
35	 m/z: 2431.2089 [MONO,perMe,Na,0,freeEnd] HexNAc4Hex5NeuAc1	1227.0991	$[M+2Na]^{2+}$	35	35	✓✓
36	 m/z: 2472.2355 [MONO,perMe,Na,0,freeEnd] HexNAc5Hex4NeuAc1	1247.6123	$[M+2Na]^{2+}$	52	-	✓✓
37	 m/z: 2489.2508 [MONO,perMe,Na,0,freeEnd] HexNAc5Hex5Fuc1	1256.1200	$[M+2Na]^{2+}$	27	27	-
38	 m/z: 2519.2613 [MONO,perMe,Na,0,freeEnd] HexNAc5Hex6	1271.1253	$[M+2Na]^{2+}$	72	-	-
39	 m/z: 2530.2773 [MONO,perMe,Na,0,freeEnd] HexNAc6Hex4Fuc1	1276.6333	$[M+2Na]^{2+}$	27	-	-

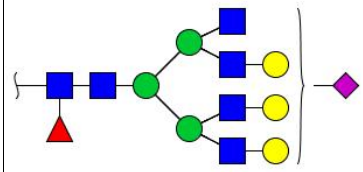
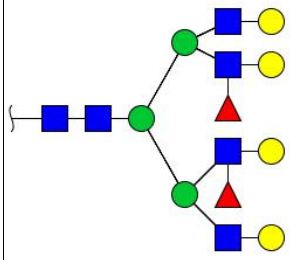
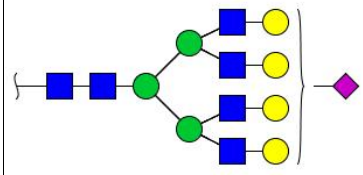
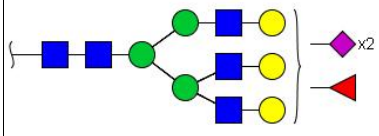
40	 m/z: 2564.2716 [MONO,perMe,Na,0,freeEnd] HexNAc3Hex6Fuc1NeuAc1	1293.6304*	$[M+2Na]^{2+}$	27	-	✓✓
41	 m/z: 2571.3039 [MONO,perMe,Na,0,freeEnd] HexNAc7Hex3Fuc1	1297.1465	$[M+2Na]^{2+}$	75	-	*
42	 m/z: 2600.2815 [MONO,perMe,Na,0,freeEnd] HexNAc2Hex10	1311.6353	$[M+2Na]^{2+}$	52	-	✓
43	 m/z: 2601.3144 [MONO,perMe,Na,0,freeEnd] HexNAc7Hex4	1312.1518	$[M+2Na]^{2+}$	72	-	✓
44	 m/z: 2605.2981 [MONO,perMe,Na,0,freeEnd] HexNAc4Hex5Fuc1NeuAc1	1314.1437	$[M+2Na]^{2+}$	44	58	✓✓

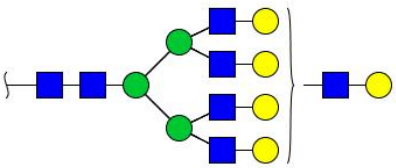
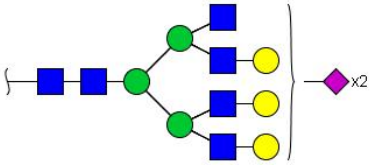
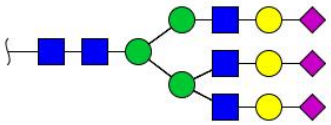
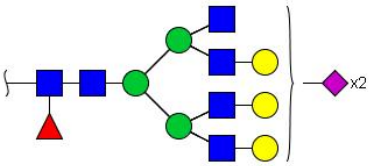
45	 m/z: 2622.3134 [MONO,perMe,Na,0,freeEnd] HexNAc4Hex6Fuc2	1322.6513	$[M+2Na]^{2+}$	27	-	-
46	 m/z: 2635.3087 [MONO,perMe,Na,0,freeEnd] HexNAc4Hex5Fuc1NeuGc1	1329.149	$[M+2Na]^{2+}$	27	-	-
47	 m/z: 2646.3247 [MONO,perMe,Na,0,freeEnd] HexNAc5Hex4Fuc1NeuAc1	1334.6569*	$[M+2Na]^{2+}$	27	-	-
48	 m/z: 2663.3400 [MONO,perMe,Na,0,freeEnd] HexNAc5Hex5Fuc2	903.1061	$[M+3Na]^{3+}$	27	27	-
49	 m/z: 2676.3352 [MONO,perMe,Na,0,freeEnd] HexNAc5Hex5NeuAc1	907.4379*	$[M+3Na]^{3+}$	35	35	✓

