Kinetics and oligomer products of the multi-phase reactions of hydroxyacetone with atmospheric amines, ammonium sulfate, and cloud processing: Supplemental Information

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Figures S1-S4, Table S1, 7 pages total

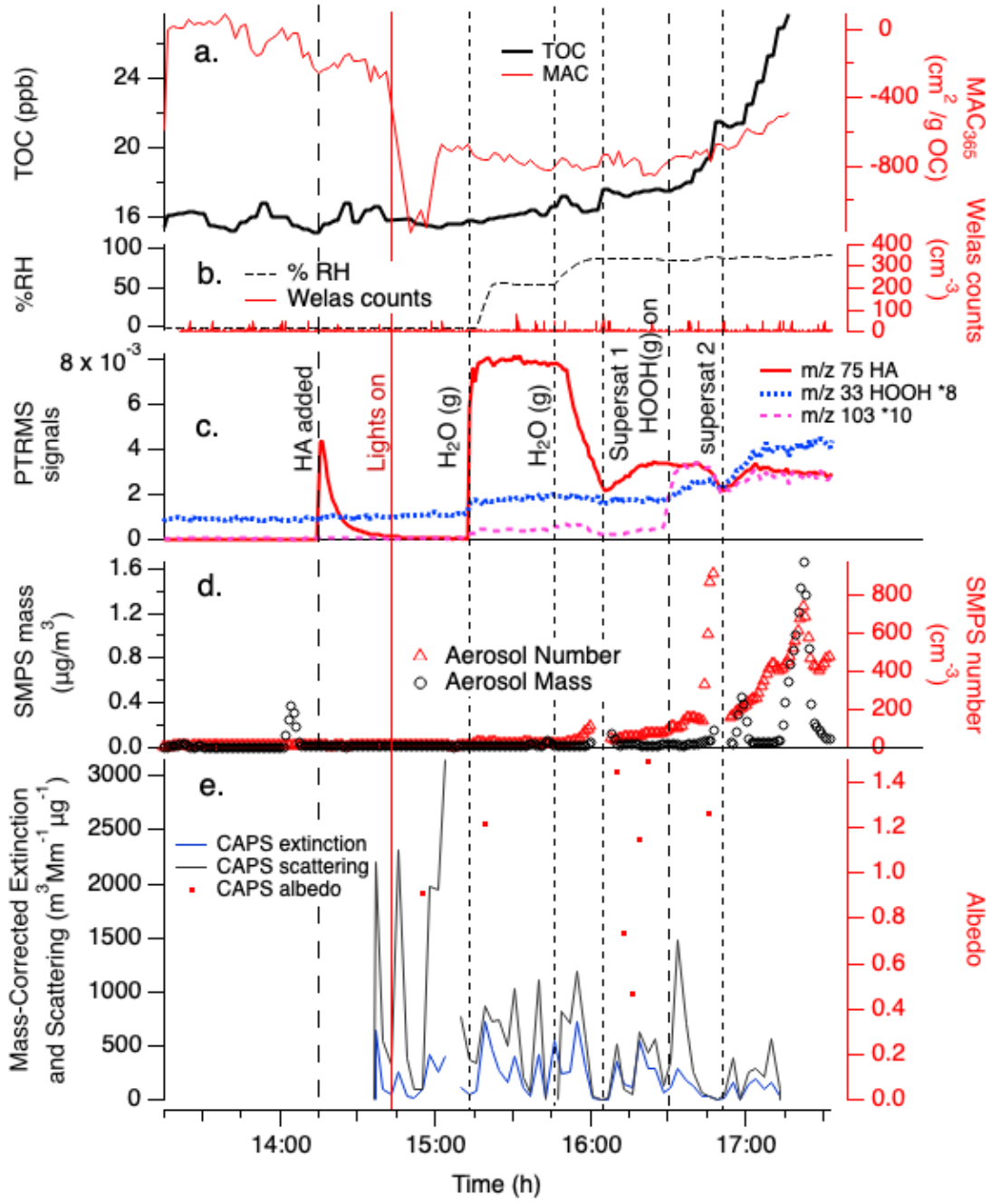

Figure S1. Expt. A with gas-phase hydroxyacetone, photolysis, cloud processing, and HOOH oxidation without seed particles in the CESAM chamber. HA addition, start of chamber illumination and HOOH(g) addition, two water vapor additions, and two water supersaturation events are labeled. Panel **a**: total organic carbon readings and mass absorption coefficients at 365 nm from PILS/waveguide UV-vis, color coded to axes. **b**: chamber RH and droplet spectrometer counts, color coded to axes. **c**: water-corrected PTR-MS data (*m/z* 75 HA, red line, *m/z* 33 HOOH fragment ×8, blue dotted line, *m/z* 103 ×10, pink dash). **d**: dilution- and wall-loss-corrected SMPS total mass (assuming density = 1 g/cm^3) and counts, color-coded to axes. **e**: CAPS-ssa data at 450 nm (mass-corrected extinction, blue line; mass-corrected scattering black line; single-scattering albedo, red dots).

