

## Supplementary Materials

Figure S1: Effect of cone voltage on positive mass spectra of [BuMeIm][Tf<sub>2</sub>N]: (a) 10V, (b) 20V, (c) 30V, (d) 40V, (e) 50V, (f) 60V.

Figure S2: Effect of cone voltage on negative mass spectra of [BuMeIm][Tf<sub>2</sub>N]: (a) 10V, (b) 20V, (c) 30V, (d) 40V, (e) 50V, (f) 60V.

Figure S3: (a) BuMeIm<sup>+</sup> concentration before and after 2.0 MGy radiolysis determined by HPLC and (b) Tf<sub>2</sub>N<sup>-</sup> concentrations before and after 2.0 MGy radiolysis determined by <sup>19</sup>F NMR in "dry" [BuMeIm][Tf<sub>2</sub>N], ½ w pre-eq [BuMeIm][Tf<sub>2</sub>N] and w pre-eq [BuMeIm][Tf<sub>2</sub>N].

Figure S4: Evolution of X<sup>-</sup> (X<sup>-</sup>: Tf<sub>2</sub>N<sup>-</sup>, TfO<sup>-</sup>, PF<sub>6</sub><sup>-</sup> and BF<sub>4</sub><sup>-</sup>) concentration as a function of the irradiation dose for [BuMeIm][Tf<sub>2</sub>N], [BuMeIm][TfO], [BuMeIm][PF<sub>6</sub>] and [BuMeIm][BF<sub>4</sub>].

Figure S5: Positive ESI-MS spectra of (a) [BuMeIm][Tf<sub>2</sub>N], (b) [BuMeIm][TfO], (c) [BuMeIm][PF<sub>6</sub>] and (d) [BuMeIm][BF<sub>4</sub>] before radiolysis.

Figure S6: Positive ESI-MS spectra of (a) [BuMeIm][Tf<sub>2</sub>N], (b) [BuMeIm][TfO], (c) [BuMeIm][PF<sub>6</sub>] and (d) [BuMeIm][BF<sub>4</sub>] after 2.0 MGy radiolysis.

Figure S7: MS/MS spectrum of ion at m/z 207.1.

Figure S8: MS/MS spectrum of ion at m/z 157.1.

Figure S9: MS/MS spectrum of ion at m/z 556.1.

Figure S10: Positive ESI-MS spectra of (a) "dry" [BuMeIm][Tf<sub>2</sub>N], (b) ½ w. pre-eq [BuMeIm][Tf<sub>2</sub>N] and (c) w. pre-eq [BuMeIm][Tf<sub>2</sub>N] after 2.0 MGy radiolysis.

Figure S11: (a) UV spectra of [BuMeIm][Tf<sub>2</sub>N] before and after 2.0 MGy radiolysis (b) Evolution of 290 nm light absorbance as a function of the irradiation dose for irradiated [BuMeIm][Tf<sub>2</sub>N].

Figure S12: HPLC chromatograms of (a) [BuMeIm][Tf<sub>2</sub>N] after 2.0 MGy radiolysis at 210 nm and 290 nm light absorbance (b) [BuMeIm][TfO] after 2.0 MGy radiolysis at 210 nm and 290 nm light absorbance, (c) [BuMeIm][PF<sub>6</sub>] after 2.0 MGy radiolysis at 210 nm and 290 nm light absorbance and (d) [BuMeIm][BF<sub>4</sub>] after 2.0 MGy radiolysis at 210 nm and 290 nm light absorbance.

Figure S13: Total ion current gas chromatogram between 8.0 to 18.0 minutes of (a) [BuMeIm][Tf<sub>2</sub>N], (b) [BuMeIm][TfO], (c) [BuMeIm][PF<sub>6</sub>], (d) [BuMeIm][BF<sub>4</sub>] after 50 kGy radiolysis on Rt-MSieve/Rt-Q PLOT columns.

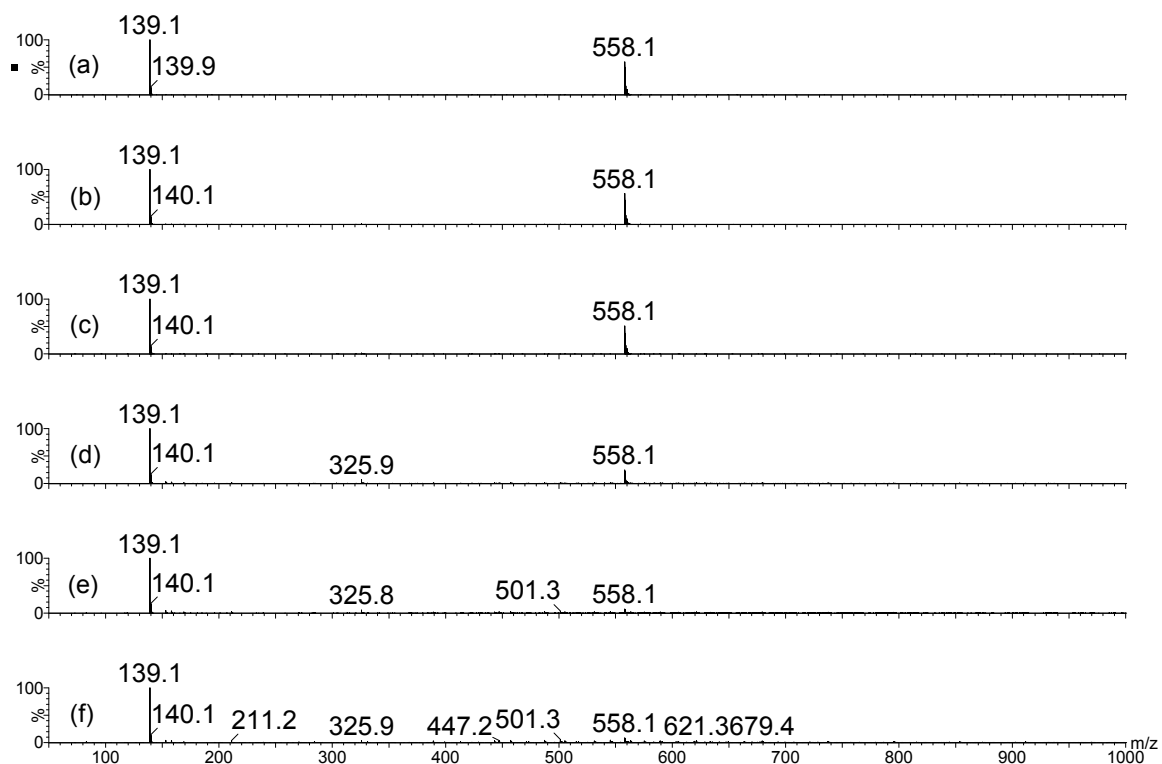


Figure S1: Effect of cone voltage on positive mass spectra of [BuMeIm][Tf<sub>2</sub>N]: (a) 10V, (b) 20V, (c) 30V, (d) 40V, (e) 50V, (f) 60V.

