

Supplementary Material

Sonochemical degradation of antibiotics from representative classes- Considerations on structural effects, initial transformation products, antimicrobial activity and matrix

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Text SM1. About selection of experimental conditions

The experimental conditions of volume, concentration, temperature and pH were selected based on previous works. For a reactor of 500 mL capacity, 300 mL of sample is a typical volume [1–3]; thus, in our work this value was used. Many papers about sonochemical treatment of organic pollutants are developed using concentration lower than 100 μM [1,4–7]; consequently, 40 μM was the chosen concentration, which also allows the pollutants to be easily quantified by HPLC apparatus equipped with a DAD detector.

Usually, under high frequency ultrasound, when the liquid temperature increases the elimination of pollutants is favored [8]; however, ultrasonic reactors for water treatment are commonly operated at temperatures between 20 and 25°C [1–4,9,10]. Therefore, our system was operated at 20°C. On the other hand, as the main objective of this research was to compare the degradation of antibiotics with different chemical structure, and changes of the solution pH can modify the sonochemical degradation [8], to avoid interferences the initial pH was fixed at 6.5.

Text SM2. Conditions for elucidation of primary transformation products

The chromatographic separation was performed using a Cortecs BEH C18 analytical column (2.1 mm \times 100 mm, 2.1 μm) from Waters. The mobile phase employed was composed by a mixture of methanol acidified with 0.01% formic acid (A) and water acidified with 0.01% formic acid (B), at a flow rate of 300 $\mu\text{L}/\text{min}$. The initial percentage of A was 10%, which was linearly increased to 90% in 14 min, followed by a 2 min isocratic period, and then returned to initial conditions over 2 min. The QTOF MS was operated in both ionization modes under the following conditions: capillary voltages of 700 (ESI+) and 2000 V (ESI-), cone voltage of 20 V, desolvation temperature set to 600 °C, source temperature to 130 °C and column temperature to 40 °C.

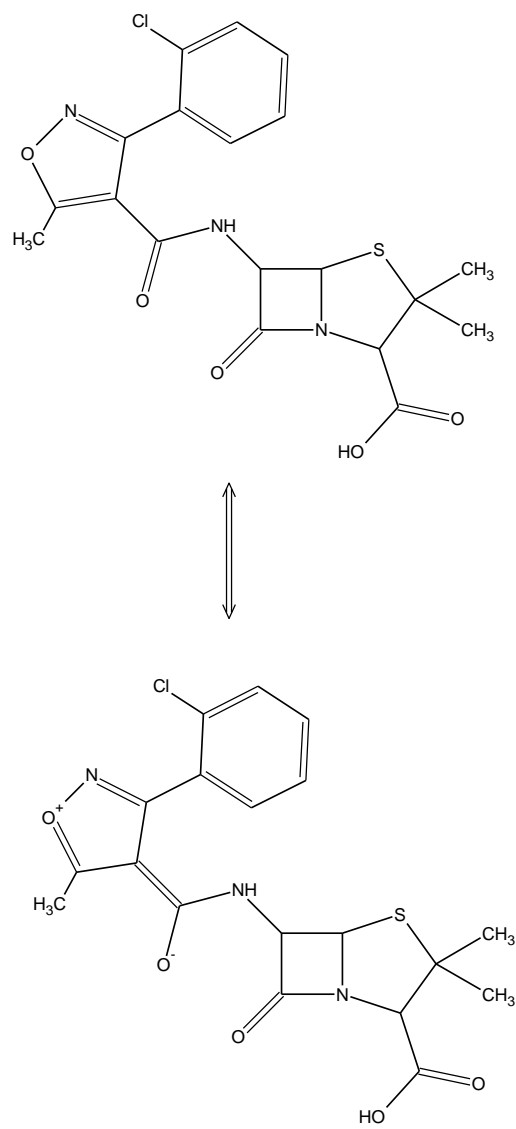
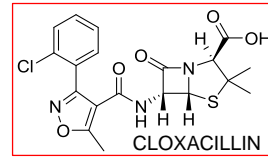


Figure SM1. Inductive and resonant effects generated by the oxazolyl substituent on CLX.

MS/MS data

84 udea (Cloxacillin, 0 min tratamiento US)
MIM_DEGRAD_US_057_358 (9.554) Cm (357:360)

ESI+



TOF MSMS 436.00ES+
1.56e6

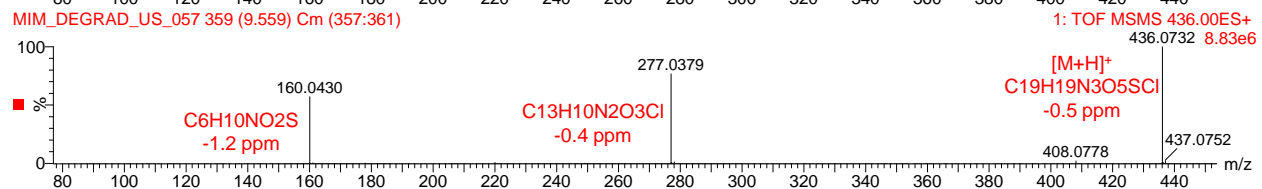
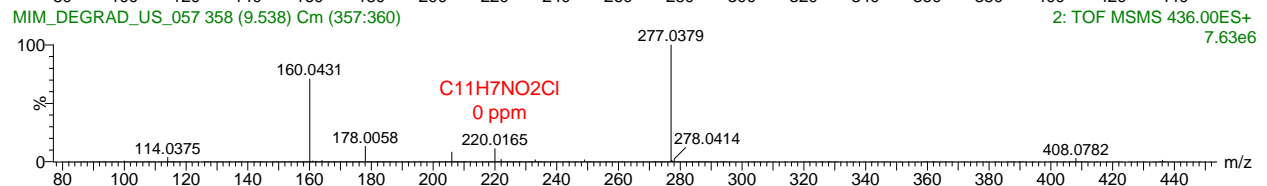
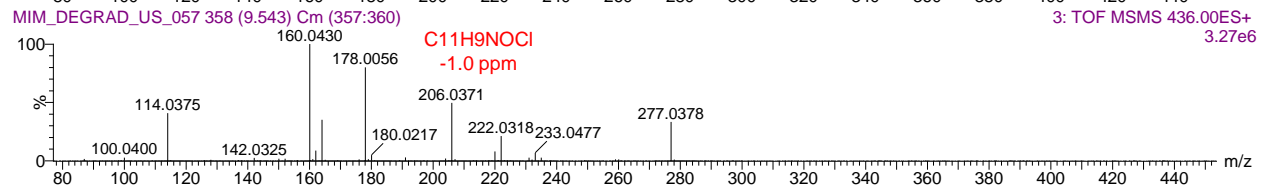
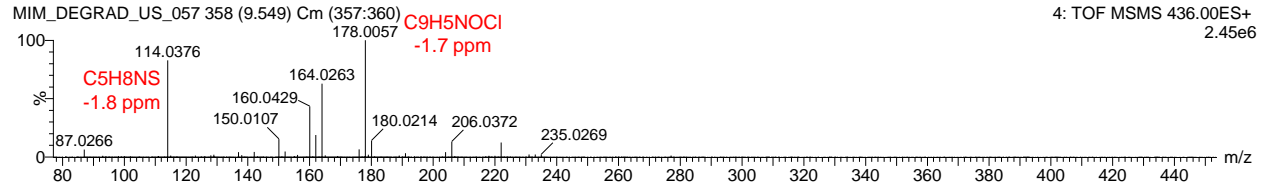
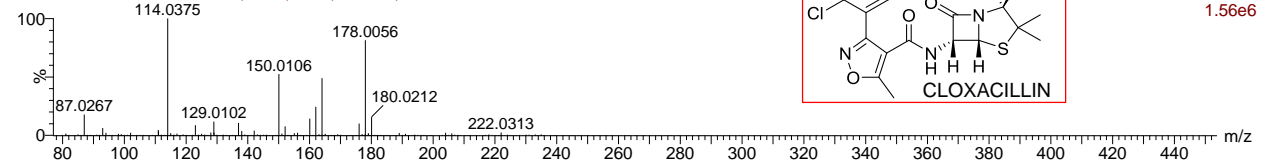
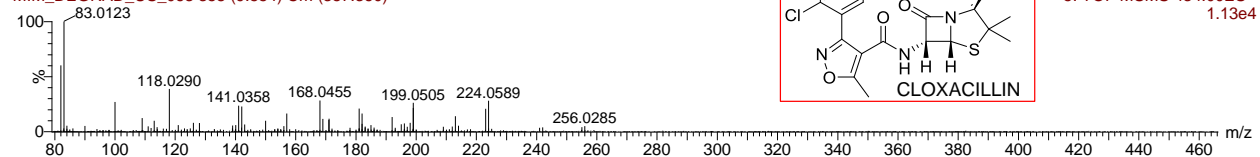


