Supporting Information for

"Degradation of Organic UV filters in Chlorinated Seawater Swimming Pools: Transformation Pathways and Bromoform Formation"

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This document contains:

- 13 pages (S1–S13)
- 3 tables (S1, S2, S3)
- 1 figure (S1)

Table S1. UV Filter Retention time (RT) and MS/MS operating conditions

Analyte	RT (min)	Parent Ion $[M+H]^+$	Cone Voltage (V)	Fixed CE* Value (V)	Fragments
DIOXY	3.65	245.1	25	6	151.0397, 121.0293
OXY	3.83	229.1	30	7	105.0341, 151.0394
OC	4.08	362.2	30	1	232.0764, 250.0872
AVO	4.26	311.2	25	8	135.0443, 161.0965
OMC	4.29	291.2	15	1	161.0601, 179.0708
BD-10 (surrogate)	3.85	193.1	20	8	82.0703, 110.0650

*CE: Collision Energy

Table S2. LLE-LC-MSMS method performance characteristics for the analysis of UV filters

Analyte	Recovery (%) (n=3)	Precision (%) (repeatability) (n=3)	Linearity (r^2)	Range (ng/L)	LOD (ng/L)	LOQ (ng/L)
BP-3	93	13	0.997	5-1000	1	5
BP-8	89	16	0.992	10-1000	8	20
Avobenzone	97	8	0.998	15-1000	5	15
OMC	102	11	0.998	25-1000	5	15
OC	117	14	0.995	20-1000	5	15
BP-d10	94	10	0.991	10-1000	10	30

Table S3. Physicochemical parameters, bromide concentration, free and combined chlorine

Pool	Temperature (°C)	pH	[Br-] (mg L^{-1})	Conductivity (mS cm^{-1})	Free Chlorine (mg L^{-1})	Combined chlorine (mg L^{-1})
Adults' Pool	26.8	8.08	73.2	56.2	1.7	0.6
Children's Pool	29.6	8.04	68.1	55.7	3.1	1.8

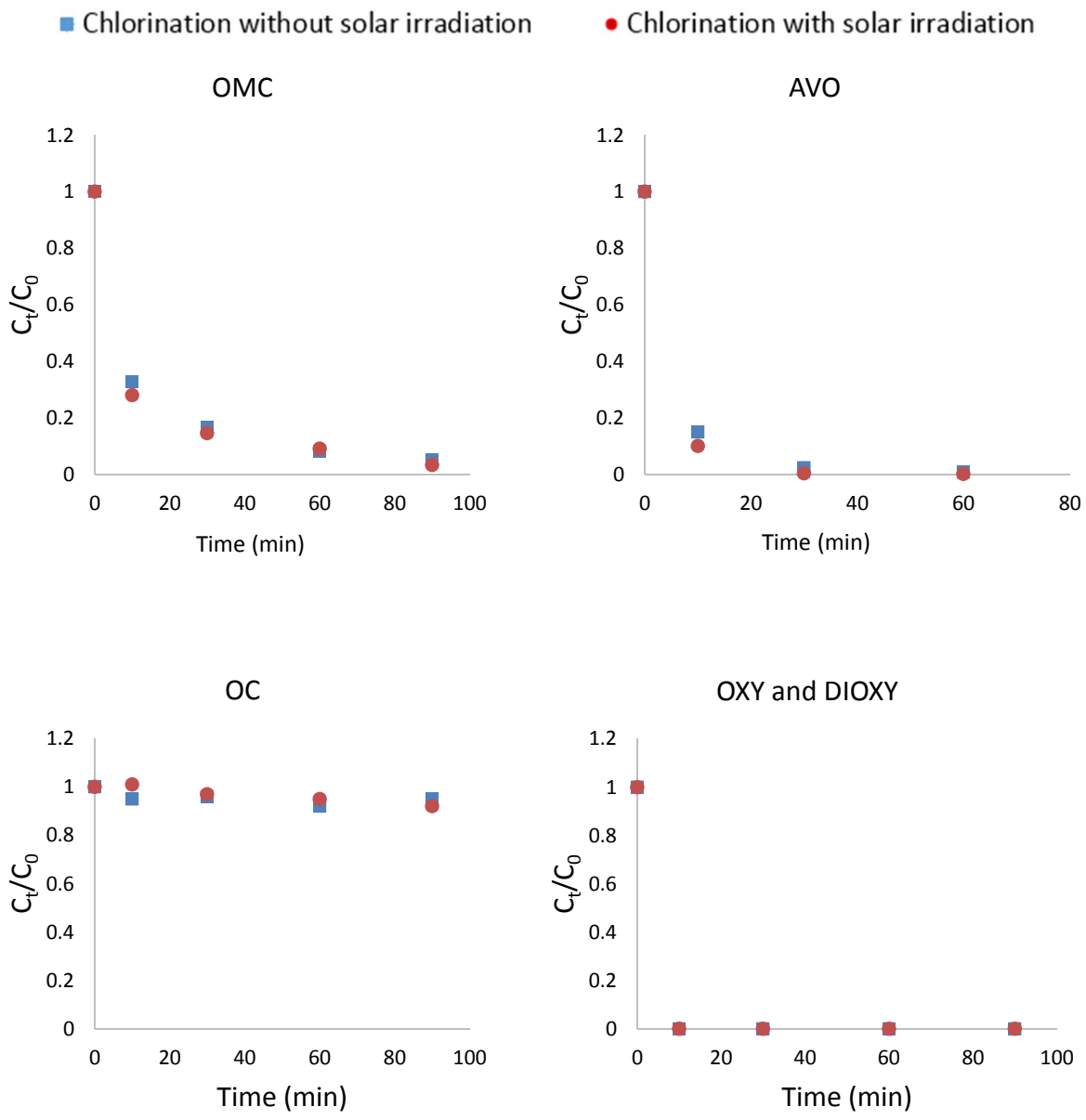


Figure S1. Disappearance of UV filters in chlorination reactions with solar irradiation (red points) and without solar irradiation (blue points). Chlorination reactions were conducted according to the protocol described in the manuscript at a ratio of UV filter:chlorine concentration of 1:25.