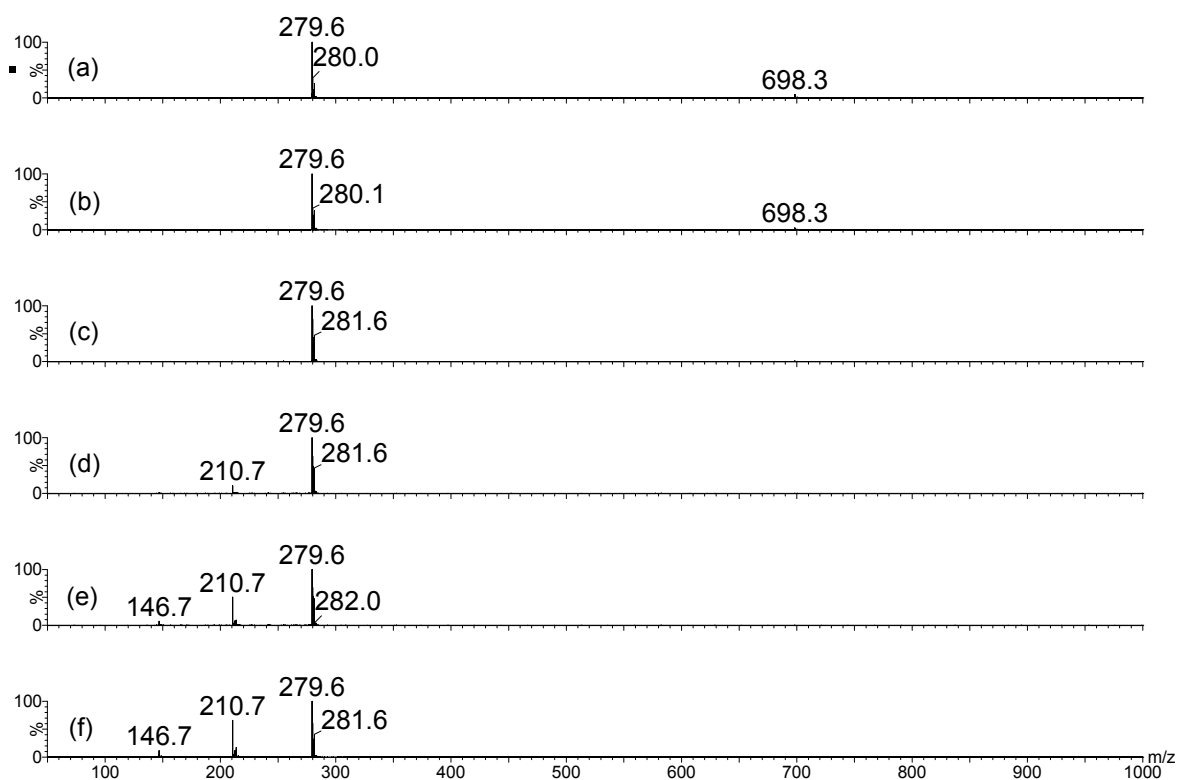


Figure S2: Effect of cone voltage on negative mass spectra of [BuMeIm][Tf<sub>2</sub>N]: (a) 10V, (b) 20V, (c) 30V, (d) 40V, (e) 50V, (f) 60V.

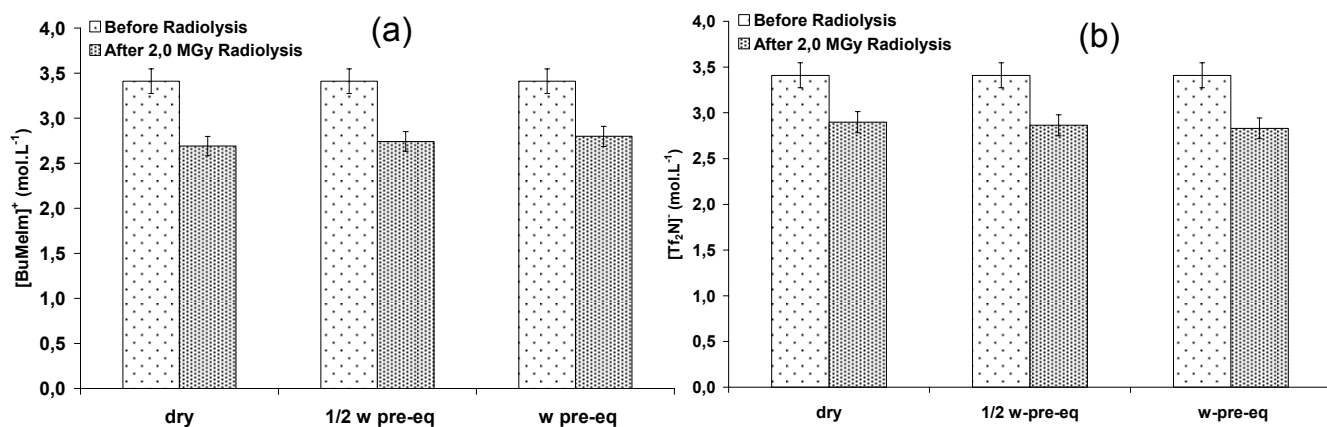


Figure S3 : (a) BuMeIm<sup>+</sup> concentration before and after 2.0 MGy radiolysis determined by HPLC and (b) Tf<sub>2</sub>N<sup>-</sup> concentrations before and after 2.0 MGy radiolysis determined by <sup>19</sup>F NMR in "dry" [BuMeIm][Tf<sub>2</sub>N], 1/2 w pre-eq [BuMeIm][Tf<sub>2</sub>N] and w pre-eq [BuMeIm][Tf<sub>2</sub>N].

