Electronic Supplementary Material (ESI) for Analytical Methods.

Supporting Information

Polyurea-Magnetic Hierarchical Porous Composites for Profiling of Anionic Metabolites

Contents

1. Experiment Section 1

Materials 1

Preparation of Polyurea-Magnetic Hierarchical Porous Composites (PMCs) 1

Characterization 1

Adsorption Experiments 2

Desorption Experiments 3

MS Analysis 3

Sample Preparation 3

Method Validation 4

Adsorption of anionic metabolites with PMC-HMDA 4

2. Supporting Figures and Tables 6

References 56

1. Experiment Section

Materials

LC-MS grade acetonitrile, formic acid, ammonium hydroxide solution (25.0% NH_3 basis), and water were purchased from Thermo Fisher Scientific (Waltham, MA, USA). 1,3-Diaminopropane, 1,4-Diaminobutane, 1,6-Hexamethylenedia-mine, m-Phenylenediamine, and N, N-Dimethylformamide were purchased from Aladdin Reagent Co. (Shanghai, China). N, N'-Carbonyldiimidazole was obtained from Macklin (Shanghai, China). The standards were purchased from Sigma-Aldrich (St. Louis, MO, USA) and Aladdin Reagent Co. (Shanghai, China). All agents were used without further purification.

Preparation of Polyurea-Magnetic Hierarchical Porous Composites (PMCs)

The magnetic particles (MPs) of Fe_3O_4 were prepared by hydrothermal method with minor modification. $FeCl_3 \cdot 6H_2O$ (0.729 g) was dissolved in 40 mL of ethylene glycol under magnetic stirring for 30 min. Then, sodium acetate trihydrate (1.920 g) were added into above solution under magnetic stirring for 60 min. The brown solution was transferred into an autoclave and heated to 200°C for 16 h. The product was magnetically separated and washed several times with ethanol and water. Fe_3O_4 were coated by SiO_2 through the Stöber sol–gel method. Amino-magnetic particles (MPs-NH_2) were prepared according to our previous study.[1]

Diamine (0.124 mmol) and N, N'-Carbonyldiimidazole (CDI, 0.248 mmol) were dissolved in 1 mL of N, N-Dimethylformamide (DMF) under shaking 1 h, MPs-NH_2 (10 mg, was dispersed in 1 mL of DMF) and diamine (0.124 mmol) were successively dispersed in the above mixture. After shaking for 3 h, the product was washed with DMF and water, finally dispersed in water under shaking more than 3 h.[1] The obtained MPs-Diamine was dispersed in 5 mL of 50% acetonitrile (ACN) for use.

Characterization

The morphology and structure were characterized by Scanning electron microscopy (SEM, Hitachi-SU8010, Japan). The Fourier transform infrared spectra (FTIR) was recorded on a Magna-550 (Nicolet, USA) spectrometer. Spectra were scanned over the range of 400–4000 cm^{-1}. The X-ray diffraction (XRD) was performed on a Rigaku SmartLab (Japan). Thermogravimetric analysis (TGA, TG/DTA7300, Hitachi, Japan) was carried out in nitrogen with a heating rate of 20°C min^{-1}. The zeta potential data were recorded via DLS (Zetasizer Nano ZS90, UK). Biological samples were analyzed by a Fourier transform ion cyclotron resonance mass spectrometer

(FTICR MS, 7.0 T, Solarix XR, Bruker Daltonics, Billerica, USA). It was a high-precision mass spectrum equipped with electrospray ionization (ESI), the error was less than 1ppm, and the resolution was 160 000 at m/z 400.

Adsorption Experiments

To optimize the adsorption and desorption for various anionic metabolites in a biological sample, seven standards from different kinds of anionic metabolites were mixed to generate a standard mixture, including adenosine monophosphate (AMP), 3',5'-cyclic monophosphate (cAMP), 2'-deoxy-5'-adenosine monophosphate (dAMP), flavin adenine dinucleotide (FAD), nicotinamide adenine dinucleotide phosphate (NADP), malic acid (MA), and citric acid (CA), which was used to adsorb and desorb under different conditions. The desorbed samples were analyzed by MS, and the peak area of each MS/MS base peak of standard was used to evaluate the efficiencies of different conditions. We optimized the adsorption conditions including formic acid (FA) proportion, organic phase proportion for ACN, and temperature, as well as the desorption conditions including ammonium hydroxide proportion.

All the experiments were performed under optimized adsorption conditions. Briefly, 0.5 mg PMCs were incubated with 1.2 mL of AMP mixed 95% ACN aqueous solution at different concentrations (100 μM, 130 μM, 200 μM) under shaking 3 h. In the adsorbing stage, the samples were magnetically separated and 50 μL of supernatant was sampled at specified intervals up to 3 h. The supernatant was diluted with 50% ACN aqueous solution (2‰ NH_4OH, (v/v)) and final AMP concentration were detected by MS and calculated by peak areas.

The amount of adsorption at equilibrium, q_e (μmol g^{-1}), was calculated as

$$q_e = \frac{(C_0 - C_e)V}{M}$$

where c_0 and c_e (μmol L^{-1}) are the initial and equilibrium AMP concentrations in samples, respectively; V (L) is the volume of samples; and M (g) is the mass of the adsorbent used.[2]

The thermodynamic parameters are calculated mainly according to the following formulae:

$$\Delta G^0 = -RT\ln K$$

$$K = \frac{q_e}{c_e}$$

$$\ln K = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$

where R and K are the universal gas constant and thermodynamic equilibrium constant; T is the temperature of adsorption.[2]

The formula used to fit the pseudo-second-order kinetics model has been reported in the study:

$$\frac{t}{q_t} = \frac{1}{k \cdot q_e^2} + \frac{1}{q_e} \cdot t$$

where q_t is the amount of adsorption at time t, and k is the pseudo-second-order rate constant.[2]

Desorption Experiments

After the equilibrium of the adsorbent site, the sediment was desorbed by 1.2 mL of 50% ACN aqueous solution (2‰ NH_4OH, (v/v)) under optimized desorption conditions. Similarly, 50 μL of supernatant was diluted with 50% ACN aqueous solution, the AMP concentrations in them were analyzed by MS and calculated by peak areas.

The standard (AMP, 1 μmol·L^{-1}) and 0.5 mg of PMC-HMDA were added to the 95% acetonitrile aqueous (containing 0.5% formic acid, v/v) followed by shaking at 303 K with 5 min. After wash and separation, PMC-HMDA were re-dispersed in 500 μL of 50% acetonitrile aqueous solution (containing 2‰ NH_4OH, v/v). The supernatant was collected by magnetic separation and centrifuged at 15000 g for 20 min at 4 °C for MS detection. We Repeated the above steps five times to complete the recovery experiment.

MS Analysis

Optimization of enrichment and separation methods were carried out using HPLC/ESI-MS/MS system consisting of an Agilent 1200 series capillary system (Agilent, Santa Clara, USA) and LTQ XLTM linear Ion Trap MS (Thermo Fisher Scientific, Waltham, MA, USA). Further qualitative identification was performed on an amide column (2.1 × 100 mm, 3.5 μm, BEH Amide). The column temperature was maintained at 25°C. Mobile phase A and B were 2‰ NH_4OH aqueous solution and NH_4OH/ACN solution (2‰). And the gradient was set as follows: 0 min, 95% B; 2 min, 90% B; 5 min, 80% B; 8 min, 80% B; 10 min, 75% B; 11 min, 60% B; 12 min, 60% B; 13 min, 95% B; 15 min, 95% B. The flow rate was 0.3 mL min^{-1}.

The mass spectrometry detection was performed in the negative ESI mode. And

parameters were set as: spray voltage at 4 kV, sheath gas flow rate at 40 arb, capillary temperature at 300°C. The full MS scan was recorded over the m/z range of 100-1000 m/z.

Sample Preparation

A total of 50 μL of the mixed serum was diluted with 450 μL cold methanol (containing 50 μL aqueous) to remove the proteins by centrifugation at 15000 g for 5 min at 4°C. The extraction was repeated three times and the supernatant was lyophilized under a CV300 vacuum centrifugal concentrator.

About 30 mg rat liver was placed in a 1.5 mL centrifuge tube and 100 μL aqueous was added. Homogenization was performed using a handheld homogenizer (TissueMasterTM) for 2 min. Then, protein precipitation was performed by adding 400 μL methanol. The following steps are the same as above.

The 293T and HUVEC cell (1×10^6 cells per sample) were washed three times with phosphate buffered saline and harvested in an 80% aqueous methanol solution. The following steps are described above.

Method Validation

A mixed stock solution of nine standards was prepared in 95% acetonitrile aqueous (containing 0.5% formic acid, v/v, the concentrations of each standard were 10 μM), including AMP, inosine monophosphate (IMP), guanosine monophosphate (GMP), cAMP, ribose 5-phosphate (R5P), NADP, cytidine diphosphate (CDP), MA, and CA. The mixed standard solution was subjected to a gradient dilution. In the section of method validation, the blank matrix was 95% acetonitrile aqueous (containing 0.5% formic acid, v/v) without standards. And the direct infusion ESI-FTICR MS was used to demonstrate the reliability of the method. The mixed standard solution was subjected to a gradient dilution. Methodological data acquisition was performed by direct injection mass spectrometry (DIMS), the injection volume was 1 μL, and the flow rate was 8 μL min^{-1}. The peak area of each MS/MS base peak of standard was ordinate values, and the concentration was abscissa values. The calibration curve was plotted, and the equation of calibration curve and coefficient of determination (R^2) were obtained. The concentration at a signal-to-noise ratio of 3 was the limit of detection (LOD) of the method. Standard solutions were profiled at three times of the day and on three consecutive days to obtain precision. Three concentrations of mixed standard solutions of high (1.2 μM), middle (1.0 μM), and low (0.8 μM) were prepared (AMP, IMP, GMP, cAMP, R5P, NADP, CDP, MA, and CA). The

concentration of the compound was obtained by calibration curve, and the ratio of the calculated concentration to the actual concentration was the recovery.

Adsorption of anionic metabolites with PMC-HMDA

The PMC-HMDA 0.5 mg were dispersed in 200 μL of 95% acetonitrile aqueous (containing 0.5% formic acid, v/v) and transferred to the pretreated biological samples, and then shaken for 5 min at 303 K. After adsorption, the PMC-HMDA trapped anionic metabolites were collected and isolated from the mixture using a magnet and respectively washed twice each with 80% and 50% acetonitrile aqueous solutions. After that, the PMC-HMDA were eluted with 500 μL of 50% acetonitrile aqueous solution (containing 2‰ NH_4OH, v/v). The supernatant was collected by magnetic separation and centrifuged at 15000 g for 20 min at 4 °C for MS detection.

2. Supporting Figures and Tables

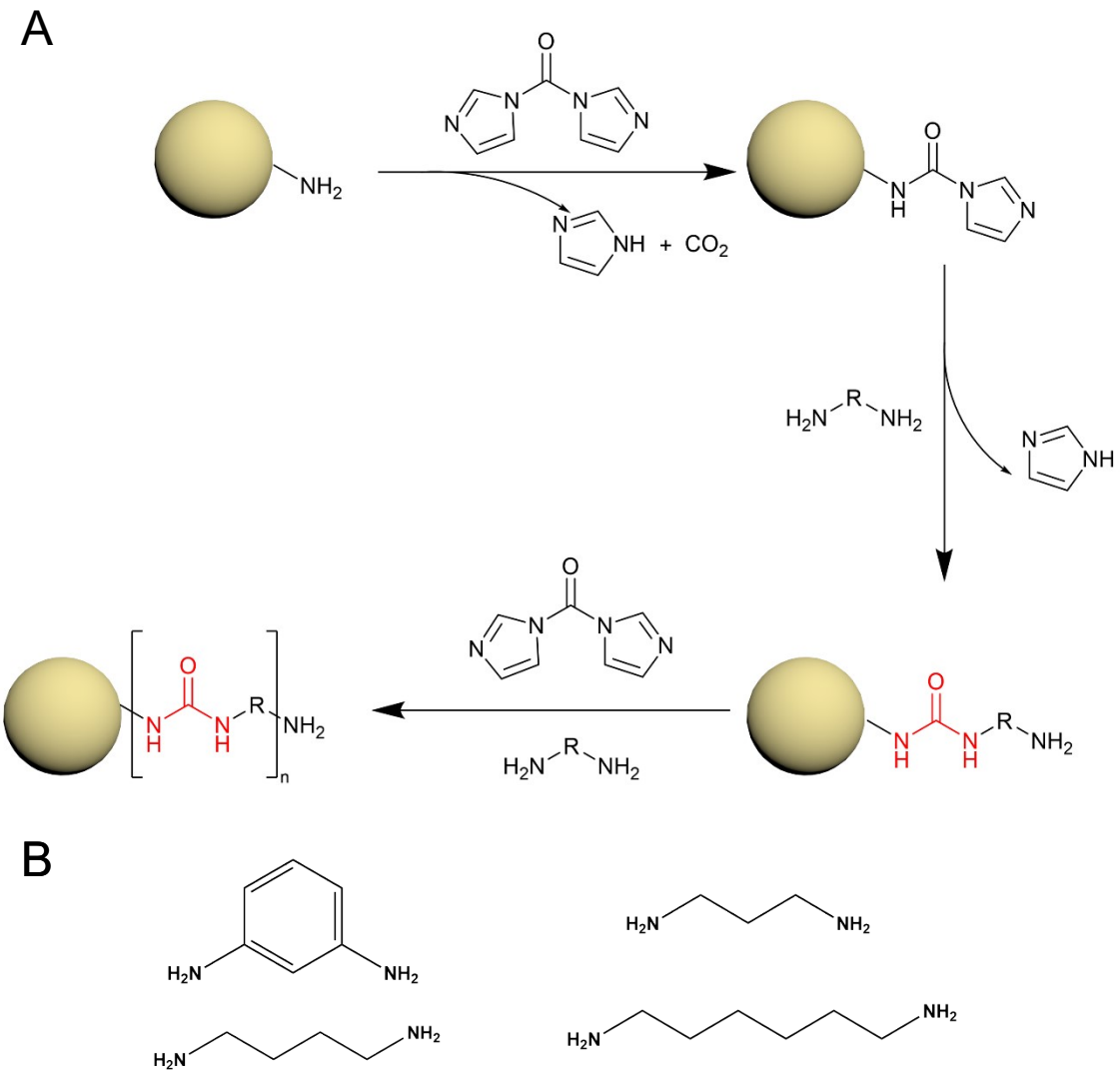

Figure S1. Conversion of diamine with N, N'-carbonyldiimidazole (A). Four kinds of monomers (B).

