SUPPORTING INFORMATION

EXPERIMENTAL SECTION

1. Materials

N, N-Diisopropylethylamine (DIPEA) was purchased from Fluorochem (Derbyshire, UK). Sodium cyanoborohydride ($NaBH_3CN$) was obtained from Aladdin (Shanghai, China). Glacial acetic acid, sodium dithionite ($Na_2S_2O_4$), L-methionine (Met), L-leucine (Leu), L-tryptophan (Trp), L-alanyl-L-alanine (Ala-ala), 2-(7-aza-1H-benzotriazole-1-yl)-1,1,3,3-tetramethyluronium-hexafluorophosphate (HATU), phenylethylamine, p-anisidine, L-proline (Pro), acetanilide and isobutylamine were obtained from J&K (Shanghai, China). Methanol and acetonitrile were purchased from Merck (Dermstadt, Germany). Isopropanol was obtained from Tedia (Fairfield, OH). Water was purified by Milli-Q system (Millipore, Milford, MA). 4-Nitroaniline, 4-dimethylaminobenzoic acid, cyclohexylamine, heptylamine, N-acetyl-L-glutamic acid, 4-nitrophenol, 2-phenylphenol and N-hydroxysuccinimide (NHS) were purchased from Alfa Aesar (Tianjin, China). Formaldehyde-d_2 solution (25%), hexadecyltrimethyl ammonium bromide (CTAB), formic acid (FA), tetraethoxysilane (TEOS), 4-aminobenzoic acid, aminopropyltriethoxysilane (APTES), glycine (Gly), 4-aminobutyric acid (GABA), 3-ethyl-5-methylphenol, 1-phenylethanolamine, oleamide, and dansyl chloride were obtained from Sigma (St. Louis, MO). d_6-Dansyl chloride was purchased from International Laboratory USA (South San Francisco, CA, USA). Propylamine and 2-phenylacetamide were obtained from TCI (Tokyo, Japan). Guaiacol was purchased from Acros (Morris Plains, NJ, USA)，and N-methyltyramine was from chromadex (Irvine, CA, USA). Other chemical reagents were all analytical grade. The amino acids mixture are each 500 ng/mL Met, Gly, Leu, Trp, Ala-ala; the aliphatic amines mixture are each 500 ng/mL isobutylamine, propylamine, cyclohexylamine, and heptylamine; the aromatic amines mixture are each 5 ug/mL N-methyltyramine, dopamine, p-anisidine, N-methylanthranilic acid and 1-phenylethanolamine; the amides mixture are each 5 μg/mL oleamide, 2-phenylacetamide, N-acetyl-L-glutamic acid, and acetanilide; the phenolic hydroxyl standards are each 5 μg/mL guaiacol, 4-nitrophenol, 3-ethyl-5-methylphenol and 2-phenylphenol；The mixed amino standards are composed by 1 μg/mL Ala-ala, Met, GABA, Leu, Trp, isobutylamine, propylamine, cyclohexylamine, heptylamine, N-methyltyramine, dopamine, Pro, p-anisidine, N-methylanthranilic acid and tyramine.

2. Synthesis and purification of cleavable azobenzene linker

The synthetic scheme was shown as Figure S1, 2.76 g 4-nitroaniline was dissolved in 600 mL CH_3OH: H_2O (2:1, v/v) in ice bath, then added newly prepared HNO_2 under stirring which was synthesized with $NaNO_2$ (1.38g) and 3.5 mL HCl (37%) in 20 mL H_2O at 0 °C. After one hour, the product was transferred into 400 mL 4-dimethylaminobenzoic acid (3.3 g) methanol solution directly in ice bath. The reaction was last for over night in stirring. [1] The precipitated product was filtered and washed with water for several times, then dried in vacuum at 60 °C and purified with SiO_2 column chromatography with ethyl acetate and cyclohexane as eluent to obtain 4-(dimethylamino)-3-((4-nitrophenyl)diazenyl)benzoic acid (donated as NO_2-azobenzene-COOH). ^{1}H NMR spectrum of NO_2-azobenzene-COOH in DMSO-d_6 is δ 12.59 (s, 1H, COOH), 8.4 (d, 2H,

J=9.2Hz, ArH), 8.25 (d, 1H, J=2, ArH), 8.02 (d, 2H, J=8.8 Hz, ArH), 7.87 (dd, 1H, J=2, 9.2 Hz, ArH), 7.12 (d, 1H, J=9.2 Hz, ArH), 3.29 (s, 6H, NCH_3).

D_4-4-Dimethylaminobenzoic acid was prepared with the previous method [2] (Figure S1c) and D_4-NO_2-azobenzene-COOH was synthesized with the above-mentioned procedure. The H_4/D_4 tagged NO_2-azobenzene-COOH were mixed at the same molar ratio and dissolved in 90 mL ethanol. Their nitro groups were reduced into amino groups with two equivalent Na_2S at refluxing temperature at 90 °C for 3 hour to produce H_4/D_4 tagged 3-((4-aminophenyl)diazenyl)-4-(dimethylamino)benzoic acid (donated as NH_2-azobenzene-COOH) [3] (Figure S1d).

3. Synthesis of $mSiO_2$@azobenzene-COOH nanoprobes.

0.3 g CTAB was dissolved in 150 mL H_2O, then 1.05 mL 2 M NaOH was added to adjust pH after the temperature of reaction solution was elevated to 60 ℃. 1.5 mL TEOS was added into reaction solution under stirring, and the reaction was last for 2 hours at 60 ℃. The products were centrifuged (14000 rpm, 10 min) and washed with ethanol for several times, subsequently dispersed into 0.5 mg/mL NH_4NO_3/ethanol solution to remove CTAB at 70 ℃ for 3 hours under stirring. The products were washed with methanol for several times and dried under vacuum (60 ℃) to get $mSiO_2$ nanoparticles. 1 g $mSiO_2$ nanoparticles were dispersed into 600 mL isopropanol, then 10 mL APTES was added and the reaction was last for overnight at room temperature under argon protection and stirring. The products were centrifuged (14000 rpm, 10 min) and washed with methanol for several times, and then dispersed into 300 mL acetic acid/methanol (1:125, v/v), 10 mL 25% glutaraldehyde was added after the temperature was elevated to 40 ℃. The reaction was last for overnight at 40 ℃ under stirring. The obtained products obtained were centrifuged (14000 rpm, 10 min) and washed with 30 mL acetic acid/methanol (1:125, v/v) for two times and then redispersed into 300 mL acetic acid/methanol (1:125, v/v). 50 mL 1:1 molar ratio H_4/D_4-NH_2-azobenzene-COOH (0.05 mmoL each) and 500 mg $NaBH_3CN$ were added at 40 ℃ under stirring. The reaction was last for overnight. The products were washed with methanol, ethanol, water and acetonitrile for several times to get $mSiO_2$@azobenzene-COOH nanoprobes.

