Supplemental Information S1: MS/MS spectra of in vitro modified peptides identified in BSA and Histone H4. The modified residue is in bold and underlined. Ethyl E,  $^{-19}K$ ,  $^{108}C$ ,  $^{Glycerol}E$ , and  $^{Glycerol}D$  represent ethylation of Glutamic acid, loss of 19 Da from Lysine, addition of 108 on Cysteine, esterification of Glutamic acid by glycerol, and esterification of Aspartic acid by glycerol respectively. Oxidation of Cysteine and Methionine are labeled as  $^{O}M$  and  $^{OOO}C$ , respectively. The symbols ^, \* in spectral labeling represent b or y ions with ammonium and water loss, respectively.

The peptide sequence, charge state, mass shift, and retention time are listed in each MS/MS spectrum.

- A. MS/MS spectra of EthylE peptides identified in BSA.
- A1. MS/MS spectrum of "DAIPENLPPLTADFA<sup>Ethyl</sup><u>E</u>DK" that identified E + ethylation in BSA SDS-PAGE gel band destained either with acetic acid/ethanol/water (10%:50%:40%), or ethanol/water (50%:50%).
- A2. MS/MS spectrum of "<sup>Ethyl</sup>KQTALVELLK" that identified E + ethylation in BSA SDS-PAGE gel band destained with acetic acid/ethanol/water (10%:50%:40%).
- <u>B. MS/MS spectra of <sup>-19</sup>K peptides identified in Histone H4 SDS-PAGE gel band</u> <u>destained with ethanol/water (50%:50%).</u>
- B1. MS/MS spectrum of "EIAQDF<sup>-19</sup><u>K</u>TDLR" that identified K 19 in Histone H4 SDS-PAGE gel band destained with ethanol/water (50%:50%).
- B2. MS/MS spectrum of "KQLAT<sup>-19</sup><u>K</u>AAR" that identified K 19 in Histone H4 SDS-PAGE gel band destained with ethanol/water (50%:50%).
- B3. MS/MS spectrum of "RYQ<sup>-19</sup><u>K</u>STELLIR" that identified K 19 in Histone H4 SDS-PAGE gel band destained with ethanol/water (50%:50%).
- B4. MS/MS spectrum of "RVTIMP<sup>-19</sup><u>K</u>DIQLAR" that identified K 19 in Histone H4 SDS-PAGE gel band destained with ethanol/water (50%:50%).
- B5. MS/MS spectrum of "VTIMP<sup>-19</sup><u>K</u>DIQLAR" that identified K 19 in Histone H4 SDS-PAGE gel band destained with ethanol/water (50%:50%).
- B6. MS/MS spectrum of "DAVTYTEHA<sup>-19</sup><u>K</u>R" that identified K 19 in Histone H4 SDS-PAGE gel band destained with ethanol/water (50%:50%).
- B7. MS/MS spectrum of "KTVTAMDWYAL<sup>-19</sup><u>K</u>R" that identified K 19 in Histone H4 SDS-PAGE gel band destained with ethanol/water (50%:50%).

# <u>C. MS/MS spectra of <sup>108</sup>C peptides identified in BSA gel band destained with ethanol/water (50%:50%).</u>

- C1. MS/MS spectrum of "<sup>O</sup>MP<sup>108</sup><u>C</u>AEDYLSLILNR" peptides identified in BSA SDS-PAGE gel band destained with ethanol/water (50%:50%).
- C2. MS/MS spectrum of "LKPDPNTL<sup>108</sup>CDEFK" peptides identified in BSA SDS-PAGE gel band destained with ethanol/water (50%:50%).
- C3. MS/MS spectrum of "LKE<sup>108</sup><u>C</u>CDKPLLEK" peptides identified in BSA SDS-PAGE gel band destained with ethanol/water (50%:50%).

- C4. MS/MS spectrum of "LKEC<sup>108</sup><u>C</u>DKPLLEK" peptides identified in BSA SDS-PAGE gel band destained with ethanol/water (50%:50%).
- C5. MS/MS spectrum of "DDPHA<sup>108</sup>CYSTVFDK" peptides identified in BSA SDS-PAGE gel band destained with ethanol/water (50%:50%).
- C6. MS/MS spectrum of "QN<sup>108</sup>CDQFEK" peptides identified in BSA SDS-PAGE gel band destained with ethanol/water (50%:50%).
- C7. MS/MS spectrum of "VGTR<sup>108</sup><u>C</u>CTKPESER" peptides identified in BSA SDS-PAGE gel band destained with ethanol/water (50%:50%).
- C8. MS/MS spectrum of "VGTRC<sup>108</sup><u>C</u>TKPESER" peptides identified in BSA SDS-PAGE gel band destained with ethanol/water (50%:50%).
- C9. MS/MS spectrum of "<sup>O</sup>MP<sup>108</sup><u>C</u>AEDYLSLILNR" peptides identified in BSA SDS-PAGE gel band destained with ethanol/water (50%:50%).
- C10. MS/MS spectrum of "L<sup>108</sup><u>C</u>VLHEK" peptides identified in BSA SDS-PAGE gel band destained with ethanol/water (50%:50%).
- C11. MS/MS spectrum of "RP<sup>108</sup><u>C</u>FSALTPDETYVPK" peptides identified in BSA SDS-PAGE gel band destained with ethanol/water (50%:50%).
- C12. MS/MS spectrum of "T<sup>000</sup>CVADESHAG<sup>108</sup><u>C</u>EK" peptides identified in BSA SDS-PAGE gel band destained with ethanol/water (50%:50%).
- C13. MS/MS spectrum of "YNGVFQE<sup>108</sup><u>C</u>CQAEDK" peptides identified in BSA SDS-PAGE gel band destained with ethanol/water (50%:50%).
- C14. MS/MS spectrum of "QN<sup>108</sup>CDQFEK" peptides identified in BSA SDS-PAGE gel band destained with ethanol/water (50%:50%).
- C15. MS/MS spectrum of "YI<sup>108</sup>CDN<sup>1</sup>QDTISSK" peptides identified in BSA SDS-PAGE gel band destained with ethanol/water (50%:50%).
- C16. MS/MS spectrum of "<sup>108</sup><u>C</u>CTESLVNR" peptides identified in BSA SDS-PAGE gel band destained with ethanol/water (50%:50%).
- C17. MS/MS spectrum of "<sup>108</sup><u>C</u>CTKPESER" peptides identified in BSA SDS-PAGE gel band destained with ethanol/water (50%:50%).
- D. MS/MS spectra of <sup>glycerol</sup>D/E peptides identified in BSA incubated with 20% glycerol 50 mM ammonium bicarbonate solution at 4 °C for 7 days, followed by in solution digestion with trypsin.
- D1. MS/MS spectrum of "KQTALV<sup>glycerol</sup><u>E</u>LLK" peptides identified in BSA in 20% glycerol solution.
- D2. MS/MS spectrum of "DTHKS<sup>glycerol</sup><u>E</u>IAHR" peptides identified in BSA in 20% glycerol solution.
- D3. MS/MS spectrum of "FKDLGE<sup>glycerol</sup><u>E</u>HFK" peptides identified in BSA in 20% glycerol solution.
- D4. MS/MS spectrum of "DLG<sup>glycerol</sup><u>E</u>EHFK" peptides identified in BSA in 20% glycerol solution.
- D5. MS/MS spectrum of "LVN<sup>glycerol</sup><u>E</u>LTEFAK" peptides identified in BSA in 20% glycerol solution.
- D6. MS/MS spectrum of "LVNELT<sup>glycerol</sup><u>E</u>FAK" peptides identified in BSA in 20% glycerol solution.

