Supporting Information

Figure S1. Annotated mass spectrum of oligosaccharides in caprine milk. (a) Unmodified (b) Permethylation modification.

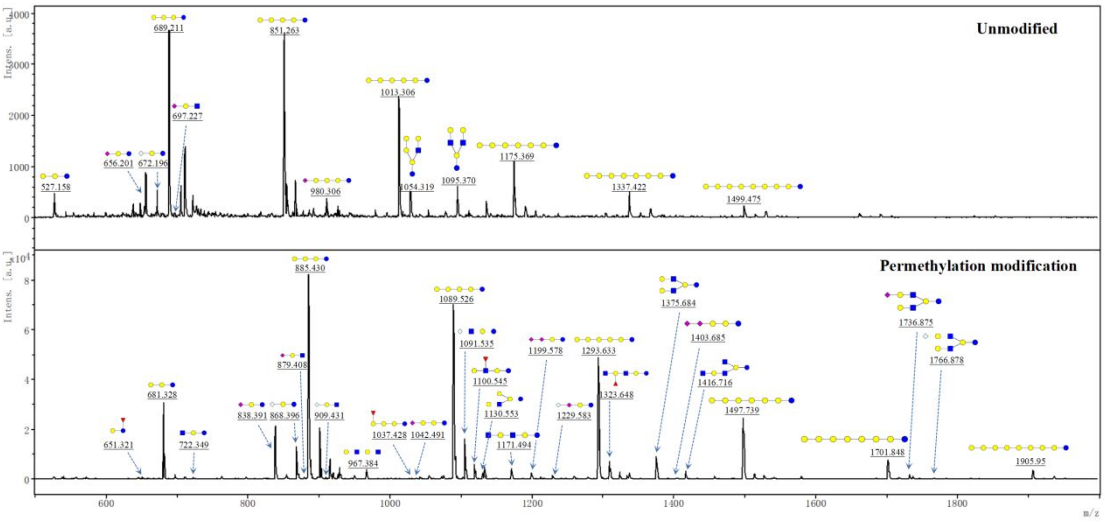

Figure S2. The fragment ion signal generated by 3'-SL (m/z 632) at different collision voltages. (a) 40eV; (b) 35eV; (c) 30eV; (d) 25eV; (e) 20eV; (f) 15 eV; (g) 10 eV.

