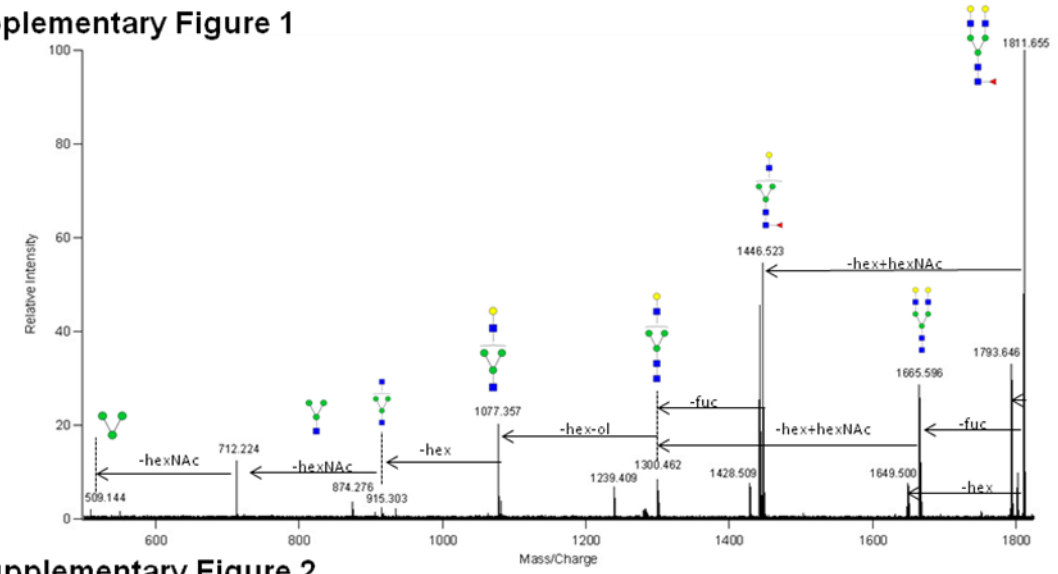
Supplementary Figure 1: Positive Mode CID MALDI FT-ICR MS/MS Spectrum of m/z 1811.6 $[M+Na]^{+}$. Tandem MS is used to confirm the composition of N-glycans and connectivity of the monosaccharides.

Supplementary Figure 2: Extracted Ion Chromatogram before and after reduction of glycan corresponding to 4Hex, 4HexNAc, 1Fuc. A: EIC of m/z 813.2 $[M+2H]^{+2}$ shows four peaks with anomer contribution. B: EIC of m/z 814.2 $[M+2H]^{+2}$ shows two peaks after sodium borohydride reduction.

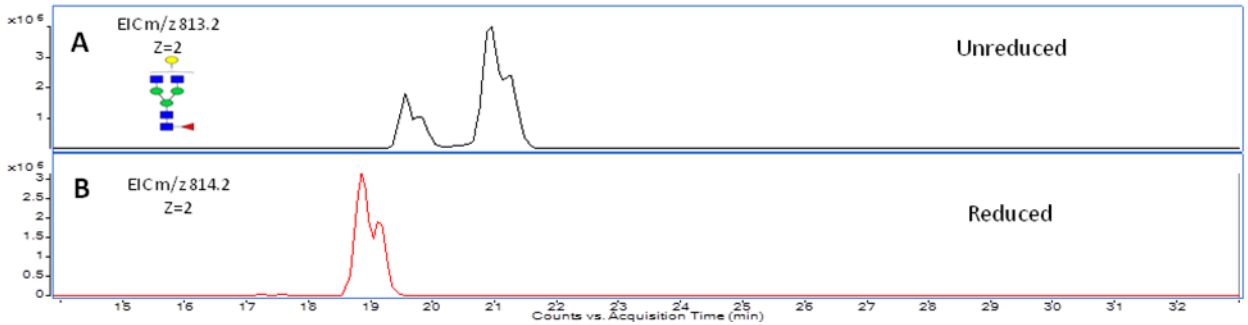
Supplementary Figure 3: Global Glycan Pool Zoom-Ins. A: Zoom-in between RT 16.8 minutes and 22.8 minutes with high mannose glycans elution highlighted. B: Zoom-in between RT 21.0 minutes and 30.5 minutes to highlight the elution of larger highly-sialylated glycans.

Supplementary Table 1: Glycan Library containing list of most abundant compounds annotated with accurate mass, retention time, glycan structure, glycan type, glycan composition, and protein source.