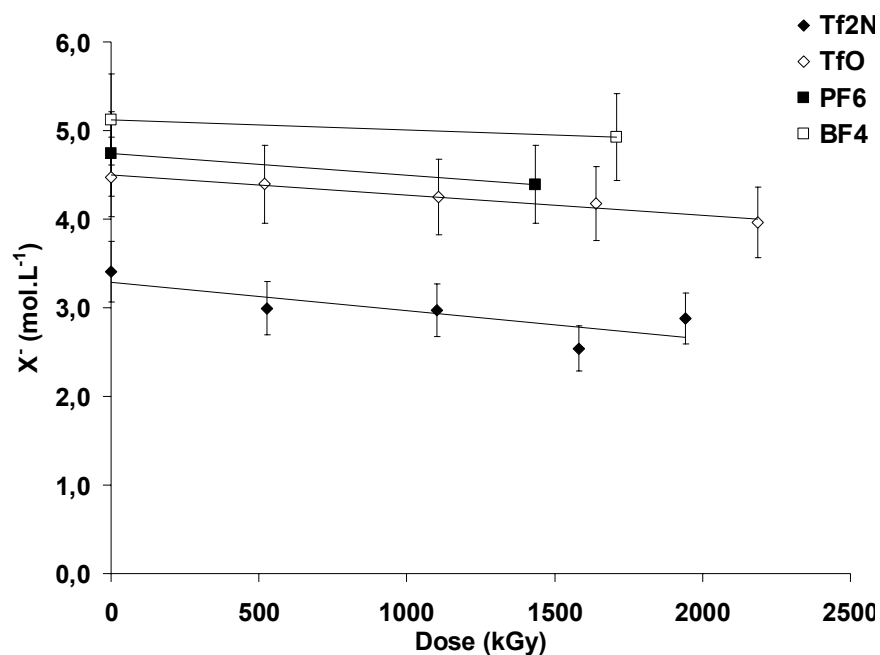


Figure S4: Evolution of  $X^-$  ( $X^-$ :  $\text{Tf}_2\text{N}^-$ ,  $\text{TfO}^-$ ,  $\text{PF}_6^-$  and  $\text{BF}_4^-$ ) concentration as a function of the irradiation dose for  $[\text{BuMeIm}][\text{Tf}_2\text{N}]$ ,  $[\text{BuMeIm}][\text{TfO}]$ ,  $[\text{BuMeIm}][\text{PF}_6]$  and  $[\text{BuMeIm}][\text{BF}_4]$ .

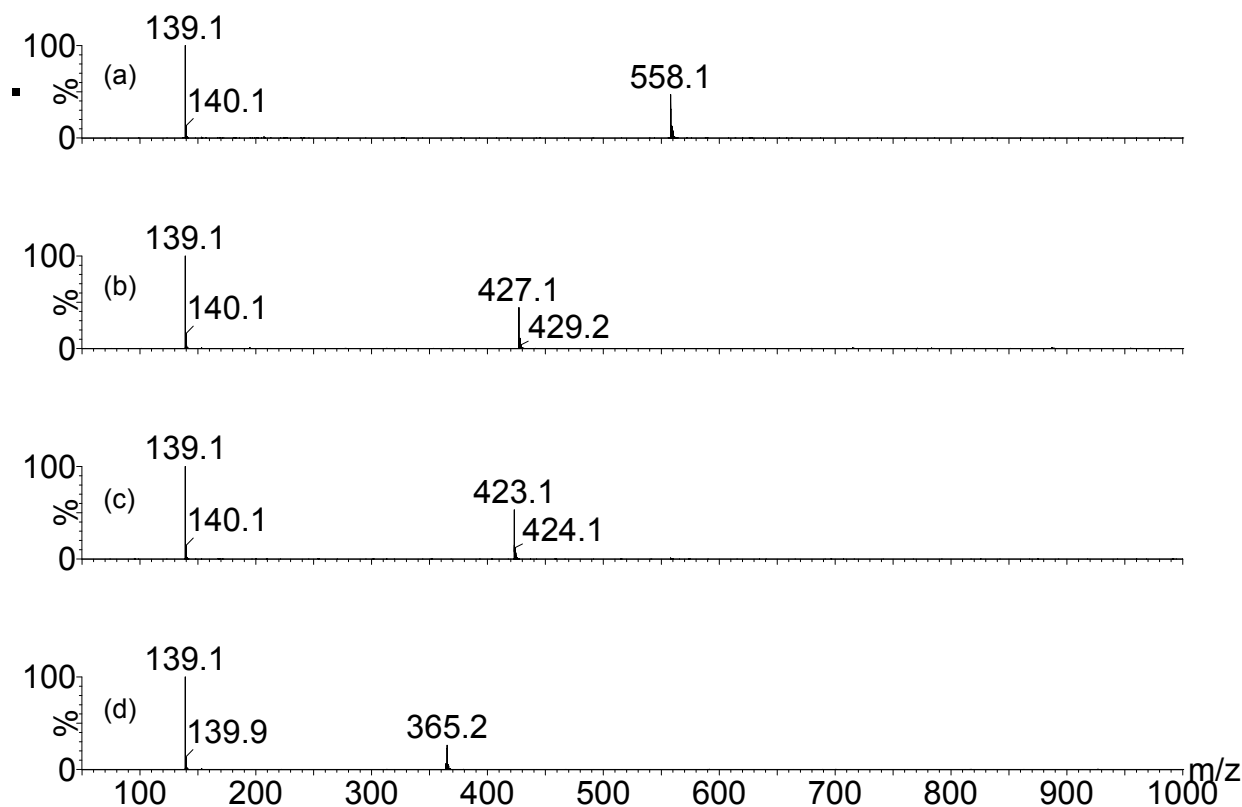
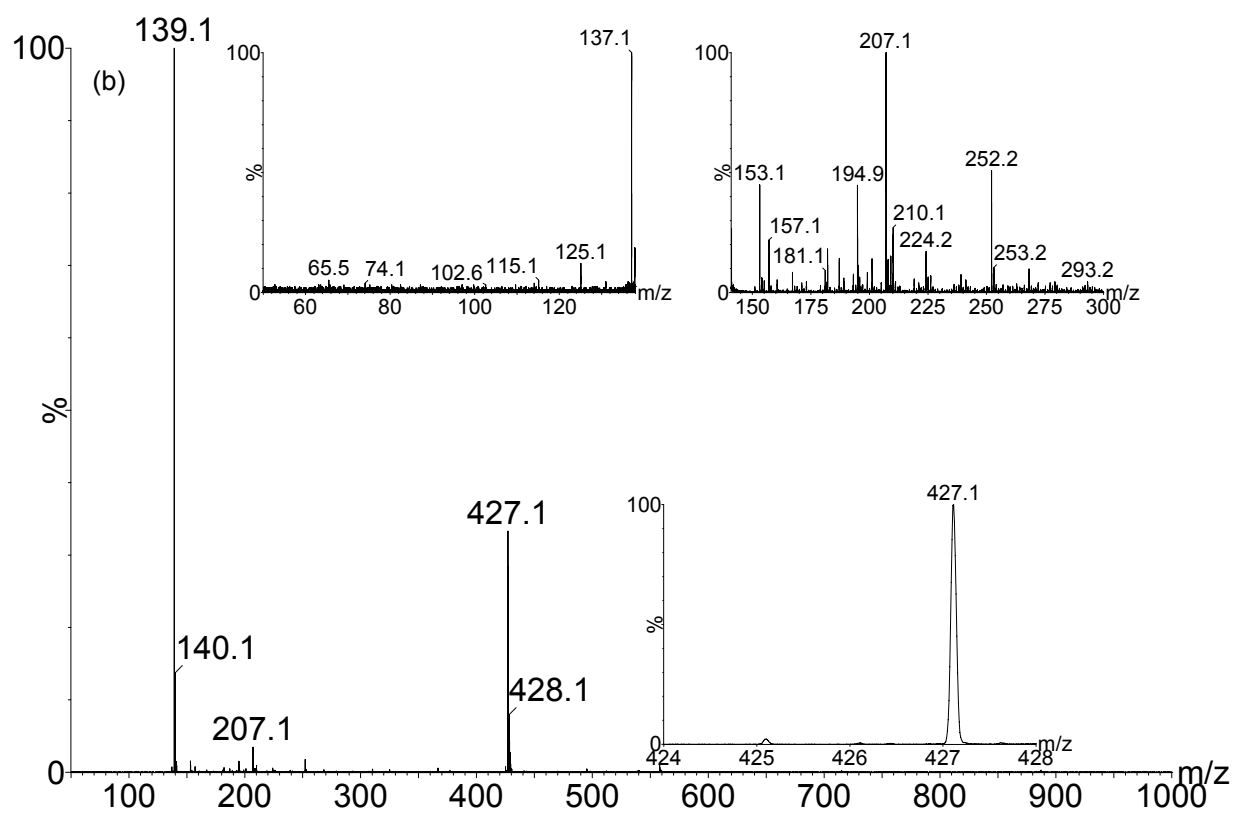
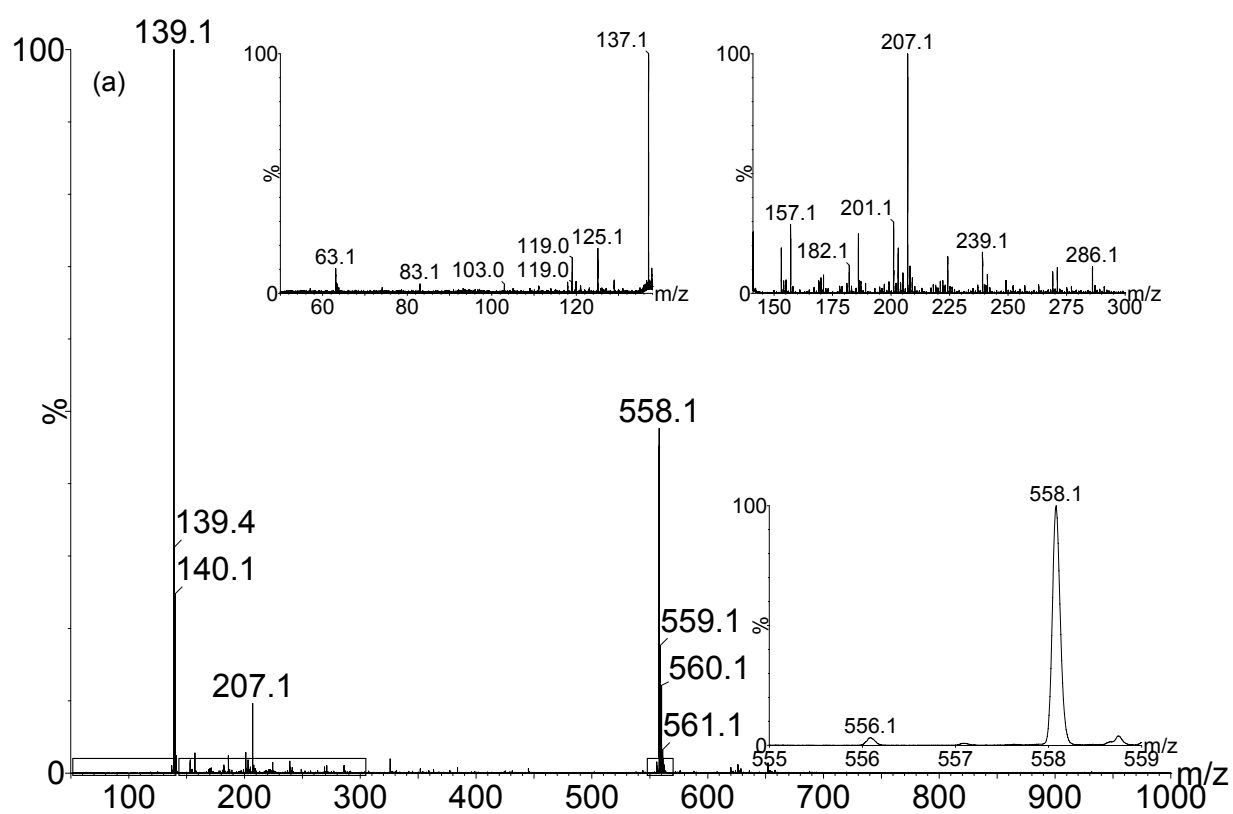