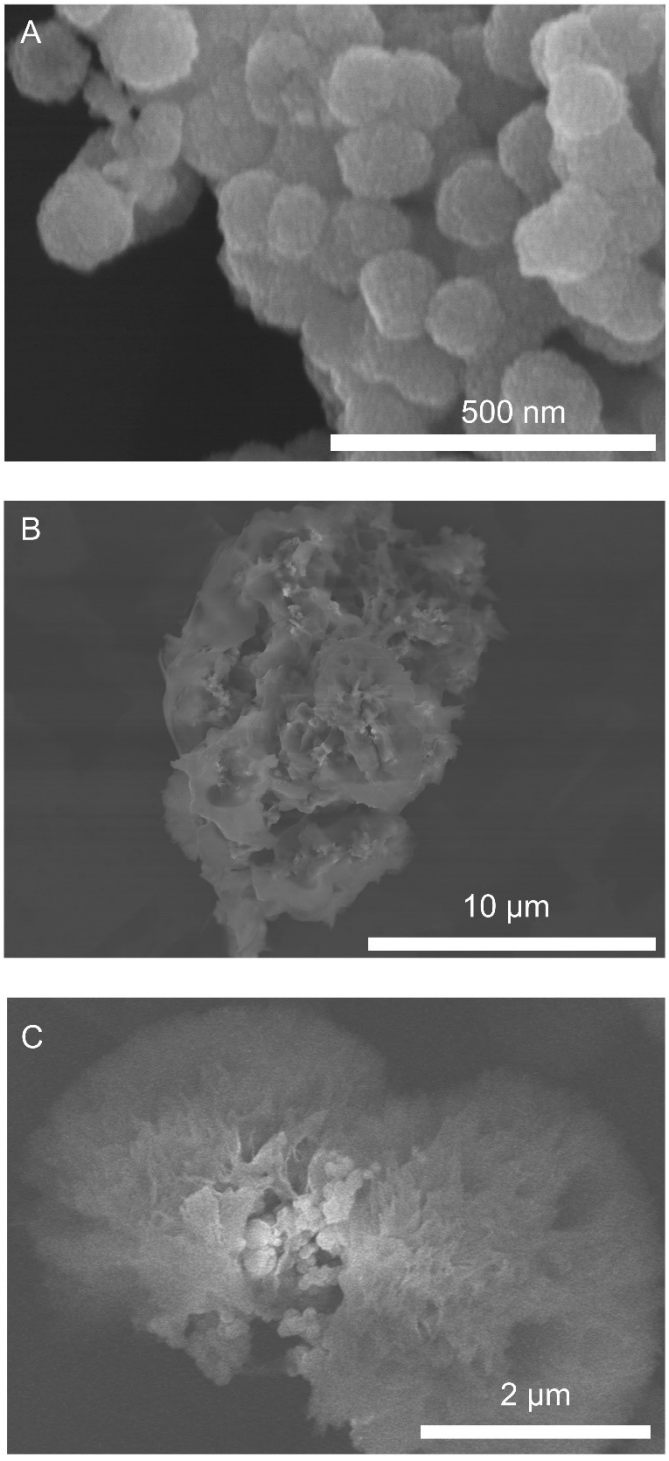

Figure S2. SEM of PMC-MPDA (A), PMC-DAP (B), and PMC-DAB (C).

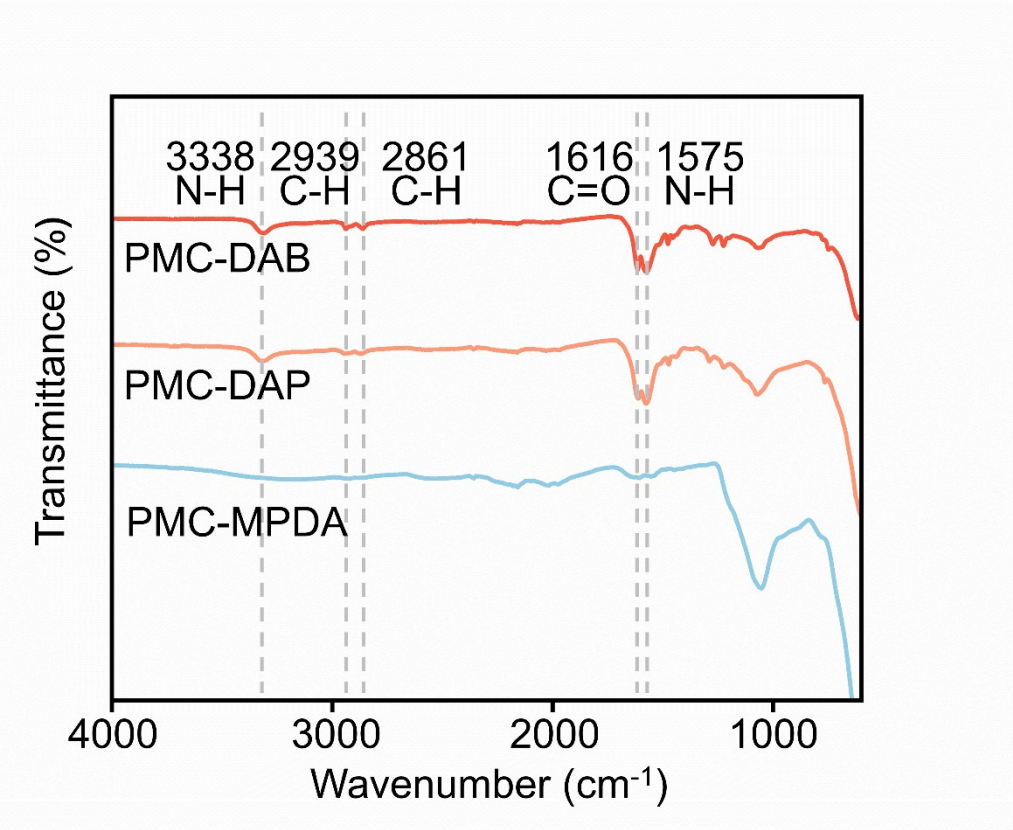

Figure S3. FTIR spectra of PMCs.

Table S1. Structural assignments for the peaks observed in the MALDI-TOF mass spectrum of polyurea synthesized with 1,6-Hexamethylenediamine and CDI.

	Examples	Series	m/z	Propoesd oligomer structure
●	1111 (n=7) 1253 (n=8) 1395 (n=9)	1	n*142+1+115+1	H-[ ]$_n$-NHCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$NH$_2$ +H$^+$
▲	1137 (n=8) 1279 (n=9) 1421 (n=10)	2	n*142+1	Macrocyclic +H$^+$
⬟	1163 (n=8) 1305 (n=9) 1447 (n=10)	3	n*142+1+25+1	H-[ ]$_n$-C≡CH +H$^+$
◆	1180 (n=8) 1322 (n=9) 1464 (n=10)	4	n*142+1+43	H-[ ]$_n$-NHC≡O$^+$

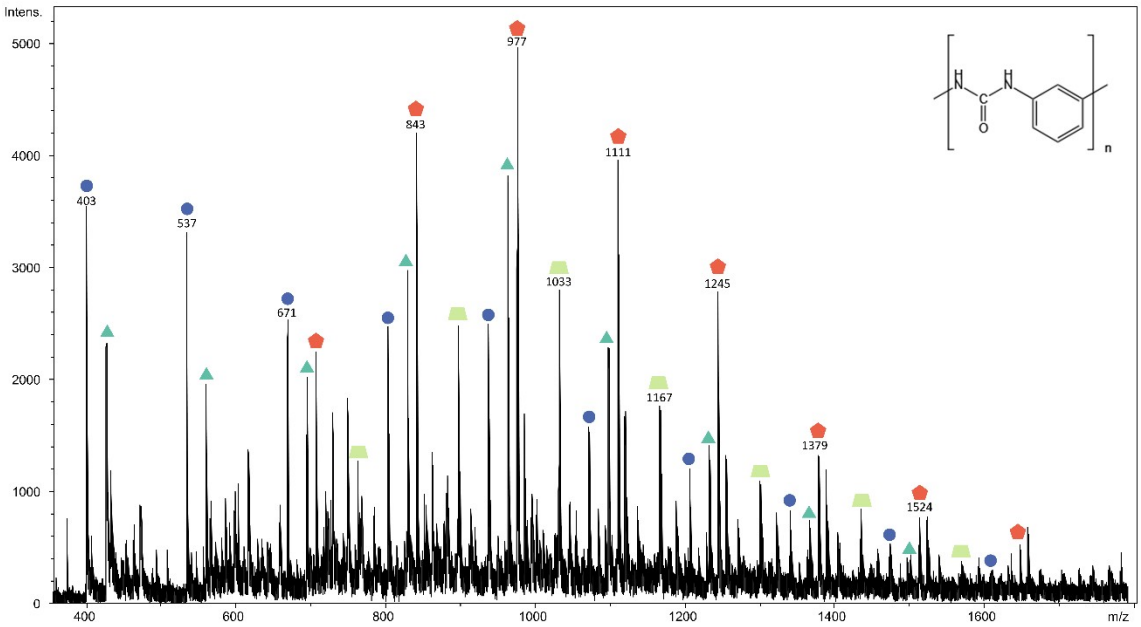

Figure S4. MALDI-TOF mass spectrum of polyurea synthesized with m-Phenylenediamine and CDI.

Table S2. Structural assignments for the peaks observed in the MALDI-TOF mass spectrum of polyurea synthesized with m-Phenylenediamine and CDI.

	Examples	Series	m/z	Proposed oligomer structure
●	939 (n=7) 1073 (n=8) 1207 (n=9)	1	n*134+1	Macrocyclic $+H^+$
▲	965 (n=8) 1099 (n=9) 1233 (n=10)	2	n*134+15+15-18+1	CH_3-[ ]$_n$-CH_3 $+H^+$
⬟	1163 (n=8) 1305 (n=9) 1447 (n=10)	3	n*134+1+71+23	H-[ ]$_n$-$CH_2CH_2CH_2CH_2CH_3$ $+H^+$
◆	1180 (n=8) 1322 (n=9) 1464 (n=10)	4	n*134+1+15+23	H-[ ]$_n$-CH_3 $+Na^+$

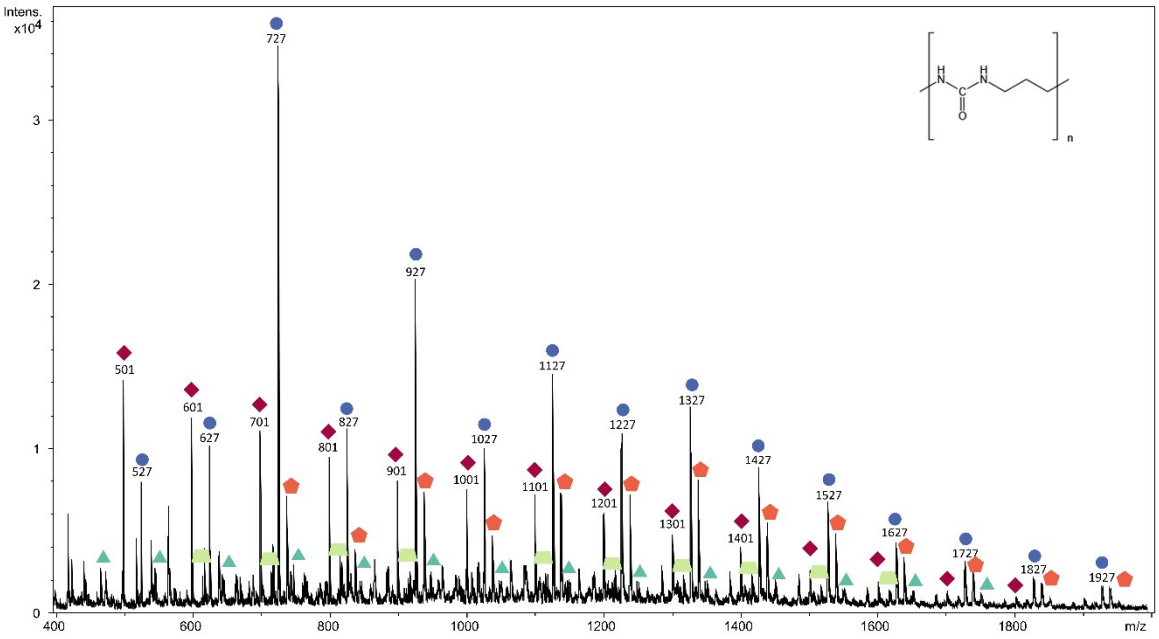

Figure S5. MALDI-TOF mass spectrum of polyurea synthesized with 1,3-Diaminopropane and CDI.

Table S3. Structural assignments for the peaks observed in the MALDI-TOF mass spectrum of polyurea synthesized with 1,3-Diaminopropane and CDI.

	Examples	Series	m/z	Proposed oligomer structure
●	627 (n=6) 727 (n=7) 827 (n=8)	1	n*100+1+42-17+1	H-[ ]$_n$-NHCH=CH$_2$ -NH$_3$+H$^+$
▲	649 (n=6) 749 (n=7) 849 (n=8)	2	n*100+1+42-17+23	H-[ ]$_n$-NHCH=CH$_2$ -NH$_3$+Na$^+$
▰	717 (n=7) 817 (n=8) 917 (n=9)	3	n*100+15+1+1	H-[ ]$_n$- CH$_3$ +H$^+$
⬟	739 (n=7) 839 (n=8) 939 (n=9)	4	n*100+15+1+23	H-[ ]$_n$-CH$_3$ +Na$^+$
◆	601 (n=6) 701 (n=7) 801 (n=8)	5	n*100+1	Macrocyclic +H$^+$

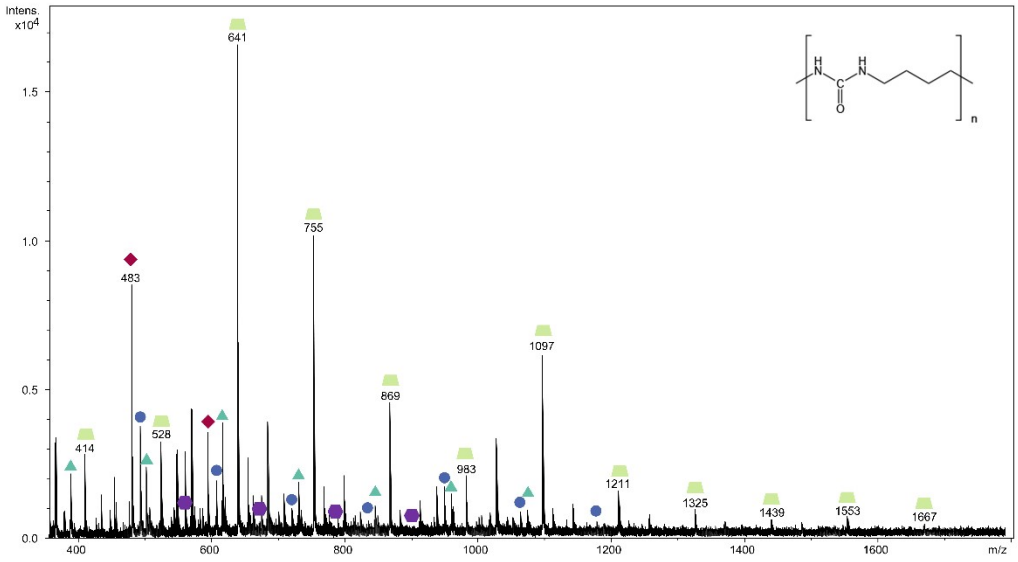

Figure S6. MALDI-TOF mass spectrum of polyurea synthesized with 1,4-Diaminobutane and CDI

Table S4. Structural assignments for the peaks observed in the MALDI-TOF mass spectrum of polyurea synthesized with 1,4-Diaminobutane and CDI.

