Supplementary Information

Network Capture Effect-Driven Enhanced Activation of Peroxymonosulfate by Iron-Doped Carbon Quantum Dots Derived from Ferrous Gluconate for Efficient Ciprofloxacin Degradation: DFT Calculations and Mechanism Analysis

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Text S1. Chemicals

Ferrous gluconate (FG, 98%), sodium percarbonate (SPC, ≥13.0% active oxygen), p-benzoquinone (p-BQ, 99%) were purchased from Aladdin Industrial Corporation (Shanghai, China). Acetaminophen (ACE, 99%), ciprofloxacin (CIP, 99%), carbamazepine (CIP, 99%), bisphenol A (BPA, 99%), peroxymonosulfate (PMS, 42%~46% $KHSO_5$ basis) were purchased from Shanghai Yien Chemical Technology Co., Ltd (Shanghai, China). Sodium azide (NaN_3, 99%), norfloxacin (NOR, 98%) were purchased from Hefei Bomei Biotechnology Co., Ltd (Hefei, China). Tetracycline hydrochloride (TC, biotechnology grade) was purchased from Shanghai Macklin Biochemical Co., Ltd (Shanghai, China). Sulfamethoxazole (SMX, 99%) was purchased from Kuer Chemical (Technology) Beijing Co., Ltd (Beijing, China). Glucose (99%), ferric trichloride hexahydrate ($FeCl_3 \cdot 6H_2O$, 99%), ethylenediamine (99%), sodium thiosulfate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$, 99%), methanol (99.9%), isopropanol (IPA, 99%), ethylenediaminetetraacetic acid disodium salt (EDTA-2Na, 99%), potassium dichromate ($K_2Cr_2O_7$, 99%), dimethyl sulfoxide (DMSO, 99%), 5,5-Dimethyl-1-pyrroline N-oxide (DMPO, 99%), sodium chloride (NaCl, 99.5%), sodium sulphate (Na_2SO_4, ≥99%), sodium nitrate ($NaNO_3$, 99%), natrium bicarbonate ($NaHCO_3$, ≥99.5%), sodium carbonate (Na_2CO_3, ≥99.8%), trisodium phosphate (Na_3PO_4, 98%), ammonium chloride (NH_4Cl, 99%), potassium chloride (KCl, ≥99.5%), calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$, 99%), magnesium chloride ($MgCl_2$, ≥99%)，hydrogen peroxide (H_2O_2, 30 wt%), sodium persulfate (PDS, ≥98%), ammonium acetate (≥98%), acetic acid (≥99%), potassium iodide (KI, ≥99%), 1,10-Phenanthroline monohydrate (≥99%), ammonium iron(II) sulfate (≥99%), hydroxylamine hydrochloride (≥99%) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). All the chemicals in this research were of analytical grade and need no further purification. Ultrapure water was used throughout the experiment.

Text S2. Characterization

Transmission electron microscopy (TEM) micrographs and high-resolution TEM (HRTEM) images of catalyst samples were recorded on a Themis Z (3.2) aberration-corrected scanning transmission electron microscopy. The X-ray diffraction (XRD) measurements were carried out on Japan Rigaku Mini flex600 X-ray diffractometer using Cu-K_α radiation at a scanning rate of 2° min^{-1} to investigate the crystalline structure of the as-prepared photocatalyst. The Raman spectra were carried out on a HORIBA JY LabRAM HR Evolution spectrometer equipped with an excitation wavelength of 532 nm. Element compositions and chemical states of the samples were obtained on an AXIS-Ultra (Kratos, Manchester, England) X-ray photoelectron spectroscopy (XPS) by using Al Kα as radiance source at 15 kV and 15 mA. Fourier transformed infrared spectra (FTIR) was obtained on iS10 FT-IR spectrometer (Nicolet, USA) with the scanning range from 400 cm-1 to 4000 cm-1. The electron spin resonance (ESR) signals of radicals spin-trapped were examined on a Bruker model ESR JES-FA200 spectrometer by spin-trap reagent DMPO in water and methanol. The Brunauer-Emmett-Teller (BET, ASAP2460) surface area was calculated according to the nitrogen adsorption desorption isotherm and the Barrett- Joyner-Halenda (BJH) was used to obtain the pore size distribution of samples through adsorption isotherm branch. An electrochemical workstation (versaSTAT3, Princeton, UK) was utilized to analyze photoelectrochemistry (PEC) properties. All photo-electrochemical characteristic for the catalysts were performed by a three-electrode electrochemical workstation (CHI660E, Shanghai Chenhua Ltd., China).

Text S3. Identification of by-products on CIP degradation

The by-products of CIP were analyzed by an Agilent 1290 series UPLC coupled to a QTOF 6550 mass spectrometer (Agilent Technologies, USA). Separation of intermediate products was accomplished using a water BEH C18 column (1.7 μm, 2.1*100 mm). Elution was performed at a flow rate of 0.3 mL min-1 with H2O containing 0.1 % (v/v) formic acid, as eluent A, and acetonitrile as eluent B; 80% A and 20% B were used for 15 minutes. Mass spectrometry analysis was conducted in positive mode using an electrospray ionization (ESI) source. The optimized parameters were as follows: capillary voltage of 4 kV; sheath gas (nitrogen, P 99.99%) flow of 12 L min^{-1}; temperature of 350 ^{o}C; scan range in full scan mode (m/z range 50-500). Once a potential product was identified, product ion scan MS/MS was performed for structure elucidation.

Text S4. Determination method of PMS concentration

The concentration of PMS in the solution was determined using a spectrophotometric method based on iodine measurement. First, 100 g KI and 5g $NaHCO_3$ were added to a 1 L capacity ($NaHCO_3$ is added to avoid oxidation of iodides) and dilute to the mark to prepare potassium iodide solution. Take 5 ml of potassium iodide solution prepared, add 1 ml of the test solution to it. React for 15 minutes, and measure its absorbance at 395 nm.

The concentration calculation formula for PMS is as follows:

$$C_{PMS} = \frac{Abs - B}{A}$$

where A is the slope and B is the intercept. The optimal wavelength for measuring PMS using this method is 395 nm, and concentrations of CO_3^{2-}, SO_4^{2-}, and Cl^- below 500 mg/L have almost no effect on this measurement method.

Text S5. Computational details

For ACE structure and Fukin function, all density functional theory (DFT) calculations were conducted using Gaussian16 software package, Revision A.031. The geometry optimization and single point calculations were performed with M06-2X functional2 and Ahlrichs' def2-TZVP basis set3. The Fukui function values in real space were generated by Multiwfn 3.8(dev)4. All figures were rendered by Visual Molecular Dynamics5 (VMD) 1.9.3.

