Supporting information for:

Sequencing Heparan Sulfate Using HILIC LC-NETD-MS/MS

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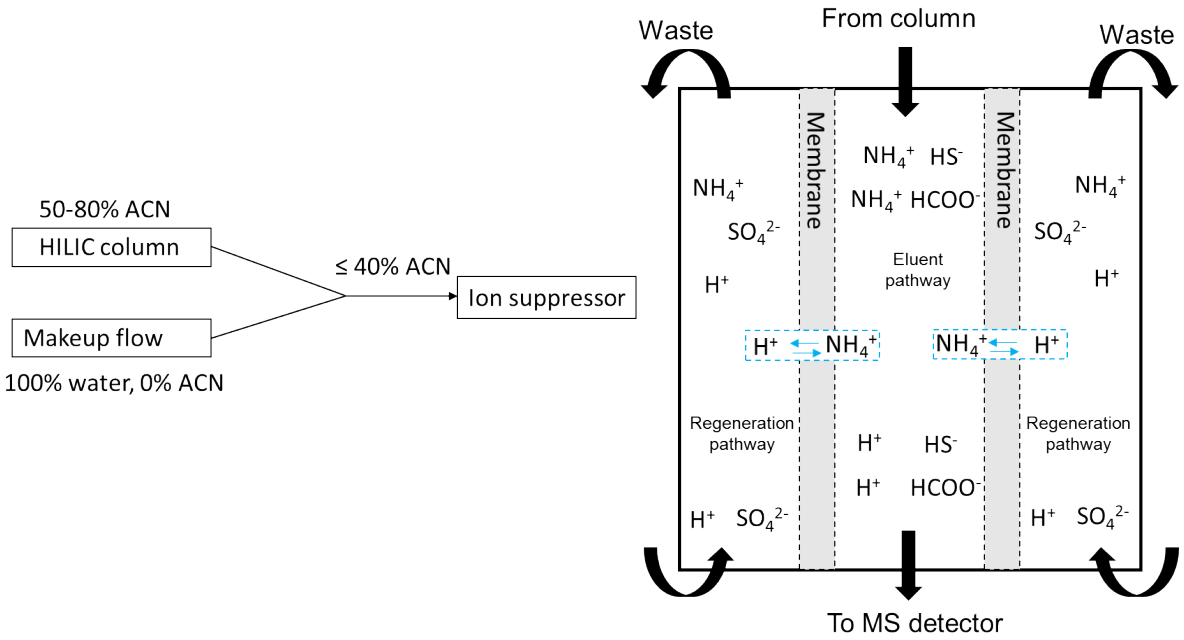

Figure S1. The LC flow path and the scheme of ion exchange in ion suppressor. HS^- indicates the anions of HS oligosaccharides.

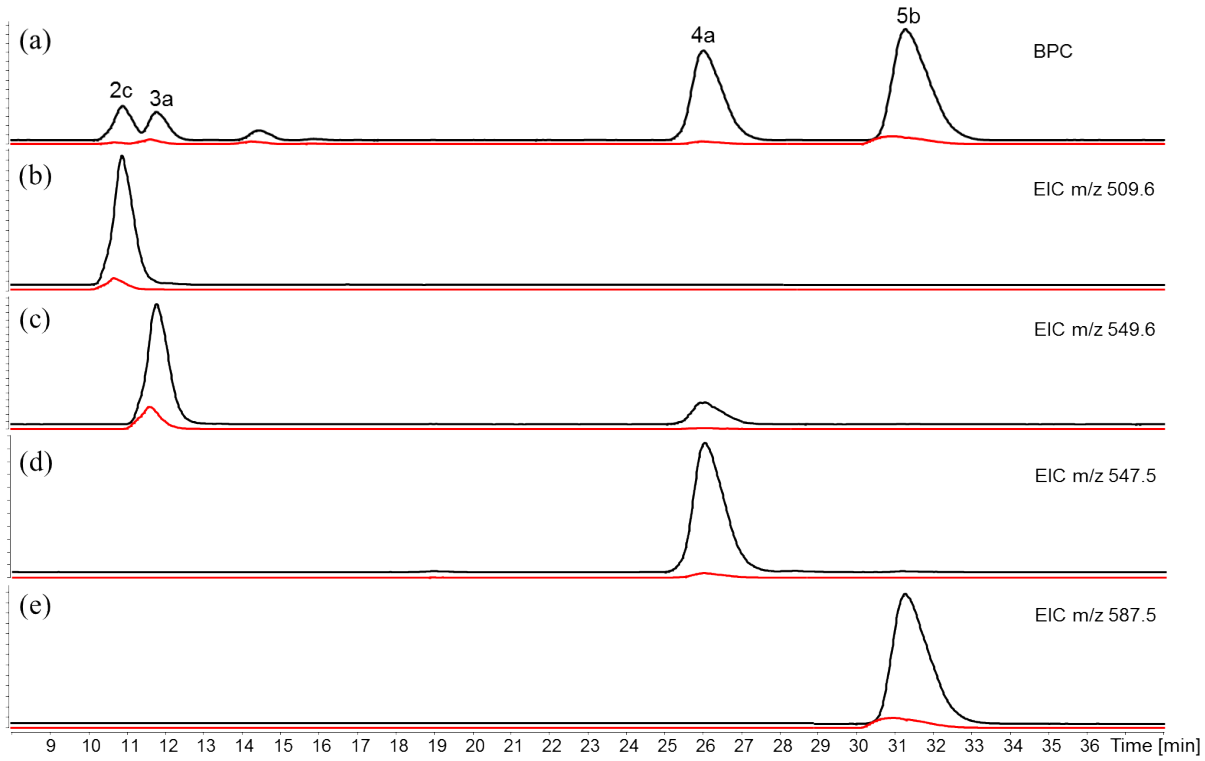

Figure S2. Influence of the use of the ion suppressor on LC peak width and signal intensity. The comparison of LC chromatograms were shown in panels. Red, without the ion suppressor; black, with the ion suppressor.

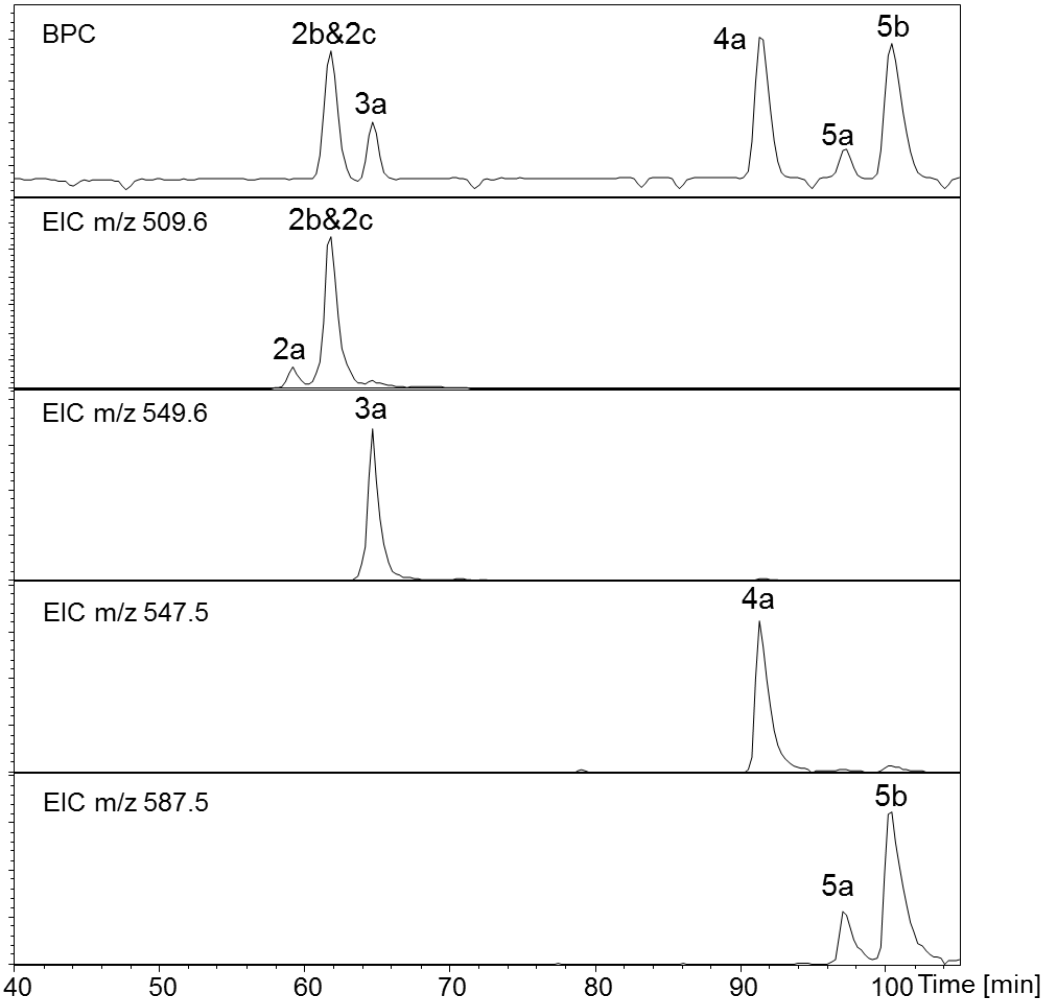

Figure S3. HILIC separation of the tetramers. **2a** was not shown in the BPC due to low abundance.