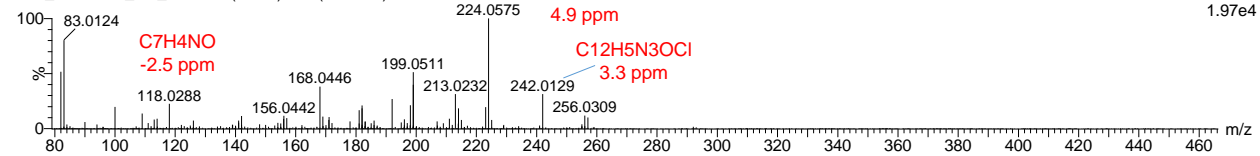
Figure SM2. MS/MS spectra of cloxacillin at (from bottom to top) 10, 20, 30, 40 and 50 eV, in positive ionization mode.

84 udea (Cloxacillin, 0 min tratamiento US)

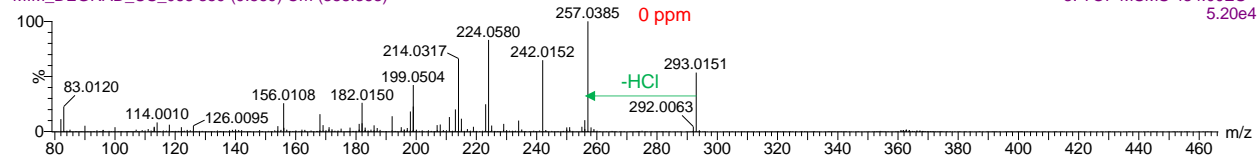
MIM_DEGRAD_US_063 358 (9.554) Cm (357:360)



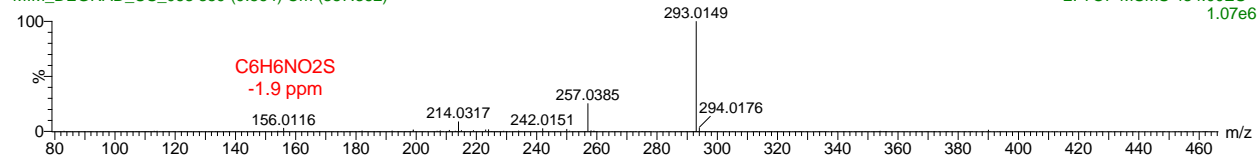
MIM_DEGRAD_US_063 359 (9.575) Cm (358:361)



MIM_DEGRAD_US_063 359 (9.569) Cm (358:363)



MIM_DEGRAD_US_063 359 (9.564) Cm (357:362)



MIM_DEGRAD_US_063 359 (9.559) Cm (358:362)

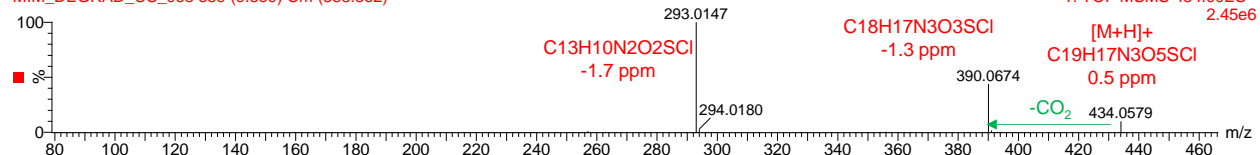
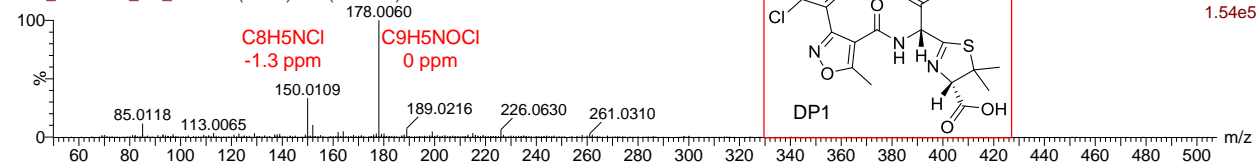


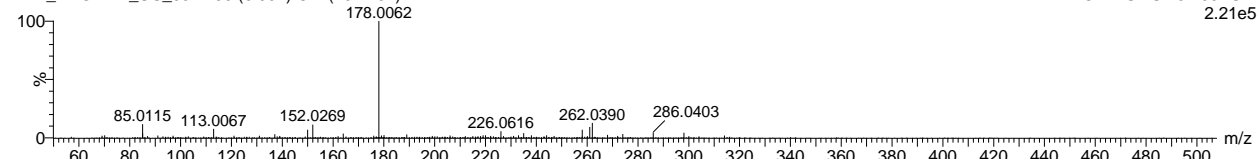
Figure SM3. MS/MS spectra of cloxacillin (from bottom to top) 10, 20, 30, 40 and 50 eV, in negative ionization mode.

85 udea (Cloxacillin, 25 min tratamiento US)

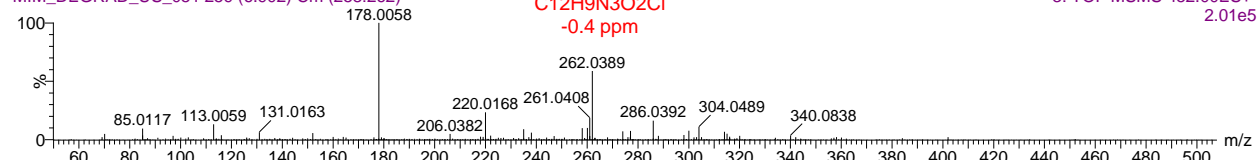
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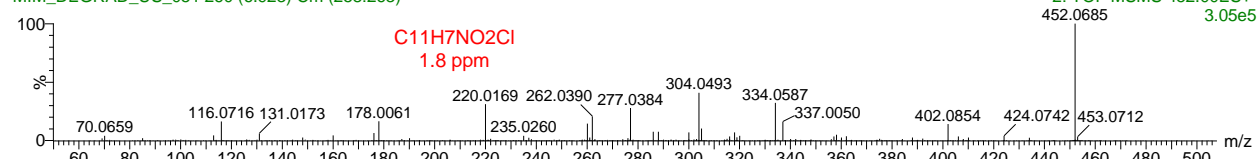
MIM_DEGRAD_US_051 259 (6.907) Cm (257:261)



MIM_DEGRAD_US_051 259 (6.902) Cm (258:262)



MIM_DEGRAD_US_051 260 (6.923) Cm (258:263)



MIM_DEGRAD_US_051 260 (6.918) Cm (258:263)

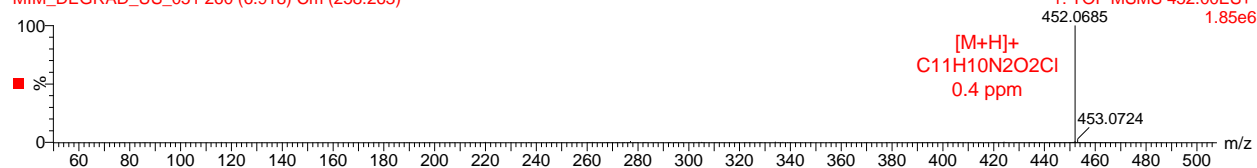


Figure SM4. MS/MS spectra of DP1 at (from bottom to top) 10, 20, 30, 40 and 50 eV, in positive ionization mode.

