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Yields and molecular composition of gas-phase and secondary organic aerosol from the photooxidation of the volatile consumer product benzyl alcohol: formation of highly oxygenated and hydroxy nitro-aromatic compounds

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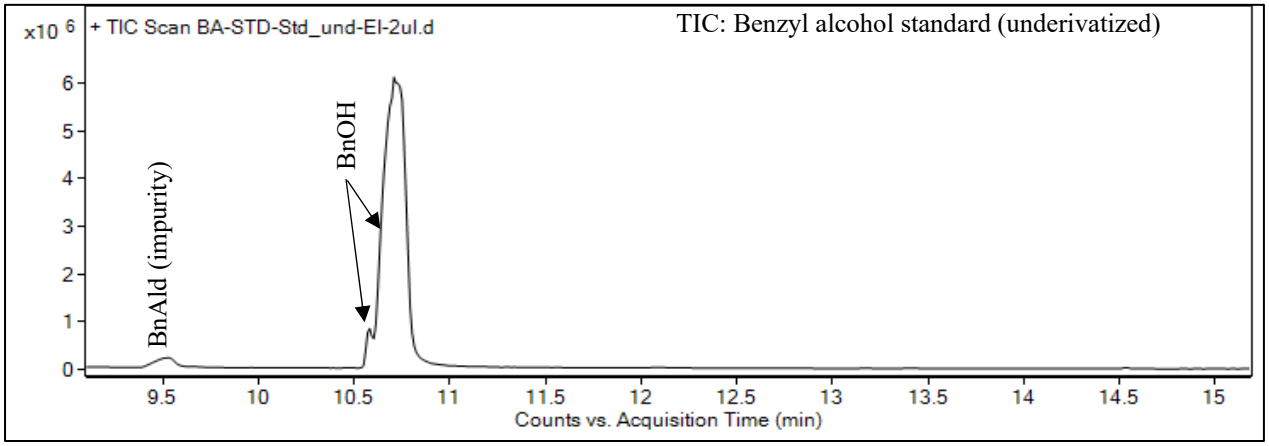
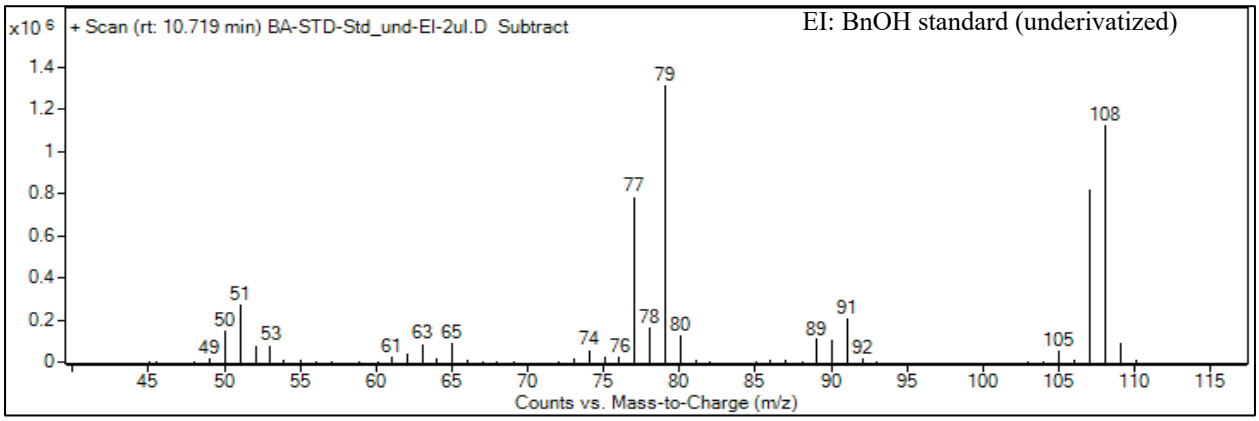
Section 1. Purity of benzyl alcohol

Benzyl alcohol (BnOH) was purchased at the highest purity commercially available (Sigma aldrich, anhydrous, 99.8%), and kept in the refrigerator when not in use. BnOH oxidizes slowly to one of the main toxic oxidation product benzaldehyde (BnAld) when exposed to air (Urakami et al., 2000). To a lesser extent, additional impurities were reported including benzoic acid, benzyl benzoate and dibenzyl ether (Ferri et al., 2006; Abend et al., 2004). In this study, the purity of BnOH was investigated by GC-MS analysis. A stock solution of BnOH at 345.86 μg/ml was prepared by dissolving 10 ul of standard BnOH in 30 ml acetonitrile. Two working solutions at 6.78 and 3.39 μg/ml, respectively, were prepared from the stock solution by diluting 10 and 5 μl in 0.5 ml methanol. The three solutions were analyzed using the same GC-MS parameters reported in the main manuscript for underivatized extracts (2 ul was injected from each solution), with an on-column injected mass of 692, 14 and 7 ng, respectively.

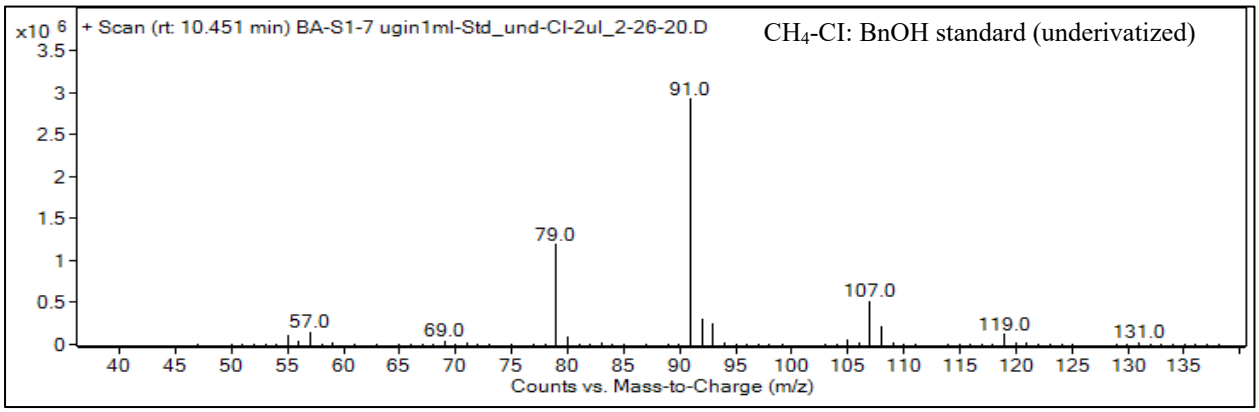
Two peaks associated with BnOH (isomers) were detected at 10.6 (small peak) and 10.7 (large peak) minutes, in addition to a small peak of BnAld eluted at 9.5 min (Figure S1). Figure S1 shows the TIC chromatogram obtained from analysing the stock solution (692 ng on column: highest amount injected). Figure S1 also shows the mass spectra associated with BnOH and BnAld in EI and CI mode. No benzoic acid or other impurities were observed when underivatized sample was analyzed. To check for benzoic acid (BnCOOH) impurity, BSTFA derivatization was conducted using the same procedure described in the main paper. Figure S2 shows chromatograms and mass spectra associated with BnOH and BnCOOH in EI and CI mode as BSTFA derivatives.



