Electronic Supplementary Material (ESI) for Analyst.


# Polydopamine-capped AgNPs as a novel matrix overcoming the ion suppression of phosphatidylcholine for MALDI MS comprehensively imaging of glycerophospholipids and sphingolipids in impact-induced injured brain

Chao Han[a, b] Shumu Li[a], Qingwei Yue[a, b], Na Li[a, b], Hui Yang[a, b], Zhenwen Zhao[*a, b]

[a] Beijing National Laboratory for Molecular Sciences, CAS Research/Education Center for Excellence in Molecular Sciences, Key Laboratory of Analytical Chemistry for Living Biosystems, Institute of Chemistry Chinese Academy of Sciences, Beijing Mass Spectrum Center, Beijing 100190, China.

[b] Graduate School, University of Chinese Academy of Sciences, Beijing 100049, China.

[*]**Corresponding Author**

Phone: +86-10-62561239. Fax: +86-10-62561285. E-mail: zhenwenzhao@iccas.ac.cn.

## Notes

The authors declare no competing financial interest.

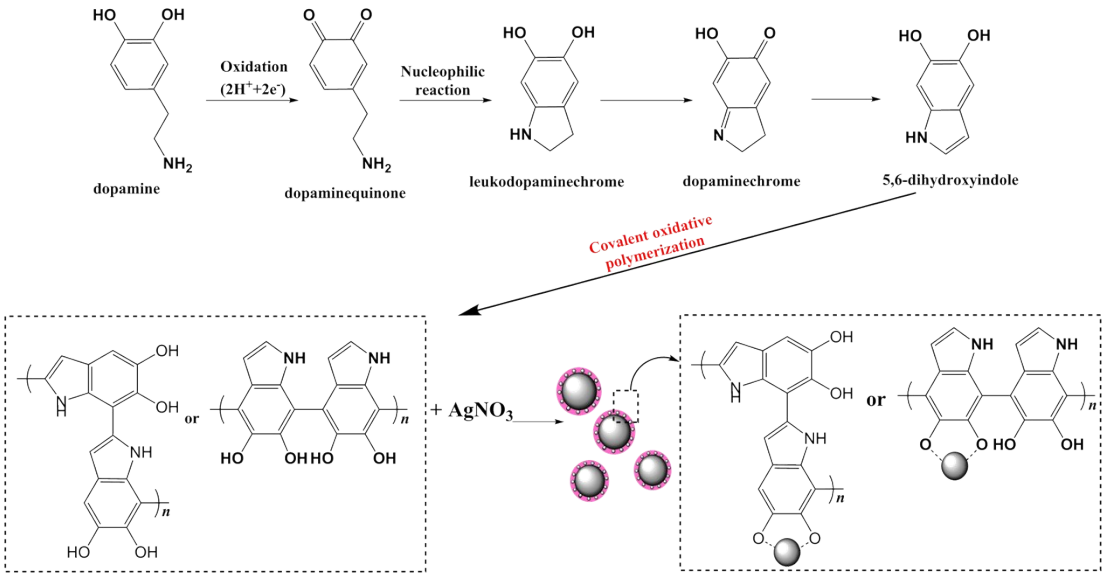



**Figure S1** The flow chart for preparation of AgNPs@PDA.

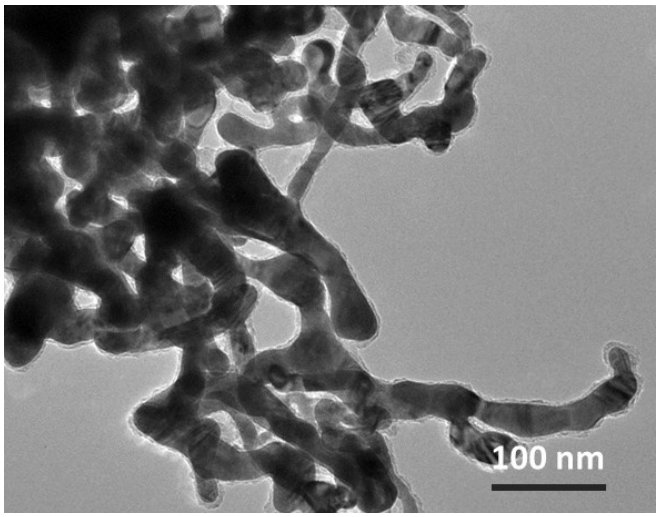



**Figure S2.** Transmission electron microscopy (TEM, JEOL, Japan) image of AgNPs@PDA. The AgNPs@PDA was synthesized by the following steps: 0.4 g $AgNO_3$ was directly added into 25 mL freshly prepared DA solution (16 mg/mL, dissolved in 10 mM tris solution with pH at 7.8 at 60°C) under stirring conditions for 24 h, the products were collected by centrifugation. The transmission electron microscope (TEM) use the electron beam as the light source (the wavelength of the electron beam is much shorter than that of visible and ultraviolet light), which improves the resolution of the microscope, allowing fine structures smaller than 0.2 μm to be observed clearly.

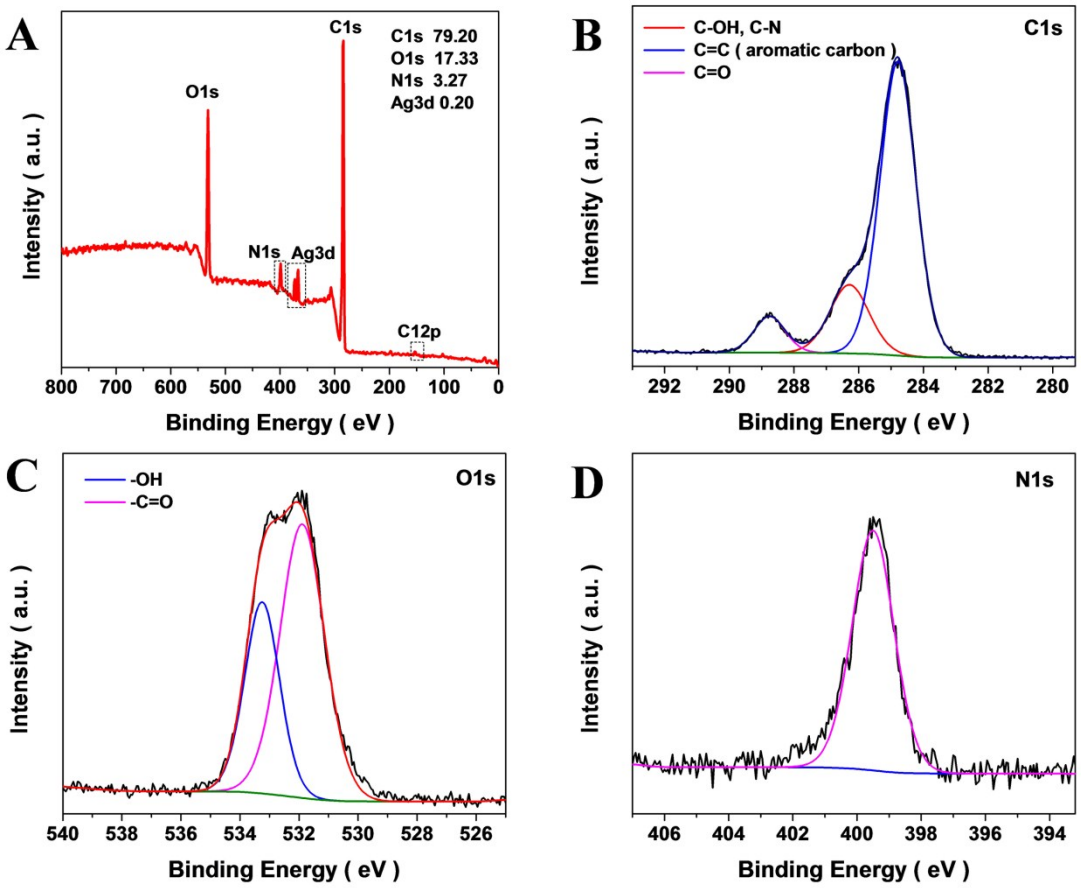



**Figure S3.** XPS spectra of AgNPs@PDA: survey (A) and high resolution spectra for C (B), O (C) and N (D).

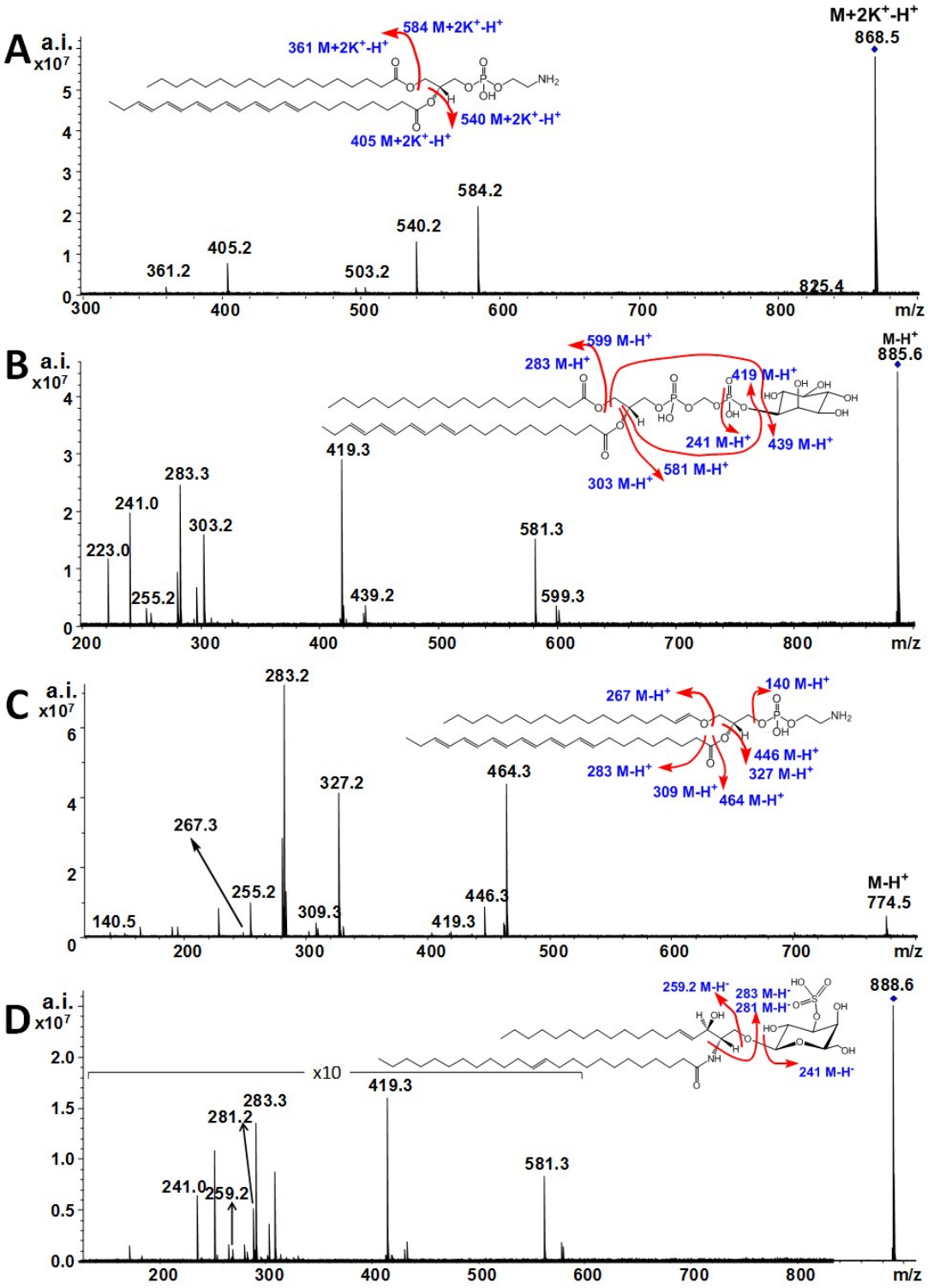



**Figure S4.** The MS/MS spectrum of (A) PE(18:0/22:6), (B) PI(18:0/20:4), (C) PE(P-18:0/22:6), and (D) ST(d18:1/24:1). A was detected in positive ion mode; B, C and D were detected in negative ion mode.