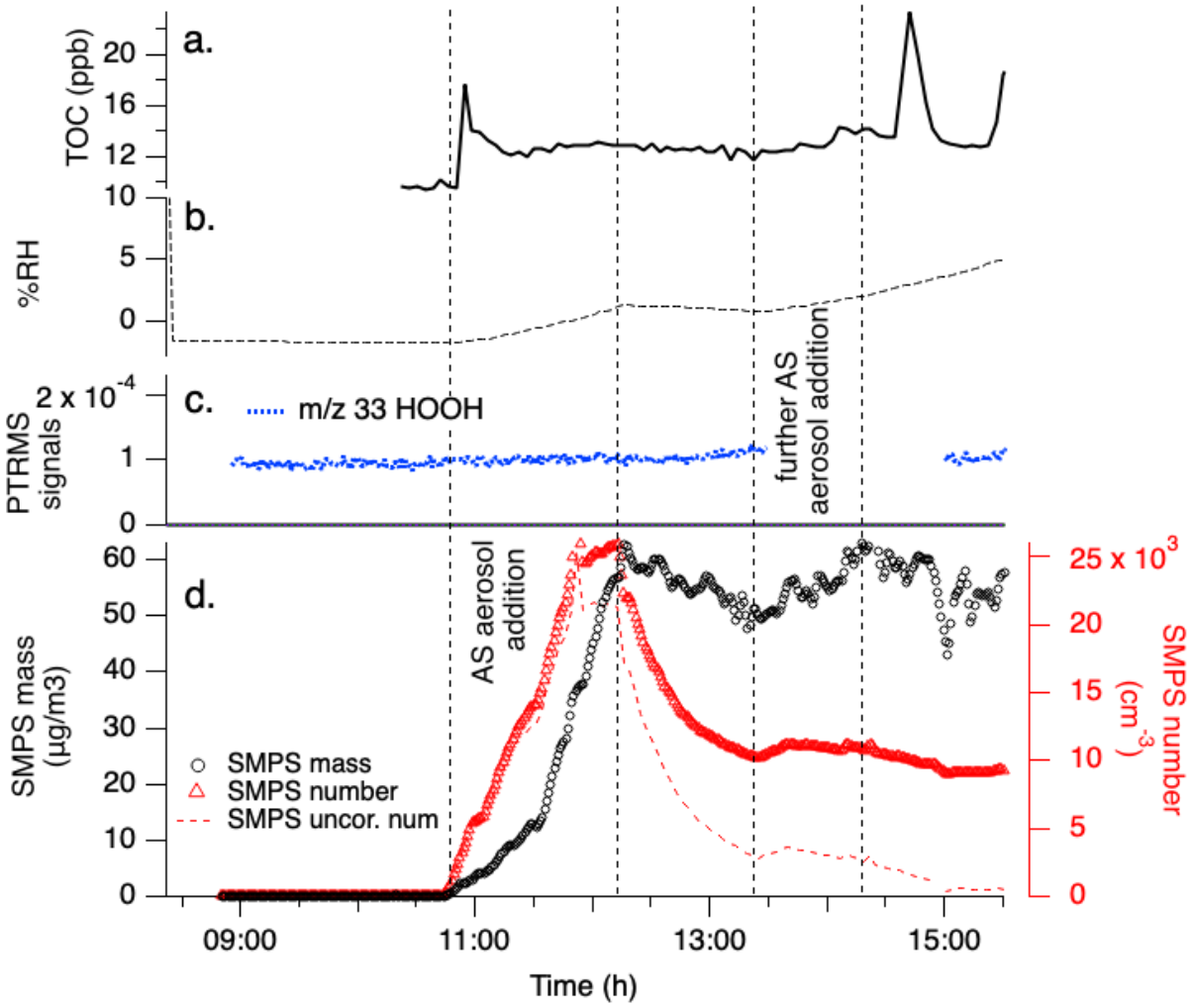

Figure S2. Experiment E (control) with AS seed particles in the CESAM chamber. Two AS addition periods are labeled. Panel **a**: total organic carbon readings in ppb from PILS sampling (black). No waveguide absorbance data was collected. **b**: chamber RH (black dashed line). **c**: water-corrected PTR-MS data for *m/z* 33 HOOH frag (blue dotted line). **d**: dilution- and wall-loss-corrected SMPS total mass (assuming density = 1 g/cm^3) and counts, color-coded to axes. Uncorrected SMPS counts also shown (red dashed line). No CAPS-ssa data was collected.

