Supplementary Materials

Photocatalytic Degradation of Norfloxacin on Different TiO2-X Polymorphs under Visible Light in Water

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Preparation of different TiO_{2-x}polymorps

Preparation of Cat.I-A: The synthetic procedure of Cat.I-A was reported elsewhere [1]. Typically, 0.7 g of L-ascorbic acid was added to 70 mL of deionized water, and the mixture was stirred for 10 min using a magnetic stirrer. Subsequently, 3.1 mL of $TiCl_3$ was added and a purple solution was formed. Then, NaOH solution (1 mol/L) was added to raise the pH to 4. After stirring for another 30 min, the as-resulted mixture was transferred to a 100 mL Teflon-lined stainless steel autoclave and heated at 180 °C for 12 h. The obtained precipitate was collected by centrifugation, rinsed with water and ethanol for several times. After drying at 80°C overnight, the sample was obtained without further treatment.

Preparation of Cat.II-R: The method was reported elsewhere [2]. Typically, titanium powder (0.300 g) and hydrochloric acid (10 mL, 2 mol/L) were mixed in a 50 mL pyrex beaker and magnetically stirred for 15 min. The mixture was then transferred to a Teflon-lined stainless-steel autoclave (23 mL capacity) and hydrothermally treated for 12 h at 220°C. The sample was then collected and washed three times with distilled water and ethanol.

Preparation of Cat.III-B: In a typical synthetic process [3], TiH_2(0.256 g) and H_2O (2 mL) were mixed in a 50 mL round-bottomed flask, and the mixture was magnetically stirred for 5 min for the generation of a dark gray suspension. Then H_2O_2(30 mL, 30.0 wt%) as an oxidation agent was added dropwise, and the as-obtained mixture was vigorously stirred for 12 h to reach a yellowish gel-like state. After that, double distilled water (40 mL) was added under continuous magnetic stirring. As pH regulator, a certain amount of NaOH (1.0 M) solution was added gradually until the pH of this transparent solution which was light yellow in color reached 9.0. As a reducing agent, $NaBH_4$(0.4 g) was added and the mixture was immediately transferred to a Teflon-lined stainless-steel autoclave and hydrothermally treated at 180°C for 24 h. The harvested material was then immerged in HCl (50.0 mL, 1.0 M) solution to eliminate the sodium boron compound. After 10 h of stirring, the powder was separated and was washed with distilled water and ethanol repetitively to

remove impurities such as Na^+, Cl^-, and BO_3^{2-}. The as-obtained precipitate was dried under vacuum for 12 h to yield TiO_2nanocrystalsin the form of grey blue powder. Post annealing of the TiO_{2-x} sample was conducted in a flow of argon using a tube furnace at 500 °C for 3 h to generate the Cat.III-B sample.

Preparation of Cat.IV-A&R: In a typical synthetic procedure [4], ethanol (10.00 g), 2-ethylimidazole (0.1-1.80 g), and hydrochloric acid (2.50 g) were mixed in a 50 mL pyrex beaker and magnetically stirred for 15 min to generate a clear solution. Then titanium (IV) isopropoxide (2.00g) was added dropwise, and the resulted mixture was stirred for another 15 min. The beaker with its content was then placed in a preheated oven (500 °C) for the contentto undergo combustion. After 5 h, Cat IV was obtained with no further treatment. Different amounts of 2-ethylimidazole were used correspondingly to synthesize a variety of catalysts, i.e. 1.8 g for Cat.IV-1, 1.0 g for Cat.IV-2, 0.3 g for Cat.IV-3 and 0.1 g for Cat.IV-4.

Reference

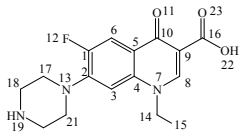
[1] M.W. Shah, Y.Q. Zhu, X.Y. Fan, J. Zhao, Y.X. Li, S. Asim, C.Y. Wang*, Sci. Rep*. 5 (2015)15804-15812.

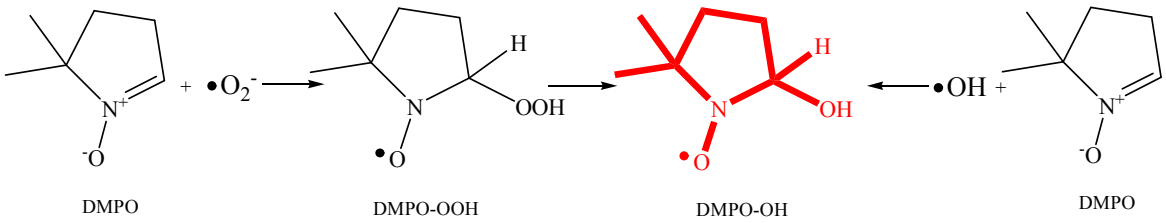
[2] F. Zuo, K. Bozhilov, R.J. Dillon, L. Wang, P. Smith, X. Zhao, C. Bardeen, P.Y. Feng*, Angew. Chem. Int. Edit.* 51 (2012) 6223-6226.

[3] X.Y. Xin, T. Xu, L. Wang, C.Y. Wang*, Sci. Rep*. 6 (2016) 23684-23692.

[4] F. Zuo, L. Wang, T. Wu, Z.Y. Zhang, D. Borchardt, P.Y. Feng*, J. Am. Chem. Soc.* 132 (2010) 11856-11857.

Table S1 Point charges (PCs) and frontier electron densities (FEDs) on atoms of *Nor* calculated by Gaussian 03 program at B3LYP/6-31G* level.

Atoms				
	$2FED_{HOMO}^2$	$2FED_{LUMO}^2$	$FED_{HOMO}^2+FED_{LUMO}^2$	PCs
C1	**0.2072**	0.0584	0.1328	0.3827
C2	0.0764	**0.2956**	**0.1860**	0.3509
C3	0.0116	**0.3202**	**0.1659**	-0.0312
C4	0.0896	0.0014	0.0455	0.4778
C5	**0.2510**	0.0686	**0.1598**	-0.2324
C6	0.0178	**0.4048**	**0.2113**	0.1305
N7	**0.1976**	0.1290	0.1633	**-1.0801**
C8	0.0006	**0.4666**	**0.2336**	**0.6766**
C9	0.1346	0.0566	0.0956	-0.4368
C10	0.0048	0.1662	0.0865	**0.6568**
O11	**0.1730**	0.1860	**0.1795**	**-0.6139**
F12	0.0574	0.0054	0.0314	-0.4057
N13	**0.2060**	0.0436	0.1248	**-0.8332**
C14	0.0020	0.0158	0.0089	0.3334
C15	0.0004	0.0038	0.0021	0.0445
C16	0.0010	0.0074	0.0042	**0.9415**
C17	0.0094	0.0452	0.0273	0.2340
C18	0.0032	0.0114	0.0083	0.2476
N19	0.0092	0.0044	0.0068	-0.3950
C20	0.0070	0.0054	0.0062	0.2499
C21	0.0048	0.0032	0.0040	0.2217
O22	0.0012	0.0010	0.0011	-0.3210
O23	0.0168	0.0114	0.0141	**-0.5985**



