

## SUPPLEMENTARY MATERIAL

### **Degradation of seventeen contaminants of emerging concern in municipal wastewater effluents by sonochemical advanced oxidation processes**

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## SUPPLEMENTARY TEXTS

**Text SM1.** Details of reagents used in the work

(Information taken from (Botero-Coy et al., 2018)).

Pharmaceutical reference standards were acquired from Sigma-Aldrich, LGC Promochem, Toronto Research Chemicals, Across Organics, Bayer Hispania, and Aventis Pharma. All reference standards were of 93% purity or higher. Individual standard stock solutions were prepared at concentrations between 50 at 500 mg/L. Intermediate solutions of 10 mg/L were prepared by dilution with methanol. Mixed working solutions containing all analytes at the  $\mu\text{g/L}$  level were prepared weekly from intermediate solutions by appropriate dilutions with water and were used for preparation of the aqueous standard calibrations and for spiking samples used as quality control.

Isotopically labelled internal standard (ILIS) acetaminophen-d4, diclofenac-d4, valsartan-d8, erythromycin-13C-d3, irbesartan-d6, venlafaxine-d6, carbamazepine 10,11-epoxide-d10 were from CDN Isotopes (Quebec, Canada); sulfamethoxazole-13C6, azithromycin-d3, ciprofloxacin-d8, norfloxacin-d5 and trimethoprim-13C3 were from Cambridge Isotope Laboratories (Andover, MA, USA). Individual ILIS stock solutions between 50 and 500 mg/L were prepared in MeOH. Intermediate mix ILIS between 1 and 0.1 mg/L were prepared by dilution with MeOH. A working mix ILIS solution at 2  $\mu\text{g/L}$  was prepared in MeOH for its use in the analysis of samples. All solutions were stored in amber glass bottles at  $-20\text{ }^{\circ}\text{C}$ . HPLC-grade methanol (MeOH), HPLC-grade acetonitrile (ACN), formic acid (HCOOH, content N98%) and ammonium acetate (NH<sub>4</sub>AC, reagent grade), were purchased from Scharlab (Barcelona, Spain).

HPLC-grade water was obtained from distilled water that was passed through a Milli-Q water purification system (Millipore, Bedford, MA, USA).

## **Reference**

Botero-Coy, A.M., Martínez-Pachón, D., Boix, C., Rincón, J.R., Castillo, N., Arias-Marín, L.P., Manrique-Losada, L., Torres-Palma, R.A., Moncayo-Lasso, A., Hernández, F., 2018. An investigation into the occurrence and removal of pharmaceuticals in colombian wastewater. *Sci. Total Environ.* 62, 842–853.

### Text SM2. Method for H<sub>2</sub>O<sub>2</sub> quantification

Hydrogen peroxide accumulation can be determined by iodometry. An aliquot of 600  $\mu\text{L}$  from the sonochemical reactor is added to a quartz cell (1 cm pathlength) containing 1350  $\mu\text{L}$  of potassium iodide (0.1 M) and 50  $\mu\text{L}$  of ammonium heptamolybdate (0.01 M, as catalyst of reaction). After 5 min of reaction, the absorbance at 350 nm was measured in a spectrophotometer to determine the  $\text{I}_3^-$  (which has a molar absorptivity: 26400  $\text{M}^{-1} \text{cm}^{-1}$ ) production (Eq. SM1-SM2) using the Beer-Lambert law. Then, according to the ~~and~~-stoichiometry of the reactions the hydrogen peroxide concentration can be established (Eq. SM3).



$$[\text{H}_2\text{O}_2]: (\text{Absorbance at 350 nm}/26400\text{M}^{-1}) * (2000/600) \quad (\text{SM3})$$

**Text SM3.** Determination of role of suspended solids on valsartan degradation

To determine the role of suspended solids on the sonochemical process, the solids from effluent sample were removed by centrifugation at 2800 rpm during 10 min using a Centaur 2 centrifuge. The model substance (valsartan) was spiked to both waters with and without solids; subsequently, the sonochemical degradation was carried out. Then, the valsartan removal from the two waters (with and without solids) by the ultrasound process was compared (see Figure SM3).

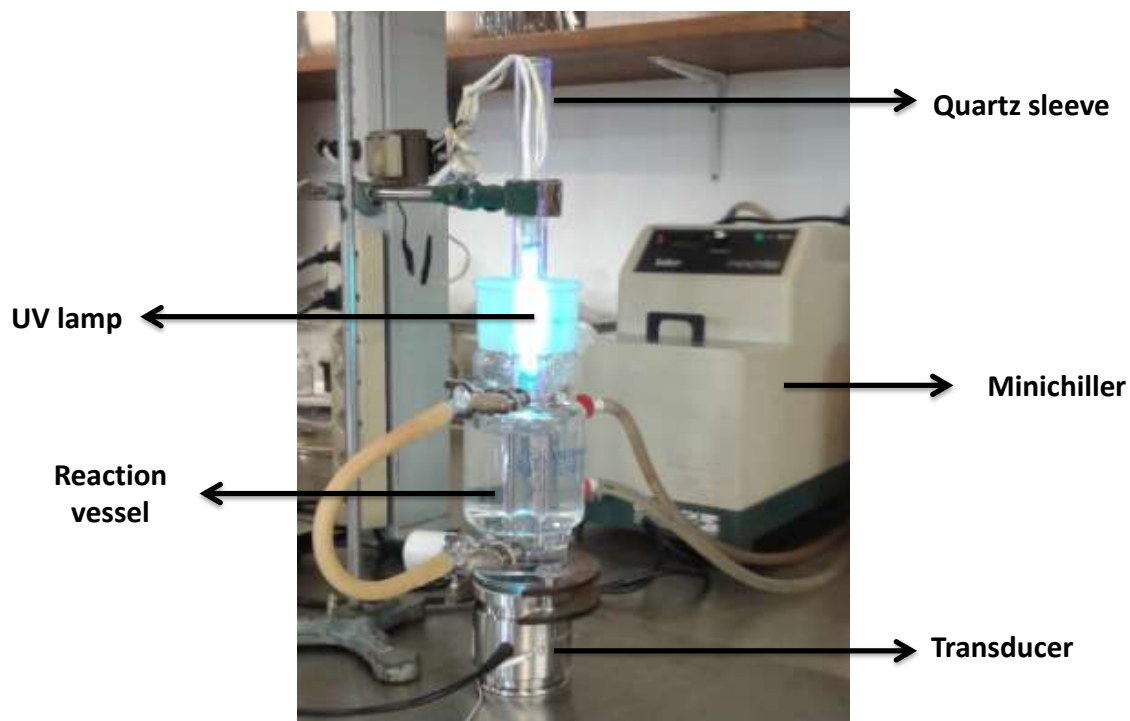
**Text SM4.** Absorption of UVA light by the matrix components