4. Characterization.

Nitrogen sorption measurements (Quadrasorbsi, USA)，fourier transform infrared spectra (Equinox 55, Bruker, Germany)，zeta-potential (Zetasizer Nano, Malvern, United Kingdom)，transmission electron microscopy (JEM-2000EX, JEOL, Japan)，and ^1H nuclear magnetic resonance (400MHz, Bruker, Switzerland) were used for the characterization of the synthetic materials.

5. Optimization of the extraction and cleavage conditions

Eight mg $mSiO_2$@azobenzene-COOH nanoprobes were activated with each 200 μL of a certain concentration of HATU, DIPEA and NHS，and the activating time was optimized from 2 min to 120 min. After activated, the nanoprobes were centrifuged (18920 g for 3 min) and washed with 1 mL 80% ACN for three times and 1 mL ACN for two times. One mL phenylethylamine solution (100 μg/mL) was subsequently added for extracting. The coupling time of nanoprobes with phenylethylamine was optimized from 2 min to 240 min. Nanoprobes were then collected with centrifuge and the residual phenethylamine in supernatant was detected with MS. The coupling nanoprobes were then washed with 80% ACN for three times and dispersed into 300 μL ACN，

after dispersed by ultrasound for 1 min，an equal volume of various concentrations of $Na_2S_2O_4$ (from 0.01 M to 0.5 M) was used to cleave the azo bond. The resulting solution was extracted three times with 300 μL ethyl acetate. The extracts were combined, lyophilized and reconstituted with 40 μL 80% ACN before MS analysis.

6. Treatment of mixed standards, blank and serum

Forty mg $mSiO_2$@azobenzene-COOH nanoprobes were activated with each 200 μL of 10 mM HATU, DIPEA, NHS for 2 min, the nanoprobes were collected by centrifuge, and then washed with 80% ACN (three times) and ACN (two times). 100 μL of the amino acids, aliphatic amines, aromatic amines，amides mixture or phenolic hydroxyl standards were diluted to 1 mL with ACN and added subsequently into the activated nanoprobes. After dispersed by ultrasound for 1 min and shaken for 5 min, the nanoprobes were separated, washed and cleaved with 0.2 M $Na_2S_2O_4$ as the above mentioned. 1 ml ACN (as the blank) was also treated by $mSiO_2$@azobenzene-COOH nanoprobes with the same process. For comparison, 100 μL of the mixed amino and phenolic hydroxyl standards were derivatized with dansyl chloride as the literature reported.[4]

20 μL thawed serum was filtered with centrifugal filter (3000 Da cutoff, Millipore, USA) to remove proteins and most peptides, and the residue was washed three times with 200 μL H_2O. The filtrate was transferred to phospholipid removal 96-well plate (Phenomenex, USA) directly to remove matrix effects. The filtrate was lyophilized and reconstituted with 1 mL ACN and then treated with $mSiO_2$@azobenzene-COOH nanoprobes or reconstituted with 20 μL H_2O and derivatized with dansyl chloride/d_6-dansyl chloride (equimolar ratio).

7. Method validation

To investigate the linearity of the method, 1 mL mixed standards including Leu-d_3，Trp-d_5，Met-d_3 from 1ng/mL to 1000 ng/mL were respectively extracted with the nanoprobes. 980 μL of 200 ng/mL Leu-d_3, Trp-d_5, Met-d_3 standards were added into 20 μL serum or H_2O to verify the recovery and precision. After mixed for 1min and centrifuged at 18920g for 10 min, the solution or the supernatant was extracted with $mSiO_2$@azobenzene-COOH nanoprobes. The mixed amino standards (1 μg/mL) were diluted 2-100000 fold and then derivatized with dansyl chloride and $mSiO_2$@azobenzene-COOH nanoprobes respectively to study the LOD (S/N=3).

8. LC/MS analysis

To optimize the extraction and cleavage conditions, Agilent 1200 UHPLC equipped with 6510 Q-TOF mass spectrometer was used. An isocratic separation was performed on a C_8 column (2.1×100 mm, 1.7 μm, Waters, Ireland) with ACN and 0.1% FA water (2:3, v/v) as mobile phases at 0.3 mL/min for 3 min. The injection volume was 1 μL and the column temperature was set at 40 °C. The MS detection was at positive mode and the ions of m/z 122.0964 and 284.1757 were used to monitor phenylethylamine and its derivatized product respectively. Other MS parameters were the same as the previous work.[5]

For mixed standards, blank and serum sample analysis, Acquity UPLC (waters, USA) liquid system coupled with LTQ-Orbitrap XL (Thermo Fisher Scientific, Rockford, IL, USA) was used. All of the samples were separated on a C_8 column (2.1×100 mm, 1.7 μm, Waters, Ireland). The injection volume was 10 μL and the column temperature was set at 40 °C. The mobile phases were water containing 0.1% FA and ACN at flow rate of 0.3 mL/min. A relatively fast gradient

separation was applied to the mixed standard analysis. The initial gradient (2% ACN) was increased linearly to 80% ACN in 6 min，followed with column washing for 3 min at 80% ACN, then was returned to the initial gradient and rebalanced for 6 min. The blank and serum samples were separated with a slow gradient to reduce peaks overlap. The initial gradient (2% ACN) was increased linearly to 98% ACN in 25 min，then kept for 3 min and returned to the initial for re-equilibrium for 3 min. The MS parameters were as follows: source voltage at 4.5 kV, capillary voltage at 32 V, and capillary temperature at 325 °C. The mass scan range was from 100 to 800 in positive mode and the resolution was set at 30,000.

