

Broomeanamides: Cyclic Octapeptides from an Isolate of Fungicolous *Sphaerostilbella broomeana* (Hypocreales, Ascomycota) from India

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List of Supporting Information

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Figure S2. Maximum likelihood phylogeny of the *Sphaerostilbella broomeana*-group based on translation elongation factor (TEF; 1232 bp) and ITS-LSU (1461 bp) ribosomal DNA sequences³. *Sphaerostilbella parabroomeana* was used as an outgroup; bootstrap support values >95% indicated above the branches.

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Figure S4. ¹³C NMR Spectrum of Broomeamide A (**1**; 400 MHz, CDCl₃)

Figure S5. TOCSY Spectrum of Broomeamide A (**1**; 600 MHz, CDCl₃)

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Figure S16. ¹H NMR Spectrum of Broomeanamide C (**3**; 500 MHz, CDCl₃)

Figure S17. TOCSY Spectrum of Broomeanamide C (**3**; 500 MHz, CDCl₃)

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Figure S26. ¹H NMR Spectrum of **6** (600 MHz, CDCl₃)

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Table S1. NMR spectroscopic data of broomeanamide B (**2**) in CDCl₃

Table S2. NMR spectroscopic data of broomeanamide C (**3**) in CDCl₃

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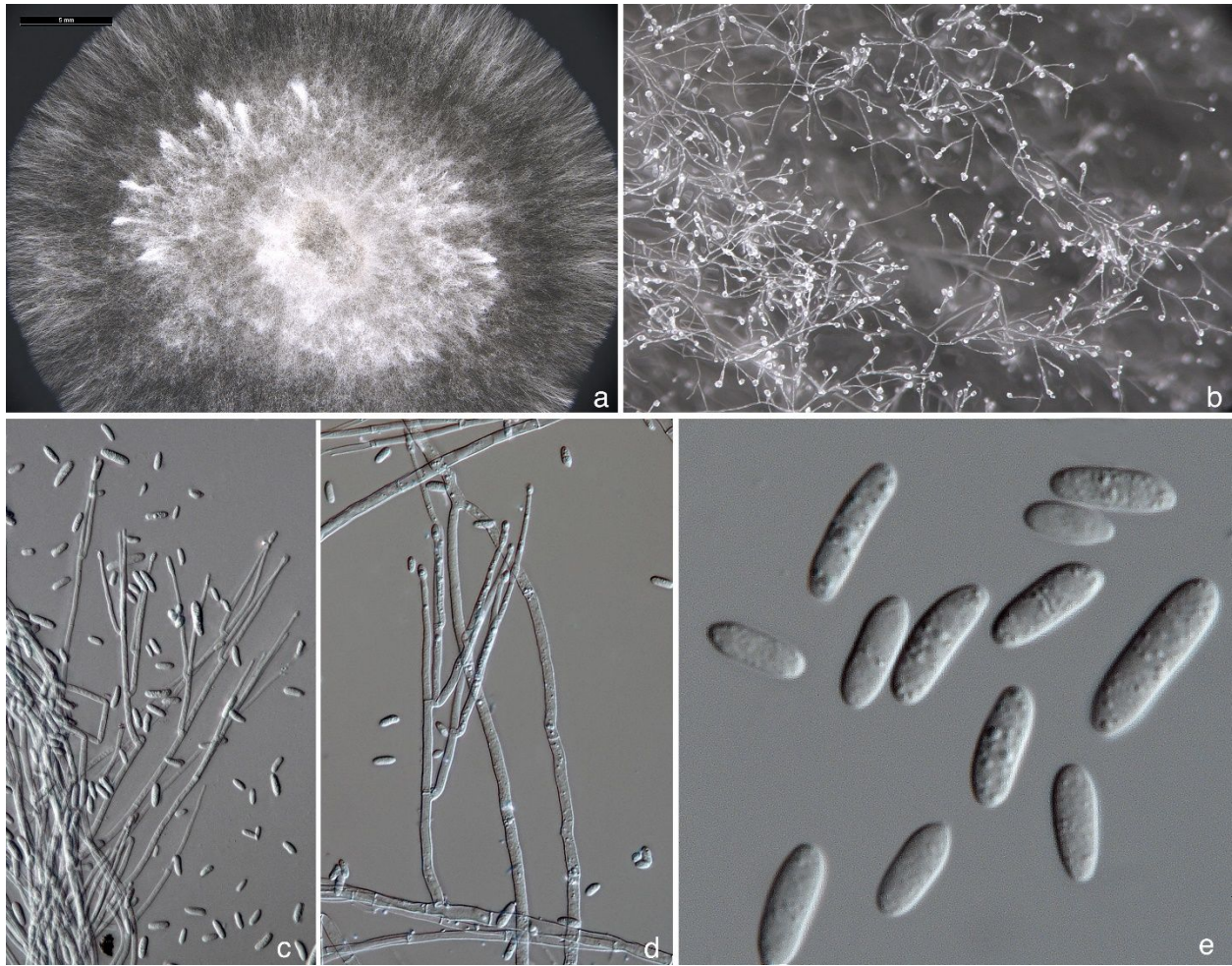


Figure S1. Isolate TFC201724 grown for 5d on MEA; a – colony, b–d conidiophores, e – conidia.

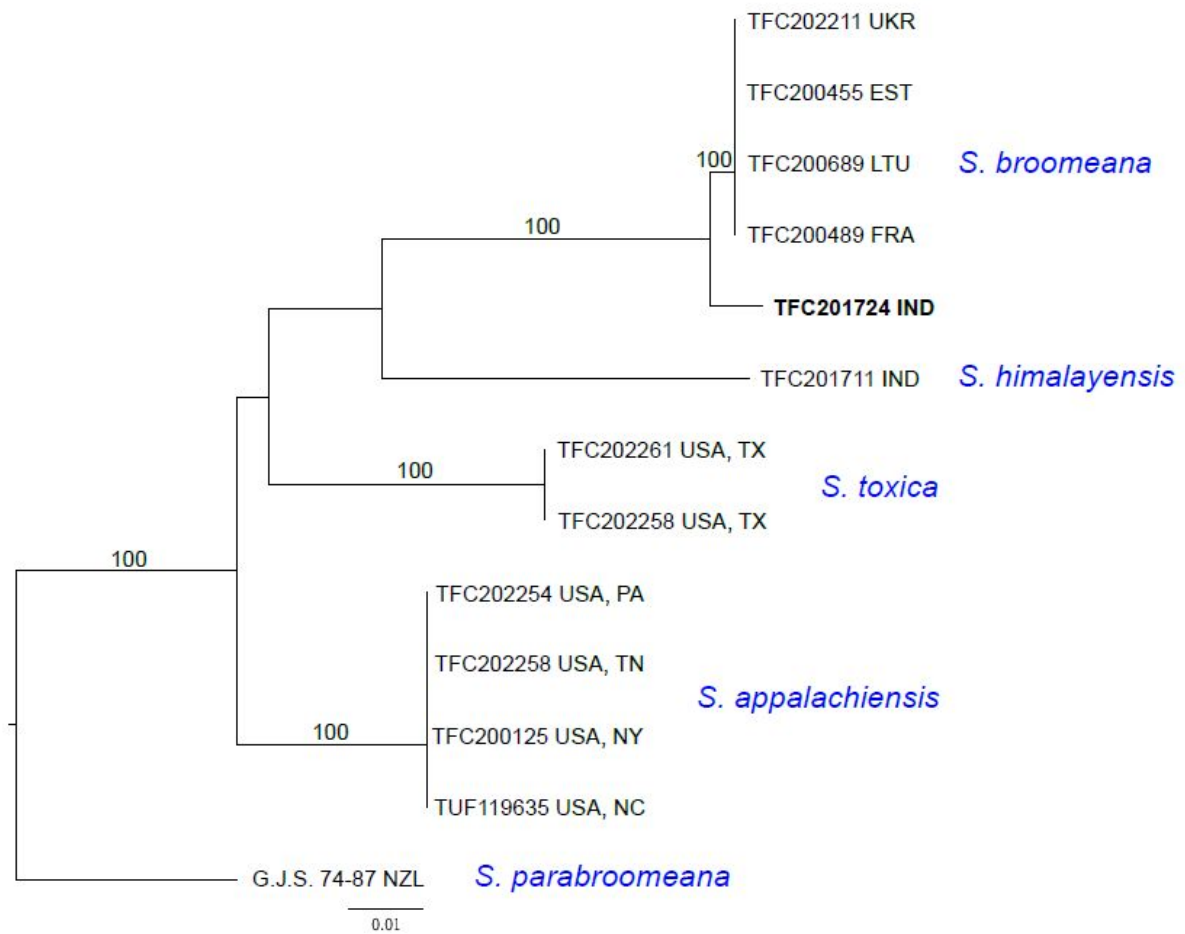


Figure S2. Maximum likelihood phylogeny of the *Sphaerostilbella broomeana*-group based on translation elongation factor (TEF; 1232 bp) and ITS-LSU (1461 bp) ribosomal DNA sequences³. *Sphaerostilbella parabroomeana* was used as an outgroup; bootstrap support values >95%