TIC: Benzyl alcohol standard (underivatized)



EI: BnOH standard (underivatized)



CH_4-CI: BnOH standard (underivatized)

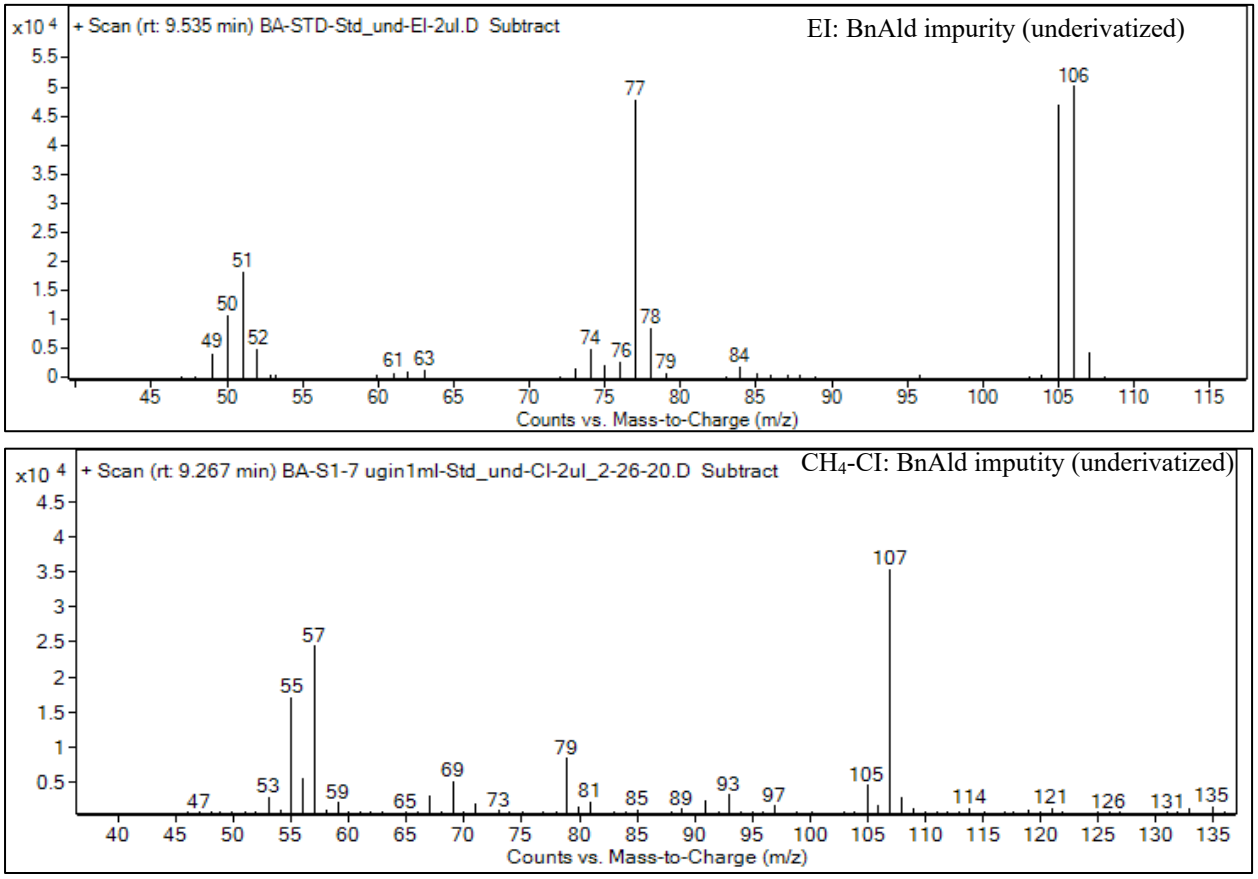
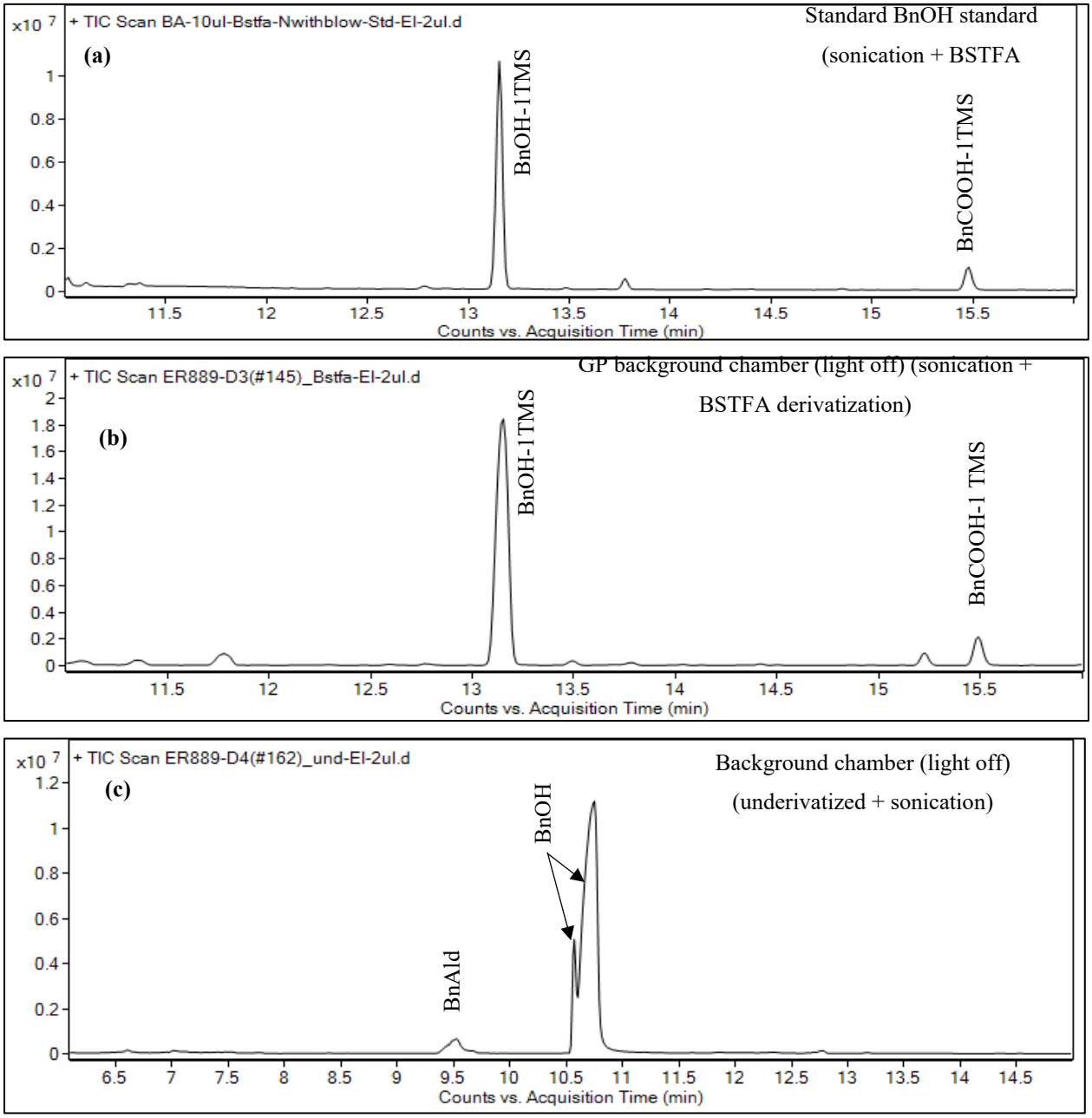
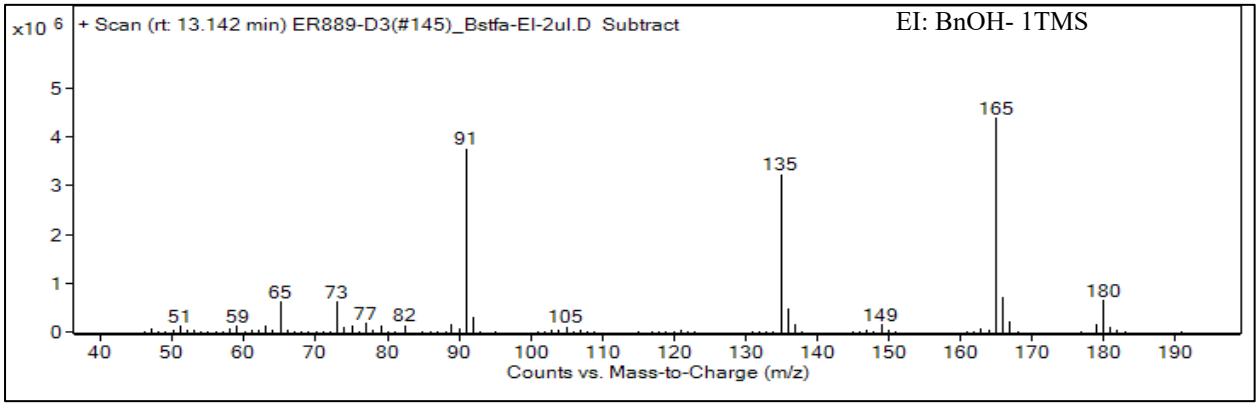


