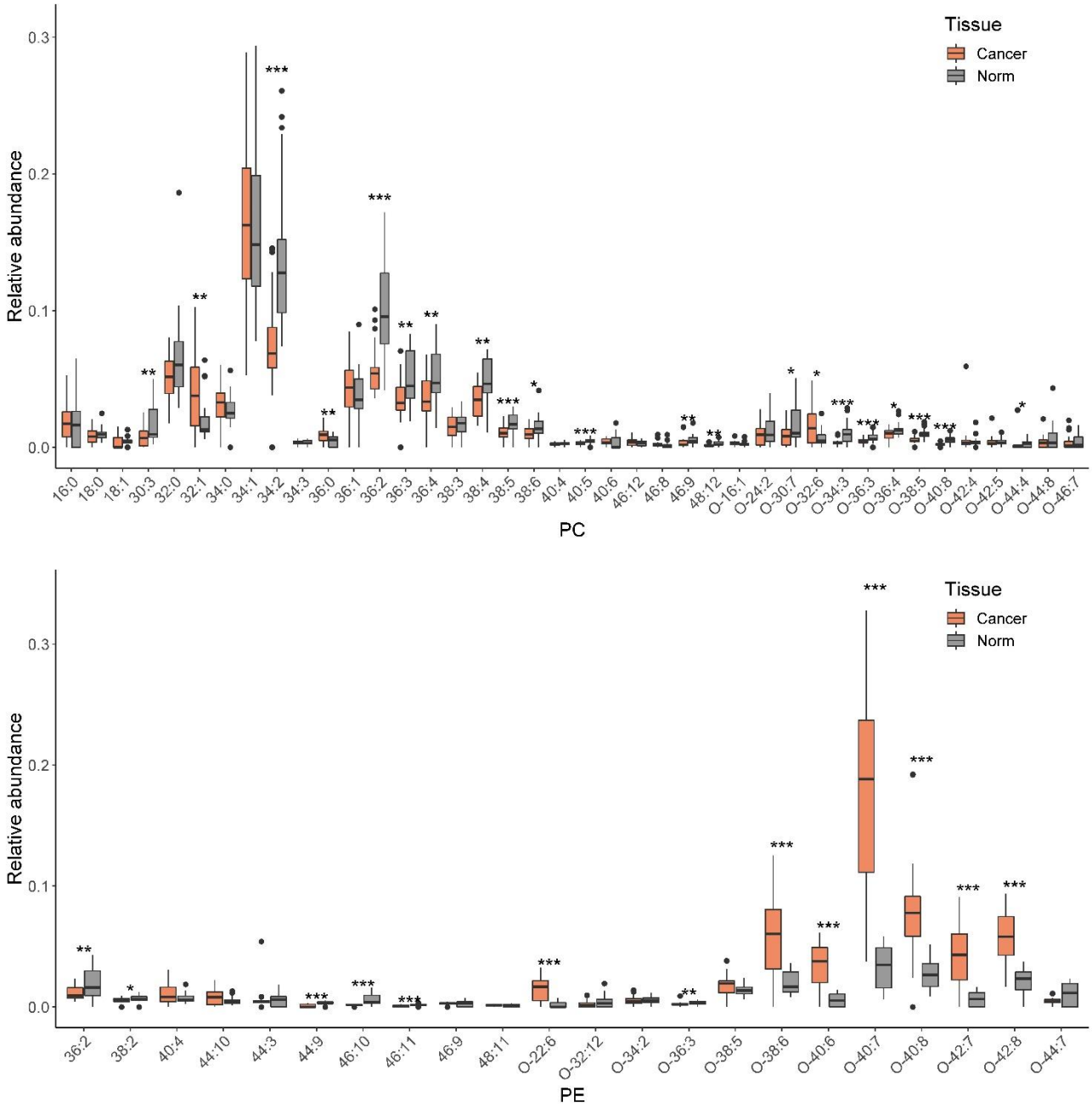
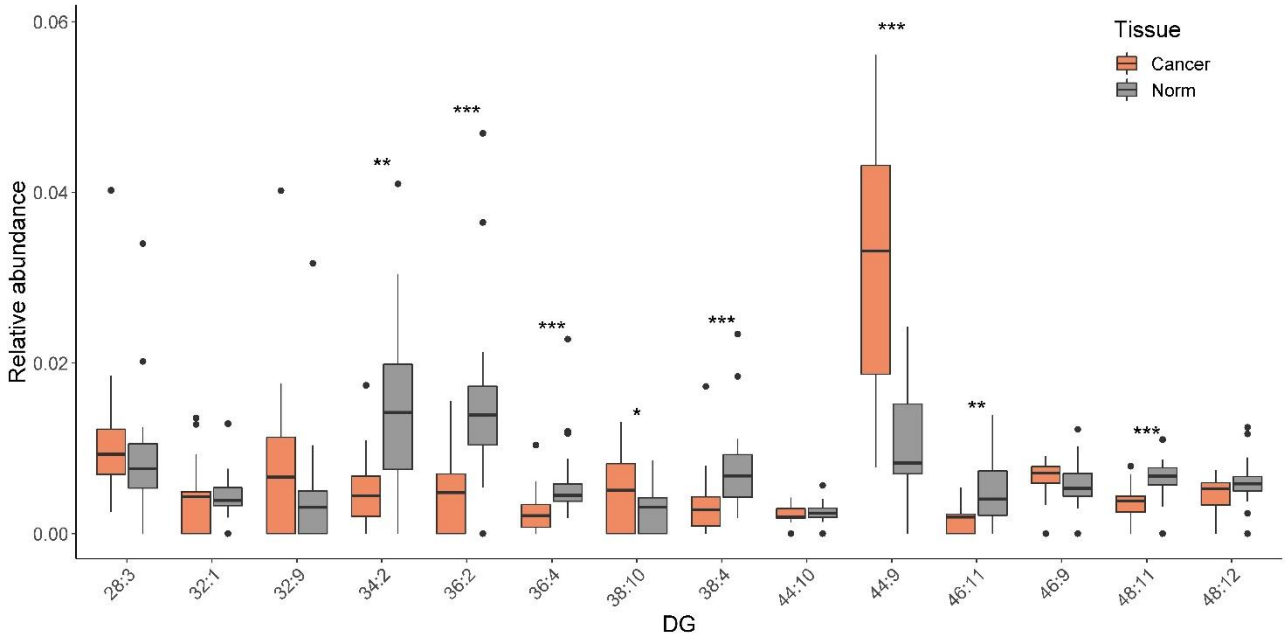
