Supporting Information for:

Towards Automatic and Comprehensive Glycan Characterization by On-line PGC-LC-EED MS/MS

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Manual determination of Man4, Man6, Man8, and Man9 putative structures

Three chromatographic peaks are observed for Man4 isomers (Figure 1a), with their EED spectra shown in Figure S1. For isomer 1, the presence of a series of C-2H, or $C^‡$ ions, including $C_1^‡$ (Hex_1), $C_2^‡$ (Hex_2), $C_3^‡$ (Hex_3), $C_4^‡$ (Hex_4), suggests a linear tri-mannose chain attached to the R0 residue. Further, the absence of $^{0,4}A$ and $^{3,5}A$ ions suggests that the trisaccharide is located at the 3-antenna, thus establishing the structure of isomer 1 as $4A_3B_3$. For isomer 2, observed C ions include $C_{1\alpha'}^‡$ (Hex), $C_{2\alpha}^‡$ (Hex_3), and $C_3^‡$ (Hex_4), but not C (Hex_2), and this indicates a branched tri-mannose antenna attached to the core mannose. Branched sub-structure can only exist at the 6-antenna, an assignment that is also supported by the presence of $^{0,4}A_2$, $^{3,5}A_2$, and $^{3,5}A_3$ ions. Thus isomer 2 can be assigned as $4A_{1,2}$. For isomer 3, observed C ions included $C_{1\alpha}^‡$ (Hex_1), $C_{2\alpha}^‡$ (Hex_2), and $C_3^‡$ (Hex_4), but not C (Hex_3), and this establishes a branched topology with two antennae consisting of one and two mannose residues, respectively. The observation of $^{0,4}A_{2\alpha}$, $^{3,5}A_{2\alpha}$, $^{0,4}A_3$, and $^{3,5}A_3$ ions may be used to establish the di-mannose branch as a 1→6-linked disaccharide at the 6-antenna, and the structure of isomer 3 as $4A_1$.

Three chromatographic peaks are observed for Man6 isomers (Figure 1c), with their EED spectra shown in Figure S2. For the major Man6 isomer, or isomer 1, the presence of $^{0,4}A_3$ and $^{3,5}A_3$ ions at *m/z* 709.325 and 737.357 suggests a tri-mannose 6-antenna, and a di-mannose 3-antenna. Further, the presence of $^{0,4}A_{2\alpha}$ and $^{3,5}A_{2\alpha}$ ions at *m/z* 301.126 and 329.157 indicates that the 6-antenna consists of a branched tri-mannose, thus establishing its structure as $6A_{1,2,3}$. For the two minor Man6 isomers, isomer 2 and isomer 3, the presence of a $^{3,5}A_4$ ion at *m/z* 941.456 suggests a tetra-mannose 6-antenna and a mono-mannose 3-antenna. The C6 substituent of the R6 residue may be determined as a di-mannose for isomer 2, based on the presence of $^{0,4}A_{3\alpha}$ and $^{3,5}A_{3\alpha}$ ions at *m/z* 505.226 and 533.257, and as a single mannose residue for isomer 3, based on the presence of $^{0,4}A_{2\alpha}$ and $^{3,5}A_{2\alpha}$ ions at *m/z* 301.126 and 329.157. Thus, isomers 2 and 3 may be assigned as $6A_{1,2}B_1$ and $6A_{1,2}B_2$, respectively.

Three chromatographic peaks are observed for Man8 isomers (Figure 1e), with their EED spectra shown in Figure S3. For the major isomer, isomer 3, the observation of a $^{3,5}A_4$ ion at *m/z* 1145.556 establishes a penta-mannose 6-antenna, and a di-mannose 3-antenna. Further, the presence of $^{0,4}A_{3\alpha}$ and $^{3,5}A_{3\alpha}$ ions at *m/z* 505.226 and 533.257 suggests that the 6-antenna consists of two di-mannose branches attached to the R6 residue. Thus, isomer 3 can be assigned as $8A_{1,2,3}B_{1,2}$. For the two minor Man8 isomers, isomer 1 and isomer 2, the presence of $^{0,4}A_4$ and $^{3,5}A_4$ ions at *m/z* and 913.425 and 941.456 suggests a tetra-mannose 6-antenna and a di-mannose 3-antenna. The C6 substituew fcnt of the R6 residue may be determined as a single mannose residue for isomer 1, based on the presence of $^{0,4}A_{2\alpha}$ and $^{3,5}A_{2\alpha}$ ions at *m/z* 301.126 and 329.157, and as a di-mannose for isomer 2, based on the presence of $^{0,4}A_{3\alpha}$ and $^{3,5}A_{3\alpha}$ ions at *m/z* 505.226 and 533.257. Thus, isomers1 and 2 may be assigned as $8A_{1,2,3}B_{2,3}$ and $8A_{1,2,3}B_{1,3}$, respectively.

Only one chromatographic peak was observed for Man9 (Figure 1f), with its EED spectrum shown in Figure S4. The presence of $^{0,4}A_4$ and $^{3,5}A_4$ ions at *m/z* 1117.524 and 1145.555 establishes a penta-hexose branch at the 6-antenna and a tri-hexose branch at the 3-antenna (also supported by the presence of a $C_4/Z_{3\beta}$ ion at *m/z* 1247.588 and a $^{1,3}A_4$ ion at *m/z* 723.340). The presence of a $C_{3\alpha}/Z_{4\alpha''}$ ion at *m/z* 635.288 is consistent with a 6-antenna consisting of two di-hexose branches, with one located at the C3 position, and the other at the C6 position based on the observation of $^{0,4}A_3$ and $^{3,5}A_3$ ions at *m/z* 505.225 and 533.257. Thus, the Man9 structure may be assigned as $9A_{1,2,3}B_{1,2,3}$. Note that eight different Man9 structures in five different topologies (Topologies A to E, Figure S5a) may be produced from the tetradecameric *N*-glycan precursor. Here, GlycoDeNovo was able to identify $9A_{1,2,3}B_{1,2,3}$ (Topology A, Figure S5a, or Topology 2,

Figure S5b) as the only one among the top-ranked candidate topologies (Topologies 1 to 5, Figure S5b) based on the observed C-ion series with compositions of Hex, Hex_2, Hex_3, Hex_5, Hex_9, and $Hex_9HexNAc$.

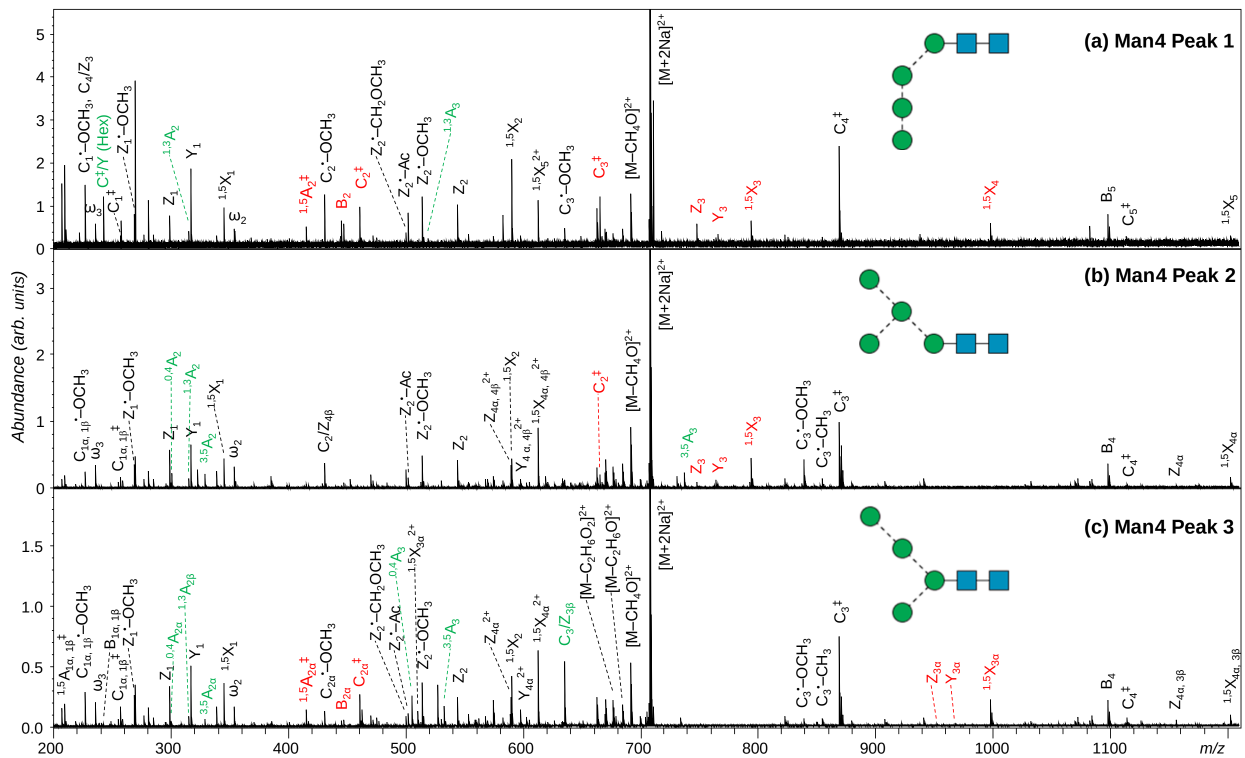


Figure S1. EED spectra of the three Man4 isomers, acquired at retention times marked in Figure 1a. Glycosidic and 1,5-cross ring fragments unique to each topology are labeled in red; linkage-diagnostic cross-ring and secondary fragments are labeled in green. Complete lists of assigned fragments can be found in Supporting Tables S10-12.

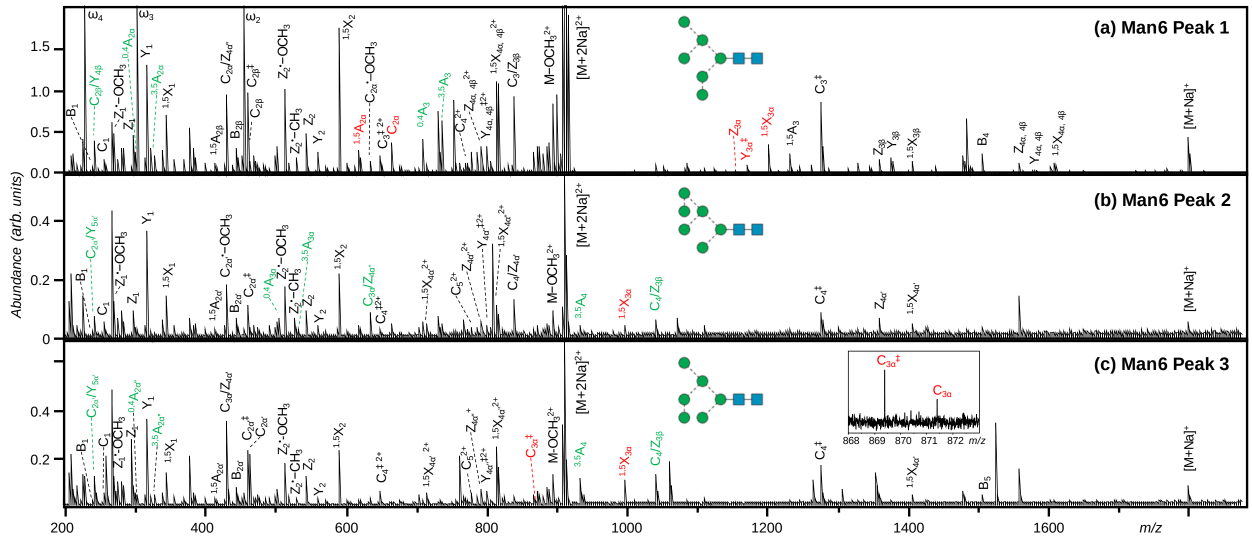


Figure S2. EED spectra of the three Man6 isomers, acquired at retention times marked in Figure 1c. Glycosidic and 1,5-cross ring fragments unique to each topology are labeled in red; linkage-diagnostic cross-ring and secondary fragments are labeled in green. Inset shows the zoomed-in region where $C_{3\alpha}$ and $C_{3\alpha}^{‡}$ ions were observed (but not identified by SNAP). Complete lists of assigned fragments can be found in Supporting Tables S13-15.

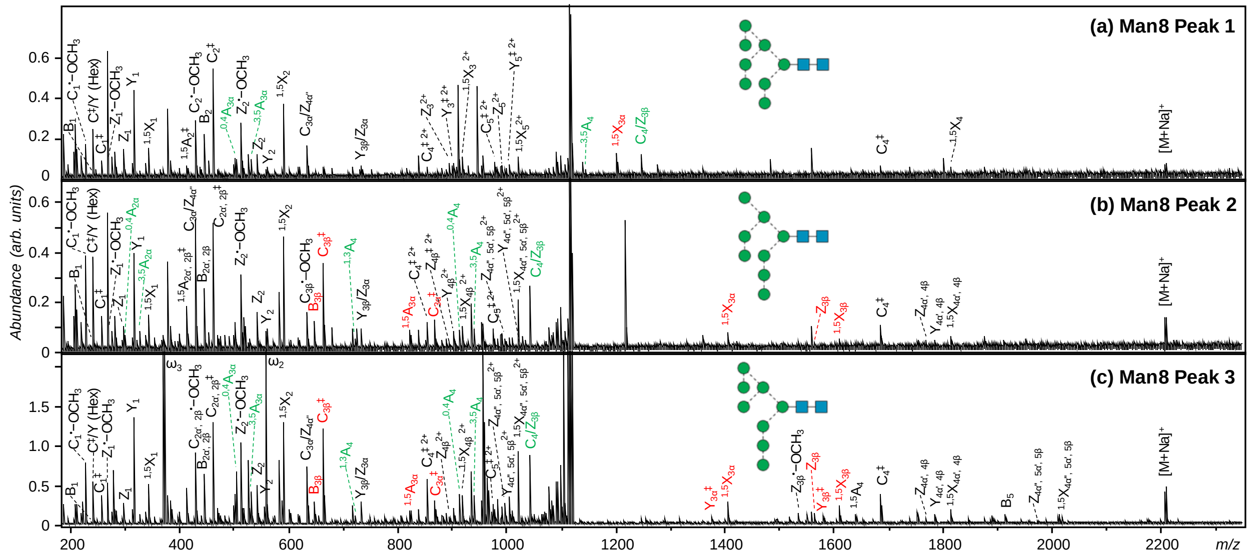


Figure S3. EED spectra of the three Man8 isomers, acquired at retention times marked in Figure 1e. Glycosidic and 1,5-cross ring fragments unique to each topology are labeled in red; linkage-diagnostic cross-ring and secondary fragments are labeled in green. Complete lists of assigned fragments can be found in Supporting Tables S16-18.

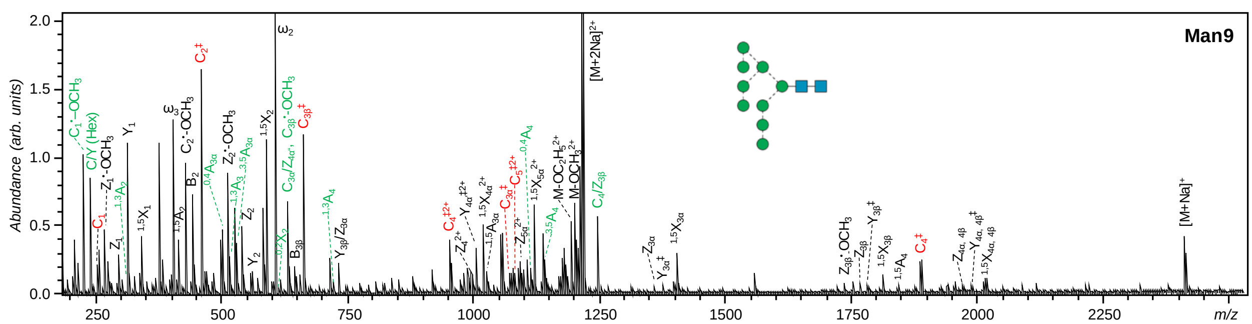
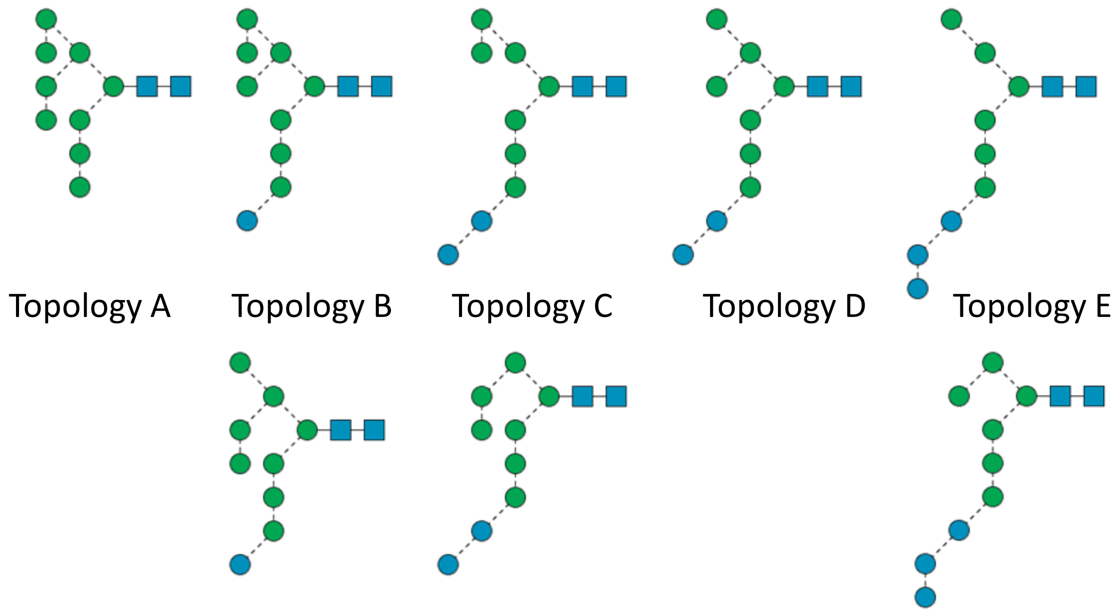


Figure S4. The EED spectrum of the Man9 structure acquired at the retention time marked in Figure 1f. Glycosidic and 1,5-cross ring fragments unique to each topology are labeled in red; linkage-diagnostic cross-ring and secondary fragments are labeled in green. A complete list of assigned fragments can be found in Supporting Tables S19.

(a)



(b)

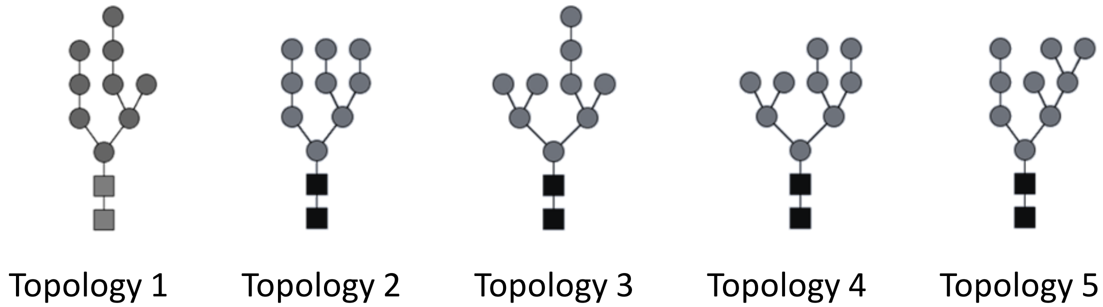
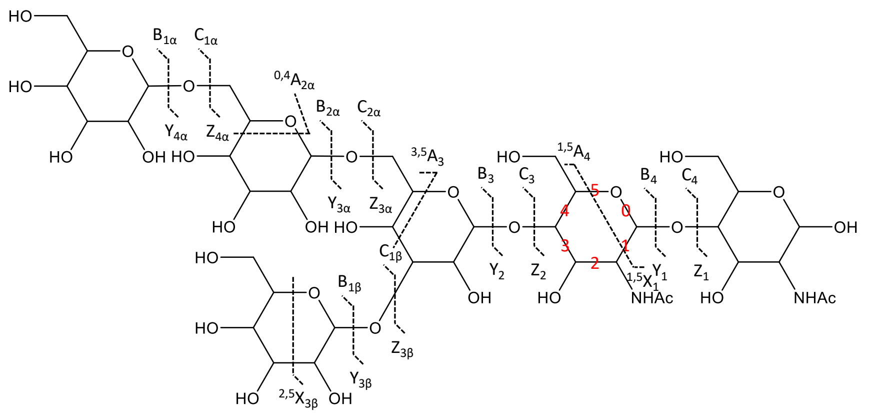
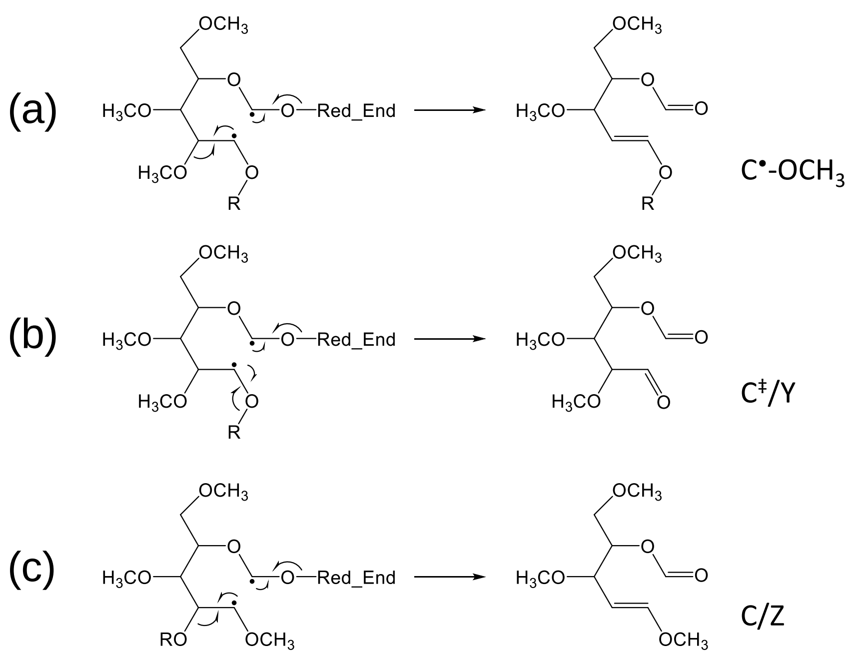


Figure S5. (a) Five different Man9 topologies (A-E) may be derived from the tetradecameric *N*-glycan precursor; (b) Five top-ranked topology candidates as determined by GlycoDeNovo based on the EED tandem mass spectrum of Man9 from RNase B. Note that these candidate topologies are the same as those identified by GlycoDeNovo from the EED tandem mass spectrum of the Man9 glycan standard.[1]



Scheme S1. Illustration of the Domon-Costello nomenclature for glycan fragmentation. Glycosidic fragments are labeled as B-, C- (non-reducing-end), and Y-, Z- (reducing-end) ions, whereas cross-ring fragments are labeled as A- (non-reducing-end) and X- (reducing-end) ions. Superscripts indicate the bonds cleaved in cross-ring fragments (bond indices are shown in the internal GlcNAc residue), whereas the Greek letters α, β, (and γ if necessary) are used to index the primary branches (in decreasing order of their mass values). For secondary branching, ′ (prime) and ″ (double prime) are used as branch indices.