Figure S5: Positive ESI-MS spectra of (a)  $[\text{BuMeIm}][\text{Tf}_2\text{N}]$ , (b)  $[\text{BuMeIm}][\text{TfO}]$ , (c)  $[\text{BuMeIm}][\text{PF}_6]$  and (d)  $[\text{BuMeIm}][\text{BF}_4]$  before radiolysis.



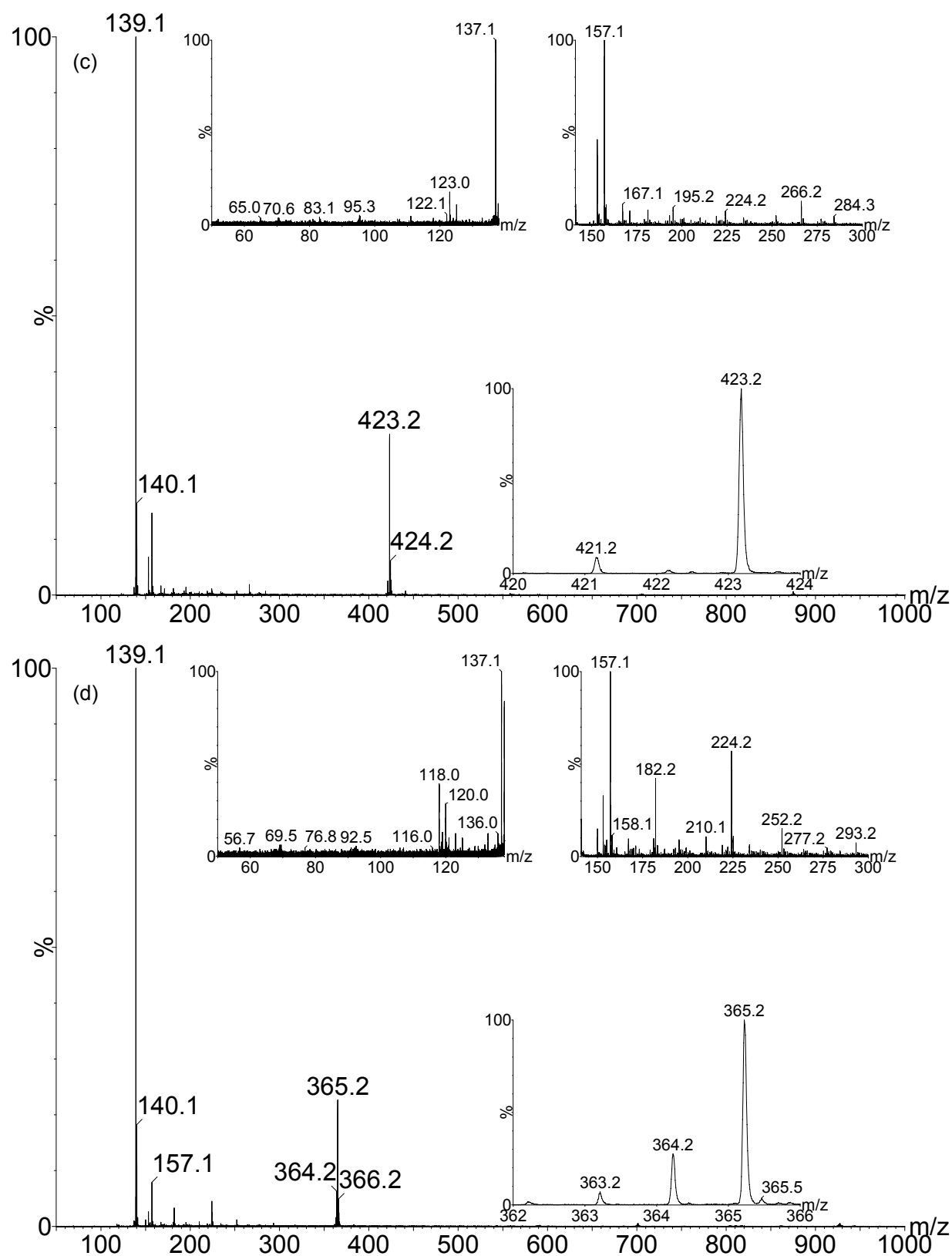


Figure S6: Positive ESI-MS spectra of (a) [BuMeIm][Tf<sub>2</sub>N], (b) [BuMeIm][TfO], (c) [BuMeIm][PF<sub>6</sub>] and (d) [BuMeIm][BF<sub>4</sub>] after 2.0 MGy radiolysis.

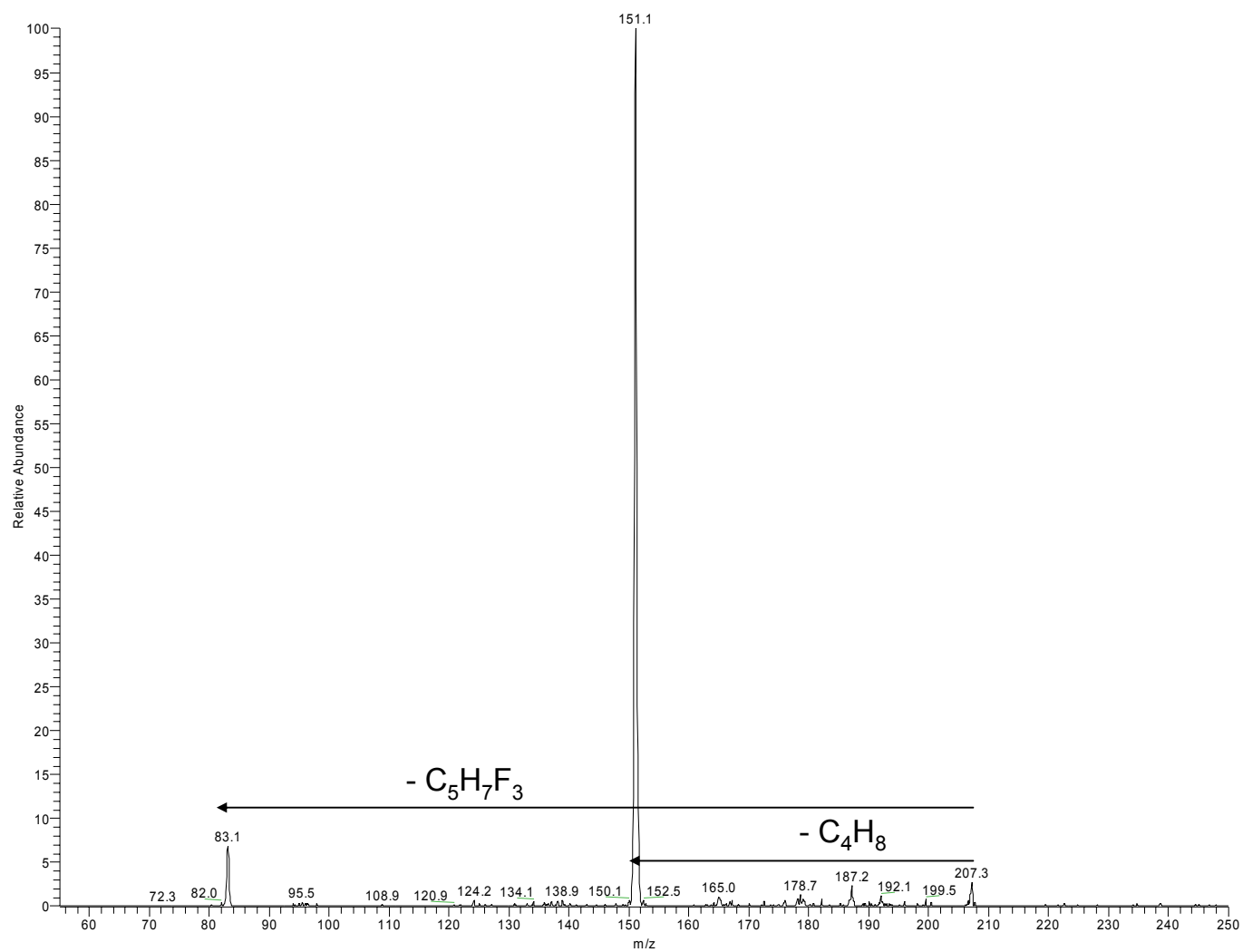


Figure S7: MS/MS spectrum of ion at m/z 207.1.

