Electronic Supplementary Information (ESI)

Anaerobic oxidation of aldehydes to carboxylic acids under hydrothermal conditions

Yiju Liao,[a] Alexandria Aspin,[a] Ziming Yang [a]*

[a] Department of Chemistry, Oakland University, Rochester, MI 48309, USA

*Correspondence: zimingyang@oakland.edu

I. Experimental Section

Materials

Aldehydes including benzaldehyde (99%), 2-(trifluoromethyl)benzaldehyde (98%), 2-bromobenzaldehyde (98%), 4-bromobenzaldehyde (99%), hydrocinnamaldehyde (90%), *p*-tolualdehyde (97%), 4-methoxybenzaldehyde (98%), cyclohexanecarboxaldehyde (97%), cinnamaldehyde (95%) and 2-naphthaldehyde (98%) were purchased from Sigma-Aldrich and used without purification. Carboxylic acids including benzoic acid (99%), 2-(trifluoromethyl)benzoic acid (98%), 2-bromobenzoic acid (97%), 4-bromobenzoic acid (98%), hydrocinnamic acid (99%), *p*-toluic acid (98%), 4-methoxybenzoic acid (99%), cyclohexanecarboxylic acid (98%), *trans*-cinnamic acid (97%), and 2-naphthoic acid (98%) were also obtained from Sigma-Aldrich and used as standards for product identification and quantification. Metal salts including ferric nitrate (99%), cupric nitrate (99%), cupric sulfate (99%), cupric chloride (99%), sodium nitrate (99%), magnesium nitrate hexahydrate (99%), and calcium nitrate tetrahydrate (99%) were obtained from Sigma-Aldrich and used as received. Dichloromethane (DCM) (99.9%) was obtained from VWR, and n-decane (99%) was purchased from Sigma-Aldrich and used as the gas chromatography (GC) internal standard. Deionized water was obtained from a Barnstead Nanopure system with a resistivity of 18.2 MΩ·cm.

Methods

General experimental procedure for the hydrothermal oxidation of aldehydes is as follows: the aldehyde (0.03 mol) was first loaded to a fused silica glass tube (2 mm ID and 6 mm OD), followed by the addition of 0.3 mL of N_2-purged deionized water or metal salt solution (0.03 – 0.06 mol). Then the tube was placed in liquid nitrogen, evacuated through three freeze-pump-thaw cycles to remove air/oxygen, and sealed with an oxyhydrogen flame.[1] The reaction mixture in the

tube was then heated in a GC oven at 200 °C and 15 bar (P_{sat}, calculated using SUPCRT92)[2] for up to 24 h, and the reaction was quenched by submerging the silica tubes in a cold water bath. The products were extracted with 3.0 mL DCM containing 8.8 mM decane, and the pH of the aqueous layer was adjusted to ~2 with HCl solution before the extraction. An Agilent 7820A GC system equipped with an autosampler and a flame-ionization detector was used to analyze and quantify the carboxylic acid products and the remaining of the starting aldehydes. The concentration of each aldehyde and carboxylic acid was quantified by GC using calibration curves established with authentic samples. The product identification was further confirmed by a gas chromatograph-mass spectrometer (Agilent 7890A/5975C) based on fragmentation patterns in the mass spectra. Small amounts of by-product include nitro compounds (from nitrate experiments), C–C cleavage products, and possible isomer structures were also detected.

II. Thermodynamic Calculations

Thermodynamic calculations on aqueous oxidation of aldehyde were conducted using the software SUPCRT92,[2] with the revised Helgeson-Kirkham-Flowers equation of state.[3, 4] Acetaldehyde was chosen as a representative aldehyde structure based on its availability in the geochemical database. Equilibrium constants (log K_{eq}) were calculated for the oxidation of acetaldehyde to acetic acid in pure water (Eqn 1) and in the presence of $Fe(NO_3)_3$ (Eqn 2), respectively, at temperatures from 0 to 300 °C at P_{sat}.

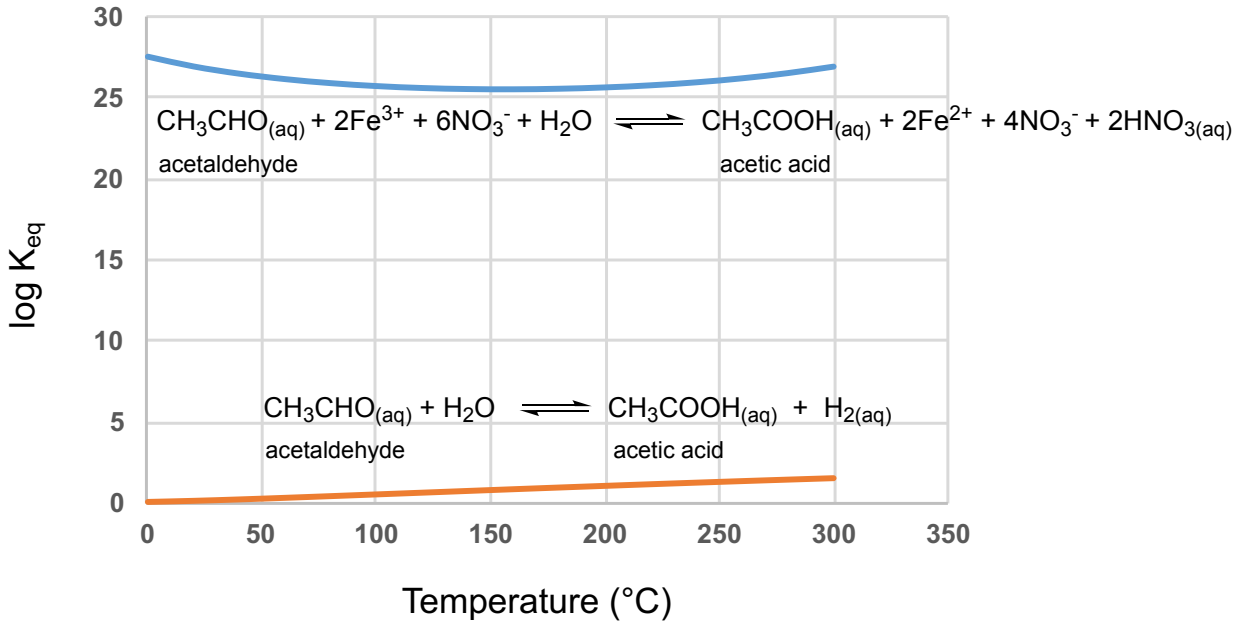
$$\underset{\text{acetaldehyde}}{CH_3CHO_{(aq)}} + H_2O \rightleftharpoons \underset{\text{acetic acid}}{CH_3COOH_{(aq)}} + H_{2(aq)} \qquad (1)$$

$$K_{eq1} = \frac{a(\text{acetic acid}_{(aq)})\, aH_{2(aq)}}{a(\text{acetaldehyde}_{(aq)})}$$

$$\underset{\text{acetaldehyde}}{CH_3CHO_{(aq)}} + 2Fe^{3+} + 6NO_3^- + H_2O \rightleftharpoons \underset{\text{acetic acid}}{CH_3COOH_{(aq)}} + 2Fe^{2+} + 4NO_3^- + 2HNO_{3(aq)} \quad (2)$$

