

Supplementary Information

Construction of a hydrophilic porphyrin-based MOF@COF hybrid via post-synthetic modification for N-glycopeptides analysis in human serum

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Characterization

Scanning electron microscopy (SEM) was characterized by Keol 2012 microscope. Transmission electron microscopy (TEM) was characterized by JEOL 1011 microscopy (Japan). Fourier transform infrared spectra (FT-IR) was characterized by Thermo Fisher Scientific 10 infrared spectrometer analysis. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) was used in an autoflex max (Bruker, USA). Nanoflow liquid chromatography–tandem mass spectrometry (Nano-LC-MS/MS) was used in Thermo Scientific TM Orbitrap Fusion Lumos (Thermo Scientific, USA).

Tryptic digestion of the standard proteins and actual sample.

HRP (1 mg) and BSA (2 mg) were dissolved in 100 μ L of deionized water. After 10 minutes of ultrasound, the protein was denatured in boiling water at 100 °C for 10 minutes. Then 100 μ L of ammonium bicarbonate (50 mM) was added together with the addition of trypsin at protein to trypsin ratio of 40: 1 and incubated the solution for 16 h at 37 °C to fully digest the protein. The obtained solution is collected in a centrifuge tube and stored at -20 °C for further use.

Serum (1 mg) was diluted in NH_4HCO_3 (50 mM) buffer and denatured in boiling water at 100 °C for 10 minutes. The mixture was reduced with DTT (200 mM) and NH_4HCO_3 (50 mM) at 37 °C for 1 h and alkylated with IAA (400 mM) and NH_4HCO_3 (50 mM) at 37 °C for 1 h in the dark. Then, the resulting mixture was incubated with trypsin (trypsin/protein is 1/40, w/w) at 37 °C for 16 h. Tryptic digests were lyophilized for further enrichment and analysis.

MALDI-TOF MS, nano-LC-MS/MS and data analysis.

This part of data search and analysis refers to our group's previous work, and the specific information can be found in References² and 18.

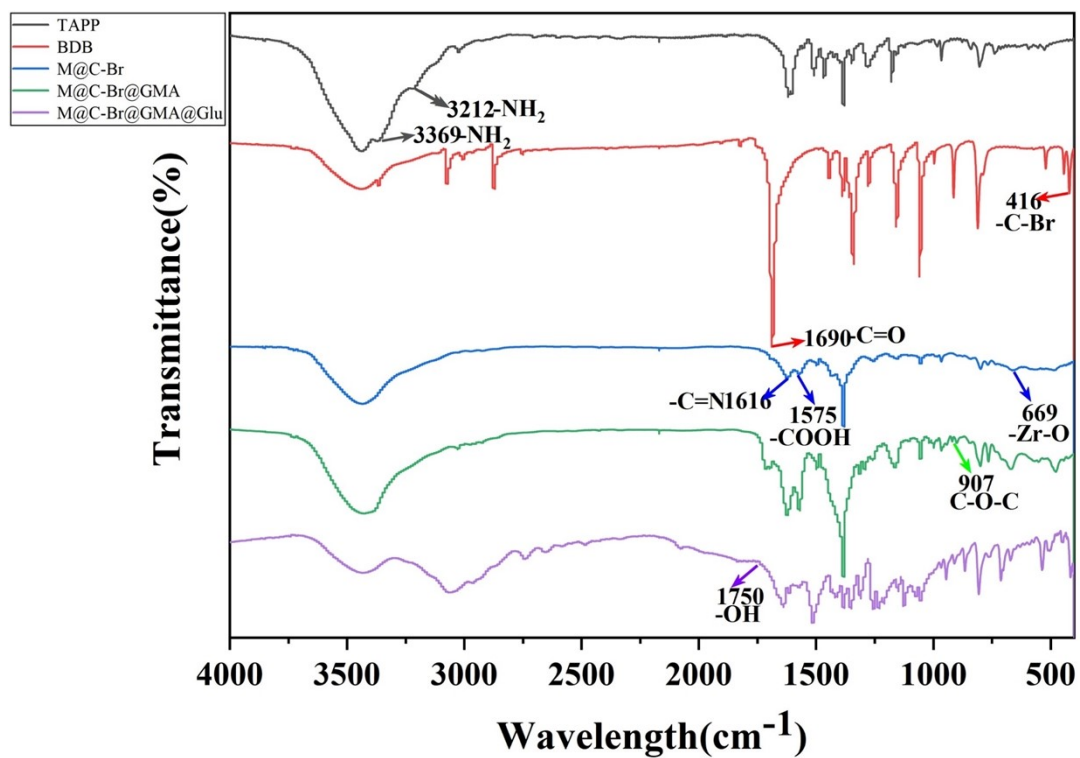


Fig. S1. The FT-IR spectra of TAPBB, BDB, M@C-Br, M@C-Br@GMA, and M@C-Br@GMA@Glu.

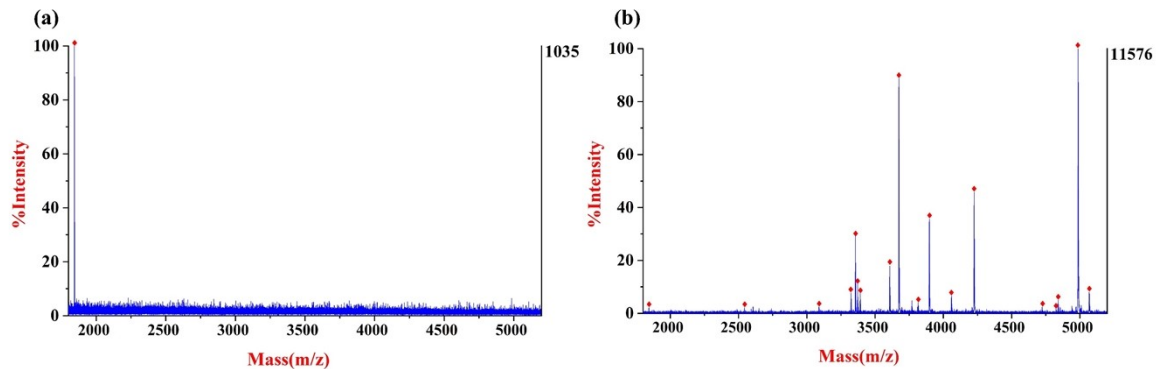


Fig. S2. MALDI-TOF mass spectra of HRP digests (a) before enrichment and (b) after enrichment with M@C-Br@GMA@Glu, glycopeptides peaks are signed as “◆”.

