Electronic Supplementary Information (ESI)

Three Cyclic Pentapeptides and a Cyclic Lipopeptide Produced by Endophytic *Fusarium decemcellulare* LG53

Gang Li,[a] Souvik Kusari,*[a] Christopher Golz,[b] Carsten Strohmann[b] and Michael Spiteller*[a]

[a]Institute of Environmental Research (INFU), Department of Chemistry and Chemical Biology, Chair of Environmental Chemistry and Analytical Chemistry, TU Dortmund, Otto-Hahn-Straße 6, 44221 Dortmund, Germany

[b]Inorganic Chemistry, Department of Chemistry and Chemical Biology, TU Dortmund, Otto-Hahn-Straße 6, 44221 Dortmund, Germany

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References

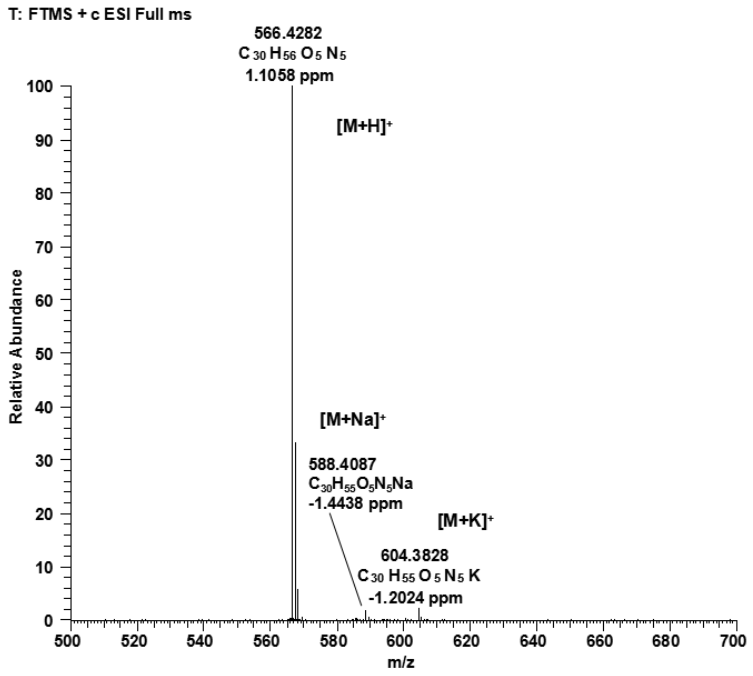


Fig. S1. Positive ESI-HRMS spectrum of compound **1**.

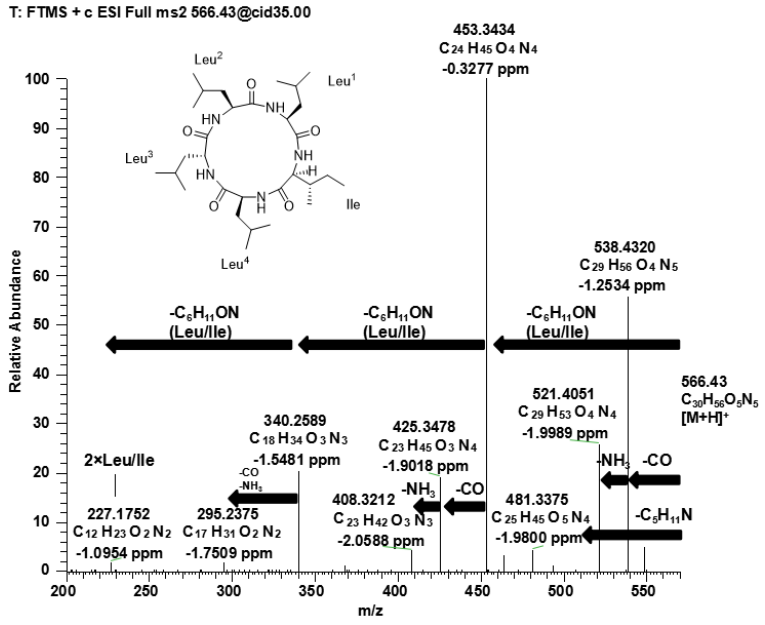


Fig. S2. Positive ESI-HRMS/MS spectrum of compound **1**.

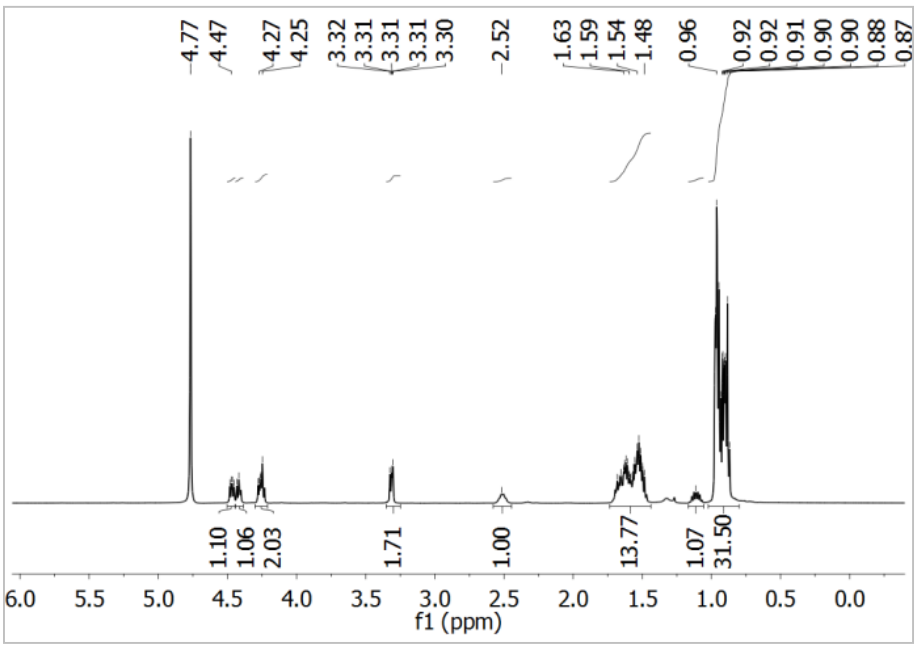


Fig. S3. ^{1}H NMR spectrum of compound **1** in $CDCl_3/CD_3OD$ (1:3).

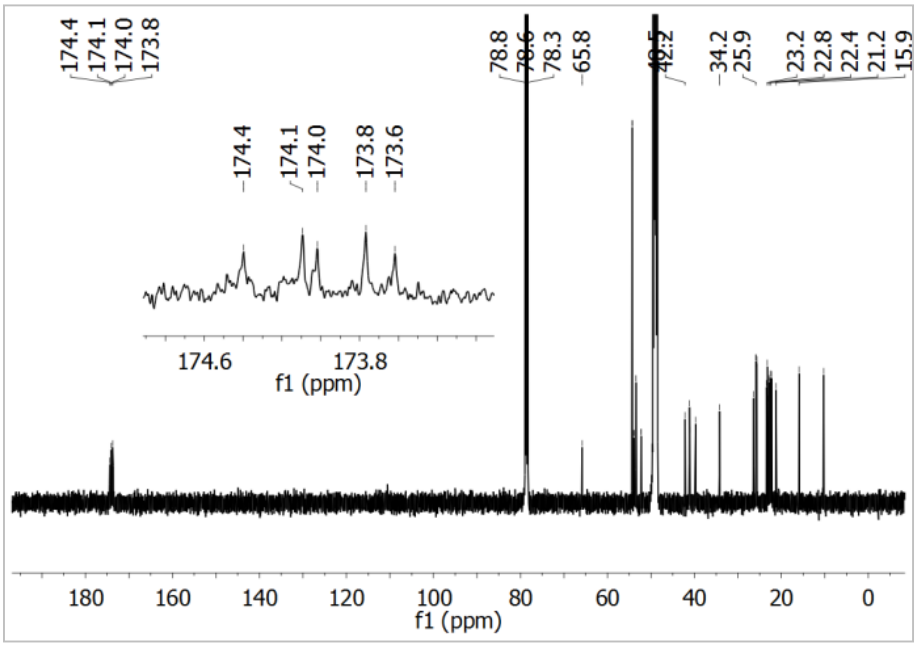


Fig. S4. ^{13}C NMR spectrum of compound **1** in $CDCl_3/CD_3OD$ (1:3).

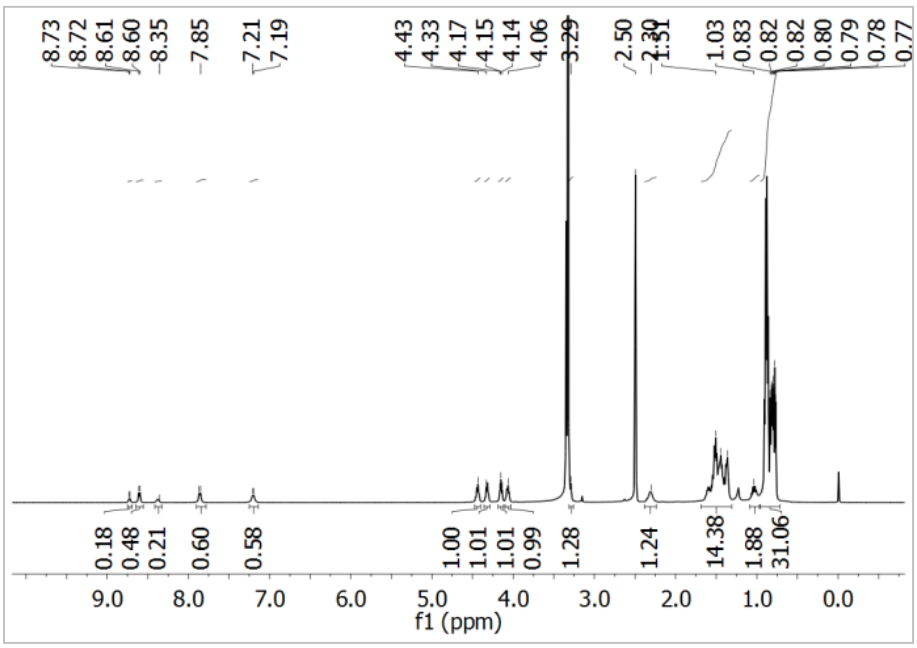


Fig. S5. ^{1}H NMR spectrum of compound **1** in DMSO-d_6.

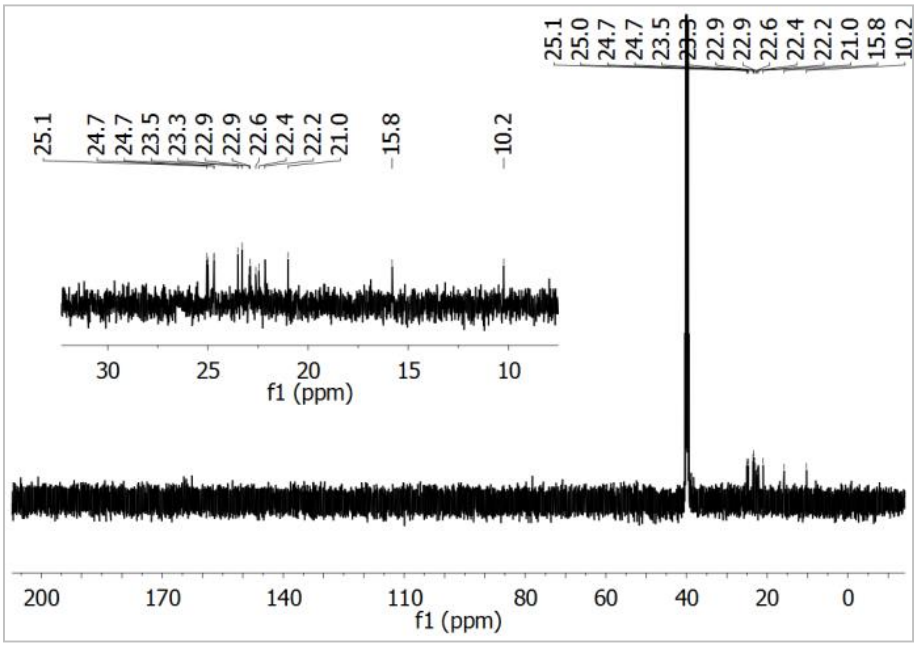


Fig. S6. ^{13}C NMR spectrum of compound **1** in DMSO-d_6.

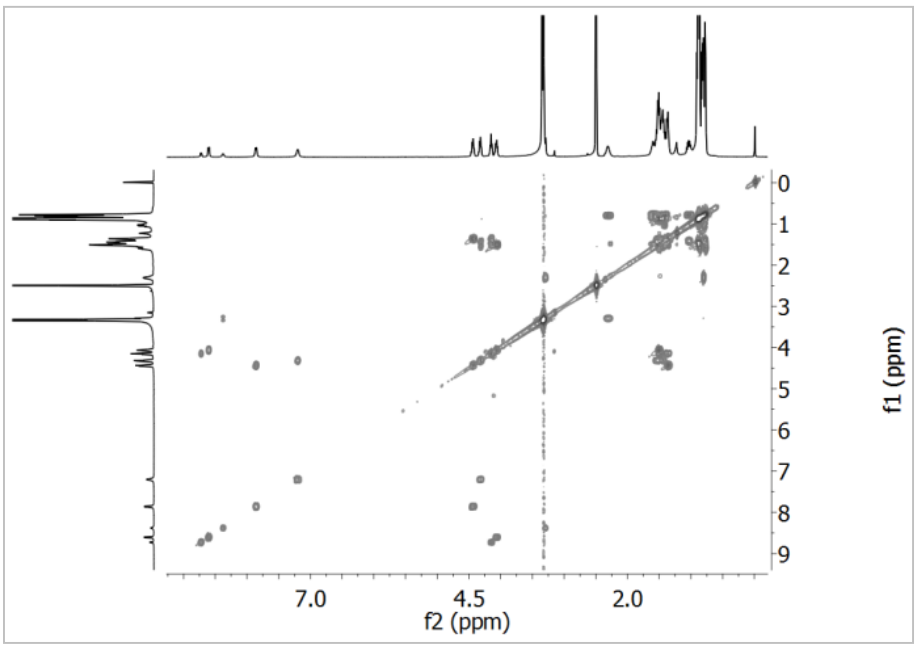


Fig. S7. ^{1}H-^{1}H COSY spectrum of compound **1** in DMSO-d_6.