SI-1. Operating Conditions for UHPLC-ESI-MS Analysis

Separation of analytes were achieved using a CORTECS UPLC column (Waters Acquity C18 2.1×100 mm, 1.6 μM) at 40 °C. The mobile phase consisted of A: water and B: methanol (ULC/MS grade, Bisolve). Both solvents A and B contained 5 mM ammonium formate. Elution was performed at a flow rate of 0.4 ml min^{-1} with a gradient starting at 15% of B and increasing to reach 100% within 6 min and held for 1 min. The sample injection volume was 5 μL. The ESI source contained two individual orthogonal sprays. One spray was for the column eluent while the other was for the internal standard (lockmass). During each chromatographic run, leucine enkephalin (2 mg L^{-1}, $C_{28}H_{37}N_5O_7$, MW 555.27, Waters Q-ToF product) was used for lock-mass correction to obtain accurate masses for each organic component eluting from the column. A solution of sodium formate (HCOONa, Waters Q-ToF product) was infused daily in the ESI source to calibrate the instrument. Optimum ESI conditions were found using a 2.5 kV capillary voltage, 450 °C desolvation temperature, 120 °C source temperature, 20 L h^{-1} cone gas flow rate and 800 L h^{-1} desolvation gas flow rate. The optimum sample cone voltage for each analyte is described in Table S1. The ESI source has been optimized directly with the samples. These parameters allowed increasing the signal to noise ratio maintaining soft ionization technique. Data were collected from 50 to 600 Da in the positive and negative ionization modes. The mass spectrometer was used in its resolution mode. Compounds responding in positive mode were detected as their protonated molecules ($[M + H]^+$) or sodium adducts ($[M + Na]^+$) or potassium adducts ($[M + K]^+$) while compounds responding in the negative mode were detected as deprotonated molecules ($[M - H]^-$).

SI-2. Operating Conditions for GC-ECD Analysis

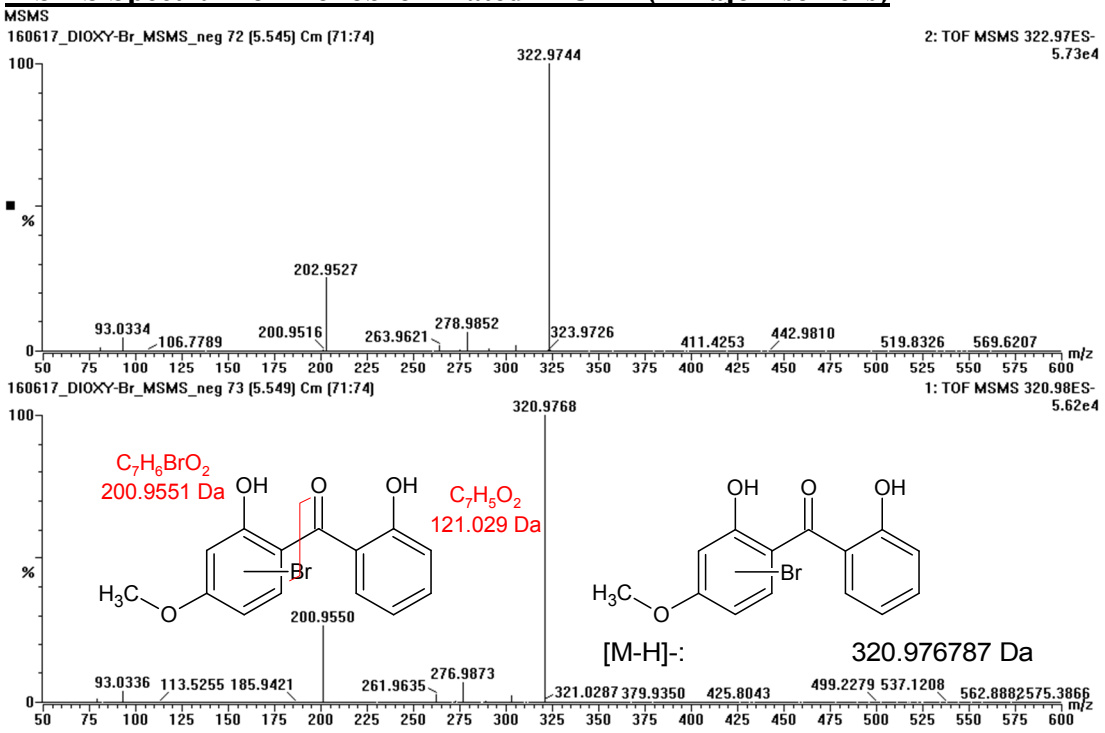
Target analytes were separated on a capillary column DB5-ms (30 m × 0.25 mm × 1 μm). Helium 5.0 was used as a carrier gas at a programmed flow of 1 ml min^{-1} and nitrogen as make-up gas at a flow of 30 ml min^{-1}. Injection volume was 1 μL and injector temperature was 200 °C. Detector temperature was adjusted to 290 °C. The GC oven temperature started at 35 °C, held for 22 min, increased to 145 °C at 20°C min^{-1} and held for 2 min, then increased to 225 °C at 20 °C min^{-1} and held for 15 min, finally temperature increased to 260 °C at 10 °C min^{-1} and held for 2 min.

