

## Supporting Information

### **1,8-di(piperidinyl)-naphthalene – Rationally Designed MAILD/MALDI Matrix for Metabolomics and Imaging Mass Spectrometry**

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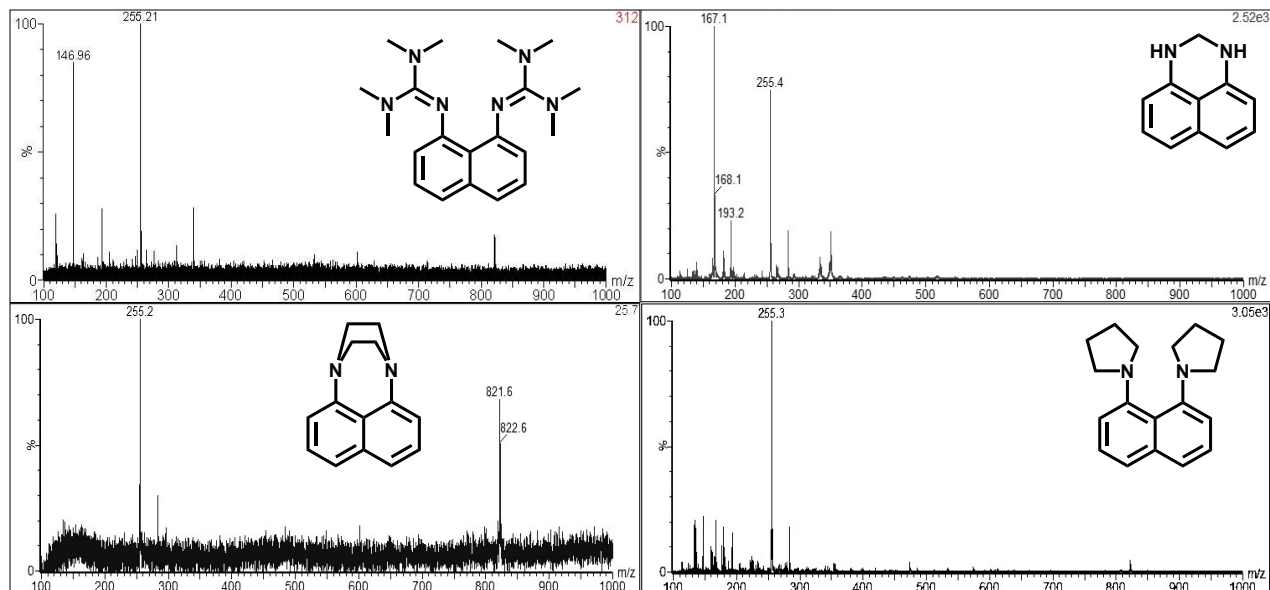
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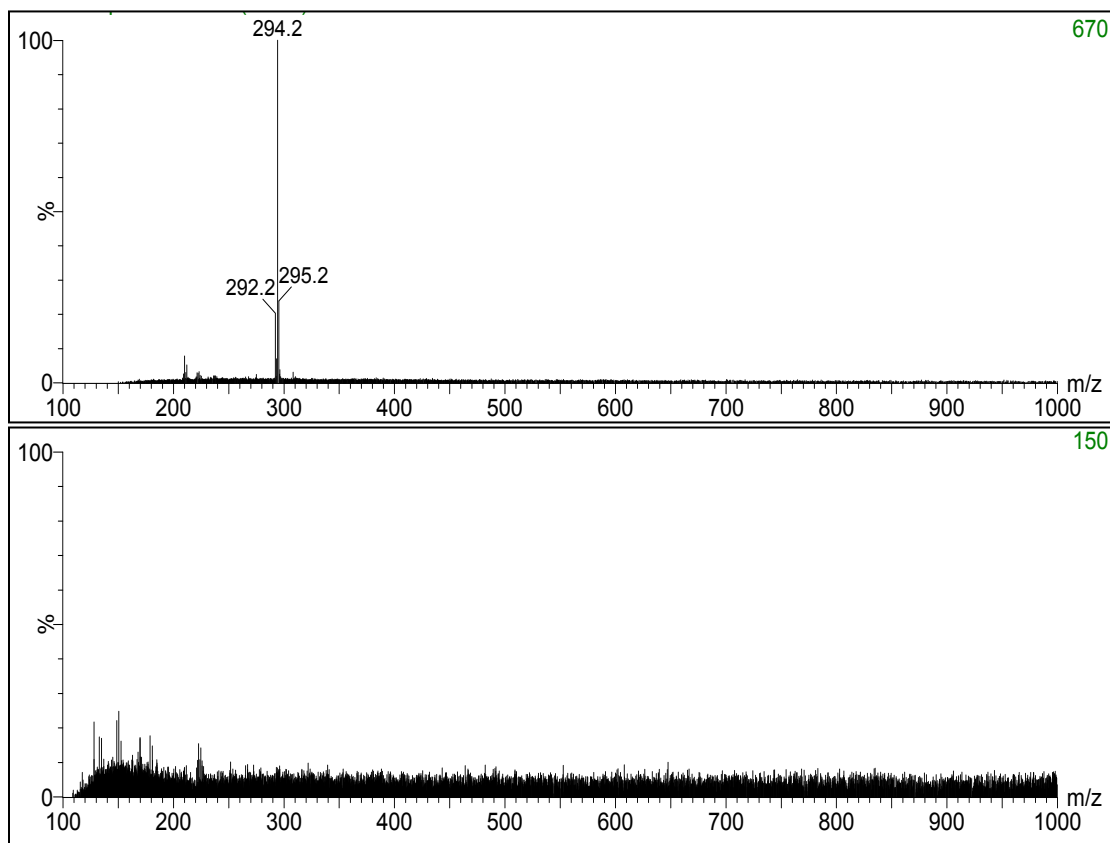
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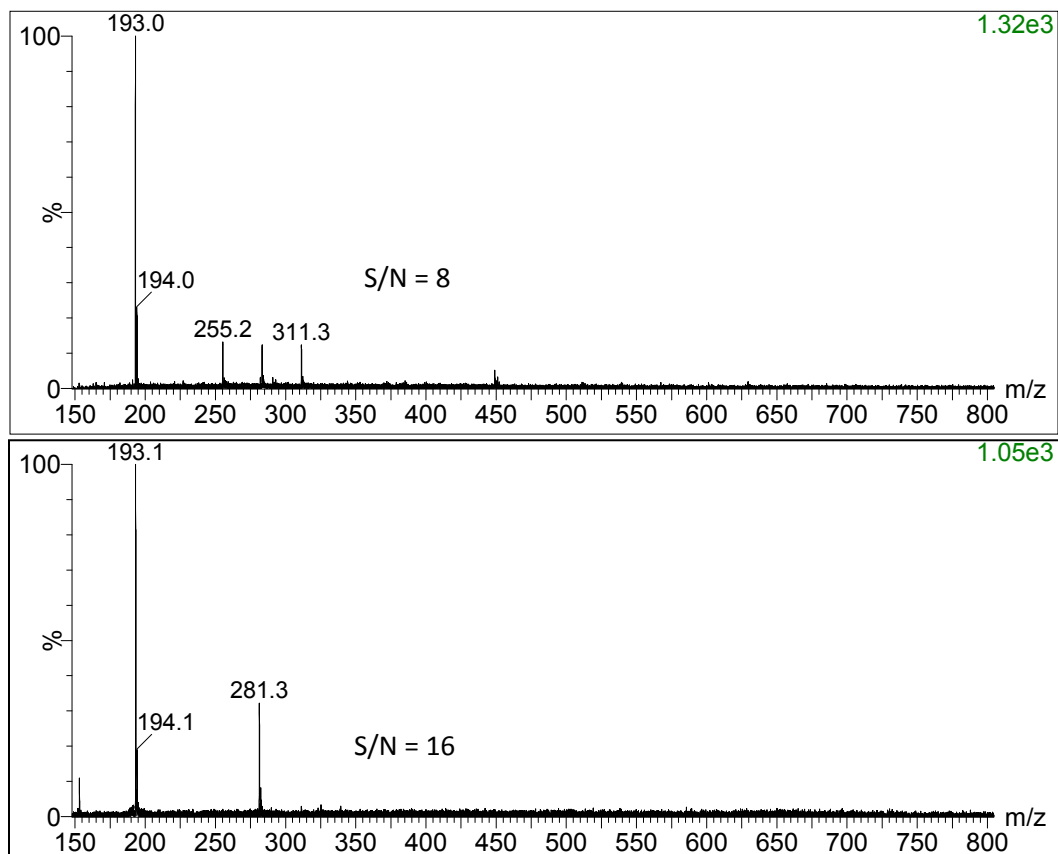
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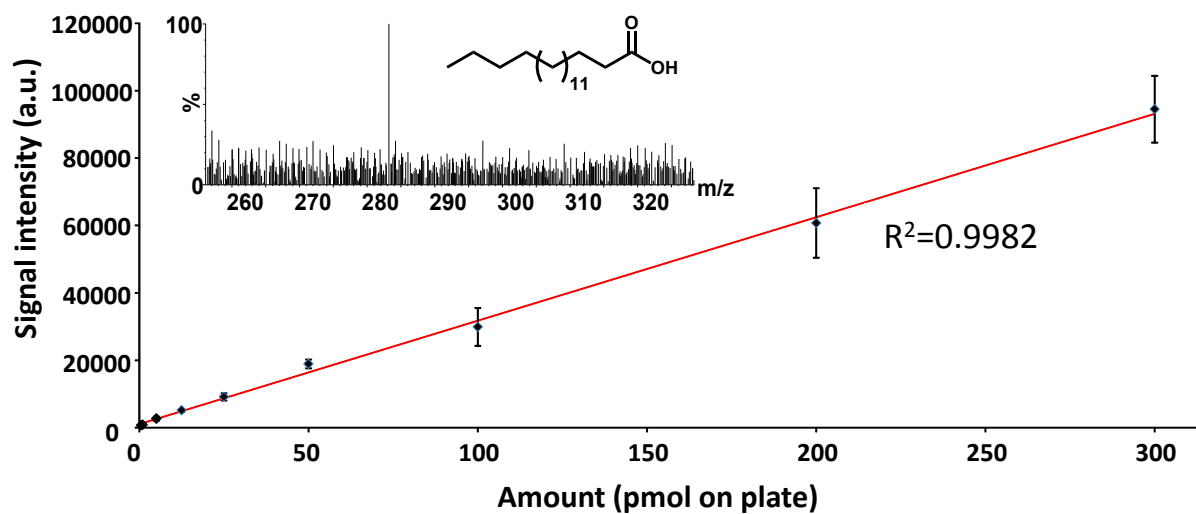
**Figure S 1.** Mass spectrum of palmitic acid ( $[M-H]^-$ ,  $m/z$  255) when recorded with various matrices in 1:1 molar ratio (top left: TMGN, 175 pmol; top right: compound **4**, 500pmol; bottom left: compound **6**, 500pmol; bottom right: compound **7**, 125 pmol) (MALDI-TOF MS, neg. ion mode)



