

Supporting information

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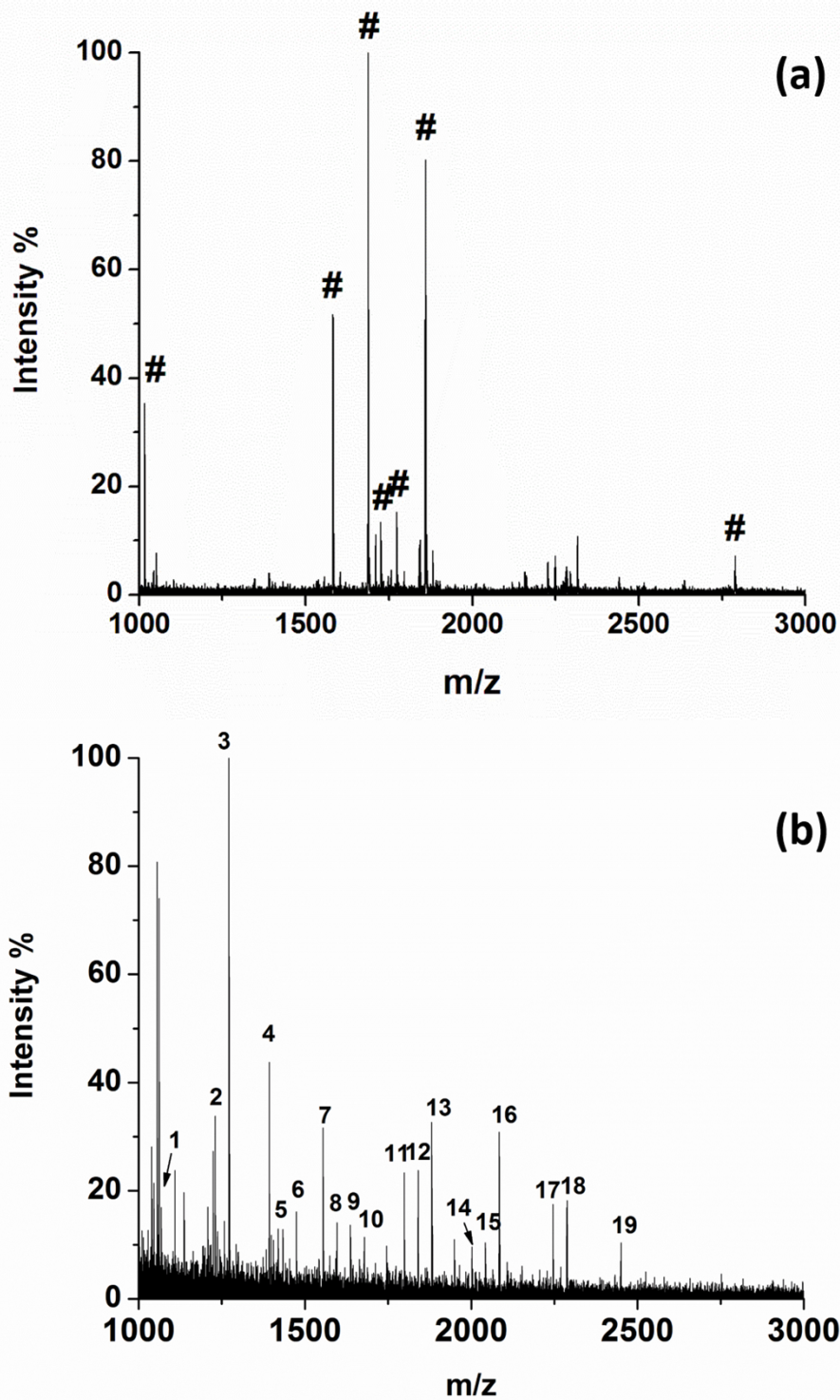


Figure S1. MALDI-TOF mass spectra of the mixture of tryptic deglycosylated peptides and N-linked glycans of ovalbumin (a) direct analysis with DHB matrix and (b) after HYNIC-derivatization and using the excess HYNIC as the matrix. Peaks labeled with # are ovalbumin peptides and peaks labeled with arabic numerals are N-linked glycans of ovalbumin.

