

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

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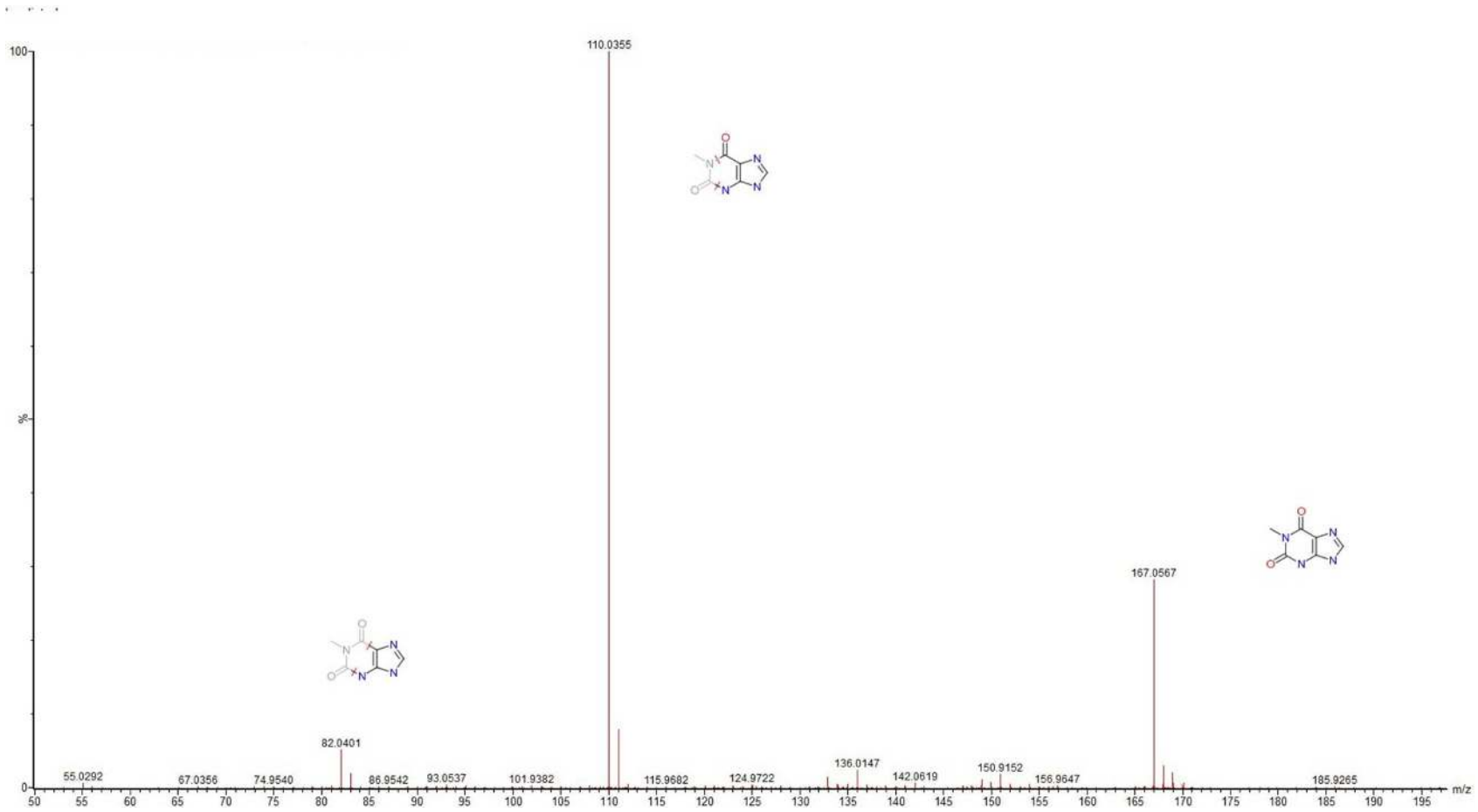
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**(Electronic Supplementary Information)**

**Table S1** - The spectral and kinetic parameters of the reaction of  $\bullet\text{OH}$ ,  $\text{SO}_4^{\bullet-}$ ,  $\text{N}_3^{\bullet}$  and  $\text{O}^{\bullet-}$  with theophylline

Radical	pH	$\lambda_{\text{max}} / \text{nm}$	$k_2 / 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
$\bullet\text{OH}$	5.9	330, 500	$8.22 \pm 0.03$
	10.2	340	$7.11 \pm 0.07$
$\text{SO}_4^{\bullet-}$	6	350	$7.51 \pm 0.04$
	9.3	350	$5.37 \pm 0.03$
$\text{N}_3^{\bullet}$	4	350	$4.05 \pm 0.02$
	6.1	340	$7.61 \pm 0.02$
	9.6	350	$8.42 \pm 0.06$
$\text{O}^{\bullet-}$	~ 13	320, 350	$1.95 \pm 0.02$



