

2-Amino-9*H*-pyrido[2,3-*b*]indole (A $\alpha$ C) Adducts and Thiol Oxidation of Serum Albumin as Potential Biomarkers of Tobacco Smoke

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**Supplemental data**

## SUPPLEMENTAL FIGURE LEGENDS

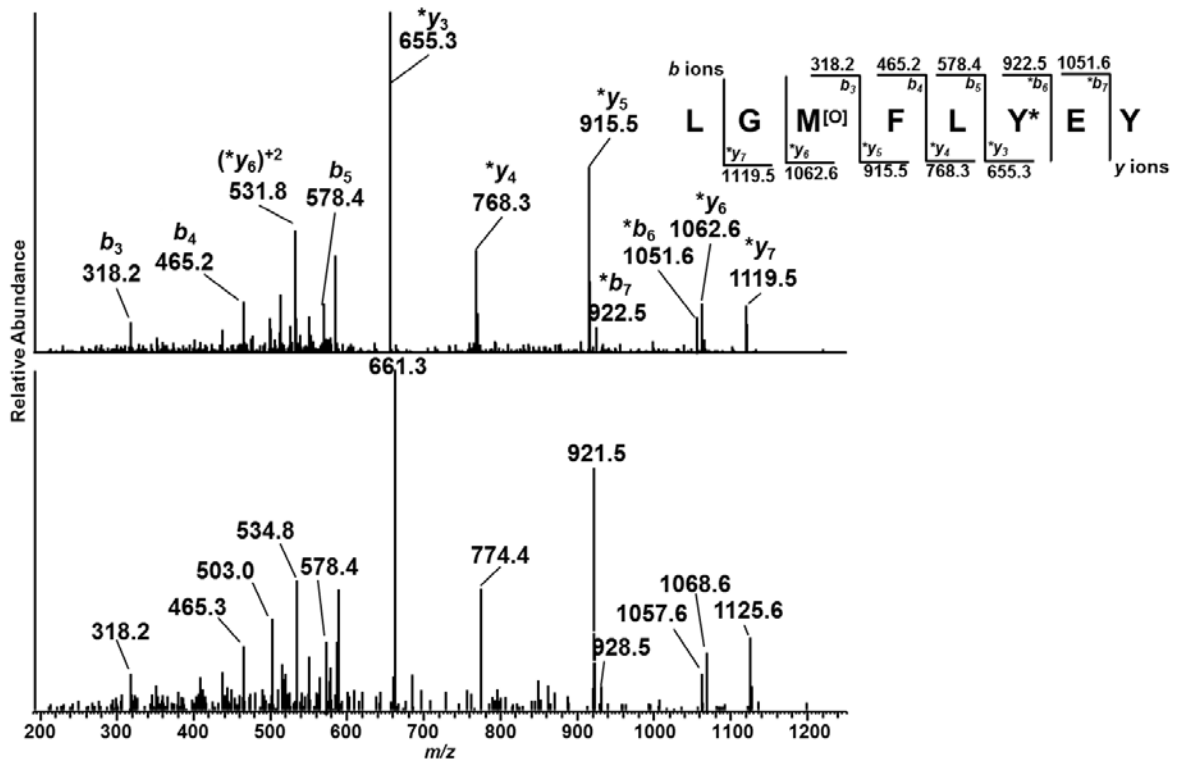
**SUPPLEMENTAL FIG. 1S.** Product ion spectra of LGMFL\*Y<sup>[AαC]</sup>EY adduct (P6) [M+2H]<sup>2+</sup> at *m/z* 616.5 of SA modified with *N*-acetoxy-AαC (upper panel) and LGMFL\*Y<sup>[AαC]</sup>EY adduct (P6) [M+2H]<sup>2+</sup> at *m/z* *m/z* 619.5 of SA modified with *N*-acetoxy-[<sup>13</sup>C<sub>6</sub>]AαC (lower panel), following trypsin-chymotrypsin digestion of SA.

