Supporting information

Imaging the Metabolic and N-glycan Alterations in Colorectal Cancer using Matrix-Assisted Laser Desorption/Ionization Mass Spectrometry

Yaqi Zhang[a, b,#], Qiangjun Chen[d,#], Lei Wang[a, b], Haoyuan Geng[a, b], Zihan Zhu[a], Cancan Lv[b], Yisheng Zhao[a, b], Xiao Wang[a, b], Chenglong Sun[a, b], Panpan Chen[a, b*], and Chao Zhang[c*]

[a] Shandong Engineering Research Center for Innovation and Application of General Technology for Separation of Natural Products, Shandong Analysis and Test Center, Qilu University of Technology (Shandong Academy of Sciences), Jinan, 250014, China
[b] Key Laboratory for Natural Active Pharmaceutical Constituents Research in Universities of Shandong Province, School of Pharmaceutical Sciences, Qilu University of Technology (Shandong Academy of Sciences), Jinan, 250014, China
[c] Department of Pediatrics, Qilu Hospital of Shandong University, Jinan 250012, China
[d] Department of Breast and Thyroid Surgery, Yi Du Central Hospital of Weifang, No.5168 Jiangjunshan Road, Weifang 262500, Shangdong Province, China
[#] These authors contributed equally
[*] Corresponding author: Panpan Chen and Chao Zhang
Tel.: +86-18560084071.
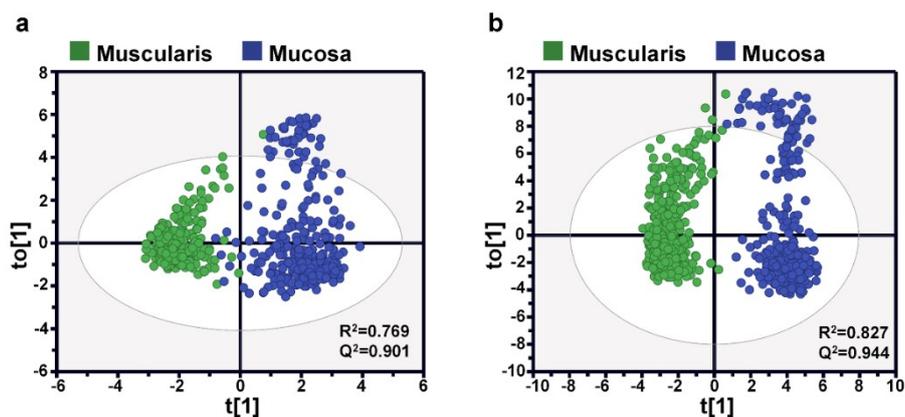E-mail address: chenpanpan1203@163.com (Panpan Chen);zczuqiu@163.com (Chao Zhang);

Figure S1. OPLS-DA score plots based on MALDI-MSI from different colorectal cancer tissue regions in positive (a) and negative (b) ions.
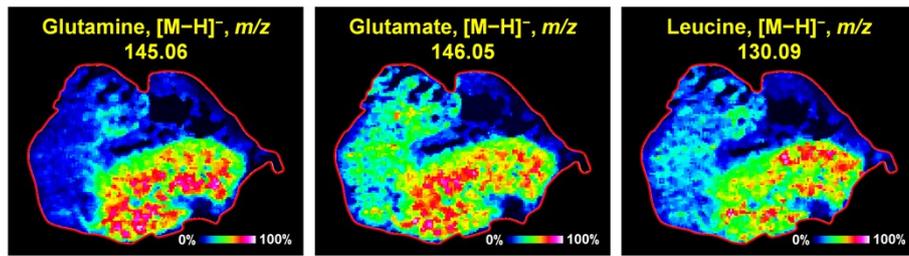
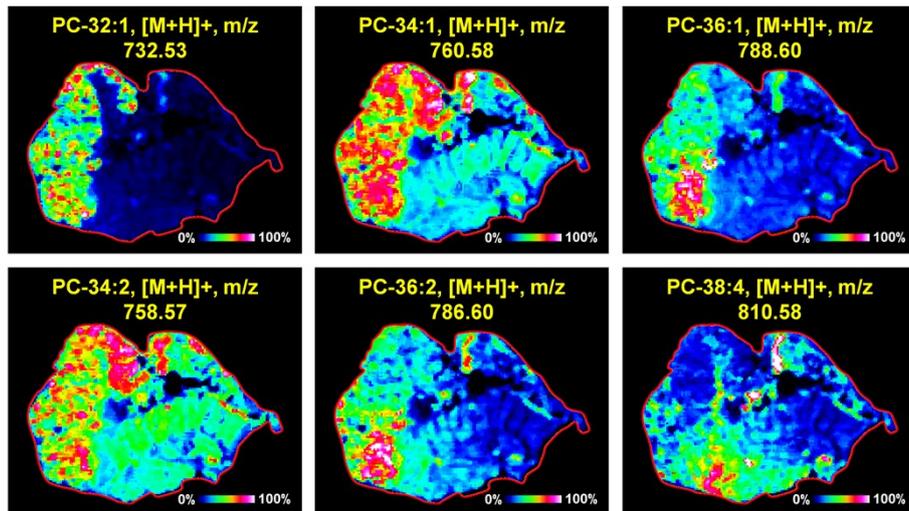**Figure S2**. MS images of glutamine, glutamate and leucine in colorectal cancer.

