Supporting Information for

Carbonate Radical Oxidation of Cylindrospermopsin (Cyanotoxin): Kinetic Studies and Mechanistic Consideration

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Table S1. List of abbreviation.

AOM	algal organic matters
AOPs	advanced oxidation processes
ATR	atrazine
BDE	bond dissociation energies
$CO_3^{\bullet-}$	carbonate radical
CTC	carbonatotetrammine cobaltic chloride
CYN	cylindrospermospsin
DFT	density functional theory
DIC	dissolved inorganic carbonate
DOM	dissolved organic matter
$^3DOM^*$	triplet dissolved organic matter
D_{RIs}	the relative reactivity of CYN with the DOM intermediates
ESI	electrospray ionization source
$HO^{\bullet}$	hydroxyl radical
HPLC-QTOF-MS	quadrupole time-of-flight mass spectrometry
IF	inhibition factors
IPU	isoproturon
MPP	mass profiler professional
PLFA	Pony Lake fulvic acid
RIs_{DOM}	reactive intermediates
$SO_4^{\bullet-}$	sulfate radical
SRDOM	Suwannee River dissolved organic matter
SRHA	Suwannee River humic acid
TBA	t-butanol
$k_{CYN_{dep.}-CO_3^{\bullet-}}$	second-order rate constant of deprotonated CYN
$k_{CYN_{neu.}-CO_3^{\bullet-}}$	second-order rate constant of neutral CYN
$k_{CYN_{IPU.}-CO_3^{\bullet-}}$	second-order rate constant of IPU
$k_{uracil_{dep.}-CO_3^{\bullet-}}$	second-order rate constant of deprotonated uracil

$k_{uracil_{neu.}-CO_3^{\bullet-}}$	second-order rate constant of neutral uracil
k_{CYN}^{app}	apparent second-order rate constant for the CYN
k_{uracil}^{app}	apparent second-order rate constants of uracil
$k'_{DOM+DIC}$	the first-order decay rate of CYN with DOM and DIC
k'_{DOM}	the first-order decay rate of CYN with DOM
$k'_{CO_3^{\bullet-}}$	the first-order decay rate of CYN with $CO_3^{\bullet-}$
$k'^{3}_{DOM^*}$	the first-order decay rate of CYN with $^3DOM^*$
$[CO_3^{\bullet-}]_{ss}$	the steady state concentration of $CO_3^{\bullet-}$
$[DOM]_{1/2}$	the concentration of DOM at IF=0.5

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Text S1. Isolation of the algal organic matters (AOM).

AOM was prepared by following an established procedure.[1-4] A culture of *Microcystis aeruginosa 905* was purchased from the Institute of Hydrobiology, Chinese Academy of Sciences (Wuhan, China). The algae were cultivated for 15 days to allow algal cells to grow into the stationary growth phase. Algal cells were then separated from the algal suspensions by following the procedure: centrifuged at 5000 rpm (Backman Coulter, US), remove the supernatant, and added ultrapure water. After repeating three times, the algal solution was then sonicated with an ultrasonic cell disrupter (JY 88-IIN, Scientz Instruments, China) for ten minutes. After cell disruption, the solution was centrifuged at 5000 rpm to obtain the supernatant. Finally, the supernatant was filtered through a 0.22 μm filter (Whatman) to get the AOM. The TOC of AOM was measured as 19.8 mg_C L^{-1} (Sievers M9, TOC Analyzers).

Text S2. The synthesis of Carbonatotetrammine cobaltic chloride (Co $(NH_3)_4CO_3Cl$, CTC).

The CTC salt was prepared according to the literature.[5] The detailed procedure was described as following:

(1) 40.0 g of $CoCO_3$ was dissolved in 115 mL of 1:1 HCl warming solution. Then diluted into 200 mL with DI water.

(2) 200.0 g of $(NH_4)_2CO_3$ was dissolved in Solution (1), then mixed with 500 mL of concentrated NH_4OH (28%), finally diluted to 1600 mL with DI water.

(3) Solution (2) was transferred to a porcelain dish and evaporated on a water-bath, with the addition of 5-6.0 g lumps of $(NH_4)_2CO_3$ at 5-minute intervals, the solution was concentrated to a volume not greater than 500 mL, then filtered while warm. After filtration, the solution was cooled in an ice-bath and diluted into 600 mL with a solution containing 36.0 g of NH_4Cl in the required amount of DI water.

(4) Solution (3) was treated with 1500 mL of cold alcohol (95 %) with ice-bath, added in 100 mL portions at 10-minute intervals. The product, separated in good crystalline form, was collected on a suction filter, washed with cold alcohol (70 %), and dried in the open air. After two times of recrystallization, the product was crystallized once from water without the addition of alcohol. The crystal was then dried in desiccator for 48 hr.

The dried product was sent to analyze the content of cobalt and chlorine. The measured value is 26.31 % and 15.89 %, respectively. They are consistent with the calculated value for Co $(NH_3)_4CO_3Cl$: 26.49 % and 15.93 %. Based on the measured Co %, the calculated purity of CTC is > 99 %. The quantum yield of $CO_3^{\bullet-}$ generated by UV_{254} irradiated of CTC in neutral solution was reported as 0.06.[6]

Text S3. Determination of reaction rate constant of $CO_3^{\bullet-}$ with CYN and Uracil

The reaction rate constant of CYN with $CO_3^{\bullet-}$ was measured using competition kinetics method. Firstly, IPU and CYN were mixed in phosphate buffer as the working solutions. Then, the CTC stock solution (0.5 mM) was spiked into the working solution, and immediately send to UV irradiation. The HPLC analysis should be finished in 15 mins to minimize CTC auto-oxidation (less than 0.5 % of IPU loss). According to the pre-experiment data, the direct photodegradation of IPU can be ignored due to the short irradiation time (the maxima irradiation time is 5 min for each sample). The equations for the depletion of IPU or CYN induced by its reaction with $CO_3^{\bullet-}$ are given by the following expression (Eq. S1-4).

$$CO_3^{\bullet-} + CYN \rightarrow CO_3^{2-} + Compound_{CYN} \qquad k_{CO_3^{\bullet-}-CYN} \qquad \text{(S1)}$$

$$CO_3^{\bullet-} + IPU \rightarrow CO_3^{2-} + Compound_{IPU} \qquad k_{CO_3^{\bullet-}-IPU} \qquad \text{(S2)}$$

$$\frac{d[CYN]}{dt} = -k_{CO_3^{\bullet-}-CYN}[CO_3^{\bullet-}][CYN] \qquad \text{(S3)}$$

$$\frac{d[IPU]}{dt} = -k_{CO_3^{\bullet-}-IPU}[CO_3^{\bullet-}][IPU] \qquad \text{(S4)}$$

where, $k_{CO_3^{\bullet-}-CYN}$ and $k_{CO_3^{\bullet-}-IPU}$ are the second-order rate constants for the reaction of $CO_3^{\bullet-}$ with CYN and IPU. Rearrangement and integration of Eq. S3 and Eq. S4 can be transformed to Eq. S5 and Eq. S6, respectively.

$$ln\frac{[CYN]}{[CYN]_0} = -k_{CO_3^{\bullet-}-CYN}\int[CO_3^{\bullet-}]\,dt \qquad \text{(S5)}$$

$$ln\frac{[IPU]}{[IPU]_0} = -k_{CO_3^{\bullet-}-IPU}\int[CO_3^{\bullet-}]\,dt \qquad \text{(S6)}$$

Eq. S6 divided by Eq. S5 could lead to Eq. S7. Finally, $k_{CO_3^{\bullet-}-CYN}$ values were calculated by the k value got from the $ln\frac{[IPU]}{[IPU]_0}$ v.s. $ln\frac{[CYN]}{[CYN]_0}$ plots.

$$ln\frac{[IPU]}{[IPU]_0} = \frac{k_{CO_3^{\bullet-}-IPU}}{k_{CO_3^{\bullet-}-CYN}} ln\frac{[CYN]}{[CYN]_0} \qquad \text{(S7)}$$

The reaction rate constant of uracil with $CO_3^{\bullet-}$ was also measured using competition kinetics method.

The HPLC analysis finished in 15 mins. According to the pre-experiment data, the direct photodegradation of uracil can be ignored due to the short irradiation time (the maxima irradiation time is 5 min for each sample). Otherwise, when pH is lower than 9, atrazine was chosen as the competitor. Other details were given as same as the IPU.

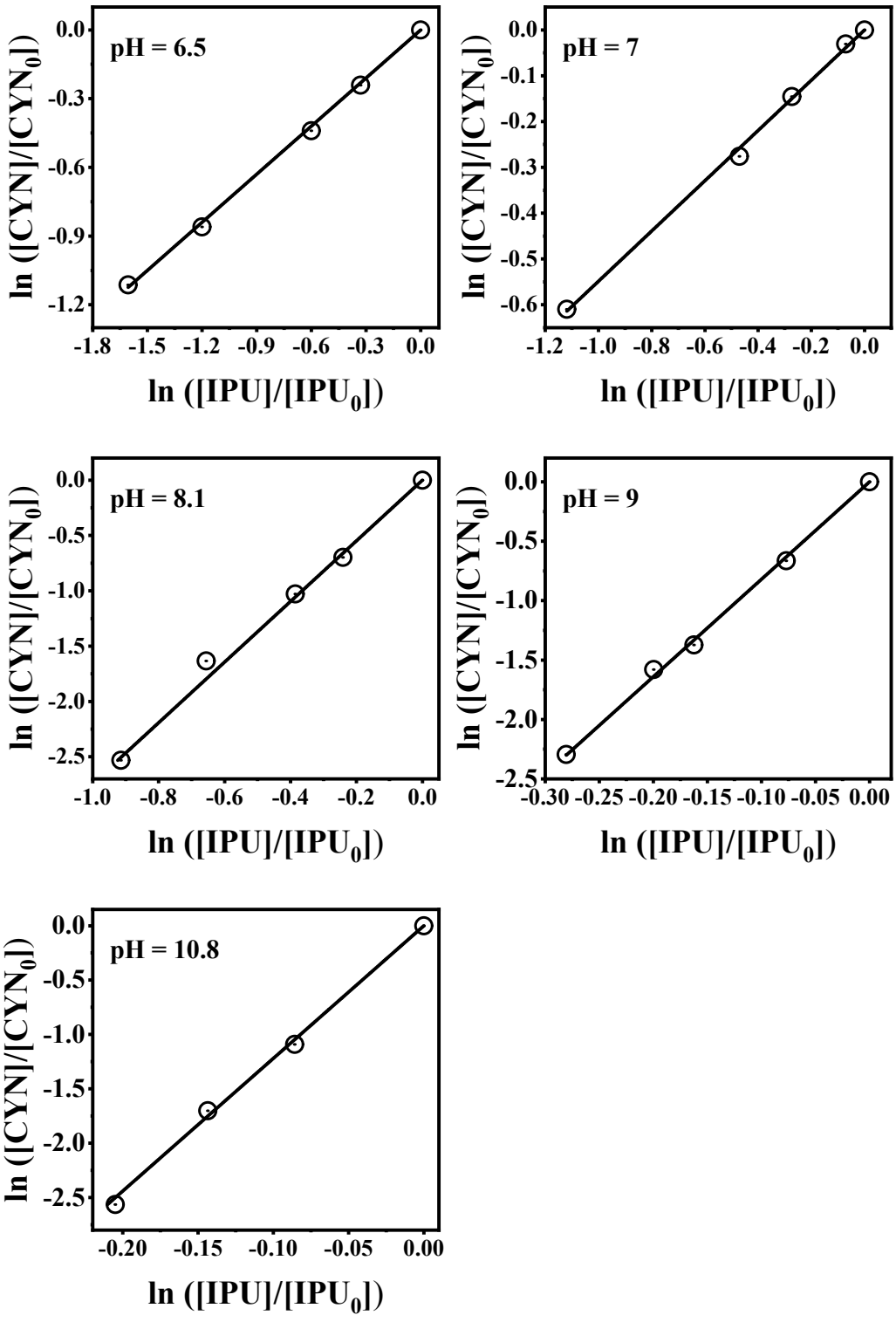
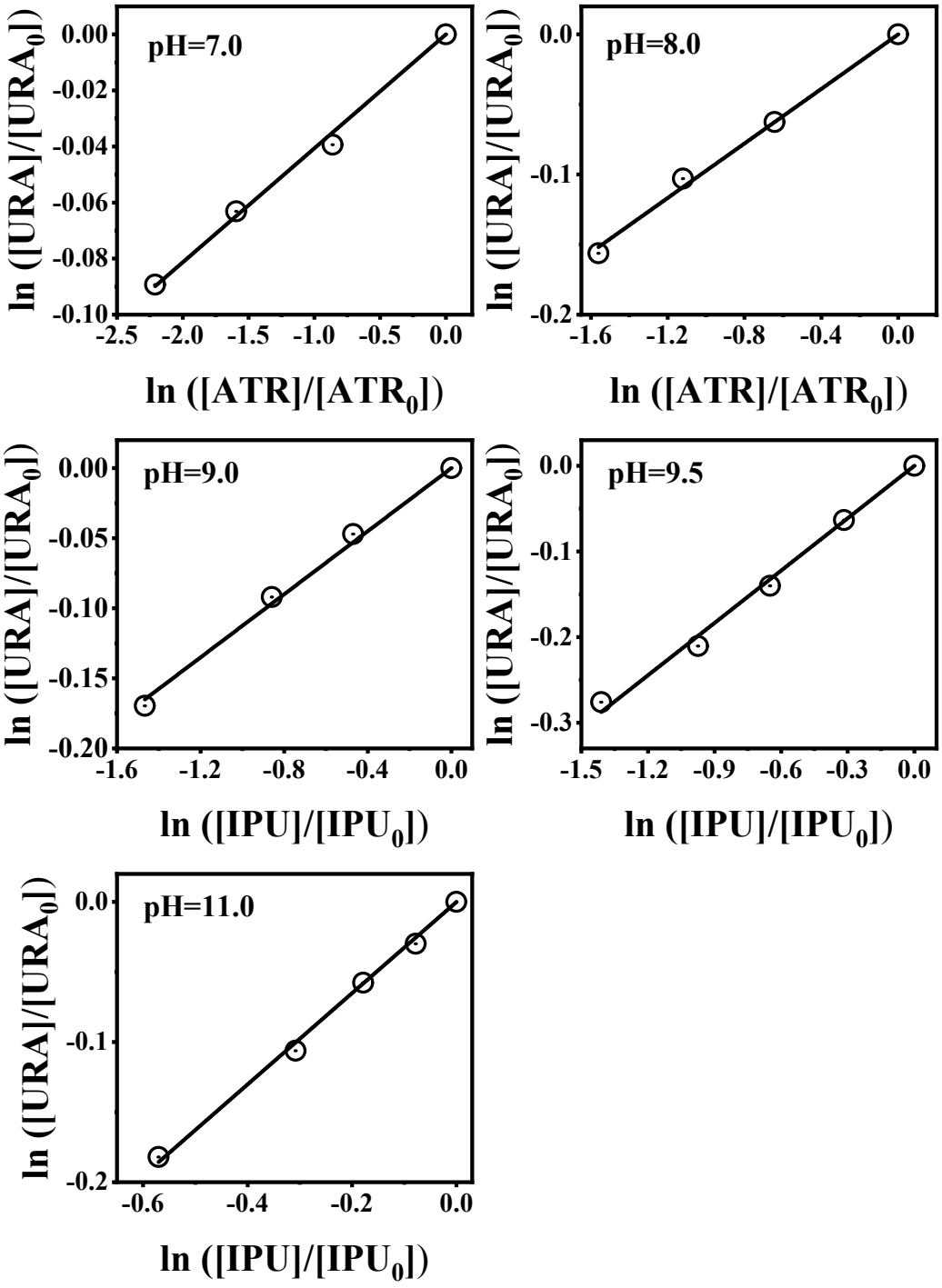


Figure S1. Competition kinetics of IPU and CYN with $CO_3^{\bullet-}$ at pH 6.5, 7.0, 8.1, 9.0 and 10.8.