**SUPPLEMENTAL FIG. 2S.** UPLC-ESI/MS<sup>2</sup> chromatograms AαC-peptide adducts from commercial SA (A) and plasma SA (B) modified with 1 mole equivalent *N*-acetoxy-AαC following digestion with trypsin/chymotrypsin: LQQ\*C<sup>[AαC]</sup>PF sulfenamide ([M+2H]<sup>2+</sup> at *m/z* 458.7), LQQ\*C<sup>[SOAαC]</sup>PF sulfenamide ([M+2H]<sup>2+</sup> at *m/z* 466.7), LQQ\*C<sup>[SO<sub>2</sub>AαC]</sup>PF sulfenamide ([M+2H]<sup>2+</sup> at *m/z* 474.7), LQQ\*C<sup>[SOAαC]</sup>PFEDHVK sulfenamide ([M+3H]<sup>3+</sup> at *m/z* 514.2), LQQ\*C<sup>[SO<sub>2</sub>AαC]</sup>PFEDHVK sulfenamide ([M+3H]<sup>3+</sup> at *m/z* 519.6), L\*Y<sup>[AαC]</sup>EIAR ([M+2H]<sup>2+</sup> at *m/z* 473.3), F\*Y<sup>[AαC]</sup>PELL ([M+2H]<sup>2+</sup> at *m/z* 517.3) and full scan spectrum of AαC ([M+H]<sup>+</sup> at *m/z* 184.1) were used to construct the ion chromatograms.

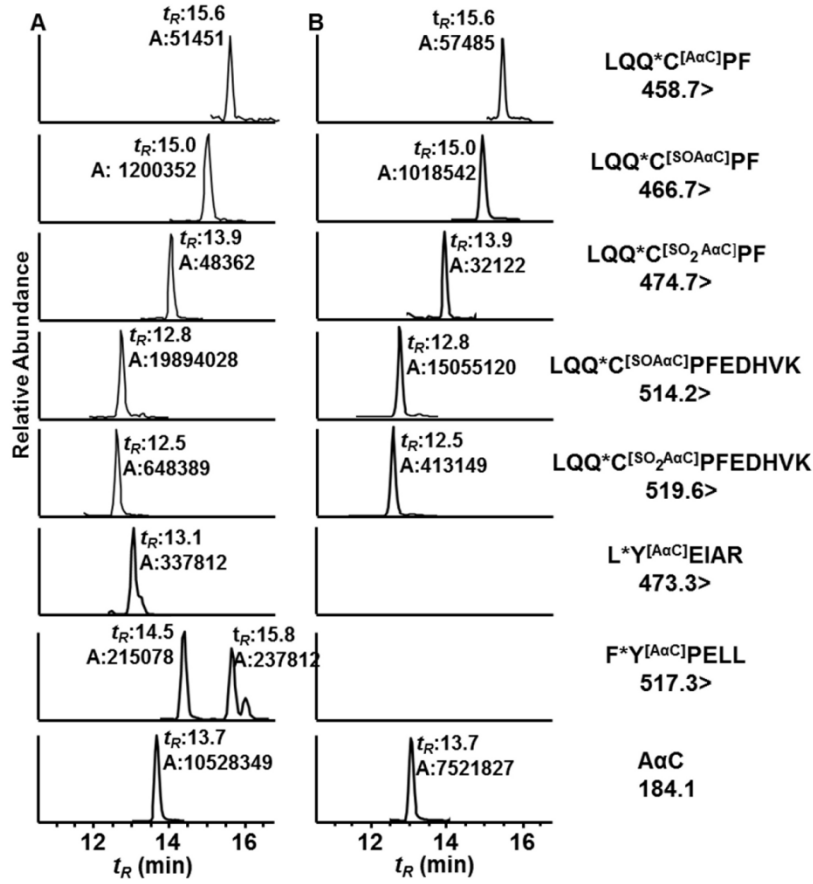
**SUPPLEMENTAL FIG. 3S.** Product ion spectra of (A) LQQ\*C<sup>[AαC]</sup>PF sulfenamide ([M+2H]<sup>2+</sup> at *m/z* 458.7, upper level) and LQQ\*C<sup>[<sup>13</sup>C<sub>6</sub>AαC]</sup>PF sulfenamide *m/z* 461.7, lower panel), (B) LQQ\*C<sup>[SOAαC]</sup>PF sulfenamide ([M+H]<sup>+</sup> at *m/z* 932.4, upper panel) and LQQ\*C<sup>[SO<sup>13</sup>C<sub>6</sub>AαC]</sup>PF sulfenamide ([M+H]<sup>+</sup> at *m/z* 938.4, lower panel); and (C) LQQ\*C<sup>[SOAαC]</sup>PFEDHVK sulfenamide ([M+3H]<sup>3+</sup> at *m/z* 514.2, upper panel) and LQQ\*C<sup>[SO<sup>13</sup>C<sub>6</sub>AαC]</sup>PFEDHVK sulfenamide ([M+3H]<sup>3+</sup> at *m/z* 516.2, lower panel) obtained from trypsin/chymotrypsin digest of SA obtained from human hepatocytes treated with 50 μM of an equimolar mixture of AαC and [<sup>13</sup>C<sub>6</sub>]-AαC.