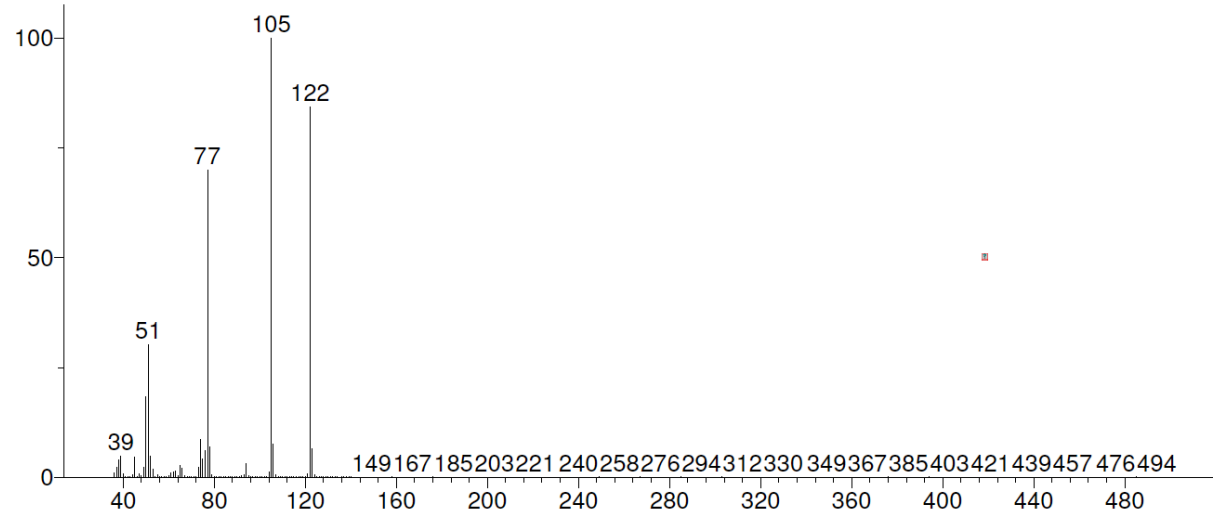
$$K_{eq2} = \frac{a(\text{acetic acid}_{(aq)})\, a(Fe^{2+})^2\, a(HNO_{3(aq)})^2}{a(\text{acetaldehyde}_{(aq)})\, a(Fe^{3+})^2\, a(NO_3^-)^2}$$

Figure S1. Calculated equilibrium constant (log K_{eq}) for oxidation of acetaldehyde to acetic acid in water with (blue) and without (orange) $Fe(NO_3)_3$, as a function of temperature at water saturation vapor pressure, using SUPCRT92.[2]



III. Characterization of Carboxylic Acid Products by GC-MS

Figure S2. GC-MS data for reaction of Compound 1.



(Text File) Scan 3070 (16.620 min): BA4.d\data.ms

Name: Scan 3070 (16.620 min): BA4.d\data.ms
MW: N/A ID#: 3762 DB: Text File
Comment: 1FN
10 largest peaks:
105 999 | 122 842 | 77 700 | 51 303 | 50 183 | 74 86 | 106 76 | 78 68 | 123 65 | 76 61 |

Database matching:

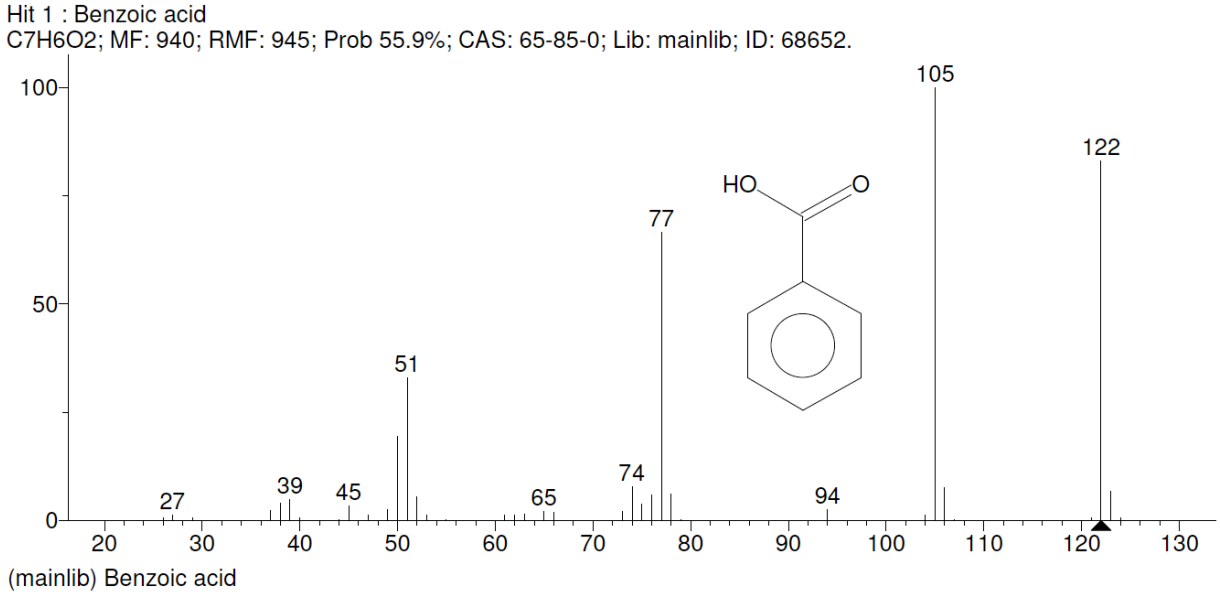
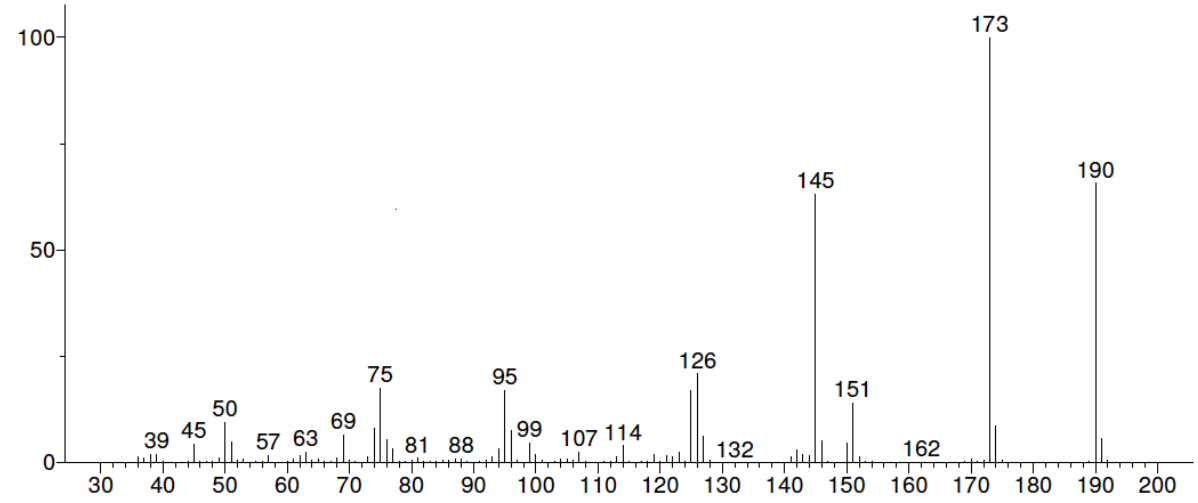