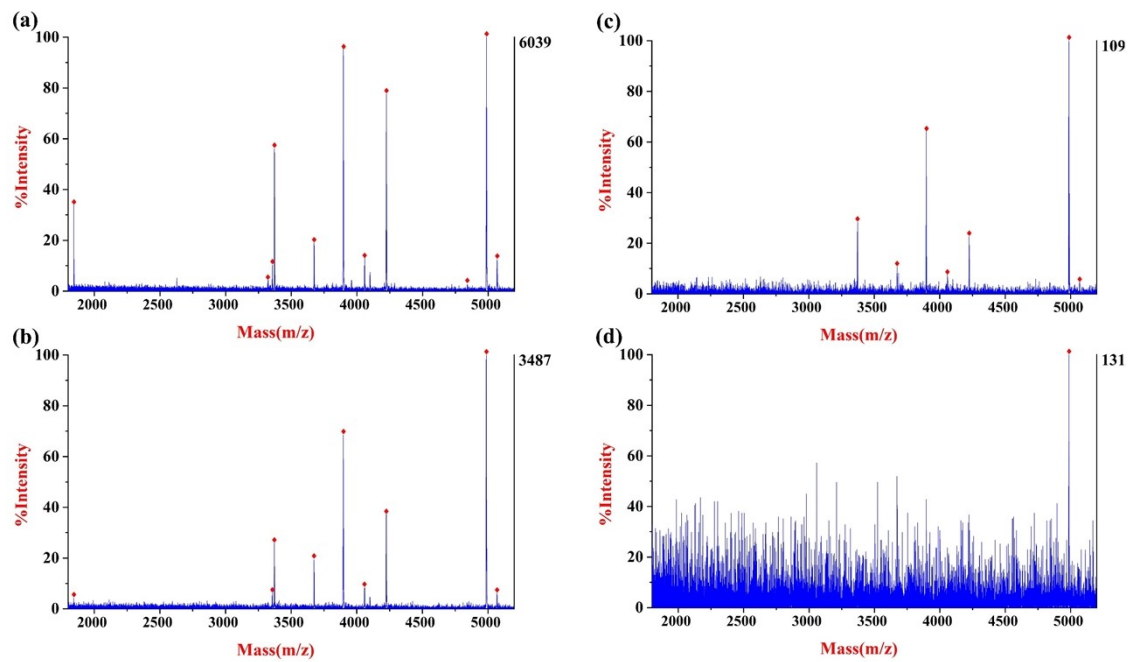


Fig. S3. MALDI-TOF Mass spectra of enriched glycopeptides from a mixture of HRP and BSA with a molar ratio, (a) 1:250, (b) 1:500, (c) 1:1000, (d) 1:2000, glycopeptide peaks are signed as “◆”.

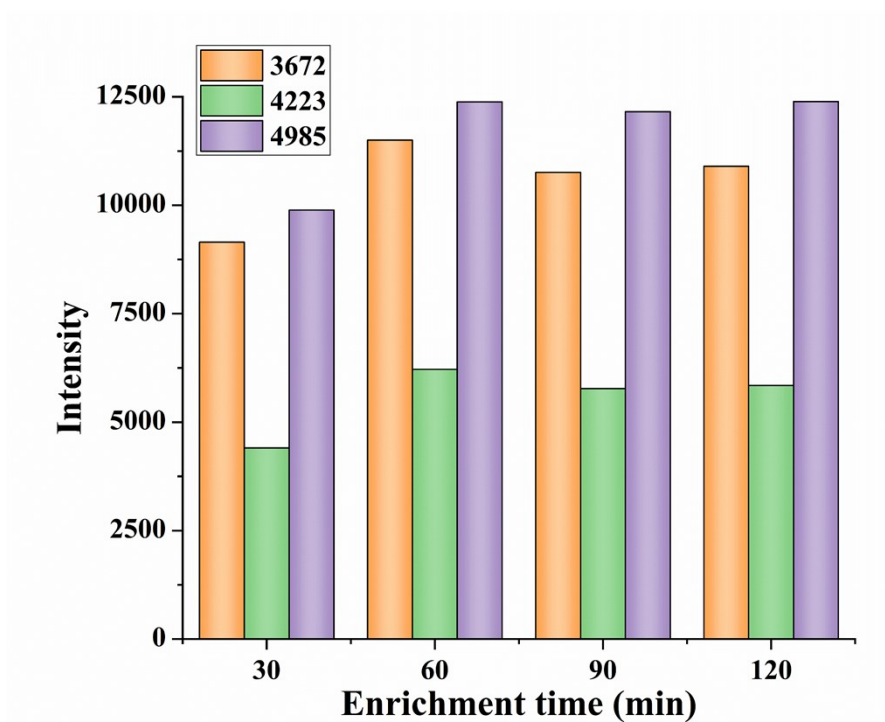


Fig. S4. MALDI-TOF MS spectra of HRP tryptic digest eluted with different time (30 min, 60 min, 90 min, 120 min) by M@C-Br@GMA@Glu.

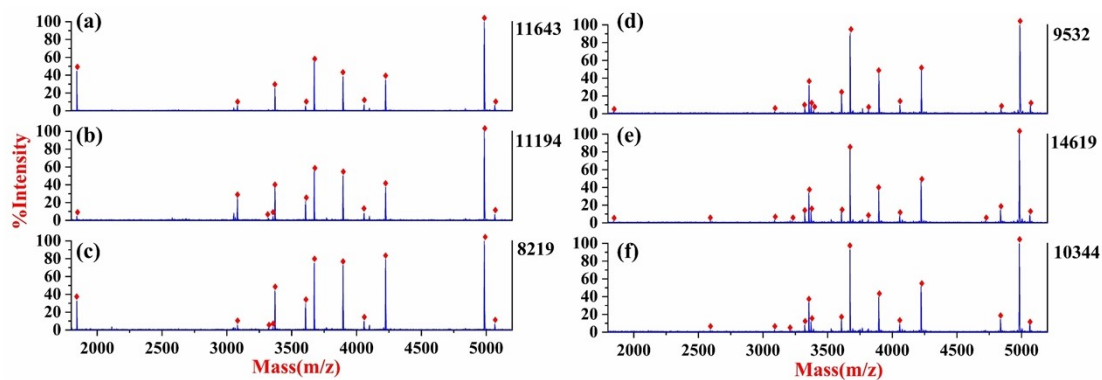


Fig. S5. MALDI-TOF MS spectra of HRP tryptic digest eluted with different loading buffer by M@C-Br@GMA@Glu: (a) for 0.5% TFA dissolved in 90% ACN aqueous solution, (b) for 1% TFA dissolved in 90% ACN aqueous solution, (c) for 3% TFA dissolved in 90% ACN aqueous solution, (d) for 0.5% TFA dissolved in 95% ACN aqueous solution, (e) for 1% TFA dissolved in 95% ACN aqueous solution, (f) for 3% TFA dissolved in 95% ACN aqueous solution, glycopeptides peaks are signed as “◆”.