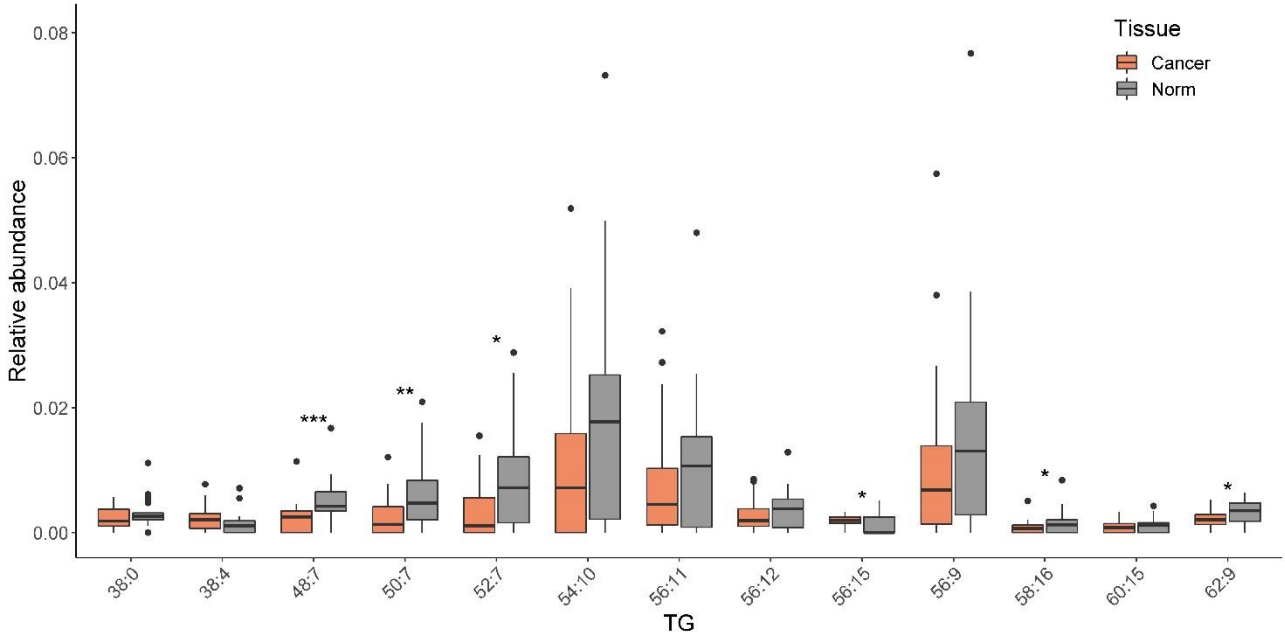
# Validation of breast cancer margins by tissue spray mass spectrometry