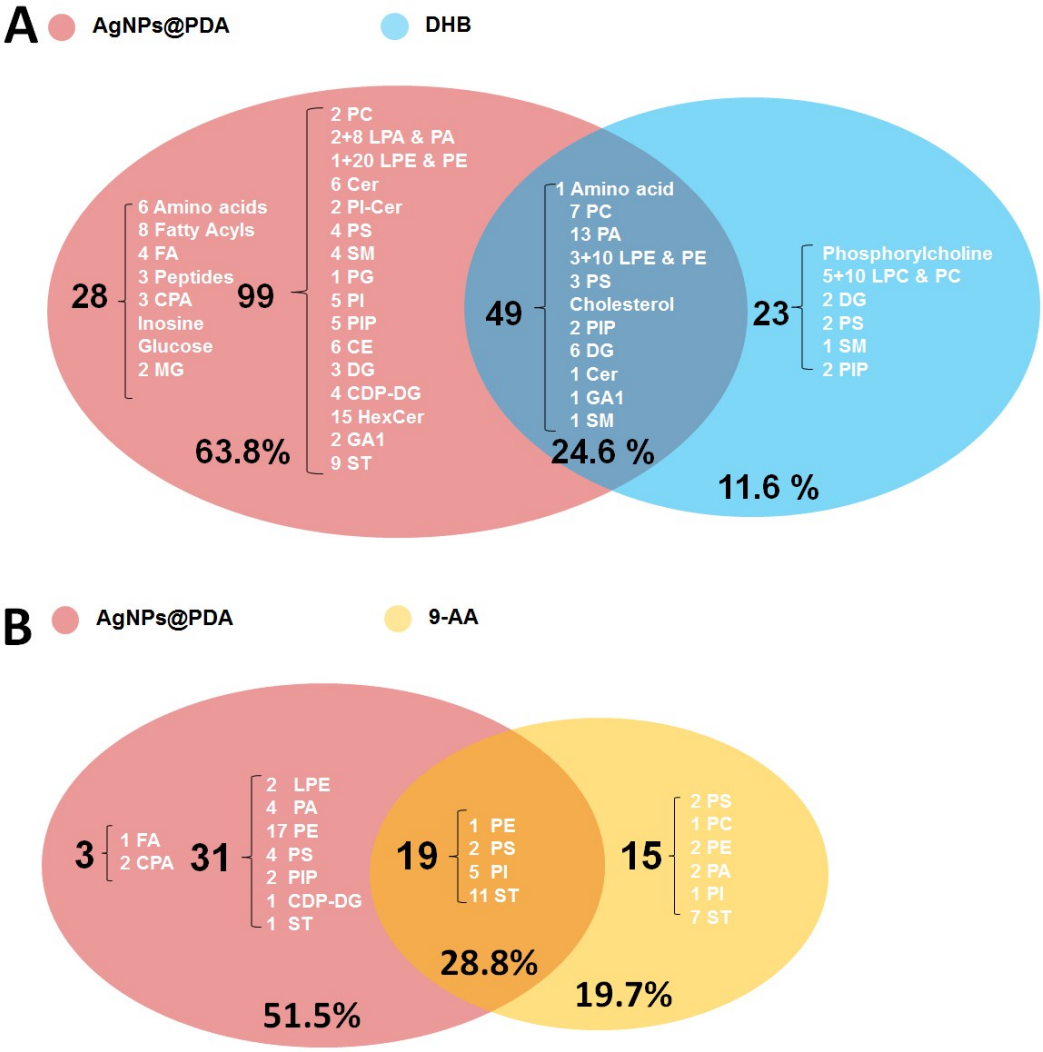



**Figure S5.** Venn diagram illustrating the classes and numbers of identified or putatively identified molecules detected by MALDI MS with AgNPs@PDA, DHB and 9-AA as the MALDI matrix. A) operating in positive ion detect mode. B) operating in negative ion detect mode.

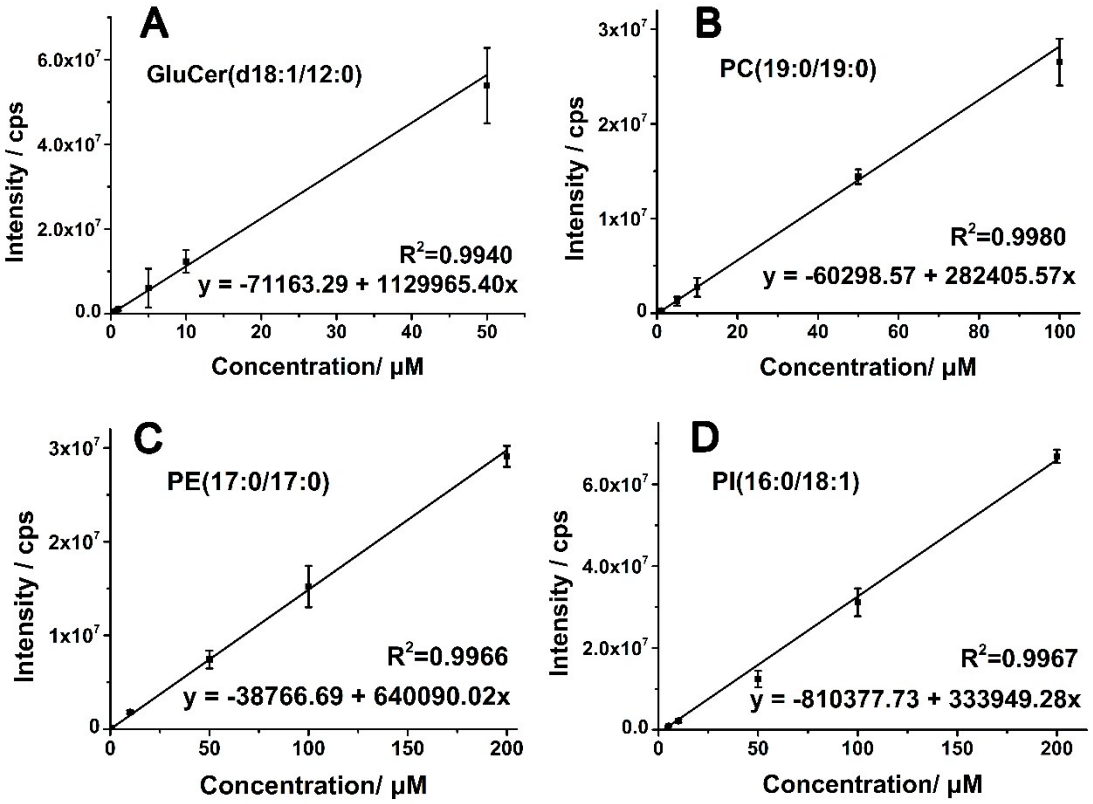



**Figure S6.** The standard curves of (A) GluCer(d18:1/12:0), (B) PC(19:0/19:0), (C) PE(17:0/17:0) and (D) PI(16:0/18:1). A, B, and C were obtained by MALDI FTICR MS in positive ion detect mode and D was obtained in negative ion detect mode.

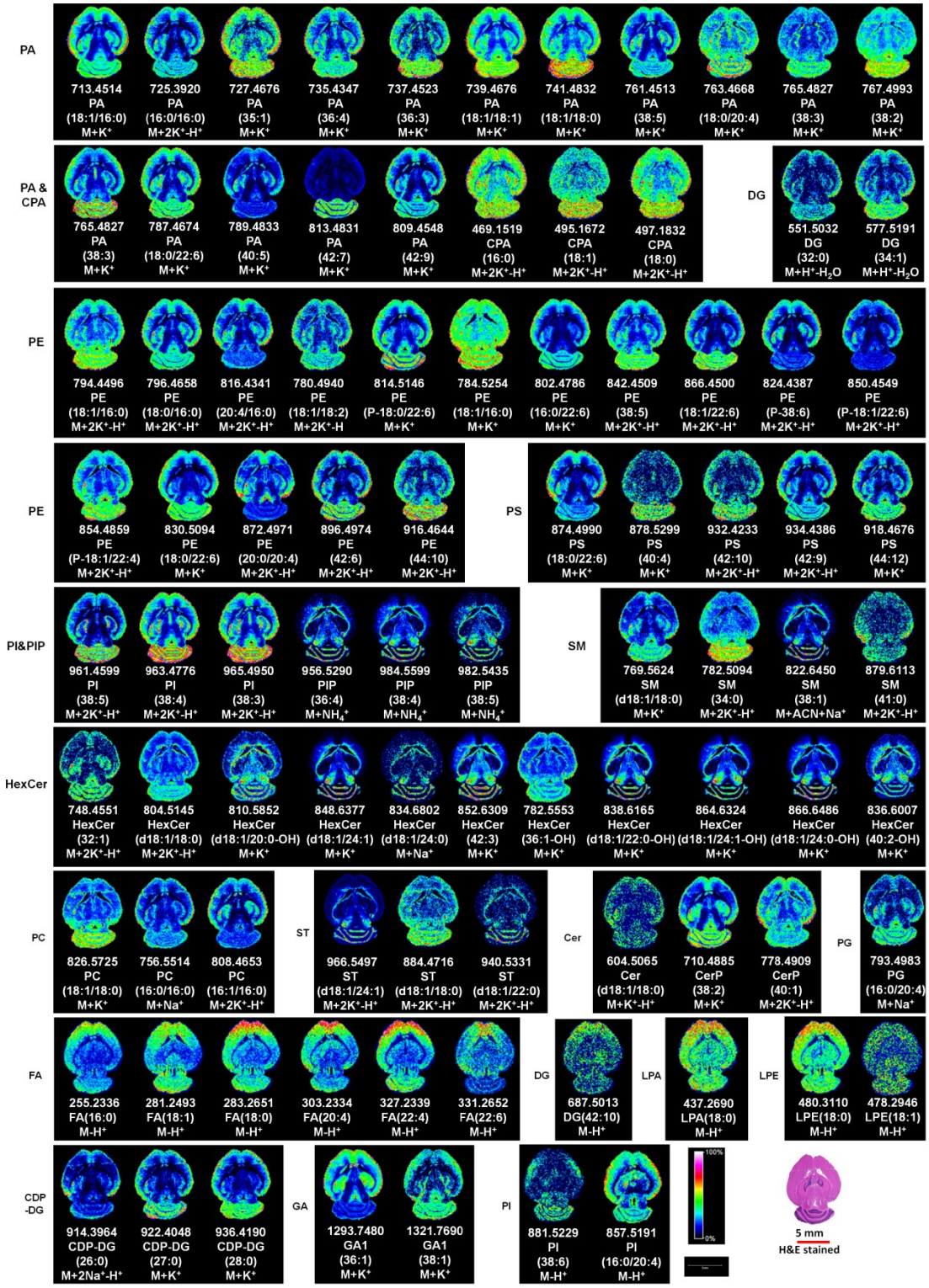



**Figure S7.** The distribution of lipids and metabolites in mouse brain tissue section obtained by MALDI FTICR MSI using AgNPs@PDA as the matrix with a laser raster step size of 120 μm.

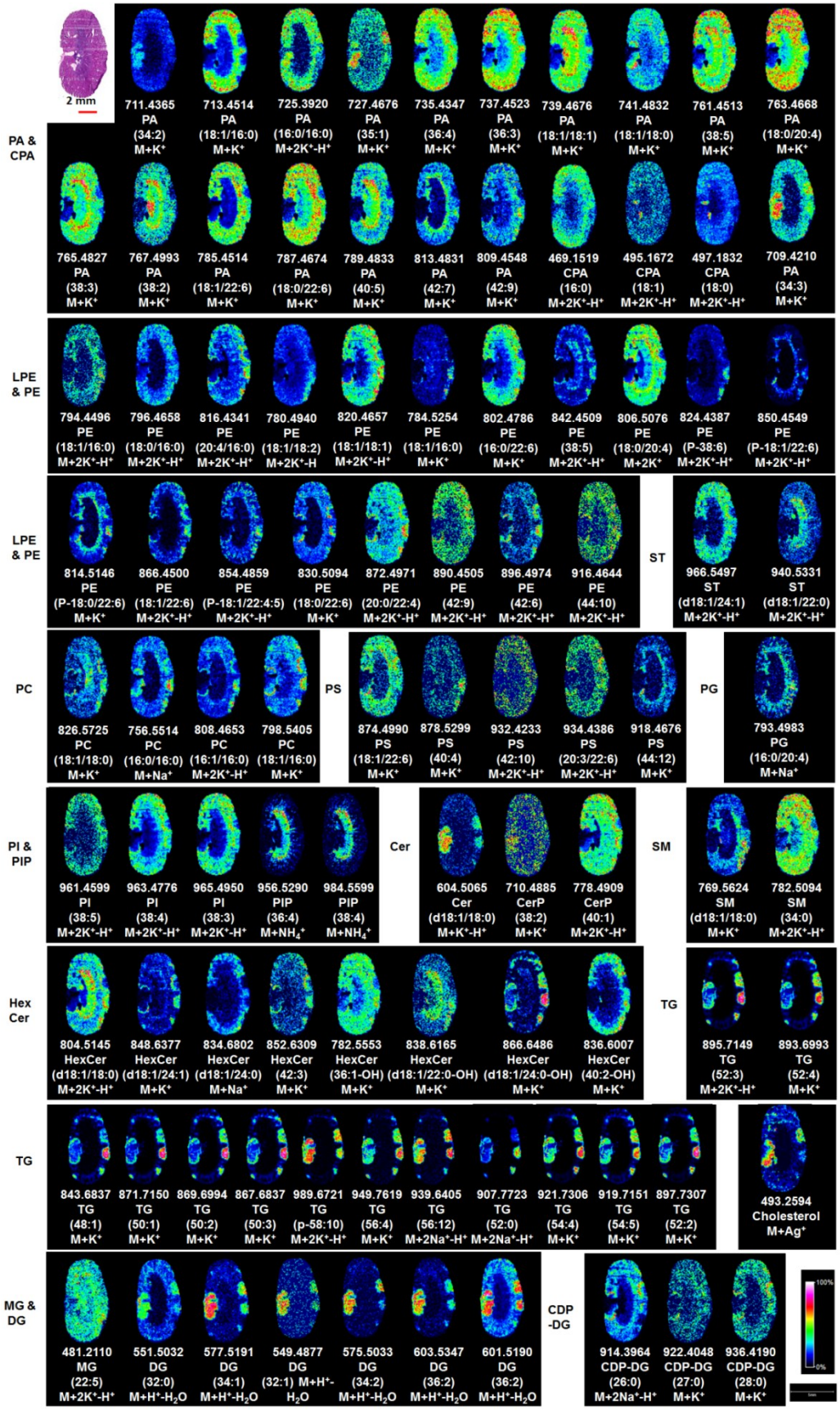



**Figure S8.** The distribution of lipids and metabolites in mouse kidney tissue section obtained by MALDI FTICR MSI using AgNPs@PDA as the matrix with a laser raster step size of 100 μm.