We have employed the first-principles [1,2] to perform all Spin-polarization density functional theory (DFT) calculations within the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) [3] formulation. We have chosen the projected augmented wave (PAW) potentials [4,5] to describe the ionic cores and take valence electrons into account using a plane wave basis set with a kinetic energy cutoff of 450 eV. Van der Waals interactions have been considered using the DFT-D3 method of Grimme [6,7]. The electronic energy was considered self-consistent when the energy change was smaller than 10^{-5} eV. A geometry optimization was considered convergent when the energy change was smaller than 0.02 eV $Å^{-1}$. The cluster was located in a 22 ×22 × 19 Å cubic supercell. During the relaxation, the Brillouin zone with a 1 × 1 × 1 Gamma centered grid was used. The 15 Å vacuum layer was normally added to the surface to eliminate the artificial interactions between periodic images. Spin polarized calculations were performed for this calculation.

For each elementary step, the Gibbs reaction free energy Δ G is defined as the difference between free energies of the initial and final states and is given by the expression:

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S$$

where ΔE is the reaction energy of reactant and product molecules adsorbed on catalyst surface, obtained from DFT calculations; Δ ZPE and Δ S are the change in zero-point energies and entropy due to the reaction.

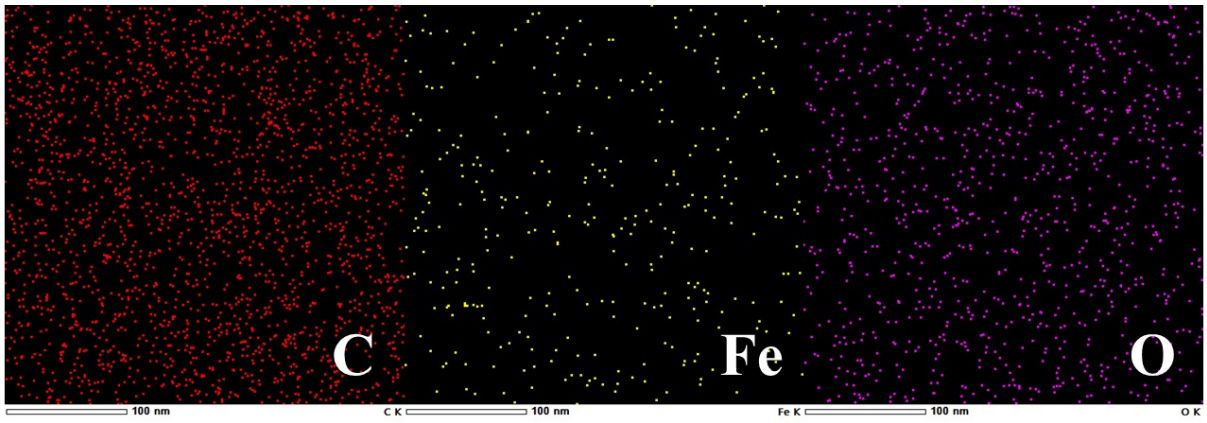


Fig. S1. EDS mapping of Fe-CQDs.

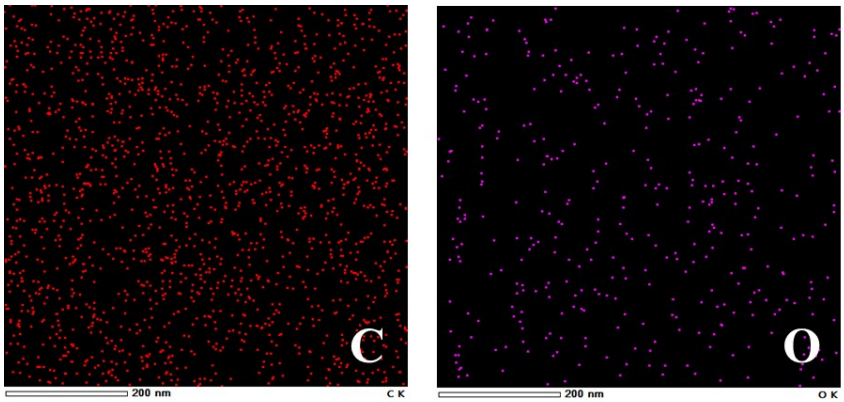


Fig. S2. EDS mapping of CQDs.

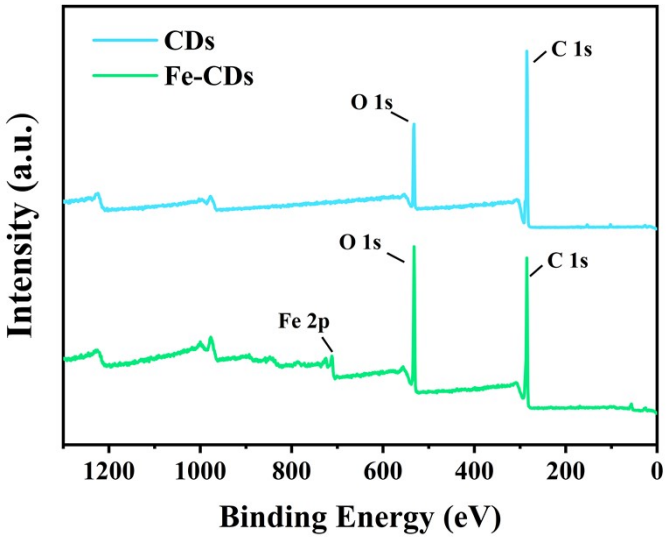


Fig. S3. XPS survey spectra of CQDs and Fe-CQDs.

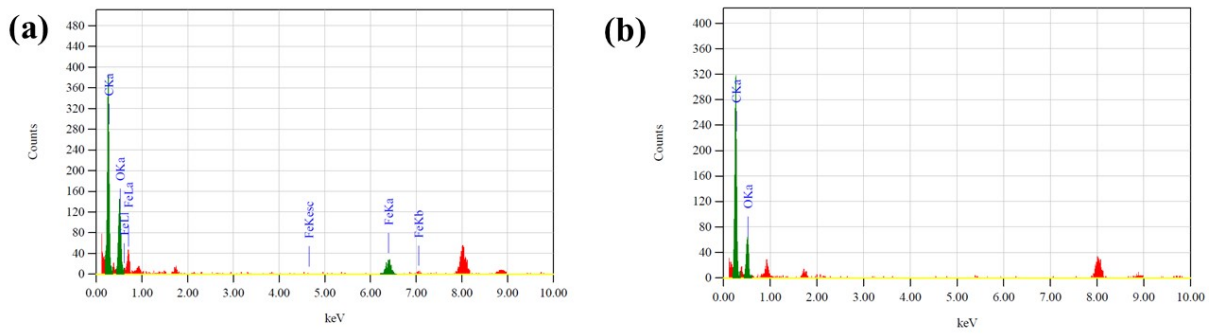


Fig. S4. Energy dispersive spectrometer (EDS) spectra of (a) Fe-CQDs and (b) CQDs.

