# Supporting Information

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NMR Spectra of Synthesized Compounds

Figure S1. $^1$H NMR spectrum (600 MHz, 300 K, D$_2$O) of H-D-$\gamma$-Glu(OMe)-Mdha-d-Ala-Leu-OH 3. 2 $\mu$L of acetone were added as an internal standard for calibration of $^{13}$C chemical shifts.

Figure S2. $^{13}$C NMR spectrum (151 MHz, 300 K, D$_2$O) of H-D-$\gamma$-Glu(OMe)-Mdha-d-Ala-Leu-OH 3. 2 $\mu$L of acetone were added as an internal standard for calibration of $^{13}$C chemical shifts.
Figure S3. $^1$H NMR spectrum (600 MHz, 305 K, D$_2$O) of thioether derivative 5. 4 µL of acetone were added as an internal standard for calibration of $^{13}$C chemical shifts.

Figure S4. $^{13}$C NMR spectrum (151 MHz, 305 K, D$_2$O) of thioether derivative 5. 4 µL of acetone were added as an internal standard for calibration of $^{13}$C chemical shifts.
Figure S5. $^1$H NMR spectrum (400 MHz, 300 K, D$_2$O) of H-D-$\gamma$-Glu-Mdha-d-Ala-Leu-OH 6.

Figure S6. $^1$H NMR spectrum (600 MHz, 300 K, D$_2$O) of 8. 2 µL of acetone were added as an internal standard for calibration of $^{13}$C chemical shifts.
Figure S7. $^{13}$C NMR spectrum (151 MHz, 300 K, D$_2$O) of 8. 2 µL of acetone were added as an internal standard for calibration of $^{13}$C chemical shifts.

Figure S8. DQF-COSY spectrum (600 MHz, 300 K, D$_2$O) of 8. 2 µL of acetone were added as an internal standard for calibration of $^{13}$C chemical shifts.
Figure S9. HSQC spectrum (151 MHz, 300 K, D$_2$O) of 8. 2 μL of acetone were added as an internal standard for calibration of $^{13}$C chemical shifts.

Figure S10. HMBC spectrum (151 MHz, 300 K, D$_2$O) of 8. 2 μL of acetone were added as an internal standard for calibration of $^{13}$C chemical shifts.
Figure S11. $^1$H NMR spectrum (600 MHz, 360 K, [D$_6$]-DMSO) of Z-D-$\gamma$-Glu(OMe)-Mdha-D-Ala-L-Leu-OtBu 11.

![NMR Spectrum 1](image1)

Figure S12. $^{13}$C NMR spectrum (151 MHz, 360 K, [D$_6$]-DMSO) of Z-D-$\gamma$-Glu(OMe)-Mdha-D-Ala-L-Leu-OtBu 11.

![NMR Spectrum 2](image2)
**Figure S13.** $^1$H NMR spectrum (600 MHz, 360 K, [D$_6$]DMSO) of Z-D-$\gamma$-Glu(OMe)-Mdha-D-Ala-L-Leu-OH 12.

**Figure S14.** $^{13}$C NMR spectrum (151 MHz, 360 K, [D$_6$]DMSO) of Z-D-$\gamma$-Glu(OMe)-Mdha-D-Ala-L-Leu-OH 12.
Figure S15. $^1$H NMR spectrum (600 MHz, 300 K, D$_2$O) of thioether derivative 13.

Figure S16. $^1$H NMR spectrum (400 MHz, 300 K, [D$_6$]DMSO) of Z-D-Gln(Me)-OH 15.
Figure S17. $^{13}$C NMR spectrum (101 MHz, 300 K, [D$_6$]DMSO) of Z-D-Gln(Me)-OH 15.

The identity of 15 was validated by comparison to an authentic synthetic sample that was prepared according to Scheme S1. Figures S18 and S19 show a comparison of the $^1$H and $^{13}$C NMR spectra of both samples.

Scheme S1. Synthesis of an authentic sample of Z-Gln(Me)-OH.
Figure S18. $^1$H NMR spectra (400 MHz, 300 K, [D$_6$]DMSO) of Z-D-Gln(Me)-OH 15 (top) and authentic sample synthesized according to Scheme S1 (bottom).

Figure S19. $^{13}$C NMR spectra (101 MHz, 300 K, [D$_6$]DMSO) of Z-D-Gln(Me)-OH 15 (top) and authentic sample synthesized according to Scheme S1 (bottom).
Figure S20. $^1$H NMR spectrum (400 MHz, 300 K, D$_2$O) of Z-D-$\gamma$-Glu,D,L-Mapa-D-Ala-L-Leu-OH 17.
Figure S21. $^1$H NMR spectrum (600 MHz, 300 K, CD$_3$OD) of microcystin-LF–GSH conjugate 18.
**LC-MS Chromatograms**

Figure S22. LC-MS chromatogram of microcystin-LF 1 (gradient: 50-100% BFA in 15 min) used for preparation of 18.

Figure S23. LC-MS chromatogram of a sample taken from the reaction mixture of 1 with an excess of GSH after 1h. (gradient: 35-70% BFA in 15 min).