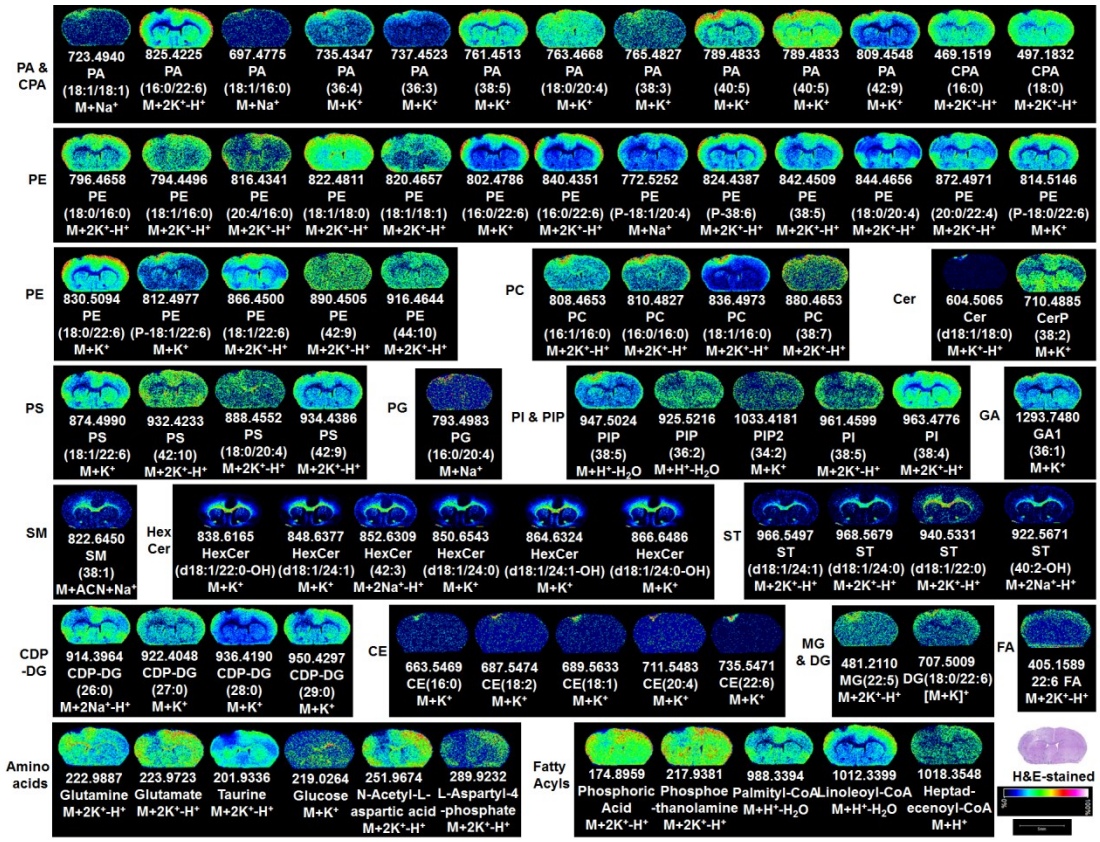



**Figure S9.** MALDI MSI analysis of GPLs, SPLs and others in mouse brain following traumatic brain injury using AgNPs@PDA as matrix.

**Table S1** List of identified or putatively identified analytes detected in mouse brain using AgNPs@PDA-assisted LDI MS or using DHB assisted LDI MS. Operating in positive ion detect mode; Precise m/z and mass accuracy (Δppm) of measurements and their corresponding product ions are reported. The compounds highlighted with light red are only detected by using AgNPs@PDA as the matrix, the compounds highlighted with light blue are only detected by using DHB as the matrix.

| Analyte chemical class | Compound | Detected ions | Detected Mass | Exact Mass | Delta /Δppm | The product ions |
|---|---|---|---|---|---|---|
| **AgNPs@PDA assisted MALDI MS Positive mode** | | | | | | □ |
| Amino acids | Taurine | $[M+2K-H]^+$ | 201.9336 | 201.9337 | -0.5 | □ |
| | Creatine | $[M+2K-H]^+$ | 207.9885 | 207.9885 | 0.0 | □ |
| | Glutamine | $[M+2K-H]^+$ | 222.9887 | 222.9887 | -0.1 | □ |
| | Glutamate | $[M+2K-H]^+$ | 223.9723 | 223.9721 | 0.9 | □ |
| | Phosphoserine | $[M+2K-H]^+$ | 261.9277 | 261.9280 | -1.1 | □ |
| | N-Acetyl-L -aspartic acid | $[M+2K-H]^+$ | 251.9674 | 251.9671 | 1.2 | □ |
| | L-Aspartyl-4 -phosphate | $[M+2K-H]^+$ | 289.9232 | 289.9229 | 1.0 | □ |
| Fatty Acyls | Phosphoethanol -amine | $[M+2K-H]^+$ | 217.9381 | 217.9381 | 0.0 | □ |
| | Phosphoric acid | $[M+2K-H]^+$ | 174.8959 | 174.8959 | 0.0 | □ |
| | Oleamide | $[M+K]^+$ | 320.2350 | 320.2350 | 0.0 | □ |
| | Isoglobotriaose | $[M+H]^+$ | 503.1974 | 503.1970 | 0.8 | □ |
| | | $[M+Na]^+$ | 525.1784 | 525.1790 | -1.1 | □ |
| | Palmityl-CoA | $[M+H-H_2O]^+$ | 988.3394 | 988.3405 | -1.1 | □ |
| | Oleoyl-CoA | $[M+H-2H_2O]^+$ | 996.3499 | 996.3478 | 2.1 | □ |
| | Linoleoyl-CoA | $[M+H-H_2O]^+$ | 1012.3399 | 1012.3422 | -2.2 | □ |
| | Heptadecenoyl -CoA | $[M+H]^+$ | 1018.3548 | 1018.3522 | 2.6 | □ |
| □ | Inosine | $[M+K]^+$ | 307.0442 | 307.0439 | 0.9 | □ |
| □ | Glucose | $[M+K]^+$ | 219.0264 | 219.0265 | -0.5 | □ |
| Fatty acid | Palmitic acid/FA(16:0) | $[M+2K-H]^+$ | 333.1592 | 333.1593 | -0.3 | □ |
| | Stearic acid/FA(18:0) | $[M+2K-H]^+$ | 361.1907 | 361.1906 | 0.3 | □ |
| | Docosahexaenoic acid/FA(22:6) | $[M+K]^+$ | 367.2031 | 367.2034 | -0.8 | □ |
| | | $[M+2K-H]^+$ | 405.1589 | 405.1593 | -1.0 | □ |
| | Arachidonic acid/FA(20:4) | $[M+K]^+$ | 343.2034 | 343.2034 | 0.0 | □ |
| | | $[M+2K-H]^+$ | 381.1593 | 381.1593 | 0.0 | □ |
| CPA | CPA(16:0) | $[M+K]^+$ | 431.1955 | 431.1959 | -0.9 | □ |
| | | $[M+2K-H]^+$ | 469.1519 | 469.1518 | 0.2 | □ |
| | CPA(18:1) | $[M+K]^+$ | 457.2117 | 457.2116 | 0.2 | □ |

| Analyte chemical class | Compound | Detected ions | Detected Mass | Exact Mass | Delta /Δppm | The product ions |
|---|---|---|---|---|---|---|
| | | $[M+2K-H]^+$ | 495.1672 | 495.1675 | -0.6 | □ |
| | CPA(18:0) | $[M+K]^+$ | 459.2275 | 459.2272 | 0.7 | □ |
| | | $[M+2K-H]^+$ | 497.1832 | 497.1831 | 0.2 | □ |
| Cholesterol | Cholesterol | $[M+H-H_2O]^+$ | 369.3520 | 369.3522 | -0.5 | □ |
| | | $[M+Na]^+$ | 409.3443 | 409.3441 | 0.5 | |
| | | $[M+Ag]^+$ | 493.2594 | 493.2594 | 0.0 | |
| Peptides | Glycyl-Lysine | $[2M+Na]^+$ | 429.2434 | 429.2432 | 0.4 | □ |
| | Arginyl -Arginine | $[2M+Na]^+$ | 683.4149 | 683.4148 | 0.1 | □ |
| | Neuromedin B (4-10) | $[M+2K-H]^+$ | 930.4398 | 930.4403 | -0.5 | □ |
| LPA | LysoPA(18:0) | $[M+2K-H]^+$ | 515.1938 | 515.1937 | 0.2 | □ |
| | LysoPA(18:1) | $[M+2K-H]^+$ | 513.1783 | 513.1780 | 0.5 | □ |
| LPE | LysoPE(18:0) | $[M+2K-H]^+$ | 558.2359 | 558.2359 | 0.0 | 109.10, 123.12, 341.30 |
| | LysoPE(18:1) | $[M+2K-H]^+$ | 556.2202 | 556.2202 | 0.0 | □ |
| | LysoPE(22:6) | $[M+2K-H]^+$ | 602.2043 | 602.2046 | -0.5 | □ |
| | LysoPE(20:4) | $[M+K]^+$ | 540.2490 | 540.2487 | 0.5 | □ |
| □ | PA(16:0/16:0) | $[M+2Na-H]^+$ | 693.4445 | 693.4442 | 0.4 | 468.2, 627.4 |
| | | $[M+2K-H]^+$ | 725.3920 | 725.3920 | 0.0 | |
| | PA(34:2) | $[M+Na]^+$ | 695.4627 | 695.4622 | 0.7 | □ |
| | | $[M+K]^+$ | 711.4365 | 711.4362 | 0.4 | □ |
| | | $[M+2K-H]^+$ | 749.3910 | 749.3920 | -1.3 | □ |
| | PA(18:1/16:0) | $[M+Na]^+$ | 697.4775 | 697.4779 | -0.6 | 441.2, 599.5 |
| | | $[M+K]^+$ | 713.4514 | 713.4518 | -0.6 | |
| | | $[M+2Na-H]^+$ | 719.4594 | 719.4598 | -0.6 | |
| | | $[M+2K-H]^+$ | 751.4077 | 751.4077 | 0.0 | |
| | PA(34:3) | $[M+K]^+$ | 709.4210 | 709.4205 | 0.7 | □ |
| | | $[M+2K-H]^+$ | 747.3755 | 747.3764 | -1.2 | □ |
| | PA(35:1) | $[M+K]^+$ | 727.4676 | 727.4675 | 0.1 | □ |
| | PA(36:4) | $[M+K]^+$ | 735.4347 | 735.4362 | -2.1 | □ |
| | | $[M+2K-H]^+$ | 773.3923 | 773.3920 | 0.4 | |
| | PA(36:3) | $[M+K]^+$ | 737.4523 | 737.4518 | 0.6 | □ |
| | | $[M+2K-H]^+$ | 775.4070 | 775.4077 | -0.9 | |
| | PA(18:1/18:1) | $[M+Na]^+$ | 723.4940 | 723.4935 | 0.7 | 441.2, 625.5 |
| | | $[M+K]^+$ | 739.4676 | 739.4675 | 0.1 | |
| | | $[M+2K-H]^+$ | 777.4227 | 777.4233 | -0.8 | |
| | PA(18:1/18:0) | $[M+K]^+$ | 741.4832 | 741.4831 | 0.1 | 341.2, 681.4 |
| | | $[M+2K-H]^+$ | 779.4390 | 779.4390 | 0.1 | |
| | PA(37:4) | $[M+K]^+$ | 749.4515 | 749.4518 | -0.4 | □ |
| | PA(38:5) | $[M+K]^+$ | 761.4513 | 761.4519 | -0.8 | □ |

| Analyte chemical class | Compound | Detected ions | Detected Mass | Exact Mass | Delta /Δppm | The product ions |
|---|---|---|---|---|---|---|
| | | $[M+2K-H]^+$ | 799.4070 | 799.4077 | -0.9 | |
| | PA(18:0/20:4) | $[M+K]^+$ | 763.4668 | 763.4675 | -0.9 | 343.2, 703.4 |
| | | $[M+2K-H]^+$ | 801.4229 | 801.4233 | -0.5 | |
| | PA(38:3) | $[M+K]^+$ | 765.4827 | 765.4832 | -0.7 | □ |
| | PA(38:2) | $[M+K]^+$ | 767.4993 | 767.4988 | 0.7 | □ |
| | PA(40:8) | $[M+K]^+$ | 783.4356 | 783.4362 | -0.7 | □ |
| | PA(40:7) | $[M+K]^+$ | 785.4514 | 785.4518 | -0.5 | □ |
| | | $[M+2K-H]^+$ | 823.4073 | 823.4077 | -0.5 | |
| | PA(18:0/22:6) | $[M+K]^+$ | 787.4674 | 787.4675 | -0.1 | 343.2, 727.4 |
| | | $[M+2K-H]^+$ | 825.4225 | 825.4233 | -1.0 | |
| | PA(40:5) | $[M+K]^+$ | 789.4833 | 789.4832 | 0.1 | □ |
| | PA(38:6) | $[M+2K-H]^+$ | 797.3924 | 797.3920 | 0.5 | □ |
| | PA(42:9) | $[M+K]^+$ | 809.4506 | 809.4518 | -1.5 | □ |
| | | $[M+2K-H]^+$ | 847.4063 | 847.4077 | -1.7 | |
| | PA(42:7) | $[M+K]^+$ | 813.4831 | 813.4831 | 0.0 | □ |
| MG | MG(22:6) | $[M+2K-H]^+$ | 479.1955 | 479.1961 | -1.3 | □ |
| | MG(22:5) | $[M+2K-H]^+$ | 481.2110 | 481.2117 | -1.5 | □ |
| DG | DG(32:0) | $[M+H-H_2O]^+$ | 551.5032 | 551.5040 | -1.4 | □ |
| | | $[M+K]^+$ | 607.4688 | 607.4698 | -1.6 | |
| | DG(34:0) | $[M+H-H_2O]^+$ | 579.5350 | 579.5353 | -0.4 | □ |
| | DG(34:1) | $[M+H-H_2O]^+$ | 577.5191 | 577.5190 | 0.2 | □ |
| | | $[M+Na]^+$ | 617.5117 | 617.5115 | 0.3 | |
| | | $[M+K]^+$ | 633.4855 | 633.4855 | 0.0 | |
| | DG(36:1) | $[M+Na]^+$ | 645.5432 | 645.5428 | 0.6 | □ |
| | | $[M+K]^+$ | 661.5167 | 661.5168 | -0.2 | |
| | DG(38:4) | $[M+H-H_2O]^+$ | 627.5348 | 627.5347 | 0.1 | □ |
| | | $[M+Na]^+$ | 667.5269 | 667.5272 | -0.5 | |
| | | $[M+K]^+$ | 683.5011 | 683.5011 | 0.0 | |
| | DG(P-18:1/18:1) or DG(P-18:2/18:0) | $[M+K]^+$ | 643.5070 | 643.5062 | 1.2 | 265.25, 267.27 |
| | DG(18:0/22:6) | $[M+H-H_2O]^+$ | 651.5344 | 651.5347 | -0.4 | 239.27, 311.23 |
| | | $[M+K]^+$ | 707.5009 | 707.5011 | -0.3 | |
| | DG(18:2/18:2) | $[M+H-H_2O]^+$ | 599.5029 | 599.5034 | -0.9 | 337.27 |
| | | $[M+K]^+$ | 655.4697 | 655.4698 | -0.1 | |
| | DG(36:2) | $[M+H-H_2O]^+$ | 603.5344 | 603.5346 | -0.4 | □ |
| | | $[M+K]^+$ | 659.5006 | 659.5011 | -0.8 | |
| Ceramide | Cer (36:2) | $[M+Na]^+$ | 586.5169 | 586.5170 | -0.2 | □ |
| | | $[M+K]^+$ | 602.4907 | 602.4909 | -0.3 | |
| | Cer(d18:1/18:0) | $[M+K]^+$ | 604.5065 | 604.5066 | -0.2 | 252.27, 264.27, 282.28 |