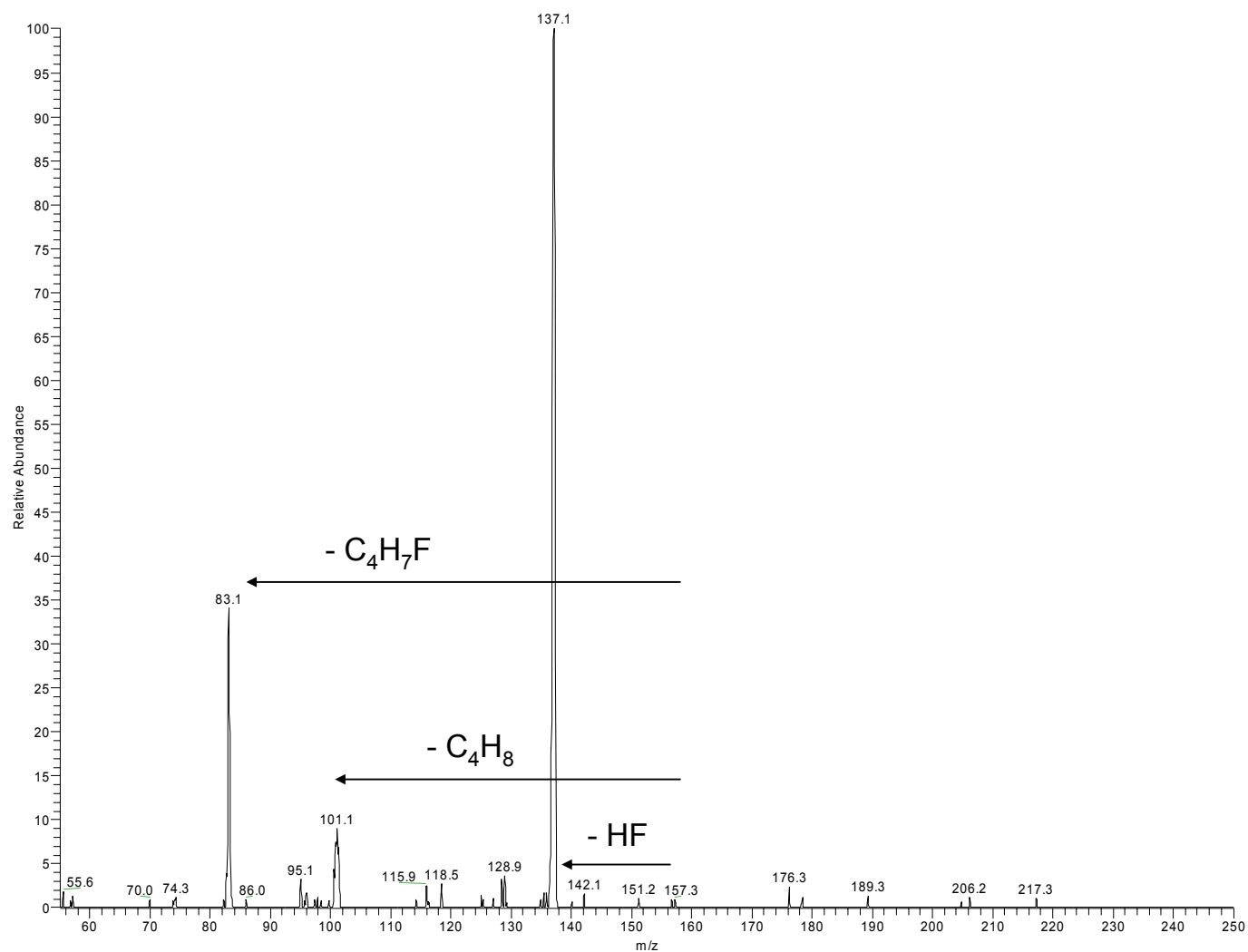


Figure S8: MS/MS spectrum of ion at m/z 157.1.



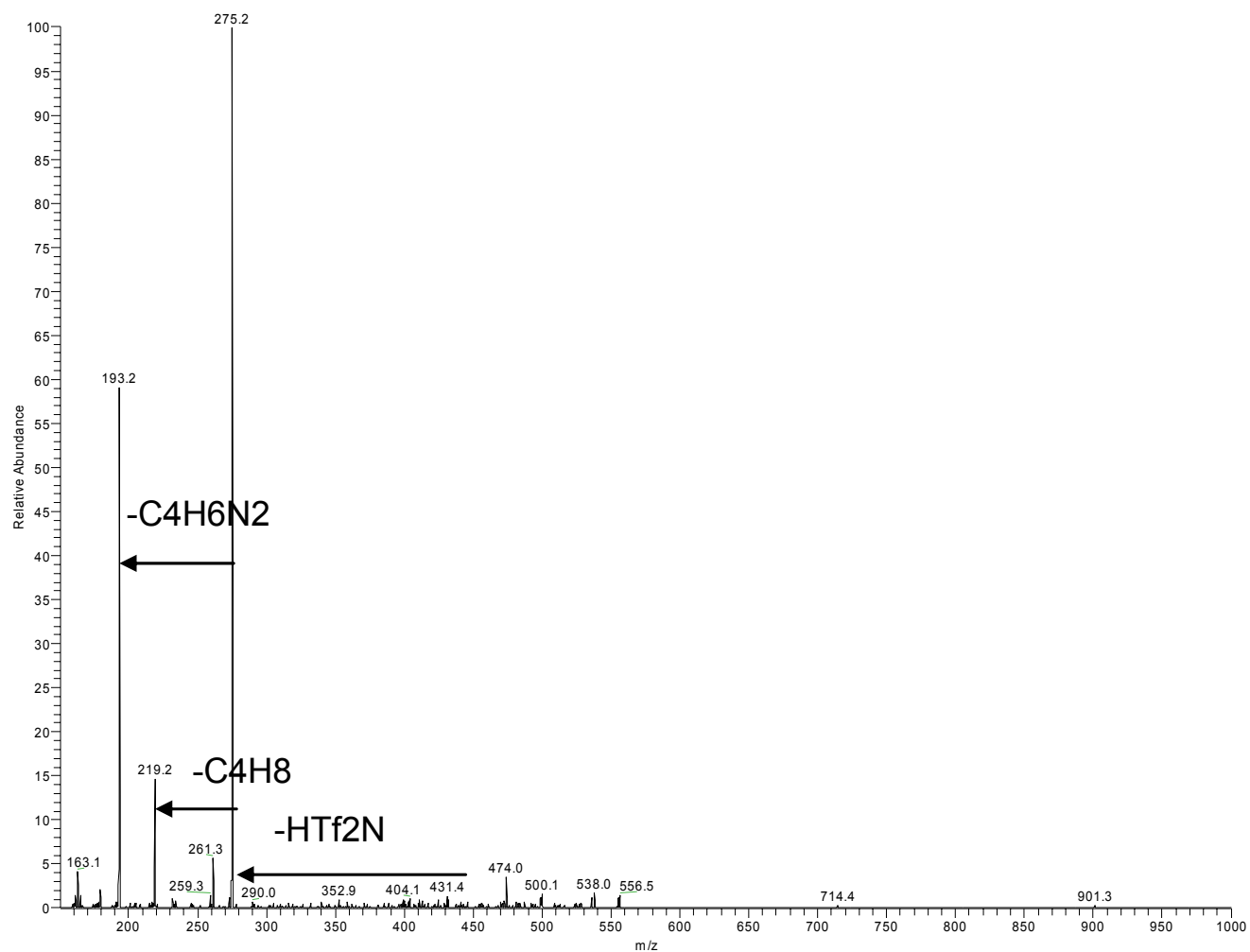


Figure S9: MS/MS spectrum of ion at m/z 556.1.