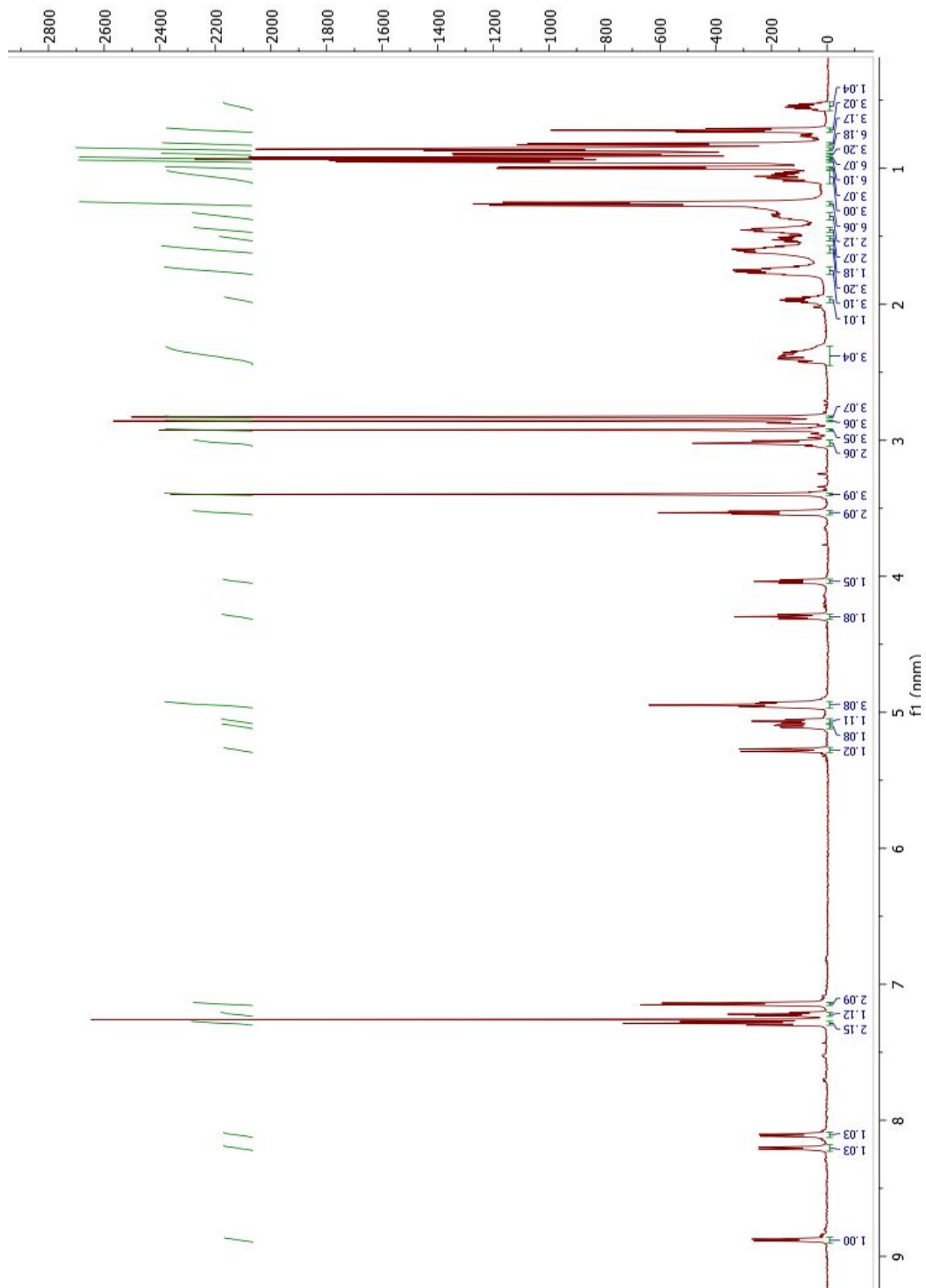


Figure S3. ^1H NMR Spectrum of Broomeanamic

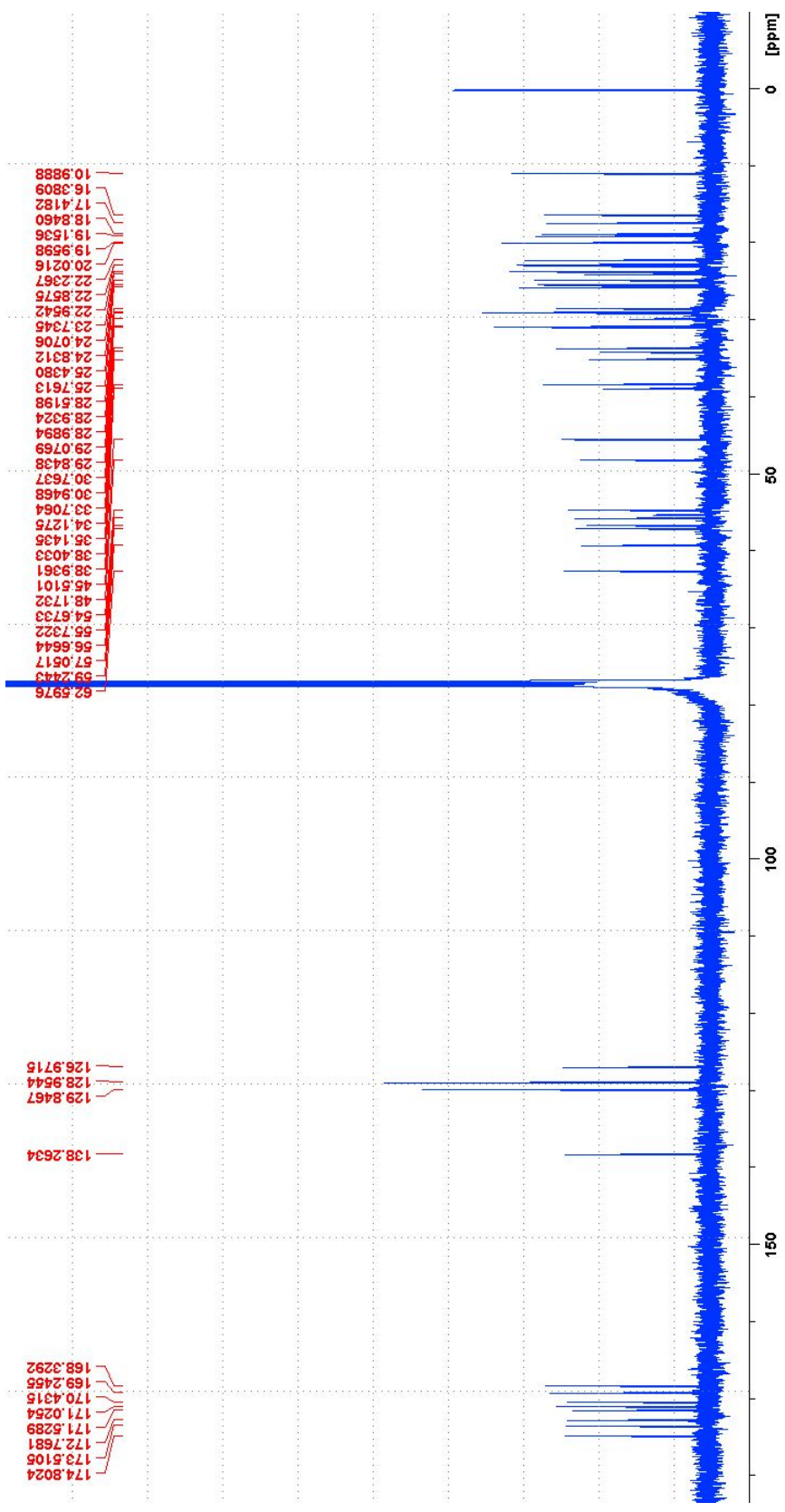


Figure S4. ^{13}C NMR Spectrum of Broomeamide A (1)

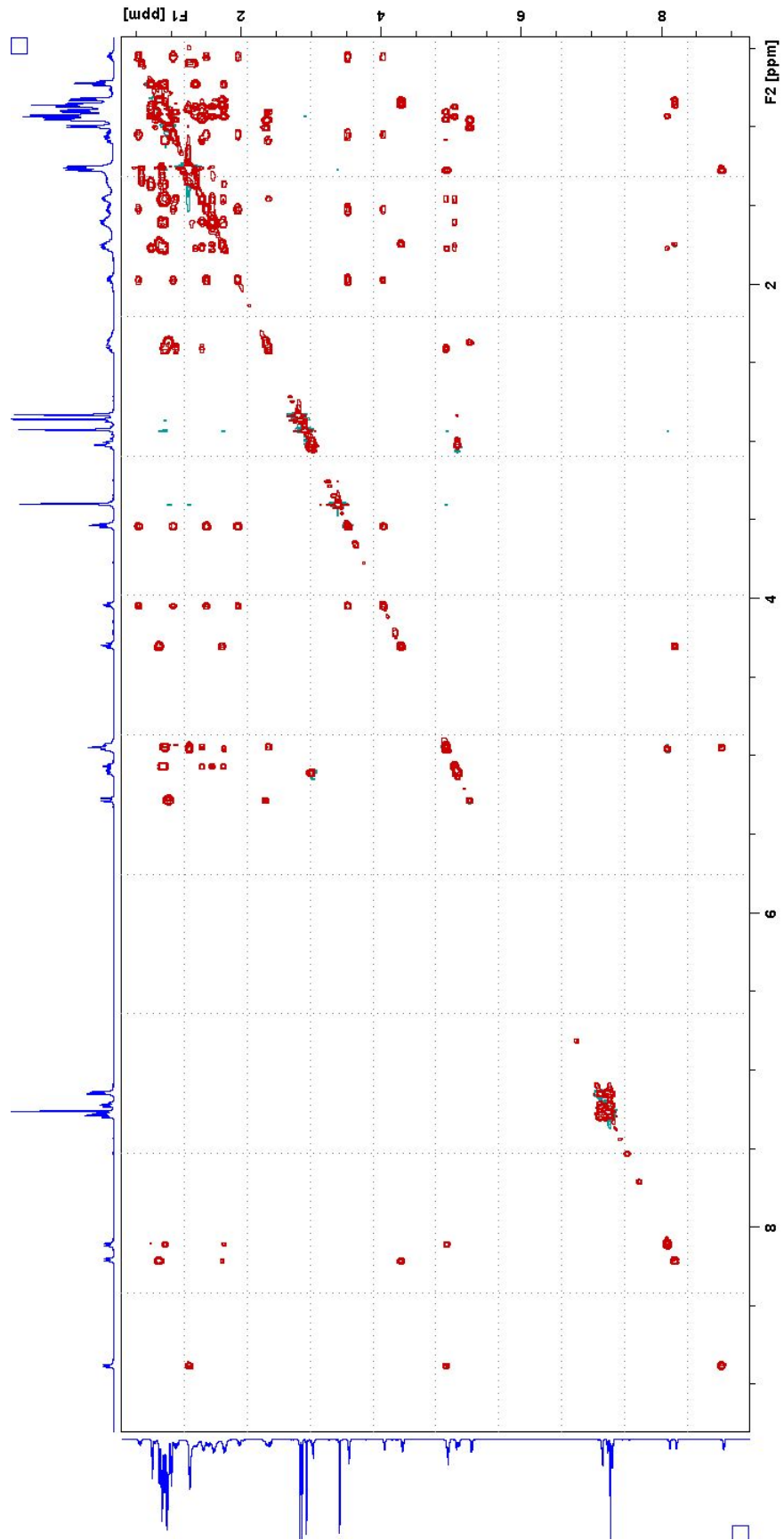


Figure S5. TOCSY Spectrum of Broomeamide A (1; 6)

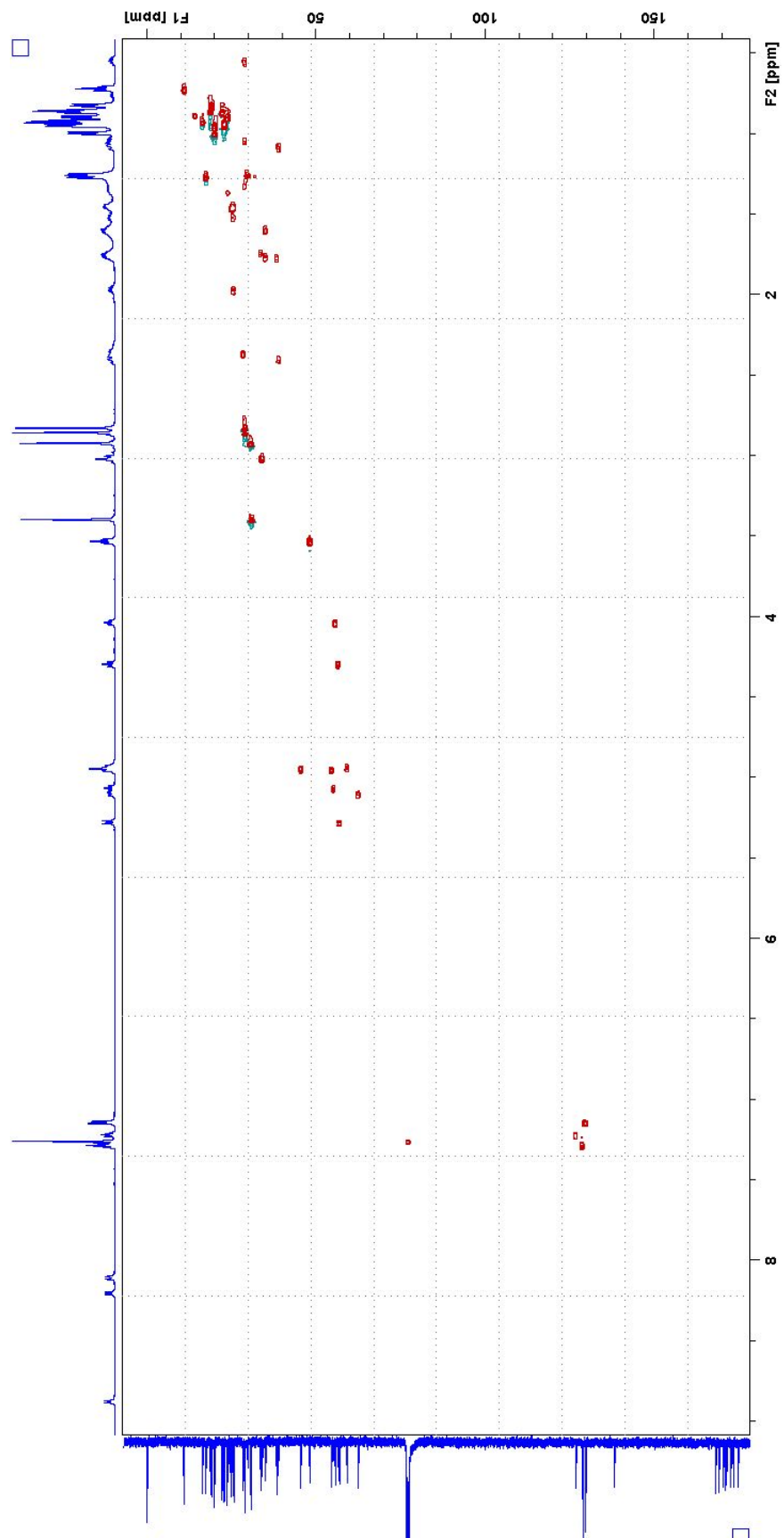


Figure S6. HSQC Spectrum of Broomeamide A (1; 600)

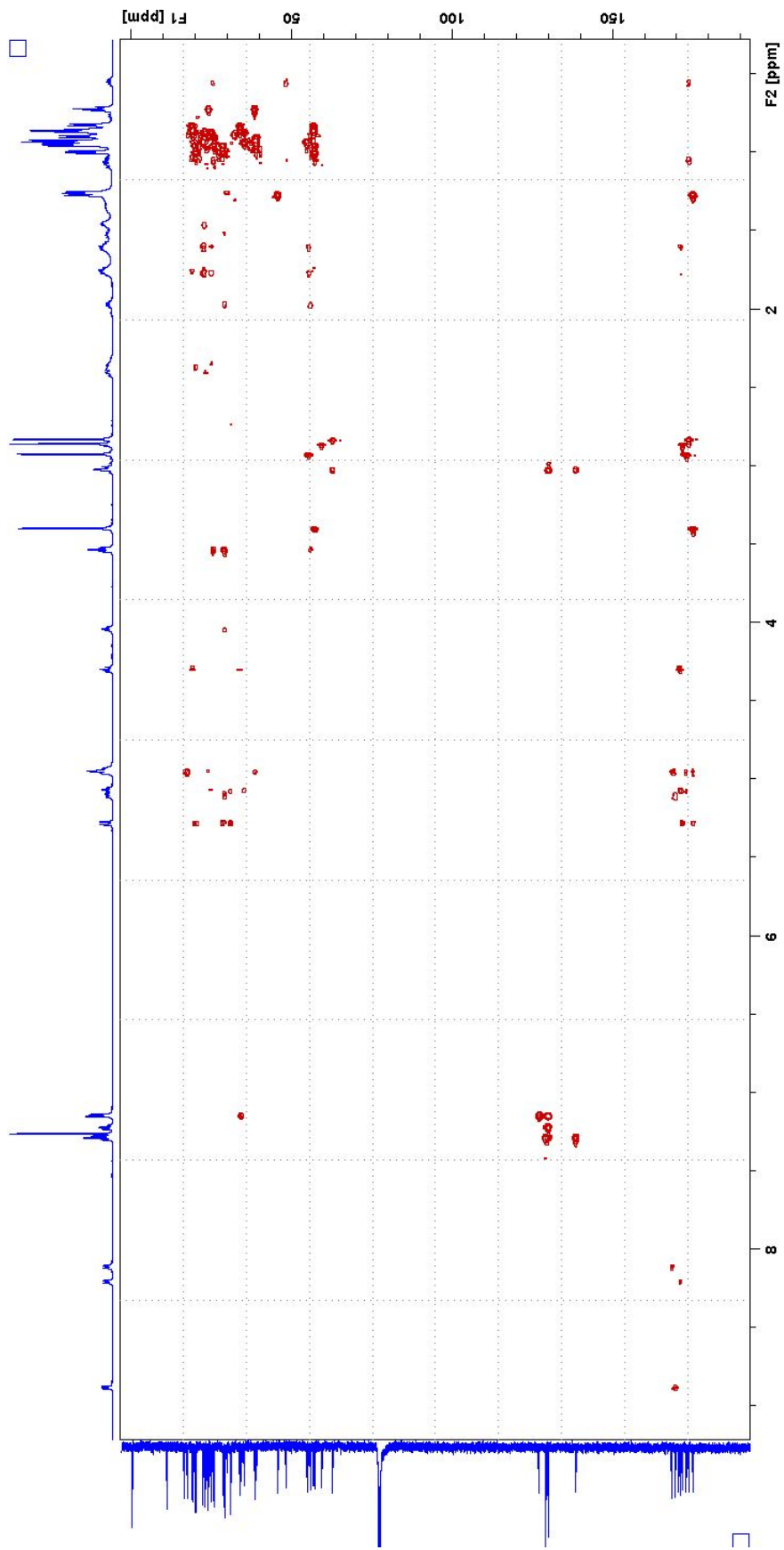


Figure S7. HMBC Spectrum of Broomeamide A (1; 60)

