Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Hydroxyl Radical Induced Oxidation of Theophylline in Water: A Kinetic and Mechanistic Study

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(Electronic Supplementary Information)

Table S1 - The spectral and kinetic parameters of the reaction of $^{\bullet}OH$, $SO_4^{\bullet-}$, $N_3^{\bullet}$ and $O^{\bullet-}$ with theophylline

Radical	**pH**	**λ_{max} / nm**	**k_2 / 10^9 dm^3 mol^{-1} s^{-1}**
$^{\bullet}OH$	5.9	330, 500	8.22 ± 0.03
	10.2	340	7.11 ± 0.07
$SO_4^{\bullet-}$	6	350	7.51 ± 0.04
	9.3	350	5.37 ± 0.03
$N_3^{\bullet}$	4	350	4.05 ± 0.02
	6.1	340	7.61 ± 0.02
	9.6	350	8.42 ± 0.06
$O^{\bullet-}$	~ 13	320, 350	1.95 ± 0.02

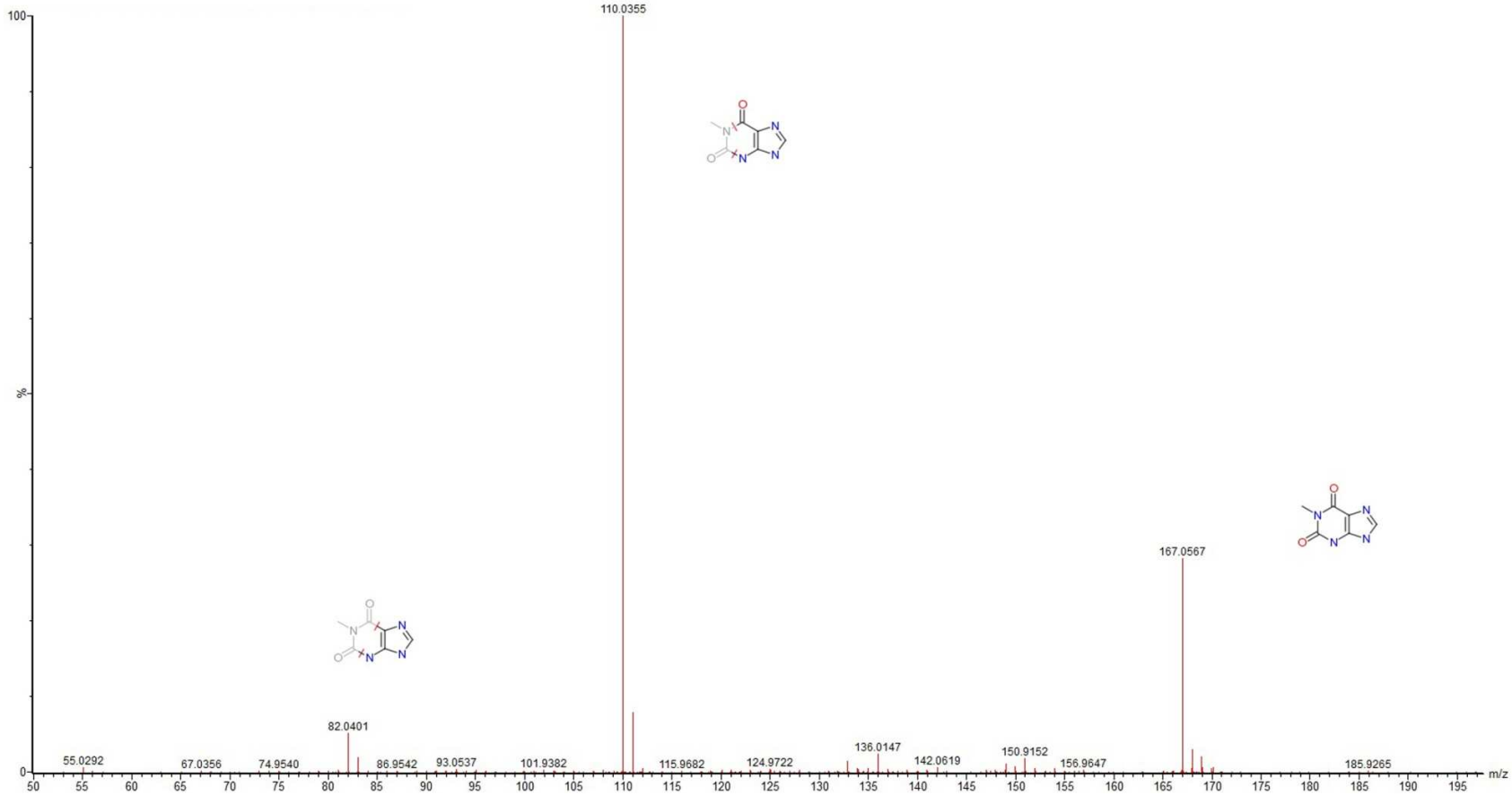

Figure S1 – MS/MS spectrum of 1-methylxanthine (**ii**)

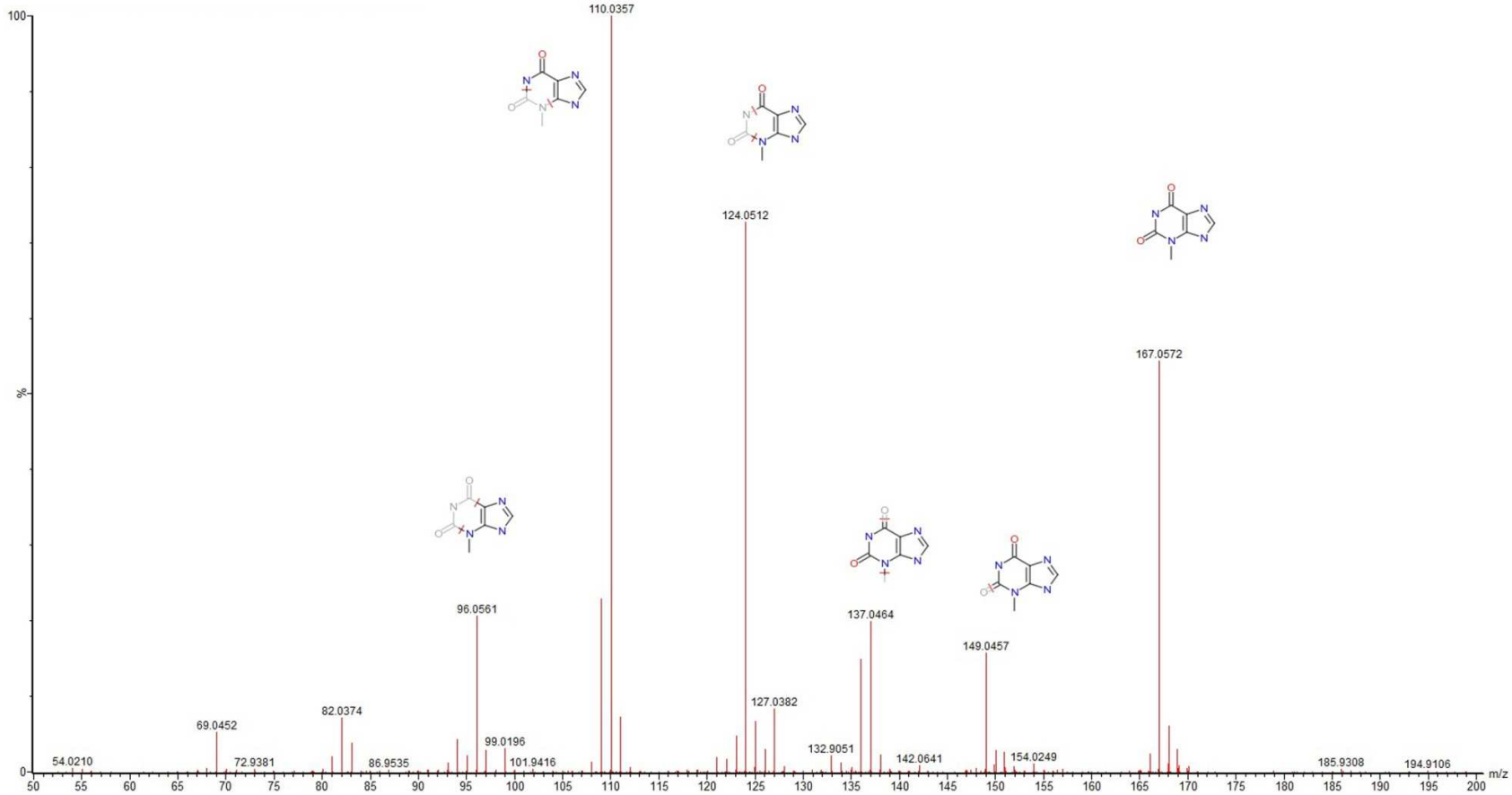

Figure S2 - MS/MS spectrum of 3-methylxanthine (**iii**)