Scheme S2. Proposed EED mechanisms for the formation of (a) C•-OCH_3, (b) C‡/Y, and (c) C/Z ions from the C1-C2 di-radical.

Table S1. LC-MS data used to generate the bar diagram and pie charts shown in Figure 5. The peak area of each isomer in its respective EIC was used to calculate its percentage abundance. (a-c) Percentage abundance of each isomer calculated from each of the three LC-MS run; (d) averaged percentage abundance and standard deviation of each isomer calculated from three technical triplicates.

(a)

Run #1	Man4	Man5	Man6	Man7	Man8	Man9
isomer 1	0.53	0.65	21.51	0.23	0.31	5.44
isomer 2	5.9	1.47	0.64	1.44	0.35	
isomer 3	2.07	41.41	0.8	3.55	11.39	
isomer 4				1.37		
isomer 5				0.94		
Sum	8.5	43.53	22.94	7.53	12.06	5.44

(b)

Run #2	Man4	Man5	Man6	Man7	Man8	Man9
isomer 1	0.58	0.73	18.86	0.24	0.33	5.45
isomer 2	6.76	1.73	0.58	1.58	0.43	
isomer 3	2.46	42.39	0.83	3.87	11.01	
isomer 4				1.44		
isomer 5				0.72		
Sum	9.8	44.86	20.27	7.86	11.76	5.45

(c)

Run #3	Man4	Man5	Man6	Man7	Man8	Man9
isomer 1	0.52	0.71	18.94	0.25	0.27	5.7
isomer 2	6.75	1.7	0.64	1.47	0.39	
isomer 3	2.41	42.09	0.94	3.84	11.36	
isomer 4				1.44		
isomer 5				0.65		
Sum	9.68	44.5	20.52	7.65	12.01	5.7

(d)

average	Man4	Man5	Man6	Man7	Man8	Man9
isomer 1	0.54 ± 0.03	0.70 ± 0.03	19.77 ± 1.23	0.24 ± 0.01	0.30 ± 0.02	5.53 ± 0.12
isomer 2	6.47 ± 0.40	1.63 ± 0.12	0.62 ± 0.03	1.50 ± 0.06	0.39 ± 0.03	
isomer 3	2.31 ± 0.17	41.96 ± 0.41	0.86 ± 0.06	3.75 ± 0.14	11.25 ± 0.17	
isomer 4				1.42 ± 0.03		
isomer 5				0.77 ± 0.12		
Sum	9.33 ± 0.59	44.30 ± 0.56	21.24 ± 1.20	7.68 ± 0.14	11.94 ± 0.13	5.53 ± 0.12

Table S2. List of assigned EED fragments in Figure 3a. All fragments are sodium adducts unless labeled otherwise. Multiple assignments are separated by commas; ω indicates harmonics; the double dagger symbol (‡) indicates that the fragment has two fewer hydrogens than the canonical structures; the double prime symbol (") indicates that the fragment has two more hydrogens than the canonical structure; the dot symbol (•) indicates a radical.

z	Exptl. *m/z*	Theo. *m/z*	Assignment	Δppm	Intensity	*S/N*
1+	211.0940	211.0941	$B_1^{\bullet}$-CH_3O	-0.40	2873742	72.7
1+	227.0889	227.0890	$C_1^{\bullet}$-CH_3O, $C_{2\alpha}/Z_{4\alpha}$	-0.28	7065568	173.7
1+	237.1322	237.1319	$Z_1^{‡\bullet}$-$C_2H_5O_2$	1.29	221641	5.4
1+	241.1046	241.1046	B_1	-0.39	1204942	30.8
1+	243.0838	243.0839	$C_1^{\bullet}$-CH_3, $C_{2\beta}^{‡}/Y_{4\beta}$	-0.29	4814282	118.1
1+	255.1425	255.1424	$Z_1^{\bullet}$-C_2H_5O	0.32	1296933	31.3
1+	257.0995	257.0996	$C_1^{‡}$	-0.19	2378836	57.2
1+	259.1152	259.1152	C_1	0.04	787400	18.9
1+	269.1582	269.1582	$Z_1^{\bullet}$-CH_3O	-0.01	5959412	142.1
1+	285.1531	285.1531	$Z_1^{\bullet}$-CH_3	-0.08	3110948	72.7
1+	299.1688	299.1687	Z_1	0.02	6174722	143.7
1+	315.1414	315.1414	$^{1,3}A_2$, $^{2,4}A_2$	-0.08	2348182	54.5
1+	315.1637	315.1637	$Y_1^{‡}$	0.07	2692867	62.5
1+	317.1793	317.1793	Y_1	0.04	12713578	294.9
1+	345.1743	345.1742	$^{1,5}X_1$	0.08	6450310	148.9
1+	355.1727	355.1726	$^{1,5}A_{2\alpha, 2\beta}$-$C_2H_5O_2$	0.13	525412	12.1
1+	357.1527	357.1520	$^{1,4}A_{2\alpha, 2\beta}^{‡}$	1.93	352527	8.1
1+	371.1676	371.1677	$^{1,5}A_{2\alpha, 2\beta}$-$C_2H_5O$	-0.33	1186438	27.0
1+	379.1341	379.1346	$^{1,4}A_{2\alpha, 2\beta}^{‡}$ + 2Na - H	-1.29	7124488	134.2
1+	385.1833	385.1833	$B_{2\alpha, 2\beta}^{\bullet}$-$C_2H_5O_2$	-0.15	1151389	25.9
1+	401.1774	401.1781	$C_{2\alpha, 2\beta}^{\bullet}$-$C_2H_5O_2$	-1.88	809886	17.8
1+	415.1938	415.1939	$^{1,5}A_{2\alpha, 2\beta}^{‡}$	-0.06	3541254	76.5
1+	417.1733	417.1732	$C_{2\alpha, 2\beta}^{\bullet}$-$C_2H_5O$	0.35	1044355	22.6
1+	417.2095	417.2095	$^{1,5}A_{2\alpha, 2\beta}$	-0.10	2102364	45.4
1+	431.1886	431.1888	$C_{2\alpha, 2\beta}^{\bullet}$-$CH_3O$	-0.30	4566826	98.2
1+	445.2043	445.2044	$B_{2\alpha, 2\beta}$	-0.20	3731052	79.7
1+	447.1837	447.1837	$C_{2\alpha, 2\beta}^{\bullet}$-$CH_3$	-0.05	1275545	27.2
1+	458.2600	458.2583	$^{0,3}X_1$	3.74	285324	6.1
1+	461.1993	461.1993	$C_{2\alpha, 2\beta}^{‡}$	-0.05	13378716	284.7
1+	463.2150	463.2150	$C_{2\alpha, 2\beta}$	0.08	3847508	81.9
1+	484.2740	484.2740	$Z_2^{\bullet}$-$C_2H_5O_2$	0.03	961898	20.1
1+	500.2690	500.2688	$Z_2^{\bullet}$- C_2H_5O	0.38	2063426	42.2

1+	502.2846	502.2845	$Z_2^{\bullet}$-Ac	0.18	3062035	62.7
1+	505.2256	505.2256	$^{0,4}A_3$	0.00	3988789	81.6
1+	514.2846	514.2845	$Z_2^{\bullet}$-CH_3O	0.20	8661585	175.5
1+	519.2412	519.2412	$^{1,3}A_3$, $^{2,4}A_3$	0.00	1553424	31.5
1+	527.2077	527.2081	$^{0,4}A_3$ + 2Na - H	-0.62	699.4572	116.0
1+	530.2796	530.2794	$Z_2^{\bullet}$-CH_3	0.22	1628087	32.7
1+	533.2568	533.2568	$^{3,5}A_3$	-0.03	3814683	76.6
1+	544.2952	544.2951	Z_2	0.26	5061577	100.8
1+	547.2374	547.2361	$^{0,3}A_3^{‡}$	2.33	203949	4.1
2+	549.2517	549.2518	C_3	-0.04	404388	8.1
1+	560.2893	560.2900	$Y_2^{‡}$	-1.14	692690	13.7
1+	561.2523	561.2518	$^{1,4}A_3^{‡}$	0.98	559768	11.1
1+	562.3057	562.3056	Y_2	0.03	2795911	55.3
1+	590.3005	590.3005	$^{1,5}X_2$	-0.08	10477073	202.4
2+	598.7975	598.7971	$Y_{3\alpha,\ 3\beta}$	0.64	355556	6.9
2+	612.7947	612.7945	$^{1,5}X_{3\alpha,\ 3\beta}$	0.17	2468150	46.9
1+	618.3315	618.3318	$^{0,2}X_2$	-0.58	444551	14.1
2+	626.8102	626.8102	$^{0,2}X_{3\alpha,\ 3\beta}$	0.04	150668	2.8
1+	633.2736	633.2729	$C_3^{‡}/Z_{3\beta}$	1.07	812789	15.3
1+	635.2886	635.2885	$C_3/Z_{3\beta}$	0.11	9676599	181.6
1+	651.2844	651.2835	$C_3^{‡}/Y_{3\beta}$	1.51	1392638	25.8
2+	662.8098	662.8096	B_4	0.28	289323	5.4
2+	671.8155	671.8149	C_4	0.87	683674	12.4
1+	679.2790	679.2784	$C_3^{‡}/^{1,5}X_{3\beta}$	0.91	1910368	34.7
1+	681.2938	681.2940	$C_3/^{1,5}X_{3\beta}$	-0.35	724925	13.2
2+	691.8419	691.8417	Z_4	0.24	2875935	51.2
2+	714.8446	714.8444	$^{1,5}X_{4\alpha,\ 4\beta}$	0.22	5736413	100.2
2+	728.8604	728.8601	$^{0,2}X_{4\alpha,\ 4\beta}$	0.44	476334	8.3
1+	734.3793	734.3792	$Y_{3\alpha}/Z_{3\beta}$	0.19	2618777	45.7
2+	736.8463	736.8464	$^{0,2}A_5$	-0.15	535328	9.3
1+	750.3740	750.3741	$Y_{3\alpha}/Y_{3\beta}^{‡}$	-0.15	161816	2.8
2+	772.8868	772.8863	$^{0,4}X_{4\alpha,\ 4\beta}$	0.67	2572913	43.6
2+	809.9048	809.9047	M	0.17	2.21E+08	3710.9
1+	837.3737	837.3727	$C_3^{‡}/Z_{4\beta,4\alpha}$	1.20	566628	9.4
1+	839.3881	839.3883	$C_3/Z_{4\beta,4\alpha}$	-0.30	899309	15.0
1+	880.4147	880.4149	$C_4/Z_{3\beta,3\alpha}$	-0.19	1137246	18.7
1+	1027.4946	1027.4932	$^{1,5}A_3^{‡}$	1.38	832485	12.6

1+	1029.4727	1029.4725	$C_3^{\bullet}$-C_2H_5O	0.14	240826	3.6
1+	1029.5102	1029.5088	$^{1,5}A_3$	1.35	943822	14.3
1+	1041.4741	1041.4725	$C_3^{\ddagger\bullet}$-CH_3O	1.62	466149	7.1
1+	1043.4885	1043.4881	$C_3^{\bullet}$-CH_3O	0.43	1387132	21.0
1+	1059.4831	1059.4830	$C_3^{\bullet}$-CH_3	0.07	759880	11.1
1+	1073.5005	1073.4987	$C_3^{\ddagger}$	1.70	12147318	177.3
1+	1126.5838	1126.5838	$Z_{3\beta,3\alpha}^{\bullet}$-$CH_3O$	-0.04	1689504	23.8
1+	1142.5784	1142.5788	$Z_{3\beta,3\alpha}^{\bullet}$-$CH_3$	-0.29	991560	14.0
1+	1145.5563	1145.5562	$^{3,5}A_4$	0.15	762870	10.7
1+	1156.5877	1156.5944	$Z_{3\beta,3\alpha}$	-5.76	2260766	69.0
1+	1172.5908	1172.5893	$Y_{3\beta,3\alpha}^{\ddagger}$	1.31	1174105	16.5
1+	1174.6054	1174.6050	$Y_{3\beta,3\alpha}$	0.38	299088	4.2
1+	1202.6005	1202.5999	$^{1,5}X_{3\alpha,3\beta}$	0.49	5245769	70.9
1+	1274.6366	1274.6351	$^{1,5}A_4$	1.11	210208	2.7
1+	1286.5997	1286.5988	$C_4^{\ddagger\bullet}$-CH_3O	0.75	1140849	14.8
1+	1302.6305	1302.6301	B_4	0.33	3069241	39.9
1+	1318.6253	1318.6250	$C_4^{\ddagger}$	0.23	1052044	13.7
1+	1330.6826	1330.6836	$Z_{4\alpha,4\beta}^{\bullet}$-$CH_3O$	-0.77	447767	5.8
1+	1346.6797	1346.6785	$Z_{4\alpha,4\beta}^{\bullet}$-$CH_3$	0.84	511886	6.7
1+	1360.6975	1360.6942	$Z_{4\alpha,4\beta}$	2.47	559153	7.0
1+	1376.6908	1376.6891	$Y_{4\alpha,4\beta}^{\ddagger}$	1.25	210316	2.6
1+	1406.6994	1406.6996	$^{1,5}X_{4\alpha,4\beta}$	-0.20	1045958	13.1
1+	1534.7845	1534.7833	M-$C_2H_6O_2$	0.78	233494	2.8
1+	1564.7948	1564.7939	M-CH_4O	0.57	396924	4.8
1+	1596.8212	1596.8201	M	0.63	4163465	48.0

Table S3. List of assigned EED fragments in Figure 3b. All fragments are sodium adducts unless labeled otherwise. Multiple assignments are separated by commas; ω indicates harmonics; the double dagger symbol (‡) indicates that the fragment has two fewer hydrogens than the canonical structures; the double prime symbol (") indicates that the fragment has two more hydrogens than the canonical structure; the dot symbol (•) indicates a radical.

z	Exptl. *m/z*	Theo. *m/z*	Assignment	Δppm	Intensity	*S/N*
1+	211.0940	211.0941	$B_1^{\bullet}$-CH_3O	-0.54	1964612	49.9
1+	213.0733	213.0734	$C_1^{\bullet}$-CH_3O, $C_{2\alpha}/Z_{4\alpha}$	-0.75	355917	9.1
1+	227.0889	227.0890	$C_1^{\bullet}$-C_2H_5O	-0.33	4041060	99.2
1+	241.1046	241.1046	B_1	-0.39	735006	17.9
1+	243.0832	243.0839	$C_1^{\bullet}$-CH_3, $C_{2\beta}^{\ddagger}/Y_{4\beta}$	-3.08	3682156	191.9
1+	255.1430	255.1424	$Z_1^{\bullet}$-C_2H_5O	2.16	858820	20.8
1+	257.0995	257.0996	$C_1^{\ddagger}$	-0.15	1710004	41.4
1+	259.1148	259.1152	C_1	-1.58	1079389	52.6
1+	269.1582	269.1582	$Z_1^{\bullet}$-CH_3O	-0.09	4979386	119.1
1+	285.1531	285.1531	$Z_1^{\bullet}$-CH_3	-0.26	2797937	66.3
1+	296.1104	296.1105	$B_4/^{1,5}X_2$	-0.06	761092	18.0
1+	299.1688	299.1687	Z_1	0.29	4992278	118.3
1+	301.1258	301.1258	$^{0,4}A_{2\alpha}$	-0.08	1306170	30.9
1+	315.1414	315.1414	$^{1,3}A_{2\beta}$, $^{2,4}A_{2\beta}$	-0.14	1157585	26.7
1+	315.1637	315.1637	$Y_1^{\ddagger}$	0.00	1679168	38.7
1+	317.1793	317.1793	Y_1	-0.06	11701574	269.9
1+	323.1077	323.1084	$^{0,4}A_{2\alpha}$ + 2Na - H	-0.29	510571	11.0
1+	329.1571	329.1571	$^{3,5}A_{2\alpha}$	0.08	2609897	59.1
1+	345.1523	345.1520	$^{0,3}A_{2\beta}$	0.93	186375	4.2
1+	345.1742	345.1742	$^{1,5}X_1$	-0.01	5883602	132.8
1+	357.1519	357.1520	$^{1,4}A_{2\beta}^{\ddagger}$	-0.31	485664	11.0
1+	371.1676	371.1676	$^{2,5}A_{2\alpha}^{\ddagger}$	-0.11	929183	21.2
1+	379.1340	379.1346	$^{1,4}A_{2\beta}^{\ddagger}$ + 2Na - H	-0.29	4426286	93.8
1+	401.1779	401.1781	$C_{2\alpha,\,2\beta}^{\bullet}$-$C_2H_5O_2$	-0.48	822935	18.3
1+	415.1938	415.1939	$^{1,5}A_{2\alpha,\,2\beta}^{\ddagger}$	-0.13	2526446	55.4
1+	417.1732	417.1732	$C_{2\alpha,\,2\beta}^{\bullet}$-$C_2H_5O$	0.02	899378	19.7
1+	417.2095	417.2095	$^{1,5}A_{2\alpha,\,2\beta}$	-0.06	1250871	27.4
1+	431.1887	431.1888	$C_{2\alpha,\,2\beta}^{\bullet}$-$CH_3O$	-0.25	5162347	112.2

1+	445.2044	445.2044	$B_{2\alpha, 2\beta}$	-0.15	3342667	71.7
1+	447.1838	447.1837	$C_{2\alpha, 2\beta}{}^{\bullet}$-$CH_3$	0.17	876116	18.8
1+	458.2579	458.2583	$^{0,3}X_1$	-0.80	311587	6.6
1+	461.1993	461.1993	$C_{2\alpha, 2\beta}{}^{\ddagger}$	-0.14	12016012	255.8
1+	463.2150	463.2150	$C_{2\alpha, 2\beta}$	0.01	3256405	69.1
1+	500.2688	500.2688	$Z_2{}^{\bullet}$- C_2H_5O	0.04	1484287	30.3
1+	502.2845	502.2845	$Z_2{}^{\bullet}$-Ac	-0.02	2679921	54.8
1+	503.2107	503.2099	$^{0,4}A_3{}^{\ddagger}$	1.53	102578	2.1
1+	505.2259	505.2256	$^{0,4}A_3$	0.59	5238566	107.1
1+	514.2846	514.2845	$Z_2{}^{\bullet}$-CH_3O	0.20	6694641	135.5
1+	519.2387	519.2412	$^{1,3}A_3$, $^{2,4}A_3$	-4.73	789087	16.0
1+	527.2077	527.2076	$^{0,4}A_3$ + 2Na - H	0.28	5278229	100.0
1+	530.2794	530.2794	$Z_2{}^{\bullet}$-CH_3	-0.07	1403994	28.2
1+	533.2568	533.2568	$^{3,5}A_3$	-0.07	2719874	54.7
1+	544.2955	544.2951	Z_2	0.83	3996890	80.0
2+	549.2518	549.2518	C_3	0.05	366282	7.3
1+	560.2901	560.2900	$Y_2{}^{\ddagger}$	0.14	433864	8.6
1+	562.3057	562.3056	Y_2	0.07	2080188	41.4
1+	590.3006	590.3005	$^{1,5}X_2$	0.09	8360624	163.3
2+	612.7946	612.7945	$^{1,5}X_{3\alpha, 3\beta}$	0.14	1643673	31.7
1+	633.2733	633.2729	$C_3{}^{\ddagger}/Z_{3\beta}$	0.68	629639	12.0
1+	635.2885	635.2885	$C_3/Z_{3\beta}$	-0.05	8222604	156.2
1+	651.2833	651.2835	$C_3{}^{\ddagger}/Y_{3\beta}$	-0.21	1176072	22.0
2+	662.8097	662.8096	B_4	0.13	292446	5.5
2+	671.8153	671.8149	C_4	0.62	513635	9.4
1+	679.2791	679.2784	$C_3{}^{\ddagger}/{}^{1,5}X_{3\beta}$	1.04	1272322	23.3
2+	691.8419	691.8417	Z_4	0.27	1809543	32.5
2+	700.8484	700.8470	Y_4	2.05	273046	4.9
2+	714.8446	714.8444	$^{1,5}X_{4\alpha, 4\beta}$	0.26	5811758	102.5
2+	728.8597	728.8601	$^{0,2}X_{4\alpha, 4\beta}$	-0.54	502063	8.9
1+	734.3782	734.3792	$Y_{3\alpha}/Z_{3\beta}$	-1.32	2303110	40.6
2+	736.8468	736.8464	$^{0,2}A_5$	0.46	745837	13.2
2+	743.8661	743.8654	$^{1,4}X_{4\alpha, 4\beta}$	0.94	133246	2.3
1+	750.3746	750.3741	$Y_{3\alpha}/Y_{3\beta}{}^{\ddagger}$	0.63	157456	2.7