Scheme S1 DMPO-OH production from 5,5-dimethly-1-pyrroline *N*-oxide (DMPO)

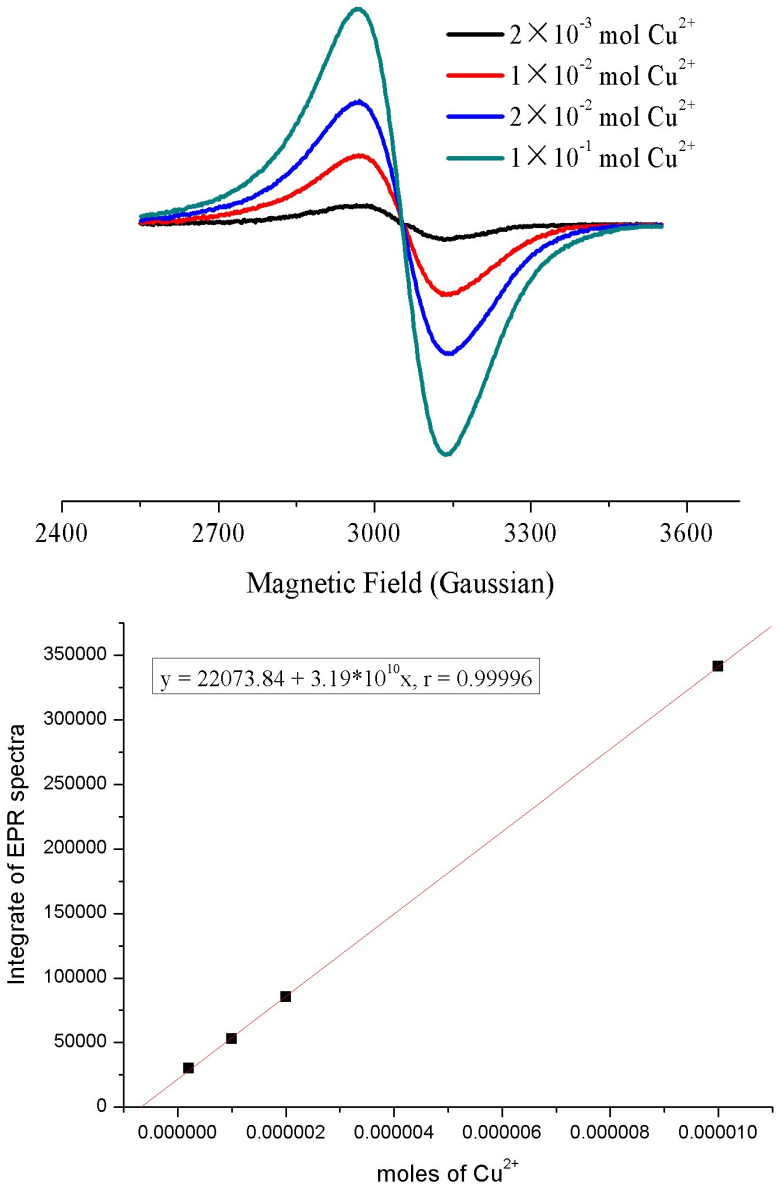


Fig.S1 EPR spectra of Cu^{2+} and the calibration curve used to determine Ti^{3+} concentration

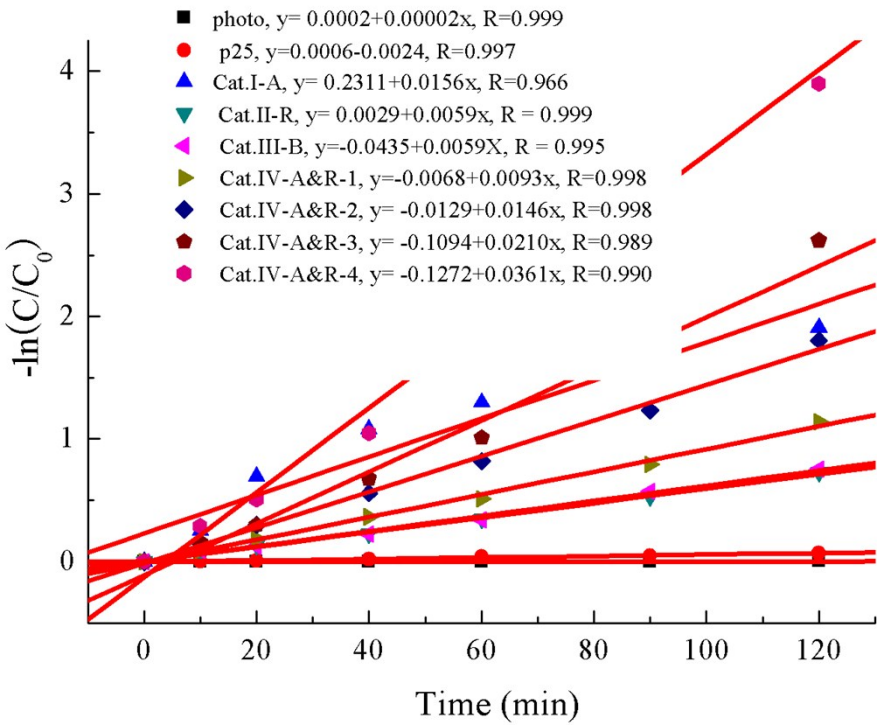


Fig. S2 The plots of –ln(C/C_0) versus reaction time (min) for degradation curves under different catalytic system

In order to obtain the adsorption isotherms of Nor on different TiO_{2-x}, 50 mL of *Nor* aqueous solutions with various initial concentrations of 25 μM, 50 μM, 100 μM, 200 μM, 400 μM, 600 μM and 800 μM were placed in contact with 0.05 g of TiO_{2-x}. After 24 h of magnetic stirring in the dark, the aqueous samples were filtered through 0.45 μm membranes to remove TiO_{2-x} powder before analyzing the concentration of *Nor* by HPLC.