Tissue
Cancer
Norm
Relative abundance
0.06
0.04
0.02
0.00
***
**
***
***
*
***
***
**
***
28:3
32:1
32:9
34:2
36:2
36:4
38:10
38:4
44:10
44:9
46:11
46:9
48:11
48:12
DG


Tissue
Cancer
Norm
Relative abundance
0.08
0.06
0.04
0.02
0.00
***
**
*
*
*
*
38:0
38:4
48:7
50:7
52:7
54:10
56:11
56:12
56:15
56:9
58:16
60:15
62:9
TG

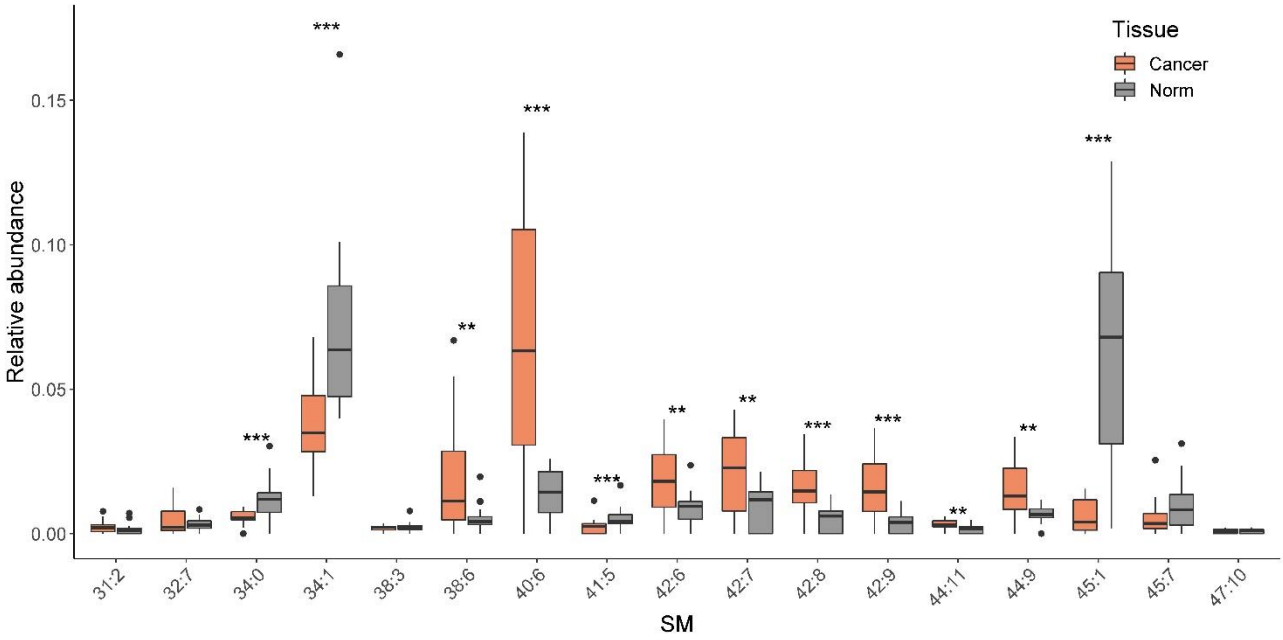
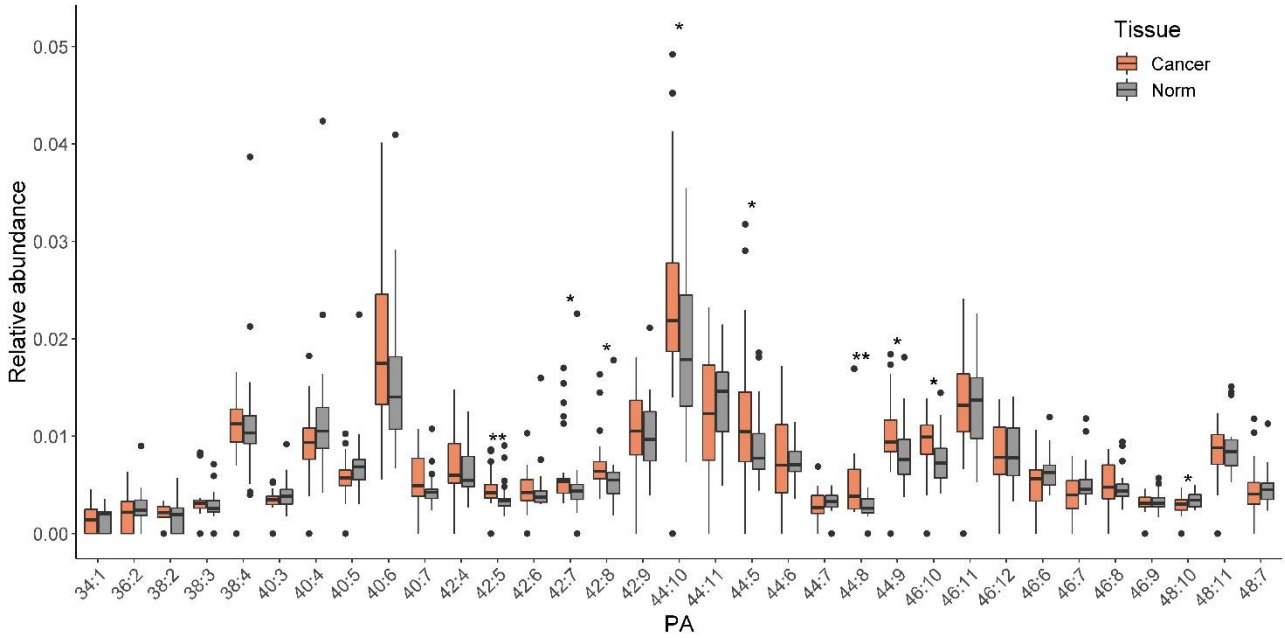
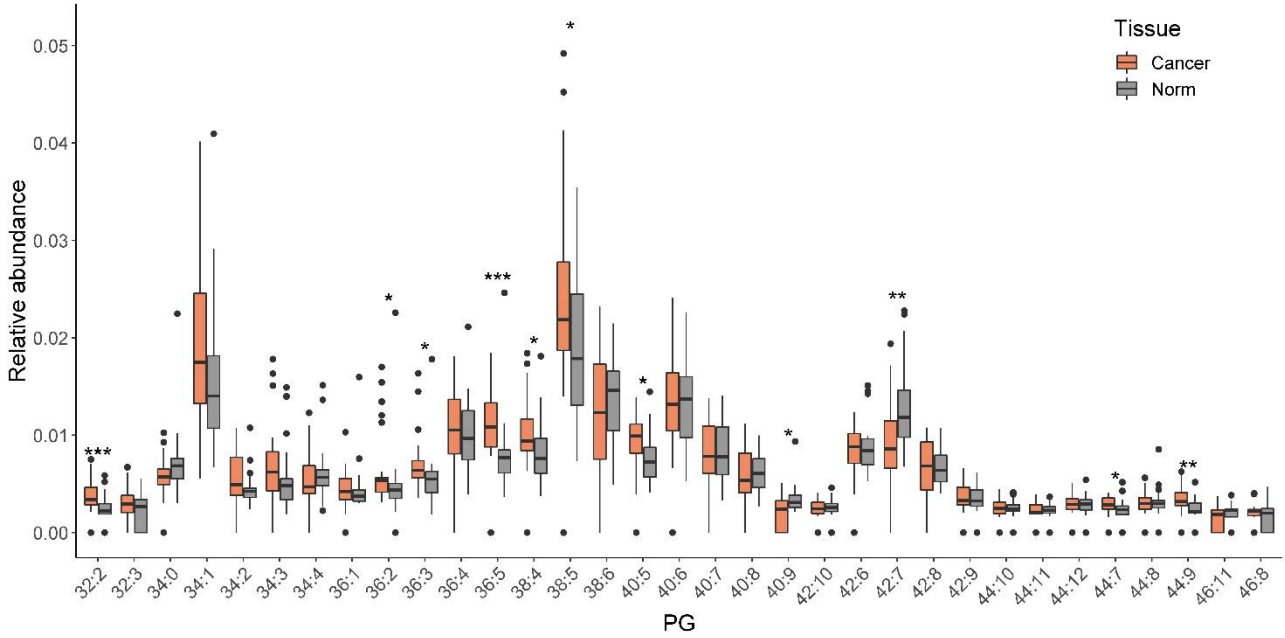



