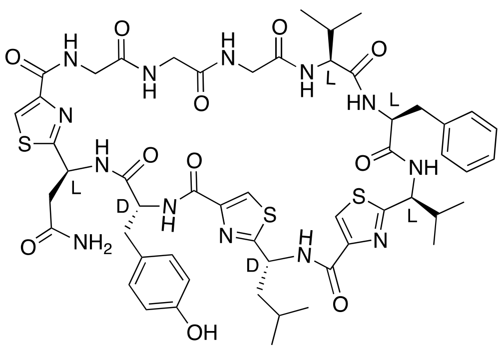
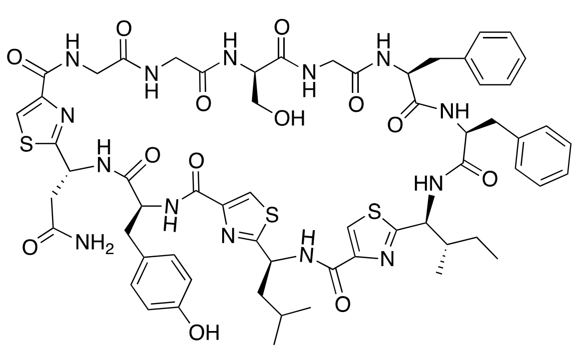
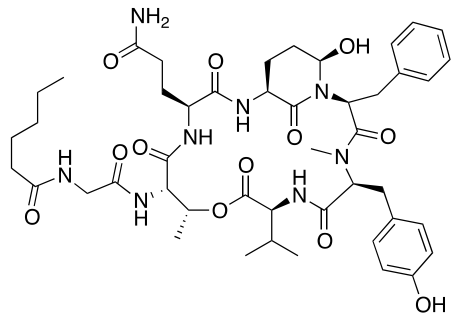
Supplementary Information



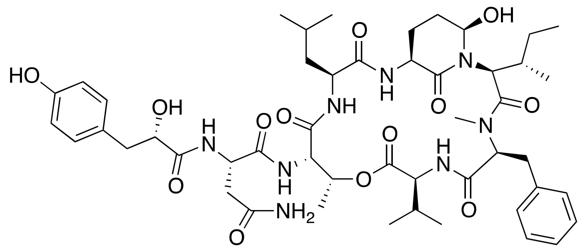
Aeruginazole A



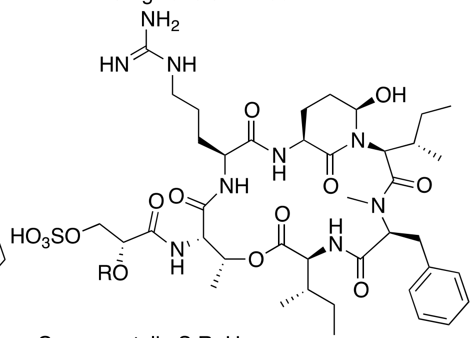
Aeruginazole DA1304



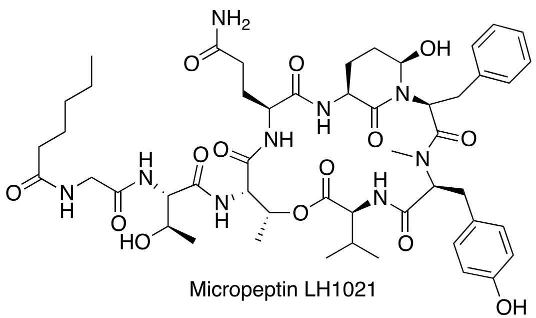
Micropeptin LH920



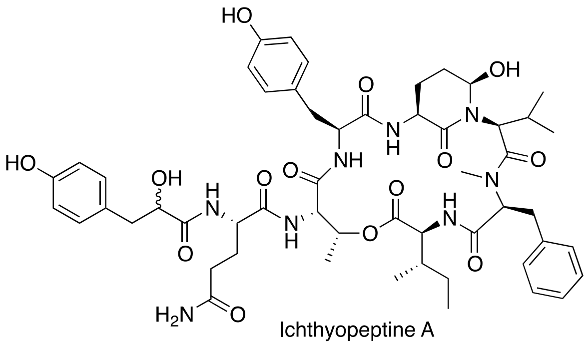
Micropeptin HM978



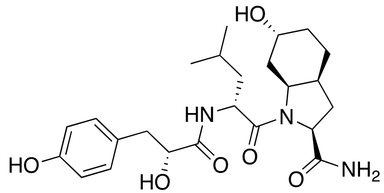
Cyanopeptolin S R=H
Cyanopeptolin SS R=SO_3H



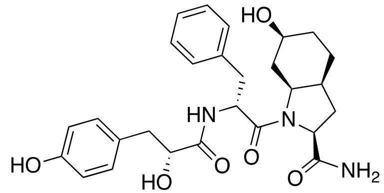
Micropeptin LH1021



Ichthyopeptine A



Aeruginosin 298B



Aeruginosin DA495A

Figure S1. Structures of Known Metabolites Isolated from the Extract of IL-381—Plate I.

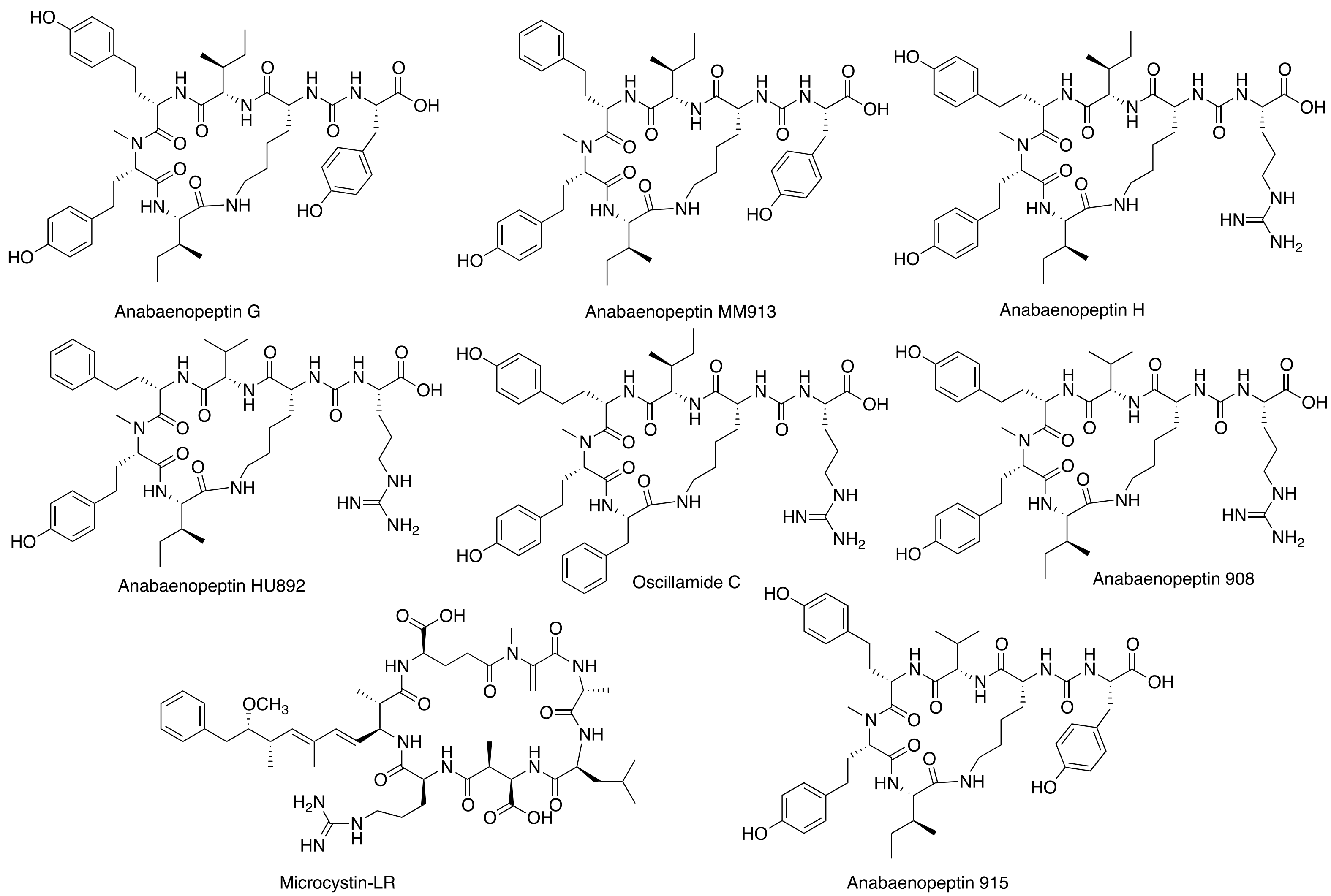


Figure S2. Structures of Known Metabolites Isolated from the Extract of IL-381—Plate II.

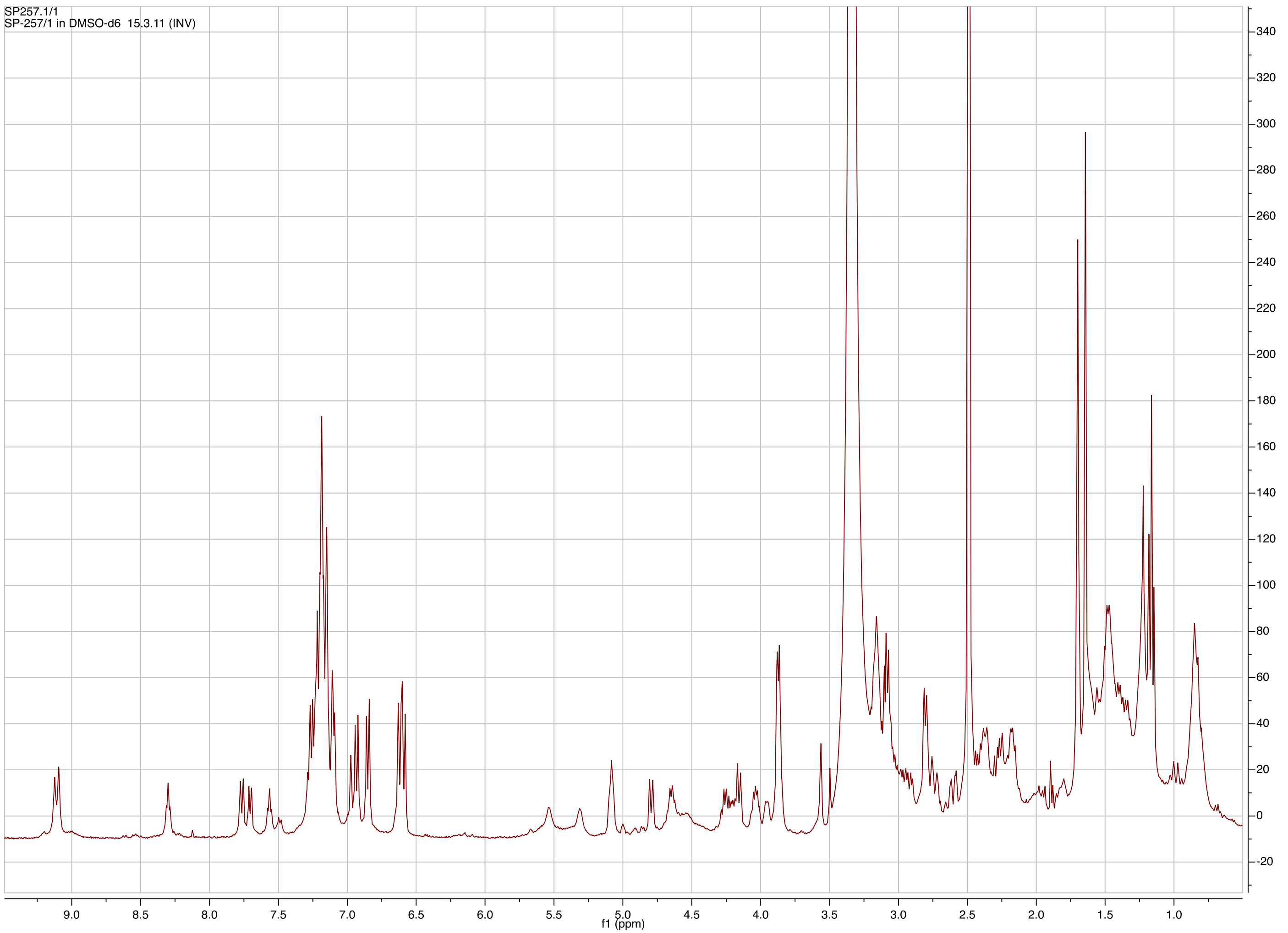


Figure S3. ^{1}H NMR Spectrum (500 MHz) of Aeruginosin KB676 (**1**) in DMSO-d_6.

