

Supplementary Materials

Stochastic Dynamics Mass Spectrometric Analysis of Ozone Depletion Reactions of Pharmaceuticals

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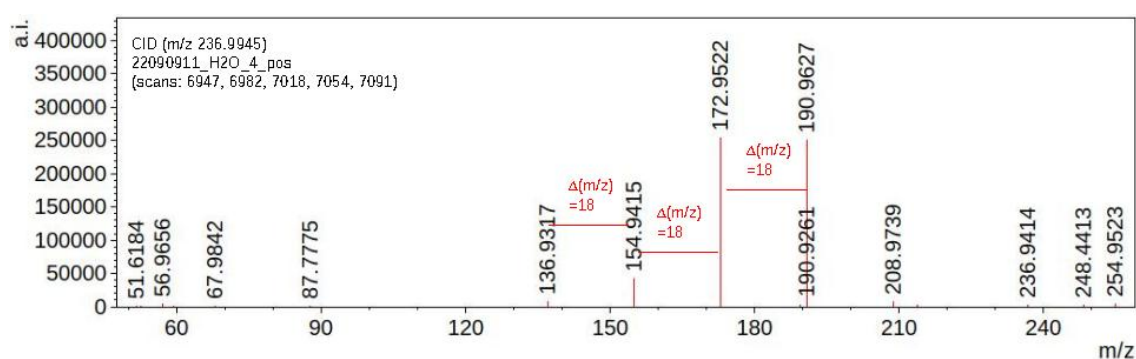


Figure S1. Experimental CID mass spectrum of the ion at m/z 236.9945 of sample 22090901_H2O_4_pos, depending on retention time or scan number.

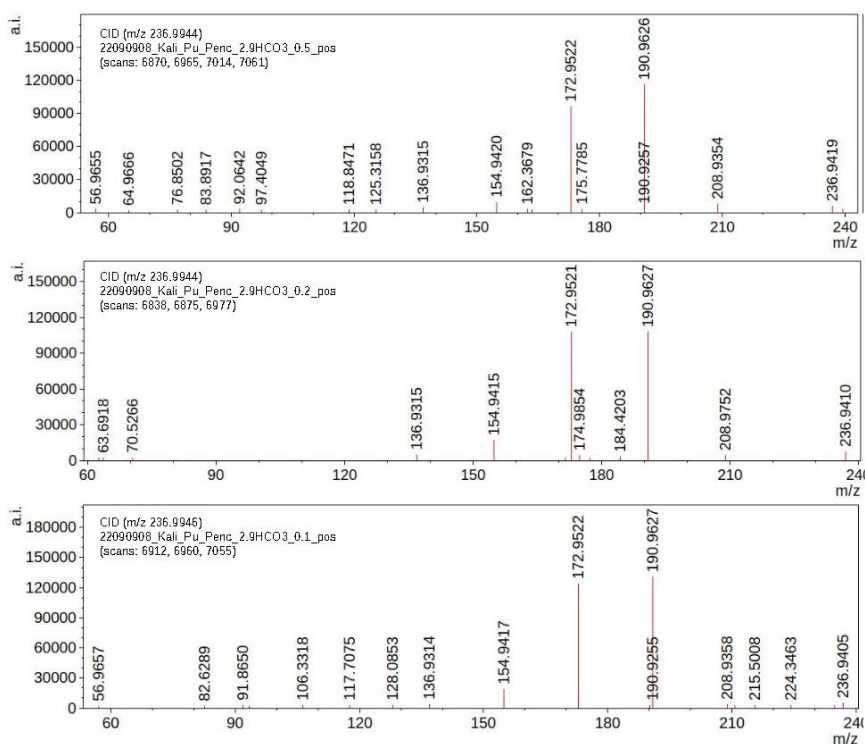


Figure S2. Experimental CID mass spectra of the ion at m/z 236.9945 of sample 22090901_H2O_4_pos depending on retention time or scan number.



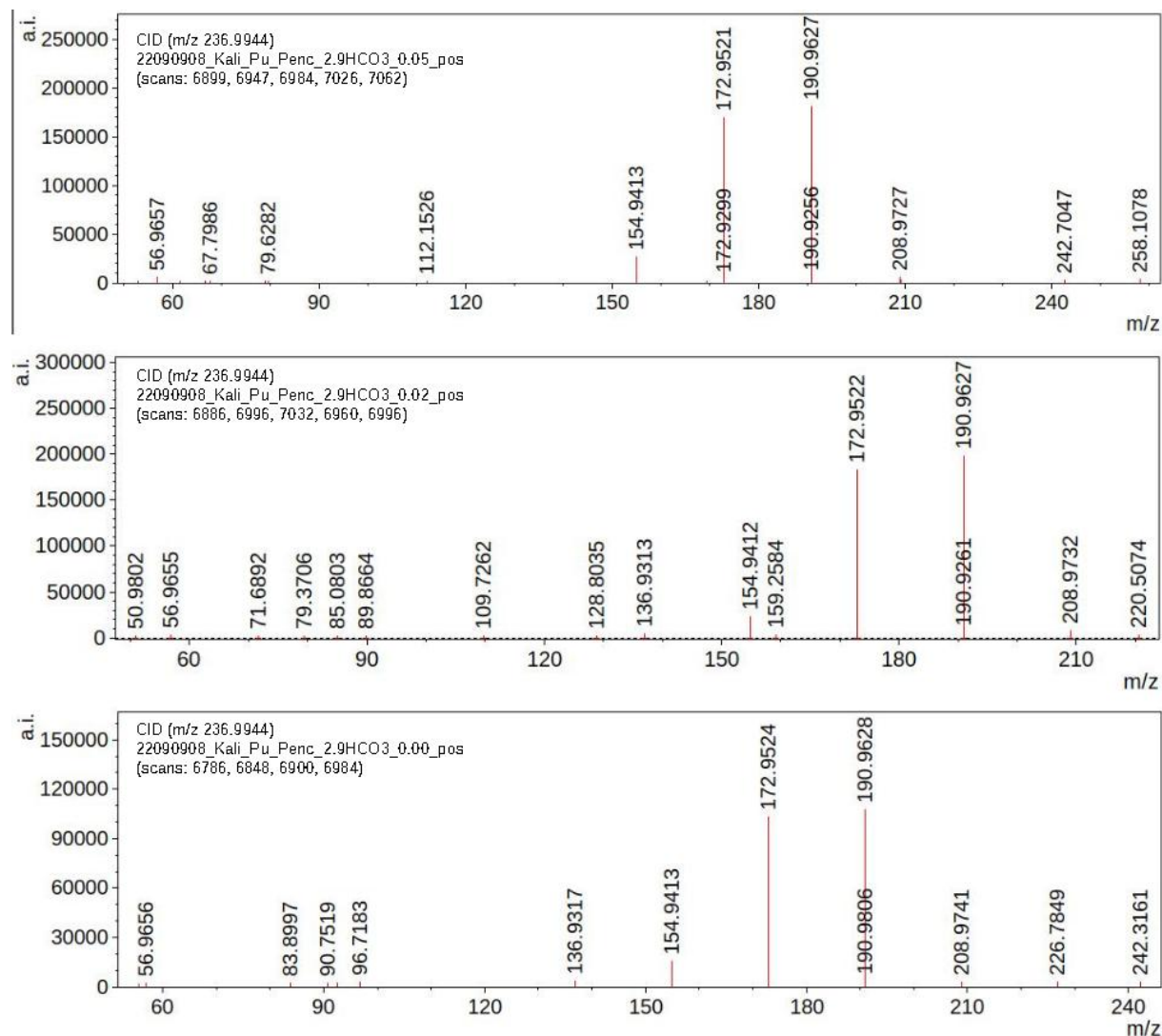


Figure S3. Experimental CID mass spectra of ion at m/z 236.9946 of samples 22090908_Kali_Pu_Penc_2.9HCO3_0.05_pos, 22090908_Kali_Pu_Penc_2.9HCO3_0.02_pos, and 22090908_Kali_Pu_Penc_2.9HCO3_0.00_pos depending on retention time or scan number.

