Supplementary Information

Figure S1. ^{1}H NMR Spectrum for milnamide E (**1**) in DMSO-d_6.

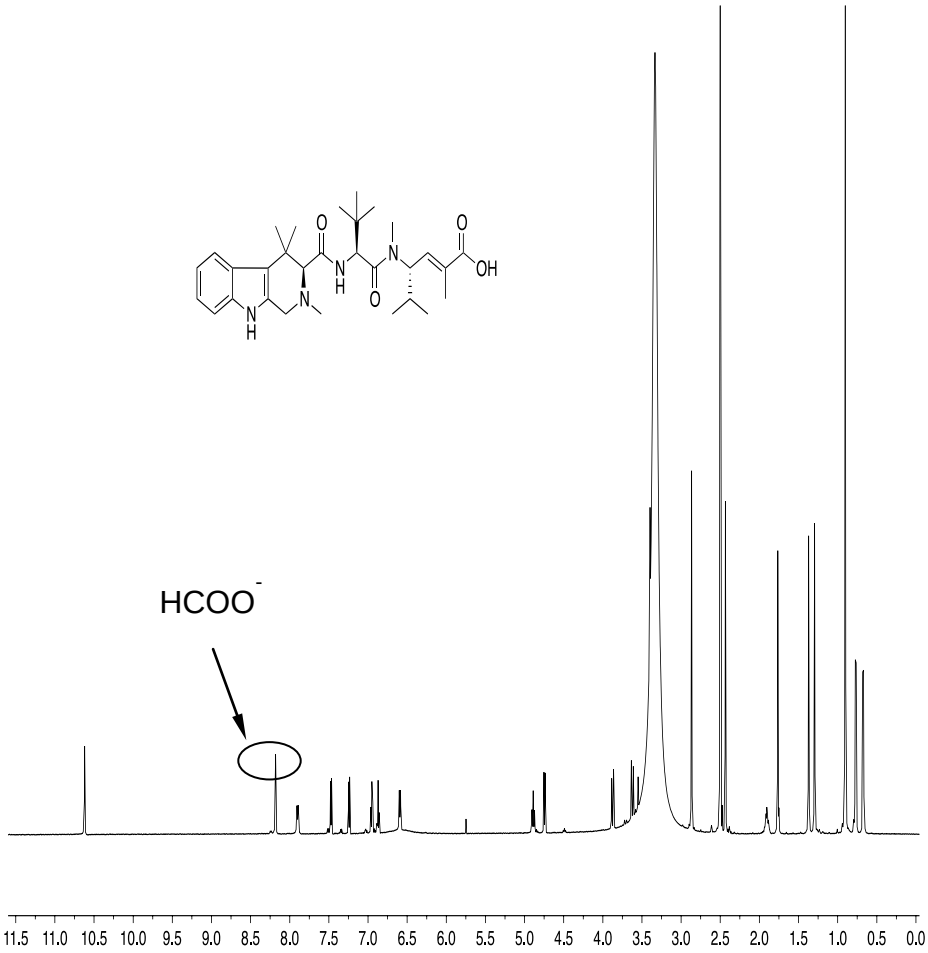


Figure S2. ^{13}C NMR Spectrum for milnamide E (**1**) in DMSO-d_6.

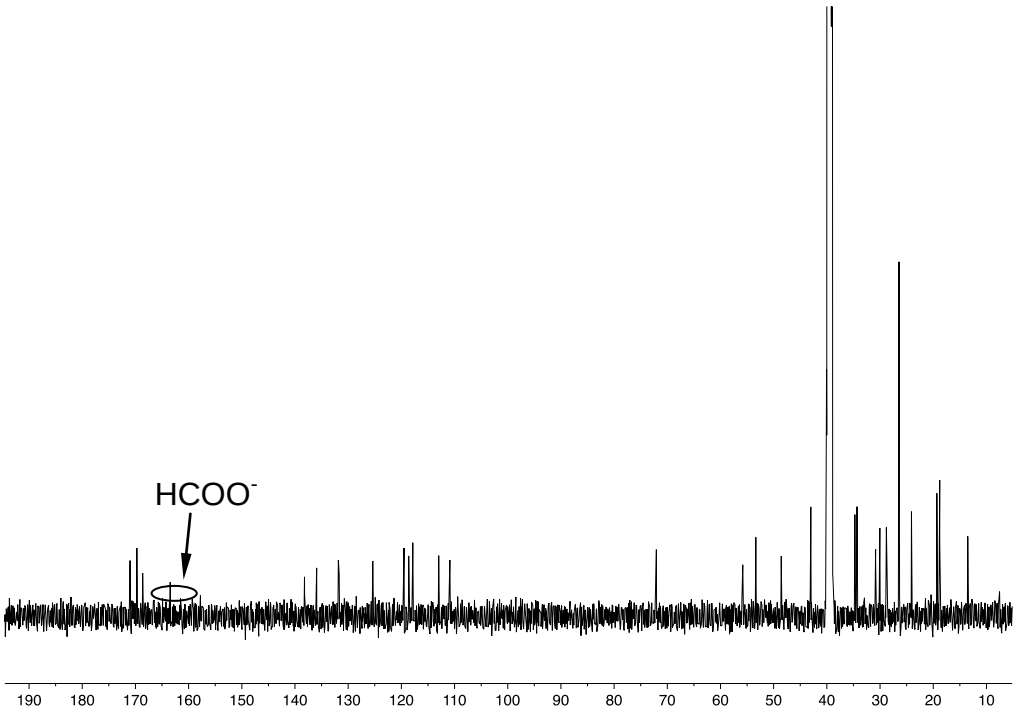


Figure S3. gHSQCAD Spectrum for milnamide E (**1**) in DMSO-d_6.

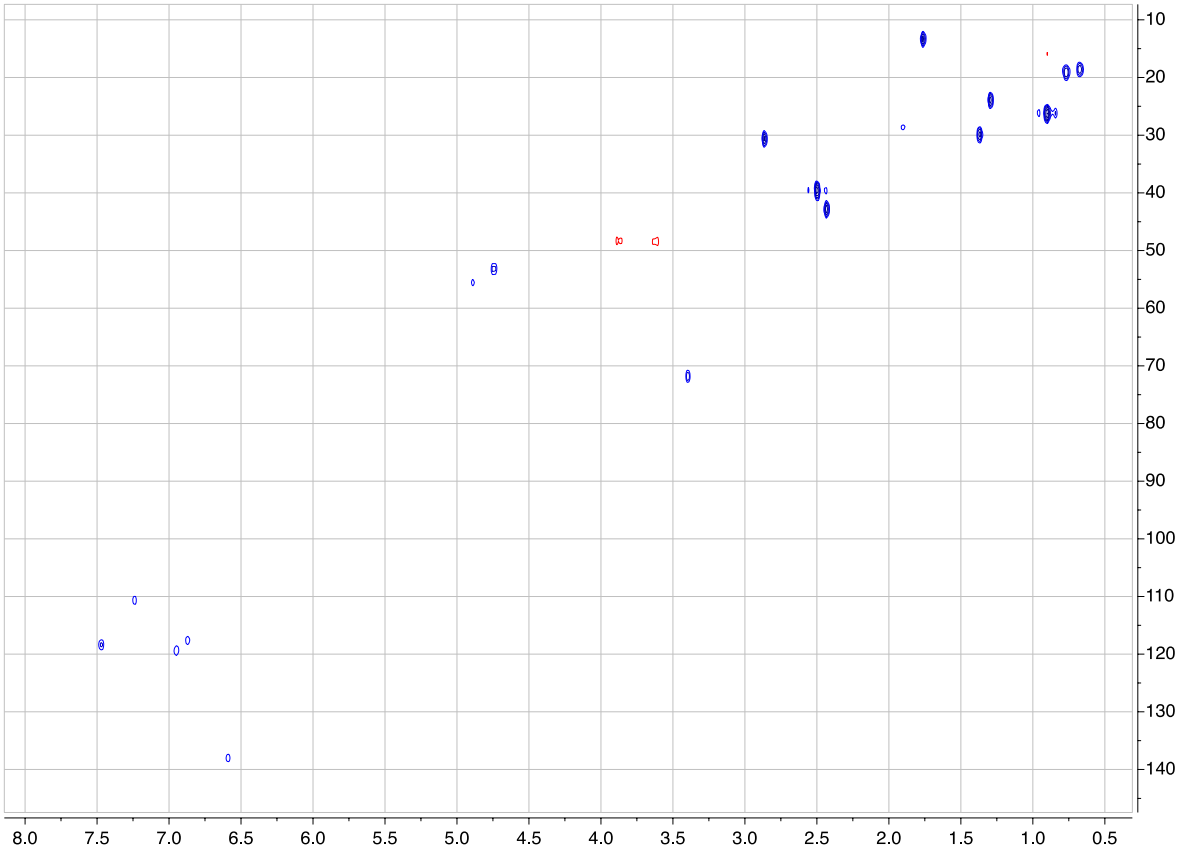


Figure S4. gHMBCAD Spectrum for milnamide E (**1**) in DMSO-d_6.