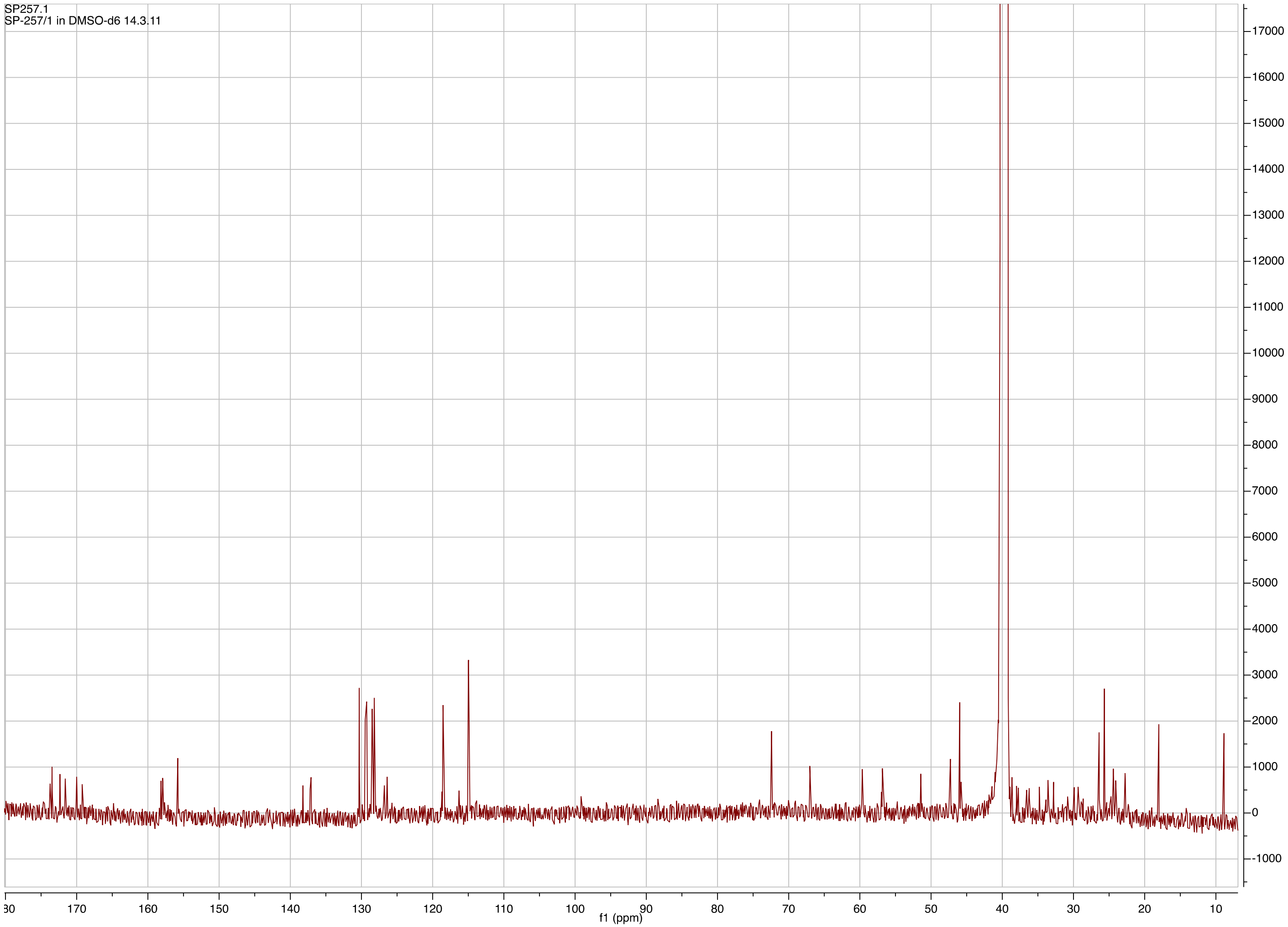


Figure S4. ^{13}C NMR Spectrum (125 MHz) of Aeruginosin KB676 (**1**) in DMSO-d_6.

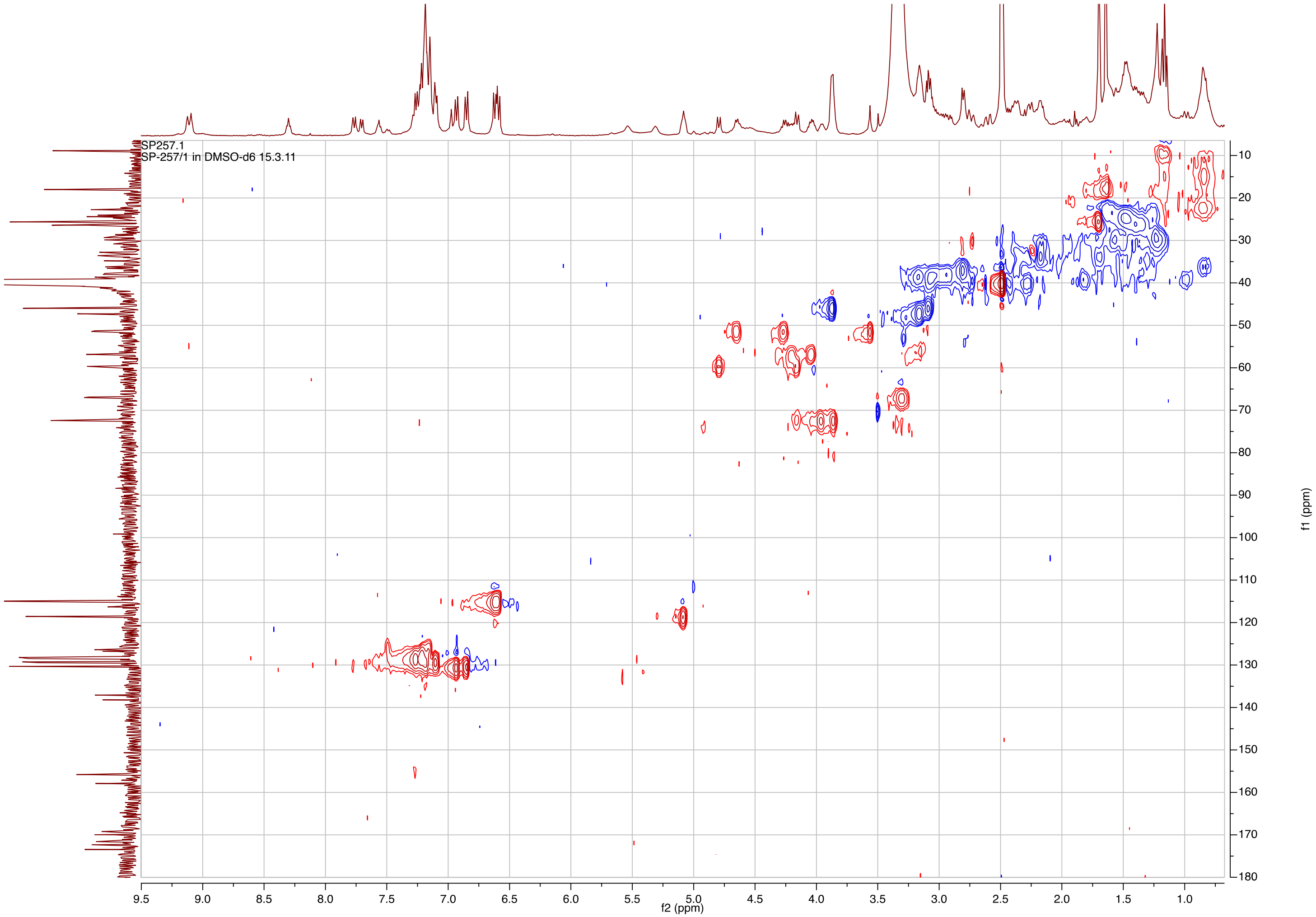


Figure S5. HSQC Spectrum of Aeruginosin KB676 (**1**) in DMSO-d_6 (Red: CH, CH_3; Blue: CH_2).

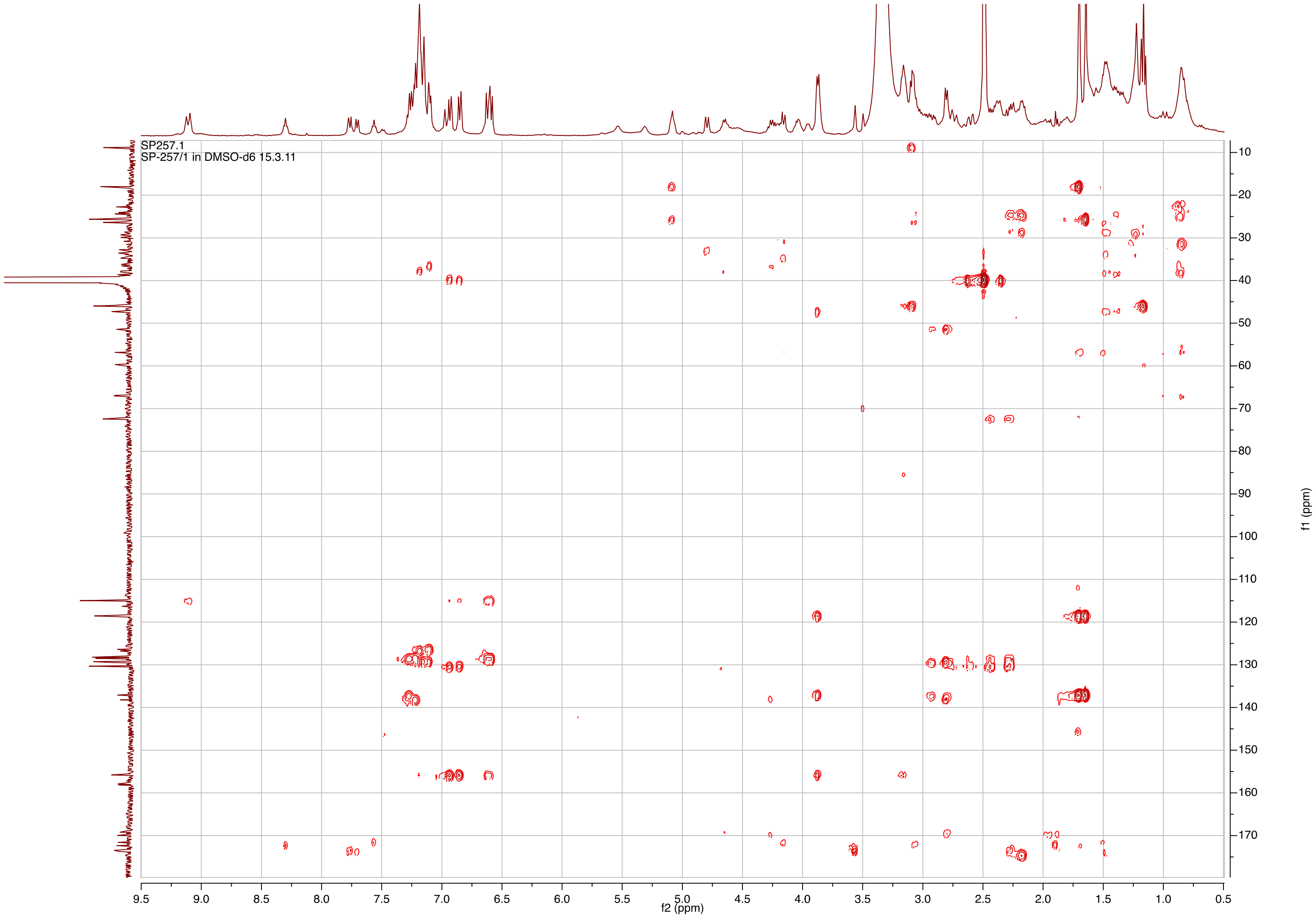


Figure S6. HMBC Spectrum of Aeruginosin KB676 (**1**) in DMSO-d_6.

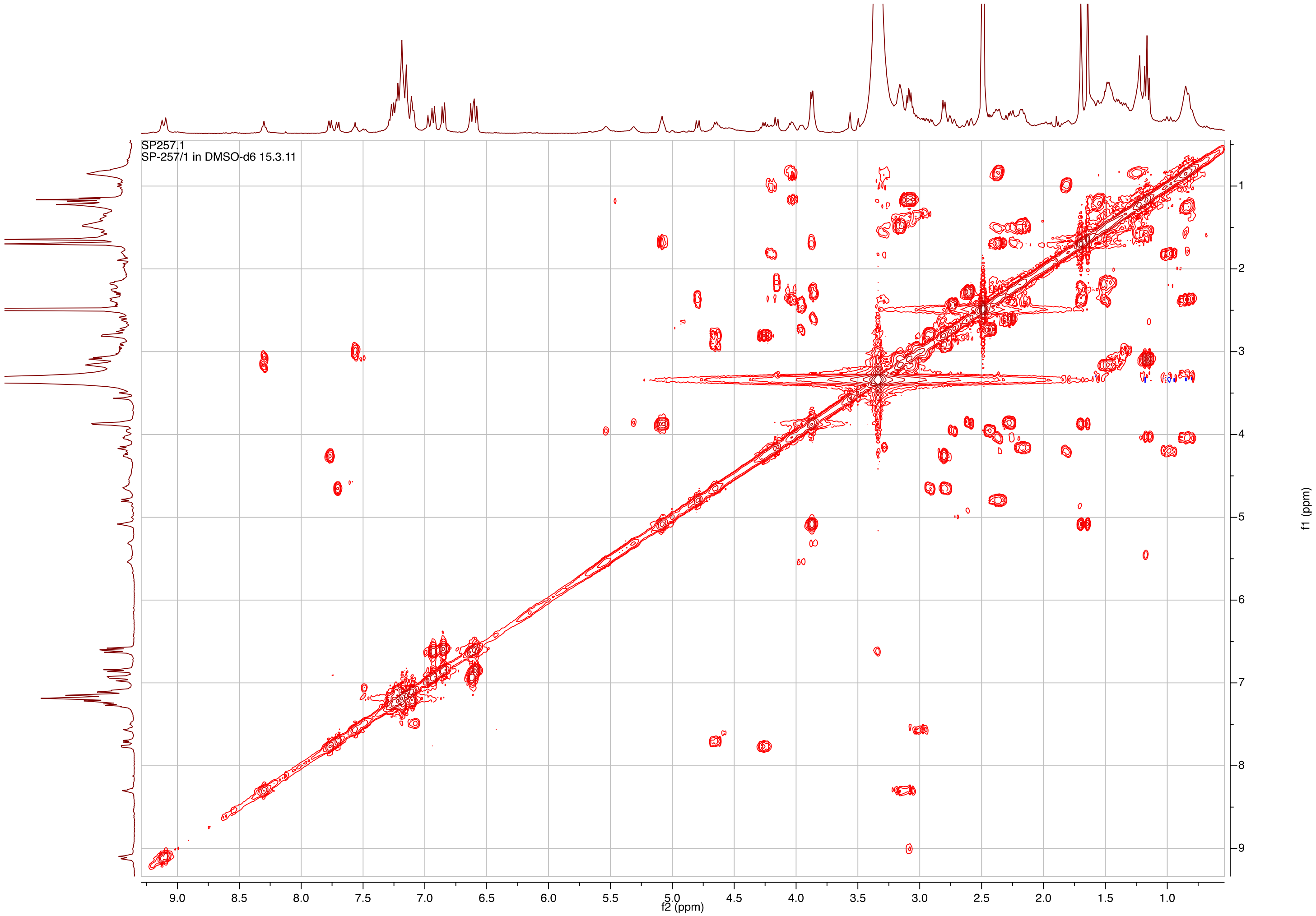


Figure S7. COSY Spectrum of Aeruginosin KB676 (**1**) in DMSO-d_6.