9. Data Processing.

The peaks from blank and serum samples were picked with Sieve X86 software (Thermo Fisher Scientific, USA). The retention time period 1-5 min, 5-10 min, 10-15 min, 15-20 min and 20-28min were processed separately. The maximum frames number was 5,000. Those ions from m/z 185-800 with a frame time width of 0.5 min, m/z width of 15 ppm, and ion intensity more than 3000 were picked out. The obtained peak table with retention time and m/z value information was processed by in-house developed software for picking those ion pairs with m/z difference of 4.0252±0.001 and drift of the retention time shorter than 15 s between H_4 and D_4 tagged derivatization products. Unknown compounds were identified through Metlin (http://metlin.scripps.edu/index.php) and HMDB (http://www.hmdb.ca) databases. 21 amino metabolite standards were derivatized individually with mSiO_2@azobenzene-COOH nanoprobes for verification.

References

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[3] Kim, T.; Jung, J.; Jang, K.; Yoon, S.; Kim, M. Synthesis and application of alkyl-substituted high chroma yellow dyes for unmodified polypropylene fiber. *Fiber Polym.* 2009, 10, 148-153

[4] Guo, K.; Li, L. Differential 12C-/13C-isotope dansylation labeling and fast liquid chromatography/mass spectrometry for absolute and relative quantification of the metabolome. *Anal. Chem.* 2009, 81, 3919-3932.

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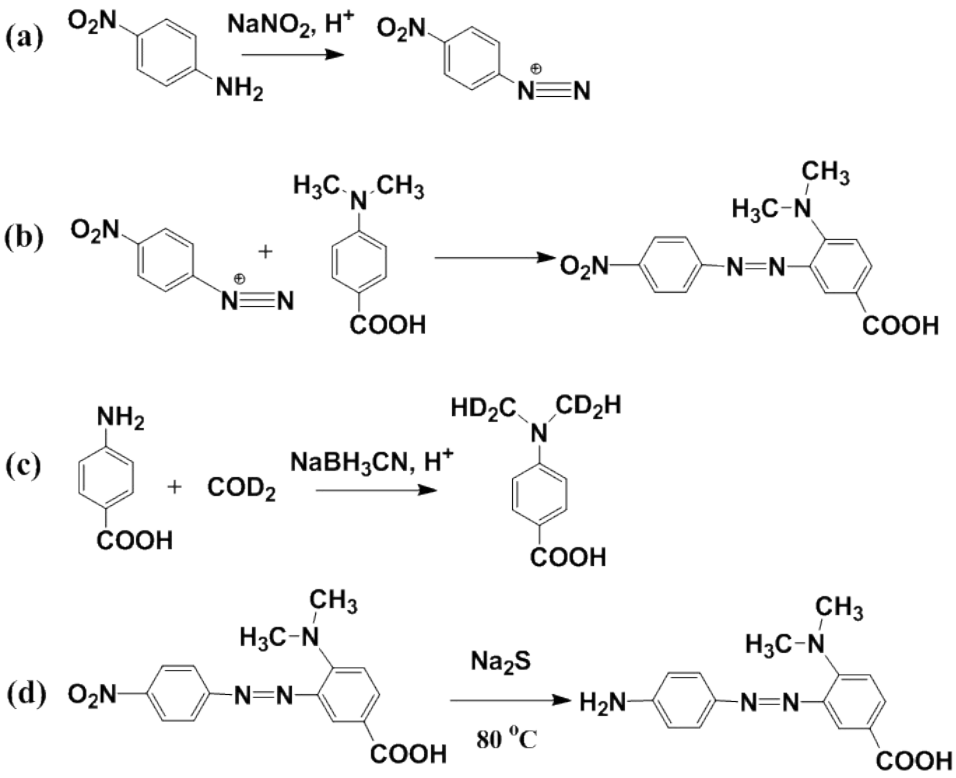
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O2N
NaNO2, H+
NH2
N≡N
(b)
H3C N CH3
COOH
CH3
H3C–N
N=N
(c)
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COOH
+ COD2
NaBH3CN, H+
HD2C N CD2H
(d)
Na2S
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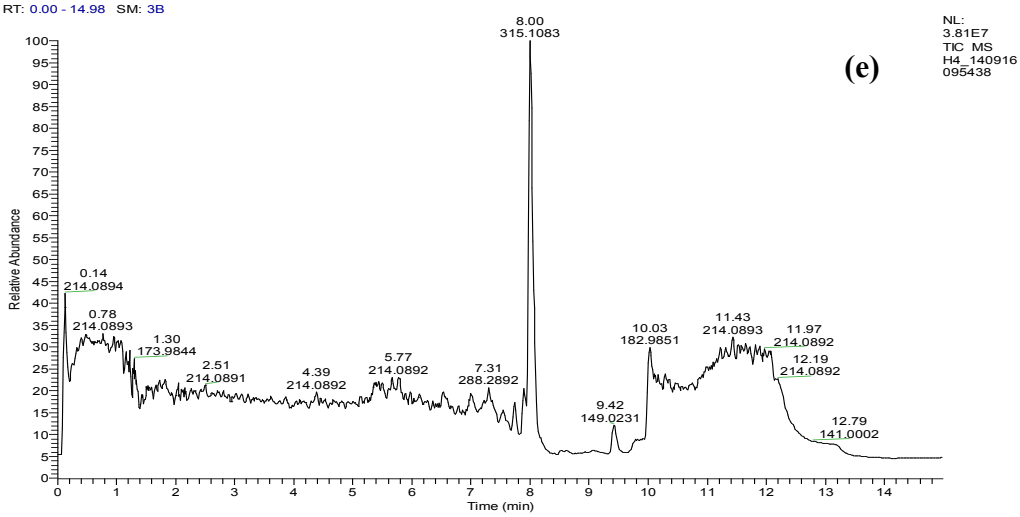
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5.77
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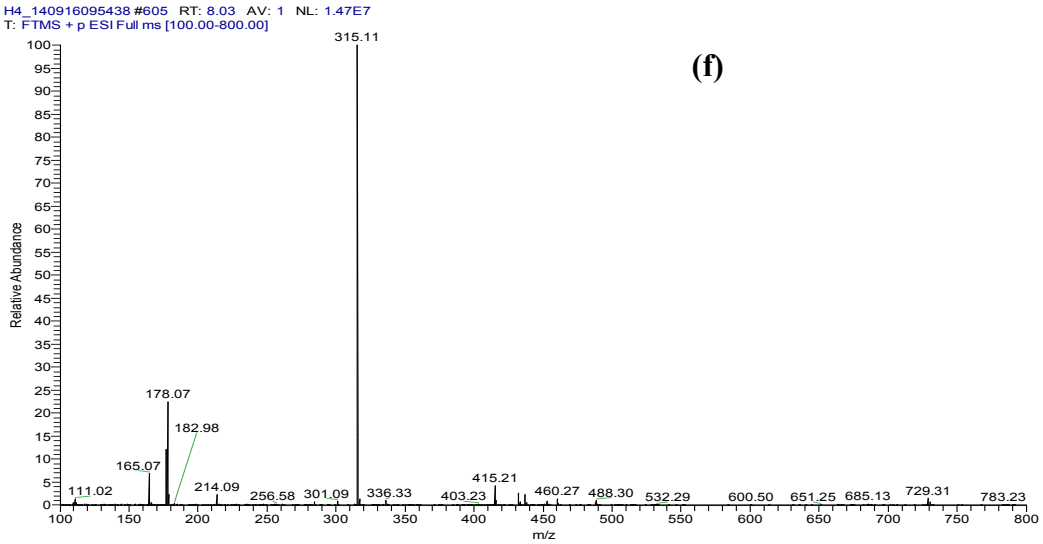
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403.23
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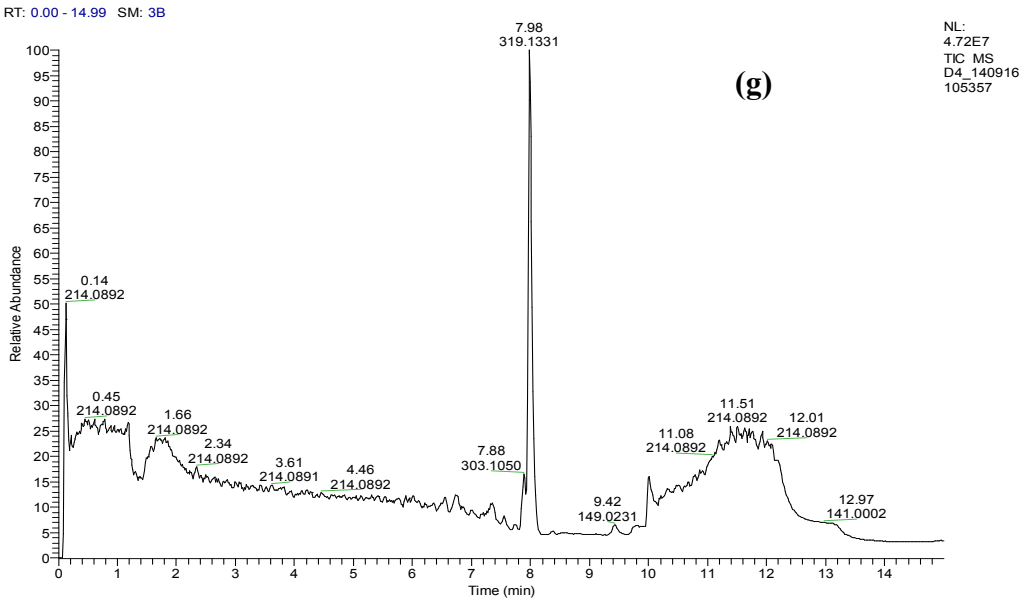
Relative Abundance
m/z