2+	772.8868	772.8863	$^{0,4}X_{4\alpha, 4\beta}$	0.67	2013864	34.1
2+	809.9047	809.9047	M	0.07	1.67E+08	2783.1
1+	837.3736	837.3727	$C_3^{\ddagger}/Z_{4\beta,4\alpha}$	1.16	385998	6.4
1+	839.3887	839.3883	$C_3/Z_{4\beta,4\alpha}$	0.41	714603	11.8
1+	855.3844	855.3832	$C_3^{\ddagger}/Y_{4\beta,4\alpha}$	1.39	551698	9.1
1+	880.4151	880.4149	$C_4/Z_{3\beta,3\alpha}$	0.21	711735	11.5
1+	1027.4944	1027.4932	$^{1,5}A_3^{\ddagger}$	1.18	738329	11.1
1+	1029.5094	1029.5088	$^{1,5}A_3$	0.55	806133	12.1
1+	1041.4727	1041.4725	$C_3^{\ddagger\bullet}$-CH_3O	0.19	479437	7.2
1+	1043.4884	1043.4881	$C_3^{\bullet}$-CH_3O	0.27	1554097	23.4
1+	1059.4829	1059.4830	$C_3^{\bullet}$-CH_3	-0.07	859731	12.4
1+	1073.5002	1073.4987	$C_3^{\ddagger}$	1.44	9500072	137.5
1+	1126.5841	1126.5838	$Z_{3\beta,3\alpha}^{\bullet}$-$CH_3O$	0.25	770422	10.8
1+	1142.5804	1142.5787	$Z_{3\beta,3\alpha}^{\bullet}$-$CH_3$	1.47	539508	7.5
1+	1145.5559	1145.5562	$^{3,5}A_4$	-0.22	732848	10.3
1+	1156.5939	1156.5944	$Z_{3\beta,3\alpha}$	-0.46	930737	13.0
1+	1172.5907	1172.5893	$Y_{3\beta,3\alpha}^{\ddagger}$	1.21	828507	11.6
1+	1174.6058	1174.6050	$Y_{3\beta,3\alpha}$	0.69	349303	4.9
1+	1202.6001	1202.5999	$^{1,5}X_{3\alpha, 3\beta}$	0.17	3204361	43.2
1+	1274.6358	1274.6351	$^{1,5}A_4$	0.50	327922	4.3
1+	1286.5999	1286.5988	$C_4^{\bullet\ddagger}$-CH_3O	0.88	1201965	15.6
1+	1302.6297	1302.6301	B_4	-0.32	2688109	35.0
1+	1318.6252	1318.6250	$C_4^{\ddagger}$	0.14	1088242	14.2
1+	1406.7013	1406.6996	$^{1,5}X_{4\alpha, 4\beta}$	1.17	770838	9.7
1+	1534.7764	1534.7833	M-$C_2H_6O_2$	-4.48	205359	2.5
1+	1552.7900	1552.7939	M-C_2H_6O	-2.56	177809	2.2
1+	1564.7944	1564.7939	M-CH_4O	0.28	519313	6.3
1+	1596.8209	1596.8201	M	0.46	3462592	40.4

Table S4. List of assigned EED fragments in Figure 3c. All fragments are sodium adducts unless labeled otherwise. Multiple assignments are separated by commas; ω indicates harmonics; the double dagger symbol (‡) indicates that the fragment has two fewer hydrogens than the canonical structures; the double prime symbol (") indicates that the fragment has two more hydrogens than the canonical structure; the dot symbol (•) indicates a radical.

z	Exptl. *m/z*	Theo. *m/z*	Assignment	Δppm	Intensity	*S/N*
1+	211.0940	211.0941	$B_1^{\bullet}$-CH_3O	-0.69	1647187	80.2
1+	213.0732	213.0734	$C_1^{\bullet}$-$C_2H_5O_2$	-0.84	401616	15.8
1+	227.0889	227.0890	$C_1^{\bullet}$-CH_3O	-0.48	6602338	336.4
1+	236.0893	236.0894	$C_4^{\ddagger}$/$Z_2^{\bullet}$-CH_3	-0.55	471343	19.4
1+	237.1320	237.1319	$Z_1^{\ddagger\bullet}$-$C_2H_5O_2$	0.03	479253	19.8
1+	238.1049	238.1050	C_4/$Z_2^{\bullet}$-CH_3	-0.52	849975	39.0
1+	239.1475	239.1476	$Z_1^{\bullet}$-$C_2H_5O_2$	-0.43	1058638	49.8
1+	241.1045	241.1046	B_1	-0.43	1456488	70.4
1+	253.1268	253.1269	$Z_1^{\ddagger\bullet}$-C_2H_5O	-0.45	388208	15.1
1+	254.0998	254.0999	$C_1^{\bullet}$-CH_3	-0.58	449043	18.3
1+	255.1425	255.1425	$Z_1^{\bullet}$-C_2H_5O	-0.13	1100916	52.0
1+	257.0995	257.0996	$C_1^{\ddagger}$	-0.27	4525083	229.0
1+	259.1152	259.1152	C_1	-0.11	3214072	161.2
1+	268.1154	268.1155	C_4/Z_2	-0.39	1007005	47.1
1+	269.1581	269.1582	$Z_1^{\bullet}$-CH_3O	-0.39	9260723	473.8
1+	285.1531	285.1531	$Z_1^{\bullet}$-CH_3	-0.33	4473650	224.7
1+	296.1104	296.1105	B_4/$^{1,5}X_2$	-0.26	1150634	53.6
1+	299.1687	299.1687	Z_1	-0.18	10032741	505.4
1+	301.1257	301.1258	$^{0,4}A_{2\alpha}$	-0.21	4885688	242.9
1+	315.1413	315.1414	$^{1,3}A_{2\alpha, 2\beta}$, $^{2,4}A_{2\alpha, 2\beta}$	-0.30	1843856	87.7
1+	315.1636	315.1637	$Y_1^{\ddagger}$	-0.36	3331345	162.4
1+	317.1792	317.1793	Y_1	-0.19	17699662	883.7
1+	323.1077	323.1078	$^{0,4}A_{2\alpha}$ + 2Na - H	-0.29	5236821	114.1
1+	329.1570	329.1571	$^{3,5}A_{2\alpha}$	-0.38	4747952	231.8
1+	341.1569	341.1571	$^{2,5}A_{2\alpha}$/$Z_{4\alpha, 3\beta}$	-0.33	1121335	50.6
1+	345.1741	345.1742	$^{1,5}X_2$	-0.27	9980800	486.8
1+	353.1569	353.1571	$^{1,5}A_{2\alpha}^{\ddagger}$/$Z_{4\alpha}^{\bullet}$-$CH_3O$	-0.66	466721	18.0
1+	355.1726	355.1728	$^{1,5}A_{2\alpha}$/$Z_{4\alpha}^{\bullet}$-CH_3O	-0.48	2212701	103.2
1+	369.1518	369.1520	$C_{2\alpha}$/$Z_{4\alpha}^{\bullet}$-$C_2H_5O_2$	-0.37	758484	31.8

1+	371.1675	371.1677	$^{1,5}A_{2\alpha}/Y_{4\alpha}{}^{\bullet}\text{-}CH_3O$	-0.36	1732078	79.0
1+	383.1676	383.1677	$C_{2\alpha}{}^{\ddagger}/Z_{4\alpha}{}^{\bullet}\text{-}C_2H_5O$	-0.35	1213431	53.3
1+	385.1467	385.1470	$C_{2\alpha}/Z_{4\alpha}{}^{\bullet}\text{-}C_2H_5O$	-0.70	894140	38.0
1+	385.1832	385.1833	$^{1,5}A_{2\alpha}/Z_{4\alpha}$	-0.36	4350751	203.8
1+	399.1624	399.1626	$C_{2\alpha}{}^{\ddagger}/Z_{4\alpha}{}^{\bullet}\text{-}CH_3O$	-0.35	1340301	58.7
1+	401.1780	401.1783	$C_{2\alpha}/Z_{4\alpha}{}^{\bullet}\text{-}CH_3O$	-0.57	1650441	73.4
1+	403.1938	403.1939	$^{1,5}A_{2\alpha}/Y_{4\alpha}$	-0.16	428377	15.4
1+	413.1780	413.1782	$B_{2\alpha}/Z_{4\alpha}$	-0.40	1048466	44.3
1+	414.2319	414.2321	$^{0,3}X_1{}^{\bullet}\text{-}C_2H_5O$	-0.55	921187	38.3
1+	415.1573	415.1574	$C_{2\alpha}{}^{\ddagger}/{}^{1,5}X_{4\alpha}{}^{\bullet}\text{-}C_2H_5O_2$	-0.36	512446	19.1
1+	417.1730	417.1731	$C_{2\alpha}{}^{\ddagger}/Y_{4\alpha}{}^{\bullet}\text{-}CH_3O$	-0.25	949086	39.6
1+	428.2475	428.2478	$^{0,3}X_1{}^{\bullet}\text{-}CH_3O$	-0.58	903541	37.2
1+	429.1730	429.1731	$C_{2\alpha}{}^{\ddagger}/Z_{4\alpha''}$	-0.18	1623043	70.8
1+	431.1886	431.1888	$C_{2\alpha}/Z_{4\alpha''}$	-0.51	10088251	465.9
1+	447.1835	447.1837	$C_{2\alpha}{}^{\ddagger}/Y_{4\alpha}$	-0.53	2595410	114.7
1+	449.1992	449.1993	$C_{2\alpha}/Y_{4\alpha}$	-0.30	1087601	45.2
1+	453.1712	453.1708	$C_{2\alpha}/Z_{4\alpha''}$ + 2Na - H	0.86	1737426	37.0
1+	458.2581	458.2583	$^{0,3}X_1$	-0.34	571892	21.2
1+	459.1835	459.1837	$B_{2\alpha}/{}^{1,5}X_{4\alpha}$	-0.33	467938	16.5
1+	470.2582	470.2583	$Z_2{}^{\bullet}\text{-}C_3H_7O_2$	-0.29	3208600	140.8
1+	472.2738	472.2739	$Z_2{}^{''\bullet}\text{-}C_3H_7O_2$	-0.29	2505702	108.9
1+	473.1993	473.1993	$^{0,4}A_{3\alpha}/Z_{4\alpha}$	0.01	627878	23.4
1+	475.1784	475.1787	$C_{2\alpha}/{}^{2,5}X_{4\alpha}{}^{\bullet}\text{-}C_2H_5O$	-0.55	3606382	157.5
1+	477.1941	477.1942	$C_{2\alpha}/{}^{1,5}X_{4\alpha}$	-0.35	2223511	95.2
1+	482.2584	482.2583	$Z_2{}^{\ddagger\bullet}\text{-}C_2H_5O_2$	0.30	516640	18.3
1+	484.2737	484.2740	$Z_2{}^{\bullet}\text{-}C_2H_5O_2$	-0.55	1300204	53.6
1+	487.2145	487.2150	$^{2,4}A_{3\alpha}/Z_{4\alpha}$	-0.91	448793	15.1
1+	491.2098	491.2099	$^{0,4}A_{3\alpha}/Y_{4\alpha}$	-0.30	1531173	63.4
1+	500.2687	500.2689	$Z_2{}^{\bullet}$- C_2H_5O	-0.33	2392493	101.0
1+	502.2843	502.2845	$Z_2{}^{\bullet}$-Ac	-0.29	4120549	177.4
1+	503.2094	503.2099	$B_{2\alpha}/{}^{2,5}X_{4\alpha}$	-0.93	549011	19.4
1+	512.2689	512.2689	$Z_2{}^{\ddagger\bullet}\text{-}CH_3O$	0.03	591915	21.0
1+	514.2843	514.2846	$Z_2{}^{\bullet}\text{-}CH_3O$	-0.46	11465812	497.7
1+	519.2046	519.2049	$C_{2\alpha}/{}^{2,5}X_{4\alpha}{}^{\bullet}\text{-}C_2H_5O$	-0.46	1638468	66.9

1+	529.2255	529.2256	$B_{2\alpha}{}^{\bullet}$-CH_3/$^{2,4}X_{4\alpha}$	-0.14	654269	23.5
1+	530.2793	530.2795	$Z_2{}^{\bullet}$-CH_3	-0.35	2629396	109.2
1+	544.2949	544.2951	Z_2	-0.32	8216068	348.0
1+	545.2567	545.2569	$^{2,5}A_{3\alpha}$/$Z_{4\alpha}$	-0.33	587700	20.4
1+	547.2358	547.2361	$B_{2\alpha}$/$^{3,5}X_{4\alpha}$	-0.63	1666232	66.7
1+	559.2724	559.2725	$^{1,5}A_{2\alpha}{}^{\bullet}$-$C_2H_5O$	-0.17	426964	13.3
1+	560.2899	560.2900	$Y_2{}^{‡}$	-0.26	1142142	43.7
1+	561.2513	561.2518	$^{0,2}A_{3\alpha}$/$Z_{4\alpha}$	-0.79	714206	25.5
1+	562.3054	562.3056	Y_2	-0.38	2588801	105.1
1+	567.7785	567.7790	$Z_{3\beta}{}^{\bullet}$-CH_3O	-0.90	768813	27.8
1+	573.2515	573.2518	$B_{2\alpha}{}^{‡}$/$^{0,4}X_{4\alpha}$	-0.56	1676121	65.6
1+	575.2669	575.2674	$B_{2\alpha}$/$^{0,4}X_{4\alpha}$	-0.82	927723	34.1
1+	590.3003	590.3005	$^{1,5}X_2$	-0.48	13528799	556.7
1+	603.2620	603.2624	$C_{2\alpha}{}^{‡\bullet}$-$C_2H_5O_2$	-0.73	1882890	72.4
1+	605.2772	605.2780	$C_{2\alpha}{}^{\bullet}$-$C_2H_5O_2$	-1.18	1118721	41.1
1+	614.2785	614.2783	C_4/$Z_{3\beta}{}^{\bullet}$-$C_2H_5O_2$	0.32	458781	14.0
1+	618.3315	618.3318	$^{0,2}X_2$	-0.58	798860	27.9
1+	619.2933	619.2937	$^{1,5}A_{2\alpha}{}^{‡}$	-0.70	3455088	136.8
1+	621.2727	621.2730	$C_{2\alpha}{}^{\bullet}$-C_2H_5O	-0.38	1022139	37.1
1+	621.3090	621.3093	$^{1,5}A_{2\alpha}$	-0.45	3232413	127.7
1+	633.2727	633.2729	$C_{2\alpha}{}^{‡\bullet}$-CH_3O	-0.34	841844	29.3
1+	635.2882	635.2886	$C_{2\alpha}{}^{\bullet}$-CH_3O	-0.56	1163032	42.3
1+	649.3040	649.3042	$B_{2\alpha}$	-0.25	936522	31.1
1+	651.2835	651.2835	$C_{2\alpha}{}^{\bullet}$-CH_3	0.04	738452	23.5
2+	654.8231	654.8236	$Z_{4\alpha}{}^{\bullet}$-$C_3H_6O_2$	-0.76	561843	16.8
1+	665.2988	665.2991	$C_{2\alpha}{}^{‡}$	-0.51	5427695	189.3
2+	655.8014	655.8021	$C_4{}^{\bullet}$-CH_3O	-1.10	2124705	76.2
2+	660.8231	660.8236	$Z_{4\alpha}{}^{‡\bullet}$-$C_2H_5O_2$	-0.77	781366	25.1
2+	661.8312	661.8314	$Z_{4\alpha}{}^{\bullet}$-$C_2H_5O_2$	-0.29	978408	32.6
1+	667.3146	667.3148	$C_{2\alpha}$	-0.28	3317750	114.0
2+	668.8204	668.8211	$Z_{4\alpha}{}^{‡\bullet}$-C_2H_5O	-1.02	974140	30.5
2+	669.8283	669.8289	$Z_{4\alpha}{}^{\bullet}$-C_2H_5O	-0.84	2825825	96.5
2+	671.8147	671.8152	C_4	-0.76	2016361	67.6
2+	676.8363	676.8367	$Z_{4\alpha}{}^{\bullet}$-CH_3O	-0.70	6609414	231.4

2+	683.8255	683.8263	$Z_{4\alpha, 3\beta}^{\ddagger\bullet}-CH_3$	-1.16	816341	24.8
2+	684.8339	684.8342	$Z_{4\alpha, 3\beta}^{\bullet}-CH_3$	-0.38	2892606	98.8
2+	691.8416	691.8420	$Z_{4\alpha, 3\beta}$	-0.58	6765116	222.3
2+	699.8393	699.8395	$^{1,5}X_{4\alpha}-CH_3O$	-0.30	4379086	142.4
1+	704.3097	704.3100	$B_4/^{1,5}X_{4\alpha}$	-0.38	3571359	115.4
1+	709.3248	709.3253	$^{0,4}A_3$	-0.69	7041628	231.5
2+	714.8441	714.8447	$^{1,5}X_{4\alpha, 3\beta}$	-0.91	18353794	572.0
2+	728.8601	728.8604	$^{0,2}X_{4\alpha, 3\beta}$	-0.41	1091315	30.3
1+	731.3070	731.3073	$^{0,4}A_3$ + 2Na - H	-0.48	11962754	371.4
1+	734.3789	734.3792	$Y_{3\alpha}/Z_{3\beta}$	-0.34	2466867	73.5
2+	735.8675	735.8682	$^{0,3}X_{4\alpha}-CH_3$	-1.00	1793287	52.3
1+	737.3565	737.3566	$^{3,5}A_3$	-0.19	4477020	136.5
2+	742.8566	742.8578	$^{3,4}X_{4\alpha}-CH_3O$	-1.61	829596	20.7
2+	743.8650	743.8657	$^{1,5}X_{4\alpha, 3\beta}$	-0.82	437563	9.2
2+	749.8648	749.8657	$^{0,3}X_{4\alpha, 3\beta}-2H$	-1.20	677969	16.2
2+	756.8732	756.8735	$^{0,4}X_{4\alpha, 3\beta}-CH_3O$	-0.43	458285	9.7
2+	765.8773	765.8788	$^{1,3}X_{4\alpha, 3\beta}$	-1.85	1866801	51.1
2+	771.8780	771.8788	$M-C_3H_6O_2$	-1.02	3722016	98.9
2+	772.8865	772.8866	$^{0,4}X_{4\alpha, 3\beta}$	-0.12	4496429	120.2
2+	778.8861	778.8866	$M-C_2H_6O_2$	-0.67	4284023	114.4
2+	786.8836	786.8841	$M-C_2H_6O$	-0.65	5277520	141.7
1+	791.3676	791.3672	$^{1,5}A_3^{\ddagger}/Z_{3\beta}$	0.48	539637	11.3
1+	793.3821	793.3828	$^{1,5}A_3/Z_{3\beta}$	-0.93	2023665	52.1
2+	793.8912	793.8919	$M-CH_4O$	-0.86	11798102	321.2
2+	801.8889	801.8894	$M-CH_4$	-0.62	2088985	52.2
2+	809.9047	809.9047	M	0.05	2849046272	75853.4
1+	839.3880	839.3883	$C_3/Z_{3\beta}$	-0.39	13325132	369.6
1+	855.3830	855.3832	$C_3^{\ddagger}/Y_{3\beta}$	-0.25	1573691	40.3
1+	883.3776	883.3782	$C_3/^{2,5}X_{4\alpha}^{\bullet}-C_2H_5O$	-0.64	3253004	92.7
1+	908.4679	908.4684	$Z_{3\alpha}^{\bullet}-C_2H_5O$	-0.52	1146433	30.0
1+	910.4840	910.4840	$^{0,4}X_{2\beta}$	-0.11	695106	16.6
1+	922.4832	922.4841	$Z_{3\alpha}^{\bullet}-CH_3O$	-0.99	539720	12.8
1+	938.4792	938.4790	$Z_{3\alpha}^{\bullet}-CH_3$	0.21	545839	13.0
1+	952.4945	952.4946	$Z_{3\alpha}$	-0.10	1115516	31.1

1+	955.4357	955.4357	$B_3/^{3,5}X_{4\alpha,\,3\beta}$	0.08	509621	12.8
1+	968.4897	968.4896	$Y_{3\alpha}{}^{‡}$	0.09	1579545	49.6
1+	998.4996	998.5001	$^{1,5}X_{3\alpha}$	-0.49	7903364	267.2
1+	1011.4616	1011.4619	$C_3{}^{‡\bullet}$-$C_2H_5O_2$	-0.33	629658	16.5
1+	1013.4744	1013.4774	$C_3{}^{\bullet}$-$C_2H_5O_2$	-2.98	458754	10.7
1+	1027.4935	1027.4932	$^{1,5}A_3{}^{‡}$	0.27	1492620	45.4
1+	1029.5094	1029.5088	$^{1,5}A_3$	0.57	1127810	33.2
1+	1041.4725	1041.4725	$C_3{}^{‡\bullet}$-CH_3O	0.03	1147636	33.8
1+	1043.4886	1043.4881	$C_3{}^{\bullet}$-CH_3O	0.48	1294448	38.7
1+	1052.4884	1052.4884	$C_4/Z_{3\beta}{}^{\bullet}$-$CH_3O$	0.00	485687	11.6
1+	1057.5033	1057.5037	B_3	-0.43	449714	10.3
1+	1059.4824	1059.4830	$C_3{}^{\bullet}$-CH_3	-0.61	1688684	50.6
1+	1066.5032	1066.5041	$B_4/Z_{3\beta}$	-0.83	516141	12.2
1+	1073.4984	1073.4987	$C_3{}^{‡}$	-0.28	15357848	497.9
1+	1075.5153	1075.5143	C_3	0.89	4832515	153.5
1+	1084.5148	1084.5146	$C_4/Z_{3\beta}$	0.13	1319147	38.5
1+	1112.5092	1112.5096	$B_4/^{1,5}X_{3\beta}$	-0.31	2170512	66.3
1+	1142.5789	1142.5787	$Y_{4\alpha'}/Z_{4\alpha''}$	0.12	690849	17.3
1+	1145.5560	1145.5562	$^{3,5}A_4$	-0.16	1638224	47.4
1+	1274.6365	1274.6351	$^{1,5}A_4$	1.08	1017111	25.0
1+	1276.6136	1276.6144	$C_4{}^{‡\bullet}$-$C_2H_5O_2$	-0.68	3924661	109.8
1+	1286.5985	1286.5988	$C_4{}^{‡\bullet}$-CH_3O	-0.25	1285552	32.8
1+	1288.6136	1288.6144	$C_4{}^{\bullet}$-CH_3O	-0.68	1300945	33.3
1+	1302.6296	1302.6301	B_4	-0.35	4915037	138.6
1+	1318.6247	1318.6250	$C_4{}^{‡}$	-0.22	1658910	43.6
1+	1330.6817	1330.6837	$Z_{4\alpha,\,3\beta}{}^{\bullet}$-$CH_3O$	-1.49	1059375	26.1
1+	1346.6791	1346.6786	$Z_{4\alpha,\,3\beta}{}^{\bullet}$-$CH_3$	0.39	684842	15.2
1+	1360.6965	1360.6942	$Z_{4\alpha,\,3\beta}$	1.69	1216143	30.0
1+	1376.6882	1376.6668	$^{2,4}A_5$	15.52	751526	16.7
1+	1378.7056	1378.7047	$Y_{4\alpha,\,3\beta}$	0.65	1914688	49.9
1+	1406.6988	1406.6996	$^{1,5}X_{4\alpha,\,3\beta}$	-0.62	3157117	85.3
1+	1520.7673	1520.7678	$^{0,4}X_{4\alpha,\,3\beta}{}^{‡}$	-0.29	683584	14.3
1+	1522.7832	1522.7834	$^{0,4}X_{4\alpha,\,3\beta}$	-0.12	735320	15.7
1+	1534.7828	1534.7833	M-$C_2H_6O_2$	-0.33	654024	13.5