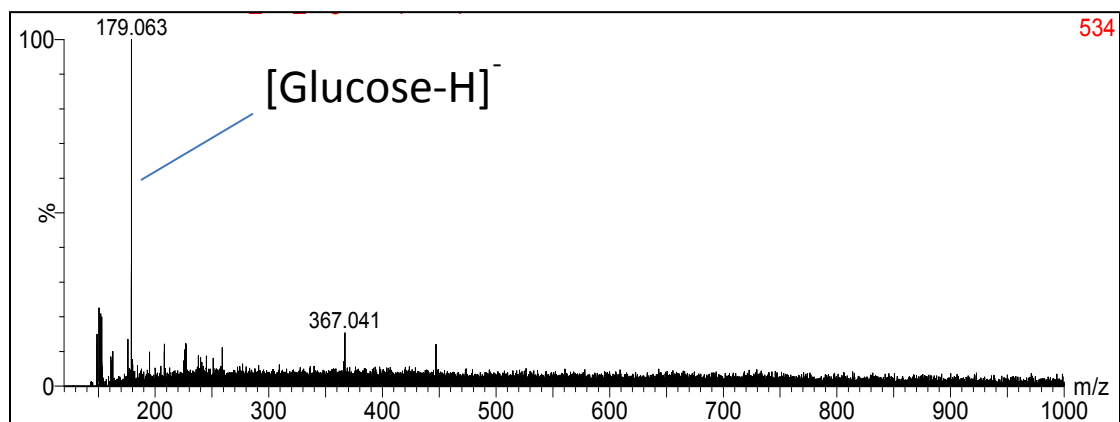
**Figure S 2.** Mass spectrum (LDI-TOF MS) of pure DPN (1 nmol on plate) recorded in positive (top) and negative (bottom) ion mode



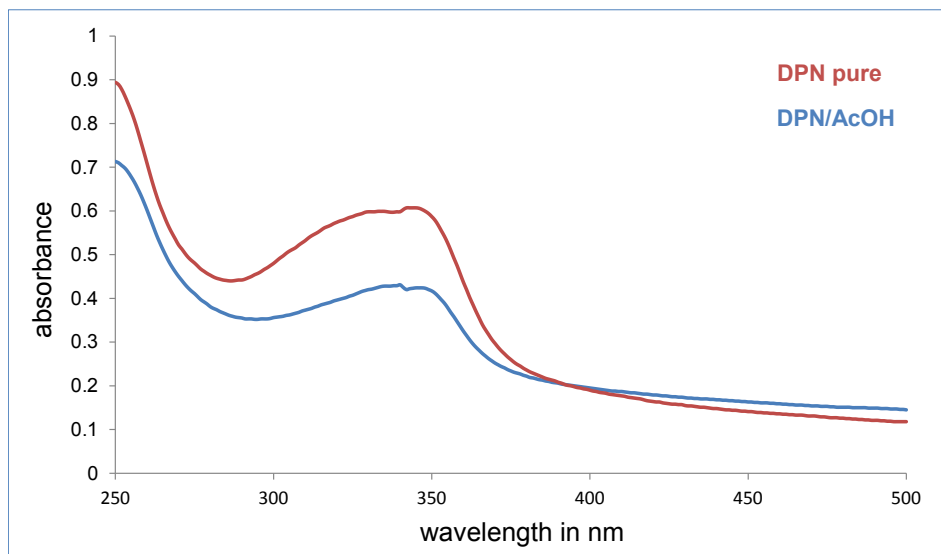
**Figure S 3.** Mass spectra of a mixture of palmitic, stearic and arachidic acid (top, 50 pmol on plate each) and oleic acid (bottom, 125 pmol) recorded using 9-aminoachridine as matrix (MALDI-TOF MS, neg. ion mode)