The UVA lamp used for the sono-photo-Fenton process emitted light mainly at 365 nm. Then, to analyze the interfering effects of matrix components, specially the suspended solid, the absorbance of the effluent with and without solids (removed by centrifugation as described in Text SM3) was measured, which values are summarized in the following table:

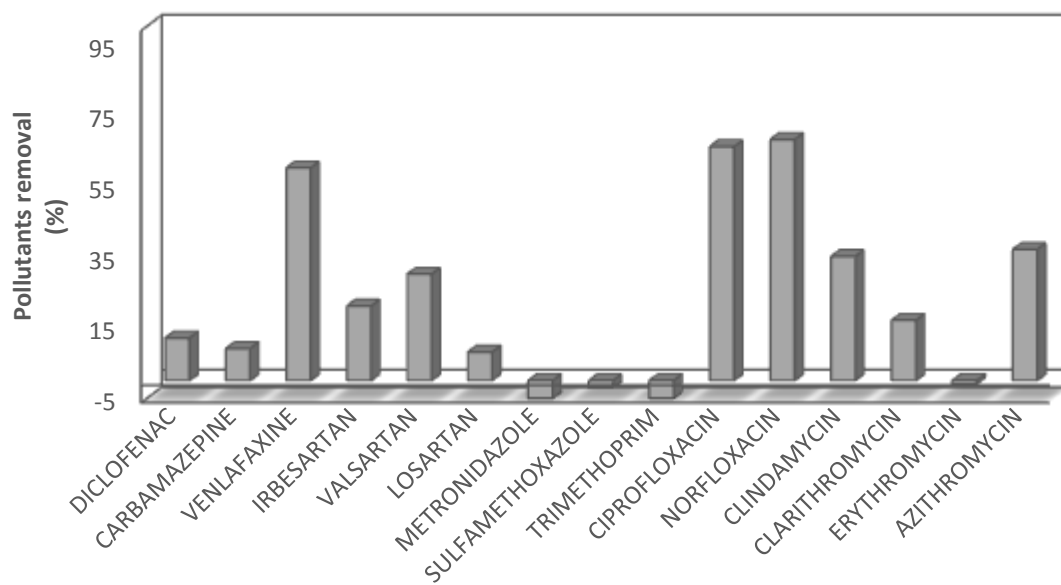
<b>Effluent</b>	<b>With solids</b>	<b>Without solids</b>
<b>Absorbance at 365 nm</b>	0.227	0.164

It can be noted that the effluent with solids presented low UVA absorbance (0.227) and this had little difference with the water without solids (0.164), which suggested a low inference by the solids in matrix toward the UVA light used in the processes.

## SUPPLEMENTARY FIGURES



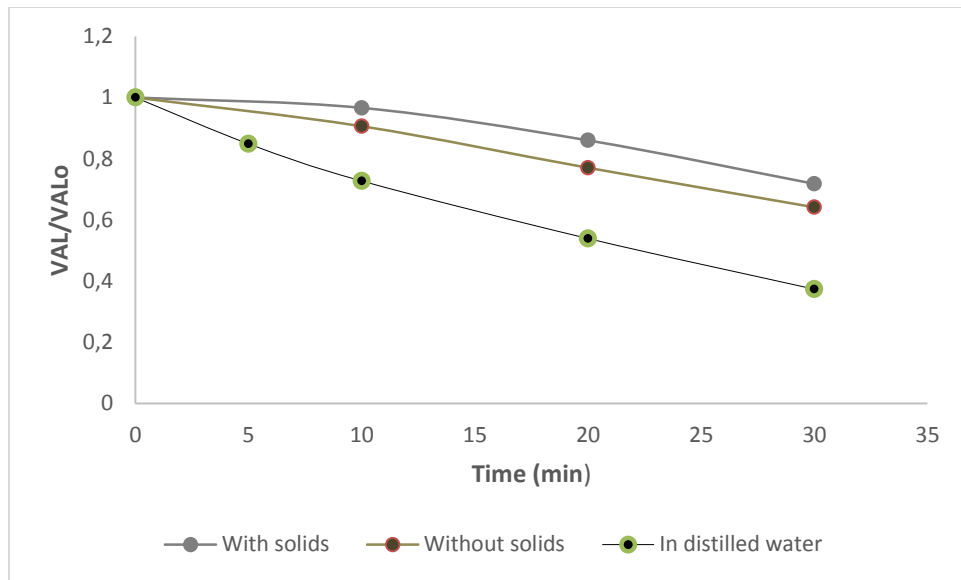
**Figure SM1.** Reactor design for combinations of ultrasound with Fenton Based systems.