102

103 **Figure S2**. Competition kinetics of IPU (atrazine) and uracil with $CO_3^{\bullet-}$ at pH 7.0, 8.0, 9.0, 9.5 and 11.0.

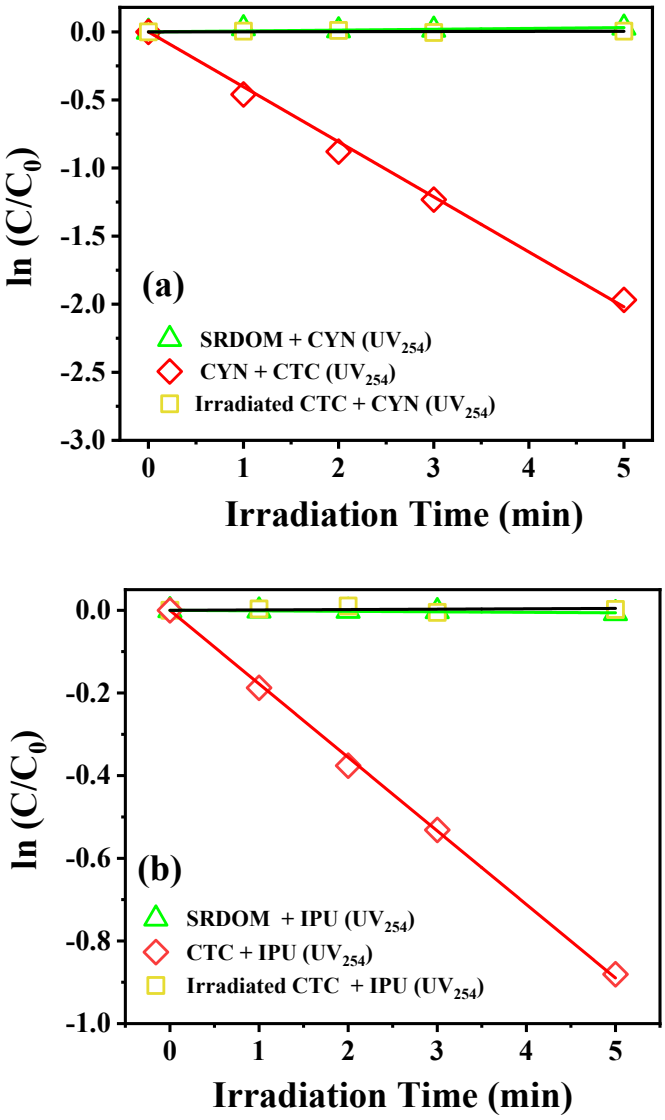


Figure S3. (a) Control experiments: the degradation of CYN under irradiation of UV_{254} with 5 mg_C L^{-1} of SRDOM and with pre-irradiated CTC solution (0.1 mM CTC was pre-irradiated 30 mins before CYN spiking). The degradation curve of CYN under UV254 irradiation of CTC solution has been added for comparison purpose. (b) Control experiments: the degradation of IPU under irradiation of UV_{254} with 5 mg_C L^{-1} of SRDOM and with pre-irradiated CTC solution (0.1 mM CTC was pre-irradiated 30 mins before IPU spiking). The degradation curve of IPU under UV_{254} irradiation of CTC solution has been added for comparison purpose. Note: within the time range of our experiment, no observed degradation of CYN and IPU in CTC solution under dark condition. (data not shown)

Table S2. Parameters for HPLC analysis.

Organic compound	Eluent composition (%)		Flow rate (mL/min)	Injection volume (μL)	Absorption wavelength (nm)
	water	methanol			
CYN	95	5	1	100	262
IPU	65	35	1	100	254
Uracil	95	5	1	100	260
Atrazine	65	35	1	100	230

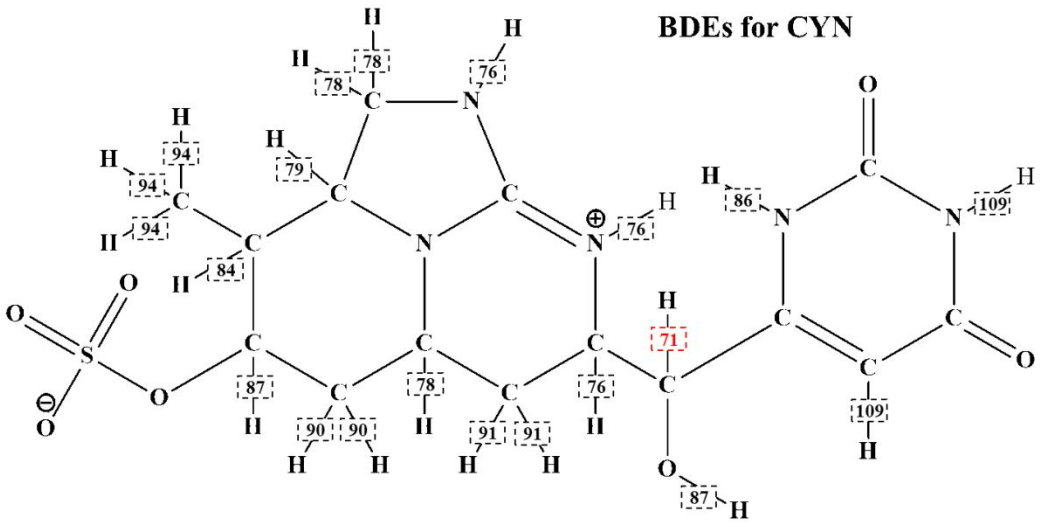
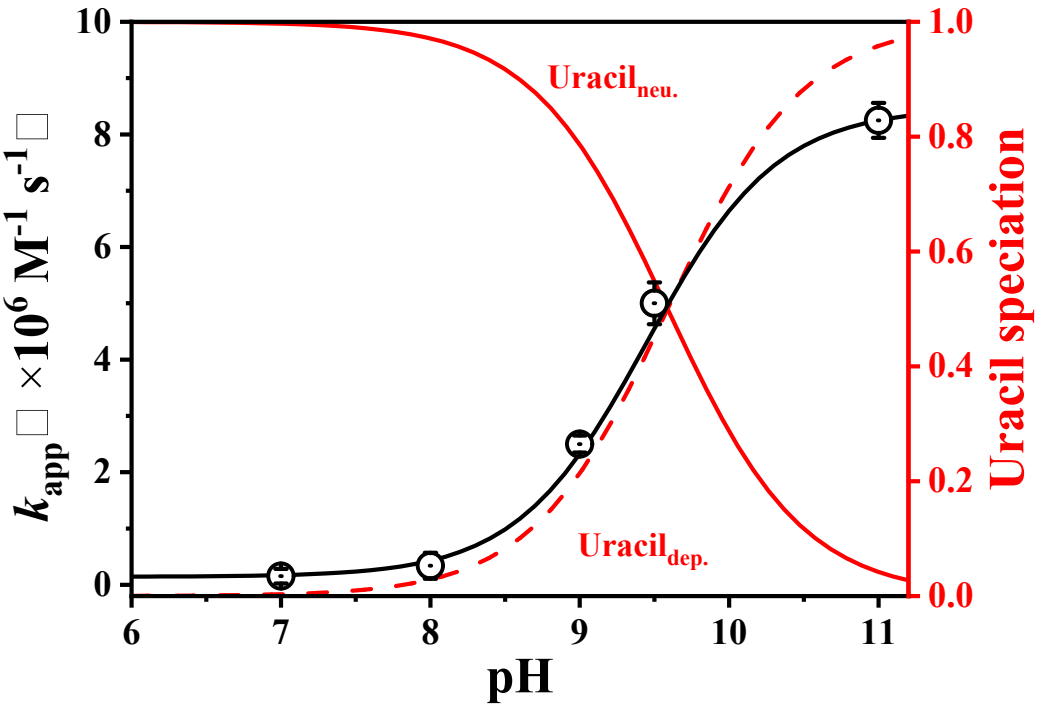


Figure S4. The calculated bond dissociation energies (BDEs, kcal mol^{-1}) for CYN by using Gaussian 09.



119

120 **Figure S5**. Apparent second-order rate constants for the reactions between $CO_3^{\bullet-}$ and Uracil depend on
121 pH. The model *k* is based on two species: Uacil$_{neu.}$, a neutral amine, and Uracil$_{dep.}$, a deprotonated amine.
122 (solid black lines, model *k*; red lines, speciation; symbols, measured *k*)

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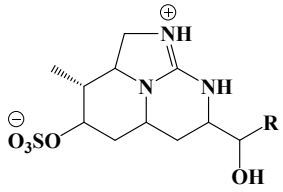
Table S3. General information regarding the identified products of CYN oxidized by $CO_3^{\bullet-}$.

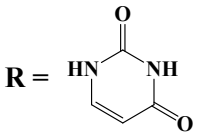
No.	Compound name	Formula	Retention time (min)	m/z (theoretical)	m/z (measured)	Mass error (ppm)	Levels
1	CYN	$C_{15}H_{21}N_5O_7S$	4.55	416.1235	416.1236	0.2	1
2	P_{156}	$C_5H_4N_2O_4$	3.56	155.0098	155.0094	-2.6	2b
3	P_{289}	$C_{10}H_{15}N_3O_5S$	3.75	290.0805	290.0803	-0.7	2b
4	P_{291}	$C_{10}H_{17}N_3O_5S$	4.96	292.0962	292.0961	-0.3	2b
5	P_{305a}	$C_{10}H_{15}N_3O_6S$	3.75	306.0754	306.0753	-0.3	3
6	P_{305b}	$C_{10}H_{15}N_3O_6S$	3.75	306.0754	306.0753	-0.3	3
7	P_{307a}	$C_{10}H_{17}N_3O_6S$	3.75	308.0911	308.0908	-1.0	3
8	P_{307b}	$C_{10}H_{17}N_3O_6S$	4.14	308.0911	308.0909	-0.6	3
9	P_{321}	$C_{10}H_{15}N_3O_7S$	3.75	322.0703	322.0712	2.8	3
10	P_{323}	$C_{10}H_{17}N_3O_7S$	3.75	324.0860	324.0855	-1.5	3
11	P_{413}	$C_{15}H_{19}N_5O_7S$	9.50	414.1083	414.1073	-2.4	2b
12	P_{429a}	$C_{15}H_{19}N_5O_8S$	3.80	430.1027	430.1030	0.7	3
13	P_{429b}	$C_{15}H_{19}N_5O_8S$	4.50	430.1027	430.1030	0.7	3
14	P_{431a}	$C_{15}H_{21}N_5O_8S$	3.75	432.1184	432.1173	-2.5	2b
15	P_{431b}	$C_{15}H_{21}N_5O_8S$	3.90	432.1184	432.1180	-0.9	2b
16	P_{445}	$C_{15}H_{19}N_5O_9S$	3.77	446.0976	446.0979	0.7	3
17	P_{447}	$C_{15}H_{21}N_5O_9S$	3.76	448.1133	448.1129	-0.9	2b
18	P_{461}	$C_{15}H_{19}N_5O_{10}S$	3.75	462.0931	462.0921	-2.2	3
19	P_{463}	$C_{15}H_{21}N_5O_{10}S$	3.73	464.1087	464.1080	-1.5	3

Text S4. Structure elucidation based on the HPLC-qTOF-MS/MS data.

S4.1 Compound name: CYN, Formula: $C_{15}H_{21}N_5O_7S$, Theoretical m/z: 416.1235

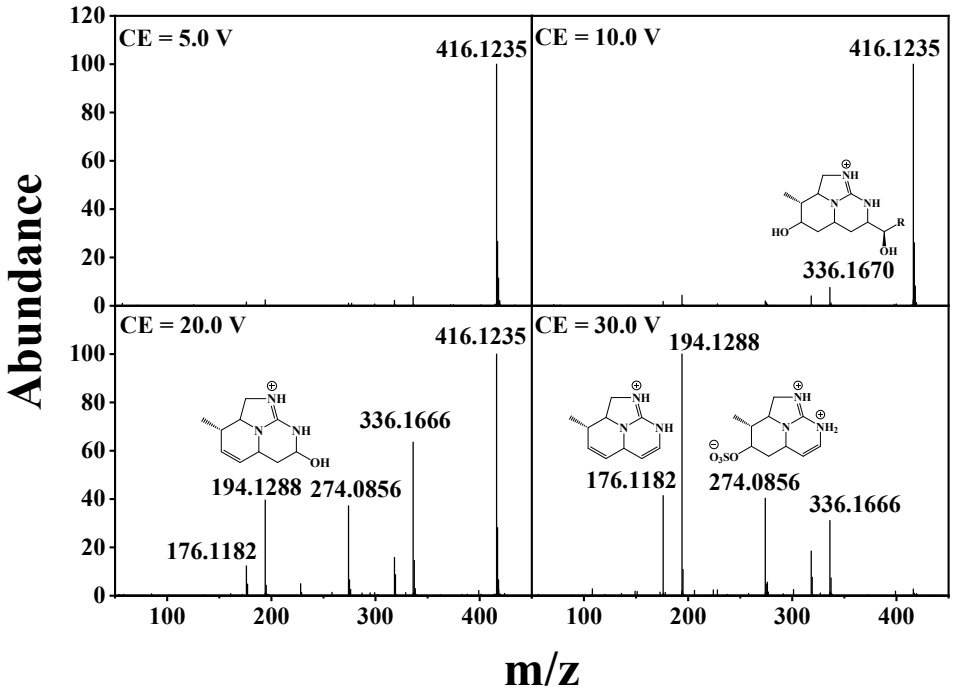
Structure:





Confidence Level:
Level 1
Parent compound

MS/MS spectra



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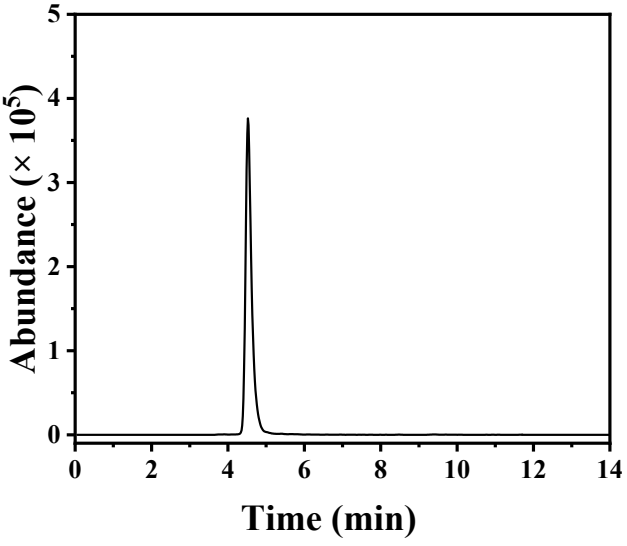

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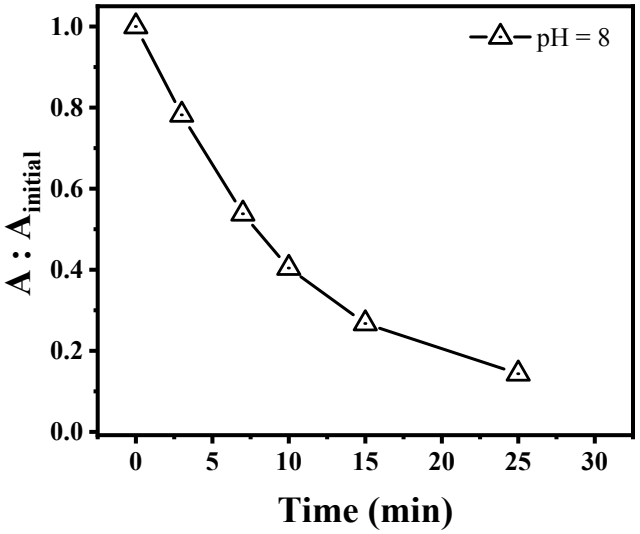
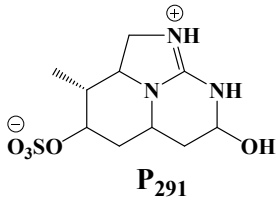


