Electronic Supplementary Material (ESI) for Molecular BioSystems

SUPPORTING INFORMATION

High resolution spatial mapping of brominated pyrrole-2-aminoimidazole alkaloids distributions in the marine sponge *Stylissa flabellata* via MALDI-Mass Spectrometry imaging.

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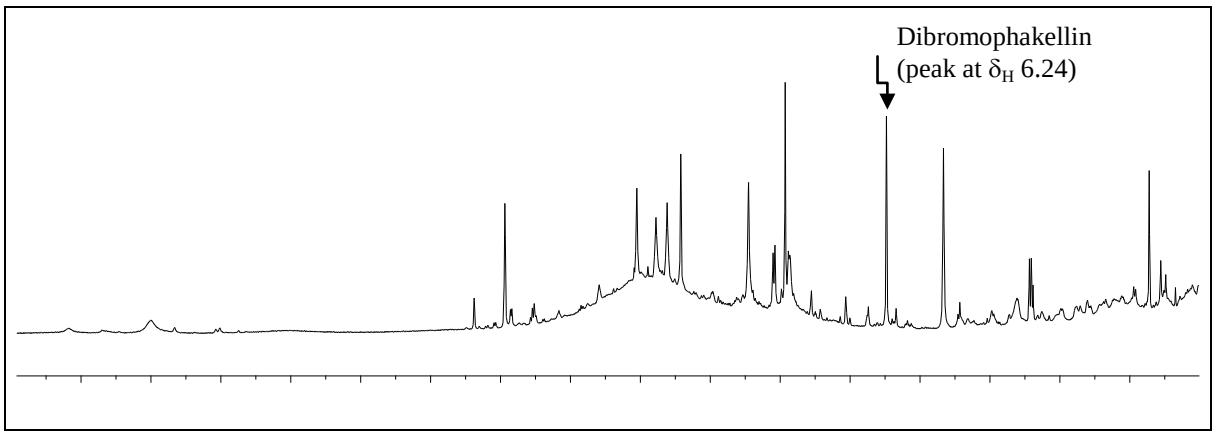


Figure S1. ^{1}H NMR spectrum of Sample 1 (Heron Island, G329565)

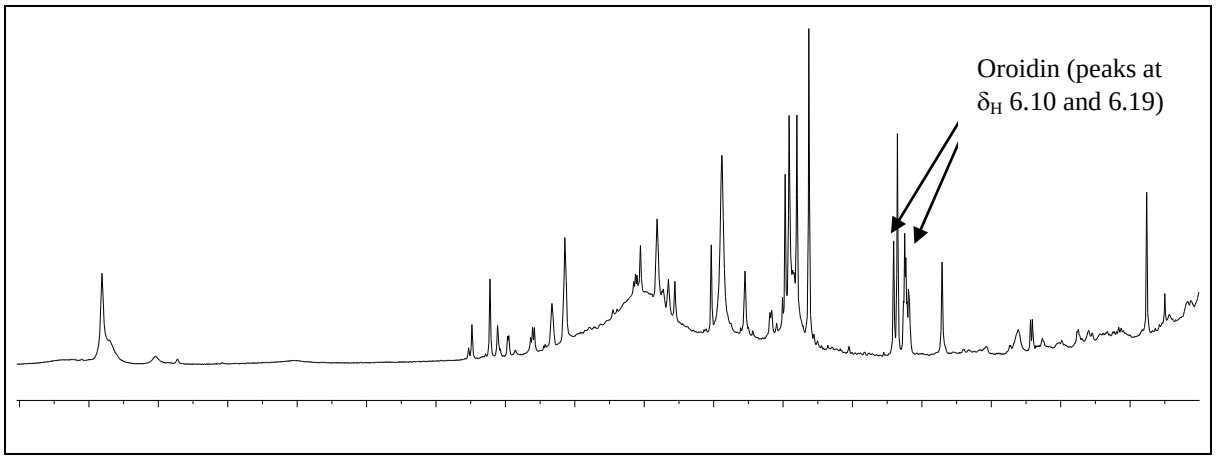


Figure S2. ^{1}H NMR spectrum of Sample 3 (Lizard Island, G330843)

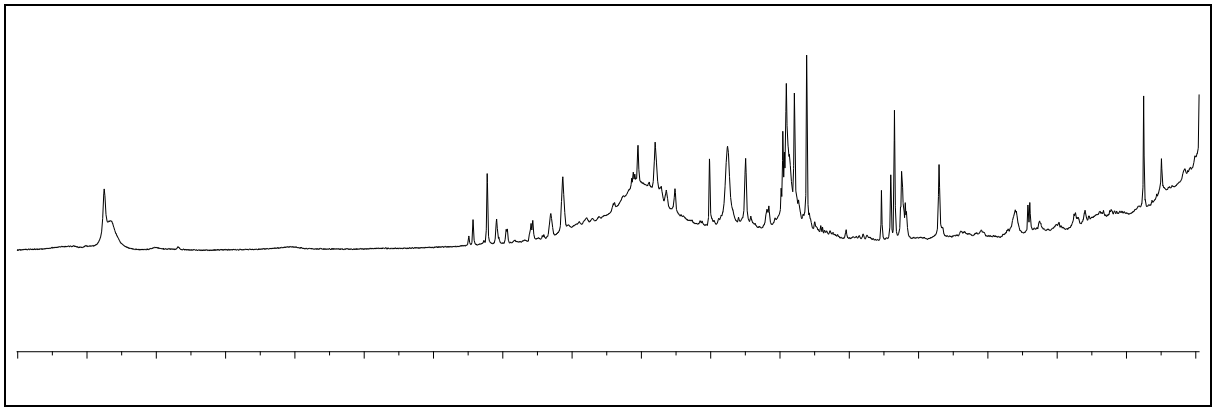


Figure S3. ^{1}H NMR spectrum of Sample 4 (Lizard Island, G330940)

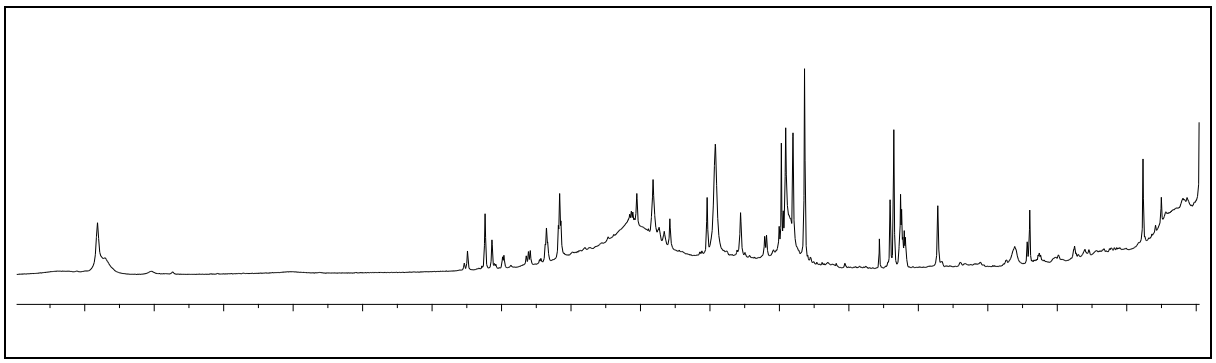


Figure S4. ^{1}H NMR spectrum of Sample 2 (Lizard Island, G330956)

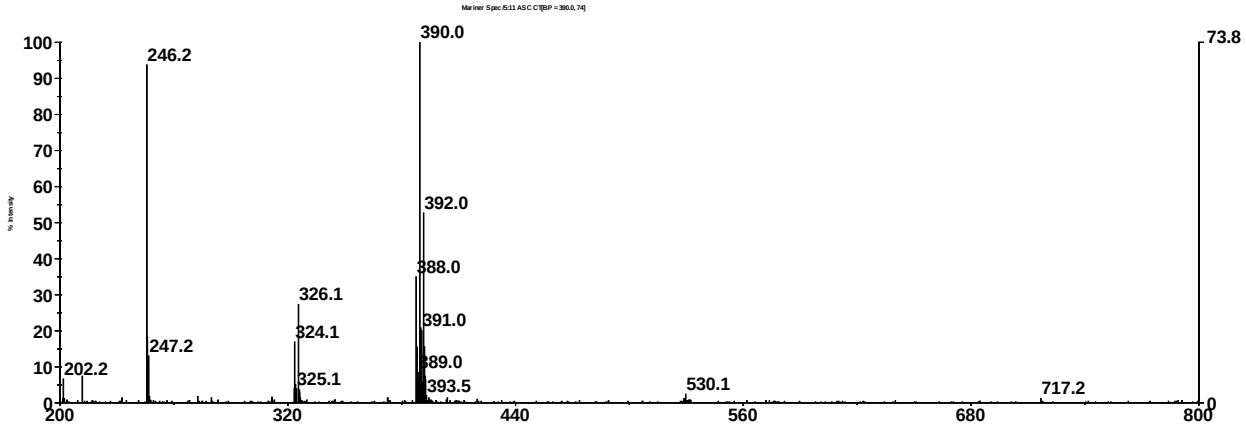


Figure S5. (+) ESI-MS spectrum of *S. flabellata* MeOH extract for Sample 1.

