

Supplementary Materials

Figures captions

Figure 1S. ACN vs ACN-H₂O: Diode array chromatograms of anolyte, after 2 F anodic oxidation with respect to caffeine, of ACN (a) and ACN-H₂O (b) caffeine solutions. Divided cell, Pt electrodes, r.t., N₂ atmosphere, caffeine 0.02 M.

Figure 2S. ACN-H₂O: Diode array chromatograms of catholyte before (a), after 1 F (b) and after 2 F anodic oxidation (c), with respect to caffeine, in ACN-H₂O. Divided cell, Pt electrodes, r.t., N₂ atmosphere, caffeine 0.02 M in ACN-0.1 M Et₄NBF₄ containing 0.02 M water. $E = +1.85$ V, *vs* SCE.

Figure 3S. Compound 1: R.T. 2.75 min, calculated mass M = 250.09 Da; UV-vis spectrum, positive Electrospray ionization (pESI) MS spectrum, pESI fragmentation MS spectra at different collision energies (C.E.), fragmentation pattern, proposed structure.

Figure 4S. Compound 2, R.T. 3.35 min, calculated mass M = 188.09 Da; UV-vis spectrum, positive and negative Electrospray ionization (pESI, nESI) MS spectra, pESI and nESI fragmentation MS spectra at different collision energies (C.E.), fragmentation patterns, proposed structure.

Figure 5S. Compound 4: R.T. 6.94 min, calculated mass M = 213.07 Da; UV-vis spectrum, negative Electrospray ionization (nESI) MS spectra, nESI fragmentation MS spectra at different collision energies (C.E.), fragmentation patterns, proposed structure.

Figure 6S. Compound 5: R.T. 8.37 min, calculated mass M = 228.09 Da; UV-vis spectrum, positive Electrospray ionization (pESI) MS spectra, pESI fragmentation MS spectra at different collision energies (C.E.), fragmentation patterns, proposed structure.