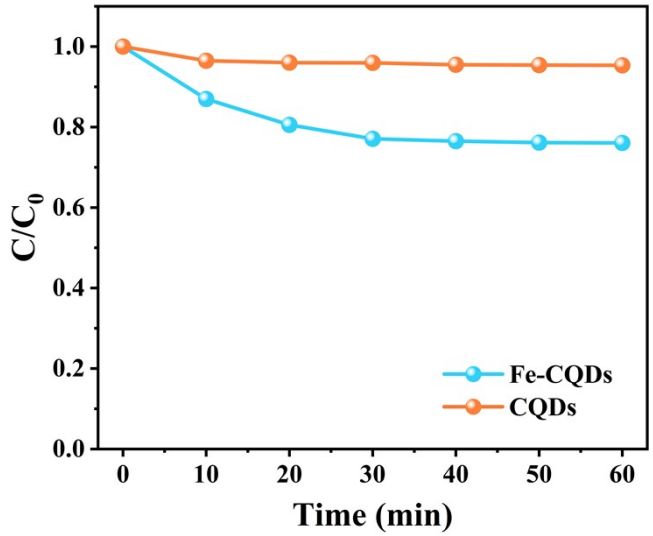


Fig. S5. Adsorption-desorption capacity of Fe-CQDs and CQDs.

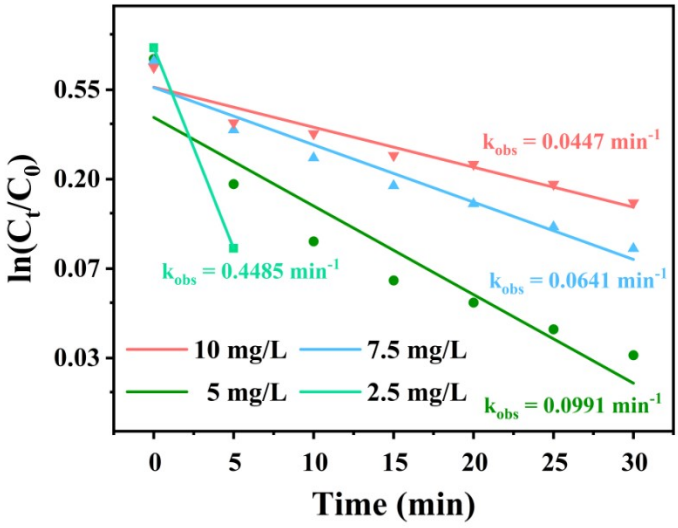


Fig. S6. Pseudo-first-order kinetic curves of initial CIP concentration on CIP degradation.

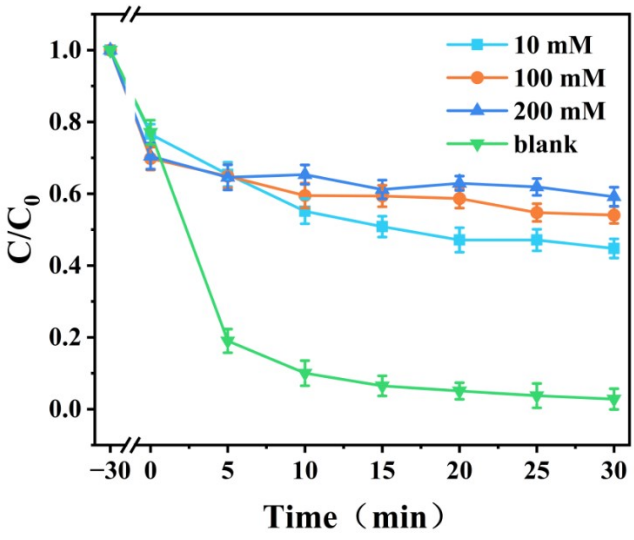


Fig. S6. Degradation performance of CIP with different concentration of IPA.

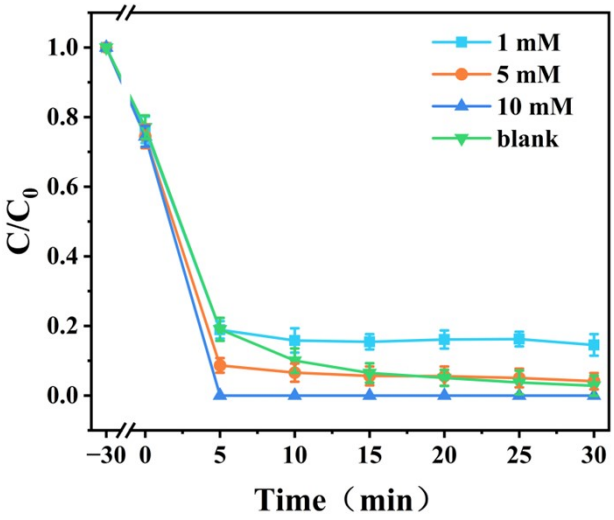


Fig. S7. Degradation performance of CIP with different concentration of $K_2Cr_2O_7$.

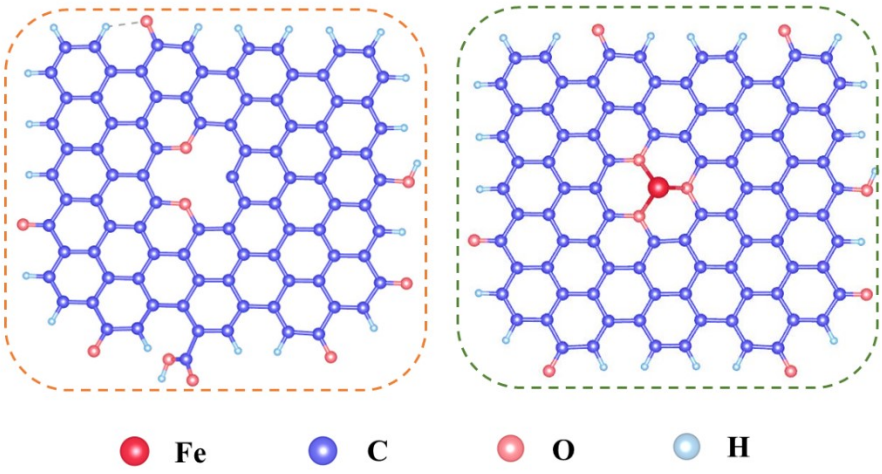


Fig. S8. Optimized modeling of CQDs (left) and Fe-CQDs (right).