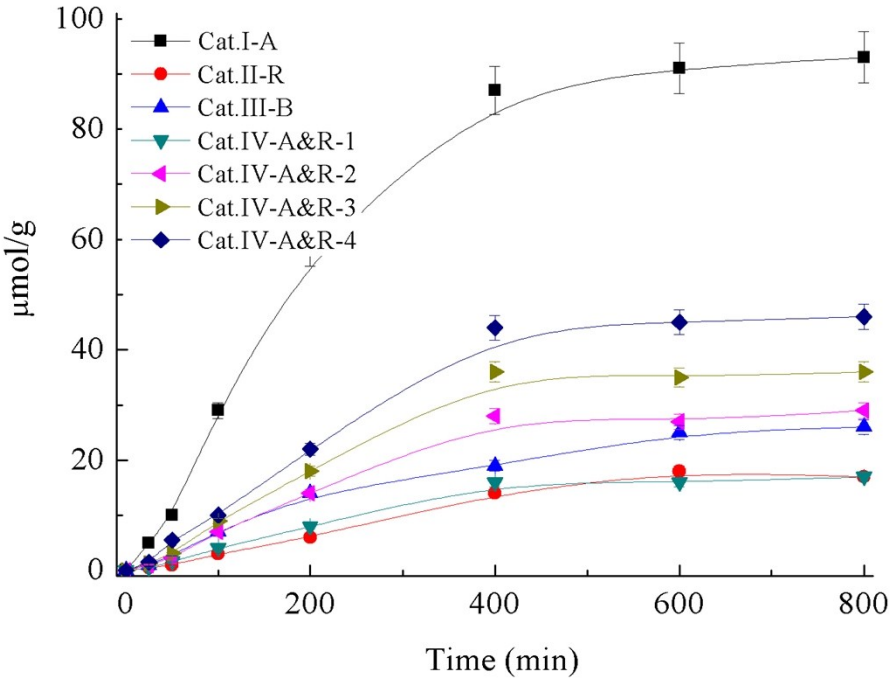
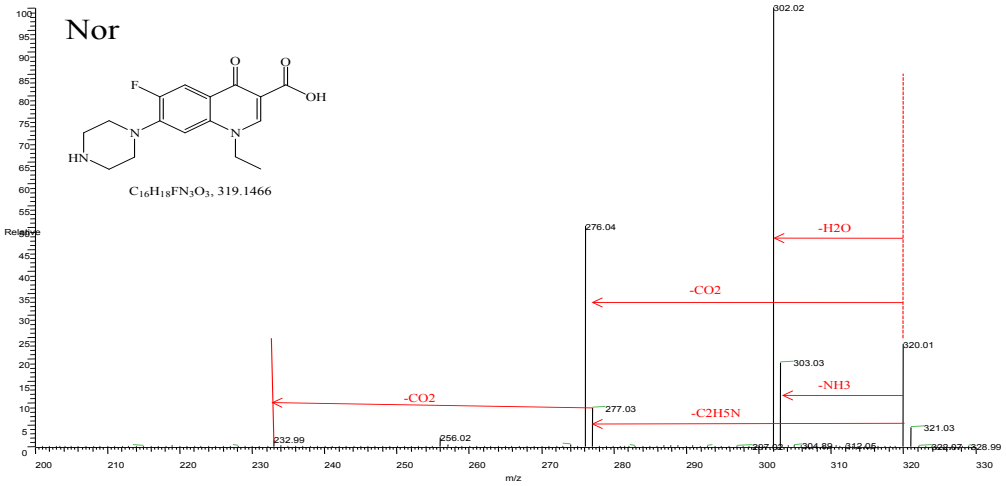
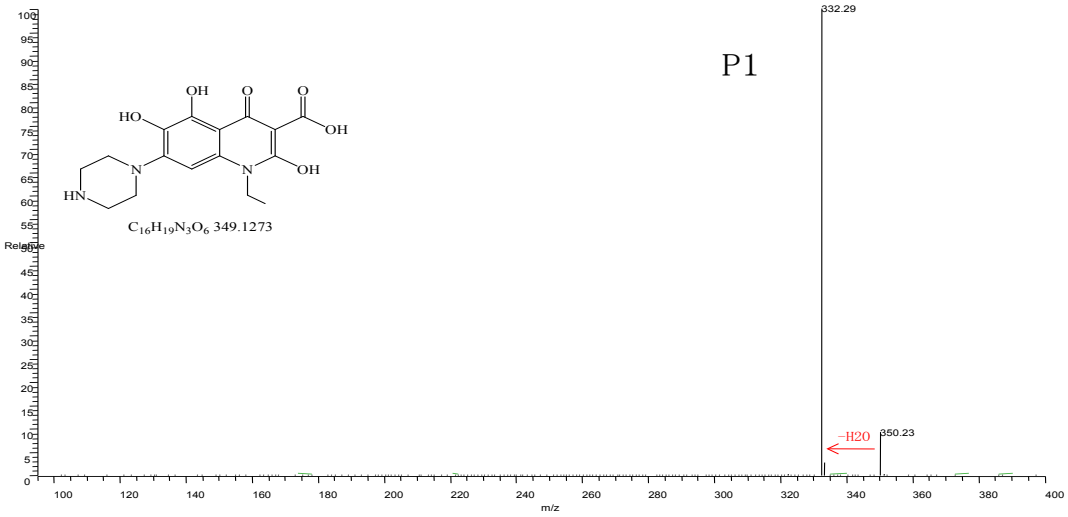
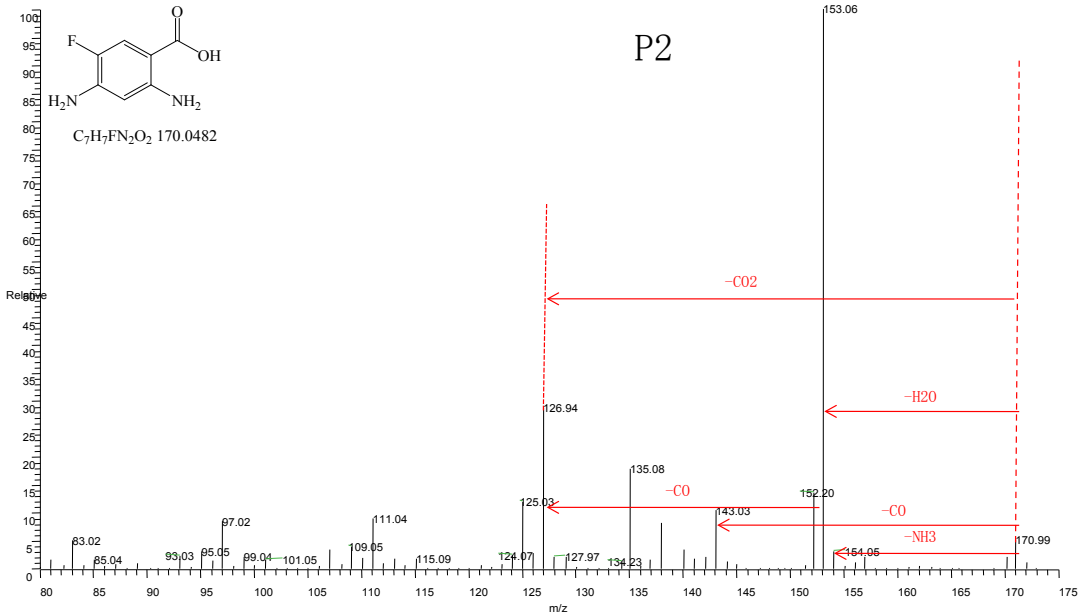