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

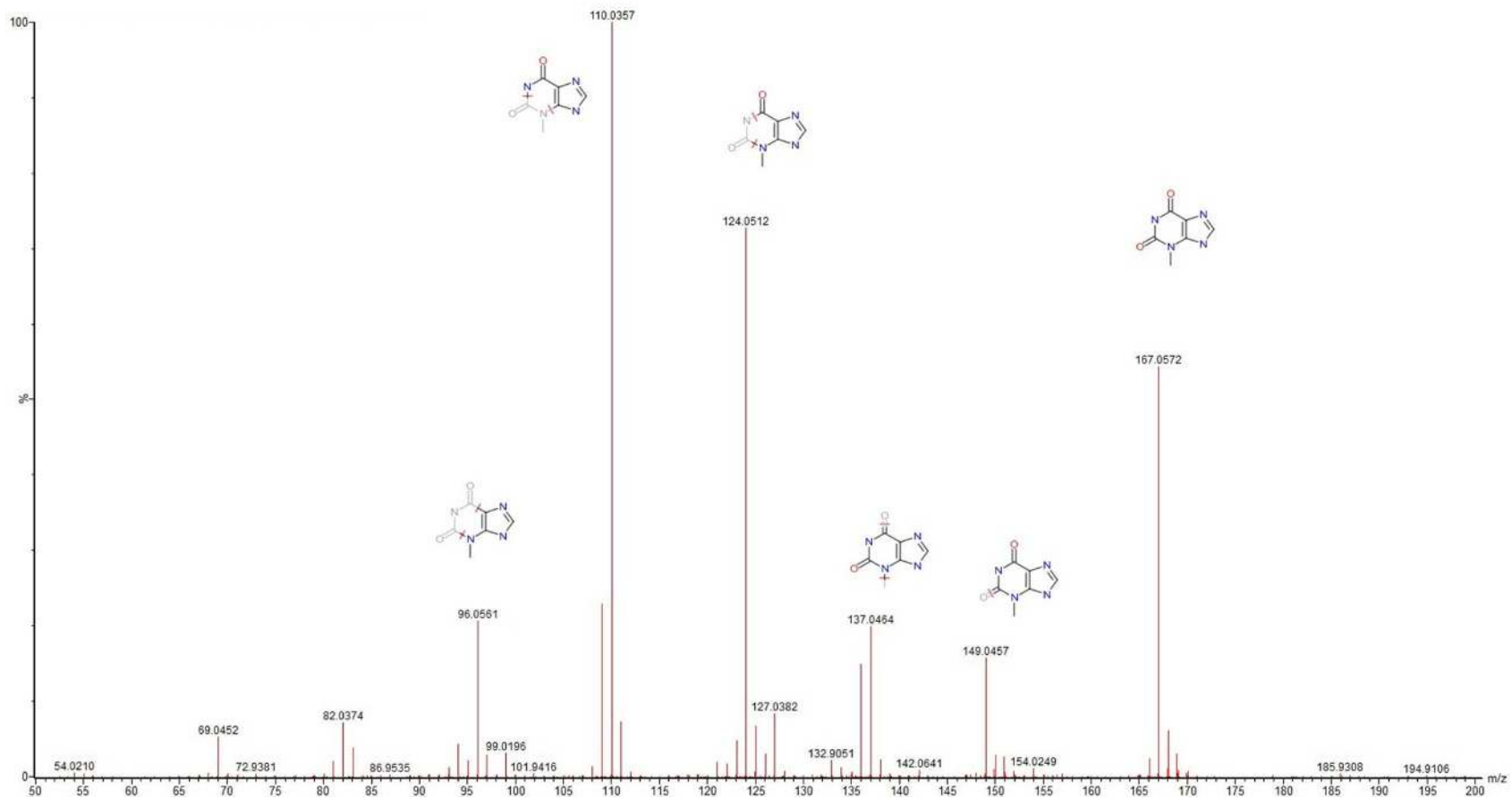
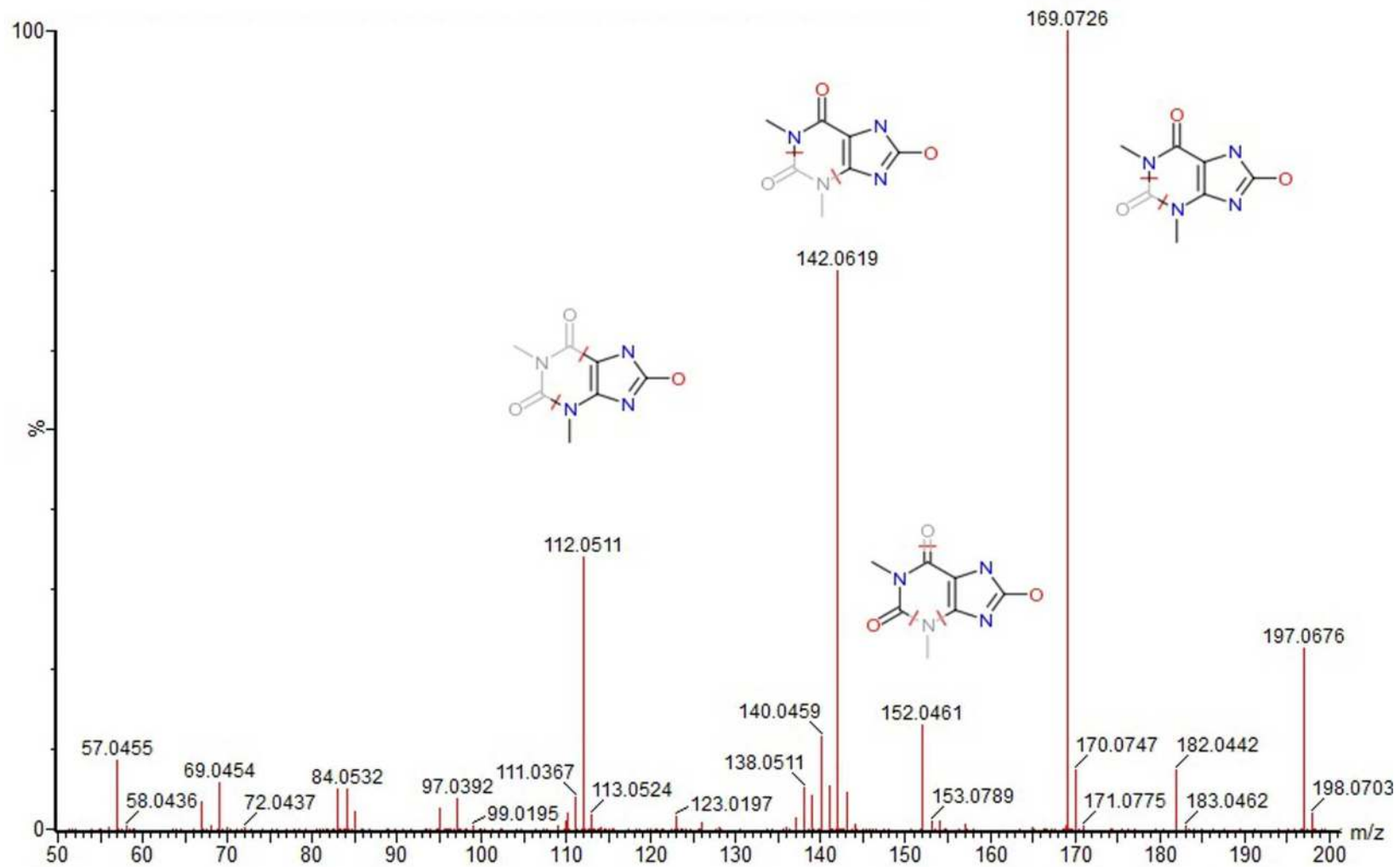
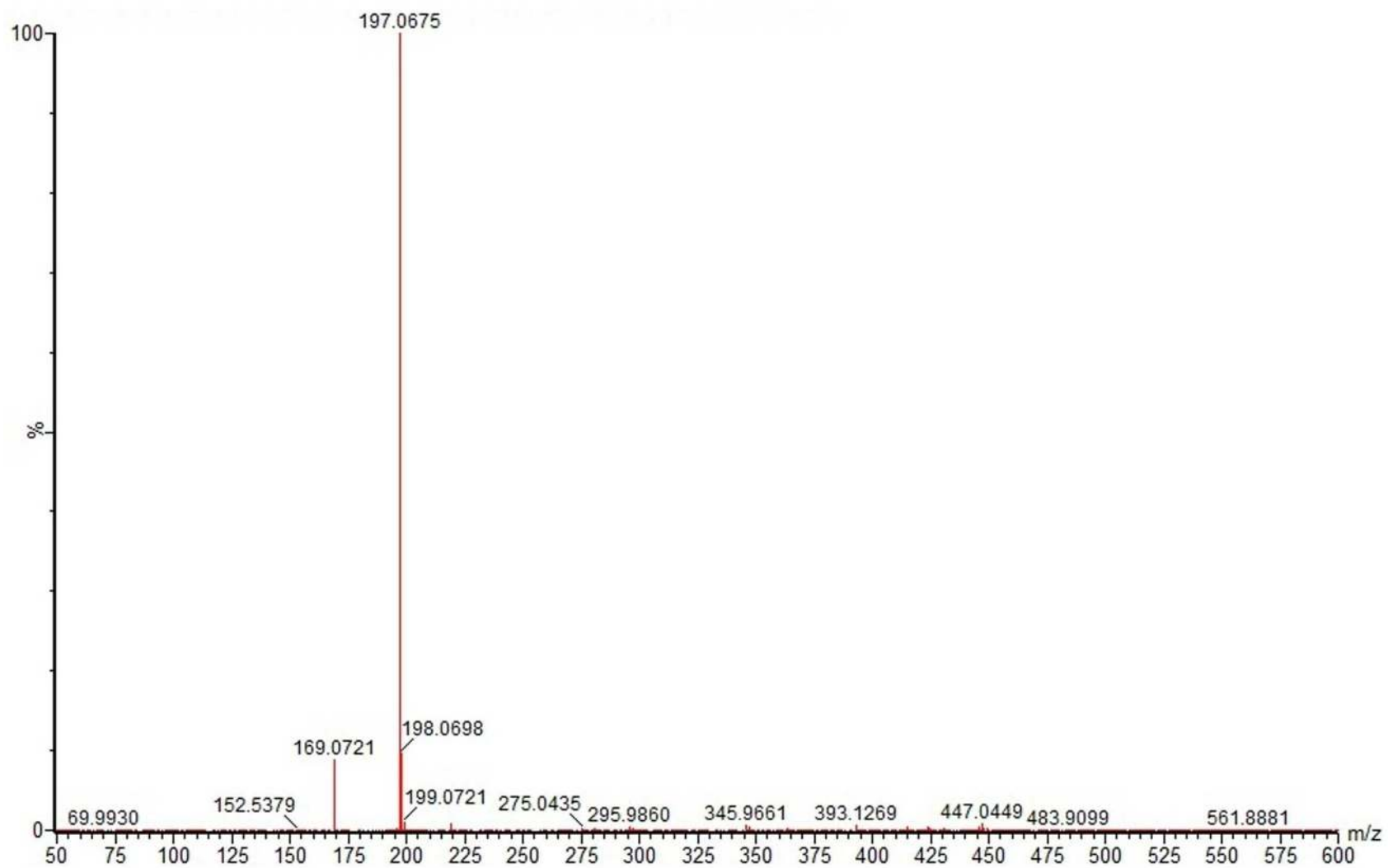


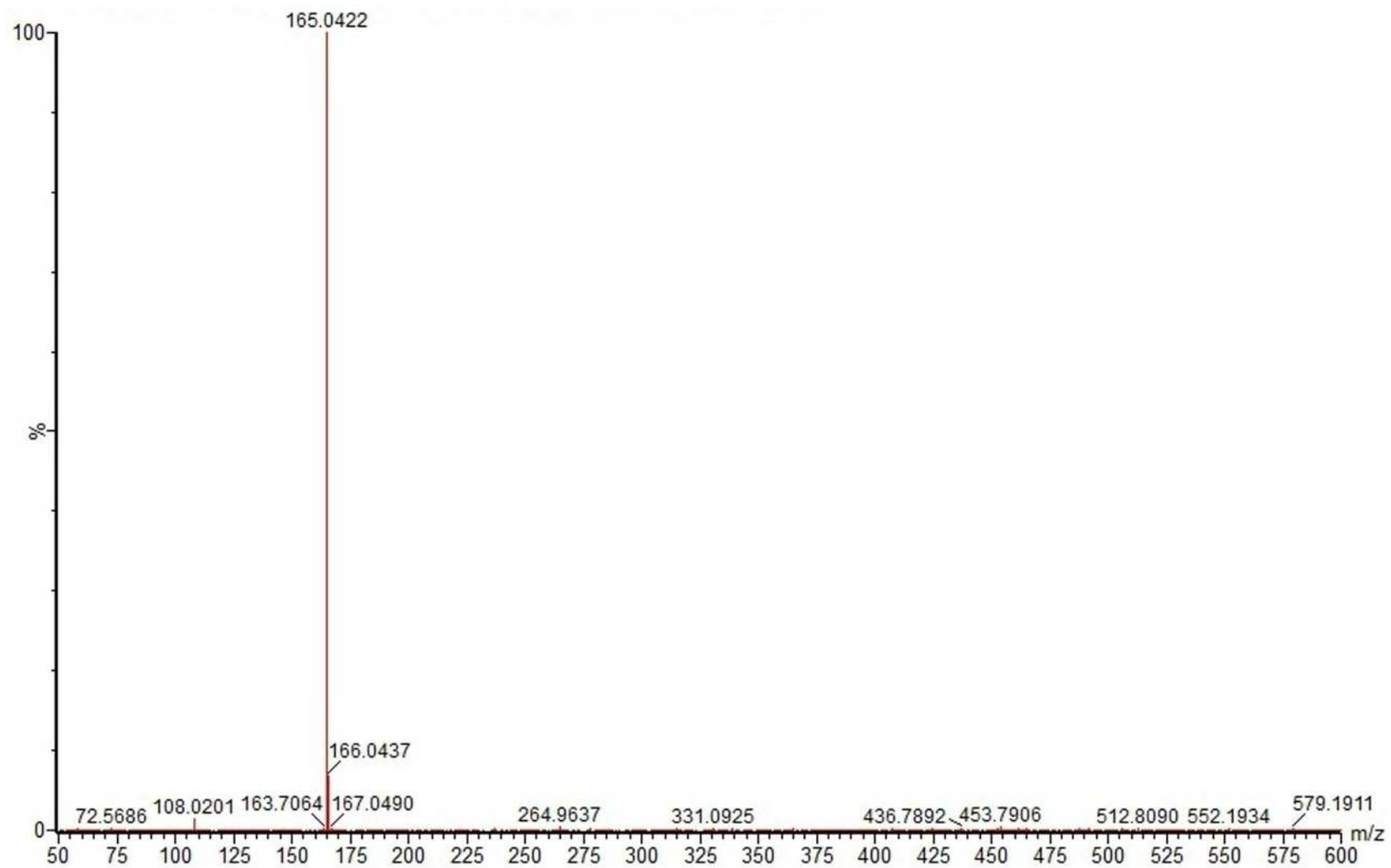
Figure S2 - MS/MS spectrum of 3-methylxanthine (iii)