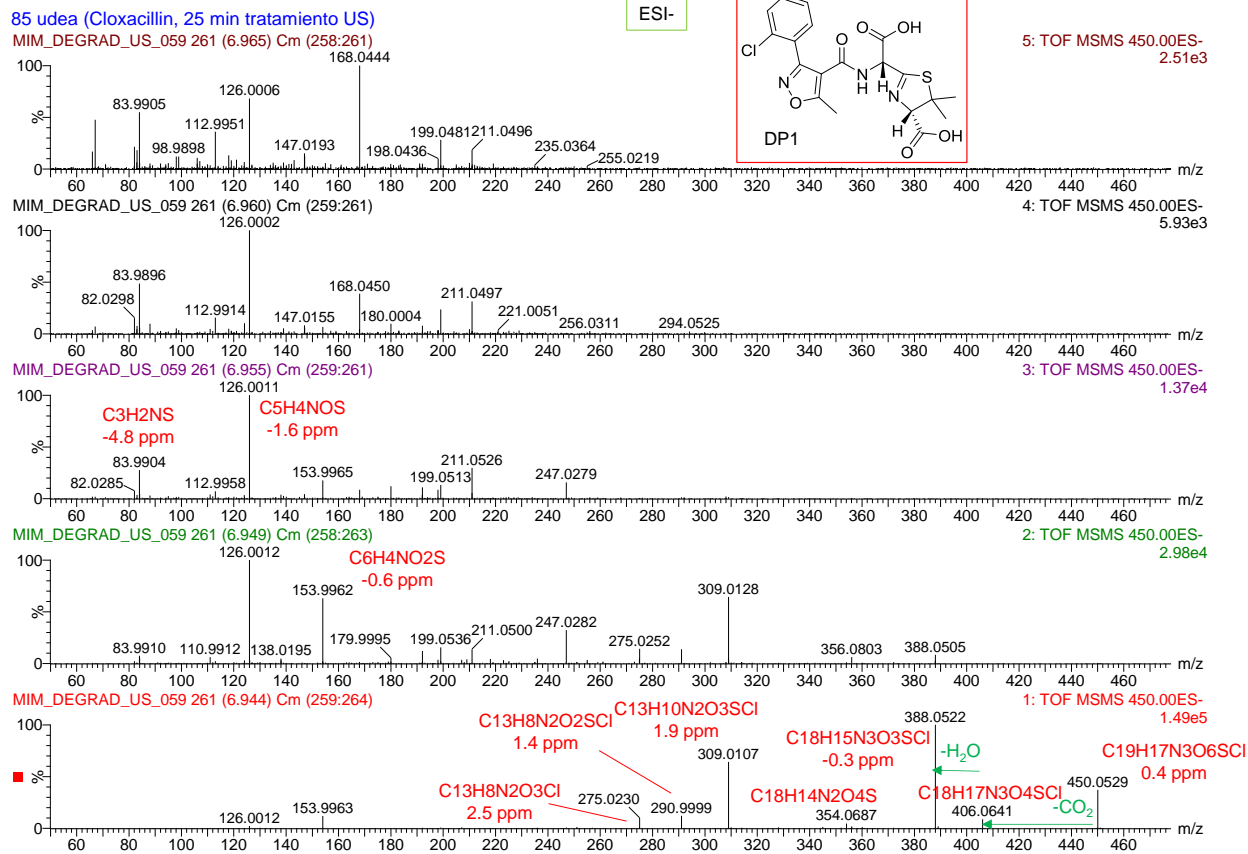
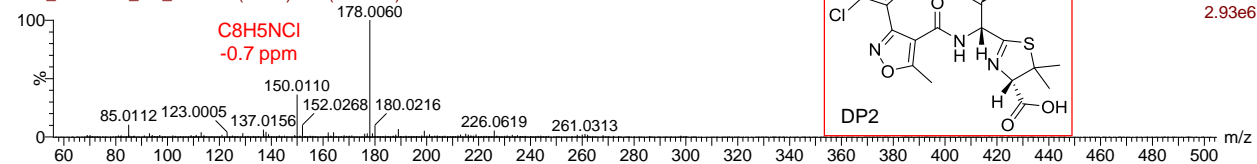


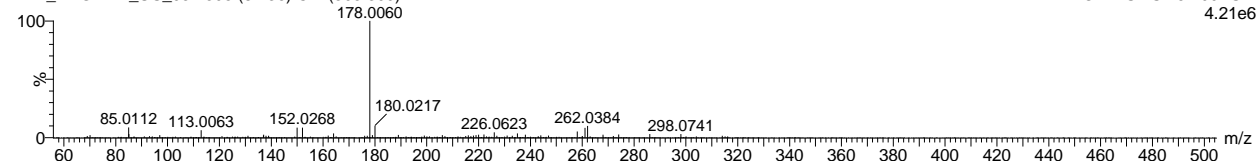
Figure SM5. MS/MS spectra of DP1 at (from bottom to top) 10, 20, 30, 40 and 50 eV, in negative ionization mode.

85 udea (Cloxacillin, 25 min tratamiento US)

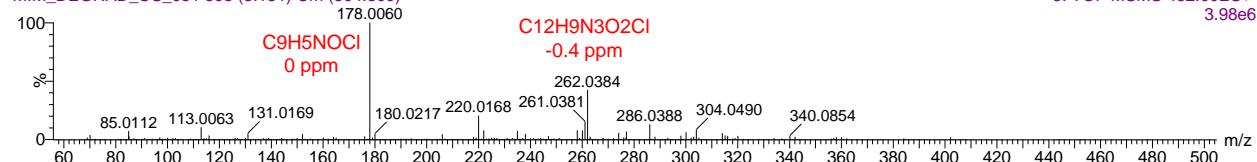
MIM_DEGRAD_US_051 305 (8.142) Cm (301:309)



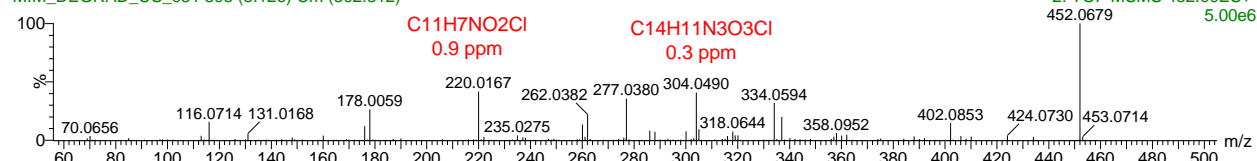
MIM_DEGRAD_US_051 305 (8.136) Cm (303:309)



MIM_DEGRAD_US_051 305 (8.131) Cm (304:309)



MIM_DEGRAD_US_051 305 (8.126) Cm (302:312)



MIM_DEGRAD_US_051 305 (8.121) Cm (301:311)

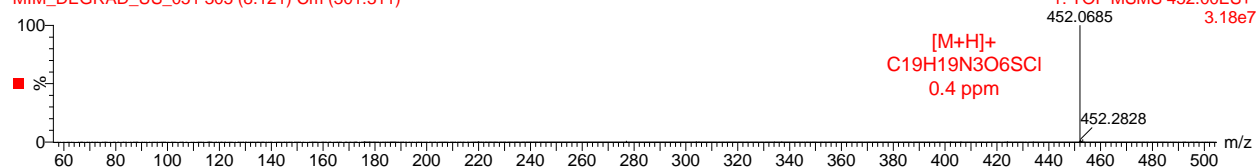


Figure SM6. MS/MS spectra of DP2 at (from bottom to top) 10, 20, 30, 40 and 50 eV, in positive ionization mode.