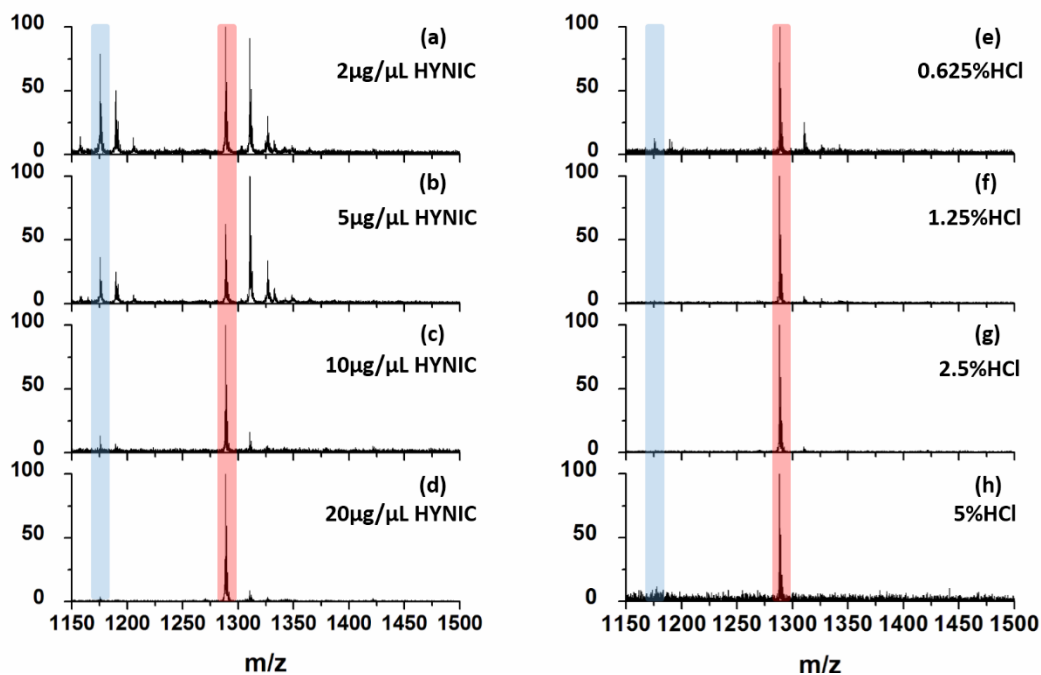


Figure S2. Optimization of reaction conditions for the derivatization of oligosaccharides including the concentration of HYNIC (left panel) and the volume fraction of HCl (right panel).

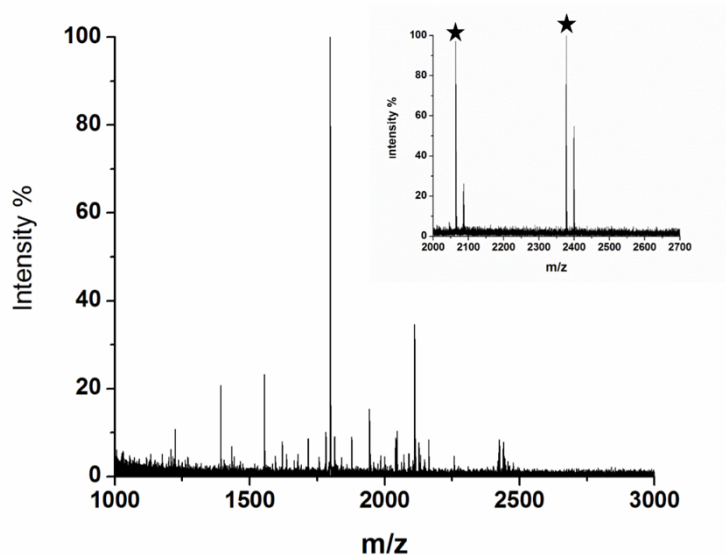


Figure S3. MALDI-TOF-MS spectrum of HYNIC derivatized N-glycans of human serum. The insert MS spectrum shows the signals detected under negative mode. ★ denotes $[M-H]^-$ signals of derivatized N-glycans.

Table S1. HYNIC-derivatized N-linked glycans released from RNase B.


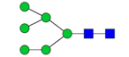



Peak No.	Theoretical m/z of native glycans	Theoretical m/z of HYNIC-derivatized glycans	Observed m/z of HYNIC-derivatized glycans	Composition
1	1257.4	1392.4	1392.4	
2	1419.5	1554.5	1554.5	
3	1581.5	1716.5	1716.5	
4	1743.6	1878.6	1878.5	
5	1905.6	2040.6	2040.6	

Table S2. HYNIC-derivatized N-linked glycans released from ovalbumin.

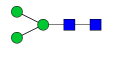
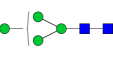

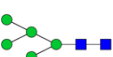




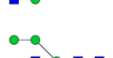



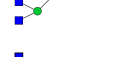




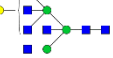
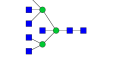
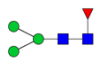
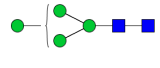
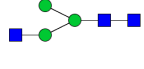