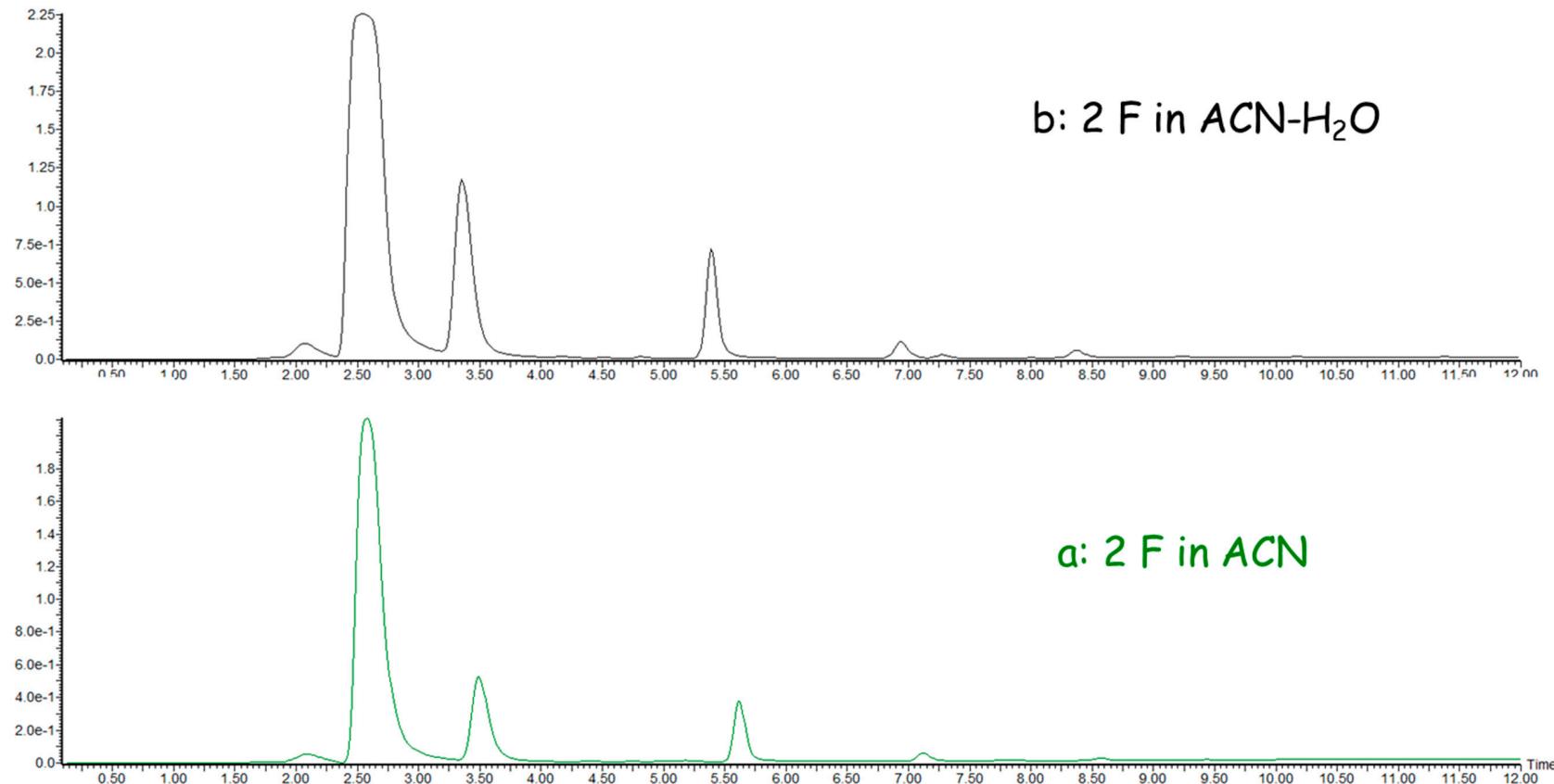


Figure 1S. ACN vs ACN-H₂O: Diode array chromatograms of anolyte, after 2 F anodic oxidation with respect to caffeine, of ACN (a) and ACN-H₂O (b) caffeine solutions. Divided cell, Pt electrodes, r.t., N₂ atmosphere, caffeine 0.02 M.

