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 Wang[2], Song Guo[2], Yun Lin[4], Mario Gomez-Hermandez[1,5], Jianfei Peng[4], Yixin Li[1], Jeremiah Secrest[1], Misti L. Zamora[4,6], Yuan Wang[7], Taicheng An[3], and Renyi Zhang[1,4*]

[1]Department of Chemistry, Texas A&M University, College Station, Texas, 77840
[2]State 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
[3]Guangzhou 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
[4]Departments of Atmospheric Sciences, Texas A&M University, College Station, TX 77843, USA
[5]Department of Chemistry and Biochemistry, Florida International University, Miami, FL 33199
[6]Environmental Health & Engineering, Johns Hopkins School of Public Health, Johns Hopkins University, MD 21218
[7]Division 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	$C_3H_5O_2$	0.00	0.67	1.67	1.5	0.3
✓		104	$C_4H_{10}O_2N$	0.25	0.50	2.50	0.5	-0.8
✓	✓	111	$C_6H_{11}N_2$	0.33	0.00	1.83	2.5	0.1
	✓	124	$C_7H_{10}ON$	0.14	0.14	1.43	3.5	0.4
✓	✓	125	$C_7H_{13}N_2$	0.29	0.00	1.86	2.5	0.1
	✓	137	$C_8H_{13}N_2$	0.25	0.00	1.63	3.5	0.3
✓		140						
	✓	153	$C_8H_{13}ON_2$	0.25	0.13	1.63	3.5	0.2
	✓	155	$C_8H_{15}ON_2$	0.25	0.13	1.88	2.5	0.0
	✓	170	$C_8H_{16}ON_3$	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
		Average		*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	$C_2H_5O_3$	0.00	1.50	2.50	0.5	-2.00
✓		83						
✓		90	$C_3H_8O_2N$	0.33	0.67	2.67	0.5	-1.50
✓		97	$C_5H_9N_2$	0.40	0.00	1.80	2.5	0.17
✓		111						
✓		125	$C_6H_9ON_2$	0.33	0.17	1.50	3.5	0.29
✓	✓	143	$C_6H_{10}O_2N_2$	0.33	0.33	1.67	3.0	0.00
	✓	214	$C_9H_{15}O_3N_3$	0.33	0.33	1.67	4.0	-0.11
	✓	227	$C_{10}H_{18}O_2N_4$	0.40	0.20	1.80	4.0	-0.20
	✓	245	$C_{10}H_{20}O_3N_4$	0.40	0.30	2.00	3.0	-0.56
	✓	246	$C_{10}H_{20}O_3N_4$	0.40	0.30	2.00	3.0	-0.56
		Average		*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	$C_3H_5O_2$	0.00	0.67	1.67	1.5	0.3
✓		89	$C_3H_5O_3$	0.00	1.00	1.67	1.5	0.0
	✓	101	$C_5H_{13}N_2$	0.40	0.00	2.60	0.5	-0.5
✓	✓	102	$C_5H_{12}ON$	0.20	0.20	2.40	0.5	-0.3
✓		112						
	✓	116	$C_6H_{14}ON$	0.17	0.17	2.33	0.5	-0.2
✓	✓	118	$C_5H_{12}O_2N$	0.20	0.40	2.40	0.5	-0.5
