Supplementary table 1 Network statistics for islets of Langerhans in Figure 3. Statistics were calculated with Cytoscape's plugin NetworkAnalyzer.

network name	cell type	clustering coef.	centralization	char. path length	avg. neighbors	nodes	edges	density	heterogeneity
islet A	alpha	0.871	0.429	1.321	4.75	8	19	0.679	0.311
islet A	beta	0.788	0.495	1.429	8	15	60	0.571	0.332
islet B	alpha	0.795	0.467	1.333	4	7	14	0.667	0.299
islet B	beta	0.81	0.515	1.436	6.769	13	44	0.564	0.414
islet C	alpha	0.848	0.238	1.179	5.75	8	23	0.821	0.19
islet C	beta	0.848	0.393	1.306	5.556	9	25	0.694	0.307
islet D	alpha	1	0	1	2	3	3	1	0
islet D	beta	1	0	1	2	3	3	1	0
islet E	alpha	0.879	0.218	1.187	10.571	14	74	0.813	0.211
islet E	beta	0.871	0.25	1.194	6.444	9	29	0.806	0.208

Supplementary table 2 Network statistics for gastric cancer tissues in Figure 6. Statistics were calculated with Cytoscape's plugin NetworkAnalyzer.

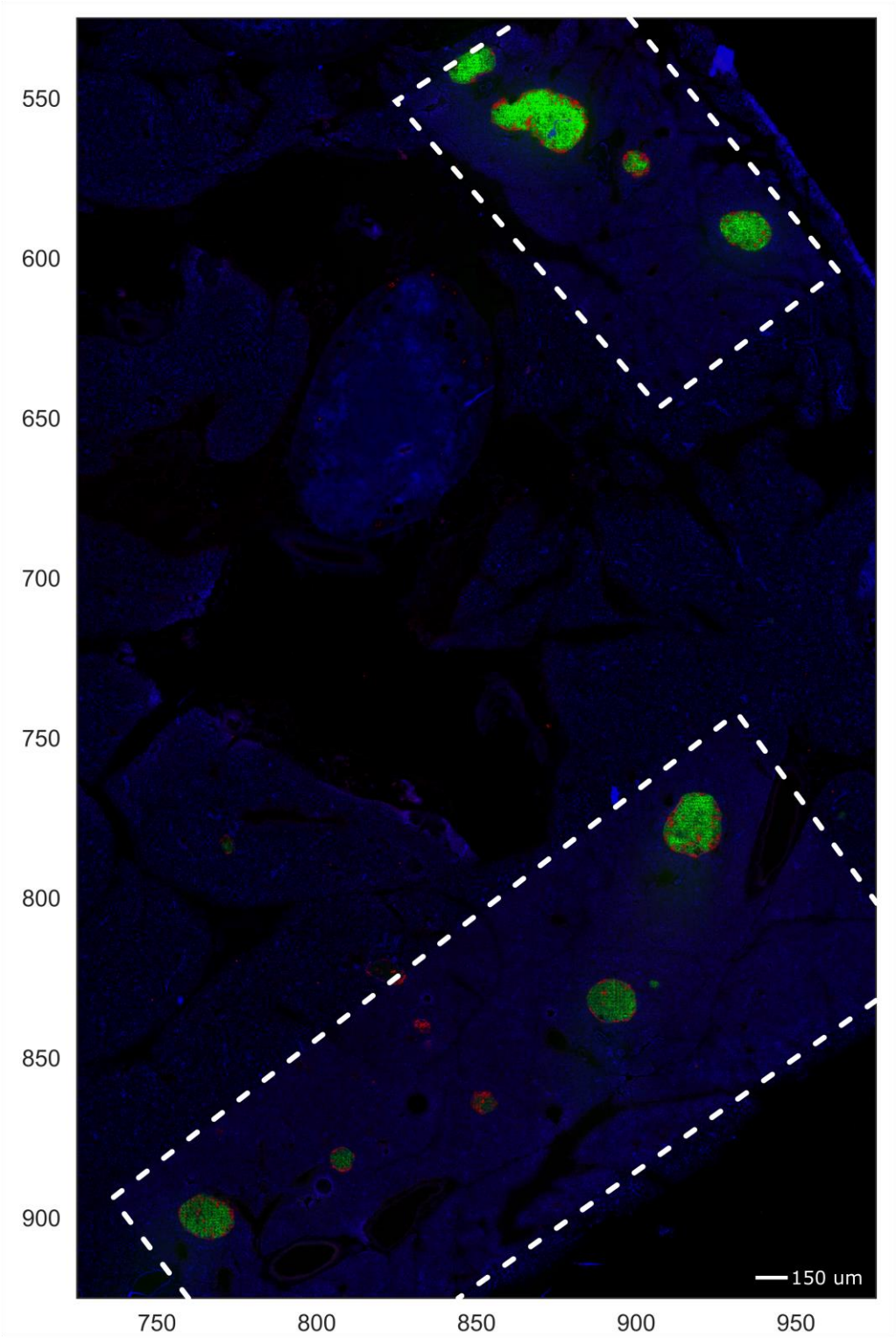
network name	HER2/ neu	clustering coef.	centralization	char. path length	avg. neighbors	nodes	edges	density	heterogeneity
A	positive	0.411	0.302	2.282	8.687	67	291	0.132	0.806
A	negative	0.317	0.32	2.7	7.239	71	257	0.103	0.89
B	positive	0.388	0.295	2.694	21.512	164	1764	0.132	1.003
B	negative	0.379	0.289	2.682	20.412	171	1746	0.12	1.047
C	positive	0.722	0.318	1.518	46.581	86	2003	0.548	0.417
C	negative	0.595	0.321	1.681	30.963	81	1254	0.387	0.469

Supplementary table 3 Network statistics for gastric cancer tissues in Figure 7. Statistics were calculated with Cytoscape's plugin NetworkAnalyzer.

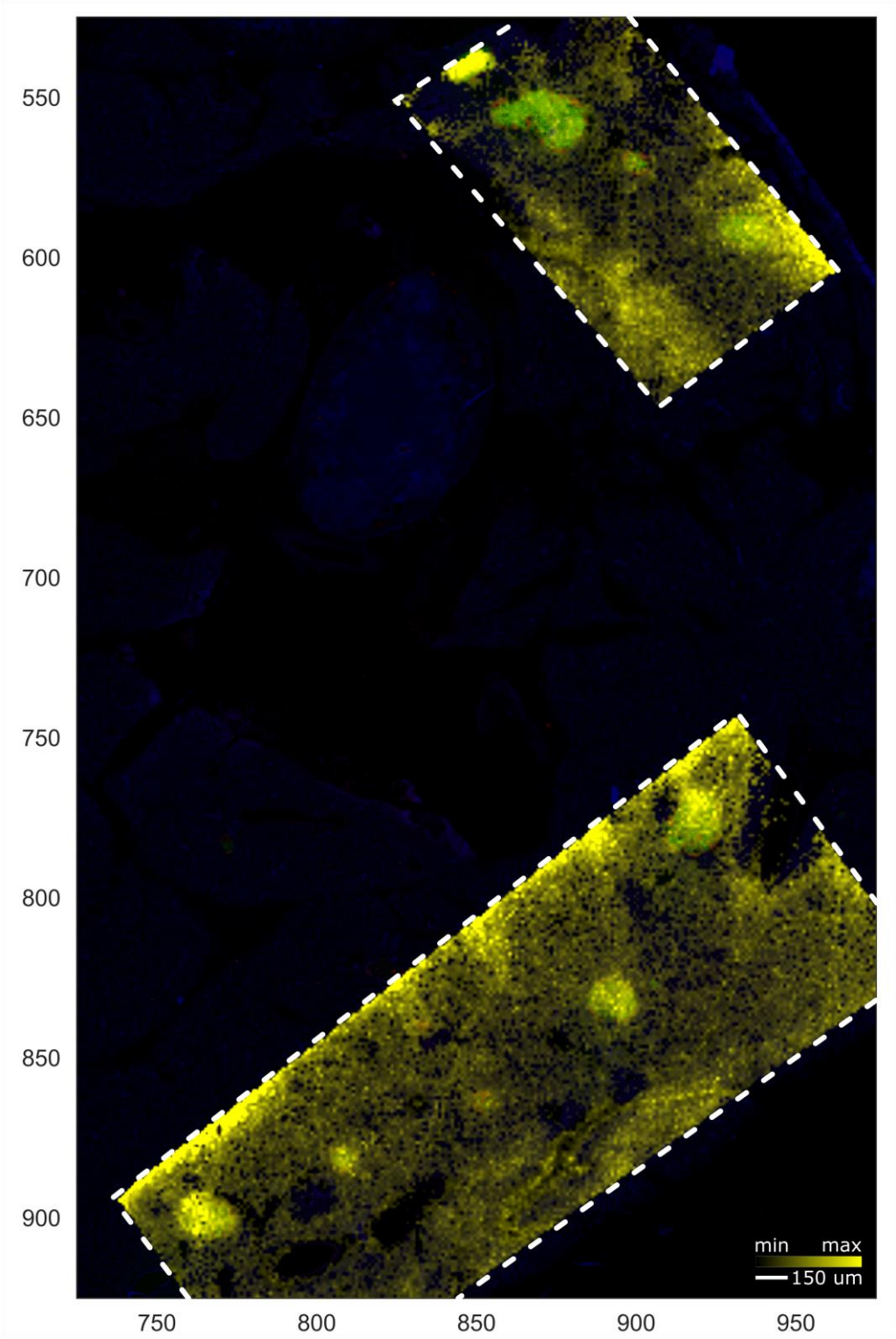
network name	HER2/ neu	clustering coef.	centralization	char. path length	avg. neighbors	nodes	edges	density	heterogeneity
A	positive	0.335	0.305	2.659	5.529	34	94	0.168	0.781
B	positive	0.418	0.207	2.44	2.4	30	36	0.083	0.702
C	positive	0.39	0.197	3.262	3.897	39	76	0.103	0.777
D	positive	0.257	0.103	4.71	2.611	36	47	0.075	0.544
E	positive	0.483	0.335	2.947	3.939	33	65	0.123	0.807