| Analyte chemical class | Compound | Detected ions | Detected Mass | Exact Mass | Delta /Δppm | The product ions |
|---|---|---|---|---|---|---|
| | Cer(d18:1/24:1) | $[M+K]^+$ | 686.5846 | 686.5848 | -0.3 | 252.27, 264.27, 282.28 |
| CerP | CerP(38:2) | $[M+K]^+$ | 710.4885 | 710.4885 | 0.0 | □ |
| | CerP(40:1) | $[M+2K-H]^+$ | 778.4909 | 778.4914 | -0.6 | □ |
| | CerP(42:2) | $[M+2K-H]^+$ | 804.5065 | 804.5070 | -0.7 | □ |
| | CerP(44:2) | $[M+K]^+$ | 822.6144 | 822.6137 | 0.9 | □ |
| HexCer | HexCer(32:1) | $[M+2K-H]^+$ | 748.4551 | 748.4527 | 3.2 | □ |
| | HexCer (d18:1/18:0) | $[M+K]^+$ | 766.5591 | 766.5594 | -0.4 | 500.30,528.29, 586.50, 602.50 |
| | | $[M+2K-H]^+$ | 804.5145 | 804.5153 | -1.0 | |
| | HexCer(40:2) | $[M+K]^+$ | 820.6068 | 820.6063 | 0.6 | □ |
| | HexCer (42:3) | $[M+K]^+$ | 846.6218 | 846.6220 | -0.2 | □ |
| | | $[M+2Na-H]^+$ | 852.6307 | 852.6300 | 0.8 | |
| | HexCer (d18:1/24:1) | $[M+Na]^+$ | 832.6645 | 832.6637 | 1.0 | 484.33, 513.32, 652.60, 670.61 |
| | | $[M+K]^+$ | 848.6377 | 848.6376 | 0.2 | |
| | | $[M+2K-H]^+$ | 886.5926 | 886.5935 | -1.0 | |
| | HexCer (d18:1/24:0) | $[M+Na]^+$ | 834.6802 | 834.6793 | 1.1 | 484.33, 513.32, 654.62, 672.63 |
| | | $[M+K]^+$ | 850.6543 | 850.6533 | 1.2 | |
| | HexCer (36:1-OH) | $[M+K]^+$ | 782.5549 | 782.5543 | 0.8 | □ |
| | HexCer (d18:1/20:0-OH) | $[M+K]^+$ | 810.5852 | 810.5856 | -0.5 | 484.33, 513.32, 632.56 |
| | | $[M+Na]^+$ | 794.6116 | 794.6116 | 0.0 | |
| | HexCer (40:2-OH) | $[M+K]^+$ | 836.6007 | 836.6012 | -0.6 | □ |
| | HexCer (d18:1/22:0-OH) | $[M+Na]^+$ | 822.6425 | 822.6430 | -0.6 | 484.33, 513.32, 642.62, 660.63 |
| | | $[M+K]^+$ | 838.6165 | 838.6169 | -0.5 | |
| | HexCer (d18:1/23:0-OH) | $[M+K]^+$ | 852.6320 | 852.6325 | -0.6 | □ |
| | HexCer (d18:1/24:0-OH) | $[M+Na]^+$ | 850.6743 | 850.6742 | 0.1 | 484.33, 513.32, 670.61,688.62 |
| | | $[M+K]^+$ | 866.6486 | 866.6482 | 0.5 | |
| | HexCer (d18:1/24:1-OH) | $[M+K]^+$ | 864.6324 | 864.6325 | -0.1 | 500.30,528.29, 684.57, 702.58 |
| | HexCer (d18:1/25:0-OH) | $[M+K]^+$ | 880.6632 | 880.6638 | -0.7 | 500.30,528.29, 700.60.718.61 |
| | HexCer (44:2-OH) | $[M+K]^+$ | 892.6626 | 892.6638 | -1.3 | □ |
| PI-Cer | PI-Cer(38:0) | $[M+Na]^+$ | 860.5981 | 860.5987 | -0.7 | □ |
| | | $[M+K]^+$ | 876.5734 | 876.5727 | 0.8 | |
| | PI-Cer(40:0) | $[M+Na]^+$ | 888.6324 | 888.6300 | 2.7 | □ |
| | | $[M+K]^+$ | 904.6045 | 904.6040 | 0.6 | |
| CE | CE(22:6) | $[M+K]^+$ | 735.5471 | 735.5477 | -0.8 | □ |
| | CE(20:5) | $[M+2K-H]^+$ | 747.4886 | 747.4879 | 0.9 | □ |

| Analyte chemical class | Compound | Detected ions | Detected Mass | Exact Mass | Delta /Δppm | The product ions |
|---|---|---|---|---|---|---|
| | CE(16:0) | $[M+K]^+$ | 663.5469 | 663.5477 | -1.3 | □ |
| | CE(18:2) | $[M+K]^+$ | 687.5474 | 687.5477 | -0.4 | □ |
| | CE(18:1) | $[M+K]^+$ | 689.5633 | 689.5633 | 0.0 | □ |
| | CE(20:4) | $[M+K]^+$ | 711.5483 | 711.5477 | 0.8 | □ |
| PS | PS(18:0/22:6) | $[M+K]^+$ | 874.4990 | 874.4995 | -0.5 | 341.31, 385.27, 651.53 |
| | | $[M+2K-H]^+$ | 912.4562 | 912.4554 | 0.9 | |
| | PS(40:4) | $[M+K]^+$ | 878.5299 | 878.5308 | -1.0 | □ |
| | PS(18:0/20:4) | $[M+2K-H]^+$ | 888.4552 | 888.4554 | -0.2 | 339.29, 649.52 |
| | PS(38:1) | $[M+K]^+$ | 856.5458 | 856.5464 | -0.7 | □ |
| | | $[M+2K-H]^+$ | 894.5008 | 894.5023 | -1.7 | |
| | PS(44:12) | $[M+K]^+$ | 918.4676 | 918.4682 | -0.7 | □ |
| | PS(42:10) | $[M+2K-H]^+$ | 932.4233 | 932.4241 | -0.8 | □ |
| | PS(42:9) | $[M+2K-H]^+$ | 934.4386 | 934.4397 | -1.2 | □ |
| SM | SM(d18:1/18:0) | $[M+Na]^+$ | 753.5888 | 753.5881 | 0.9 | 125.00, 184.07 |
| | | $[M+K]^+$ | 769.5624 | 769.5624 | 0.0 | |
| | SM(34:0) | $[M+2K-H]^+$ | 782.5094 | 782.5101 | -0.9 | □ |
| | SM(38:1) | $[M+ACN+Na]^+$ | 822.6450 | 822.6459 | -1.1 | □ |
| | SM(40:1) | $[M+ACN+Na]^+$ | 850.6749 | 850.6772 | -2.7 | □ |
| | SM(41:0) | $[M+2K-H]^+$ | 879.6113 | 879.6118 | -0.6 | □ |
| PE | PE(18:1/16:0) | $[M+K]^+$ | 756.4931 | 756.4940 | -1.2 | 313.27, 339.29, 577.52 |
| | | $[M+2K-H]^+$ | 794.4496 | 794.4499 | -0.4 | |
| | PE(18:0/16:0) | $[M+K]^+$ | 758.5095 | 758.5097 | -0.3 | 313.27, 341.29, 579.52 |
| | | $[M+2Na-H]^+$ | 764.5176 | 764.5177 | -0.1 | |
| | | $[M+2K-H]^+$ | 796.4658 | 796.4655 | 0.4 | |
| | PE(P-16:0/18:1) | $[M+2K-H]^+$ | 778.4545 | 778.4550 | -0.6 | 339.29, 364.26 |
| | PE(P-16:0/20:4) | $[M+K]^+$ | 762.4835 | 762.4834 | 0.1 | 361.27, 364.26, 420.29, 438.30, 583.51 |
| | PE(P-18:1/18:1) | $[M+2K-H]^+$ | 804.4709 | 804.4706 | 0.4 | 120.97, 164.01, 339.29, 587.54, 609.52, 707.50 |
| | PE(P-18:1/18:0) | $[M+K]^+$ | 768.5305 | 768.5304 | 0.1 | 339.29, 392.29 |
| | PE(P-38:6) | $[M+K]^+$ | 786.4840 | 786.4834 | 0.8 | □ |
| | PE(P-18:1/20:4) | $[M+Na]^+$ | 772.5252 | 772.5252 | 0.0 | 361.27, 390.28, 609.52 |
| | | $[M+K]^+$ | 788.4987 | 788.4991 | -0.5 | |
| | | $[M+2K-H]^+$ | 826.4557 | 826.4550 | 0.8 | |
| | PE(P-38:4) | $[M+K]^+$ | 790.5143 | 790.5147 | -0.5 | □ |
| | PE(P-38:2) | $[M+K]^+$ | 794.5468 | 794.5460 | 1.0 | □ |
| | | $[M+2K-H]^+$ | 832.5013 | 832.5019 | -0.7 | |
| | PE(20:4/16:0) | $[M+2K-H]^+$ | 816.4341 | 816.4342 | -0.2 | 313.27, 361.27, 599.50 |
| | PE(18:1/18:2) | $[M+K]^+$ | 780.4940 | 780.4940 | 0.0 | 337.27, 339.29, 623.50 |
| | PE(18:1/18:1) | $[M+2K-H]^+$ | 820.4657 | 820.4655 | 0.2 | 339.29, 625.52 |

| Analyte chemical class | Compound | Detected ions | Detected Mass | Exact Mass | Delta /Δppm | The product ions |
|---|---|---|---|---|---|---|
| | PE(18:1/18:0) | $[M+K]^+$ | 784.5254 | 784.5253 | 0.1 | 164.01, 339.29, 341.31, 605.55, 627.53 |
| | | $[M+2K-H]^+$ | 822.4811 | 822.4812 | -0.1 | |
| | PE(16:0/22:6) | $[M+K]^+$ | 802.4786 | 802.4784 | 0.2 | 313.27, 385.27, 623.50 |
| | | $[M+2K-H]^+$ | 840.4351 | 840.4342 | 1.1 | |
| | PE(38:5) | $[M+2K-H]^+$ | 842.4509 | 842.4499 | 1.2 | □ |
| | PE(18:0/20:4) | $[M+K]^+$ | 806.5076 | 806.5097 | -2.6 | 164.01, 341.31, 627.54, 649.52 or |
| | or PE(18:1/20:3) | $[M+2K-H]^+$ | 844.4656 | 844.4655 | 0.1 | 164.01, 339.29, 627.54, 649.52 |
| | PE(38:2) | $[M+2K-H]^+$ | 848.4966 | 848.4968 | -0.2 | □ |
| | PE(38:1) | $[M+2K-H]^+$ | 850.5135 | 850.5125 | 1.2 | □ |
| | PE(P-18:1/22:6) | $[M+K]^+$ | 812.4977 | 812.4991 | -1.7 | 633.52, 731.50, 385.27, 390.28, 446.30, 464.31 |
| | | $[M+2K-H]^+$ | 850.4549 | 850.4550 | -0.1 | |
| | PE(P-18:0/22:6) | $[M+K]^+$ | 814.5146 | 814.5147 | -0.1 | 385.27, 392.29, 448.32, 466.33 |
| | | $[M+2Na-H]^+$ | 820.5242 | 820.5228 | 1.7 | |
| | | $[M+2K-H]^+$ | 852.4718 | 852.4706 | 1.4 | |
| | PE(P-18:1/22:4) | $[M+K]^+$ | 816.5293 | 816.5304 | -1.3 | 389.31, 390.28, 464.31, 637.56 |
| | | $[M+2K-H]^+$ | 854.4859 | 854.4863 | -0.5 | |
| | PE(P-18:0/22:4) | $[M+K]^+$ | 818.5452 | 818.5460 | -1.0 | 389.31, 392.29, 466.33 |
| | | $[M+2Na-H]^+$ | 824.5548 | 824.5541 | 0.8 | |
| | | $[M+2K-H]^+$ | 856.5029 | 856.5019 | 1.2 | |
| | PE(16:0/20:4) | $[M+2K-H]^+$ | 816.4358 | 816.4342 | 2.0 | 313.27, 361.27, 599.50 |
| | PE(18:1/18:1) | $[M+2K-H]^+$ | 820.4657 | 820.4655 | 0.2 | 339.29, 603.54 |
| | PE(18:1:22:6) | $[M+K]^+$ | 828.4929 | 828.4940 | -1.3 | 339.29, 385.27, 649.52 |
| | | $[M+2K-H]^+$ | 866.4500 | 866.4499 | 0.1 | |
| | PE(18:0/22:6) | $[M+K]^+$ | 830.5094 | 830.5097 | -0.4 | 385.27, 392.29, 448.32, 466.33 |
| | | $[M+2K-H]^+$ | 868.4654 | 868.4655 | -0.1 | |
| | PE(20:0/20:4) | $[M+K]^+$ | 834.5398 | 834.5410 | -1.4 | 341.31, 655.57 |
| | | $[M+2K-H]^+$ | 872.4971 | 872.4968 | 0.3 | |
| | PE(42:9) | $[M+K]^+$ | 852.4926 | 852.4940 | -1.7 | □ |
| | | $[M+2K-H]^+$ | 890.4505 | 890.4499 | 0.7 | |
| | PE(42:7) | $[M+2K-H]^+$ | 894.4807 | 894.4812 | -0.6 | □ |
| | PE(42:6) | $[M+2K-H]^+$ | 896.4974 | 896.4968 | 0.7 | □ |
| | PE(44:10) | $[M+2K-H]^+$ | 916.4644 | 916.4655 | -1.2 | □ |
| PC | PC(16:1/16:0) | $[M+2K-H]^+$ | 808.4653 | 808.4655 | -0.3 | 125.00, 184.07 |
| | PC(16:0/16:0) | $[M+Na]^+$ | 756.5514 | 756.5514 | 0.0 | 125.00, 184.07, 720.59 |
| | | $[M+2K-H]^+$ | 810.4827 | 810.4812 | 1.9 | |
| | PC(18:1/16:0) | $[M+Na]^+$ | 782.5674 | 782.5670 | 0.5 | 125.00, 184.07, 760.59 |
| | | $[M+K]^+$ | 798.5405 | 798.5410 | -0.6 | |
| | | $[M+2Na-H]^+$ | 804.5501 | 804.5490 | 1.4 | |
| | | $[M+2K-H]^+$ | 836.4973 | 836.4968 | 0.6 | |
| | PC(P-38:6) | $[M+K]^+$ | 828.5309 | 828.5304 | 0.6 | □ |