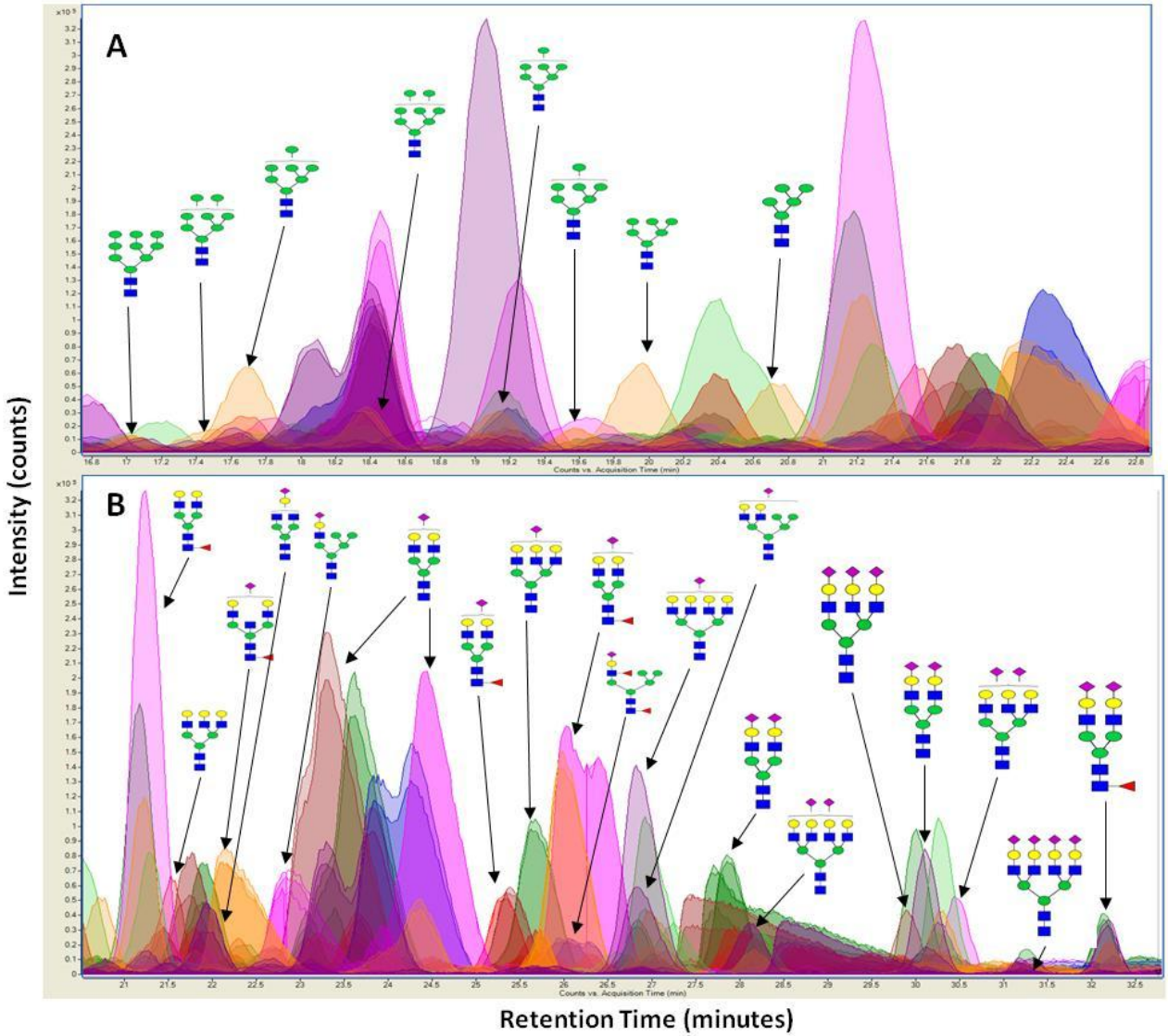
Supplementary Figure 1



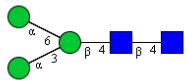
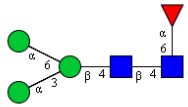
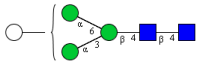
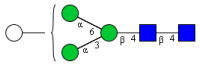
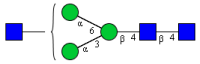
Supplementary Figure 2

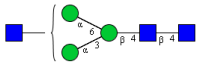
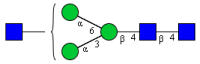
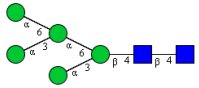
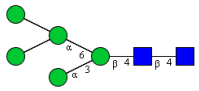
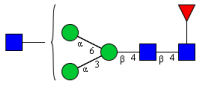


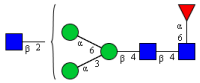
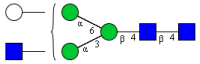
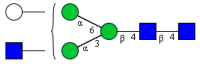
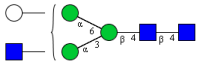
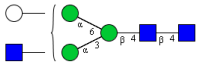
Supplementary Figure3

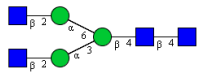
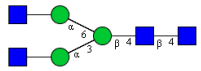
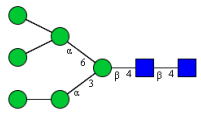
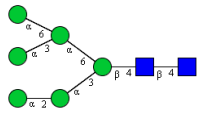
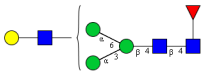


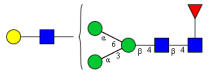
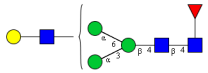
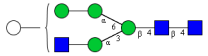
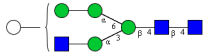
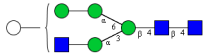
Supplementary Table 1

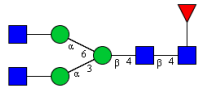
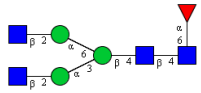
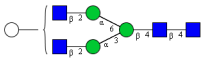
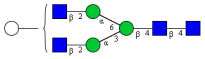
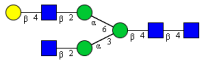
Number	Mass	RT	Structure	Glycan Type	Composition	Protein
1	912.3	18.1		Complex	H_3N_2	IgA, IgM, IgG, anti-trypsin, Transferrin, AGP, alpha-2-macro
2	1058.4	22.1		Complex	$H_3N_2F_1$	IgA
3	1074.4	13.6		High Mannose	H_4N_2	IgM, IgA, alpha-2-macro
4	1074.4	18.0		High Mannose	H_4N_2	IgM, alpha-2-macro
5	1115.4	20.7		Complex	H_3N_3	anti-trypsin, IgA, alpha-2-macro

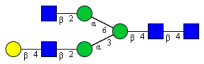
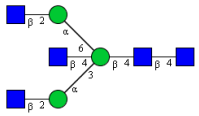
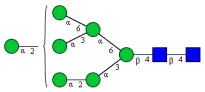
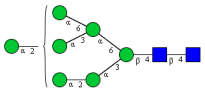
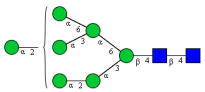
6	1115.4	23.6		Complex	H_3N_3	anti-trypsin, IgA, Transferrin
7	1115.4	18.9		Complex	H_3N_3	IgG
8	1236.5	20.6		High Mannose	H_5N_2	IgM, AGP, alpha-2-macro, IgA
9	1236.5	18.1		High Mannose	H_5N_2	IgM, alpha-2-macro
10	1261.5	22.1		Complex	$H_3N_3F_1$	IgA, alpha-2-macro

