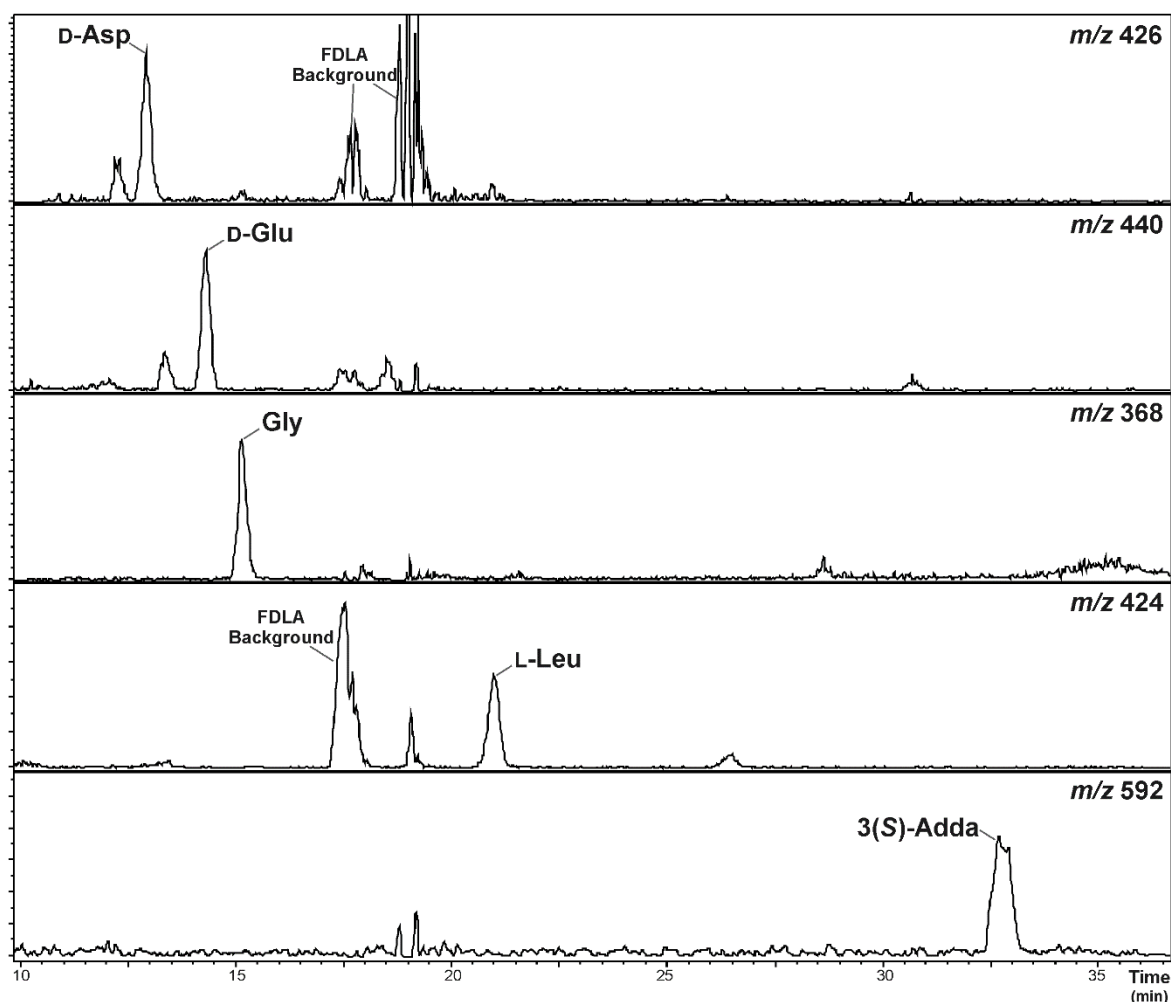


## Supplementary Information

**Table S1.** High resolution mass spectrometry (HRMS) analysis of the Antarctic microcystins and mass deviations from the proposed structures.