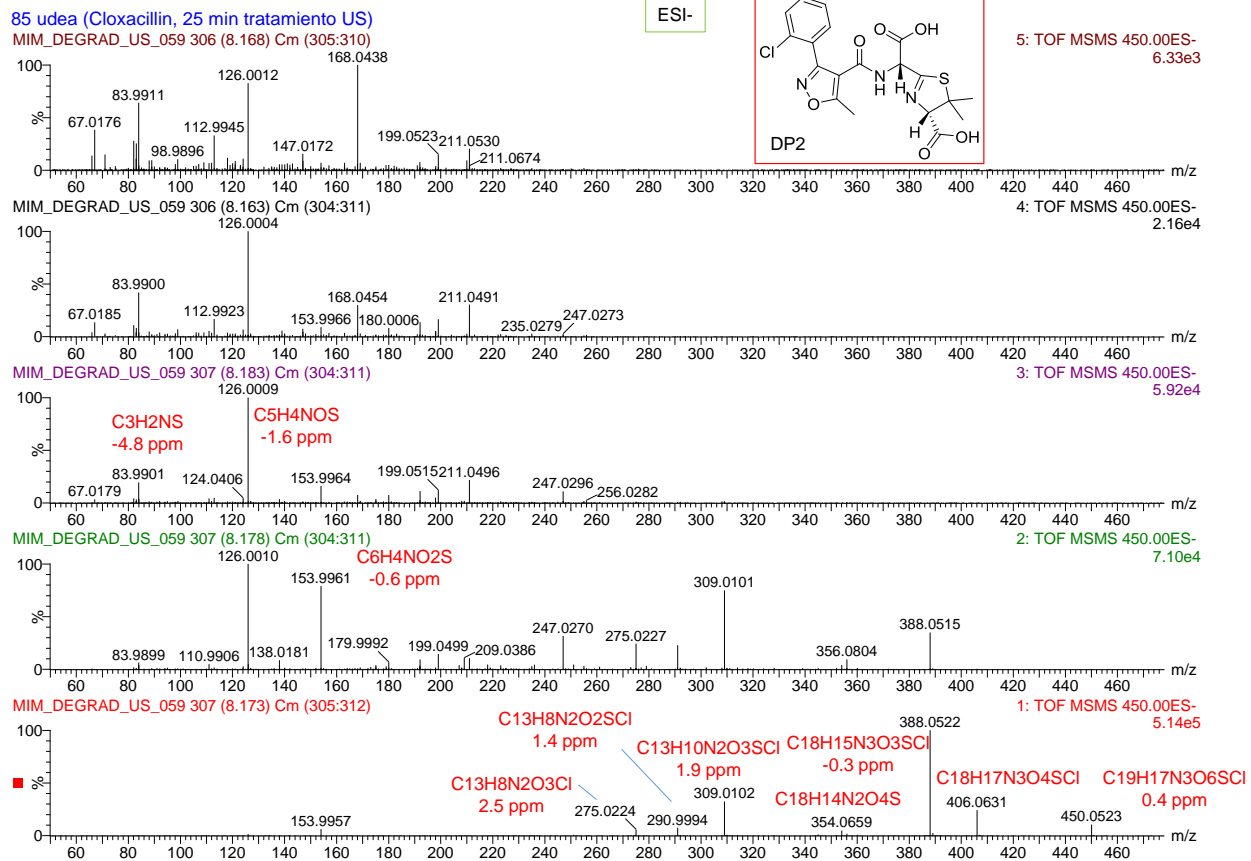


Figure SM7. MS/MS spectra of DP2 at (from bottom to top) 10, 20, 30, 40 and 50 eV, in negative ionization mode.

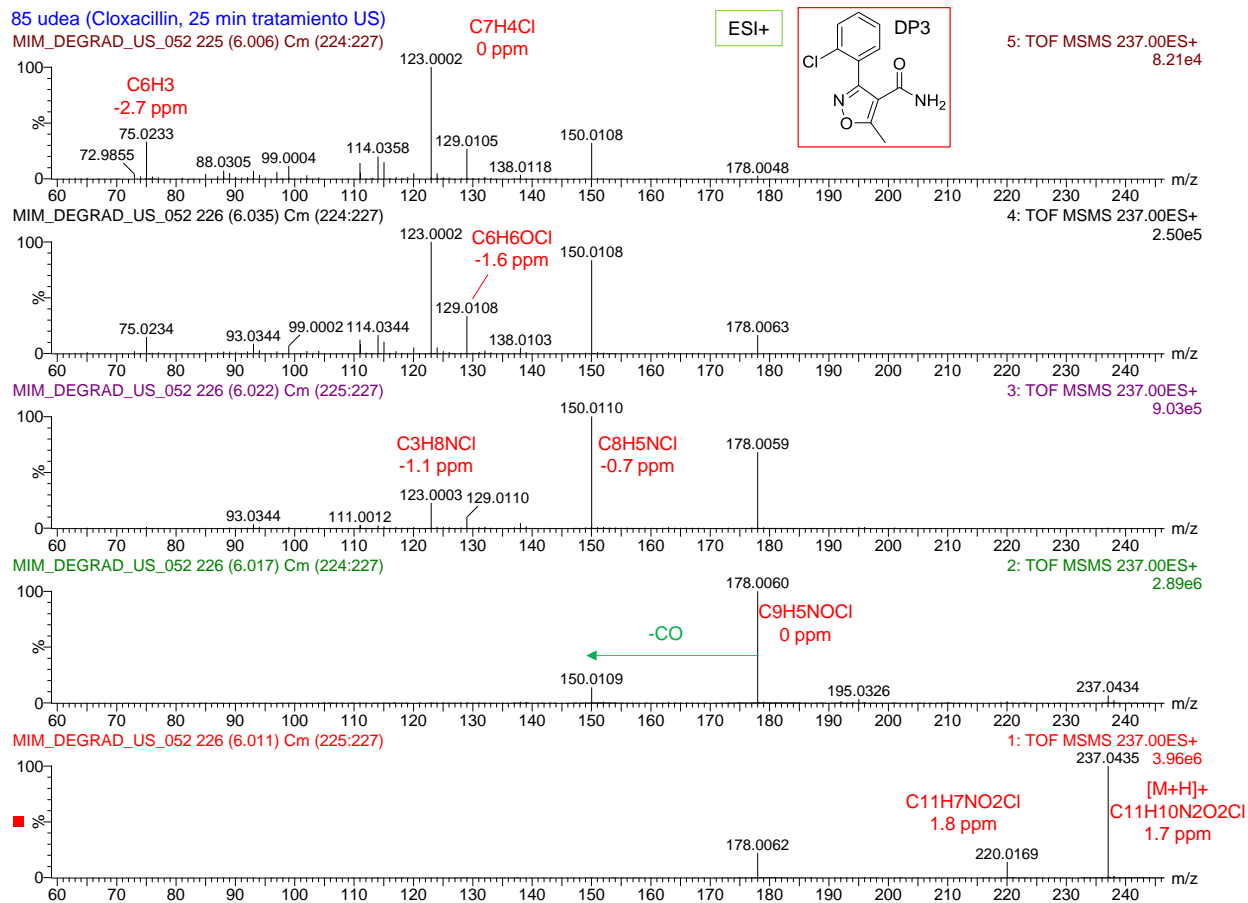
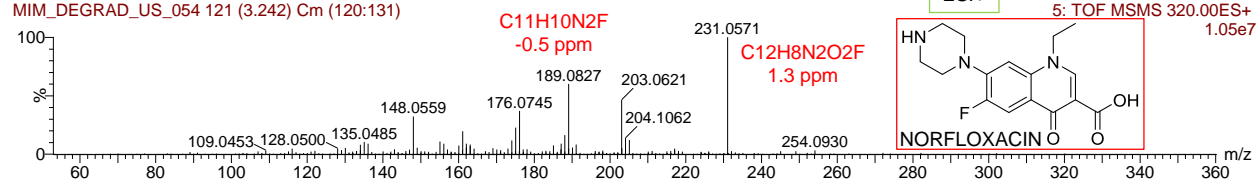


