

Supplemental Material

Nontargeted Analysis of DNA Adducts by Mass-Tag MS:

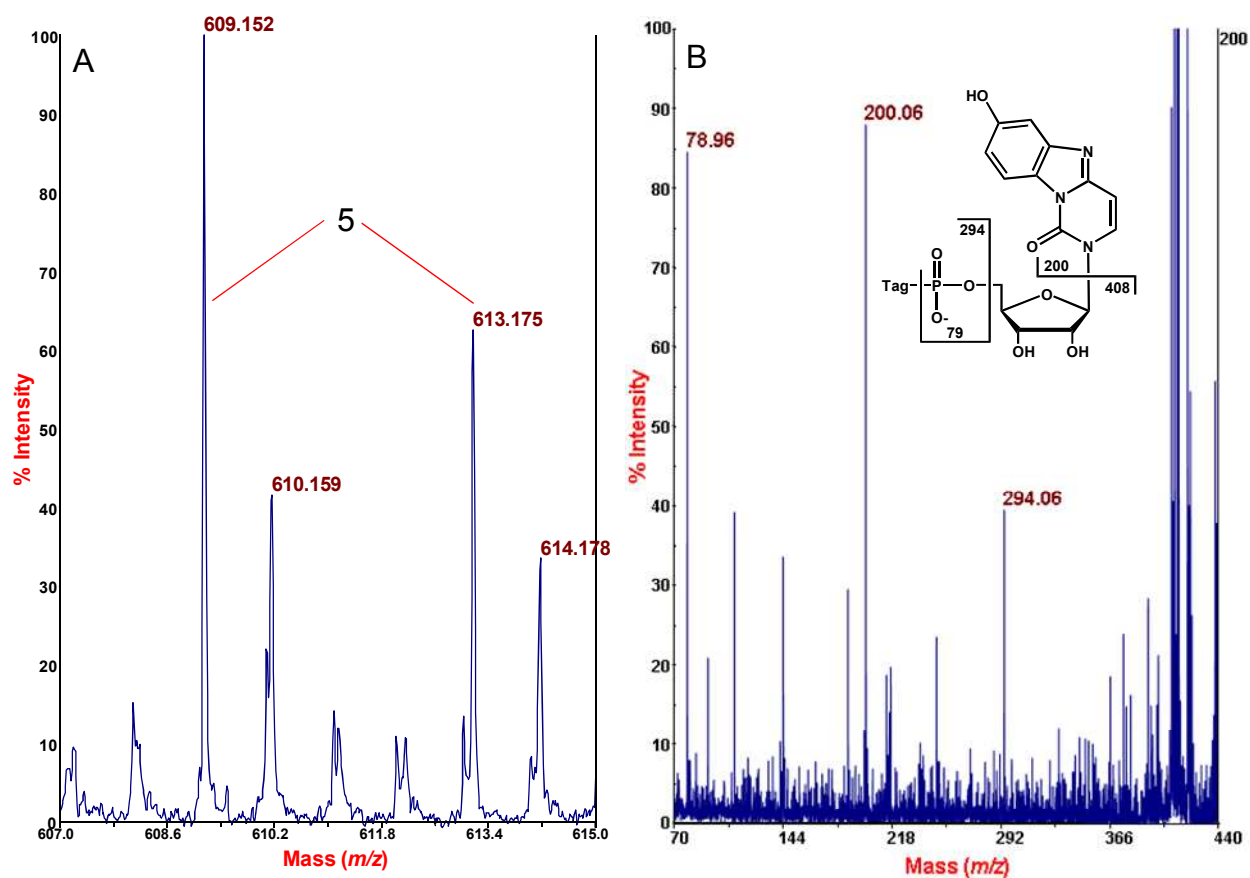
Reaction of *p*-Benzoquinone with DNA