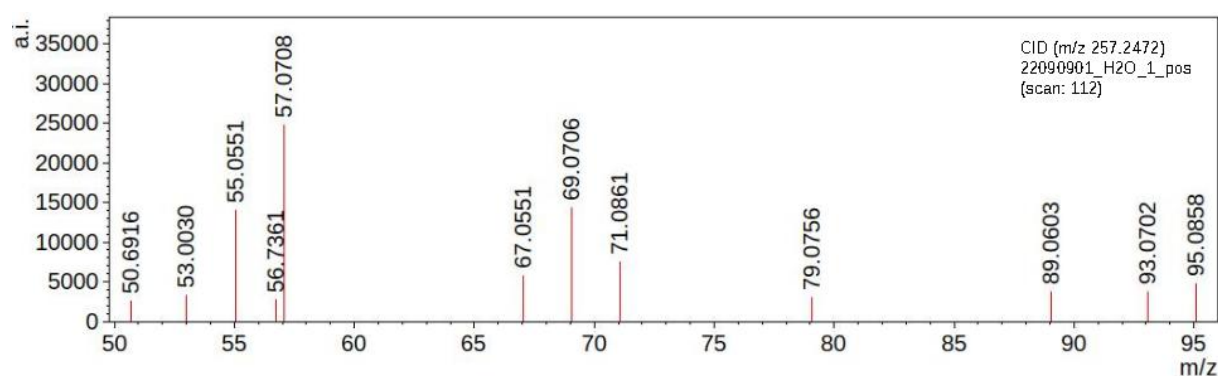


Figure S4. Experimental CID mass spectrum of ion at m/z 257.2472 of sample 22090901_H2O_1_pos of scan number 112.

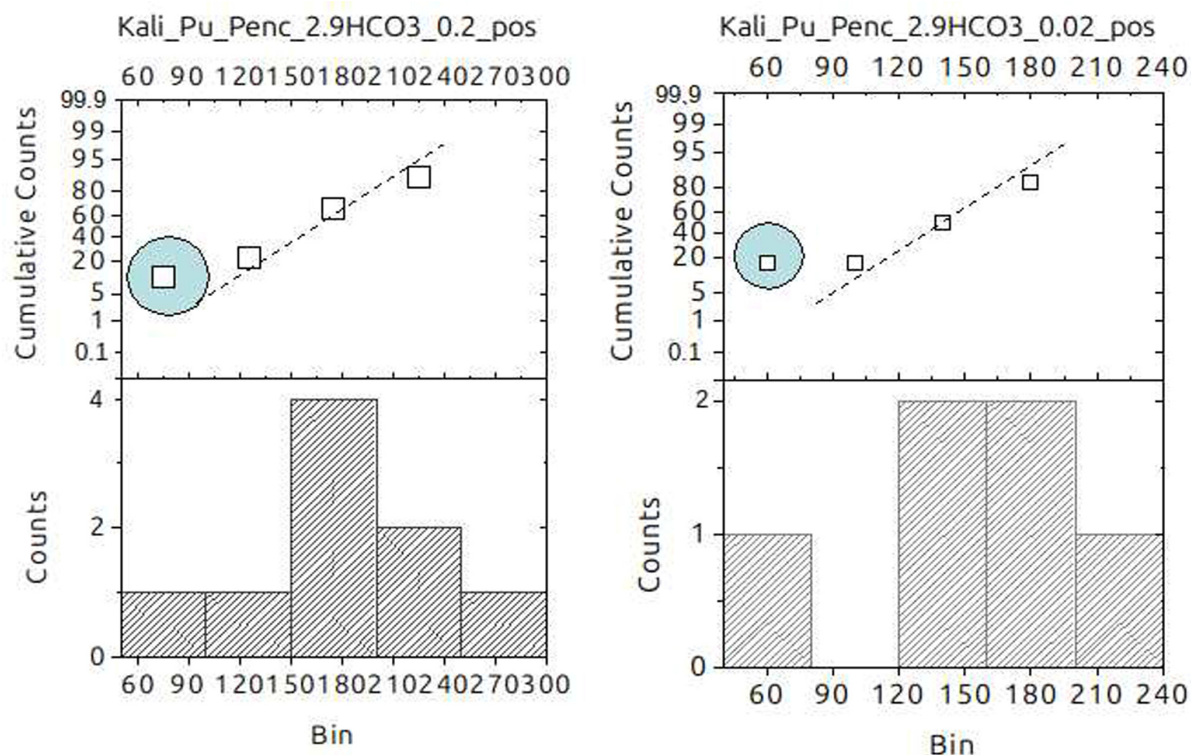


Figure S5. Histograms and probability plots of the measured variables of the shown samples.