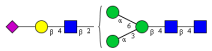
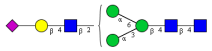
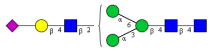
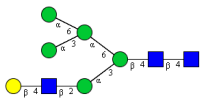
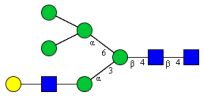
11	1261.5	19.7		Complex	$H_3N_3F_1$	IgM, IgG, anti-trypsin
12	1277.5	22.1		Complex	H_4N_3	IgA
13	1277.5	24.6		Complex	H_4N_3	alpha-2-macro, anti-trypsin, IgA
14	1277.5	17.3		Complex	H_4N_3	Transferrin
15	1277.5	20.1		Complex	H_4N_3	IgM, anti-trypsin, AGP

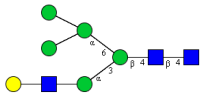
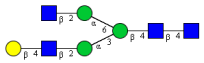
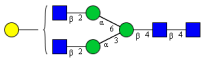
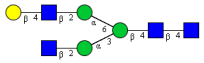
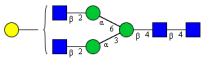
16	1318.5	17.9		Complex	H_3N_4	IgG, Transferrin
17	1318.5	15.4		Complex	H_3N_4	IgA
18	1398.5	21.4		High Mannose	H_6N_2	alpha-2-macro, IgM
19	1398.5	18.1		High Mannose	H_6N_2	IgM, IgA, AGP
20	1423.5	22.1		Complex	$H_4N_3F_1$	IgG, alpha-2-macro

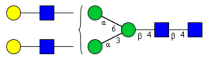
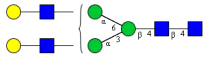
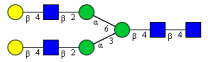
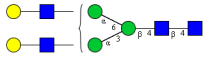
21	1423.5	19.1		Complex	$H_4N_3F_1$	IgM
22	1423.5	15.6		Complex	$H_4N_3F_1$	IgA
23	1439.5	17.9		Hybrid	H_5N_3	IgA, alpha-2-macro
24	1439.5	18.3		Hybrid	H_5N_3	IgM
25	1439.5	15.8		Hybrid	H_5N_3	AGP, Transferrin, anti-trypsin, IgA, IgG

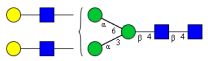
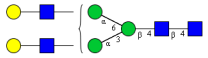
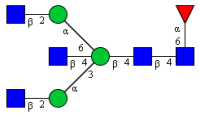
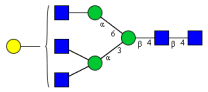
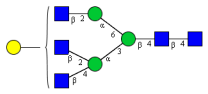
26	1464.6	15.9		Complex	$H_3N_4F_1$	IgG
27	1464.6	20.5		Complex	$H_3N_4F_1$	IgM, IgG, Transferrin, IgA
28	1480.6	22.8		Complex	H_4N_4	anti-trypsin, AGP
29	1480.6	20.7		Complex	H_4N_4	AGP, Transferrin
30	1480.6	18.9		Complex	H_4N_4	IgG, IgM, AGP, Transferrin

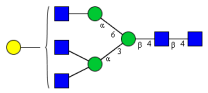
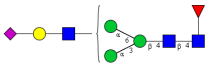
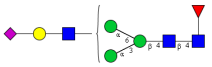
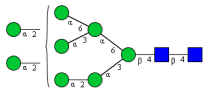
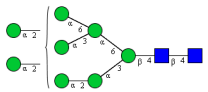
31	1480.6	19.2		Complex	H_4N_4	IgA, IgG, Transferrin, AGP, anti-trypsin
32	1521.6	14.4		Complex	H_3N_5	IgG, IgA
33	1560.6	19.2		High Mannose	H_7N_2	IgM, alpha-2-macro
34	1560.6	17.7		High Mannose	H_7N_2	IgM, alpha-2-macro
35	1560.6	18.3		High Mannose	H_7N_2	IgM, IgA, AGP

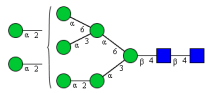
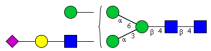
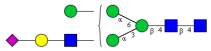
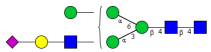
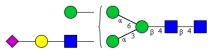
36	1568.6	25.8		Complex	$H_4N_3S_1$	anti-trypsin, Transferrin
37	1568.6	23.7		Complex	$H_4N_3S_1$	anti-trypsin, IgA, Transferrin, alpha-2-macro
38	1568.6	16.0		Complex	$H_4N_3S_1$	alpha-2-macro
39	1601.6	19.4		Hybrid	H_6N_3	IgM, alpha-2-macro, IgA
40	1601.6	13.5		Hybrid	H_6N_3	alpha-2-macro

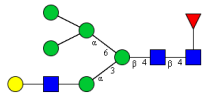
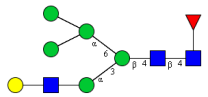
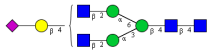
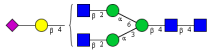
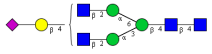
41	1601.6	18.3		Hybrid	H_6N_3	alpha-2-macro, IgM, IgA
42	1626.6	22.2		Complex	$H_4N_4F_1$	IgM, IgA,IgG
43	1626.6	17.1		Complex	$H_4N_4F_1$	IgM, IgG
44	1626.6	21.3		Complex	$H_4N_4F_1$	IgA, Transferrin, alpha-2-macro, IgG
45	1626.6	14.6		Complex	$H_4N_4F_1$	IgG, IgM