	Examples	Series	m/z	Proposed oligomer structure
●	611 (n=5) 725 (n=6) 839 (n=7)	1	n*114+1+17+23	H-[ ]$_n$-NH_3 +Na^+
▲	619 (n=5) 733 (n=6) 847 (n=7)	2	n*114+1+43-18+23	H-[ ]$_n$-$CH_2CH_2CH_3$ -H_2O+Na^+
▰	641 (n=5) 755 (n=6) 869 (n=7)	3	n*114+1+70	H-[ ]$_n$-$CH_2CH_2CH2C{\equiv}O^+$
◆	711 (n=6) 825 (n=7) 939 (n=8)	5	n*114+1+25+1	H-[ ]$_n$-C≡CH +H^+
⬢	685 (n=6) 799 (n=7) 913 (n=8)	6	n*114+1	Macrocyclic +H^+

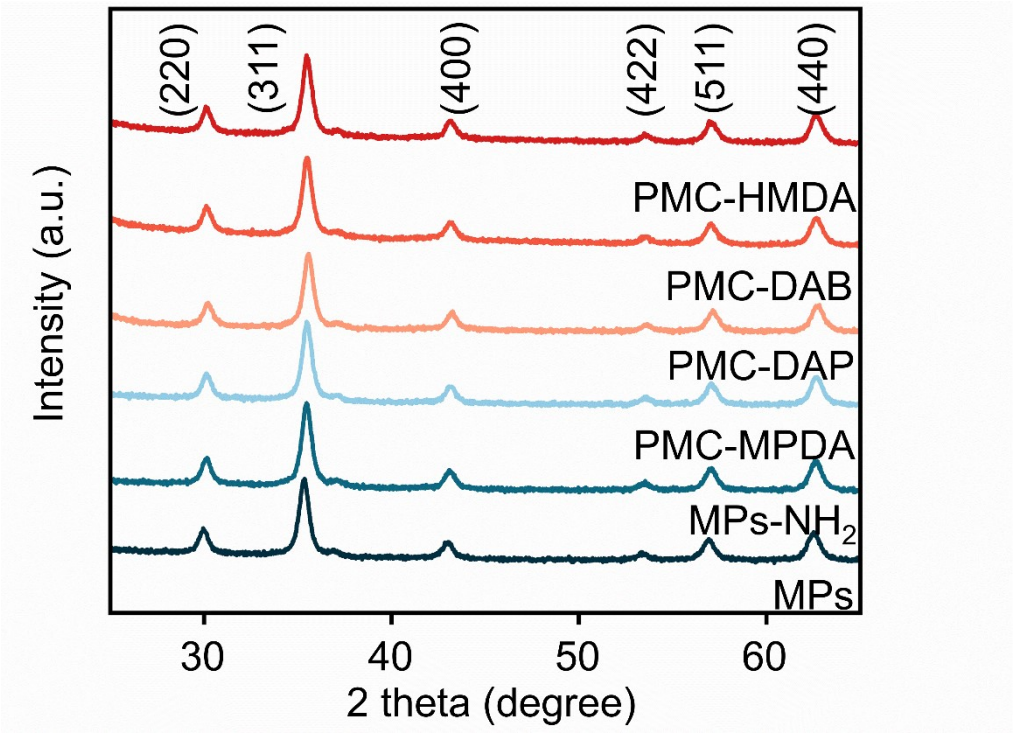

Figure S7. XRD patterns of MPs and PMCs

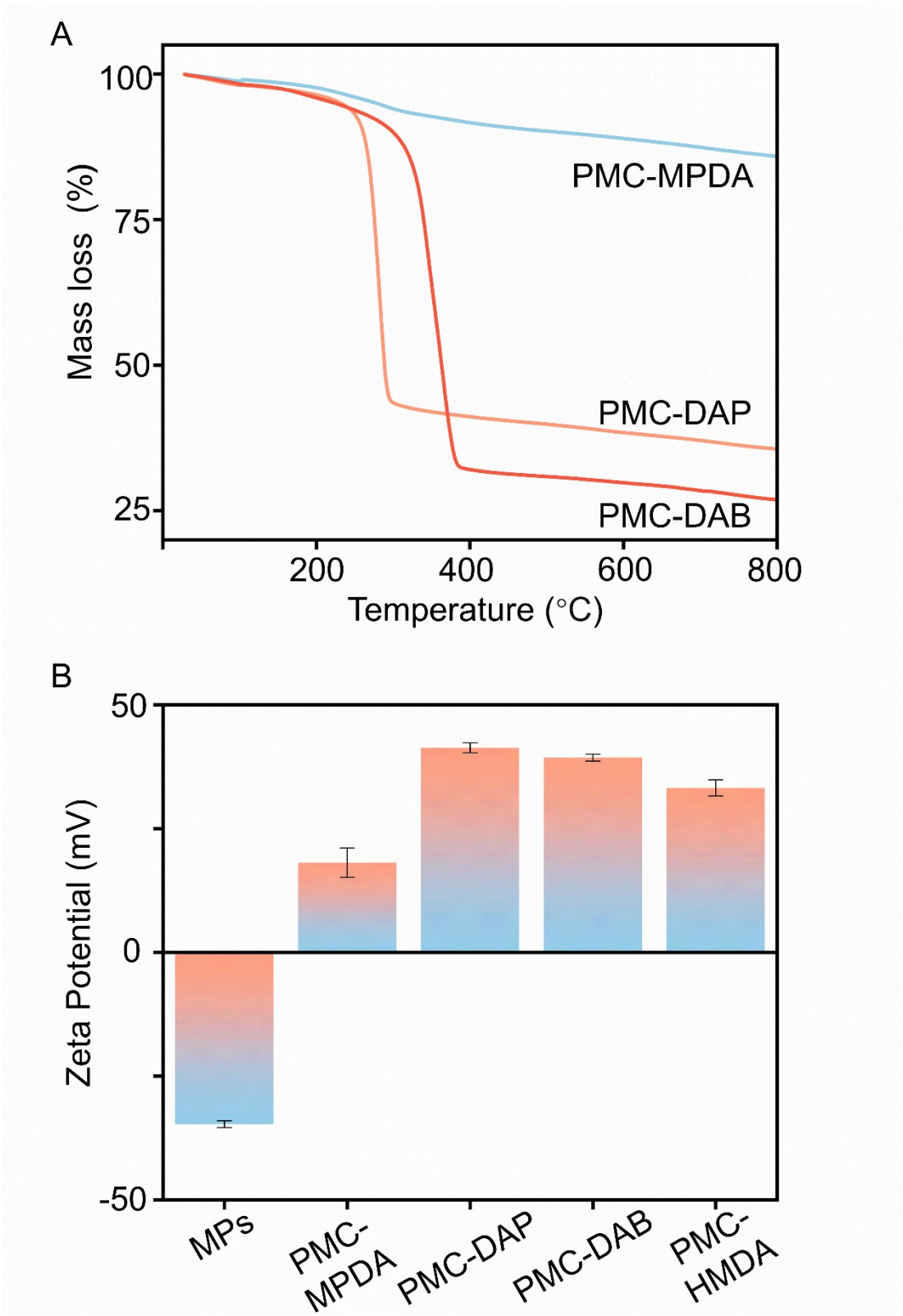

Figure S8. TGA curves (A) of PMCs. Zeta potential determinations (B) of MPs and PMCs.

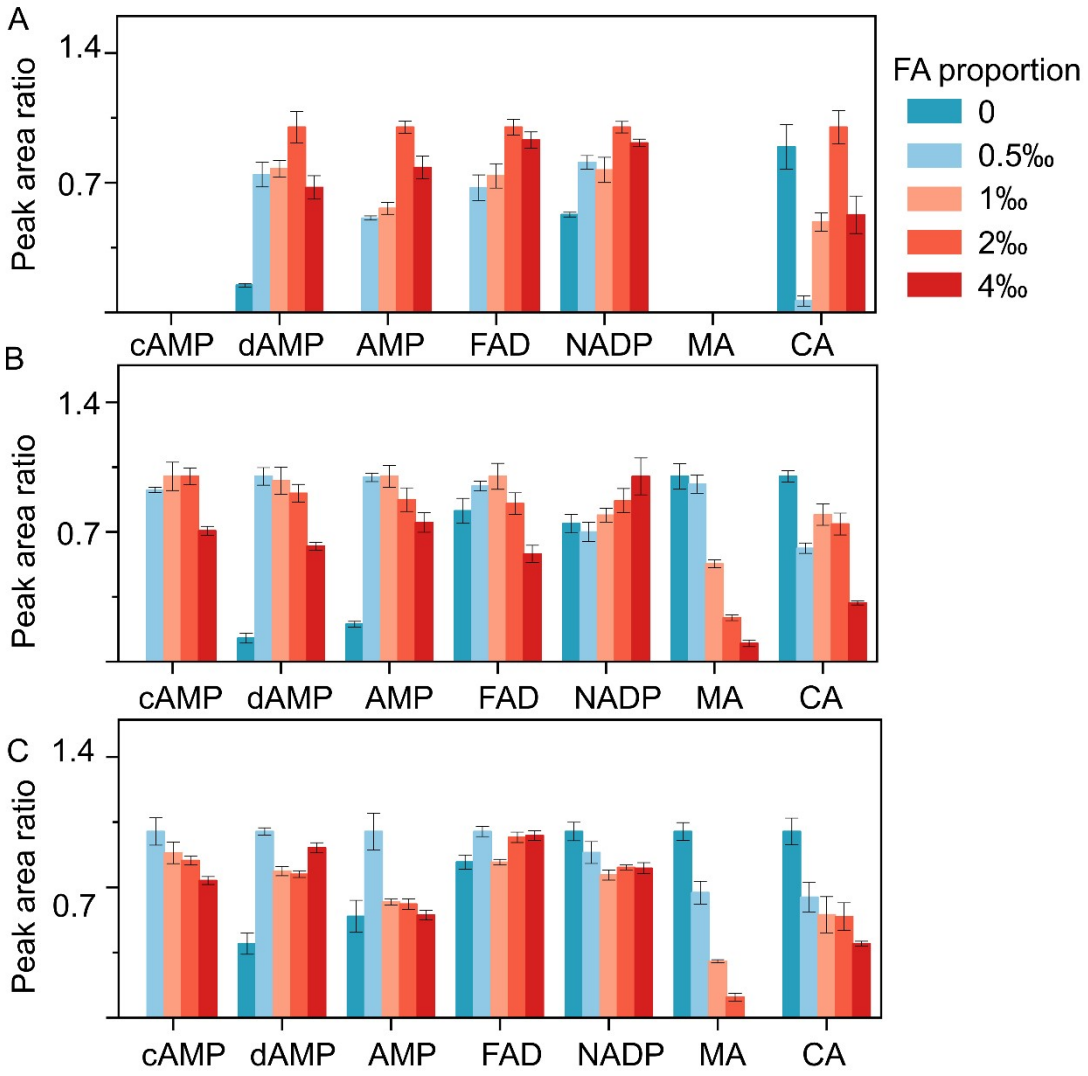

Figure S9. The optimization of formic acid proportion for adsorption of PMC-MPDA (A), PMC-DAP (B), and PMC-DAB (C).

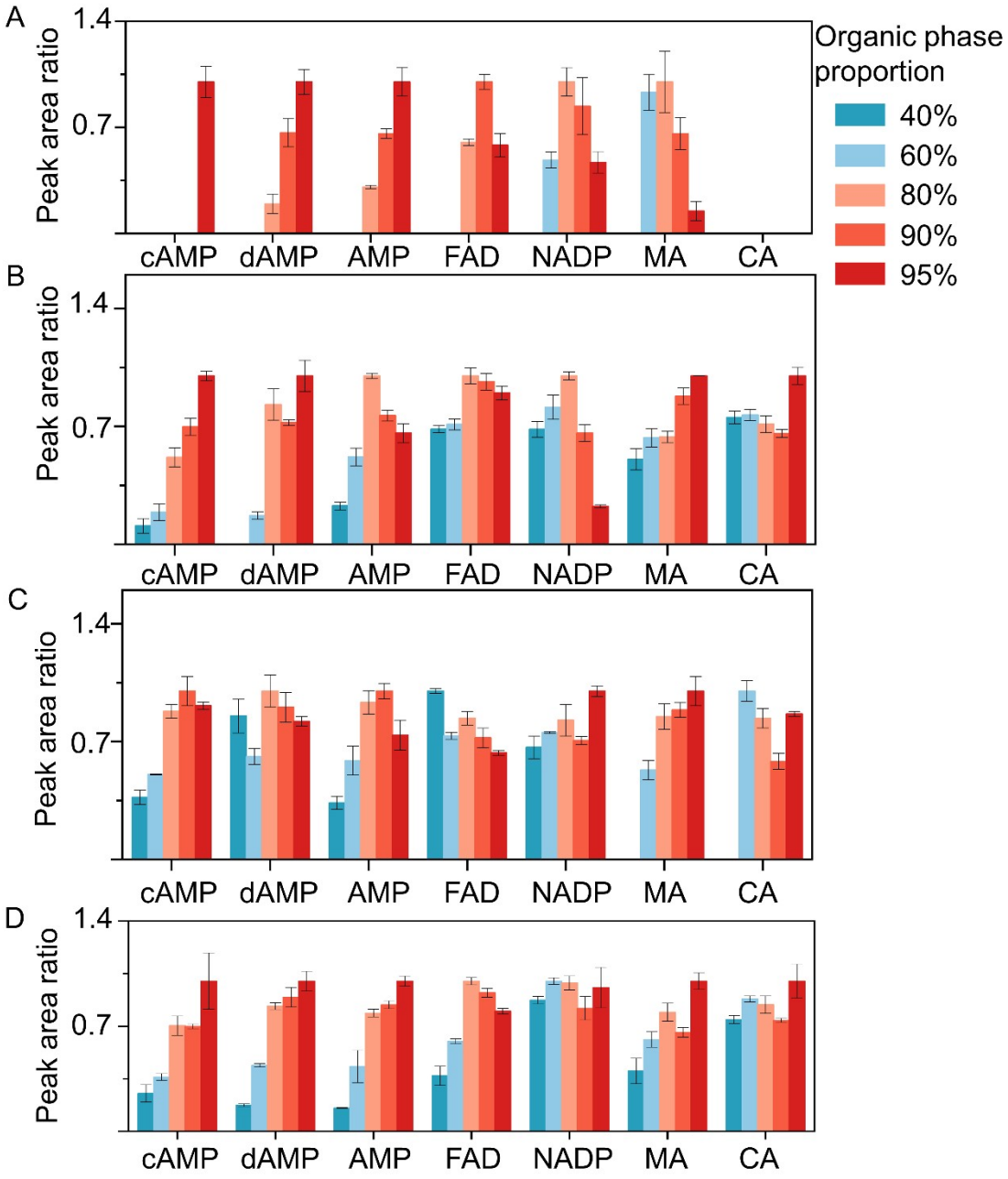

Figure S10. The optimization of organic phase proportion for adsorption of PMC-MPDA (A), PMC-DAP (B), PMC-DAB (C), and PMC-HMDA (D).