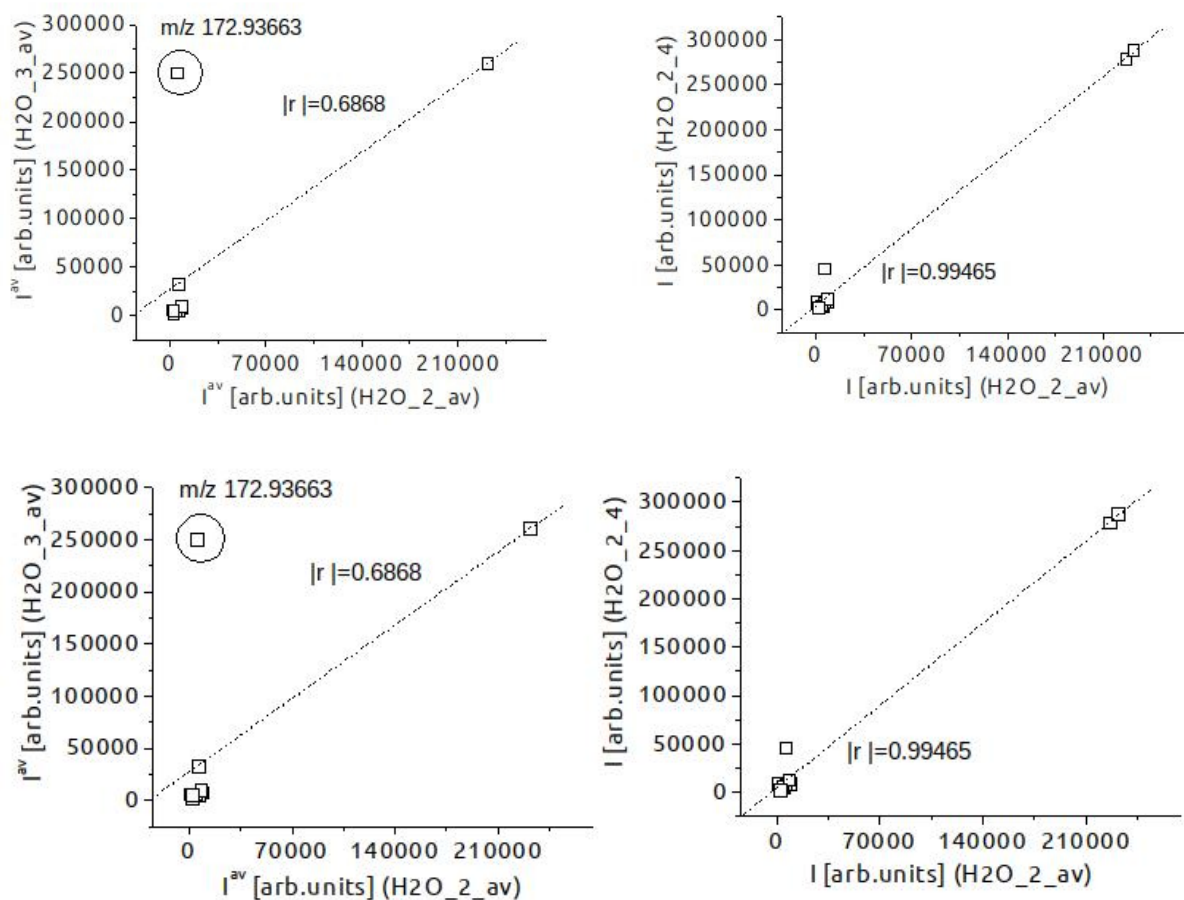


Figure S6. Linear relation between average intensity data on ion at m/z 172.93663 per shown sample sets of variables (Table S5); chemometrics.

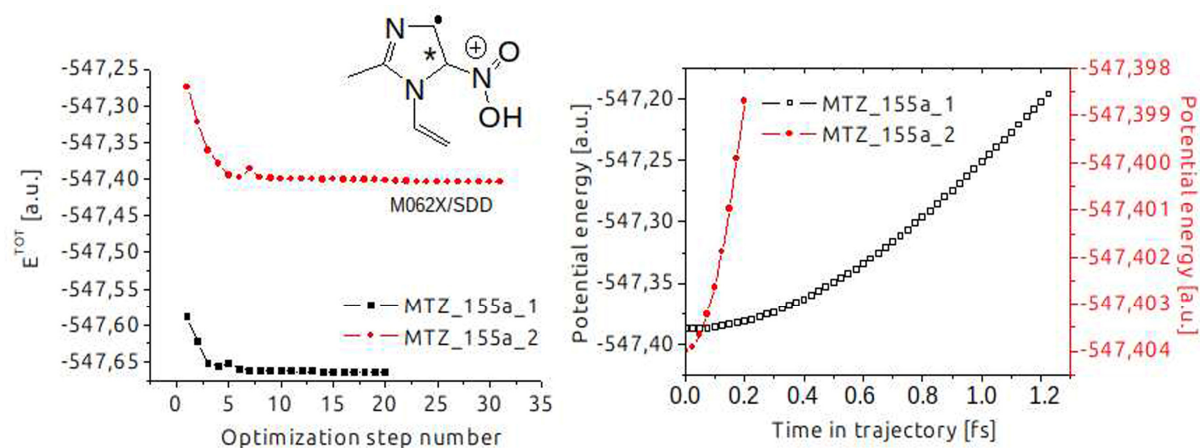


Figure S7. Theoretical ion-radical optimization: Total energy (E^{TOT} [a.u.]) with respect to optimization step number; and, BOMD DFT data on the same level of theory: Potential energy [a.u.] versus time in trajectory [fs] of enantiomers of ion at m/z 155 shown as MTZ_155_a1 and MTZ_155_a2; chemical diagram of the species.

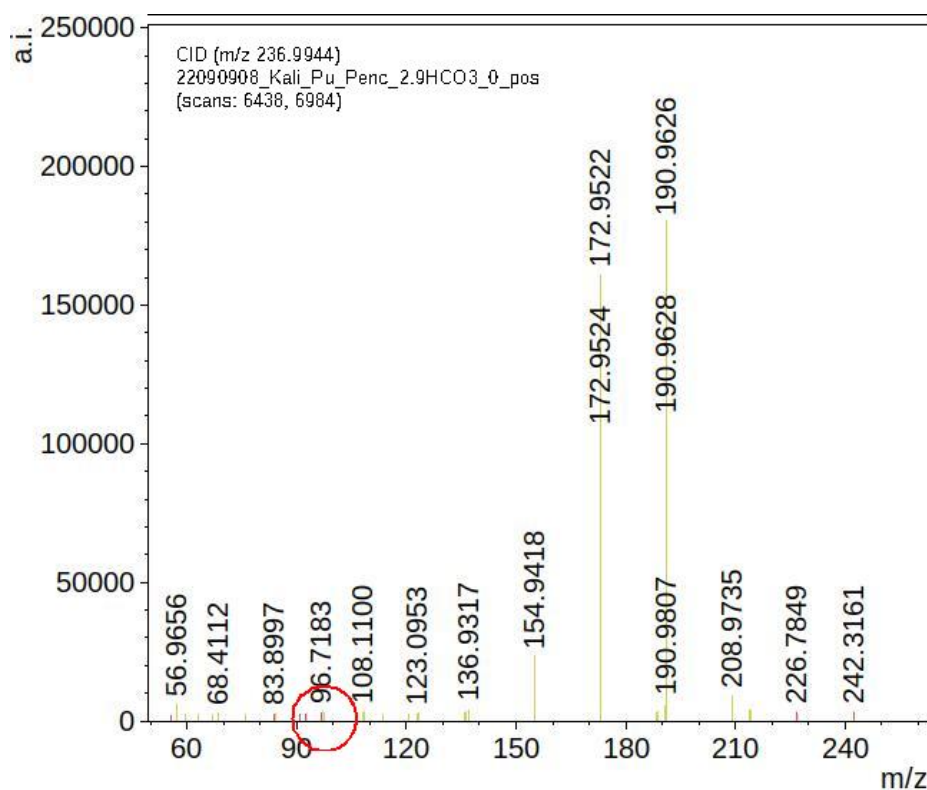


Figure S8. Experimental CID mass spectra of the ion at m/z 236.9946 of sample 22090908_Kali_Pu_Penc_2.9HCO3_0_pos depending on scan numbers.

Table S1. Mass spectrometric experimental conditions of measurements.