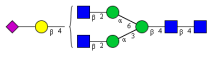
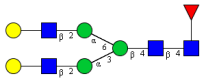
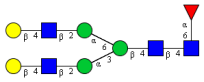
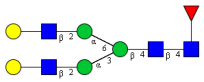
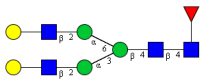
46	1642.6	17.2		Complex	H_5N_4	alpha-2-macro, AGP
47	1642.6	22.1		Complex	H_5N_4	IgG, AGP, alpha-2-macro, Transferrin, IgM
48	1642.6	20.0		Complex	H_5N_4	IgG, anti-trypsin, AGP, alpha-2-macro, IgA, IgM, Transferrin
49	1642.6	24.2		Complex	H_5N_4	IgA, alpha-2-macro, Transferrin
50	1642.6	13.9		Complex	H_5N_4	IgM, IgG, Transferrin, alpha-2-macro, anti-trypsin, IgA, AGP

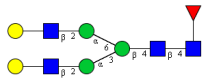
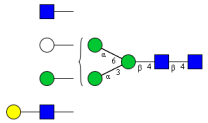
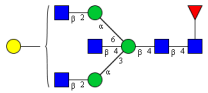
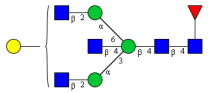
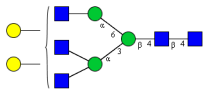
51	1642.6	16.4		Complex	H_5N_4	IgM
52	1642.6	15.1		Complex	H_5N_4	IgA, IgM
53	1667.6	17.2		Complex	$H_3N_5F_1$	IgG, IgM, IgA
54	1683.6	17.5		Complex	H_4N_5	IgA
55	1683.6	15.4		Complex	H_4N_5	IgM, IgG, IgA, alpha-2-macro, Transferrin

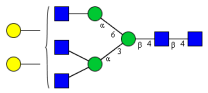
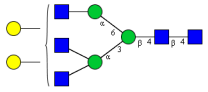
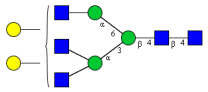
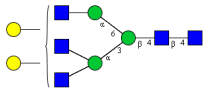
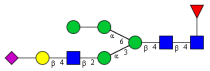
56	1683.6	20.5		Complex	H_4N_5	Transferrin
57	1714.6	28.2		Complex	$H_4N_3F_1S_1$	alpha-2-macro
58	1714.6	25.9		Complex	$H_4N_3F_1S_1$	IgM, IgA, IgA, Transferrin
59	1722.6	19.5		High Mannose	H_8N_2	IgM
60	1722.6	18.4		High Mannose	H_8N_2	IgM, alpha-2-macro, IgA

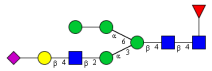
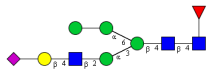
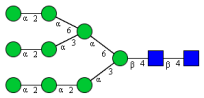
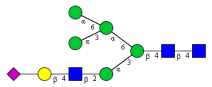
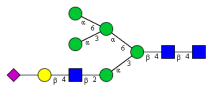
61	1722.6	17.8		High Mannose	H_8N_2	IgM, IgA
62	1729.6	22.9		Hybrid	$H_5N_3S_1$	IgA, alpha-2-macro
63	1729.6	15.9		Hybrid	$H_5N_3S_1$	alpha-2-macro, IgA
64	1729.6	20.8		Hybrid	$H_5N_3S_1$	IgA, Transferrin, anti-trypsin
65	1729.6	16.7		Hybrid	$H_5N_3S_1$	anti-trypsin

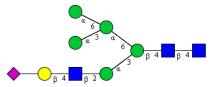
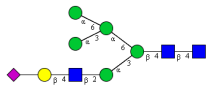
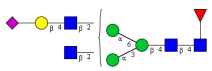
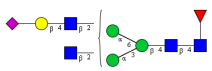
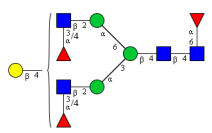
66	1747.6	14.6		Hybrid	$H_6N_3F_1$	IgM, alpha-2-macro
67	1747.6	15.2		Hybrid	$H_6N_3F_1$	Transferrin, IgM
68	1771.6	23.9		Complex	$H_4N_4S_1$	alpha-2-macro, IgA, Transferrin
69	1771.6	23.2		Complex	$H_4N_4S_1$	Transferrin, anti-trypsin
70	1771.6	22.7		Complex	$H_4N_4S_1$	Transferrin, IgM, anti-trypsin

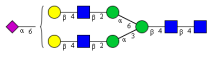
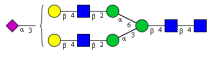
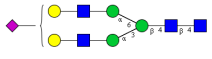
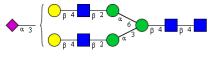
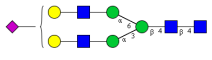
71	1771.7	16.3		Complex	$H_4N_4S_1$	alpha-2-macro, anti-trypsin, IgA, Transferrin
72	1788.7	16.3		Complex	$H_5N_4F_1$	alpha-2-macro
73	1788.7	22.1		Complex	$H_5N_4F_1$	IgM, IgG, alpha-2-macro, IgA, Transferrin, anti-trypsin, AGP
74	1788.7	18.0		Complex	$H_5N_4F_1$	IgA, IgM, alpha-2-macro
75	1788.7	15.5		Complex	$H_5N_4F_1$	alpha-2-macro, IgA, IgG, Transferrin, IgM

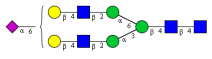
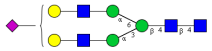
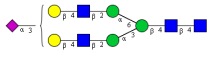
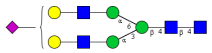
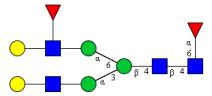
76	1788.7	19.9		Complex	$H_5N_4F_1$	IgA, alpha-2-macro, Transferrin, anti-trypsin, IgM, AGP
77	1804.7	21.1		Hybrid	H_6N_4	Transferrin
78	1829.7	18.0		Complex	H_4N_5	IgA, IgM, alpha-2-macro
79	1829.7	14.3		Complex	H_4N_5	IgM, IgA
80	1845.7	20.7		Complex	H_5N_5	IgA, Transferrin, AGP