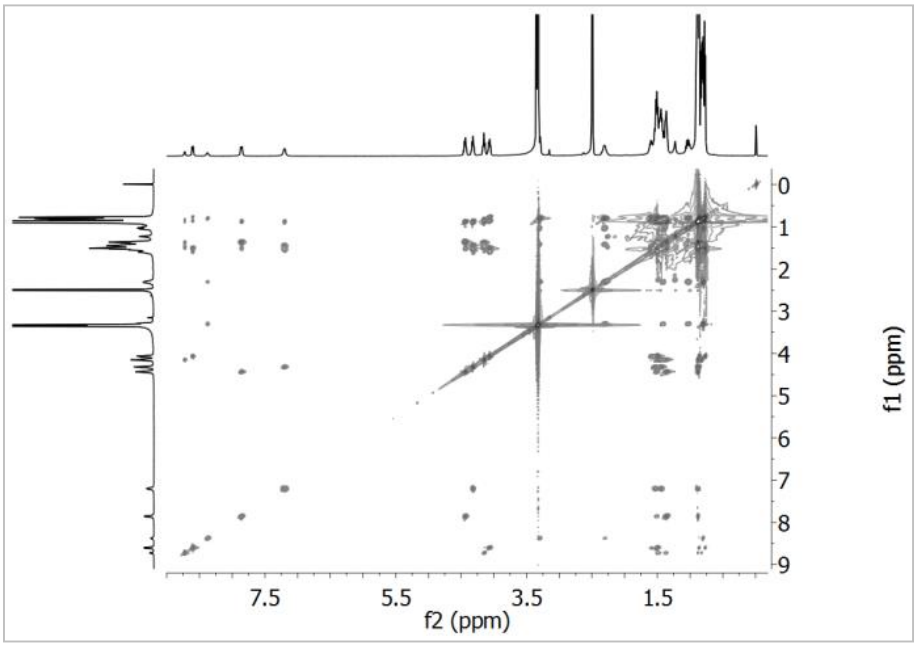


Fig. S8. TOCSY spectrum of compound **1** in DMSO-d_6.

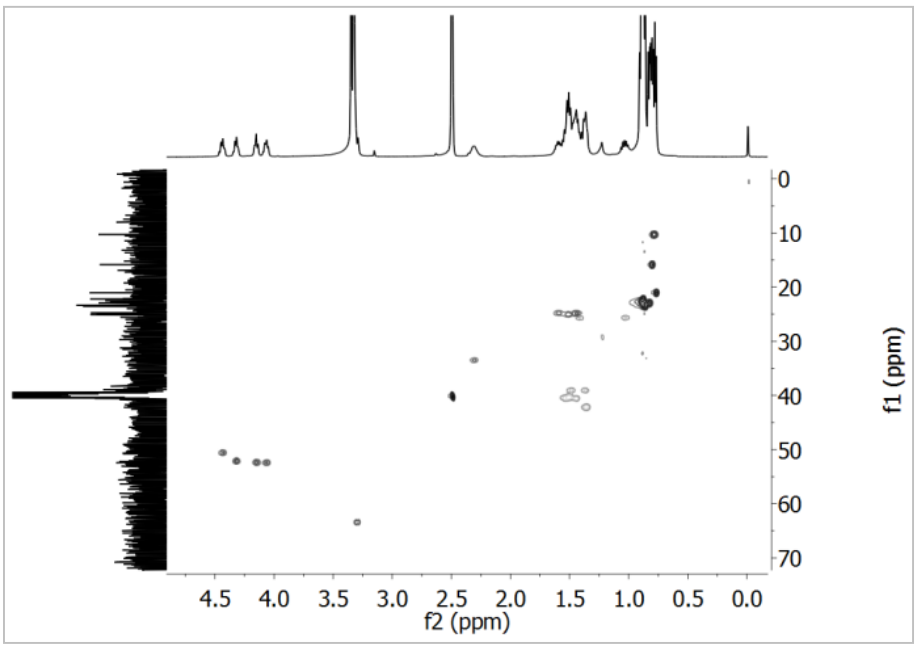


Fig. S9. HSQC spectrum of compound **1** in DMSO-d_6.

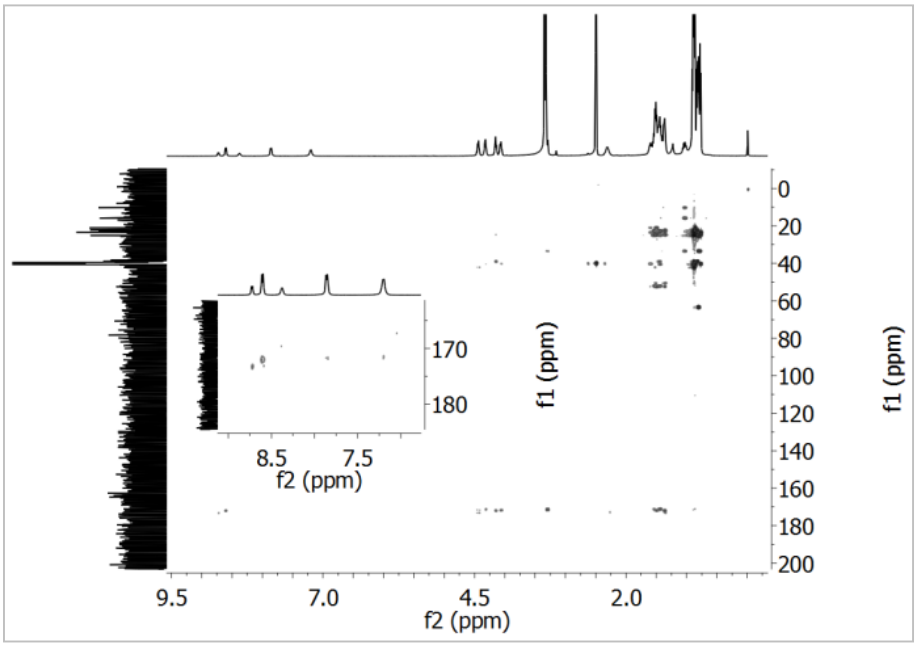


Fig. S10. HMBC spectrum of compound **1** in DMSO-d_6.

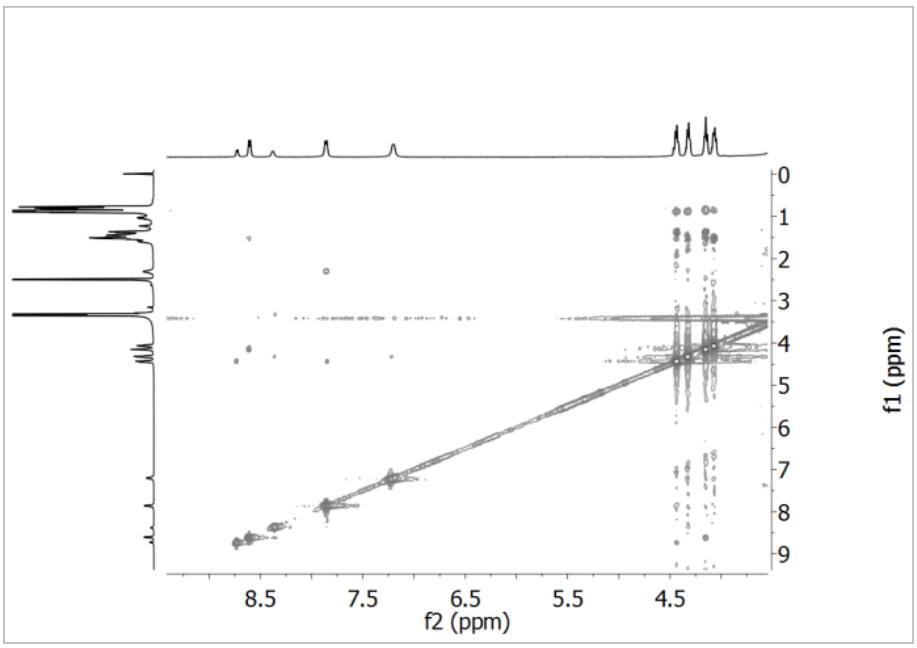


Fig. S11. NOESY spectrum of compound **1** in DMSO-d_6.

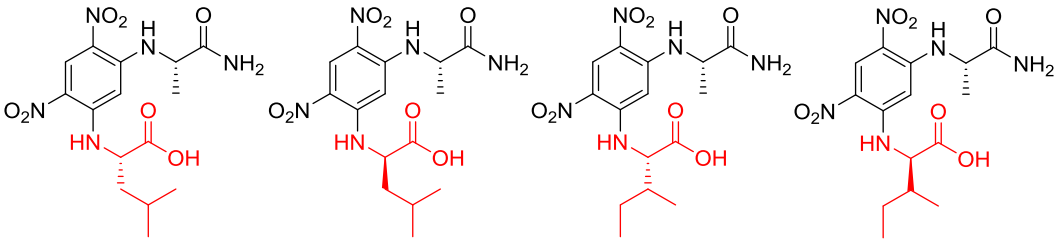
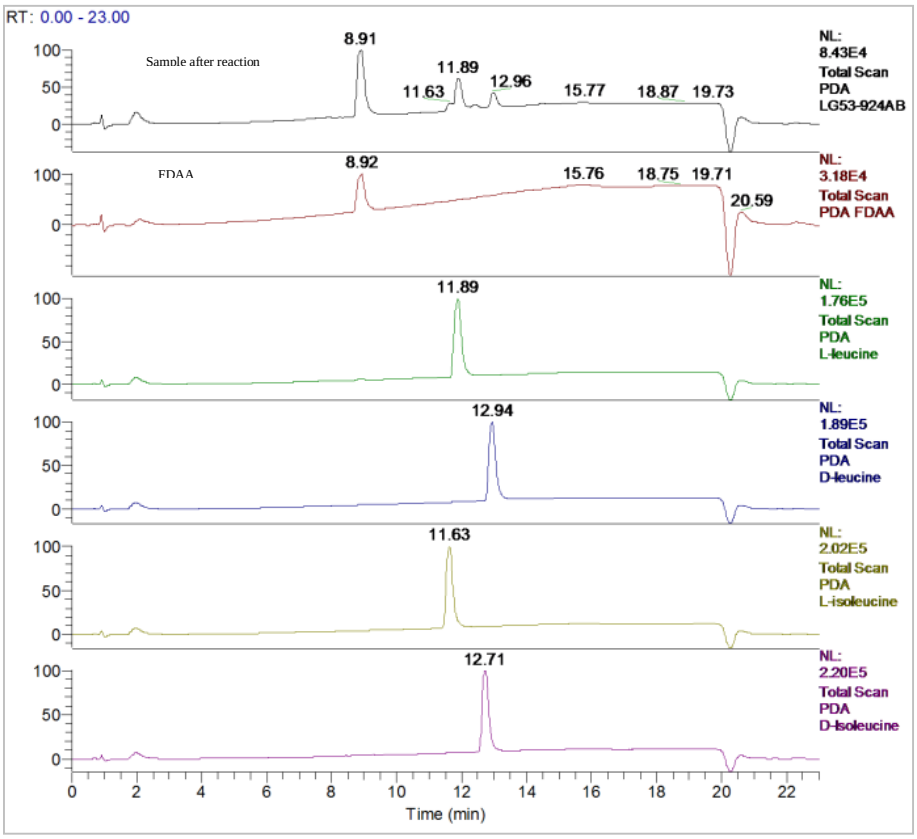


Fig. S12. Marfey's reagent FDAA-derived amino acid standards (from left to right: L-Leucine, D-Leucine, L-Isoleucine, and D-Isoleucine).



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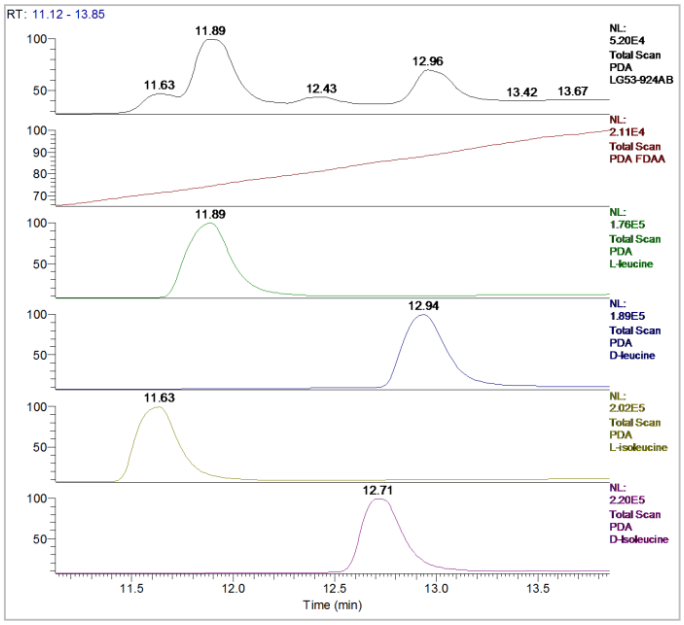


Fig. S13. LC-MS analysis for FDAA derivatives of the hydrolysis of **1** and amino acid standards. The Marfey's method is for assigning the absolute configurations of amino acid residues.