Polarity	Positive
Syringe type	Hamilton
Flow rate [mL.min ⁻¹]	3.000
Inner diameter [mm]	2.303
Volume [mL]	250
Dynamic exclusion [s]	3
Intensity threshold	1.6×10^4
In-source CID [eV]	0
Minimum AGC target	8.102

Table S2. ANOVA data on average values of mass spectrometric variables of peaks of samples H2O_i_pos.raw (I = 2–4) as depicted in Figures 2 and S1.

Dataset	N	Mean	sd(yEr±)	se(yEr±)	
H2O_4 H2O_2	14	164.87211	46.9842	12.55705	
H2O_4 H2O_2	13	179.94954	49.46043	13.71786	
H ₀ : The means of all selected datasets are equal					
H ₁ : The means of one or more selected datasets are different					
Source	DoF	Sum of square	Mean square	F-value	P-values
Model	1	1532.36365	1532.36365	0.65989	0.42427
Error	25	58,053.7025	2322.14810		
At the 0,05 level, the population means are not significantly different.					
Means comparison using the Bonferroni test					
Dataset	Mean	Diff. between means	Simultan. confidence intervals		Signif. at 0.05 level
H2O_4 H2O_2	164.87211		Lower limit	Upper limit	
H2O_4 H2O_2	179.94954	−15.07742	−53.30362	23.14877	No
Dataset	N	Mean	sd (yEr±)	se (yEr±)	
H2O_2 H2O_3	13	179.94954	49.46043	13.71786	
H2O_2 H2O_3	12	175.02653	47.06219	13.58568	
H ₀ : The means of all selected datasets are equal					
H ₁ : The means of one or more selected datasets are different					
Source	DoF	Sum of square	Mean square	F-value	P-values
Model	1	151.232539	151.232539	0.06475	0.80140
Error	23	53,719.3612	2335.62440		
At the 0,05 level, the population means are not significantly different.					
Means comparison using the Bonferroni test					
Dataset	Mean	Diff. between means	Simultan. confidence intervals		Signif. at 0,05 level
H2O_2 H2O_3	179.94954		Lower limit	Upper limit	
H2O_2 H2O_3	175.02653	4.92301	−35.09891	44.94492	No

Table S3. Experimental average intensity data (I^{av} [arb.units]) on CID-MS/MS peaks of ion at *m/z* 236.9944 within a set of Kali_Pu_Penc_2.9HCO₃_i_pos (i = 0–0.5) samples with respect to analyte concentration [ng·mL⁻¹].

Conc. [ng·mL ⁻¹]	I ^{av} [arb.units]					
	<i>m/z</i>					
	57	137	154	172	191	237
0	-	4618.109	14,119.74	10,5887.7	-	-
0.01	2378.107	-	14,321.79	10,4252.8	-	-
0.02	-	-	-	-	201,957.5	-
0.05	-	-	-	-	172,047.8	-
0.1	1971.139	4930.923	16,408.26	113,025.6	117,074.2	7790.585
0.2	1657.605	5151.472	20,122.25	122,307.4	4762.9	5860.342
0.5	-	-	-	-	-	2722.879

Table S4. Normality Shapiro–Wilk test data on measurable variables of a set of Kali_Pu_Penc_2.9HCO3_i_pos (I = 0–0.5) samples.

Dataset	N	W	P-value	Decision
Kali_Pu_Penc_2.9HCO3_0_pos	6	0.90689	0.39959	Normal at 0.05 level
Kali_Pu_Penc_2.9HCO3_0.01_pos	8	0.93037	0.52419	Normal at 0.05 level
Kali_Pu_Penc_2.9HCO3_0.02_pos	6	0.90678	0.39890	Normal at 0.05 level
Kali_Pu_Penc_2.9HCO3_0.05_pos	7	0.94872	0.73317	Normal at 0.05 level
Kali_Pu_Penc_2.9HCO3_0.2_pos	9	0.94939	0.67695	Normal at 0.05 level
Kali_Pu_Penc_2.9HCO3_0.5_pos	8	0.95649	0.77682	Normal at 0.05 level

Table S5. Experimental average intensity data (I^{av} [arb.units]) on CID-MS/MS peaks of ion at m/z 172.93663 of CID-MS/MS spectra of peak at m/z 236.9944 and RT = 12.35–12.37 mins within a set of H2O_i_pos (i = 2–4) samples.

H2O 2 pos		H2O 3 pos		H2O 4 pos	
m/z	I [arb.units]	m/z	I [arb.units]	m/z	I [arb.units]
56.96558	5720.842	56.96557	5132.995	56.96567	8344.425
92.0646	1197.106	-	-	-	-
136.9315	9090.176	136.9315	7420.001	136.9315	8239.521
154.7856	1286.463	154.9077	5598.097	154.9079	8195.65
154.908	6484.534	154.9415	32516.67	154.9414	45,431.96
154.9413	37925.75	-	-	-	-
172.9366	5517.312	172.9523	249883.4	172.9376	4150.114
172.9522	226,896.9	-	-	172.9522	278,450.7
174.9853	2393.142	174.9861	1706.941	-	-
190.9258	6744.511	190.9262	4575.465	190.9262	7508.939
190.9627	232093.6	190.9627	260,192.4	190.9627	287798.3
-	-	195.9683	2415.503	-	-
208.9359	4439.535	208.9362	5234.383	208.9357	4730.306
208.9735	8634.116	208.9733	9629.666	208.974	12,198.8
-	-	-	-	213.942	2552.525
236.9412	2404.237	236.9415	4939.987	236.9416	1914.974
-	-	254.9512	4072.26	-	-

Table S6. Experimental measurable variables of a set of Kali_Pu_Penc_2.9HCO3_i_pos (i = 0–0.5) samples per span of scan time or scan number; m/z and absolute intensity (I [arb.units]) data on CID-MS/MS peaks; descriptive statistics; data on Equation (2).

