The proteoglycan bikunin has a defined sequence

Mellisa Ly,[1] Franklin E. Leach III,[2] Tatiana N. Laremore,[1] Toshihiko Toida,[3] I. Jonathan Amster,[2] Robert J. Linhardt,[1,4,5,6]

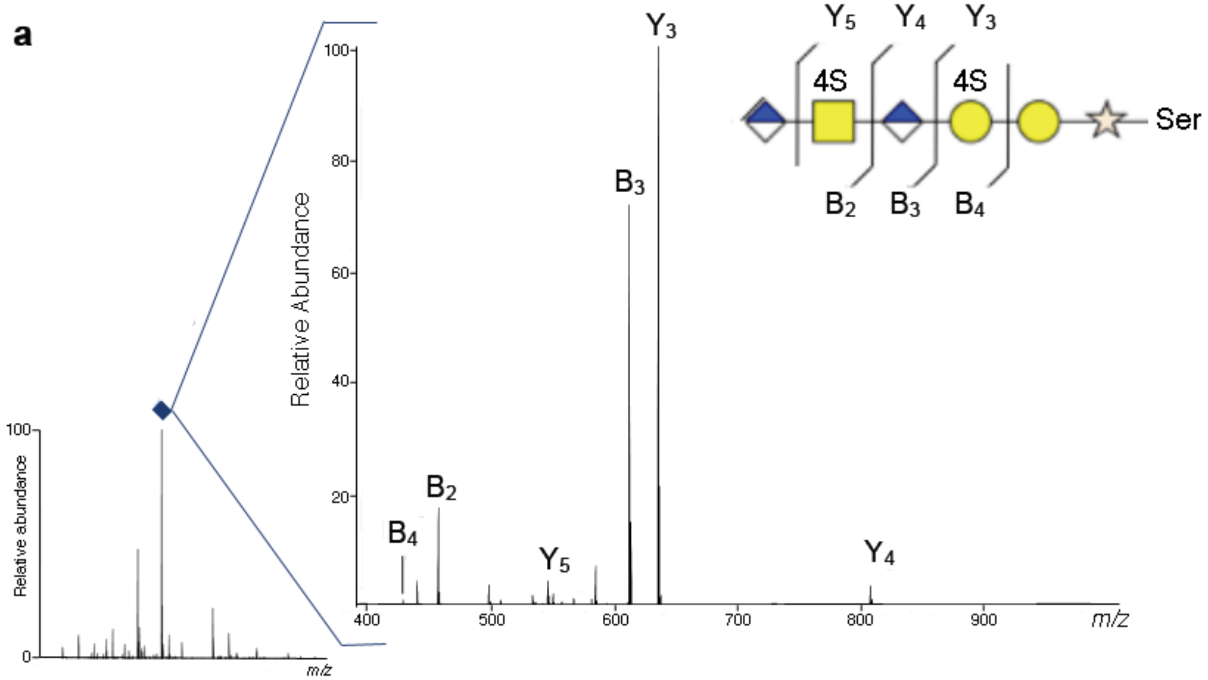
Departments of [1]Chemistry and Chemical Biology, [4]Chemical and Biological Engineering, [5]Biology, [6]Biomedical Engineering, Center for Biocatalysis and Interdisciplinary Studies, Rensselaer Polytechnic Institute, Troy, NY 12180, USA

[2]University of Georgia, Department of Chemistry, Athens, GA 30602, USA

[3]Graduate School of Pharmaceutical Sciences, Chiba University, 263-8522 Chiba, Japan

SUPPLEMENTARY INFORMATION

SUPPLEMENTARY RESULTS



b

Cleavage	m/z	Relative Intensity	Ion	Accuracy (ppm)	M_{exp}	M_{theor}
B2	458.0607	17.23	HexA1HexNAc1S1-B	0.5	459.0685	459.0683
B3	616.0823	73.67	HexA2HexNAc1S1-B	0.5	617.0901	617.0898
B4	428.5422	0.79	HexA2HexNAc1Hex1S2-B	0.8	859.1001	859.0994
B6Y3	553.1078	1.87	Hex2Pen1S1-BY	0.6	554.1156	554.1153
Y3	640.1393	100	Y-Hex2Pen1S1-Ser	-0.3	641.1471	641.1473
Y4	816.1709	3.33	Y-HexA1Hex2Pen1S1	-1.2	817.1787	817.1797
Y5	549.1001	4.15	Y-HexNAc1HexA1Hex2Pen1S2-Ser	0.2	1100.2159	1100.2156

Supplementary Figure 1. FTMS analysis of linkage region. **a**. Negative-ion mode FTMS showed the hexasaccharide with single composition ΔUA-GalNAc4S-GlcA-Gal4S-Gal-Xyl-Ser was most abundant. CID-FTMS/MS analysis of the hexasaccharide with m/z 628.1118. **b**. Assignment of fragment ions identified include B_2, B_3, B_4, B_6Y_3, Y_3, Y_4, Y_5 which afforded the uniform composition of the linkage region with a single serine residue on the reducing end. Mass spectra were acquired on the orbitrap FT mass spectrometer.

***m/z*$_{\text{Exp}}$**	***z***	**M$_{\text{Exp}}$**	**M$_{\text{Theor}}$**	**Accuracy (ppm)**	**Chain**
833.6725	6	5008.0818	5008.0784	-0.68	dp24-6-Ser
854.1919	6	5131.1982	5131.2009	0.53	dp25-5-Ser
1025.0322	5	5131.2078	5131.2009	-1.34	dp25-5-Ser
1041.2226	5	5211.1520	5211.1577	1.09	dp25-6-Ser
867.5181	6	5211.1554	5211.1577	0.44	dp25-6-Ser
743.4437	7	5211.1605	5211.1577	-0.54	dp25-6-Ser
883.5303	6	5307.2286	5307.2331	0.85	dp26-5-Ser
896.8565	6	5387.1858	5387.1899	0.76	dp26-6-Ser
687.7814	8	5510.3136	5510.3124	-0.22	dp27-5-Ser
611.2495	9	5510.3157	5510.3124	-0.60	dp27-5-Ser
786.1802	7	5510.3160	5510.3124	-0.65	dp27-5-Ser
917.2105	6	5510.3176	5510.3124	-0.94	dp27-5-Ser
1100.8552	5	5510.3228	5510.3124	-1.89	dp27-5-Ser
797.6020	7	5590.2686	5590.2692	0.11	dp27-6-Ser
930.7039	6	5590.2702	5590.2692	-0.18	dp27-6-Ser
620.1334	9	5590.2708	5590.2692	-0.29	dp27-6-Ser
1117.0464	5	5590.2710	5590.2692	-0.32	dp27-6-Ser
944.0296	6	5670.2244	5670.2260	0.28	dp27-7-Ser
809.0252	7	5670.2310	5670.2260	-0.88	dp27-7-Ser
946.5494	6	5686.3510	5686.3446	-1.13	dp28-5-Ser
822.7499	7	5766.3039	5766.3014	-0.43	dp28-6-Ser
960.0435	6	5766.3078	5766.3014	-1.11	dp28-6-Ser
967.2366	6	5809.4664	5809.4671	0.12	dp29-4-Ser
1161.0852	5	5809.4572	5809.4671	1.70	dp29-4-Ser
1176.6742	5	5889.4178	5889.4239	1.04	dp29-5-Ser
653.2613	9	5889.4297	5889.4239	-0.98	dp29-5-Ser
735.1698	8	5889.4208	5889.4239	0.53	dp29-5-Ser
840.3384	7	5889.4234	5889.4239	0.08	dp29-5-Ser
980.5628	6	5889.4236	5889.4239	0.05	dp29-5-Ser
1192.8677	5	5969.3775	5969.3807	0.54	dp29-6-Ser
745.1645	8	5969.3784	5969.3807	0.39	dp29-6-Ser
595.9302	10	5969.3800	5969.3807	0.12	dp29-6-Ser
993.8889	6	5969.3802	5969.3807	0.08	dp29-6-Ser
662.2568	9	5969.3814	5969.3807	-0.12	dp29-6-Ser
851.7610	7	5969.3816	5969.3807	-0.15	dp29-6-Ser

Supplementary Table 1. FT-ICR MS quadrupole windowing identifications of 47 compositions and their charge states ranging from dp24-6-Ser to dp43-7-Ser and (z =5-12) respectively. Identified monoisotopic peaks for each envelope listed with its experimental mass (M$_{\text{Exp}}$), theoretical mass (M$_{\text{Theor}}$), accuracy in ppm, and component.

m/z_{Exp}	z	M_{Exp}	M_{Theor}	Accuracy (ppm)	Chain
1007.2148	6	6049.3356	6049.3375	0.31	dp29-7-Ser
863.1837	7	6049.3405	6049.3375	-0.50	dp29-7-Ser
865.4864	7	6065.4594	6065.4561	-0.54	dp30-5-Ser
1009.7349	6	6065.4640	6065.4651	0.18	dp30-5-Ser
876.7647	7	6145.4153	6145.4129	-0.39	dp30-6-Ser
1023.0605	6	6145.4176	6145.4129	-0.76	dp30-6-Ser
1030.4219	6	6188.5782	6188.5786	0.06	dp31-4-Ser
695.4953	9	6268.5279	6268.5354	1.20	dp31-5-Ser
625.8452	10	6268.5300	6268.5354	0.86	dp31-5-Ser
1252.6987	5	6268.5325	6268.5354	0.46	dp31-5-Ser
1043.7479	6	6268.5342	6268.5354	0.19	dp31-5-Ser
894.4976	7	6268.5378	6268.5354	-0.38	dp31-5-Ser
782.5596	8	6268.5392	6268.5354	-0.61	dp31-5-Ser
633.8409	10	6348.4870	6348.4922	0.82	dp31-6-Ser
792.5534	8	6348.4896	6348.4922	0.41	dp31-6-Ser
1057.0740	6	6348.4908	6348.4922	0.22	dp31-6-Ser
905.9196	7	6348.4918	6348.4922	0.06	dp31-6-Ser
1268.6913	5	6348.4955	6348.4922	-0.52	dp31-6-Ser
704.3806	9	6348.4956	6348.4922	-0.54	dp31-6-Ser
802.5480	8	6428.4464	6428.4490	0.40	dp31-7-Ser
917.3419	7	6428.4479	6428.4490	0.17	dp31-7-Ser
641.8370	10	6428.4480	6428.4490	0.16	dp31-7-Ser
1070.4003	6	6428.4486	6428.4490	0.06	dp31-7-Ser
715.0547	9	6444.5625	6444.5676	0.79	dp32-5-Ser
919.6443	7	6444.5647	6444.5676	0.45	dp32-5-Ser
1073.0865	6	6444.5658	6444.5676	0.28	dp32-5-Ser
928.7650	7	6508.4096	6508.4058	-0.58	dp31-8-Ser
931.0663	7	6524.5187	6524.5244	0.87	dp32-6-Ser
814.5571	8	6524.5192	6524.5244	0.80	dp32-6-Ser
1086.4134	6	6524.5272	6524.5244	-0.43	dp32-6-Ser
942.4891	7	6604.4783	6604.4812	0.44	dp32-7-Ser
1099.7388	6	6604.4796	6604.4812	0.24	dp32-7-Ser
824.5524	8	6604.4816	6604.4812	-0.06	dp32-7-Ser
1328.5199	5	6647.6385	6647.6469	1.26	dp33-5-Ser
948.6556	7	6647.6438	6647.6469	0.47	dp33-5-Ser
663.7569	10	6647.6470	6647.6469	-0.02	dp33-5-Ser
1106.9334	6	6647.6472	6647.6469	-0.05	dp33-5-Ser
829.9486	8	6647.6512	6647.6469	-0.65	dp33-5-Ser
737.6204	9	6647.6538	6647.6469	-1.04	dp33-5-Ser

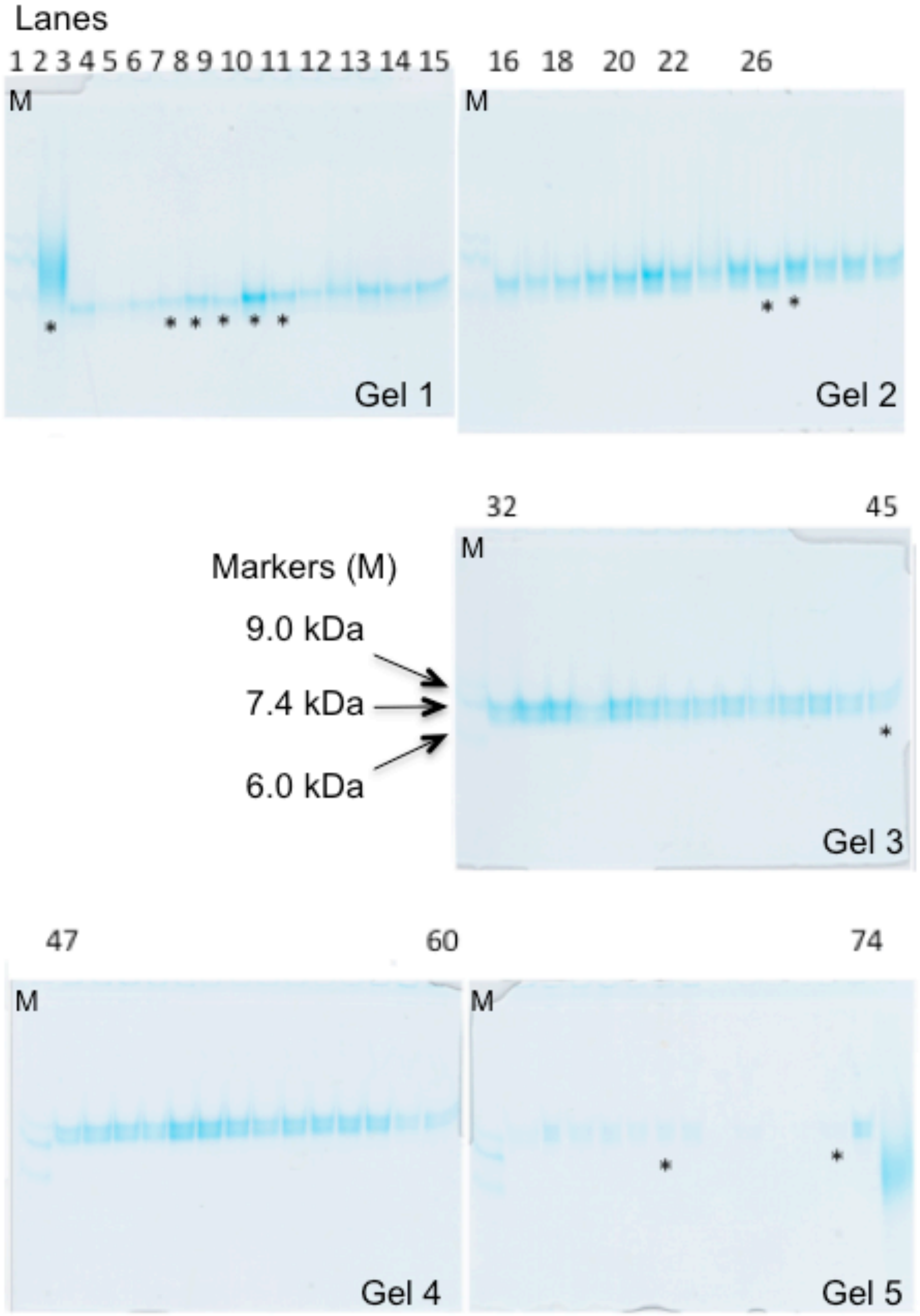
Supplementary Table 1. (Continued).

***m/z*$_{\mathrm{Exp}}$**	***z***	**M$_{\mathrm{Exp}}$**	**M$_{\mathrm{Theor}}$**	**Accuracy (ppm)**	**Chain**
839.9425	8	6727.6024	6727.6037	0.19	dp33-6-Ser
610.5925	11	6727.6033	6727.6037	0.06	dp33-6-Ser
746.5037	9	6727.6035	6727.6037	0.03	dp33-6-Ser
1120.2596	6	6727.6044	6727.6037	-0.10	dp33-6-Ser
960.0787	7	6727.6055	6727.6037	-0.27	dp33-6-Ser
1344.5134	5	6727.6060	6727.6037	-0.34	dp33-6-Ser
671.7529	10	6727.6070	6727.6037	-0.49	dp33-6-Ser
971.5004	7	6807.5574	6807.5605	0.46	dp33-7-Ser
1133.5853	6	6807.5586	6807.5605	0.28	dp33-7-Ser
617.8612	11	6807.5590	6807.5605	0.22	dp33-7-Ser
849.9382	8	6807.5680	6807.5605	-1.10	dp33-7-Ser
973.8019	7	6823.6679	6823.6791	1.64	dp34-5-Ser
982.9241	7	6887.5233	6887.5173	-0.87	dp33-8-Ser
1149.5981	6	6903.6354	6903.6359	0.07	dp34-6-Ser
985.2259	7	6903.6359	6903.6359	0.00	dp34-6-Ser
1162.9233	6	6983.5866	6983.5927	0.87	dp34-7-Ser
996.6481	7	6983.5913	6983.5927	0.20	dp34-7-Ser
871.9420	8	6983.5984	6983.5927	-0.82	dp34-7-Ser
701.6668	10	7026.7460	7026.7584	1.76	dp35-5-Ser
637.7879	11	7026.7527	7026.7584	0.81	dp35-5-Ser
779.7425	9	7026.7527	7026.7584	0.81	dp35-5-Ser
877.3371	8	7026.7592	7026.7584	-0.11	dp35-5-Ser
1002.8153	7	7026.7617	7026.7584	-0.47	dp35-5-Ser
1170.1199	6	7026.7662	7026.7584	-1.11	dp35-5-Ser
1014.2371	7	7106.7143	7106.7152	0.13	dp35-6-Ser
709.6640	10	7106.7180	7106.7152	-0.39	dp35-6-Ser
1183.4452	6	7106.7180	7106.7152	-0.39	dp35-6-Ser
645.0576	11	7106.7194	7106.7152	-0.59	dp35-6-Ser
887.3324	8	7106.7216	7106.7152	-0.90	dp35-6-Ser
788.6283	9	7106.7249	7106.7152	-1.36	dp35-6-Ser
797.3998	9	7186.6762	7186.6720	-0.58	dp35-7-Ser
1196.6037	6	7186.6768	7186.6720	-0.67	dp35-7-Ser
897.3259	8	7186.6696	7186.6720	0.33	dp35-7-Ser
1025.6595	7	7186.6711	7186.6720	0.13	dp35-7-Ser
652.3268	11	7186.6806	7186.6720	-1.20	dp35-7-Ser

Supplementary Table 1. (Continued).

m/z_{Exp}	z	$\mathrm{M}_{\mathrm{Exp}}$	$\mathrm{M}_{\mathrm{Theor}}$	**Accuracy (ppm)**	**Chain**
909.2097	8	7282.7478	7282.7474	-0.05	dp36-6-Ser
1039.2416	7	7282.7536	7282.7474	-0.85	dp36-6-Ser
1212.6172	6	7282.7578	7282.7474	-1.43	dp36-6-Ser
1226.1088	6	7362.6996	7362.7042	0.62	dp36-7-Ser
1050.8076	7	7362.7078	7362.7042	-0.49	dp36-7-Ser
919.3310	8	7362.7104	7362.7042	-0.84	dp36-7-Ser
1233.1369	6	7405.8760	7405.8699	-0.82	dp37-5-Ser
672.1623	11	7405.8789	7405.8699	-1.22	dp37-5-Ser
622.8109	12	7485.8244	7485.8267	0.31	dp37-6-Ser
1068.3960	7	7485.8266	7485.8267	0.01	dp37-6-Ser
679.5221	11	7485.8289	7485.8267	-0.29	dp37-6-Ser
934.7209	8	7485.8296	7485.8267	-0.39	dp37-6-Ser
747.5753	10	7485.8310	7485.8267	-0.57	dp37-6-Ser
830.7512	9	7485.8310	7485.8267	-0.57	dp37-6-Ser
1246.6312	6	7485.8340	7485.8267	-0.98	dp37-6-Ser
1079.8179	7	7565.7799	7565.7835	0.48	dp37-7-Ser
944.7151	8	7565.7832	7565.7835	0.04	dp37-7-Ser
686.7907	11	7565.7835	7565.7835	0.00	dp37-7-Ser
956.7238	8	7661.8528	7661.8589	0.80	dp38-6-Ser
1275.9678	6	7661.8536	7661.8589	0.69	dp38-6-Ser
1093.5435	7	7661.8591	7661.8589	-0.03	dp38-6-Ser
966.7197	8	7741.8200	7741.8157	-0.56	dp38-7-Ser
1110.9875	7	7784.9749	7784.9814	0.83	dp39-5-Ser
981.9833	8	7864.9366	7864.9382	0.20	dp39-6-Ser
713.8952	11	7864.9408	7864.9382	-0.33	dp39-6-Ser
1309.8139	6	7864.9302	7864.9382	1.02	dp39-6-Ser
1122.5545	7	7864.9361	7864.9382	0.27	dp39-6-Ser
654.4039	12	7864.9404	7864.9382	-0.28	dp39-6-Ser
881.7559	9	7944.8733	7944.8950	2.73	dp39-7-Ser
992.1039	8	7944.8936	7944.8950	0.18	dp39-7-Ser
1133.9771	7	7944.8943	7944.8950	0.09	dp39-7-Ser
1323.1422	6	7944.9000	7944.8950	-0.63	dp39-7-Ser
685.9952	12	8244.0360	8244.0497	1.66	dp41-6-Ser
1176.7135	7	8244.0491	8244.0497	0.07	dp41-6-Ser
1029.4986	8	8244.0512	8244.0497	-0.18	dp41-6-Ser
1039.4928	8	8324.0048	8324.0065	0.20	dp41-7-Ser
1188.1367	7	8324.0115	8324.0065	-0.60	dp41-7-Ser
1242.1497	7	8703.1103	8703.1180	0.88	dp43-7-Ser
1086.8827	8	8703.1240	8703.1180	-0.69	dp43-7-Ser

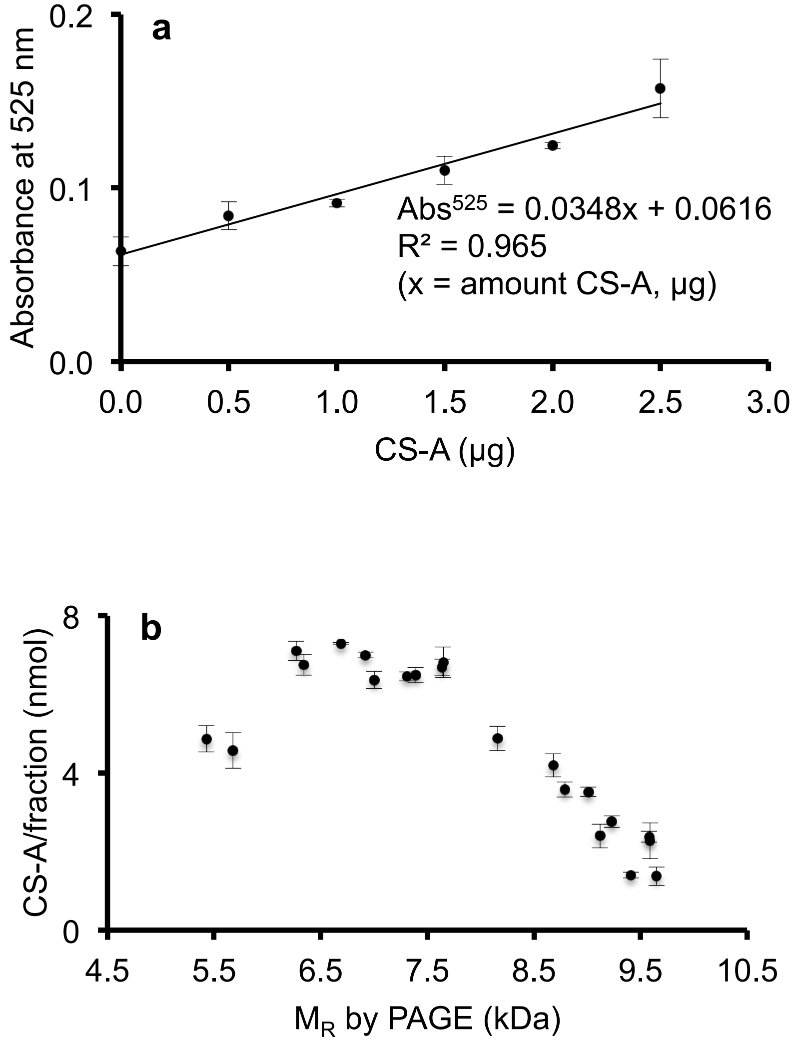
Supplementary Table 1. (Continued).



Supplementary Figure 2. Analytical PAGE analysis of bikunin pG. 15% PAGE numbered as Gel 1-5 allowed both M_N and M_W calculation of bikunin pG and M_R determination of gel bands. For bikunin pG, Gel 1 used markers, highest abundant compositions from lanes 7, 8, 9, 10, and 11, and Gel 5 used markers and lanes 57, 58, and 60. Starred bands(*) analyzed by FTMS or FT-ICR MS.

Gel	Lane	Fraction	M_R by PAGE
1	3	50	5.37
	4	51	5.43
	5	52	5.55
	6	53	5.68
	7	**54**	**5.74**
	8	**55**	**5.80**
	9	**56**	**5.87**
	10	**57**	**5.93**
	11	**58**	**6.06**
	12	59	6.13
	13	60	6.20
	14	61	6.27
	15	62	6.34
2	17	63	6.41
	18	64	6.48
	19	65	6.62
	20	66	6.69
	21	67	6.77
	22	68	6.84
	23	69	6.92
	24	70	7.00
	25	71	7.15
	26	**72**	**7.23**
	27	**73**	**7.31**
	28	74	7.39
	29	75	7.47
	30	76	7.56
3	32	77	7.39
	33	78	7.47
	34	79	7.56
	35	80	7.64
	36	81	7.64
	37	82	7.73
	38	83	7.81
	39	84	7.81
	40	85	7.81
	41	86	7.81
	42	87	7.90
	43	88	7.99
	44	89	8.07
	45	**90**	**8.16**
4	47	91	8.47
	48	92	8.57
	49	93	8.68
	50	94	8.68
	51	95	8.79
	52	96	8.90
	53	97	9.01
	54	98	9.01
	55	99	9.12
	56	100	9.23
	57	**101**	**9.46**
	58	102	9.58
	59	103	9.58
	60	**104**	**9.58**
5	62	105	9.32
	63	106	9.29
	64	107	9.41
	65	108	9.29
	66	109	9.29
	67	110	9.41
	68	111	9.41
	69	112	9.41
	70	113	9.41
	71	114	9.65
	72	115	9.65
	73	**116**	**9.65**
	74	117	9.77

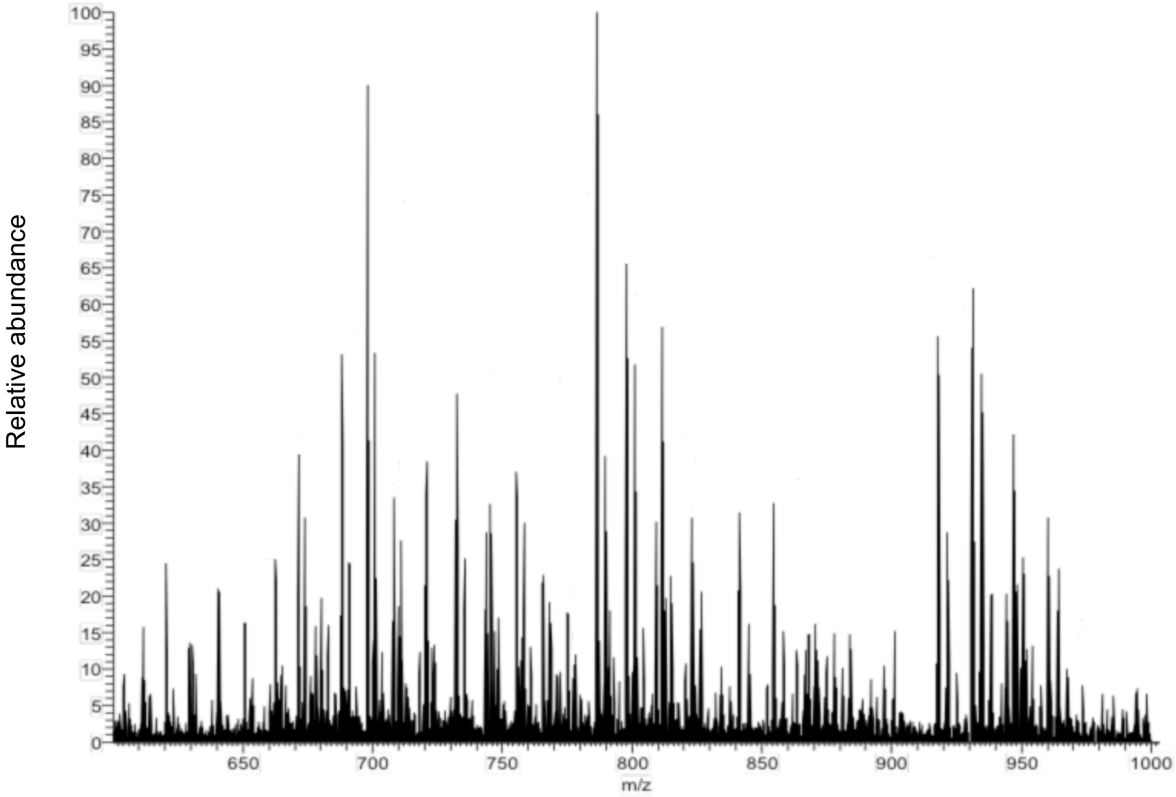
Supplementary Table 2. M_R-values of fractions #50-117, based on molecular mass densitometry analysis against CSA standards. Their respective lane loadings from Supplementary Figure 2 are listed with rows in bold analyzed by FTMS or FT-ICR MS.



Supplementary Figure 3. Microcarbazole assay results quantified GAG based on uronic acid content. **a**. Standard curve using CS-A from bovine trachea. **b**. Quantity of pG (nmol) plotted against their respective M_R by PAGE. In both cases values plotted are expressed as mean ± s.d.

Sample (n = 3)	**Absorbance at 525 nm**	**pG, µg/fraction**	**nmol/fraction**
CS-A Standard 1, 0.0 µg	0.0635 ± 0.0084		
CS-A Standard 2, 0.5 µg	0.0841 ± 0.0081		
CS-A Standard 3, 1.0 µg	0.0913 ± 0.0022		
CS-A Standard 4, 1.5 µg	0.1100 ± 0.0081		
CS-A Standard 5, 2.0 µg	0.1250 ± 0.0019		
CS-A Standard 6, 2.5 µg	0.1507 ± 0.0170		
5.43 kDa by PAGE, f51	0.0692 ± 0.0048	26.4 ± 1.8	4.9 ± 0.33
5.68 kDa by PAGE, f53	0.0689 ± 0.0068	26.0 ± 2.5	4.6 ± 0.45
6.27 kDa by PAGE, f61	0.0813 ± 0.0028	44.6 ± 1.5	7.1 ± 0.24
6.34 kDa by PAGE, f62	0.0801 ± 0.0031	42.8 ± 1.6	6.7 ± 0.26
6.69 kDa by PAGE, f66	0.0841 ± 0.0002	48.8 ± 0.12	7.3 ± 0.02
6.92 kDa by PAGE, f69	0.0839 ± 0.0009	48.5 ± 0.50	7.0 ± 0.07
7.00 kDa by PAGE, f70	0.0813 ± 0.0027	44.6 ± 1.5	6.4 ± 0.22
7.31 kDa by PAGE, f73	0.0831 ± 0.0015	47.2 ± 0.85	6.5 ± 0.12
7.39 kDa by PAGE, f74	0.0836 ± 0.0025	48.0 ± 1.4	6.5 ± 0.19
7.64 kDa by PAGE, f80	0.0856 ± 0.0027	51.1 ± 1.6	6.7 ± 0.21
7.65 kDa by PAGE, f81	0.0864 ± 0.0049	52.2 ± 3.0	6.8 ± 0.39
8.16 kDa by PAGE, f90	0.0649 ± 0.0042	39.8 ± 2.6	4.9 ± 0.32
8.68 kDa by PAGE, f93	0.0637 ± 0.0045	36.4 ± 2.6	4.2 ± 0.29
8.79 kDa by PAGE, f95	0.0726 ± 0.0039	31.5 ± 1.7	3.6 ± 0.19
9.01 kDa by PAGE, f97	0.0727 ± 0.0024	31.7 ± 1.0	3.5 ± 0.11
9.12 kDa by PAGE, f99	0.0662 ± 0.0083	21.9 ± 2.8	2.4 ± 0.30
9.23 kDa by PAGE, f100	0.0686 ± 0.0036	25.5 ± 1.3	2.8 ± 0.15
9.58 kDa by PAGE, f102	0.0668 ± 0.0039	22.8 ± 1.3	2.4 ± 0.14
9.59 kDa by PAGE, f104	0.0661 ± 0.0132	21.8 ± 4.4	2.3 ± 0.45
9.41 kDa by PAGE, f110	0.0604 ± 0.0032	13.2 ± 0.71	1.4 ± 0.07
9.65 kDa by PAGE, f116	0.0604 ± 0.0103	13.3 ± 2.3	1.4 ± 0.23

Supplementary Table 3. Carbazole assay results of various fractions showing absorbance, µg/fraction, and nmol bikunin pG/fraction as listed (n=3 in all cases, with data expressed as mean ± s.d.).