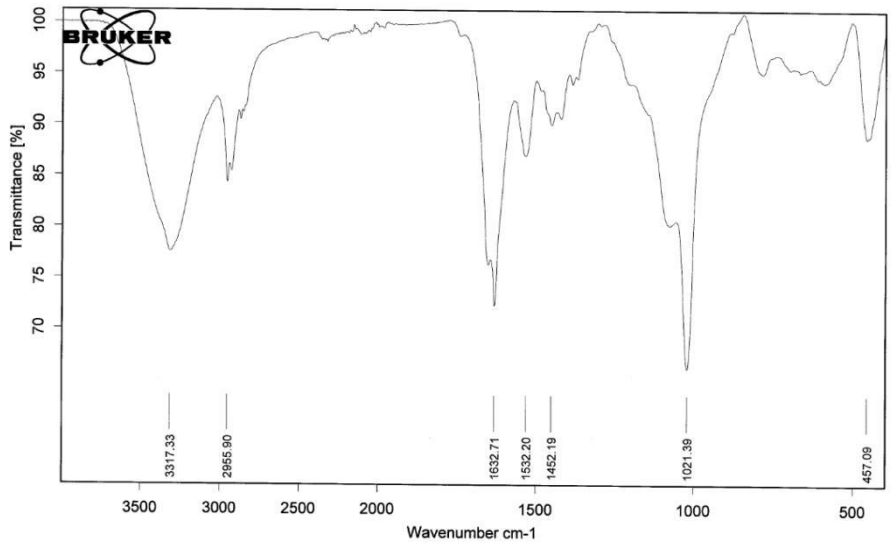


Fig. S14. IR spectrum of compound **1**.

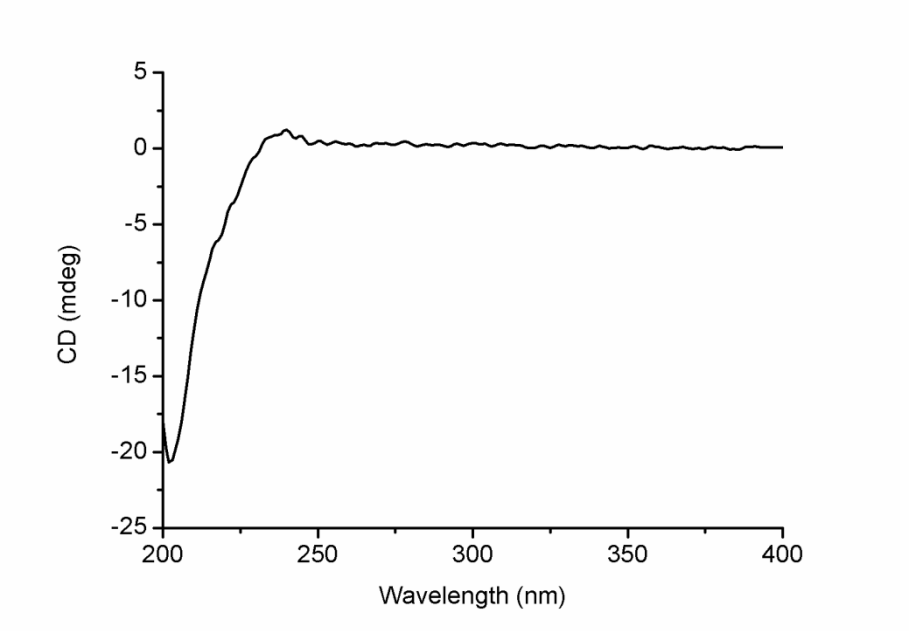


Fig. S15. CD spectrum of compound **1**.

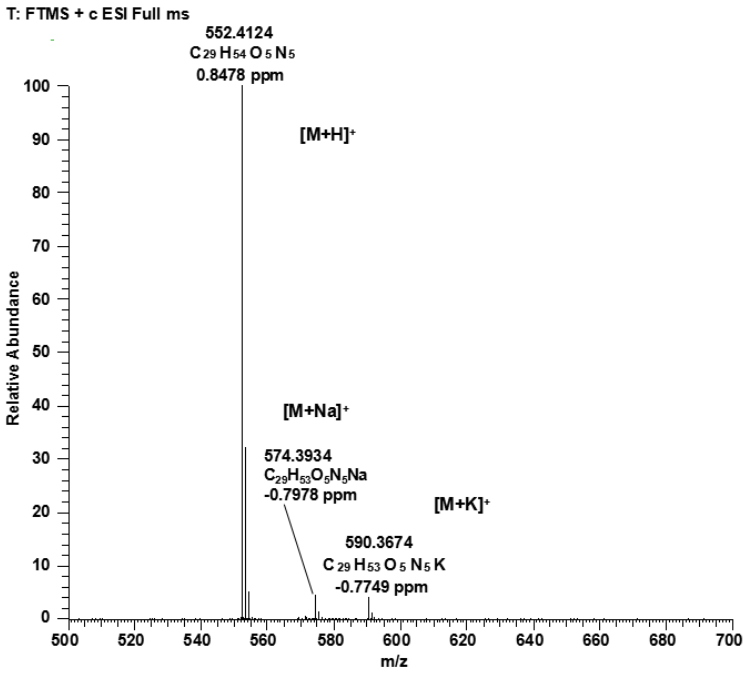


Fig. S16. Positive ESI-HRMS spectrum of compound **2**.

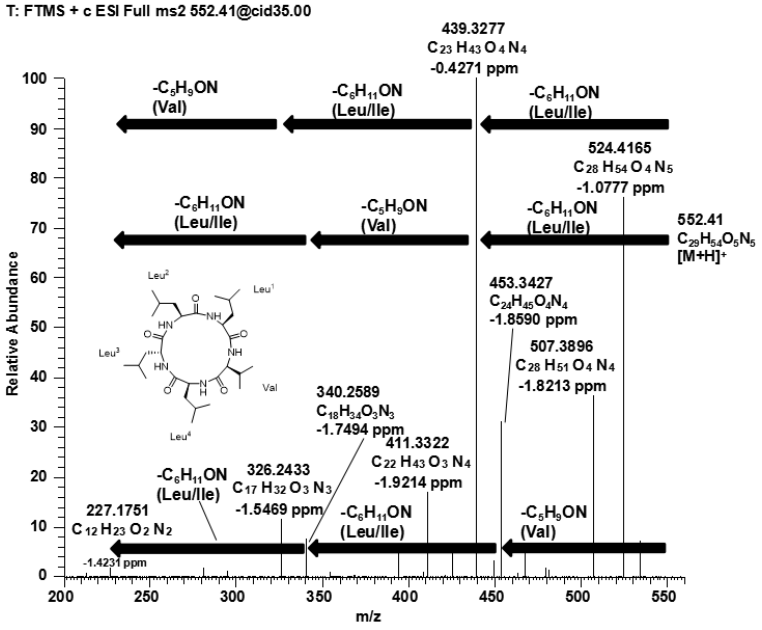


Fig. S17. Positive ESI-HRMS/MS spectrum of compound **2**.

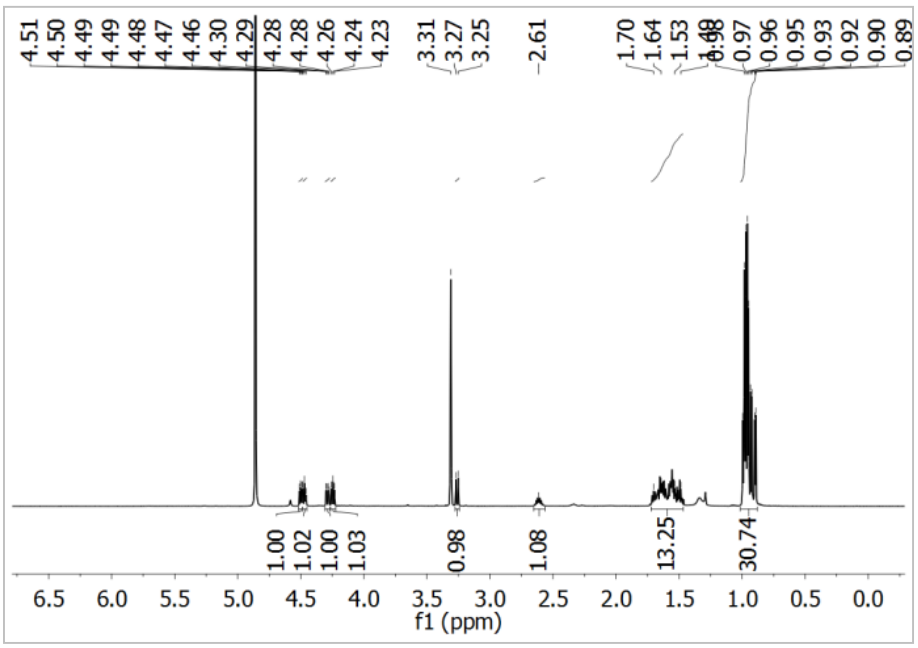


Fig. S18. ^{1}H NMR spectrum of compound **2** in CD_3OD.

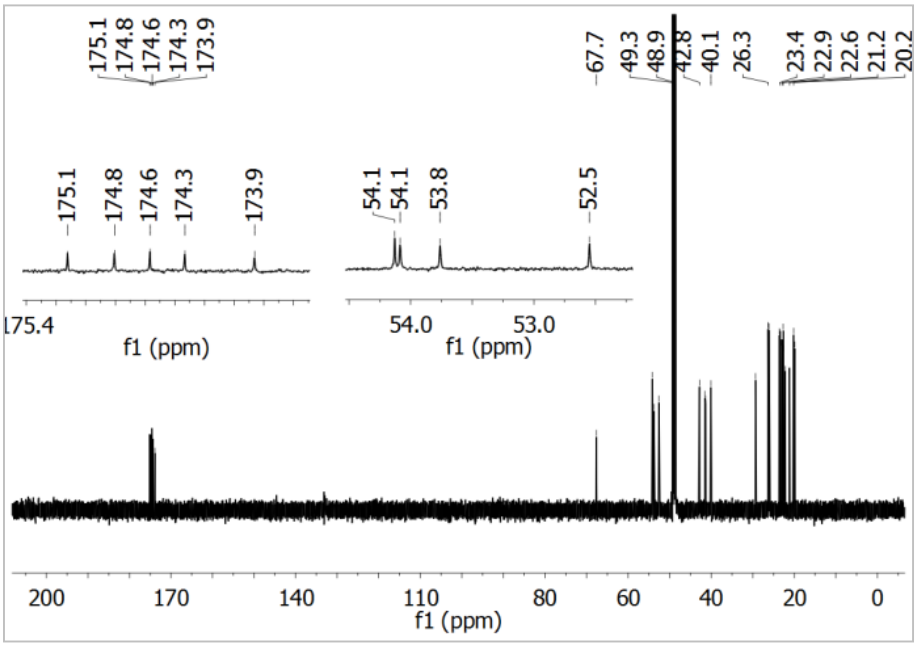


Fig. S19. ^{13}C NMR spectrum of compound **2** in CD_3OD.

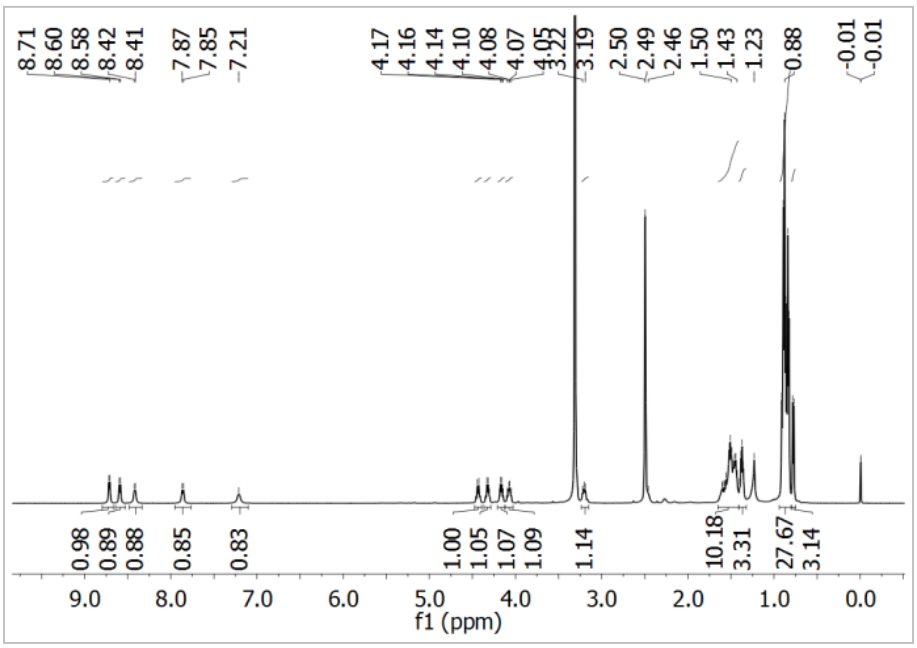


Fig. S20. ^{1}H NMR spectrum of compound **2** in DMSO-d_6.