(f)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141.0002
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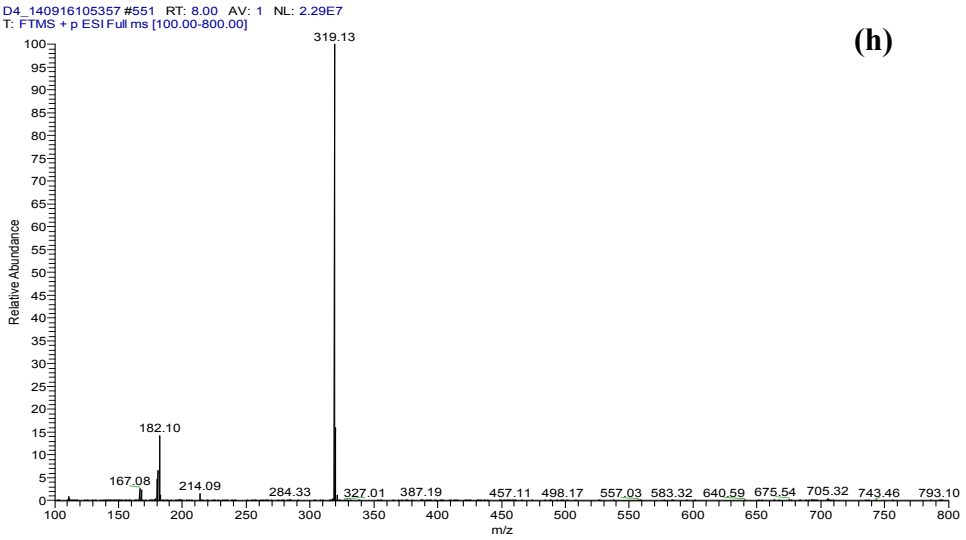
Time (min)