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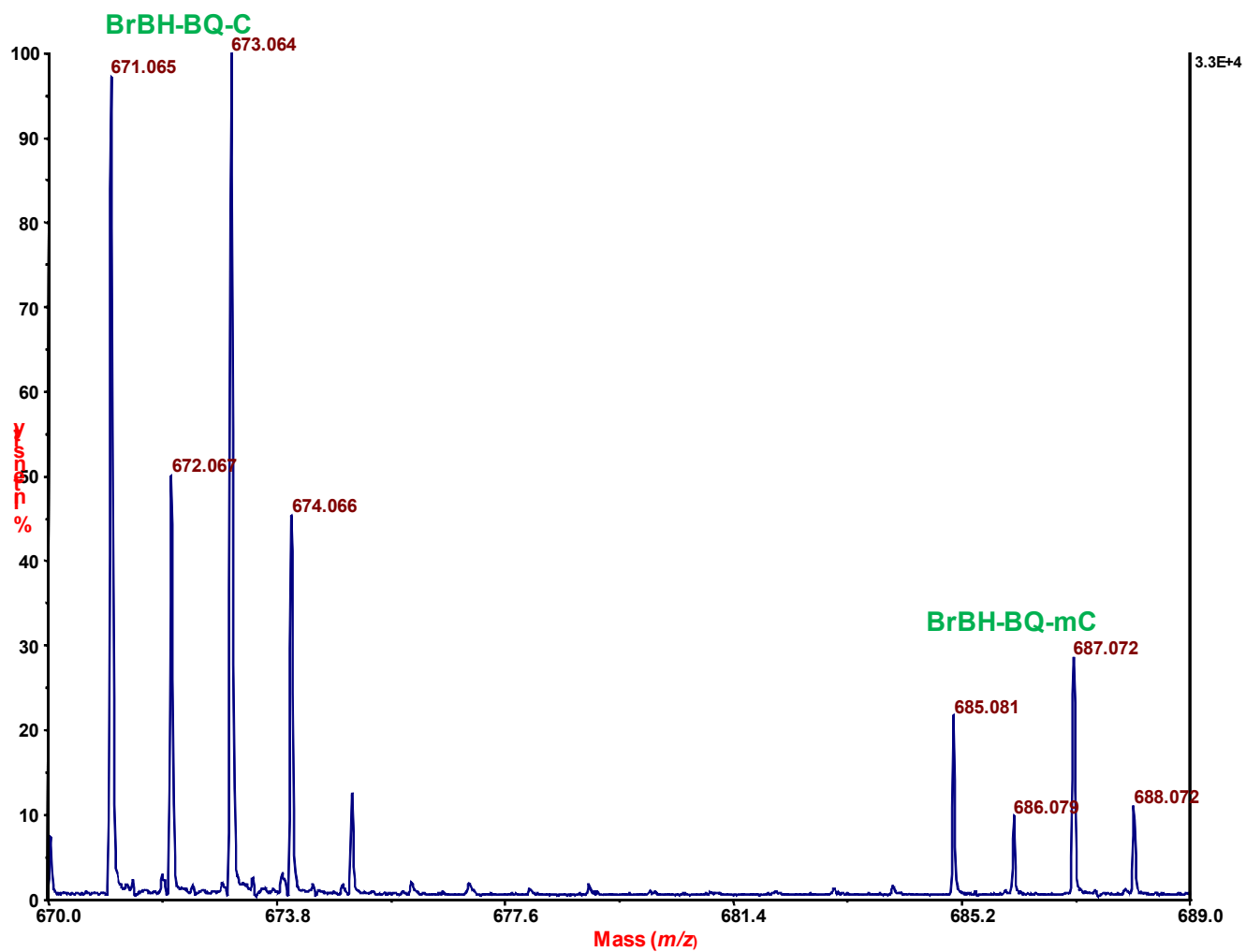
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MALDI-TOF-MS and MALDI-TOF/TOF-MS Spectra