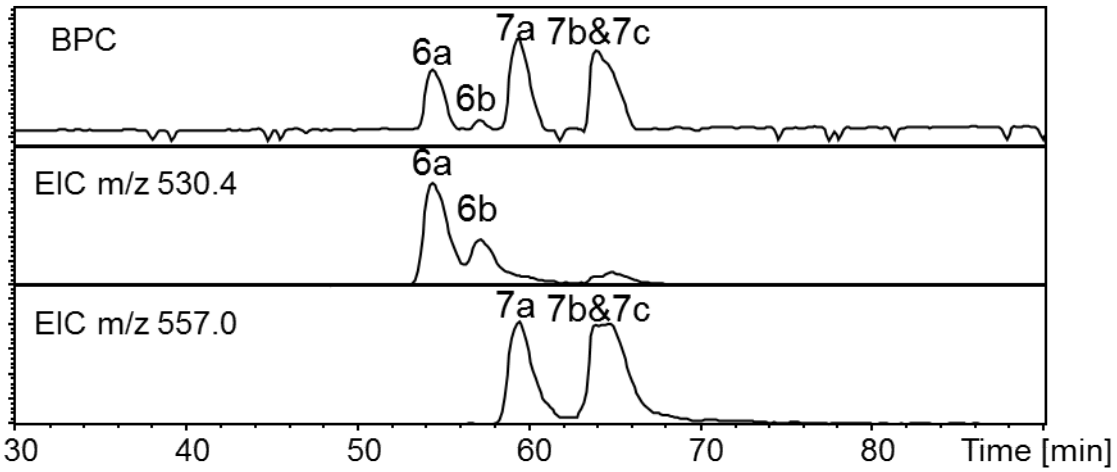

Figure S4. HILIC separation of the hexamers.

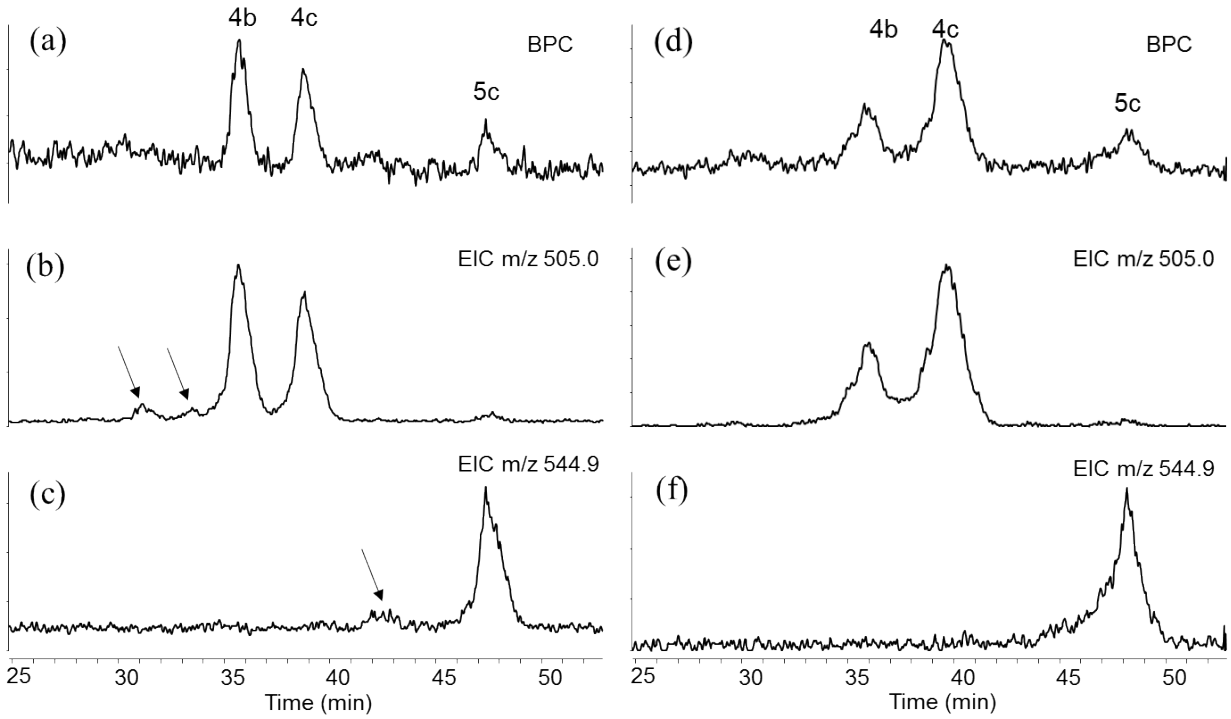

Figure S5. HILIC separation of tetramers without reducing end modification at different temperatures. Left panels, 25 °C; Right panels, 55 °C. Small anomeric peaks were observed and indicated with arrows in panel b and c.

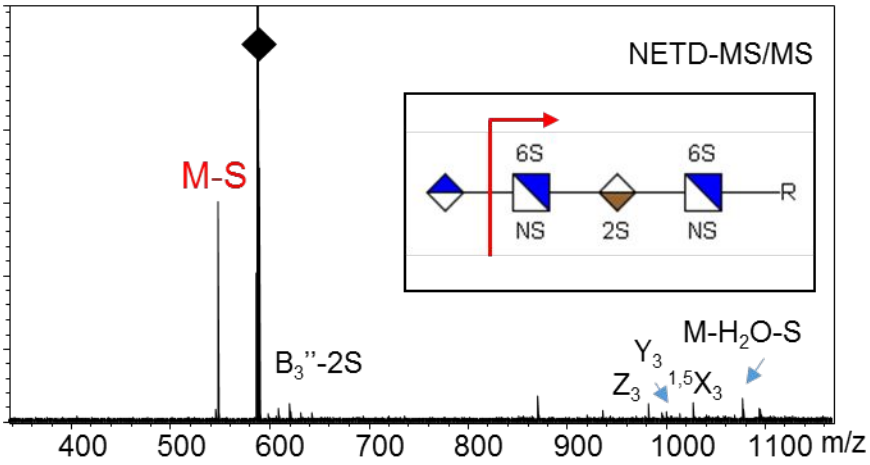

Figure S6. NETD-MS/MS spectrum of **5b** using the $[M-2H]^{2-}$ precursor.

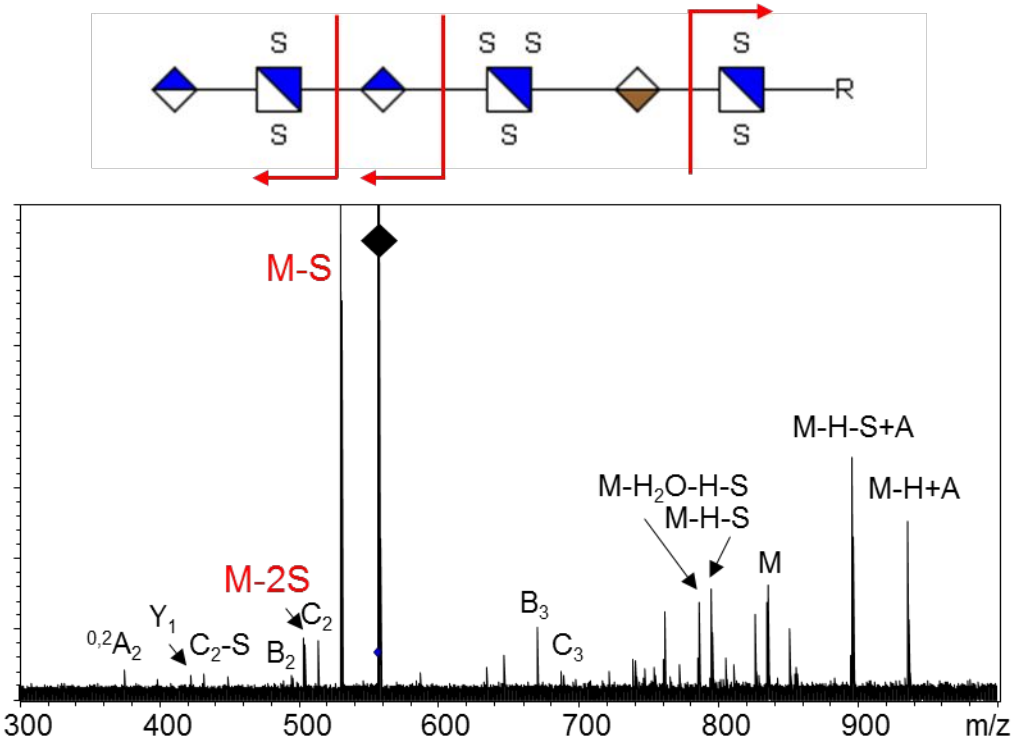

Figure S7. NETD-MS/MS spectrum of **7a** using the $[M-3H]^{3-}$ precursor.