1+	1550.7802	1550.7783	M-C_2H_6O	1.16	542227	10.3
1+	1564.7937	1564.7939	M-CH_4O	-0.18	1331505	31.6
1+	1596.8192	1596.8201	M	-0.57	8028314	214.4

Table S5. List of assigned EED fragments in Figure 4a. All fragments are sodium adducts unless labeled otherwise. Multiple assignments are separated by commas; ω indicates harmonics; the double dagger symbol (‡) indicates that the fragment has two fewer hydrogens than the canonical structures; the double prime symbol (") indicates that the fragment has two more hydrogens than the canonical structure; the dot symbol (•) indicates a radical.

z	Exptl. *m/z*	Theo. *m/z*	Assignment	Δppm	Intensity	*S/N*
1+	211.0940	211.0941	$B_1^{\bullet}$-CH_3O	-0.45	1055191	32.6
1+	227.0889	227.0890	$C_1^{\bullet}$-CH_3O or $C_{3\alpha}/Z_{4\alpha}$	-0.28	2814648	85.2
1+	241.1045	241.1046	B_1	-0.56	320719	14.8
1+	243.0839	243.0839	$C_{2\beta, 2\alpha}^{‡}/Y_{5\beta, 5\alpha}$	-0.24	2871041	86.3
1+	259.1151	259.1152	C_1	-0.27	422941	21.5
1+	269.1578	269.1582	$Z_1^{\bullet}$-CH_3O	-1.65	5109139	328.9
1+	285.1531	285.1531	$Z_1^{\bullet}$-CH_3	0.06	861134	25.3
1+	299.1688	299.1687	Z_1	0.29	976914	28.2
1+	315.1637	315.1637	$Y_1^{‡}$	0.26	494156	14.2
1+	317.1794	317.1793	Y_1	0.16	4023138	115.4
1+	345.1743	345.1742	$^{1,5}X_1$	0.25	1519902	43.8
1+	415.1938	415.1939	$^{1,5}A_{2\alpha, 2\beta}^{‡}$	-0.23	1251157	34.3
1+	417.1715	417.1732	$C_2^{\bullet}$-C_2H_5O	-4.13	349829	9.6
1+	417.2097	417.2095	$^{1,5}A_{2\alpha, 2\beta}$	0.49	492772	13.5
1+	431.1888	431.1888	$C_2^{\bullet}$-CH_3O	0.07	2977497	81.2
1+	445.2045	445.2044	B_2	0.14	1447751	38.9
1+	447.1838	447.1837	$C_2^{\bullet}$-CH_3	0.22	760957	20.4
1+	461.1994	461.1993	$C_2^{‡}$	0.12	3672059	97.2
1+	463.2151	463.2150	C_2	0.19	719571	35.6
1+	484.2748	484.2740	$Z_2^{\bullet}$-$C_2H_5O_2$	1.74	165490	4.3
1+	502.2847	502.2845	$Z_2^{\bullet}$-Ac	0.24	1240317	31.9
1+	514.2847	514.2845	$Z_2^{\bullet}$-CH_3O	0.40	2183949	55.8
1+	519.2412	519.2412	$^{1,3}A_3$, $^{2,4}A_3$	0.06	629363	16.1
1+	544.2957	544.2951	Z_2	1.16	1234656	30.7
1+	562.3058	562.3056	Y_2	0.37	509542	12.5
1+	590.3006	590.3005	$^{1,5}X_2$	0.14	2838203	67.9
1+	619.2939	619.2936	$^{1,5}A_3^{‡}$	0.41	555355	13.1
1+	621.3075	621.3093	$^{1,5}A_3$	-2.91	494165	20.3
1+	635.2888	635.2885	$C_3^{\bullet}$-CH_3O	0.36	514830	12.0
1+	649.3045	649.3042	B_3	0.43	586959	13.5

1+	665.2999	665.2991	$C_3^‡$	1.12	3117244	71.0
1+	667.3146	667.3148	C_3	-0.28	635339	14.5
1+	709.3232	709.3253	$^{0,4}A_4$	-3.02	1085660	49.3
2+	714.8451	714.8444	$^{1,5}X_{3\alpha, 3\beta}$	0.87	338438	7.6
1+	723.3390	723.3410	$^{1,3}A_{4\beta}$, $^{2,4}A_{4\beta}$	-2.74	410707	14.6
1+	731.3049	731.3073	$^{0,4}A_4$ + 2Na - H	-3.31	1521600	70.5
1+	734.3796	734.3792	$Y_{3\alpha}/Z_{3\beta}$	0.61	504915	11.3
1+	737.3567	737.3566	$^{3,5}A_4$	0.04	725807	16.2
2+	816.8950	816.8943	$^{1,5}X_{4\alpha, 4\beta}$	0.82	555717	11.6
1+	839.3884	839.3883	$C_4/Z_{3\beta}$	0.10	2573351	52.4
2+	895.9371	895.9415	$Z_{5\alpha, 5\beta}$	-4.92	216858	4.3
2+	932.9603	932.9599	$^{0,2}X_{5\alpha, 5\beta}$	0.45	130040	2.5
2+	976.9854	976.9861	$^{0,4}X_{5\alpha, 5\beta}$	-0.73	619465	11.6
2+	1014.0046	1014.0045	M	0.11	42215732	771.4
1+	1330.6822	1330.6836	$Z_{3\alpha, 3\beta}{}^{\bullet}$-$CH_3O$	-1.05	200581	3.2
1+	1360.6891	1360.6942	$Z_{3\alpha, 3\beta}$	-3.70	594482	9.1
1+	1376.6913	1376.6891	$Y_{3\alpha, 3\beta}^‡$	1.64	223257	3.4
1+	1406.6992	1406.6996	$^{1,5}X_{3\alpha, 3\beta}$	-0.31	1052571	16.2
1+	1481.6988	1481.6982	$C_4^‡$	0.42	1033515	15.3
1+	1564.7954	1564.7939	$Z_{4\alpha, 4\beta}$	0.95	244007	3.4
1+	1580.7911	1580.7888	$Y_{4\alpha, 4\beta}^‡$	1.39	215404	3.0
1+	1610.7974	1610.7994	$^{1,5}X_{4\alpha, 4\beta}$	-1.23	405091	5.7
1+	1710.8251	1710.8296	B_5	-2.64	289943	3.8
1+	2005.0179	2005.0197	M	-0.92	902317	11.3

Table S6. List of assigned EED fragments in Figure 4b. All fragments are sodium adducts unless labeled otherwise. Multiple assignments are separated by commas; ω indicates harmonics; the double dagger symbol (‡) indicates that the fragment has two fewer hydrogens than the canonical structures; the double prime symbol (") indicates that the fragment has two more hydrogens than the canonical structure; the dot symbol (•) indicates a radical.

z	Exptl. *m/z*	Theo. *m/z*	Assignment	Δppm	Intensity	*S/N*
1+	211.0939	211.0941	$B_1^{\bullet}$-CH_3O	-1.06	4367299	131.6
1+	227.0888	227.0890	$C_1^{\bullet}$-CH_3O	-0.81	5803067	176.3
1+	239.0892	239.0890	$B_1^{‡}$	0.94	123360	3.7
1+	241.1045	241.1046	B_1	-0.60	1199589	36.2
1+	243.0838	243.0839	$C_1^{\bullet}$-CH_3, $C_{2\beta, 2\alpha'}^{‡}/Y_{4\beta, 5\alpha'}$	-0.66	9892578	298.1
1+	257.0994	257.0996	$C_1^{‡}$	-0.46	3073907	89.6
1+	259.1151	259.1152	C_1	-0.42	1300205	37.9
1+	269.1581	269.1582	$Z_1^{\bullet}$-CH_3O	-0.39	4952915	144.4
1+	285.1531	285.1531	$Z_1^{\bullet}$-CH_3	-0.19	2336968	67.8
1+	296.1104	296.1105	$B_5/^{1,5}X_2$	-0.26	815517	23.4
1+	299.1688	299.1687	Z_1	0.15	3868784	111.1
1+	301.1257	301.1258	$^{0,4}A_{2\alpha''}$	-0.21	2499591	71.8
1+	315.1414	315.1414	$^{1,3}A_{2\alpha',2\beta}$, $^{2,4}A_{2\alpha',2\beta}$	-0.03	1935269	55.1
1+	315.1636	315.1637	$Y_1^{‡}$	-0.15	1535072	43.7
1+	317.1793	317.1793	Y_1	-0.12	13718496	390.3
1+	323.1073	323.1078	$^{0,4}A_{2\alpha''}$ + 2Na - H	-1.53	1990387	119
1+	329.1570	329.1571	$^{3,5}A_{2\alpha''}$	-0.23	2074830	58.4
1+	343.1364	343.1363	$^{0,3}A_{2\alpha',2\beta}^{‡}$	0.18	495824	13.7
1+	345.1742	345.1742	$^{1,5}X_1$	-0.15	6200687	171.0
1+	387.1990	387.1990	$^{1,5}A_{2\alpha', 2\beta}^{‡}$ -CH_3O	0.04	712325	19.1
1+	401.1782	401.1781	$C_{2\alpha',2\beta}^{\bullet}$-$C_2H_5O_2$	0.17	1505349	40.3
1+	413.1782	413.1782	$B_{2\alpha''}/Z_{4\alpha'}$	-0.08	963896	25.6
1+	415.1938	415.1939	$^{1,5}A_{2\alpha', 2\beta}^{‡}$	-0.23	1819341	48.3
1+	417.1730	417.1732	$C_{2\alpha',2\beta}^{\bullet}$-$C_2H_5O$	-0.37	1153996	30.6
1+	417.2094	417.2095	$^{1,5}A_{2\alpha', 2\beta}$	-0.18	1638113	43.5
1+	429.1730	429.1731	$C_{3\alpha}^{‡}/Z_{4\alpha'}$	-0.25	728673	19.2
1+	431.1888	431.1888	$C_{3\alpha}/Z_{4\alpha'}$	0.00	10685049	281.2
1+	445.2043	445.2044	$B_{2\alpha',2\beta}$	-0.22	6132700	160.1
1+	447.1836	447.1837	$C_{2\alpha',2\beta}^{\bullet}$-$CH_3$	-0.19	2021576	52.8

1+	461.1992	461.1993	$C_{2\alpha',2\beta}^{‡}$	-0.20	21401918	554.7
1+	463.2149	463.2150	$C_{2\alpha',2\beta}$	-0.14	3671208	94.9
1+	484.2739	484.2740	$Z_2^{\bullet}$-$C_2H_5O_2$	-0.05	945413	24.3
1+	502.2845	502.2845	$Z_2^{\bullet}$-Ac	-0.16	3993509	101.1
1+	514.2846	514.2845	$Z_2^{\bullet}$-CH_3O	0.24	8685159	217.9
1+	519.2411	519.2412	$^{1,3}A_{3\alpha',3\beta}$, $^{2,4}A_{3\alpha',3\beta}$	-0.19	2772697	69.6
1+	530.2796	530.2794	$Z_2^{\bullet}$-CH_3	0.22	1752167	43.4
1+	544.2955	544.2951	Z_2	0.74	5432477	133.0
1+	560.2903	560.2900	$Y_2^{‡}$	0.50	766153	18.7
1+	562.3056	562.3056	Y_2	-0.07	2423319	59.0
1+	590.3004	590.3005	$^{1,5}X_2$	-0.18	12985275	312.5
2+	612.7945	612.7945	$^{1,5}X_{3\alpha}$	-0.09	452698	10.8
1+	618.3311	618.3318	$^{0,2}X_2$	-1.16	632260	15.1
1+	635.2890	635.2885	C_4/$Z_{4\alpha}$	0.74	1876780	44.1
1+	734.3793	734.3792	$Y_{3\alpha}$/$Z_{3\beta}$	0.15	2025212	43.2
2+	793.8882	793.8916	$Z_{4\alpha', 3\beta}$	-4.29	737398	15.0
2+	816.8943	816.8943	$^{1,5}X_{3\beta}$	-0.01	3256585	64.2
1+	825.3725	825.3727	$C_{3\alpha}^{\bullet}$-C_2H_5O	-0.28	750060	14.8
1+	825.4091	825.4091	$^{1,5}A_{3\alpha}$	0.00	1786031	35.2
1+	839.3882	839.3883	$C_{3\alpha}^{\bullet}$-CH_3O	-0.09	690395	13.3
2+	852.9088	852.9120	$^{1,5}A_5$	-3.68	351960	6.8
1+	869.3997	869.3989	$C_{3\alpha}^{‡}$	0.89	1821835	35.0
1+	871.4149	871.4145	$C_{3\alpha}$	0.40	1217776	23.4
2+	895.9376	895.9415	$Z_{4\alpha'', 5\alpha',4\beta}$	-4.31	2191200	41.1
1+	913.4252	913.4251	$^{0,4}A_4$	0.06	3170175	58.4
2+	918.9438	918.9442	$^{1,5}X_{4\alpha'', 5\alpha',4\beta}$	-0.41	7120822	131.2
2+	932.9589	932.9599	$^{0,2}X_{4\alpha'', 5\alpha',4\beta}$	-1.01	875924	16.1
1+	935.4045	935.4071	$^{0,4}A_4$ + 2Na - H	-2.80	8142842	152.2
2+	940.9500	940.9462	$^{2,5}X_{4\alpha'', 5\alpha',4\beta}$	4.03	1965728	36.2
1+	941.4566	941.4564	$^{3,5}A_4$	0.20	1508877	27.8
2+	976.9853	976.9861	$^{0,4}X_{4\alpha'', 5\alpha',4\beta}$	-0.77	2660931	48.0
2+	1014.0039	1014.0045	M	-0.59	1.75E+08	3077.5
1+	1043.4875	1043.4881	C_4/$Z_{3\beta}$	-0.56	7656820	135.0
1+	1126.5835	1126.5838	$Z_{3\alpha}^{\bullet}$-CH_3O	-0.26	310056	5.1

1+	1142.5796	1142.5788	$Z_{3\alpha}{}^{\bullet}$-CH_3	0.76	256130	4.3
1+	1156.5933	1156.5944	$Z_{3\alpha}$	-0.97	1035269	17.2
1+	1172.5910	1172.5893	$Y_{3\alpha}{}^{\ddagger}$	1.45	705345	11.7
1+	1202.5989	1202.5999	${}^{1,5}X_{3\alpha}$	-0.77	3627753	58.4
1+	1435.6915	1435.6927	${}^{1,5}A_4{}^{\ddagger}$	-0.83	479304	7.2
1+	1437.7065	1437.7084	${}^{1,5}A_4$	-1.30	1122125	16.9
1+	1467.6816	1467.6826	$C_4{}^{\bullet}$-CH_3	-0.63	598791	8.6
1+	1481.6978	1481.6982	$C_4{}^{\ddagger}$	-0.27	3995069	57.6
1+	1520.7667	1520.7676	$Z_{4\alpha',3\beta}{}^{\ddagger\bullet}$-$C_2H_5O$	-0.62	632160	9.1
1+	1534.7799	1534.7834	$Z_{4\alpha',3\beta}{}^{\bullet}$-$CH_3O$	-2.26	1236467	17.8
1+	1550.7754	1550.7783	$Z_{4\alpha',3\beta}{}^{\bullet}$-$CH_3$	-1.88	775358	11.2
1+	1564.7940	1564.7939	$Z_{4\alpha',3\beta}$	0.02	1838389	25.5
1+	1580.7874	1580.7888	$Y_{4\alpha',3\beta}{}^{\ddagger}$	-0.94	686319	9.5
1+	1582.8011	1582.8045	$Y_{4\alpha',3\beta}$	-2.16	539158	7.5
1+	1610.7975	1610.7994	${}^{1,5}X_{4\alpha',3\beta}$	-1.19	2144525	29.8
1+	1710.8273	1710.8296	B_5	-1.33	1049794	13.7
1+	1768.8890	1768.8937	$Z_{4\alpha'',5\alpha',4\beta}$	-2.64	262411	3.4
1+	1814.8954	1814.8992	${}^{1,5}X_{4\alpha'',5\alpha',4\beta}$	-2.11	890385	11.6
1+	1972.9933	1972.9935	M-CH_4O	-0.09	488415	6.0
1+	2005.0141	2005.0197	M	-2.78	4057732	50.0

Table S7. List of assigned EED fragments in Figure 4c. All fragments are sodium adducts unless labeled otherwise. Multiple assignments are separated by commas; ω indicates harmonics; the double dagger symbol (‡) indicates that the fragment has two fewer hydrogens than the canonical structures; the double prime symbol (") indicates that the fragment has two more hydrogens than the canonical structure; the dot symbol (•) indicates a radical.

z	Exptl. *m/z*	Theo. *m/z*	Assignment	Δppm	Intensity	*S/N*
1+	211.0939	211.0941	$B_1^{\bullet}$-CH_3O	-0.73	4312810	75.9
1+	227.0889	227.0890	$C_1^{\bullet}$-CH_3O	-0.55	7412889	128.2
1+	241.1045	241.1046	B_1	-0.48	1370988	23.3
1+	243.0838	243.0839	$C_1^{\bullet}$-CH_3, $C_{2\beta, 2\alpha}^{‡}/Y_{5\beta, 5\alpha}$	-0.53	7675213	130.6
1+	257.0994	257.0996	$C_1^{‡}$	-0.46	2375195	39.7
1+	259.1151	259.1152	C_1	-0.50	1136401	40.2
1+	269.1581	269.1582	$Z_1^{\bullet}$-CH_3O	-0.24	5810771	98.6
1+	285.1531	285.1531	$Z_1^{\bullet}$-CH_3	-0.08	3273250	54.6
1+	299.1688	299.1687	Z_1	0.25	4726915	77.1
1+	315.1414	315.1414	$^{1,3}A_{2\alpha',2\beta}$, $^{2,4}A_{2\alpha',2\beta}$	0.02	2473658	39.3
1+	315.1637	315.1637	$Y_1^{‡}$	0.23	1972634	31.3
1+	317.1793	317.1793	Y_1	-0.03	17629158	280.1
1+	345.1742	345.1742	$^{1,5}X_1$	0.05	7754856	120.8
1+	401.1782	401.1781	$C_{2\alpha',2\beta}^{\bullet}$-$C_2H_5O_2$	0.14	1532910	24.0
1+	414.2322	414.2321	$^{0,2}X_1$	0.24	575320	8.9
1+	415.1940	415.1939	$^{1,5}A_{2\alpha', 2\beta}^{‡}$	0.38	1795182	27.6
1+	417.1730	417.1732	$C_{2\alpha',2\beta}^{\bullet}$-$C_2H_5O$	-0.34	1291490	19.9
1+	417.2096	417.2095	$^{1,5}A_{2\alpha', 2\beta}$	0.16	1694285	26.1
1+	429.1730	429.1731	$C_{2\alpha',2\beta}^{‡\bullet}$-$CH_3O$	-0.28	1435573	21.8
1+	431.1888	431.1888	$C_{2\alpha',2\beta}^{\bullet}$-$CH_3O$	-0.02	8642389	131.5
1+	445.2044	445.2044	$B_{2\alpha',2\beta}$	0.00	7177136	107.2
1+	447.1837	447.1837	$C_{2\alpha',2\beta}^{\bullet}$-$CH_3$	-0.05	1715162	25.6
1+	461.1993	461.1993	$C_{2\alpha',2\beta}^{‡}$	-0.09	22590436	332.6
1+	463.2150	463.2150	$C_{2\alpha',2\beta}$	0.06	5418068	78.7
1+	484.2741	484.2740	$Z_2^{\bullet}$-$C_2H_5O_2$	0.19	1391920	20.0
1+	505.2258	505.2255	$^{0,4}A_{3\alpha'}$	0.54	7307940	102.9
1+	514.2846	514.2845	$Z_2^{\bullet}$-CH_3O	0.20	11505350	161.0
1+	519.2414	519.2412	$^{1,3}A_{3\beta}$ or $^{2,4}A_{3\beta}$	0.33	1447705	20.3
1+	527.2077	527.2076	$^{0,4}A_{3\alpha'}$ + 2Na - H	0.31	9911296	318.4