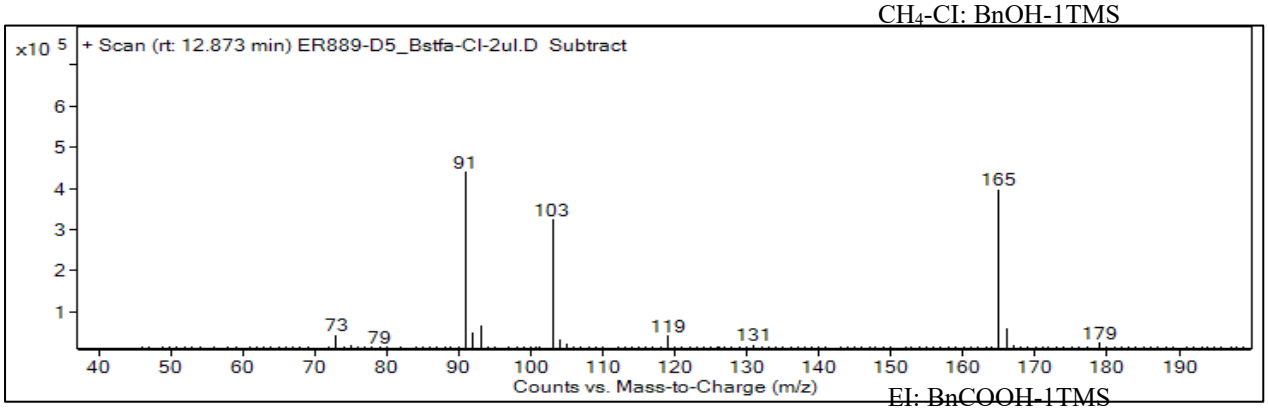
Figure S1. GC-MS chromatograms of benzyl alcohol standard, and EI and methane-CI mass spectra of benzylalcohol and benzaldehyde (underivatized).