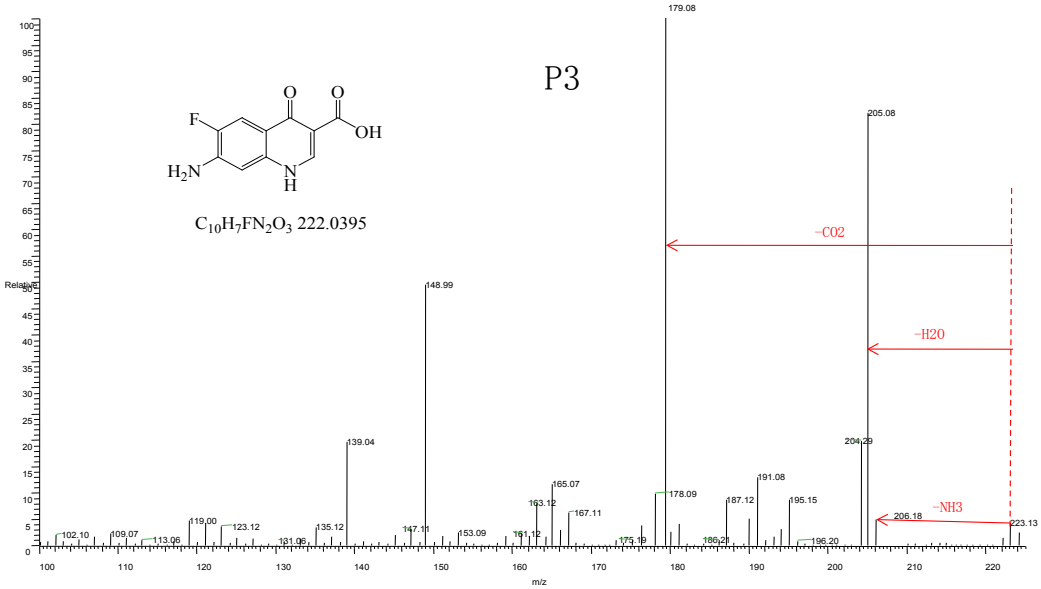
Fig.S3 Adsorption isotherm of *Nor* on different TiO_{2-x}. ([TiO_{2-x}] = 1.0 g/L, pH value = 7.0±0.2)

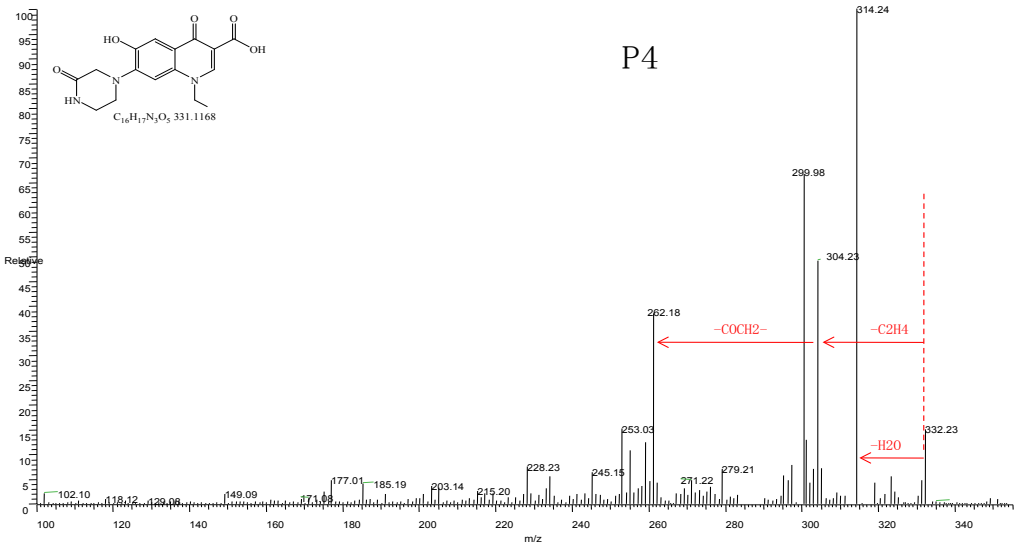
Mass spectra of *Nor* and *P1* to *P19*:

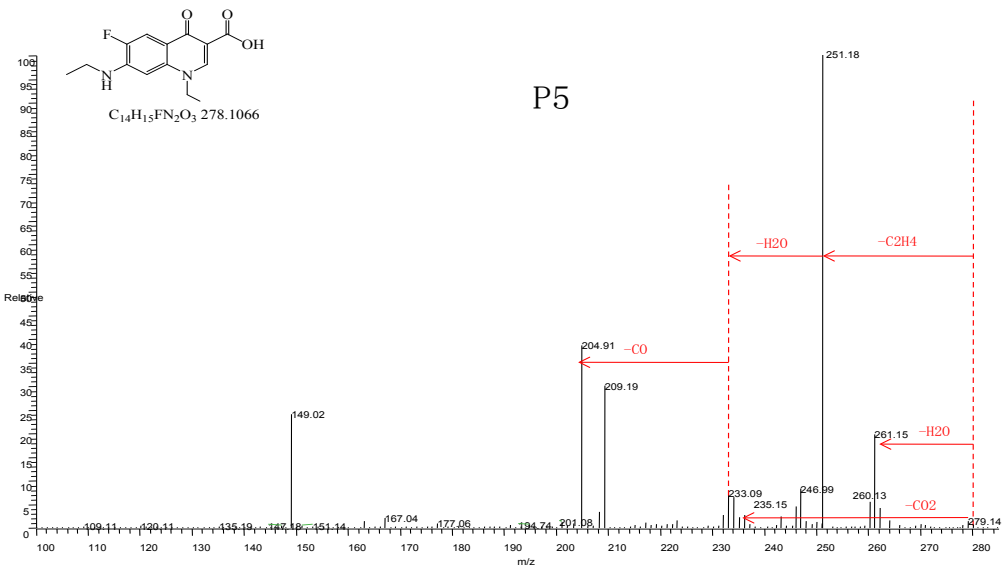




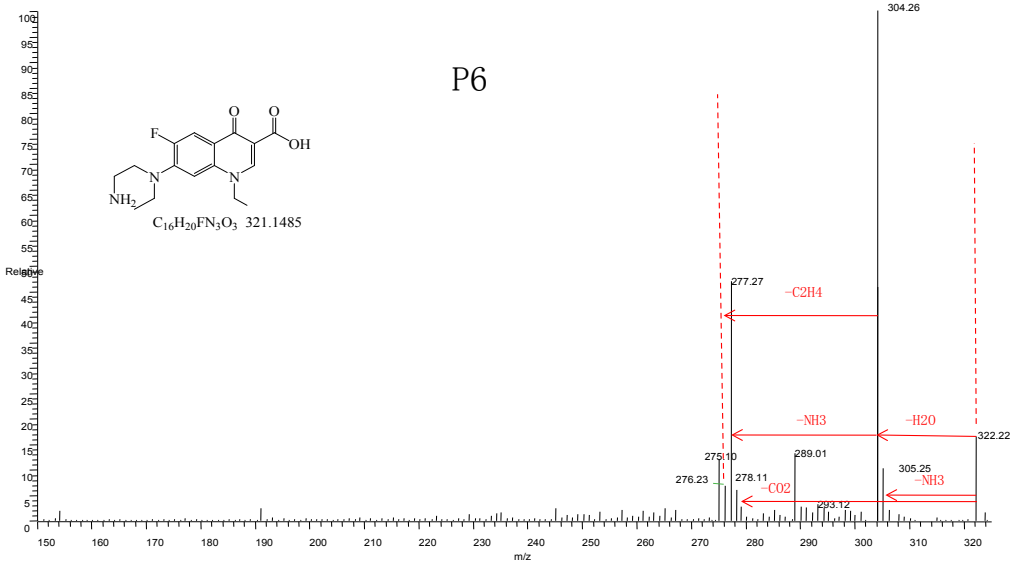



P3
C10H7FN2O3 222.0395
-CO2
-H20
-NH3
Relative
m/z


P4
C16H17N3O5 331.1168
-COCH2-
-C2H4
-H20
Relative
m/z

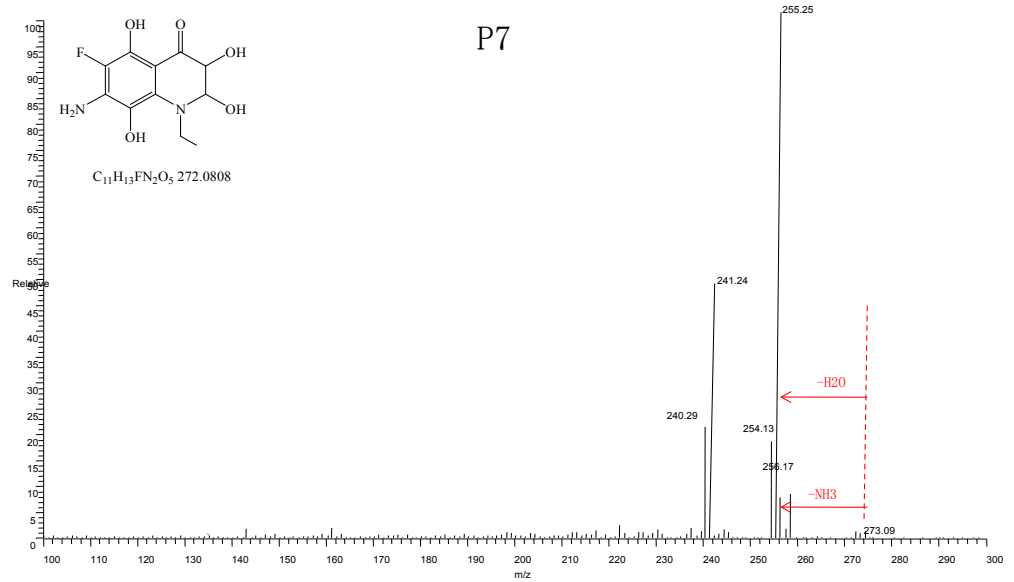

P5
C14H15FN2O3 278.1066
-H20
-C2H4
-CO
-H20
-CO2
Relative
m/z

P6



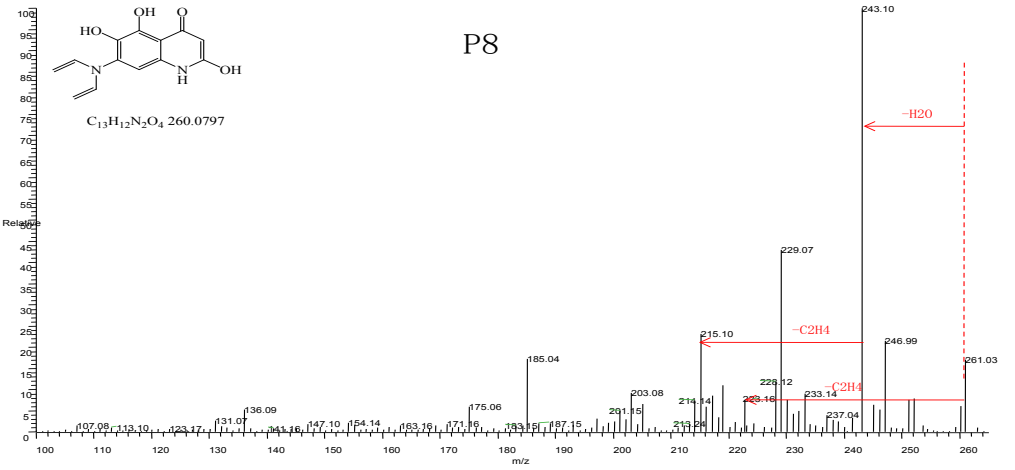