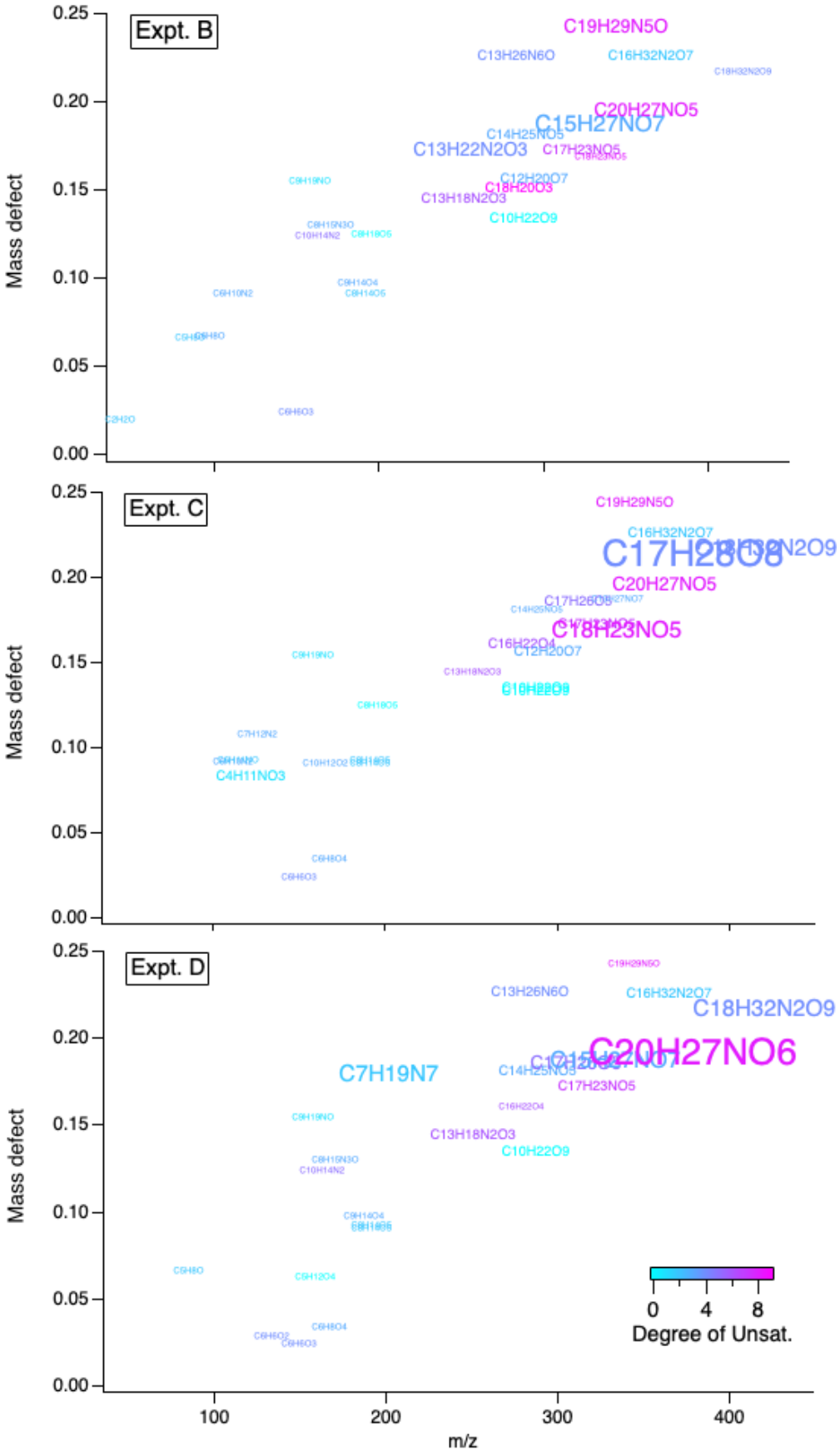

Figure S3. Kendrick mass defect plot showing differences from unit mass of each UHPLC-(+)ESI-HRMS peak with an assigned chemical formula in aerosol collected at the end of Expts. B-D. Colors and symbols indicate degree of unsaturation, and font size is proportional to peak area.