22090908 Kali_Pu_Penc_2.9HCO3_0_pos								
Scan	m/z	I	m/z	m/z	I	m/z	I	
6786	190.9628	94,799.52	172.9522	100516.9	154.9419	10,471.08	136.9317	5238.761
6848	190.9627	114,977.4	172.9522	113892.1	154.9412	14,779.72	136.9313	5015.042
6900	190.9629	95,165.75	172.9522	105016.8	154.9413	14,969.45	136.9309	4196.147
6984	190.9628	108,119.3	172.9524	104036.3	154.9413	16,284.14	136.9317	4348.084
Mean	190.9628	-	172.9522	-	154.9414	-	136.9314	-
sd(yEr±)	$9.08 \cdot 10^{-5}$	-	$8.15 \cdot 10^{-5}$	-	3.03×10^{-4}	-	3.77×10^{-4}	-
se(yEr±)	$4.54 \cdot 10^{-5}$	-	$4.08 \cdot 10^{-5}$	-	1.52×10^{-4}	-	1.89×10^{-4}	-
<I>	-	103,265.5	-	105,865.5	-	14,126.1	-	4699.508
<I> ²	-	1.07×10^{10}	-	1.12×10^{10}	-	2.00×10^8	-	2.21×10^7
<I ² >	-	1.07×10^{10}	-	1.12×10^{10}	-	2.04×10^8	-	2.23×10^7
<I ² >-<I> ²	-	7.45×10^7	-	2.43×10^7	-	4.79×10^6	-	191,890.9
D ² _{SD}	-	1.97×10^{-9}	-	6.41×10^{-10}	-	1.26×10^{-10}	-	5.06×10^{-12}
22090908 Kali_Pu_Penc_2.9HCO3_0.01_pos								
Scan	m/z	I	m/z	I	scan	m/z	I	
6846	1.55×10^2	12,746.74	1.37×10^2	5696.719	6838	-	190.9627	108,118.2
6900	154.9409	15686.28	136.931	5057.069	6875	-	190.9625	102,440.5
6996	154.9418	$1.25 \cdot 10^4$	-	-	6977	-	190.9626	138,291.3
7032	154.9414	$1.61 \cdot 10^4$	136.9309	4.49×10^3	-	-	-	-
Mean	154.9415	-	136.9311	-	-	-	190.9626	-
sd(yEr±)	4.24×10^{-4}	-	$4.18 \cdot 10^{-4}$	-	-	-	6.83×10^{-5}	-
se(yEr±)	2.12×10^{-4}	-	$2.42 \cdot 10^{-4}$	-	-	-	3.95×10^{-5}	-
<I>	-	14,259.4	-	5080.261	-	-	-	1.16×10^5
<I> ²	-	2.03×10^8	-	2.58×10^7	-	-	-	1.35×10^{10}
<I ² >	-	2.06×10^8	-	2.61×10^7	-	-	-	1.38×10^{10}

$\langle I^2 \rangle - \langle I \rangle^2$	-	2.70×10^6	-	244,214.9	-	-	-	2.48×10^8
D''_{SD}	-	7.11×10^{-11}	-	6.44×10^{-12}	-	-	-	6.53×10^{-9}
22090908 Kali Pu Penc 2.9HCO3 0.1 pos								
Scan	m/z	I	m/z	I	m/z	I	m/z	I
6912			172.9522	124,106.6	154.9417	19,448.14	136.9314	3911.171
6960			172.9522	105,954.7	154.9422	16,688.77	136.9312	4781.951
7055			172.9522	109,017.7	154.9419	13,187.52	136.931	6164.307
Mean			1.73×10^2	-	1.55×10^2	-	1.37×10^2	-
sd(yEr±)			1.61×10^{-5}	-	2.63×10^{-4}	-	1.86×10^{-4}	-
se(yEr±)			9.30×10^{-6}	-	1.52×10^{-4}	-	1.07×10^{-4}	-
$\langle I \rangle$	-		1.13×10^5	-	1.64×10^4	-	4.95×10^3	
$\langle I \rangle^2$	-		1.28×10^{10}	-	2.70×10^8	-	2.45×10^7	
$\langle I^2 \rangle$	-		1.28×10^{10}	-	2.77×10^8	-	2.54×10^7	
$\langle I^2 \rangle - \langle I \rangle^2$	-		6.30×10^7	-	6.56×10^6	-	8.61×10^5	
D''_{SD}	-		1.66×10^{-9}	-	1.73×10^{-10}	-	2.27×10^{-11}	
22090908 Kali Pu Penc 2.9HCO3 0.5 pos								
Scan	m/z	I	m/z	I	m/z	I		
6870	190.9625	106,181.2	172.9522	111,567.8	154.9411	21,753.58	-	-
6965	190.9626	154,672.2	172.9521	147,775.1	154.9414	21,179.83	-	-
7014	190.9627	96,203.68	172.9522	97,410.2	154.9418	17,728.27	-	-
7061	190.9626	116,411.1	172.9522	96,655.97	154.942	9,919.188	-	-
Mean	190.9626	-	172.9522	-	154.9416	-	-	-
sd(yEr±)	8.25×10^{-5}	-	6.82×10^{-5}	-	3.96×10^{-4}	-	-	-
se(yEr±)	4.12×10^{-5}	-	3.41×10^{-5}	-	1.98×10^{-4}	-	-	-
$\langle I \rangle$	-	118,367.1	-	113,352.3	-	17,645.22	-	-
$\langle I \rangle^2$	-	1.40×10^{10}	-	1.28×10^{10}	-	3.11×10^8	-	-
$\langle I^2 \rangle$	-	1.45×10^{10}	-	1.33×10^{10}	-	3.34×10^8	-	-
$\langle I^2 \rangle - \langle I \rangle^2$	-	4.90×10^8	-	4.30×10^8	-	2.23×10^7	-	-
D''_{SD}	-	1.29×10^{-8}	-	1.13×10^{-8}	-	5.87×10^{10}	-	-

Table S7. Thermochemistry (M062X/SDD) of ions of analytes at GS and TS in gas-phase, depending on molecular conformations, isomerism, and protomers; Z-matrixes are given in Table S8.

	m/z 137		m/z 97		m/z 155	
	MTZ_137		MTZ_97		MTZ_155 b1	
	GS	TS	GS	TS	GS	TS
E _{ZPVE}	82.54695	80.62289	56.45498	55.83237	99.48070	98.86015
E _{corr}	0.140506	0.137016	0.096399	0.095390	0.169419	0.167805
H _{corr}	0.141450	0.137961	0.097343	0.096334	0.170363	0.168749
G _{corr}	0.097105	0.094332	0.059597	0.058625	0.120368	0.119722
e ₀	0.131547	0.128481	0.089967	0.088975	0.158533	0.157544
E	-471.802417	-471.471214	-339.431652	-339.41855	-547.856404	-547.849287
H	-471.801473	-471.470270	-339.430708	-339.41761	-547.855460	-547.848343
G	-471.845818	-471.513899	-339.468454	-339.45532	-547.905455	-547.897370
	m/z 155		m/z 155		m/z 155	
	MTZ_155 b2		MTZ_155 a2		MTZ_155 a1	
	GS	TS	GS	TS	GS	TS
E _{ZPVE}	99.47977	98.74987	92.17500	91.47661	91.18166	91.42647
E _{corr}	0.169418	0.167937	0.157181	0.155690	0.145307	0.155300
H _{corr}	0.170362	0.168881	0.158125	0.156635	0.155748	0.156244
G _{corr}	0.120366	0.119846	0.110338	0.108300	0.156692	0.109970
e ₀	0.158531	0.157368	0.146890	0.145777	0.145307	0.145697
E	-547.856405	-547.843565	-547.246822	-547.23847	-547.507333	-547.226116
H	-547.855461	-547.842620	-547.245877	-547.23753	-547.506389	-547.225172
G	-547.905457	-547.891656	-547.293664	-547.28586	-547.555045	-547.271446

E_{ZPVE}—zero-point vibration energy [kcal·mol⁻¹]; e₀—zero-point correction [Hartree·(partice)⁻¹]; E_{corr}—thermal correction to energy [Hartree·(partice)⁻¹]; H_{corr}—thermal correction to enthalpy [Hartree·(partice)⁻¹]; G_{corr}—thermal correction to free energy [Hartree·(partice)⁻¹]; E—sum of electronic and thermal energies [Hartree·(partice)⁻¹]; H—sum of electronic and thermal enthalpies [Hartree·(partice)⁻¹]; G—sum of electronic and thermal free energies [Hartree·(partice)⁻¹].