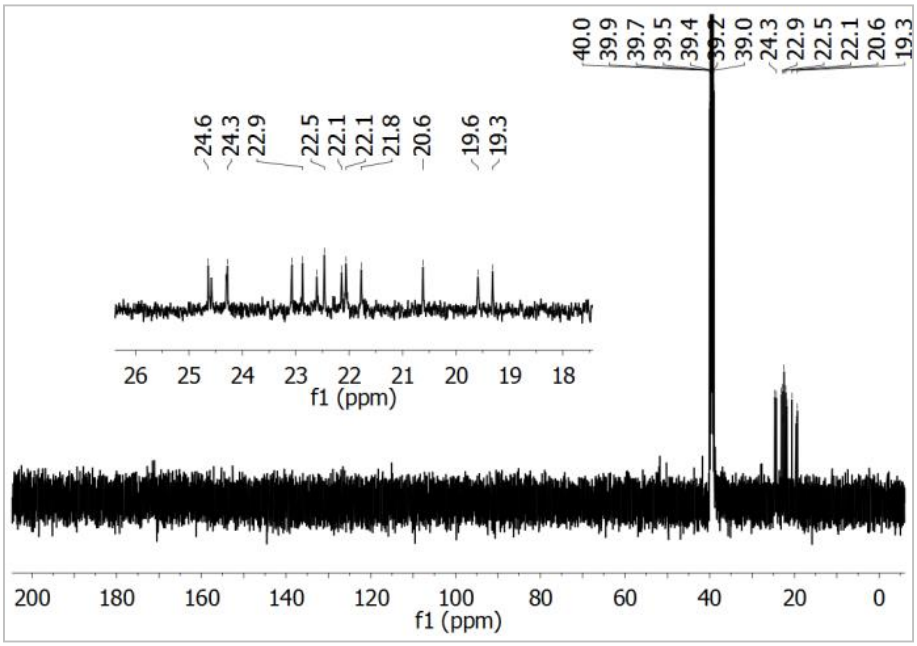


Fig. S21. ^{13}C NMR spectrum of compound **2** in DMSO-d_6.

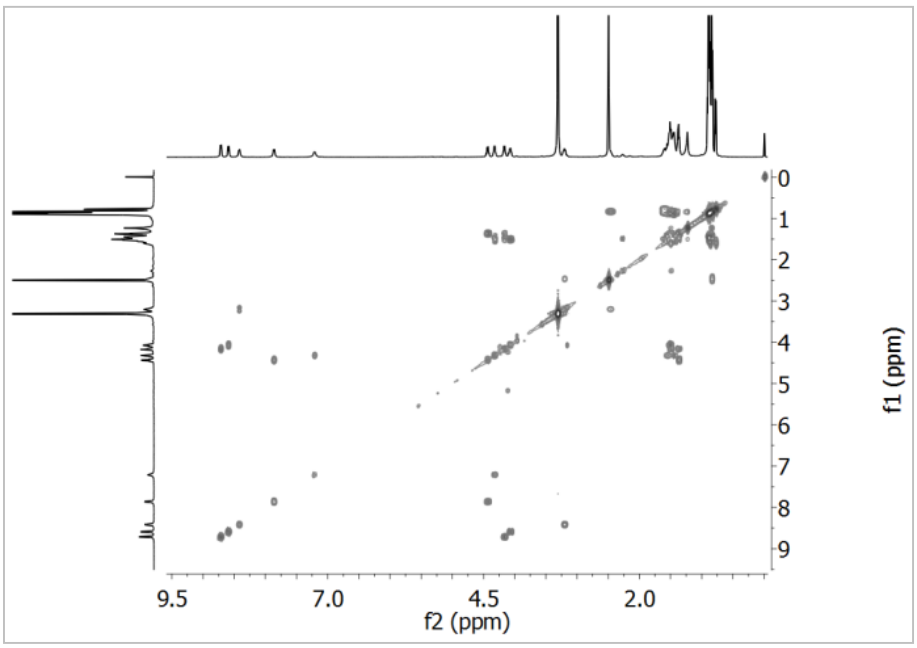


Fig. S22. ^{1}H-^{1}H COSY spectrum of compound **2** in DMSO-d_6.

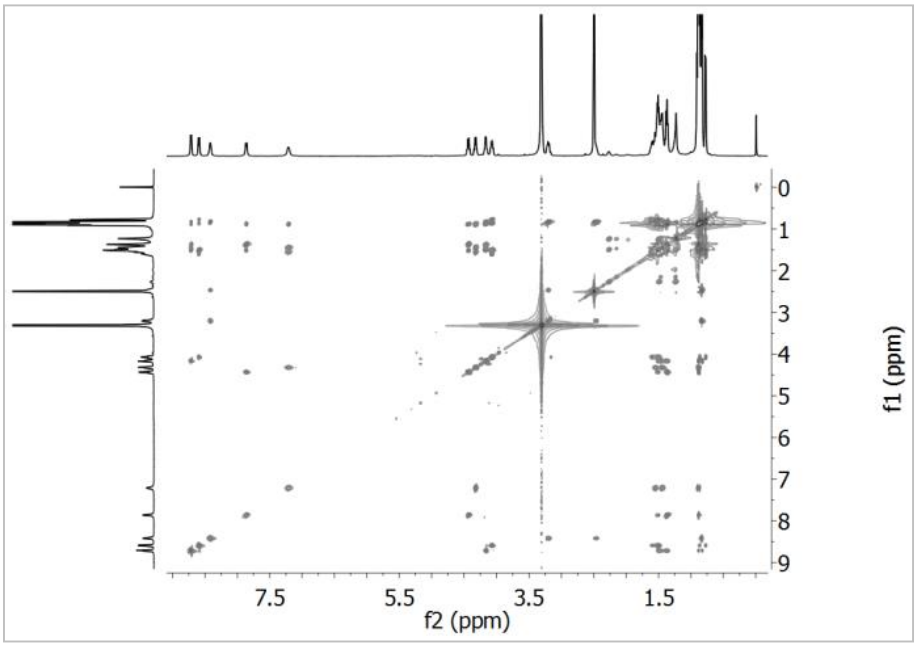


Fig. S23. TOCSY spectrum of compound **2** in DMSO-d_6.

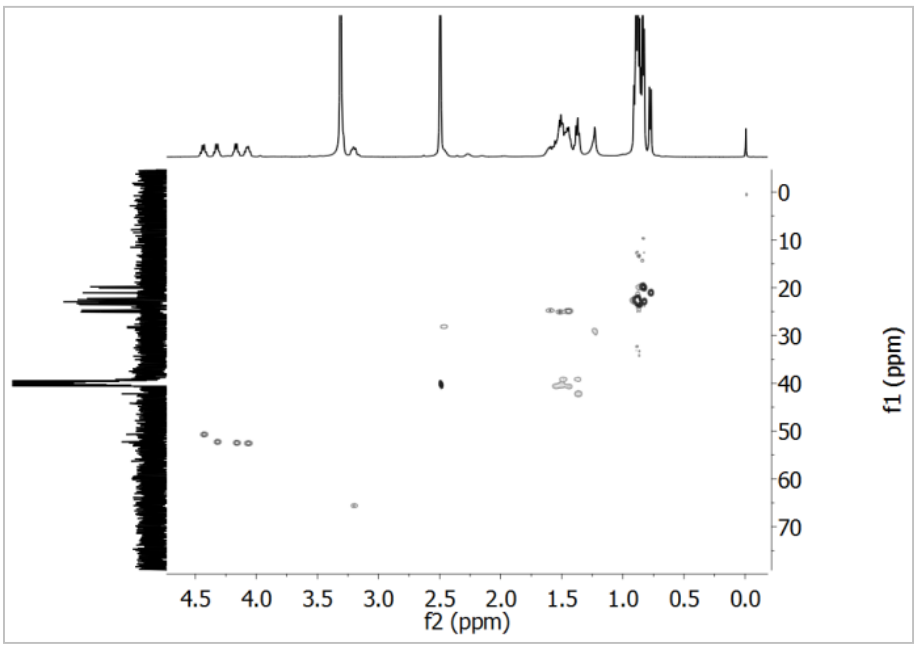


Fig. S24. HSQC spectrum of compound **2** in DMSO-d_6.

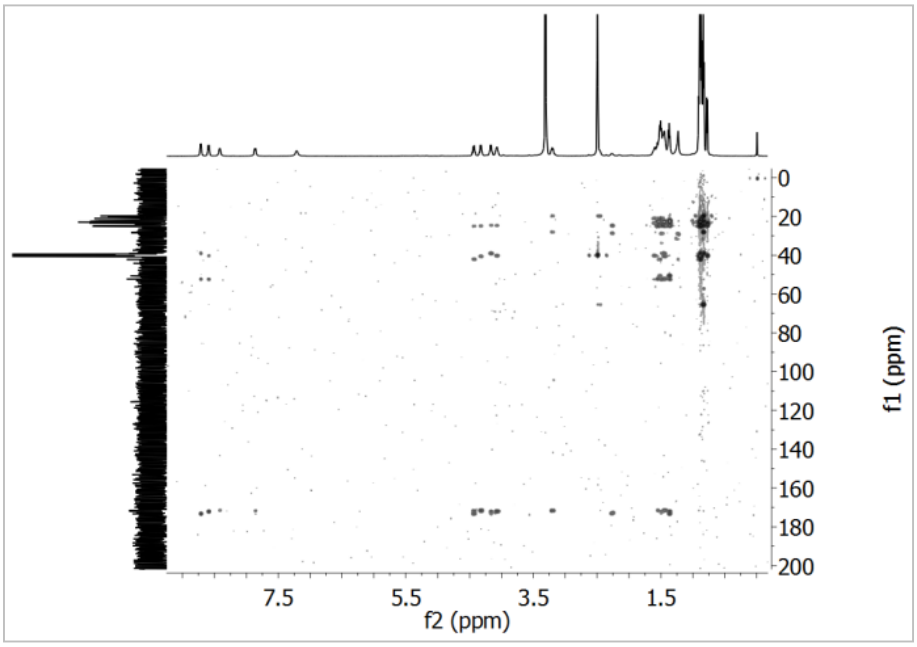


Fig. S25. HMBC spectrum of compound **2** in DMSO-d_6.

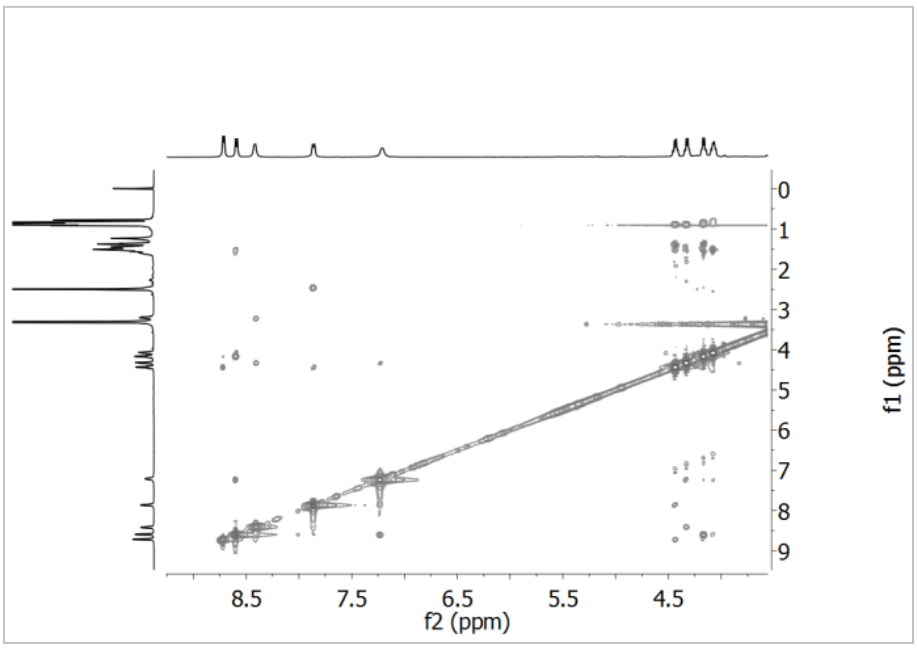


Fig. S26. NOESY spectrum of compound **2** in DMSO-d_6.

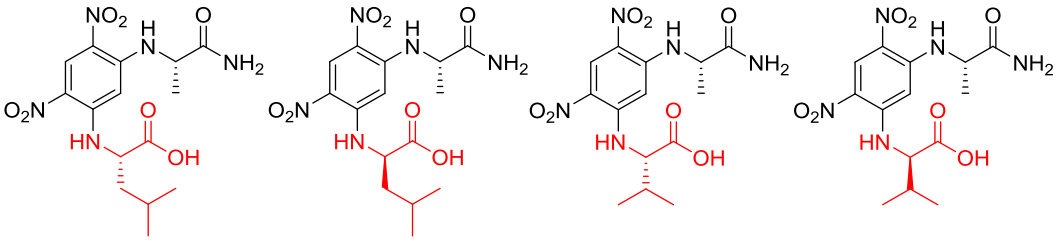


Fig. S27. Marfey's reagent FDAA-derived amino acid standards (from left to right: L-Leucine, D-Leucine, L-Valine, and D-Valine).

