

**Table S2.** Product ion assignments from the fragmentation of the unlabeled and <sup>15</sup>N-labeled protonated anabaenolysin A. Accurate mass measurements were made with LTQ Orbitrap (ThermoFisher Scientific) using nanospray infusion of the purified 1 and both collision induced dissociation (CID) and higher energy collisional dissociation (HCD) to produce product ions.

Ion trap measurement		Number of N	Accurate mass measurement			Assigned ion structure without H <sup>+</sup>
Ion (m/z) <sup>a</sup> <sup>14</sup> N	<sup>15</sup> N		Experimental mass	Calculated mass	Error (ppm)	
559	563	4	559,27600	559,27623	-0,42	M
542	545	3				M-NH <sub>3</sub>
541	545	4	541,26428	541,26567	-2,57	M-H <sub>2</sub> O
531	535	4	531,28009	531,28132	-2,32	M-CO
524	527	3				M-(H <sub>2</sub> O+NH <sub>3</sub> )
514	517	3				M-(CO+NH <sub>3</sub> )
513	517	4	513,26959	513,27076	-2,27	M-(CO+H <sub>2</sub> O)
497	499	2				M-(CO+2NH <sub>3</sub> )
496	499	3				M-(CO+H <sub>2</sub> O+NH <sub>3</sub> )
502	505	3				M-Gly
485	487	2	485,22717	485,22822	-2,17	M-(Gly+NH <sub>3</sub> )
467	469	2				M-(Gly+H <sub>2</sub> O+NH <sub>3</sub> )
465	469	4	465,19702	465,19798	-2,07	M-C <sub>7</sub> H <sub>10</sub>
457	459	2	457,23315	457,23331	-0,35	M-(Gly+CO+NH <sub>3</sub> )
439	441	2				M-(Gly+CO+H <sub>2</sub> O+NH <sub>3</sub> )
417	419	2	417,23834	417,23839	-0,13	M-(Gly-Gly+CO)
411	415	4	411,15030	411,15103	-1,79	M-C <sub>11</sub> H <sub>16</sub>
397	401	4	397,13531	397,13538	-0,19	M-C <sub>12</sub> H <sub>18</sub>
383	387	4				M-(C <sub>11</sub> H <sub>16</sub> +CO)
369	373	4	369,14041	369,14047	-0,16	M-(C <sub>12</sub> H <sub>18</sub> +CO)
357	359	2				M-(AOFHA+CO+NH <sub>3</sub> )
357	361	4				M-C <sub>15</sub> H <sub>22</sub>
340	343	3				M-(C <sub>12</sub> H <sub>18</sub> +CO+29)
312			312,11896	312,11901	-0,15	M-(C <sub>12</sub> H <sub>18</sub> +Gly+CO)
300	301	1				M-(Gly-AOFHA+CO+NH <sub>3</sub> )
300	303	3				M-(C <sub>15</sub> H <sub>22</sub> +Gly)
289	293	4				M-(AHOPA+NH <sub>3</sub> )
272	275	3	272,08771	272,08771	0,01	M-AHOPA
270	271	1				AHOPA-(2H <sub>2</sub> O)
260	261	1	260,20087	260,20089	-0,07	M-(Gly-Gly-AOFHA+CO)
253	253	0	253,15871	253,15869	0,08	AHOPA-(2H <sub>2</sub> O+NH <sub>3</sub> )
244	247	3	244,09285	244,09279	0,23	M-(AHOPA+CO)
242	243	1				M-(Gly-Gly-AOFHA+CO+H <sub>2</sub> O)
230	231	1	230,19006	230,19033	-1,15	C <sub>16</sub> H <sub>23</sub> N from AHOPA
225	225	0	225,16383	225,16378	0,24	AHOPA-(CO+2H <sub>2</sub> O+NH <sub>3</sub> )
215	217	2	215,06630	215,06624	0,26	M-(AHOPA-Gly)

<sup>a</sup> = In <sup>14</sup>N column are product ions from unlabelled Abl-A and in <sup>15</sup>N column are product ions from <sup>15</sup>N labelled Abl-A.