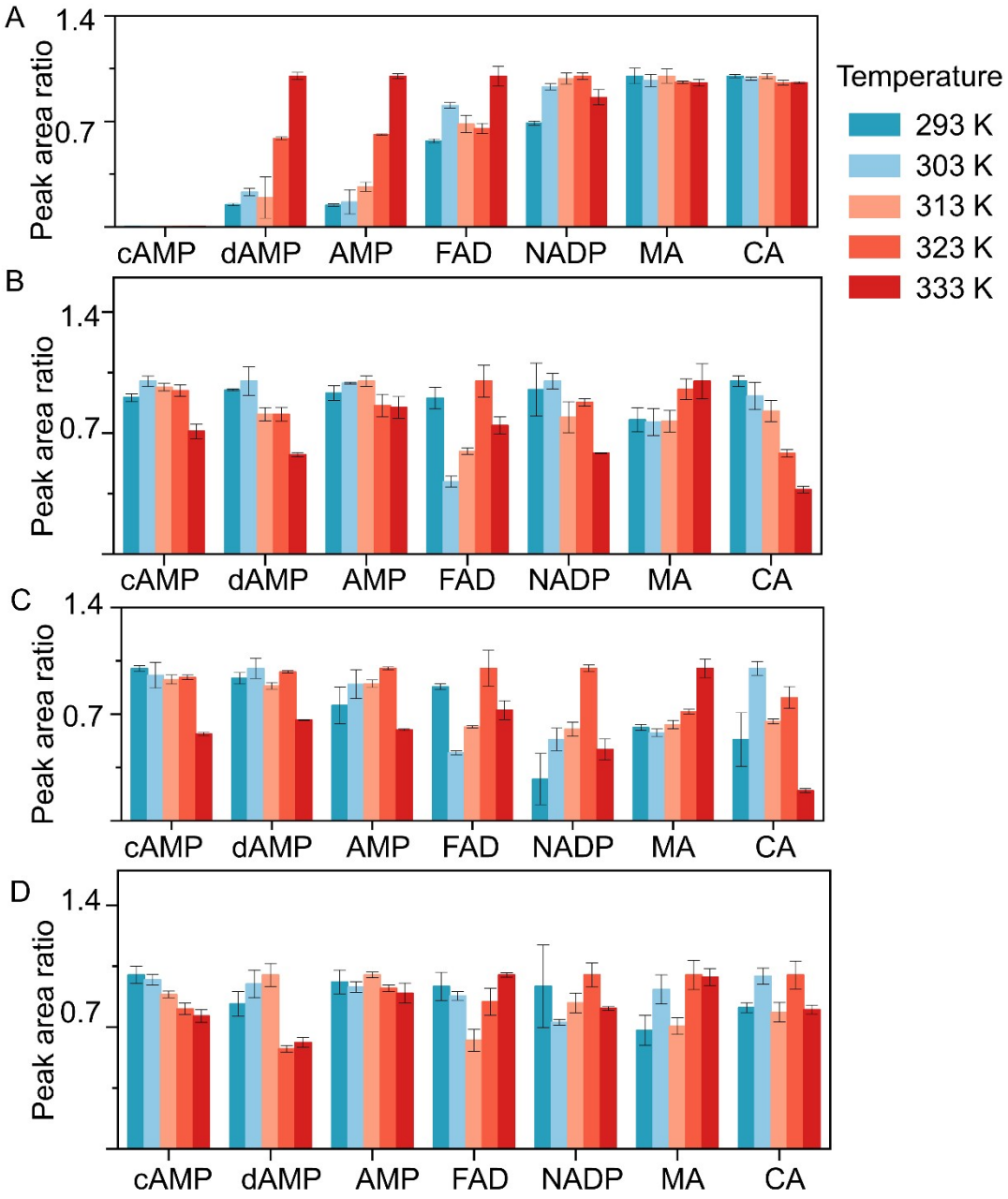

Figure S11. The optimization of temperature for adsorption of PMC-MPDA (A), PMC-DAP (B), PMC-DAB (C), and PMC-HMDA (D).

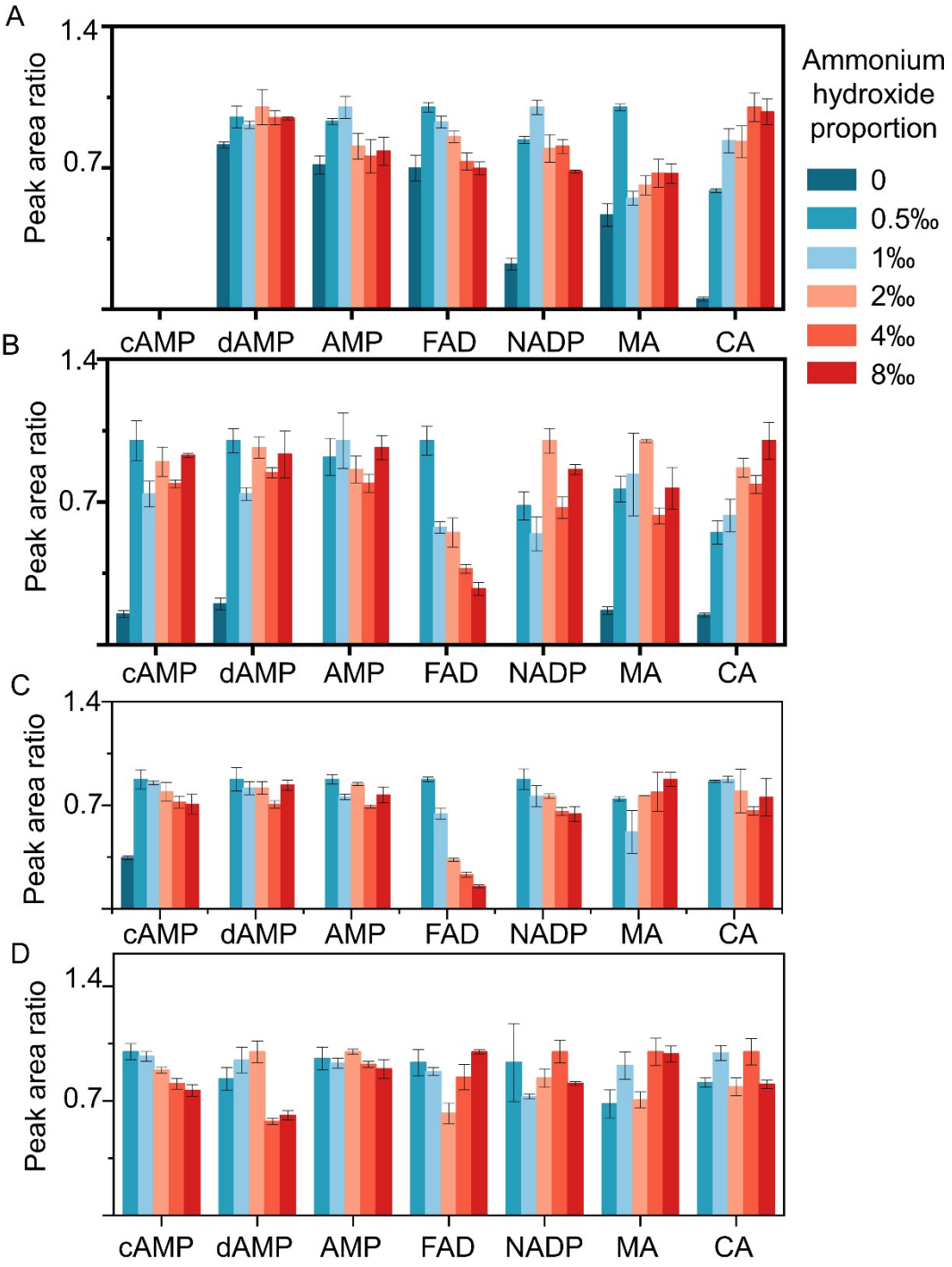

Figure S12. The optimization of ammonium hydroxide proportion for desorption of PMC-MPDA (A), PMC-DAP (B), PMC-DAB (C), and PMC-HMDA (D).

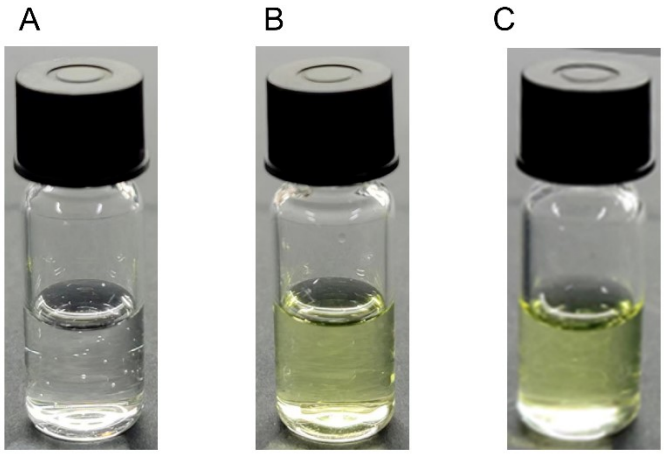

Figure S13. The adsorption (A) and desorption (B) phenomena can be observed visually in highly concentrated flavin adenine dinucleotide (FAD) solutions (C).

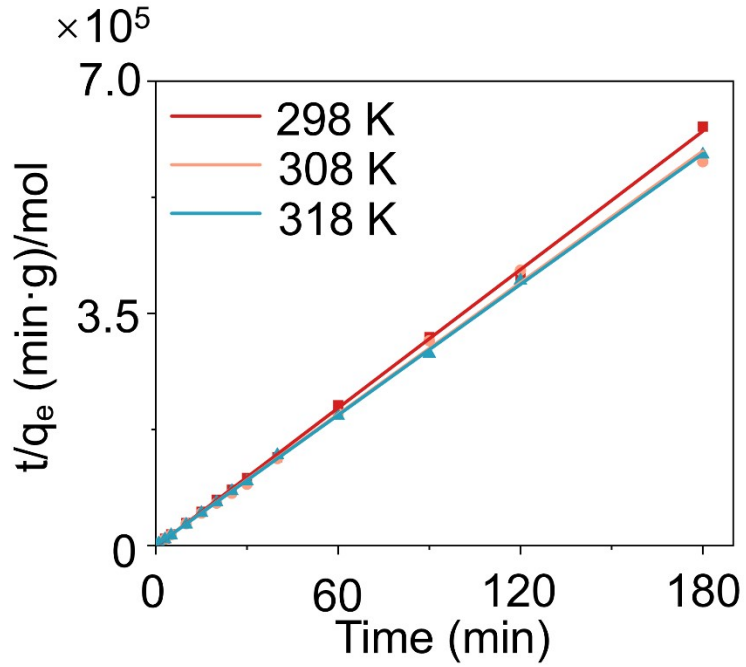

Figure S14. The enrichment performance of AMP solution with the same concentration at 298 K, 308 K, and 318 K.

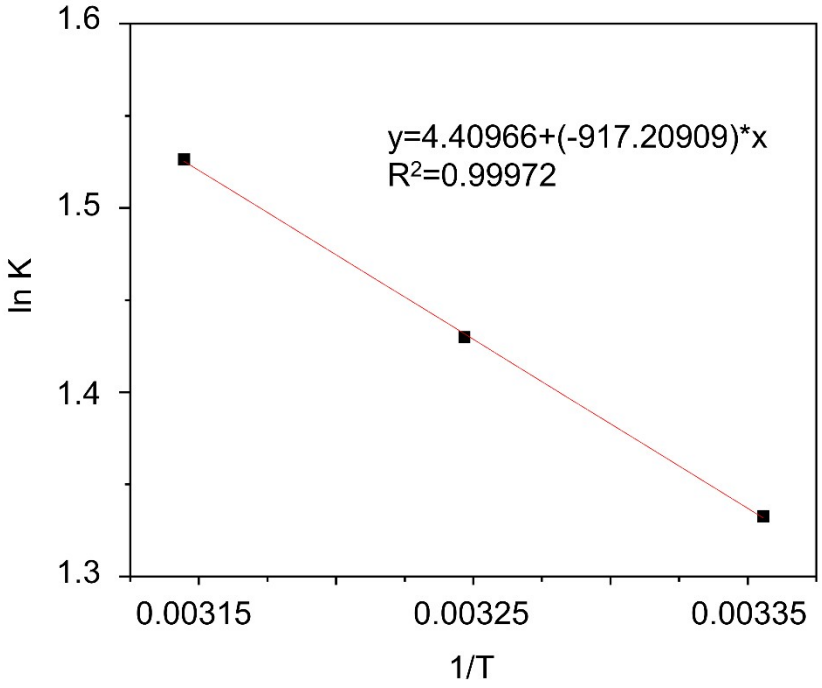

Figure S15. The enrichment performance of AMP solution with the same concentration at 298 K, 308 K, and 318 K: plot of 1/T and ln K.

Table S5. Thermodynamics parameters for adsorption of AMP on PMC-HMDA.

T	$\mathbf{q_e}$	ΔG^0	ΔH^0	ΔS^0	$\mathbf{R^2}$
K	μmol / g	kJ / mol	kJ / mol	J / (mol K)	
298	287.65	-14.12			0.99941
308	302.65	-14.67	7.63	36.66	0.99803
318	304.71	-15.23			0.99973

Table S6. Parameters of pseudo-second-order kinetics model for adsorption of AMP on PMC-HMDA at various initial concentrations

$\mathbf{C_0}$	$\mathbf{q_e}$	$\mathbf{R^2}$
μmol / L	μmol / g	
100	190.12	0.99995
130	215.28	0.99985
200	287.65	0.99941

Table S7. The LOD, linear range of the analysis method using LC-MS with PMC-HMDA.

Analytes	LODs	Linear range	Calibration equation	R^2
	pmol	$\mu mol \cdot L^{-1}$		
AMP	0.2	0.05 - 10	y = -7.68488E-4 + 2.15723E-5*x	0.99845
IMP	0.5	0.05 – 10	y = 1.42975E-4 + 2.66932E-5*x	0.99859
GMP	2	0.5 – 6	y = 4.83081E-4 + 5.93532E-6*x	0.99791
cAMP	2	0.4 - 2	y = 1.79205E-4 + 5.34048E-6*x	0.99704
R5P	2	0.4 - 6	y = -6.40298E-4 + 4.20061E-6*x	0.99728
NADP	2	0.4 – 6	y = -0.00174 + 9.10526E-6*x	0.99927
CDP	2	0.4 – 6	y = -3.8988E-4 + 7.71932E-6*x	0.99831
Malic acid	0.5	0.5 - 2	y = 0.00704 + 1.27824E-5*x	0.99886
Citric acid	1	0.2 - 6	y = -0.00599 + 3.09103E-5*x	0.99984

Table S8. The precision of the analysis method using LC-MS with PMC-HMDA.

Analytes	Intra-day			Inter-day		
	experimental nmol·L^{-1}	theoretical nmol·L^{-1}	RSDs	experimental nmol·L^{-1}	theoretical nmol·L^{-1}	RSDs
AMP	616.62	600.00	2.77%	639.66	600.00	6.61%
IMP	610,38	600.00	1.73%	631.26	600.00	5.21%
GMP	2126.40	2000.00	6.32%	2037.40	2000.00	1.87%
cAMP	1040.70	1000.00	4.07%	1029.00	1000.00	2.90%
R5P	2062.80	2000.00	3.14%	2053.20	2000.00	2.66%
NADP	2072.60	2000.00	3.63%	2208.40	2000.00	10.42%
CDP	2169.40	2000.00	8.47%	2121.80	2000.00	6.09%
Malic acid	1039.90	1000.00	3.99%	1041.10	1000.00	4.11%
Citric acid	2047.80	2000.00	2.39%	2016.40	2000.00	0.82%

Table S9. The accuracy of the analysis method using LC-MS with PMC-HMDA.