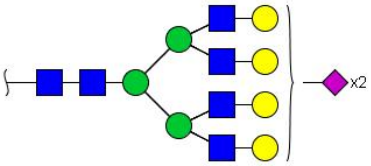
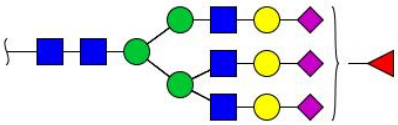
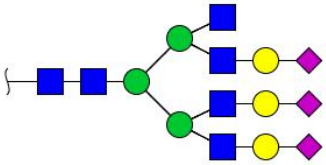
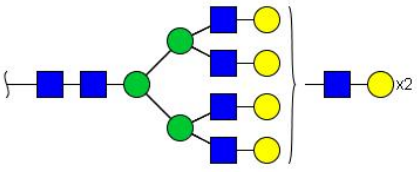
50	 m/z: 2693.3506 [MONO,perMe,Na,0,freeEnd] HexNAc5Hex6Fuc1	913.1097	$[M+3Na]^{3+}$	27	-	✓
51	 m/z: 2764.3877 [MONO,perMe,Na,0,freeEnd] HexNAc6Hex6	936.7887	$[M+3Na]^{3+}$	72	35	✓
52	 m/z: 2792.3826 [MONO,perMe,Na,0,freeEnd] HexNAc4Hex5NeuAc2	1407.6859	$[M+2Na]^{2+}$	52	52	✓✓
53	 m/z: 2850.4244 [MONO,perMe,Na,0,freeEnd] HexNAc5Hex5Fuc1NeuAc1	965.4676	$[M+3Na]^{3+}$	27	35	✓✓
54	 m/z: 2867.4398 [MONO,perMe,Na,0,freeEnd] HexNAc5Hex6Fuc2	971.1394	$[M+3Na]^{3+}$	27	-	-

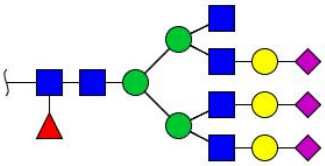
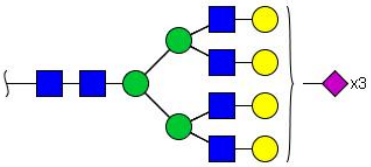
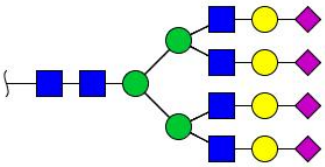
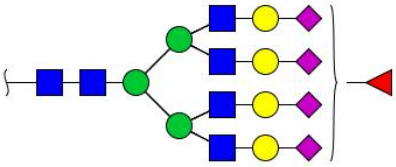
55	 m/z: 2880.4350 [MONO,perMe,Na,0,freeEnd] HexNAc5Hex6NeuAc1	975.4711	$[M+3Na]^{3+}$	72	-	✓✓
56	 m/z: 2908.4663 [MONO,perMe,Na,0,freeEnd] HexNAc6Hex5Fuc2	984.8149	$[M+3Na]^{3+}$	27	-	✓
57	 m/z: 2938.4769 [MONO,perMe,Na,0,freeEnd] HexNAc6Hex6Fuc1	994.8184	$[M+3Na]^{3+}$	27	-	✓
58	 m/z: 2966.4718 [MONO,perMe,Na,0,freeEnd] HexNAc4Hex5Fuc1NeuAc2	1004.1501	$[M+3Na]^{3+}$	27	58	✓✓
59	 m/z: 3026.4929 [MONO,perMe,Na,0,freeEnd] HexNAc4Hex5Fuc1NeuGc1	1532.728	$[M+Na+K]^{2+}$	27	-	-
60	 m/z: 3037.5089 [MONO,perMe,Na,0,freeEnd]	1027.8291	$[M+3Na]^{3+}$	52	-	-