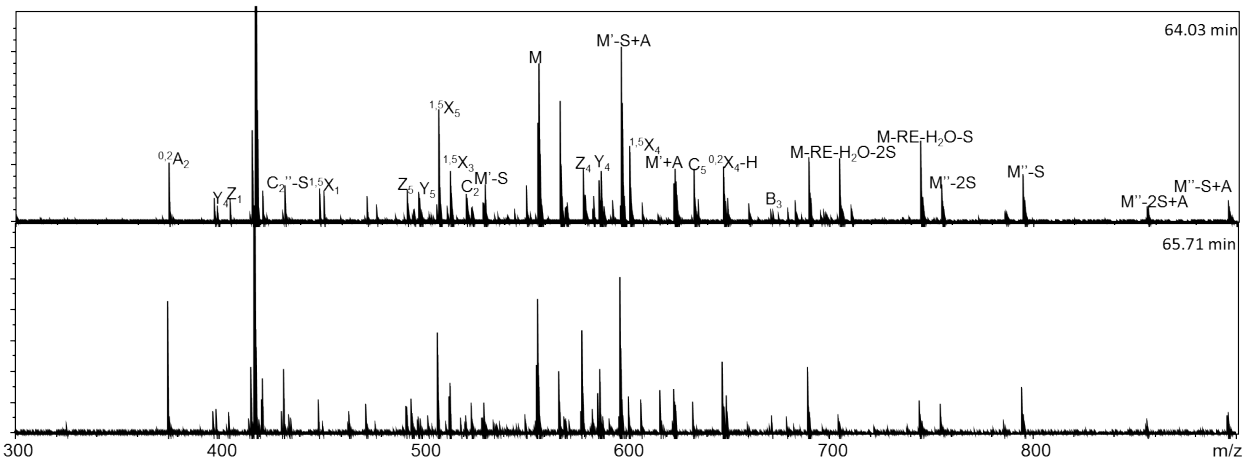

Figure S8. Annotated LC-MS/MS spectra of overlapped **7b** and **7c** at 64.03 and 65.71 min**.**

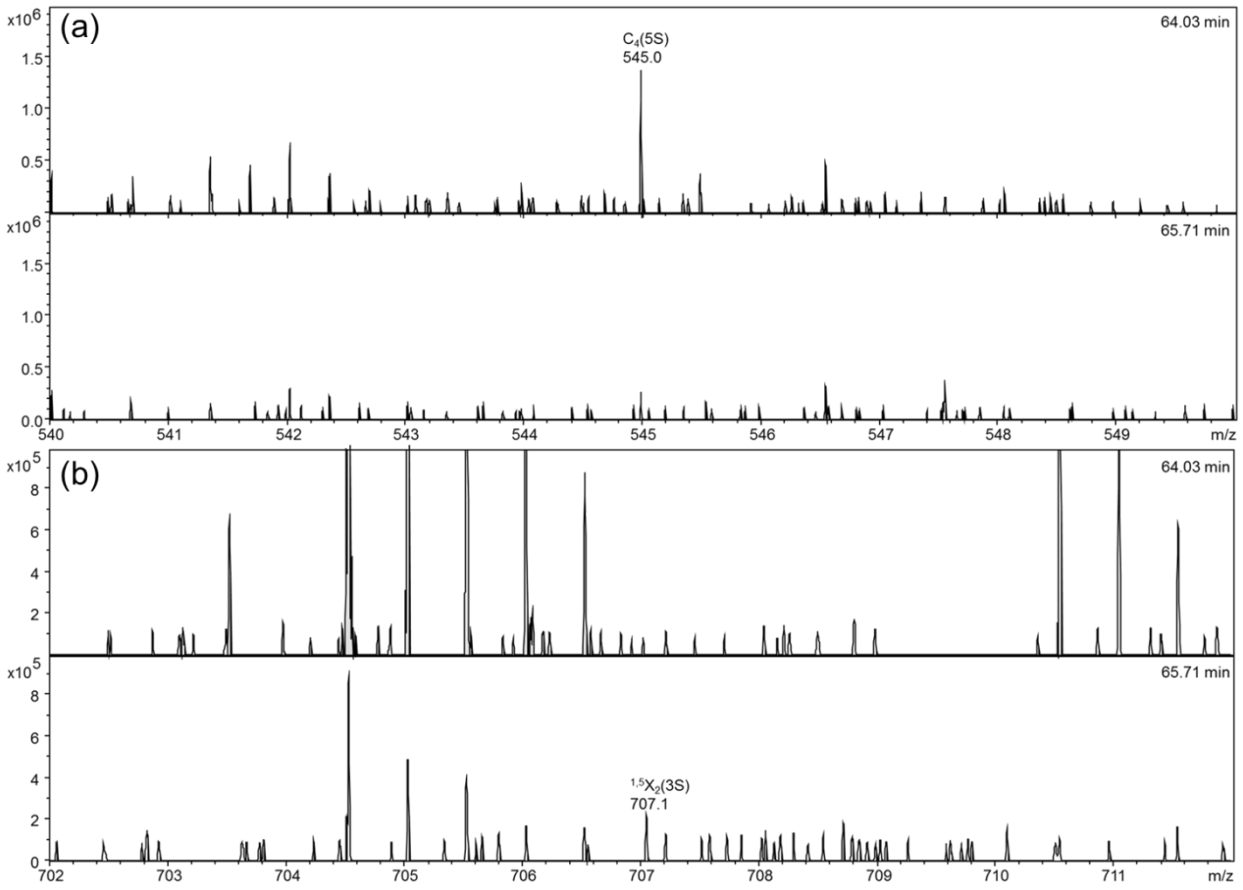

Figure S9. Zoom-in LC-MS/MS spectra of overlapped **7b** and **7c** at 64.03 and 65.71 min for selected diagnostic ions. (a), C_4(5S) at *m/z* 545.0; (b), $^{1,5}X_2$(3S) at *m/z* 707.1.

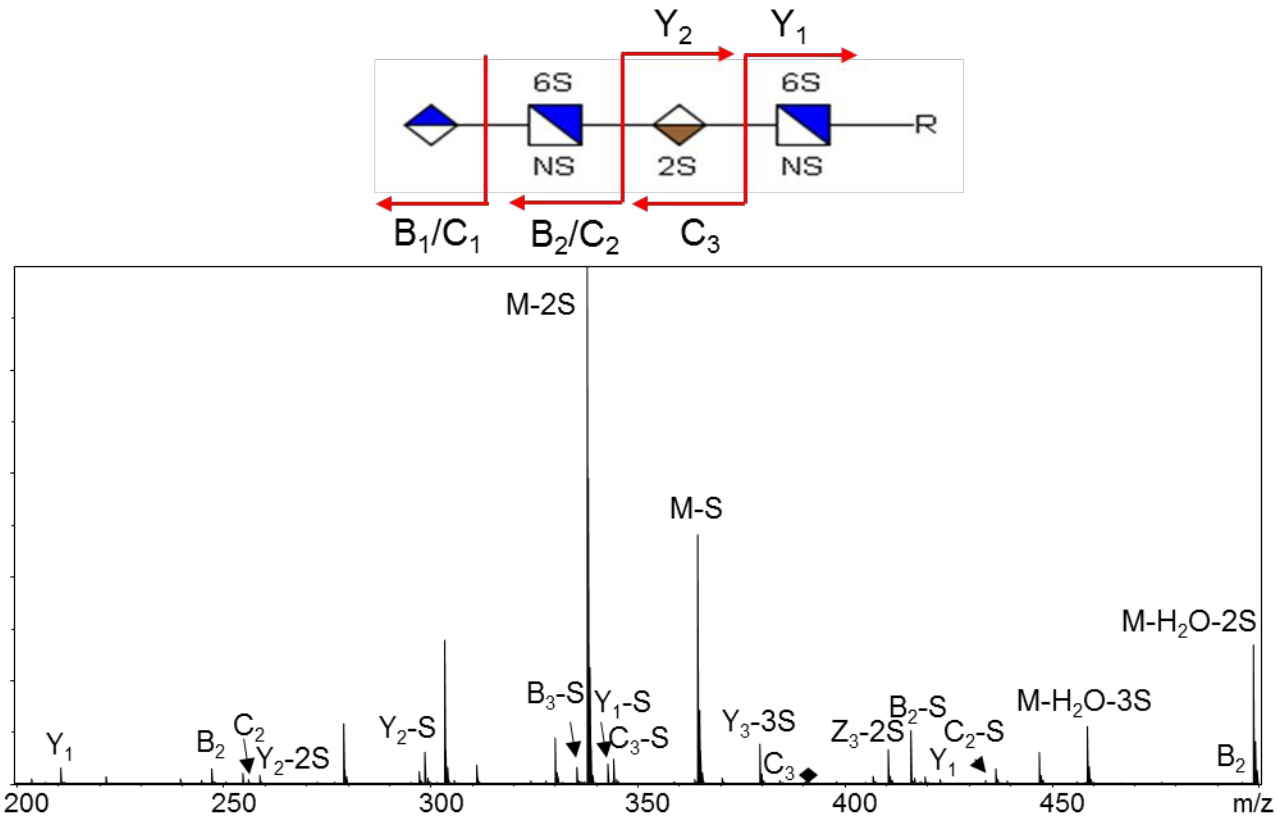

Figure S10. CID-MS/MS spectrum of **5b** using the $[M-3H]^{3-}$ precursor.