Analytes	Low concentration			Middle concentration			High concentration			Average recovery rate
	experimental nmol·L^{-1}	theoretical nmol·L^{-1}	recovery rate	experimental nmol·L^{-1}	theoretical nmol·L^{-1}	recovery rate	experimental nmol·L^{-1}	theoretical nmol·L^{-1}	recovery rate	
AMP	517.92	480.00	119.12%	598.11	600.00	99.41%	743.84	720.00	105.44%	107.99%
IMP	449.63	480.00	91.14%	617.15	600.00	103.71%	606.72	720.00	80.57%	91.80%
GMP	1355.28	1600.00	78.35%	1788.03	2000.00	86.15%	2322.49	2400.00	95.98%	86.83%
cAMP	795.84	800.00	98.80%	970.46	1000.00	94.58%	1274.25	1200.00	109.97%	101.11%
R5P	1536.78	1600.00	94.36%	1938.42	2000.00	95.95%	2194.11	2400.00	89.28%	93.20%
NADP	1482.29	1600.00	90.52%	1719.75	2000.00	82.93%	2423.45	2400.00	101.15%	91.53%
CDP	1511.72	1600.00	93.53%	1882.40	2000.00	93.34%	2324.69	2400.00	96.52%	94.46%
Malic acid	697.16	800.00	80.51%	976.00	1000.00	96.70%	1173.19	1200.00	97.11%	91.44%
Citric acid	1391.80	1600.00	82.21%	1571.23	2000.00	72.70%	2338.62	2400.00	96.89%	83.93%

Table S10. The precision at LLOQ of the analysis method using LC-MS with PMC-HMDA.

Analytes	Intra-day			Inter-day		
	experimental nmol·L^{-1}	theoretical nmol·L^{-1}	RSDs	experimental nmol·L^{-1}	theoretical nmol·L^{-1}	RSDs
AMP	56.04	50.00	12.08%	57.07	50.00	14,14%
IMP	48.38	50.00	3.25%	47.81	50.00	4.38%
GMP	482.15	500.00	3.57%	477.05	500.00	4.59%
cAMP	368.24	400.00	7.94%	356.76	400.00	10.81%
R5P	343.48	400.00	14.13%	321.16	400.00	19.71%
NADP	364.28	400.00	8.93%	343.80	400.00	14.05%
CDP	373.20	400.00	6.70%	345.88	400.00	13.53%
Malic acid	522.80	500.00	4.56%	531.05	500.00	6.21%
Citric acid	221.24	200.00	10.62%	232.92	200.00	16.46%

Table S11. The accuracy at LLOQ of the analysis method using LC-MS with PMC-HMDA.

Analytes	**Low concentration**			**Middle concentration**			**High concentration**			**Average recovery rate**
	experimental $nmol \cdot L^{-1}$	theoretical $nmol \cdot L^{-1}$	recovery rate	experimental $nmol \cdot L^{-1}$	theoretical $nmol \cdot L^{-1}$	recovery rate	experimental $nmol \cdot L^{-1}$	theoretical $nmol \cdot L^{-1}$	recovery rate	
AMP	56.95	40.00	142.38%	65.62	50.00	131.24%	80.09	80.00	100.11%	124.58%
IMP	32.12	40.00	80.30%	44.25	50.00	88.50%	78.49	80.00	80.57%	83.12%
GMP	355.99	400.00	89.00%	379.67	500.00	74.73%	748.40	800.00	93.55%	85.76%
cAMP	231.40	300.00	77.13%	354.17	400.00	88.54%	509.07	500.00	101.81%	89.16%
R5P	313.15	300.00	104.38%	364.85	400.00	91.21%	383.10	500.00	76.62%	90.74%
NADP	319.33	300.00	106.44%	341.21	400.00	85.30%	601.41	500.00	120.28%	104.01%
CDP	264.61	300.00	88.10%	356.69	400.00	89.17%	581.21	500.00	116.24%	97.84%
Malic acid	411.81	400.00	102.95%	497.40	500.00	99.48%	778.03	800.00	94.88%	90.10%
Citric acid	135.60	100.00	135.60%	228.25	200.00	114.12%	423.01	400.00	105.75%	118.49%

Table S12. The retention time of the standards and cell using HPLC-MS/MS with PMC-HMDA.

Analytes	Retention time (min)	
	standards	**cell**
AMP	9.46	9.54
IMP	9.96	9.93
GMP	9.80	9.86
ADP	10.14	10.06
CDP	10.16	10.07
ATP	13.58	13.50
NAD	11.97	12.11

Table S13. The list of anionic metabolites putatively identified based on accurate mass match with the HMDB metabolites.

No.	Metabolites	Molecular formula	Theoretical	Experimental	Accuracy	Samples		
			m/z	m/z	ppm	Cell	Liver	Serum
	Nucleotides							
1	AMP/dGMP	$C_{10}H_{14}N_5O_7P$	346.0558	346.0557	-0.3	√	√	√
2	GMP	$C_{10}H_{14}N_5O_8P$	362.0507	362.0506	-0.3	√	√	
3	CMP	$C_9H_{14}N_3O_8P$	322.0446	322.0444	-0.6	√	√	
4	UMP	$C_9H_{13}N_2O_9P$	323.0286	323.0285	-0.3	√	√	
5	ADP	$C_{10}H_{15}N_5O_{10}P_2$	426.0221	426.0222	0.2	√	√	√
6	GDP	$C_{10}H_{15}N_5O_{11}P_2$	442.0171	442.0171	0.0	√	√	√
7	UDP	$C_9H_{14}N_2O_{12}P_2$	402.9949	402.9949	0.0	√	√	
8	CDP	$C_9H_{15}N_3O_{11}P_2$	402.0109	402.0109	0.0	√	√	
9	ATP/dGTP	$C_{10}H_{16}N_5O_{13}P_3$	505.9885	505.9885	0.0	√	√	
10	GTP	$C_{10}H_{16}N_5O_{14}P_3$	521.9834	521.9835	0.2	√	√	
11	CTP	$C_9H_{16}N_3O_{14}P_3$	481.9772	481.9773	0.2	√		
12	UTP	$C_9H_{15}N_2O_{15}P_3$	482.9613	482.9614	0.2	√		
13	dAMP	$C_{10}H_{14}N_5O_6P$	330.0609	330.0609	0.0	√		
14	dTMP	$C_{10}H_{15}N_2O_8P$	321.0493	321.0493	-0.1	√		

No.	Metabolites	Molecular formula	Theoretical	Experimental	Accuracy	Intensity		
			m/z	m/z	ppm	Cell	Liver	Serum
15	dADP	$C_{10}H_{15}N_5O_9P_2$	410.0272	410.0273	0.2	√	√	√
16	dUDP	$C_9H_{14}N_2O_{11}P_2$	387.000006	387.0002	0.5	√	√	
17	dTDP	$C_{10}H_{16}N_2O_{11}P_2$	401.0157	401.0157	0.0	√		√
18	dCDP	$C_9H_{15}N_3O_{10}P_2$	386.016	386.0160	0.0	√		√
19	dATP	$C_{10}H_{16}N_5O_{12}P_3$	489.9936	489.9938	0.4	√		
20	dTTP	$C_{10}H_{17}N_2O_{14}P_3$	480.982	480.9820	0.0	√		
21	dCTP	$C_9H_{16}N_3O_{13}P_3$	465.9823	465.9825	0.4	√		
22	dUTP	$C_9H_{15}N_2O_{14}P_3$	466.966337	466.9671	1.6	√		
23	dIDP	$C_{10}H_{14}N_4O_{10}P_2$	411.011239	411.0114	0.3			√
24	CH_3-AMP	$C_{10}H_{14}N_5O_7P$-CH_3	360.071458	360.0713	-0.4	√	√	√
25	CH_2OH-AMP	$C_{10}H_{14}N_5O_7P$-CH_2OH	376.066373	376.0664	0.2	√		
26	CH_3-GMP	$C_{10}H_{14}N_5O_8P$	362.050723	362.0507	0.0	√	√	√
27	NADP	$C_{21}H_{28}N_7O_{17}P_3$	742.0682	742.0679	-0.5	√		
28	NADP	$C_{21}H_{28}N_7O_{17}P_3$	370.5305	370.5305	0.0	√	√	
29	NADPH	$C_{21}H_{30}N_7O_{17}P_3$	744.083826	744.0838	0.0	√		

No.	Metabolites	Molecular formula	Theoretical	Experimental	Accuracy	Intensity		
			m/z	m/z	ppm	Cell	Liver	Serum
30	NADPH	$C_{21}H_{30}N_7O_{17}P_3$	371.538	371.5382	0.5	√	√	
31	NAD	$C_{21}H_{27}N_7O_{14}P_2$	662.1018	662.1021	0.5	√	√	
32	FAD	$C_{27}H_{33}N_9O_{15}P_2$	391.5713	391.5713	0.1	√	√	√
33	FAD	$C_{27}H_{33}N_9O_{15}P_2$	784.1499	784.1493	-0.8	√		
34	cFMN	$C_{17}H_{19}N_4O_8P$	437.086774	437.0867	-0.1		√	
35	AICAR	$C_9H_{15}N_4O_8P$	337.055474	337.0558	1.0		√	
36	SAICAR	$C_{13}H_{19}N_4O_{12}P$	453.066432	453.0665	0.2		√	
37	IMP	$C_{10}H_{13}N_4O_8P$	347.0398	347.0398	0.0	√	√	
38	AP4A	$C_{20}H_{28}N_{10}O_{19}P_4$	835.040988	835.0409	-0.1	√		
39	cADPR	$C_{15}H_{21}N_5O_{13}P_2$	540.0538	540.0537	-0.1	√	√	
40	cTMP	$C_{10}H_{13}N_2O_7P$	303.038761	303.0387	-0.2	√		
41	cAMP	$C_{10}H_{12}N_5O_6P$	328.045243	328.0452	0.0	√	√	
42	cGMP	$C_{10}H_{12}N_5O_7P$	344.040158	344.0404	0.6			√
43	IAA-RP	$C_{10}H_{15}N_2O_9P$	337.0442	337.0441	-0.2		√	
	Carbohydrates							
44	G6P	$C_6H_{13}O_9P$	259.0224	259.0225	0.3	√		

No.	Metabolites	Molecular formula	Theoretical	Experimental	Accuracy	Intensity		
			m/z	m/z	ppm	Cell	Liver	Serum
45	Rib-1,5-P2	$C_5H_{12}O_11P_2$	308.978208	308.9779	-1.1	√		
46	GLCN-6-P	$C_6H_{14}NO_8P$	258.0384	258.0384	-0.2	√		
47	6PG	$C_6H_{13}O_{10}P$	275.0174	275.0171	-1.0	√		
48	FDP	$C_6H_{13}O_{10}P$	338.9888	338.9887	-0.2	√	√	√
49	PRPP	$C_5H_{13}O_{14}P_3$	388.944538	388.9447	0.3	√		
50	UDPG/UDP-GLC	$C_{15}H_{24}N_2O_{17}P_2$	565.0477	565.0477	-0.1	√	√	
51	UDP-Glc-Nac	$C_{17}H_{27}N_3O_{17}P_2$	302.5335	302.5334	-0.3	√	√	
52	UDP-Glc-Nac	$C_{17}H_{27}N_3O_{17}P_2$	606.0743	606.0743	0.1	√	√	√
53	UDP-GlcUA	$C_{15}H_{22}N_2O_{18}P_2$	579.027008	579.0272	0.3	√	√	
54	dTDP-D-glucose	$C_{16}H_{26}N_2O_{16}P_2$	563.0685	563.0685	0.0	√	√	
55	Adenylsuccinic acid	$C_{14}H_{18}N_5O_{11}P$	462.066767	462.0670	0.4	√	√	
56	UDP-Apiose	$C_{14}H_{22}N_2O_{16}P_2$	535.037179	535.0371	-0.1	√	√	
57	Sedoheptulose-7-P	$C_7H_{15}O_{10}P$	289.033	289.0327	-1.0	√	√	
58	GlcNAc6p	$C_8H_{16}NO_9P$	300.049	300.0487	-1.2	√	√	
59	GDP-fucose	$C_{16}H_{25}N_5O_{15}P_2$	588.074962	588.0750	0.0	√	√	
60	monophospho-n-acetylneuraminic acid	$C_{11}H_{20}NO_{12}P$	388.065035	388.0652	0.3	√	√	

No.	Metabolites	Molecular formula	Theoretical	Experimental	Accuracy	Intensity		
			m/z	m/z	ppm	Cell	Liver	Serum
61	I6P	$C_6H_{13}O_9P$	259.022442	259.0225	0.2	√	√	
62	D-myo-Inositol 1,4-bisphosphate	$C_6H_{14}O_{12}P_2$	338.988772	338.9887	-0.2	√		√
63	IP3	$C_6H_{15}O_{15}P_3$	418.955103	418.9552	0.2	√		
64	GroPIns	$C_9H_{19}O_{11}P$	333.05922	333.0590	-0.8	√	√	
65	DHAP(O-18:0)	$C_{21}H_{43}O_6P$	421.272449	421.2724	-0.1			√
66	D-4'-phosphopantothenate	$C_9H_{18}NO_8P$	298.0697	298.0696	-0.3		√	
67	Nicotinamide ribotide	$C_{11}H_{16}N_2O_8P$	334.055808	334.0557	-0.3			√
68	D-myo-Inositol 1,4-bisphosphate	$C_6H_{14}O_{12}P_2$	338.988773	338.9887	-0.2	√	√	
69	Diphosphoglucuronic acid	$C_6H_{12}O_{13}P_2$	352.968037	352.9681	0.2		√	
	phosphate ester							
70	Phosphoribosyl-AMP	$C_{15}H_{23}N_5O_{14}P_2$	558.064397	558.0644	0.0	√	√	
71	CDP-ethanolamine	$C_{11}H_{20}N_4O_{11}P_2$	445.053104	445.0531	0.1		√	
72	ADP-ribose 2'-phosphate	$C_{15}H_{24}N_5O_{17}P_3$	638.030727	638.0308	0.1	√	√	
73	Cmp-nana	$C_{20}H_{31}N_4O_{16}P$	613.139991	613.1399	-0.2	√		
74	O-acetyl-ADP-ribose	$C_{17}H_{25}N_5O_{15}P_2$	600.074962	600.07439	-1.0		√	
75	Guanosine diphosphate mannose	$C_{16}H_{25}N_5O_{16}P_2$	604.069877	604.06933	-0.9	√	√	

No.	Metabolites	Molecular formula	Theoretical m/z	Experimental m/z	Accuracy ppm	Intensity Cell	Liver	Serum
76	Uridine diphosphate-N-acetylgalactosamine	$C_{17}H_{27}N_3O_{17}P_2$	606.074293	606.07414	-0.3	√		
	Cholic acid							
77	Deoxycholic acid	$C_{24}H_{40}O_4$	391.285383	391.2854	0.0	√	√	√
78	Cholic acid	$C_{24}H_{40}O_5$	407.280298	407.2802	-0.4		√	√
79	Glycocholic acid	$C_{26}H_{43}NO_6$	464.301762	464.3016	-0.5	√	√	√
80	Deoxycholic acid 3-glucuronide	$C_{30}H_{48}O_{10}$	567.317471	567.3175	0.0			√
81	Deoxycholic acid glycine conjugate	$C_{26}H_{43}NO_5$	448.306847	448.3068	-0.2			√
82	Bilirubin	$C_{33}H_{36}N_4O_6$	583.256208	583.2566	0.6		√	
83	3b-Hydroxy-5-cholenoic acid	$C_{24}H_{38}O_3$	373.274819	373.2748	0.1		√	
84	24-Nor Ursodeoxycholic Acid	$C_{23}H_{38}O_4$	377.269733	377.2697	0.0	√	√	√
85	12-Ketodeoxycholic acid	$C_{24}H_{38}O_4$	389.269733	389.2697	0.0	√	√	√
86	7alpha-Hydroxy-3-oxo-4-cholestenoate	$C_{27}H_{42}O_4$	429.301033	429.3010	0.0	√		√
87	Deoxycholylalanine	$C_{27}H_{45}NO_5$	462.322497	462.3227	0.4			√
88	Chenodeoxycholic acid sulfate	$C_{24}H_{40}O_7S$	471.242198	471.2422	-0.1		√	
89	7-Sulfocholic acid	$C_{24}H_{40}O_8S$	487.237113	487.2372	0.2		√	
90	Deoxycholylthreonine	$C_{28}H_{47}NO_6$	492.333062	492.3333	0.5	√		√