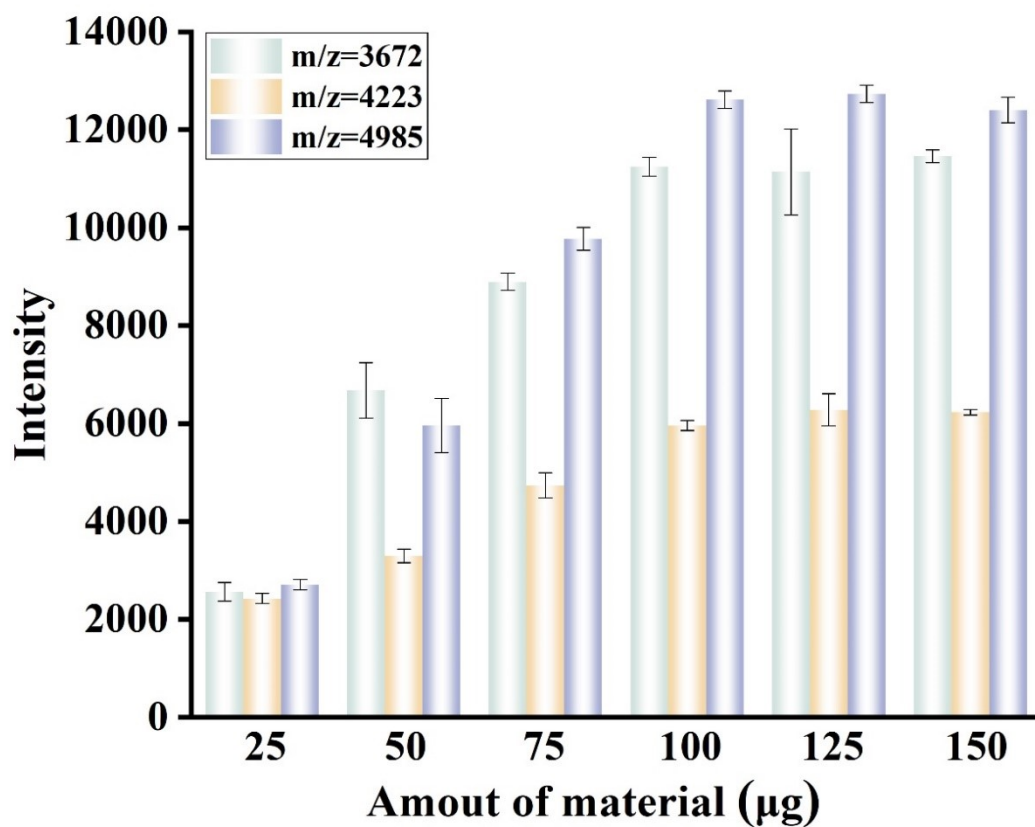


Fig. S6. Evaluation of the loading capacity of M@C-Br@GMA@Glu composites through enrichment for glycopeptides from HRP digests by different amounts of the composites.

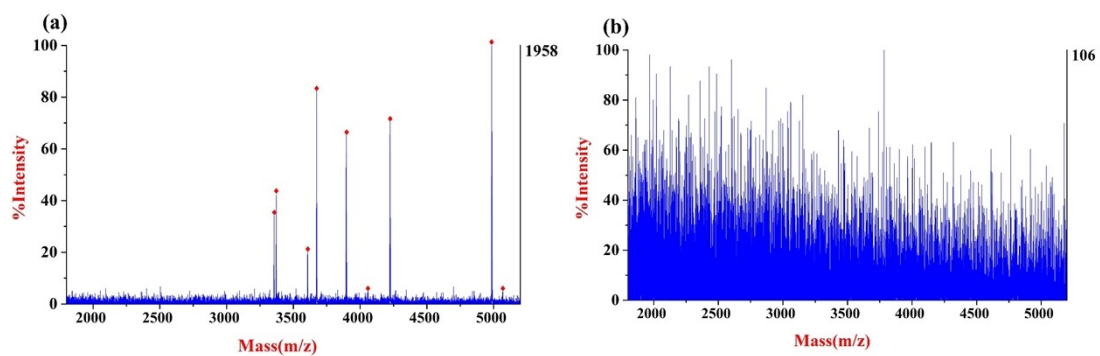


Fig. S7. MALDI-TOF MS spectra of the supernatant after the enriched by M@C-Br@GMA@Glu: (a) 75 µg, (b) 100 µg. Glycopeptide peaks are signed as “◆”.

Table S1. The detailed information of glycopeptides derived from HRP after enrichment by M@C-Br@GMA@Glu. #: Glycosylation site.

Num.	m/z	Amino acid sequence	Glycan composition
1	1843.1	NVGLN#R	XylMan3FucGlcNAc2
2	2542.6	SSPN#ATDTIPLVR	XylMan3FucGlcNAc2
3	3088.9	GLCPLNGN#LSALVDFDLR	XylMan3FucGlcNAc2
4	3323.1	QLTPTFYDNSCPN#VSNIVR	XylMan3FucGlcNAc2
5	3355.1	SFAN#STQTFNFVAFVEAMDR	XylMan3FucGlcNAc2
6	3371.1	SFAN#STQTFNFVAFVEAM*DR	XylMan3FucuGlcNAc2
7	3390.2	DSFRNVGLN#R	XylMan6Fuc2GlcNAc4
8	3607.4	NQCRGLCPLNGN#LSALVDFDLR	XylMan3FucGlcNAc2
9	3674.5	GLIQSDQELFSSPN#ATDTIPLVR	XylMan3FucGlcNAc2
10	3815.7	LHFHDCFVNGCDASILLDN#TTSFR	XylMan3FucGlcNAc2
11	3897.6	LHFHDCFVNGCDASILLDN#TTSFR	XylMan3FucGlcNAc2
12	4059.7	QLTPTFYDNSC(AAVESACPR)PN#VSNIVR-H2O	XylMan3GlcNAc2
13	4224.9	QLTPTFYDNSC(AAVESACPR)PN#VSNIVR	XylMan3FucGlcNAc2
14	4722.6	LYN#FSNTGLPDPTLN#TTYLQTLR	Man3FucGlcNAc2, Man3FucGlcNAc2
15	4825.8	LYN#FSNTGLPDPTLN#TTYLQTLR	XylMan2FucGlcNAc, XylMan2GlcNAc2
16	4840.7	LYN#FSNTGLPDPTLN#TTYLQTLR	XylMan3FucGlcNAc2
17	4986.9	LYN#FSNTGLPDPTLN#TTYLQTLR	XylMan3FucGlcNAc2, XylMan3FucGlcNAc2

18	5068.9	QLTPTFYDNSC(AAVESACPR)PN#VSNIVR	XylMan3GlcNAc2
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Table S2. The RSD of three parallel trials on the load capacity of M@C-Br@GMA@Glu.

Amount of material	m/z = 3672		m/z = 4223		m/z = 4985	
	Average \pm S. D.	RSD (%)	Average \pm S. D.	RSD (%)	Average \pm S. D.	RSD (%)
25 μ g	2565.0 \pm 189.6	7.4	2427.7 \pm 177.9	7.3	2709.7 \pm 106.3	3.9
50 μ g	6678.0 \pm 567.3	8.5	3294.0 \pm 139.2	4.2	5961.7 \pm 556.1	9.3
75 μ g	8898.3 \pm 175.9	1.9	4736.7 \pm 257.7	5.4	9771.0 \pm 235.0	2.4
100 μ g	11248.7 \pm 195.3	1.7	5960.7 \pm 101.3	1.7	12616.7 \pm 181.7	1.4
125 μ g	11140.7 \pm 881.1	7.9	6280.7 \pm 331.1	5.3	12735.7 \pm 176.8	1.4
150 μ g	11459.7 \pm 127.4	1.1	6231.7 \pm 54.1	0.9	12406.0 \pm 258.8	2.1

Table S3. The comparison table of M@C-Br@GMA@Glu and other previous materials in references.