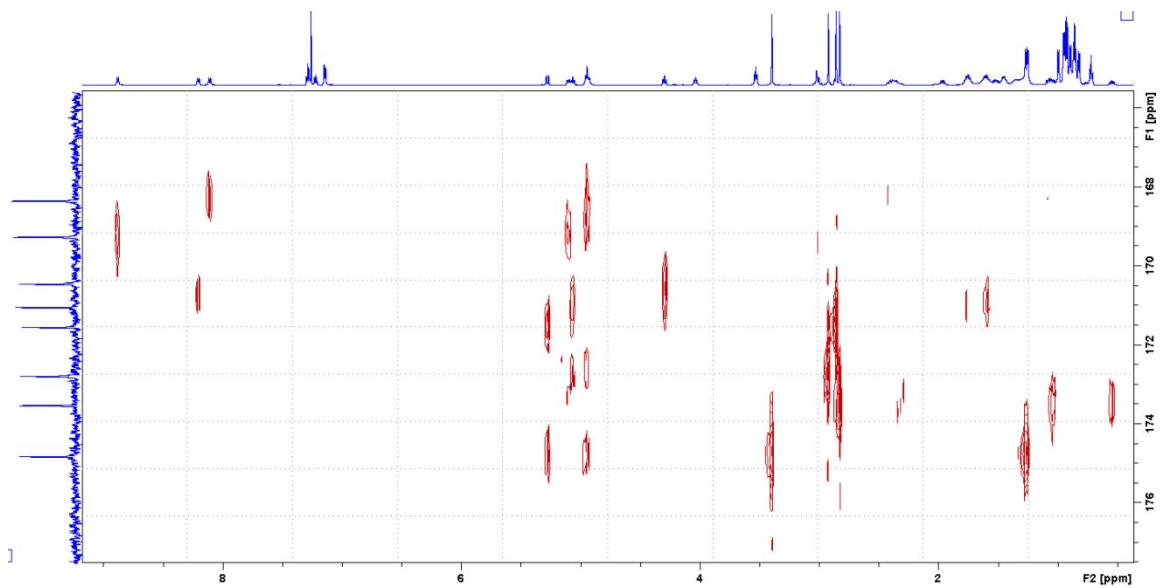


Figure S8. Expanded Carbonyl Region of the HMBC Spectrum of Broomeamide A (**1**; 600 MHz, CDCl₃)

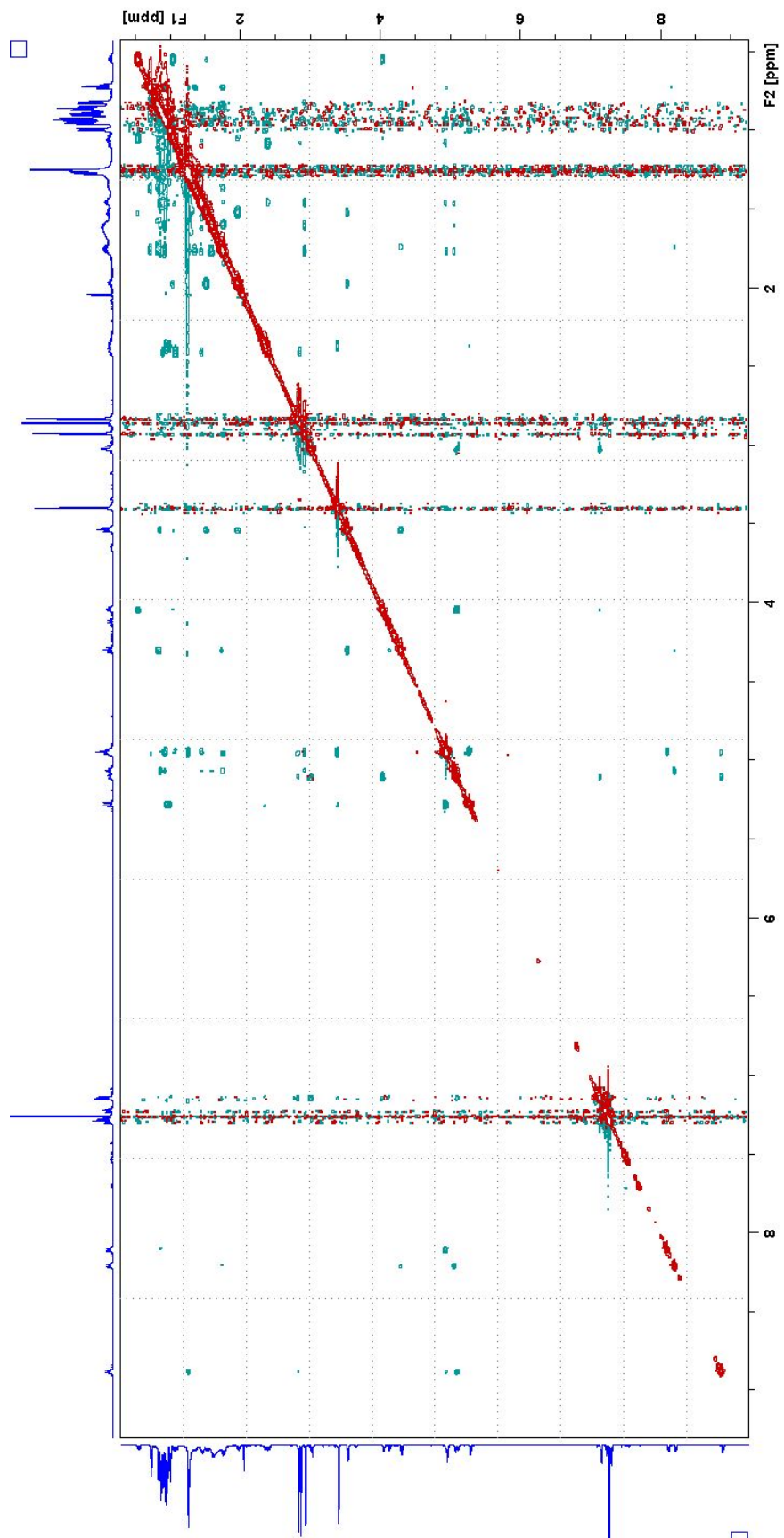


Figure S9. ROESY Spectrum of Broomeamide A (1; 6)

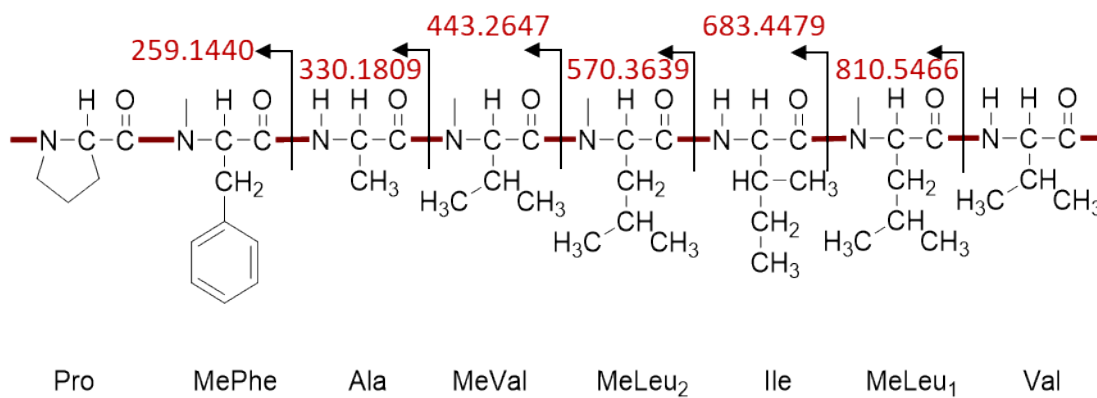
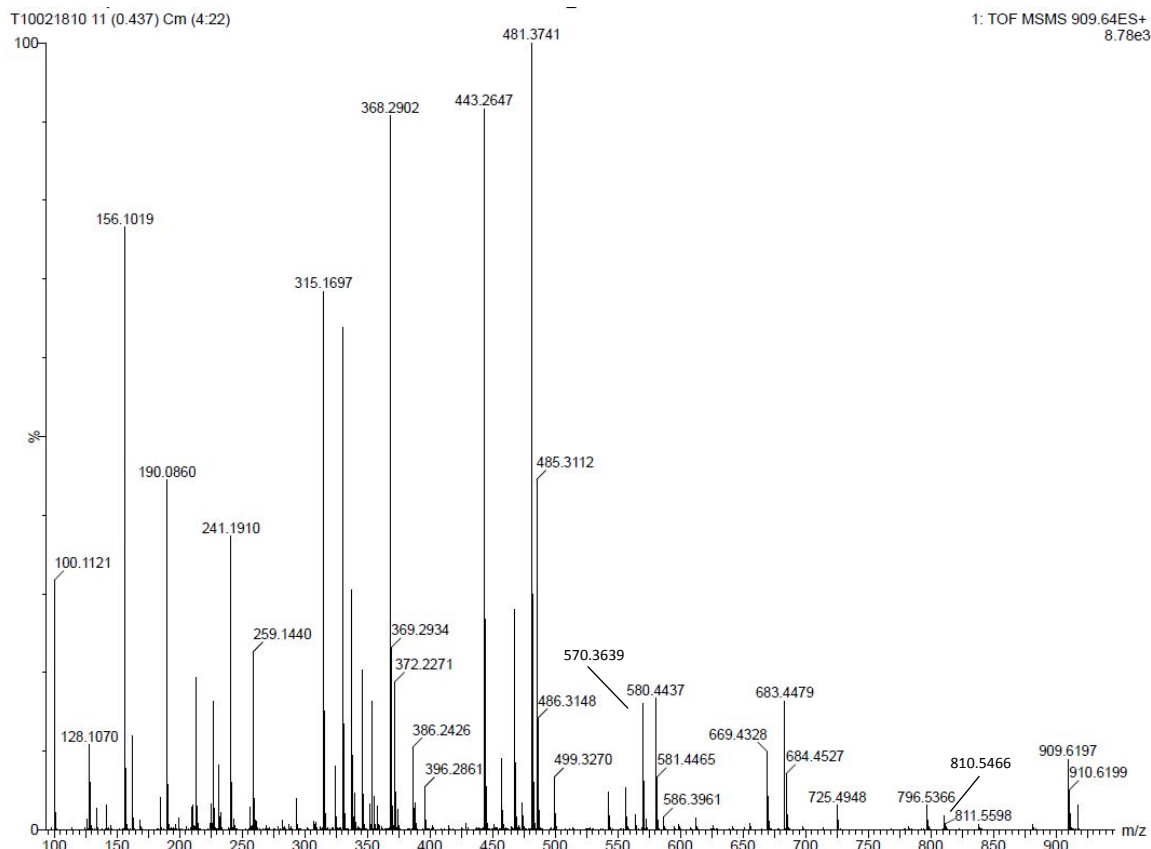
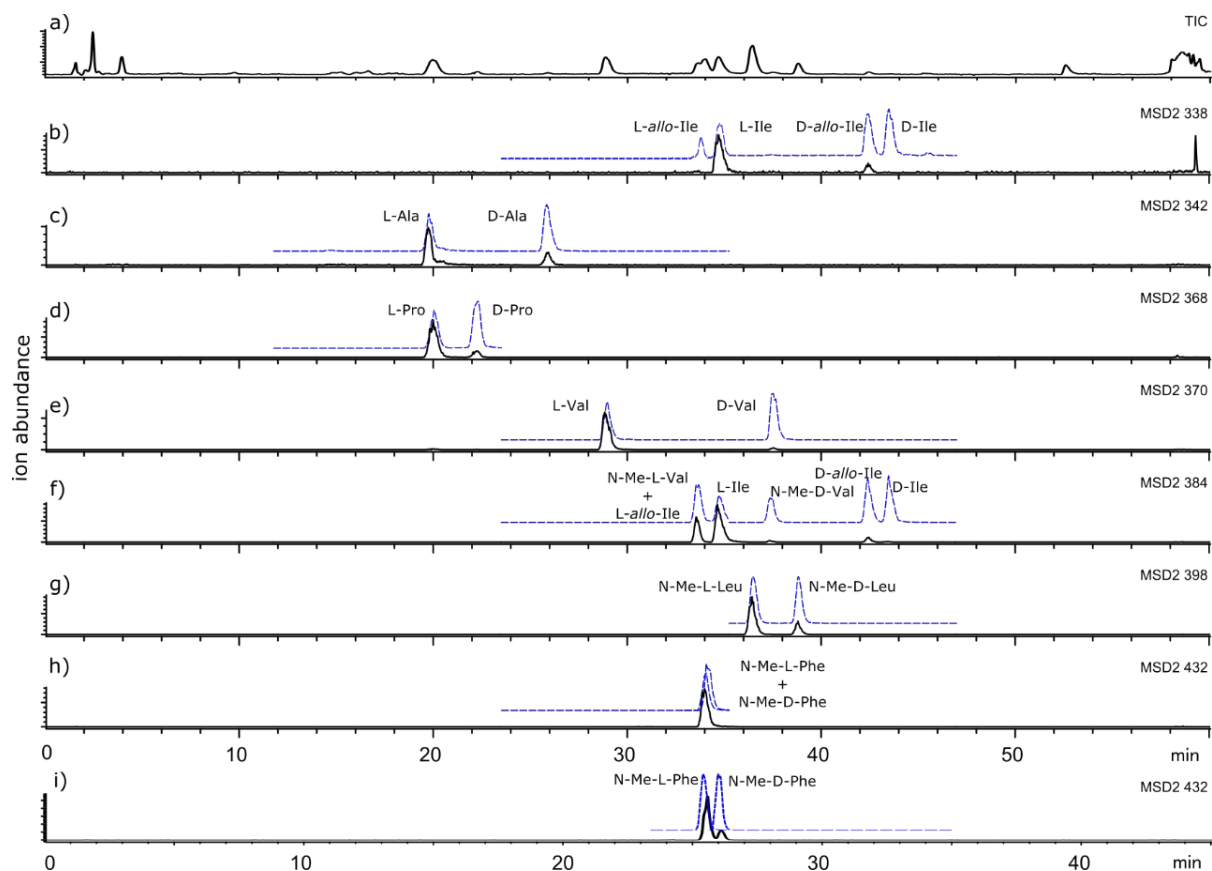


Figure S10. HRESIMSMS data for Broomeanamide A (1)



a) Total Ion Chromatogram using C_3 column; b) EIC (extracted ion current; m/z 338) for L-FDAA-L-Ile; c) EIC (m/z 342) for L-FDAA-L-Ala; d) EIC (m/z 368) for L-FDAA-L-Pro; e) EIC (m/z 370) for L-FDAA-L-Val; f) EIC (m/z 384) for L-FDAA-N-Me-L-Val (note the co-extraction of ions for the isomeric Ile residues); g) EIC (m/z 396) for L-FDAA-N-Me-L-Leu; h) EIC (m/z 432) for L-FDAA-N-Me-L-Phe; i) EIC spectrum (m/z 432) from C_{18} Marfey's analysis of **1** for characterization of L-FDAA-N-Me-L-Phe. For b)-i), L-FDAA derivatives of D- and L-amino acid standards are displayed as blue dotted lines.