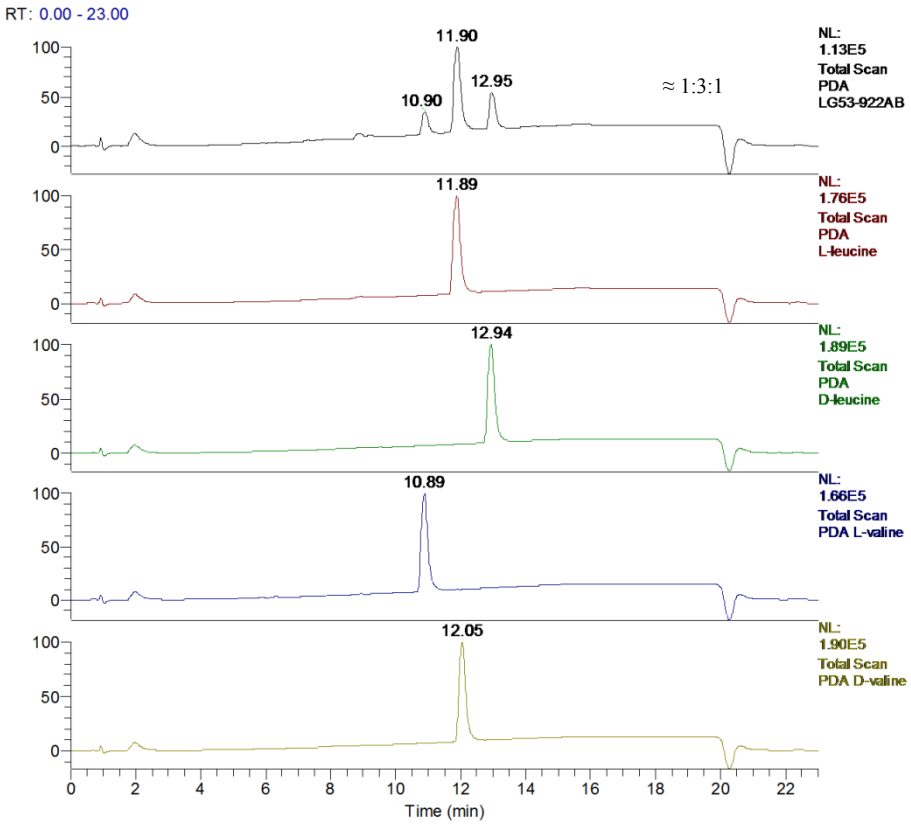


Fig. S28. LC-MS analysis for FDAA derivatives of the hydrolysis of **2** and amino acid standards. The Marfey's method is for assigning the absolute configurations of amino acid residues.

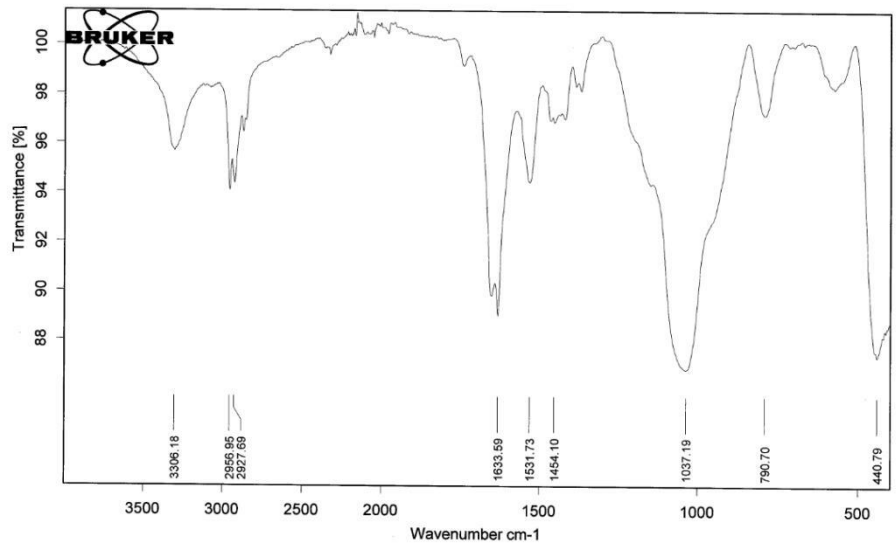


Fig. S29. IR spectrum of compound **2**.

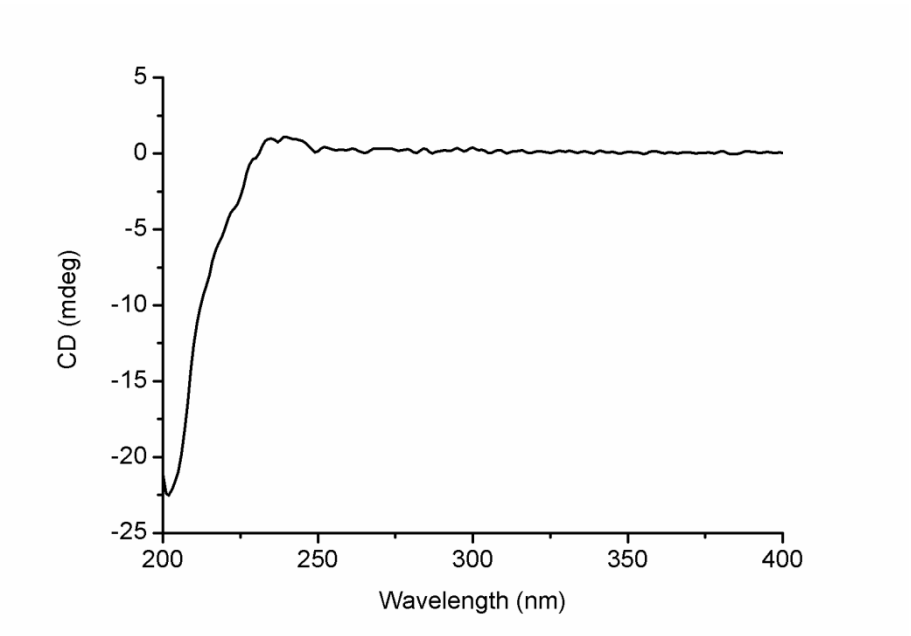


Fig. S30. CD spectrum of compound **2**.

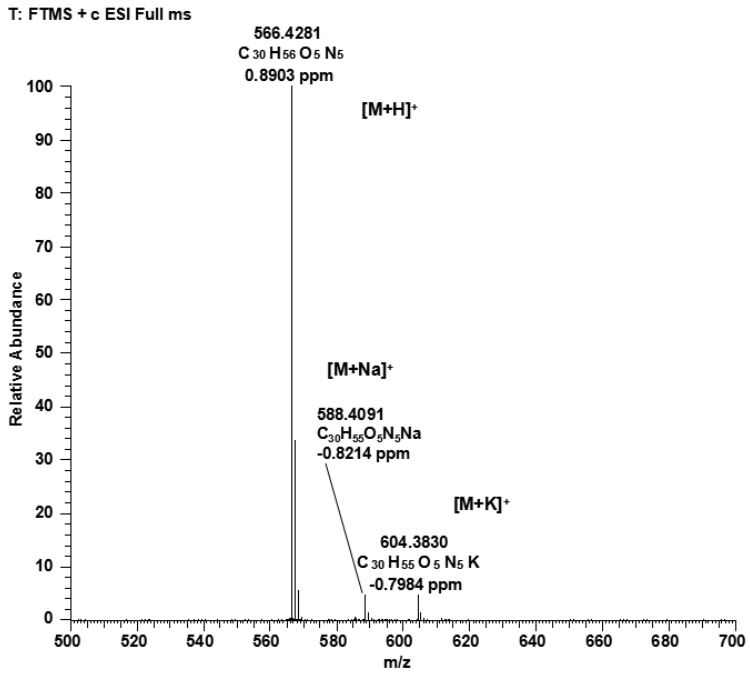


Fig. S31. Positive ESI-HRMS spectrum of compound **3**.

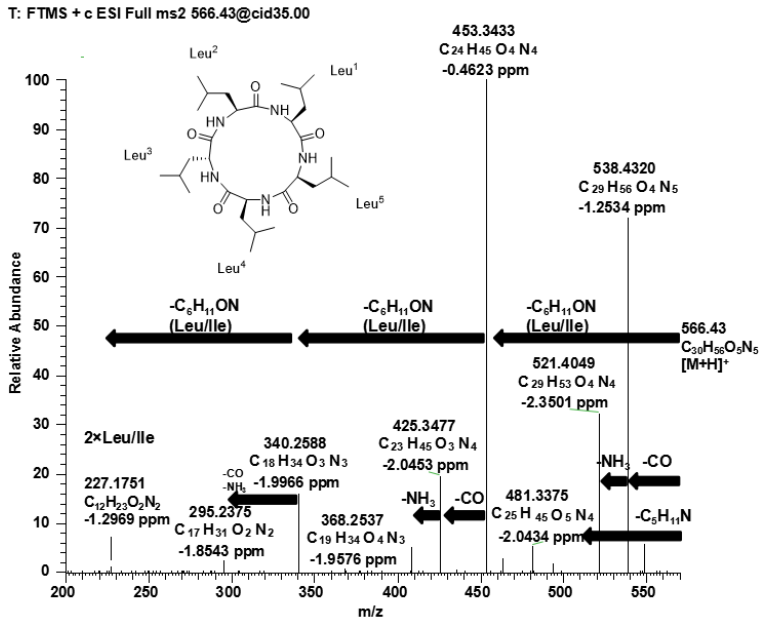


Fig. S32. Positive ESI-HRMS/MS spectrum of compound **3**.

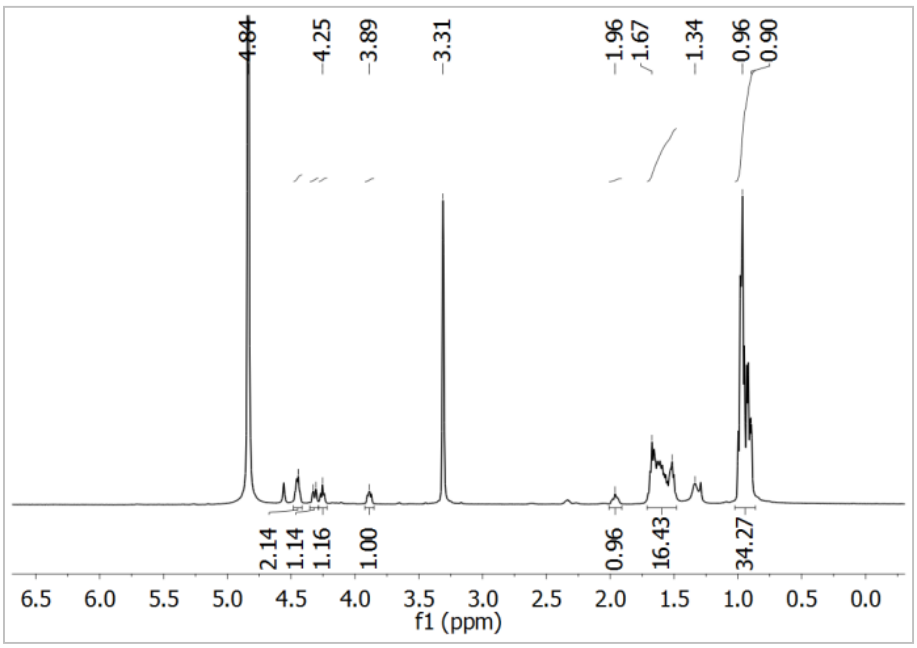


Fig. S33. ^{1}H NMR spectrum of compound **3** in CD_3OD.

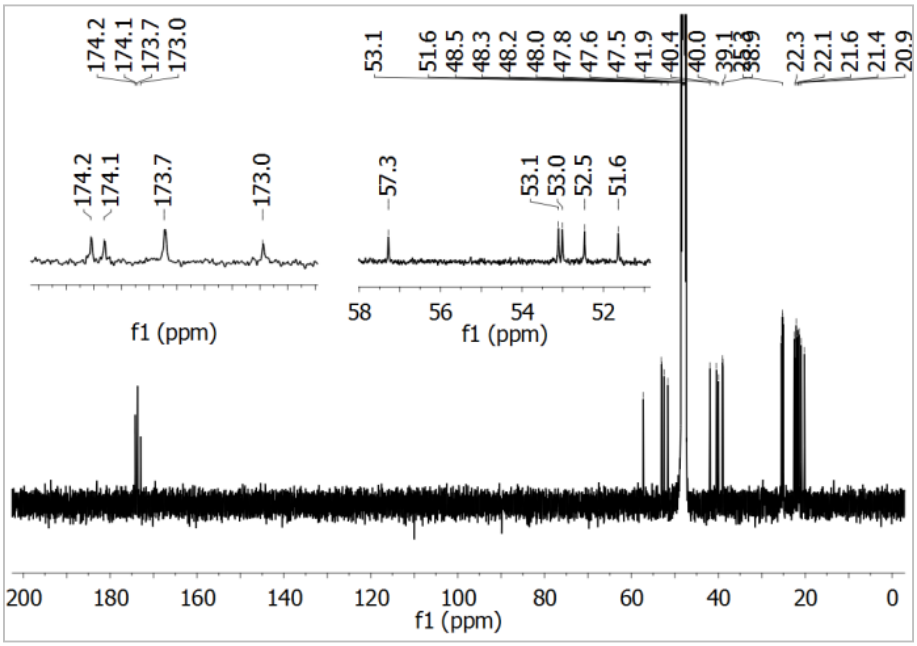


Fig. S34. ^{13}C NMR spectrum of compound **3** in CD_3OD.

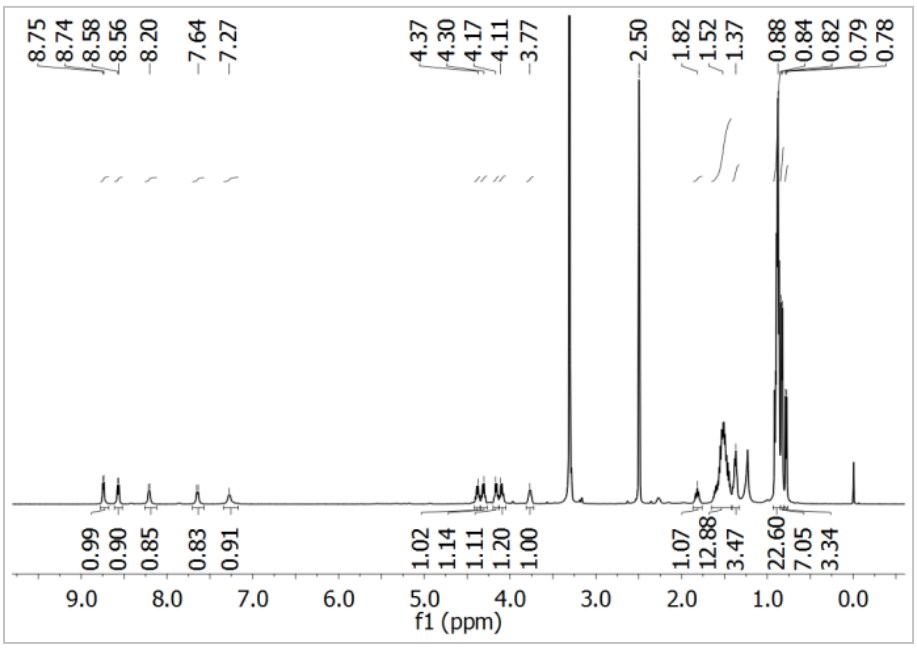


Fig. S35. ^{1}H NMR spectrum of compound **3** in DMSO-d_6.