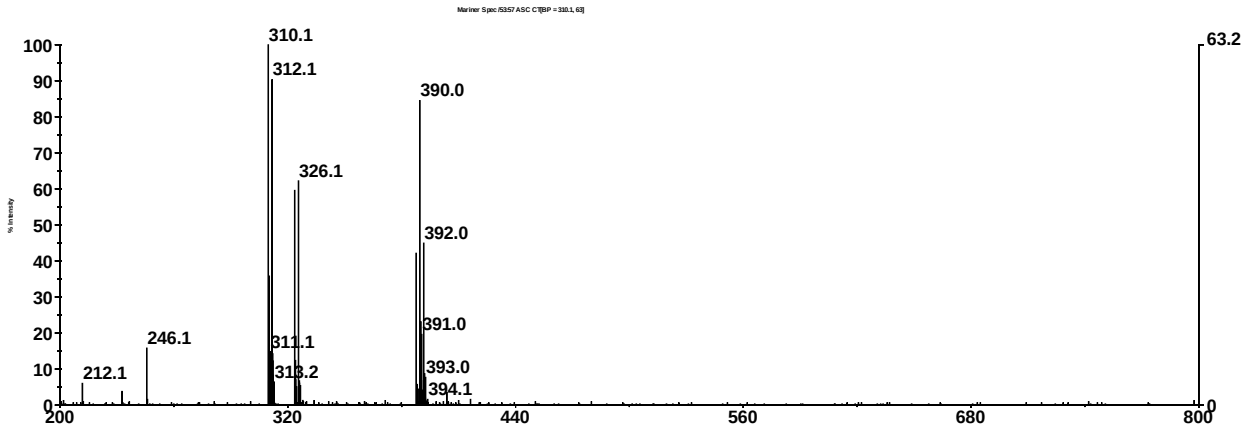


Figure S6. (+) ESI-MS spectrum of *S. flabellata* MeOH extract for Sample 2.

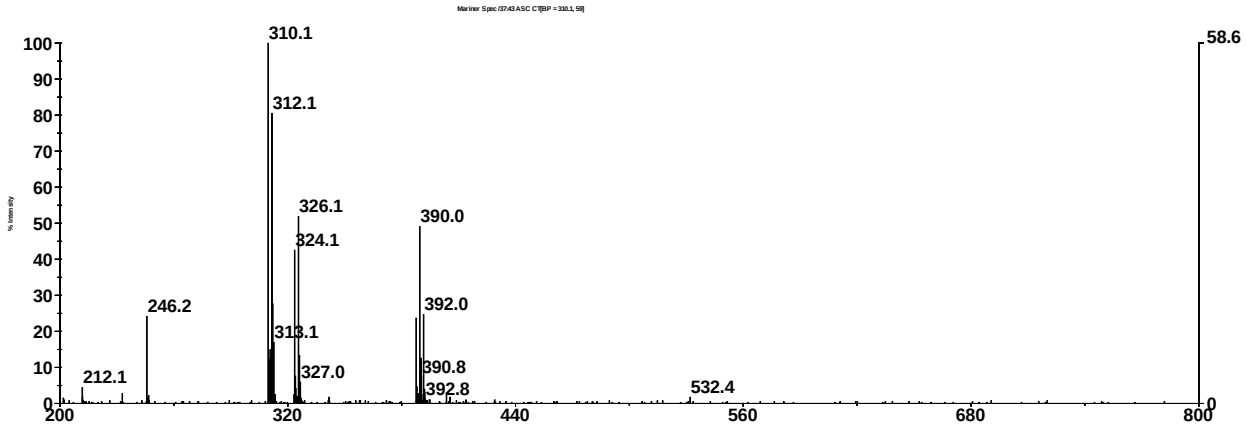


Figure S7. (+) ESI-MS spectrum of *S. flabellata* MeOH extract for Sample 3.

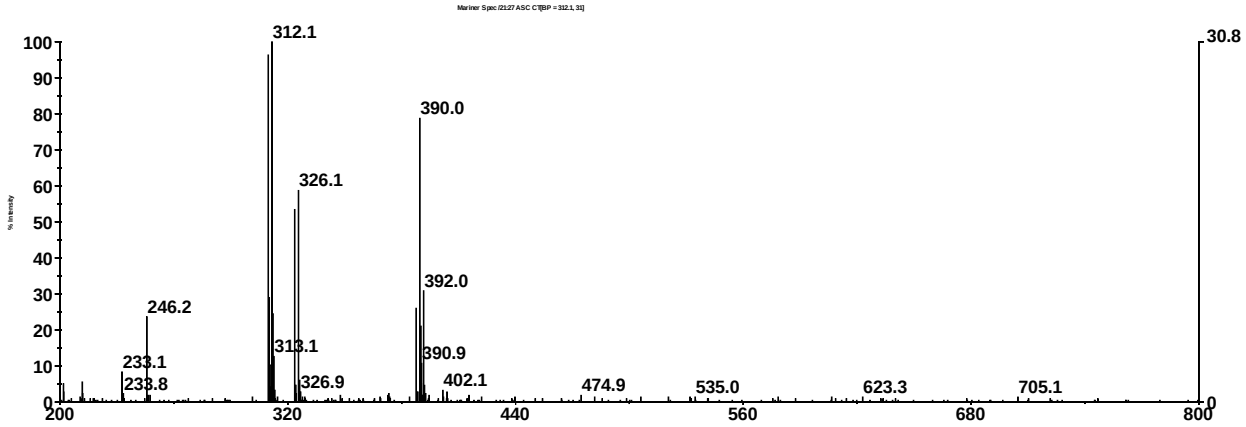


Figure S8. (+) ESI-MS spectrum of *S. flabellata* MeOH extract for Sample 4.

