

SUPPLEMENTAL INFORMATION

Formation and optical properties of brown carbon from small α -dicarbonyls and amines

Wilmarie Marrero-Ortiz^{1,‡}, Min Hu^{2*}, Zhuofei Du^{2,‡}, Yuemeng Ji^{3*}, Yujue Wang², Song Guo², Yun Lin⁴, Mario Gomez-Hernandez^{1,5}, Jianfei Peng⁴, Yixin Li¹, Jeremiah Secrest¹, Misti L. Zamora^{4,6}, Yuan Wang⁷, Taicheng An³, and Renyi Zhang^{1,4*}

¹Department of Chemistry, Texas A&M University, College Station, Texas, 77840

²State Key Joint Laboratory of Environmental Simulation and Pollution Control, College of Environmental Sciences and Engineering, Peking University, Beijing, 100871, China

Department of Atmospheric Sciences, Texas A&M University, College Station, Texas, 77843

³Guangzhou Key Laboratory of Environmental Catalysis and Pollution Control, School of Environmental Science and Engineering, Institute of Environmental Health and Pollution Control, Guangdong University of Technology, Guangzhou 510006, China

⁴Departments of Atmospheric Sciences, Texas A&M University, College Station, TX 77843, USA

⁵Department of Chemistry and Biochemistry, Florida International University, Miami, FL 33199

⁶Environmental Health & Engineering, Johns Hopkins School of Public Health, Johns Hopkins University, MD 21218

⁷Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125

[‡] The authors contributed equally to this work

This supplemental information contains 11 pages, with 8 tables (Tables S1 – S8) and 7 figures (Figs. S1-S7)

Table S1: Size-selected effective densities (g cm^{-3}) measurement for each mixture. The uncertainties correspond to one standard deviation.

Size	MG-MA	MG-DA	MG-TA	GL-MA	GL-DA	GL-TA
150	1.24	1.33	1.35	1.18	0.93	1.24
200	1.29	1.35	1.39	1.22	0.97	1.30
250	1.30	1.37	1.40	1.23	1.01	1.28
300	1.29	1.35	1.37	1.23	1.02	1.28
350	1.28	1.35	1.35	1.23	0.96	1.29
Average	1.28 ± 0.02	1.35 ± 0.01	1.37 ± 0.02	1.22 ± 0.02	0.98 ± 0.04	1.28 ± 0.02
Average	1.25 ± 0.14					

Table S2: Peaks detected for the **MG-MA** mixture with their corresponding mass to charge ratio (m/z), chemical formula, nitrogen to carbon ratio (N/C), oxygen to carbon ratio (O/C), hydrogen to carbon ratio (H/C), double bond equivalent (DBE) and aromaticity. The structures identified are labeled in red.

TD-ID-CIMS	Orbitrap-MS	m/z	Formula	N/C	O/C	H/C	DBE	Aromaticity
✓		73	C₃H₅O₂	0.00	0.67	1.67	1.5	0.3
✓		104	C₄H₁₀O₂N	0.25	0.50	2.50	0.5	-0.8
✓	✓	111	C₆H₁₁N₂	0.33	0.00	1.83	2.5	0.1
	✓	124	C ₇ H ₁₀ ON	0.14	0.14	1.43	3.5	0.4
✓	✓	125	C₇H₁₃N₂	0.29	0.00	1.86	2.5	0.1
	✓	137	C₈H₁₃N₂	0.25	0.00	1.63	3.5	0.3
✓		140						
	✓	153	C₈H₁₃ON₂	0.25	0.13	1.63	3.5	0.2
	✓	155	C ₈ H ₁₅ ON ₂	0.25	0.13	1.88	2.5	0.0
	✓	170	C ₈ H ₁₆ ON ₃	0.38	0.13	2.00	2.5	-0.2
	✓	232	C ₁₃ H ₁₈ ON ₃	0.23	0.08	1.38	6.5	0.3
<i>Average</i>				0.24	0.18	1.78	2.90	0.06

Table S3: Peaks detected for the **GL-MA** mixture with their corresponding mass to charge ratio (m/z), chemical formula, nitrogen to carbon ratio (N/C), oxygen to carbon ratio (O/C), hydrogen to carbon ratio (H/C), double bond equivalent (DBE) and aromaticity. The structures identified are labeled in red.

