SUPPORTING INFORMATION

Stable Isotope labeling of Prodiginines and Serratamolides Produced by *Serratia marcescens* Directly on Agar and Simultaneous Visualization by Matrix-Assisted Laser Desorption/Ionization Imaging High-Resolution Mass Spectrometry

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Fig. S7. MALDI-imaging-HRMS of bacterial endophyte *S. marcescens* MSRBB2 grown on nutrient agar with a thin layer of agar supplemented with [methyl-D_3]-L-methionine (1 mg/mL). Optical image with assigned scan areas and comparison of labeled and unlabeled prodigiosin (**3**, $[M+H]^+$ ± 2 ppm).

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Fig. S47. HRMS spectra of 2-methyl-3-nonyl prodiginine with incorporated ^{15}N derived from $^{15}NH_4Cl$ from labeled nutrient agar (compound **7** $[M+H]^+$: *m/z* 381, $C_{24}H_{34}N_2{}^{15}NO$).

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Fig. S54. HRMS spectra of 2-methyl-3-nonyl prodiginine with incorporated [1-^{13}C]-L-proline from labeled nutrient agar (compound **7** $[M+H]^+$: *m/z* 381, $C_{23}{}^{13}CH_{34}N_3O$).

Fig. S55. HRMS spectra of 2-methyl-3-propyl prodiginine with incorporated ^{15}N-L-serine from labeled nutrient agar (compound **1** $[M+H]^+$: *m/z* 296, $C_{18}H_{22}N_3O$).

Fig. S56. HRMS spectra of 2-methyl-3-butyl prodiginine with incorporated ^{15}N-L-serine from labeled nutrient agar (compound **2** $[M+H]^+$: *m/z* 310, $C_{19}H_{24}N_3O$).

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Fig. S64. HRMS spectra of prodigiosin with incorporated methyl-D_3 group derived from 0.5 mg/mL [methyl-D_3]-L-methionine on nutrient agar (compound **3** $[M+H]^+$: *m/z* 327, $C_{20}H_{23}D_3N_3O$).

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Fig. S74. HRMS spectra of 2-methyl-3-propyl prodiginine with incorporated methyl-D_3 group derived from 1 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **1** $[M+H]^+$: *m/z* 299, $C_{18}H_{19}D_3N_3O$).

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Fig. S77. HRMS spectra of 2-methyl-3-hexyl prodiginine with incorporated methyl-D_3 group derived from 1 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **4** $[M+H]^+$: *m/z* 341, $C_{21}H_{25}D_3N_3O$).

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Fig. S80. HRMS spectra of 2-methyl-3-propyl prodiginine with incorporated ^{15}N derived from $^{15}NH_4Cl$ from labeled potato dextrose agar (compound **1** $[M+H]^+$: *m/z* 297, $C_{18}H_{22}N_2{}^{15}NO$).

Fig. S81. HRMS spectra of 2-methyl-3-butyl prodiginine with incorporated ^{15}N derived from $^{15}NH_4Cl$ from labeled potato dextrose agar (compound **2** $[M+H]^+$: *m/z* 311, $C_{19}H_{24}N_2{}^{15}NO$).

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Fig. S85. HRMS spectra of 2-methyl-3-propyl prodiginine with incorporated [1-^{13}C]-L-proline from labeled potato dextrose agar (compound **1** $[M+H]^+$: *m/z* 297, $C_{17}{}^{13}CH_{22}N_3O$).

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Fig. S90. HRMS spectra of 2-methyl-3-propyl prodiginine with incorporated ^{15}N-L-serine from labeled potato dextrose agar (compound **1** $[M+H]^+$: *m/z* 296, $C_{18}H_{22}N_3O$).

Fig. S91. HRMS spectra of 2-methyl-3-butyl prodiginine with incorporated ^{15}N-L-serine from labeled potato dextrose agar (compound **2** $[M+H]^+$: *m/z* 310, $C_{19}H_{24}N_3O$).

Fig. S92. HRMS spectra of prodigiosin with incorporated ^{15}N-L-serine from labeled potato dextrose agar (compound **3** $[M+H]^+$: *m/z* 324, $C_{20}H_{26}N_3O$).

Fig. S93. HRMS spectra of 2-methyl-3-hexyl prodiginine with incorporated ^{15}N-L-serine from labeled potato dextrose agar (compound **4** $[M+H]^+$: *m/z* 338, $C_{21}H_{28}N_3O$).

Fig. S94. HRMS spectra of 2-methyl-3-heptyl prodiginine with incorporated ^{15}N-L-serine from labeled potato dextrose agar (compound **5** $[M+H]^+$: *m/z* 352, $C_{22}H_{30}N_3O$).

Fig. S95. HRMS spectra of 2-methyl-3-propyl prodiginine with incorporated methyl-D_3 group derived from 0.5 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **1** $[M+H]^+$: *m/z* 299, $C_{18}H_{19}D_3N_3O$).

Fig. S96. HRMS spectra of 2-methyl-3-butyl prodiginine with incorporated methyl-D_3 group derived from 0.5 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **2** $[M+H]^+$: *m/z* 313, $C_{19}H_{21}D_3N_3O$).

Fig. S97. HRMS spectra of prodigiosin with incorporated methyl-D_3 group derived from 0.5 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **3** $[M+H]^+$: *m/z* 327, $C_{20}H_{23}D_3N_3O$).

Fig. S98. HRMS spectra of 2-methyl-3-hexyl prodiginine with incorporated methyl-D_3 group derived from 0.5 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **4** $[M+H]^+$: *m/z* 341, $C_{21}H_{25}D_3N_3O$).

Fig. S99. HRMS spectra of 2-methyl-3-heptyl prodiginine with incorporated methyl-D_3 group derived from 0.5 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **5** $[M+H]^+$: *m/z* 355, $C_{22}H_{27}D_3N_3O$).

Fig. S100. HRMS spectra of 2-methyl-3-nonyl prodiginine with incorporated methyl-D_3 group derived from 0.5 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **7** $[M+H]^+$: *m/z* 383, $C_{24}H_{31}D_3N_3O$).

Fig. S101. HRMS spectra of 2-methyl-3-propyl prodiginine with incorporated methyl-D_3 group derived from 2 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **1** $[M+H]^+$: *m/z* 299, $C_{18}H_{19}D_3N_3O$).

Fig. S102. HRMS spectra of 2-methyl-3-butyl prodiginine with incorporated methyl-D_3 group derived from 2 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **2** $[M+H]^+$: *m/z* 313, $C_{19}H_{21}D_3N_3O$).

Fig. S103. HRMS spectra of prodigiosin with incorporated methyl-D_3 group derived from 2 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **3** $[M+H]^+$: *m/z* 327, $C_{20}H_{23}D_3N_3O$).

Fig. S104. HRMS spectra of 2-methyl-3-hexyl prodiginine with incorporated methyl-D_3 group derived from 2 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **4** $[M+H]^+$: *m/z* 341, $C_{21}H_{25}D_3N_3O$).

Fig. S105. HRMS spectra of 2-methyl-3-heptyl prodiginine with incorporated methyl-D_3 group derived from 2 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **5** $[M+H]^+$: *m/z* 355, $C_{22}H_{27}D_3N_3O$).

Fig. S106. HRMS spectra of 2-methyl-3-nonyl prodiginine with incorporated methyl-D_3 group derived from 2 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **7** $[M+H]^+$: *m/z* 383, $C_{24}H_{31}D_3N_3O$).

Fig. S107. HRMS spectra of 4-methoxy-2,2'-bipyrrole-5-carbaldehyde (MBC) with incorporated ^{15}N-L-serine from labeled nutrient agar (compound **8** $[M+H]^+$: *m/z* 192, $C_{10}H_{11}N^{15}NO_2$).

Fig. S108. HRMS spectra of 4-methoxy-2,2'-bipyrrole-5-carbaldehyde (MBC) with incorporated methyl-D_3 group derived from 1 mg/mL [methyl-D_3]-L-methionine on nutrient agar (compound **8** $[M+H]^+$: *m/z* 194, $C_{10}H_8D_3N_2O_2$).

Fig. S109. HRMS spectra of 4-methoxy-2,2'-bipyrrole-5-carbaldehyde (MBC) with incorporated methyl-D_3 group derived from 2 mg/mL [methyl-D_3]-L-methionine on nutrient agar (compound **8** $[M+H]^+$: *m/z* 194, $C_{10}H_8D_3N_2O_2$).

Fig. S110. HRMS spectra of 4-methoxy-2,2'-bipyrrole-5-carbaldehyde (MBC) with incorporated methyl-D_3 group derived from 0.5 mg/mL [methyl-D_3]-L-methionine on nutrient agar (compound **8** $[M+H]^+$: *m/z* 194, $C_{10}H_8D_3N_2O_2$).

Fig. S111. HRMS spectra of 4-methoxy-2,2'-bipyrrole-5-carbaldehyde (MBC) with incorporated [1-^{13}C]-L-proline from labeled nutrient agar (compound **8** $[M+H]^+$: *m/z* 192, $C_9{}^{13}CH_{11}N_2O_2$).

Fig. S112. HRMS spectra of 4-methoxy-2,2'-bipyrrole-5-carbaldehyde (MBC) with incorporated ^{15}N-L-serine from labeled potato dextrose agar (compound **8** $[M+H]^+$: *m/z* 192, $C_{10}H_{11}N^{15}NO_2$).

Fig. S113. HRMS spectra of 4-methoxy-2,2'-bipyrrole-5-carbaldehyde (MBC) with incorporated methyl-D_3 group derived from 1 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **8** $[M+H]^+$: *m/z* 194, $C_{10}H_8D_3N_2O_2$).

Fig. S114. HRMS spectra of 4-methoxy-2,2'-bipyrrole-5-carbaldehyde (MBC) with incorporated methyl-D_3 group derived from 2 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **8** $[M+H]^+$: *m/z* 194, $C_{10}H_8D_3N_2O_2$).

Fig. S115. HRMS spectra of 4-methoxy-2,2'-bipyrrole-5-carbaldehyde (MBC) with incorporated methyl-D_3 group derived from 0.5 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **8** $[M+H]^+$: *m/z* 194, $C_{10}H_8D_3N_2O_2$).

Fig. S116. HRMS spectra of 4-methoxy-2,2'-bipyrrole-5-carbaldehyde (MBC) with incorporated [1-^{13}C]-L-proline from labeled potato dextrose agar (compound **8** $[M+H]^+$: *m/z* 192, $C_9{}^{13}CH_{11}N_2O_2$).

Fig. S117. $HRMS^2$ of 2-methyl-3-butyl prodiginine with incorporated methyl-D_3 group derived from 1 mg/mL [methyl-D_3]-L-methionine on nutrient agar (compound **2** $[M+H]^+$: *m/z* 313, $C_{19}H_{21}D_3N_3O$).

Fig. S118. $HRMS^2$ of prodigiosin with incorporated methyl-D_3 group derived from 1 mg/mL [methyl-D_3]-L-methionine on nutrient agar (compound **3** $[M+H]^+$: *m/z* 327, $C_{20}H_{23}D_3N_3O$).

Fig. S119. $HRMS^2$ of 2-methyl-3-hexyl prodiginine with incorporated methyl-D_3 group derived from 1 mg/mL [methyl-D_3]-L-methionine on nutrient agar (compound **4** $[M+H]^+$: *m/z* 341, $C_{21}H_{25}D_3N_3O$).

Fig. S120. $HRMS^2$ of 2-methyl-3-heptyl prodiginine with incorporated methyl-D_3 group derived from 1 mg/mL [methyl-D_3]-L-methionine on nutrient agar (compound **5** $[M+H]^+$: *m/z* 355, $C_{22}H_{27}D_3N_3O$).

Fig. S121. $HRMS^2$ of 2-methyl-3-butyl prodiginine with incorporated methyl-D_3 group derived from 0.5 mg/mL [methyl-D_3]-L-methionine on nutrient agar (compound **2** $[M+H]^+$: *m/z* 313, $C_{19}H_{21}D_3N_3O$).

Fig. S122. $HRMS^2$ of prodigiosin with incorporated methyl-D_3 group derived from 0.5 mg/mL [methyl-D_3]-L-methionine on nutrient agar (compound **3** $[M+H]^+$: *m/z* 327, $C_{20}H_{23}D_3N_3O$).

Fig. S123. $HRMS^2$ of 2-methyl-3-hexyl prodiginine with incorporated methyl-D_3 group derived from 0.5 mg/mL [methyl-D_3]-L-methionine on nutrient agar (compound **4** $[M+H]^+$: *m/z* 341, $C_{21}H_{25}D_3N_3O$).

Fig. S124. $HRMS^2$ of 2-methyl-3-heptyl prodiginine with incorporated methyl-D_3 group derived from 0.5 mg/mL [methyl-D_3]-L-methionine on nutrient agar (compound **5** $[M+H]^+$: *m/z* 355, $C_{22}H_{27}D_3N_3O$).

Fig. S125. $HRMS^2$ of 2-methyl-3-propyl prodiginine with incorporated methyl-D_3 group derived from 2 mg/mL [methyl-D_3]-L-methionine on nutrient agar (compound **1** $[M+H]^+$: *m/z* 299, $C_{18}H_{19}D_3N_3O$).

Fig. S126. $HRMS^2$ of 2-methyl-3-butyl prodiginine with incorporated methyl-D_3 group derived from 2 mg/mL [methyl-D_3]-L-methionine on nutrient agar (compound **2** $[M+H]^+$: *m/z* 313, $C_{19}H_{21}D_3N_3O$).

Fig. S127. $HRMS^2$ of prodigiosin with incorporated methyl-D_3 group derived from 2 mg/mL [methyl-D_3]-L-methionine on nutrient agar (compound **3** $[M+H]^+$: *m/z* 327, $C_{20}H_{23}D_3N_3O$).

Fig. S128. $HRMS^2$ of 2-methyl-3-hexyl prodiginine with incorporated methyl-D_3 group derived from 2 mg/mL [methyl-D_3]-L-methionine on nutrient agar (compound **4** $[M+H]^+$: *m/z* 341, $C_{21}H_{25}D_3N_3O$).

Fig. S129. $HRMS^2$ of 2-methyl-3-heptyl prodiginine with incorporated methyl-D_3 group derived from 2 mg/mL [methyl-D_3]-L-methionine on nutrient agar (compound **5** $[M+H]^+$: *m/z* 355, $C_{22}H_{27}D_3N_3O$).

Fig. S130. $HRMS^2$ of 2-methyl-3-propyl prodiginine with incorporated methyl-D_3 group derived from 1 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **1** $[M+H]^+$: *m/z* 299, $C_{18}H_{19}D_3N_3O$).

Fig. S131. $HRMS^2$ of 2-methyl-3-butyl prodiginine with incorporated methyl-D_3 group derived from 1 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **2** $[M+H]^+$: *m/z* 313, $C_{19}H_{21}D_3N_3O$).

Fig. S132. $HRMS^2$ of prodigiosin with incorporated methyl-D_3 group derived from 1 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **3** $[M+H]^+$: *m/z* 327, $C_{20}H_{23}D_3N_3O$).

Fig. S133. $HRMS^2$ of 2-methyl-3-hexyl prodiginine with incorporated methyl-D_3 group derived from 1 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **4** $[M+H]^+$: *m/z* 341, $C_{21}H_{25}D_3N_3O$).

Fig. S134. $HRMS^2$ of 2-methyl-3-heptyl prodiginine with incorporated methyl-D_3 group derived from 1 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **5** $[M+H]^+$: *m/z* 355, $C_{22}H_{27}D_3N_3O$).

Fig. S135. $HRMS^2$ of 2-methyl-3-propyl prodiginine with incorporated methyl-D_3 group derived from 0.5 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **1** $[M+H]^+$: *m/z* 299, $C_{18}H_{19}D_3N_3O$).

Fig. S136. $HRMS^2$ of 2-methyl-3-butyl prodiginine with incorporated methyl-D_3 group derived from 0.5 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **2** $[M+H]^+$: *m/z* 313, $C_{19}H_{21}D_3N_3O$).

Fig. S137. $HRMS^2$ of prodigiosin with incorporated methyl-D_3 group derived from 0.5 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **3** $[M+H]^+$: *m/z* 327, $C_{20}H_{23}D_3N_3O$).

Fig. S138. $HRMS^2$ of 2-methyl-3-hexyl prodiginine with incorporated methyl-D_3 group derived from 0.5 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **4** $[M+H]^+$: *m/z* 341, $C_{21}H_{25}D_3N_3O$).

Fig. S139. $HRMS^2$ of 2-methyl-3-heptyl prodiginine with incorporated methyl-D_3 group derived from 0.5 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **5** $[M+H]^+$: *m/z* 355, $C_{22}H_{27}D_3N_3O$).

Fig. S140. $HRMS^2$ of 2-methyl-3-propyl prodiginine with incorporated methyl-D_3 group derived from 2 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **1** $[M+H]^+$: *m/z* 299, $C_{18}H_{19}D_3N_3O$).

Fig. S141. $HRMS^2$ of 2-methyl-3-butyl prodiginine with incorporated methyl-D_3 group derived from 2 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **2** $[M+H]^+$: *m/z* 313, $C_{19}H_{21}D_3N_3O$).

Fig. S142. HRMS^2 of prodigiosin with incorporated methyl-D_3 group derived from 2 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **3** $[M+H]^+$: *m/z* 327, $C_{20}H_{23}D_3N_3O$).

Fig. S143. HRMS^2 of 2-methyl-3-hexyl prodiginine with incorporated methyl-D_3 group derived from 2 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **4** $[M+H]^+$: *m/z* 341, $C_{21}H_{25}D_3N_3O$).

Fig. S144. HRMS^2 of 2-methyl-3-heptyl prodiginine with incorporated methyl-D_3 group derived from 2 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **5** $[M+H]^+$: *m/z* 355, $C_{22}H_{27}D_3N_3O$).

Fig. S145. HRMS spectra of 2-methyl-3-propyl prodiginine with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (compound **1** $[M+H]^+$: *m/z* 296, $C_{18}H_{22}N_3O$).

Fig. S146. HRMS spectra of 2-methyl-3-butyl prodiginine with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (compound **2** $[M+H]^+$: *m/z* 310, $C_{19}H_{24}N_3O$).

Fig. S147. HRMS spectra of prodigiosin with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (compound **3** $[M+H]^+$: *m/z* 324, $C_{20}H_{26}N_3O$).

Fig. S148. HRMS spectra of 2-methyl-3-hexyl prodiginine with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (compound **4** $[M+H]^+$: *m/z* 338, $C_{21}H_{28}N_3O$).

Fig. S149. HRMS spectra of 2-methyl-3-heptyl prodiginine with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (compound **5** $[M+H]^+$: *m/z* 352, $C_{22}H_{30}N_3O$).

Fig. S150. HRMS spectra of 2-methyl-3-nonyl prodiginine with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (compound **7** $[M+H]^+$: *m/z* 380, $C_{24}H_{34}N_3O$).

Fig. S151. HRMS spectra of 4-methoxy-2,2'-bipyrrole-5-carbaldehyde (MBC) with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (compound **8** $[M+H]^+$: *m/z* 192, $C_{10}H_{11}N^{15}NO_2$).

Fig. S152. HRMS spectra of 2-methyl-3-amylpyrrole (MAP) with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (compound **9** $[M+H]^+$: *m/z* 153, $C_{10}H_{18}{}^{15}N$).

Fig. S153. HRMS^2 spectra of 2-methyl-3-propyl prodiginine with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (compound **1** $[M+H]^+$: *m/z* 297, $C_{18}H_{22}N_2{}^{15}NO$).

Fig. S154. $HRMS^2$ spectra of 2-methyl-3-butyl prodiginine with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (compound **2** $[M+H]^+$: *m/z* 311, $C_{19}H_{24}N_2{}^{15}NO$).

Fig. S155. $HRMS^2$ spectra of prodigiosin with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (compound **3** $[M+H]^+$: *m/z* 325, $C_{20}H_{26}N_2{}^{15}NO$).

Fig. S156. $HRMS^2$ spectra of 2-methyl-3-hexyl prodiginine with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (compound **4** $[M+H]^+$: *m/z* 339, $C_{21}H_{28}N_2{}^{15}NO$).

Fig. S157. $HRMS^2$ spectra of 2-methyl-3-heptyl prodiginine with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (compound **5** $[M+H]^+$: *m/z* 353, $C_{22}H_{30}N_2{}^{15}NO$).

Fig. S158. MALDI-imaging-HRMS of abundant serratamolides (A: serrawettin W1 (**10**); B: C_{10}+C_{12} (**12**); C: C_{10}+$C_{12:1}$ (**16**)) produced by *S. marcescens* MSRBB2 on potato dextrose agar supplemented with [^{15}N]-L-serine. Optical image with assigned scan area and localization of unlabeled serratamolides along with one and two incorporations of [^{15}N]-L-serine ($[M+K]^+$ ± 3 ppm).

Fig. S159. MALDI-imaging-HRMS of abundant serratamolides (A: serrawettin W1 (**10**); B: C_{10}+C_{12} (**12**); C: C_{10}+$C_{12:1}$ (**16**)) produced by *S. marcescens* MSRBB2 on potato dextrose agar supplemented with [^{15}N]-L-serine. Optical image with assigned scan area and localization of unlabeled serratamolides along with one and two incorporations of [^{15}N]-L-serine ($[M+K]^+$ ± 3 ppm).

Fig. S160. HRMS of serrawettin W1 / serratamolide C_{10}+C_{10} with incorporated ^{15}N-L-serine from labeled nutrient agar (compound **10** $[M+H]^+$: *m/z* 515, $C_{26}H_{47}N_2O_8$).

Fig. S161. HRMS of serratamolide C_{10}+C_{11} with incorporated ^{15}N-L-serine from labeled nutrient agar (compound **11** $[M+H]^+$: *m/z* 529, $C_{27}H_{49}N_2O_8$).

Fig. S162. HRMS of serratamolide C_{10}+C_{12} with incorporated ^{15}N-L-serine from labeled nutrient agar (compound **12** $[M+H]^+$: *m/z* 543, $C_{28}H_{51}N_2O_8$).

Fig. S163. HRMS of serratamolide C_{11}+C_{12} with incorporated ^{15}N-L-serine from labeled nutrient agar (compound **13** $[M+H]^+$: *m/z* 557, $C_{29}H_{53}N_2O_8$).

Fig. S164. HRMS of serratamolide C_{12}+C_{12} with incorporated ^{15}N-L-serine from labeled nutrient agar (compound **14** $[M+H]^+$: *m/z* 571, $C_{30}H_{55}N_2O_8$).

Fig. S165. HRMS of serratamolide C_{10}+$C_{11:1}$ with incorporated ^{15}N-L-serine from labeled nutrient agar (compound **15** $[M+H]^+$: *m/z* 527, $C_{27}H_{47}N_2O_8$).

Fig. S166. HRMS of serratamolide C_{10}+$C_{12:1}$ with incorporated ^{15}N-L-serine from labeled nutrient agar (compound **16** $[M+H]^+$: *m/z* 541, $C_{28}H_{49}N_2O_8$).

Fig. S167. HRMS of serratamolide C_{11}+$C_{12:1}$ with incorporated ^{15}N-L-serine from labeled nutrient agar (compound **17** $[M+H]^+$: *m/z* 555, $C_{29}H_{51}N_2O_8$).

Fig. S168. HRMS of serratamolide C_{12}+$C_{12:1}$ with incorporated ^{15}N-L-serine from labeled nutrient agar (compound **18** $[M+H]^+$: *m/z* 569, $C_{30}H_{53}N_2O_8$).

Fig. S169. HRMS of ring-opened serratamolide C_{10}+C_{10} with incorporated ^{15}N-L-serine from labeled nutrient agar (compound **19** $[M+H]^+$: *m/z* 533, $C_{26}H_{49}N_2O_9$).

Fig. S170. HRMS of ring-opened serratamolide C_{10}+C_{11} with incorporated ^{15}N-L-serine from labeled nutrient agar (compound **20** $[M+H]^+$: *m/z* 547, $C_{27}H_{51}N_2O_9$).

Fig. S171. HRMS of ring-opened serratamolide C_{10}+C_{12} with incorporated ^{15}N-L-serine from labeled nutrient agar (compound **21** $[M+H]^+$: *m/z* 561, $C_{28}H_{53}N_2O_9$).

Fig. S172. HRMS of ring-opened serratamolide C_{10}+$C_{12:1}$ with incorporated ^{15}N-L-serine from labeled nutrient agar (compound **22** $[M+H]^+$: *m/z* 559, $C_{28}H_{51}N_2O_9$).

Fig. S173. $HRMS^2$ of ring-opened serratamolide C_{10}+C_{13} with incorporated ^{15}N-L-serine from labeled nutrient agar (compound **23** $[M+H]^+$: *m/z* 575, $C_{29}H_{55}N_2O_9$).

Fig. S174. HRMS of ring-opened serratamolide C_{12}+C_{12} with incorporated ^{15}N-L-serine from labeled nutrient agar (compound **24** $[M+H]^+$: *m/z* 589, $C_{30}H_{57}N_2O_9$).

Fig. S175. HRMS of ring-opened serratamolide C_{12}+C_{13} with incorporated ^{15}N-L-serine from labeled nutrient agar (compound **25** $[M+H]^+$: *m/z* 603, $C_{31}H_{59}N_2O_9$).

Fig. S176. HRMS of ring-opened serratamolide C_{10}+$C_{13:1}$ with incorporated ^{15}N-L-serine from labeled nutrient agar (compound **26** $[M+H]^+$: *m/z* 573, $C_{29}H_{53}N_2O_9$).

Fig. S177. HRMS of ring-opened serratamolide C_{12}+$C_{12:1}$ with incorporated ^{15}N-L-serine from labeled nutrient agar (compound **27** $[M+H]^+$: *m/z* 587, $C_{30}H_{55}N_2O_9$).

Fig. S178. HRMS of ring-opened serratamolide C_{13}+$C_{12:1}$ with incorporated ^{15}N-L-serine from labeled nutrient agar (compound **28** $[M+H]^+$: *m/z* 601, $C_{31}H_{57}N_2O_9$).

Fig. S179. HRMS of serratamic acid with incorporated ^{15}N-L-serine from labeled nutrient agar (N-(D-3-hydroxydecanoyl)-L-serine, compound **29** $[M+H]^+$: *m/z* 276, $C_{13}H_{26}NO_5$).

Fig. S180. HRMS of serratamic acid derivative with incorporated ^{15}N-L-serine from labeled nutrient agar (hydroxydodecanoyl-serine, compound **30** $[M+H]^+$: *m/z* 304, $C_{15}H_{30}NO_5$).

Fig. S181. HRMS of serratamic acid derivative with double bond with incorporated ^{15}N-L-serine from labeled nutrient agar (hydroxydodecenoyl-serine, compound **31** $[M+H]^+$: *m/z* 302, $C_{15}H_{28}NO_5$).

Fig. S182. HRMS of serrawettin W1 / serratamolide C_{10}+C_{10} with incorporated ^{15}N-L-serine from labeled potato dextrose agar (compound **10** $[M+H]^+$: *m/z* 515, $C_{26}H_{47}N_2O_8$).

Fig. S183. HRMS of serratamolide C_{10}+C_{11} with incorporated ^{15}N-L-serine from labeled potato dextrose agar (compound **11** $[M+H]^+$: *m/z* 529, $C_{27}H_{49}N_2O_8$).

Fig. S184. HRMS of serratamolide C_{10}+C_{12} with incorporated ^{15}N-L-serine from labeled potato dextrose agar (compound **12** $[M+H]^+$: *m/z* 543, $C_{28}H_{51}N_2O_8$).

Fig. S185. HRMS of serratamolide C_{11}+C_{12} with incorporated ^{15}N-L-serine from labeled potato dextrose agar (compound **13** $[M+H]^+$: *m/z* 557, $C_{29}H_{53}N_2O_8$).

Fig. S186. HRMS of serratamolide C_{12}+C_{12} with incorporated ^{15}N-L-serine from labeled potato dextrose agar (compound **14** $[M+H]^+$: *m/z* 571, $C_{30}H_{55}N_2O_8$).

Fig. S187. HRMS of serratamolide C_{10}+$C_{11:1}$ with incorporated ^{15}N-L-serine from labeled potato dextrose agar (compound **15** $[M+H]^+$: *m/z* 527, $C_{27}H_{47}N_2O_8$).

Fig. S188. HRMS of serratamolide C_{10}+$C_{12:1}$ with incorporated ^{15}N-L-serine from labeled potato dextrose agar (compound **16** $[M+H]^+$: *m/z* 541, $C_{28}H_{49}N_2O_8$).

Fig. S189. HRMS of serratamolide C_{11}+$C_{12:1}$ with incorporated ^{15}N-L-serine from labeled potato dextrose agar (compound **17** $[M+H]^+$: *m/z* 555, $C_{29}H_{51}N_2O_8$).

Fig. S190. HRMS of serratamolide C_{12}+$C_{12:1}$ with incorporated ^{15}N-L-serine from labeled potato dextrose agar (compound **18** $[M+H]^+$: *m/z* 569, $C_{30}H_{53}N_2O_8$).

Fig. S191. HRMS of ring-opened serratamolide C_{10}+C_{10} with incorporated ^{15}N-L-serine from labeled potato dextrose agar (compound **19** $[M+H]^+$: *m/z* 533, $C_{26}H_{49}N_2O_9$).

Fig. S192. HRMS of ring-opened serratamolide C_{10}+C_{11} with incorporated ^{15}N-L-serine from labeled potato dextrose agar (compound **20** $[M+H]^+$: *m/z* 547, $C_{27}H_{51}N_2O_9$).

Fig. S193. HRMS of ring-opened serratamolide C_{10}+C_{12} with incorporated ^{15}N-L-serine from labeled potato dextrose agar (compound **21** $[M+H]^+$: *m/z* 561, $C_{28}H_{53}N_2O_9$).

Fig. S194. HRMS of ring-opened serratamolide C_{10}+$C_{12:1}$ with incorporated ^{15}N-L-serine from labeled potato dextrose agar (compound **22** $[M+H]^+$: *m/z* 559, $C_{28}H_{51}N_2O_9$).

Fig. S195. HRMS^2 of ring-opened serratamolide C_{10}+C_{13} with incorporated ^{15}N-L-serine from labeled potato dextrose agar (compound **23** $[M+H]^+$: *m/z* 575, $C_{29}H_{55}N_2O_9$).

Fig. S196. HRMS of ring-opened serratamolide C_{12}+C_{12} with incorporated ^{15}N-L-serine from labeled potato dextrose agar (compound **24** $[M+H]^+$: *m/z* 589, $C_{30}H_{57}N_2O_9$).

Fig. S197. HRMS of ring-opened serratamolide C_{12}+C_{13} with incorporated ^{15}N-L-serine from labeled potato dextrose agar (compound **25** $[M+H]^+$: *m/z* 603, $C_{31}H_{59}N_2O_9$).

Fig. S198. HRMS of ring-opened serratamolide C_{10}+$C_{13:1}$ with incorporated ^{15}N-L-serine from labeled potato dextrose agar (compound **26** $[M+H]^+$: *m/z* 573, $C_{29}H_{53}N_2O_9$).

Fig. S199. HRMS of ring-opened serratamolide C_{12}+$C_{12:1}$ with incorporated ^{15}N-L-serine from labeled potato dextrose agar (compound **27** $[M+H]^+$: *m/z* 587, $C_{30}H_{55}N_2O_9$).

Fig. S200. HRMS of ring-opened serratamolide C_{13}+$C_{12:1}$ with incorporated ^{15}N-L-serine from labeled potato dextrose agar (compound **28** $[M+H]^+$: *m/z* 601, $C_{31}H_{57}N_2O_9$).

Fig. S201. HRMS of serratamic acid with incorporated ^{15}N-L-serine from labeled potato dextrose agar (N-(D-3-hydroxydecanoyl)-L-serine, compound **29** $[M+H]^+$: *m/z* 276, $C_{13}H_{26}NO_5$).

Fig. S202. HRMS of serratamic acid derivative with incorporated ^{15}N-L-serine from labeled potato dextrose agar (hydroxydodecanoyl-serine, compound **30** $[M+H]^+$: *m/z* 304, $C_{15}H_{30}NO_5$).

Fig. S203. HRMS of serratamic acid derivative with double bond with incorporated ^{15}N-L-serine from labeled potato dextrose agar (hydroxydodecenoyl-serine, compound **31** $[M+H]^+$: *m/z* 302, $C_{15}H_{28}NO_5$).

Fig. S204. HRMS of serrawettin W1 / serratamolide C_{10}+C_{10} with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (compound **10** $[M+H]^+$: *m/z* 515, $C_{26}H_{47}N_2O_8$).

Fig. S205. HRMS of serratamolide C_{10}+C_{11} with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (compound **11** $[M+H]^+$: *m/z* 529, $C_{27}H_{49}N_2O_8$).

Fig. S206. HRMS of serratamolide C_{10}+C_{12} with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (compound **12** $[M+H]^+$: *m/z* 543, $C_{28}H_{51}N_2O_8$).

Fig. S207. HRMS of serratamolide C_{11}+C_{12} with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (compound **13** $[M+H]^+$: *m/z* 557, $C_{29}H_{53}N_2O_8$).

Fig. S208. HRMS of serratamolide C_{12}+C_{12} with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (compound **14** $[M+H]^+$: *m/z* 571, $C_{30}H_{55}N_2O_8$).

Fig. S209. HRMS of serratamolide C_{10}+$C_{12:1}$ with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (compound **16** $[M+H]^+$: *m/z* 541, $C_{28}H_{49}N_2O_8$).

Fig. S210. HRMS of serratamolide C_{12}+$C_{12:1}$ with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (compound **18** $[M+H]^+$: *m/z* 569, $C_{30}H_{53}N_2O_8$).

Fig. S211. HRMS of ring-opened serratamolide C_{10}+C_{10} with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (compound **19** $[M+H]^+$: *m/z* 533, $C_{26}H_{49}N_2O_9$).

Fig. S212. HRMS of ring-opened serratamolide C_{10}+C_{12} with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (compound **21** $[M+H]^+$: *m/z* 561, $C_{28}H_{53}N_2O_9$).

Fig. S213. HRMS of ring-opened serratamolide C_{10}+$C_{12:1}$ with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (compound **22** $[M+H]^+$: *m/z* 559, $C_{28}H_{51}N_2O_9$).

Fig. S214. HRMS of ring-opened serratamolide C_{12}+C_{12} with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (compound **24** $[M+H]^+$: *m/z* 589, $C_{30}H_{57}N_2O_9$).

Fig. S215. HRMS of ring-opened serratamolide C_{12}+$C_{12:1}$ with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (compound **27** $[M+H]^+$: *m/z* 587, $C_{30}H_{55}N_2O_9$).

Fig. S216. HRMS of serratamic acid with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (N-(D-3-hydroxydecanoyl)-L-serine, compound **29** $[M+H]^+$: *m/z* 276, $C_{13}H_{26}NO_5$).

Fig. S217. HRMS of serratamic acid derivative with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (hydroxydodecanoyl-serine, compound **30** $[M+H]^+$: *m/z* 304, $C_{15}H_{30}NO_5$).

Fig. S218. HRMS of serratamic acid derivative with double bond with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (hydroxydodecenoyl-serine, compound **31** $[M+H]^+$: *m/z* 302, $C_{15}H_{28}NO_5$).

Fig. S219. MALDI-imaging-HRMS control of abundant serratamolides (A: serrawettin W1 (**10**); B: C_{10}+C_{12} (**12**); C: C_{10}+$C_{12:1}$ (**16**)) produced by *S. marcescens* MSRBB2 on potato dextrose agar. Optical image with assigned scan area and localization of unlabeled serratamolides along with one and two incorporations of [^{15}N]-L-serine ($[M+K]^+$ ± 3 ppm).

III. SUPPLEMENTARY TABLES

Table S1. Peak height ratios obtained from HPLC-HRMS by comparison of labeled and unlabeled prodiginines and MBC produced by *S. marcescens*. Different labeling studies with $^{15}NH_4Cl$, [1-^{13}C]-L-proline, [methyl-D_3]-L-methionine, and [^{15}N]-L-serine on nutrient agar (NA) and potato dextrose agar (PDA).

Table S2. Peak height ratios obtained from HPLC-HRMS by comparison of labeled (1x ^{15}N) and unlabeled serratamolides produced by *S. marcescens*. Different labeling studies with [^{15}N]-L-serine on nutrient agar (NA) and potato dextrose agar (PDA), as well as nutrient broth (NB) incubation under static conditions.

IV. SUPPLEMENTARY REFERENCES

I. METHODS

Labeling studies with stable isotope precursors on agar (see Figure 1 in the manuscript for a schematic representation of the workflow).

Nutrient agar (NA) and potato dextrose agar (PDA) was prepared as per producers specifications in Petri dishes (60 x 15 mm^2) with a thickness of approximately 4 mm (Fig. 1, step 1). We used small Petri dishes (60 x 15 mm^2) instead of the standard sized dishes (94 x 16 mm^2) to reduce the amounts of labeled compounds required. At the onset, we optimized the thickness of agar to 4-5 mm required for easy, accurate and reproducible MALDI-imaging-HRMS. Thinner agar would break or crack during the drying and/or matrix application process and thicker agar would waste media and compounds supplemented in the agar. After the agar has solidified, another thin layer (ca. 1-2 mm, 2-3 mL per Petri dish) of the respective agar amended with respective stable isotope labeled supplement(s) was poured on top (Fig. 1, step 2). $^{15}NH_4Cl$ (98% ^{15}N), [1-^{13}C]-L-proline (99% ^{13}C), [methyl-D_3]-L-methionine (98% D), and [^{15}N]-L-serine (98% ^{15}N) (Cambridge Isotope Laboratories, Inc., Tewksbury, USA) were used with a concentration of 1 mg/mL as supplements. The labeled compounds were added to the media before autoclaving. Additionally, experiments were performed with [methyl-D_3]-L-methionine in concentrations of 0.5 and 2 mg/mL. The agar was allowed to solidify and then inoculated with *S. marcescens* [1] and incubated at 30°C for 3 (NA) or 7 (PDA) days, respectively (Fig. 1, step 3). For MALDI-imaging studies, the samples were photographed with the digital microscope VHX-5000 (Keyence Deutschland GMBH, Germany), cut to a square sample size of approx. 8 x 8 mm, transferred to a glass slide, fixed with a thin 25 µm adhesive tape, and dried under a N_2 gas flow (Fig. 1, steps 4 and 5). Note that the agar containing seeded bacterium samples were cut out as square samples (square agar plugs), because during the drying process the agar can shrink by losing its water content. For a square samples, the size reduction is uniform for all sides and the measured ion

images fits onto the original optical images. In contrast, rectangular samples are more likely to be deformed during the drying. We achieved an optimum and homogenous drying of the samples amenable to MALDI-imaging-HRMS using a constant flow of nitrogen gas. The matrix application and MALDI-imaging measurements were performed under previously published methods [1] (Fig. 1, steps 5-10). Briefly, we utilized a SMALDI Prep spray device (TransMIT GmbH, Germany) for matrix application. The matrix used was HCCA (alpha-cyano-4-hydroxycinnamic acid, 7 mg/mL) in acetone:water 1:1 (*v:v*) containing 0.1 % FA, which was sprayed using the following parameters: 20 µL/min matrix flow rate, 3 L/min gas (N_2) flow rate, 30 min spray cycle, and 100 rpm sample plate revolution speed.

The MALDI-imaging high resolution mass spectrometry experiments were carried out with an atmospheric pressure scanning microprobe matrix-assisted laser desorption/ionization source (AP-SMALDI) (TransMIT GmbH, Germany) coupled to a Q Exactive high-resolution mass spectrometer (Thermo Scientific Inc., Bremen, Germany) with a 60 Hz pulsed N_2 laser MNL 100 series (LTB Lasertechnik GmbH, Germany) for UV beam generation at 337.1 nm [1]. The scan resolution was adjusted to 40 µm for each sample and measured in full scan positive ion mode at *m/z* 100–1000 mass range with internal lock mass correction utilizing the exact mass of $[HCCA+K]^+$ at *m/z* 228.00575. The measurements were performed with a mass resolution of 140000 @ *m/z* 200, S-lens level 65, a spray voltage of 2.0 kV, an injection time of 200–300 ms, and the attenuator value of the AP ion source was set at 20˚. MS^2 measurements of deuterium labeled prodigiosin $[M+H]^+$ were executed with an ion filter of *m/z* 327.2264 ± 0.5 amu with a scan range of *m/z* 100 – 340, higher-energy collisional dissociation (HCD, 45 eV) and a resolution of 35 000 @ *m/z* 200. The mapping of mass pixels corresponding to the target compounds or fragments, and the data processing was done with the software package ImageQuest (v. 1.1.0; Thermo Fisher Scientific, Germany). Mass pixels are shown as false colors.

In addition to the MALDI experiments, one or two incubated plates were extracted with methanol (thrice with 15 min ultra-sonication) after 3 (NA) or 7 (PDA) days, respectively, concentrated and analyzed by HPLC-HRMS using previously established procedures [1].

Feeding study of ^{15}N-L-serine in nutrient broth.

The bacterial endophyte *S. marcescens* was incubated with 50 mL diluted nutrient broth (1/2 strength of the specified composition) (Nutrient broth No 1, Sigma-Aldrich, Steinheim, Germany) at 30°C under stationary (static) conditions, with addition of 100 mg of filter-sterilized ^{15}N-L-serine (98% ^{15}N, Cambridge Isotope Laboratories, Inc., Tewksbury, USA) after 3 days of seeding the bacterium. After 10 days, the water was evaporated using a rotary evaporator (Laborota 4001, Heidolph, Schwabach, Germany) in a 40 °C water bath at 150 rpm. The extracts were dissolved in methanol and analyzed by HPLC-HRMS using previously established procedures [1].

II. SUPPLEMENTARY FIGURES

Fig. S1. Chemical structures of secondary metabolites produced by endophytic *S. marcescens* MSRBB2.

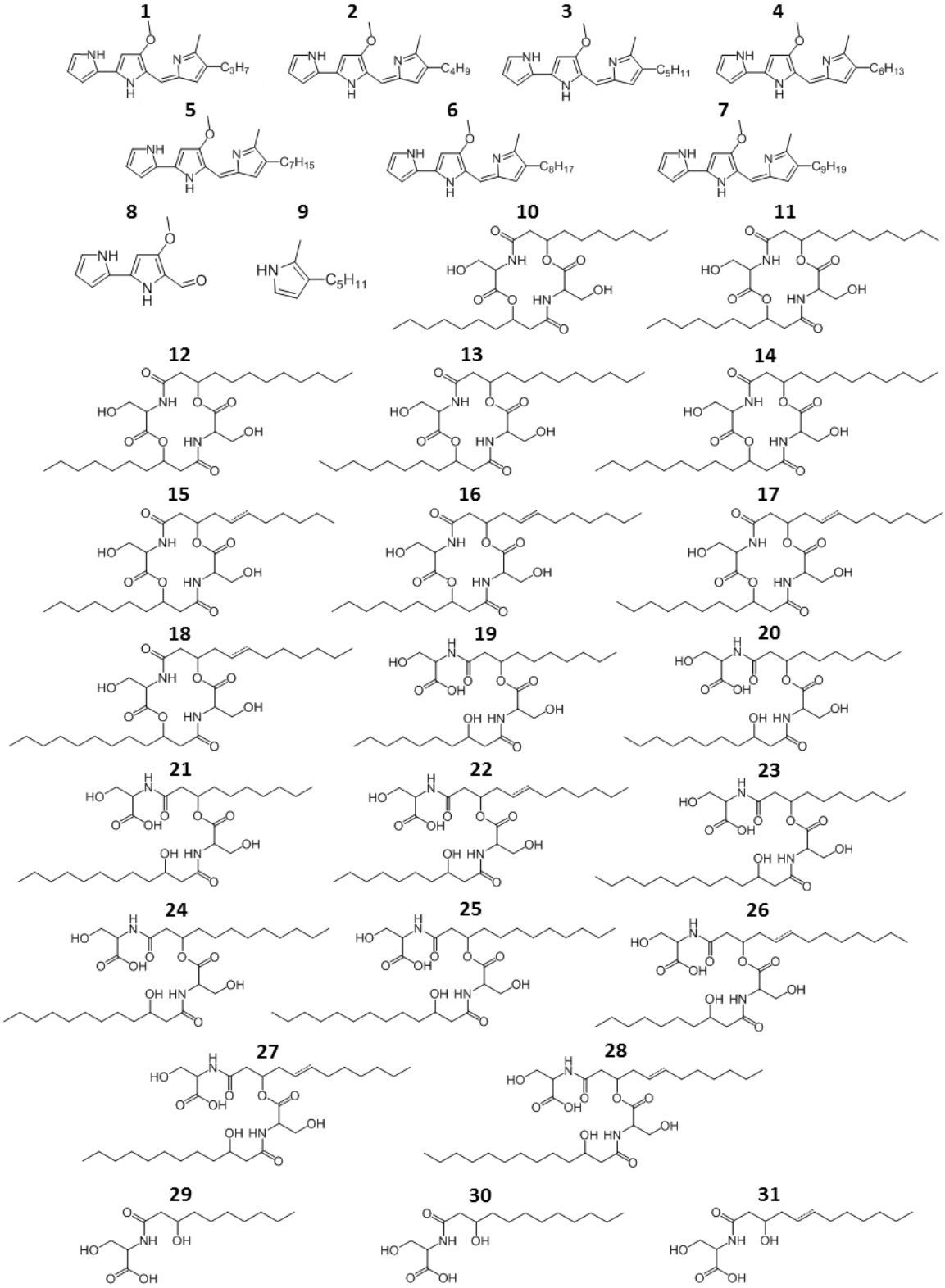


Fig. S2. MALDI-imaging-HRMS of bacterial endophyte *S. marcescens* MSRBB2 grown on nutrient agar with a thin layer of agar supplemented with [methyl-D_3]-L-methionine (1 mg/mL). Optical image with assigned scan area and localization of labeled and unlabeled prodigiosin (**3**, $[M+H]^+$ ± 2 ppm, (A)). Characteristic fragments of MALDI-imaging-$HRMS^2$ of labeled prodigiosin $C_{20}H_{23}D_3N_3O$ (**3**, $[M+H]^+$ ± 3 ppm, (B)).

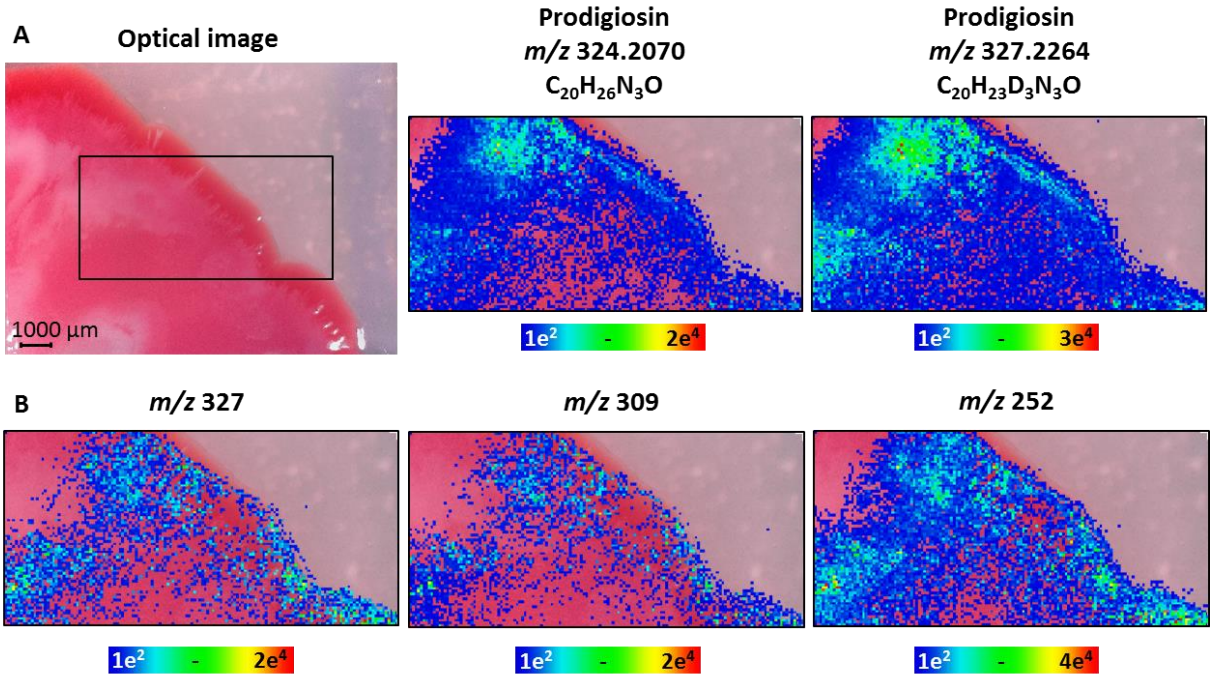


Fig. S3. MALDI-imaging-HRMS of bacterial endophyte *S. marcescens* MSRBB2 grown on nutrient agar with a thin layer of agar supplemented with [methyl-D_3]-L-methionine (1 mg/mL). Optical image with assigned scan area and localization of labeled and unlabeled prodigiosin (**3**, $[M+H]^+$ ± 2 ppm, (A)). Characteristic fragments of MALDI-imaging-$HRMS^2$ of labeled prodigiosin $C_{20}H_{23}D_3N_3O$ (**3**, $[M+H]^+$ ± 3 ppm, (B)).

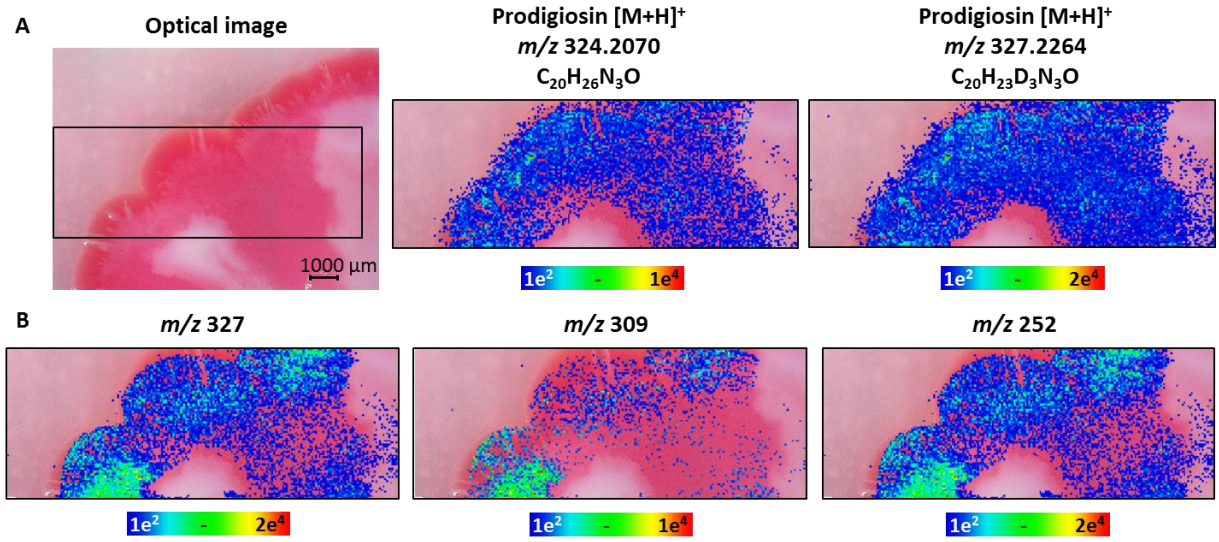


Fig. S4. MALDI-imaging-HRMS of bacterial endophyte *S. marcescens* MSRBB2 grown on nutrient agar with a thin layer of agar supplemented with [methyl-D_3]-L-methionine (1 mg/mL). Optical image with assigned scan area and localization of labeled and unlabeled prodigiosin (**3**, $[M+H]^+$ ± 2 ppm, (A)). Characteristic fragments of MALDI-imaging-$HRMS^2$ of labeled prodigiosin $C_{20}H_{23}D_3N_3O$ (**3**, $[M+H]^+$ ± 3 ppm, (B)).

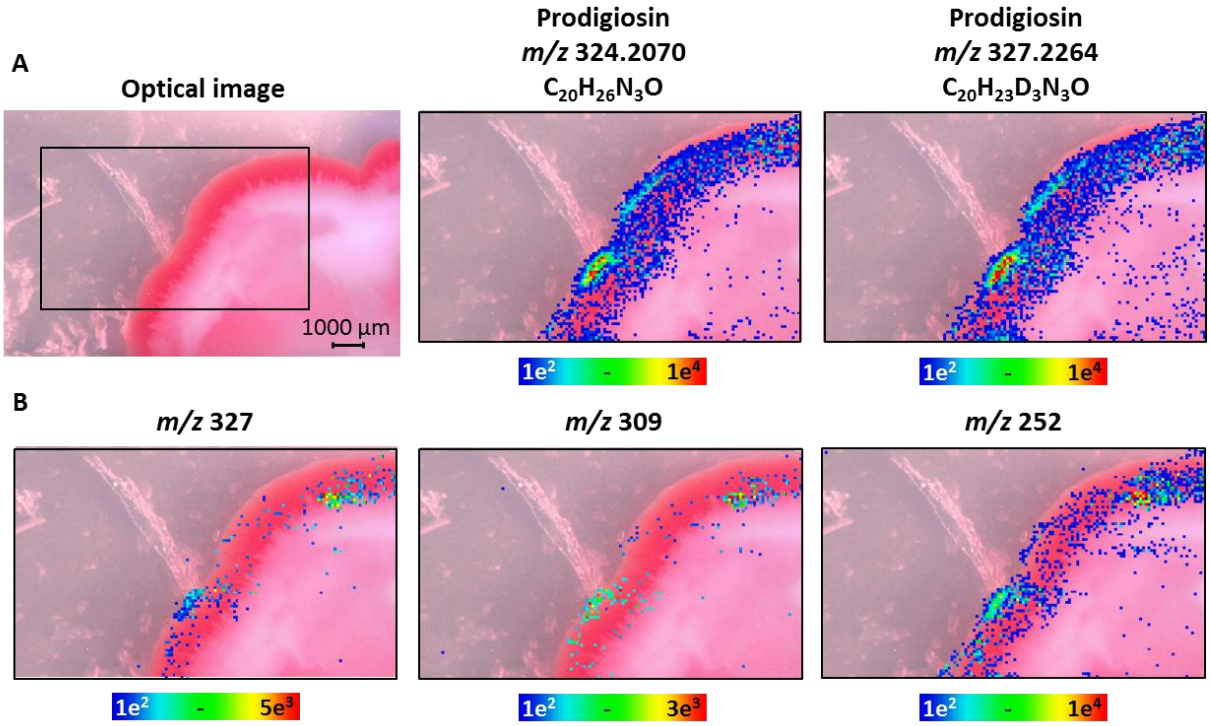


Fig. S5. MALDI-imaging-HRMS of bacterial endophyte *S. marcescens* MSRBB2 grown on nutrient agar with a thin layer of agar supplemented with [methyl-D_3]-L-methionine (1 mg/mL). Optical image with assigned scan area and localization of labeled and unlabeled prodigiosin (**3**, $[M+H]^+$ ± 2 ppm, (A)). Characteristic fragments of MALDI-imaging-$HRMS^2$ of labeled prodigiosin $C_{20}H_{23}D_3N_3O$ (**3**, $[M+H]^+$ ± 3 ppm, (B)).

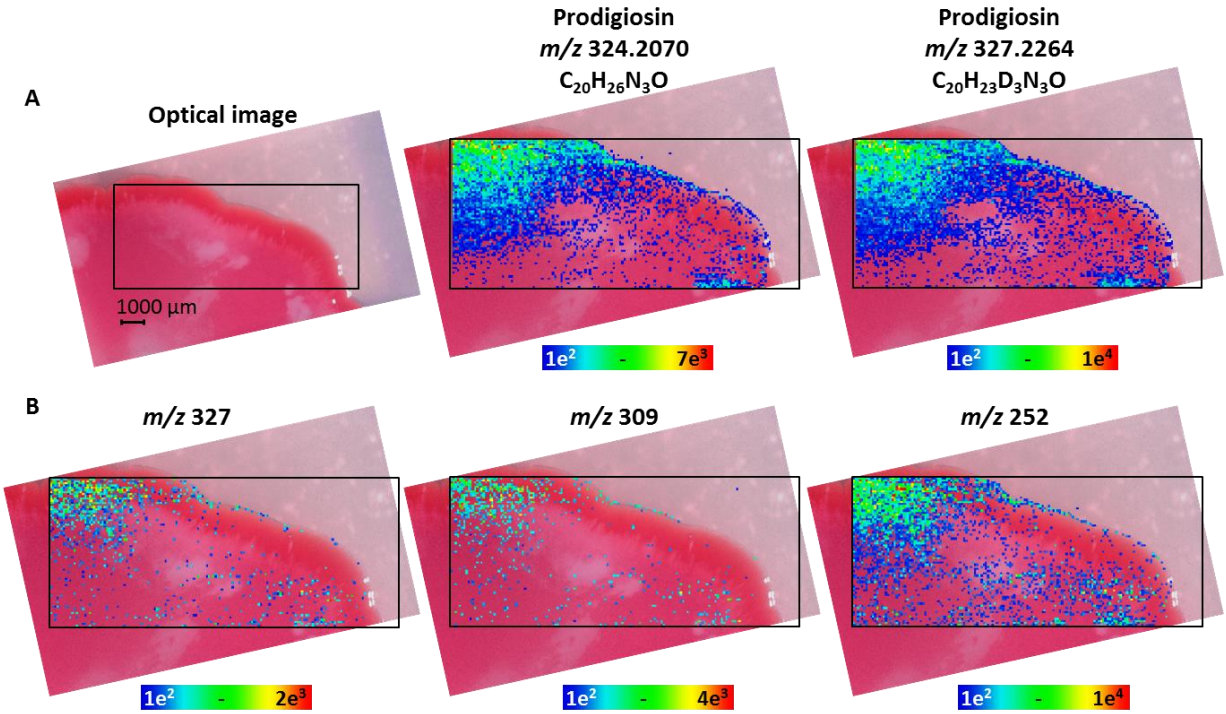


Fig. S6. MALDI-imaging-HRMS of bacterial endophyte *S. marcescens* MSRBB2 grown on nutrient agar with a thin layer of agar supplemented with [methyl-D_3]-L-methionine (1 mg/mL). Optical image with assigned scan area and localization of labeled and unlabeled prodigiosin (**3**, $[M+H]^+$ ± 2 ppm, (A)). Characteristic fragments of MALDI-imaging-$HRMS^2$ of labeled prodigiosin $C_{20}H_{23}D_3N_3O$ (**3**, $[M+H]^+$ ± 3 ppm, (B)).

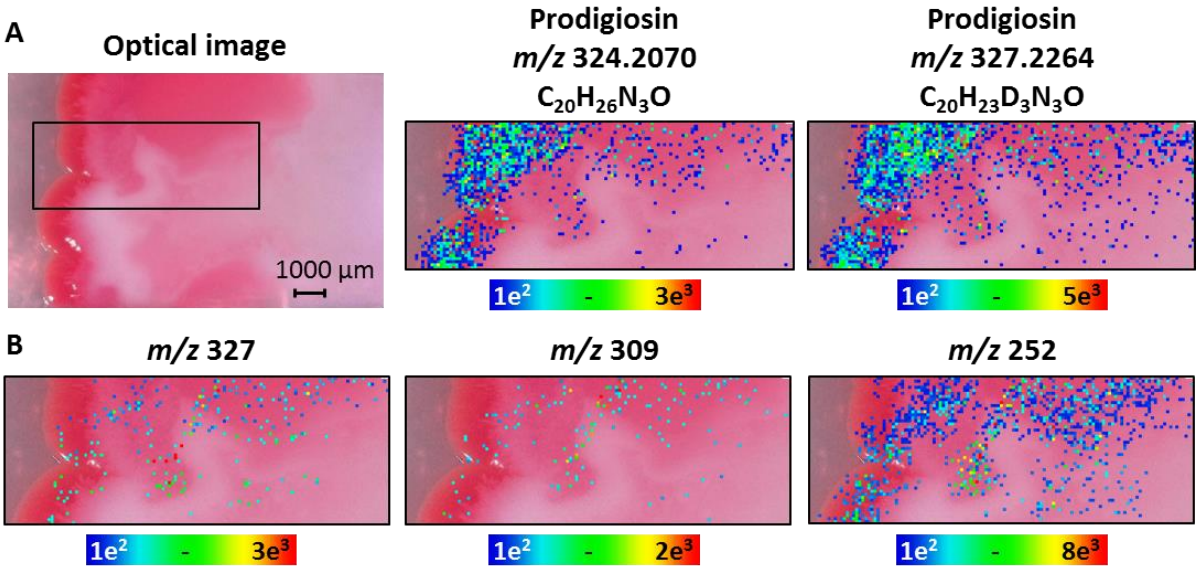


Fig. S7. MALDI-imaging-HRMS of bacterial endophyte *S. marcescens* MSRBB2 grown on nutrient agar with a thin layer of agar supplemented with [methyl-D_3]-L-methionine (1 mg/mL). Optical image with assigned scan areas and comparison of labeled and unlabeled prodigiosin (**3**, $[M+H]^+$ ± 2 ppm).

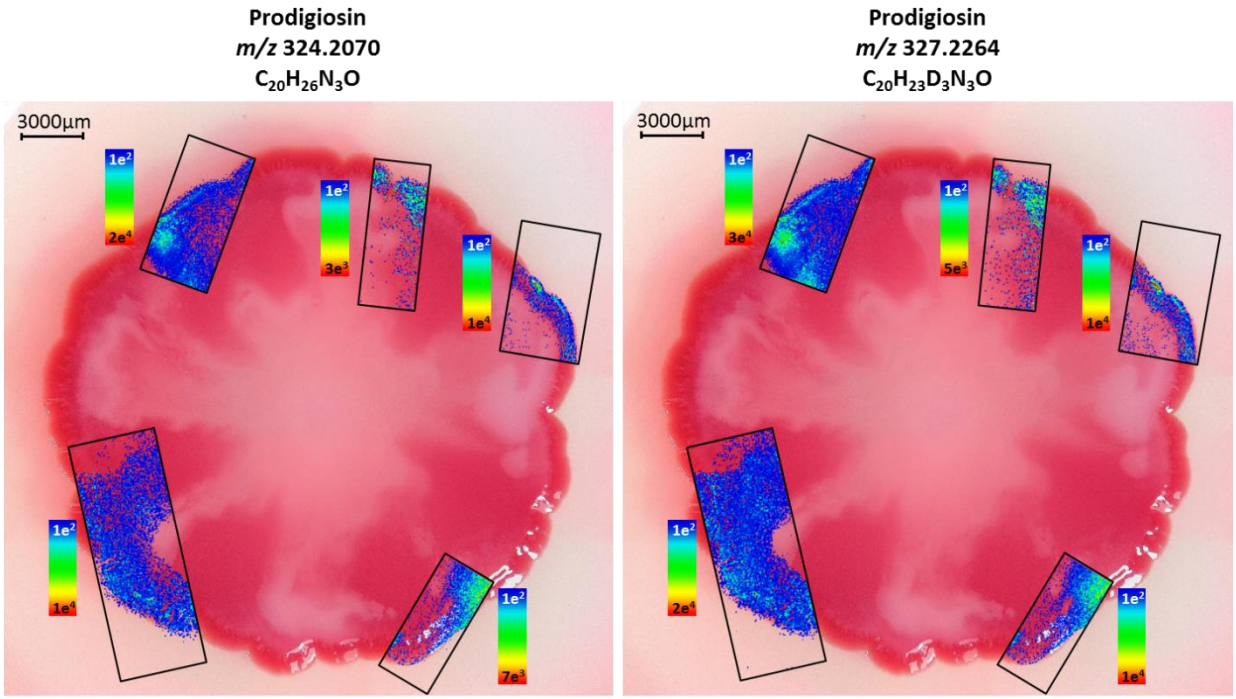


Fig. S8. MALDI-imaging-HRMS of bacterial endophyte *S. marcescens* MSRBB2 grown on nutrient agar with a thin layer of agar supplemented with $^{15}NH_4Cl$ (1 mg/mL). Optical image with assigned scan area and localization of labeled, unlabeled, and natural ^{13}C-isotopic prodigiosin (**3**, $[M+H]^+$ ± 2 ppm)

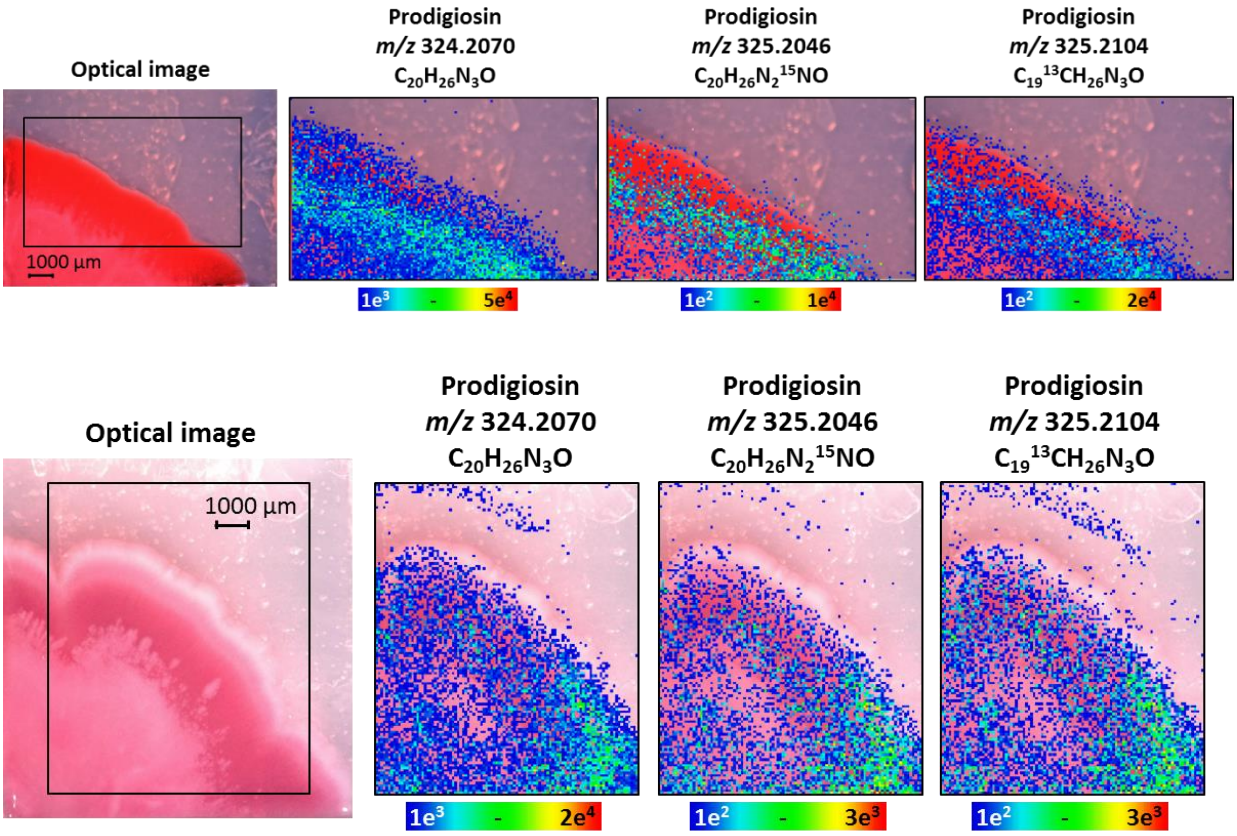


Fig. S9. MALDI-imaging-HRMS of bacterial endophyte *S. marcescens* MSRBB2 grown on nutrient agar with a thin layer of agar supplemented with [1-^{13}C]-L-proline (1 mg/mL). Optical image with assigned scan area and localization of labeled and unlabeled prodigiosin (**3**, $[M+H]^+$ ± 2 ppm, (A)). Characteristic fragments of MALDI-imaging-HRMS^2 of labeled prodigiosin $C_{19}{}^{13}CH_{23}N_3O$ (**3**, $[M+H]^+$ ± 3 ppm, (B)).

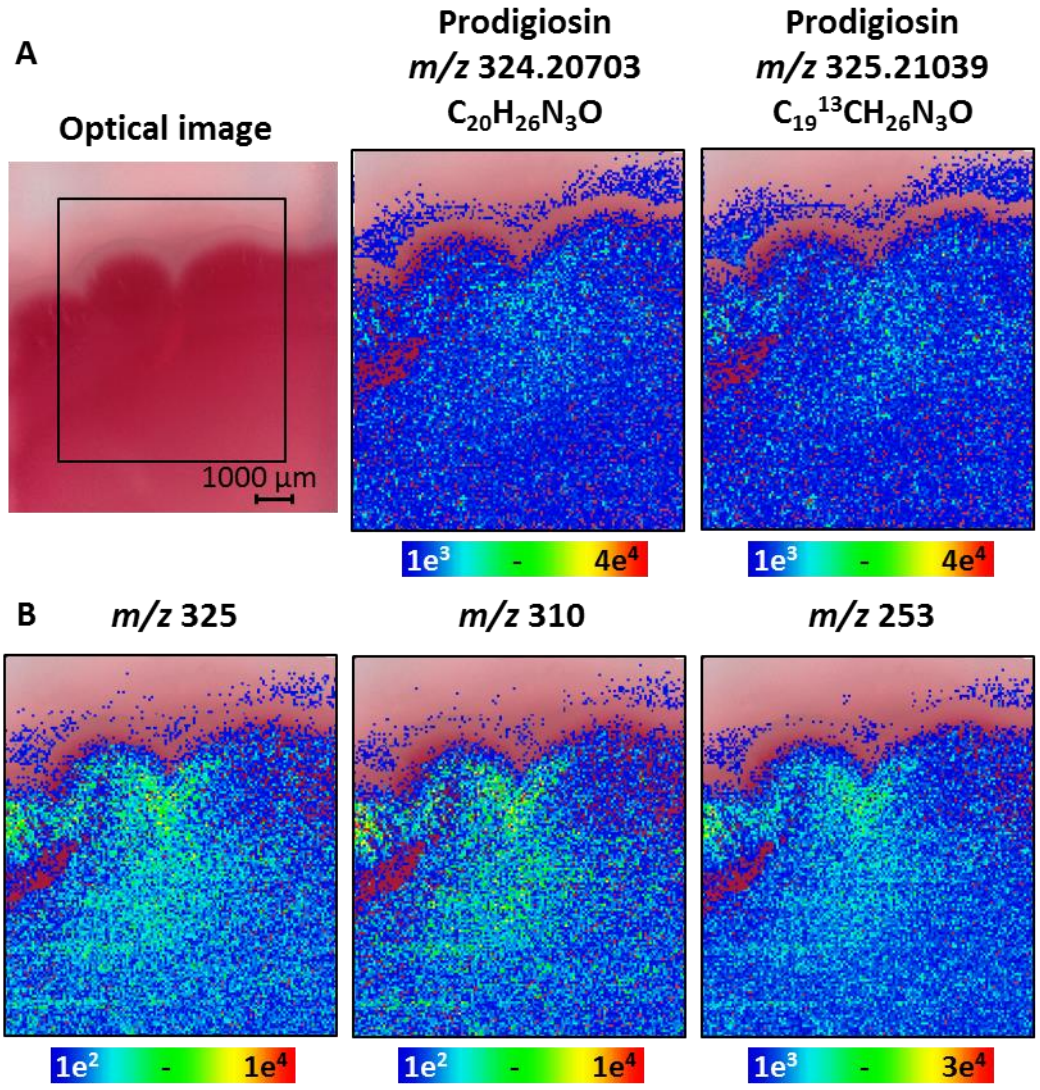


Fig. S10. MALDI-imaging-HRMS of bacterial endophyte *S. marcescens* MSRBB2 grown on nutrient agar with a thin layer of agar supplemented with ^{15}N-L-serine (1 mg/mL). Optical image with assigned scan area and localization of labeled, unlabeled, and natural ^{13}C-isotopic prodigiosin (**3**, $[M+H]^+$ ± 2 ppm)

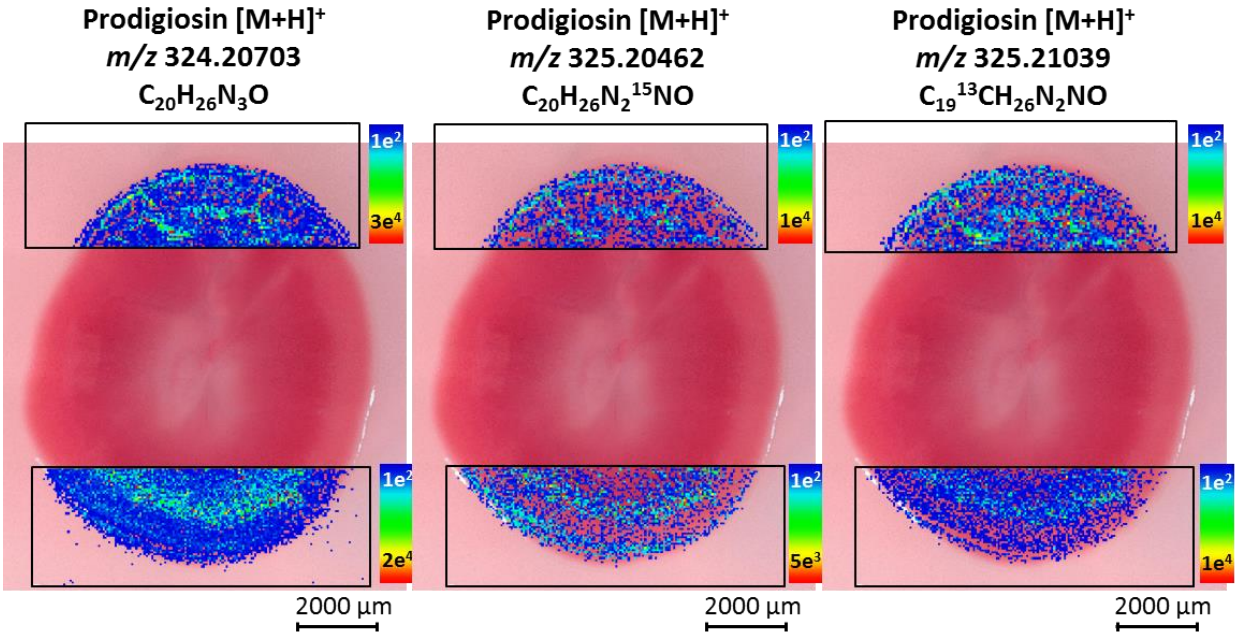


Fig. S11. MALDI-imaging-HRMS of bacterial endophyte *S. marcescens* MSRBB2 grown on nutrient agar with a thin layer of agar supplemented with [methyl-D_3]-L-methionine (0.5 mg/mL). Optical image with assigned scan area and localization of labeled and unlabeled prodigiosin (**3**, $[M+H]^+$ ± 2 ppm, (A)). Characteristic fragments of MALDI-imaging-HRMS^2 of labeled prodigiosin $C_{20}H_{23}D_3N_3O$ (**3**, $[M+H]^+$ ± 3 ppm, (B)).

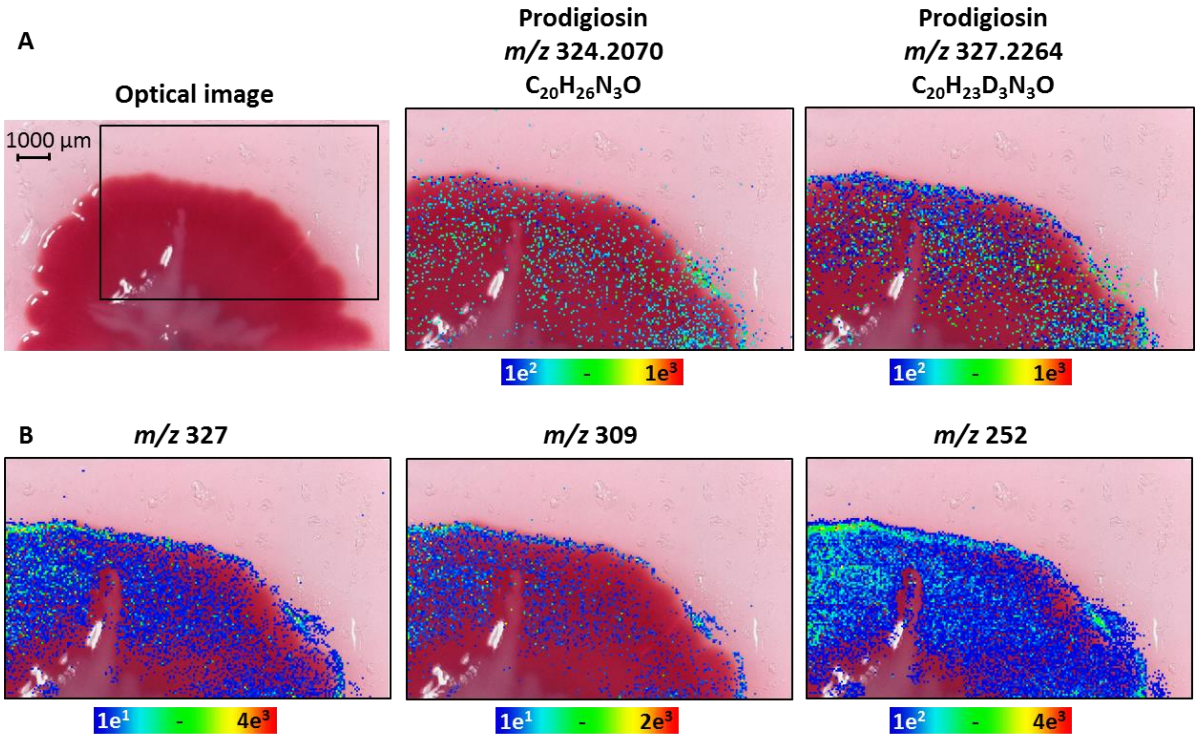


Fig. S12. MALDI-imaging-HRMS of bacterial endophyte *S. marcescens* MSRBB2 grown on nutrient agar with a thin layer of agar supplemented with [methyl-D_3]-L-methionine (0.5 mg/mL). Optical image with assigned scan area and localization of labeled and unlabeled prodigiosin (**3**, $[M+H]^+$ ± 2 ppm, (A)). Characteristic fragments of MALDI-imaging-$HRMS^2$ of labeled prodigiosin $C_{20}H_{23}D_3N_3O$ (**3**, $[M+H]^+$ ± 3 ppm, (B)).

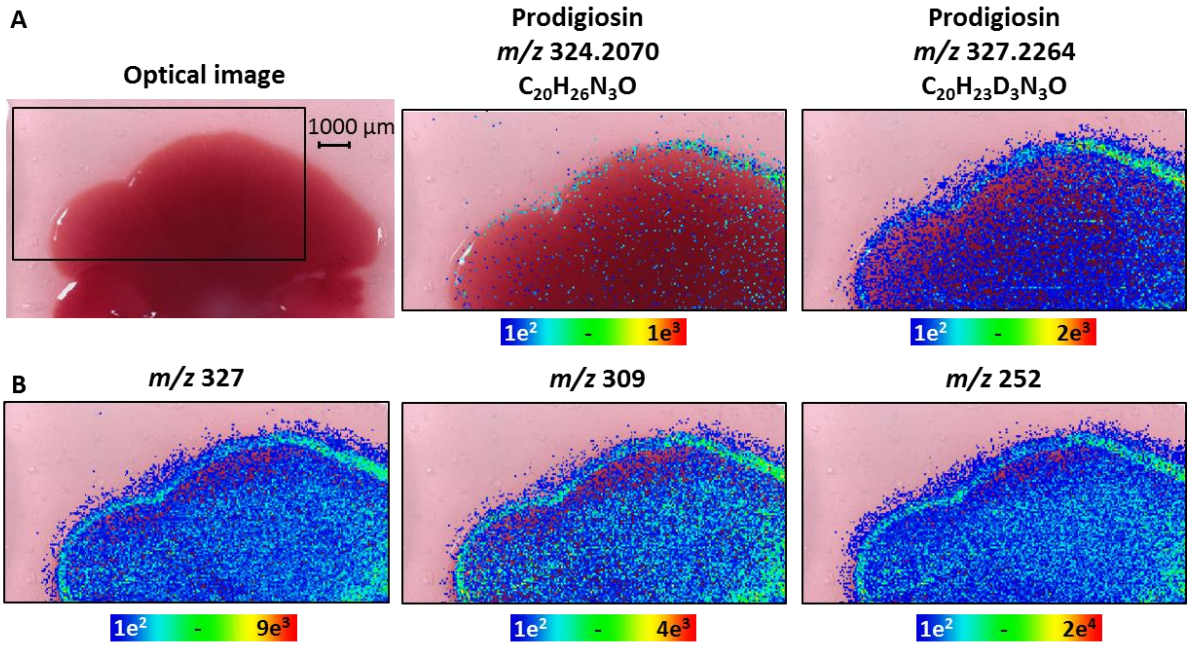


Fig. S13. MALDI-imaging-HRMS of bacterial endophyte *S. marcescens* MSRBB2 grown on nutrient agar with a thin layer of agar supplemented with [methyl-D_3]-L-methionine (2 mg/mL). Optical image with assigned scan area and localization of labeled and unlabeled prodigiosin (**3**, $[M+H]^+$ ± 2 ppm, (A)). Characteristic fragments of MALDI-imaging-HRMS^2 of labeled prodigiosin $C_{20}H_{23}D_3N_3O$ (**3**, $[M+H]^+$ ± 3 ppm, (B)).

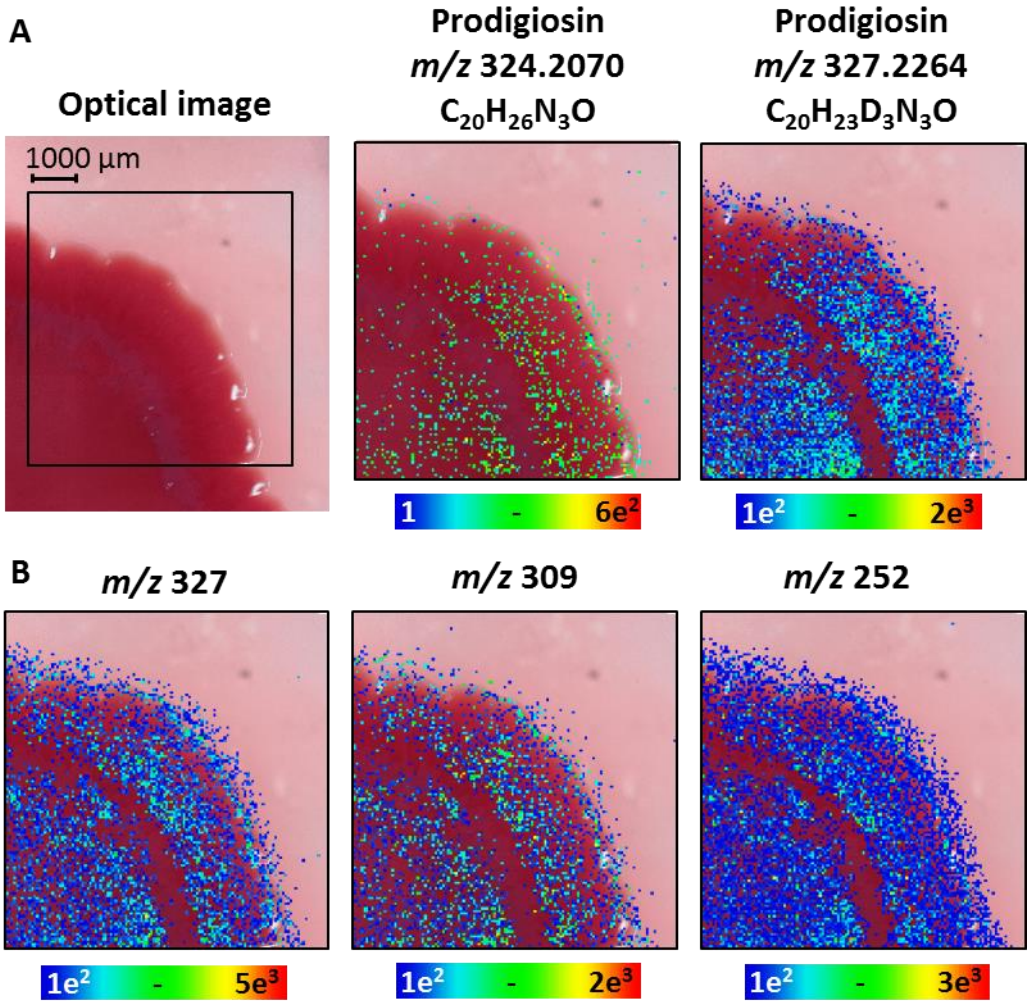


Fig. S14. MALDI-imaging-HRMS of bacterial endophyte *S. marcescens* MSRBB2 grown on nutrient agar with a thin layer of agar supplemented with [methyl-D_3]-L-methionine (2 mg/mL). Optical image with assigned scan area and localization of labeled and unlabeled prodigiosin (**3**, $[M+H]^+$ ± 2 ppm, (A)). Characteristic fragments of MALDI-imaging-$HRMS^2$ of labeled prodigiosin $C_{20}H_{23}D_3N_3O$ (**3**, $[M+H]^+$ ± 3 ppm, (B)).

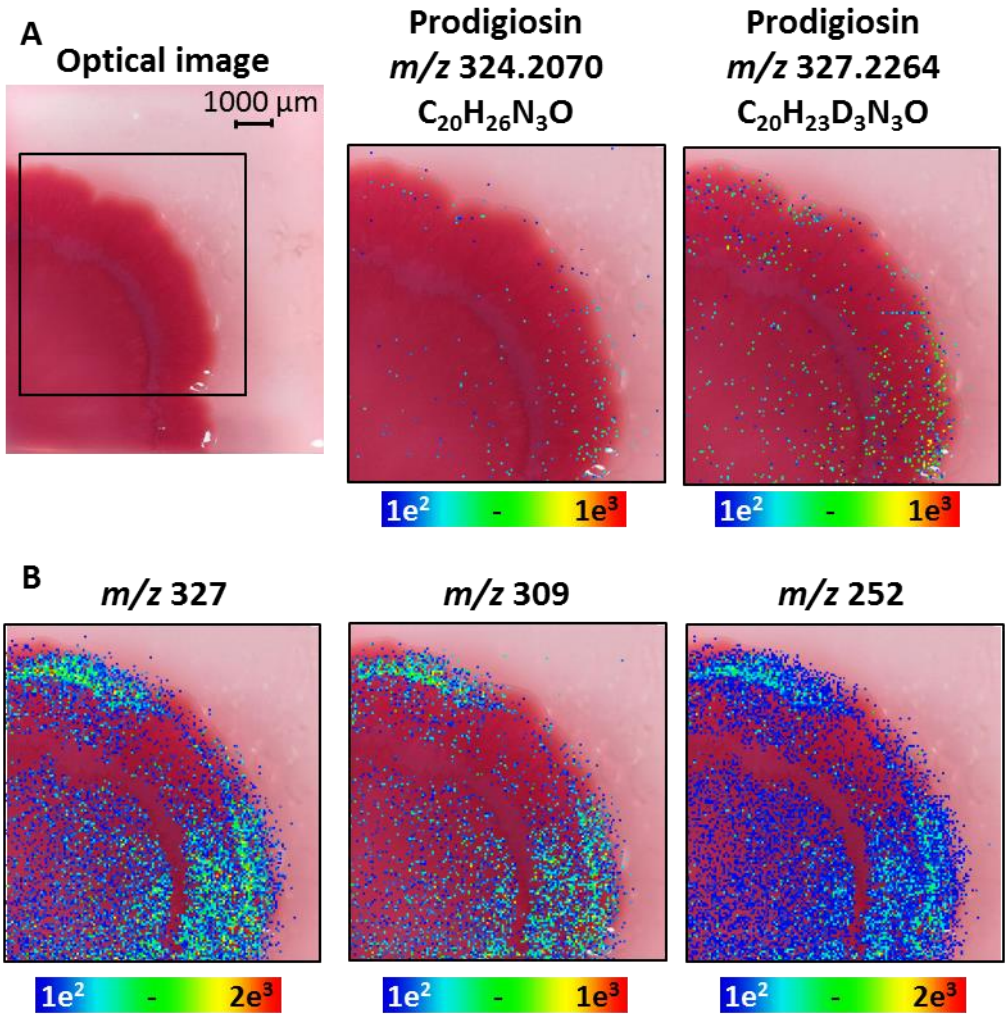


Fig. S15. MALDI-imaging-HRMS of bacterial endophyte *S. marcescens* MSRBB2 grown on nutrient agar with a thin layer of agar supplemented with [methyl-D_3]-L-methionine (2 mg/mL). Optical image with assigned scan area and localization of labeled and unlabeled prodigiosin (**3**, $[M+H]^+$ ± 2 ppm, (A)). Characteristic fragments of MALDI-imaging-$HRMS^2$ of labeled prodigiosin $C_{20}H_{23}D_3N_3O$ (**3**, $[M+H]^+$ ± 3 ppm, (B)).