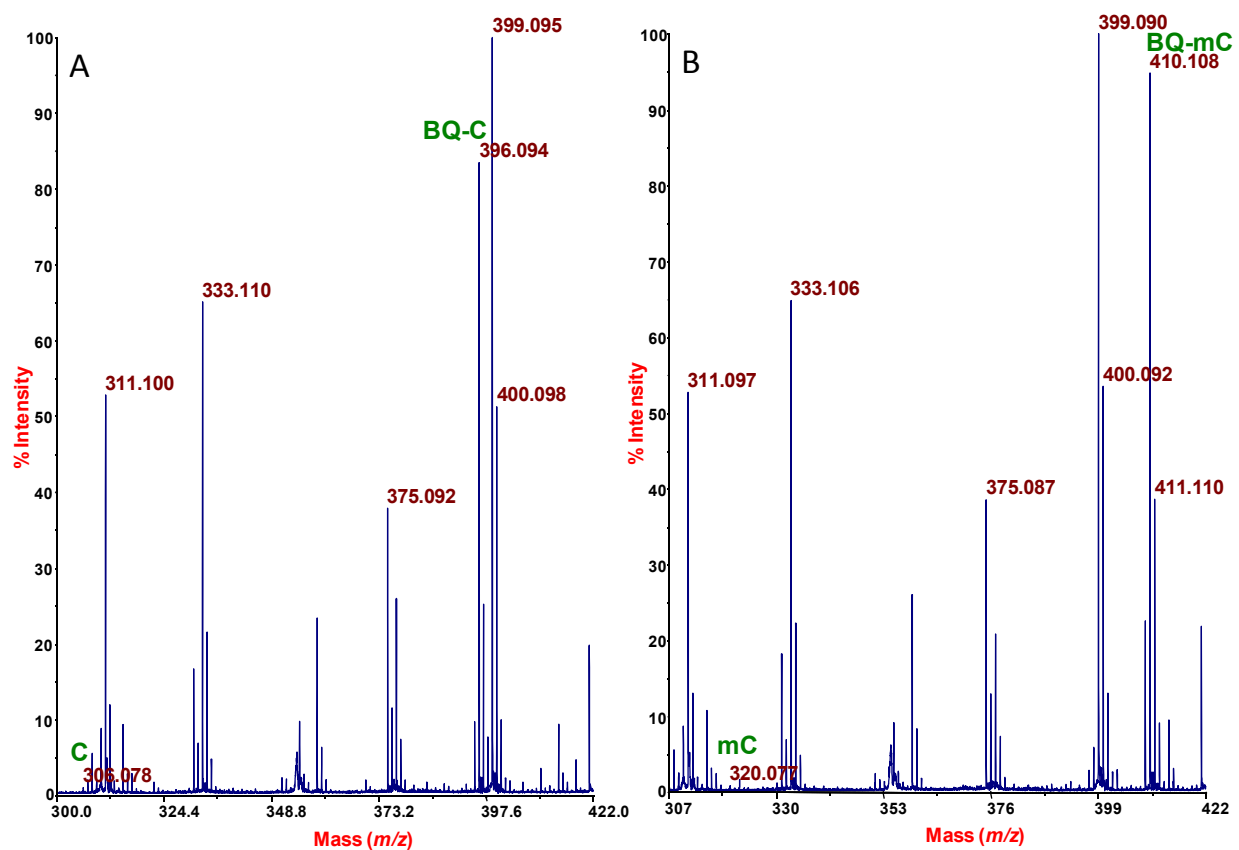
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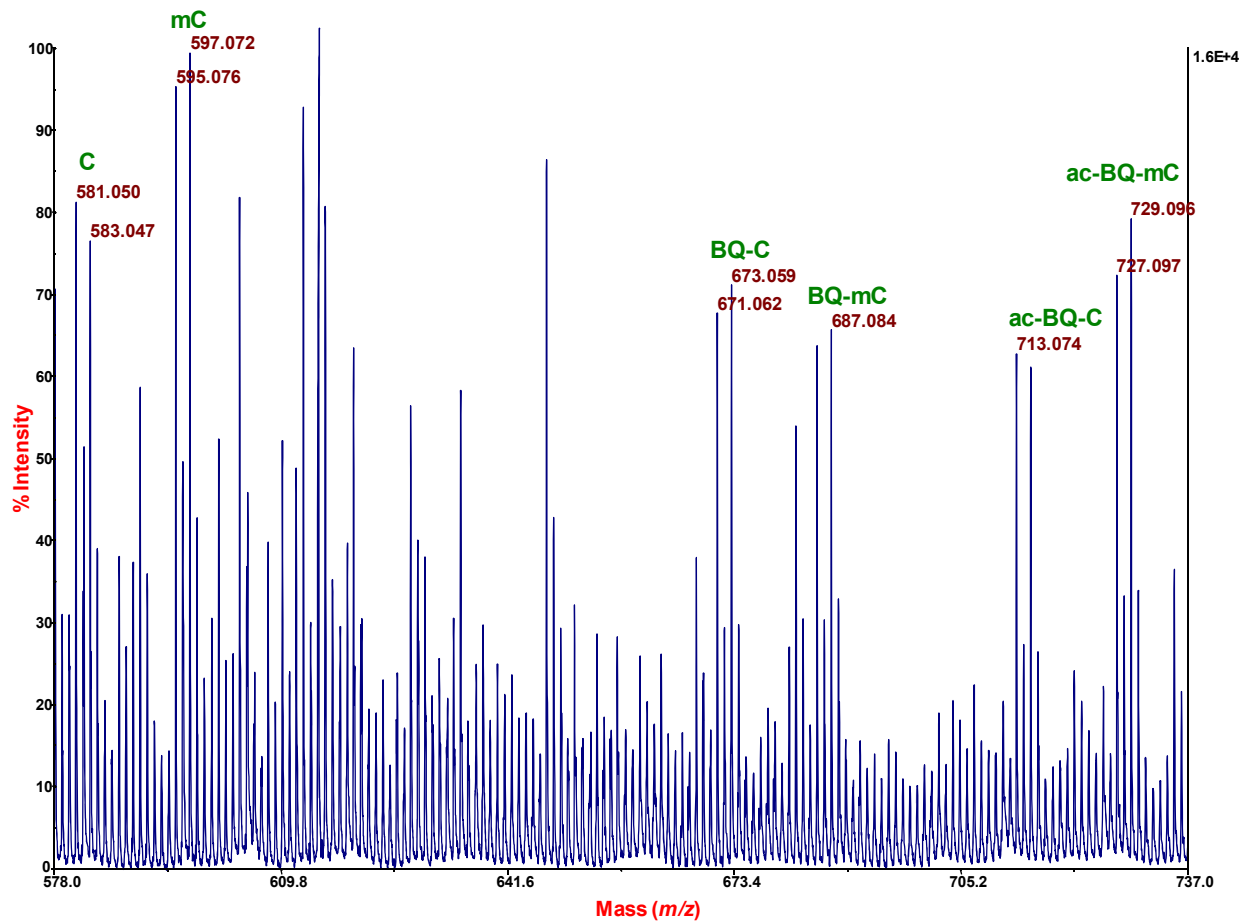
Supplemental Figure 1. **A.** Detection by MALDI-TOF-MS of ribonucleotide BQ-CMP (**5**) as a conjugate of BH at m/z 609.152, and as a conjugate of BH(d_4) at m/z 613.175, formed by reacting BQ with calf thymus DNA contaminated with RNA. **B.** Fragmentation analysis of m/z 609.152.