SI-3. Operating Conditions for GC-MS Analysis

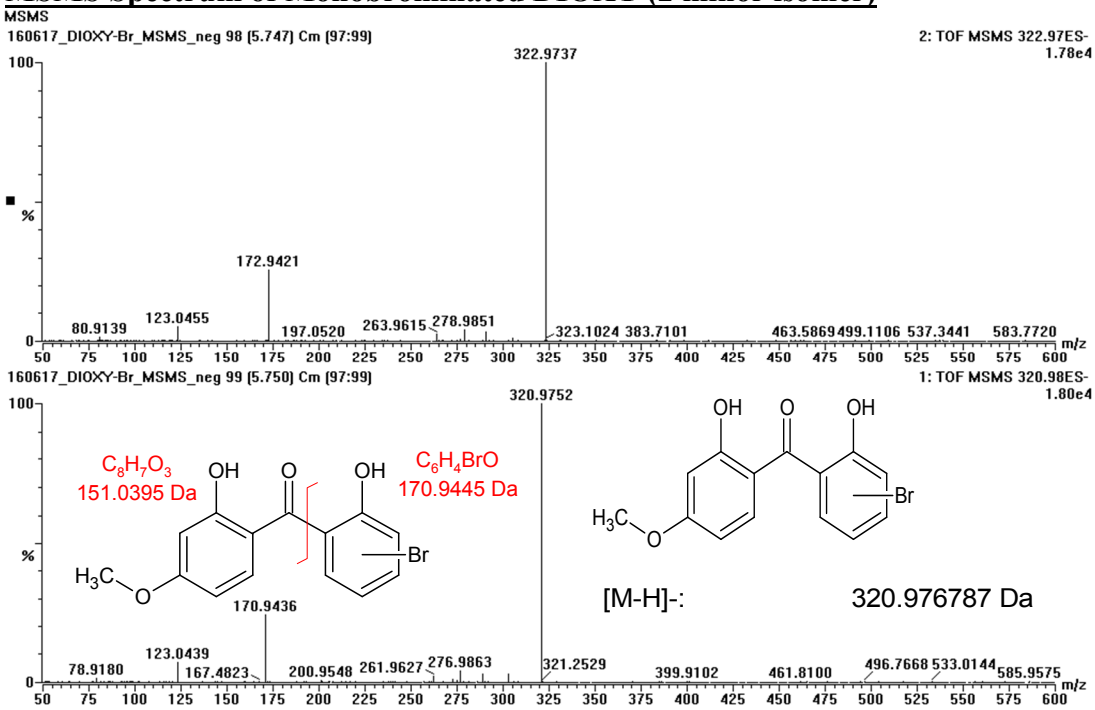
The chromatographic separation was accomplished on a TR-5MS capillary column (Thermo Electron, 30 m × 0.25 mm × 0.25 μm). Samples (2 μL) were injected at 280 °C in splitless mode. Helium was used as a carrier gas at a flow of 1 mL min^{-1}. Oven program was adjusted according to U.S.EPA Method 551.1 (1995). Data was recorded in the full scan mode in the mass range m/z 50–600.

SI-4. Mass Spectra of DIOXY Transformation Products

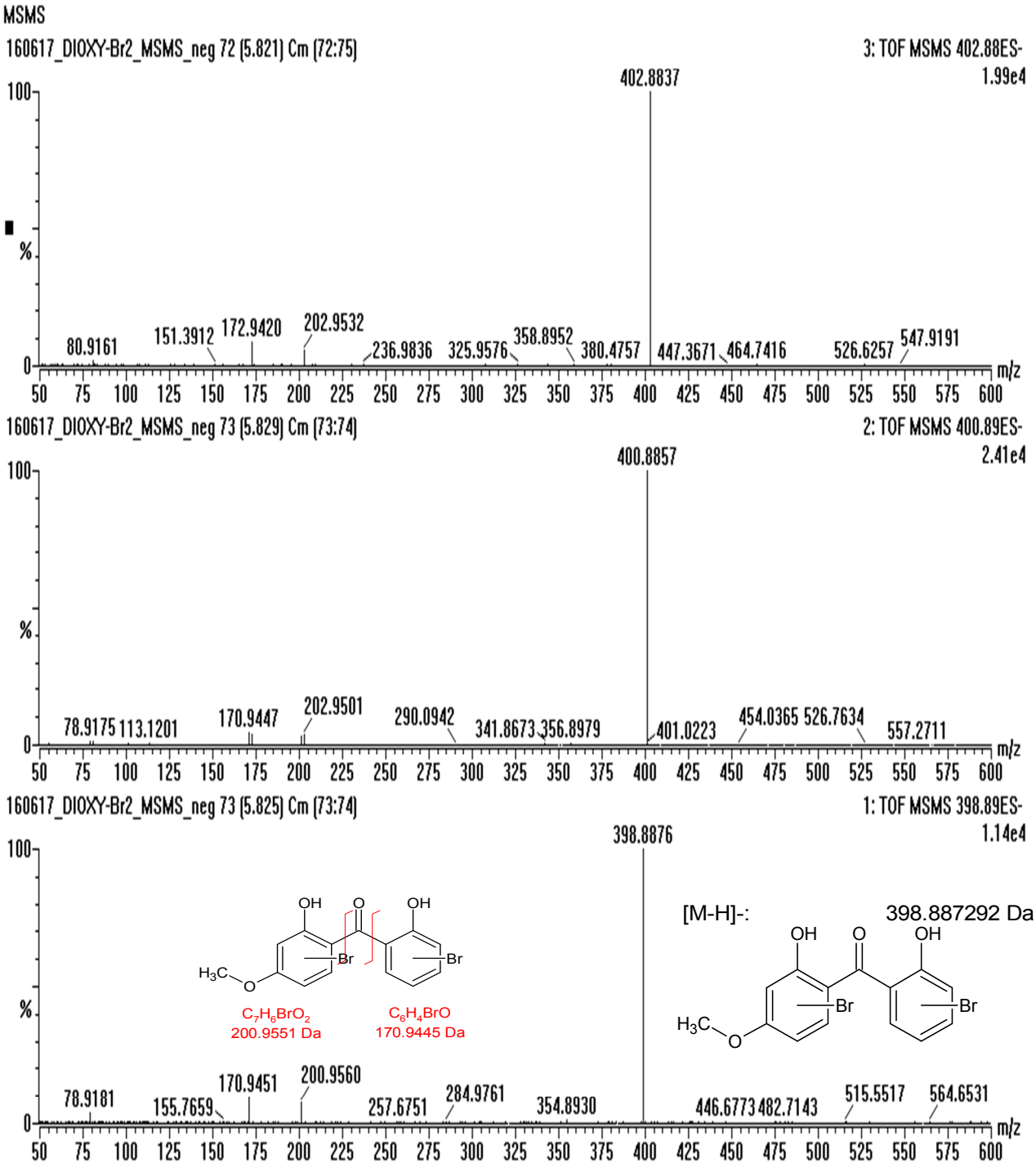
MSMS Spectrum of Monobrominated DIOXY (2 major isomers)