- D7. MS/MS spectrum of "AEFV<sup>glycerol</sup><u>E</u>VTK" peptides identified in BSA in 20% glycerol solution.
- D8. MS/MS spectrum of "RHP<sup>glycerol</sup><u>E</u>YAVSLLR" peptides identified in BSA in 20% glycerol solution.
- D9. MS/MS spectrum of "HLVD<sup>glycerol</sup><u>E</u>PQNLIK" peptides identified in BSA in 20% glycerol solution.
- D10. MS/MS spectrum of "QTALV<sup>glycerol</sup><u>E</u>LLK" peptides identified in BSA in 20% glycerol solution.
- D11. MS/MS spectrum of "KQTALV<sup>glycerol</sup><u>E</u>LLK" peptides identified in BSA in 20% glycerol solution.

D12. MS/MS spectrum of "LVT<sup>glycerol</sup> $\underline{D}$ LTK" peptides identified in BSA in 20% glycerol solution.



	10	0	0.1120	D. C. MILO	01120	D 14110	ooq.	J	1	J · · · 120	J 14110	5120	JINIO J	
1							D	1983.96	992.48	983.48	983.97	1965.95	1966.93	18
2	187.07				169.06		A	1868.93	934.97	925.96	926.46	1850.92	1851.91	17
3	300.16				282.15			1797.9	899.45	890.45	890.94	1779.88	1780.87	16
4	397.21				379.2		Ρ	1684.81	842.91	833.9	834.4	1666.8	1667.78	15
5	526.25				508.24		E	1587.76	794.38	785.38	785.87	1569.75	1570.73	14
6	640.29	320.65	311.65	312.14	622.28	623.27	Ν	1458.72	729.86	720.86	721.35	1440.7	1441.69	13
7	753.38	377.19	368.19	368.68	735.37	736.35	L	1344.67	672.84	663.83	664.33	1326.66	1327.65	12
8	850.43	425.72	416.71	417.21	832.42	833.4	Ρ	1231.59	616.3	607.29	607.78	1213.58	1214.56	11
9	947.48	474.25	465.24	465.73	929.47	930.46	Ρ	1134.54	567.77	558.77	559.26	1116.53	1117.51	10
10	1060.57	530.79	521.78	522.27	1042.56	1043.54	L	1037.48	519.25	510.24	510.73	1019.47	1020.46	9
11	1161.62	581.31	572.31	572.8	1143.6	1144.59	Т	924.4	462.7	453.7	454.19	906.39	907.37	8
12	1232.65	616.83	607.82	608.32	1214.64	1215.63	A	823.35	412.18	403.17	403.67	805.34	806.32	7
13	1347.68	674.34	665.34	665.83	1329.67	1330.65	D	752.31	376.66	367.66	368.15	734.3	735.29	6
14	1494.75	747.88	738.87	739.36	1476.74	1477.72	F	637.29	319.15	310.14	310.63	619.28	620.26	5
15	1565.79	783.4	774.39	774.88	1547.77	1548.76	A	490.22				472.21	473.19	4
16	1722.83	861.92	852.91	853.4	1704.82	1705.8	E"	419.18				401.17	402.16	3
17	1837.85	919.43	910.43	910.92	1819.84	1820.83	D	262.14				244.13	245.11	2
18							K	147.11					130.09	1



A2. K.KQTALVELLK.H (+2) · Mod : 28.00 at K(1) · Retention time : 52.98 min · Precursor m/z : 586.37 · Precursor int. : 18741.700 · Basepeak int. : 4392.190

#	b	b++	b++-H2O	b++-NH3	b-H2O	b-NH3	Seq.	у	y++	y++-H2O	y++-NH3	y-H2O	y-NH3	#
1							Κ"	1170.71	585.86	576.86	577.35	1152.7	1153.69	10
2	285.16					268.13	Q	1014.62	507.81	498.81	499.3	996.61	997.59	9
3	386.21				368.2	369.18	Т	886.56	443.78	434.78	435.27	868.55	869.53	8
4	457.25				439.24	440.22	А	785.51	393.26	384.25	384.75	767.5	768.49	- 7
5	570.33				552.32	553.3	L	714.48	357.74	348.74	349.23	696.46	697.45	6
6	669.4	335.2	326.2	326.69	651.39	652.37	V	601.39	301.2	292.19	292.69	583.38	584.36	-5
7	798.44	399.72	390.72	391.21	780.43	781.41	E	502.32				484.31	485.3	4
8	911.53	456.27	447.26	447.75	893.51	894.5	L	373.28					356.25	3
9	1024.61	512.81	503.8	504.3	1006.6	1007.58	L	260.2					243.17	2
10							K	147.11					130.09	1