Figure S1. Lipids identified in cancer/ surrounding tissues using tissue-spray MS in positive mode: phosphatidylcholines (PC), phosphatidylethanolamines (PE), diacylglycerols (DG) and triacylglycerols (DG), sphingomyelins (SM). Statistically significant differences according to U-test are indicated by an asterisk: * - p-value < 0.05; ** - p-value < 0.01; *** - p-value < 0.001.


Tissue
Cancer
Norm
Relative abundance
0.05
0.04
0.03
0.02
0.01
0.00
34:1 36:2 38:2 38:3 38:4 40:3 40:4 40:5 40:6 40:7 42:4 42:5 42:6 42:7 42:8 42:9 44:10 44:11 44:5 44:6 44:7 44:8 44:9 46:10 46:11 46:12 46:6 46:7 46:8 46:9 48:10 48:11 48:7
PA


Tissue
Cancer
Norm
Relative abundance
0.05
0.04
0.03
0.02
0.01
0.00
32:2 32:3 34:0 34:1 34:2 34:3 34:4 36:1 36:2 36:3 36:4 36:5 38:4 38:5 38:6 40:5 40:6 40:7 40:8 40:9 42:10 42:6 42:7 42:8 42:9 44:10 44:11 44:12 44:7 44:8 44:9 46:11 46:8
PG