Supplementary Figure 4. FTMS of fraction 5.74 kDa (by PAGE) corresponding to 20 composition identifications listed in Supplementary Table 4.

m/z	**Intensity**	*z*	M_{Exp}	M_{Theor}	**Accuracy (ppm)**	**Chain**
791.0083	7.89E+03	6	4752.0968	4752.0910	1.2	dp23-5-Ser
720.5985	2.91E+04	7	5051.2443	5051.2525	-1.6	dp25-4-Ser
840.8673	3.15E+04	6	5051.2508	5051.2525	-0.3	dp25-4-Ser
732.0211	2.79E+04	7	5131.2025	5131.2025	0.0	dp25-5-Ser
854.1933	1.76E+04	6	5131.2068	5131.2025	0.8	dp25-5-Ser
640.3933	1.57E+04	8	5131.2090	5131.2025	1.3	dp25-5-Ser
857.8574	1.06E+04	6	5153.1914	5153.1845	1.3	dp25-5-Ser + Na
735.1638	1.27E+04	7	5153.2014	5153.1845	3.3	dp25-5-Ser + Na
743.4441	1.41E+04	7	5211.1635	5211.1525	2.1	dp25-6-Ser
660.5115	7.05E+03	8	5292.1546	5292.1103	8.4	dp25-7-Ser
870.2047	1.49E+04	6	5227.2752	5227.2846	-1.8	dp26-4-Ser
883.5289	1.17E+04	6	5307.2204	5307.2346	-2.7	dp26-5-Ser
757.1675	9.94E+03	7	5307.2273	5307.2346	-1.4	dp26-5-Ser
897.0251	1.04E+04	6	5388.1976	5388.1924	1.0	dp26-6-Ser
677.7837	9.57E+03	8	5430.3322	5430.3640	-5.9	dp27-4-Ser
774.7591	9.49E+03	7	5430.3685	5430.3640	0.8	dp27-4-Ser
611.2465	1.64E+04	9	5510.2889	5510.3140	-4.6	dp27-5-Ser
917.3785	2.11E+04	6	5510.3180	5510.3140	0.7	dp27-5-Ser
786.1808	6.18E+04	7	5510.3204	5510.3140	1.2	dp27-5-Ser
687.7824	3.41E+04	8	5510.3218	5510.3140	1.4	dp27-5-Ser
620.1336	1.20E+04	9	5590.2728	5590.2640	1.6	dp27-6-Ser
697.7768	5.28E+04	8	5590.2770	5590.2640	2.3	dp27-6-Ser
930.7057	4.03E+04	6	5590.2812	5590.2640	3.1	dp27-6-Ser
797.6038	4.20E+04	7	5590.2814	5590.2640	3.1	dp27-6-Ser
707.7708	8.42E+03	8	5670.2290	5670.2140	2.6	dp27-7-Ser
629.0177	1.00E+04	9	5670.2297	5670.2140	2.8	dp27-7-Ser
799.9031	1.13E+04	7	5606.3765	5606.3961	-3.5	dp28-4-Ser
946.7166	1.99E+04	6	5686.3466	5686.3461	0.1	dp28-5-Ser
709.7858	1.84E+04	8	5686.3490	5686.3461	0.5	dp28-5-Ser
811.3279	3.47E+04	7	5686.3501	5686.3461	0.7	dp28-5-Ser
822.7477	1.15E+04	7	5766.2887	5766.2961	-1.3	dp28-6-Ser
960.0419	1.38E+04	6	5766.2984	5766.2961	0.4	dp28-6-Ser
719.7811	1.02E+04	8	5766.3114	5766.2961	2.7	dp28-6-Ser
834.3162	1.16E+04	7	5847.2682	5847.2539	2.4	dp28-7-Ser
729.9008	6.86E+03	8	5847.2690	5847.2539	2.6	dp28-7-Ser
653.3691	9.04E+03	9	5889.3923	5889.4255	-5.6	dp29-5-Ser
662.2541	1.12E+04	9	5969.3573	5969.3755	-3.0	dp29-6-Ser
745.1632	1.06E+04	8	5969.3682	5969.3755	-1.2	dp29-6-Ser
671.1390	9.41E+03	9	6049.3214	6049.3255	-0.7	dp29-7-Ser
863.1846	9.76E+03	7	6049.3470	6049.3255	3.5	dp29-7-Ser
680.0267	1.71E+04	9	6129.3107	6129.2800	5.0	dp29-8-Ser

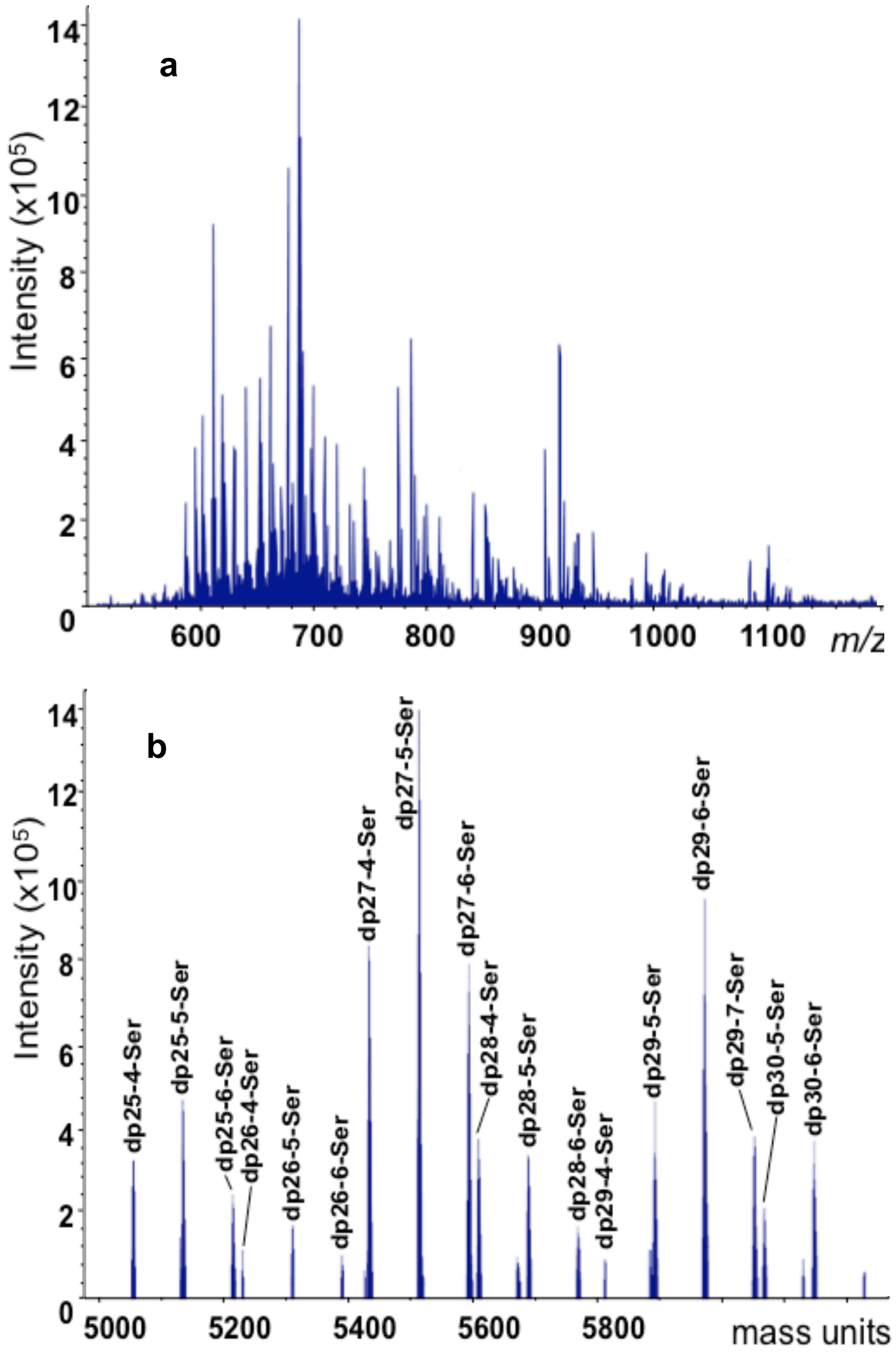
Supplementary Table 4. Accurate mass measurements for 20 compositions identified by FTMS of 5.74 kDa (by PAGE). Data acquired on the orbitrap FT mass spectrometer.

m/z	***z***	$\mathbf{M_{Exp}}$	$\mathbf{M_{Theor}}$	**Accuracy (ppm)**	**Chain**
777.6793	6	4672.1226	4672.1326	2.1	dp23-4-Ser
666.4402	7	4672.1360	4672.1326	-0.7	dp23-4-Ser
583.0099	8	4672.1416	4672.1326	-1.9	dp23-4-Ser
593.0024	8	4752.0816	4752.0894	1.6	dp23-5-Ser
691.5894	7	4848.1804	4848.1648	-3.2	dp24-4-Ser
720.5973	7	5051.2357	5051.2441	1.7	dp25-4-Ser
630.2728	8	5051.2526	5051.2441	-1.7	dp25-4-Ser
840.8694	6	5051.2632	5051.2441	-3.8	dp25-4-Ser
1009.0482	5	5051.2878	5051.2441	-8.7	dp25-4-Ser
640.3914	8	5131.1936	5131.2009	1.4	dp25-5-Ser
854.1915	6	5131.1958	5131.2009	1.0	dp25-5-Ser
569.1256	9	5131.2006	5131.2009	0.1	dp25-5-Ser
732.0230	7	5131.2156	5131.2009	-2.9	dp25-5-Ser
743.4434	7	5211.1584	5211.1577	-0.1	dp25-6-Ser
578.0101	9	5211.1611	5211.1577	-0.7	dp25-6-Ser
867.5197	6	5211.1650	5211.1577	-1.4	dp25-6-Ser
652.4009	8	5227.2696	5227.2763	1.3	dp26-4-Ser
579.8003	9	5227.2729	5227.2763	0.7	dp26-4-Ser
870.2049	6	5227.2762	5227.2763	0.0	dp26-4-Ser
745.7469	7	5227.2829	5227.2763	-1.3	dp26-4-Ser
757.1680	7	5307.2306	5307.2331	0.5	dp26-5-Ser
662.3950	8	5307.2224	5307.2331	2.0	dp26-5-Ser
588.6839	9	5307.2253	5307.2331	1.5	dp26-5-Ser
883.5362	6	5307.2640	5307.2331	-5.8	dp26-5-Ser
903.8808	6	5430.3394	5430.3556	3.0	dp27-4-Ser
774.7557	7	5430.3445	5430.3556	2.0	dp27-4-Ser
602.2532	9	5430.3568	5430.3556	-0.2	dp27-4-Ser
677.7872	8	5430.3600	5430.3556	-0.8	dp27-4-Ser
687.7809	8	5510.3096	5510.3124	0.5	dp27-5-Ser
786.1798	7	5510.3132	5510.3124	-0.1	dp27-5-Ser
917.3778	6	5510.3136	5510.3124	-0.2	dp27-5-Ser
611.2495	9	5510.3157	5510.3124	-0.6	dp27-5-Ser
550.0249	10	5510.3270	5510.3124	-2.6	dp27-5-Ser
697.7751	8	5590.2632	5590.2692	1.1	dp27-6-Ser
620.1319	9	5590.2573	5590.2692	2.1	dp27-6-Ser
930.5360	6	5590.2706	5590.2692	-0.3	dp27-6-Ser
557.9190	10	5590.2758	5590.2692	-1.2	dp27-6-Ser
797.6041	7	5590.2833	5590.2692	-2.5	dp27-6-Ser
799.9029	7	5606.3749	5606.3878	2.3	dp28-4-Ser
621.9252	9	5606.3970	5606.3878	-1.6	dp28-4-Ser
699.6670	8	5606.4062	5606.3878	-3.3	dp28-4-Ser
933.2293	6	5606.4304	5606.3878	-7.6	dp28-4-Ser

Supplementary Table 5. Accurate mass measurements for 18 compositions identified by FT-ICR MS of 5.80 kDa (by PAGE). Mass spectrum was acquired on the Bruker Bruker FT-ICR mass spectrometer. This table corresponds to identifications in spectra from Figure 3a.

m/z	***z***	**M_{Exp}**	**M_{Theor}**	**Accuracy (ppm)**	**Chain**
811.3261	7	5686.3373	5686.3446	1.3	dp28-5-Ser
709.7839	8	5686.3336	5686.3446	1.9	dp28-5-Ser
567.6270	10	5686.3480	5686.3446	-0.6	dp28-5-Ser
630.8087	9	5686.3485	5686.3446	-0.7	dp28-5-Ser
946.7230	6	5686.3848	5686.3446	-7.1	dp28-5-Ser
639.6926	9	5766.3036	5766.3014	-0.4	dp28-6-Ser
575.6236	10	5766.3140	5766.3014	-2.2	dp28-6-Ser
719.7824	8	5766.3216	5766.3014	-3.5	dp28-6-Ser
587.9346	10	5889.4240	5889.4239	0.0	dp29-5-Ser
662.2553	9	5969.3679	5969.3807	2.1	dp29-6-Ser
851.7596	7	5969.3718	5969.3807	1.5	dp29-6-Ser
541.6634	11	5969.3832	5969.3807	-0.4	dp29-6-Ser
595.9308	10	5969.3860	5969.3807	-0.9	dp29-6-Ser
745.1672	8	5969.4000	5969.3807	-3.2	dp29-6-Ser
603.9257	10	6049.3350	6049.3375	0.4	dp29-7-Ser
548.9323	11	6049.3411	6049.3375	-0.6	dp29-7-Ser
671.1414	9	6049.3428	6049.3375	-0.9	dp29-7-Ser
863.1855	7	6049.3531	6049.3375	-2.6	dp29-7-Ser
755.1622	8	6049.3600	6049.3375	-3.7	dp29-7-Ser
767.1672	8	6145.4000	6145.4129	2.1	dp30-6-Ser
876.9111	7	6145.4323	6145.4129	-3.2	dp30-6-Ser

Supplementary Table 5. (Continued).



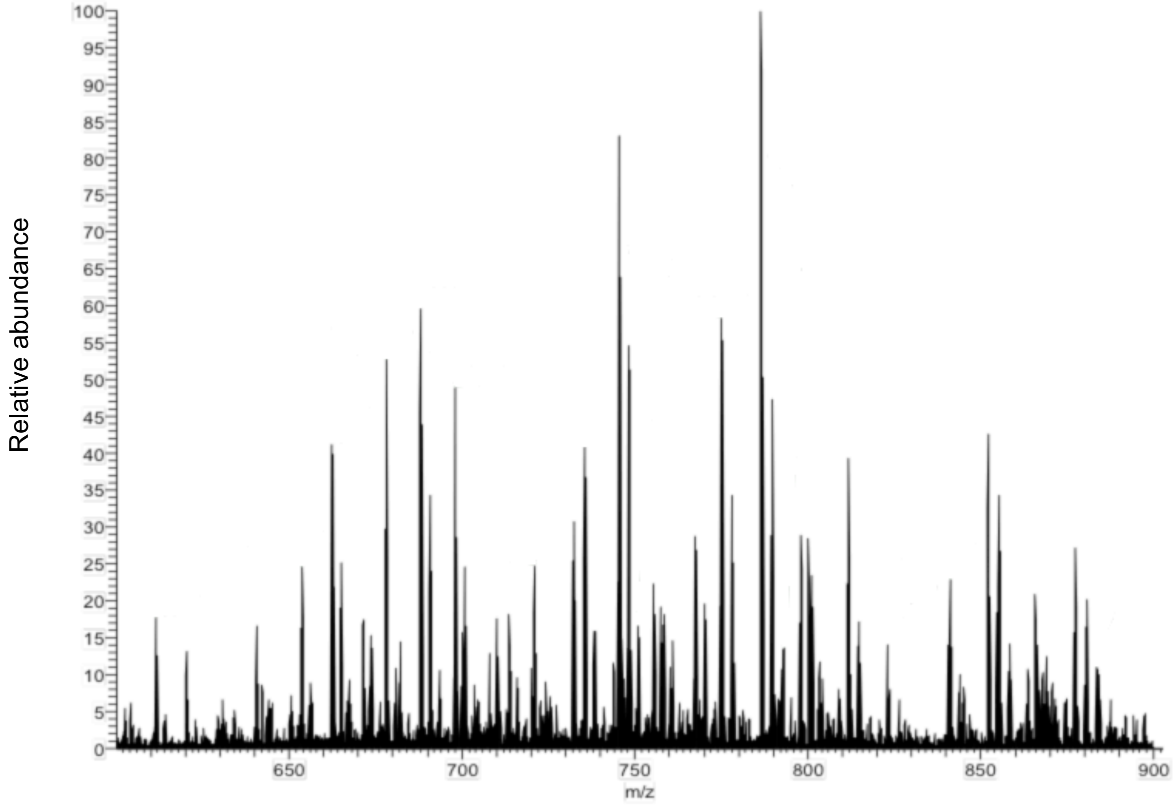
Supplementary Figure 5. FTMS of fraction 5.87 kDa (by PAGE) corresponding to 20 composition identifications listed in Supplementary Table 6. **a**. FT mass spectrum, **b**. deconvoluted spectrum.

m/z	*z*	M_{Exp}	M_{Theor}	Accuracy (ppm)	Chain
666.4416	7	4672.1460	4672.1400	1.3	dp23-4-S
840.8677	6	5051.2532	5051.2500	0.6	dp25-4-S
720.5996	7	5051.2520	5051.2500	0.4	dp25-4-S
630.3991	8	5051.2554	5051.2500	1.1	dp25-4-S
854.1970	6	5131.2290	5131.2000	5.6	dp25-5-S
732.0216	7	5131.2060	5131.2000	1.2	dp25-5-S
640.3935	8	5131.2106	5131.2000	2.1	dp25-5-S
650.3894	8	5211.1778	5211.1500	5.3	dp25-6-S
652.5281	8	5228.2874	5228.2924	-1.0	dp26-4-S
662.3968	8	5307.2370	5307.2346	0.5	dp26-5-S
768.7354	7	5388.2026	5388.1924	1.9	dp26-6-S
672.5172	8	5388.2002	5388.1924	1.4	dp26-6-S
904.0526	6	5430.3626	5430.3600	0.5	dp27-4-S
774.7586	7	5430.3650	5430.3600	0.9	dp27-4-S
677.7879	8	5430.3658	5430.3600	1.1	dp27-4-S
602.3661	9	5430.3653	5430.3600	1.0	dp27-4-S
917.3785	6	5510.3180	5510.3100	1.4	dp27-5-S
786.1809	7	5510.3211	5510.3100	2.0	dp27-5-S
687.7826	8	5510.3234	5510.3100	2.4	dp27-5-S
611.2500	9	5510.3204	5510.3100	1.9	dp27-5-S
930.7049	6	5590.2764	5590.2600	2.9	dp27-6-S
797.6043	7	5590.2849	5590.2600	4.4	dp27-6-S
697.7784	8	5590.2898	5590.2600	5.3	dp27-6-S
620.1358	9	5590.2926	5590.2600	5.8	dp27-6-S
699.7916	8	5606.3954	5606.3961	-0.1	dp28-4-S
621.9257	9	5606.4017	5606.3961	1.0	dp28-4-S
811.3285	7	5686.3543	5686.3461	1.4	dp28-5-S
709.7859	8	5686.3498	5686.3461	0.7	dp28-5-S
946.8843	6	5687.3528	5687.3539	-0.2	dp28-5-S
719.7803	8	5766.3050	5766.2961	1.5	dp28-6-S
822.8946	7	5767.3170	5767.3039	2.3	dp28-6-S
639.8057	9	5767.3217	5767.3039	3.1	dp28-6-S
644.5976	9	5810.4488	5810.4833	-5.9	dp29-4-S
735.1710	8	5889.4306	5889.4300	0.1	dp29-5-S
653.3737	9	5889.4337	5889.4300	0.6	dp29-5-S
588.1350	10	5891.4283	5891.4457	-3.0	dp29-5-S

Supplementary Table 6. Accurate mass measurements for 20 compositions identified by FTMS of 5.87 kDa (by PAGE). Mass spectrum was acquired on the orbitrap FT mass spectrometer.

m/z	*z*	M_{Exp}	M_{Theor}	Accuracy (ppm)	Chain
851.7626	7	5969.3930	5969.3800	2.2	dp29-6-S
745.1654	8	5969.3858	5969.3800	1.0	dp29-6-S
662.2586	9	5969.3978	5969.3800	3.0	dp29-6-S
596.0324	10	5970.4023	5970.3878	2.4	dp29-6-S
671.1434	9	6049.3610	6049.3255	5.9	dp29-7-S
604.1288	10	6051.3663	6051.3457	3.4	dp29-7-S
672.9308	9	6065.4476	6065.4576	-1.6	dp30-5-S
865.6283	7	6066.4529	6066.4654	-2.1	dp30-5-S
681.8154	9	6145.4090	6145.4076	0.2	dp30-6-S
877.0534	7	6146.4286	6146.4154	2.1	dp30-6-S
767.2950	8	6146.4226	6146.4154	1.2	dp30-6-S
613.7356	10	6147.4343	6147.4232	1.8	dp30-6-S
690.9246	9	6227.3918	6227.3732	3.0	dp30-7-S

Supplementary Table 6. (Continued).



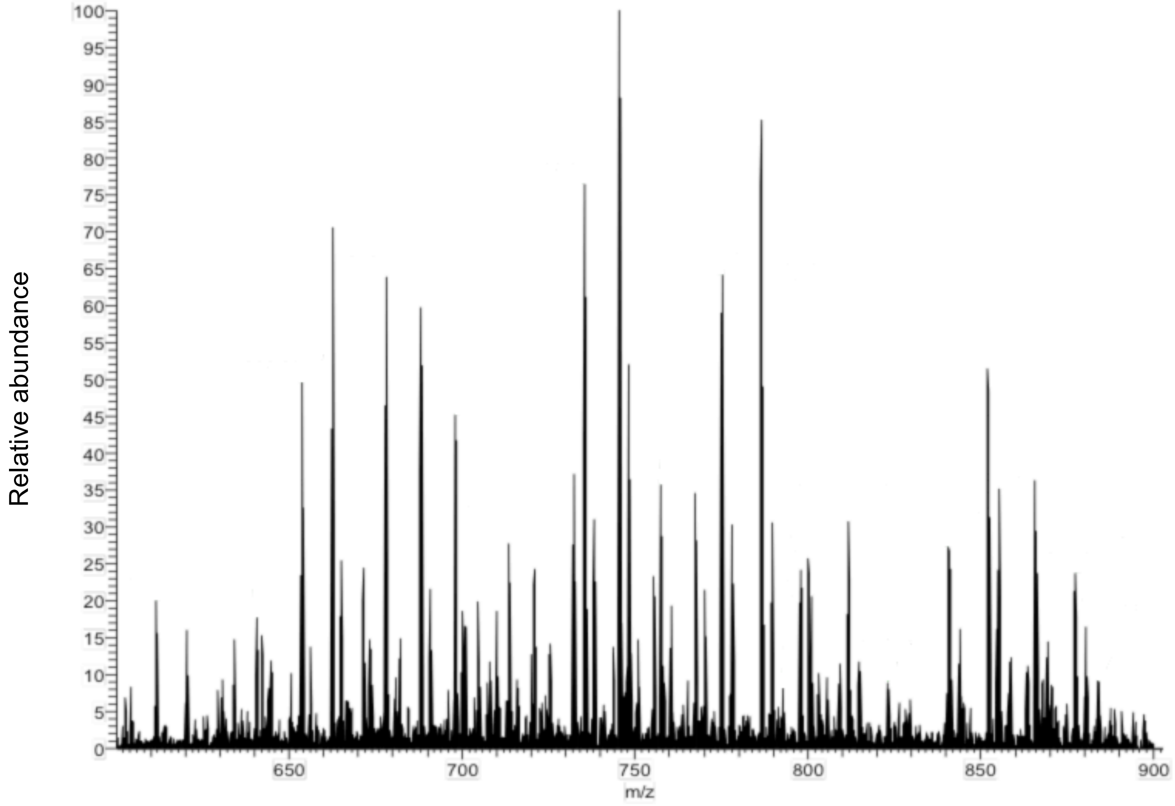
Supplementary Figure 6. FTMS of fraction 5.93 kDa (by PAGE) corresponding to 25 composition identifications listed in Supplementary Table 7.

m/z	*z*	M_{Exp}	M_{Theor}	Accuracy (ppm)	Chain
666.4411	7	4672.1425	4672.1410	0.3	dp23-4-Ser
807.1886	6	4849.1786	4849.1809	-0.5	dp24-4-Ser
840.8679	6	5051.2544	5051.2525	0.4	dp25-4-Ser
720.5993	7	5051.2499	5051.2525	-0.5	dp25-4-Ser
630.3980	8	5051.2466	5051.2525	-1.2	dp25-4-Ser
732.0219	7	5131.2081	5131.2025	1.1	dp25-5-Ser
640.3931	8	5131.2074	5131.2025	1.0	dp25-5-Ser
650.3883	8	5211.1690	5211.1525	3.2	dp25-6-Ser
867.6880	6	5212.1750	5212.1603	2.8	dp25-6-Ser
743.5873	7	5212.1659	5212.1603	1.1	dp25-6-Ser
870.2041	6	5227.2716	5227.2846	-2.5	dp26-4-Ser
883.5306	6	5307.2306	5307.2346	-0.8	dp26-5-Ser
757.1715	7	5307.2553	5307.2346	3.9	dp26-5-Ser
897.0262	6	5388.2042	5388.1924	2.2	dp26-6-Ser
768.7359	7	5388.2061	5388.1924	2.5	dp26-6-Ser
774.7577	7	5430.3587	5430.3640	-1.0	dp27-4-Ser
677.7879	8	5430.3658	5430.3640	0.3	dp27-4-Ser
602.4741	9	5431.3373	5431.3718	-6.4	dp27-4-Ser
786.1808	7	5510.3204	5510.3140	1.2	dp27-5-Ser
687.7824	8	5510.3218	5510.3140	1.4	dp27-5-Ser
611.2495	9	5510.3159	5510.3140	0.3	dp27-5-Ser
797.6035	7	5590.2793	5590.2640	2.7	dp27-6-Ser
697.7771	8	5590.2794	5590.2640	2.8	dp27-6-Ser
620.2460	9	5591.2844	5591.2718	2.3	dp27-6-Ser
629.0187	9	5670.2387	5670.2140	4.4	dp27-7-Ser
707.8967	8	5671.2362	5671.2218	2.5	dp27-7-Ser
822.8938	7	5767.3114	5767.3039	1.3	dp28--6-Ser
719.9053	8	5767.3050	5767.3039	0.2	dp28--6-Ser
799.9049	7	5606.3891	5606.3961	-1.3	dp28-4-Ser
699.7916	8	5606.3954	5606.3961	-0.1	dp28-4-Ser
811.3275	7	5686.3473	5686.3461	0.2	dp28-5-Ser
709.7854	8	5686.3458	5686.3461	-0.1	dp28-5-Ser
644.5973	9	5810.4461	5810.4833	-6.4	dp29-4-Ser
735.1656	8	5889.3874	5889.4255	-6.5	dp29-5-Ser
653.3739	9	5889.4355	5889.4255	1.7	dp29-5-Ser
840.4821	7	5890.4295	5890.4333	-0.7	dp29-5-Ser

Supplementary Table 7. Accurate mass measurements for 25 compositions identified by FTMS of 5.93 kDa (by PAGE). Mass spectrum was acquired on the orbitrap FT mass spectrometer.

m/z	***z***	**M_{Exp}**	**M_{Theor}**	**Accuracy (ppm)**	**Chain**
745.1664	8	5969.3938	5969.3755	3.1	dp29-6-Ser
662.2574	9	5969.3870	5969.3755	1.9	dp29-6-Ser
755.1579	8	6049.3258	6049.3255	0.0	dp29-7-Ser
671.1436	9	6049.3628	6049.3255	6.2	dp29-7-Ser
603.9272	10	6049.3503	6049.3255	4.1	dp29-7-Ser
747.3000	8	5986.4626	5986.5154	-8.8	dp30-4-Ser
865.4876	7	6065.4680	6065.4576	1.7	dp30-5-Ser
757.3013	8	6066.4730	6066.4654	1.3	dp30-5-Ser
673.0438	9	6066.4646	6066.4654	-0.1	dp30-5-Ser
876.9091	7	6145.4185	6145.4076	1.8	dp30-6-Ser
767.1702	8	6145.4242	6145.4076	2.7	dp30-6-Ser
681.8166	9	6145.4198	6145.4076	2.0	dp30-6-Ser
888.6191	7	6227.3885	6227.3732	2.4	dp30-7-Ser
704.4916	9	6349.4948	6349.4948	0.0	dp31-6-Ser
633.9401	10	6349.4793	6349.4948	-2.5	dp31-6-Ser
713.2660	9	6428.4644	6428.4370	4.3	dp31-7-Ser
802.6738	8	6429.4530	6429.4448	1.3	dp31-7-Ser
641.9377	10	6429.4553	6429.4448	1.6	dp31-7-Ser

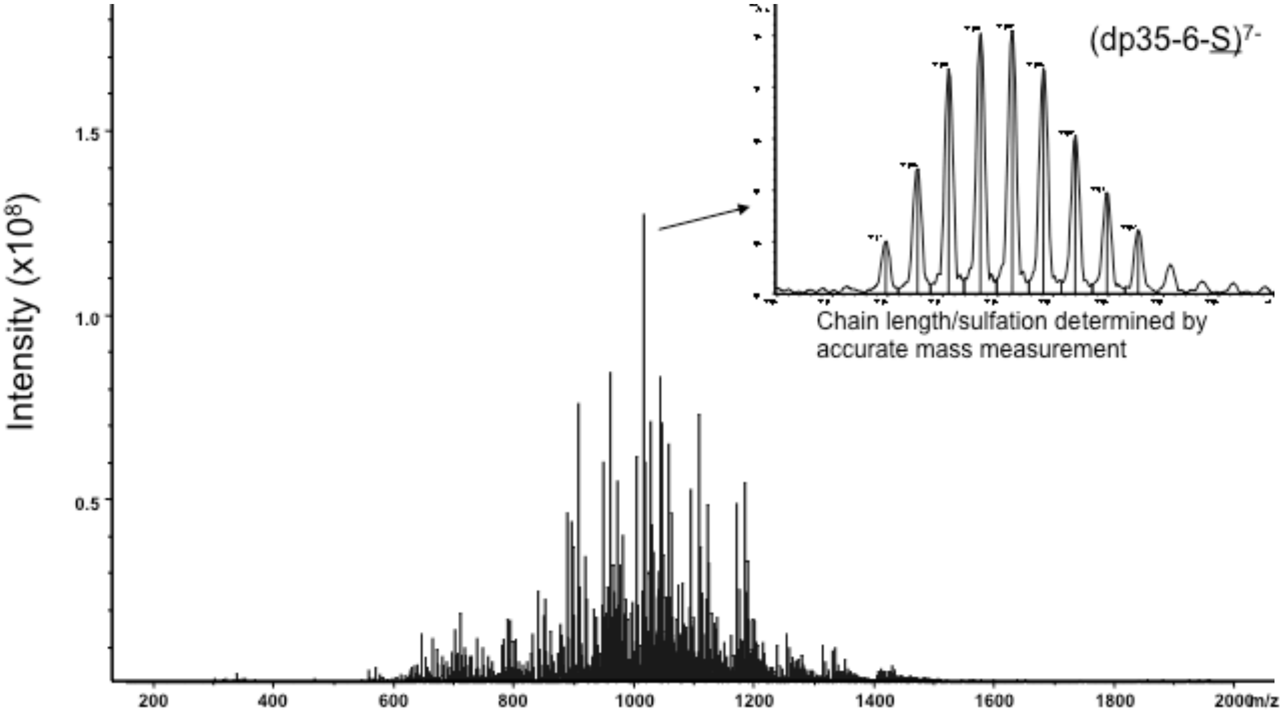
Supplementary Table 7. (Continued).



Supplementary Figure 7. FTMS of fraction 6.06 kDa (by PAGE) corresponding to 20 composition identifications listed in Supplementary Table 8.

m/z	*z*	M_{Exp}	M_{Theor}	Accuracy (ppm)	Chain
666.5848	7	4673.1484	4673.1488	-0.1	dp23-4-Ser
840.8683	6	5051.2568	5051.2525	0.8	dp25-4-Ser
720.5997	7	5051.2527	5051.2525	0.0	dp25-4-Ser
630.3975	8	5051.2426	5051.2525	-2.0	dp25-4-Ser
732.0219	7	5131.2081	5131.2025	1.1	dp25-5-Ser
743.4461	7	5211.1775	5211.1525	4.8	dp25-6-Ser
650.3885	8	5211.1706	5211.1525	3.5	dp25-6-Ser
757.1735	7	5307.2693	5307.2346	6.5	dp26-5-Ser
774.9020	7	5431.3688	5431.3718	-0.6	dp27-4-Ser
687.7819	8	5510.3178	5510.3140	0.7	dp27-5-Ser
797.7469	7	5591.2831	5591.2718	2.0	dp27-6-Ser
697.9027	8	5591.2842	5591.2718	2.2	dp27-6-Ser
799.9048	7	5606.3884	5606.3961	-1.4	dp28-4-Ser
699.7905	8	5606.3866	5606.3961	-1.7	dp28-4-Ser
811.4718	7	5687.3574	5687.3539	0.6	dp28-5-Ser
709.9115	8	5687.3546	5687.3539	0.1	dp28-5-Ser
719.9065	8	5767.3146	5767.3039	1.9	dp28-6-Ser
644.5983	9	5810.4551	5810.4833	-4.9	dp29-4-Ser
851.7631	7	5969.3965	5969.3755	3.5	dp29-6-Ser
745.1670	8	5969.3986	5969.3755	3.9	dp29-6-Ser
755.1648	8	6049.3810	6049.3255	9.2	dp29-7-Ser
854.1977	7	5986.4387	5986.5154	-12.8	dp30-4-Ser
747.3016	8	5986.4754	5986.5154	-6.7	dp30-4-Ser
664.1592	9	5986.5032	5986.5154	-2.0	dp30-4-Ser
865.4865	7	6065.4603	6065.4576	0.4	dp30-5-Ser
876.9095	7	6145.4213	6145.4076	2.2	dp30-6-Ser
633.9422	10	6349.5003	6349.4948	0.9	dp31-6-Ser
802.6744	8	6429.4578	6429.4448	2.0	dp31-7-Ser
713.3768	9	6429.4616	6429.4448	2.6	dp31-7-Ser
641.9383	10	6429.4613	6429.4448	2.6	dp31-7-Ser
824.8048	8	6606.5010	6606.4847	2.5	dp32-7-Ser

Supplementary Table 8. Accurate mass measurements for 20 compositions identified by FTMS of 6.06 kDa (by PAGE). Mass spectrum was acquired on the orbitrap FT mass spectrometer.



