

SUPPORTING INFORMATION

**Analysis of Sialic Acid Linkage, Chain and Blood-Group Type,
and Branching Pattern of Sialylated Oligosaccharides
by Negative-Ion Electrospray Tandem Mass Spectrometry**

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Table S-1. Linkage and monosaccharide composition assignment from methylation analysis of DSMFLND.

Figure S-1. ES-CID-MS/MS spectra of de-*N*-acetylated sialyllactose. (a) 3'-deAc-SL, (b) 6'-deAc-SL. Fragmentation is similar to that shown in Fig. 1.

Figure S-2. ES-CID-MS/MS spectra of sialylated *N*-acetyllactosamines. (a) 3'-SLN, (b) 6'-SLN. Fragmentation is similar to that shown in Fig. 1.

Figure S-3. ES-CID-MS/MS spectra of 3'SLNFP II and 3'SLNFP III using $[M-2H+Na]^-$ as precursors.

Figure S-4. ES-CID-MS/MS spectra of branched monosialylated and monofucosylated hexaose. (a) $[M-H]^-$ of MSMFLNnH, and (b) $[M-H]^-$ of MSMFLNH. Fragmentation is shown in Fig. 5.

Figure S-5. ES-CID-MS/MS of branched disialylated and monofucosylated hexaose, $[M-H]^-$ of DSMFLNH. Fragmentation is shown in Fig. 6.

Figure S-6. ES-CID-MS/MS spectrum from 500 fmol (a) and 5 pmol (b) of 6'-SLN.

Table S-1. Linkage and monosaccharide composition assignment from methylation analysis of DSMFLND.

PMAAs ^a	Linkages	Molar ratio ^b	
		Observed	Theoretical
Fucitol			
1,5-Di- <i>O</i> -acetyl	Fuc1-	0.9	1
Glucitol			
4-Mono- <i>O</i> -acetyl	-4Glc1	0.8	1
Galactitiol			
1,5-Di- <i>O</i> -acetyl	Gal1-	1.7	2
1,3,5-Tri- <i>O</i> -acetyl	-3Gal1-	1.2	1
1,3,5,6-Tetra- <i>O</i> -acetyl	-3,6Gal1-	2.0	2
N-Acetylglucosaminitol			
1,3,5-Tri- <i>O</i> -acetyl	-3GlcNAc1-	1.3	1
1,4,5-Tri- <i>O</i> -acetyl	-4GlcNAc1-	1.3	1
1,3,4,5-Tetra- <i>O</i> -acetyl	-3,4GlcNAc1-	1.2	1
1,3,4,6-Tetra- <i>O</i> -acetyl	-3,6GlcNAc1-	0.8	1

^a PMAA partially methylated alditol acetates.

^b Molar ratios relative to 1,5-di-*O*-acetyl-2,3,4,6-tetra-*O*-methyl-galactitol.