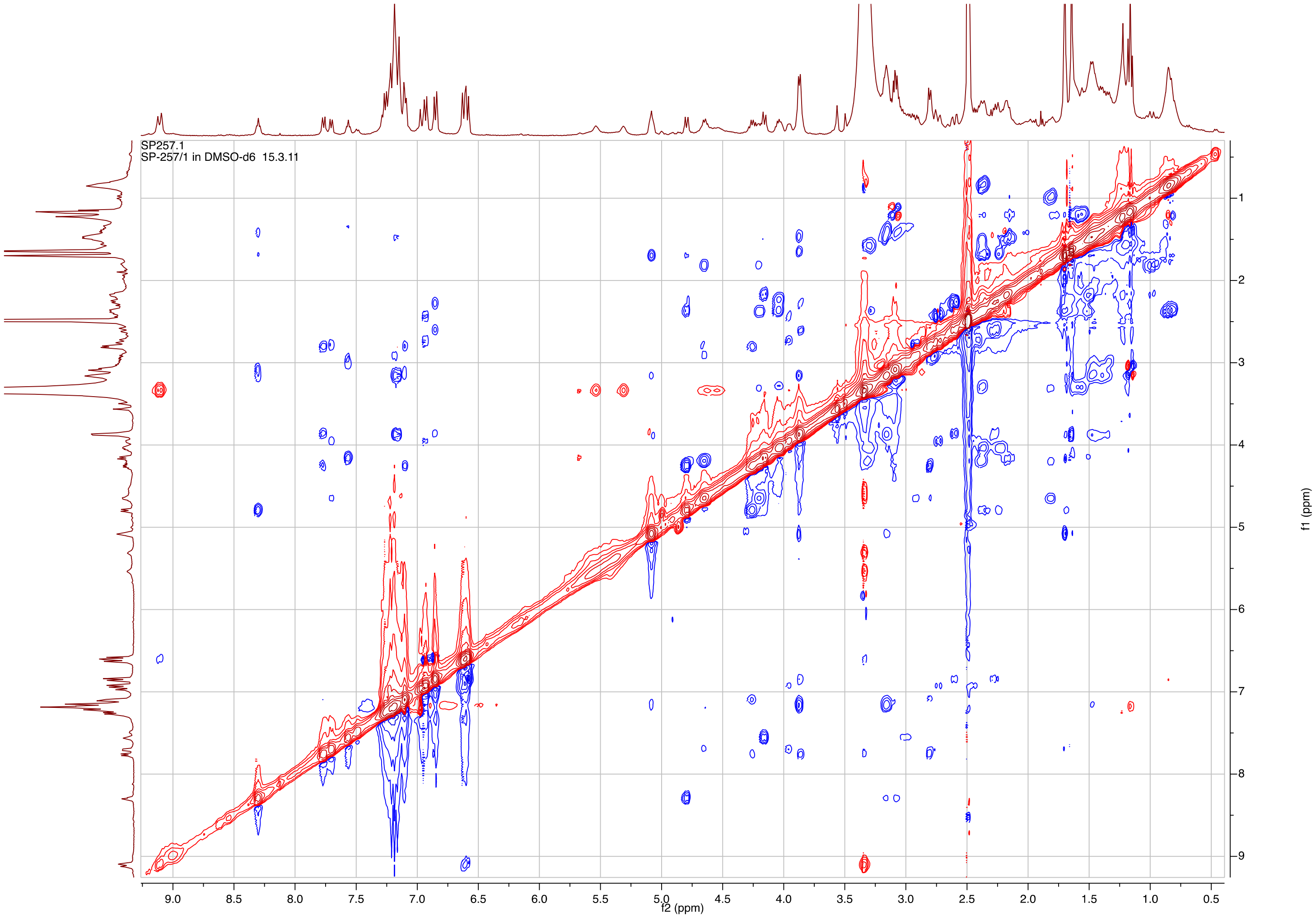


Figure S8. ROESY Spectrum of Aeruginosin KB676 (**1**) in DMSO-d_6 (Blue: NOE correlation).

Table S1. NMR Data of the minor rotamer of Aeruginosin KB676 (**1**) in DMSO-d_6.

Position	δ_C mult. [b]	δ_H mult. [b] *J* in Hz	HMBC Correlations [c]	NOE Correlations [d]
Hpla 1	173.7, qC	-		
2	72.4, CH	3.95, m		Hpla-3,3′,5,5′; Phe-*N*H
3	39.5, CH_2	2.72, dd (14.5,3.3)	Hpla-1,2,4,5,5′	Hpla-2,3′,5,5′
		2.44, m	Hpla-1,2,4,5,5′	Hpla-2,3,5,5′
4	128.6, qC	-		
5,5′	130.5, CH	6.93, d (8.3)	Hpla-3,6,6′,7	Hpla-2,3,3′,6,6′
6,6′	115.0, CH	6.62, d (8.3)	Hpla-4,7	Hpla-5,5′,7-*O*H
7	155.9, qC	-		
2-*O*H	-	5.36, brs		
7-*O*H	-	9.12, s	Hpla-7	Hpla-6,6′
Phe 1	169.2, qC	-		
2	51.3, CH	4.65, q (6.0)	Phe-1,3	Phe-3,3′5,5′,*N*H; Choi-7,7a; Agm-1-*N*H
3	37.7, CH_2	2.92, m	Phe-1,4	Phe-2,3′,5,5′,7
		2.78, m	Phe-1,4	Phe-2,3,5,5′,7,*N*H
4	137.2, qC	-		
5,5′	129.5, CH	7.18, m	Phe-3,7	Phe-2,3,6,6′; Choi-7a
6,6′	128.5, CH	7.27, m	Phe-4	Phe-5,5′
7	126.8, CH	7.18, m	Phe-5	Phe-6,6′; Choi-7a
*N*H	-	7.70, d (8.0)	Hpla-1; Phe-2	Phe-2,3; Hpla-2
Choi 1	171.6, qC	-		
2	59.6, CH	4.16, d (9.0)	Choi-1,3	Choi-3,3′,3a; Agm-1-*N*H
3	33.6, CH_2	2.16, m (ax)		Choi-2,3′,3a,4,
		1.50, m (eq)	Choi-7a	Choi-2,3,3a
3a	34.8, CH	2.38, m		Choi-2,3,3′,4,7a
4	22.8, CH_2	1.63, m (2H)		Choi-3,3a,5,7a

Table S1. *Cont.*

5	29.9, CH_2	1.53, m (eq)		Choi-5′,6,
		1.16, m (ax)		Choi-5; Agm-1,4
6	66.9, CH	3.32, m		Choi-5,7eq,7a
6-*O*H	-	4.52, brs		
7	39.0, CH_2	1.80, m (eq)		Choi-6,7ax,7a
		0.98, m (ax)	Choi-6,7a	Choi-5ax,7eq
7a	57.0, CH	4.19, m		Choi-3a,4,7eq
^{4}*N*-prenyl-Agm 1	38.0, CH_2	3.02, m		Agm-1′,2,3,4,7,1-*N*H
		2.95, m	Agm-3	Agm-1,2,1-*N*H
2	26.4, CH_2	1.33, m	Agm-1	Agm-1,1′,4,6,1-*N*H
3	24.4, CH_2	1.45, m	Agm-1	Agm-1,4,6,7,1-*N*H
4	47.3, CH_2	3.16, m	Agm-5	Agm-1′,2,3,6,7,1-*N*H
5	155.8, qC	-		
6	45.8, CH_2	3.87, brd (6.0)	Agm-4,5,7,8	Agm-2,3,4,7,9,10
7	118.6, CH	5.08, brt (6.0)	Agm-9	Agm-1,1′,3,4,6,9
8	137.1, qC	-		
9	25.7, CH_3	1.70, brs	Agm-7,8	Agm-6,7
10	18.0, CH_3	1.64, brs	Agm-7,8	Agm-6,1-*N*H
1-*N*H	-	7.55, t (5.5)	Choi-1	Agm-1,1′,2,3,4,10; Choi-2
5-*N*H,*N*H_2	-	7.25, brm		

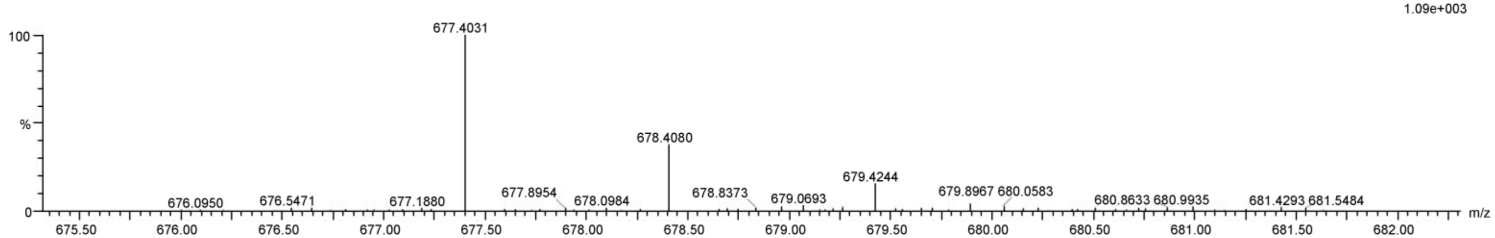
[a] 125 MHz for carbons and 500 MHz for protons; [b] Multiplicity and assignment from HSQC experiment; [c] Determined from HMBC experiment, $^nJ_{CH}$ = 8 Hz, recycle time 1 s; [d] Selected NOE's from ROESY experiment.

Elemental Composition Report

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
190 formula(e) evaluated with 8 results within limits (up to 4 best isotopic matches for each mass)
Elements Used:
C: 30-50 H: 40-60 N: 0-10 O: 0-10

SP-257/1 Shira Peer
carmeli359c 28 (1.244) Cm (27:29) 1: TOF MS ES+ 1.09e+003



		mDa	PPM	DBE			
Minimum:				-1.5			
Maximum:		5.0	10.0	50.0			

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
677.4031	677.4027	0.4	0.6	14.5	143.7	1.5	C37 H53 N6 O6
	677.4013	1.8	2.7	9.5	143.5	1.2	C36 H57 N2 O10
	677.4053	-2.2	-3.2	13.5	143.4	1.1	C41 H57 O8
	677.4067	-3.6	-5.3	18.5	144.0	1.8	C42 H53 N4 O4

Figure S9. HR ESI MS data of Aeruginosin KB676 (**1**).

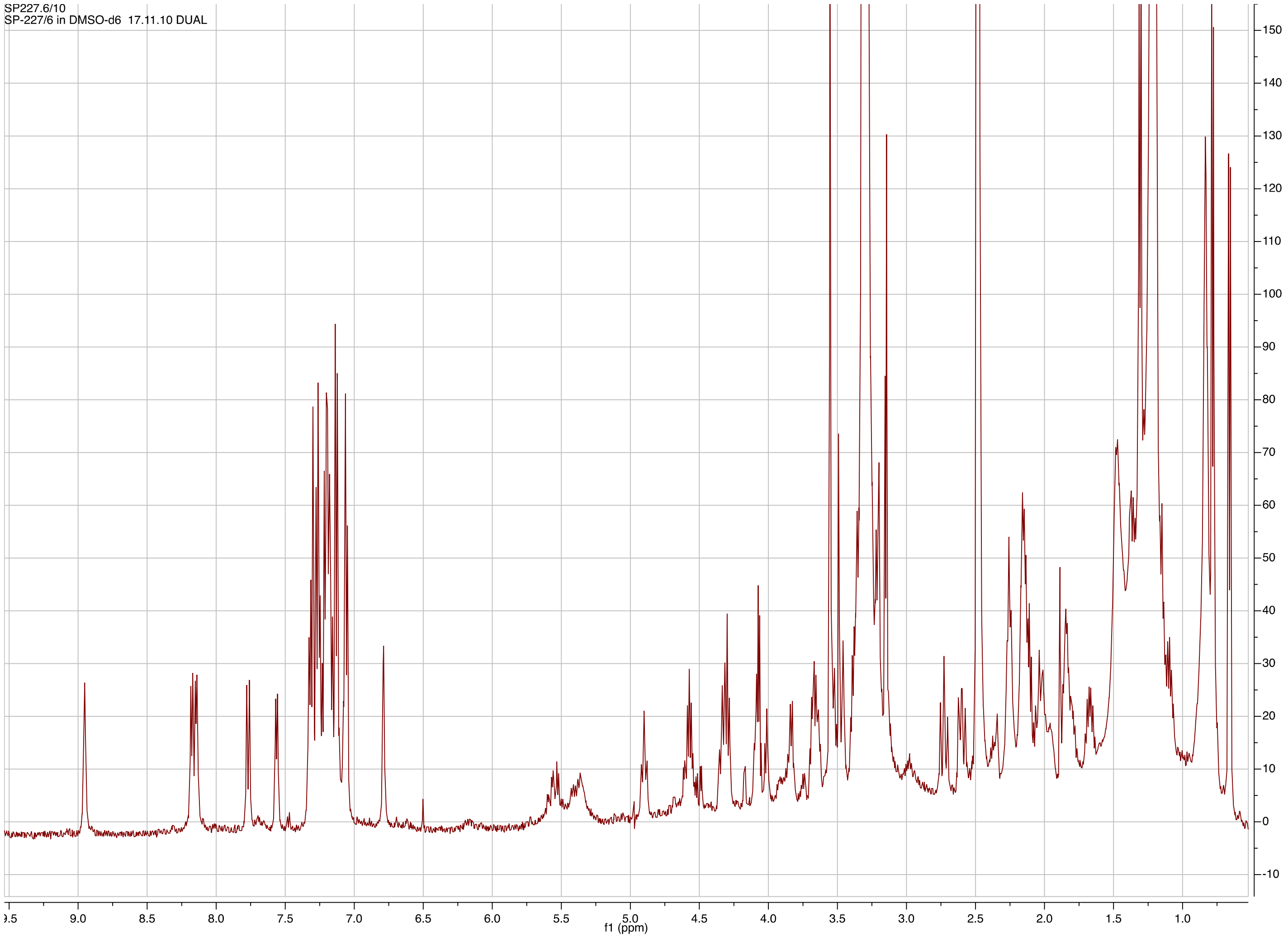


Figure S10. ^{1}H NMR Spectrum (500 MHz) of Microphycin KB921 (**2**) in DMSO-d_6.