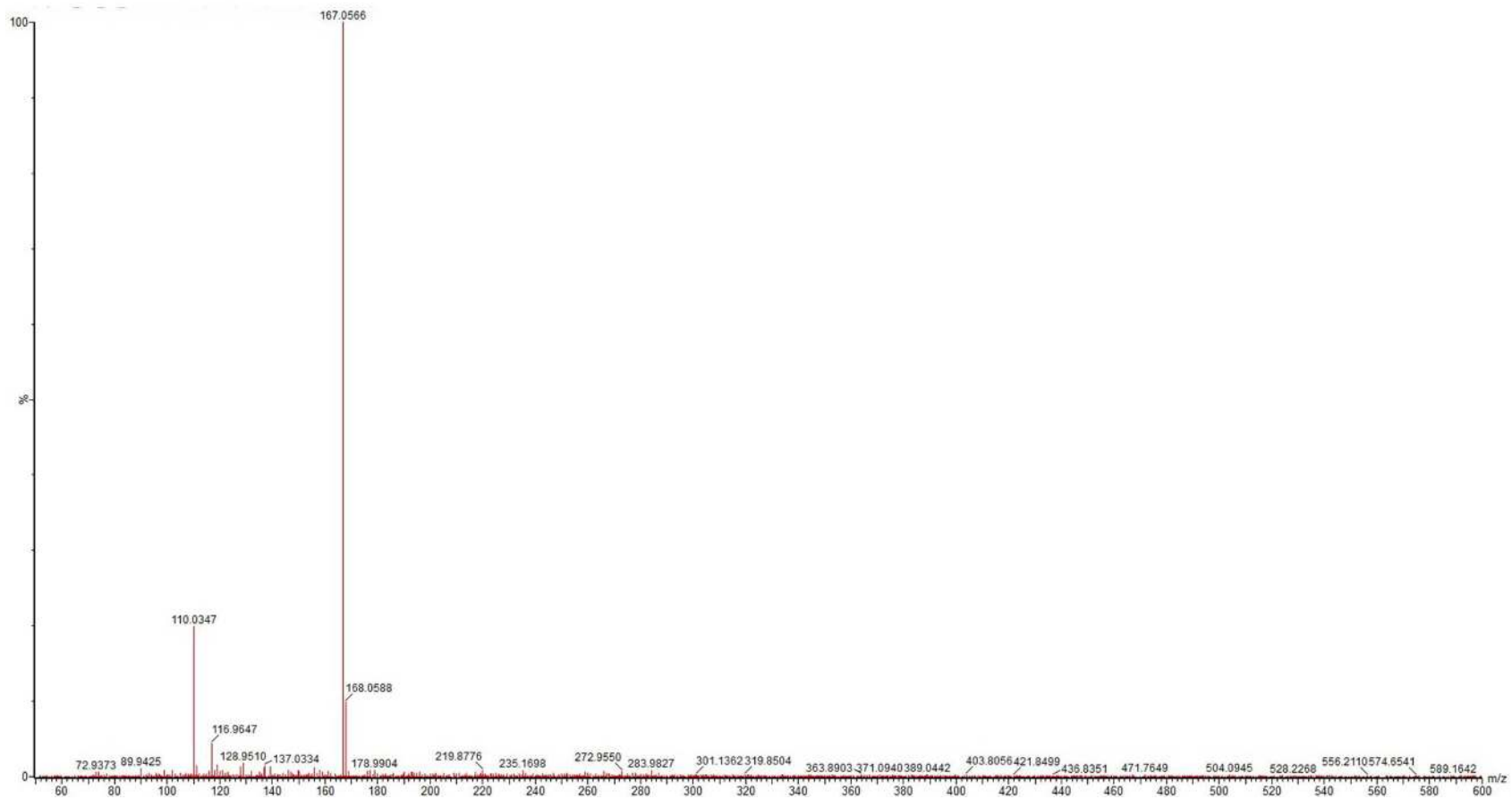
**Figure S3** - MS/MS spectrum of 1,3-dimethyluric acid (i)



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

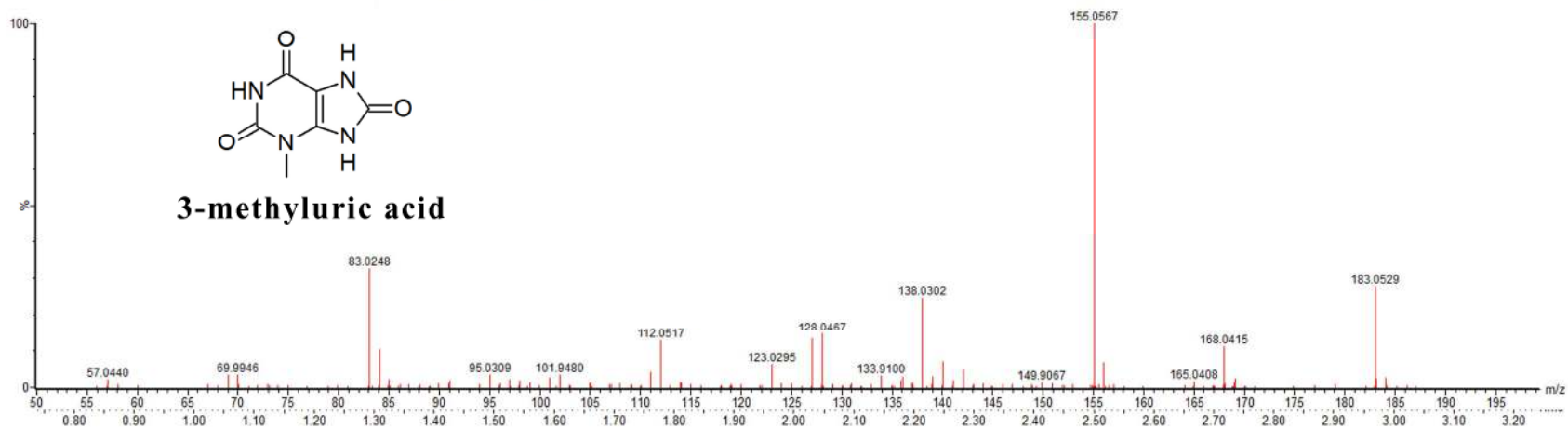
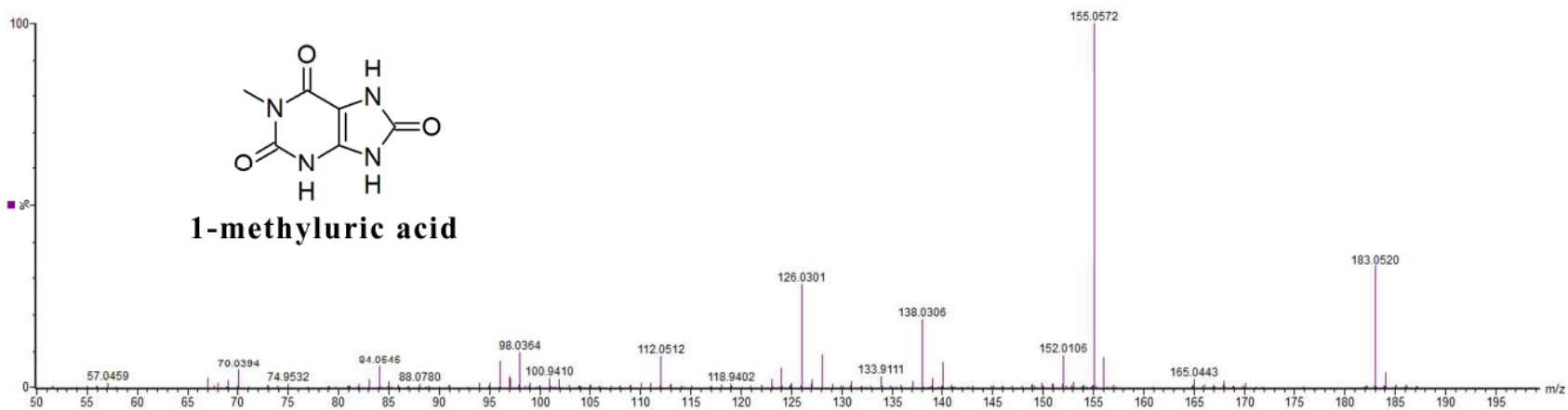