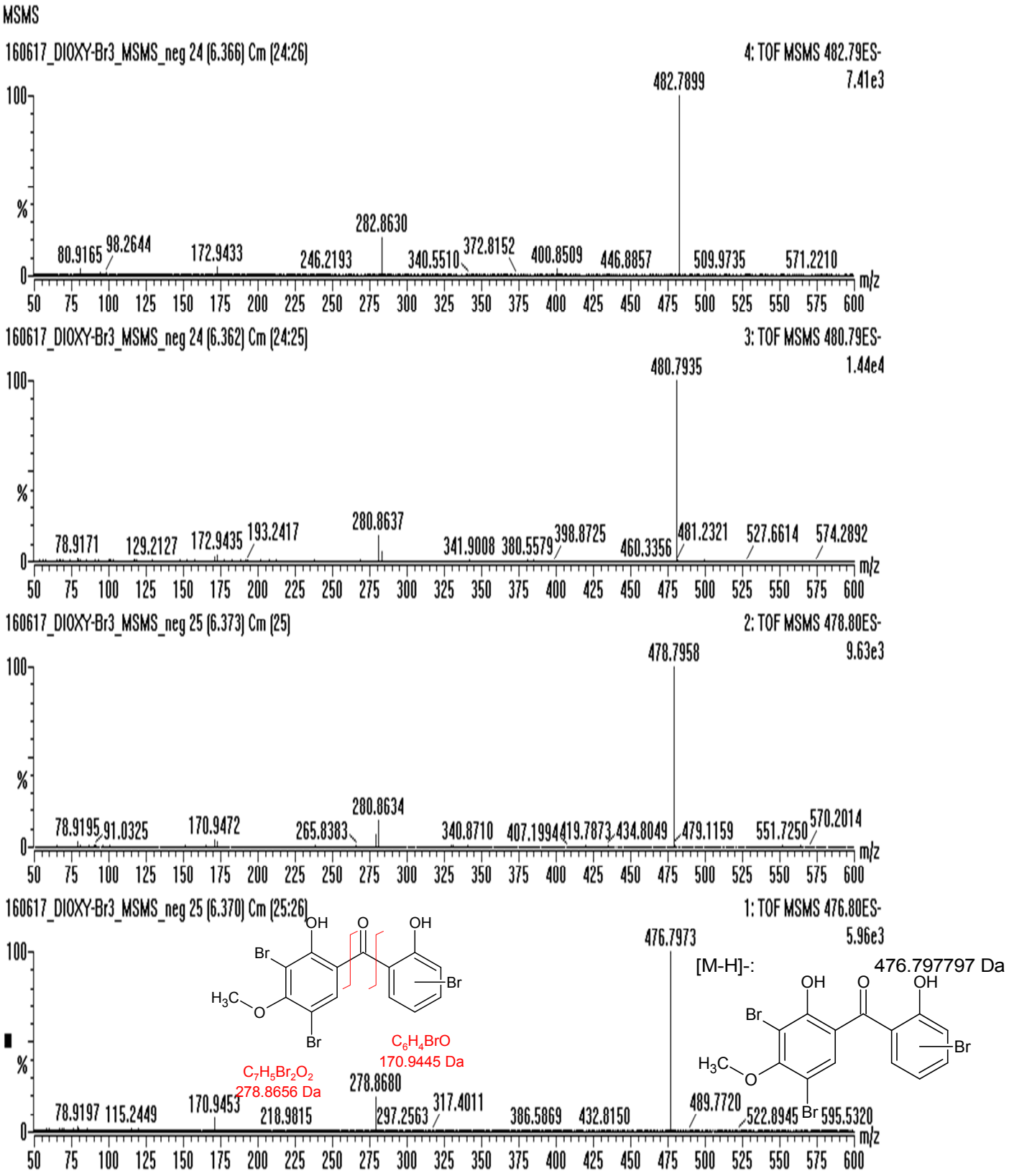
MSMS Spectrum of Monobrominated DIOXY (2 minor isomer)