Explanation of network metrics in tables 1-3:

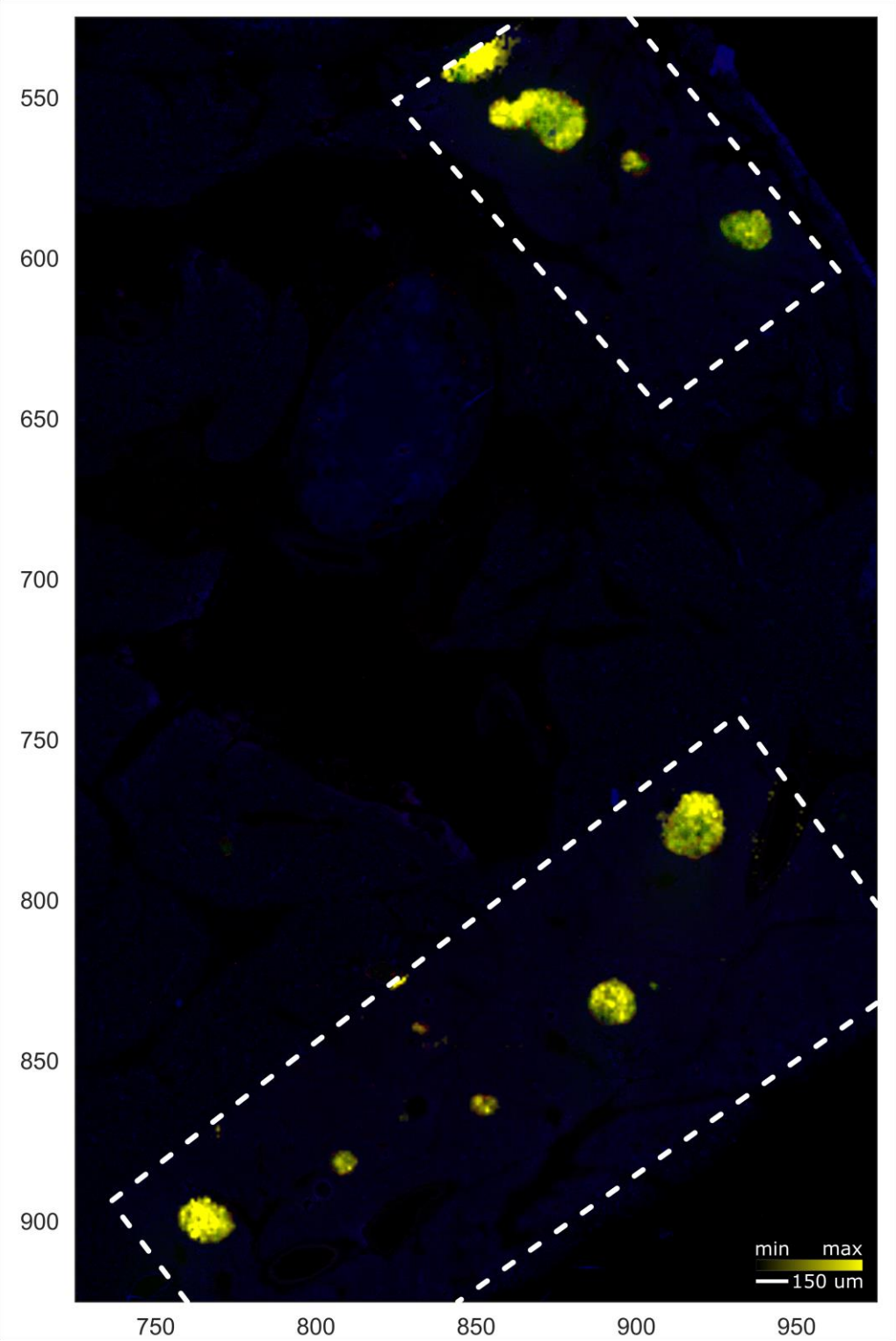
- The clustering coefficient (0-1) describes, whether nodes in a network tend to form clusters.
- The centralization (0-1) of a network describes, whether the network has a center (star shaped).
- The network's characteristic path length is the average of the shortest path length between any pair of nodes.
- The density (0-1) describes how densely the network is populated with edges.
- The heterogeneity (0-1) of a network reflects, whether a network tends to contain hub nodes (i.e. well connected nodes).



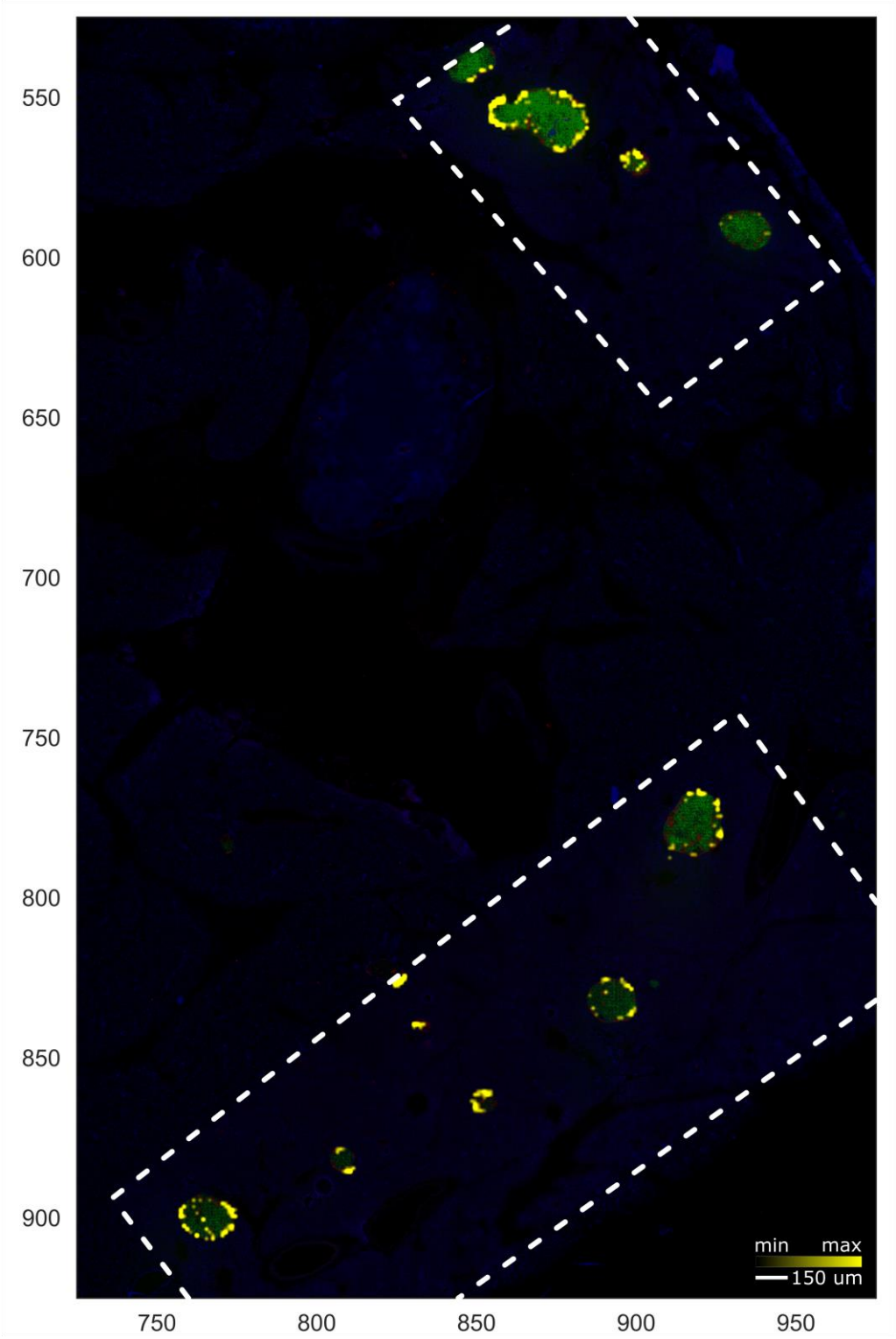
Supplementary figure 1 **Immunohistochemistry staining of mouse pancreas**: glucagon (red), insulin (green), DAPI (blue). The highlighted regions were analyzed with MALDI imaging prior to immunostaining.