Figure S3. GC-MS data for reaction of Compound 2.

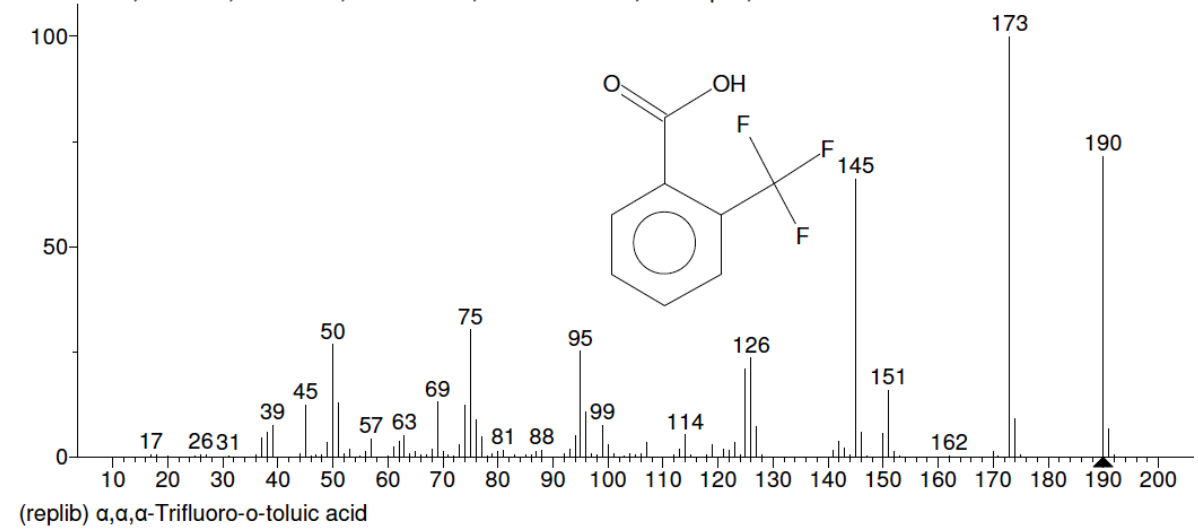


(Text File) Scan 3198 (17.268 min): BA6.d\data.ms

Name: Scan 3198 (17.268 min): BA6.d\data.ms
MW: N/A ID#: 3771 DB: Text File
Comment: 2FN
10 largest peaks:
173 999 | 190 658 | 145 632 | 126 210 | 75 176 | 95 171 | 125 168 | 151 141 | 50 97 | 174 85 |

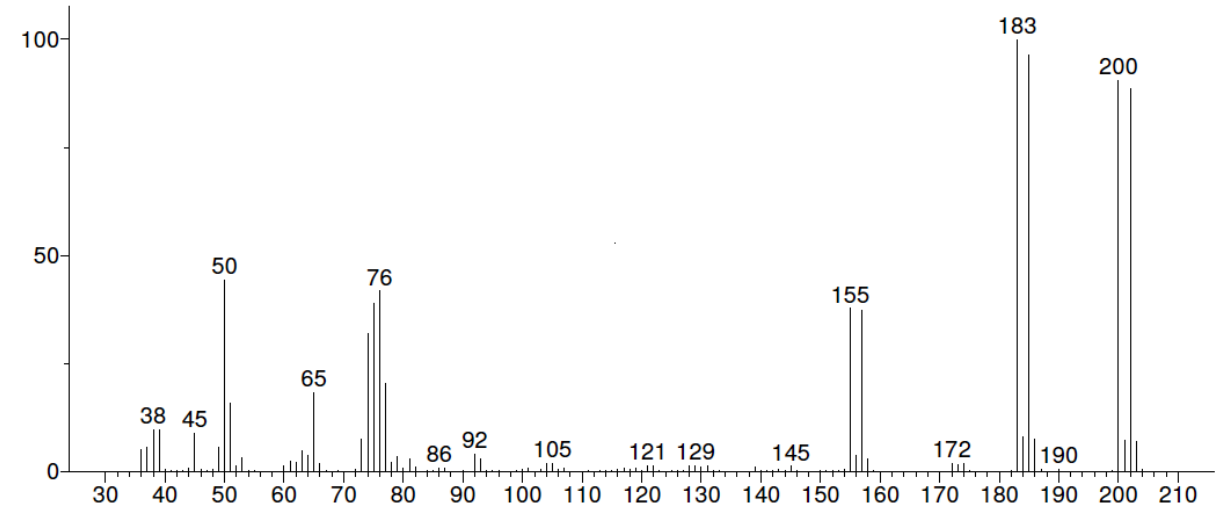
Database matching:

Hit 1 : α,α,α-Trifluoro-o-toluic acid
C8H5F3O2; MF: 941; RMF: 942; Prob 77.2%; CAS: 433-97-6; Lib: replib; ID: 22428.