Figure S3. MS images of representative phosphatidylcholines in colorectal cancer.
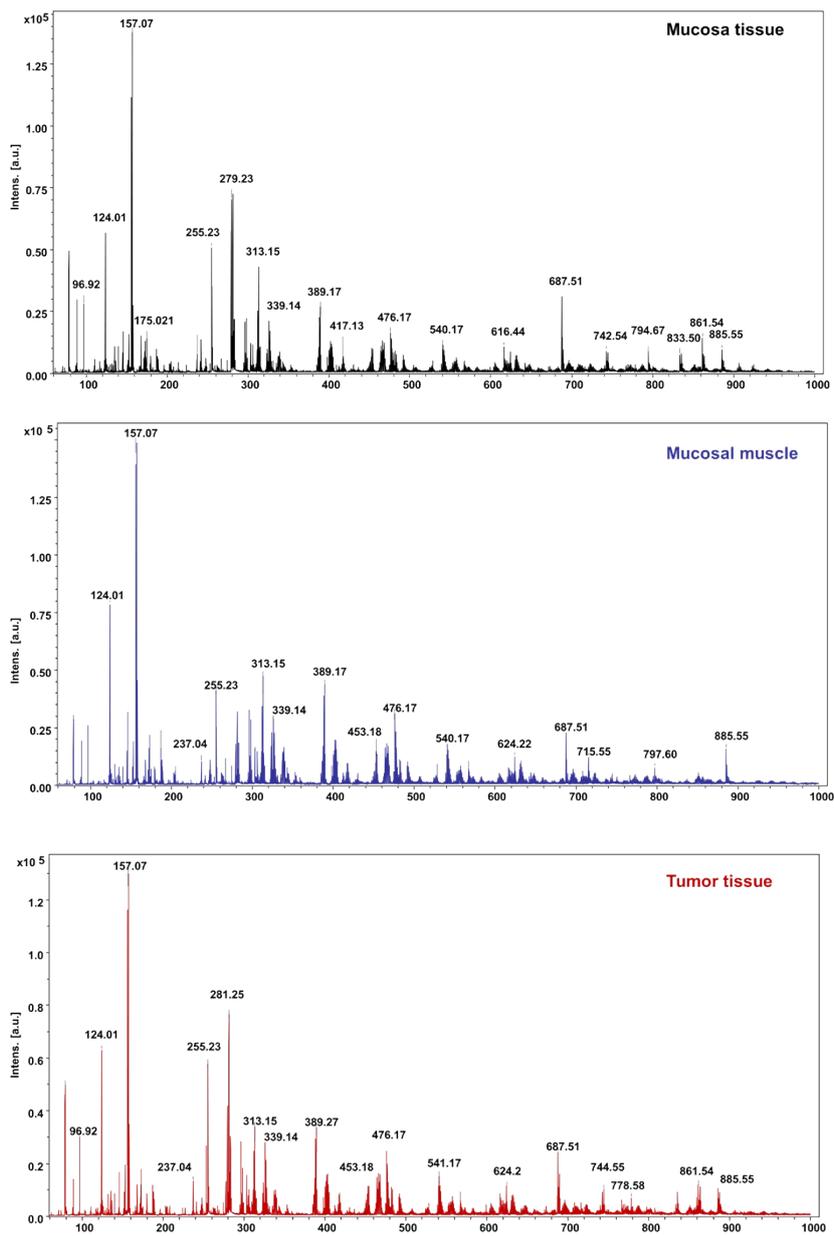
Figure S4. MALDI-MS spectra of mucosa tissue, mucosal muscle and tumor tissue in colorectal cancer.
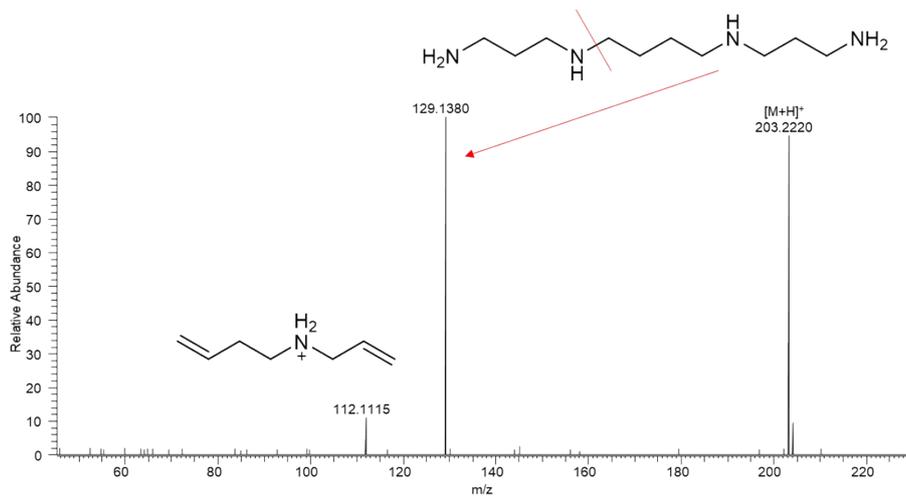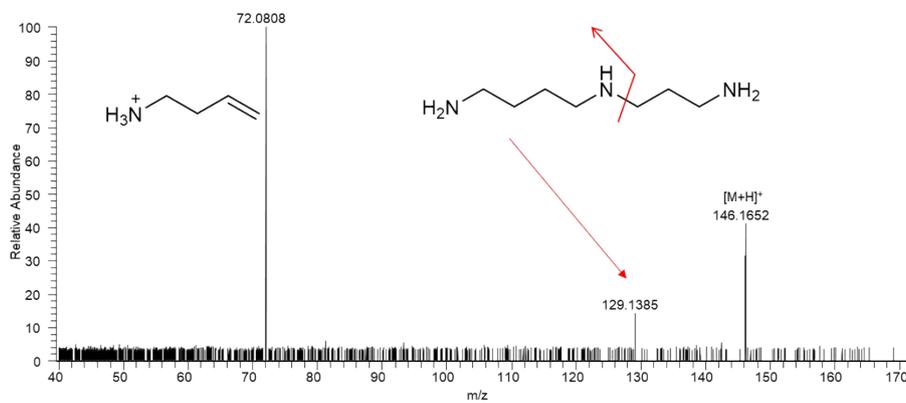
Figure S5. The MS/MS spectrum of spermine.