**Figure S5** - Mass spectrum of 1-methylxanthine (**ii**) in negative ionization mode

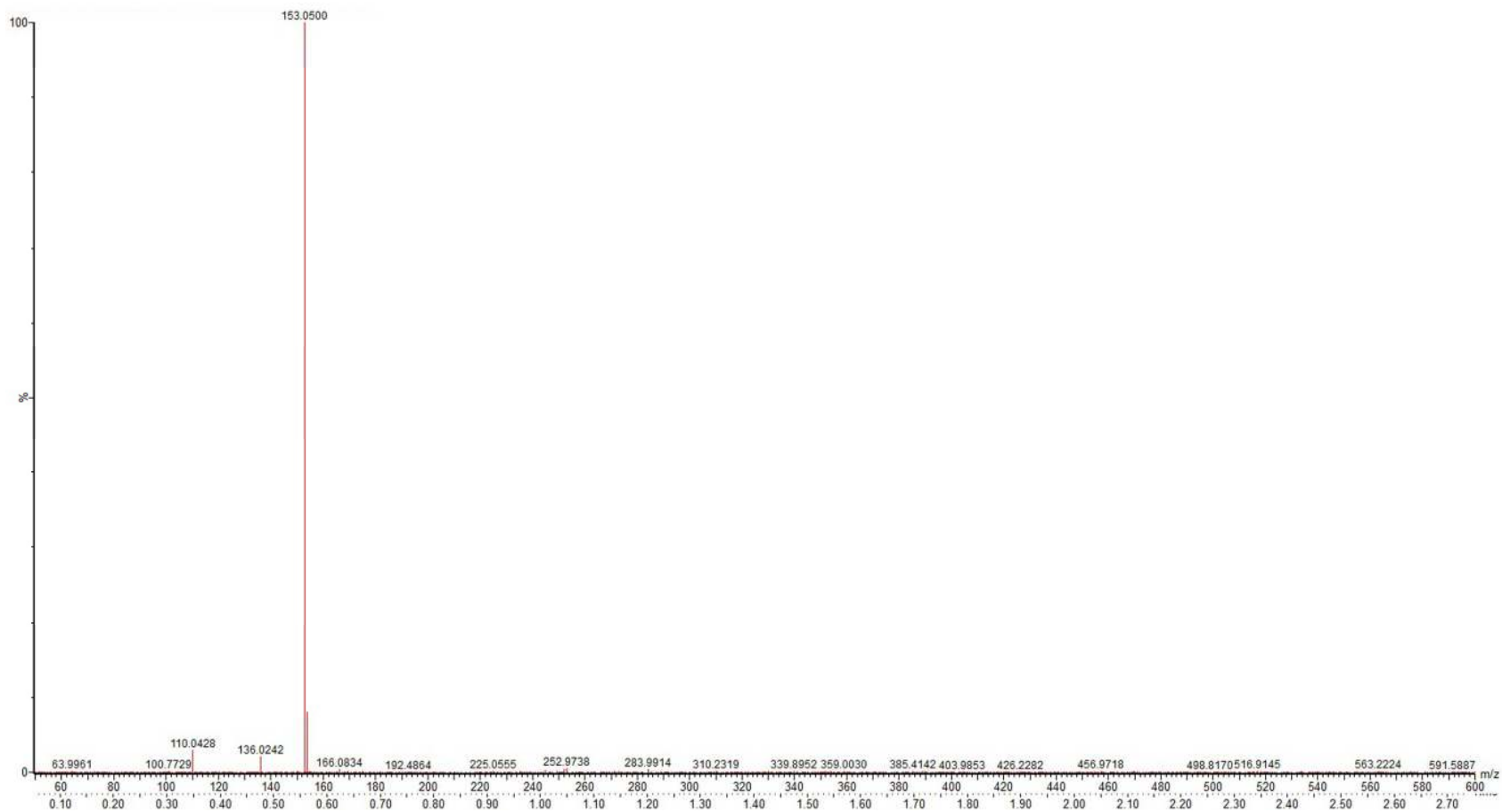


**Figure S6** - Mass spectrum of 3-methylxanthine (**iii**) in positive ionization mode





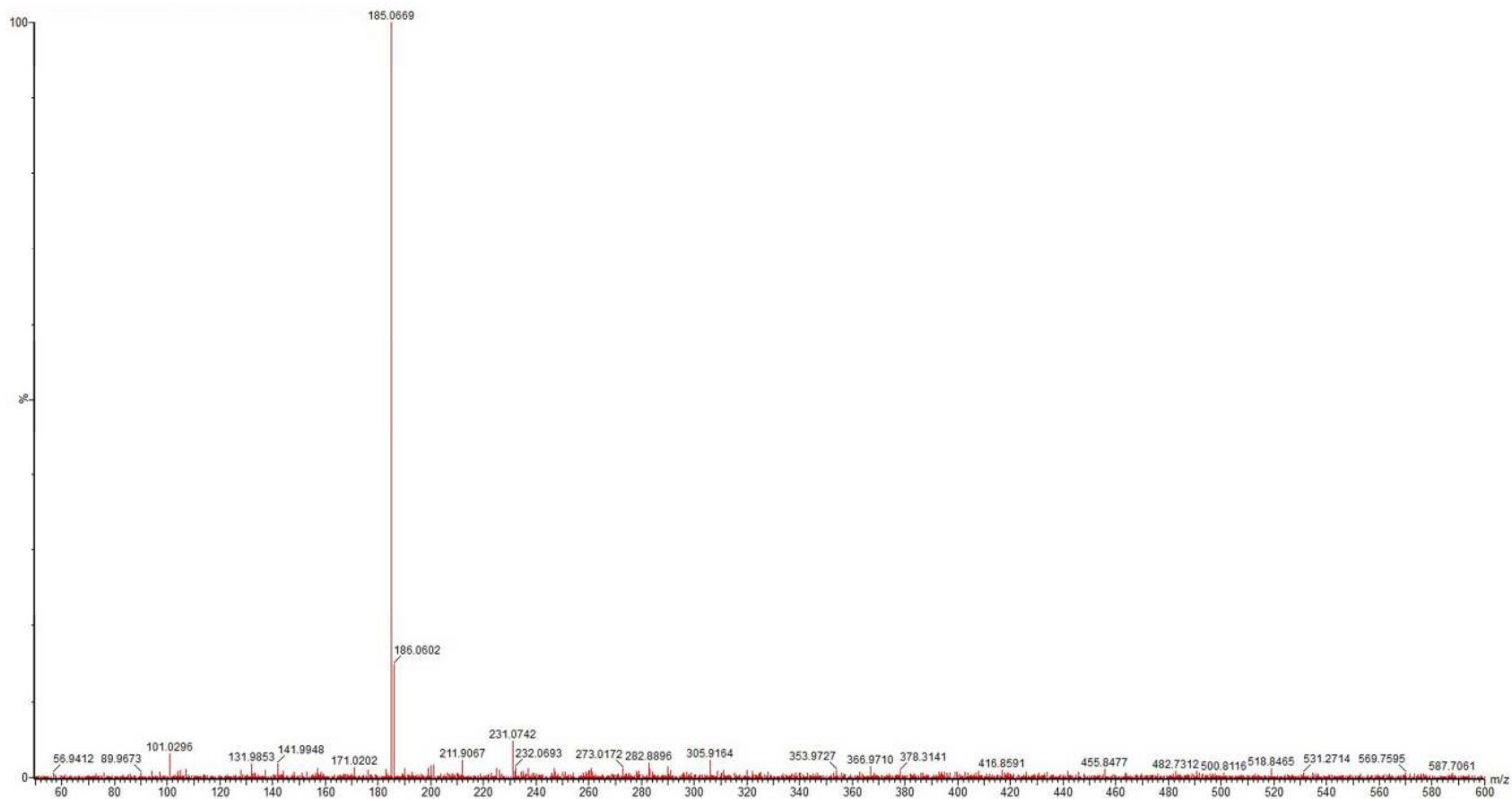
**Figure S7** - MS/MS spectrum of 1-dimethyluric acid (**iv**) and 3-dimethyluric acid (**v**) in positive ionization mode



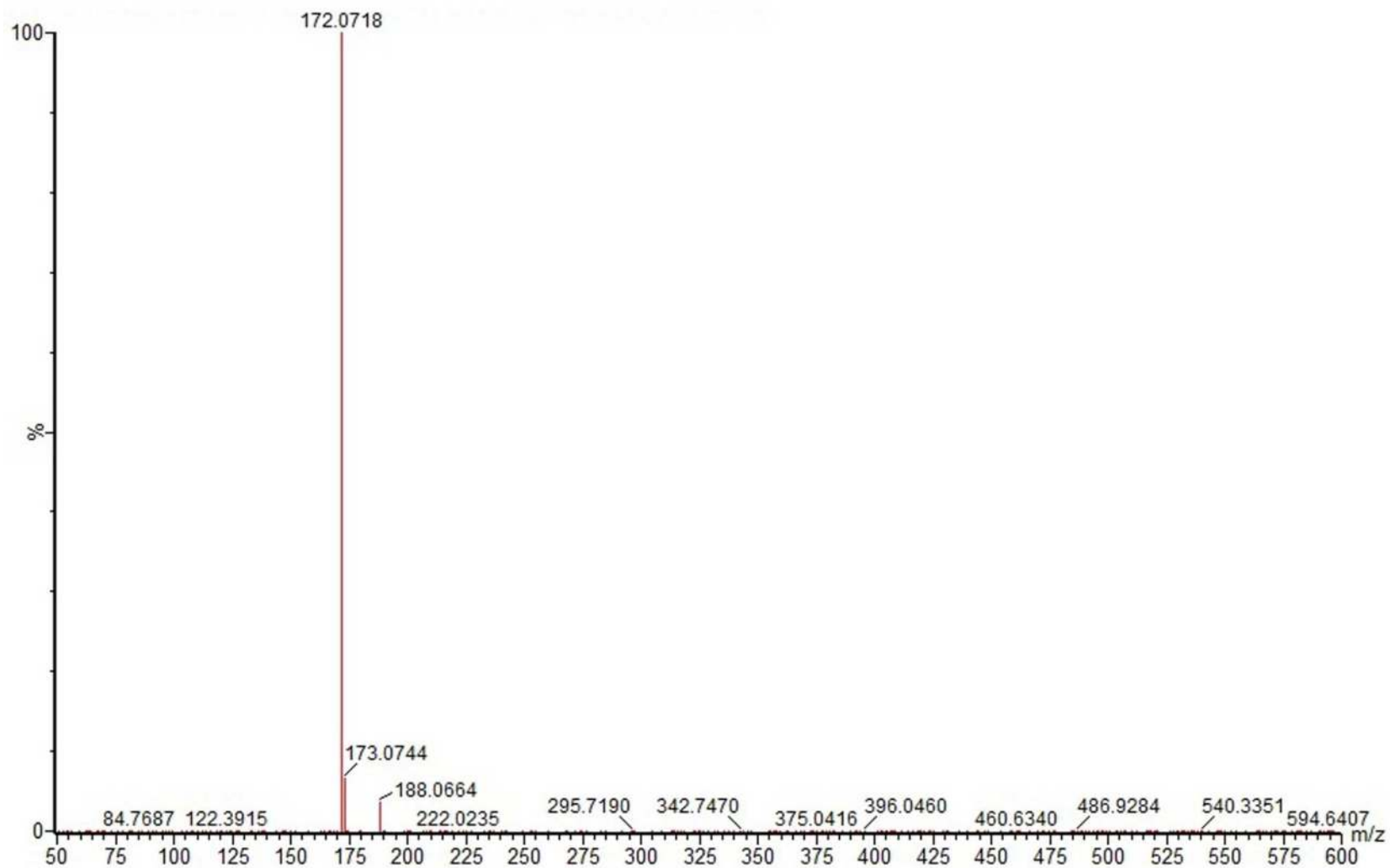
**Figure S8** - Mass spectrum of xanthine (vi) in positive ionization mode