| Analyte chemical class | Compound | Detected ions | Detected Mass | Exact Mass | Delta /Δppm | The product ions |
|---|---|---|---|---|---|---|
| | PC(18:1/18:0) | $[M+Na]^+$ | 810.5981 | 810.5983 | -0.2 | 125.00, 184.07 |
| | | $[M+K]^+$ | 826.5725 | 826.5723 | 0.2 | |
| | PC(16:0/20:4) | $[M+K]^+$ | 820.5242 | 820.5253 | -1.3 | 125.00, 184.07 |
| | PC(16:0/22:6) | $[M+K]^+$ | 844.5252 | 844.5253 | -0.1 | 125.00, 184.07 |
| | PC(38:7) | $[M+2K-H]^+$ | 880.4653 | 880.4655 | -0.3 | □ |
| | PC(18:0/22:6) | $[M+K]^+$ | 872.5559 | 872.5566 | -0.8 | 184.07, 341.30, 385.27, 651.53 |
| PG | PG(16:0/20:4) | $[M+Na]^+$ | 793.4983 | 793.4990 | -0.9 | 155.01, 305.24, 313.27, 599.50 |
| | ST(33:1) | $[M+H]^+$ | 766.5140 | 766.5134 | 0.8 | □ |
| | | $[M+Na]^+$ | 804.4709 | 804.4692 | 2.1 | |
| | | $[M+K]^+$ | 788.4963 | 788.4953 | 1.3 | |
| | ST(36:2) | $[M+2K-H]^+$ | 882.4576 | 882.4564 | 1.4 | □ |
| | ST(d18:1/18:0) | $[M+2K-H]^+$ | 884.4716 | 884.4721 | -0.6 | 259.00, 267.26, 340.30 |
| | ST(40:2) | $[M+H]^+$ | 862.6078 | 862.6073 | 0.5 | □ |
| ST | ST(d18:1/22:0) | $[M+2K-H]^+$ | 940.5331 | 940.5347 | -1.7 | 243.00, 259.00, 323.32, 366.36, 627.38 |
| | ST(d18:1/24:1) | $[M+2K-H]^+$ | 966.5497 | 966.5503 | -0.6 | 243.00, 259.00, 392.38 |
| | ST(d18:1/24:0) | $[M+2K-H]^+$ | 968.5679 | 968.5660 | 2.0 | 243.00, 259.00, 394.39 |
| | ST(40:2-OH) | $[M+2Na-H]^+$ | 922.5671 | 922.5661 | 1.1 | □ |
| | ST (d18:1/24:0-OH) | $[M+2Na-H]^+$ | 952.6136 | 952.6130 | 0.6 | 243.00, 339.35, 524.28, 542.29, 570.28 |
| | PI(28:3) | $[M+K]^+$ | 787.3789 | 787.3794 | -0.6 | □ |
| | PI(36:4) | $[M+K]^+$ | 897.4868 | 897.4890 | -2.5 | □ |
| PI | PI(38:5) | $[M+2K-H]^+$ | 961.4599 | 961.4605 | -0.6 | □ |
| | PI(38:4) | $[M+K]^+$ | 925.5199 | 925.5203 | -0.4 | □ |
| | | $[M+2K-H]^+$ | 963.4776 | 963.4762 | 1.4 | |
| | PI(38:3) | $[M+2K-H]^+$ | 965.4950 | 965.4918 | 3.3 | □ |
| | PIP(28:3-OH) | $[M+K]^+$ | 883.3412 | 883.3407 | 0.6 | □ |
| | PIP(36:4) | $[M+NH_4]^+$ | 956.5290 | 956.5260 | 3.1 | □ |
| | PIP(36:2) | $[M+H-2H_2O]^+$ | 925.5216 | 925.5208 | 0.9 | □ |
| | PIP(38:5) | $[M+H-H_2O]^+$ | 947.5024 | 947.5051 | -2.9 | □ |
| PIP | | $[M+NH_4]^+$ | 982.5435 | 982.5416 | 1.9 | |
| | PIP(38:4) | $[M+NH_4]^+$ | 984.5599 | 984.5573 | 2.6 | □ |
| | PIP(34:1) | $[M+H-H_2O]^+$ | 897.4868 | 897.4895 | -3.0 | □ |
| | PIP2(34:2) | $[M+H-H_2O]^+$ | 959.4446 | 959.4458 | -1.2 | □ |
| | | $[M+K]^+$ | 1033.4181 | 1033.4216 | -3.4 | |
| | CDP-DG(26:0) | $[M+K]^+$ | 908.3841 | 908.3836 | 0.6 | □ |
| | | $[M+2Na-H]^+$ | 914.3964 | 914.3916 | 5.2 | |
| CDP-DG | CDP-DG(28:0) | $[M+K]^+$ | 936.4190 | 936.4149 | 4.4 | □ |
| | | $[M+2Na-H]^+$ | 942.4270 | 942.4229 | 4.4 | |
| | CDP-DG(27:0) | $[M+K]^+$ | 922.4048 | 922.3992 | 6.1 | □ |

| Analyte chemical class | Compound | Detected ions | Detected Mass | Exact Mass | Delta /Δppm | The product ions |
|---|---|---|---|---|---|---|
| | | $[M+2Na-H]^+$ | 928.4015 | 928.4072 | -6.1 | |
| | CDP-DG(29:0) | $[M+K]^+$ | 950.4297 | 950.4305 | -0.8 | □ |
| GA1 | Ganglioside GA1(36:1) | $[M+Na]^+$ | 1277.7746 | 1277.7705 | 3.2 | □ |
| | | $[M+K]^+$ | 1293.7480 | 1293.7444 | 2.7 | |
| | Ganglioside GA1(36:2) | $[M+Na]^+$ | 1275.7605 | 1275.7548 | 4.5 | □ |
| | | $[M+K]^+$ | 1291.7322 | 1291.7287 | 2.7 | |
| | Ganglioside GA1(38:1) | $[M+Na]^+$ | 1305.8054 | 1305.8018 | 2.8 | □ |
| | | $[M+K]^+$ | 1321.7690 | 1321.7757 | -5.0 | |
| **DHB assisted MALDI MS Positive mode** | | | | | | □ |
| □ | Phosphoryl -choline | $[M+H]^+$ | 184.0736 | 184.0739 | -1.6 | □ |
| | | $[M+Na]^+$ | 206.0557 | 206.0558 | -0.6 | |
| | | $[M+K]^+$ | 222.0298 | 222.0298 | 0.0 | |
| Amino acid | Taurine | $[M+2K-H]^+$ | 201.9341 | 201.9337 | 2.0 | □ |
| Chol | Cholesterol | $[M+H-H_2O]^+$ | 369.3523 | 369.3522 | 0.3 | □ |
| LPC | LysoPC(16:0) | $[M+H-H_2O]^+$ | 478.3304 | 478.3298 | 1.3 | □ |
| | | $[M+K]^+$ | 534.2969 | 534.2956 | 2.4 | |
| | LysoPC(18:1) | $[M+H-H_2O]^+$ | 504.3454 | 504.3454 | 0.0 | □ |
| | | $[M+H]^+$ | 522.3563 | 522.3554 | 1.7 | |
| | | $[M+K]^+$ | 560.3123 | 560.3113 | 1.8 | |
| | LysoPC(18:0) | $[M+H]^+$ | 524.3725 | 524.3711 | 2.7 | □ |
| | | $[M+K]^+$ | 562.3280 | 562.3269 | 2.0 | |
| | LysoPC(20:4) | $[M+H]^+$ | 544.3393 | 544.3398 | -0.9 | □ |
| | LysoPC(22:6) | $[M+H]^+$ | 568.3410 | 568.3398 | 2.1 | □ |
| | | $[M+K]^+$ | 606.2965 | 606.2956 | 1.5 | |
| LPE | LysoPE(18:1) | $[M+K]^+$ | 518.2643 | 518.2643 | 0.0 | □ |
| | | $[M+2K-H]^+$ | 556.2219 | 556.2202 | 3.1 | |
| | LysoPE(20:4) | $[M+K]^+$ | 540.2508 | 540.2487 | 3.9 | □ |
| | LysoPE(22:6) | $[M+K]^+$ | 564.2500 | 564.2487 | 2.3 | □ |
| | | $[M+2K-H]^+$ | 602.2049 | 602.2046 | 0.5 | |
| Cer | Cer (36:1) | $[M+H-H_2O]^+$ | 548.5415 | 548.5407 | 1.5 | □ |
| | | $[M+K]^+$ | 604.5080 | 604.5066 | 2.3 | |
| DG | DG(32:0) | $[M+H-H_2O]^+$ | 551.5047 | 551.5040 | 1.3 | □ |
| | DG(34:1) | $[M+H-H_2O]^+$ | 577.5204 | 577.5196 | 1.4 | □ |
| | DG(36:4) | $[M+H-H_2O]^+$ | 599.5036 | 599.5040 | -0.7 | □ |
| | DG(36:1) | $[M+H-H_2O]^+$ | 605.5521 | 605.5509 | 2.0 | □ |
| | DG(38:6) | $[M+H-H_2O]^+$ | 623.5052 | 623.5040 | 1.9 | □ |
| | DG(38:5) | $[M+H-H_2O]^+$ | 625.5222 | 625.5196 | 4.2 | □ |
| | DG(38:4) | $[M+H-H_2O]^+$ | 627.5382 | 627.5353 | 4.6 | □ |
| | DG(40:6) | $[M+H-H_2O]^+$ | 651.5367 | 651.5353 | 2.1 | □ |
| PA | PA(36:4) | $[M+H]^+$ | 697.4824 | 697.4803 | 3.0 | □ |

| Analyte chemical class | Compound | Detected ions | Detected Mass | Exact Mass | Delta /Δppm | The product ions |
|---|---|---|---|---|---|---|
| | | $[M+K]^+$ | 735.4385 | 735.4362 | 3.1 | |
| | PA(34:1) | $[M+K]^+$ | 713.4530 | 713.4518 | 1.7 | □ |
| | | $[M+2K-H]^+$ | 751.4107 | 751.4077 | 4.0 | |
| | PA(36:3) | $[M+K]^+$ | 737.4540 | 737.4518 | 3.0 | □ |
| | PA(36:2) | $[M+K]^+$ | 739.4692 | 739.4675 | 2.3 | □ |
| | | $[M+2K-H]^+$ | 777.4245 | 777.4233 | 1.5 | □ |
| | PA(38:3) | $[M+Na]^+$ | 749.5093 | 749.5092 | 0.1 | □ |
| | | $[M+K]^+$ | 765.4856 | 765.4831 | 3.3 | |
| | PA(40:5) | $[M+H]^+$ | 751.5302 | 751.5272 | 4.0 | □ |
| | | $[M+K]^+$ | 789.4819 | 789.4831 | -1.5 | |
| | PA(38:5) | $[M+K]^+$ | 761.4531 | 761.4518 | 1.7 | □ |
| | PA(38:4) | $[M+K]^+$ | 763.4710 | 763.4675 | 4.6 | □ |
| | PA(38:2) | $[M+K]^+$ | 767.4999 | 767.4988 | 1.4 | □ |
| | PA(40:7) | $[M+K]^+$ | 785.4537 | 785.4518 | 2.4 | □ |
| | PA(36:1) | $[M+K]^+$ | 741.4830 | 741.4831 | -0.1 | □ |
| | | $[M+2K-H]^+$ | 779.4381 | 779.4390 | -1.2 | |
| | PA(40:6) | $[M+K]^+$ | 787.4703 | 787.4675 | 3.6 | □ |
| | | $[M+2K-H]^+$ | 825.4239 | 825.4233 | 0.7 | |
| | PA(42:7) | $[M+K]^+$ | 813.4841 | 813.4831 | 1.2 | □ |
| PS | PS(34:6) | $[M+H]^+$ | 716.4319 | 716.4297 | 3.1 | □ |
| | PS(44:12) | $[M+H]^+$ | 880.5114 | 880.5123 | -1.0 | □ |
| | | $[M+K]^+$ | 918.4657 | 918.4682 | -2.7 | |
| | PS(42:9) | $[M+K]^+$ | 896.4842 | 896.4838 | 0.4 | □ |
| | PS(40:6) | $[M+K]^+$ | 874.5039 | 874.4995 | 5.0 | □ |
| | | $[M+2K-H]^+$ | 912.4582 | 912.4554 | 3.1 | |
| | PS(42:2) | $[M+2K-H]^+$ | 948.5521 | 948.5493 | 3.0 | □ |
| SM | SM(36:1) | $[M+H]^+$ | 731.6081 | 731.6067 | 1.9 | □ |
| | | $[M+Na]^+$ | 753.5901 | 753.5886 | 2.0 | |
| | SM(42:2) | $[M+Na]^+$ | 835.6702 | 835.6663 | 4.7 | □ |
| | | $[M+K]^+$ | 851.6415 | 851.6403 | 1.4 | |
| PE | PE(40:7) | $[M+H-H_2O]^+$ | 772.5307 | 772.5282 | 3.2 | □ |
| | | $[M+H]^+$ | 828.4980 | 828.4940 | 4.8 | |
| | PE(38:1) | $[M+H]^+$ | 774.6020 | 774.6007 | 1.7 | □ |
| | PE(P-38:5) | $[M+K]^+$ | 788.4998 | 788.4991 | 0.9 | □ |
| | PE(34:1) | $[M+2K-H]^+$ | 794.4530 | 794.4499 | 3.9 | □ |
| | PE(38:6) | $[M+K]^+$ | 802.4813 | 802.4784 | 3.6 | □ |
| | | $[M+2K-H]^+$ | 840.4366 | 840.4342 | 2.9 | |
| | PE(38:4) | $[M+H-H_2O]^+$ | 806.5153 | 806.5125 | 3.5 | □ |
| | PE(P-40:6) | $[M+K]^+$ | 814.5151 | 814.5147 | 0.5 | □ |
| | PE(P-40:4) | $[M+K]^+$ | 818.5493 | 818.5460 | 4.0 | □ |