No.	Materials used	LOD	Selectivity	The load capacity	Standard protein	Ref.
1	Fe ₃ O ₄ @Au-GSH	10 fmol μL ⁻¹	HRP: BSA = 1:100	-	HRP, IgG	[1]
2	Fe ₃ O ₄ @CS@Au-l-Cys	0.5 fmol μL ⁻¹	HRP: BSA = 1:1000	-	HRP	[2]
3	magCDP@Ada-MSA	0.1 fmol μL ⁻¹	HRP: BSA= 1:500	-	HRP	[3]
4	MU ₂ O ₇ -66-NH ₂ /PA	1 fmol μL ⁻¹	HRP: BSA = 1:1000	-	HRP, IgG	[4]
5	L-Cys-Fe ₃ O ₄ @mSiO ₂	1 fmol μL ⁻¹	HRP: BSA = 1:100	-	HRP, IgG	[5]
6	M@C-Br@GMA@Glu	0.2 fmol μL ⁻¹	HRP: BSA= 1:2000	100 mg/g	HRP	this work

“-” indicates that there is no mention.

Table S4. Details of enriched glycopeptides derived from serum of the normal controls and CC patients by M@C-Br@GMA@Glu nanospheres.

Num.	Annotated Sequence	Protein Group Accessions	Theo. MH ⁺ [Da]
Glycopeptides detected in normal control serum			
1	[R].LSLHRPALEDLLLGSEANLTCTLTGLR.[D]	P01876; P0DOX2	2964.582
2	[K].FNLTETSEAEIHQSFQHLLR.[T]	P01011	2401.178
3	[K].MVSHHNLTTGATLINEQWLLTTAK.[N]	P00739; P00738	2680.376
4	[K].SLGNVNFTVSAEALSEQELCGTEVPSVPEHGR.[K]	P01023	3414.612
5	[R].FSLLGHASISCTVENETIGVWRPSPPTCEK.[I]	P04003	3373.619
6	[K].ELHHLQEQNVSNAFLDKGEFYIGSK.[Y]	P00450	2904.416
7	[K].AALAAFNAQNGSNFQLEEISR.[A]	P02765	2366.137
8	[K].THTNISESHPNATFSAVGEASICEDDWSNGER.[F]	P01871	3520.483
9	[K].MVSHHNLTTGATLINEQWLLTTAK.[N]	P00739; P00738	2696.371
10	[K].VGQLQLSHNLSLVLPQNLK.[H]	P05155	2314.349
11	[R].QQQHLLFGSNVTDCSGNFCLFR.[S]	P02787	2516.108
12	[K].VVLHPNYSQVDIGLIK.[L]	P00738	1795.995
13	[R].QDQCIYNTTYLNVQR.[E]	P02763	1916.881
14	[K].LQAPLNYTEFQKPICLPSK.[G]	P03952	2248.168
15	[K].LDAPTNLQFVNETDSTVLVLR.[W]	P02751	2233.135
16	[R].KVCQDCPLLAPLNDTR.[V]	P02765	1900.926
17	[R].VIDFNCTTSSVSSALANTK.[D]	P04196	2015.959
18	[K].DIVEYYNDSNGSHVLQGR.[F]	P25311	2066.941
19	[K].AALAAFNAQNGSNFQLEEISR.[A]	P02765	2367.121
20	[R].ADGTVNQIEGEATPVNLTEPAK.[L]	P05090	2255.104
21	[K].AVLQLNEEGVDTAGSTGVTLNLTSPILR.[F]	P08185	3111.678
22	[K].AALAAFNAQNGSNFQLEEISR.[A]	P02765	2368.105
23	[K].VCQDCPLLAPLNDTR.[V]	P02765	1772.831
24	[R].FEVDSPVYNATWSASLK.[N]	P04114	1914.912
25	[R].FSDGLESNSSTQFEVK.[K]	P0C0L4; P0C0L5	1775.797
26	[K].AVLQLNEEGVDTAGSTGVTLNLTSPILR.[F]	P08185	3110.694
27	[K].MVSHHNLTTGATLINEQWLLTTAK.[N]	P00739; P00738	2681.360
28	[R].DESFAELHSKFLNEDYKSVFMKNISFDK.[I]	P21105	3545.624
29	[R].ADGTVNQIEGEATPVNLTEPAKLEVK.[F]	P05090	2724.394
30	[R].QNQCFYNSSYLNVQR.[E]	P19652	1921.850
31	[K].ENLTAPGSDSAVFFEQGTTR.[I]	P00450	2127.983
32	[R].QNQCFYNSSYLNVQR.[E]	P19652	1922.834
33	[R].KLPPGLLANFTLLR.[T]	P02750	1553.941
34	[R].LAGKPTHVNVSVVMAEVDGTCY.[-]	P01876	2348.126
35	[K].EHEGAIYPDNTTDFQR.[A]	P00450	1893.825
36	[R].LANLTQGEDQYYLR.[V]	P10909	1684.818
37	[R].VNQNLVYESGSLNFSK.[L]	P04114	1799.881
38	[R].VLSNNSDANLELINTWVAK.[N]	P05155	2102.076