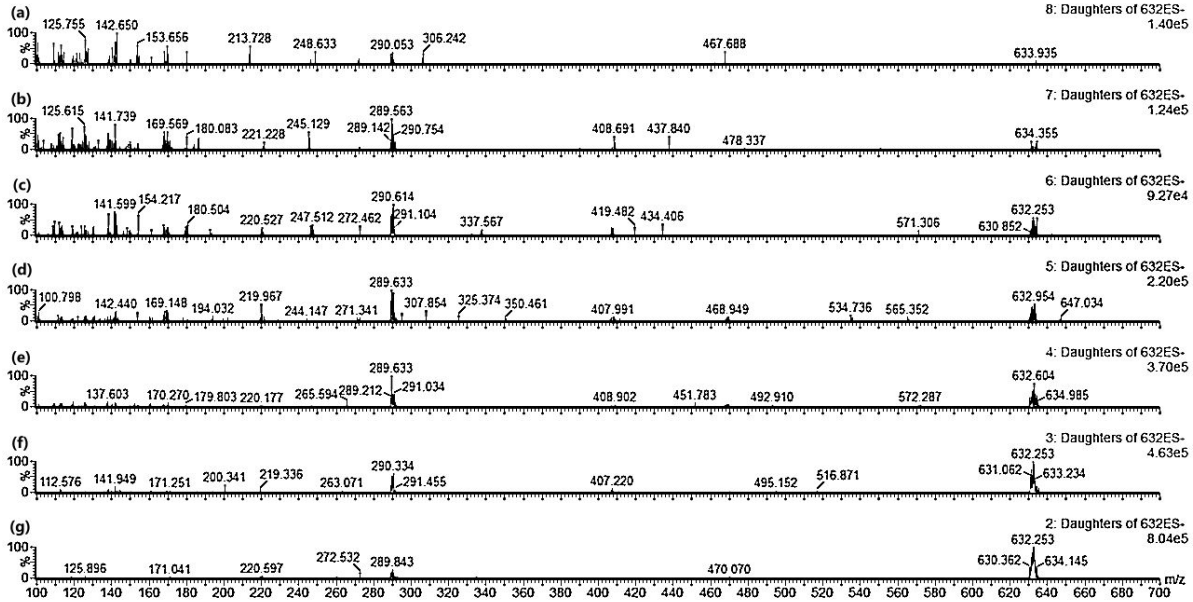

Figure S3. Typical extracted ion chromatograms (a-f) Extracted ion chromatograms of oligosaccharide standards. (i,j) Extracted ion chromatograms of LNnT and LNT in human milk. (k,l) Extracted ion chromatograms of 3'-SL and 6'-SL in caprine milk.(m,n) Extracted ion chromatograms of DSL and 3'-GL in ovine milk. (o,p) Extracted ion chromatograms of 2'-FL and 3-FL in camel milk.

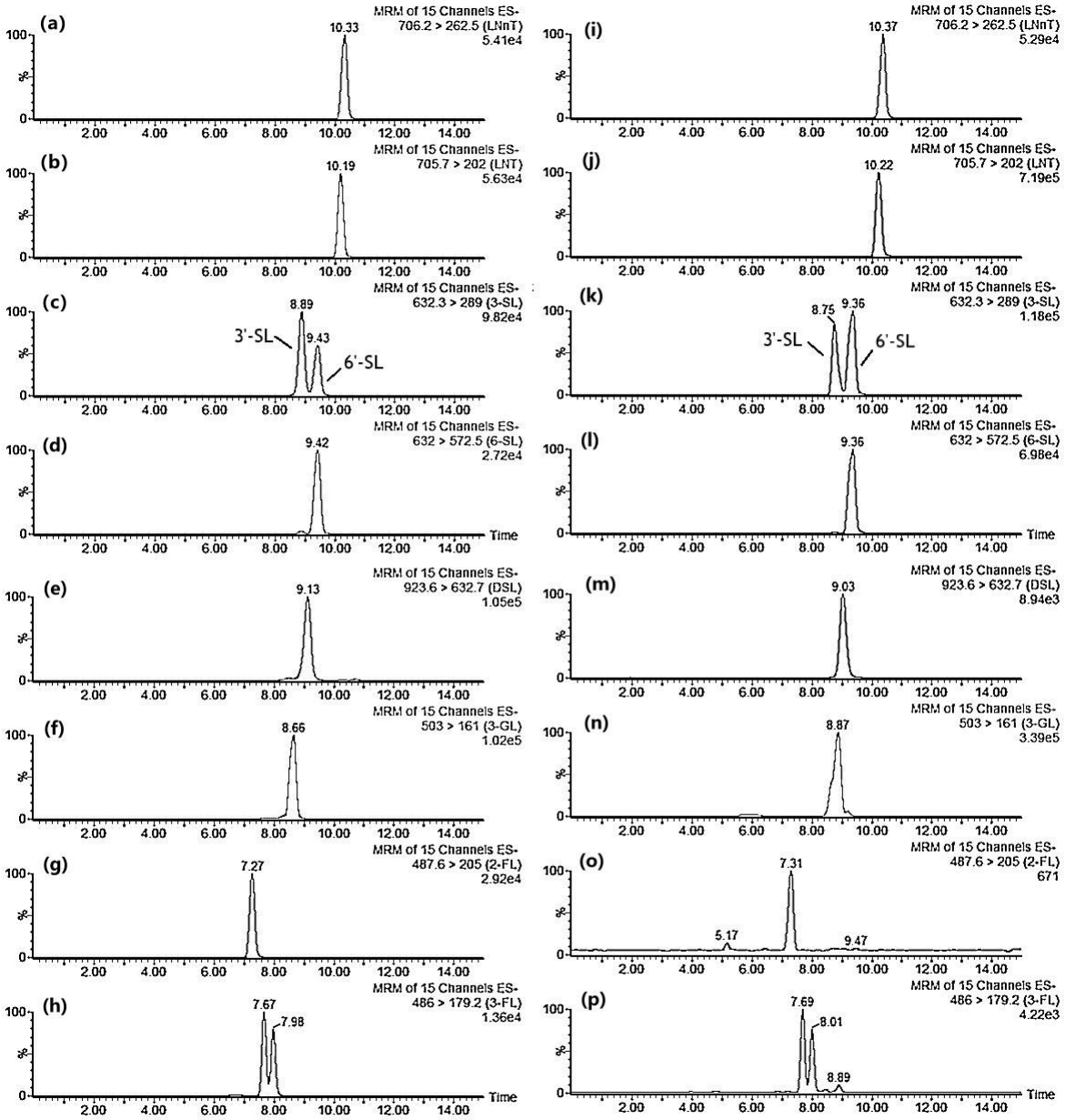

Figure S4. Total ion current trace of oligosaccharide in milk samples in full scan mode. (a) bovine milk; (b) caprine milk; (c) ovine milk; (d) camel milk; (e) human millk.