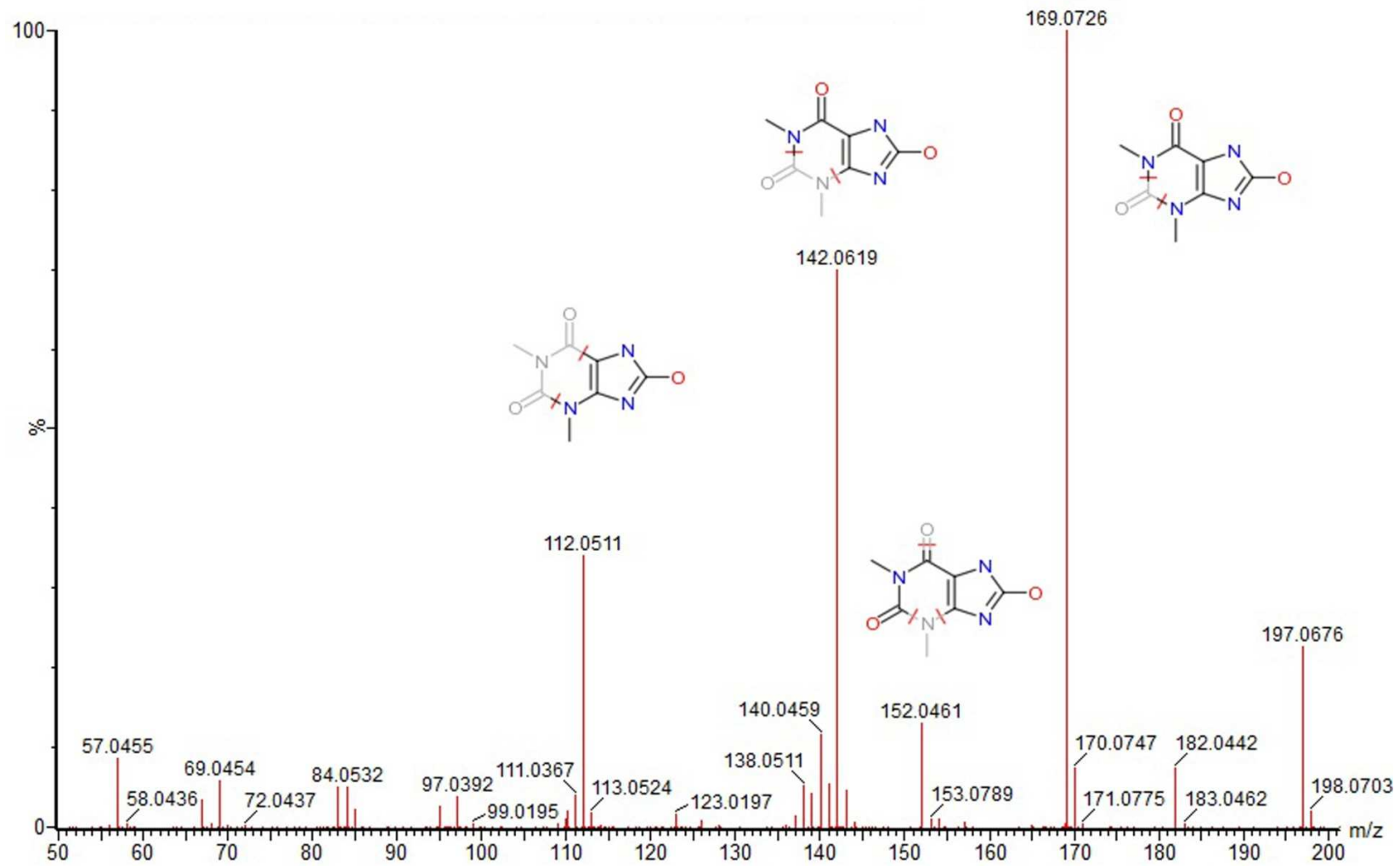

Figure S3 - MS/MS spectrum of 1,3-dimethyluric acid (**i**)

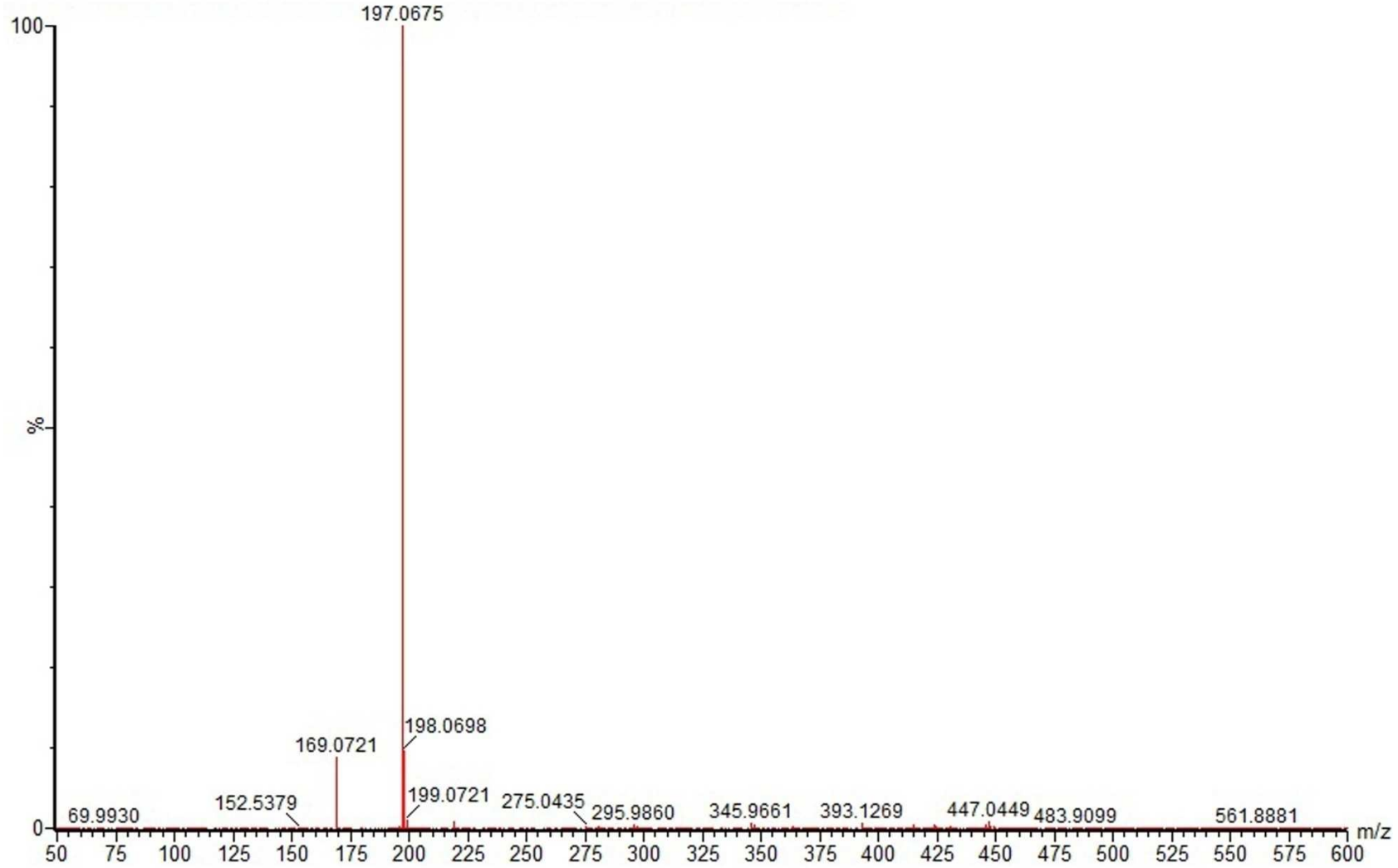

Figure S4 - Mass spectrum of 1,3-dimethyluric acid (**i**) in positive ionization mode