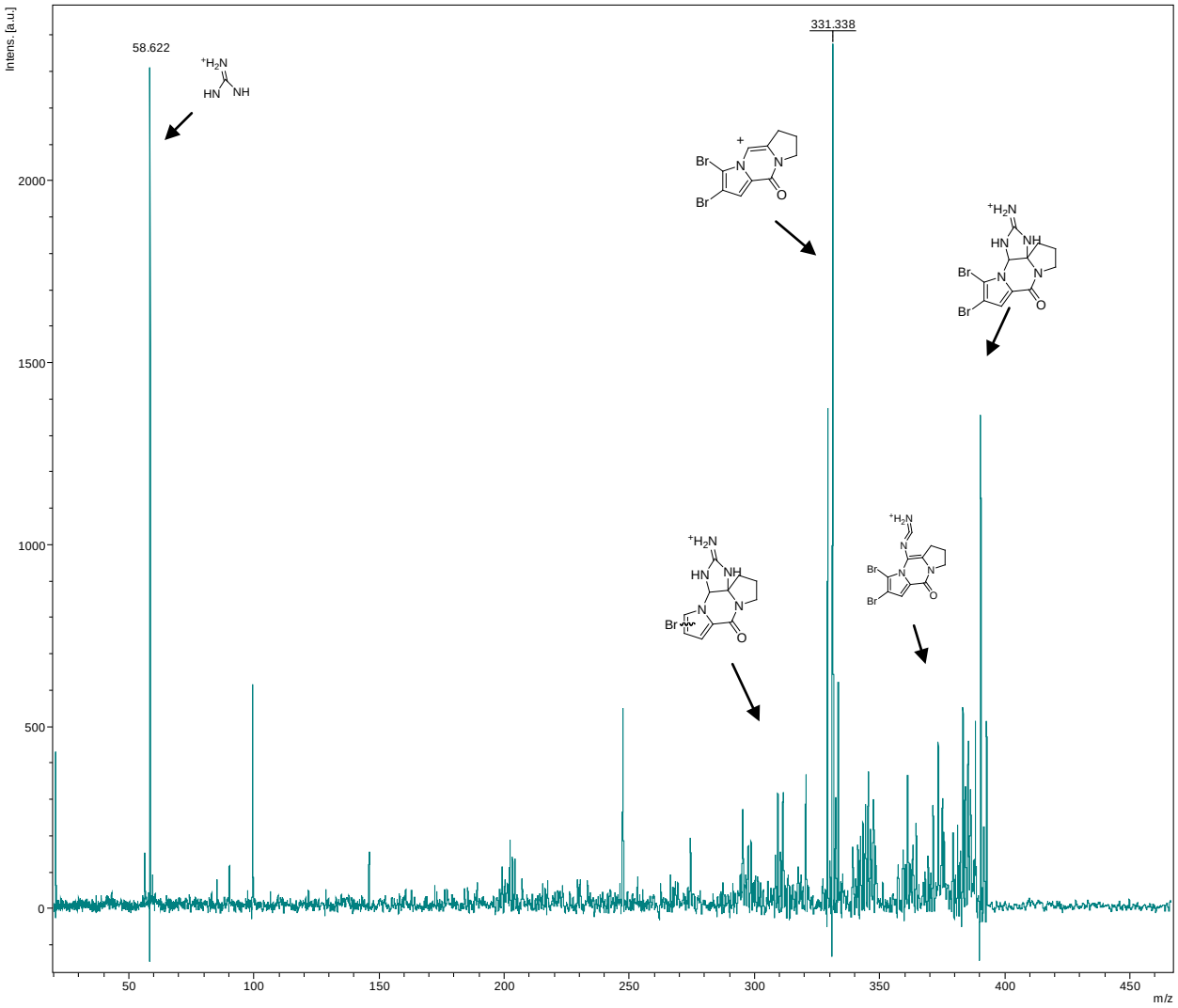


Figure S9. MS-MS fragmentation spectra for dibromophakellin obtained directly off 20µm *S. flabellata* tissue (*m/z* 390).

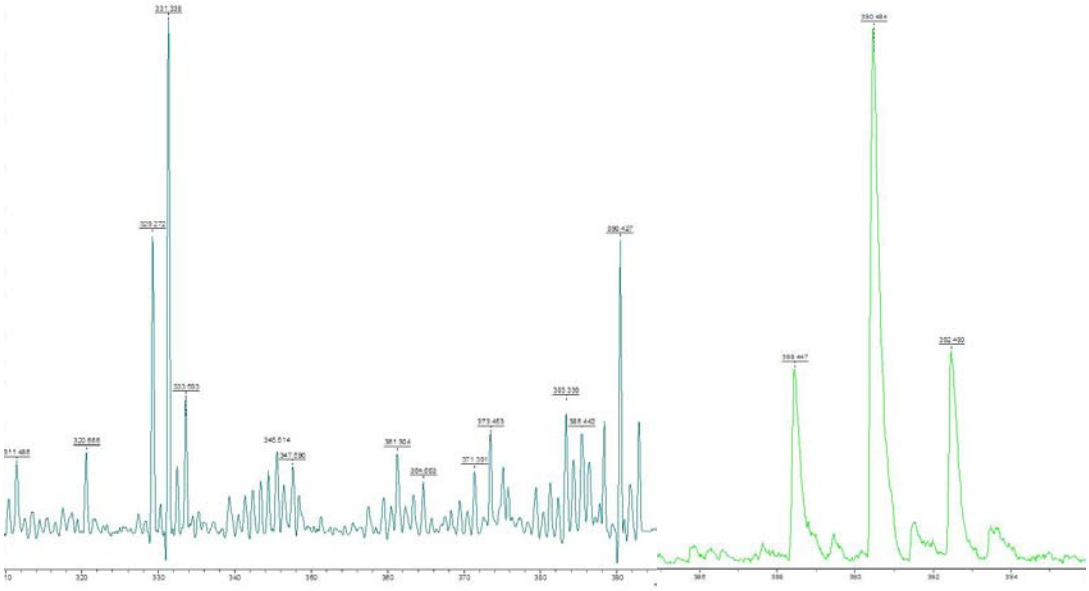


Figure S10. Expanded MS-MS fragmentation spectra for dibromophakellin obtained directly off 20µm *S. flabellata* tissue (*m/z* 390) showing major fragment ion peaks.

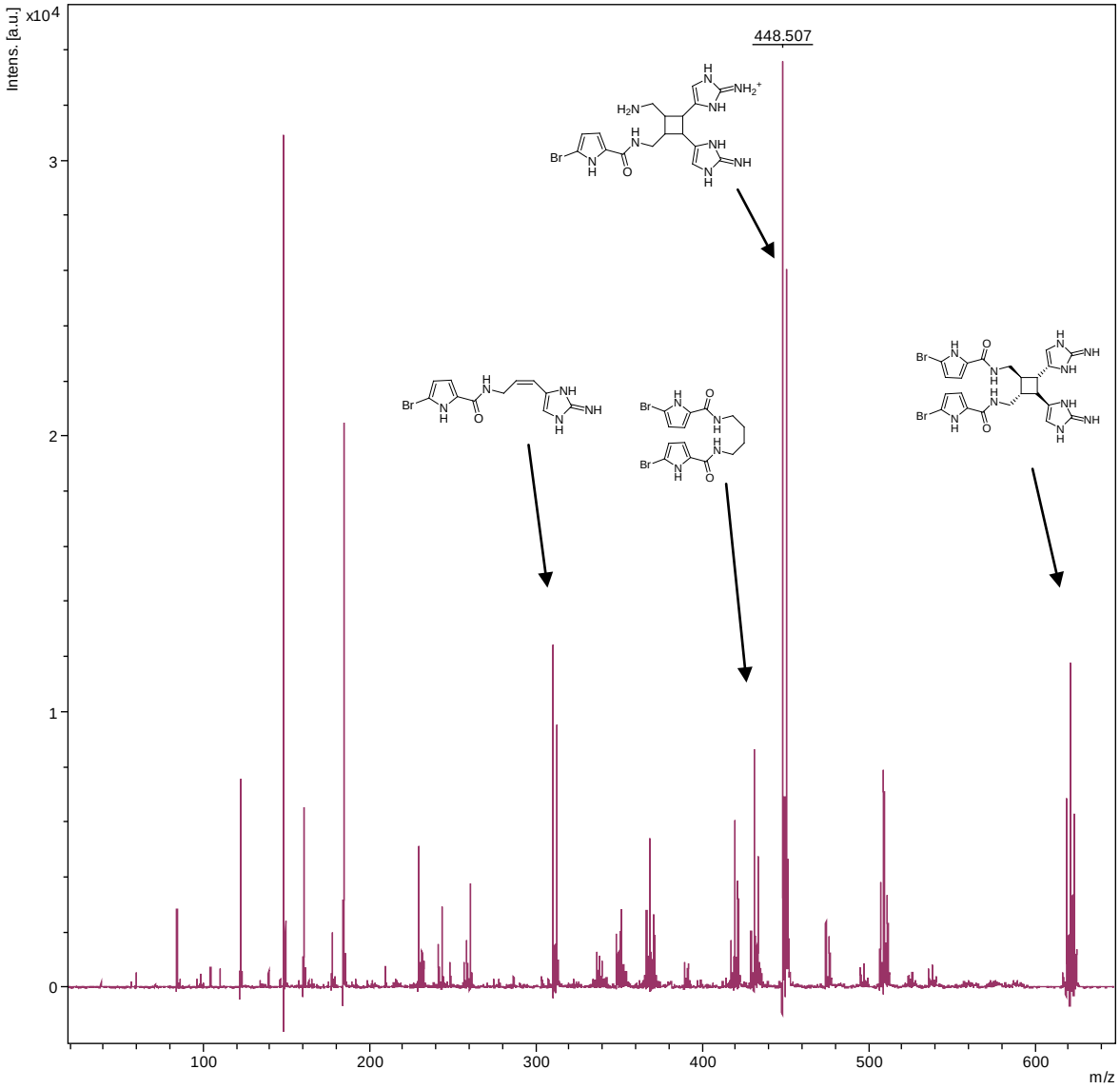


Figure S11. Full MS-MS fragmentation spectra for sceptrin obtained directly off 20µm *S. flabellata* tissue (*m/z* 621).