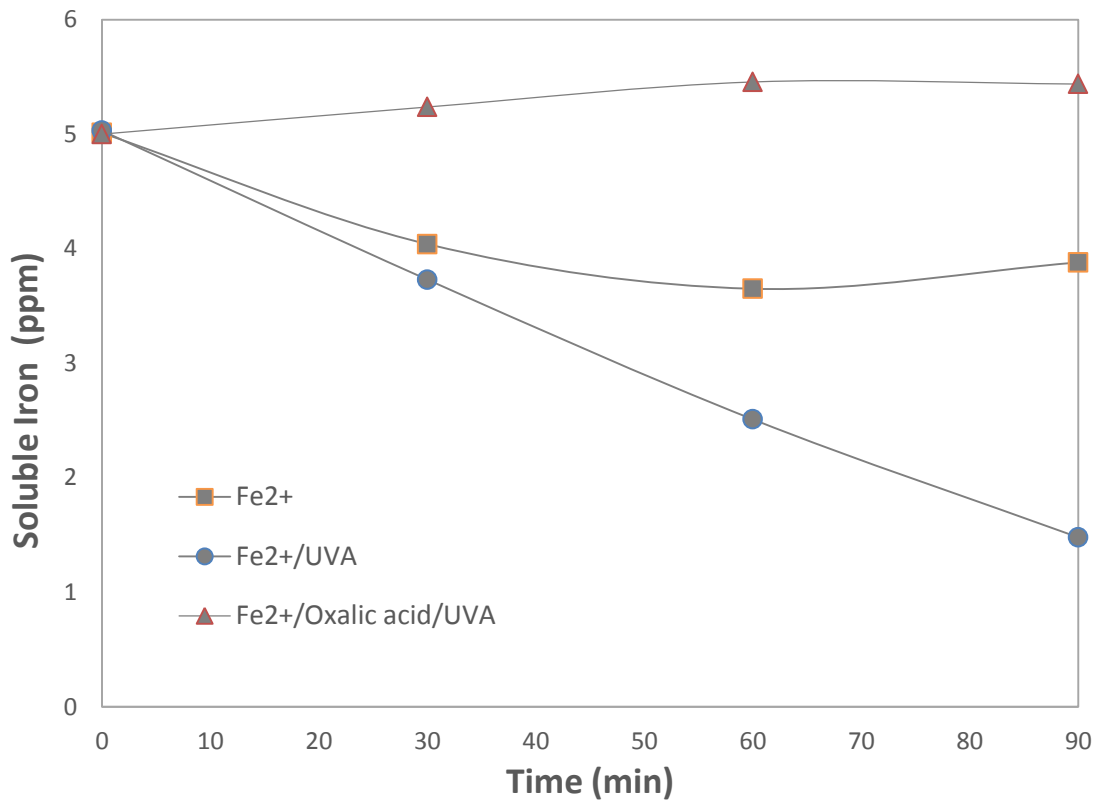
**Figure SM2.** Pharmaceuticals removal by El salitre MWTP.

Adapted from reference (Botero-Coy et al., 2018).

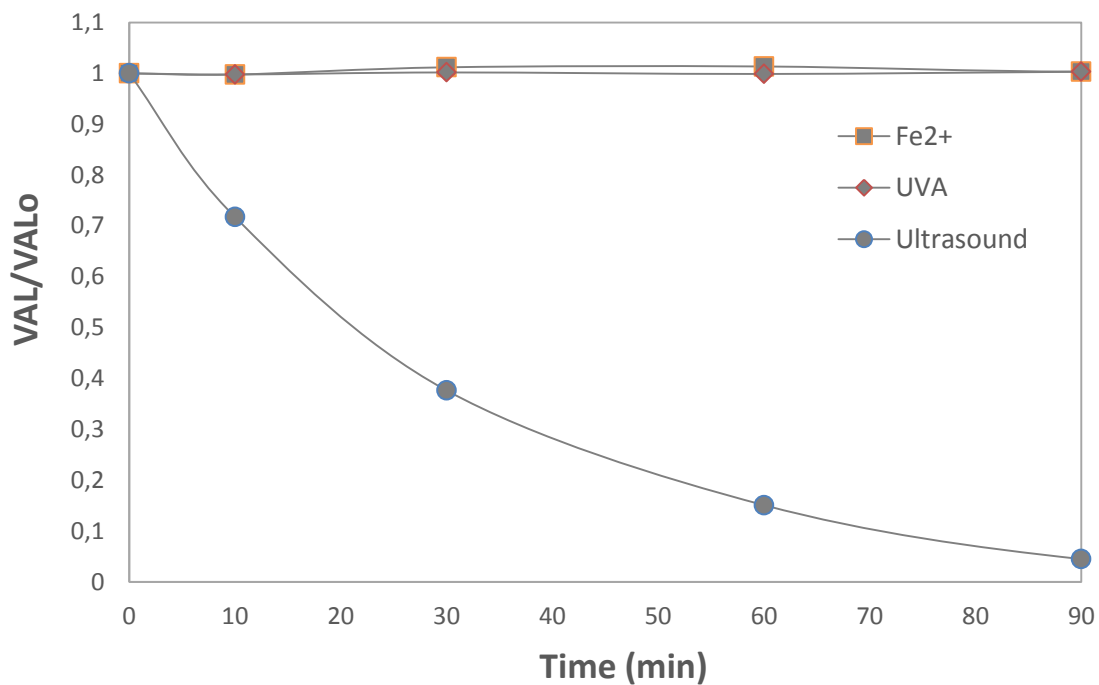




**Figure SM3.** Comparison of valsartan (VAL) degradation in both effluents (with and without solids) and distilled water. Conditions: Actual power density:  $88.0 \text{ W L}^{-1}$ ,  $f$ : 375 kHz,  $V$ : 300 mL,  $[\text{Valsartan}]$ :  $40 \mu\text{M}$ ,  $\text{pH}_{\text{initial}}$  in wastewater:  $7.1 \pm 0.1$ .  $\text{pH}_{\text{initial}}$  in distilled water :6.5.



**Figure SM4.** Soluble iron in the effluent for different systems. Effluent and iron (II) ( $\text{Fe}^{2+}$ ); effluent, iron (II) and UVA ( $\text{Fe}^{2+}/\text{UVA}$ ); effluent, iron (II), UVA and oxalic acid ( $\text{Fe}^{2+}/\text{UVA}/\text{Oxalic acid}$ ). Initial conditions=  $[\text{Fe}^{2+}]$ :  $5 \text{ mg L}^{-1}$ ,  $[\text{Oxalic acid}]$ :  $2 \text{ mg L}^{-1}$ .



**Figure SM5.** Control experiments for valsartan (VAL) degradation in distilled water.

From Figure SM5 can be noted that the  $\text{Fe}^{2+}$  or UVA light individually had no degrading effect on valsartan (VAL), demonstrating that these components take relevance only in the combination with ultrasound.

## MS/MS SUPPLEMENTARY SPECTRA FOR THE SONODEGRADATION PRODUCTS OF VALSARTAN

In order to elucidate the sonodegradation products of valsartan, an exhaustive study of the fragmentation pathway of the parent compounds was required. The MS/MS spectrum (Figure SM6) of **valsartan** ( $C_{24}H_{30}N_5O_3$  expressed as protonated molecule) at 10 eV showed initial losses of water ( $m/z$  418) and  $N_2$  ( $m/z$  408). At 20 eV, minor product ions at  $m/z$  362 (obtained after consecutive losses of  $N_2$  and formic acid) and at  $m/z$  352 (corresponding to the loss of the pentanal chain) were observed. The most important product ions were found at  $m/z$  235 (corresponding to the 5-(4'-methyl-[1,1'-biphenyl]-2-yl)-1H-tetrazole group), 207 (corresponding to the loss of  $N_2$  from 235) and 291 (obtained after the loss of the 2-methylpropan-1-imine from  $m/z$  362). A product ion at  $m/z$  306 was also observed, corresponding to the loss of formic acid from  $m/z$  352. At higher collision energies, product ions at  $m/z$  190 and 180 were found, corresponding to losses of hydrogen cyanide acid and ammonia from  $m/z$  207, respectively. The proposed fragmentation pathway for the valsartan parent compound can be seen in Figure SM7.