Supplementary Figure 8. FT-ICR MS of fraction 7.23 kDa (by PAGE) corresponding to 34 composition identifications listed in Supplementary Table 9. Zoom inset shows an example of the high resolution allowing accurate mass measurement of dp35-6-Ser with *m/z* = 1014.2332 (*z* = 7).

m/z	***z***	**M_{Exp}**	**M_{Theor}**	**Accuracy (ppm)**	**Chain**
828.7751	7	5809.4881	5809.4671	-3.6	dp29-4-Ser
725.0519	8	5809.4854	5809.4671	-3.2	dp29-4-Ser
967.2364	6	5809.4652	5809.4671	0.3	dp29-4-Ser
1160.8820	5	5809.4490	5809.4671	3.1	dp29-4-Ser
840.3401	7	5889.4353	5889.4239	-1.9	dp29-5-Ser
653.3713	9	5889.4119	5889.4239	2.0	dp29-5-Ser
735.1683	8	5889.4088	5889.4239	2.6	dp29-5-Ser
980.5581	6	5889.3954	5889.4239	4.8	dp29-5-Ser
993.8924	6	5969.4012	5969.3807	-3.4	dp29-6-Ser
745.1649	8	5969.3816	5969.3807	-0.2	dp29-6-Ser
851.7572	7	5969.3550	5969.3807	4.3	dp29-6-Ser
854.0693	7	5985.5397	5985.4993	-6.7	dp30-4-Ser
1009.9061	6	6065.4834	6065.4561	-4.5	dp30-5-Ser
865.4866	7	6065.4608	6065.4561	-0.8	dp30-5-Ser
1030.4260	6	6188.6028	6188.5786	-3.9	dp31-4-Ser
882.9329	7	6188.5927	6188.5786	-2.3	dp31-4-Ser
1236.7021	5	6188.5495	6188.5786	4.7	dp31-4-Ser
695.4984	9	6268.5558	6268.5354	-3.3	dp31-5-Ser
894.4987	7	6268.5455	6268.5354	-1.6	dp31-5-Ser
782.5588	8	6268.5328	6268.5354	0.4	dp31-5-Ser
625.8448	10	6268.5260	6268.5354	1.5	dp31-5-Ser
1043.7442	6	6268.5120	6268.5354	3.7	dp31-5-Ser
1252.6908	5	6268.4930	6268.5354	6.8	dp31-5-Ser
1057.0776	6	6348.5124	6348.4922	-3.2	dp31-6-Ser
905.9216	7	6348.5058	6348.4922	-2.1	dp31-6-Ser
792.5540	8	6348.4944	6348.4922	-0.3	dp31-6-Ser
704.3801	9	6348.4911	6348.4922	0.2	dp31-6-Ser
633.8409	10	6348.4870	6348.4922	0.8	dp31-6-Ser
706.1751	9	6364.6461	6364.6108	-5.5	dp32-4-Ser
1059.7653	6	6364.6386	6364.6108	-4.4	dp32-4-Ser
1070.4028	6	6428.4636	6428.4490	-2.3	dp31-7-Ser
641.8377	10	6428.4550	6428.4490	-0.9	dp31-7-Ser
917.3429	7	6428.4549	6428.4490	-0.9	dp31-7-Ser
802.5490	8	6428.4544	6428.4490	-0.8	dp31-7-Ser
713.2613	9	6428.4219	6428.4490	4.2	dp31-7-Ser

Supplementary Table 9. Accurate mass measurements for 34 compositions identified by FT-ICR MS of 7.23 kDa (by PAGE). Mass spectrum was acquired on the Bruker FT-ICR mass spectrometer.

m/z	***z***	**M_{Exp}**	**M_{Theor}**	**Accuracy (ppm)**	**Chain**
919.6471	7	6444.5843	6444.5676	-2.6	dp32-5-Ser
715.0564	9	6444.5778	6444.5676	-1.6	dp32-5-Ser
804.4376	8	6444.5710	6444.5676	-0.5	dp32-5-Ser
643.3482	10	6444.5678	6444.5676	0.0	dp32-5-Ser
1073.0849	6	6444.5562	6444.5676	1.8	dp32-5-Ser
928.6156	7	6508.3716	6508.4058	5.3	dp31-8-Ser
812.5380	8	6508.3664	6508.4058	6.1	dp31-8-Ser
723.9410	9	6524.5392	6524.5244	-2.3	dp32-6-Ser
814.5589	8	6524.5336	6524.5244	-1.4	dp32-6-Ser
651.4448	10	6524.5260	6524.5244	-0.2	dp32-6-Ser
931.0662	7	6524.5180	6524.5244	1.0	dp32-6-Ser
1086.4091	6	6524.5014	6524.5244	3.5	dp32-6-Ser
819.9543	8	6567.6968	6567.6901	-1.0	dp33-4-Ser
728.7358	9	6567.6924	6567.6901	-0.4	dp33-4-Ser
1093.6074	6	6567.6912	6567.6901	-0.2	dp33-4-Ser
1312.5304	5	6567.6910	6567.6901	-0.1	dp33-4-Ser
937.2332	7	6567.6870	6567.6901	0.5	dp33-4-Ser
655.7589	10	6567.6670	6567.6901	3.5	dp33-4-Ser
737.6214	9	6647.6628	6647.6469	-2.4	dp33-5-Ser
829.9492	8	6647.6560	6647.6469	-1.4	dp33-5-Ser
663.7577	10	6647.6550	6647.6469	-1.2	dp33-5-Ser
948.6539	7	6647.6319	6647.6469	2.3	dp33-5-Ser
1106.9276	6	6647.6124	6647.6469	5.2	dp33-5-Ser
1328.5144	5	6647.6110	6647.6469	5.4	dp33-5-Ser
839.9436	8	6727.6112	6727.6037	-1.1	dp33-6-Ser
671.7527	10	6727.6050	6727.6037	-0.2	dp33-6-Ser
1344.5129	5	6727.6035	6727.6037	0.0	dp33-6-Ser
960.0777	7	6727.5985	6727.6037	0.8	dp33-6-Ser
746.5024	9	6727.5918	6727.6037	1.8	dp33-6-Ser
610.5908	11	6727.5846	6727.6037	2.8	dp33-6-Ser
1120.2523	6	6727.5606	6727.6037	6.4	dp33-6-Ser
1122.7794	6	6743.7310	6743.7223	-1.3	dp34-4-Ser
755.3900	9	6807.5802	6807.5605	-2.9	dp33-7-Ser
849.9373	8	6807.5608	6807.5605	0.0	dp33-7-Ser
971.4990	7	6807.5476	6807.5605	1.9	dp33-7-Ser
617.8601	11	6807.5469	6807.5605	2.0	dp33-7-Ser
679.7468	10	6807.5460	6807.5605	2.1	dp33-7-Ser
1133.5782	6	6807.5160	6807.5605	6.5	dp33-7-Ser
973.6594	7	6823.6782	6823.6791	0.1	dp34-5-Ser
1136.1032	6	6823.6738	6823.6791	0.8	dp34-5-Ser

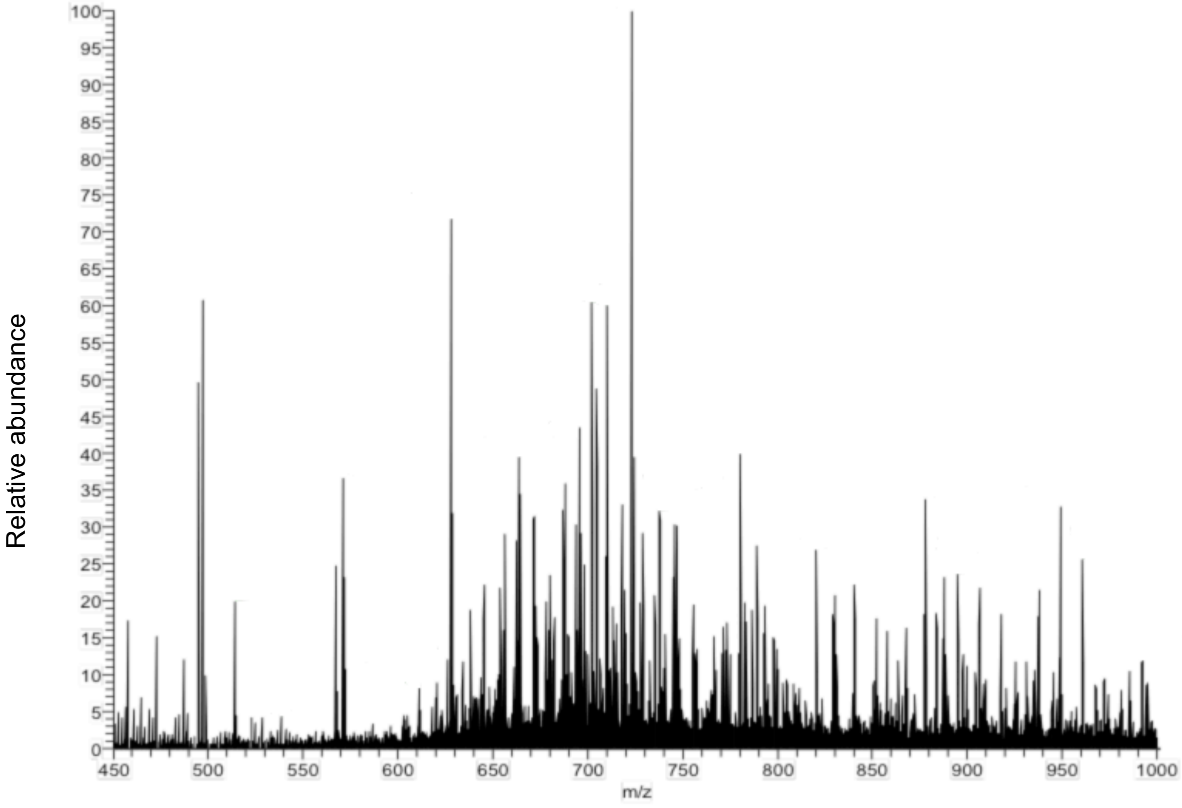
Supplementary Table 9. (Continued).

m/z	*z*	M_{Exp}	M_{Theor}	Accuracy (ppm)	Chain
859.9325	8	6887.5224	6887.5173	-0.7	dp33-8-Ser
687.7436	10	6887.5140	6887.5173	0.5	dp33-8-Ser
982.9215	7	6887.5051	6887.5173	1.8	dp33-8-Ser
1146.9078	6	6887.4936	6887.5173	3.4	dp33-8-Ser
764.2687	9	6887.4885	6887.5173	4.2	dp33-8-Ser
985.2305	7	6903.6681	6903.6359	-4.7	dp34-6-Ser
1149.5995	6	6903.6438	6903.6359	-1.1	dp34-6-Ser
861.8204	8	6903.6334	6903.6359	0.4	dp34-6-Ser
1162.9251	6	6983.5974	6983.5927	-0.7	dp34-7-Ser
871.8153	8	6983.5926	6983.5927	0.0	dp34-7-Ser
774.8336	9	6983.5804	6983.5927	1.8	dp34-7-Ser
996.6457	7	6983.5745	6983.5927	2.6	dp34-7-Ser
697.2487	10	6983.5728	6983.5927	2.8	dp34-7-Ser
1404.3476	5	7026.7770	7026.7584	-2.6	dp35-5-Ser
1002.8174	7	7026.7764	7026.7584	-2.6	dp35-5-Ser
877.3379	8	7026.7656	7026.7584	-1.0	dp35-5-Ser
1170.1186	6	7026.7584	7026.7584	0.0	dp35-5-Ser
637.7875	11	7026.7483	7026.7584	1.4	dp35-5-Ser
779.7410	9	7026.7392	7026.7584	2.7	dp35-5-Ser
701.6659	10	7026.7370	7026.7584	3.0	dp35-5-Ser
1183.4484	6	7106.7372	7106.7152	-3.1	dp35-6-Ser
1420.3384	5	7106.7310	7106.7152	-2.2	dp35-6-Ser
887.3332	8	7106.7280	7106.7152	-1.8	dp35-6-Ser
709.6639	10	7106.7170	7106.7152	-0.3	dp35-6-Ser
788.6274	9	7106.7168	7106.7152	-0.2	dp35-6-Ser
645.0573	11	7106.7161	7106.7152	-0.1	dp35-6-Ser
1014.2332	7	7106.6870	7106.7152	4.0	dp35-6-Ser
1196.7754	6	7186.6992	7186.6720	-3.8	dp35-7-Ser
797.5136	9	7186.6926	7186.6720	-2.9	dp35-7-Ser
652.3257	11	7186.6685	7186.6720	0.5	dp35-7-Ser
597.8797	12	7186.6500	7186.6720	3.1	dp35-7-Ser
717.6569	10	7186.6470	7186.6720	3.5	dp35-7-Ser
1025.6560	7	7186.6466	7186.6720	3.5	dp35-7-Ser
897.3227	8	7186.6440	7186.6720	3.9	dp35-7-Ser
1027.8237	7	7202.8283	7202.7906	-5.2	dp36-5-Ser
899.2187	8	7202.8198	7202.7906	-4.1	dp36-5-Ser
1199.2937	6	7202.8168	7202.7906	-3.6	dp36-5-Ser
719.1715	10	7202.8008	7202.7906	-1.4	dp36-5-Ser
799.1905	9	7202.7925	7202.7906	-0.3	dp36-5-Ser
653.6982	11	7202.7738	7202.7906	2.3	dp36-5-Ser

Supplementary Table 9. (Continued).

m/z	***z***	**M_{Exp}**	**M_{Theor}**	**Accuracy (ppm)**	**Chain**
1210.1052	6	7266.6780	7266.6288	-6.8	dp35-8-Ser
659.5955	11	7266.6363	7266.6288	-1.0	dp35-8-Ser
907.3211	8	7266.6312	7266.6288	-0.3	dp35-8-Ser
1037.0820	7	7266.6286	7266.6288	0.0	dp35-8-Ser
806.3944	9	7266.6198	7266.6288	1.2	dp35-8-Ser
725.6526	10	7266.6040	7266.6288	3.4	dp35-8-Ser
1212.7873	6	7282.7706	7282.7474	-3.2	dp36-6-Ser
727.2677	10	7282.7550	7282.7474	-1.0	dp36-6-Ser
661.0605	11	7282.7513	7282.7474	-0.5	dp36-6-Ser
808.1813	9	7282.7019	7282.7474	6.2	dp36-6-Ser
1226.1114	6	7362.7152	7362.7042	-1.5	dp36-7-Ser
1050.6639	7	7362.7097	7362.7042	-0.7	dp36-7-Ser
735.1620	10	7362.7058	7362.7042	-0.2	dp36-7-Ser
668.3288	11	7362.7026	7362.7042	0.2	dp36-7-Ser
817.0675	9	7362.6777	7362.7042	3.6	dp36-7-Ser
1068.2615	7	7485.8929	7485.8267	-8.8	dp37-6-Ser
747.4771	10	7485.8568	7485.8267	-4.0	dp37-6-Ser
622.7295	12	7485.8554	7485.8267	-3.8	dp37-6-Ser
679.4317	11	7485.8423	7485.8267	-2.1	dp37-6-Ser
1259.9605	6	7565.8098	7565.7835	-3.5	dp37-7-Ser
1079.8218	7	7565.8072	7565.7835	-3.1	dp37-7-Ser
944.7168	8	7565.7968	7565.7835	-1.8	dp37-7-Ser
629.4741	12	7565.7828	7565.7835	0.1	dp37-7-Ser
686.7888	11	7565.7626	7565.7835	2.8	dp37-7-Ser
954.7129	8	7645.7656	7645.7403	-3.3	dp37-8-Ser
848.5215	9	7645.7637	7645.7403	-3.1	dp37-8-Ser
1091.2439	7	7645.7619	7645.7403	-2.8	dp37-8-Ser
636.1368	12	7645.7352	7645.7403	0.7	dp37-8-Ser
694.0574	11	7645.7172	7645.7403	3.0	dp37-8-Ser
763.5617	10	7645.6950	7645.7403	5.9	dp37-8-Ser
1102.6669	7	7725.7229	7725.6791	-5.7	dp37-9-Ser
964.7026	8	7725.6832	7725.6791	-0.5	dp37-9-Ser
857.3997	9	7725.6675	7725.6791	1.5	dp37-9-Ser
1104.8227	7	7741.8213	7741.8157	-0.7	dp38-7-Ser
859.0815	9	7741.8115	7741.8157	0.5	dp38-7-Ser
702.7007	11	7741.8013	7741.8157	1.9	dp38-7-Ser

Supplementary Table 9. (Continued).



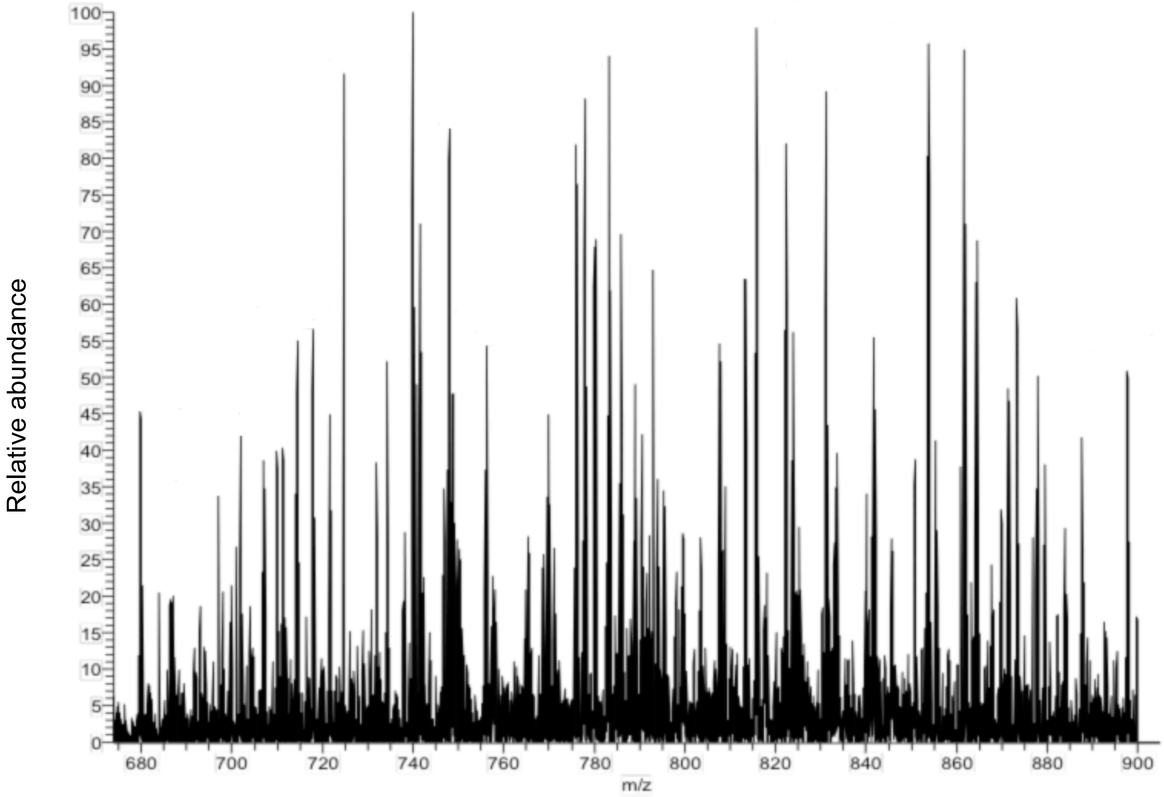
Supplementary Figure 9. FTMS of fraction 7.31 kDa (by PAGE) corresponding to 32 composition identifications listed in Supplementary Table 10.

m/z	***z***	$\mathbf{M_{Exp}}$	$\mathbf{M_{Theor}}$	**Accuracy (ppm)**	**Chain**
904.2179	6	5431.3544	5431.3718	-3.2	dp27-4-Ser
774.9013	7	5431.3639	5431.3718	-1.5	dp27-4-Ser
687.7808	8	5510.3090	5510.3140	-0.9	dp27-5-Ser
917.3776	6	5510.3126	5510.3140	-0.3	dp27-5-Ser
786.1801	7	5510.3155	5510.3140	0.3	dp27-5-Ser
930.8713	6	5591.2748	5591.2718	0.5	dp27-6-Ser
811.3275	7	5686.3473	5686.3461	0.2	dp28-5-Ser
719.9057	8	5767.3082	5767.3039	0.7	dp28-6-Ser
829.0595	7	5810.4713	5810.4833	-2.1	dp29-4-Ser
967.4047	6	5810.4752	5810.4833	-1.4	dp29-4-Ser
980.5635	6	5889.4280	5889.4255	0.4	dp29-5-Ser
735.1716	8	5889.4354	5889.4255	1.7	dp29-5-Ser
840.4814	7	5890.4246	5890.4333	-1.5	dp29-5-Ser
653.4840	9	5890.4264	5890.4333	-1.2	dp29-5-Ser
662.2570	9	5969.3834	5969.3755	1.3	dp29-6-Ser
745.2909	8	5970.3898	5970.3833	1.1	dp29-6-Ser
671.1418	9	6049.3466	6049.3255	3.5	dp29-7-Ser
863.3282	7	6050.3522	6050.3333	3.1	dp29-7-Ser
686.6124	9	6188.5820	6188.5870	-0.8	dp31-4-Ser
883.0777	7	6188.5987	6188.5870	1.9	dp31-4-Ser
782.5576	8	6268.5234	6268.5370	-2.2	dp31-5-Ser
894.6401	7	6269.5355	6269.5478	-2.0	dp31-5-Ser
704.3825	9	6348.5129	6348.4870	4.1	dp31-6-Ser
906.0640	7	6349.5028	6349.4978	0.8	dp31-6-Ser
792.6809	8	6349.5098	6349.4978	1.9	dp31-6-Ser
802.7999	8	6430.4618	6430.4527	1.4	dp31-7-Ser
706.2832	9	6365.6192	6365.6269	-1.2	dp32-4-Ser
794.8198	8	6366.6210	6366.6347	-2.2	dp32-4-Ser
919.9308	7	6446.5704	6446.5847	-2.2	dp32-5-Ser
804.8145	8	6446.5786	6446.5847	-1.0	dp32-5-Ser
724.0518	9	6525.5366	6525.5269	1.5	dp32-6-Ser
655.7592	10	6567.6703	6567.6970	-4.1	dp33-4-Ser
728.7354	9	6567.6890	6567.6970	-1.2	dp33-4-Ser
820.0778	8	6568.6850	6568.7048	-3.0	dp33-4-Ser
737.6174	9	6647.6270	6647.6500	-3.5	dp33-5-Ser
829.9471	8	6647.6394	6647.6500	-1.6	dp33-5-Ser
663.7575	10	6647.6533	6647.6500	0.5	dp33-5-Ser
948.6570	7	6647.6538	6647.6500	0.6	dp33-5-Ser

Supplementary Table 10. Accurate mass measurements for 32 compositions identified by FTMS of 7.31 kDa (by PAGE). Mass spectrum was acquired on the orbitrap FT mass spectrometer.

m/z	*z*	M_{Exp}	M_{Theor}	Accuracy (ppm)	Chain
746.5047	9	6727.6127	6727.5970	2.3	dp33-6-Ser
671.7543	10	6727.6213	6727.5970	3.6	dp33-6-Ser
840.0684	8	6728.6098	6728.6048	0.7	dp33-6-Ser
850.0638	8	6808.5730	6808.5548	2.7	dp33-7-Ser
679.8501	10	6808.5793	6808.5548	3.6	dp33-7-Ser
673.5639	10	6745.7173	6745.7447	-4.1	dp34-4-Ser
689.4566	10	6904.6443	6904.6369	1.1	dp34-6-Ser
766.1759	9	6904.6535	6904.6369	2.4	dp34-6-Ser
867.3425	8	6946.8026	6946.8070	-0.6	dp35-4-Ser
693.6743	10	6946.8213	6946.8070	2.1	dp35-4-Ser
991.5308	7	6947.7704	6947.8148	-6.4	dp35-4-Ser
637.8779	11	7027.7430	7027.7678	-3.5	dp35-5-Ser
701.6666	10	7026.7443	7026.7570	-1.8	dp35-5-Ser
779.7431	9	7026.7583	7026.7570	0.2	dp35-5-Ser
877.3374	8	7026.7618	7026.7570	0.7	dp35-5-Ser
709.6628	10	7106.7063	7106.7070	-0.1	dp35-6-Ser
887.3352	8	7106.7442	7106.7070	5.2	dp35-6-Ser
717.6582	10	7186.6603	7186.6570	0.5	dp35-7-Ser
889.4720	8	7123.8386	7123.8469	-1.2	dp36-4-Ser
719.2692	10	7202.7703	7202.7891	-2.6	dp36-5-Ser
653.7910	11	7202.7871	7202.7891	-0.3	dp36-5-Ser
909.4616	8	7283.7554	7283.7469	1.2	dp36-6-Ser
924.9781	8	7407.8874	7407.8827	0.6	dp37-5-Ser
679.5236	11	7485.8457	7485.8170	3.8	dp37-6-Ser
686.8822	11	7566.7903	7566.7748	2.0	dp37-7-Ser
839.7471	9	7566.7943	7566.7748	2.6	dp37-7-Ser
944.8430	8	7566.8066	7566.7748	4.2	dp37-7-Ser

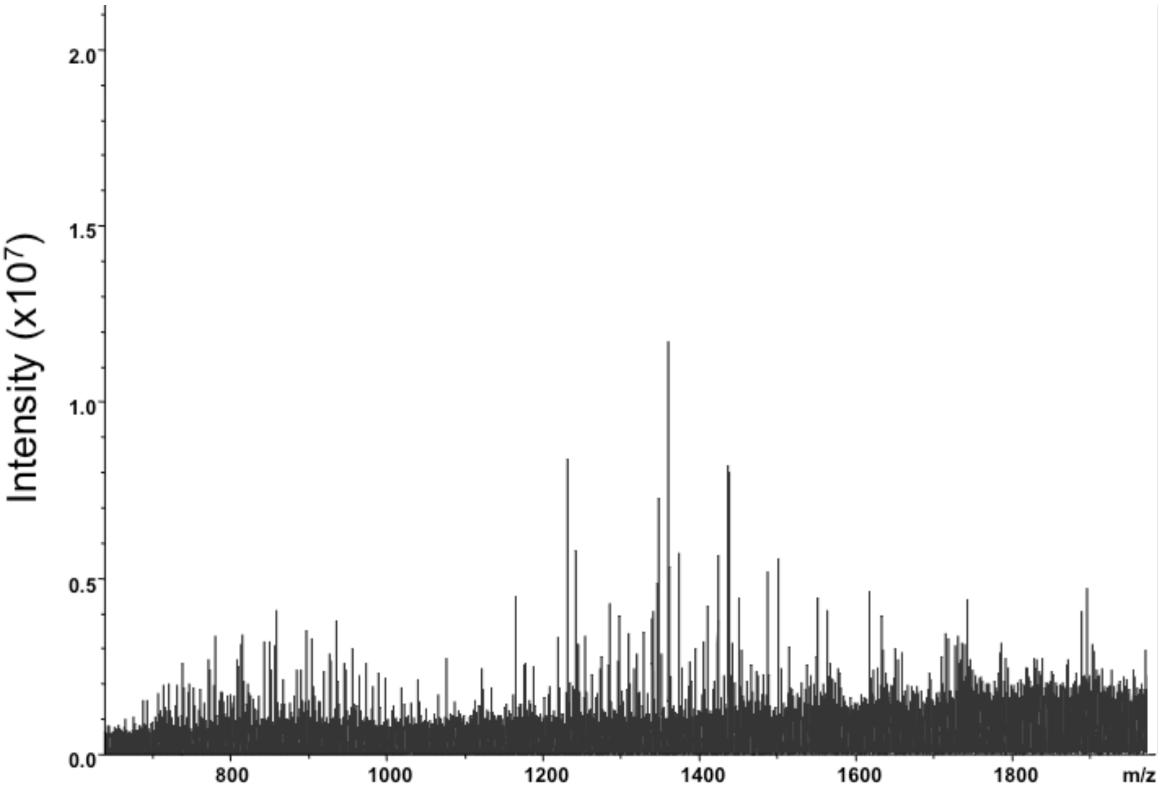
Supplementary Table 10. (Continued).



Supplementary Figure 10. FTMS of fraction 8.16 kDa (by PAGE) corresponding to 34 composition identifications listed in Supplementary Table 11.

m/z	*z*	M_{Exp}	M_{Theor}	Accuracy (ppm)	Chain
737.6179	9	6647.6315	6647.6470	-2.3	dp33-5-Ser
746.6155	9	6728.6099	6728.6048	0.8	dp33-6-Ser
770.9690	9	6947.7914	6947.8148	-3.4	dp35-4-Ser
877.3353	8	7026.7450	7026.7570	-1.7	dp35-5-Ser
788.6285	9	7106.7269	7106.7070	2.8	dp35-6-Ser
797.7322	9	7188.6602	7188.6727	-1.7	dp35-7-Ser
731.5814	10	7325.8923	7325.9170	-3.4	dp37-4-Ser
739.5772	10	7405.8503	7405.8670	-2.3	dp37-5-Ser
821.8686	9	7405.8878	7405.8670	2.8	dp37-5-Ser
830.7504	9	7485.8240	7485.8170	0.9	dp37-6-Ser
747.5780	10	7485.8583	7485.8170	5.5	dp37-6-Ser
755.5726	10	7565.8043	7565.7670	4.9	dp37-7-Ser
832.6491	9	7502.9123	7502.9569	-5.9	dp38-4-Ser
757.1806	10	7581.8843	7581.8991	-2.0	dp38-5-Ser
765.2793	10	7662.8713	7662.8569	1.9	dp38-6-Ser
769.5941	10	7706.0193	7706.0348	-2.0	dp39-4-Ser
699.5402	11	7706.0283	7706.0348	-0.8	dp39-4-Ser
777.4848	10	7784.9263	7784.9770	-6.5	dp39-5-Ser
872.8734	9	7864.9310	7864.9270	0.5	dp39-6-Ser
713.9867	11	7864.9398	7864.9270	1.6	dp39-6-Ser
785.5820	10	7865.8983	7865.9348	-4.6	dp39-6-Ser
721.2539	11	7944.8790	7944.8770	0.2	dp39-7-Ser
793.5823	10	7945.9013	7945.8848	2.1	dp39-7-Ser
795.0907	10	7960.9853	7961.0091	-3.0	dp40-4-Ser
892.5455	9	8041.9799	8041.9669	1.6	dp40-6-Ser
733.9995	11	8085.0806	8085.1448	-7.9	dp41-4-Ser
807.5049	10	8085.1273	8085.1448	-2.2	dp41-4-Ser
897.3401	9	8085.1313	8085.1448	-1.7	dp41-4-Ser
815.3996	10	8164.0743	8164.0870	-1.6	dp41-5-Ser
748.5409	11	8245.0360	8245.0448	-1.1	dp41-6-Ser
692.8252	12	8325.9963	8326.0027	-0.8	dp41-7-Ser
833.3025	10	8343.1033	8343.1426	-4.7	dp42-5-Ser
768.5592	11	8465.2373	8465.2627	-3.0	dp43-4-Ser
853.3098	10	8543.1763	8543.1970	-2.4	dp43-5-Ser
717.6721	12	8624.1591	8624.1548	0.5	dp43-6-Ser
790.2783	11	8704.1474	8704.1048	4.9	dp43-7-Ser
863.2181	10	8642.2593	8642.3026	-5.0	dp44-4-Ser
871.0173	10	8720.2513	8720.2369	1.6	dp44-5-Ser
879.1125	10	8801.2033	8801.1947	1.0	dp44-6-Ser
810.2007	11	8923.2938	8923.3148	-2.4	dp45-5-Ser
817.4708	11	9003.2649	9003.2648	0.0	dp45-6-Ser
691.5525	13	9003.2842	9003.2648	2.2	dp45-6-Ser
697.7809	13	9084.2534	9084.2227	3.4	dp45-7-Ser

Supplementary Table 11. Accurate mass measurements of compositions by FTMS of 8.16 kDa (by PAGE), acquired on the orbitrap FT mass spectrometer.