1+	530.2796	530.2794	$Z_2^{\bullet}$-CH_3	0.23	2697415	37.5
1+	533.2571	533.2568	$^{3,5}A_{3\alpha'}$	0.45	4898734	68.1
1+	544.2955	544.2951	Z_2	0.80	6585251	91.1
1+	560.2894	560.2900	$Y_2^{\ddagger}$	-1.13	1183909	16.3
1+	562.3058	562.3056	Y_2	0.34	3457909	47.7
1+	590.3008	590.3005	$^{1,5}X_2$	0.36	17784598	241.7
2+	612.7945	612.7945	$^{1,5}X_{3\alpha}$	-0.04	328345	4.4
1+	618.3321	618.3318	$^{0,2}X_2$	0.46	630549	8.5
1+	635.2888	635.2885	$C_{3\alpha'}/Z_{4\alpha''}$	0.33	7318534	97.4
1+	651.2840	651.2835	$C_{3\alpha'}/Y_{4\alpha''}$	0.79	1433059	18.8
1+	734.3794	734.3792	$Y_{3\alpha}/Z_{3\beta}$	0.29	3204971	39.0
2+	788.3723	788.3725	$^{3,5}A_5$	-0.25	433420	4.8
2+	793.8892	793.8916	$Z_{4\alpha', 3\beta}$	-3.01	637928	7.1
2+	800.8806	800.8812	$^{1,5}X_{4\alpha', 3\beta}$	-0.77	604240	6.4
1+	809.3777	809.3777	$C_{3\alpha}^{\bullet}$-C_2H_5O	0.04	1032968	10.9
2+	816.8945	816.8943	$^{1,5}X_{3\beta}$	0.24	3950350	41.7
1+	825.4093	825.4091	$^{1,5}A_{3\alpha}$	0.30	1604466	16.9
1+	839.3914	839.3883	$C_{3\alpha}^{\bullet}$-CH_3O	3.67	543964	5.5
1+	855.3865	855.3832	$C_{3\alpha}^{\bullet}$-CH_3	3.85	652646	6.6
1+	869.3986	869.3989	$C_{3\alpha}^{\ddagger}$	-0.31	3237171	32.7
1+	871.4168	871.4145	$C_{3\alpha}$	2.65	1151423	11.2
2+	895.9408	895.9415	$Z_{4\alpha'', 5\alpha', 4\beta}$	-0.70	4714825	45.9
1+	913.4253	913.4251	$^{0,4}A_4$	0.19	4153723	39.5
2+	918.9297	918.9331	$^{0,3}A_6$	-3.74	1850811	17.6
2+	918.9445	918.9442	$^{1,5}X_{4\alpha'', 5\alpha', 4\beta}$	0.27	11906868	113.4
2+	932.9604	932.9599	$^{0,2}X_{4\alpha'', 5\alpha',4\beta}$	0.56	854613	8.1
2+	940.9506	940.9462	$^{0,2}A_6$	4.66	2946282	28.0
1+	941.4571	941.4564	$^{3,5}A_4$	0.70	2302433	21.9
2+	976.9861	976.9861	$^{0,4}X_{4\alpha'', 5\alpha', 4\beta}$	0.02	4376939	41.0
2+	1014.0041	1014.0045	M	-0.36	1.72E+09	16042.1
1+	1043.4879	1043.4881	$C_4/Z_{3\beta}$	-0.23	10055260	93.5
1+	1126.5818	1126.5838	$Z_{3\alpha}^{\bullet}$-CH_3O	-1.85	371794	3.4
1+	1142.5780	1142.5788	$Z_{3\alpha}^{\bullet}$-CH_3	-0.65	637457	5.8
1+	1156.5913	1156.5944	$Z_{3\alpha}$	-2.66	814608	7.5
1+	1172.5905	1172.5893	$Y_{3\alpha}^{\ddagger}$	1.03	1130909	10.4

1+	1202.5999	1202.5999	$^{1,5}X_{3\alpha}$	0.04	4043076	36.6
1+	1435.6945	1435.6927	$^{1,5}A_4^{\ddagger}$	1.21	651505	5.6
1+	1437.7070	1437.7084	$^{1,5}A_4$	-0.94	1490058	12.8
1+	1451.6859	1451.6876	$C_4^{\bullet}$-CH_3O	-1.17	918824	7.7
1+	1467.6832	1467.6826	$C_4^{\bullet}$-CH_3	0.44	818793	6.8
1+	1481.6989	1481.6982	$C_4^{\ddagger}$	0.46	6477604	54.0
1+	1534.7833	1534.7834	$Z_{4\alpha',3\beta}^{\bullet}$-$CH_3O$	-0.06	1356381	11.3
1+	1550.7776	1550.7783	$Z_{4\alpha',3\beta}^{\bullet}$-$CH_3$	-0.46	1070269	8.9
1+	1564.7962	1564.7939	$Z_{4\alpha',3\beta}$	1.45	1637605	13.1
1+	1580.7890	1580.7888	$Y_{4\alpha',3\beta}^{\ddagger}$	0.11	1143657	9.2
1+	1610.7979	1610.7994	$^{1,5}X_{4\alpha',3\beta}$	-0.93	2792559	22.4
1+	1710.8293	1710.8296	B_5	-0.16	1717779	13.2
1+	1768.8935	1768.8937	$Z_{4\alpha'',5\alpha',4\beta}$	-0.12	626023	4.8
1+	1814.8969	1814.8992	$^{1,5}X_{4\alpha'',5\alpha',4\beta}$	-1.27	1124511	8.6
1+	1930.9817	1930.9829	$^{0,4}X_{4\alpha'',5\alpha',4\beta}$	-0.65	299859	2.2
1+	1972.9921	1972.9935	M-CH_4O	-0.69	665589	4.9
1+	2005.0188	2005.0197	M	-0.47	5626437	41.4

Table S8. List of assigned EED fragments in Figure 4d. All fragments are sodium adducts unless labeled otherwise. Multiple assignments are separated by commas; ω indicates harmonics; the double dagger symbol (‡) indicates that the fragment has two fewer hydrogens than the canonical structures; the double prime symbol (") indicates that the fragment has two more hydrogens than the canonical structure; the dot symbol (•) indicates a radical.

z	Exptl. *m/z*	Theo. *m/z*	Assignment	Δppm	Intensity	*S/N*
1+	211.0939	211.0941	$B_1^{\bullet}$-CH_3O	-0.73	4594087	131.4
1+	227.0889	227.089	$C_1^{\bullet}$-CH_3O	-0.59	15503128	428.3
1+	241.1045	241.1046	B_1	-0.56	1525854	42.4
1+	243.0838	243.0839	$C_1^{\bullet}$-CH_3, $C_{2\beta}^{‡}/Y_{5\beta}$	-0.53	9149023	253.9
1+	255.1424	255.1424	$Z_1^{‡\bullet}$-C_2H_5O	-0.11	824204	22.6
1+	257.0995	257.0996	$C_1^{‡}$	-0.31	4425565	121.3
1+	259.1151	259.1152	C_1	-0.54	2921008	171.1
1+	269.1582	269.1582	$Z_1^{\bullet}$-CH_3O	-0.16	7002440	191.6
1+	285.1531	285.1531	$Z_1^{\bullet}$-CH_3	-0.26	4167532	109.5
1+	296.1105	296.1105	$B_5/^{1,5}X_2$	0.01	1351565	35.3
1+	299.1689	299.1687	Z_1	0.39	5705639	148.9
1+	301.1257	301.1258	$^{0,4}A_{2\alpha}$	-0.21	3786775	99
1+	315.1414	315.1414	$^{1,3}A_{2\alpha, 2\beta}$, $^{2,4}A_{2\alpha, 2\beta}$	0.02	2813393	73.3
1+	315.1636	315.1637	$Y_1^{‡}$	-0.09	2560997	66.8
1+	317.1793	317.1793	Y_1	-0.12	19546054	509.5
1+	323.1077	323.1078	$^{0,4}A_{2\alpha}$ + 2Na - H	-0.23	5212497	298.7
1+	329.1571	329.1571	$^{3,5}A_{2\alpha}$	-0.04	2743775	71.8
1+	345.1742	345.1742	$^{1,5}X_1$	-0.07	8424097	218.7
1+	359.1683	359.1676	$^{1,4}A_{2\alpha, 2\beta}$	1.70	238718	6.2
1+	371.1676	371.1676	$B_{2\beta}/^{0,4}X_{4\beta}$	-0.08	2123097	54.7
1+	385.1834	385.1833	$B_{2\beta}^{\bullet}$-$C_2H_5O_2$	0.16	4778245	120.4
1+	387.199	387.199	$^{1,5}A_{2\beta}$ - CH_3O	0.15	793843	20
1+	401.1781	401.1781	$C_{2\beta}^{\bullet}$-$C_2H_5O_2$	0.07	2310509	56.8
1+	415.194	415.1939	$^{1,5}A_{2\beta}^{‡}$	0.30	6928051	167.9
1+	417.1731	417.1732	$C_{2\beta}^{\bullet}$-C_2H_5O	-0.15	1710442	41.5
1+	417.2095	417.2095	$^{1,5}A_{2\beta}$	0.09	1874339	45.4
1+	429.1732	429.1731	$C_{2\beta}^{‡\bullet}$-CH_3O	0.20	1291027	31.1
1+	431.1887	431.1888	$C_{2\beta}^{\bullet}$-CH_3O, $C_{2\alpha}/Z_{4\alpha}$	-0.20	17382242	419.1
1+	443.1888	443.1888	$B_{2\beta}^{‡}$	0.03	349260	8.3

1+	445.2047	445.2044	$B_{2\beta}$	0.54	5549172	131.9
1+	447.1837	447.1837	$C_{2\beta}^{\bullet}-CH_3$	0.10	4357378	103.6
1+	458.2584	458.2583	$^{0,3}X_1$	0.31	693883	16.4
1+	459.184	459.1837	$B_{3\beta}/^{1,5}X_{5\beta}$	0.78	614397	14.5
1+	461.1993	461.1993	$C_{2\beta}^{\ddagger}$	-0.18	11719190	276.6
1+	463.215	463.215	$C_{2\beta}$	-0.03	1458389	34.3
1+	484.2739	484.274	$Z_2^{\bullet}-C_2H_5O_2$	-0.12	1435577	33.3
1+	502.2846	502.2845	$Z_2^{\bullet}$-Ac	0.04	4205359	96.6
1+	514.2847	514.2845	$Z_2^{\bullet}-CH_3O$	0.30	12804381	291.4
1+	519.2413	519.2412	$^{1,3}A_{3\beta}$, $^{2,4}A_{3\beta}$	0.24	2137748	48.7
1+	530.2795	530.2794	$Z_2^{\bullet}-CH_3$	0.06	3115772	70.3
1+	544.2953	544.2951	Z_2	0.47	6325363	141.6
1+	560.2904	560.29	$Y_2^{\ddagger}$	0.75	1143262	25.3
1+	561.252	561.2518	$^{1,4}A_{3\beta}^{\ddagger}$	0.33	715670	15.9
1+	562.3058	562.3056	Y_2	0.26	3137635	69.5
1+	590.3007	590.3005	$^{1,5}X_2$	0.23	21185914	457.3
1+	605.2781	605.2779	$C_{2\alpha, 3\beta}^{\bullet}-C_2H_5O_2$	0.34	1411935	30.5
1+	619.2943	619.2936	$^{1,5}A_{2\alpha, 3\beta}^{\ddagger}$	1.02	3618963	77
1+	621.2736	621.273	$C_{2\alpha, 3\beta}^{\bullet}-C_2H_5O$	1.10	1526305	32.5
1+	621.3095	621.3093	$^{1,5}A_{2\alpha, 3\beta}$	0.29	2705293	57.6
1+	635.2891	635.2885	$C_{2\alpha, 3\beta}^{\bullet}-CH_3O$	0.91	3341655	69.7
1+	647.2865	647.2885	$B_{2\alpha, 3\beta}^{\ddagger}$	-3.14	238135	4.9
1+	649.3049	649.3042	$B_{2\alpha, 3\beta}$	1.12	3634408	74.5
1+	651.284	651.2835	$C_{2\alpha, 3\beta}^{\bullet}-CH_3$	0.90	1256385	25.8
1+	665.2992	665.2991	$C_{2\alpha, 3\beta}^{\ddagger}$	0.14	16103262	326
1+	667.315	667.3148	$C_{2\alpha, 3\beta}$	0.32	4989881	101
2+	691.8412	691.8417	$Z_{3\alpha, 3\beta}$	-0.68	285618	5.7
1+	707.3114	707.3097	$^{0,4}A_3^{\ddagger}$	2.43	318401	6.3
1+	709.3254	709.3253	$^{0,4}A_3$	0.05	5227728	104.1
2+	714.8446	714.8444	$^{1,5}X_{3\alpha, 3\beta}$	0.28	2213369	43.2
1+	723.3411	723.341	$^{1,3}A_{4\beta}$, $^{2,4}A_{4\beta}$	0.16	3224848	62.9
1+	731.3073	731.3073	$^{0,4}A_3$ + 2Na - H	-0.03	10721002	461.8
1+	734.3795	734.3792	$Y_{3\alpha}/Z_{3\beta}$	0.37	3932710	76.7
1+	737.3569	737.3566	$^{3,5}A_3$	0.31	5316280	103.7

2+	816.8947	816.8943	$^{1,5}X_{4\beta}$	0.46	1643410	29.7
1+	839.3884	839.3883	$C_4/Z_{3\beta}$	0.04	12071547	212.5
2+	852.9088	852.912	$^{1,5}A_4$	-3.69	416235	7.3
2+	866.9083	866.9094	B_4	-1.24	430826	7.6
1+	885.394	885.3938	$C_4/^{1,5}X_{3\beta}$	0.19	462695	7.9
2+	895.9404	895.9415	$Z_{4\alpha, 5\beta}$	-1.14	3317514	56.7
2+	918.9443	918.9442	$^{1,5}X_{4\alpha, 5\beta}$	0.06	10079623	167.5
2+	932.9601	932.9599	$^{0,2}X_{4\alpha, 5\beta}$	0.25	966361	16.1
2+	940.9453	940.9462	$^{0,2}A_5$	-0.96	619365	10.3
2+	976.9863	976.9861	$^{0,4}X_{4\alpha, 5\beta}$	0.23	4104121	66.8
1+	995.466	995.467	$^{1,5}A_5$	-0.96	211553	3.4
1+	1247.588	1247.588	$C_4/Z_{4\alpha}$	0.30	866362	12.8
1+	1316.669	1316.668	$Z_{3\alpha, 3\beta}^{\bullet}$-$C_2H_5O$	0.59	988762	14.2
1+	1330.683	1330.684	$Z_{3\alpha, 3\beta}^{\bullet}$-$CH_3O$	-0.76	2538331	36.3
1+	1346.681	1346.679	$Z_{3\alpha, 3\beta}^{\bullet}$-$CH_3$	1.46	1443757	20.7
1+	1360.696	1360.694	$Z_{3\alpha, 3\beta}$	1.28	2932544	40.7
1+	1376.691	1376.689	$Y_{3\alpha, 3\beta}^{\ddagger}$	1.63	1852947	25.7
1+	1378.704	1378.705	$Y_{3\alpha, 3\beta}$	-0.46	417607	5.8
1+	1406.7	1406.7	$^{1,5}X_{3\alpha, 3\beta}$	-0.04	5628905	78.2
1+	1435.695	1435.693	$^{1,5}A_4^{\ddagger}$	1.44	685397	9.5
1+	1437.708	1437.708	$^{1,5}A_4$	-0.27	2062070	28.6
1+	1451.688	1451.688	$C_4^{\bullet}$-CH_3O	0.16	1075615	14.4
1+	1467.682	1467.683	$C_4^{\bullet}$-CH_3	-0.69	1002850	13.5
1+	1481.699	1481.698	$C_4^{\ddagger}$	0.80	6322948	84.8
1+	1534.782	1534.783	$Z_{4\beta}^{\bullet}$-CH_3O	-0.76	762791	10.2
1+	1550.777	1550.778	$Z_{4\beta}^{\bullet}$-CH_3	-1.05	2209302	29.6
1+	1564.794	1564.794	$Z_{4\beta}$	0.21	1133744	15.2
1+	1580.79	1580.789	$Y_{4\beta}^{\ddagger}$	0.46	1233418	15.9
1+	1610.799	1610.799	$^{1,5}X_{4\beta}$	-0.48	1924410	24.8
1+	1710.829	1710.83	B_5	-0.46	1543853	18.9
1+	1728.84	1728.84	C_5	0.13	171242	2.1
1+	1738.885	1738.883	$Z_{4\alpha}^{\bullet}$-CH_3O	0.81	378986	4.6
1+	1768.896	1768.894	$Z_{4\alpha, 5\beta}$	1.11	311446	3.8
1+	1784.885	1784.889	$Y_{4\alpha, 5\beta}^{\ddagger}$	-1.98	296330	3.6

1+	1814.899	1814.899	$^{1,5}X_{\mathbf{4\alpha,\ 5\beta}}$	-0.16	1096319	13.4
1+	1930.982	1930.983	$^{0,4}X_{4\alpha,\ 5\beta}$	-0.62	325811	3.8
1+	1942.98	1942.983	M-$C_2H_6O_2$	-1.58	287338	3.3
1+	1958.979	1958.978	M-C_2H_6O	0.62	356494	4.1
1+	1972.994	1972.993	M-CH_4O	0.33	596513	6.9
1+	2005.018	2005.02	M	-0.78	5496154	63.6

Table S9. List of assigned EED fragments in Figure 4e. All fragments are sodium adducts unless labeled otherwise. Multiple assignments are separated by commas; ω indicates harmonics; the double dagger symbol (‡) indicates that the fragment has two fewer hydrogens than the canonical structures; the double prime symbol (") indicates that the fragment has two more hydrogens than the canonical structure; the dot symbol (•) indicates a radical.

z	Exptl. *m/z*	Theo. *m/z*	Assignment	Δppm	Intensity	*S/N*
1+	211.0940	211.0941	$B_1^{\bullet}$-CH_3O	-0.45	1203080	40.8
1+	227.0889	227.0890	$C_1^{\bullet}$-CH_3O	-0.37	3437079	113.4
1+	241.1045	241.1046	B_1	-0.72	450148	25.2
1+	243.0838	243.0839	$C_1^{\bullet}$-CH_3, $C_{2\beta, 2\alpha}^{‡}/Y_{5\beta, 5\alpha}$	-0.41	2336125	78.1
1+	259.1150	259.1152	C_1	-0.69	245683	10.7
1+	269.1581	269.1582	$Z_1^{\bullet}$-CH_3O	-0.27	1437579	45.9
1+	285.1531	285.1531	$Z_1^{\bullet}$-CH_3	-0.26	864759	27.3
1+	299.1689	299.1687	Z_1	0.46	1033385	32.8
1+	315.1637	315.1637	$Y_1^{‡}$	-0.03	782873	24.8
1+	317.1794	317.1793	Y_1	0.35	4851238	154.0
1+	345.1742	345.1742	$^{1,5}X_1$	-0.01	1834612	56.9
1+	415.1925	415.1939	$^{1,5}A_2^{‡}$	-3.21	1224969	35.6
1+	417.2086	417.2095	$^{1,5}A_2$	-2.26	232399	6.8
1+	431.1887	431.1888	$C_2^{\bullet}$-CH_3O	-0.18	2501493	72.7
1+	445.2045	445.2044	B_2	0.27	1635645	47.3
1+	447.1836	447.1837	$C_2^{\bullet}$-CH_3	-0.14	941784	27.2
1+	461.1991	461.1993	$C_2^{‡}$	-0.48	4513437	130.0
1+	463.2151	463.2150	C_2	0.27	748582	21.4
1+	502.2847	502.2845	$Z_2''^{\bullet}$-$C_2H_5O_2$	0.30	3115160	86.2
1+	505.2256	505.2255	$^{0,4}A_{3\alpha}$	0.00	959460	26.6
1+	514.2846	514.2845	$Z_2^{\bullet}$-CH_3O	0.07	2537556	69.9
1+	519.2416	519.2412	$^{1,3}A_{3\beta}$, $^{2,4}A_{3\beta}$	0.72	465555	12.8
1+	527.2075	527.2076	$^{0,4}A_{3\alpha}$ + 2Na - H	-0.13	797492	41.9
1+	533.2569	533.2568	$^{3,5}A_{3\alpha}$	0.04	1243467	34.0
1+	544.2956	544.2951	Z_2	0.94	1536277	41.7
1+	562.3057	562.3056	Y_2	0.16	604405	16.4
1+	590.3007	590.3005	$^{1,5}X_2$	0.21	2984647	80.3
1+	619.2942	619.2936	$^{1,5}A_{3\alpha, 3\beta}^{‡}$	0.89	1024914	27.3
1+	635.2888	635.2885	$C_3^{\bullet}$-CH_3O	0.37	1245750	32.7

1+	649.3049	649.3042	B_3	1.07	908090	23.6
1+	651.2836	651.2835	$C_3^{\bullet}$-CH_3	0.19	339807	8.8
1+	665.2993	665.2991	$C_3^{\ddagger}$	0.25	4503148	115.1
1+	667.3150	667.3148	C_3	0.32	1016177	26.0
1+	709.3253	709.3253	$^{0,4}A_4$	-0.02	1681420	42.3
2+	714.8443	714.8444	$^{1,5}X_{3\alpha,\ 3\beta}$	-0.15	326085	8.1
1+	723.3412	723.3410	$^{1,3}A_{4\beta}$, $^{2,4}A_{4\beta}$	0.30	269429	6.7
1+	731.3073	731.3073	$^{0,4}A_4$ + 2Na - H	-0.03	2711610	142.0
1+	734.3794	734.3792	$Y_{3\alpha}$ /$Z_{3\beta}$	0.30	1006051	24.9
1+	737.3569	737.3566	$^{3,5}A_4$	0.40	1065106	26.4
2+	753.3532	753.3515	C_4	2.21	222815	5.4
1+	765.3513	765.3515	$^{1,4}A_{4\beta}^{\ddagger}$	-0.32	148770	3.6
2+	816.8942	816.8943	$^{1,5}X_{4\alpha,\ 4\beta}$	-0.17	785383	18.2
1+	839.3883	839.3883	C_4/$Z_{3\beta}$	0.02	3887717	88.2
2+	866.9075	866.9094	B_5	-2.23	149525	3.4
2+	895.9377	895.9415	$Z_{5\alpha,\ 5\beta}$	-4.19	395067	8.7
2+	903.9387	903.9411	$Y_{5\alpha,\ 5\beta}^{\ddagger}$	-2.71	700217	15.4
2+	918.9444	918.9442	$^{1,5}X_{5\alpha,\ 5\beta}$	0.20	1661473	35.4
2+	947.9642	947.9651	$^{1,4}X_{5\alpha,\ 5\beta}$	-0.97	139132	3.0
2+	1014.0047	1014.0045	M	0.21	53525336	1067.8
1+	1330.6782	1330.6836	$Z_{3\alpha,\ 3\beta}^{\bullet}$-$CH_3O$	-4.10	343969	6.0
1+	1360.6920	1360.6942	$Z_{3\alpha,\ 3\beta}$	-1.58	768870	23.7
1+	1376.6899	1376.6891	$Y_{3\alpha,\ 3\beta}^{\ddagger}$	0.61	388145	6.5
1+	1406.7003	1406.6996	$^{1,5}X_{3\alpha,\ 3\beta}$	0.45	1047642	17.5
1+	1451.6835	1451.6876	$C_4^{\bullet}$-CH_3O	-2.84	147463	2.4
1+	1481.6998	1481.6982	$C_4^{\ddagger}$	1.09	1315539	21.0
1+	1550.7756	1550.7783	$Z_{4\alpha,\ 4\beta}^{\bullet}$-$CH_3$	-1.72	252321	4.0
1+	1564.7894	1564.7939	$Z_{4\alpha,\ 4\beta}$	-2.92	179174	2.7
1+	1580.7870	1580.7888	$Y_{4\alpha,\ 4\beta}^{\ddagger}$	-1.16	178413	2.7
1+	1610.7993	1610.7994	$^{1,5}X_{4\alpha,\ 4\beta}$	-0.06	887038	26.3
1+	1710.8290	1710.8296	B_5	-0.33	336340	4.8
1+	1726.8226	1726.8245	$C_5^{\ddagger}$	-1.10	169588	2.4
1+	1814.8987	1814.8992	$^{1,5}X_{5\alpha,\ 5\beta}$	-0.25	199522	2.9
1+	2005.0177	2005.0197	M	-0.99	1257983	17.1