S4.2 Compound name: P_{291}, Formula: $C_{10}H_{17}N_3O_5S$, Theoretical m/z: 292.0962

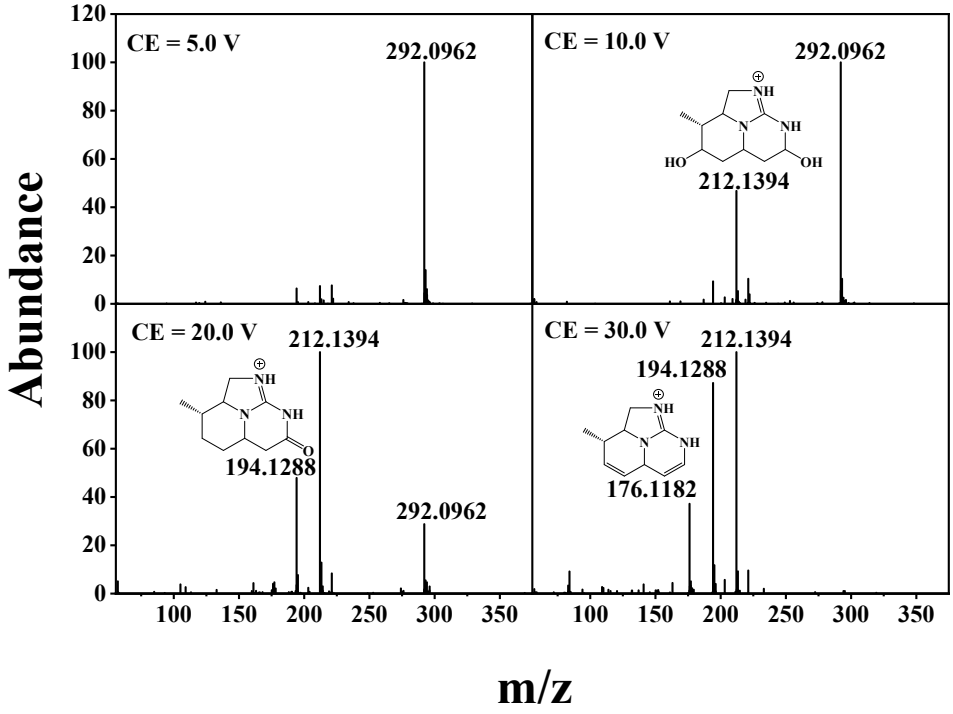
Structure:



P_{291}

Confidence Level:
Level 2b
Diagnostic evidence

MS/MS spectra



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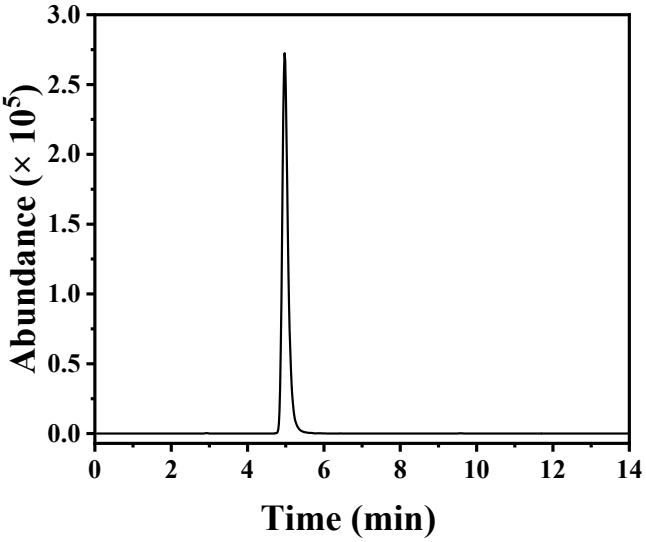

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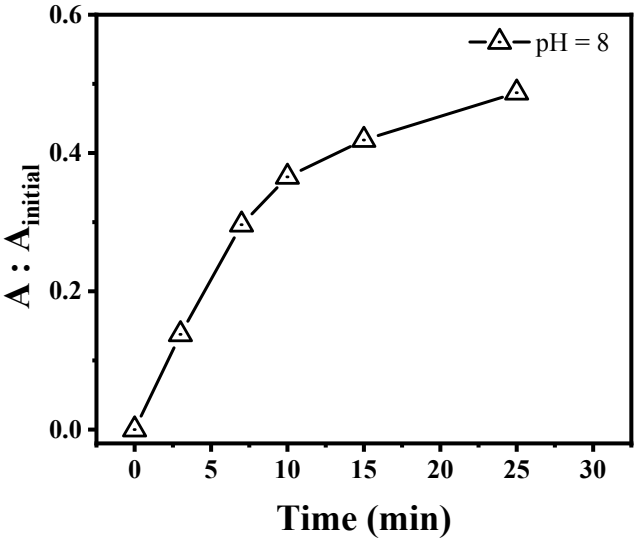

S4.3 Compound name: P_{289}, Formula: $C_{10}H_{15}N_3O_5S$, Theoretical m/z: 290.0805

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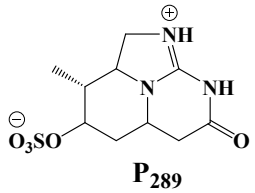
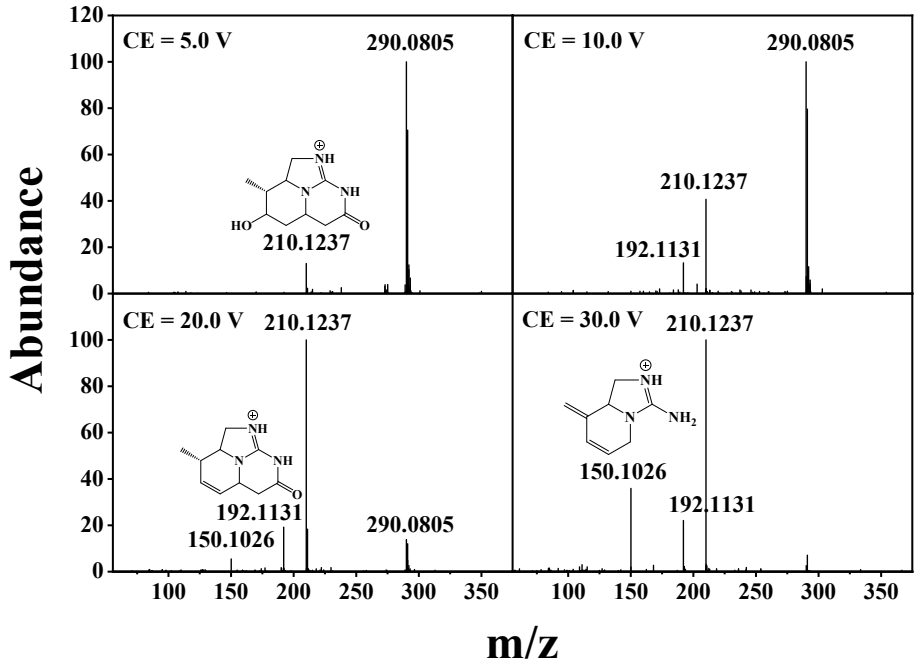


P_{289}

Confidence Level:
Level 2b
Diagnostic evidence

MS/MS spectra



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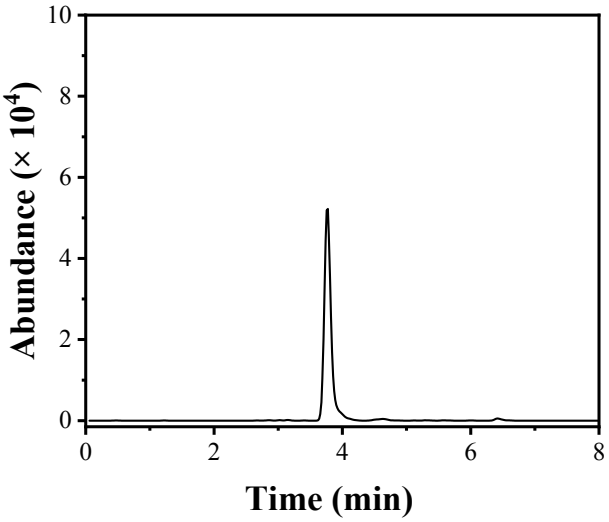

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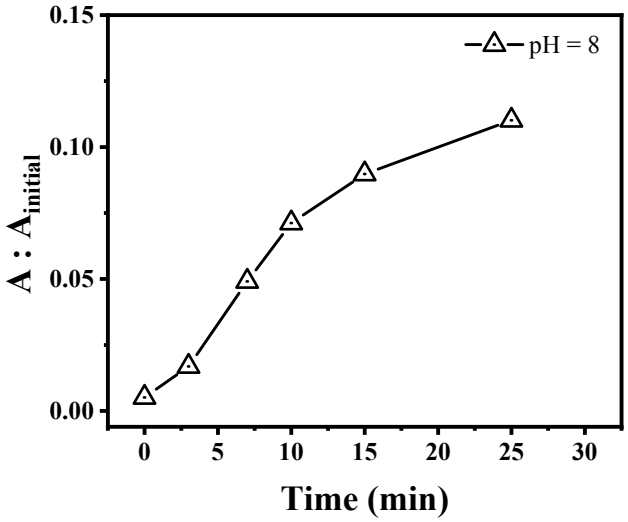
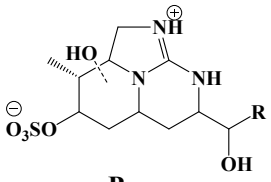


S4.4 Compound name: $P_{431a/b}$, Formula: $C_{15}H_{21}N_5O_8S$, Theoretical m/z: 432.1184

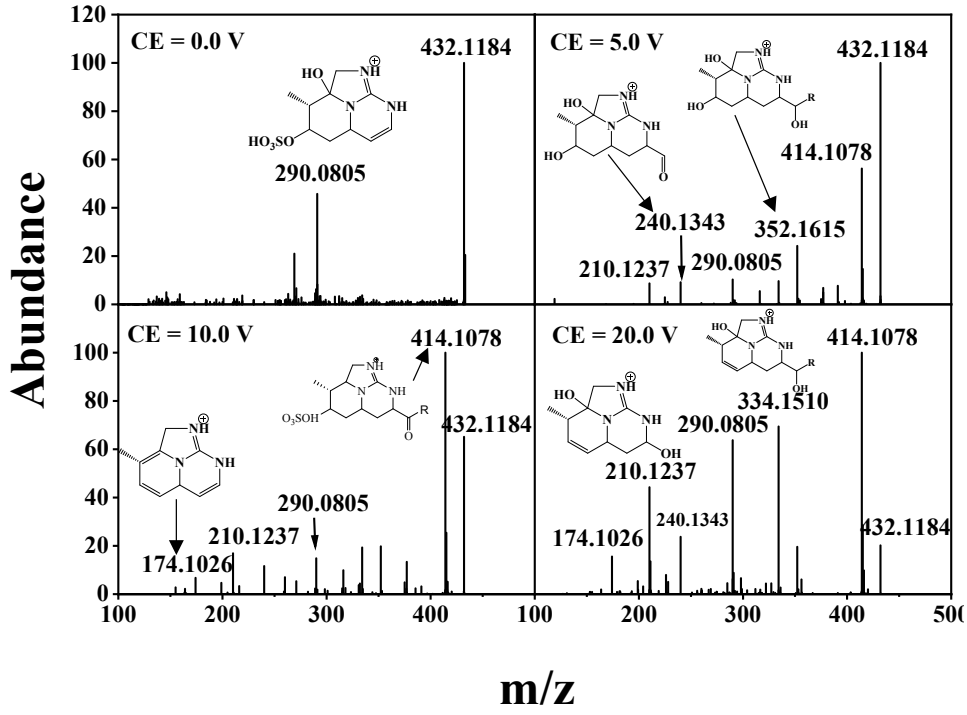
Structure:



$P_{431a/b}$

Confidence Level:
Level 2b
Diagnostic evidence

MS/MS spectra



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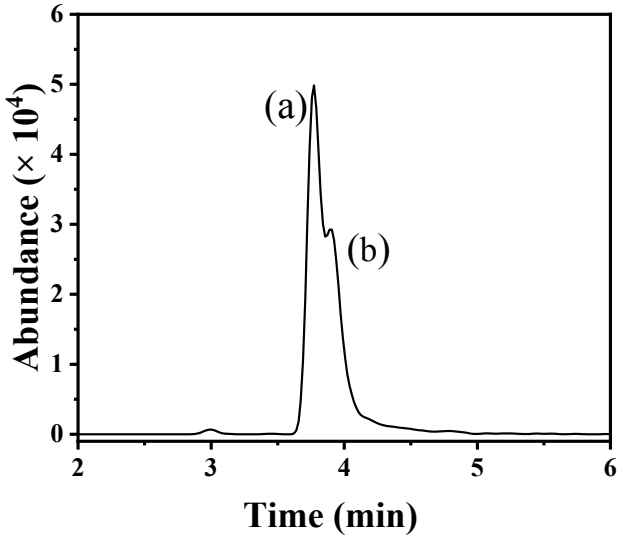

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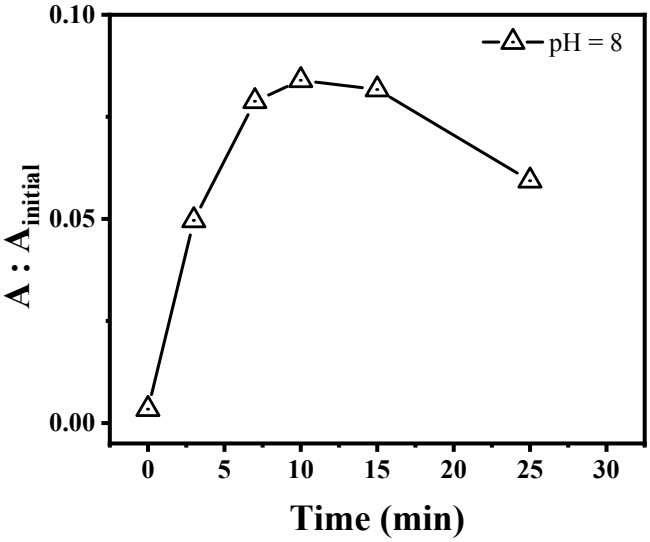
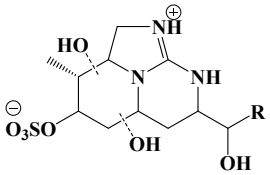


S4.5 Compound name: P_{447}, Formula:$C_{15}H_{21}N_5O_9S$, Theoretical m/z: 448.1133