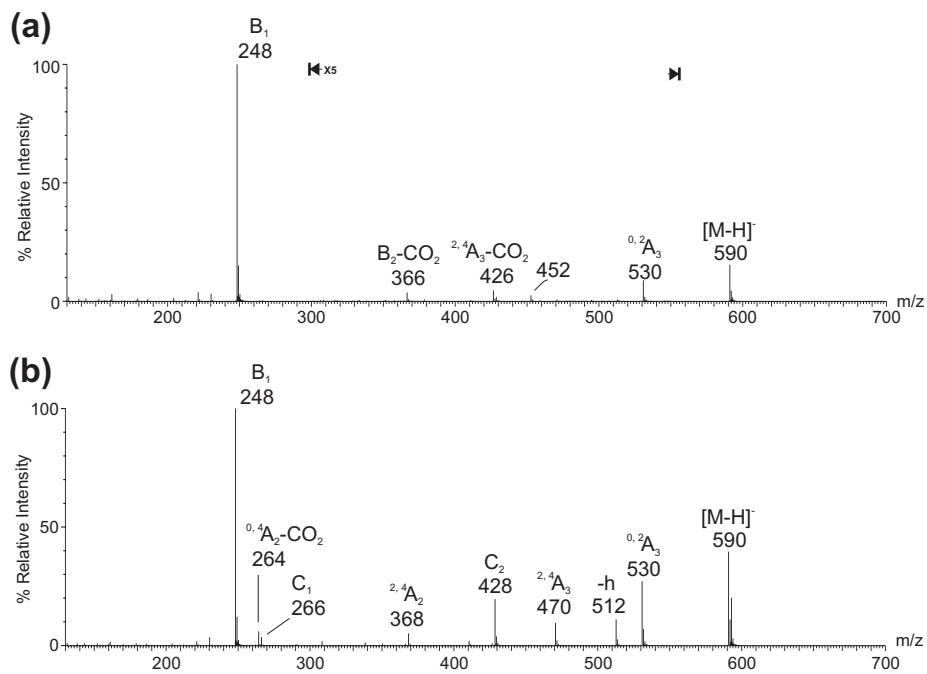


Figure S-1. ES-CID-MS/MS spectra of de-*N*-acetylated sialyllactose. (a) 3'-deAc-SL, (b) 6'-deAc-SL. Fragmentation is similar to that shown in Fig. 1.

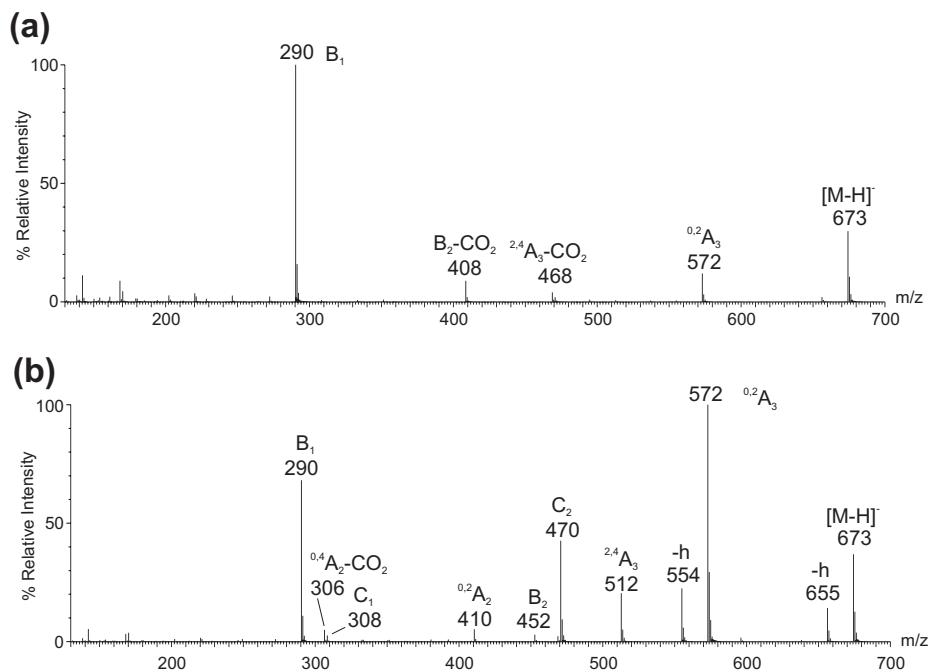


Figure S-2. ES-CID-MS/MS spectra of sialylated *N*-acetyllactosamines. (a) 3'-SLN, (b) 6'-SLN. Fragmentation is similar to that shown in Fig. 1.