R.EIAQDFKTDLR.F (+1) · Mod : -19.00 at K(7) · Retention time : 61.73 min · Precursor m/z : 1319.61 · Precursor int. : 7861.340 · Basepeak int. : 6513.940

m/z Seq. y E b++-H20 b++-NH3 b-H20 b-NH3 y++-H20 y++-NH3 y-H20 y-NH3 # b # b++ y++ 1316.69 658.85 1187.65 594.33 649.84 650.34 1298.68 1299.66 11 1 243.13 225.12 296.16 585.32 528.78 585.81 1169.64 1170.62 10 529.27 1056.55 1057.54 9 2 Ι A 1074.56 537.79

	014.17				200.10			1074.00	- JOL 10	520.70	0Z0.Zr	1000.001	1007.04	~
4	442.23				424.22	425.2	Q	1003.53	502.27	493.26	493.75	985.52	986.5	8
5	557.26				539.25	540.23	D	875.47	438.24	429.23	429.72	857.46	858.44	7
6	704.33	352.67	343.66	344.15	686.31	687.3	F	760.44	380.72	371.72	372.21	742.43	743.41	6
7	813.42	407.21	398.21	398.7	795.41	796.39	K"	613.37	307.19	298.18	298.68	595.36	596.35	5
8	914.47	457.74	448.73	449.22	896.46	897.44	Т	504.28				486.27	487.25	4
9	1029.5	515.25	506.25	506.74	1011.48	1012.47	D	403.23				385.22	386.2	ω
10	1142.58	571.79	562.79	563.28	1124.57	1125.55	L	288.2					271.18	2
11							R	175.12					158 09	1

### B1.





#	b	b++	b++-H2O	b++-NH3	b-H2O	b-NH3	Seq.	у	y++	y++-H2O	y++-NH3	y-H2O	y-NH3	#
1							К	967.61	484.31	475.3	475.8	949.6	950.58	9
2	257.16					240.13	Q	839.52	420.26	411.26	411.75	821.5	822.49	8
3	370.25					353.22	L	711.46	356.23	347.23	347.72	693.45	694.43	7
4	441.28					424.26	A	598.37				580.36	581.35	6
5	542.33				524.32	525.3	Т	527.34				509.32	510.31	5
6	651.43	326.22	317.21	317.7	633.41	634.4	K"	426.29					409.26	4
7	722.46	361.73	352.73	353.22	704.45	705.44	A	317.19					300.17	3
8	793.5	397.25	388.25	388.74	775.49	776.47	A	246.16					229.13	2
9							R	175.12					158.09	1





#	b	b++	b++-H2O	b++-NH3	b-H2O	b-NH3	Seq.	у	y++	y++-H2O	y++-NH3	y-H2O	y-NH3	#
1							R	1387.81	694.41	685.4	685.9	1369.8	1370.78	11
2	320.17					303.15	γ	1231.71	616.36	607.35	607.85	1213.7	1214.68	10
3	448.23					431.2	Q	1068.65	534.83	525.82	526.31	1050.64	1051.62	9
4	557.33					540.3	K"	940.59	470.8	461.79	462.28	922.58	923.56	8
5	644.36	322.68	313.68	314.17	626.35	627.33	S	831.49	416.25	407.24	407.74	813.48	814.47	- 7
6	745.41	373.21	364.2	364.69	727.39	728.38	Т	744.46	372.73	363.73	364.22	726.45	727.43	6
7	874.45	437.73	428.72	429.21	856.44	857.42	E	643.41	322.21	313.2	313.7	625.4	626.39	5
8	987.53	494.27	485.26	485.76	969.52	970.51	L	514.37					497.34	4
9	1100.62	550.81	541.81	542.3	1082.61	1083.59	L	401.29					384.26	3
10	1213.7	607.35	598.35	598.84	1195.69	1196.67		288.2					271.18	2
11							R	175.12					158.09	1



#	b	b++	b++-H2O	b++-NH3	b-H2O	b-NH3	Seq.	У	y++	y++-H2O	у++-NHЗ	y-H2O	y-NH3	#
1							R	1521.9	761.45	752.45	752.94	1503.89	1504.87	13
2	256.18					239.15	V	1365.8	683.4	674.4	674.89	1347.79	1348.77	12
3	357.23				339.21	340.2	Т	1266.73	633.87	624.86	625.35	1248.72	1249.7	11
4	470.31				452.3	453.28	I	1165.68	583.34	574.34	574.83	1147.67	1148.65	10
5	601.35	301.18	292.17	292.67	583.34	584.32	М	1052.6	526.8	517.8	518.29	1034.59	1035.57	9
6	698.4	349.7	340.7	341.19	680.39	681.38	Р	921.56	461.28	452.28	452.77	903.55	904.53	8
7	807.5	404.25	395.25	395.74	789.49	790.47	К"	824.5	412.76	403.75	404.24	806.49	807.48	- 7
8	922.52	461.77	452.76	453.25	904.51	905.5	D	715.41	358.21	349.2	349.69	697.4	698.38	6
9	1035.61	518.31	509.3	509.79	1017.6	1018.58	Ι	600.38	300.69		292.18		583.36	5
10	1163.67	582.34	573.33	573.82	1145.66	1146.64	Q	487.3					470.27	4
11	1276.75	638.88	629.87	630.37	1258.74	1259.72	L	359.24					342.21	3
12	1347.79	674.4	665.39	665.88	1329.78	1330.76	A	246.16					229.13	2
13							R	175.12					158.09	1



#	b	b++	b++-H2O	b++-NH3	b-H2O	b-NH3	Seq.	у	y++	y++-H2O	y++-NH3	y-H2O	y-NH3	#
1							V	1365.8	683.4	674.4	674.89	1347.79	1348.77	12
2	201.12				183.11		Т	1266.73	633.87	624.86	625.35	1248.72	1249.7	11
3	314.21				296.2		1	1165.68	583.34	574.34	574.83	1147.67	1148.65	10
4	445.25				427.24		М	1052.6	526.8	517.8	518.29	1034.59	1035.57	9
5	542.3				524.29		Р	921.56	461.28	452.28	452.77	903.55	904.53	8
6	651.4	326.2	317.2	317.69	633.39	634.37	K"	824.5	412.76	403.75	404.24	806.49	807.48	7
7	766.42	383.72	374.71	375.2	748.41	749.4	D	715.41	358.21	349.2	349.69	697.4	698.38	6
8	879.51	440.26	431.25	431.74	861.5	862.48	I	600.38	300.69		292.18		583.36	5
9	1007.57	504.29	495.28	495.77	989.56	990.54	Q	487.3					470.27	4
10	1120.65	560.83	551.82	552.32	1102.64	1103.62	L	359.24					342.21	3
11	1191.69	596.35	587.34	587.83	1173.68	1174.66	А	246.16					229.13	2
12							R	175.12					158.09	1

B5.