| Analyte chemical class | Compound | Detected ions | Detected Mass | Exact Mass | Delta /Δppm | The product ions |
|---|---|---|---|---|---|---|
| | PE(40:6) | $[M+K]^+$ | 830.5124 | 830.5097 | 3.3 | □ |
| | | $[M+2K-H]^+$ | 868.4673 | 868.4655 | 2.1 | |
| | PE(42:9) | $[M+K]^+$ | 852.4971 | 852.4940 | 3.6 | □ |
| PC | PC(32:0) | $[M+H]^+$ | 734.5726 | 734.5694 | 4.4 | □ |
| | | $[M+Na]^+$ | 756.5533 | 756.5514 | 2.5 | |
| | | $[M+K]^+$ | 772.5276 | 772.5253 | 3.0 | |
| | PC(34:1) | $[M+H]^+$ | 760.5871 | 760.5851 | 2.6 | □ |
| | | $[M+Na]^+$ | 782.5724 | 782.5694 | 3.8 | |
| | | $[M+K]^+$ | 798.5445 | 798.5410 | 4.4 | |
| | PC(36:4) | $[M+Na]^+$ | 804.5538 | 804.5514 | 3.0 | □ |
| | | $[M+K]^+$ | 820.5273 | 820.5253 | 2.4 | |
| | PC(36:2) | $[M+H]^+$ | 786.6041 | 786.6007 | 4.3 | □ |
| | | $[M+Na]^+$ | 808.5845 | 808.5827 | 2.2 | |
| | | $[M+K]^+$ | 824.5604 | 824.5566 | 4.6 | |
| | PC(36:1) | $[M+H]^+$ | 788.6188 | 788.6164 | 3.0 | □ |
| | | $[M+Na]^+$ | 810.6012 | 810.5983 | 3.6 | |
| | | $[M+K]^+$ | 826.5761 | 826.5723 | 4.6 | |
| | PC(34:2) | $[M+Na]^+$ | 780.5528 | 780.5514 | 1.8 | □ |
| | | $[M+K]^+$ | 796.5266 | 796.5253 | 1.6 | |
| | PC(38:6) | $[M+H]^+$ | 806.5713 | 806.5694 | 2.4 | □ |
| | | $[M+Na]^+$ | 828.5529 | 828.5514 | 1.8 | |
| | | $[M+K]^+$ | 844.5276 | 844.5253 | 2.7 | |
| | PC(32:1) | $[M+H]^+$ | 732.5562 | 732.5538 | 3.3 | □ |
| | | $[M+Na]^+$ | 754.5377 | 754.5357 | 2.7 | |
| | | $[M+K]^+$ | 770.5127 | 770.5097 | 3.9 | |
| | PC(38:4) | $[M+Na]^+$ | 832.5866 | 832.5827 | 4.7 | □ |
| | | $[M+K]^+$ | 848.5606 | 848.5566 | 4.7 | |
| | PC(38:1) | $[M+H]^+$ | 816.6463 | 816.6477 | -1.7 | □ |
| | | $[M+K]^+$ | 854.6050 | 854.6036 | 1.6 | |
| | PC(40:7) | $[M+Na]^+$ | 854.5682 | 854.5670 | 1.4 | □ |
| | | $[M+K]^+$ | 870.5453 | 870.5410 | 4.9 | |
| | PC(40:6) | $[M+H]^+$ | 834.6024 | 834.6007 | 2.0 | □ |
| | | $[M+Na]^+$ | 856.5862 | 856.5827 | 4.1 | |
| | | $[M+K]^+$ | 872.5593 | 872.5566 | 3.1 | |
| | PC(34:0) | $[M+H]^+$ | 762.6001 | 762.6007 | -0.8 | □ |
| | | $[M+Na]^+$ | 784.5832 | 784.5827 | 0.6 | |
| | | $[M+K]^+$ | 800.5548 | 800.5566 | -2.2 | |
| | | $[M+2K-H]^+$ | 838.5129 | 838.5125 | 0.5 | |
| | PC(38:2) | $[M+Na]^+$ | 836.6160 | 836.6140 | 2.4 | □ |
| | | $[M+K]^+$ | 852.5912 | 852.5879 | 3.9 | |

| Analyte chemical class | Compound | Detected ions | Detected Mass | Exact Mass | Delta /Δppm | The product ions |
|---|---|---|---|---|---|---|
| | PC(40:2) | $[M+K]^+$ | 880.6227 | 880.6192 | 4.0 | □ |
| | PC(42:1) | $[M+K]^+$ | 910.6699 | 910.6662 | 4.1 | □ |
| | PC(44:12) | $[M+K]^+$ | 916.5304 | 916.5253 | 5.6 | □ |
| PIP | PIP(36:3) | $[M+H-H_2O]^+$ | 923.5060 | 923.5051 | 1.0 | □ |
| | PIP(36:2) | $[M+H-H_2O]^+$ | 925.5233 | 925.5208 | 2.7 | □ |
| | PIP(38:5) | $[M+H-H_2O]^+$ | 947.5040 | 947.5051 | -1.2 | □ |
| | PIP2(34:1) | $[M+H]^+$ | 961.4631 | 961.4614 | 1.8 | □ |
| GA1 | Ganglioside GA1(36:1) | $[M+Na]^+$ | 1277.7756 | 1277.7705 | 4.0 | □ |
| | | $[M+K]^+$ | 1293.7573 | 1293.7444 | 10.0 | □ |

**Table S2.** List of identified or putatively identified analytes detected in mouse brain using AgNPs@PDA-assisted LDI MS or using 9-AA assisted LDI MS in negative ion detect mode. Precise m/z and mass accuracy (Δppm) of measurements and their corresponding product are reported. The compounds highlighted with light red are only detected by using AgNPs@PDA as the matrix, and the compounds highlighted with light orange are only detected by using 9-AA as the matrix.

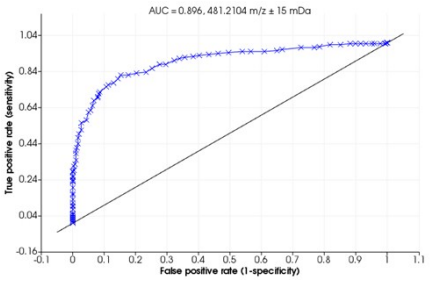
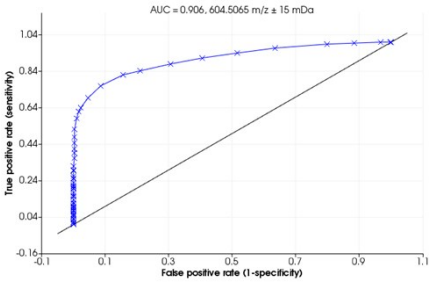
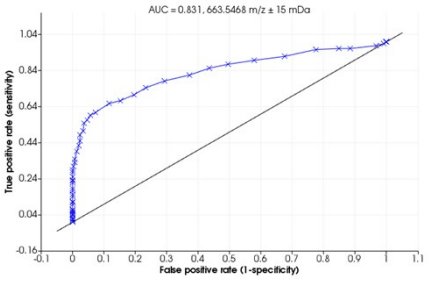
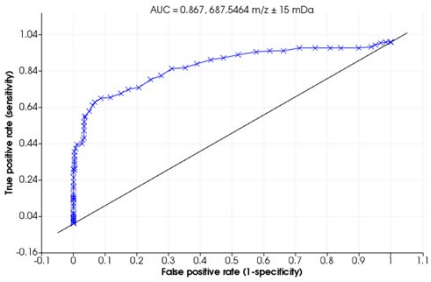
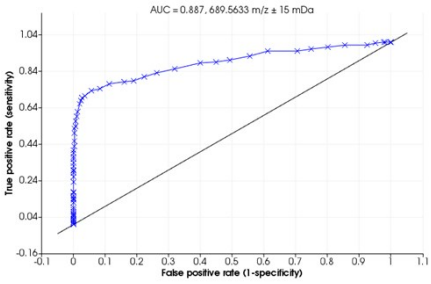
| Analyte chemical class | Compound | Detected ions | Detected Mass | Exact Mass | Delta /Δppm | The product ions |
|---|---|---|---|---|---|---|
| **AgNPs@PDA assisted MALDI MS negative mode** | | | | | | □ |
| FA | Palmitic acid/FA(16:0) | $[M-H]^-$ | 255.2336 | 255.2330 | 2.5 | □ |
| | Oleic acid/FA(18:1) | $[M-H]^-$ | 281.2493 | 281.2486 | 2.5 | □ |
| | Stearic acid/FA(18:0) | $[M-H]^-$ | 283.2651 | 283.2643 | 2.8 | □ |
| | Arachidonic acid /FA(20:4) | $[M-H]^-$ | 303.2334 | 303.2330 | 1.3 | □ |
| | Docosahexaenoic acid/FA(22:6) | $[M-H]^-$ | 327.2340 | 327.2330 | 2.9 | □ |
| | Adrenic acid/FA(22:4) | $[M-H]^-$ | 331.2652 | 331.2643 | 2.7 | □ |
| DG | DG(42:10) | $[M-H]^-$ | 687.5013 | 687.4994 | 2.8 | □ |
| PA&LPA | LPA(18:0) | $[M-H]^-$ | 437.2690 | 437.2674 | 3.7 | □ |
| | PA(34:1) | $[M-H]^-$ | 673.4821 | 673.4814 | 1.0 | □ |
| | PA(36:2) | $[M-H]^-$ | 699.4996 | 699.4970 | 3.7 | □ |
| | PA(36:1) | $[M-H]^-$ | 701.5109 | 701.5127 | -2.6 | □ |
| | PA(18:0/22:6) | $[M-H]^-$ | 747.4947 | 747.4970 | -3.1 | 283.26, 327.23, 419.25, 437.27 |
| | CPA(16:0) | $[M-H]^-$ | 391.2266 | 391.2255 | 2.9 | □ |
| | CPA(18:1) | $[M-H]^-$ | 417.2413 | 417.2411 | 0.5 | □ |
| | CPA(18:0) | $[M-H]^-$ | 419.2576 | 419.2568 | 1.9 | □ |
| LPE | LPE(18:0) | $[M-H_2O-H]^-$ | 462.2999 | 462.2984 | 3.2 | 196.04, 283.26, 480.31 |
| | | $[M-H]^-$ | 480.3110 | 480.3096 | 2.9 | |
| | LPE(18:1) | $[M-H]^-$ | 478.2946 | 478.2939 | 1.5 | 196.04, 281.25, 478.29 |
| PE | PE(34:1) | $[M-H]^-$ | 716.5263 | 716.5236 | 3.8 | □ |
| | PE(18:0/16:0) | $[M-H]^-$ | 718.5414 | 718.5392 | 3.1 | 255.23, 462.30, 480.31 |
| | PE(36:2) | $[M-H]^-$ | 742.5413 | 742.5392 | 2.8 | □ |
| | PE(18:1/18:0) or PE(16:0/20:1) | $[M-H]^-$ | 744.5573 | 744.5549 | 3.2 | 281.25, 283.27, 462.30, 480.311 or 255.23, 488.32, 506.32 |
| | PE(16:0/22:6) | $[M-H]^-$ | 762.5092 | 762.5079 | 1.7 | 196.04, 255.2, 283.24, 327.23, 391.23, 452.28 |
| | PE(18:1/20:4) | $[M-H]^-$ | 764.5229 | 764.5236 | -0.9 | 196.04, 259.24, 281.25, 303.23, |
| | PE(18:0/20:4) | $[M-H]^-$ | 766.5414 | 766.5392 | 2.9 | 196.04, 259.24, 283.26, 303.23, |