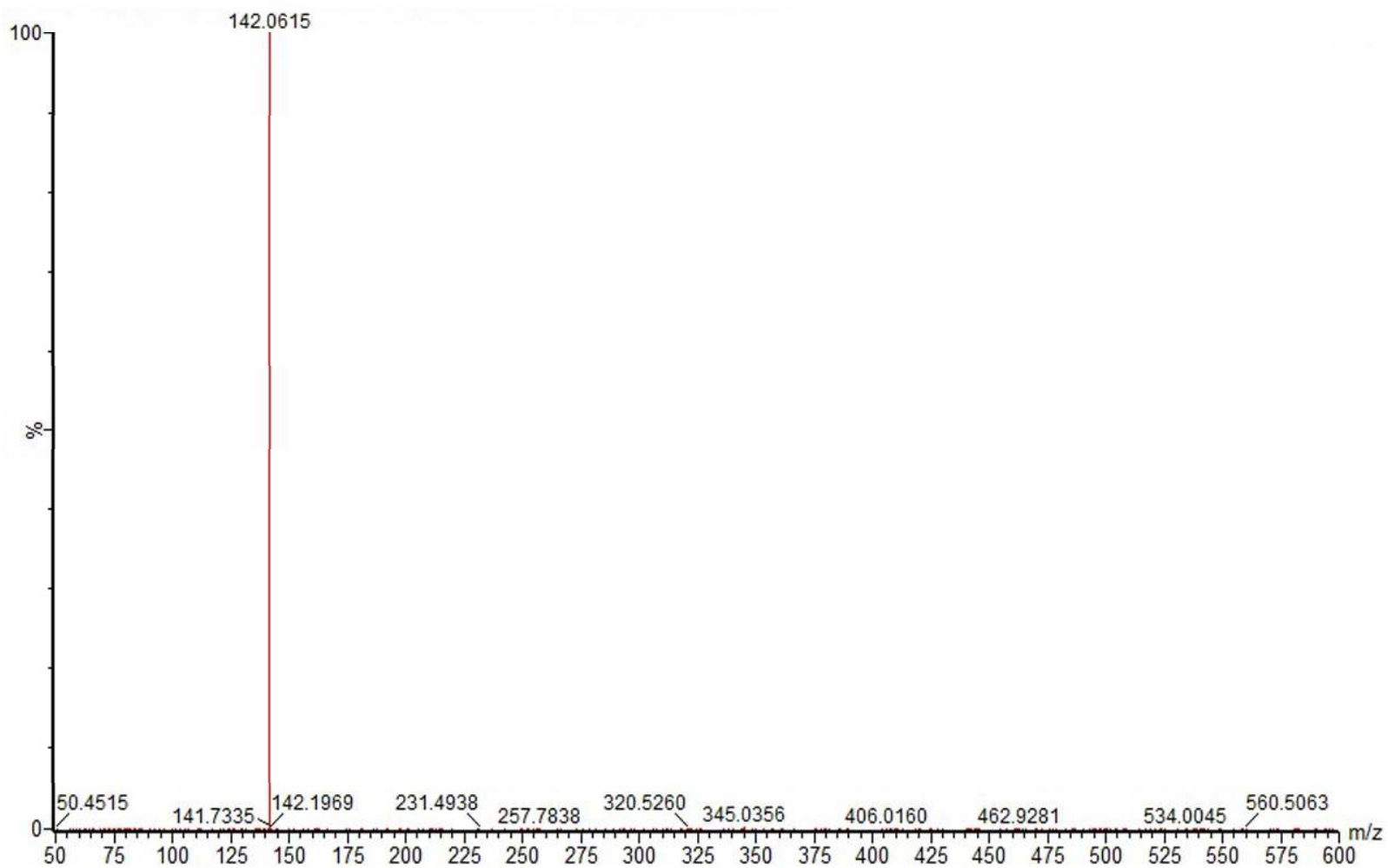
**Figure S9** - Mass spectrum of 1/3-methyl tetrahydro-1H-purine-2,6-dione (**vii**) in negative ionization mode



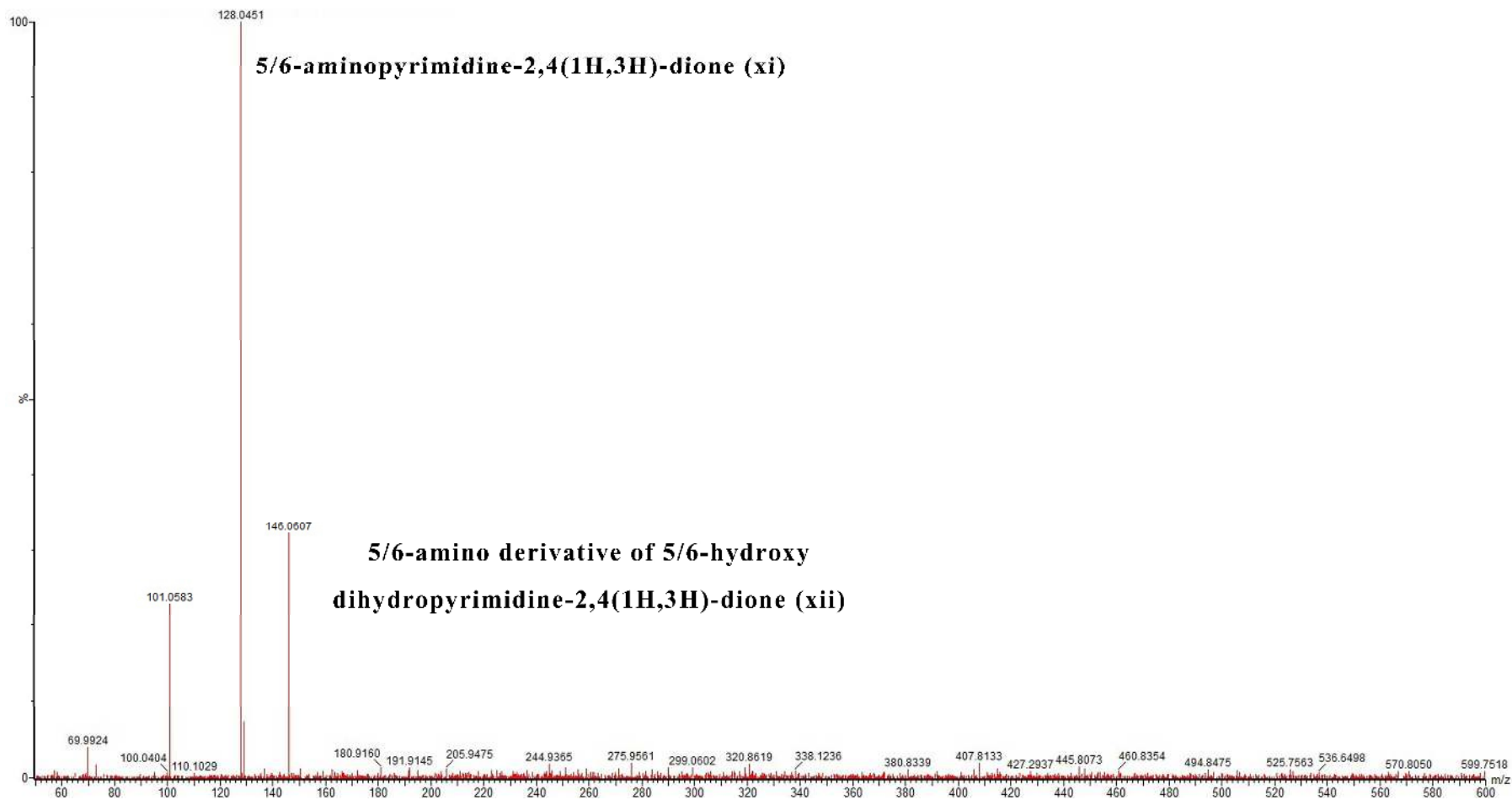
**Figure S10** - Mass spectrum of 8-hydroxy-1/3-methyl-3,7,8,9-tetrahydro-1H-purine-2,6-dione (**viii**) in positive ionization mode