#	b	b++	b++-H2O	b++-NH3	b-H2O	b-NH3	Seq.	у	y++	y++-H2O	y++-NH3	y-H2O	y-NH3	#
1							D	1271.64	636.33	627.32	627.81	1253.63	1254.62	11
2	187.07				169.06		A	1156.62	578.81	569.81	570.3	1138.61	1139.59	10
3	286.14				268.13		V	1085.58	543.29	534.29	534.78	1067.57	1068.55	9
4	387.19				369.18		Т	986.51	493.76	484.75	485.25	968.5	969.48	8
-5	550.25				532.24		γ	885.46	443.24	434.23	434.72	867.45	868.44	7
6	651.3	326.15	317.15		633.29		Т	722.4	361.7	352.7	353.19	704.39	705.37	6
- 7	780.34	390.67	381.67		762.33		E	621.35	311.18	302.17	302.67	603.34	604.33	5
8	917.4	459.2	450.2		899.39		Н	492.31					475.28	4
9	988.44	494.72	485.72		970.43		A	355.25					338.22	3
10	1097.53	549.27	540.26	540.76	1079.52	1080.51	Κ"	284.21					267.19	2
11							R	175.12					158.09	1



#	b	b++	b++-H2O	b++-NH3	b-H2O	b-NH3	Seq.	у	y++	y++-H2O	у++-NH3	y-H2O	y-NH3	#
1							К	1575.9	788.45	779.45	779.94	1557.89	1558.87	14
2	230.15				212.14	213.12	Т	1447.8	724.41	715.4	715.89	1429.79	1430.78	13
3	329.22				311.21	312.19	V	1346.76	673.88	664.88	665.37	1328.74	1329.73	12
4	430.27				412.26	413.24	Т	1247.69	624.35	615.34	615.83	1229.68	1230.66	11
- 5	501.3				483.29	484.28	A	1146.64	573.82	564.82	565.31	1128.63	1129.61	10
6	632.34	316.68	307.67	308.16	614.33	615.32	M	1075.6	538.3	529.3	529.79	1057.59	1058.58	9
7	747.37	374.19	365.18	365.68	729.36	730.34	D	944.56	472.78	463.78	464.27	926.55	927.54	8
8	846.44	423.72	414.72	415.21	828.43	829.41	V	829.53	415.27		406.76		812.51	- 7
9	945.51	473.26	464.25	464.74	927.5	928.48	V	730.47	365.74		357.22		713.44	6
10	1108.57	554.79	545.78	546.28	1090.56	1091.54	γ	631.4	316.2		307.69		614.37	5
11	1179.61	590.31	581.3	581.79	1161.6	1162.58	А	468.33					451.31	4
12	1292.69	646.85	637.84	638.34	1274.68	1275.67	L	397.3					380.27	3
13	1401.79	701.4	692.39	692.88	1383.78	1384.76	K"	284.21					267.19	2
14							R	175.12					158.09	1





#	b	b++	b++-H2O	b++-NH3	b-H2O	b-NH3	Seq.	у	y++	y++-H2O	у++-NH3	y-H2O	y-NH3	#
1							L	1627.75	814.38	805.37	805.86	1609.74	1610.72	13
2	242.19					225.16	К	1514.66	757.83	748.83	749.32	1496.65	1497.64	12
3	339.24					322.21	Ρ	1386.57	693.79	684.78	685.27	1368.56	1369.54	11
4	454.27				436.26	437.24	D	1289.51	645.26	636.26	636.75	1271.5	1272.49	10
5	551.32				533.31	534.29	Р	1174.49	587.75	578.74	579.23	1156.48	1157.46	9
6	665.36	333.18	324.18	324.67	647.35	648.34	Ν	1077.43	539.22	530.22	530.71	1059.42	1060.41	8
- 7	766.41	383.71	374.7	375.2	748.4	749.38	Т	963.39	482.2	473.19	473.69	945.38	946.36	- 7
8	879.49	440.25	431.25	431.74	861.48	862.47	L	862.34	431.68	422.67	423.16	844.33	845.32	6
9	1090.5	545.76	536.75	537.24	1072.49	1073.48	С"	749.26	375.13	366.13	366.62	731.25	732.23	- 5
10	1205.53	603.27	594.26	594.76	1187.52	1188.5	D	538.25				520.24	521.22	4
11	1334.57	667.79	658.78	659.28	1316.56	1317.55	E	423.22				405.21	406.2	3
12	1481.64	741.32	732.32	732.81	1463.63	1464.61	F	294.18					277.15	2
13							К	147.11					130.09	1



C3. K.LKEC(+108)CDKPLLEK.S (+3) - Mod : 1.15 at 0(-1) - Retention time : 38.19 min - Precursor m/z : 509.97 - Precursor int. : 4343.400 - Basepeak int. : 8463.640



#	b	b++	b++-H2O	b++-NH3	b-H2O	b-NH3	Seq.	у	y++	y++-H2O	у++-NHЗ	y-H2O	y-NH3	#
1							L	1526.74	763.87	754.87	755.36	1508.73	1509.71	12
2	242.19					225.16	К	1413.65	707.33	698.33	698.82	1395.64	1396.63	11
3	371.23				353.22	354.2	E	1285.56	643.28	634.28	634.77	1267.55	1268.53	10
4	474.24				456.23	457.21	С	1156.52	578.76	569.76	570.25	1138.51	1139.49	9
5	685.25	343.13	334.12	334.61	667.24	668.22	С"	1053.51	527.26	518.25	518.74	1035.5	1036.48	8
6	800.27	400.64	391.64	392.13	782.26	783.25	D	842.5	421.75	412.75	413.24	824.49	825.47	- 7
7	928.37	464.69	455.68	456.18	910.36	911.34	К	727.47	364.24	355.23	355.73	709.46	710.44	6
8	1025.42	513.21	504.21	504.7	1007.41	1008.4	Р	599.38				581.37	582.35	- 5
9	1138.51	569.76	560.75	561.24	1120.5	1121.48	L	502.32				484.31	485.3	4
10	1251.59	626.3	617.29	617.79	1233.58	1234.56	L	389.24				371.23	372.21	3
11	1380.63	690.82	681.81	682.31	1362.62	1363.61	E	276.15				258.14	259.13	2
12							K	147.11					130.09	1