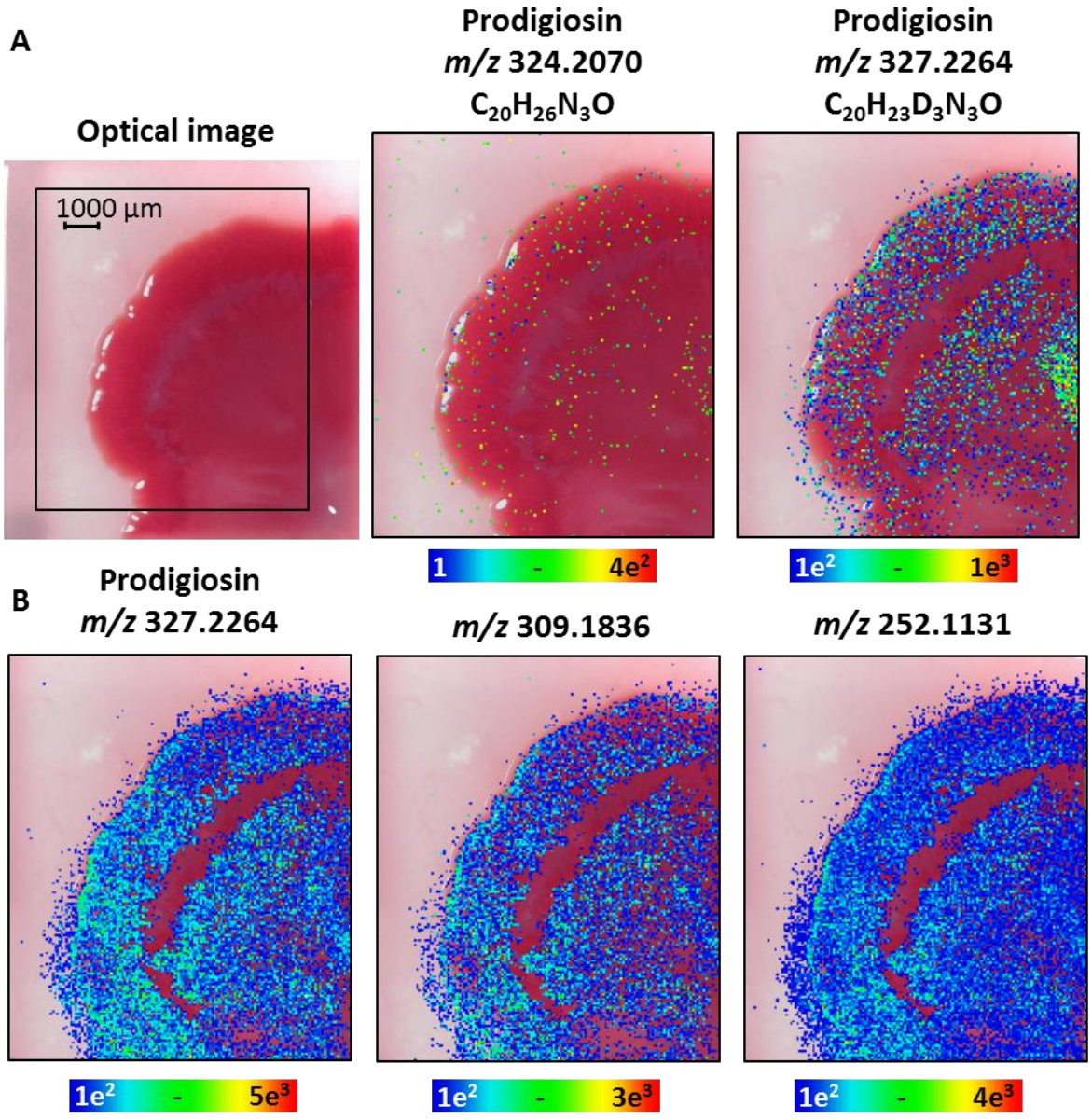


Fig. S16. MALDI-imaging-HRMS of bacterial endophyte *S. marcescens* MSRBB2 grown on potato dextrose agar with a thin layer of agar supplemented with [methyl-D_3]-L-methionine (1 mg/mL). Optical image with assigned scan area (C) and localization of labeled (A) and unlabeled (B) prodiginines ($[M+H]^+$ ± 2 ppm).

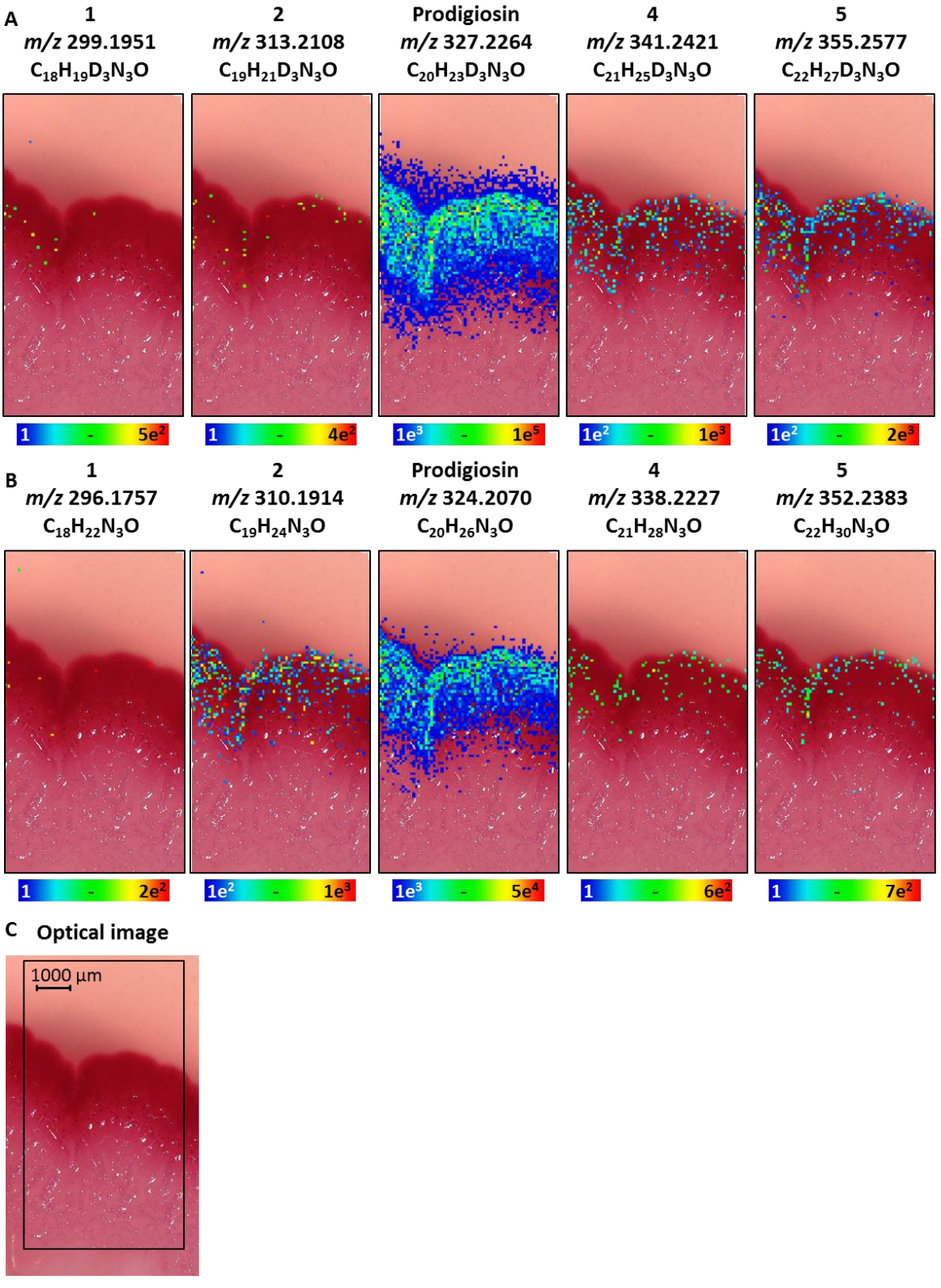


Fig. S17. MALDI-imaging-HRMS of bacterial endophyte *S. marcescens* MSRBB2 grown on potato dextrose agar with a thin layer of agar supplemented with [methyl-D_3]-L-methionine (1 mg/mL). Optical image with assigned scan area and localization of characteristic fragments of MALDI-imaging-HRMS^2 of labeled prodigiosin $C_{20}H_{23}D_3N_3O$ (**3**, $[M+H]^+$ ± 3 ppm).

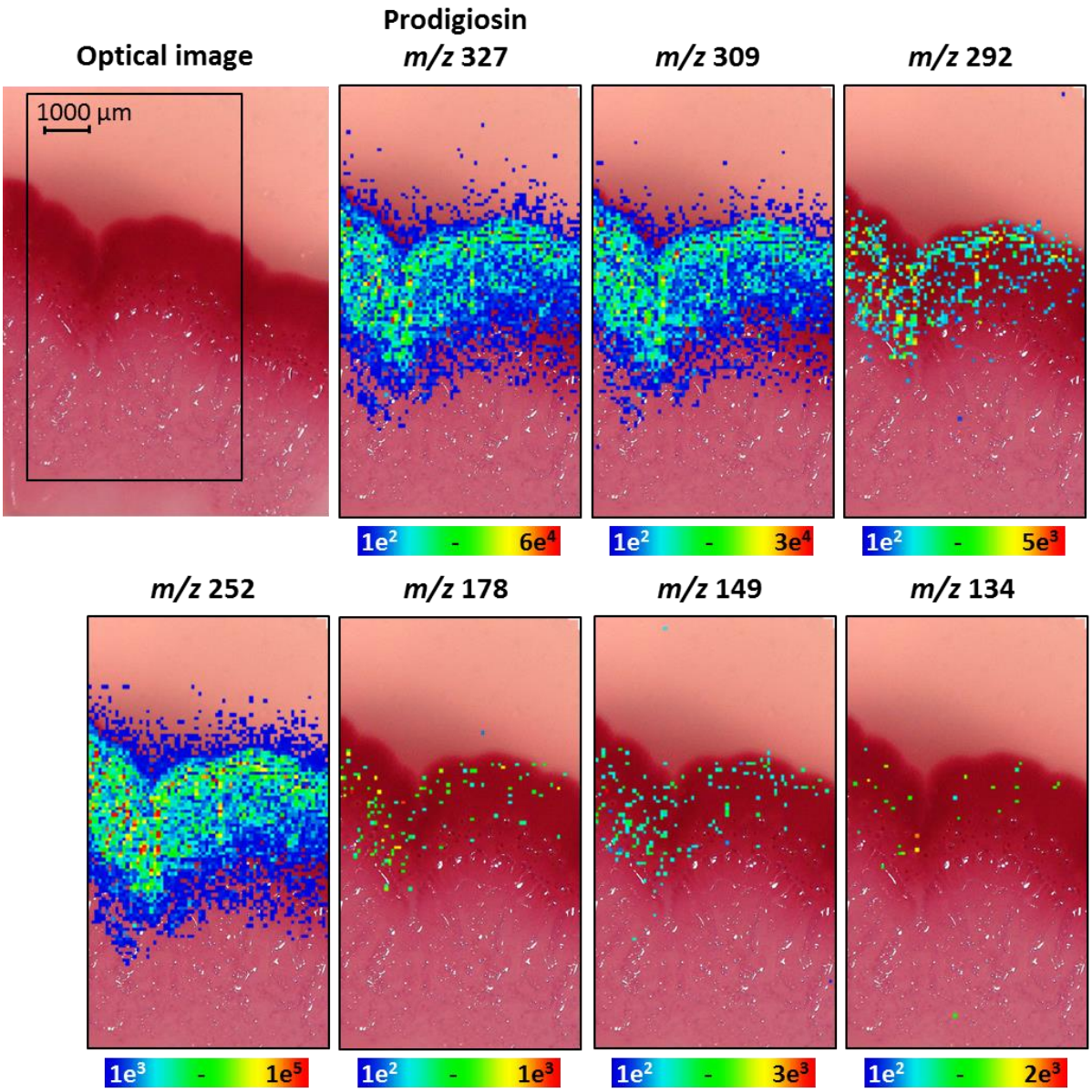


Fig. S18. MALDI-imaging-HRMS of bacterial endophyte *S. marcescens* MSRBB2 grown on potato dextrose agar with a thin layer of agar supplemented with [methyl-D_3]-L-methionine (1 mg/mL). Optical image with assigned scan area (C) and localization of labeled (A) and unlabeled (B) prodiginines ($[M+H]^+$ ± 2 ppm).

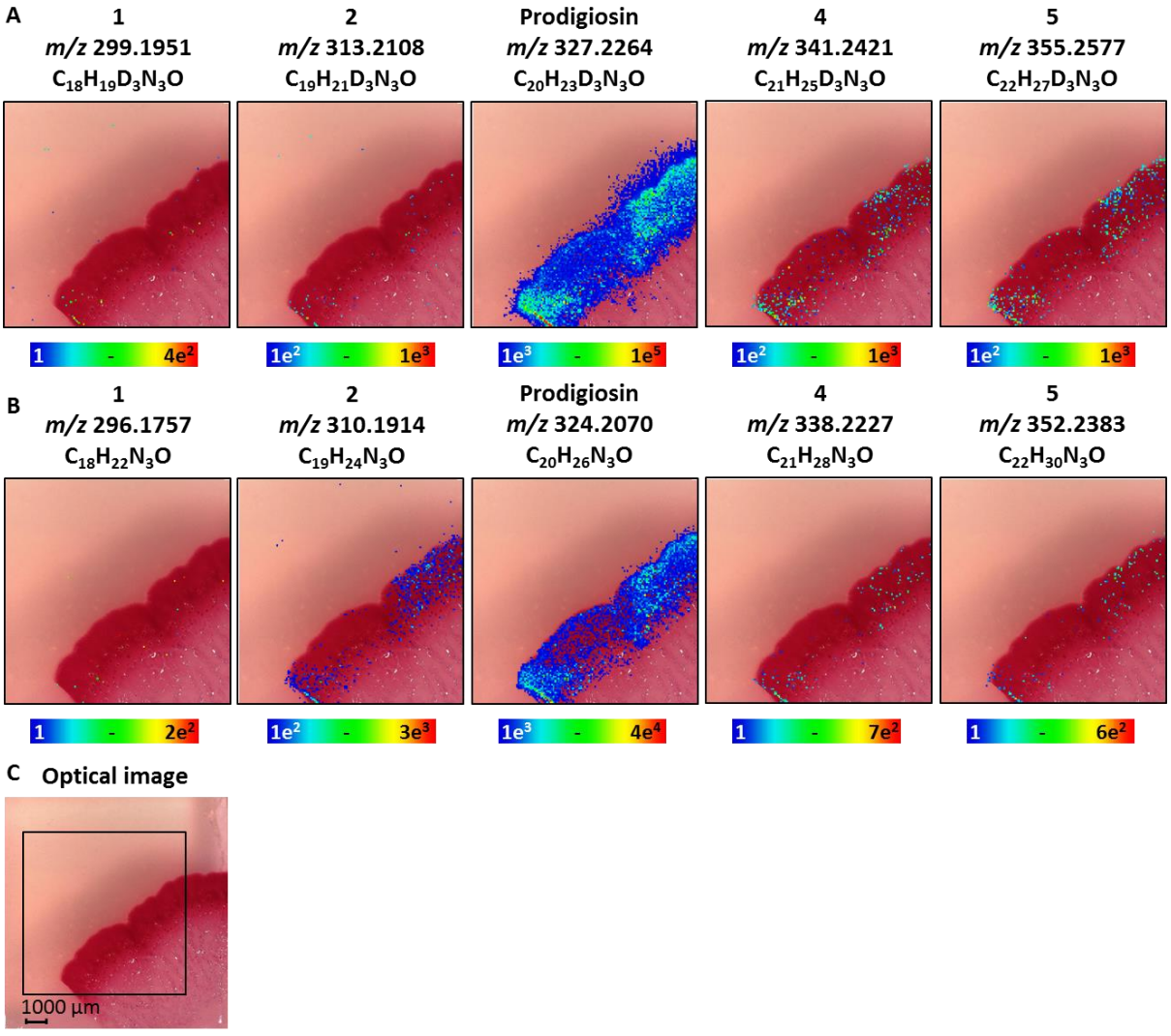


Fig. S19. MALDI-imaging-HRMS of bacterial endophyte *S. marcescens* MSRBB2 grown on potato dextrose agar with a thin layer of agar supplemented with [methyl-D_3]-L-methionine (1 mg/mL). Optical image with assigned scan area and localization of characteristic fragments of MALDI-imaging-HRMS^2 of labeled prodigiosin $C_{20}H_{23}D_3N_3O$ (**3**, $[M+H]^+$ ± 3 ppm).

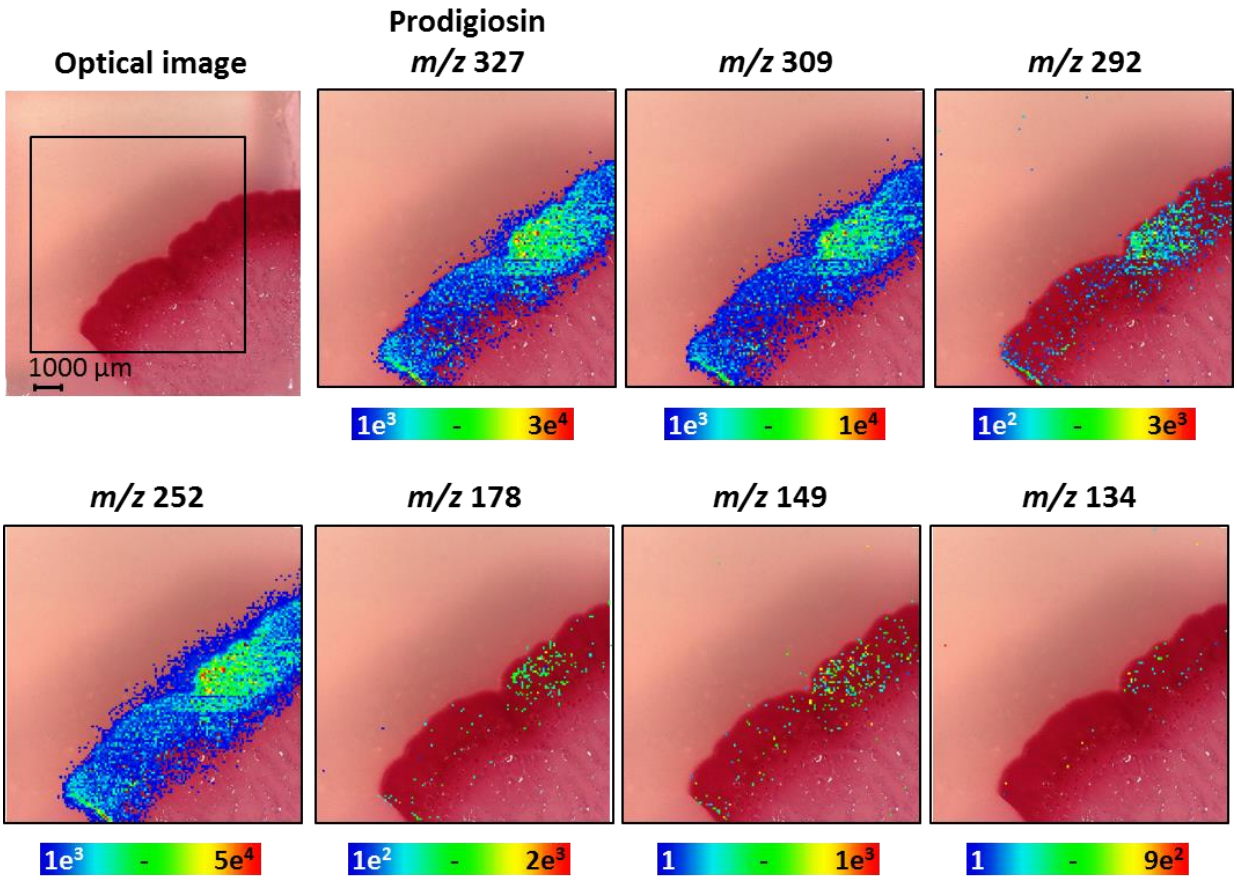


Fig. S20. MALDI-imaging-HRMS of bacterial endophyte *S. marcescens* MSRBB2 grown on potato dextrose agar with a thin layer of agar supplemented with [methyl-D_3]-L-methionine (1 mg/mL). Optical image with assigned scan area (C) and localization of labeled (A) and unlabeled (B) prodiginines ($[M+H]^+$ ± 2 ppm).

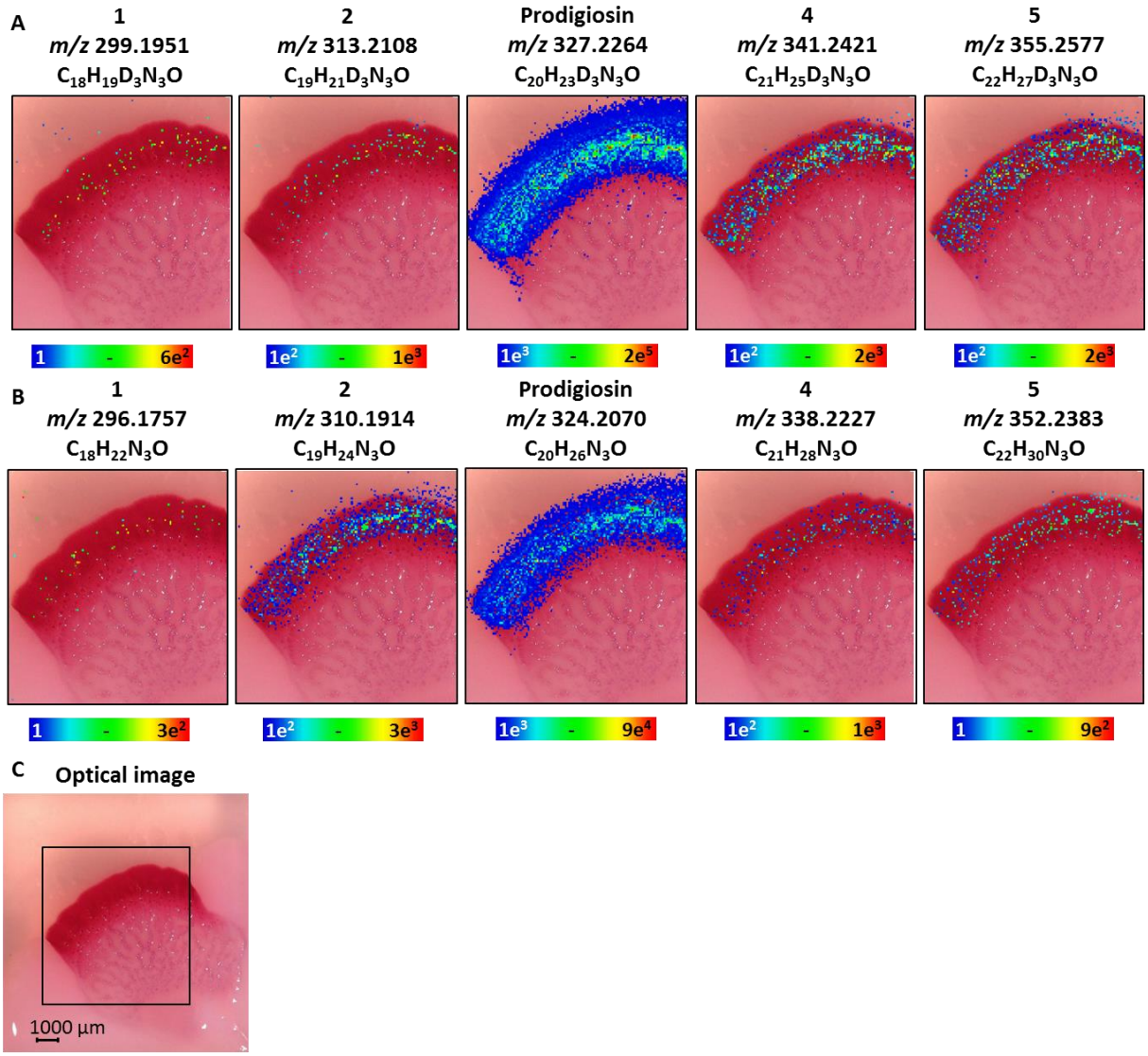


Fig. S21. MALDI-imaging-HRMS of bacterial endophyte *S. marcescens* MSRBB2 grown on potato dextrose agar with a thin layer of agar supplemented with [methyl-D_3]-L-methionine (1 mg/mL). Optical image with assigned scan area and localization of characteristic fragments of MALDI-imaging-HRMS^2 of labeled prodigiosin $C_{20}H_{23}D_3N_3O$ (**3**, $[M+H]^+$ ± 3 ppm).

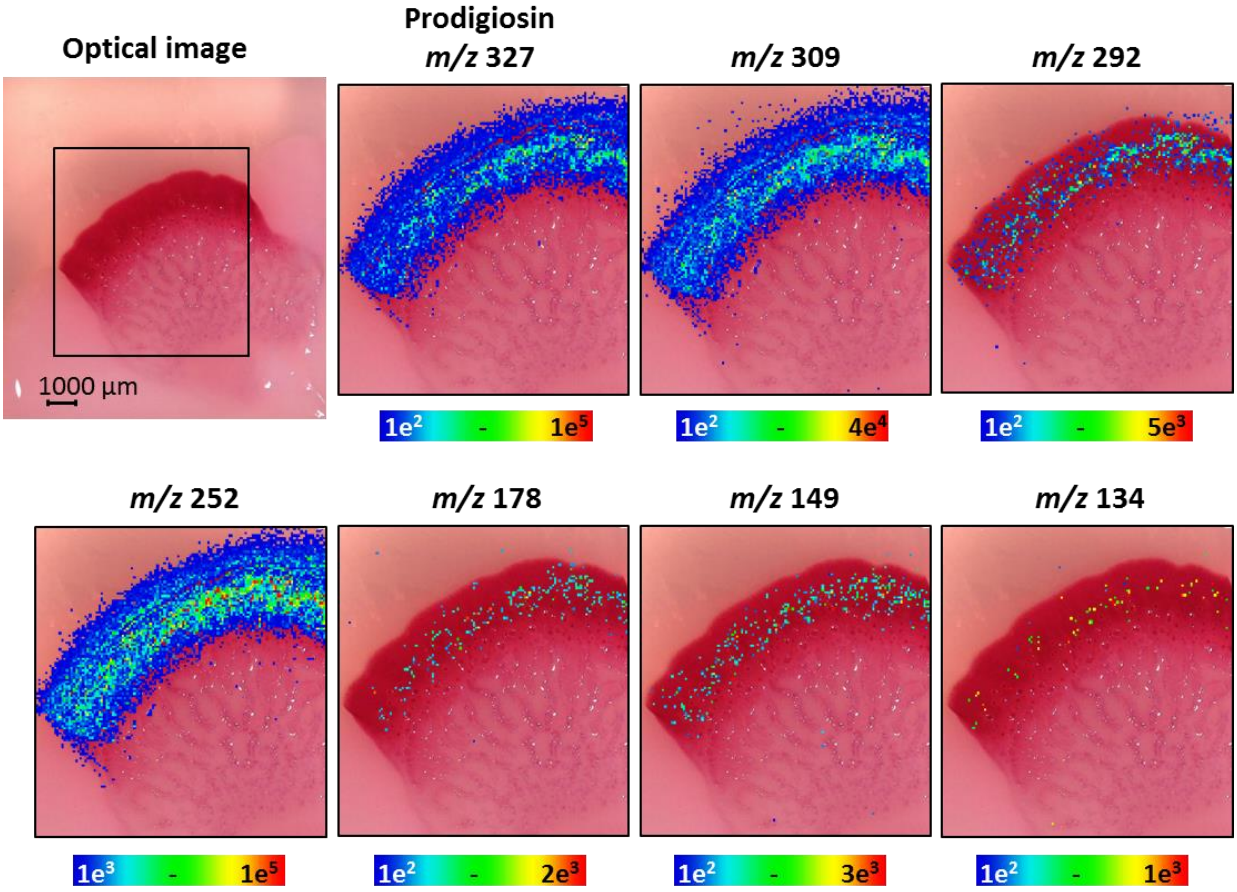


Fig. S22. MALDI-imaging-HRMS of bacterial endophyte *S. marcescens* MSRBB2 grown on potato dextrose agar with a thin layer of agar supplemented with $^{15}NH_4Cl$ (1 mg/mL). Optical image with assigned scan area and localization of labeled, unlabeled, and natural ^{13}C-isotopic prodigiosin (**3**, $[M+H]^+$ ± 2 ppm).

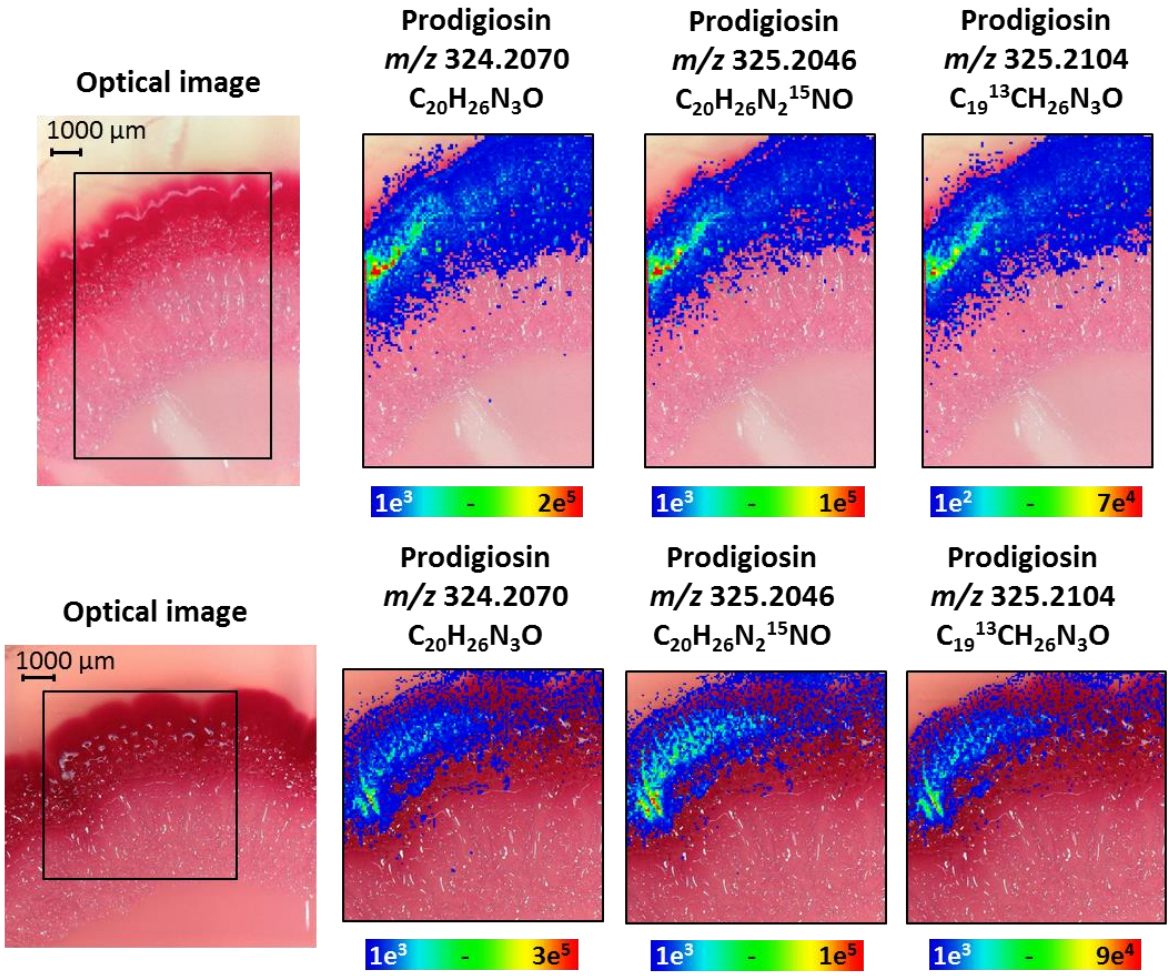


Fig. S23. MALDI-imaging-HRMS of bacterial endophyte *S. marcescens* MSRBB2 grown on potato dextrose agar with a thin layer of agar supplemented with [1-^{13}C]-L-proline (1 mg/mL). Optical image with assigned scan area (C) and localization of labeled (A) and unlabeled (B) prodiginines ($[M+H]^+$ ± 2 ppm).

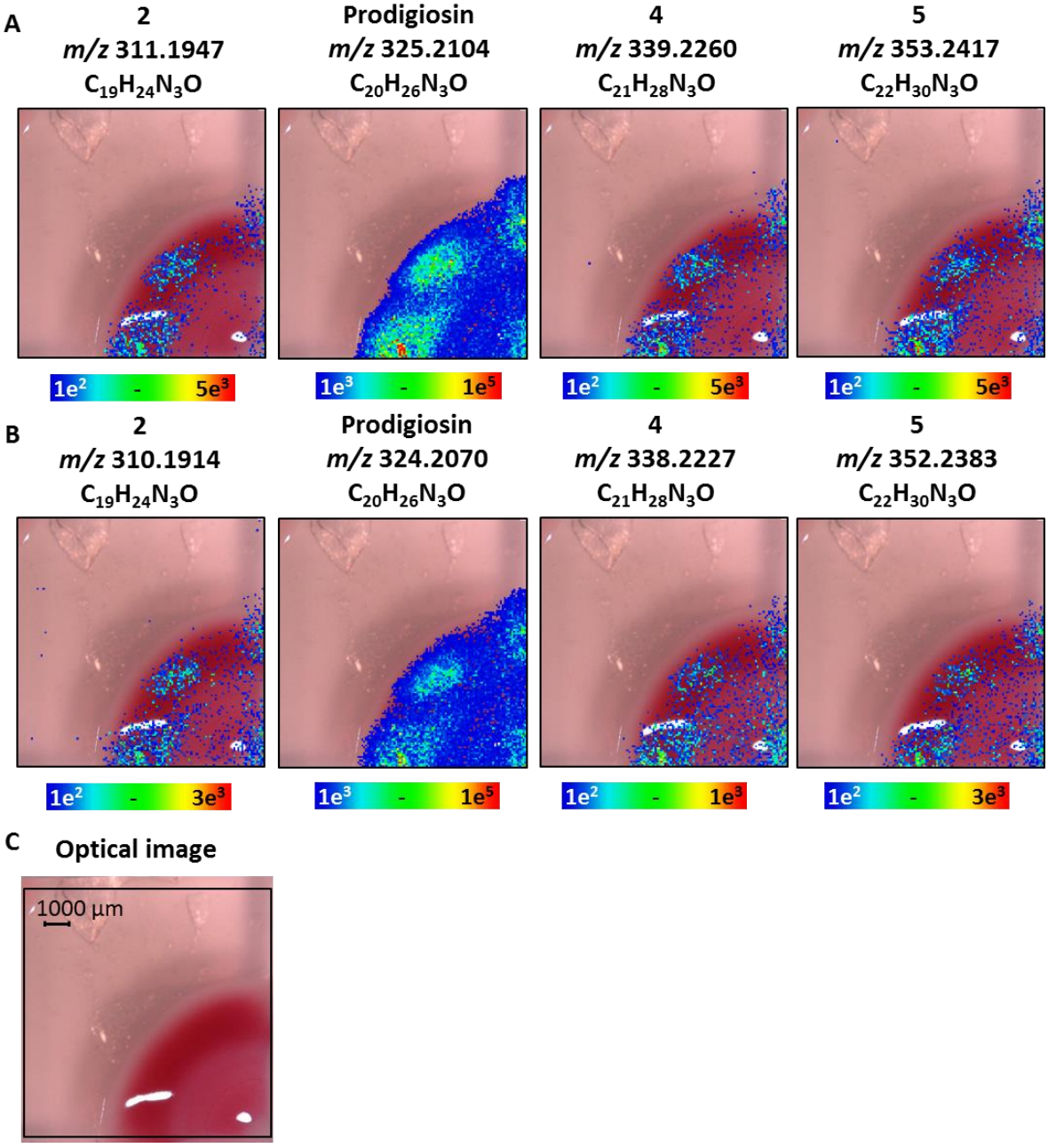


Fig. S24. MALDI-imaging-HRMS of bacterial endophyte *S. marcescens* MSRBB2 grown on potato dextrose agar with a thin layer of agar supplemented with [1-^{13}C]-L-proline (1 mg/mL). Optical image with assigned scan area (C) and localization of labeled (A) and unlabeled (B) prodiginines ($[M+H]^+$ ± 2 ppm).

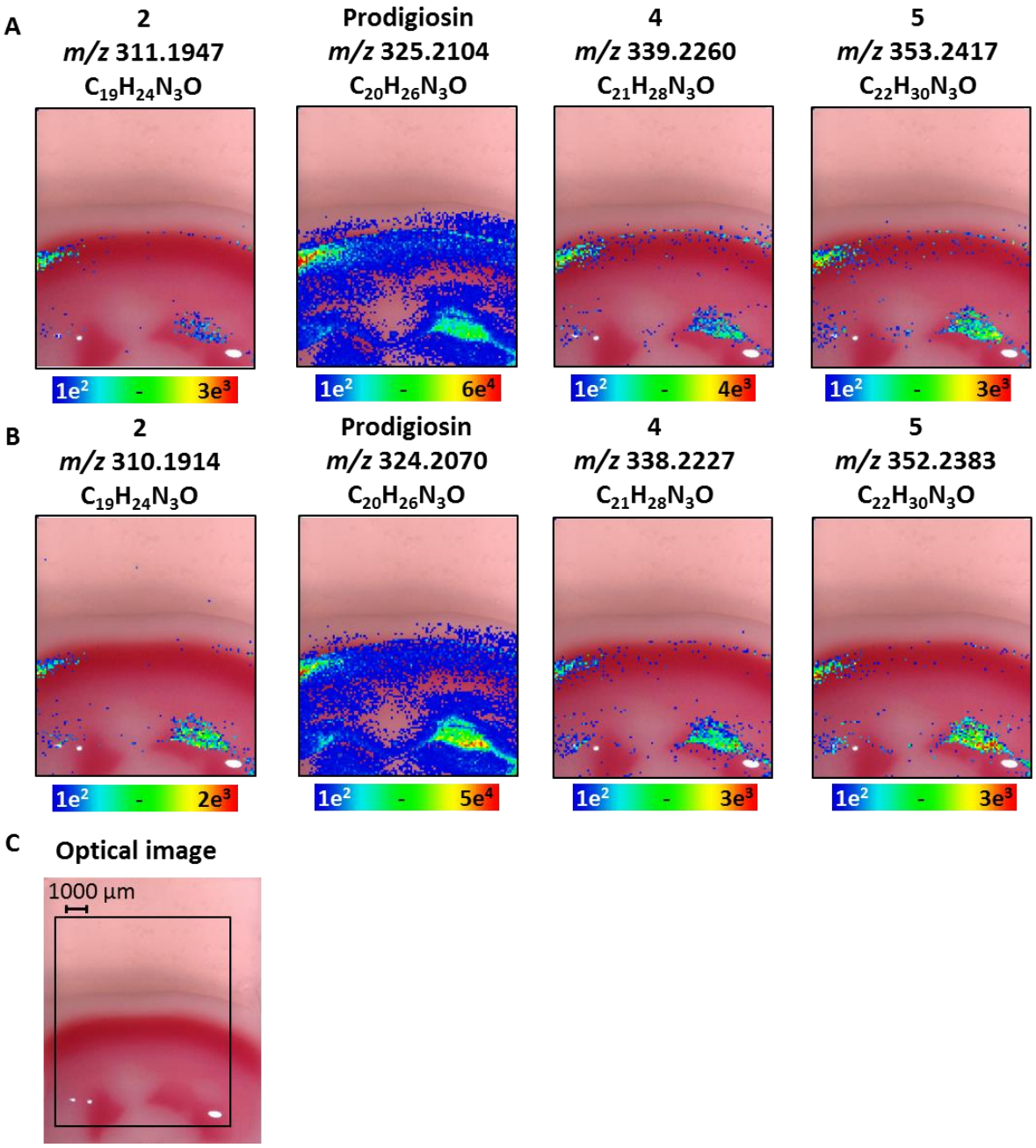


Fig. S25. MALDI-imaging-HRMS of bacterial endophyte *S. marcescens* MSRBB2 grown on potato dextrose agar with a thin layer of agar supplemented with ^{15}N-L-serine (1 mg/mL). Optical image with assigned scan area and localization of labeled, unlabeled, and natural ^{13}C-isotopic prodigiosin (**3**, $[M+H]^+$ ± 2 ppm)

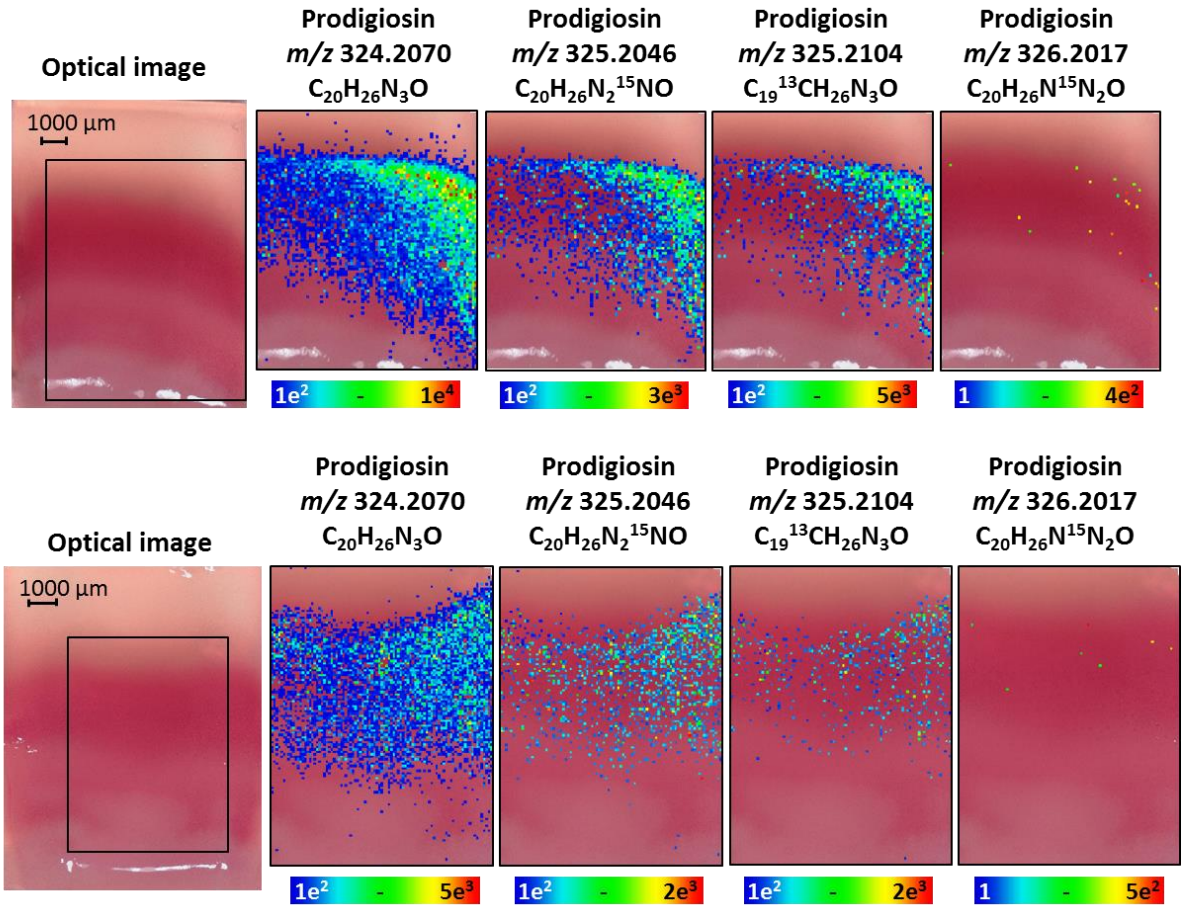


Fig. S26. MALDI-imaging-HRMS of bacterial endophyte *S. marcescens* MSRBB2 grown on potato dextrose agar with a thin layer of agar supplemented with ^{15}N-L-serine (1 mg/mL). Optical image with assigned scan area and localization of labeled, unlabeled, and natural ^{13}C-isotopic prodigiosin (**3**, $[M+H]^+$ ± 2 ppm)

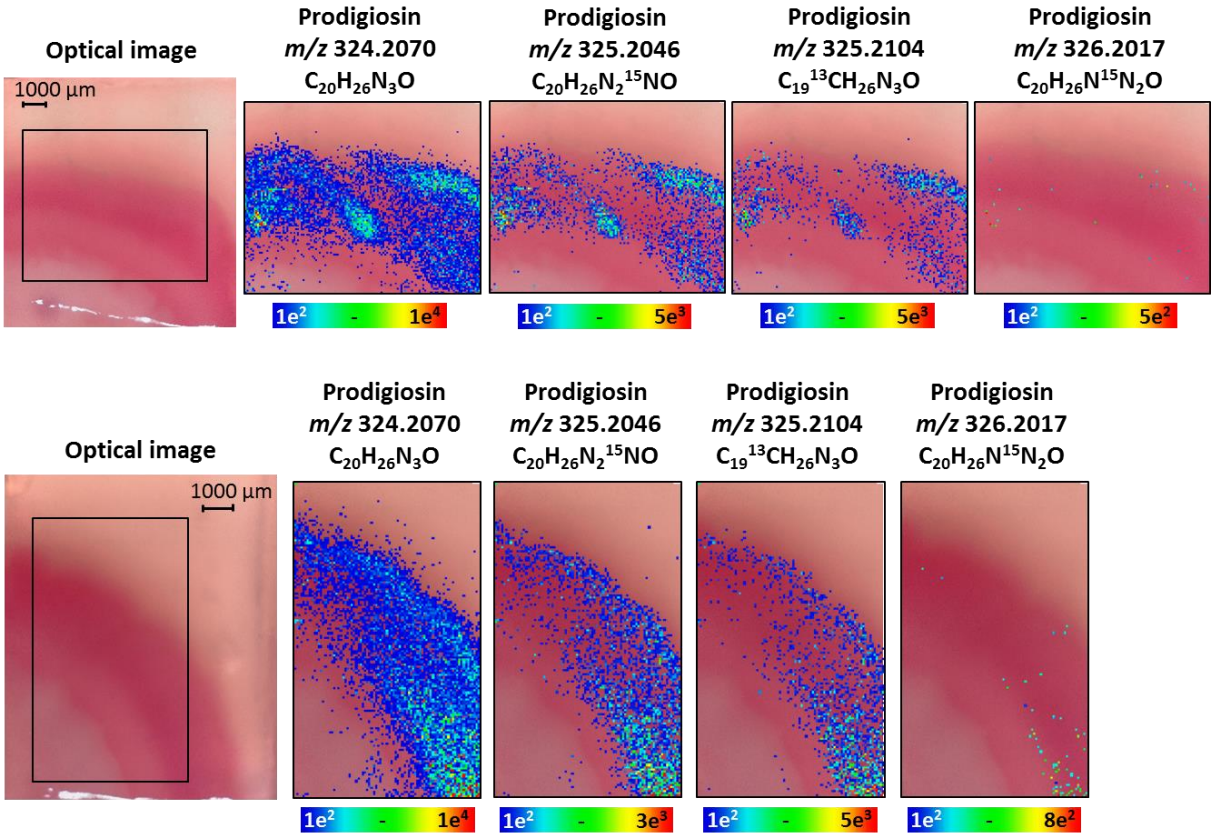


Fig. S27. MALDI-imaging-HRMS of bacterial endophyte *S. marcescens* MSRBB2 grown on potato dextrose agar with a thin layer of agar supplemented with ^{15}N-L-serine (1 mg/mL). Optical image with assigned scan area and localization of labeled, unlabeled, and natural ^{13}C-isotopic prodigiosin (**3**, $[M+H]^+$ ± 2 ppm)

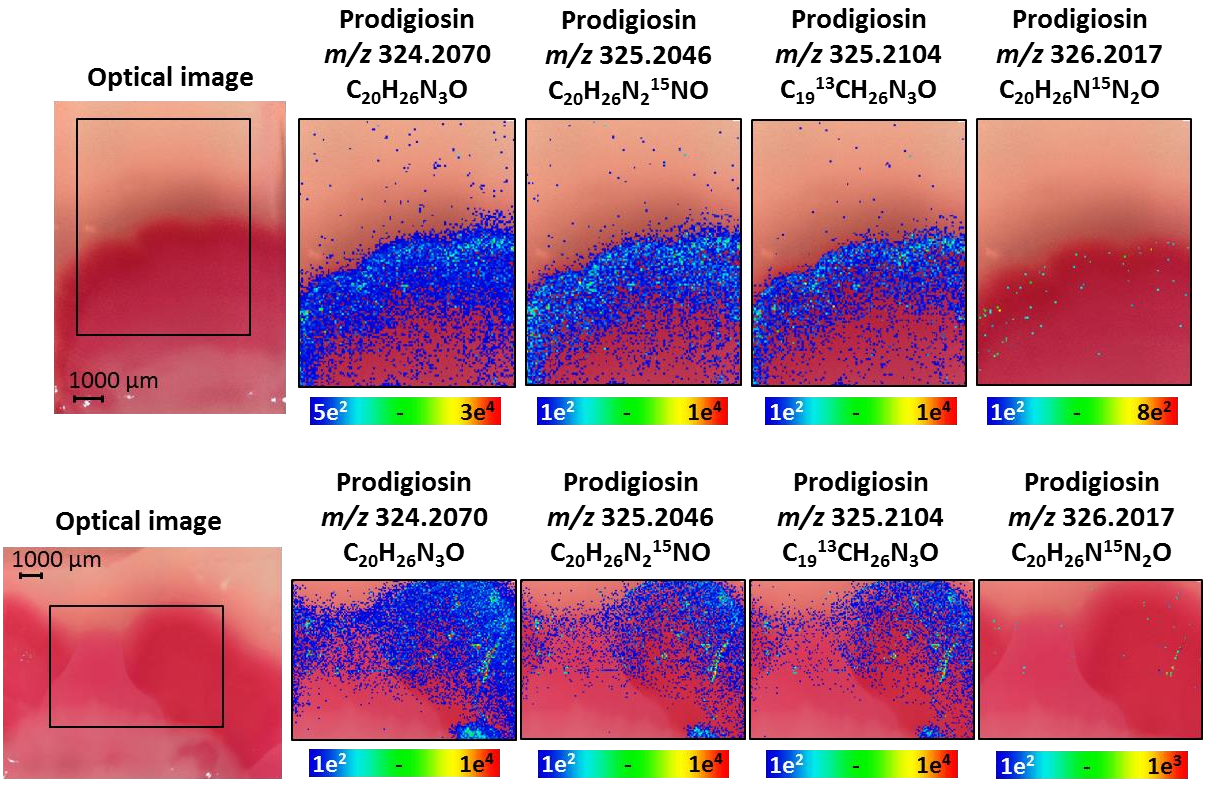


Fig. S28. MALDI-imaging-HRMS of bacterial endophyte *S. marcescens* MSRBB2 grown on potato dextrose agar with a thin layer of agar supplemented with [methyl-D_3]-L-methionine (0.5 mg/mL). Optical image with assigned scan area and localization of labeled and unlabeled prodigiosin (**3**, $[M+H]^+$ ± 2 ppm, (A)). Characteristic fragments of MALDI-imaging-$HRMS^2$ of labeled prodigiosin $C_{20}H_{23}D_3N_3O$ (**3**, $[M+H]^+$ ± 3 ppm, (B)).

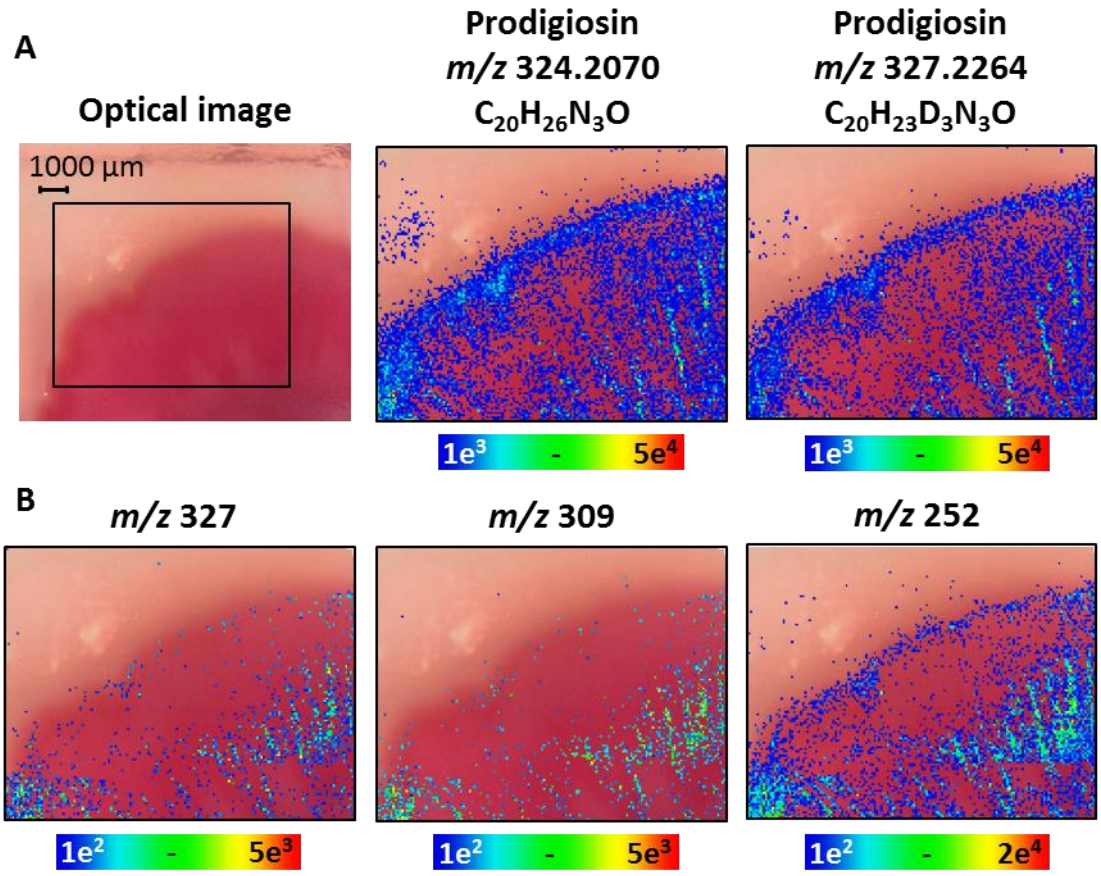


Fig. S29. MALDI-imaging-HRMS of bacterial endophyte *S. marcescens* MSRBB2 grown on potato dextrose agar with a thin layer of agar supplemented with [methyl-D_3]-L-methionine (0.5 mg/mL). Optical image with assigned scan area and localization of labeled and unlabeled prodigiosin (**3**, $[M+H]^+$ ± 2 ppm, (A)). Characteristic fragments of MALDI-imaging-$HRMS^2$ of labeled prodigiosin $C_{20}H_{23}D_3N_3O$ (**3**, $[M+H]^+$ ± 3 ppm, (B)).

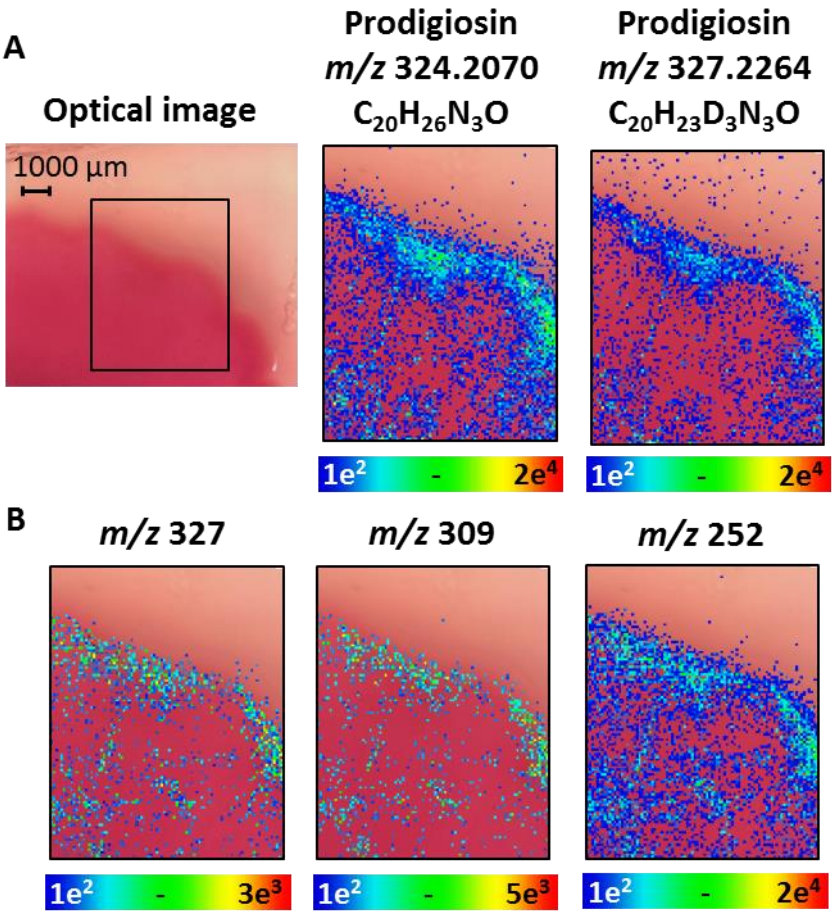


Fig. S30. MALDI-imaging-HRMS of bacterial endophyte *S. marcescens* MSRBB2 grown on potato dextrose agar with a thin layer of agar supplemented with [methyl-D_3]-L-methionine (2 mg/mL). Optical image with assigned scan area and localization of labeled and unlabeled prodigiosin (**3**, $[M+H]^+$ ± 2 ppm, (A)). Characteristic fragments of MALDI-imaging-$HRMS^2$ of labeled prodigiosin $C_{20}H_{23}D_3N_3O$ (**3**, $[M+H]^+$ ± 3 ppm, (B)).

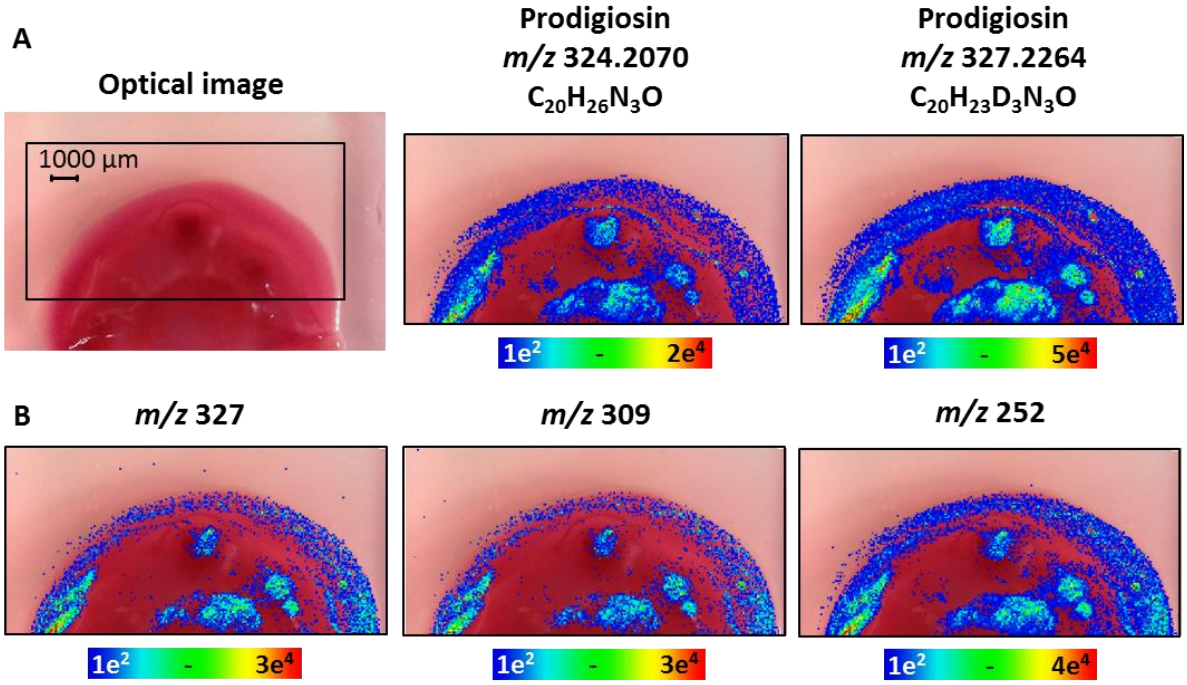


Fig. S31. MALDI-imaging-HRMS of bacterial endophyte *S. marcescens* MSRBB2 grown on potato dextrose agar with a thin layer of agar supplemented with [methyl-D_3]-L-methionine (2 mg/mL). Optical image with assigned scan area and localization of labeled and unlabeled prodigiosin (**3**, $[M+H]^+$ ± 2 ppm, (A)). Characteristic fragments of MALDI-imaging-$HRMS^2$ of labeled prodigiosin $C_{20}H_{23}D_3N_3O$ (**3**, $[M+H]^+$ ± 3 ppm, (B)).

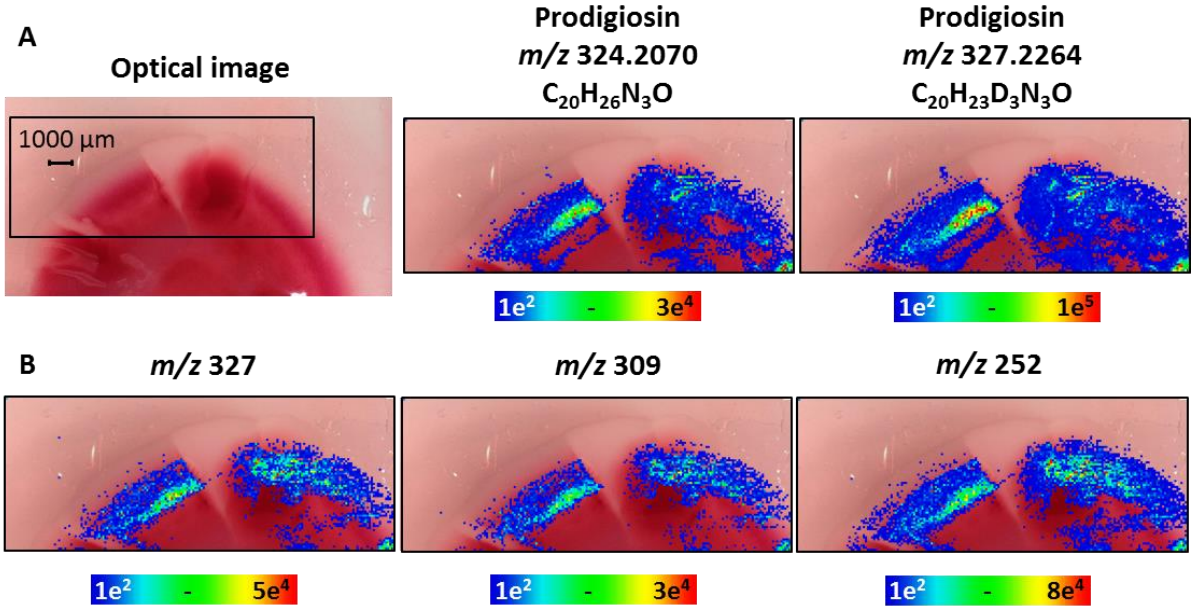


Fig. S32. MALDI-imaging-HRMS of bacterial endophyte *S. marcescens* MSRBB2 grown on potato dextrose agar with a thin layer of agar supplemented with [methyl-D_3]-L-methionine (2 mg/mL). Optical image with assigned scan area and localization of labeled and unlabeled prodigiosin (**3**, $[M+H]^+$ ± 2 ppm, (A)). Characteristic fragments of MALDI-imaging-$HRMS^2$ of labeled prodigiosin $C_{20}H_{23}D_3N_3O$ (**3**, $[M+H]^+$ ± 3 ppm, (B)).

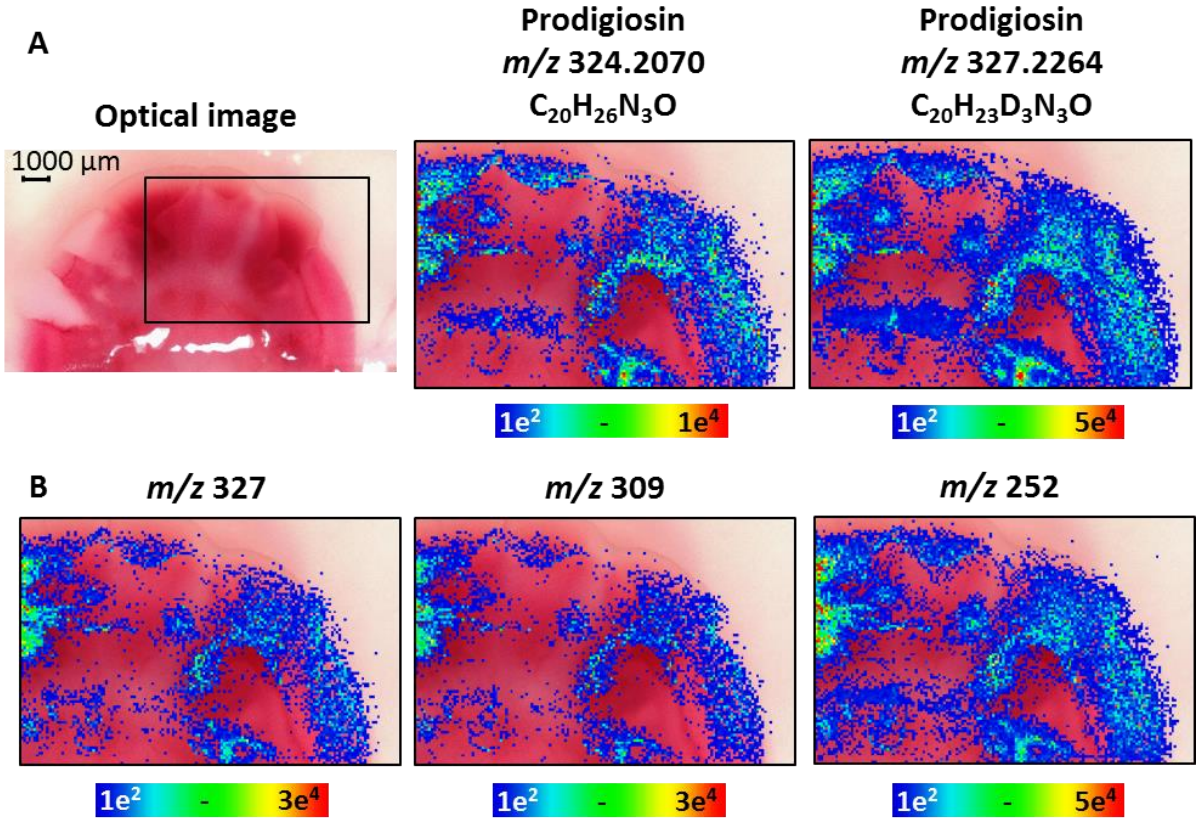


Fig. S33. MALDI-imaging-HRMS of bacterial endophyte *S. marcescens* MSRBB2 grown on potato dextrose agar with a thin layer of agar supplemented with [methyl-D_3]-L-methionine (2 mg/mL). Optical image with assigned scan area and localization of labeled and unlabeled prodigiosin (**3**, $[M+H]^+$ ± 2 ppm, (A)). Characteristic fragments of MALDI-imaging-$HRMS^2$ of labeled prodigiosin $C_{20}H_{23}D_3N_3O$ (**3**, $[M+H]^+$ ± 3 ppm, (B)).

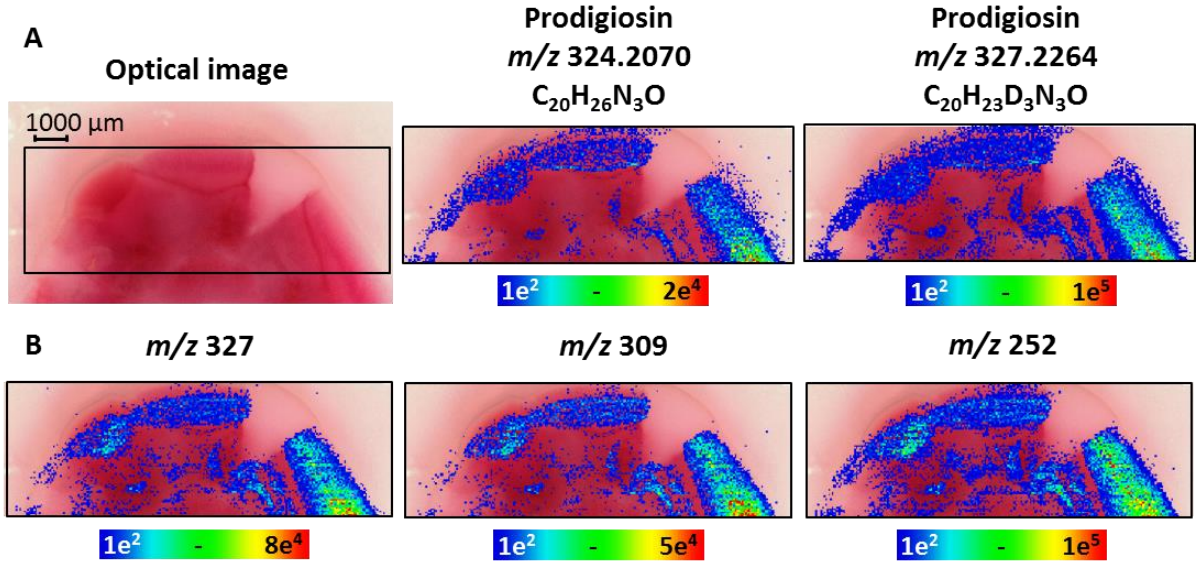


Fig. S34. MALDI-imaging-HRMS control of bacterial endophyte *S. marcescens* MSRBB2 grown on nutrient agar without stable isotope supplements. Optical image with assigned scan area and localization of labeled, unlabeled, and natural ^{13}C-isotopic prodigiosin (**3**, $[M+H]^+$ ± 2 ppm).

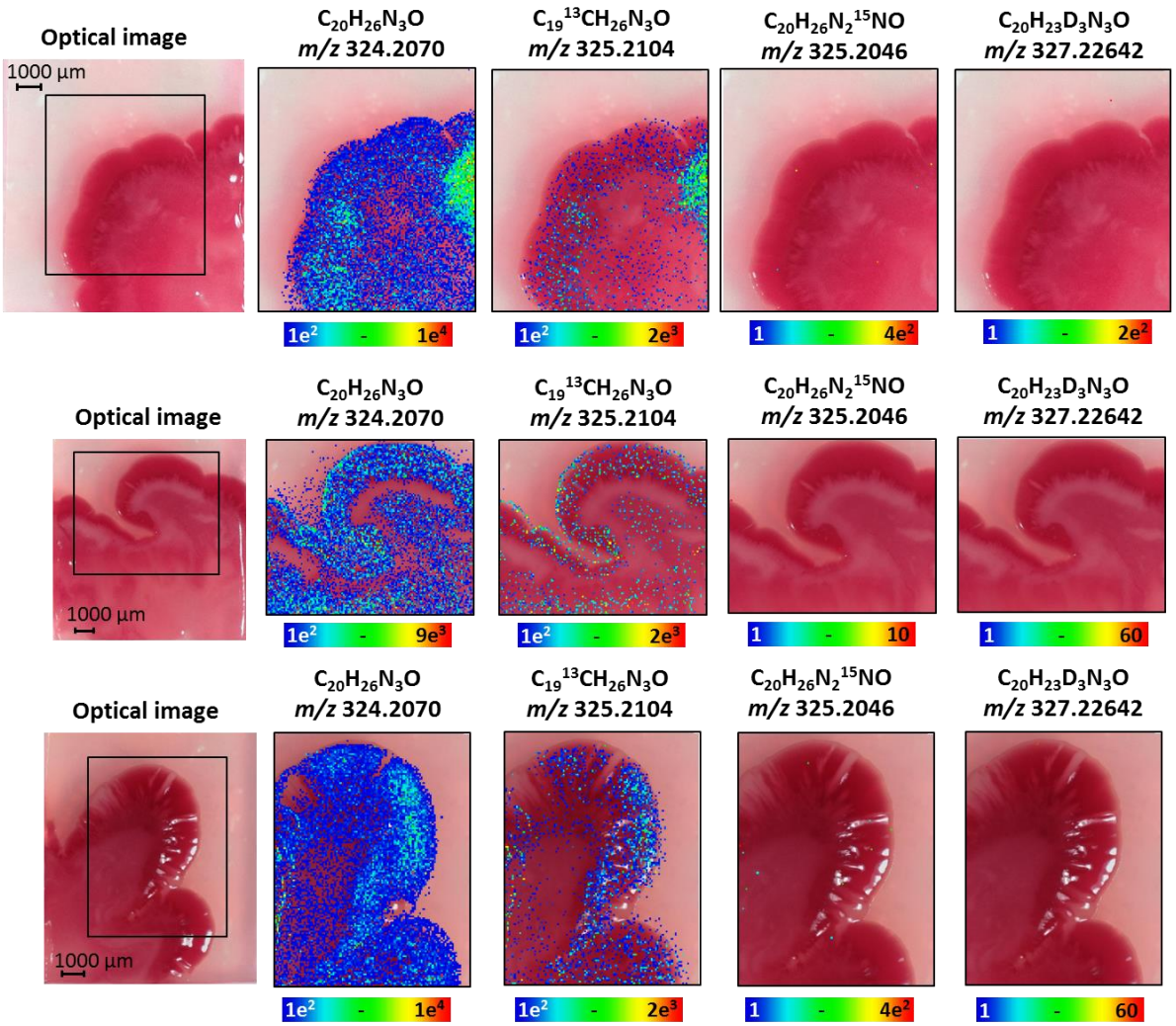


Fig. S35. MALDI-imaging-HRMS control of bacterial endophyte *S. marcescens* MSRBB2 grown on potato dextrose agar without stable isotope supplements for 14 days. Optical image with assigned scan area and localization of labeled, unlabeled, and natural ^{13}C-isotopic prodigiosin (**3**, $[M+H]^+$ ± 2 ppm).

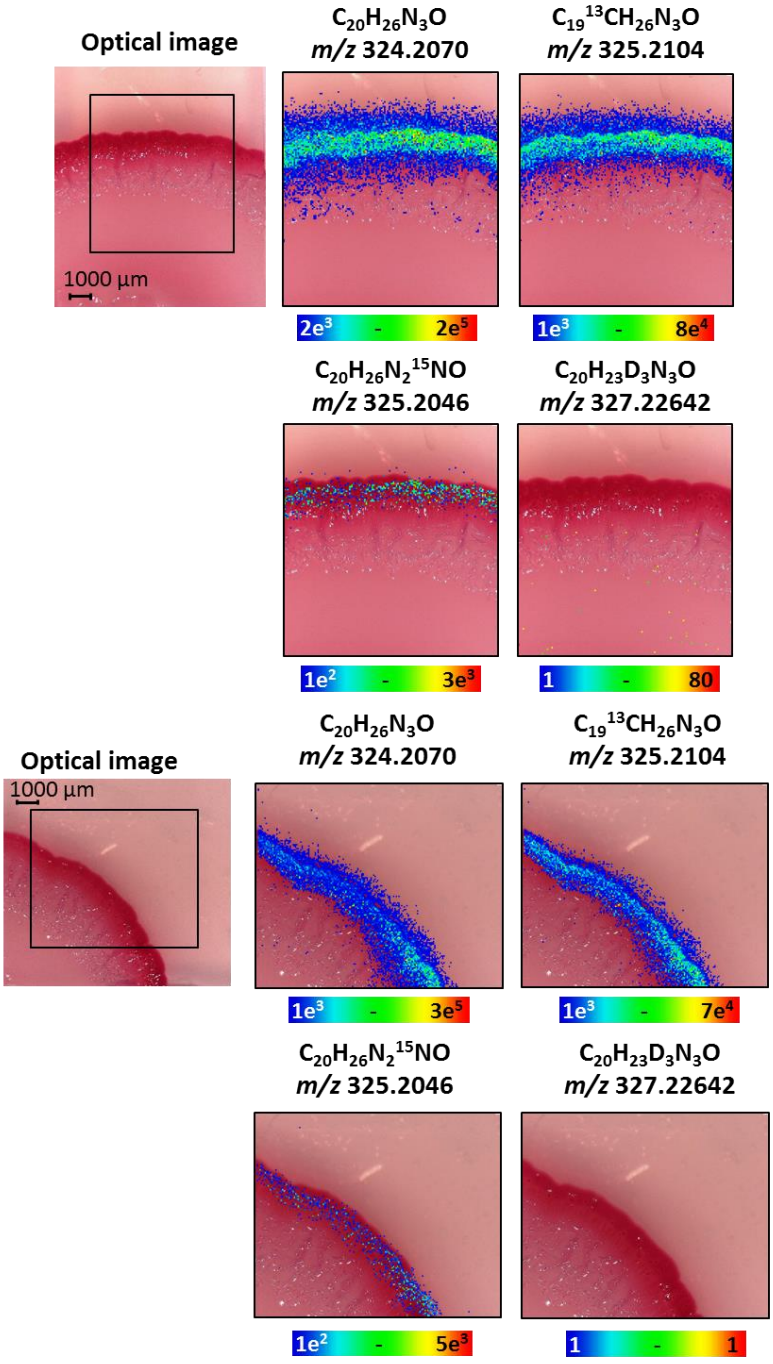


Fig. S36. HRMS spectra of 2-methyl-3-propyl prodiginine with incorporated methyl-D_3 group derived from 1 mg/mL [methyl-D_3]-L-methionine on nutrient agar (compound **1** $[M+H]^+$: *m/z* 299, $C_{18}H_{19}D_3N_3O$).

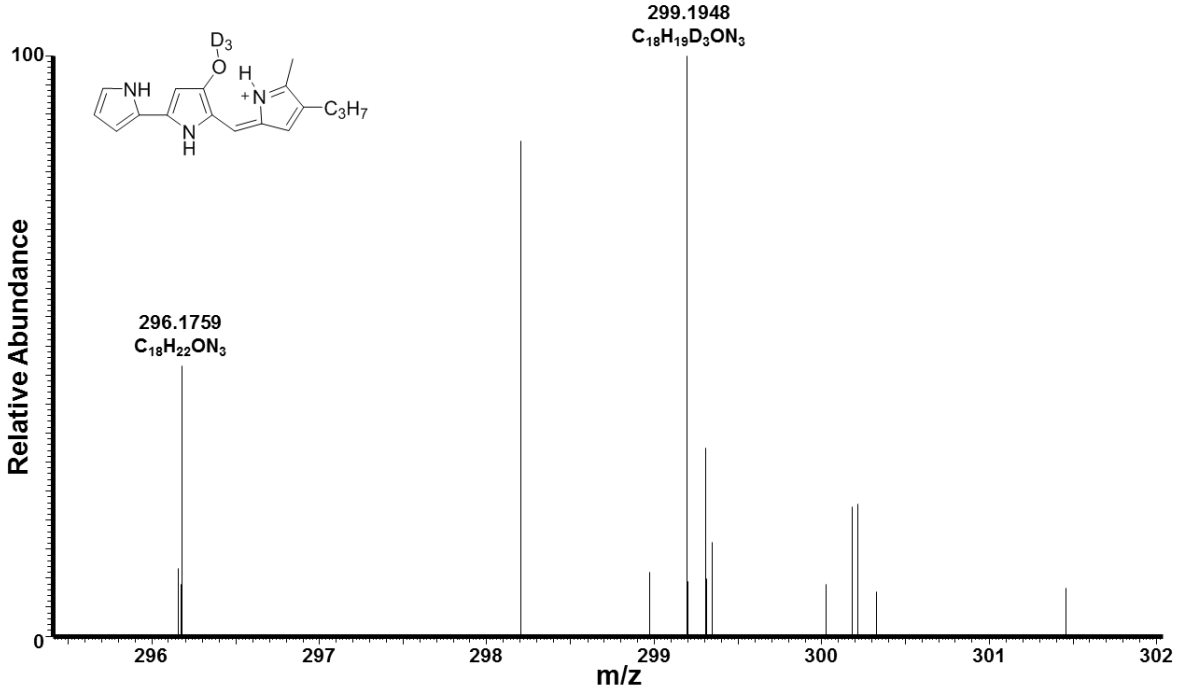


Fig. S37. HRMS spectra of 2-methyl-3-butyl prodiginine with incorporated methyl-D_3 group derived from 1 mg/mL [methyl-D_3]-L-methionine on nutrient agar (compound **2** $[M+H]^+$: *m/z* 313, $C_{19}H_{21}D_3N_3O$).

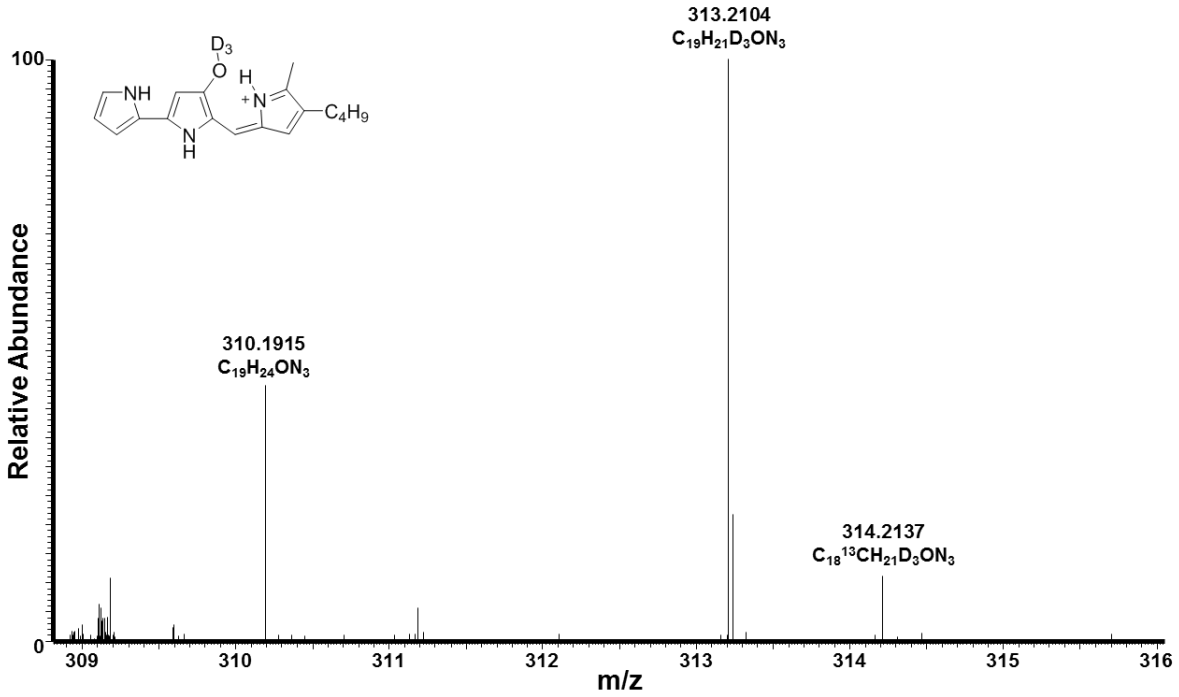


Fig. S38. HRMS spectra of prodigiosin with incorporated methyl-D_3 group derived from 1 mg/mL [methyl-D_3]-L-methionine on nutrient agar (compound **3** $[M+H]^+$: *m/z* 327, $C_{20}H_{23}D_3N_3O$).

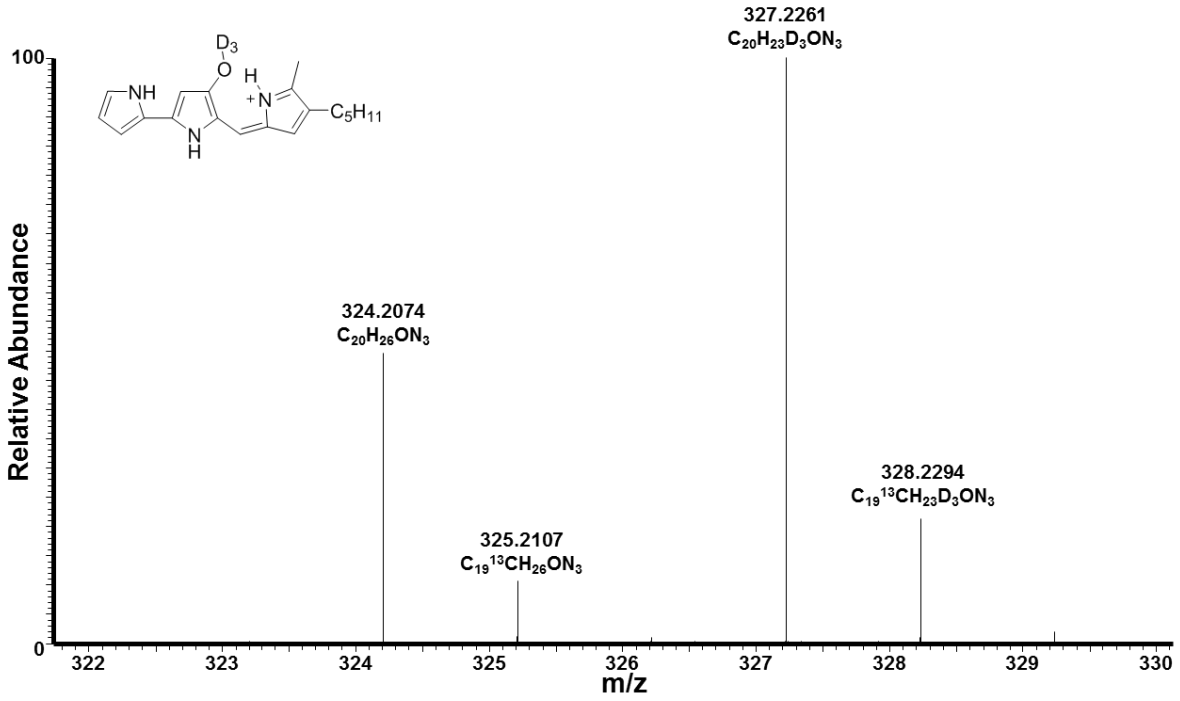


Fig. S39. HRMS spectra of 2-methyl-3-hexyl prodiginine with incorporated methyl-D_3 group derived from 1 mg/mL [methyl-D_3]-L-methionine on nutrient agar (compound **4** $[M+H]^+$: *m/z* 341, $C_{21}H_{25}D_3N_3O$).

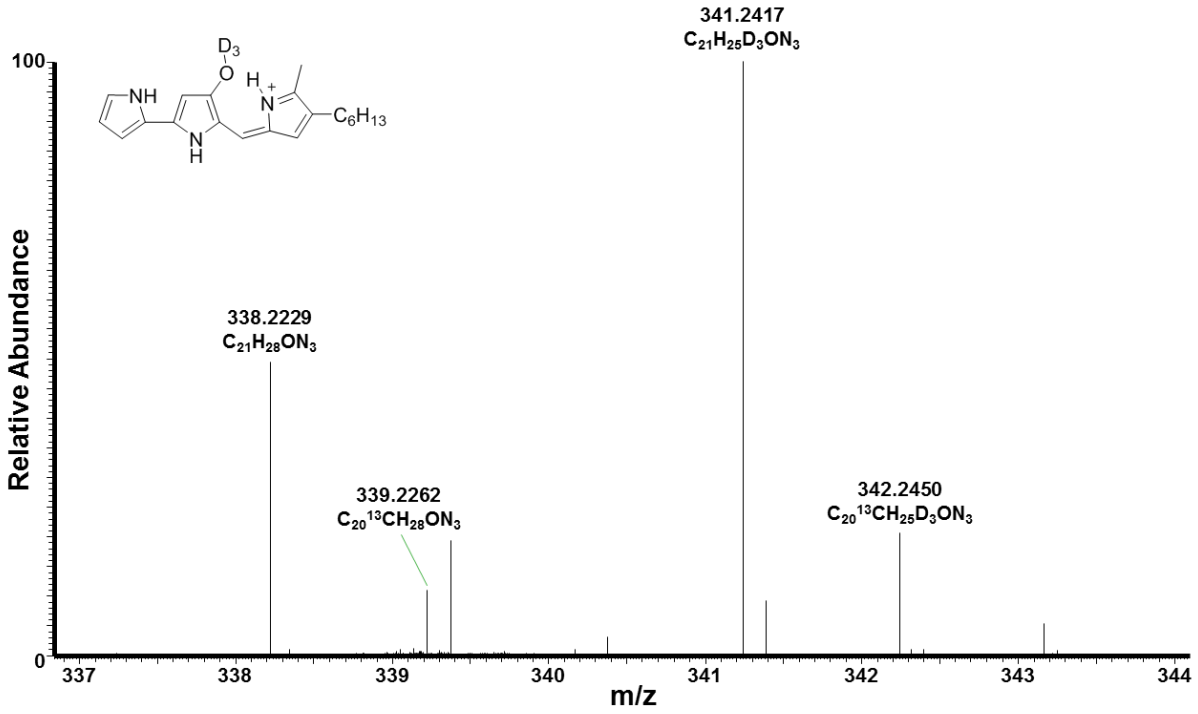


Fig. S40. HRMS spectra of 2-methyl-3-heptyl prodiginine with incorporated methyl-D_3 group derived from 1 mg/mL [methyl-D_3]-L-methionine on nutrient agar (compound **5** $[M+H]^+$: *m/z* 355, $C_{22}H_{27}D_3N_3O$).