Table S8. Atomic coordinates of species of mass spectrometric ions of Table S7 of ground and transition states.

MTZ 97				MTZ 97			
TS				GS			
Atom	x	y	z	x	y	Z	
C	1.54493	0.38216	0.01613	C	1.56781	0.41004	0.00008
C	−0.67171	−0.54682	−0.0321	C	−0.6648	−0.55644	−0.00004
C	1.53929	−1.01937	0.04809	C	1.53016	−0.9595	−0.00003
N	0.10397	−1.46451	0.05934	N	0.18164	−1.50173	−0.00005
C	−2.15634	−0.43646	0.00003	C	−2.1281	−0.4193	0.00003
N	0.19877	0.80292	0.00002	N	0.22702	0.82008	0.00002
O	−0.26964	1.93453	−0.00006	O	−0.2414	1.95169	−0.00006
H	2.36024	1.09255	0.00017	H	2.38849	1.10972	0.00016
H	2.33709	−1.664	0.00002	H	2.36504	−1.64652	0.0000
H	−2.60212	−1.43251	0.00011	H	−2.57391	−1.41535	0.0001
H	−2.49811	0.11361	−0.88483	H	−2.46984	0.13078	−0.88485
H	−2.4979	0.11344	0.8851	H	−2.46967	0.13061	0.8851

MTZ 137				MTZ 137			
TS				GS			
Atom	x	y	z	x	y	Z	
N	1.73661063	−1.37262241	0.01595197	N	1.68618300	−1.41708200	0.00004400
C	1.61414367	0.00546673	−0.03435166	C	1.54612000	−0.07835800	−0.00000600
C	0.50357299	−1.92002138	0.05153344	C	0.41817600	−1.92934500	−0.00001100
N	0.20698969	0.42015871	0.06357813	N	0.21478000	0.30676800	−0.00004000
C	2.74758637	0.92069646	0.00001842	C	2.70239900	0.86557200	0.00002400
C	−0.10413004	1.74278882	−0.00004560	C	−0.14929200	1.68759100	−0.00005100
C	−0.48837346	−0.85180991	−0.00002738	C	−0.53341400	−0.90692600	−0.00004100
N	−1.84357167	−1.17593904	−0.00003124	N	−1.88887000	−1.23122600	−0.00003200
C	−1.32251073	2.29879418	0.00002248	C	−1.36770600	2.24367100	0.00002200
O	−2.70958505	−0.25904683	0.00005581	O	−2.75476900	−0.31411700	0.00005500
H	0.25556288	−2.93206192	0.00003867	H	0.21035300	−2.98677800	−0.00000600
H	3.65673614	0.31950156	−0.00022694	H	3.61153700	0.26435100	−0.00022500
H	2.75242680	1.56132138	0.88827889	H	2.70728500	1.50617700	0.88825800
H	2.75224148	1.56177048	−0.88791208	H	2.70705700	1.50659900	−0.88789700
H	0.77416881	2.37773386	−0.00011796	H	0.72902600	2.32261500	−0.00011600
H	−1.38042191	3.38145904	0.00002259	H	−1.42550900	3.32637800	0.00003800
H	−2.23889149	1.72643657	0.00009676	H	−2.28394100	1.67113400	0.00008500

MTZ 155 b2				MTZ 155 b2			
TS				GS			
Atom	x	y	z	x	y	Z	
N	−0.53025	1.94579	−0.17919	N	−0.40024800	1.94578600	−0.17919000
C	0.77832	1.56702	−0.81578	C	0.77831500	1.56702300	−0.81578100
C	−1.16477	0.86797	0.13239	C	−1.16477300	0.86797400	0.13239300
C	0.80485	0.07802	−0.78244	C	0.80484900	0.07801700	−0.78244300
C	−2.48341	0.92546	0.81417	C	−2.48340500	0.92546300	0.81417400
N	1.88262	−0.39658	0.28963	N	1.88262200	−0.39658000	0.28962900
N	−0.52705	−0.24584	−0.28226	N	−0.52704800	−0.24583600	−0.28225900
C	−0.96732	−1.60966	−0.1067	C	−0.96732000	−1.60965800	−0.10669900
O	3.04976	−0.49134	−0.14362	O	3.04976500	−0.49134300	−0.14361900
O	1.47492	−0.57493	1.46444	O	1.47491900	−0.57492700	1.46444300
C	−2.11647	−2.05724	−0.62379	C	−2.11646900	−2.05723800	−0.62378800
H	−0.66613	2.90427	0.02456	H	−0.66612800	2.90426700	0.02456100
H	1.53342	2.24993	−1.16816	H	1.53342300	2.24993400	−1.16816000
H	1.09891	−0.44618	−1.69302	H	1.09890900	−0.44617600	−1.69301600
H	−3.30001	0.87101	0.08636	H	−3.30001200	0.87101000	0.08635500
H	−2.58584	1.85656	1.37527	H	−2.58584000	1.85655500	1.37527400
H	−2.58992	0.08119	1.50007	H	−2.58992000	0.08118600	1.50006500
H	−0.29444	−2.21833	0.48887	H	−0.29444200	−2.21832500	0.48886700
H	−2.42099	−3.08264	−0.44857	H	−2.42098700	−3.08264500	−0.44857000
H	−2.76693	−1.43872	−1.23636	H	−2.76693100	−1.43871700	−1.23635500