	✓	119	$C_5H_{15}ON_2$	0.40	0.20	3.00	-0.5	-1.2
✓		143	$C_8H_{19}N_2$	0.25	0.00	2.38	0.5	-0.3
	✓	148	$C_6H_{14}O_3N$	0.17	0.50	2.33	0.5	-0.6
	✓	162	$C_7H_{16}O_3N$	0.14	0.43	2.29	0.5	-0.4
	✓	163	$C_7H_{19}O_2N_2$	0.29	0.29	2.71	-0.5	-0.9
	✓	174	$C_8H_{16}O_3N$	0.13	0.38	2.00	1.5	-0.2
	✓	229	$C_{11}H_{21}O_3N_2$	0.18	0.27	1.91	2.5	-0.1
	✓	246	$C_{11}H_{20}O_5N$	0.09	0.45	1.82	2.5	-0.1
	✓	271	$C_{13}H_{23}O_4N_2$	0.15	0.31	1.77	3.5	-0.1
	✓	292	$C_{12}H_{22}O_7N$	0.08	0.58	1.83	2.5	-0.3
		Average		*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	$C_2H_5O_3$	0.00	1.50	2.50	0.5	-2.00
✓	✓	104	$C_4H_9O_2N$	0.25	0.50	2.25	1.0	-0.50
✓	✓	131	$C_6H_{14}ON_2$	0.33	0.17	2.33	1.0	-0.43
	✓	149	$C_6H_{16}O_2N_2$	0.33	0.33	2.67	0.0	-1.00
		Average		*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	$C_3H_5O_2$	0.00	0.67	1.67	1.5	0.3
	✓	76	$C_3H_{10}ON$	0.33	0.33	3.33	-0.5	-1.3
✓		89	$C_3H_5O_3$	0.00	1.00	1.67	1.5	0.0
✓		97						
✓		111						
	✓	115	$C_6H_{15}N_2$	0.33	0.00	2.50	0.5	-0.4
	✓	131	$C_6H_{11}O_3$	0.00	0.50	1.83	1.5	0.0
	✓	132	$C_6H_{14}O_2N$	0.17	0.33	2.33	0.5	-0.4
✓		180						
	✓	199	$C_9H_{11}O_5$	0.00	0.56	1.22	4.5	0.3
	✓	207	$C_9H_{23}O_3N_2$	0.22	0.33	2.56	-0.5	-0.7
	✓	217	$C_9H_{13}O_6$	0.00	0.67	1.44	3.5	0.1
	✓	260	$C_{12}H_{22}O_5N$	0.08	0.42	1.83	2.5	-0.1
	✓	276	$C_{12}H_{22}O_6N$	0.08	0.50	1.83	2.5	-0.2
	✓	292	$C_{12}H_{22}O_7N$	0.08	0.58	1.83	2.5	-0.3
	✓	332	$C_{15}H_{26}O_7N$	0.07	0.47	1.73	3.5	-0.1
	✓	348	$C_{15}H_{26}O_8N$	0.07	0.53	1.73	3.5	-0.2
		Average		*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	$C_2H_5O_3$	0.00	1.50	2.50	0.5	-2.00
	✓	115.12	$C_6H_{15}N_2$	0.33	0.00	2.50	0.5	-0.38
✓		136	$C_5H_{14}O_3N$	0.20	0.60	2.80	-0.5	-1.20
			Average	*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.

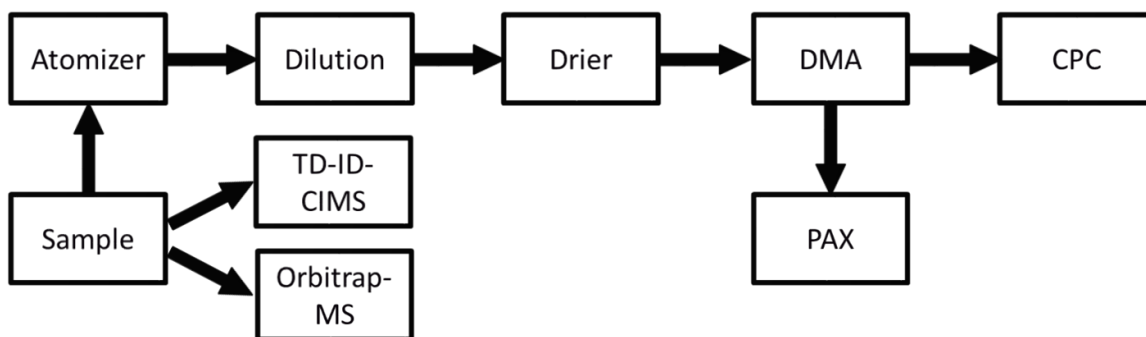|	N/C	O/C	H/C	DBE	Aromaticity	SSA
MG-MA	0.24	0.18	1.78	2.90	0.06	0.73
MG-DA	0.18	0.37	2.19	1.13	-0.34	0.90
MG-TA	*0.10*	*0.49*	*1.97*	*1.93*	*-0.21*	0.97
GL-MA	0.33	0.42	1.96	2.67	-0.50	0.99
GL-DA	0.23	0.63	2.44	0.63	-0.98	0.98
GL-TA	0.18	0.70	2.60	0.17	-1.19	0.99

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.