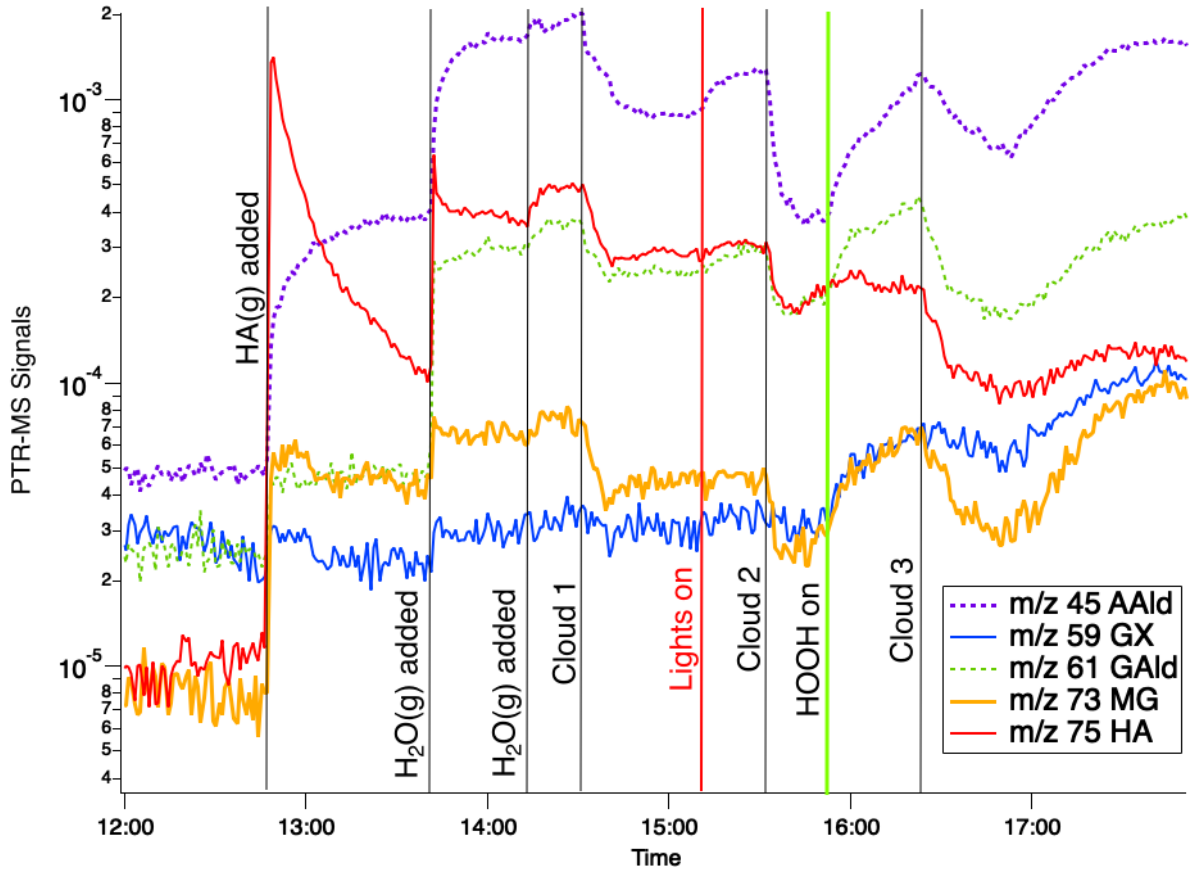

Figure S4: PTR-MS traces for *m/z* 75 hydroxyacetone (red trace) and various aldehyde species in Experiment B, showing responses to turning chamber lights on (red vertical line) and adding HOOH as an OH radical source (green vertical line). PTR-MS signals at *m/z* 45, acetaldehyde (purple dashes); *m/z* 59, glyoxal (blue); *m/z* 61, glycolaldehyde (green dashes); and *m/z* 73, methylglyoxal with some contribution from HA fragments (orange). Experimental events in chamber are noted with labelled vertical lines.

Table S1: Major Organic Species Detected in Aerosol Phase at End of Chamber Experiments