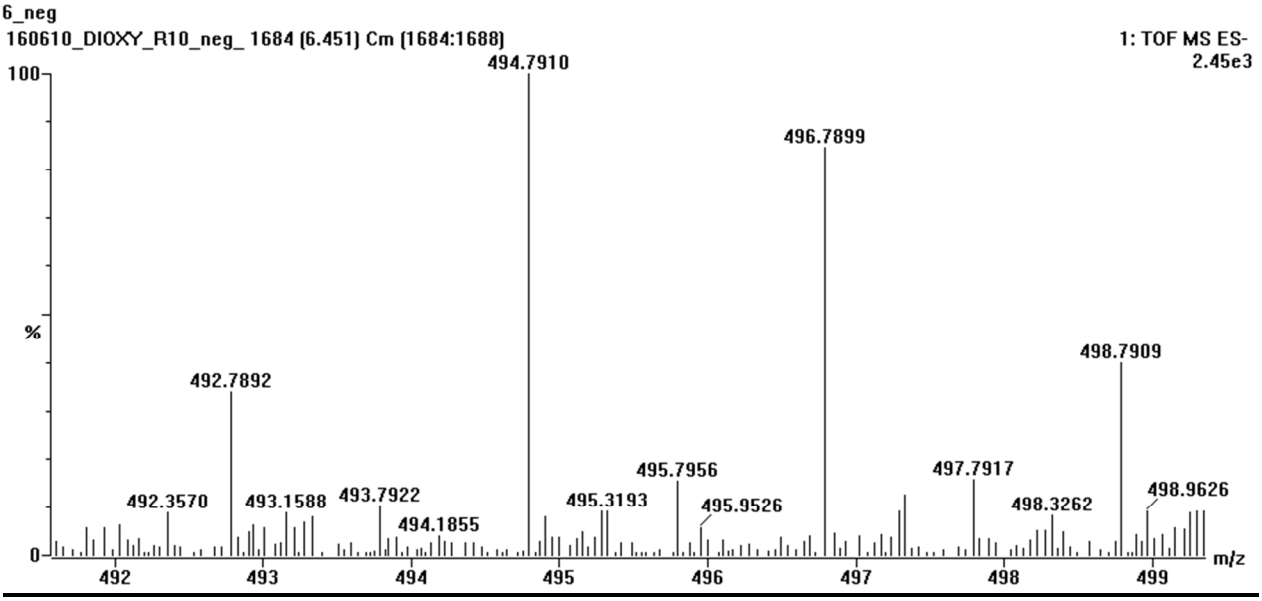
MSMS Spectrum of dibrominated DIOXY



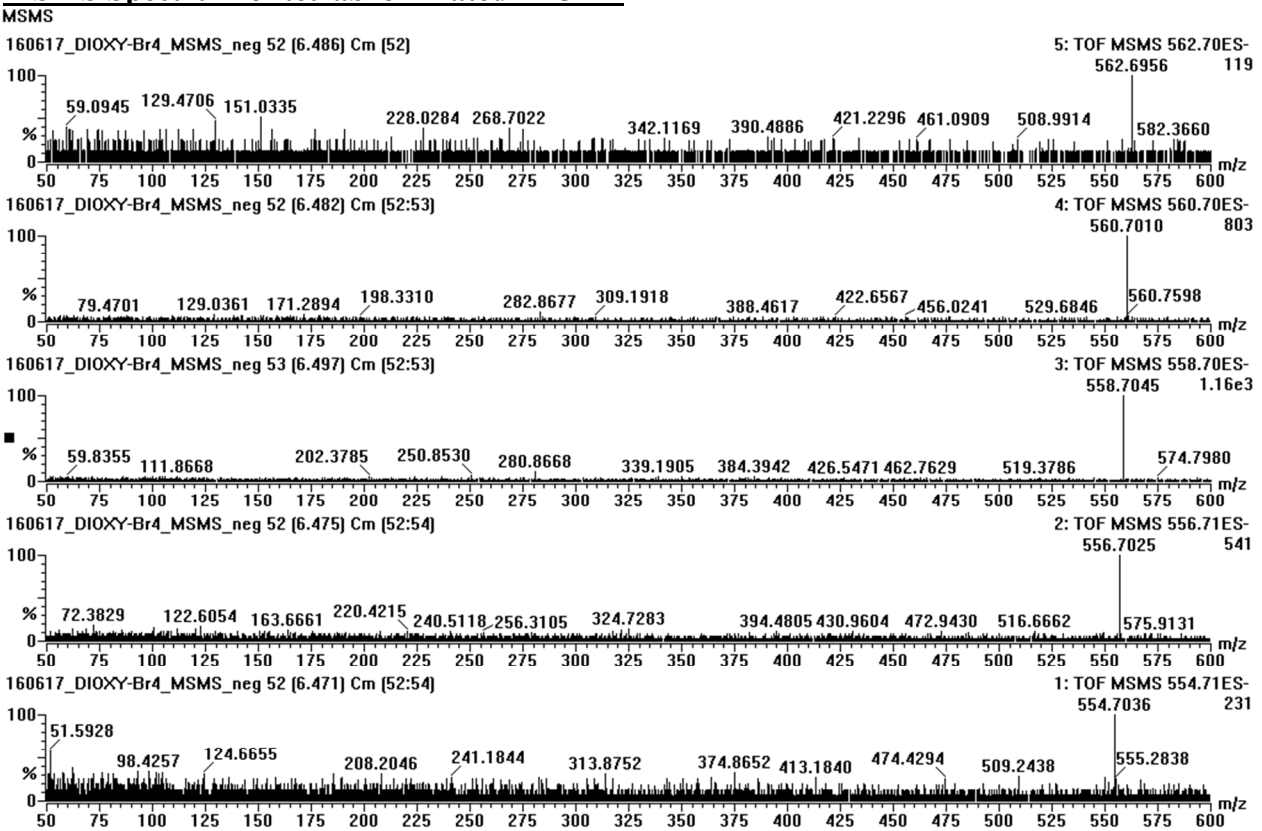
MSMS Spectrum of tribrominated DIOXY



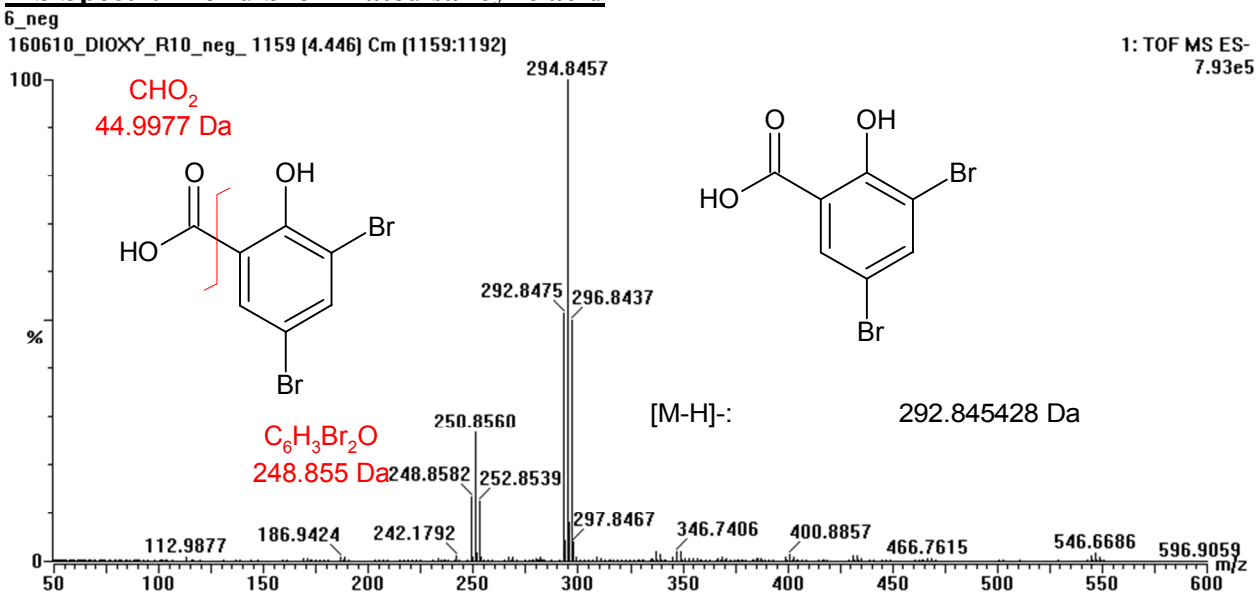
MS Spectrum of tribrominated oxidized DIOXY