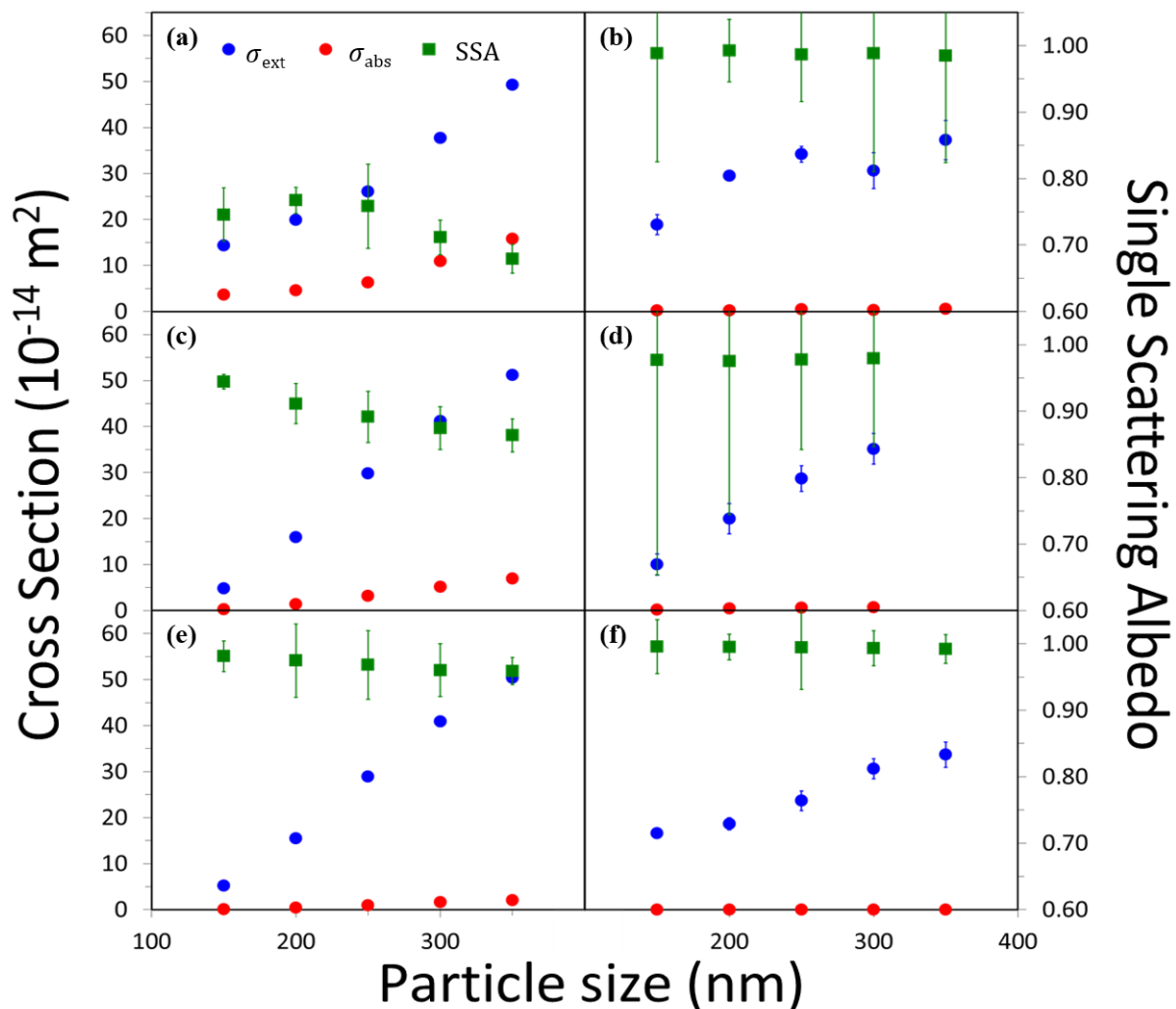
Figure S2: Summary of the optical properties measurements as a function of particle size. The left axis corresponds to the extinction cross section (blue circles) and the absorption cross section (red circles). The right axis corresponds to the single scattering albedo (green squares). The error bars 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).