Microcystin	Measured $m/z$ <sup>a</sup>	Molecular Formula	Calculated $m/z$	Error (ppm)
[Gly <sup>1</sup> , Asp <sup>3</sup> , Dhb <sup>7</sup> ] MC-LR (3)	967.5285	C <sub>47</sub> H <sub>71</sub> N <sub>10</sub> O <sub>12</sub>	967.5247	+3.86
[Gly <sup>1</sup> , Asp <sup>3</sup> , Dhb <sup>7</sup> ] MC-LHar (4)	981.5413	C <sub>48</sub> H <sub>73</sub> N <sub>10</sub> O <sub>12</sub>	967.5404	+0.87
[Gly <sup>1</sup> , Asp <sup>3</sup> , ADMAdda <sup>5</sup> , Dhb <sup>7</sup> ] MC-LR (5)	995.5206	C <sub>48</sub> H <sub>71</sub> N <sub>10</sub> O <sub>13</sub>	995.5197	-0.94
[Gly <sup>1</sup> , Asp <sup>3</sup> , ADMAdda <sup>5</sup> , Dhb <sup>7</sup> ] MC-LHar (6)	1009.5348	C <sub>49</sub> H <sub>73</sub> N <sub>10</sub> O <sub>13</sub>	1,009.5353	+0.47
[Gly <sup>1</sup> , Asp <sup>3</sup> , Dhb <sup>7</sup> ] MC-RR (7)	1010.5442	C <sub>47</sub> H <sub>72</sub> N <sub>13</sub> O <sub>12</sub>	1,010.5418	-2.44
[Gly <sup>1</sup> , Asp <sup>3</sup> , Dhb <sup>7</sup> ] MC-RHar (8)	1024.5569	C <sub>48</sub> H <sub>74</sub> N <sub>13</sub> O <sub>12</sub>	1,024.5574	+0.53
[Gly <sup>1</sup> , Asp <sup>3</sup> , ADMAdda <sup>5</sup> , Dhb <sup>7</sup> ] MC-RR (9)	1038.5405	C <sub>48</sub> H <sub>72</sub> N <sub>13</sub> O <sub>13</sub>	1,038.5367	-3.82
[Gly <sup>1</sup> , Asp <sup>3</sup> , ADMAdda <sup>5</sup> , Dhb <sup>7</sup> ] MC-RHar (10)	1052.5541	C <sub>49</sub> H <sub>74</sub> N <sub>13</sub> O <sub>13</sub>	1,052.5524	-1.60

<sup>a</sup> All HRMS measurements were made using the singularly-protonated molecular ion.



**Figure S1.** Advanced Marfey's amino acid analysis of the Antarctic-LR microcystin congeners; extracted ion chromatograms of hydrolysates derivatized with L-FDLA (1-fluoro-2,4-dinitrophenyl-5-leucine).