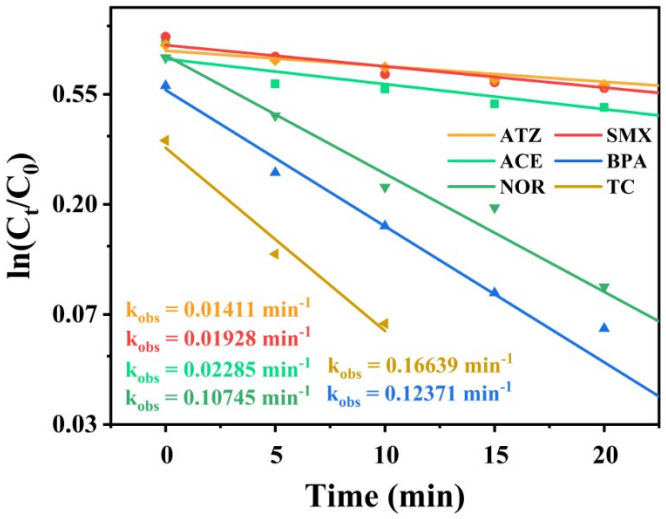


Fig. S9. Pseudo-first-order kinetic curves of different pollutants in Fe-CQDs/PMS system.

Table S1 HPLC conditions for organic analysis

Compounds	Eluents	Flow rate (mL/min)	Wavelength (nm)
ACE	0.1% acetic acid: methanol=70:30	0.8	243
SMX	0.1% acetic acid: methanol=47.5:52.5	1.0	264
BPA	water: acetonitrile=30:70	1.0	278
TC	oxalic acid: acetonitrile=72.5:27.5	1.0	352
CBZ	water: methanol=30:70	1.0	285
NOR	phosphoric acid: acetonitrile=80:20	1.0	352
CIP	formic acid: acetonitrile=80:20	0.9	278

Table S2 Fukin index of BPA

Atom	q(N)	q(N+1)	q(N-1)	f^-	f^+	f^0	CDD
1(C)	-0.0561	-0.1228	-0.0143	0.0418	0.0666	0.0542	0.0248
2(C)	0.066	0.035	0.1339	0.0678	0.031	0.0494	-0.0368
3(C)	-0.0561	-0.1228	-0.0143	0.0418	0.0666	0.0542	0.0248
4(C)	-0.0442	-0.0989	-0.0078	0.0364	0.0547	0.0456	0.0183
5(C)	-0.0009	-0.015	0.0529	0.0538	0.0141	0.034	-0.0397
6(C)	-0.0442	-0.0989	-0.0078	0.0364	0.0547	0.0456	0.0183
7(H)	0.0437	0.0082	0.072	0.0282	0.0356	0.0319	0.0073
8(H)	0.0437	0.0082	0.072	0.0282	0.0356	0.0319	0.0073
9(H)	0.0375	0.0113	0.0585	0.021	0.0261	0.0236	0.0051
10(H)	0.0375	0.0113	0.0585	0.021	0.0261	0.0236	0.0051
11(C)	0.0302	0.0298	0.0327	0.0025	0.0004	0.0015	-0.0021
12(C)	-0.0009	-0.015	0.0529	0.0538	0.0141	0.034	-0.0397
13(C)	-0.0442	-0.0989	-0.0078	0.0364	0.0547	0.0456	0.0183
14(C)	-0.0442	-0.0989	-0.0078	0.0364	0.0547	0.0456	0.0183
15(C)	-0.0561	-0.1228	-0.0143	0.0418	0.0666	0.0542	0.0248
16(H)	0.0375	0.0113	0.0585	0.021	0.0261	0.0236	0.0051
17(C)	-0.0561	-0.1228	-0.0143	0.0418	0.0666	0.0542	0.0248
18(H)	0.0375	0.0113	0.0585	0.021	0.0261	0.0236	0.0051
19(C)	0.066	0.035	0.1339	0.0678	0.031	0.0494	-0.0368
20(H)	0.0437	0.0082	0.072	0.0282	0.0356	0.0319	0.0073
21(H)	0.0437	0.0082	0.072	0.0282	0.0356	0.0319	0.0073
22(C)	-0.085	-0.0927	-0.0775	0.0075	0.0077	0.0076	0.0001
23(C)	-0.085	-0.0927	-0.0775	0.0075	0.0077	0.0076	0.0001
24(H)	0.0279	0.022	0.0352	0.0073	0.0059	0.0066	-0.0014
25(H)	0.0308	0.0153	0.0464	0.0156	0.0155	0.0155	-0.0001
26(H)	0.0308	0.0153	0.0464	0.0156	0.0155	0.0155	-0.0001
27(H)	0.0308	0.0153	0.0464	0.0156	0.0155	0.0155	-0.0001
28(H)	0.0279	0.022	0.0352	0.0073	0.0059	0.0066	-0.0014
29(H)	0.0308	0.0153	0.0464	0.0156	0.0155	0.0155	-0.0001
30(O)	-0.222	-0.247	-0.1745	0.0475	0.025	0.0363	-0.0225
31(H)	0.1758	0.1567	0.2043	0.0286	0.019	0.0238	-0.0095
32(O)	-0.222	-0.247	-0.1745	0.0475	0.025	0.0363	-0.0225
33(H)	0.1758	0.1567	0.2043	0.0286	0.019	0.0238	-0.0095