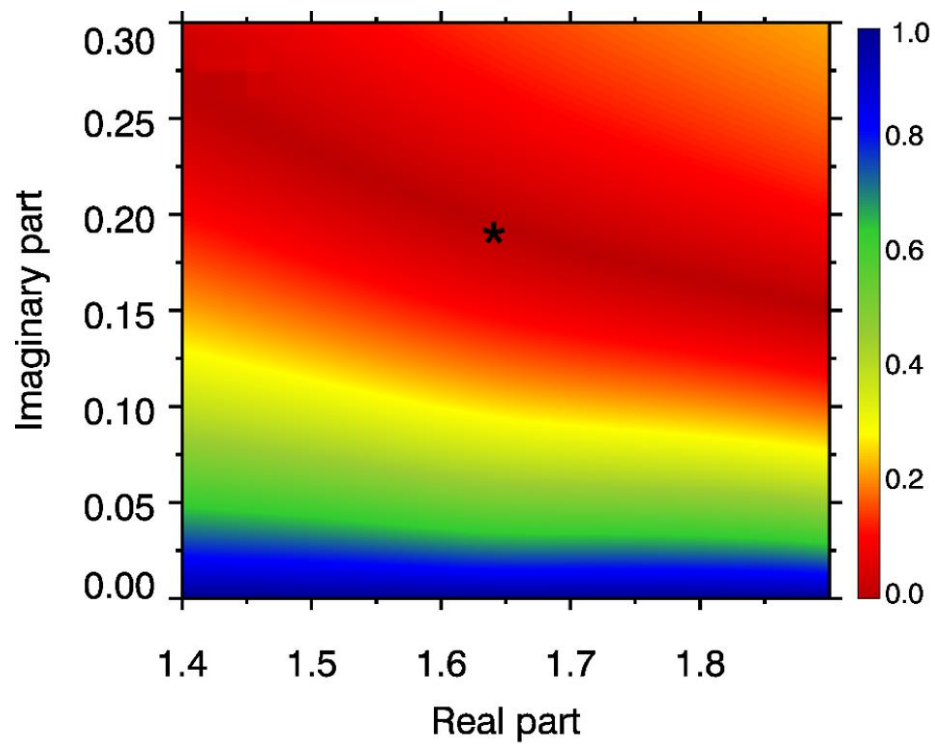
Figure S3: Contour of *CFD* as a function of *n* (real part) and *k* (imaginary part) used for refractive index retrieval for MG-MA. The reddest color corresponds to the lowest *CFD*.