(g)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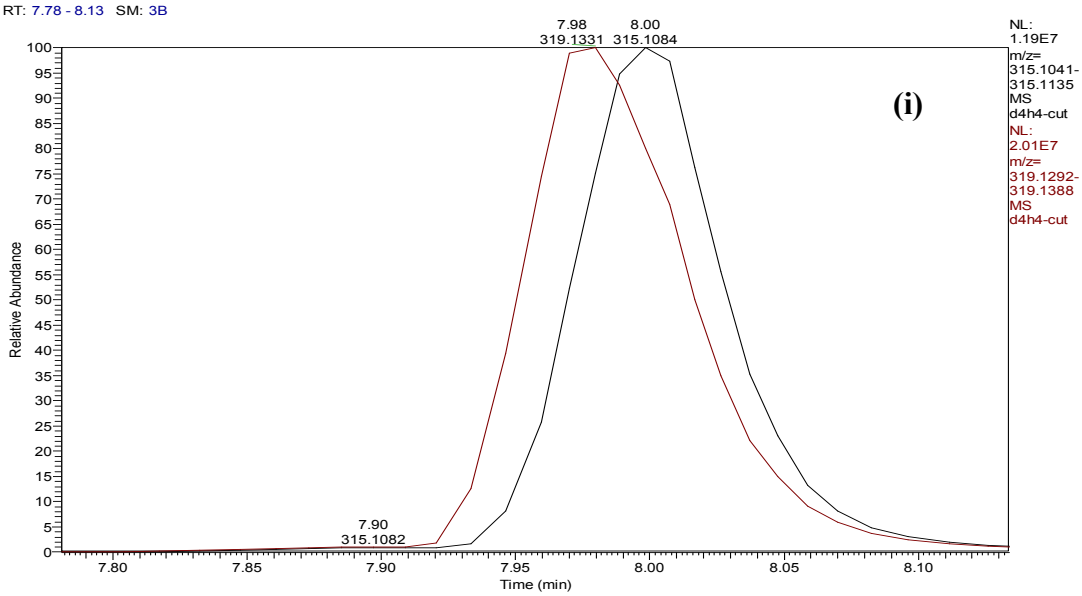
Relative Abundance
m/z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MS
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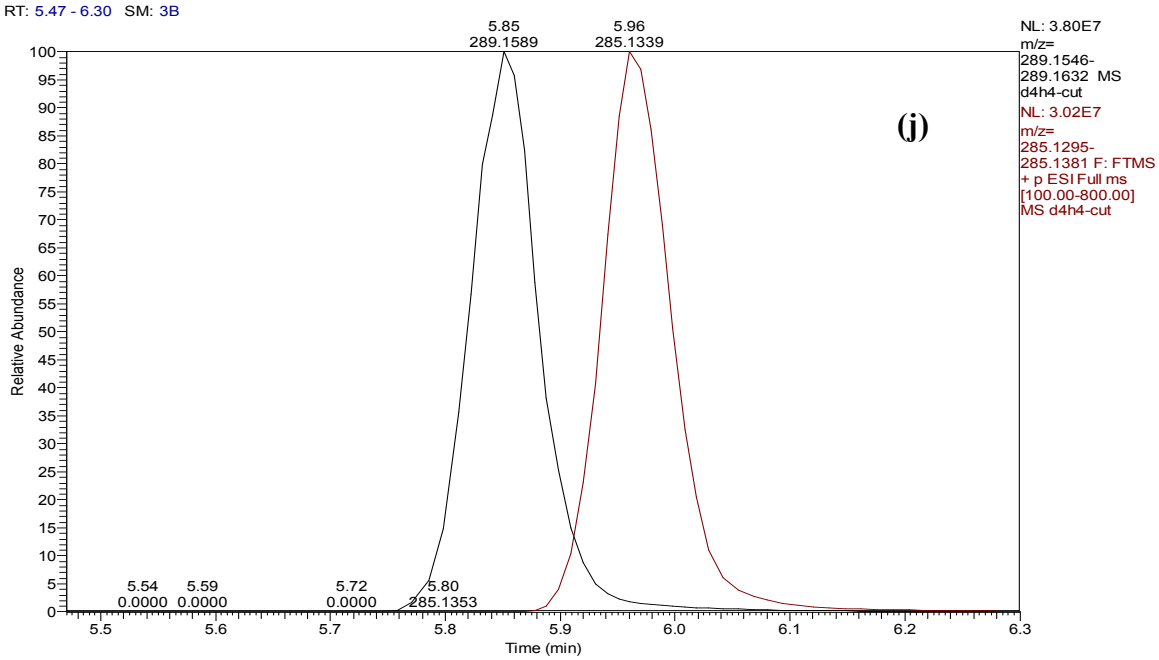
Relative Abundance
Time (min)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MS d4h4-cut
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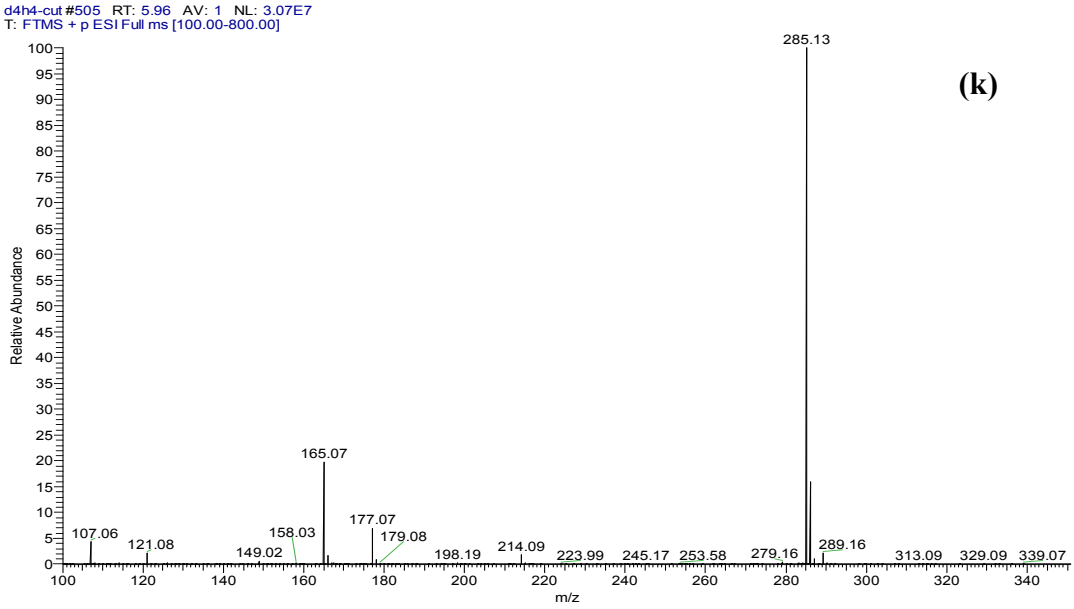
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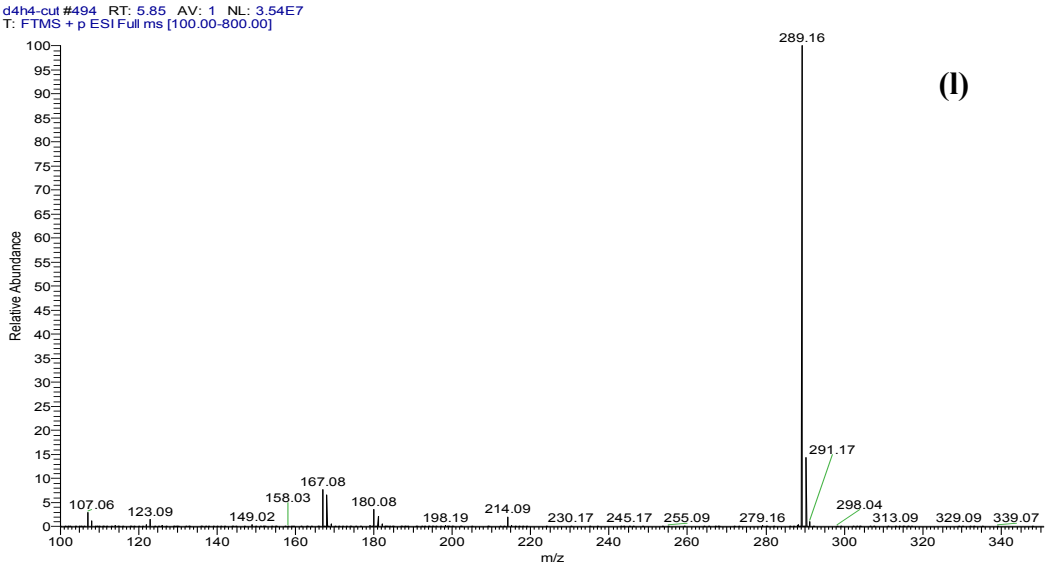