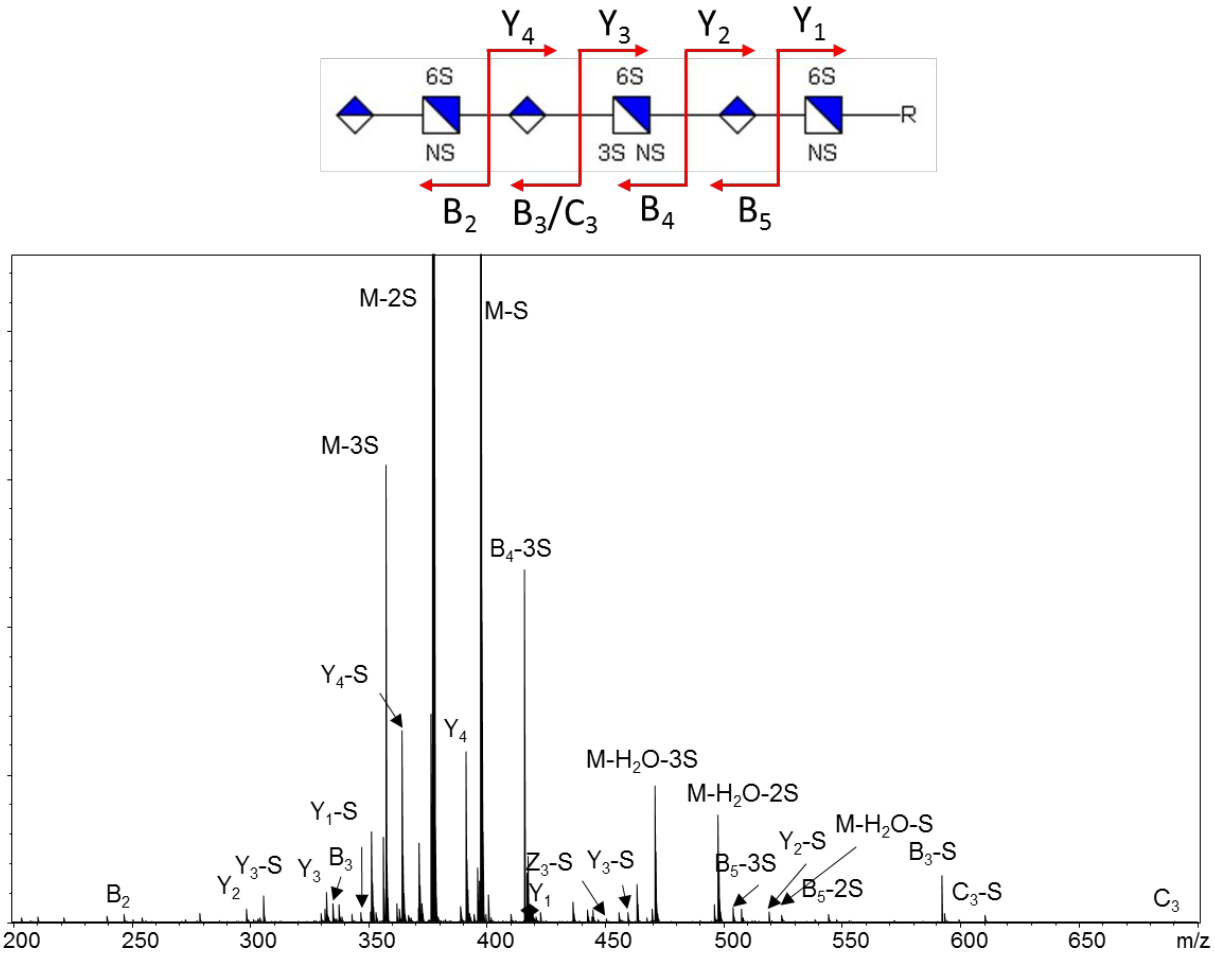

Figure S11. CID-MS/MS spectrum of **7a** using the $[M-4H]^{4-}$ precursor.

Table S1. Observed precursor of highest charge state of each compound in LC-MS. Compounds of charge state enhanced were marked in bold.

		Without ion suppressor		With ion suppressor	
	No. of Sulfate containing	Highest charge state	No. of free proton remaining	Highest charge state	No. of free proton remaining
2a	2	2-	0	2-	0
2b	2	2-	0	2-	0
2c	2	2-	0	2-	0
3a	3	2-	1	2-	1
4a	4	**2-**	2	**3-**	1
5a	5	**2-**	3	**3-**	2
5b	5	**2-**	3	**3-**	2
6a	6	**2-**	4	**4-**	2
6b	6	**2-**	4	**4-**	2
7a	7	**3-**	4	**4-**	3
7b	7	**3-**	4	**4-**	3
7c	7	**3-**	4	**4-**	3

Table S2. List of assigned peaks in the NETD-MS/MS spectrum of **2b**, $[M - 2H]^{2-}$. Relative intensities were normalized to the total intensity in the spectrum, same below. RE, reducing end modification; A, NETD reagent.

m/z	Intensity	Charge	Error (ppm)	Assignment
365.1042	0.002%	-1	4.91	Z1"
375.0228	0.003%	-1	-2.79	0,2A2
385.1282	0.060%	-1	-1.02	Y1
430.0658	0.012%	-1	-0.67	1,5A2
457.0529	0.003%	-1	-0.65	B2'
458.0607	0.034%	-1	-0.60	B2
474.0556	0.156%	-1	-0.70	C2"
475.0635	0.072%	-1	-0.55	C2'
476.0715	0.066%	-1	-0.13	C2
543.1500	0.002%	-1	-0.33	Z2
546.0763	0.020%	-1	-1.35	3,5A3
554.1365	0.007%	-1	0.43	B3-S
561.1611	0.004%	-1	0.62	Y2
562.0722	0.003%	-1	0.46	0,3A3
570.1305	0.007%	-1	-1.23	C3"-S
592.0825	0.006%	-1	-0.07	0,2A3
633.0844	0.079%	-1	-1.28	B3'
634.0923	0.042%	-1	-1.30	B3
650.0873	0.056%	-1	-1.14	C3"
651.0949	0.032%	-1	-1.47	C3'
652.1034	0.018%	-1	-0.39	C3
784.1739	0.010%	-1	-2.41	2,4X2
809.1815	0.025%	-1	4.83	M"-RE-CO2-SO3
810.1857	0.006%	-1	0.39	M'-RE-CO2-SO3
826.1847	0.145%	-1	-1.99	Z3
837.1707	0.003%	-1	-2.12	M-RE-H2O-SO3
842.1794	0.155%	-1	-2.25	Y3"
843.1856	0.105%	-1	-4.13	Y3'
844.1949	0.059%	-1	-2.40	Y3
853.1670	0.004%	-1	-0.45	M"-RE-SO3
872.1896	0.081%	-1	-2.55	1,5X3
886.2052	0.010%	-1	-2.59	0,2X3
890.1414	0.007%	-1	-0.86	M'-RE-CO2
894.2651	0.004%	-1	-1.76	M"-CO2-SO3
916.2161	0.040%	-1	-2.05	0,3X3