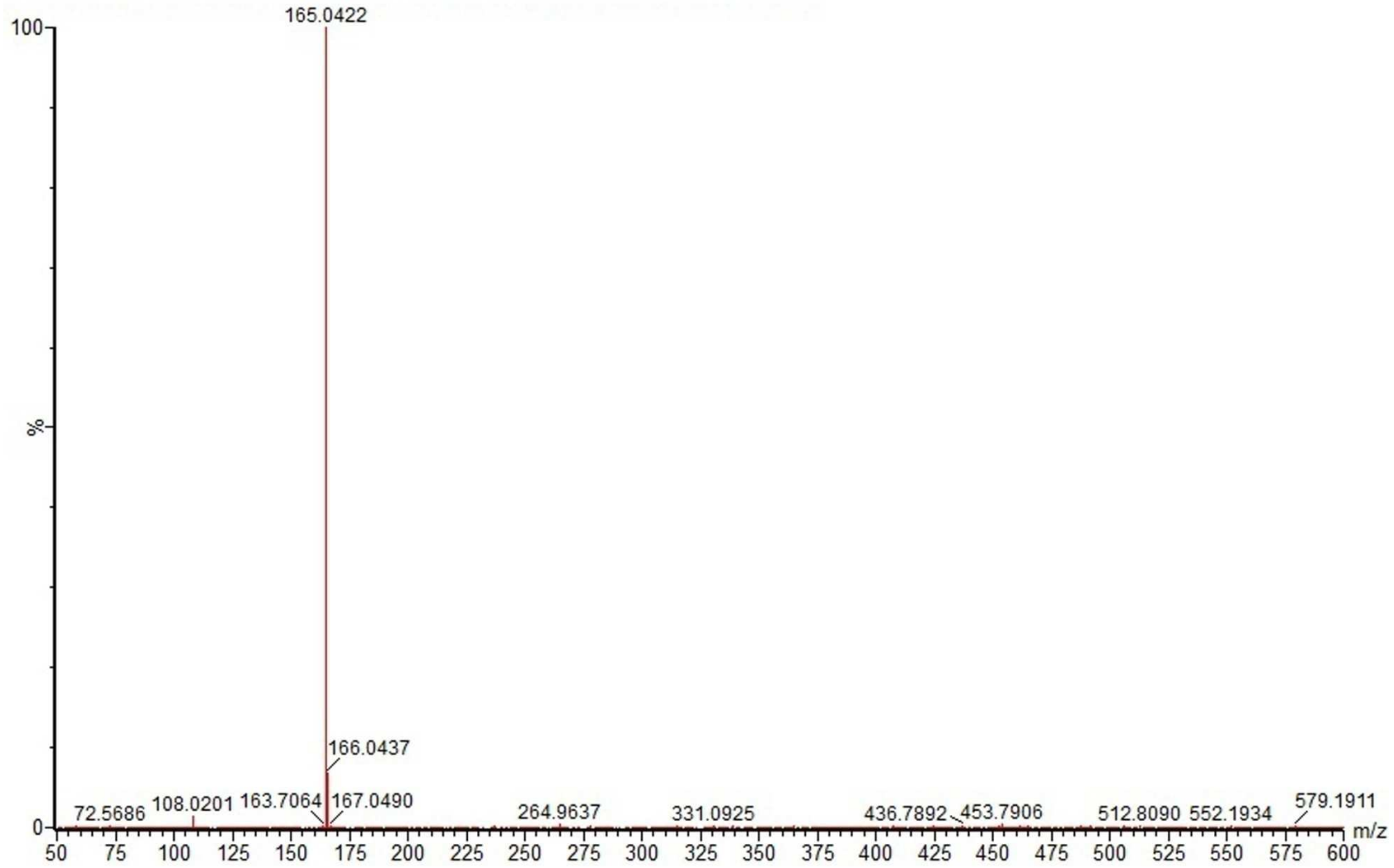

Figure S5 - Mass spectrum of 1-methylxanthine (**ii**) in negative ionization mode

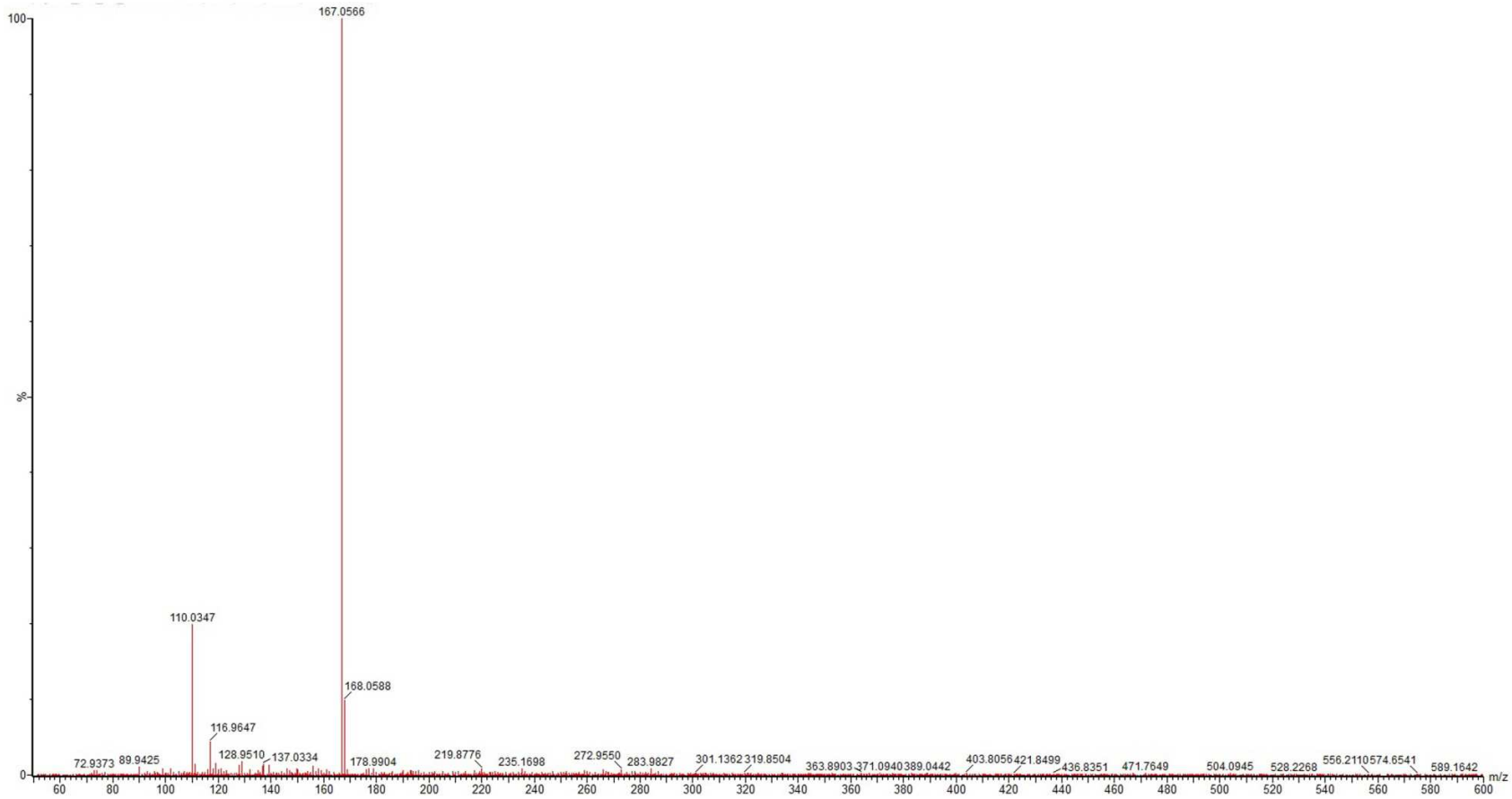

Figure S6 - Mass spectrum of 3-methylxanthine (**iii**) in positive ionization mode