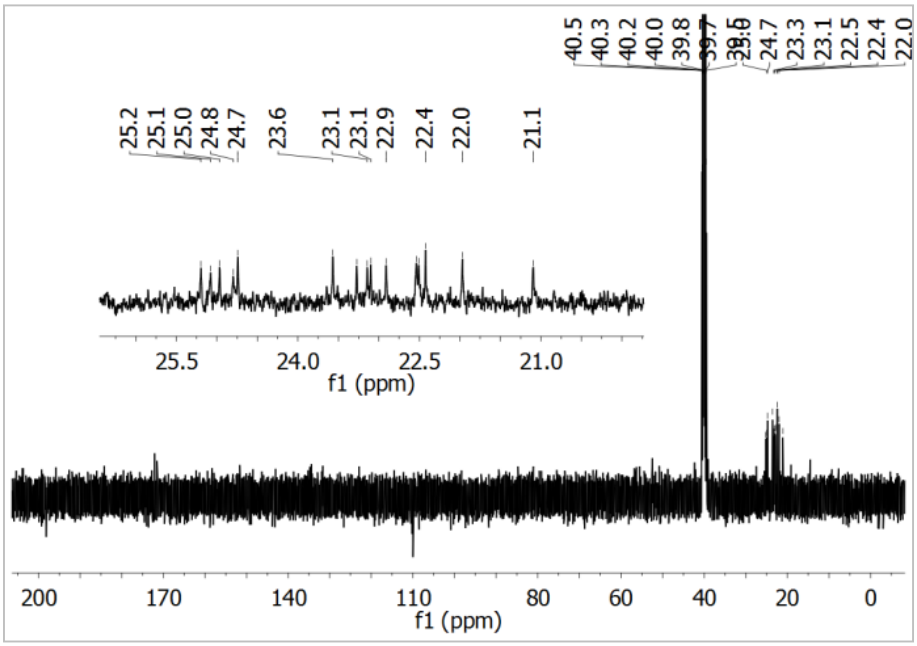


Fig. S36. ^{13}C NMR spectrum of compound **3** in DMSO-d_6.

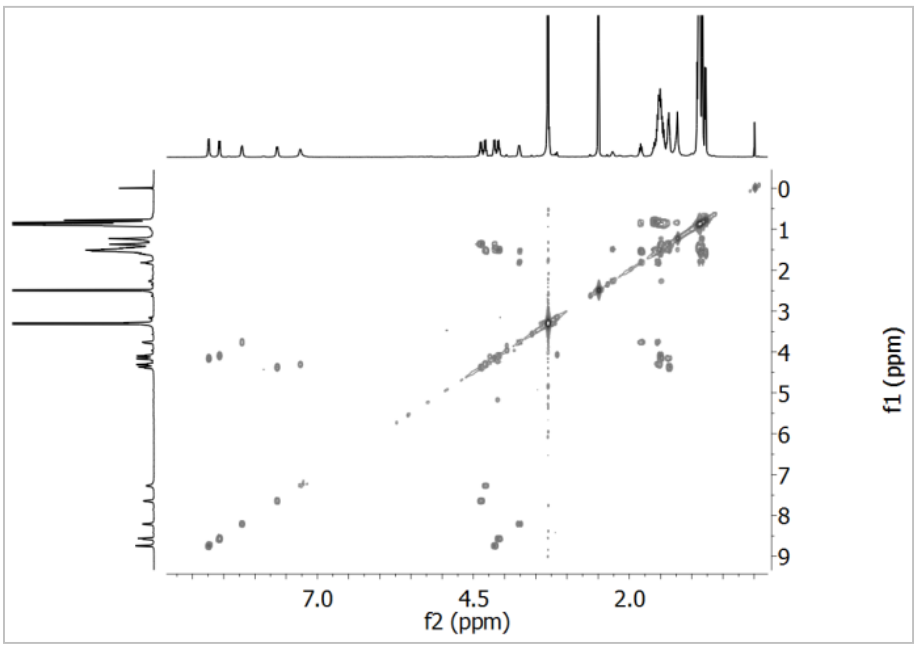


Fig. S37. ^{1}H-^{1}H COSY spectrum of compound **3** in DMSO-d_6.

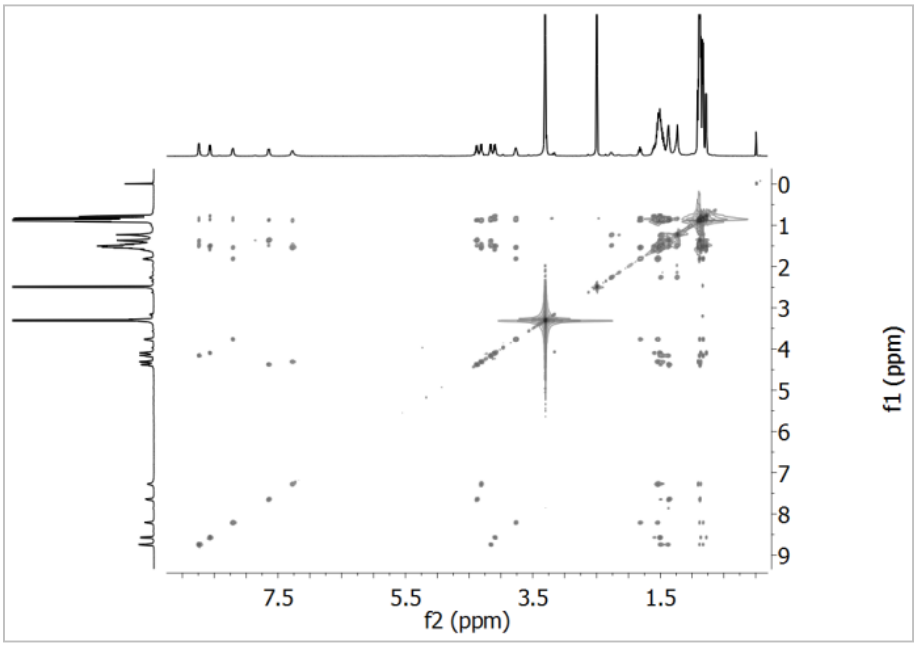
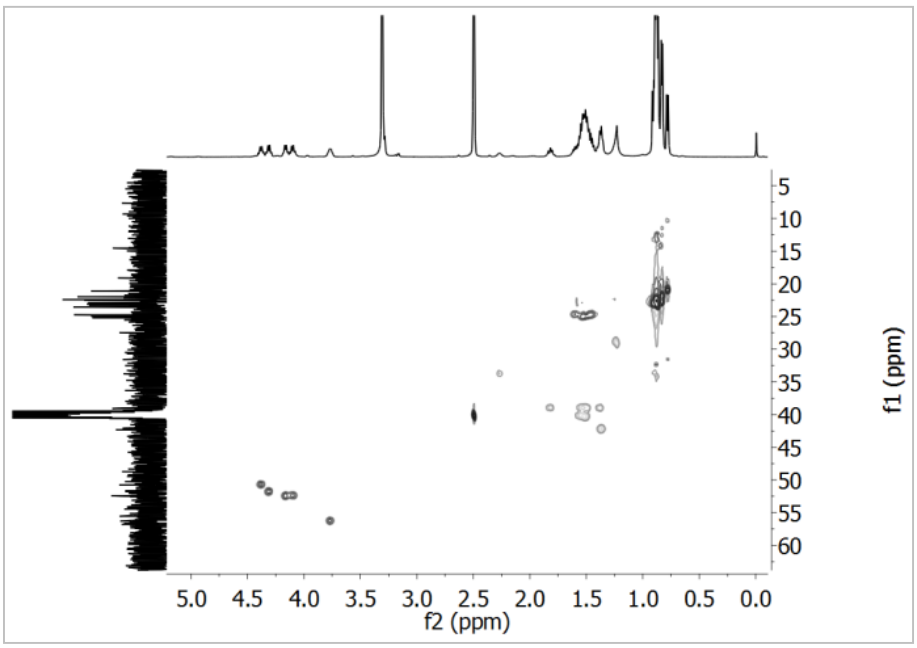


Fig. S38. TOCSY spectrum of compound **3** in DMSO-d_6.



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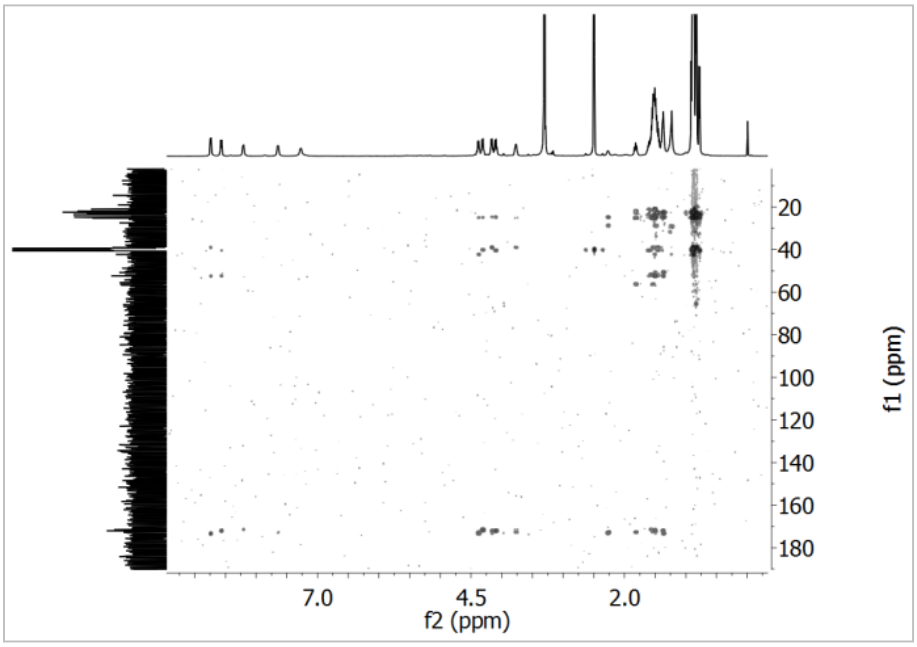

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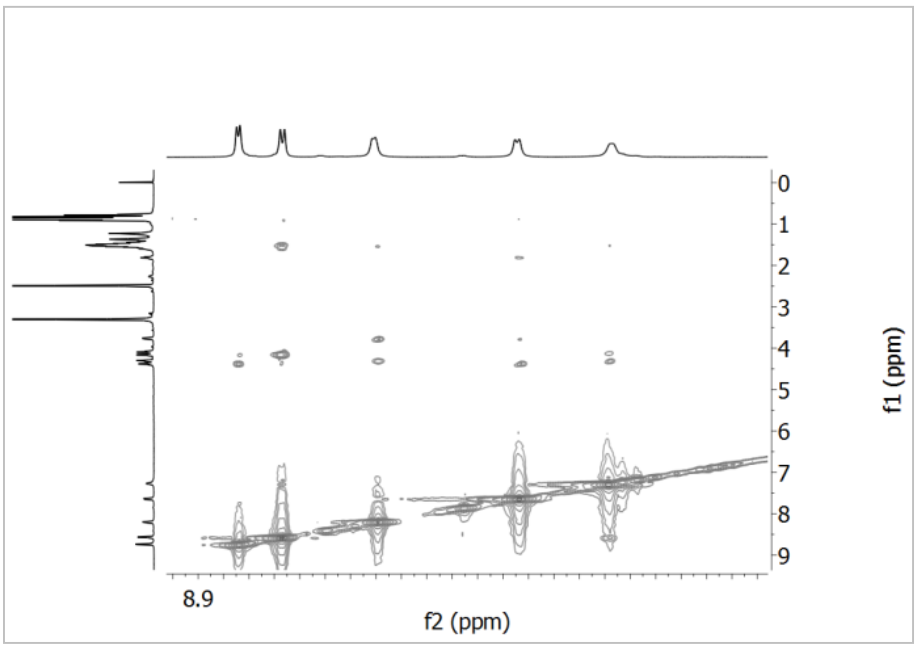

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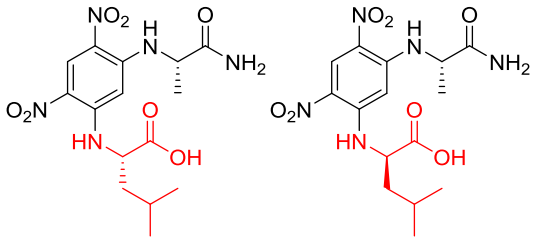