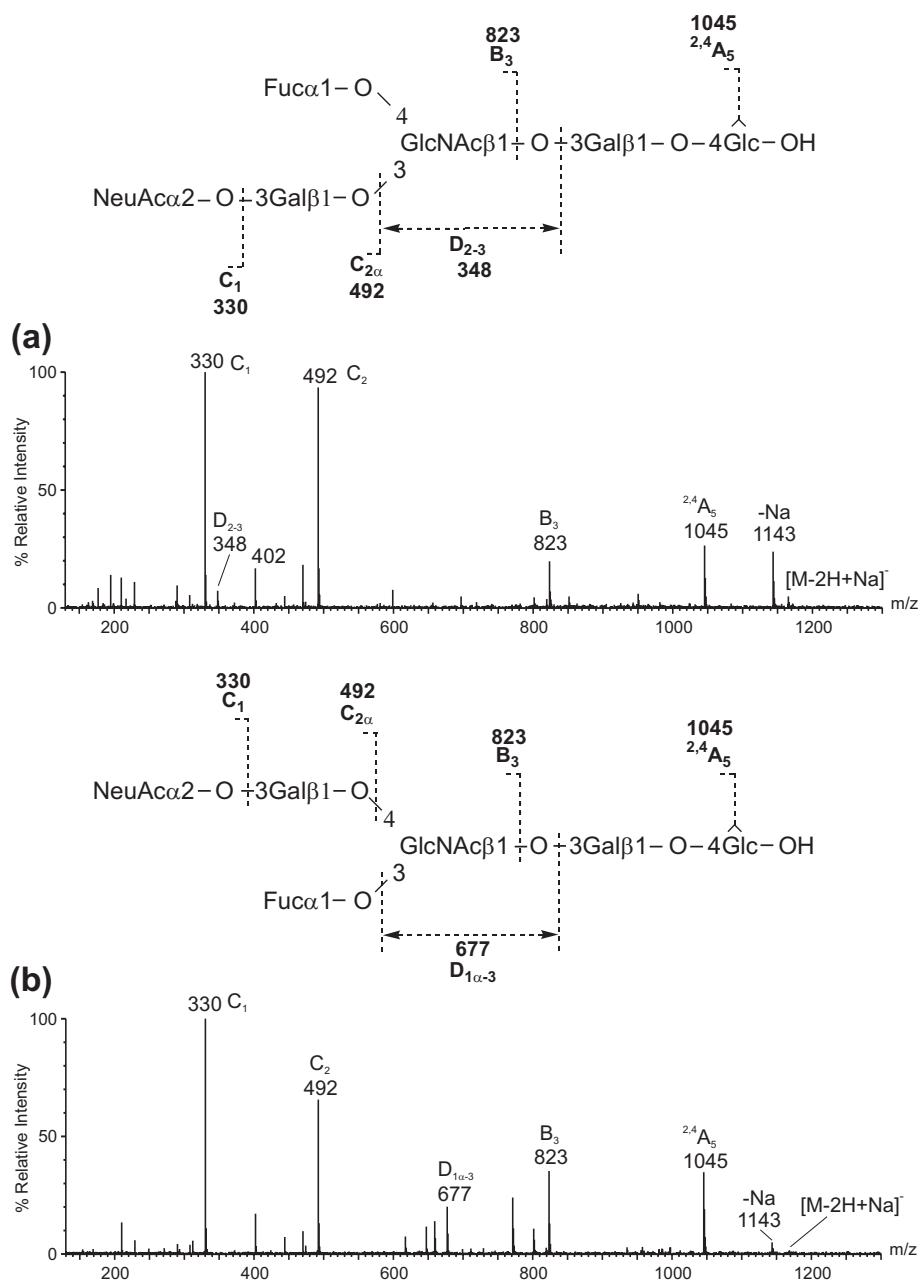


Figure S-3. ES-CID-MS/MS spectra of 3'SLNFP II and 3'SLNFP III using $[\text{M}-2\text{H}+\text{Na}]^-$ as precursors.