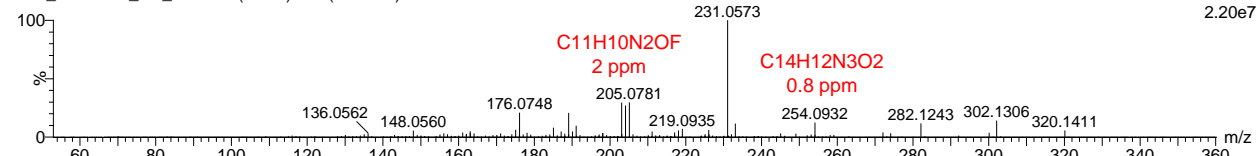
Figure SM8. MS/MS spectra of DP3 at (from bottom to top) 10, 20, 30, 40 and 50 eV, in positive ionization mode.

82 udea (Norfloxacin, 0 min tratamiento US)

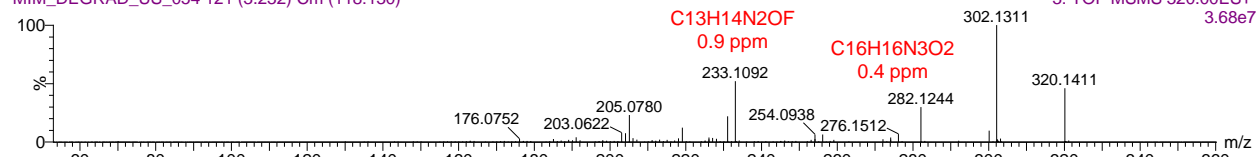
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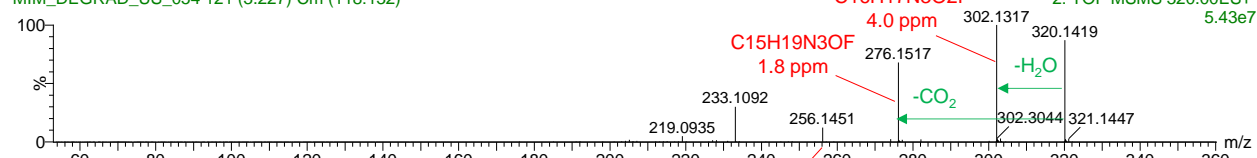
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MIM_DEGRAD_US_054 121 (3.232) Cm (118:130)



MIM_DEGRAD_US_054 121 (3.227) Cm (118:132)



MIM_DEGRAD_US_054 134 (3.570) Cm (134:136)

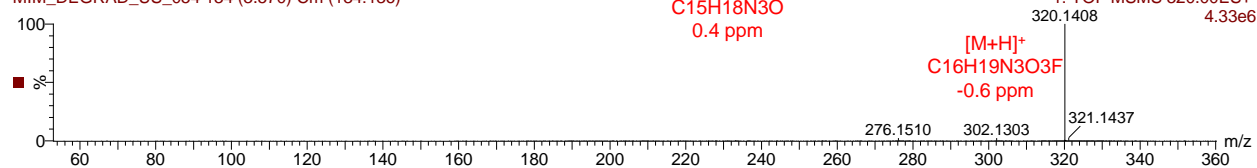
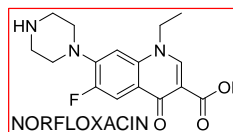


Figure SM9. MS/MS spectra of norfloxacin at (from bottom to top) 10, 20, 30, 40 and 50 eV, in positive ionization mode.

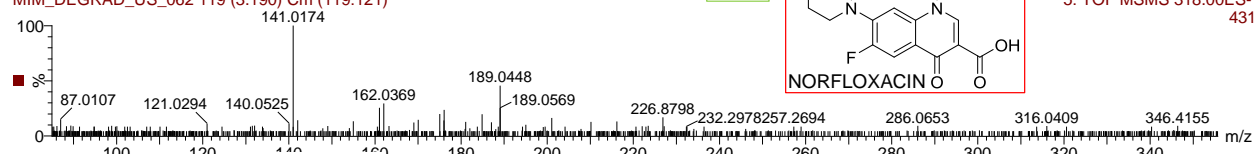
82 udea (Norfloxacin, 0 min tratamiento US)

MIM_DEGRAD_US_062 119 (3.190) Cm (119:121)

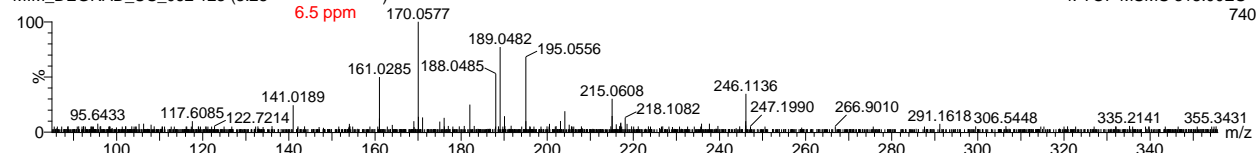
ESI-



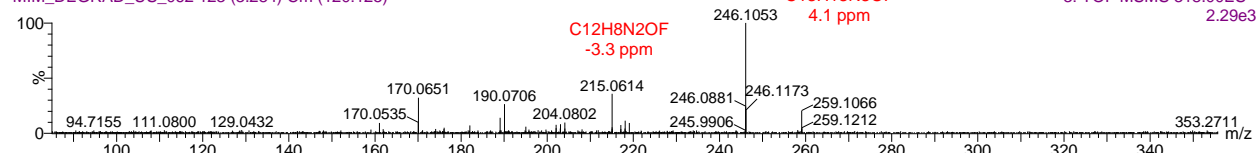
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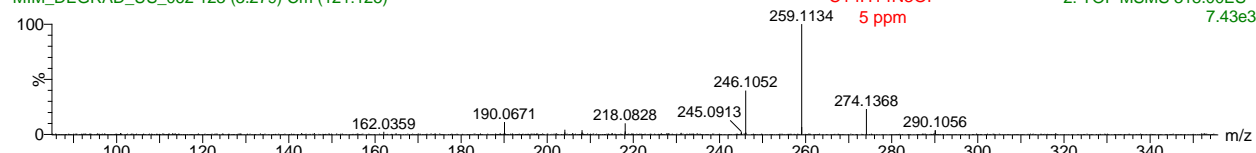
MIM_DEGRAD_US_062 123 (3.28) Cm (120:125)