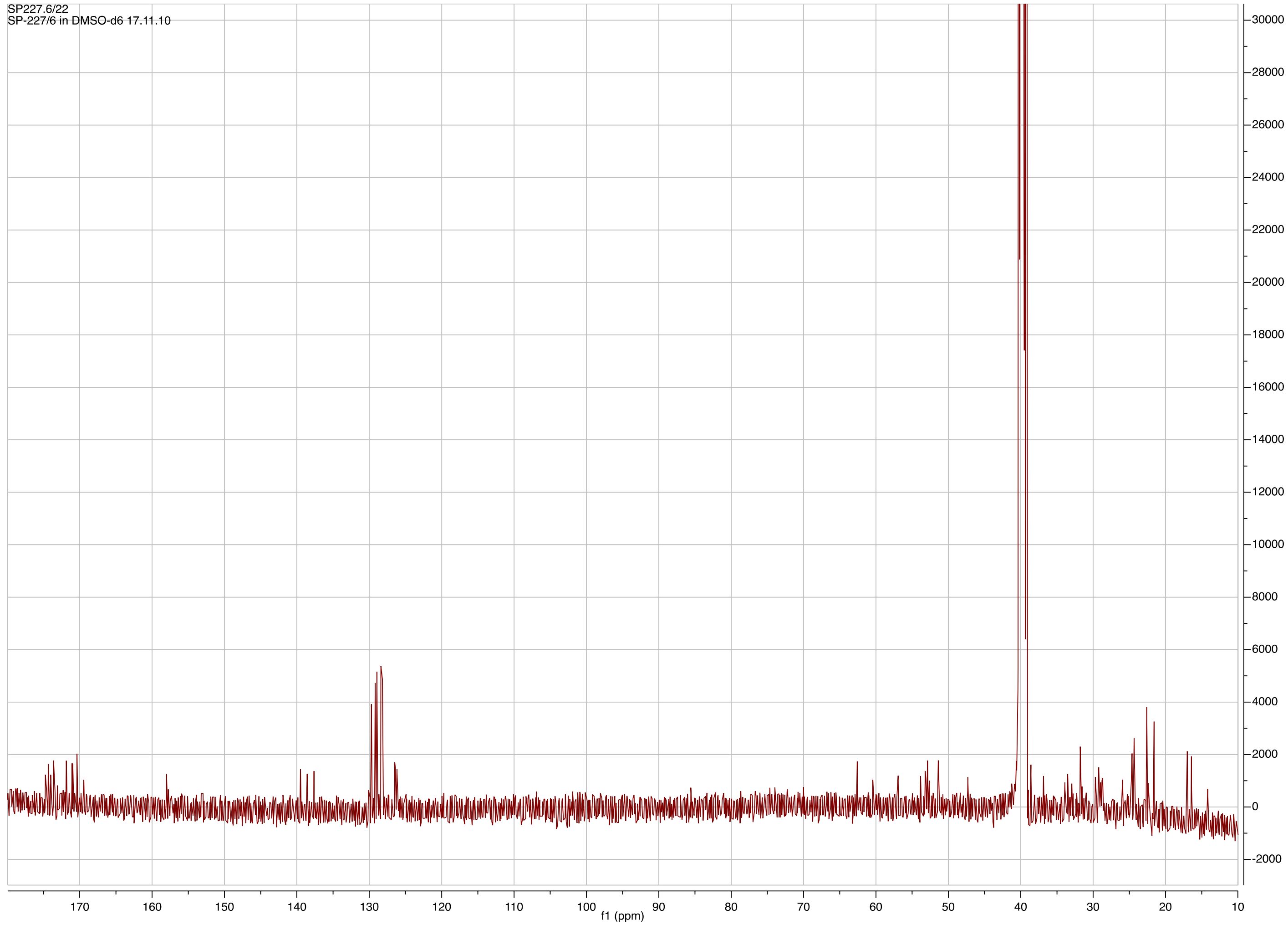


Figure S11. ^{13}C NMR Spectrum (125 MHz) of Microphycin KB921 (**2**) in DMSO-d_6.

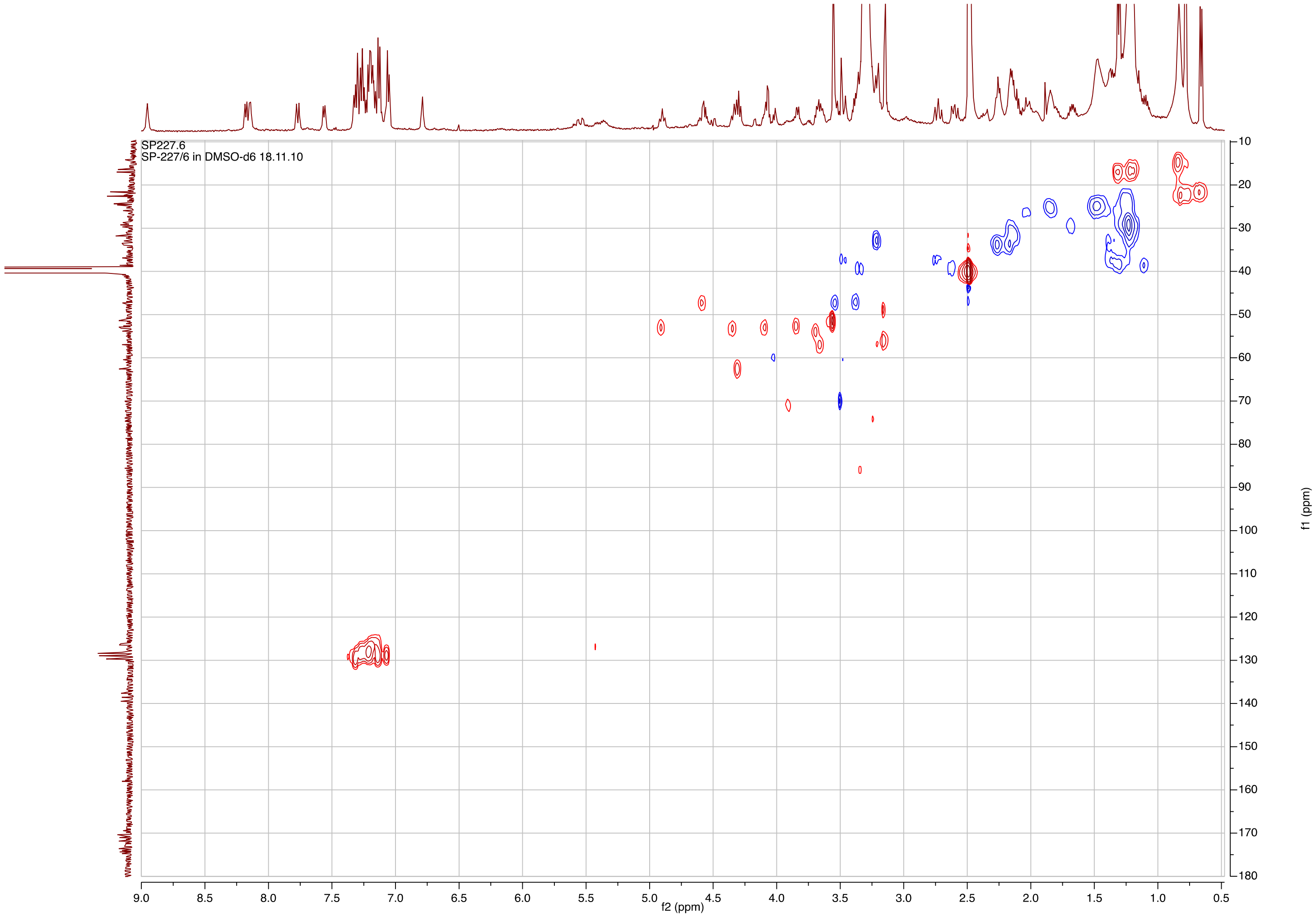


Figure S12. HSQC Spectrum of Microphycin KB921 (**2**) in DMSO-d_6 (Red: CH, CH_3; Blue: CH_2).

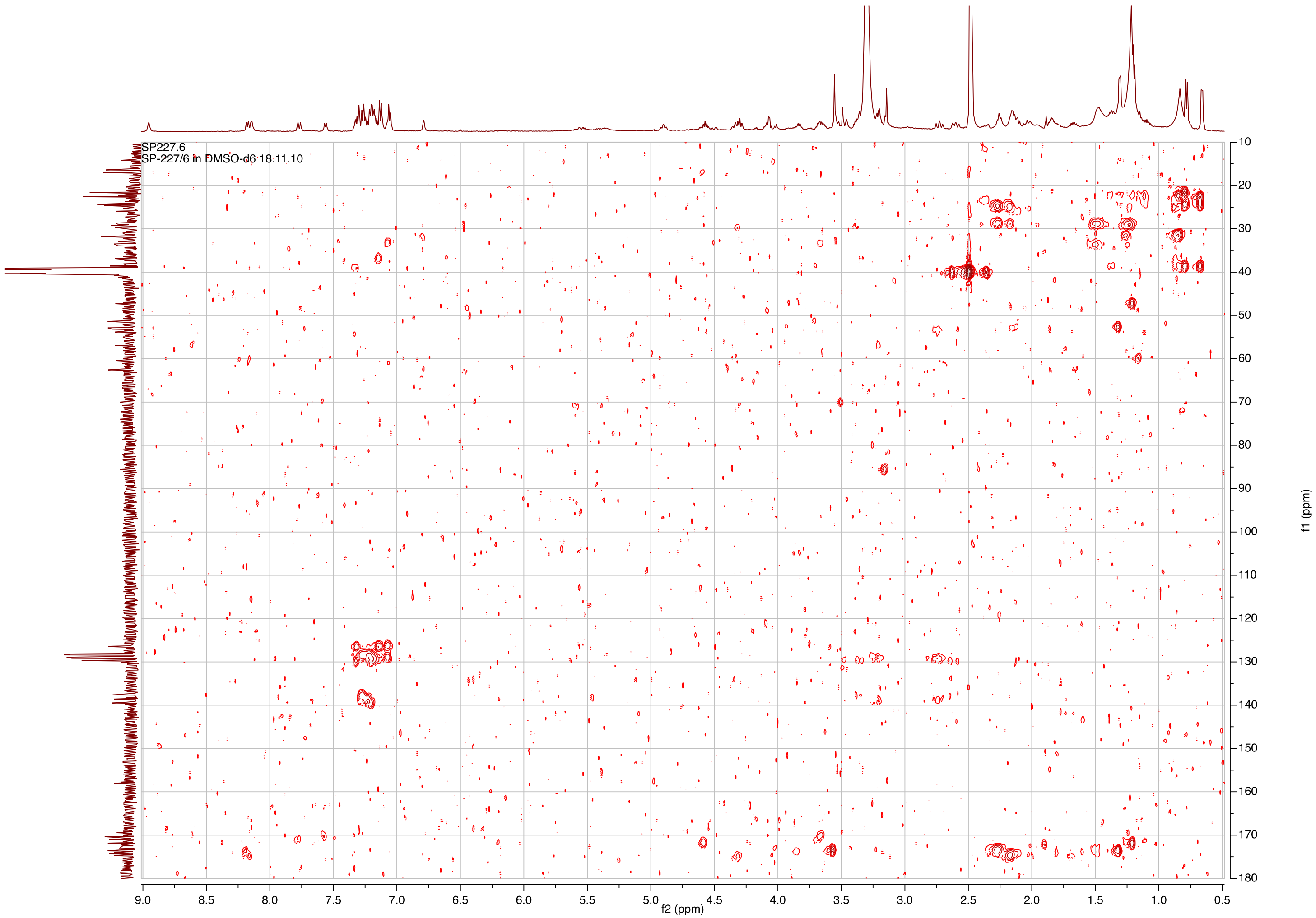


Figure S13. HMBC Spectrum of Microphycin KB921 (**2**) in DMSO-d_6.

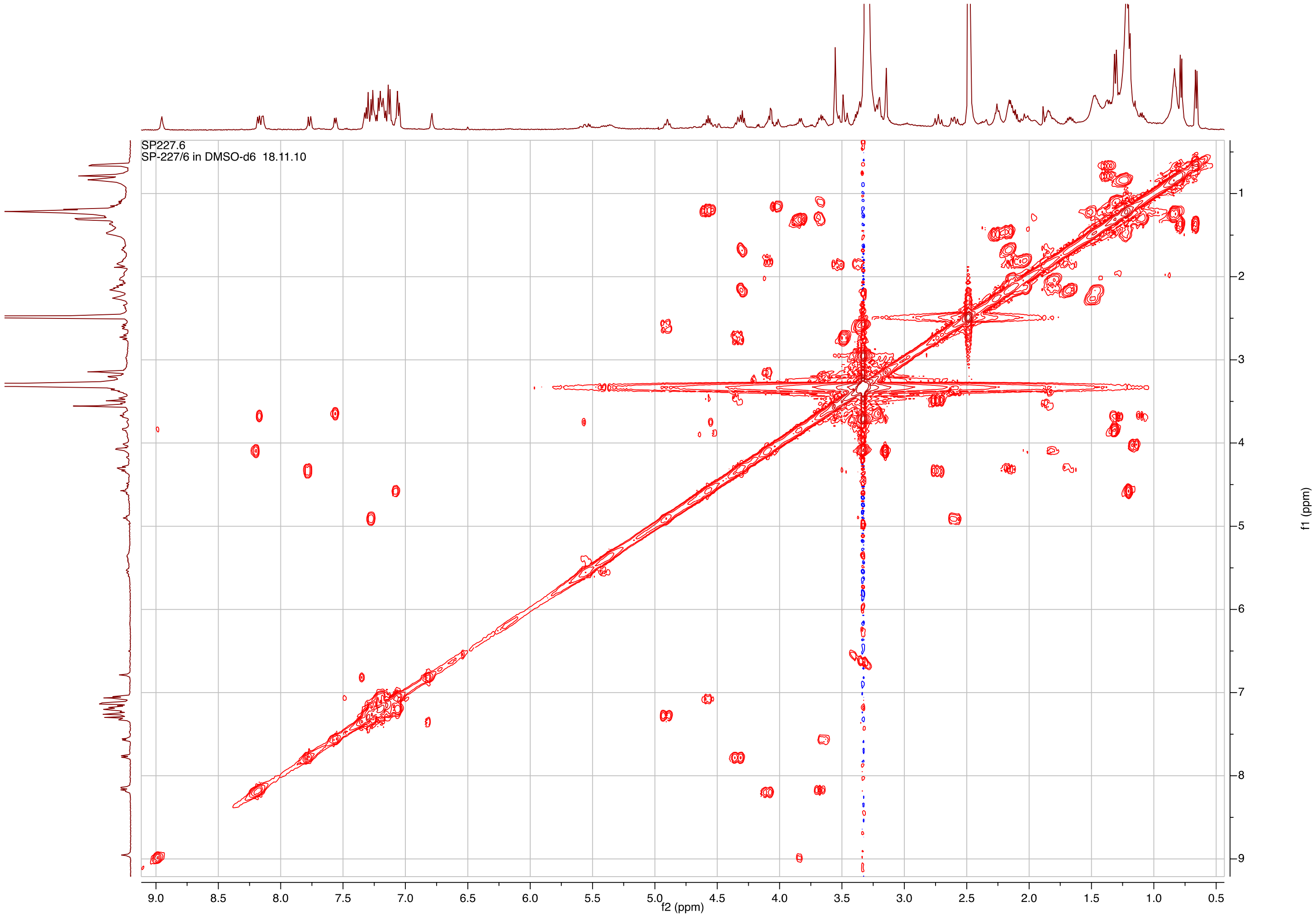


Figure S14. COSY Spectrum of Microphycin KB921 (**2**) in DMSO-d_6.