(replib) α,α,α-Trifluoro-o-toluic acid

Figure S4. GC-MS data for reaction of Compound 3.

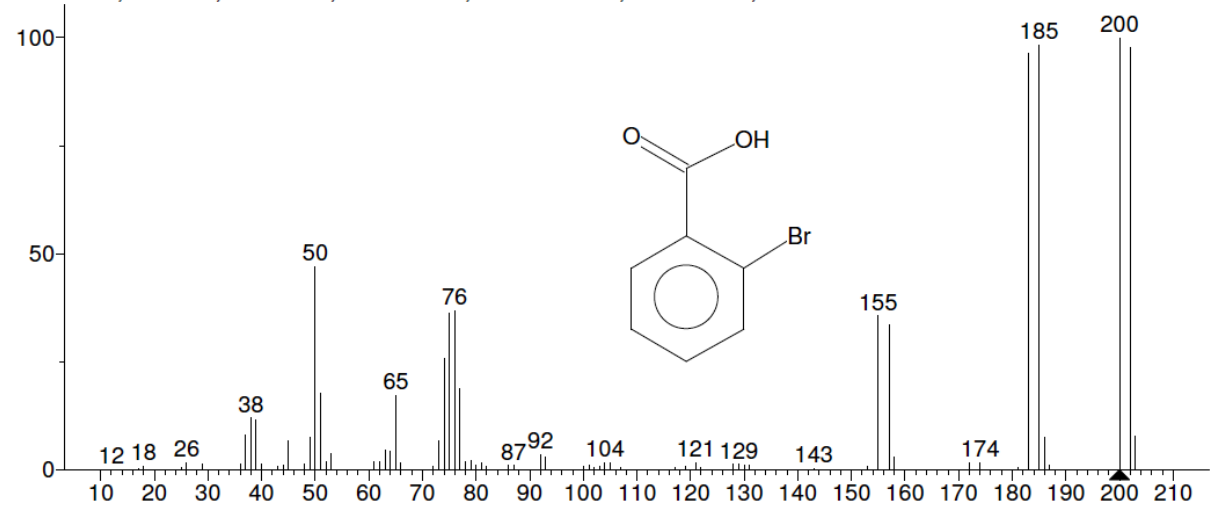


(Text File) Scan 3741 (20.443 min): BA8.d\data.ms

Name: Scan 3741 (20.443 min): BA8.d\data.ms
MW: N/A ID#: 3784 DB: Text File
Comment: 3FN
10 largest peaks:
183 999 | 185 962 | 200 905 | 202 882 | 50 445 | 76 419 | 75 388 | 155 379 | 157 372 | 74 318 |

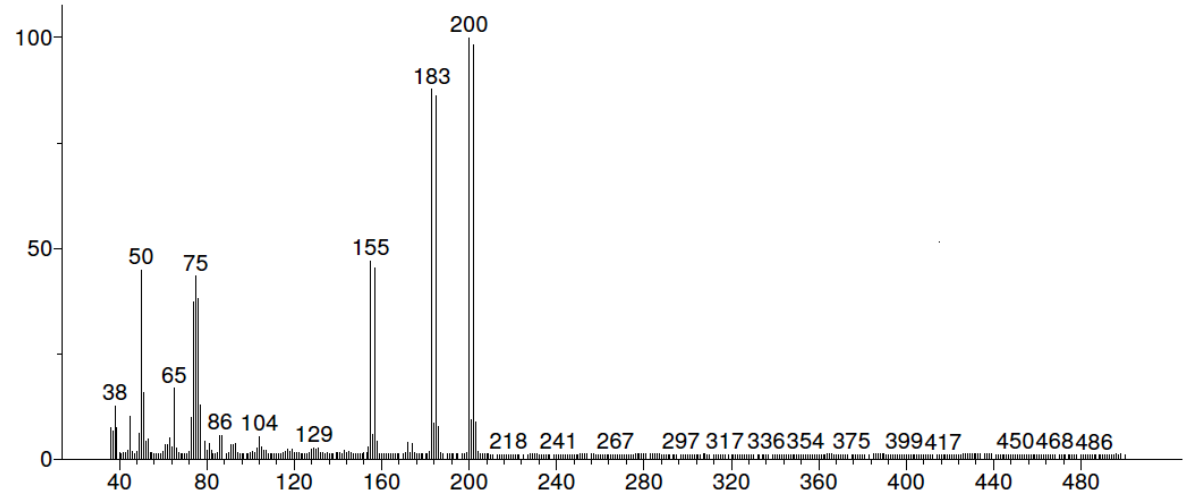
Database matching:

Hit 1 : Benzoic acid, 2-bromo-
C7H5BrO2; MF: 919; RMF: 945; Prob 42.3%; CAS: 88-65-3; Lib: mainlib; ID: 145777.



(mainlib) Benzoic acid, 2-bromo-

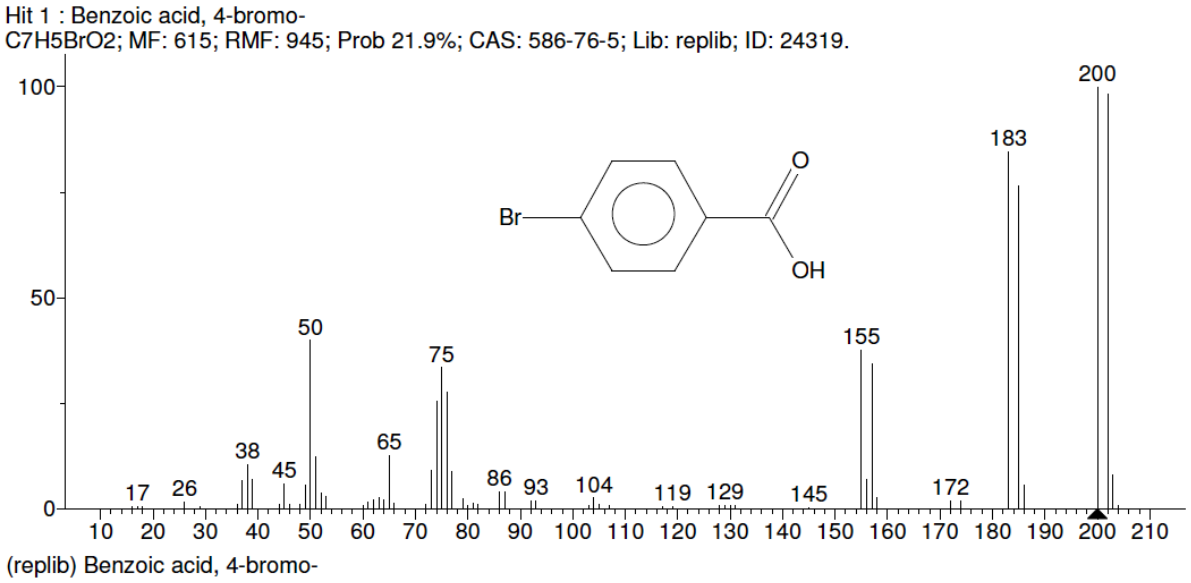
Figure S5. GC-MS data for reaction of Compound 4.