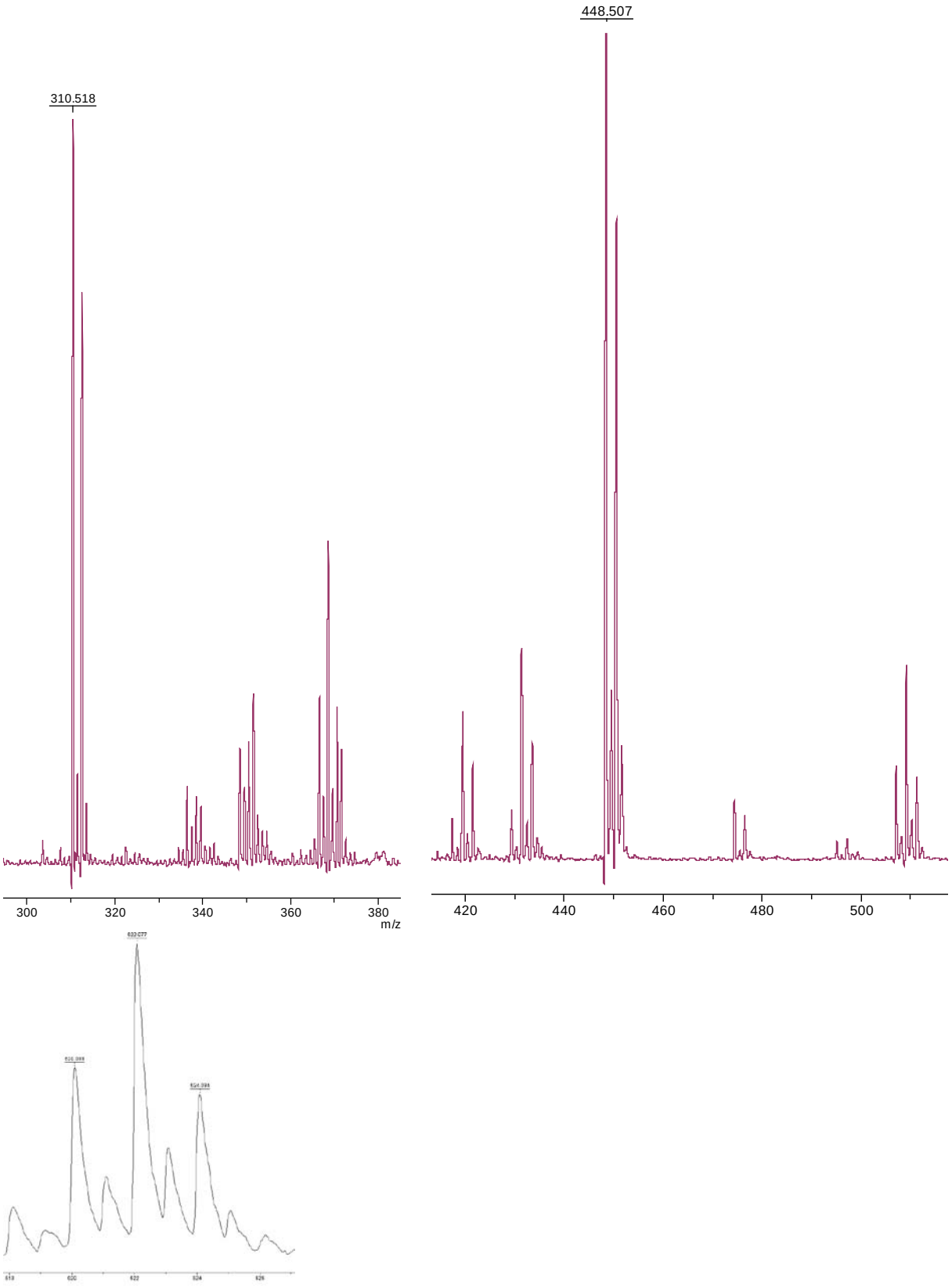


Figure S12. Expanded MS-MS fragmentation spectra for sceptrin obtained directly off 20µm *S. flabellata* tissue (*m/z* 621) showing major fragment ion peaks.

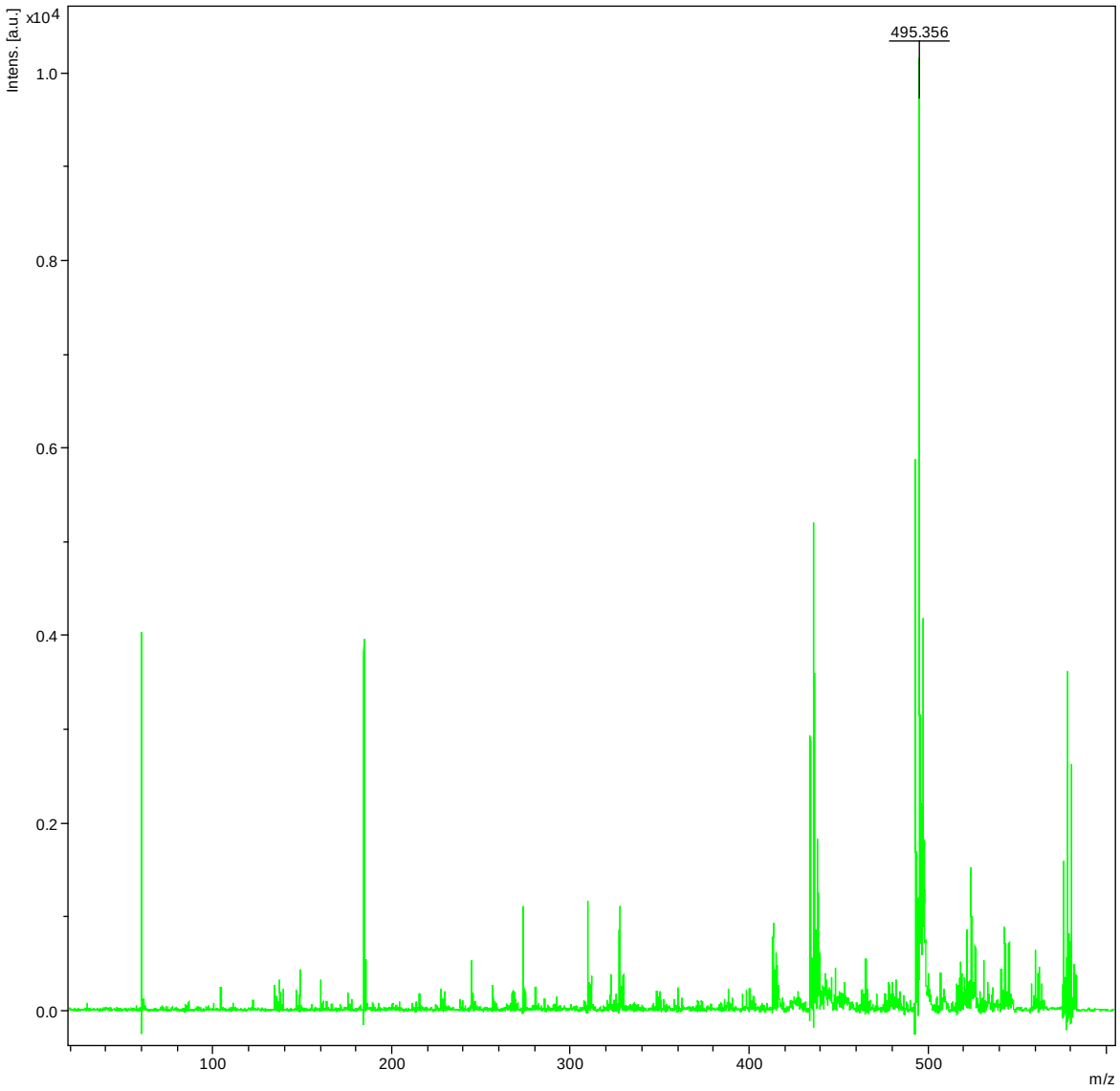


Figure S13. MS-MS fragmentation spectra for dibromopalau'amine obtained directly off 20µm *S. flabellata* tissue (*m/z* 578). MS/MS reported for palau'amine (R.B. Kinnel, H.-P. Gehrken, R. Swali, G. Skoropowski, P. J. Scheuer *J. Org. Chem.*, 1998, **63**, 3281-3286.): *m/z* **420, 402, 361, 337, 278**, 229, 94, 60. The peaks highlighted in bold are directly equivalent to 576/578/580, 558/560/562, 523,525,527, 493/495/497, 434/436/438 in dibromopalau'amine.