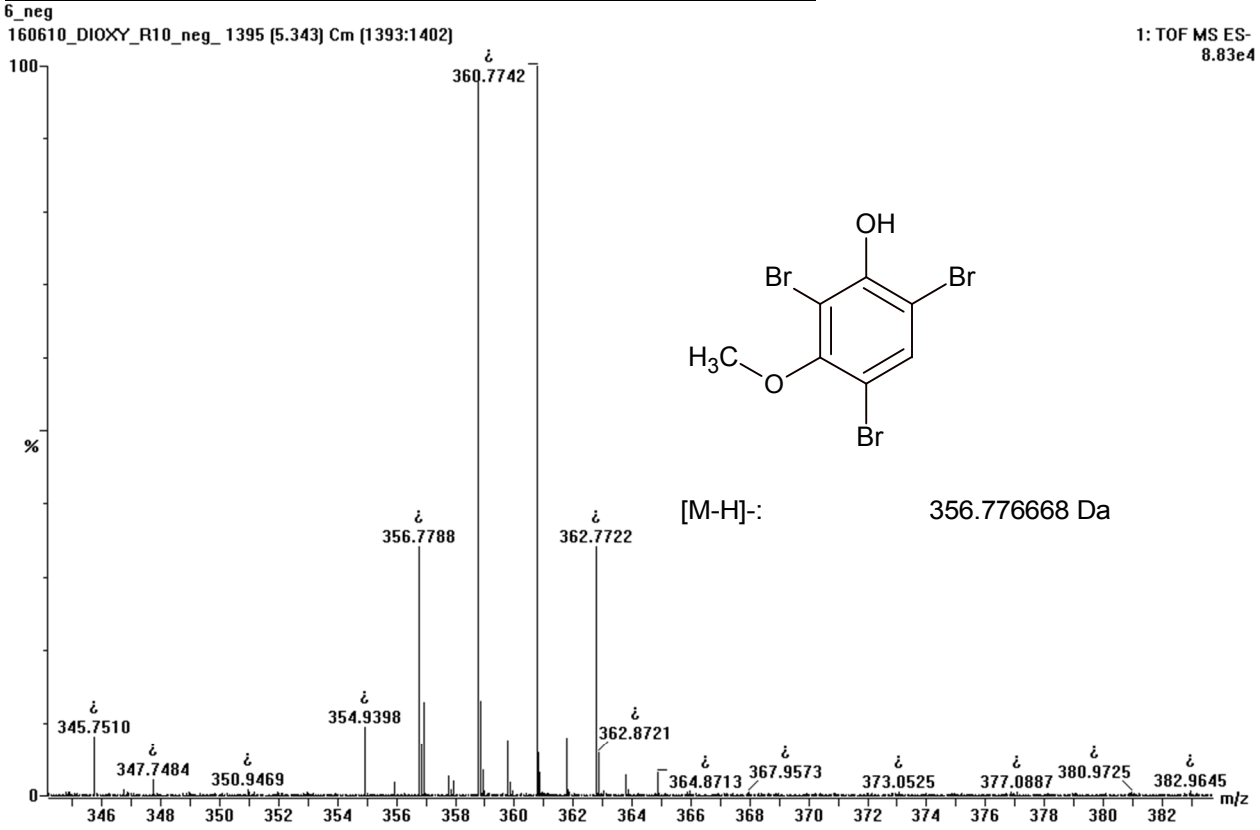
MSMS Spectrum of tetrabrominated DIOXY



MS Spectrum of dibrominated salicylic acid

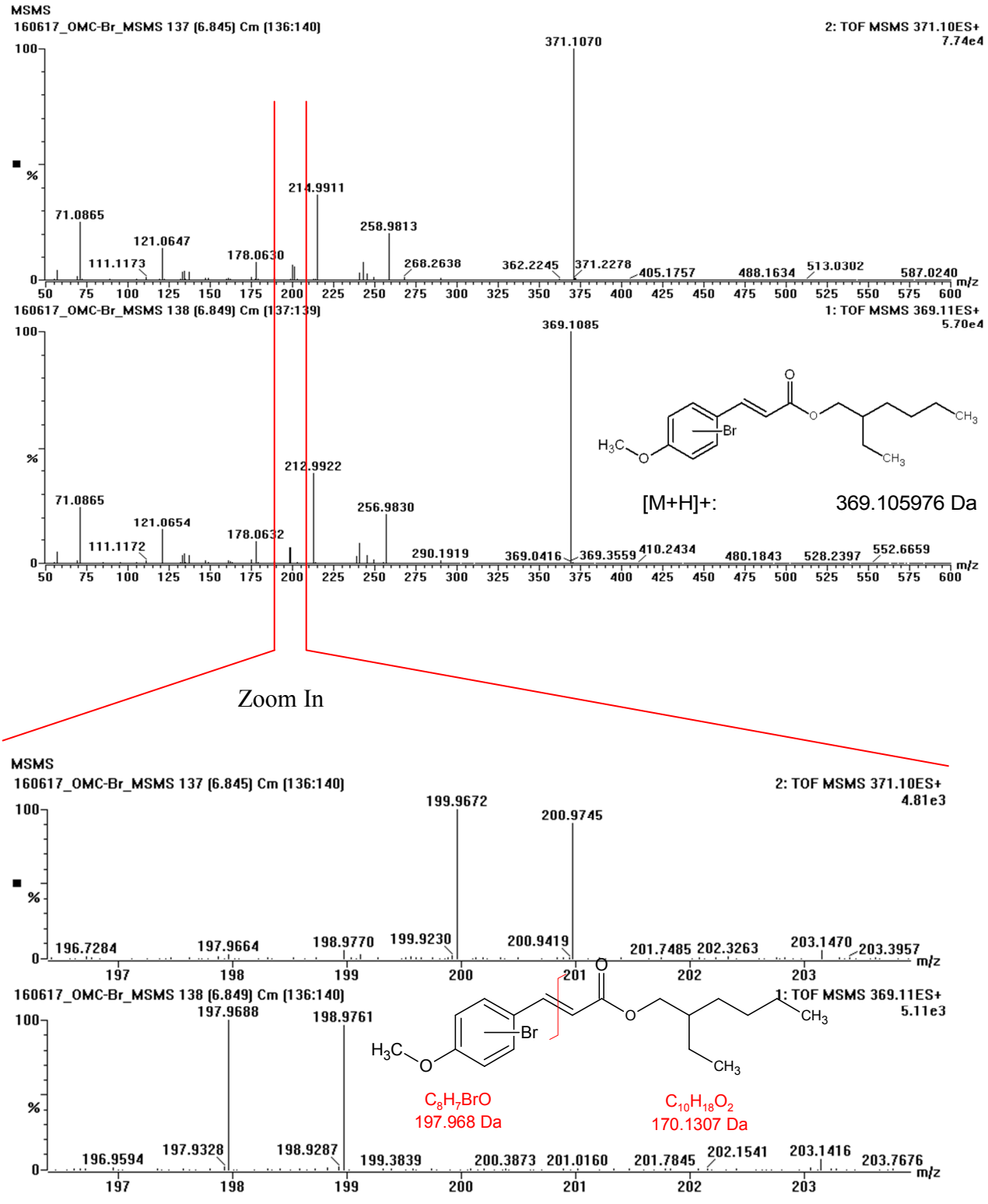


MS Spectrum of 2,4,6-Tribromo-3-methoxyphenol (TBMP)