TD-ID-CIMS	Orbitrap-MS	m/z	Formula	N/C	O/C	H/C	DBE	Aromaticity
✓		77	C₂H₅O₃	0.00	1.50	2.50	0.5	-2.00
✓		83						
✓		90	C₃H₈O₂N	0.33	0.67	2.67	0.5	-1.50
✓		97	C₅H₉N₂	0.40	0.00	1.80	2.5	0.17
✓		111						
✓		125	C₆H₉ON₂	0.33	0.17	1.50	3.5	0.29
✓	✓	143	C₆H₁₀O₂N₂	0.33	0.33	1.67	3.0	0.00
	✓	214	C₉H₁₅O₃N₃	0.33	0.33	1.67	4.0	-0.11
	✓	227	C₁₀H₁₈O₂N₄	0.40	0.20	1.80	4.0	-0.20
	✓	245	C₁₀H₂₀O₃N₄	0.40	0.30	2.00	3.0	-0.56
	✓	246	C₁₀H₂₀O₃N₄	0.40	0.30	2.00	3.0	-0.56
<i>Average</i>				0.33	0.42	1.96	2.67	-0.50

Table S4: Peaks detected for the **MG-DA** mixture with their corresponding mass to charge ratio (m/z), chemical formula, nitrogen to carbon ratio (N/C), oxygen to carbon ratio (O/C), hydrogen to carbon ratio (H/C), double bond equivalent (DBE) and aromaticity. The structures identified are labeled in red.

TD-ID-CIMS	Orbitrap-MS	m/z	Formula	N/C	O/C	H/C	DBE	Aromaticity
✓		73	C₃H₅O₂	0.00	0.67	1.67	1.5	0.3
✓		89	C₃H₅O₃	0.00	1.00	1.67	1.5	0.0
	✓	101	C₅H₁₃N₂	0.40	0.00	2.60	0.5	-0.5
✓	✓	102	C₅H₁₂ON	0.20	0.20	2.40	0.5	-0.3
✓		112						
	✓	116	C₆H₁₄ON	0.17	0.17	2.33	0.5	-0.2
✓	✓	118	C₅H₁₂O₂N	0.20	0.40	2.40	0.5	-0.5
	✓	119	C₅H₁₅ON₂	0.40	0.20	3.00	-0.5	-1.2
✓		143	C₈H₁₉N₂	0.25	0.00	2.38	0.5	-0.3
	✓	148	C₆H₁₄O₃N	0.17	0.50	2.33	0.5	-0.6
	✓	162	C₇H₁₆O₃N	0.14	0.43	2.29	0.5	-0.4
	✓	163	C₇H₁₉O₂N₂	0.29	0.29	2.71	-0.5	-0.9
	✓	174	C₈H₁₆O₃N	0.13	0.38	2.00	1.5	-0.2
	✓	229	C₁₁H₂₁O₃N₂	0.18	0.27	1.91	2.5	-0.1
	✓	246	C₁₁H₂₀O₅N	0.09	0.45	1.82	2.5	-0.1
	✓	271	C₁₃H₂₃O₄N₂	0.15	0.31	1.77	3.5	-0.1
	✓	292	C₁₂H₂₂O₇N	0.08	0.58	1.83	2.5	-0.3
<i>Average</i>				0.18	0.37	2.19	1.13	-0.34

Table S5: Peaks detected for the **GL-DA** mixture with their corresponding mass to charge ratio (m/z), chemical formula, nitrogen to carbon ratio (N/C), oxygen to carbon ratio (O/C), hydrogen to carbon ratio (H/C), double bond equivalent (DBE) and aromaticity. The structures identified are labeled in red.

TD-ID-CIMS	Orbitrap-MS	m/z	Formula	N/C	O/C	H/C	DBE	Aromaticity
✓		77	C₂H₅O₃	0.00	1.50	2.50	0.5	-2.00
✓	✓	104	C₄H₉O₂N	0.25	0.50	2.25	1.0	-0.50
✓	✓	131	C₆H₁₄ON₂	0.33	0.17	2.33	1.0	-0.43
	✓	149	C₆H₁₆O₂N₂	0.33	0.33	2.67	0.0	-1.00
<i>Average</i>				0.23	0.63	2.44	0.63	-0.98

Table S6: Peaks detected for the **MG-TA** mixture with their corresponding mass to charge ratio (m/z), chemical formula, nitrogen to carbon ratio (N/C), oxygen to carbon ratio (O/C), hydrogen to carbon ratio (H/C), double bond equivalent (DBE) and aromaticity. The structures identified are labeled in red.