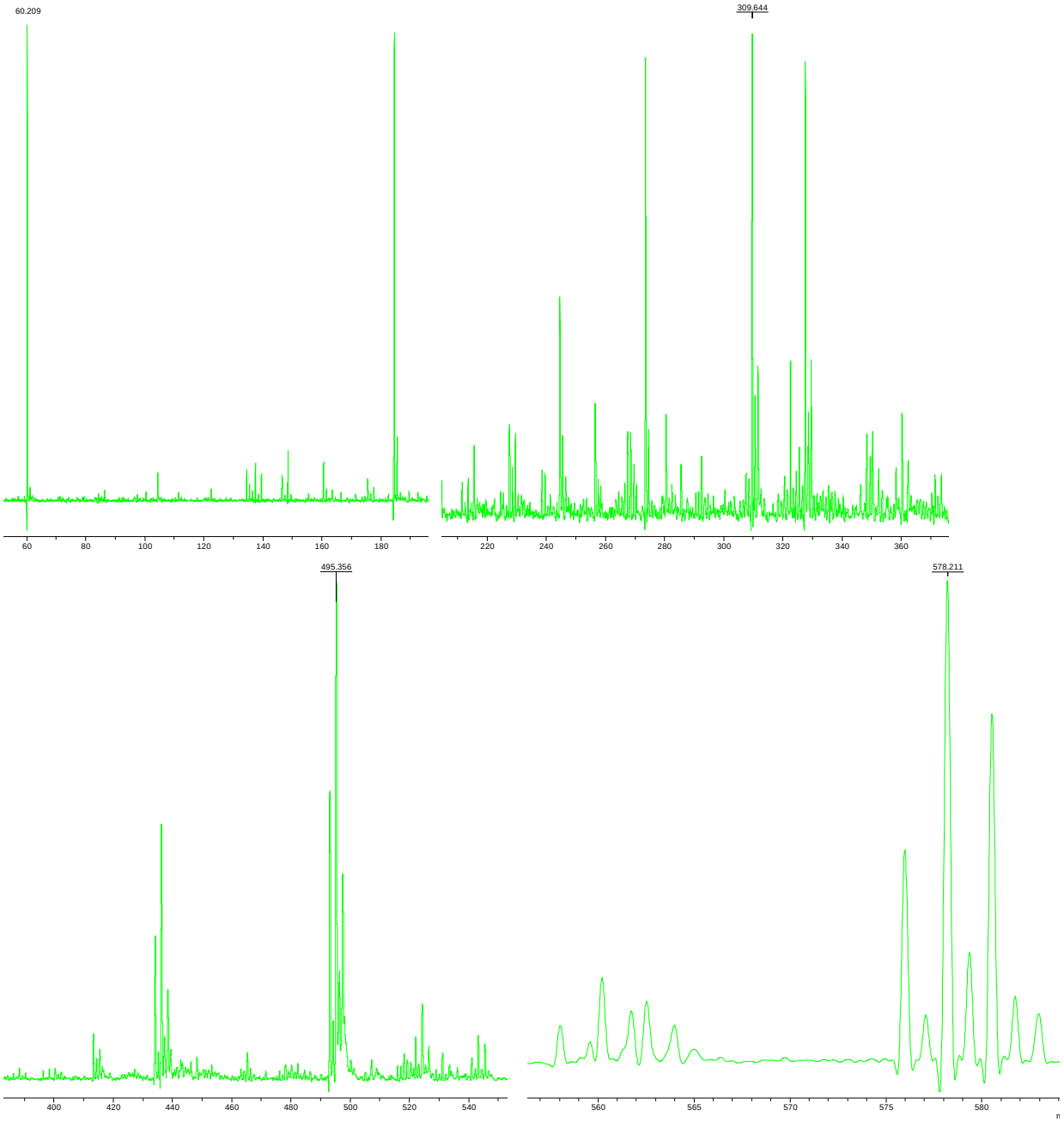


Figure S14. Expanded MS-MS fragmentation spectra for dibromopalau'amine obtained directly off 20µm *S. flabellata* tissue (*m/z* 578) showing major fragment ion peaks.

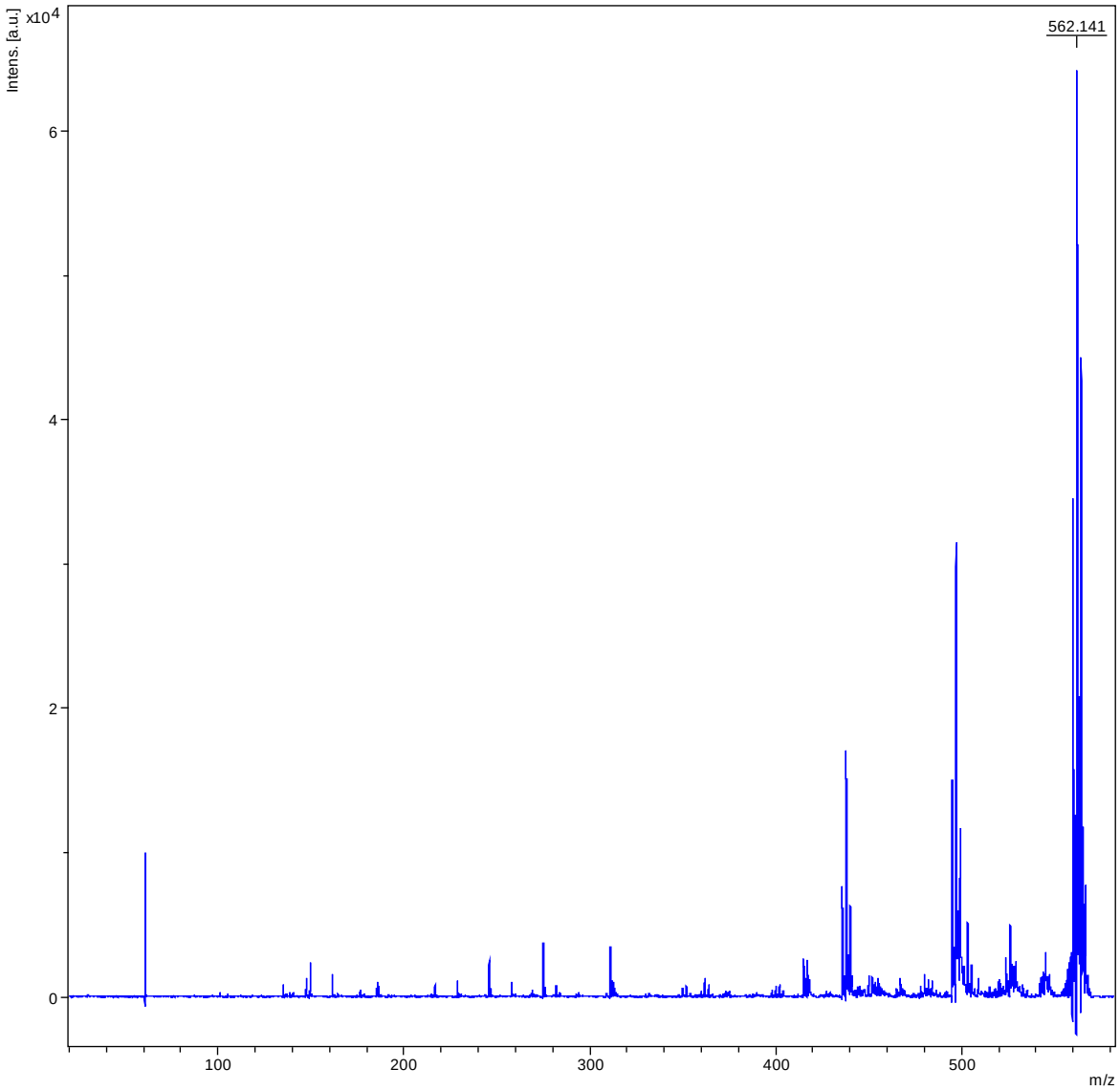


Figure S15. MS-MS fragmentation spectra for a possible deoxygenated dibromopalau'amine analogue obtained directly off 20µm *S. flabellata* tissue (*m/z* 562). The major fragmentation pattern for this compound is similar to that observed for dibromopalau'amine suggesting a similar structure.