No.	Metabolites	Molecular formula	Theoretical m/z	Experimental m/z	Accuracy ppm	Intensity		
						Cell	Liver	Serum
91	Sulfolithocholylglycine	$C_{26}H_{43}NO_7S$	512.268747	512.2687	0.0		√	√
92	Cholylisoleucine	$C_{30}H_{51}NO_6$	520.364362	520.3639	-0.9	√		√
93	Cholic acid glucuronide	$C_{30}H_{48}O_{11}$	583.312386	583.31239	0.0		√	√
	Others							
94	Malic acid	$C_4H_6O_5$	133.014247	133.0144	1.3	√		
95	3-Fluoro-2-oxopropanoic acid	$C_3H_3FO_3$	104.999346	104.9993	-0.3	√		
96	3-Furoic acid	$C_5H_4O_3$	111.008768	111.0088	0.4	√		
97	4-Carboxypyrazole	$C_4H_4N_2O_2$	111.020001	111.0201	0.5	√		
98	2,3-Dihydro-1H-pyrrole-2-carboxylic acid	$C_5H_7NO_2$	112.040402	112.0406	1.8	√		
99	Fumaric acid	$C_4H_4O_4$	115.003682	115.0037	0.0	√		
100	(3S)-3-Amino-4-oxobutanoic acid	$C_4H_7NO_3$	116.035317	116.0353	-0.5	√		
101	D-beta-Homoserine	$C_4H_9NO_3$	118.050967	118.0509	-0.9	√		
102	Benzoic acid	$C_7H_6O_2$	121.029503	121.0297	1.4	√		
103	Phosphoric acid hydroxymethyl ester	CH_5O_5P	126.980183	126.9800	-1.1	√		
104	(2S)-3,4-Dioxoazetidine-2-carboxylic acid	$C_4H_3NO_4$	127.998931	127.9988	-0.9	√		
105	M-toluic Acid	$C_8H_8O_2$	135.045153	135.0453	1.2			√

No.	Metabolites	Molecular formula	Theoretical	Experimental	Accuracy	Intensity		
			m/z	m/z	ppm	Cell	Liver	Serum
106	4-Hydroxybenzoic acid	$C_7H_6O_3$	137.024418	137.0246	1.5		√	
107	Phenylpropiolic acid	$C_9H_6O_2$	145.029503	145.0297	1.4			√
108	4-hydroxyheptanoic acid	$C_7H_{14}O_3$	145.087018	145.0873	2.0			√
109	D-Arabinose	$C_5H_{10}O_5$	149.045547	149.0455	-0.1			√
110	2-Aminomuconic acid	$C_6H_7NO_4$	156.030231	156.03049	1.7		√	
111	2-(Phosphonomethyl)pentanedioic acid	$C_6H_{11}O_7P$	225.016963	225.0168	-0.5	√		√
112	Chorismate	$C_{10}H_{10}O_6$	225.040462	225.0402	-1.1			√
113	Glyceric acid 1,3-biphosphate	$C_3H_8O_{10}P_2$	264.951993	264.9516	-1.4	√	√	
114	$C_{18}H_{32}O_3$	$C_{18}H_{32}O_3$	295.227868	295.2279	0.0			√
115	3,8-Dihydroxy-1-methylanthraquinone-2-carboxylic acid	$C_{16}H_{10}O_6$	297.040462	297.0405	0.1	√		√
116	5-Oxooctadecanoic acid	$C_{18}H_{34}O_3$	297.243518	297.2438	0.9		√	√
117	9-hydroxyoctadecanoic acid	$C_{18}H_{36}O_3$	299.259169	299.2590	-0.4	√		
118	xi-7-Hydroxyhexadecanedioic acid	$C_{16}H_{30}O_5$	301.202048	301.2019	-0.4	√		
119	Eicosapentaenoic acid	$C_{20}H_{30}O_2$	301.217304	301.2173	0.0	√		
120	Arachidonic acid	$C_{20}H_{32}O_2$	303.232954	303.2329	0.0	√		
121	5'-Carboxy-gamma-chromanol	$C_{18}H_{26}O_4$	305.175833	305.1758	-0.3	√		

No.	Metabolites	Molecular formula	Theoretical	Experimental	Accuracy	Intensity		
			m/z	m/z	ppm	Cell	Liver	Serum
122	5,8,11-Eicosatrienoic acid	$C_{20}H_{34}O_2$	305.248604	305.2486	-0.1	√		
123	Penilloic acid	$C_{15}H_{20}N_2O_3S$	307.112187	307.1121	-0.3	√		
124	Hydroxy-3-oxooctadecatrienoic acid	$C_{18}H_{28}O_4$	307.191483	307.1914	-0.3	√		
125	Eicosadienoic acid	$C_{20}H_{36}O_2$	307.264254	307.2643	0.1	√		
126	Indoxyl glucuronide	$C_{14}H_{15}NO_7$	308.077575	308.0775	-0.3	√	√	
127	3h-Sialic acid	$C_{11}H_{19}NO_9$	308.098705	308.0985	-0.6	√		
128	Octadeca-2,4-dienedioic acid	$C_{18}H_{30}O_4$	309.207133	309.2071	-0.2	√		
129	Pteroic acid	$C_{14}H_{12}N_6O_3$	311.089812	311.0899	0.2	√		
130	18-Hydroperoxyoctadeca-2,4-dienoic acid	$C_{18}H_{32}O_4$	311.222783	311.2227	-0.4	√		
131	3D,7D,11D-Phytanic acid	$C_{20}H_{40}O_2$	311.295554	311.2954	-0.4	√	√	
132	Gibberellin A120	$C_{19}H_{22}O_4$	313.144533	313.1446	0.1	√		
133	9,10-DHOME	$C_{18}H_{34}O_4$	313.238433	313.2383	-0.3	√	√	
134	3-hydroxypristanic acid	$C_{19}H_{38}O_3$	313.274819	313.2747	-0.4	√	√	
135	N-Myristoyl Serine	$C_{17}H_{33}NO_4$	314.233682	314.2336	-0.1	√		
136	Beta-Citryl-L-glutamic acid	$C_{11}H_{15}NO_{10}$	320.062319	320.0622	-0.3	√		
137	Bis(2-ethylhexyl) hydrogen phosphate	$C_{16}H_{35}O_4P$	321.22002	321.2200	0.0	√		

No.	Metabolites	Molecular formula	Theoretical	Experimental	Accuracy	Intensity		
			m/z	m/z	ppm	Cell	Liver	Serum
138	Cibaric acid	$C_{18}H_{28}O_5$	323.186398	323.1864	-0.1	√		
139	Z)-15-Oxo-11-eicosenoic acid	$C_{20}H_{36}O_3$	323.259169	323.2591	-0.1	√		
140	Dihyroxy-1H-indole glucuronide I	$C_{14}H_{15}NO_8$	324.07249	324.0724	-0.2	√	√	
141	N-Myristoyl Proline	$C_{19}H_{35}NO_3$	324.254418	324.2544	0.0	√		
142	3-[4-Hydroxy-3-[3-(4-hydroxyphenyl)prop-2-enoyloxy]phenyl]prop-2-enoic acid	$C_{18}H_{14}O_6$	325.071762	325.0718	0.1		√	
143	3-hydroxyicos-13-enoic acid	$C_{20}H_{38}O_3$	325.274819	325.2748	-0.2	√	√	
144	Margaroylglycine	$C_{19}H_{37}NO_3$	326.270068	326.2700	-0.1	√		
145	Rhamnalpinogenin	$C_{17}H_{12}O_7$	327.051026	327.0511	0.2	√		
146	Prostaglandin M	$C_{16}H_{24}O_7$	327.144927	327.1450	0.1	√		
147	Corchorifatty acid F	$C_{18}H_{32}O_5$	327.217698	327.2176	-0.3	√		
148	Docosahexaenoic acid	$C_{22}H_{32}O_2$	327.232954	327.2329	-0.2	√	√	
149	Blighinone	$C_{16}H_{10}O_8$	329.030291	329.0302	-0.3	√		
150	Penicillin G	$C_{16}H_{18}N_2O_4S$	333.091452	333.0915	0.1	√		
151	ent-16beta-Methoxy-19-kauranoic acid	$C_{21}H_{34}O_3$	333.243518	333.2435	0.0	√		
152	Docosatrienoic acid	$C_{22}H_{38}O_2$	333.279904	333.2798	-0.3	√		
153	Dattelic acid	$C_{16}H_{16}O_8$	335.077241	335.0772	-0.2	√		

No.	Metabolites	Molecular formula	Theoretical	Experimental	Accuracy	Intensity		
			m/z	m/z	ppm	Cell	Liver	Serum
154	Erucic acid	$C_{22}H_{42}O_2$	337.311204	337.3112	0.0	√	√	
155	11-Dehydro-2,3-dinor-txb2	$C_{18}H_{28}O_6$	339.181312	339.1813	0.0	√		
156	19(20)-EpDPE	$C_{22}H_{32}O_3$	343.227868	343.2278	-0.3	√		
157	Sebacoyl-L-carnitine	$C_{17}H_{31}NO_6$	344.207861	344.2078	-0.3	√		
158	Ginkgoic acid	$C_{22}H_{34}O_3$	345.243518	345.2436	0.2	√		
159	3-Dibenzofuran-3-yl-2-(phosphonomethylamino)propanoic acid	$C_{16}H_{16}NO_6P$	348.064247	348.0643	0.0	√	√	
160	S-(Formylmethyl)glutathione	$C_{12}H_{19}N_3O_7S$	348.087095	348.0871	-0.1	√	√	
161	3-Feruloyl-1,5-quinolactone	$C_{17}H_{18}O_8$	349.092891	349.0929	0.1	√		
162	9S-hydroxy-11,15-dioxo-5Z,13E-prostadienoic acid	$C_{20}H_{30}O_5$	349.202048	349.2020	0.0	√	√	
163	3,4-Dimethyl-5-pentyl-2-furanundecanoic	$C_{22}H_{38}O_3$	349.274819	349.2748	0.0	√	√	
164	S-(2-Hydroxyethyl)glutathione	$C_{12}H_{21}N_3O_7S$	350.102745	350.1027	0.0	√		
165	Penicilloic acid	$C_{16}H_{20}N_2O_5S$	351.102016	351.1021	0.1	√		
166	2,3-Dimethoxy-5-methyl-6-(9'-carboxynonyl)-1,4-benzoquinone	$C_{19}H_{28}O_6$	351.181312	351.1813	-0.2	√	√	
167	1-dodecanoyl-glycero-3-phosphate	$C_{15}H_{31}O_7P$	353.173464	353.1728	-1.8	√	√	
168	Prostaglandin E1	$C_{20}H_{34}O_5$	353.233348	353.2334	0.1	√	√	

No.	Metabolites	Molecular formula	Theoretical	Experimental	Accuracy	Intensity		
			m/z	m/z	ppm	Cell	Liver	Serum
169	Succinyldisalicylic acid	$C_{18}H_{14}O_8$	357.061591	357.0615	-0.3	√		
170	Pantetheine 4'-phosphate	$C_{11}H_{23}N_2O_7PS$	357.089082	357.0891	0.2	√	√	
171	(S)-2-Biphenyl-4-yl-1-(1H-tetrazol-5-yl)ethylaminomethyl phosphonic acid	$C_{16}H_{18}N_5O_3P$	358.10745	358.1075	0.2		√	
172	10S,17S-DiHDoHE	$C_{22}H_{32}O_4$	359.222783	359.2227	-0.1	√		
173	Acifluorfen	$C_{14}H_7ClF_3NO_5$	359.989208	359.9892	-0.1	√	√	
174	Levofloxacin	$C_{18}H_{20}FN_3O_4$	360.136508	360.1364	-0.4	√		
175	Gibberellin A115	$C_{20}H_{26}O_6$	361.165662	361.1657	0.0	√		
176	19,20-DiHDPA	$C_{22}H_{34}O_4$	361.238433	361.2385	0.0	√		
177	Clinprost	$C_{22}H_{36}O_4$	363.254083	363.2541	0.1	√		
178	2-S-glutathionyl acetate	$C_{12}H_{19}N_3O_8S$	364.082009	364.0820	0.1	√	√	
179	Cefaclor	$C_{15}H_{14}ClN_3O_4S$	366.032078	366.0320	-0.2	√		
180	Zeanoside B	$C_{16}H_{17}NO_9$	366.083055	366.0831	0.2	√		
181	19-hydroxyprostaglandin H2(1-)	$C_{20}H_{32}O_6$	367.212612	367.2127	0.2	√	√	
182	Grifolic acid	$C_{23}H_{32}O_4$	371.222783	371.2228	-0.1	√		√
183	Menadiol disuccinate	$C_{19}H_{18}O_8$	373.092891	373.0928	-0.2	√		

No.	Metabolites	Molecular formula	Theoretical	Experimental	Accuracy	Intensity		
			m/z	m/z	ppm	Cell	Liver	Serum
184	Cicaprost	$C_{22}H_{30}O_5$	373.202048	373.2021	0.1	√	√	√
185	Calcitroic acid	$C_{23}H_{34}O_4$	373.238433	373.2384	0.0	√		
186	14-Hydroxy-E4-neuroprostane	$C_{22}H_{32}O_5$	375.217698	375.2176	-0.3		√	
187	S-Pyruvylglutathione	$C_{13}H_{19}N_3O_8S$	376.082009	376.08201	0.0		√	
188	5-oxo-pentanoic acid	$C_{14}H_{23}N_3O_7S$	376.118395	376.1184	0.0	√		
189	(2E)-2-[(4,5-Dimethoxy-2-methyl-3,6-dioxocyclohexa-1,4-dien-1-yl)methylidene]undecanoic acid	$C_{21}H_{30}O_6$	377.196962	377.1970	0.2	√	√	√
190	Dhv-PGE2	$C_{22}H_{34}O_5$	377.233348	377.2331	-0.6	√		√
191	6-Thioguanosine monophosphate	$C_{10}H_{14}N_5O_7PS$	378.027879	378.0276	-0.8		√	
192	S-Lactoylglutathione	$C_{13}H_{21}N_3O_8S$	378.097659	378.0978	0.3	√	√	
193	Sphingosine 1-phosphate	$C_{18}H_{38}NO_5P$	378.241483	378.2414	-0.2			√
194	Meticillin	$C_{17}H_{20}N_2O_6S$	379.096931	379.0968	-0.2	√		
195	Norbixin	$C_{24}H_{28}O_4$	379.191483	379.1916	0.2	√		
196	20-Cooh ltb4	$C_{21}H_{32}O_6$	379.212612	379.2126	0.0	√	√	√
197	Glufosfamide	$C_{10}H_{21}Cl_2N_2O_7P$	381.039067	381.0385	-1.4	√	√	√
198	12-Oxo-20-trihydroxy-leukotriene B4	$C_{20}H_{30}O_7$	381.191877	381.1918	-0.1	√	√	√