$C_{16}H_{20}FN_3O_3$ 321.1485

P7

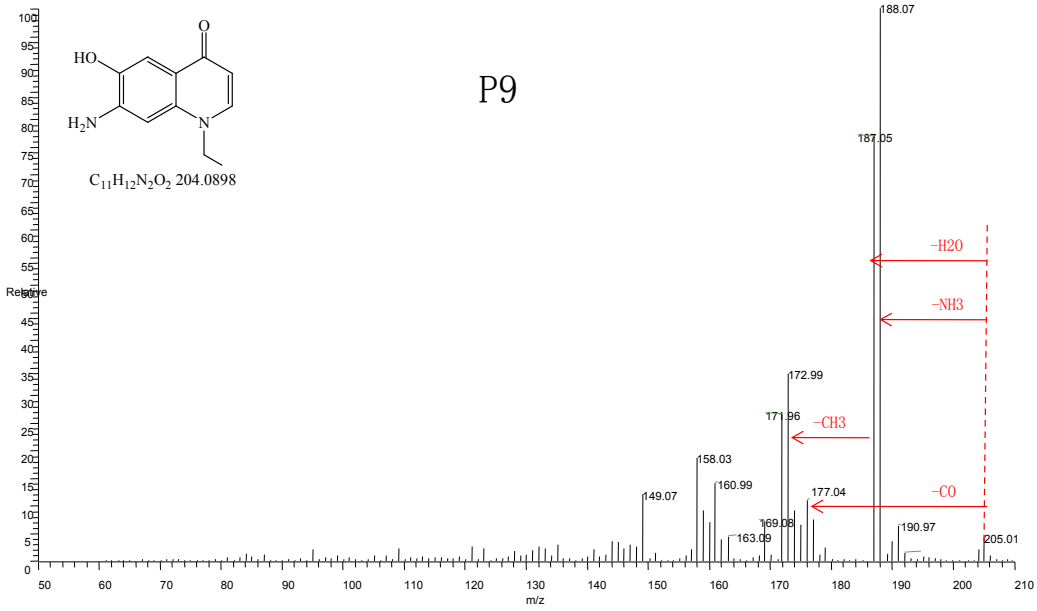


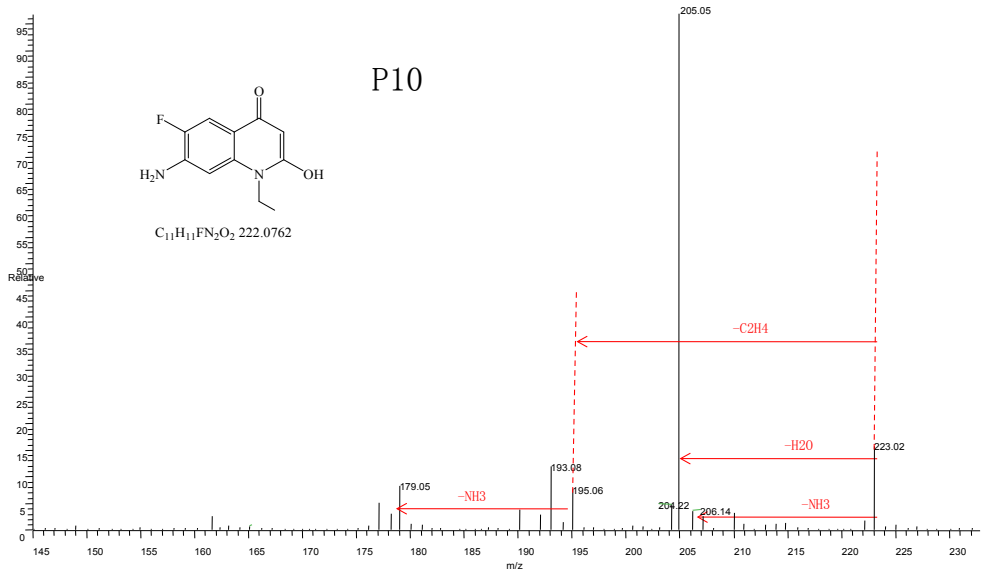
$C_{11}H_{13}FN_2O_5$ 272.0808

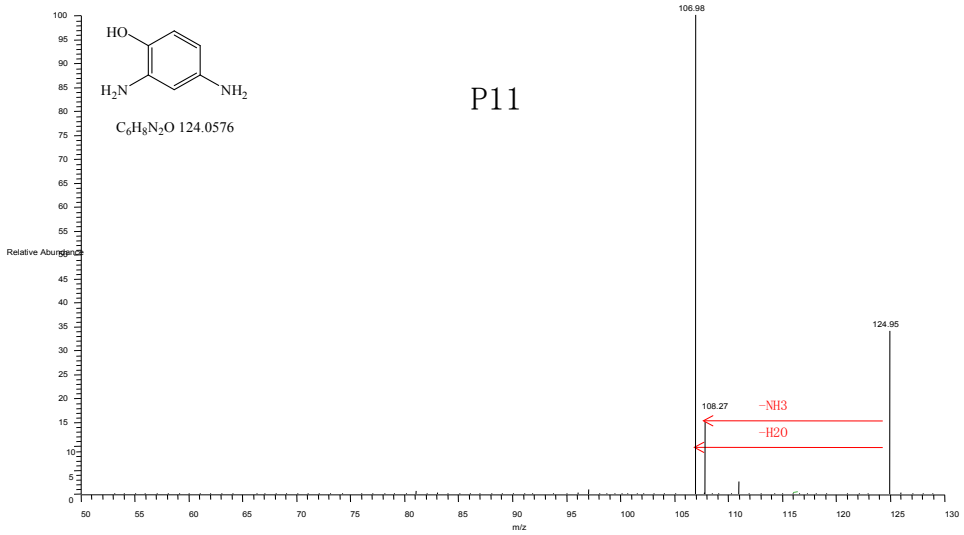
P8

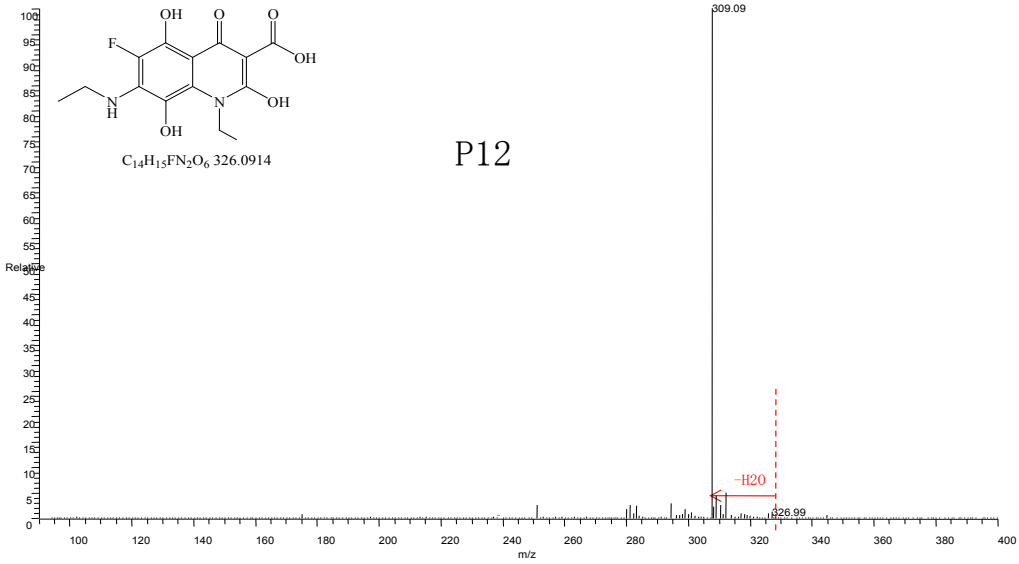


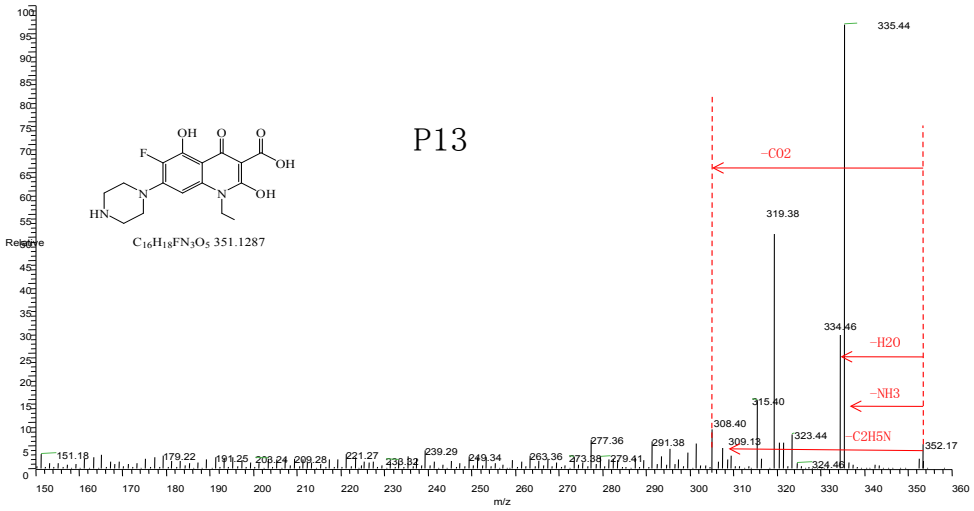
$C_{13}H_{12}N_2O_4$ 260.0797