x10 7
+ TIC Scan BA-10ul-Bstfa-Nwithblow-Std-EI-2ul.d
(a)
Standard BnOH standard
(sonication + BSTFA
BnOH-1TMS
BnCOOH-1TMS
Counts vs. Acquisition Time (min)
+ TIC Scan ER889-D3(#145)_Bstfa-EI-2ul.d
(b)
GP background chamber (light off) (sonication +
BSTFA derivatization)
BnOH-1TMS
BnCOOH-1 TMS
Counts vs. Acquisition Time (min)
+ TIC Scan ER889-D4(#162)_und-EI-2ul.d
(c)
Background chamber (light off)
(underivatized + sonication)
BnOH
BnAld
Counts vs. Acquisition Time (min)

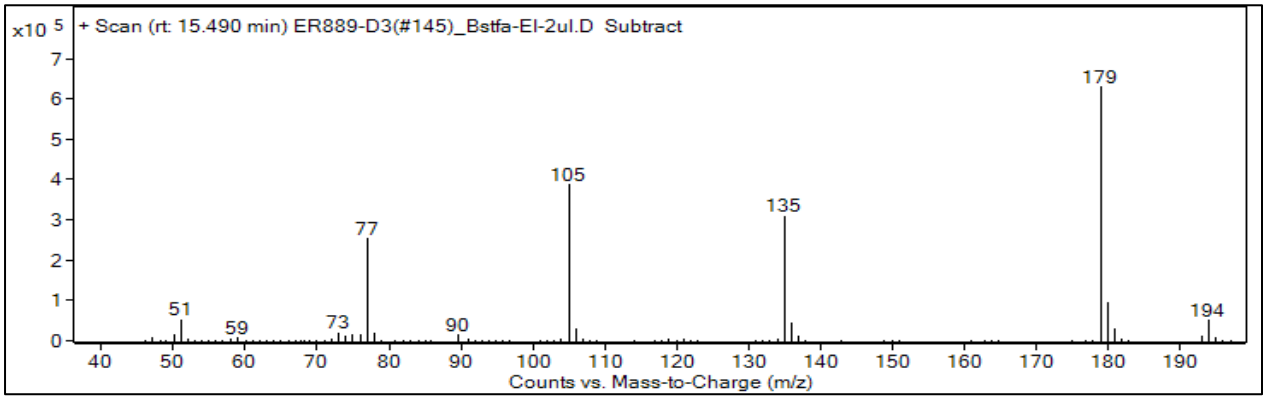
EI: BnOH- 1TMS



CH_4-CI: BnOH-1TMS



EI: BnCOOH-1TMS



CH_4-CI: BnCOOH-1TMS

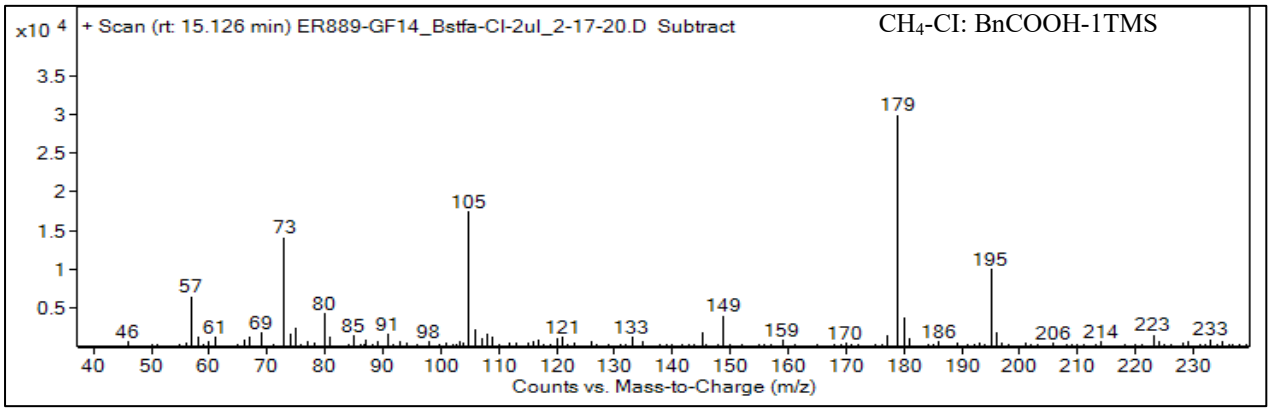


Figure S2. Artefacts associated with BnOH when exposed to chamber air, sonication, and/or BSTFA derivatization. (a) GC-MS chromatograms originated from BSTFA derivatization of stock solution. (b) GC-MS chromatogram originated from BSTFA derivatization of GP chamber background extract (light off). (c) GC-MS chromatogram originated from underivatized GP chamber background extract (light off). Mass spectra in EI and CH_4-CI associated with BnOH and benzoic acid (BnCOOH).