TD-ID-CIMS	Orbitrap-MS	m/z	Formula	N/C	O/C	H/C	DBE	Aromaticity
✓		73	C₃H₅O₂	0.00	0.67	1.67	1.5	0.3
	✓	76	C₃H₁₀ON	0.33	0.33	3.33	-0.5	-1.3
✓		89	C₃H₅O₃	0.00	1.00	1.67	1.5	0.0
✓		97						
✓		111						
	✓	115	C ₆ H ₁₅ N ₂	0.33	0.00	2.50	0.5	-0.4
	✓	131	C ₆ H ₁₁ O ₃	0.00	0.50	1.83	1.5	0.0
	✓	132	C₆H₁₄O₂N	0.17	0.33	2.33	0.5	-0.4
✓		180						
	✓	199	C ₉ H ₁₁ O ₅	0.00	0.56	1.22	4.5	0.3
	✓	207	C ₉ H ₂₃ O ₃ N ₂	0.22	0.33	2.56	-0.5	-0.7
	✓	217	C ₉ H ₁₃ O ₆	0.00	0.67	1.44	3.5	0.1
	✓	260	C ₁₂ H ₂₂ O ₅ N	0.08	0.42	1.83	2.5	-0.1
	✓	276	C ₁₂ H ₂₂ O ₆ N	0.08	0.50	1.83	2.5	-0.2
	✓	292	C ₁₂ H ₂₂ O ₇ N	0.08	0.58	1.83	2.5	-0.3
	✓	332	C ₁₅ H ₂₆ O ₇ N	0.07	0.47	1.73	3.5	-0.1
	✓	348	C ₁₅ H ₂₆ O ₈ N	0.07	0.53	1.73	3.5	-0.2
<i>Average</i>				0.10	0.49	1.97	1.93	-0.21

Table S7: Peaks detected for the **GL-TA** mixture with their corresponding mass to charge ratio (m/z), chemical formula, nitrogen to carbon ratio (N/C), oxygen to carbon ratio (O/C), hydrogen to carbon ratio (H/C), double bond equivalent (DBE) and aromaticity. The structures identified are labeled in red.

TD-ID-CIMS	Orbitrap-MS	m/z	Formula	N/C	O/C	H/C	DBE	Aromaticity
✓		77	C₂H₅O₃	0.00	1.50	2.50	0.5	-2.00
	✓	115.12	C ₆ H ₁₅ N ₂	0.33	0.00	2.50	0.5	-0.38
✓		136	C₅H₁₄O₃N	0.20	0.60	2.80	-0.5	-1.20
<i>Average</i>				0.18	0.70	2.60	0.17	-1.19

Table S8: Summary of the average nitrogen to carbon ratio (N/C), oxygen to carbon ratio (O/C), hydrogen to carbon ratio (H/C), double bond equivalent (DBE), aromaticity, and single scattering albedo (SSA) at 405 nm for the α -dicarbonyl-amine mixtures.

	N/C	O/C	H/C	DBE	Aromaticity	SSA
MG-MA	0.24	0.18	1.78	2.90	0.06	0.73
MG-DA	0.18	0.37	2.19	1.13	-0.34	0.90
MG-TA	<i>0.10</i>	<i>0.49</i>	<i>1.97</i>	<i>1.93</i>	<i>-0.21</i>	0.97
GL-MA	0.33	0.42	1.96	2.67	-0.50	0.99
GL-DA	0.23	0.63	2.44	0.63	-0.98	0.98
GL-TA	0.18	0.70	2.60	0.17	-1.19	0.99