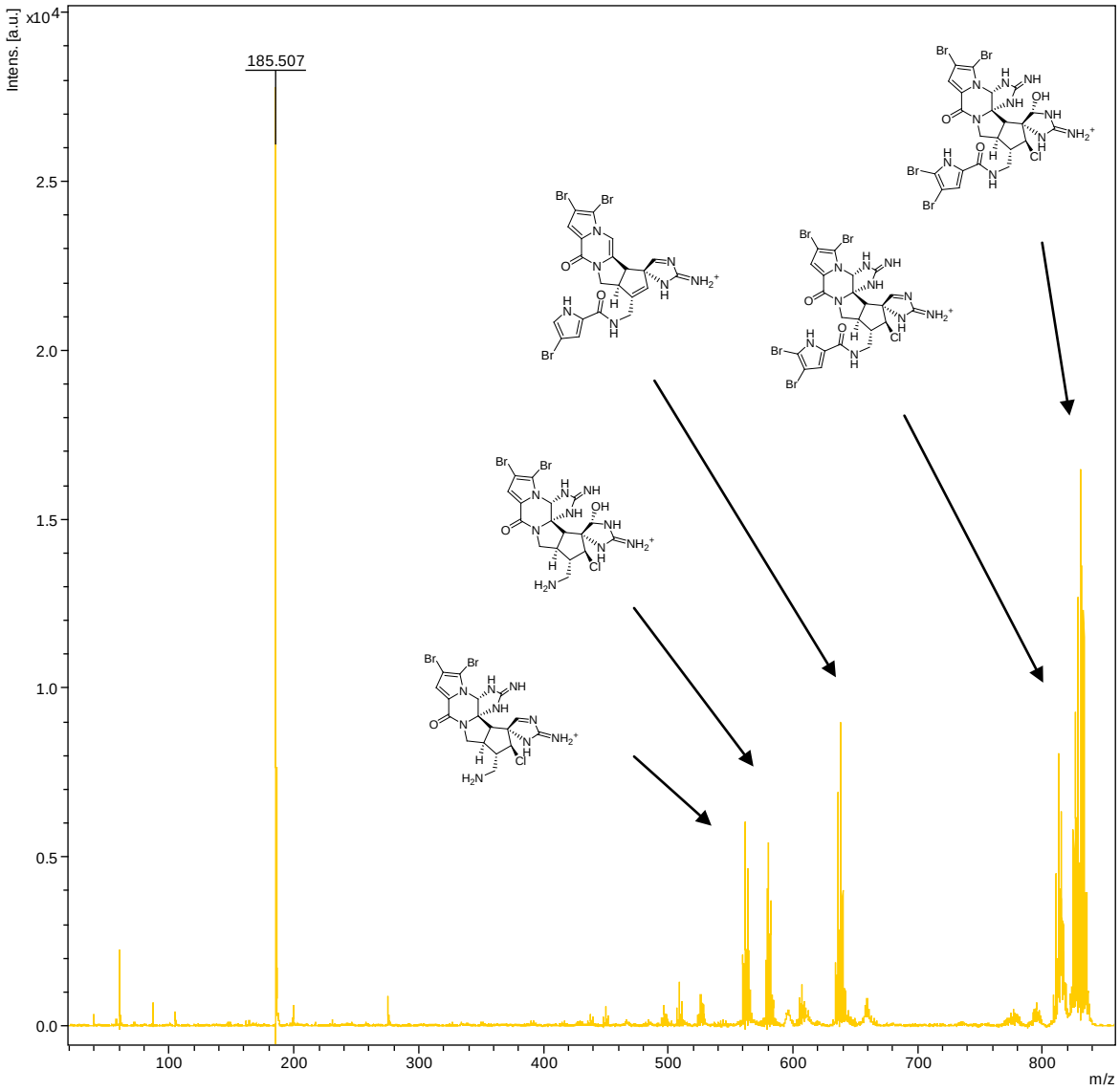
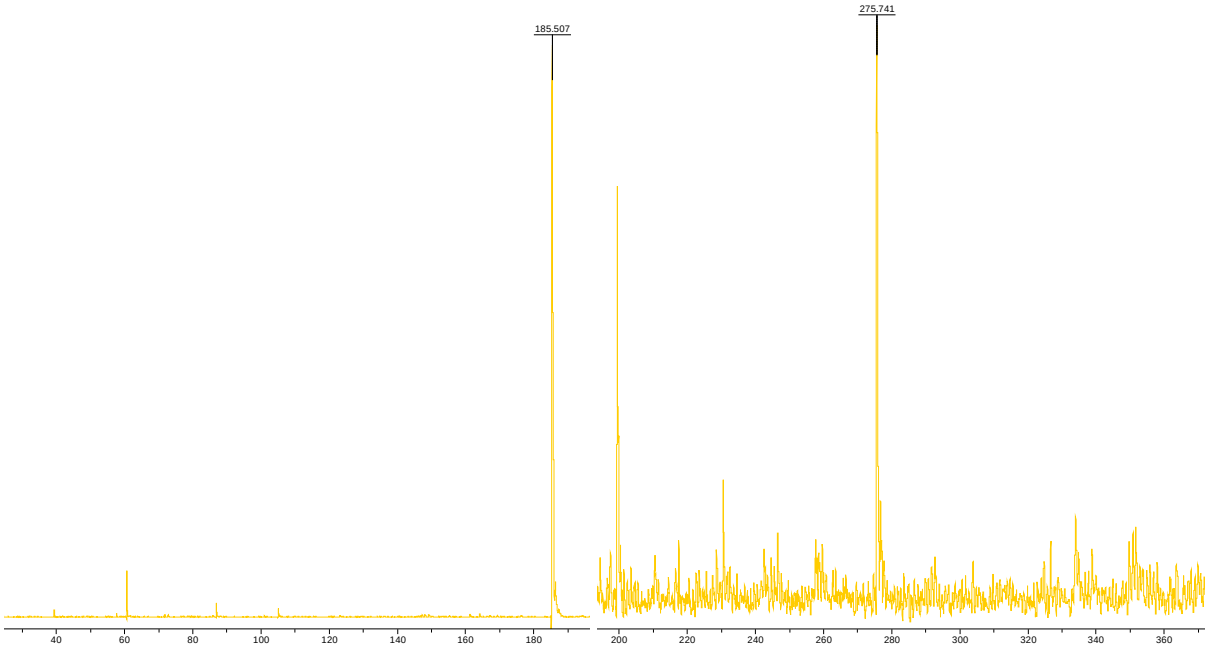


Figure S16. MS-MS fragmentation spectra for konbu'acidin B obtained directly off 20µm *S. flabellata* sections (*m/z* 825-835).