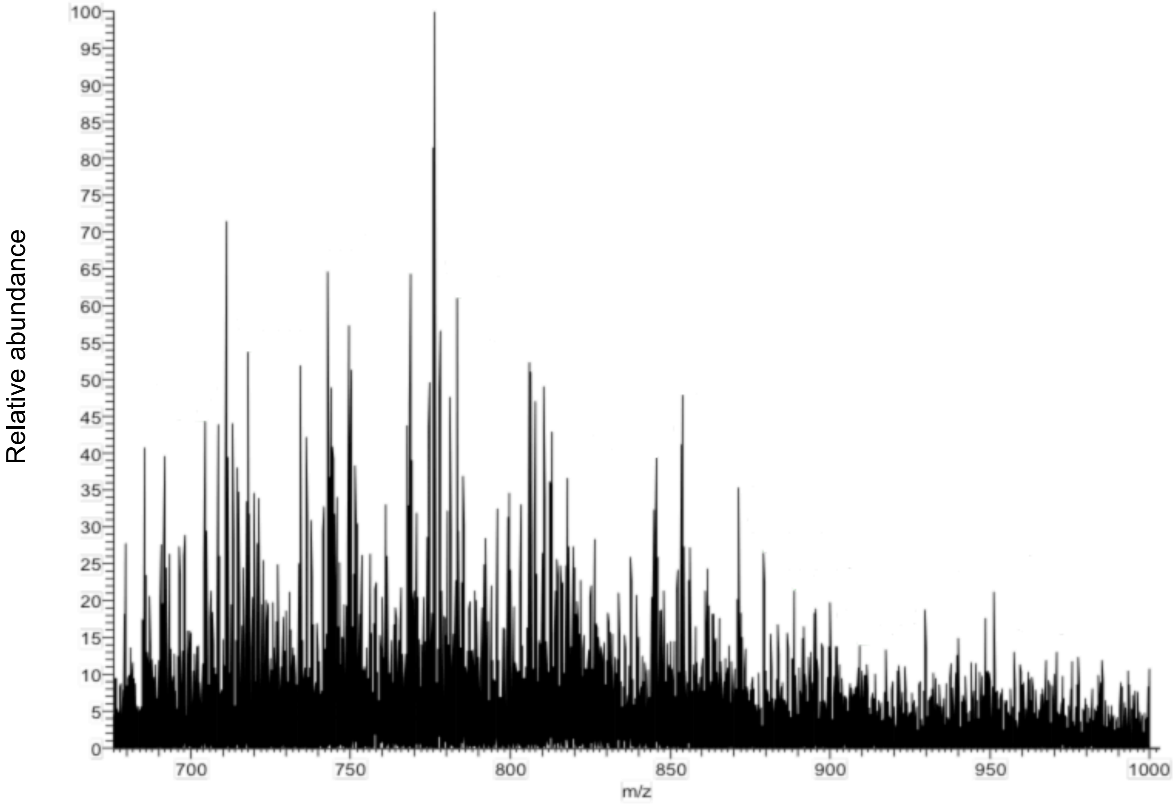
Supplementary Figure 11. FT-ICR MS of fraction 9.46 kDa (by PAGE) corresponding to 20 composition identifications listed in Supplementary Table 12.

m/z	***z***	**M_{Exp}**	**M_{Theor}**	**Accuracy (ppm)**	**Chain**
1539.7989	5	7705.0413	7705.0246	-2.2	dp39-4-Ser
1346.3453	6	8084.1186	8084.1361	2.2	dp41-4-Ser
741.0896	11	8164.0792	8164.0929	1.7	dp41-5-Ser
1631.6065	5	8164.0793	8164.0929	1.7	dp41-5-Ser
1165.1487	7	8164.1025	8164.0929	-1.2	dp41-5-Ser
906.0031	9	8164.1059	8164.0929	-1.6	dp41-5-Ser
815.3029	10	8164.1148	8164.0929	-2.7	dp41-5-Ser
1372.8324	6	8244.0490	8244.0497	0.1	dp41-6-Ser
1176.7183	7	8244.0827	8244.0497	-4.0	dp41-6-Ser
1386.3316	6	8324.0364	8324.0065	-3.6	dp41-7-Ser
775.5549	11	8543.1975	8543.2044	0.8	dp43-5-Ser
1422.6941	6	8543.2192	8543.2044	-1.7	dp43-5-Ser
853.2144	10	8543.2298	8543.2044	-3.0	dp43-5-Ser
948.1307	9	8543.2543	8543.2044	-5.8	dp43-5-Ser
1436.1846	6	8623.1544	8623.1612	0.8	dp43-6-Ser
861.3081	10	8623.1590	8623.1612	0.3	dp43-6-Ser
717.5890	12	8623.1616	8623.1612	0.0	dp43-6-Ser
957.1217	9	8623.1655	8623.1612	-0.5	dp43-6-Ser
1723.6254	5	8623.1660	8623.1612	-0.6	dp43-6-Ser
1076.8936	8	8623.2112	8623.1612	-5.8	dp43-6-Ser
1230.8853	7	8623.2517	8623.1612	-10.5	dp43-6-Ser
965.8933	9	8703.1177	8703.1180	0.0	dp43-7-Ser
869.3048	10	8703.1260	8703.1180	-0.9	dp43-7-Ser
790.0950	11	8703.1386	8703.1180	-2.4	dp43-7-Ser
1242.2987	7	8703.1455	8703.1180	-3.2	dp43-7-Ser
1449.5191	6	8703.1614	8703.1180	-5.0	dp43-7-Ser
1452.0488	6	8719.3474	8719.2366	-12.7	dp44-5-Ser
1253.7151	7	8783.0603	8783.0748	1.7	dp43-8-Ser
1465.3559	6	8799.1900	8799.1934	0.4	dp44-6-Ser
798.8273	11	8799.1939	8799.1934	-0.1	dp44-6-Ser
810.0217	11	8922.3323	8922.3159	-1.8	dp45-5-Ser
891.1265	10	8922.3508	8922.3159	-3.9	dp45-5-Ser
1485.8926	6	8922.4102	8922.3159	-10.6	dp45-5-Ser

Supplementary Table 12. Accurate mass measurements for 20 compositions identified by FT-ICR MS of 9.46 kDa (by PAGE). Mass spectrum was acquired on the Bruker FT-ICR mass spectrometer.

m/z	*z*	M_{Exp}	M_{Theor}	Accuracy (ppm)	Chain
1499.3674	6	9002.2512	9002.2727	2.4	dp45-6-Ser
817.3795	11	9002.2603	9002.2727	1.4	dp45-6-Ser
1285.0304	7	9002.2674	9002.2727	0.6	dp45-6-Ser
1296.4648	7	9082.3082	9082.2295	-8.7	dp45-7-Ser
1512.7146	6	9082.3344	9082.2295	-11.6	dp45-7-Ser
1307.8728	7	9162.1642	9162.1863	2.4	dp45-8-Ser
1327.6226	7	9301.4206	9301.4274	0.7	dp47-5-Ser
844.4850	11	9301.4286	9301.4274	-0.1	dp47-5-Ser
774.0287	12	9301.4458	9301.4274	-2.0	dp47-5-Ser
929.0363	10	9301.4488	9301.4274	-2.3	dp47-5-Ser
1549.0714	6	9301.4830	9301.4274	-6.0	dp47-5-Ser
780.7732	12	9381.3720	9381.3842	1.3	dp47-6-Ser
937.1298	10	9381.3760	9381.3842	0.9	dp47-6-Ser
720.6374	13	9381.3876	9381.3842	-0.4	dp47-6-Ser
1339.1996	7	9381.4518	9381.3842	-7.2	dp47-6-Ser
1350.7518	7	9461.3094	9461.3410	3.3	dp47-7-Ser
859.1162	11	9461.3640	9461.3410	-2.4	dp47-7-Ser
812.3652	12	9760.4760	9760.4957	2.0	dp49-6-Ser
1393.2025	7	9760.4799	9760.4957	1.6	dp49-6-Ser
1404.6382	7	9840.5298	9840.4525	-7.9	dp49-7-Ser

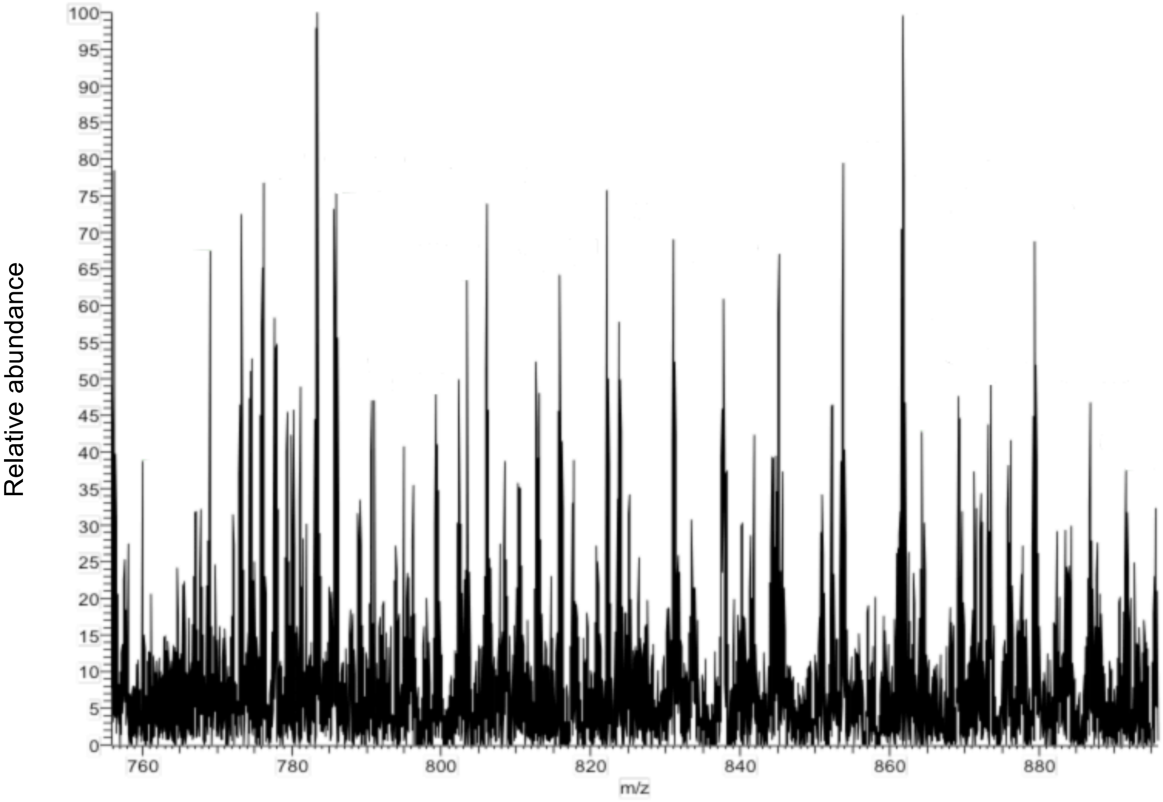
Supplementary Table 12. (Continued).



Supplementary Figure 12. FTMS of fraction 9.58 kDa (by PAGE) corresponding to 18 composition identifications listed in Supplementary Table 13.

m/z	***z***	**M_{Exp}**	**M_{Theor}**	**Accuracy (ppm)**	**Chain**
734.0053	11	8085.1444	8085.1448	-0.1	dp41-4-Ser
741.2746	11	8165.1067	8165.0948	1.5	dp41-5-Ser
748.6348	11	8246.0689	8246.0527	2.0	dp41-6-Ser
704.2630	12	8463.2499	8463.2470	0.3	dp43-4-Ser
775.6491	11	8543.2262	8543.1970	3.4	dp43-5-Ser
717.6748	12	8624.1915	8624.1548	4.3	dp43-6-Ser
863.1251	10	8641.3293	8641.2947	4.0	dp44-4-Ser
871.1175	10	8721.2533	8721.2447	1.0	dp44-5-Ser
802.9348	11	8843.3689	8843.3648	0.5	dp45-4-Ser
742.6040	12	8923.3419	8923.3148	3.0	dp45-5-Ser
749.1837	12	9002.2983	9002.2570	4.6	dp45-6-Ser
767.4461	12	9221.4471	9221.4670	-2.2	dp47-4-Ser
774.1947	12	9302.4303	9302.4248	0.6	dp47-5-Ser
780.8594	12	9382.4067	9382.3748	3.4	dp47-6-Ser
737.5744	13	9601.5689	9601.5848	-1.7	dp49-4-Ser
805.7859	12	9681.5247	9681.5348	-1.0	dp49-5-Ser
812.5344	12	9762.5067	9762.4927	1.4	dp49-6-Ser
895.2251	11	9858.5622	9858.5747	-1.3	dp50-5-Ser

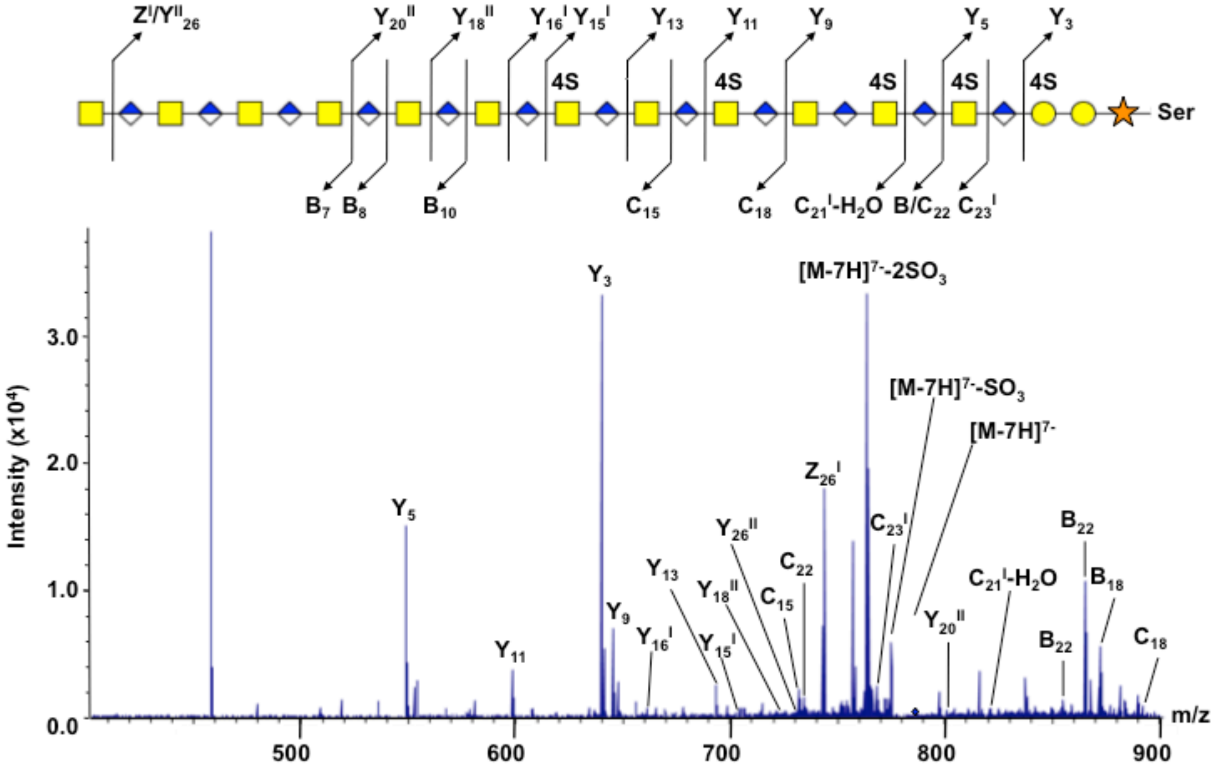
Supplementary Table 13. Accurate mass measurements for 18 compositions identified by FTMS of 9.58 kDa (by PAGE). Mass spectrum was acquired on the orbitrap FT mass spectrometer.



Supplementary Figure 13. FTMS of fraction 9.65 kDa (by PAGE) corresponding to 25 composition identifications listed in Supplementary Table 14.

m/z	*z*	M_{Exp}	M_{Theor}	Accuracy (ppm)	Chain
830.7524	9	7485.8420	7485.8170	3.3	dp37-6-Ser
755.8747	10	7568.8253	7568.7905	4.6	dp37-7-Ser
864.2142	9	7786.9982	7786.9927	0.7	dp39-5-Ser
872.9875	9	7865.9579	7865.9348	2.9	dp39-6-Ser
785.5897	10	7865.9753	7865.9348	5.1	dp39-6-Ser
793.6863	10	7946.9413	7946.8927	6.1	dp39-7-Ser
815.4051	10	8164.1293	8164.0870	5.2	dp41-5-Ser
823.5031	10	8245.1093	8245.0478	7.4	dp41-6-Ser
833.1003	10	8341.0813	8341.1269	-5.5	dp42-5-Ser
775.6450	11	8543.1811	8543.1970	-1.9	dp43-5-Ser
853.4135	10	8544.2133	8544.2048	1.0	dp43-5-Ser
861.3097	10	8623.1753	8623.1470	3.3	dp43-6-Ser
790.2759	11	8704.1210	8704.1048	1.9	dp43-7-Ser
883.2233	10	8842.3113	8842.3570	-5.2	dp45-4-Ser
891.2281	10	8922.3593	8922.3070	5.9	dp45-5-Ser
817.4731	11	9003.2902	9003.2648	2.8	dp45-6-Ser
774.1066	12	9301.3731	9301.4170	-4.7	dp47-5-Ser
851.9390	11	9382.4151	9382.3748	4.3	dp47-6-Ser
871.8595	11	9601.5406	9601.5848	-4.6	dp49-4-Ser
805.7017	12	9680.5143	9680.5270	-1.3	dp49-5-Ser
886.4050	11	9761.5411	9761.4848	5.8	dp49-6-Ser
779.1193	13	10141.6526	10141.6027	4.9	dp51-6-Ser
862.4748	12	10361.7915	10361.8205	-2.8	dp53-4-Ser
801.9744	13	10438.7689	10438.7470	2.1	dp53-5-Ser
808.2047	13	10519.7628	10519.7048	5.5	dp53-6-Ser
771.9138	14	10820.9028	10820.8805	2.1	dp55-5-Ser

Supplementary Table 14. Accurate mass measurements for 25 compositions identified by FTMS of 9.65 kDa (by PAGE). Mass spectrum was acquired on the orbitrap FT mass spectrometer.



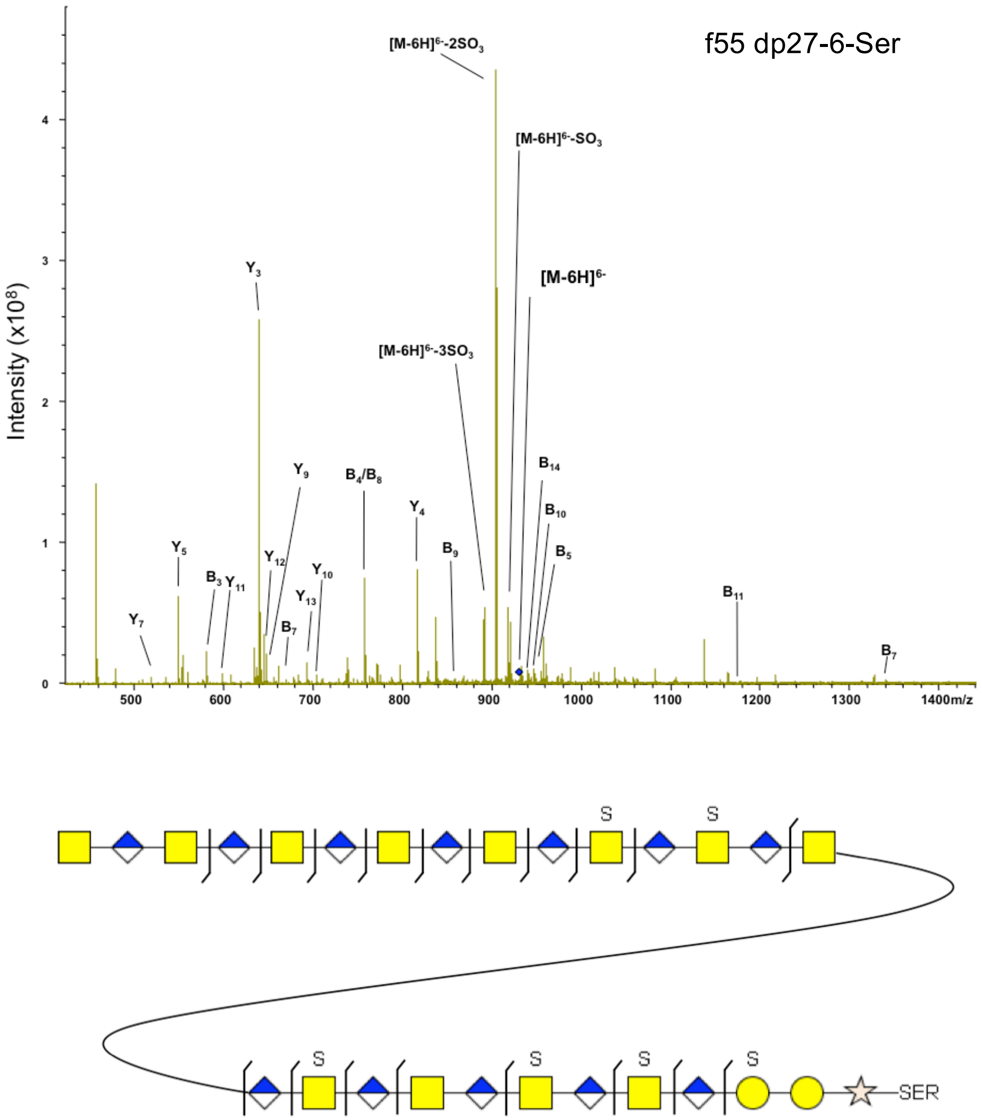
Supplementary Figure 14. Annotated spectra from CID-FTMS/MS in negative ion mode of UTI bikunin pG parent ion *m/z z* 786.18 (*z* = 7) and its fragmentation pattern providing sequence for composition dp27-5-Ser. Fragment ions assigned in Supplementary Table 15. CID mass spectra were acquired on the orbitrap FT mass spectrometer. Observed fragment ions included C_n, Z_n,Y_n or B_n type.

Cleavage	***m/z***	**Relative Intensity**	**Ion**	**Accuracy (ppm)**	$\mathbf{M_{exp}}$	$\mathbf{M_{theor}}$
B7	678.2048	1.59	HexA3HexNAc4-B	0.3	1358.4253	1358.4249
B8	757.2153	35	HexA4HexNAc4-B	0.3	1516.4463	1516.4458
B10	636.8481	1.15	HexA5HexNAc5-B	-1.5	1913.5678	1913.5706
B18^{I}	871.9817	7.13	HexA9HexNAc9S1-B	-0.5	3491.9581	3491.9600
B22^{I}	865.0192	11.85	HexA11HexNA11S2-B	-1.1	4330.1351	4330.1397
B22^{II}	849.0267	0.59	HexA11HexNA11S1-B	-2.4	4250.1726	4250.1829
C15	733.1945	1.15	HexA7HexNAc8S1-C	-2.4	2936.8093	2936.8164
C18	891.9718	0.88	HexA9HexNAc9S2-C	0.5	3571.9185	3571.9168
C21^{I}-H_2O	820.8017	1.67	HexA10HexNAc11S1-C	-0.5	4109.0476	4109.0498
C22	734.0065	1.95	HexA11HexNA11S3-C	-2.4	4410.0860	4410.0965
C23^{I}	767.8521	1.62	HexA11HexNA12S3-C	-3.5	4613.1596	4613.1759
CY	458.0606	91.42	HexA1HexNAc1S1	-0.9	459.0684	459.0688
CY	607.6377	1.54	HexA3HexNAc3S1	-0.1	1217.2911	1217.2912
B3Y1^{V}	860.8431	0.62	Hex2HexA11HexNAc10	-1.9	4309.2546	4309.2629
B4Y1^{I}	738.1683	0.72	Hex2HexA10HexNAc10S4	2.1	4435.0568	4435.0475
Y3	640.1395	84.36	Y-Hex2Pen1S1-Ser	-0.8	641.1473	641.1479
Y5	549.1001	40.06	Y-Hex2HexA1HexNAc1Pen1S2-Ser	-0.8	1100.2159	1100.2167
Y9	645.1238	19.94	Y-Hex2HexA3HexNAc3Pen1S3-Ser	-0.2	1938.3949	1938.3953
Y1^{1}	598.3579	6.82	Y-Hex2HexA4HexNAc4Pen1S4-Ser	-0.3	2397.4629	2397.4636
Y13	693.1347	6.76	Y-Hex2HexA5HexNAc5Pen1S4-Ser	-1.8	2776.5701	2776.5751
Y15^{I}	705.9506	1.21	Y-Hex2HexA6HexNAc6Pen1S4-Ser	-1.7	3534.7921	3534.7980
Y16^{I}	665.3348	1.87	Y-Hex2HexA7HexNAc6Pen1S4-Ser	-2.3	3331.7131	3331.7208
Y18^{II}	725.3646	0.54	Y-Hex2HexA8HexNAc7Pen1S3-Ser	-6.0	3631.8621	3631.8838
Y20^{II}	800.9877	0.48	Y-Hex2HexA9HexNAc8Pen1S3-Ser	-2.5	4009.9776	4009.9875
Y26^{II}	731.7460	0.58	Y-Hex2HexA12HexNAc11Pen1S3-Ser	-6.2	5129.2768	5129.3085
Z26^{I}	743.1721	10.07	Z-Hex2HexA12HexNAc11Pen1S4-Ser	-1.1	5209.2595	5209.2654
Y27^{I}	774.7559	11.65	Y-Hex2HexA12HexNAc12Pen1S4-Ser	-3.3	5430.3461	5430.3640
Y27^{II}	763.3340	17.23	Y-Hex2HexA12HexNAc12Pen1S3-Ser	-4.0	5350.3928	5350.4140

Supplementary Table 15. Assignment of fragment ions resulted from CID of *m/z* 786.18 (*z* = 7) corresponding to composition dp27-5-Ser. CID mass spectra were acquired on the orbitrap FT mass spectrometer. Ion compositions for Tables S13-S34 are written as Hex#HexA#HexNAc#Pen#S#-AA, where Hex# is number of hexoses (Gal), HexA# is number of hexuronic acids (GlcA), HexNAc# is the number of *N*-acetyl-hexosamines (GalNAc), Pen# is the number of pentoses (Xyl), S# is the number of sulfo groups, and AA is the amino acid on the reducing end. B_n,C_n,Y_n, and Z_n ions were observed from FTMS whereas only B_n and Y_n ions were observed from FT-ICR MS.

Cleavage	***m/z***	**Relative Intensity**	**Ion**	**Accuracy (ppm)**	***m/z*theor**	***z***
B03	581.1830	5.45	HexA1HexNAc2-B	1.0	581.1836	1
B04	757.2148	20.46	HexA2HexNAc2-B	1.1	757.2156	1
B05	960.2947	5.18	HexA2HexNAc3-B	0.3	960.2950	1
B06	567.6595	0.23	HexA3HexNAc3-B	0.7	567.6599	2
B06	1136.3257	2.94	HexA3HexNAc3-B	1.2	1136.3271	1
B07	669.1994	1.25	HexA3HexNAc4-B	0.3	669.1996	2
B07	1339.4088	1.45	HexA3HexNAc4-B	-1.7	1339.4065	1
B08	757.2148	20.46	HexA4HexNAc4-B	1.1	757.2156	2
B09	858.7547	1.02	HexA4HexNAc5-B	0.7	858.7553	2
B10	946.7711	4.49	HexA5HexNAc5-B	0.3	946.7714	2
B11	1048.3102	1.39	HexA5HexNAc6-B	0.8	1048.3111	2
B12	567.6595	0.23	HexA6HexNAc6-B	0.7	567.6599	4
B12	757.2148	20.46	HexA6HexNAc6-B	1.1	757.2156	3
B12	1136.3257	2.94	HexA6HexNAc6-B	1.2	1136.3271	2
B13	851.5608	0.45	HexA6HexNAc7S1-B	0.3	851.5610	3
B14	910.2375	0.93	HexA7HexNAc7S1-B	1.0	910.2384	3
B14	1365.8619	0.19	HexA7HexNAc7S1-B	-0.5	1365.8612	2
B15	977.9313	0.50	HexA7HexNAc8S1-B	0.2	977.9315	3
B17	847.9640	0.38	HexA8HexNAc9S2-B	-0.1	847.9639	4
B19	942.7411	1.12	HexA9HexNAc10S2-B	0.7	942.7418	4
B20	986.7489	0.28	HexA10HexNAc10S2-B	0.9	986.7498	4
B22	881.0108	0.72	HexA11HexNAc11S3-B	1.4	881.0120	5
B24	810.5200	0.53	HexA12HexNAc12S4-B	0.2	810.5202	6
B24	972.8247	0.14	HexA12HexNAc12S4-B	1.0	972.8257	5
B24	1216.2847	1.60	HexA12HexNAc12S4-B	-0.6	1216.2839	4
Y03	640.1392	83.31	Y-Hex2Pen1S1-Ser	1.3	640.1400	1
Y04	816.1711	9.98	Y-Hex2HexA1Pen1S1-Ser	1.2	816.1721	1
Y05	549.1003	13.84	Y-Hex2HexA1HexNAc1Pen1S2-Ser	0.4	549.1005	2
Y06	637.1159	0.99	Y-Hex2HexA2HexNAc1Pen1S2-Ser	1.0	637.1165	2
Y08	577.4308	0.15	Y-Hex2HexA3HexNAc2Pen1S3-Ser	1.0	577.4314	3
Y09	645.1240	6.66	Y-Hex2HexA3HexNAc3Pen1S3-Ser	0.8	645.1245	3
Y10	703.8015	1.31	Y-Hex2HexA4HexNAc3Pen1S3-Ser	0.5	703.8019	3
Y11	598.3586	1.52	Y-Hex2HexA4HexNAc4Pen1S4-Ser	0.0	598.3586	4
Y13	693.1358	1.46	Y-Hex2HexA5HexNAc5Pen1S4-Ser	1.0	693.1365	4
Y14	737.1436	0.15	Y-Hex2HexA6HexNAc5Pen1S4-Ser	1.2	737.1445	4

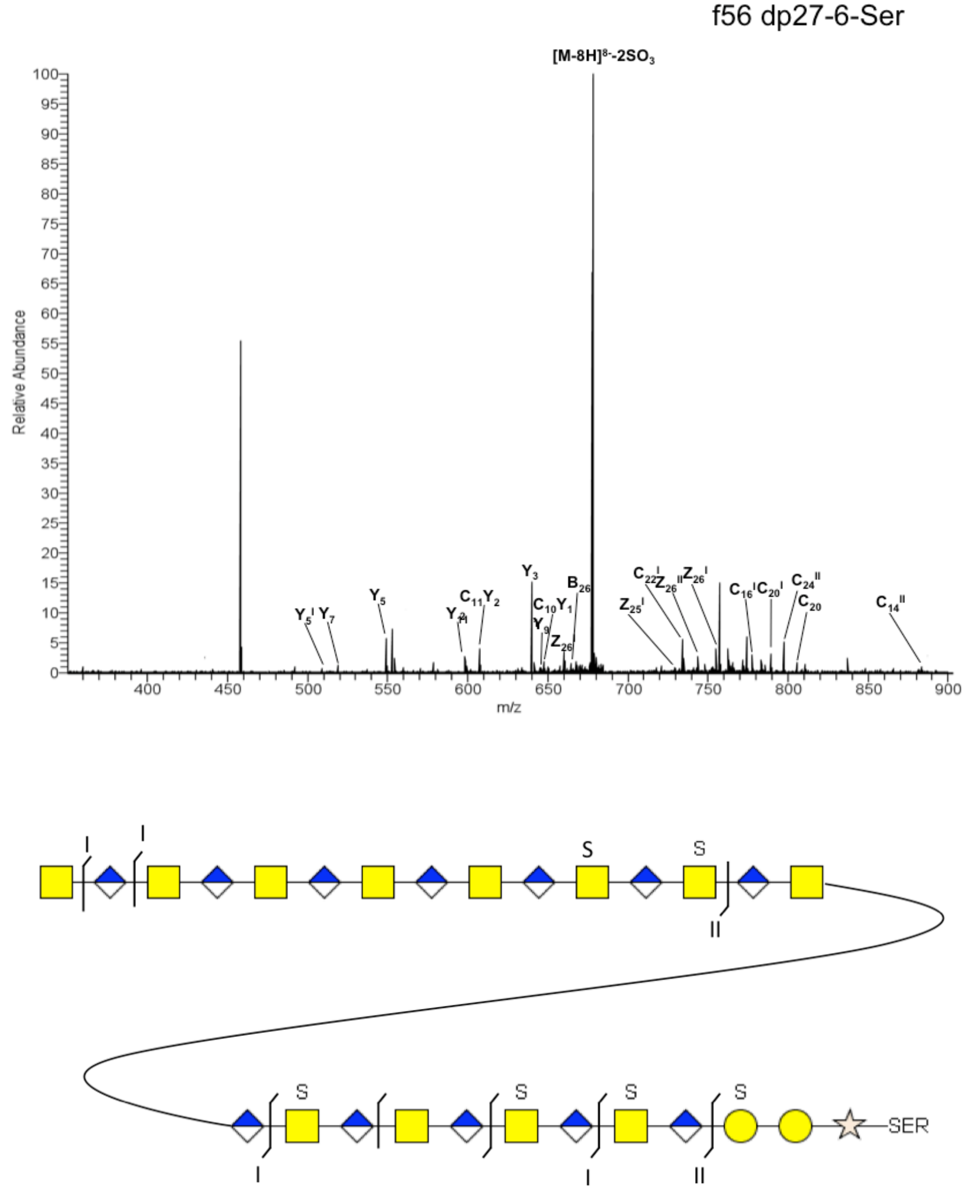
Supplementary Table 16. Assignment of fragment ions resulted from CID of parent ion *m/z* 917.38 (*z* = 6) corresponding to composition dp27-5-Ser. CID mass spectra were acquired on the Bruker FT-ICR mass spectrometer. The corresponding spectra is in Figure 3c.



Supplementary Figure 15. Annotated spectra of CID-FT-ICR MS/MS in negative ion mode of UTI bikunin pG parent ion *m/z* 930.70 (*z* = 6) corresponding to composition dp27-6-Ser and its fragmentation showing sequence. Fragment ions assigned in Supplementary Table 17. All fragment ions were Y_n or B_n type.