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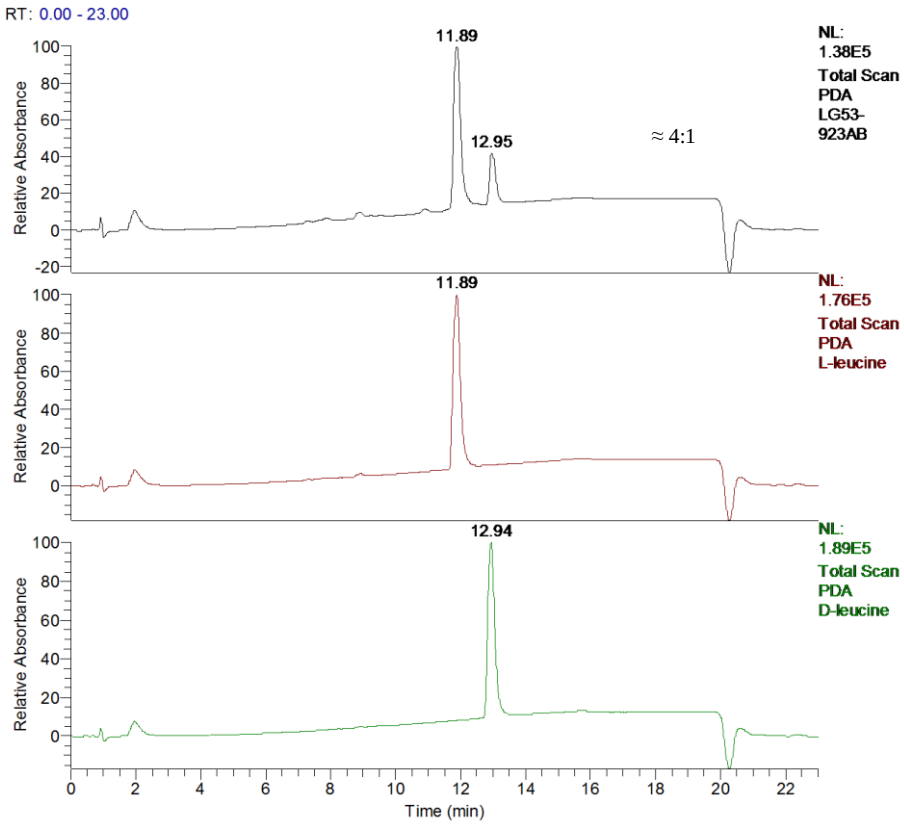

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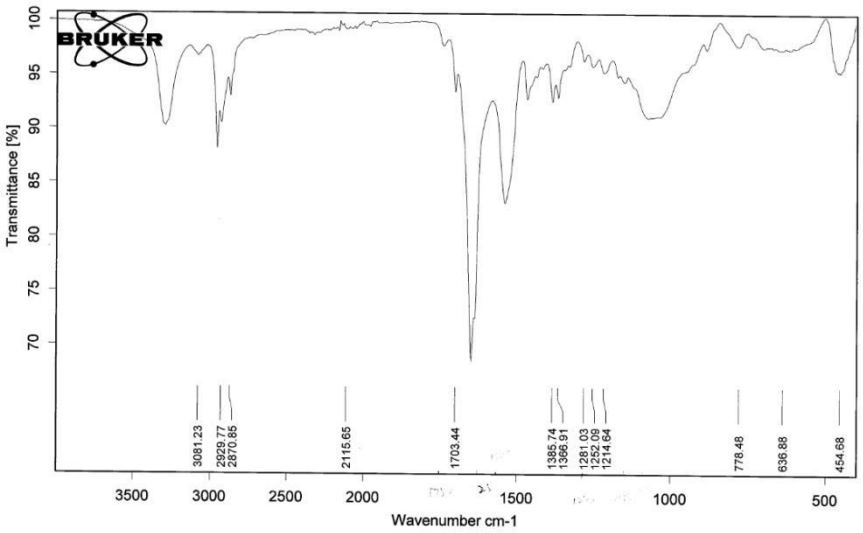

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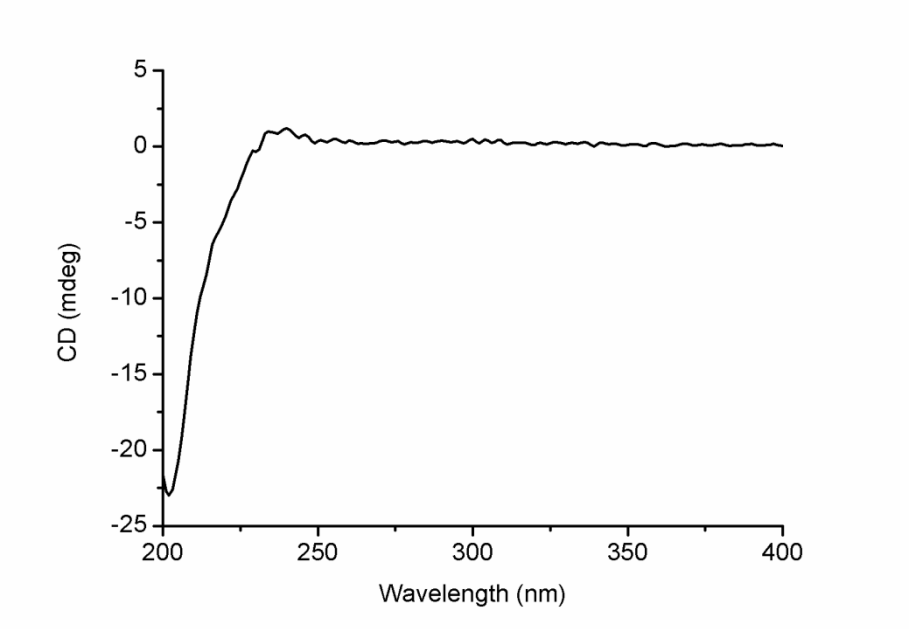


Fig. S45. CD spectrum of compound **3**.

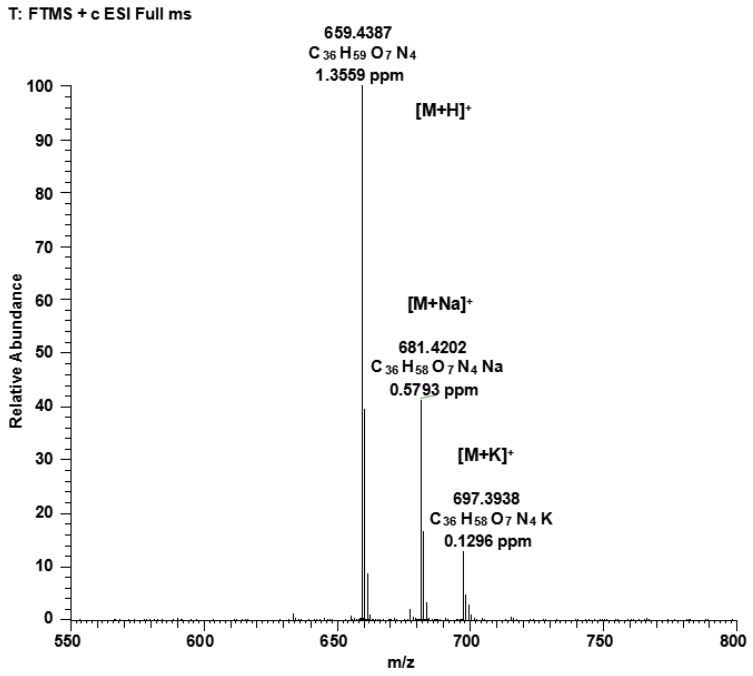


Fig. S46. Positive ESI-HRMS spectrum of compound **4**.

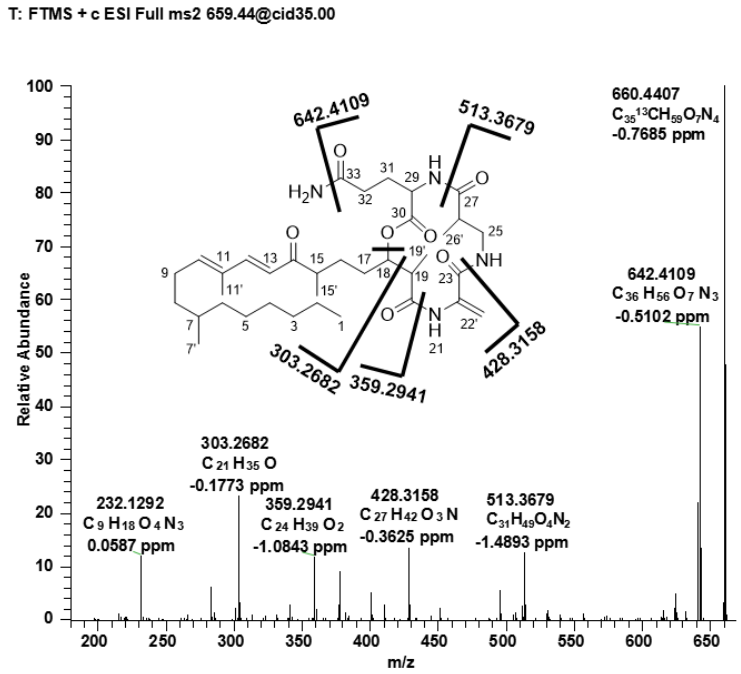


Fig. S47. Positive ESI-HRMS/MS spectrum of compound **4**.

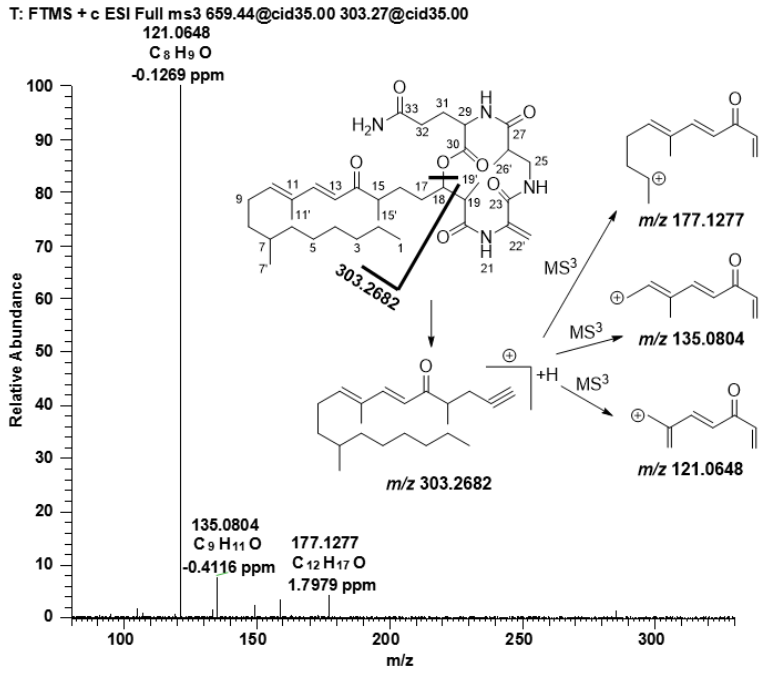


Fig. S48. Positive ESI-HR-MS^3 spectrum of compound **4**.

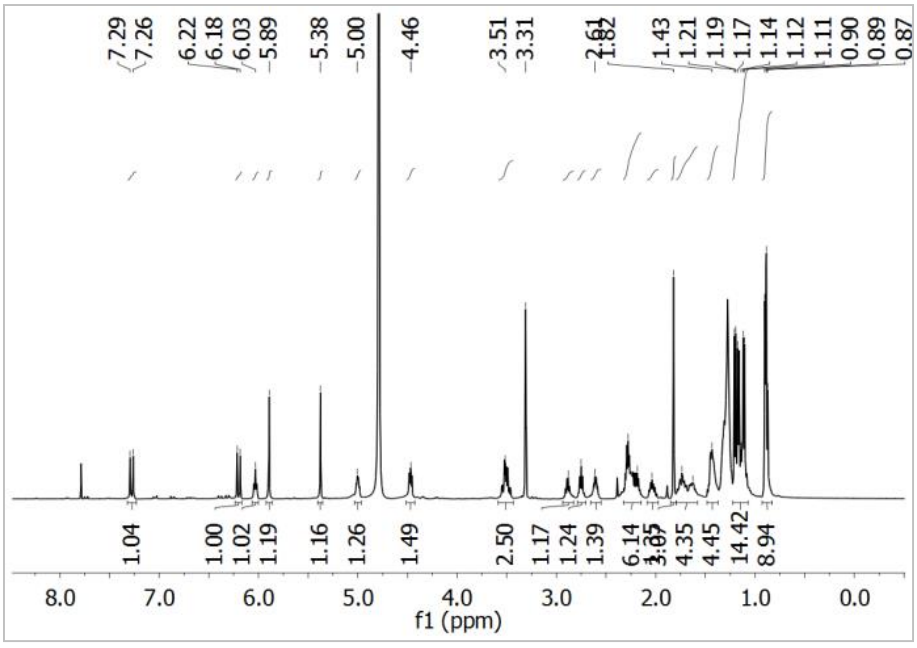


Fig. S49. ^{1}H NMR spectrum of compound **4** in $CDCl_3$/CD_3OD (1:3).