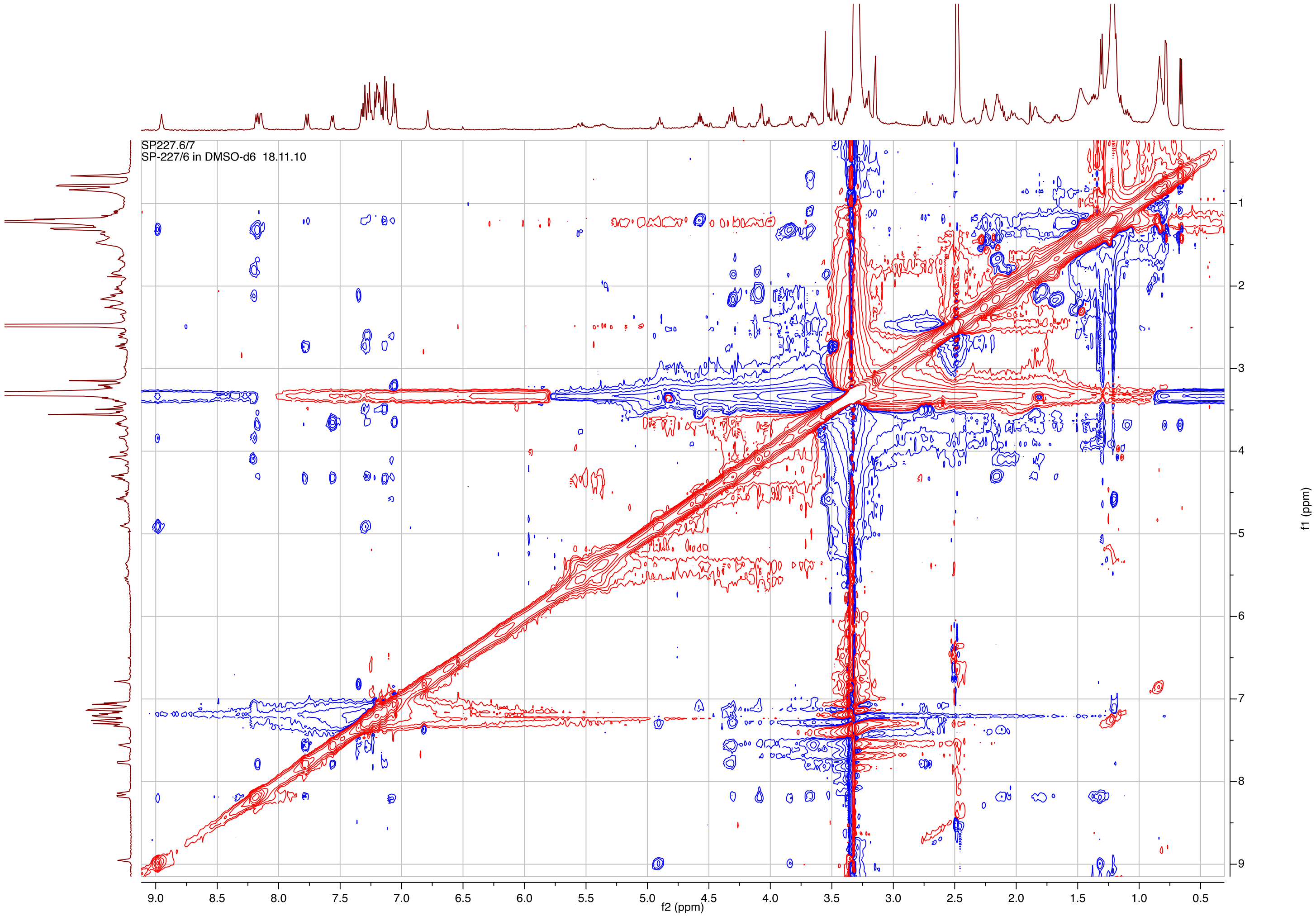


Figure S15. ROESY Spectrum of Microphycin KB921 (**2**) in DMSO-d_6 (Blue: NOE correlation).

Table S2. NMR Data of Microphycin KB921 (**2**) in DMSO-d_6.

Position	δ_C mult. [b]	δ_H mult. [b] *J* in Hz	HMBC Correlations [c]	NOE Correlations [d]
[1]Phe 1	171.1, qC			
2	52.9, CH	4.91, brdd (11.0,8.5)	[1]Phe-1	[1]Phe1- 3a,*N*H; [2]Ala-*N*H
3	39.0, CH_2	3.38, m	[1]Phe-4,5,5′	[1]Phe1-2,3b
		2.62, t (11.0)	[1]Phe-5,5′	[1]Phe1-3a,5,5′,6,6′,*N*H
4	137.7, qC	-		
5,5′	129.7, CH	7.31, m	[1]Phe-3,7	[1]Phe1-3b,6,6′,7
6,6′	128.2, CH	7.27, m	[1]Phe-4	[1]Phe1-3b,5,5′,7
7	126.5, CH	7.20, m	[1]Phe-5,5′	[1]Phe1-5,5′,6,6′
*N*H		7.27, m	[1]Phe-3; [8]Phe-1	[1]Phe1-2,3b; [8]Phe-*N*H
[2]Ala 1	173.6, qC	-		
2	52.6, CH	3.84, dq (4.0,7.5)	[2]Ala-1	[2]Ala-3,*N*H
3	17.0, CH_3	1.31, d (7.5)	[2]Ala-1,2	[2]Ala-2,*N*H; Gln-*N*H
*N*H		8.96, m		[2]Ala-2,3; [1]Phe-*N*H
[3]Gln 1	174.0, qC	-		
2	53.1, CH	4.08, dt (5.5,7.0)		Gln-3a,3b,4,*N*H
3	29.7, CH_2	2.12, m	Gln-1	Gln-2,3b,*N*H_2(b),*N*H
		1.84, m	Gln-1,2	Gln-2,3a,4,*N*H_2(b),*N*H
4	31.8, CH_2	2.14, m	Gln-5	Gln-2,3b,*N*H_2(b),*N*H
5	174.3, qC	-		
*N*H	-	8.18, d (7.0)	[2]Ala-1	Gln-2,3a,3b,4; [2]Ala-3
NH_2 ab	-	6.80, s	Gln-4,5	Gln-*N*H_2(b)
		7.33, s		Gln-3a,3b,4,*N*H_2(a)
[4]Ala 1	171.9, qC	-		
2	47.2, CH	4.58, dq (6.5,7.1)	[4]Ala-1,3	[4]Ala-3,*N*H
3	16.4, CH_3	1.21, d (7.1)	[4]Ala-1,2	[4]Ala-2,*N*H

Table S2. *Cont.*

*N*H	-	7.07, m		^{4}Ala-2,3; Pro-5a
^{5}Pro 1	174.8, qC	-		
2	62.8, CH	4.31, t (8.0)	Pro-1,3	Pro-3a,4a,5a
3	29.2, CH_2	2.15, dd (9.0,8.0)	Pro-4,5	Pro-2,3b,4a,4b
		1.67, m		Pro-3a,4a,4b
4	24.6, CH_2	1.85, m	Pro-2	Pro-2,3a,3b,5a
		1.47, m		Pro-3a,3b
5	47.3, CH_2	3.54, m		Pro-2,4a,5b; ^{4}Ala-*N*H
		3.38, m		Pro-5a
^{6}Leu 1	171.0, qC	-		
2	53.8, CH	3.67, m	Leu-1	Leu-3a,3b,4,5,6,NH
3	38.6, CH_2	1.30, m		Leu-2,3b,5,6,*N*H
		1.11, m	Leu-1,2,4,5	Leu-2,3a,4
4	24.3, CH	1.33, m	Leu-3	Leu-2,3b,5,6,*N*H
5	22.6, CH_3	0.79, d (6.5)	Leu-3,4,6	Leu-2,3a,4,6
6	21.6, CH_3	0.67, d (6.5)	Leu-3,4,5	Leu-2,3a,4,5
*N*H	-	8.16, d (6.5)	Pro-1	Leu-2,3a,4; ^{7}Phe-*N*H
^{7}Phe 1	170. 4, qC	-		
2	53.2, CH	4.32, brdd (13.0,10.0)	^{7}Phe-1	^{7}Phe-3a,5,5′; ^{8}Phe3-*N*H
3	36.9, CH_2	3.47, m		^{7}Phe-2,3b,5,5′
		2.73, t (13.0)	^{7}Phe-2,4,5,5′	^{7}Phe-3a,*N*H
4	138.6, qC	-		
5,5′	129.2, CH	7.14, m	^{7}Phe-3,7	^{7}Phe-2,3a,6,6′,7
6,6′	128.2, CH	7.22, m	^{7}Phe-4	^{7}Phe-5,5′,7
7	126.4, CH	7.17, m	^{7}Phe-5,5′	^{7}Phe-5,5′,6,6′
*N*H	-	7.78, d (10.0)	Leu-1	^{7}Phe-2,3b; Leu-*N*H; ^{8}Phe3-*N*H

Table S2. *Cont.*

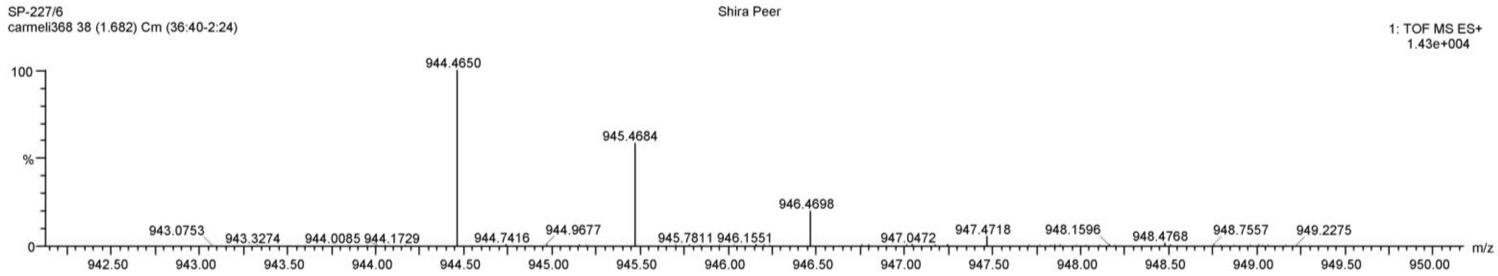
^{8}Phe 1	169.5, qC			
2	56.9, CH	3.65, m	^{7}Phe-1	^{8}Phe-3,5,5′,*N*H
3	32.6, CH_2	3.22, m	^{8}Phe-2,4,5,5′	^{8}Phe-2,5,5′
4	139.5, qC	-		
5,5′	129.0, CH	7.07, m	^{8}Phe-3,4,7	^{8}Phe-2,3,6,6′,7
6,6′	128.4, CH	7.20, m	^{8}Phe-4	^{8}Phe-5,5′,7
7	126.2, CH	7.18, m	^{8}Phe-5,5′	^{8}Phe-5,5′,6,6′
*N*H	-	7.57, d (7.0)	^{7}Phe-1	^{8}Phe-2,*N*H; ^{7}Phe-2,*N*H

[a] 125 MHz for carbons and 500 MHz for protons; [b] Multiplicity and assignment from HSQC experiment; [c] Determined from HMBC experiment, $^{n}J_{CH}$ = 8 Hz, recycle time 1 s; [d] Selected NOE's from ROESY experiment.

Elemental Composition Report

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
443 formula(e) evaluated with 10 results within limits (up to 4 best isotopic matches for each mass)
Elements Used:
C: 35-50 H: 50-80 N: 5-15 O: 5-15 Na: 0-1



Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
Minimum:				-1.5			
Maximum:		5.0	10.0	50.0			
944.4650	944.4657	-0.7	-0.7	20.5	119.0	0.4	C50 H66 N5 O13
	944.4646	0.4	0.4	22.5	120.3	1.6	C49 H63 N9 O9 Na
	944.4644	0.6	0.6	26.5	121.5	2.9	C47 H58 N15 O7
	944.4660	-1.0	-1.1	27.5	122.2	3.5	C50 H59 N13 O5 Na

Figure S16. HR ESI MS data of Microphycin KB921 (**2**).