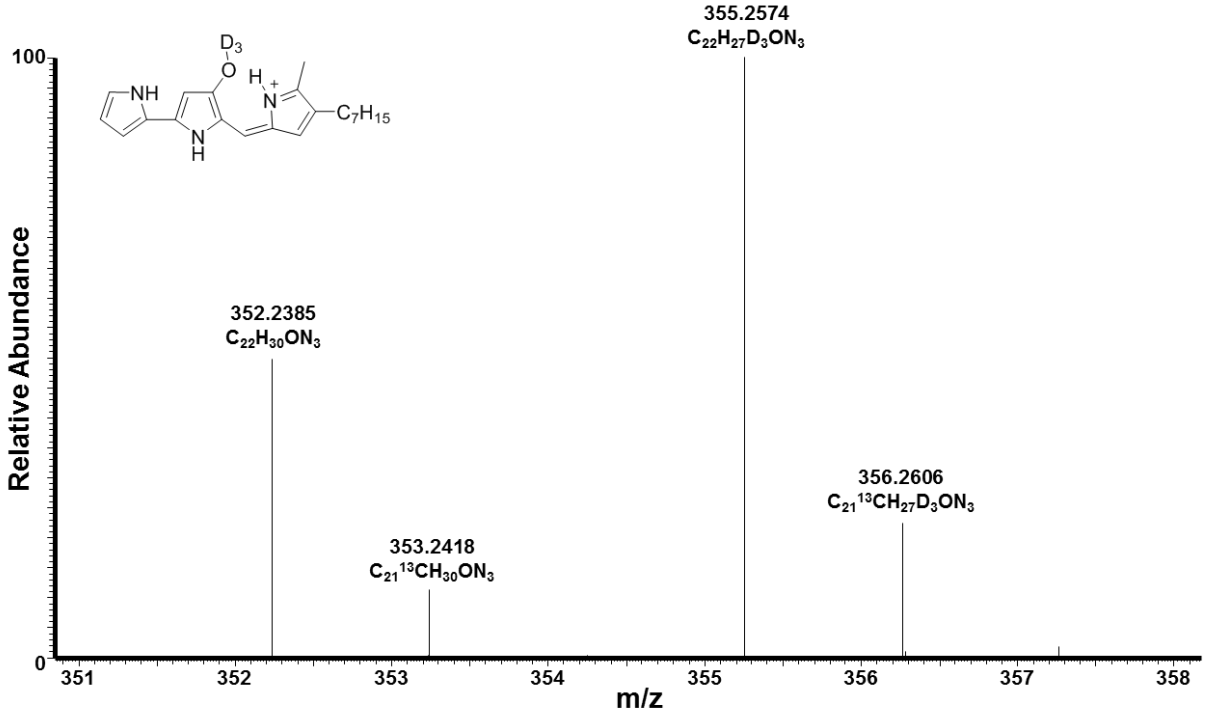


Fig. S41. HRMS spectra of 2-methyl-3-propyl prodiginine with incorporated ^{15}N derived from $^{15}NH_4Cl$ from labeled nutrient agar (compound **1** $[M+H]^+$: *m/z* 297, $C_{18}H_{22}N_2{}^{15}NO$).

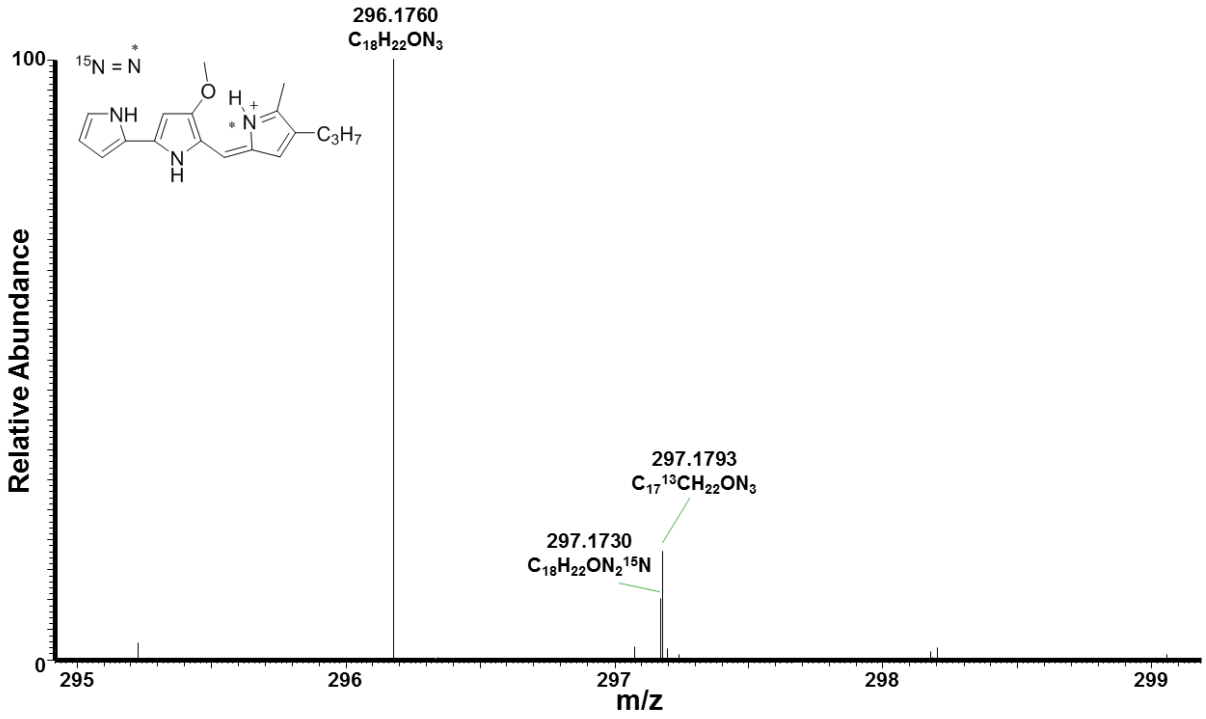


Fig. S42. HRMS spectra of 2-methyl-3-butyl prodiginine with incorporated ^{15}N derived from $^{15}NH_4Cl$ from labeled nutrient agar (compound **2** $[M+H]^+$: *m/z* 311, $C_{19}H_{24}N_2{}^{15}NO$).

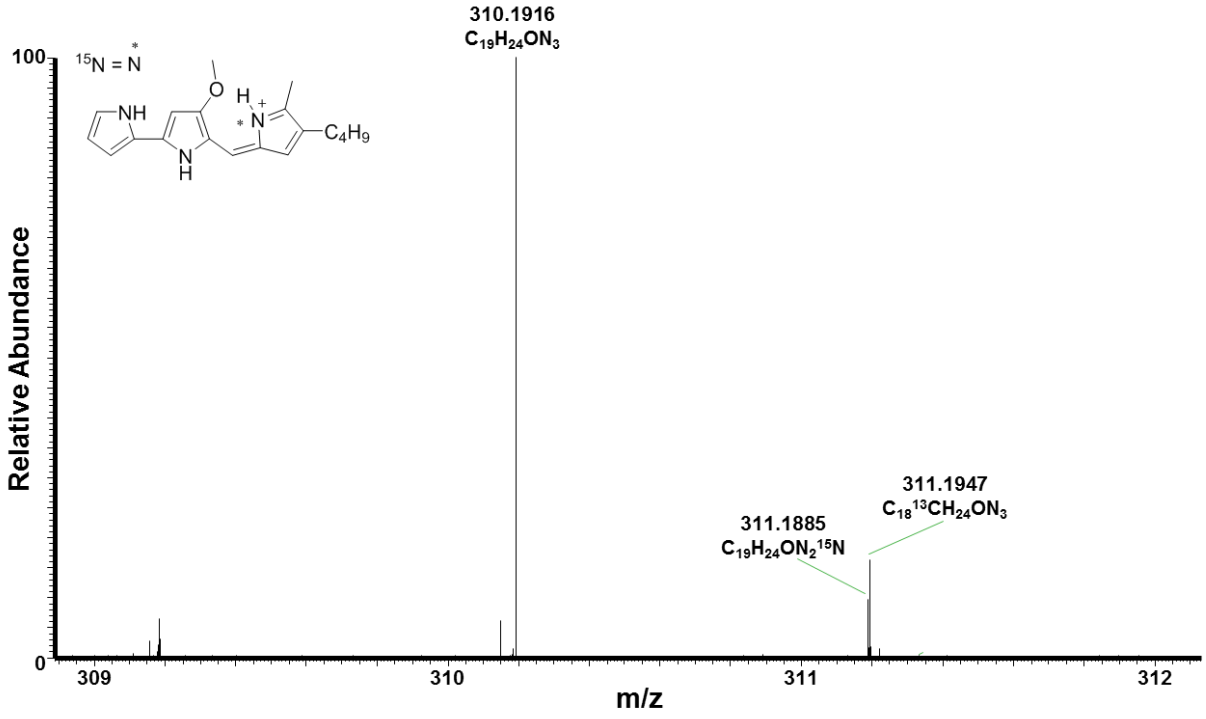


Fig. S43. HRMS spectra of prodigiosin with incorporated ^{15}N derived from $^{15}NH_4Cl$ from labeled nutrient agar (compound **3** $[M+H]^+$: *m/z* 325, $C_{20}H_{26}N_2{}^{15}NO$).

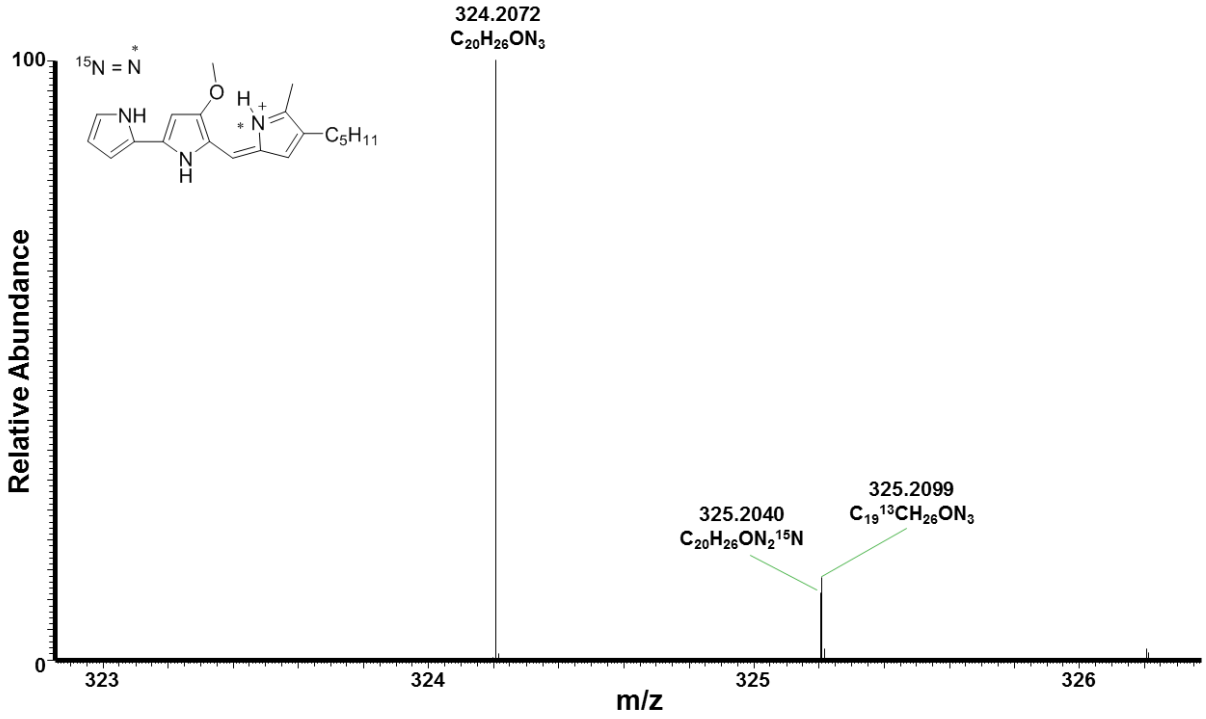


Fig. S44. HRMS spectra of 2-methyl-3-hexyl prodiginine with incorporated ^{15}N derived from $^{15}NH_4Cl$ from labeled nutrient agar (compound **4** $[M+H]^+$: *m/z* 339, $C_{21}H_{28}N_2{}^{15}NO$).

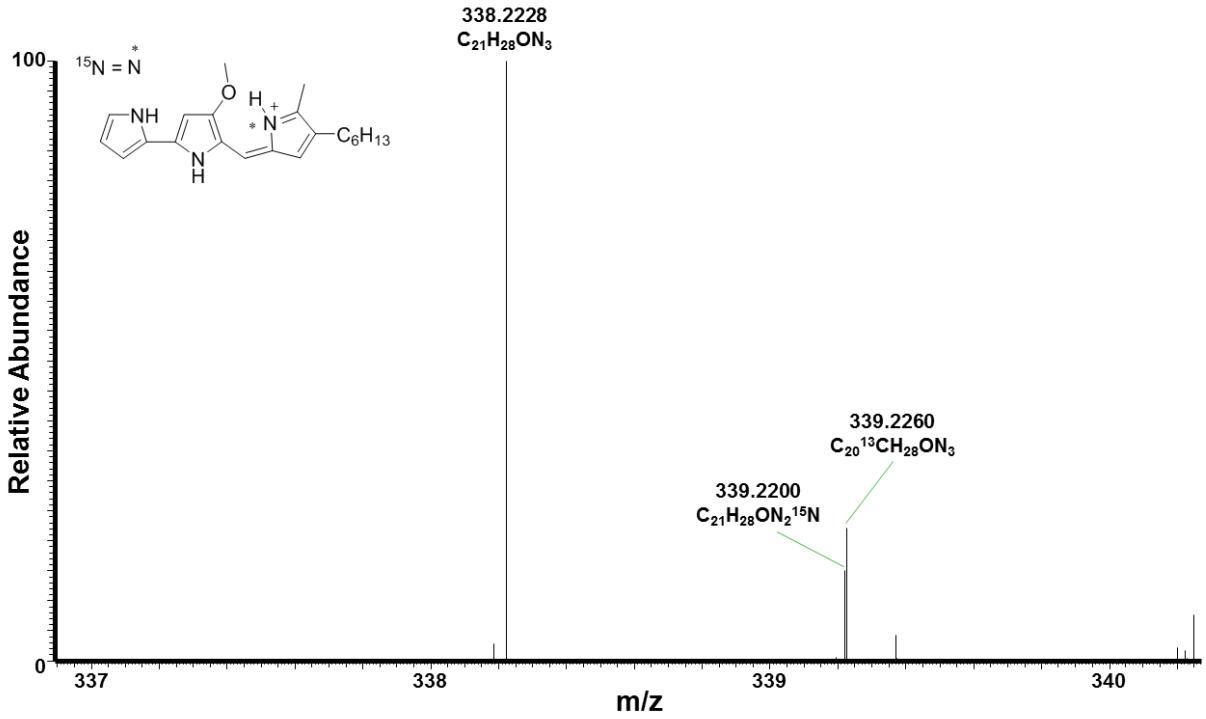


Fig. S45. HRMS spectra of 2-methyl-3-heptyl prodiginine with incorporated ^{15}N derived from $^{15}NH_4Cl$ from labeled nutrient agar (compound **5** $[M+H]^+$: *m/z* 353, $C_{22}H_{30}N_2{}^{15}NO$).

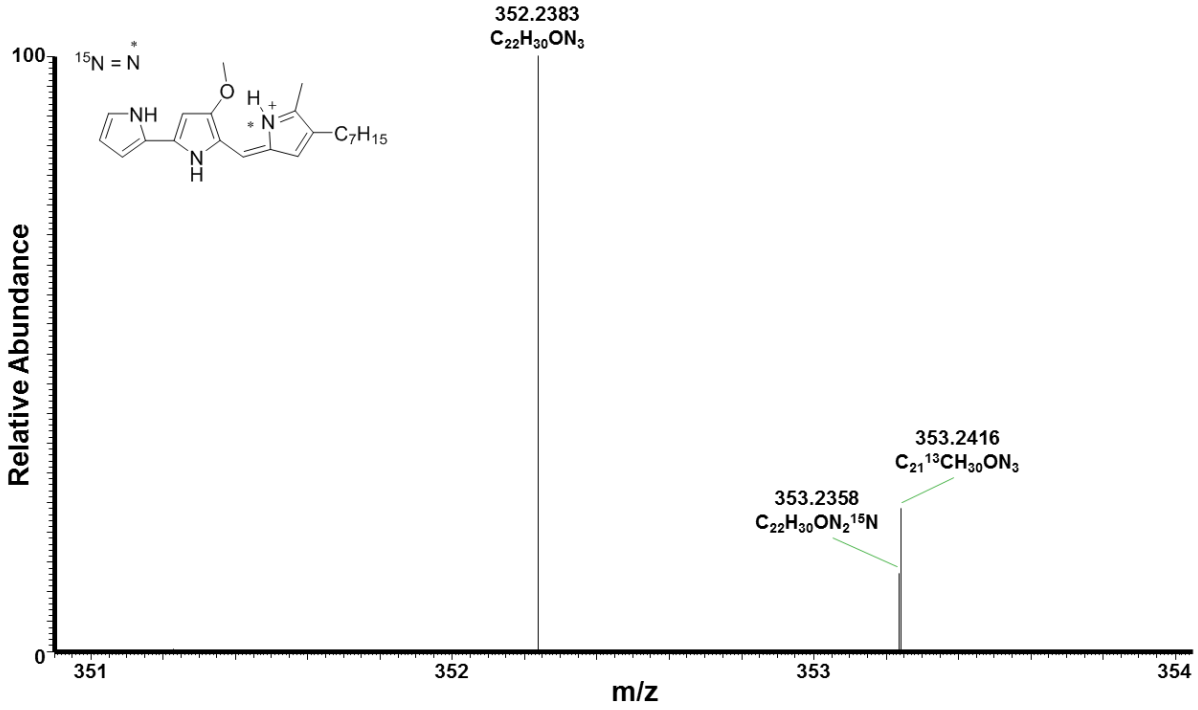


Fig. S46. HRMS spectra of 2-methyl-3-octyl prodiginine with incorporated ^{15}N derived from $^{15}NH_4Cl$ from labeled nutrient agar (compound **6** $[M+H]^+$: *m/z* 367, $C_{23}H_{32}N_2{}^{15}NO$).

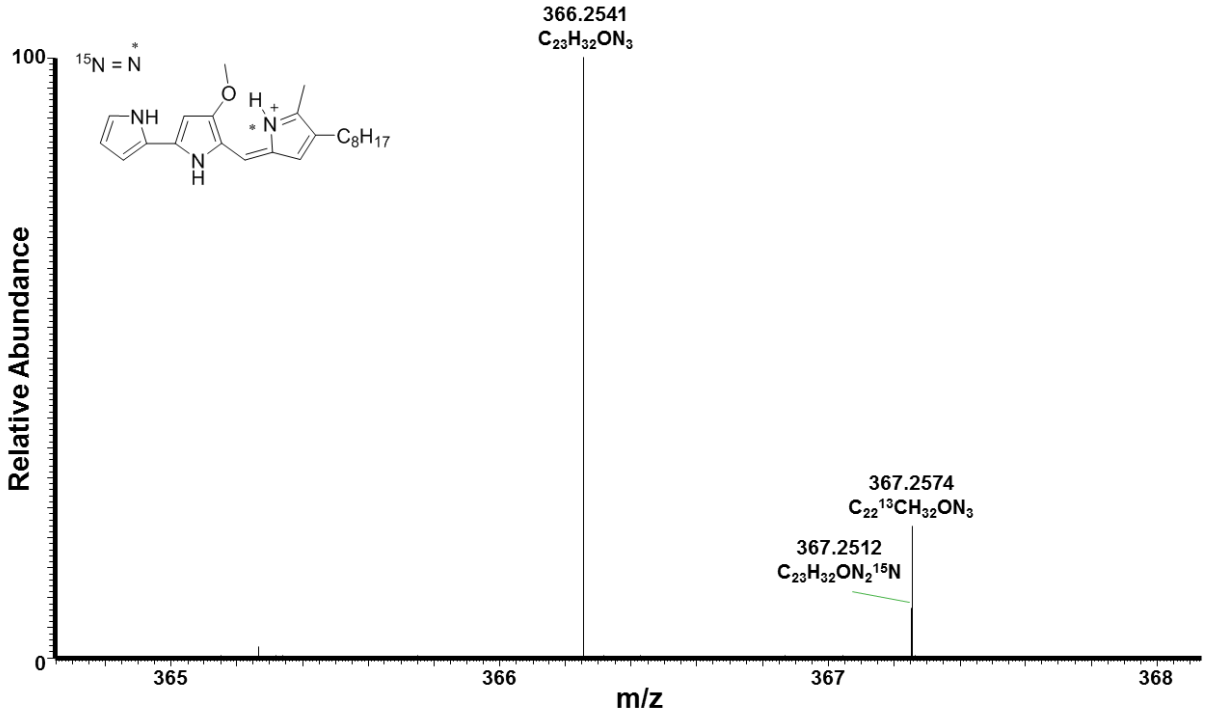


Fig. S47. HRMS spectra of 2-methyl-3-nonyl prodiginine with incorporated ^{15}N derived from $^{15}NH_4Cl$ from labeled nutrient agar (compound **7** $[M+H]^+$: *m/z* 381, $C_{24}H_{34}N_2{}^{15}NO$).

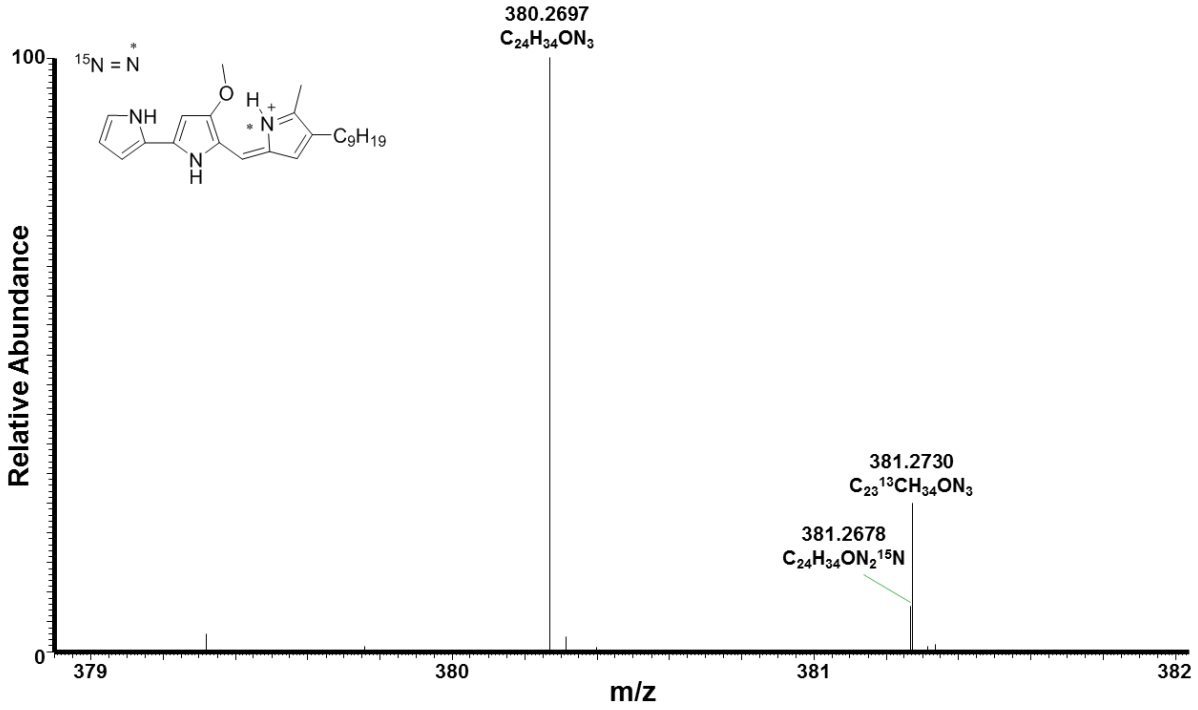


Fig. S48. HRMS spectra of 2-methyl-3-propyl prodiginine with incorporated [1-^{13}C]-L-proline from labeled nutrient agar (compound **1** $[M+H]^+$: *m/z* 297, $C_{17}{}^{13}CH_{22}N_3O$).

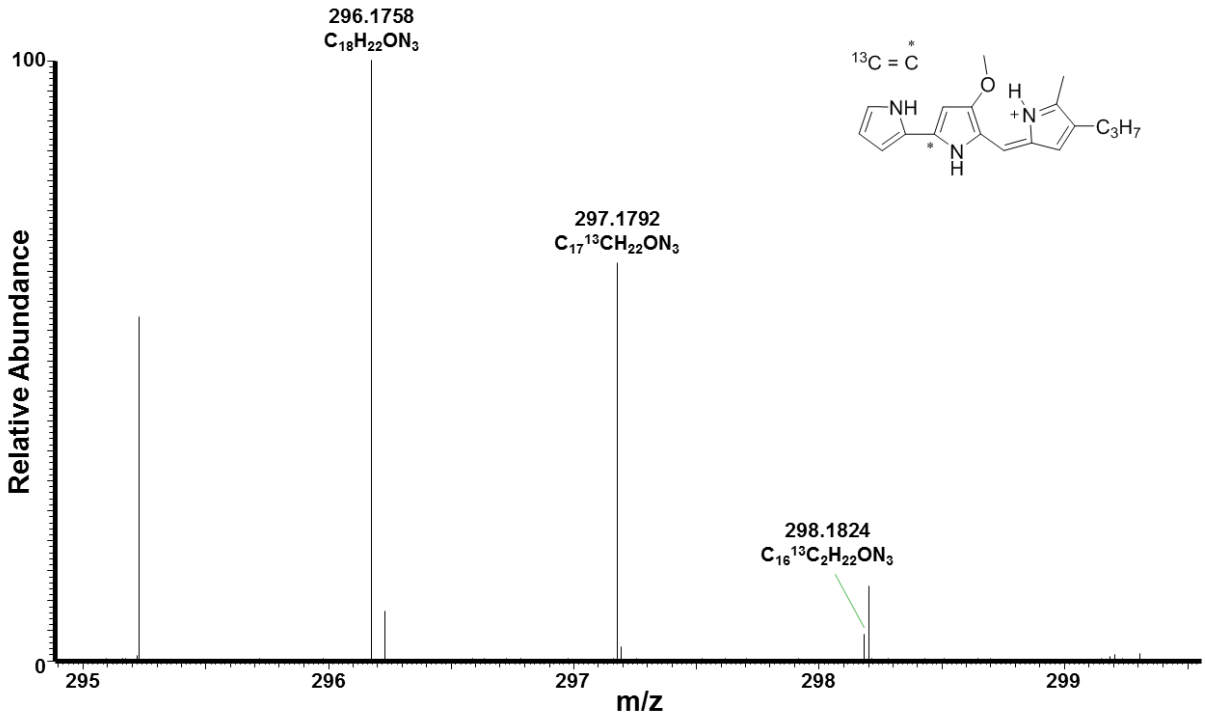


Fig. S49. HRMS spectra of 2-methyl-3-butyl prodiginine with incorporated [1-^{13}C]-L-proline from labeled nutrient agar (compound **2** $[M+H]^+$: *m/z* 311, $C_{18}{}^{13}CH_{24}N_3O$).

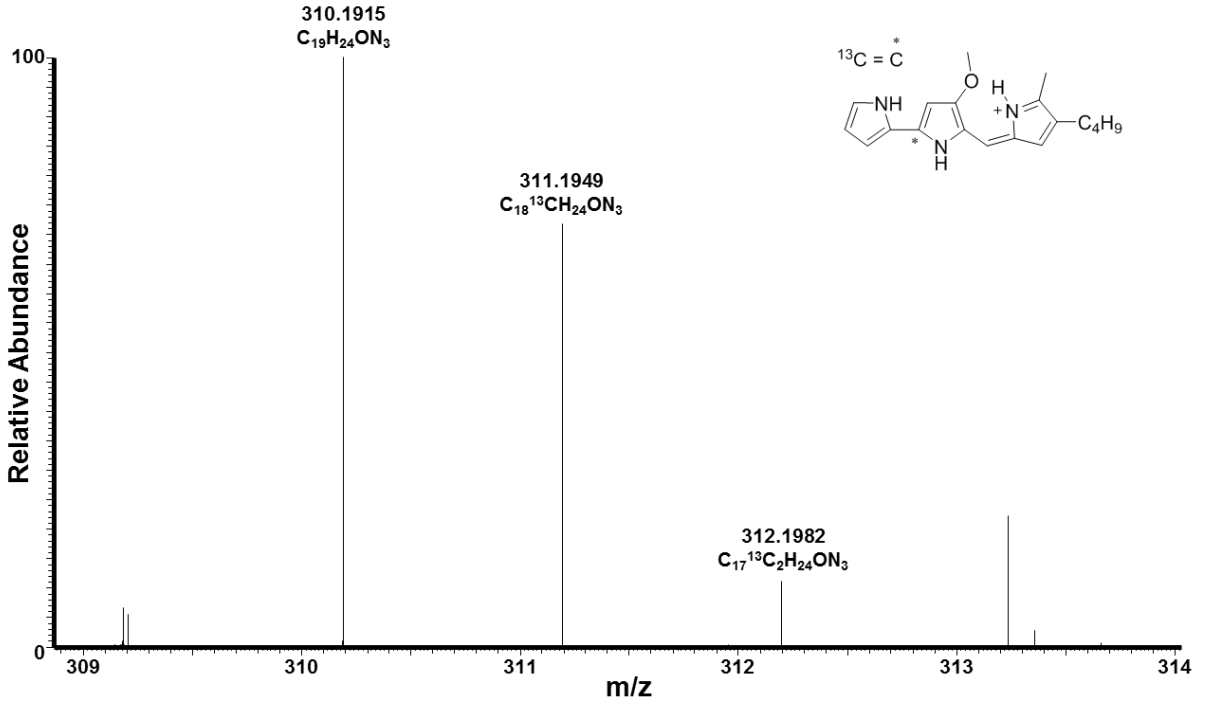


Fig. S50. HRMS spectra of prodigiosin with incorporated [1-^{13}C]-L-proline from labeled nutrient agar (compound **3** $[M+H]^+$: *m/z* 325, $C_{19}{}^{13}CH_{26}N_3O$).

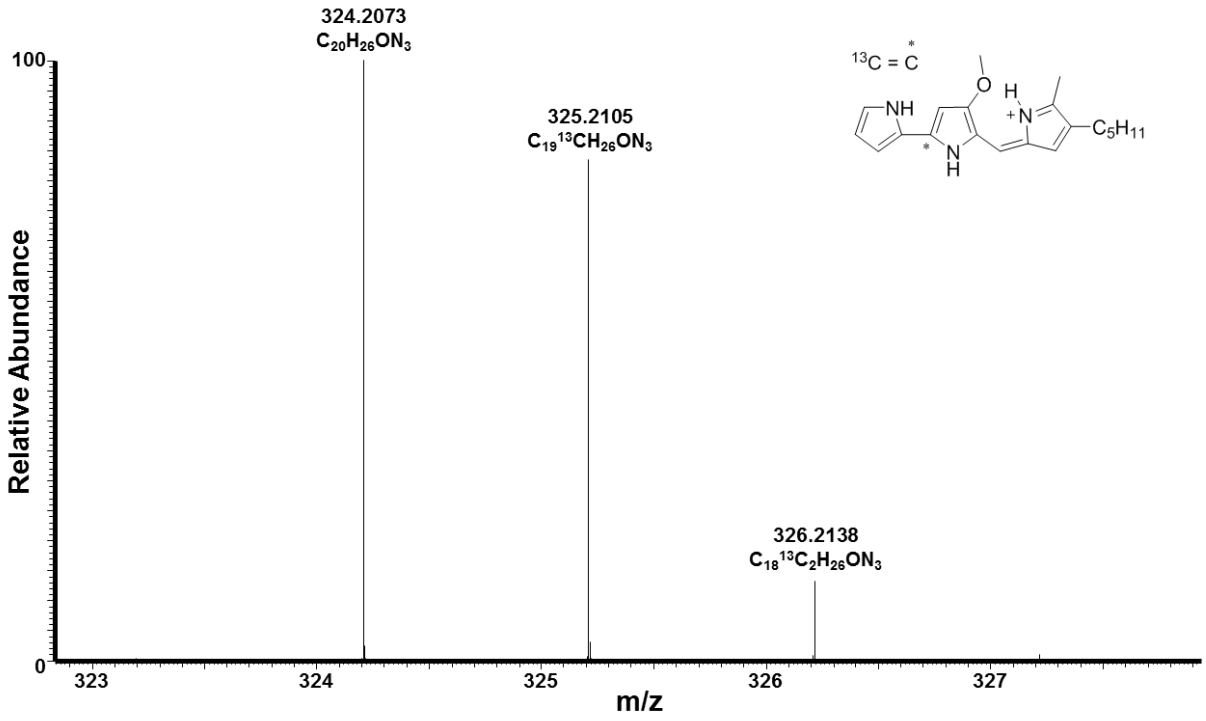


Fig. S51. HRMS spectra of 2-methyl-3-hexyl prodiginine with incorporated [1-^{13}C]-L-proline from labeled nutrient agar (compound **4** $[M+H]^+$: *m/z* 339, $C_{20}{}^{13}CH_{28}N_3O$).

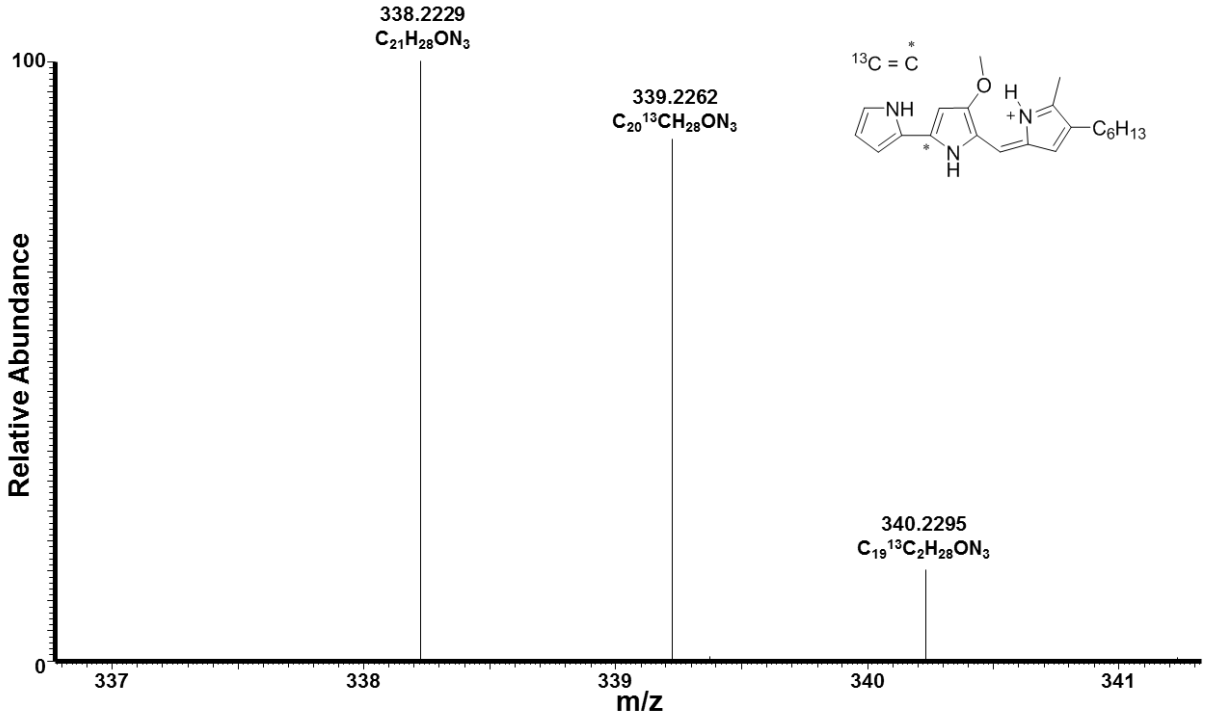


Fig. S52. HRMS spectra of 2-methyl-3-heptyl prodiginine with incorporated [1-^{13}C]-L-proline from labeled nutrient agar (compound **5** $[M+H]^+$: *m/z* 353, $C_{21}{}^{13}CH_{30}N_3O$).

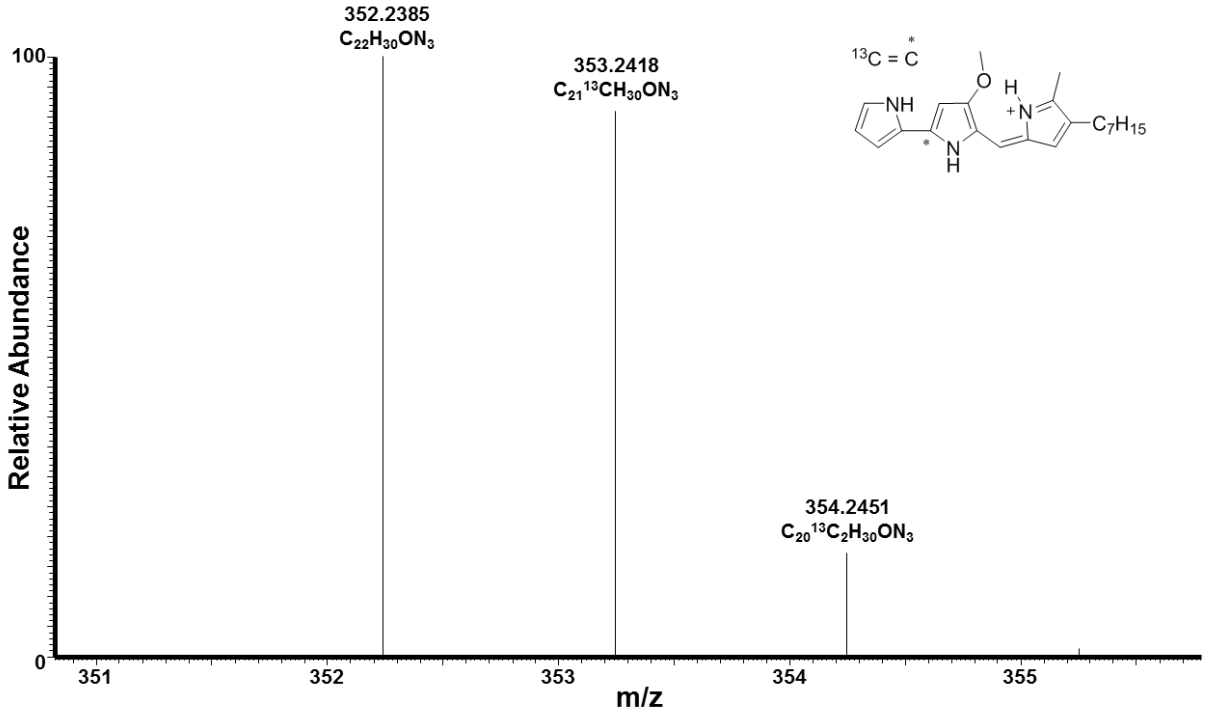


Fig. S53. HRMS spectra of 2-methyl-3-octyl prodiginine with incorporated [1-^{13}C]-L-proline from labeled nutrient agar (compound **6** $[M+H]^+$: *m/z* 367, $C_{22}{}^{13}CH_{32}N_3O$).

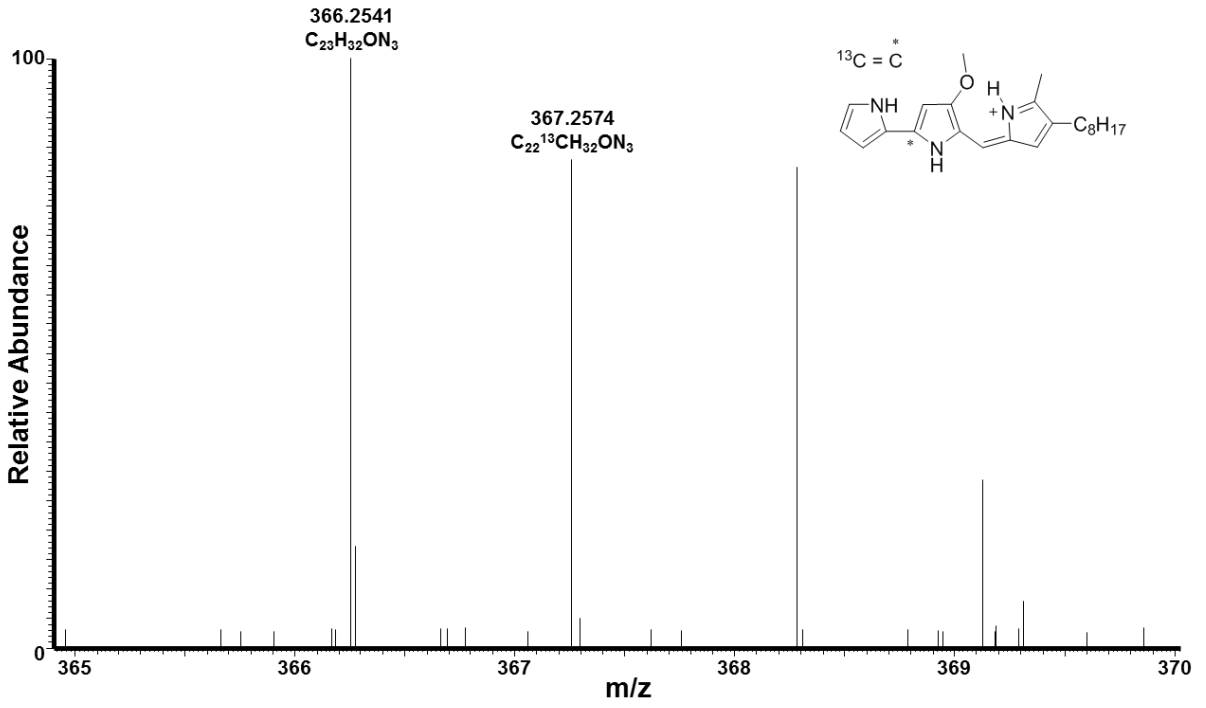


Fig. S54. HRMS spectra of 2-methyl-3-nonyl prodiginine with incorporated [1-^{13}C]-L-proline from labeled nutrient agar (compound **7** $[M+H]^+$: *m/z* 381, $C_{23}{}^{13}CH_{34}N_3O$).

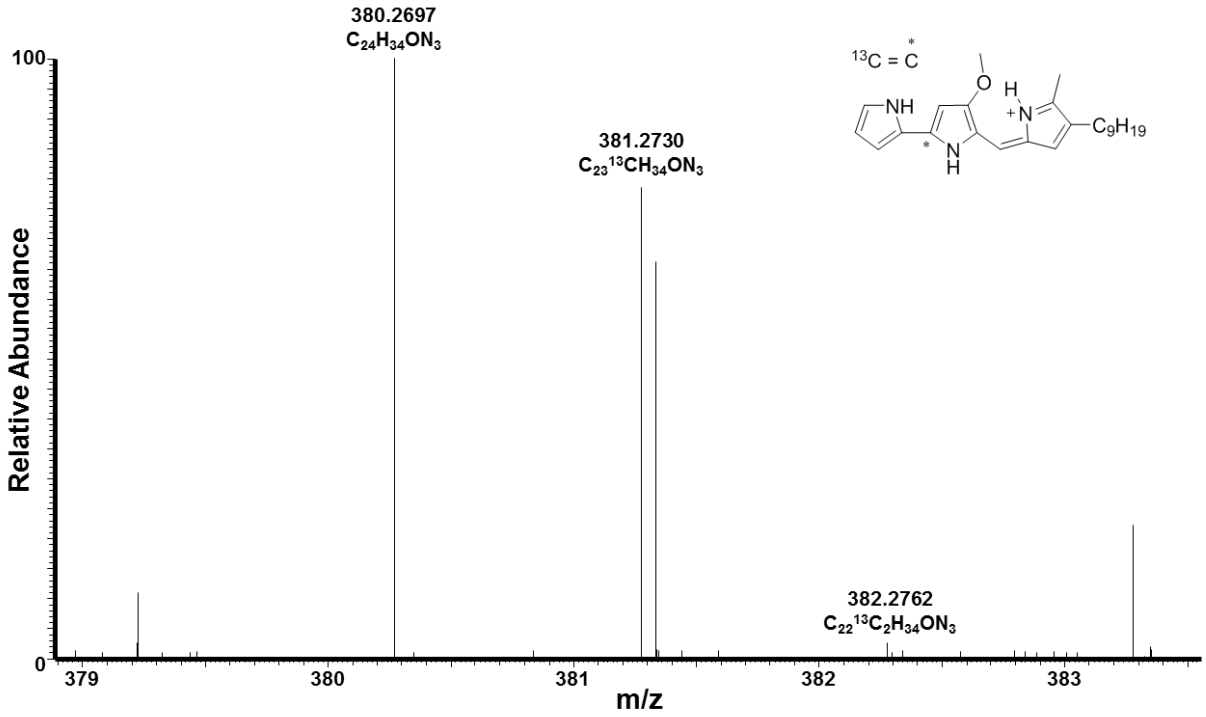


Fig. S55. HRMS spectra of 2-methyl-3-propyl prodiginine with incorporated ^{15}N-L-serine from labeled nutrient agar (compound **1** $[M+H]^+$: *m/z* 296, $C_{18}H_{22}N_3O$).

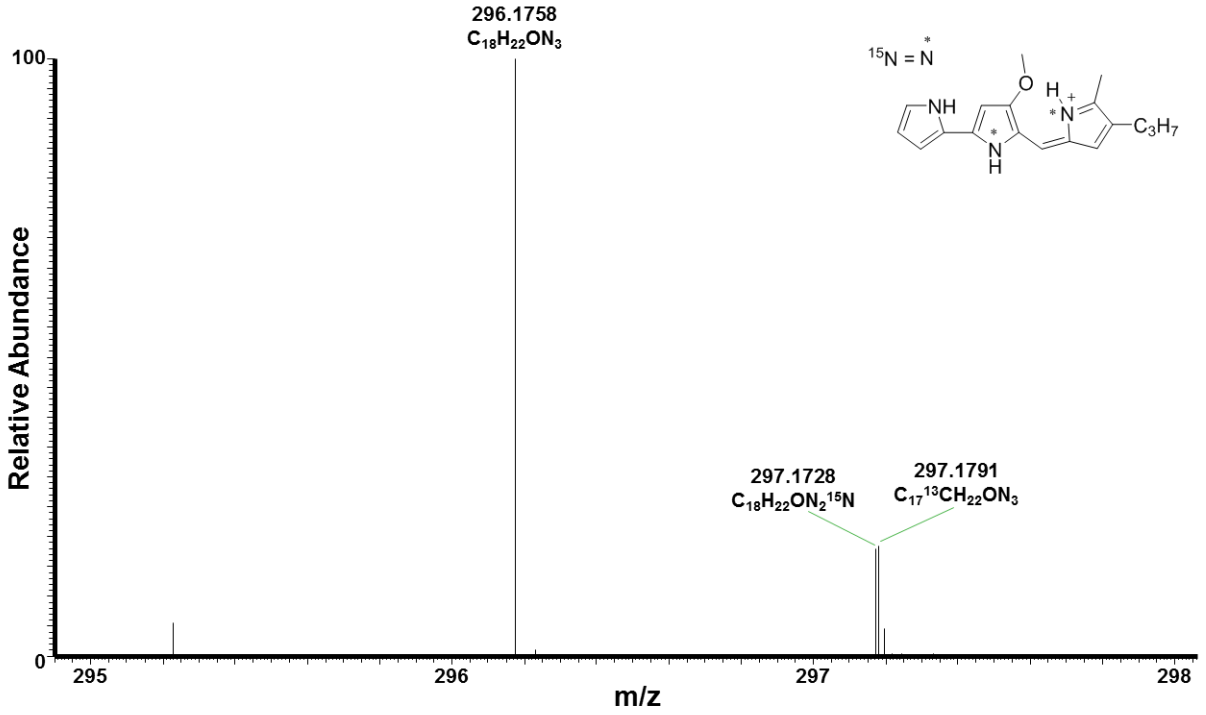


Fig. S56. HRMS spectra of 2-methyl-3-butyl prodiginine with incorporated ^{15}N-L-serine from labeled nutrient agar (compound **2** $[M+H]^+$: *m/z* 310, $C_{19}H_{24}N_3O$).

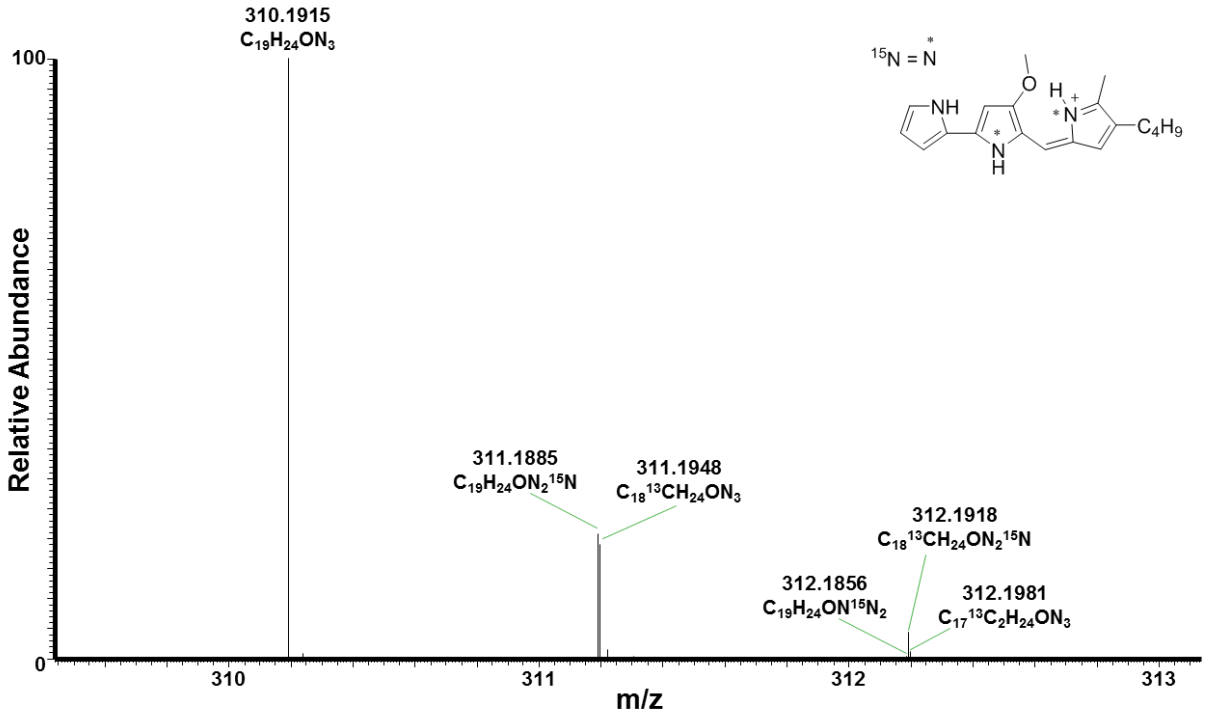


Fig. S57. HRMS spectra of prodigiosin with incorporated ^{15}N-L-serine from labeled nutrient agar (compound **3** $[M+H]^+$: *m/z* 324, $C_{20}H_{26}N_3O$).

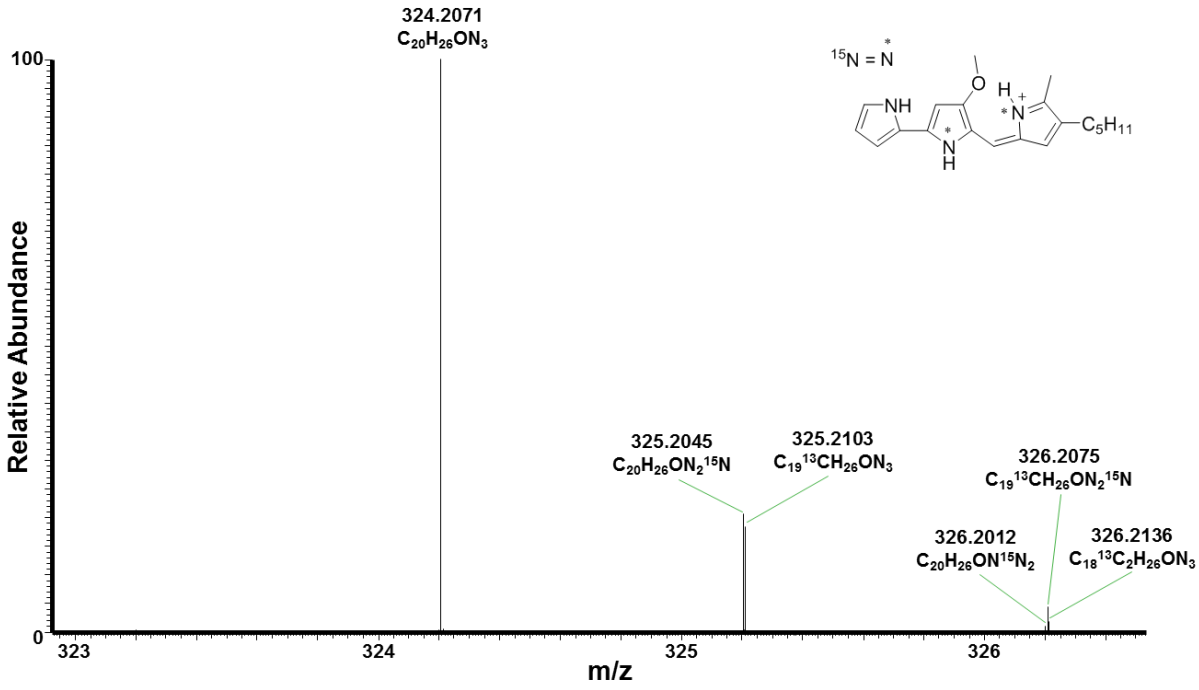


Fig. S58. HRMS spectra of 2-methyl-3-hexyl prodiginine with incorporated ^{15}N-L-serine from labeled nutrient agar (compound **4** $[M+H]^+$: *m/z* 338, $C_{21}H_{28}N_3O$).

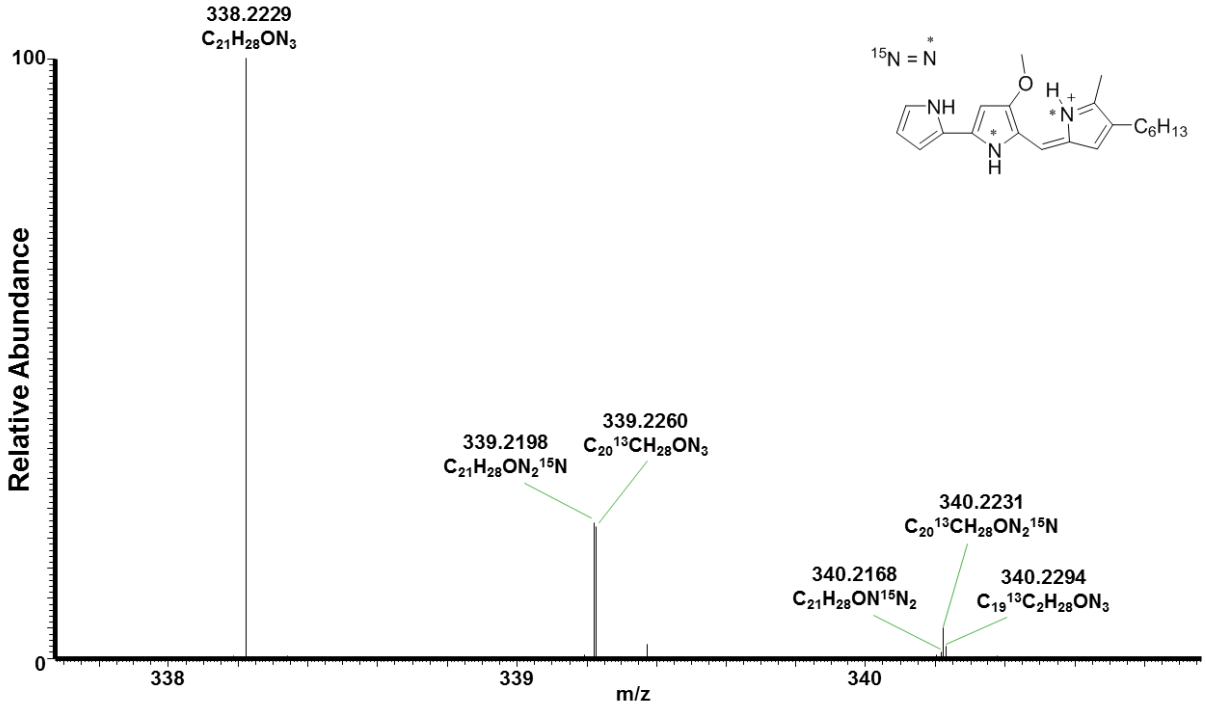


Fig. S59. HRMS spectra of 2-methyl-3-heptyl prodiginine with incorporated ^{15}N-L-serine from labeled nutrient agar (compound **5** $[M+H]^+$: *m/z* 352, $C_{22}H_{30}N_3O$).

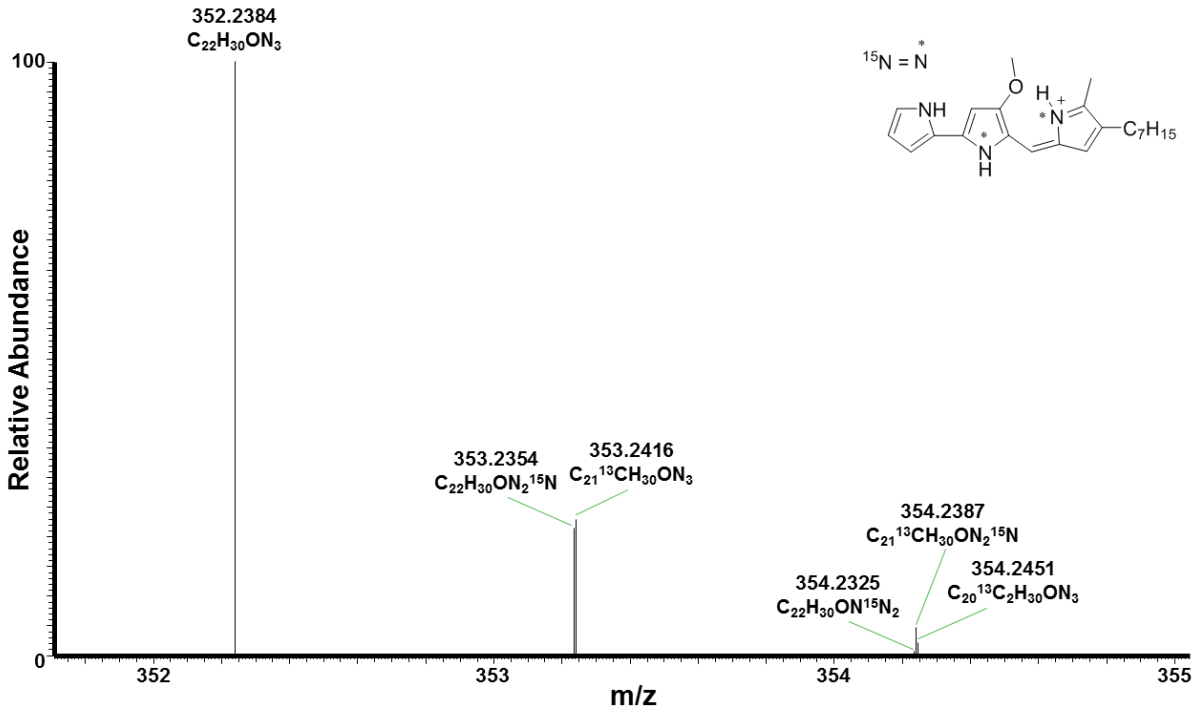


Fig. S60. HRMS spectra of 2-methyl-3-octyl prodiginine with incorporated ^{15}N-L-serine from labeled nutrient agar (compound **6** $[M+H]^+$: *m/z* 366, $C_{23}H_{32}N_3O$).

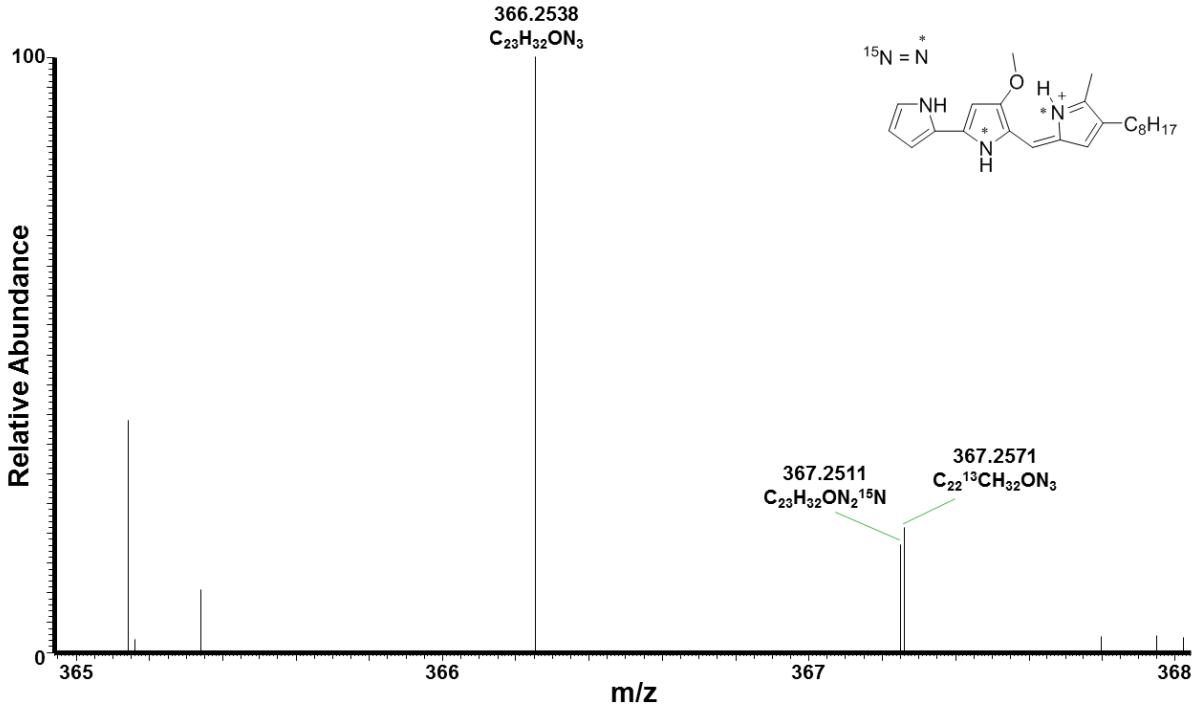


Fig. S61. HRMS spectra of 2-methyl-3-nonyl prodiginine with incorporated ^{15}N-L-serine from labeled nutrient agar (compound **7** $[M+H]^+$: *m/z* 380, $C_{24}H_{34}N_3O$).

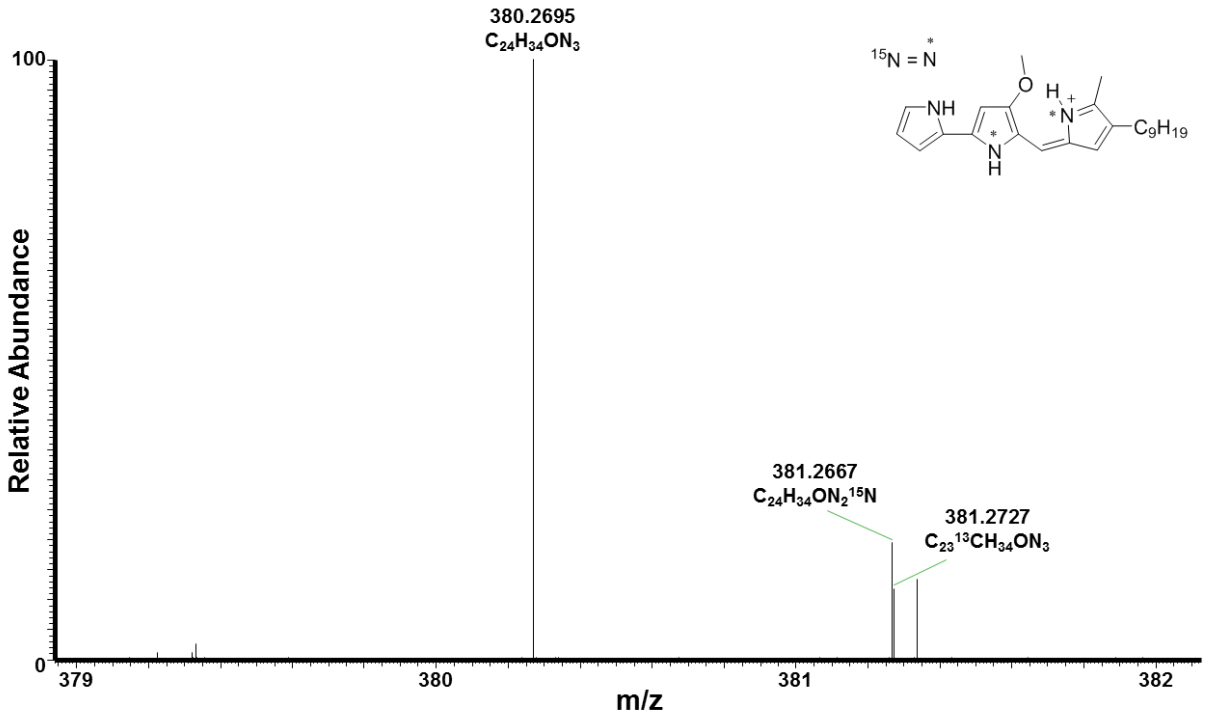


Fig. S62. HRMS spectra of 2-methyl-3-propyl prodiginine with incorporated methyl-D_3 group derived from 0.5 mg/mL [methyl-D_3]-L-methionine on nutrient agar (compound **1** $[M+H]^+$: *m/z* 299, $C_{18}H_{19}D_3N_3O$).

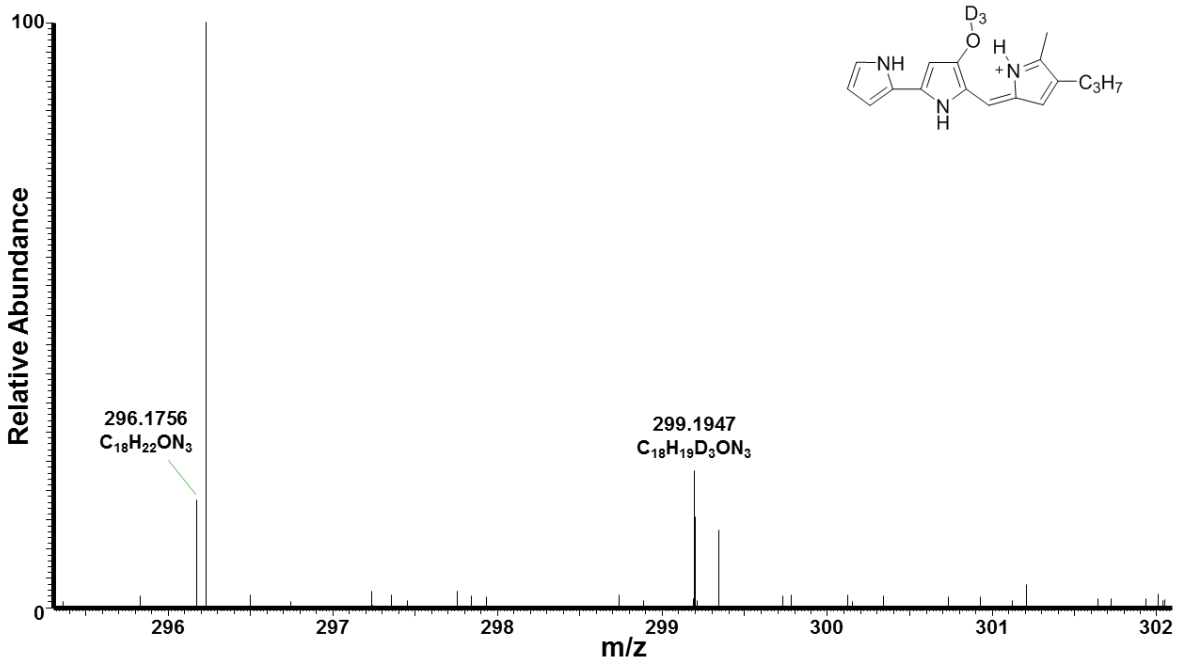


Fig. S63. HRMS spectra of 2-methyl-3-butyl prodiginine with incorporated methyl-D_3 group derived from 0.5 mg/mL [methyl-D_3]-L-methionine on nutrient agar (compound **2** $[M+H]^+$: *m/z* 313, $C_{19}H_{21}D_3N_3O$).

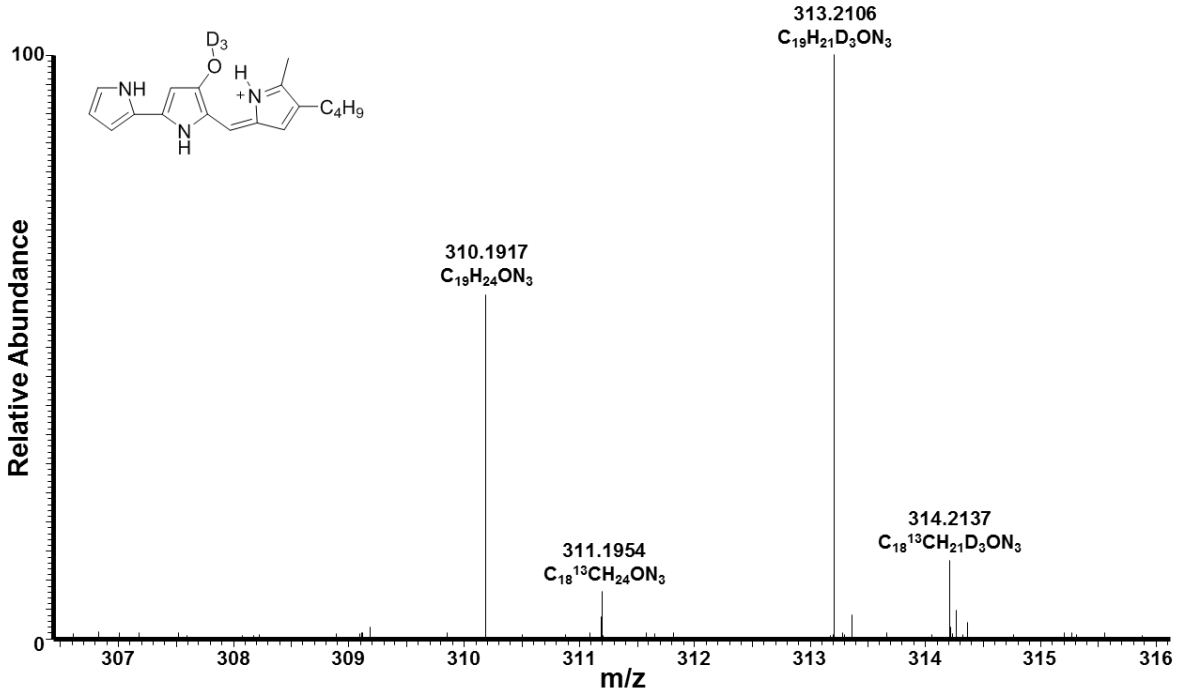


Fig. S64. HRMS spectra of prodigiosin with incorporated methyl-D_3 group derived from 0.5 mg/mL [methyl-D_3]-L-methionine on nutrient agar (compound **3** $[M+H]^+$: *m/z* 327, $C_{20}H_{23}D_3N_3O$).

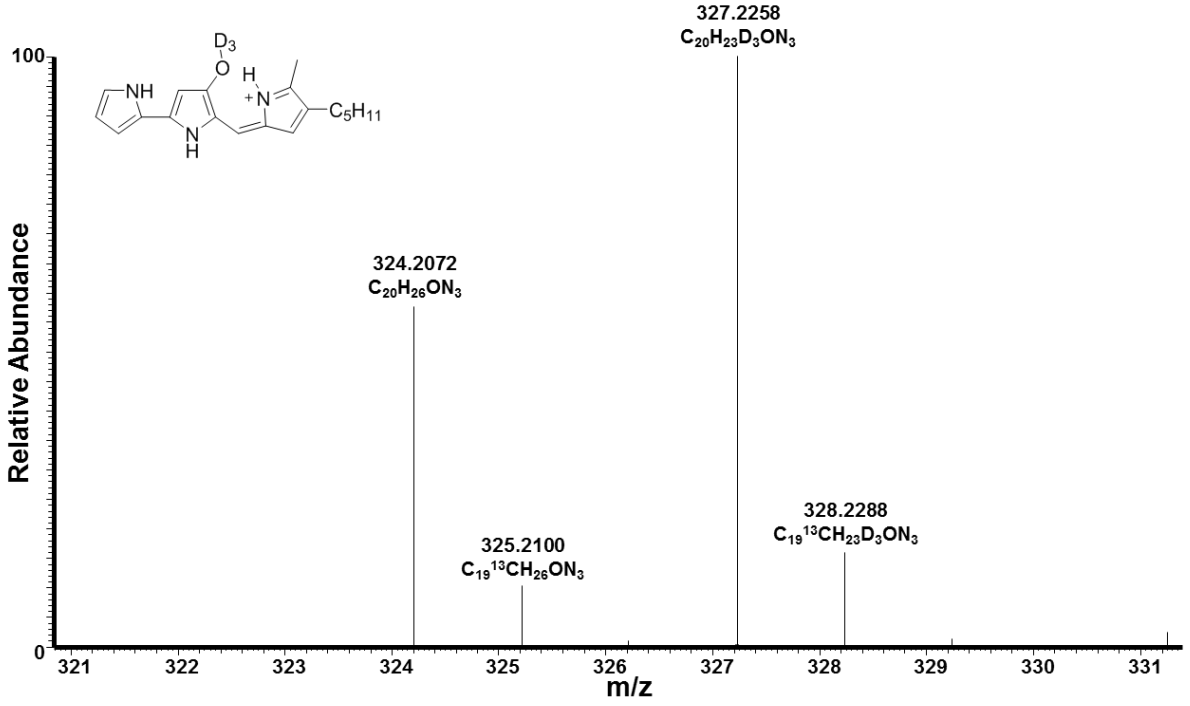


Fig. S65. HRMS spectra of 2-methyl-3-hexyl prodiginine with incorporated methyl-D_3 group derived from 0.5 mg/mL [methyl-D_3]-L-methionine on nutrient agar (compound **4** $[M+H]^+$: *m/z* 341, $C_{21}H_{25}D_3N_3O$).

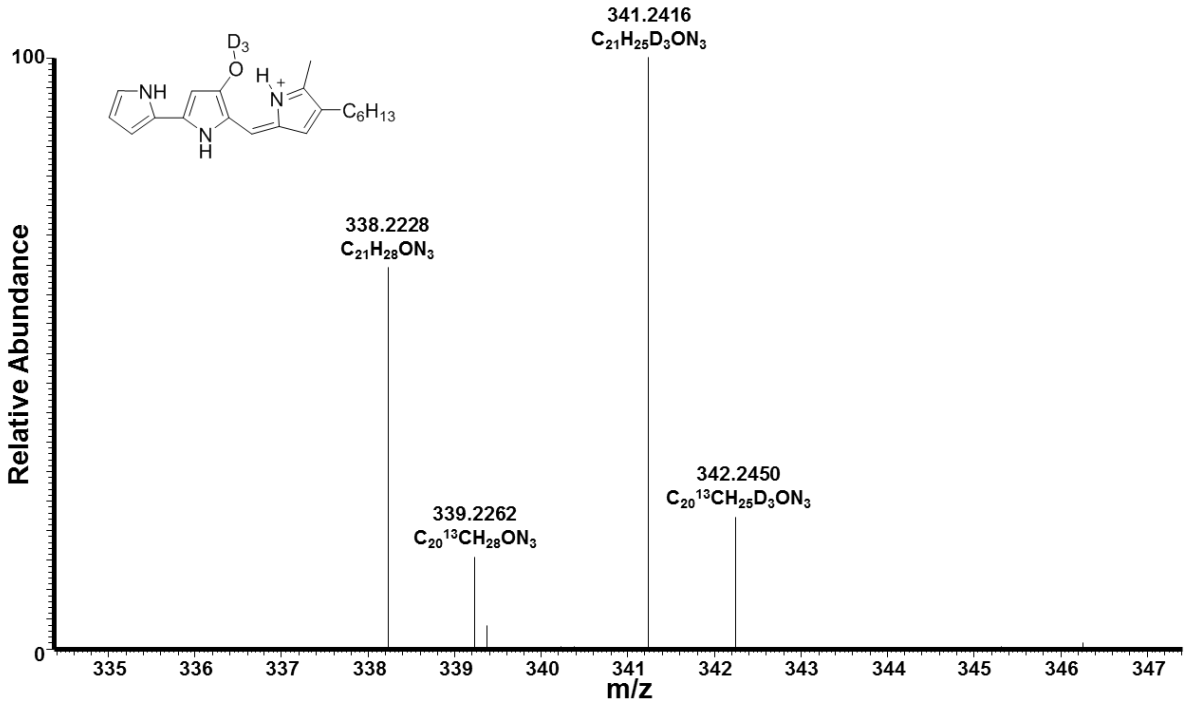


Fig. S66. HRMS spectra of 2-methyl-3-heptyl prodiginine with incorporated methyl-D_3 group derived from 0.5 mg/mL [methyl-D_3]-L-methionine on nutrient agar (compound **5** $[M+H]^+$: *m/z* 355, $C_{22}H_{27}D_3N_3O$).

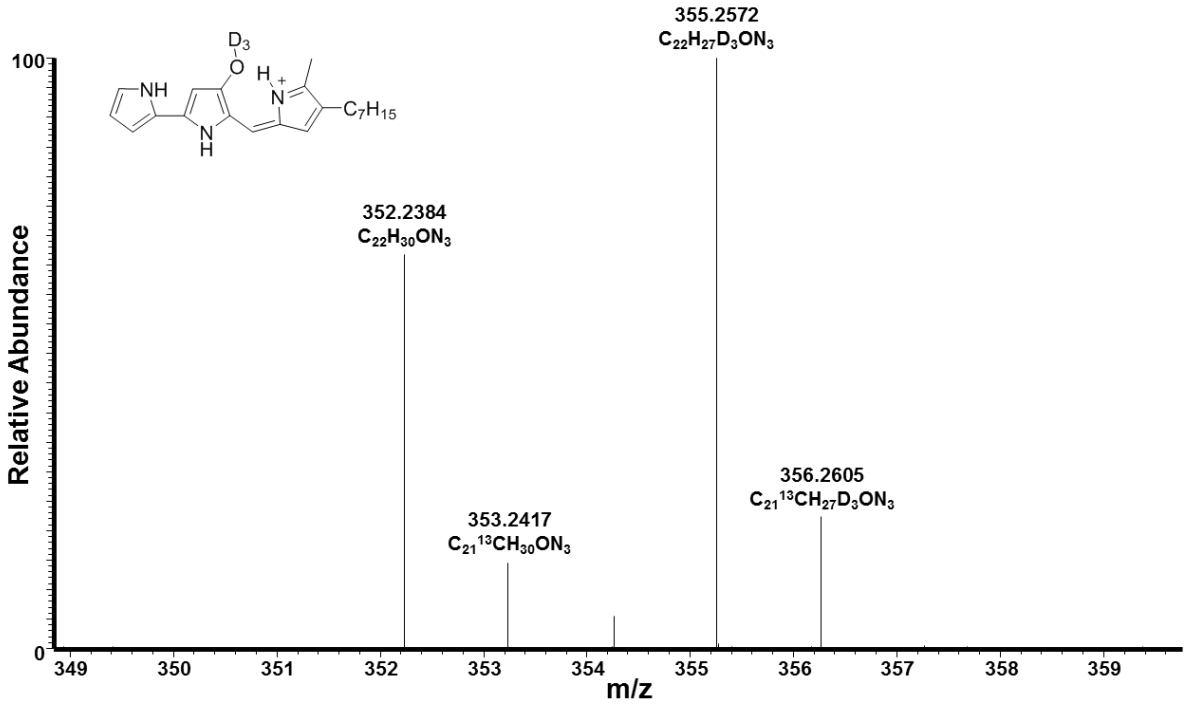


Fig. S67. HRMS spectra of 2-methyl-3-propyl prodiginine with incorporated methyl-D_3 group derived from 2 mg/mL [methyl-D_3]-L-methionine on nutrient agar (compound **1** $[M+H]^+$: *m/z* 299, $C_{18}H_{19}D_3N_3O$).

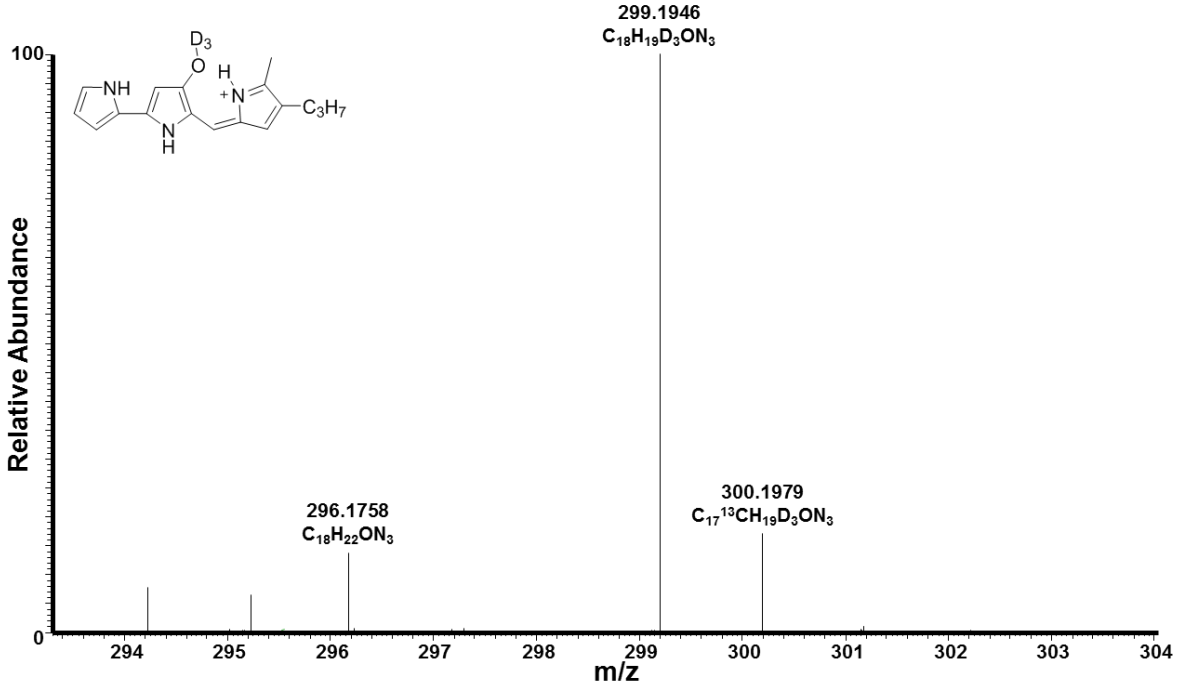


Fig. S68. HRMS spectra of 2-methyl-3-butyl prodiginine with incorporated methyl-D_3 group derived from 2 mg/mL [methyl-D_3]-L-methionine on nutrient agar (compound **2** $[M+H]^+$: *m/z* 313, $C_{19}H_{21}D_3N_3O$).

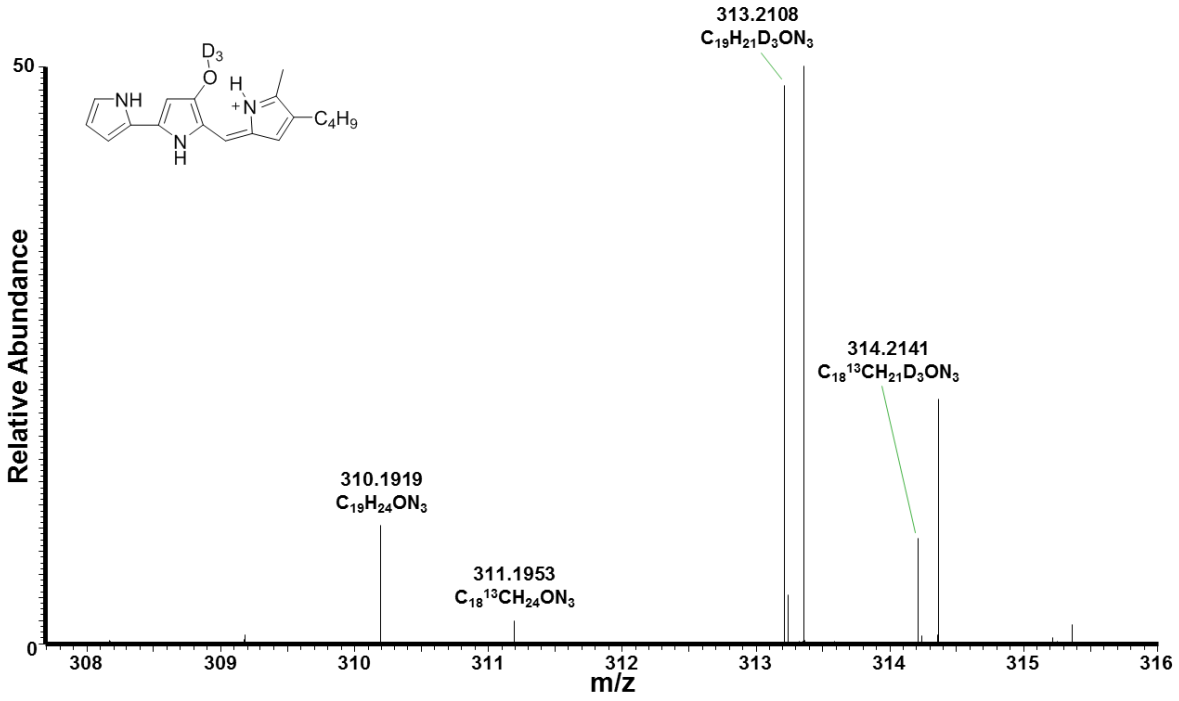


Fig. S69. HRMS spectra of prodigiosin with incorporated methyl-D_3 group derived from 2 mg/mL [methyl-D_3]-L-methionine on nutrient agar (compound **3** $[M+H]^+$: *m/z* 327, $C_{20}H_{23}D_3N_3O$).

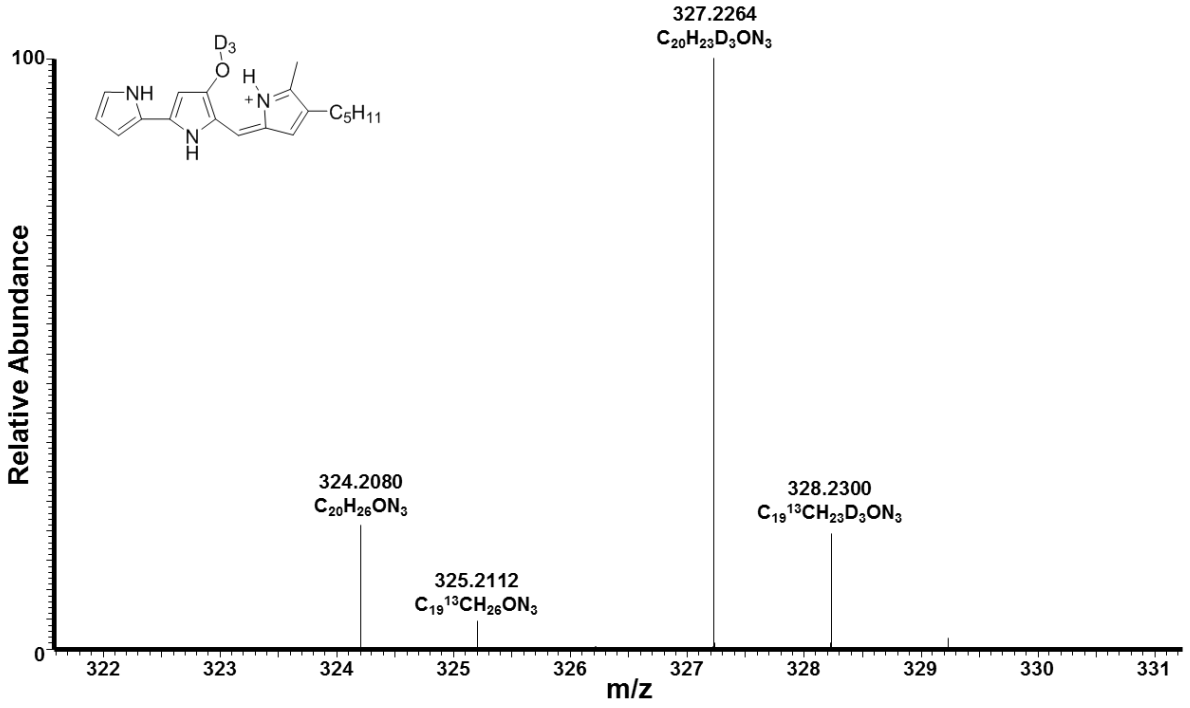


Fig. S70. HRMS spectra of 2-methyl-3-hexyl prodiginine with incorporated methyl-D_3 group derived from 2 mg/mL [methyl-D_3]-L-methionine on nutrient agar (compound **4** $[M+H]^+$: *m/z* 341, $C_{21}H_{25}D_3N_3O$).