Section S2

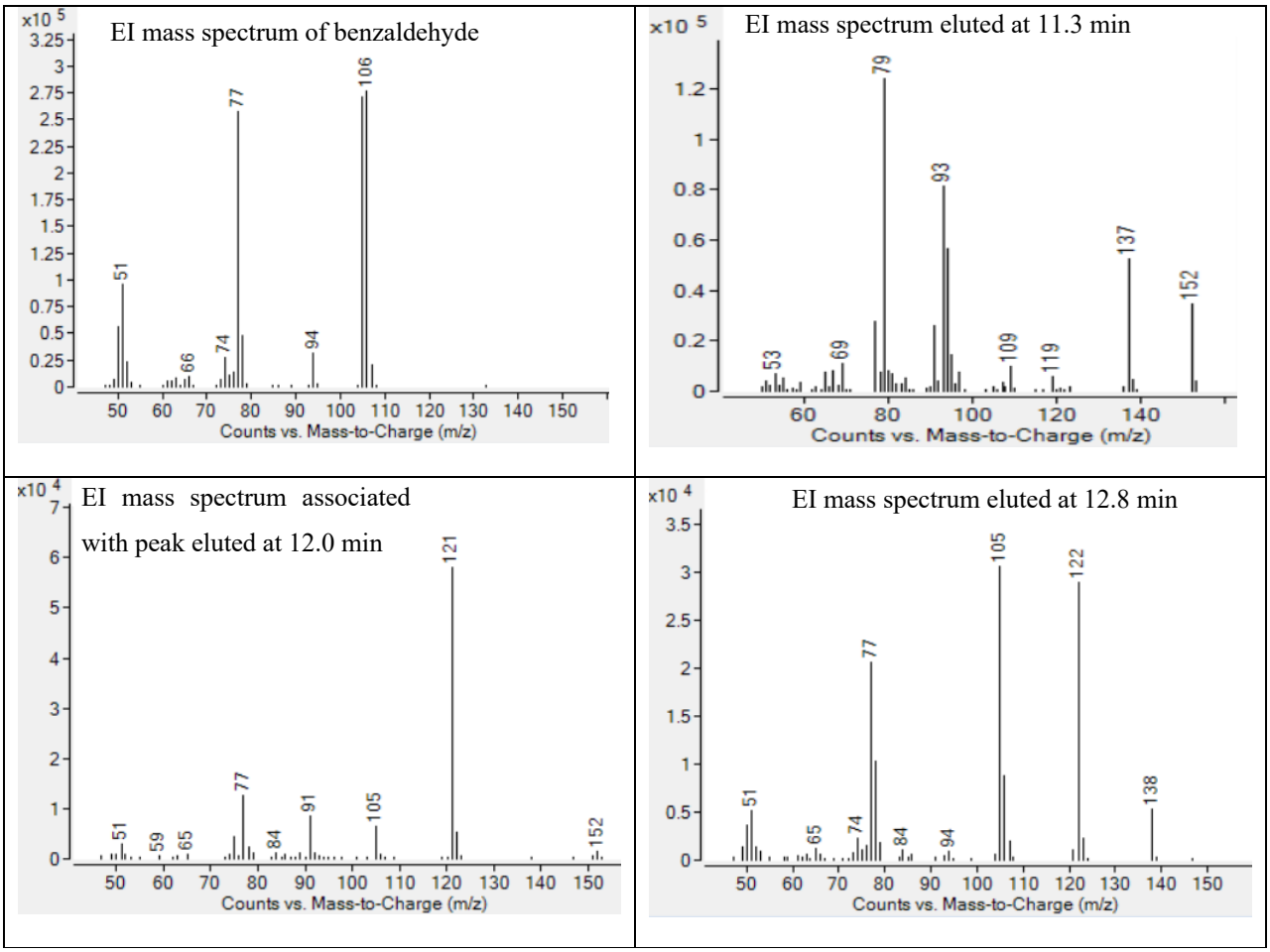


Figure S3. Selected EI mass spectra associated with peaks observed in the BnOH/H_2O_2 and/or BnOH/NOx underivatized denuder extracts eluting at retention time of 9.3 min (benzaldehyde), 11.3 min; 12.0 min; and 12.8 min.

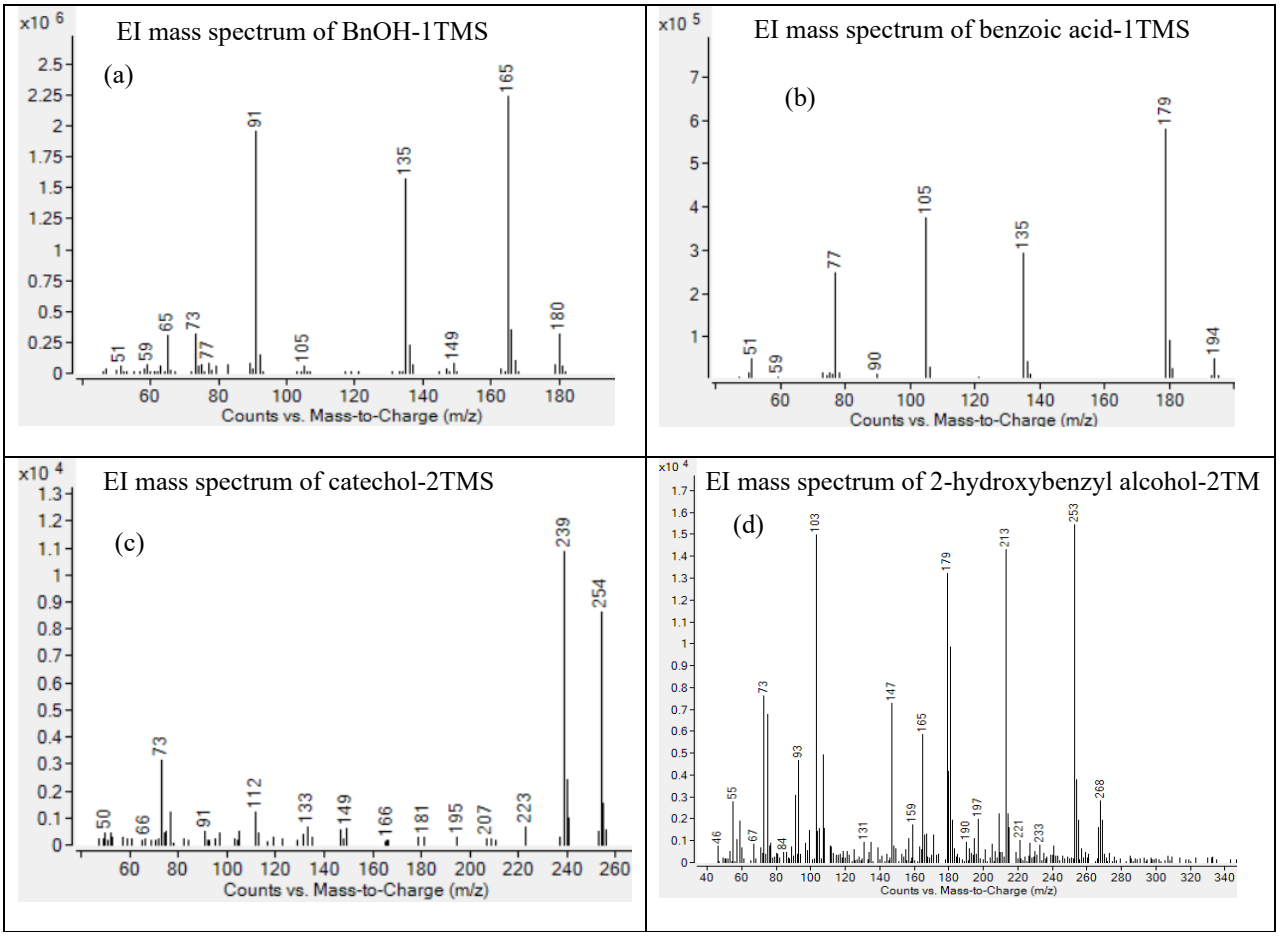


Figure S4. Selected EI mass spectra associated with peaks observed in the BnOH/H_2O_2 and/or BnOH/NOx BSTFA derivatized denuder extracts.