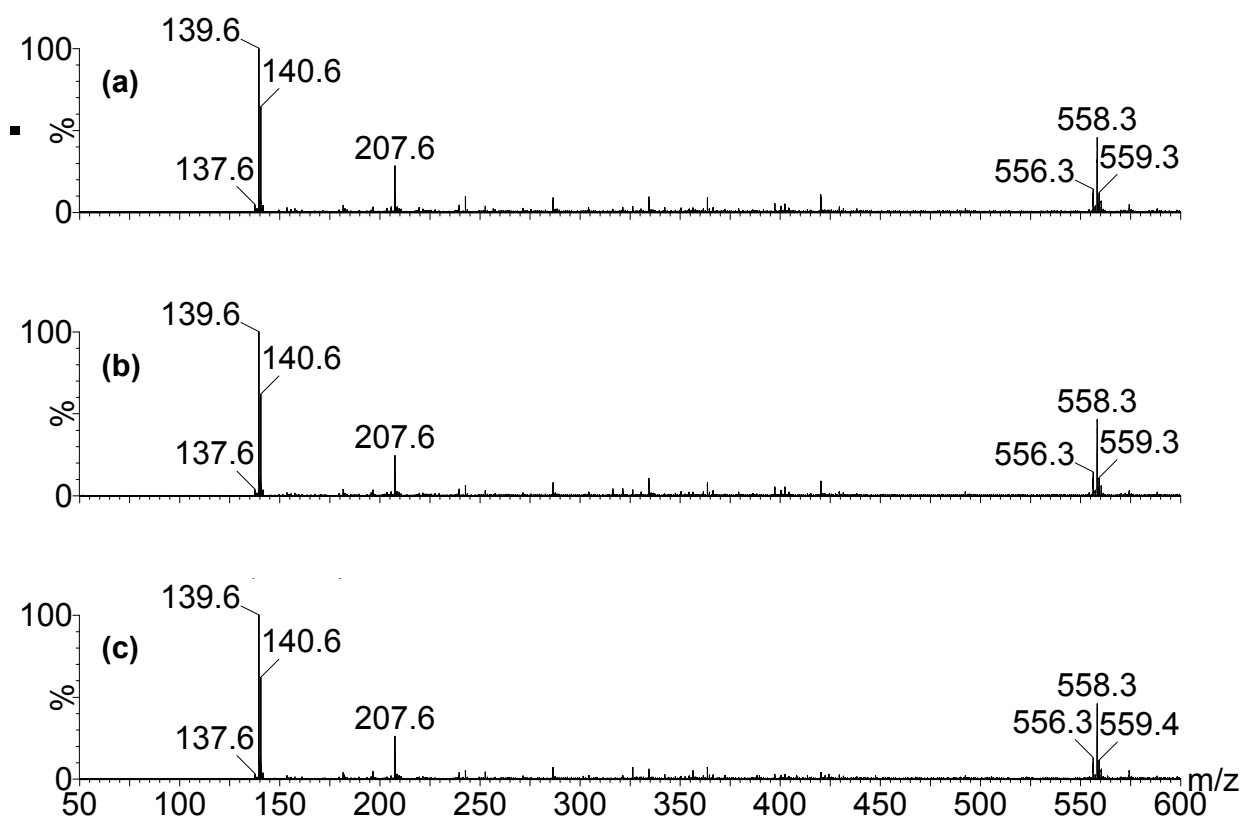


Figure S10: Positive ESI-MS spectra of (a) "dry" [BuMeIm][Tf<sub>2</sub>N], (b) 1/2 w. pre-eq [BuMeIm][Tf<sub>2</sub>N] and (c) w. pre-eq [BuMeIm][Tf<sub>2</sub>N] after 2.0 MGy radiolysis.

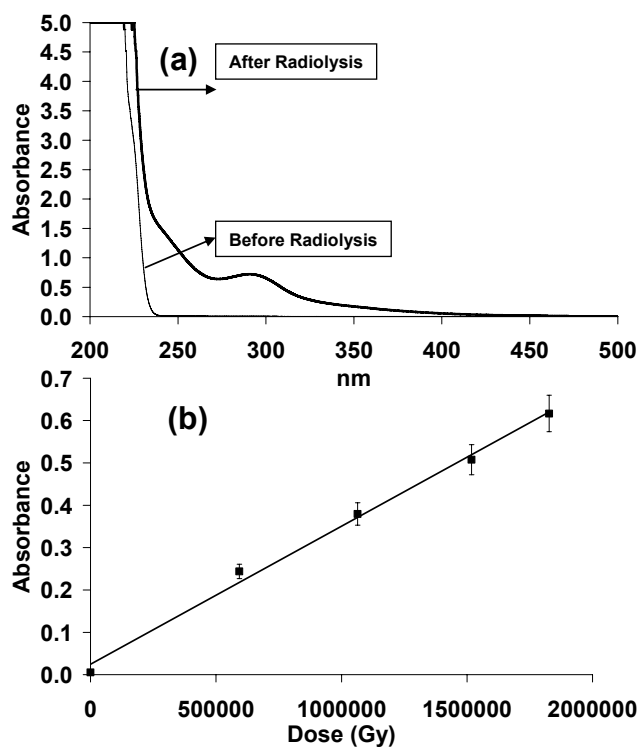


Figure S11: (a) UV spectra of [BuMeIm][Tf<sub>2</sub>N] before and after 2.0 MGy radiolysis (b) Evolution of 290 nm light absorbance as a function of the irradiation dose for irradiated [BuMeIm][Tf<sub>2</sub>N].