Cleavage	***m/z***	**Relative Intensity**	**Ion**	**Accuracy (ppm)**	m/z_{theor}	*z*
B03	581.1832	5.65	HexA1HexNAc2-B	0.6	581.1836	1
B04	757.2148	17.57	HexA2HexNAc2-B	1.1	757.2156	1
B05	960.2949	3.39	HexA2HexNAc3-B	0.1	960.2950	1
B07	669.1992	0.78	HexA3HexNAc4-B	0.6	669.1996	2
B07	1339.4076	0.72	HexA3HexNAc4-B	-0.8	1339.4065	1
B08	757.2148	17.57	HexA4HexNAc4-B	1.1	757.2156	2
B09	858.7543	0.65	HexA4HexNAc5-B	1.2	858.7553	2
B10	946.7715	2.08	HexA5HexNAc5-B	-0.1	946.7714	2
B11	1176.3052	0.71	HexA6HexNAc6S1-B	0.3	1176.3055	2
B14	936.8905	0.46	HexA7HexNAc7S2-B	0.2	936.8907	3
Y03	640.1394	60.71	Y-Hex2Pen1S1-Ser	1.0	640.1400	1
Y04	816.1714	18.78	Y-Hex2HexA1Pen1S1-Ser	0.9	816.1721	1
Y05	549.1000	13.17	Y-Hex2HexA1HexNAc1Pen1S2-Ser	0.9	549.1005	2
Y07	518.7537	0.84	Y-Hex2HexA2HexNAc2Pen1S3-Ser	0.6	518.7540	3
Y09	645.1241	5.99	Y-Hex2HexA3HexNAc3Pen1S3-Ser	0.6	645.1245	3
Y10	703.8012	1.32	Y-Hex2HexA4HexNAc3Pen1S3-Ser	0.9	703.8019	3
Y11	598.3584	0.87	Y-Hex2HexA4HexNAc4Pen1S4-Ser	0.4	598.3586	4
Y12	642.3661	0.77	Y-Hex2HexA5HexNAc4Pen1S4-Ser	0.8	642.3666	4
Y13	693.1359	3.33	Y-Hex2HexA5HexNAc5Pen1S4-Ser	0.8	693.1365	4

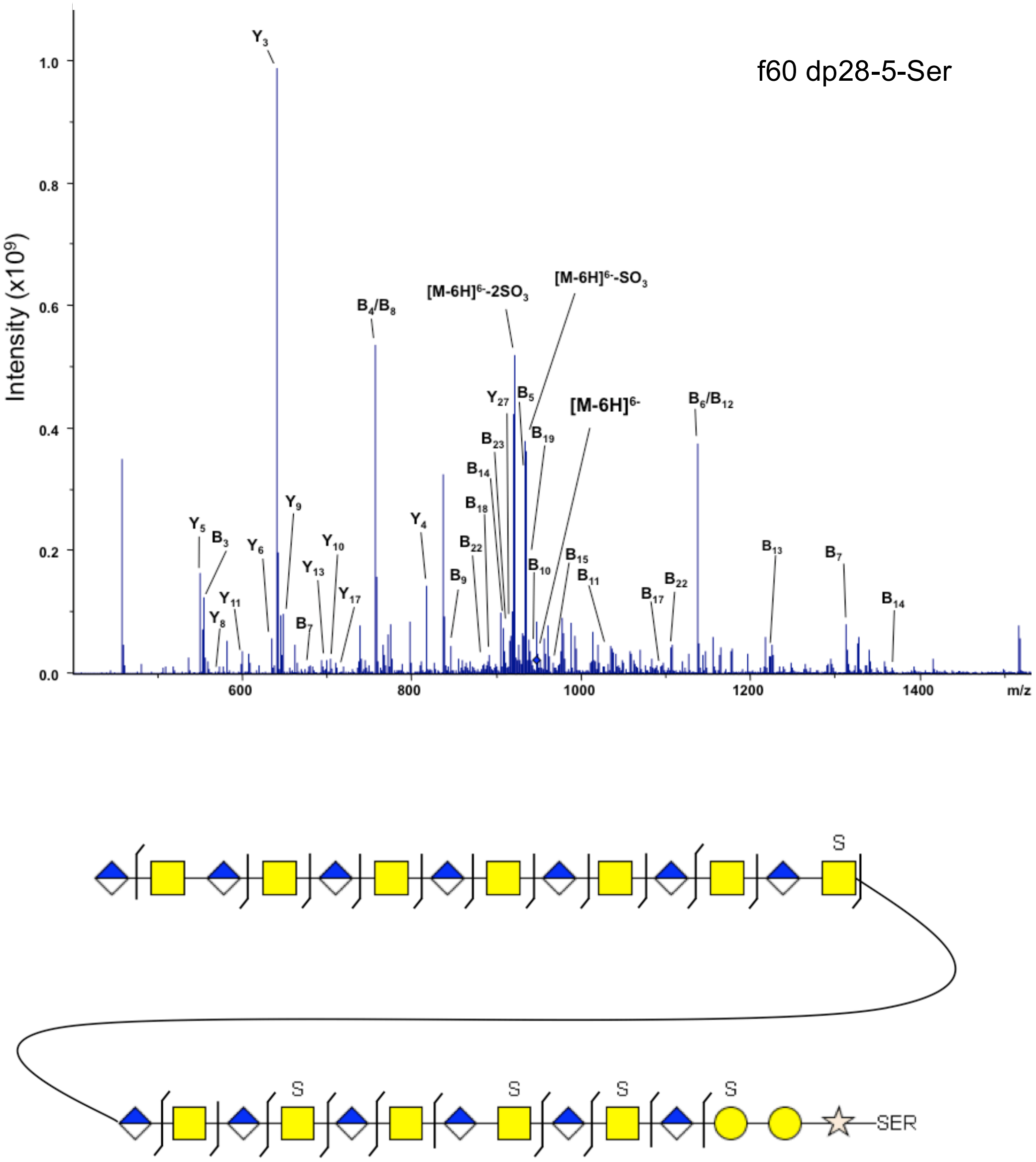
Supplementary Table 17. Assignment of fragment ions resulted from CID of parent ion *m/z* 930.70 (*z* = 6) corresponding to composition dp27-6-Ser. CID mass spectra were acquired on the Bruker FT-ICR mass spectrometer.



Supplementary Figure 16. Annotated spectra from CID-FTMS/MS in negative ion mode of UTI bikunin pG parent ion *m/z* 697.78 (z = 8) and its fragmentation pattern providing sequence for composition dp27-6-Ser. Fragment ions assigned in Supplementary Table 18. Observed fragment ions included C_n, Z_n, Y_n or B_n type.

Cleavage	***m/z***	**Relative Intensity**	**Ion**	**Accuracy (ppm)**	$\mathbf{M_{exp}}$	$\mathbf{M_{theor}}$
CY	458.0610	55.47	HexA3HexNAc4S1	1.2	459.0688	459.0683
C11Y22	607.6383	4.06	HexA3HexNAc3S1	0.9	1217.2923	1217.2912
C10Y11	647.6166	2.04	HexA3HexNAc3S2	0.6	1297.2489	1297.2480
C14$^{\mathrm{II}}$	883.5849	1.00	HexA7HexNAc7-C	-0.8	2653.7782	2653.7802
C16$^{\mathrm{I}}$	777.2045	3.12	HexA8HexNAc8S1-C	0.3	3112.8493	3112.8485
C20$^{\mathrm{I}}$	657.4976	1.16	HexA10HexNAc10S2-C	1.1	3951.0326	3951.0282
C20$^{\mathrm{I}}$	789.1983	1.64	HexA10HexNAc10S2-C	0.6	3951.0306	3951.0282
C20	805.1896	0.48	HexA10HexNAc10S3-C	0.5	4030.9871	4030.9851
C22$^{\mathrm{I}}$	734.0072	1.69	HexA11HexNAc11S3-C	-1.4	4410.0902	4410.0965
C24$^{\mathrm{II}}$	797.1937	5.39	HexA12HexNAc12S3-C	0.2	4789.2092	4789.2080
B26$^{\mathrm{I}}$	667.2733	0.56	HexA13HexNAc13-B	1.0	5346.2490	5346.2436
Y3	640.1399	15.52	Y-Hex2Pen1S1-Ser	0.6	641.1477	641.1473
Y5$^{\mathrm{I}}$	509.1221	0.77	Y-Hex2HexA1HexNAc1Pen1S1-Ser	1.0	1020.2599	1020.2588
Y5	549.1003	6.05	Y-Hex2HexA1HexNAc1Pen1S2-Ser	0.6	1100.2163	1100.2156
Y7	518.7533	1.40	Y-Hex2HexA2HexNAc2Pen1S3-Ser	-0.3	1559.2834	1559.2839
Y9	645.1246	1.02	Y-Hex2HexA3HexNAc3Pen1S3-Ser	1.0	1938.3973	1938.3953
Y11$^{\mathrm{I}}$	578.3693	1.79	Y-Hex2HexA4HexNAc4Pen1S3-Ser	0.7	2317.5085	2317.5068
Y11	598.3580	2.86	Y-Hex2HexA4HexNAc4Pen1S4-Ser	-0.1	2397.4633	2397.4636
Z25$^{\mathrm{I}}$	729.4451	0.95	Z-Hex2HexA11HexNAc11Pen1S5-Ser	-4.2	5113.1705	5113.1919
Z26$^{\mathrm{II}}$	743.1725	0.95	Z-Hex2HexA12HexNAc11Pen1S4-Ser	-0.6	5209.2623	5209.2654
Z26$^{\mathrm{I}}$	660.1451	1.25	Z-Hex2HexA12HexNAc11Pen1S5-Ser	0.2	5289.2234	5289.2222
Z26$^{\mathrm{I}}$	754.5948	3.16	Z-Hex2HexA12HexNAc11Pen1S5-Ser	-0.7	5289.2184	5289.2222
Y27$^{\mathrm{II}}$	677.7868	31.44	Y-Hex2HexA12HexNAc12Pen1S4-Ser	-1.3	5430.3570	5430.3640

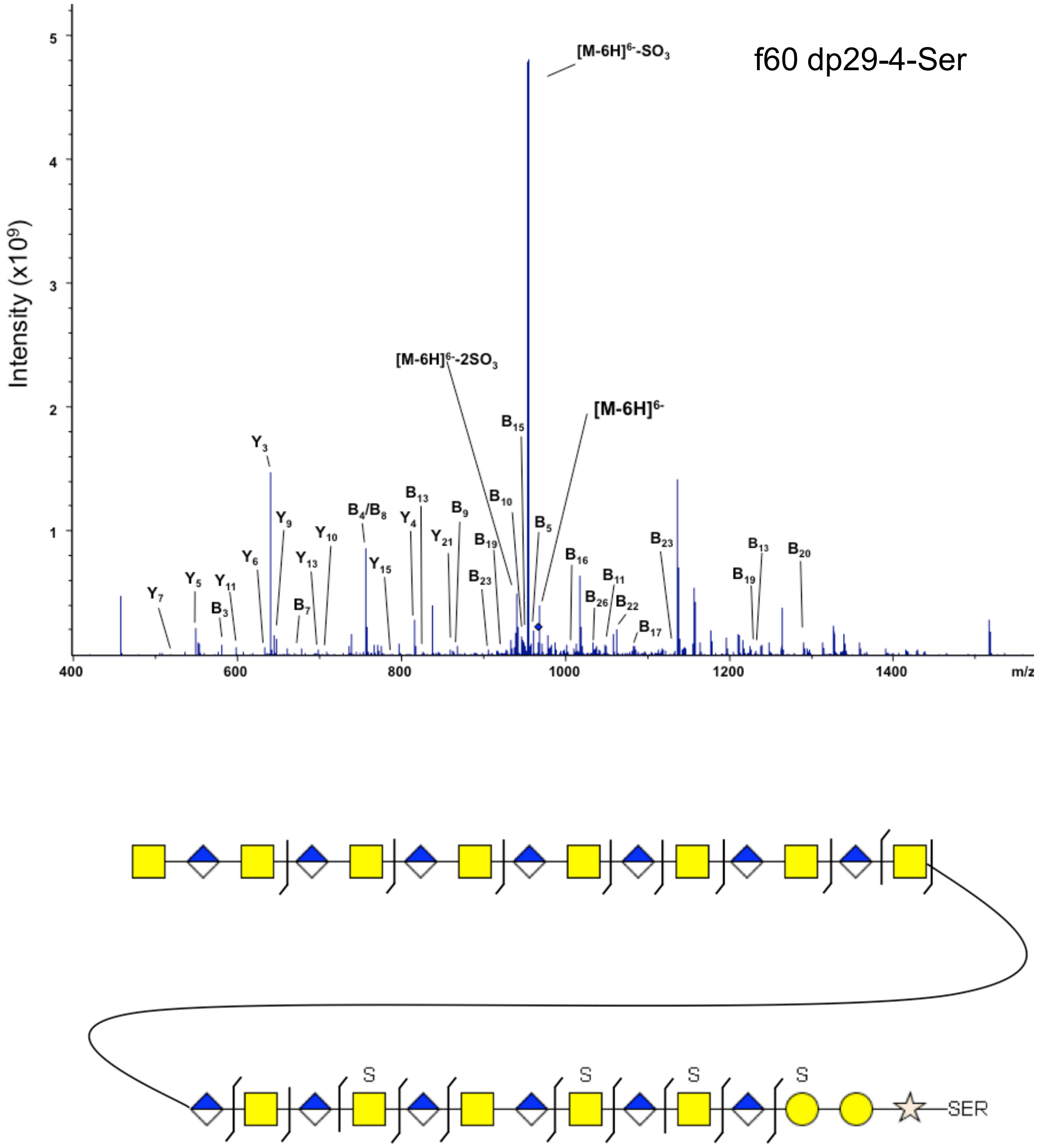
Supplementary Table 18. Assignment of fragment ions resulted from CID of parent ion *m/z* 697.78 ($z = 8$) corresponding to composition dp27-6-Ser. CID mass spectra were acquired on the orbitrap FT mass spectrometer.



Supplementary Figure 17. Annotated spectra from CID-FT-ICR MS/MS negative ion mode of UTI bikunin pG parent ion *m/z* 946.88 (z = 6) and its fragmentation pattern providing sequence for composition dp28-5-Ser. Fragment ions assigned in Supplementary Table 19. All fragment ions were Y_n or B_n type.

Cleavage	***m/z***	**Relative Intensity**	**Ion**	**Accuracy (ppm)**	m/z_{theor}	***z***
B03	554.1357	12.95	HexA2HexNAc1-B	1.0	554.1363	1
B04	757.2151	54.34	HexA2HexNAc2-B	0.7	757.2156	1
B06	1136.3271	24.26	HexA3HexNAc3-B	0.0	1136.3271	1
B07	655.6754	0.73	HexA4HexNAc3-B	0.9	655.6760	2
B07	1312.3586	7.58	HexA4HexNAc3-B	0.5	1312.3592	1
B08	757.2151	54.34	HexA4HexNAc4-B	0.7	757.2156	2
B09	845.2312	4.06	HexA5HexNAc4-B	0.6	845.2317	2
B10	946.7712	7.67	HexA5HexNAc5-B	0.2	946.7714	2
B11	1034.7873	4.52	HexA6HexNAc5-B	0.1	1034.7874	2
B12	1136.3271	24.26	HexA6HexNAc6-B	0.0	1136.3271	2
B13	1224.3432	5.22	HexA7HexNAc6-B	0.0	1224.3431	2
B14	910.2374	1.51	HexA7HexNAc7S1-B	1.1	910.2384	3
B14	1365.8614	1.17	HexA7HexNAc7S1-B	-0.1	1365.8612	2
B15	968.9153	0.94	HexA8HexNAc7S1-B	0.5	968.9158	3
B16	1036.6087	3.47	HexA8HexNAc8S1-B	0.2	1036.6089	3
B17	1095.2859	1.76	HexA9HexNAc8S1-B	0.3	1095.2863	3
B18	891.9707	0.99	HexA9HexNAc9S2-B	1.4	891.9719	4
B19	935.9795	0.40	HexA10HexNAc9S2-B	0.5	935.9799	4
B22	881.0113	0.80	HexA11HexNAc11S3-B	0.8	881.0120	5
B22	1101.5164	0.76	HexA11HexNAc11S3-B	0.4	1101.5169	4
B23	916.2178	0.63	HexA12HexNAc11S3-B	0.7	916.2184	5
B5	933.2473	14.25	HexA3HexNAc2-B	0.5	933.2477	1
Y03	640.1394	100.00	Y-Hex2Pen1S1-Ser	1.0	640.1400	1
Y04	816.1716	14.27	Y-Hex2HexA1Pen1S1-Ser	0.6	816.1721	1
Y05	549.1001	15.49	Y-Hex2HexA1HexNAc1Pen1S2-Ser	0.7	549.1005	2
Y06	637.1161	1.15	Y-Hex2HexA2HexNAc1Pen1S2-Ser	0.7	637.1165	2
Y08	577.4310	0.42	Y-Hex2HexA3HexNAc2Pen1S2-Ser	-0.2	577.4309	3
Y09	645.1241	8.16	Y-Hex2HexA3HexNAc3Pen1S3-Ser	0.6	645.1245	3
Y10	703.8016	2.21	Y-Hex2HexA4HexNAc3Pen1S3-Ser	0.4	703.8019	3
Y11	598.3576	1.58	Y-Hex2HexA4HexNAc4Pen1S4-Ser	1.7	598.3586	4
Y13	693.1359	2.25	Y-Hex2HexA5HexNAc5Pen1S4-Ser	0.8	693.1365	4
Y17	721.9424	0.31	Y-Hex2HexA7HexNAc7Pen1S5-Ser	1.8	721.9437	5
Y27	917.3771	10.34	Y-Hex2HexA12HexNAc12Pen1S5-Ser	1.1	917.3781	6

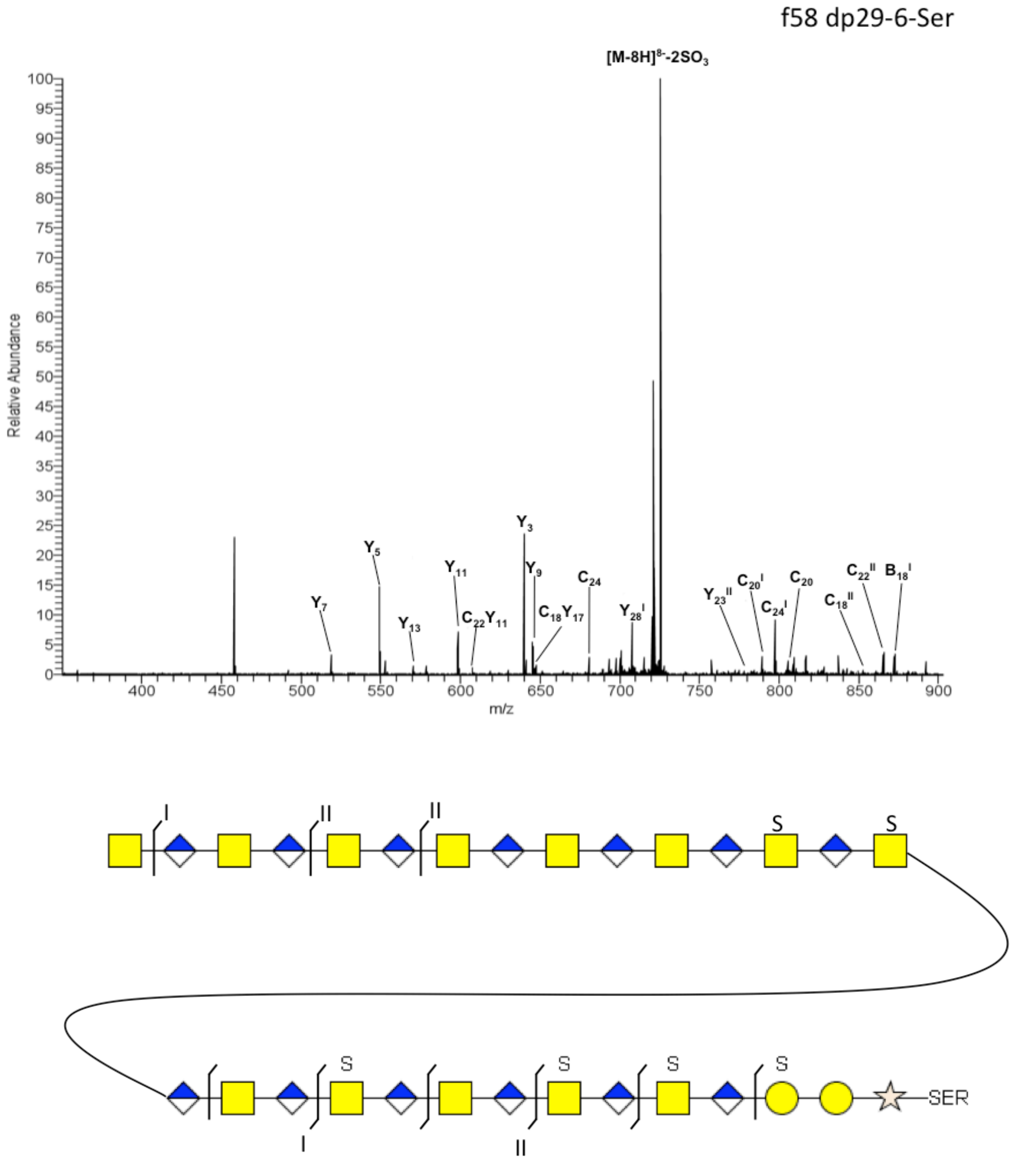
Supplementary Table 19. Assignment of fragment ions resulted from CID of parent ion *m/z* 946.88 (*z* = 6) corresponding to composition dp28-5-Ser. CID mass spectra were acquired on the Bruker FT-ICR mass spectrometer.



Supplementary Figure 18. Annotated spectra from CID-FT-ICR MS/MS in negative ion mode of UTI bikunin pG parent ion *m/z* 967.24 ($z = 6$) and its fragmentation pattern providing sequence for composition dp29-4-Ser. Fragment ions assigned in Supplementary Table 20. All fragment ions were Y_n or B_n type.

Cleavage	*m/z*	Relative Intensity	Ion	Accuracy (ppm)	m/z_{theor}	*z*
B03	581.1838	1.87	HexA1HexNAc2-B	-0.4	581.1836	1
B04	757.2150	18.92	HexA2HexNAc2-B	0.9	757.2156	1
B05	960.2941	4.03	HexA2HexNAc3-B	1.0	960.2950	1
B07	669.1991	0.44	HexA3HexNAc4-B	0.7	669.1996	2
B08	757.2150	18.92	HexA4HexNAc4-B	0.9	757.2156	2
B09	858.7544	0.98	HexA4HexNAc5-B	1.1	858.7553	2
B10	946.7710	2.94	HexA5HexNAc5-B	0.4	946.7714	2
B11	1048.3113	1.80	HexA5HexNAc6-B	-0.2	1048.3111	2
B13	824.9079	0.26	HexA6HexNAc7-B	1.1	824.9088	3
B13	1237.8671	1.83	HexA6HexNAc7-B	-0.2	1237.8668	2
B15	951.2784	0.46	HexA7HexNAc8-B	0.9	951.2793	3
B16	1009.9564	1.27	HexA8HexNAc8-B	0.2	1009.9566	3
B17	1077.6491	0.65	HexA8HexNAc9-B	0.6	1077.6497	3
B19	922.7513	0.34	HexA9HexNAc10S1-B	1.4	922.7526	4
B19	1230.6744	0.81	HexA9HexNAc10S1-B	-1.5	1230.6725	3
B20	1289.3513	2.12	HexA10HexNAc10S1-B	-1.1	1289.3499	3
B22	1061.5387	4.39	HexA11HexNAc11S1-B	-0.2	1061.5384	4
B23	905.6352	1.01	HexA11HexNAc12S2-B	1.5	905.6365	5
B23	1132.2974	0.82	HexA11HexNAc12S2-B	0.1	1132.2975	4
B26	1032.6558	2.25	HexA13HexNAc13S3-B	0.8	1032.6566	5
Y03	640.1396	32.21	Y-Hex2Pen1S1-Ser	0.6	640.1400	1
Y04	816.1709	5.80	Y-Hex2HexA1Pen1S1-Ser	1.5	816.1721	1
Y05	549.1011	4.31	Y-Hex2HexA1HexNAc1Pen1S2-Ser	-1.1	549.1005	2
Y06	637.1165	0.43	Y-Hex2HexA2HexNAc1Pen1S2-Ser	0.1	637.1165	2
Y07	518.7549	0.17	Y-Hex2HexA2HexNAc2Pen1S3-Ser	-1.7	518.7540	3
Y09	645.1245	2.81	Y-Hex2HexA3HexNAc3Pen1S3-Ser	0.0	645.1245	3
Y10	703.8014	0.18	Y-Hex2HexA4HexNAc3Pen1S3-Ser	0.6	703.8019	3
Y11	598.3587	0.13	Y-Hex2HexA4HexNAc4Pen1S4-Ser	-0.1	598.3586	4
Y13	693.1360	0.26	Y-Hex2HexA5HexNAc5Pen1S4-Ser	0.7	693.1365	4
Y15	787.9136	0.15	Y-Hex2HexA6HexNAc6Pen1S4-Ser	0.9	787.9143	4
Y21	857.5959	0.09	Y-Hex2HexA9HexNAc9Pen1S4-Ser	1.2	857.5969	5

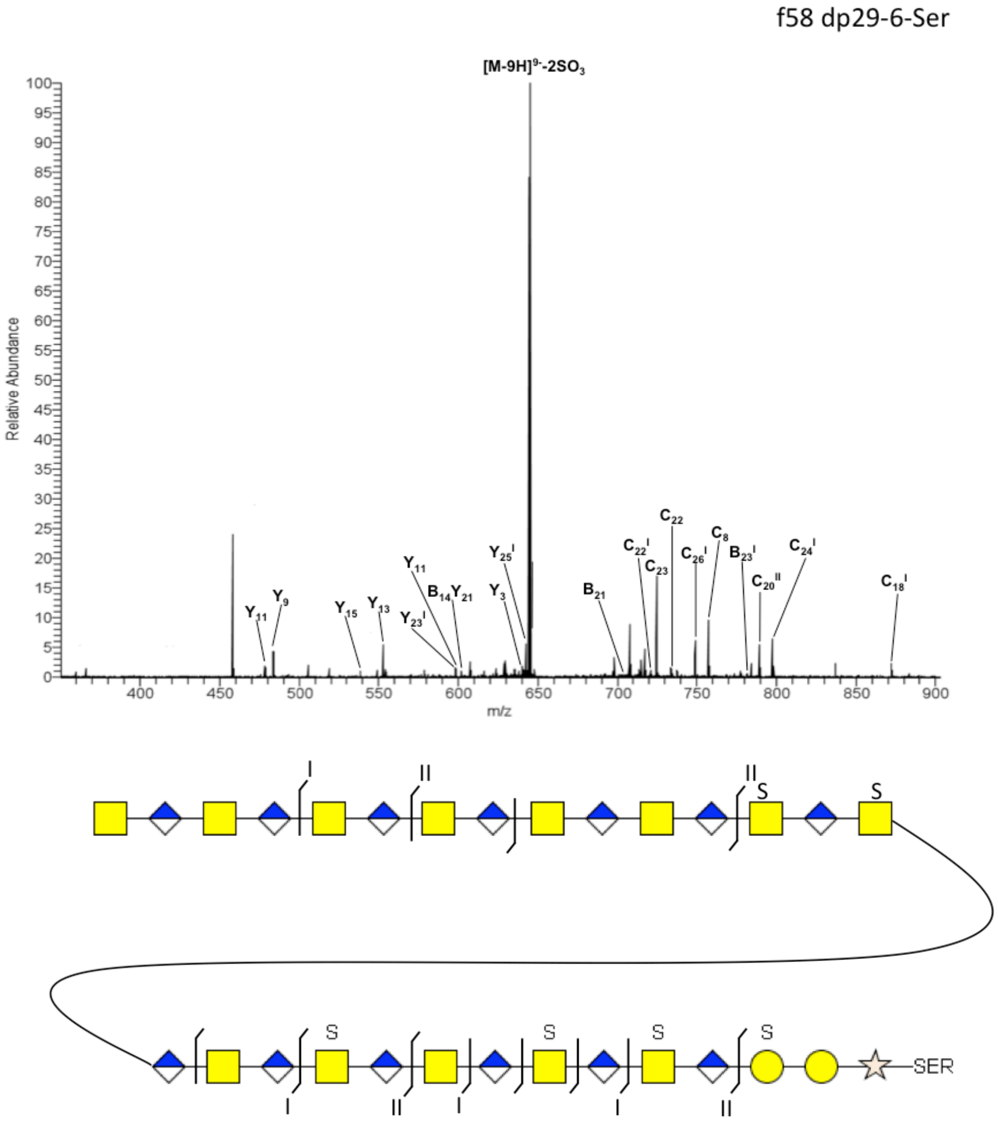
Supplementary Table 20. Assignment of fragment ions resulted from CID of parent ion *m/z* 967.24 ($z = 6$) corresponding to composition dp29-4-Ser. CID mass spectra were acquired on the Bruker FT-ICR mass spectrometer.



Supplementary Figure 19. Annotated spectra from CID-FTMS/MS in negative ion mode of UTI bikunin pG parent ion *m/z* 745.16 (z = 8) and its fragmentation pattern providing sequence for composition dp29-6-Ser. Fragment ions assigned in Supplementary Table 21. Observed fragment ions included C_n, Z_n, Y_n or B_n type.

Cleavage	***m/z***	**Relative Intensity**	**Ion**	**Accuracy (ppm)**	**M_{exp}**	**M_{theor}**
CY	458.0610	23.04	HexA1HexNAc1S1	1.2	459.0688	459.0683
B22Y21	607.6382	1.22	HexA3HexNAc3S1	0.7	1217.2921	1217.2912
C18Y17	647.6166	1.68	HexA3HexNAc3S2	0.6	1297.2489	1297.2480
C18^{II}	851.9982	0.23	HexA9HexNAc9-C	6.1	3412.0241	3412.0031
B18^{I}	871.9815	2.69	HexA9HexNAc9S1-B	-0.8	3491.9573	3491.9600
C20^{I}	789.1962	0.24	HexA10HexNAc10S2-C	-2.1	3951.0201	3951.0282
C20	805.1893	0.79	HexA10HexNAc10S3-C	0.1	4030.9856	4030.9851
C22^{II}	865.0189	0.53	HexA11HexNAc11S2-C	-1.4	4330.1336	4330.1397
C24^{I}	797.1934	5.69	HexA12HexNAc12S3-C	-0.1	4789.2074	4789.2080
C24	689.0156	0.32	HexA12HexNAc12S4-C	2.1	4830.1640	4830.1539
Y3	640.1401	24.36	Y-Hex2Pen1S1-Ser	1.0	641.1479	641.1473
Y5	549.1005	15.19	Y-Hex2HexA1HexNAc1Pen1S2-Ser	0.0	1100.2167	1100.2167
Y7	518.7539	3.38	Y-Hex2HexA2HexNAc2Pen1S3-Ser	0.8	1559.2852	1559.2839
Y9	645.1240	5.6	Y-Hex2HexA3HexNAc3Pen1S3-Ser	0.1	1938.3955	1938.3953
Y11^{I}	578.3689	0.52	Y-Hex2HexA4HexNAc4Pen1S3-Ser	0.0	2317.5069	2317.5068
Y11	598.3584	4.73	Y-Hex2HexA4HexNAc4Pen1S4-Ser	0.5	2397.4649	2397.4636
Y13	570.2988	1.49	Y-Hex2HexA5HexNAc5Pen1S4-Ser	0.4	2856.5331	2856.5319
Y23^{II}	777.6795	0.25	Y-Hex2HexA10HexNAc10Pen1S4-Ser	-3.6	4672.1240	4672.1410
Y25^{III}	709.1740	0.8	Y-Hex2HexA11HexNAc11Pen1S3-Ser	-6.0	4971.2728	4971.3025
Y25^{II}	720.5986	10.14	Y-Hex2HexA11HexNAc11Pen1S4-Ser	-1.5	5051.2450	5051.2525
Y28^{I}	707.5343	1.14	Y-Hex2HexA13HexNAc12Pen1S5-Ser	0.6	5668.3370	5668.3336
Y29^{II}	725.1756	21.66	Y-Hex2HexA13HexNAc13Pen1S4-Ser	-1.4	5809.4674	5809.4755

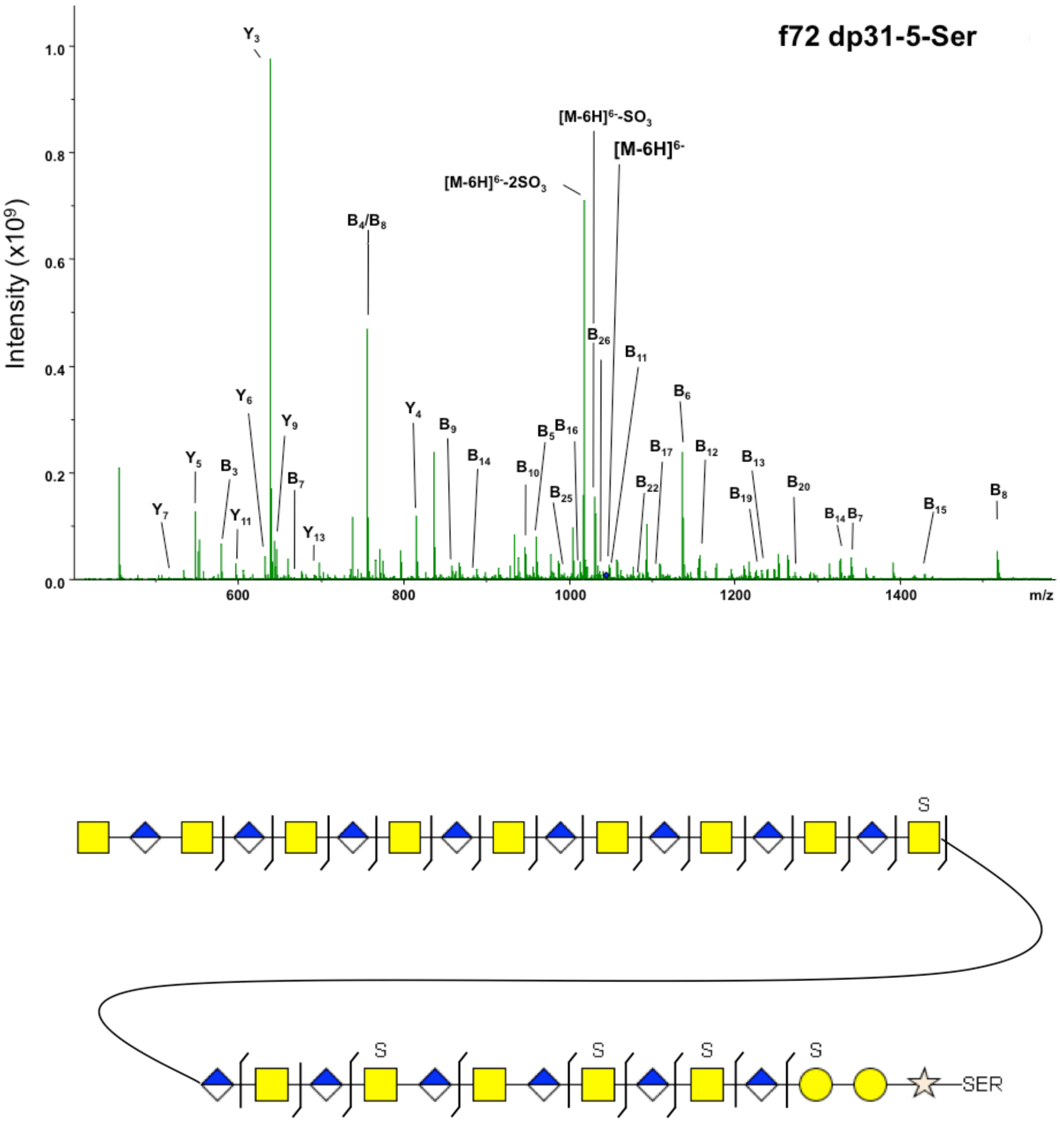
Supplementary Table 21. Assignment of fragment ions resulted from CID of parent ion *m/z* 745.16 ($z = 8$) corresponding to composition dp29-6-Ser. CID mass spectra were acquired on the orbitrap FT mass spectrometer.



Supplementary Figure 20. Annotated spectra from CID-FTMS/MS in negative ion mode of UTI bikunin pG parent ion *m/z* 662.26 (*z* = 9) and its fragmentation pattern providing sequence for composition dp 29-6-Ser. Fragment ions assigned in Supplementary Table 22. Observed fragment ions included C_n, Z_n, Y_n or B_n type.