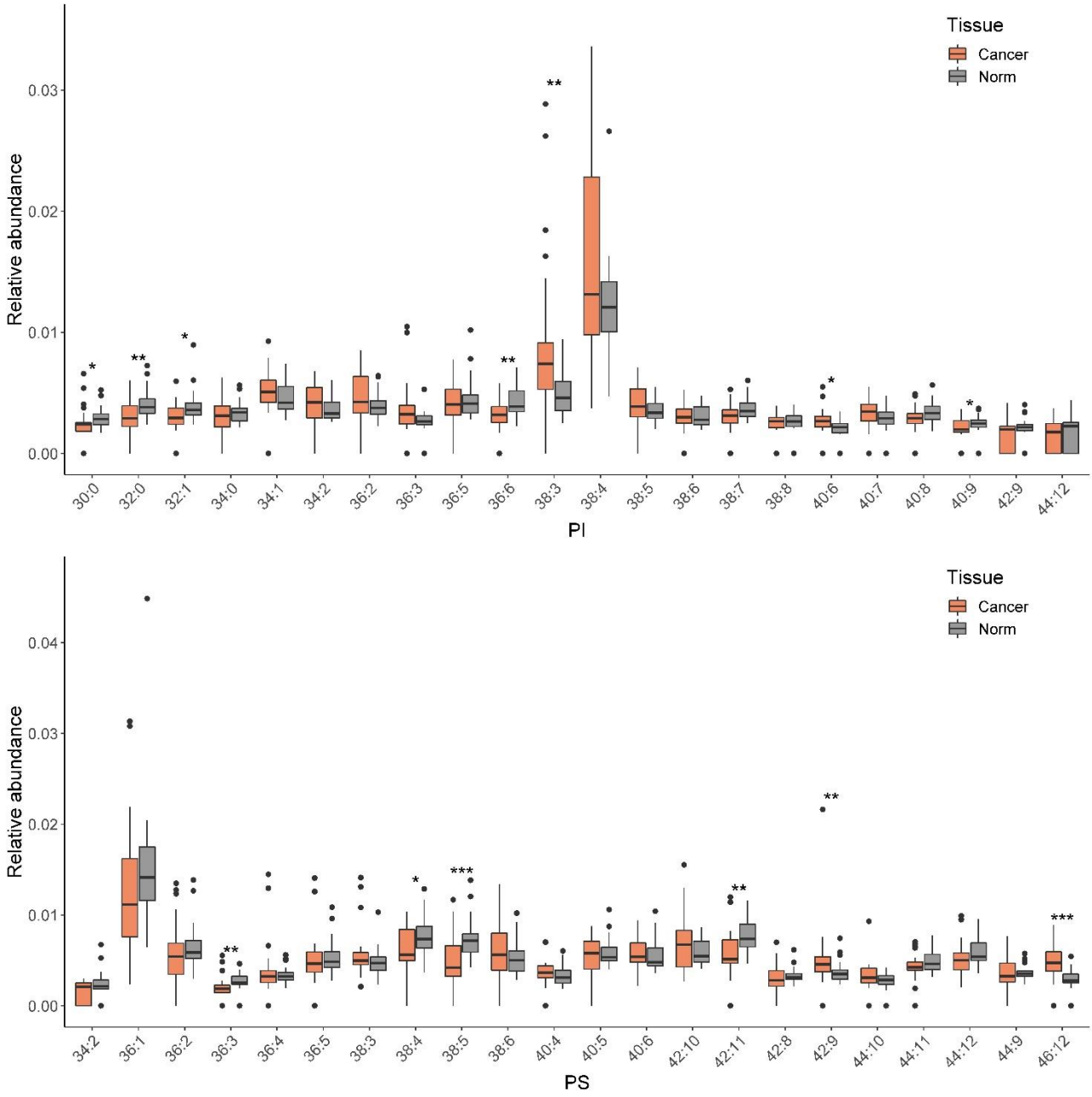



Figure S2. Lipids identified in cancer/ surrounding tissues using tissue-spray MS in negative mode: phosphatidic acids (PA), phosphatidylglycerols (PG), phosphatidylinositols (PI), phosphatidylserines (PS). Statistically significant differences according to U-test are indicated by an asterisk: * - p-value < 0.05; ** - p-value < 0.01; *** - p-value < 0.001.

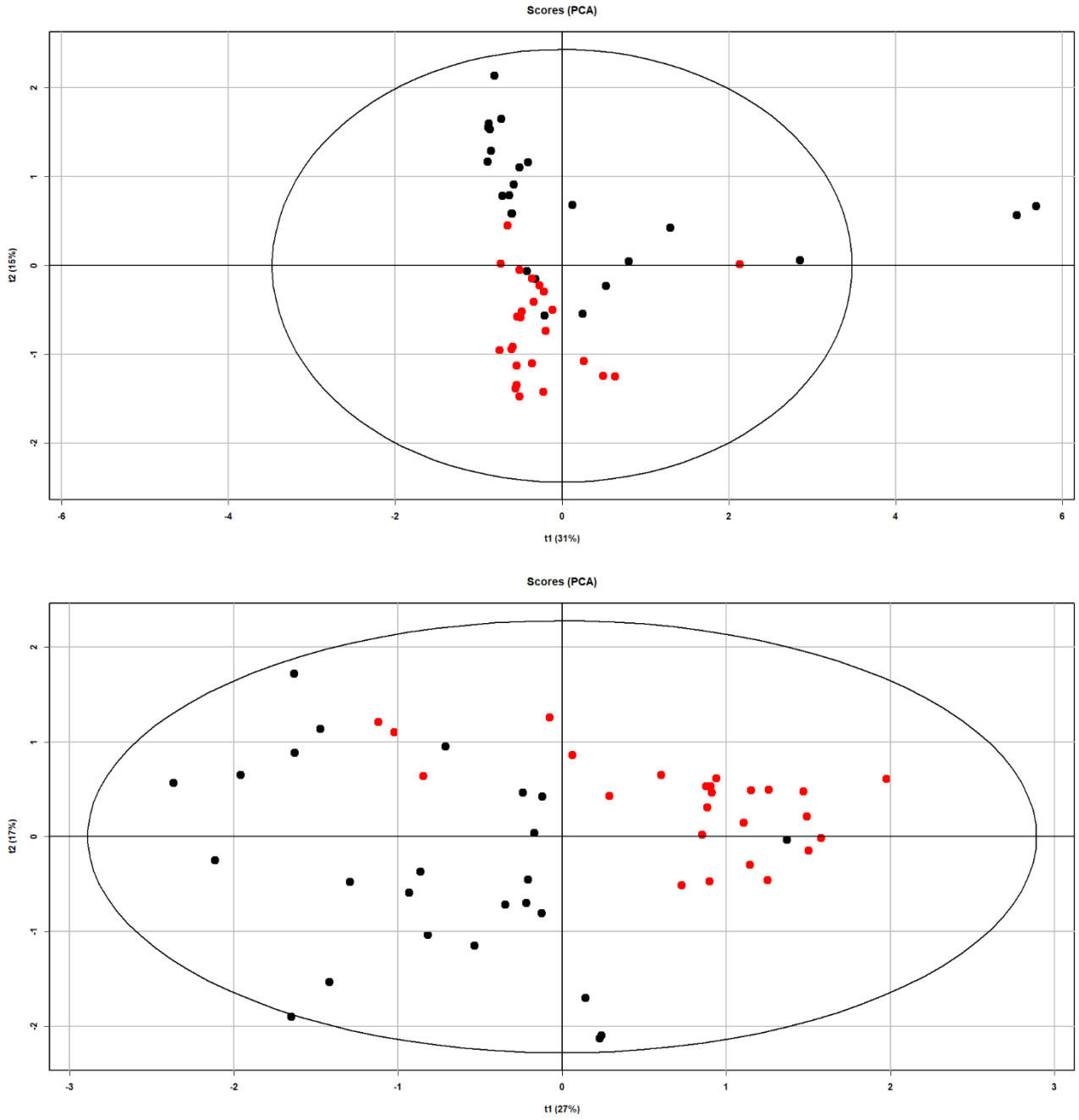



Figure S3. PCA score plots of positive and negative MS.