Figure S11. HPLC-MS data from Marfey's analysis of **1**.

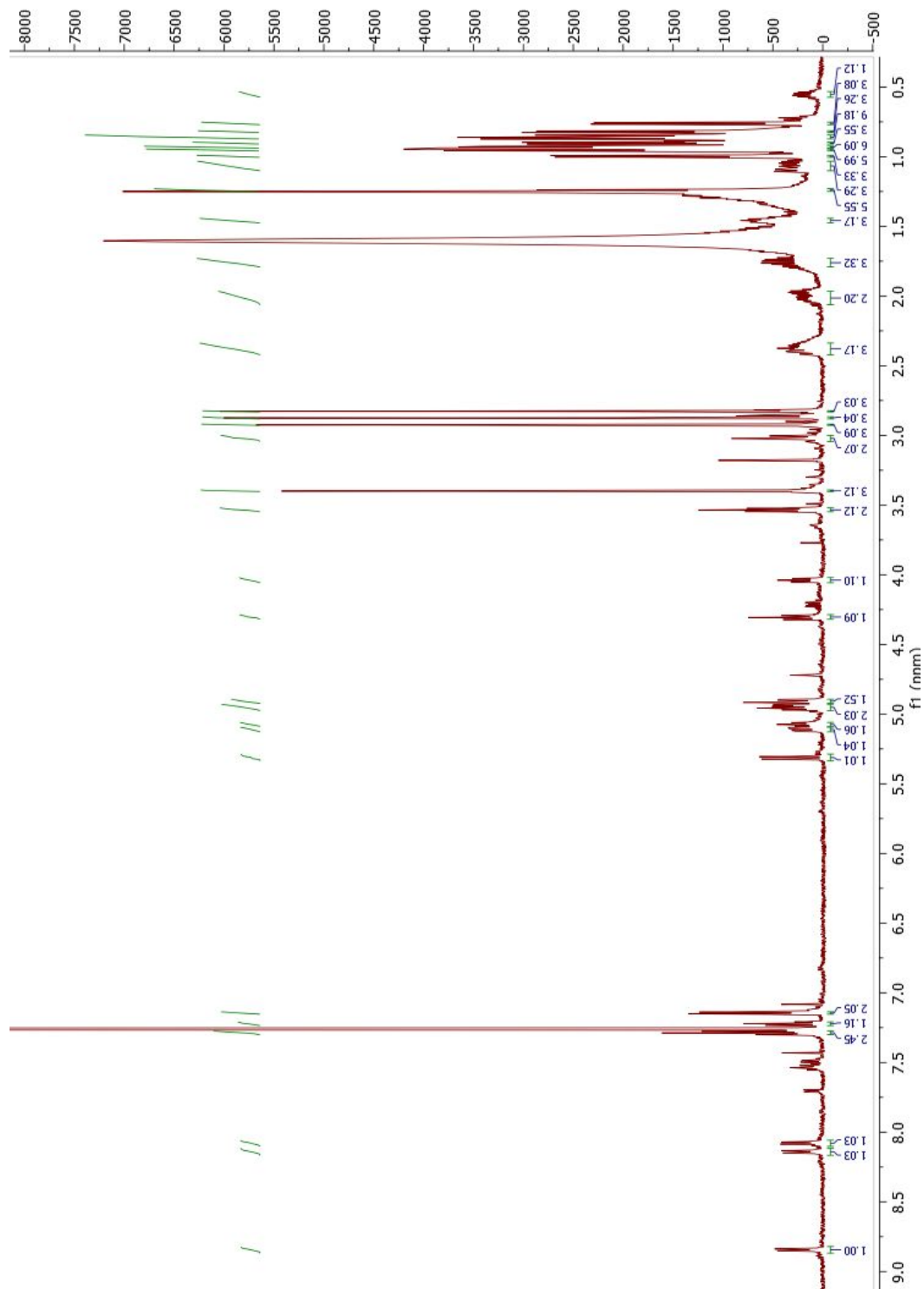


Figure S12. ^1H NMR Spectrum of Broom

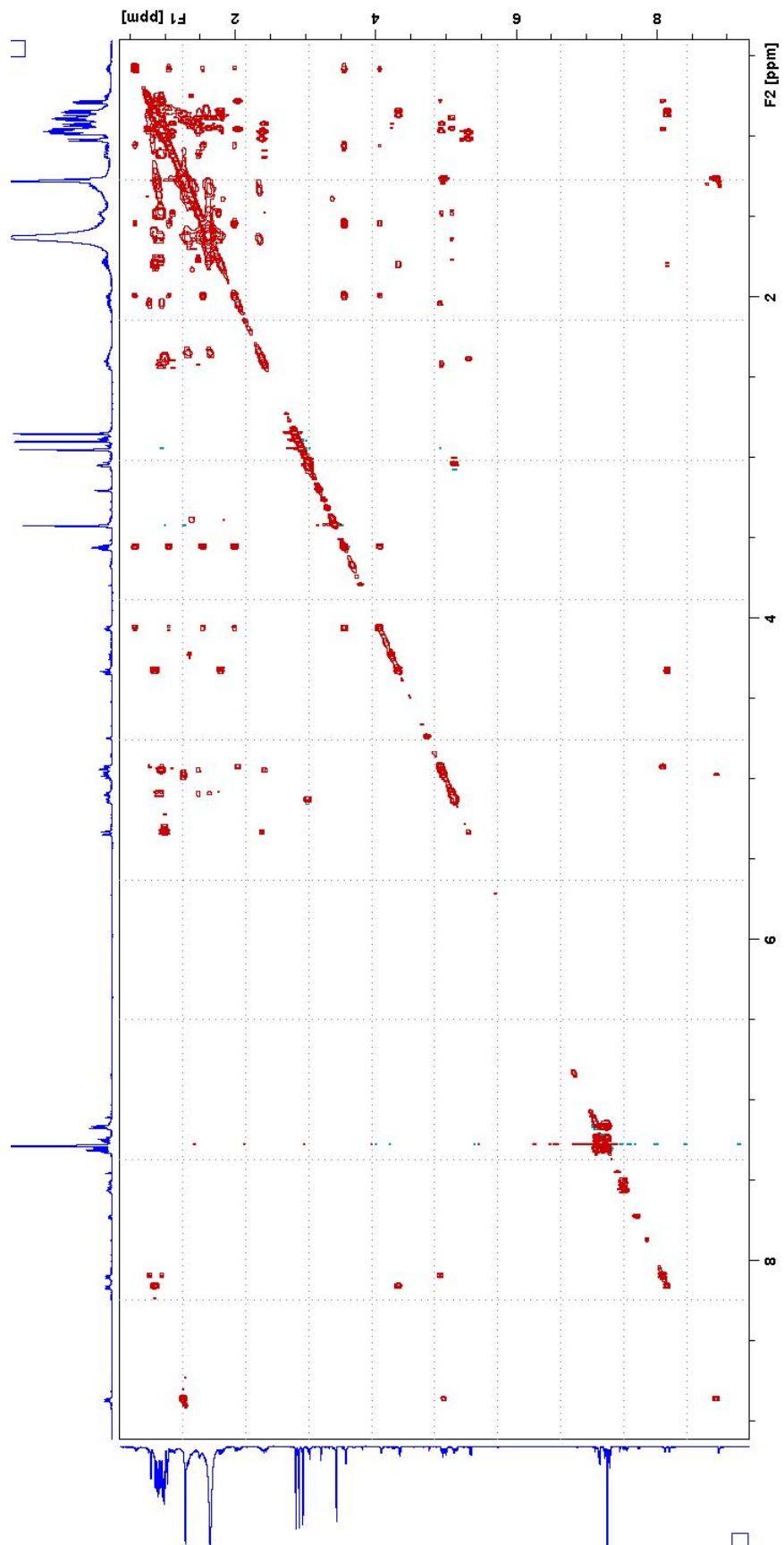


Figure S13. TOCSY Spectrum of Broomeamide B (2)

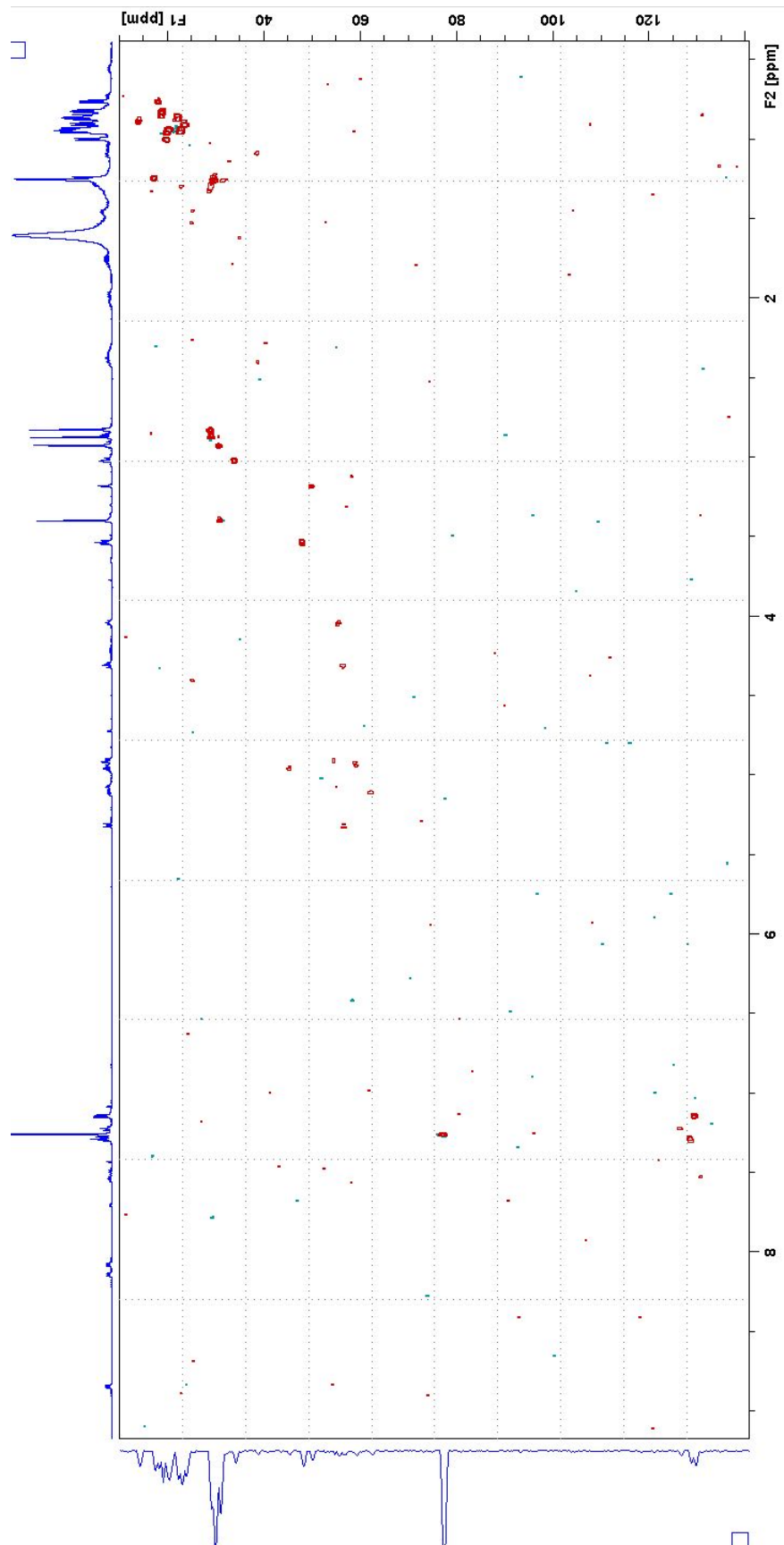


Figure S14. HSQC Spectrum of Broomeamide B (2; 5)

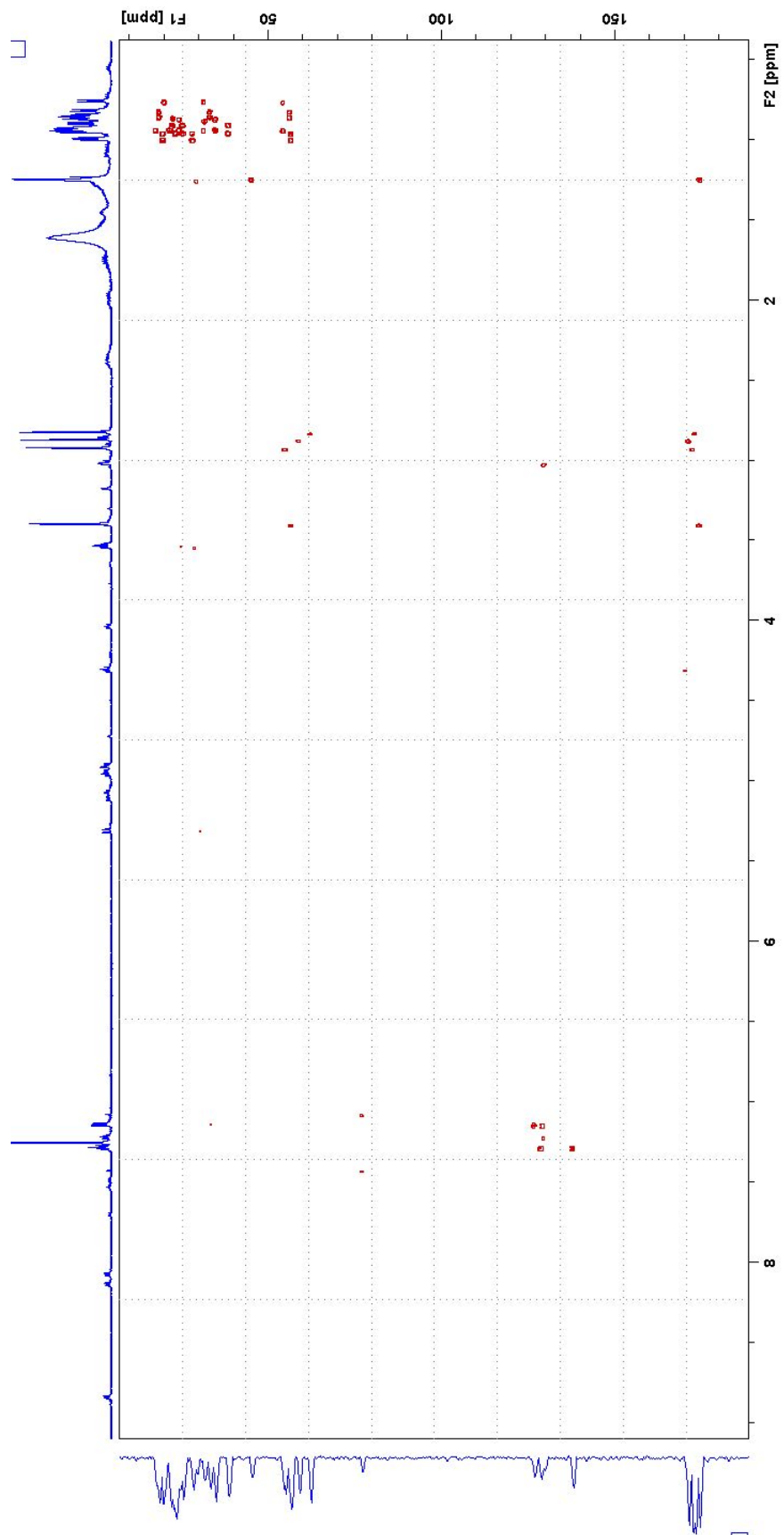


Figure S15. HMBC Spectrum of Broomeamide B (2);