(Text File) Scan 3755 (20.228 min): 11FN.d\data.ms

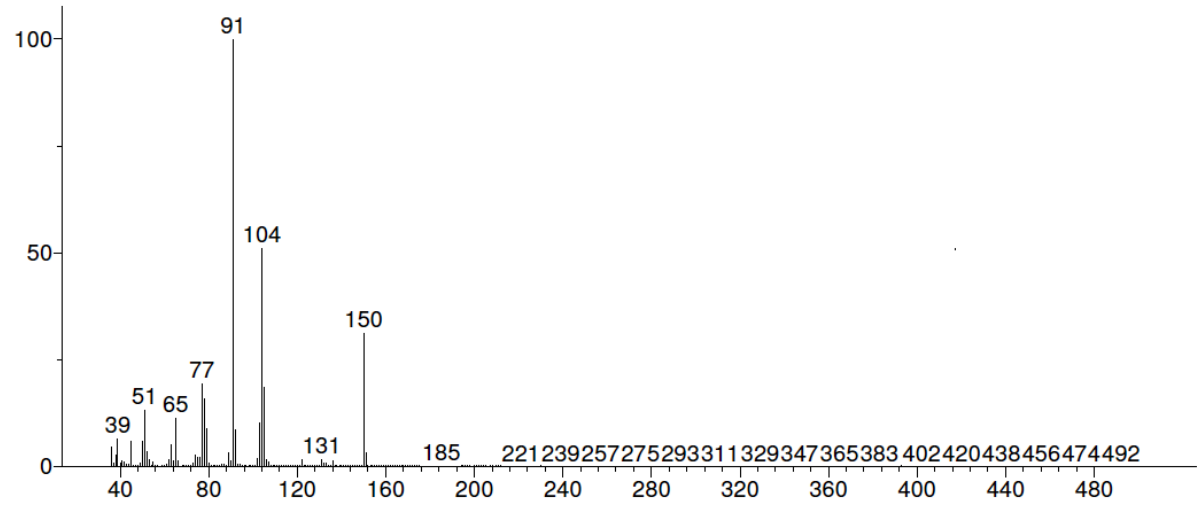
Name: Scan 3755 (20.228 min): 11FN.d\data.ms
MW: N/A ID#: 3974 DB: Text File
Comment: 11FN
10 largest peaks:
200 999 | 202 981 | 183 877 | 185 860 | 155 470 | 157 452 | 50 450 | 75 435 | 76 379 | 74 372 |

Database matching:



(replib) Benzoic acid, 4-bromo-

Figure S6. GC-MS data for reaction of Compound 5.

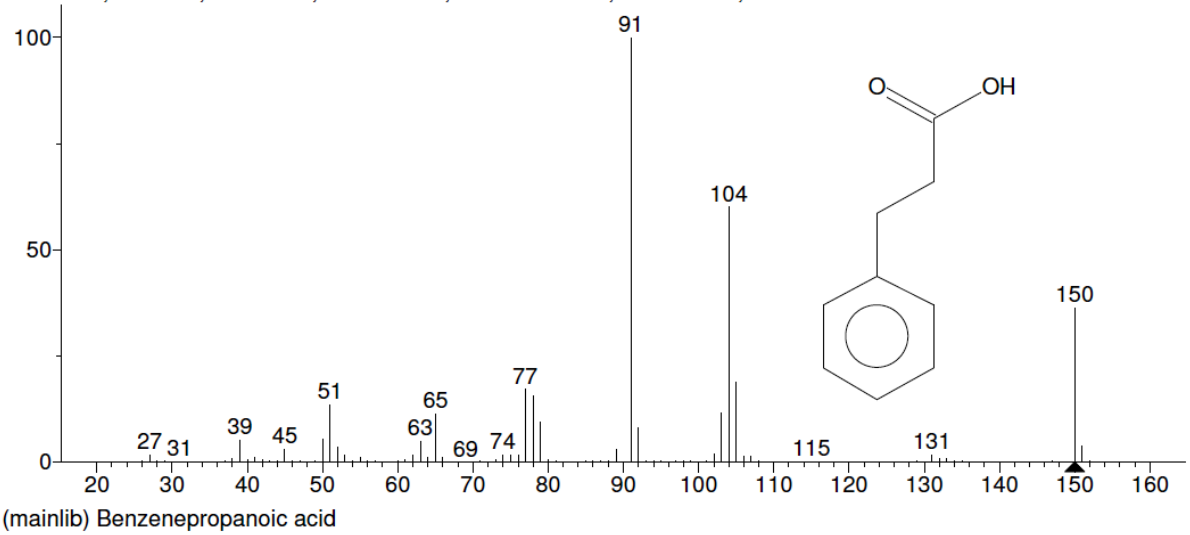


(Text File) Scan 3364 (18.728 min): BA0.d\data.ms

Name: Scan 3364 (18.728 min): BA0.d\data.ms
MW: N/A ID#: 3802 DB: Text File
Comment: 4FN
10 largest peaks:
91 999 | 104 512 | 150 313 | 77 196 | 105 185 | 78 156 | 51 134 | 65 115 | 103 103 | 79 88 |