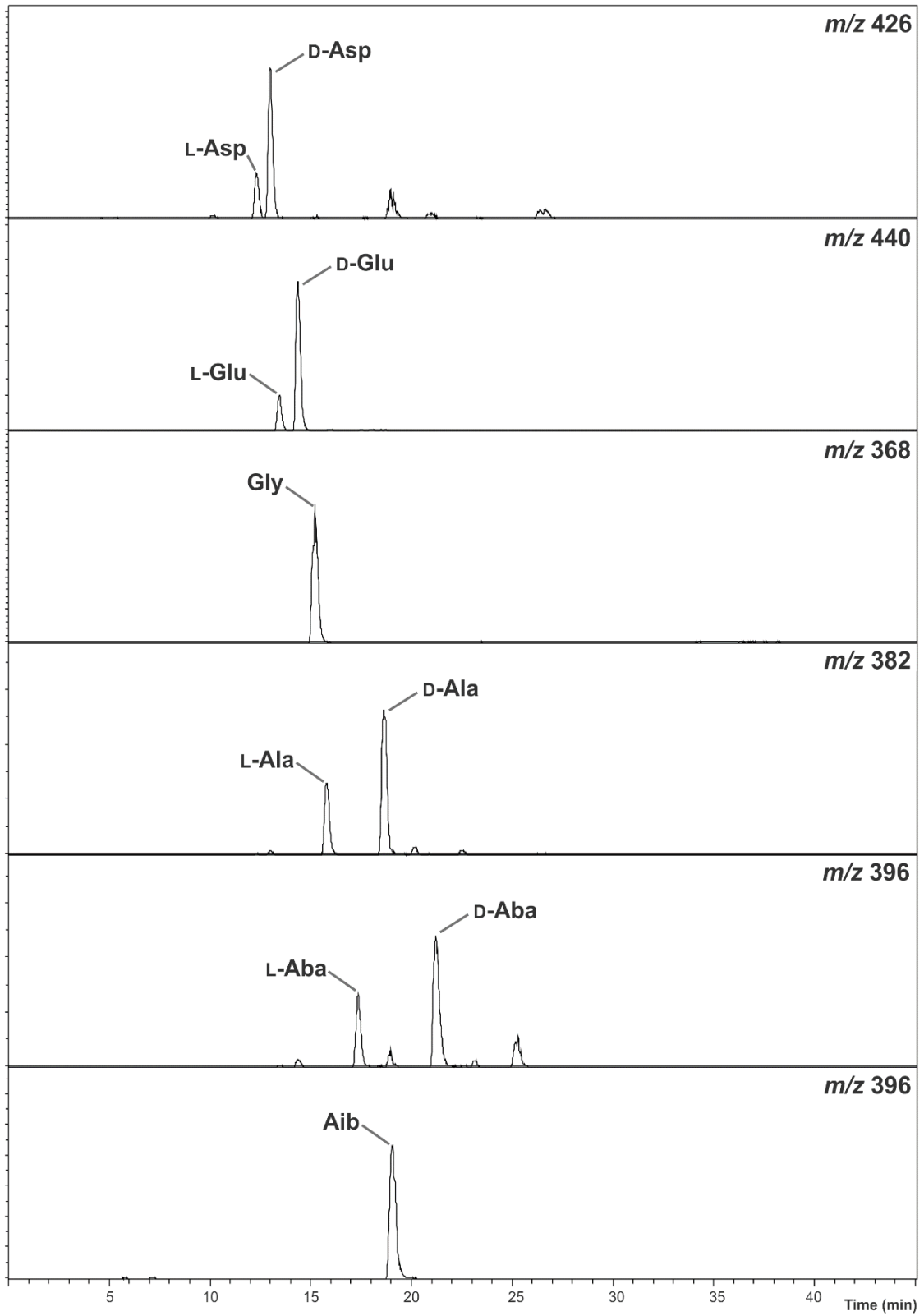
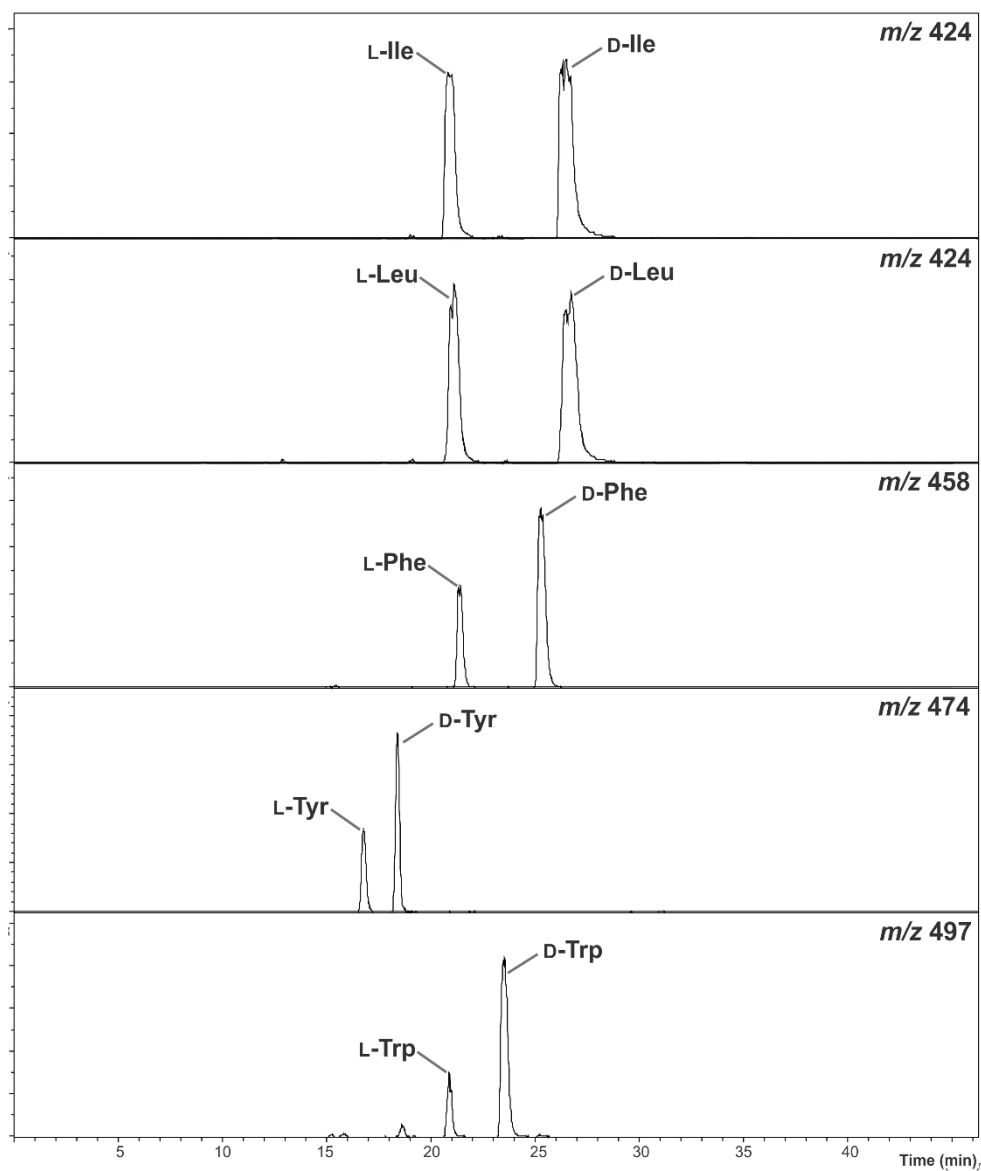