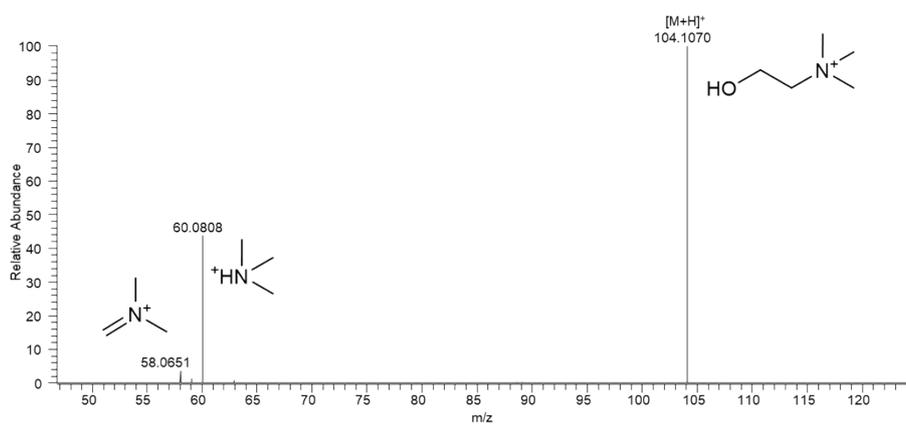**Figure S6**. The MS/MS spectrum of spermidine.