Table S3 Fukin index of CIP

Atom	q(N)	q(N+1)	q(N-1)	f^-	f^+	f^0	CDD
1(N)	0.0068	-0.0255	0.0359	0.0291	0.0324	0.0307	0.0033
2(C)	0.0475	-0.0386	0.0692	0.0217	0.0861	0.0539	0.0644
3(C)	-0.0627	-0.0911	-0.0296	0.0330	0.0284	0.0307	-0.0046
4(C)	0.1154	0.0399	0.1394	0.0240	0.0755	0.0498	0.0516
5(C)	-0.0306	-0.0432	0.0240	0.0546	0.0126	0.0336	-0.0420
06(C)	-0.0407	-0.1030	-0.0127	0.0280	0.0623	0.0451	0.0343
7(C)	0.0873	0.0495	0.1420	0.0547	0.0378	0.0462	-0.0168
8(C)	0.0430	-0.0144	0.0639	0.0209	0.0574	0.0391	0.0365
9(C)	-0.0755	-0.1277	-0.0553	0.0202	0.0522	0.0362	0.0320
10(C)	0.0461	0.0317	0.0715	0.0253	0.0144	0.0199	-0.0109
11(C)	0.1925	0.1789	0.2044	0.0119	0.0136	0.0127	0.0017
12(O)	-0.3009	-0.3420	-0.2580	0.0429	0.0411	0.0420	-0.0018
13(O)	-0.1949	-0.2253	-0.1705	0.0243	0.0305	0.0274	0.0062
14(N)	-0.0716	-0.0907	0.0058	0.0774	0.0191	0.0483	-0.0583
15(C)	-0.0081	-0.0161	0.0066	0.0147	0.0079	0.0113	-0.0067
16(C)	-0.0116	-0.0188	0.0008	0.0124	0.0073	0.0098	-0.0051
17(N)	-0.1634	-0.1696	-0.1302	0.0332	0.0062	0.0197	-0.027
18(C)	-0.0114	-0.0189	0.0018	0.0132	0.0074	0.0103	-0.0058
19(C)	-0.0058	-0.0106	0.0083	0.0141	0.0048	0.0095	-0.0093
20(O)	-0.2617	-0.3494	-0.1744	0.0873	0.0878	0.0875	0.0005
21(F)	-0.0874	-0.1198	-0.0454	0.0420	0.0324	0.0372	-0.0097
22(C)	0.0188	0.0179	0.0195	0.0008	0.0009	0.0008	0.0001
23(C)	-0.0654	-0.0781	-0.0560	0.0094	0.0127	0.0110	0.0033
24(C)	-0.0599	-0.0753	-0.0447	0.0152	0.0154	0.0153	0.0001
25(H)	0.0608	0.0261	0.0778	0.0171	0.0347	0.0259	0.0176
26(H)	0.0608	0.0313	0.0821	0.0213	0.0295	0.0254	0.0082
27(H)	0.0370	0.0142	0.0511	0.0141	0.0227	0.0184	0.0086
28(H)	0.1326	0.1216	0.1406	0.0080	0.0110	0.0095	0.0030
29(H)	0.0358	0.0310	0.0477	0.0119	0.0048	0.0084	-0.0071
30(H)	0.0239	0.0111	0.0524	0.0285	0.0128	0.0206	-0.0157
31(H)	0.0203	0.0130	0.0377	0.0174	0.0073	0.0124	-0.0101
32(H)	0.0390	0.0252	0.0588	0.0198	0.0137	0.0168	-0.0061
33(H)	0.1077	0.0942	0.1306	0.0229	0.0134	0.0182	-0.0095
34(H)	0.0373	0.0238	0.0570	0.0196	0.0135	0.0166	-0.0061
35(H)	0.0192	0.0114	0.0369	0.0177	0.0078	0.0127	-0.0099
36(H)	0.0236	0.0136	0.0507	0.0271	0.0100	0.0186	-0.0172
37(H)	0.0371	0.0332	0.0512	0.0141	0.0039	0.0090	-0.0103
38(H)	0.0499	0.0320	0.0622	0.0123	0.0179	0.0151	0.0056
39(H)	0.0494	0.0325	0.0599	0.0104	0.0169	0.0137	0.0065
40(H)	0.0511	0.0450	0.0544	0.0033	0.0060	0.0047	0.0028
41(H)	0.0547	0.0458	0.0631	0.0085	0.0088	0.0086	0.0004
42(H)	0.0537	0.0348	0.0693	0.0156	0.0189	0.0172	0.0033

Table S4 Fukin index of NOR

Atom	q(N)	q(N+1)	q(N-1)	f^-	f^+	f^0	CDD
1(C)	0.0914	0.0553	0.1219	0.0305	0.0362	0.0333	0.0057
2(C)	-0.0387	-0.1078	-0.0144	0.0243	0.0691	0.0467	0.0448
3(C)	-0.0207	-0.0393	-0.0001	0.0205	0.0186	0.0196	-0.0020
4(C)	0.0409	0.0257	0.0577	0.0169	0.0151	0.0160	-0.0017
5(C)	-0.0580	-0.1303	-0.0346	0.0234	0.0723	0.0478	0.0489
6(C)	0.0361	-0.0249	0.0483	0.0121	0.0610	0.0366	0.0489
7(H)	0.0593	0.0276	0.0770	0.0177	0.0317	0.0247	0.0140
8(C)	0.1150	0.0516	0.1371	0.0221	0.0635	0.0428	0.0413
9(H)	0.0427	0.0097	0.0571	0.0144	0.0330	0.0237	0.0186
10(C)	0.0437	-0.0413	0.0666	0.0229	0.0851	0.0540	0.0622
11(C)	-0.0621	-0.0923	-0.0023	0.0598	0.0302	0.0450	-0.0296
12(H)	0.0532	0.0206	0.0686	0.0154	0.0326	0.0240	0.0172
13(N)	-0.1025	-0.1059	-0.0627	0.0398	0.0034	0.0216	-0.0364
14(N)	0.0004	-0.028	0.0454	0.0449	0.0284	0.0367	-0.0165
15(F)	-0.0952	-0.1285	-0.0677	0.0275	0.0333	0.0304	0.0058
16(O)	-0.2790	-0.3702	-0.1959	0.0831	0.0912	0.0872	0.0081
17(C)	0.2008	0.1832	0.2156	0.0148	0.0176	0.0162	0.0028
18(C)	-0.0179	-0.0227	-0.0009	0.017	0.0048	0.0109	-0.0122
19(H)	0.0154	0.0081	0.0346	0.0192	0.0073	0.0133	-0.0119
20(H)	0.0327	0.0292	0.0499	0.0171	0.0035	0.0103	-0.0136
21(C)	-0.0179	-0.0227	-0.0002	0.0177	0.0048	0.0112	-0.0129
22(H)	0.0154	0.0081	0.0361	0.0207	0.0073	0.0140	-0.0134
23(H)	0.0327	0.0292	0.0500	0.0173	0.0035	0.0104	-0.0138
24(C)	-0.0113	-0.019	0.0086	0.0199	0.0077	0.0138	-0.0123
25(H)	0.0357	0.0217	0.0595	0.0238	0.0140	0.0189	-0.0098
26(H)	0.0292	0.0223	0.0492	0.0199	0.0069	0.0134	-0.0130
27(C)	-0.0113	-0.019	0.0073	0.0186	0.0077	0.0131	-0.0109
28(H)	0.0357	0.0217	0.0585	0.0228	0.0140	0.0184	-0.0089
29(H)	0.0292	0.0223	0.0487	0.0194	0.0069	0.0132	-0.0125
30(O)	-0.3060	-0.3467	-0.2586	0.0474	0.0406	0.0440	-0.0068
31(O)	-0.1646	-0.1821	-0.1487	0.0159	0.0176	0.0167	0.0017
32(H)	0.1821	0.1592	0.2002	0.0182	0.0229	0.0205	0.0047
33(C)	0.0181	0.0094	0.0264	0.0084	0.0086	0.0085	0.0002
34(H)	0.0424	0.0260	0.0557	0.0132	0.0165	0.0149	0.0032
35(H)	0.0424	0.0260	0.0557	0.0133	0.0165	0.0149	0.0032
36(C)	-0.0747	-0.0837	-0.0673	0.0073	0.0090	0.0082	0.0016
37(H)	0.0437	0.0346	0.0515	0.0078	0.0091	0.0085	0.0013
38(H)	0.0437	0.0346	0.0515	0.0078	0.0091	0.0085	0.0013
39(H)	0.0471	0.0268	0.0620	0.0150	0.0203	0.0176	0.0053
40(N)	-0.1656	-0.1772	-0.0742	0.0914	0.0116	0.0515	-0.0798
41(H)	0.0966	0.0891	0.1272	0.0305	0.0076	0.0190	-0.0230