MTZ 155 b1				MTZ 155 b1			
TS				GS			
Atom	x	y	z	x	y	Z	
N	0.48063	1.94295	-0.17427	N	0.40012900	1.94581200	-0.17913200
C	-0.68498	1.59284	-0.84773	C	-0.77839100	1.56691700	-0.81572100
C	1.2707	0.83939	0.16354	C	1.16471700	0.86805500	0.13255600
C	-0.77018	0.12902	-0.73876	C	-0.80478500	0.07790900	-0.78233800
C	2.55987	0.93063	0.8077	C	2.48326300	0.92571300	0.81449900
N	-1.80607	-0.39184	0.28278	N	-1.88266800	-0.39676500	0.28958300
N	0.60368	-0.24089	-0.28885	N	0.52708400	-0.24581400	-0.28204400
C	1.04428	-1.60466	-0.11347	C	0.96768600	-1.60958200	-0.10666300
O	-2.97331	-0.48557	-0.15047	O	-3.04990800	-0.49049200	-0.14366100
O	-1.39839	-0.57132	1.45741	O	-1.47498800	-0.57624300	1.46421200
C	2.19328	-2.05197	-0.63114	C	2.11668100	-2.05689000	-0.62433300
H	0.74255	2.90922	0.01777	H	0.66593500	2.90432400	0.02457700
H	-1.45692	2.2547	-1.1751	H	-1.53350000	2.24973000	-1.16828100
H	-1.02209	-0.44129	-1.69958	H	-1.09871500	-0.44632300	-1.69293500
H	2.66645	0.08633	1.49354	H	2.58982600	0.08140400	1.50034200
H	2.66204	1.8617	1.36888	H	2.58544300	1.85678300	1.37569200
H	3.3766	0.87639	0.08	H	3.29999200	0.87146800	0.08680700
H	0.37178	-2.21345	0.48239	H	0.29518200	-2.21836600	0.48919400
H	2.49805	-3.07736	-0.45623	H	2.42145000	-3.08227900	-0.44942200
H	2.84331	-1.43331	-1.24402	H	2.76671400	-1.43822800	-1.23721400
MTZ 155 a1				MTZ 155 a1			
TS				GS			
Atom	x	y	z	x	y	Z	
N	0.47905	2.02191	-0.0769	N	0.40257600	2.03817700	-0.07865900
C	1.25629	0.95314	0.07473	C	1.17036900	0.94856700	0.09977000
C	-0.67509	1.61527	-0.61955	C	-0.77019400	1.65032000	-0.64036100
C	2.55496	0.98698	0.77244	C	2.51181700	0.96401100	0.74249100
C	-0.74041	0.13843	-0.77001	C	-0.81409300	0.14906300	-0.76330800
N	-1.80418	-0.423	0.26677	N	-1.87786800	-0.41237900	0.27346800
N	0.59296	-0.22081	-0.37009	N	0.51924300	-0.21021000	-0.36339800
C	1.02845	-1.56494	-0.35487	C	0.95475900	-1.55429400	-0.34816600
O	-2.99759	-0.40779	-0.13496	O	-3.07129300	-0.39716200	-0.12824900
O	-1.40941	-0.77964	1.40471	O	-1.48311100	-0.76901300	1.41141800
C	2.29839	-1.99158	-0.43665	C	2.22469100	-1.98095300	-0.42995200
H	-1.49944	2.31357	-0.89679	H	-1.57317600	2.32421700	-0.89011400
H	2.69207	0.12668	1.44521	H	2.61839600	0.13731900	1.45192600
H	2.69515	1.9036	1.25983	H	2.62144000	1.91413900	1.26648600
H	3.39302	0.87562	-0.00136	H	3.31939100	0.88623100	0.00529400
H	-1.09122	-0.28519	-1.71305	H	-1.16495500	-0.27459900	-1.70631500
H	0.21551	-2.27965	-0.2561	H	0.14181200	-2.26903100	-0.24939700
H	2.5035	-3.05342	-0.37981	H	2.42981200	-3.04279200	-0.37309500
H	3.14446	-1.32613	-0.55958	H	3.07075200	-1.31549200	-0.55286500
MTZ 155 a2				MTZ 155 a2			
TS				GS			
Atom	x	y	z	x	y	Z	
N	0.92852	-1.94673	0.19216	N	0.86202100	-1.96068200	0.18807600
C	1.49717	-0.60828	-0.02604	C	1.41778900	-0.65099500	0.00674400
C	-0.27876	-1.92949	-0.18833	C	-0.37074000	-1.91762700	-0.21853500
C	2.83252	-0.29723	0.41876	C	2.81191600	-0.36514600	0.37596600
C	-0.68479	-0.49907	-0.71593	C	-0.74738200	-0.52079100	-0.70834100
N	-1.73178	0.11425	0.22225	N	-1.79437600	0.09252900	0.22983600
N	0.59422	0.20011	-0.53386	N	0.53162400	0.17838300	-0.52627200
C	0.74449	1.61206	-0.83081	C	0.68189500	1.59033100	-0.82321800
O	-1.31279	0.49767	1.34372	O	-1.37538300	0.47594600	1.35130900
O	-2.90242	0.13937	-0.21175	O	-2.96501000	0.11764300	-0.20416100
C	0.90044	2.50505	0.1541	C	0.83784600	2.48332000	0.16168400
H	-0.97975	-2.74565	-0.20502	H	-1.04234200	-2.76732600	-0.19745500
H	3.21195	0.63515	0.02864	H	3.14935100	0.61336400	0.03620800
H	3.51358	-1.13938	-0.02835	H	3.45112500	-1.16128000	-0.02086200
H	2.96577	-0.40385	1.46224	H	2.90318900	-0.42557400	1.46966200
H	-1.0804	-0.44253	-1.73263	H	-1.14299700	-0.46424400	-1.72504100
H	0.69981	1.85658	-1.88593	H	0.63721700	1.83485900	-1.87834600
H	1.00953	3.55652	-0.08745	H	0.94693400	3.53479000	-0.07986400
H	0.90044	2.22226	1.20365	H	0.83784600	2.20053600	1.21124100

Table S9. Frequency analysis of species of mass spectrometric ions of Table S7 of ground and transition states.

		MTZ 97			MTZ 97	
		TS			GS	
Freq.	−183.7012	114.7517	156.0437	91.8094	193.0722	247.7487
Freq.	247.1805	272.6430	390.7232	307.8247	421.9938	462.2612
Freq.	576.0871	624.3574	639.2417	585.7070	632.6793	665.1950
Freq.	708.7406	779.7238	811.3151	809.7528	813.8416	925.2989
Freq.	864.1052	924.8208	1058.3856	981.5838	1021.4514	1073.0057
Freq.	1080.5140	1091.4649	1186.4523	1096.3072	1142.9434	1215.7035
Freq.	1246.3793	1438.9595	1452.2248	1337.2509	1448.5537	1471.2200
Freq.	1484.3753	1490.8899	1675.4278	1474.4661	1543.9365	1688.7738
Freq.	2116.4180	3068.7633	3154.4816	1786.4128	3068.1916	3153.3242
Freq.	3203.1633	3290.5682	3907.1068	3199.8524	3304.8083	3325.8607
		MTZ 137			MTZ 137	
		TS			GS	
Freq.	−170.2772	69.0974	175.9204	51.9919	92.3398	206.2044
Freq.	213.9140	231.3638	252.9792	209.0404	235.2508	264.5252
Freq.	267.9815	348.1596	454.6593	294.0812	349.3480	415.5603
Freq.	479.3225	504.4144	587.4894	497.7583	544.8839	662.5918
Freq.	595.4848	665.3170	674.6251	662.8694	685.1511	697.6584
Freq.	723.1265	739.2086	794.4764	766.7322	825.0025	949.4438
Freq.	838.3447	939.3554	996.8238	981.1675	1035.1978	1042.7474
Freq.	1042.9281	1074.5389	1110.1704	1049.7194	1099.2427	1121.7483
Freq.	1116.6302	1123.5425	1187.8718	1201.6841	1272.5901	1302.4795
Freq.	1305.1604	1347.7569	1377.3911	1347.6133	1423.0344	1454.5973
Freq.	1408.8766	1448.5410	1462.2258	1459.0525	1476.9968	1504.6668
Freq.	1468.6543	1502.6474	1522.2675	1520.5554	1531.1347	1550.1545
Freq.	1547.5725	1770.7673	3086.7494	1571.4802	1739.2718	3089.7700
Freq.	3167.6944	3220.8323	3222.6096	3168.4456	3214.6101	3220.2229
Freq.	3277.4009	3352.7500	3698.8874	3278.7863	3333.0429	3341.9858
		MTZ 155 b2			MTZ 155 b2	
		TS			GS	
Freq.	−5.6309	39.8929	61.8458	46.3437	57.4774	81.2603
Freq.	116.7031	137.6233	158.8839	116.4656	133.7436	193.7835
Freq.	238.8396	296.1955	315.0877	243.0292	290.4459	352.3586
Freq.	342.3087	358.3113	413.4036	353.9710	422.0876	466.5068
Freq.	459.6714	475.1337	588.9186	495.6477	605.3419	638.7011
Freq.	637.2201	678.7992	722.4012	676.9799	717.7225	749.9799
Freq.	746.4881	759.1666	794.4412	757.0393	763.2813	792.7966
Freq.	842.1932	909.2660	1011.6245	919.7788	1009.3849	1014.9540
Freq.	1026.8352	1060.0027	1068.5220	1015.8336	1061.9549	1069.4375
Freq.	1083.2674	1097.8763	1150.1403	1090.1336	1132.3592	1175.5129
Freq.	1206.1438	1243.0390	1274.6907	1221.7077	1258.8688	1319.9684
Freq.	1295.2633	1340.2572	1352.4229	1340.3457	1346.0160	1398.2334
Freq.	1381.3087	1466.2598	1468.1021	1406.3211	1462.8403	1466.1210
Freq.	1496.4261	1513.5556	1583.8816	1493.4394	1507.5950	1577.9134
Freq.	1600.8541	1734.1848	1781.6953	1586.5367	1619.5894	1733.7686
Freq.	3083.4214	3173.2312	3181.8689	3081.5087	3170.2246	3181.5835
Freq.	3197.8576	3202.2200	3246.1525	3198.1801	3203.4634	3250.0192
Freq.	3314.0894	3362.6375	3985.9165	3315.0913	3348.2431	3655.2239