39	[R].GLNVTLSSSTGRNGFK.[S]	P0C0L4; P0C0L5	1552.797
40	[K].WFYIASAFRNEEYNK.[S]	P02763; P19652	1938.902
41	[K].EGYSNISYIVVNHQGISSR.[L]	P49908	2124.036
42	[R].DQCIVDDITYNVNDTFHK.[R]	Q28749; P02751	2197.971
43	[R].FNSSYLQGTNQITGR.[Y]	P04114	1686.808
44	[K].SLGNVNFTVSAEAELESQELCGTEVPSVPEHGR.[K]	P01023	3415.596
45	[K].GCVLLSYLNETVTVSASLESVR.[G]	P01023	2398.217
46	[R].VYKPSAGNNSLYR.[D]	P02749	1469.738
47	[R].GFGVAIVGNYTAALPTEAALR.[T]	Q96PD5	2092.107
48	[K].NLFLNHSENATAK.[D]	P00739; P00738	1460.702
49	[R].FSYSKNETYQLFLSYSSK.[K]	P02748	2193.039
50	[K].LNAENNATFYFK.[I]	P01042	1432.674
51	[K].AGLQAFFVQVECNK.[S]	P00450	1640.774
52	[R].IYSGILNLSDITK.[D]	P03952	1437.784
53	[K].LATALSLSNKFVEGSHNSTVSLTTK.[N]	P04114	2607.351
54	[K].VTQVYAENGTVLQGSTVASVYK.[G]	P27169	2315.177
55	[K].YTGNASALFILPDQDK.[M]	P01011	1753.864
56	[K].ALGISPFHEHAEVVFTANDSGPR.[R]	P02766	2452.189
57	[K].YNSQNQSNNQFVLYR.[I]	P01042	1875.862
58	[K].WFYIASAFRNEEYNK.[S]	P02763; P19652	1939.886
59	[K].NLFLNHSENATAK.[D]	P00739; P00738	1461.686
60	[R].AQLLQGLGFNLTER.[S]	P08185	1560.838
61	[K].NTTCQDLQIEVTVK.[G]	P0C0L4; P0C0L5	1649.805
62	[K].DIVEYYNDSNGSHVLQGR.[F]	P25311	2067.925
63	[K].TPLTANITK.[S]	P0DOX2	959.541
64	[R].SQILEGLGFNLTESESDVHR.[G]	Q5RRCR2	2345.162
65	[R].LSHNELADSGIPGNSFNSSLVELDLSYNK.[L]	P51884	3221.548
66	[K].ELHHLQEQNVSNAFLDK.[G]	P00450	2022.988
67	[R].SPYYNVSDEISFHCYDGYTLR.[G]	Q864V9	2587.108
68	[K].ALPQPQNVTSLLGCTH.[-]	P02790	1736.864
69	[K].LNAENNATFYFK.[I]	P01042	1433.658
70	[K].HANWTLTPLK.[S]	P27169	1181.631
71	[K].LATALSLSNKFVEGSHNSTVSLTTK.[N]	P04114	2606.367
72	[K].LPTQNITFQTESSVAEQEAEFQSPK.[Y]	Q14624	2810.337
73	[K].LYLGSNLTLALHPALFQNLK.[L]	P22792	2316.223
74	[K].LDAPTNLQFVNEDSTVLVVR.[W]	P02751	2234.119
75	[R].GLNVTLSSSTGR.[N]	P0C0L4; P0C0L5	1105.585
76	[R].ITYSIVQTNCSK.[E]	P01042	1414.688
77	[K].CGLVPVLAENYNK.[SN]	P02787	1477.736
78	[K].GAFISNFSMTVDGK.[T]	P19823	1474.688
79	[R].SWPAVGNCSALR.[W]	P02790	1405.653
80	[R].EEQYNSTYR.[V]	P0DOX5	1190.496
81	[R].EEQFNSTFR.[V]	P01859	1158.506

82	[R].ENISDPTSPLR.[T]	P01591	1229.601
83	[R].QQQHFLFGSNVTDCSGNFCLFR.[S]	P02787	2517.092
84	[K].YDFNSSMLYSTAK.[G]	P04114	1527.667
85	[K].IYPGVDFGGEELNVTFVK.[G]	P03952	1984.990
86	[R].GLCVNASAVSR.[L]	P17936	1134.557
87	[R].ALGFENATQALGR.[A]	Q08380	1348.686
88	[R].EEQFNSTYR.[V]	P01861	1174.501
89	[K].TVLTPATNHMGNVFTTIPANR.[E]	P01024	2256.144
90	[K].VGQLQLSHNLSLVILVPQNLK.[H]	P05155	2315.333
91	[K].IDSTGNVTNELR.[V]	O75882	1319.644
92	[K].YNSQNQSNNQFVLYR.[I]	P01042	1876.846
93	[K].FEAAVNKAYNK.[S]	Q180E9	1255.632
94	[R].VLSNNSDANLELINTWVAK.[N]	P05155	2104.044
95	[R].DIENFNSTQK.[F]	P43652	1196.543
96	[R].SPYYNVSDEISFHCYDGYTLR.[G]	P00751	2587.108
97	[K].ADTHDEILEGLNFNLTEIPEAQIHEGFQELLR.[T]	P01009	3692.808
98	[K].NNATVHEQVGGPSLTSDLQAQSK.[G]	P04004	2382.153
99	[R].ESVTDHVNLTIPLEKPLQNFTLCFR.[A]	P02743	2972.519
100	[K].VSNQTLSLFFTVLQDVPVR.[D]	P01023	2164.165
101	[K].ELHHLQEQNVSN AFLDKGEFYIGSK.[Y]	P00450	2905.400
102	[K].LGSFEGLVNLTFIHLQHNR.[L]	P51884	2196.156
103	[K].NNATVHEQVGGPSLTSDLQAQSK.[G]	P04004	2383.137
104	[R].QQQHFLFGSNVTDCSGNFCLFR.[S]	P02787	2516.108
105	[K].LGACNDTLQQLMEVFKFDTISEK.[T]	P01008	2688.290
106	[R].DQCIVDDITYNVNDTFHK.[R]	Q28749; P02751	2198.955
107	[K].THTNISESHPNATFSAVGEASICEDDDWSGER.[F]	P0DOX6	3521.467
108	[K].ADTHDEILEGLNFNLTEIPEAQIHEGFQELLR.[T]	P01009	3693.792
109	[K].AFENVTDLQWLILDHNLLENSK.[I]	P51884	2613.320
110	[R].GGSSGWSGGLAQNR.[S]	P07357	1334.608
111	[R].SRYPHKPEINSTTHPGADLQENFCR.[N]	P00734	2955.380
112	[R].EEQYNSTYRVVSVLTVLHQDWLNGK.[E]	P0DOX5	2980.469
113	[R].LEPVHLQLQCMSQEQLAQAANATK.[E]	Q96PD5	2808.402
114	[K].NCGVNCSDVFTALIGEIASPNYPKYPENS.[C]	P09871	3527.621
115	[K].QVFPGLNYCTSGAYSNASSTDSASYYPPLTGDTR.[L]	P04114	3552.538
116	[K].DTLTSRPAQGVVTTLENVSPPR.[R]	P02751	2339.220
117	[K].LYLGSNNLTALHPALFQNLK.[L]	P22792	2317.207
118	[R].YPHKPEINSTTHPGADLQENFCR.[N]	P00734	2712.247
119	[K].YLGNATAIFFLPDEGK.[L]	P01009	1756.879
120	[K].DIVEYYNDSNGSHVLQGR.[F]	P25311	2066.941
121	[K].SRPANHCVYFYGDEISFSCHETSR.[F]	P04003	2920.241
122	[K].QVFPGLNYCTSGAYSNASSTDSASYYPPLTGDTR.[L]	P04114	3551.554