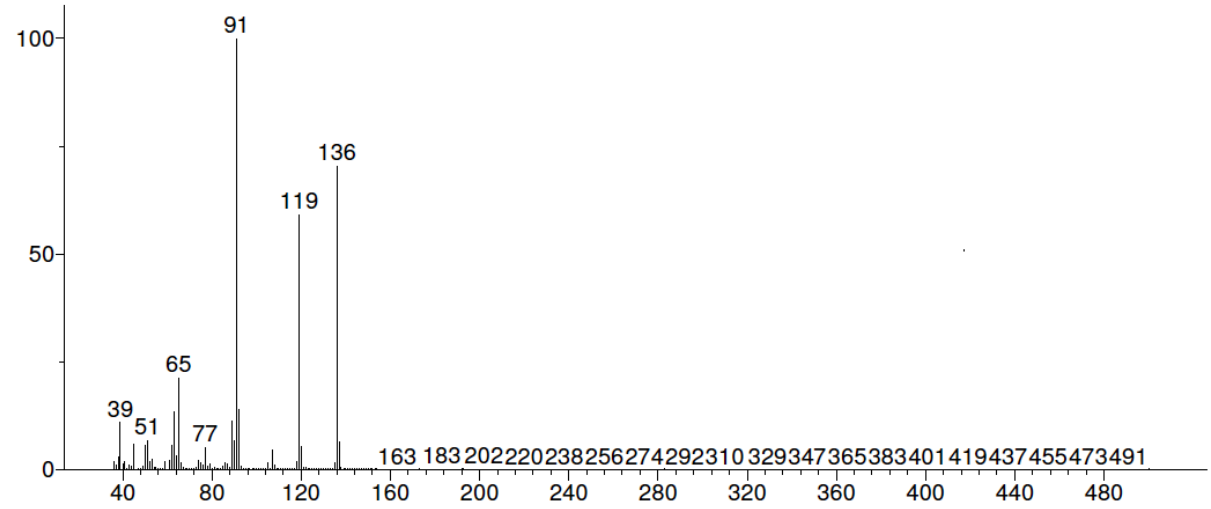
Database matching:

Hit 1 : Benzenepropanoic acid
C9H10O2; MF: 926; RMF: 949; Prob 70.1%; CAS: 501-52-0; Lib: mainlib; ID: 51978.



(mainlib) Benzenepropanoic acid

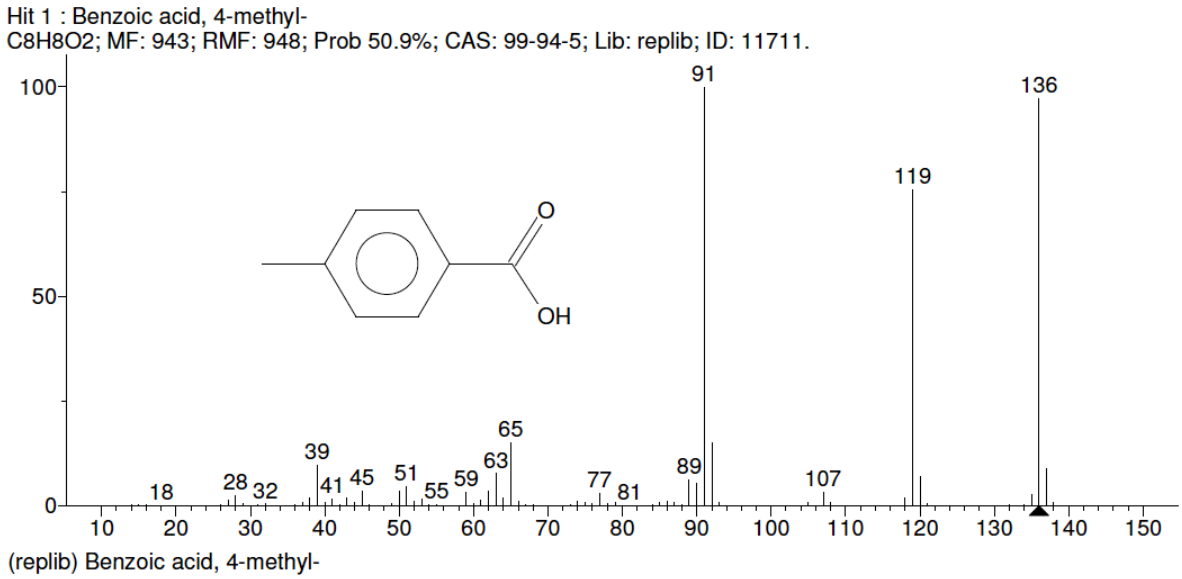
Figure S7. GC-MS data for reaction of Compound 6.



(Text File) Scan 2830 (18.223 min): PTA.D\data.ms

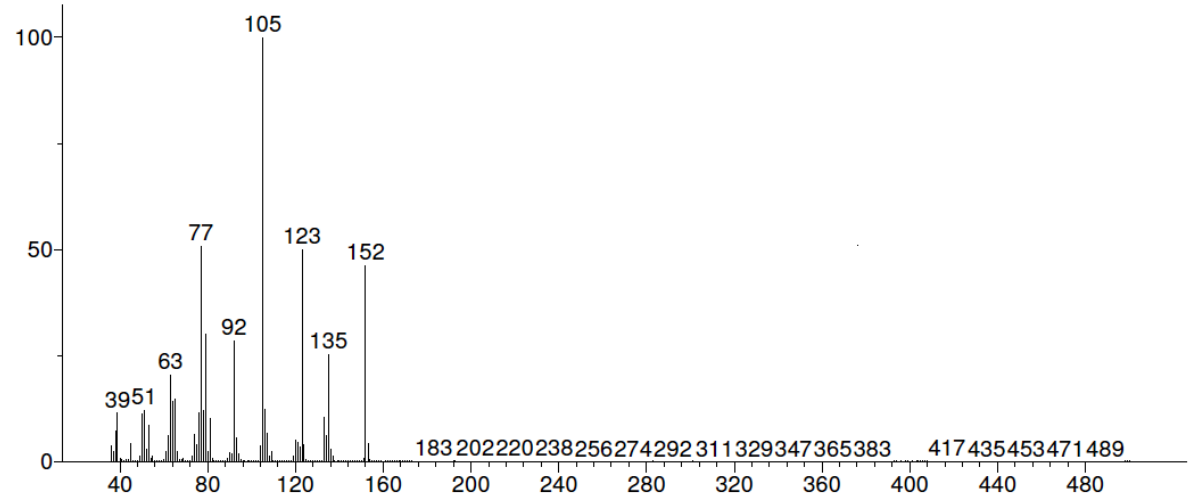
Name: Scan 2830 (18.223 min): PTA.D\data.ms
MW: N/A ID#: 3998 DB: Text File
Comment: P-TOLUIC ACID
10 largest peaks:
91 999 | 136 705 | 119 592 | 65 215 | 92 138 | 63 134 | 89 113 | 39 111 | 51 69 | 90 67 |

Database matching:



(replib) Benzoic acid, 4-methyl-

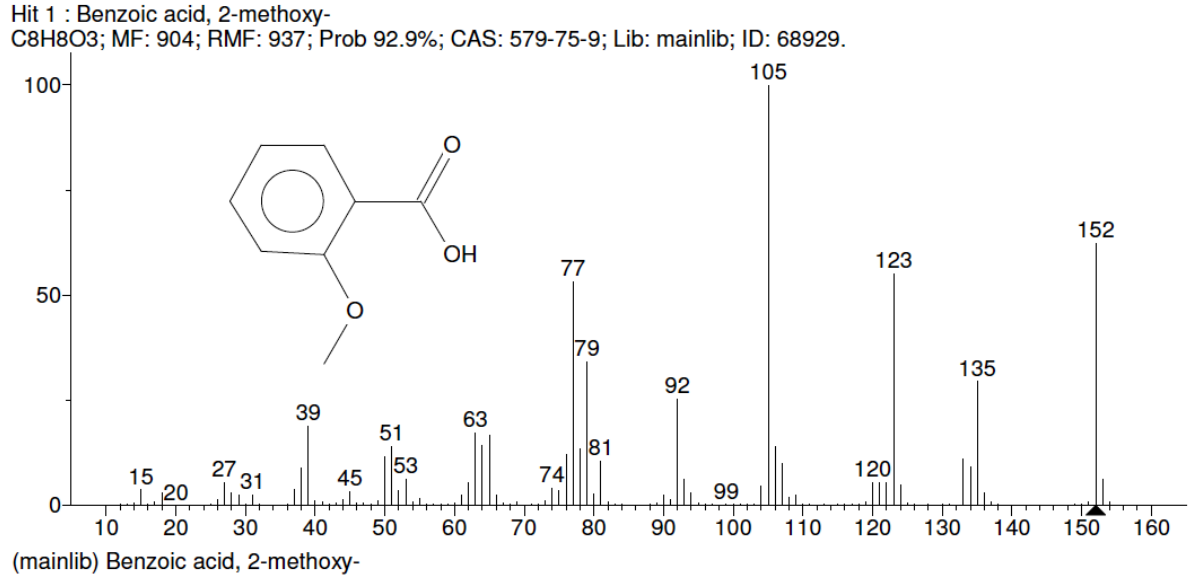
Figure S8. GC-MS data for reaction of Compound 7.



(Text File) Scan 3828 (20.709 min): BA4.d\data.ms

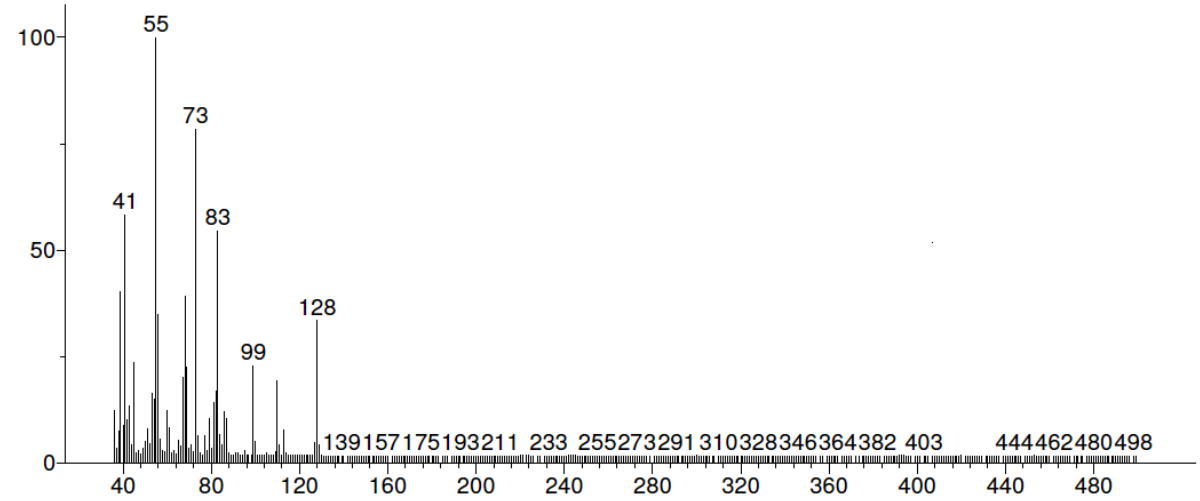
Name: Scan 3828 (20.709 min): BA4.d\data.ms
MW: N/A ID#: 3845 DB: Text File
Comment: 7FN
10 largest peaks:
105 999 | 77 508 | 123 502 | 152 464 | 79 299 | 92 286 | 135 255 | 63 207 | 65 146 | 64 141 |

Database matching:



(mainlib) Benzoic acid, 2-methoxy-

Figure S9. GC-MS data for reaction of Compound 8.

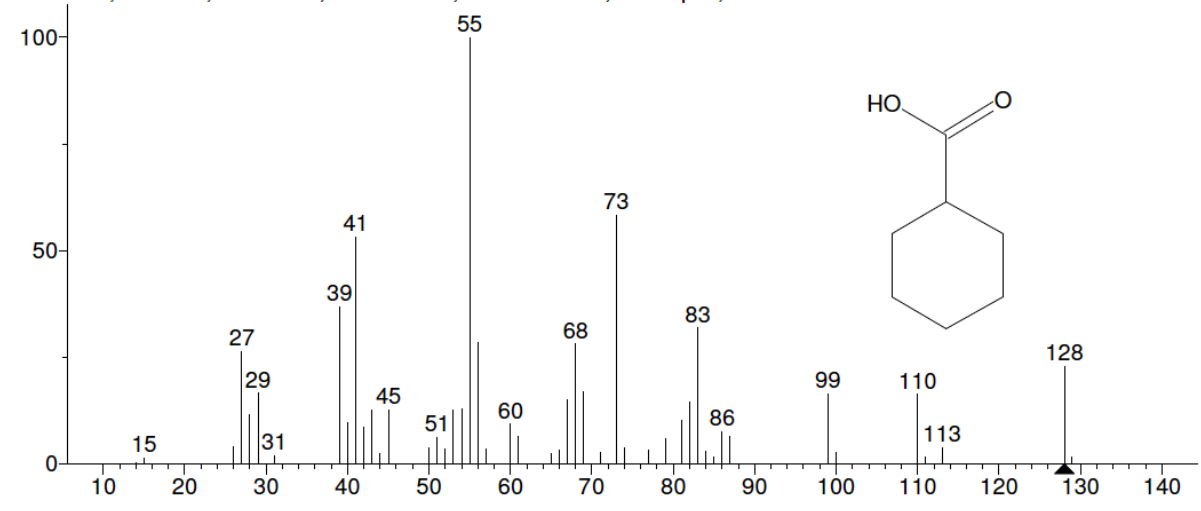


(Text File) Scan 2859 (15.433 min): BA6.d\data.ms

Name: Scan 2859 (15.433 min): BA6.d\data.ms
MW: N/A ID#: 3886 DB: Text File
Comment: 8FN
10 largest peaks:
55 999 | 73 784 | 41 584 | 83 546 | 39 400 | 68 391 | 56 348 | 128 336 | 45 235 | 99 230 |