C4. K.LKECC(+108)DKPLLEK.S (+3) · Mod : 0.38 at 0(-1) · Retention time : 38.57 min · Precursor m/z : 509.71 · Precursor int. : 5839.170 · Basepeak int. : 6788.780



#	Ь	b++	b++-H2O	b-H2O	Seq.	У	y++	y++-H2O	y++-NH3	y-H2O	y-NH3	#
1					D	1605.63	803.32	794.31	794.81	1587.62	1588.6	13
2	231.06			213.05	D	1490.6	745.81	736.8	737.29	1472.59	1473.58	12
3	328.11			310.1	Ρ	1375.58	688.29	679.29	679.78	1357.57	1358.55	11
4	465.17			447.16	Н	1278.52	639.77	630.76	631.25	1260.51	1261.5	10
5	536.21			518.2	A	1141.47	571.24	562.23	562.72	1123.45	1124.44	9
6	747.22	374.11	365.11	729.21	С"	1070.43	535.72	526.71	527.2	1052.42	1053.4	8
- 7	910.28	455.65	446.64	892.27	γ	859.42	430.21	421.21	421.7	841.41	842.39	7
8	997.32	499.16	490.16	979.3	S	696.36	348.68	339.68	340.17	678.35	679.33	6
9	1098.36	549.68	540.68	1080.35	Т	609.32	305.17	296.16	296.65	591.31	592.3	5
10	1197.43	599.22	590.21	1179.42	V	508.28				490.27	491.25	4
11	1344.5	672.75	663.75	1326.49	F	409.21				391.2	392.18	3
12	1459.53	730.27	721.26	1441.52	D	262.14				244.13	245.11	2
13					K	147.11					130.09	1

 $C6. \\ \texttt{K.QNC(+108)DQFEK.L (+2) } \cdot \texttt{Mod} : 0.56 \texttt{ at } 0(-1) \cdot \texttt{Retention time} : 13.90 \texttt{ min} \cdot \texttt{Precursor m/z} : 560.49 \cdot \texttt{Precursor int} : 828920.000 \cdot \texttt{Basepeak int} : 1169110.000$ 



#	b	b++	b++-H2O	b++-NH3	b-H2O	b-NH3	Seq.	у	y++	y++-H2O	y++-NH3	y-H2O	y-NH3	#
1							Q	1119.42	560.21	551.21	551.7	1101.41	1102.39	8
2	243.11					226.08	N	991.36	496.18	487.18	487.67	973.35	974.33	7
3	454.12					437.09	С"	877.32	439.16	430.16	430.65	859.31	860.29	6
4	569.15				551.13	552.12	D	666.31	333.66	324.65	325.14	648.3	649.28	5
5	697.2	349.11	340.1	340.59	679.19	680.18	Q	551.28				533.27	534.26	4
6	844.27	422.64	413.63	414.13	826.26	827.25	F	423.22				405.21	406.2	3
7	973.32	487.16	478.16	478.65	955.3	956.29	E	276.15				258.14	259.13	2
8							K	147.11					130.09	1



304.16

175.12

R

286.15

287.13 2

158.09 1

12 1399.58 700.29

13

691.29

691.78 1381.57 1382.55 E







#	b	b++	b++-H2O	b++-NH3	b-H2O	b-NH3	Seq.	у	y++	y++-H2O	y++-NH3	y-H2O	y-NH3	#
1							V	1573.69	787.35	778.34	778.83	1555.68	1556.66	13
2	157.1						G	1474.62	737.81	728.81	729.3	1456.61	1457.59	12
3	258.15				240.13		Т	1417.6	709.3	700.3	700.79	1399.59	1400.57	11
4	414.25				396.24	397.22	R	1316.55	658.78	649.77	650.27	1298.54	1299.52	10
- 5	517.26				499.25	500.23	С	1160.45	580.73	571.72	572.22	1142.44	1143.42	9
6	728.26	364.64	355.63	356.12	710.25	711.24	С"	1057.44	529.22	520.22	520.71	1039.43	1040.41	8
- 7	829.31	415.16	406.15	406.65	811.3	812.29	Т	846.43	423.72	414.71	415.21	828.42	829.4	7
8	957.41	479.21	470.2	470.69	939.4	940.38	К	745.38	373.2	364.19	364.68	727.37	728.36	6
9	1054.46	527.73	518.73	519.22	1036.45	1037.43	Ρ	617.29	309.15	300.14	300.63	599.28	600.26	5
10	1183.5	592.26	583.25	583.74	1165.49	1166.48	E	520.24				502.23	503.21	4
11	1270.53	635.77	626.77	627.26	1252.52	1253.51	S	391.19				373.18	374.17	3
12	1399.58	700.29	691.29	691.78	1381.57	1382.55	E	304.16				286.15	287.13	2
13							R	175.12					158.09	1







#	b	b++	b++-H2O	b-H2O	Seq.	у	y++	y++-H2O	y++-NH3	y-H2O	y-NH3	#
1					L	949.46	475.23	466.23	466.72	931.45	932.43	7
2	325.1				C"	836.38	418.69	409.69	410.18	818.36	819.35	6
3	424.17				V	625.37	313.19	304.18	304.67	607.36	608.34	5
4	537.25				L	526.3				508.29	509.27	4
5	674.31	337.66			Н	413.21				395.2	396.19	3
6	803.36	402.18	393.18	785.34	E	276.15				258.14	259.13	2
7					K	147.11					130.09	1