Three chromatographic peaks were observed at 10.61 min (**DP1**), 9.96 (**DP2**) and 9.02 (**DP3**), all of them with accurate masses of  $m/z$  452.2312, 452.2308 and 452.2316, corresponding to an elemental composition of  $C_{24}H_{30}N_5O_4$ , expressed as protonated molecule (mass errors ranging from 2.2. to 4.0 ppm). These would correspond to hydroxylations of the parent compound. In order to locate the hydroxylation position, the MS/MS spectra were carefully revised.

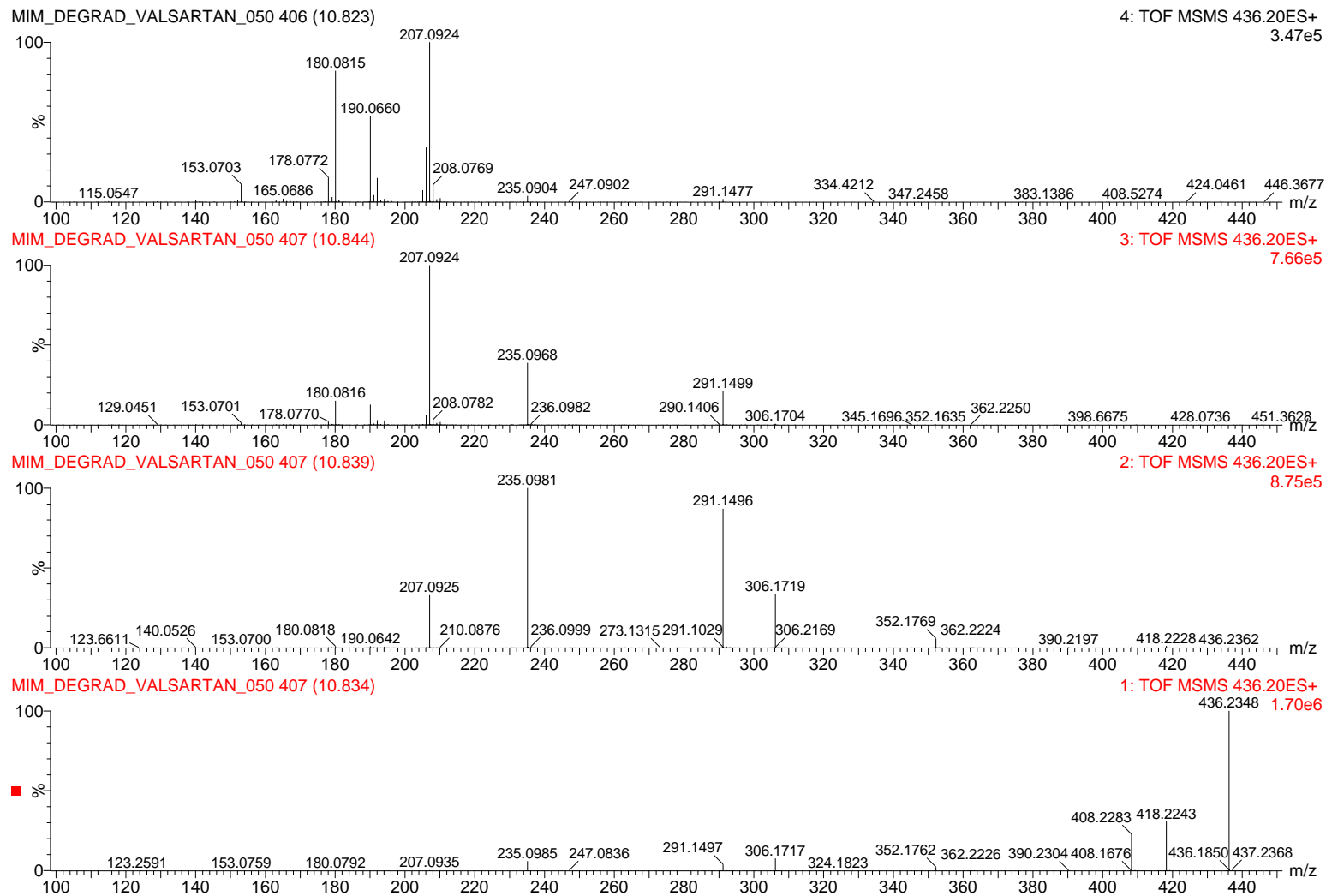
**DP1** presented product ions at  $m/z$  251 and 223 (shift of 16 respect to the 235 and 207 of the parent compound) (Figure SM8), indicating that the hydroxylation has occurred in the 5-(4'-methyl-[1,1'-biphenyl]-2-yl)-1H-tetrazole group. However, the product ion at 180 remained unaltered. Therefore, the hydroxyl group was located in the amine group of the tetrazole.

**DP2** also presented the product ions at  $m/z$  251 and 223, but also at 196 (a shift of 16 amu respect to the 180) (Figure SM9), therefore indicating that the hydroxyl group was located in any of the two aromatic rings.