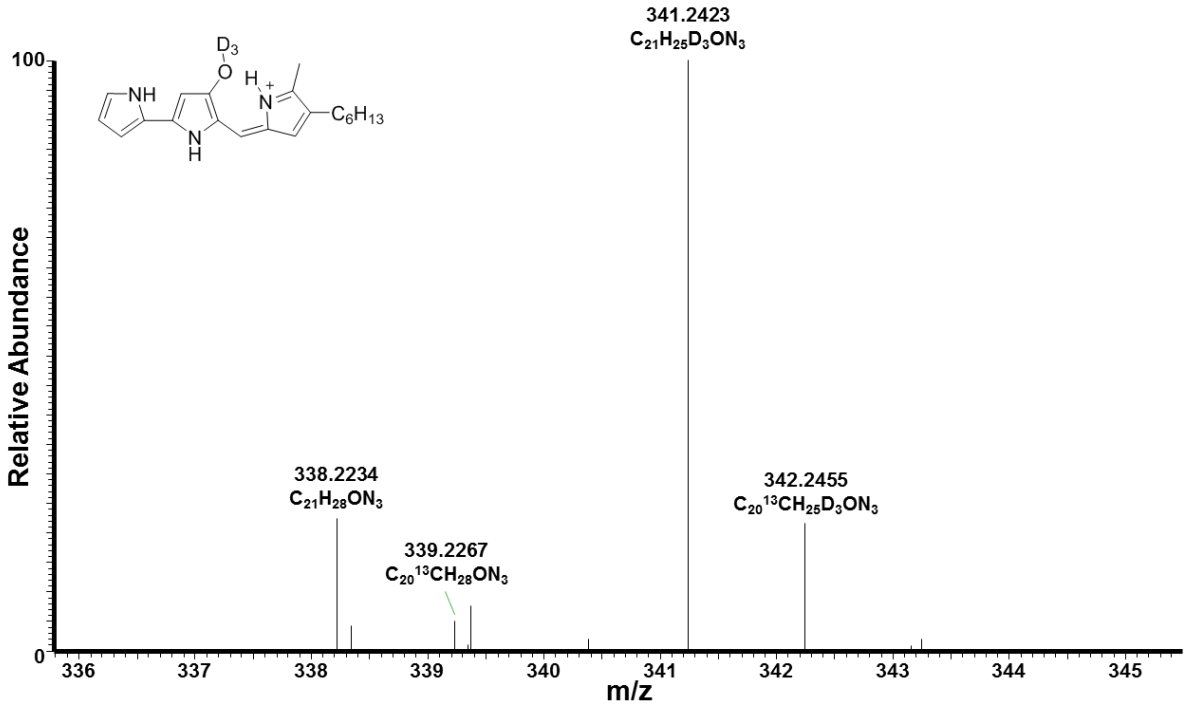


Fig. S71. HRMS spectra of 2-methyl-3-heptyl prodiginine with incorporated methyl-D_3 group derived from 2 mg/mL [methyl-D_3]-L-methionine on nutrient agar (compound **5** $[M+H]^+$: *m/z* 355, $C_{22}H_{27}D_3N_3O$).

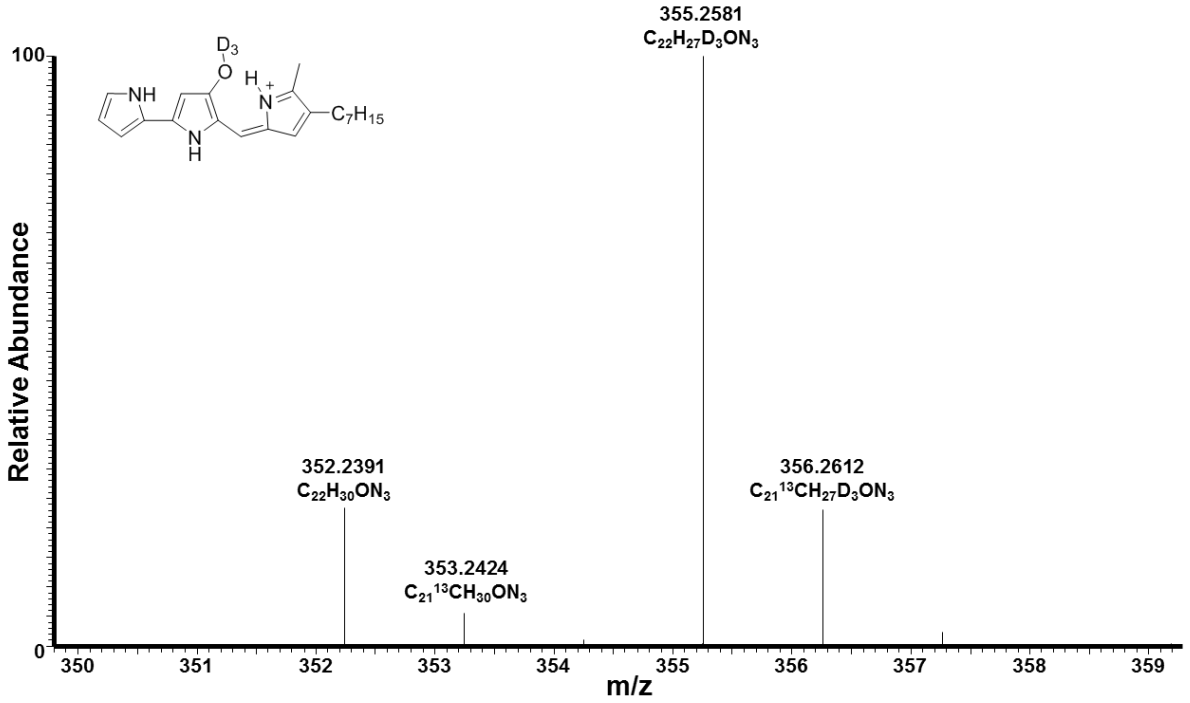


Fig. S72. HRMS spectra of 2-methyl-3-octyl prodiginine with incorporated methyl-D_3 group derived from 2 mg/mL [methyl-D_3]-L-methionine on nutrient agar (compound **6** $[M+H]^+$: *m/z* 369, $C_{23}H_{29}D_3N_3O$).

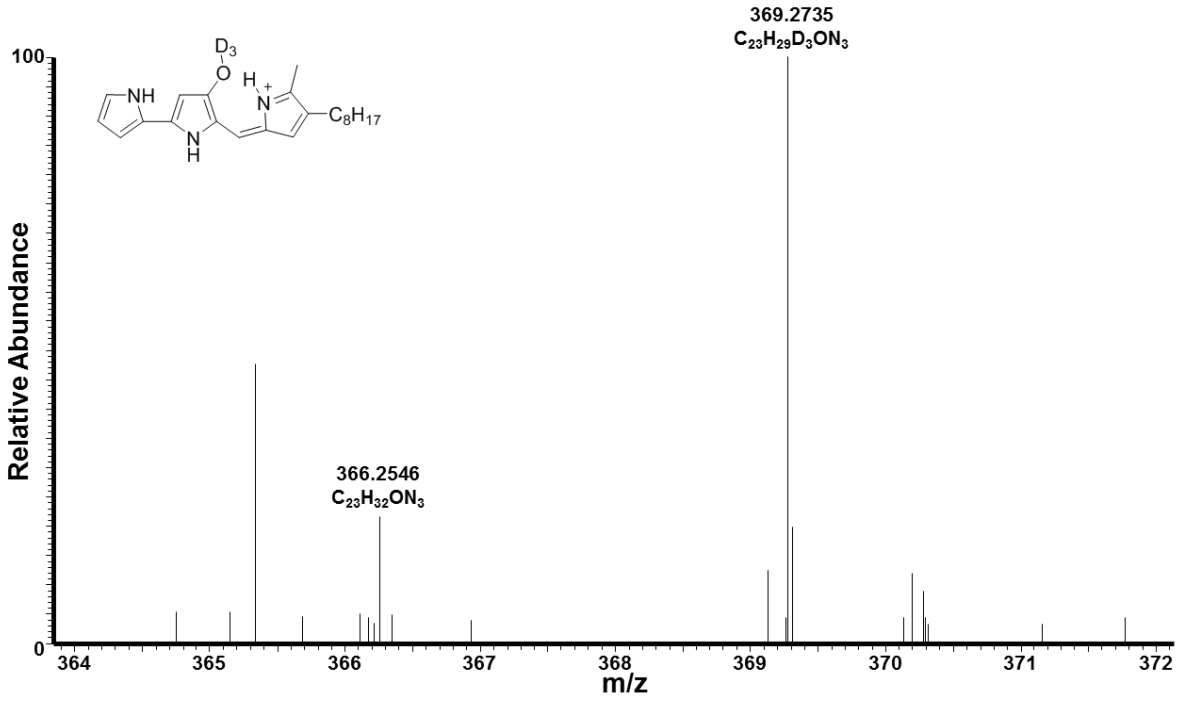


Fig. S73. HRMS spectra of 2-methyl-3-nonyl prodiginine with incorporated methyl-D_3 group derived from 2 mg/mL [methyl-D_3]-L-methionine on nutrient agar (compound **7** $[M+H]^+$: *m/z* 383, $C_{24}H_{31}D_3N_3O$).

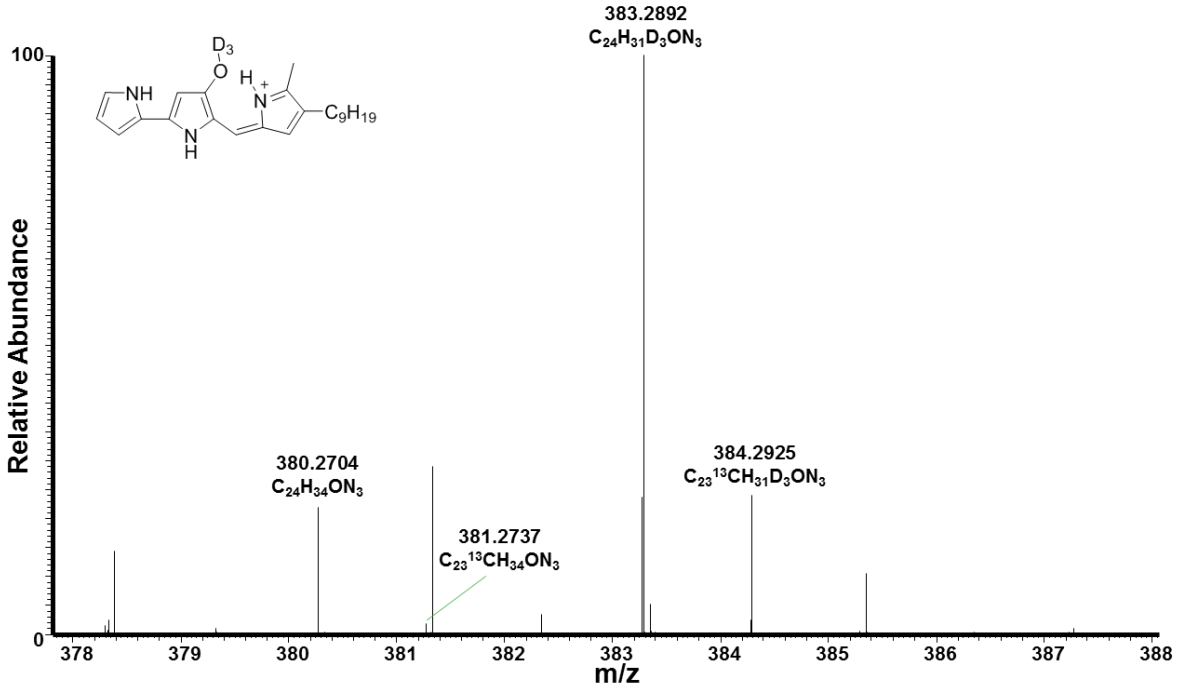


Fig. S74. HRMS spectra of 2-methyl-3-propyl prodiginine with incorporated methyl-D_3 group derived from 1 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **1** $[M+H]^+$: *m/z* 299, $C_{18}H_{19}D_3N_3O$).

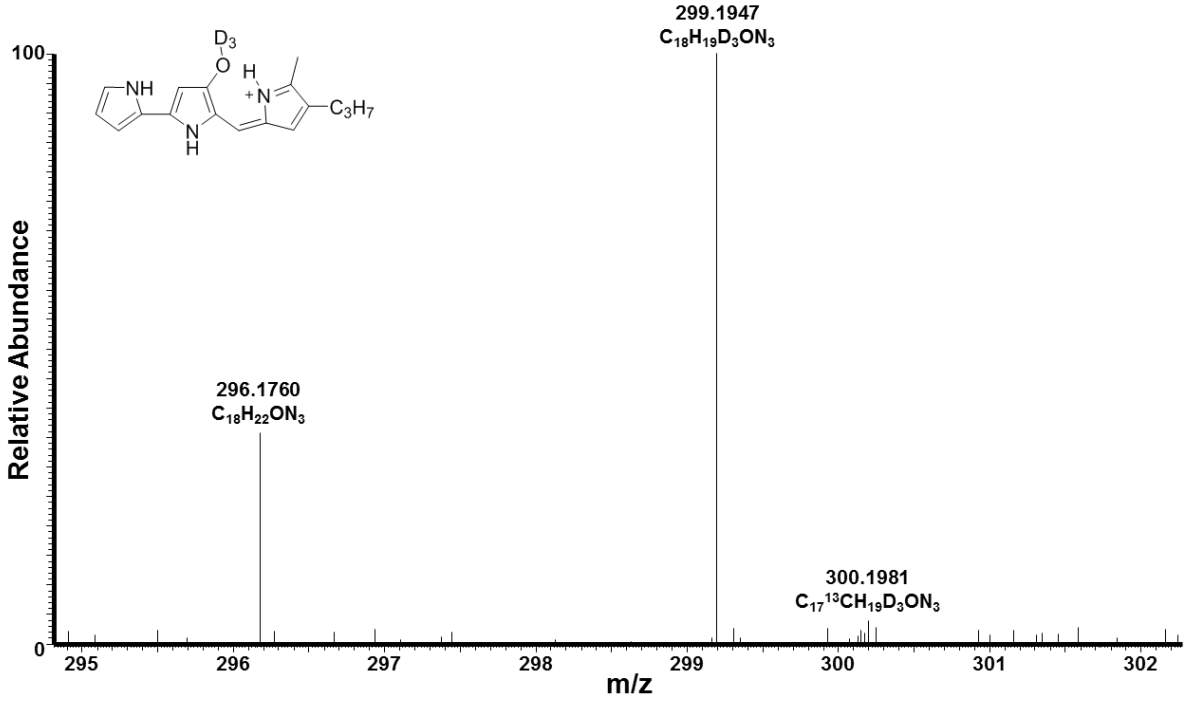


Fig. S75. HRMS spectra of 2-methyl-3-butyl prodiginine with incorporated methyl-D_3 group derived from 1 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **2** $[M+H]^+$: *m/z* 313, $C_{19}H_{21}D_3N_3O$).

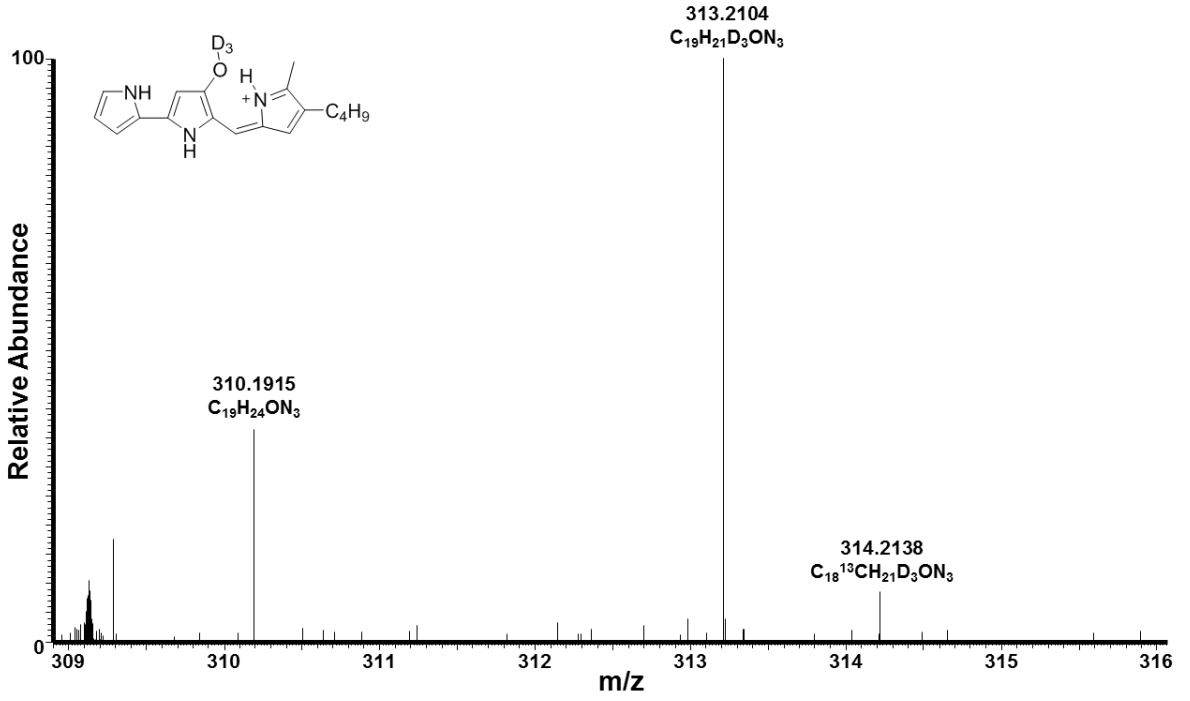


Fig. S76. HRMS spectra of prodigiosin with incorporated methyl-D_3 group derived from 1 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **3** $[M+H]^+$: *m/z* 327, $C_{20}H_{23}D_3N_3O$).

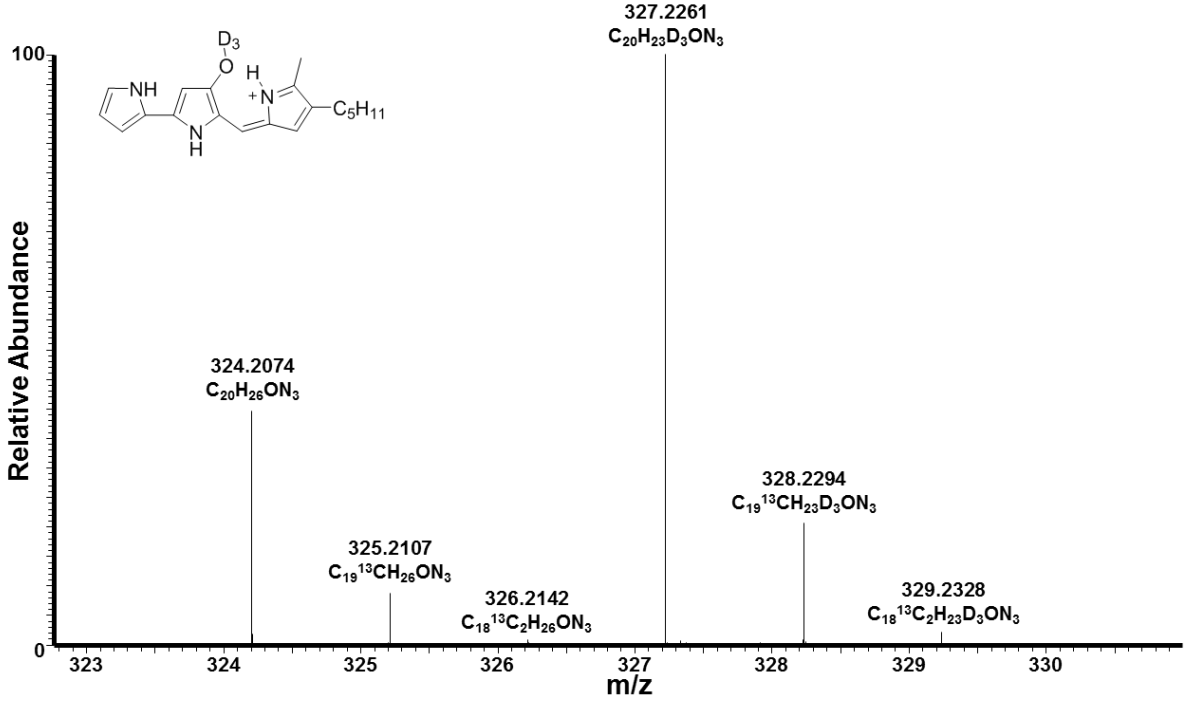


Fig. S77. HRMS spectra of 2-methyl-3-hexyl prodiginine with incorporated methyl-D_3 group derived from 1 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **4** $[M+H]^+$: *m/z* 341, $C_{21}H_{25}D_3N_3O$).

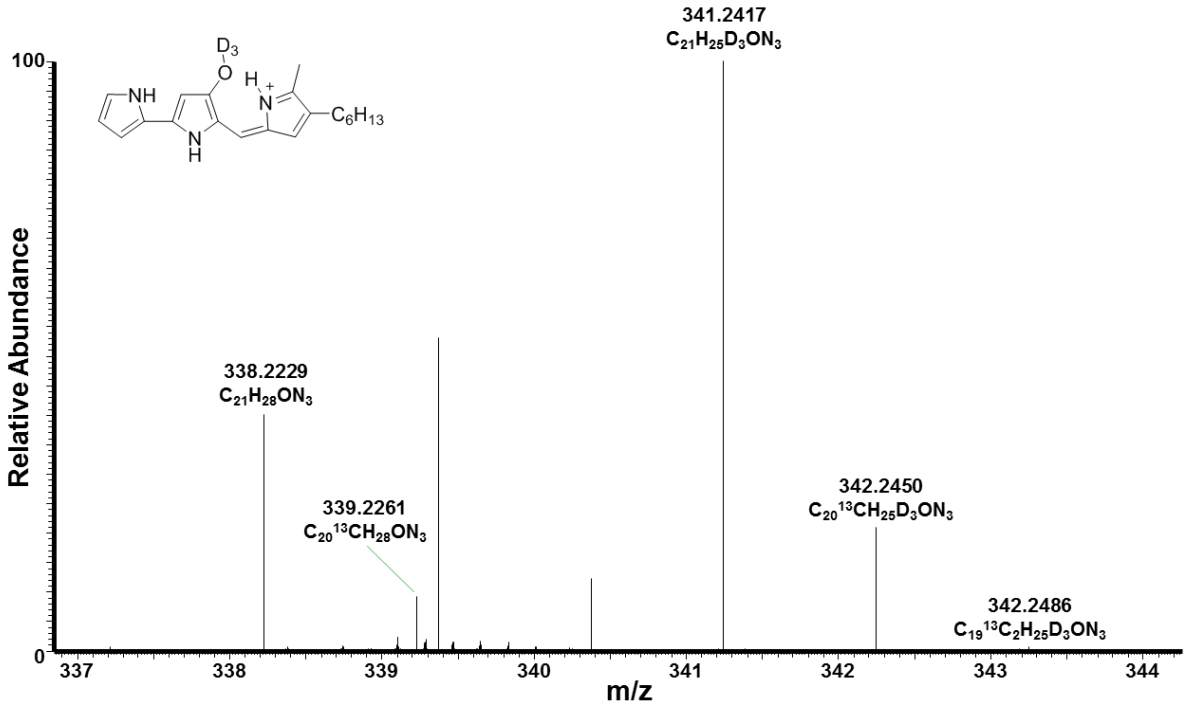


Fig. S78. HRMS spectra of 2-methyl-3-heptyl prodiginine with incorporated methyl-D_3 group derived from 1 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **5** $[M+H]^+$: *m/z* 355, $C_{22}H_{27}D_3N_3O$).

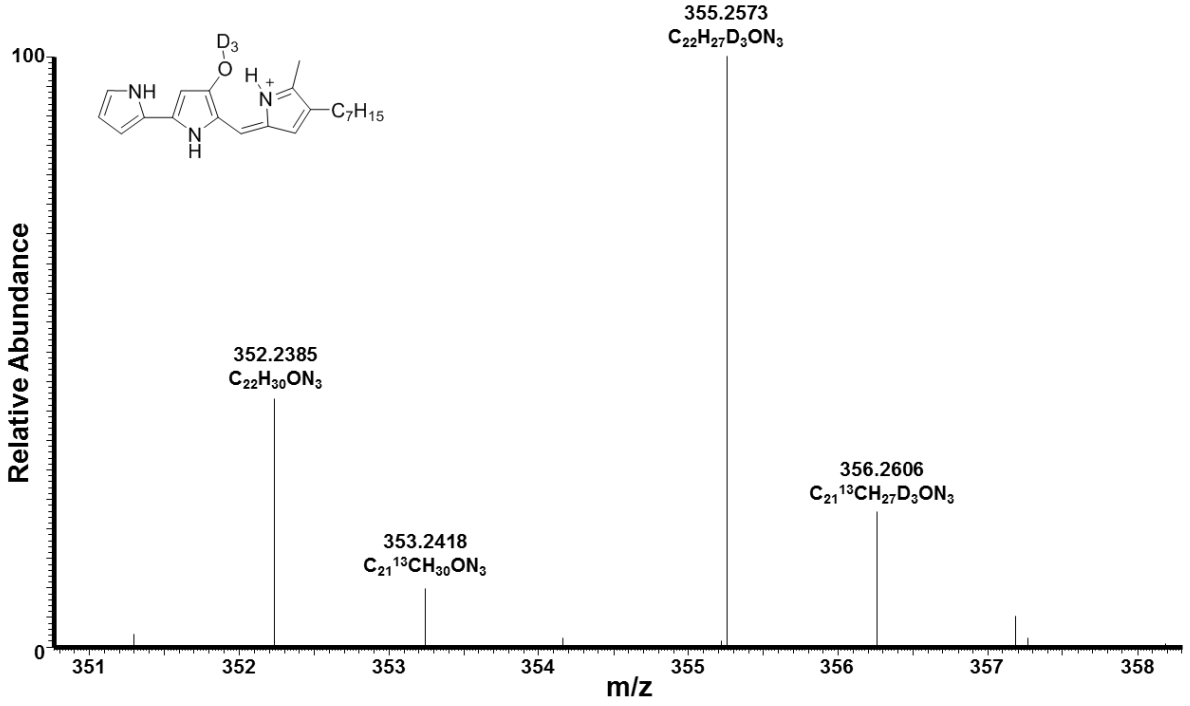


Fig. S79. HRMS spectra of 2-methyl-3-nonyl prodiginine with incorporated methyl-D_3 group derived from 1 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **7** $[M+H]^+$: *m/z* 383, $C_{24}H_{31}D_3N_3O$).

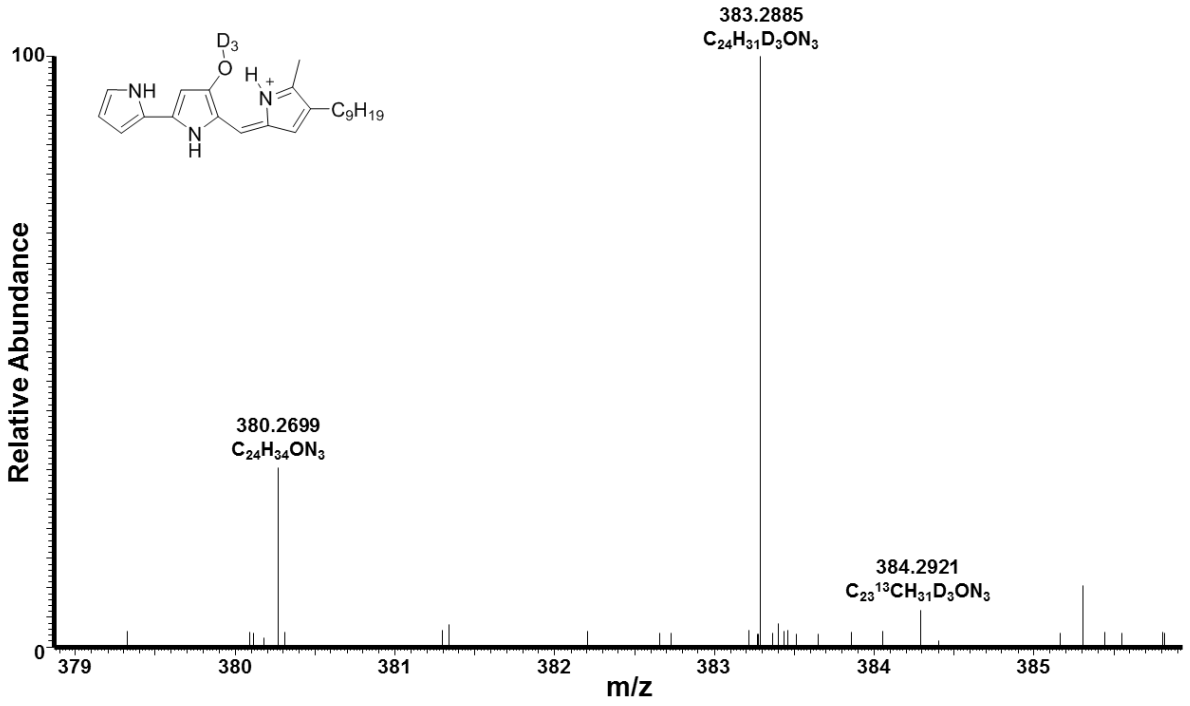


Fig. S80. HRMS spectra of 2-methyl-3-propyl prodiginine with incorporated ^{15}N derived from $^{15}NH_4Cl$ from labeled potato dextrose agar (compound **1** $[M+H]^+$: *m/z* 297, $C_{18}H_{22}N_2{}^{15}NO$).

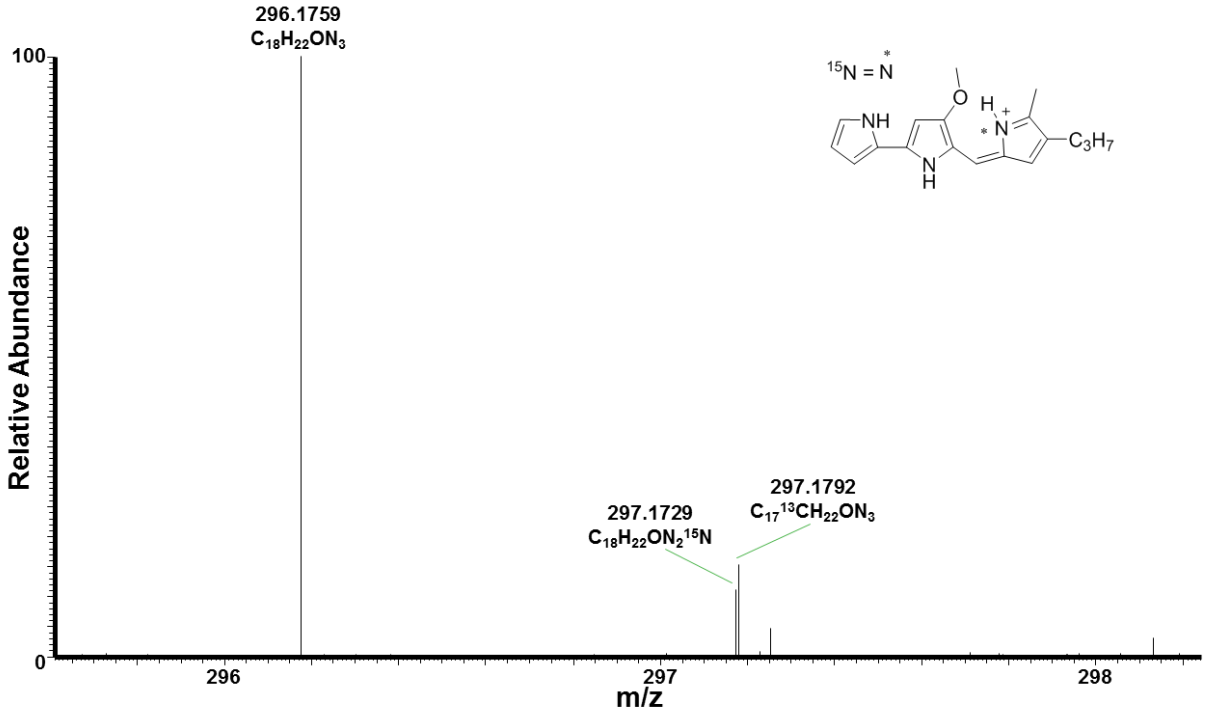


Fig. S81. HRMS spectra of 2-methyl-3-butyl prodiginine with incorporated ^{15}N derived from $^{15}NH_4Cl$ from labeled potato dextrose agar (compound **2** $[M+H]^+$: *m/z* 311, $C_{19}H_{24}N_2{}^{15}NO$).

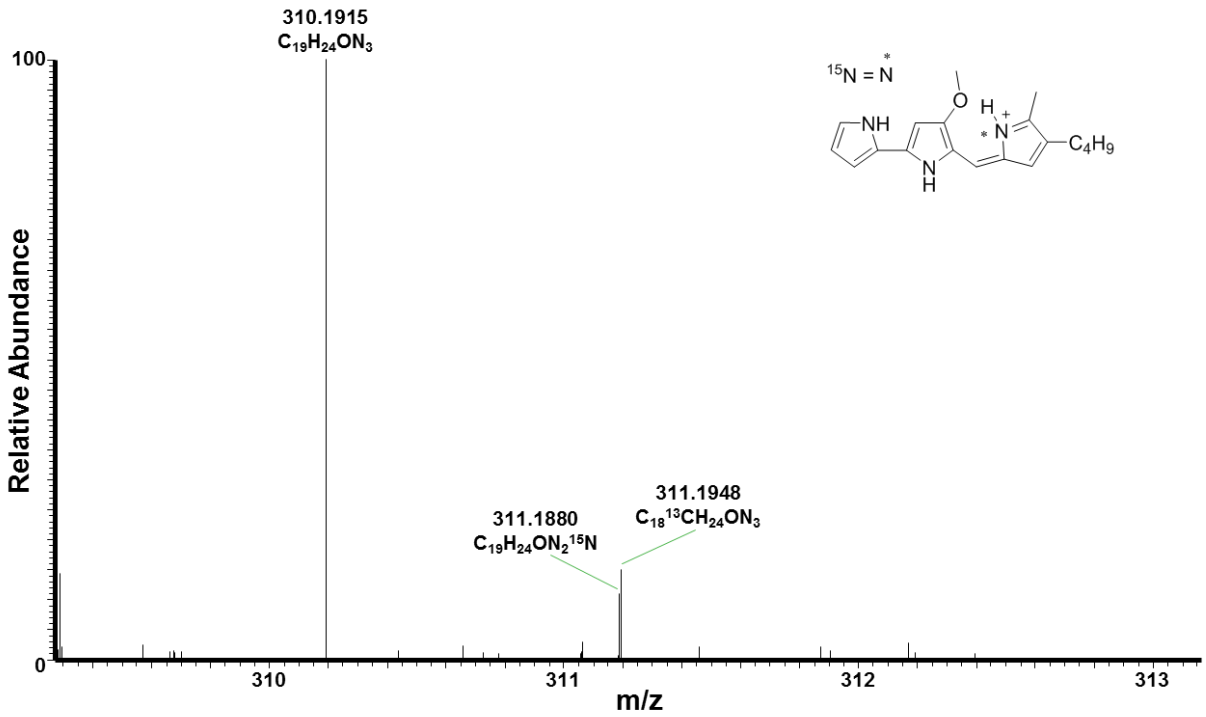


Fig. S82. HRMS spectra of prodigiosin with incorporated ^{15}N derived from $^{15}NH_4Cl$ from labeled potato dextrose agar (compound **3** $[M+H]^+$: *m/z* 325, $C_{20}H_{26}N_2{}^{15}NO$).

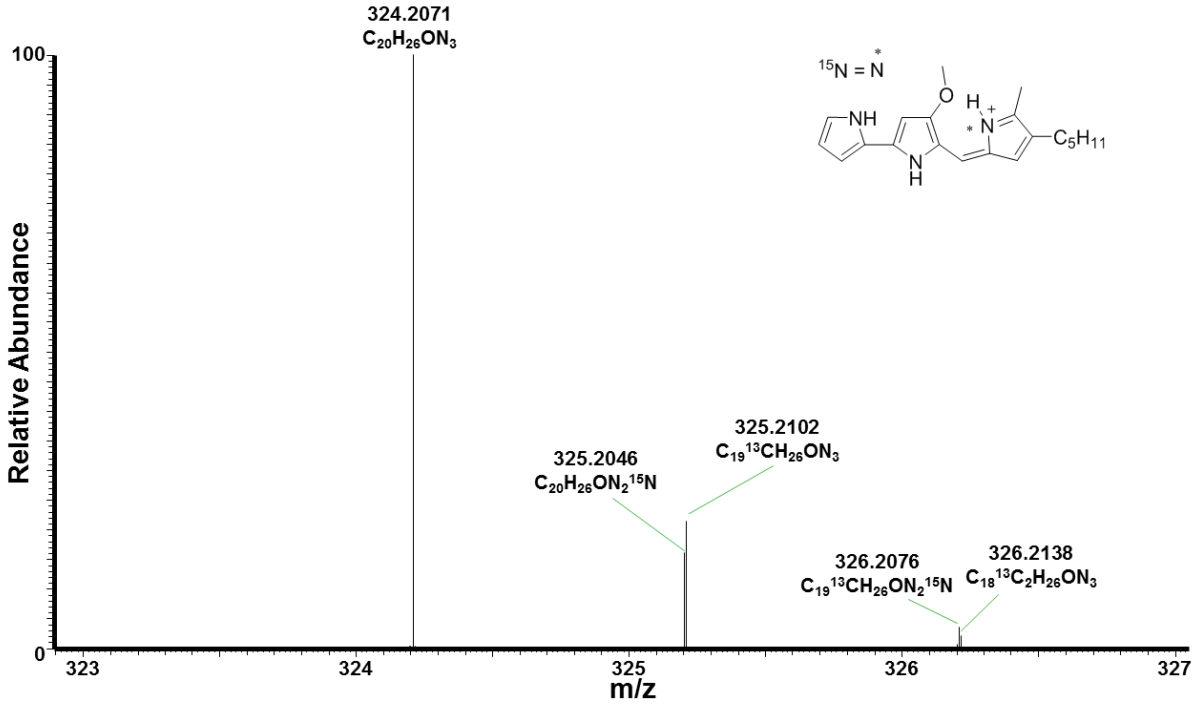


Fig. S83. HRMS spectra of 2-methyl-3-hexyl prodiginine with incorporated ^{15}N derived from $^{15}NH_4Cl$ from labeled potato dextrose agar (compound **4** $[M+H]^+$: *m/z* 339, $C_{21}H_{28}N_2{}^{15}NO$).

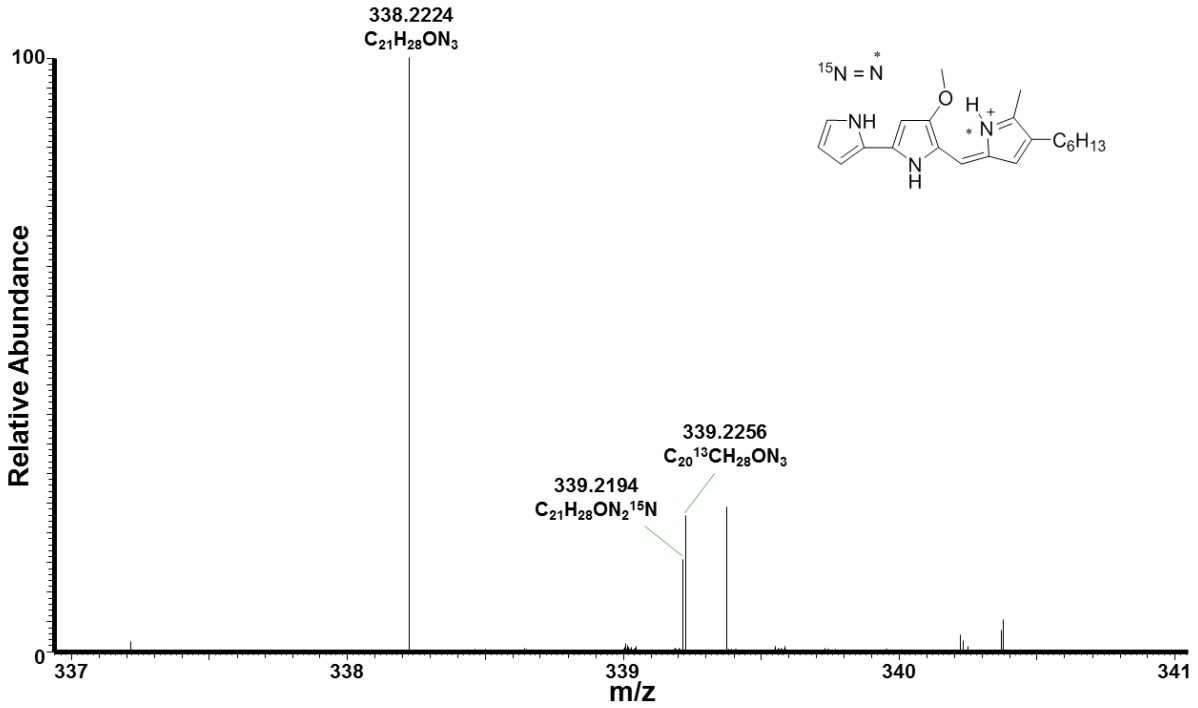


Fig. S84. HRMS spectra of 2-methyl-3-heptyl prodiginine with incorporated ^{15}N derived from $^{15}NH_4Cl$ from labeled potato dextrose agar (compound **5** $[M+H]^+$: *m/z* 353, $C_{22}H_{30}N_2{}^{15}NO$).

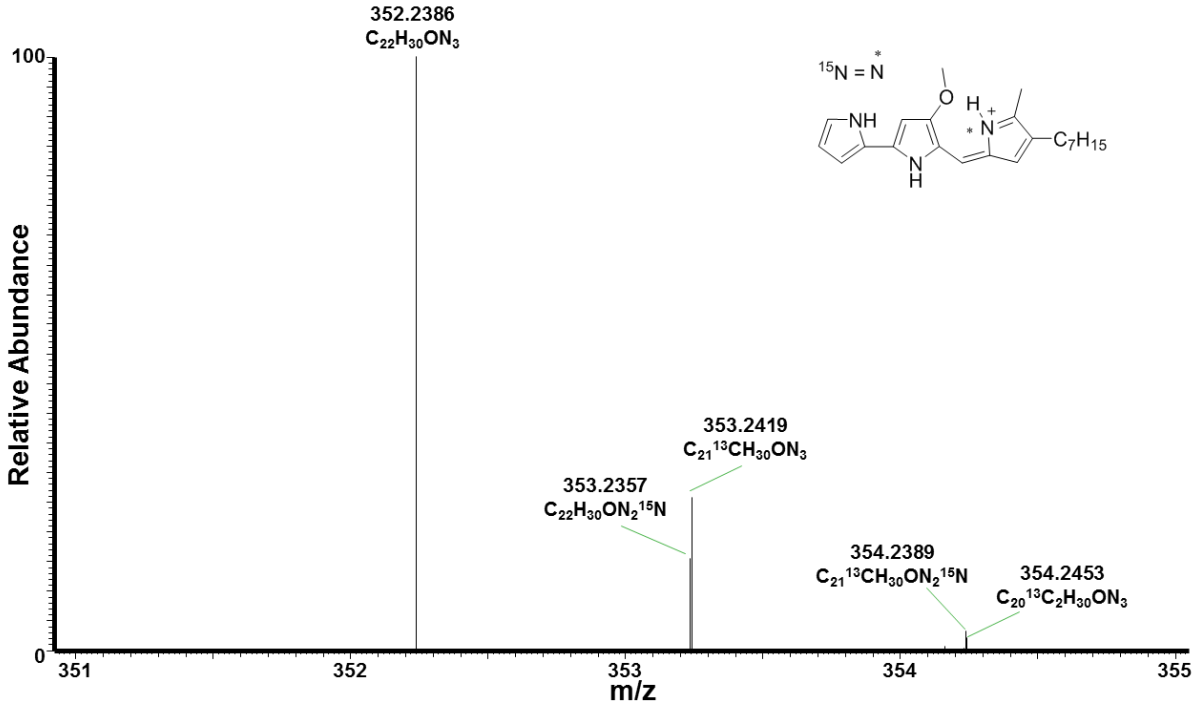


Fig. S85. HRMS spectra of 2-methyl-3-propyl prodiginine with incorporated [1-^{13}C]-L-proline from labeled potato dextrose agar (compound **1** $[M+H]^+$: *m/z* 297, $C_{17}{}^{13}CH_{22}N_3O$).

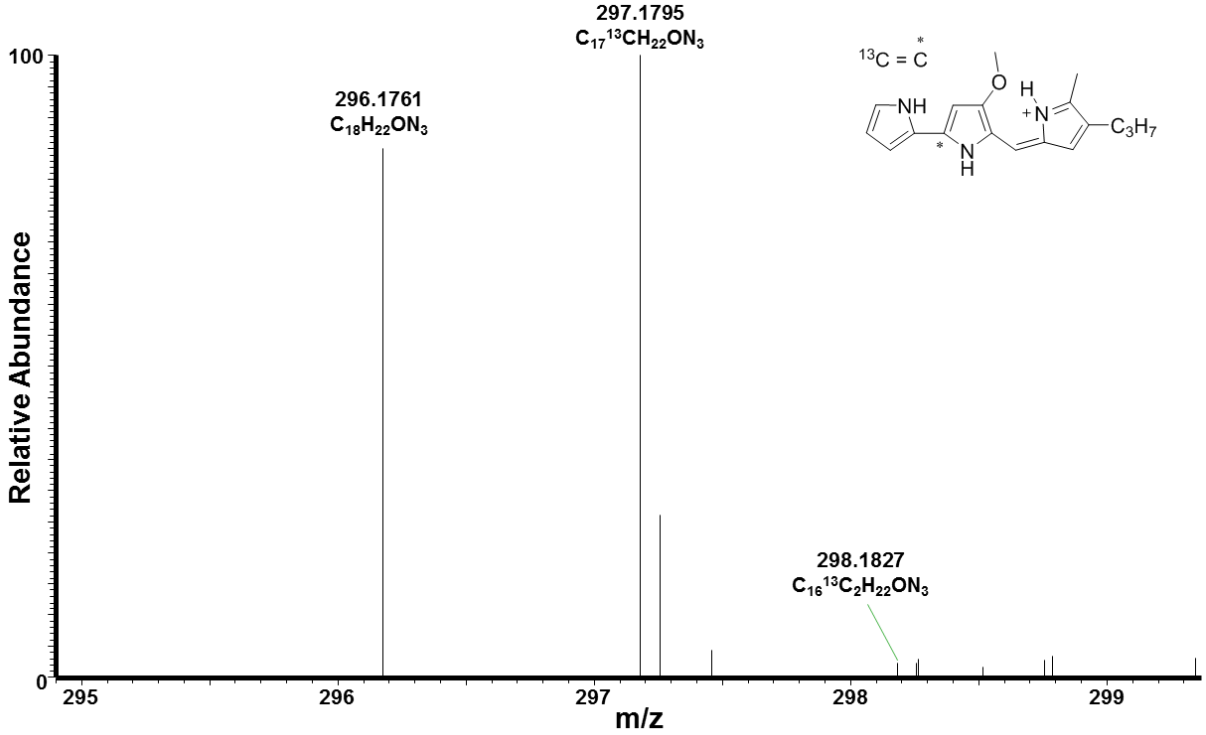


Fig. S86. HRMS spectra of 2-methyl-3-butyl prodiginine with incorporated [1-^{13}C]-L-proline from labeled potato dextrose agar (compound **2** $[M+H]^+$: *m/z* 311, $C_{18}{}^{13}CH_{24}N_3O$).

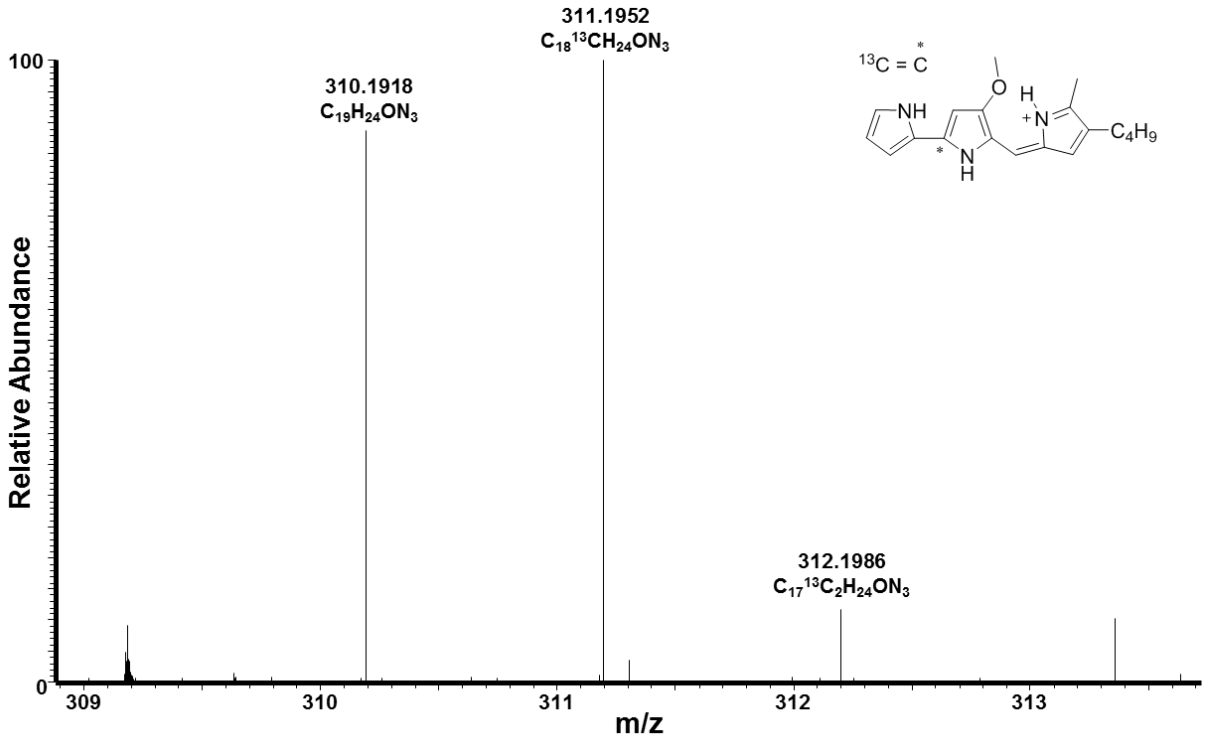


Fig. S87. HRMS spectra of prodigiosin with incorporated [1-^{13}C]-L-proline from labeled potato dextrose agar (compound **3** $[M+H]^+$: *m/z* 325, $C_{19}{}^{13}CH_{26}N_3O$).

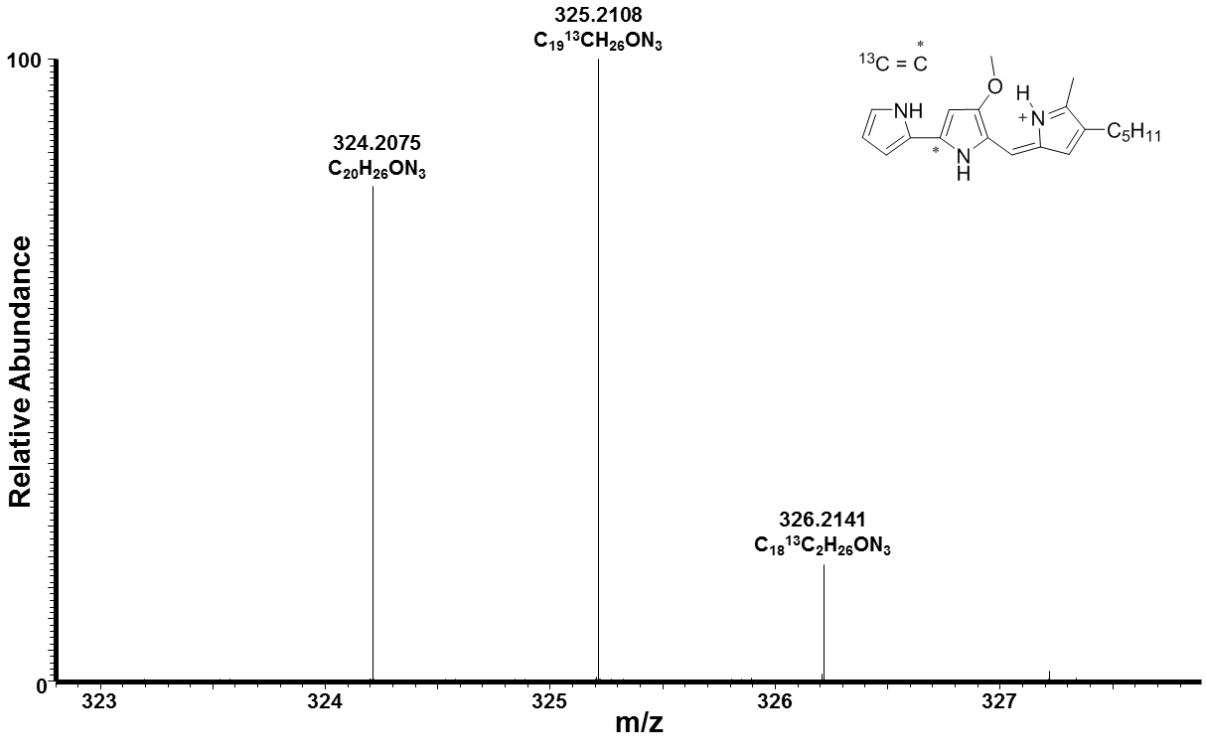


Fig. S88. HRMS spectra of 2-methyl-3-hexyl prodiginine with incorporated [1-^{13}C]-L-proline from labeled potato dextrose agar (compound **4** $[M+H]^+$: *m/z* 339, $C_{20}{}^{13}CH_{28}N_3O$).

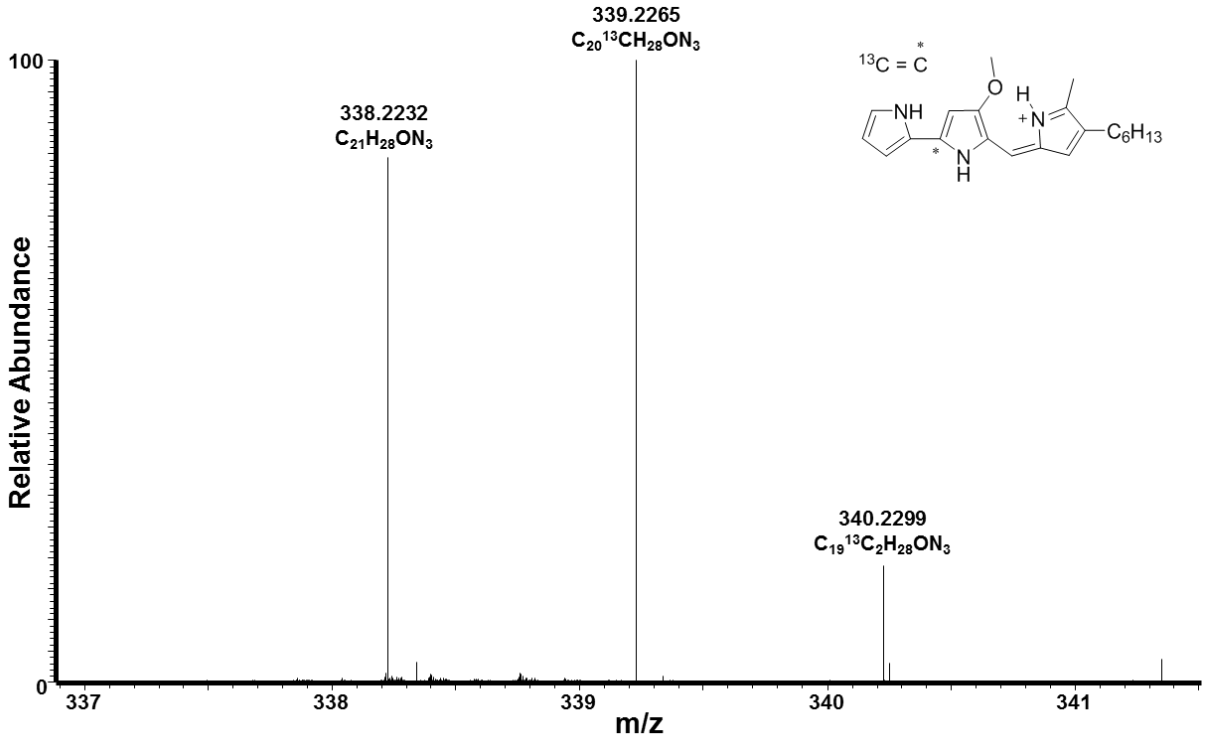


Fig. S89. HRMS spectra of 2-methyl-3-heptyl prodiginine with incorporated [1-^{13}C]-L-proline from labeled potato dextrose agar (compound **5** $[M+H]^+$: *m/z* 353, $C_{21}{}^{13}CH_{30}N_3O$).

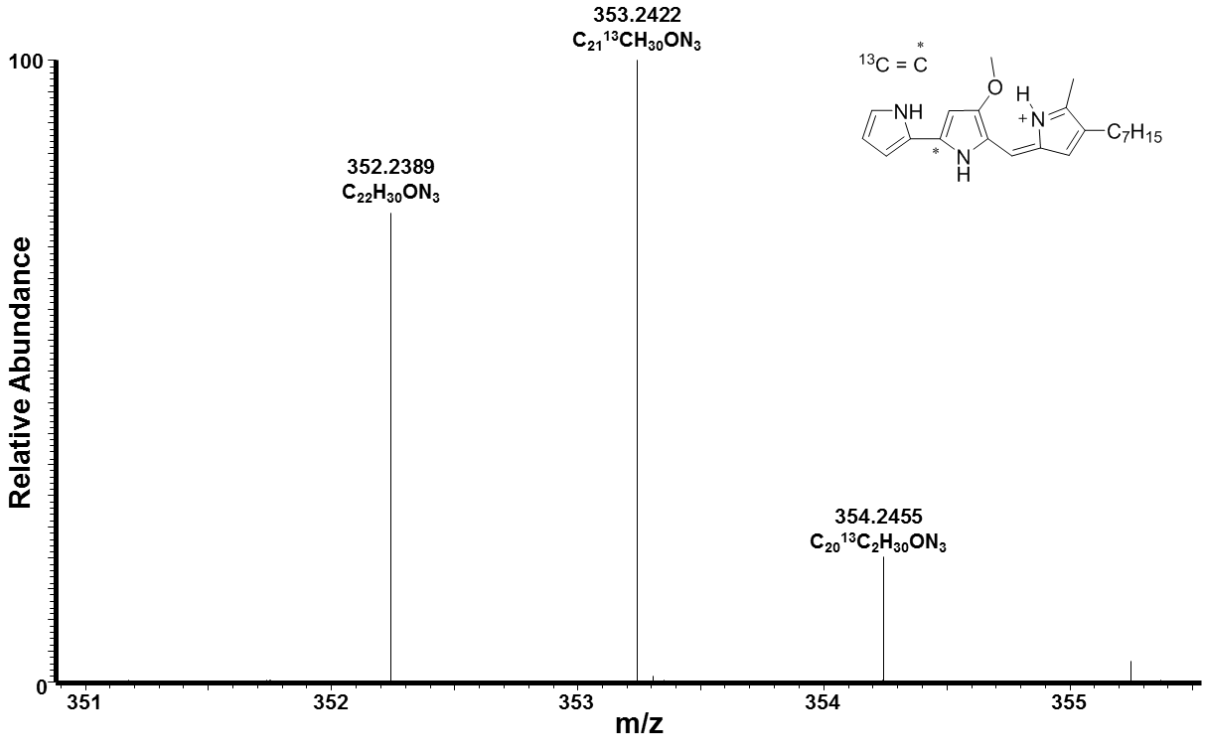


Fig. S90. HRMS spectra of 2-methyl-3-propyl prodiginine with incorporated ^{15}N-L-serine from labeled potato dextrose agar (compound **1** $[M+H]^+$: *m/z* 296, $C_{18}H_{22}N_3O$).

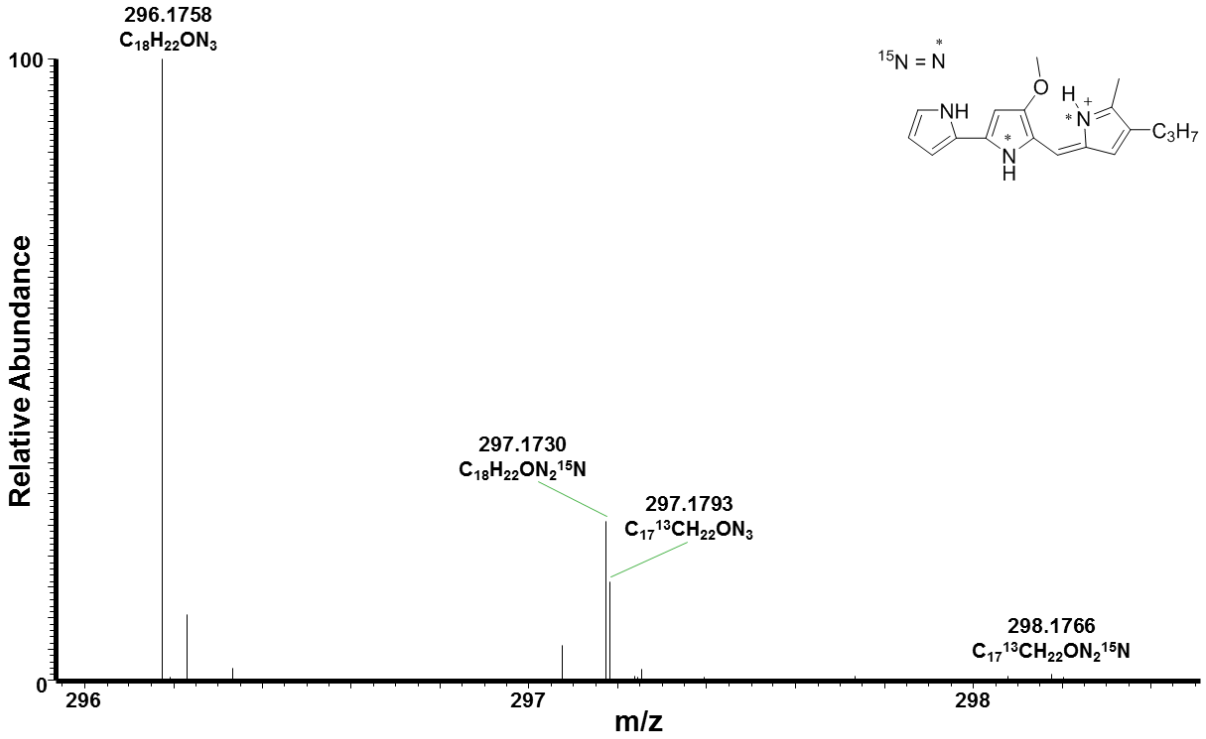


Fig. S91. HRMS spectra of 2-methyl-3-butyl prodiginine with incorporated ^{15}N-L-serine from labeled potato dextrose agar (compound **2** $[M+H]^+$: *m/z* 310, $C_{19}H_{24}N_3O$).

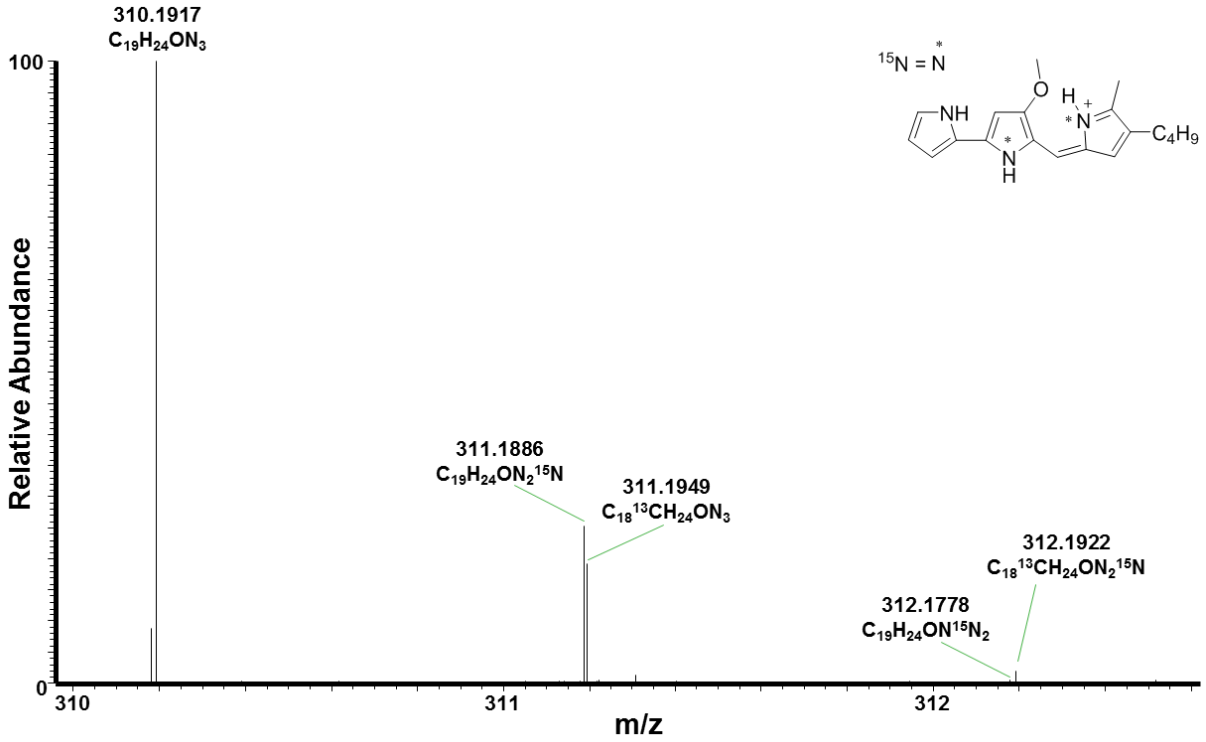


Fig. S92. HRMS spectra of prodigiosin with incorporated ^{15}N-L-serine from labeled potato dextrose agar (compound **3** $[M+H]^+$: *m/z* 324, $C_{20}H_{26}N_3O$).

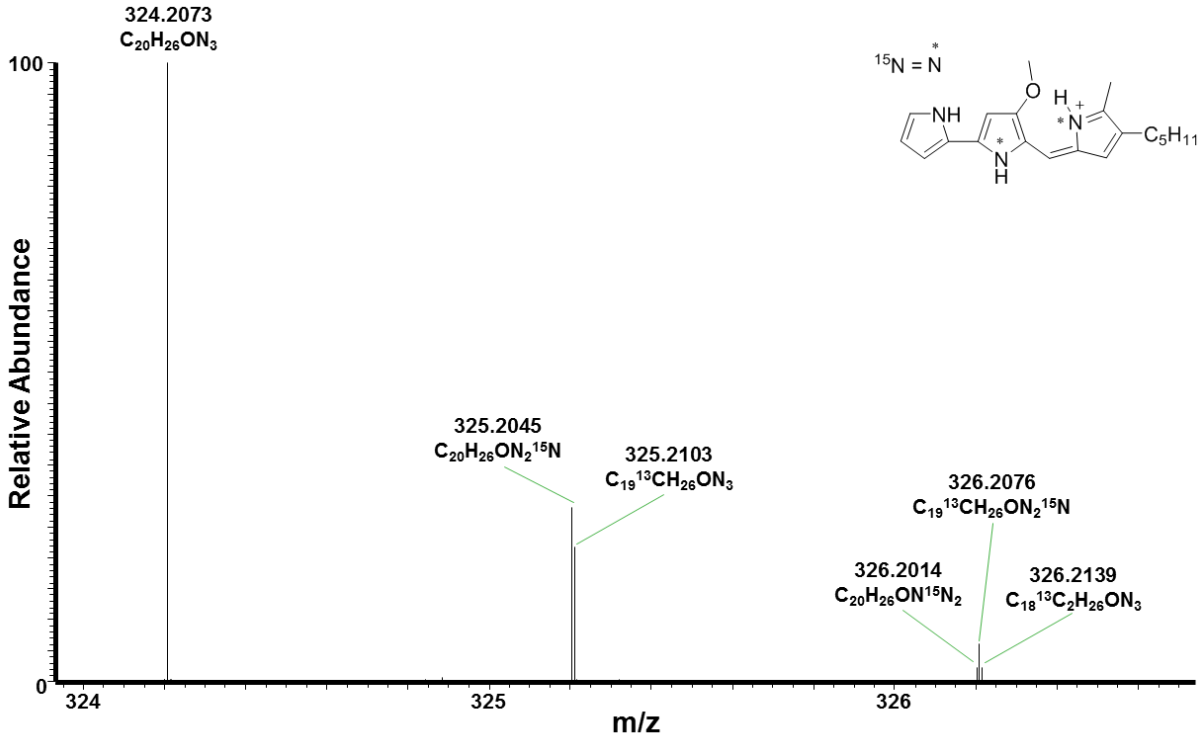


Fig. S93. HRMS spectra of 2-methyl-3-hexyl prodiginine with incorporated ^{15}N-L-serine from labeled potato dextrose agar (compound **4** $[M+H]^+$: *m/z* 338, $C_{21}H_{28}N_3O$).

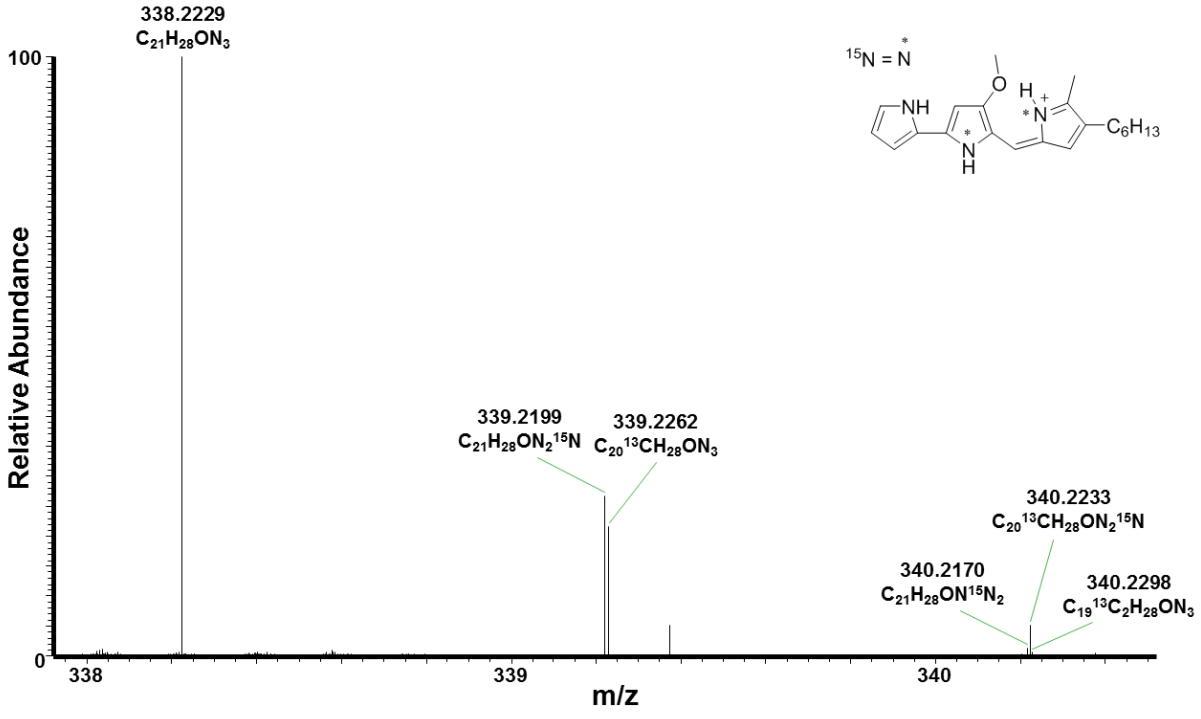


Fig. S94. HRMS spectra of 2-methyl-3-heptyl prodiginine with incorporated ^{15}N-L-serine from labeled potato dextrose agar (compound **5** $[M+H]^+$: *m/z* 352, $C_{22}H_{30}N_3O$).

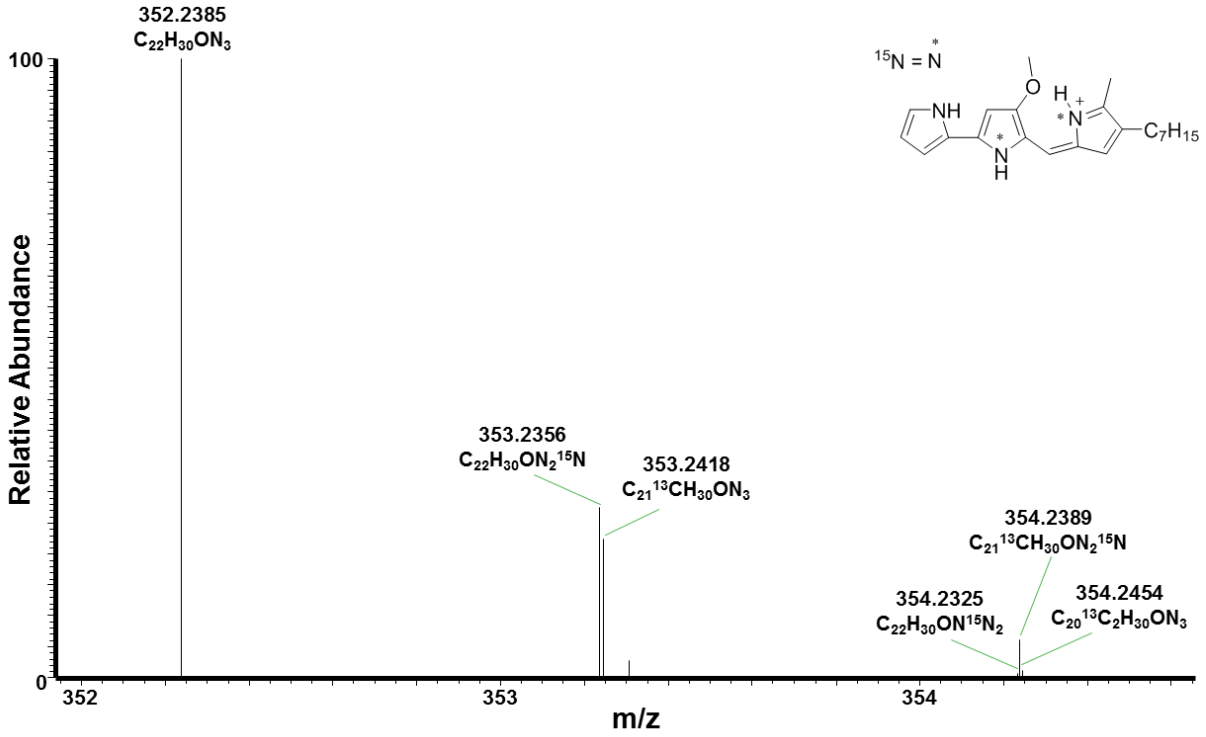


Fig. S95. HRMS spectra of 2-methyl-3-propyl prodiginine with incorporated methyl-D_3 group derived from 0.5 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **1** $[M+H]^+$: *m/z* 299, $C_{18}H_{19}D_3N_3O$).

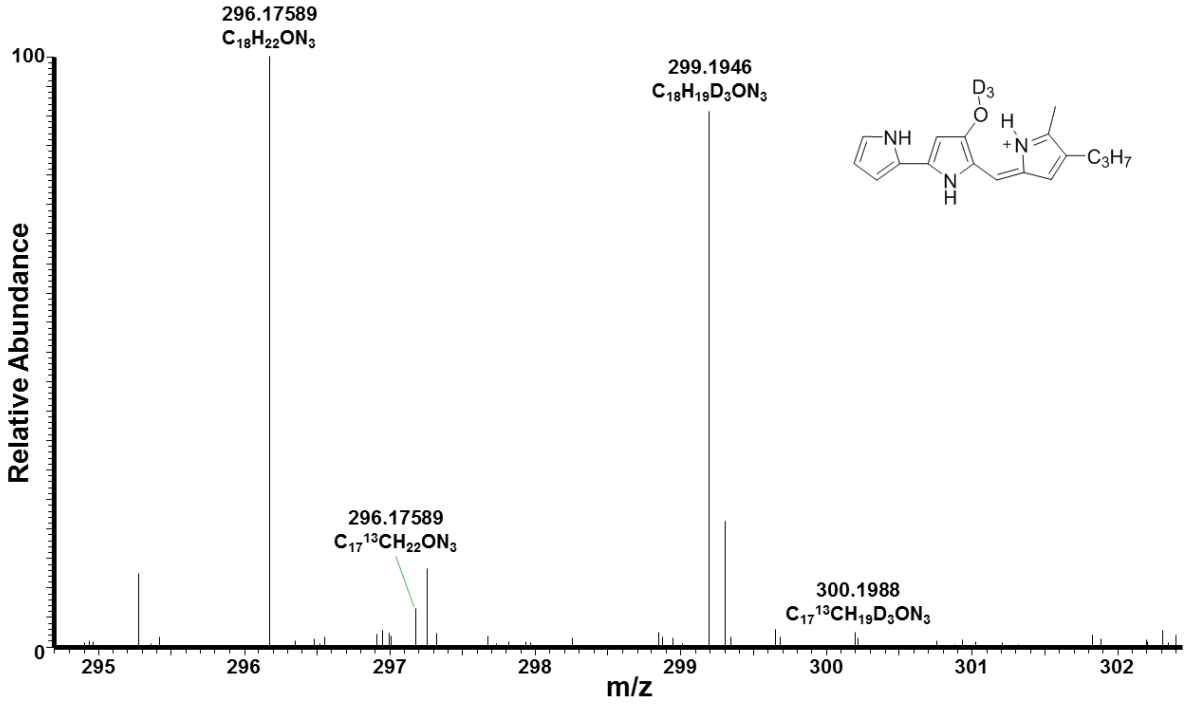


Fig. S96. HRMS spectra of 2-methyl-3-butyl prodiginine with incorporated methyl-D_3 group derived from 0.5 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **2** $[M+H]^+$: *m/z* 313, $C_{19}H_{21}D_3N_3O$).

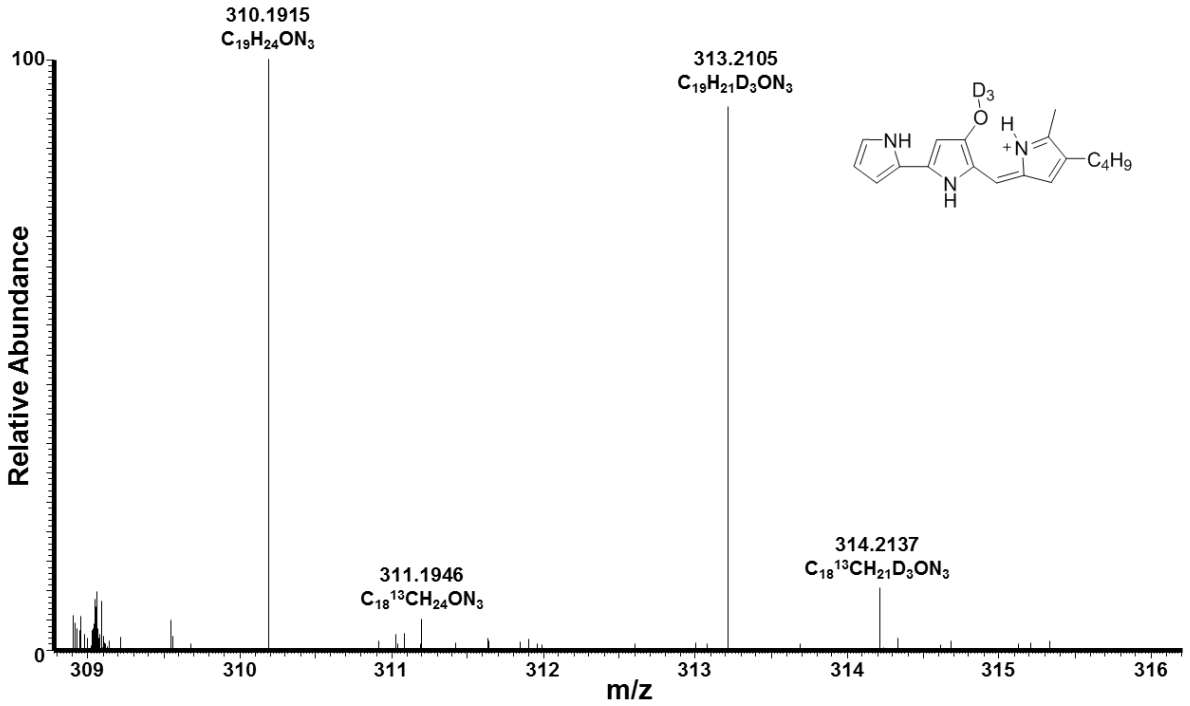


Fig. S97. HRMS spectra of prodigiosin with incorporated methyl-D_3 group derived from 0.5 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **3** $[M+H]^+$: *m/z* 327, $C_{20}H_{23}D_3N_3O$).

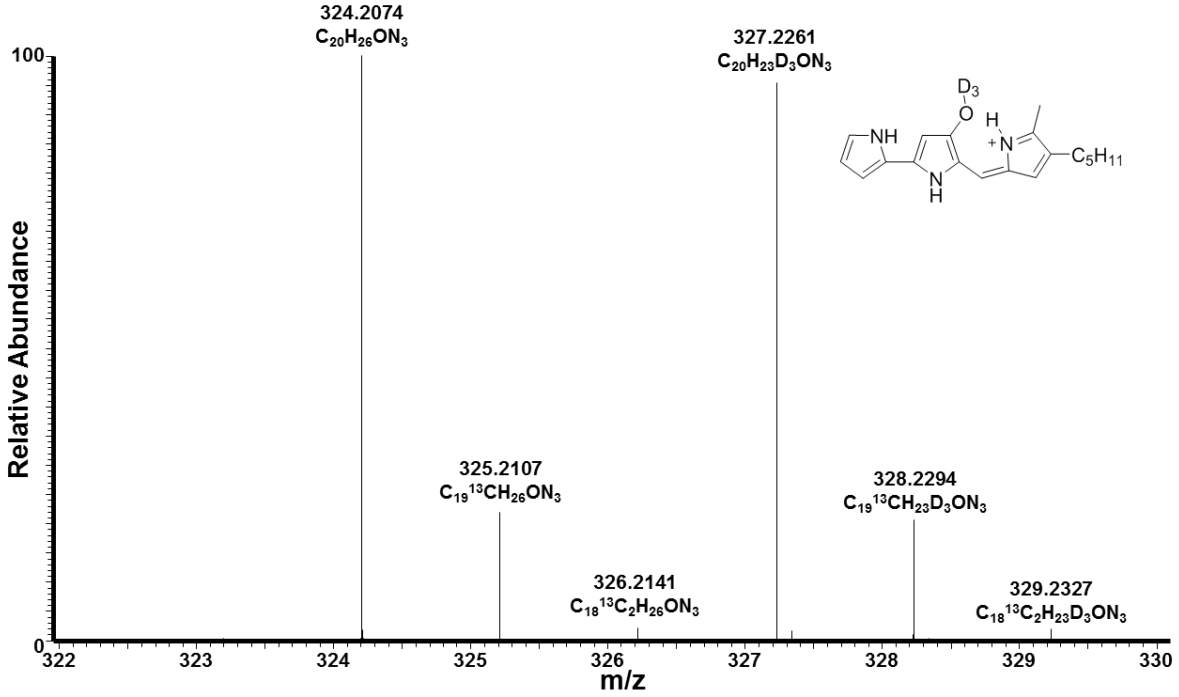


Fig. S98. HRMS spectra of 2-methyl-3-hexyl prodiginine with incorporated methyl-D_3 group derived from 0.5 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **4** $[M+H]^+$: *m/z* 341, $C_{21}H_{25}D_3N_3O$).

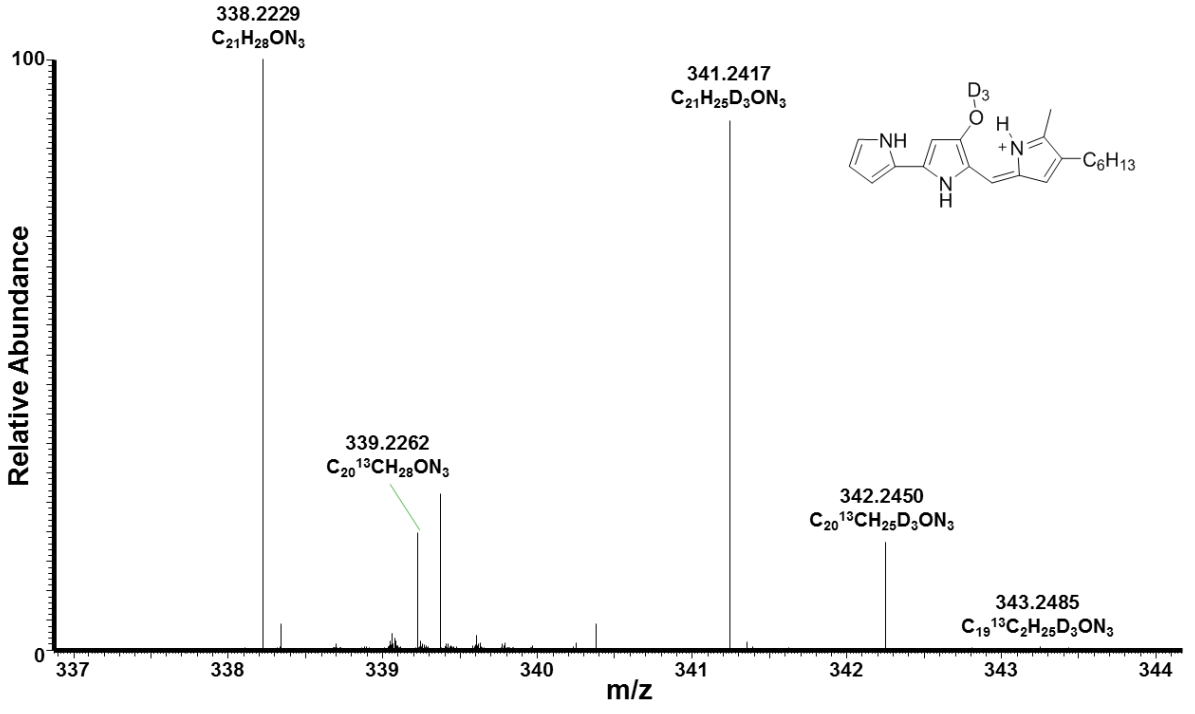


Fig. S99. HRMS spectra of 2-methyl-3-heptyl prodiginine with incorporated methyl-D_3 group derived from 0.5 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **5** $[M+H]^+$: *m/z* 355, $C_{22}H_{27}D_3N_3O$).

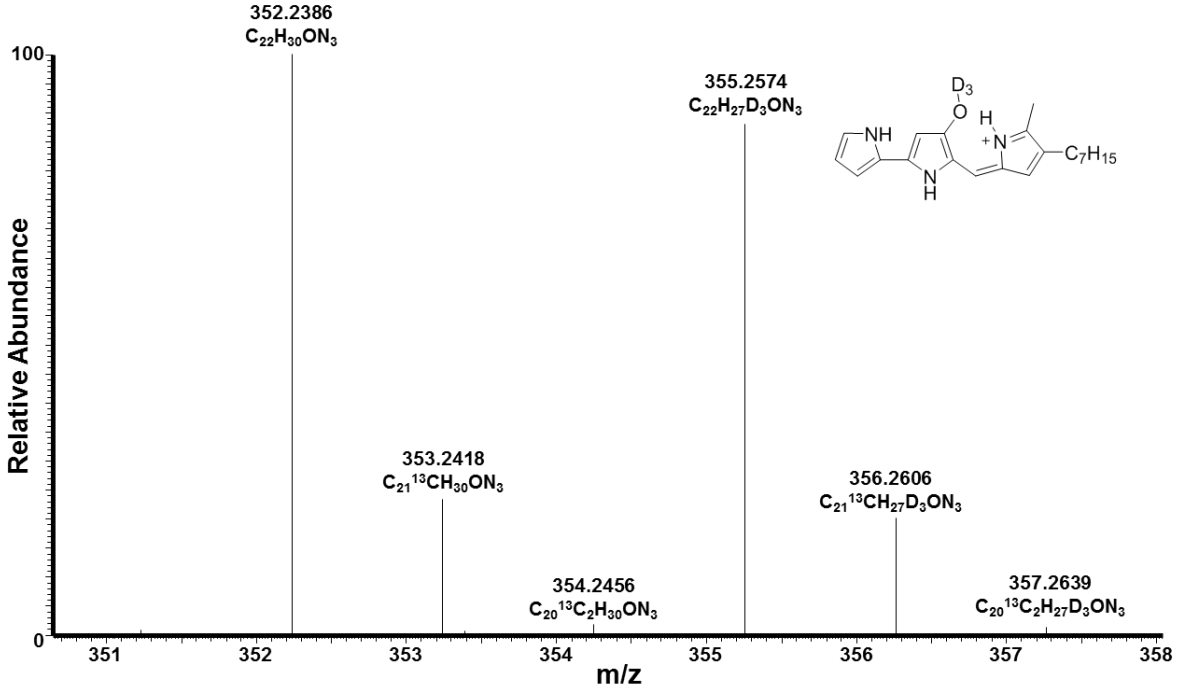


Fig. S100. HRMS spectra of 2-methyl-3-nonyl prodiginine with incorporated methyl-D_3 group derived from 0.5 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **7** $[M+H]^+$: *m/z* 383, $C_{24}H_{31}D_3N_3O$).