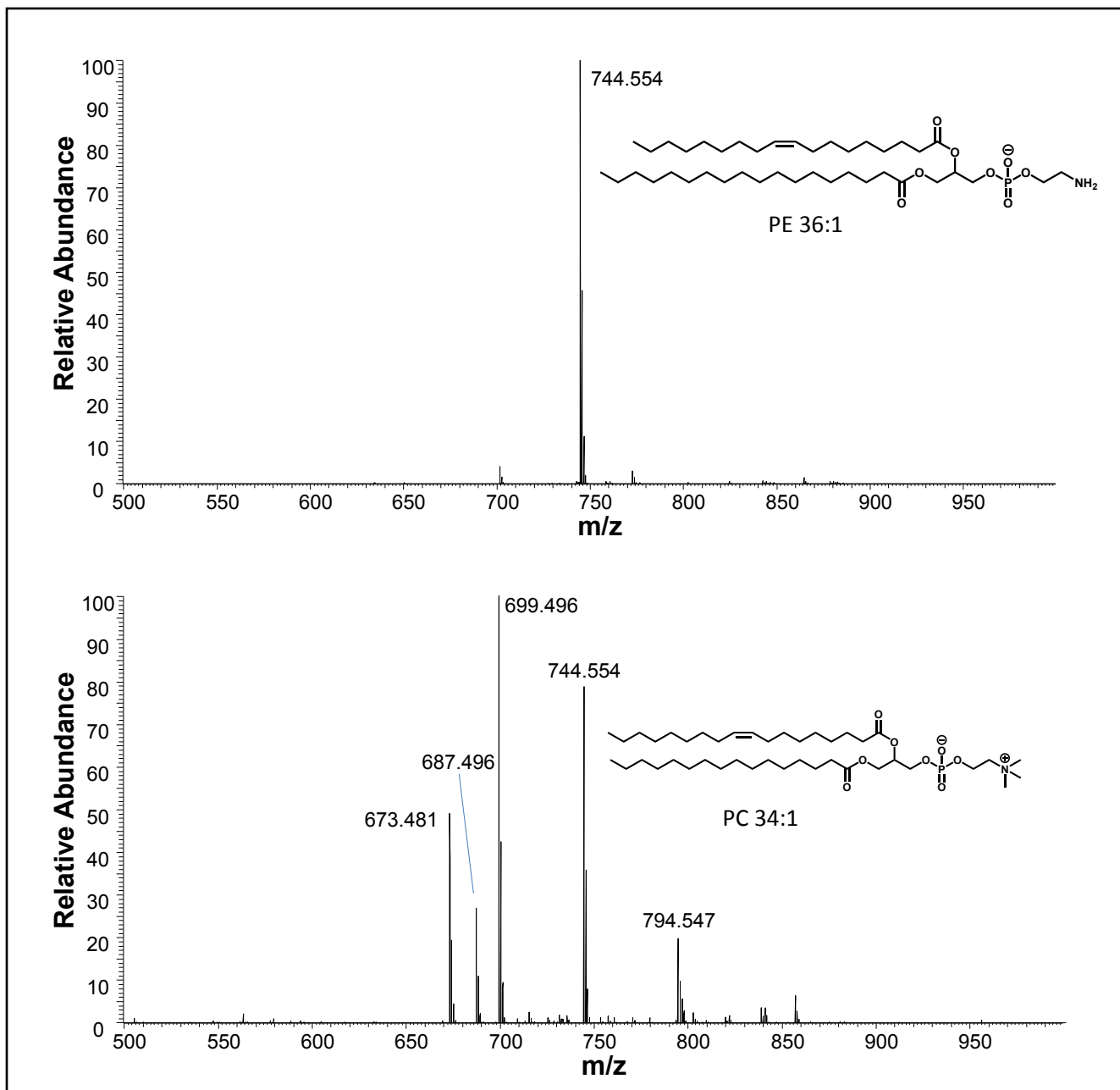
**Figure S 4.** TOF-detector response curve for increasing concentrations of stearic acid recorded with DPN as matrix. The inset shows a spectrum of stearic acid at 500fmol on plate (S/N=4).



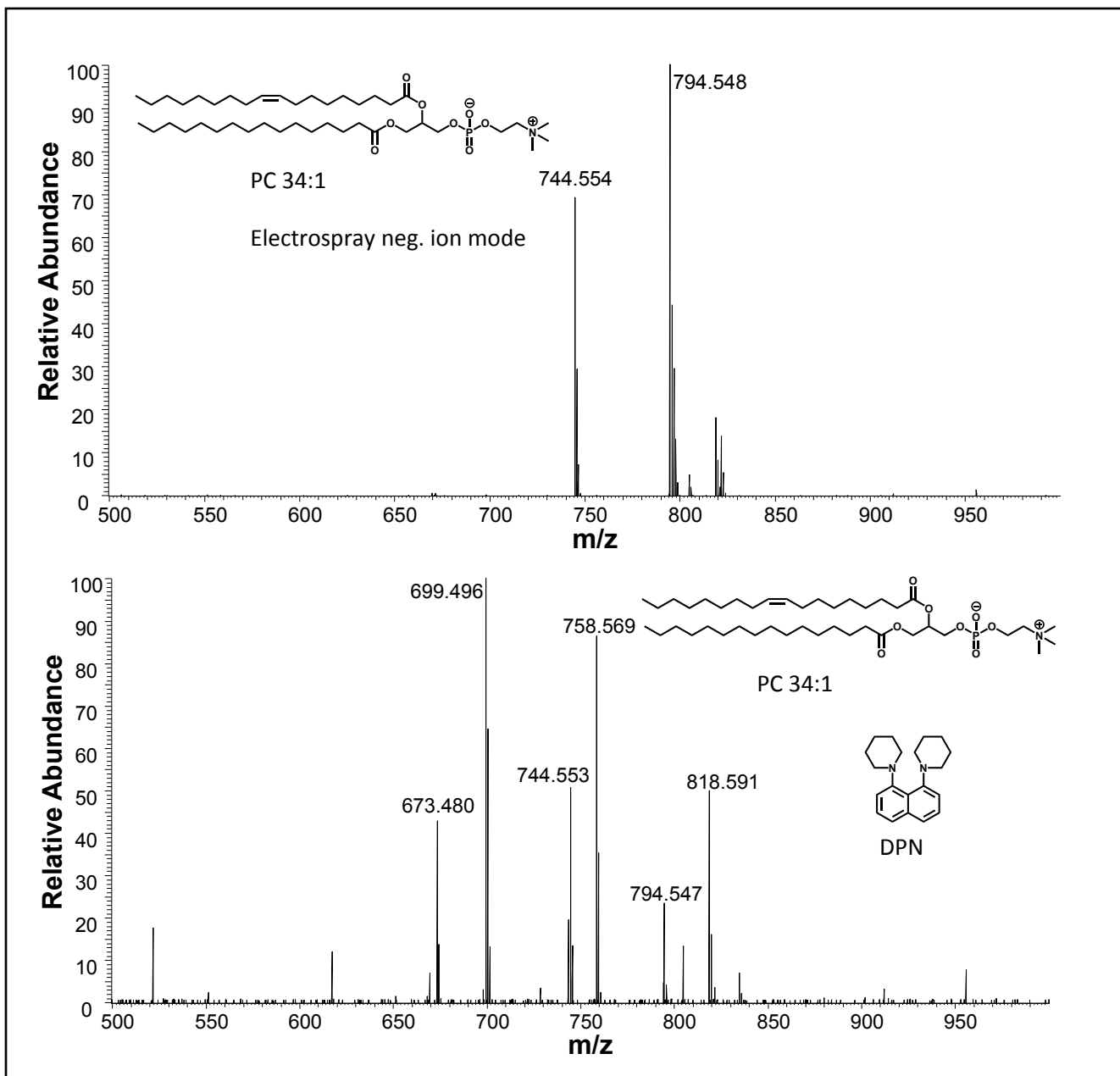
**Figure S 5.** Mass spectrum of glucose (500 pmol on plate) recorded using DPN as matrix (MALDI-TOF MS, neg. ion mode)



**Figure S 6.** UV-Vis spectra of pure DPN (red) and DPN cocrystallized with acetic acid (1:1,blue) recorded in solid state



**Figure S 7.** AP-MALDI-FTMS spectra of PE 36:1 (top) and PC 34:1 (bottom) recorded with DPN as matrix (not normalized, negative ion mode)