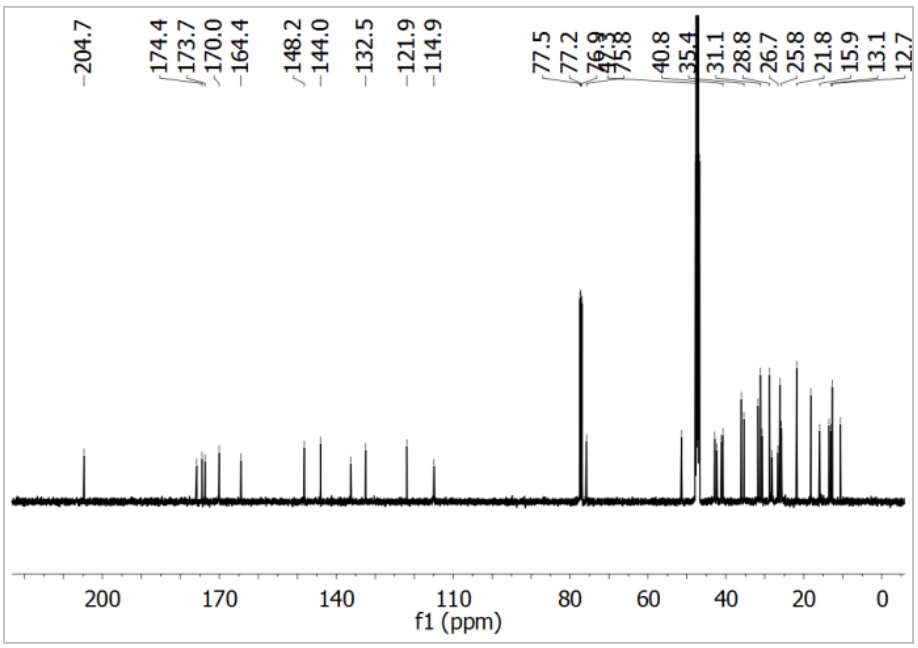


Fig. S50. ^{13}C NMR spectrum of compound **4** in $CDCl_3/CD_3OD$ (1:3).

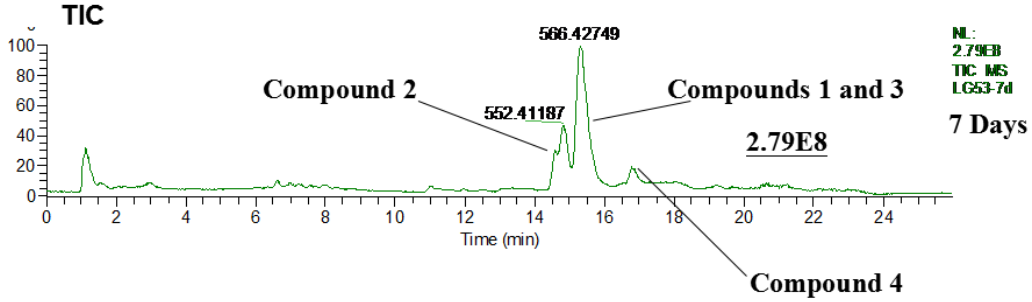


Fig. S51. LC-HRMS positive full-scan chromatogram of compounds **1**–**4** from *Fusarium decemcellulare* LG53 on PDA medium.

Fig. S52. High resolution EICs (extracted ion chromatograms) of the selected mass of compound **4** (*m/z* 659.4378, $[M+H]^+$) of the extracts from fungi on PDA.

Note: all the fungal cultures in Petri dishes (7 days, PDA media) were processed for LC-MS measurement in the same way. They were extracted by 50 mL MeOH and then concentrated to get a 5 mL MeOH extract. 200 μL MeOH extract was used and then diluted into 800 μL MeOH for LC-MS measurement. The concentration of compound **4** for LC-MS measurement was 10 μg/mL. The experiment was done in triplicate.

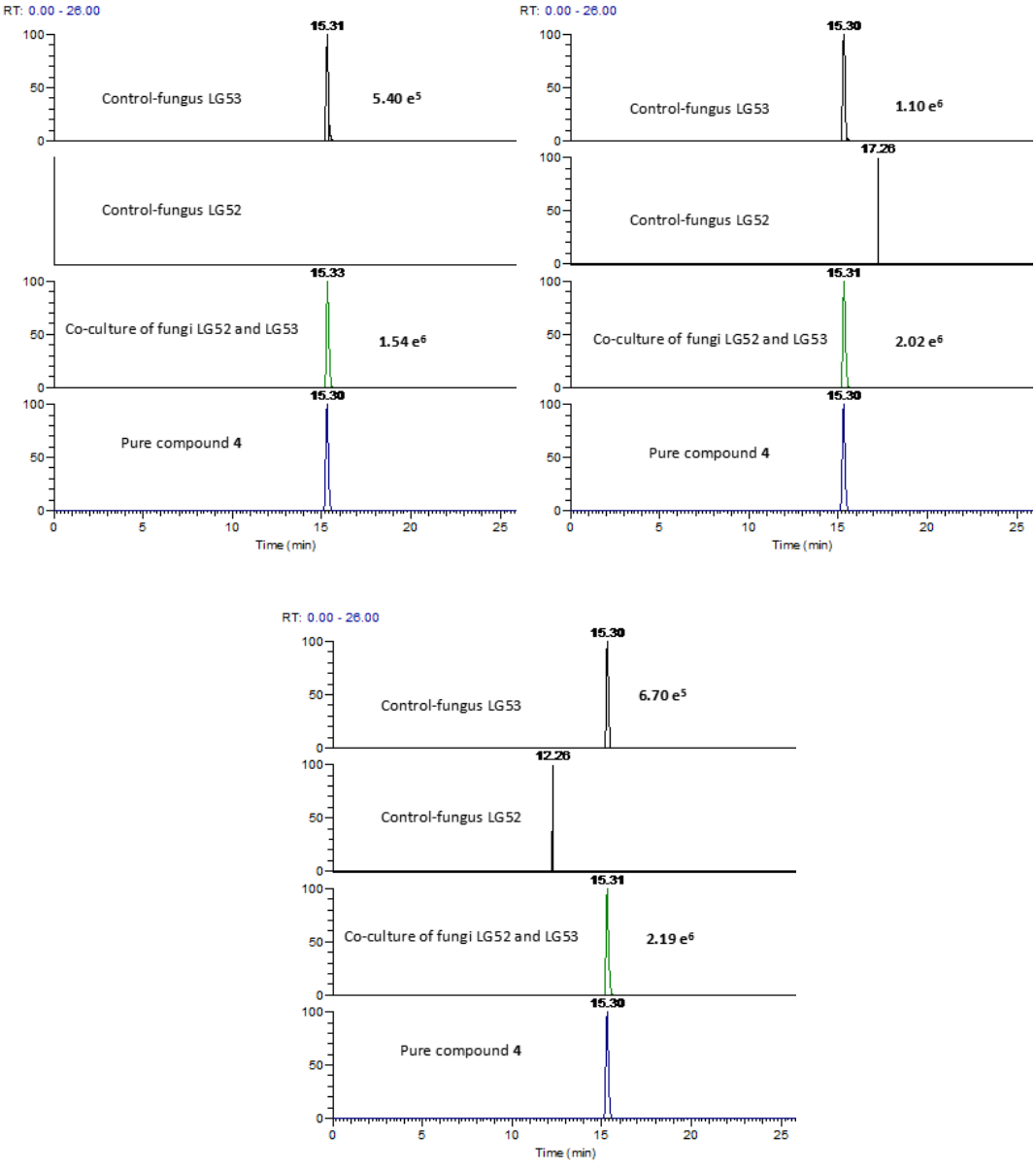


Fig. S53. High resolution EICs (extracted ion chromatograms) of the selected mass of compound **4** (*m/z* 659.4378, $[M+H]^+$) of the extracts from fungi in liquid PDB media.

Note: all the fungal cultures in 100 mL PDB media (7 days) were processed for LC-MS measurement in the same way. They were extracted by 100 mL EtOAc and then concentrated to get a dry extract. 5 mL MeOH was employed to dissolve the extract. 200 μL MeOH extract was used and then diluted into 800 μL MeOH for LC-MS measurement. The concentration of compound **4** for LC-MS measurement was 10 μg/mL. The experiment was done twice.

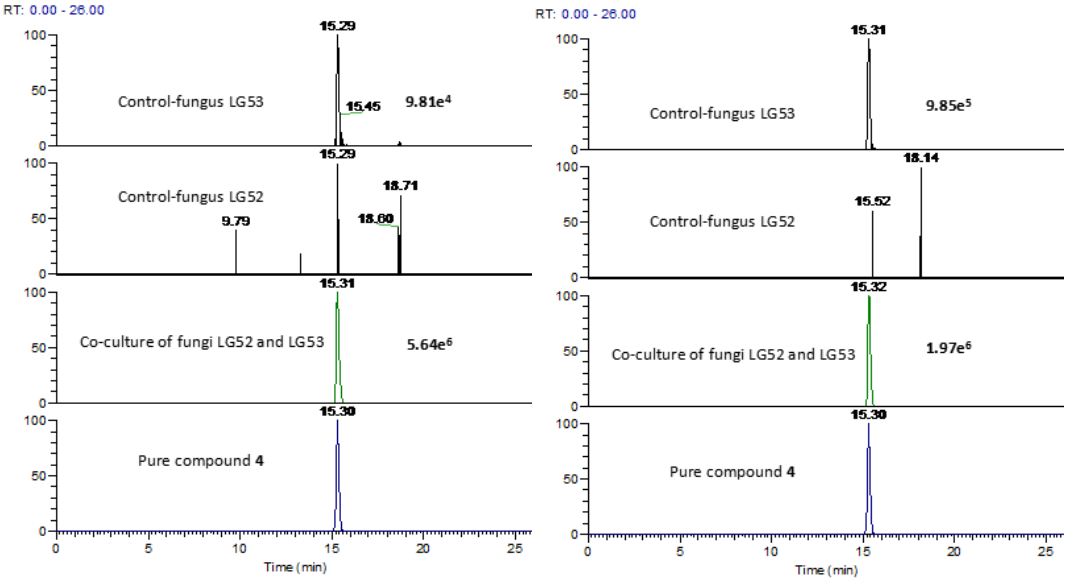
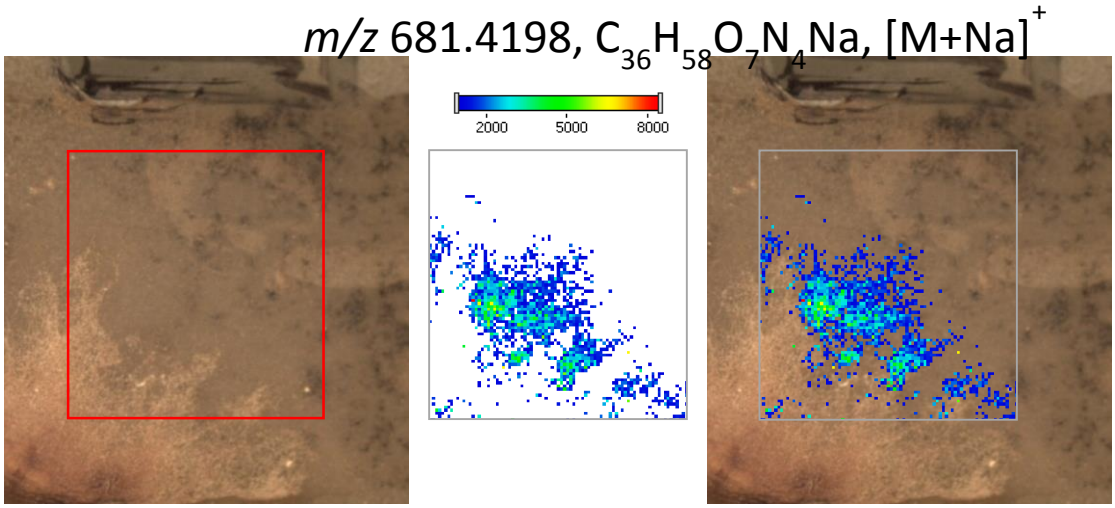


Fig. S54. The positive control of *F. decemcellulare* LG53 (7 days culture) for MALDI-imaging-MS.

Note: the red box indicates the measured area.



S55. Identification of the endophytic fungi.

For identification, the fungal strain LG53 was cultured on potato dextrose agar (PDA) at 28 ± 2 ºC for one week in an incubator. The total genomic DNA (gDNA) of the fungus was then extracted using peqGOLD fungal DNA mini kit (Peqlab Biotechnologie GmbH, Germany) strictly following the manufacturer's guidelines. The DNA was then subjected to PCR amplification using primers ITS4 and ITS5 according to White *et al*. (1990).[1] The amplified fragment consisted of ITS1, 5.8S and ITS2 regions of the rDNA. The PCR reaction was performed in 50 µL reaction mixture containing 45 µL Red Taq DNA Polymerase Master Mix (1.1x), 0.5 µL forward primer (100 µM), 0.5 µL reverse primer (100 µM), 3 µL template DNA and 1 µL of sterile

double-distilled water. The PCR cycling protocol consisted of an initial denaturation at 95 ºC for 2 min, 30 cycles of denaturation, annealing and elongation at 95 ºC for 30 s, 54 ºC for 40 s and 72 ºC for 30 s. This was followed by a final elongation step at 72 ºC for 5 min. As a negative control, the template DNA was replaced by sterile double-distilled water. The PCR amplified products spanning approximately 500-600 bp (base pairs) were checked by gel electrophoresis. The PCR products were purified using GFX^{TM} PCR DNA and Gel Band Purification kit (GE Healthcare Life Sciences, Germany) following the manufacturer's instructions, and sequenced from both directions at GATC Biotech (Cologne, Germany).

The fungal strain LG52 was also identified using a similar method. Briefly, the fungus was cultured on PDA at 28 ± 2 ºC for one week in an incubator. The total gDNA of the fungus was then extracted by mechanical decomposition and following purification with the DNA-Purification solution from Applichem A34180, strictly following the manufacturer's guidelines. The DNA was then subjected to PCR amplification using primers ITS1 and ITS4 according to White *et al*. (1990).[1] The amplified fragment consisted of ITS1, 5.8S and ITS2 regions of the rDNA. The PCR products were purified using with the kit Chargeswitch (Invitrogen) following the manufacturer's instructions, and sequenced from both directions at LGC GmbH (Berlin, Germany).

References

1. T. J. White, T. D. Bruns, S. Lee and J. W. Taylor, In *Protocols: a guide to methods and applications*. PCR Academic Press: San Diego, 1990; pp 315–322.