Table S10. List of assigned EED fragments in Figure S1a. All fragments are sodium adducts unless labeled otherwise. Multiple assignments are separated by commas; ω indicates harmonics; the double dagger symbol (‡) indicates that the fragment has two fewer hydrogens than the canonical structures; the double prime symbol (") indicates that the fragment has two more hydrogens than the canonical structure; the dot symbol (•) indicates a radical.

z	Exptl. *m/z*	Theo. *m/z*	Assignment	Δppm	Intensity	*S/N*
1+	227.0889	227.0890	$C_1^{\bullet}$-CH_3O, C_4/Z_3	-0.46	1380016	38.1
1+	243.0838	243.0839	$C^{‡}$/Y (Hex)	-0.45	1115815	30.9
1+	269.1581	269.1582	$Z_1^{\bullet}$-CH_3O	-0.41	804009	42.4
1+	299.1687	299.1687	Z_1	-0.18	777119	39.9
1+	315.1413	315.1414	$^{1,3}A_2$, $^{2,4}A_2$	-0.55	228402	7.6
1+	317.1792	317.1793	Y_1	-0.41	1742926	45.9
1+	345.1742	345.1742	$^{1,5}X_1$	-0.21	863069	22.3
1+	415.1936	415.1939	$^{1,5}A_2^{‡}$	-0.54	540035	23.6
1+	431.1886	431.1888	$C_2^{\bullet}$-CH_3O	-0.39	1117818	27.6
1+	445.2042	445.2044	B_2	-0.56	669895	30.1
1+	447.1834	447.1837	$C_2^{\bullet}$-CH_3	-0.66	484771	11.7
1+	461.1992	461.1993	$C_2^{‡}$	-0.40	853759	20.6
1+	500.2690	500.2688	$Z_2^{\bullet}$- C_2H_5O	0.52	967526	29.9
1+	502.2841	502.2845	$Z_2^{\bullet}$-Ac	-0.78	710202	16.6
1+	514.2843	514.2845	$Z_2^{\bullet}$-CH_3O	-0.46	1067378	24.7
1+	519.2412	519.2412	$^{1,3}A_3$, $^{2,4}A_3$	-0.08	267994	8.1
1+	544.2948	544.2951	Z_2	-0.51	887160	20.1
1+	590.3003	590.3005	$^{1,5}X_2$	-0.42	1896463	41.8
1+	635.2882	635.2885	$C_3^{\bullet}$-CH_3O	-0.59	377332	8.1
1+	665.2992	665.2991	$C_3^{‡}$	0.19	1051164	22.1
2+	691.8414	691.8418	M-CH_4O	-0.58	1282765	54.7
2+	707.8545	707.8548	M	-0.49	28591048	595.4
1+	718.3834	718.3843	$Z_3^{\bullet}$-CH_3O	-1.25	306118	6.3
1+	748.3937	748.3948	Z_3	-1.47	458452	9.4
1+	766.4043	766.4054	Y_3	-1.44	364181	10.9
1+	794.3994	794.4003	$^{1,5}X_3$	-1.21	525405	10.6
1+	869.3991	869.3989	$C_4^{‡}$	0.22	2158072	41.0
1+	938.4784	938.4790	$Z_4^{\bullet}$-CH_3	-0.66	240649	4.5
1+	998.4996	998.5001	$^{1,5}X_4$	-0.51	459888	8.1
1+	1082.4988	1082.4990	$C_5^{‡\bullet}$-CH_3O	-0.16	373709	6.4

1+	1098.5293	1098.5303	B_5	-0.86	652854	11.1
1+	1202.5999	1202.5999	$^{1,5}X_5$	0.02	168187	2.7
1+	1392.7213	1392.7204	M	0.63	428883	9.2

Table S11. List of assigned EED fragments in Figure S1b. All fragments are sodium adducts unless labeled otherwise. Multiple assignments are separated by commas; ω indicates harmonics; the double dagger symbol (‡) indicates that the fragment has two fewer hydrogens than the canonical structures; the double prime symbol (") indicates that the fragment has two more hydrogens than the canonical structure; the dot symbol (•) indicates a radical.

z	Exptl. *m/z*	Theo. *m/z*	Assignment	Δppm	Intensity	*S/N*
1+	227.0890	227.0890	$C_{1\alpha,1\beta}^{\bullet}$-$CH_3O$	-0.11	2783076	110.5
1+	241.1047	241.1046	$B_{1\alpha,1\beta}$	0.10	473571	15.6
1+	255.1426	255.1424	$Z_1^{\ddagger\bullet}$-C_2H_5O	0.59	978952	17.6
1+	257.0996	257.0996	$C_{1\alpha,1\beta}^{\ddagger}$	0.27	1790223	32.0
1+	259.1152	259.1152	$C_{1\alpha,1\beta}$	-0.04	1343838	51.3
1+	269.1583	269.1582	$Z_1^{\bullet}$-CH_3O	0.25	4043355	71.5
1+	285.1532	285.1531	$Z_1^{\bullet}$-CH_3	0.20	1427021	25.5
1+	299.1688	299.1687	Z_1	0.22	6544182	116.1
1+	301.1258	301.1258	$^{0,4}A_2$	0.19	2462148	43.7
1+	315.1415	315.1414	$^{1,3}A_2$, $^{2,4}A_2$	0.18	584720	10.2
1+	315.1638	315.1637	$Y_1^{\ddagger}$	0.29	1535230	26.8
1+	317.1794	317.1793	Y_1	0.35	7380774	128.2
1+	323.1078	323.1078	$^{0,4}A_2$ + 2Na - H	0.08	3237565	123.1
1+	329.1571	329.1571	$^{3,5}A_2$	0.08	2353812	40.4
1+	345.1743	345.1742	$^{1,5}X_1$	0.28	4975036	84.4
1+	414.2324	414.2321	$^{0,2}X_1$	0.74	316367	5.1
1+	431.1888	431.1888	C_2/$Z_{4\beta}$	0.17	4187774	68.1
1+	484.2741	484.2740	$Z_2^{\bullet}$-$C_2H_5O_2$	0.23	842143	13.5
1+	500.2104	500.2102	B_4/$^{1,5}X_3$	0.24	3041701	47.8
1	500.2688	500.2688	$Z_2^{\bullet}$- C_2H_5O	0.06	1006552	41.5
1+	502.2847	502.2845	$Z_2^{\bullet}$-Ac	0.40	1720689	27.0
1+	514.2848	514.2845	$Z_2^{\bullet}$-CH_3O	0.49	5428147	84.0
1+	530.2796	530.2794	$Z_2^{\bullet}$-CH_3	0.37	1170464	17.8
1+	544.2951	544.2951	Z_2	0.04	4770224	71.7
1+	560.2892	560.2900	$Y_2^{\ddagger}$	-1.34	308521	4.6
2+	560.7601	560.7598	$B_{4\alpha,4\beta}$	0.65	258632	3.8
1+	562.3058	562.3056	Y_2	0.26	636280	9.4
2+	569.7655	569.7650	$C_{4\alpha,4\beta}$	0.87	1411412	20.7
2+	589.7918	589.7918	$Z_{4\alpha,4\beta}$	0.01	3816949	55.2
1+	590.3007	590.3005	$^{1,5}X_2$	0.23	4905638	70.9

2+	598.7978	598.7971	$Y_{4\alpha,4\beta}$	1.19	641682	9.3
2+	612.7949	612.7945	$^{1,5}X_{4\alpha,4\beta}$	0.52	9956921	142.1
1+	618.3325	618.3318	$^{0,2}X_2$	0.98	451548	6.4
1+	621.3095	621.3093	$^{1,5}A_{2\alpha}$	0.42	920705	13.1
2+	626.8107	626.8102	$^{0,2}X_{4\alpha,4\beta}$	0.74	574667	8.1
2+	634.7966	634.7965	$^{0,2}A_5$	0.09	1173677	16.5
1+	635.2887	635.2885	$C_2^{\bullet}$-CH_3O	0.26	1303094	18.3
1+	651.2844	651.2835	$C_2^{\bullet}$-CH_3	1.39	566942	7.8
1+	665.3002	665.2991	$C_2^{\ddagger}$	1.61	2167957	29.6
1+	667.3155	667.3148	C_2	1.07	1031088	14.1
2+	670.8372	670.8364	$^{0,4}X_{4\alpha,4\beta}$	1.18	4429429	60.4
2+	707.8553	707.8548	M	0.65	2.06E+08	2777.7
1+	718.3852	718.3843	$Z_3^{\bullet}$-CH_3O	1.21	512838	6.8
1+	731.3075	731.3073	$^{0,4}A_3$ + 2Na - H	0.27	2069570	58.5
1+	737.3572	737.3566	$^{3,5}A_3$	0.72	2580940	34.4
1+	748.3951	748.3948	Z_3	0.35	1087166	28.8
1+	764.3913	764.3898	$Y_3^{\ddagger}$	2.05	1380350	18.2
1+	766.4062	766.4054	Y_3	1.06	484103	6.3
1+	794.4006	794.4003	$^{1,5}X_3$	0.34	4842378	63.0
1+	809.3783	809.3777	$C_3^{\bullet}$-$C_2H_5O_2$	0.82	481885	6.2
1+	823.3946	823.3934	$^{1,5}A_3^{\ddagger}$	1.41	1513351	19.4
1+	839.3888	839.3883	$C_3^{\bullet}$-CH_3O	0.53	4886783	61.5
1+	853.4033	853.4040	B_3	-0.84	427370	5.4
1+	855.3833	855.3832	$C_3^{\bullet}$-CH_3	0.09	1441688	18.2
1+	869.3992	869.3989	$C_3^{\ddagger}$	0.41	11444902	141.5
1+	871.4152	871.4145	C_3	0.72	6640976	82.1
1+	938.4785	938.4790	$Y_{4\alpha}/Y_{4\beta}$	-0.47	497461	6.0
1+	941.4572	941.4564	$^{3,5}A_3^{\ddagger}$	0.90	1467469	17.8
1+	1070.5359	1070.5354	$^{1,5}A_4$	0.51	1057625	11.9
1+	1084.5157	1084.5146	$C_4^{\bullet}$-CH_3O	0.99	1282352	14.4
1+	1098.5310	1098.5303	B_4	0.62	3866560	43.4
1+	1114.5269	1114.5252	$C_4^{\ddagger}$	1.50	533187	5.8
1+	1126.5853	1126.5838	$Z_{4\alpha,4\beta}^{\bullet}$-$CH_3O$	1.32	434171	4.7
1+	1142.5779	1142.5788	$Z_{4\alpha,4\beta}^{\bullet}$-$CH_3$	-0.78	272466	3.0
1+	1156.5967	1156.5944	$Z_{4\alpha,4\beta}$	2.01	372368	4.1

1+	1172.5907	1172.5893	$Y_{4\alpha,4\beta}^{\ddagger}$	1.18	287570	3.0
1+	1202.6001	1202.5999	$^{1,5}X_{4\alpha,4\beta}$	0.19	1633858	17.2
1+	1360.6977	1360.6942	M-CH_4O	2.62	331550	3.2
1+	1392.7219	1392.7204	M	1.09	2373368	23.2

Table S12. List of assigned EED fragments in Figure S1c. All fragments are sodium adducts unless labeled otherwise. Multiple assignments are separated by commas; ω indicates harmonics; the double dagger symbol (‡) indicates that the fragment has two fewer hydrogens than the canonical structures; the double prime symbol (") indicates that the fragment has two more hydrogens than the canonical structure; the dot symbol (•) indicates a radical.

z	Exptl. *m/z*	Theo. *m/z*	Assignment	Δppm	Intensity	*S/N*
1+	211.0940	211.0941	$B_{1\alpha,1\beta}{}^{\bullet}$-$CH_3O$	-0.45	462578	11.6
1+	227.0889	227.0890	$C_{1\alpha,1\beta}{}^{\bullet}$-$CH_3O$	-0.33	2957972	71.9
1+	241.1046	241.1046	$B_{1\alpha,1\beta}$	-0.31	413385	17.2
1+	257.0996	257.0996	$C_{1\alpha,1\beta}{}^{‡}$	0.08	1789985	43.5
1+	259.1152	259.1152	$C_{1\alpha,1\beta}$	-0.15	738317	34.6
1+	269.1582	269.1582	$Z_1{}^{\bullet}$-CH_3O	0.02	2771893	66.2
1+	299.1685	299.1687	Z_1	-0.85	3300388	78.6
1+	301.1257	301.1258	$^{0,4}A_{2\alpha}$	-0.28	365861	14.1
1+	315.1415	315.1414	$^{1,3}A_{2\beta}$, $^{2,4}A_{2\beta}$	0.15	732154	17.2
1+	315.1637	315.1637	$Y_1{}^{‡}$	0.07	865219	20.3
1+	317.1793	317.1793	Y_1	-0.09	5417656	125.9
1+	329.1570	329.1571	$^{3,5}A_{2\alpha}$	-0.23	747570	33.4
1+	345.1743	345.1742	$^{1,5}X_1$	0.08	3848254	88.1
1+	415.1939	415.1939	$^{1,5}A_{2\alpha}{}^{‡}$	0.02	1527131	33.8
1+	431.1888	431.1888	$C_{2\alpha}{}^{\bullet}$-CH_3O	0.03	1360776	29.9
1+	461.1993	461.1993	$C_{2\alpha}{}^{‡}$	-0.05	2859089	61.5
1+	463.2150	463.2150	$C_{2\alpha}$	0.04	1465637	31.3
1+	500.2688	500.2688	$Z_2{}^{\bullet}$- C_2H_5O	0.06	1006552	41.5
1+	502.2844	502.2845	$Z_2{}^{\bullet}$-Ac	-0.18	1086009	22.4
1+	505.2256	505.2255	$^{0,4}A_3$	0.14	2693408	55.6
2+	510.7447	510.7447	$^{1,5}X_{3\alpha}$	-0.01	1259043	25.7
1+	514.2846	514.2845	$Z_2{}^{\bullet}$-CH_3O	0.10	3845487	78.6
1+	527.2075	527.2075	$^{0,4}A_3$ + 2Na - H	-0.09	3902946	172.7
1+	530.2792	530.2794	$Z_2{}^{\bullet}$-CH_3	-0.43	661993	13.3
1+	533.2569	533.2568	$^{3,5}A_3$	0.12	1793027	36.1
1+	544.2953	544.2951	Z_2	0.34	2565246	50.9
1+	560.2907	560.2900	$Y_2{}^{‡}$	1.23	331386	6.5
2+	560.7572	560.7598	B_4	-4.63	218597	4.3
1+	562.3044	562.3056	Y_2	-2.14	661877	13.0

2+	569.7654	569.7650	C_4	0.64	413360	8.0
2+	589.7917	589.7918	$Z_{4\alpha, 3\beta}$	-0.19	2550903	48.9
1+	590.3006	590.3005	$^{1,5}X_2$	0.14	4447175	85.2
2+	612.7945	612.7945	$^{1,5}X_{4\alpha, 3\beta}$	-0.12	6412388	121.8
2+	626.8100	626.8102	$^{0,2}X_{4\alpha, 3\beta}$	-0.25	381142	7.2
2+	670.8370	670.8364	$^{0,4}X_{4\alpha, 3\beta}$	0.82	2280636	41.7
2+	707.8550	707.8548	M	0.33	1.07E+08	1935.1
1+	734.3793	734.3792	$Y_{3\alpha}/Z_{3\beta}$	0.12	730132	13.1
1+	823.3943	823.3934	$^{1,5}A_3^{\ddagger}$	1.12	898105	15.7
1+	825.4091	825.4091	$^{1,5}A_3$	0.04	285087	5.0
1+	839.3886	839.3883	$C_3^{\bullet}$-CH_3O	0.28	671892	11.6
1+	855.3835	855.3832	$C_3^{\bullet}$-CH_3	0.34	679209	11.7
1+	869.3987	869.3989	$C_3^{\ddagger}$	-0.20	7751766	131.2
1+	871.4151	871.4145	C_3	0.60	2538225	43.0
1+	941.4563	941.4564	$^{3,5}A_4$	-0.06	713158	11.8
1+	952.4949	952.4946	$Z_{3\alpha}$	0.28	261662	4.2
1+	968.4894	968.4895	$Y_{3\alpha}^{\ddagger}$	-0.13	249805	4.0
1+	998.5000	998.5001	$^{1,5}X_{3\alpha}$	-0.13	2368191	36.5
1+	1070.5370	1070.5354	$^{1,5}A_4$	1.53	371592	5.5
1+	1098.5299	1098.5303	B_4	-0.34	2266598	33.8
1+	1114.5254	1114.5252	$C_4^{\ddagger}$	0.14	686152	9.9
1+	1126.5847	1126.5838	$Z_{4\alpha, 3\beta}^{\bullet}$-$CH_3O$	0.80	433261	6.3
1+	1172.5875	1172.5893	$Z_{4\alpha,4\beta}$	-1.55	316011	5.7
1+	1202.6002	1202.5999	$^{1,5}X_{4\alpha, 3\beta}$	0.24	856339	12.0
1+	1360.6947	1360.6942	M-CH_4O	0.38	202911	2.7
1+	1392.7202	1392.7204	M	-0.13	1429924	18.7

Table S13. List of assigned EED fragments in Figure S2a. All fragments are sodium adducts unless labeled otherwise. Multiple assignments are separated by commas; ω indicates harmonics; the double dagger symbol (‡) indicates that the fragment has two fewer hydrogens than the canonical structures; the double prime symbol (") indicates that the fragment has two more hydrogens than the canonical structure; the dot symbol (•) indicates a radical.

z	Exptl. *m/z*	Theo. *m/z*	Assignment	Δppm	Intensity	*S/N*
1+	211.0934	211.0941	$B_1^{\bullet}$-CH_3O	-3.34	2461427	47.7
1+	227.0883	227.0890	$C_1^{\bullet}$-CH_3O	-2.93	4867073	89.7
1+	241.1046	241.1046	B_1	-0.23	849379	15.7
1+	243.0834	243.0839	$C_1^{\bullet}$-CH_3, $C_{2\beta}^{‡}$/$Y_{4\beta}$	-2.05	3928313	72.8
1+	259.1150	259.1152	C_1	-1.00	1306114	24.1
1+	269.1581	269.1582	$Z_1^{\bullet}$-CH_3O	-0.53	4822340	87.7
1+	285.1531	285.1531	$Z_1^{\bullet}$-CH_3	-0.12	2814129	50.1
1+	299.1687	299.1687	Z_1	-0.15	4879694	84.0
1+	301.1259	301.1258	$^{0,4}A_{2\alpha}$	0.29	2944244	50.3
1+	315.1416	315.1414	$^{1,3}A_{2\alpha,\,2\beta}$, $^{2,4}A_{2\alpha,\,2\beta}$	0.68	1993545	34.1
1+	315.1639	315.1637	$Y_1^{‡}$	0.61	2535854	43.4
1+	317.1795	317.1793	Y_1	0.60	13833557	236.6
1+	323.108	323.1078	$^{0,4}A_{2\alpha}$ + 2Na - H	0.63	3227342	74.5
1+	329.1572	329.1571	$^{3,5}A_{2\alpha}$	0.50	2515376	43.6
1+	345.1744	345.1742	$^{1,5}X_1$	0.60	7456714	129.8
1+	371.1682	371.1676	$B_{2\beta}$/$^{0,4}X_{4\beta}$	1.62	1649345	28.4
1+	385.1839	385.1833	$B_{2\beta}^{\bullet}$-$C_2H_5O_2$	1.43	3395620	57.9
1+	401.1788	401.1781	$C_{2\beta}^{\bullet}$-$C_2H_5O_2$	1.81	1587441	26.5
1+	414.2328	414.2321	$^{0,2}X_1$	1.85	635546	10.2
1+	415.1943	415.1939	$^{1,5}A_{2\beta}^{‡}$	1.00	2030646	32.6
1+	417.2101	417.2095	$^{1,5}A_{2\beta}$	1.33	830681	13.3
1+	431.1896	431.1888	$C_{2\alpha}$/$\mathbf{Z_{4\alpha''}}$	2.00	11120905	175.5
1+	445.2052	445.2044	$B_{2\beta}$	1.82	3583703	54.8
1+	447.1844	447.1837	$C_{2\beta}^{\bullet}$-CH_3	1.51	2006639	30.7
1+	453.1718	453.1708	$C_{2\alpha}$/$\mathbf{Z_{4\alpha''}}$ + 2Na - H	2.23	1667266	32.4
1+	461.2003	461.1993	$C_{2\beta}^{‡}$	2.03	12128542	185.9
1+	463.2159	463.2150	$C_{2\beta}$	1.91	1957535	30.1
1+	475.1797	475.1786	$C_{2\alpha}^{‡}$/$^{1,5}X_{4\alpha''}$	2.34	1167474	18.0
1+	484.2751	484.2740	$Z_2^{\bullet}$-$C_2H_5O_2$	2.34	1088225	16.8
1+	491.2110	491.2099	$Y_{4\alpha'}$/$^{0,4}A_{4\alpha''}$	2.14	848797	13.2