Cleavage	***m/z***	**Relative Intensity**	**Ion**	**Accuracy (ppm)**	**M_{exp}**	**M_{theor}**	***z***
CY	458.0611	23.97	HexA1HexNAc1S1	1.4	459.0689	459.0683	1
B14Y21	607.6385	2.63	HexA3HexNAc3S1	1.2	1217.2927	1217.2912	2
C8	757.2158	9.92	HexA4HexNAc-C	0.9	1516.4473	1516.4458	2
C18^{I}	871.9818	0.82	HexA9HexNAc9S1-C	-0.4	3491.9585	3491.9600	4
C20^{II}	789.1983	2.88	HexA10HexNAc10S2-C	0.6	3951.0306	3951.0282	5
B21	704.6683	0.33	HexA10HexNAc11S3-B	-1.8	4234.0568	4234.0644	6
C22^{I}	720.6806	0.19	HexA11HexNAc11S2-C	-2.1	4330.1306	4330.1397	6
C22	734.0083	0.44	HexA11HexNAc11S3-C	0.1	4410.0968	4410.0965	6
C23	723.6012	0.18	HexA11HexNAc12S4-C	3.7	5072.2632	5072.2442	7
C24^{I}	797.1939	1.33	HexA12HexNAc12S3-C	0.5	4789.2104	4789.2080	6
C26^{II}	748.7462	1.32	HexA13HexNAc13S4-C	0.4	5248.2782	5248.2763	7
Y3	640.1402	2.06	Y-Hex2Pen1S1-Ser	1.1	641.1480	641.1473	1
Y9	483.5914	4.52	Y-Hex2HexA3HexNAc3Pen1S3-Ser	0.8	1938.3969	1938.3953	4
Y11^{I}	578.3689	0.76	Y-Hex2HexA4HexNAc4Pen1S3-Ser	0.0	2317.5069	2317.5068	4
Y11	478.4849	1.94	Y-Hex2HexA4HexNAc4Pen1S4-Ser	0.0	2397.4636	2397.4636	5
Y11	598.3587	1.74	Y-Hex2HexA4HexNAc4Pen1S4-Ser	1.0	2397.4661	2397.4636	4
Y13	554.3074	1.05	Y-Hex2HexA5HexNAc5Pen1S4-Ser	-2.7	2776.5761	2776.5835	5
Y15	538.2665	0.5	Y-Hex2HexA6HexNAc6Pen1S4-Ser	0.3	3235.6460	3235.6450	6
Y23^{II}	781.3475	0.48	Y-Hex2HexA10HexNAc10Pen1S4-Ser	1.9	4694.1320	4694.1230	6
Y23^{I}	593.0026	0.27	Y-Hex2HexA10HexNAc10Pen1S5-Ser	-1.6	4752.0834	4752.0910	8
Y25^{I}	640.3947	0.21	Y-Hex2HexA11HexNAc11Pen1S5-Ser	3.4	5131.2202	5131.2025	8
Y29^{II}	644.4885	15.53	Y-Hex2HexA13HexNAc13Pen1S4-Ser	-1.5	5809.4669	5809.4755	9

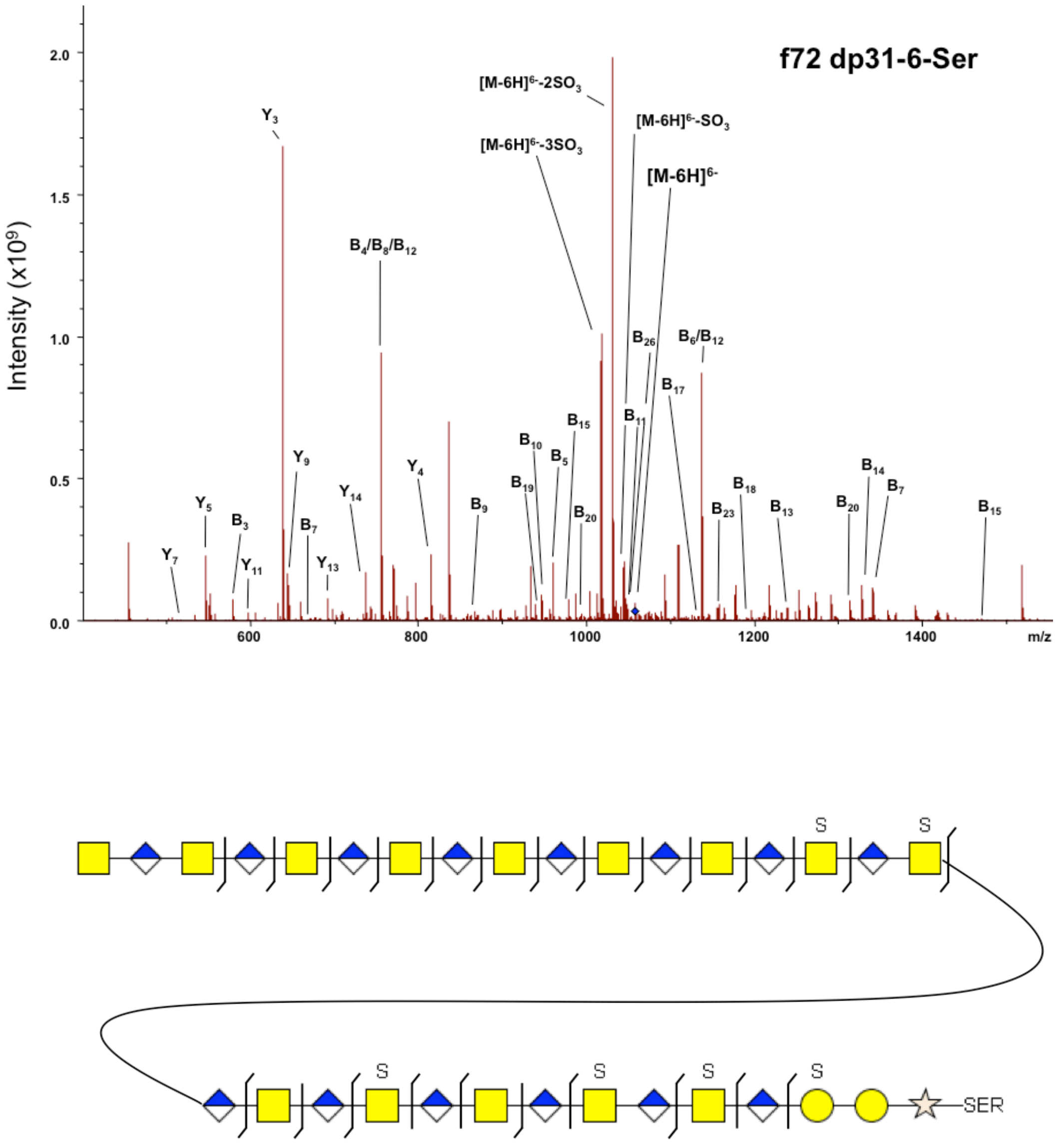
Supplementary Table 22. Assignment of fragment ions resulted from CID of parent ion *m/z* 662.26 (z = 9) corresponding to composition dp29-6-Ser. CID mass spectra were acquired on the orbitrap FT mass spectrometer.



Supplementary Figure 21. Annotated spectra from CID-FT-ICR MS/MS negative ion mode of UTI bikunin pG parent ion *m/z* 1043.74 (z = 6) and its fragmentation pattern providing sequence for composition dp31-5-Ser. Fragment ions assigned in Supplementary Table 23. All fragment ions were Y_n or B_n type.

Cleavage	***m/z***	**Relative Intensity**	**Ion**	**Accuracy (ppm)**	***m/z*$_{\text{theor}}$**	***z***
B03	581.1831	7.01	HexA1HexNAc2-B	0.8	581.1836	1
B04	757.2147	47.59	HexA2HexNAc2-B	1.2	757.2156	1
B05	960.2945	8.20	HexA2HexNAc3-B	0.5	960.2950	1
B06	1136.3271	15.99	HexA3HexNAc3-B	0.0	1136.3271	1
B07	669.1991	0.42	HexA3HexNAc4-B	0.7	669.1996	2
B07	1339.4073	4.10	HexA3HexNAc4-B	-0.6	1339.4065	1
B08	757.2147	47.59	HexA4HexNAc4-B	1.2	757.2156	2
B08	1515.4405	5.08	HexA4HexNAc4-B	-1.3	1515.4386	1
B09	858.7550	2.22	HexA4HexNAc5-B	0.4	858.7553	2
B10	946.7715	5.43	HexA5HexNAc5-B	-0.1	946.7714	2
B11	1048.3109	2.56	HexA5HexNAc6-B	0.2	1048.3111	2
B12	1136.3271	15.99	HexA6HexNAc6-B	0.0	1136.3271	2
B13	1237.8674	2.06	HexA6HexNAc7-B	-0.5	1237.8668	2
B14	883.5869	0.21	HexA7HexNAc7-B	-0.9	883.5861	3
B14	1325.8837	4.12	HexA7HexNAc7-B	-0.7	1325.8828	2
B15	1427.4243	1.12	HexA7HexNAc8-B	-1.2	1427.4225	2
B16	1009.9562	0.89	HexA8HexNAc8-B	0.4	1009.9566	3
B17	1104.3021	0.48	HexA8HexNAc9S1-B	-0.1	1104.3020	3
B19	1230.6724	0.33	HexA9HexNAc10S1-B	0.1	1230.6725	3
B20	1289.3504	1.57	HexA10HexNAc10S1-B	-0.4	1289.3499	3
B22	1081.5278	0.69	HexA11HexNAc11S2-B	-0.1	1081.5276	4
B25	997.4502	0.52	HexA12HexNAc13S3-B	0.0	997.4502	5
B26	1032.6563	0.66	HexA13HexNAc13S3-B	0.3	1032.6566	5
Y03	640.1394	100.00	Y-Hex2Pen1S1-Ser	1.0	640.1400	1
Y04	816.1715	12.01	Y-Hex2HexA1Pen1S1-Ser	0.7	816.1721	1
Y05	549.1001	12.00	Y-Hex2HexA1HexNAc1Pen1S2-Ser	0.7	549.1005	2
Y06	637.1162	0.88	Y-Hex2HexA2HexNAc1Pen1S2-Ser	0.5	637.1165	2
Y07	518.7537	0.28	Y-Hex2HexA2HexNAc2Pen1S3-Ser	0.6	518.7540	3
Y09	645.1242	6.32	Y-Hex2HexA3HexNAc3Pen1S3-Ser	0.4	645.1245	3
Y11	598.3582	0.41	Y-Hex2HexA4HexNAc4Pen1S4-Ser	0.7	598.3586	4
Y13	693.1355	0.82	Y-Hex2HexA5HexNAc5Pen1S4-Ser	1.4	693.1365	4

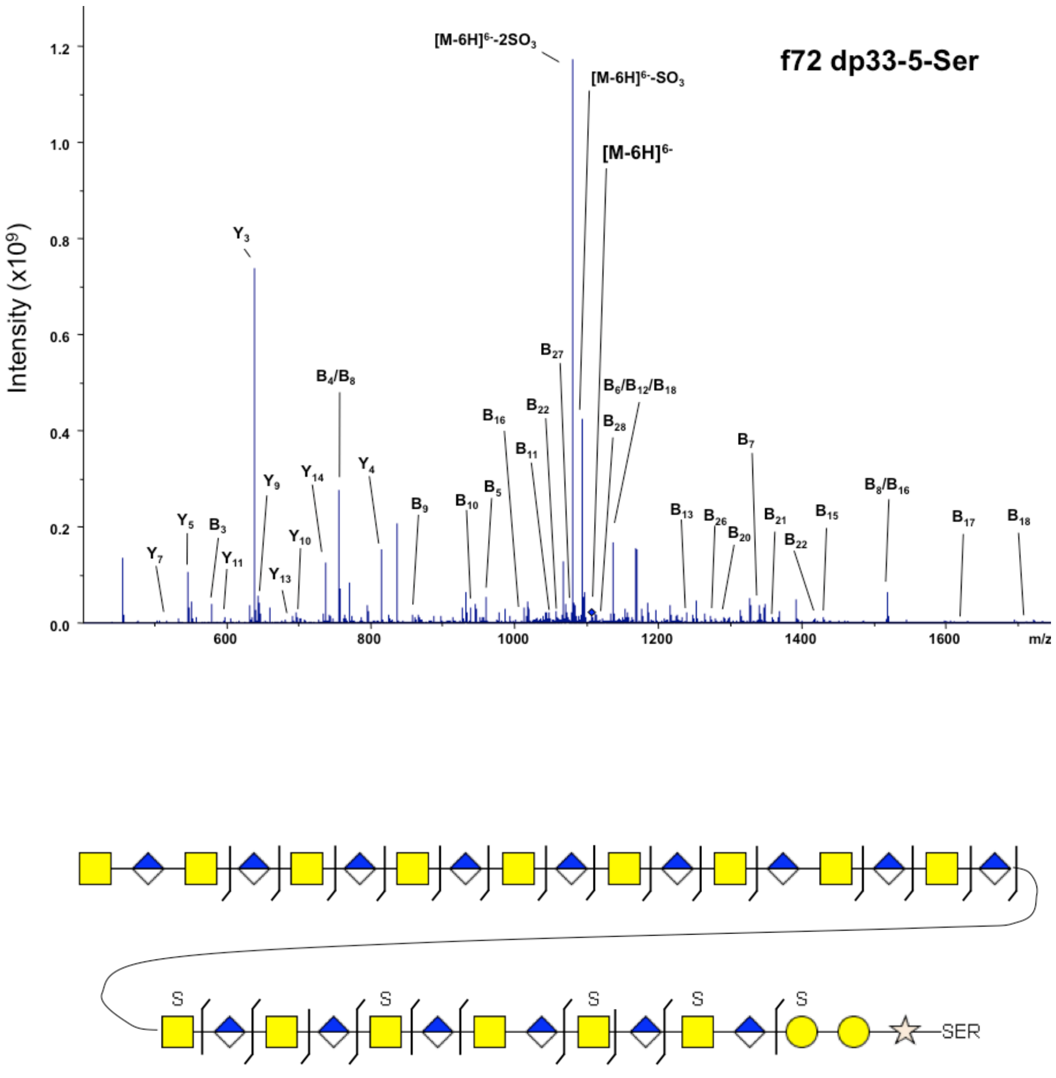
Supplementary Table 23. Assignment of fragment ions resulted from CID of parent ion *m/z* 1043.74 (*z* = 6) corresponding to composition dp31-5-Ser. CID mass spectra were acquired on the Bruker FT-ICR mass spectrometer.



Supplementary Figure 22. Annotated spectra from CID-FT-ICR MS/MS in negative ion mode of UTI bikunin pG parent ion *m/z* 1057.08 (*z* = 6) and its fragmentation pattern providing sequence for composition dp31-6-Ser. Fragment ions assigned in Supplementary Table 24. All fragment ions were Y_n or B_n type.

Cleavage	*m/z*	Relative Intensity	Ion	Accuracy (ppm)	m/z_{theor}	*z*
B03	581.1833	3.80	HexA1HexNAc2-B	0.4	581.1836	1
B04	757.2146	46.51	HexA2HexNAc2-B	1.4	757.2156	1
B05	960.2941	9.87	HexA2HexNAc3-B	1.0	960.2950	1
B06	1136.3268	25.92	HexA3HexNAc3-B	0.3	1136.3271	1
B07	669.1994	0.21	HexA3HexNAc4-B	0.3	669.1996	2
B07	1339.4084	5.40	HexA3HexNAc4-B	-1.4	1339.4065	1
B08	757.2146	46.51	HexA4HexNAc4-B	1.4	757.2156	2
B09	858.7549	1.10	HexA4HexNAc5-B	0.5	858.7553	2
B10	946.7707	4.04	HexA5HexNAc5-B	0.7	946.7714	2
B11	1048.3117	2.21	HexA5HexNAc6-B	-0.6	1048.3111	2
B12	757.2146	46.51	HexA6HexNAc6-B	1.4	757.2156	3
B12	1136.3268	25.92	HexA6HexNAc6-B	0.3	1136.3271	2
B13	1237.8660	2.41	HexA6HexNAc7-B	0.6	1237.8668	2
B14	1325.8836	6.27	HexA7HexNAc7-B	-0.6	1325.8828	2
B15	977.9321	0.35	HexA7HexNAc8S1-B	-0.6	977.9315	3
B15	1467.4019	0.29	HexA7HexNAc8S1-B	-0.7	1467.4009	2
B17	1130.9552	0.18	HexA8HexNAc9S2-B	-0.8	1130.9543	3
B18	1189.6323	0.57	HexA9HexNAc9S2-B	-0.5	1189.6316	3
B19	942.7412	0.22	HexA9HexNAc10S2-B	0.6	942.7418	4
B20	986.7495	0.97	HexA10HexNAc10S2-B	0.3	986.7498	4
B20	1316.0032	0.37	HexA10HexNAc10S2-B	-0.8	1316.0021	3
B23	1152.2863	0.22	HexA11HexNAc12S3-B	0.3	1152.2867	4
B26	1048.6492	0.14	HexA13HexNAc13S4-B	-1.2	1048.6480	5
Y03	640.1392	83.82	Y-Hex2Pen1S1-Ser	1.3	640.1400	1
Y04	816.1711	11.34	Y-Hex2HexA1Pen1S1-Ser	1.2	816.1721	1
Y05	549.1003	10.41	Y-Hex2HexA1HexNAc1Pen1S2-Ser	0.4	549.1005	2
Y07	518.7540	0.20	Y-Hex2HexA2HexNAc2Pen1S3-Ser	0.0	518.7540	3
Y09	645.1240	6.58	Y-Hex2HexA3HexNAc3Pen1S3-Ser	0.8	645.1245	3
Y10	703.8016	0.78	Y-Hex2HexA4HexNAc3Pen1S3-Ser	0.4	703.8019	3
Y11	598.3580	0.27	Y-Hex2HexA4HexNAc4Pen1S4-Ser	1.0	598.3586	4
Y13	693.1362	4.05	Y-Hex2HexA5HexNAc5Pen1S4-Ser	0.4	693.1365	4
Y14	737.1436	0.41	Y-Hex2HexA6HexNAc5Pen1S4-Ser	1.2	737.1445	4

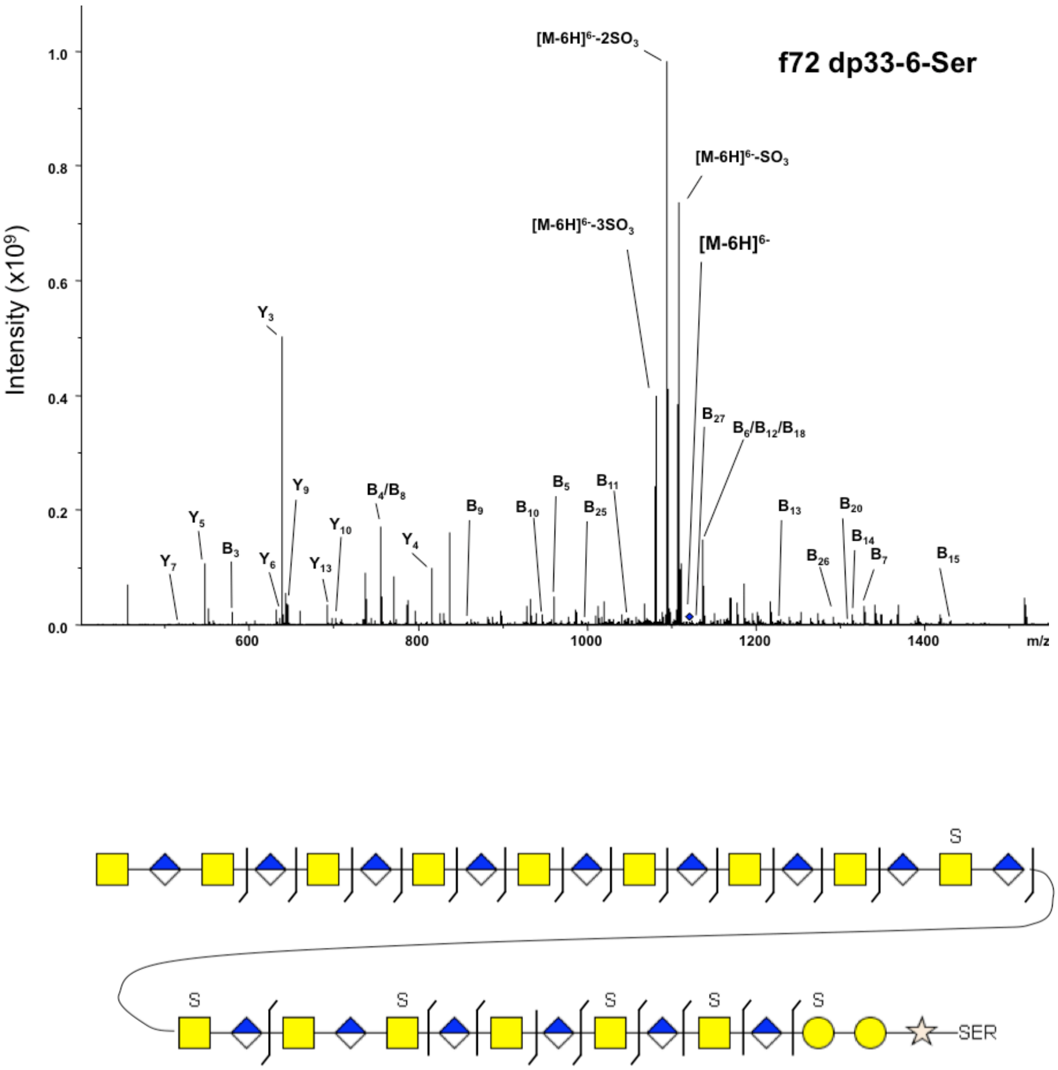
Supplementary Table 24. Assignment of fragment ions resulted from CID of parent ion *m/z* 1057.08 (*z* = 6) corresponding to composition dp31-6-Ser. CID mass spectra were acquired on the Bruker FT-ICR mass spectrometer.



Supplementary Figure 23. Annotated spectra from CID-FT-ICR MS/MS in negative ion mode of UTI bikunin pG parent ion *m/z* 1106.93 ($z = 6$) and its fragmentation pattern providing sequence for composition dp33-5-Ser. Fragment ions assigned in Supplementary Table 25. All fragment ions were Y_n or B_n type.

Cleavage	***m/z***	**Relative Intensity**	**Ion**	**Accuracy (ppm)**	***m/z*theor**	***z***
B03	581.1832	3.43	HexA1HexNAc2-B	0.6	581.1836	1
B04	757.2146	23.50	HexA2HexNAc2-B	1.4	757.2156	1
B05	960.2943	4.69	HexA2HexNAc3-B	0.7	960.2950	1
B06	1136.3261	9.49	HexA3HexNAc3-B	0.9	1136.3271	1
B07	1339.4069	3.00	HexA3HexNAc4-B	-0.3	1339.4065	1
B08	757.2146	23.50	HexA4HexNAc4-B	1.4	757.2156	2
B08	1515.4389	1.73	HexA4HexNAc4-B	-0.2	1515.4386	1
B09	858.7549	1.21	HexA4HexNAc5-B	0.5	858.7553	2
B10	946.7713	2.93	HexA5HexNAc5-B	0.1	946.7714	2
B11	1048.3104	1.77	HexA5HexNAc6-B	0.6	1048.3111	2
B12	1136.3261	9.49	HexA6HexNAc6-B	0.9	1136.3271	2
B13	1237.8660	2.03	HexA6HexNAc7-B	0.6	1237.8668	2
B15	1427.4240	1.01	HexA7HexNAc8-B	-1.0	1427.4225	2
B16	1009.9564	0.38	HexA8HexNAc8-B	0.2	1009.9566	3
B16	1515.4389	1.73	HexA8HexNAc8-B	-0.2	1515.4386	2
B17	1616.9780	0.21	HexA8HexNAc9-B	0.2	1616.9783	2
B18	1136.3261	9.49	HexA9HexNAc9-B	0.9	1136.3271	3
B18	1704.9902	0.24	HexA9HexNAc9-B	2.4	1704.9943	2
B20	1289.3495	1.22	HexA10HexNAc10S1-B	0.3	1289.3499	3
B21	1357.0428	0.40	HexA10HexNAc11S1-B	0.1	1357.0430	3
B22	1061.5379	0.50	HexA11HexNAc11S1-B	0.5	1061.5384	4
B22	1415.7202	0.90	HexA11HexNAc11S1-B	0.1	1415.7204	3
B26	1271.0833	1.29	HexA13HexNAc13S2-B	0.1	1271.0834	4
B27	1073.2718	0.57	HexA13HexNAc14S3-B	0.6	1073.2725	5
B28	1108.4781	0.93	HexA14HexNAc14S3-B	0.7	1108.4789	5
Y03	640.1393	63.05	Y-Hex2Pen1S1-Ser	1.1	640.1400	1
Y04	816.1712	12.93	Y-Hex2HexA1Pen1S1-Ser	1.1	816.1721	1
Y05	549.1000	8.20	Y-Hex2HexA1HexNAc1Pen1S2-Ser	0.9	549.1005	2
Y07	518.7537	0.30	Y-Hex2HexA2HexNAc2Pen1S3-Ser	0.6	518.7540	3
Y09	645.1241	4.15	Y-Hex2HexA3HexNAc3Pen1S3-Ser	0.6	645.1245	3
Y10	703.8014	0.78	Y-Hex2HexA4HexNAc3Pen1S3-Ser	0.6	703.8019	3
Y11	598.3580	0.31	Y-Hex2HexA4HexNAc4Pen1S4-Ser	1.0	598.3586	4
Y13	693.1360	1.20	Y-Hex2HexA5HexNAc5Pen1S4-Ser	0.7	693.1365	4
Y14	737.1436	0.25	Y-Hex2HexA6HexNAc5Pen1S4-Ser	1.2	737.1445	4

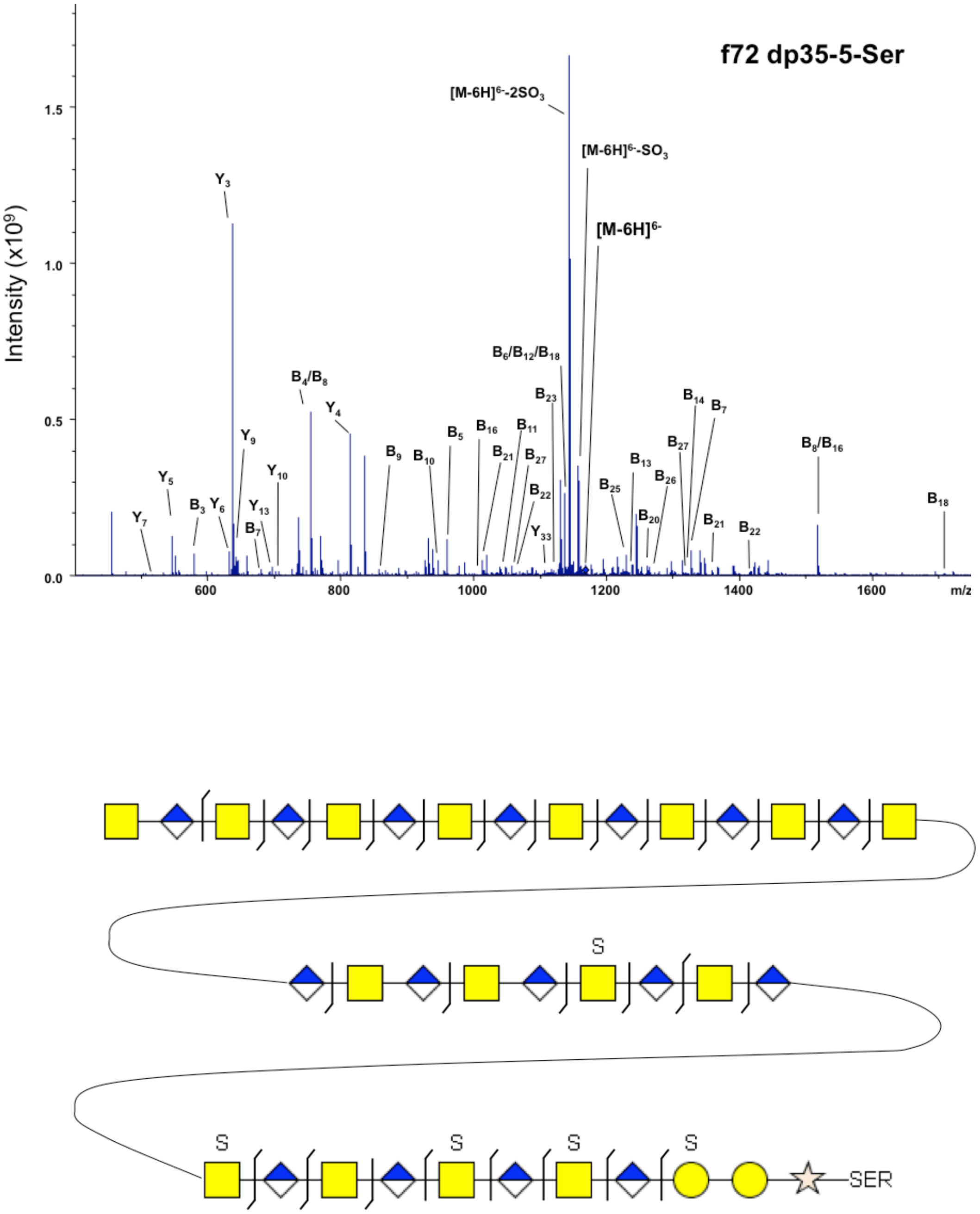
Supplementary Table 25. Assignment of fragment ions resulted from CID of parent ion *m/z* 1106.93 (*z* = 6) corresponding to composition dp33-5-Ser. CID mass spectra were acquired on the Bruker FT-ICR mass spectrometer.



Supplementary Figure 24. Annotated spectra from CID-FT-ICR MS/MS in negative ion mode of UTI bikunin pG parent ion *m/z* 1120.25 ($z = 6$) and its fragmentation pattern providing sequence for composition dp33-6-Ser. Fragment ions assigned in Supplementary Table 26. All fragment ions were Y_n or B_n type.

Cleavage	***m/z***	**Relative Intensity**	**Ion**	**Accuracy (ppm)**	***m/z*$_{\text{theor}}$**	***z***
B03	581.1832	2.29	HexA1HexNAc2-B	0.6	581.1836	1
B04	757.2151	17.42	HexA2HexNAc2-B	0.7	757.2156	1
B05	960.2944	4.88	HexA2HexNAc3-B	0.6	960.2950	1
B06	1136.3272	9.22	HexA3HexNAc3-B	-0.1	1136.3271	1
B07	1339.4077	3.44	HexA3HexNAc4-B	-0.9	1339.4065	1
B08	757.2151	17.42	HexA4HexNAc4-B	0.7	757.2156	2
B09	858.7547	0.52	HexA4HexNAc5-B	0.7	858.7553	2
B10	946.7709	1.66	HexA5HexNAc5-B	0.5	946.7714	2
B11	1048.3114	1.29	HexA5HexNAc6-B	-0.3	1048.3111	2
B12	1136.3272	9.22	HexA6HexNAc6-B	-0.1	1136.3271	2
B12	1136.3272	9.22	HexA9HexNAc9-B	-0.1	1136.3271	3
B13	1237.8669	1.41	HexA6HexNAc7-B	-0.1	1237.8668	2
B14	1325.8836	3.33	HexA7HexNAc7-B	-0.6	1325.8828	2
B15	1427.4239	0.78	HexA7HexNAc8-B	-1.0	1427.4225	2
B18	1162.9790	0.94	HexA9HexNAc9S1-B	0.3	1162.9794	3
B20	1316.0028	0.40	HexA10HexNAc10S2-B	-0.5	1316.0021	3
B25	997.4492	0.31	HexA12HexNAc13S3-B	1.0	997.4502	5
B26	1291.0732	0.39	HexA13HexNAc13S3-B	-0.5	1291.0726	4
B27	1124.4699	0.32	HexA14HexNAc14S4-B	0.3	1124.4703	5
Y03	640.1393	50.93	Y-Hex2Pen1S1-Ser	1.1	640.1400	1
Y04	816.1713	9.74	Y-Hex2HexA1Pen1S1-Ser	1.0	816.1721	1
Y05	549.1000	10.23	Y-Hex2HexA1HexNAc1Pen1S2-Ser	0.9	549.1005	2
Y06	637.1160	1.14	Y-Hex2HexA2HexNAc1Pen1S2-Ser	0.9	637.1165	2
Y07	518.7535	0.31	Y-Hex2HexA2HexNAc2Pen1S3-Ser	1.0	518.7540	3
Y09	645.1239	4.57	Y-Hex2HexA3HexNAc3Pen1S3-Ser	0.9	645.1245	3
Y10	703.8013	1.07	Y-Hex2HexA4HexNAc3Pen1S3-Ser	0.8	703.8019	3
Y13	693.1361	3.49	Y-Hex2HexA5HexNAc5Pen1S4-Ser	0.6	693.1365	4

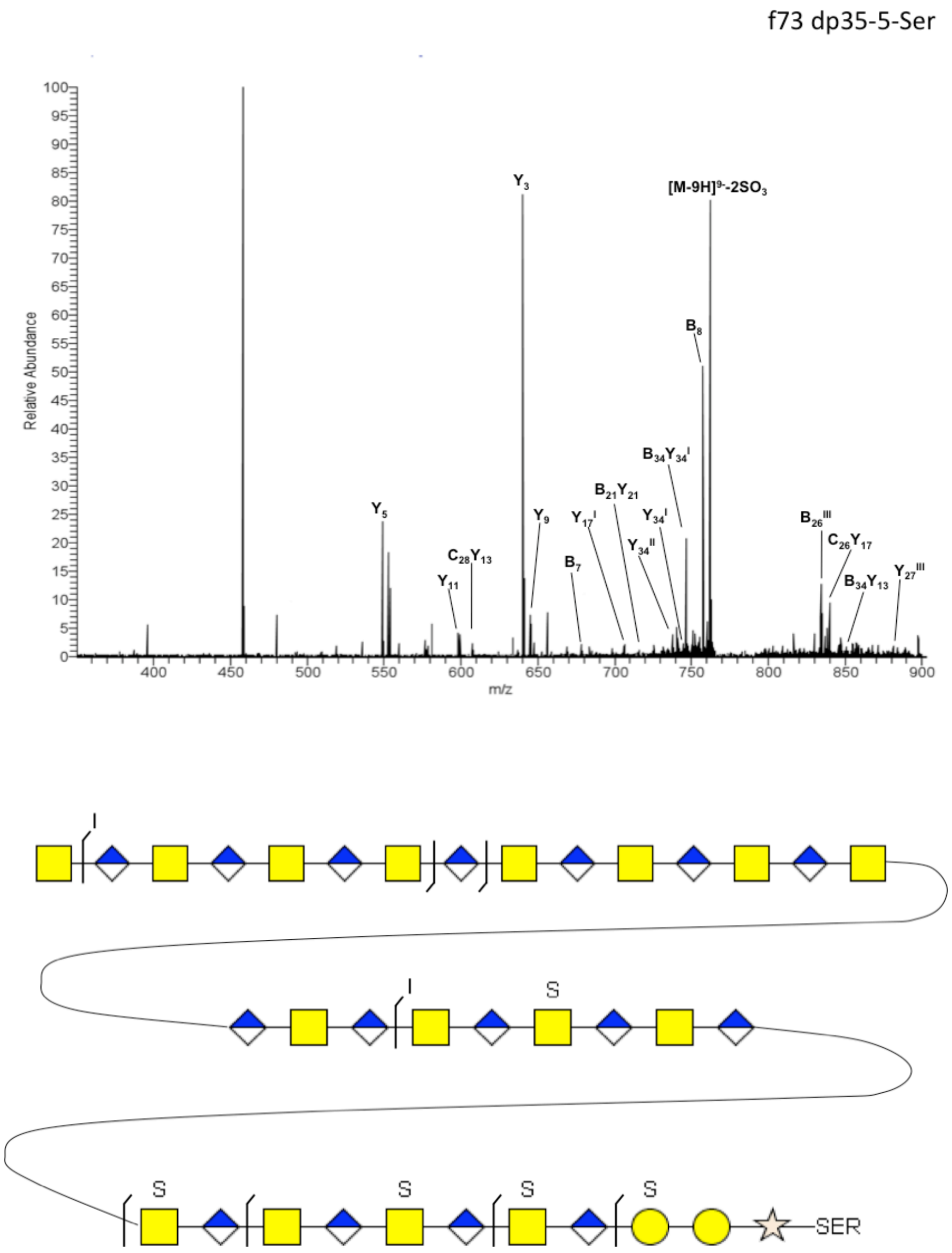
Supplementary Table 26. Assignment of fragment ions resulted from CID of parent ion *m/z* 1120.25 (*z* = 6) corresponding to composition dp33-6-Ser. CID mass spectra were acquired on the Bruker FT-ICR mass spectrometer.