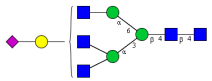
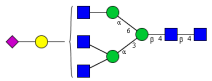
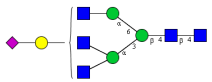
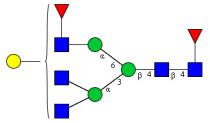
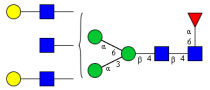
81	1845.7	18.5		Complex	H_5N_5	IgA, IgM
82	1845.7	16.5		Complex	H_5N_5	IgA, IgG, Transferrin, IgM, alpha-2-macro
83	1845.7	22.0		Complex	H_5N_5	Transferrin, AGP
84	1845.7	13.0		Complex	H_5N_5	alpha-2-macro, IgM
85	1876.7	17.5		Hybrid	$H_5N_3F_1S_1$	alpha-2-macro

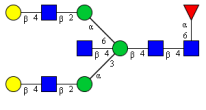
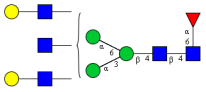
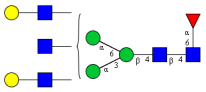
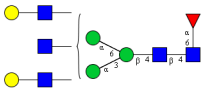
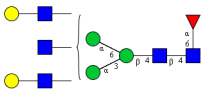
86	1876.7	27.9		Hybrid	$H_5N_3F_1S_1$	alpha-2-macro
87	1876.7	24.9		Hybrid	$H_5N_3F_1S_1$	IgM, alpha-2-macro
88	1884.7	17.9		High Mannose	H_9N_2	IgM, AGP, alpha-2-macro
89	1892.7	27.2		Hybrid	$H_6N_3S_1$	alpha-2-macro
90	1892.7	24.0		Hybrid	$H_6N_3S_1$	alpha-2-macro

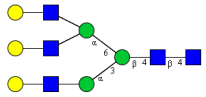
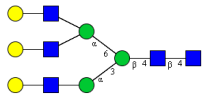
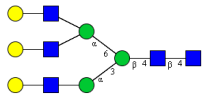
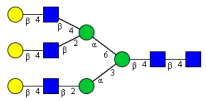
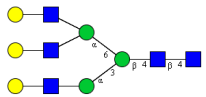
91	1892.7	23.1		Hybrid	$H_6N_3S_1$	alpha-2-macro
92	1892.7	17.1		Hybrid	$H_6N_3S_1$	alpha-2-macro
93	1917.7	25.7		Hybrid	$H_4N_4F_1S_1$	IgA, IgM, IgG
94	1917.7	28.3		Hybrid	$H_4N_4F_1S_1$	alpha-2-macro
95	1918.7	16.9		Complex	$H_4N_4F_3$	AGP, anti-trypsin

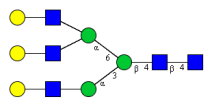
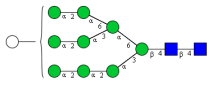
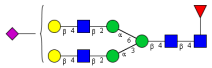
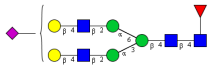
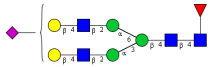
96	1933.7	24.7		Complex	$H_5H_4S_1$	alpha-2-macro, Transferrin, IgG
97	1933.7	23.6		Complex	$H_5H_4S_1$	anti-trypsin, AGP
98	1933.7	27.4		Complex	$H_5H_4S_1$	Transferrin, anti-trypsin
99	1933.7	26.5		Complex	$H_5H_4S_1$	IgM
10	1933.7	17.2		Complex	$H_5H_4S_1$	alpha-2-macro, IgA

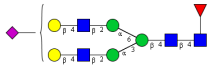
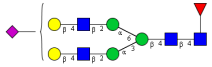
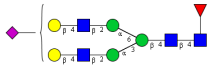
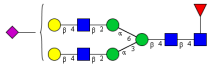
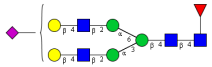
101	1933.7	24.1		Complex	$H_5H_4S_1$	Transferrin
102	1933.7	19.9		Complex	$H_5H_4S_1$	alpha-2-macro, anti-trypsin, IgA
103	1933.7	20.7		Complex	$H_5H_4S_1$	anti-trypsin, alpha-2-macro
104	1933.7	18.6		Complex	$H_5H_4S_1$	anti-trypsin
105	1934.7	21.7		Complex	$H_5N_4F_2$	IgA

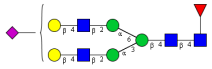
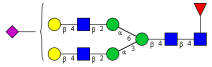
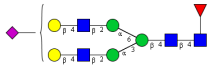
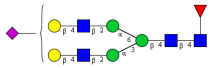
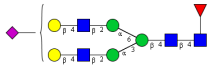
106	1974.7	19.8		Complex	$H_4N_5S_1$	IgA, IgM
107	1974.7	14.6		Complex	$H_4N_5S_1$	IgA
108	1974.7	15.4		Complex	$H_4N_5S_1$	IgA
109	1975.8	17.4		Complex	H_4N_F2	IgG
110	1991.7	22.4		Complex	$H_5N_5F_1$	IgA, IgM