922.2571	0.011%	-1	-4.90	M-H2O-SO3
930.2310	0.003%	-1	-2.85	M"-2CO2
934.1308	0.007%	-1	-1.34	M'-RE
938.2530	0.011%	-1	-3.77	M"-SO3
939.2610	0.007%	-1	-3.52	M'-SO3
956.2149	0.004%	-1	2.04	M"-H2O-CO2
957.2190	0.006%	-1	-1.86	M'-H2O-CO2
958.2261	0.009%	-1	-2.62	M-H2O-CO2
960.2048	0.009%	-1	-3.22	2,4X3
974.2198	0.019%	-1	-3.81	M"-CO2
975.2282	0.072%	-1	-3.19	M'-CO2
1001.2085	0.004%	-1	-2.13	M'-H2O
1002.2162	0.005%	-1	-2.23	M-H2O
1018.2096	0.049%	-1	-3.63	M"
1019.2176	0.295%	-1	-3.52	M'
1141.3380	0.009%	-1	-4.07	M'-SO3+A
1221.2942	0.172%	-1	-4.30	M'+A

Table S3. List of assigned peaks in the NETD-MS/MS spectrum of **2c**, $[M - 2H]^{2-}$.

m/z	Intensity	Charge	Error (ppm)	Assignment
385.1283	0.022%	-1	-0.80	Y1
396.1147	0.003%	-1	-0.11	C2
537.1065	0.007%	-1	-0.20	0,3X1
554.1363	0.004%	-1	0.05	B3-S
570.1303	0.009%	-1	-1.54	C3''-S
623.1067	0.008%	-1	-0.47	Z2
633.0833	0.003%	-1	-3.12	B3'
634.0924	0.020%	-1	-1.08	B3
639.1003	0.005%	-1	-2.46	Y2''
641.1178	0.003%	-1	0.36	Y2
650.0870	0.022%	-1	-1.56	C3''
651.0960	0.020%	-1	0.32	C3'
652.1029	0.021%	-1	-1.16	C3
669.1119	0.427%	-1	-0.78	1,5X2
770.1615	0.004%	-1	1.75	3,5X2
787.0770	0.006%	-1	-2.34	3,5A4-H
788.0856	0.009%	-1	-1.41	3,5A4
809.1748	0.004%	-1	-3.44	M''-RE-CO2-SO3
826.1860	0.171%	-1	-0.36	Z3
834.0897	0.006%	-1	-2.93	0,2A4
837.1713	0.003%	-1	-1.36	M-RE-H2O-SO3
842.1807	0.073%	-1	-0.63	Y3''
843.1875	0.063%	-1	-1.85	Y3'
844.1966	0.047%	-1	-0.35	Y3
853.1667	0.008%	-1	-0.78	M''-RE-SO3
854.1729	0.004%	-1	-2.63	M'-RE-SO3
872.1908	0.033%	-1	-1.12	1,5X3
885.1996	0.004%	-1	-0.01	0,2X3-H
886.2072	0.013%	-1	-0.34	0,2X3
888.1263	0.012%	-1	-0.31	1,5A4-H
916.1211	0.061%	-1	-0.34	M'-RE-H2O
916.2179	0.023%	-1	-0.19	0,3X3
917.1257	0.017%	-1	-3.85	M-RE-H2O
921.2514	0.003%	-1	-2.59	M'-H2O-SO3
922.2607	0.013%	-1	-0.99	M-H2O-SO3
931.2031	0.003%	-1	-2.19	3,5X3-H
933.1228	0.003%	-1	-1.45	M''-RE
934.1322	0.004%	-1	0.16	M'-RE

938.2556	0.068%	-1	-1.01	M''-SO3
939.2605	0.022%	-1	-4.08	M'-SO3
956.2129	0.006%	-1	-0.08	M''-H2O-CO2
974.2236	0.021%	-1	0.12	M''-CO2
975.2307	0.090%	-1	-0.67	M'-CO2
1018.2126	0.013%	-1	-0.76	M''
1019.2214	0.160%	-1	0.20	M'
1020.2278	0.185%	-1	-1.13	M
1140.3383	0.004%	-1	3.10	M''-SO3+A
1141.3410	0.005%	-1	-1.37	M'-SO3+A
1220.2889	0.004%	-1	-2.18	M''+A
1221.3010	0.166%	-1	1.26	M'+A
1222.3038	0.097%	-1	-2.79	M+A

Table S4. List of assigned peaks in the NETD-MS/MS spectrum of **5b**, $[M - 3H]^{3-}$.

m/z	Intensity	Charge	Error (ppm)	Assignment
329.0176	0.014%	-1	-2.35	3,5A2
335.5157	0.077%	-2	-1.07	B3-S
339.0279	0.143%	-2	-0.91	Y2
343.1177	0.035%	-1	-0.91	Y1-S
344.5212	0.015%	-2	-0.25	C3-S
373.0081	0.016%	-1	-0.29	0,2A2-2H
375.0237	2.666%	-1	-0.51	0,2A2
375.4942	0.068%	-2	-0.53	B3
383.4916	0.012%	-2	-0.69	C3''
384.4994	0.076%	-2	-0.73	C3
386.0398	0.011%	-1	-0.20	1,5A2-S-2H
403.0487	0.019%	-1	0.05	Z1''
404.0562	0.253%	-1	-0.66	Z1'
405.0642	0.324%	-1	-0.17	Z1
414.0344	0.029%	-1	-0.92	B2''-S
415.0186	0.097%	-2	3.29	1,4X2
415.0424	0.111%	-1	-0.50	B2'-S
416.0502	0.208%	-1	-0.48	B2-S
419.5631	0.012%	-2	1.10	Y3-2S
421.0592	0.045%	-1	-0.07	Y1''
422.0666	0.018%	-1	-1.03	Y1'
423.0746	0.248%	-1	-0.54	Y1
432.0452	0.557%	-1	-0.44	C2''-S
433.5607	0.009%	-2	1.44	1,5X3-2S
434.0608	0.040%	-1	-0.41	C2-S
435.5154	0.084%	-2	-0.46	0,2A4-S
449.5279	0.070%	-2	-0.20	Z3''-S
450.0318	0.021%	-2	-0.10	Z3'-S
450.5356	0.072%	-2	-0.35	Z3-S
451.0693	0.030%	-1	-1.01	1,5X1
452.4914	0.010%	-2	0.44	3,5A4
455.0209	0.049%	-2	-0.25	M''-RE-H2O-2SO3
455.5243	0.020%	-2	-1.34	M'-RE-H2O-2SO3
456.0286	0.064%	-2	-0.43	M-RE-H2O-2SO3
458.5330	0.137%	-2	-0.43	Y3''-S
459.5407	0.116%	-2	-0.74	Y3-S
467.0042	0.013%	-1	-0.62	1,5A2-H
473.5383	0.326%	-2	-0.39	1,5X3-S
475.4931	0.020%	-2	-1.81	0,2A4

480.0422	0.015%	-2	-0.44	0,2X3-S-H
489.5070	0.016%	-2	1.38	Z3''
490.0101	0.068%	-2	-0.27	Z3'
490.5139	0.114%	-2	-0.56	Z3
493.9913	0.027%	-1	-0.70	B2''
494.9992	0.310%	-2	-0.45	M''-RE-H2O-SO3
494.9992	0.310%	-1	-0.45	B2'
495.5032	0.186%	-2	-0.34	M'-RE-H2O-SO3
495.5526	0.011%	-2	1.88	0,3X3-S
496.0073	0.432%	-1	0.14	B2
496.0073	0.432%	-2	0.14	M-RE-H2O-SO3
497.5648	0.025%	-2	-1.51	M''-H2O-2SO3
498.5111	0.086%	-2	-0.99	Y3''
498.5731	0.357%	-2	-0.61	M-H2O-2SO3
499.0131	0.016%	-2	-4.95	Y3'
499.5193	0.196%	-2	-0.38	Y3
502.5407	0.056%	-2	-1.02	1,4X3-S
504.0047	0.020%	-2	-0.08	M''-RE-SO3
504.0661	0.025%	-1	-0.67	3,5A3-S
506.5706	0.133%	-2	-0.50	M''-2SO3
507.0727	0.034%	-2	-4.19	M'-2SO3
507.5785	0.126%	-2	-0.37	M-2SO3
512.0018	0.250%	-1	-0.72	C2''
513.5165	1.198%	-2	-0.78	1,5X3
514.0178	0.507%	-1	-0.01	C2
515.5488	0.071%	-2	-0.60	M''-H2O-CO2-SO3
516.0511	0.023%	-2	-3.58	M'-H2O-CO2-SO3
520.0203	0.056%	-2	-0.98	0,2X3-H
520.5235	0.023%	-2	-2.50	0,2X3
524.5541	0.031%	-2	-0.59	M''-CO2-SO3
525.0577	0.019%	-2	-1.14	M'-CO2-SO3
535.4814	0.039%	-2	-0.69	M'-RE-H2O
535.5297	0.026%	-2	-0.59	0,3X3
535.9857	0.012%	-2	0.14	M-RE-H2O
537.5430	0.051%	-2	-1.82	M''-H2O-SO3
538.5514	0.520%	-2	-0.82	M-H2O-SO3
542.5191	0.101%	-2	-1.07	1,4X3
543.0209	0.022%	-2	-4.90	3,5X3-H
546.5487	0.547%	-2	-1.15	M''-SO3
547.0517	0.290%	-2	-2.67	M'-SO3
547.5566	0.943%	-2	-0.95	M-SO3