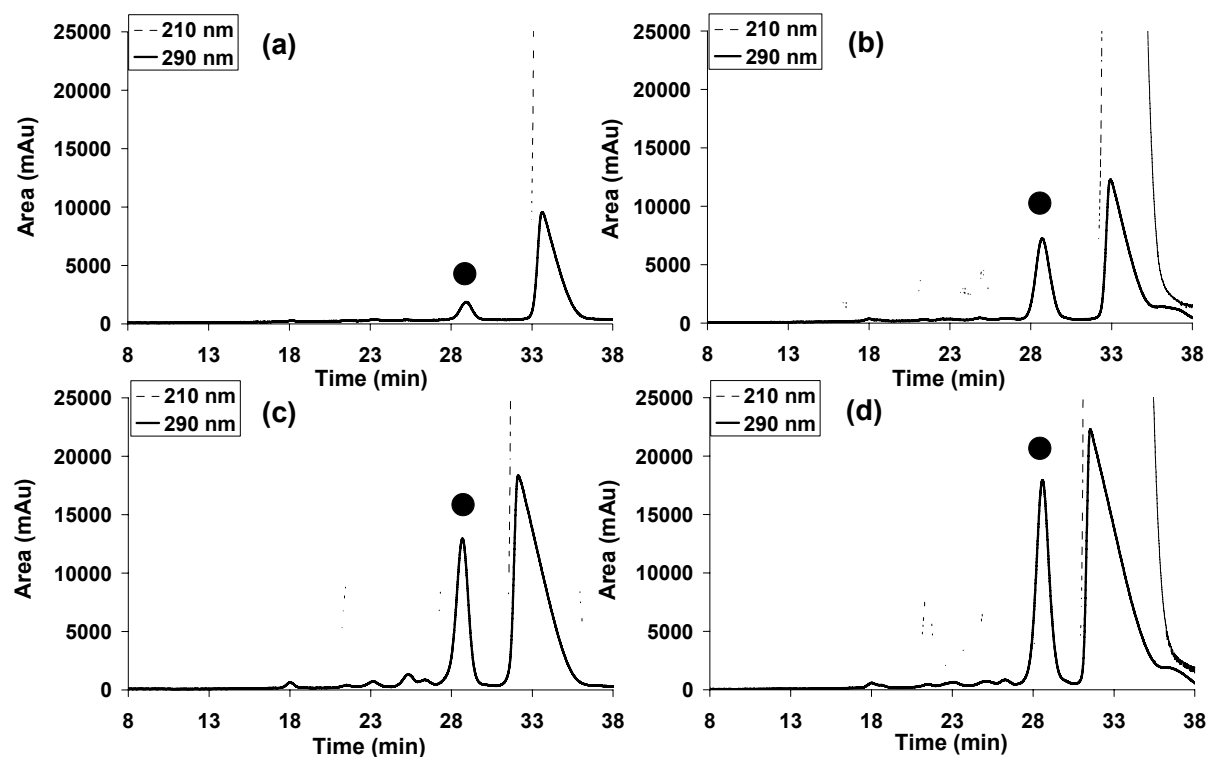


Figure S12: HPLC chromatograms of (a) [BuMeIm][Tf<sub>2</sub>N] after 2.0 MGy radiolysis at 210 nm and 290 nm light absorbance (b) [BuMeIm][TfO] after 2.0 MGy radiolysis at 210 nm and 290 nm light absorbance, (c) [BuMeIm][PF<sub>6</sub>] after 2.0 MGy radiolysis at 210 nm and 290 nm light absorbance and (d) [BuMeIm][BF<sub>4</sub>] after 2.0 MGy radiolysis at 210 nm and 290 nm light absorbance.

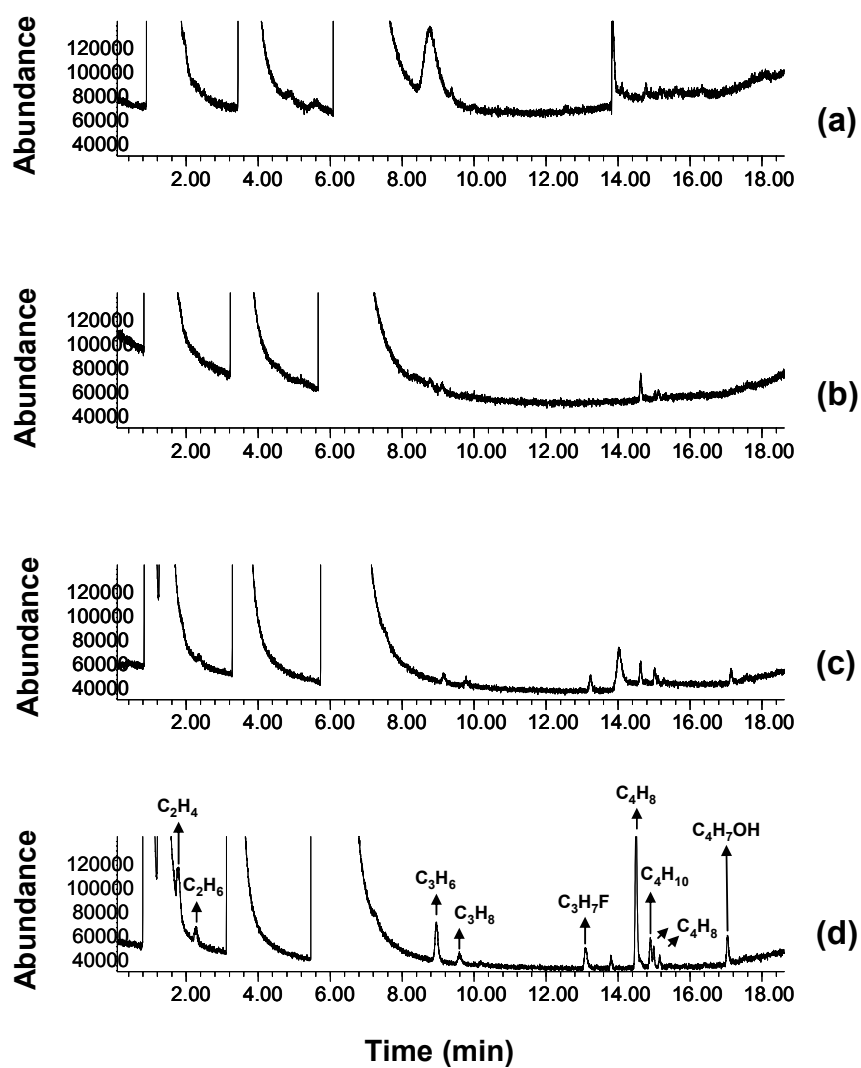


Figure S13: Total ion current gas chromatogram between 8.0 to 18.0 minutes of (a) [BuMeIm][Tf2N], (b) [BuMeIm][TfO], (c) [BuMeIm][PF6], (d) [BuMeIm][BF4] after 50 kGy radiolysis on Rt-MSieve/Rt-Q PLOT columns.