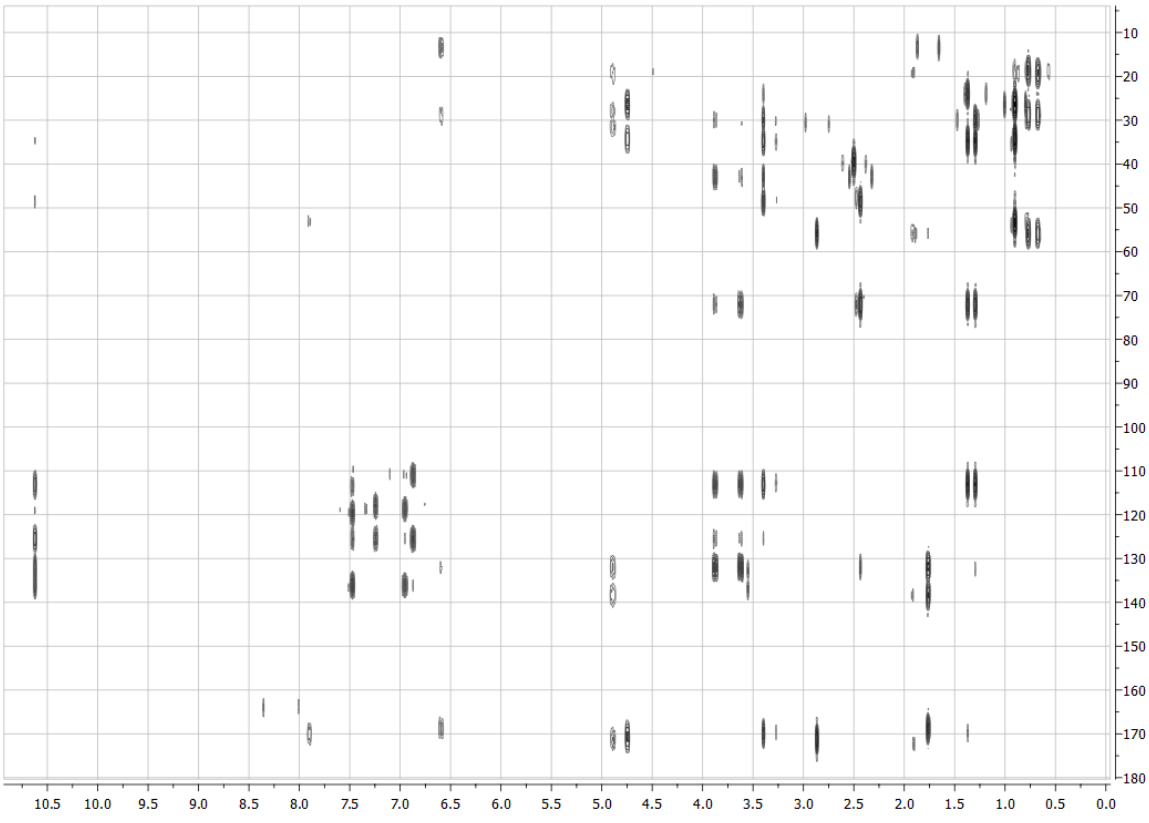


Figure S5. gCOSY Spectrum for milnamide E (**1**) in DMSO-d_6.

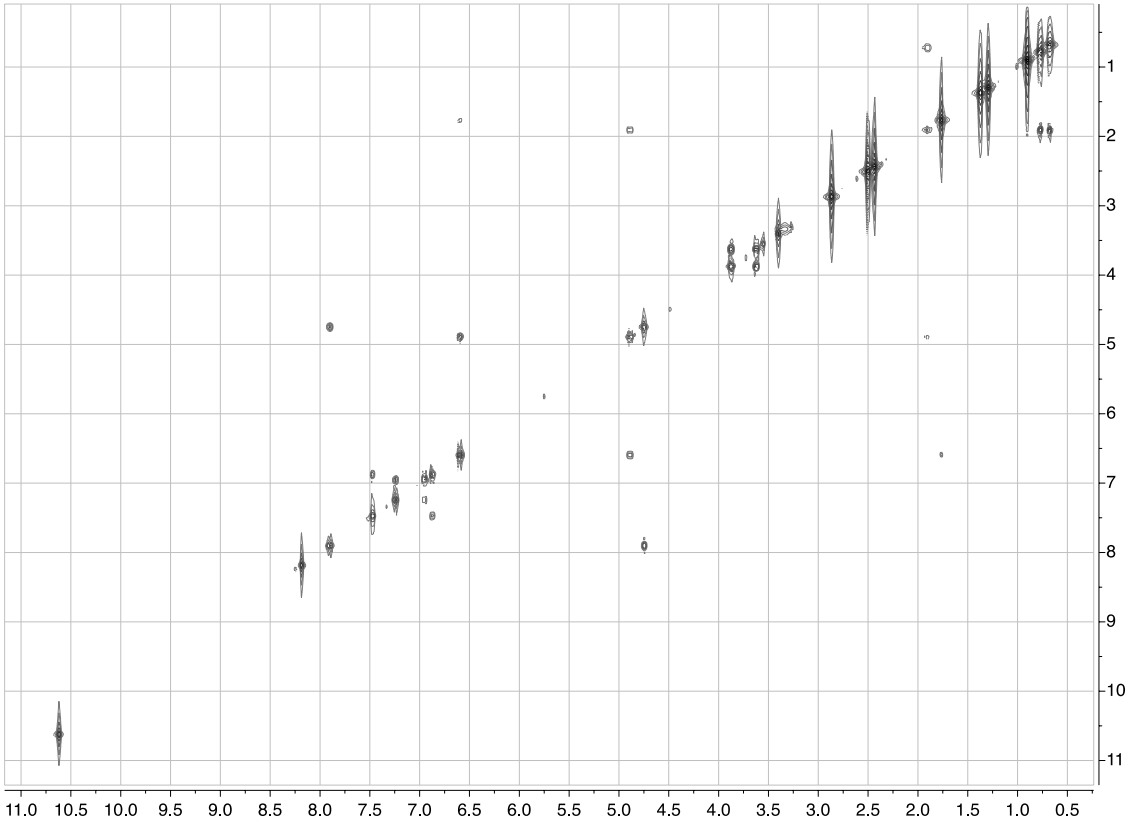


Figure S6. ROESY Spectrum for milnamide E (**1**) in DMSO-d_6.

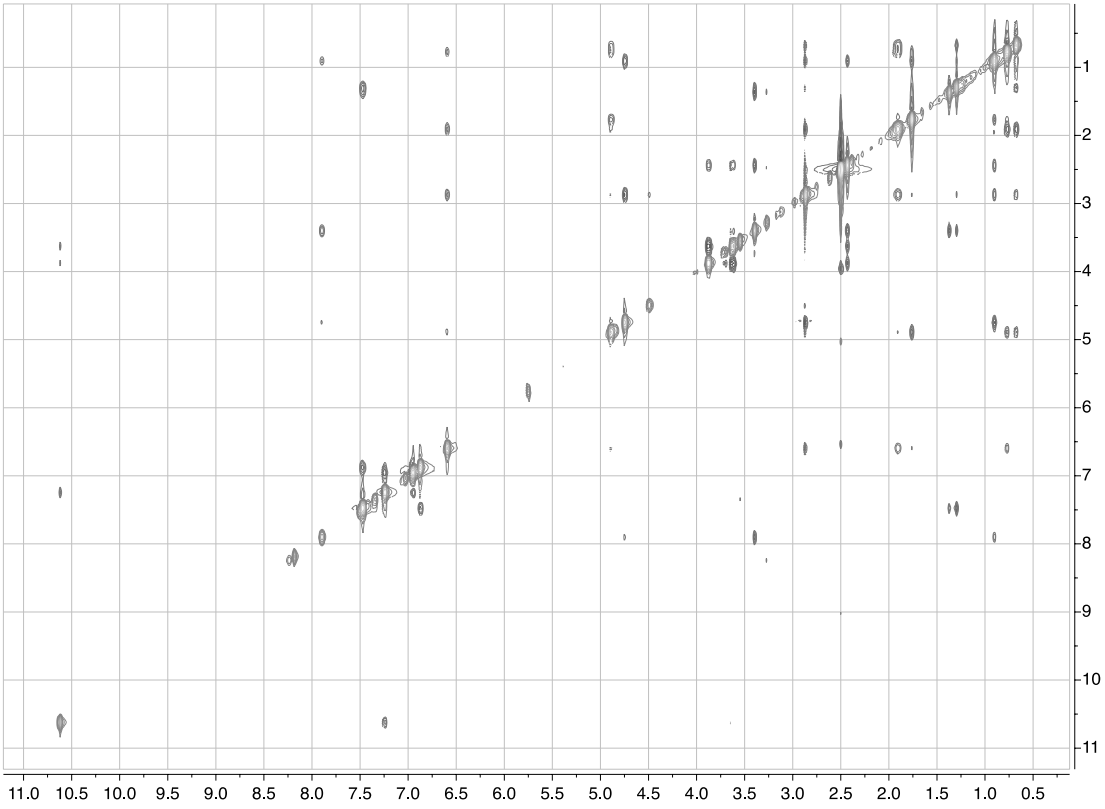


Figure S7. ^{1}H NMR Spectrum for milnamide F (**2**) in DMSO-d_6.