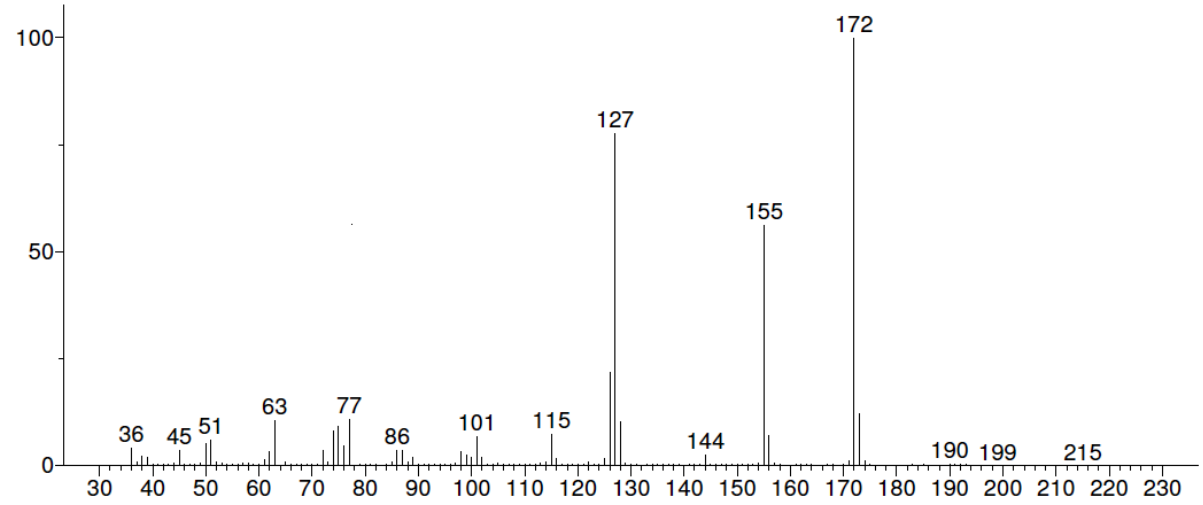
Database matching:

Hit 15 : Cyclohexanecarboxylic acid
C7H12O2; MF: 479; RMF: 945; Prob 1.13%; CAS: 98-89-5; Lib: replib; ID: 4546.



(replib) Cyclohexanecarboxylic acid

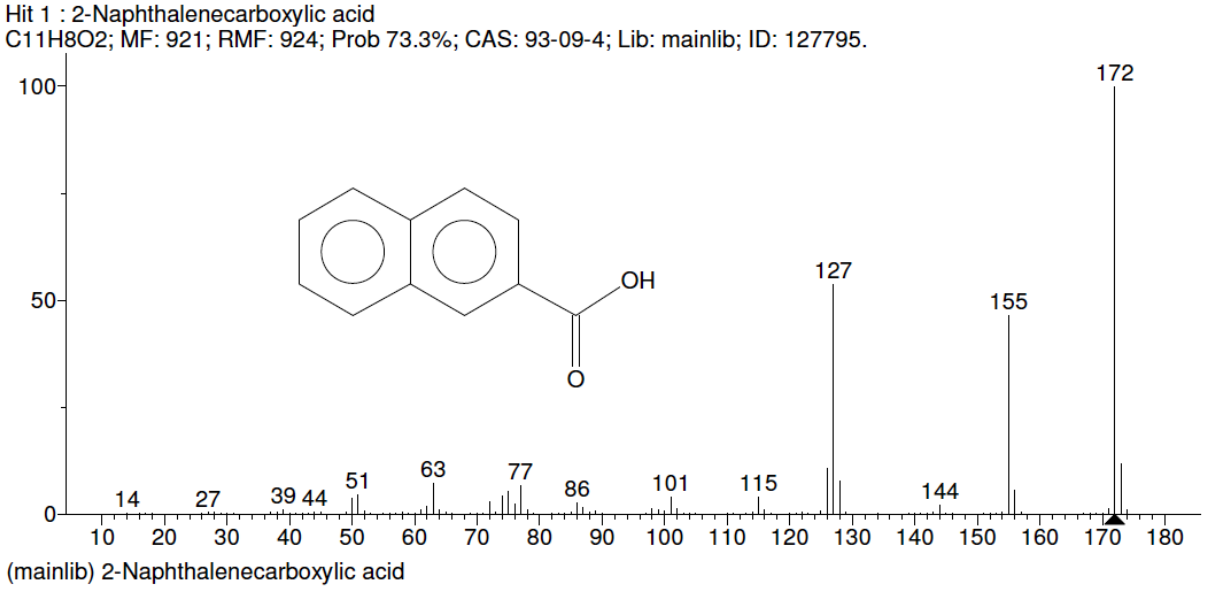
Figure S10. GC-MS data for reaction of Compound 10.



(Text File) Scan 4317 (23.441 min): 10FN.d\data.ms

Name: Scan 4317 (23.441 min): 10FN.d\data.ms
MW: N/A ID#: 3926 DB: Text File
Comment: 10FN
10 largest peaks:
172 999 | 127 776 | 155 562 | 126 217 | 173 120 | 77 109 | 63 107 | 128 101 | 75 91 | 74 80 |

Database matching:



(mainlib) 2-Naphthalenecarboxylic acid

References

1. X. Fu, Y. Liao, C. R. Glein, M. Jamison, K. Hayes, J. Zaporski and Z. Yang, *ACS Earth and Space Chemistry*, 2020, **4**, 722-729.
2. J. W. Johnson, E. H. Oelkers and H. C. Helgeson, *Computers & Geosciences*, 1992, **18**, 899-947.
3. D. A. Sverjensky, E. L. Shock and H. C. Helgeson, *Geochimica et Cosmochimica Acta*, 1997, **61**, 1359-1412.
4. E. L. Shock, D. C. Sassani, M. Willis and D. A. Sverjensky, *Geochimica et Cosmochimica Acta*, 1997, **61**, 907-950.