555.5270	0.039%	-2	-0.87	M''-H2O-CO2
556.0288	0.018%	-1	0.82	2,4A3
556.5638	0.028%	-2	-0.44	M'-RE-H2O-2SO3+A
564.5330	0.025%	-2	0.40	M''-CO2
565.0354	0.018%	-2	-2.24	M'-CO2
578.0255	0.083%	-2	-1.40	M'-H2O
578.5276	0.035%	-2	-4.46	M-H2O
580.0879	0.046%	-1	-1.18	Z2'-S
581.0958	0.036%	-1	-1.07	Z2-S
584.0222	0.034%	-1	-1.85	3,5A3
586.5268	0.117%	-2	-1.53	M''
587.0307	0.391%	-2	-1.51	M'
587.5346	0.960%	-2	-1.62	M
589.0341	0.057%	-1	3.46	1,4X1
590.0661	0.050%	-1	-1.26	B3''-2S
591.0737	0.052%	-1	-1.75	B3'-2S
592.0821	0.053%	-1	-0.63	B3-2S
596.5408	0.017%	-2	-2.81	M'-RE-H2O-SO3+A
597.0905	0.049%	-1	-1.42	Y2''-S
599.1060	0.115%	-1	-1.58	Y2-S
608.0766	0.351%	-1	-1.38	C3''-2S
608.1131	0.444%	-2	-1.39	M'-2SO3+A
627.1007	0.052%	-1	-1.96	1,5X2-S
647.5856	0.033%	-2	-4.26	M''-SO3+A
648.0910	0.855%	-2	-2.04	M'-SO3+A
660.0439	0.023%	-1	-2.31	Z2'
661.0517	0.055%	-1	-2.27	Z2
670.0222	0.068%	-1	-2.26	B3''-S
671.0297	0.219%	-1	-2.67	B3'-S
672.0376	0.139%	-1	-2.56	B3-S
677.0461	0.166%	-1	-3.06	Y2''
679.0621	0.343%	-1	-2.51	Y2
688.0321	0.099%	-1	-3.16	C3''-S
690.0487	0.026%	-1	-1.76	C3-S
707.0567	0.377%	-1	-2.81	1,5X2
751.9938	0.020%	-1	-3.18	B3
770.0034	0.033%	-1	-4.31	C3
868.1247	0.010%	-1	-3.20	1,5X3-2S
998.1512	0.008%	-1	-2.90	M-H2O-2SO3

Table S5. List of assigned peaks in the NETD-MS/MS spectrum of **7a**, $[M - 4H]^{4-}$.

m/z	Intensity	Charge	Error (ppm)	Assignment
191.0198	0.010%	-1	0.27	C1"
329.0181	0.008%	-1	0.94	3,5A2
375.0234	0.180%	-1	-1.23	0,2A2
391.3542	0.297%	-3	-0.94	Y4
403.0481	0.047%	-1	-1.48	Z1"
404.0559	0.050%	-1	-1.42	Z1'
405.0637	0.767%	-1	-1.40	Z1
415.0182	0.028%	-2	2.35	1,4X2
415.042	0.045%	-1	-1.38	B2'
416.0498	0.135%	-2	-1.47	B4-3S
416.0498	0.135%	-1	-1.47	B2-S
418.3912	0.023%	-3	-1.61	Y5-3S
418.5542	0.017%	-2	-1.49	Y3"-2S
419.562	0.056%	-2	-1.54	Y3-2S
421.0587	0.213%	-1	-1.30	Y1"
421.5158	0.414%	-2	2.30	3,5X2-S-2H
421.6683	0.033%	-3	-1.43	C5
423.0743	0.033%	-1	-1.46	Y1
432.0448	0.305%	-1	-1.18	C2"-S
434.0603	0.038%	-1	-1.69	C2-S
451.0693	0.154%	-1	-1.14	1,5X1
459.5403	0.019%	-2	-1.74	Y3-S
464.0256	0.011%	-2	-1.60	C4"-2S
464.0769	0.012%	-1	-1.60	0,2X1-H
466.9958	0.004%	-3	1.62	3,5A6
471.0237	0.014%	-3	-1.91	Y5"-S
473.5377	0.021%	-2	-1.78	1,5X3-S
481.0273	0.089%	-3	-1.69	1,5X5-S
482.331	0.011%	-3	-1.61	0,2A6
490.5134	0.041%	-2	-1.59	Z3
492.0082	0.162%	-3	-2.07	Z5'
492.3444	0.096%	-3	-1.66	Z5
494.9986	0.052%	-2	-1.65	B4"-S
494.9986	0.052%	-1	-1.65	B2'
495.5026	0.051%	-2	-1.44	B4'-S
495.6706	0.013%	-3	-1.45	M'-RE-H2O-SO3
496.0067	0.214%	-3	-1.16	M-RE-H2O-SO3
496.0067	0.214%	-1	-1.16	B2
496.0067	0.214%	-2	-1.16	B4-S
497.6761	0.263%	-3	-1.57	Y5"

497.7172	0.035%	-3	-1.59	M-H2O-2SO3
498.3474	0.227%	-3	-2.72	Y5
499.0141	0.084%	-2	-2.87	Y3'
499.5187	0.106%	-2	-1.62	Y3
503.0489	0.065%	-3	-1.62	M"-2SO3
504.0039	0.025%	-2	-1.64	C4"-S
504.0657	0.046%	-1	-1.63	3,5A3-S
504.0657	0.046%	-2	-1.63	B5-3S
505.0117	0.060%	-2	-1.69	C4-S
507.3219	0.016%	-3	-4.90	M"-RE-H2O-CO2
507.6795	0.999%	-3	-1.70	1,5X5
512.0027	0.043%	-1	1.13	C2"
512.0153	0.083%	-3	-1.94	0,2X5-H
512.3502	0.034%	-3	-3.95	0,2X5
513.0112	0.022%	-1	2.37	C2'
513.0112	0.022%	-2	-3.53	1,5X3-H
513.516	0.510%	-2	-1.81	1,5X3
514.0176	0.194%	-1	-0.49	C2
520.0202	0.020%	-2	-1.16	0,2X3-H
521.6815	0.111%	-3	-4.55	0,3X5-2H
522.3228	0.036%	-3	-1.53	M'-RE-H2O
522.6586	0.021%	-3	-1.73	M-RE-H2O
523.6976	0.025%	-3	-1.64	M"-H2O-SO3
527.0146	0.012%	-3	-1.77	3,5X5
529.7013	0.179%	-3	-1.27	M"-SO3
530.0368	0.118%	-3	-2.12	M'-SO3
530.3731	0.386%	-3	-1.30	M'-SO3
535.0248	0.021%	-2	-2.56	0,3X3-H
535.6862	0.011%	-3	-2.31	M"-H2O-CO2
536.0222	0.016%	-3	-2.17	M'-H2O-CO2
537.0181	0.038%	-3	-1.71	2,4X5
538.5508	0.045%	-2	-1.91	Z4-S
540.0143	0.043%	-2	-1.74	3,5A5-S
541.6899	0.041%	-3	-1.99	M"-CO2
542.0261	0.040%	-3	-1.37	M'-CO2
543.9822	0.018%	-2	-1.75	C4"
544.99	0.117%	-2	-1.77	C4
546.5483	0.063%	-2	-1.87	Y4"-S
547.5561	0.058%	-2	-1.83	Y4-S
550.3498	0.036%	-3	-1.68	M"-H2O
550.6856	0.475%	-3	-1.89	M'-H2O
551.02	0.202%	-3	-4.65	M-H2O
556.3532	0.142%	-3	-1.86	M"