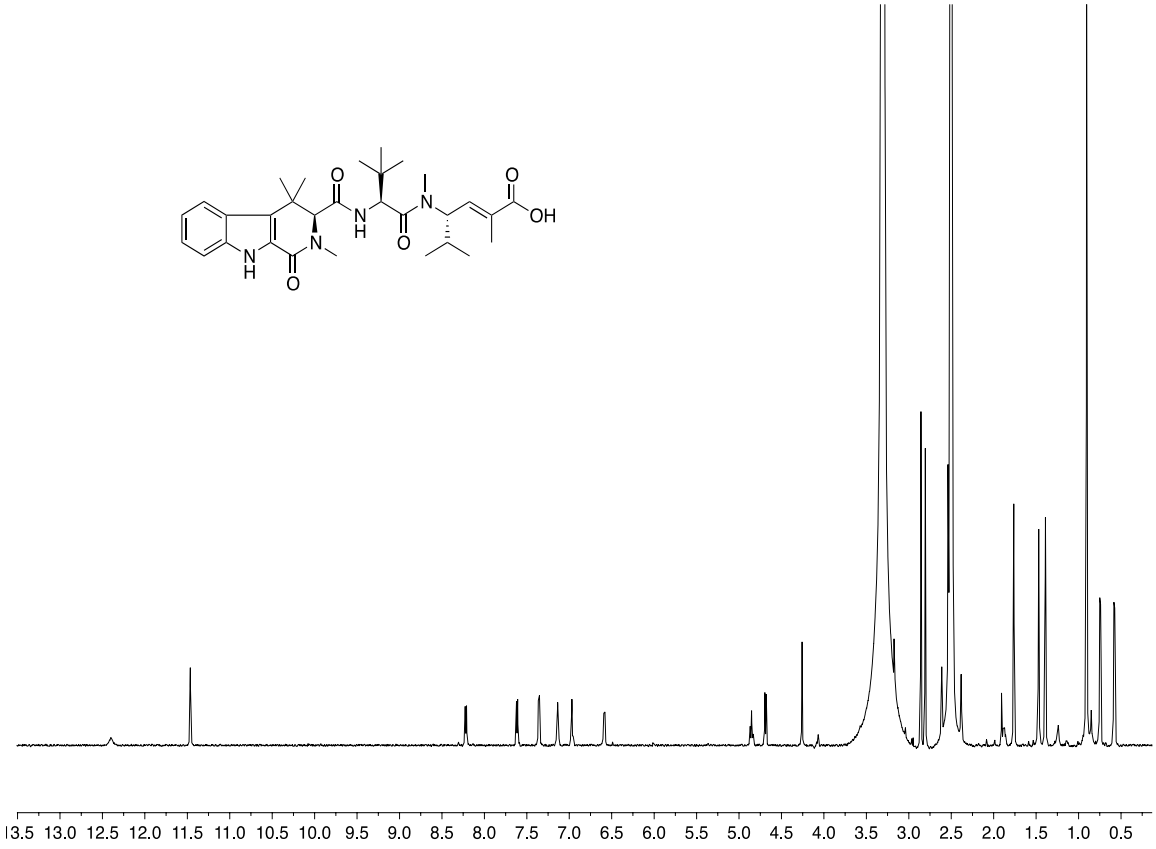


Figure S8. gHSQCAD Spectrum for milnamide F (**2**) in DMSO-d_6.

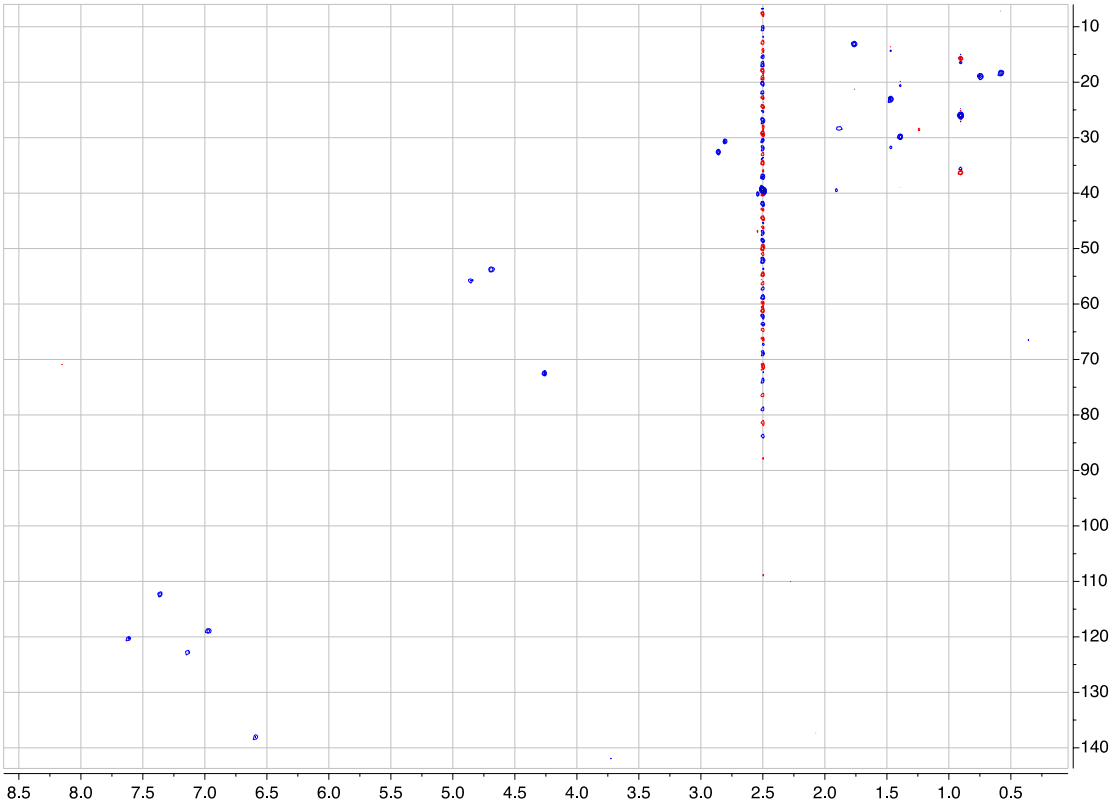


Figure S9. gHMBCAD Spectrum for milnamide F (2) in DMSO-d_6.

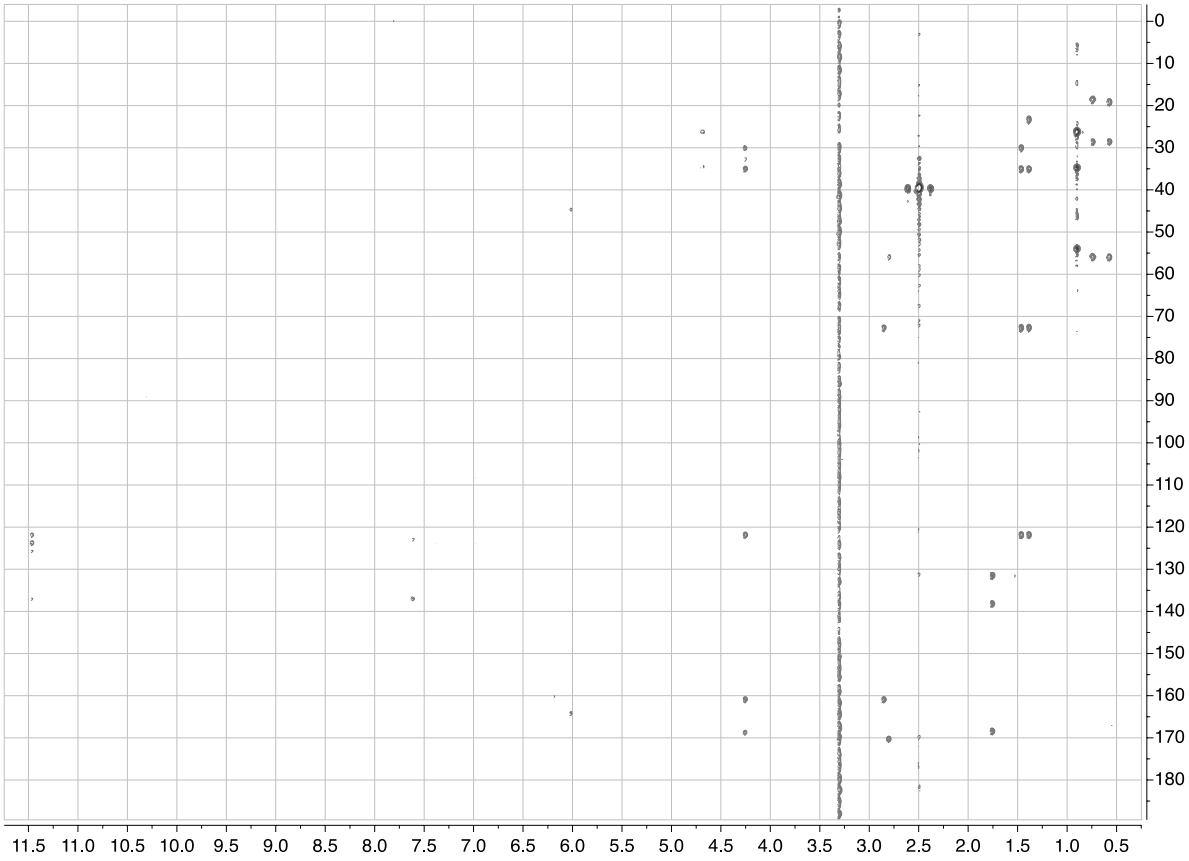


Figure S10. gCOSY Spectrum for milnamide F (**2**) in DMSO-d_6.