MTZ_155_b1						
TS			MTZ_155_b1			
Freq.				GS		
Freq.	-13.0702	22.9494	61.0055	46.3082	57.5357	81.2564
Freq.	113.0922	138.2024	173.7640	116.4553	133.7220	193.7723
Freq.	233.4556	270.2008	342.8060	243.0690	290.4068	352.3206
Freq.	346.9459	408.5826	432.4575	353.9795	422.1584	466.5388
Freq.	481.8187	611.3602	646.8472	495.7863	605.3139	638.6811
Freq.	681.5828	723.7373	752.3424	676.9759	717.7110	750.0069
Freq.	754.7587	775.0479	856.5141	757.0480	763.2667	792.8204
Freq.	925.8286	982.0619	1013.3193	919.7762	1009.4629	1014.9494
Freq.	1057.2646	1068.3292	1074.7564	1015.8626	1061.9749	1069.4926
Freq.	1088.2880	1119.0795	1145.3144	1090.1339	1132.3558	1175.5226
Freq.	1241.8042	1306.7296	1337.1180	1221.7258	1258.8791	1319.9660
Freq.	1361.4850	1390.0907	1408.8294	1340.3581	1346.0272	1398.2270
Freq.	1440.6707	1463.0012	1473.2309	1406.3226	1462.8434	1466.1413
Freq.	1482.7655	1504.0393	1531.4172	1493.4385	1507.5957	1577.8760
Freq.	1596.9430	1657.5036	1732.5998	1586.5617	1619.6130	1733.7113
Freq.	2688.0491	3079.3723	3165.3592	3081.4997	3170.2192	3181.5135
Freq.	3195.0765	3203.6211	3250.6336	3198.1624	3203.5078	3250.2609
Freq.	3315.2389	3417.9595	3608.4323	3315.1189	3348.3102	3655.2226
MTZ_155_a1						
TS			MTZ_155_a1			
Freq.				GS		
Freq.	-107.2424	51.8536	81.8194	56.0586	68.4653	86.0336
Freq.	122.3601	151.7095	197.5196	142.4484	188.7391	228.5305
Freq.	239.2959	325.5388	327.8045	241.7697	298.2008	348.7946
Freq.	390.2511	450.7692	500.6245	367.9133	401.0753	494.6606
Freq.	632.2415	657.0742	666.3759	613.0649	635.0313	648.8719
Freq.	723.6374	737.2412	757.7083	676.3727	723.5686	739.4486
Freq.	806.4704	890.4782	975.8457	758.6739	809.8597	894.2119
Freq.	991.9748	1010.0285	1042.8836	977.7913	999.8983	1009.2278
Freq.	1047.8084	1067.6938	1097.7157	1018.6863	1057.5927	1074.9954
Freq.	1181.5172	1209.0868	1258.6379	1187.6279	1209.9364	1230.6670
Freq.	1277.3923	1306.4927	1343.3091	1280.0081	1302.5326	1342.6935
Freq.	1371.2365	1434.6172	1446.7001	1363.3906	1374.7296	1449.5192
Freq.	1450.0556	1477.0036	1481.8027	1462.4929	1488.6730	1503.1023
Freq.	1507.6183	1536.2324	1623.9438	1520.5676	1534.9407	1567.9126
Freq.	1718.9647	2691.8325	3040.3845	1739.0707	3070.3283	3149.6177
Freq.	3076.8924	3191.6758	3210.2758	3168.2455	3202.8154	3207.7822
Freq.	3223.5191	3324.7118	3625.1192	3222.4999	3319.4330	3323.9268
MTZ_155_a2						
TS			MTZ_155_a2			
Freq.				GS		
Freq.	-248.6202	13.8276	48.8156	49.3004	82.2894	91.7014
Freq.	107.8099	147.8049	178.3759	137.3306	155.9285	197.7378
Freq.	244.4903	272.0666	355.5367	249.2877	301.8438	365.9227
Freq.	376.6419	443.7486	510.6427	381.7474	441.7900	513.7498
Freq.	611.3741	651.0623	673.4031	639.1791	655.0167	676.2068
Freq.	699.2103	716.7312	776.5844	703.4875	726.7972	783.4960
Freq.	812.7980	884.5872	925.2465	843.8079	928.9209	969.2661
Freq.	960.9197	963.6876	996.1576	970.6339	995.6778	1015.1870
Freq.	1026.2384	1065.0927	1090.0201	1061.7905	1082.3875	1089.8931
Freq.	1154.8417	1188.0051	1219.9646	1153.1155	1205.8325	1238.9148
Freq.	1264.7191	1283.2120	1330.7995	1277.6923	1304.7208	1334.7349
Freq.	1337.8599	1392.7979	1427.2938	1339.8615	1400.6645	1445.0373
Freq.	1466.4274	1479.9165	1526.5405	1467.3560	1475.3752	1484.0218
Freq.	1592.8092	1701.1062	1714.2716	1589.8220	1603.6447	1657.6565
Freq.	1760.6515	2483.3721	3186.6639	1710.5810	3066.9570	3141.2292
Freq.	3203.5215	3258.4332	3287.7359	3182.4463	3203.1562	3224.5613
Freq.	3317.1397	3337.8253	3520.0399	3257.8922	3285.0222	3316.6753