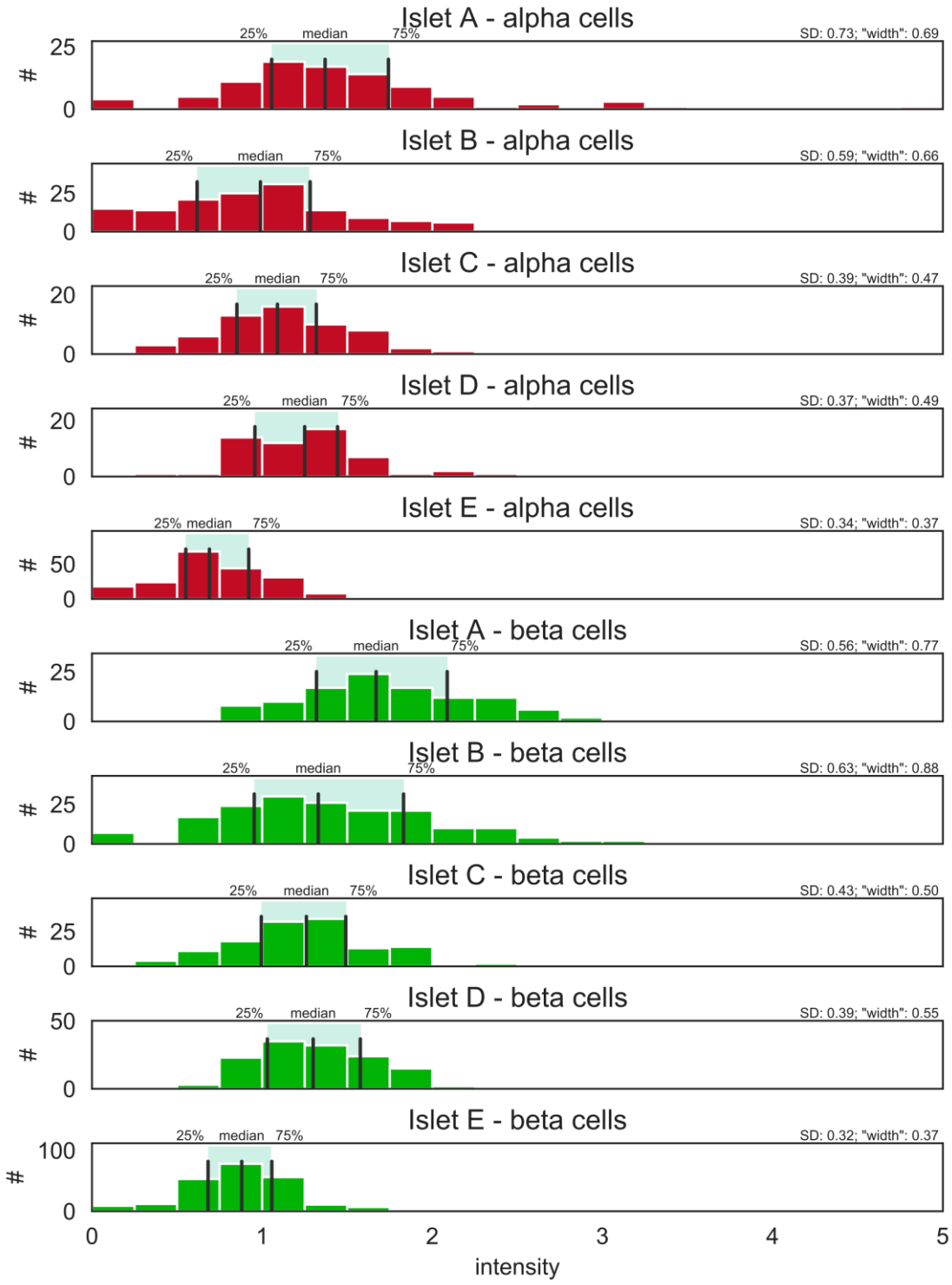
Supplementary figure 2 **Immunohistochemistry staining of mouse pancreas superimposed by molecular distribution of adenosine diphosphate (yellow).** Glucagon (red), insulin (green), DAPI (blue). The highlighted regions were analyzed with MALDI imaging prior to immunostaining.



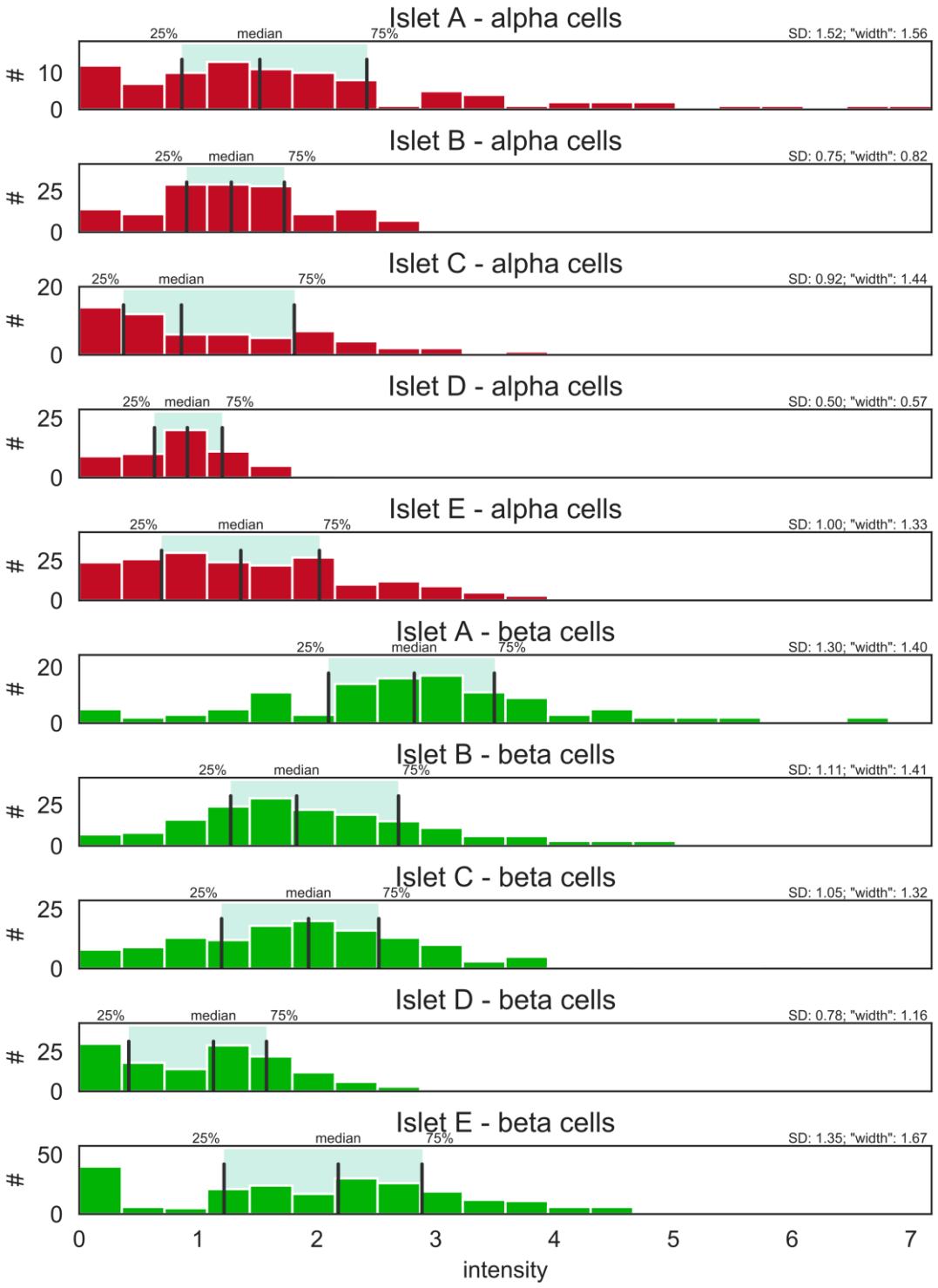
Supplementary figure 3 **Immunohistochemistry staining of mouse pancreas superimposed by molecular distribution of cholesterol sulfate (yellow).** Glucagon (red), insulin (green), DAPI (blue). The highlighted regions were analyzed with MALDI imaging prior to immunostaining.