Figure S1. Synthetic approach of azobenzoic acid linkers (a-d); the total ion chromatogram of NO_2-azobenzene-COOH and its m/z spectrum (e-f); the total ion chromatogram of D_4-NO_2-azobenzene-COOH and its m/z spectrum (g-h); the extracted ion chromatograms of NO_2-azobenzene-COOH and D_4-NO_2-azobenzene-COOH mixture (i); extracted ion chromatograms of NH_2-azobenzene-COOH and D_4-NH_2-azobenzene-COOH mixture (j); m/z spectrum of NH_2-azobenzene-COOH (k) and D_4-NH_2-azobenzene-COOH (l).

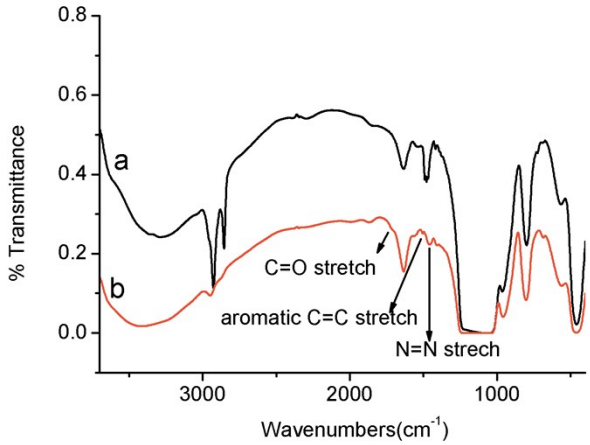

Figure S2. FT-IR spectroscopy of $mSiO_2$-NH_2 (a) and $mSiO_2$@azobenzene-COOH (b) nanoparticles