**Figure S 8.** ESI-FTMS spectra of pure PC 34:1 (0.1  $\mu\text{mol/ml}$  in MeOH, top) and PC 34:1 mixed with DPN (1:1(v/v), 500  $\mu\text{mol/ml}$  in MeOH, bottom) (not normalized, negative ion mode)

m/z	Assignment	detected as	detected by		
			DMAN	DPN	
105.01 8	C <sub>3</sub> H <sub>5</sub> O <sub>4</sub>	Glyceric acid	[M-H] <sup>-</sup>	+	+
	C <sub>4</sub> H <sub>9</sub> O <sub>2</sub> N <sub>2</sub>	Uracile	[M-H] <sup>-</sup>	-	+
	C <sub>5</sub> H <sub>7</sub> O <sub>3</sub>	3/5-keto valeric acid	[M-H] <sup>-</sup>	+	+
111.01 9	C <sub>5</sub> H <sub>10</sub> O <sub>2</sub> N	Valine	[M-H] <sup>-</sup>	+	+
	C <sub>4</sub> H <sub>9</sub> O <sub>3</sub> N	Threonine	[M-H] <sup>-</sup>	+	+
	C <sub>7</sub> H <sub>5</sub> O <sub>2</sub>	Benzoic acid	[M-H] <sup>-</sup>	++	+++
115.03 9	C <sub>6</sub> H <sub>6</sub> O <sub>3</sub> N	Pyroglutamic acid	[M-H] <sup>-</sup>	+	+
	C <sub>5</sub> H <sub>9</sub> O <sub>3</sub> N	Hydroxyproline	[M-H] <sup>-</sup>	-	+
	C <sub>6</sub> H <sub>12</sub> O <sub>2</sub> N	Leucine/Isoleucine	[M-H] <sup>-</sup>	+	+
116.07 1	C <sub>4</sub> H <sub>7</sub> O <sub>3</sub> N <sub>2</sub>	Asparagine	[M-H] <sup>-</sup>	+	+
	C <sub>5</sub> H <sub>11</sub> O <sub>2</sub> N <sub>2</sub>	Ornithine	[M-H] <sup>-</sup>	+	+
	C <sub>4</sub> H <sub>6</sub> O <sub>4</sub> N	Aspartic acid	[M-H] <sup>-</sup>	+	+
118.05 0	C <sub>5</sub> H <sub>7</sub> O <sub>5</sub>	Threonine/erythronic acid	[M-H] <sup>-</sup>	++	++
	C <sub>7</sub> H <sub>5</sub> O <sub>2</sub> N	Anthranilic acid	[M-H] <sup>-</sup>	-	+
	C <sub>7</sub> H <sub>5</sub> O <sub>3</sub>	2/3/4-Hydroxy benzoic acid	[M-H] <sup>-</sup>	-	++
121.02 8	C <sub>5</sub> H <sub>9</sub> O <sub>2</sub> NNa	acid	[M-]	-	+
	C <sub>5</sub> H <sub>9</sub> O <sub>3</sub> N <sub>2</sub>	Valine	[2H+Na] <sup>+</sup>	++	++
		Glutamine	[M-H] <sup>-</sup>		
128.03 4	C <sub>5</sub> H <sub>8</sub> O <sub>4</sub> N	Dipeptide[Ala+Gly]		+++	+++
	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub> N <sub>3</sub>	Glutamic acid	[M-H] <sup>-</sup>	++	+
	C <sub>9</sub> H <sub>8</sub> O <sub>2</sub> N	Histidine	[M-H] <sup>-</sup>	-	+
130.05 0	C <sub>5</sub> H <sub>12</sub> O <sub>2</sub> N <sub>2</sub>	3-Indole carboxylic acid	[M-H] <sup>-</sup>	++	+++
	Cl	Ornithine	[M+Cl] <sup>+</sup>	+	+
	C <sub>4</sub> H <sub>11</sub> O <sub>4</sub> NP	Phosphocholine	[M-H] <sup>-</sup>	-	+
130.08 6	C <sub>6</sub> H <sub>7</sub> O <sub>4</sub> N <sub>2</sub>	Hydantoin-5-propionic acid	[M-H] <sup>-</sup>	-	+
	C <sub>7</sub> H <sub>11</sub> O <sub>3</sub> N <sub>2</sub>		[M-H] <sup>-</sup>	-	+
	C <sub>9</sub> H <sub>8</sub> O <sub>3</sub> N	Dipeptide[Pro+Gly]	[M-H] <sup>-</sup>	+	+
131.04 5	C <sub>6</sub> H <sub>11</sub> O <sub>6</sub>	Hippuric acid	[M-H] <sup>-</sup>	-	+
	C <sub>9</sub> H <sub>10</sub> O <sub>3</sub> N	Glucose	[M-H] <sup>-</sup>	-	++
	C <sub>5</sub> H <sub>12</sub> O <sub>4</sub> NS	Tyrosine	[M-H] <sup>-</sup>	-	+
131.08 1	C <sub>8</sub> H <sub>13</sub> O <sub>3</sub> N <sub>2</sub>	Choline sulfate	[M-H] <sup>-</sup>	-	+
	C <sub>7</sub> H <sub>11</sub> O <sub>4</sub> N <sub>2</sub>	Dipeptide[Pro+Ala]	[M-H] <sup>-</sup>	-	+
	C <sub>5</sub> H <sub>10</sub> O <sub>4</sub> N <sub>2</sub>	Dipeptide[Hyp+Gly]	[M+Cl] <sup>+</sup>	-	+
132.02 9	Cl	Dipeptide[Gly+Ser]	[M-H] <sup>-</sup>		
	C <sub>8</sub> H <sub>13</sub> O <sub>4</sub> N <sub>2</sub>	Dipeptide[Pro+Ser]		+	+
		Dipeptide[Hyp+Ala]	[M-H] <sup>-</sup>	++++	++++
135.03 0	C <sub>5</sub> H <sub>10</sub> O <sub>7</sub> P	Deoxyribosephosphates	[M+Cl] <sup>+</sup>	-	+
	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub> Cl	Glucose	[M-H] <sup>-</sup>	-	+
	C <sub>9</sub> H <sub>13</sub> O <sub>4</sub> N <sub>3</sub>	Deoxycytidine	[M-H] <sup>-</sup>	-	+
136.03 9	C <sub>10</sub> H <sub>15</sub> O <sub>4</sub> N <sub>2</sub>	Dipeptide[Pro+Hyp]	[M-H] <sup>-</sup>	+	+
	C <sub>11</sub> H <sub>19</sub> O <sub>3</sub> N <sub>2</sub>	Dipeptide[Leu/Ile+Pro]	[M-H] <sup>-</sup>	-	+
	C <sub>14</sub> H <sub>27</sub> O <sub>2</sub>	Myristic acid	[M-H] <sup>-</sup>		
137.02 3	C <sub>10</sub> H <sub>16</sub> O <sub>4</sub> N <sub>3</sub>	Dipeptide[Gln+Pro]		-	+
		Tripeptide[Gly+Pro+Ala]	[M+Cl] <sup>+</sup>	-	+
	C <sub>9</sub> H <sub>18</sub> O <sub>4</sub> N <sub>2</sub>	Dipeptide[Val+Thr]	[M-H] <sup>-</sup>	+	++
138.05 5	Cl	FA (16:1)	[M-H] <sup>-</sup>	-	+++
	C <sub>16</sub> H <sub>29</sub> O <sub>2</sub>	Palmitic acid	[M-H] <sup>-</sup>	+	-
	C <sub>16</sub> H <sub>31</sub> O <sub>2</sub>	Glycerophosphocholine	[M-H] <sup>-</sup>	++	++
145.06 1	C <sub>8</sub> H <sub>15</sub> O <sub>6</sub> NP	Dipeptide[Pro+Phe]	[M-H] <sup>-</sup>	-	+
	C <sub>14</sub> H <sub>17</sub> O <sub>3</sub> N <sub>2</sub>	Dipeptide[His+Asp]	[M-H] <sup>-</sup>	-	+
	C <sub>10</sub> H <sub>13</sub> O <sub>5</sub> N <sub>4</sub>	Heptadecanoic acid	[M-H] <sup>-</sup>	-	+
146.04 5	C <sub>17</sub> H <sub>33</sub> O <sub>2</sub>	Tripeptide[Gly+Pro+Val]	[M+Cl] <sup>+</sup>	-	++
	C <sub>12</sub> H <sub>20</sub> O <sub>4</sub> N <sub>3</sub>	Dipeptide[Phe+Ala]	[M-H] <sup>-</sup>	-	+
	C <sub>12</sub> H <sub>16</sub> O <sub>3</sub> N <sub>2</sub>	Thyronine	[M-H] <sup>-</sup>		
154.06 1	Cl	Tripeptide[Gly+Pro+Thr]		-	+
	C <sub>15</sub> H <sub>14</sub> O <sub>4</sub> N	Tripeptide[Ala+Pro+Ser]	[M-H] <sup>-</sup>	-	+
	C <sub>11</sub> H <sub>18</sub> O <sub>5</sub> N <sub>3</sub>	Dipeptide[Gln+Glu]	[M-H] <sup>-</sup>	-	+
160.04 0		Dipeptide[Arg+Cys]	[M-H] <sup>-</sup>	-	+
	C <sub>10</sub> H <sub>15</sub> O <sub>6</sub> N <sub>3</sub>	Dipeptide[Pro+Glu]	[M+Cl] <sup>+</sup>		
	C <sub>9</sub> H <sub>18</sub> O <sub>3</sub> N <sub>5</sub> S	Dipeptide[Gln+Pro]		-	+
167.06 1	C <sub>10</sub> H <sub>14</sub> O <sub>5</sub> N <sub>2</sub>	Tripeptide[Gly+Pro+Ala]	[M+Cl] <sup>+</sup>	+	++
	C <sub>10</sub> H <sub>17</sub> O <sub>4</sub> N <sub>3</sub>	Dipeptide[Lys+Pro]	[M-H] <sup>-</sup>	-	+
	Cl	FA (18:2)	[M+Cl] <sup>+</sup>		
168.04 2		Dipeptide[Gln+Val]			
	C <sub>11</sub> H <sub>21</sub> O <sub>3</sub> N <sub>3</sub>	Dipeptide[Leu/Ile+Asn]			
	Cl	Tripeptide[2xGly+Ile/Leu]		+	++
171.04 0	C <sub>18</sub> H <sub>31</sub> O <sub>2</sub>	Tripeptide[Gly+Val+Ala]	[M-H] <sup>-</sup>	+	++
	C <sub>10</sub> H <sub>19</sub> O <sub>4</sub> N <sub>3</sub>	FA (18:1)	[M-H] <sup>-</sup>	-	+
	Cl	Stearic acid	[M-H] <sup>-</sup>		
171.07 7		Tripeptide[Pro+Gly+Ile]			
		Tripeptide[Pro+Gly+Leu]			
	C <sub>18</sub> H <sub>33</sub> O <sub>2</sub>	Tripeptide[Pro+Val+Ala]	[M+Cl] <sup>+</sup>	-	+
178.05 0	C <sub>18</sub> H <sub>35</sub> O <sub>2</sub>	Deoxyadenosine	[M-H] <sup>-</sup>	+	+
	C <sub>13</sub> H <sub>22</sub> O <sub>4</sub> N <sub>3</sub>	Tripeptide[Pro+Thr+Ala]	[M+Cl] <sup>+</sup>	+	+
		Tripeptide[Pro+2xAla]	[M-H] <sup>-</sup>	-	+
		Phosphopantothenic acid	[M-H] <sup>-</sup>	-	+
		Tripeptide[2xPro+Ser]	[M-H] <sup>-</sup>		