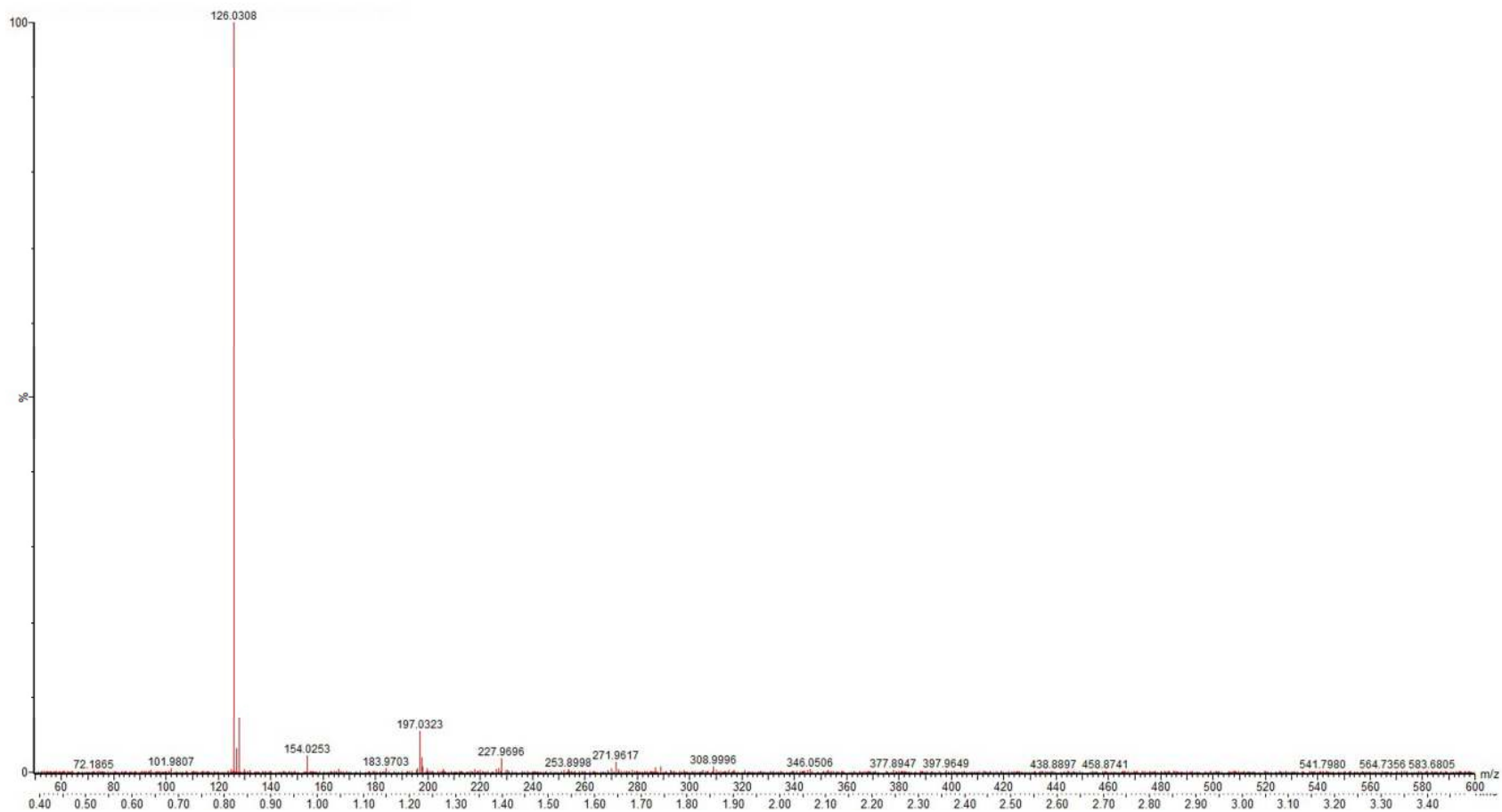
**Figure S11** - Mass spectrum of 5/6-amino derivative of 5/6-hydroxy-1,3-dimethylpyrimidine-2,4(1H,3H)-dione (**ix**) in positive ionization mode



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

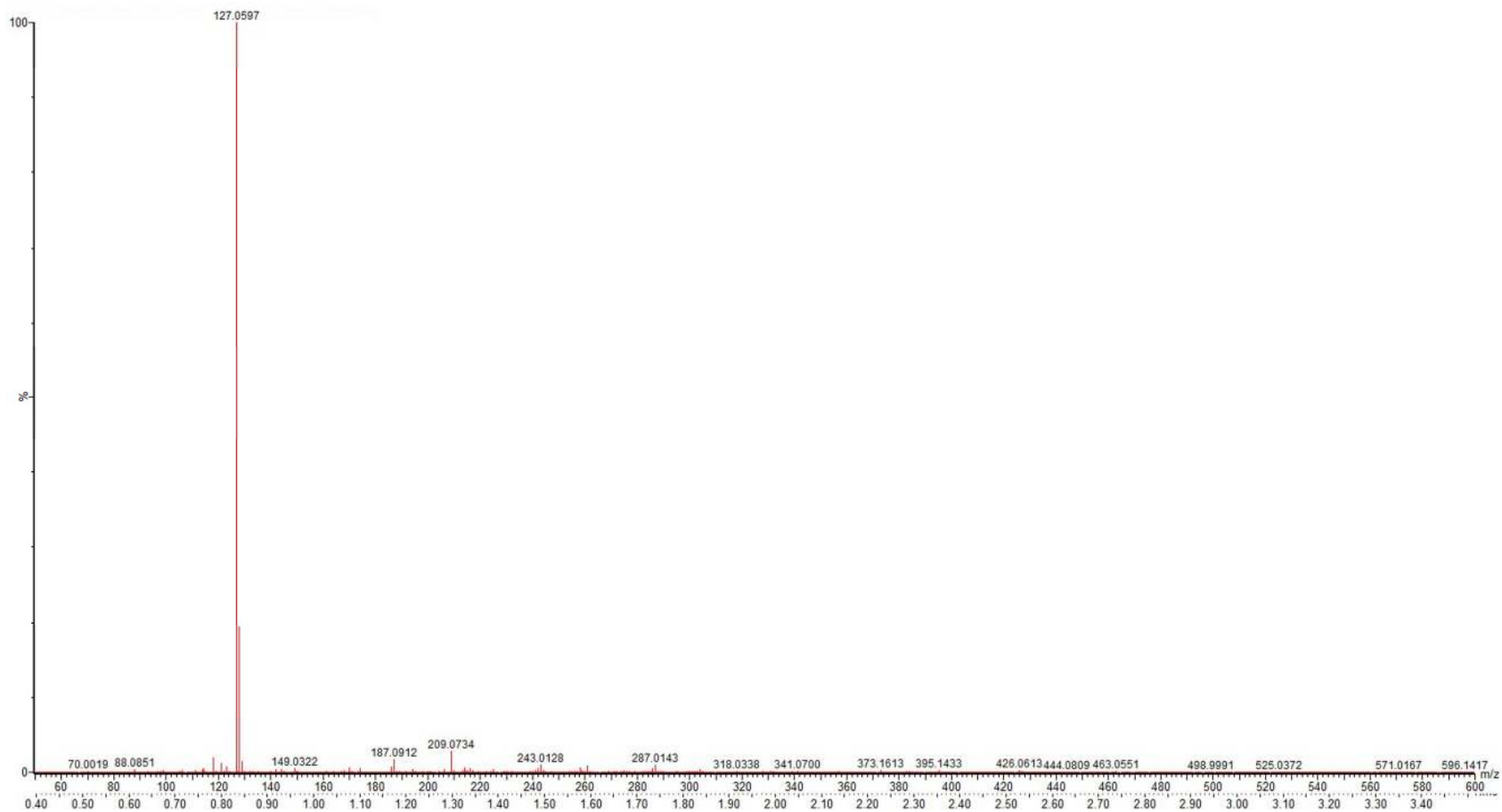


**Figure S13** - Mass spectrum of 5/6-aminopyrimidine-2,4(1H,3H)-dione (**xi**) and 5/6-amino derivative of 5/6-hydroxydihydropyrimidine-2,4(1H,3H)-dione (**xii**) in positive ionization mode