No.	Metabolites	Molecular formula	Theoretical	Experimental	Accuracy	Intensity		
			m/z	m/z	ppm	Cell	Liver	Serum
199	serofendic acid	$C_{21}H_{34}O_4S$	381.210504	381.2107	0.5			√
200	N6-Succinyl Adenosine	$C_{14}H_{17}N_5O_8$	382.100436	382.1004	0.0	√	√	√
201	(S)-2,3-Dihydro-3,5-dihydroxy-2-oxo-3-indoleacetic acid 5-glucoside	$C_{16}H_{19}NO_{10}$	384.093619	384.0936	-0.2	√	√	√
202	3-Hydroxydodec-6-enedioylcarnitine	$C_{19}H_{33}NO_7$	386.218426	386.2184	0.0	√		√
203	Rosmic acid	$C_{21}H_{26}O_7$	389.160577	389.1605	-0.1	√		√
204	10-Hydroperoxy-H4-neuroprostane	$C_{22}H_{32}O_6$	391.212612	391.2127	0.1	√	√	√
205	gamma-L-Glutamyl-S-(2-carboxy-1-propyl)cysteinylglycine	$C_{14}H_{23}N_3O_8S$	392.113309	392.1135	0.4	√	√	
206	1-Hydroxypyrene glucuronide	$C_{22}H_{18}O_7$	393.097976	393.0981	0.4	√		√
207	(9S,10S)-10-hydroxy-9-(phosphonooxy)octadecanoate	$C_{18}H_{37}O_7P$	395.220414	395.2206	0.5	√	√	
208	1-hexadecyl-glycero-3-phosphate	$C_{19}H_{41}O_6P$	395.256799	395.2568	-0.1	√		
209	S-adenosyl-4-methylthio-2-oxobutanoate	$C_{15}H_{20}N_5O_6S$	397.106153	397.1062	0.1	√		
210	beraprost	$C_{24}H_{30}O_5$	397.202048	397.2021	0.1	√		
211	Tris(2-butoxyethyl) phosphate	$C_{18}H_{39}O_7P$	397.236064	397.2359	-0.3	√	√	
212	3-(Acetyloxy)-2-hydroxypropyl octadecanoate	$C_{23}H_{44}O_5$	399.311598	399.3119	0.7	√		
213	Shoyuflavone B	$C_{19}H_{14}O_{10}$	401.05142	401.0512	-0.5	√	√	√

No.	Metabolites	Molecular formula	Theoretical	Experimental	Accuracy	Intensity		
			m/z	m/z	ppm	Cell	Liver	Serum
214	Dihydroresveratrol 3-glucuronide	$C_{20}H_{22}O_9$	405.119106	405.1194	0.8	√		√
215	6,8-Dihydroxy-1,7-diprenylxanthone-2-carboxylic acid	$C_{24}H_{24}O_6$	407.150012	407.1503	0.6	√		√
216	1-palmitoyl-dihydroxyacetone-phosphate	$C_{19}H_{37}O_7P$	407.220414	407.2208	0.9	√	√	
217	N-Docosahexaenoyl GABA	$C_{26}H_{39}NO_3$	412.285718	412.2859	0.3			√
218	Cephalosporin C	$C_{16}H_{21}N_3O_8S$	414.097659	414.0977	0.0		√	
219	Armillaric acid	$C_{23}H_{28}O_7$	415.176227	415.1763	0.1	√		√
220	Gaylussacin	$C_{21}H_{22}O_9$	417.119106	417.1194	0.8	√	√	
221	Artelinate	$C_{23}H_{30}O_7$	417.191877	417.1919	0.0	√		√
222	1-Piperidinyloxy, 4-(((dodecyloxy)hydroxyphosphinyl)oxy)	$C_{21}H_{43}NO_5P$	419.280609	419.2807	0.3			√
223	6-Ethylchenodeoxycholic acid	$C_{26}H_{44}O_4$	419.316683	419.3167	0.1		√	
224	Lovastatin acid	$C_{24}H_{38}O_6$	421.259562	421.2597	0.3		√	√
225	Gemcitabine diphosphate	$C_9H_{13}F_2N_3O_{10}P_2$	421.997147	421.9971	-0.1			√
226	S-(1,2-Dicarboxyethyl)glutathione	$C_{14}H_{21}N_3O_{10}S$	422.087488	422.0876	0.2	√	√	
227	Cysteineglutathione disulfide	$C_{13}H_{22}N_4O_8S_2$	425.080629	425.0807	0.1	√	√	
228	4α-carboxy-5α-cholesta-8,24-dien-3β-ol	$C_{28}H_{44}O_3$	427.321769	427.3218	0.2	√	√	√

No.	Metabolites	Molecular formula	Theoretical m/z	Experimental m/z	Accuracy ppm	Intensity Cell	Intensity Liver	Intensity Serum
229	4alpha-Carboxy-5alpha-cholesta-8-en-3beta-ol	$C_{28}H_{46}O_3$	429.337419	429.3375	0.2	√	√	√
230	Asperulosidic acid	$C_{18}H_{24}O_{12}$	431.1195	431.1191	-0.9			√
231	Aleglitazar	$C_{24}H_{23}NO_5S$	436.122417	436.1227	0.7	√	√	
232	Nonacosanoic acid	$C_{29}H_{58}O_2$	437.436405	437.4366	0.5	√		√
233	gamma-CEHC glucuronide	$C_{21}H_{28}O_{10}$	439.160971	439.1609	-0.2			√
234	Folic acid	$C_{19}H_{19}N_7O_6$	440.132405	440.1324	0.0	√	√	
235	2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9-Hexadecafluorononanoic acid	$C_9H_2F_{16}O_2$	444.972654	444.9723	-0.8			√
236	Lucuminic acid	$C_{19}H_{26}O_{12}$	445.13515	445.1347	-1.0			√
237	Corticosterone-21-hemisuccinate	$C_{25}H_{34}O_7$	445.223177	445.2233	0.3	√		
238	13'-Carboxy-gamma-tocopherol	$C_28H_{46}O_4$	445.332334	445.3324	0.1	√		√
239	Torvanol A	$C_{20}H_{20}O_{10}S$	451.070441	451.0704	-0.2			√
240	Ceanothenic acid	$C_{29}H_{42}O_4$	453.301033	453.3011	0.1			√
241	(6R)-5,10-Methylenetetrahydrofolate	$C_{20}H_{23}N_7O_6$	456.163705	456.1634	-0.6	√	√	

No.	Metabolites	Molecular formula	Theoretical	Experimental	Accuracy	Intensity		
			m/z	m/z	ppm	Cell	Liver	Serum
242	Methyltetrahydrofolic acid	$C_{20}H_{25}N_7O_6$	458.179355	458.1794	0.0		√	
243	Prednisolone hemisuccinate	$C_{25}H_{32}O_8$	459.202442	459.2025	0.1	√	√	
244	13'-Carboxy-alpha-tocopherol	$C_{29}H_{48}O_4$	459.347984	459.3480	0.1	√		√
245	Dihydroisomorphine-3-glucuronide	$C_{23}H_{29}NO_9$	462.176955	462.1770	0.1			√
246	Biotripyrrin-b	$C_{25}H_{27}N_3O_6$	464.182709	464.1827	-0.1		√	
247	Catechin 7-glucuronide	$C_{21}H_{22}O_{12}$	465.10385	465.1042	0.8		√	
248	3alpha-Androstanediol glucuronide	$C_{25}H_{40}O_8$	467.265042	467.2652	0.3			√
249	Bucladesine	$C_{18}H_{24}N_5O_8P$	468.128973	468.1293	0.7	√	√	
250	27-Hydroxyisomangiferolic acid	$C_{30}H_{48}O_4$	471.347984	471.3480	0.1	√	√	√
251	2-({4-[({2-amino-8-methyl-4,9-dioxo-6H,7H-pyrazino[1,2-a][1,3,5]triazin-dioic acid	$C_{20}H_{23}N_7O_7$	472.15862	472.1587	0.2		√	
252	Chicoric acid	$C_{22}H_{18}O_{12}$	473.07255	473.0725	0.0		√	
253	Enterolactone 3'-glucuronide	$C_{24}H_{26}O_{10}$	473.145321	473.1452	-0.3			√
254	1-O-all-trans-retinoyl-beta-glucuronic Acid	$C_{26}H_{36}O_8$	475.233742	475.2337	0.0			√
255	Enterodiol glucuronide	$C_{24}H_{30}O_{10}$	477.176621	477.1766	0.0			√
256	Cholylalanine	$C_{27}H_{45}NO_6$	478.317412	478.3170	-0.9	√		√
257	Cholesteryl hemisuccinate	$C_{31}H_{50}O_4$	485.363634	485.3636	0.0	√	√	√

No.	Metabolites	Molecular formula	Theoretical	Experimental	Accuracy	Intensity		
			m/z	m/z	ppm	Cell	Liver	Serum
258	Cytidine-5'-diphosphocholine	$C_{14}H_{26}N_4O_{11}P_2$	487.100054	487.1002	0.2	√	√	
259	Arjunolic acid	$C_{30}H_{48}O_5$	487.342898	487.3429	0.0	√		√
260	6-Methoxyluteolin 7-glucuronide	$C_{22}H_{20}O_{13}$	491.083114	491.0828	-0.6		√	
261	Pregnanediol 3-O-glucuronide	$C_{27}H_{44}O_8$	495.296342	495.2963	-0.1			√
262	N, N'-Bis(gamma-glutamyl)cystine	$C_{16}H_{26}N_4O_{10}S_2$	497.101759	497.1017	-0.2		√	
263	Medicagenic acid	$C_{30}H_{46}O_6$	501.322163	501.3222	0.1			√
264	4-O-beta-Laminaribiosyl-D-glucose	$C_{18}H_{32}O_{16}$	503.161758	503.1617	-0.2		√	
265	Protobassic acid	$C_{30}H_{48}O_6$	503.337813	503.3379	0.1			√
266	Daidzein 4'-glucuronide-7-sulfate	$C_{21}H_{18}O_{13}S$	509.039535	509.0402	1.2			√
267	Pregnanetriol 3a-O-b-D-glucuronide	$C_{27}H_{44}O_9$	511.291257	511.2911	-0.3			√
268	1-Stearoylglycerophosphoglycerol	$C_{24}H_{49}O_9P$	511.304143	511.3044	0.6	√	√	
269	Lucidenic acid D2	$C_{29}H_{38}O_8$	513.249392	513.2494	0.1	√		√
270	Tsugaric acid C	$C_{32}H_{50}O_5$	513.358548	513.3586	0.0	√		√
271	Fusidic Acid	$C_{31}H_{48}O_6$	515.337813	515.3376	-0.4			√
272	Ganosporeric acid A	$C_{30}H_{38}O_8$	525.249392	525.2493	-0.1	√		√
273	(24E)-15alpha-Acetoxy-3alpha-hydroxy-23-oxo-7,9(11),24-lanostatrien-26-oic acid	$C_{32}H_{46}O_6$	525.322163	525.3222	0.0	√		√

No.	Metabolites	Molecular formula	Theoretical	Experimental	Accuracy	Intensity		
			m/z	m/z	ppm	Cell	Liver	Serum
274	8-oxo-GTP	$C_{10}H_{12}N_5O_{15}P_3$	533.946998	533.9466	-0.8	√		
275	Formamidopyrimidine nucleoside triphosphate	$C_{10}H_{18}N_5O_{15}P_3$	539.993948	539.9938	-0.3	√	√	
276	Letermovir	$C_{29}H_{28}F_4N_4O_4$	571.197392	571.19746	0.1			√
277	Vitamin D2 3-glucuronide	$C_{34}H_{52}O_7$	571.364028	571.3641	0.1			√
278	Phosphoribulosylformimino-AICAR-P	$C_{15}H_{25}N_5O_{15}P_2$	576.074962	576.0748	-0.3		√	
279	Biliverdin	$C_{33}H_{34}N_4O_6$	581.240558	581.24006	-0.9		√	
280	Cadazolid	$C_{29}H_{29}F_2N_3O_8$	584.184995	584.18471	-0.5	√		√
281	18-Dehydroursolic acid 3-arabinoside	$C_{35}H_{54}O_7$	585.379678	585.37987	0.3	√		√
282	25-Hydroxyvitamin D2-25-glucuronide	$C_{34}H_{52}O_8$	587.358942	587.35882	-0.2	√		√
283	Oxidized glutathione	$C_{20}H_{32}N_6O_{12}S_2$	611.144686	611.14485	0.3	√	√	√
284	Cholestane-3,7,12,25-tetrol-3-glucuronide	$C_{33}H_{56}O_{10}$	611.380072	611.38078	1.2			√
285	Perfluorododecanoic acid	$C_{12}HF_{23}O_2$	612.953652	612.95375	0.2			√
286	APC	$C_{33}H_{38}N_4O_8$	617.261688	617.26164	-0.1			√
287	CMP-N-glycoloylneuraminate	$C_{20}H_{31}N_4O_{17}P$	629.134906	629.13451	-0.6		√	
288	Dihydrotestosterone diglucuronide	$C_{31}H_{46}O_{14}$	641.28148	641.28118	-0.5			√

No.	Metabolites	Molecular formula	Theoretical	Experimental	Accuracy	Intensity		
			m/z	m/z	ppm	Cell	Liver	Serum
289	Esculentoside E	$C_{35}H_{54}O_{11}$	649.359336	649.35901	-0.5		√	
290	Cefpimizole	$C_{28}H_{26}N_6O_{10}S_2$	669.107907	669.10721	-1.0	√		
291	Gomphrenin II	$C_{33}H_{32}N_2O_{15}$	695.172992	695.17257	-0.6			√
292	a-L-threo-4-Hex-4-enopyranuronosyl-D-galacturonic acid	$C_{12}H_{16}O_{12}$	351.0569	351.0570	0.3		√	
293	GSH	$C_{10}H_{17}N_3O_6S$	306.07653	306.0766	0.1	√	√	
294	Cholesterol sulfate	$C_{27}H_{46}O_4S$	465.3044	465.3045	0.2	√	√	√
295	Asp-ala	$C_7H_{12}N_2O_5$	203.067365	203.0674	0.2			√
296	GSSG	$C_{20}H_{32}N_6O_{12}S_2$	611.144685	611.1447	0.0	√	√	√
	LPA							
297	LPA(a-13:0)	$C_{16}H_{33}O_7P$	367.189113	367.1887	-1.2	√	√	
298	LPA(16:0)	$C_{19}H_{39}O_7P$	409.236064	409.2362	0.3	√	√	√
299	LPA(18:2)	$C_{21}H_{39}O_7P$	433.236064	433.2361	0.1			√
300	LPA(18:0)	$C_{21}H_{43}O_7P$	437.267364	437.2677	0.7	√	√	√
301	LPA(20:4)	$C_{23}H_{39}O_7P$	457.236064	457.2362	0.3			√
302	LPA(22:6)	$C_{25}H_{39}O_7P$	481.236064	481.2361	0.1			√