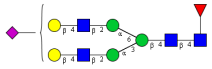
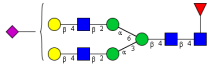
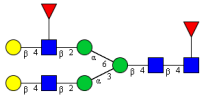
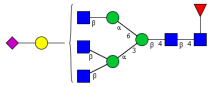
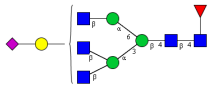
111	1991.7	18.6		Complex	$H_5N_5F_1$	IgM, alpha-2-macro, IgA, IgG, AGP, Transferrin
112	1991.7	19.7		Complex	$H_5N_5F_1$	alpha-2-macro
113	1991.7	19.0		Complex	$H_5N_5F_1$	alpha-2-macro
114	1991.7	14.6		Complex	$H_5N_5F_1$	IgM, alpha-2-macro, IgA
115	1991.7	15.9		Complex	$H_5N_5F_1$	IgA, IgM

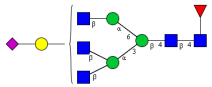
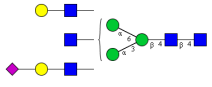
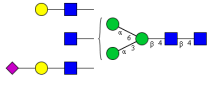
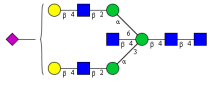
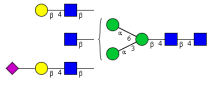
116	2007.7	16.3		Complex	H_6N_5	alpha-2-macro, Transferrin
117	2007.7	21.1		Complex	H_6N_5	alpha-2-macro, IgA
118	2007.7	19.4		Complex	H_6N_5	IgM, IgG, IgA
119	2007.7	22.6		Complex	H_6N_5	anti-trypsin, IgA, IgM, AGP, Transferrin
120	2007.7	23.5		Complex	H_6N_5	AGP

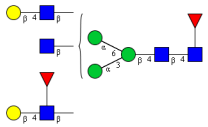
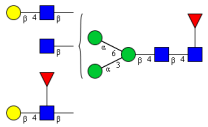
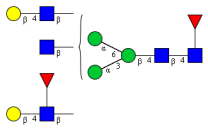
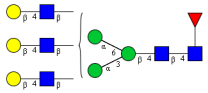
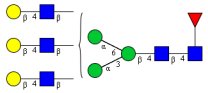
121	2007.7	21.3		Complex	H_6N_5	AGP, anti-trypsin, Transferrin
122	2046.7	18.7		High Mannose	$H_{10}N_2$	IgM
123	2079.8	28.2		Complex	$H_5N_4F_1S_1$	IgA, Transferrin
124	2079.8	24.1		Complex	$H_5N_4F_1S_1$	alpha-2-macro, IgA
125	2079.8	25.7		Complex	$H_5N_4F_1S_1$	IgA, anti-trypsin

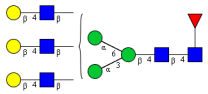
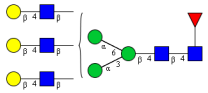
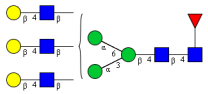
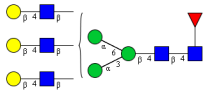
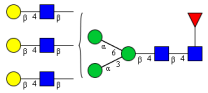
126	2079.8	26.2		Complex	$H_5N_4F_1S_1$	IgA, alpha-2-macro, anti-trypsin, IgM, IgG
127	2079.8	28.5		Complex	$H_5N_4F_1S_1$	alpha-2-macro, IgM
128	2079.8	16.6		Complex	$H_5N_4F_1S_1$	alpha-2-macro
129	2079.8	21.0		Complex	$H_5N_4F_1S_1$	alpha-2-macro, anti-trypsin
130	2079.8	26.6		Complex	$H_5N_4F_1S_1$	Transferrin, IgG

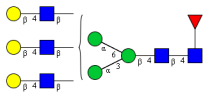
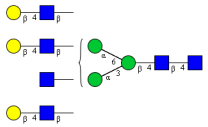
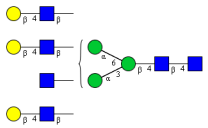
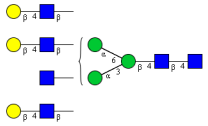
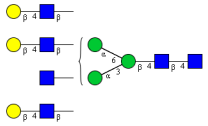
131	2079.8	21.5		Complex	$H_5N_4F_1S_1$	alpha-2-macro
132	2079.8	23.3		Complex	$H_5N_4F_1S_1$	alpha-2-macro, anti-trypsin
133	2079.8	18.8		Complex	$H_5N_4F_1S_1$	IgA
134	2079.8	18.6		Complex	$H_5N_4F_1S_1$	alpha-2-macro, IgA
135	2079.8	26.2		Complex	$H_5N_4F_1S_1$	Transferrin

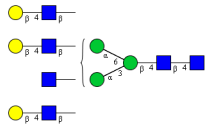
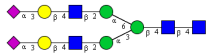
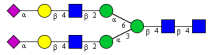
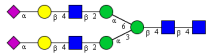
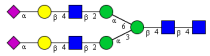
136	2079.8	18.6		Complex	$H_5N_4F_1S_1$	IgM
137	2079.8	21.0		Complex	$H_5N_4F_1S_1$	IgA, AGP
138	2080.8	20.8		Complex	$H_5N_4F_3$	AGP
139	2120.8	22.6		Complex	$H_4N_5F_1S_1$	IgM, IgA
140	2120.8	21.8		Complex	$H_4N_5F_1S_1$	IgA, IgM

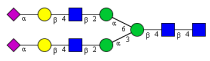
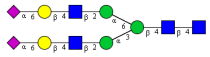
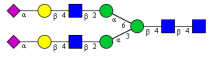
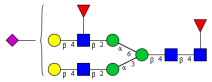
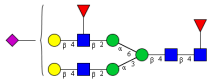
141	2120.8	16.9		Complex	$H_4N_5F_1S_1$	IgA
142	2136.8	22.4		Complex	$H_5N_5S_1$	IgA, IgG, IgM
143	2136.8	25.6		Complex	$H_5N_5S_1$	AGP
144	2136.8	20.7		Complex	$H_5N_5S_1$	IgM, alpha-2-macro, AGP, IgG, IgA
145	2136.8	15.5		Complex	$H_5N_5S_1$	IgA