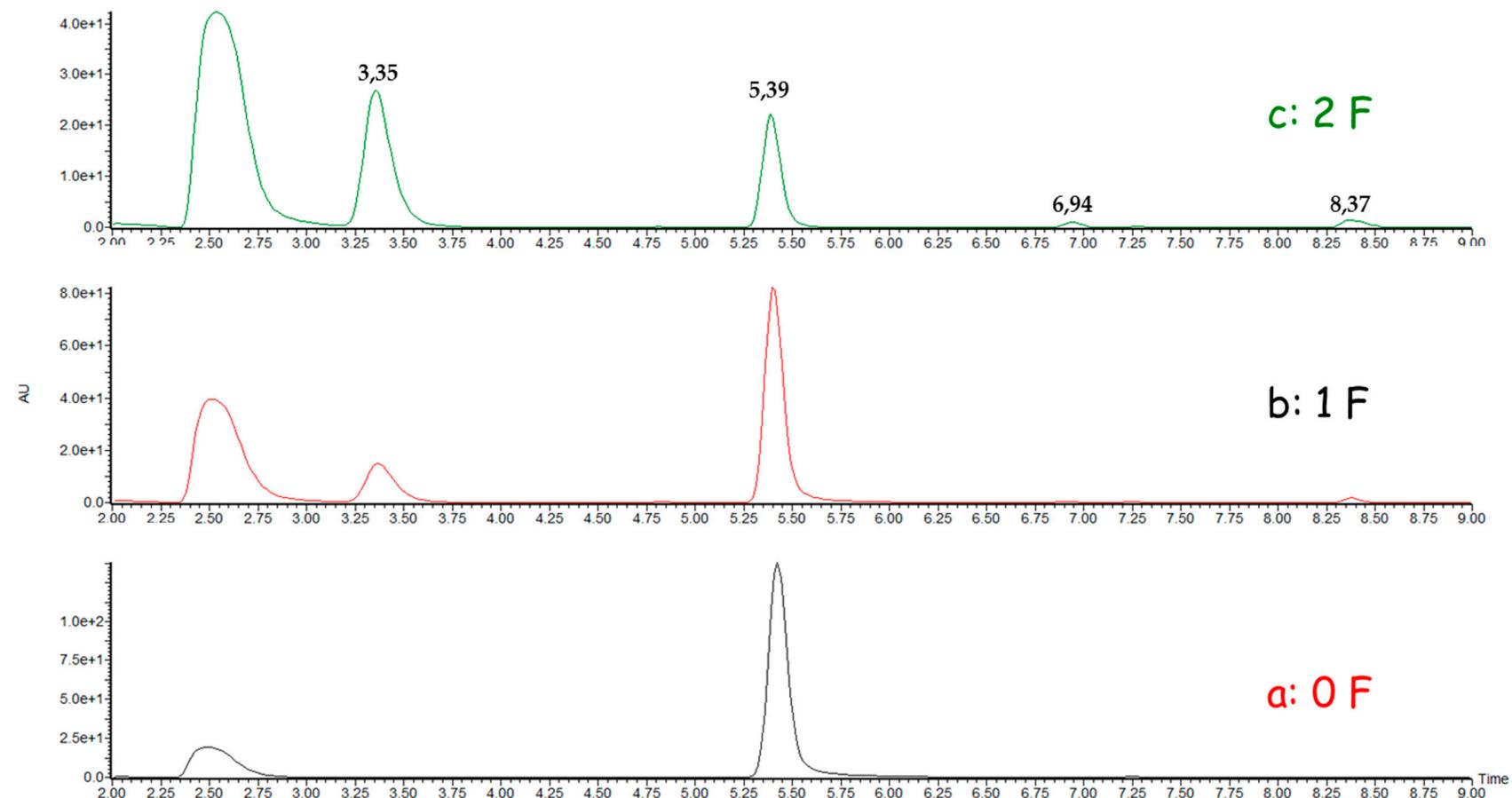
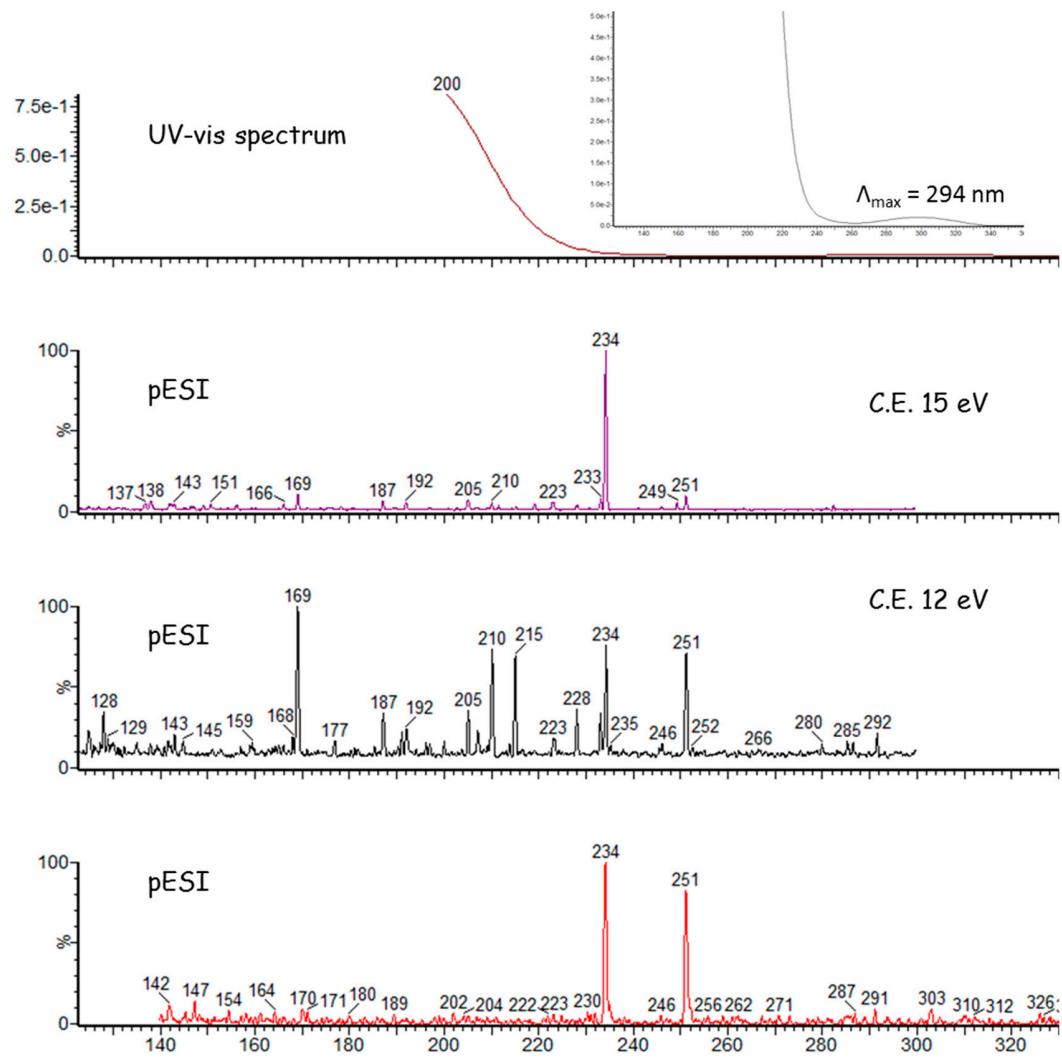
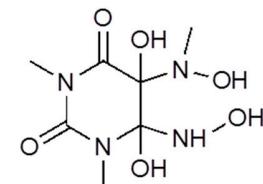