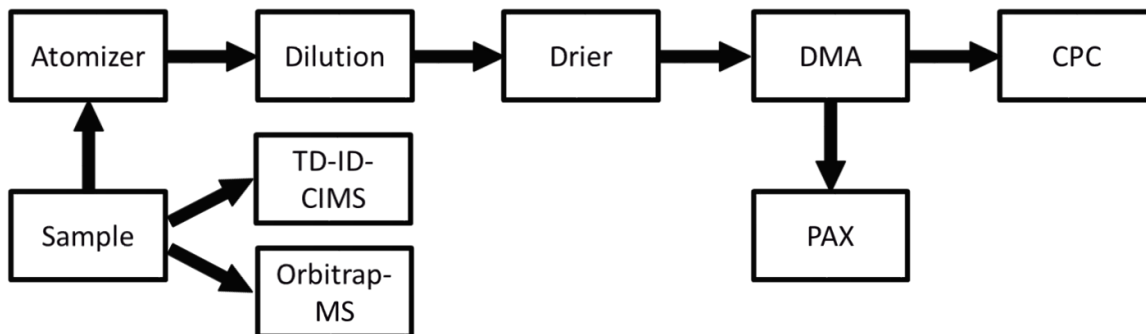


Figure S1: Experimental setup for the optical properties and chemical composition analysis. There is an exhaust (not shown) from the atomizer, and the flow rate to the atomizer is about 5-10 l min⁻¹. The output line from the DMA is split between the CPC and PAX to detect the concentration and optical properties, respectively.