1+	500.2699	500.2688	$Z_2^{\bullet}$- C_2H_5O	2.32	2041165	31.6
1+	502.2856	502.2845	$Z_2^{\bullet}$-Ac	2.17	3282636	50.7
1+	514.2858	514.2845	$Z_2^{\bullet}$-CH_3O	2.44	10482719	161.3
1+	519.2422	519.2412	$^{1,3}A_{3\beta}$, $^{2,4}A_{3\beta}$	1.83	1501063	23.1
1+	530.2809	530.2794	$Z_2^{\bullet}$-CH_3	2.67	2039061	31.3
1+	544.2967	544.2951	Z_2	2.93	5725663	87.2
1+	560.2889	560.2900	$Y_2^{‡}$	-1.88	758609	11.5
1+	562.3068	562.3056	Y_2	2.11	2824116	42.6
1+	575.2688	575.2674	$^{2,5}A_{2\alpha}^{‡}$	2.36	988828	14.8
1+	590.3020	590.3005	$^{1,5}X_2$	2.41	18637936	274.9
1+	605.2792	605.2779	$C_{2\alpha}^{\bullet}$-$C_2H_5O_2$	2.14	721711	10.6
2+	612.7957	612.7945	$^{1,5}X_{3\alpha}$	1.95	920701	13.3
1+	619.2960	619.2936	$^{1,5}A_{2\alpha}^{‡}$	3.78	2981754	43.1
1+	621.2749	621.2730	$C_{2\alpha}^{\bullet}$-C_2H_5O	3.10	502265	7.3
1+	621.3113	621.3093	$^{1,5}A_{2\alpha}$	3.30	1783490	25.8
1+	635.2916	635.2885	$C_{2\alpha}^{\bullet}$-CH_3O	4.78	1542163	21.8
2+	651.3038	651.3016	C_3	3.33	872728	11.9
1+	665.3010	665.2991	$C_{2\alpha}^{‡}$	2.86	4787549	63.2
1+	667.3166	667.3148	$C_{2\alpha}$	2.75	2648819	35.0
1+	709.3272	709.3253	$^{0,4}A_3$	2.59	4855292	61.7
2+	714.8457	714.8444	$^{1,5}X_{3\beta}$	1.83	1355086	16.5
1+	731.3098	731.3073	$^{0,4}A_3$ + 2Na - H	3.36	1312671	20.0
1+	734.3808	734.3792	$Y_{3\alpha}$ /$Z_{3\beta}$	2.22	3178970	38.6
1+	737.3585	737.3566	$^{3,5}A_3$	2.59	6861491	83.3
2+	750.8600	750.8621	$^{1,5}A_4$	-2.80	441908	5.0
2+	764.8584	764.8595	B_4	-1.50	543629	6.1
2+	793.8941	793.8916	$Z_{4\alpha, 4\beta}$	3.13	3396053	36.3
2+	816.8966	816.8943	$^{1,5}X_{4\alpha, 4\beta}$	2.77	11178151	115.7
2+	830.9141	830.9100	$^{0,2}X_{4\alpha, 4\beta}$	4.94	758834	7.9
2+	838.8936	838.8963	$^{0,2}A_5$	-3.25	5412996	54.4
1+	839.3899	839.3883	C_3/$Z_{3\beta}$	1.92	4894115	49.2
2+	874.9382	874.9362	$^{0,4}X_{4\alpha, 4\beta}$	2.34	3570014	36.0
2+	911.9559	911.9546	M	1.47	3.74E+09	38683.4
1+	1043.4895	1043.4881	$C_3^{‡\bullet}$-CH_3O	1.37	1158935	12.2

1+	1059.4848	1059.4830	$C_3^{\bullet}$-CH_3	1.65	464292	4.9
1+	1084.5160	1084.5146	C_3	1.26	549503	5.8
1+	1126.5809	1126.5838	$Z_{3\alpha}^{\bullet}$-CH_3O	-2.58	756735	7.8
1+	1156.5958	1156.5944	$Z_{3\alpha}$	1.20	709671	7.3
1+	1172.5903	1172.5893	$Y_{3\alpha}^{\ddagger}$	0.89	976543	10.0
1+	1202.5996	1202.5999	$^{1,5}X_{3\alpha}$	-0.22	3254020	32.7
1+	1231.5950	1231.5929	$^{1,5}A_3^{\ddagger}$	1.66	665755	6.7
1+	1233.6087	1233.6086	$^{1,5}A_3$	0.11	2374781	23.8
1+	1277.5988	1277.5984	$C_3^{\ddagger}$	0.32	9293675	90.9
1+	1330.6840	1330.6836	$Z_{3\beta}^{\bullet}$-CH_3O	0.32	1612447	15.8
1+	1349.6573	1349.6559	$^{3,5}A_4$	0.99	555852	5.4
1+	1360.6933	1360.6942	$Z_{3\beta}$	-0.65	1583308	15.0
1+	1376.6905	1376.6891	$Y_{3\beta}^{\ddagger}$	1.05	630114	6.0
1+	1378.7050	1378.7047	$Y_{3\beta}$	0.21	1530119	14.5
1+	1406.6984	1406.6996	$^{1,5}X_{3\beta}$	-0.86	2111782	20.1
1+	1506.7293	1506.7298	B_4	-0.36	2147603	19.7
1+	1564.7948	1564.7939	$Z_{4\alpha,\ 4\beta}$	0.56	616009	12.7
1+	1582.7981	1582.8045	$Y_{4\alpha,\ 4\beta}$	-4.04	415549	3.7
1+	1610.7955	1610.7994	$^{1,5}X_{4\alpha,\ 4\beta}$	-2.44	1558936	13.8
1+	1768.8937	1768.8937	M-CH_4O	-0.01	649836	5.5
1+	1800.9140	1800.9199	M	-3.29	5382990	45.2

Table S14. List of assigned EED fragments in Figure S2b. All fragments are sodium adducts unless labeled otherwise. Multiple assignments are separated by commas; ω indicates harmonics; the double dagger symbol (‡) indicates that the fragment has two fewer hydrogens than the canonical structures; the double prime symbol ('') indicates that the fragment has two more hydrogens than the canonical structure; the dot symbol (•) indicates a radical.

z	Exptl. *m/z*	Theo. *m/z*	Assignment	Δppm	Intensity	*S/N*
1+	227.0890	227.0888	$C_1^{\bullet}$-CH_3O	1.01	1394461	29.8
1+	241.1046	241.1046	B_1	-0.31	436877	10.5
1+	243.0839	243.0839	$C_1^{\bullet}$-CH_3, $C_{2\alpha'}^{‡}/Y_{5\alpha}$	0.04	947744	26.0
1+	257.0996	257.0997	$C_1^{‡}$	-0.08	508863	10.7
1+	259.1151	259.1152	C_1	-0.54	469992	11.5
1+	299.1688	299.1687	Z_1	0.30	882859	18.0
1+	317.1793	317.1792	Y_1	0.32	3511068	72.0
1+	345.1742	345.1742	$^{1,5}X_1$	0.00	1371685	27.5
1+	415.1938	415.1939	$^{1,5}A_{2\alpha'}^{‡}$	-0.13	484312	10.6
1+	431.1887	431.1887	$C_{2\alpha'}^{\bullet}$-CH_3O	0.00	1728668	33.1
1+	445.2045	445.2045	$B_{2\alpha'}$	-0.11	646959	12.4
1+	447.1852	447.1859	$C_{2\alpha'}^{\bullet}$-CH_3	-1.41	274171	5.2
1+	461.1992	461.2008	$C_{2\alpha'}^{‡}$	-3.43	1073998	20.5
1+	463.2156	463.2164	$C_{2\alpha'}$	-1.75	335841	6.4
1+	502.2846	502.2843	$Z_2^{\bullet}$-Ac	0.66	538081	9.9
1+	505.2254	505.2255	$^{0,4}A_{3\alpha'}$	-0.20	647503	11.9
1+	514.2847	514.2846	$Z_2^{\bullet}$-CH_3O	0.16	1683460	30.6
1+	530.2795	530.2797	$Z_2^{\bullet}$-CH_3	-0.34	312570	5.6
1+	533.2570	533.2571	$^{3,5}A_{3\alpha'}$	-0.15	309353	5.5
1+	544.2951	544.2949	Z_2	0.26	855435	15.2
2+	562.3058	562.3056	Y_2	0.32	322999	5.7
1+	590.3007	590.3005	$^{1,5}X_2$	0.34	2072446	35.4
1+	635.2888	635.2885	$C_{3\alpha}/Z_{4\alpha''}$	0.44	1097338	24.3
2+	651.3027	651.3022	C_4	0.68	168173	2.8
2+	793.8922	793.8920	$Z_{5\alpha', 4\alpha'', 3\beta}$	0.26	532943	8.2
2+	816.8943	816.8939	$^{1,5}X_{5\alpha', 4\alpha'', 3\beta}$	0.53	1018092	15.3
1+	839.3887	839.3883	$C_4/Z_{3\alpha'}$	0.50	1178967	17.3
1+	874.9365	874.9362	$^{0,4}X_{4\alpha', 4\alpha'', 3\beta}$	0.39	372991	5.3
2+	911.9552	911.9547	M	0.58	23592078	329.5

1+	913.4255	913.4251	$^{0,4}A_4$	0.42	867365	12.1
1+	935.4060	935.4071	$^{0,4}A_4$ + 2Na - H	-1.19	986016	20.8
1+	941.4547	941.4552	$^{3,5}A_4$	-0.56	237377	2.6
1+	998.5005	998.4996	$^{1,5}X_{3\alpha}$	0.98	520514	5.5
1+	1043.4887	1043.4873	$C_4/Z_{3\beta}$	1.38	596691	6.2
1+	1277.6003	1277.5975	$C_4^{‡}$	2.22	1033891	9.4
1+	1360.6946	1360.6898	$Z_{4\alpha'}$	3.53	572988	5.1
1+	1406.7003	1406.6998	$^{1,5}X_{4\alpha'}$	0.38	380576	3.4
1+	1506.7391	1506.7343	B_5	3.19	245325	2.1
1+	1800.9223	1800.9178	M	2.50	435781	4.3

Table S15. List of assigned EED fragments in Figure S2c. All fragments are sodium adducts unless labeled otherwise. Multiple assignments are separated by commas; ω indicates harmonics; the double dagger symbol (‡) indicates that the fragment has two fewer hydrogens than the canonical structures; the double prime symbol (") indicates that the fragment has two more hydrogens than the canonical structure; the dot symbol (•) indicates a radical.

z	Exptl. *m/z*	Theo. *m/z*	Assignment	Δppm	Intensity	*S/N*
1+	227.0890	227.0890	$C_1^{\bullet}$-CH_3O	0.20	1212647	43.8
1+	241.1046	241.1046	B_1	-0.23	300695	14.8
1+	243.0840	243.0839	$C_1^{\bullet}$-CH_3, $C_{2\alpha'}^{‡}/Y_{5\alpha}$	0.21	1107137	40.2
1+	257.0996	257.0996	$C_1^{‡}$	0.20	500007	17.8
1+	269.1582	269.1582	$Z_1^{\bullet}$-CH_3O	0.10	1133127	39.3
1+	299.1688	299.1687	Z_1	0.20	920668	58.9
1+	301.1253	301.1258	$^{0,4}A_{2\alpha}$	-1.57	582721	14.1
1+	317.1793	317.1793	Y_1	0.07	3269107	114.5
1+	345.1742	345.1742	$^{1,5}X_1$	0.05	1272727	43.4
1+	415.1936	415.1939	$^{1,5}A_{2\alpha'}^{‡}$	-0.71	366219	17.3
1+	417.1729	417.1732	$C_{2\alpha'}^{\bullet}$-C_2H_5O	-0.58	181771	5.9
1+	431.1887	431.1888	$C_{2\alpha'}^{\bullet}$-CH_3O, $C_{3\alpha}/Z_{4\alpha'}$	-0.23	1839747	59.5
1+	445.2044	445.2044	$B_{2\alpha'}$	-0.11	586204	18.6
1+	461.1993	461.1993	$C_{2\alpha'}^{‡}$	-0.12	2067356	64.9
1+	502.2844	502.2845	$Z_2^{\bullet}$-Ac	-0.36	622586	19.0
1+	514.2844	514.2845	$Z_2^{\bullet}$-CH_3O	-0.19	1562169	47.4
1+	519.2408	519.2412	$^{1,3}A_{3\alpha'}$, $^{2,4}A_{3\alpha'}$	-0.75	338951	10.3
1+	530.2794	530.2794	$Z_2^{\bullet}$-CH_3	-0.18	265475	8.0
1+	544.2950	544.2951	Z_2	-0.05	1043738	31.2
1+	562.3055	562.3056	Y_2	-0.27	378934	16.3
1+	590.3005	590.3005	$^{1,5}X_2$	-0.09	2045757	59.9
2+	714.8445	714.8444	$^{1,5}X_{4\alpha'}$	0.03	300059	8.1
2+	773.8646	773.8648	C_5	-0.29	188147	4.8
2+	793.8913	793.8916	$Z_{5\alpha', 4\alpha'', 3\beta}$	-0.40	527417	13.6
2+	816.8943	816.8943	$^{1,5}X_{5\alpha', 4\alpha'', 3\beta}$	-0.08	1887249	47.6
2+	830.9107	830.9100	$^{0,2}X_{5\alpha', 4\alpha'', 3\beta}$	0.92	92528	2.3
1+	839.3883	839.3883	$C_{3\alpha}^{\bullet}$-CH_3O	0.02	121167	3.0
1+	869.3985	869.3989	$C_{3\alpha}^{‡}$	-0.39	356202	8.8
2+	874.9359	874.9362	$^{0,4}X_{5\alpha', 4\alpha'', 3\beta}$	-0.31	430943	10.4
2+	911.9547	911.9546	M	0.12	32684054	771.0

1+	913.4266	913.4251	$^{0,4}A_4$	1.67	1086778	25.6
1+	1335.6406	1335.6403	$^{2,4}A_5$	0.24	110576	2.1
1+	941.4515	941.4552	$^{3,5}A_4$	-4.02	335376	7.9
1+	998.5003	998.4996	$^{1,5}X_{3\alpha}$	0.69	902261	20.8
1+	1043.4883	1043.4873	$C_4/Z_{3\beta}$	0.95	1053154	23.5
1+	1277.5989	1277.5975	$C_4^{\ddagger}$	1.11	1398678	26.9
1+	1360.6898	1360.6933	$Z_{4\alpha'}$	-2.58	195995	3.6
1+	1406.6998	1406.6986	$^{1,5}X_{4\alpha'}$	0.87	284986	5.3
1+	1506.7343	1506.7312	B_5	2.04	266175	4.7
1+	1800.9215	1800.9178	M	2.05	657706	10.5

Table S16. List of assigned EED fragments in Figure S3a. All fragments are sodium adducts unless labeled otherwise. Multiple assignments are separated by commas; ω indicates harmonics; the double dagger symbol (‡) indicates that the fragment has two fewer hydrogens than the canonical structures; the double prime symbol (") indicates that the fragment has two more hydrogens than the canonical structure; the dot symbol (•) indicates a radical.

z	Exptl. *m/z*	Theo. *m/z*	Assignment	Δppm	Intensity	*S/N*
1+	227.0884	227.0890	$C_1^{\bullet}$-CH_3O	-2.49	1824395	63.9
1+	241.1040	241.1046	B_1	-2.84	579721	17.9
1+	243.0839	243.0839	$C_1^{\bullet}$-CH_3, $C_{2\beta, 2\alpha}{}^{‡}/Y_{5\beta, 5\alpha}$	-0.24	2315792	40.4
1+	257.0989	257.0996	$C_1^{‡}$	-2.72	944566	31.4
1+	259.1156	259.1152	C_1	1.35	278065	4.7
1+	269.1582	269.1582	$Z_1^{\bullet}$-CH_3O	-0.09	1034626	17.5
1+	299.1687	299.1687	Z_1	-0.15	1434823	51.4
1+	317.1793	317.1793	Y_1	-0.03	4349914	68.5
1+	345.1742	345.1742	$^{1,5}X_1$	0.05	4158642	70.0
1+	417.2088	417.2095	$^{1,5}A_{2\alpha', 2\alpha'', 2\beta}$	-1.78	402701	6.3
1+	431.1886	431.1888	$C_{2\alpha', 2\alpha'', 2\beta}{}^{‡\bullet}$-$CH_3O$	-0.37	2773351	43.2
1+	445.2045	445.2044	$B_{2\alpha', 2\alpha'', 2\beta}$	0.18	2026681	31.4
1+	461.1997	461.1993	$C_{2\alpha', 2\alpha'', 2\beta}{}^{‡}$	0.71	4278156	66.4
1+	463.2150	463.2150	$C_{2\alpha', 2\alpha'', 2\beta}$	0.08	1348793	20.9
1+	505.2256	505.2256	$^{0,4}A_{3\alpha'}$	0.05	875778	13.4
1+	514.2845	514.2845	$Z_2^{\bullet}$-CH_3O	0.01	2638883	40.0
1+	527.2075	527.2076	$^{0,4}A_{3\alpha'}$ + 2Na - H	-0.12	1259692	36.4
1+	530.2800	530.2794	$Z_2^{\bullet}$-CH_3	0.95	352120	5.3
1+	533.2570	533.2568	$^{3,5}A_{3\alpha'}$	0.25	995079	14.9
1+	544.2955	544.2951	Z_2	0.87	1071132	15.8
1+	560.2894	560.2900	$Y_2^{‡}$	-1.06	259307	3.8
1+	562.3056	562.3056	Y_2	0.02	530167	7.7
1+	590.3005	590.3005	$^{1,5}X_2$	-0.06	3425827	48.7
1+	635.2884	635.2885	$C_{3\alpha}/Z_{4\alpha''}$	-0.24	1536134	21.5
1+	734.3797	734.3792	$Y_{3\alpha}/Z_{3\beta}$	0.68	531711	7.0
2+	854.3881	854.3936	$C_4^{‡}$	-6.45	621671	13.0
2+	895.9404	895.9415	$Z_{4\alpha', 3\beta}$	-1.23	485813	5.7
2+	918.9443	918.9442	$^{1,5}X_{4\alpha', 4\alpha'', 3\beta}$	0.12	807427	9.2
2+	977.9622	977.9646	B_5	-2.47	314352	3.5
2+	1020.9938	1020.9941	$^{1,5}X_{5\alpha'', 5\alpha', 4\beta}$	-0.33	977781	10.4

2+	1116.0542	1116.0543	M	-0.09	30855028	320.3
1+	1139.5074	1139.5069	$^{0,4}A_4$ + 2Na - H	0.44	856792	16.3
1+	1145.5543	1145.5562	$^{3,5}A_4$	-1.60	370453	3.7
1+	1202.5993	1202.5999	$^{1,5}X_{3\alpha}$	-0.51	1041855	10.2
1+	1247.5881	1247.5879	$C_4/Z_{3\beta}$	0.21	1027858	10.1
1+	1685.7939	1685.7980	$C_4^{\ddagger}$	-2.43	440655	3.7
1+	1738.8783	1738.8832	$Z_{4\alpha'', 4\alpha', 3\beta}^{\bullet}$-$CH_3O$	-2.82	392021	3.1
1+	1814.8982	1814.8992	$^{1,5}X_{4\alpha', 4\alpha'', 3\beta}$	-0.55	319226	2.5
1+	2209.1180	2209.1195	M	-0.69	538742	3.9

Table S17. List of assigned EED fragments in Figure S3b. All fragments are sodium adducts unless labeled otherwise. Multiple assignments are separated by commas; ω indicates harmonics; the double dagger symbol (‡) indicates that the fragment has two fewer hydrogens than the canonical structures; the double prime symbol (") indicates that the fragment has two more hydrogens than the canonical structure; the dot symbol (•) indicates a radical.

z	Exptl. *m/z*	Theo. *m/z*	Assignment	Δppm	Intensity	*S/N*
1+	227.0889	227.0890	$C_1^{\bullet}$-CH_3O	-0.24	3615028	80.0
1+	241.1041	241.1046	B_1	-2.38	365187	11.8
1+	243.0839	243.0839	$C_1^{\bullet}$-CH_3, $C_{2\beta, 2\alpha'}^{‡}/Y_{4\beta, 5\alpha'}$	-0.20	3541806	76.5
1+	259.1149	259.1152	C_1	-1.35	431193	8.1
1+	269.1582	269.1582	$Z_1^{\bullet}$-CH_3O	-0.16	1124361	24.0
1+	285.1524	285.1531	$Z_1^{\bullet}$-CH_3	-2.71	385817	8.2
1+	299.1687	299.1687	Z_1	-0.15	895894	19.0
1+	301.1251	301.1258	$^{0,4}A_{2\alpha''}$	-2.34	674662	24.8
1+	315.1413	315.1414	$^{1,3}A_{2\alpha', 2\beta}$ or $^{2,4}A_{2\alpha', 2\beta}$	-0.50	460577	9.6
1+	329.1562	329.1571	$^{3,5}A_{2\alpha''}$	-2.60	615096	21.9
1+	317.1792	317.1793	Y_1	-0.28	3712570	77.1
1+	343.1357	343.1363	$^{0,3}A_{2\alpha', 2\beta}^{‡}$	-1.83	165648	3.4
1+	345.1741	345.1742	$^{1,5}X_1$	-0.39	1325820	27.0
1+	385.1831	385.1833	$B_{2\alpha', 2\beta}^{\bullet}$-$C_2H_5O_2$	-0.59	876569	17.8
1+	387.1990	387.1990	$^{1,5}A_{2\alpha', 2\beta}^{‡}$ -CH_3O	0.07	182706	3.7
1+	415.1938	415.1939	$^{1,5}A_{2\alpha', 2\beta}^{‡}$	-0.23	1683901	32.9
1+	417.2092	417.2095	$^{1,5}A_{2\alpha', 2\beta}$	-0.80	575774	11.2
1+	431.1885	431.1888	$C_3/Z_{4\alpha'}$, $C_{2\alpha',2\beta}^{\bullet}$-$CH_3O$	-0.69	4950089	95.9
1+	445.2042	445.2044	$B_{2\alpha', 2\beta}$	-0.54	2286658	44.0
1+	447.1835	447.1837	$C_{2\alpha', 2\beta}^{\bullet}$-$CH_3$	-0.52	1321437	25.4
1+	461.1992	461.1993	$C_{2\alpha', 2\beta}^{‡}$	-0.38	4779982	91.8
1+	463.2148	463.2150	$C_{2\alpha', 2\beta}$	-0.42	922451	17.7
1+	514.2843	514.2845	$Z_2^{\bullet}$-CH_3O	-0.40	2798328	51.7
1+	519.2408	519.2412	$^{1,3}A_{3\alpha', 3\beta}$, $^{2,4}A_{3\alpha', 3\beta}$	-0.73	1162091	21.5
1+	544.2951	544.2951	Z_2	0.08	1385340	25.3
1+	562.3036	562.3056	Y_2	-3.65	974837	31.9
1+	590.3002	590.3005	$^{1,5}X_2$	-0.54	4155918	74.7
1+	619.2957	619.2936	$^{1,5}A_{3\beta}^{‡}$	3.40	444997	7.9
1+	635.2880	635.2885	$C_{3\beta}^{\bullet}$-CH_3O	-0.79	1385684	24.1