No.	Metabolites	Molecular formula	Theoretical	Experimental	Accuracy	Intensity		
			m/z	m/z	ppm	Cell	Liver	Serum
303	LPA(p-16:0)	$C_{19}H_{39}O_6P$	393.241149	393.2412	0.2	√		√
304	LPA(O-18:0)	$C_{21}H_{45}O_6P$	423.288099	423.2880	-0.3	√		
	LPE							
305	LPE(16:0)	$C_{21}H_{44}NO_7P$	452.278263	452.2783	0.0		√	
306	LPE(18:0)	$C_{23}H_{48}NO_7P$	480.309563	480.3098	0.5	√	√	√
307	LPE(18:1)	$C_{23}H_{46}NO_7P$	478.293913	478.2940	0.1		√	√
308	LPE(18:2)	$C_{23}H_{44}NO_7P$	476.278263	476.2783	0.1		√	
309	LPE(20:4)	$C_{25}H_{44}NO_7P$	500.278263	500.2785	0.4		√	√
310	LPE(22:2)	$C_{27}H_{52}NO_7P$	532.340863	532.3407	-0.3	√		
311	LPE(p-16:0)	$C_{21}H_{44}NO_6P$	436.283348	436.2838	1.1			√
	LPI							
312	LPI(16:0)	$C_{25}H_{49}O_{12}P$	571.288887	571.2885	-0.7	√	√	
313	LPI(17:0)	$C_{26}H_{51}O_{12}P$	585.304537	585.3042	-0.6	√	√	
314	LPI(18:0)	$C_{27}H_{53}O_{12}P$	599.320187	599.3206	0.7			√
315	LPI(18:1)	$C_{27}H_{51}O_{12}P$	597.304537	597.3040	-0.9		√	
316	LPI(18:2)	$C_{27}H_{49}O_{12}P$	595.288887	595.2883	-0.9		√	

No.	Metabolites	Molecular formula	Theoretical	Experimental	Accuracy	Intensity		
			m/z	m/z	ppm	Cell	Liver	Serum
317	LPI(18:3)	$C_{27}H_{45}O_{12}P$	591.257587	591.2574	-0.4	√		
318	LPI(20:3)	$C_{29}H_{51}O_{12}P$	621.304537	621.3044	-0.2	√		√
319	LPI(20:1)	$C_{29}H_{55}O_{12}P$	625.335837	625.3356	-0.3	√		
320	LPI(20:0)	$C_{29}H_{57}O_{12}P$	627.351487	627.3516	0.1	√	√	
321	LPI(22:4)	$C_{31}H_{53}O_{12}P$	647.320187	647.3201	-0.1	√		
322	LPI(22:5)	$C_{31}H_{51}O_{12}P$	645.304537	645.3046	0.1	√	√	
323	LPI(22:6)	$C_{31}H_{49}O_{12}P$	643.288887	643.2882	-1.0		√	
	PE							
324	PE(34:2)	$C_{39}H_{74}NO_8P$	714.507928	714.5073	-0.9		√	
325	PE(36:4)	$C_{41}H_{74}NO_8P$	738.507928	738.5071	-1.1		√	
326	PE(36:3)	$C_{41}H_{76}NO_8P$	740.523578	740.5235	-0.1	√		
327	PE(36:2)	$C_{41}H_{78}NO_8P$	742.539229	742.5392	-0.1			√
328	PE(38:4)	$C_{43}H_{78}NO_8P$	766.539229	766.5398	0.8			√
	PS							
329	PS(36:4)	$C_{42}H_{74}NO_{10}P$	782.497758	782.4977	0.0			√
	LPS							

No.	Metabolites	Molecular formula	Theoretical	Experimental	Accuracy	Intensity		
			m/z	m/z	ppm	Cell	Liver	Serum
330	LPS(16:0/0:0)	$C_{22}H_{44}NO_9P$	496.268092	496.2683	0.3	√		
331	LPS(18:2(9Z,12Z)/0:0)	$C_{24}H_{44}NO_9P$	520.268092	520.2680	-0.1	√	√	
332	LPS(18:1(9Z)/0:0)	$C_{24}H_{46}NO_9P$	522.283742	522.2839	0.2	√	√	
333	LPS(18:0/0:0)	$C_{24}H_{48}NO_9P$	524.299392	524.2994	0.0	√	√	
	PI							
334	PI(32:2)	$C_{41}H_{77}O_{13}P$	807.502903	807.5029	0.0			√
335	PI(32:1)	$C_{41}H_{79}O_{13}P$	809.518553	809.5181	-0.6			√
336	PI(34:3)	$C_{43}H_{77}O_{13}P$	831.502903	831.5024	-0.6			√
337	PI(34:2)	$C_{43}H_{79}O_{13}P$	833.518553	833.5184	-0.2			√
338	PI(36:2)	$C_{45}H_{83}O_{13}P$	861.549853	861.5495	-0.4			√
339	PI(38:5)	$C_{47}H_{81}O_{13}P$	883.534203	883.5347	0.6			√
340	PI(38:4)	$C_{47}H_{83}O_{13}P$	885.549853	885.5499	0.1		√	
	PG							
341	PG(34:2)	$C_{40}H_{75}O_{10}P$	745.502509	745.5022	-0.5			√
342	PG(34:1)	$C_{40}H_{77}O_{10}P$	747.518159	747.5188	0.9			√
343	PG(36:1)	$C_{42}H_{81}O_{10}P$	775.549459	775.5493	-0.3	√		

No.	Metabolites	Molecular formula	Theoretical m/z	Experimental m/z	Accuracy ppm	Intensity Cell	Intensity Liver	Intensity Serum
344	PG(38:3)	$C_{44}H_{81}O_{10}P$	799.549459	799.5496	0.1	√		
345	PG(38:1)	$C_{44}H_{85}O_{10}P$	803.580759	803.5804	-0.5	√		
	LPG							
346	LPG(16:0/0:0)	$C_{22}H_{45}O_9P$	483.272843	483.2729	0.0	√	√	
347	LPG(18:2(9Z,12Z)/0:0)	$C_{24}H_{45}O_9P$	507.272843	507.2731	0.5		√	
348	LPG(18:1(9Z)/0:0)	$C_{24}H_{47}O_9P$	509.288493	509.2886	0.1	√	√	
	PA							
349	PA(8:0/16:0)	$C_{27}H_{53}O_8P$	535.340529	535.3405	-0.1	√		
350	PA(30:2)	$C_{33}H_{61}O_8P$	615.403129	615.4037	0.9		√	
351	PA(30:1)	$C_{33}H_{63}O_8P$	617.418779	617.4184	-0.5	√	√	
352	PA(30:0)	$C_{33}H_{65}O_8P$	619.434429	619.4342	-0.3	√		
353	PA(32:2)	$C_{35}H_{65}O_8P$	643.434429	643.4340	-0.6		√	
354	PA(34:2)	$C_{37}H_{69}O_8P$	671.465729	671.4653	-0.7		√	
355	PA(36:4)	$C_{39}H_{69}O_8P$	695.465729	695.4654	-0.5		√	
356	PA(36:2)	$C_{39}H_{73}O_8P$	699.497029	699.4974	0.5		√	√
	FA							

No.	Metabolites	Molecular formula	Theoretical	Experimental	Accuracy	Intensity		
			m/z	m/z	ppm	Cell	Liver	Serum
357	FA(16:0(-OH))	$C_{16}H_{32}O_3$	271.227868	271.2276	-0.9	√	√	√
358	FA(20:2)	$C_{18}H_{32}O_2$	279.232954	279.2329	-0.3	√	√	√
359	FA(22:0)	$C_{22}H_{44}O_2$	339.326854	339.3267	-0.4	√	√	
360	FA(23:0)	$C_{23}H_{46}O_2$	353.342504	353.3425	0.0	√	√	√
	FAHFA							
361	FAHFA(16:0/9-O-16:0)	$C_{32}H_{62}O_4$	509.457534	509.4576	0.2			√
362	FAHFA(16:1(9Z)/9-O-18:0)	$C_{34}H_{64}O_4$	535.473184	535.4731	-0.1	√		
363	FAHFA(16:0/9-O-18:0)	$C_{34}H_{66}O_4$	537.488834	537.4888	0.0	√		
364	FAHFA(18:1(9Z)/12-O-18:0)	$C_{36}H_{68}O_4$	563.504484	563.5045	0.0	√	√	√
	CPA							
365	CPA(16:0)	$C_{19}H_{37}O_6P$	391.225499	391.2255	0.1	√	√	√
366	CPA(18:2(9Z,12Z)/0:0)	$C_{21}H_{37}O_6P$	415.225499	415.2251	-1.1		√	
367	CPA(18:1(11Z)/0:0)	$C_{21}H_{39}O_6P$	417.241149	417.2411	-0.2	√		
368	CPA(18:0/0:0)	$C_{21}H_{41}O_6P$	419.256799	419.2569	0.1	√		√
	Total of 368 anionic metabolites					**252**	**173**	**136**

Table S14. The list of isotopic internal standards identified by FTICR MS in 3 biological samples based on standards.

Isotopic internal standards	Molecular formula	Theoretical m/z
UTP	$^{13}C_9H_{15}{}^{15}N_2O_{15}P_3$	493.985478
GTP	$^{13}C_{10}H_{16}N_5O_{14}P_3$	532.016894
dGMP	$^{13}C_{10}H_{14}{}^{15}N_5O_7P$	361.074488
UMP	$C_9H_{13}{}^{15}N_2O_9P$	325.022658

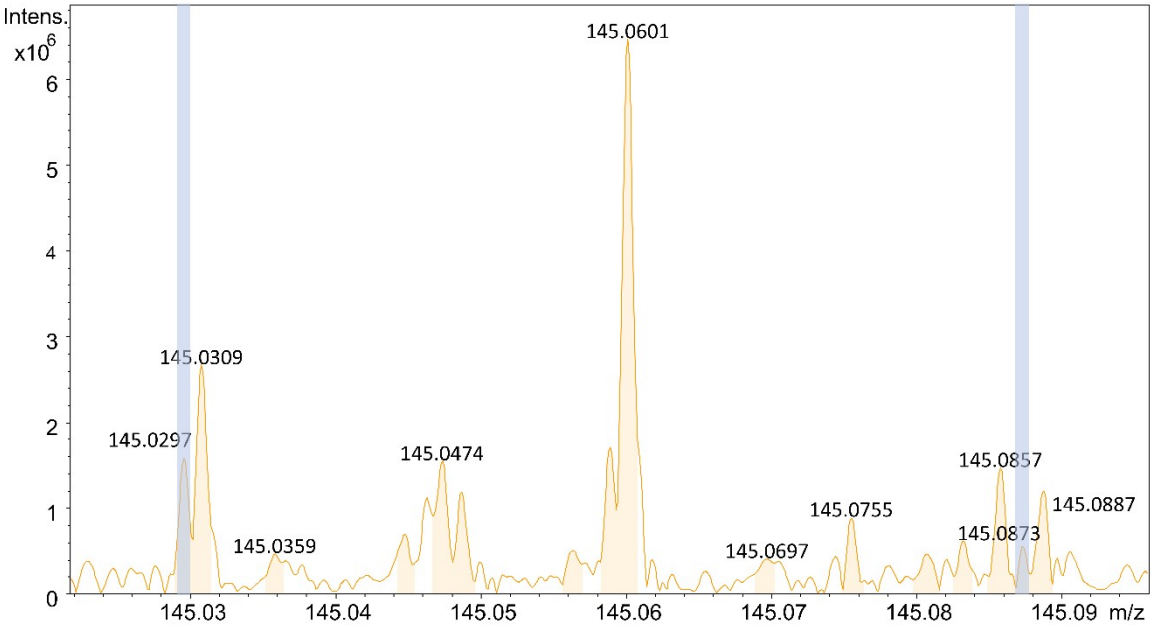

Fig S16. The FTICR MS can be differ the isomer with similar mass data such as 145.0297 to 145.0873.

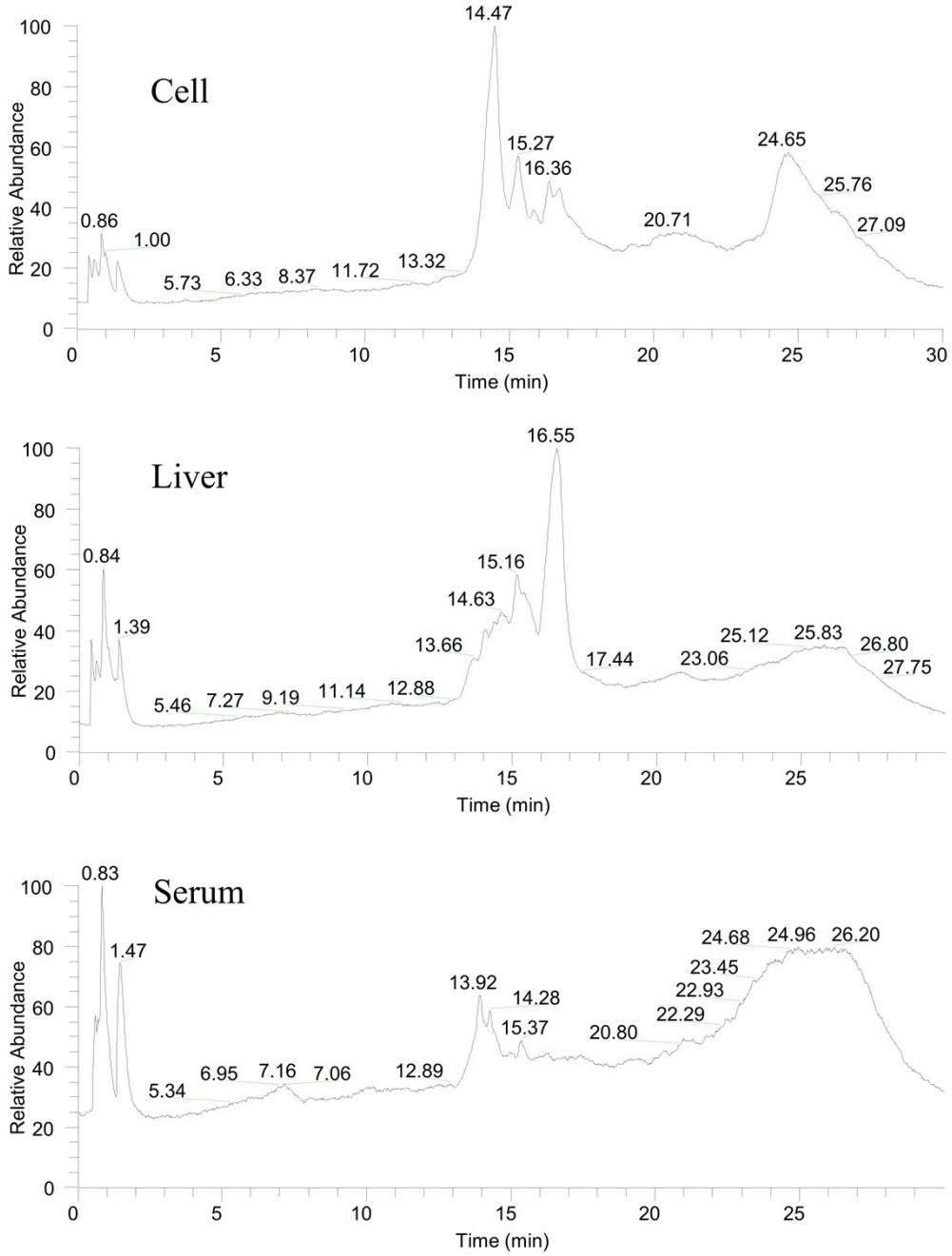

Fig S17. The typical HPLC chromatogram of different biological samples.

References

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