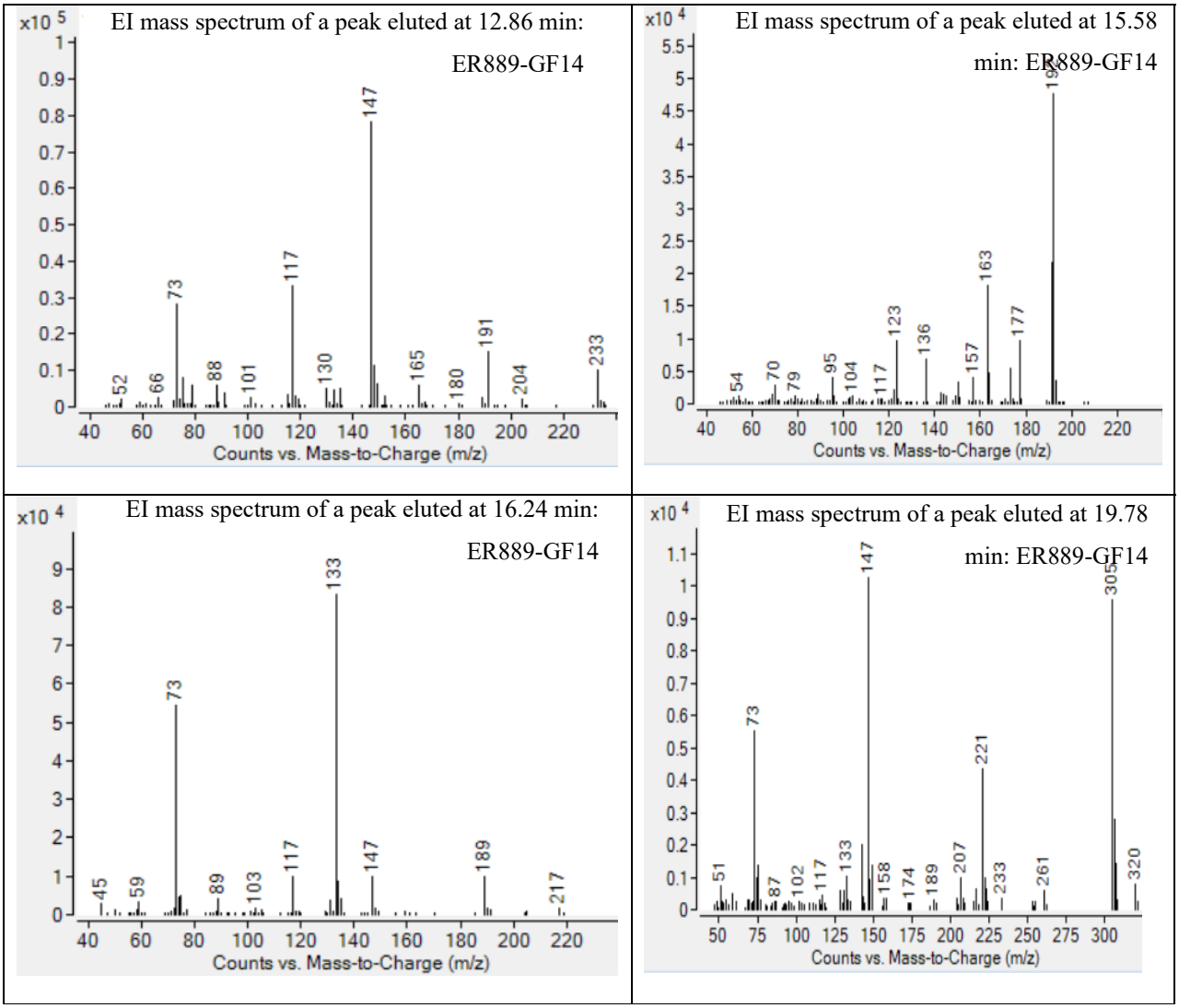
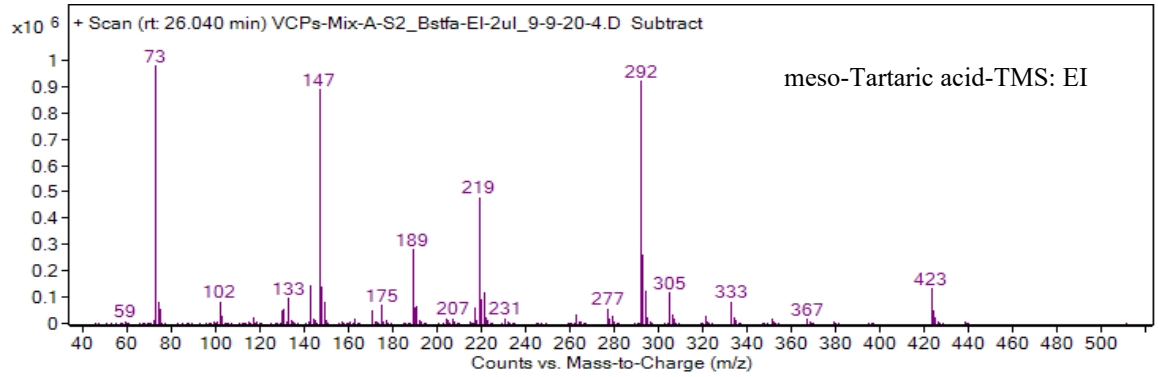
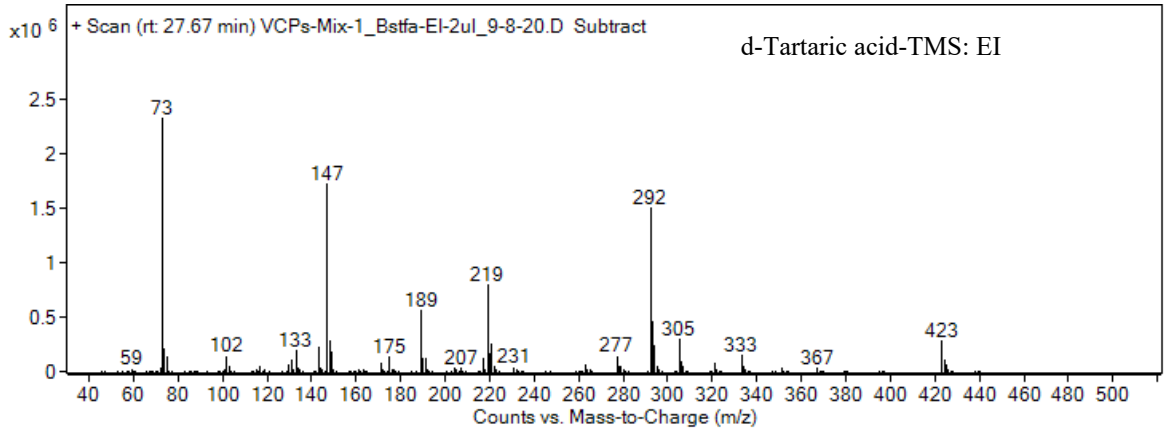
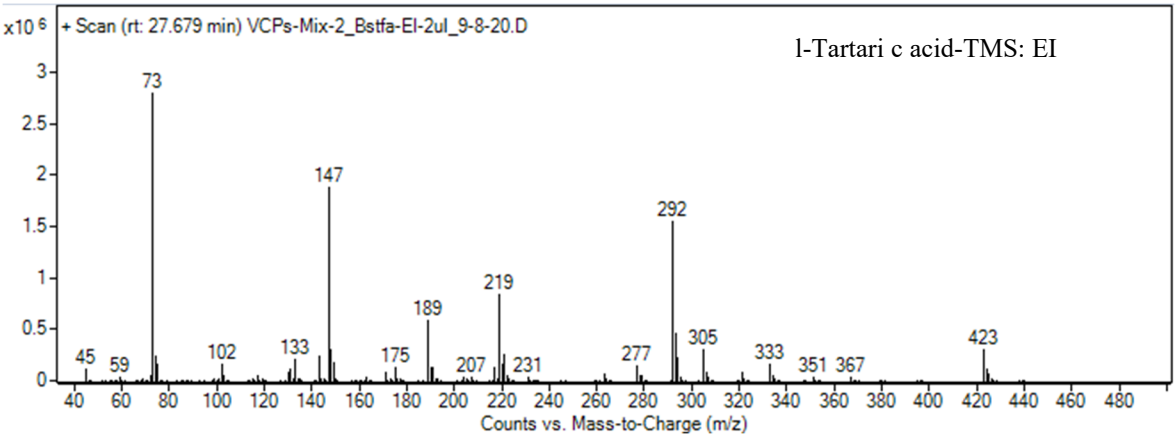