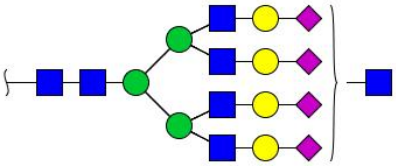
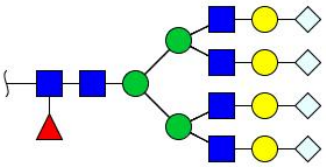
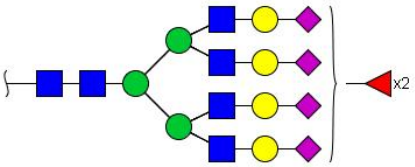
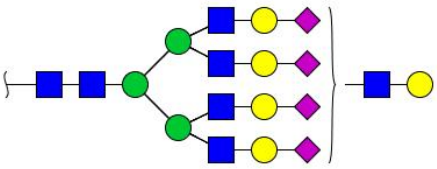
	HexNAc5Hex5NeuAc2					
61	 m/z: 3054.5242 [MONO,perMe,Na,0,freeEnd] HexNAc5Hex6Fuc1NeuAc1	1033.5009*	$[M+3Na]^{3+}$	27	-	✓
62	 m/z: 3125.5613 [MONO,perMe,Na,0,freeEnd] HexNAc6Hex6NeuAc1	1057.1799	$[M+3Na]^{3+}$	72	-	-
63	 m/z: 3142.5766 [MONO,perMe,Na,0,freeEnd] HexNAc6Hex7Fuc1	1062.8517	$[M+3Na]^{3+}$	27	-	-
64	 m/z: 3211.5981 [MONO,perMe,Na,0,freeEnd] HexNAc5Hex5Fuc1NeuAc2	1617.2937	$[M+2Na]^{2+}$	27	64	✓
65	 m/z: 3241.6087 [MONO,perMe,Na,0,freeEnd]	1095.8624	$[M+3Na]^{3+}$	72	52	-

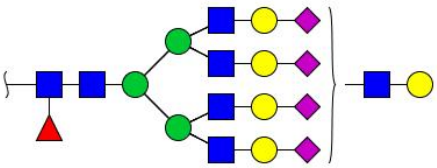
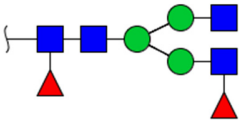
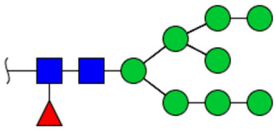
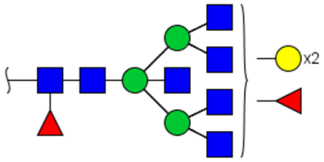
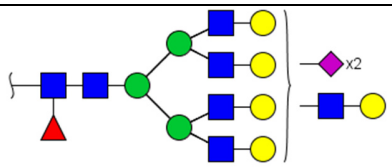
	HexNAc5Hex6NeuAc2					
66	 m/z: 3299.6505 [MONO,perMe,Na,0,freeEnd] HexNAc6Hex6Fuc1NeuAc1	1115.2096	$[M+3Na]^{3+}$	27	-	✓
67	 m/z: 3316.6659 [MONO,perMe,Na,0,freeEnd] HexNAc6Hex7Fuc2	1669.8275*	$[M+2Na]^{2+}$	27	-	✓
68	 m/z: 3329.6611 [MONO,perMe,Na,0,freeEnd] HexNAc6Hex7NeuAc1	1125.2132	$[M+3Na]^{3+}$	80	-	-
69	 m/z: 3415.6979 [MONO,perMe,Na,0,freeEnd]	1153.8921	$[M+3Na]^{3+}$	27	52	✓

	HexNAc5Hex6Fuc1NeuAc2					
70	 m/z: 3417.7135 [MONO,perMe,Na,0,freeEnd] HexNAc7Hex8	1154.5640*	$[M+3Na]^{3+}$	80	-	✓
71	 m/z: 3486.7350 [MONO,perMe,Na,0,freeEnd] HexNAc6Hex6NeuAc2	1177.5711*	$[M+3Na]^{3+}$	72	-	-
72	 m/z: 3602.7823 [MONO,perMe,Na,0,freeEnd] HexNAc5Hex6NeuAc3	1216.2536	$[M+3Na]^{3+}$	72	72	✓✓
73	 m/z: 3660.8242 [MONO,perMe,Na,0,freeEnd] HexNAc6Hex6Fuc1NeuAc2	1235.6009*	$[M+3Na]^{3+}$	27	-	-