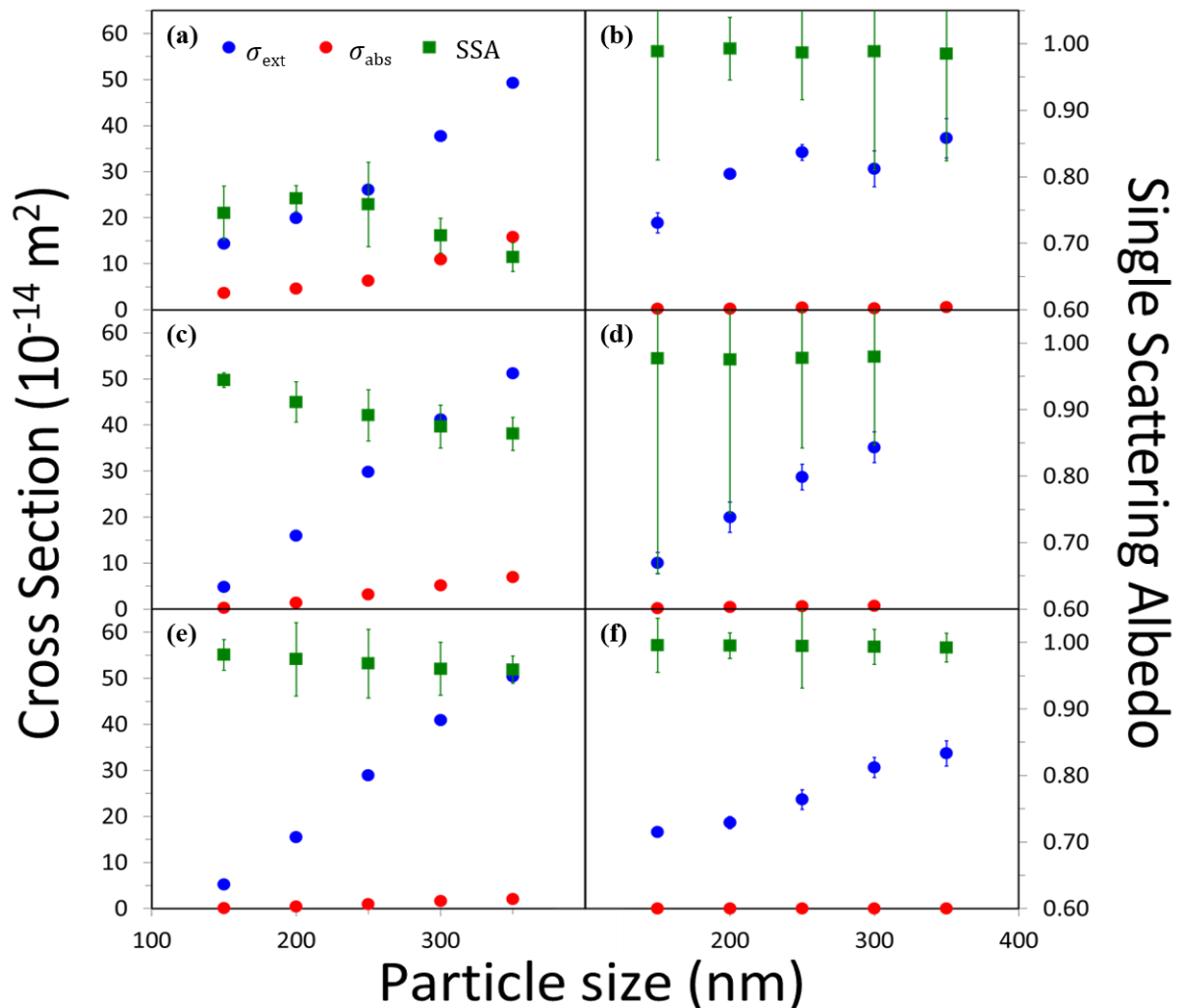


Figure S2: Summary of the optical properties measurements as a function of particle size. The left axis corresponds to the extinction cross section (blue circles) and the absorption cross section (red circles). The right axis corresponds to the single scattering albedo (green squares). The error bars correspond to the uncertainties of the measurements. The left column corresponds to the MG mixtures with MA (a), DA (c), and TA (e), while the right column corresponds to the GL mixtures with MA (b), DA (d), and TA (f).

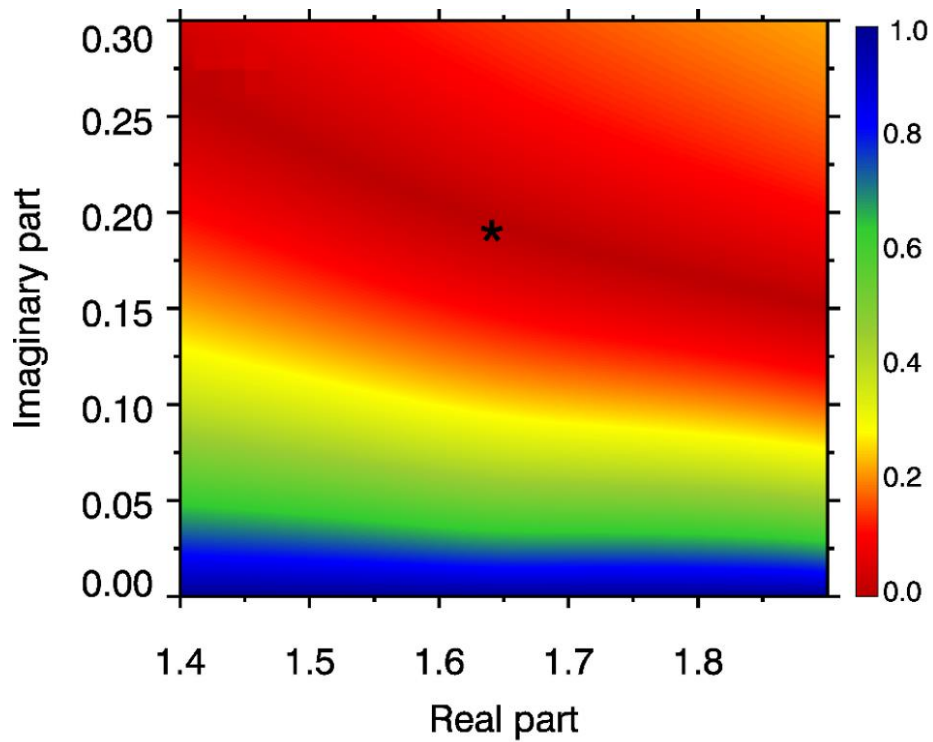


Figure S3: Contour of CFD as a function of n (real part) and k (imaginary part) used for refractive index retrieval for MG-MA. The reddest color corresponds to the lowest CFD .