**Table S1.** Lipids identified in positive ion tissue-spray mass spectra of breast samples.

| Lipid Name | Calculated m/z | Experimental m/z | Error, ppm |
|---|---|---|---|
| DG 28:3 | 529.3863 | 529.3912 | 9 |
| DG 32:1 | 589.4802 | 589.4802 | 0 |
| DG 32:9 | 573.3550 | 573.3618 | 12 |
| DG 34:2 | 615.4959 | 615.5004 | 7 |
| DG 36:2 | 643.5272 | 643.5256 | 2 |
| DG 36:4 | 639.4959 | 639.4921 | 6 |
| DG 38:10 | 655.4333 | 655.4241 | 14 |
| DG 38:4 | 667.5272 | 667.5349 | 12 |
| DG 44:10 | 739.5272 | 739.5371 | 13 |
| DG 44:9 | 741.5428 | 741.5479 | 7 |
| DG 46:11 | 765.5428 | 765.5460 | 4 |
| DG 46:9 | 769.5741 | 769.5696 | 6 |
| DG 48:11 | 793.5741 | 793.5701 | 5 |
| DG 48:12 | 791.5585 | 791.5695 | 14 |
| LPC 16:0 | 518.3217 | 518.3271 | 10 |
| LPC 18:0 | 546.3530 | 546.3568 | 7 |
| LPC 18:1 | 544.3374 | 544.3435 | 11 |
| LPC O-16:1 | 502.3268 | 502.3226 | 8 |
| LPC O-24:2 | 612.4363 | 612.4373 | 2 |
| LPE O-22:6 | 534.2955 | 534.3016 | 11 |
| PC 30:3 | 722.4731 | 722.4791 | 8 |
| PC 32:0 | 756.5514 | 756.5557 | 6 |
| PC 32:1 | 754.5357 | 754.5424 | 9 |
| PC 34:0 | 784.5827 | 784.5852 | 3 |
| PC 34:1 | 782.5670 | 782.5728 | 7 |
| PC 34:2 | 780.5514 | 780.5574 | 8 |
| PC 34:3 | 778.5357 | 778.5454 | 12 |
| PC 36:0 | 812.6140 | 812.6046 | 12 |
| PC 36:1 | 810.5983 | 810.6020 | 5 |
| PC 36:2 | 808.5827 | 808.5880 | 7 |
| PC 36:3 | 806.5670 | 806.5710 | 5 |
| PC 36:4 | 804.5514 | 804.5560 | 6 |
| PC 38:3 | 834.5983 | 834.6010 | 3 |
| PC 38:4 | 832.5827 | 832.5864 | 4 |
| PC 38:5 | 830.5670 | 830.5706 | 4 |
| PC 38:6 | 828.5514 | 828.5623 | 13 |
| PC 40:4 | 860.6140 | 860.6205 | 8 |
| PC 40:5 | 858.5983 | 858.6005 | 3 |
| PC 40:6 | 856.5827 | 856.5828 | 0 |
| PC 46:12 | 928.5827 | 928.5888 | 7 |

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|---|---|---|---|
| PC 46:8 | 936.6453 | 936.6396 | 6 |
| PC 46:9 | 934.6296 | 934.6313 | 2 |
| PC 48:12 | 956.6140 | 956.6258 | 12 |
| PC O-30:7 | 700.4313 | 700.4382 | 10 |
| PC O-32:6 | 730.4782 | 730.4858 | 10 |
| PC O-34:3 | 764.5565 | 764.5455 | 14 |
| PC O-36:3 | 792.5878 | 792.5826 | 7 |
| PC O-36:4 | 790.5721 | 790.5694 | 3 |
| PC O-38:5 | 816.5878 | 816.5940 | 8 |
| PC O-40:8 | 838.5721 | 838.5631 | 11 |
| PC O-42:4 | 874.6660 | 874.6584 | 9 |
| PC O-42:5 | 872.6504 | 872.6433 | 8 |
| PC O-44:4 | 902.6973 | 902.7042 | 8 |
| PC O-44:8 | 894.6347 | 894.6323 | 3 |
| PC O-46:7 | 924.6817 | 924.6868 | 6 |
| PE 36:2 | 766.5357 | 766.5370 | 2 |
| PE 38:2 | 794.5670 | 794.5752 | 10 |
| PE 40:4 | 818.5670 | 818.5565 | 13 |
| PE 44:10 | 862.5357 | 862.5353 | 1 |
| PE 44:3 | 876.6453 | 876.6390 | 7 |
| PE 44:9 | 864.5514 | 864.5392 | 14 |
| PE 46:10 | 890.5670 | 890.5547 | 14 |
| PE 46:11 | 888.5514 | 888.5537 | 3 |
| PE 46:9 | 892.5827 | 892.5753 | 8 |
| PE 48:11 | 916.5827 | 916.5812 | 2 |
| PE O-32:12 | 676.3374 | 676.3317 | 8 |
| PE O-34:2 | 724.5252 | 724.5292 | 6 |
| PE O-36:3 | 750.5408 | 750.5472 | 8 |
| PE O-38:5 | 774.5408 | 774.5316 | 12 |
| PE O-38:6 | 772.5252 | 772.5364 | 15 |
| PE O-40:6 | 800.5565 | 800.5570 | 1 |
| PE O-40:7 | 798.5408 | 798.5459 | 6 |
| PE O-40:8 | 796.5252 | 796.5345 | 12 |
| PE O-42:7 | 826.5721 | 826.5815 | 11 |
| PE O-42:8 | 824.5565 | 824.5558 | 1 |
| PE O-44:7 | 854.6034 | 854.5914 | 14 |
| SM 31:2 | 681.4942 | 681.5012 | 10 |
| SM 32:7 | 685.4316 | 685.4234 | 12 |
| SM 34:0 | 727.5724 | 727.5634 | 12 |
| SM 34:1 | 725.5568 | 725.5611 | 6 |
| SM 38:3 | 777.5881 | 777.5899 | 2 |
| SM 38:6 | 771.5411 | 771.5391 | 3 |
| SM 40:6 | 799.5724 | 799.5635 | 11 |