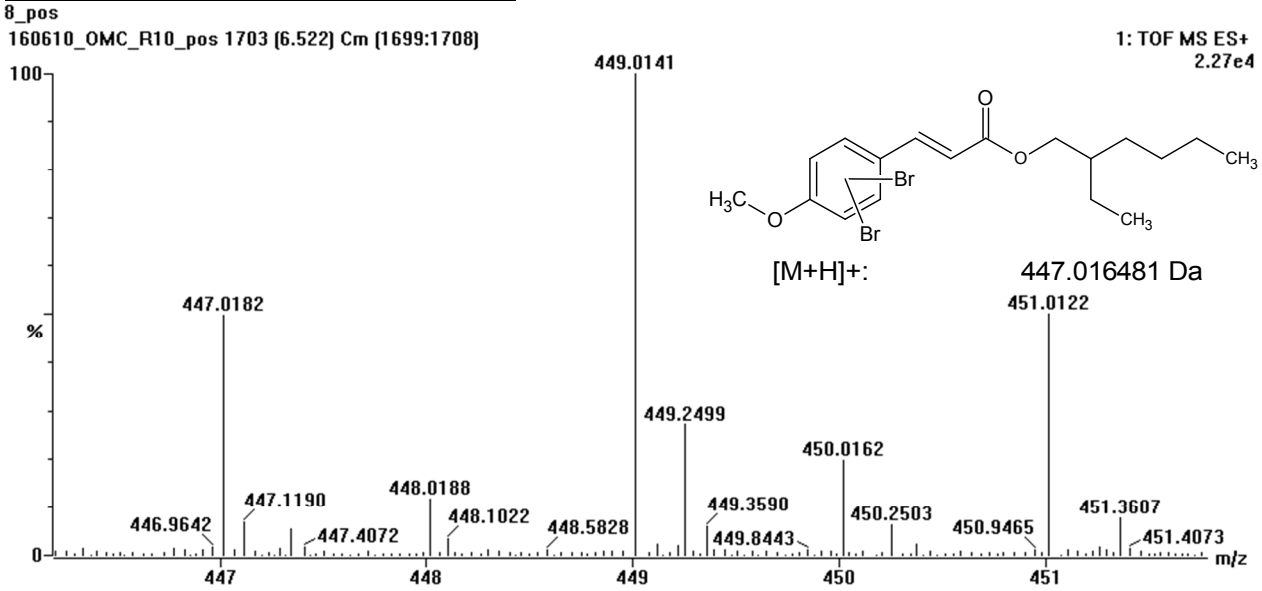


SI-5. Mass Spectra of OMC Transformation Products

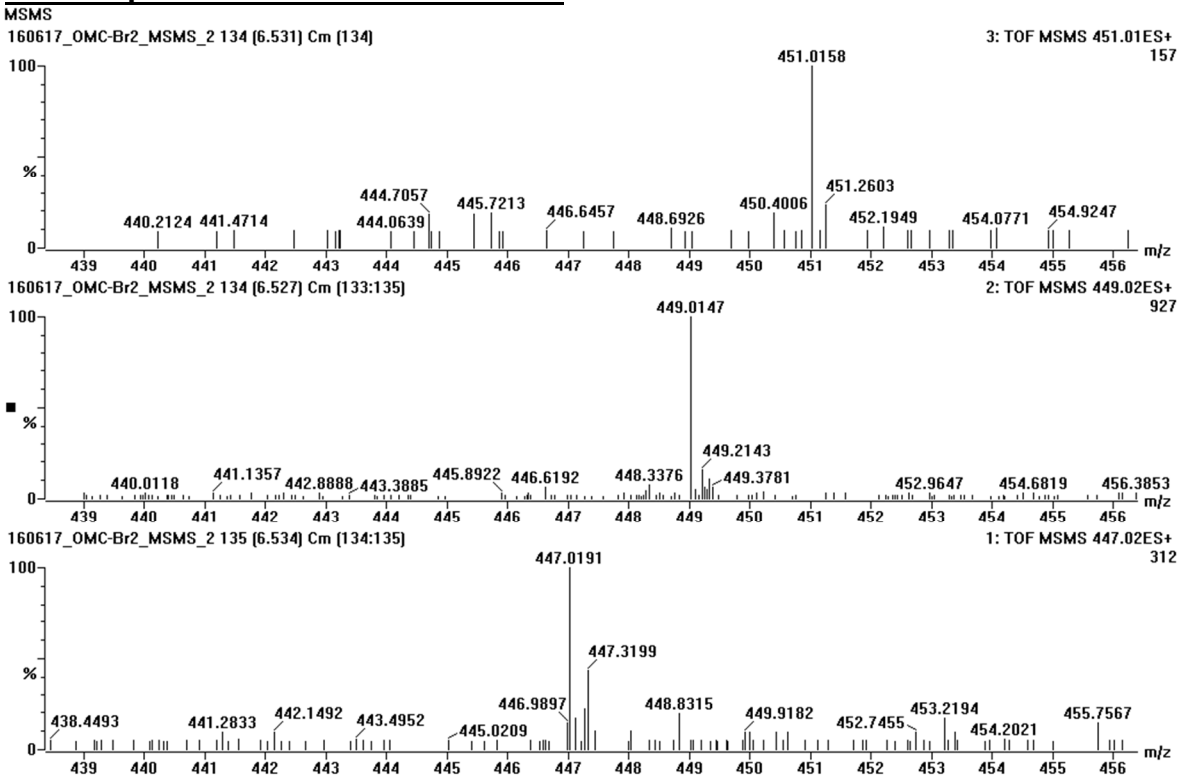
MSMS Spectrum of Monobrominated OMC



MS Spectrum of Dibrominated OMC