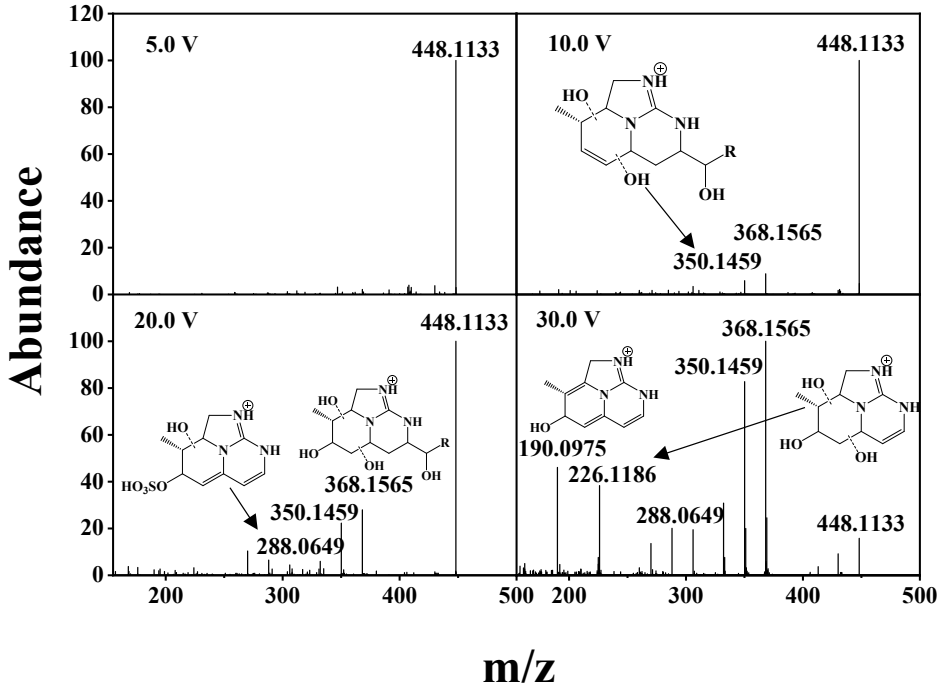
Structure:



P_{447}

Confidence Level:
Level 2b
Diagnostic evidence

MS/MS spectra



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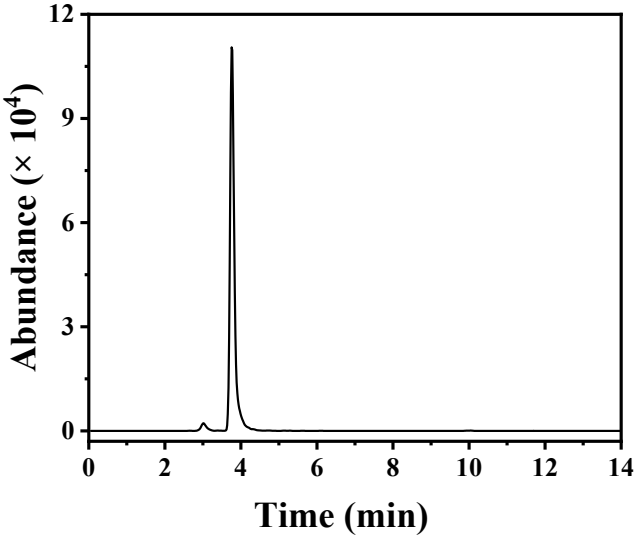

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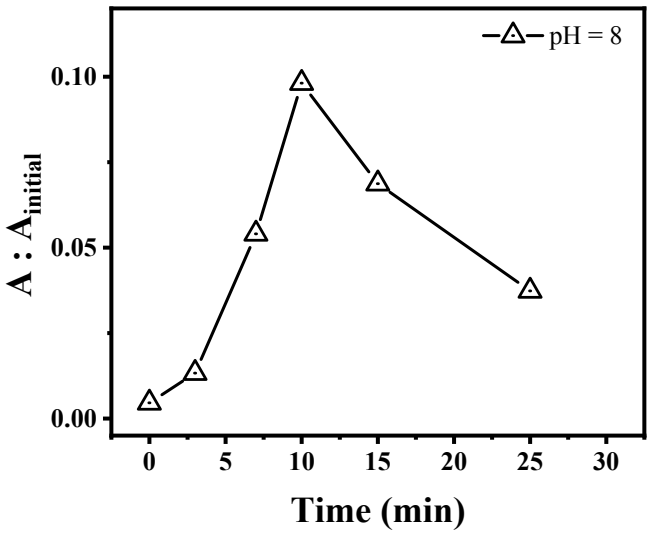
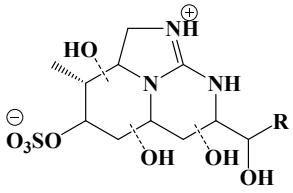


S4.6 Compound name: P_{463}, Formula: $C_{15}H_{21}N_5O_{10}S$, Theoretical m/z: 464.1087

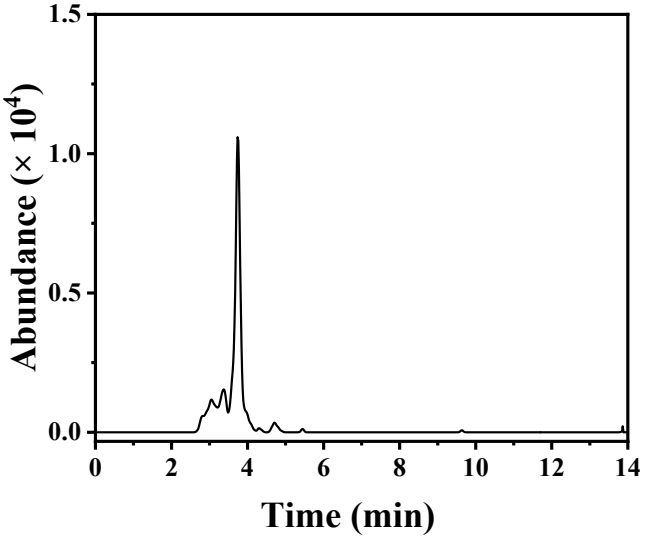
Structure:



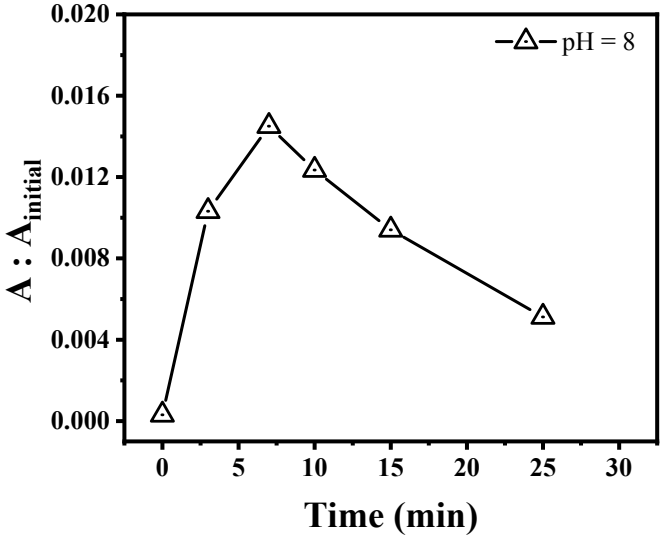
P_{463}

Confidence Level:
Level 3
Proposed Structure

Chromatogram.

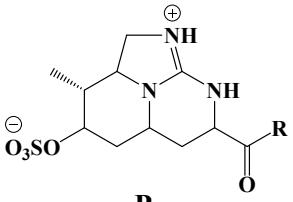


Reaction profile.



S4.7 Compound name: P_{413}, Formula: $C_{15}H_{19}N_5O_7S$, Theoretical m/z: 414.1078

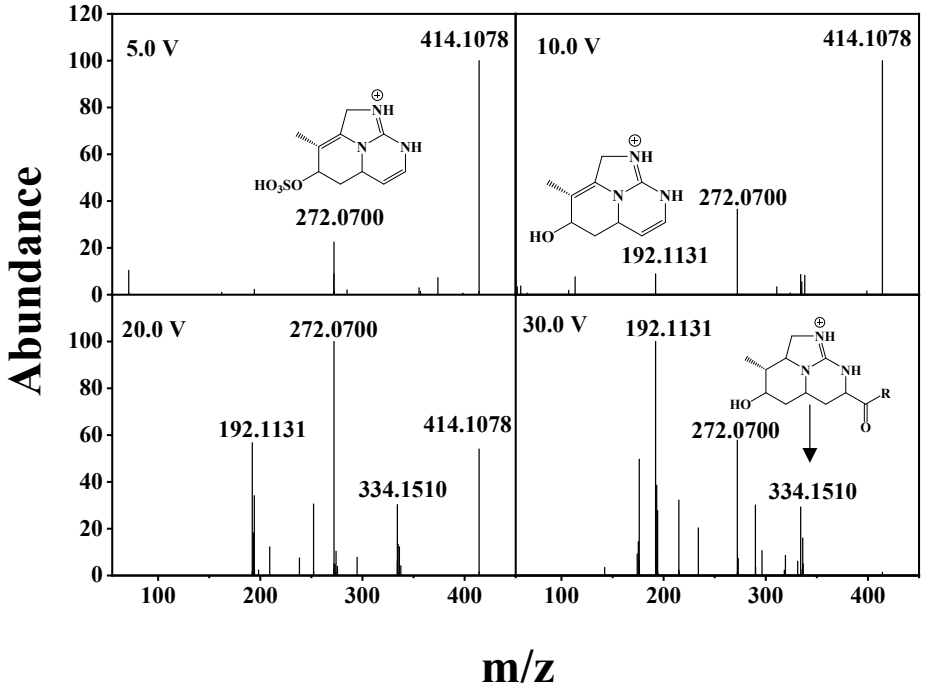
Structure:



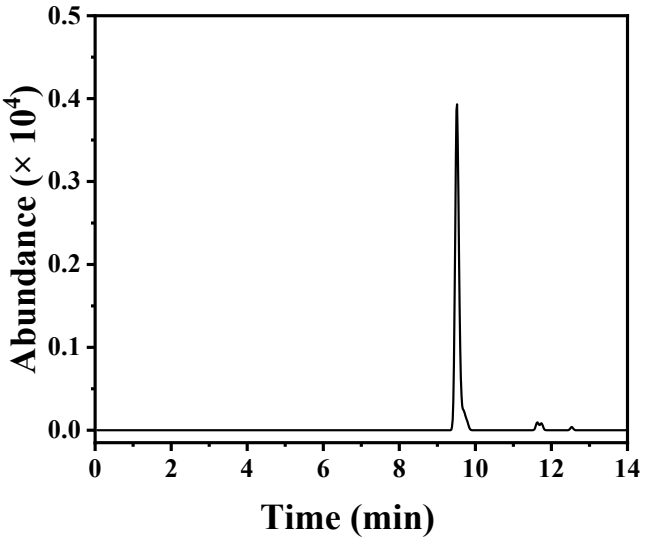
P_{413}

Confidence Level:
Level 2b
Diagnostic evidence

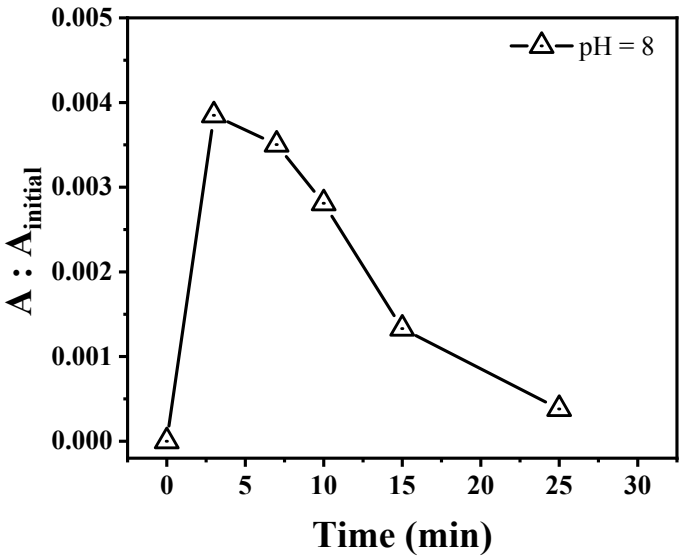
MS/MS spectra



Chromatogram.

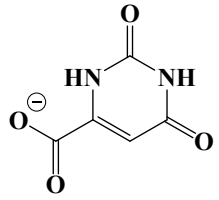


Reaction profile.



S4.8 Compound name: P_{156}, Formula: $C_5H_4N_2O_4$, Theoretical m/z: 155.0098

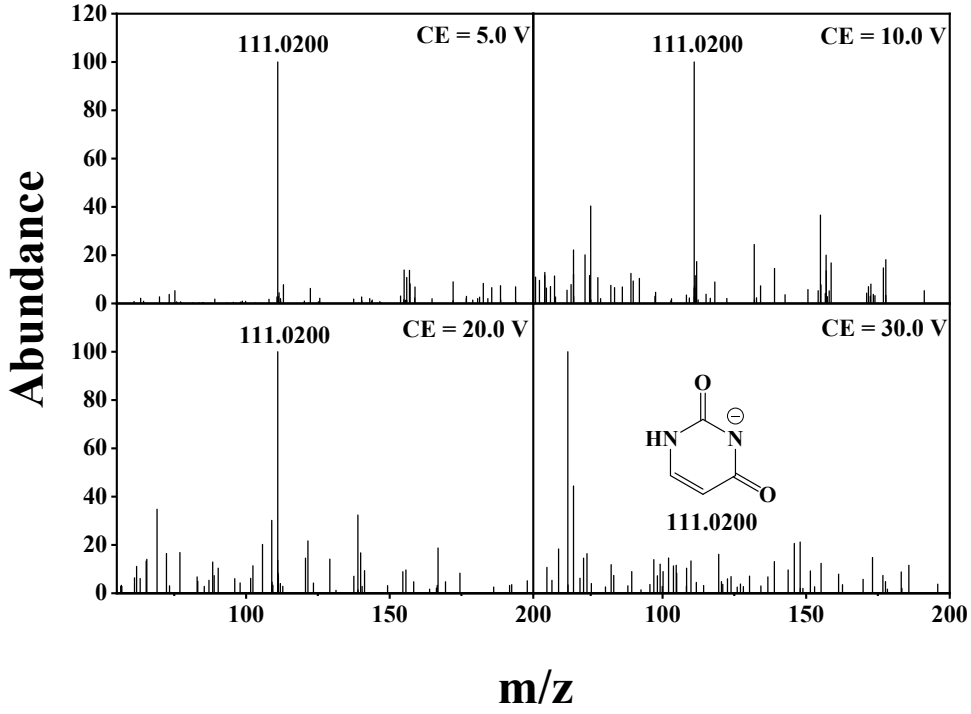
Structure:



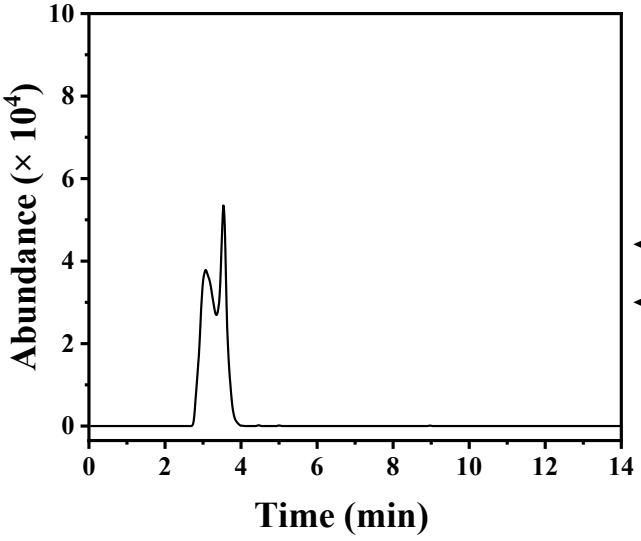
P_{156}

Confidence Level:
Level 2b
Diagnostic evidence

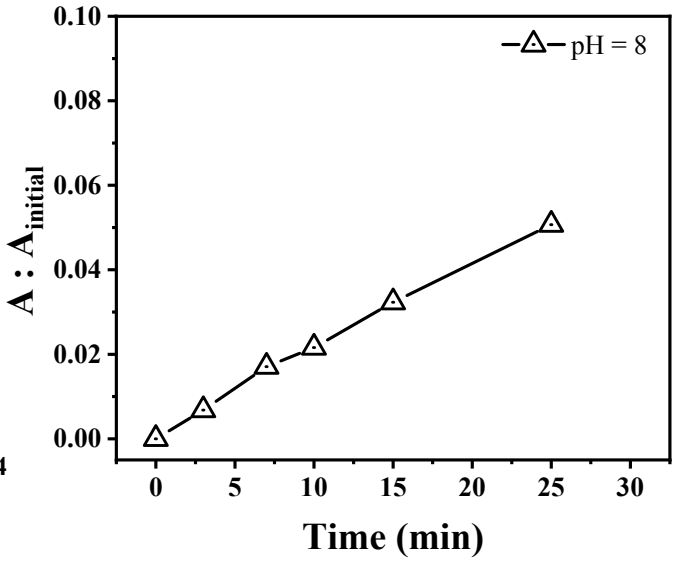
MS/MS spectra



Chromatogram.