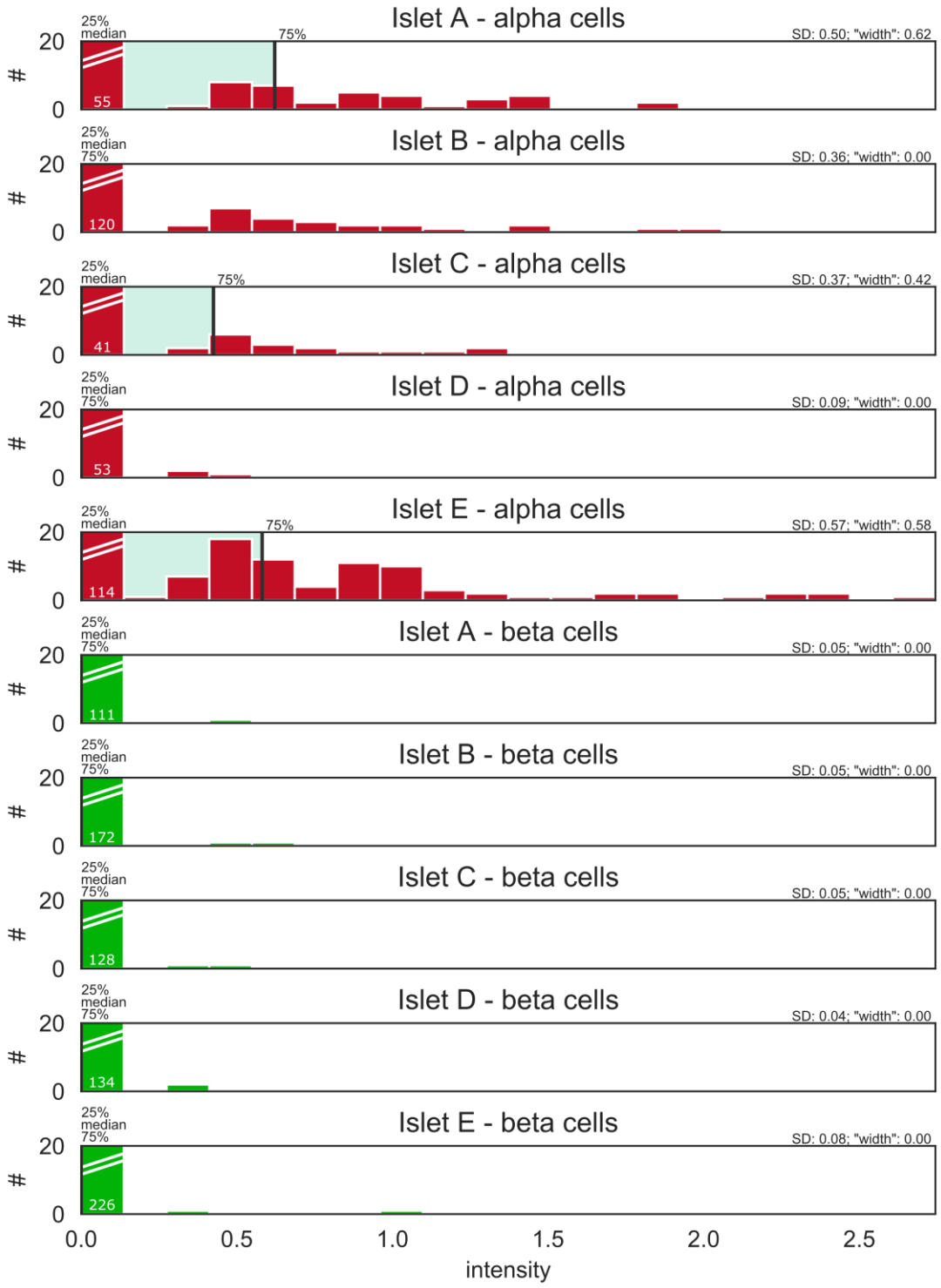
Supplementary figure 4 **Immunohistochemistry staining of mouse pancreas superimposed by molecular distribution of 3-O-sulfogalactosylceramide (yellow).** Glucagon (red), insulin (green), DAPI (blue). The highlighted regions were analyzed with MALDI imaging prior to immunostaining.



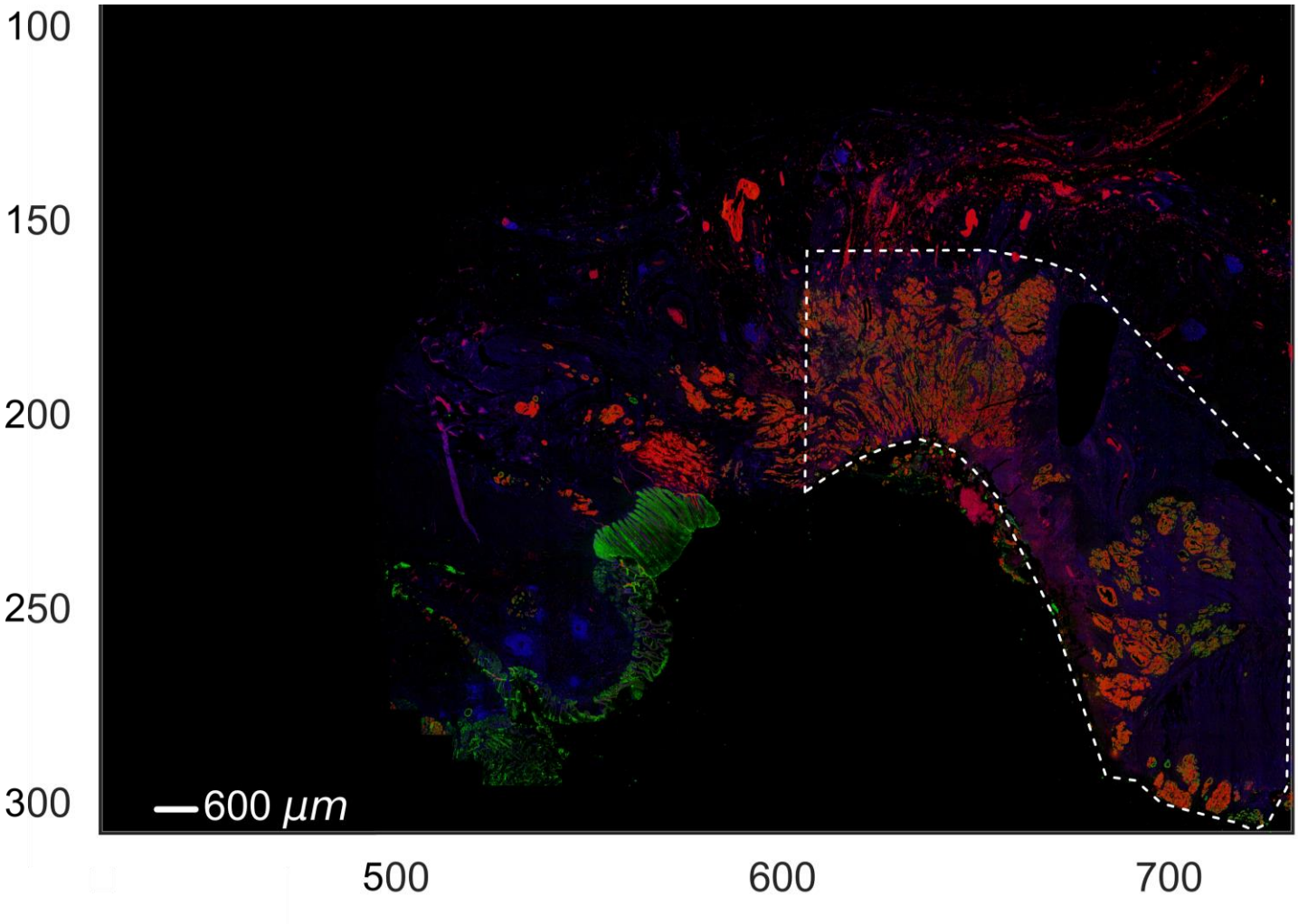
Supplementary figure 5 **Intensity distribution per islet of Langerhans and cell type for adenosine diphosphate.** The 25th percentile, median and 75th percentile are highlighted. SD: standard deviation; width: 75th percentile – 25th percentile.



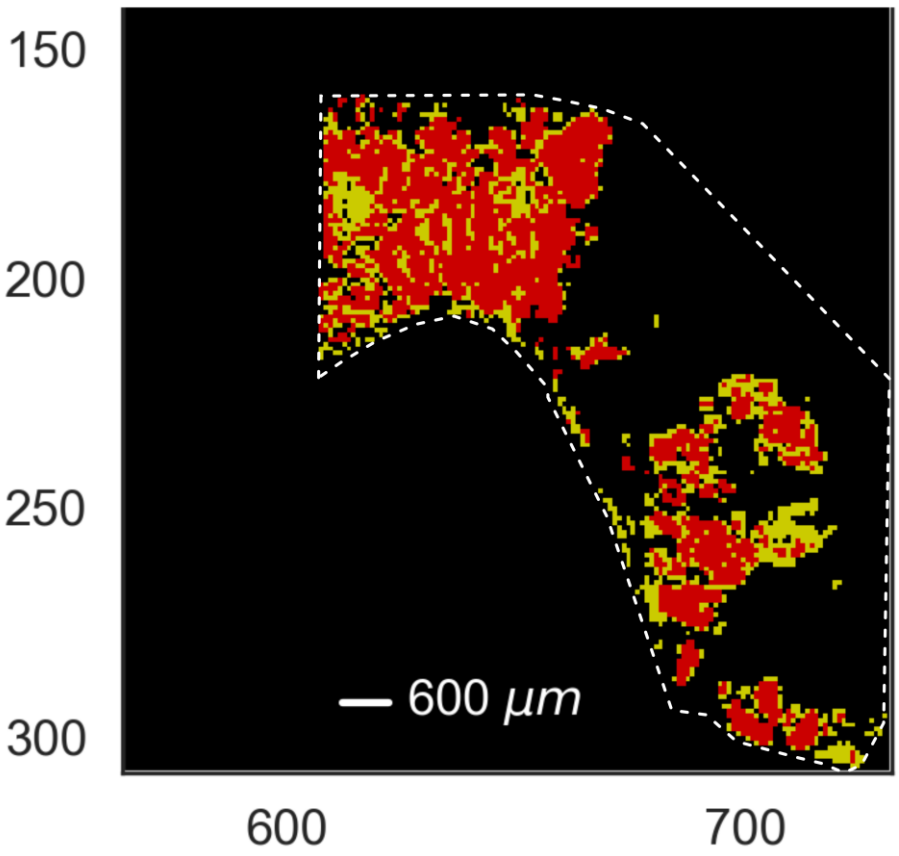
Supplementary figure 6 **Intensity distribution per islet of Langerhans and cell type for cholesterol sulfate.** The 25th percentile, median and 75th percentile are highlighted. SD: standard deviation; width: 75th percentile – 25th percentile.