**SUPPLEMENTAL FIG. 4S.** Product ion spectra of (A) LQQ\*C<sup>[SO<sub>2</sub>H]</sup>PFEDHVK sulfinic acid [M+2H]<sup>2+</sup> at *m/z* 688.3, (B) LQQ\*C[SO<sub>3</sub>H]PFEDHVK sulfonic acid [M+2H]<sup>2+</sup> at *m/z* 696.3, (C) DVFLGM<sup>[O]</sup>F [M+H]<sup>+</sup> at *m/z* 844.3 obtained from trypsin/chymotrypsin digest of SA of human hepatocytes treated with 50 μM of an equimolar mixture of AαC and [<sup>13</sup>C<sub>6</sub>]AαC.

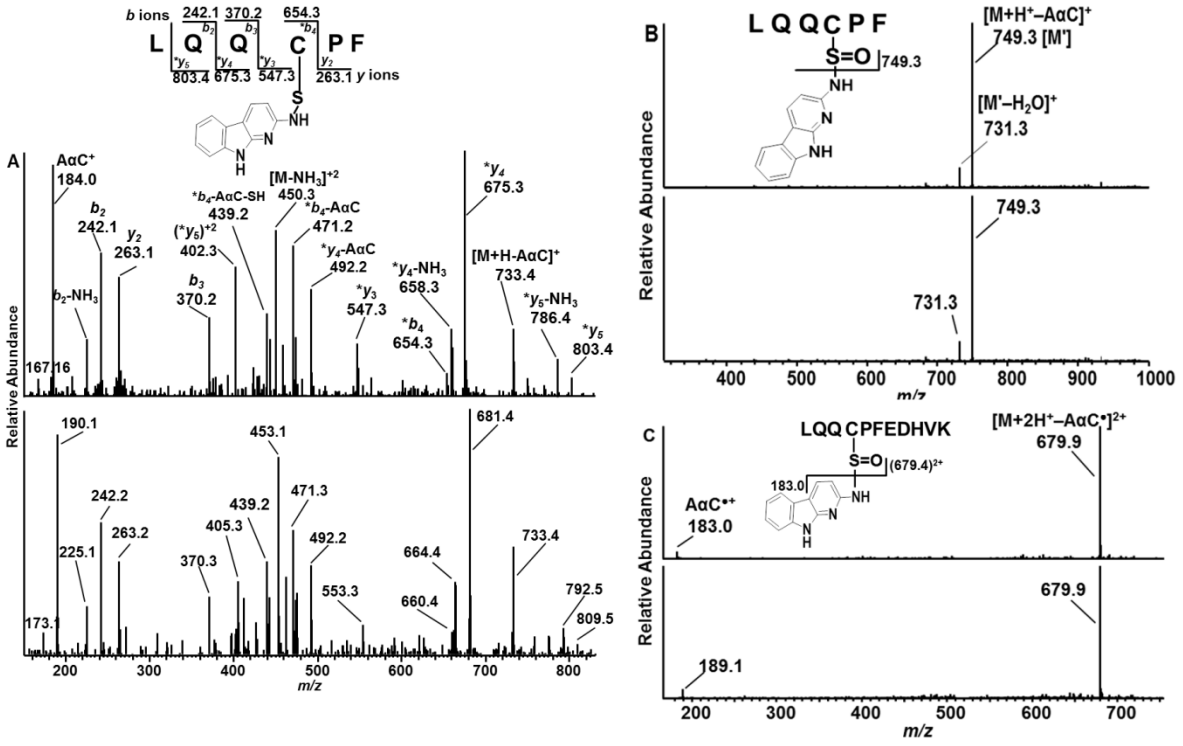
Supplemental Fig. 1S



Supplemental Fig. 2S



Supplemental Fig. 3S



Supplemental Fig. 4S