Figure 2S. ACN-H₂O: Diode array chromatograms of catholyte before (a), after 1 F (b) and after 2 F anodic oxidation (c), with respect to caffeine, in ACN-H₂O. Divided cell, Pt electrodes, r.t., N₂ atmosphere, caffeine 0.02 M in ACN-0.1 M Et₄NBF₄ containing 0.02 M water. $E = +1.85$ V, vs SCE.



R.T. = 2.75 min



$M = 250 \text{ Da}$

Figure 3S. Compound 1: R.T. 2.75 min, calculated monoisotopic mass $M = 250.09 \text{ Da}$; UV-vis spectrum, positive Electrospray ionization (pESI) MS spectrum, pESI fragmentation MS spectra at different collision energies (C.E.), fragmentation pattern, proposed structure.

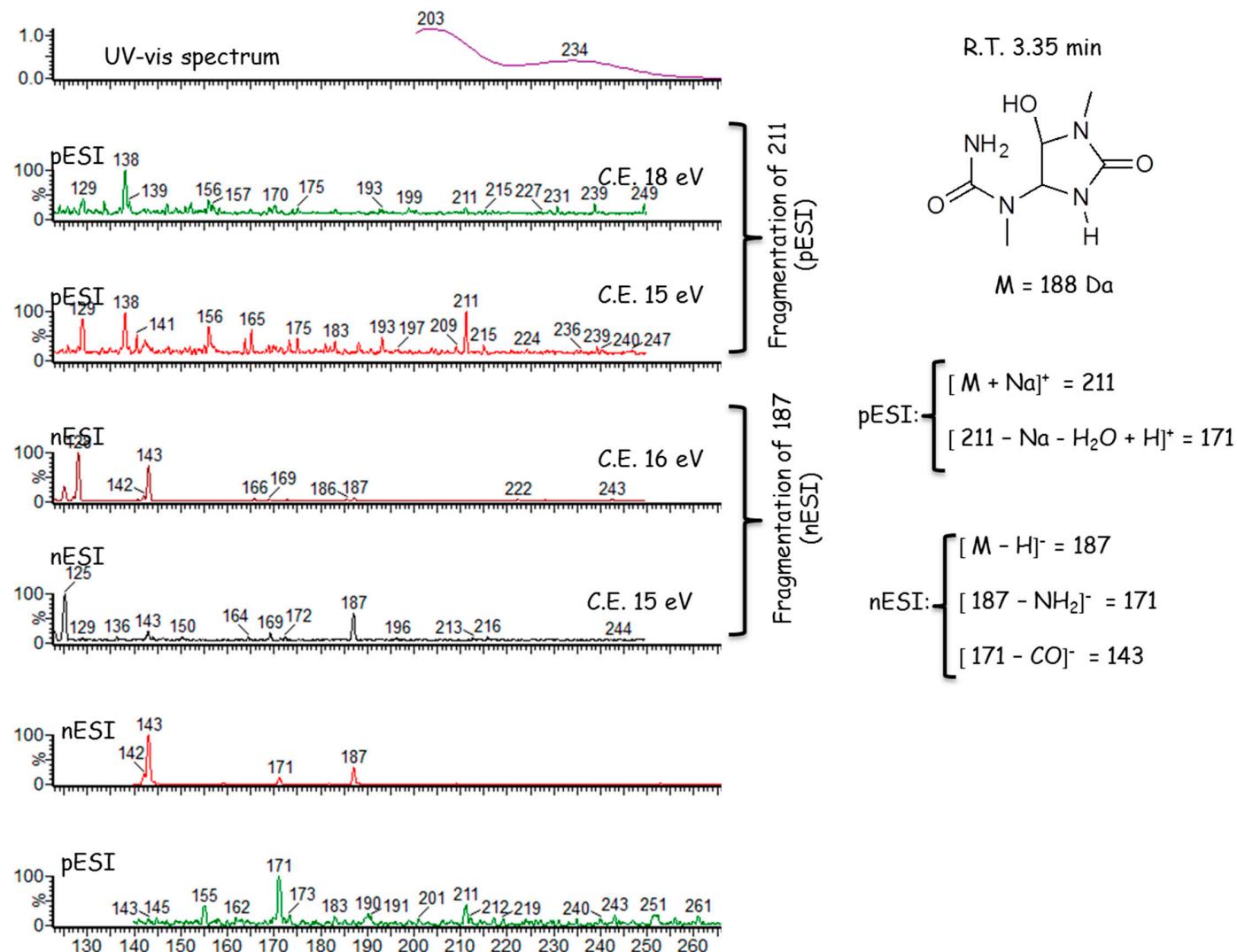


Figure 4S. Compound 2, R.T. 3.35 min, calculated monoisotopic mass M = 188.09 Da; UV-vis spectrum, positive and negative Electrospray ionization (pESI, nESI) MS spectra, pESI and nESI fragmentation MS spectra at different collision energies (C.E.), fragmentation patterns, proposed structure.