556.6893	0.908%	-3	-1.51	M'
557.0251	1.473%	-3	-1.74	M
561.5533	0.027%	-2	-2.20	1,5X4-S
570.407	0.061%	-3	-3.64	M"-2SO3+A
570.7442	0.208%	-3	-1.46	M'-2SO3+A
571.0781	0.128%	-3	-4.99	M-2SO3+A
577.5216	0.018%	-2	-1.43	Z4"
578.0252	0.031%	-2	-1.86	Z4'
578.5294	0.514%	-2	-1.38	Z4
579.9925	0.151%	-2	-2.10	3,5A5
580.0877	0.013%	-1	-1.59	Z2'
581.0952	0.016%	-1	-2.01	Z2
583.0142	0.017%	-2	-2.20	B5"-S
583.0142	0.017%	-1	-2.20	3,5A3-H
583.5185	0.165%	-2	-1.56	B5'-S
584.0224	0.229%	-1	-1.53	3,5A3
584.0224	0.229%	-2	-1.53	B5-S
586.5267	0.259%	-2	-1.61	Y4"
587.5342	0.242%	-2	-2.19	Y4
589.6817	0.051%	-3	-2.12	M'-RE-H2O+A
590.0162	0.024%	-3	-4.62	M-RE-H2O+A
591.0735	0.023%	-1	-1.99	B3'-S
592.0196	0.136%	-2	-1.99	C5"-S
592.0817	0.028%	-1	-1.42	B3-S
593.0272	0.224%	-2	-2.32	C5-S
597.0587	0.105%	-3	-4.52	M"-SO3+A
597.3961	1.794%	-3	-1.92	M'-SO3+A
597.7307	1.087%	-3	-4.21	M-SO3+A
599.1058	0.042%	-1	-1.95	Y2
601.5319	0.327%	-2	-1.74	1,5X4
607.5436	0.044%	-2	-2.08	0,2X4-S-H
608.076	0.029%	-1	-2.31	C3"-S
623.4967	0.503%	-2	-1.77	B5'
623.7112	0.016%	-3	-3.89	M"+A
623.9989	0.185%	-2	-4.50	B5
624.0484	0.442%	-3	-1.94	M'+A
624.3829	0.278%	-3	-4.20	M+A
631.9977	0.131%	-2	-2.31	C5"
633.0059	0.677%	-2	-1.68	C5
647.522	0.162%	-2	-1.96	0,2X4-H
658.0555	0.019%	-2	-1.94	Z5"-2S
659.0637	0.014%	-2	-1.40	Z5-2S
670.0222	0.011%	-1	-2.22	B3"

671.0301	0.089%	-2	0.29	3,5X4
671.0301	0.089%	-1	-2.06	B3'
672.0376	0.075%	-1	-2.61	B3
682.066	0.011%	-2	-2.08	1,5X5-2S
688.0327	0.057%	-1	-2.23	C3"
697.0736	0.026%	-2	1.39	2,5X5-2S
698.0337	0.029%	-2	-2.17	Z5"-S
698.537	0.017%	-2	-3.08	Z5'-S
699.0416	0.042%	-2	-2.04	Z5-S
700.4928	0.014%	-2	-2.57	3,5A6-H
703.5267	0.033%	-2	-2.22	M"-RE-H2O-2SO3
704.5348	0.828%	-2	-1.89	M-RE-H2O-2SO3
707.0394	0.014%	-2	-1.59	Y5"-S
712.5318	0.013%	-2	-2.51	M"-RE-2SO3
722.0438	0.024%	-2	-2.68	1,5X5-S
739.0195	0.022%	-2	-2.63	Z5
743.5048	0.026%	-2	-2.50	M"-RE-H2O-SO3
744.5127	1.058%	-2	-2.42	M-RE-H2O-SO3
746.071	0.124%	-2	-2.45	M"-H2O-2SO3
747.077	0.022%	-2	-4.98	M-H2O-2SO3
752.51	0.011%	-2	-2.55	M"-RE-SO3
755.0764	0.231%	-2	-2.24	M"-2SO3
762.0219	0.016%	-2	-2.95	1,5X5
773.0595	0.024%	-2	-2.70	M"-CO2-SO3
786.0491	0.093%	-2	-2.72	M"-H2O-SO3
795.0544	0.545%	-2	-2.67	M"-SO3
820.104	0.023%	-1	-2.84	Z3"-2S
835.0327	0.030%	-2	-2.71	M"
835.5349	0.023%	-2	-4.77	M'
856.1148	0.101%	-2	-2.92	M"-2SO3+A
896.0929	0.194%	-2	-3.06	M"-SO3+A
896.5952	0.149%	-2	-4.93	M'-SO3+A
911.0467	0.022%	-1	-2.87	B4"-2S
936.0712	0.032%	-2	-3.11	M"+A
936.5738	0.032%	-2	-4.49	M'+A

Table S6. List of assigned peaks in the NETD-MS/MS spectrum of **7c**, $[M - 4H]^{4-}$.

m/z	Intensity	Charge	Error (ppm)	Assignment
256.5051	0.053%	-2	-0.82	C2
329.0179	0.033%	-1	-1.63	3,5A2
334.5076	0.024%	-2	-1.91	B3"
375.0232	1.524%	-1	-1.96	0,2A2
404.0556	0.115%	-1	-2.07	Z1'
405.0631	0.113%	-1	-2.94	Z1
412.5124	0.005%	-2	1.02	3,5A4
414.0339	0.035%	-1	-2.24	B2"-S
415.0179	0.045%	-2	1.55	1,4X2
415.0417	0.025%	-1	-2.18	B2'-S
416.0497	0.209%	-2	-1.86	B4-2S
416.0497	0.209%	-1	-1.86	B2-S
419.0569	0.129%	-2	-4.40	Y3'-2S
419.5618	0.064%	-2	-1.94	Y3-2S
421.0583	0.133%	-1	-2.31	Y1"
423.074	0.022%	-1	-2.14	Y1
432.0444	0.731%	-1	-2.13	C2"-S
434.0597	0.049%	-1	-2.89	C2-S
435.5145	0.110%	-2	-2.38	0,2A4
451.0686	0.019%	-1	-2.73	1,5X1
455.5238	0.014%	-2	-2.37	B4'-S
459.5401	0.014%	-2	-2.19	Y3-S
464.0252	0.298%	-2	-2.43	C4"-S
465.0233	0.028%	-3	4.74	Z5"-S
465.692	0.019%	-3	-2.03	Z5-S
466.9954	0.005%	-3	2.47	3,5A6
471.6952	0.014%	-3	-2.69	Y5-S
473.5372	0.032%	-2	-2.70	1,5X3-S
481.0268	0.036%	-3	-2.62	1,5X5-S
490.009	0.026%	-2	-2.60	Z3'
490.513	0.057%	-2	-2.39	Z3
492.0081	0.040%	-3	-2.47	Z5'
492.3439	0.367%	-3	-2.65	Z5
494.9982	0.376%	-1	-2.57	B2'
494.9982	0.376%	-2	-2.57	B4"
495.502	0.239%	-2	-2.76	B4'
497.6754	0.030%	-3	-2.85	Y5"
497.7168	0.020%	-3	-2.39	M-H2O-2SO3
498.3475	0.086%	-3	-2.51	Y5
499.5181	0.091%	-2	-2.75	Y3

503.0484	0.109%	-3	-2.60	M"-2SO3
504.0035	0.035%	-2	-2.45	C4"
504.0652	0.034%	-1	-2.61	3,5A3-S
504.508	0.015%	-2	-1.28	C4'
505.0112	0.132%	-2	-2.67	C4
507.6792	0.754%	-3	-2.32	1,5X5
512.0009	0.111%	-1	-2.50	C2"
512.3506	0.045%	-3	-3.28	0,2X5
513.5155	0.180%	-2	-2.79	1,5X3
514.0164	0.609%	-1	-2.71	C2
520.0211	0.043%	-2	0.45	0,2X3-H
520.5237	0.037%	-2	-2.01	0,2X3
521.6819	0.033%	-3	-3.87	0,3X5-2H
523.6971	0.025%	-3	-2.49	M"-H2O-SO3
524.0325	0.017%	-3	-3.45	M'-H2O-SO3
526.0182	0.020%	-2	0.82	2,4A5
529.7003	0.149%	-3	-3.05	M"-SO3
530.0358	0.102%	-3	-3.98	M'-SO3
530.3725	0.404%	-3	-2.55	M-SO3
535.024	0.070%	-2	-3.94	0,3X3-H
535.5284	0.030%	-2	-3.08	0,3X3
535.685	0.015%	-3	-4.56	M"-H2O-CO2
536.0216	0.043%	-3	-3.21	M'-H2O-CO2
538.5503	0.140%	-2	-2.78	Z4-S
540.0138	0.044%	-2	-2.79	3,5A5
541.6893	0.038%	-3	-3.04	M"-CO2
542.0246	0.021%	-3	-4.17	M'-CO2
546.5477	0.082%	-2	-2.93	Y4"-S
547.5551	0.107%	-2	-3.61	Y4-S
550.6853	0.211%	-3	-2.48	M'-H2O
556.0269	0.053%	-1	-2.67	2,4A3
556.3526	0.123%	-3	-2.94	M"
556.6887	0.672%	-3	-2.63	M'
557.0246	1.145%	-3	-2.65	M
561.5529	0.057%	-2	-2.93	1,5X4-S
570.0238	0.212%	-2	-3.61	1,5A5-S
570.7432	0.174%	-3	-3.22	M'-2SO3+A
577.5205	0.049%	-2	-3.29	Z4"
578.0248	0.212%	-2	-2.57	Z4'
578.5284	1.346%	-2	-3.08	Z4
583.0136	0.044%	-2	-3.14	B5"-S
584.0212	0.155%	-1	-3.63	3,5A3
584.0212	0.155%	-2	-3.63	B5-S