Supplementary Figure 25. Annotated spectra from CID-FT-ICR MS/MS in negative ion mode of UTI bikunin pG parent ion *m/z* 1170.12 (z = 6) and its fragmentation pattern providing sequence for composition dp35-5-Ser. Fragment ions assigned in Supplementary Table 27. All fragment ions were Y_n or B_n type.

Cleavage	***m/z***	**Relative Intensity**	**Ion**	**Accuracy (ppm)**	m/z_{theor}	*z*
B03	581.1832	4.36	HexA1HexNAc2-B	0.6	581.1836	1
B04	757.2145	32.10	HexA2HexNAc2-B	1.5	757.2156	1
B05	960.2944	7.11	HexA2HexNAc3-B	0.6	960.2950	1
B06	1136.3258	10.11	HexA3HexNAc3-B	1.1	1136.3271	1
B07	669.1993	0.16	HexA3HexNAc4-B	0.4	669.1996	2
B07	1339.4072	4.62	HexA3HexNAc4-B	-0.5	1339.4065	1
B08	757.2145	32.10	HexA4HexNAc4-B	1.5	757.2156	2
B08	1515.4399	2.80	HexA4HexNAc4-B	-0.9	1515.4386	1
B09	858.7546	0.63	HexA4HexNAc5-B	0.9	858.7553	2
B10	946.7716	2.59	HexA5HexNAc5-B	-0.2	946.7714	2
B11	1048.3106	1.66	HexA5HexNAc6-B	0.4	1048.3111	2
B12	1136.3258	10.11	HexA6HexNAc6-B	1.1	1136.3271	2
B13	1237.8665	2.35	HexA6HexNAc7-B	0.2	1237.8668	2
B14	1325.8821	1.16	HexA7HexNAc7-B	0.6	1325.8828	2
B16	1009.9570	0.22	HexA8HexNAc8-B	-0.4	1009.9566	3
B16	1515.4399	2.80	HexA8HexNAc8-B	-0.9	1515.4386	2
B18	1136.3258	10.11	HexA9HexNAc9-B	1.1	1136.3271	3
B18	1704.9968	0.42	HexA9HexNAc9-B	-1.5	1704.9943	2
B20	1262.6986	1.65	HexA10HexNAc10-B	-0.8	1262.6976	3
B21	1017.5302	0.44	HexA10HexNAc11S1-B	0.2	1017.5304	4
B21	1357.0444	0.87	HexA10HexNAc11S1-B	-1.0	1357.0430	3
B22	1061.5384	0.45	HexA11HexNAc11S1-B	0.0	1061.5384	4
B22	1415.7211	0.78	HexA11HexNAc11S1-B	-0.5	1415.7204	3
B23	1112.3080	0.73	HexA11HexNAc12S1-B	0.3	1112.3083	4
B25	1227.0772	0.40	HexA12HexNAc13S2-B	-1.5	1227.0754	4
B26	1271.0837	0.62	HexA13HexNAc13S2-B	-0.3	1271.0834	4
B27	1057.2818	0.40	HexA13HexNAc14S2-B	-0.6	1057.2811	5
B27	1321.8537	0.36	HexA13HexNAc14S2-B	-0.4	1321.8532	4
Y03	640.1393	69.46	Y-Hex2Pen1S1-Ser	1.1	640.1400	1
Y04	816.1712	27.15	Y-Hex2HexA1Pen1S1-Ser	1.1	816.1721	1
Y05	549.1001	7.21	Y-Hex2HexA1HexNAc1Pen1S2-Ser	0.7	549.1005	2
Y06	637.1163	1.17	Y-Hex2HexA2HexNAc1Pen1S2-Ser	0.4	637.1165	2
Y07	518.7535	0.17	Y-Hex2HexA2HexNAc2Pen1S3-Ser	1.0	518.7540	3
Y09	645.1243	3.19	Y-Hex2HexA3HexNAc3Pen1S3-Ser	0.3	645.1245	3
Y10	703.8018	0.77	Y-Hex2HexA4HexNAc3Pen1S3-Ser	0.1	703.8019	3
Y13	693.1359	0.54	Y-Hex2HexA5HexNAc5Pen1S4-Ser	0.8	693.1365	4
Y33	1106.9333	0.64	Y-Hex2HexA15HexNAc15Pen1S5-Ser	0.5	1106.9338	6

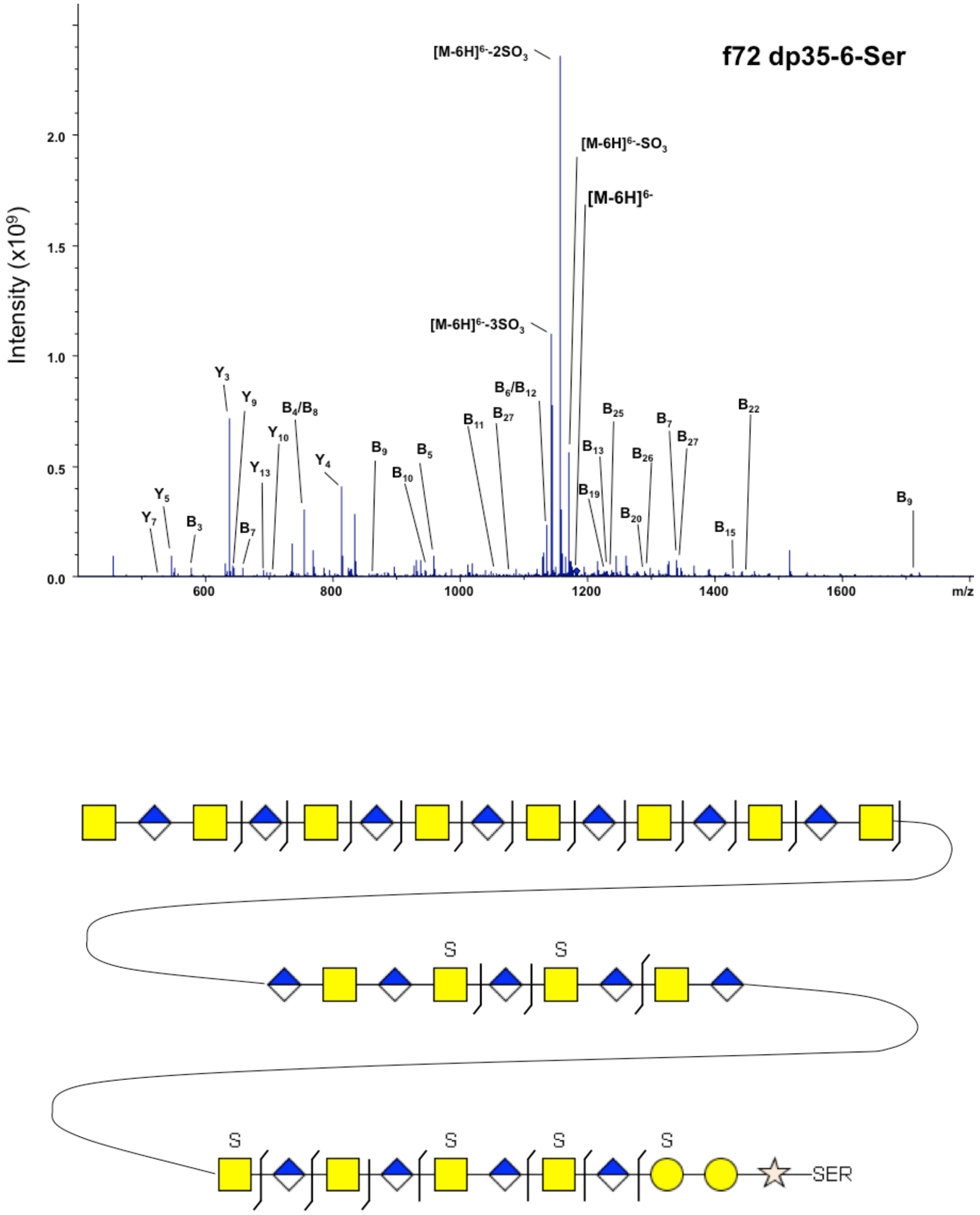
Supplementary Table 27. Assignment of fragment ions resulted from CID of parent ion *m/z* 1170.12 (*z* = 6) corresponding to composition dp35-5-Ser. CID mass spectra were acquired on the Bruker FT-ICR mass spectrometer.



Supplementary Figure 26. Annotated spectra from CID-FTMS/MS in negative ion mode of UTI bikunin pG parent ion *m/z* 779.74 ($z = 9$) and its fragmentation pattern providing sequence for composition dp35-5-Ser. Fragment ions assigned in Supplementary Table 28. Observed fragment ions include C_n, Z_n, Y_n or B_n type.

Cleavage	***m/z***	**Relative Intensity**	**Ion**	**Accuracy (ppm)**	$\mathbf{M_{exp}}$	$\mathbf{M_{theor}}$
CY	458.0610	100	HexA1HexNAc1S1-C	1.2	459.0688	459.0683
C28Y13	607.6384	2.3	HexA3HexNAc3S1	1.0	1217.2925	1217.2912
B21Y21	718.1791	0.78	HexA3HexNAc5S1	-5.1	1438.3739	1438.3811
C26Y17	837.1722	3.61	HexA4HexNAc4S2	0.3	1676.3601	1676.3595
B34Y13	851.4906	1.06	Hex2HexA5HexNAc5S4	-2.2	2557.4953	2557.5008
B34Y34^{I}	746.5166	17.13	Hex2HexA16HexNAc15S4	-1.0	6727.7198	6727.7268
B7	678.2046	2.15	HexA3HexNAc4-B	0.0	1358.4249	1358.4249
B8	757.2155	52.89	HexA4HexNAc4-B	0.5	1516.4467	1516.4458
B26^{III}	833.7269	2.09	HexA13HexNAc13S1-C	0.5	5008.4084	5008.4058
Y3	640.1400	83.12	Y-Hex2Pen1S1-Ser	0.8	641.1478	641.1473
Y5	549.1005	24.47	Y-Hex2HexA1HexNAc1Pen1S2-Ser	0.0	1100.2167	1100.2167
Y9	645.1241	7.43	Y-Hex2HexA3HexNAc3Pen1S3-Ser	0.2	1938.3958	1938.3953
Y11^{I}	578.3692	1.54	Y-Hex2HexA4HexNAc4Pen1S3-Ser	0.6	2317.5081	2317.5068
Y11	598.3583	4.34	Y-Hex2HexA4HexNAc4Pen1S4-Ser	0.4	2397.4645	2397.4636
Y17^{I}	705.9550	1.01	Y-Hex2HexA7HexNAc7Pen1S4-Ser	4.6	3534.8141	3534.7980
Y27^{III}	881.0646	0.68	Y-Hex2HexA12HexNAc12Pen1S2-Ser	-2.2	5292.4346	5292.4460
Y34^{II}	737.4091	1.38	Y-Hex2HexA16HexNAc15Pen1S3-Ser	-0.3	6645.7523	6645.7543
Y34^{I}	746.2939	1.54	Y-Hex2HexA16HexNAc15Pen1S4-Ser	0.6	6725.7155	6725.7112
Y35^{II}	761.9752	17.55	Y-Hex2HexA16HexNAc16Pen1S3-Ser	-1.4	6866.8472	6866.8570

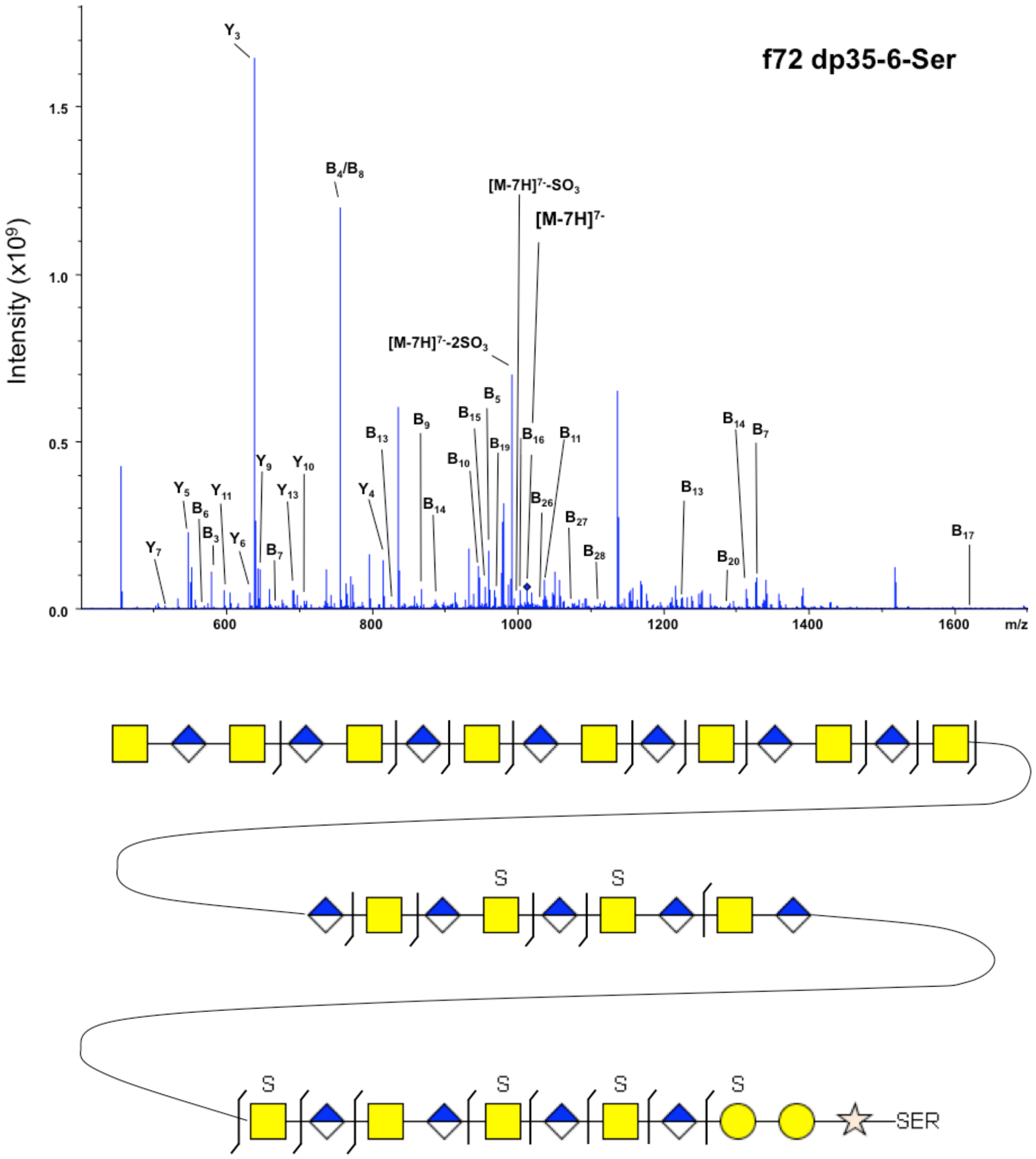
Supplementary Table 28. Assignment of fragment ions resulted from CID of parent ion *m/z* 779.74 (z = 9) corresponding to composition dp35-5-Ser. CID mass spectra were acquired on the orbitrap FT mass spectrometer.



Supplementary Figure 27. Annotated spectra from CID-FT-ICR MS/MS in negative ion mode of UTI bikunin pG parent ion *m/z* 1183.45 (z = 6) and its fragmentation pattern providing sequence for dp35-6-Ser. Fragment ions assigned in Supplementary Table 29. All fragment ions were Y_n or B_n type.

Cleavage	***m/z***	**Relative Intensity**	**Ion**	**Accuracy (ppm)**	***m/z*$_{theor}$**	***z***
B03	581.1833	1.59	HexA1HexNAc2-B	0.4	581.1836	1
B04	757.2149	12.43	HexA2HexNAc2-B	1.0	757.2156	1
B05	960.2943	3.92	HexA2HexNAc3-B	0.7	960.2950	1
B06	1136.3272	5.81	HexA3HexNAc3-B	-0.1	1136.3271	1
B07	669.1991	0.09	HexA3HexNAc4-B	0.7	669.1996	2
B07	1339.4077	2.86	HexA3HexNAc4-B	-0.9	1339.4065	1
B08	757.2149	12.43	HexA4HexNAc4-B	1.0	757.2156	2
B09	858.7551	0.42	HexA4HexNAc5-B	0.3	858.7553	2
B09	1718.5196	0.64	HexA4HexNAc5-B	-1.0	1718.5179	1
B10	946.7709	1.08	HexA5HexNAc5-B	0.5	946.7714	2
B11	1048.3118	1.07	HexA5HexNAc6-B	-0.7	1048.3111	2
B12	1136.3272	5.81	HexA6HexNAc6-B	-0.1	1136.3271	2
B13	1237.8658	1.35	HexA6HexNAc7-B	0.8	1237.8668	2
B15	1427.4243	0.96	HexA7HexNAc8-B	-1.2	1427.4225	2
B19	1230.6742	1.03	HexA9HexNAc10S1-B	-1.4	1230.6725	3
B20	1289.3494	0.91	HexA10HexNAc10S1-B	0.4	1289.3499	3
B22	1442.3734	0.18	HexA11HexNAc11S2-B	-0.5	1442.3726	3
B25	1247.0653	0.14	HexA12HexNAc13S3-B	-0.6	1247.0646	4
B26	1291.0730	0.14	HexA13HexNAc13S3-B	-0.3	1291.0726	4
B27	1073.2719	0.19	HexA13HexNAc14S3-B	0.5	1073.2725	5
B27	1341.8430	0.20	HexA13HexNAc14S3-B	-0.4	1341.8424	4
Y03	640.1394	29.90	Y-Hex2Pen1S1-Ser	1.0	640.1400	1
Y04	816.1710	16.30	Y-Hex2HexA1Pen1S1-Ser	1.3	816.1721	1
Y05	549.1003	3.63	Y-Hex2HexA1HexNAc1Pen1S2-Ser	0.4	549.1005	2
Y07	518.7538	0.08	Y-Hex2HexA2HexNAc2Pen1S3-Ser	0.4	518.7540	3
Y09	645.1241	1.68	Y-Hex2HexA3HexNAc3Pen1S3-Ser	0.6	645.1245	3
Y10	703.8015	0.70	Y-Hex2HexA4HexNAc3Pen1S3-Ser	0.5	703.8019	3
Y13	693.1363	1.24	Y-Hex2HexA5HexNAc5Pen1S4-Ser	0.3	693.1365	4

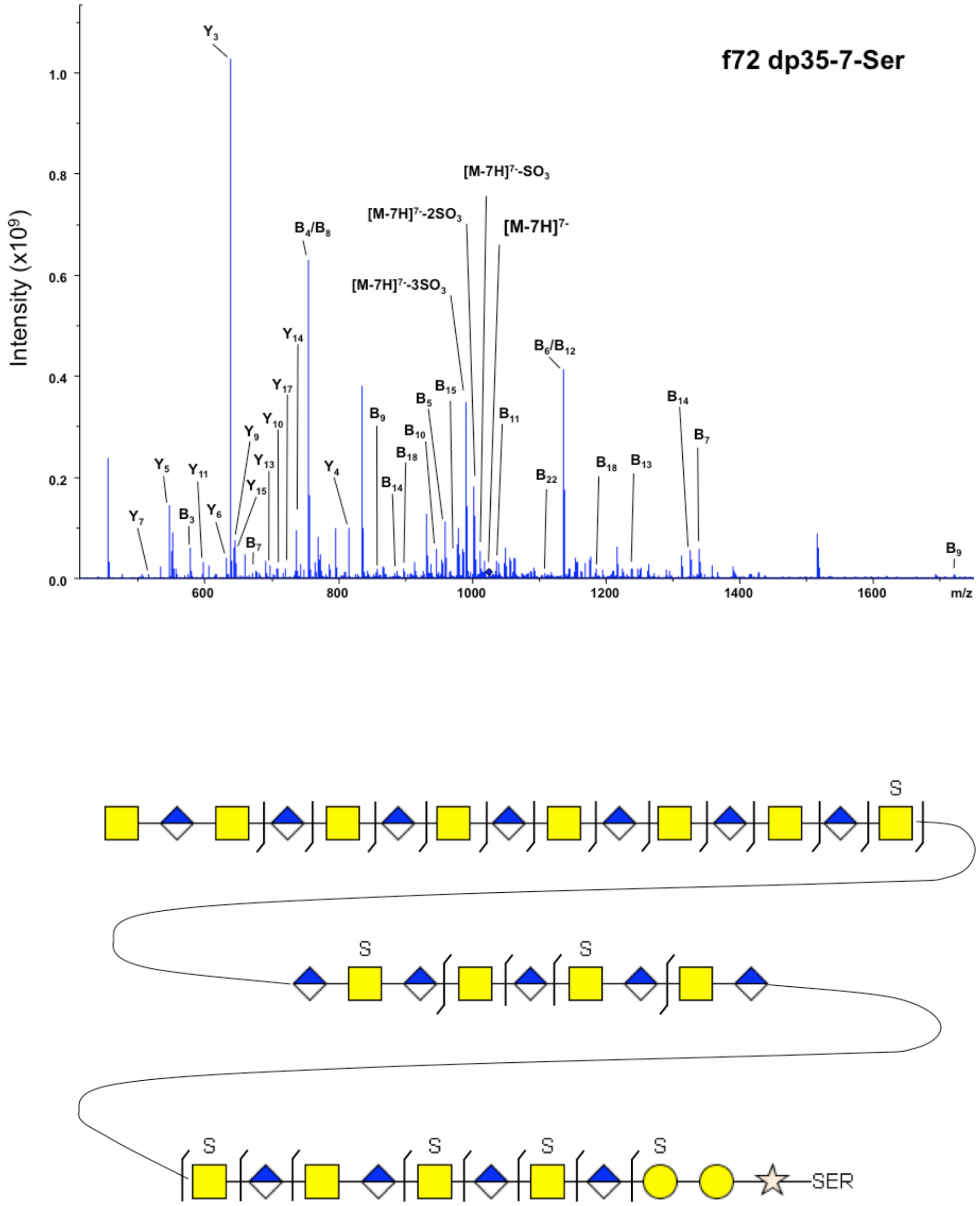
Supplementary Table 29. Assignment of fragment ions resulted from CID of parent ion *m/z* 1183.45 (*z* = 6) corresponding to composition dp35-6-Ser. CID mass spectra were acquired on the Bruker FT-ICR mass spectrometer.



Supplementary Figure 28. Annotated spectra from CID-FT-ICR MS/MS in negative ion mode of UTI bikunin pG parent ion *m/z* 1014.23 (z = 7) and its fragmentation pattern providing sequence for composition dp35-6-Ser. Fragment ions assigned in Supplementary Table 30. All fragment ions were Y_n or B_n type.

Cleavage	***m/z***	**Relative Intensity**	**Ion**	**Accuracy (ppm)**	***m/z*$_{theor}$**	***z***
B03	581.1831	6.94	HexA1HexNAc2-B	0.8	581.1836	1
B05	960.2945	10.13	HexA2HexNAc3-B	0.5	960.2950	1
B06	567.6595	0.16	HexA3HexNAc3-B	0.7	567.6599	2
B07	669.1990	0.57	HexA3HexNAc4-B	0.9	669.1996	2
B07	1339.4074	5.02	HexA3HexNAc4-B	-0.7	1339.4065	1
B09	858.7544	2.00	HexA4HexNAc5-B	1.1	858.7553	2
B10	946.7714	6.72	HexA5HexNAc5-B	0.0	946.7714	2
B11	1048.3103	2.75	HexA5HexNAc6-B	0.7	1048.3111	2
B13	824.9081	0.19	HexA6HexNAc7-B	0.8	824.9088	3
B13	1237.8664	2.47	HexA6HexNAc7-B	0.3	1237.8668	2
B14	883.5861	0.38	HexA7HexNAc7-B	0.0	883.5861	3
B14	1325.8819	1.59	HexA7HexNAc7-B	0.7	1325.8828	2
B15	951.2794	0.38	HexA7HexNAc8-B	-0.2	951.2793	3
B16	1009.9565	1.24	HexA8HexNAc8-B	0.1	1009.9566	3
B17	1616.9791	0.22	HexA8HexNAc9-B	-0.5	1616.9783	2
B19	966.7605	0.31	HexA10HexNAc10S1-B	0.1	966.7606	4
B20	1289.3506	1.09	HexA10HexNAc10S1-B	-0.6	1289.3499	3
B26	1032.6561	0.39	HexA13HexNAc13S3-B	0.5	1032.6566	5
B27	1073.2737	0.22	HexA13HexNAc14S3-B	-1.1	1073.2725	5
B28	1108.4785	0.44	HexA14HexNAc14S3-B	0.4	1108.4789	5
Y03	640.1392	100.00	Y-Hex2Pen1S1-Ser	1.3	640.1400	1
Y04	816.1714	8.73	Y-Hex2HexA1Pen1S1-Ser	0.9	816.1721	1
Y05	549.1000	12.91	Y-Hex2HexA1HexNAc1Pen1S2-Ser	0.9	549.1005	2
Y06	637.1163	0.54	Y-Hex2HexA2HexNAc1Pen1S2-Ser	0.4	637.1165	2
Y07	518.7534	0.44	Y-Hex2HexA2HexNAc2Pen1S3-Ser	1.2	518.7540	3
Y09	645.1243	5.98	Y-Hex2HexA3HexNAc3Pen1S3-Ser	0.3	645.1245	3
Y10	703.8016	0.63	Y-Hex2HexA4HexNAc3Pen1S3-Ser	0.4	703.8019	3
Y11	598.3581	0.59	Y-Hex2HexA4HexNAc4Pen1S4-Ser	0.9	598.3586	4
Y13	693.1361	3.34	Y-Hex2HexA5HexNAc5Pen1S4-Ser	0.6	693.1365	4

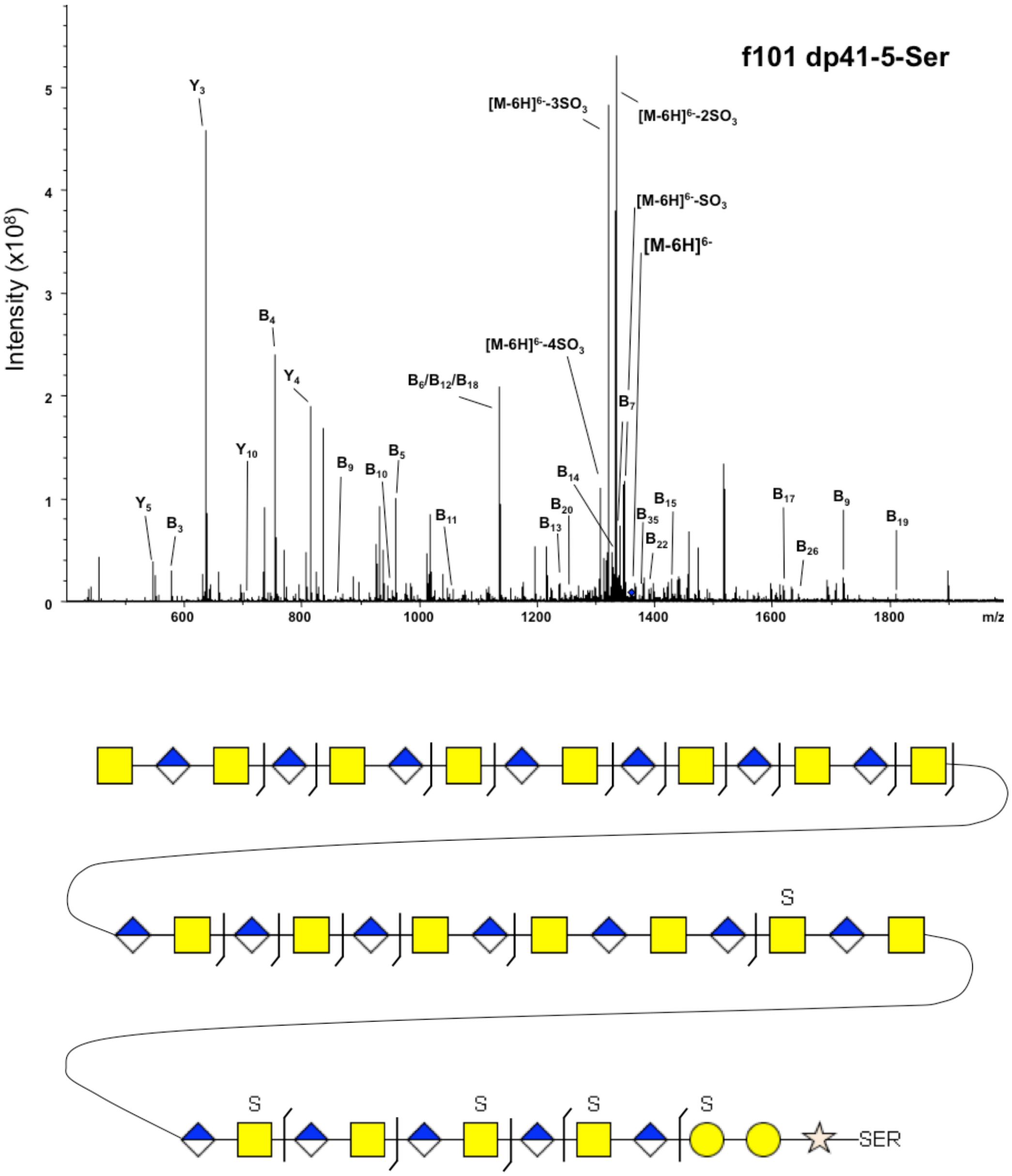
Supplementary Table 30. Assignment of fragment ions resulted from CID of parent ion *m/z* 1014.23 (*z* = 7) corresponding to composition dp35-6-Ser. CID mass spectra were acquired on the Bruker FT-ICR mass spectrometer.



Supplementary Figure 29. Annotated spectra from CID-FT-ICR MS/MS in negative ion mode of UTI bikunin pG parent ion *m/z* 1025.66 (z = 7) and its fragmentation pattern providing sequence for composition dp35-7-Ser. Fragment ions assigned in Supplementary Table 31. All fragment ions were Y_n or B_n type.