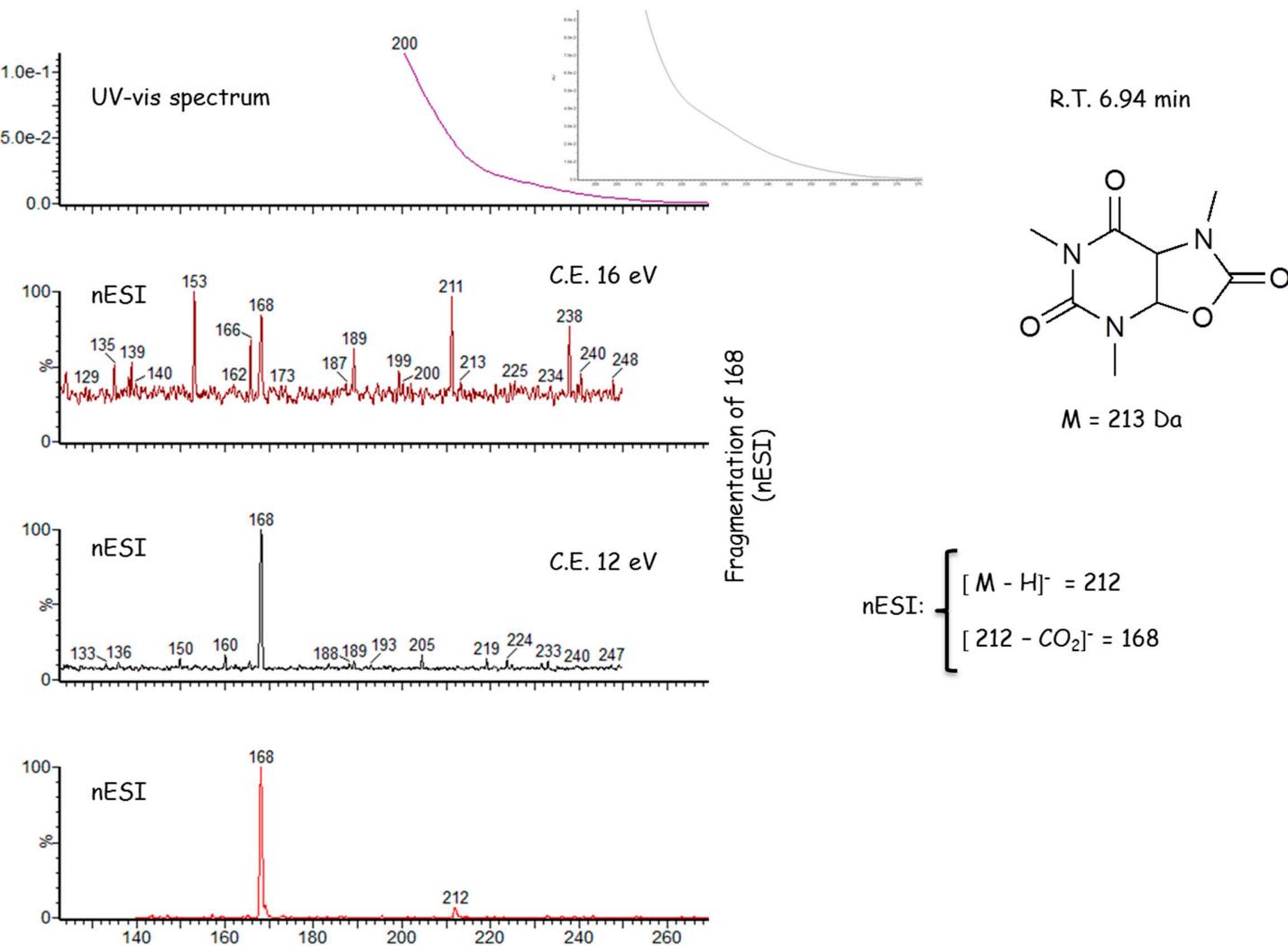
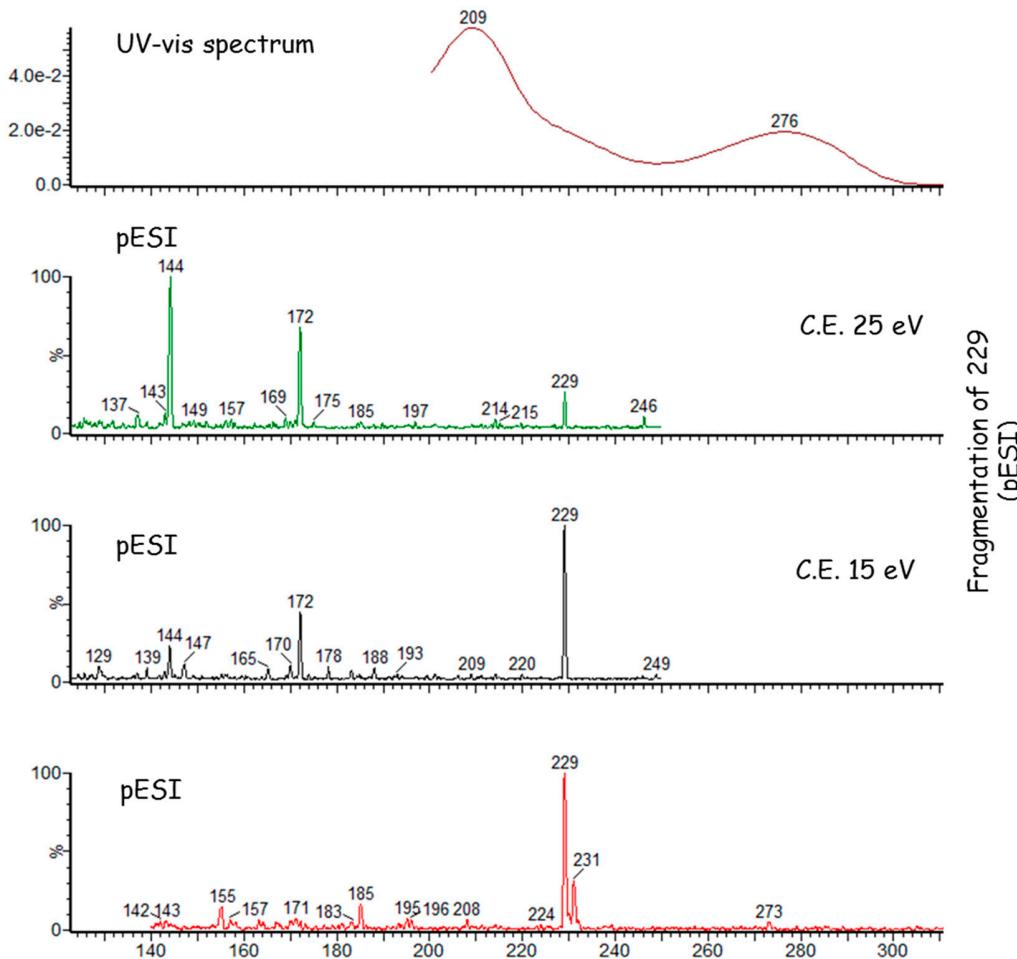
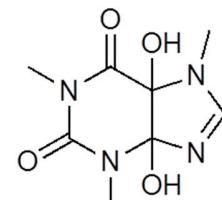


Figure 5S. Compound 4: R.T. 6.94 min, calculated monoisotopic mass $M = 213.07 \text{ Da}$; UV-vis spectrum, negative Electrospray ionization (nESI) MS spectra, nESI fragmentation MS spectra at different collision energies (C.E.), fragmentation patterns, proposed structure.



R.T. 8.37 min



$M = 228$ Da

pESI:

$$\begin{cases} [M + H]^+ = 229 \\ [229 - CH_3]^+ = 214 \\ [229 - CONCH_3]^+ = 172 \\ [172 - CO]^+ = 144 \end{cases}$$

Figure 6S. Compound 5: R.T. 8.37 min, calculated monoisotopic mass $M = 228.09$ Da; UV-vis spectrum, positive Electrospray ionization (pESI) MS spectra, pESI fragmentation MS spectra at different collision energies (C.E.), fragmentation patterns, proposed structure.