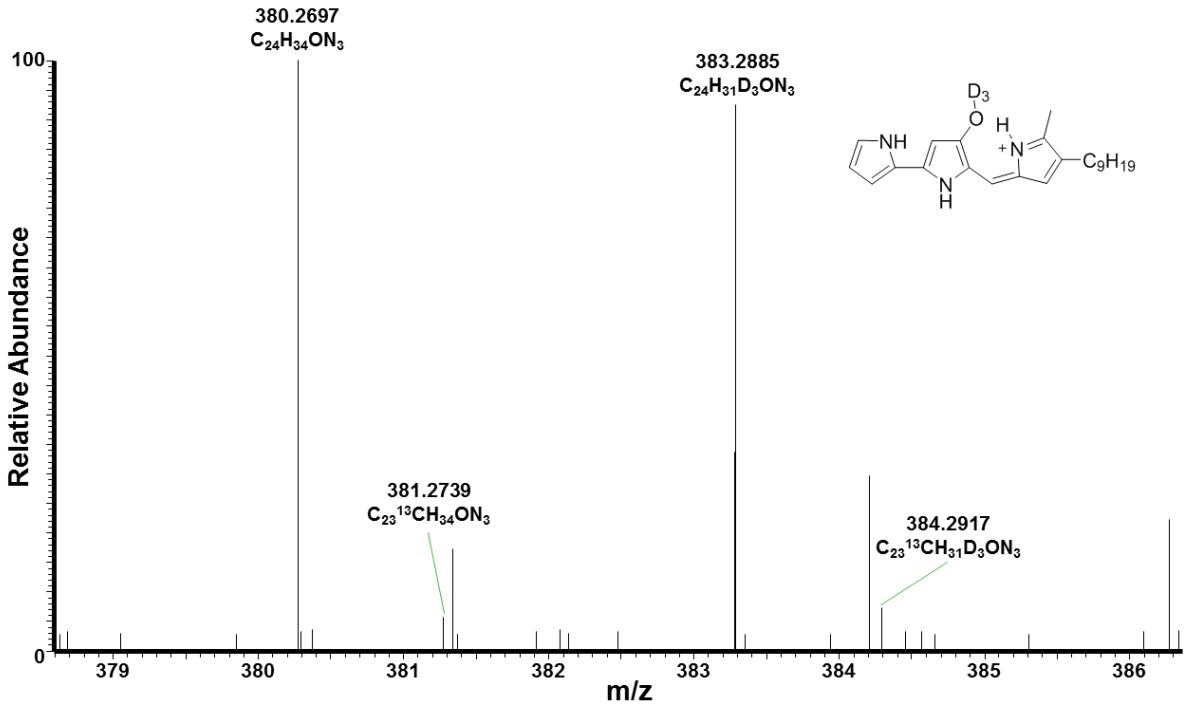


Fig. S101. HRMS spectra of 2-methyl-3-propyl prodiginine with incorporated methyl-D_3 group derived from 2 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **1** $[M+H]^+$: *m/z* 299, $C_{18}H_{19}D_3N_3O$).

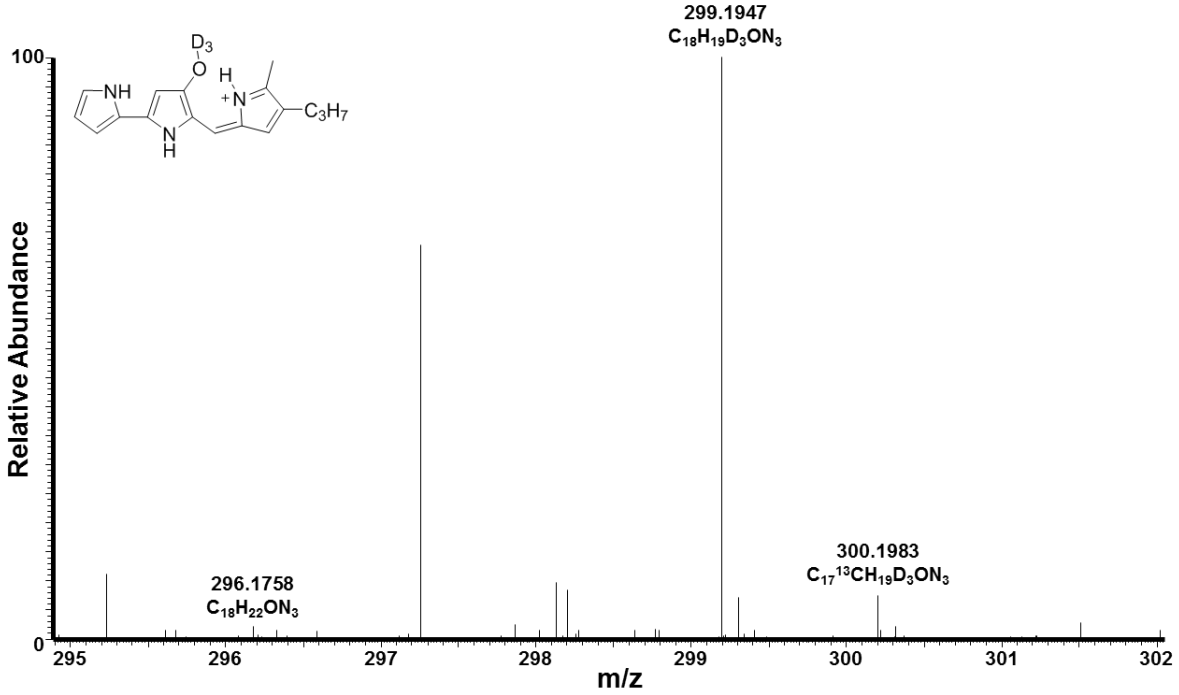


Fig. S102. HRMS spectra of 2-methyl-3-butyl prodiginine with incorporated methyl-D_3 group derived from 2 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **2** $[M+H]^+$: *m/z* 313, $C_{19}H_{21}D_3N_3O$).

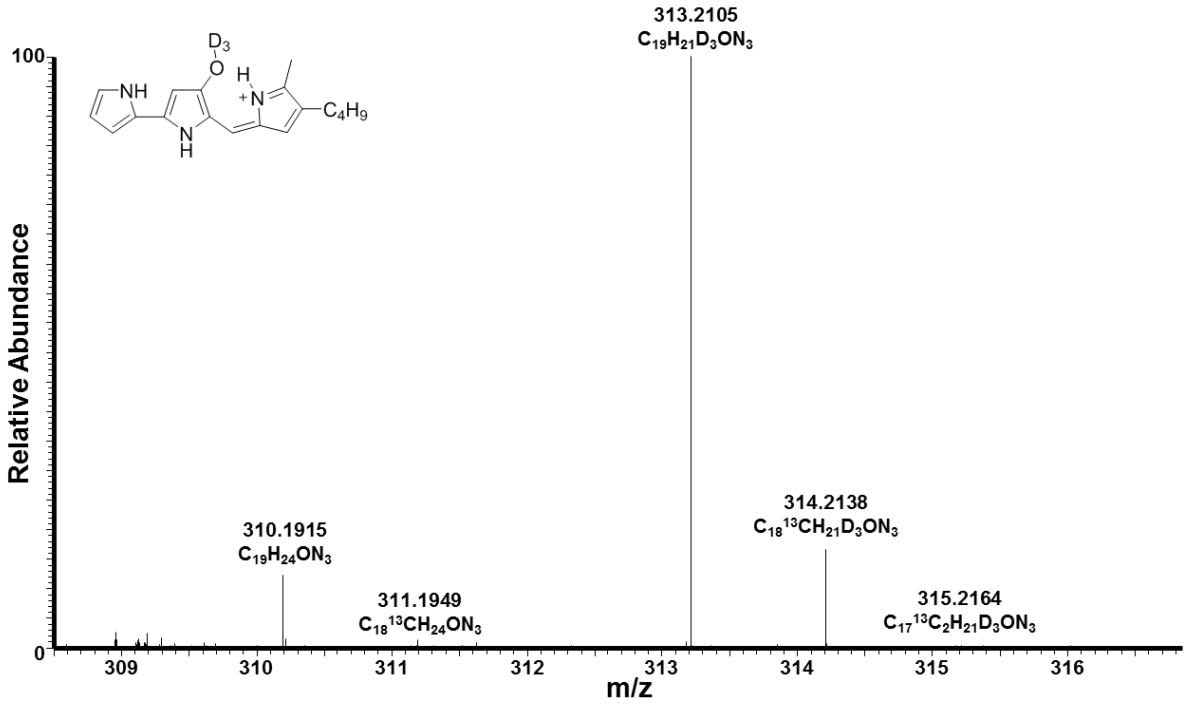


Fig. S103. HRMS spectra of prodigiosin with incorporated methyl-D_3 group derived from 2 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **3** $[M+H]^+$: *m/z* 327, $C_{20}H_{23}D_3N_3O$).

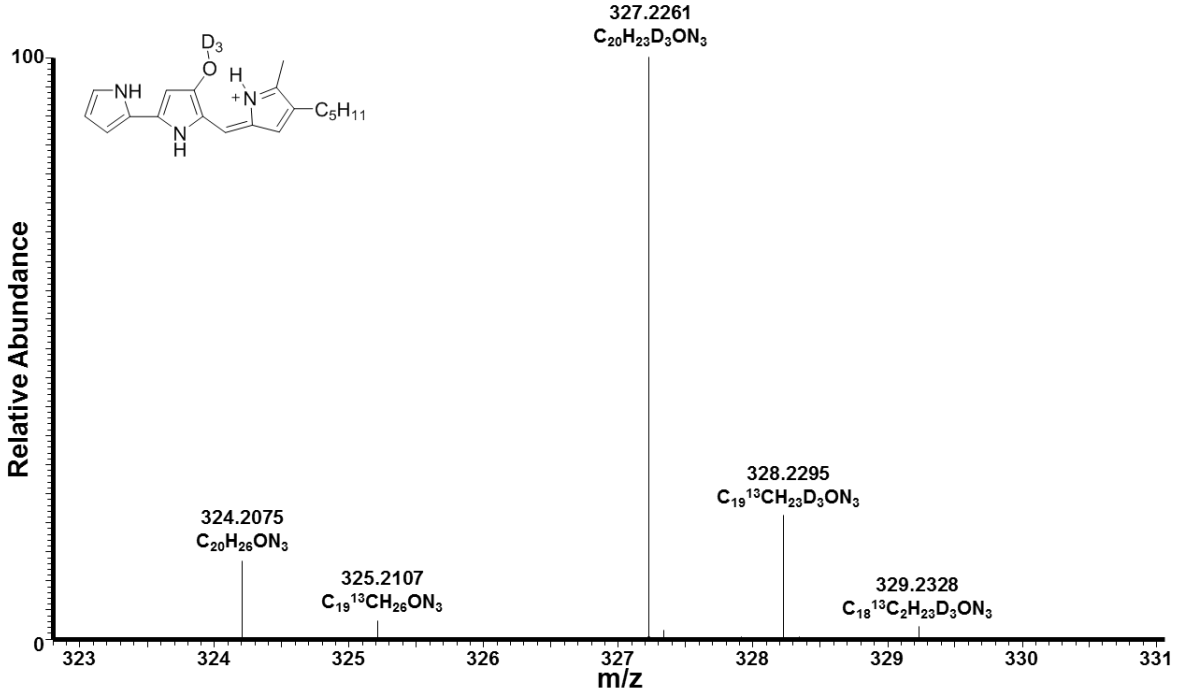


Fig. S104. HRMS spectra of 2-methyl-3-hexyl prodiginine with incorporated methyl-D_3 group derived from 2 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **4** $[M+H]^+$: *m/z* 341, $C_{21}H_{25}D_3N_3O$).

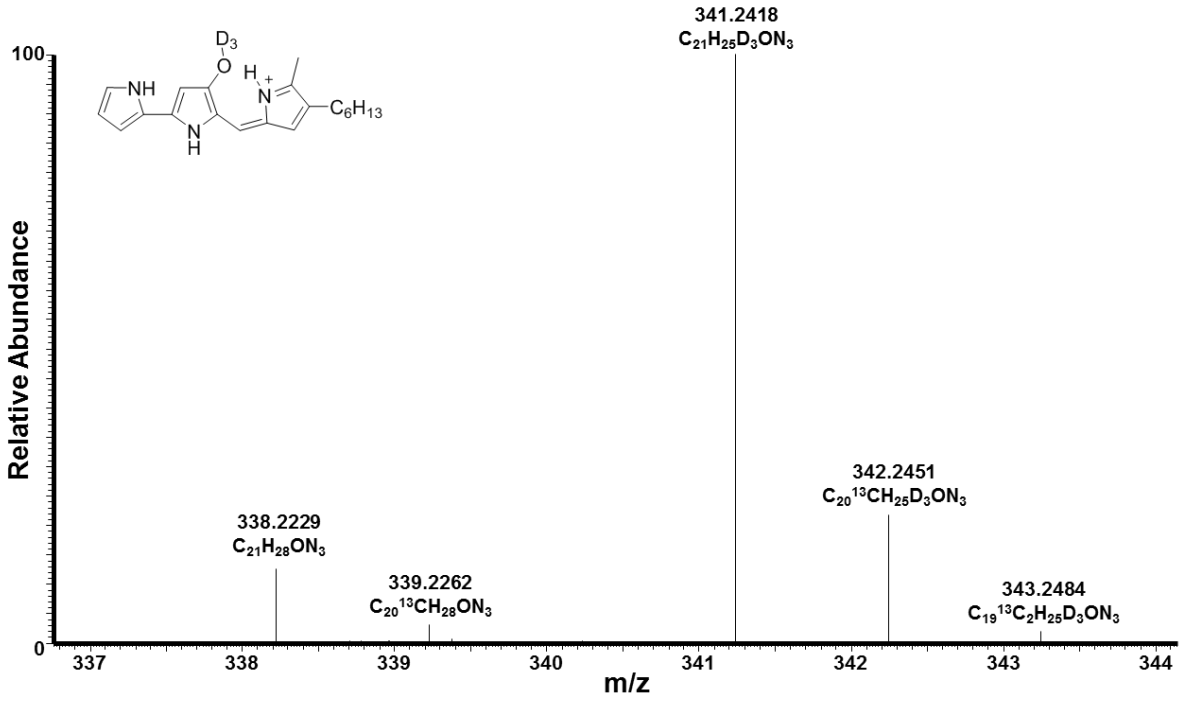


Fig. S105. HRMS spectra of 2-methyl-3-heptyl prodiginine with incorporated methyl-D_3 group derived from 2 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **5** $[M+H]^+$: *m/z* 355, $C_{22}H_{27}D_3N_3O$).

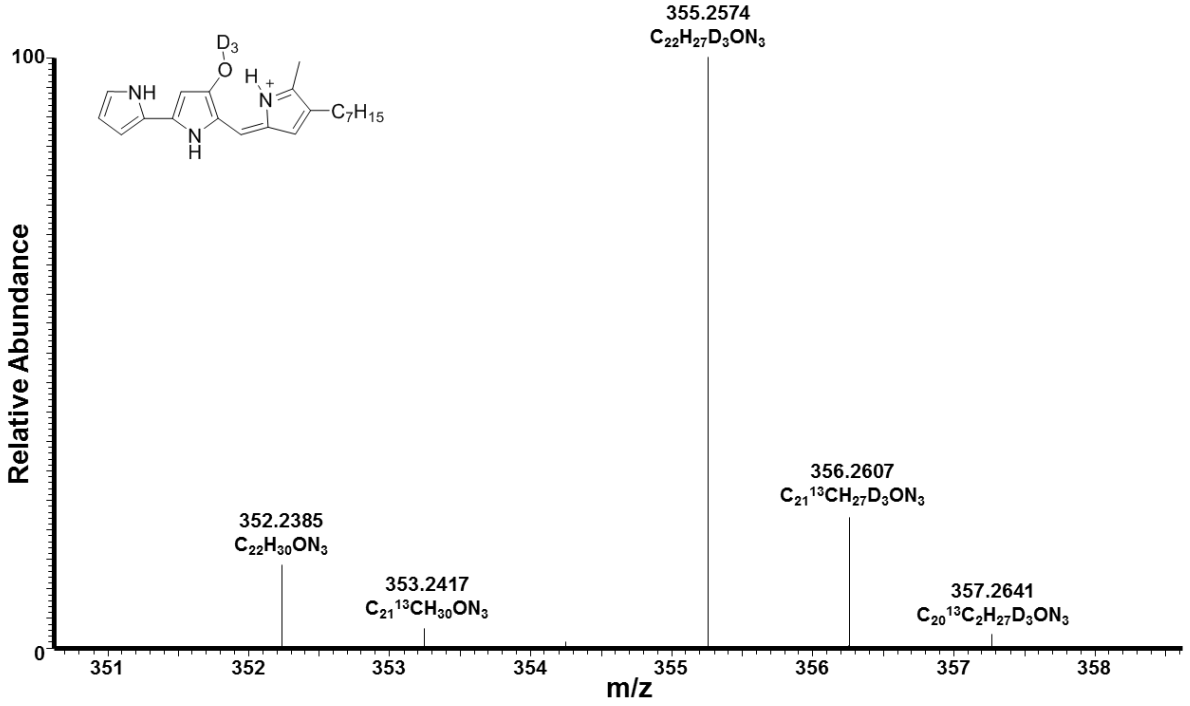


Fig. S106. HRMS spectra of 2-methyl-3-nonyl prodiginine with incorporated methyl-D_3 group derived from 2 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **7** $[M+H]^+$: *m/z* 383, $C_{24}H_{31}D_3N_3O$).

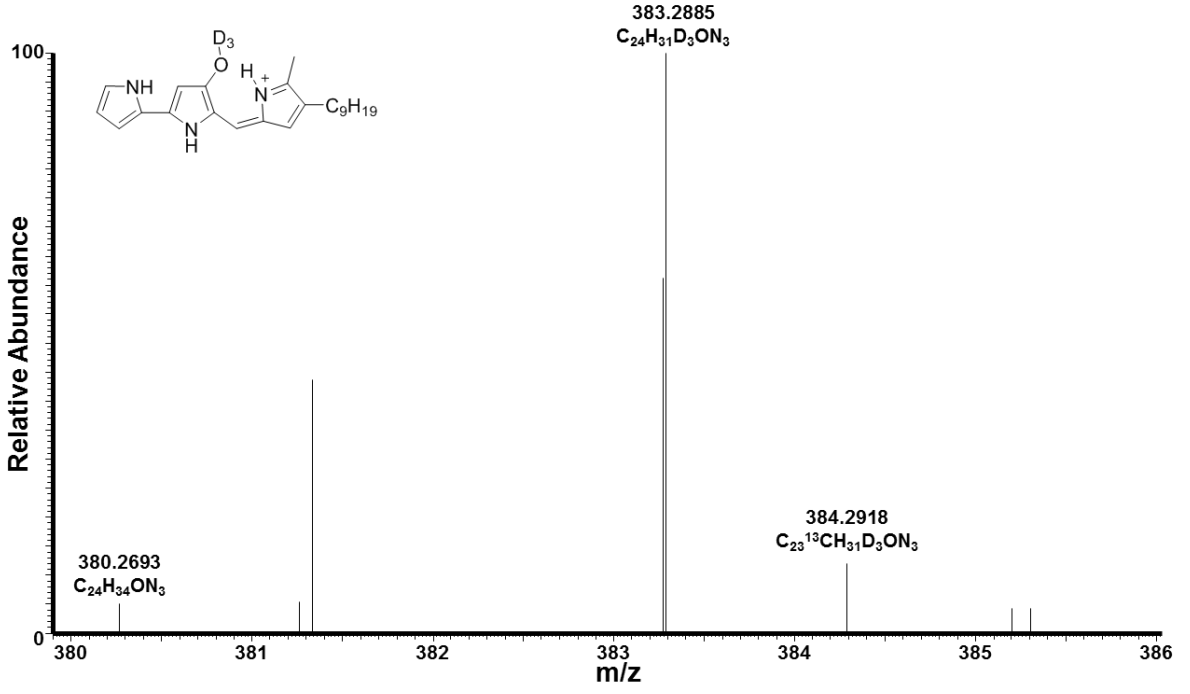


Fig. S107. HRMS spectra of 4-methoxy-2,2'-bipyrrole-5-carbaldehyde (MBC) with incorporated ^{15}N-L-serine from labeled nutrient agar (compound **8** $[M+H]^+$: *m/z* 192, $C_{10}H_{11}N^{15}NO_2$).

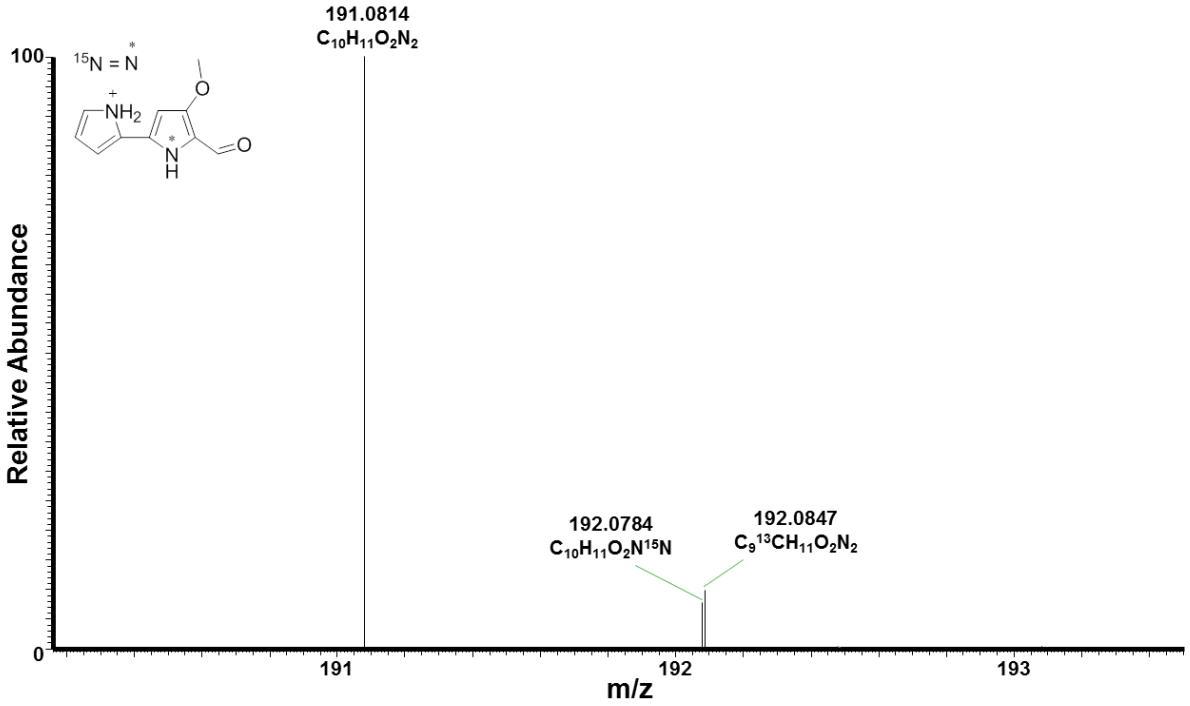


Fig. S108. HRMS spectra of 4-methoxy-2,2'-bipyrrole-5-carbaldehyde (MBC) with incorporated methyl-D_3 group derived from 1 mg/mL [methyl-D_3]-L-methionine on nutrient agar (compound **8** $[M+H]^+$: *m/z* 194, $C_{10}H_8D_3N_2O_2$).

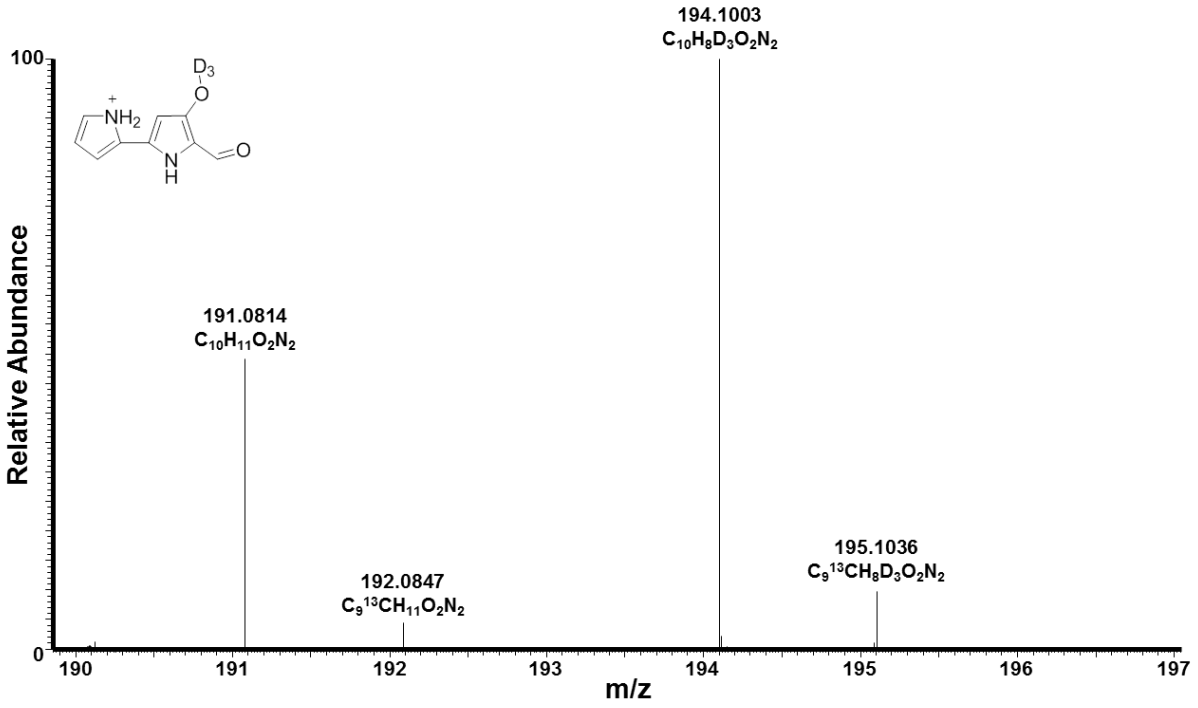


Fig. S109. HRMS spectra of 4-methoxy-2,2'-bipyrrole-5-carbaldehyde (MBC) with incorporated methyl-D_3 group derived from 2 mg/mL [methyl-D_3]-L-methionine on nutrient agar (compound **8** $[M+H]^+$: *m/z* 194, $C_{10}H_8D_3N_2O_2$).

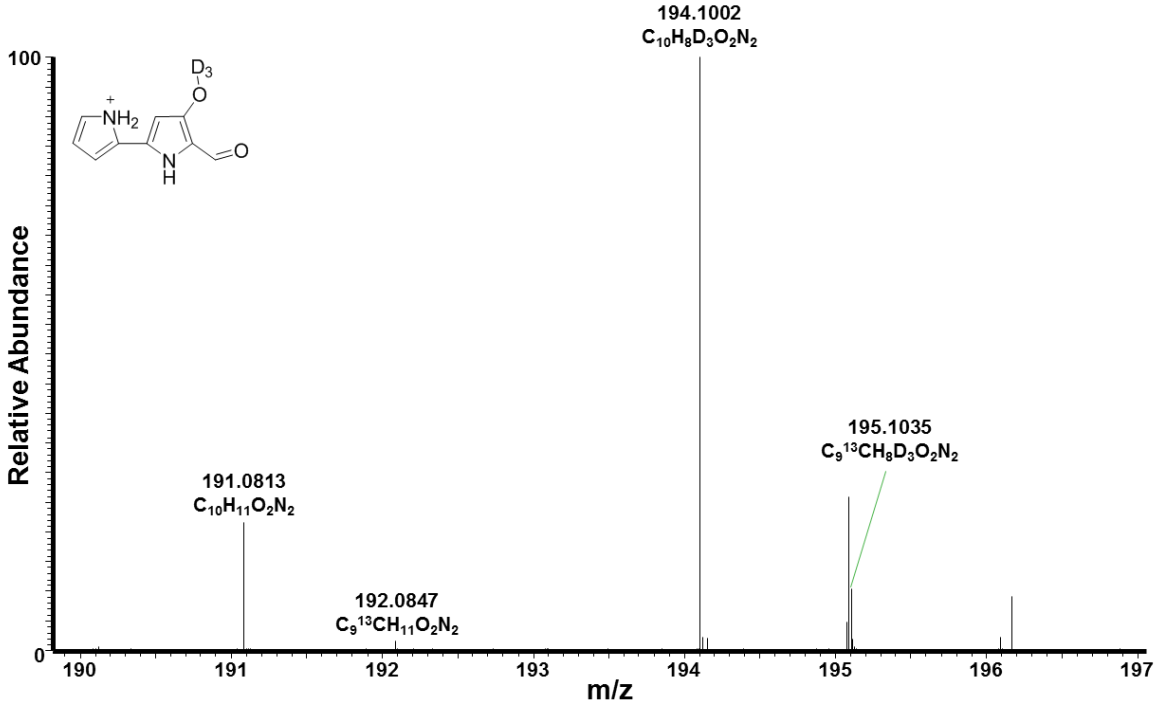


Fig. S110. HRMS spectra of 4-methoxy-2,2'-bipyrrole-5-carbaldehyde (MBC) with incorporated methyl-D_3 group derived from 0.5 mg/mL [methyl-D_3]-L-methionine on nutrient agar (compound **8** $[M+H]^+$: *m/z* 194, $C_{10}H_8D_3N_2O_2$).

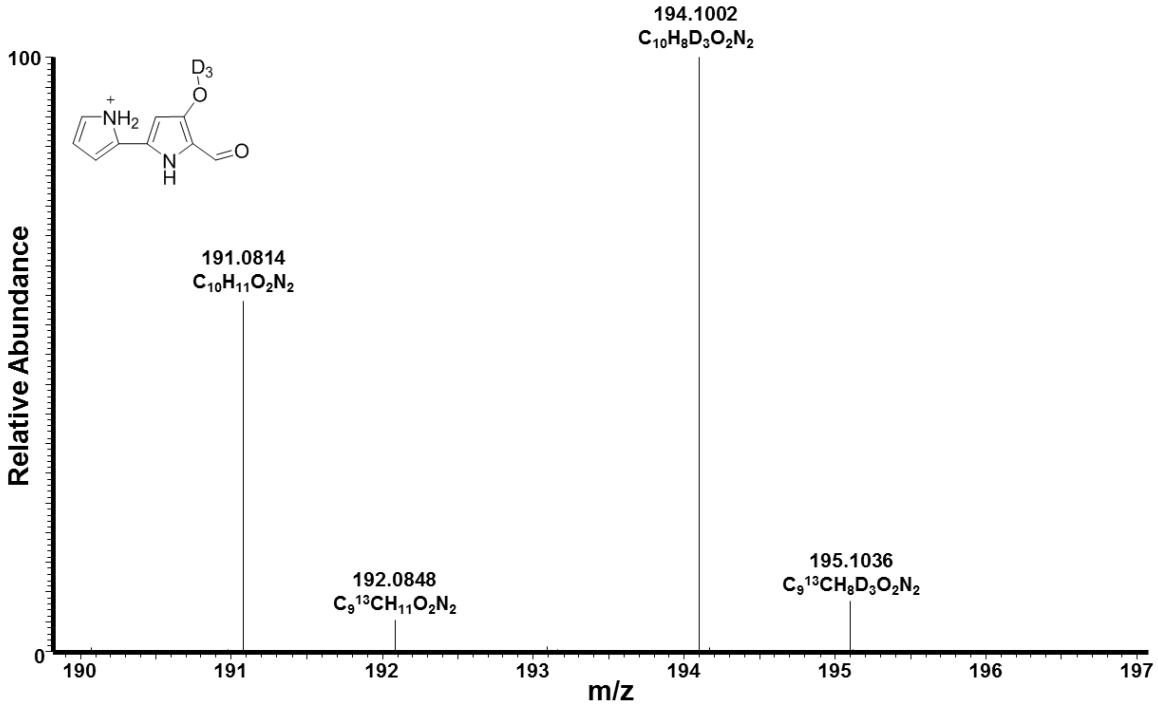


Fig. S111. HRMS spectra of 4-methoxy-2,2'-bipyrrole-5-carbaldehyde (MBC) with incorporated [1-^{13}C]-L-proline from labeled nutrient agar (compound **8** $[M+H]^+$: *m/z* 192, $C_9{}^{13}CH_{11}N_2O_2$).

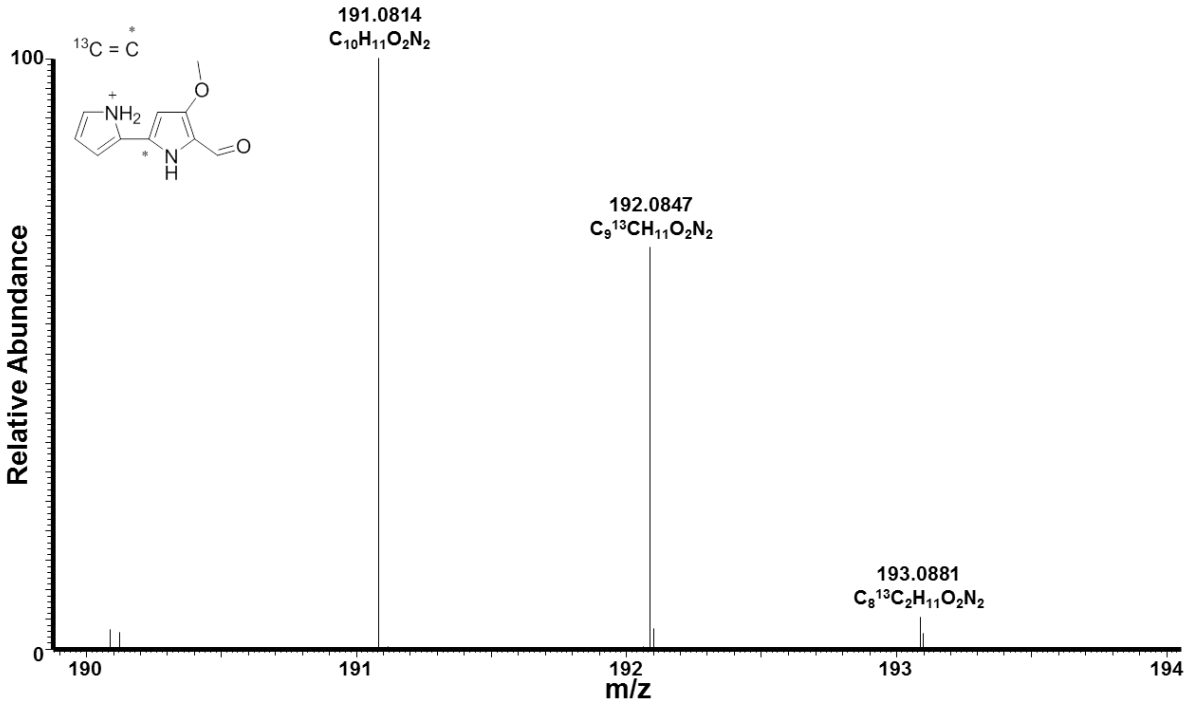


Fig. S112. HRMS spectra of 4-methoxy-2,2'-bipyrrole-5-carbaldehyde (MBC) with incorporated ^{15}N-L-serine from labeled potato dextrose agar (compound **8** $[M+H]^+$: *m/z* 192, $C_{10}H_{11}N^{15}NO_2$).

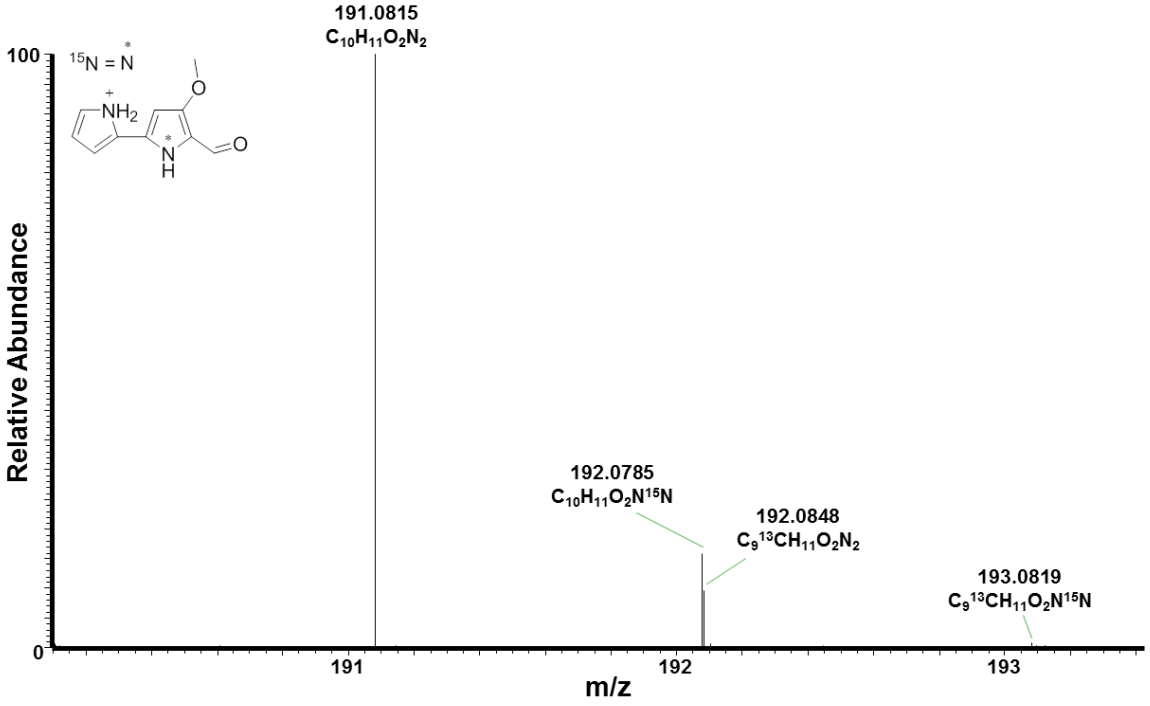


Fig. S113. HRMS spectra of 4-methoxy-2,2'-bipyrrole-5-carbaldehyde (MBC) with incorporated methyl-D_3 group derived from 1 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **8** $[M+H]^+$: *m/z* 194, $C_{10}H_8D_3N_2O_2$).

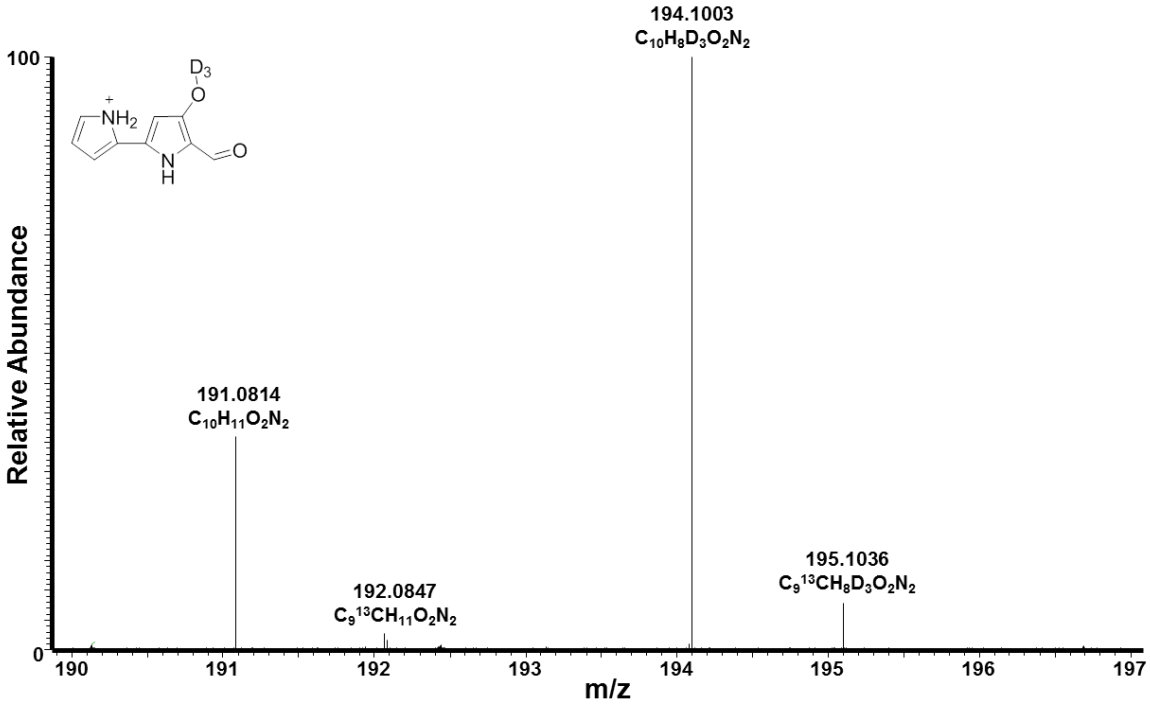


Fig. S114. HRMS spectra of 4-methoxy-2,2'-bipyrrole-5-carbaldehyde (MBC) with incorporated methyl-D_3 group derived from 2 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **8** $[M+H]^+$: *m/z* 194, $C_{10}H_8D_3N_2O_2$).

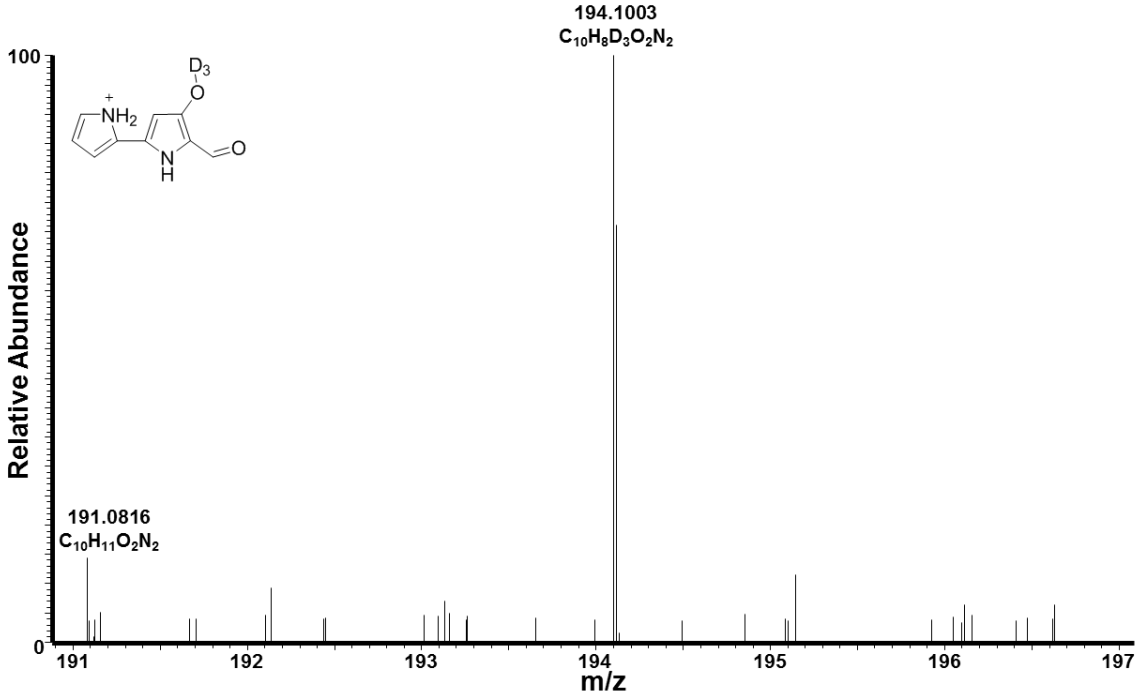


Fig. S115. HRMS spectra of 4-methoxy-2,2'-bipyrrole-5-carbaldehyde (MBC) with incorporated methyl-D_3 group derived from 0.5 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **8** $[M+H]^+$: *m/z* 194, $C_{10}H_8D_3N_2O_2$).

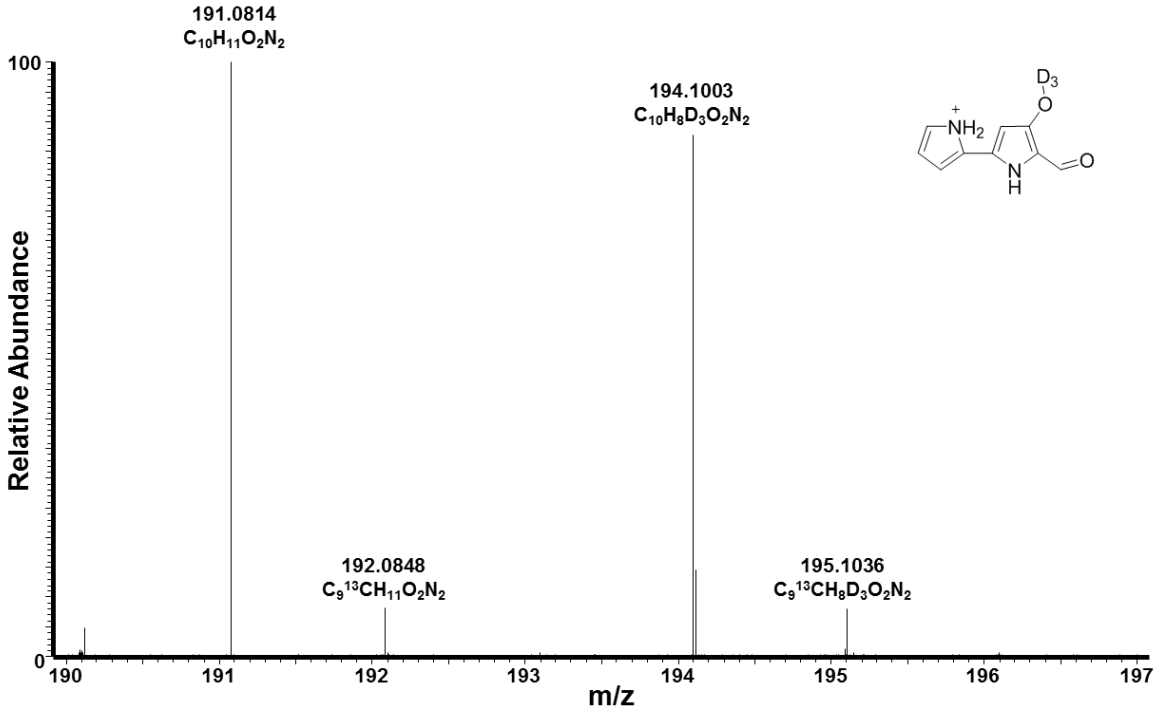


Fig. S116. HRMS spectra of 4-methoxy-2,2'-bipyrrole-5-carbaldehyde (MBC) with incorporated [1-^{13}C]-L-proline from labeled potato dextrose agar (compound **8** $[M+H]^+$: *m/z* 192, $C_9{}^{13}CH_{11}N_2O_2$).

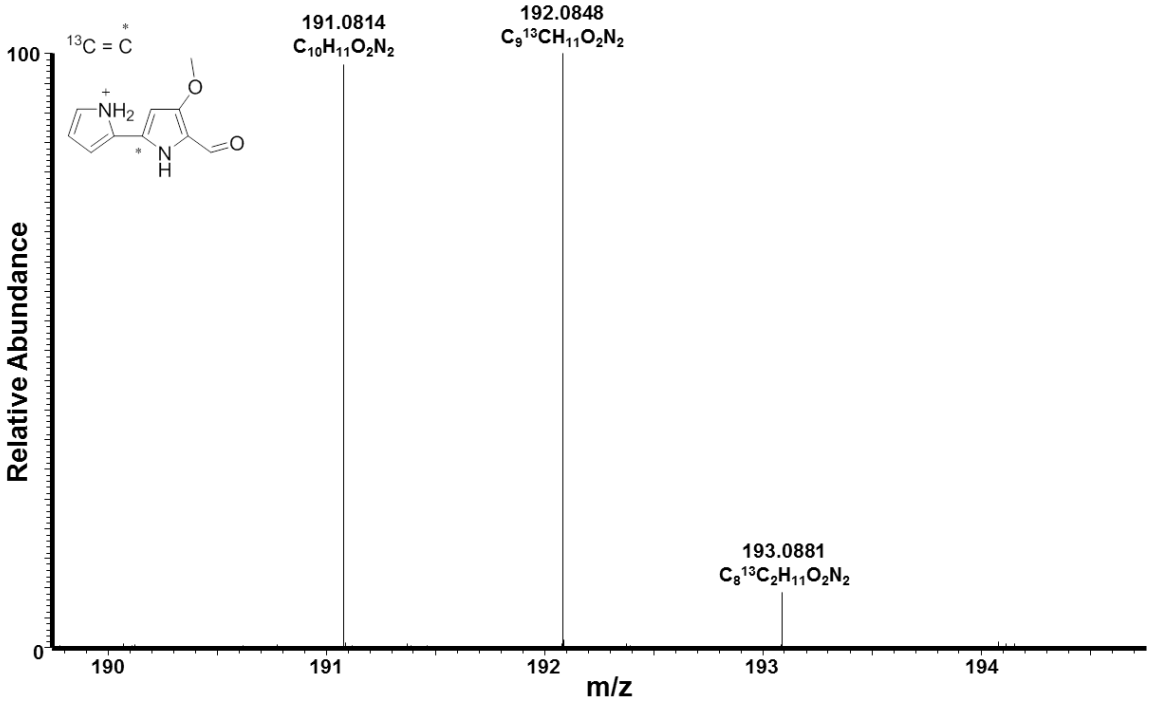


Fig. S117. HRMS^2 of 2-methyl-3-butyl prodiginine with incorporated methyl-D_3 group derived from 1 mg/mL [methyl-D_3]-L-methionine on nutrient agar (compound **2** $[M+H]^+$: *m/z* 313, $C_{19}H_{21}D_3N_3O$).

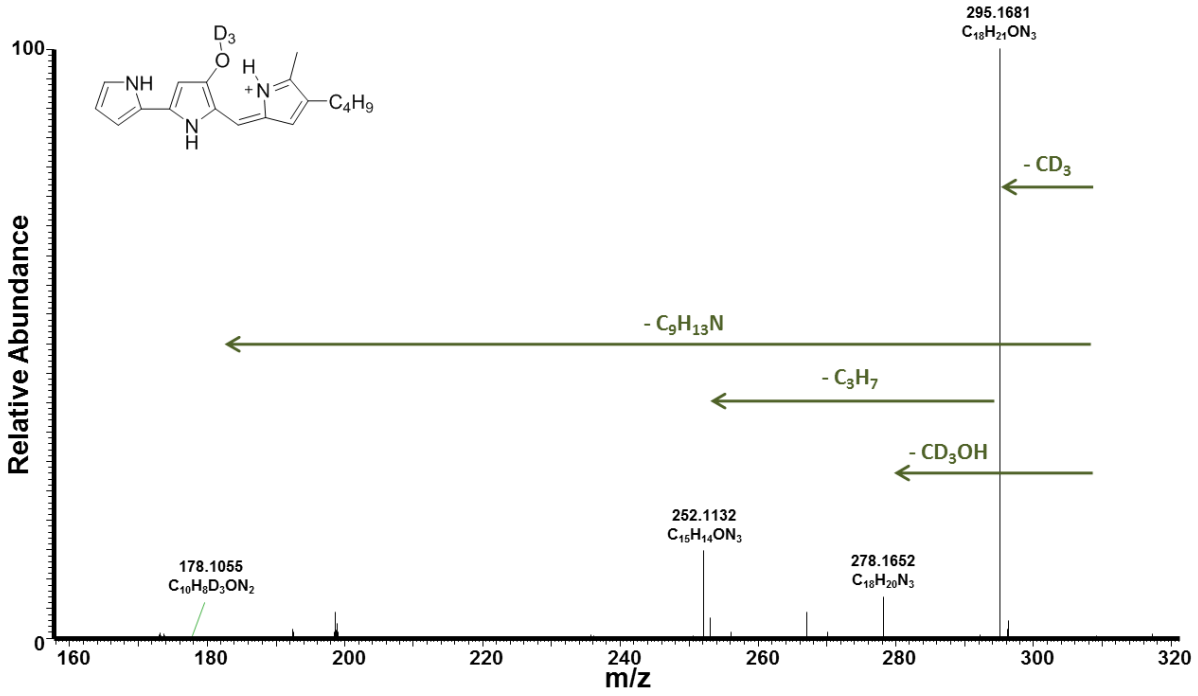


Fig. S118. HRMS^2 of prodigiosin with incorporated methyl-D_3 group derived from 1 mg/mL [methyl-D_3]-L-methionine on nutrient agar (compound **3** $[M+H]^+$: *m/z* 327, $C_{20}H_{23}D_3N_3O$).

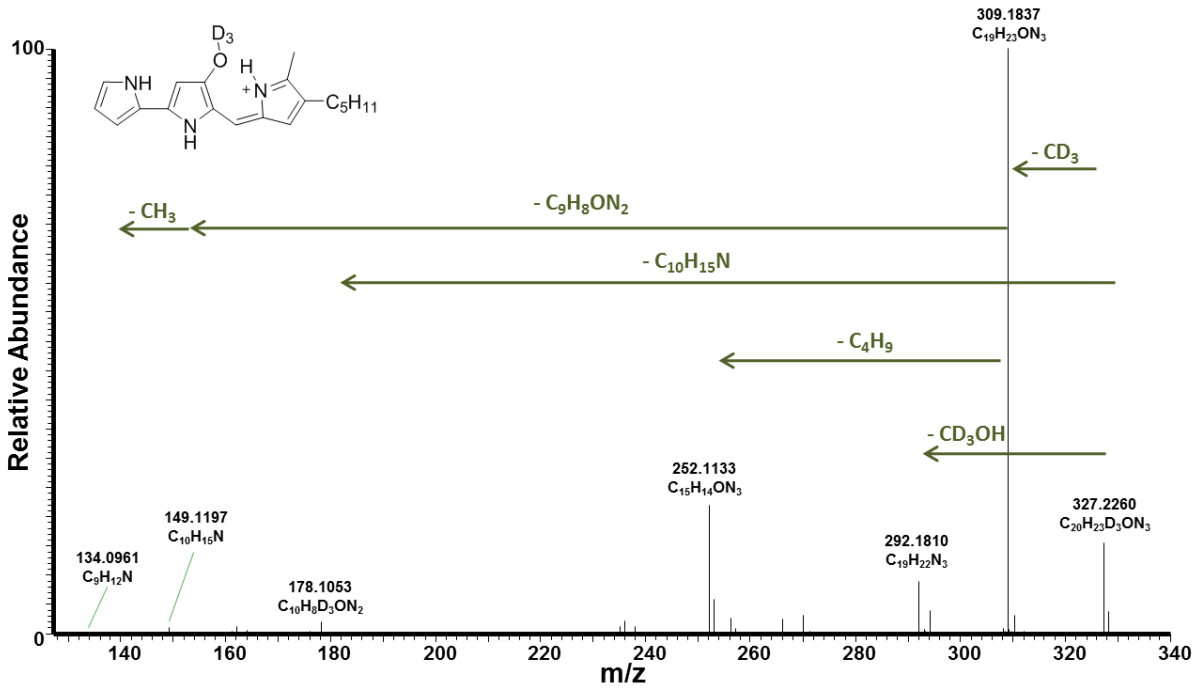


Fig. S119. HRMS^2 of 2-methyl-3-hexyl prodiginine with incorporated methyl-D_3 group derived from 1 mg/mL [methyl-D_3]-L-methionine on nutrient agar (compound **4** $[M+H]^+$: *m/z* 341, $C_{21}H_{25}D_3N_3O$).

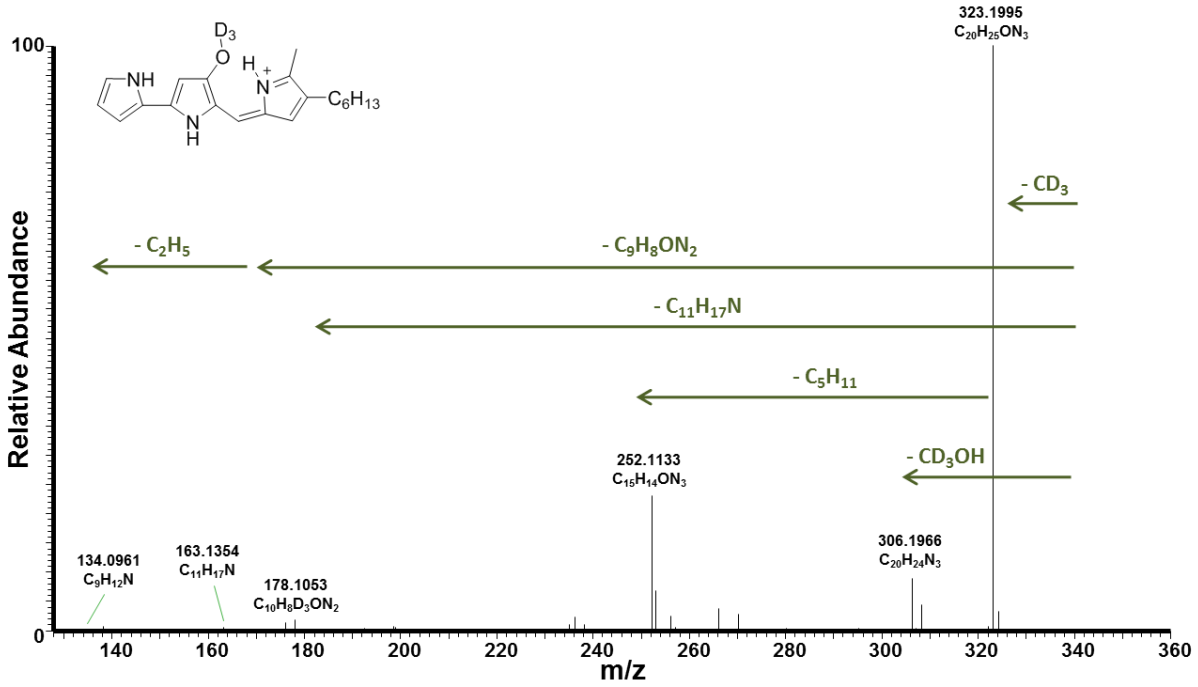


Fig. S120. HRMS^2 of 2-methyl-3-heptyl prodiginine with incorporated methyl-D_3 group derived from 1 mg/mL [methyl-D_3]-L-methionine on nutrient agar (compound **5** $[M+H]^+$: *m/z* 355, $C_{22}H_{27}D_3N_3O$).

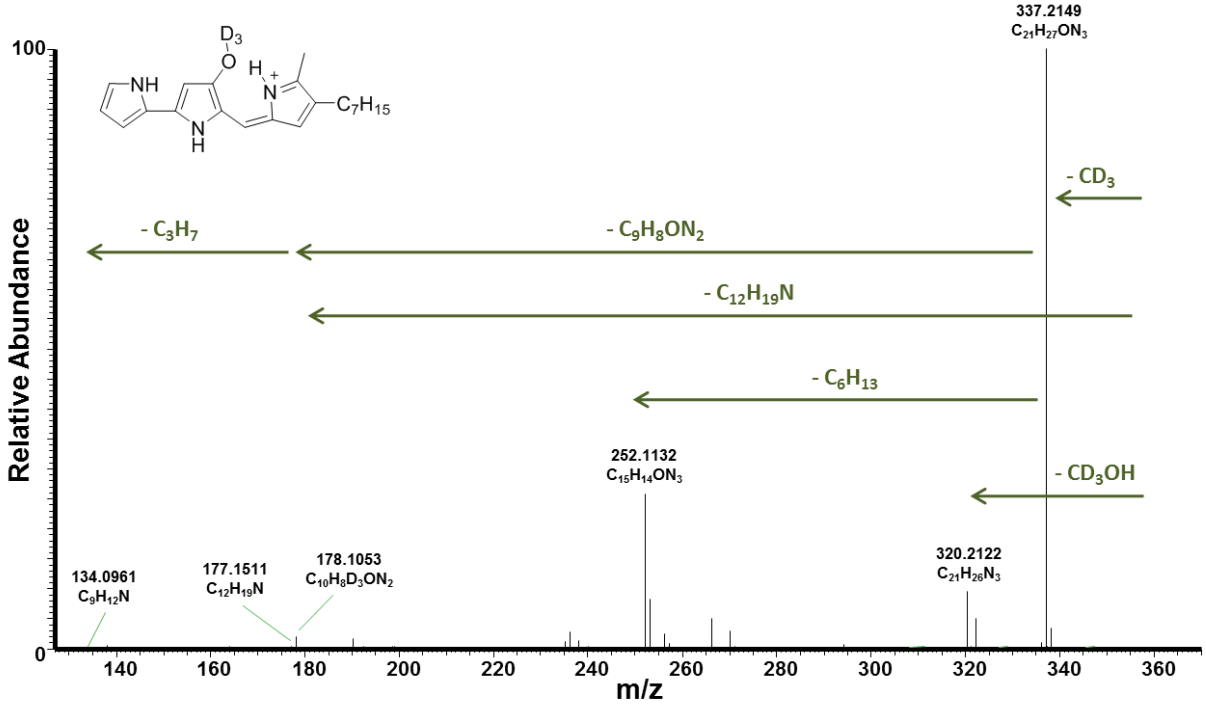


Fig. S121. HRMS^2 of 2-methyl-3-butyl prodiginine with incorporated methyl-D_3 group derived from 0.5 mg/mL [methyl-D_3]-L-methionine on nutrient agar (compound **2** $[M+H]^+$: *m/z* 313, $C_{19}H_{21}D_3N_3O$).

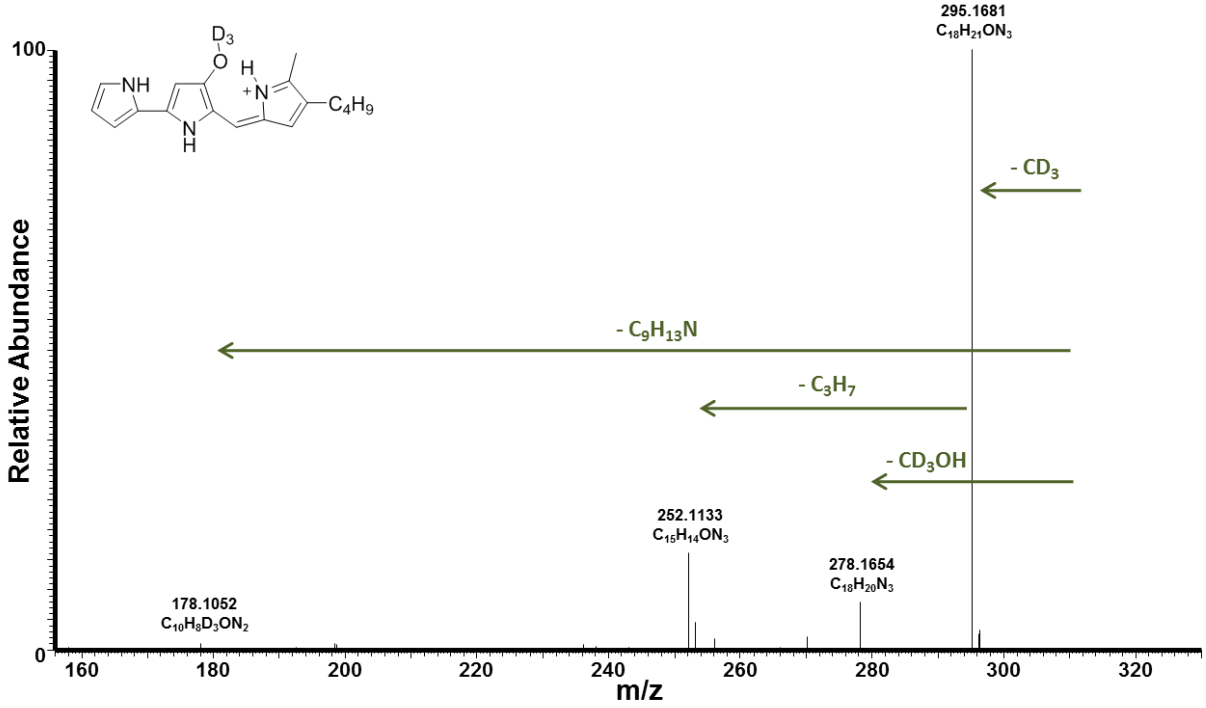


Fig. S122. HRMS^2 of prodigiosin with incorporated methyl-D_3 group derived from 0.5 mg/mL [methyl-D_3]-L-methionine on nutrient agar (compound **3** $[M+H]^+$: *m/z* 327, $C_{20}H_{23}D_3N_3O$).

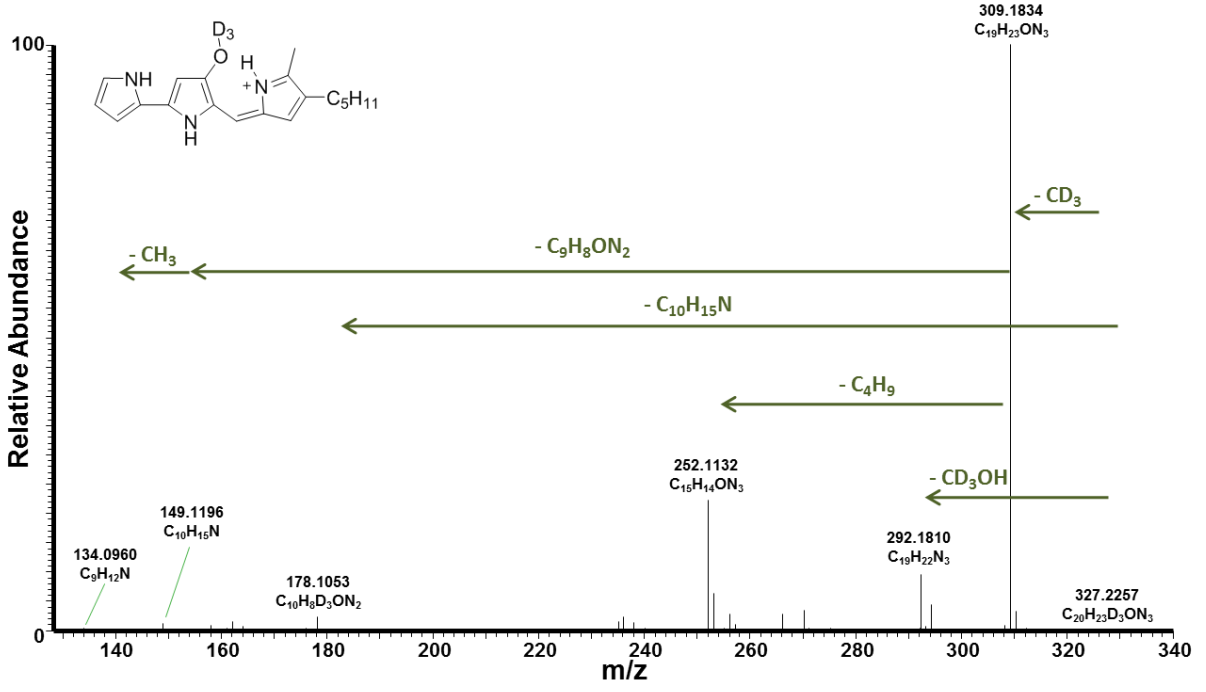


Fig. S123. HRMS^2 of 2-methyl-3-hexyl prodiginine with incorporated methyl-D_3 group derived from 0.5 mg/mL [methyl-D_3]-L-methionine on nutrient agar (compound **4** $[M+H]^+$: *m/z* 341, $C_{21}H_{25}D_3N_3O$).

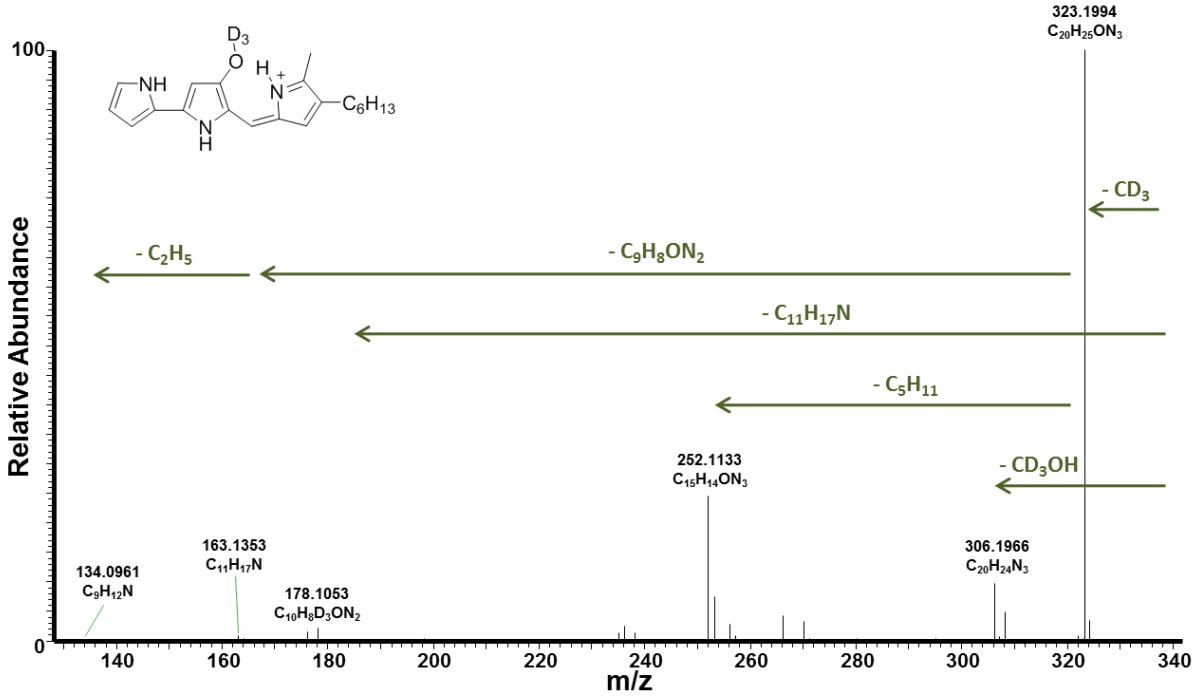


Fig. S124. HRMS^2 of 2-methyl-3-heptyl prodiginine with incorporated methyl-D_3 group derived from 0.5 mg/mL [methyl-D_3]-L-methionine on nutrient agar (compound **5** $[M+H]^+$: *m/z* 355, $C_{22}H_{27}D_3N_3O$).

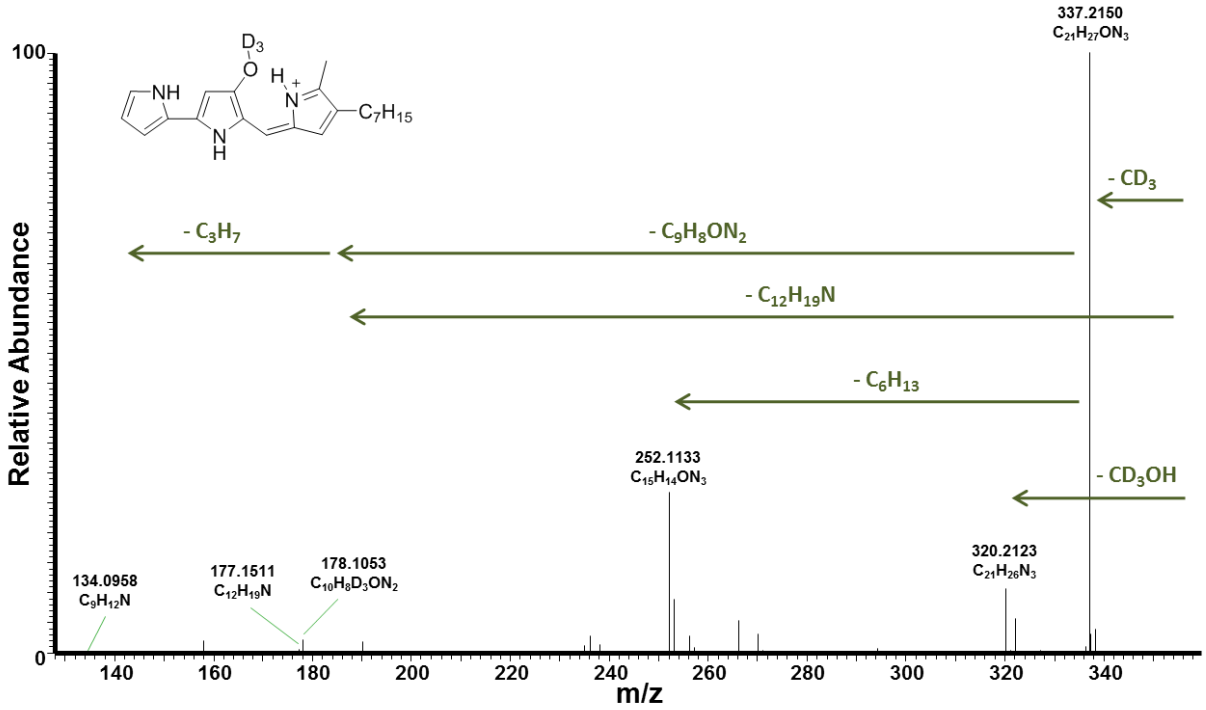


Fig. S125. HRMS^2 of 2-methyl-3-propyl prodiginine with incorporated methyl-D_3 group derived from 2 mg/mL [methyl-D_3]-L-methionine on nutrient agar (compound **1** $[M+H]^+$: *m/z* 299, $C_{18}H_{19}D_3N_3O$).

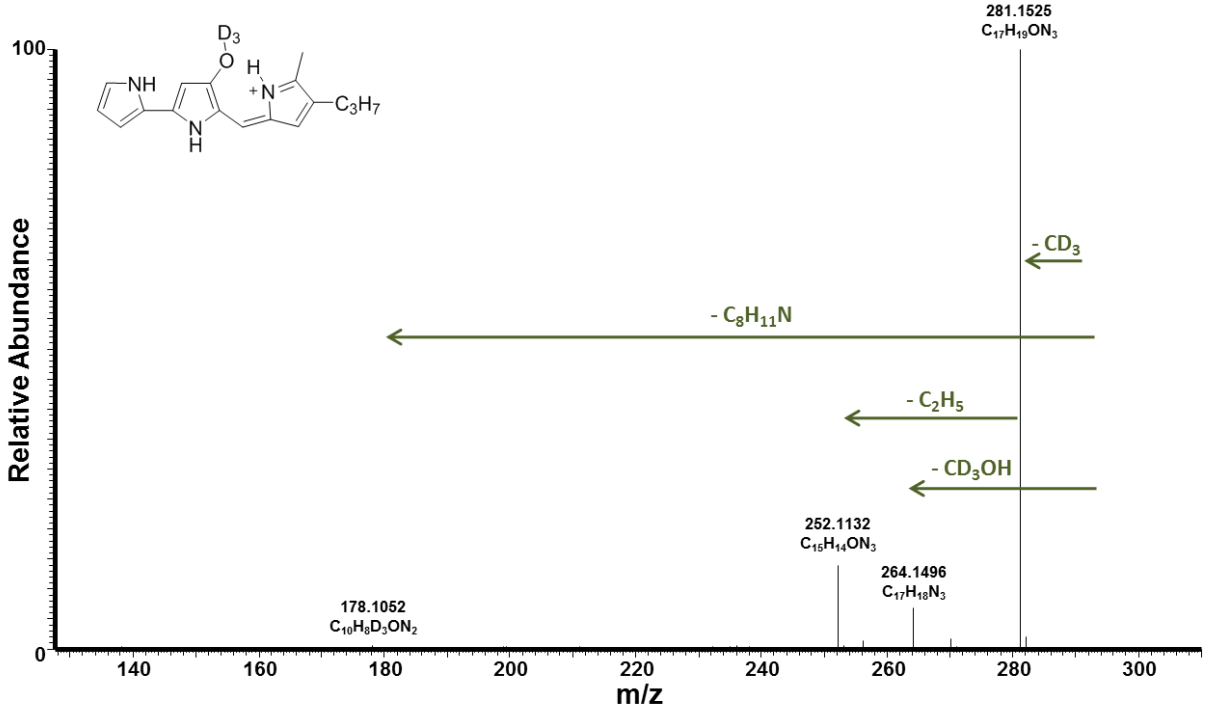


Fig. S126. HRMS^2 of 2-methyl-3-butyl prodiginine with incorporated methyl-D_3 group derived from 2 mg/mL [methyl-D_3]-L-methionine on nutrient agar (compound **2** $[M+H]^+$: *m/z* 313, $C_{19}H_{21}D_3N_3O$).

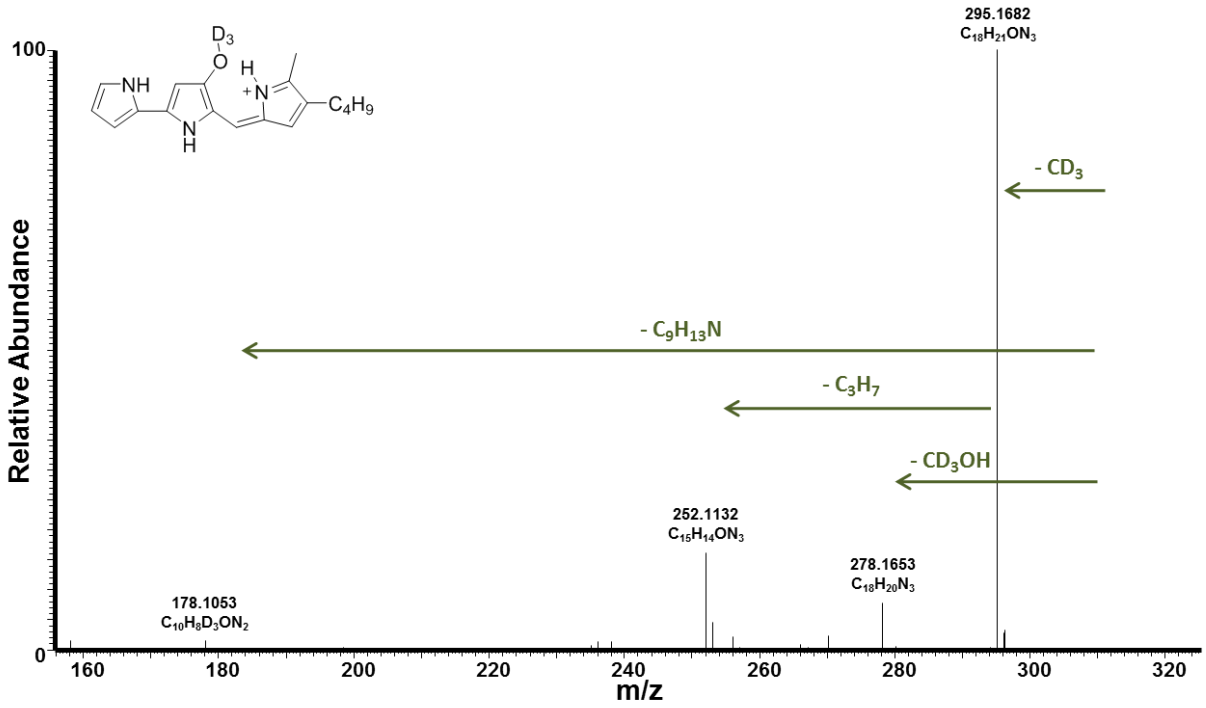


Fig. S127. HRMS^2 of prodigiosin with incorporated methyl-D_3 group derived from 2 mg/mL [methyl-D_3]-L-methionine on nutrient agar (compound **3** $[M+H]^+$: *m/z* 327, $C_{20}H_{23}D_3N_3O$).

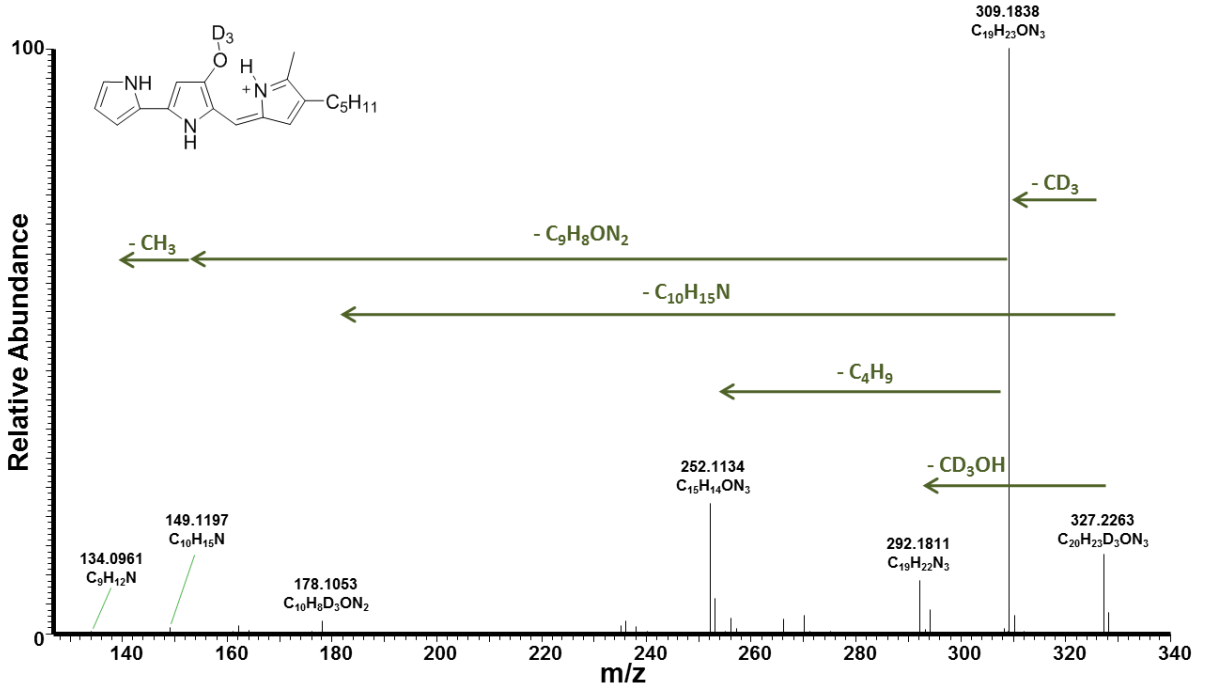


Fig. S128. HRMS^2 of 2-methyl-3-hexyl prodiginine with incorporated methyl-D_3 group derived from 2 mg/mL [methyl-D_3]-L-methionine on nutrient agar (compound **4** $[M+H]^+$: *m/z* 341, $C_{21}H_{25}D_3N_3O$).

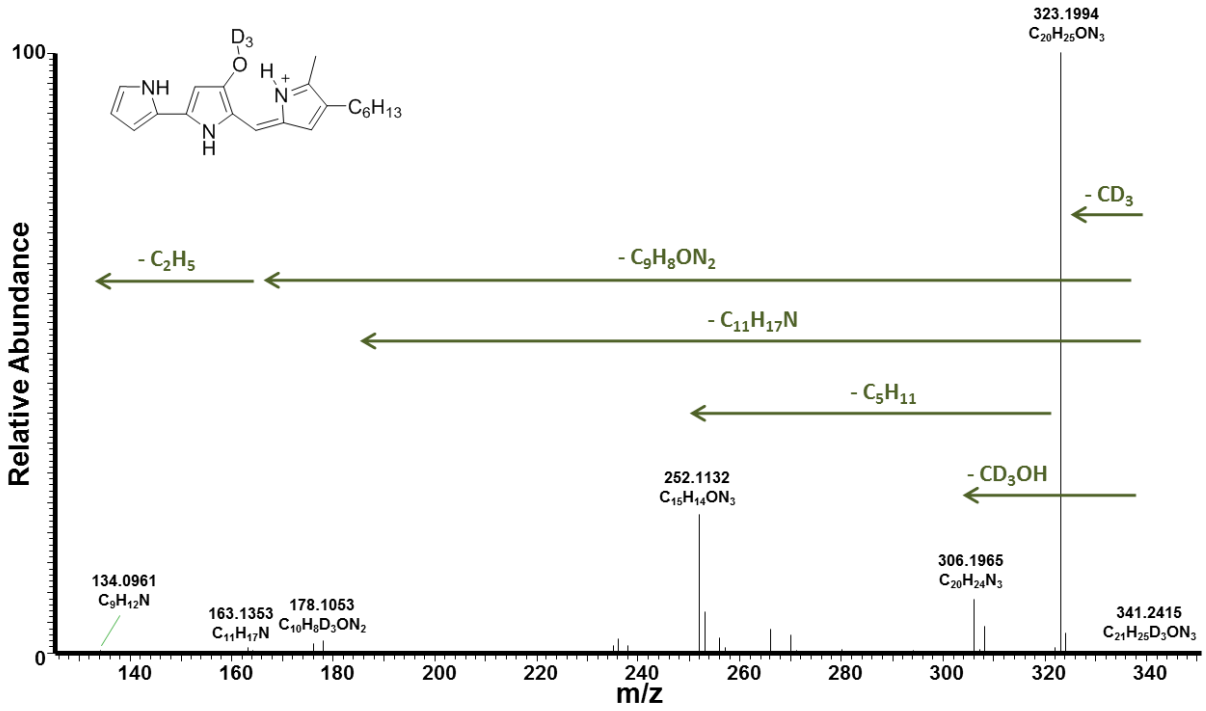


Fig. S129. HRMS^2 of 2-methyl-3-heptyl prodiginine with incorporated methyl-D_3 group derived from 2 mg/mL [methyl-D_3]-L-methionine on nutrient agar (compound **5** $[M+H]^+$: *m/z* 355, $C_{22}H_{27}D_3N_3O$).

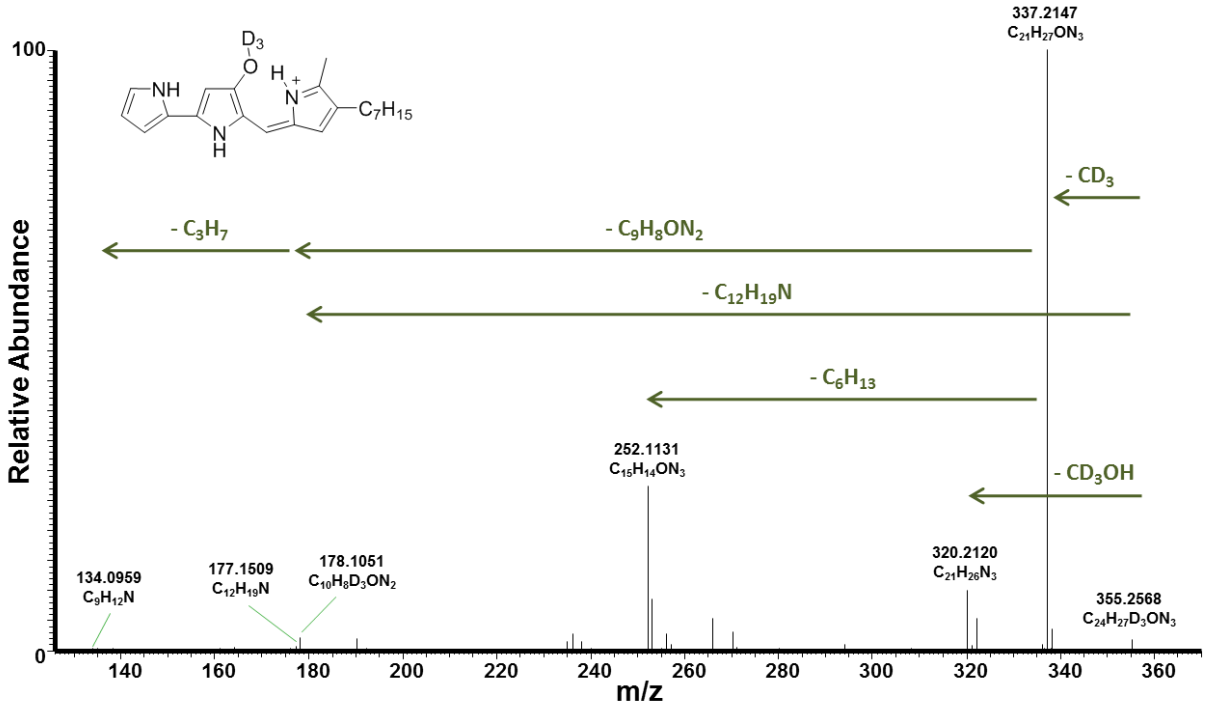


Fig. S130. HRMS^2 of 2-methyl-3-propyl prodiginine with incorporated methyl-D_3 group derived from 1 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **1** $[M+H]^+$: *m/z* 299, $C_{18}H_{19}D_3N_3O$).

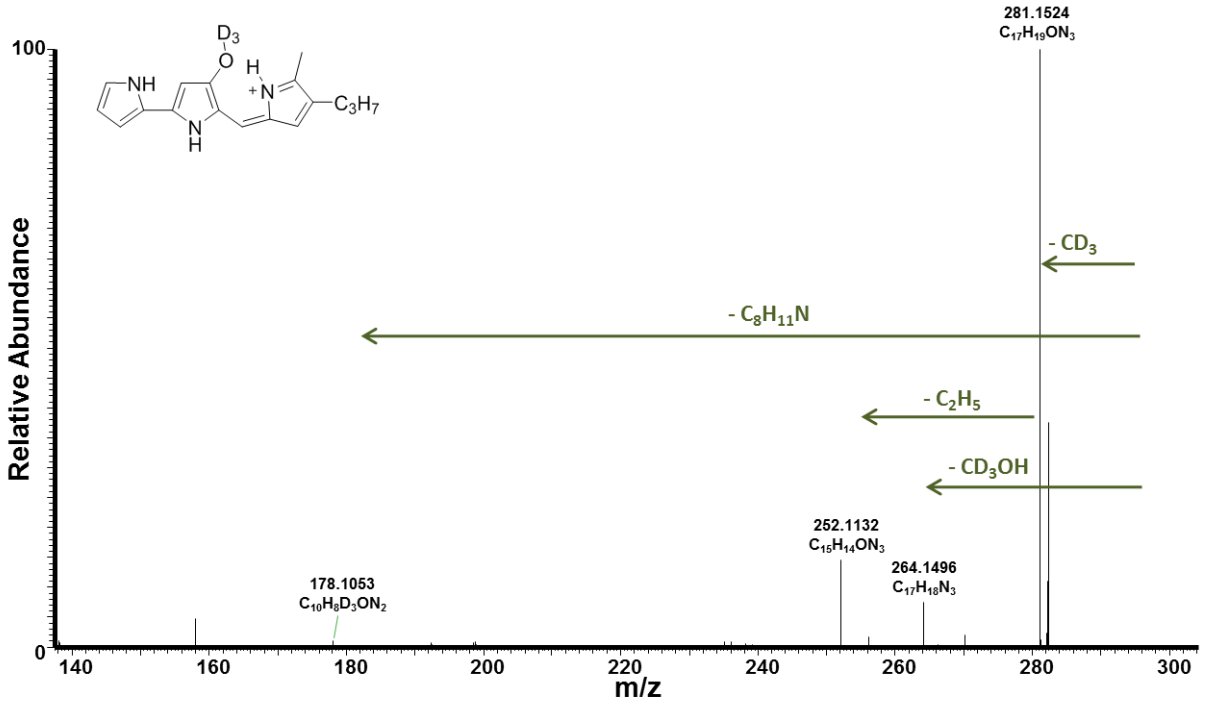


Fig. S131. HRMS^2 of 2-methyl-3-butyl prodiginine with incorporated methyl-D_3 group derived from 1 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **2** $[M+H]^+$: *m/z* 313, $C_{19}H_{21}D_3N_3O$).