Figure S5. Selected EI mass spectra associated with peaks observed in the BnOH/H_2O_2 and/or BnOH/NOx BSTFA derivatized filter extracts.


x10 6
+ Scan (rt: 26.040 min) VCPs-Mix-A-S2_Bstfa-EI-2ul_9-9-20-4.D Subtract
meso-Tartaric acid-TMS: EI
73
147
292
219
189
59
102
133
175
207
231
277
305
333
367
423
Counts vs. Mass-to-Charge (m/z)


x10 6
+ Scan (rt: 27.67 min) VCPs-Mix-1_Bstfa-EI-2ul_9-8-20.D Subtract
d-Tartaric acid-TMS: EI
73
147
292
219
189
59
102
133
175
207
231
277
305
333
367
423
Counts vs. Mass-to-Charge (m/z)


x10 6
+ Scan (rt: 27.679 min) VCPs-Mix-2_Bstfa-EI-2ul_9-8-20.D
l-Tartari c acid-TMS: EI
73
147
292
219
189
45
59
102
133
175
207
231
277
305
333
351
367
423
Counts vs. Mass-to-Charge (m/z)

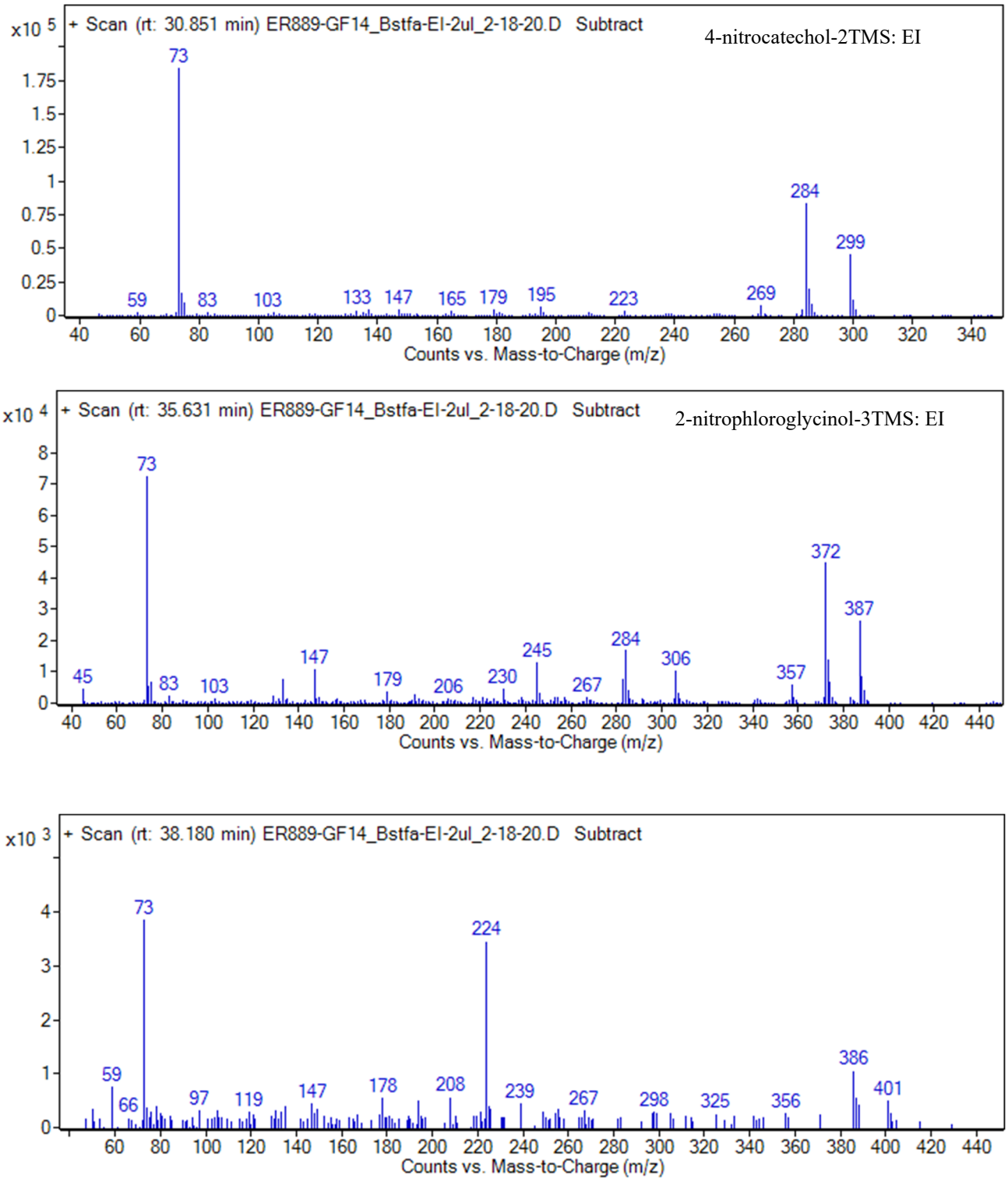
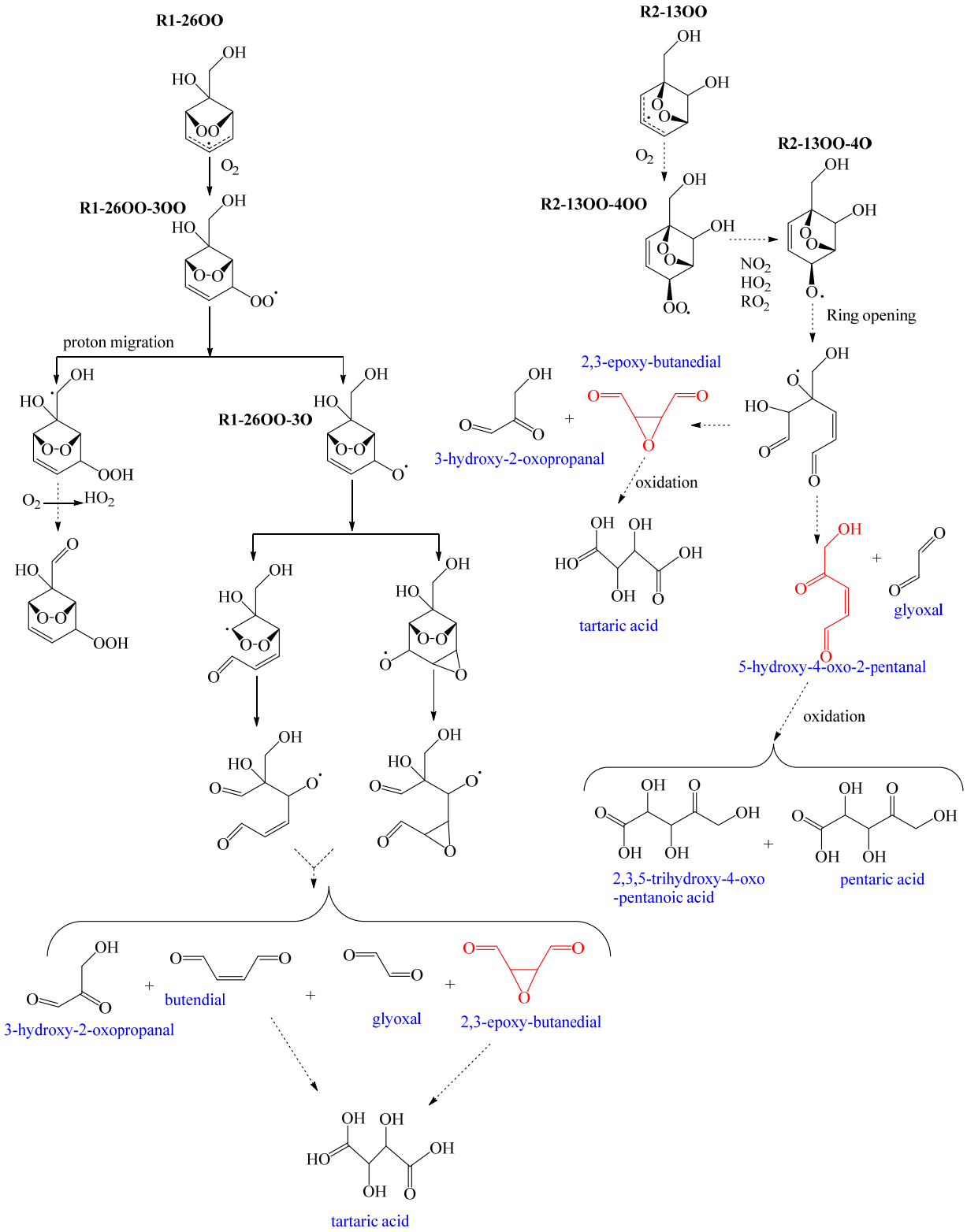


Figure S6. EI mass spectra associated with BSTFA derivatives of meso-tartaric acid, *L*-tartaric acid, d-tartaric acid standards, 4-nitrocatechol, 2-nitrophloroglucinol (isomer), and a peak eluted at 38.18 min.



Scheme S1. Proposed reaction pathways leading to some intermediate products from the reaction of R1-23OO and R2-16OO.

References (SI)

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