C11. R.RPC(+108)FSALTPDETYVPK.A (+3) - Mod : 2.62 at 0(-1) - Betenion time : 49.07 min - Precursor m/z : 645.51 - Precursor int. : 678263.000 - Basepeak int. : 90640.800 492.94

1							R	1931.9	966.45	957.45	957.94	1913.89	1914.87	1Ŀ
2	254.16					237.14	Р	1775.8	888.4	879.4	879.89	1757.79	1758.77	15
3	465.17					448.14	C"	1678.75	839.88	830.87	831.36	1660.73	1661.72	14
4	612.24	306.62		298.11		595.21	F	1467.74	734.37	725.37	725.86	1449.73	1450.71	13
5	699.27	350.14	341.13	341.63	681.26	682.24	S	1320.67	660.84	651.83	652.32	1302.66	1303.64	12
6	770.31	385.66	376.65	377.14	752.3	753.28	A	1233.64	617.32	608.32	608.81	1215.63	1216.61	11
-7	883.39	442.2	433.19	433.69	865.38	866.37	L	1162.6	581.8	572.8	573.29	1144.59	1145.57	10
8	984.44	492.72	483.72	484.21	966.43	967.41	Т	1049.51	525.26	516.26	516.75	1031.5	1032.49	9
9	1081.49	541.25	532.24	532.74	1063.48	1064.47	Ρ	948.47	474.74	465.73	466.22	930.46	931.44	8
10	1196.52	598.76	589.76	590.25	1178.51	1179.49	D	851.41	426.21	417.21	417.7	833.4	834.39	- 7
11	1325.56	663.28	654.28	654.77	1307.55	1308.54	E	736.39	368.7	359.69	360.18	718.38	719.36	6
12	1426.61	713.81	704.8	705.3	1408.6	1409.58	Т	607.34	304.18	295.17	295.66	589.33	590.32	- 5
13	1589.67	795.34	786.34	786.83	1571.66	1572.65	Y	506.3					489.27	- 4
14	1688.74	844.87	835.87	836.36	1670.73	1671.72	V	343.23					326.21	3
15	1785.79	893.4	884.4	884.89	1767.78	1768.77	Р	244.17					227.14	2
16							K	147 11					130.09	1



#	b	b++	b++~H2O	b-H2O	Seq.	у	y++	y++-H2O	y++-NH3	y-H2O	y-NH3	#
1					Т	1505.55	753.28	744.27	744.76	1487.54	1488.52	13
2	253.06			235.05	C(48)	1404.5	702.75	693.75	694.24	1386.49	1387.47	12
3	352.13			334.12	$\vee$	1253.49	627.25	618.24	618.73	1235.48	1236.46	11
4	423.17			405.16	A	1154.42	577.71	568.71	569.2	1136.41	1137.39	10
5	538.2			520.19	D	1083.38	542.2	533.19	533.68	1065.37	1066.36	9
6	667.24	334.12	325.12	649.23	E	968.36	484.68	475.68	476.17	950.35	951.33	8
7	754.27	377.64	368.63	736.26	S	839.31	420.16	411.16	411.65	821.3	822.29	7
8	891.33	446.17	437.16	873.32	Н	752.28	376.64	367.64	368.13	734.27	735.25	6
9	962.37	481.69	472.68	944.36	A	615.22	308.11	299.11	299.6	597.21	598.2	5
10	1019.39	510.2	501.19	1001.38	G	544.19				526.17	527.16	4
11	1230.4	615.7	606.7	1212.39	С"	487.16				469.15	470.14	3
12	1359.44	680.22	671.22	1341.43	E	276.15				258.14	259.13	2
13					K	147.11					130.09	1



#	b	b++	b++~H2O	b++-NH3	b-H2O	b-NH3	Seq.	у	y++	y++-H2O	y++-NH3	y-H2O	y-NH3	#
1							Υ	1817.66	909.33	900.33	900.82	1799.65	1800.64	14
2	278.11					261.09	Ν	1654.6	827.8	818.8	819.29	1636.59	1637.57	13
3	335.14					318.11	G	1540.56	770.78	761.78	762.27	1522.54	1523.53	12
4	434.2					417.18	$\vee$	1483.53	742.27	733.27	733.76	1465.52	1466.51	11
5	581.27					564.25	F	1384.47	692.74	683.73	684.22	1366.45	1367.44	10
6	709.33	355.17		346.66		692.3	Q	1237.4	619.2	610.2	610.69	1219.39	1220.37	9
- 7	838.37	419.69	410.69	411.18	820.36	821.35	E	1109.34	555.17	546.17	546.66	1091.33	1092.31	8
8	1049.38	525.2	516.19	516.68	1031.37	1032.36	С"	980.3	490.65	481.65	482.14	962.29	963.27	- 7
9	1228.39	614.7	605.69	606.19	1210.38	1211.37	C(76)	769.29	385.15	376.14	376.63	751.28	752.26	6
10	1356.45	678.73	669.72	670.22	1338.44	1339.42	Q	590.28				572.27	573.25	- 5
11	1427.49	714.25	705.24	705.73	1409.48	1410.46	А	462.22				444.21	445.19	4
12	1556.53	778.77	769.76	770.26	1538.52	1539.5	E	391.18				373.17	374.16	3
13	1671.56	836.28	827.28	827.77	1653.55	1654.53	D	262.14				244.13	245.11	2
14							K	147.11					130.09	1

## C13.



C14. K.QNC(+108)DQFEK.L (+2) · Mod : ·17.00 at N(2) · Retention time : 40.77 min · Precursor m/z : 551.90 · Precursor int. : 56926.000 · Basepeak int. : 12381.700



K.YIC(+108)DNQDTISSK.L (+2) - Mod : 1.00 at Q(6) - Retention time : 44.56 min - Precursor m/z : 748.38 - Precursor int. : 31833.700 - Basepeak int. : 2618.420

C15.