**Table S 1:** Assignments of peaks of the mass spectra recorded via AP-MALDI-FT-MS of diluted fresh blood. The peaks were assigned via their accurate mass with <5 ppm mass accuracy (<10 ppm below 200 *m/z*) and their isotopic pattern. Peaks of an intensity below 100 a.u. were ignored. (PA: phosphatidic acid, PE: phosphatidylethanolamine, PI: phosphatidylinositol, PS: phosphatidylserine, PG: phosphatidylglycerol, PC: phosphatidylcholine, SM: sphingomyelin, Cer: cerebroside, CerP: ceramide phosphate, PE-Cer: ceramide phosphoethanolamine). Metabolites with \* were additionally confirmed via MS/MS.



179.05 5	C <sub>10</sub> H <sub>13</sub> O <sub>3</sub> N <sub>5</sub> ClC <sub>12</sub> H <sub>20</sub> O <sub>5</sub> N <sub>3</sub>	Tripeptide[Ala+Leu/Ile+Pr o]			
180.06 6	C <sub>11</sub> H <sub>19</sub> O <sub>4</sub> N <sub>3</sub> Cl C <sub>9</sub> H <sub>17</sub> O <sub>8</sub> NP				
182.04 8	C <sub>13</sub> H <sub>20</sub> O <sub>5</sub> N <sub>3</sub> C <sub>14</sub> H <sub>24</sub> O <sub>4</sub> N <sub>3</sub>				
185.09 2					
187.07 2					
197.03 5					
201.08 8					
213.01 7					
215.03 2					
226.08 3					
227.10 4					
227.14 0					
227.20 1					
242.11 5					
253.09 8					
253.21 8					
255.23 3					
256.09 8					
261.12 5					
269.08 8					
269.24 9					
270.14 6					
271.08 5					
272.09 3					
272.12 6					
273.09 7					
276.11					

2					
278.067					
278.092					
278.128					
279.233					
280.107					
281.249					
283.265					
284.162					
286.072					
286.141					
292.107					
298.070					
298.141					
298.178					
m/z	Assignment	detected as	detected by DMAN	detected by DPN	