123	[K].QEPERNECFLQHK.[D]	P02768; P02770	1715.781
124	[R].VYKPSAGNNSLYR.[D]	P02749	1470.722
125	[K].SLGPNSCSANGPLYLIHGPNLYCYSDVEK.[L]	P02790	3283.503
126	[K].LNAENNATFYFK.[I]	P01042	1432.674
127	[K].SPDVINGSPISQK.[I]	P08603	1342.685
128	[K].GVTSVSQIFHSPDLAIRDTFVNASR.[T]	P05155	2718.385
129	[K].MLNTSSLLEQLNEQFNWVSR.[L]	P10909	2426.166
130	[K].MVSHHNLTTGATLINEQWLLTTAK.[N]	P00739; P00738	2697.355
131	[K].AALAAFNAQNGSNFQLEEISR.[A]	P02765	2368.105
132	[K].YKNNSDISSTR.[G]	P01871	1286.586
133	[K].YKNNSDISSTR.[G]	P01871	1285.602
134	[R].NHSCEPCQTLAVR.[S]	P00748	1572.689
135	[K].AKVGQLQLSHNLSLVILVPQNLK.[H]	P05155	2513.481
136	[R].YAEDKFNETTEK.[S]	P43652	1475.654
137	[K].ISNSSDTVECECSENWK.[G]	O75882	2045.806
138	[K].SLTFNETYQDISELVYGAK.[L]	P01008	2179.044
139	[R].AVNITSENLIDDVVSLIR.[G]	P02748	1972.060
140	[K].HQDFNSAVQLVENFCR.[N]	P00734	1964.892
141	[K].QSVPAHFVALNGSK.[L]	Q863A0	1455.759
142	[K].NLSMPLLPADFHK.[E]	P05546	1483.761
143	[R].NCCNTENPPGCYR.[Y]	P43652	1642.604
144	[K].VSNVSCQASVSR.[M]	P55058	1294.606
145	[K].HYTNSSQDVTVPCR.[V]	P0DOX2	1664.733
146	[K].RNNQTIFEQTINDLTFDGSFIK.[E]	A1YG99	2603.262
147	[K].TKPREEQYNSTYR.[V]	P0DOX5	1672.793
148	[R].NLTTSLTESVDR.[N]	P80108	1336.659
149	[R].FNDTEVLQR.[L]	P43251	1122.543
150	[R].LQNNENNISCVER.[G]	P36980; Q03591	1591.702
151	[R].FGCEIENNR.[S]	P25311	1139.479
152	[K].FLNNGTCTAEGK.[F]	P05156	1312.584
153	[R].ISEENETTCYMGK.[W]	P08603	1562.635
154	[R].EEQYNSTFR.[V]	P01860	1174.501
155	[K].LGNWSAMPSCCK.[A]	P02749	1251.550
156	[K].EDALNETR.[E]	P10909	948.427
157	[R].WFSAGLASNSSWLR.[E]	Q8WNM0	1582.765
158	[R].LQNNENNISCVER.[G]	P36980; Q03591	1590.718
159	[K].WSDIWNATK.[Y]	P06276	1121.526
160	[R].DTFVNASR.[T]	P05155	910.426
161	[K].LGNWSAMPSCCK.[A]	P02749	1267.545
162	[K].FVEGSHNSTVSLTTK.[N]	P04114	1607.791
163	[K].FSPSLGILKNGSTALHAAVMGGSLKAVDLLLKA NADPALPNTNNELPR.[D]	Q502M6	4914.603
164	[K].VDKDLQSLEDILHQVENK.[T]	P02679	2124.082

165	[K].YLGNATAIFFLPDEGKLQHLENELTHDIITK.[F]	P01009	3541.821
166	[K].ADTHDEILEGLNFNLTEIPEAQIHEGFQELLR.[T]	P01009	3692.808
167	[K].GLKFNLTTETSEAEIHQSFQHLLR.[T]	P01011	2699.379
168	[K].SVQEIQATFFYFTPNKTEDTIFLR.[E]	P02763; P19652	2896.440
169	[R].EGDHEFLEVPEAQEDVEATFPVHQPGNYSCSYR.[T]	P04217	3837.661
170	[K].WNPSPPACEPNSCINLPDIPHASWETYPRPTK.[E]	P04003	3733.705
171	[K].WNPSPPACEPNSCINLPDIPHASWETYPRPTK.[E]	P04003	3732.721
172	[K].DFVNASSKYEITTIHNLFR.[K]	P05546	2256.130
173	[R].NEEYNKSVQEIQATFFYFTPNKTEDTIFLR.[E]	P02763; P19652	3674.754
174	[K].NNATVHEQVGGPSLTSDLQAQSK.[G]	P04004	2382.153
175	[K].SLGNVNFTVSAEAELESQELCGTEVPSVPEHGRK.[D]	P01023	3542.707
176	[K].KLSSWVLLMKYLGNATAIFFLPDEGKLQHLENE LTHDIITK.[F]	P01009	4727.516
177	[R].QLAHQSNSTNIFFSPVSIATAFAMLSLGTK.[A]	P01009	3183.603
178	[K].DLQSLEDILHQVENKTSEVK.[Q]	P02679	2326.177
179	[K].DLQSLEDILHQVENK.[T]	P02679	1781.892
180	[K].AGLQAFFVQECNKSSSK.[D]	P00450	2029.965
181	[R].QLAHQSNSTNIFFSPVSIATAFAMLSLGTK.[A]	P01009	3182.619
182	[K].AALAAFNAQNGSNFQLEEISR.[A]	P02765	2368.105
183	[K].SLGPNSCSANGPLYLIHGPNLYCYSYDVEK.[L]	P02790	3284.487
184	[K].YLGNATAIFFLPDEGKLQHLENELTHDIITK.[F]	P01009	3542.805
185	[R].WVLTAAHCLLYPPWDKNFTENDLLVR.[I]	P00734	3172.592
186	[R].QKDVDKEFYLFPTVFDENESLLEDNIR.[M]	P00450	3417.674
187	[R].LQAILGVPWKDKNCTSR.[L]	Q9GLN8	1987.043
188	[K].NCGVNCSDVFTALIGEIASPNYPKYPENSR.[C]	P09871	3528.605
189	[K].LNAENNATFYFK.[I]	P01042	1433.658
190	[R].WVLTAAHCLLYPPWDKNFTENDLLVR.[I]	P00734	3173.576
191	[R].FNSSYLQGTNQITGR.[Y]	P04114	1687.792
192	[R].NETGPYQCEIR.[D]	P11464	1367.590
193	[K].VTACHSSQP NATLYK.[M]	P05543	1677.790
194	[R].ETAYSNASLLIQNVTR.[E]	P11464	1781.892
195	[R].VLYLAAYNCTLRPVSK.[K]	Q9UGM5	1868.994
196	[R].LQNNENNISCVER.[G]	P36980; Q03591	1591.702
197	[R].KLPDHHSPALFQDCMNASIHFLK.[A]	Q5VUY2	2707.312
198	[R].FSDGLESNSSTQFEVK.[K]	P0C0L5	1775.797
199	[R].DNCCILDER.[F]	P02679	1195.472
200	[K].FLNNGTCTAEGK.[F]	P05156	1313.568
201	[K].VPGNVTAVLGETLK.[V]	P01833	1398.784
202	[K].NGSLFAFR.[G]	P04004	912.457
203	[R].FSGSTSGNTTTLTISR.[V]	A0A075B6J6	1630.792
204	[R].GLNVTLSSSTGR.[N]	P0C0L5	1105.585