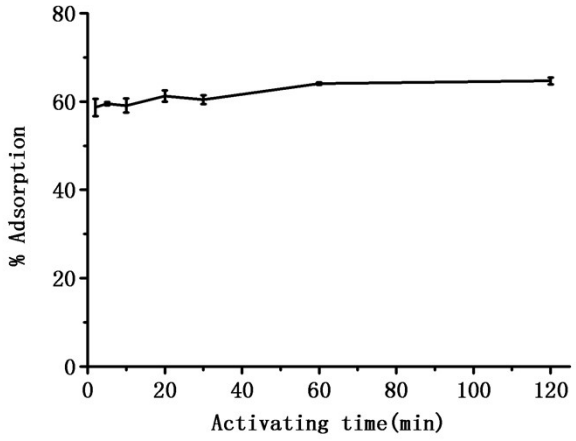

Figure S3. Optimization of activating time

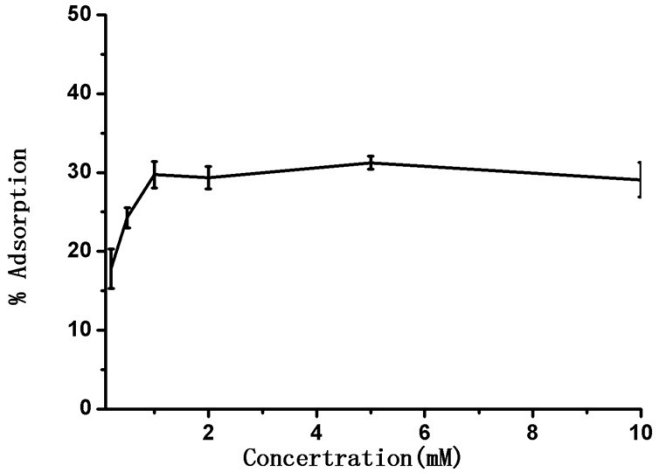

Figure S4. Optimization of the concentration of activator

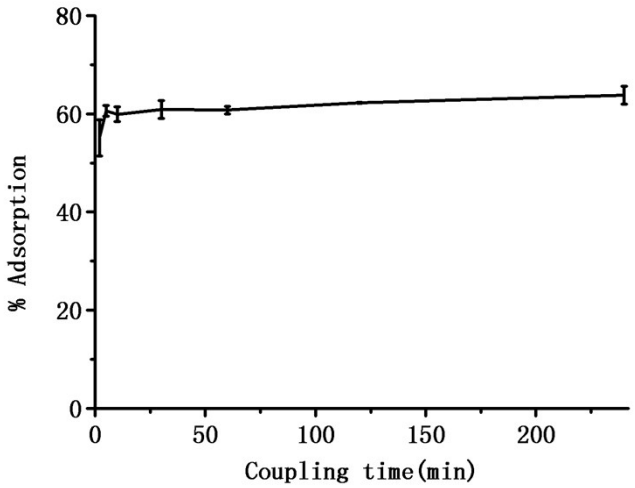

Figure S5. Optimization of the coupling time

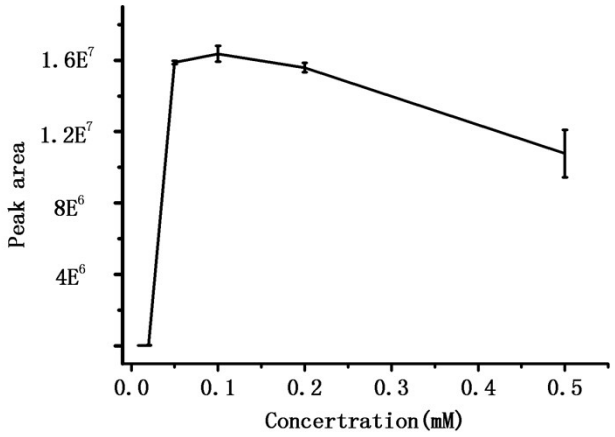

Figure S6. Optimization of $Na_2S_2O_4$ concentration

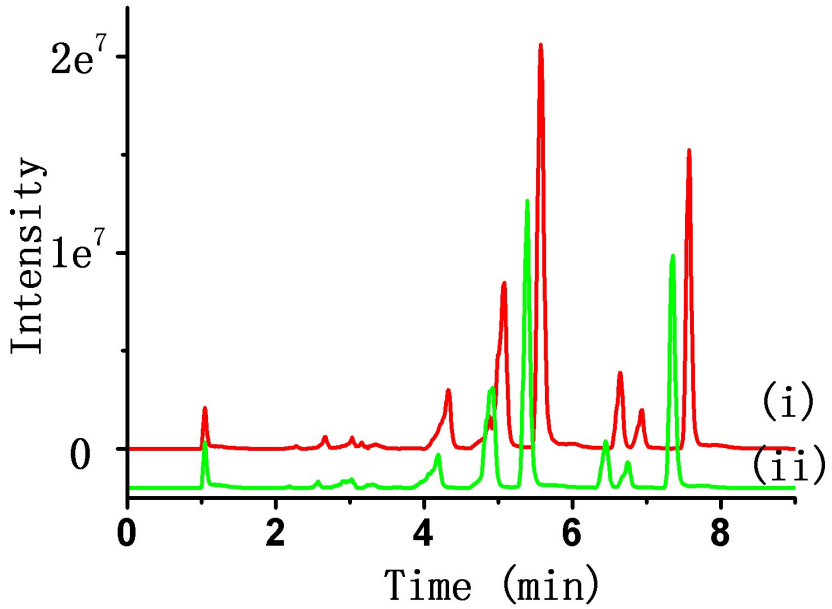

Figure S7. Extracted ion chromatograms of amino metabolites H_4-tagged (i) and D_4-tagged (ii) derivatization products

Table S1. LOD and MS sensitivity enhanced folds of the mixed amino standards before and after $mSiO_2$@azobenzene-COOH nanoprobes and dansyl chloride derivatization

Compounds	LOD			Enhanced folds		
	without derivatization (ng/mL)	dansyl chloride derivatization (ng/mL)	nanoprobe derivatization (ng/mL)	dansyl chloride derivatization	nanoprobe derivatization	nanoprobe /dansyl chloride
Propylamine	-	2	0.5	significantly increased	significantly increased	4
Isobutylamine	-	2	0.1	significantly increased	significantly increased	20
Cyclohexylamine	50	10	0.2	5	250	50
Heptylamine	5	10	0.1	0.5	50	100
N-methyltyramine	2	500	10	0.004	0.2	50
Tyramine	10	20	0.5	0.5	20	40
Dopamine	20	500	10	0.04	2	50
p-Anisidine	0.5	50	0.2	0.01	2.5	250
N-methylanthranilic acid	5	2	50	2.5	0.1	0.04
Leu	10	5	0.5	2	20	10
Met	200	5	0.02	40	10000	250
Trp	100	10	1	10	100	10
GABA	500	0.5	1	1000	500	0.5
Ala-ala	200	2	5	100	40	0.4
Pro	50	10	500	5	0.1	0.02

Table S2. Linearity, recovery and precision of deuterated amino acids with $mSiO_2$@azobenzene-COOH derivatization.

Standard	Linear range (ng/mL)	R^2	Recovery (%)	Precision (RSD%)
L-leucinie-d3	1~1000	0.9980	97.25	5.7
Tryptophan-d5	1~1000	0.9970	86.98	4.9
L-methionine-d3	1~1000	0.9984	90.70	0.48

Table S3 Derivatization products of amino metabolites defined from 20 μL serum with $mSiO_2$@azobenzene-COOH probes

D_4-tagged derivatization product		H_4-tagged derivatization product		Compound molecular weight	Amino metabolites	Error ppm
Precursor ion	t_R (min)	Precursor ion	t_R (min)			
228.1647	1.07	224.1396	1.08	61.0530	ethanolamine *[b]	4
352.1788	1.08	348.1535	1.07	185.0669	fucosamine [a]	3
330.1965	1.08	326.1716	1.07	163.0851	dimethylaminopurine [b]	4
272.1549	1.08	268.1296	1.07	105.0430	serine *[b]	4
256.1598	1.08	252.1346	1.08	89.0480	alanine *[b]	6
282.1754	1.10	278.1500	1.10	115.0634	4-amino-2-methylenebutanoic acid [b]	1
242.1437	1.33	238.1186	1.33	75.0320	glycine *[b]	0
242.1438	2.25	238.1189	2.34	75.0323	acetohydroxamic acid [b]	5
360.1972	2.33	356.1719	2.42	193.0853	4-(nitrosoamino)-1-(3-pyridinyl)-1-butanone	1
198.1540	2.34	194.1290	2.42	31.0421	methylamine	7
327.1966	2.64	323.1714	2.71	160.084	ala-ala *[b]	0
330.1964	2.69	326.1715	2.79	163.0849	fucosamine	2
286.1703	2.71	282.1451	2.81	119.0585	homoserine*[b]	2
259.1596	2.94	255.1342	3.14	92.0476	Unknown [b]	
282.1753	3.49	278.1504	3.64	115.0638	proline*[b]	5
240.1634	3.54	236.1390	3.59	73.0524	aminoacetone[b]	-4
270.2118	3.59	266.1865	3.71	103.0999	2-amino-3-methyl-1-butanol[b]	2
270.1654	3.75	266.1500	3.85	103.0643	3-Aminobutanoic acid	1
270.1754	3.91	266.1500	4.06	103.0634	GABA*[b]	2
348.1862	4.03	344.1611	4.18	181.0714	3-amino-3-(4-hydroxyphenyl)propanoate	1
323.1654	4.04	319.1403	4.05	156.0537	imidazole lactate*[b]	2
229.1361	4.08	225.1104	4.28	62.0238	Unknown	
249.1149	4.08	245.0899	4.27	82.0033	Unknown	
348.1853	4.30	344.1611	4.44	181.0745	tyrosine*[b]	3
300.1493	4.44	296.1241	4.62	133.0375	aspartic acid [b]	0
296.1910	4.64	292.1659	4.82	129.0793	pipecolinic acid*[b]	3
284.1910	4.74	280.1658	4.91	117.0792	aminopentanoic acid[b]	0
316.1626	5.00	312.1379	5.07	149.0513	methionine*[b]	2
284.1908	5.01	280.1656	5.19	117.0790	valine*[b]	0
254.1804	5.34	250.1550	5.35	87.0684	4-aminobutyraldehyde[b]	0