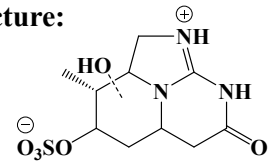


Reaction profile.



S4.9 Compound name: $P_{305a/b}$, Formula: $C_{10}H_{15}N_3O_6S$, Theoretical m/z: 306.0754

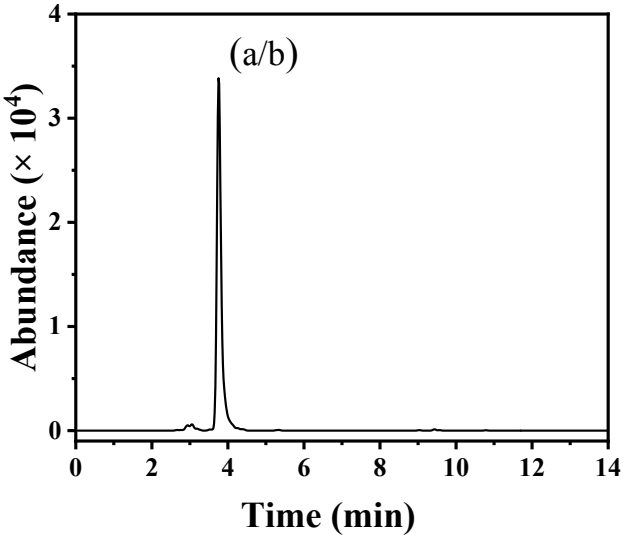
Structure:



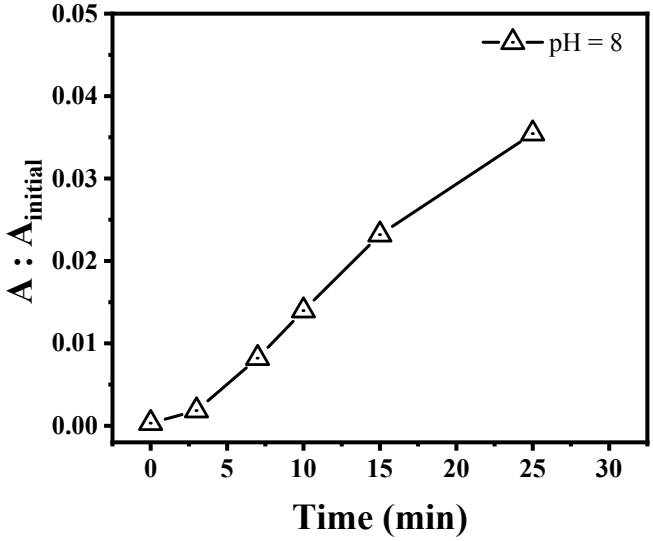
$P_{305a/b}$

Confidence Level:
Level 3
Proposed Structure

Chromatogram.

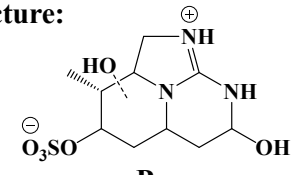


Reaction profile.



S4.10 Compound name: $P_{307a/b}$, Formula: $C_{10}H_{17}N_3O_6S$, Theoretical m/z: 308.0911

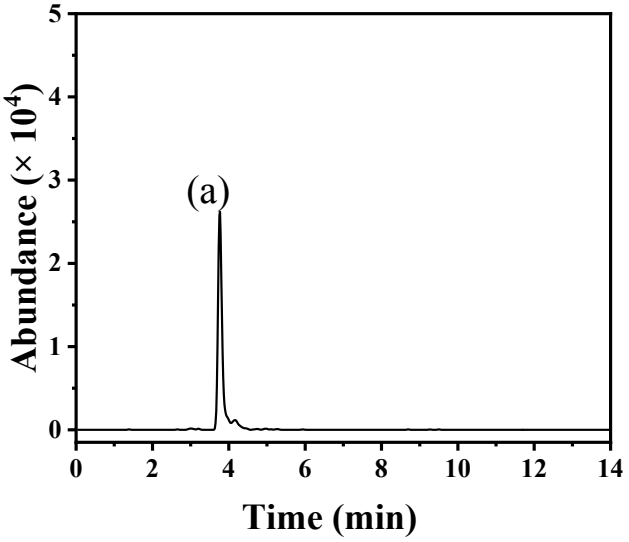
Structure:



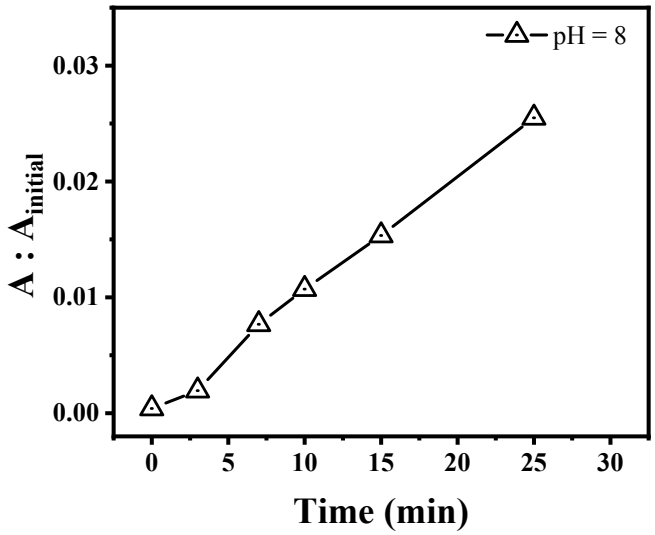
$P_{307a/b}$

Confidence Level:
Level 3
Proposed Structure

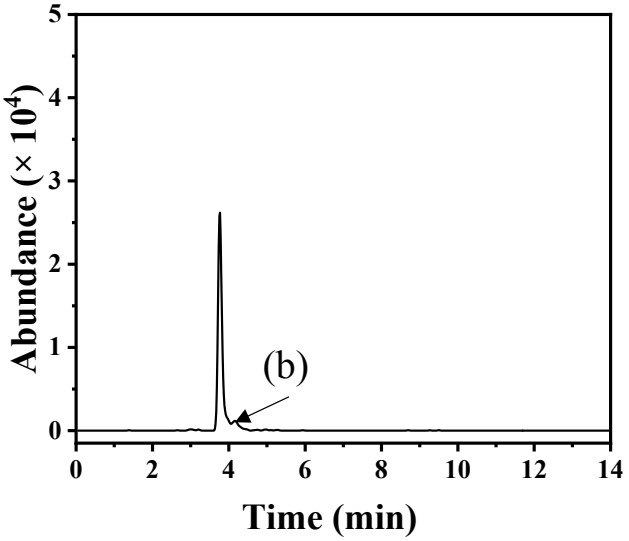
Chromatogram.



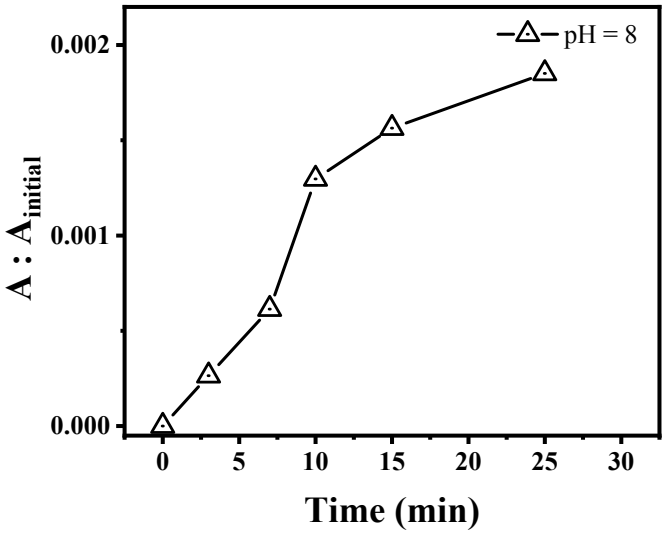
Reaction profile.



Chromatogram.

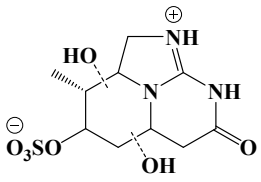


Reaction profile.



S4.11 Compound name: P_{321}, Formula: $C_{10}H_{15}N_3O_7S$, Theoretical m/z: 322.0703

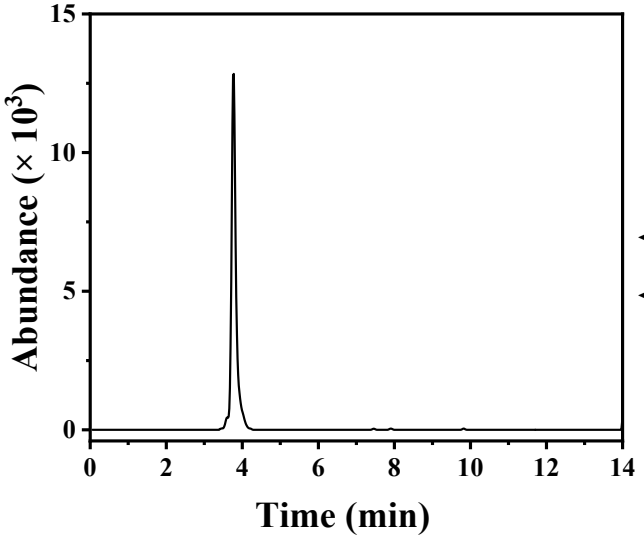
Structure:



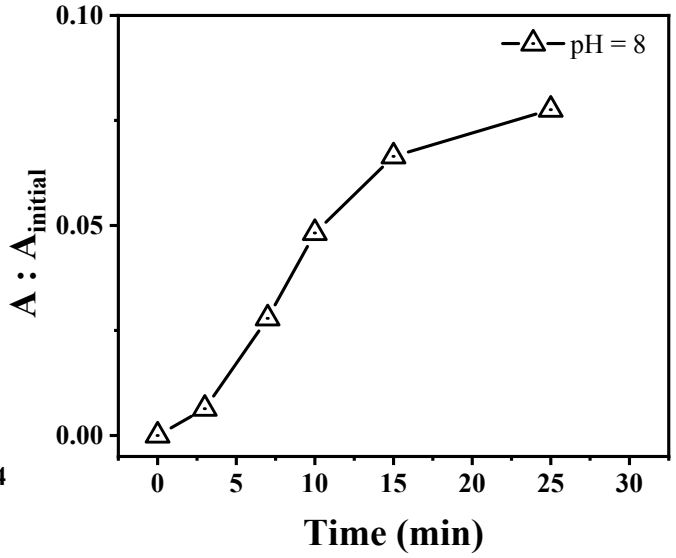
P_{321}

Confidence Level:
Level 3
Proposed Structure

Chromatogram

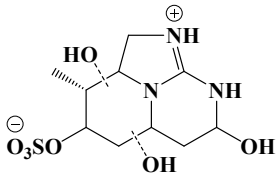


Reaction profile.



S4.12 Compound name: P_{323}, Formula: $C_{10}H_{17}N_3O_7S$, Theoretical m/z: 324.0860

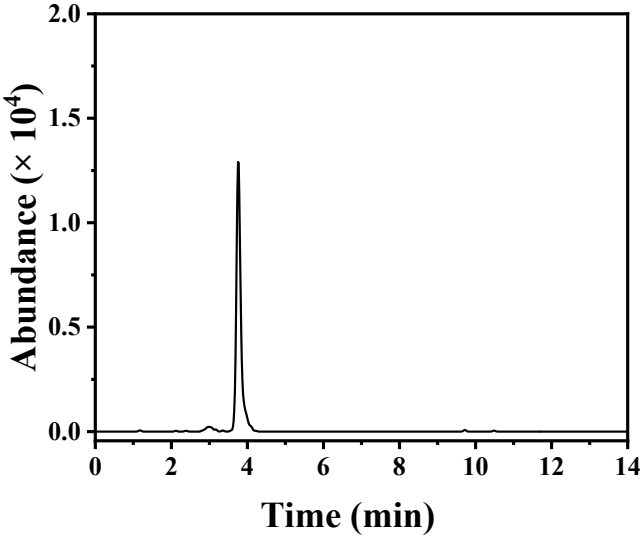
Structure:



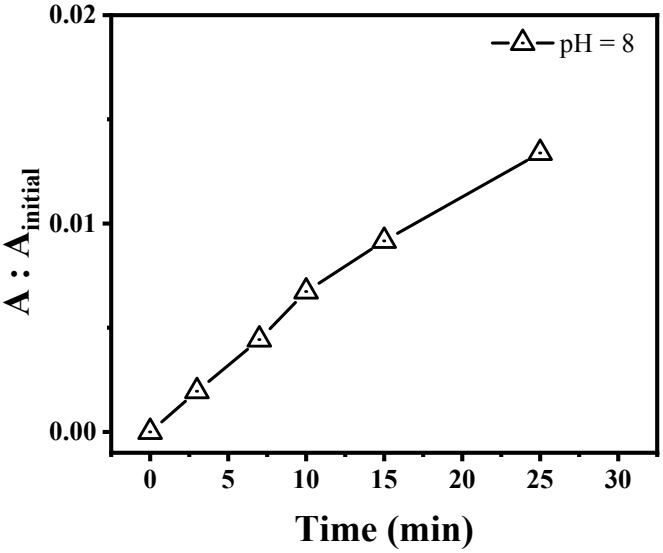
P_{323}

Confidence Level:
Level 3
Proposed Structure

Chromatogram.

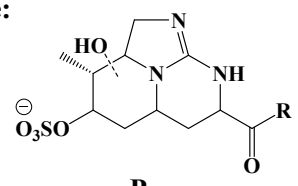


Reaction profile.