Table S5 Fukin index of SMX

Atom	q(N)	q(N+1)	q(N-1)	f^-	f^+	f^0	CDD
1(C)	0.0592	0.0300	0.1080	0.0487	0.0293	0.0390	-0.0194
2(C)	-0.0589	-0.1241	-0.0021	0.0569	0.0651	0.0610	0.0082
3(C)	-0.0221	-0.0828	0.0082	0.0302	0.0607	0.0455	0.0304
4(C)	-0.0474	-0.0614	0.0161	0.0635	0.0140	0.0388	-0.0495
5(C)	-0.0281	-0.0918	0.0068	0.0349	0.0637	0.0493	0.0289
6(C)	-0.0630	-0.1336	-0.0057	0.0572	0.0707	0.0639	0.0134
7(H)	0.0449	0.0115	0.0750	0.0301	0.0333	0.0317	0.0032
8(H)	0.0516	0.0270	0.0717	0.0201	0.0246	0.0224	0.0045
9(H)	0.0518	0.0213	0.0764	0.0246	0.0304	0.0275	0.0058
10(H)	0.0432	0.0068	0.0743	0.0311	0.0363	0.0337	0.0052
11(N)	-0.1642	-0.1912	-0.0479	0.1163	0.0270	0.0716	-0.0893
12(S)	0.5167	0.5009	0.5362	0.0195	0.0158	0.0177	-0.0037
13(O)	-0.3268	-0.3624	-0.2817	0.0451	0.0356	0.0403	-0.0095
14(O)	-0.3105	-0.3388	-0.2604	0.0500	0.0283	0.0392	-0.0217
15(N)	-0.1344	-0.1480	-0.0783	0.0561	0.0137	0.0349	-0.0424
16(H)	0.1355	0.1187	0.1613	0.0259	0.0167	0.0213	-0.0092
17(H)	0.1277	0.1077	0.1684	0.0407	0.0200	0.0304	-0.0207
18(H)	0.1272	0.1061	0.1684	0.0412	0.0211	0.0311	-0.0201
19(C)	0.0720	0.0325	0.0893	0.0173	0.0395	0.0284	0.0222
20(C)	-0.1019	-0.1492	-0.0824	0.0194	0.0473	0.0334	0.0278
21(C)	0.0823	0.0106	0.1100	0.0277	0.0717	0.0497	0.0440
22(C)	-0.0712	-0.0959	-0.0599	0.0114	0.0246	0.0180	0.0132
23(N)	-0.1244	-0.1745	-0.0880	0.0364	0.0501	0.0432	0.0136
24(O)	-0.0658	-0.1152	-0.0290	0.0368	0.0493	0.0431	0.0125
25(H)	0.0557	0.0261	0.0735	0.0178	0.0297	0.0237	0.0119
26(H)	0.0507	0.0198	0.0643	0.0136	0.0309	0.0222	0.0172
27(H)	0.0488	0.0284	0.0620	0.0132	0.0204	0.0168	0.0073
28(H)	0.0516	0.0215	0.0657	0.0141	0.0301	0.0221	0.0161

Table S6 Fukin index of TC

Atom	q(N)	q(N+1)	q(N-1)	f^-	f^+	f^0	CDD
1(C)	-0.0694	-0.0948	-0.0450	0.0244	0.0254	0.0249	0.0010
2(C)	0.0920	0.0774	0.1098	0.0178	0.0146	0.0162	-0.0032
3(C)	-0.0306	-0.0402	-0.0177	0.0129	0.0096	0.0113	-0.0033
4(C)	-0.0059	-0.0187	0.0050	0.0109	0.0129	0.0119	0.0019
5(C)	-0.0657	-0.0802	-0.0393	0.0264	0.0146	0.0205	-0.0118
6(C)	-0.0366	-0.0734	-0.0022	0.0344	0.0368	0.0356	0.0024
7(C)	0.1286	0.0959	0.1675	0.0389	0.0327	0.0358	-0.0062
8(C)	0.0906	0.0889	0.0912	0.0006	0.0017	0.0012	0.0012
9(C)	-0.0173	-0.0193	-0.0118	0.0055	0.0020	0.0038	-0.0035
10(C)	-0.0539	-0.0690	-0.0376	0.0163	0.0151	0.0157	-0.0012
11(C)	0.0877	0.0777	0.1126	0.0249	0.0099	0.0174	-0.0150
12(C)	-0.0508	-0.0572	-0.0431	0.0077	0.0064	0.0071	-0.0013
13(H)	0.0403	0.0224	0.0602	0.0199	0.0179	0.0189	-0.0020
14(H)	0.0357	0.0241	0.0521	0.0164	0.0116	0.0140	-0.0048
15(H)	0.0459	0.0253	0.0674	0.0215	0.0206	0.0211	-0.0009
16(H)	0.0345	0.0232	0.0477	0.0132	0.0112	0.0122	-0.0020
17(C)	0.0671	0.0604	0.0720	0.0049	0.0067	0.0058	0.0018
18(C)	0.1371	0.0683	0.1391	0.0020	0.0688	0.0354	0.0668
19(C)	0.1291	0.0391	0.1297	0.0006	0.0900	0.0453	0.0895
20(C)	-0.0229	-0.0253	-0.0195	0.0033	0.0024	0.0029	-0.0010
21(C)	0.0207	0.0144	0.0265	0.0058	0.0063	0.0060	0.0005
22(O)	-0.1688	-0.1806	-0.1499	0.0189	0.0118	0.0153	-0.0071
23(H)	0.1776	0.1644	0.1974	0.0197	0.0133	0.0165	-0.0064
24(O)	-0.2513	-0.3005	-0.0929	0.1584	0.0492	0.1038	-0.1092
25(O)	-0.1601	-0.1800	-0.1352	0.0249	0.0199	0.0224	-0.0050
26(H)	0.1544	0.1461	0.1703	0.0159	0.0083	0.0121	-0.0077
27(O)	-0.2382	-0.3236	-0.2127	0.0255	0.0854	0.0555	0.0599
28(C)	-0.0777	-0.1058	-0.0645	0.0132	0.0281	0.0206	0.0149
29(C)	0.1767	0.1631	0.1817	0.0050	0.0136	0.0093	0.0086
30(O)	-0.2571	-0.2957	-0.2372	0.0199	0.0386	0.0293	0.0187
31(N)	-0.1393	-0.1543	-0.1311	0.0082	0.0150	0.0116	0.0067
32(H)	0.1341	0.1127	0.1462	0.0121	0.0214	0.0168	0.0093
33(H)	0.1303	0.1196	0.1351	0.0048	0.0107	0.0077	0.0059
34(O)	-0.1447	-0.2035	-0.1394	0.0053	0.0589	0.0321	0.0535
35(H)	0.1378	0.1199	0.1456	0.0077	0.0179	0.0128	0.0102
36(N)	-0.0857	-0.0922	0.0000	0.0857	0.0065	0.0461	-0.0792
37(C)	-0.0466	-0.0523	-0.0272	0.0194	0.0057	0.0126	-0.0137
38(H)	0.0286	0.0130	0.0503	0.0218	0.0155	0.0186	-0.0062
39(H)	0.0149	0.0074	0.0466	0.0317	0.0076	0.0196	-0.0241
40(H)	0.0302	0.0264	0.0413	0.0111	0.0038	0.0074	-0.0074
41(C)	-0.0466	-0.0519	-0.0274	0.0192	0.0053	0.0123	-0.0138
42(H)	0.0111	0.0053	0.0422	0.0311	0.0057	0.0184	-0.0254
43(H)	0.0350	0.0177	0.0559	0.0210	0.0172	0.0191	-0.0038