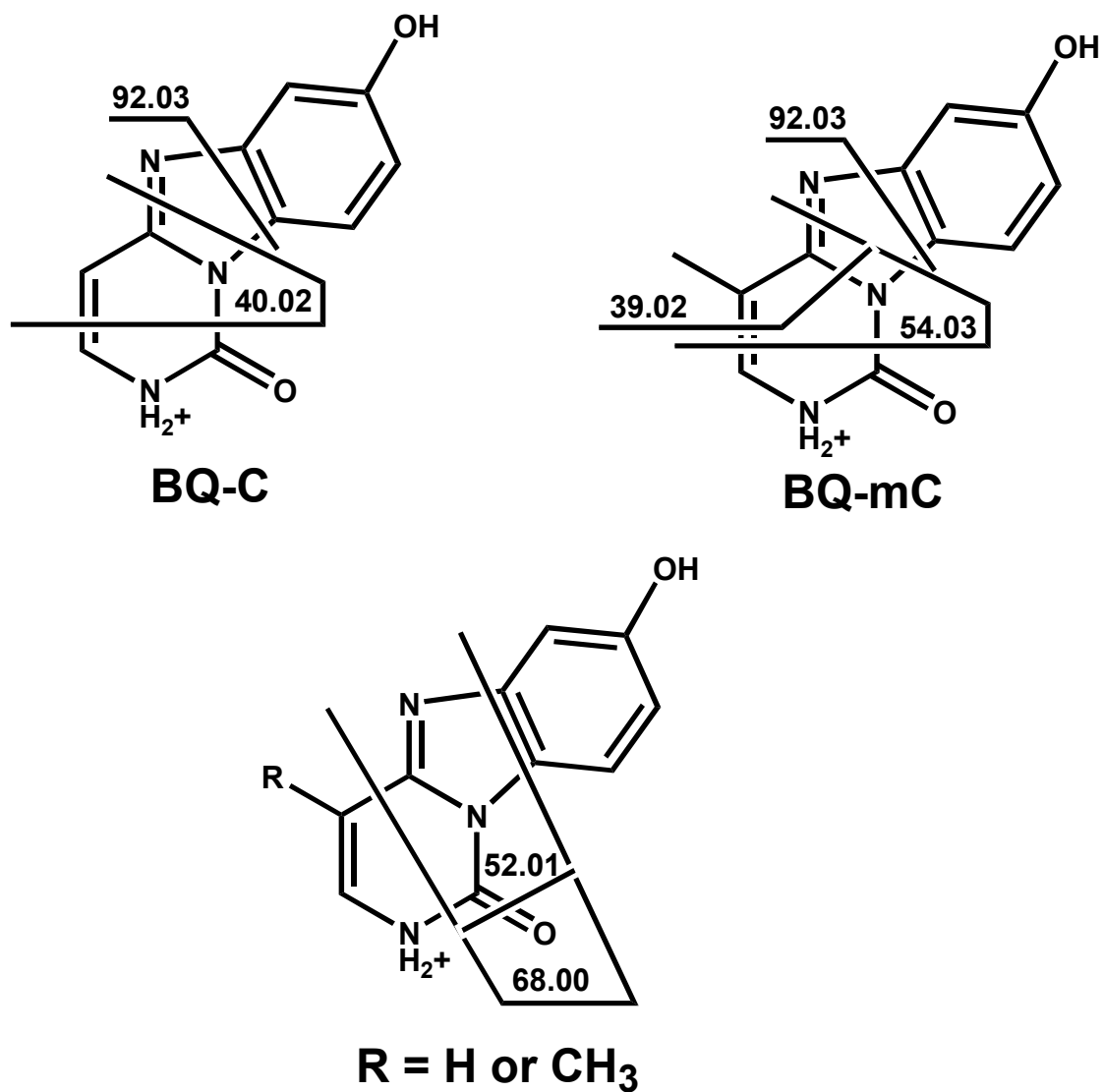
Supplemental Figure 2. Detection of BrBH-BQ-dCMP (at m/z 671.065 and 673.064), and BrBH-BQ-mdCMP (at m/z 685.081 and 687.072) from DNA reacted with hydroquinone in the presence of ferric chloride, followed by digestion, chromatography, mass tag labeling with BrBH, and MALDI-TOF-MS.