m/z	RT (min)	Peak area Expt B HA_g + AS	Peak area Expt C HA_g + AS/Gly	Peak area Expt D $MeAm_g$ + AS/HA	Formula assigned	Ion	Unsat	Delta (ppm)	Precursors
43.0190	8.28	9.1E+03			C2H2O	H+	2	14.6	unknown
85.0653	11.58	7.6E+03		7.2E+03	C5H8O	H+	2	0	2 HA - CO_2
97.0660	14.22	4.5E+04			C6H8O	H+	3	7.1	3 AAld
111.0907	7.52	1.3E+04	1.4E+04		C6H10N2	H+	3	-13.6	2 HA + 2 NH_3
114.0917	7.73		1.2E+04		C6H11NO	H+	2	-1.9	HA + AAld + Glycine - CO_2
122.0820	10.75		1.1E+06		C4H11NO3	H+	1	2.5	HA + Glycine - CO_2
125.1074	8.96		3.3E+04		C7H12N2	H+	3	-3.7	HA + 2AAld + 2 NH_3
133.0278	1.06			8.0E+04	C6H6O2	Na+	4	9.8	MG +HA
149.0233	13.42	2.5E+04	4.4E+05	5.6E+05	C6H6O3	Na+	4	12	2MG
158.1539	6.33	2.5E+05	2.5E+05	2.1E+04	C9H19NO	H+	1	-4	unknown
159.0623	9.06			7.0E+04	C5H12O4	Na+	0	-6.3	HA + AAld
163.1232	9.92	3.4E+03		3.7E+04	C10H14N2	H+	5	-1.7	2HA +2AAld +2 NH_3
165.0906	11.60		5.9E+05		C10H12O2	H+	3	-5.9	2AAld +2HA
167.0336	13.83		4.1E+04	1.2E+04	C6H8O4	Na+	3	9.6	2MG
170.1297	6.10	2.5E+04		1.6E+05	C8H15N3O	H+	3	2.2	GAld +2HA + 3NH_3
187.0967	9.72	1.2E+04		1.2E+04	C9H14O4	H+	3	-1.5	3HA
191.0902	6.81	2.2E+04	4.7E+03	2.1E+04	C8H14O5	H+	2	-8.9	GAld +2HA
191.0917	6.43		7.5E+04	9.6E+04	C8H14O5	H+	2	-1.4	GAld +2HA
195.1239	6.83	1.1E+05	3.6E+05		C8H18O5	H+	0	3.6	MG +2HA -CO_2
202.1784	7.96			5.6E+06	C7H19N7	H+	2	1.7	2GX +HA +7NH_3
251.1436	11.17	1.1E+06	3.8E+04	1.2E+06	C13H18N2O3	H+	6	16.1	2GAld +3HA +2NH_3
255.1720	11.46	3.1E+06			C13H22N2O3	H+	4	4.5	2AAld +3HA +2NH_3