205	[K].NNSDISSTR.[G]	P01871	994.444
206	[K].DVLNFTCEPK.[S]	P11464	1223.561
207	[K].NLFLNHSENATAK.[D]	P00739; P00738	1459.718
208	[K].NGTAVCATNR.[R]	P05156	1064.479
209	[K].YNSQNSNNQFVLYR.[I]	P01042	1876.846
210	[R].LDVDQALNR.[S]	P04278	1044.532
Glycopeptides detected in CC serum			
1	[K].THTNISESHPNATFSAVGEASICEDDWNSEGER.[F]	P01871	3520.483
2	[R].LSLHRPALEDLLLGSEANLTCTLTGLR.[D]	P01876; P0DOX2	2964.582
3	[K].LGACNDTLQQLMEVFKFDTISEK.[T]	P01008	2688.290
4	[K].AALAAFNAQNNGSNFQLEEISR.[A]	P02765	2366.137
5	[K].YLGNATAIFFLPDEGKLQHLENELTHDIITK.[F]	P01009	3541.821
6	[R].DQCIVDDITYNVNDTFHK.[R]	Q28749; P02751	2197.971
7	[K].SLGNVNFTVSAEALLESQELCGTEVPSVPEHGR.[K]	P01023	3414.612
8	[K].ADTHDEILEGLNFNLTEIPEAQIHEGFQELLR.[T]	P01009	3692.808
9	[R].QQQHFLFGSNVTDCSGNFCLFR.[S]	P02787	2516.108
10	[K].AALAAFNAQNNGSNFQLEEISR.[A]	P02765	2367.121
11	[K].LDAPTNLQFVNEDSTVLVLR.[W]	P02751	2233.135
12	[R].FSLLGHASISCTVENETIGVWRPSPPTCEK.[I]	P04003	3373.619
13	[K].VVLHPNYSQVDIGLIK.[L]	P00738	1795.995
14	[K].LGSFEGLVNLTFIHLQHNR.[L]	P51884	2196.156
15	[K].SVQEIQATFFYFTPNTEDTIFLR.[E]	P02763; P19652	2896.440
16	[K].THTNISESHPNATFSAVGEASICEDDDWSEGER.[F]	P0DOX6	3521.467
17	[K].ADTHDEILEGLNFNLTEIPEAQIHEGFQELLR.[T]	P01009	3693.792
18	[R].ESVTDHVNLTIPLEKPLQNFTLCFR.[A]	P02743	2972.519
19	[R].FSDGLESNSSTQFEVK.[K]	P0C0L4; P0C0L5	1775.797
20	[K].VSNQTLNLFVTLQDVPVR.[D]	P01023	2164.165
21	[R].SPYYNVSDEISFHCYDGYTLR.[G]	P00751	2587.108
22	[K].LPTQNITFQTESSVAEQEAEFQSPK.[Y]	Q14624	2810.337
23	[K].SLGNVNFTVSAEALLESQELCGTEVPSVPEHGR.[K]	P01023	3415.596
24	[K].IITILEEEMNVSVCGLYTYGKVPVPGHVTVSICR.[K]	P01023	3735.879
25	[R].FNSSYLQGTNQITGR.[Y]	P04114	1686.808
26	[R].KVCQDCPLLAPLNDTR.[V]	P02765	1900.926
27	[R].SQILEGLGFNLTESESDVHR.[G]	Q5RCR2	2345.162
28	[K].AGLQAFFVQECNK.[S]	P00450	1640.774
29	[K].VCQDCPLLAPLNDTR.[V]	P02765	1772.831
30	[K].FNLTETSEAEIHQSFQHLLR.[T]	P01011	2401.178
31	[K].NLFLNHSENATAK.[D]	P00738	1460.702
32	[R].TEVSSNHVLIYLDKVSNTLSLFFTVLQDVPVR.[D]	P01023	3762.995
33	[R].QNQCIFYNSSYLVNQR.[E]	P19652	1921.850
34	[K].YLGNATAIFFLPDEGK.[L]	P01009	1756.879
35	[K].NLFLNHSENATAK.[D]	P00738	1461.686

36	[K].YLGNATAIFFLPDEGKLQHLENELTHDIITK.[F]	P01009	3542.805
37	[R].FEVDSPVYNATWSASLK.[N]	P04114	1914.912
38	[K].EHEGAIYPDNTTDFQR.[A]	P00450	1893.825
39	[R].IYSGILNLSDITK.[D]	P03952	1437.784
40	[R].LANLTQGEDQYYLR.[V]	P10909	1684.818
41	[K].VGQLQLSHNLSLVILVPQNLK.[H]	P05155	2314.349
42	[K].YKNNSDISSTR.[G]	P01871	1286.586
43	[R].QDQCIYNTTYLNVQR.[E]	P02763	1916.881
44	[R].ADGTVNQIEGEATPVNLTEPAKLEVK.[F]	P05090	2724.394
45	[R].ADGTVNQIEGEATPVNLTEPAK.[L]	P05090	2255.104
46	[K].LNAENNATFYFK.[I]	P01042	1432.674
47	[K].LQAPLNYTEFQKPICLPSK.[G]	P03952	2248.168
48	[K].KLSSWVLLMKYLGNATAIFFLPDEGKLQHLENE LTHDIITK.[F]	P01009	4727.516
49	[R].VYKPSAGNNSLYR.[D]	P02749	1470.722
50	[R].ENISDPTSPLR.[T]	P01591	1229.601
51	[K].MVSHHNLTTGATLINEQWLLTTAK.[N]	P00738	2680.376
52	[K].MVSHHNLTTGATLINEQWLLTTAK.[N]	P00738	2696.371
53	[K].LNAENNATFYFK.[I]	P01042	1433.658
54	[K].HANWTLTPLK.[S]	P27169	1181.631
55	[K].AALAAFNAQNGSNFQLEEISR.[A]	P02765	2368.105
56	[K].DFVNASSKYEITTIHNLFR.[K]	P05546	2256.130
57	[R].GLNVTLSSTGR.[N]	P0C0L4; P0C0L5	1105.585
58	[R].IVGGTNSSWGEWPWQVSLQVK.[L]	P03952	2359.172
59	[K].NNSDISSTR.[G]	P01871	994.444
60	[K].CGLVPVLAENYNK.[SN]	P02787	1477.736
61	[R].KLPPGLLANFTLLR.[T]	P02750	1553.941
62	[R].FNSSYLQGTNQITGR.[Y]	P04114	1687.792
63	[R].GGSSGWSGGLAQNR.[S]	P07357	1334.608
64	[R].AQLLQGLGFNLTER.[S]	P08185	1560.838
65	[R].SWPAVGNCSALR.[W]	P02790	1405.653
66	[K].YKNNSDISSTR.[G]	P01871	1285.602
67	[K].AFENVTDLQWLILDHNLENSK.[I]	P51884	2613.320
68	[K].GAFISNFSMTVDGK.[T]	P19823	1474.688
69	[R].QLAHQSNSTNIFFSPVSIATAFAMLSLGTK.[A]	P01009	3182.619
70	[R].DMLDRFLGVDITSIGGNPTDSRIDGEKGALTSVG NHPNSTLAEQR.[E]	C4JTD3	4755.328
71	[K].EGYSNISYIVVNHQGISSR.[L]	P49908	2124.036
72	[K].VSDDITYVATATLPNYCRAGNGPK.[D]	P79085	2641.256
73	[R].RSDLPGGLAGPRGGLNTR.[S]	Q02080	1881.989
74	[R].ALGFENATQALGR.[A]	Q08380	1348.686
75	[K].AIDLNLENFHIIIIGDAINLSTYFK.[N]	Q9F411	2737.397
76	[K].FLNNGTCTAEGK.[F]	P05156	1312.584