44(H)	0.0316	0.0276	0.0467	0.0151	0.0040	0.0096	-0.0111
Atom	**q(N)**	**q(N+1)**	**q(N-1)**	**f^-**	**f^+**	**f^0**	**CDD**
45(H)	0.0295	0.0202	0.0407	0.0111	0.0094	0.0102	-0.0017
46(O)	-0.2326	-0.2585	-0.2147	0.0179	0.0260	0.0219	0.0081
47(H)	0.1395	0.1261	0.1503	0.0108	0.0134	0.0121	0.0026
48(H)	0.0317	0.0206	0.0424	0.0107	0.0111	0.0109	0.0004
49(O)	-0.2034	-0.2027	-0.2034	0.0000	-0.0007	-0.0004	-0.0008
50(H)	0.1615	0.1512	0.1695	0.0080	0.0103	0.0091	0.0023
51(C)	-0.0935	-0.0984	-0.0881	0.0054	0.0049	0.0051	-0.0005
52(H)	0.0290	0.0194	0.0390	0.0099	0.0096	0.0098	-0.0003
53(H)	0.0350	0.0265	0.0443	0.0093	0.0085	0.0089	-0.0008
54(H)	0.0344	0.0310	0.0365	0.0021	0.0033	0.0027	0.0012
55(H)	0.0273	0.0167	0.0356	0.0083	0.0106	0.0094	0.0022
56(H)	0.0392	0.0260	0.0416	0.0024	0.0132	0.0078	0.0108

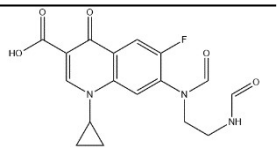
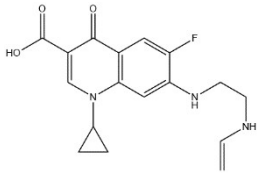
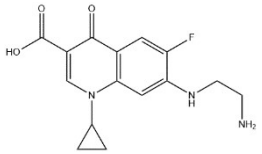
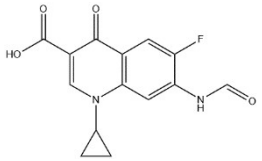
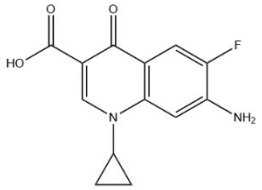
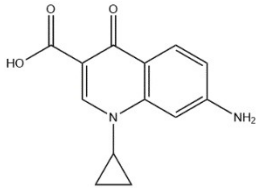
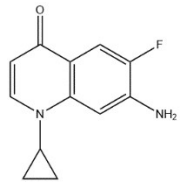
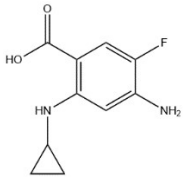
Table S7 Fukin index of ATZ