Supplemental Figure 3. Analysis (without mass tagging) by MALDI-TOF-MS of two reaction mixtures: (A) dCMP plus BQ, where a tiny peak for unreacted dCMP is seen at m/z 306.078, and a peak for BQ-dCMP is seen at m/z 396.094; and (B) mdCMP plus BQ, where a tiny peak for residual mdCMP is seen at m/z 320.077, and a peak for BQ-mdCMP is seen at m/z 410.108.



Supplemental Figure 4. Spectrum obtained by combining the two reaction mixtures of Supplemental Figure 3, labeling with BrBH, and subjecting the resulting mixture to MALDI-TOF-MS. Peak assignments (some of which are not labeled in the figure because of space limitations): 581.050 and 583.047 (BrBH-BQ-dCMP), 595.076 and 597.072 (BrBH-BQ-mdCMP), 671.062 and 673.059 (BrBH-BQ-dCMP), 685.086 and 687.084 (BrBH-BQ-mdCMP), 713.074 and 715.067 (BrBH-acetylBQ-dCMP), and 727.097 and 729.096 (BrBH-acetylBQ-mdCMP).



Supplemental Figure 5. Additional fragment ion assignments in regard to Figure 5: m/z 40.02 (C₂H₂N) for BQ-C; m/z 54.03 (C₃H₄N) and 39.02 (C₃H₃) for BQ-mC; and m/z 52.01 (C₂N₂), 68.00 (C₂N₂O), and 92.03 (C₆H₄O) common for both.