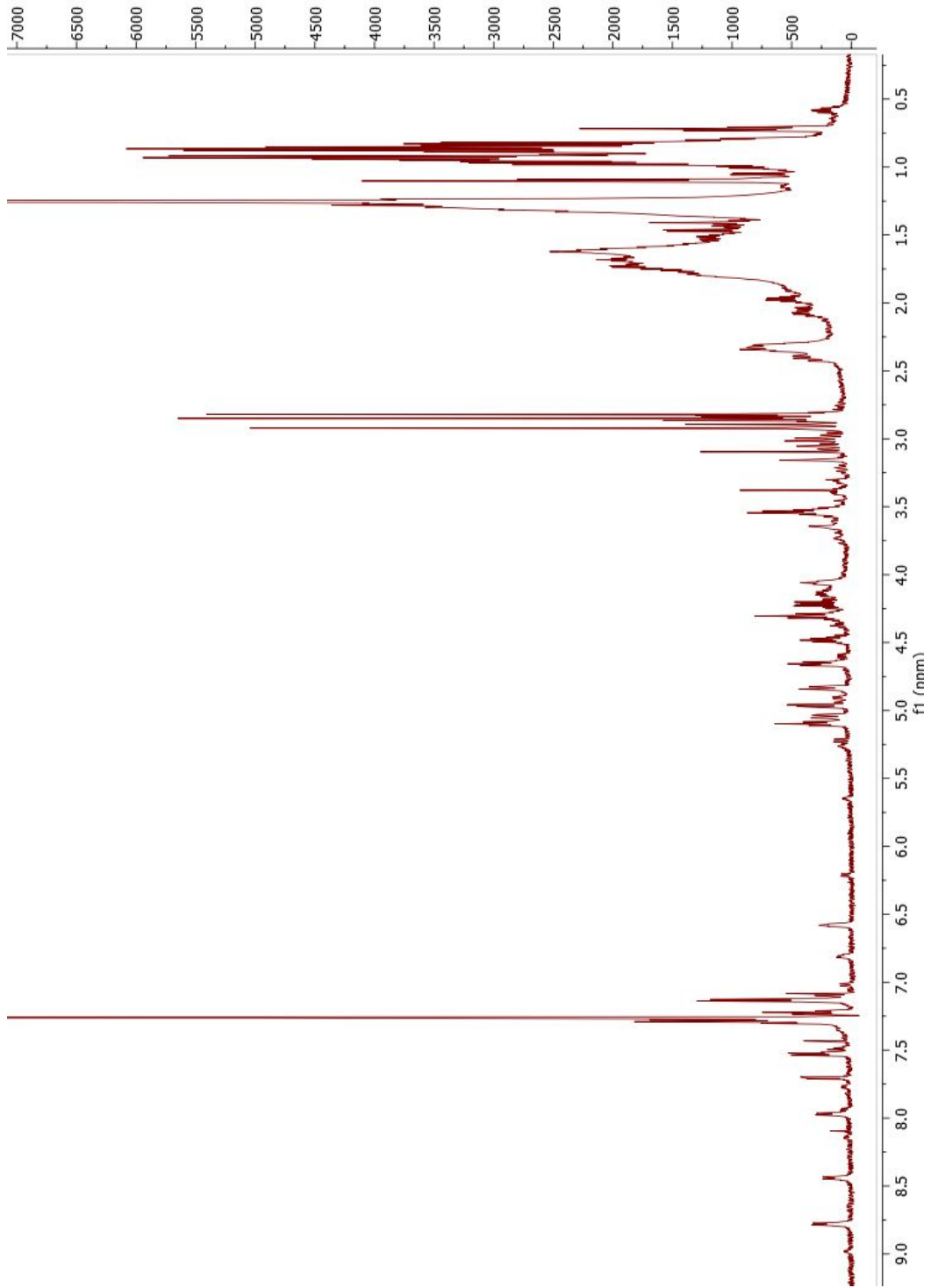


Figure S16. ^1H NMR Spectrum of Broomea

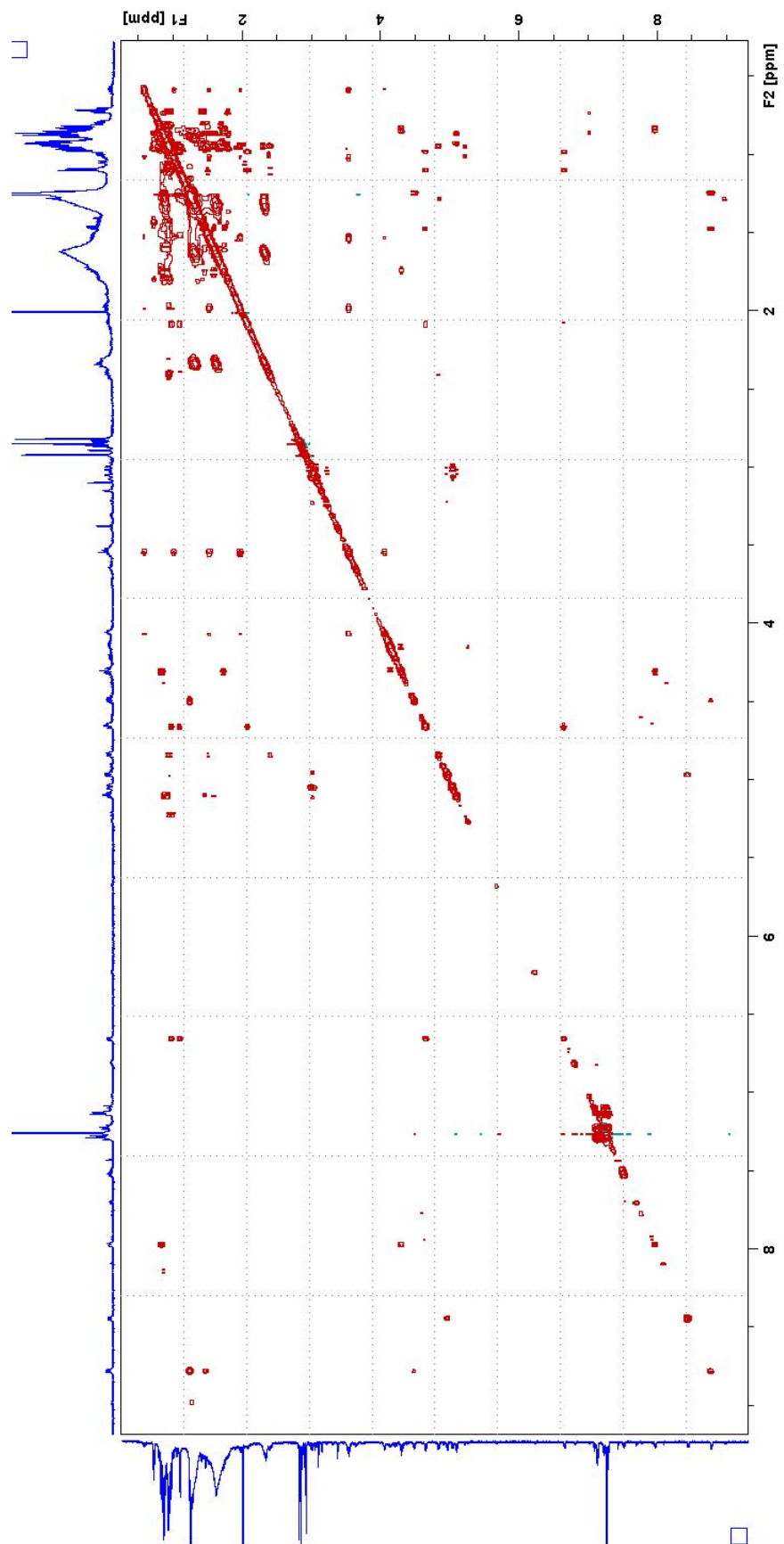


Figure S17. TOCSY Spectrum of Broomeamide C (3);

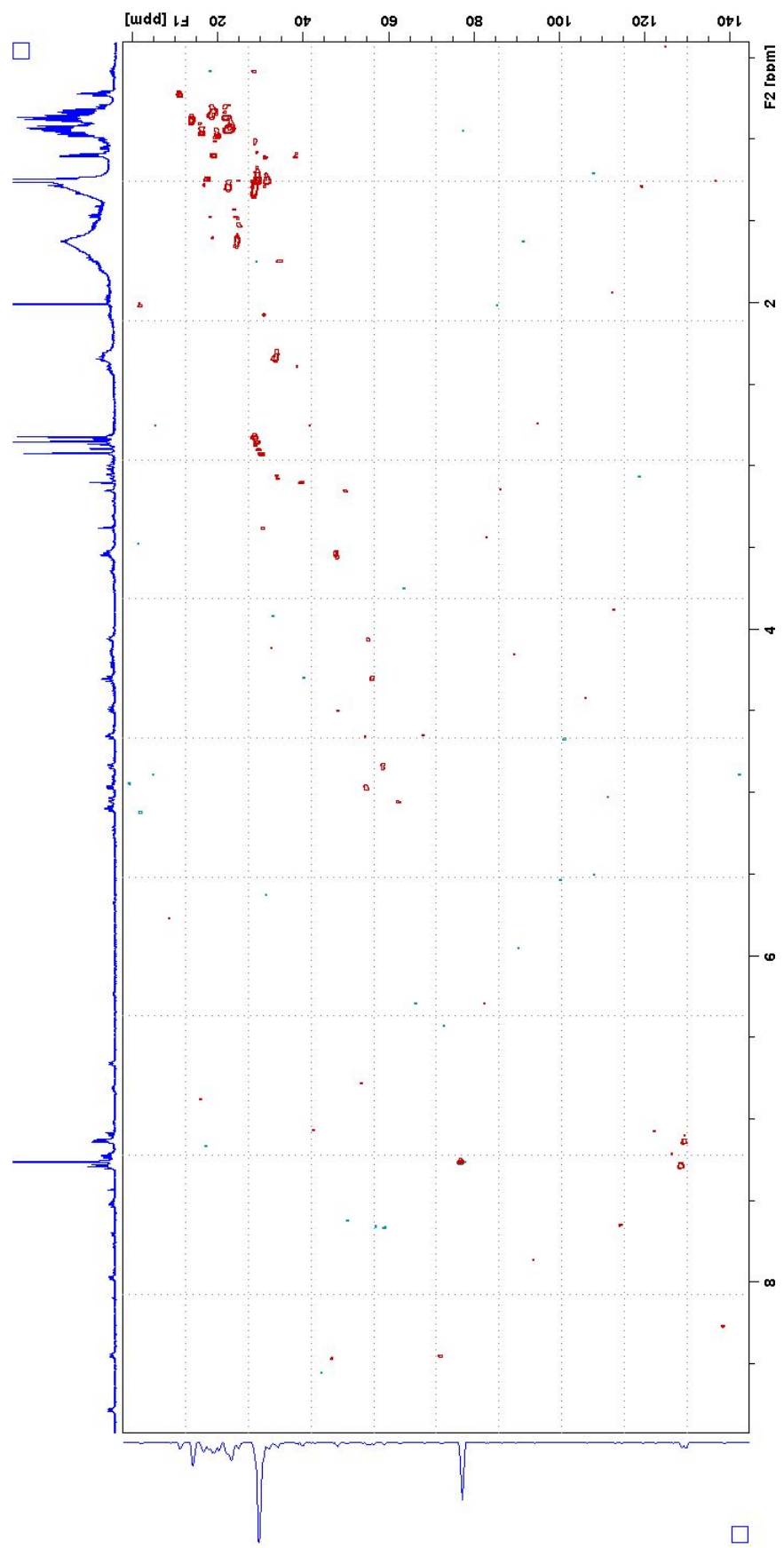


Figure S18. HSQC Spectrum of Broomeamide C (3; 5)