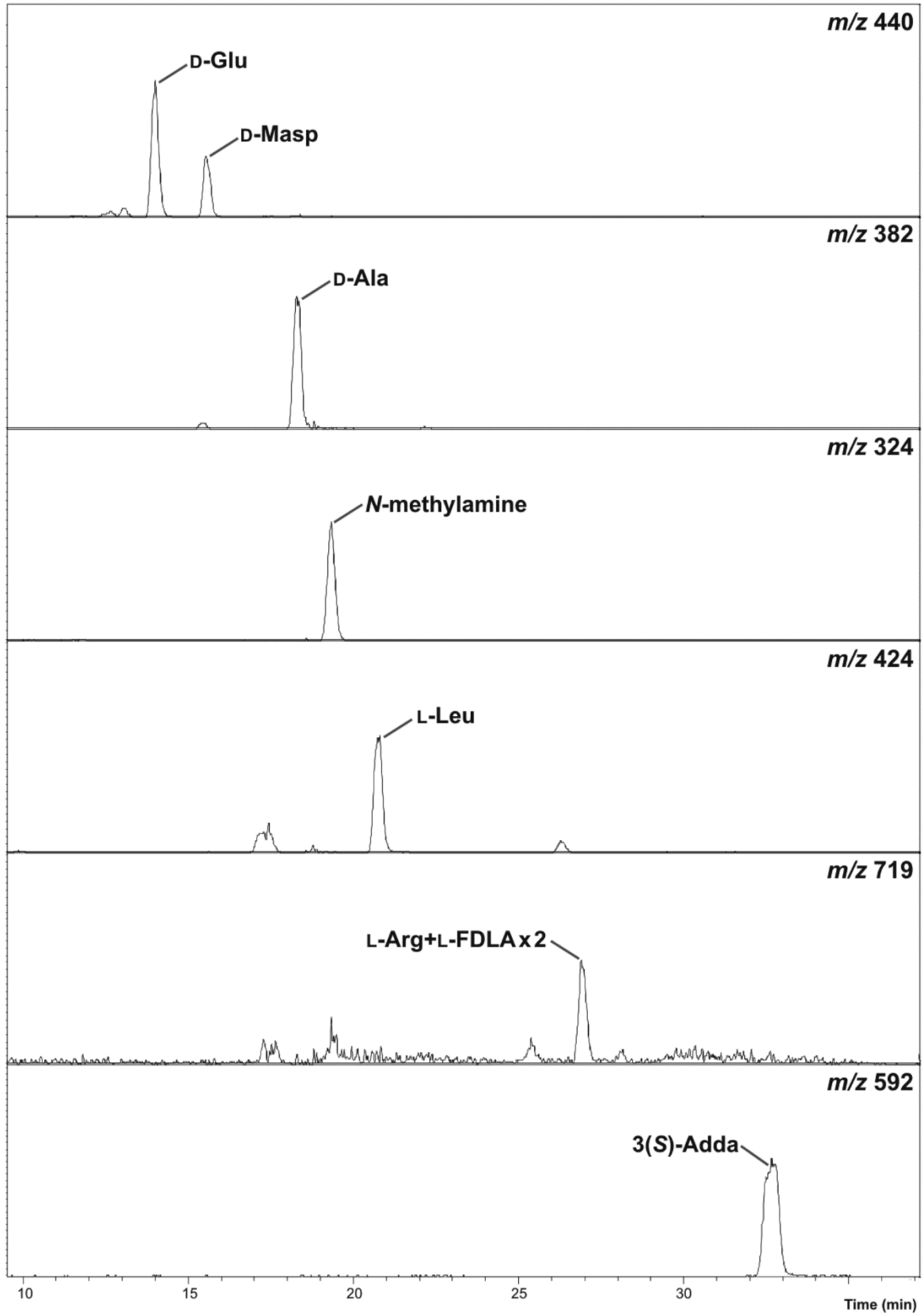