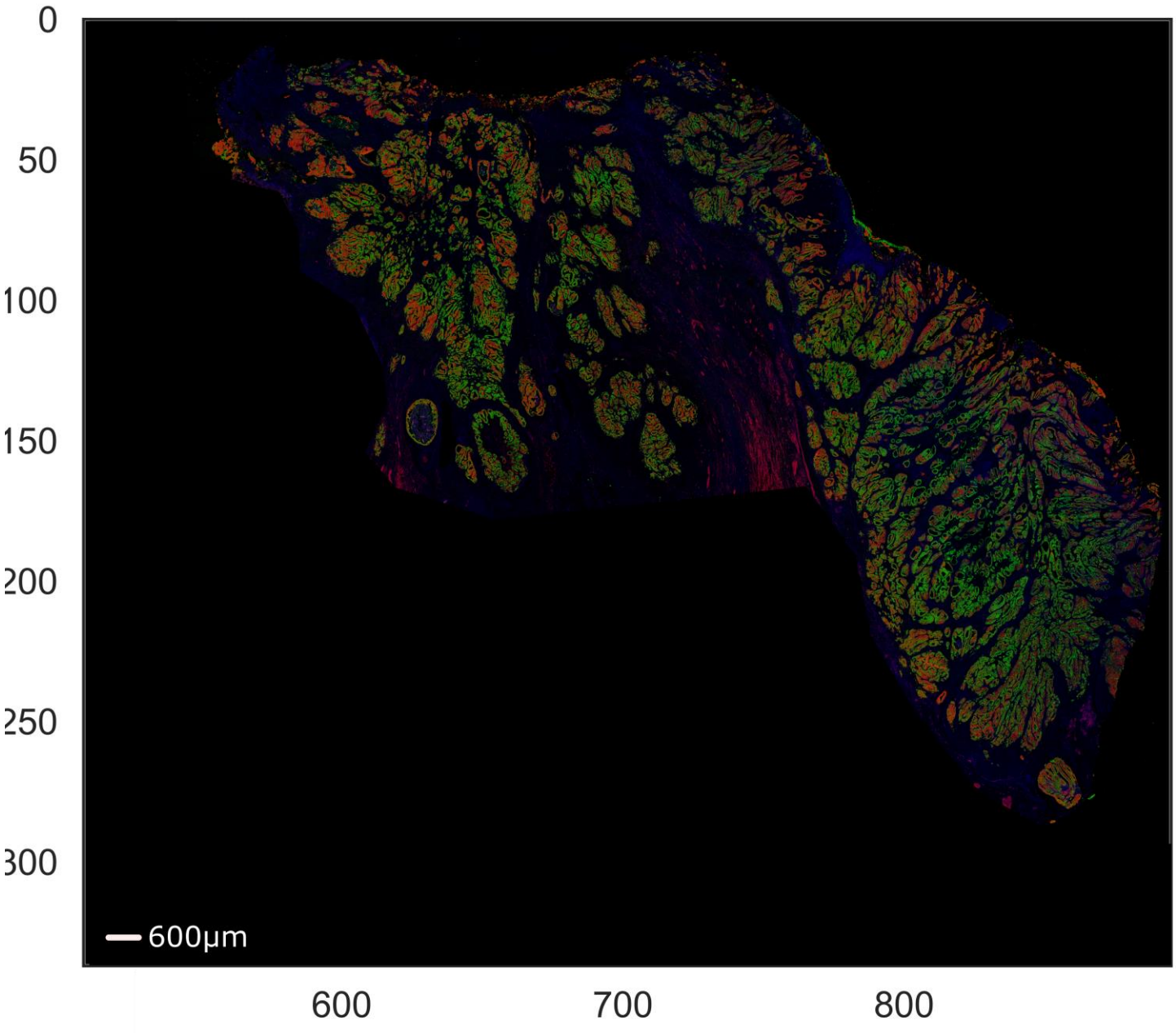
Supplementary figure 7 **Intensity distribution per islet of Langerhans and cell type for 3-O-sulfogalactosylceramide.** The 25th percentile, median and 75th percentile are highlighted. SD: standard deviation; width: 75th percentile – 25th percentile. The heights of the bars that exceed the y-axis limit of 20 is written per bar.



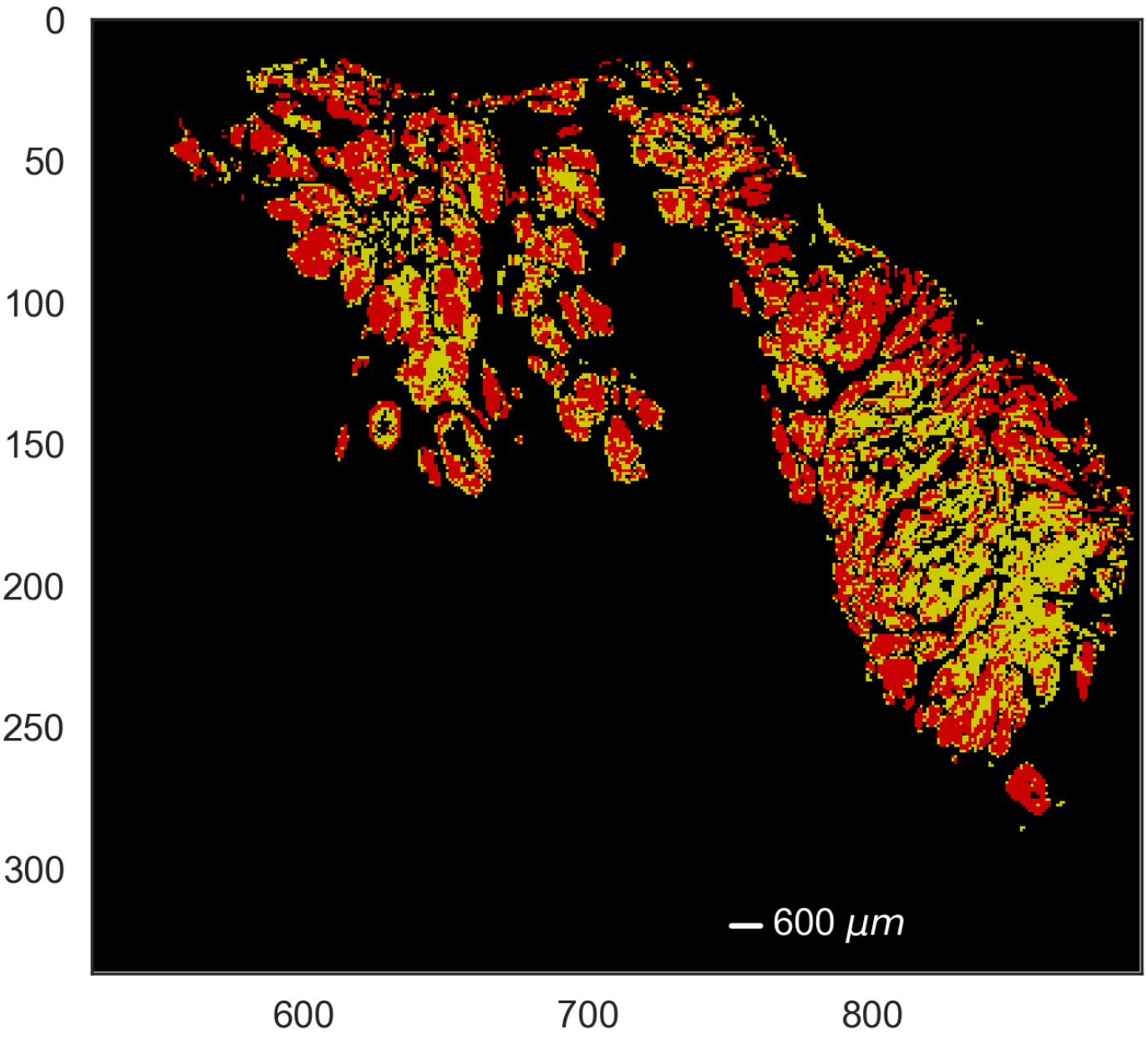
Supplementary figure 8 I**mmunohistochemistry staining of a human gastric cancer tissue slide**: DAPI (blue), pancytokeratin (green), HER2/neu (red). The highlighted regions were analyzed with MALDI imaging prior to immunostaining. Tissue folds were excluded (black).