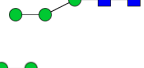

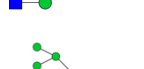






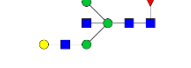


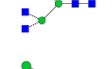


Peak No.	Theoretical m/z of native glycans	Theoretical m/z of HYNIC-derivatized glycans	Observed m/z of HYNIC-derivatized glycans	Composition
1	933.3	1068.3	1068.3	
2	1095.4	1230.4	1230.3	
3	1136.4	1271.4	1271.4	
4	1257.4	1392.4	1392.4	
5	1298.4	1433.4	1433.4	
6	1339.5	1474.5	1474.5	
7	1419.5	1554.5	1554.5	
8	1460.5	1595.5	1595.5	
9	1501.5	1636.5	1636.5	
10	1542.6	1677.6	1677.5	
11	1663.6	1798.6	1798.6	
12	1704.6	1839.6	1839.6	
13	1745.6	1880.6	1880.6	
14	1866.7	2001.7	2001.7	
15	1907.7	2042.7	2042.7	
16	1948.7	2083.7	2083.7	
17	2110.8	2245.8	2245.8	
18	2151.8	2286.8	2286.8	
19	2313.8	2448.8	2448.8	

Table S3. Observed m/z value in Figure 4b and corresponding fragmentation type of HYNIC-derivatized DP7 (BY ions are not included).

Peak No.	Observed m/z value	Fragmentation type
1	260.2	C ^{2,5} X _{Glc}
2	319.3	Z1
3	363.3	C2
4	419.4	B ^{1,4} X _{Glc}
5	467.4	C ^{0,4} X _{Glc}
6	525.5	C3
7	581.5	B ^{0,3} X _{Glc}
8	629.5	C ^{0,4} X _{Glc}
9	687.6	C4
10	743.7	B ^{0,3} X _{Glc}
11	791.7	C ^{0,4} X _{Glc}
12	849.7	C5
13	907.9	C ^{2,5} X _{Glc}
14	953.9	C ^{0,4} X _{Glc}
15	1012.0	C6
16	1111.6	^{2,4} X _{Glc}

Table S4. HYNIC-derivatized N-linked glycans released from human serum.

No.	Theoretical m/z of native glycans	Theoretical m/z of HYNIC-derivatized glycans	Observed m/z of HYNIC-derivatized glycans	Composition
1	1079.4	1214.4	1214.4	
2	1095.4	1230.4	1230.2	
3	1136.4	1271.4	1271.4	
4	1257.4	1392.4	1392.4	
5	1282.5	1417.5	1417.5	
6	1298.4	1433.4	1433.4	
7	1419.5	1554.5	1554.5	
8	1340.5	1475.5	1475.5	
9	1460.5	1595.5	1595.5	
10	1485.5	1620.5	1620.5	
11	1501.5	1636.5	1636.5	
12	1542.6	1677.6	1677.5	
13	1581.5	1716.5	1716.5	
14	1622.6	1757.6	1757.5	
15	1630.6	1765.6	1765.6	
16	1647.6	1782.6	1782.6	
17	1663.6	1798.6	1798.6	
18	1688.6	1823.6	1823.6	
19	1704.6	1839.6	1839.6	
20	1743.6	1878.6	1878.5	


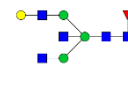
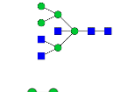


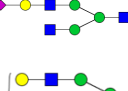
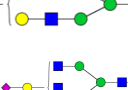
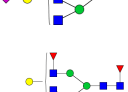
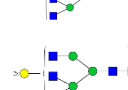
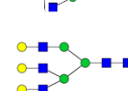
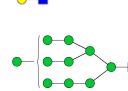
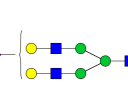
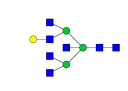
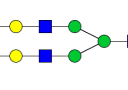
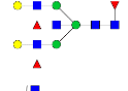
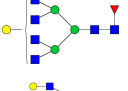
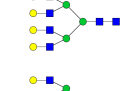
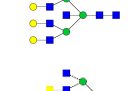


21	1825.6	1960.6	1960.6	
22	1850.7	1985.7	1985.7	
23	1866.7	2001.7	2001.6	
24	1905.6	2040.6	2040.6	
25	1914.7	2049.7	2049.7	
26	1939.8	2074.8	2074.8	
27	1954.7	2089.7	2089.7	
28	1995.7	2130.7	2130.7	
29	1997.0	2132.0	2132.0	
30	2012.7	2147.7	2147.7	
31	2028.7	2163.7	2163.7	
32	2067.6	2202.6	2202.6	
33	2100.9	2235.9	2235.9	
34	2110.7	2245.7	2245.7	
35	2246.0	2381.0	2381.0	
36	2304.8	2439.8	2439.8	
37	2380.8	2515.8	2515.8	
38	2395.2	2530.2	2530.2	
39	2598.0	2733.0	2733.0	
40	2679.0	2814.0	2814.0	

Table S5. Observed m/z value in Figure 5 and corresponding fragmentation type of derivatized-NA2 (Y ions not included).

Peak No.	Observed m/z value	Fragmentation type
1	204.1	B2Y5
2	366.2	B2
3	528.2	B3
4	893.4	B5Y3
5	1055.7	B5Y4
6	1276.7	C5Y5
7	1462.1	Z ^{1,5} X _{Gal}
8	1666.1	^{1,5} X _{Gal}