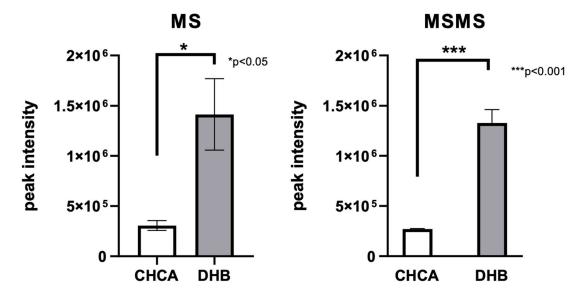
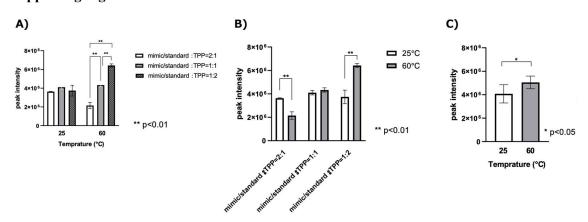


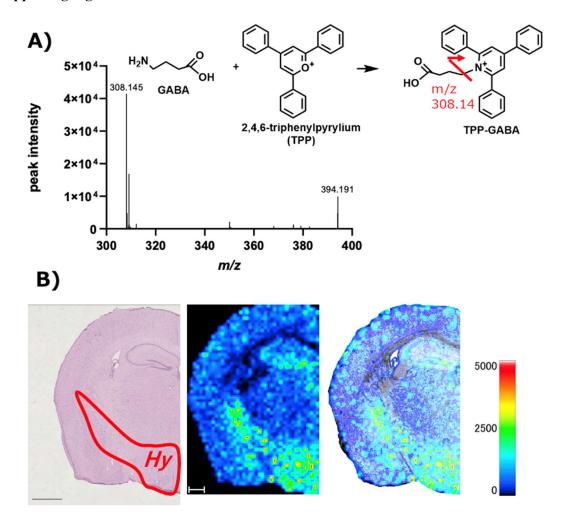
TPP-DA-d4 mass spectrum. The molecular structure of TPP-DA-d4 is formed by the reaction of TPP and DA-d4. *m/z* 308.14 derived from TPP reagent is detected in the product ion spectrum of TPP-DA-d4.



Optimization of matrix conditions. The peak intensity of TPP-DA was significantly increased when DHB was used compared to when CHCA was used as the matrix. A) MS measurement B) MSMS measurement

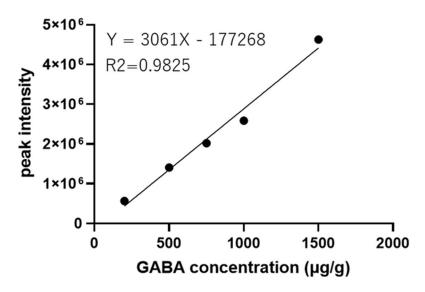


Improvement of DA detection intensity by examining derivatization conditions A) and B) show the reaction of standard solution/mimic sample mixture and TPP solution in a tube, followed by the addition of matrix. C) shows the standard solution/mimic sample mixture was spotted on ITO glass, and the derivatization reagent and matrix were supplied by spraying in the same way as in the TPP-DA determination described in the main text. A) the intensity of TPP-DA detection at different TPP supply rates and derivatization reaction temperatures. At 25°C, the intensity of TPP-DA detection remained unchanged regardless of the TPP supply rate, but at 60°C, the intensity of TPP-DA detection increased with increasing TPP supply rate. B) TPP-DA detection intensity under **TPP** sufficiently increased the heated condition when supplied was (mimic/standard:TPP=1:1 or higher). C) Compares the derivatization reaction at 25°C and 60°C under the conditions of TPP-DA quantification described in the main text, and shows that the TPP-DA detection intensity significantly increased under the heated condition.



Mass spectrum of γ -aminobutyric acid (GABA) and MALDI-MSI results. A) Molecular structure of TPP-GABA formed by the reaction of TPP and GABA. m/z 308.14 derived from TPP reagent is detected in the product ion spectrum of TPP-GABA. Distribution of TPP-DA in coronal sections of mouse brain tissue. B) TPP-DA is localized in the hypothalamus (Hy) when compared to hematoxylin and eosin staining (HE staining) of post-measured sections. Scale bar is 500 μ m.





GABA conc.	average peak	quantitative value	accuracy	RSD
(µg/g)	intensity (n=3)	(µg/g)	(%)	(%)
1500	4627386	1569.6	-4.6	16.7
1000	2586142	902.8	9.7	12.7
750	2018752	717.4	4.3	6.5
500	1407784	517.8	-3.6	7.0
200	565192	242.6	-21.3	7.4

Quantitative determination of TPP-GABA in mouse brain thalamus. The coefficient of determination of linearity (R^2) was set to be greater than 0.98, accuracy within $\pm 30\%$, and RSD within $\pm 20\%$ in MALDI-MSI.