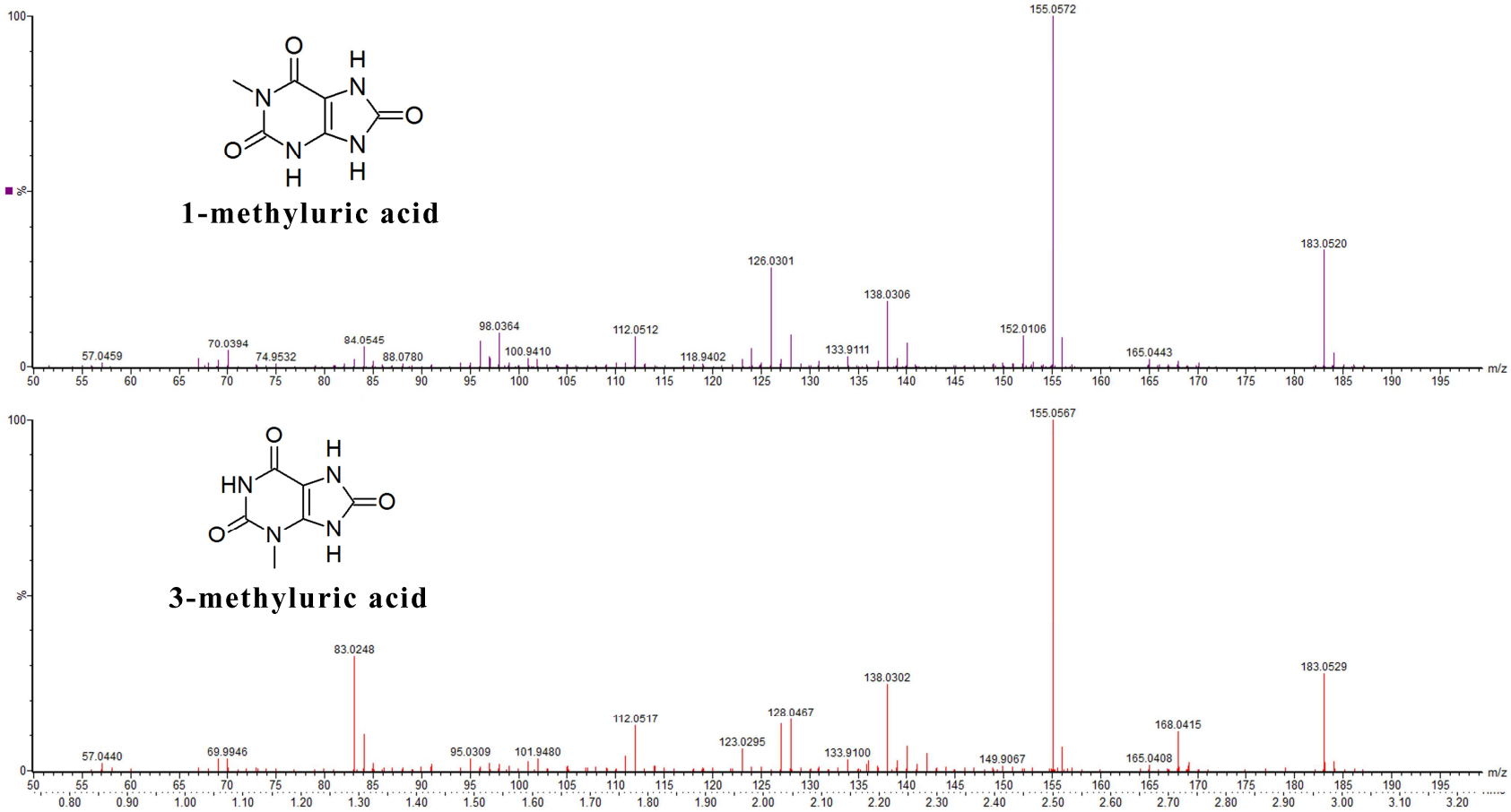

Figure S7 - MS/MS spectrum of 1-dimethyluric acid (**iv**) and 3-dimethyluric acid (**v**) in positive ionization mode

Figure S8 - Mass spectrum of xanthine (**vi**) in positive ionization mode

Figure S9 - Mass spectrum of 1/3-methyl tetrahydro-1H-purine-2,6-dione (**vii**) in negative ionization mode

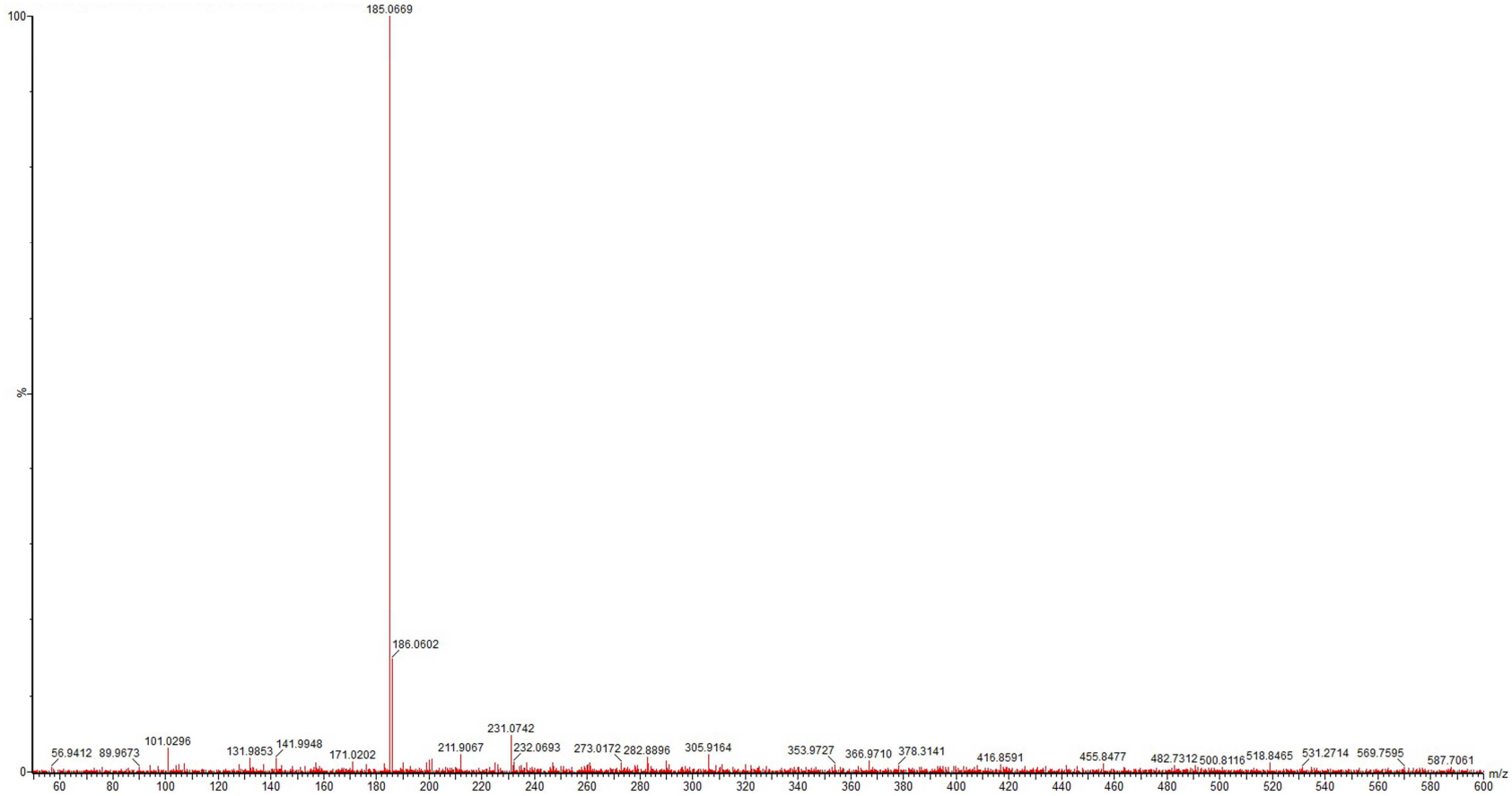

Figure S10 - Mass spectrum of 8-hydroxy-1/3-methyl-3,7,8,9-tetrahydro-1H-purine-2,6-dione (**viii**) in positive ionization mode