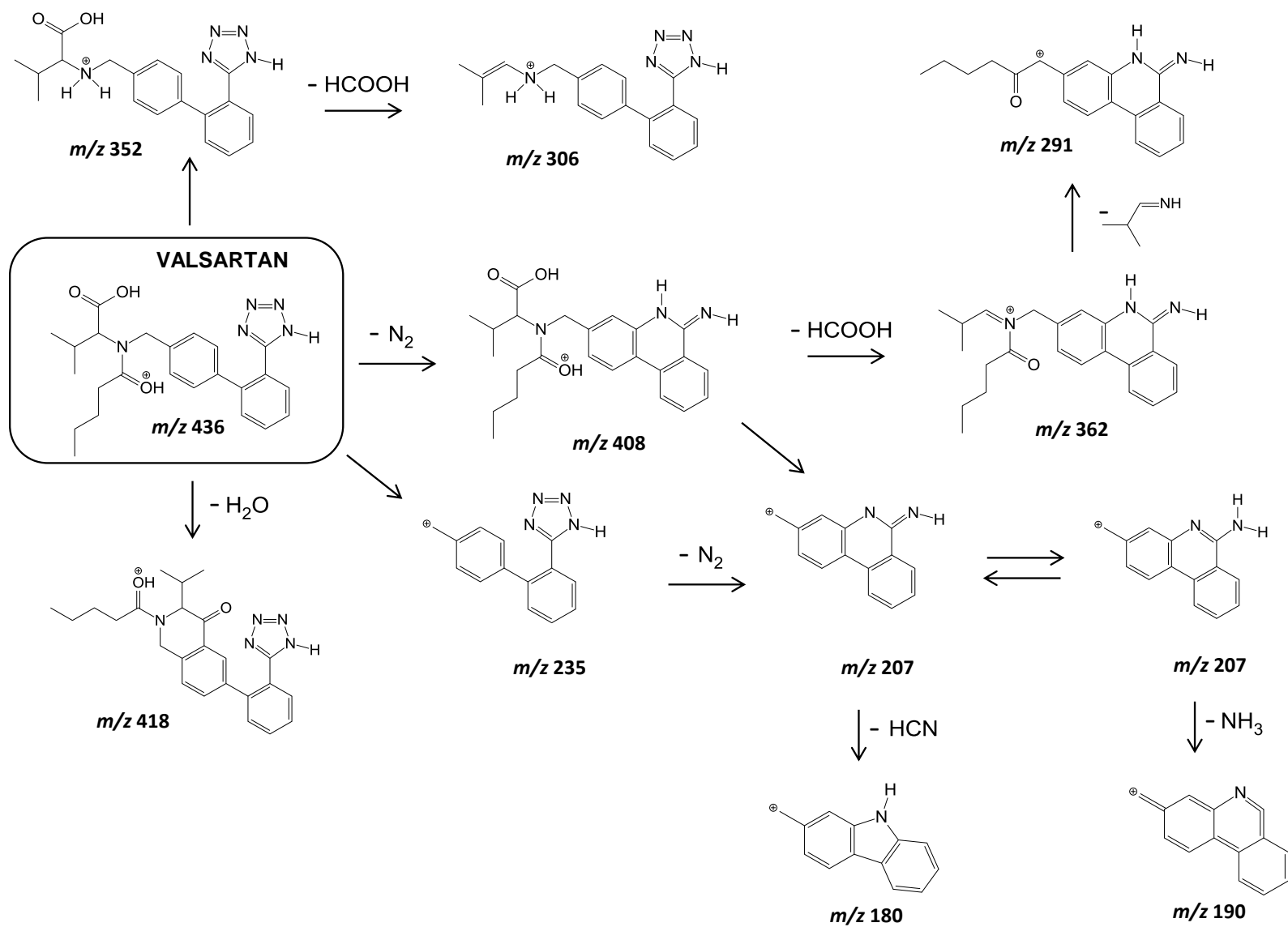
**DP3** instead presented product ions at  $m/z$  235, 207, 180 and 190 (Figure SM10), likely to the parent compound, therefore indicating that the hydroxylation has not occurred in this part of the molecule. Moreover, the product ion at  $m/z$  306 was also observed, therefore indicating that the valine group remained unaltered. Therefore, the hydroxylation should occur in the pentanamide moiety.

Regarding **DP4** (9.05 min), an accurate mass of 450.2152 was obtained. This would correspond to an elemental composition  $C_{24}H_{28}N_5O_4$ , this is, to the reduction of one of the hydroxylated DPs. Product ions at  $m/z$  305 (instead of 307), 235, 207, 190 and 180 were observed (Figure SM11).

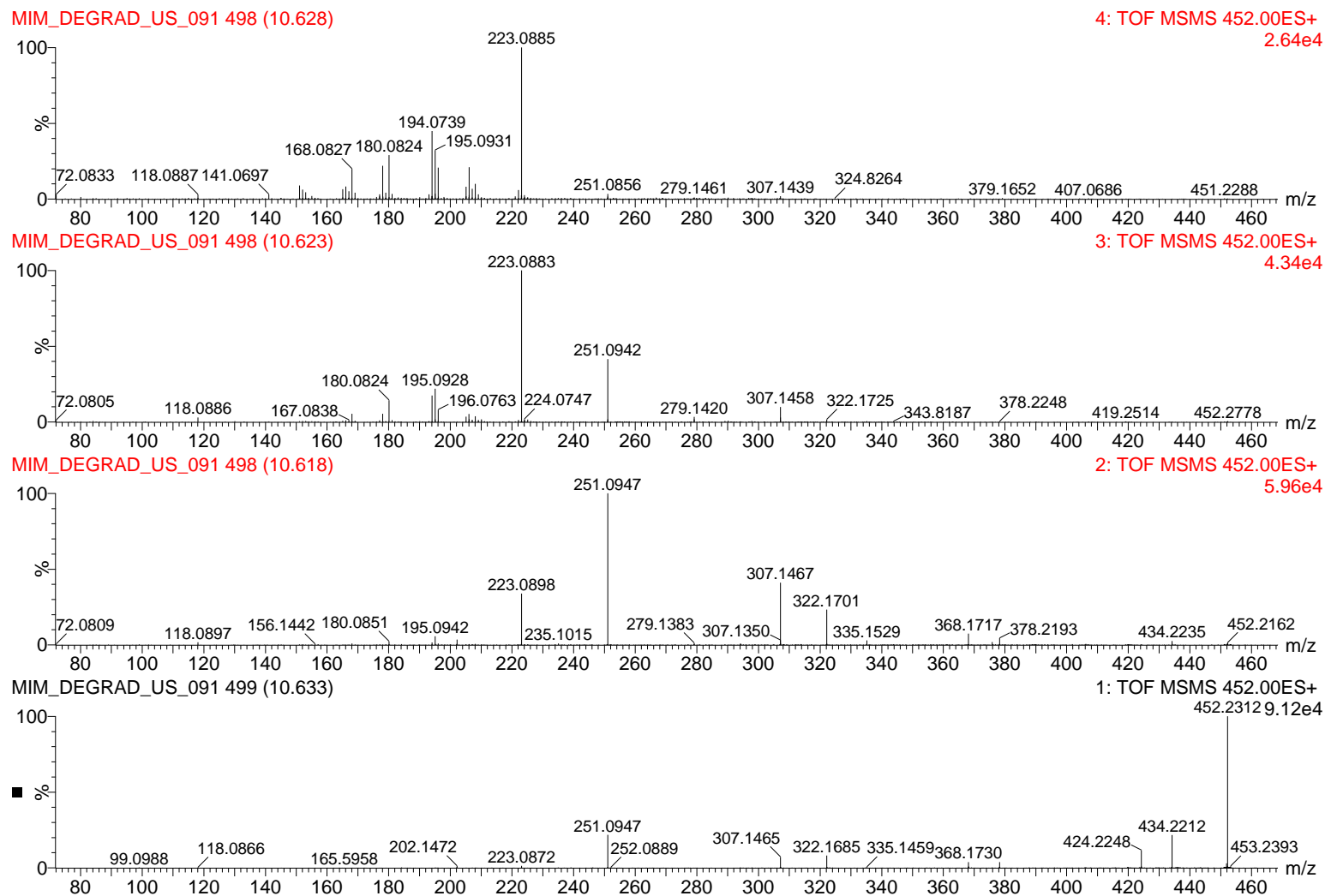
Finally, **DP5** was found at 5.26 min, and its elemental composition matched with an elemental composition of  $C_{19}H_{22}N_5O_2$  (1.4 ppm mass error). This was in accordance with the N-dealkylation of the pentanamide group from the parent compound. Product ions at  $m/z$  235, 207, 190 and 180 (Figure SM12) remained unaltered.