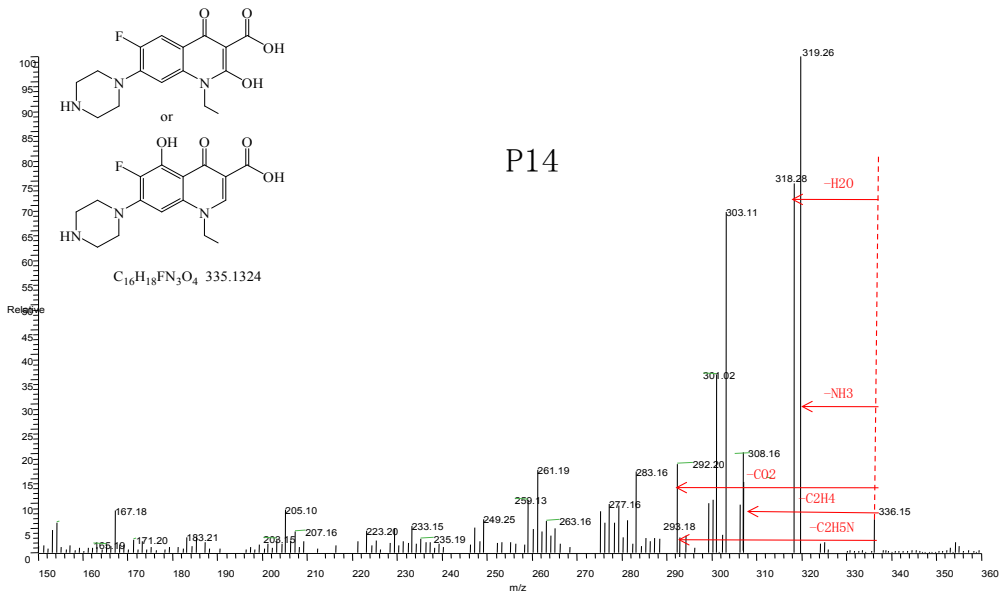

P9
C11H12N2O2 204.0898
188.07
187.05
-H2O
-NH3
172.99
171.96
-CH3
158.03
160.99
149.07
177.04
-CO
169.08
163.09
190.97
205.01
Relative
m/z

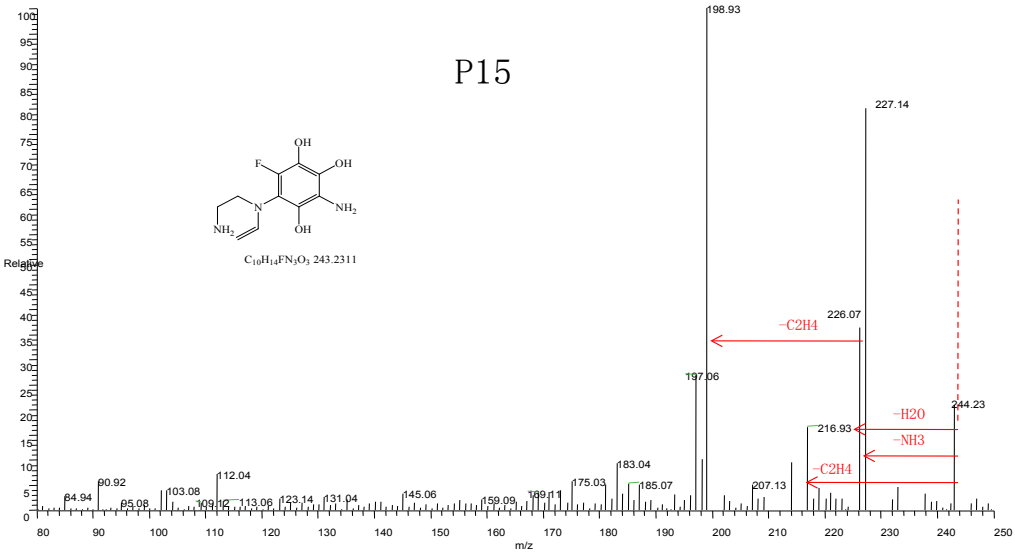

P10
C11H11FN2O2 222.0762
205.05
-C2H4
-H2O
223.02
193.08
179.05
-NH3
195.06
204.22
206.14
-NH3
Relative
m/z