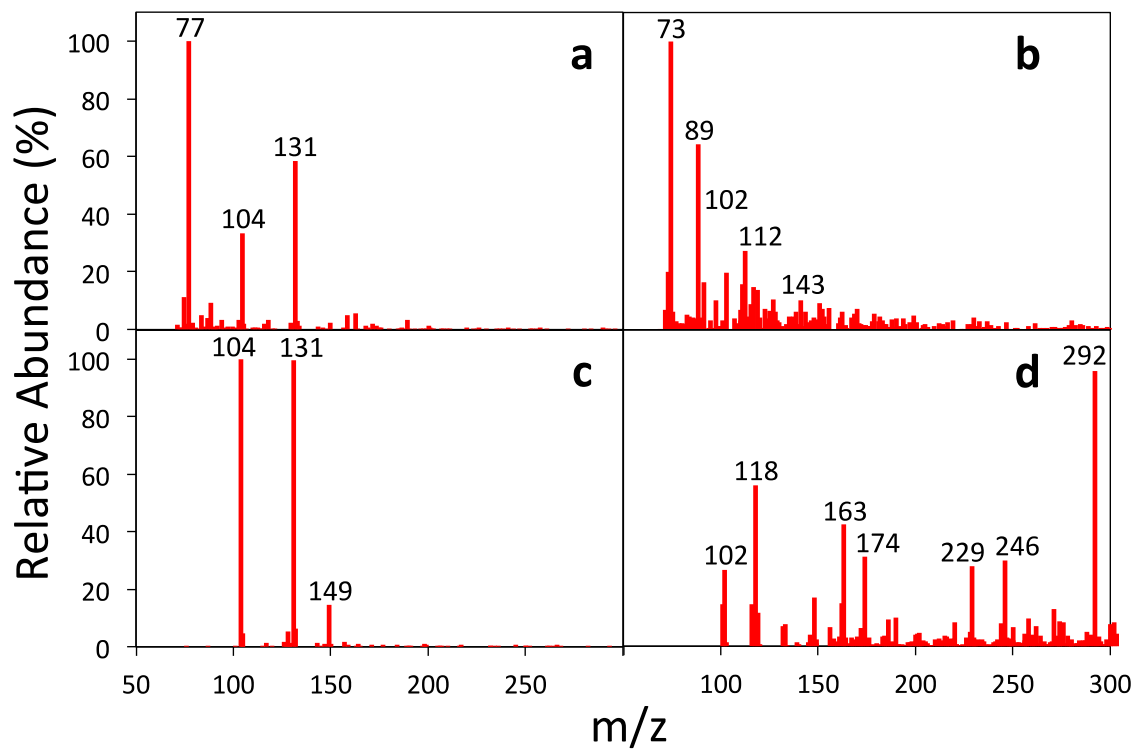


Figure S4: Mass spectra from the TD-ID-CIMS for GL-DA (a) and MG-DA (b) and from the Orbitrap-MS for GL-DA (c) and MG-DA (d).