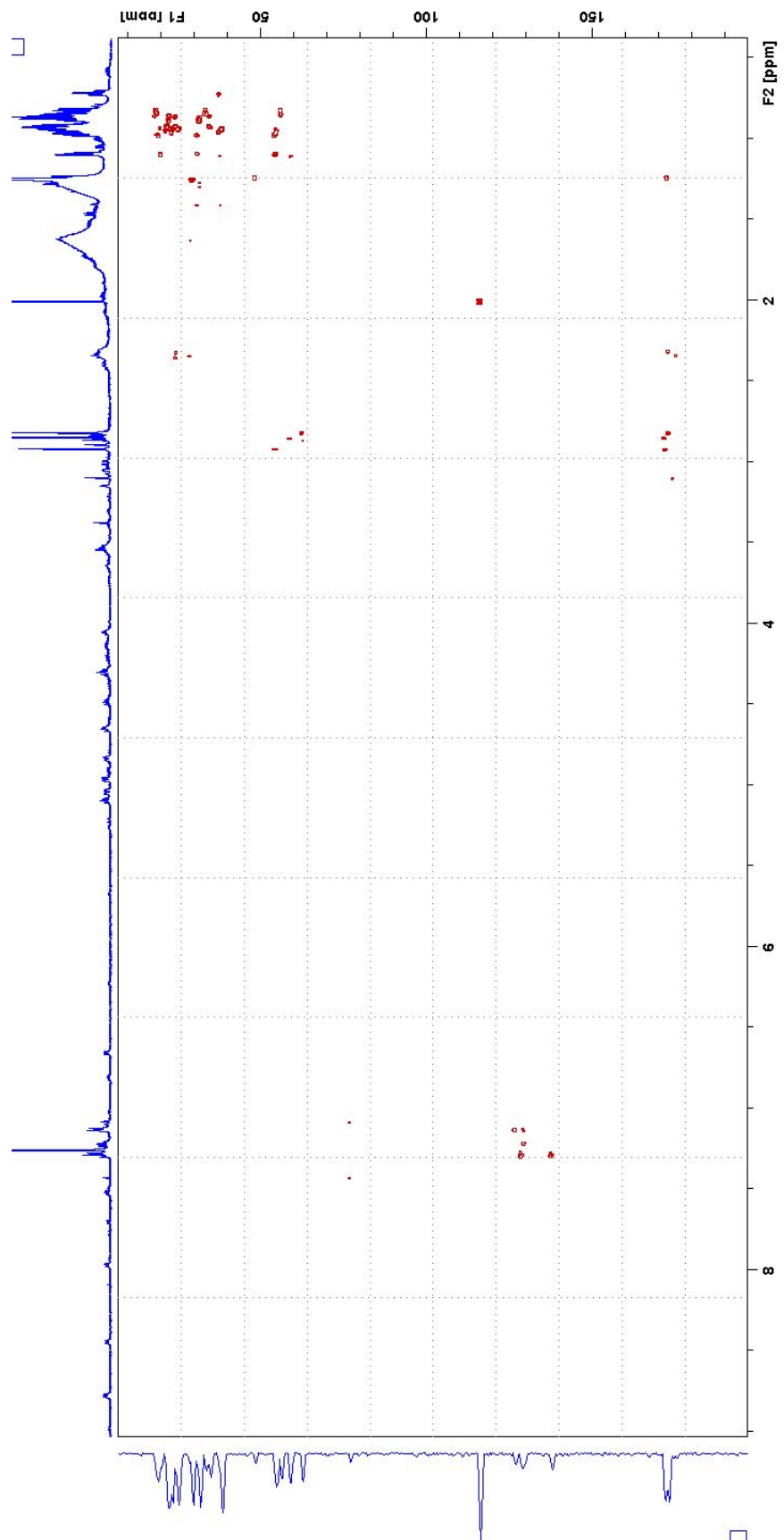
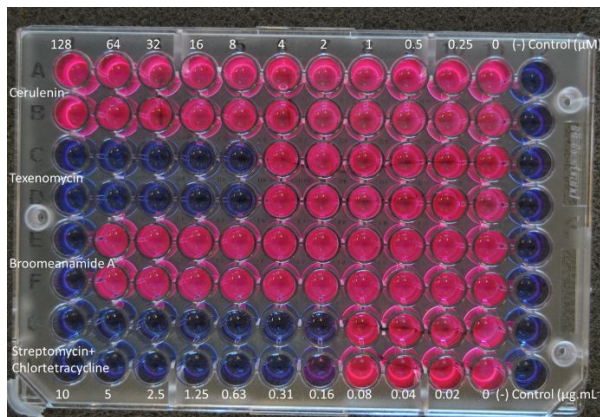
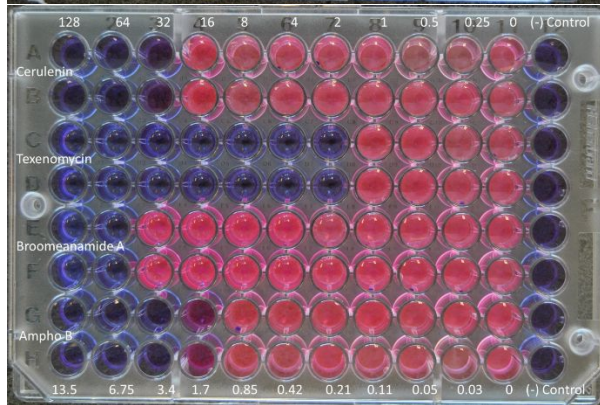


Figure S19. HMBC Spectrum of Broomeamide C (3);

S. aureus 23°C



C. albicans 23°C



C. neoformans 23°C

C. neoformans 37°C

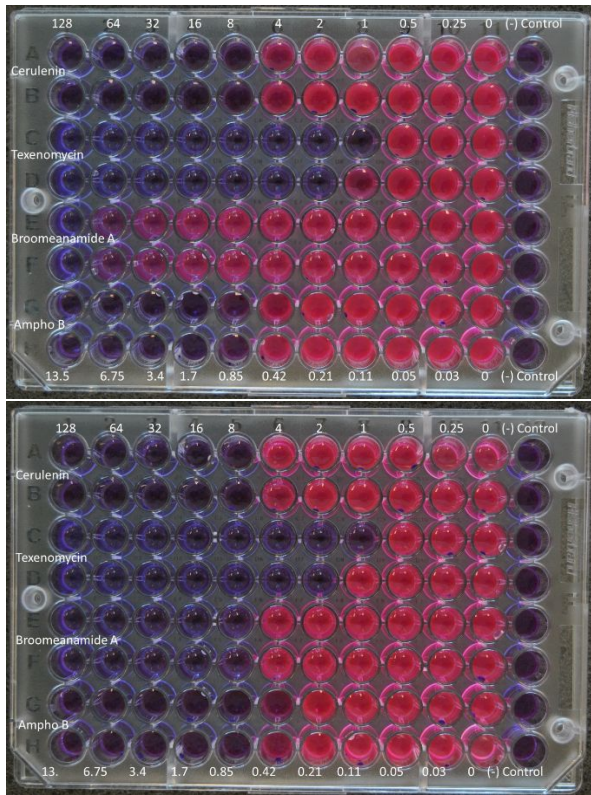


Figure S20. MIC data

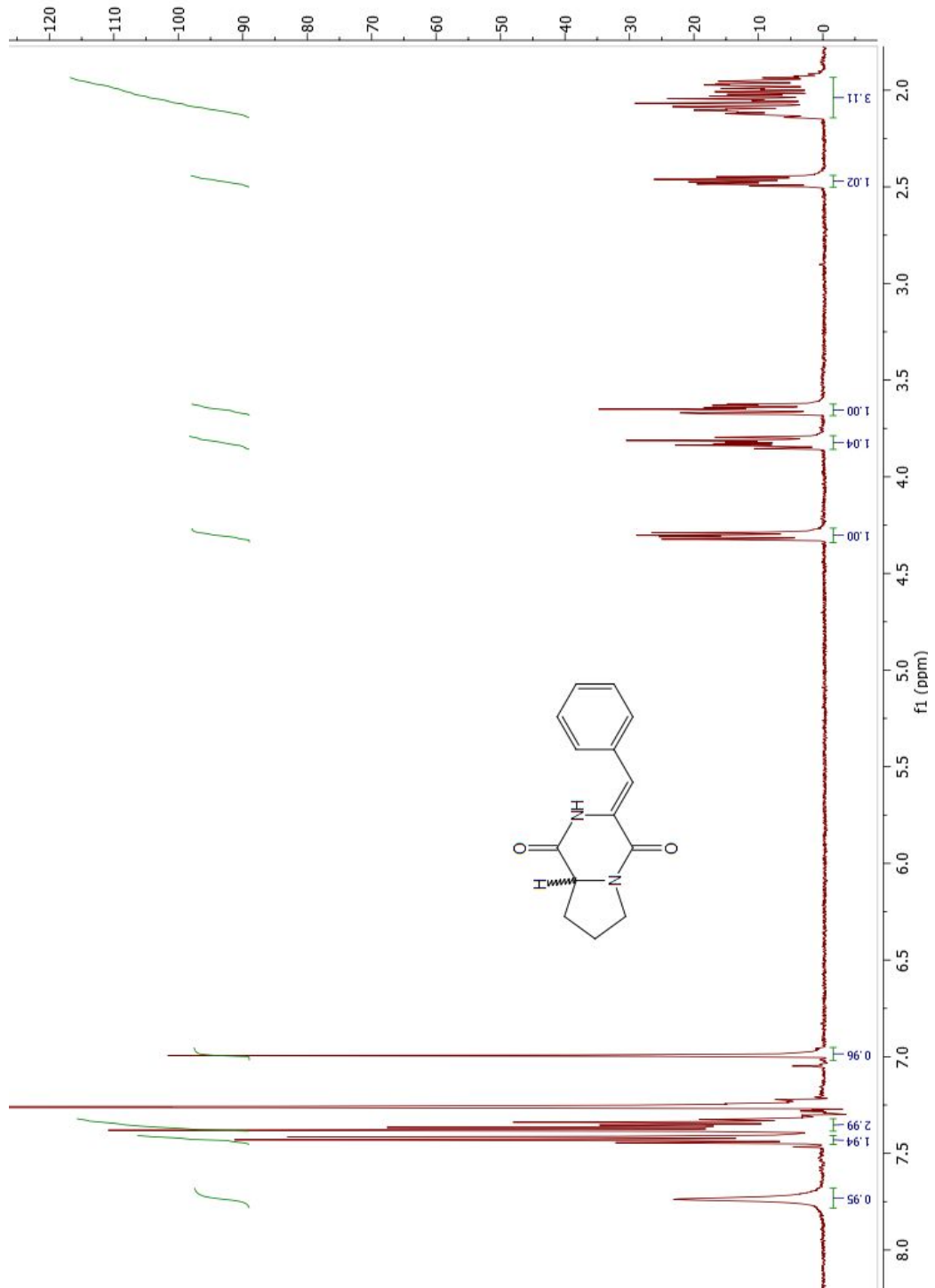


Figure S21. ¹H NMR Spectrum of **4** (600 MHz, CDCl₃)

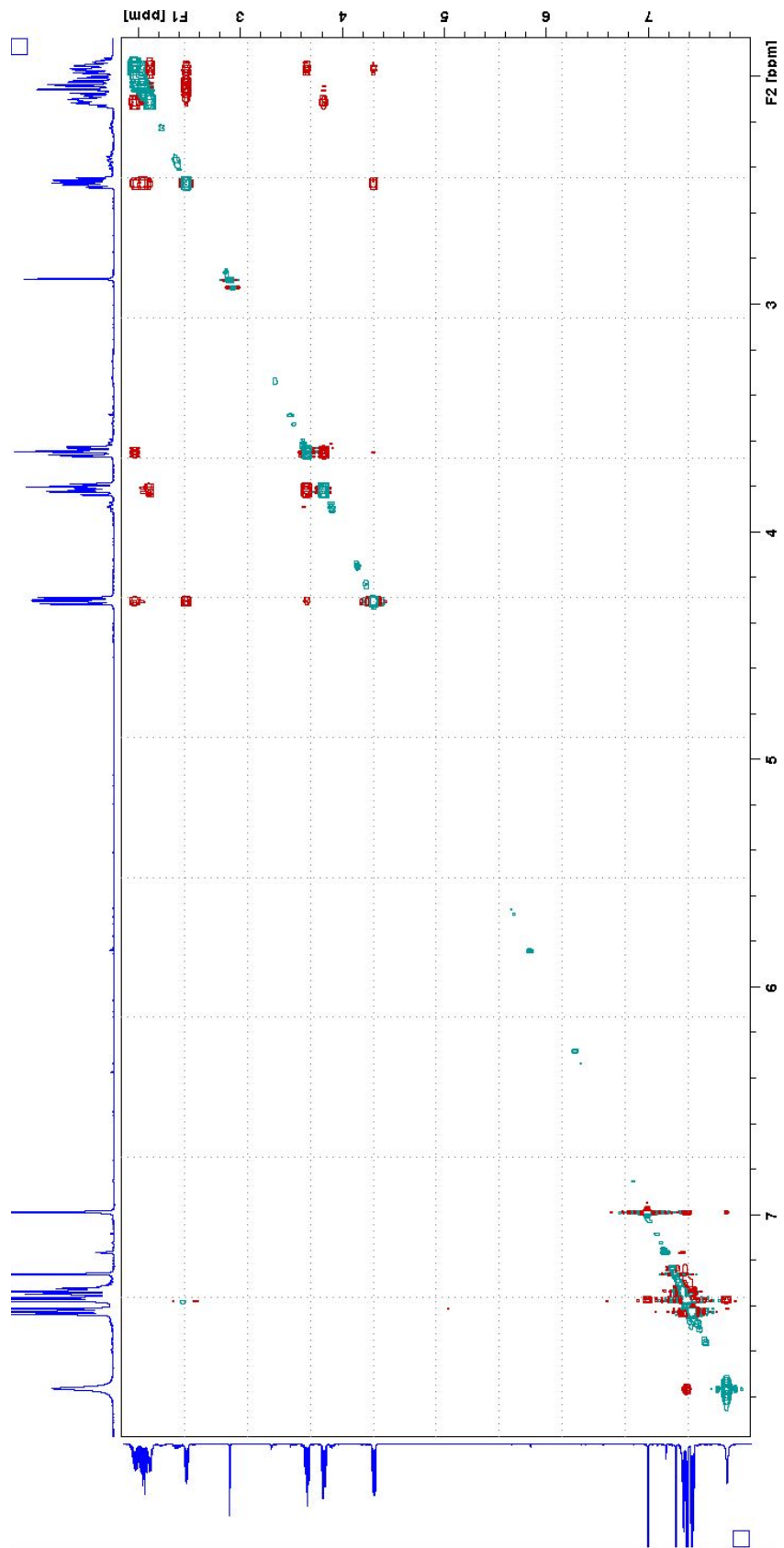


Figure S22. NOESY Spectrum of **4** (150 MHz, CDCl₃)