279.1601	12.91		1.8E+06	4.9E+05	C16H22O4	H+	6	1.6	5AAld +2HA
283.2251	12.18	1.1E+06		1.0E+06	C13H26N6O	H+	4	1.8	2GAld +3HA +6NH_3
285.1496	11.12	2.2E+06			C18H20O3	H+	9	1.8	GAld +8AAld
287.1324	10.53	1.3E+06	1.4E+06		C10H22O9	H+	0	-6.3	2GAld +2HA
287.1337	11.57		1.4E+06	1.3E+06	C10H22O9*	H+	0	-1.8	2GAld +2HA
288.1800	11.04	2.3E+06	8.4E+04	2.3E+06	C14H25NO5	H+	3	-3.7	GAld +2AAld +2HA +NH3
294.1551	8.01	1.1E+06	1.1E+06		C12H20O7	NH_4+	3	-0.6	MG +3HA
311.1852	11.72		1.7E+06	3.0E+06	C17H26O5*	H+	5	-2	HA +7AAld
322.1712	10.52	2.3E+06	2.3E+06	2.3E+06	C17H23NO5*	H+	7	17.7	GAld +5HA +NH_3
334.1677	10.15	7.9E+05	4.6E+06		C18H23NO5	H+	8	6.6	MG +5HA +NH_3
334.1866	10.30	4.5E+06	2.6E+05	4.4E+06	C15H27NO7*	H+	3	0.2	5HA +NH3
344.2425	13.10	2.9E+06	2.3E+06	4.7E+05	C19H29N5O	H+	8	-7.3	AAld +GAld+5HA +5NH_3
362.1952	11.45	4.1E+06	3.8E+06		C20H27NO5	H+	8	-4.4	AAld +6HA +NH_3
365.2250	9.30	2.2E+06	1.9E+06	2.2E+06	C16H32N2O7	H+	2	-10.4	2AAld +4HA +2NH_3

378.1908	11.65			9.6E+06	C20H27NO6	H+	8	-2.4	GAld +6HA +NH_3
378.2125	11.77		1.0E+07		C17H28O8	NH_4+	4	-0.6	AAld +5HA
421.2161	12.21	6.2E+04	4.6E+06	4.3E+06	C18H32N2O9*	H+	4	-6	2MG +4HA +2NH_3

Notes: *m/z* = detected mass-to-charge ratio is positive ion ESI mode. RT = UPLC retention time. Ion = ionization. Unsat = degrees of unsaturation. Delta = difference between predicted and detected exact mass, in ppm. * = recommended tracer ions for HA oligomerization chemistry.