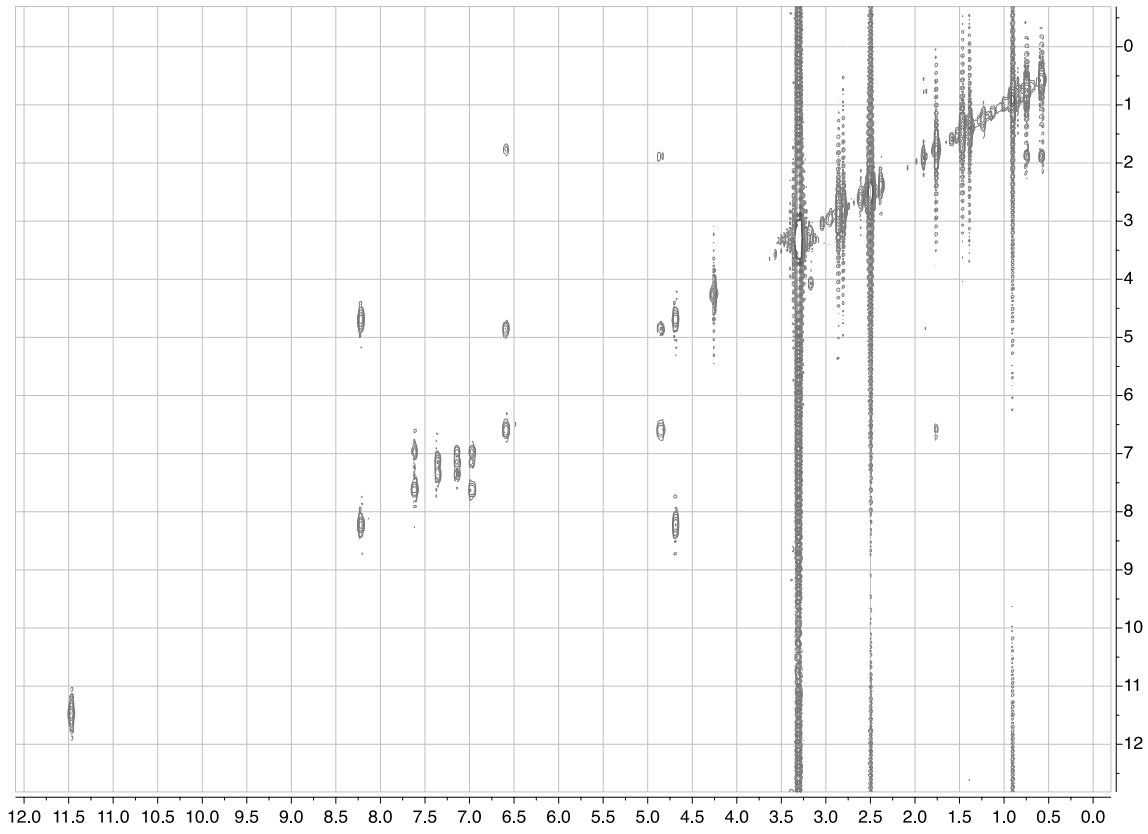


Figure S11. ROESY Spectrum for milnamide F (**2**) in DMSO-d_6.

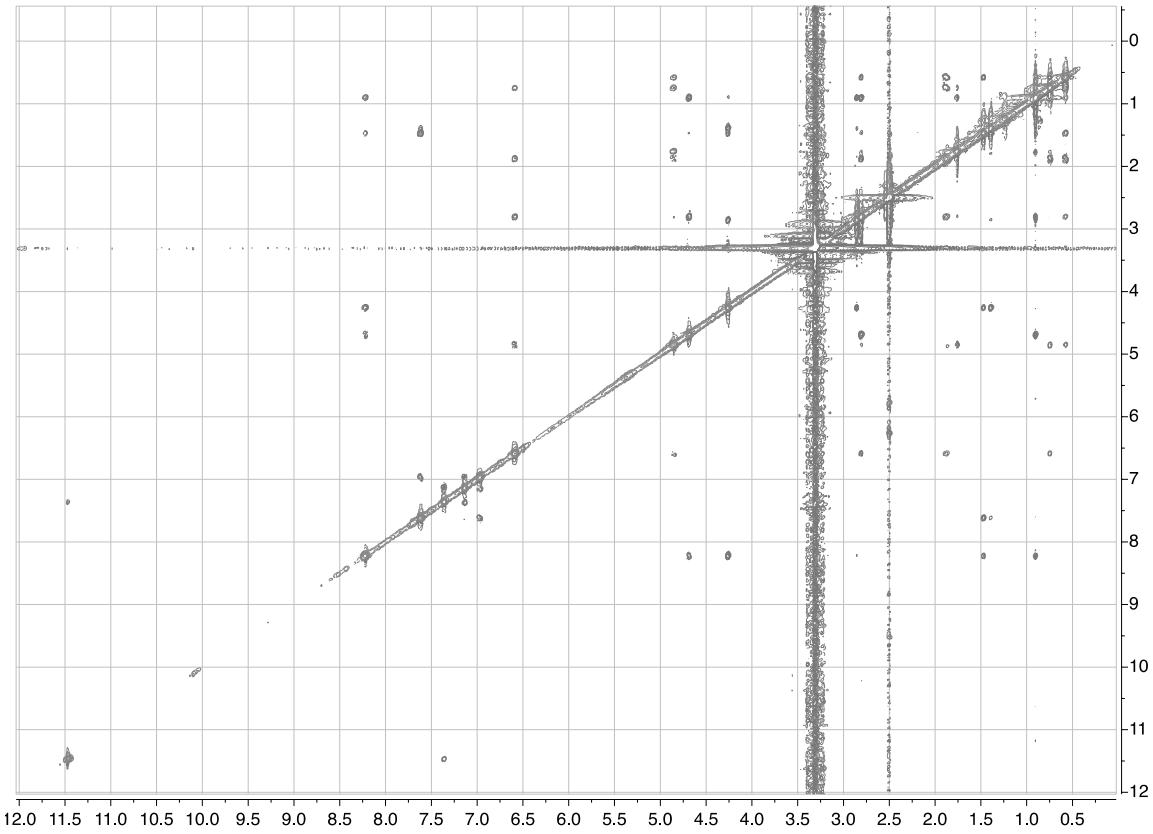


Figure S12. ^{1}H NMR Spectrum for milnamide G (**3**) in DMSO-d_6.

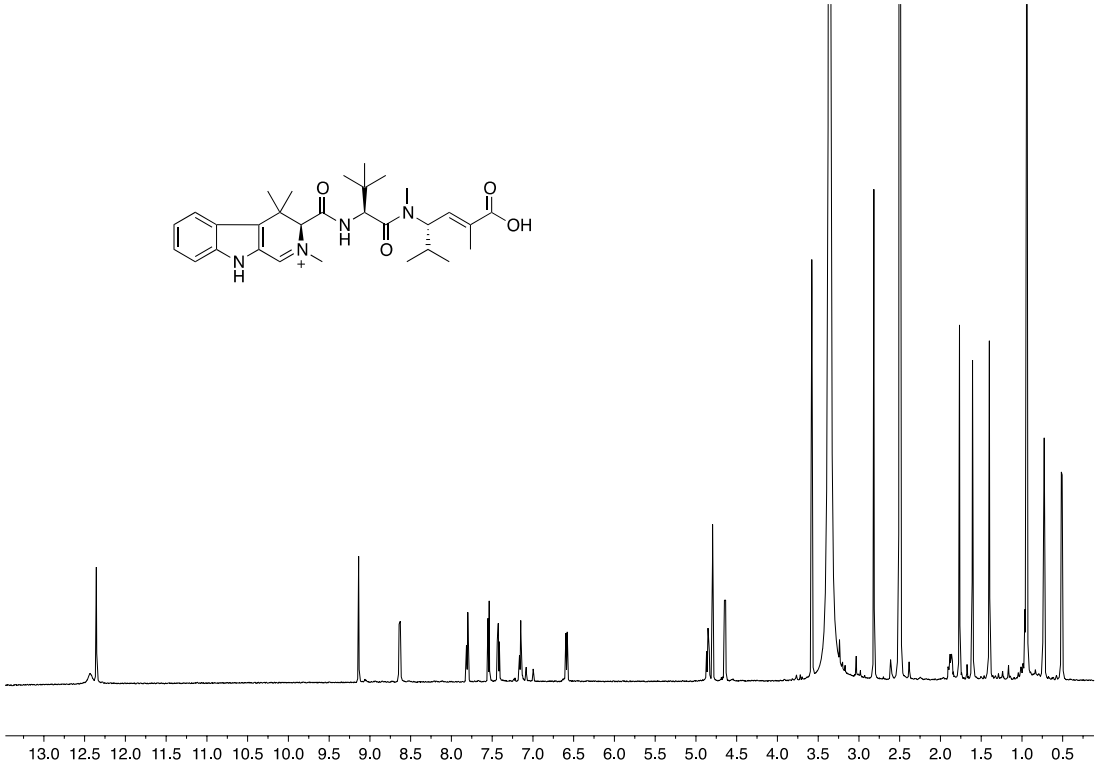


Figure S13. gHSQCAD Spectrum for milnamide G (**3**) in DMSO-d_6.