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|---|---|---|---|
| SM 41:5 | 815.6037 | 815.6088 | 6 |
| SM 42:6 | 827.6037 | 827.6073 | 4 |
| SM 42:7 | 825.5881 | 825.5807 | 9 |
| SM 42:8 | 823.5724 | 823.5633 | 11 |
| SM 42:9 | 821.5568 | 821.5610 | 5 |
| SM 44:11 | 845.5568 | 845.5557 | 1 |
| SM 44:9 | 849.5881 | 849.5927 | 5 |
| SM 45:1 | 879.7289 | 879.7186 | 12 |
| SM 45:7 | 867.6350 | 867.6341 | 1 |
| SM 47:10 | 889.6194 | 889.6076 | 13 |
| TG 38:0 | 689.5691 | 689.5768 | 11 |
| TG 38:4 | 681.5065 | 681.5012 | 8 |
| TG 48:7 | 815.6160 | 815.6088 | 9 |
| TG 50:7 | 843.6473 | 843.6499 | 3 |
| TG 52:7 | 871.6786 | 871.6900 | 13 |
| TG 54:10 | 893.6630 | 893.6685 | 6 |
| TG 56:11 | 919.6786 | 919.6858 | 8 |
| TG 56:12 | 917.6630 | 917.6697 | 7 |
| TG 56:15 | 911.6160 | 911.6099 | 7 |
| TG 56:9 | 923.7099 | 923.7148 | 5 |
| TG 58:16 | 937.6317 | 937.6273 | 5 |
| TG 60:15 | 967.6786 | 967.6663 | 13 |
| TG 62:9 | 1007.8038 | 1007.7893 | 14 |

**Table S2.** Lipids identified in negative ion tissue-spray mass spectra of breast samples.

| Lipid Name | Calculated m/z | Experimental m/z | Error, ppm |
|---|---|---|---|
| FA 16:0 | 255.2330 | 255.2296 | 13 |
| FA 16:1 | 253.2173 | 253.2151 | 9 |
| FA 18:0 | 283.2643 | 283.2611 | 11 |
| FA 18:1 | 281.2486 | 281.2455 | 11 |
| FA 20:2 | 307.2643 | 307.2616 | 9 |
| FA 20:3 | 305.2486 | 305.2456 | 10 |
| FA 20:5 | 301.2173 | 301.2152 | 7 |
| FA 22:4 | 331.2643 | 331.2615 | 8 |
| FA 22:5 | 329.2486 | 329.2451 | 11 |
| FA 22:6 | 327.2330 | 327.2304 | 8 |
| LPE O-16:1 | 436.2833 | 436.2802 | 7 |
| LPE O-26:2 | 574.4242 | 574.4189 | 9 |
| PA 34:1 | 673.4814 | 673.4750 | 10 |
| PA 38:3 | 725.5127 | 725.5031 | 13 |
| PA 40:3 | 753.5440 | 753.5380 | 8 |
| PA 40:6 | 747.4970 | 747.4889 | 11 |
| PA 40:7 | 745.4814 | 745.4727 | 12 |
| PA 42:4 | 779.5596 | 779.5536 | 8 |
| PA 42:5 | 777.5440 | 777.5349 | 12 |
| PA 42:9 | 769.4814 | 769.4752 | 8 |
| PA 44:11 | 793.4814 | 793.4711 | 13 |
| PA 44:5 | 805.5753 | 805.5685 | 8 |
| PA 44:6 | 803.5596 | 803.5519 | 10 |
| PA 44:7 | 801.5440 | 801.5357 | 10 |
| PA 44:8 | 799.5283 | 799.5185 | 12 |
| PA 46:6 | 831.5909 | 831.5824 | 10 |
| PA 46:7 | 829.5753 | 829.5650 | 12 |
| PA 46:8 | 827.5596 | 827.5506 | 11 |
| PA 46:9 | 825.5440 | 825.5355 | 10 |
| PA 48:10 | 851.5596 | 851.5498 | 12 |
| PA 48:11 | 849.5440 | 849.5372 | 8 |
| PA 48:7 | 857.6066 | 857.5950 | 13 |
| PA O-32:3 | 627.4395 | 627.4332 | 10 |
| PA O-36:2 | 685.5178 | 685.5113 | 9 |
| PA O-38:4 | 709.5178 | 709.5082 | 13 |
| PA O-40:5 | 735.5334 | 735.5236 | 13 |
| PA O-44:9 | 783.5334 | 783.5239 | 12 |
| PE 36:2 | 742.5392 | 742.5312 | 11 |
| PE 36:3 | 740.5236 | 740.5162 | 10 |
| PE 38:4 | 766.5392 | 766.5317 | 10 |