77	[R].QQQHFLFGSNVTDCSGNFCLFR.[S]	P02787	2517.092
78	[K].QVFPGLNYCTSGAYSNASSTDSASYPLTGDTR.[L]	P04114	3551.554
79	[K].QVLFLDTVYGNCSHFVTK.[T]	P04114	2230.085
80	[R].EEQFNSTFR.[V]	P01859	1158.506
81	[K].VHNGSEILFSYFQDLVITLPFELR.[K]	P04114	2838.471
82	[R].ITYSIVQTNCSK.[E]	P01042	1414.688
83	[K].IGGIWTVWGTNK.[S]	P14151	1332.695
84	[R].RGSNLASGRRTPPNCAAEDIK.[A]	Q9ULD9	2271.126
85	[K].LYLGSNNLTALHPALFQNLK.[L]	P22792	2316.223
86	[K].CGLVPVLAENYK.[SN]	P02787	1478.720
87	[R].NISDGFDPDNVDAALALPAHSYSGR.[E]	P04004	2773.306
88	[K].ALPQPQNVTSLLGCTH.[-]	P02790	1736.864
89	[K].ELHHLQEQNVSNAFLDKGEFYIGSK.[Y]	P00450	2905.400
90	[R].WFSAGLASNSSWLR.[E]	Q8WNM0	1582.765
91	[R].SGNYPSSLSNETDR.[L]	Q9NS86	1527.656
92	[K].AAIPSALDTNSSK.[S]	Q08380	1275.643
93	[K].YNSQNSNNQFVLYR.[I]	P01042	1876.846
94	[R].DTFVNASR.[T]	P05155	910.426
95	[R].VELEDFNGNR.[T]	O75636	1194.527
96	[R].DIENFNSTQK.[F]	P43652	1196.543
97	[K].WVSNKTEGR.[I]	P01008	1077.532
98	[R].EEQYNSTYR.[V]	P01857	1190.496
99	[K].LPPGLLANFTLLR.[T]	P02750	1425.846
100	[R].VITVQVANFTLR.[L]	Q9Y6R7	1361.779
101	[K].WSDIWNATK.[Y]	P06276	1121.526
102	[K].NGTAVCATNR.[R]	P05156	1064.479
103	[R].NGTLVAFR.[G]	Q92954	878.473
104	[R].AFGSNPNLTK.[V]	P22792	1049.526
105	[K].EDALNETR.[E]	P10909	948.427
106	[R].EEQYNSTFR.[V]	P01860	1174.501
107	[K].IDSTGNVTNELR.[V]	O75882	1319.644
108	[R].NECFLOHK.[D]	P02768; P02770	1076.483
109	[K].ELLETVVNR.[T]	P55056	1073.584
110	[R].FNDTEVLQR.[L]	P43251	1122.543
111	[K].DFYVDENTTVR.[V]	Q5RCR2	1359.606
112	[R].LDVDQALNR.[S]	P04278	1044.532
113	[K].YSRKNMLYMNSSEK.[D]	Q8IM30	1768.788
114	[R].FSGSTSGNTTTLTISR.[V]	A0A075B6J6	1630.792
115	[R].QQQHFLFGSNVTDCSGNFCLFR.[S]	P02787	2516.108
116	[K].MVSHHNLTTGATLINEQWLLTTAK.[N]	P00739; P00738	2680.376
117	[K].NNATVHEQVGGPSLTSDLQAQSK.[G]	P04004	2382.153
118	[R].FQSPAGTEALFELHNISVADSANYSCVYVDLKPP	P04217	4630.172

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119	[K].AALAAFNAQNNGSNFQLEEISR.[A]	P02765	2367.121
120	[K].NLFLNHSENATAK.[D]	P00739; P00738	1460.702
121	[K].ENLTAPGSDSAVFFEQGTR.[I]	P00450	2127.983
122	[R].SQILEGLGFNLTESESDVHR.[G]	P29622	2345.162
123	[K].SLTFNETYQDISELVYGAK.[L]	P01008	2179.044
124	[K].LNAENNATFYFK.[I]	P01042	1432.674
125	[R].LGHCPDPVLVNGEFSSSGPVNVSDK.[I]	P20851	2612.230
126	[K].NLFLNHSENATAK.[D]	P00739; P00738	1461.686
127	[K].MVSHHNLTTGATLINEQWLLTTAK.[N]	P00739; P00738	2696.371
128	[K].KDPFTSYAAFVVPPIVPKDLHFKEVCNTEYK.[D]	P68875	3754.883
129	[K].LPFLQSGSLLILGPNGCGKSSIQRIIAEIWPVYN K.[N]	P41909	4014.152
130	[K].CGLVPVLAENYNK.[SN]	P02787	1477.736
131	[R].LAGKPTHVNVSVVMAEVDGTCY.[-]	P01876	2348.126
132	[K].MVSHHNLTTGATLINEQWLLTTAK.[N]	P00739; P00738	2681.360
133	[K].VTQVYAENGTVLQGSTVASVYK.[G]	P27169	2315.177
134	[R].VYKPSAGNNSLYR.[D]	P02749	1469.738
135	[K].NNATVHEQVGGPSLTSDLQAQSK.[G]	P04004	2383.137
136	[R].AVNITSENLIDDVVSILR.[G]	P02748	1972.060
137	[R].LHNMSEAMAVTAYHQYSK.[G]	Q8TDX9	2113.932
138	[R].YAEDKFNETTEK.[S]	P43652	1475.654
139	[K].SPDVINGSPISQK.[I]	P08603	1342.685
140	[R].NLTTSLTESVDR.[N]	P80108	1336.659
141	[K].AALAAFNAQNNGSNFQLEEISR.[A]	P02765	2366.137
142	[R].LGHCPDPVLVNGEFSSSGPVNVSDK.[I]	P20851	2613.214
143	[R].SPYYNVSDEISFHCYDGYTLR.[G]	Q864V9	2587.108
144	[K].ALGISPFHEHAEVVFTANDSGPR.[R]	P02766	2452.189
145	[K].HQDFNSAVQLVENFCR.[N]	P00734	1964.892
146	[K].LDAPTNLQFVNEDSTVLVR.[W]	P02751	2234.119
147	[K].VDNALQSGNSQESVTEQDSK.[D]	P01834	2137.937
148	[K].DIVEYYNDSNGSHVLQGR.[F]	P25311	2067.925
149	[K].AALAAFNAQNNGSNFQLEEISR.[A]	P02765	2368.105
150	[K].WFYIASAFRNEEYNK.[S]	P02763; P19652	1939.886
151	[K].VPGNVTAVLGETLK.[V]	P01833	1398.784
152	[R].FAPLNSWPDNVSLDK.[A]	A1AIC1	1704.812
153	[R].EVNTSGFAPARPPPQPGSTTFWAWSVLR.[V]	P0DOX3	3057.522
154	[K].RNNQTIFEQTINDLTFDGSFIK.[E]	A1YG99	2603.262
155	[K].LNAENNATFYFK.[I]	P01042	1433.658
156	[K].FVEGSHNSTVSLTTK.[N]	P04114	1607.791

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