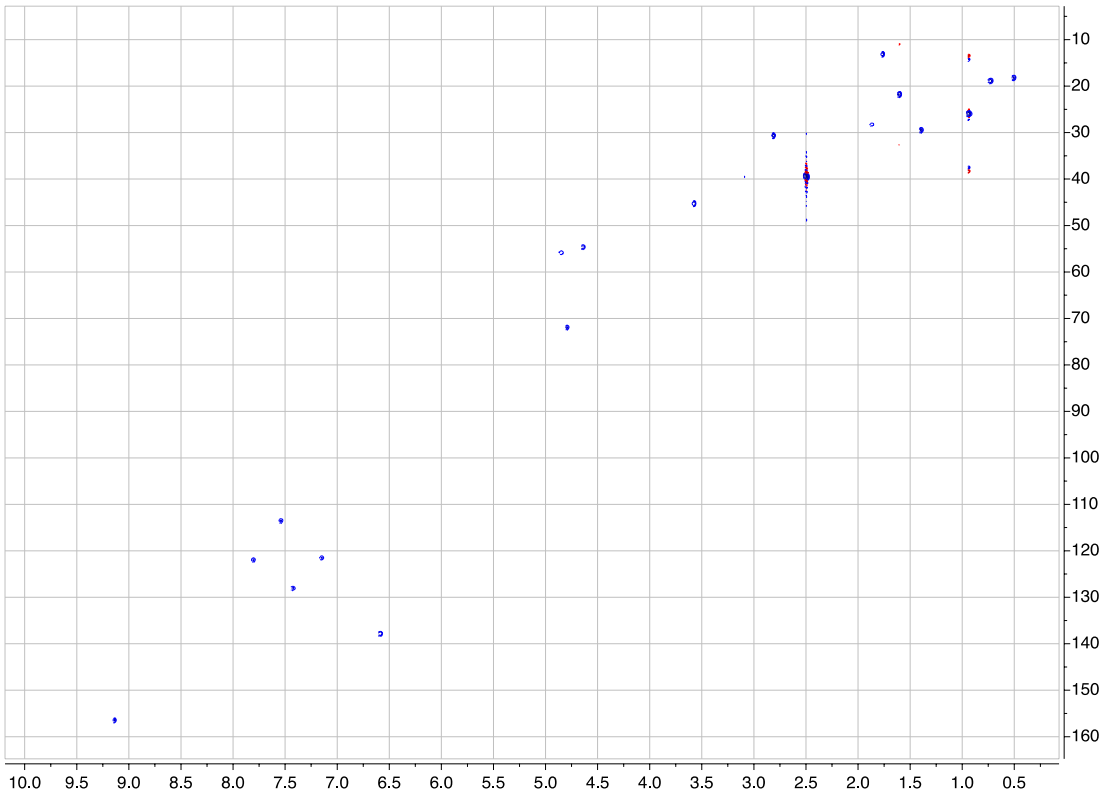


Figure S14. gHMBCAD Spectrum for milnamide G (**3**) in DMSO-d_6.

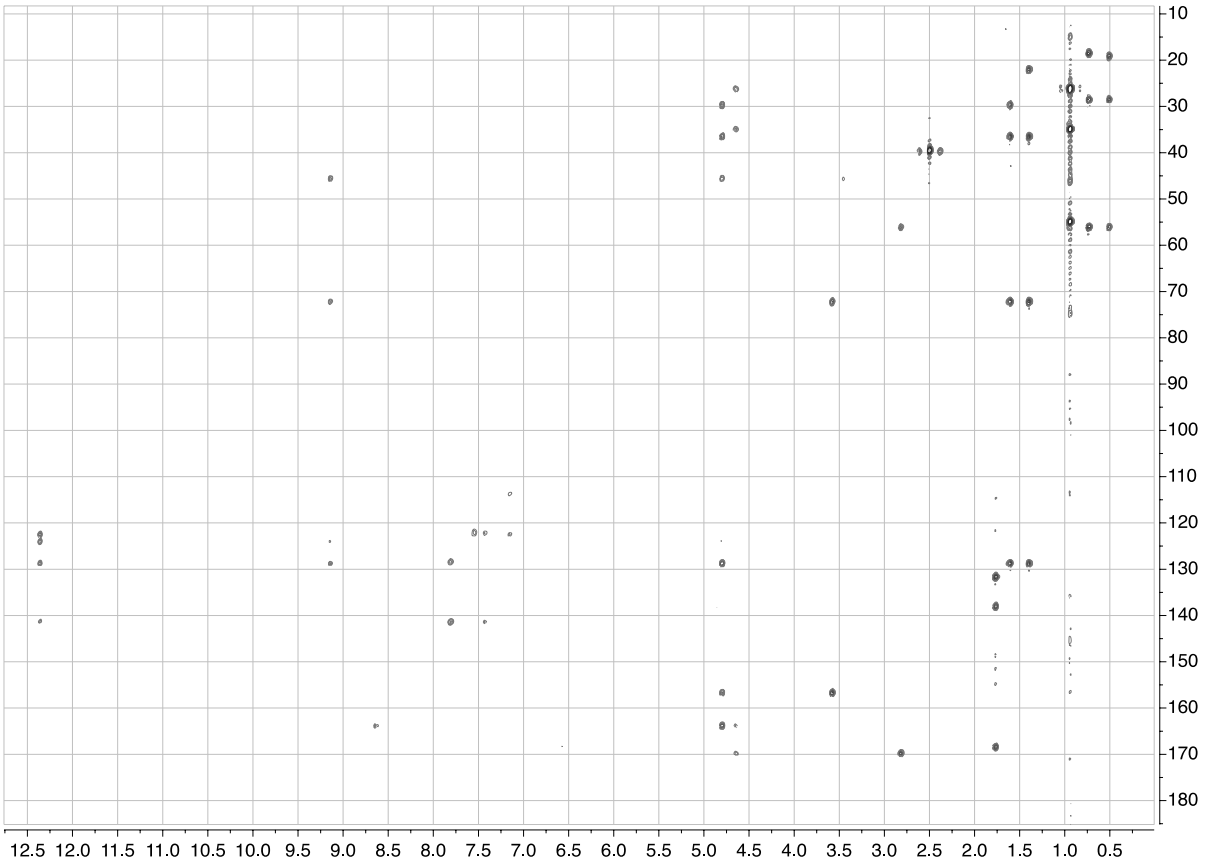


Figure S15. gCOSY Spectrum for milnamide G (**3**) in DMSO-d_6.

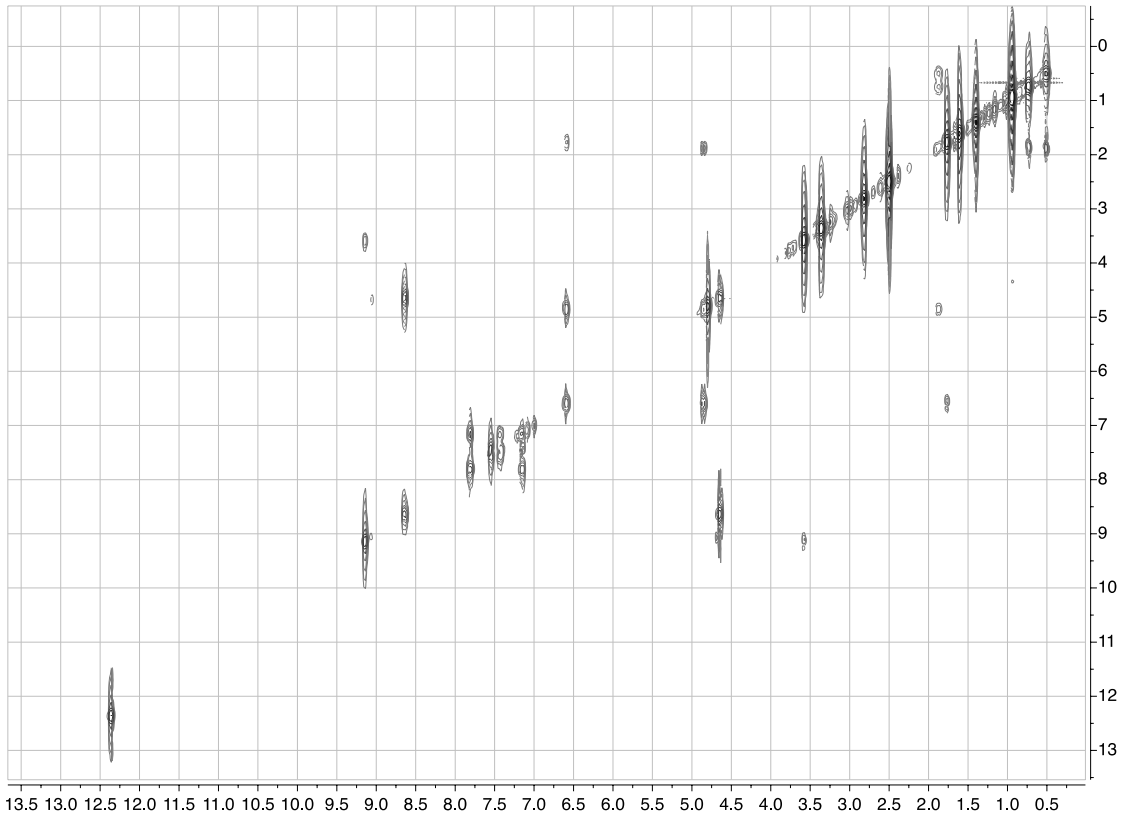


Figure S16. ROESY Spectrum for milnamide G (**3**) in DMSO-d_6.