**Figure SM6.** MS/MS spectra at different collision energies (10, 20, 30 and 40 eV, from bottom to top) for valsartan

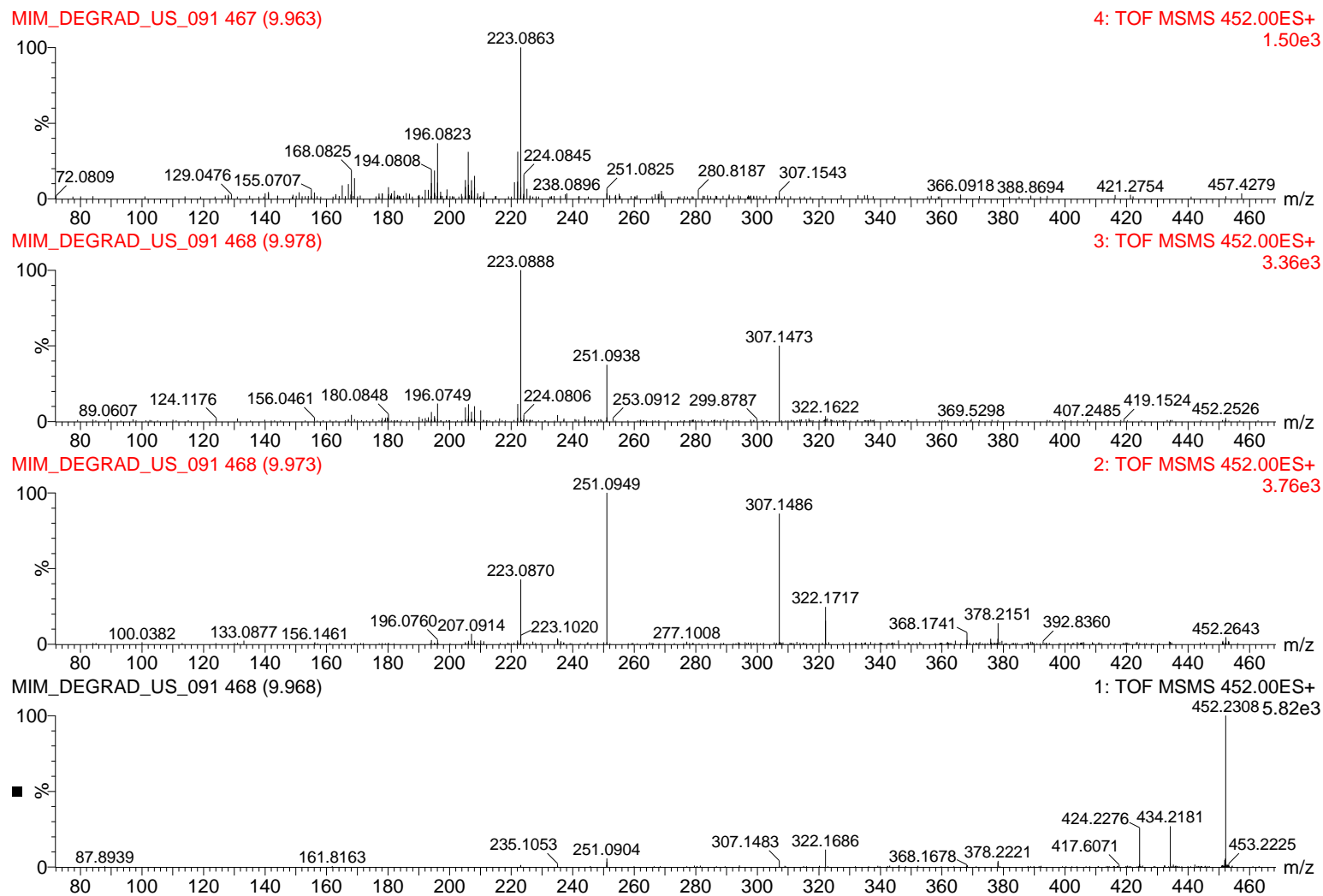


**Figure SM7.** Proposed fragmentation pathway for valsartan parent compound

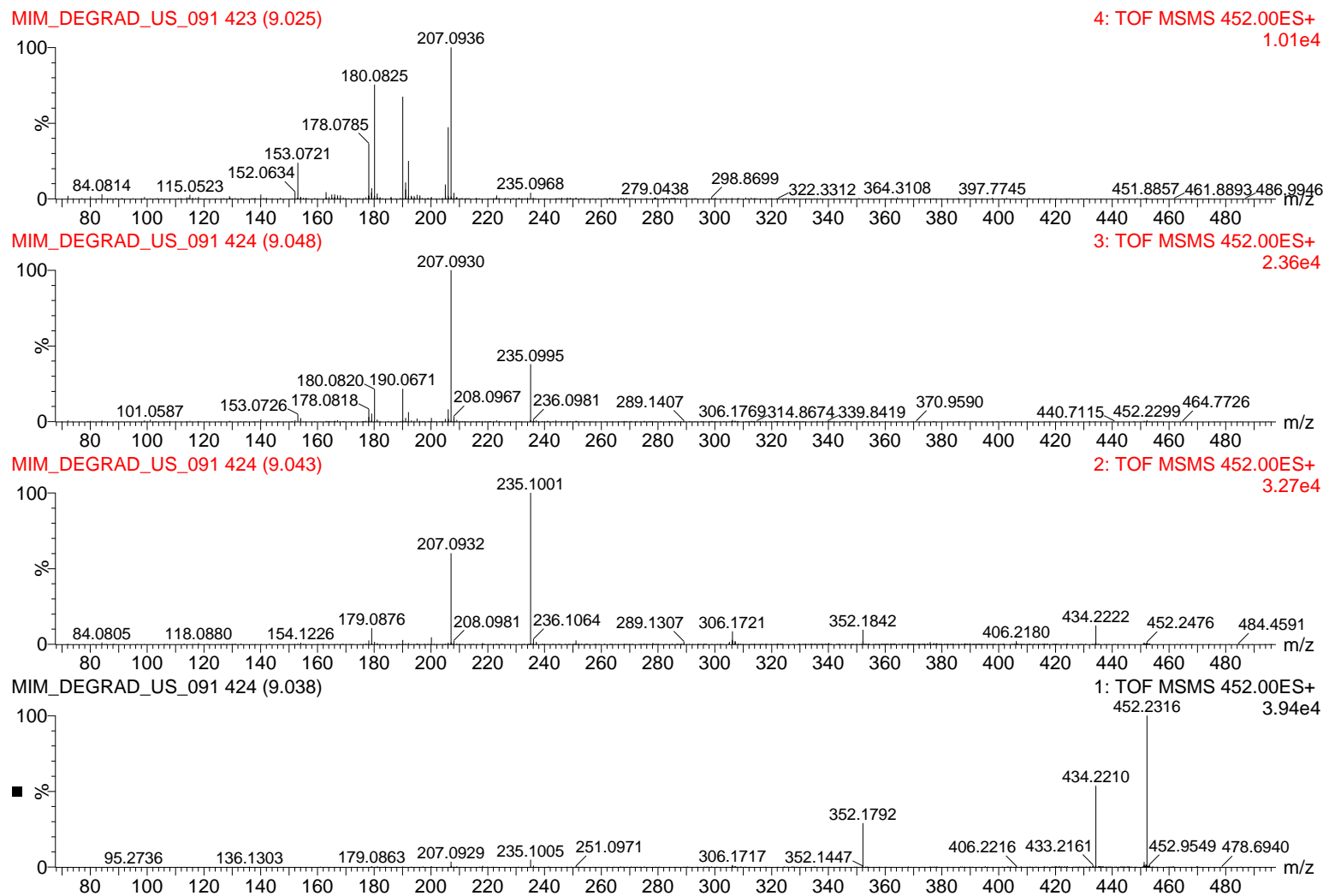


**Figure SM8.** MS/MS spectra at different collision energies (10, 20, 30 and 40 eV, from bottom to top) for DP1

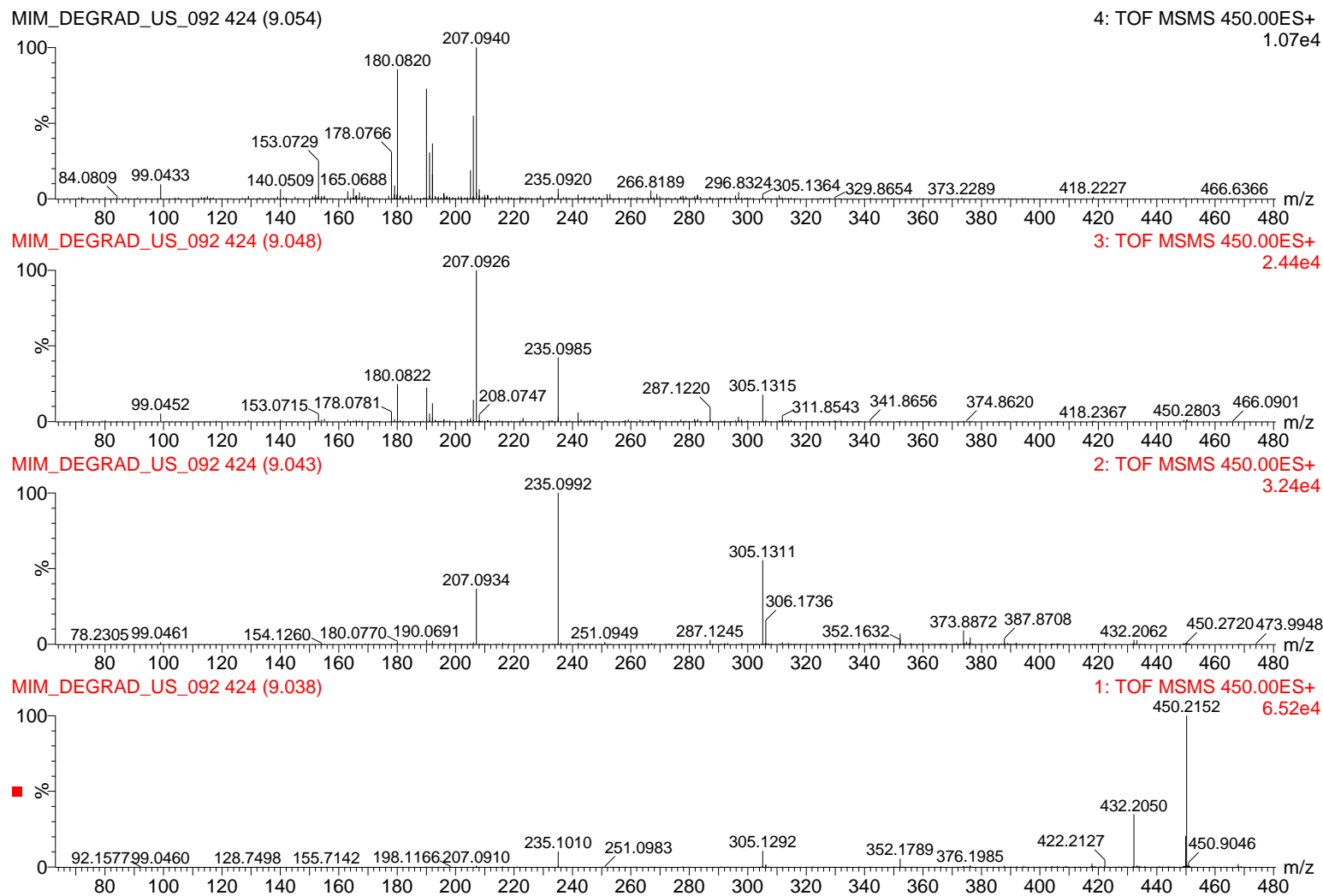




**Figure SM9.** MS/MS spectra at different collision energies (10, 20, 30 and 40 eV, from bottom to top) for DP2



**Figure SM10.