586.0382	0.014%	-1	-1.20	1,4A3
586.5258	0.626%	-2	-3.17	Y4"
587.5337	0.778%	-2	-3.03	Y4
589.0346	0.054%	-1	4.22	3,5X1
590.0654	0.042%	-1	-2.48	B3"-S
592.0191	0.265%	-2	-2.78	C5"-S
592.0805	0.028%	-1	-3.33	B3-S
597.0587	0.081%	-3	-4.52	M"-SO3+A
597.3957	1.626%	-3	-2.67	M'-SO3+A
599.1054	0.018%	-1	-2.53	Y2-S
601.5313	0.235%	-2	-2.83	1,5X4
607.5429	0.350%	-2	-3.28	0,2X4-S-H
608.5418	0.085%	-2	1.69	0,2X4-S
623.9995	0.025%	-2	-3.49	B5
624.0475	0.462%	-3	-3.31	M'+A
630.0268	0.022%	-1	-3.18	0,2A3
631.9969	0.017%	-2	-3.54	C5"
633.0046	0.045%	-2	-3.71	C5
658.0544	0.023%	-2	-3.64	Z5"-2S
659.0627	0.015%	-2	-2.90	Z5-2S
661.0508	0.065%	-1	-3.68	Z2
670.0213	0.071%	-1	-3.52	B3"
671.0295	0.056%	-2	-0.58	3,5X4
671.0295	0.056%	-1	-2.93	B3'
672.0367	0.144%	-1	-3.88	B3
677.0455	0.024%	-1	-3.93	Y2"
679.0612	0.105%	-1	-3.80	Y2
681.0575	0.016%	-2	-3.05	1,5X5-2S-2H
688.0319	0.033%	-1	-3.35	C3"
688.0684	0.013%	-2	1.46	0,2X5-2S-2H
697.075	0.083%	-2	3.42	2,5X5-2S
698.0323	0.030%	-2	-4.20	Z5"-S
699.0405	0.076%	-2	-3.62	Z5-S
704.5336	0.037%	-2	-3.62	M-RE-H2O-2SO3
707.0559	0.108%	-1	-4.00	1,5X2
719.0796	0.013%	-1	-4.01	0,2X2-S-H
722.0432	0.028%	-2	-3.62	1,5X5-S
724.075	0.022%	-2	-4.02	M"-H2O-CO2-2SO3
728.0428	0.015%	-2	-4.11	0,2X5-S-2H
729.0558	0.020%	-2	2.95	0,2X5-S
738.5148	0.013%	-2	-3.74	Z5'
739.0186	0.046%	-2	-3.83	Z5
744.5118	0.025%	-2	-3.60	M-RE-H2O-SO3

746.0699	0.102%	-2	-3.90	M"-H2O-2SO3
755.0751	0.325%	-2	-3.99	M"-2SO3
762.0206	0.014%	-2	-4.68	1,5X5
764.0533	0.038%	-2	-3.96	M"-H2O-CO2-SO3
773.0592	0.027%	-2	-3.20	M"-CO2-SO3
786.0481	0.111%	-2	-4.00	M"-H2O-SO3
795.0532	0.636%	-2	-4.20	M"-SO3
799.0363	0.047%	-1	-3.78	0,2X2-H
835.032	0.014%	-2	-3.52	M"
847.6118	0.013%	-2	-4.86	M'-H2O-2SO3+A
856.1136	0.123%	-2	-4.30	M"-2SO3+A
883.0564	0.084%	-1	2.26	1,5A4-S-2H
884.0608	0.022%	-1	-1.58	1,5A4-S-H
896.0916	0.281%	-2	-4.50	M"-SO3+A
911.0451	0.040%	-1	-4.64	B4"-S
929.0556	0.163%	-1	-4.63	C4"-S
936.0698	0.051%	-2	-4.62	M"+A

Table S7. List of assigned peaks in the CID-MS/MS spectrum of **5b**, $[M - 3H]^{3-}$.

m/z	Intensity	Charge	Error (ppm)	Assignment
175.0248	0.036%	-1	-0.34	B1
193.0352	0.007%	-1	-0.81	C1
211.0335	0.426%	-2	-1.27	Y1
247.4995	0.353%	-2	-1.97	B2
256.5047	0.058%	-2	-2.24	C2
259.0709	0.204%	-2	-2.19	Y2-2S
277.5100	0.003%	-2	-1.97	2,4A3
299.0491	0.798%	-2	-2.39	Y2-S
335.5150	0.340%	-2	-3.19	B3-S
336.0926	0.018%	-1	-2.95	B2-2S
339.0269	0.044%	-2	-4.00	Y2
343.1169	0.459%	-1	-3.28	Y1-S
344.5202	0.575%	-2	-3.34	C3-S
354.1032	0.001%	-1	-2.91	C2-2S
370.5776	0.114%	-2	-3.69	Z3-3S
379.5828	1.016%	-2	-3.70	Y3-3S
384.4983	0.018%	-2	-3.69	C3
410.5558	0.715%	-2	-3.72	Z3-2S
416.0488	1.288%	-1	-3.98	B2-S
419.5610	0.112%	-2	-3.88	Y3-2S
423.0733	0.035%	-1	-3.77	Y1
434.0593	0.076%	-1	-3.80	C2-S
439.1916	0.065%	-1	-4.05	Y2-3S
456.0271	0.035%	-2	-3.92	M-RE-H2O-2SO3
496.0051	0.040%	-1	-4.31	B2
496.0051	0.040%	-2	-4.31	M-RE-H2O-SO3
498.5711	3.476%	-2	-4.59	M-H2O-2SO3
501.1374	0.010%	-1	-4.45	Z2-2S
512.1235	0.042%	-1	-4.31	C2-3S
519.1477	0.256%	-1	-4.79	Y2-2S

Table S8. List of assigned peaks in the CID-MS/MS spectrum of **7a**, $[M - 4H]^{4-}$.

m/z	Intensity	Charge	Error (ppm)	Assignment
416.0512	1.810%	-1	1.77	B2-S
416.0512	1.810%	-2	1.77	B4-3S
364.7029	0.976%	-3	1.63	Y4-S
391.3553	0.886%	-3	1.74	Y4
471.0666	0.659%	-3	1.86	M-H2O-3SO3
497.7190	0.510%	-3	1.90	M-H2O-2SO3
592.0839	0.233%	-1	2.35	B3-S
332.6778	0.136%	-3	1.67	Y3
306.0255	0.133%	-3	1.91	Y3-S
389.0138	0.082%	-3	1.79	B5-S
335.5166	0.078%	-2	1.67	B3
362.3614	0.068%	-3	1.67	B5-2S
299.0503	0.067%	-2	1.37	Y2
496.0082	0.065%	-1	1.98	B2
496.0082	0.065%	-2	1.98	B4-S
496.0082	0.065%	-3	1.98	M-RE-H2O-SO3
419.5635	0.057%	-2	2.06	Y3-2S
338.0506	0.053%	-3	1.68	Y4-2S
418.3927	0.052%	-3	1.95	Y5-3S
519.1512	0.051%	-1	2.01	Y2-S
456.0298	0.047%	-2	2.18	B4-2S
442.7036	0.047%	-3	1.95	M-RE-H2O-3SO3
507.5798	0.045%	-2	2.12	Y4-2S
544.0461	0.039%	-2	2.15	B5-2S
395.0174	0.039%	-3	1.97	C5-S
410.5581	0.039%	-2	1.75	Z3-2S
610.0947	0.034%	-1	2.58	C3-S
524.3714	0.033%	-3	2.14	M-H2O-SO3
459.5418	0.031%	-2	1.61	Y3-S
445.0450	0.025%	-3	1.75	Y5-2S
247.5002	0.024%	-2	0.94	B2
330.3363	0.023%	-3	1.58	B4-S
504.0675	0.019%	-1	2.06	3,5A4-S
504.0675	0.019%	-2	2.06	B5-3S
450.5367	0.019%	-2	1.96	Z3-S
303.6839	0.017%	-3	1.36	B4-2S
538.5531	0.012%	-2	2.29	Z4-S
279.3730	0.011%	-3	1.18	Y3-2S

412.3892	0.009%	-3	1.96	Z5-3S
423.0757	0.009%	-1	2.04	Y1
368.3650	0.008%	-3	1.66	C5-2S
415.6661	0.006%	-3	1.71	B5
379.5849	0.004%	-2	1.81	Y3-3S
467.6012	0.004%	-2	1.94	Y4-3S
690.0516	0.002%	-1	2.46	C3
343.1186	0.001%	-1	1.64	Y1-S
356.9886	0.000%	-3	1.66	B4