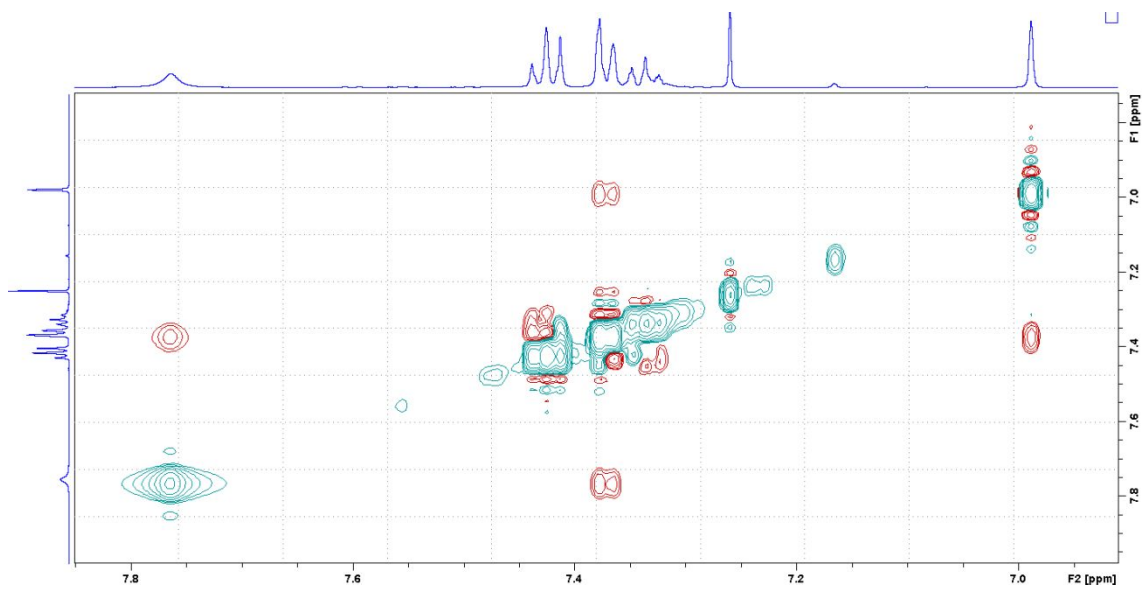
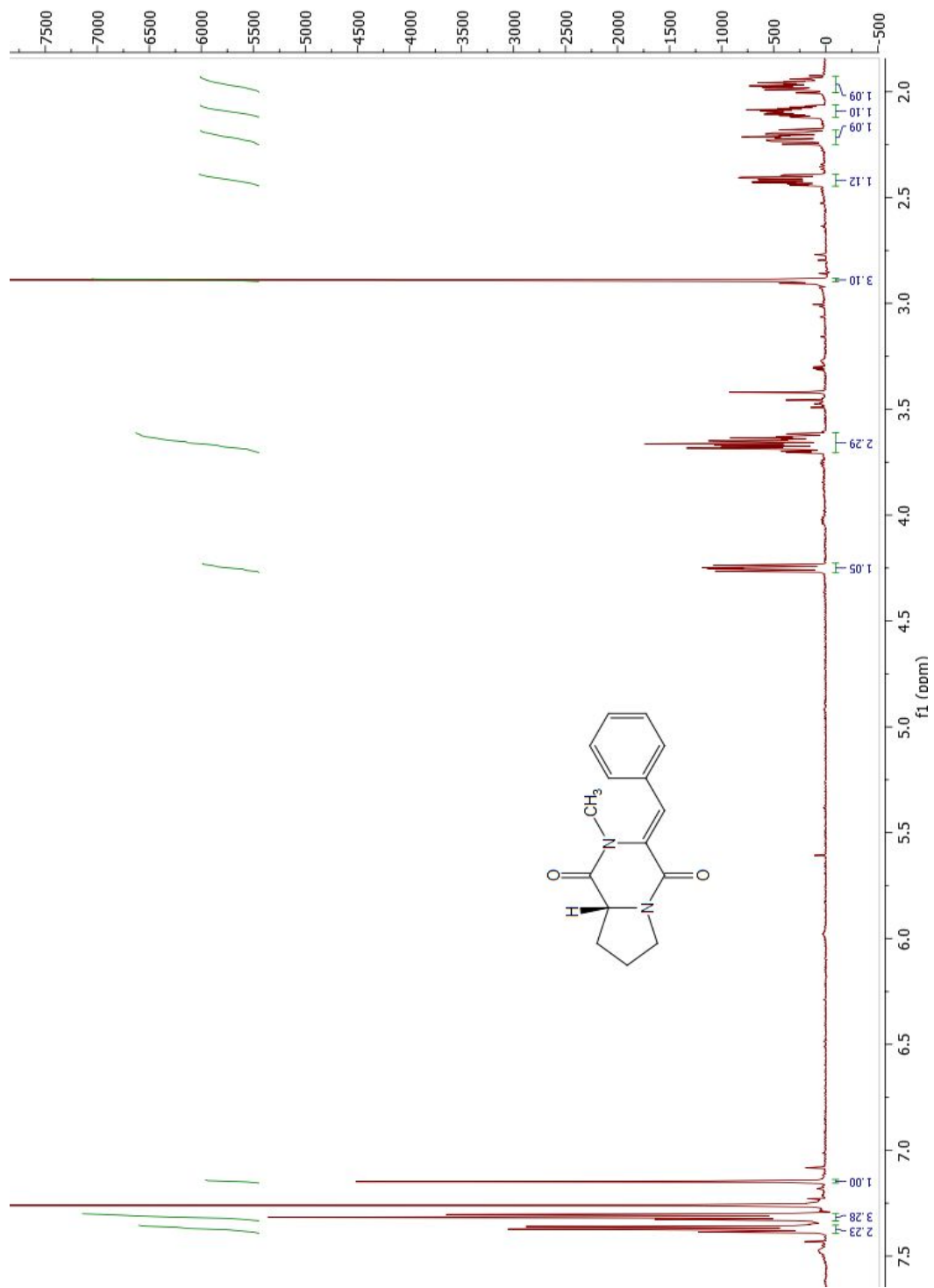


Figure S23. Expanded Aromatic Region of the NOESY Spectrum of **4** (**4**; 600 MHz, CDCl₃)



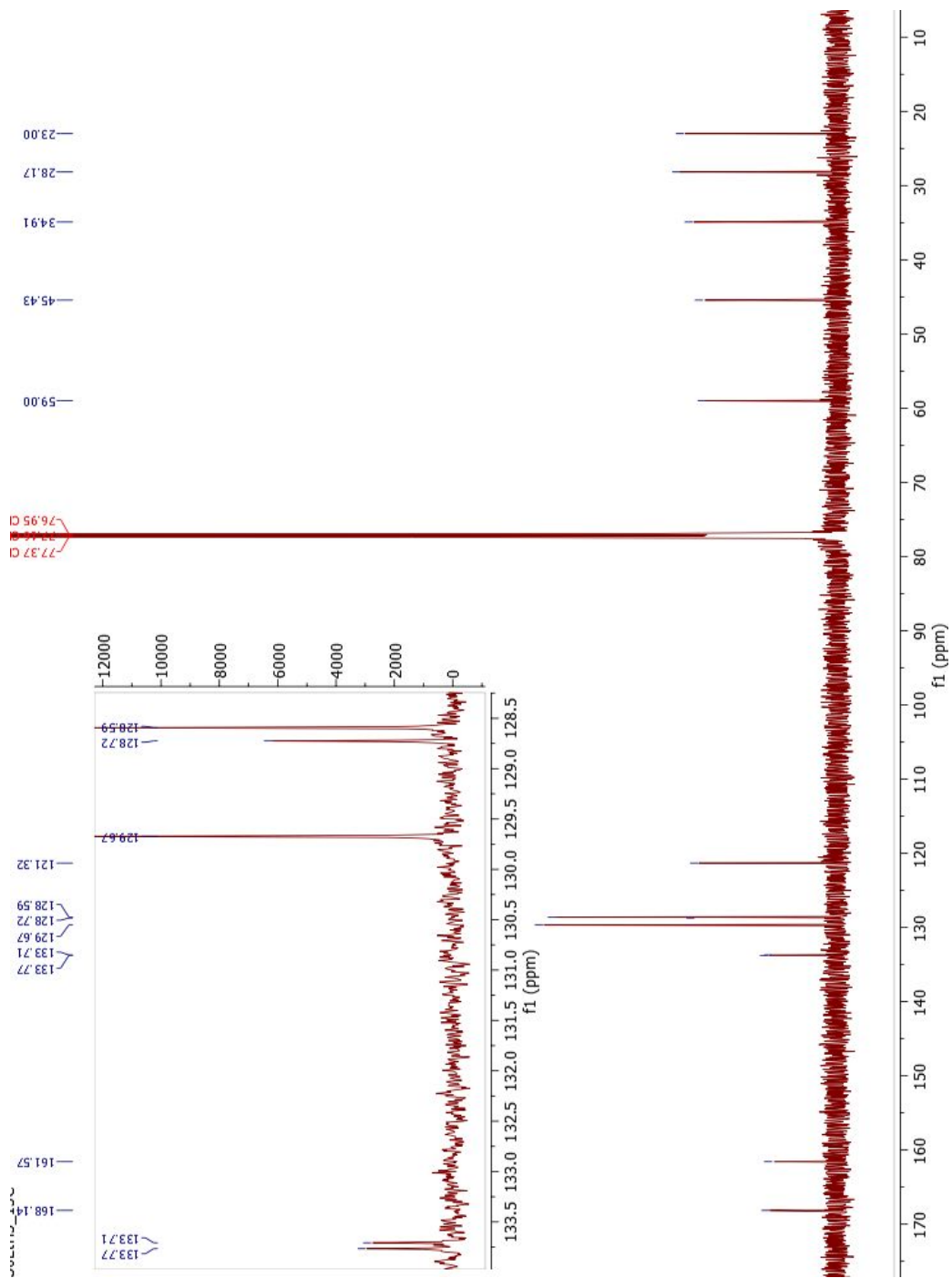


Figure S25. ^{13}C NMR Spectrum of 5 (150 MHz,

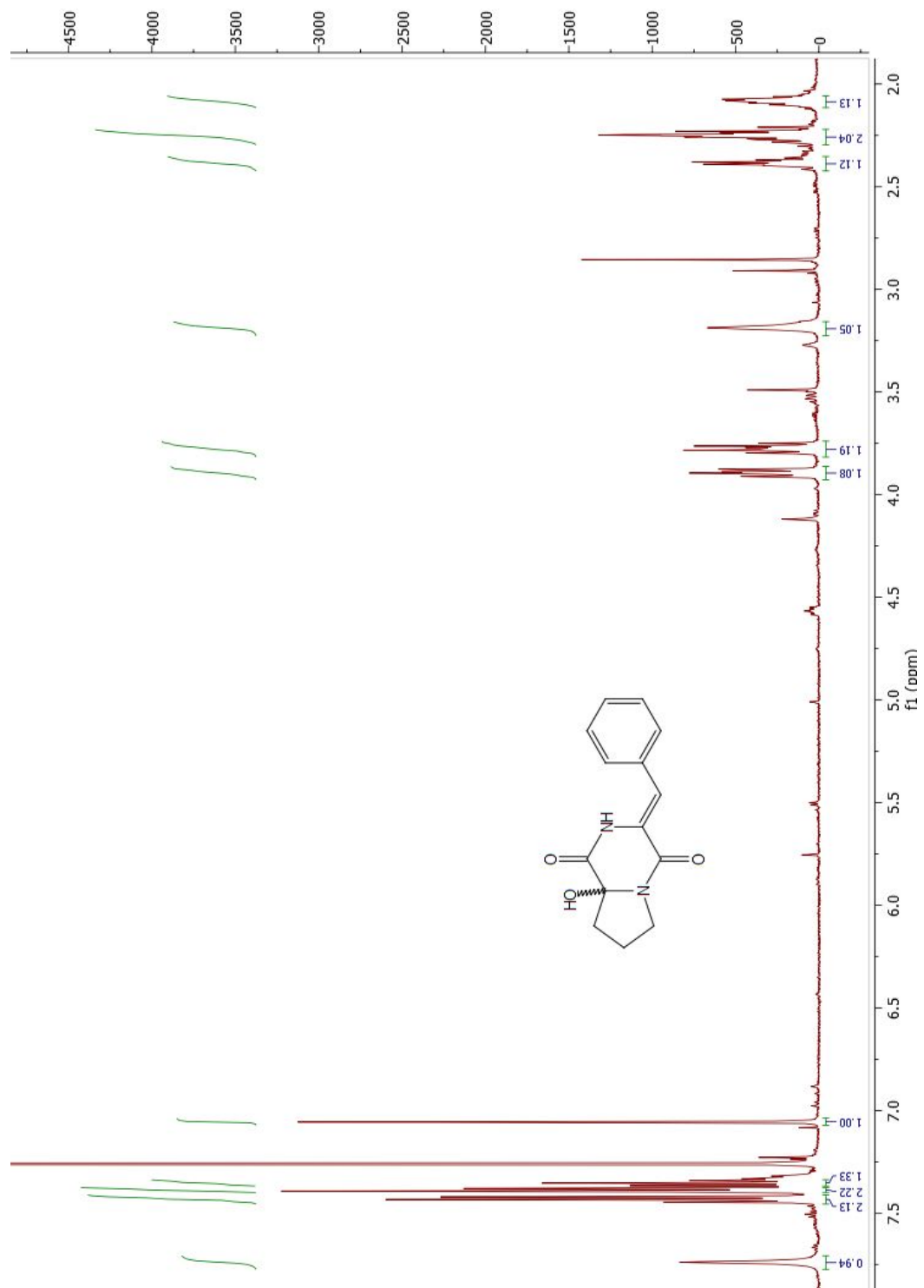


Figure S26. ^1H NMR Spectrum of **6** (600 MHz, CDCl_3)