** MS/MS spectra at different collision energies (10, 20, 30 and 40 eV, from bottom to top) for DP3



**Figure SM11.** MS/MS spectra at different collision energies (10, 20, 30 and 40 eV, from bottom to top) for DP4

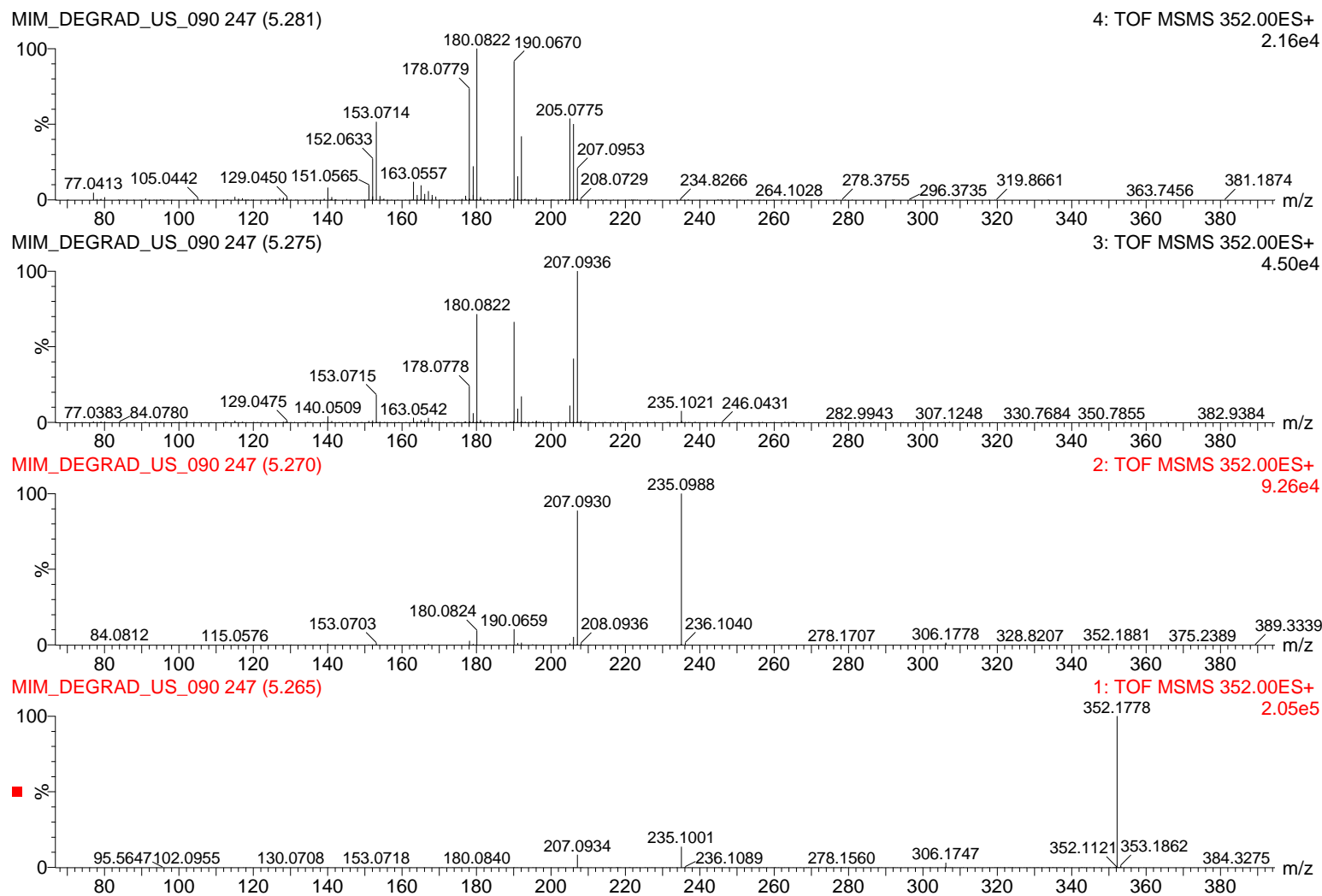


Figure SM12. MS/MS spectra at different collision energies (10, 20, 30 and 40 eV, from bottom to top) for DP5

## SUPPLEMENTARY TABLES

**Table SM1.** Basic global parameters of the effluent from El salitre MWTP.

<b>Parameter</b>	<b>COD (mg O<sub>2</sub> L<sup>-1</sup>)</b>	<b>TOC (mg C L<sup>-1</sup>)</b>	<b>pH</b>	<b>Suspended solids (mg L<sup>-1</sup>)</b>	<b>Absorbance at 365 nm</b>
<b>Value</b>	153.96	40.11	7.48	90.01	0.227

**Table SM2.** Changes of pH during combined processes.

<b>Pollutants in the effluent</b>				
<b>System</b>	<b>Sonochemistry</b>	<b>Sono-Fenton</b>	<b>Sono-photo-Fenton</b>	<b>Sono-photo-Fenton/oxalic acid</b>
Initial pH	7.48			
Final pH	7.52	7.51	7.54	7.52
<b>Valsartan in distilled water</b>				
<b>System</b>	<b>Sonochemistry</b>	<b>Sono-Fenton</b>	<b>Sono-photo-Fenton</b>	<b>Sono-photo-Fenton/oxalic acid</b>
Initial pH	6.5			
Final pH	3.95	3.79	3.77	6.2