C16. K.CCTESLVNR.R (+2) - Mod : 108.00 at C(1) - Retention time : 41.32 min - Precursor m/z : 566.95 - Precursor int. : 107184.000 - Basepeak int. : 24559.700



#	b	b++	b++~H2O	b++-NH3	b-H2O	b-NH3	Seq.	у	y++	y++-H2O	у++-NH3	y-H2O	y-NH3	#
1							С"	1160.45	580.73	571.72	572.22	1142.44	1143.42	9
2	315.03						С	949.44	475.22	466.22	466.71	931.43	932.41	8
3	416.07				398.06		Т	846.43	423.72	414.71	415.21	828.42	829.4	7
4	544.17				526.16	527.14	К	745.38	373.2	364.19	364.68	727.37	728.36	6
5	641.22	321.11	312.11	312.6	623.21	624.2	Ρ	617.29	309.15	300.14	300.63	599.28	600.26	5
6	770.26	385.64	376.63	377.12	752.25	753.24	E	520.24				502.23	503.21	4
7	857.3	429.15	420.15	420.64	839.29	840.27	S	391.19				373.18	374.17	3
8	986.34	493.67	484.67	485.16	968.33	969.31	E	304.16				286.15	287.13	2
9							R	175.12					158.09	1



K.KQTALVELLK.H (+1) - Mod : 74.00 at E(7) - Retention time : 36.25 min - Precursor m/z : 1216.55 - Precursor int. : 2392540.000 - Basepeak int. : 58088.800

D1.



 $\begin{array}{l} \textbf{D2.} \\ \textbf{R.DTHKSEIAHR.F (+2) \cdot Mod: 74.00 \ at \ E(6) \cdot \textbf{Retention time}: 3.88 \ \text{min} \cdot \textbf{Precursor m/z}: 634.40 \cdot \textbf{Precursor int.}: 17090.100 \cdot \textbf{Basepeak int.}: 6144.300 \end{array}$ 

#	b	b++	b++-H2O	b++-NH3	b-H2O	b-NH3	Seq.	у	y++	y++-H2O	y++-NH3	y-H2O	y-NH3	#
1							D	1267.6	634.3	625.3	625.79	1249.59	1250.58	10
2	217.08				199.07		Т	1152.57	576.79	567.79	568.28	1134.56	1135.55	9
3	354.14				336.13		Н	1051.53	526.27	517.26	517.75	1033.52	1034.5	8
4	482.24				464.23	465.21	К	914.47	457.74	448.73	449.22	896.46	897.44	- 7
5	569.27				551.26	552.24	S	786.37	393.69	384.68	385.18	768.36	769.35	6
6	772.31	386.66	377.65	378.15	754.3	755.28	E"	699.34	350.17	341.17	341.66	681.33	682.31	-5
7	885.39	443.2	434.2	434.69	867.38	868.37	1	496.3					479.27	4
8	956.43	478.72	469.71	470.21	938.42	939.41	А	383.21					366.19	3
9	1093.49	547.25	538.24	538.74	1075.48	1076.46	Н	312.18					295.15	2
10							R	175.12					158.09	1

D3. R.FKDLGEEHFK.G (+2) - Mod : 74.00 at E(7) - Retention time : 32.21 min - Precursor m/z : 662.39 - Precursor int. : 198169.000 - Basepeak int. : 87264.400



#	b	b++	b++-H2O	b++-NH3	b-H2O	b-NH3	Seq.	у	y++	y++-H2O	y++-NH3	y-H2O	y-NH3	#
1							F	1323.62	662.31	653.31	653.8	1305.61	1306.59	10
2	276.17					259.14	К	1176.55	588.78	579.77	580.27	1158.54	1159.53	9
3	391.2				373.19	374.17	D	1048.46	524.73	515.73	516.22	1030.45	1031.43	8
4	504.28				486.27	487.26	L	933.43	467.22	458.21	458.71	915.42	916.4	7
5	561.3				543.29	544.28	G	820.35	410.68	401.67	402.16	802.34	803.32	6
6	690.35	345.68	336.67	337.16	672.34	673.32	E	763.32	382.17	373.16	373.65	745.31	746.3	5
7	893.39	447.2	438.19	438.68	875.38	876.36	E"	634.28	317.64	308.64	309.13	616.27	617.26	4
8	1030.45	515.73	506.72	507.21	1012.44	1013.42	Н	431.24					414.21	3
9	1177.52	589.26	580.26	580.75	1159.51	1160.49	F	294.18					277.15	2
10							K	147.11					130.09	1



K.DLGEEHFK.G (+2) - Mod : 74.00 at E(4) - Retention time : 31.19 min - Precursor m/z : 524.96 - Precursor int. : 102253.000 - Basepeak int. : 29628.700

#	b	b++	b++-H2O	b-H2O	Seq.	у	y++	y++-H2O	у++-NHЗ	y-H2O	y-NH3	#
1					D	1048.46	524.73	515.73	516.22	1030.45	1031.43	8
2	229.12			211.11	L	933.43	467.22	458.21	458.71	915.42	916.4	7
3	286.14			268.13	G	820.35	410.68	401.67	402.16	802.34	803.32	6
4	415.18			397.17	E	763.32	382.17	373.16	373.65	745.31	746.3	5
5	618.23	309.62	300.61	600.21	E"	634.28	317.64	308.64	309.13	616.27	617.26	4
6	755.28	378.15	369.14	737.27	Н	431.24					414.21	3
7	902.35	451.68	442.67	884.34	F	294.18					277.15	2
8					K	147.11					130.09	1

D4.



#	b	b++	b++-H2O	b++-NH3	b-H2O	b-NH3	Seq.	у	y++	y++-H2O	у++-NH3	y-H2O	y-NH3	#
1							L	1237.63	619.32	610.31	610.81	1219.62	1220.6	10
2	213.16						V	1124.55	562.78	553.77	554.26	1106.54	1107.52	9
3	327.2					310.18	Ν	1025.48	513.24	504.24	504.73	1007.47	1008.45	8
4	530.25				512.24	513.22	E"	911.43	456.22	447.22	447.71	893.42	894.41	- 7
- 5	643.33	322.17	313.16	313.66	625.32	626.3	L	708.39	354.7	345.69	346.19	690.38	691.37	6
6	744.38	372.69	363.69	364.18	726.37	727.35	Т	595.31				577.3	578.28	5
7	873.42	437.21	428.21	428.7	855.41	856.39	E	494.26				476.25	477.23	4
8	1020.49	510.75	501.74	502.23	1002.48	1003.46	F	365.22					348.19	3
9	1091.53	546.27	537.26	537.75	1073.52	1074.5	A	218.15					201.12	2
10							К	147.11					130.09	1