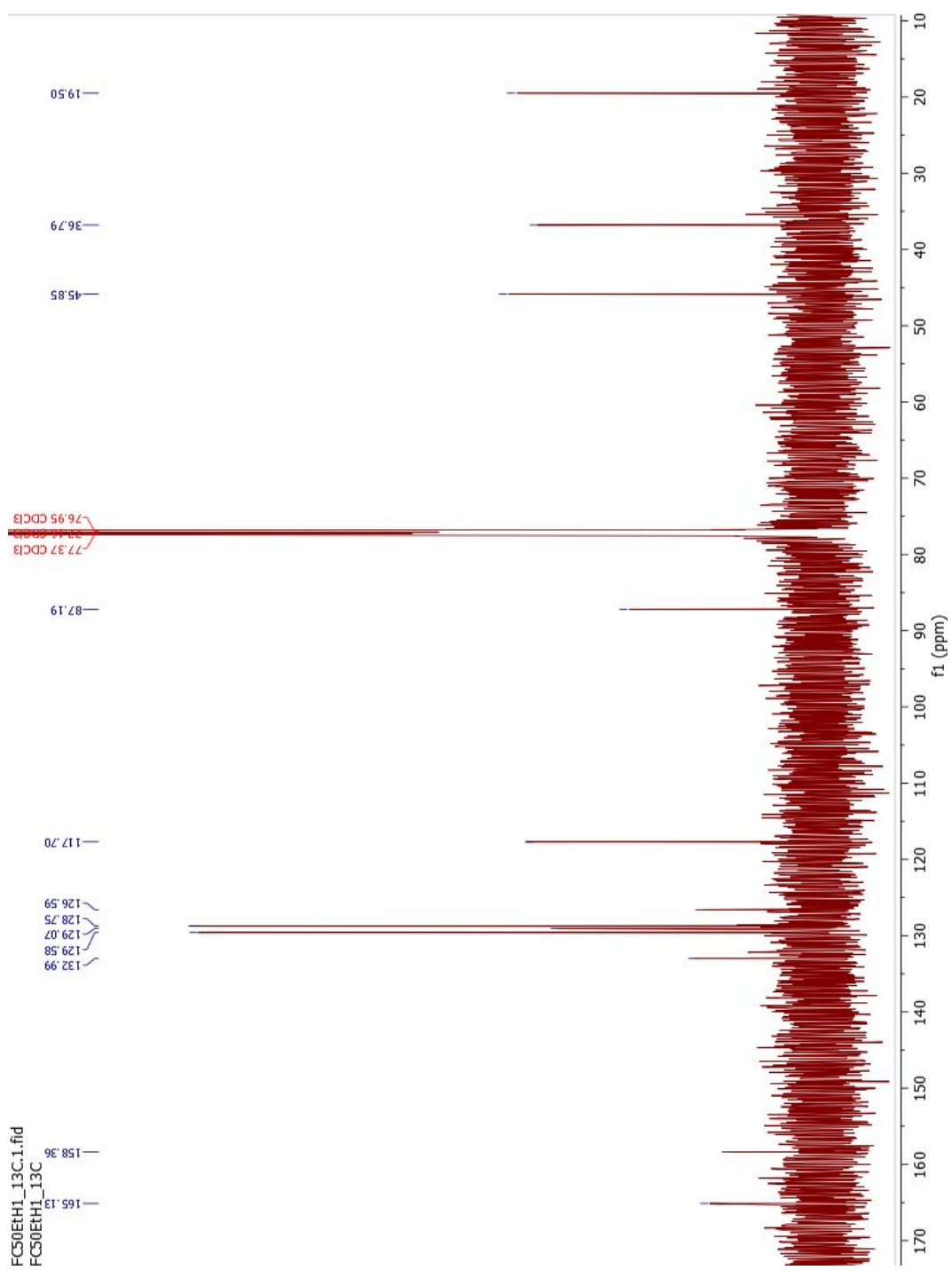


Figure S27. ^{13}C NMR Spectrum of **6** (150 MHz, CDCl_3)

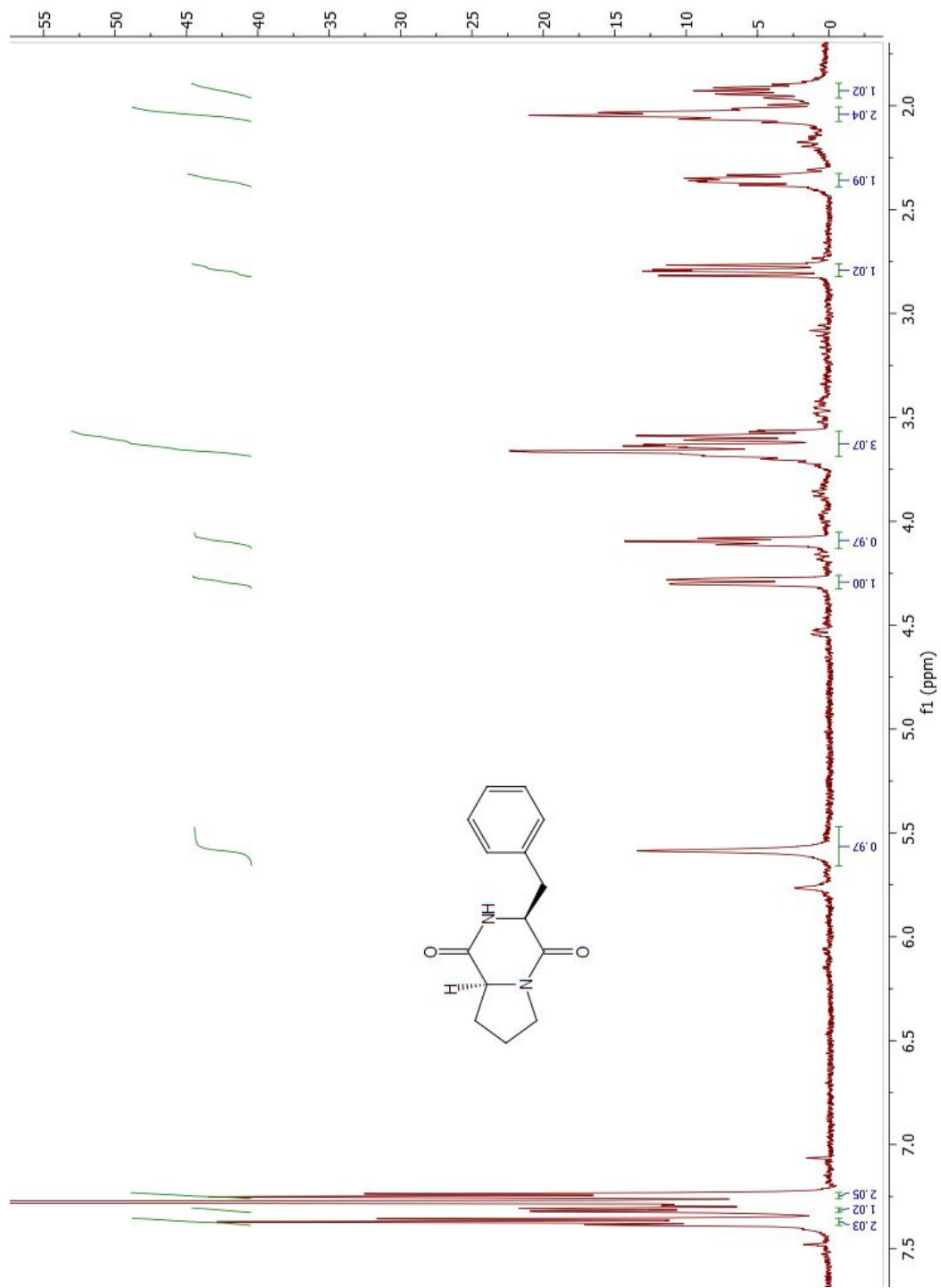


Figure S28. ^1H NMR Spectrum of **7** (500 MHz, CDCl_3)

Table S1. NMR spectroscopic data of broomeanamide B (**2**) in CDCl₃

Amino acid	position	¹³ C ^a	¹ H (mult., <i>J</i> in Hz) ^b	HMBC
Pro	CO	173.5	-	-
	α-CH	55.8	4.04 (br t, 7.3)	-
	β ₁ -CH ₂	28.8	1.07 (m)	-
	β ₂ -CH ₂	28.8	0.55 (m)	-
	γ ₁ -CH ₂	25.5	2.00 (m)	-
	γ ₂ -CH ₂	25.5	1.52 (m)	-
	δ-CH ₂	48.2	3.54 (t, 6.7)	28.8
<i>N</i> -MePhe	CO	-	-	-
	N-CH ₃	28.8	2.83 (s)	173.5, 62.5
	α-CH	62.5	5.11 (dd, 10.3, 4.1)	-
	β-CH ₂	34.0	3.02 (m)	129.6, 62.5
	γ-C (ar.)	138.3	-	-
	δ-CH ₂ (ar.)	129.6	7.14 (d, 7.1)	129.6, 126.9, 34.0
	ε-CH ₂ (ar.)	128.9	7.29 (t, 7.3)	138.3, 129.6
	ζ-CH (ar.)	126.9	7.22 (t, 7.6)	129.6
Ala	CO	174.9	-	-
	NH	-	8.85 (d, 7.5)	-
	α-CH	45.7	4.96 (m)	-
	β-CH ₃	17.1	1.24 (d, 6.5)	174.9, 45.7
<i>N</i> -MeVal	CO	171.6	-	-
	N-CH ₃	31.0	3.40 (s)	174.9, 56.8
	α-CH	56.8	5.31 (d, 10.6)	-
	β-CH	38.7	2.40 (m)	-
	γ ₁ -CH ₃	19.8	1.00 (d, 6.5)	56.8, 38.7, 20.0
	γ ₂ -CH ₃	20.0	0.95 (d, 6.5)	56.8, 38.7, 19.8
<i>N</i> -MeLeu ²	CO	-	-	-
	N-CH ₃	29.2	2.87 (s)	171.6, 59.1
	α-CH	59.1	4.93 (m)	-
	β ₁ -CH ₂	38.7	2.40 (m)	-
	β ₂ -CH ₂	38.7	1.08 (m)	-
	γ-CH	25.5	1.45 (m)	-
	δ ₁ -CH ₃	23.6	0.90 (d, 6.5)	38.7, 25.5, 22.7
	δ ₂ -CH ₃	22.7	0.94 (d, 6.5)	38.7, 25.5
Val ¹	CO	172.8	-	-
	NH	-	8.08 (d, 8.2)	-
	α-CH	54.6	4.90 (m)	-
	β-CH	33.6	1.78 (m)	-
	γ ₁ -CH ₃	17.9	0.76 (d, 6.5)	54.6, 31.7, 20.5
	γ ₂ -CH ₃	22.7	0.93(d, 6.5)	54.6, 31.7, 17.9
	<i>N</i> -MeLeu ¹	CO	-	-
N-CH ₃		30.9	2.92 (s)	172.8, 55.2
α-CH		55.2	5.07 (brt, 7.5)	-
β ₁ -CH ₂		34.9	1.75 (m)	-
β ₂ -CH ₂		34.9	1.61	-
γ-CH		25.5	1.45 (m)	-
δ ₁ -CH ₃		22.1	0.86 (d, 6.5)	34.9, 25.5, 20.1
δ ₂ -CH ₃		20.1	0.93 (d, 6.5)	34.9, 25.5, 22.1
Val ²		CO	170.9	-
	NH	-	8.14 (d, 8.1)	-
	α-CH	56.6	4.31 (br t, 8.5)	170.9
	β-CH	34.6	1.74 (m)	-
	γ ₁ -CH ₃	18.9	0.82 (d, 6.5)	56.6, 34.6, 18.7
	γ ₂ -CH ₃	18.7	0.85 (d, 6.5)	56.6, 34.6, 18.9

^a150 MHz; ^b600 MHz.

Table S2. NMR spectroscopic data of broomeanamide C (**3**) in CDCl₃

Amino acid	position	¹³ C ^a	¹ H (mult., <i>J</i> in Hz) ^b	HMBC
Pro	CO	173.3	-	-
	α-CH	55.2	4.06 (t, 6.7)	-
	β ₁ -CH ₂	29.0	1.00 (m)	-
	β ₂ -CH ₂	29.0	0.57 (m)	-
	γ ₁ -CH ₂	25.3	1.97 (m)	-
	γ ₂ -CH ₂	25.3	1.54 (m)	-
	δ-CH ₂	48.1	3.53 (m)	-
<i>N</i> -MePhe	CO	-	-	-
	N-CH ₃	29.0	2.82 (s)	173.3, 62.4
	α-CH	62.4	5.04(dd, 11.8, 3.0)	-
	β-CH ₂	34.2	3.07 (m)	-
	γ-C (ar.)	138.2	-	-
	δ-CH ₂ (ar.)	129.5	7.13 (d, 7.3)	126.8
	ε-CH ₂ (ar.)	128.7	7.29 (t, 7.6)	129.5, 138.2
	ζ-CH (ar.)	126.8	7.21 (t, 6.7)	129.5
Ala	CO	-	-	-
	NH	-	8.80 (d, 8.3)	-
	α-CH	48.5	4.50 (m)	-
	β-CH ₃	17.7	1.27 (d, 6.3)	172.9, 48.5
Val ²	CO	172.0	-	-
	N-H	-	6.65 (d, 8.3)	-
	α-CH	54.7	4.66 (m)	-
	β-CH	33.8	2.10 (m)	-
	γ ₁ -CH ₃	19.3	1.10 (d, 6.4)	54.7, 20.2
	γ ₂ -CH ₃	20.2	0.97 (d, 6.4)	54.7, 19.3
<i>N</i> -MeLeu ²	CO	-	-	-
	N-CH ₃	29.4	2.85 (s)	172.0, 59.1
	α-CH	59.1	4.84 (dd, 11.0, 2.3)	-
	β ₁ -CH ₂	38.3	2.41 (m)	-
	β ₂ -CH ₂	38.3	1.30 (m)	-
	γ-CH	25.3	1.54 (m)	-
	δ ₁ -CH ₃	23.3	0.89 (d, 6.4)	22.3
	δ ₂ -CH ₃	22.3	0.94 (d, 6.4)	23.3
Ile	CO	172.4	-	-
	NH	-	8.45 (d, 8.3)	-
	α-CH	54.9	4.97 (m)	-
	β-CH	37.6	1.79 (m)	-
	γ-CH ₃	22.8	0.92 (d, 6.3)	-
	γ-CH ₂	28.4	1.32 (m)	-
	δ-CH ₃	11.3	0.72 (t, 7.3)	37.6
	<i>N</i> -MeLeu ¹	CO	-	-
N-CH ₃		30.4	2.92 (s)	172.4, 54.4
α-CH		54.4	5.10 (t, 7.8)	-
β ₁ -CH ₂		34.7	1.74 (m)	-
β ₂ -CH ₂		34.7	1.62 (m)	-
γ-CH		25.3	1.45 (m)	-
δ ₁ -CH ₃		22.3	0.86 (d, 6.4)	22.9
δ ₂ -CH ₃		22.8	0.92 (d, 6.4)	25.3
Val ¹	CO	-	-	-
	NH	-	7.97 (d, 8.3)	-
	α-CH	56.5	4.30 (t, 8.8)	-
	β-CH	34.7	1.74 (m)	-
	γ ₁ -CH ₃	22.5	0.82 (d, 6.3)	56.5, 34.7, 18.6
	γ ₂ -CH ₃	18.6	0.85 (d, 6.3)	34.7, 22.5

^a150 MHz; ^b600 MHz.