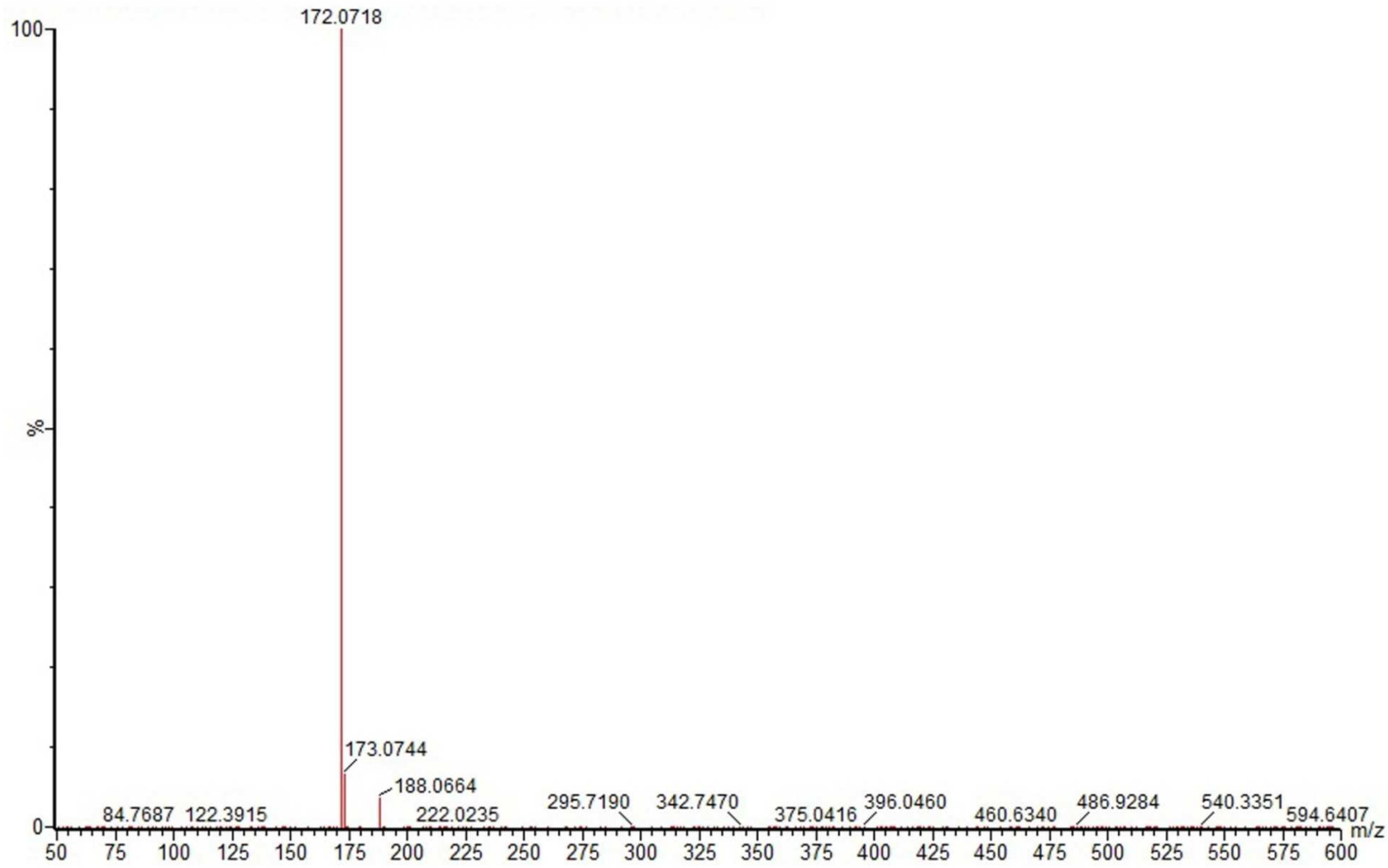

Figure S11 - Mass spectrum of 5/6-amino derivative of 5/6-hydroxy-1,3-dimethylpyrimidine-2,4(1H,3H)-dione (**ix**) in positive ionization mode

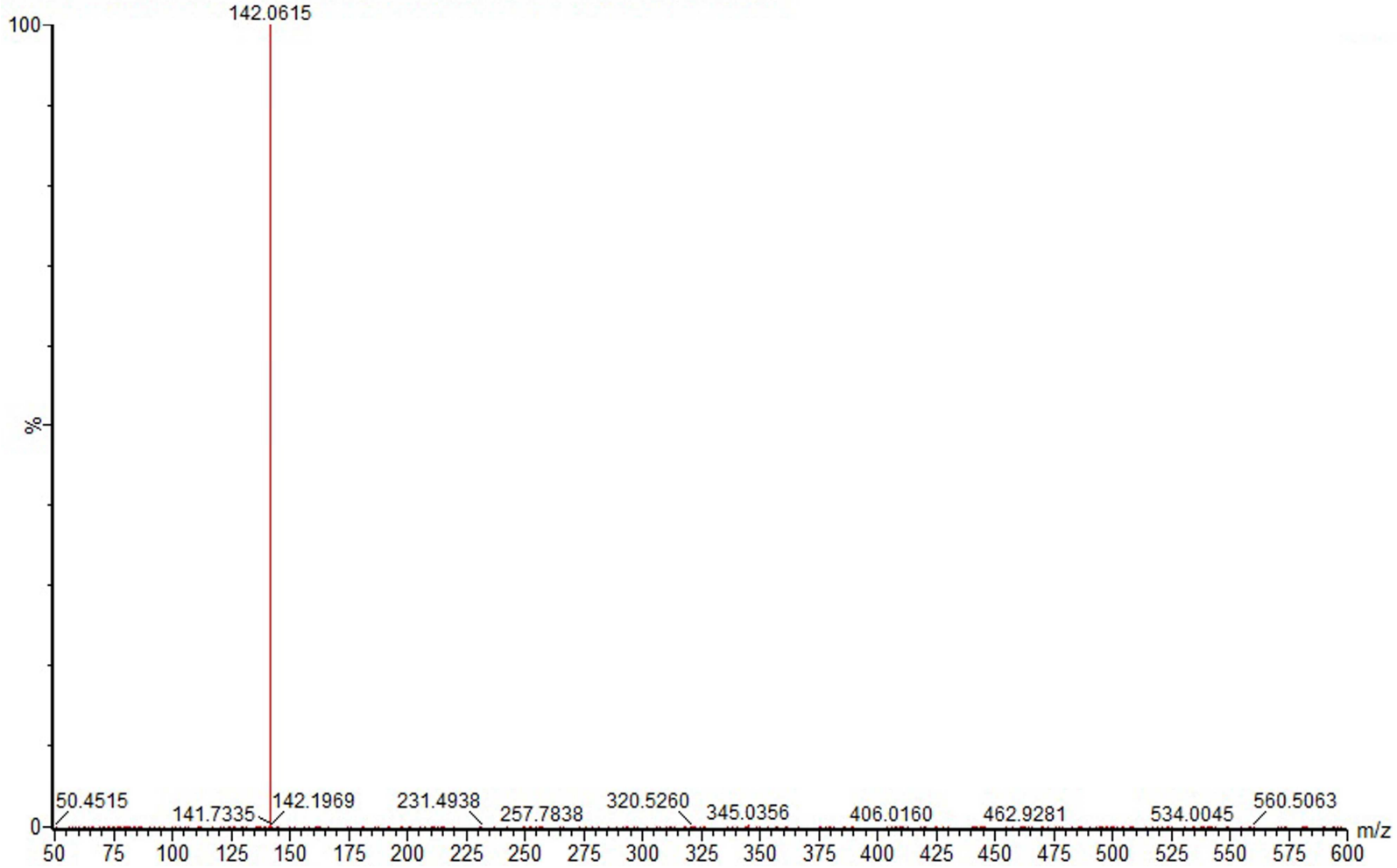

Figure S12 - Mass spectrum of 5/6-amino derivative of 1/3- methylpyrimidine-2,4(1H,3H)-dione (**x**) in positive ionization mode