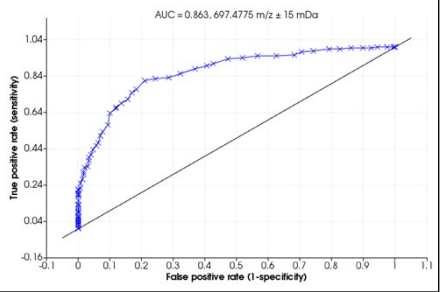
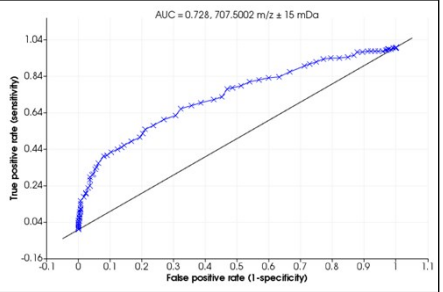
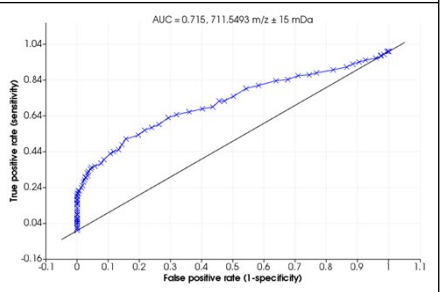
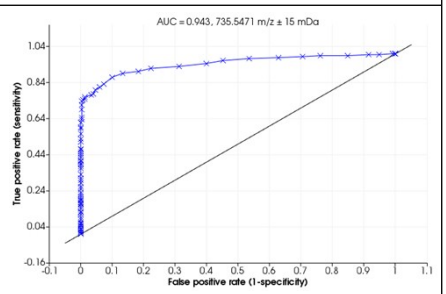
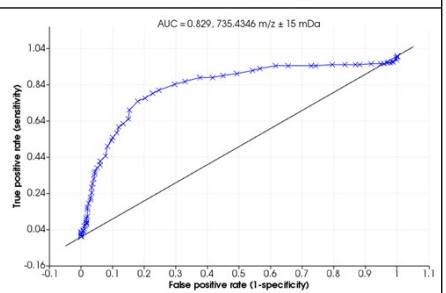
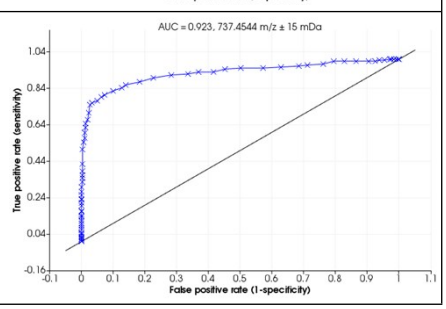
| Analyte chemical class | Compound | Detected ions | Detected Mass | Exact Mass | Delta /Δppm | The product ions |
|---|---|---|---|---|---|---|
| | | | | | | 462.30, 480.31 |
| | PE(38:1) | $[M-H]^-$ | 772.5894 | 772.5862 | 4.1 | □ |
| | PE(18:1/22:6) | $[M-H]^-$ | 788.5222 | 788.5236 | -1.8 | 153.00, 196.04, 281.25, 327.23, 524.28 |
| | PE(18:0/22:6) | $[M-H]^-$ | 790.5417 | 790.5392 | 3.2 | 283.24, 325.31, 329.24, 341.31, 466.32 |
| | PE(20:0/20:4) | $[M-H]^-$ | 794.5724 | 794.5705 | 2.4 | 153.00, 196.04, 303.23, 311.30, 482.27, 500.28 |
| | PE(44:8) | $[M-H_2O-H]^-$ | 822.5454 | 822.5438 | 1.9 | □ |
| | PE(P-34:1) | $[M-H]^-$ | 700.5306 | 700.5287 | 2.7 | □ |
| | PE(P-18:1/18:1) | $[M-H]^-$ | 726.5457 | 726.5443 | 1.9 | 281.25, 419.26, 444.29, 462.30 |
| | PE(P-18:0/18:1) | $[M-H]^-$ | 728.5635 | 728.5600 | 4.8 | 281.25, 446.30, 464.32 |
| | PE(P-18:1/20:5) | $[M-H]^-$ | 746.5164 | 746.5130 | 4.6 | 283.21, 444.29, 462.29, 480.25 |
| | PE(P-18:1:20:4) | [M-H]- | 748.5319 | 748.5287 | 4.3 | □ |
| | PE(P-18:1/20:3) | $[M-H]^-$ | 750.5465 | 750.5443 | 2.9 | □ |
| | PE(P-38:2) | $[M-H]^-$ | 754.5802 | 754.5756 | 6.1 | □ |
| | PE(P-38:1) | $[M-H]^-$ | 756.5937 | 756.5913 | 3.2 | □ |
| | PE(P-18:0/22:6) | $[M-H]^-$ | 774.5470 | 774.5443 | 3.5 | 140.50, 267.27, 283.24, 309.31, 327.23, 446.30, 464.31 |
| | PE(P-40:4) | $[M-H]^-$ | 778.5770 | 778.5756 | 1.8 | □ |
| PS | PS(18:1/18:1) or PS(18:0/18:2) | $[M-H]^-$ | 786.5321 | 786.5291 | 3.8 | 281.25, 417.24, 435.25 or 279.23, 283.27, 419.26, 437.27 |
| | PS(18:1/20:3) | $[M-H]^-$ | 810.5273 | 810.5291 | -2.2 | 281.25, 417.24, 459.25, 546.28, 723.50 |
| | PS(38:1) | $[M-H]^-$ | 788.5468 | 788.5436 | 4.1 | □ |
| | PS(18:1/22:5) | $[M-H]^-$ | 834.5331 | 834.5291 | 4.8 | 153.00, 281.25, 747.50 |
| | | $[M+K-2H]^-$ | 872.4853 | 872.4849 | 0.5 | |
| | PS(42:9) | $[M-H]^-$ | 856.5101 | 856.5134 | -3.9 | □ |
| | PS(42:1) | $[M-H]^-$ | 872.6347 | 872.6386 | -4.5 | □ |
| | PS(44:10) | $[M-H]^-$ | 882.5261 | 882.5291 | -3.4 | □ |
| ST | ST(36:3) | $[M-H]^-$ | 802.5177 | 802.5145 | 4.0 | □ |
| | ST(d18:1/18:0) | $[M-H]^-$ | 806.5477 | 806.5458 | 2.4 | 257.00, 265.26, 308.30 |
| | ST(40:2) | $[M-H]^-$ | 860.5939 | 860.5927 | 1.4 | □ |
| | ST(d18:1/22:0) | $[M-H]^-$ | 862.6113 | 862.6084 | 3.4 | 241.00, 257.00, 321.32, 364.36, 625.38 |
| | ST(41:1) | $[M-H]^-$ | 876.6198 | 876.6240 | -4.8 | □ |
| | ST(42:3) | $[M-H]^-$ | 886.6102 | 886.6084 | 2.0 | □ |
| | ST(d18:1/24:1) | $[M-H]^-$ | 888.6273 | 888.6240 | 3.7 | 241.00, 259.20, 281.25, 283.27 |
| | | $[M+K-2H]^-$ | 926.5812 | 926.5799 | 1.4 | |
| | ST(d18:1/24:0) | $[M-H]^-$ | 890.6387 | 890.6397 | -1.1 | 241.00, 257.00, 392.39 |

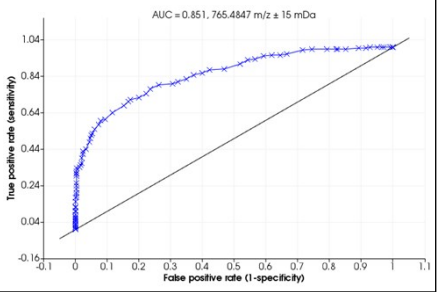
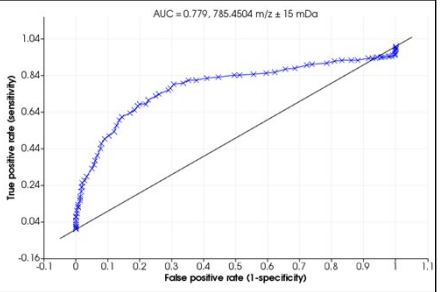
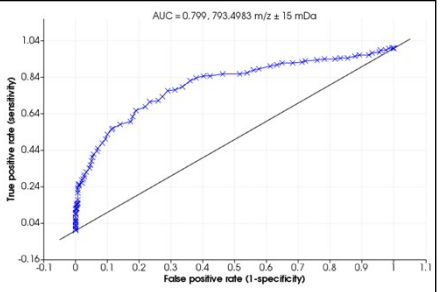
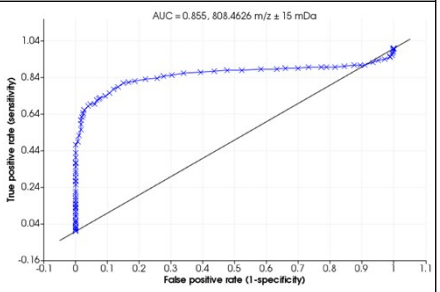
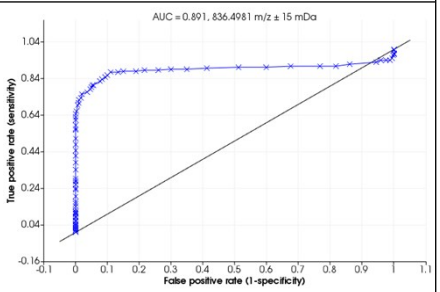
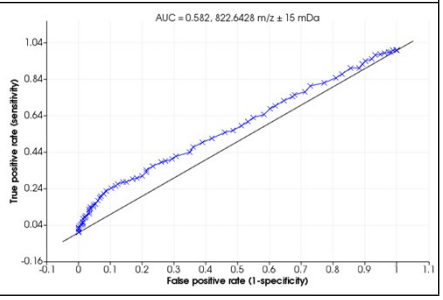
| Analyte chemical class | Compound | Detected ions | Detected Mass | Exact Mass | Delta /Δppm | The product ions |
|---|---|---|---|---|---|---|
| | ST(38:1-OH) | $[M-H]^-$ | 850.5732 | 850.5720 | 1.4 | □ |
| | ST(40:2-OH) | $[M-H]^-$ | 876.5890 | 876.5876 | 1.6 | □ |
| | ST(d18:1/22:0-OH) | $[M-H]^-$ | 878.6048 | 878.6033 | 1.7 | 241.00, 257.00, 321.32, 364.36 |
| | ST(d18:1/24:1-OH) | $[M-H]^-$ | 904.6221 | 904.6189 | 3.5 | 241.00, 335.33, 522.28 |
| | ST(d18:1/24:0-OH) | $[M-H]^-$ | 906.6374 | 906.6346 | 3.1 | 241.00, 337.35, 522.28 |
| PI | PI(34:1) | $[M-H]^-$ | 835.5360 | 835.5342 | 2.2 | □ |
| | PI(16:0/20:4) | $[M-H]^-$ | 857.5191 | 857.5186 | 0.6 | 241.01, 255.23, 303.23, 409.24, 439.23, 553.28, 571.29 |
| | PI(38:6) | $[M-H]^-$ | 881.5229 | 881.5186 | 4.9 | □ |
| | PI(18:1/20:4) | $[M-H]^-$ | 883.5371 | 883.5342 | 3.3 | 241.01, 281.25, 303.23, 417.24, 439.23, 579.30, 597.31 |
| | PI(18:0/20:4) | $[M-H]^-$ | 885.5520 | 885.5499 | 2.4 | 241.01, 283.27, 303.23, 419.26, 439.23, 581.31, 599.32 |
| | PI(40:6) | $[M-H]^-$ | 909.5543 | 909.5499 | 4.8 | □ |
| PIP | PIP(38:4) | $[M-H]^-$ | 965.5163 | 965.5162 | 0.1 | □ |
| | | $[M+Na-2H]^-$ | 987.4980 | 987.4981 | -0.1 | |
| | PIP2(36:2) | $[M-H_2O-H]^-$ | 1003.4712 | 1003.4714 | -0.2 | □ |
| | PIP2(38:3) | $[M-H_2O-H]^-$ | 1029.4838 | 1029.4871 | -3.2 | □ |
| CDP-DG | CDP-DG(36:1) | $[M-H]^-$ | 1006.5509 | 1006.5540 | -3.1 | □ |
| **9-AA assisted MALDI MS Negative mode** | | | | | | |
| FA | Palmitic acid/FA(16:0) | $[M-H]^-$ | 255.2336 | 255.2330 | 2.5 | □ |
| | Oleic acid/FA(18:1) | $[M-H]^-$ | 281.2493 | 281.2486 | 2.5 | □ |
| | Stearic acid/FA(18:0) | $[M-H]^-$ | 283.2651 | 283.2643 | 2.8 | □ |
| | Arachidonic acid /FA(20:4) | $[M-H]^-$ | 303.2334 | 303.2330 | 1.3 | □ |
| | Docosahexaenoic acid/FA(22:6) | $[M-H]^-$ | 327.2340 | 327.2330 | 2.9 | □ |
| | Adrenic acid/FA(22:4) | $[M-H]^-$ | 331.2652 | 331.2643 | 2.7 | □ |
| PS | PS(36:1) | $[M-H]^-$ | 788.5439 | 788.5436 | 0.4 | □ |
| | PS(40:6) | $[M-H]^-$ | 834.5329 | 834.5291 | 4.6 | □ |
| | PS(42:9) | $[M-H]^-$ | 856.5148 | 856.5134 | 1.6 | □ |
| | PS(44:5) | $[M-H]^-$ | 892.6099 | 892.6073 | 2.9 | □ |
| PE | PE(38:4) | $[M-H]^-$ | 766.5414 | 766.5392 | 2.9 | □ |
| | PE(36:1) | $[M-H]^-$ | 744.5573 | 744.5549 | 3.2 | □ |
| | PE(P-40:6) | $[M-H]^-$ | 774.5470 | 774.5443 | 3.5 | □ |
| | PE(40:6) | $[M-H]^-$ | 790.5384 | 790.5392 | -1.0 | □ |