S4.13 Compound name: $P_{429a/b}$, Formula: $C_{15}H_{19}N_5O_8S$, Theoretical m/z: 430.1027

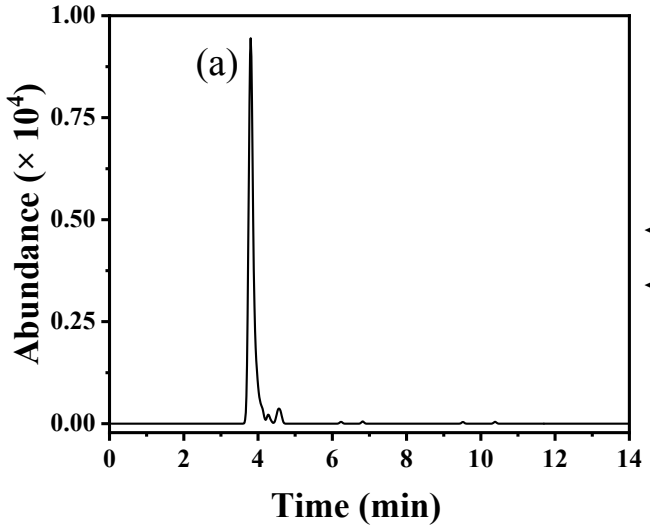
Structure:



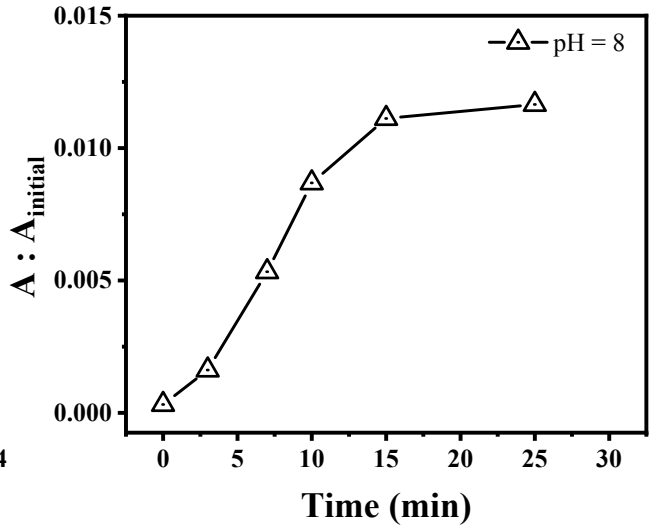
$P_{429a/b}$

Confidence Level:
Level 3
Proposed Structure

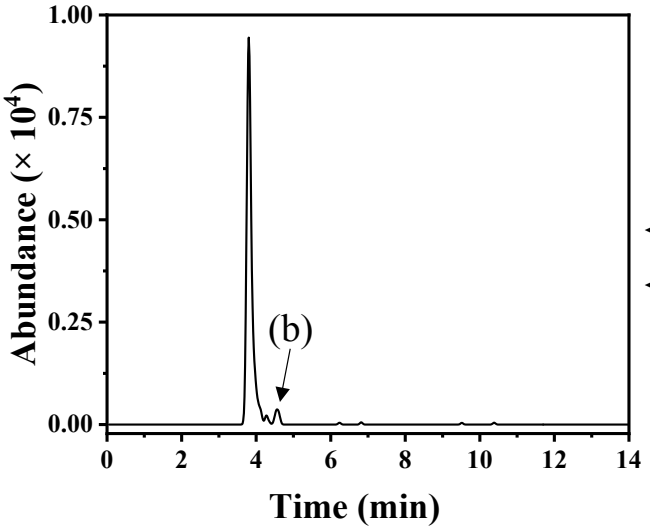
Chromatogram.



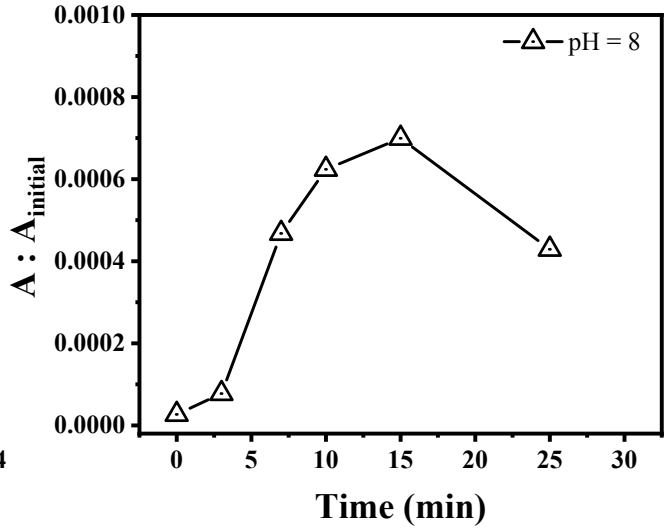
Reaction profile.



Chromatogram.

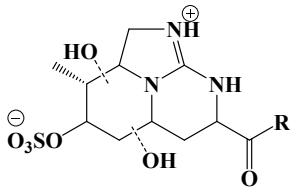


Reaction profile.



S4.14 Compound name: P_{445}, Formula: $C_{15}H_{19}N_5O_9S$, Theoretical m/z: 446.0976

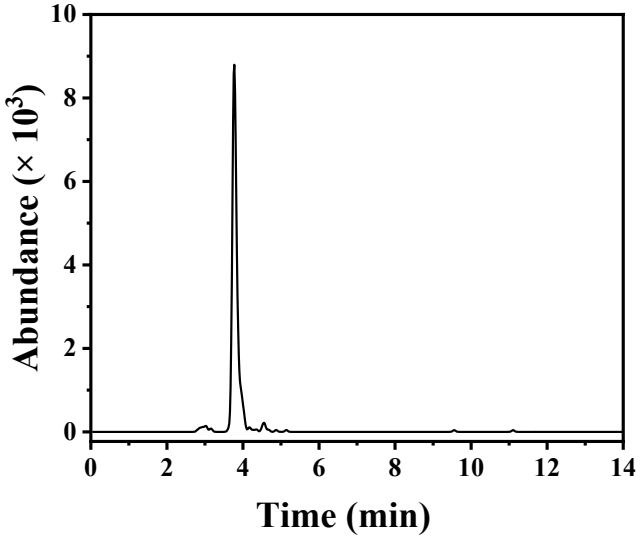
Structure:



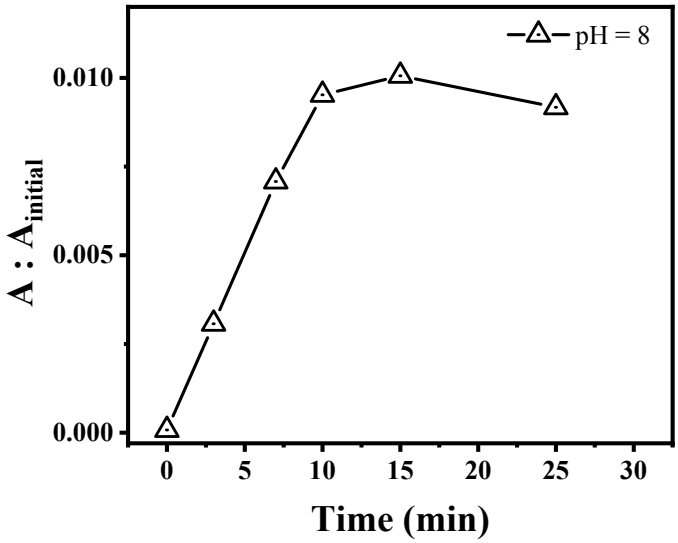
P_{445}

Confidence Level:
Level 3
Proposed Structure

Chromatogram.

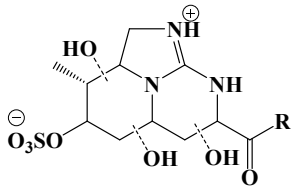


Reaction profile.



S4.15 Compound name: P_{461}, Formula: $C_{15}H_{19}N_5O_{10}S$, Theoretical m/z: 462.0931

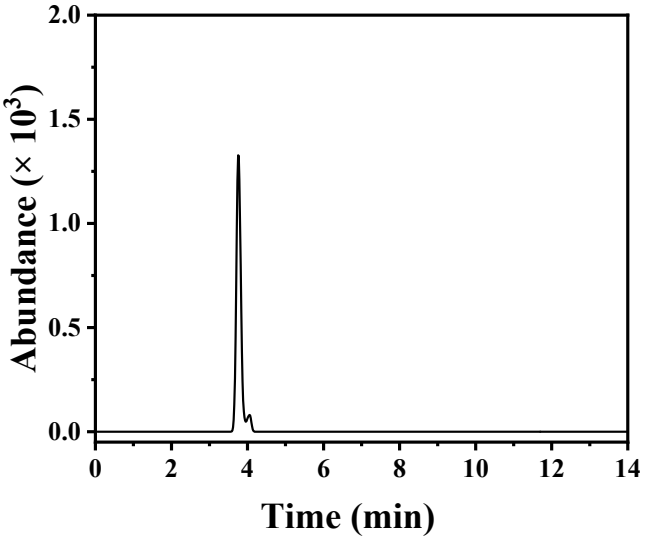
Structure:



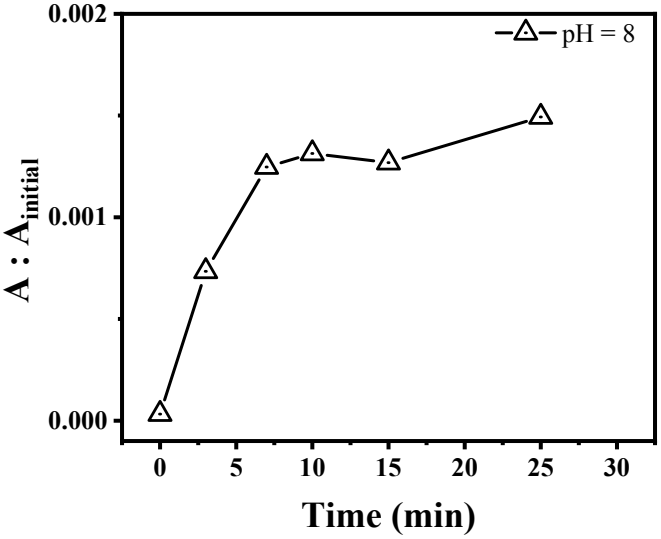
P_{461}

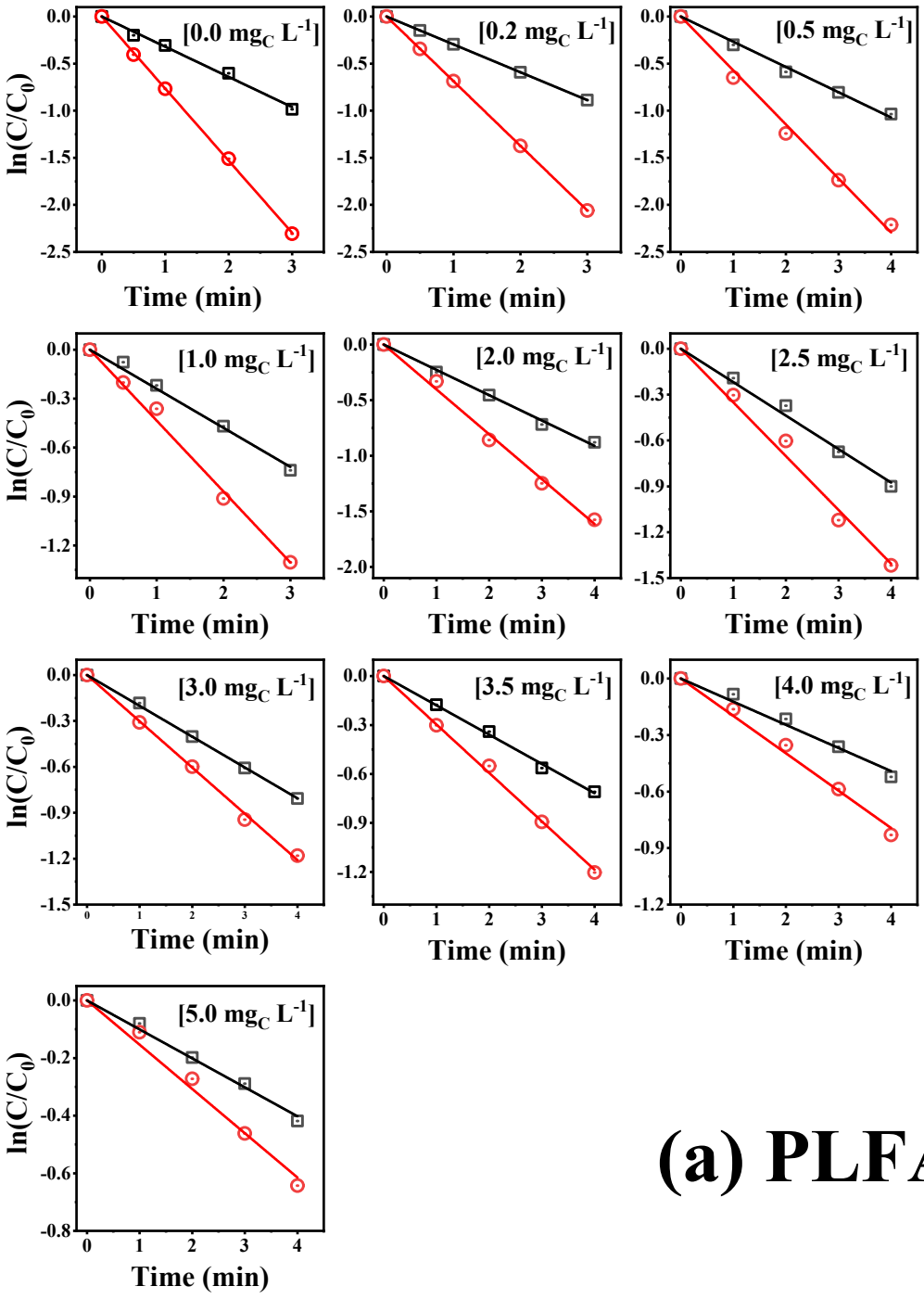
Confidence Level:
Level 3
Proposed Structure

Chromatogram.

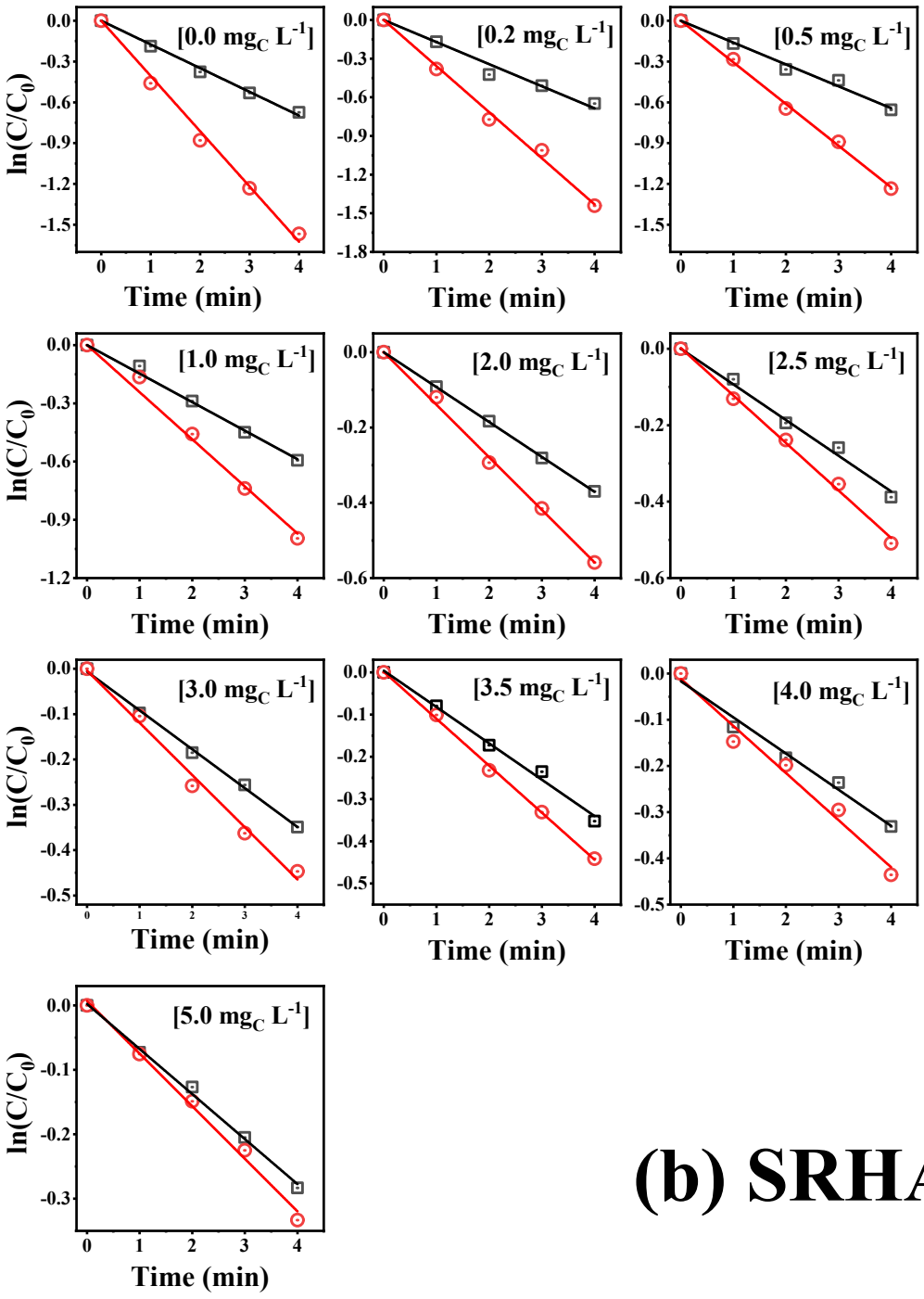


Reaction profile.