**Table S 1** contd.

299.137	C <sub>12</sub> H <sub>19</sub> O <sub>5</sub> N <sub>4</sub>	Tripeptide[Asn+Pro+Ala] Tripeptide[Gln+Pro+Glu] Tetrapeptide[2xGly+Pro+Ala]	[M-H] <sup>-</sup>	-	+
	C <sub>20</sub> H <sub>31</sub> O <sub>2</sub> C <sub>10</sub> H <sub>15</sub> O <sub>4</sub> N <sub>5</sub> Cl	Arachidonic acid Dipeptide[Asn+His] Tripeptide[2xGly+His]	[M-H] <sup>-</sup> [M+Cl] <sup>-</sup>	-	+
303.233	C <sub>10</sub> H <sub>16</sub> O <sub>6</sub> N <sub>3</sub> S	Tripeptide[Asn+Cys+Ala] Tripeptide[Gly+Cys+Glu] Glutathione	[M-H] <sup>-</sup>	++	+
304.083		Tripeptide[Gly+Pro+Val]	[M+Cl] <sup>-</sup> [M+Cl] <sup>-</sup>	-	+
	C <sub>12</sub> H <sub>21</sub> O <sub>4</sub> N <sub>3</sub> Cl C <sub>12</sub> H <sub>23</sub> O <sub>4</sub> N <sub>3</sub> Cl	Tripeptide[2xAla+Leu] Tripeptide[2xAla+Ile] Tripeptide[2xVal+Gly] Tripeptide[2xPro+Thr]	[M+Cl] <sup>-</sup> [M+Cl] <sup>-</sup>	-	+
306.077		Tripeptide[Pro+Gly+Ile] Tripeptide[Pro+Gly+Leu]	[M+Cl] <sup>-</sup>	-	+
	C <sub>14</sub> H <sub>22</sub> O <sub>5</sub> N <sub>3</sub> C <sub>13</sub> H <sub>22</sub> O <sub>4</sub> N <sub>3</sub> Cl	Tripeptide[Pro+Val+Ala] Tripeptide[Pro+Thr+Ala] Dipeptide[Phe+Tyr] Tripeptide[Ala+Leu+Pro]	[M+Cl] <sup>-</sup> [M-H] <sup>-</sup> [M+Cl] <sup>-</sup>	-	+
306.123		Tripeptide[Ala+Ile+Pro]	[M-H] <sup>-</sup>	-	+
	C <sub>12</sub> H <sub>20</sub> O <sub>5</sub> N <sub>3</sub> Cl C <sub>18</sub> H <sub>19</sub> O <sub>4</sub> N <sub>2</sub>	Tripeptide[Ser+Lys+Cys] Tripeptide[Pro+Lys+Gly] Tripeptide[Ala+Cys+Arg]	[M+Cl] <sup>-</sup> [M-H] <sup>-</sup> [M+Cl] <sup>-</sup>	-	+
308.139	C <sub>14</sub> H <sub>24</sub> O <sub>4</sub> N <sub>3</sub> Cl	Tripeptide[Gln+Pro+Ala] Tetrapeptide[2xAla+Pro+Gly]	[M+Cl] <sup>-</sup>	-	+
312.157	C <sub>12</sub> H <sub>23</sub> O <sub>5</sub> N <sub>4</sub> S	Tripeptide[Val+Pro+Asn]	[M-H] <sup>-</sup>	-	+
320.139	C <sub>13</sub> H <sub>24</sub> O <sub>4</sub> N <sub>4</sub> Cl C <sub>12</sub> H <sub>23</sub> O <sub>4</sub> N <sub>6</sub> S	Tetrapeptide[2xGly+Pro+Val] Tetrapeptide[2xAla+Pro+Gln]	[M-H] <sup>-</sup> [M+Cl] <sup>-</sup>	-	+
	C <sub>13</sub> H <sub>22</sub> O <sub>5</sub> N <sub>4</sub> Cl	Tetrapeptide[Asn+Gly+Pro+Val]	[M+Cl] <sup>-</sup>	-	+
322.118	C <sub>14</sub> H <sub>24</sub> O <sub>5</sub> N <sub>4</sub> Cl	cPA (16:0/0:0) Tripeptide[Val+His+Asn]	[M-H] <sup>-</sup>	-	+
327.136		Tetrapeptide[2xGly+His+Val]	[M-H] <sup>-</sup> [M-H] <sup>-</sup>	-	+
	C <sub>16</sub> H <sub>26</sub> O <sub>6</sub> N <sub>5</sub>	Tetrapeptide[3xAla+His]	[M-H] <sup>-</sup>	-	++
334.154		Cholestenic acid	[M-H] <sup>-</sup>	++	++
	C <sub>19</sub> H <sub>36</sub> O <sub>6</sub> P C <sub>15</sub> H <sub>24</sub> O <sub>5</sub> N <sub>6</sub> Cl	Dihydroxyvitamin D3 cPA (18:1/0:0) cPA (18:0/0:0)	[M-H] <sup>-</sup> [M-H] <sup>-</sup>	-	+
335.141		Dihydroxycholestenic acid	[M-H] <sup>-</sup>	+	-
	C <sub>27</sub> H <sub>43</sub> O <sub>3</sub>	Trihydroxyvitamin D3	[M-H] <sup>-</sup>	-	++
335.150		Dihydroxycholestanic acid	[M+Cl] <sup>-</sup>	-	+
	C <sub>21</sub> H <sub>38</sub> O <sub>6</sub> P C <sub>21</sub> H <sub>40</sub> O <sub>6</sub> P	Dihydroxyprostanic acid	[M-H] <sup>-</sup>	-	+
347.149	C <sub>27</sub> H <sub>43</sub> O <sub>4</sub>	LysoPA18:0/0:0	[M-H] <sup>-</sup>	-	+
	C <sub>27</sub> H <sub>45</sub> O <sub>4</sub>	Tetrapeptide[Lys+Gly+Pro+Ile]	[M-H] <sup>-</sup>	-	+
349.129		Tetrapeptide[Lys+Gly+Pro+Leu]	[M-H] <sup>-</sup>	-	+
	C <sub>21</sub> H <sub>42</sub> O <sub>7</sub> P C <sub>19</sub> H <sub>35</sub> O <sub>5</sub> N <sub>5</sub> Cl	Tetrapeptide[Lys+Ala+Pro+Val]	[M-H] <sup>-</sup>	-	+
363.145		Cholesterol sulfate	[M-H] <sup>-</sup>	-	+
	C <sub>27</sub> H <sub>45</sub> O <sub>4</sub> S C <sub>27</sub> H <sub>46</sub> O <sub>4</sub> Cl	Dihydroxycholestanic acid	[M-H] <sup>-</sup>	-	+
384.189	C <sub>19</sub> H <sub>37</sub> O <sub>6</sub> N <sub>8</sub>	Tetrapeptide[Lys+Ala+Thr+Arg]	[M-H] <sup>-</sup>	-	+
	C <sub>22</sub> H <sub>31</sub> O <sub>6</sub> N <sub>4</sub> S	Tetrapeptide[Cys+Pro+Val+Tyr] Tetrapeptide[Tyr+Pro+Ala+Met]	[M-H] <sup>-</sup>	-	+
391.226		Tetrapeptide[Pro+Ser+Met+Phe]	[M-H] <sup>-</sup>	-	+
	C <sub>21</sub> H <sub>42</sub> O <sub>7</sub> P C <sub>22</sub> H <sub>34</sub> O <sub>6</sub> N <sub>4</sub> S	LysoPE (18:0/0:0) Tetrapeptide[Met+Leu/Ile+Gly+Tyr]	[M-H] <sup>-</sup>	-	+
403.151		Tetrapeptide[Val+Ser+Phe+Met]	[M-H] <sup>-</sup>	-	+
415.322		Tetrapeptide[Ala+Val+Met+Tyr]	[M-H] <sup>-</sup>	-	+
	C <sub>21</sub> H <sub>42</sub> O <sub>7</sub> P C <sub>22</sub> H <sub>34</sub> O <sub>6</sub> N <sub>4</sub> S	Tetrapeptide[2xVal+Cys+Tyr]	[M-H] <sup>-</sup>	-	+
417.242		Tetrapeptide[Cys+Leu/Ile+Asp+Phe]	[M-H] <sup>-</sup>	-	+
419.25	C <sub>22</sub> H <sub>31</sub> O <sub>7</sub> N <sub>4</sub> S	Tetrapeptide[Tyr+Ser+Pr	[M-H] <sup>-</sup>	-	+

m/z	Assignment	detected as	detected by DMAN	detected by DPN
7	o +Met] Tetrapeptide[Ala+Glu+M et +Phe] Tetrapeptide[Val+Phe+C ys +Glu]			
431.31 7				
433.33 3				
437.26 8				
448.23 4				
465.30 5				
469.30 9				
473.28 3				
479.19 8				
480.31 0				
481.21 4				
495.19 3				