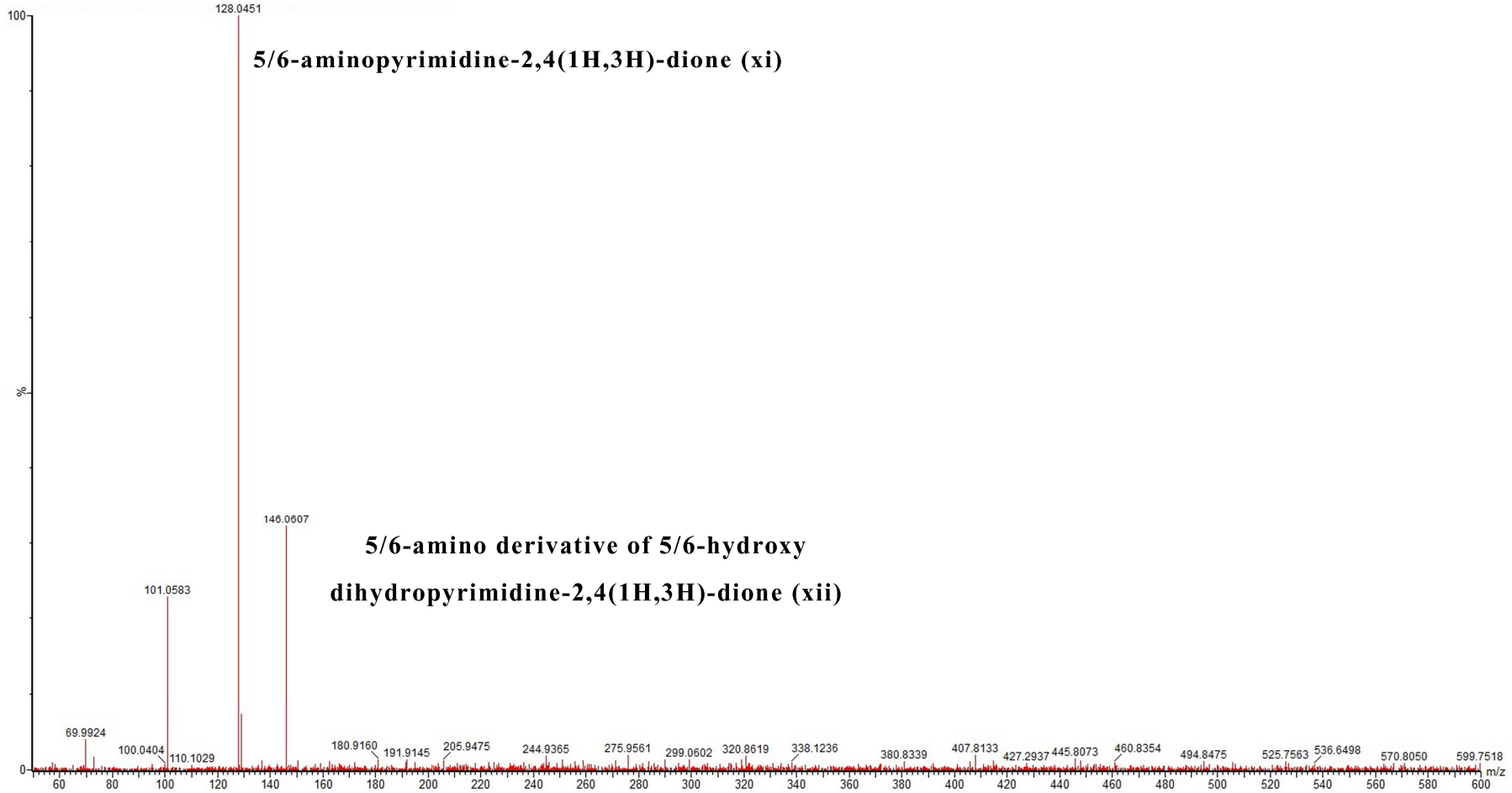

Figure S13 - Mass spectrum of 5/6-aminopyrimidine-2,4(1H,3H)-dione (**xi**) and 5/6-amino derivative of 5/6-hydroxydihydropyrimidine-2,4(1H,3H)-dione (**xii**) in positive ionization mode

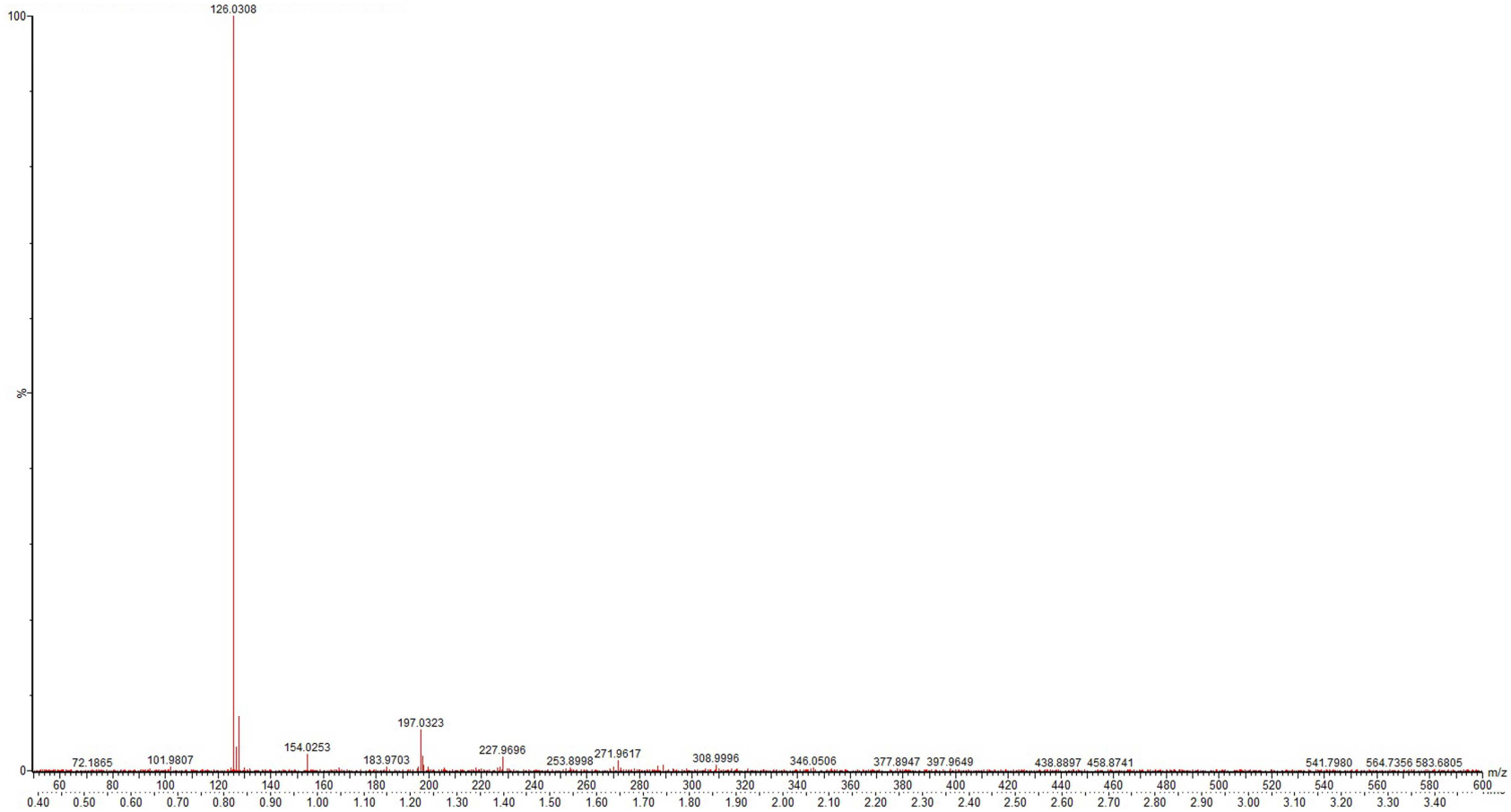

Figure S14 - Mass spectrum of 5/6-aminopyrimidine-2,4(1H,3H)-dione (**xi**) in negative ionization mode

Figure S15 - Mass spectrum of 1/3-methylpyrimidine-2,4(1H,3H)-dione **(xiii)** in positive ionization mode

Figure S16 - Mass spectrum of 5,6-diaminopyrimidine-2,4(1H,3H)-dione (**xiv**) in positive ionization mode