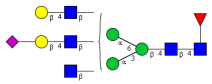
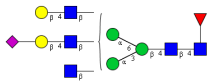
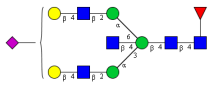
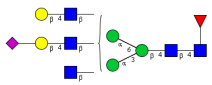
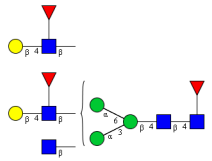
146	2137.8	21.8		Complex	$H_5N_5F_2$	alpha-2-macro
147	2137.8	20.4		Complex	$H_5N_5F_2$	alpha-2-macro
148	2137.8	18.1		Complex	$H_5N_5F_2$	IgA
149	2153.7	16.0		Complex	$H_6N_5F_1$	alpha-2-macro, Tranferrin, IgA
150	2153.8	23.7		Complex	$H_6H_5F_1$	AGP

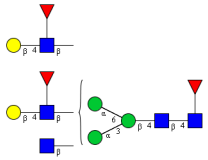
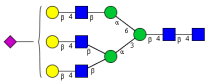
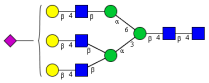
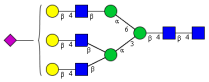
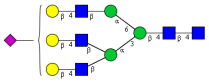
151	2153.8	20.1		Complex	$H_6H_5F_1$	IgM, IgA
152	2153.8	17.0		Complex	$H_6H_5F_1$	alpha-2-macro
153	2153.8	22.9		Complex	$H_6H_5F_1$	alpha-2-macro, IgM, IgA
154	2153.8	21.1		Complex	$H_6H_5F_1$	IgA, anti-trypsin, IgM
155	2153.8	24.5		Complex	$H_6H_5F_1$	AGP, IgA, alpha-2-macro

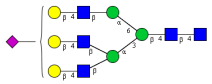
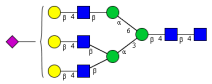
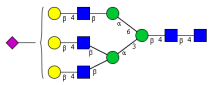
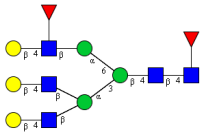
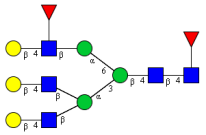
156	2153.8	21.6		Complex	$H_6H_5F_1$	AGP
157	2210.8	24.8		Complex	H_6N_6	anti-trypsin
158	2210.8	26.9		Complex	H_6N_6	anti-trypsin
159	2210.8	23.0		Complex	H_6N_6	AGP
160	2210.8	22.2		Complex	H_6N_6	AGP

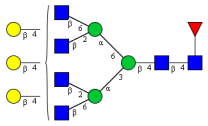
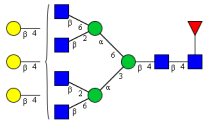
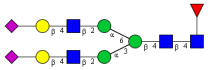
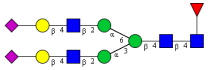
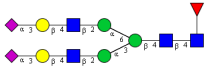
161	2210.8	28.8		Complex	H_6N_6	anti-trypsin, alpha-2-macro
162	2224.8	25.5		Complex	$H_5N_4S_2$	alpha-2-macro, Transferrin, anti-trypsin
163	2224.8	33.6		Complex	$H_5N_4S_2$	alpha-2-macro
164	2224.8	31.1		Complex	$H_5N_4S_2$	anti-trypsin
165	2224.8	29.2		Complex	$H_5N_4S_2$	alpha-2-macro, IgA, anti-trypsin, IgM, Transferrin

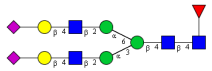
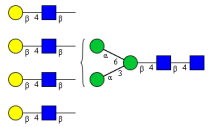
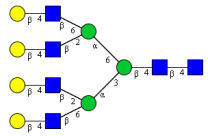
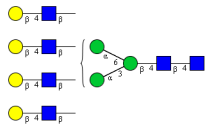
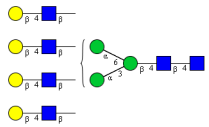
166	2224.8	27.3		Complex	$H_5N_4S_2$	anti-trypsin,Transferrin
167	2224.8	22.9		Complex	$H_5N_4S_2$	anti-trypsin, alpha-2-macro, Transferrin
168	2224.8	20.7		Complex	$H_5N_4S_2$	anti-trypsin, alpha-2-macro
169	2225.8	27.5		Complex	$H_5N_4F_2S_1$	alpha-2-macro
170	2225.8	26.1		Complex	$H_5N_4F_2S_1$	IgM

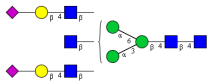
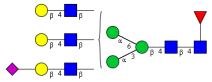
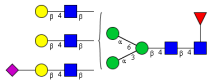
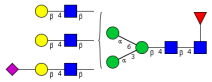
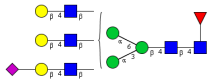
171	2282.8	25.4		Complex	$H_5N_5F_1S_1$	alpha-2-macro
172	2282.8	23.0		Complex	$H_5N_5F_1S_1$	alpha-2-macro
173	2282.8	22.4		Complex	$H_5N_5F_1S_1$	IgM, IgG, IgA
174	2282.8	17.5		Complex	$H_5N_5F_1S_1$	IgA, IgM, alpha-2-macro
175	2283.8	18.5		Complex	$H_5N_5F_3$	IgA, IgG

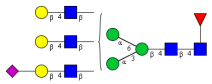
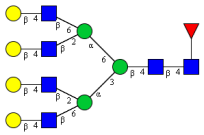
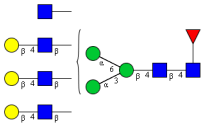
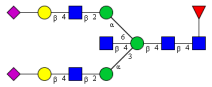
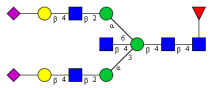
176	2283.9	20.0		Complex	$H_5N_5F_3$	AGP
177	2298.8	29.3		Complex	$H_6N_5S_1$	anti-trypsin
178	2298.8	27.5		Complex	$H_6N_5S_1$	AGP, anti-trypsin
179	2298.8	26.1		Complex	$H_6N_5S_1$	IgA, IgM
180	2298.8	25.1		Complex	$H_6N_5S_1$	Transferrin, alpha-2-macro