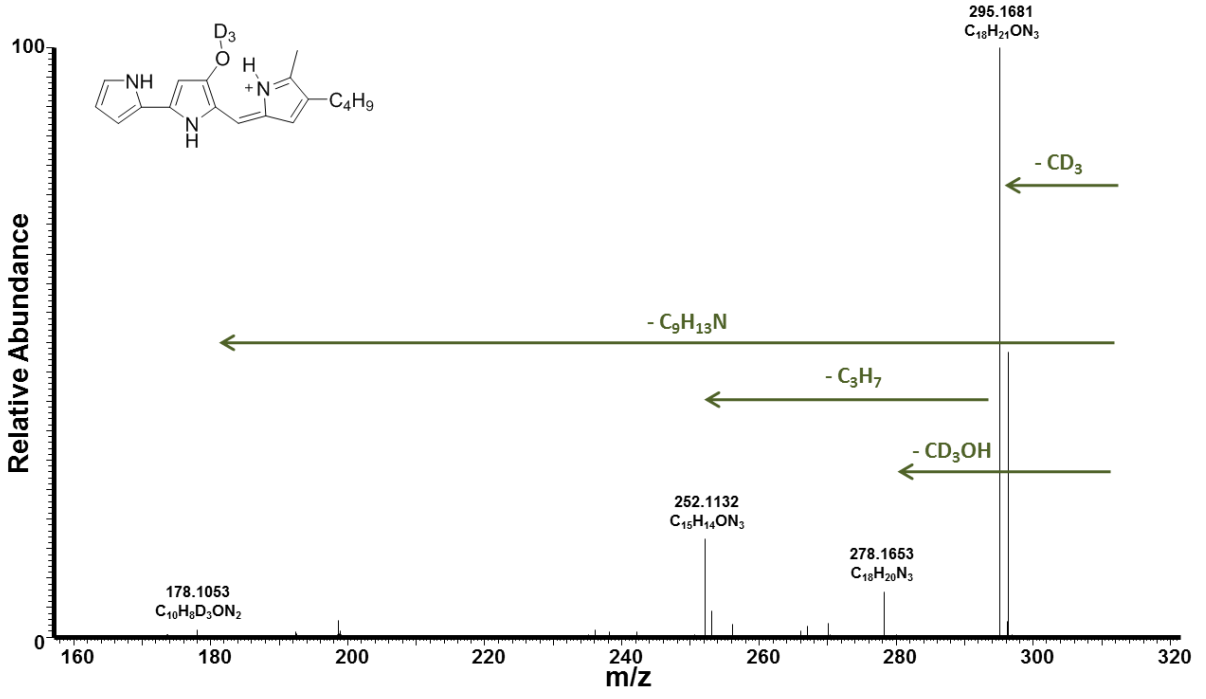


Fig. S132. HRMS^2 of prodigiosin with incorporated methyl-D_3 group derived from 1 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **3** $[M+H]^+$: *m/z* 327, $C_{20}H_{23}D_3N_3O$).

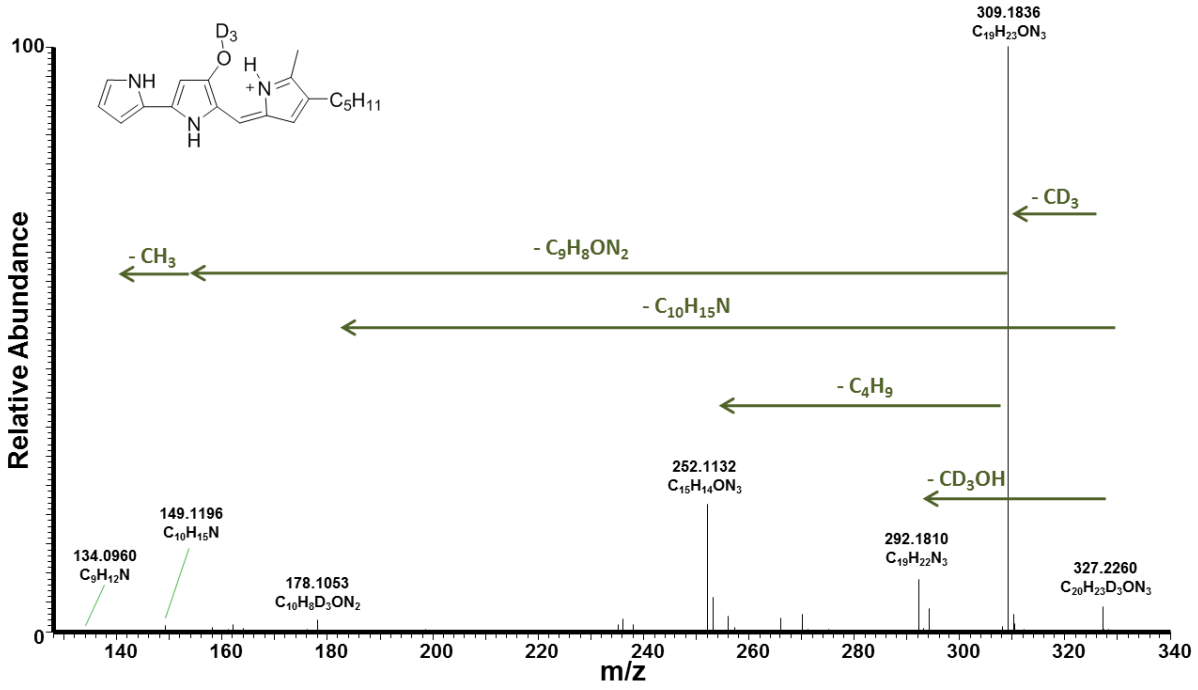


Fig. S133. HRMS^2 of 2-methyl-3-hexyl prodiginine with incorporated methyl-D_3 group derived from 1 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **4** $[M+H]^+$: *m/z* 341, $C_{21}H_{25}D_3N_3O$).

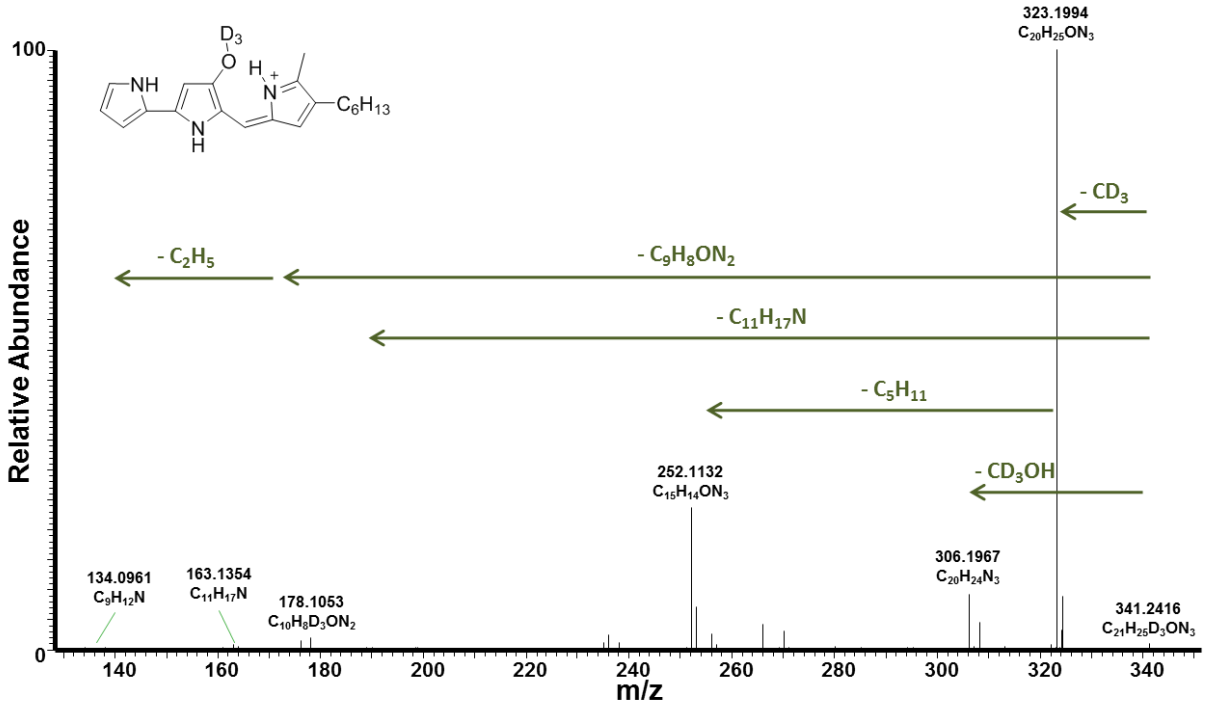


Fig. S134. HRMS^2 of 2-methyl-3-heptyl prodiginine with incorporated methyl-D_3 group derived from 1 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **5** $[M+H]^+$: *m/z* 355, $C_{22}H_{27}D_3N_3O$).

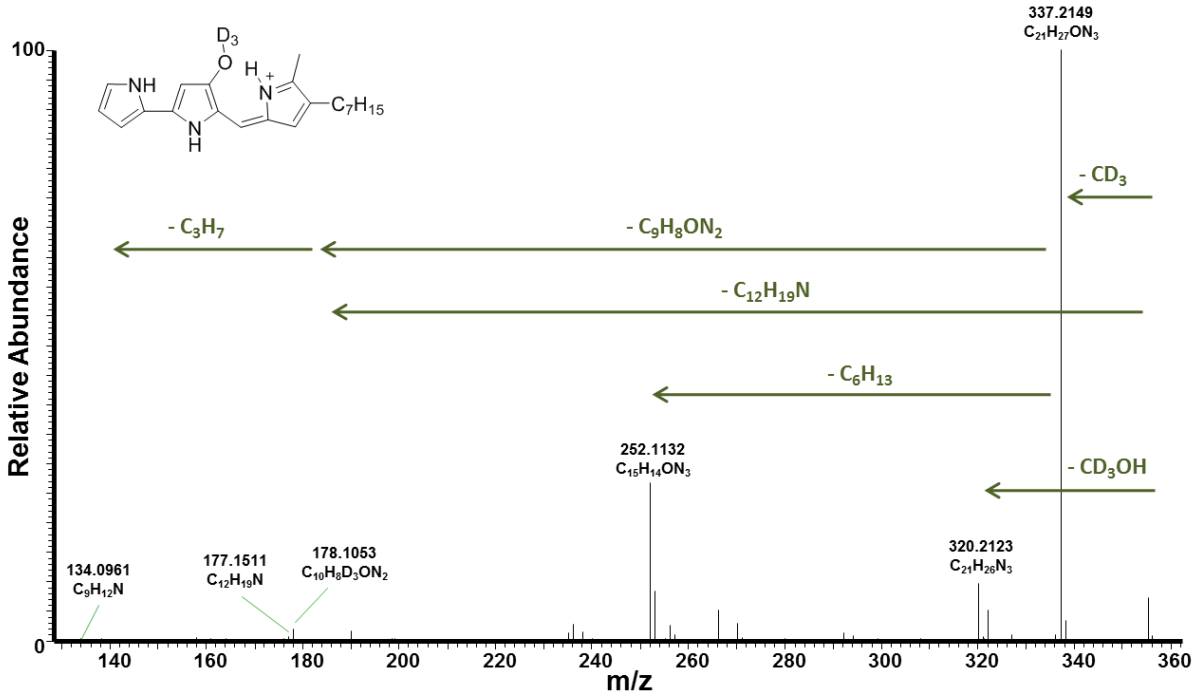


Fig. S135. HRMS^2 of 2-methyl-3-propyl prodiginine with incorporated methyl-D_3 group derived from 0.5 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **1** $[M+H]^+$: *m/z* 299, $C_{18}H_{19}D_3N_3O$).

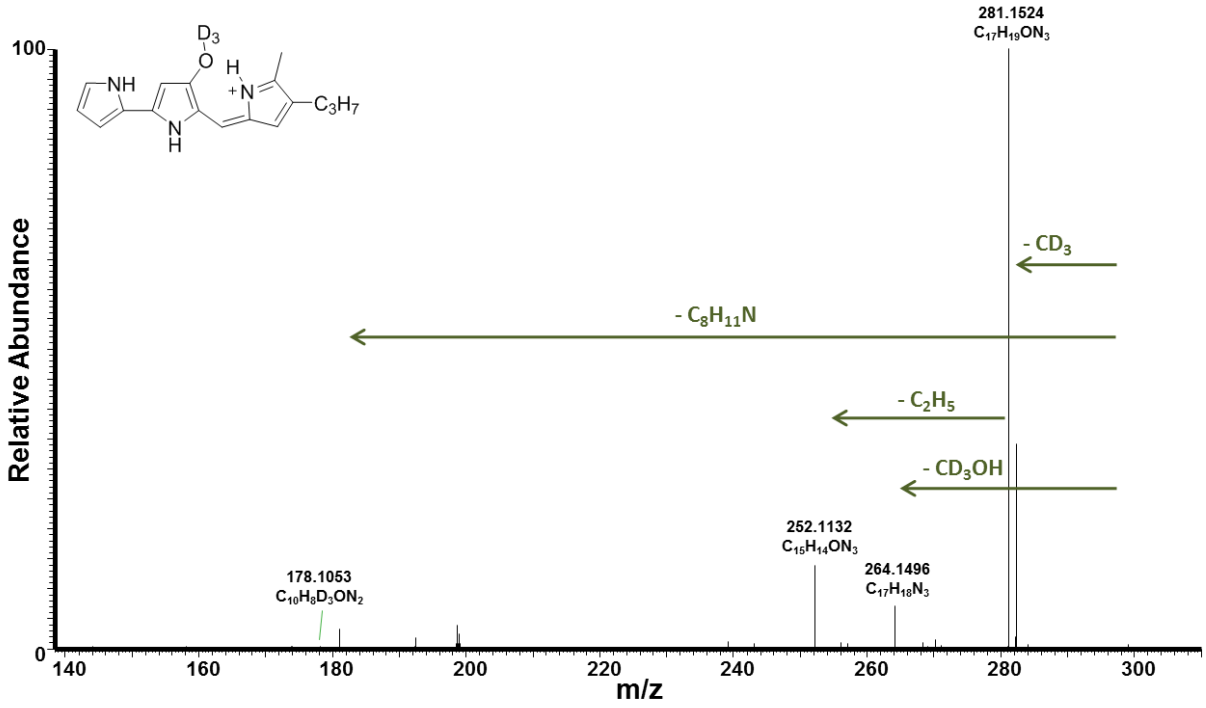


Fig. S136. HRMS^2 of 2-methyl-3-butyl prodiginine with incorporated methyl-D_3 group derived from 0.5 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **2** $[M+H]^+$: *m/z* 313, $C_{19}H_{21}D_3N_3O$).

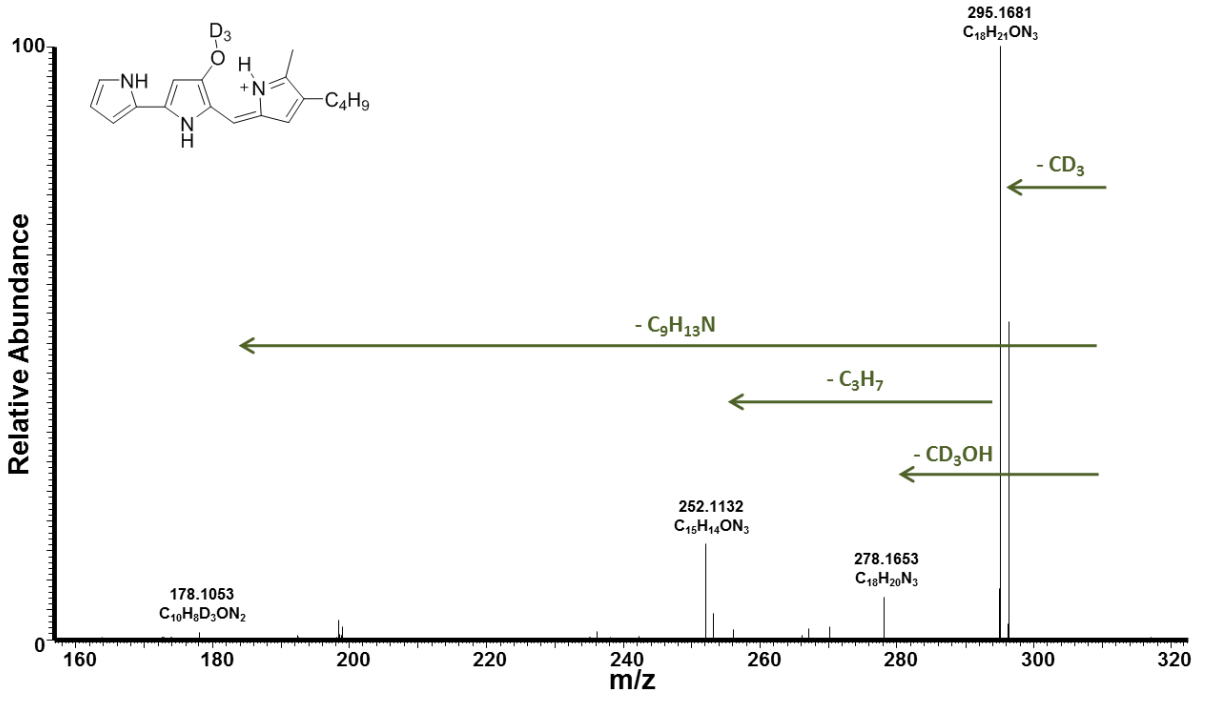


Fig. S137. HRMS^2 of prodigiosin with incorporated methyl-D_3 group derived from 0.5 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **3** $[M+H]^+$: *m/z* 327, $C_{20}H_{23}D_3N_3O$).

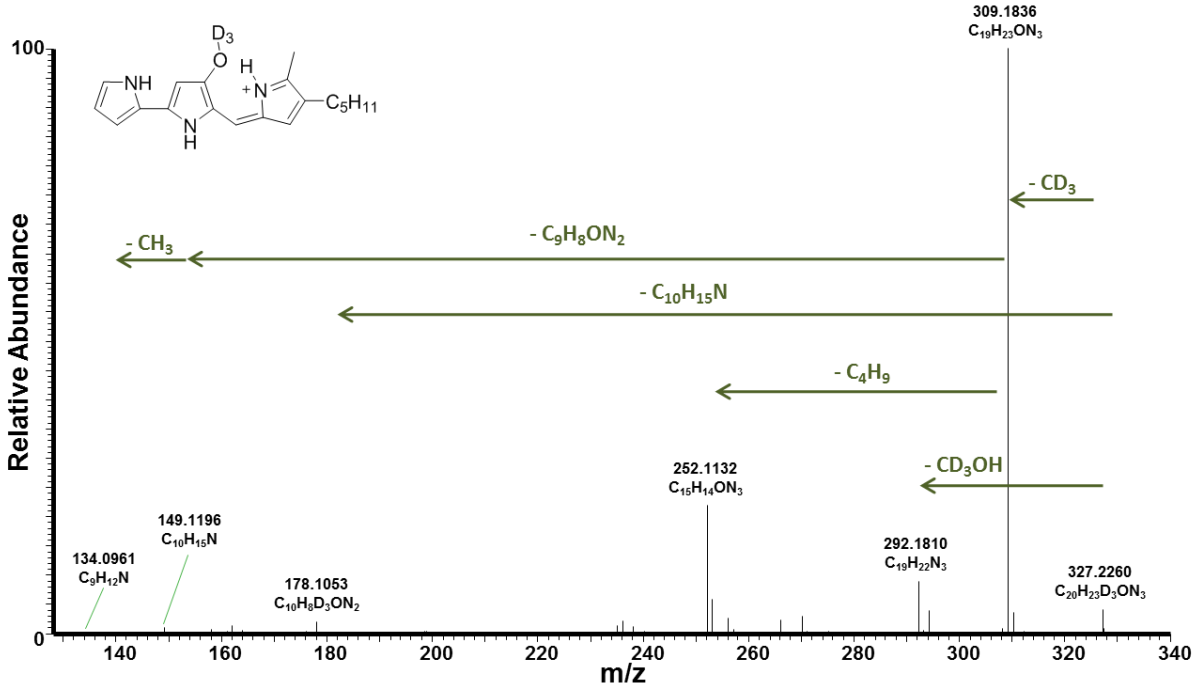


Fig. S138. HRMS^2 of 2-methyl-3-hexyl prodiginine with incorporated methyl-D_3 group derived from 0.5 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **4** $[M+H]^+$: *m/z* 341, $C_{21}H_{25}D_3N_3O$).

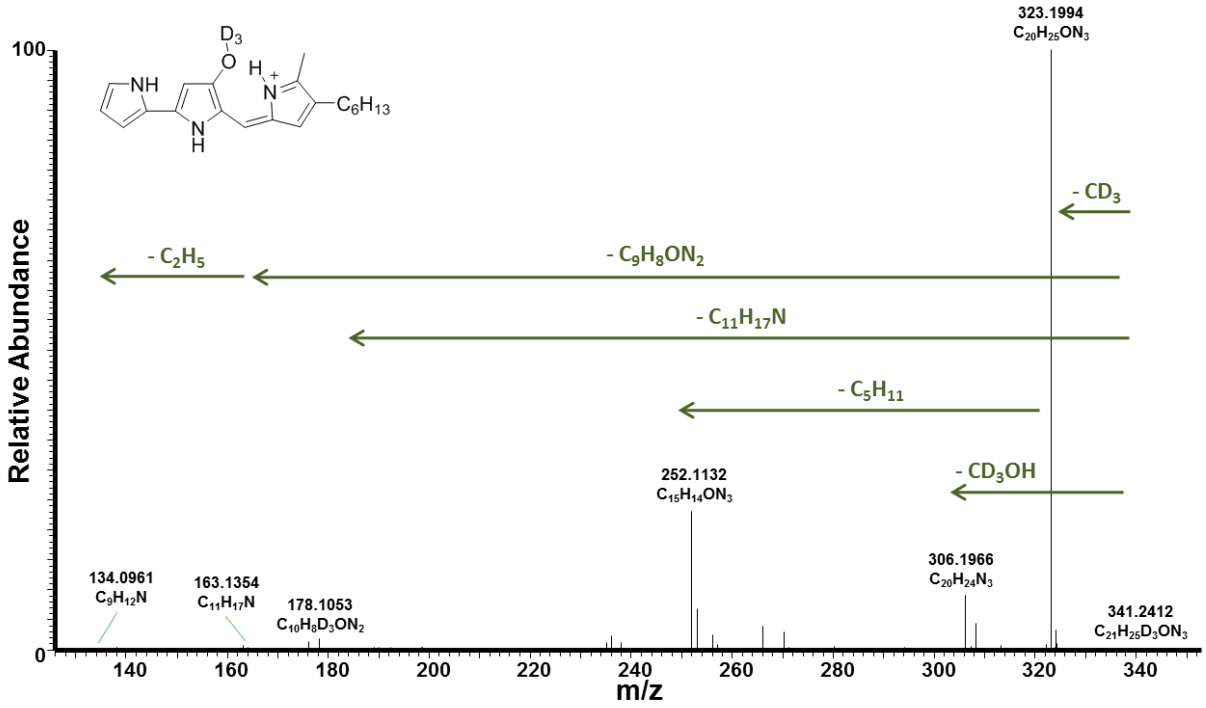


Fig. S139. HRMS^2 of 2-methyl-3-heptyl prodiginine with incorporated methyl-D_3 group derived from 0.5 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **5** $[M+H]^+$: *m/z* 355, $C_{22}H_{27}D_3N_3O$).

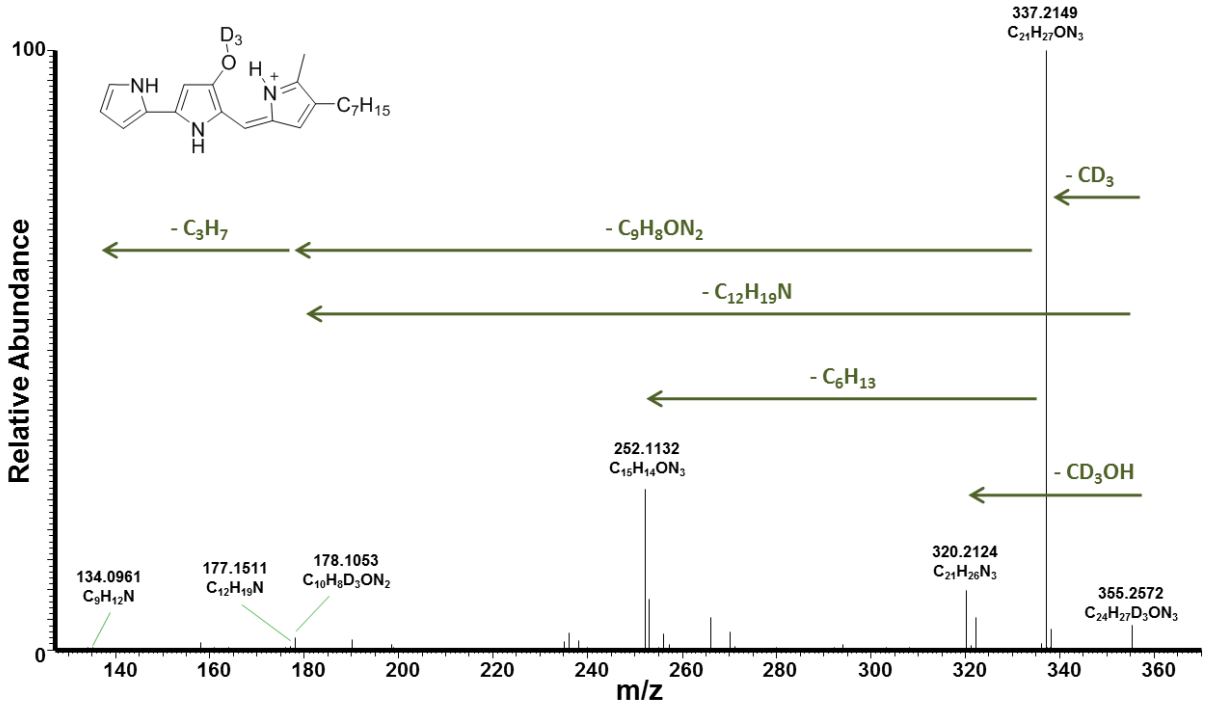


Fig. S140. HRMS^2 of 2-methyl-3-propyl prodiginine with incorporated methyl-D_3 group derived from 2 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **1** $[M+H]^+$: *m/z* 299, $C_{18}H_{19}D_3N_3O$).

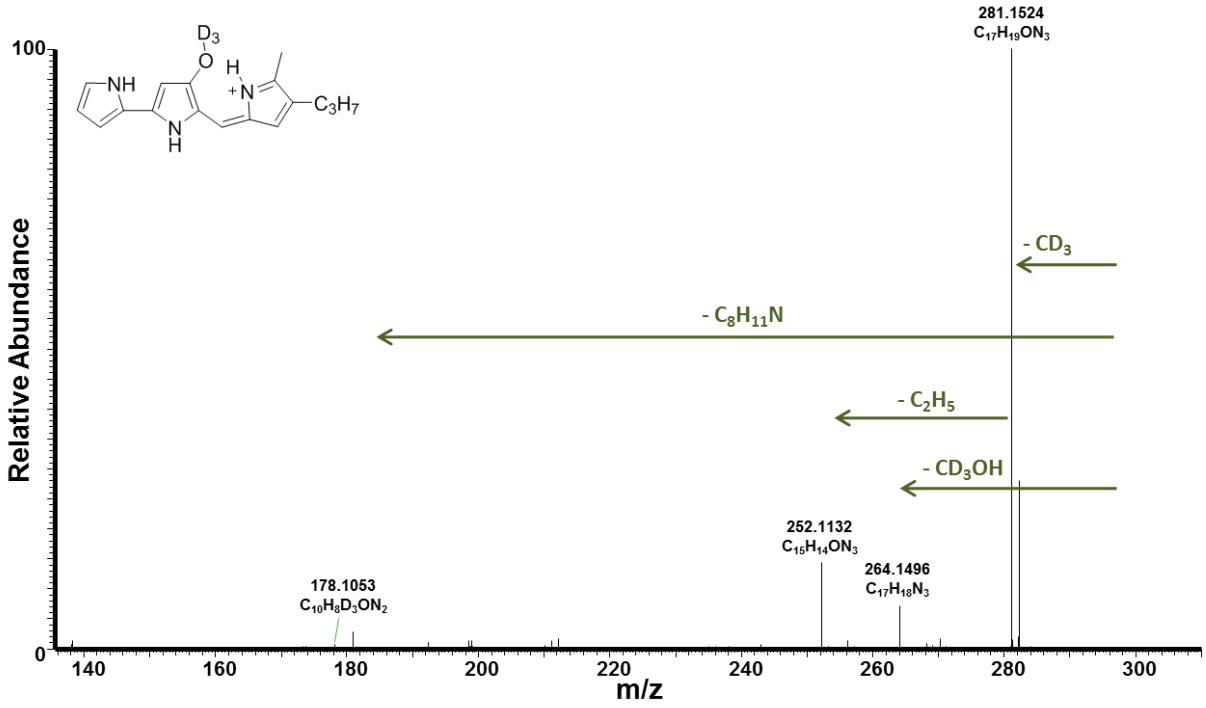


Fig. S141. HRMS^2 of 2-methyl-3-butyl prodiginine with incorporated methyl-D_3 group derived from 2 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **2** $[M+H]^+$: *m/z* 313, $C_{19}H_{21}D_3N_3O$).

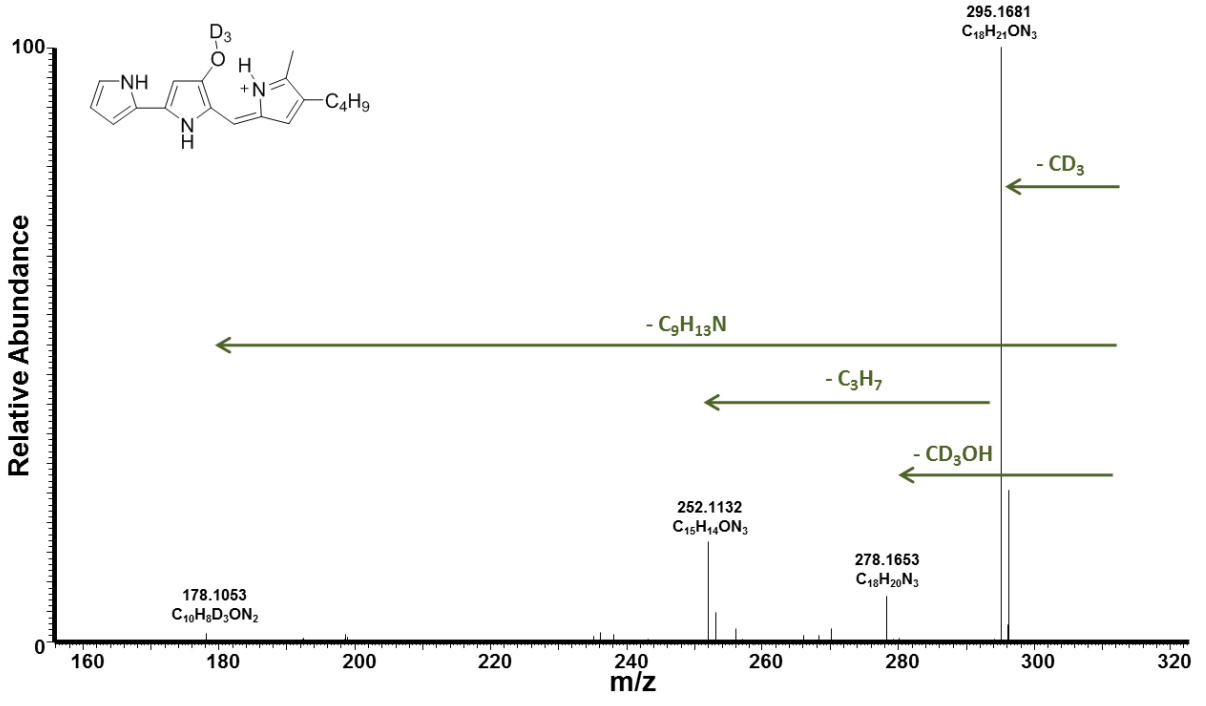


Fig. S142. HRMS^2 of prodigiosin with incorporated methyl-D_3 group derived from 2 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **3** $[M+H]^+$: *m/z* 327, $C_{20}H_{23}D_3N_3O$).

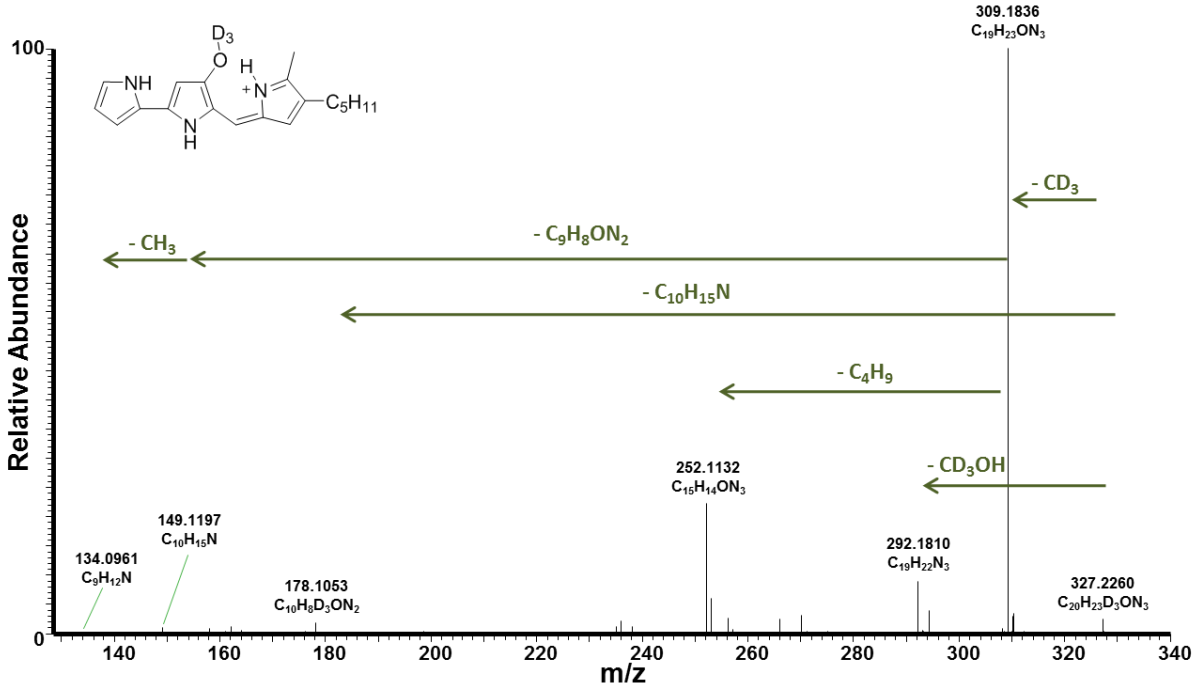


Fig. S143. HRMS^2 of 2-methyl-3-hexyl prodiginine with incorporated methyl-D_3 group derived from 2 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **4** $[M+H]^+$: *m/z* 341, $C_{21}H_{25}D_3N_3O$).

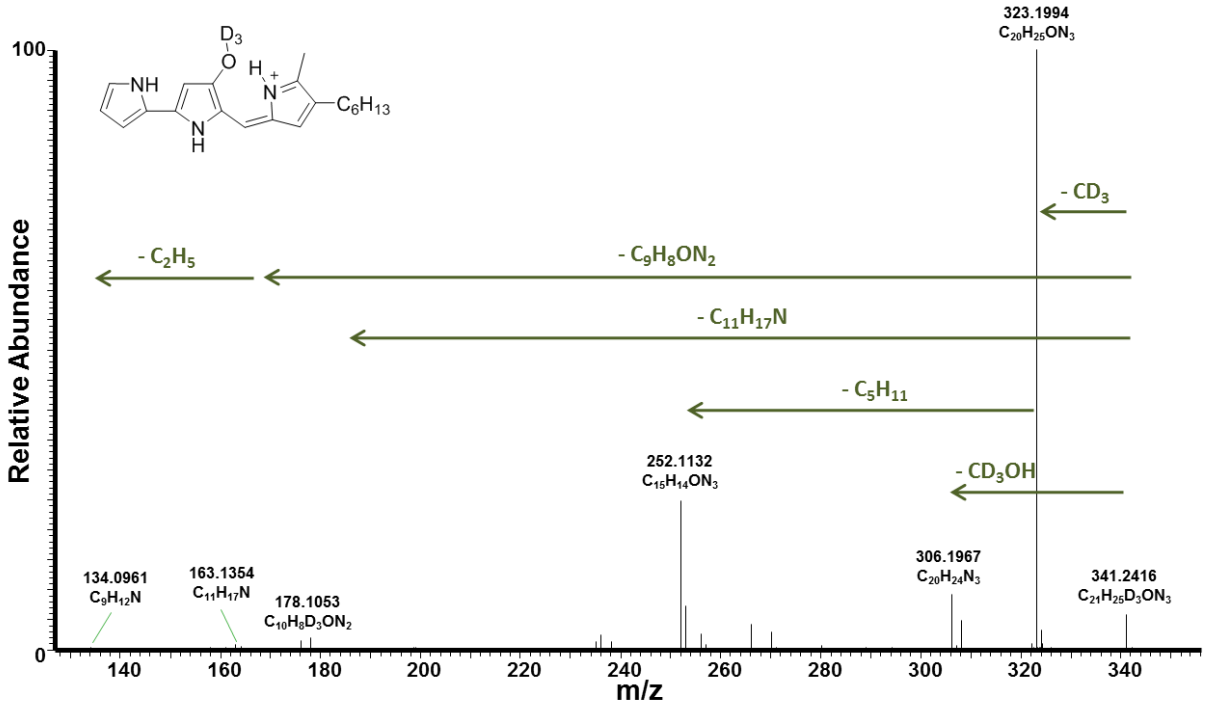


Fig. S144. HRMS^2 of 2-methyl-3-heptyl prodiginine with incorporated methyl-D_3 group derived from 2 mg/mL [methyl-D_3]-L-methionine on potato dextrose agar (compound **5** $[M+H]^+$: *m/z* 355, $C_{22}H_{27}D_3N_3O$).

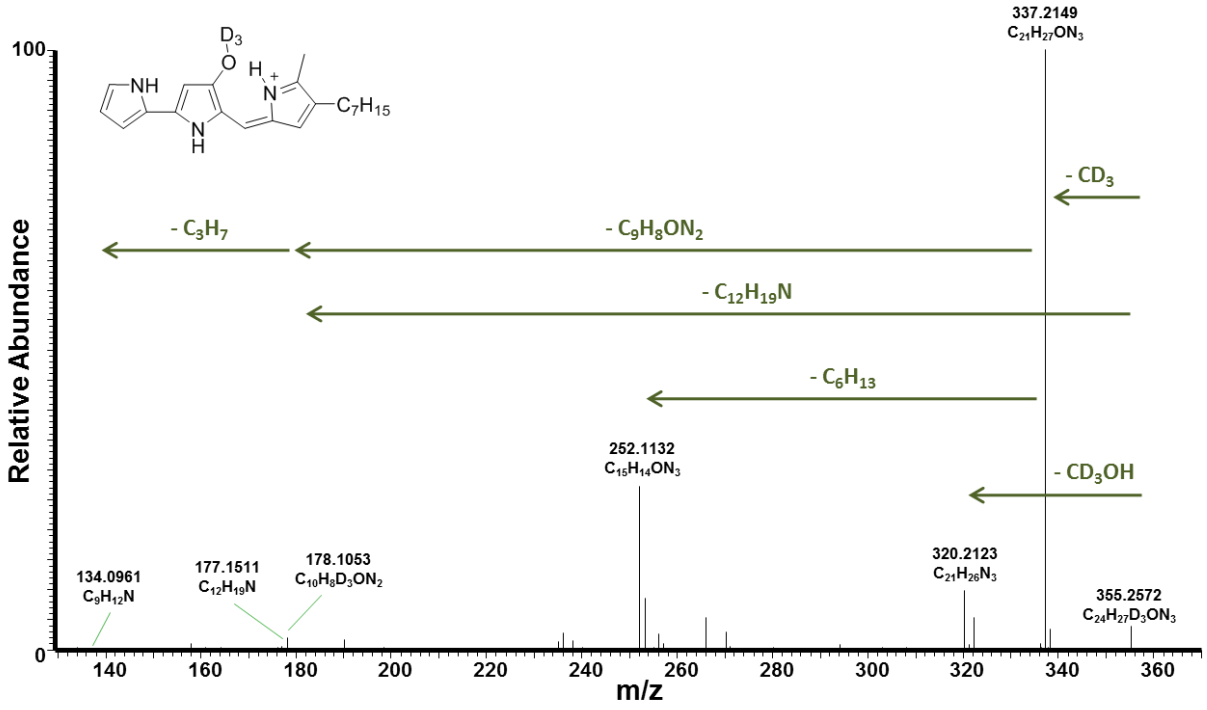


Fig. S145. HRMS spectra of 2-methyl-3-propyl prodiginine with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (compound **1** $[M+H]^+$: *m/z* 296, $C_{18}H_{22}N_3O$).

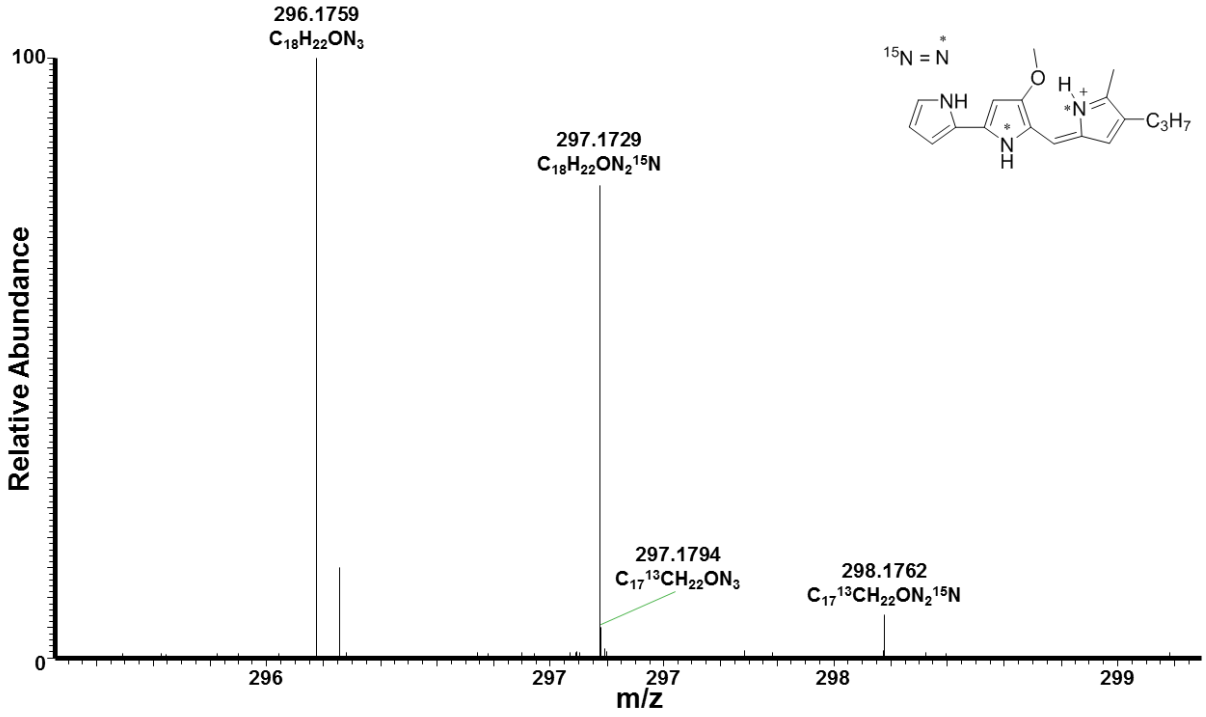


Fig. S146. HRMS spectra of 2-methyl-3-butyl prodiginine with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (compound **2** $[M+H]^+$: *m/z* 310, $C_{19}H_{24}N_3O$).

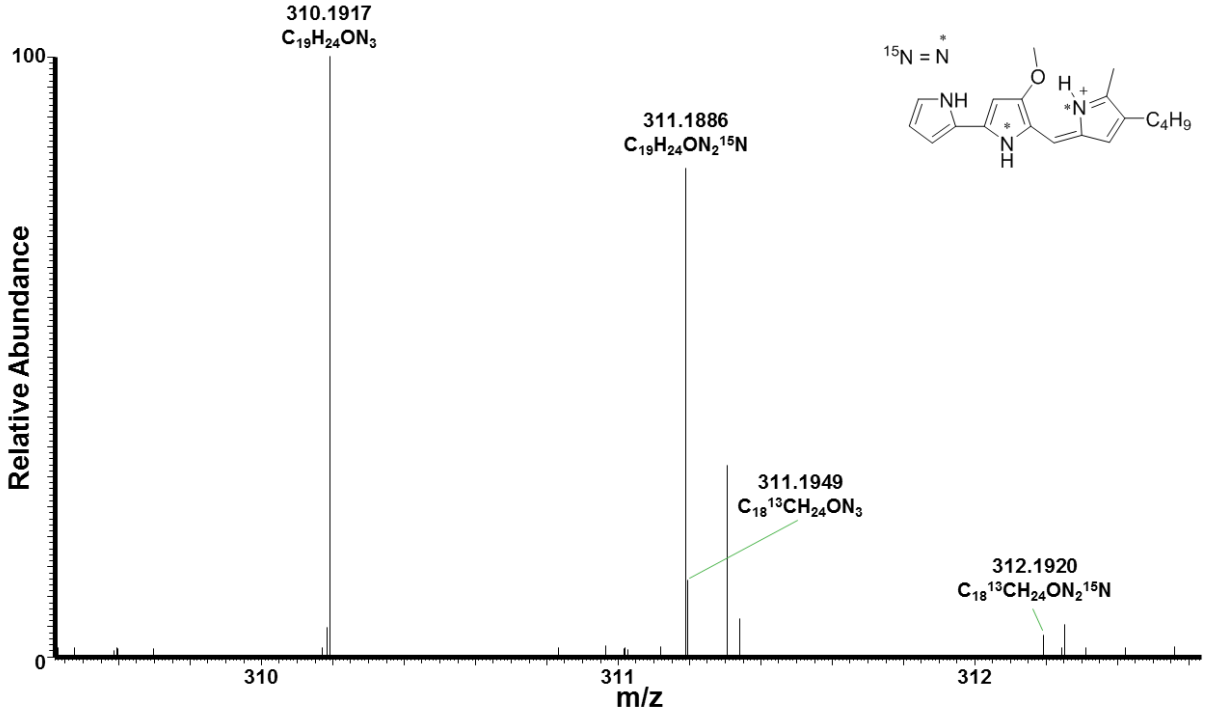


Fig. S147. HRMS spectra of prodigiosin with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (compound **3** $[M+H]^+$: *m/z* 324, $C_{20}H_{26}N_3O$).

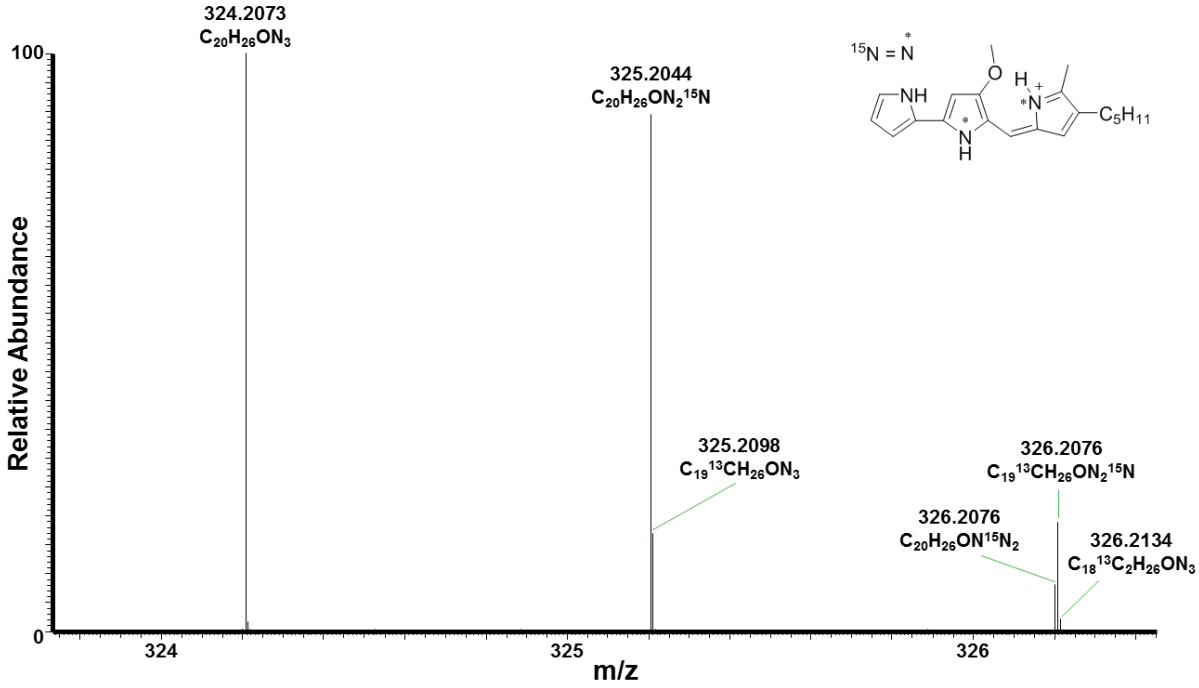


Fig. S148. HRMS spectra of 2-methyl-3-hexyl prodiginine with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (compound **4** $[M+H]^+$: *m/z* 338, $C_{21}H_{28}N_3O$).

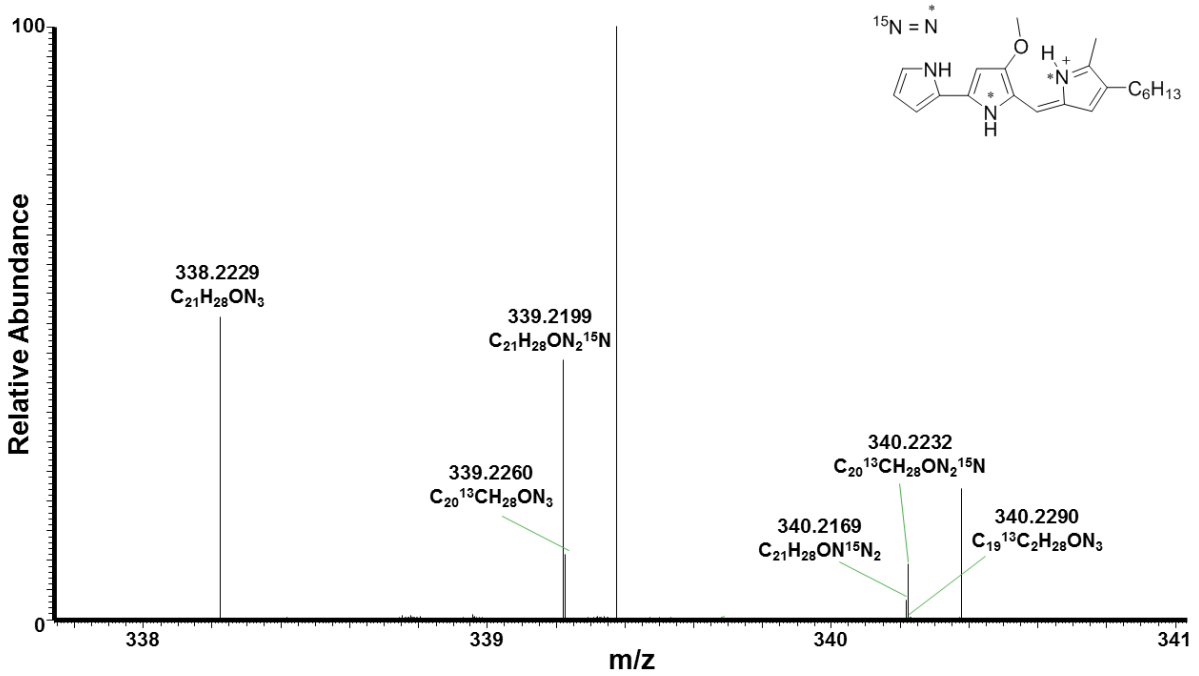


Fig. S149. HRMS spectra of 2-methyl-3-heptyl prodiginine with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (compound **5** $[M+H]^+$: *m/z* 352, $C_{22}H_{30}N_3O$).

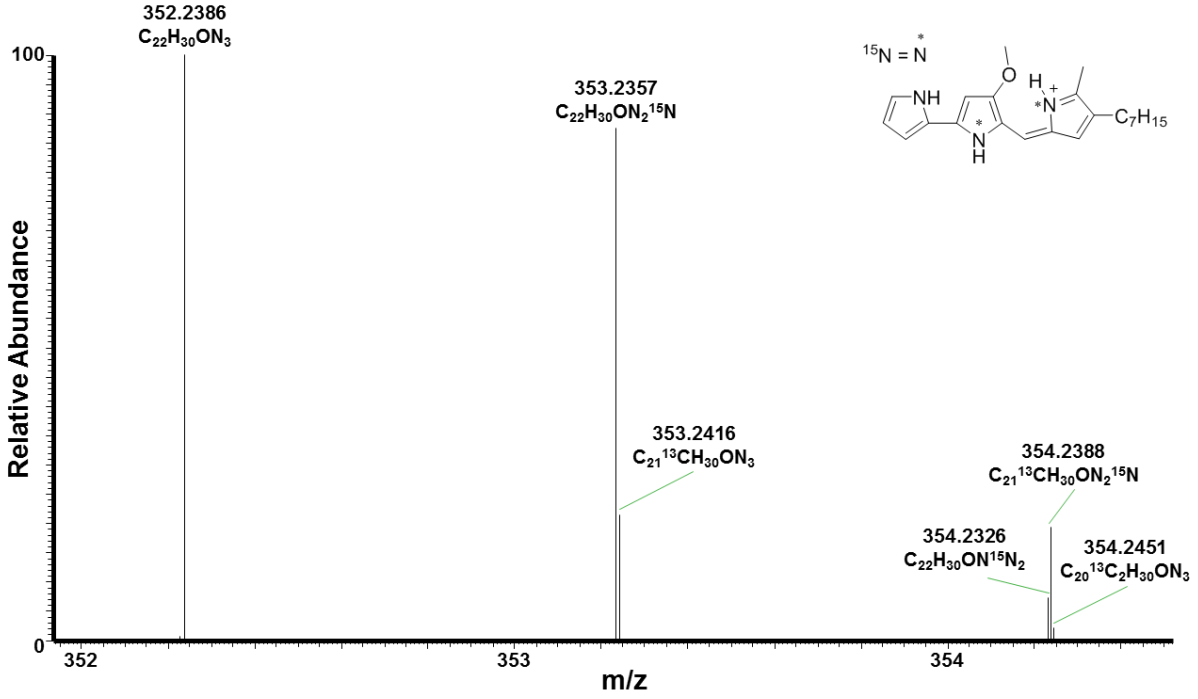


Fig. S150. HRMS spectra of 2-methyl-3-nonyl prodiginine with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (compound **7** $[M+H]^+$: *m/z* 380, $C_{24}H_{34}N_3O$).

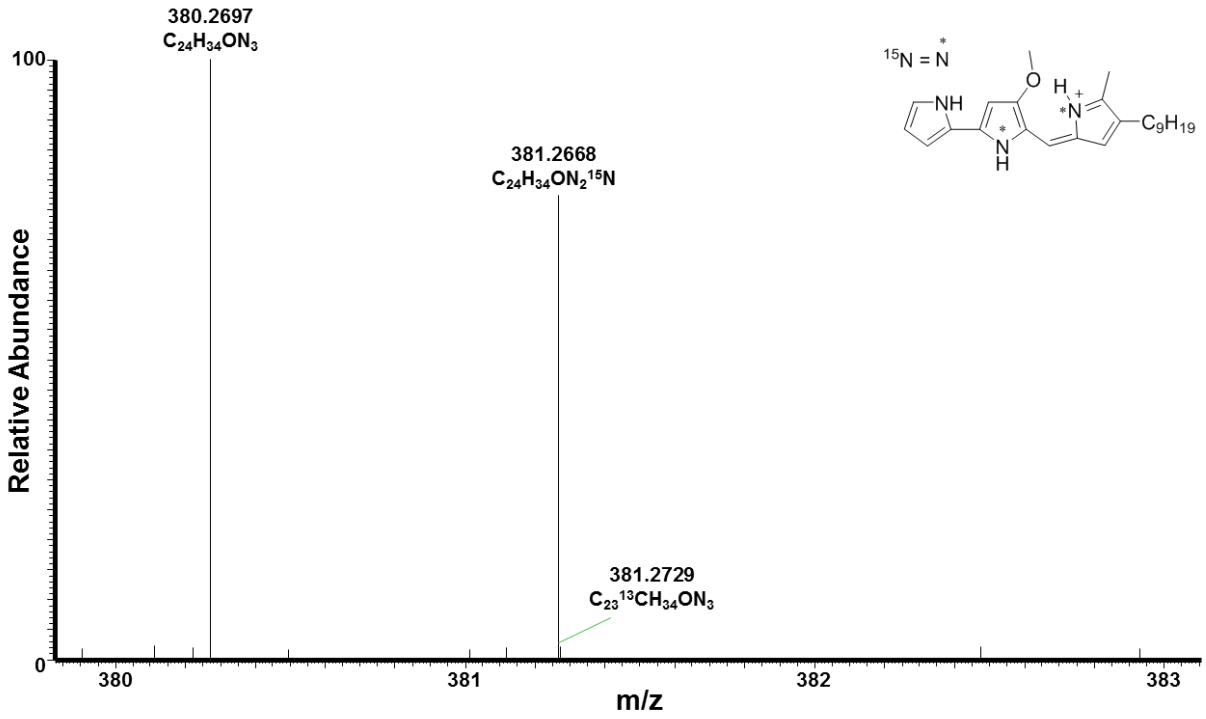


Fig. S151. HRMS spectra of 4-methoxy-2,2'-bipyrrole-5-carbaldehyde (MBC) with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (compound **8** $[M+H]^+$: *m/z* 192, $C_{10}H_{11}N^{15}NO_2$).

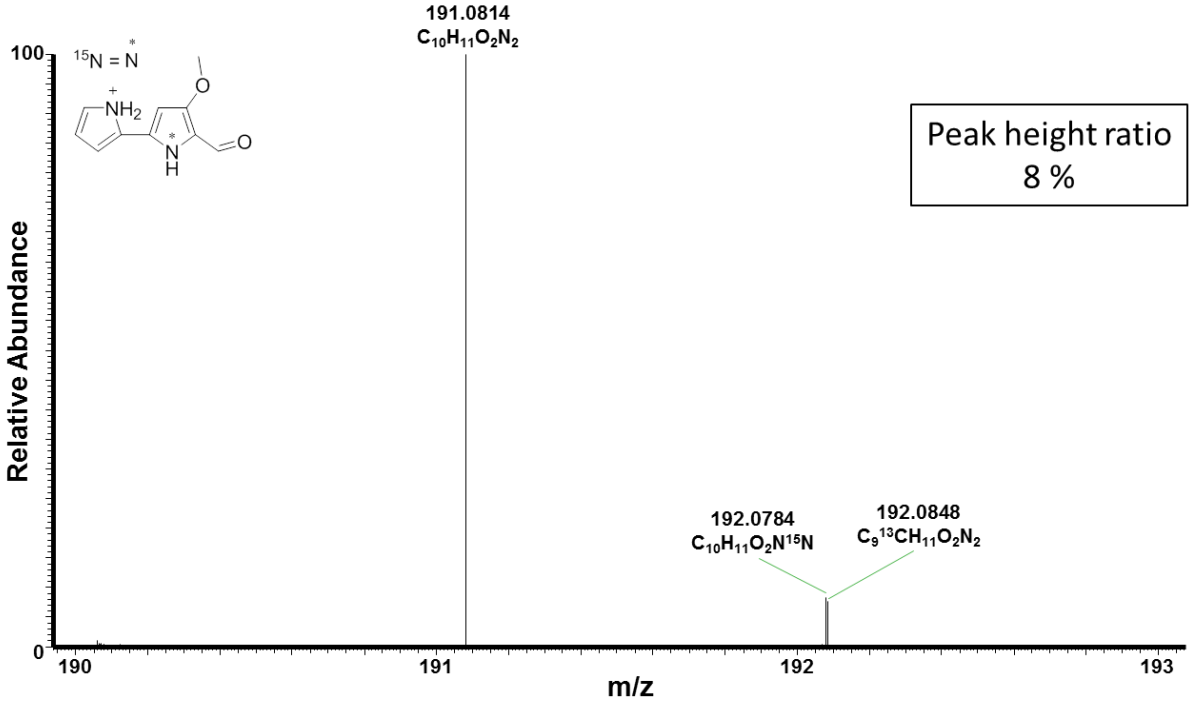


Fig. S152. HRMS spectra of 2-methyl-3-amylpyrrole (MAP) with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (compound **9** $[M+H]^+$: *m/z* 153, $C_{10}H_{18}{}^{15}N$).

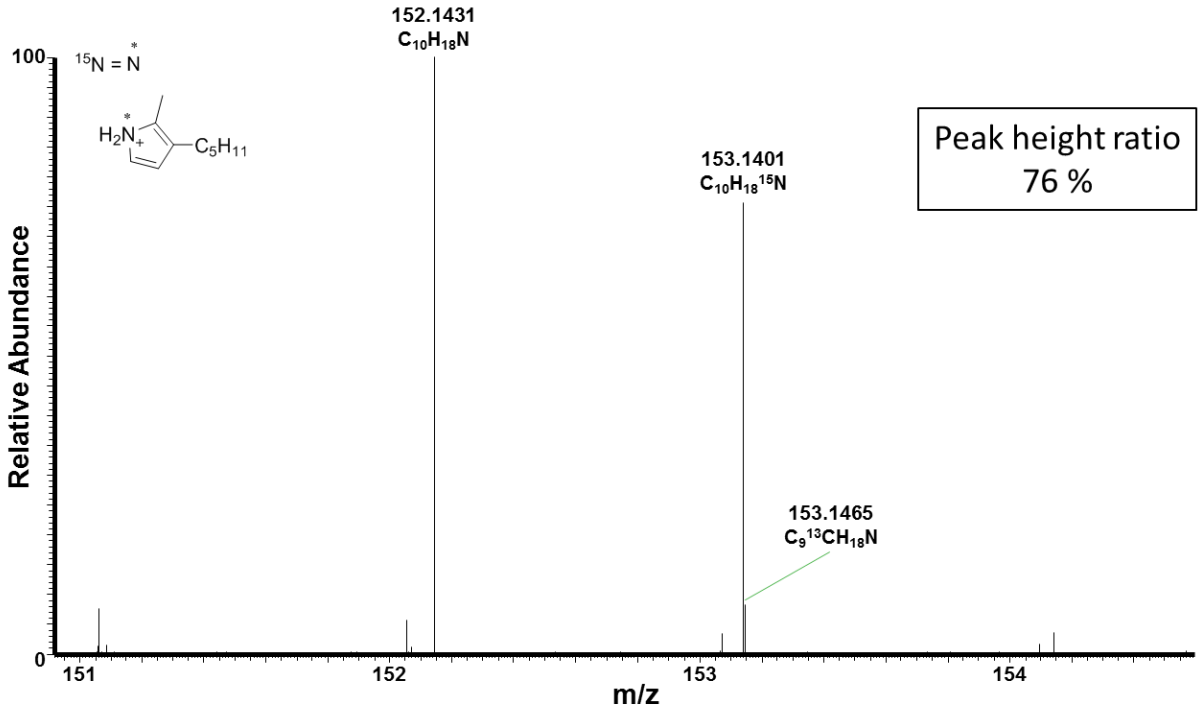


Fig. S153. HRMS^2 spectra of 2-methyl-3-propyl prodiginine with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (compound **1** $[M+H]^+$: *m/z* 297, $C_{18}H_{22}N_2{}^{15}NO$).

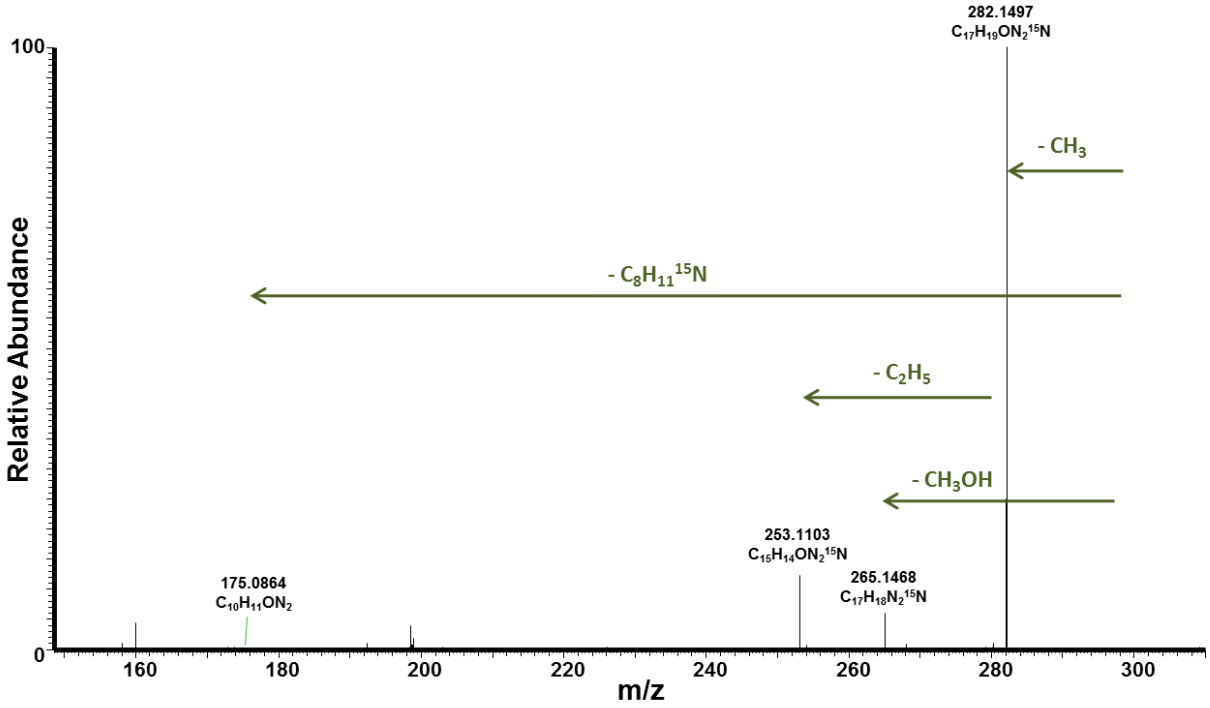


Fig. S154. HRMS^2 spectra of 2-methyl-3-butyl prodiginine with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (compound **2** $[M+H]^+$: *m/z* 311, $C_{19}H_{24}N_2{}^{15}NO$).

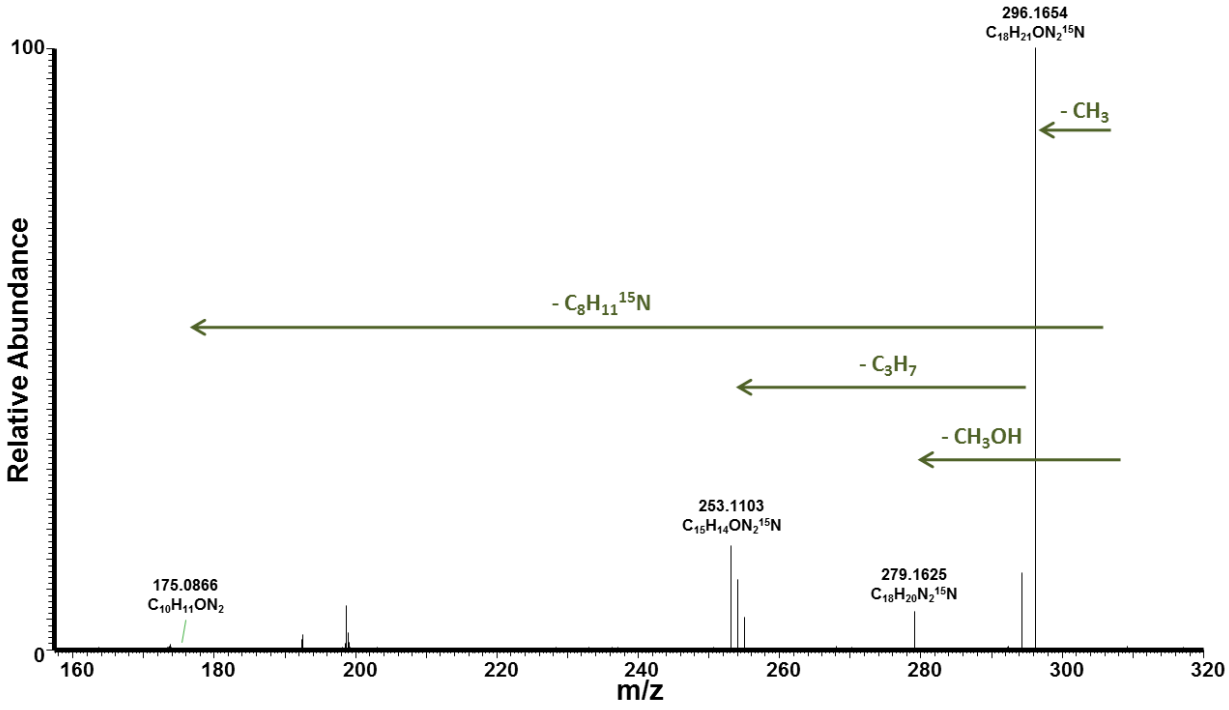


Fig. S155. HRMS^2 spectra of prodigiosin with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (compound **3** $[M+H]^+$: *m/z* 325, $C_{20}H_{26}N_2{}^{15}NO$).

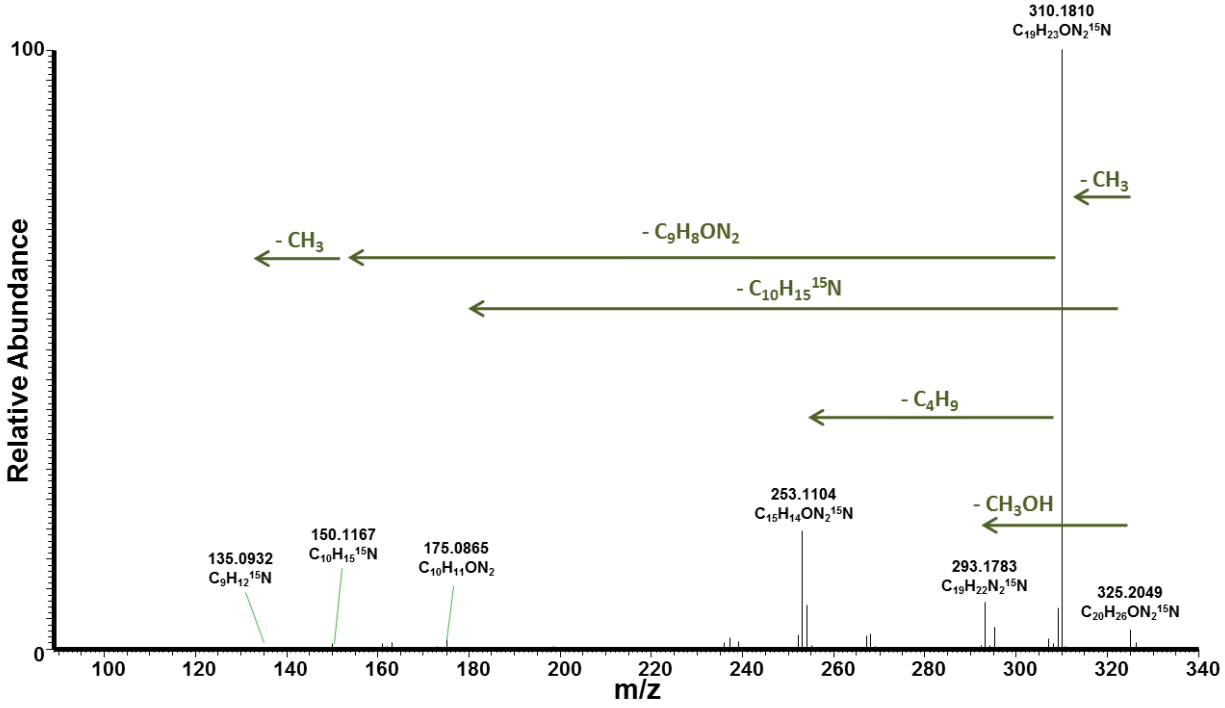


Fig. S156. HRMS^2 spectra of 2-methyl-3-hexyl prodiginine with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (compound **4** $[M+H]^+$: *m/z* 339, $C_{21}H_{28}N_2{}^{15}NO$).

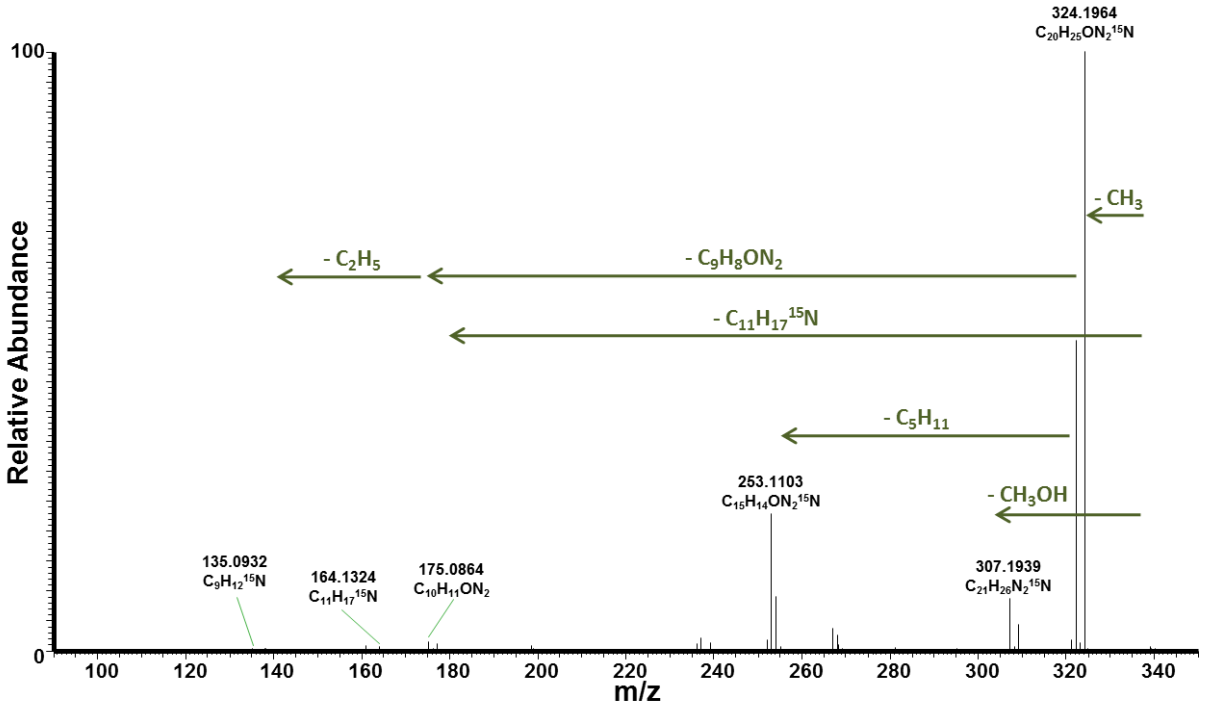


Fig. S157. HRMS^2 spectra of 2-methyl-3-heptyl prodiginine with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (compound **5** $[M+H]^+$: *m/z* 353, $C_{22}H_{30}N_2{}^{15}NO$).

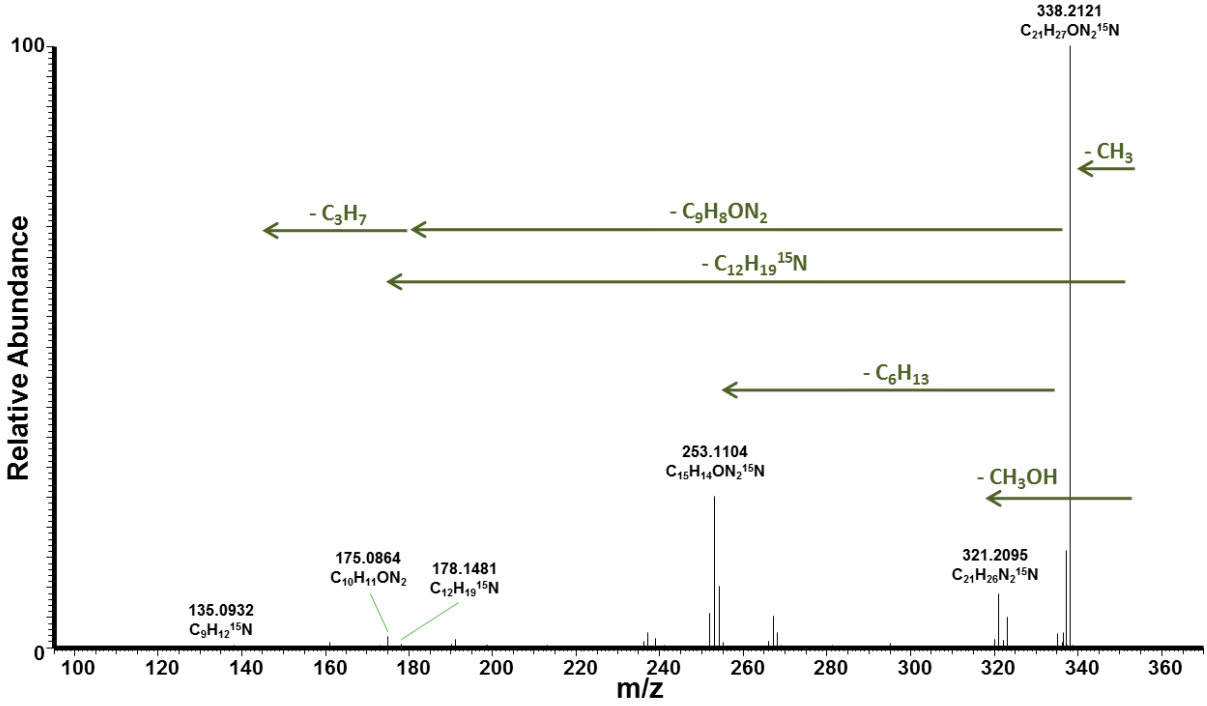


Fig. S158. MALDI-imaging-HRMS of abundant serratamolides (A: serrawettin W1 (**10**); B: C_{10}+C_{12} (**12**); C: C_{10}+$C_{12:1}$ (**16**)) produced by *S. marcescens* MSRBB2 on potato dextrose agar supplemented with [^{15}N]-L-serine. Optical image with assigned scan area and localization of unlabeled serratamolides along with one and two incorporations of [^{15}N]-L-serine ([M+K]$^+$ ± 3 ppm).

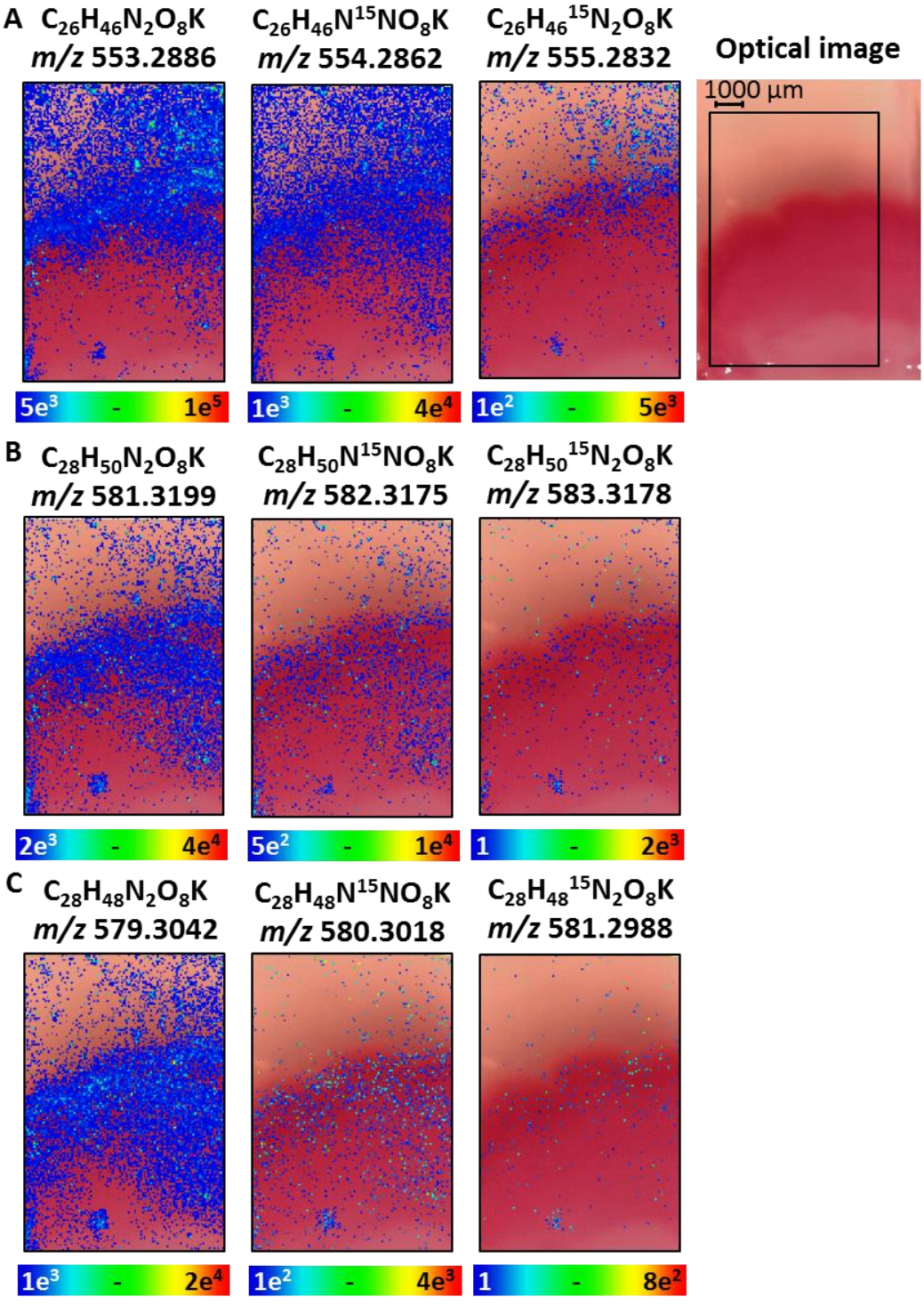


Fig. S159. MALDI-imaging-HRMS of abundant serratamolides (A: serrawettin W1 (**10**); B: C_{10}+C_{12} (**12**); C: C_{10}+$C_{12:1}$ (**16**)) produced by *S. marcescens* MSRBB2 on potato dextrose agar supplemented with [^{15}N]-L-serine. Optical image with assigned scan area and localization of unlabeled serratamolides along with one and two incorporations of [^{15}N]-L-serine ([M+K]$^+$ ± 3 ppm).

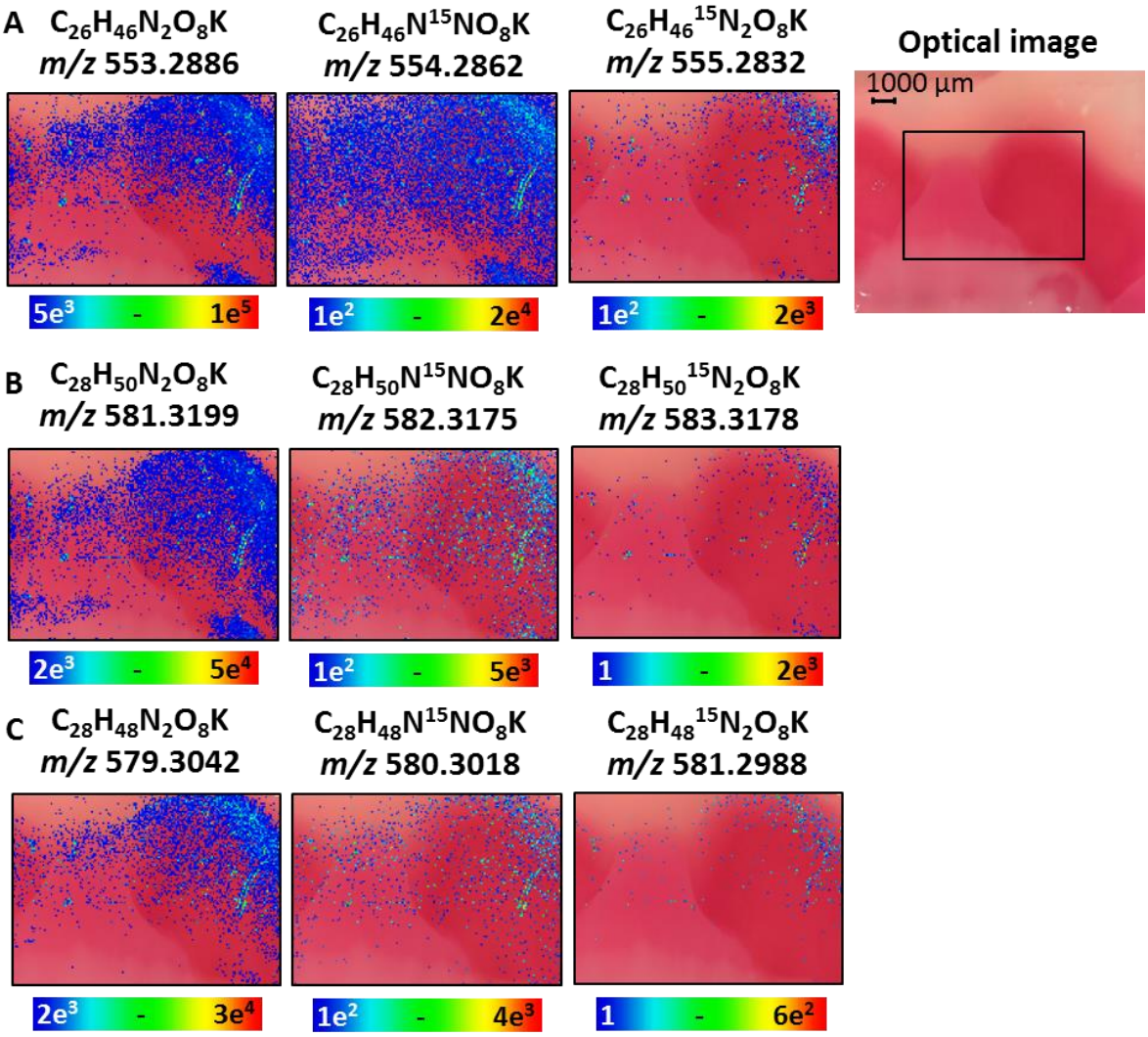


Fig. S160. HRMS of serrawettin W1 / serratamolide C_{10}+C_{10} with incorporated ^{15}N-L-serine from labeled nutrient agar (compound **10** $[M+H]^+$: *m/z* 515, $C_{26}H_{47}N_2O_8$).