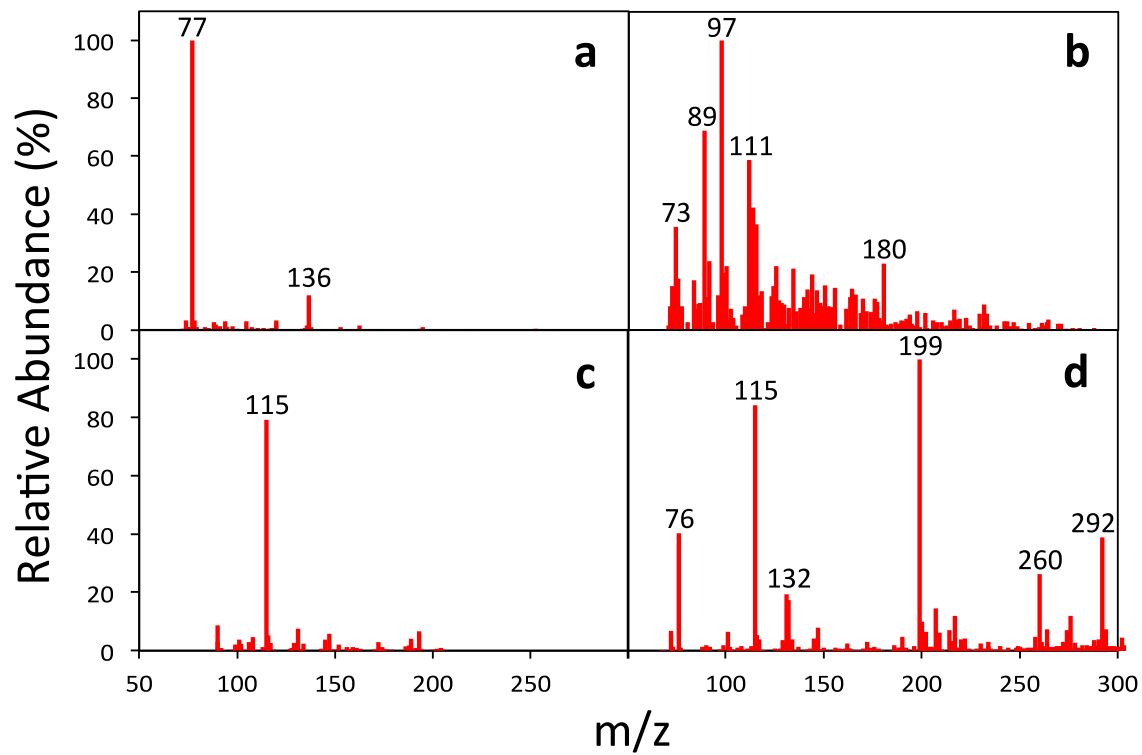


Figure S5: Mass spectra from the TD-ID-CIMS for GL-TA (a) and MG-TA (b) and from the Orbitrap-MS for GL-TA (c) and MG-TA (d).

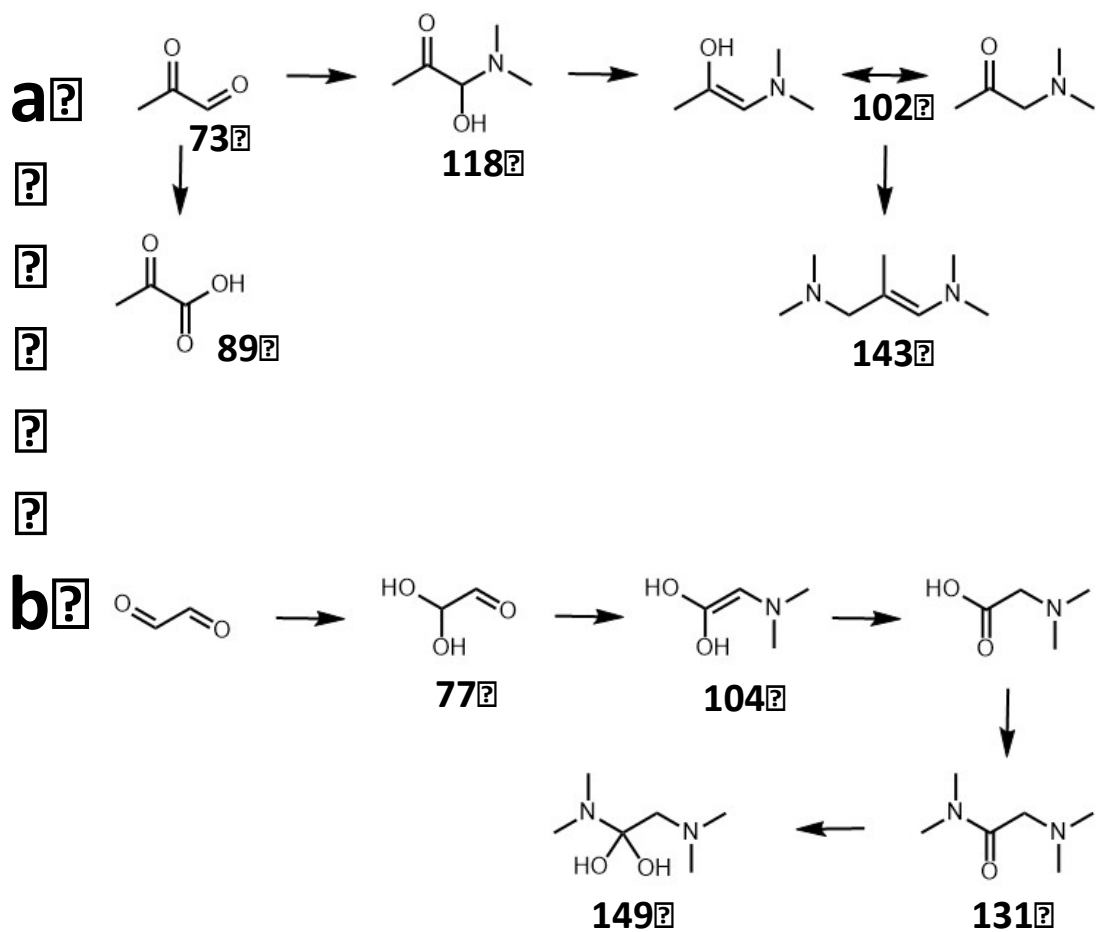


Figure S6: Proposed chemical mechanisms for dimethylamine (DA) reactions with MG (a) and GL (b). The numbers correspond to the m/z .