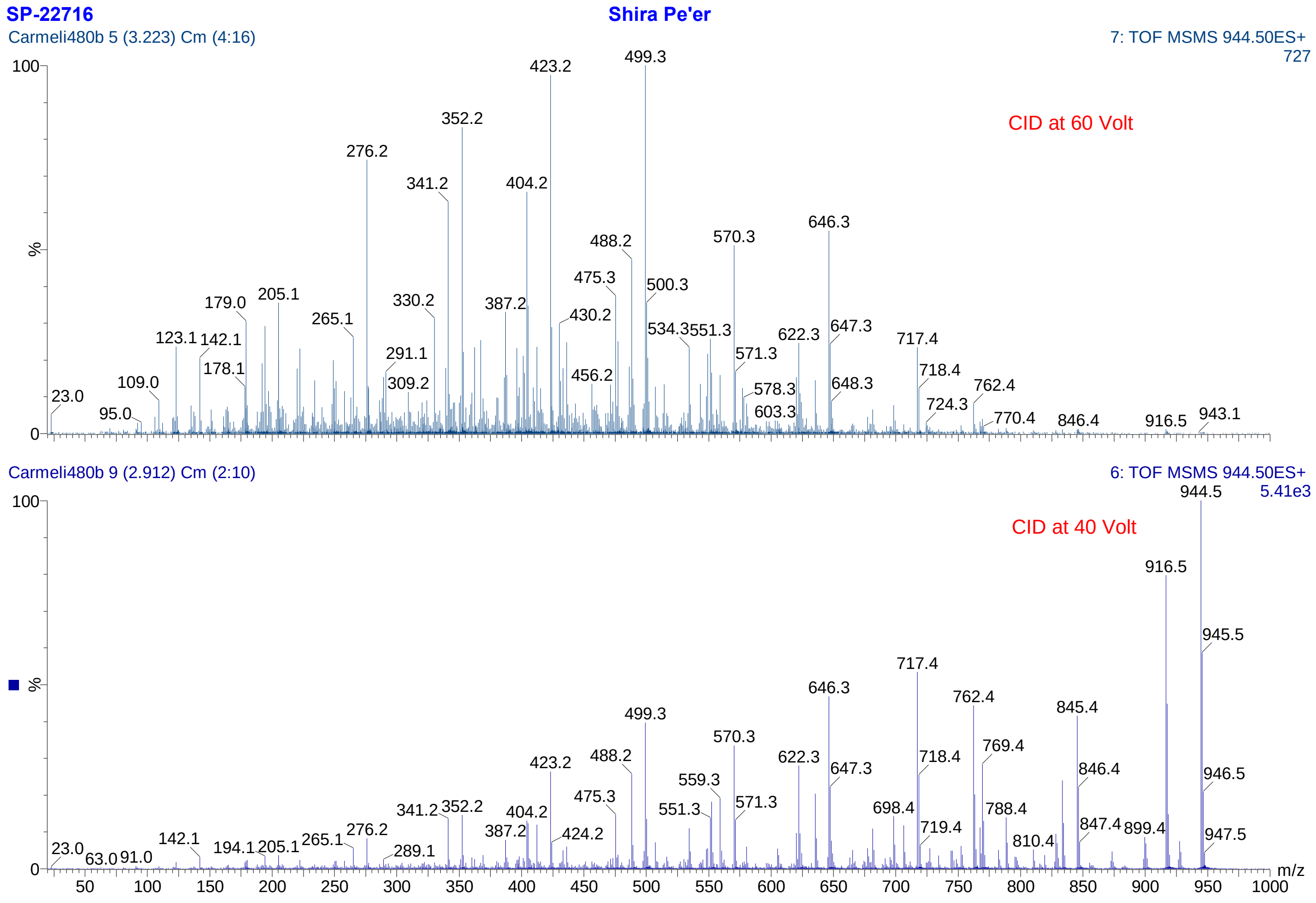


Figure S17. ESI MS/MS CID spectra of Microphycin KB921 (**2**) at 40 (lower trace) and 60 (upper trace) Volt.

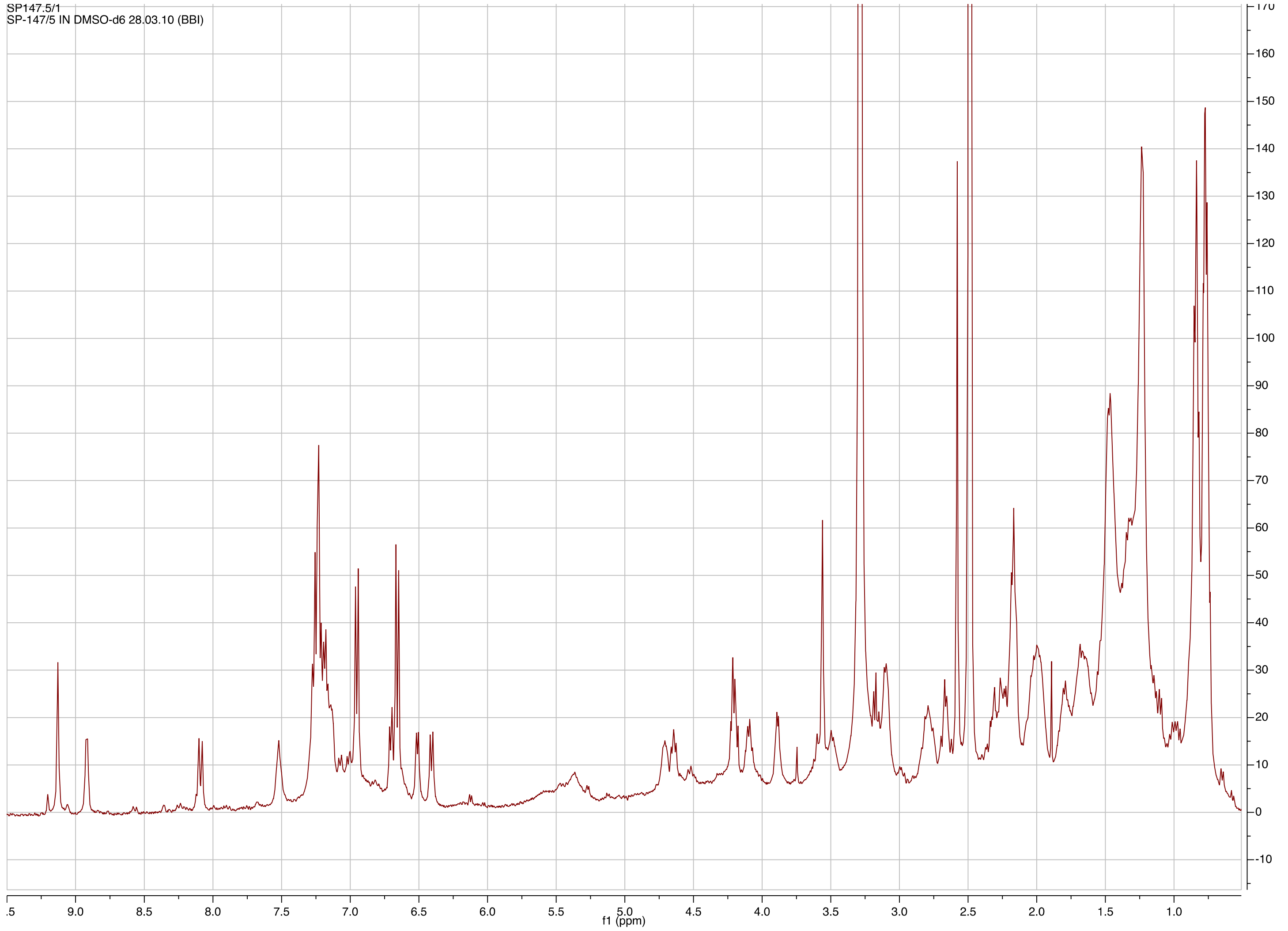


Figure S18. ^{1}H NMR Spectrum (500 MHz) of Anabaenopeptin KB906 (**3**) in DMSO-d_6.

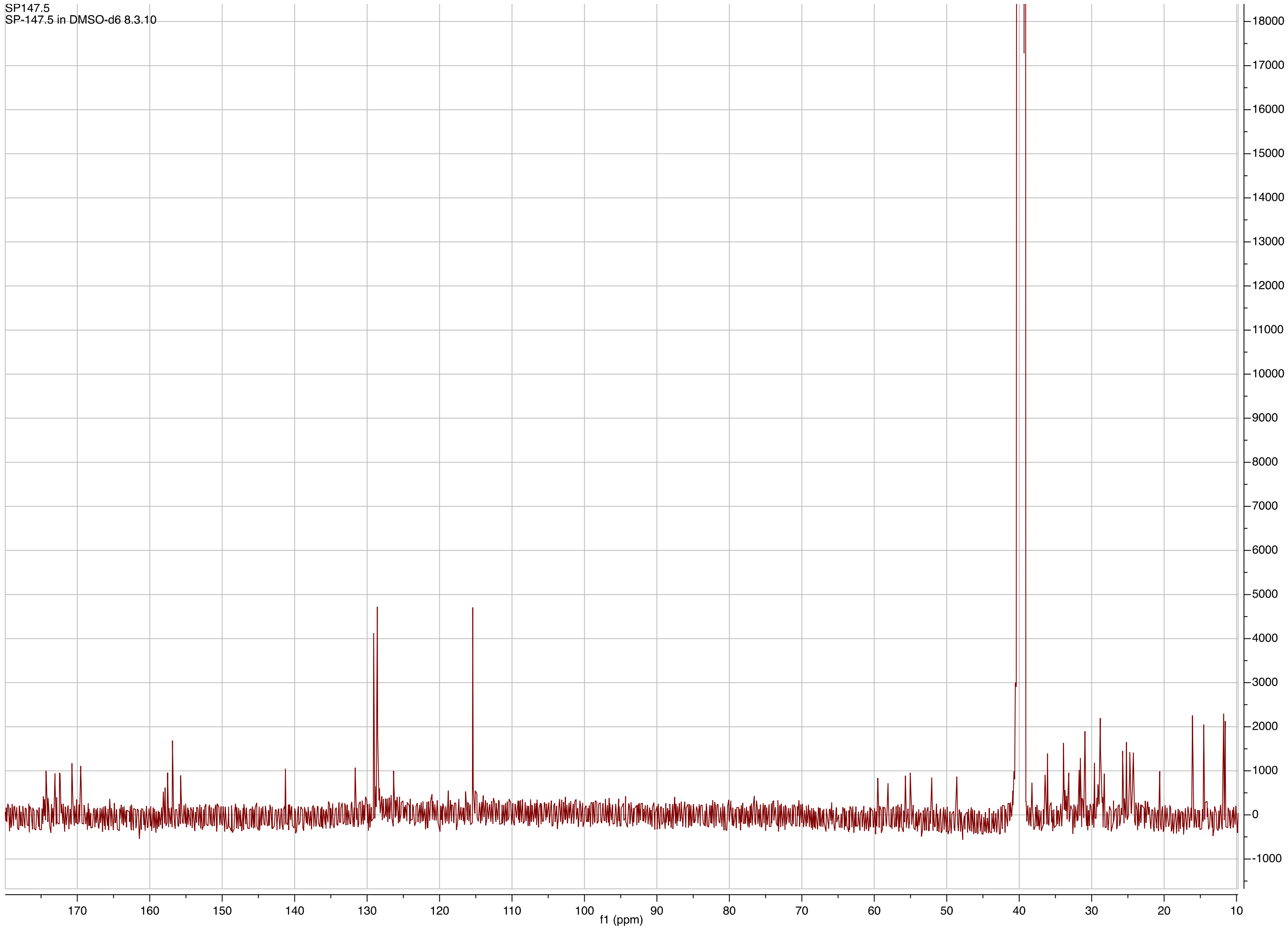


Figure S19. ^{13}C NMR Spectrum (125 MHz) of Anabaenopeptin KB906 (**3**) in DMSO-d_6.

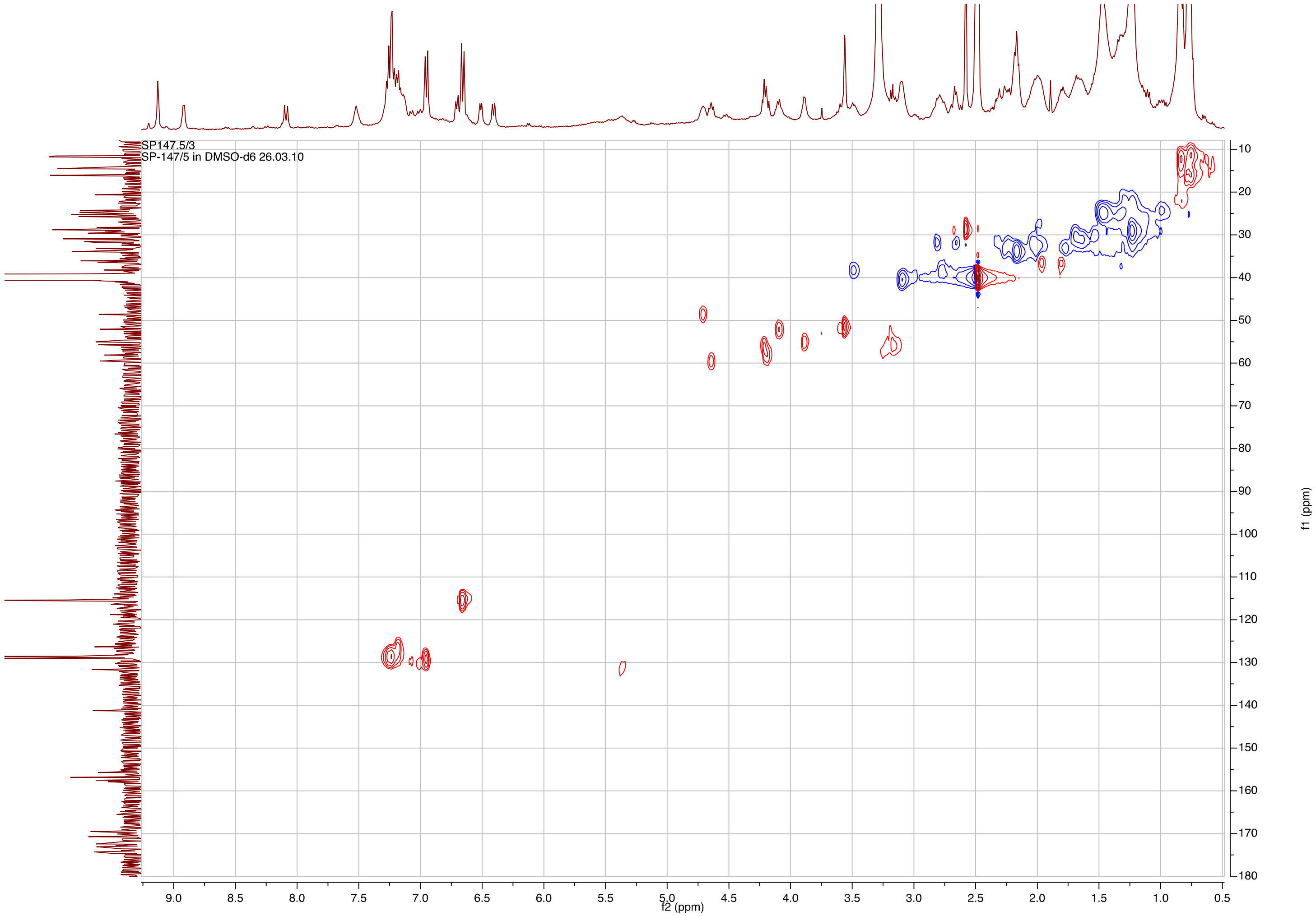


Figure S20. HSQC Spectrum of Anabaenopeptin KB906 (**3**) in DMSO-d_6 (Red: CH, CH_3; Blue: CH_2).