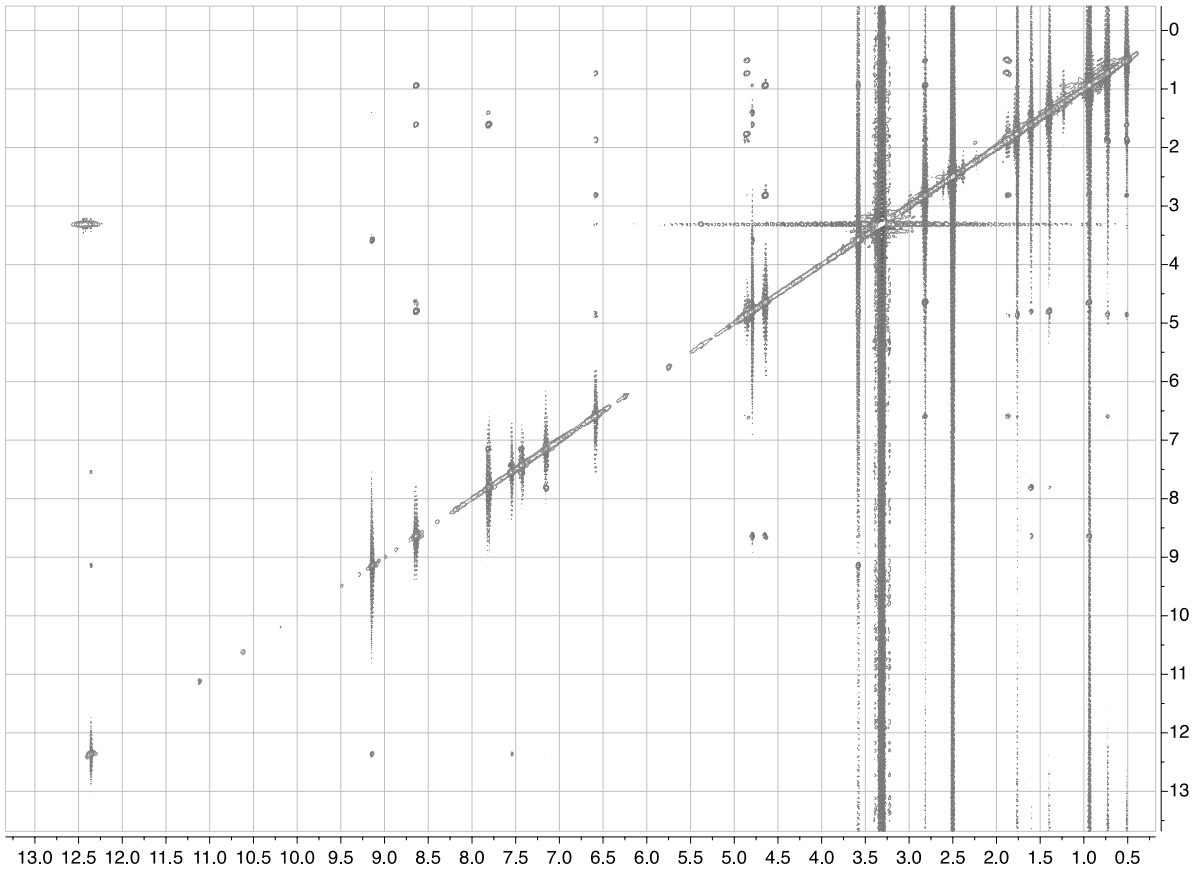


Figure S17. ^{1}H NMR Spectrum for hemiasterlin D (**4**) in DMSO-d_6.

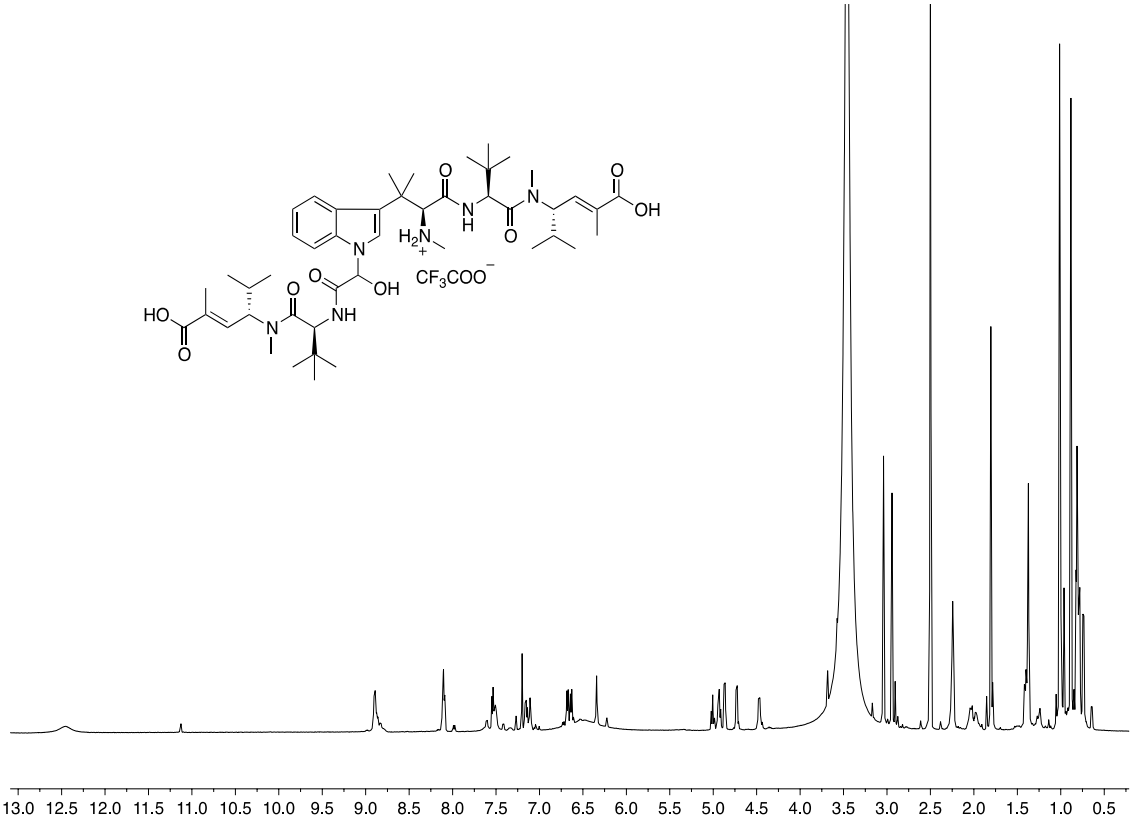


Figure S18. gHSQCAD Spectrum for hemiasterlin D (**4**) in DMSO-d_6.

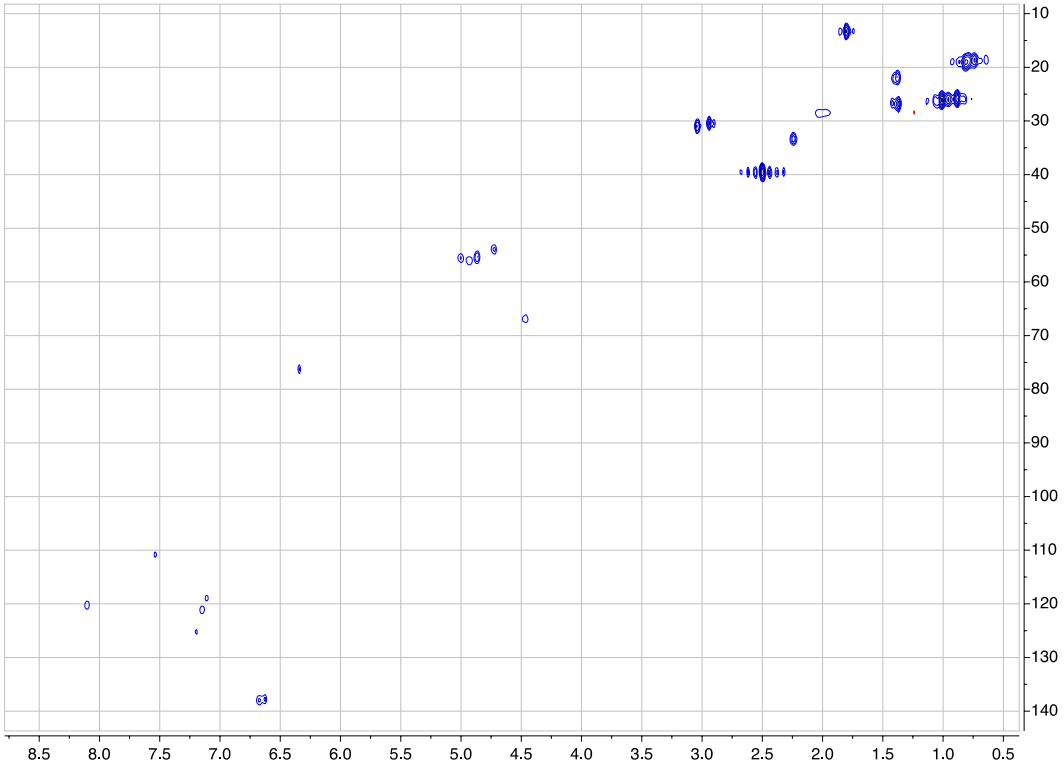


Figure S19. gHMBCAD Spectrum for hemiasterlin D (**4**) in DMSO-d_6.