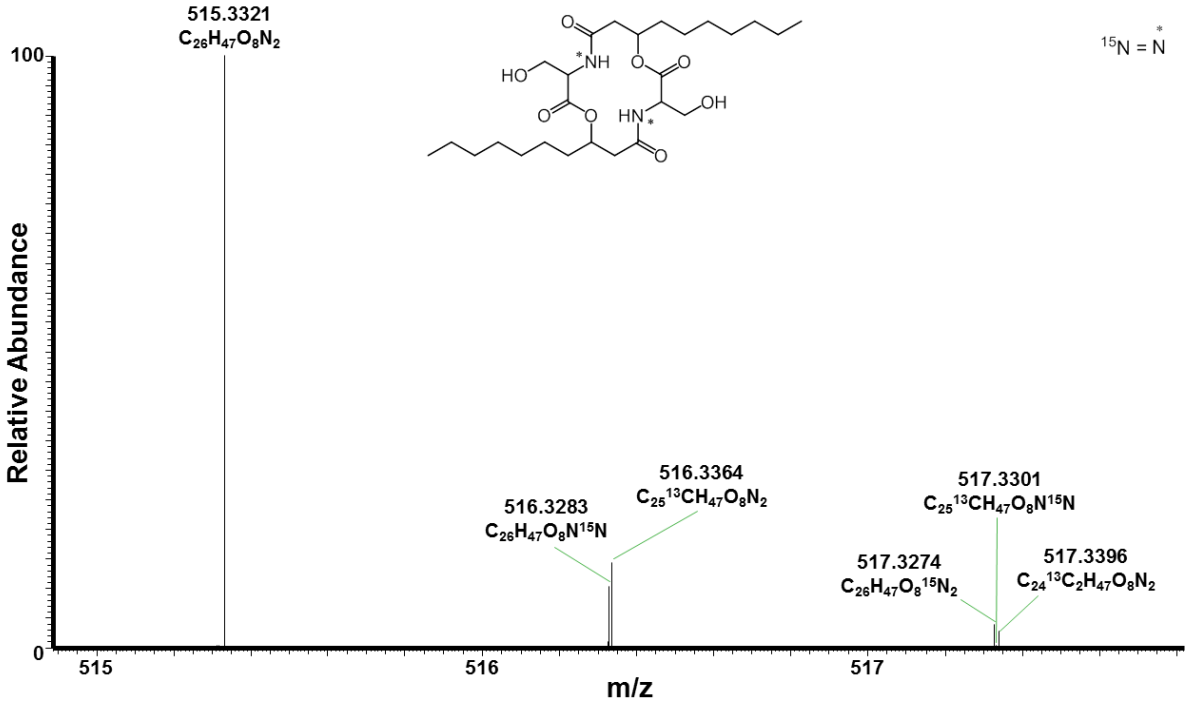


Fig. S161. HRMS of serratamolide C_{10}+C_{11} with incorporated ^{15}N-L-serine from labeled nutrient agar (compound **11** $[M+H]^+$: *m/z* 529, $C_{27}H_{49}N_2O_8$).

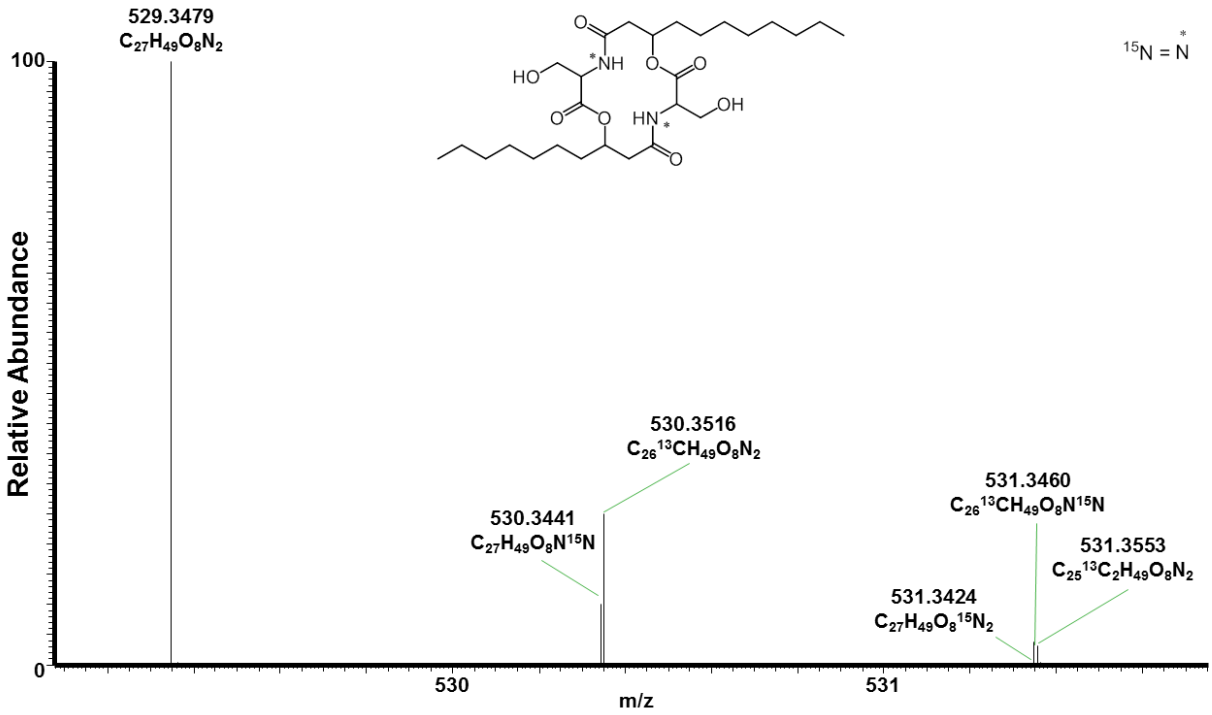


Fig. S162. HRMS of serratamolide C_{10}+C_{12} with incorporated ^{15}N-L-serine from labeled nutrient agar (compound **12** $[M+H]^+$: *m/z* 543, $C_{28}H_{51}N_2O_8$).

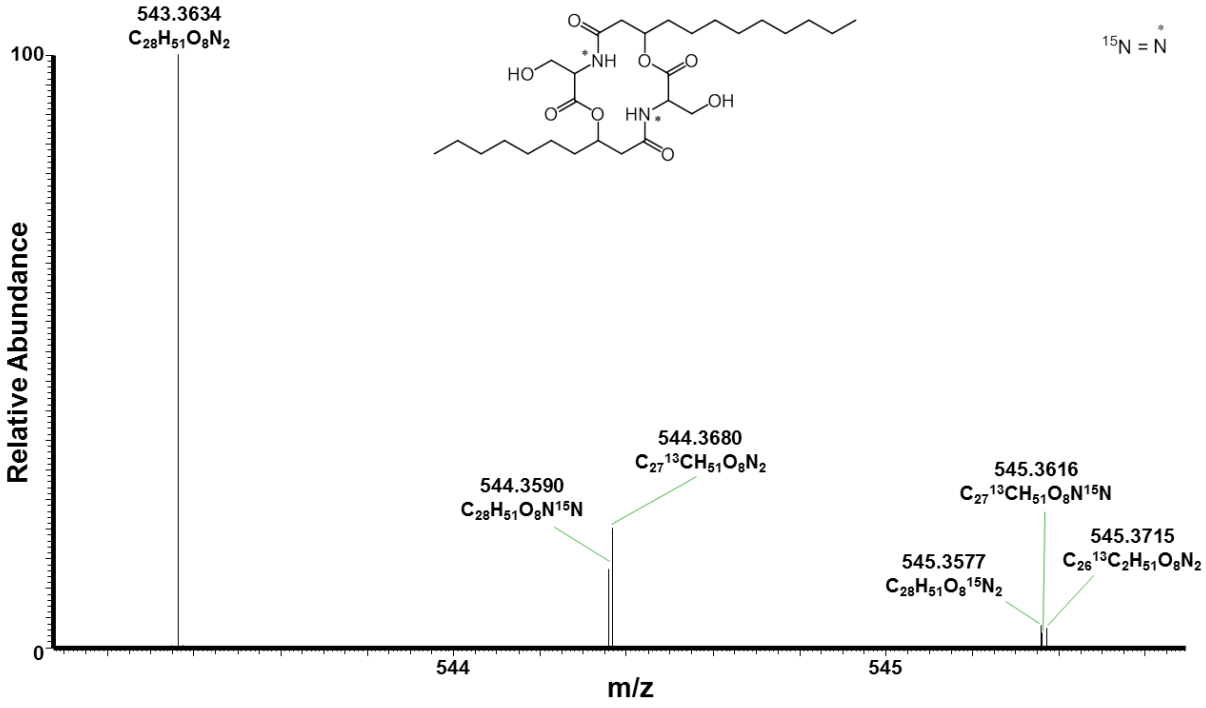


Fig. S163. HRMS of serratamolide C_{11}+C_{12} with incorporated ^{15}N-L-serine from labeled nutrient agar (compound **13** $[M+H]^+$: *m/z* 557, $C_{29}H_{53}N_2O_8$).

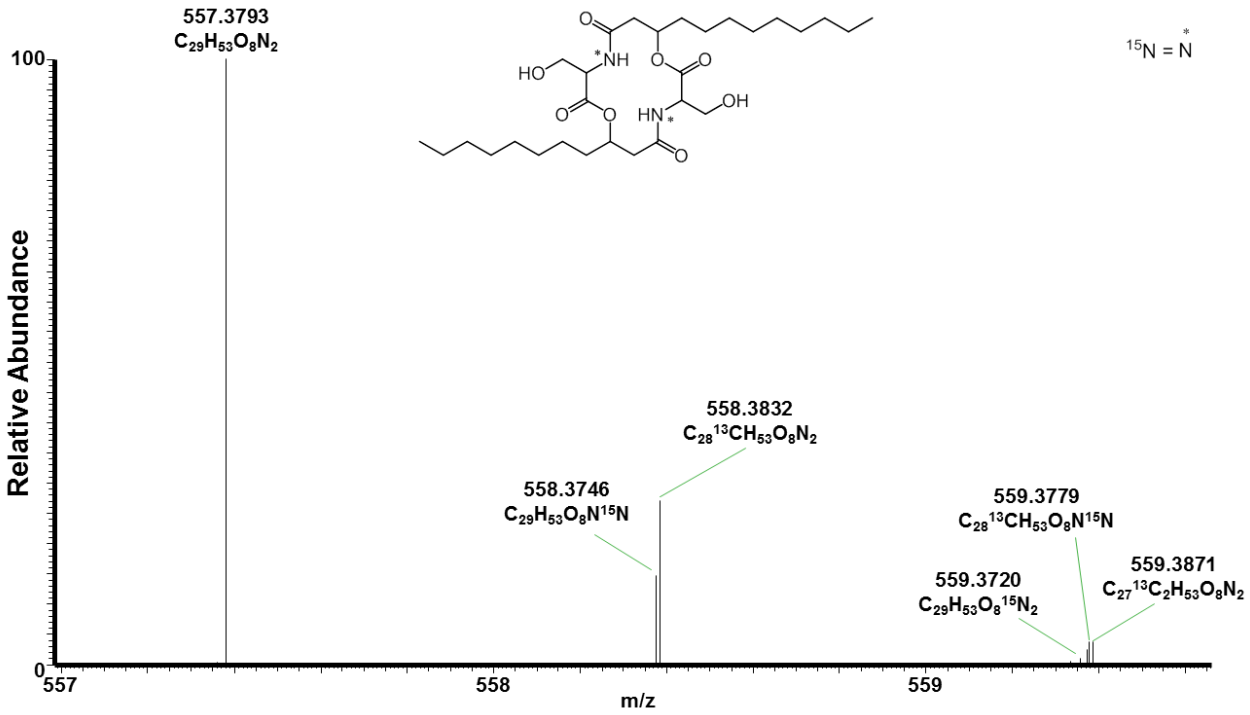


Fig. S164. HRMS of serratamolide C_{12}+C_{12} with incorporated ^{15}N-L-serine from labeled nutrient agar (compound **14** $[M+H]^+$: *m/z* 571, $C_{30}H_{55}N_2O_8$).

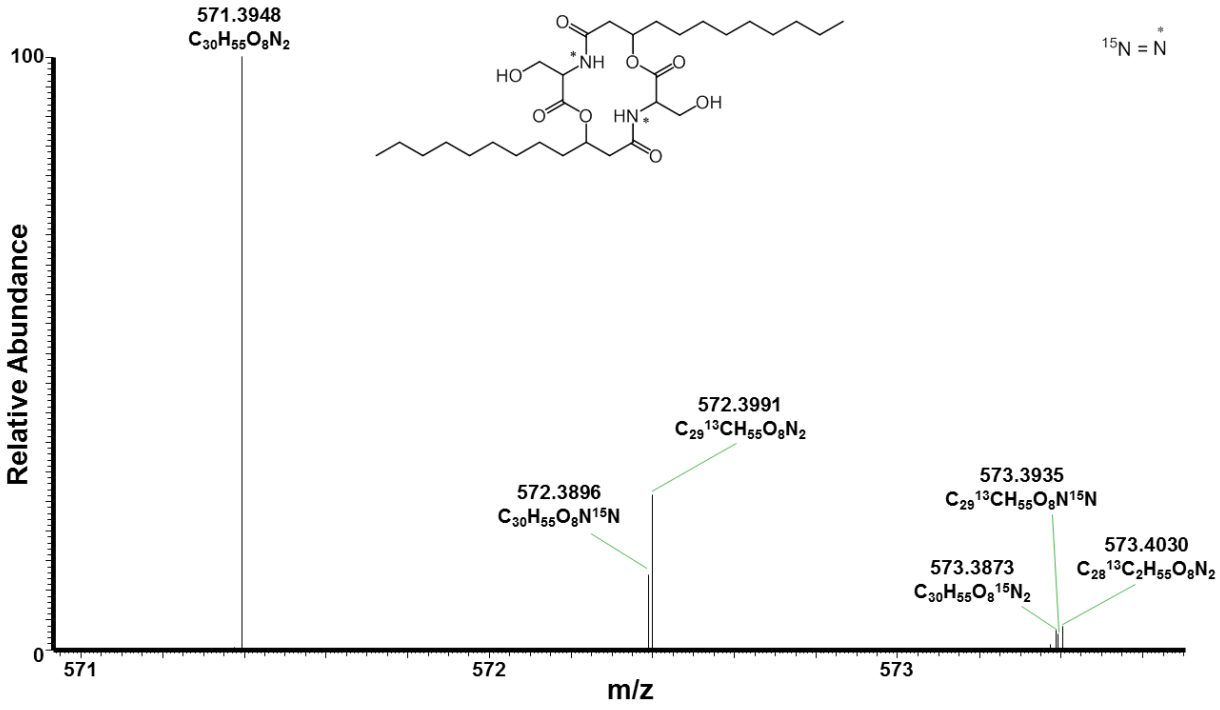


Fig. S165. HRMS of serratamolide C_{10}+$C_{11:1}$ with incorporated ^{15}N-L-serine from labeled nutrient agar (compound **15** $[M+H]^+$: *m/z* 527, $C_{27}H_{47}N_2O_8$).

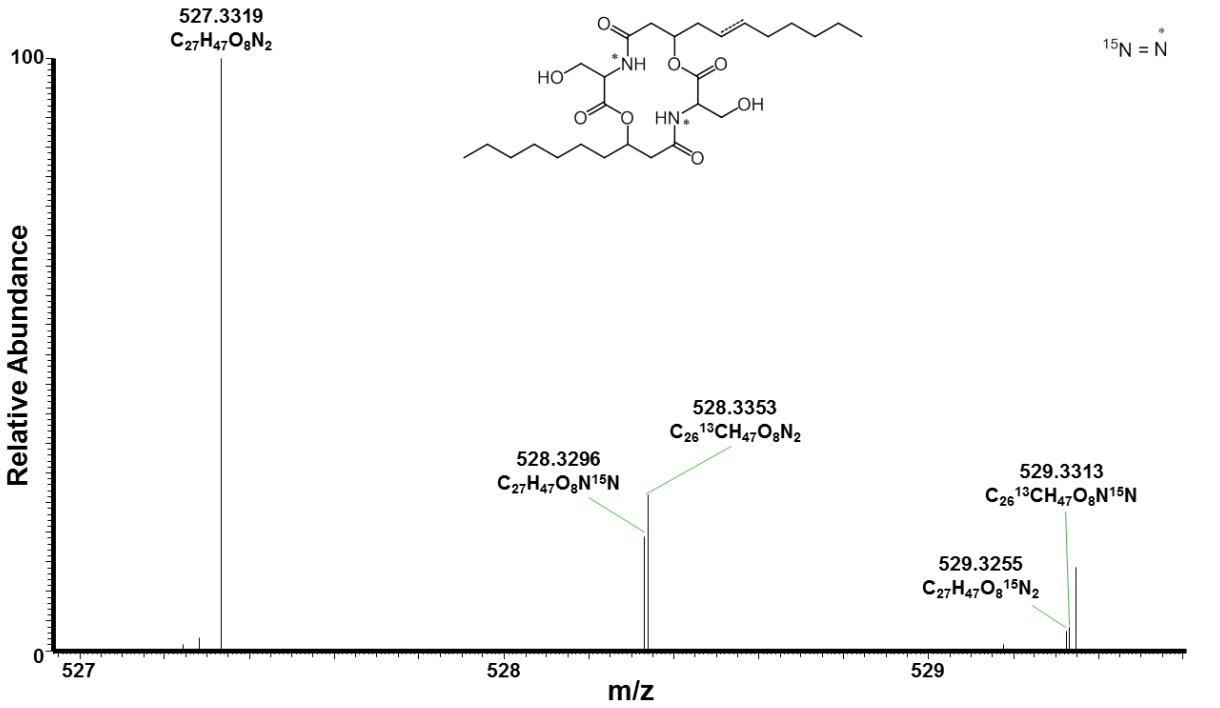


Fig. S166. HRMS of serratamolide C_{10}+$C_{12:1}$ with incorporated ^{15}N-L-serine from labeled nutrient agar (compound **16** $[M+H]^+$: *m/z* 541, $C_{28}H_{49}N_2O_8$).

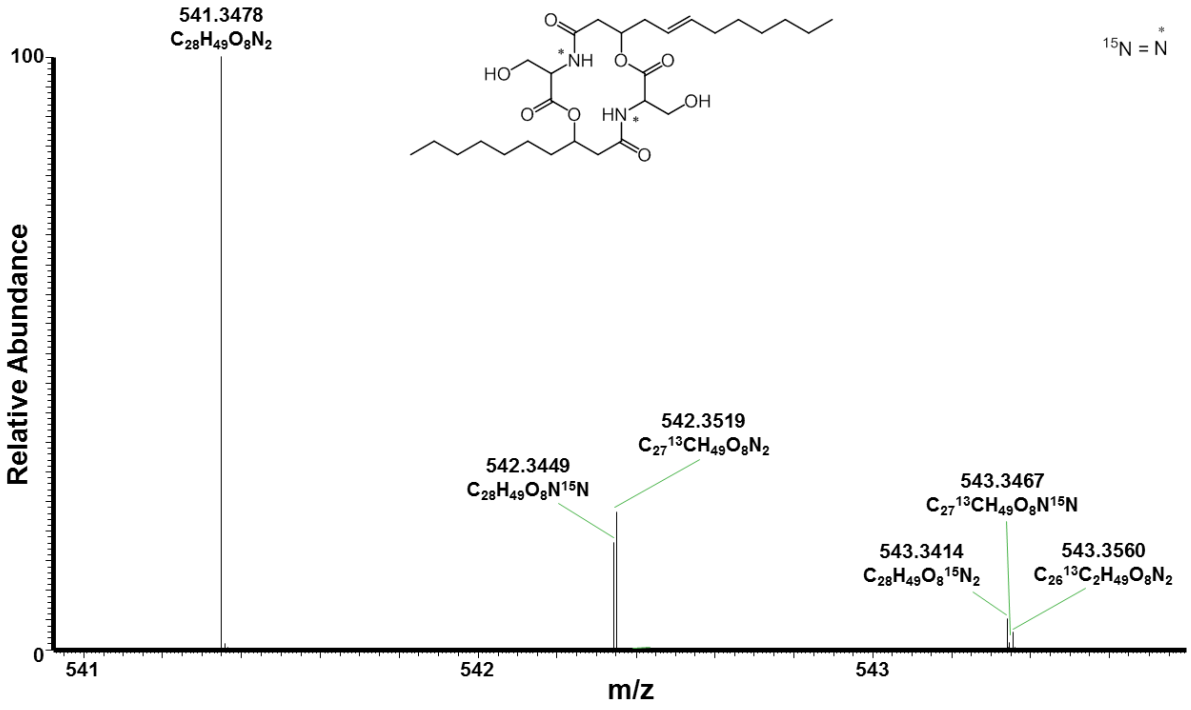


Fig. S167. HRMS of serratamolide C_{11}+$C_{12:1}$ with incorporated ^{15}N-L-serine from labeled nutrient agar (compound **17** $[M+H]^+$: *m/z* 555, $C_{29}H_{51}N_2O_8$).

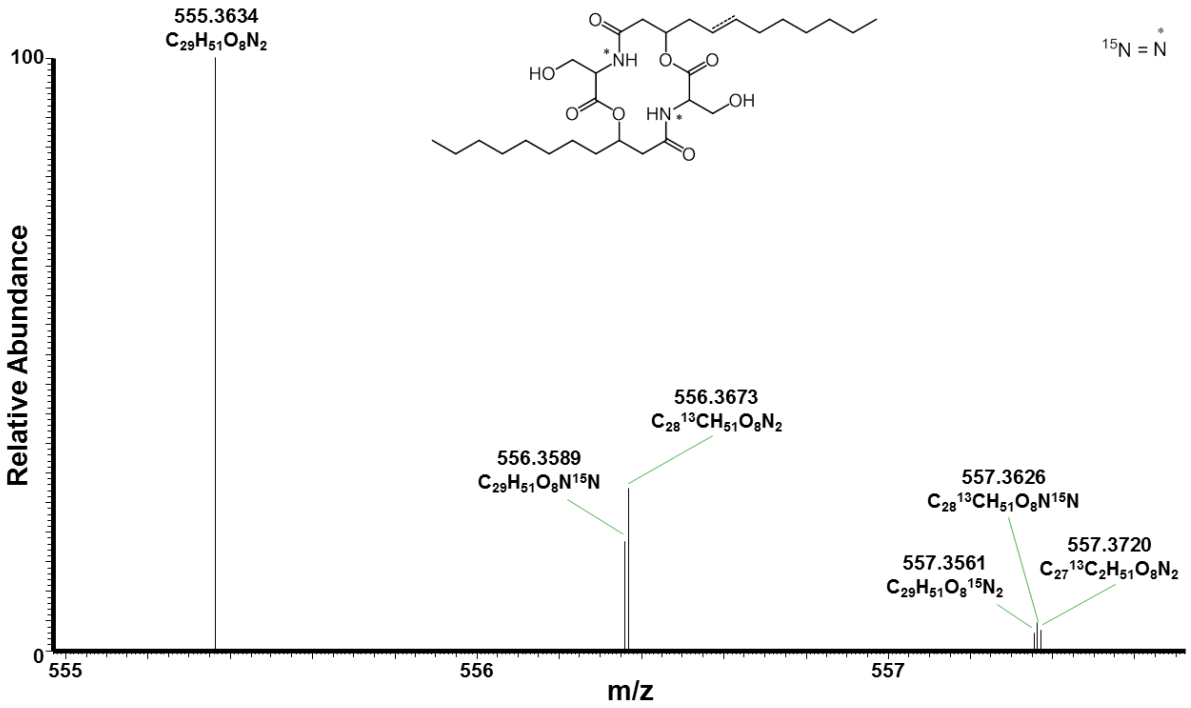


Fig. S168. HRMS of serratamolide C_{12}+$C_{12:1}$ with incorporated ^{15}N-L-serine from labeled nutrient agar (compound **18** $[M+H]^+$: *m/z* 569, $C_{30}H_{53}N_2O_8$).

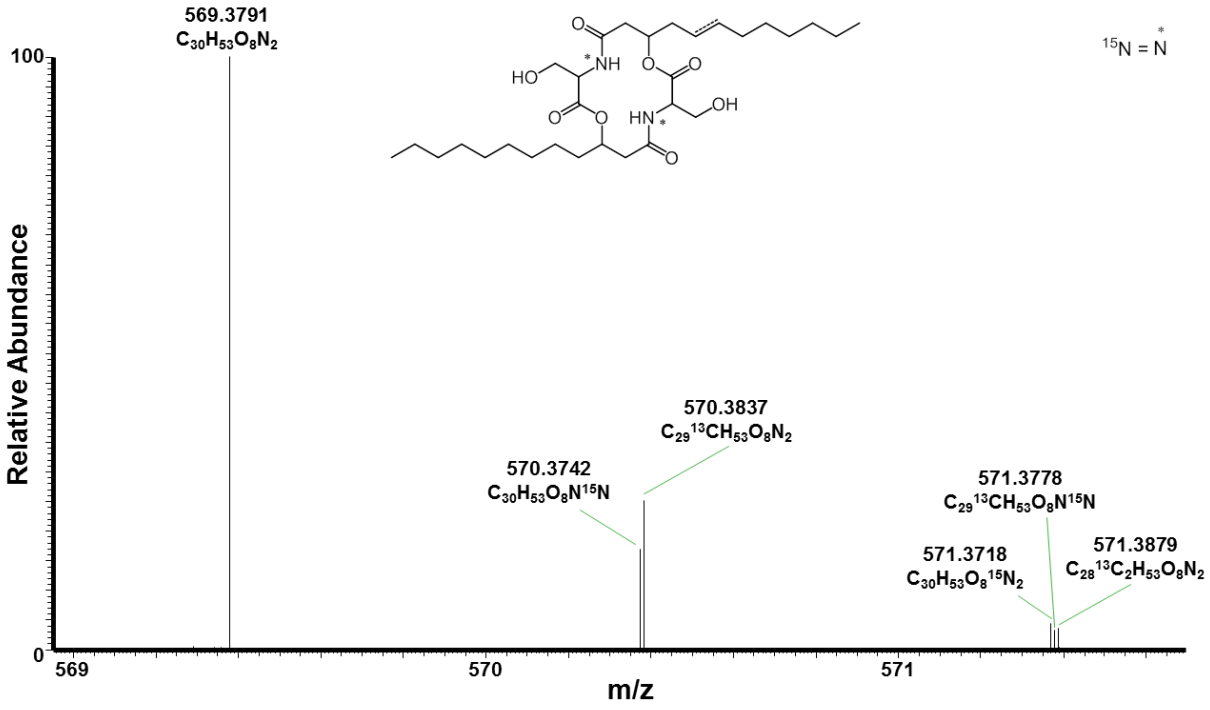


Fig. S169. HRMS of ring-opened serratamolide C_{10}+C_{10} with incorporated ^{15}N-L-serine from labeled nutrient agar (compound **19** $[M+H]^+$: *m/z* 533, $C_{26}H_{49}N_2O_9$).

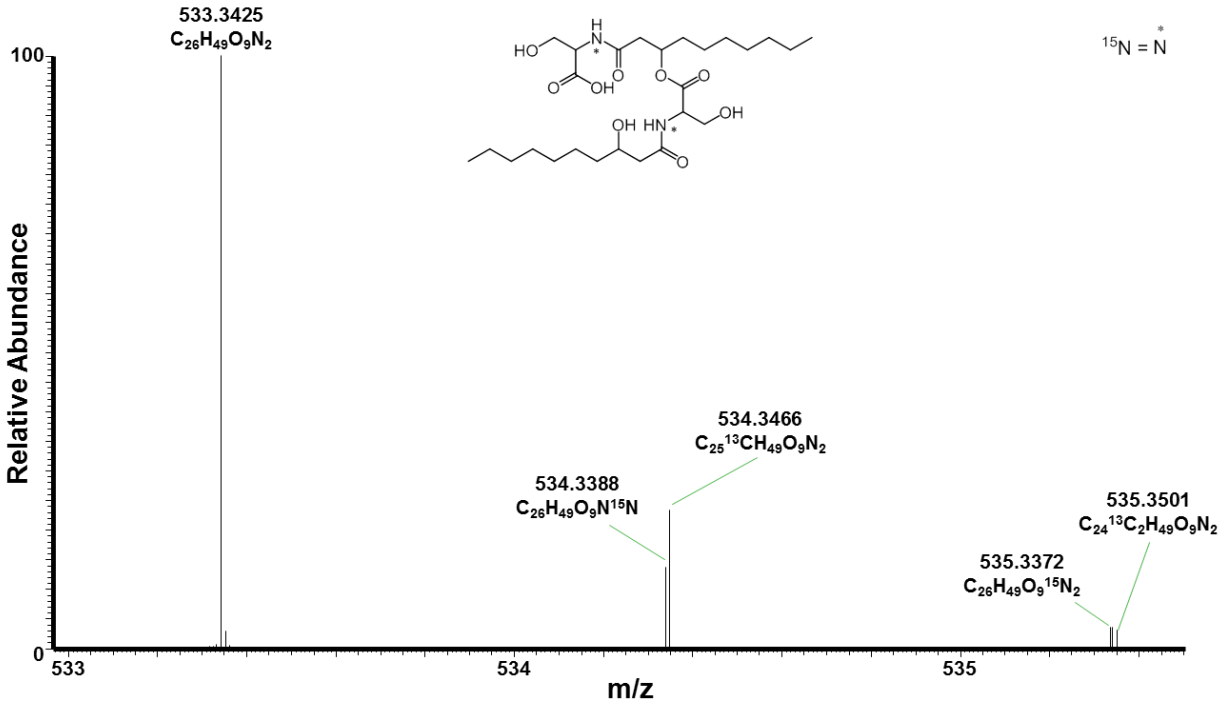


Fig. S170. HRMS of ring-opened serratamolide C_{10}+C_{11} with incorporated ^{15}N-L-serine from labeled nutrient agar (compound **20** $[M+H]^+$: *m/z* 547, $C_{27}H_{51}N_2O_9$).

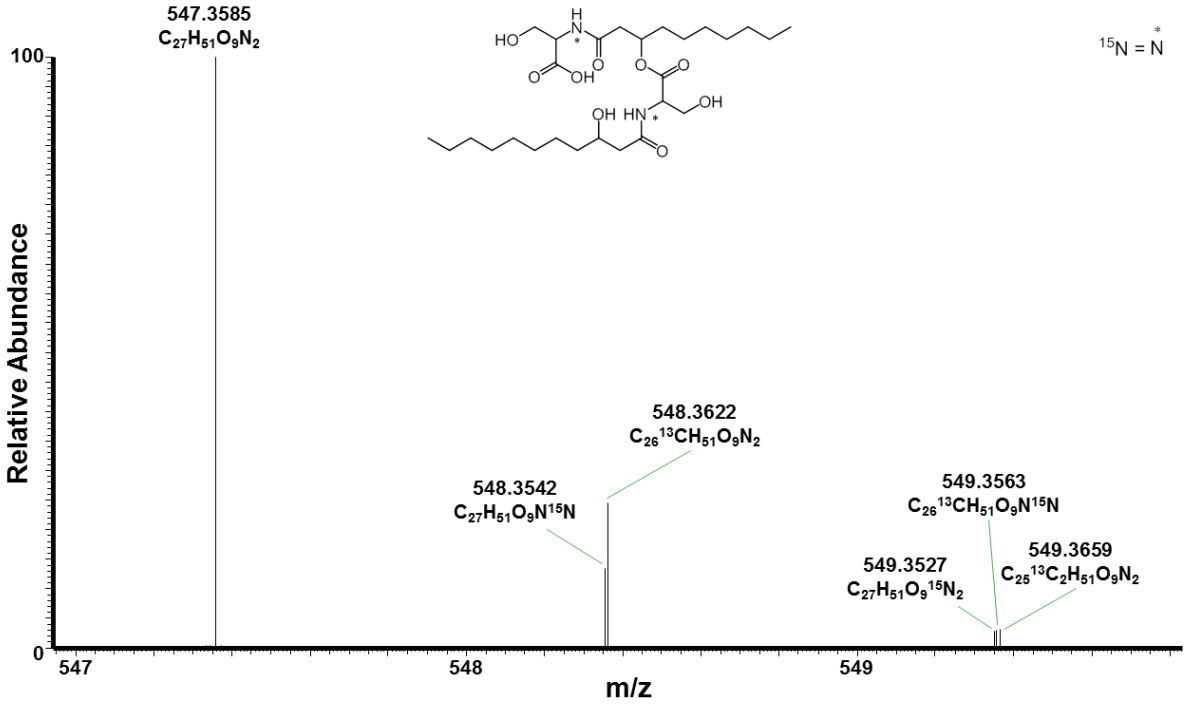


Fig. S171. HRMS of ring-opened serratamolide C_{10}+C_{12} with incorporated ^{15}N-L-serine from labeled nutrient agar (compound **21** $[M+H]^+$: *m/z* 561, $C_{28}H_{53}N_2O_9$).

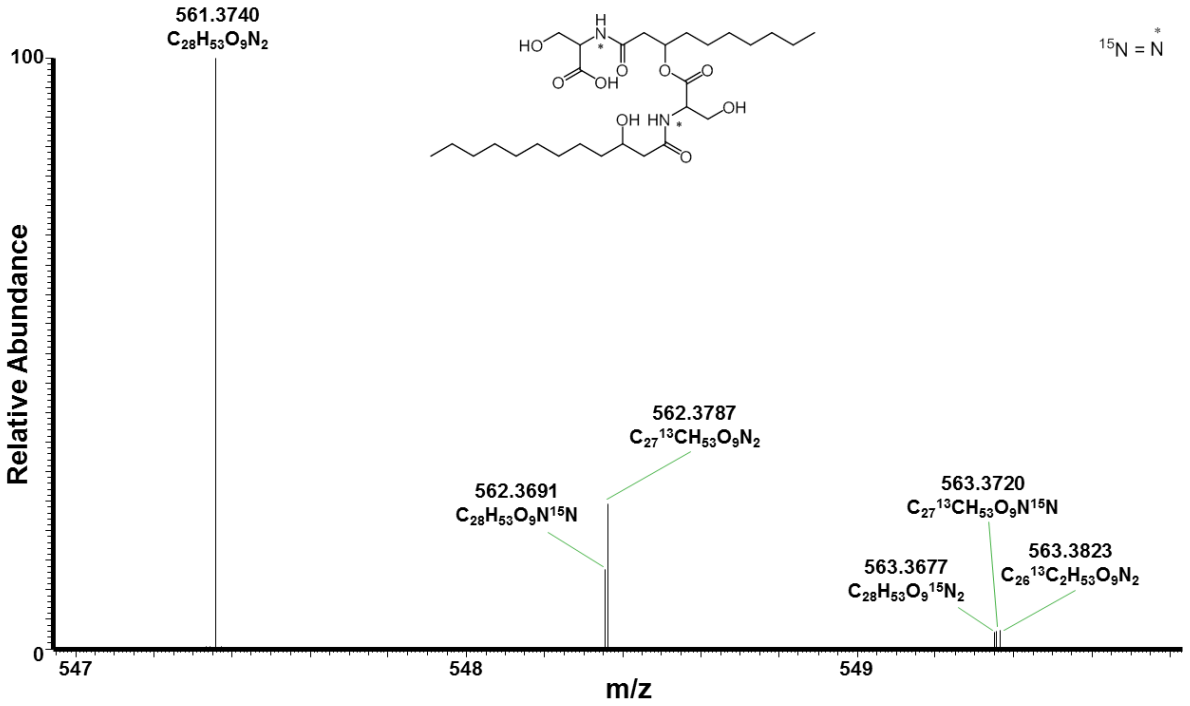


Fig. S172. HRMS of ring-opened serratamolide C_{10}+$C_{12:1}$ with incorporated ^{15}N-L-serine from labeled nutrient agar (compound **22** $[M+H]^+$: *m/z* 559, $C_{28}H_{51}N_2O_9$).

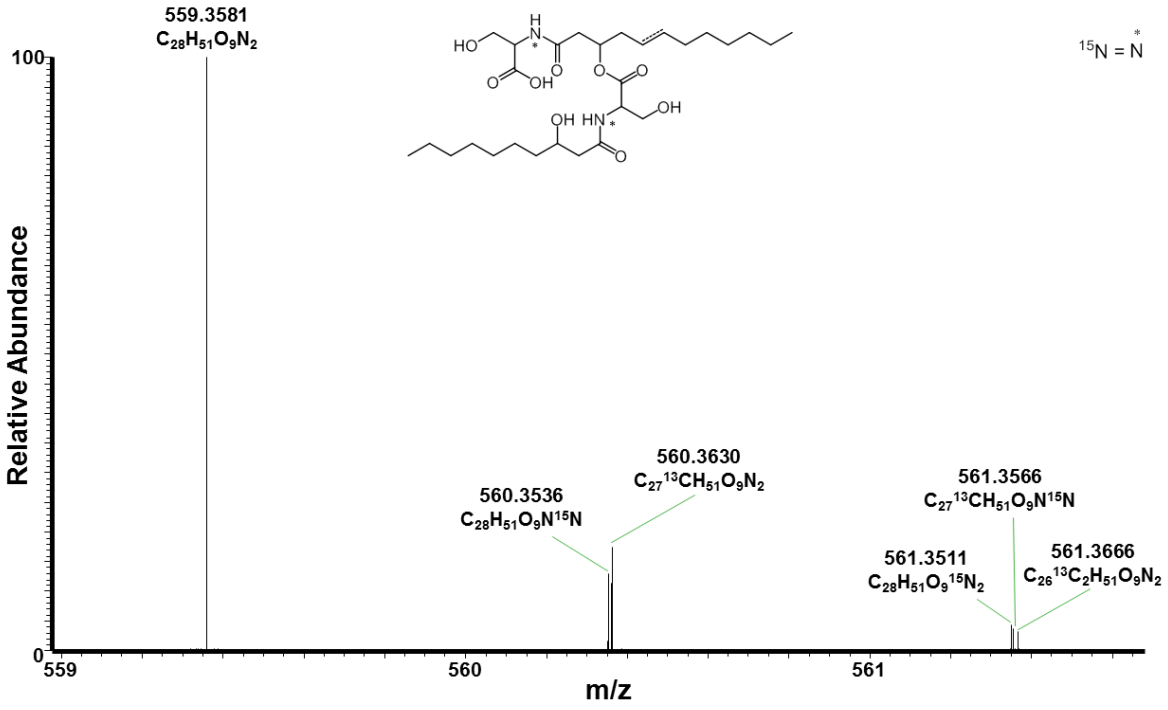


Fig. S173. HRMS^2 of ring-opened serratamolide C_{10}+C_{13} with incorporated ^{15}N-L-serine from labeled nutrient agar (compound **23** $[M+H]^+$: *m/z* 575, $C_{29}H_{55}N_2O_9$).

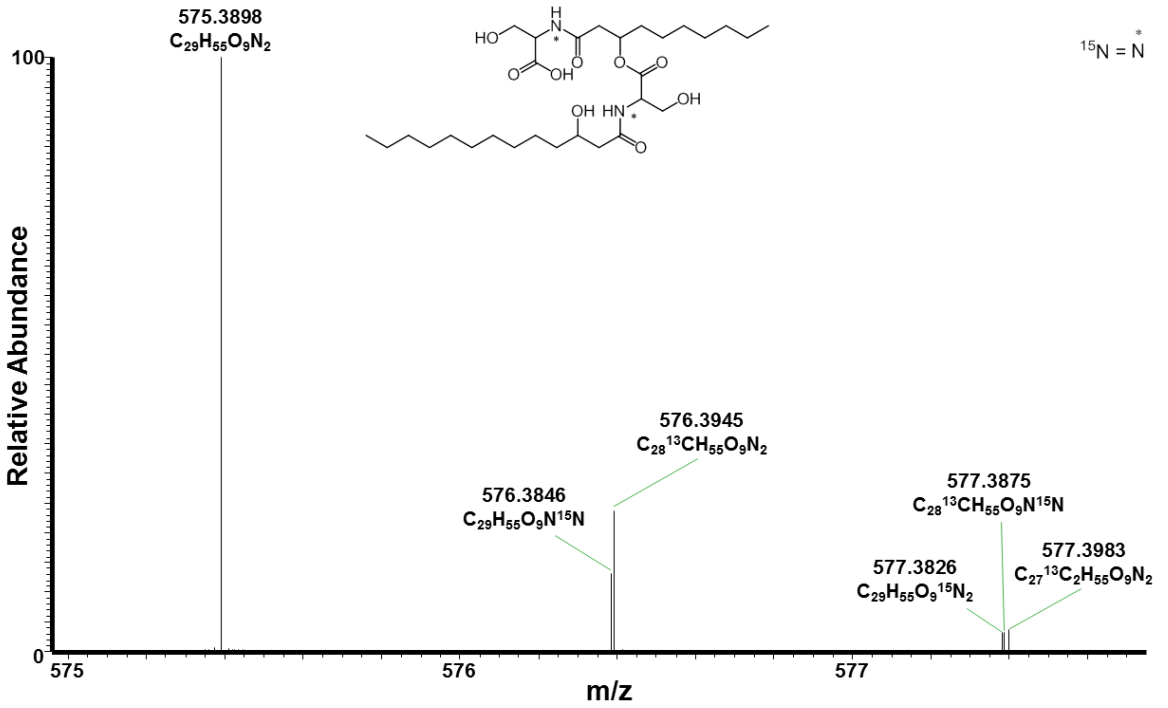


Fig. S174. HRMS of ring-opened serratamolide C_{12}+C_{12} with incorporated ^{15}N-L-serine from labeled nutrient agar (compound **24** $[M+H]^+$: *m/z* 589, $C_{30}H_{57}N_2O_9$).

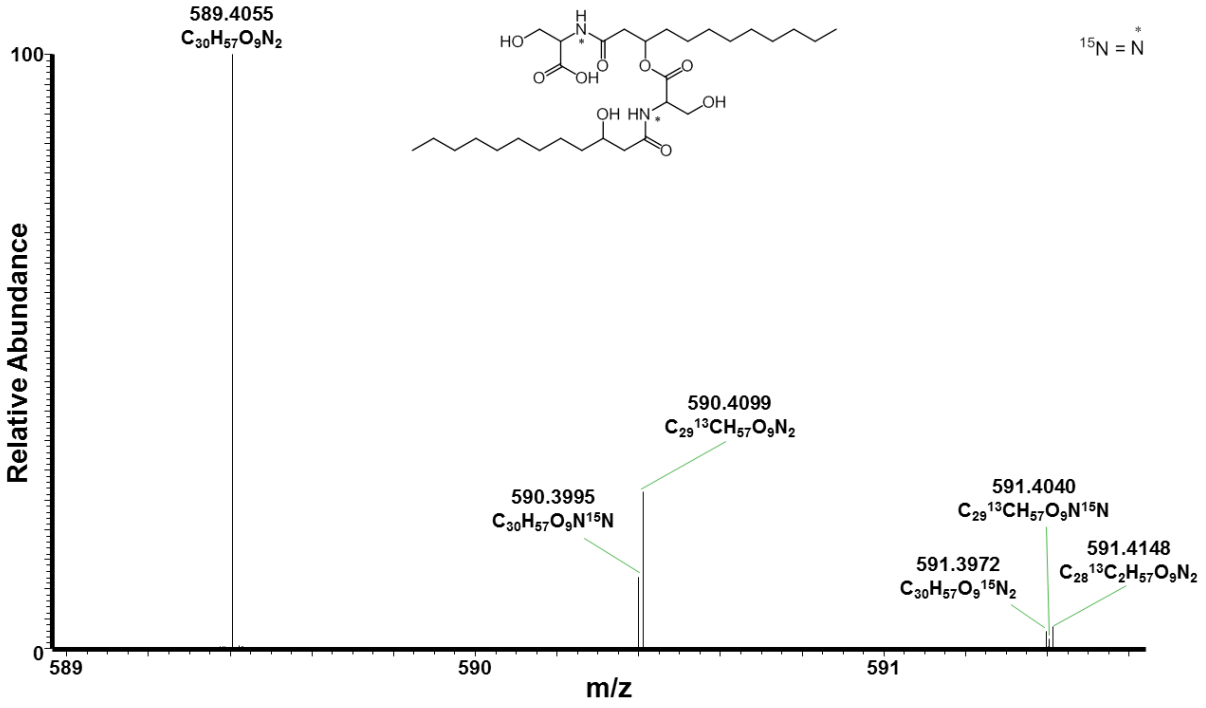


Fig. S175. HRMS of ring-opened serratamolide C_{12}+C_{13} with incorporated ^{15}N-L-serine from labeled nutrient agar (compound **25** $[M+H]^+$: *m/z* 603, $C_{31}H_{59}N_2O_9$).

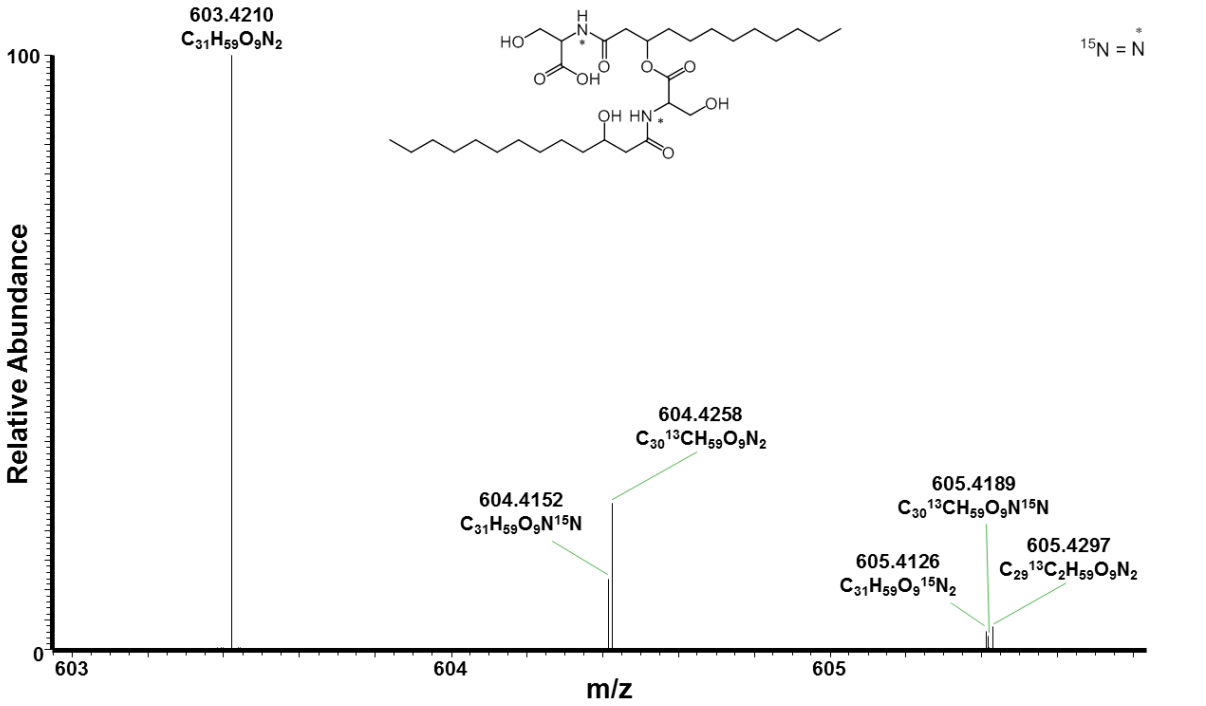


Fig. S176. HRMS of ring-opened serratamolide C_{10}+$C_{13:1}$ with incorporated ^{15}N-L-serine from labeled nutrient agar (compound **26** $[M+H]^+$: *m/z* 573, $C_{29}H_{53}N_2O_9$).

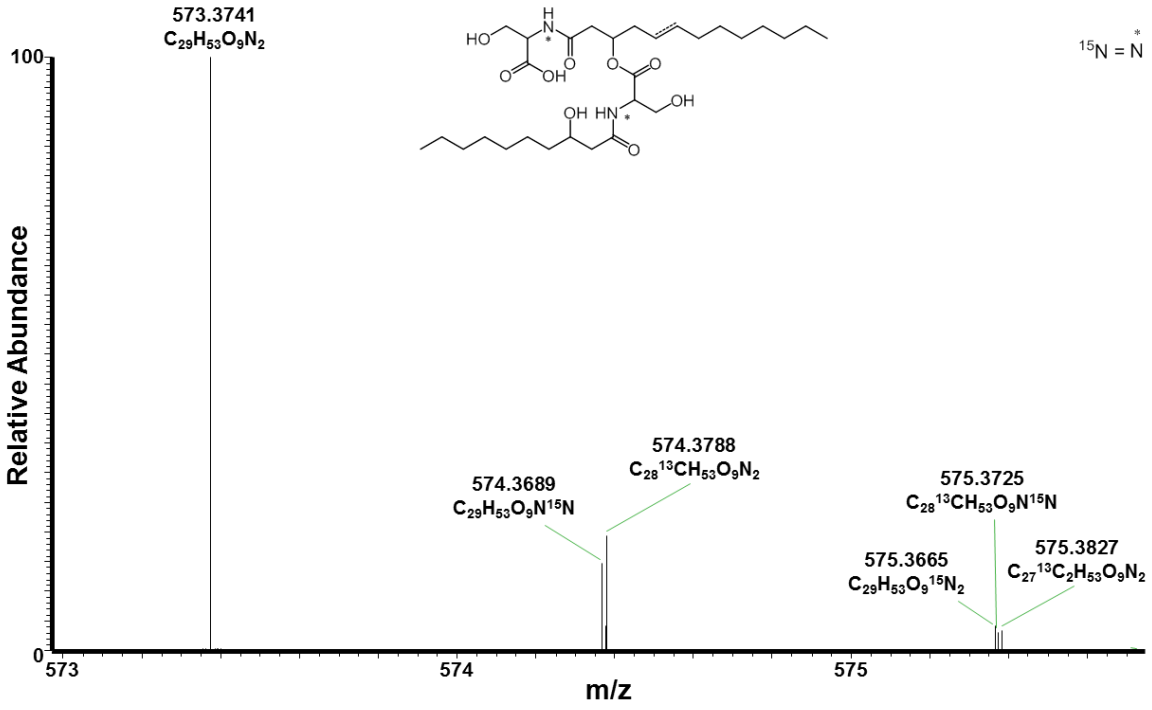


Fig. S177. HRMS of ring-opened serratamolide C_{12}+$C_{12:1}$ with incorporated ^{15}N-L-serine from labeled nutrient agar (compound **27** $[M+H]^+$: *m/z* 587, $C_{30}H_{55}N_2O_9$).

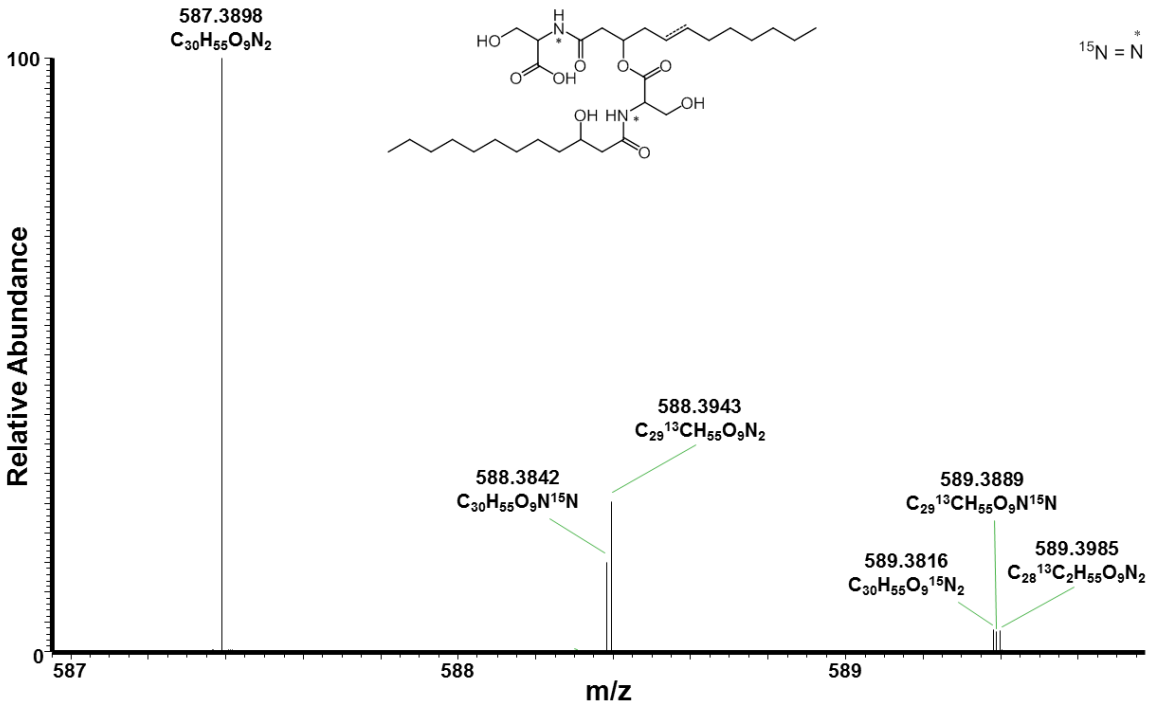


Fig. S178. HRMS of ring-opened serratamolide C_{13}+$C_{12:1}$ with incorporated ^{15}N-L-serine from labeled nutrient agar (compound **28** $[M+H]^+$: *m/z* 601, $C_{31}H_{57}N_2O_9$).

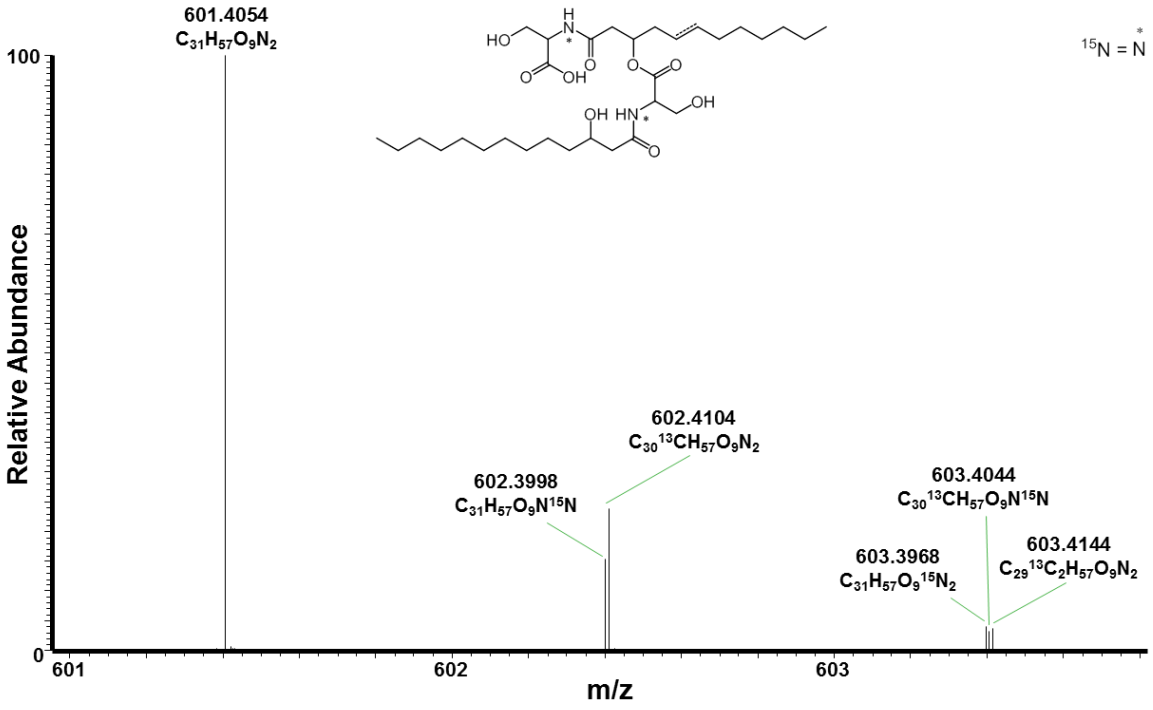


Fig. S179. HRMS of serratamic acid with incorporated ^{15}N-L-serine from labeled nutrient agar (N-(D-3-hydroxydecanoyl)-L-serine, compound **29** $[M+H]^+$: *m/z* 276, $C_{13}H_{26}NO_5$).

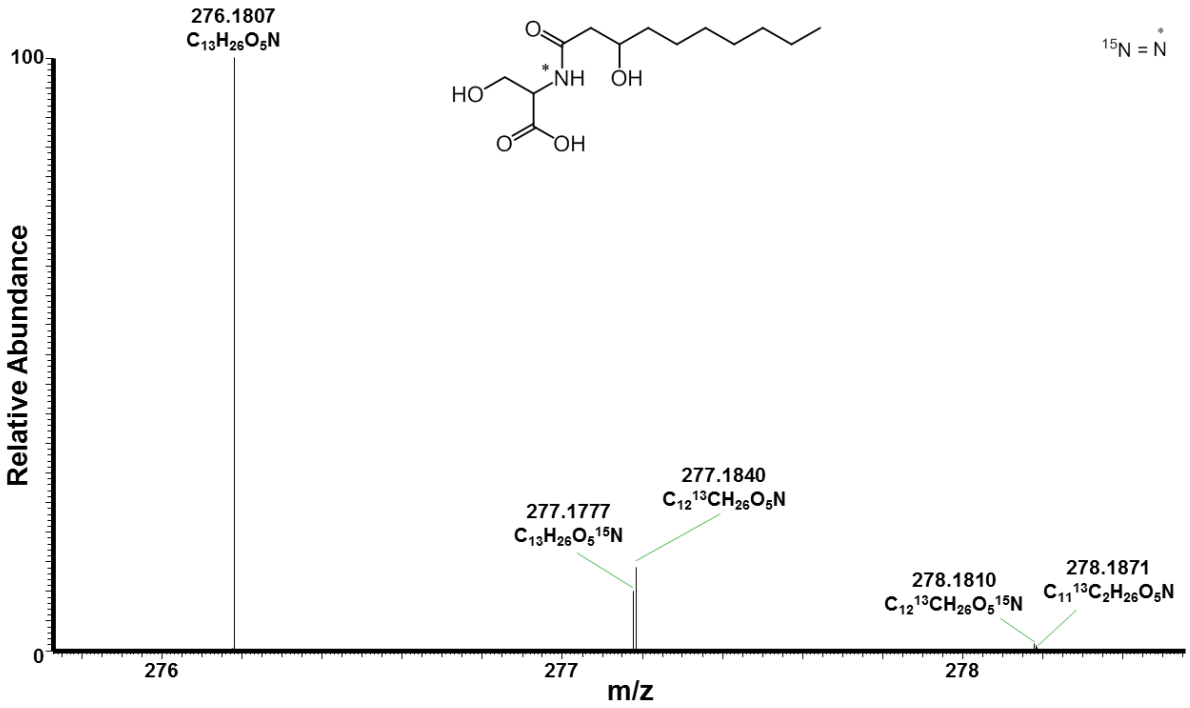


Fig. S180. HRMS of serratamic acid derivative with incorporated ^{15}N-L-serine from labeled nutrient agar (hydroxydodecanoyl-serine, compound **30** $[M+H]^+$: *m/z* 304, $C_{15}H_{30}NO_5$).

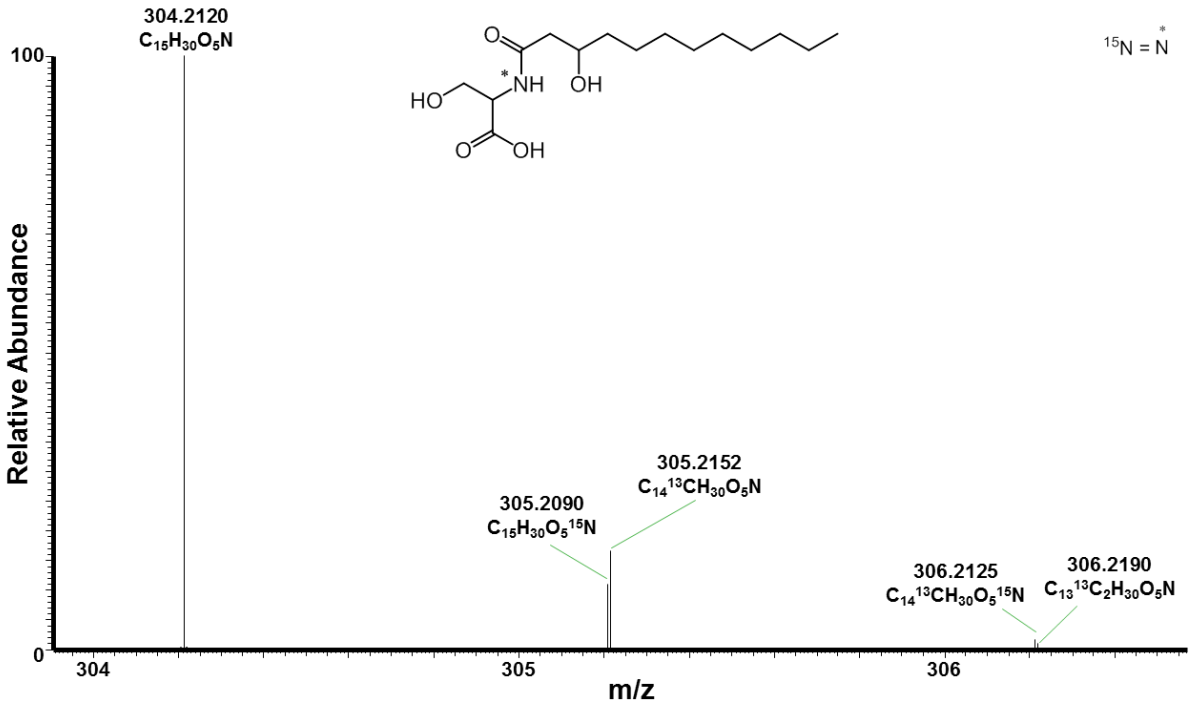


Fig. S181. HRMS of serratamic acid derivative with double bond with incorporated ^{15}N-L-serine from labeled nutrient agar (hydroxydodecenoyl-serine, compound **31** $[M+H]^+$: *m/z* 302, $C_{15}H_{28}NO_5$).

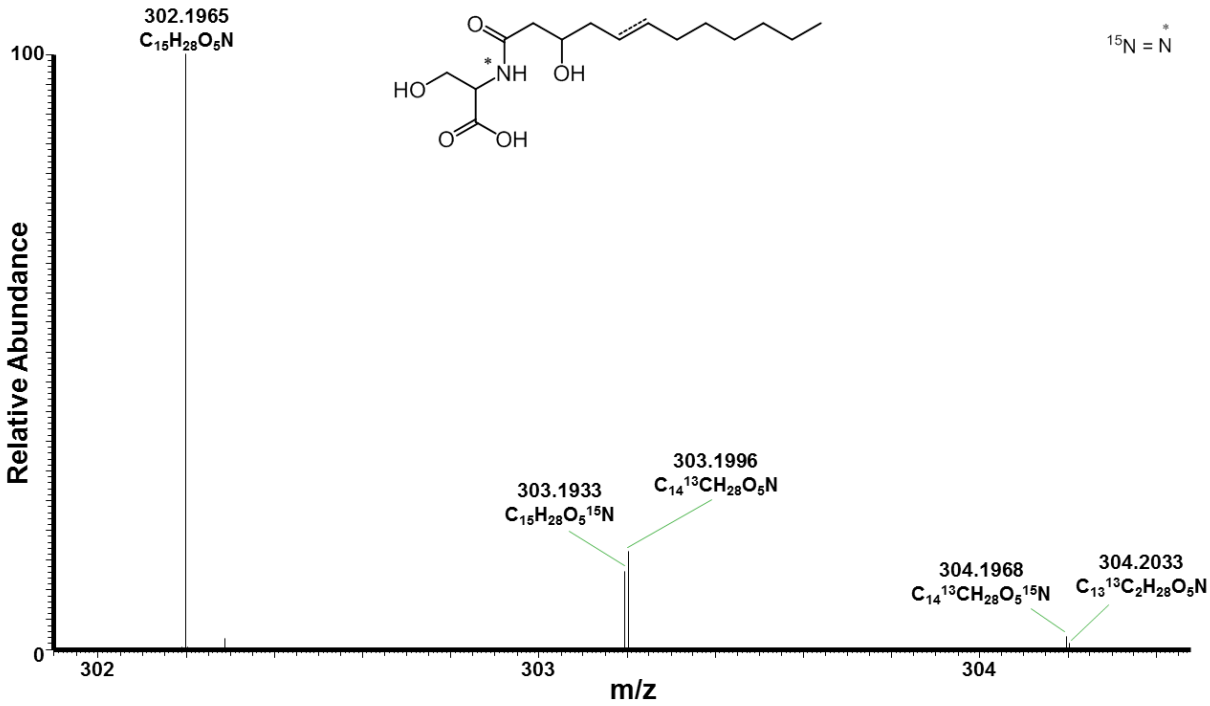


Fig. S182. HRMS of serrawettin W1 / serratamolide C_{10}+C_{10} with incorporated ^{15}N-L-serine from labeled potato dextrose agar (compound **10** $[M+H]^+$: *m/z* 515, $C_{26}H_{47}N_2O_8$).

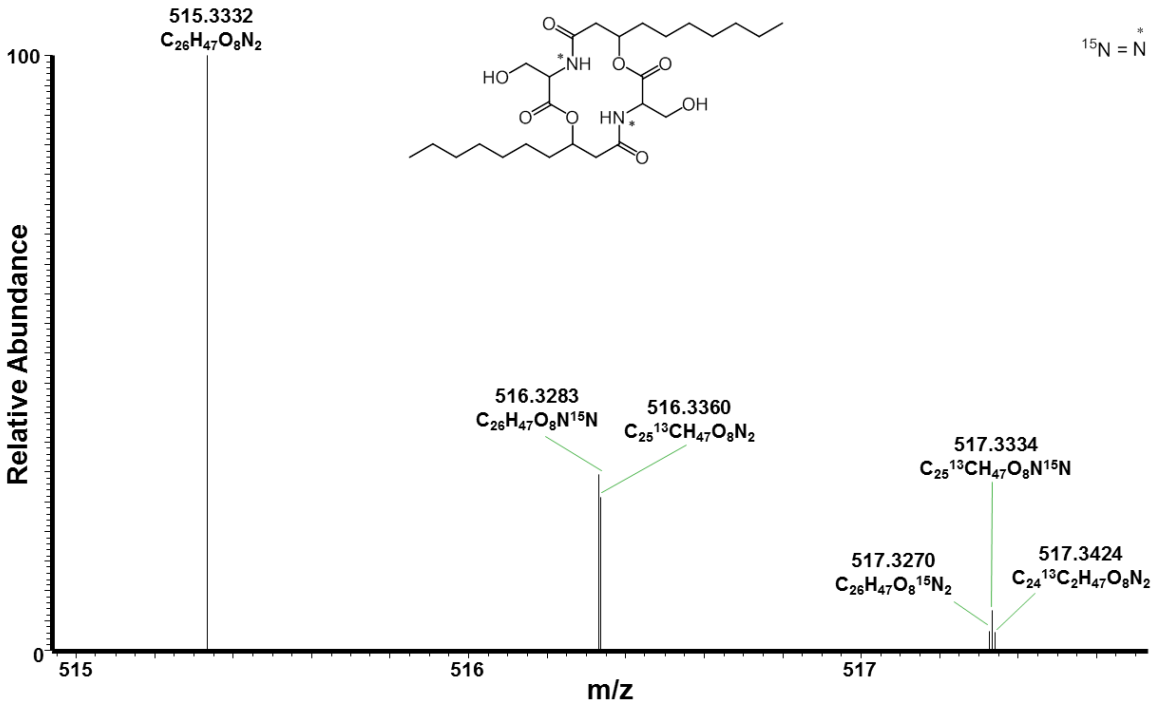


Fig. S183. HRMS of serratamolide C_{10}+C_{11} with incorporated ^{15}N-L-serine from labeled potato dextrose agar (compound **11** $[M+H]^+$: *m/z* 529, $C_{27}H_{49}N_2O_8$).

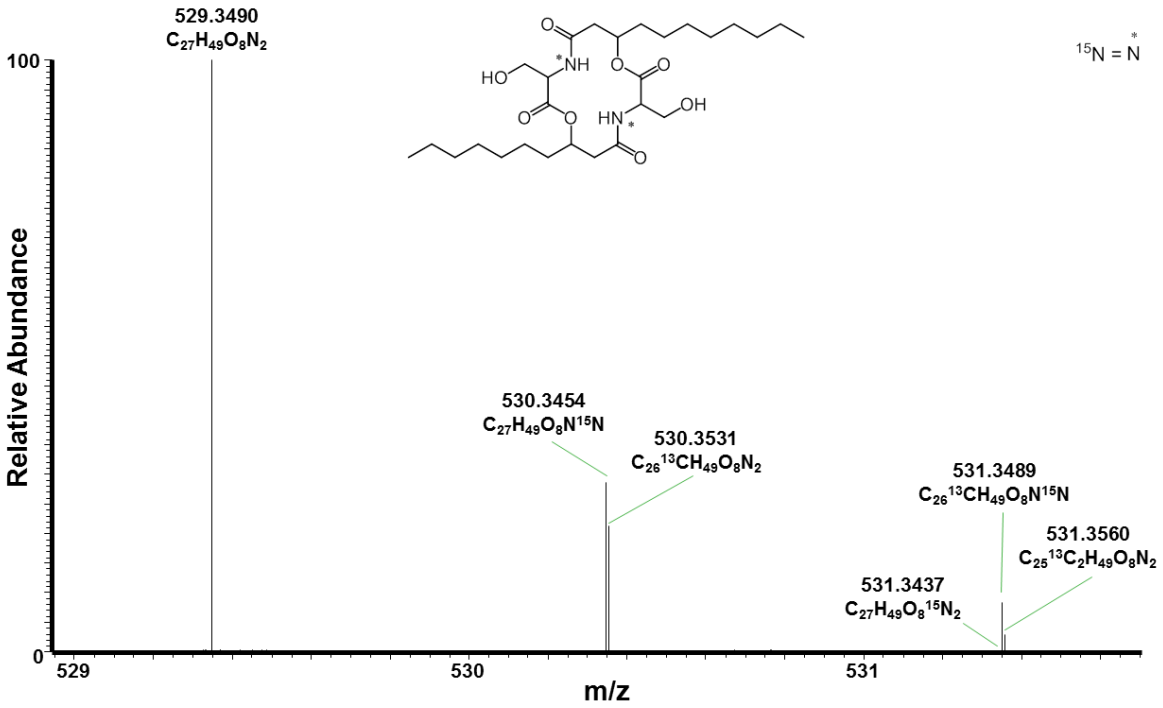


Fig. S184. HRMS of serratamolide C_{10}+C_{12} with incorporated ^{15}N-L-serine from labeled potato dextrose agar (compound **12** $[M+H]^+$: *m/z* 543, $C_{28}H_{51}N_2O_8$).

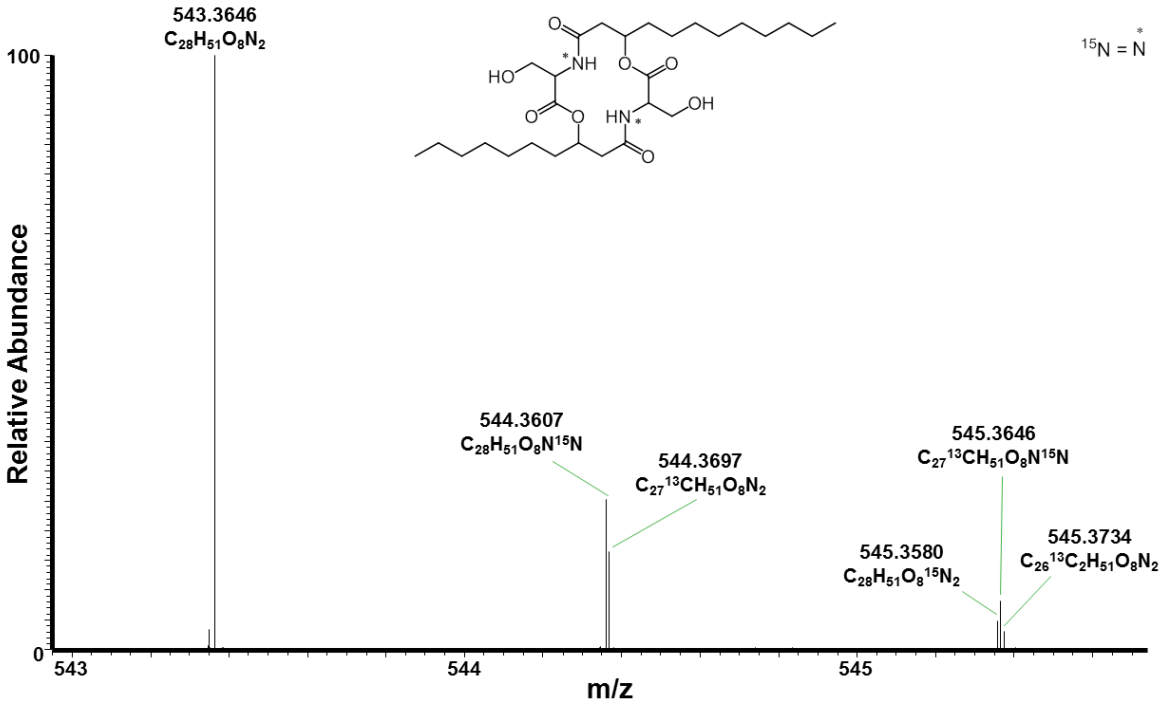


Fig. S185. HRMS of serratamolide C_{11}+C_{12} with incorporated ^{15}N-L-serine from labeled potato dextrose agar (compound **13** $[M+H]^+$: *m/z* 557, $C_{29}H_{53}N_2O_8$).

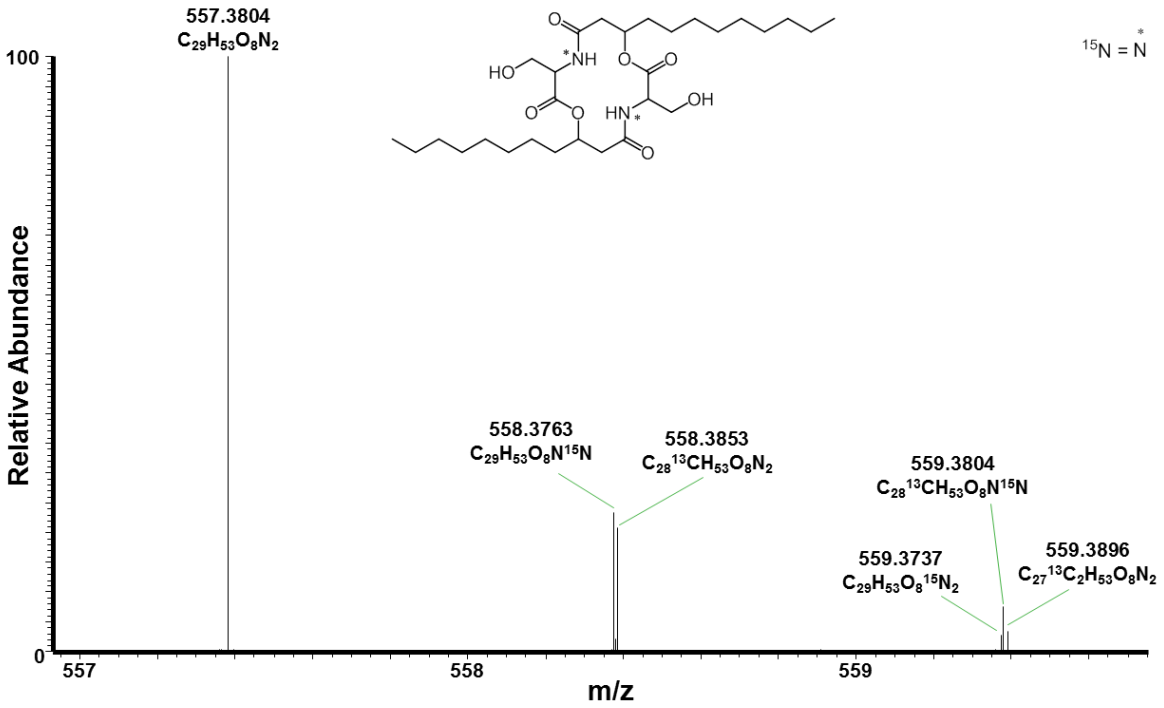


Fig. S186. HRMS of serratamolide C_{12}+C_{12} with incorporated ^{15}N-L-serine from labeled potato dextrose agar (compound **14** $[M+H]^+$: *m/z* 571, $C_{30}H_{55}N_2O_8$).

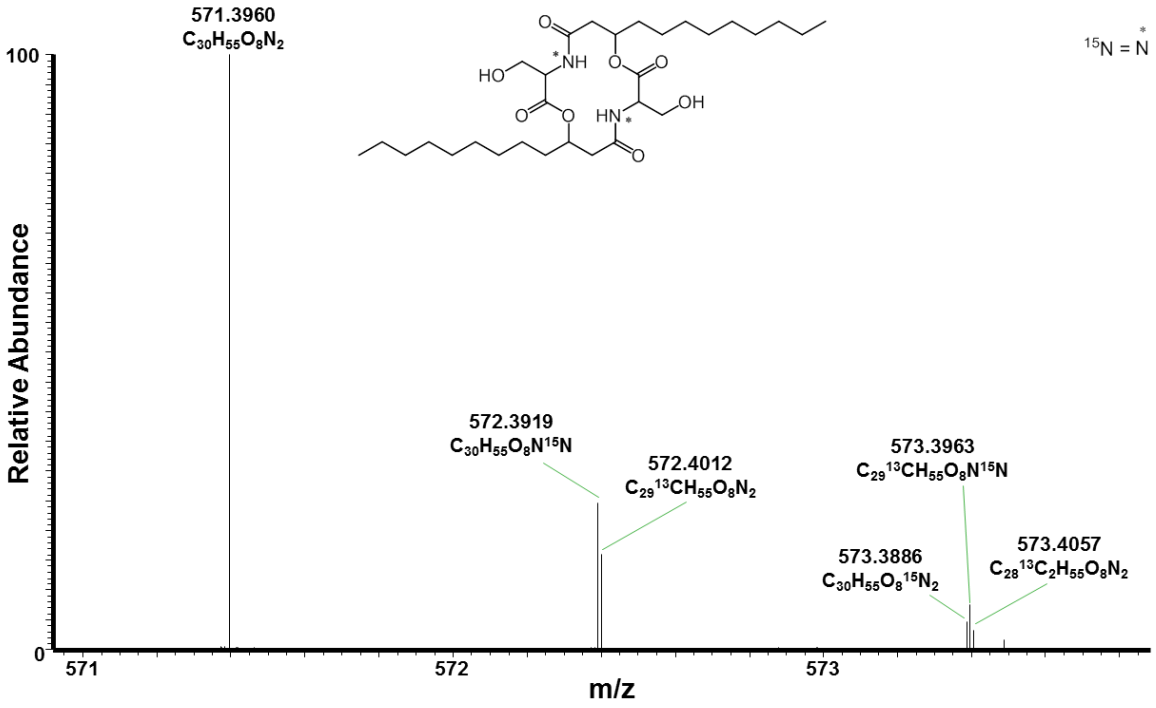


Fig. S187. HRMS of serratamolide C_{10}+$C_{11:1}$ with incorporated ^{15}N-L-serine from labeled potato dextrose agar (compound **15** $[M+H]^+$: *m/z* 527, $C_{27}H_{47}N_2O_8$).

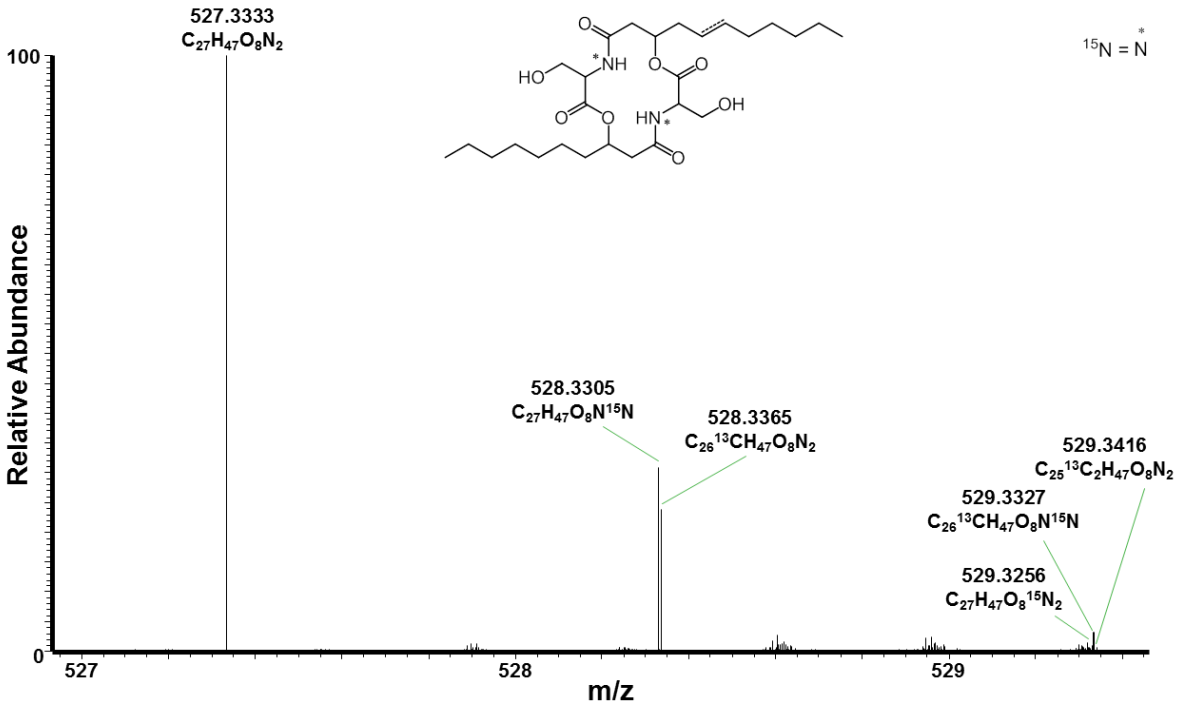


Fig. S188. HRMS of serratamolide C_{10}+$C_{12:1}$ with incorporated ^{15}N-L-serine from labeled potato dextrose agar (compound **16** $[M+H]^+$: *m/z* 541, $C_{28}H_{49}N_2O_8$).

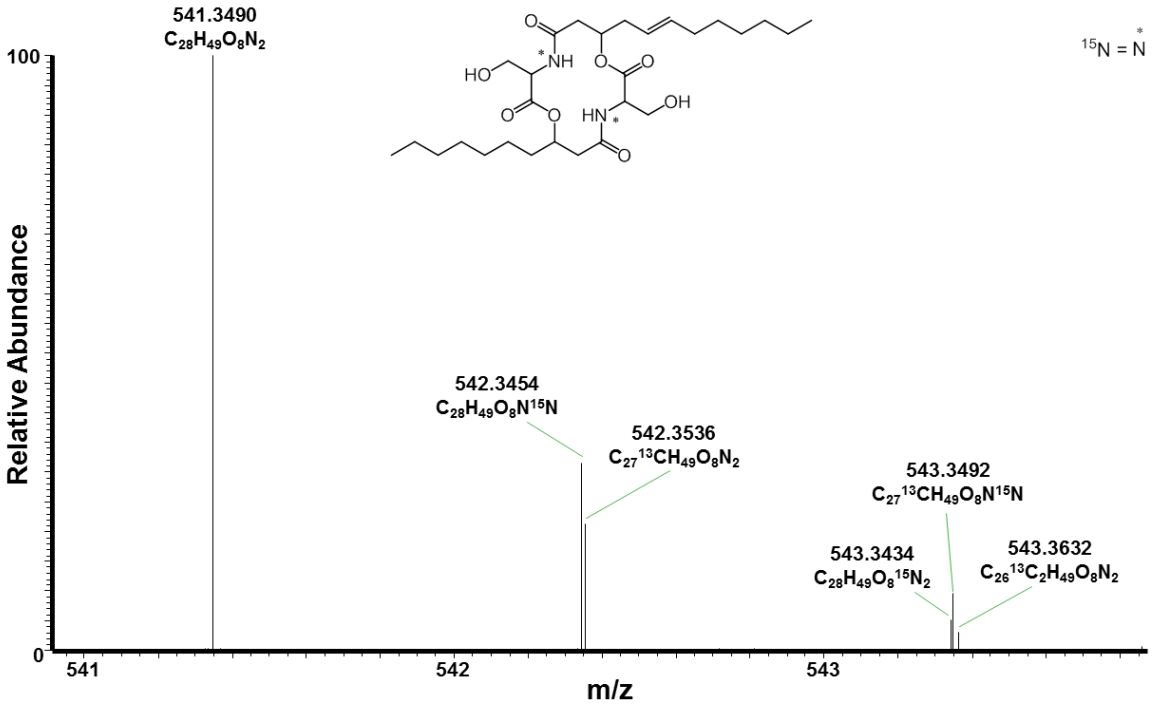


Fig. S189. HRMS of serratamolide C_{11}+$C_{12:1}$ with incorporated ^{15}N-L-serine from labeled potato dextrose agar (compound **17** $[M+H]^+$: *m/z* 555, $C_{29}H_{51}N_2O_8$).

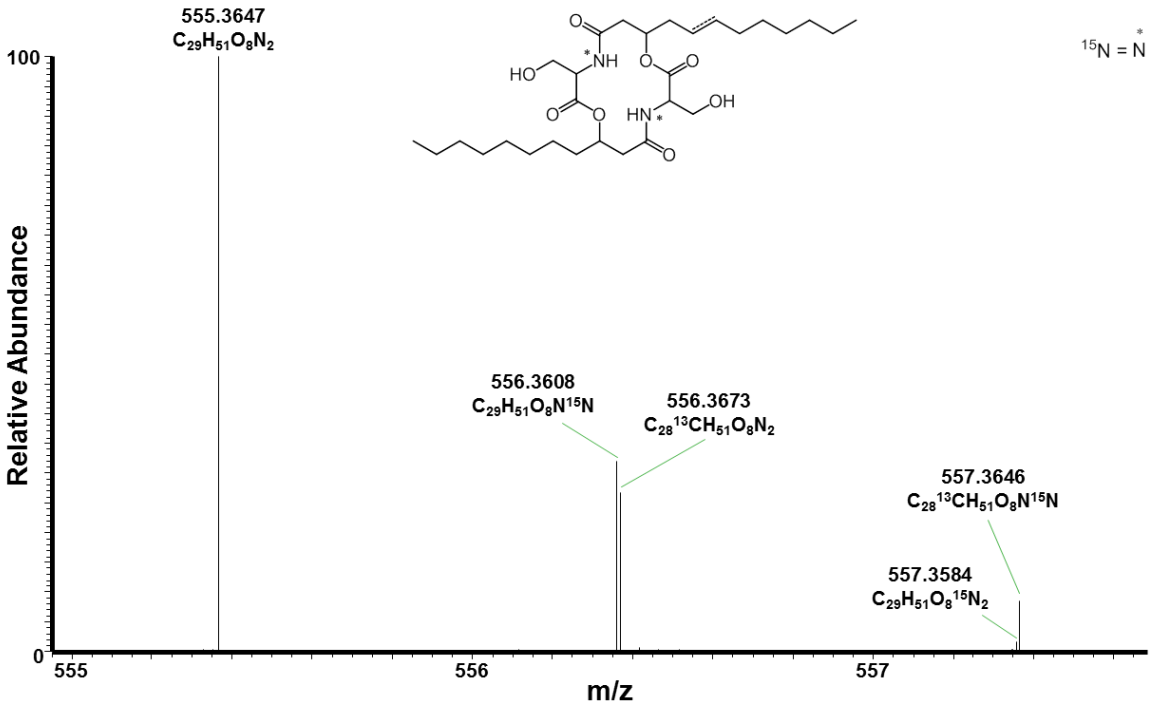


Fig. S190. HRMS of serratamolide C_{12}+$C_{12:1}$ with incorporated ^{15}N-L-serine from labeled potato dextrose agar (compound **18** $[M+H]^+$: *m/z* 569, $C_{30}H_{53}N_2O_8$).

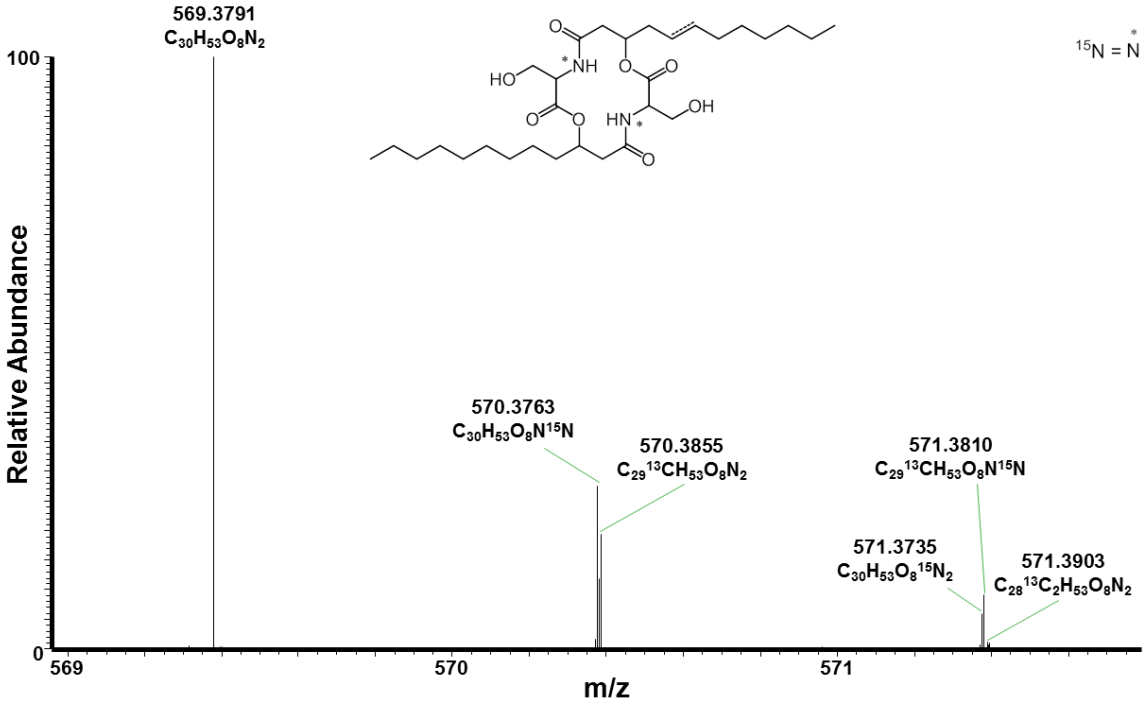


Fig. S191. HRMS of ring-opened serratamolide C_{10}+C_{10} with incorporated ^{15}N-L-serine from labeled potato dextrose agar (compound **19** $[M+H]^+$: *m/z* 533, $C_{26}H_{49}N_2O_9$).