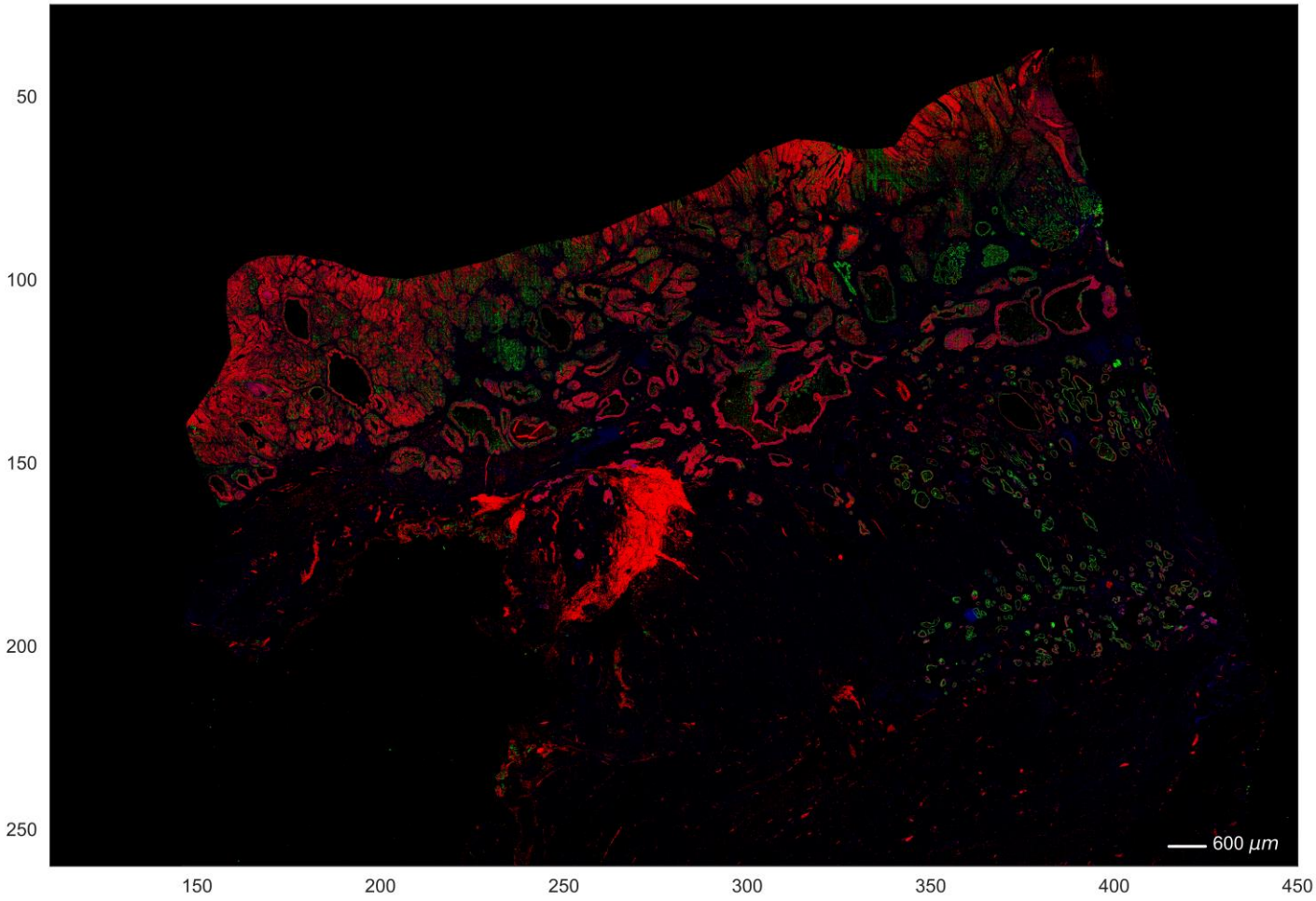
Supplementary figure 9 **HER2/neu positive (red) and negative (yellow) tumor region for the tissue depicted in Supplementary figure 8.**



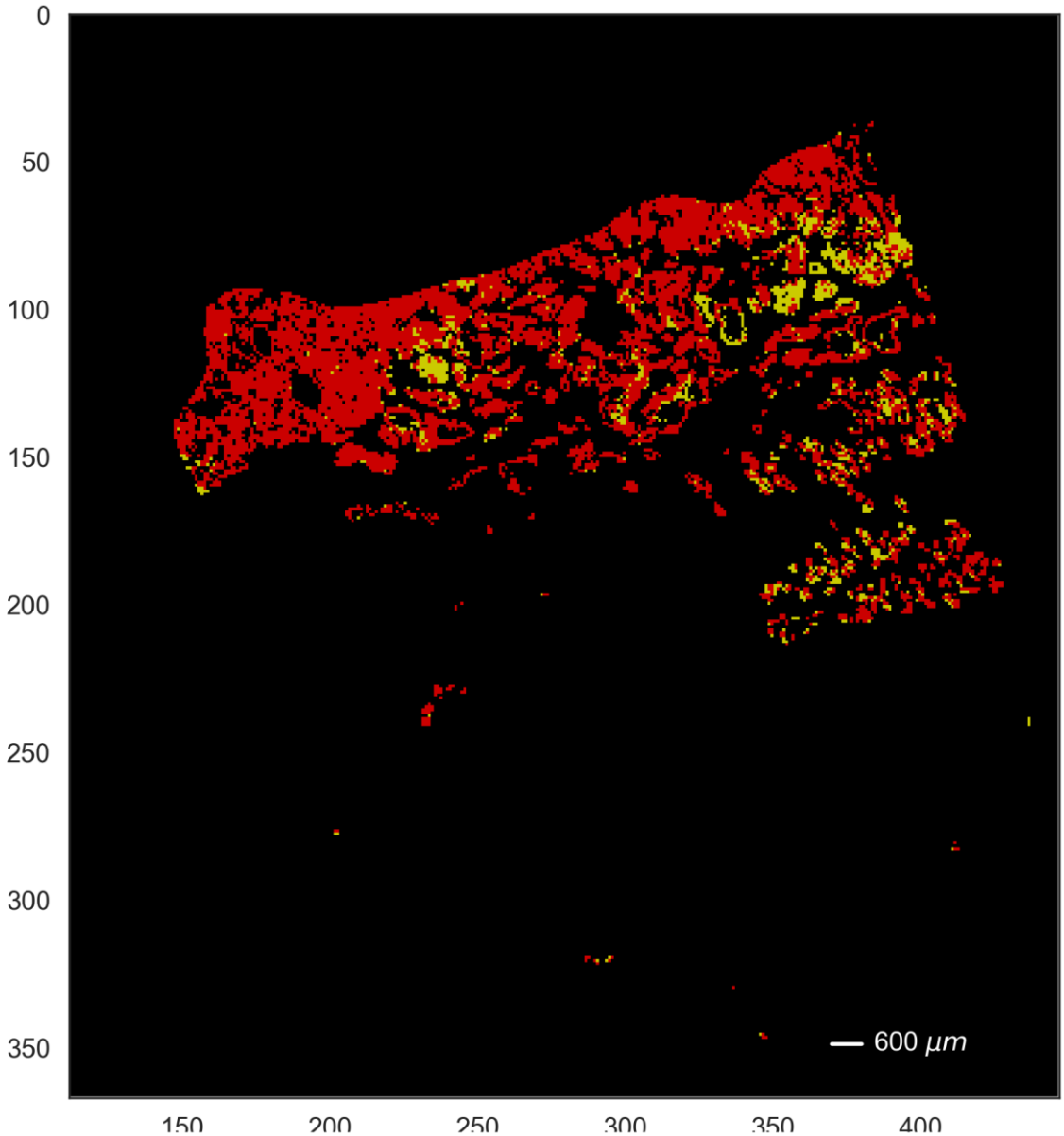
Supplementary figure 10 **Immunohistochemistry staining of a human gastric cancer tissue slide after MALDI imaging**: DAPI (blue), pancytokeratin (green), HER2/neu (red). Tissue folds and artifacts were excluded (black).