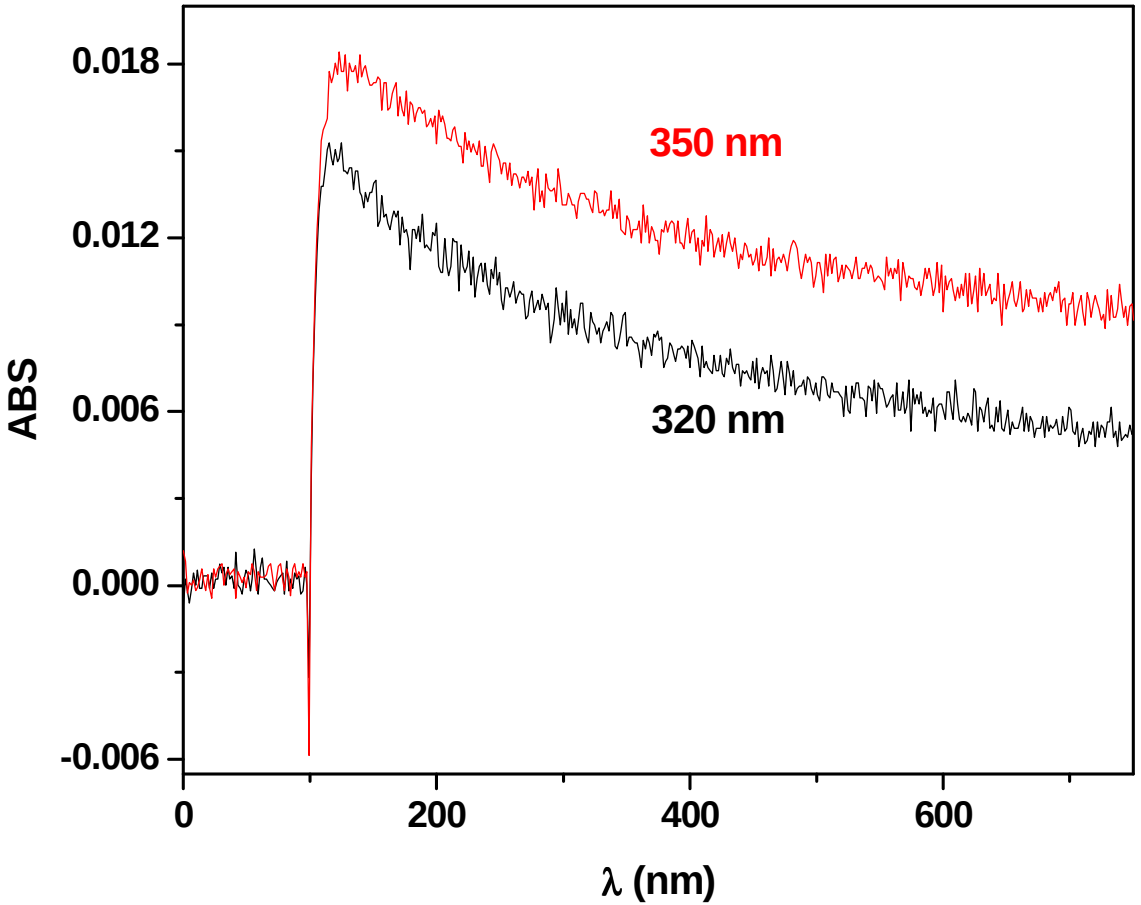

Figure S17 - Decay traces at 320 nm (Red) and 350 nm (Black) in the case of reaction of $O^{\bullet -}$ with theophylline.

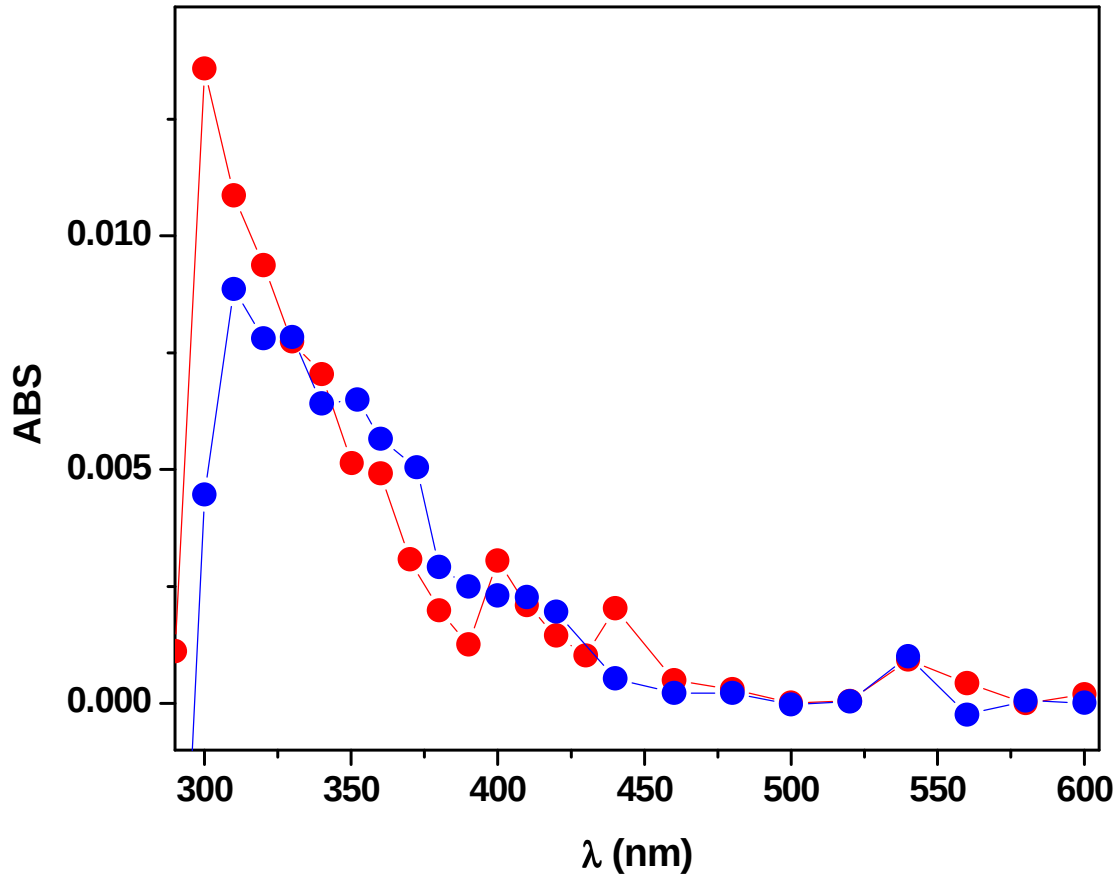

Figure S18 - Transient absorption spectrum of theophylline (1×10^{-4} mol dm^{-3}) recorded during its reaction with $SO_4^{\bullet -}$ after (●) 347 μs (pH 6.0) and with $N_3^{\bullet}$ after (●) 328 μs (pH 6.1).