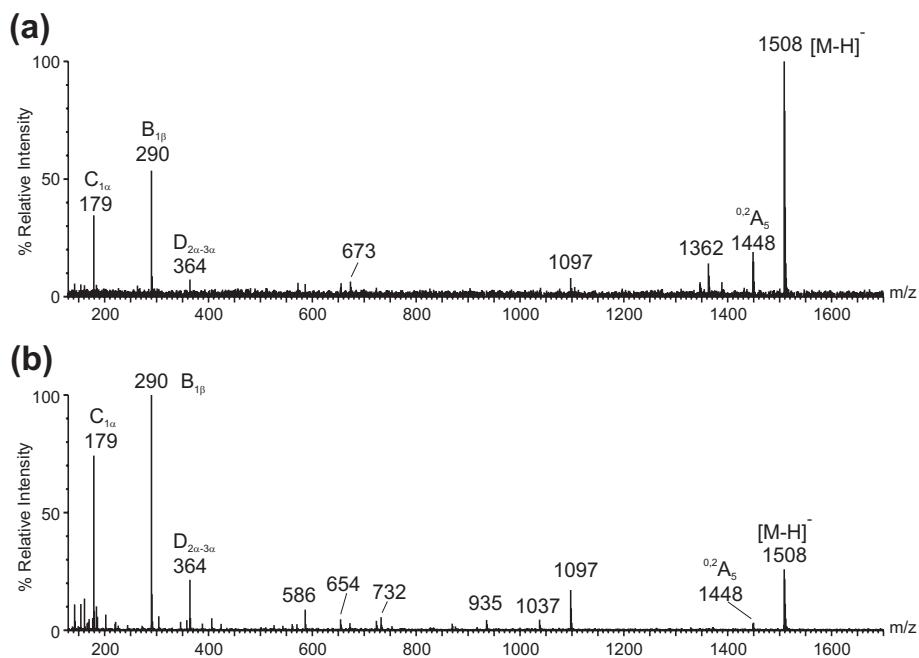


Figure S-4. ES-CID-MS/MS spectra of branched monosialylated and monofucosylated hexaose. (a) $[M-H]^-$ of MSMFLNnH, and (b) $[M-H]^-$ of MSMFLNH. Fragmentation is shown in Fig. 5.

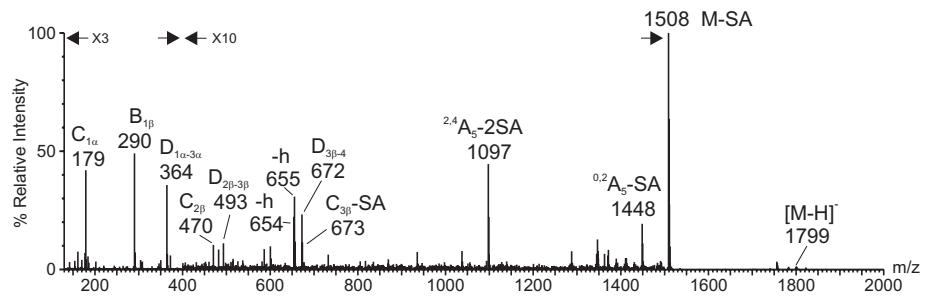


Figure S-5. ES-CID-MS/MS of branched disialylated and monofucosylated hexaose, $[M-H]^-$ of DSMFLNH. Fragmentation is shown in Fig. 6.

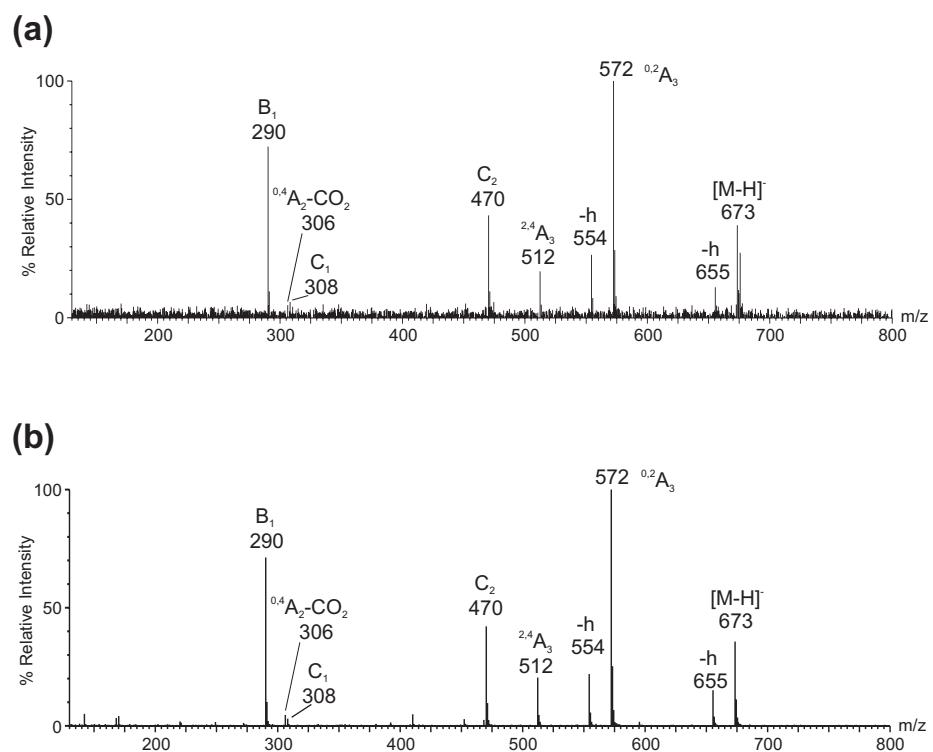


Figure S-6. ES-CID-MS/MS spectra from 500 fmol (a) and 5 pmol (b) of 6'-SLN.