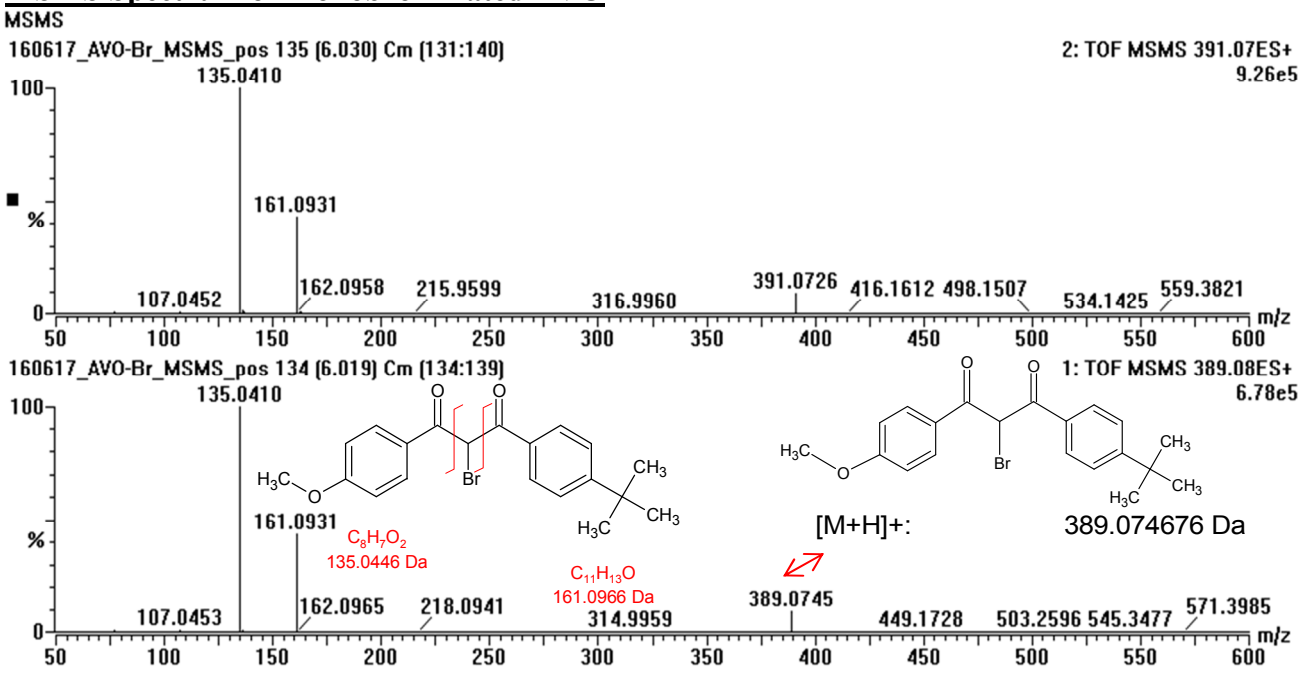


MSMS Spectrum of Dibrominated OMC



SI-5. Mass Spectra of AVO Transformation Products

MSMS Spectrum of Monobrominated AVO



MS Spectrum of Dibrominated AVO