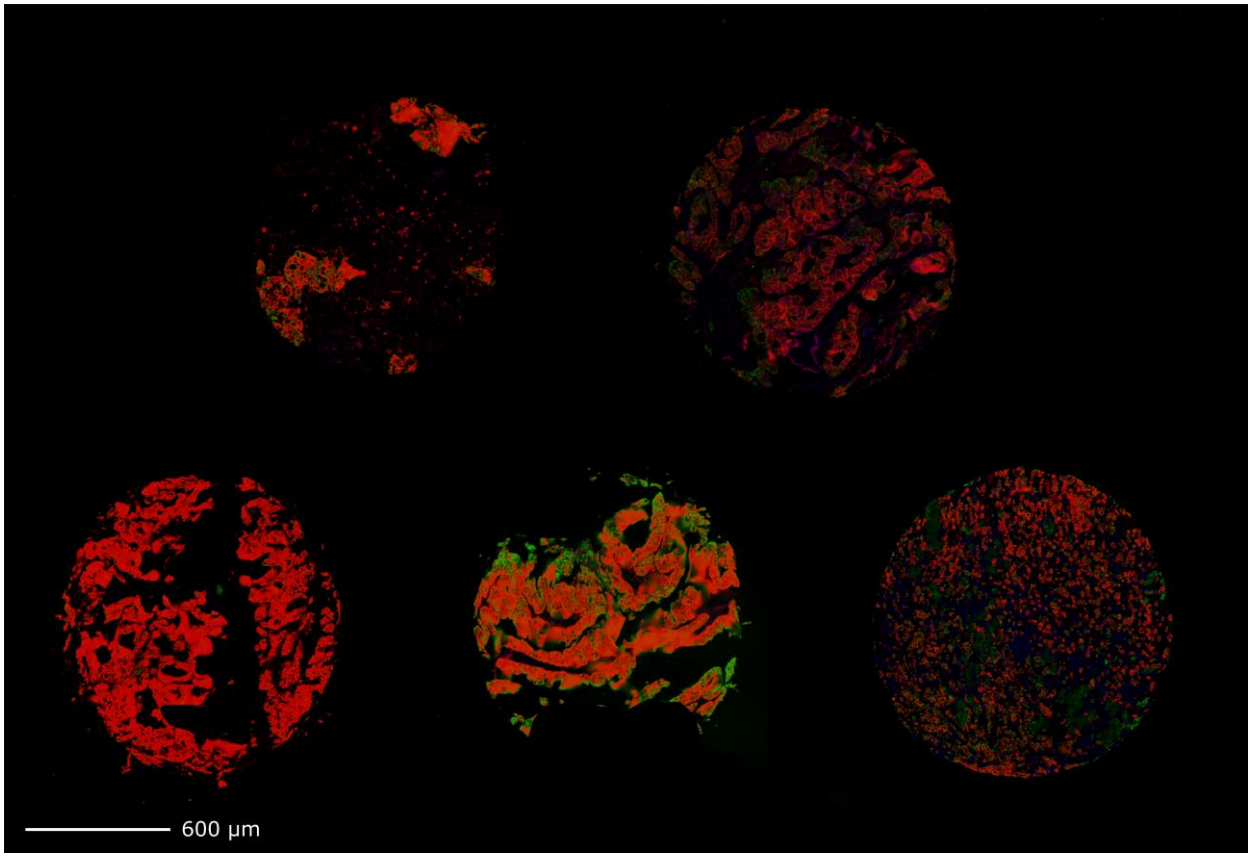
Supplementary figure 11 **HER2/neu positive (red) and negative (yellow) tumor region for the tissue depicted in Supplementary figure 10.**



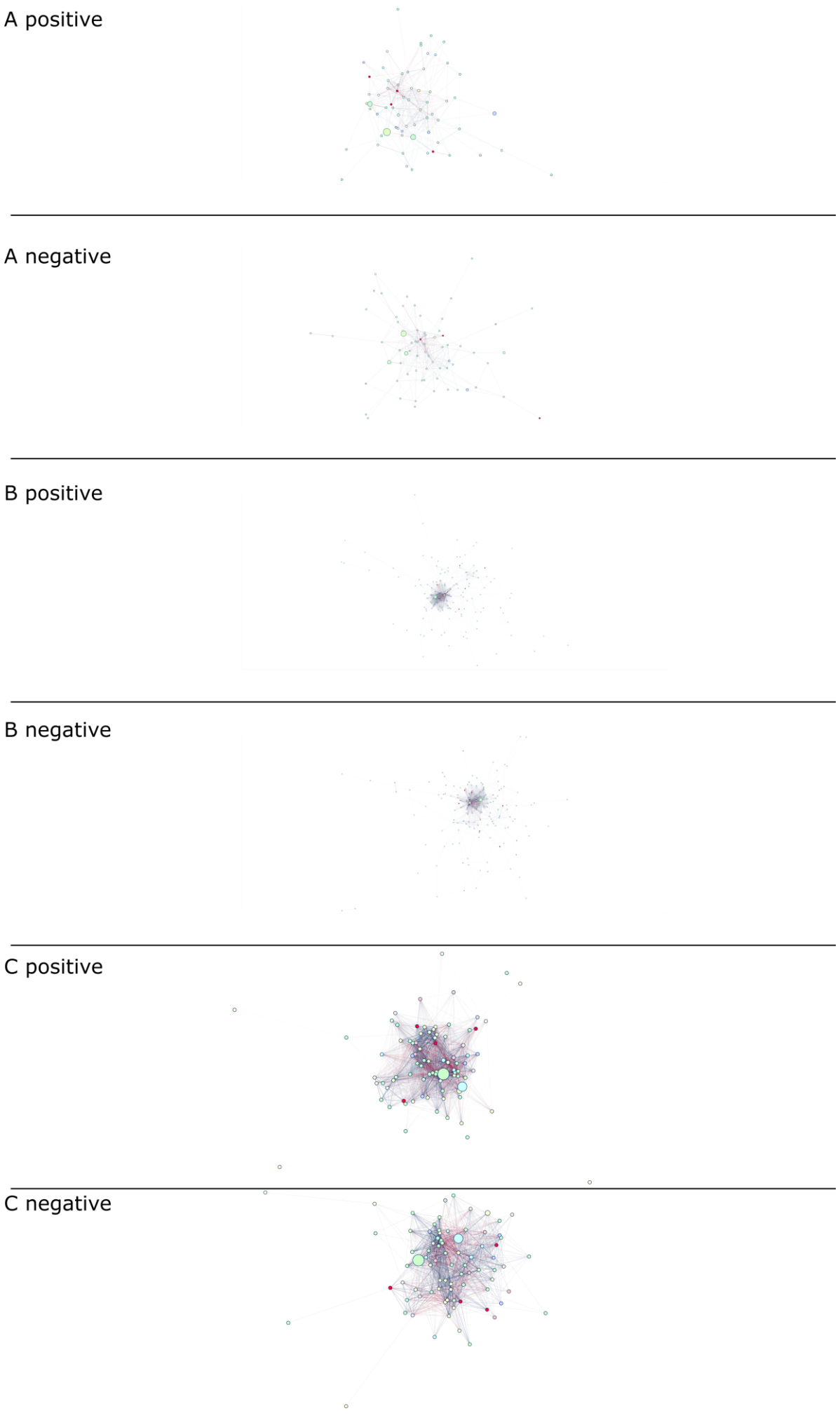
Supplementary figure 12 **Immunohistochemistry staining of a human gastric cancer tissue slide after MALDI imaging**: DAPI (blue), pancytokeratin (green), HER2/neu (red). Tissue folds, artifacts and normal epithel were excluded (black).



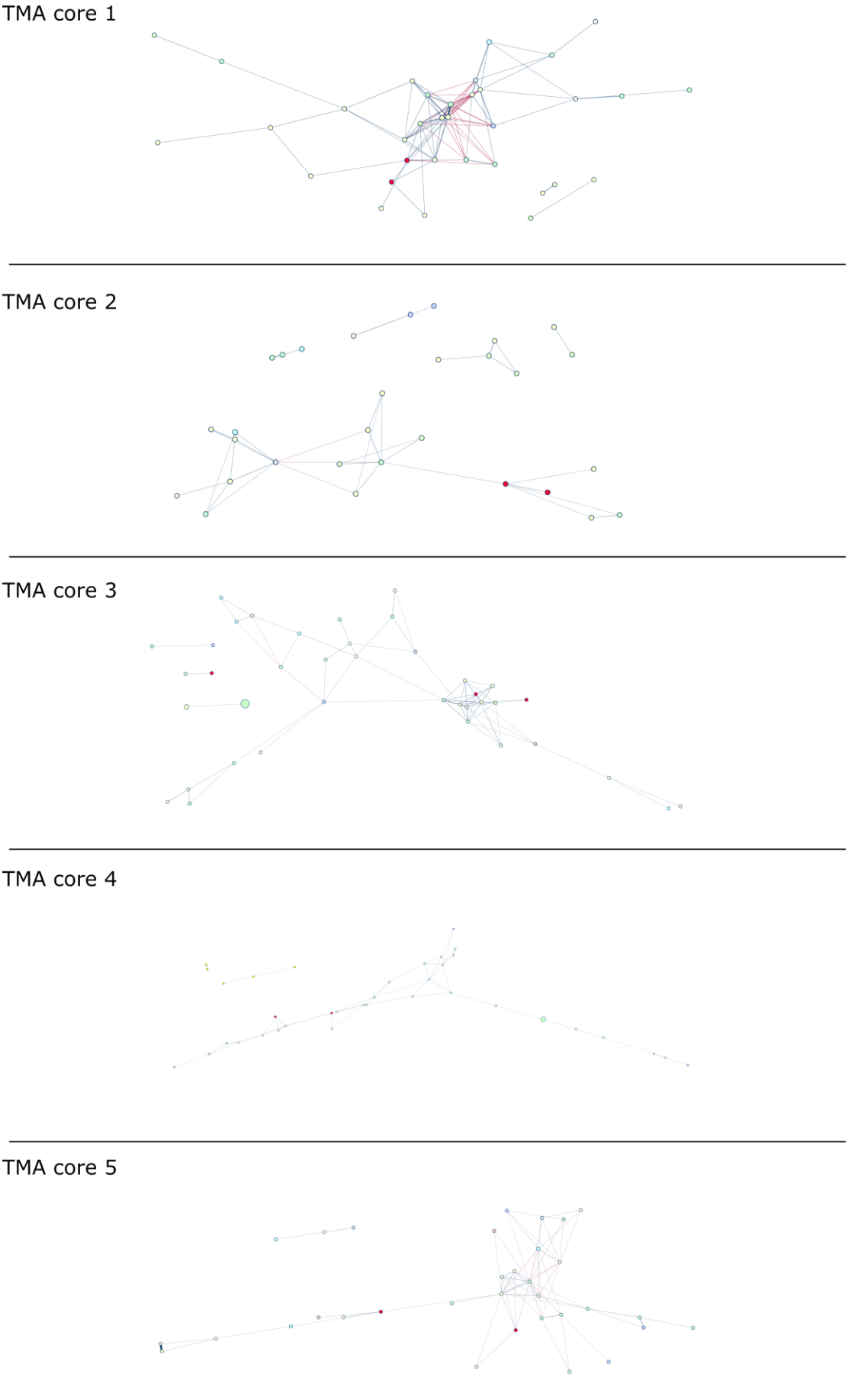
Supplementary figure 13 **HER2/neu positive (red) and negative (yellow) tumor region for the tissue depicted in Supplementary figure 12.**