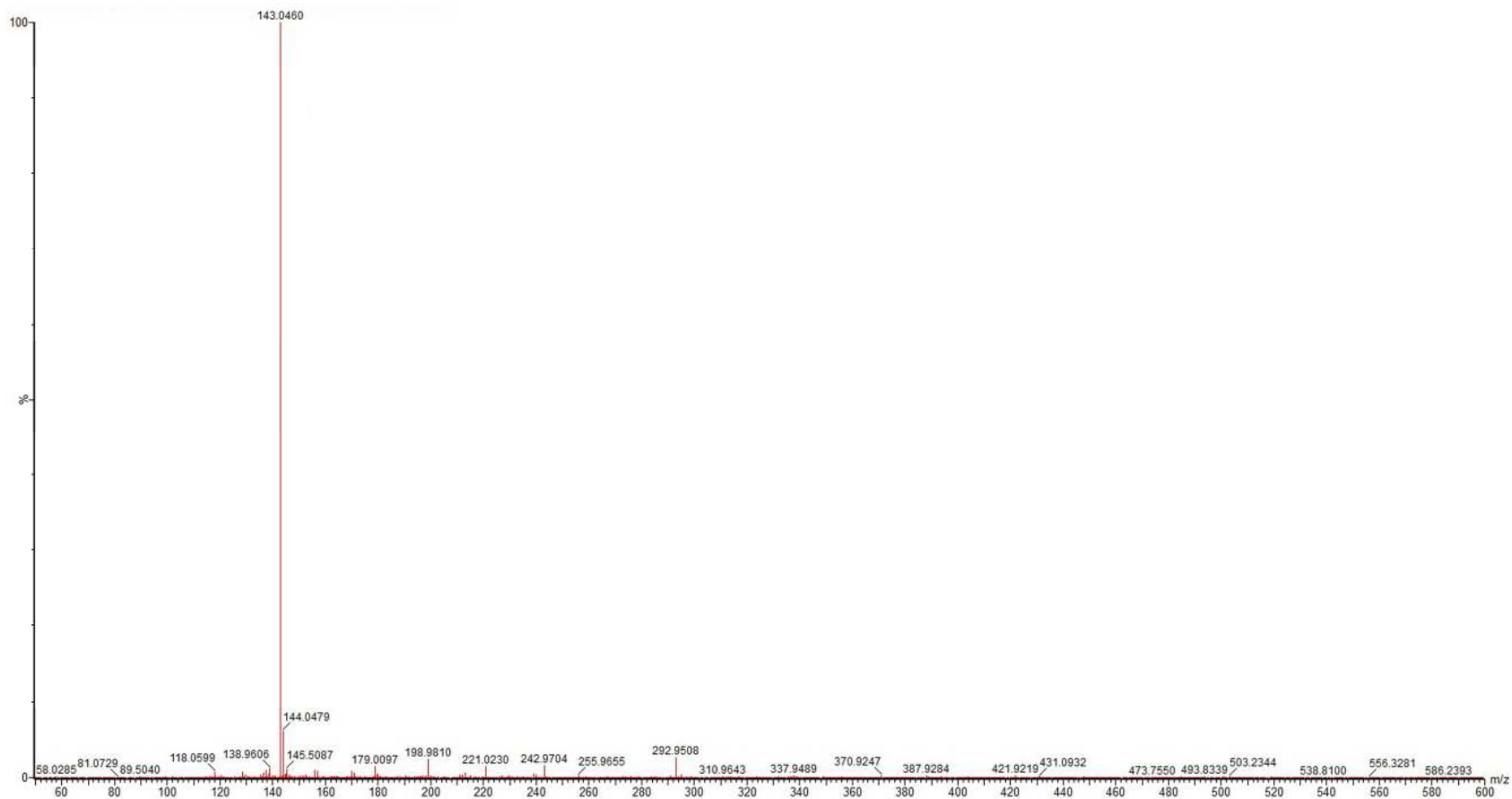


**Figure S14** - Mass spectrum of 5/6-aminopyrimidine-2,4(1H,3H)-dione (**xi**) in negative ionization mode

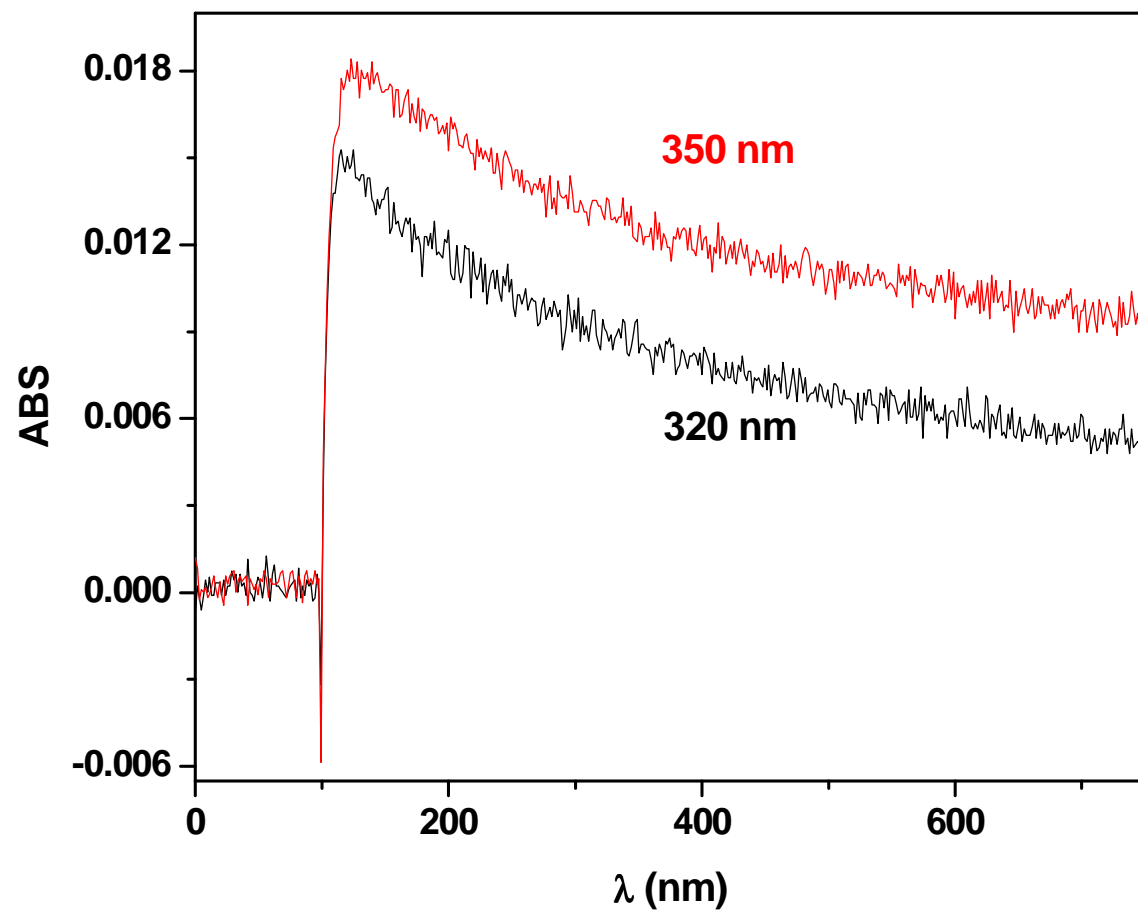




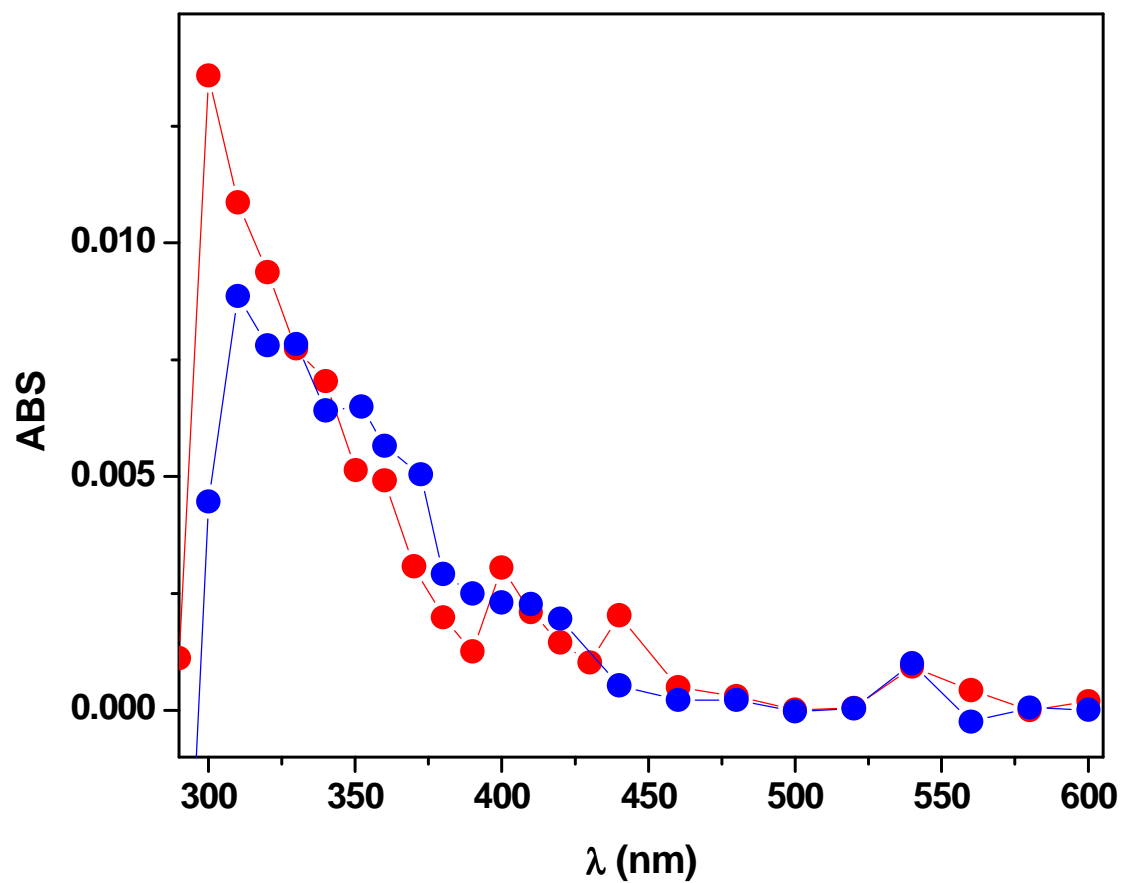
**Figure S15** - Mass spectrum of 1/3-methylpyrimidine-2,4(1H,3H)-dione (**xiii**) in positive ionization mode