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|---|---|---|---|
| PE 38:5 | 764.5236 | 764.5177 | 8 |
| PE 38:7 | 760.4923 | 760.4855 | 9 |
| PE 40:6 | 790.5392 | 790.5296 | 12 |
| PE 42:8 | 814.5392 | 814.5300 | 11 |
| PE 46:11 | 864.5549 | 864.5459 | 10 |
| PE 46:12 | 862.5392 | 862.5279 | 13 |
| PE 48:12 | 890.5705 | 890.5611 | 11 |
| PE O-34:3 | 698.5130 | 698.5043 | 13 |
| PE O-36:3 | 726.5443 | 726.5367 | 11 |
| PE O-36:5 | 722.5130 | 722.5040 | 13 |
| PE O-36:8 | 716.4661 | 716.4567 | 13 |
| PE O-36:9 | 714.4504 | 714.4405 | 14 |
| PE O-38:6 | 748.5287 | 748.5219 | 9 |
| PE O-38:7 | 746.5130 | 746.5041 | 12 |
| PE O-40:7 | 774.5443 | 774.5345 | 13 |
| PE O-40:8 | 772.5287 | 772.5219 | 9 |
| PE O-44:10 | 824.5600 | 824.5493 | 13 |
| PG 32:2 | 717.4712 | 717.4636 | 11 |
| PG 32:3 | 715.4556 | 715.4501 | 8 |
| PG 34:0 | 749.5338 | 749.5239 | 13 |
| PG 34:3 | 743.4869 | 743.4775 | 13 |
| PG 34:4 | 741.4712 | 741.4653 | 8 |
| PG 36:1 | 775.5495 | 775.5439 | 7 |
| PG 36:2 | 773.5338 | 773.5279 | 8 |
| PG 36:3 | 771.5182 | 771.5124 | 7 |
| PG 36:5 | 767.4869 | 767.4763 | 14 |
| PG 38:4 | 797.5338 | 797.5252 | 11 |
| PG 40:9 | 815.4869 | 815.4789 | 10 |
| PG 42:7 | 847.5495 | 847.5377 | 14 |
| PG 44:10 | 869.5338 | 869.5227 | 13 |
| PG 44:11 | 867.5182 | 867.5065 | 13 |
| PG 44:7 | 875.5808 | 875.5737 | 8 |
| PG 44:8 | 873.5651 | 873.5562 | 10 |
| PG 46:11 | 895.5495 | 895.5373 | 14 |
| PG 46:8 | 901.5964 | 901.5875 | 10 |
| PG O-32:4 | 699.4606 | 699.4513 | 13 |
| PG O-34:4 | 727.4919 | 727.4844 | 10 |
| PG O-34:6 | 723.4606 | 723.4515 | 13 |
| PG O-36:6 | 751.4919 | 751.4833 | 12 |
| PG O-44:11 | 853.5389 | 853.5308 | 9 |
| PI 30:0 | 781.4867 | 781.4772 | 12 |
| PI 32:0 | 809.5180 | 809.5087 | 12 |
| PI 32:1 | 807.5024 | 807.4921 | 13 |

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|---|---|---|---|
| PI 34:0 | 837.5493 | 837.5388 | 13 |
| PI 34:1 | 835.5337 | 835.5252 | 10 |
| PI 34:2 | 833.5180 | 833.5106 | 9 |
| PI 36:2 | 861.5493 | 861.5425 | 8 |
| PI 36:5 | 855.5024 | 855.4939 | 10 |
| PI 38:3 | 887.5650 | 887.5563 | 10 |
| PI 38:4 | 885.5493 | 885.5373 | 14 |
| PI 38:8 | 877.4867 | 877.4806 | 7 |
| PI 42:9 | 931.5337 | 931.5251 | 9 |
| PS 36:1 | 788.5447 | 788.5363 | 11 |
| PS 36:2 | 786.5291 | 786.5207 | 11 |
| PS 36:3 | 784.5134 | 784.5039 | 12 |
| PS 36:5 | 780.4821 | 780.4739 | 10 |
| PS 38:3 | 812.5447 | 812.5336 | 14 |
| PS 38:5 | 808.5134 | 808.5023 | 14 |
| PS 38:6 | 806.4978 | 806.4881 | 12 |
| PS 40:4 | 838.5604 | 838.5491 | 13 |
| PS 40:5 | 836.5447 | 836.5385 | 7 |
| PS 40:6 | 834.5291 | 834.5216 | 9 |
| PS 42:10 | 854.4978 | 854.4859 | 14 |
| PS 42:9 | 856.5134 | 856.5030 | 12 |
| PS 44:9 | 884.5447 | 884.5379 | 8 |
| PS O-34:5 | 738.4715 | 738.4628 | 12 |
| PS O-36:3 | 770.5341 | 770.5256 | 11 |
| PS O-38:4 | 796.5498 | 796.5387 | 14 |
| PS O-38:5 | 794.5341 | 794.5280 | 8 |
| PS O-40:5 | 822.5654 | 822.5546 | 13 |
| PS O-40:6 | 820.5498 | 820.5384 | 14 |
| PS O-40:7 | 818.5341 | 818.5233 | 13 |
| PS O-42:12 | 836.4872 | 836.4805 | 8 |
| PS O-42:7 | 846.5654 | 846.5588 | 8 |
| PS O-42:8 | 844.5498 | 844.5436 | 7 |
| PS O-42:9 | 842.5341 | 842.5276 | 8 |
| PS O-44:8 | 872.5811 | 872.5697 | 13 |
| PS O-44:9 | 870.5654 | 870.5580 | 9 |