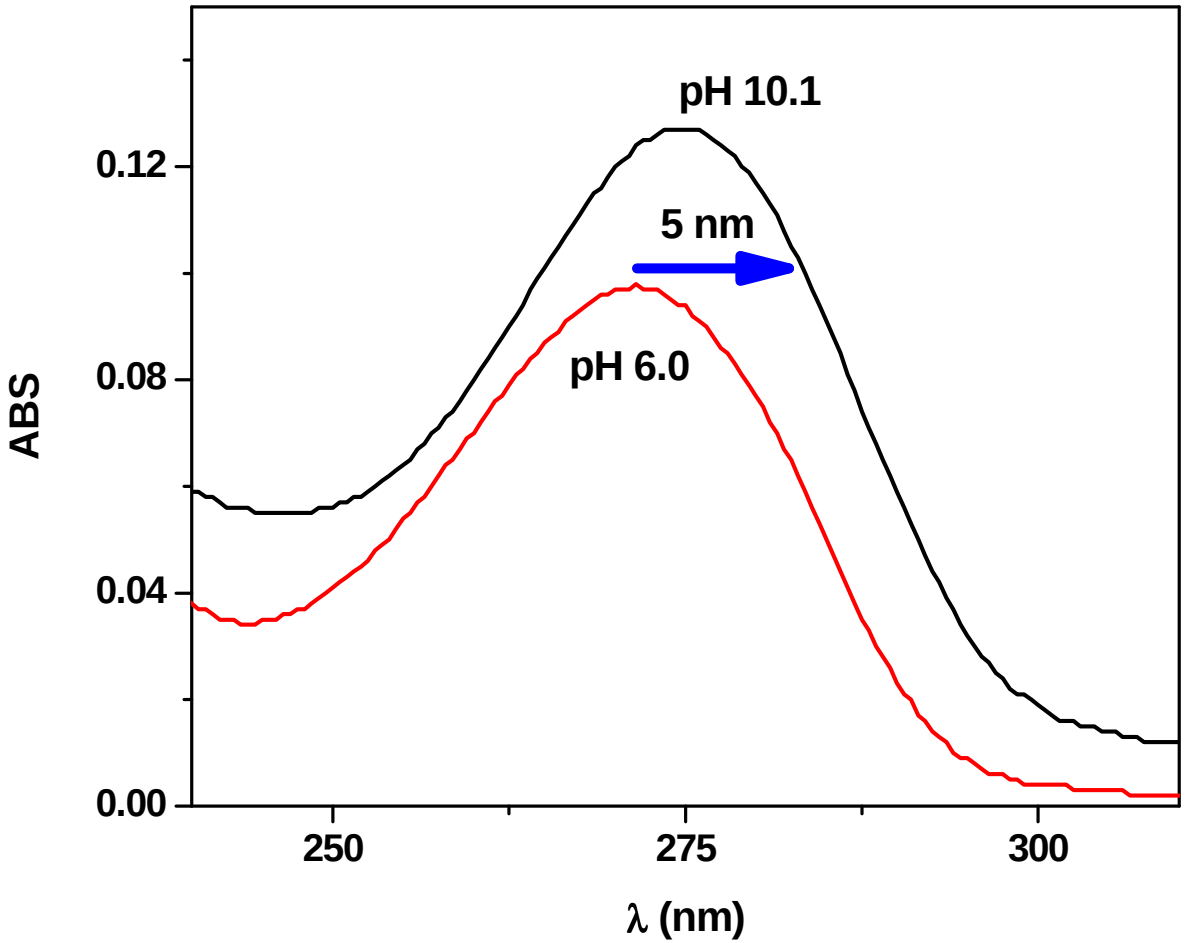

Figure S19 - UV-Vis Spectrum of theophylline at pH 6 and 10.1.

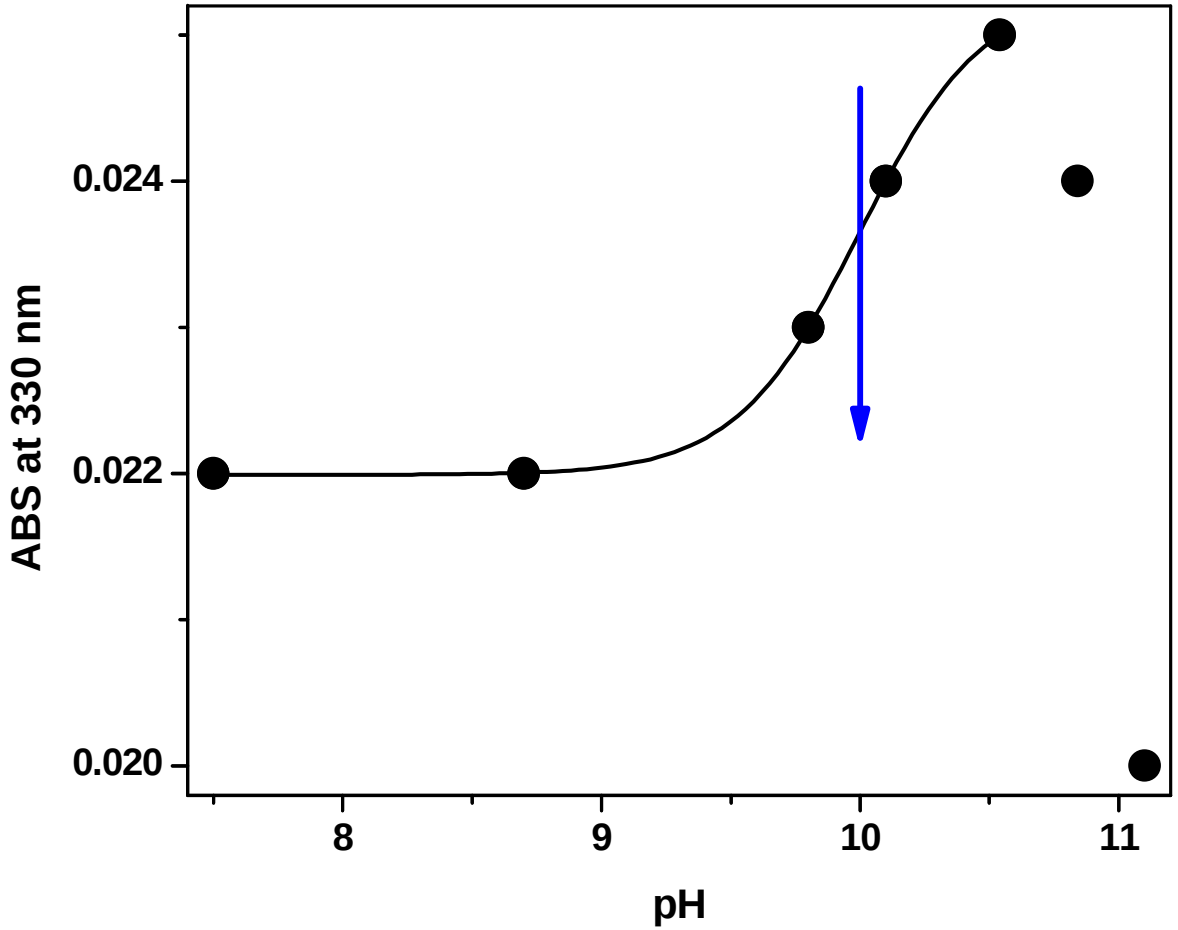

Figure S20- Plot of absorbance of transient at 330 nm obtained by the reaction of theophylline with $^{\bullet}OH$ against pH.

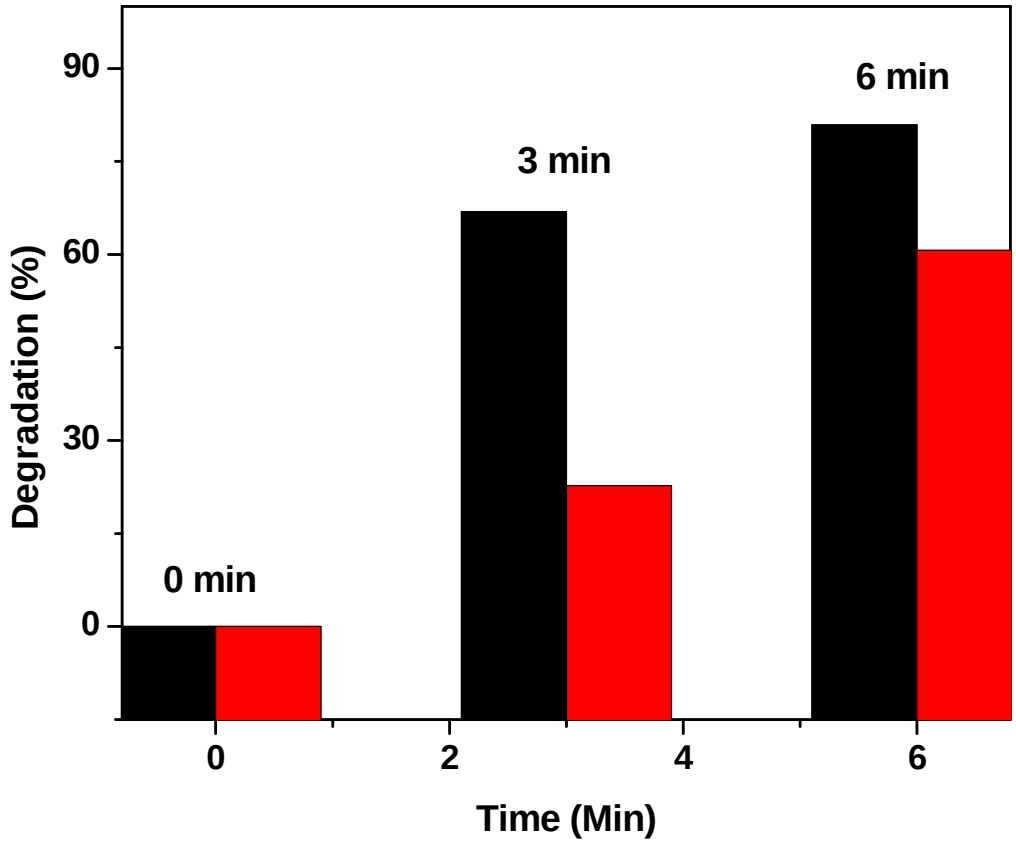

Figure S21 - Percentage degradation of theophylline in N_2 purged (Red) and aerated (Black) conditions as a function of time