MIM_DEGRAD_US_062 123 (3.284) Cm (120:125)



MIM_DEGRAD_US_062 123 (3.279) Cm (121:125)



MIM_DEGRAD_US_062 123 (3.274) Cm (122:125)

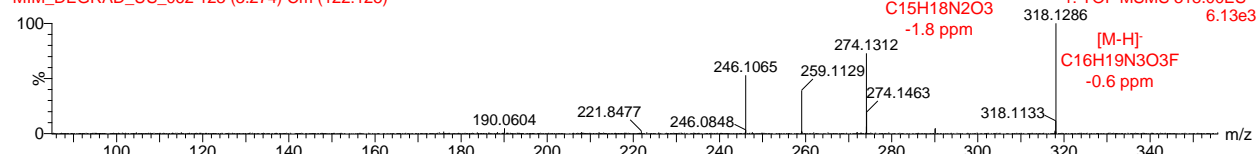
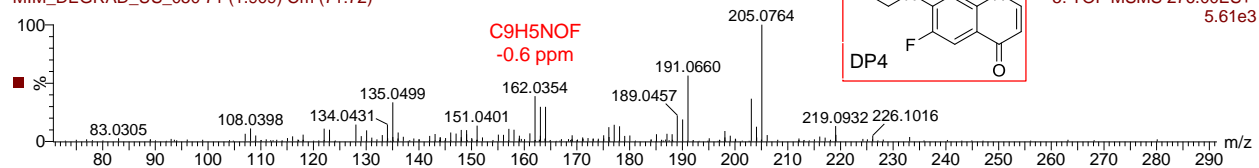


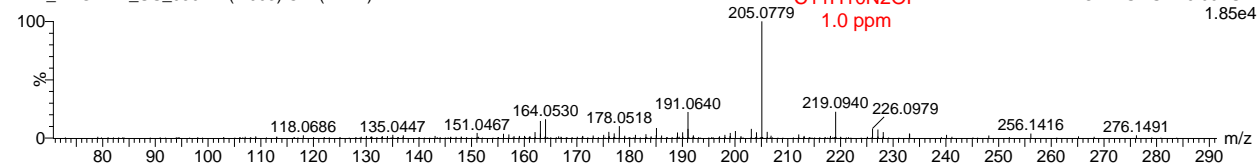
Figure SM10. MS/MS spectra of norfloxacin at (from bottom to top) 10, 20, 30, 40 and 50 eV, in negative ionization mode.

83 udea (Norfloxacin, 30 min tratamiento US)

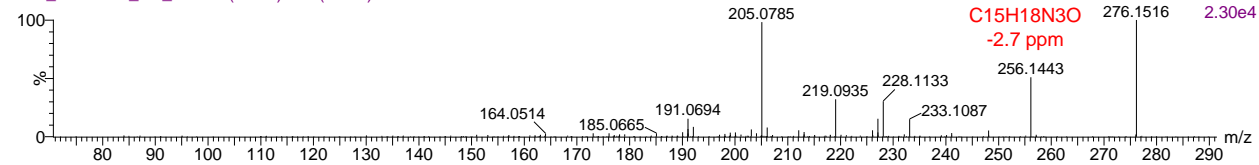
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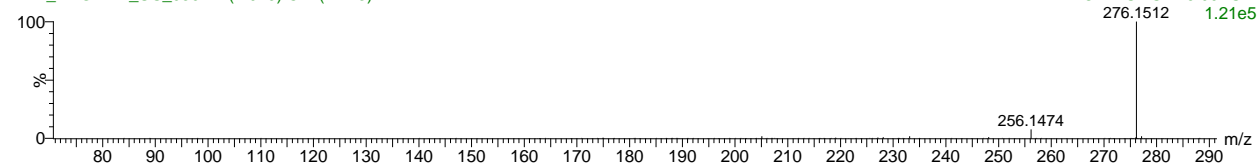
MIM_DEGRAD_US_050 71 (1.903) Cm (71:72)



MIM_DEGRAD_US_050 71 (1.898) Cm (71:72)



MIM_DEGRAD_US_050 72 (1.919) Cm (71:73)



MIM_DEGRAD_US_050 72 (1.914) Cm (71:73)

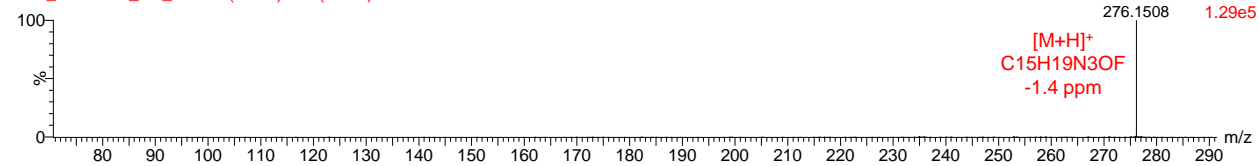
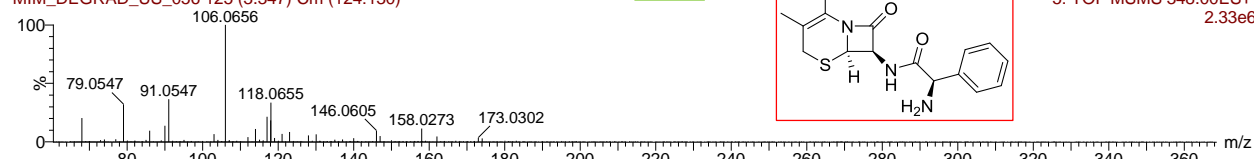


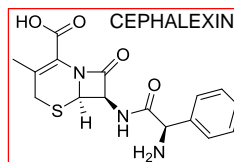
Figure SM11. MS/MS spectra of DP4 at (from bottom to top) 10, 20, 30, 40 and 50 eV, in positive ionization mode.

86 udea (Cephalexin, 0 min tratamiento US)

MIM_DEGRAD_US_056 125 (3.347) Cm (124:130)

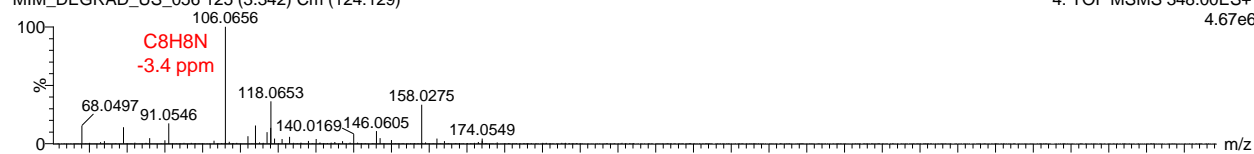


ESI+

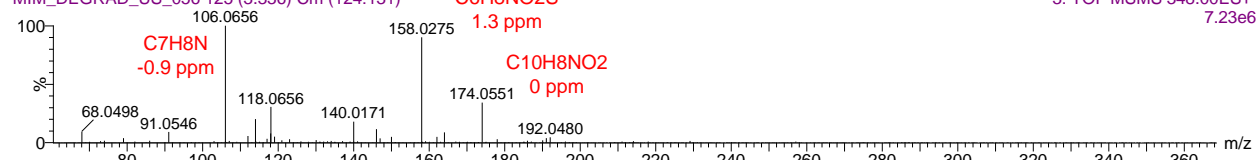


5: TOF MSMS 348.00ES+
2.33e6

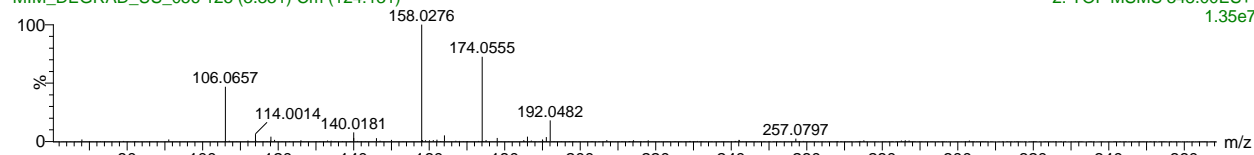
MIM_DEGRAD_US_056 125 (3.336) Cm (124:129)