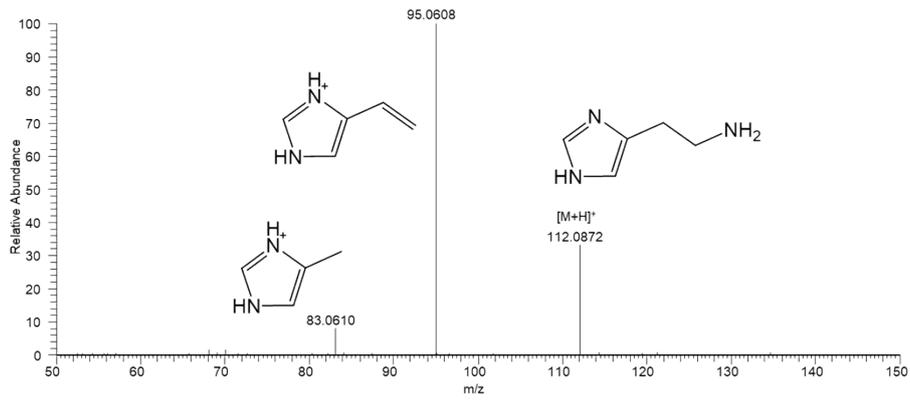**Figure S7**. The MS/MS spectrum of choline.
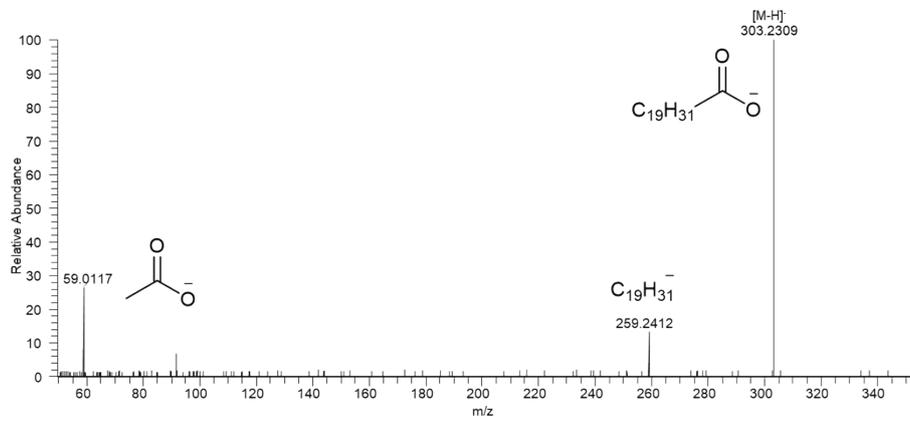
Figure S8. The MS/MS spectrum of histamine.

Figure S9. The MS/MS spectrum of FA-C20:4.

Table S1. Annotated metabolites in this study.

Name	Formula	Ion type	Theoretical m/z	Measured m/z	Relative error (ppm)
Malic acid	$C_4H_5O_5$	[M-H]$^-$	133.0142	133.0145	2.26
Glutamate	$C_5H_9NO_4$	[M-H]$^-$	146.0459	146.0462	2.05
Glutamine	$C_5H_{10}N_2O_3$	[M-H]$^-$	145.0619	145.0622	2.07
Aspartate	$C_4H_7NO_4$	[M-H]$^-$	132.0302	132.0305	2.27
FA-C16:1	$C_{16}H_{30}O_2$	[M-H]$^-$	253.2173	253.2176	1.18
FA-C18:1	$C_{18}H_{34}O_2$	[M-H]$^-$	281.2486	281.2491	1.78
FA-C20:1	$C_{20}H_{38}O_2$	[M-H]$^-$	309.2799	309.2807	2.59
FA-C16:0	$C_{16}H_{32}O_2$	[M-H]$^-$	255.233	255.2335	1.96
FA-C18:0	$C_{18}H_{36}O_2$	[M-H]$^-$	283.2643	283.265	2.47
FA-C18:2	$C_{18}H_{32}O_2$	[M-H]$^-$	279.233	279.2335	1.79
FA-C20:4	$C_{20}H_{32}O_2$	[M-H]$^-$	303.233	303.2336	1.98
FA-C20:3	$C_{20}H_{34}O_2$	[M-H]$^-$	305.2487	305.2497	3.28
FA-C20:3	$C_{20}H_{36}O_2$	[M-H]$^-$	307.2644	307.265	1.95
FA-C22:4	$C_{22}H_{36}O_2$	[M-H]$^-$	331.2649	331.2651	0.60
Choline	$C_5H_{13}NO$	[M+H]$^+$	104.107	104.1071	0.96
Phosphocholine	$C_5H_{14}NO_4P$	[M+H]$^+$	184.0733	184.0737	2.17
Spermidine	$C_7H_{19}N_3$	[M+H]$^+$	146.1651	146.1654	2.05
Spermine	$C_{10}H_{26}N_4$	[M+H]$^+$	203.2228	203.223	0.98
PC-32:0	$C_{40}H_{80}NO_8P$	[M+H]$^+$	734.5694	734.5698	0.54
PC-34:1	$C_{42}H_{82}NO_8P$	[M+H]$^+$	760.5851	760.5861	1.31
PC-34:2	$C_{42}H_{80}NO_8P$	[M+H]$^+$	758.5694	758.5671	-3.03