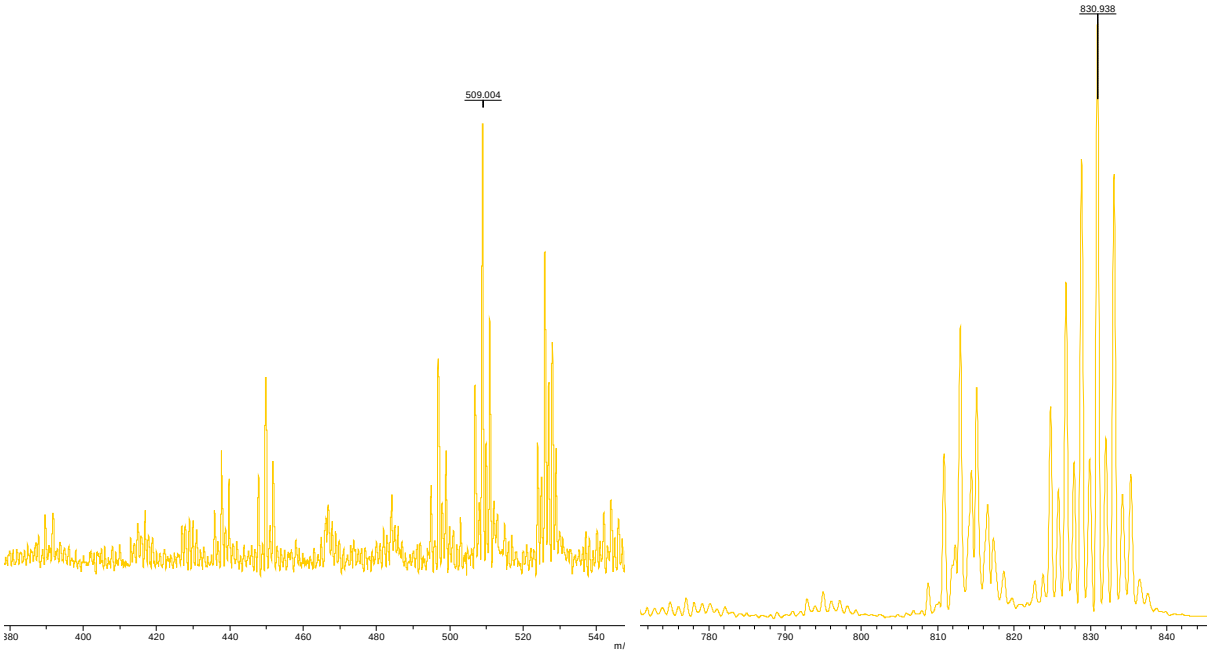


Figure S17. Expanded MS-MS fragmentation spectra for konbu'acidin B obtained directly off 20µm *S. flabellata* sections (*m/z* 825-835) showing major fragment ion peaks.

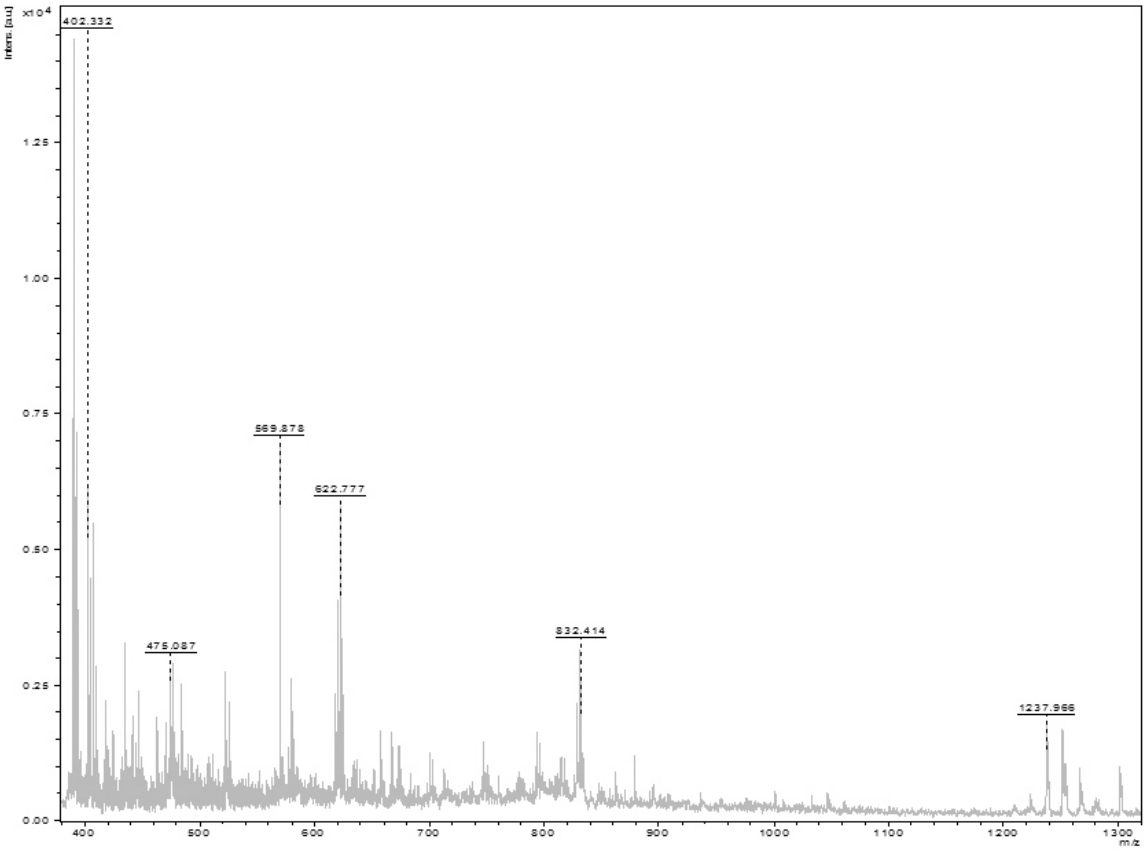


Figure S18. MALDI-MS spectrum of EtOH spot extract for *S. flabellata* Sample 1.

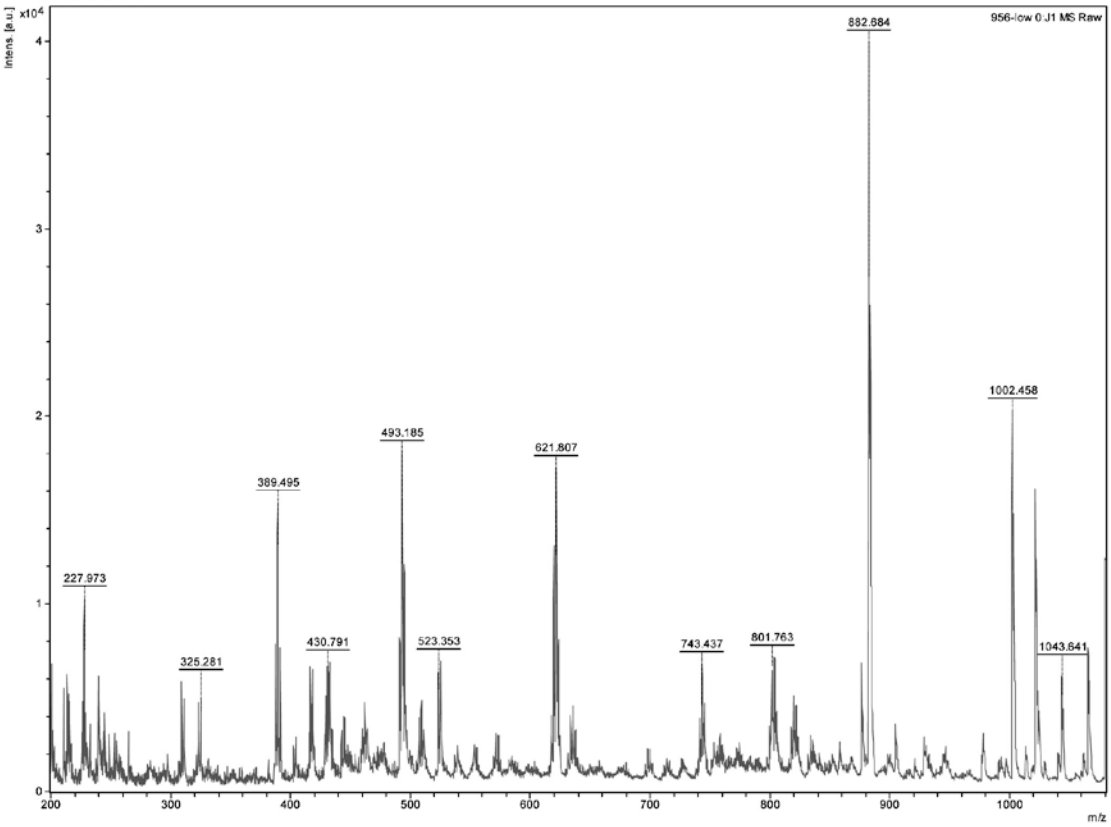


Figure S19. MALDI-MS spectrum of EtOH spot extract for *S. flabellata* Sample 2.