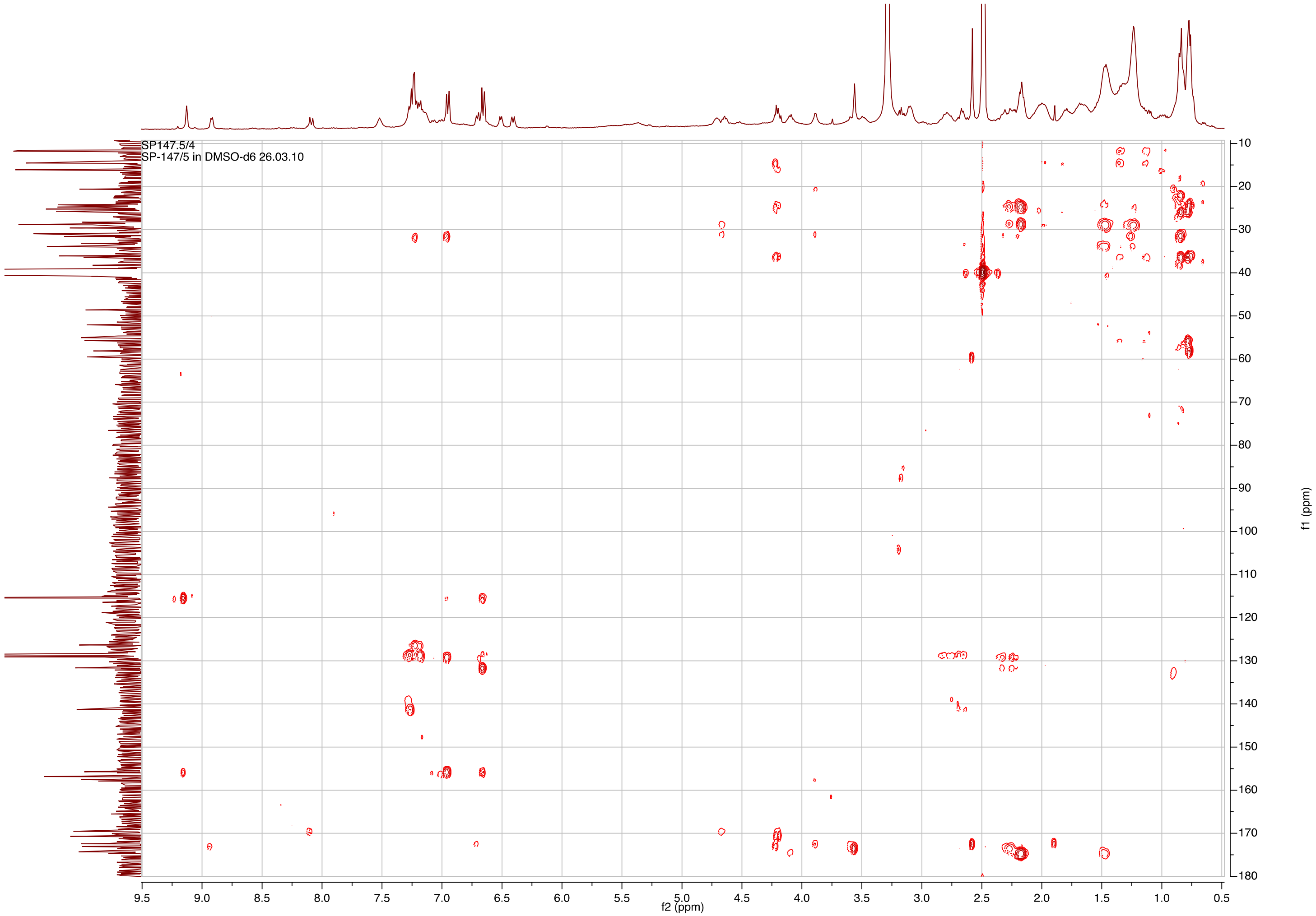


Figure S21. HMBC Spectrum of Anabaenopeptin KB906 (**3**) in DMSO-d_6.

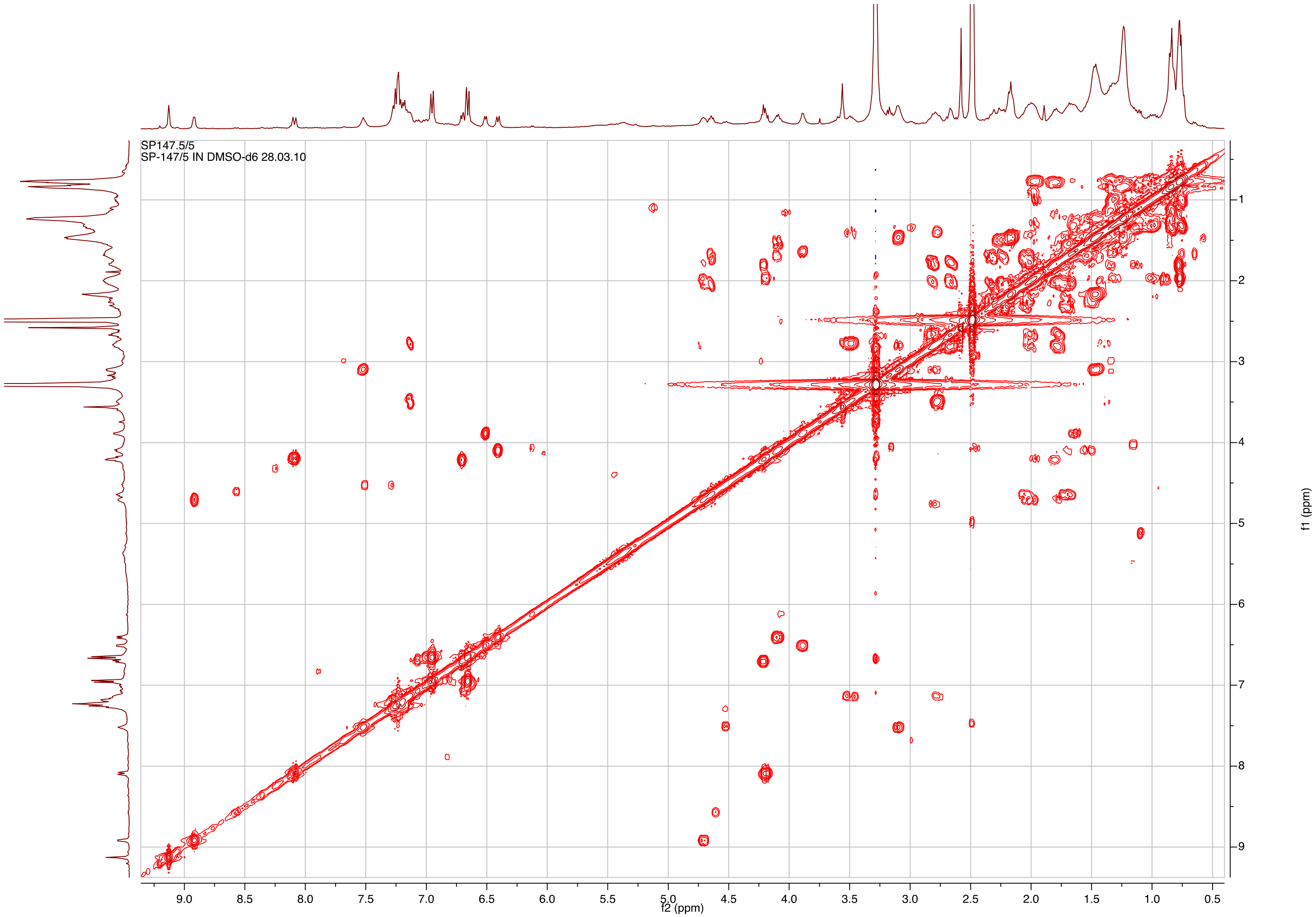


Figure S22. COSY Spectrum of Anabaenopeptin KB906 (**3**) in DMSO-d_6.

Table S3. NMR Data of Anabaenopeptin KB906 (**3**) in DMSO-d_6.

Position	δ_C mult. [b]	δ_H mult.[b] *J* in Hz	HMBC Correlations [c]	NOE Correlations [d]
[1]Ile 1	170.7, qC	-		
2	58.1, CH	4.19, m	[1]Ile-1,3,4,6	[1]Ile-3,4a,5,6,*N*H; Lys-ε-*N*H
3	36.1, CH	1.97, m		[1]Ile-2,4a,5,6,*N*H; Lys-ε-*N*H
4 ab	24.2, CH_2	1.31, m		[1]Ile-2,3,4b,5,*N*H
		0.98, m	[1]Ile-5,6	[1]Ile-4a,5,6,*N*H
5	11.6, CH_3	0.75, t (7.0)	[1]Ile-2,3,4	[1]Ile-2,3,4a,4b,*N*H
6	16.1, CH_3	0.77, d (6.5)	[1]Ile-2,3,4	[1]Ile-2,3,4b,*N*H
*N*H	-	8.10, d (9.5)	*N*MeHty-1	[1]Ile-2,3,4a,4b,5,6; Lys-ε-*N*H; *N*MeHty-2,*N*Me
[2]*N*MeHty 1	169.5, qC	-		
2	59.5, CH	4.66, t (7.0)	*N*MeHty-1,3,*N*Me; Hph-1	*N*MeHty-3a,3b,4a,4b,*N*Me; Hph-2; [1]Ile-*N*H
3 ab	30.9, CH_2	2.03, m		*N*MeHty-2,3b,4a,4b,6,6′,*N*Me
		1.70, m		*N*MeHty-2,3a,4b,6,6′,*N*Me
4 ab	31.6, CH_2	2.32, m	*N*MeHty-3,5,6,6′	*N*MeHty-2,3a,4b,6,6′
		2.23, m	*N*MeHty-5,6,6′	*N*MeHty-2,3a,3b,4a,6,6′,*N*Me
5	131.6, qC	-		
6,6′	129.1, CH	6.95, d (7.9)	*N*MeHty-4,7,7′,8	*N*MeHty-3a,3b,4a,4b,7,7′,*N*Me
7,7′	115.4, CH	6.66, d (7.9)	*N*MeHty-5,6,6′,8	*N*MeHty-6,6′,*O*H
8	155.7, qC	-		
*N*Me	28.8, CH_3	2.58, s	*N*MeHty-2; Hph-1	*N*MeHty-2,3a,3b,4b,6,6′; [1]Ile-*N*H
*O*H		9.15 s	*N*MeHty-7,7′,8	*N*MeHty-7,7′
[3]Hph 1	172.4, qC	-		
2	48.6, CH	4.71, m		Hph-3b,4b,*N*H; *N*MeHty-2
3 ab	33.2, CH_2	2.00, m		Hph-3b,4,*N*H
		1.78, m		Hph-2,3a,4a,*N*H
4 ab	31.7, CH_2	2.81, m	Hph-6,6′	Hph-3a,3b,4b,*N*H
		2.66, m	Hph-3,6,6′	Hph-2,4a,6,6′,*N*H

Table S3. *Cont.*

5	141.3, qC	-		
6,6′	128.6, CH	7.25, d (7.3)	Hph-4,7,7′	Hph-4b,7,7′,8
7,7′	128.6, CH	7.23, t (7.3)	Hph-6,6′,8	Hph-6,6′,8
8	126.4, CH	7.18, t (7.3)	Hph-6,6′,7,7′	Hph-6,6′,7,7′
*N*H	-	8.93, d (4.9)	^{4}Ile -1	Hph-2,3a,3b,4a,4b; ^{4}Ile-2
^{4}Ile	173.1, qC	-		
2	55.6, CH	4.21, t (6.4)	^{4}Ile-1,4,6	^{4}Ile-3,4a,5,6,*N*H; Hph-*N*H
3	36.4, CH	1.80, m	^{4}Ile-6	^{4}Ile-2,4a,4b,6,*N*H
4 ab	25.7, CH_2	1.34, m	^{4}Ile-2,3,5,6	^{4}Ile-2,3,4b,*N*H
		1.12 m	^{4}Ile-3,5,6	^{4}Ile-3,4a,5
5	11.8, CH_3	0.83, t (7.0)	^{4}Ile-3,4	^{4}Ile-2,4b
6	14.5, CH_3	0.78, d (6.4)	^{4}Ile-2,3,4, Lys-1	^{4}Ile-2,3
*N*H	-	6.70, d (7.0)		^{4}Ile-2,3,4a; Lys-2,3,*N*H
^{5}Lys 1	172.4, qC	-		
2	55.0, CH	3.88, ddd (6.4,5.8,4.6)	Lys-1,3,4, CO	Lys-3,4a,5,α-*N*H; ^{4}Ile-*N*H
3	30.9, CH_2	1.61, m		Lys-2,4b,α-*N*H; ^{4}Ile-*N*H
4 ab	20.6, CH_2	1.30, m		Lys-2,4b,α-*N*H,ε-*N*H
		1.24, m		Lys-3,4a,5,α-*N*H,ε-*N*H
5	28.3, CH_2	1.38, m		Lys-2,4′,6a,6b,α-*N*H,ε-*N*H
6 ab	38.2, CH_2	3.48, m	Lys-5	Lys-5,6b,ε-*N*H
		2.78, m		Lys-5,6a,ε-*N*H
δ-*N*H	-	6.51, d (5.8)		Lys-2,3,4a,4b,5; ^{4}Ile-*N*H; Arg-α-*N*H
δ-*N*H	-	7.13, m	^{1}Ile-1	Lys-4a,4b,5,6a,6b; ^{1}Ile-2,3,*N*H
^{6}Arg 1	174.3, qC	-		
2	52.1, CH	4.09, dt (8.2,5.2)	Arg-1,3	Arg-3a,3b,4,α-*N*H

Table S3. *Cont.*

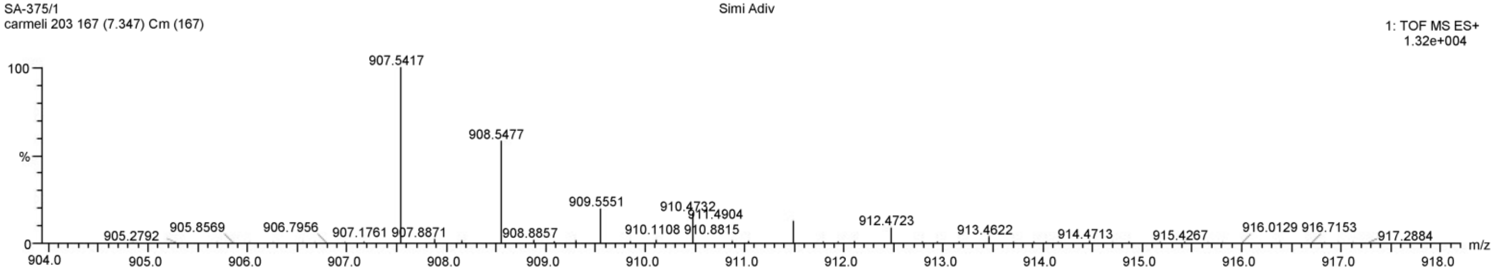
3 ab	29.6, CH_2	1.69, m	Arg-2	Arg-2,3b,5,α-*N*H
		1.52, m	Arg-2,4,5	Arg-2,3a,5,α-*N*H
4	25.2, CH_2	1.46, m	Arg-5	Arg-2,3a,5,α-NH,δ-*N*H
5	40.5, CH_2	3.09, m	Arg-6	Arg-3a,3b,4,δ-*N*H
6	156.9, qC	-		
7	-	-		
α-*N*H	-	6.42, d (8.2)	CO	Arg-2,3a,3b,4; Lys-α-*N*H
δ-*N*H	-	7.50, brm		Arg-4,5
*N*H/*N*H_2	-	6.65, brm		
		7.30, brm		
CO	157.5, qC	-		

[a] 125 MHz for carbons and 500 MHz for protons; [b] Multiplicity and assignment from HSQC experiment; [c] Determined from HMBC experiment, $^{n}J_{CH}$ = 8 Hz, recycle time 1 s; [d] Selected NOE's from ROESY experiment.