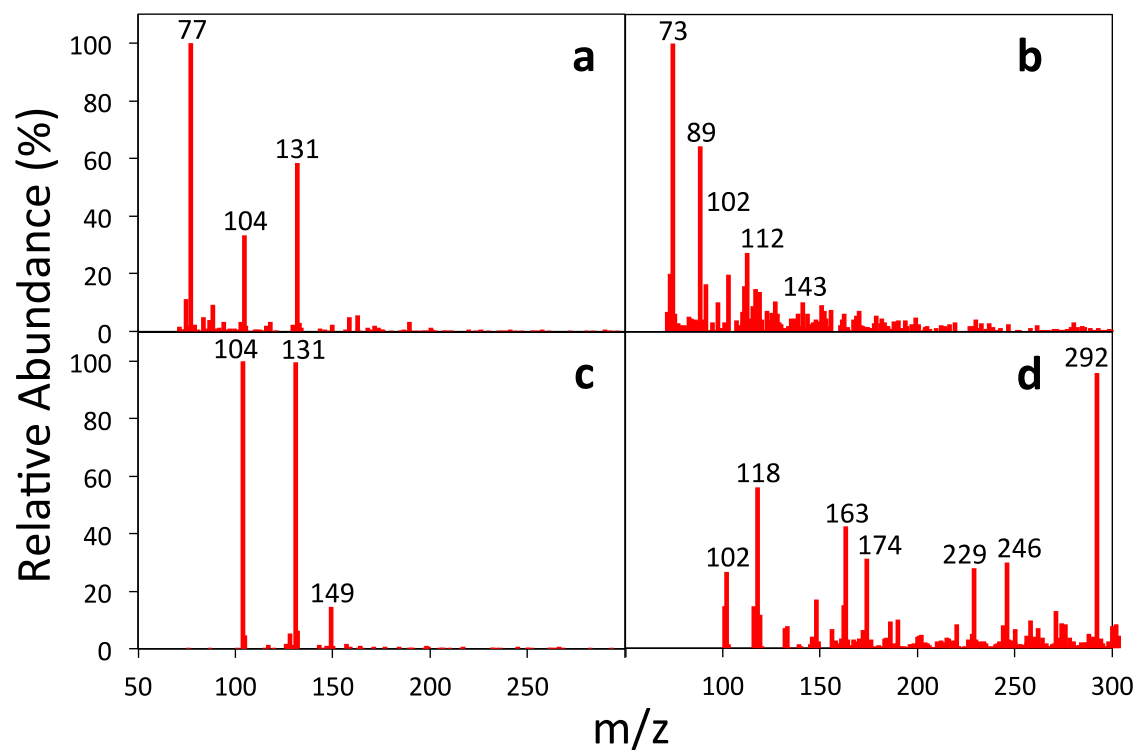
Figure S4: Mass spectra from the TD-ID-CIMS for GL-DA (a) and MG-DA (b) and from the Orbitrap-MS for GL-DA (c) and MG-DA (d).
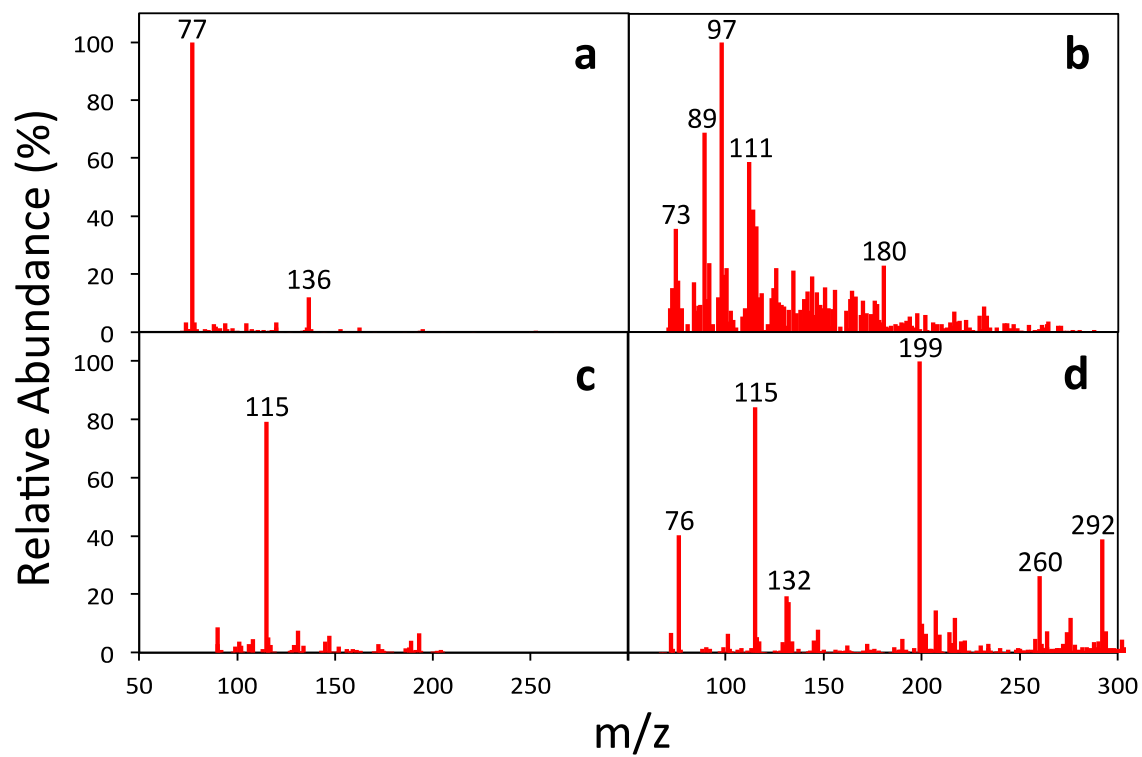
Figure S5: Mass spectra from the TD-ID-CIMS for GL-TA (a) and MG-TA (b) and from the Orbitrap-MS for GL-TA (c) and MG-TA (d).