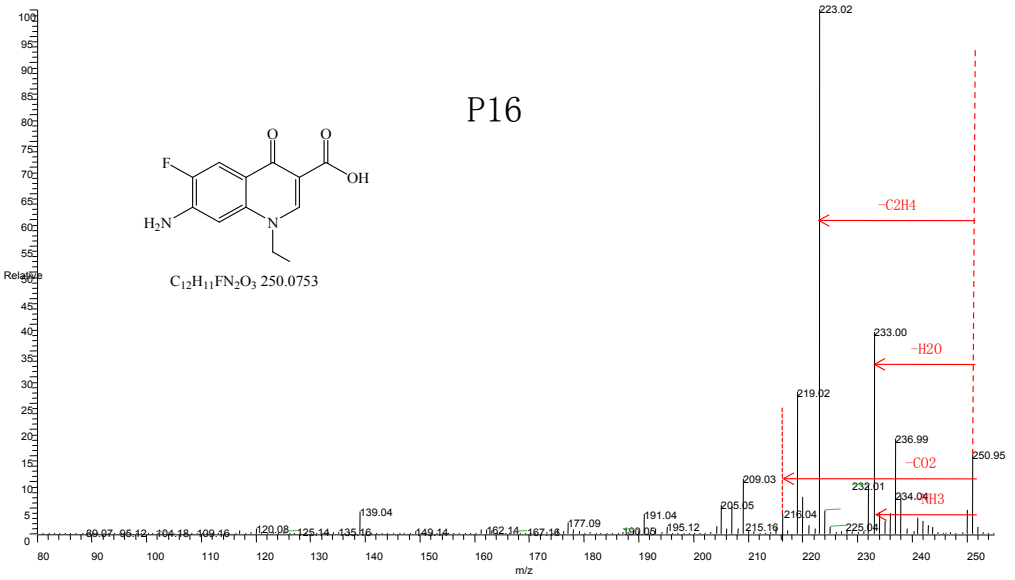

P11
C6H8N2O 124.0576
106.98
124.95
108.27
-NH3
-H2O
Relative Abundance
m/z

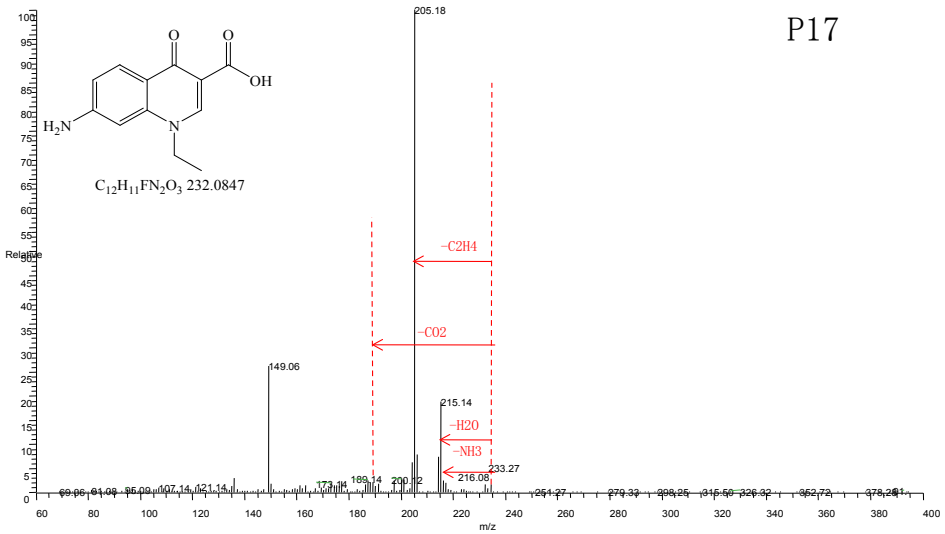

P12
C14H15FN2O6 326.0914
309.09
-H2O
326.99
Relative
m/z


P13
C16H18FN3O5 351.1287
335.44
-CO2
319.38
334.46
-H2O
-NH3
315.40
308.40
309.13
323.44
-C2H5N
352.17
277.36
291.38
151.18
179.22
Relative
m/z


P14
or
C16H18FN3O4 335.1324
319.26
318.28
-H2O
303.11
301.02
-NH3
308.16
292.20
-CO2
283.16
261.19
259.13
277.16
-C2H4
336.15
249.25
263.16
293.18
-C2H5N
205.10
167.18
207.16
223.20
233.15
235.19
Relative
m/z


P15
198.93
227.14
226.07
−C2H4
197.06
244.23
−H2O
216.93
−NH3
−C2H4
183.04
112.04
90.92
103.08
84.94
95.08
109.10
113.06
123.14
131.04
145.06
159.09
169.11
175.03
185.07
207.13
$C_{10}H_{14}FN_3O_3$ 243.2311
Relative
m/z


P16
223.02
−C2H4
233.00
−H2O
219.02
236.99
250.95
−CO2
209.03
232.01
234.04
−NH3
205.05
216.04
225.04
215.16
139.04
191.04
177.09
195.12
$C_{12}H_{11}FN_2O_3$ 250.0753
Relative
m/z


P17
205.18
−C2H4
−CO2
149.06
215.14
−H2O
−NH3
233.27
216.08
$C_{12}H_{11}FN_2O_3$ 232.0847
Relative
m/z

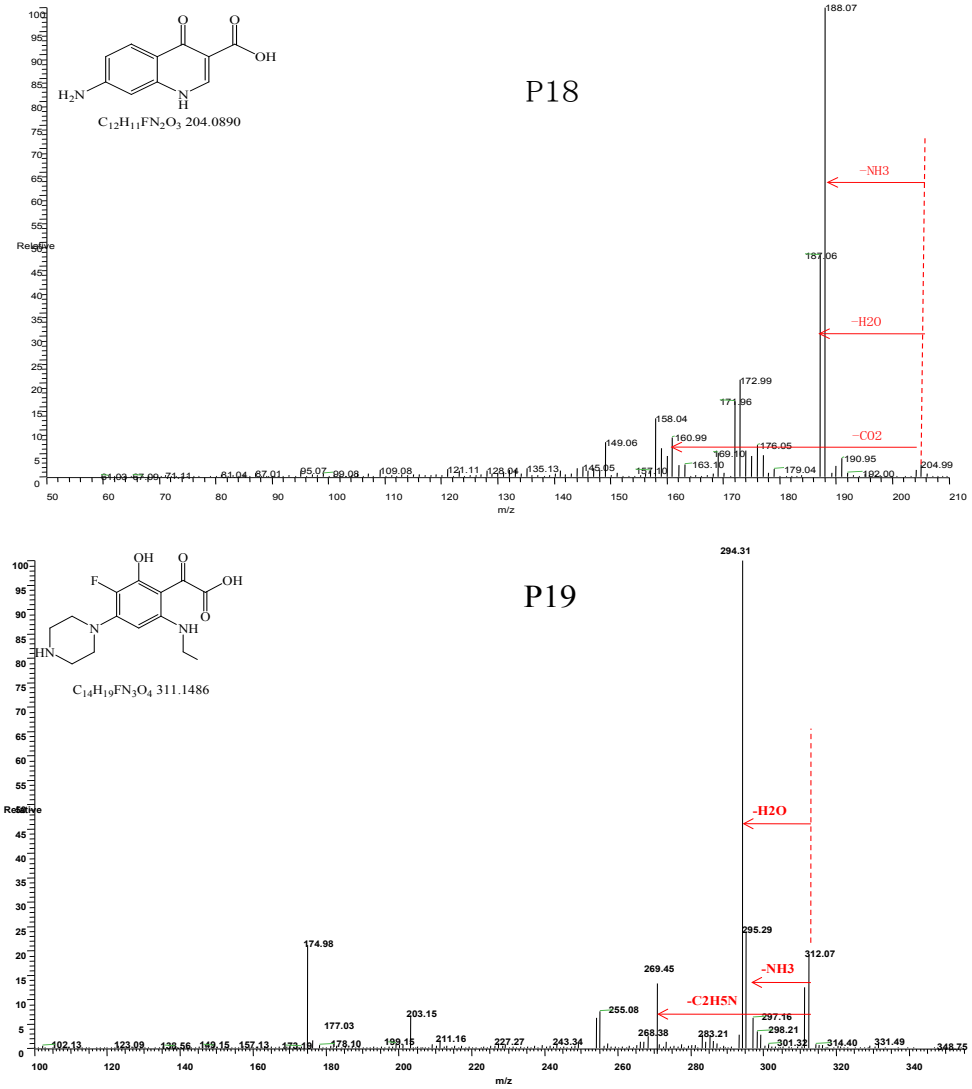


Fig.S4 Product-ion spectra (MS/MS) of the $[M+H]^+$ ions of *Nor* and its degradation intermediates *P1-P19*. The intermediates were purified by semi-preparative HPLC and the tandem mass spectra were acquired on an LTQ linear ion-trap mass spectrometer.