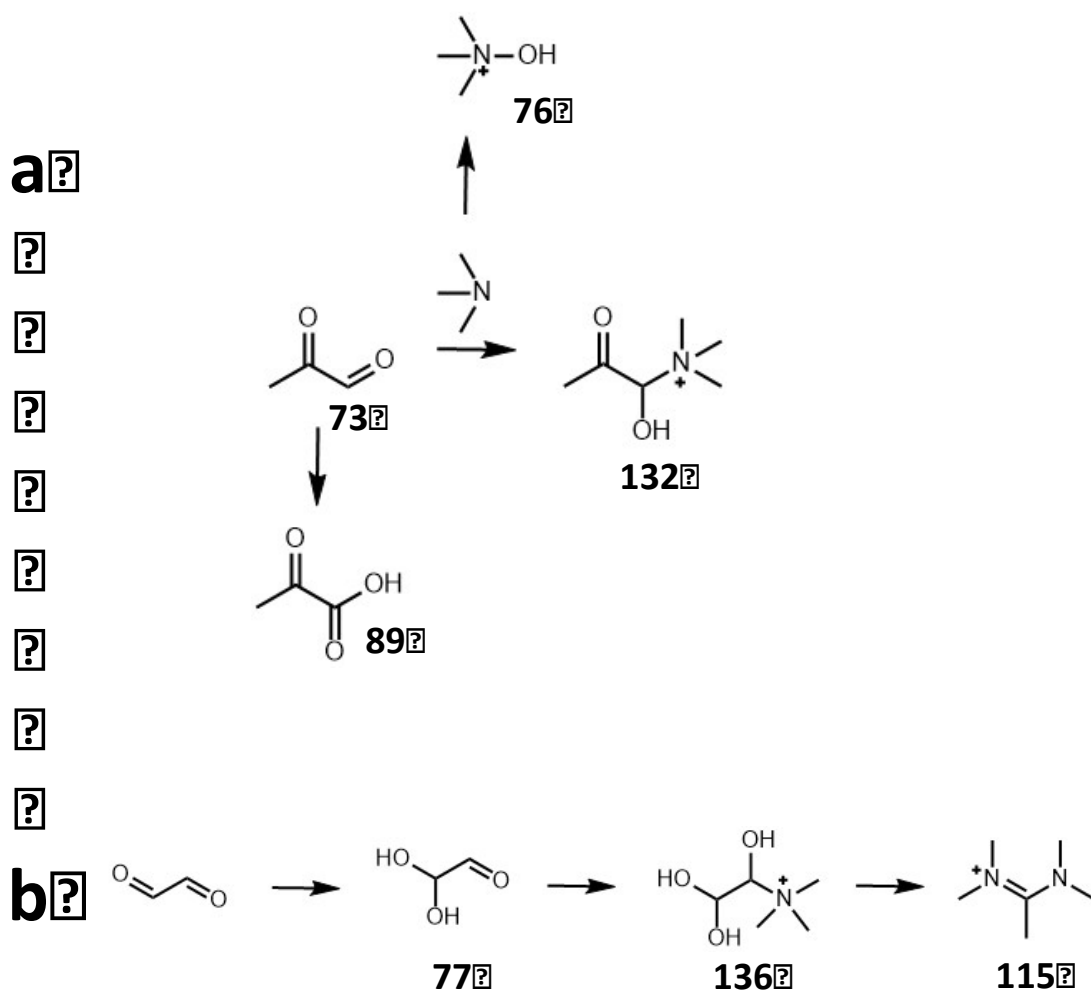


Figure S7: Proposed chemical mechanisms for trimethylamine (TA) reactions with MG (a) and GL (b). The numbers correspond to the m/z .