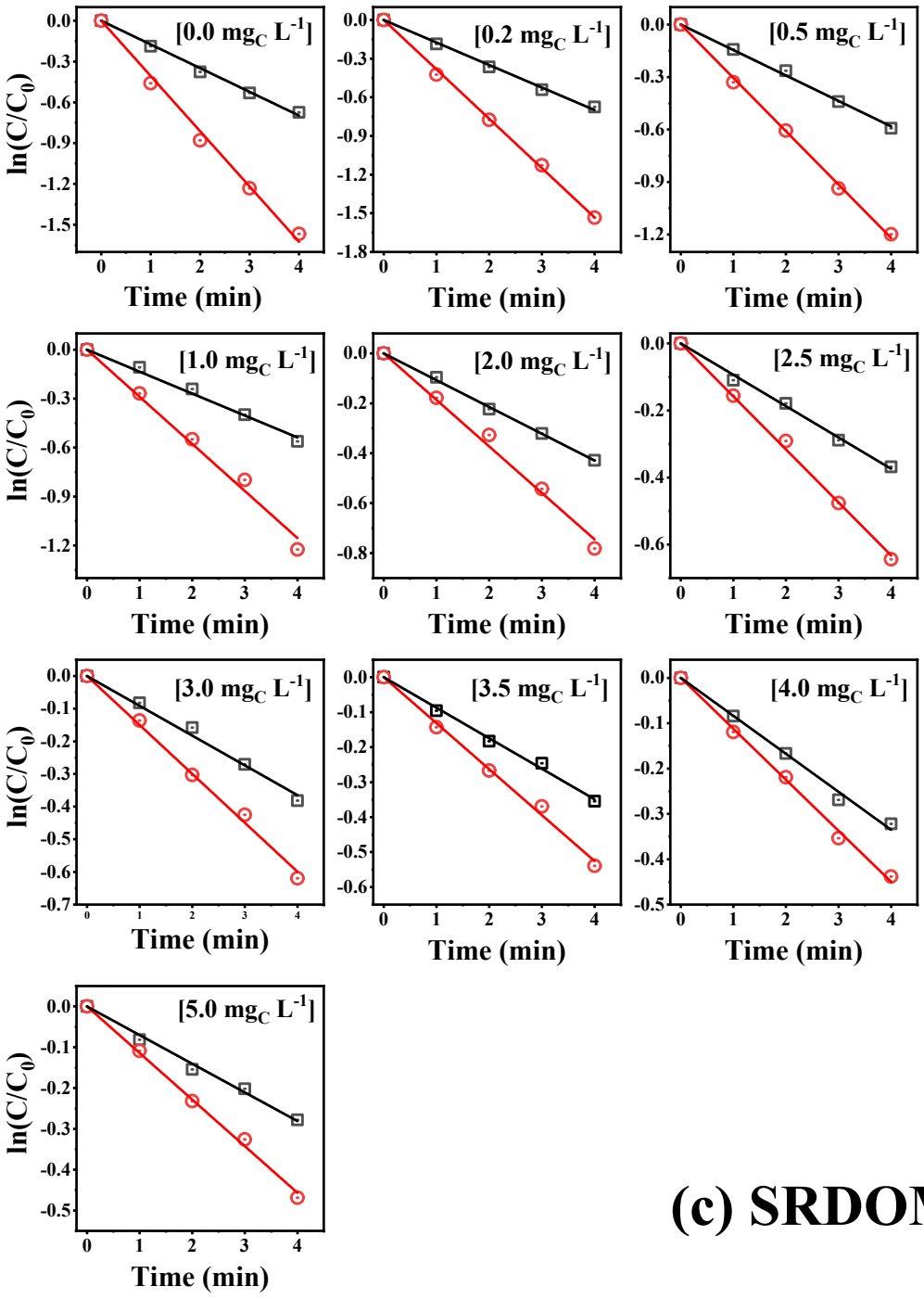



[0.0 mgC L-1]
[0.2 mgC L-1]
[0.5 mgC L-1]
[1.0 mgC L-1]
[2.0 mgC L-1]
[2.5 mgC L-1]
[3.0 mgC L-1]
[3.5 mgC L-1]
[4.0 mgC L-1]
[5.0 mgC L-1]
ln(C/C0)
Time (min)

(a) PLFA


[0.0 mg$_C$ L^{-1}]
[0.2 mg$_C$ L^{-1}]
[0.5 mg$_C$ L^{-1}]
[1.0 mg$_C$ L^{-1}]
[2.0 mg$_C$ L^{-1}]
[2.5 mg$_C$ L^{-1}]
[3.0 mg$_C$ L^{-1}]
[3.5 mg$_C$ L^{-1}]
[4.0 mg$_C$ L^{-1}]
[5.0 mg$_C$ L^{-1}]
ln(C/C$_0$)
Time (min)

(b) SRHA


[0.0 mg$_C$ L^{-1}]
[0.2 mg$_C$ L^{-1}]
[0.5 mg$_C$ L^{-1}]
[1.0 mg$_C$ L^{-1}]
[2.0 mg$_C$ L^{-1}]
[2.5 mg$_C$ L^{-1}]
[3.0 mg$_C$ L^{-1}]
[3.5 mg$_C$ L^{-1}]
[4.0 mg$_C$ L^{-1}]
[5.0 mg$_C$ L^{-1}]
ln(C/C$_0$)
Time (min)

(c) SRDOM

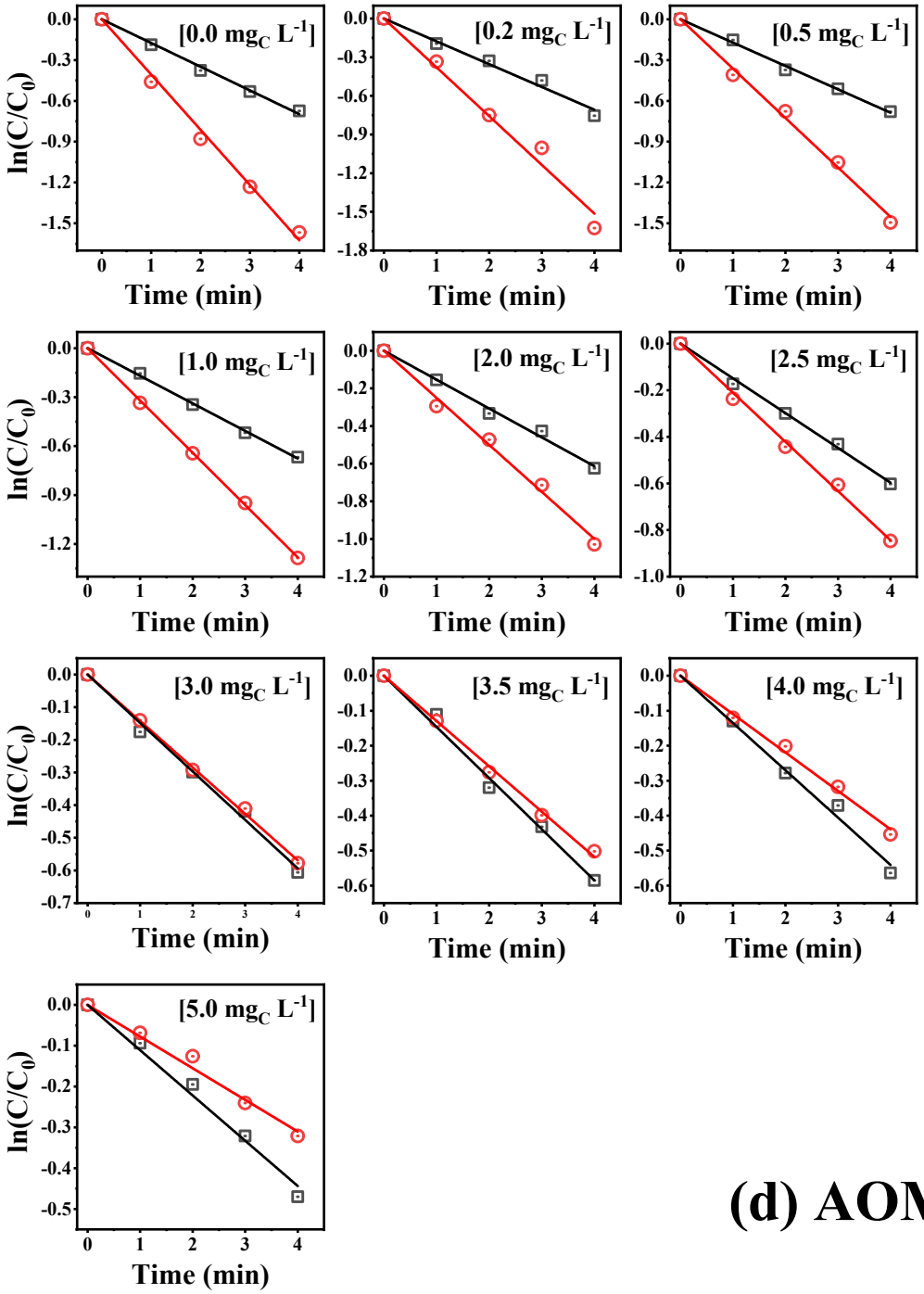
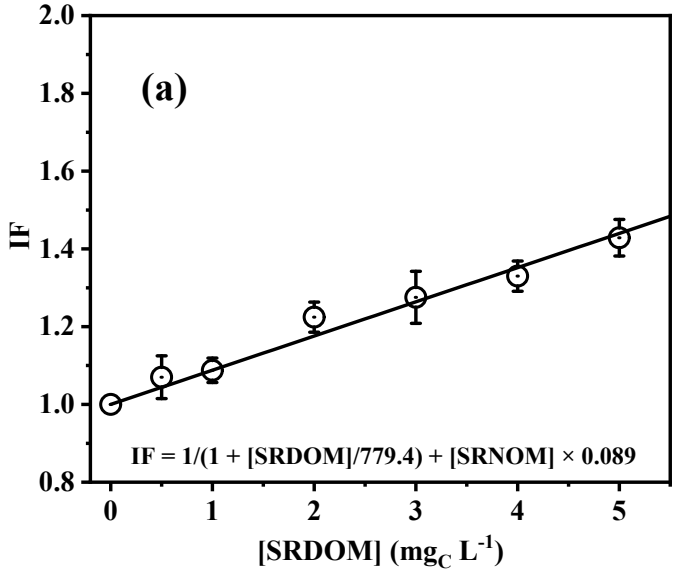
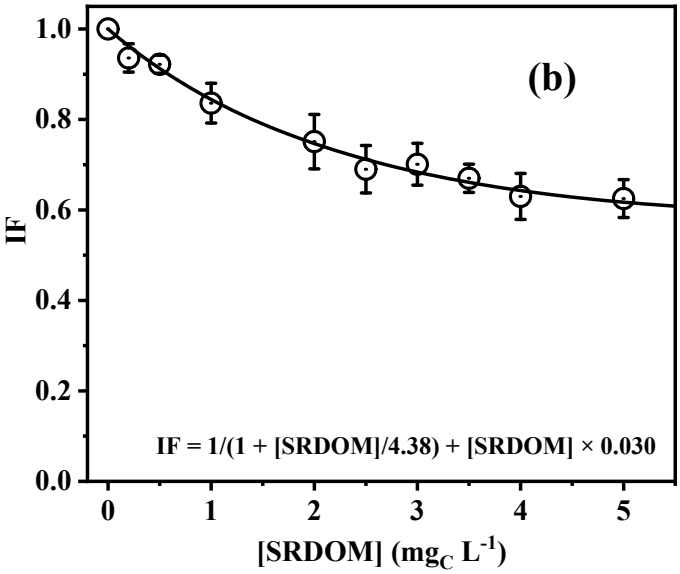


Figure S6. The degradation kinetics of CYN and IPU measured over time in various DOM concentrations ([DOM] = 0.0-5.0 mg_C L^{-1}, pH 8.0) under $CO_3^{\bullet-}$-mediated oxidation processes. (a) PLFA. (b) SRHA. (c) SRDOM (d) AOM.



157



158

159 **Figure S7. (a)**. Inhibition factors measured at various DOM concentrations in the range of 0.0-5.0 mg_C
160 L^{-1} for aqueous solutions (pH 8.0). IF values measured for SRDOM at $SO_4^{\bullet-}$-mediated oxidation processes.
161 **(b)**. Inhibition factors measured at various DOM concentrations in the range of 0.0-5.0 mg_C L^{-1} for aqueous
162 solutions (pH 9.0). IF values measured for SRDOM at $CO_3^{\bullet-}$-mediated oxidation processes.

163

164

Table S4. The concentrations of chemical components for simulated waters.

Components	Units
Cl^-	0.2 mM [a]
HCO_3^-	1 mM [a]
SO_4^{2-}	0.1 mM [a]
NO_3^-	0.02 mM [a]
pH	6 ~ 9 [a]

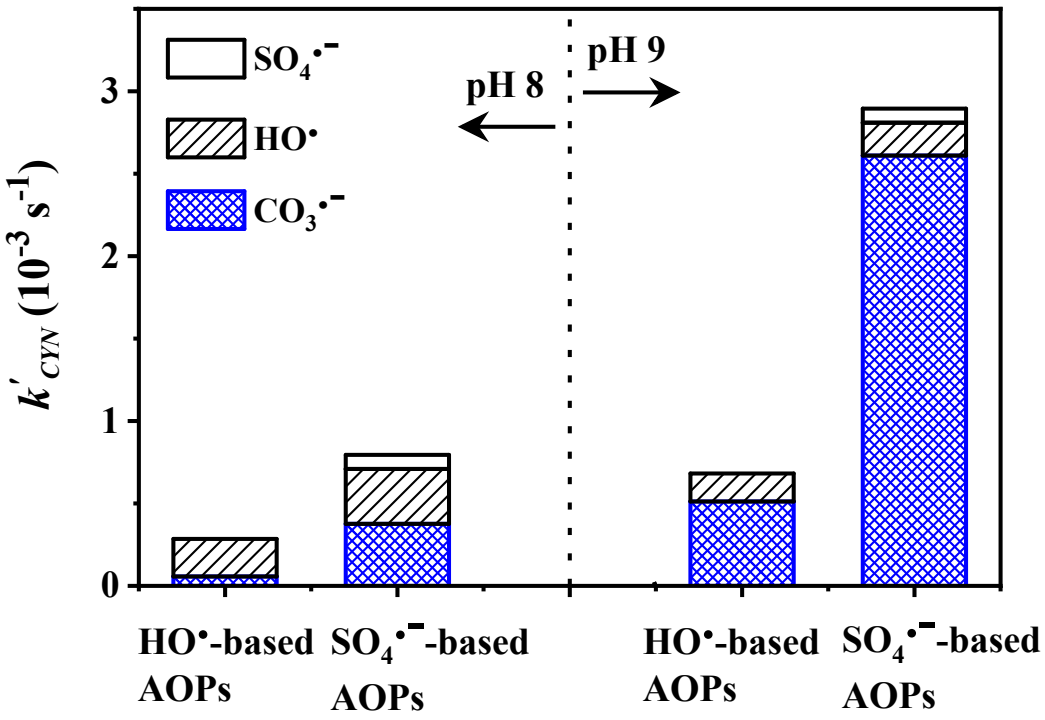
[a]Ref. [7].