MIM_DEGRAD_US_056 125 (3.331) Cm (124:131)



MIM_DEGRAD_US_056 125 (3.331) Cm (124:131)



MIM_DEGRAD_US_056 125 (3.326) Cm (124:130)

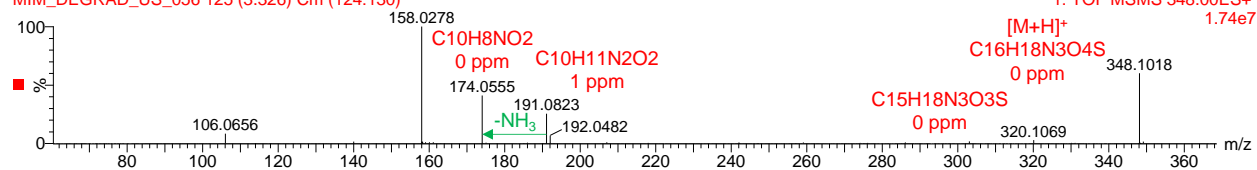
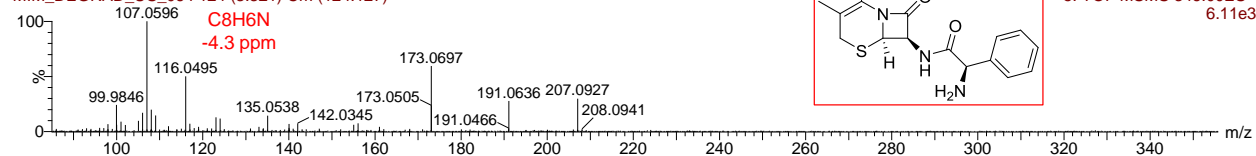


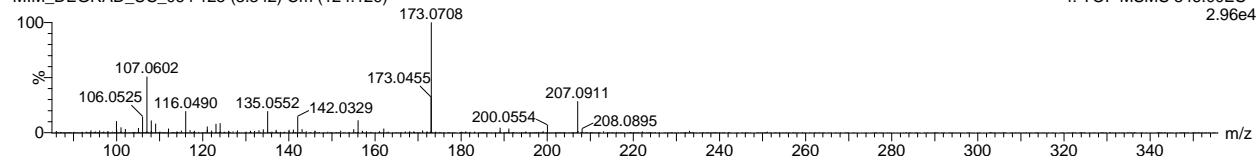
Figure SM12. MS/MS spectra of cephalexin at (from bottom to top) 10, 20, 30, 40 and 50 eV, in positive ionization mode.

86 udea (Cephalexin, 0 min tratamiento US)

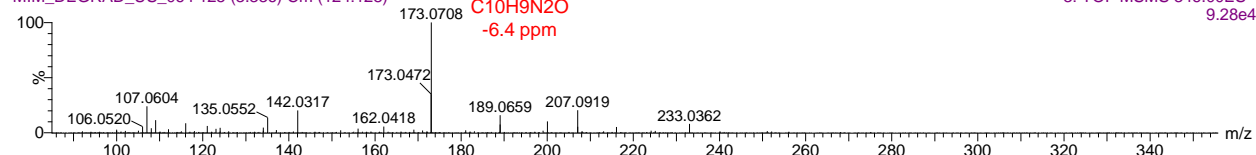
MIM_DEGRAD_US_064 124 (3.321) Cm (124:127)



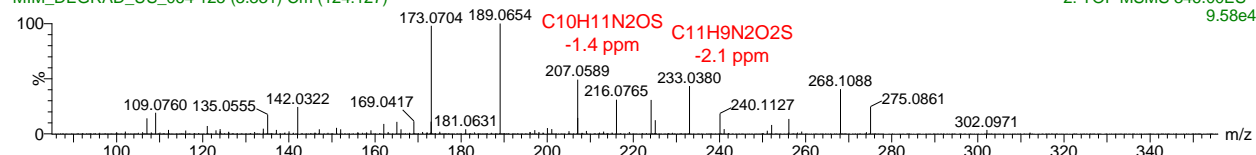
MIM_DEGRAD_US_064 125 (3.342) Cm (124:129)



MIM_DEGRAD_US_064 125 (3.336) Cm (124:128)



MIM_DEGRAD_US_064 125 (3.331) Cm (124:127)



MIM_DEGRAD_US_064 125 (3.326) Cm (124:129)

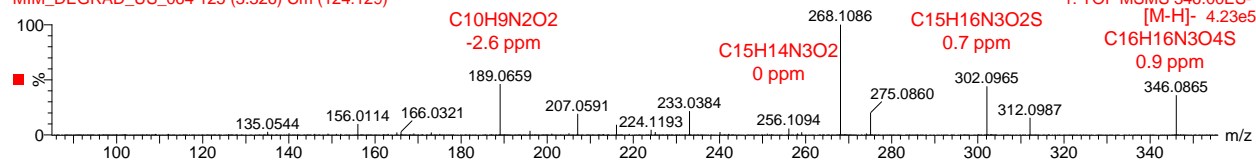
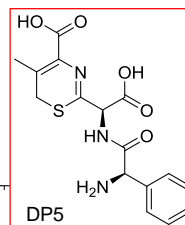


Figure SM13. MS/MS spectra of cephalexin at (from bottom to top) 10, 20, 30, 40 and 50 eV, in negative ionization mode.

87 udea (Cephalexin, 35 min tratamiento US)

MIM_DEGRAD_US_053 57 (1.542) Cm (56:59)