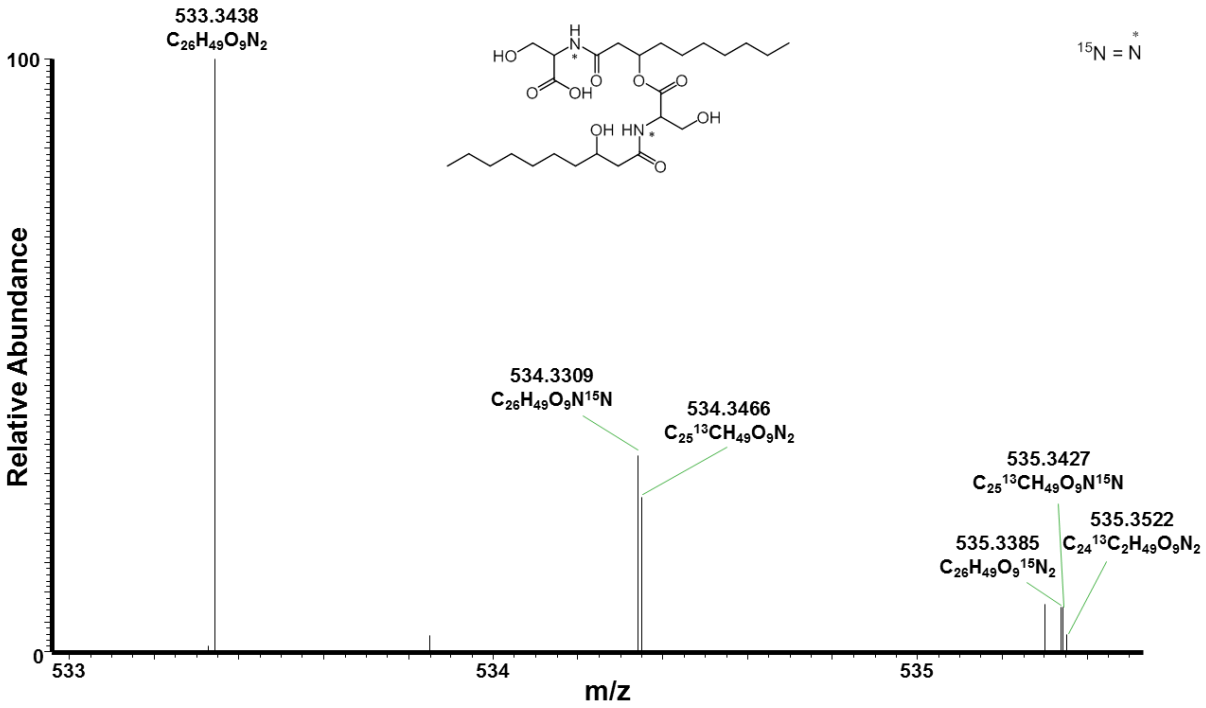


Fig. S192. HRMS of ring-opened serratamolide C_{10}+C_{11} with incorporated ^{15}N-L-serine from labeled potato dextrose agar (compound **20** $[M+H]^+$: *m/z* 547, $C_{27}H_{51}N_2O_9$).

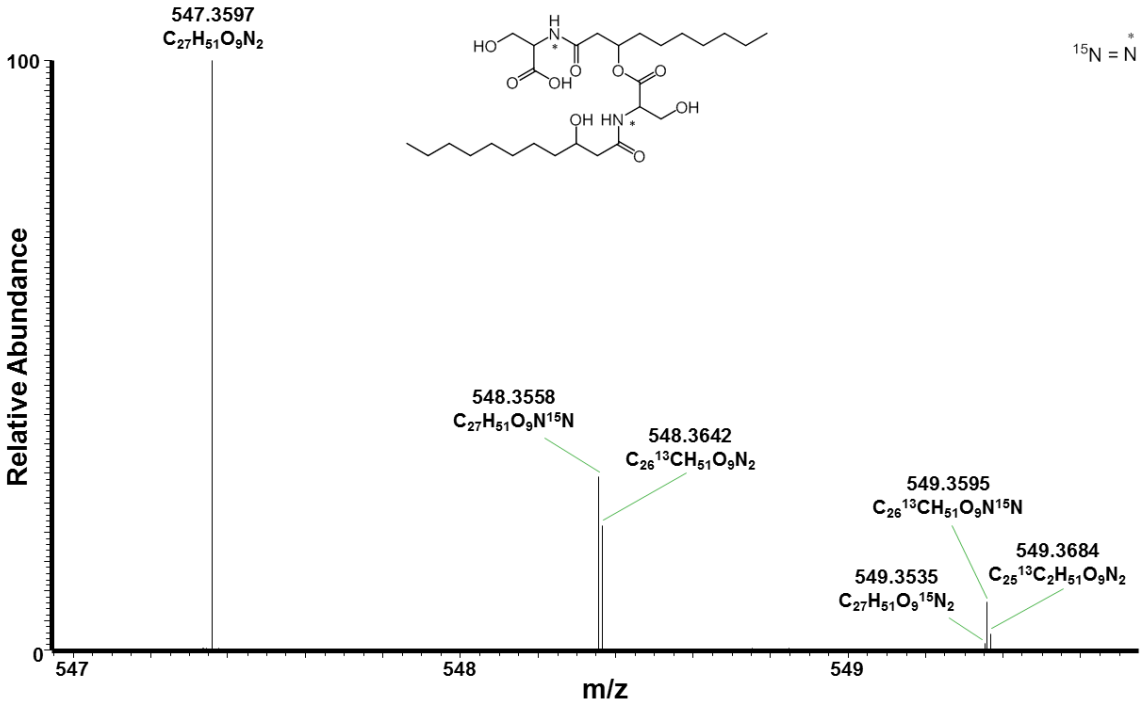


Fig. S193. HRMS of ring-opened serratamolide C_{10}+C_{12} with incorporated ^{15}N-L-serine from labeled potato dextrose agar (compound **21** $[M+H]^+$: *m/z* 561, $C_{28}H_{53}N_2O_9$).

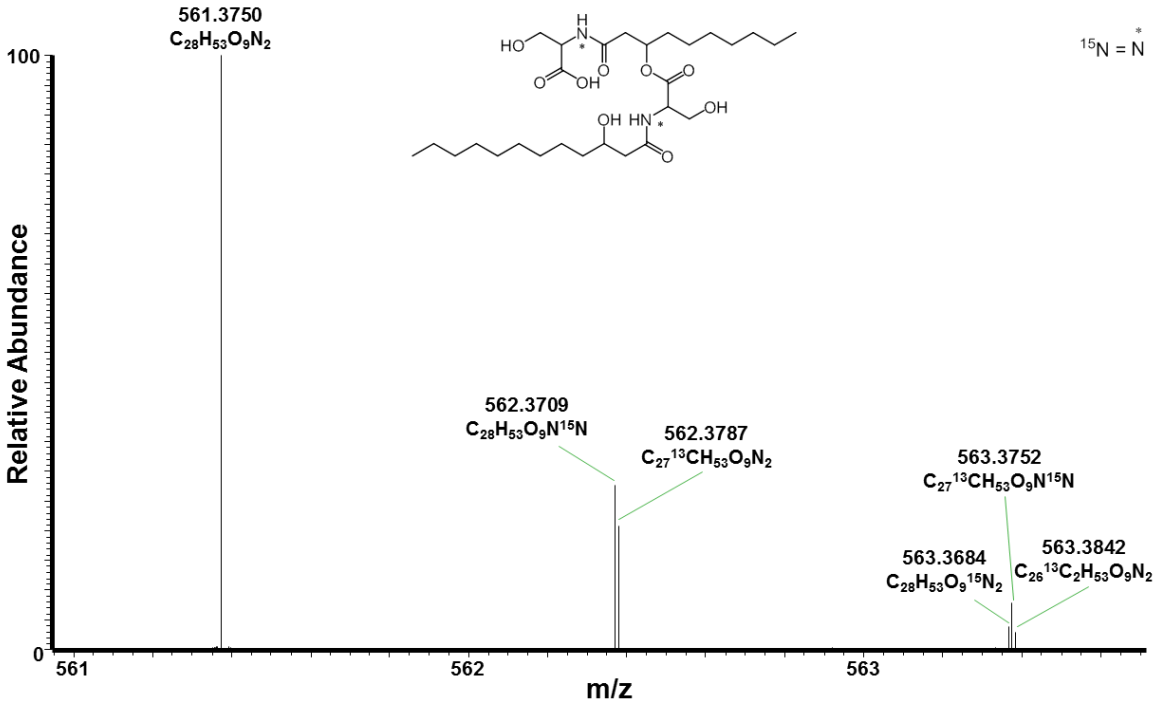


Fig. S194. HRMS of ring-opened serratamolide C_{10}+$C_{12:1}$ with incorporated ^{15}N-L-serine from labeled potato dextrose agar (compound **22** $[M+H]^+$: *m/z* 559, $C_{28}H_{51}N_2O_9$).

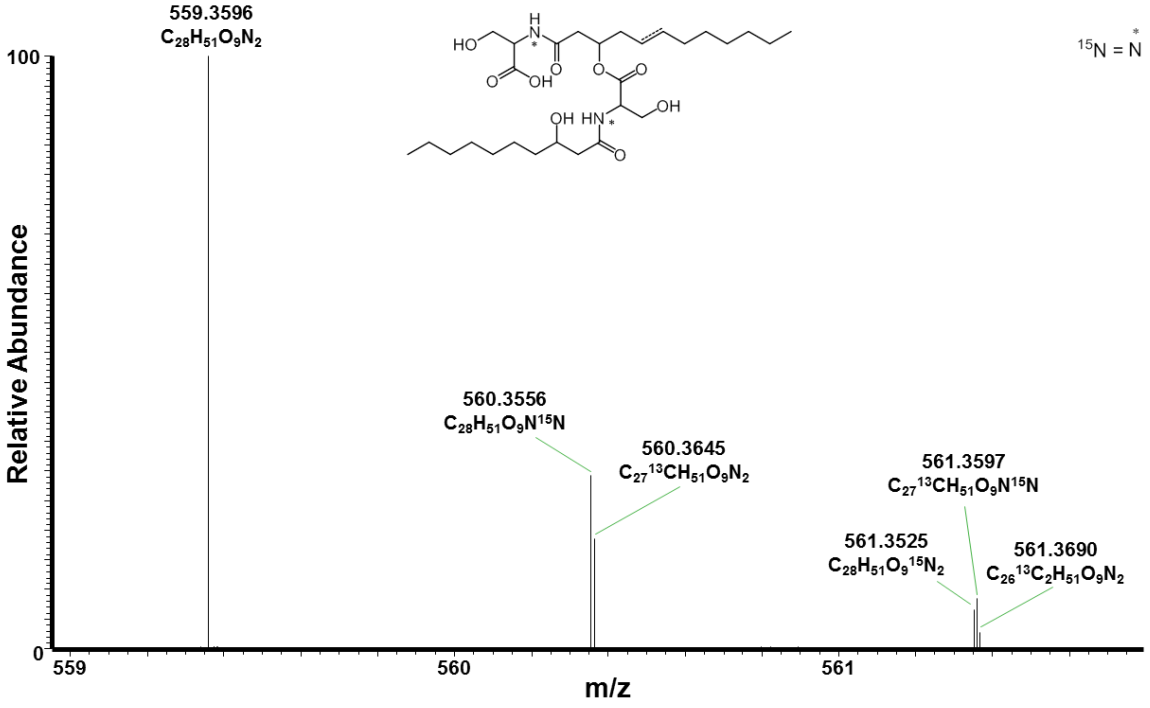


Fig. S195. HRMS^2 of ring-opened serratamolide C_{10}+C_{13} with incorporated ^{15}N-L-serine from labeled potato dextrose agar (compound **23** $[M+H]^+$: *m/z* 575, $C_{29}H_{55}N_2O_9$).

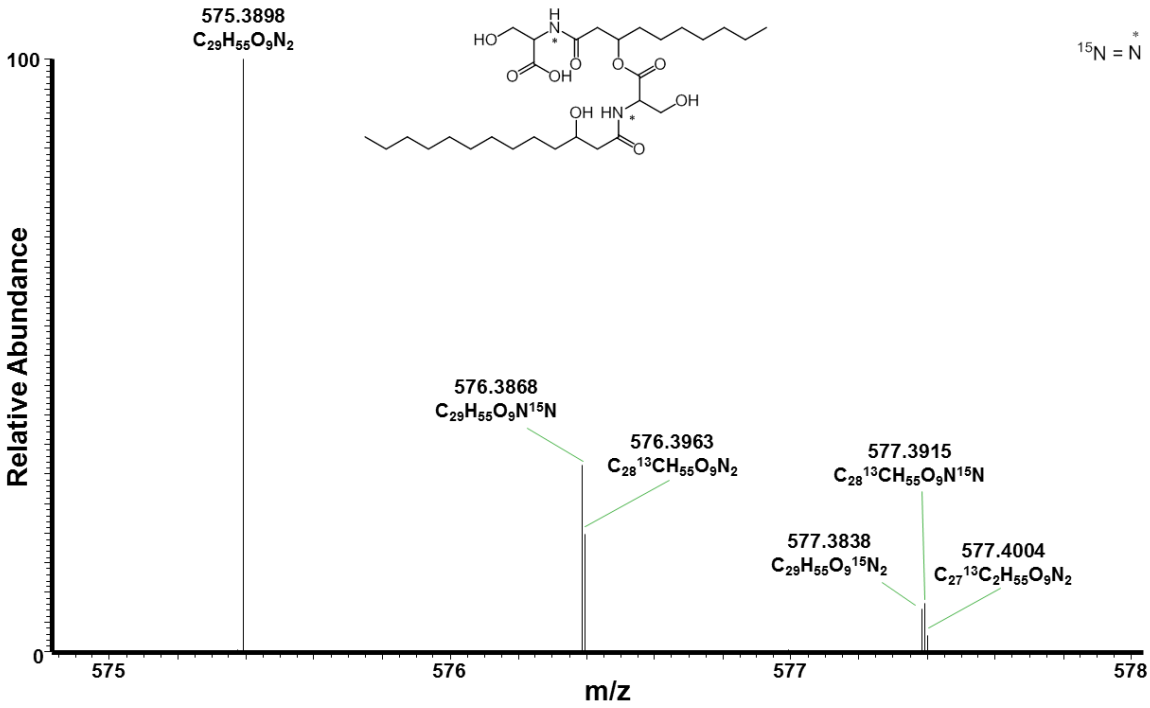


Fig. S196. HRMS of ring-opened serratamolide C_{12}+C_{12} with incorporated ^{15}N-L-serine from labeled potato dextrose agar (compound **24** $[M+H]^+$: *m/z* 589, $C_{30}H_{57}N_2O_9$).

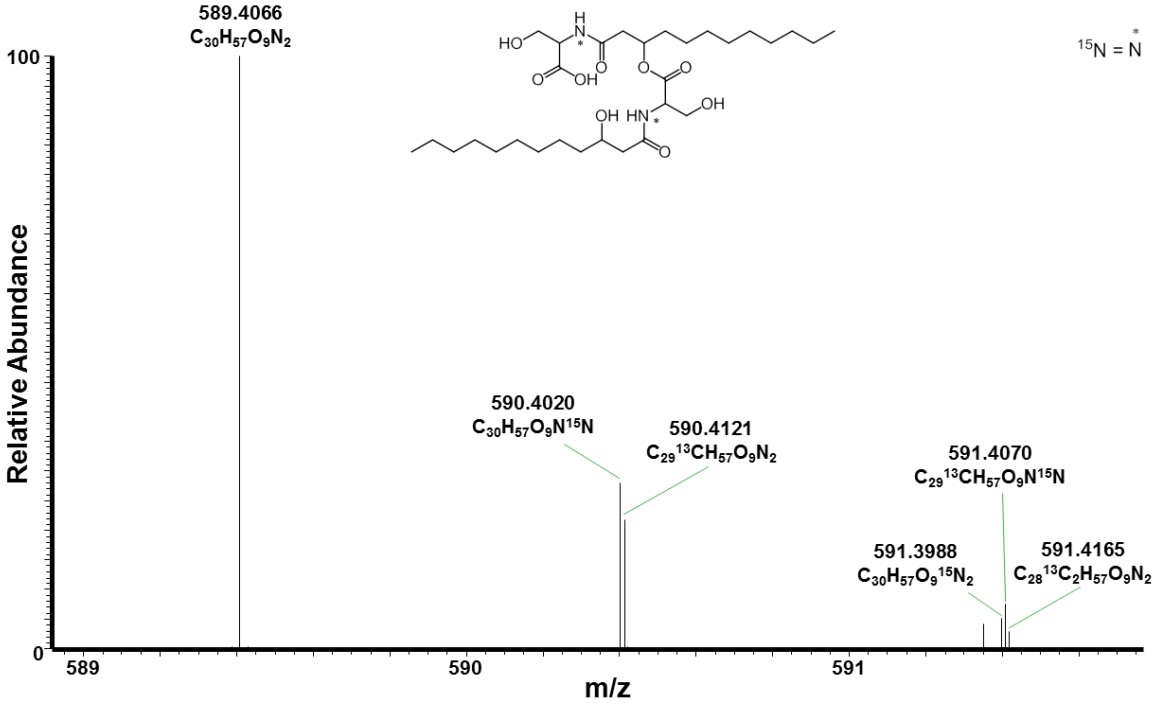


Fig. S197. HRMS of ring-opened serratamolide C_{12}+C_{13} with incorporated ^{15}N-L-serine from labeled potato dextrose agar (compound **25** $[M+H]^+$: *m/z* 603, $C_{31}H_{59}N_2O_9$).

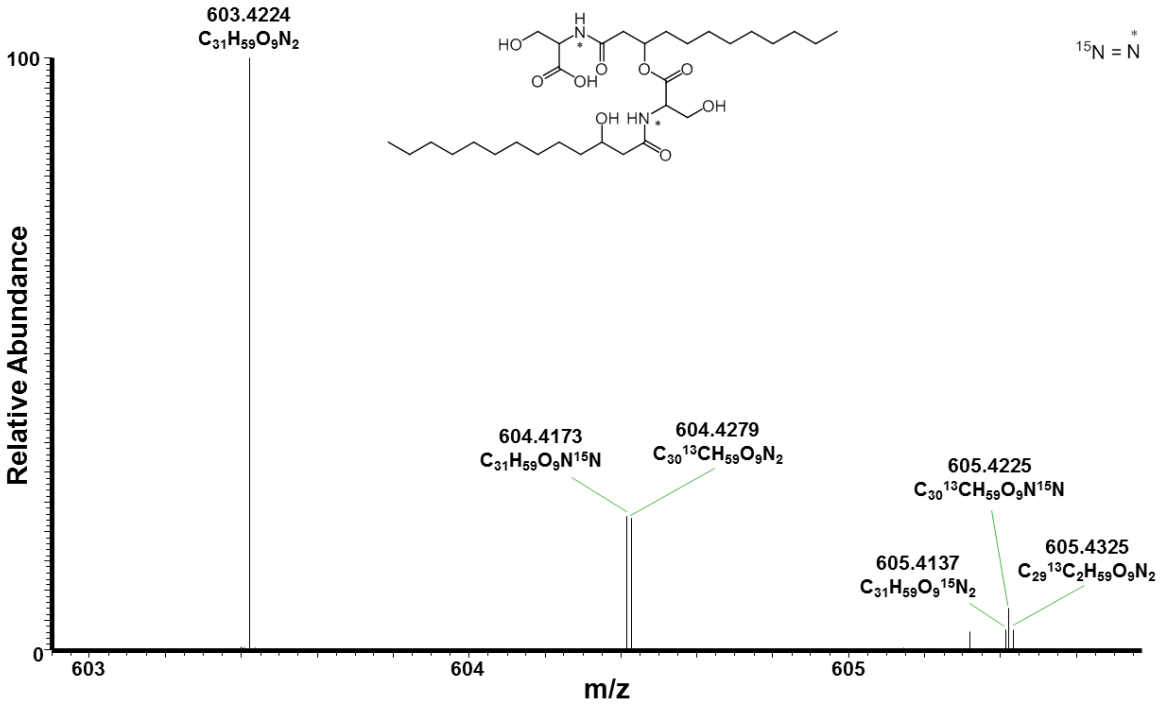


Fig. S198. HRMS of ring-opened serratamolide C_{10}+$C_{13:1}$ with incorporated ^{15}N-L-serine from labeled potato dextrose agar (compound **26** $[M+H]^+$: *m/z* 573, $C_{29}H_{53}N_2O_9$).

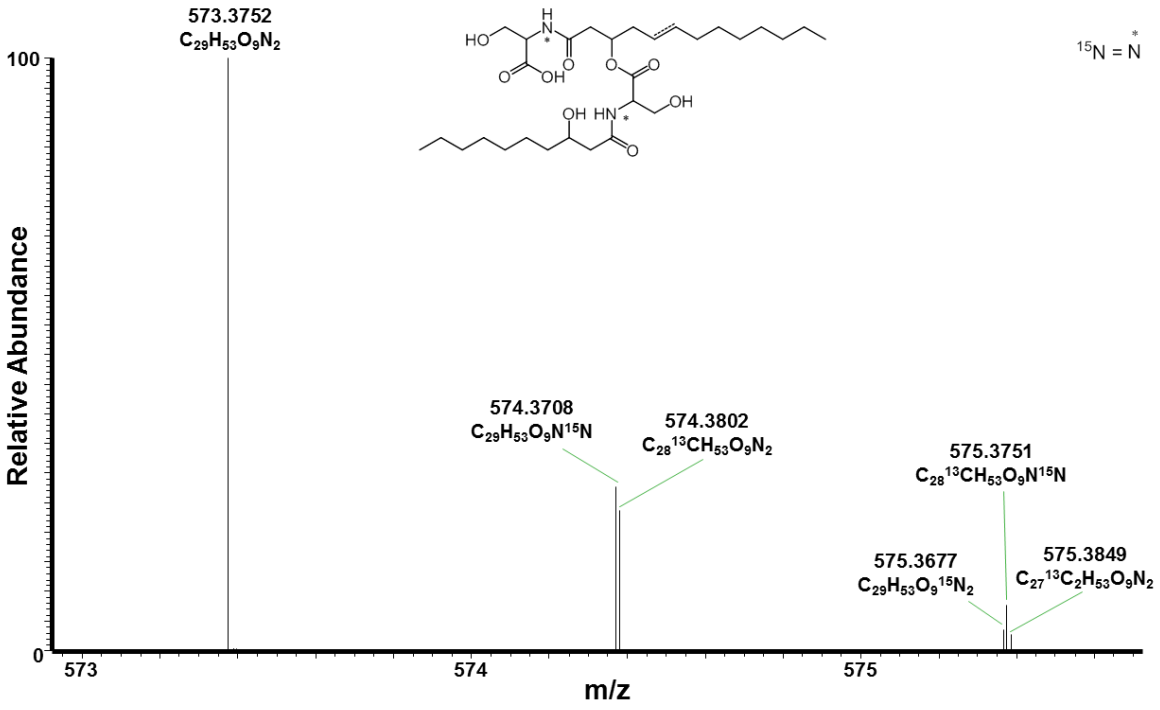


Fig. S199. HRMS of ring-opened serratamolide C_{12}+$C_{12:1}$ with incorporated ^{15}N-L-serine from labeled potato dextrose agar (compound **27** $[M+H]^+$: *m/z* 587, $C_{30}H_{55}N_2O_9$).

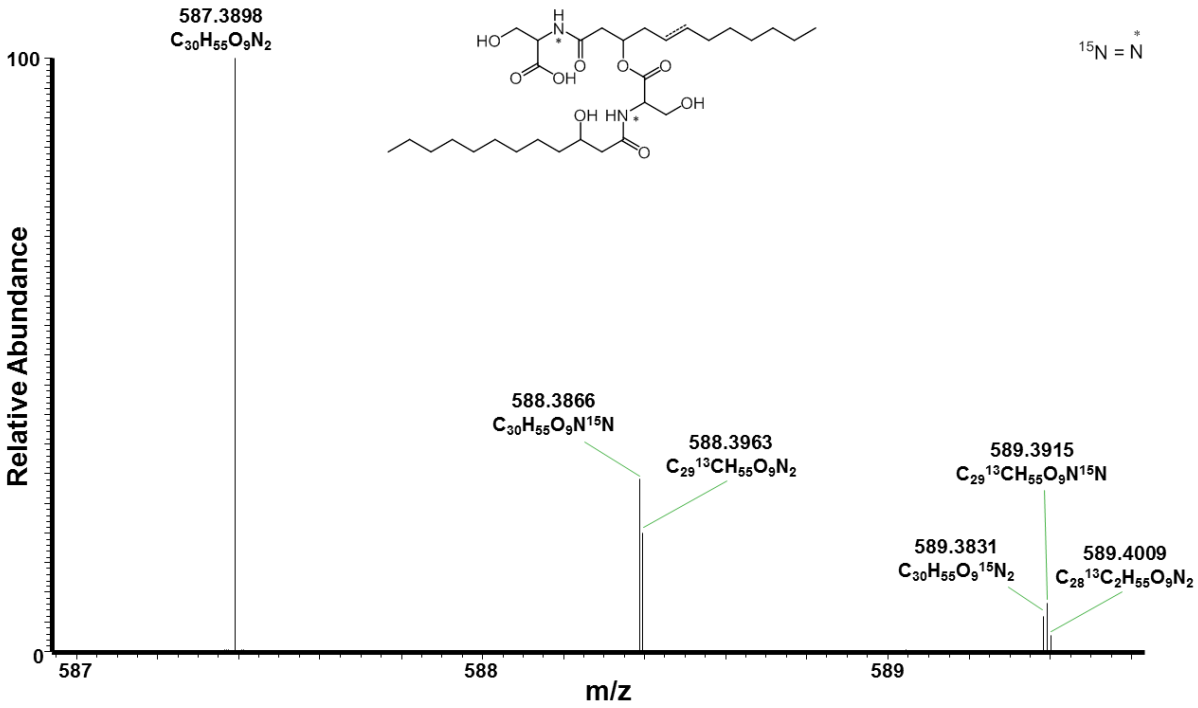


Fig. S200. HRMS of ring-opened serratamolide C_{13}+$C_{12:1}$ with incorporated ^{15}N-L-serine from labeled potato dextrose agar (compound **28** $[M+H]^+$: *m/z* 601, $C_{31}H_{57}N_2O_9$).

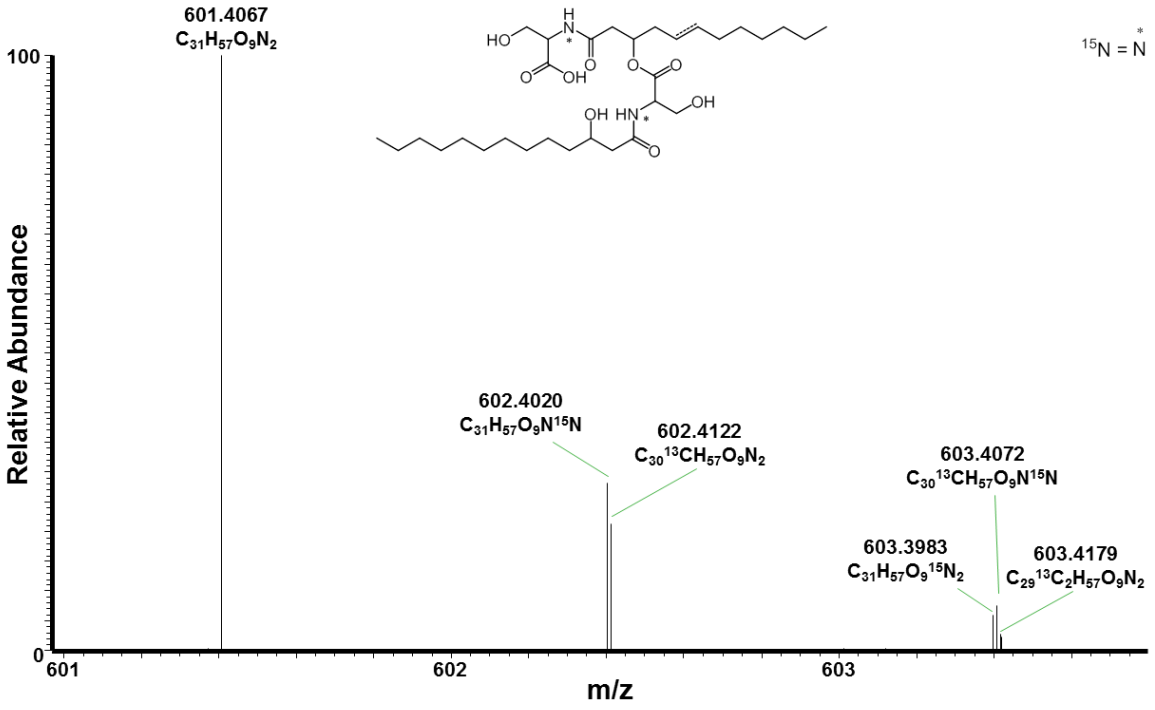


Fig. S201. HRMS of serratamic acid with incorporated ^{15}N-L-serine from labeled potato dextrose agar (N-(D-3-hydroxydecanoyl)-L-serine, compound **29** $[M+H]^+$: *m/z* 276, $C_{13}H_{26}NO_5$).

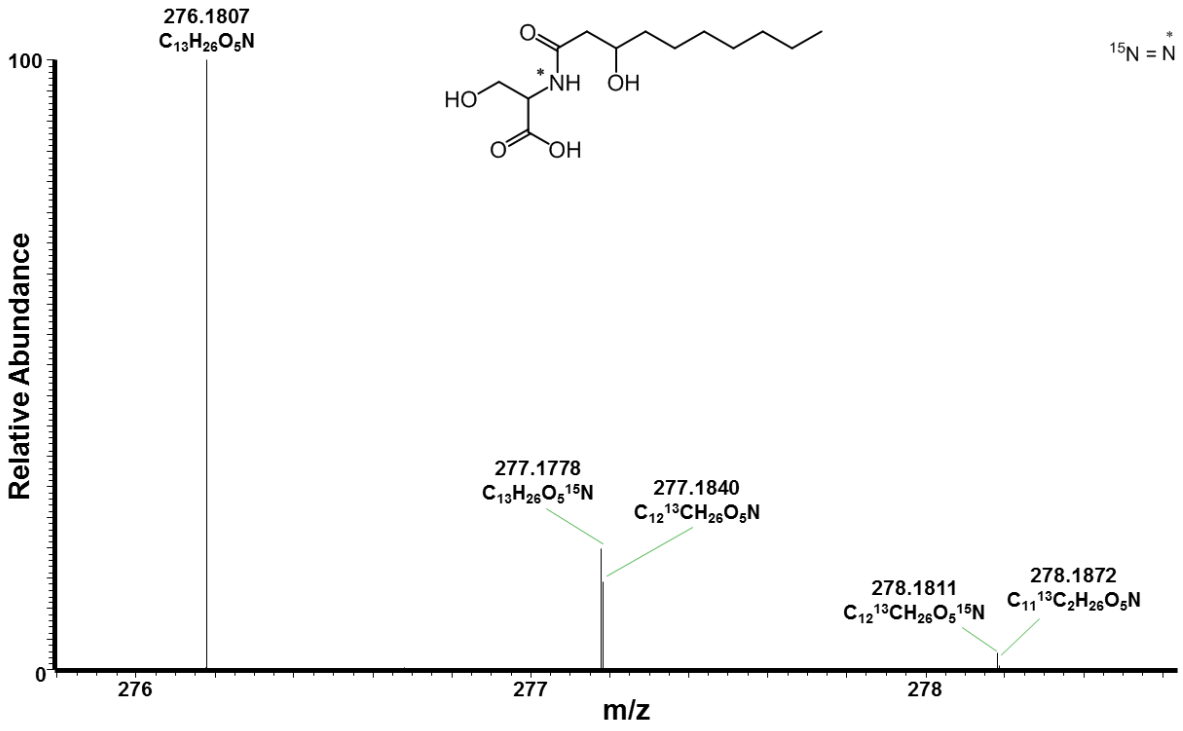


Fig. S202. HRMS of serratamic acid derivative with incorporated ^{15}N-L-serine from labeled potato dextrose agar (hydroxydodecanoyl-serine, compound **30** $[M+H]^+$: *m/z* 304, $C_{15}H_{30}NO_5$).

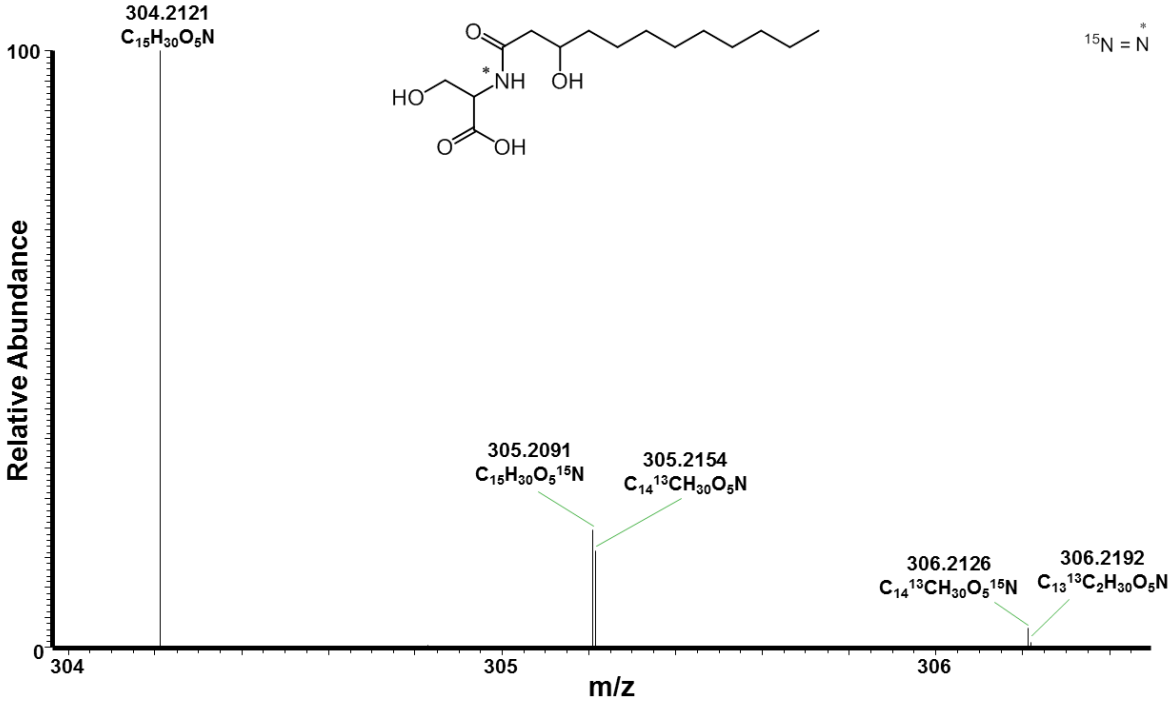


Fig. S203. HRMS of serratamic acid derivative with double bond with incorporated ^{15}N-L-serine from labeled potato dextrose agar (hydroxydodecenoyl-serine, compound **31** $[M+H]^+$: *m/z* 302, $C_{15}H_{28}NO_5$).

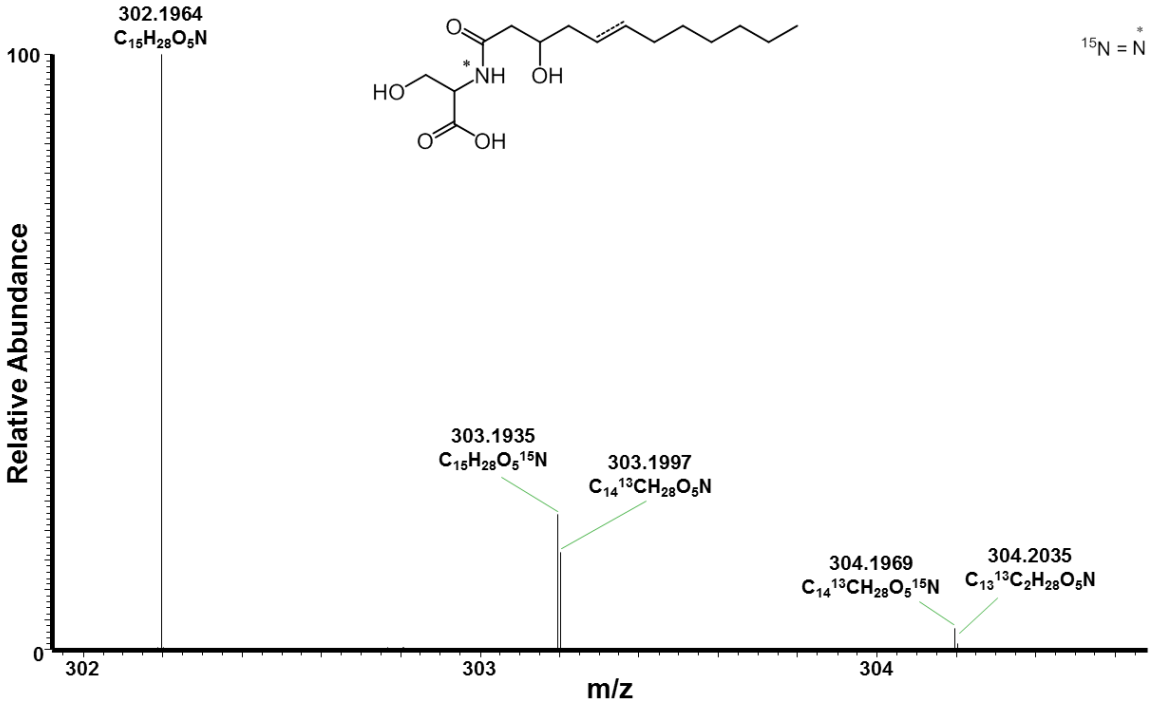


Fig. S204. HRMS of serrawettin W1 / serratamolide C_{10}+C_{10} with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (compound **10** $[M+H]^+$: *m/z* 515, $C_{26}H_{47}N_2O_8$).

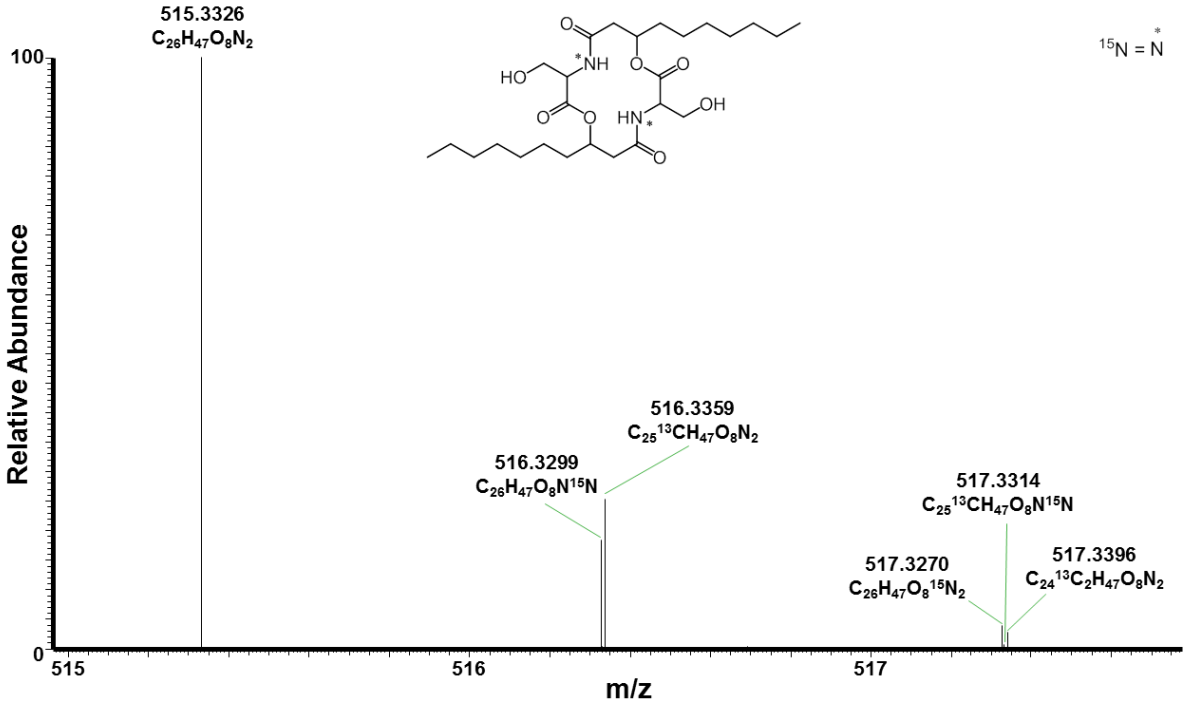


Fig. S205. HRMS of serratamolide C_{10}+C_{11} with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (compound **11** $[M+H]^+$: *m/z* 529, $C_{27}H_{49}N_2O_8$).

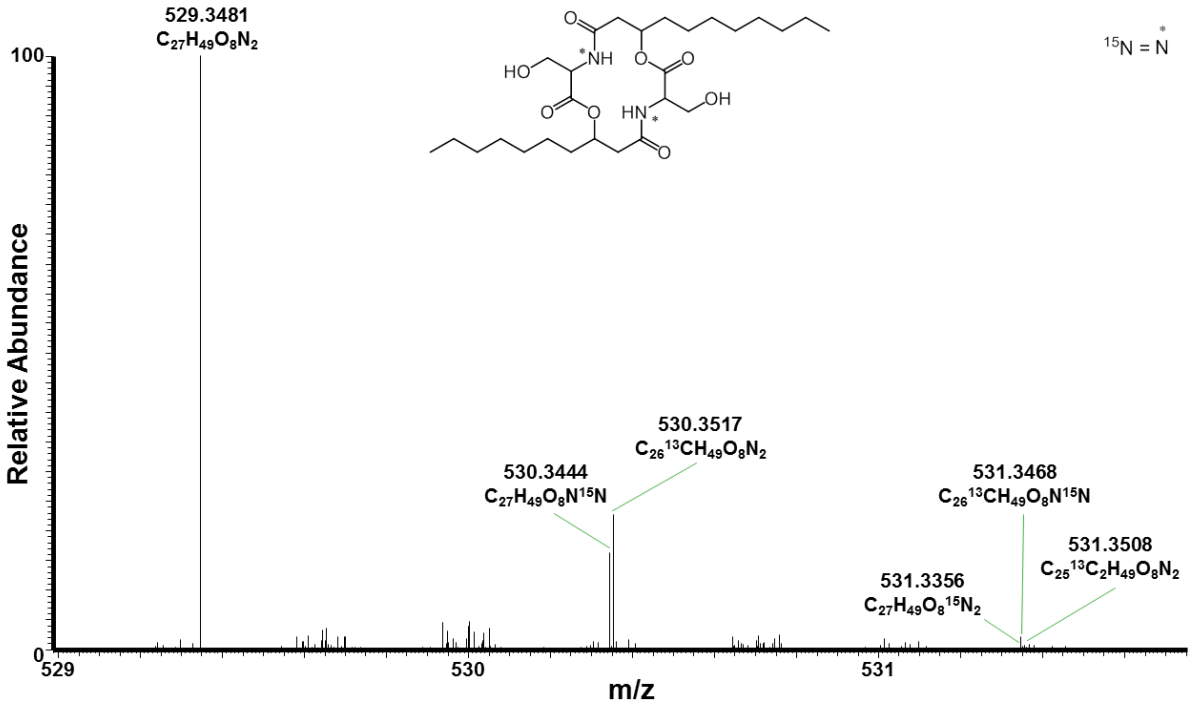


Fig. S206. HRMS of serratamolide C_{10}+C_{12} with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (compound **12** $[M+H]^+$: *m/z* 543, $C_{28}H_{51}N_2O_8$).

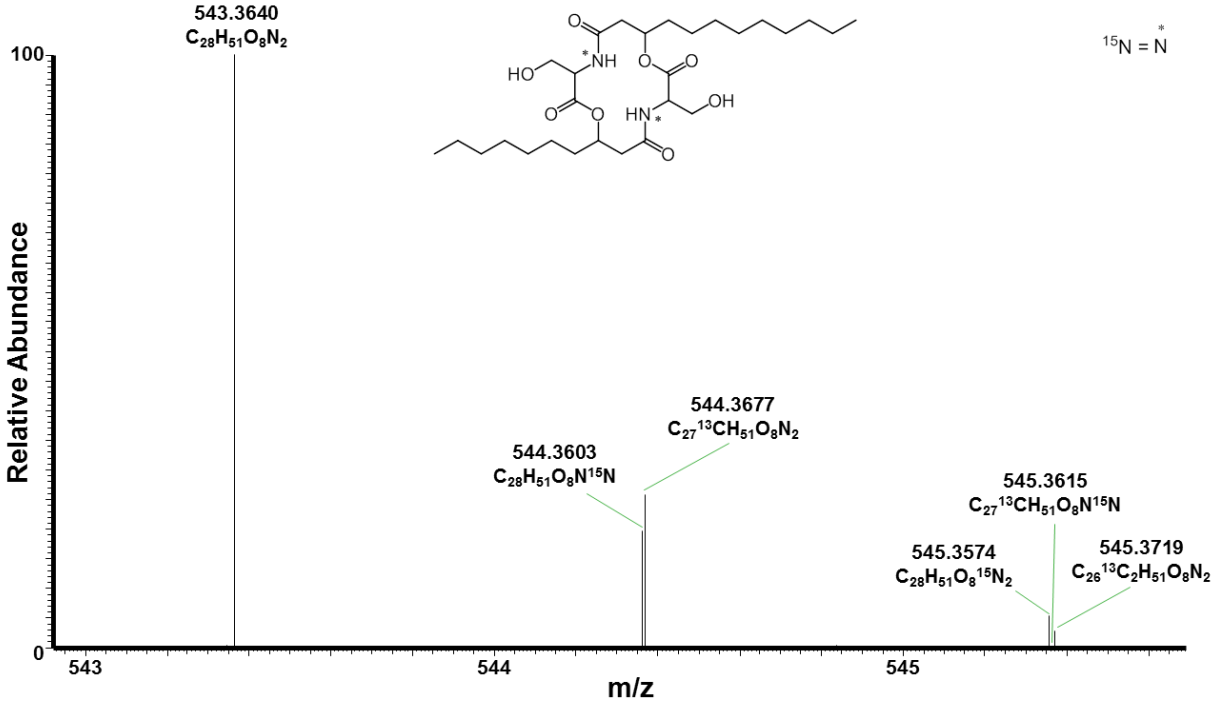


Fig. S207. HRMS of serratamolide C_{11}+C_{12} with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (compound **13** $[M+H]^+$: *m/z* 557, $C_{29}H_{53}N_2O_8$).

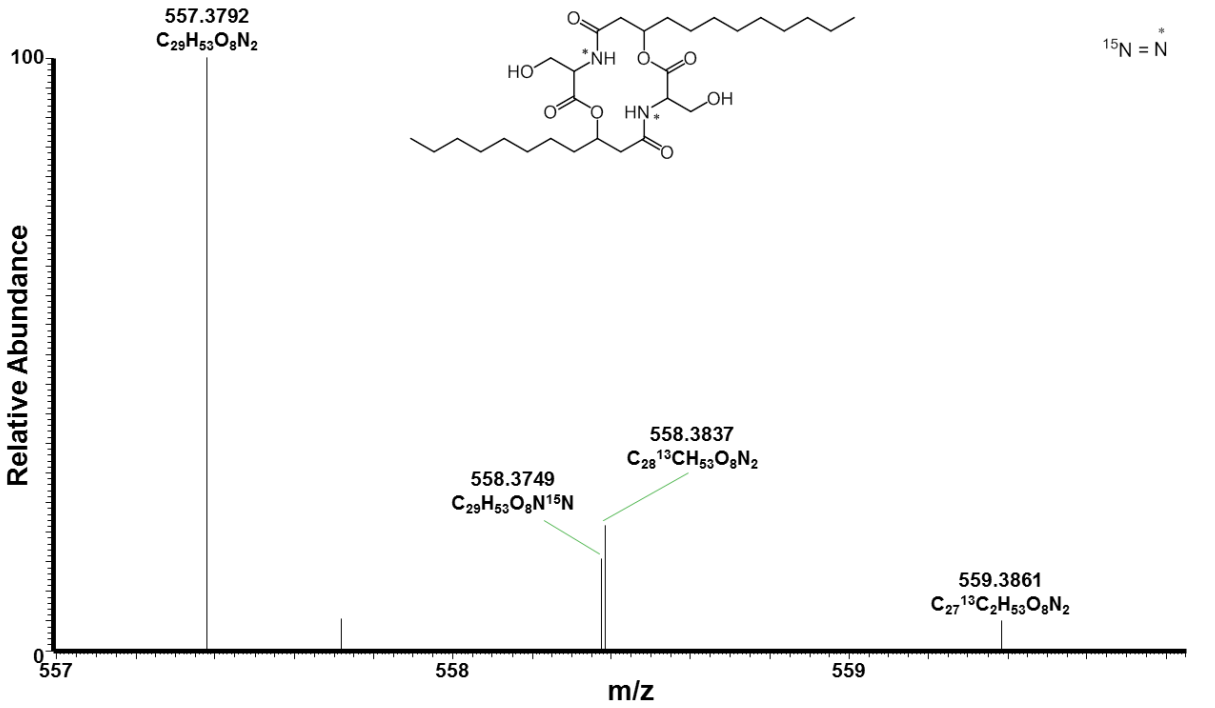


Fig. S208. HRMS of serratamolide C_{12}+C_{12} with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (compound **14** $[M+H]^+$: *m/z* 571, $C_{30}H_{55}N_2O_8$).

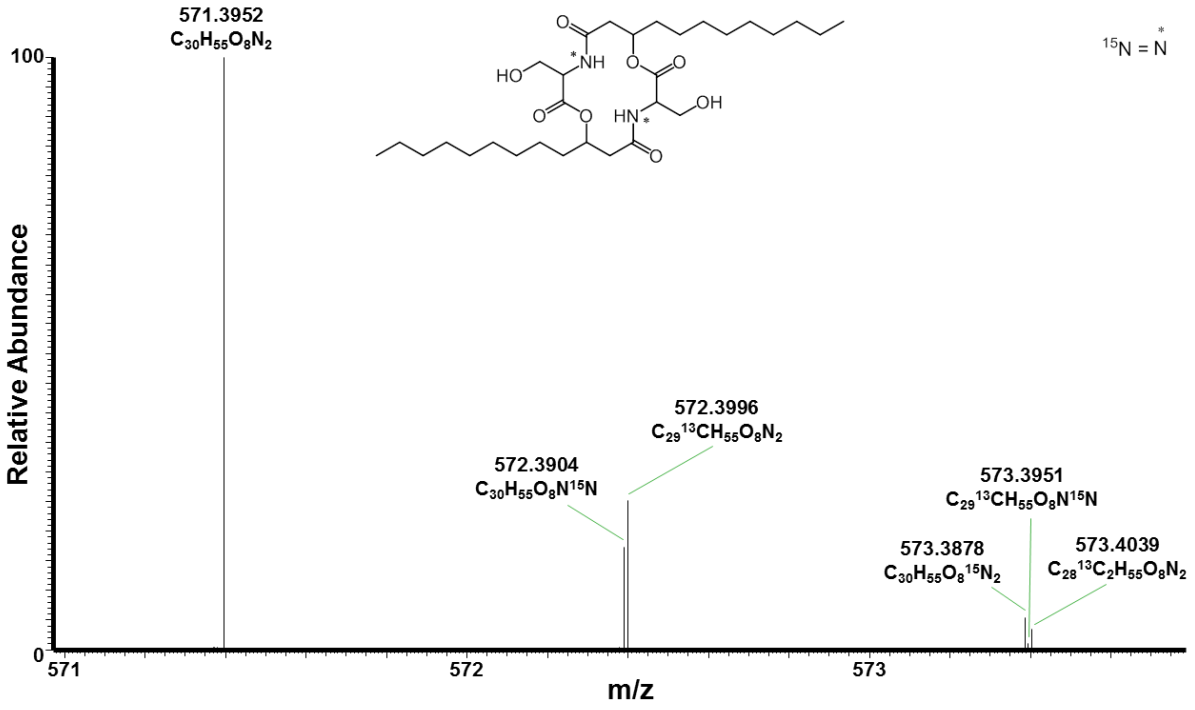


Fig. S209. HRMS of serratamolide C_{10}+$C_{12:1}$ with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (compound **16** $[M+H]^+$: *m/z* 541, $C_{28}H_{49}N_2O_8$).

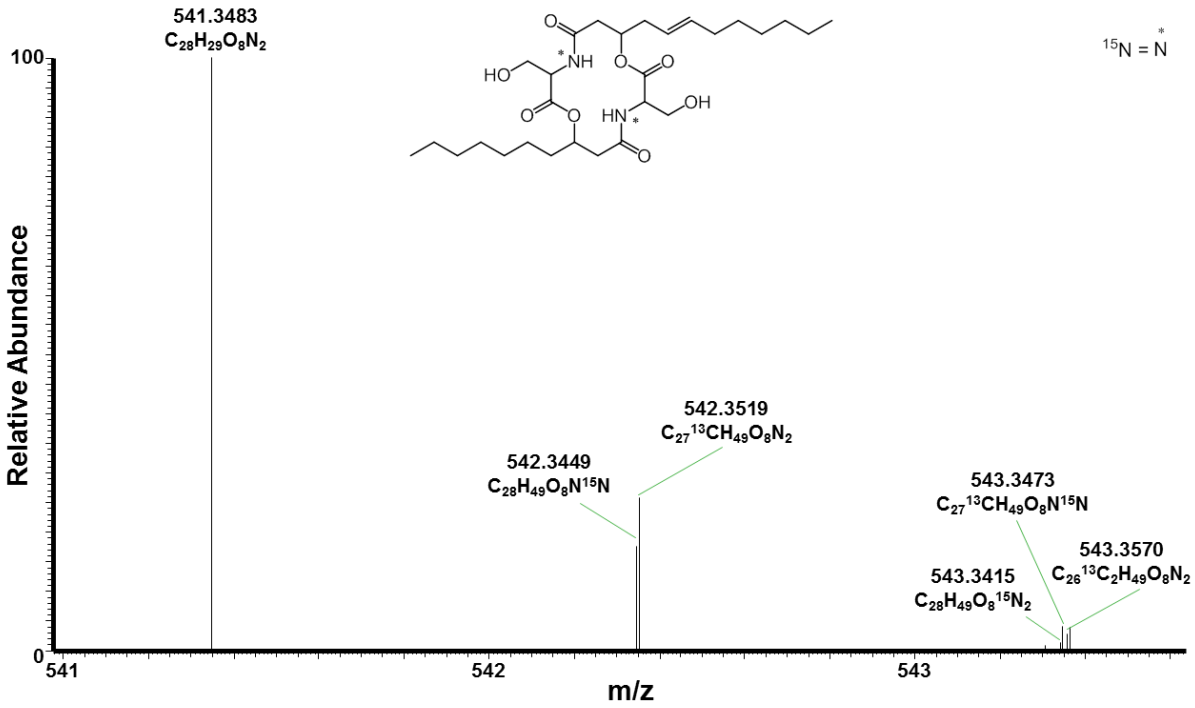


Fig. S210. HRMS of serratamolide C_{12}+$C_{12:1}$ with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (compound **18** $[M+H]^+$: *m/z* 569, $C_{30}H_{53}N_2O_8$).

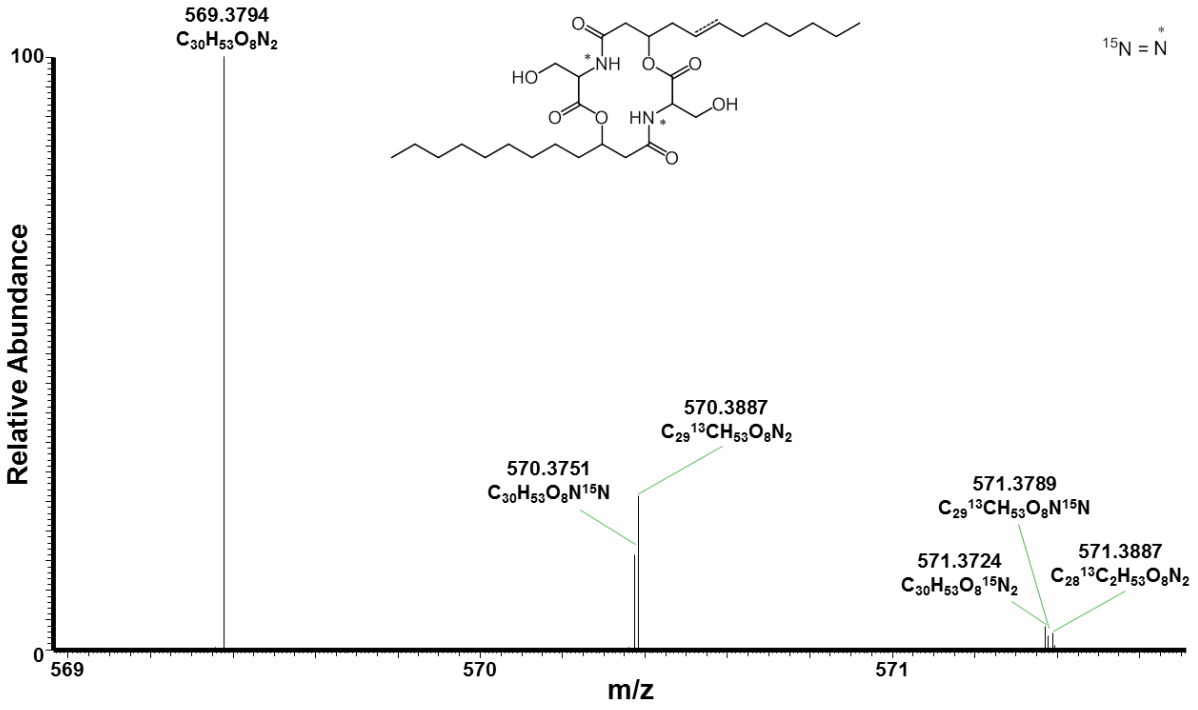


Fig. S211. HRMS of ring-opened serratamolide C_{10}+C_{10} with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (compound **19** $[M+H]^+$: *m/z* 533, $C_{26}H_{49}N_2O_9$).

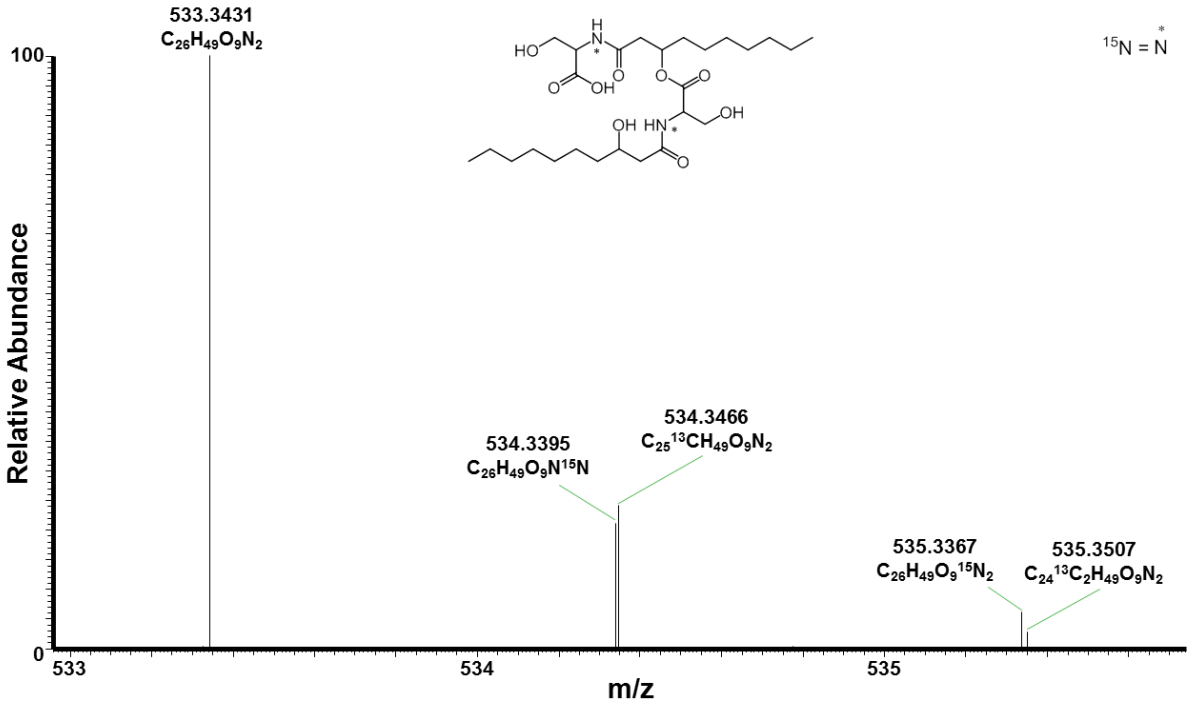


Fig. S212. HRMS of ring-opened serratamolide C_{10}+C_{12} with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (compound **21** $[M+H]^+$: *m/z* 561, $C_{28}H_{53}N_2O_9$).

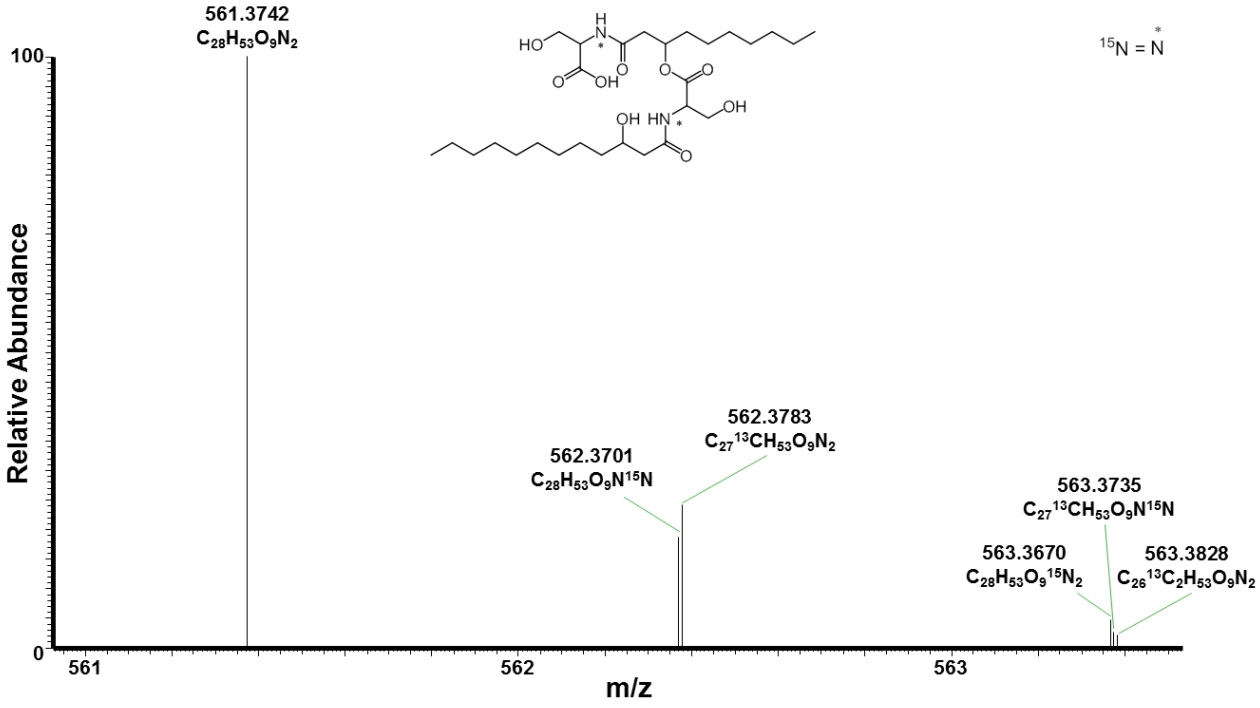


Fig. S213. HRMS of ring-opened serratamolide C_{10}+$C_{12:1}$ with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (compound **22** $[M+H]^+$: *m/z* 559, $C_{28}H_{51}N_2O_9$).

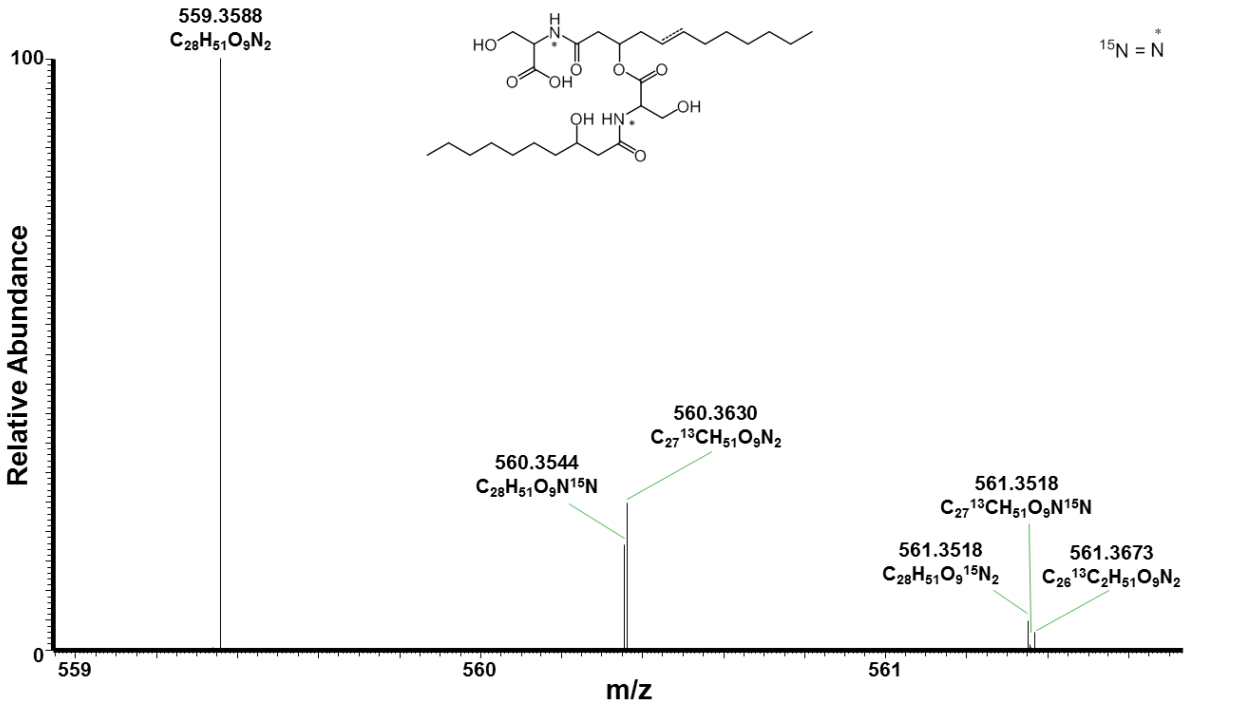


Fig. S214. HRMS of ring-opened serratamolide C_{12}+C_{12} with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (compound **24** $[M+H]^+$: *m/z* 589, $C_{30}H_{57}N_2O_9$).

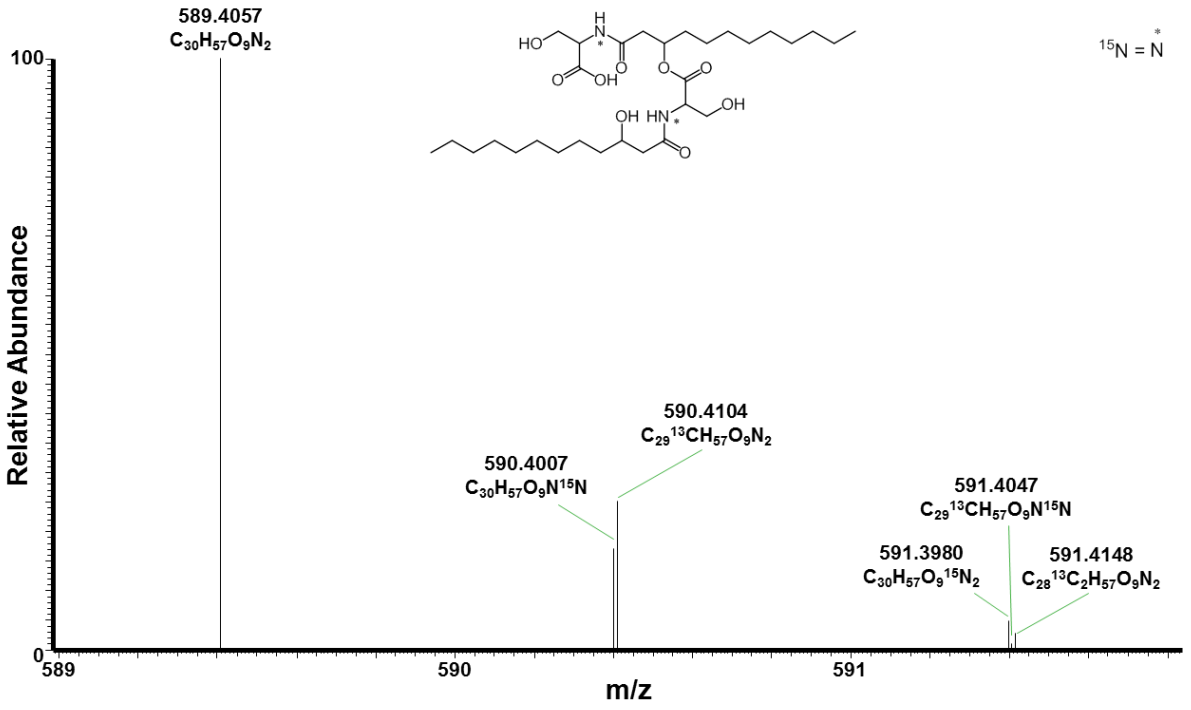


Fig. S215. HRMS of ring-opened serratamolide C_{12}+$C_{12:1}$ with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (compound **27** $[M+H]^+$: *m/z* 587, $C_{30}H_{55}N_2O_9$).

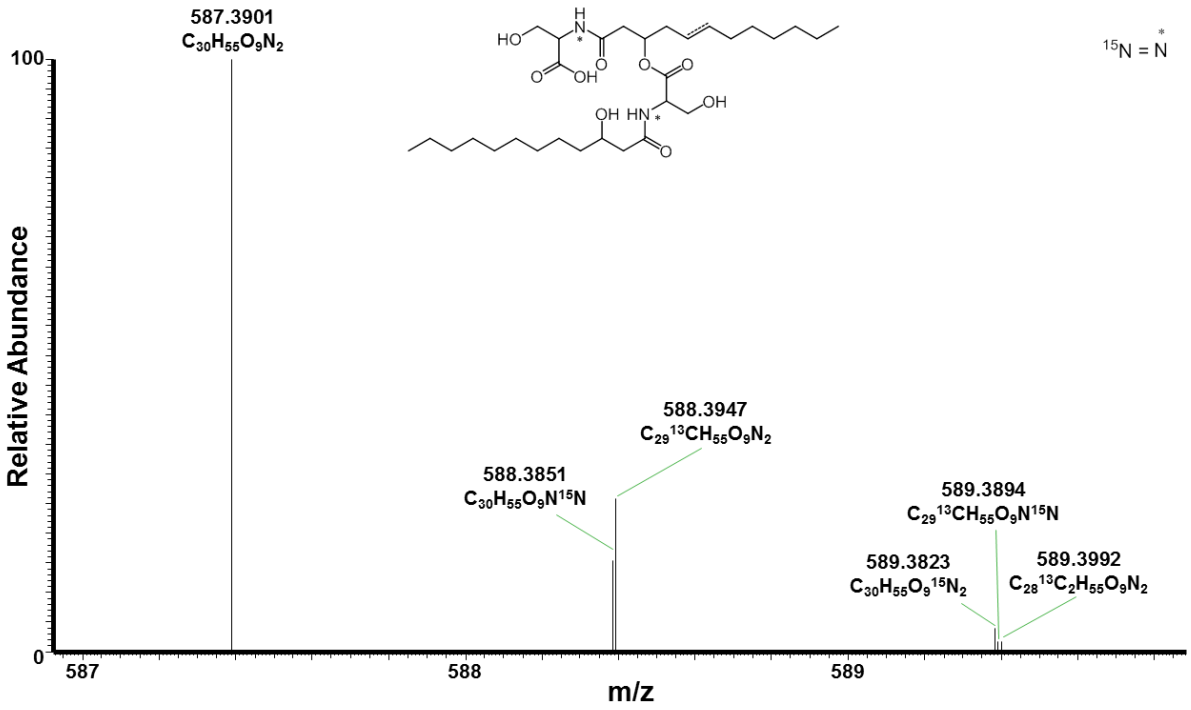


Fig. S216. HRMS of serratamic acid with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (N-(D-3-hydroxydecanoyl)-L-serine, compound **29** $[M+H]^+$: *m/z* 276, $C_{13}H_{26}NO_5$).

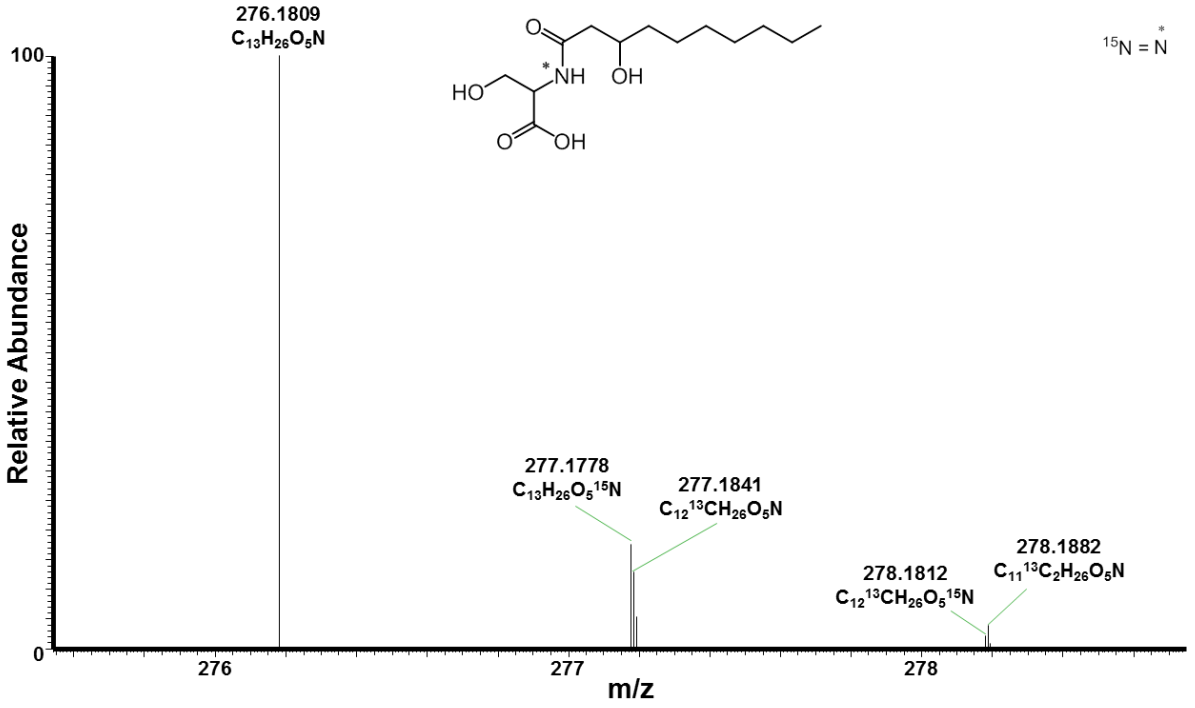


Fig. S217. HRMS of serratamic acid derivative with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (hydroxydodecanoyl-serine, compound **30** $[M+H]^+$: *m/z* 304, $C_{15}H_{30}NO_5$).

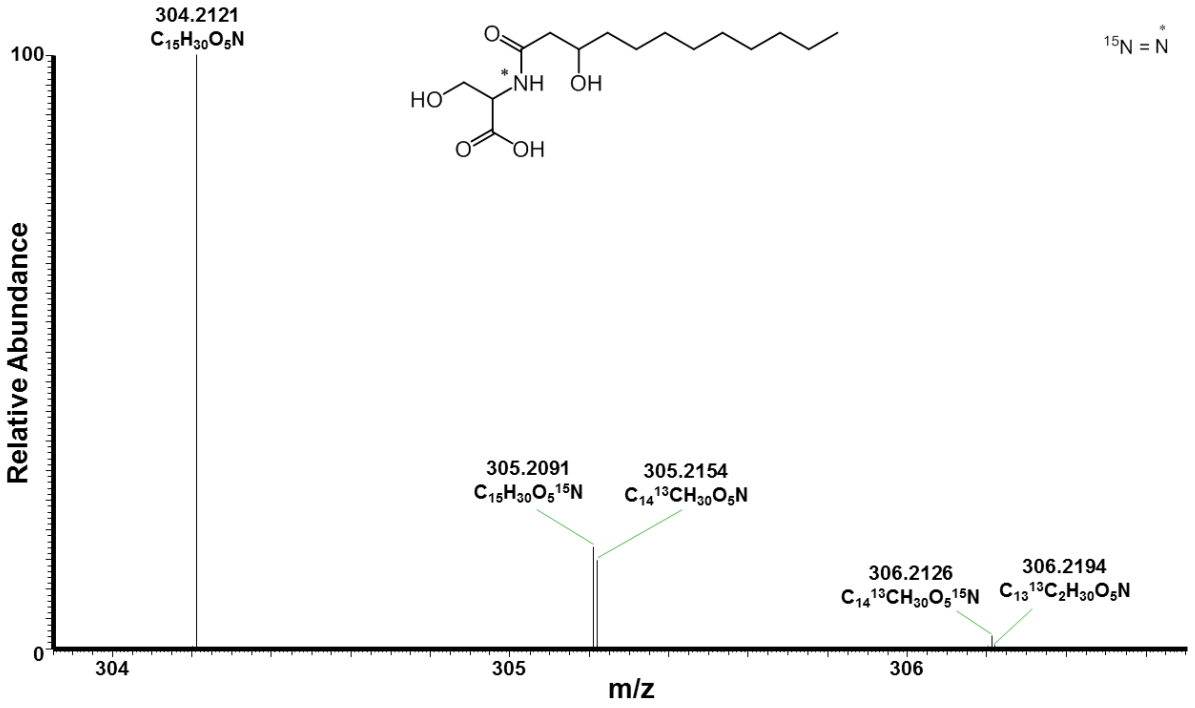


Fig. S218. HRMS of serratamic acid derivative with double bond with incorporated ^{15}N-L-serine from nutrient broth with 2 mg/mL ^{15}N-L-serine (hydroxydodecenoyl-serine, compound **31** $[M+H]^+$: *m/z* 302, $C_{15}H_{28}NO_5$).

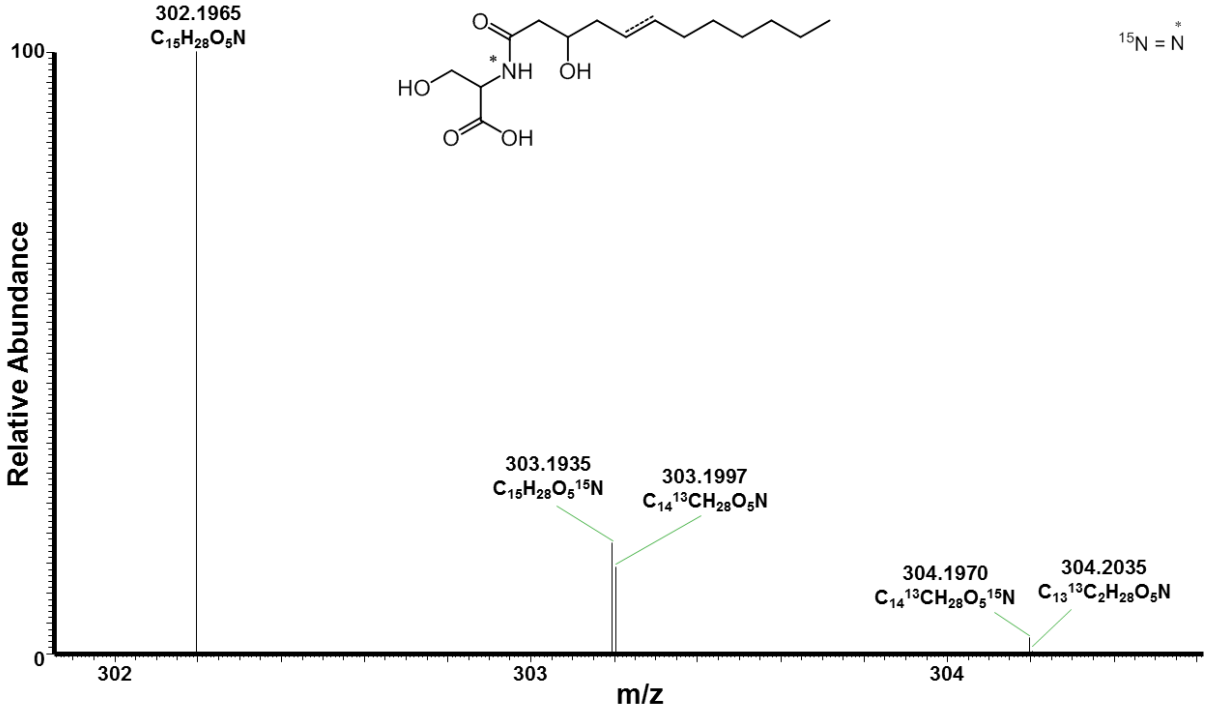
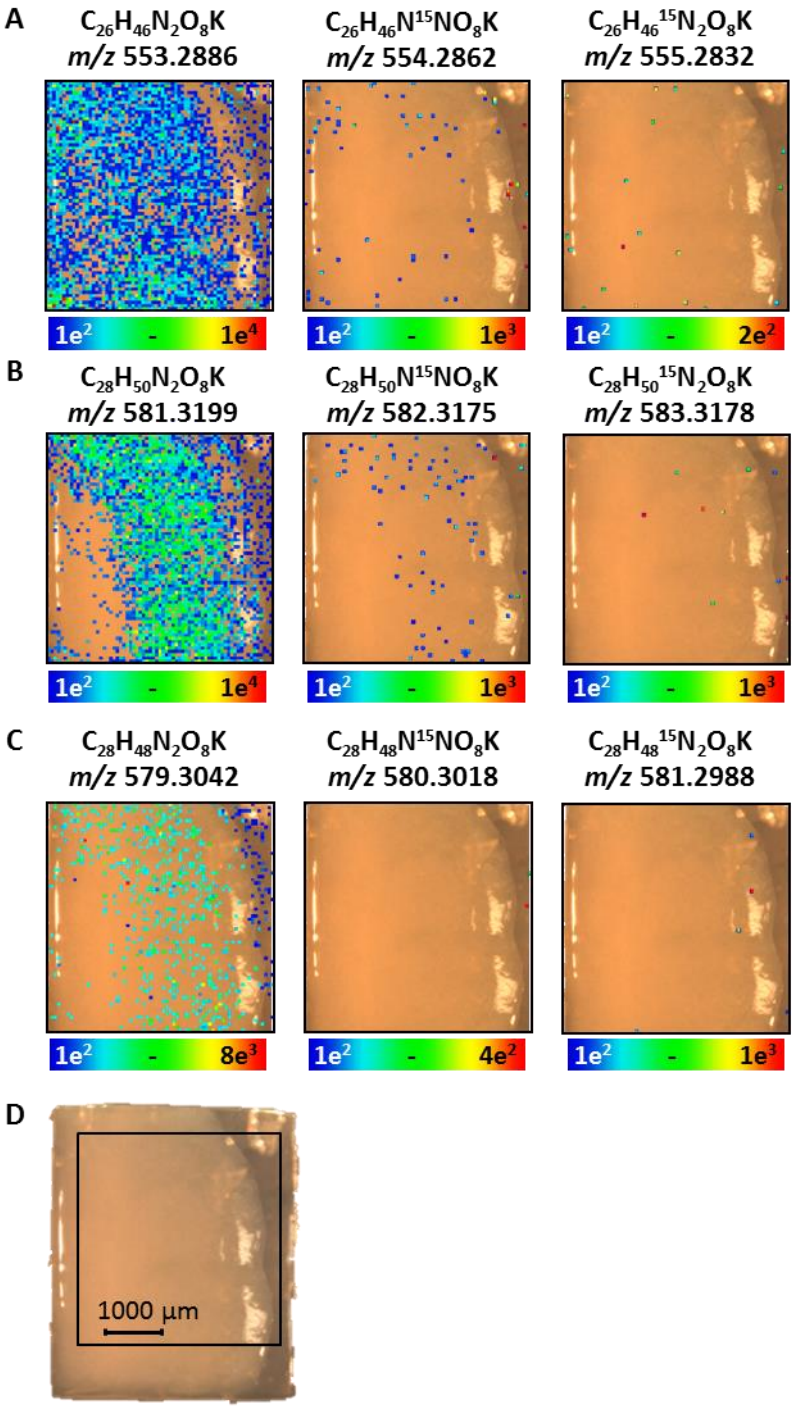


Fig. S219. MALDI-imaging-HRMS control of abundant serratamolides (A: serrawettin W1 (**10**); B: C_{10}+C_{12} (**12**); C: C_{10}+$C_{12:1}$ (**16**)) produced by *S. marcescens* MSRBB2 on potato dextrose agar. Optical image with assigned scan area (D) and localization of unlabeled serratamolides along with one and two incorporations of [^{15}N] ([M+K]$^+$ ± 3 ppm).



III. SUPPLEMENTARY TABLES

Table S1. Peak height ratios obtained from HPLC-HRMS by comparison of labeled and unlabeled prodiginines and MBC produced by *S. marcescens*. Different labeling studies with $^{15}NH_4Cl$, [1-^{13}C]-L-proline, [methyl-D_3]-L-methionine, and [^{15}N]-L-serine on nutrient agar (NA) and potato dextrose agar (PDA).

Prodiginine	Media	$^{15}NH_4Cl$	[1-^{13}C]-L-proline	^{15}N-L-serine	[methyl-D_3]-L-methionine		
		1 mg/mL [%]	1 mg/mL [%]	1 mg/mL [%]	0.5 mg/mL [%]	1 mg/mL [%]	2 mg/mL [%]
2-methyl-3-propyl-P (**1**)	NA	10	84	18	128	215	439
2-methyl-3-butyl-P (**2**)	NA	10	66	21	170	227	472
2-methyl-3-pentyl-P (**3**)	NA	11	72	23	174	202	478
2-methyl-3-hexyl-P (**4**)	NA	15	87	23	155	202	445
2-methyl-3-heptyl-P (**5**)	NA	15	91	21	145	201	429
2-methyl-3-octyl-P (**6**)	NA	8	83	18	n.d.	n.d.	464
2-methyl-3-nonyl-P (**7**)	NA	8	79	19	n.d.	n.d.	456
MBC (**8**)	NA	-	71	8	169	204	466
2-methyl-3-propyl-P (**1**)	PDA	11	118	25	91	329	>1000
2-methyl-3-butyl-P (**2**)	PDA	11	113	25	92	275	816
2-methyl-3-pentyl-P (**3**)	PDA	16	126	28	95	252	744
2-methyl-3-hexyl-P (**4**)	PDA	16	119	27	90	249	798
2-methyl-3-heptyl-P (**5**)	PDA	15	133	27	88	238	713
2-methyl-3-octyl-P (**6**)	PDA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2-methyl-3-nonyl-P (**7**)	PDA	n.d.	n.d.	n.d.	93	329	>1000
MBC (**8**)	PDA	-	102	16	88	278	703

Table S2. Peak height ratios obtained from HPLC-HRMS by comparison of labeled (1x ^{15}N) and unlabeled serratamolides produced by *S. marcescens*. Different labeling studies with [^{15}N]-L-serine on nutrient agar (NA) and potato dextrose agar (PDA), as well as nutrient broth (NB) incubation under static conditions.

Serratamolide		^{15}N-L-serine		
No.	**Sum formula**	**NA 1 mg/mL [%]**	**PDA 1 mg/mL [%]**	**NB 2 mg/mL [%]**
10	$C_{26}H_{46}N_2O_8$	10	29	18
11	$C_{27}H_{48}N_2O_8$	10	29	16
12	$C_{28}H_{50}N_2O_8$	13	25	20
13	$C_{29}H_{52}N_2O_8$	15	23	16
14	$C_{30}H_{54}N_2O_8$	13	25	17
15	$C_{27}H_{46}N_2O_8$	19	24	n.d.
16	$C_{28}H_{48}N_2O_8$	18	31	18
17	$C_{29}H_{50}N_2O_8$	18	32	n.d.
18	$C_{30}H_{52}N_2O_8$	17	27	16
19	$C_{26}H_{48}N_2O_9$	14	33	21
20	$C_{27}H_{50}N_2O_9$	13	29	n.d.
21	$C_{28}H_{52}N_2O_9$	13	28	19
22	$C_{28}H_{50}N_2O_9$	13	29	19
23	$C_{29}H_{54}N_2O_9$	13	31	n.d.
24	$C_{30}H_{56}N_2O_9$	12	28	17
25	$C_{31}H_{58}N_2O_9$	12	22	n.d.
26	$C_{29}H_{52}N_2O_9$	15	28	n.d.
27	$C_{30}H_{54}N_2O_9$	15	29	15
28	$C_{31}H_{56}N_2O_9$	15	28	n.d.
29	$C_{13}H_{25}NO_5$	10	20	18
30	$C_{15}H_{29}NO_5$	11	20	17
31	$C_{15}H_{27}NO_5$	13	23	18

IV. SUPPLEMENTARY REFERENCES

[1] Eckelmann, D.; Spiteller, M.; Kusari, S. *Sci. Rep.* **2018**, 8, 5283.