74	 m/z: 3690.8348 [MONO,perMe,Na,0,freeEnd] HexNAc6Hex7NeuAc2	1245.6044	$[M+3Na]^{3+}$	80	52	✓
75	 m/z: 3776.8716 [MONO,perMe,Na,0,freeEnd] HexNAc5Hex6Fuc1NeuAc3	1274.2833	$[M+3Na]^{3+}$	27	75	✓✓
76	 m/z: 3847.9087 [MONO,perMe,Na,0,freeEnd] HexNAc6Hex6NeuAc3	1297.9624	$[M+3Na]^{3+}$	72	-	-
77	 m/z: 3866.9396 [MONO,perMe,Na,0,freeEnd] HexNAc8Hex9	1944.9644	$[M+2Na]^{2+}$	80	-	-

78	 m/z: 4021.9979 [MONO,perMe,Na,0,freeEnd] HexNAc6Hex6Fuc1NeuAc3	1355.9921	$[M+3Na]^{3+}$	27	-	-
79	 m/z: 4052.0084 [MONO,perMe,Na,0,freeEnd] HexNAc6Hex7NeuAc3	1030.2440	$[M+4Na]^{4+}$	80	52	✓
80	 m/z: 4413.1821 [MONO,perMe,Na,0,freeEnd] HexNAc6Hex7NeuAc4	1120.5374	$[M+4Na]^{4+}$	80	72	✓✓
81	 m/z: 4587.2713 [MONO,perMe,Na,0,freeEnd] HexNAc6Hex7Fuc1NeuAc4	1164.0597	$[M+4Na]^{4+}$	80	75	✓

82	 m/z: 4658.3084 [MONO,perMe,Na,0,freeEnd] HexNAc7Hex7NeuAc4	1181.8190*	$[M+4Na]^{4+}$	80	-	-
83	 m/z: 4707.3136 [MONO,perMe,Na,0,freeEnd] HexNAc6Hex7Fuc1NeuGc4	1194.0703*	$[M+4Na]^{4+}$	80	-	-
84	 m/z: 4761.3605 [MONO,perMe,Na,0,freeEnd] HexNAc6Hex7Fuc2NeuAc4	1207.5820*	$[M+4Na]^{4+}$	80	-	-
85	 m/z: 4862.4082 [MONO,perMe,Na,0,freeEnd] HexNAc7Hex8NeuAc4	1232.8439*	$[M+4Na]^{4+}$	80	-	*

86	 m/z: 5036.4974 [MONO,perMe,Na,0,freeEnd] HexNAc7Hex8Fuc1NeuAc4	1276.3663*	$[M+4Na]^{4+}$	80	-	✓
87	 m/z: 2010.0141 [MONO,perMe,Na,0,freeEnd] HexNAc4Hex3Fuc2	1016.5017	$[M+2Na]^{2+}$	13	-	✓✓
88	 m/z: 2366.1711 [MONO,perMe,Na,0,freeEnd] HexNAc2Hex8Fuc1	1194.5802	$[M+2Na]^{2+}$	52	-	-
89	 m/z: 3153.5926 [MONO,perMe,Na,0,freeEnd] HexNAc7Hex5Fuc2	1066.5237	$[M+3Na]^{3+}$	80	-	-
90	 m/z: 4314.1501 [MONO,perMe,Na,0,freeEnd] HexNAc7Hex8Fuc1NeuAc2	1453.3762	$[M+3Na]^{3+}$	90	-	-

[a] MALDI MS based quantification was performed using masses corresponding to the $[M+Na]^{+}$ adducts only;

[b] Quantification of N-glycans isolated from tissues were performed using the heavy glycan of the same composition;

[c] one check indicates that permethylated structure was confirmed while double check indicates that both structures (permethylated and perdeuterated) were confirmed, while asterisk indicate that only perdeuterated structure was confirmed.

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Legend: ■ N-acetyl glucosamine (GlcNac), ● Mannose (Man), ● Galactose (Gal), ◀ Fucose (Fuc), ♦ Sialic acid (NeuAc).