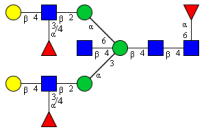
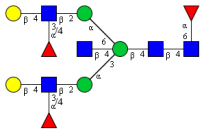
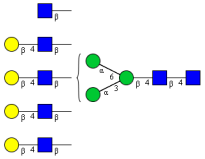
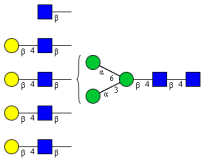
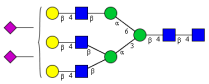
181	2298.8	26.0		Complex	$H_6N_5S_1$	anti-trypsin, AGP
182	2298.8	26.5		Complex	$H_6N_5S_1$	alpha-2-macro, Transferrin, AGP
183	2298.8	19.9		Complex	$H_6N_5S_1$	anti-trypsin, alpha-2-macro
184	2299.8	19.0		Complex	$H_6N_5F_2$	alpha-2-macro
185	2299.9	22.4		Complex	$H_6N_5F_2$	IgA, IgM

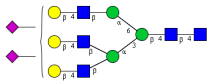
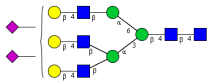
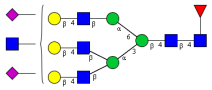
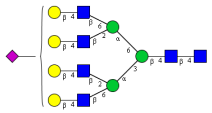
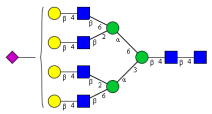
186	2356.9	29.2		Complex	$H_6N_6F_1$	alpha-2-macro
187	2356.9	20.2		Complex	$H_6N_6F_1$	IgA, alpha-2-macro
188	2370.8	32.4		Complex	$H_5N_4F_1S_2$	anti-trypsin, alpha-2-macro
189	2370.8	35.4		Complex	$H_5N_4F_1S_2$	anti-trypsin
190	2370.9	30.9		Complex	$H_5N_4F_1S_2$	IgM, Transferrin, IgA, anti-trypsin

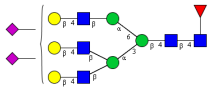
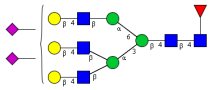
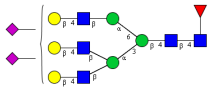
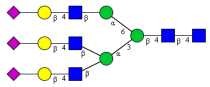
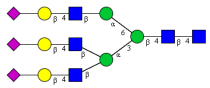
191	2370.9	22.2		Complex	$H_5N_4F_1S_2$	anti-trypsin, IgA
192	2372.9	31.4		Complex	H_7N_6	alpha-2-macro
193	2372.9	23.3		Complex	H_7N_6	AGP, IgA, alpha-2-macro
194	2372.9	25.3		Complex	H_7N_6	AGP
195	2372.9	19.9		Complex	H_7N_6	AGP

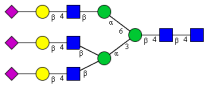
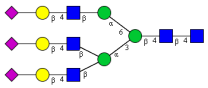
196	2425.8	26.6		Complex	$H_5N_5S_2$	IgA
197	2444.9	27.4		Complex	$H_6N_5F_1S_1$	AGP, anti-trypsin, alpha-2-macro, IgA
198	2444.9	25.2		Complex	$H_6N_5F_1S_1$	IgA
199	2444.9	28.2		Complex	$H_6N_5F_1S_1$	alpha-2-macro
200	2444.9	26.6		Complex	$H_6N_5F_1S_1$	alpha-2-macro, IgA

201	2444.9	27.7		Complex	$H_6N_5F_1S_1$	alpha-2-macro
202	2518.9	24.9		Complex	$H_7N_6F_1$	AGP
203	2559.9	17.4		Complex	$H_6N_7F_1$	IgA
204	2571.9	22.1		Complex	$H_5N_5F_1S_2$	anti-trypsin
205	2571.9	29.9		Complex	$H_5N_5F_1S_2$	anti-trypsin

206	2573.9	27.9		Complex	$H_5N_5F_1S_2$	IgA, anti-trypsin
207	2573.9	29.0		Complex	$H_5N_5F_1S_2$	IgM, alpha-2-macro
208	2575.9	22.1		Complex	H_7N_7	anti-trypsin
209	2575.9	26.7		Complex	H_7N_7	AGP
210	2589.9	30.2		Complex	$H_6N_5S_2$	anti-trypsin, IgM

211	2589.9	29.3		Complex	$H_6N_5S_2$	anti-trypsin
212	2589.9	30.9		Complex	$H_6N_5S_2$	alpha-2-macro, anti-trypsin, Transferrin
213	2648.0	23.6		Complex	$H_6N_6F_1S_1$	IgA
214	2664.0	26.3		Complex	$H_7N_6S_1$	AGP, anti-trypsin
215	2664.0	27.4		Complex	$H_7N_6S_1$	AGP

216	2736.0	23.4		Complex	$H_6N_5F_1S_1$	anti-trypsin
217	2736.0	30.6		Complex	$H_6N_5F_1S_1$	anti-trypsin
218	2736.0	29.0		Complex	$H_6N_5F_1S_1$	anti-trypsin, IgA
219	2881.0	49.5		Complex	$H_6N_5S_3$	IgM
220	2881.0	51.9		Complex	$H_6N_5S_3$	IgM, IgG

221	2881.0	52.7		Complex	$H_6N_5S_3$	IgG
222	2881.0	53.2		Complex	$H_6N_5S_3$	IgG, IgA