**Table S 1** contd.

497.209	C <sub>22</sub> H <sub>33</sub> O <sub>7</sub> N <sub>4</sub> S	Tetrapeptide[Cys+Leu/Ile+Thr+Tyr]	[M-H] <sup>-</sup>	-	+
511.188	C <sub>22</sub> H <sub>31</sub> O <sub>8</sub> N <sub>4</sub> S	Tetrapeptide[Tyr+Ser+Val+Met]	[M-H] <sup>-</sup>	-	+
513.204	C <sub>25</sub> H <sub>29</sub> O <sub>8</sub> N <sub>4</sub> S	Tetrapeptide[2xThr+Met+Phe]	[M-H] <sup>-</sup>	-	+
519.271	C <sub>23</sub> H <sub>35</sub> O <sub>6</sub> N <sub>8</sub>	Tetrapeptide[Cys+Leu/Ile+Tyr+Asp]	[M-H] <sup>-</sup>	++	+
519.271	C <sub>25</sub> H <sub>29</sub> O <sub>8</sub> N <sub>4</sub> S	Tetrapeptide[Tyr+Ala+Glu+Met]	[M-H] <sup>-</sup>	-	+
519.271	C <sub>23</sub> H <sub>35</sub> O <sub>6</sub> N <sub>8</sub>	Tetrapeptide[Ser+Glu+Met+Phe]	[M-H] <sup>-</sup>	++	+
519.271	C <sub>23</sub> H <sub>35</sub> O <sub>6</sub> N <sub>8</sub>	Tetrapeptide[Met+Phe+Asp+Thr]	[M-H] <sup>-</sup>	-	+
519.271	C <sub>23</sub> H <sub>35</sub> O <sub>6</sub> N <sub>8</sub>	Tetrapeptide[Met+Tyr+2xThr]	[M-H] <sup>-</sup>	-	+
519.271	C <sub>24</sub> H <sub>38</sub> O <sub>5</sub> N <sub>9</sub>	Tetrapeptide[Ser+Lys+Met+Arg]	[M-H] <sup>-</sup>	-	++
519.271	C <sub>26</sub> H <sub>48</sub> O <sub>9</sub> P	Tetrapeptide[Leu/Ile+Pro+Gln+Lys]	[M-H] <sup>-</sup>	-	+
519.271	C <sub>26</sub> H <sub>42</sub> O <sub>5</sub> N <sub>5</sub> S	Tetrapeptide[2xArg+Asn+Ser]	[M-H] <sup>-</sup>	-	+
519.271	C <sub>27</sub> H <sub>40</sub> O <sub>5</sub> N <sub>5</sub> S	Tetrapeptide[2xHis+Lys+Leu/Ile]	[M-H] <sup>-</sup>	-	+
530.282	C <sub>24</sub> H <sub>48</sub> O <sub>9</sub> PCl	LysoPG (20:2/0:0)	[M+Cl] <sup>-</sup>	-	+
530.282	C <sub>26</sub> H <sub>38</sub> O <sub>6</sub> N <sub>5</sub> S	Tetrapeptide[Met+Phe+Lys+Leu/Ile]	[M-H] <sup>-</sup>	-	+
532.297	C <sub>22</sub> H <sub>38</sub> O <sub>6</sub> N <sub>9</sub> Na	Tetrapeptide[Met+Val+Trp+Leu/Ile]	[M-2H+Na] <sup>-</sup>	-	++
532.297	C <sub>26</sub> H <sub>46</sub> O <sub>7</sub> NPCl	LysoPG (18:0/0:0)	[M+Cl] <sup>-</sup>	-	++
532.297	C <sub>22</sub> H <sub>41</sub> O <sub>6</sub> N <sub>9</sub> Na	Tetrapeptide[Met+Thr+Trp+Leu/Ile]	[M-2H+Na] <sup>-</sup>	-	++
535.305	C <sub>26</sub> H <sub>42</sub> O <sub>6</sub> N <sub>5</sub> S	Tetrapeptide[Lys+Arg+Glu+Pro]	[M-H] <sup>-</sup>	-	+
536.292	C <sub>23</sub> H <sub>38</sub> O <sub>11</sub> N <sub>5</sub>	LysoPC (18:4/0:0)	[M-H] <sup>-</sup>	-	+
546.277	C <sub>27</sub> H <sub>41</sub> O <sub>5</sub> N <sub>6</sub>	Tetrapeptide[Arg+Gln+Lys+Val]	[M-H] <sup>-</sup>	-	+
546.277	C <sub>24</sub> H <sub>36</sub> O <sub>7</sub> N <sub>9</sub>	Tetrapeptide[Met+Tyr+Lys+Leu/Ile]	[M-H] <sup>-</sup>	-	++
547.284	C <sub>28</sub> H <sub>52</sub> O <sub>9</sub> P	Pentapeptide[Ser+Asp+Glu+Val+Leu/Ile]	[M-H] <sup>-</sup>	-	++
547.284	C <sub>27</sub> H <sub>48</sub> O <sub>7</sub> NPCl	Tetrapeptide[Met+Trp+Lys+Val]	[M-H] <sup>-</sup>	-	+
547.284	C <sub>27</sub> H <sub>50</sub> O <sub>7</sub> NPCl	Tetrapeptide[Met+Trp+Lys+Val]	[M+Cl] <sup>-</sup>	-	+
548.256	C <sub>28</sub> H <sub>39</sub> O <sub>5</sub> N <sub>8</sub>	Tetrapeptide[Arg+Asn+Gln+Phe]	[M+Cl] <sup>-</sup>	-	+
548.256	C <sub>31</sub> H <sub>38</sub> O <sub>5</sub> N <sub>6</sub>	LysoPG (22:2/0:0)	[M-H] <sup>-</sup>	-	+
548.293	C <sub>27</sub> H <sub>38</sub> O <sub>7</sub> N <sub>5</sub> S	LysoPE (22:4/0:0)	[M-H] <sup>-</sup>	-	+
548.293	C <sub>31</sub> H <sub>41</sub> O <sub>6</sub> N <sub>6</sub>	LysoPE (22:3/0:0)	[M-H] <sup>-</sup>	-	+
548.293	C <sub>31</sub> H <sub>41</sub> O <sub>6</sub> N <sub>6</sub>	Tetrapeptide[His+Val+Lys+Trp]	[M-H] <sup>-</sup>	-	+
550.272	C <sub>24</sub> H <sub>36</sub> O <sub>8</sub> N <sub>9</sub>	Tetrapeptide[2xTrp+Ala+Leu/Ile]	[M-H] <sup>-</sup>	-	+
550.272	C <sub>22</sub> H <sub>38</sub> O <sub>8</sub> N <sub>9</sub> Na	Tetrapeptide[Trp+Met+Glu+Leu/Ile]	[M-H] <sup>-</sup>	-	++
550.308	C <sub>26</sub> H <sub>46</sub> O <sub>9</sub> NPCl	Tetrapeptide[Trp+Phe+Val+Lys]	[M-2H+Na] <sup>-</sup>	-	+
550.308	C <sub>27</sub> H <sub>50</sub> O <sub>8</sub> NPCl	Tetrapeptide[Arg+Asn+Tyr+Gln]	[M-2H+Na] <sup>-</sup>	-	+
550.308	C <sub>32</sub> H <sub>63</sub> O <sub>8</sub> NP	Tetrapeptide[Arg+Asn+Tyr+Gln]	[M+Cl] <sup>-</sup>	-	++
550.308	C <sub>30</sub> H <sub>57</sub> NO <sub>8</sub> P	Tetrapeptide[Arg+Lys+Glu+Gln]	[M+Cl] <sup>-</sup>	-	+
550.308	C <sub>32</sub> H <sub>43</sub> O <sub>5</sub> N <sub>6</sub>	Tetrapeptide[Arg+Lys+Glu+Gln]	[M-H] <sup>-</sup>	-	+
552.287	C <sub>30</sub> H <sub>56</sub> O <sub>9</sub> P	LysoPS(20:3/0:0)	[M-H] <sup>-</sup>	+	++
552.287	C <sub>24</sub> H <sub>36</sub> O <sub>9</sub> N <sub>9</sub>	LysoPE (OH-22:3/0:0)	[M-H] <sup>-</sup>	-	+
552.287	C <sub>24</sub> H <sub>40</sub> O <sub>9</sub> N <sub>9</sub>	CerP(d18:1/14:0)	[M-H] <sup>-</sup>	-	+
560.256	C <sub>24</sub> H <sub>40</sub> O <sub>9</sub> N <sub>9</sub>	fragment of PE(22:1/16:0)	[M-H] <sup>-</sup>	-	+
560.256	C <sub>24</sub> H <sub>40</sub> O <sub>9</sub> N <sub>9</sub>	Tetrapeptide[Leu/Ile+Lys+Trp+Phe]	[M-H] <sup>-</sup>	-	+
560.256	C <sub>24</sub> H <sub>40</sub> O <sub>9</sub> N <sub>9</sub>	LysoPG (24:2/0:0)	[M-H] <sup>-</sup>	-	+
561.287	C <sub>24</sub> H <sub>40</sub> O <sub>9</sub> N <sub>9</sub>	Pentapeptide[His+Pro+Ser+2xGln]	[M-H] <sup>-</sup>	-	+
561.287	C <sub>24</sub> H <sub>40</sub> O <sub>9</sub> N <sub>9</sub>	Pentapeptide[Glu+Pro+Lys+2xAsn]	[M-H] <sup>-</sup>	-	+
562.272	C <sub>24</sub> H <sub>40</sub> O <sub>9</sub> N <sub>9</sub>	Pentapeptide[Glu+Pro+Lys+2xAsn]	[M-H] <sup>-</sup>	-	+