Cleavage	***m/z***	**Relative Intensity**	**Ion**	**Accuracy (ppm)**	***m/z*theor**	***z***
B03	581.1831	5.95	HexA1HexNAc2-B	0.79	581.1836	1
B04	757.2148	60.75	HexA2HexNAc2-B	1.12	757.2156	1
B05	960.2941	10.75	HexA2HexNAc3-B	0.96	960.2950	1
B06	1136.3266	23.98	HexA3HexNAc3-B	0.44	1136.3271	1
B07	669.1990	0.50	HexA3HexNAc4-B	0.90	669.1996	2
B07	1339.4066	5.36	HexA3HexNAc4-B	-0.09	1339.4065	1
B08	757.2148	60.75	HexA4HexNAc4-B	1.12	757.2156	2
B09	858.7549	1.69	HexA4HexNAc5-B	0.50	858.7553	2
B09	1718.5184	0.77	HexA4HexNAc5-B	-0.27	1718.5179	1
B10	946.7709	5.19	HexA5HexNAc5-B	0.50	946.7714	2
B11	1048.3112	2.80	HexA5HexNAc6-B	-0.13	1048.3111	2
B12	1136.3266	23.98	HexA6HexNAc6-B	0.44	1136.3271	2
B13	1237.8659	2.13	HexA6HexNAc7-B	0.72	1237.8668	2
B14	883.5860	0.23	HexA7HexNAc7-B	0.15	883.5861	3
B14	1325.8829	5.55	HexA7HexNAc7-B	-0.05	1325.8828	2
B15	977.9314	0.35	HexA7HexNAc8S1-B	0.13	977.9315	3
B18	891.9713	0.28	HexA9HexNAc9S2-B	0.69	891.9719	4
B18	1189.6308	0.39	HexA9HexNAc9S2-B	0.71	1189.6316	3
B22	1101.5159	0.20	HexA11HexNAc11S3-B	0.86	1101.5169	4
Y03	640.1393	100.00	Y-Hex2Pen1S1-Ser	1.11	640.1400	1
Y04	816.1713	9.44	Y-Hex2HexA1Pen1S1-Ser	0.98	816.1721	1
Y05	549.1000	13.01	Y-Hex2HexA1HexNAc1Pen1S2-Ser	0.92	549.1005	2
Y06	637.1161	0.72	Y-Hex2HexA2HexNAc1Pen1S2-Ser	0.70	637.1165	2
Y07	518.7537	0.59	Y-Hex2HexA2HexNAc2Pen1S3-Ser	0.58	518.7540	3
Y09	645.1240	4.92	Y-Hex2HexA3HexNAc3Pen1S3-Ser	0.76	645.1245	3
Y10	703.8015	0.71	Y-Hex2HexA4HexNAc3Pen1S3-Ser	0.50	703.8019	3
Y11	598.3581	0.75	Y-Hex2HexA4HexNAc4Pen1S4-Ser	0.86	598.3586	4
Y13	693.1361	3.45	Y-Hex2HexA5HexNAc5Pen1S4-Ser	0.55	693.1365	4
Y14	737.1437	0.34	Y-Hex2HexA6HexNAc5Pen1S4-Ser	1.09	737.1445	4
Y15	646.1209	0.74	Y-Hex2HexA6HexNAc6Pen1S5-Ser	0.75	646.1214	5
Y17	721.9433	1.53	Y-Hex2HexA7HexNAc7Pen1S5-Ser	0.52	721.9437	5

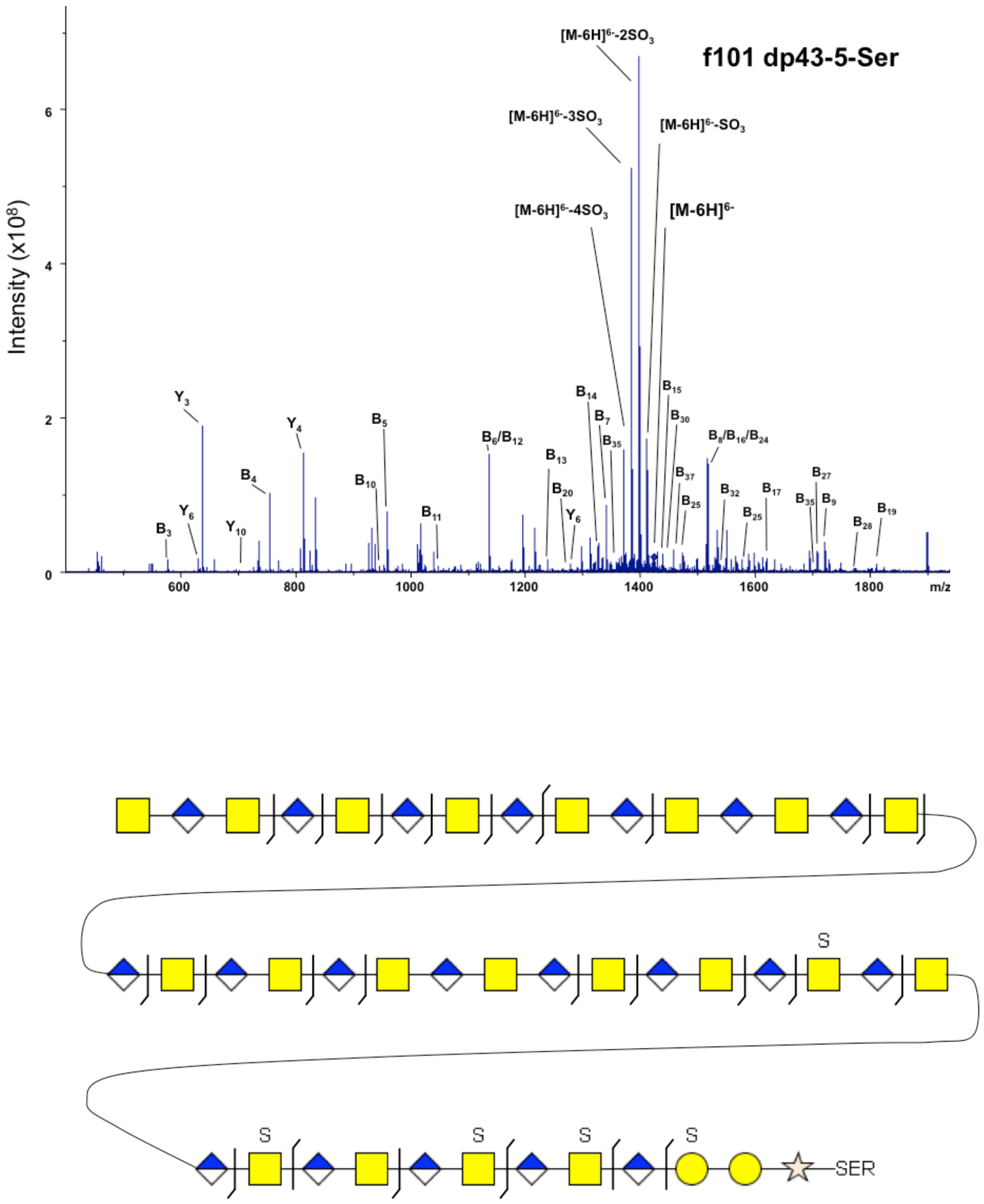
Supplementary Table 31. Assignment of fragment ions resulted from CID of parent ion *m/z* 1025.66 (*z* = 7) corresponding to composition dp35-7-Ser. CID mass spectra were acquired on the Bruker FT-ICR mass spectrometer.



Supplementary Figure 30. Annotated spectra from CID-FT-ICR MS/MS in negative ion mode of UTI bikunin pG parent ion *m/z* 1359.67 ($z = 6$) and its fragmentation pattern providing sequence for composition dp41-5-Ser. Fragment ions assigned in Supplementary Table 32. Partial sequence with 2 ambiguous sulfo groups. All fragment ions were Y_n or B_n type.

Cleavage	***m/z***	**Relative Intensity**	**Ion**	**Accuracy (ppm)**	***m/z*$_{\text{theor}}$**	***z***
B03	581.1833	5.65	HexA1HexNAc2-B	0.4	581.1836	1
B04	757.2150	44.60	HexA2HexNAc2-B	0.9	757.2156	1
B05	960.2941	18.86	HexA2HexNAc3-B	1.0	960.2950	1
B06	1136.3261	23.28	HexA3HexNAc3-B	0.9	1136.3271	1
B07	1339.4061	13.09	HexA3HexNAc4-B	0.3	1339.4065	1
B09	858.7542	0.39	HexA4HexNAc5-B	1.3	858.7553	2
B09	1718.5183	4.09	HexA4HexNAc5-B	-0.2	1718.5179	1
B10	946.7711	2.71	HexA5HexNAc5-B	0.3	946.7714	2
B11	1048.3106	2.28	HexA5HexNAc6-B	0.4	1048.3111	2
B12	1136.3261	23.28	HexA6HexNAc6-B	0.9	1136.3271	2
B13	1237.8665	3.52	HexA6HexNAc7-B	0.2	1237.8668	2
B14	1325.8820	9.08	HexA7HexNAc7-B	0.6	1325.8828	2
B15	1427.4233	4.47	HexA7HexNAc8-B	-0.5	1427.4225	2
B17	1616.9779	2.56	HexA8HexNAc9-B	0.2	1616.9783	2
B18	1136.3261	23.28	HexA9HexNAc9-B	0.9	1136.3271	3
B19	1806.5344	1.30	HexA9HexNAc10-B	-0.2	1806.5340	2
B20	1262.6968	0.94	HexA10HexNAc10-B	0.6	1262.6976	3
B22	1389.0673	1.36	HexA11HexNAc11-B	0.6	1389.0681	3
B26	1641.8108	1.32	HexA13HexNAc13-B	-1.1	1641.8091	3
B35	1376.5626	0.63	HexA17HexNAc18S3-B	-0.7	1376.5617	5
Y03	640.1394	86.13	Y-Hex2Pen1S1-Ser	1.0	640.1400	1
Y04	816.1712	34.61	Y-Hex2HexA1Pen1S1-Ser	1.1	816.1721	1
Y05	549.0999	6.59	Y-Hex2HexA1HexNAc1Pen1S2-Ser	1.1	549.1005	2
Y10	703.8014	1.10	Y-Hex2HexA4HexNAc3Pen1S3-Ser	0.6	703.8019	3

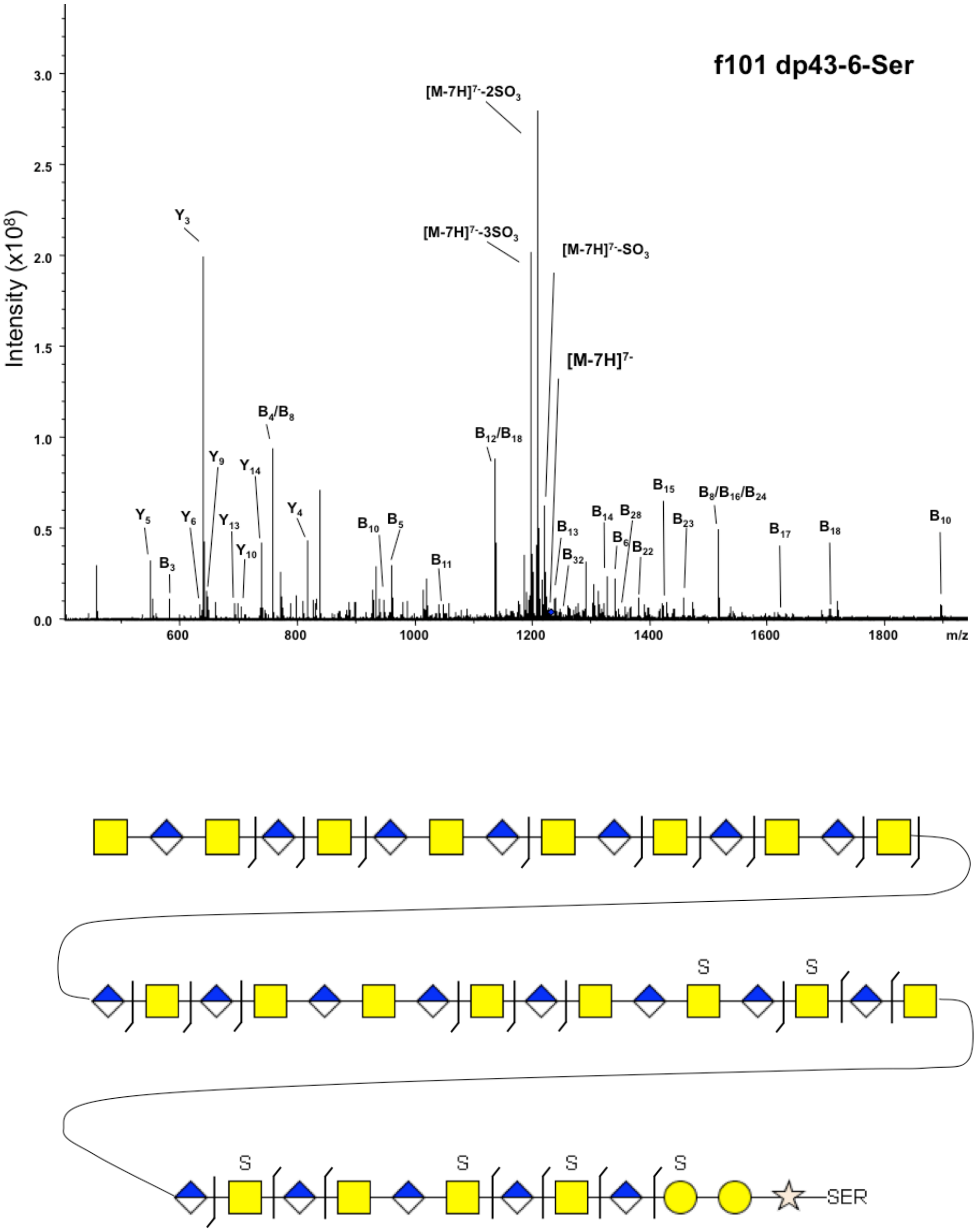
Supplementary Table 32. Assignment of fragment ions resulted from CID of parent ion *m/z* 1359.67 (*z* = 6) corresponding to composition dp41-5-Ser. CID mass spectra were acquired on the Bruker FT-ICR mass spectrometer.



Supplementary Figure 31. Annotated spectra from CID-FT-ICR MS/MS in negative ion mode of UTI bikunin pG parent ion *m/z m/z* 1422.69 (*z* = 6) and its fragmentation pattern providing sequence for composition dp43-5-Ser. Fragment ions assigned in Supplementary Table 33. All fragment ions were Y$_n$ or B$_n$ type.

Cleavage	***m/z***	**Relative Intensity**	**Ion**	**Accuracy (ppm)**	***m/z*theor**	***z***
B03	581.1833	2.62	HexA1HexNAc2-B	0.4	581.1836	1
B04	757.2151	15.81	HexA2HexNAc2-B	0.7	757.2156	3
B05	960.2945	12.07	HexA2HexNAc3-B	0.5	960.2950	6
B06	1136.3263	14.06	HexA3HexNAc3-B	0.7	1136.3271	6
B07	1339.4062	12.86	HexA3HexNAc4-B	-0.2	1339.4065	4
B08	1515.4380	14.23	HexA4HexNAc4-B	0.4	1515.4386	2
B09	1718.5178	5.58	HexA4HexNAc5-B	0.1	1718.5179	6
B10	946.7714	1.17	HexA5HexNAc5-B	0.0	946.7714	1
B11	1048.3102	1.14	HexA5HexNAc6-B	0.8	1048.3111	6
B12	1136.3263	14.06	HexA6HexNAc6-B	0.7	1136.3271	1
B13	1237.8661	2.72	HexA6HexNAc7-B	0.6	1237.8668	2
B14	1325.8820	6.26	HexA7HexNAc7-B	0.6	1325.8828	4
B15	1427.4211	4.00	HexA7HexNAc8-B	-1.0	1427.4225	5
B16	1515.4380	14.23	HexA8HexNAc8-B	0.4	1515.4386	3
B17	1616.9778	2.66	HexA8HexNAc9-B	-0.3	1616.9783	6
B19	1806.5324	1.55	HexA9HexNAc10-B	0.9	1806.5340	2
B20	1262.6976	0.52	HexA10HexNAc10-B	0.0	1262.6976	4
B24	1515.4380	14.23	HexA12HexNAc12-B	0.4	1515.4386	1
B25	1456.7608	0.93	HexA11HexNAc12-B	-0.3	1456.7612	2
B25	1583.1315	0.95	HexA12HexNAc13-B	-0.1	1583.1317	5
B27	1709.5016	0.41	HexA13HexNAc14-B	0.3	1709.5022	6
B28	1768.1788	0.90	HexA14HexNAc14-B	-0.4	1768.1795	4
B30	1440.6498	0.85	HexA15HexNAc15S1-B	0.1	1440.6499	2
B32	1535.4270	1.69	HexA16HexNAc16S1-B	-0.5	1535.4278	3
B35	1360.5692	1.50	HexA17HexNAc18S2-B	0.8	1360.5703	6
B35	1700.9638	0.76	HexA17HexNAc18S2-B	0.5	1700.9647	2
B37	1452.3829	1.24	HexA18HexNAc19S3-B	-0.7	1452.3839	6
Y03	640.1395	29.58	Y-Hex2Pen1S1-Ser	0.8	640.1400	1
Y04	816.1714	23.76	Y-Hex2HexA1Pen1S1-Ser	0.9	816.1721	1
Y06	637.1162	0.88	Y-Hex2HexA2HexNAc1Pen1S2-Ser	0.5	637.1165	2
Y06	1275.2392	0.60	Y-Hex2HexA2HexNAc1Pen1S2-Ser	0.9	1275.2404	1
Y10	703.8007	0.35	Y-Hex2HexA4HexNAc3Pen1S3-Ser	1.6	703.8019	3

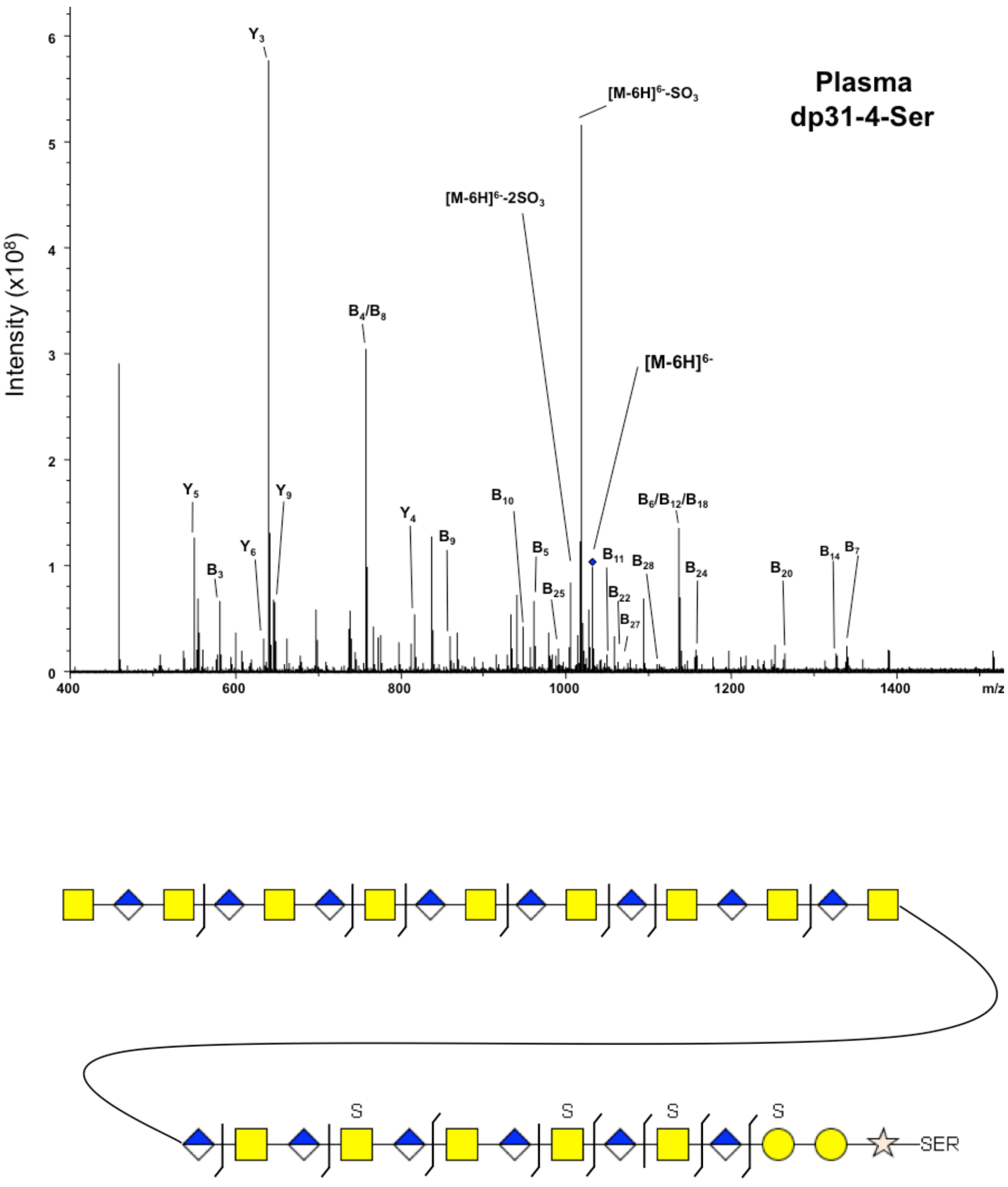
Supplementary Table 33. Assignment of fragment ions resulted from CID of parent ion *m/z* 1422.69 (*z* = 6) corresponding to composition dp43-5-Ser. CID mass spectra were acquired on the Bruker FT-ICR mass spectrometer.



Supplementary Figure 32. Annotated spectra from CID-FT-ICR MS/MS in negative ion mode of UTI bikunin pG parent ion *m/z* 1436.18 (*z* = 6) and its fragmentation pattern providing sequence for composition dp43-6-Ser. Fragment ions assigned in Supplementary Table 34. Partial sequence with 2 ambiguous sulfo groups. All fragment ions were Y_n or B_n type.

Cleavage	***m/z***	**Relative Intensity**	**Ion**	**Accuracy (ppm)**	m/z_{theor}	*z*
B03	581.1840	5.69	HexA1HexNAc2-B	0.8	581.1836	1
B04	757.2164	46.44	HexA2HexNAc2-B	1.0	757.2156	1
B05	960.2958	14.48	HexA2HexNAc3-B	0.9	960.2950	1
B06	1339.4075	10.48	HexA3HexNAc4-B	0.7	1339.4065	1
B08	757.2164	46.44	HexA4HexNAc4-B	1.0	757.2156	2
B08	1515.4373	5.66	HexA4HexNAc4-B	-0.8	1515.4386	1
B10	946.7716	4.56	HexA5HexNAc5-B	0.3	946.7714	2
B10	1894.5490	3.95	HexA5HexNAc5-B	-0.6	1894.5500	1
B11	1048.3113	3.47	HexA5HexNAc6-B	0.2	1048.3111	2
B12	1136.3274	27.26	HexA6HexNAc6-B	0.3	1136.3271	2
B13	1237.8669	6.10	HexA6HexNAc7-B	0.1	1237.8668	2
B14	1325.8828	12.41	HexA7HexNAc7-B	0.0	1325.8828	2
B15	1427.4217	4.49	HexA7HexNAc8-B	-0.5	1427.4225	2
B16	1515.4373	5.66	HexA8HexNAc8-B	-0.8	1515.4386	2
B17	1616.9790	2.00	HexA8HexNAc9-B	0.5	1616.9783	2
B18	1136.3274	27.26	HexA9HexNAc9-B	0.3	1136.3271	3
B18	1704.9916	2.81	HexA18HexNAc18-B	-1.6	1704.9943	4
B22	1389.0679	4.00	HexA11HexNAc11-B	-0.2	1389.0681	3
B23	1456.7617	1.45	HexA11HexNAc12-B	0.3	1456.7612	3
B24	1515.4373	5.66	HexA12HexNAc12-B	-0.8	1515.4386	3
B28	1345.8724	1.91	HexA14HexNAc14S1-B	0.3	1345.8720	4
B32	1244.1326	1.57	HexA16HexNAc16S2-B	0.4	1244.1321	5
Y03	640.1405	98.54	Y-Hex2Pen1S1-Ser	0.8	640.1400	1
Y04	816.1727	21.11	Y-Hex2HexA1Pen1S1-Ser	0.7	816.1721	1
Y05	549.1011	14.42	Y-Hex2HexA1HexNAc1Pen1S2-Ser	1.1	549.1005	2
Y06	637.1170	2.17	Y-Hex2HexA2HexNAc1Pen1S2-Ser	0.7	637.1165	2
Y09	645.1250	6.03	Y-Hex2HexA3HexNAc3Pen1S3-Ser	0.8	645.1245	3
Y10	703.8026	2.50	Y-Hex2HexA4HexNAc3Pen1S3-Ser	1.1	703.8019	3
Y13	693.1368	4.21	Y-Hex2HexA5HexNAc5Pen1S4-Ser	0.4	693.1365	4
Y14	737.1451	1.11	Y-Hex2HexA6HexNAc5Pen1S4-Ser	0.8	737.1445	4

Supplementary Table 34. Assignment of fragment ions resulted from CID of parent ion *m/z* 1436.18 (*z* = 6) corresponding to composition dp43-6-Ser. CID mass spectra were acquired on the Bruker FT-ICR mass spectrometer.



Supplementary Figure 33. Annotated spectra from CID-FT-ICR MS/MS in negative ion mode of pooled human plasma bikunin pG parent ion *m/z* 1030.43 (z = 6) and its fragmentation pattern providing sequence for composition dp31-4-Ser. Fragment ions assigned in Supplementary Table 35. All fragment ions were Y_n or B_n type.

Cleavage	***m/z***	**Relative Intensity**	**Ion**	**Accuracy (ppm)**	$m/z_{\textbf{theor}}$	*z*
B03	581.1831	11.89	HexA1HexNAc2-B	0.8	581.1836	1
B04	757.2150	53.01	HexA2HexNAc2-B	0.9	757.2156	1
B05	960.2945	11.21	HexA2HexNAc3-B	0.5	960.2950	1
B06	1136.3261	15.31	HexA3HexNAc3-B	0.9	1136.3271	1
B07	1339.4055	4.01	HexA3HexNAc4-B	0.7	1339.4065	1
B08	757.2150	53.01	HexA4HexNAc4-B	0.9	757.2156	2
B09	858.7550	5.57	HexA4HexNAc5-B	0.4	858.7553	2
B10	946.7709	6.54	HexA10HexNAc10-B	0.5	946.7714	4
B11	1048.3106	3.00	HexA5HexNAc6-B	0.4	1048.3111	2
B12	1136.3261	15.31	HexA6HexNAc6-B	0.9	1136.3271	2
B14	1325.8812	3.00	HexA7HexNAc7-B	1.2	1325.8828	2
B18	1136.3261	15.31	HexA9HexNAc9-B	0.9	1136.3271	3
B20	1262.6965	2.89	HexA10HexNAc10-B	0.9	1262.6976	3
B22	1061.5369	1.66	HexA11HexNAc11S1-B	1.5	1061.5384	4
B24	1156.3151	3.27	HexA12HexNAc12S1-B	1.0	1156.3163	4
B25	981.4580	2.87	HexA12HexNAc13S2-B	0.8	981.4588	5
B27	1073.2708	1.14	HexA13HexNAc14S3-B	1.6	1073.2725	5
B28	1108.4772	1.29	HexA14HexNAc14S3-B	1.5	1108.4789	5
Y03	640.1395	100.00	Y-Hex2Pen1S1-Ser	0.8	640.1400	1
Y04	816.1710	9.03	Y-Hex2HexA1Pen1S1-Ser	1.3	816.1721	1
Y05	549.1001	20.27	Y-Hex2HexA1HexNAc1Pen1S2-Ser	0.7	549.1005	2
Y06	637.1160	1.37	Y-Hex2HexA2HexNAc1Pen1S2-Ser	0.9	637.1165	2
Y09	645.1244	10.26	Y-Hex2HexA3HexNAc3Pen1S3-Ser	0.1	645.1245	3

Supplementary Table 35. Assignment of fragment ions resulted from CID of parent ion *m/z* 1030.43 (*z* = 6) corresponding to composition dp31-4-Ser of human plasma bikunin pG. CID mass spectra were acquired on the Bruker FT-ICR mass spectrometer.

dp#[a]	**Disaccharides**[b]	**Sequences possible based on:**					
		Odd and even dp[c]	**Odd or even dp**[d]	**4-9 sulfation sites**[e]	**Two less sulfation sites**[f]	**Four less sulfation sites**[g]	**MS sequencing**[h]
20	10	3.E+03	1.E+03	8.E+02	5E+02		
21			2.E+03	2.E+03	5E+02	99	
22	11	6.E+03	2.E+03	2.E+03	1E+03		
23			4.E+03	4.E+03	1E+03	120	4
24	12	1.E+04	4.E+03	4.E+03	1E+03		4
25			8.E+03	7.E+03	2E+03	219	4
26	13	2.E+04	8.E+03	7E+03	2E+03		4
27			1.E+04	1E+04	4E+03	465	4
28	14	5.E+04	2.E+04	1E+04	4E+03		4
29			3.E+04	3E+04	7E+03	957	4
30	15	1.E+05	3.E+04	3E+04	7E+03		4
31			7.E+04	5.E+04	1E+04	1914	4
32	16	2.E+05	7.E+04	5.E+04	1E+04		4
33			1.E+05	9.E+04	2E+04	3718	4
34	17	4.E+05	1.E+05	9.E+04	2E+04		4
35			3.E+05	2.E+05	4E+04	7007	4
36	18	8.E+05	3.E+05	2.E+05	4E+04		4
37			5.E+05	3.E+05	7E+04	12805	4
38	19	2.E+06	5.E+05	3.E+05	7E+04		4
39			1.E+06	4.E+05	1E+05	22698	4
40	20	3.E+06	1.E+06	4.E+05	1.E+05		4
41			2.E+06	7.E+05	2.E+05	39066	4
42	21	6.E+06	2.E+06	7.E+05	2.E+05		4
43			4.E+06	1.E+06	3.E+05	65382	4
44	22	1.E+07	4.E+06	1.E+06	3.E+05		4
45			8.E+06	2.E+06	4.E+05	106590	4
46	23	3.E+07	8.E+06	2.E+06	4.E+05		4
47			2.E+07	3.E+06	6.E+05	169575	4
48	24	5.E+07	2.E+07	3.E+06	6.E+05		4
49			3.E+07	4.E+06	9.E+05	263739	4

50	25	1.E+08	3.E+07	4.E+06	9.E+05		4
51			7.E+07	6.E+06	1.E+06	401698	4
52	26	2.E+08	7.E+07	6.E+06	1.E+06		4
53			1.E+08	8.E+06	2.E+06	600116	4
54	27	4.E+08	1.E+08	8.E+06	2.E+06		4
55			3.E+08	1.E+07	3.E+06	880693	4
56	28	8.E+08	3.E+08	1.E+07	3.E+06		4
57			5.E+08	2.E+07	4.E+06	1271325	4
58	29	2.E+09	5.E+08	2.E+07	4.E+06		4
59			1.E+09	2.E+07	5.E+06	1807455	4
60	30	3.E+09	1.E+09	2.E+07	5.E+06		4
61			2.E+09	3.E+07	6.E+06	2533635	
NUMBER OF SEQUENCES		~210 billion		~910 million	~570 million	~43 million	**~150**

Supplementary Table 36. Decreasing number of bikunin GAG chain sequences with increasing experimentally determined constraints. Summed at the bottom are the total numbers of sequences for each column of constraints.

Footnotes correspond to the following:

a Degree of polymerization number (dp #), or number of monosaccharides, is shown since there are both odd numbered and even numbered GAGs.

b Number of disaccharides ranging from 10 to 30 repeating units, as estimated by PAGE and confirmed by FTMS and FT-ICR MS.

c Number of possible sequences with repetitions allowed for both odd and even numbered chains estimated as comprising of either GalNAc4S-GlcA or GalNAc-GlcA calculated as $n^r + n^{r+1}$, where n is the types of disaccharides possible and r is the number of times either repeating unit might be chosen to determine chain length.

d Number of possible sequences allowing either odd, n^{r+1}, or even, n^r, numbered chains.

e Number of possible sequences limiting the number of sulfates to 4-9 for each size GAG using $\Sigma_n C_r$, where n is the number of sulfation sites and r is the number of sulfates.

f Number of possible sequences with two less sulfation sites from the RE to the Gal4S for each sized GAG with one less numbers of sulfates (3-8) than *e* using $\Sigma_n C_r$, where n is the number of sulfation sites and r is the number of sulfates.

g Number of possible sequences with four less sulfation sites to include the trisaccharide NRE for each sized GAG than *f* using $\Sigma_n C_r$, where n is the number of sulfation sites and r is the number of sulfates.

h Number of possible sequences based on all experimental MS observations, estimating the sulfate number on average to be 4-7 for dp23-60 (although experimentally 104 compositions were identified).

GAG length	**Number of Sulfo Groups**															
	4				**5**				**6**				**7**			
	Subdomains															
	d	**c**	**b**	**a**	**d**	**c**	**b**	**a**	**d**	**c**	**b**	**a**	**d**	**c**	**b**	**a**
dp23	0	2	0	2	0	0	0	3	0	0	2	2				
dp24	1	2	0	2	1	0	0	3	1	0	2	2				
dp25	0	3	0	2	0	1	0	3	0	1	2	2	0	-1	2	3
dp26	1	3	0	2	1	1	0	3	1	1	2	2	1	-1	2	3
dp27	0	4	0	2	**0**	**2**	**0**	**3**	**0**	**2**	**2**	**2**	0	0	2	3
dp28	1	4	0	2	1	2	0	3	1	2	2	2	1	0	2	3
dp29	**0**	**5**	**0**	**2**	0	3	0	3	**0**	**3**	**2**	**2**	0	1	2	3
dp30	1	5	0	2	1	3	0	3	1	3	2	2	1	1	2	3
dp31	**0**	**6**	**0**	**2**	**0**	**4**	**0**	**3**	**0**	**4**	**2**	**2**	0	2	2	3
dp32	1	6	0	2	1	4	0	3	1	4	2	2	1	2	2	3
dp33	0	7	0	2	**0**	**5**	**0**	**3**	**0**	**5**	**2**	**2**	0	3	2	3
dp34	1	7	0	2	1	5	0	3	1	5	2	2	1	3	2	3
dp35	0	8	0	2	**0**	**6**	**0**	**3**	**0**	**6**	**2**	**2**	**0**	**4**	**2**	**3**
dp36	1	8	0	2	1	6	0	3	1	6	2	2	1	4	2	3
dp37	0	9	0	2	0	7	0	3	0	7	2	2	0	5	2	3
dp38	1	9	0	2	1	7	0	3	1	7	2	2	1	5	2	3
dp39	0	10	0	2	0	8	0	3	0	8	2	2	0	6	2	3
dp40	1	10	0	2	1	8	0	3	1	8	2	2	1	6	2	3
dp41	0	11	0	2	**0**	**9**	**0**	**3**	0	9	2	2	0	7	2	3
dp42	1	11	0	2	1	9	0	3	1	9	2	2	1	7	2	3
dp43	0	12	0	2	**0**	**10**	**0**	**3**	**0**	**10**	**2**	**2**	0	8	2	3
dp44	1	12	0	2	1	10	0	3	1	10	2	2	1	8	2	3
dp45	0	13	0	2	0	11	0	3	0	11	2	2	0	9	2	3
dp46	1	13	0	2	1	11	0	3	1	11	2	2	1	9	2	3
dp47	0	14	0	2	0	12	0	3	0	12	2	2	0	10	2	3
dp48	1	14	0	2	1	12	0	3	1	12	2	2	1	10	2	3
dp49	0	15	0	2	0	13	0	3	0	13	2	2	0	11	2	3
dp50	1	15	0	2	1	13	0	3	1	13	2	2	1	11	2	3
dp51	0	16	0	2	0	14	0	3	0	14	2	2	0	12	2	3
dp52	1	16	0	2	1	14	0	3	1	14	2	2	1	12	2	3
dp53	0	17	0	2	0	15	0	3	0	15	2	2	0	13	2	3
dp54	1	17	0	2	1	15	0	3	1	15	2	2	1	13	2	3
dp55	0	18	0	2	0	16	0	3	0	16	2	2	0	14	2	3
dp56	1	18	0	2	1	16	0	3	1	16	2	2	1	14	2	3
dp57	0	19	0	2	0	17	0	3	0	17	2	2	0	15	2	3
dp58	1	19	0	2	1	17	0	3	1	17	2	2	1	15	2	3
dp59	0	20	0	2	0	18	0	3	0	18	2	2	0	16	2	3
dp60	1	20	0	2	1	18	0	3	1	18	2	2	1	16	2	3

Supplementary Table 37. Subdomains (d.c.b.a) in chains dp23 though dp60 with 4 to 7 sulfo groups. Structures elucidated and assigned from MS/MS experiments are shown in bold and shaded. Subdomains a and b are part of the sulfated domain near the reducing end while subdomain c is part of the nonsulfated domain near the non-reducing end. Subdomain d accounts for odd and even numbered chains.