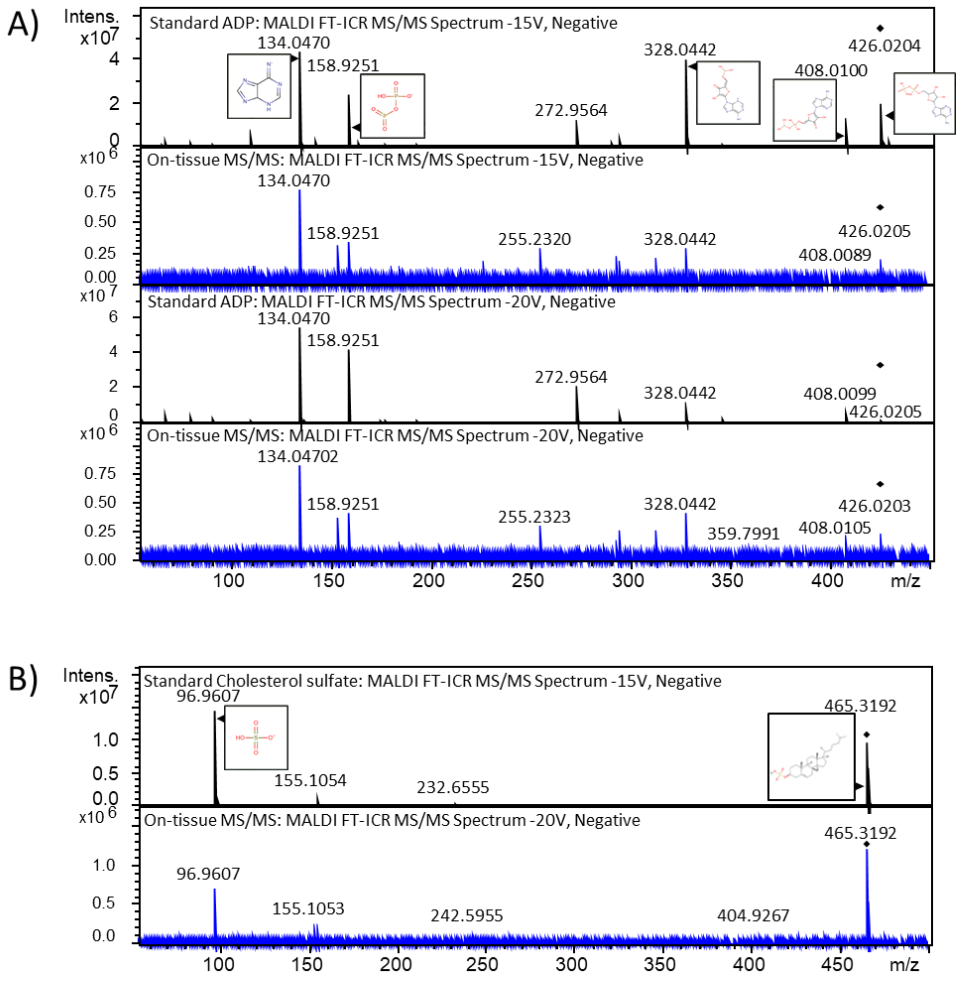
Supplementary figure 14 **Immunohistochemistry staining of human gastric cancer TMA cores after MALDI imaging**: DAPI (blue), pancytokeratin (green), HER2/neu (red). Tissue folds and artifacts were excluded (black).

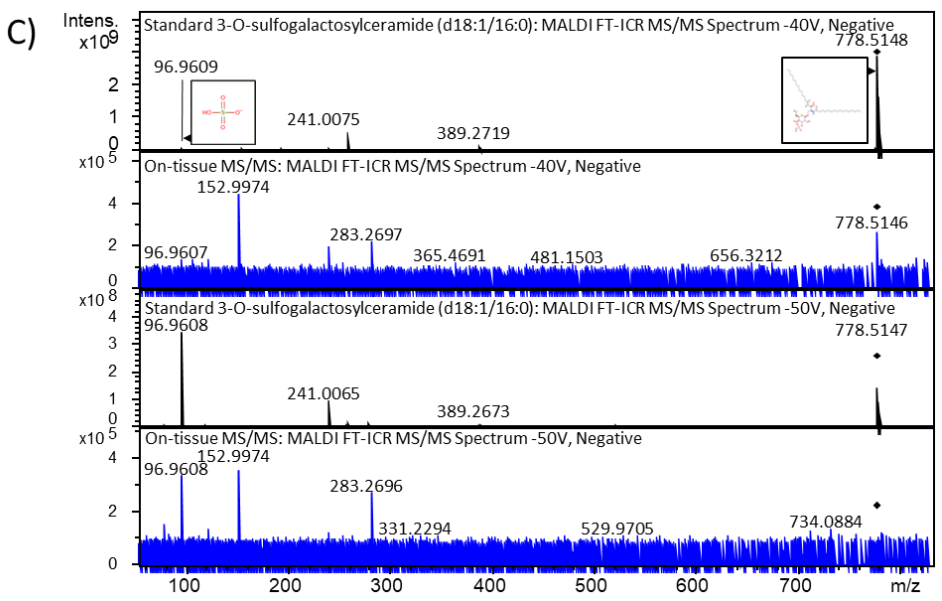


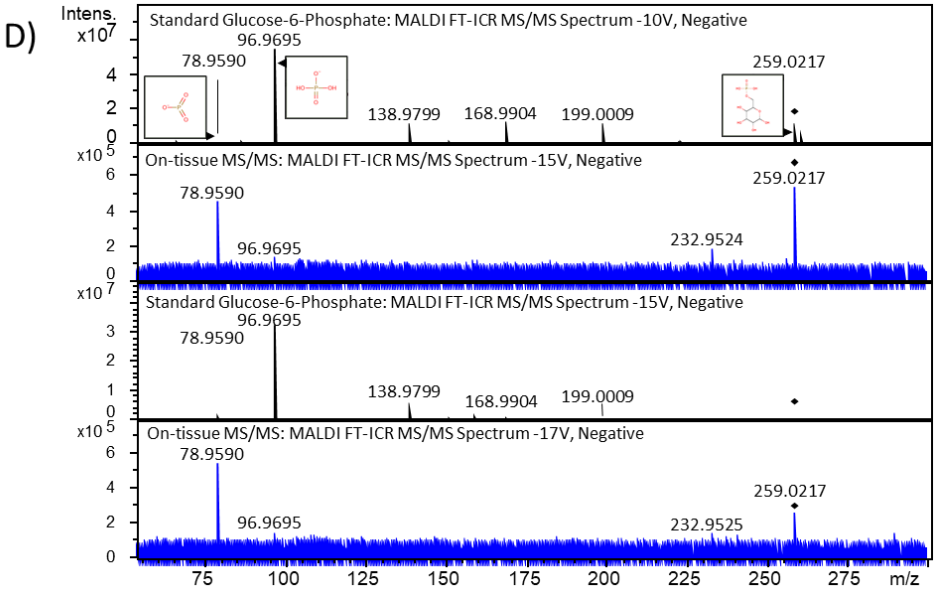
Supplementary figure 15 **Spatial correlation networks of metabolites in three human gastric tissue sections with gastroesophageal carcinomas.** Order corresponding to images in figure 6.



Supplementary figure 16 **Spatial correlation networks of metabolites in five tissue microarray cores human gastric tissue sections with gastroesophageal carcinomas.** Order corresponding to images in figure 7.







Supplementary figure 17*:* **Identification of metabolites detected on islets of Langerhans on consecutive mouse pancreatic tissue section (see MALDI images of Figures 3 and 4) compared to standard compounds**: A) ADP, B) cholesterol sulfate, C) 3-O-sulfogalactosylceramide (d18:1/16:0) and D) glucose-6-phosphate. The parent ions were isolated and fragmented by MALDI FTICR on-tissue MS/MS using quadrupole collision-induced dissociation (CID).