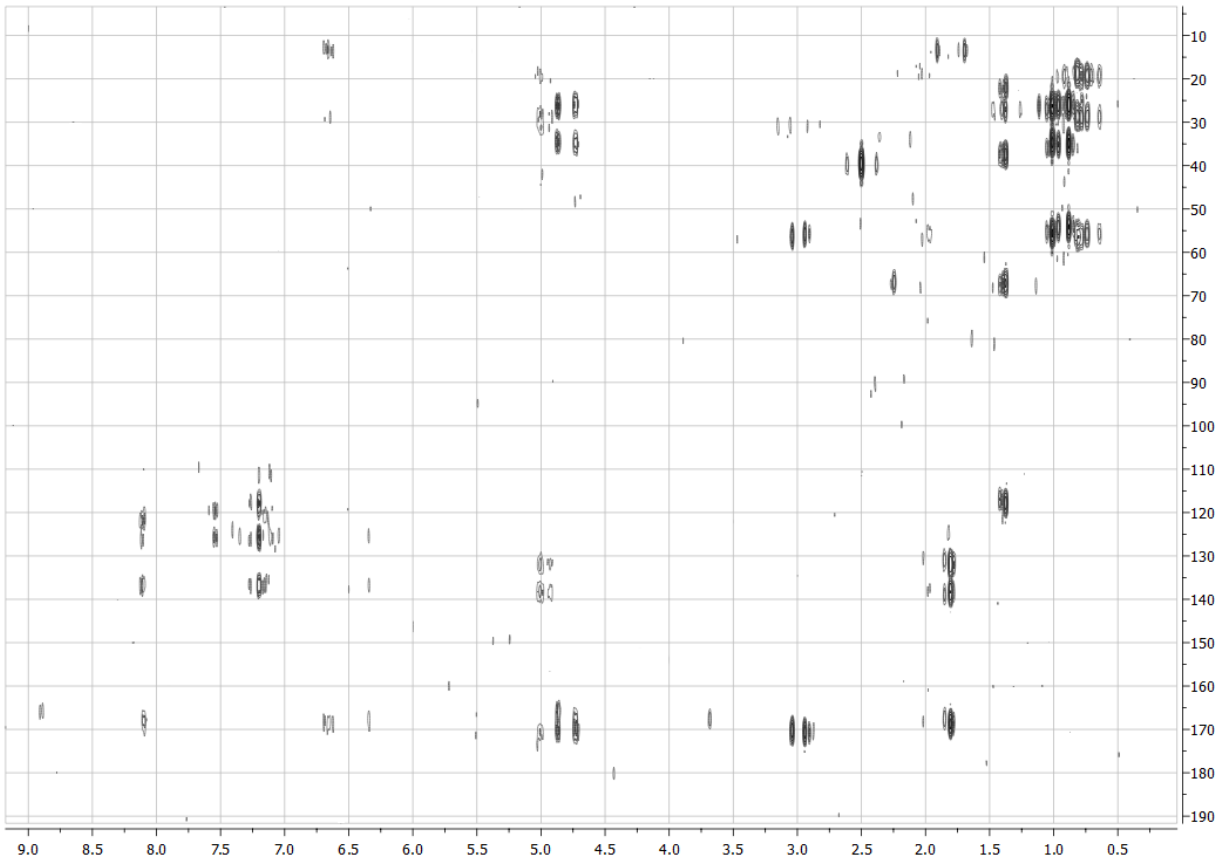


Figure S20. gCOSY Spectrum for hemiasterlin D (**4**) in DMSO-d_6.

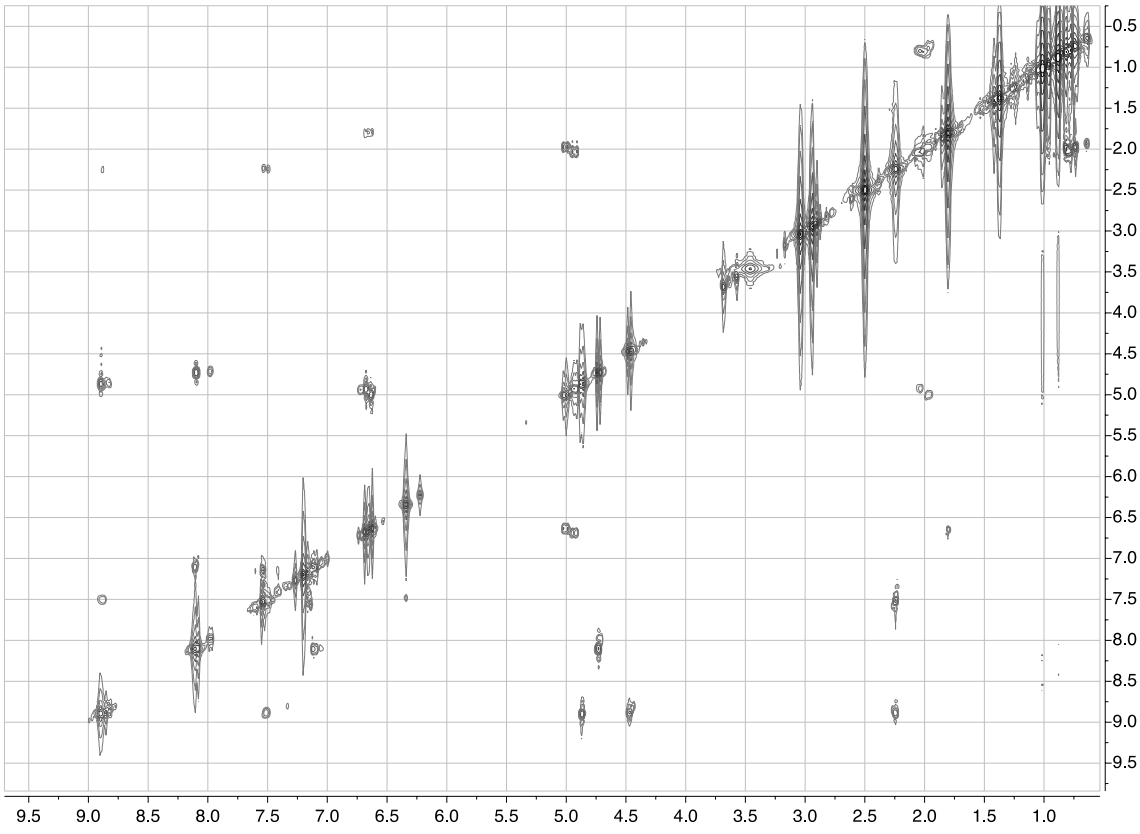


Figure S21. ROESY Spectrum for hemiasterlin D (**4**) in DMSO-d_6.

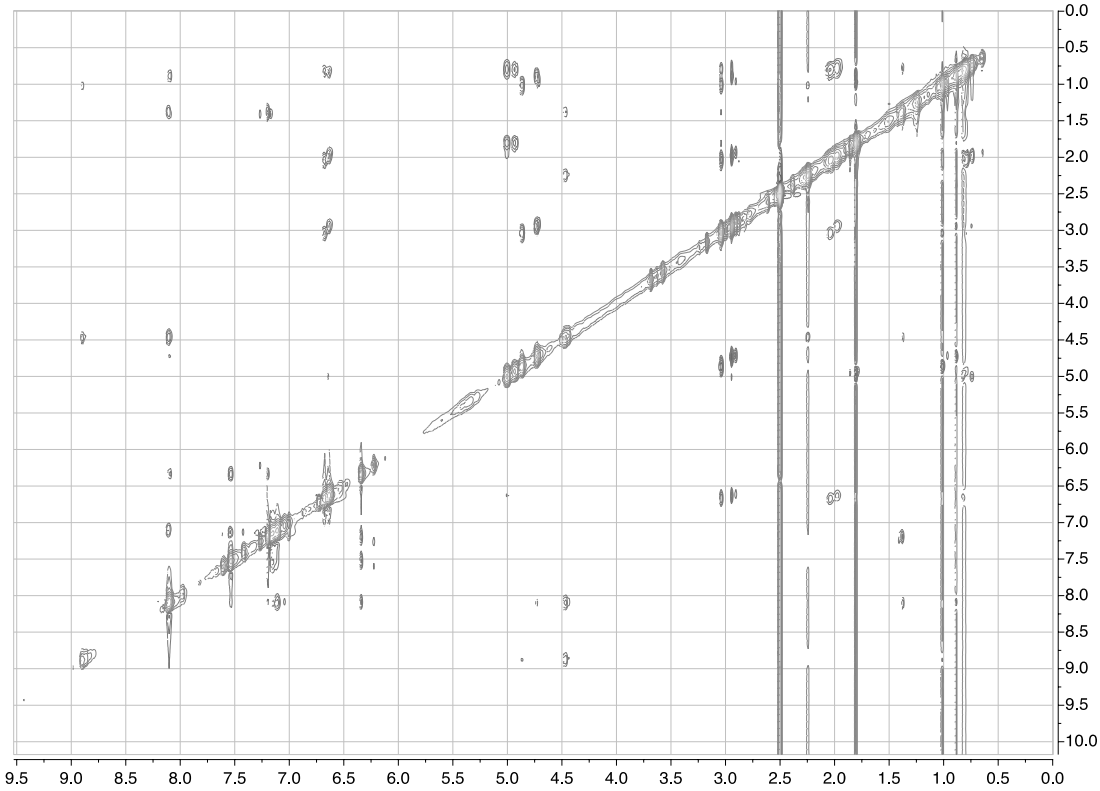


Figure S22. (+)-HRESIMS Spectrum for hemiasterlin D (**4**).