563.33  
6  
564.28  
8  
566.30  
3  
567.30  
7  
573.28  
2  
576.25  
1  
577.31  
6  
578.26  
7  
580.28  
3  
582.26  
1  
582.29  
8  
588.44  
1  
589.35  
2  
591.33  
2  
591.36  
8  
594.26  
2  
598.29  
3

m/z

Assignment

detected  
as

detected by  
DMAN DPN

**Table S 1** contd.

599.32	C <sub>27</sub> H <sub>52</sub> O <sub>12</sub> P	LysoPI (18:0/0:0)	[M-H]	+	+
2	C <sub>33</sub> H <sub>41</sub> O <sub>5</sub> N <sub>6</sub>	Tetrapeptide[Leu/Ile+Val	[M-H]	-	+
		+]			
601.31	C <sub>31</sub> H <sub>61</sub> NO <sub>8</sub> P	2xTrp]	[M-H]	-	++
3	C <sub>32</sub> H <sub>44</sub> O <sub>5</sub> N <sub>7</sub>	fragment of PE(22:/16:0)	[M-H]	+	+
	C <sub>34</sub> H <sub>31</sub> O <sub>4</sub> N <sub>4</sub> Fe	Tetrapeptide[2xLys+Phe	[M-H]	+++	+++
		+Trp]	[M-H]	-	++
605.35	C <sub>33</sub> H <sub>44</sub> O <sub>6</sub> N <sub>7</sub>	Heme B (ferrous)*	[M-H]	-	+
2	C <sub>30</sub> H <sub>43</sub> O <sub>7</sub> N <sub>8</sub>	CerP(d18:1/16:0)	[M-H]	-	+
	C <sub>35</sub> H <sub>69</sub> O <sub>6</sub> NP	Tetrapeptide[2xLys+Tyr+	[M-H]	+	++
		Trp]	[M-H]	++	+++
606.34	C <sub>34</sub> H <sub>30</sub> O <sub>4</sub> N <sub>4</sub> Fe	Tetrapeptide[2xTyr+Lys+	[M-	-	++
2	Na	Arg]	[2H+Na]	+	+++
	C <sub>36</sub> H <sub>69</sub> O <sub>6</sub> NP	CerP(d18:1/17:0)	[M-H]	-	+
615.17		Heme B (Oxo-complex)*		-	+
1	C <sub>36</sub> H <sub>71</sub> O <sub>6</sub> NP	Heme B (ferrous)	[M-H]	+	++
	C <sub>34</sub> H <sub>31</sub> O <sub>6</sub> N <sub>4</sub> Fe	CerP(d18:2/18:0)	[M-H]	++	++
616.47		CerP(d18:1/18:1)	[M-H]	++	+
2	C <sub>34</sub> H <sub>32</sub> O <sub>6</sub> N <sub>4</sub> Fe	CerP(d18:1/18:0)	[M-H]	++	++
	C <sub>34</sub> H <sub>31</sub> O <sub>4</sub> N <sub>4</sub> Fe	Heme B (oxy)	[M-H]	++	+
622.33	Cl	Heme B (hydroperoxy)*	[M+C]	-	+
7	C <sub>32</sub> H <sub>61</sub> O <sub>10</sub> NP	Hemin B	[M-H]	-	+
	C <sub>34</sub> H <sub>32</sub> O <sub>4</sub> N <sub>4</sub> Fe	PS (26:0)		-	+
627.32	Cl	Heme B (ferrous)	[M-H]	-	+
9	C <sub>28</sub> H <sub>47</sub> O <sub>8</sub> N <sub>10</sub>	Pentapeptide[Glu+Ile/Leu	[M-H]	-	+
		+Arg+His+Val]	[M-H]	+	+
630.48	C <sub>35</sub> H <sub>66</sub> O <sub>8</sub> NP	PE (30:2)	[M-H]	-	+
8	C <sub>33</sub> H <sub>61</sub> O <sub>10</sub> NP	PE-Cer(34:1)	[M-H]	-	+
	C <sub>34</sub> H <sub>65</sub> O <sub>9</sub> NP	PS (27:1)	[M-H]	-	+
631.16	C <sub>33</sub> H <sub>63</sub> O <sub>10</sub> NP	PS (P-16:0/12:0)	[M-H]	+	+++
6	C <sub>37</sub> H <sub>68</sub> O <sub>8</sub> P	PS (27:0)	[M-H]	-	+
	C <sub>37</sub> H <sub>70</sub> O <sub>8</sub> P	PA(34:2)	[M-H]	-	+
637.15	C <sub>38</sub> H <sub>76</sub> O <sub>6</sub> N <sub>2</sub> P	PA(34:1)	[M-H]	-	++
3	C <sub>39</sub> H <sub>68</sub> O <sub>8</sub> P	PE-Cer (36:1)	[M-H]	-	+
	C <sub>39</sub> H <sub>70</sub> O <sub>8</sub> P	PA (36:4)	[M-H]	-	+
642.48	C <sub>39</sub> H <sub>72</sub> O <sub>8</sub> P	PA (36:3)	[M-H]	-	+
8	C <sub>39</sub> H <sub>74</sub> O <sub>8</sub> P	PA (36:2)	[M-H]	-	+
	C <sub>40</sub> H <sub>80</sub> O <sub>6</sub> N <sub>2</sub> P	PA (36:1)	[M-H]	+	++
644.50	C <sub>39</sub> H <sub>77</sub> O <sub>8</sub> NP	PE-Cer(38:1)	[M-H]	-	+
4	C <sub>41</sub> H <sub>70</sub> O <sub>8</sub> P	PE (34:0)	[M-H]	-	+
	C <sub>41</sub> H <sub>72</sub> O <sub>8</sub> P	PA(38:5)	[M-H]	-	++
	C <sub>41</sub> H <sub>74</sub> O <sub>8</sub> P	PA(20:4/18:1)*	[M-H]	-	+
647.16	C <sub>42</sub> H <sub>81</sub> O <sub>6</sub> NP	PA(38:3)	[M-H]	-	+
1	C <sub>41</sub> H <sub>77</sub> O <sub>8</sub> NP	CerP(d18:1/24:1)	[M-H]	-	+
	C <sub>41</sub> H <sub>79</sub> O <sub>8</sub> NP	PE (36:2)	[M-H]	-	+
648.16	C <sub>43</sub> H <sub>72</sub> O <sub>8</sub> P	PE (36:1)	[M-H]	-	+
9	C <sub>43</sub> H <sub>74</sub> O <sub>8</sub> P	PA(40:6)	[M-H]	-	+
	C <sub>43</sub> H <sub>77</sub> O <sub>8</sub> NP	PA(40:5)		-	+
650.14	C <sub>43</sub> H <sub>81</sub> O <sub>8</sub> NP	PE (20:4/18:0)*		-	+
0		PE (20:2/18:0)*	[M-H]	-	+
		PE (20:1/18:1)*	[M-H]	-	+
650.40	C <sub>44</sub> H <sub>88</sub> O <sub>6</sub> N <sub>2</sub> P	PE (20:0/18:2)*	[M-H]	-	+
5	C <sub>46</sub> H <sub>90</sub> O <sub>6</sub> N <sub>2</sub> P	PE-Cer (42:1)	[M-H]	-	++
	C <sub>46</sub> H <sub>92</sub> O <sub>6</sub> N <sub>2</sub> P	PE-Cer (44:2)	[M-Na]	-	+
651.14	C <sub>44</sub> H <sub>47</sub> O <sub>10</sub> NP	PE-Cer (44:1)		-	+
7	C <sub>47</sub> H <sub>82</sub> O <sub>13</sub> P	PS (38:4)		-	+
		PI (20:4/18:0)*		-	+
651.35				-	+
6				-	+
658.44				-	+
8				-	+
659.51				-	+
5				-	+
662.40				-	+
5				-	+
662.44				-	+
2				-	+
664.42				-	+
1				-	+
671.46				-	+
7				-	+
673.48				-	+
2				-	+

687.54 6				
695.46 6				
697.48 3				
699.49 8				
701.51 4				
715.57 7				
718.54 0				
721.48 3				
723.49 9				
725.58 6				
726.58 2				
742.54 1				
744.55 6				
747.49 9				
749.51 4				
766.54 0				
770.57 2				
771.64 0				
797.65 6				
799.67 1				
810.53 0				
885.55 2				