Table S5. Principle reactions of the water matrix with $HO^{\bullet}$ or $SO_4^{\bullet-}$ in the UV/H_2O_2 or UV/$K_2S_2O_8$ AOPs in the kinetic model.

No.	Reaction	Second-order reaction constants	Reference
Photolysis of H_2O_2 or $K_2S_2O_8$			
1	$S_2O_8^{2-} \rightarrow 2SO_4^{\bullet-}$ $H_2O_2 \rightarrow 2HO^{\bullet-}$	formation rate = $2\phi I_0$ f_{parent} $(1\text{-}10^{-Al})$	8
$SO_4^{\bullet-}$ reactions			
2	$SO_4^{\bullet-}+OH^- \rightarrow SO_4^{2-}+OH^{\bullet}$	7.00×10^7 M^{-1} s^{-1}	1, 9
3	$SO_4^{\bullet-}+H_2O \rightarrow HSO_4^-+OH^{\bullet}$	6.60×10^2 s^{-1}	9
4	$SO_4^{\bullet-}+OH^{\bullet} \rightarrow HSO_5^-$	1.00×10^{10} M^{-1} s^{-1}	9
5	$SO_4^{\bullet-}+SO_5^{2-} \rightarrow SO_5^{\bullet-}+SO_4^{2-}$	1.00×10^8 M^{-1} s^{-1}	9
6	$SO_4^{\bullet-}+HSO_5^- \rightarrow SO_5^{\bullet-}+HSO_4^-$	1.00×10^6 M^{-1} s^{-1}	9
7	$SO_5^{\bullet-}+SO_5^{\bullet-} \rightarrow SO_4^{\bullet-}+SO_4^{\bullet-}+O_2$	2.10×10^8 M^{-1} s^{-1}	9
8	$SO_5^{\bullet-}+SO_5^{\bullet-} \rightarrow S_2O_8^{2-}+O_2$	2.20×10^8 M^{-1} s^{-1}	9
9	$SO_4^{\bullet-}+SO_4^{\bullet-} \rightarrow S_2O_8^{2-}$	7.00×10^8 M^{-1} s^{-1}	9
10	$SO_4^{\bullet-}+S_2O_8 \rightarrow S_2O_8^{\bullet-}+SO_4^{2-}$	6.50×10^5 M-1 s-1	9
11	$S_2O_8^{2-}+CO_3^{\bullet-} \rightarrow CO_3^{2-}+S_2O_8^{\bullet-}$	3.00×10^4 M^{-1} s^{-1}	9
12	$SO_4^{\bullet-}+HCO_3 \rightarrow CO_3^{\bullet-}+ HSO_4^-$	2.60×10^6 M^{-1} s^{-1}	9
13	$SO_4^{\bullet-}+CO_3^{2-} \rightarrow CO_3^{\bullet-}+SO_4^{2-}$	6.10×10^6 M^{-1} s^{-1}	9
14	$SO_4^{\bullet-}+NO_3^- \rightarrow NO_3^{\bullet-}+SO_4^{2-}$	2.10×10^6 M^{-1} s^{-1}	9
15	$SO_4^{\bullet-}$+DOM→product	6.70×10^3 L mg_C^{-1} s^{-1}	determined in our study
OH• reactions			
16	$OH^{\bullet}+H_2O_2 \rightarrow HO_2^{\bullet}+H_2O$	2.70×10^7 M^{-1} s^{-1}	9
17	$OH^{\bullet}+OH^{\bullet} \rightarrow H_2O_2$	5.50×10^9 M^{-1} s^{-1}	9
18	$OH^{\bullet}+O_2^{\bullet-} \rightarrow O_2+OH^-$	7.00×10^9 M^{-1} s^{-1}	9
19	$H_2O_2+O_2^{\bullet-} \rightarrow O_2+OH^{2-}+OH^{\bullet-}$	0.13 s^{-1}	9
20	$OH^{\bullet}+S_2O_8^{2-} \rightarrow S_2O_8^{\bullet-}+OH^-$	$< 1.00 \times 10^6$ M^{-1} s^{-1}	9
21	$OH^{\bullet}$+DOM→product	1.60×10^4 L mg_C^{-1} s^{-1}	determined in our study
22	$OH^{\bullet}+CO_3^{2-} \rightarrow CO_3^{\bullet-}+OH^-$	3.90×10^8 M^{-1} s^{-1}	9
23	$OH^{\bullet}+HCO_3^- \rightarrow CO_3^{\bullet-}+H_2O$	8.60×10^6 M^{-1} s^{-1}	9

24	$H_2O_2+CO_3^{\bullet-}\rightarrow HCO_3^-+HO_2^{\bullet}$	4.30×10^5 M^{-1} s^{-1}	9
25	$OH^{\bullet}+CO_3^{\bullet-}\rightarrow$product	3.00×10^9 M^{-1} s^{-1}	9
26	$O_2^{\bullet-}+CO_3^{\bullet-}\rightarrow CO_3^{2-}+O_2$	6.00×10^8 M^{-1} s^{-1}	9
27	$CO_3^{\bullet-}+CO_3^{\bullet-}\rightarrow$product	3.00×10^7 M^{-1} s^{-1}	9
28	$CO_3^{\bullet-}$+DOM→product	1.04×10^2 L mg_C^{-1} s^{-1}	10
29	$HO^{\bullet}+H_2CO_3\rightarrow CO_3^{\bullet-}+H_2O+H^+$	1.00×10^6 M^{-1} s^{-1}	9
Chloride reactions			
30	$OH^{\bullet}+Cl^-\rightarrow ClOH^{\bullet-}$	4.30×10^9 M^{-1} s^{-1}	9
31	$ClOH^{\bullet-}\rightarrow OH^{\bullet}+Cl^-$	6.10×10^9 M^{-1} s^{-1}	9
32	$SO_4^{\bullet-}+Cl^-\rightarrow SO_4+Cl^{\bullet}$	3.00×10^8 M^{-1} s^{-1}	9
33	$SO_4^{2-}+Cl^{\bullet-}\rightarrow SO_4^{\bullet-}+Cl^-$	2.50×10^8 M^{-1} s^{-1}	9
34	$ClOH^{\bullet-}+H^+\rightarrow Cl^{\bullet-}+H_2O$	2.10×10^{10} M^{-1} s^{-1}	9
35	$ClOH^{\bullet-}+Cl^-\rightarrow Cl_2^{\bullet-}+OH^-$	1.00×10^4 M^{-1} s^{-1}	9
36	$Cl^{\bullet-}+H_2O\rightarrow ClOH^{\bullet-}+H^+$	2.50×10^5 M^{-1} s^{-1}	9
37	$Cl^{\bullet}+OH^-\rightarrow ClOH^{\bullet-}$	1.80×10^{10} M^{-1} s^{-1}	9
38	$Cl^{\bullet}+H_2O_2\rightarrow HO_2^{\bullet}+H^++Cl^-$	2.00×10^9 M^{-1} s^{-1}	9
39	$Cl^{\bullet}+Cl^-\rightarrow Cl_2^{\bullet-}$	8.50×10^9 M^{-1} s^{-1}	9
40	$Cl^{\bullet}+Cl^{\bullet}\rightarrow Cl_2$	8.80×10^7 M^{-1} s^{-1}	9
41	$Cl^{\bullet-}+HOCl\rightarrow ClO^{\bullet}+H^++Cl^-$	3.00×10^9 M^{-1} s^{-1}	9
42	$Cl^{\bullet-}+OCl^-\rightarrow ClO^{\bullet}+Cl^-$	8.30×10^9 M^{-1} s^{-1}	9
43	$Cl_2^{\bullet-}\rightarrow Cl^{\bullet-}+Cl^-$	6.00×10^4 M^{-1} s^{-1}	9
44	$Cl_2^{\bullet-}+HO^{\bullet}\rightarrow HOCl+Cl^-$	1.00×10^9 M^{-1} s^{-1}	9
45	$Cl_2^{\bullet-}+Cl_2^{\bullet-}\rightarrow Cl_2+2Cl^-$	9.00×10^8 M^{-1} s^{-1}	9
46	$Cl_2^{\bullet-}+Cl^{\bullet-}\rightarrow Cl_2+Cl^-$	2.10×10^9 M^{-1} s^{-1}	9
47	$Cl_2^{\bullet-}+H_2O_2\rightarrow HO_2^{\bullet-}+2Cl+H$	1.40×10^5 M^{-1} s^{-1}	9
48	$Cl_2^{\bullet-}+O2^{\bullet-}\rightarrow O_2+2Cl^-$	2.00×10^9 M^{-1} s^{-1}	9
49	$Cl_2^{\bullet-}+H_2O\rightarrow Cl^-+HClOH$	1.30×10^3 M^{-1} s^{-1}	9
50	$Cl_2^{\bullet-}+HO^-\rightarrow ClOH^{\bullet-}+Cl^-$	4.50×10^7 M^{-1} s^{-1}	9
51	$HClOH\rightarrow ClOH^{\bullet-}+H^+$	1.00×10^8 M^{-1} s^{-1}	9
52	$HClOH\rightarrow Cl^{\bullet-}+H_2O$	1.00×10^2 M^{-1} s^{-1}	9
53	$HClOH+Cl^-\rightarrow Cl_2^{\bullet-}+H_2O$	5.00×10^9 M^{-1} s^{-1}	9
54	$Cl^-+Cl_2\rightarrow Cl_3^-$	2.00×10^4 M^{-1} s^{-1}	9
55	$Cl_3^-\rightarrow Cl_2+Cl^-$	1.10×10^5 M^{-1} s^{-1}	9

56	$Cl_3+O_2^{\bullet-}\rightarrow Cl_2^{\bullet-}+Cl^-+O_2$	$3.80\times10^9\ M^{-1}\ s^{-1}$	9
57	$Cl_2+H_2O\rightarrow Cl^-+HOCl+H^+$	$15\ M^{-1}\ s^{-1}$	9
58	$Cl_2+H_2O_2\rightarrow O_2+HCl$	$1.30\times10^4\ M^{-1}\ s^{-1}$	9
59	$Cl_2+O_2^{\bullet-}\rightarrow O_2+Cl_2^{\bullet-}$	$1.00\times10^9\ M^{-1}\ s^{-1}$	9
60	$OCl^-+H_2O_2\rightarrow O_2+Cl^-+H_2O$	$1.70\times10^5\ M^{-1}\ s^{-1}$	9
61	$OCl^-+HO^{\bullet}\rightarrow ClO^{\bullet}+OH^-$	$8.80\times10^9\ M^{-1}\ s^{-1}$	9
62	$OCl^-+O_2^{\bullet-}+H_2O\rightarrow Cl^{\bullet-}+2HO^-+O_2$	$2.00\times10^8\ M^{-1}\ s^{-1}$	9
63	$OCl^-+CO_3^{\bullet-}\rightarrow CO_3^{2-}+ClO^{\bullet}$	$5.70\times10^5\ M^{-1}\ s^{-1}$	9
64	$Cl^{\bullet}+CO_3^{2-}\rightarrow CO_3^{\bullet-}+Cl^-$	$5.00\times10^8\ M^{-1}\ s^{-1}$	9
65	$Cl^{\bullet-}+HCO_3^-\rightarrow CO_3^{\bullet-}+Cl^-+H^+$	$2.20\times10^8\ M^{-1}\ s^{-1}$	9
66	$Cl_2^{\bullet-}+HCO_3^-\rightarrow CO_3^{\bullet-}+2Cl^-+H^+$	$8.00\times10^7\ M^{-1}\ s^{-1}$	9
67	$Cl_2^{\bullet-}+CO_3^{2-}\rightarrow CO_3^{\bullet-}+2Cl^-$	$1.60\times10^8\ M^{-1}\ s^{-1}$	9
68	$Cl^{\bullet-}$+DOM→product	$1.30\times10^4\ L\ mg_C^{-1}\ s^{-1}$	9
Other reactions			
69	$NO_3^{\bullet-}+NO_3^{\bullet-}\rightarrow N_2O_6$	$7.9\times10^5\ M^{-1}\ s^{-1}$	9
70	$NO_3^{\bullet-}+Cl^{\bullet-}\rightarrow NO_3^-+Cl^{\bullet}$	$7.1\times10^7\ M^{-1}\ s^{-1}$	9
71	$SO_4^{\bullet-}+HPO_4^{2-}\rightarrow HPO_4^{\bullet-}+SO_4^{2-}$	$1.20\times10^6\ M^{-1}\ s^{-1}$	9
72	$SO_4^{\bullet-}+H_2PO_4^-\rightarrow HPO_4^{\bullet-}+HSO_4^-$	$5.0\times10^4\ M^{-1}\ s^{-1}$	9
73	$HO^{\bullet-}+HPO_4^{2-}\rightarrow HPO_4^{\bullet-}+OH^-$	$1.50\times10^5\ M^{-1}\ s^{-1}$	9
74	$HO^{\bullet-}+H_2PO_4^-\rightarrow HPO_4^{\bullet-}+H_2O$	$2.0\times10^4\ M^{-1}\ s^{-1}$	9



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172 **Figure S8**. Photodegradation of CYN in AOPs at pH 8 (left) and pH 9 (right). The black bars stand for
173 the calculated contributions for $HO^{\bullet-}$ or $SO_4^{\bullet-}$ in two synthetic matrices. (1 mg_C L^{-1} SRDOM, 1 mM DIC,
174 2 mM phosphate buffer). The blue bars stand for the calculated $CO_3^{\bullet-}$ contributions.

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Literature Cited

1. Fang, J.; Yang, X.; Ma, J.; Shang, C.; Zhao, Q., Characterization of algal organic matter and formation of DBPs from chlor(am)ination. *Water Res.* **2010,** *44*, (20), 5897-5906.
2. Zhou, S.; Shao, Y.; Gao, N.; Deng, Y.; Li, L.; Deng, J.; Tan, C., Characterization of algal organic matters of Microcystis aeruginosa: biodegradability, DBP formation and membrane fouling potential. *Water Res.* **2014,** *52*, 199-207.
3. Yang, X.; Guo, W.; Shen, Q., Formation of disinfection byproducts from chlor(am)ination of algal organic matter. *J. Hazard. Mater.* **2011,** *197*, 378-88.
4. Liu, C.; Ersan, M. S.; Plewa, M. J.; Amy, G.; Karanfil, T., Formation of regulated and unregulated disinfection byproducts during chlorination of algal organic matter extracted from freshwater and marine algae. *Water Res.* **2018,** *142*, 313-324.
5. Lamb, A. B.; Damon, E. B., The Dissociation Constants of Diaquotetrammine Cobaltic Cation as an Acid. *J. Am. Chem. Soc.* **1937,** *59*, (2), 383-390.
6. Cope, V. W.; Chen, S. N.; Hoffman, M. Z., Intermediates in the photochemistry of of carbonato-amine complexes of cobalt(III). Carbonate(-) radicals and the aquocarbonato complex. *J. Am. Chem. Soc.* **1973,** *95*, (10), 3116-3121.
7. Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M., *Environmental organic chemistry*. John Wiley & Sons: 2016.
8. Zepp, R. G., Quantum yields for reaction of pollutants in dilute aqueous solution. *Environ. Sci. Technol.* **1978,** *12*, (3), 327-329.
9. Lian, L.; Yao, B.; Hou, S.; Fang, J.; Yan, S.; Song, W., Kinetic study of hydroxyl and sulfate radical-mediated oxidation of pharmaceuticals in wastewater effluents. *Environ. Sci. Technol.* **2017,** *51*, (5), 2954-2962.
10. Yan, S.; Liu, Y.; Lian, L.; Li, R.; Ma, J.; Zhou, H.; Song, W., Photochemical formation of carbonate radical and its reaction with dissolved organic matters. *Water Res.* **2019**, 161, 288-296.