ESI+



5: TOF MSMS 364.00ES+
1.94e6

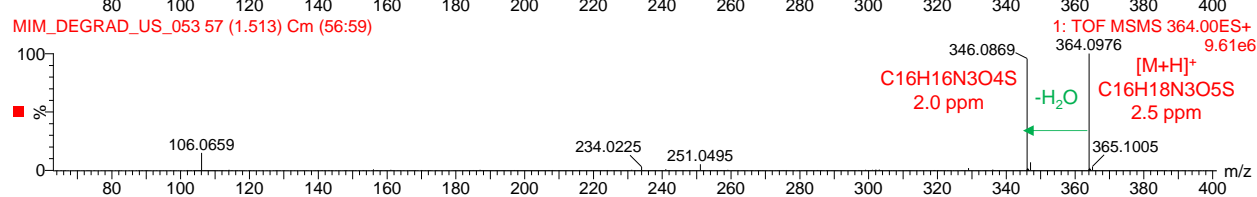
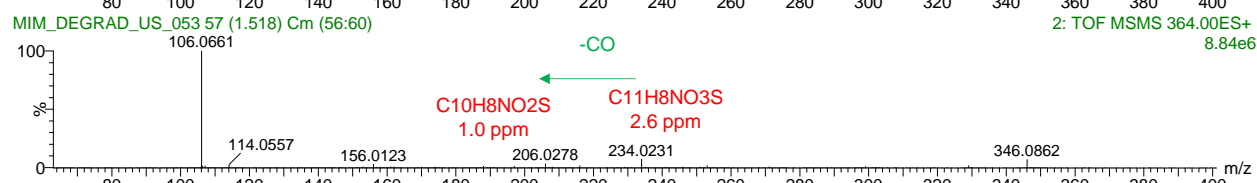
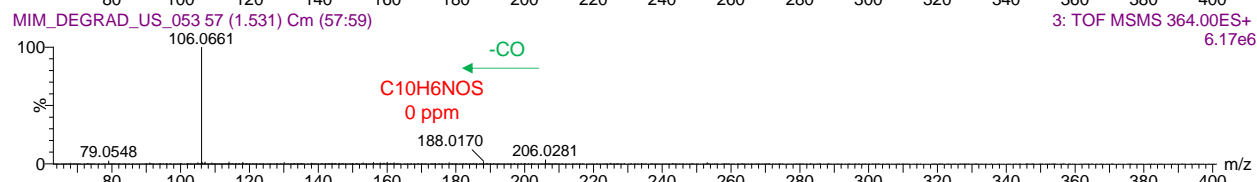
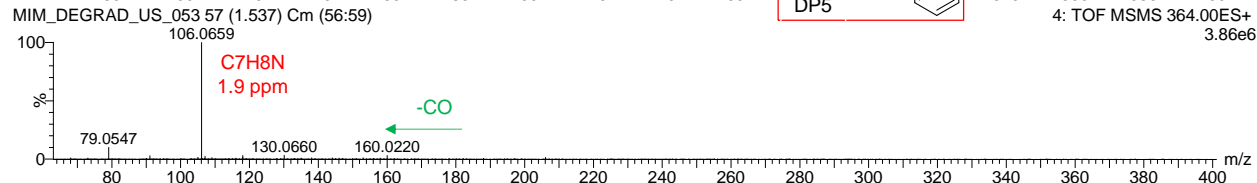
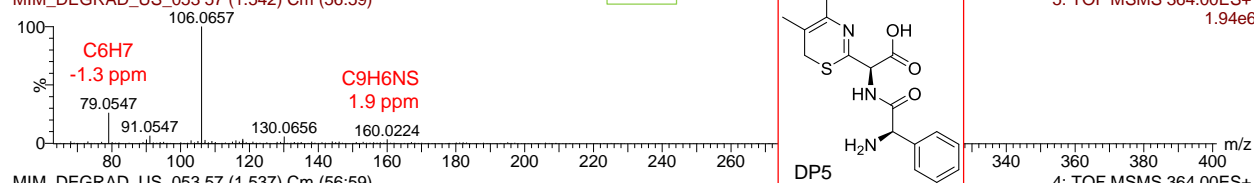
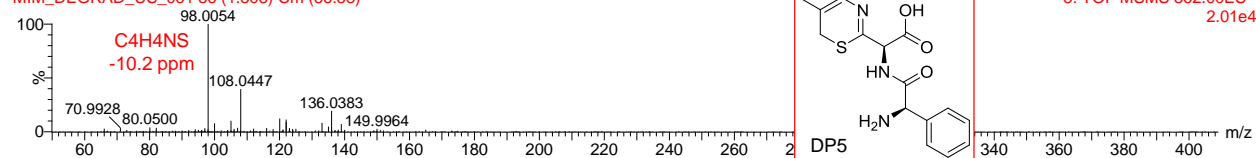


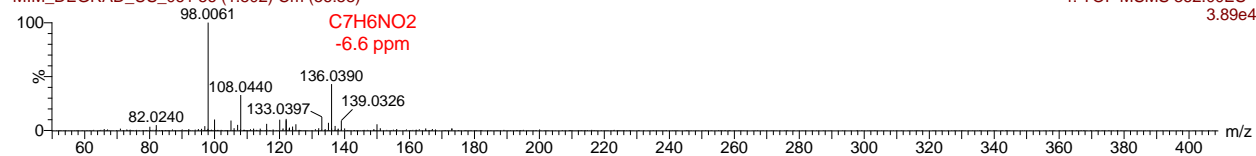
Figure SM14. MS/MS spectra of DP5 at (from bottom to top) 10, 20, 30, 40 and 50 eV, in positive ionization mode.

87 udea (Cephalexin, 35 min tratamiento US)

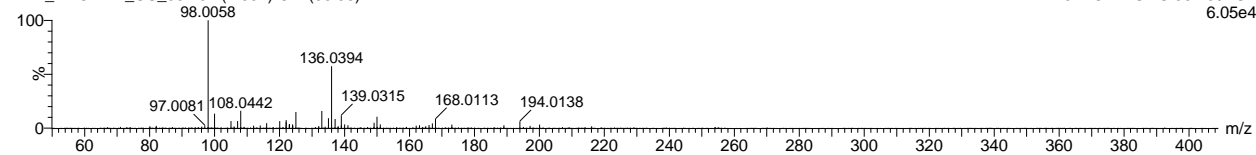
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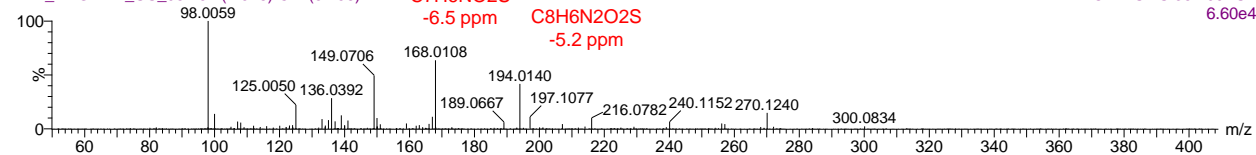
MIM_DEGRAD_US_061 56 (1.502) Cm (56:58)



MIM_DEGRAD_US_061 57 (1.532) Cm (56:58)



MIM_DEGRAD_US_061 57 (1.518) Cm (57:58)



MIM_DEGRAD_US_061 57 (1.513) Cm (56:58)

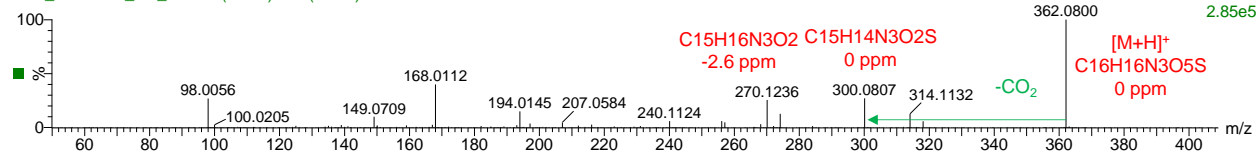


Figure SM15. MS/MS spectra of DP5 at (from bottom to top) 10, 20, 30, 40 and 50 eV, in negative ionization mode.

Table SM1. Composition of the simulated hospital wastewater (HWW) and seawater (SW).

HWW*								
Substance	NaCl	CaCl ₂	KCl	Na ₂ SO ₄	KH ₂ PO ₄	NH ₄ Cl	Urea	pH
Concentration (μmol L⁻¹)	51300	340	1340	710	370	940	21000	6.5
SW								
Substance	NaCl	MgSO ₄ -7 H ₂ O	CaCl ₂ -2H ₂ O		NaHCO ₃		pH	
Concentration (μmol L⁻¹)	500000	50000	10000		2000		6.5	

*Preparation based on [11].

Supplementary references

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