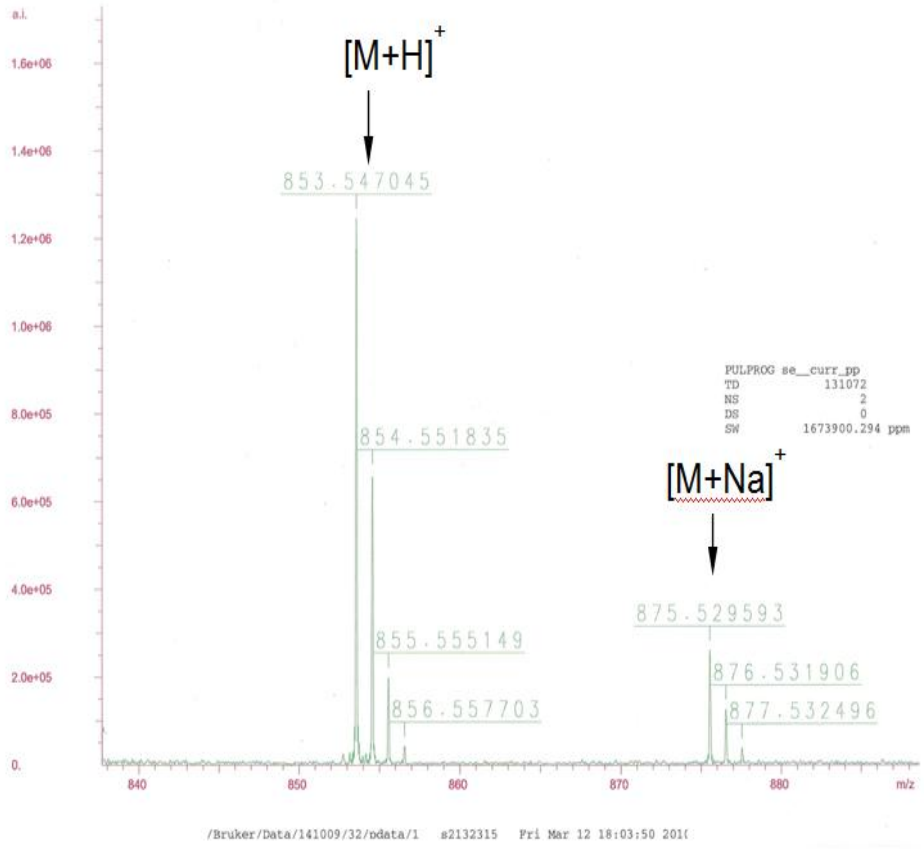


Figure S23. LC/MS Analysis of Marfey's Derivatives of compounds **1**–**4**.

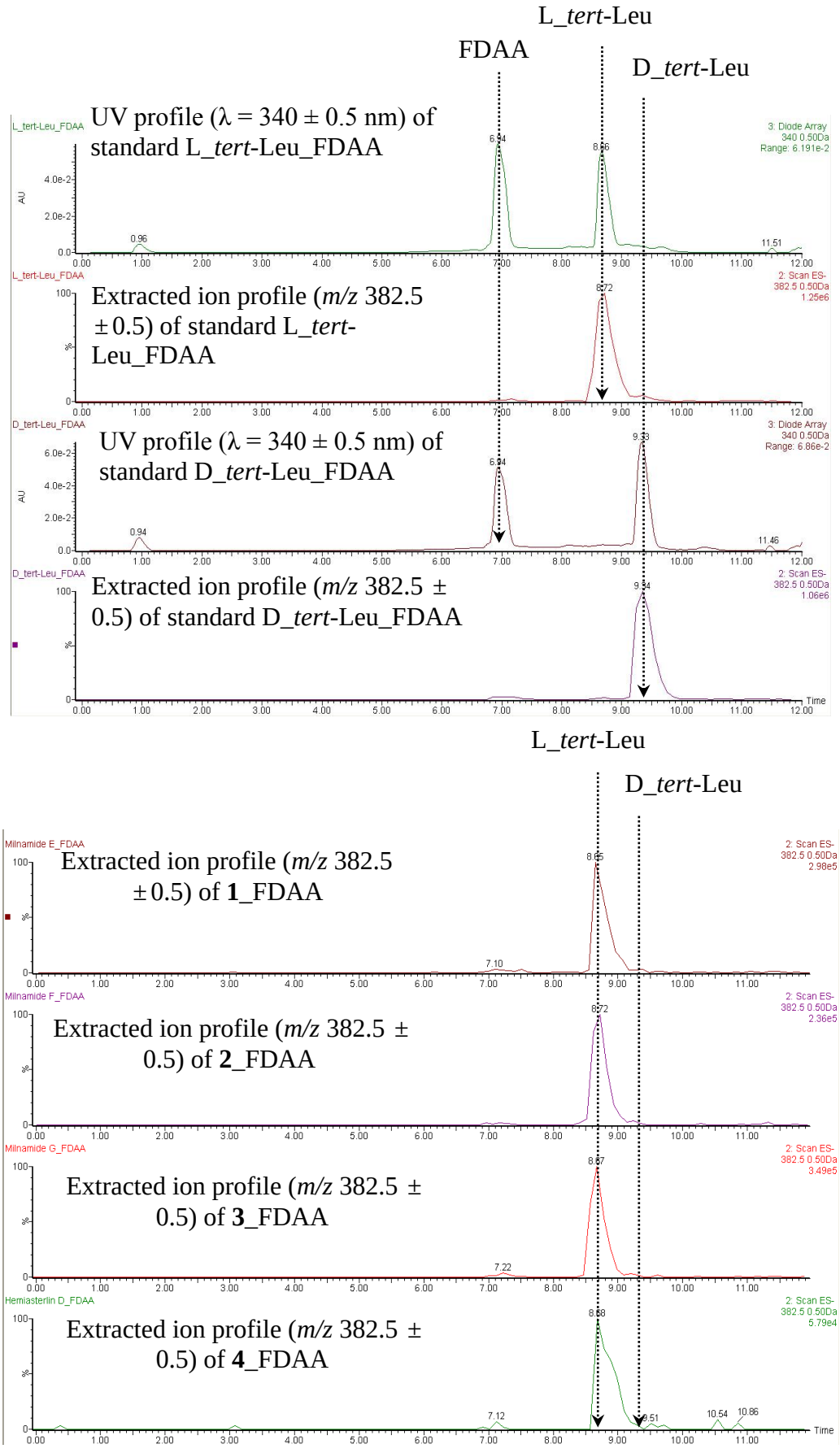
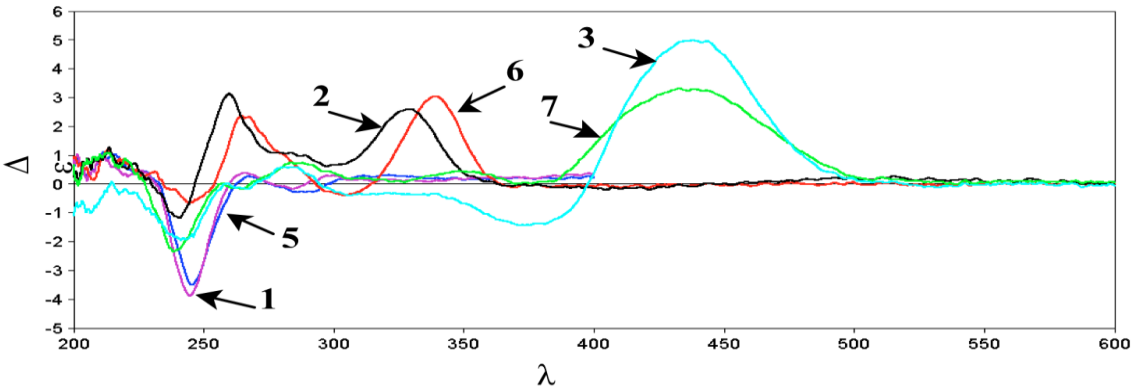


Figure S24. CD Spectra and Specific Rotations of Compounds **1**–**3** and **5**–**7**.

CD Spectra



Specific Rotations

Compound	$[\alpha]_D^{25}$	$[\alpha]_D$ (Reference)
1	+11 (*c* 0.02, MeOH)	
2	+29 (*c* 0.05, MeOH)	
3	+134 (*c* 0.04, MeOH)	
5	+38 (*c* 0.02, MeOH)	+28.8 (*c* 0.50, CH_2Cl_2) [1]
6	+49 (*c* 0.05, MeOH)	+68 (*c* 0.06, MeOH) [2]
7	+180 (*c* 0.06, MeOH)	+156 (*c* 0.39, MeOH) [3]

Figure S25. Photographs of the sponges *Pipestela candelabra*; (**A**) Photograph of the sponge *Pipestela candelabra* collected at Wilson Reef, Coral Sea; (**B**) Photograph of the sponge *Pipestela candelabra* collected at Houghton Reef, Howick Group.

(**A**)

(**B**)

References

1. Crews, P.; Farias, J.J.; Emrich, R.; Keifer, P.A. Milnamide A, an unusual cytotoxic tripeptide from the marine sponge *Auletta* cf. *constricta*. *J. Org. Chem.* **1994**, *59*, 2932–2934.
2. Sonnenschein, R.N.; Farias, J.J.; Tenney, K.; Mooberry, S.L.; Lobkovsky, E.; Clardy, J.; Crews, P. A further study of the cytotoxic constituents of a milnamide-producing sponge. *Org. Lett.* **2004**, *6*, 779–782.
3. Chevallier, C.; Richardson, A.D.; Edler, M.C.; Hamel, E.; Harper, M.K.; Ireland, C.M. A new cytotoxic and tubulin-interactive milnamide derivative from a marine sponge *Cymbastela* sp. *Org. Lett.* **2003**, *5*, 3737–3739.