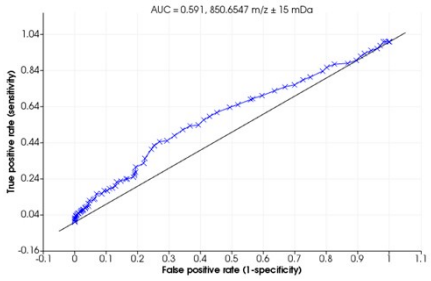
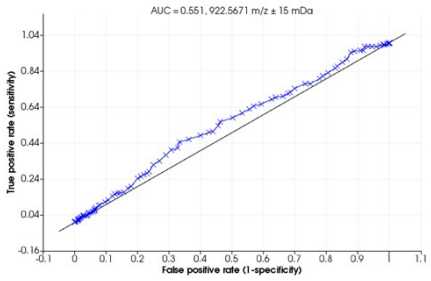
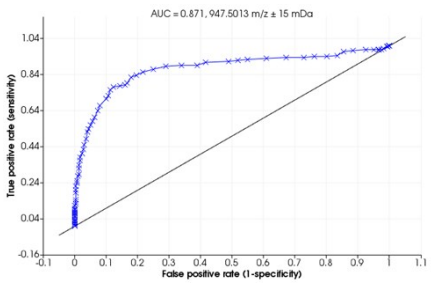
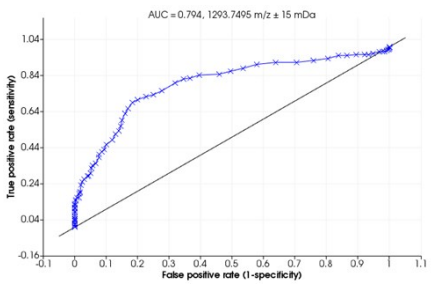
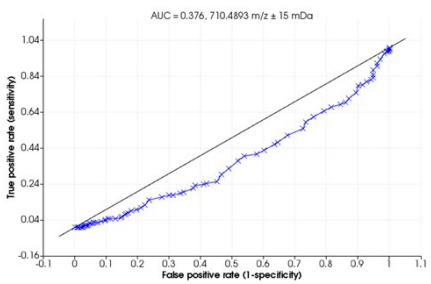
| Analyte chemical class | Compound | Detected ions | Detected Mass | Exact Mass | Delta /Δppm | The product ions |
|---|---|---|---|---|---|---|
| PC | PC(36:2) | $[M+K-2H]^-$ | 822.5398 | 822.5421 | -2.8 | □ |
| PA | LPA(18:0) | $[M-H]^-$ | 437.2690 | 437.2674 | 3.7 | □ |
| | PA(34:1) | $[M-H]^-$ | 673.4821 | 673.4814 | 1.0 | □ |
| | PA(36:2) | $[M-H]^-$ | 699.4996 | 699.4970 | 3.7 | □ |
| | PA(36:1) | $[M-H]^-$ | 701.5109 | 701.5127 | -2.6 | □ |
| | PA(40:6) | $[M-H]^-$ | 747.4947 | 747.4970 | -3.1 | □ |
| | PA(40:1) | $[M+K-2H]^-$ | 795.5343 | 795.5312 | 3.9 | □ |
| | PA(42:2) | $[M+K-2H]^-$ | 821.5504 | 821.5468 | 4.4 | □ |
| | CPA(16:0) | $[M-H]^-$ | 391.2266 | 391.2255 | 2.9 | □ |
| | CPA(18:1) | $[M-H]^-$ | 417.2413 | 417.2411 | 0.5 | □ |
| | CPA(18:0) | $[M-H]^-$ | 419.2576 | 419.2568 | 1.9 | □ |
| ST | ST(36:1) | $[M-H]^-$ | 806.5494 | 806.5458 | 4.5 | □ |
| | ST(38:1) | $[M-H]^-$ | 834.5812 | 834.5771 | 4.9 | □ |
| | ST(40:2) | $[M-H]^-$ | 860.5968 | 860.5927 | 4.8 | □ |
| | ST(40:1) | $[M-H]^-$ | 862.6073 | 862.6084 | -1.3 | □ |
| | ST(41:2) | $[M-H]^-$ | 874.6104 | 874.6084 | 2.3 | □ |
| | ST(41:1) | $[M-H]^-$ | 876.6300 | 876.6240 | 6.8 | □ |
| | ST(42:3) | $[M-H]^-$ | 886.6151 | 886.6084 | 7.6 | □ |
| | ST(42:2) | $[M-H_2O-H]^-$ | 870.6161 | 870.6129 | 3.7 | |
| | | $[M-H]^-$ | 888.6290 | 888.6240 | 5.6 | |
| | | $[M+K-2H]^-$ | 926.5816 | 926.5799 | 1.8 | □ |
| | ST(42:1) | $[M-H]^-$ | 890.6402 | 890.6397 | 0.6 | |
| | | $[M+K-2H]^-$ | 928.5954 | 928.5955 | -0.1 | □ |
| | ST(43:2) | $[M-H]^-$ | 902.6416 | 902.6397 | 2.1 | □ |
| | ST(44:2) | $[M-H]^-$ | 916.6564 | 916.6553 | 1.2 | □ |
| | ST(38:1-OH) | $[M-H]^-$ | 850.5762 | 850.5720 | 4.9 | □ |
| | ST(40:2-OH) | $[M-H]^-$ | 876.5890 | 876.5876 | 1.6 | □ |
| | ST(40:1-OH) | $[M-H]^-$ | 878.6068 | 878.6033 | 4.0 | □ |
| | ST(42:2-OH) | $[M-H]^-$ | 904.6234 | 904.6189 | 5.0 | □ |
| | ST(42:1-OH) | $[M-H]^-$ | 906.6388 | 906.6346 | 4.6 | □ |
| | ST(44:2-OH) | $[M-H]^-$ | 932.6547 | 932.6502 | 4.8 | □ |
| | ST(44:1-OH) | $[M-H]^-$ | 934.6696 | 934.6659 | 4.0 | □ |
| PI | PI(34:1) | $[M-H]^-$ | 835.5338 | 835.5342 | -0.5 | □ |
| | PI(36:4) | $[M-H]^-$ | 857.5220 | 857.5186 | 4.0 | □ |
| | PI(38:5) | $[M-H]^-$ | 883.5361 | 883.5342 | 2.2 | □ |
| | PI(38:6) | $[M-H]^-$ | 881.5184 | 881.5186 | -0.2 | □ |
| | PI(38:4) | $[M-H]^-$ | 885.5491 | 885.5499 | -0.9 | □ |
| | PI(40:6) | $[M-H]^-$ | 909.5465 | 909.5499 | -3.7 | □ |
| | PI(40:4) | $[M-H]^-$ | 913.5799 | 913.5812 | -1.4 | □ |

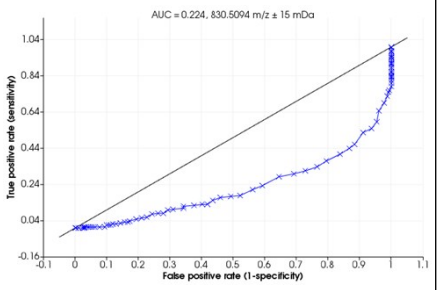
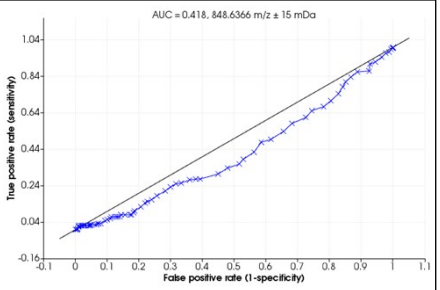
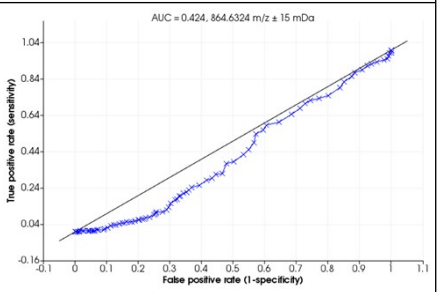
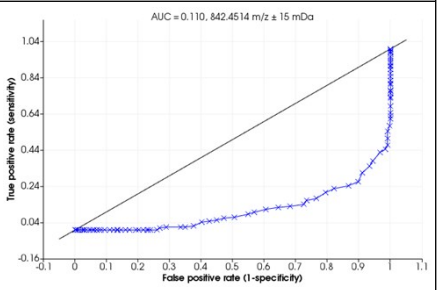
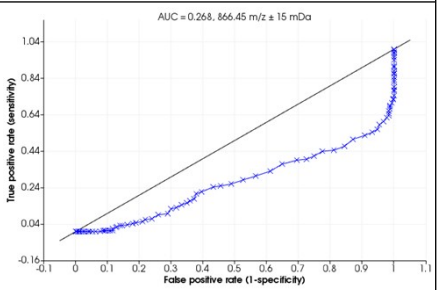
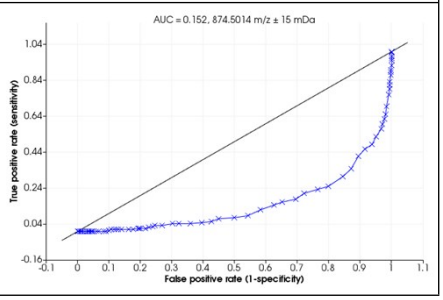
**Table S3.** Different compounds between injury region and control region obtained by ROC analysis.

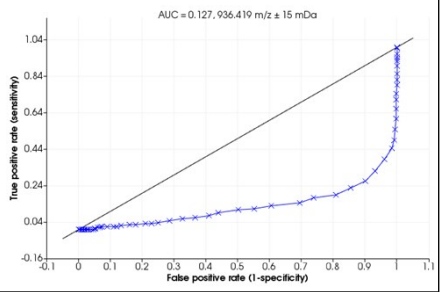
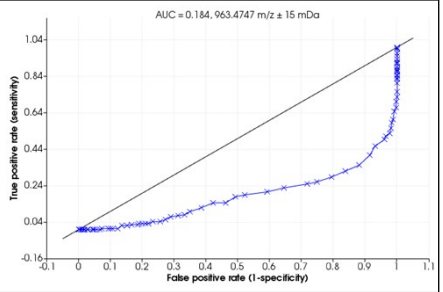
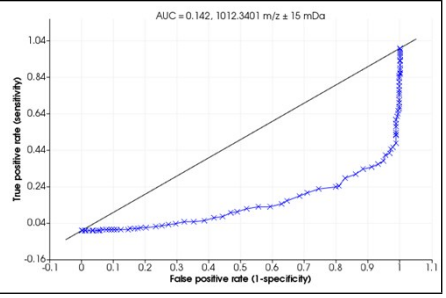
| Centroid [m/z] | ± [Da] | Compound | Maximum AUC in interval | ROC plot |
|---|---|---|---|---|
| 481.2104 | 0.015 | MG(22:5) | 0.896197 |   |
| 604.5065 | 0.015 | Cer(d18:1/18:0) | 0.905948 |   |
| 663.5468 | 0.015 | CE(16:0) | 0.831459 |   |
| 687.5464 | 0.015 | CE(18:2) | 0.867119 |   |
| 689.5633 | 0.015 | CE(18:1) | 0.886808 |   |

| Centroid [m/z] | ± [Da] | Compound | Maximum AUC in interval | ROC plot |
|---|---|---|---|---|
| 697.4775 | 0.015 | PA(16:0/16:0) | 0.862848 |   |
| 707.5002 | 0.015 | DG(18:2/18:2) | 0.727918 |   |
| 711.5493 | 0.015 | CE(20:4) | 0.71518 |   |
| 735.5471 | 0.015 | CE(22:6) | 0.943422 |   |
| 735.4346 | 0.015 | PA(36:4) | 0.82903 |   |
| 737.4544 | 0.015 | PA(36:3) | 0.923209 |   |

| Centroid [m/z] | ± [Da] | Compound | Maximum AUC in interval | ROC plot |
|---|---|---|---|---|
| 765.4847 | 0.015 | PA(38:3) | 0.85132 |   |
| 785.4504 | 0.015 | PA(18:1/22:6) | 0.779124 |   |
| 793.4983 | 0.015 | PG (16:0/20:4) | 0.798823 |   |
| 808.4626 | 0.015 | PC (16:1/16:0) | 0.85513 |   |
| 836.4981 | 0.015 | PC (18:1/16:0) | 0.890672 |   |
| 822.6428 | 0.015 | SM(38:1) | 0.515546 |   |

| Centroid [m/z] | ± [Da] | Compound | Maximum AUC in interval | ROC plot |
|---|---|---|---|---|
| 838.6165 | 0.015 | HexCer (d18:1/22:0-OH) | 0.582533 | |
| 850.6547 | 0.015 | HexCer (d18:1/24:0) | 0.590992 |  |
| 922.5671 | 0.015 | ST (d18:1/22:1-OH) | 0.55061 |  |
| 947.5013 | 0.015 | PIP(38:5) | 0.870766 |  |
| 1293.7495 | 0.015 | Ganglioside GA1 (36:1) | 0.793659 |  |
| 710.4893 | 0.015 | CerP(38:2) | 0.375975 |  |

| Centroid [m/z] | ± [Da] | Compound | Maximum AUC in interval | ROC plot |
|---|---|---|---|---|
| 830.5094 | 0.015 | PE(18:0/22:6) | 0.223639 |   |
| 848.6366 | 0.015 | HexCer (d18:1/24:1) | 0.417696 |   |
| 864.6324 | 0.015 | HexCer (d18:1/24:1-OH) | 0.424493 |   |
| 842.4514 | 0.015 | PE(38:5) | 0.110375 |   |
| 866.45 | 0.015 | PE(18:1/22:6) | 0.26838 |   |
| 874.5014 | 0.015 | PS(18:0/22:6) | 0.152327 |   |

| Centroid [m/z] | ± [Da] | Compound | Maximum AUC in interval | ROC plot |
|---|---|---|---|---|
| 936.419 | 0.015 | CDP-DG(28:0) | 0.126526 |   |
| 963.4747 | 0.015 | PI(38:4) | 0.18406 |   |
| 1012.3401 | 0.015 | Linoleoyl-CoA | 0.142478 |   |