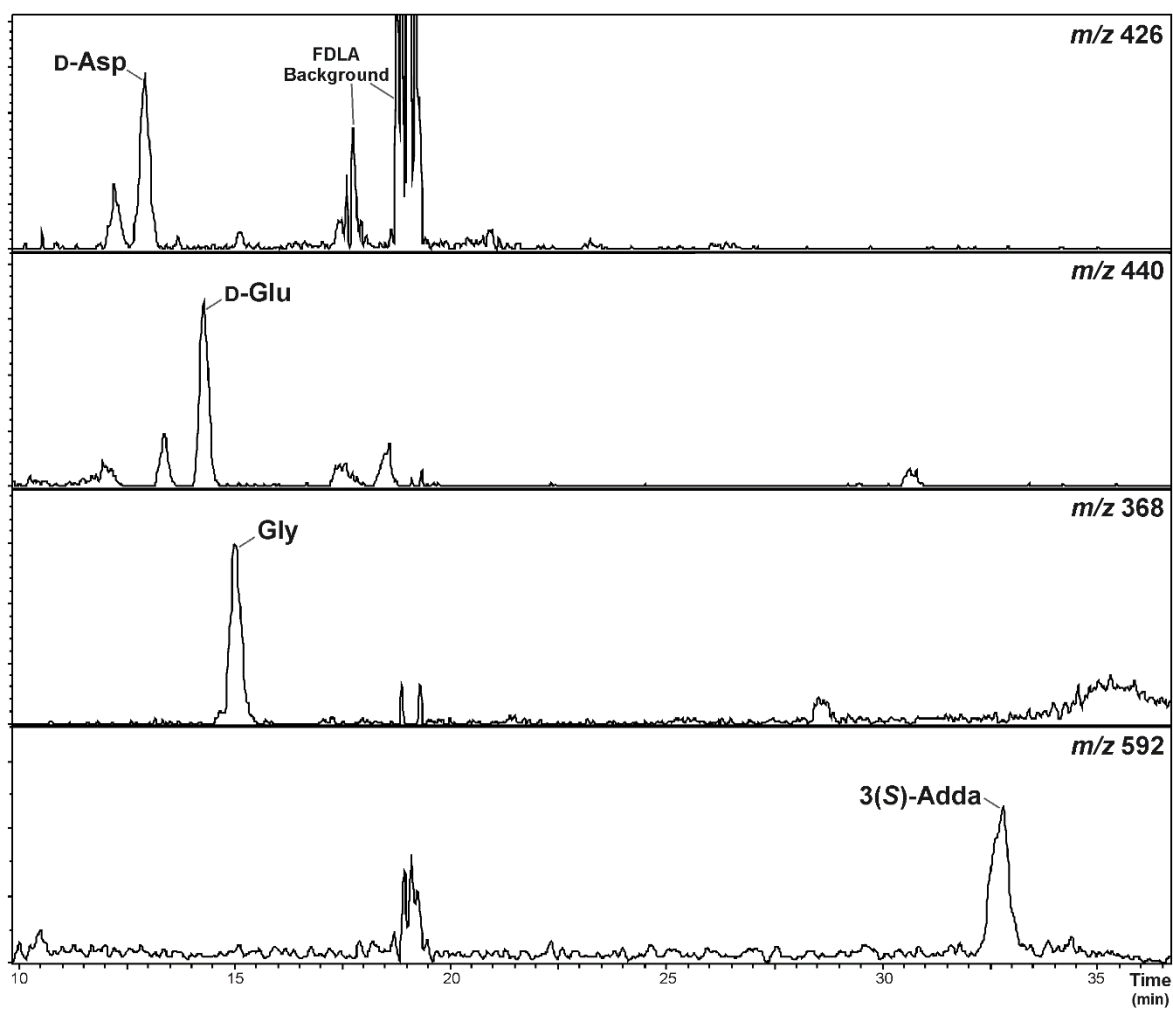
Figure S2. Cont.



**Figure S2.** Advanced Marfey's amino acid analysis of standard amino acids; extracted ion chromatograms of amino acids derivatized with DL-FDLA.



**Figure S3.** Advanced Marfey's amino acid analysis of MC-LR; extracted ion chromatograms of hydrolyzed MC-LR derivatized with L-FDLA.



**Figure S4.** Advanced Marfey's amino acid analysis of the Antarctic-RR microcystin congeners; extracted ion chromatograms of hydrolyzates derivatized with L-FDLA.