350.1623	5.68	346.1367	5.72	183.0501	5-methoxy-3-hydroxyanthranilate [ab]	16
240.2010	5.63	236.1759	5.79	73.0893	butylamine*[b]	2
295.1702	5.65	291.1456	5.90	128.0590	4-amino-4-cyano-butanoic acid[b]	3
348.1495	5.70	344.1243	5.73	181.0377	2,7-dihydroxy-2H-1,4-benzoxazinone[b]	1
302.1438	5.70	298.1190	5.74	135.0324	homocysteine[b]	2.8
326.2015	5.84	322.1765	6.03	159.0899	calystegine	2
257.1436	5.86	253.1187	6.10	90.0321	Unknown [b]	
316.1591	6.06	312.1347	6.18	149.0481	dihydroxyindole[b]	2
381.2328	6.18	377.2076	6.36	214.1210	Unknown	
298.2066	6.18	294.1815	6.37	131.0949	isoleucine*[b]	2
381.2328	6.32	377.2076	6.55	214.1210	Unknown	
298.2063	6.44	294.1815	6.64	131.0949	leucine*[b]	2
488.2812	6.47	484.2561	6.55	321.1696	Gly Phe Val	2
332.1910	6.71	328.1658	6.91	165.0792	phenylalanine*[b]	1
371.2020	6.72	367.1768	6.91	204.0902	tryptophan*[b]	2
298.2066	6.79	294.1814	7.00	131.0949	aminocaproic acid	2
425.1102	6.83	421.0851	6.97	257.9985	Unknown	
448.2135	6.84	444.1878	7.03	281.1012	N2-(gamma-Glutamyl)-4-carboxyphenylhydrazine	0
266.2168	6.93	262.1915	7.13	99.1049	cyclohexylammonium*	2
324.1493	6.97	320.1242	7.03	157.0376	aminomucoconic acid	0
355.2644	7.12	351.2387	7.30	188.1521	trimethyllysine*[b]	-1
462.2288	7.44	458.2039	7.58	295.1174	asparaginyl-Tyrosine	2
413.0921	7.56	409.0674	7.72	245.9808	eudistomin N	6
427.0974	7.56	423.0721	7.72	259.9855	Unknown [b]	
332.2273	8.24	328.2022	8.27	165.1156	Pseudoephedrine [b]	1
411.2905	8.58	407.2655	8.80	244.1789	Leu-Leu [b]	1
351.1857	9.31	347.1606	9.34	184.0740	Glu-P-2	-4
313.2063	9.34	309.1809	9.52	146.0943	Unknown[b]	
289.1490	9.56	285.1238	9.73	122.0372	Unknown	
395.2483	9.93	391.2231	10.19	228.1365	Unknown	
417.2010	10.26	413.1757	10.35	250.0891	Unknown	
335.1902	11.16	331.1652	11.18	168.0786	Unknown [b]	
534.4204	11.35	530.3954	11.35	367.3088	Unknown	
427.2745	11.69	423.2494	11.85	260.1628	Unknown	
410.2955	12.04	406.2703	12.15	243.1837	Unknown	
331.1081	12.30	327.0834	12.46	163.9968	Unknown	
367.2067	12.32	363.1817	12.49	200.0951	diaminophenyl ether	0
317.1115	12.34	313.0854	12.45	149.9988	Unknown	

331.1081	12.46	327.0834	12.58	163.9968	Unknown	2
424.3109	12.95	420.2861	13.00	257.1995	Unknown	
331.1447	12.86	327.1197	13.10	164.0331	Unknown	
347.1397	12.86	343.1146	13.11	180.0280	Unknown	
492.2651	13.87	488.2399	13.95	325.1533	Unknown	
414.1464	13.96	410.1204	14.02	247.0338	Unknown	
414.1464	14.06	410.1204	14.10	247.0338	Unknown	
632.3874	15.38	628.3629	15.38	465.2763	Leu Arg Arg	-5
363.1172	15.80	359.0900	15.93	196.0050	Unknown	
379.1121	15.81	375.0871	15.95	212.0005	2-amino-5-(5-nitro-2-furyl)-1,3,4-thiadiazole [b]	1
419.2840	16.44	415.2597	16.47	252.1731	Unknown	
417.3056	17.45	413.2801	17.51	250.1935	Unknown	
534.4197	17.84	530.3950	17.88	367.3084	Unknown	
461.3316	18.01	457.3062	18.07	294.2196	Unknown	
380.2852	18.23	376.2597	18.29	213.1731	Unknown	
534.4197	18.29	530.3950	18.42	367.3084	Unknown	
583.4552	19.45	579.4303	19.50	416.3437	Unknown	
445.3367	19.84	441.3118	19.83	278.2252	Unknown	
554.4227	20.19	550.3974	20.3	387.3108	Unknown	
584.3848	20.02	580.3599	20.06	417.2733	sphingofungin E	1
420.3527	21.10	416.3274	21.13	253.2408	Unknown	
431.3570	22.71	427.3317	22.75	264.2451	Unknown	
504.4465	24.50	500.4212	24.52	337.3346	Unknown	

Annotation： * Validated with standards

[a] Detected as $[M+Na]^+$

[b] Detected with dansyl chloride derivatization method