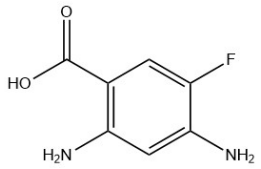
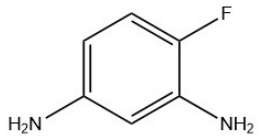
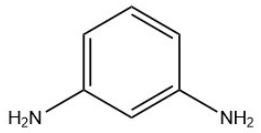
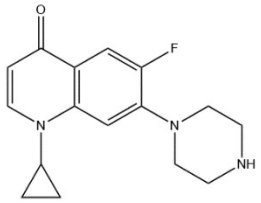
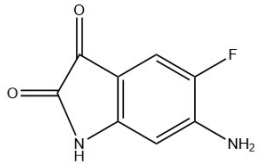
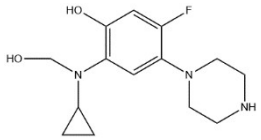
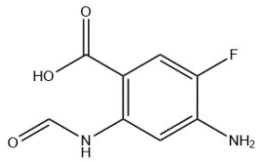
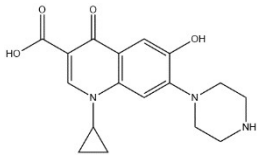
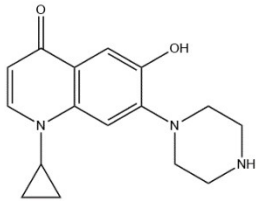
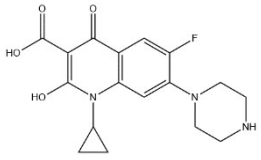
Atom	q(N)	q(N+1)	q(N-1)	f^-	f^+	f^0	CDD
1(C)	0.1577	0.0978	0.1828	0.0252	0.0599	0.0425	0.0347
2(C)	0.1370	-0.0050	0.1701	0.0332	0.1420	0.0876	0.1088
3(C)	0.1562	0.0963	0.1817	0.0255	0.0598	0.0427	0.0344
4(N)	-0.2096	-0.3014	-0.1837	0.0258	0.0918	0.0588	0.0660
5(N)	-0.0868	-0.1272	0.0006	0.0874	0.0404	0.0639	-0.0470
6(H)	0.1320	0.1067	0.1633	0.0313	0.0253	0.0283	-0.0060
7(N)	-0.0835	-0.1227	0.0188	0.1022	0.0392	0.0707	-0.0630
8(H)	0.1313	0.1066	0.1652	0.0340	0.0247	0.0293	-0.0093
9(C)	0.0383	0.0311	0.0518	0.0136	0.0072	0.0104	-0.0064
10(H)	0.0345	0.0268	0.0504	0.0160	0.0077	0.0118	-0.0083
11(C)	-0.0923	-0.1026	-0.0718	0.0205	0.0103	0.0154	-0.0102
12(H)	0.0328	0.0101	0.0600	0.0272	0.0227	0.0249	-0.0044
13(H)	0.0321	0.0310	0.0382	0.0061	0.0011	0.0036	-0.0050
14(H)	0.0288	0.0149	0.0457	0.0169	0.0139	0.0154	-0.0030
15(C)	-0.0861	-0.0959	-0.0738	0.0124	0.0097	0.0110	-0.0027
16(H)	0.0379	0.0193	0.0596	0.0217	0.0185	0.0201	-0.0032
17(H)	0.0314	0.0195	0.0453	0.0140	0.0119	0.0129	-0.0021
18(H)	0.0349	0.0263	0.0467	0.0118	0.0086	0.0102	-0.0032
19(C)	0.0061	-0.0063	0.0248	0.0186	0.0124	0.0155	-0.0062
20(H)	0.0371	0.0267	0.0545	0.0173	0.0104	0.0139	-0.0069
21(C)	-0.0837	-0.0953	-0.0712	0.0125	0.0116	0.0120	-0.0009
22(H)	0.0333	0.0211	0.0470	0.0137	0.0122	0.0129	-0.0015
23(H)	0.0400	0.0201	0.0606	0.0206	0.0199	0.0203	-0.0007
24(H)	0.0354	0.0248	0.0478	0.0124	0.0106	0.0115	-0.0018
25(N)	-0.2240	-0.2971	-0.0986	0.1254	0.0730	0.0992	-0.0524
26(N)	-0.2238	-0.2967	-0.1019	0.1219	0.0730	0.0974	-0.0489
27(H)	0.0311	0.0093	0.0628	0.0317	0.0218	0.0268	-0.0099
28(Cl)	-0.0777	-0.2380	0.0235	0.1012	0.1603	0.1308	0.0591

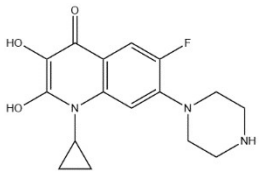
Table S8 Fukin index of ACE

Atom	q(N)	q(N+1)	q(N-1)	f^-	f^+	f^0	CDD
1(C)	-0.0669	-0.1982	0.0097	0.0766	0.1313	0.1039	0.0547
2(C)	-0.0657	-0.1925	0.0041	0.0697	0.1269	0.0983	0.0571
3(C)	0.0244	-0.0312	0.1274	0.1031	0.0555	0.0793	-0.0475
4(C)	-0.0541	-0.1872	0.0142	0.0683	0.1331	0.1007	0.0648
5(C)	-0.0674	-0.2048	0.0030	0.0703	0.1374	0.1039	0.0671
6(C)	0.0646	-0.0019	0.1650	0.1004	0.0665	0.0835	-0.0339
7(H)	0.0573	0.0023	0.0954	0.0381	0.0550	0.0466	0.0168
8(H)	0.0328	-0.0199	0.0644	0.0316	0.0527	0.0421	0.0211
9(H)	0.0589	0.0027	0.0941	0.0352	0.0562	0.0457	0.0210
10(H)	0.0530	-0.0061	0.0892	0.0362	0.0591	0.0477	0.0229
11(O)	-0.2245	-0.2497	-0.1161	0.1085	0.0251	0.0668	-0.0833
12(H)	0.2041	0.1828	0.2356	0.0316	0.0213	0.0264	-0.0103
13(N)	-0.0674	-0.0738	0.0020	0.0694	0.0064	0.0379	-0.0630
14(H)	0.1547	0.1430	0.1851	0.0303	0.0117	0.0210	-0.0186
15(C)	0.1859	0.1593	0.2092	0.0233	0.0266	0.0250	0.0033
16(O)	-0.3704	-0.3953	-0.3099	0.0605	0.0249	0.0427	-0.0355
17(C)	-0.0804	-0.0885	-0.0718	0.0087	0.0080	0.0084	-0.0006
18(H)	0.0549	0.0533	0.0680	0.0131	0.0016	0.0074	-0.0115
19(H)	0.0536	0.0519	0.0666	0.0131	0.0017	0.0074	-0.0114
20(H)	0.0526	0.0539	0.0646	0.0120	-0.0013	0.0054	-0.0133

Table S9. Identified transformation products of CIP

Number	Formula	Retention time (min)	Experimental m/z [M-H]-	Structural formula
TP1	$C_{18}H_{16}N_3O_5F$	7.26	360.9	
TP2	$C_{17}H_{18}N_3O_3F$	16.60	334	
TP3	$C_{15}H_{16}N_3O_3F$	7.26	360.9	
TP4	$C_{15}H_{11}N_2O_4F$	15.66	291	
TP5	$C_{14}H_{11}N_2O_3F$	5.86	263	
TP6	$C_{14}H_{11}N_2O_3$	10.76	245	
TP7	$C_{13}H_{10}N_2OF$	4.17	219	
TP8	$C_{10}H_{11}N_2O_2F$	28.58	211	

TP9	$C_7H_7N_2O_2F$	6.69	171	
TP10	$C_6H_8N_2F$	26.44	127	
TP11	$C_6H_8N_2$	2.21	109	
TP12	$C_{16}H_{20}N_3OF$	9.69	288	
TP13	$C_8H_5N_2O_2F$	19.80	181	
TP14	$C_{13}H_{19}N_3O_2F$	13.27	282	
TP15	$C_8H_6N_2O_3F$	21.61	200	
TP16	$C_{17}H_{19}N_3O_4$	20.78	330	
TP17	$C_{15}H_{17}N_3O_2$	13.51	285	
TP18	$C_{14}H_{17}N_3O_2F$	18.14	348	

TP19	$C_{16}H_{17}N_3O_3F$	13.84	320	
TP20	$C_{16}H_{17}N_3O_4$	18.08	318