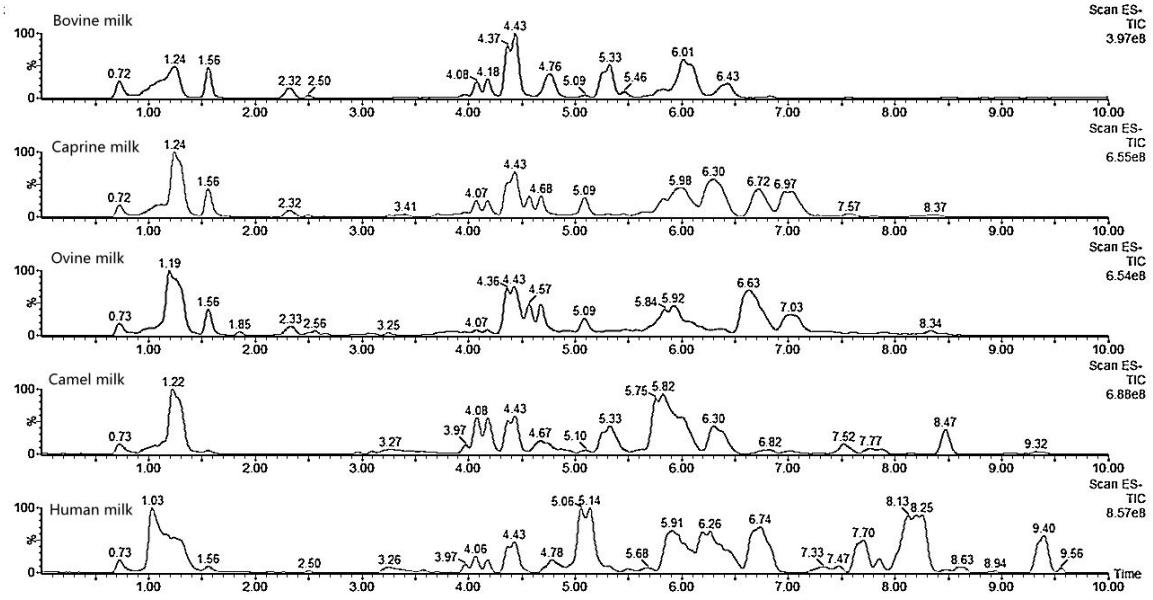

Table S1. Recovery of the UPLC-MRM-MS Method for Milk Oligosaccharides

	Endogenous level (μg/mL)	Spiked values (μg/mL)	Expected values (μg/mL)	Observed values (μg/mL)	Recovery (%)
DSL	2.76 ± 0.06	2.5	5.26	4.84 ± 0.22	92±4%
LNnT	0.31 ± 0.03	0.5	0.85	0.79 ± 0.01	92±2%
LNT	0.10 ± 0.01	0.3	0.40	0.44± 0.02	109±4%
3'-SL	58.0 ± 5.48	50	108.0	104.0 ± 3.82	96±4%
6'-SL	12.0 ± 0.48	15	27.0	29.09 ± 0.82	108±3%
α3'-GL	4.18 ± 0.05	3.5	7.68	3.73 ± 0.18	105±2%
2'-FL	/	0.1	0.1	0.10 ± 0.002	100±1%
3-FL	0.36 ± 0.07	0.3	0.66	0.59 ± 0.01	93±2%

Table S2. Validation of Matrix Effect of the UPLC-MRM-MS Method for milk oligosaccharides.

	Standard calibration (μg/mL)	Standard addition (μg/mL)	RSD (%)
DSL	2.76 ± 0.06	2.57 ± 0.03	7.1
LNnT	0.31 ± 0.03	0.31 ± 0.06	-0.7
LNT	0.10 ± 0.01	0.12 ± 0.03	-12.7
3'-SL	58.0 ± 5.48	59.99 ± 0.99	-3.3
6'-SL	12.0 ± 0.48	11.33 ± 0.63	5.7
α3'-GL	4.18 ± 0.05	3.73 ± 0.18	11.5
2'-FL	/	-0.11± 0.01	200
3-FL	0.36 ± 0.07	0.30 ± 0.06	20.1