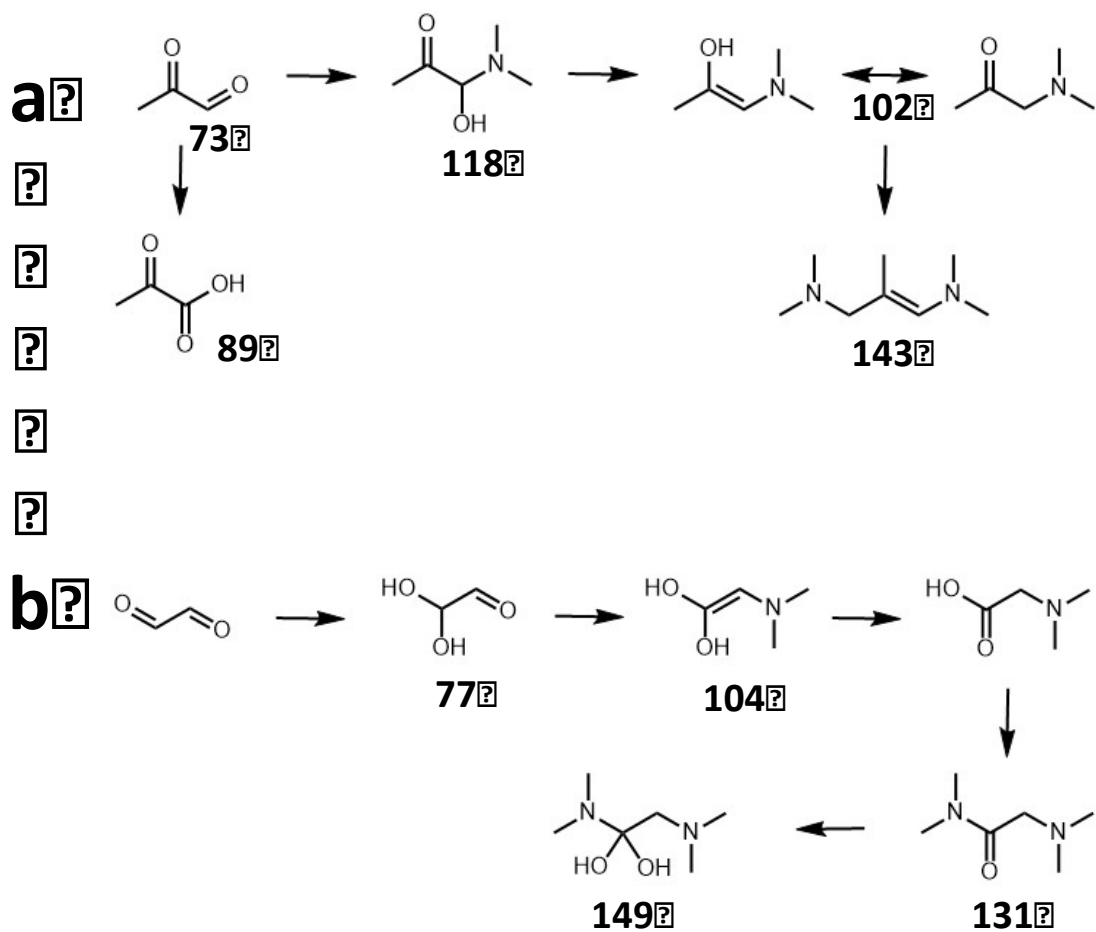
Figure S6: Proposed chemical mechanisms for dimethylamine (DA) reactions with MG (a) and GL (b). The numbers correspond to the *m/z*.