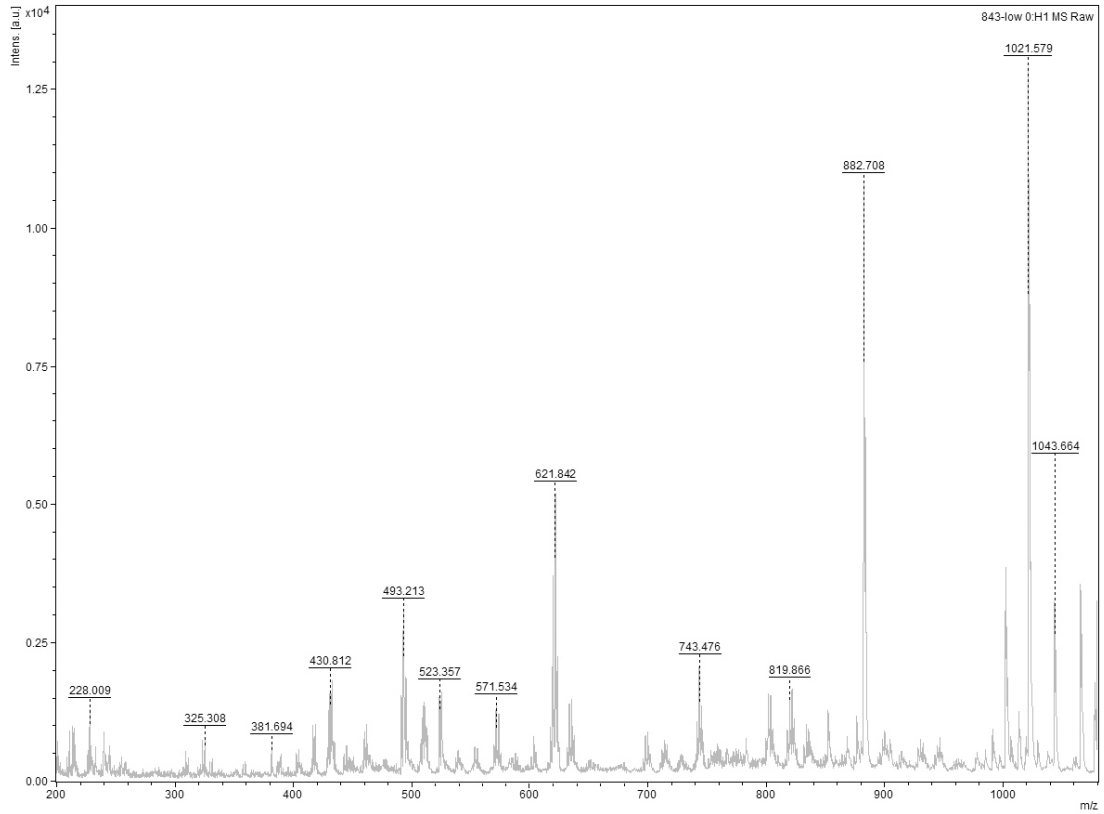


Figure S20. MALDI-MS spectrum of EtOH spot extract for *S. flabellata* Sample 3.

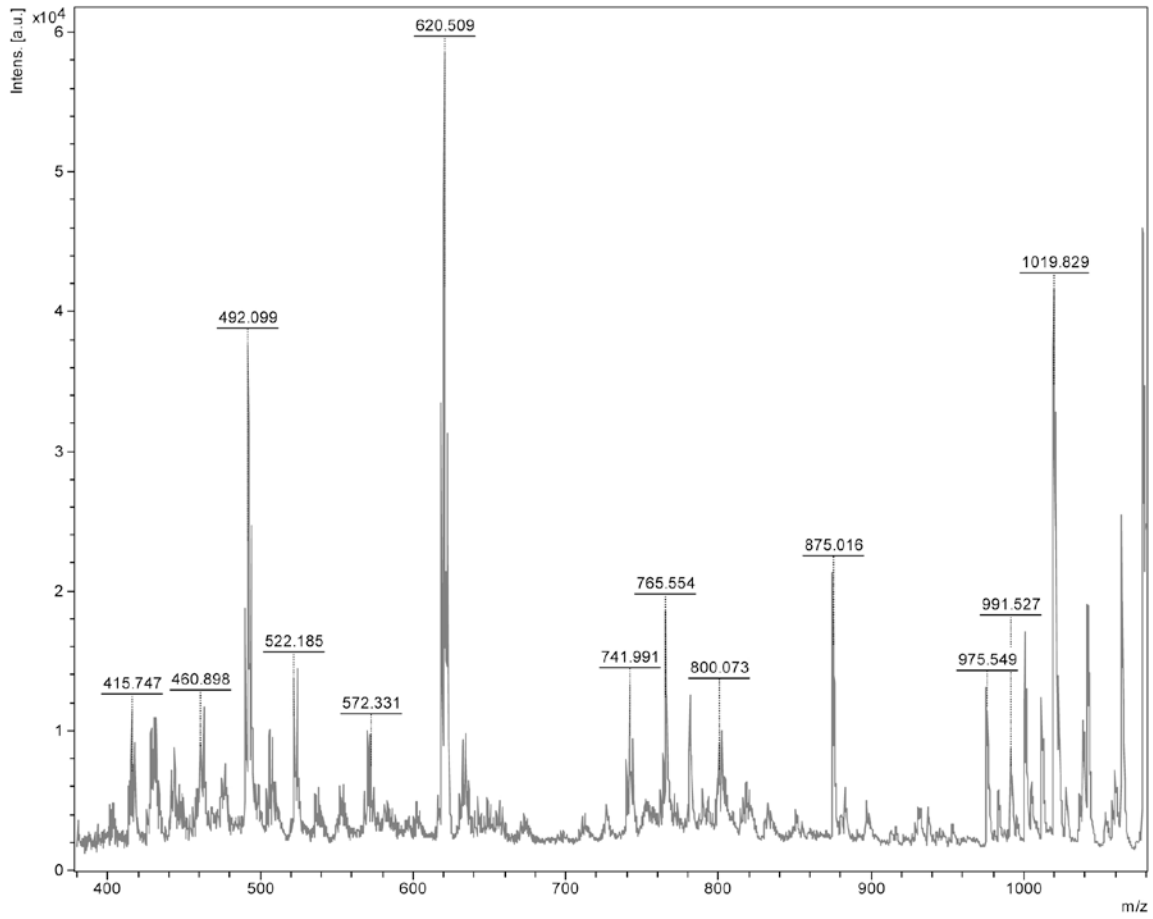


Figure S21. MALDI-MS spectrum of EtOH spot extract for *S. flabellata* Sample 4.

Table S1. Comparison of presence (+) or absence (-) of B-P-2-AIs detected in four *S. flabellata* specimens by MALDI-Imaging analysis.

Compound Number	Compound	*m/z* peak	**Sample 1** Heron Island G329565	**Sample 2** Lizard Island G330956	**Sample 3** Lizard Island G330843	**Sample 4** Lizard Island G330940
4	Dibromophakellin	388 / 390 / 392	+	+	-	-
	Mono-brominated compound	414 / 416	+	+	+	+
	Mono-brominated compound	474 / 476	-	-	+	+
	Di-brominated compound	520 / 522 / 524	-	+	+	+
	Dibromopalau'amine analogue	560 / 562 / 564	+	-	-	-
5	Dibromopalau'amine	576 / 578 / 580	+	-	-	-
6	Sceptrin	619 / 621 / 623	+	+	+	+
	Tri-brominated compound	695 / 697 / 699 / 701	+	-	-	-
	Di-brominated compound	741 / 743 / 745	+	-	-	-
	Konbu'acidin B	825 / 827 / 829 / 831 / 833 / 835	+	-	-	-