1+	649.3044	649.3042	$B_{3\beta}$	0.24	1034927	17.6
1+	665.2990	665.2991	$C_{3\beta}^{‡}$	-0.13	3254318	54.3
2+	714.8444	714.8444	$^{1,5}X_{3\alpha}$	-0.01	220718	3.6
1+	734.3791	734.3792	$Y_{3\alpha}/Z_{3\beta}$	-0.12	723462	11.8
1+	823.3938	823.3934	$^{1,5}A_{3\alpha}{}^{‡}$	0.44	695461	10.8
1+	825.4084	825.4091	$^{1,5}A_{3\alpha}$	-0.84	524790	8.1
1+	839.3877	839.3883	$C_4/Z_{3\alpha}$	-0.73	672004	10.1
1+	869.3988	869.3989	$C_{3\alpha}^{‡}$	-0.12	1067850	16.0
2+	895.9375	895.9415	$Z_{4\alpha', 4\beta}$	-4.44	202285	2.9
1+	913.4241	913.4251	$^{0,4}A_4$	-1.14	712395	10.0
2+	918.9432	918.9442	$^{1,5}X_{4\alpha', 4\beta}$	-1.06	749158	10.5
1+	935.4076	935.4071	$^{0,4}A_4$ + 2Na - H	0.54	2013621	54.5
1+	941.4557	941.4564	$^{3,5}A_4$	-0.73	747258	10.5
2+	1020.9934	1020.9941	$^{1,5}X_{4\alpha'', 5\alpha', 5\beta}$	-0.67	1791974	23.6
2+	1035.0087	1035.0097	$^{0,2}X_{4\alpha'', 5\alpha', 5\beta}$	-0.97	265883	3.5
1+	1043.4863	1043.4881	$C_4/Z_{3\beta}$	-1.75	2239479	29.5
2+	1116.0535	1116.0543	M	-0.79	47181416	603.7
1+	1406.6993	1406.6996	$^{1,5}X_{3\alpha}$	-0.28	545862	6.1
1+	1564.7863	1564.7939	$Z_{3\beta}$	-4.85	186884	2.0
1+	1610.7994	1610.7994	$^{1,5}X_{3\beta}$	-0.03	335178	3.5
1+	1685.7959	1685.7980	$C_4^{‡}$	-1.21	771236	7.9
1+	1784.8923	1784.8886	$Y_{4\alpha', 4\beta}^{‡}$	2.07	232321	2.3
1+	1814.8998	1814.8992	$^{1,5}X_{4\alpha', 4\beta}$	0.32	372858	3.6
1+	2209.1177	2209.1195	M	-0.82	1106030	9.8

Table S18. List of assigned EED fragments in Figure S3c. All fragments are sodium adducts unless labeled otherwise. Multiple assignments are separated by commas; ω indicates harmonics; the double dagger symbol (‡) indicates that the fragment has two fewer hydrogens than the canonical structures; the double prime symbol (") indicates that the fragment has two more hydrogens than the canonical structure; the dot symbol (•) indicates a radical.

z	Exptl. *m/z*	Theo. *m/z*	Assignment	Δppm	Intensity	*S/N*
1+	211.0940	211.0941	$B_1^{\bullet}$-CH_3O	-0.54	2736254	52.4
1+	227.0889	227.0890	$C_1^{\bullet}$-CH_3O	-0.46	8382834	157.7
1+	241.1045	241.1046	B_1	-0.43	1194601	45.3
1+	243.0839	243.0839	$C_1^{\bullet}$-CH_3, $C_{2\beta, 2\alpha}^{‡}/Y_{5\beta, 5\alpha}$	-0.24	5653985	107.8
1+	269.1581	269.1582	$Z_1^{\bullet}$-CH_3O	-0.20	3296951	60.2
1+	285.1530	285.1531	$Z_1^{\bullet}$-CH_3	-0.36	1694535	30.4
1+	299.1688	299.1687	Z_1	0.02	2823748	50.6
1+	315.1414	315.1414	$^{1,3}A_{2\beta, 2\alpha'}$, $^{2,4}A_{2\beta, 2\alpha'}$	0.05	1895840	33.6
1+	315.1636	315.1637	$Y_1^{‡}$	-0.19	1137135	20.1
1+	317.1793	317.1793	Y_1	0.07	13827026	245.0
1+	345.1743	345.1742	$^{1,5}X_1$	0.14	5157770	87.6
1+	385.1832	385.1833	$B_{2\alpha', 2\beta}^{\bullet}$-$C_2H_5O_2$	-0.20	2949895	48.9
1+	401.1781	401.1781	$C_{2\alpha', 2\beta}^{\bullet}$-$C_2H_5O_2$	0.02	1651135	27.3
1+	415.1937	415.1939	$^{1,5}A_{2\alpha', 2\beta}^{‡}$	-0.42	4750704	77.7
1+	417.1730	417.1732	$C_{2\alpha', 2\beta}^{\bullet}$-$C_2H_5O$	-0.49	1392257	22.8
1+	417.2095	417.2095	$^{1,5}A_{2\alpha', 2\beta}$	-0.06	1467013	24.0
1+	431.1887	431.1888	$C_{2\alpha', 2\beta}^{\bullet}$-$CH_3O$	-0.27	9150847	148.0
1+	445.2046	445.2044	$B_{2\alpha', 2\beta}$	0.32	6334171	101.8
1+	447.1837	447.1837	$C_{2\alpha', 2\beta}^{\bullet}$-$CH_3$	-0.07	2818300	45.3
1+	461.1991	461.1993	$C_{2\alpha', 2\beta}^{‡}$	-0.61	12970280	205.8
1+	463.2150	463.2150	$C_{2\alpha', 2\beta}$	-0.05	3058270	47.9
1+	500.2689	500.2688	$Z_2^{\bullet}$-C_2H_5O	0.20	2179184	32.5
1+	505.2254	505.2256	$^{0,4}A_{3\alpha'}$	-0.24	6357461	94.9
1+	514.2846	514.2845	$Z_2^{\bullet}$-CH_3O	0.07	10161803	149.1
1+	519.2411	519.2412	$^{1,3}A_{3\beta}$, $^{2,4}A_{3\beta}$	-0.11	2089811	30.7
1+	527.2075	527.2076	$^{0,4}A_{3\alpha'}$ + 2Na - H	-0.12	8333980	286.0
1+	530.2795	530.2794	$Z_2^{\bullet}$-CH_3	0.10	2067467	29.8
1+	533.2568	533.2568	$^{3,5}A_{3\alpha'}$	-0.01	4069541	58.6
1+	544.2952	544.2951	Z_2	0.21	5086288	72.3

1+	547.2364	547.2361	$^{o,3}A_{3\beta}^{\ddagger}$	0.58	624701	8.9
1+	558.2748	558.2743	ω2	0.76	28846362	411.3
1+	561.2520	561.2518	$^{1,4}A_{3\beta}^{\ddagger}$	0.33	609264	8.7
1+	562.3058	562.3056	Y_2	0.21	2479423	35.3
1+	590.3007	590.3005	$^{1,5}X_2$	0.33	12789314	184.1
1+	605.2783	605.2779	$C_{3\beta}^{\bullet}-C_2H_5O_2$	0.72	1351642	19.5
1+	619.2941	619.2936	$^{1,5}A_{3\beta}^{\ddagger}$	0.80	1174887	17.0
1+	621.2729	621.2730	$C_{3\beta}^{\bullet}-C_2H_5O$	-0.08	1111185	16.0
1+	621.3094	621.3093	$^{1,5}A_{3\beta}$	0.12	652502	9.4
1+	635.2886	635.2885	$C_{3\beta}^{\bullet}-CH_3O$	0.08	7259794	104.0
1+	649.3042	649.3042	$B_{3\beta}$	0.06	2872247	40.6
1+	665.2997	665.2991	$C_{3\beta}^{\ddagger}$	0.83	11991463	166.2
1+	667.3147	667.3148	$C_{3\beta}$	-0.16	1735094	24.1
1+	723.3412	723.3410	$^{1,3}A_4$, $^{2,4}A_4$	0.29	1197338	17.1
1+	734.3795	734.3792	$Y_{3\alpha}/Z_{3\beta}$	0.37	2792346	37.2
1+	809.3777	809.3777	$C_{3\alpha}^{\bullet}-C_2H_5O_2$	-0.01	689129	8.1
2+	816.8946	816.8943	$^{1,5}X_{3\beta}$	0.32	724653	8.5
1+	823.3895	823.3934	$^{1,5}A_{3\alpha}^{\ddagger}$	-4.77	1153224	13.6
1+	825.4096	825.4091	$^{1,5}A_{3\alpha}$	0.69	1533326	18.1
2+	854.3937	854.3936	$C_4^{\ddagger}$	0.14	5871521	126.7
1+	869.3987	869.3989	$C_{3\alpha}^{\ddagger}$	-0.24	2932887	32.5
1+	871.4155	871.4145	$C_{3\alpha}$	1.07	1626028	16.5
2+	895.9375	895.9415	$Z_{4\alpha', 4\beta}$	-4.46	660667	6.7
1+	913.4252	913.4251	$^{0,4}A_4$	0.11	3752538	35.4
2+	918.9443	918.9442	$^{1,5}X_{4\alpha', 4\beta}$	0.10	3558203	33.6
1+	935.4072	935.4071	$^{0,4}A_4$ + 2Na - H	0.11	6760764	101.8
1+	941.4568	941.4564	$^{3,5}A_4$	0.44	3754988	35.5
2+	997.9926	997.9914	$Z_{4\alpha'', 5\alpha', 5\beta}$	1.26	2670706	24.1
2+	1020.9940	1020.9941	$^{1,5}X_{4\alpha'', 5\alpha', 5\beta}$	-0.09	9010826	78.8
2+	1035.0089	1035.0097	$^{0,2}X_{4\alpha'', 5\alpha', 5\beta}$	-0.83	699422	6.1
1+	1043.4878	1043.4881	$C_4/Z_{3\beta}$	-0.27	8783704	63.6
2+	1050.0154	1050.0150	$^{1,4}X_{4\alpha'', 5\alpha', 5\beta}$	0.38	797132	7.0
2+	1116.0565	1116.0543	M	1.89	4.33E+09	38003.3
1+	1376.6910	1376.6891	$Y_{3\alpha}^{\ddagger}$	1.41	946551	8.5

1+	1406.7006	1406.6996	$^{1,5}X_{3\alpha}$	0.68	2699346	24.3
1+	1534.7850	1534.7834	$Z_{3\beta}^{\bullet}$-CH_3O	1.04	1369255	12.0
1+	1550.7758	1550.7783	$Z_{3\beta}^{\bullet}$-CH_3	-1.63	1228545	10.8
1+	1564.7935	1564.7939	$Z_{3\beta}$	-0.30	1355794	11.5
1+	1580.7904	1580.7888	$Y_{3\beta}^{\ddagger}$	0.99	1078214	9.2
1+	1610.7991	1610.7994	$^{1,5}X_{3\beta}$	-0.18	2216270	18.9
1+	1641.8100	1641.8081	$^{1,5}A_4$	1.15	972209	8.3
1+	1685.7997	1685.7980	$C_4^{\ddagger}$	1.02	3680153	31.3
1+	1738.8846	1738.8832	$Z_{4\alpha', 4\beta}^{\bullet}$-$CH_3O$	0.84	531728	4.3
1+	1754.8820	1754.8781	$Z_{4\alpha', 4\beta}^{\bullet}$-$CH_3$	2.22	1335990	10.9
1+	1768.8957	1768.8937	$Z_{4\alpha', 4\beta}$	1.10	693677	5.6
1+	1814.8982	1814.8992	$^{1,5}X_{4\alpha', 4\beta}$	-0.55	1725800	14.0
1+	1914.9295	1914.9294	B_5	0.08	1157007	9.0
1+	2019.0003	2018.9990	$^{1,5}X_{4\alpha'',5\alpha', 5\beta}$	0.68	892994	6.9
1+	2177.0998	2177.0933	M-CH_4O	2.98	631411	4.8
1+	2209.1230	2209.1195	M	1.61	4699603	35.5

Table S19. List of assigned EED fragments in Figure S4. All fragments are sodium adducts unless labeled otherwise. Multiple assignments are separated by commas; ω indicates harmonics; the double dagger symbol (‡) indicates that the fragment has two fewer hydrogens than the canonical structures; the double prime symbol (") indicates that the fragment has two more hydrogens than the canonical structure; the dot symbol (•) indicates a radical.

z	Exptl. *m/z*	Theo. *m/z*	Assignment	Δppm	Intensity	*S/N*
1+	211.0941	211.0941	$B_1^{\bullet}$-CH_3O	0.02	3647079	83.0
1+	227.0890	227.0890	$C_1^{\bullet}$-CH_3O	-0.02	9420735	211.8
1+	241.1046	241.1046	B_1	-0.10	999653	22.2
1+	243.0839	243.0839	$C^{‡}$/Y (Hex)	-0.04	7825140	173.9
1+	255.1430	255.1424	$Z_1^{‡\bullet}$-C_2H_5O	2.36	242908	5.3
1+	257.0996	257.0996	$C_1^{‡}$	0.04	1943497	42.8
1+	269.1582	269.1582	$Z_1^{\bullet}$-CH_3O	-0.13	2827002	61.6
1+	315.1636	315.1637	$Y_1^{‡}$	-0.34	1001436	21.7
1+	317.1792	317.1793	Y_1	-0.28	10089101	219.0
1+	345.1741	345.1742	$^{1,5}X_1$	-0.44	3811638	81.9
1+	357.1518	357.1520	$^{1,4}A_2^{‡}$	-0.56	260764	5.6
1+	371.1673	371.1676	$B_{2\beta}$/$^{0,4}X_{5\beta}$	-0.81	1014506	21.3
1+	385.1831	385.1833	$B_2^{\bullet}$-$C_2H_5O_2$	-0.57	2259531	46.5
1+	401.1779	401.1781	$C_2^{\bullet}$-$C_2H_5O_2$	-0.63	1240838	24.9
1+	414.2321	414.2321	$^{0,2}X_1$	-0.05	414033	8.1
1+	415.1936	415.1939	$^{1,5}A_2^{‡}$	-0.54	3596688	70.6
1+	417.1729	417.1732	$C_2^{\bullet}$-C_2H_5O	-0.77	1218533	23.9
1+	417.2093	417.2095	$^{1,5}A_2$	-0.56	1151033	22.6
1+	431.1884	431.1888	$C_2^{\bullet}$-CH_3O	-0.78	8735882	170.8
1+	445.2041	445.2044	B_2	-0.72	6623371	128.4
1+	447.1834	447.1837	$C_2^{\bullet}$-CH_3	-0.74	1956346	37.9
1+	461.1990	461.1993	$C_2^{‡}$	-0.81	14978026	290.0
1+	463.2145	463.2150	C_2	-0.98	3993569	77.0
1+	502.2841	502.2845	$Z_2^{\bullet}$-Ac	-0.88	3529647	66.1
1+	505.2252	505.2256	$^{0,4}A_{3\alpha'}$	-0.64	4247609	79.6
1+	514.2842	514.2845	$Z_2^{\bullet}$-CH_3O	-0.63	7988247	147.4
1+	519.2408	519.2412	$^{1,3}A_{3\beta, 3\alpha''}$, $^{2,4}A_{3\beta, 3\alpha''}$	-0.79	2532358	46.7
1+	527.2069	527.2076	$^{0,4}A_{3\alpha'}$ + 2Na - H	-1.26	5611797	102.2
1+	530.2790	530.2794	$Z_2^{\bullet}$-CH_3	-0.88	1400536	25.5

1+	533.2565	533.2568	${}^{3,5}A_{3\alpha'}$	-0.58	3397186	61.9
1+	544.2951	544.2951	Z_2	0.04	4588140	82.6
1+	549.2519	549.2518	${}^{o,3}A_{3\beta, 3\alpha''}$	0.27	310392	5.6
1+	560.2897	560.2900	$Y_2{}^{\ddagger}$	-0.48	609434	10.9
1+	561.2520	561.2518	${}^{1,4}A_{3\beta, 3\alpha''}{}^{\ddagger}$	0.42	537990	9.6
1+	562.3051	562.3056	Y_2	-0.91	1498814	26.9
1+	575.2669	575.2674	$B_{3\beta}/{}^{0,4}X_{5\beta}$	-0.96	1015965	18.1
1+	583.2339	583.2338	${}^{1,4}A_{3\beta, 3\alpha''}{}^{\ddagger}$ + 2Na - H	0.24	5636337	100.4
1+	590.3001	590.3005	${}^{1,5}X_2$	-0.70	10244614	181.9
1+	605.2781	605.2779	$C_{3\beta}{}^{\bullet}$-$C_2H_5O_2$	0.37	835465	14.8
1+	618.3314	618.3318	${}^{0,2}X_2$	-0.66	543244	9.5
1+	619.2936	619.2936	${}^{1,5}A_{3\beta}{}^{\ddagger}$	-0.01	889748	15.6
1+	621.2726	621.2730	$C_{3\beta}{}^{\bullet}$-C_2H_5O	-0.62	852442	15.0
1+	621.3088	621.3093	${}^{1,5}A_{3\beta}$	-0.74	810002	14.2
1+	635.2881	635.2885	$C_{3\beta}{}^{\bullet}$-CH_3O, $C_{3\alpha}/Z_{4\alpha''}$	-0.73	6106029	105.9
1+	649.3041	649.3042	$B_{3\beta}$	-0.20	1830995	31.5
1+	665.2991	665.2991	$C_{3\beta}{}^{\ddagger}$	0.05	10571215	179.1
2+	714.8445	714.8444	${}^{1,5}X_{3\alpha}$	0.15	241174	4.0
1+	723.3406	723.3410	${}^{1,3}A_{4\beta}$, ${}^{2,4}A_{4\beta}$	-0.57	934089	14.8
1+	734.3788	734.3792	$Y_{3\alpha}/Z_{3\beta}$	-0.57	1925128	31.9
1+	883.3780	883.3781	$C_4/{}^{1,5}X_{3\alpha}$	-0.21	1189084	16.9
2+	918.9438	918.9442	${}^{1,5}X_{3\beta}$	-0.47	264525	3.6
2+	956.4416	956.4435	$C_4{}^{\ddagger}$	-1.94	3425791	42.9
2+	990.9814	990.9835	$Y_{5\alpha'}/Z_{5\alpha''}$	-2.16	1616237	20.8
2+	997.9895	997.9914	$Z_{4\alpha'', 4\alpha', 4\beta}$	-1.85	1482969	19.1
2+	1020.9933	1020.9941	${}^{1,5}X_{4\alpha'', 4\alpha', 4\beta}$	-0.75	4633435	56.7
2+	1027.4895	1027.4932	${}^{1,5}A_{3\alpha}{}^{\ddagger}$	-3.62	552934	6.8
1+	1029.5087	1029.5088	${}^{1,5}A_{3\alpha}$	-0.16	1512995	18.5
1+	1073.4995	1073.4987	$C_{3\alpha}$	0.77	1337201	15.8
2+	1079.0023	1079.0067	$C_5{}^{\ddagger}$	-4.08	1323761	15.2
2+	1100.0429	1100.0412	$Z_{5\alpha'', 5\alpha', 5\beta}$	1.55	1537338	18.2
1+	1117.5238	1117.5249	${}^{0,4}A_4$	-0.94	1484645	17.5
2+	1123.0434	1123.0440	${}^{1,5}X_{5\alpha'', 5\alpha', 5\beta}$	-0.49	6029031	68.9
2+	1137.0599	1137.0596	${}^{0,2}X_{5\alpha'', 5\alpha', 5\beta}$	0.21	704621	8.1

1+	1139.5061	1139.5069	$^{0,4}A_4$ + 2Na - H	-0.70	4222158	48.3
1+	1145.5555	1145.5562	$^{3,5}A_4$	-0.59	2437099	44.8
2+	1152.0651	1152.0649	$^{1,4}X_{5\alpha'', 5\alpha', 5\beta}$	0.15	510719	5.8
2+	1218.1026	1218.1042	M	-1.31	9.19E+08	10338.0
1+	1247.5878	1247.5879	$C_4/Z_{3\beta}$	-0.08	5014663	56.4
1+	1330.6839	1330.6836	$Z_{3\alpha}^{\bullet}$-CH_3O	0.21	289645	3.2
1+	1360.6945	1360.6942	$Z_{3\alpha}$	0.28	392133	4.3
1+	1376.6912	1376.6891	$Y_{3\alpha}^{\ddagger}$	1.54	558750	6.1
1+	1406.6999	1406.6996	$^{1,5}X_{3\alpha}$	0.16	2620864	28.7
1+	1738.8876	1738.8832	$Z_{3\beta}^{\bullet}$-CH_3O	2.55	602888	5.9
1+	1754.8772	1754.8781	$Z_{3\beta}^{\bullet}$-CH_3	-0.51	631958	6.2
1+	1768.8997	1768.8937	$Z_{3\beta}$	3.38	622931	6.1
1+	1784.8903	1784.8886	$Y_{3\beta}^{\ddagger}$	0.92	565285	5.5
1+	1814.8988	1814.8992	$^{1,5}X_{3\beta}$	-0.24	1181069	11.6
1+	1845.9088	1845.9079	$^{1,5}A_4$	0.47	470221	4.6
1+	1889.8974	1889.8977	$C_4^{\ddagger}$	-0.18	2321093	21.6
1+	1942.9856	1942.9829	$Z_{4\alpha'', 4\alpha', 4\beta}^{\bullet}$-$CH_3O$	1.37	533793	5.0
1+	1972.9975	1972.9935	$Z_{4\alpha'', 4\alpha', 4\beta}^{\bullet}$	2.06	546748	5.1
1+	2019.0024	2018.9990	$^{1,5}X_{4\alpha'', 4\alpha', 4\beta}$	1.68	968409	9.0
1+	2119.0256	2119.0292	B_5	-1.67	500142	4.5
1+	2367.1813	2367.1774	M-C_2H_6O	1.61	292280	2.6
2+	2381.1853	2381.1930	M-CH_4O	-3.24	337848	3.0
1+	2413.2214	2413.2192	M	0.91	3693304	32.4

(1) Hong, P.; Sun, H.; Sha, L.; Pu, Y.; Khatri, K.; Yu, X.; Tang, Y.; Lin, C. GlycoDeNovo–an Efficient Algorithm for Accurate de novo Glycan Topology Reconstruction from Tandem Mass Spectra *J. Am. Soc. Mass. Spectrom.* **2017**, *28*, 2288-2301.