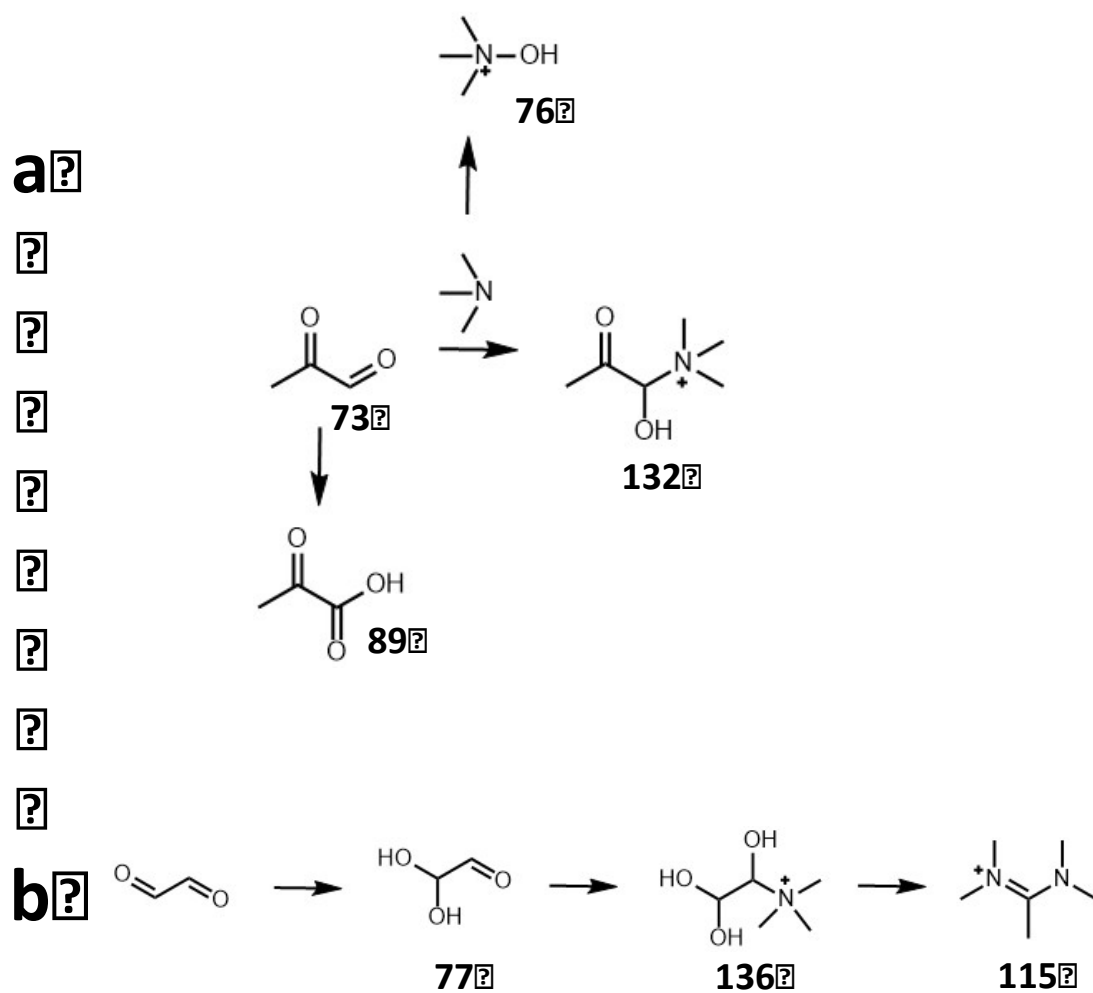
Figure S7: Proposed chemical mechanisms for trimethylamine (TA) reactions with MG (a) and GL (b). The numbers correspond to the *m/z*.