#	b	b++	b++-H2O	b++-NH3	b-H2O	b-NH3	Seq.	у	y++	y++-H2O	у++-NНЗ	y-H2O	y-NH3	#
1							L	1237.63	619.32	610.31	610.81	1219.62	1220.6	10
2	213.16						$\vee$	1124.55	562.78	553.77	554.26	1106.54	1107.52	9
3	327.2					310.18	Ν	1025.48	513.24	504.24	504.73	1007.47	1008.45	8
4	456.25				438.24	439.22	E	911.43	456.22	447.22	447.71	893.42	894.41	- 7
- 5	569.33				551.32	552.3	L	782.39	391.7	382.69	383.19	764.38	765.37	6
6	670.38	335.69	326.69	327.18	652.37	653.35	Т	669.31	335.16	326.15	326.64	651.3	652.28	5
7	873.42	437.21	428.21	428.7	855.41	856.39	E"	568.26				550.25	551.23	4
8	1020.49	510.75	501.74	502.23	1002.48	1003.46	F	365.22					348.19	3
9	1091.53	546.27	537.26	537.75	1073.52	1074.5	A	218.15					201.12	2
10							K	147.11					130.09	1

D6.





#	b	b++	b++-H2O	b-H2O	Seq.	у	y++	y++-H2O	y++-NH3	y-H2O	y-NH3	#
1					А	996.49	498.75	489.74	490.23	978.48	979.46	8
2	201.09			183.08	Ш	925.45	463.23	454.22	454.72	907.44	908.42	7
3	348.16			330.15	F	796.41	398.71	389.7	390.19	778.4	779.38	6
4	447.22			429.21	V	649.34	325.17	316.17	316.66	631.33	632.31	5
5	650.27	325.64	316.63	632.26	Ē	550.27				532.26	533.24	4
6	749.34	375.17	366.17	731.32	V	347.23				329.22	330.2	3
7	850.38	425.7	416.69	832.37	Т	248.16				230.15	231.13	2
8					K	147.11					130.09	1



#	b	b++	b++-H2O	b++-NH3	b-H2O	b-NH3	Seq.	у	y++	y++-H2O	y++-NH3	y-H2O	y-NH3	#
1							R	1513.81	757.41	748.4	748.9	1495.8	1496.79	12
2	294.17					277.14	Н	1357.71	679.36	670.35	670.85	1339.7	1340.68	11
3	391.22					374.19	Ρ	1220.65	610.83	601.82	602.32	1202.64	1203.62	10
4	594.26				576.25	577.24	E"	1123.6	562.3	553.3	553.79	1105.59	1106.57	9
- 5	757.33	379.17	370.16	370.65	739.32	740.3	γ	920.56	460.78	451.78	452.27	902.55	903.53	8
6	828.36	414.69	405.68	406.17	810.35	811.34	A	757.49	379.25	370.24	370.74	739.48	740.47	7
7	927.43	464.22	455.21	455.71	909.42	910.41	$\vee$	686.46	343.73	334.73	335.22	668.44	669.43	6
8	1014.46	507.74	498.73	499.22	996.45	997.44	S	587.39				569.38	570.36	5
9	1113.53	557.27	548.26	548.76	1095.52	1096.51	V	500.35					483.33	4
10	1226.62	613.81	604.81	605.3	1208.61	1209.59	L	401.29					384.26	3
11	1339.7	670.35	661.35	661.84	1321.69	1322.67	L	288.2					271.18	2
12							R	175.12					158.09	1



#	b	b++	b++-H2O	b++-NH3	b-H2O	b-NH3	Seq.	у	y++	y++-H2O	у++-NH3	y-H2O	y-NH3	#
1							Н	1379.72	690.36	681.36	681.85	1361.71	1362.69	11
2	251.15						L	1242.66	621.83	612.83	613.32	1224.65	1225.63	10
3	350.22						$\vee$	1129.57	565.29	556.28	556.78	1111.56	1112.55	9
4	465.25				447.24		D	1030.5	515.76	506.75	507.24	1012.49	1013.48	8
-5	668.29	334.65	325.64		650.28		E"	915.48	458.24	449.24	449.73	897.47	898.45	- 7
6	765.34	383.17	374.17		747.33		Ρ	712.43	356.72		348.21		695.41	6
- 7	893.4	447.2	438.2	438.69	875.39	876.37	Q	615.38	308.19		299.68		598.36	5
8	1007.44	504.23	495.22	495.71	989.43	990.42	N	487.32					470.3	4
9	1120.53	560.77	551.76	552.25	1102.52	1103.5	L	373.28					356.25	3
10	1233.61	617.31	608.3	608.8	1215.6	1216.58		260.2					243.17	2
11							K	147.11					130.09	1

D9. K.HLVDEPQNLIK.Q (+2) · Mod : 74.00 at E(5) · Retention time : 38.19 min · Precursor m/z : 690.59 · Precursor int. : 4499390.000 · Basepeak int. : 914565.000



D10. K.QTALVELLK.H (+2) - Mod : 74.00 at E(6) - Retention time : 42.65 min - Precursor m/z : 545.10 - Precursor int. : 302657.000 - Basepeak int. : 462649.000



D11. K.KQTALVELLK.H (+2) - Mod : 74.00 at E(7) - Retention time : 36.24 min - Precursor m/z : 609.17 - Precursor int. : 3236940.000 - Basepeak int. : 185929.000



#	b	b++	b++-H2O	b-H2O	Seq.	у	y++	y++-H2O	y++-NH3	y-H2O	y-NH3	#
1					L	863.47	432.24	423.23	423.73	845.46	846.45	7
2	213.16				V	750.39	375.7	366.69	367.18	732.38	733.36	6
3	314.21			296.2	Т	651.32	326.16	317.16	317.65	633.31	634.29	5
4	503.23			485.22	D"	550.27				532.26	533.24	4
5	616.32	308.66	299.66	598.31	L	361.24				343.23	344.22	3
6	717.37	359.19	350.18	699.36	Т	248.16				230.15	231.13	2
7					Κ	147.11					130.09	1