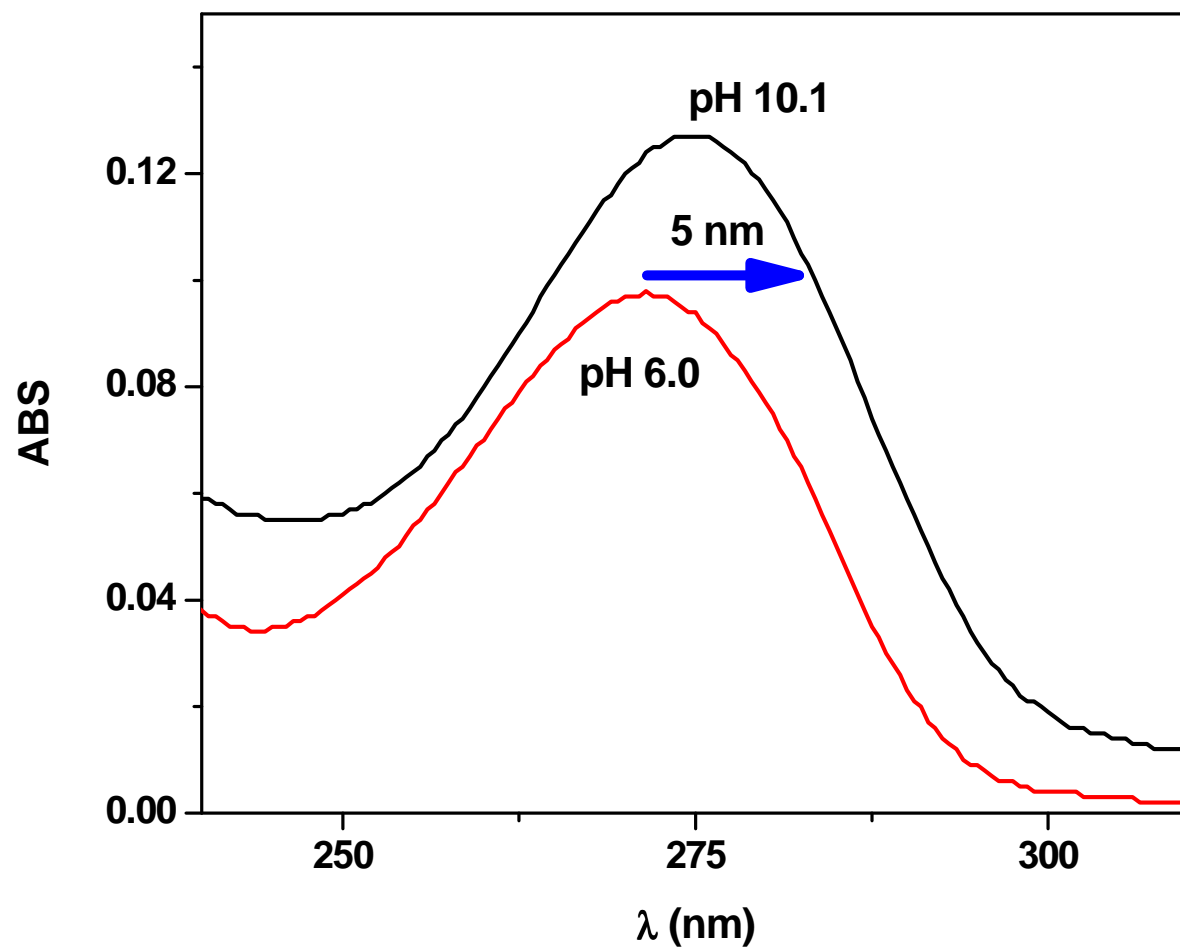
**Figure S16** - Mass spectrum of 5,6-diaminopyrimidine-2,4(1H,3H)-dione (**xiv**) in positive ionization mode



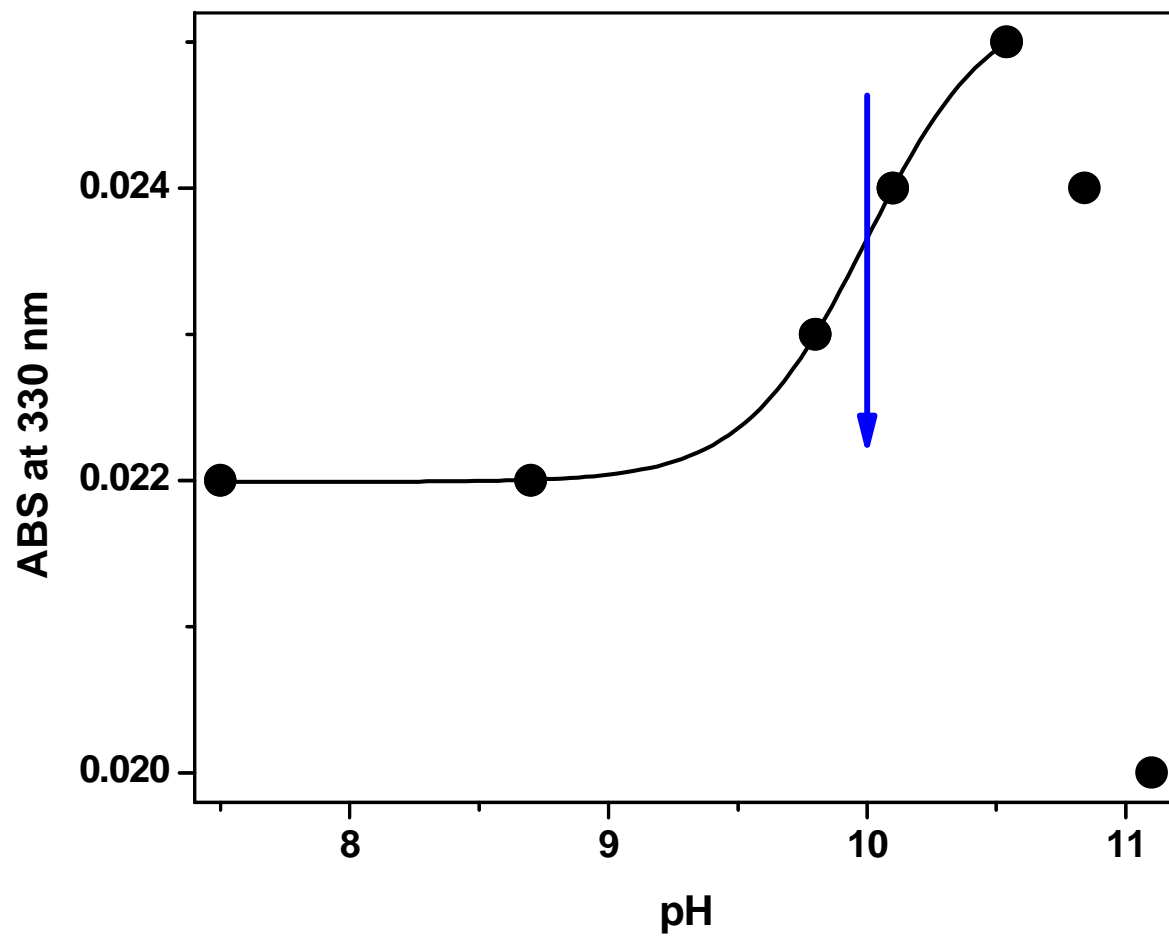
**Figure S17** - Decay traces at 320 nm (Red) and 350 nm (Black) in the case of reaction of  $O^{\bullet-}$  with theophylline.



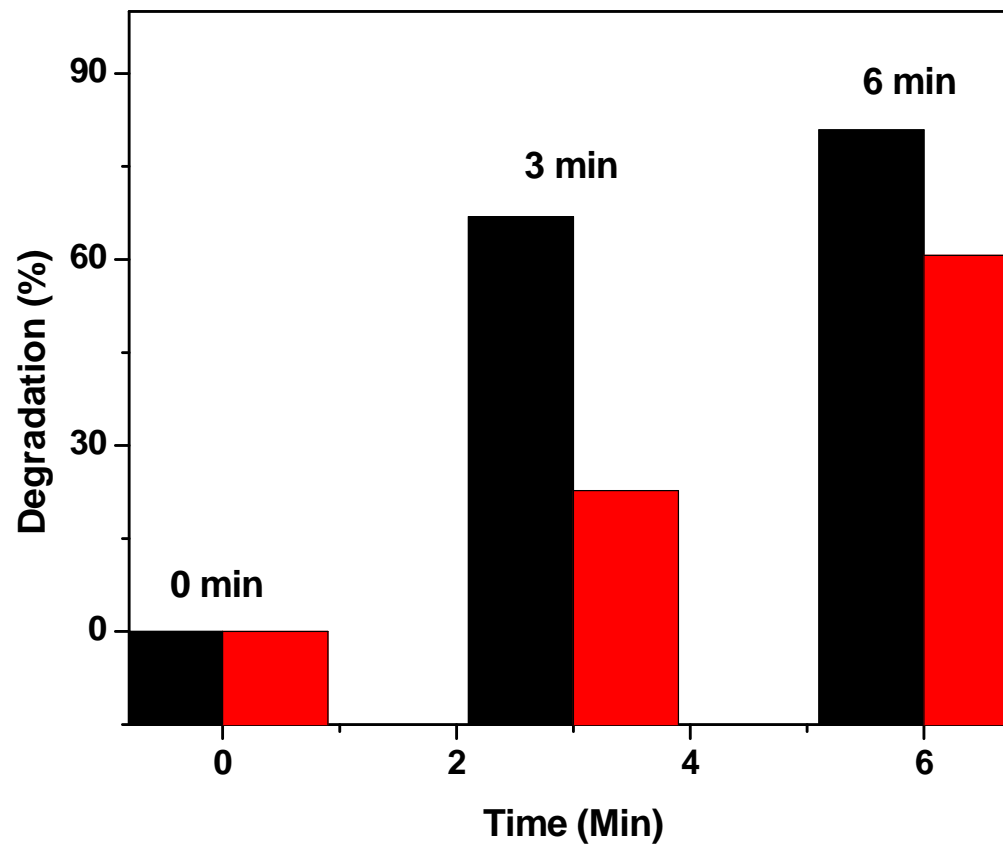
**Figure S18** - Transient absorption spectrum of theophylline ( $1 \times 10^{-4}$  mol dm $^{-3}$ ) recorded during its reaction with  $\text{SO}_4^{\bullet-}$  after (●) 347  $\mu\text{s}$  (pH 6.0) and with  $\text{N}_3^{\bullet}$  after (●) 328  $\mu\text{s}$  (pH 6.1).



**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  $\cdot\text{OH}$  against pH.



**Figure S21** - Percentage degradation of theophylline in N<sub>2</sub> purged (Red) and aerated (Black) conditions as a function of time