Elemental Composition Report

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
323 formula(e) evaluated with 4 results within limits (up to 4 best isotopic matches for each mass)
Elements Used:
C: 25-50 H: 40-75 N: 5-15 O: 0-15



Minimum:				-1.5			
Maximum:		5.0	10.0	50.0			

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
907.5417	907.5419	-0.2	-0.2	21.5	77.7	0.4	C47 H67 N14 O5
	907.5405	1.2	1.3	16.5	78.7	1.4	C46 H71 N10 O9
	907.5392	2.5	2.8	11.5	80.3	3.0	C45 H75 N6 O13
	907.5464	-4.7	-5.2	7.5	83.1	5.7	C39 H75 N10 O14

Figure S23. HR ESI MS data of Anabaenopeptin KB906 (**3**).

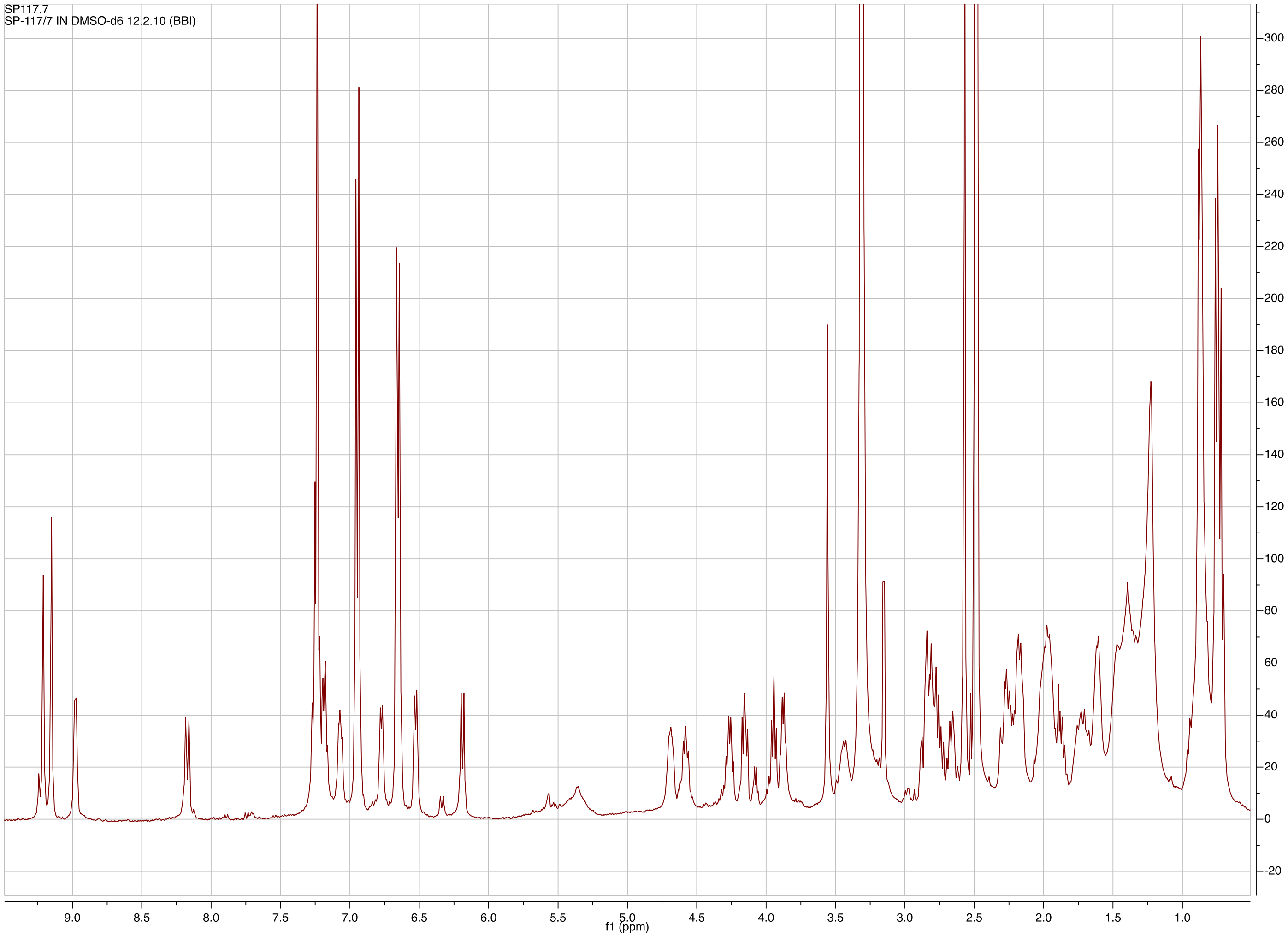


Figure S24. [1]H NMR Sp0ectrum (400 MHz) of Anabaenopeptin KB899 (**4**) in DMSO-d_6.

Figure S25. ^{13}C NMR Spectrum (100 MHz) of Anabaenopeptin KB899 (**4**) in DMSO-d_6.

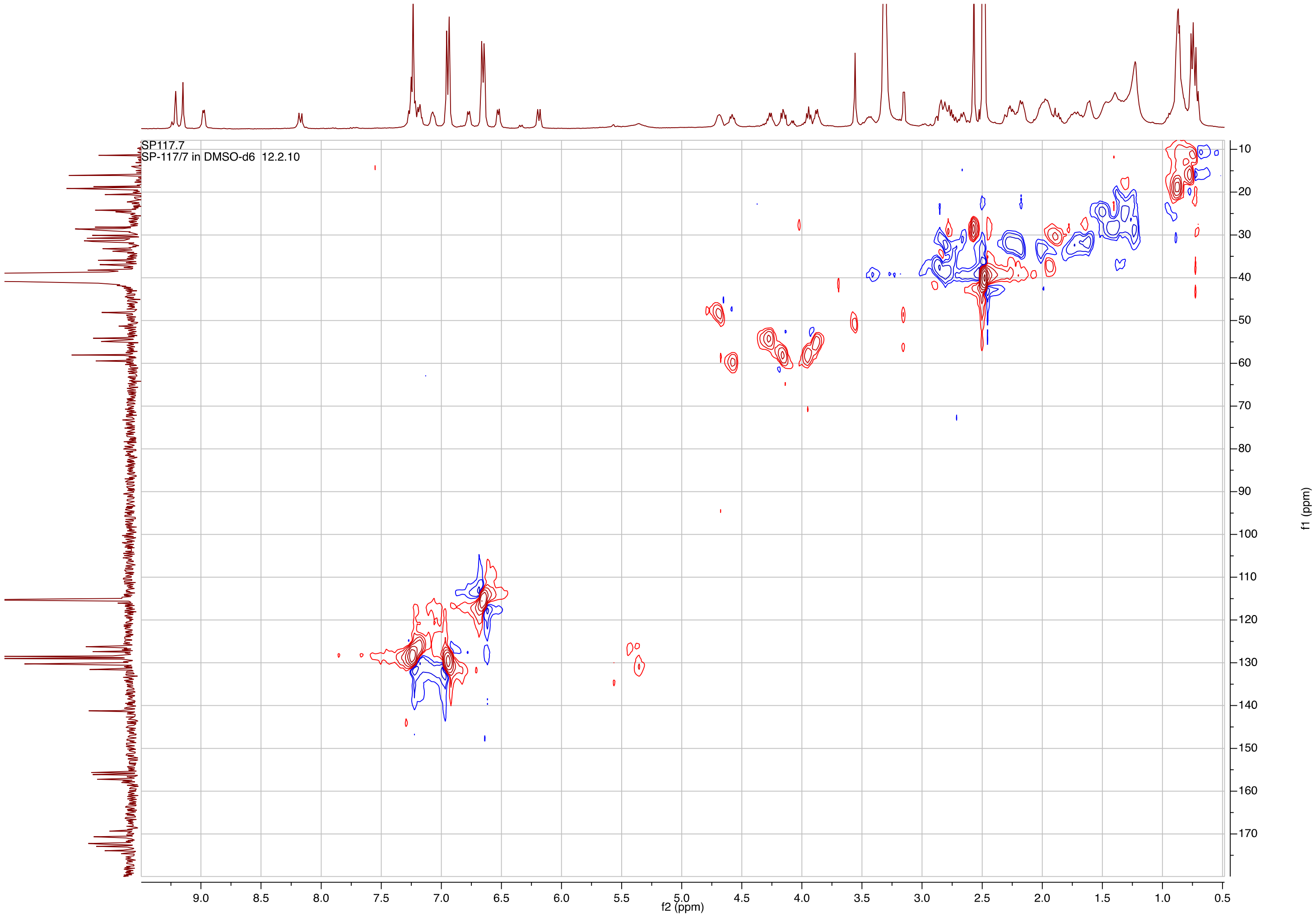


Figure S26. HSQC Spectrum of Anabaenopeptin KB899 (**4**) in DMSO-d_6 (Red: CH, CH_3; Blue: CH_2).

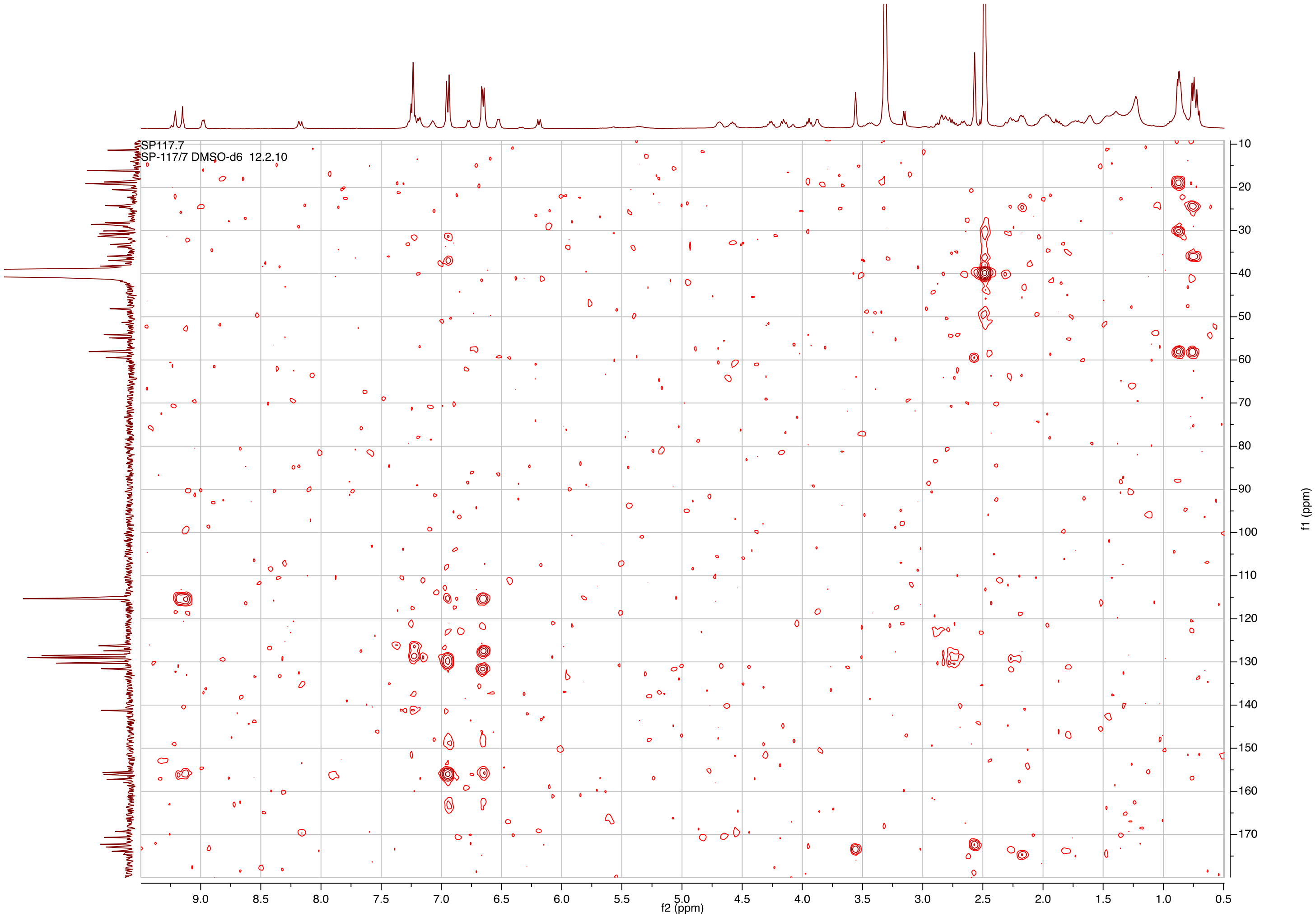


Figure S27. HMBC Spectrum of Anabaenopeptin KB899 (**4**) in DMSO-d_6.

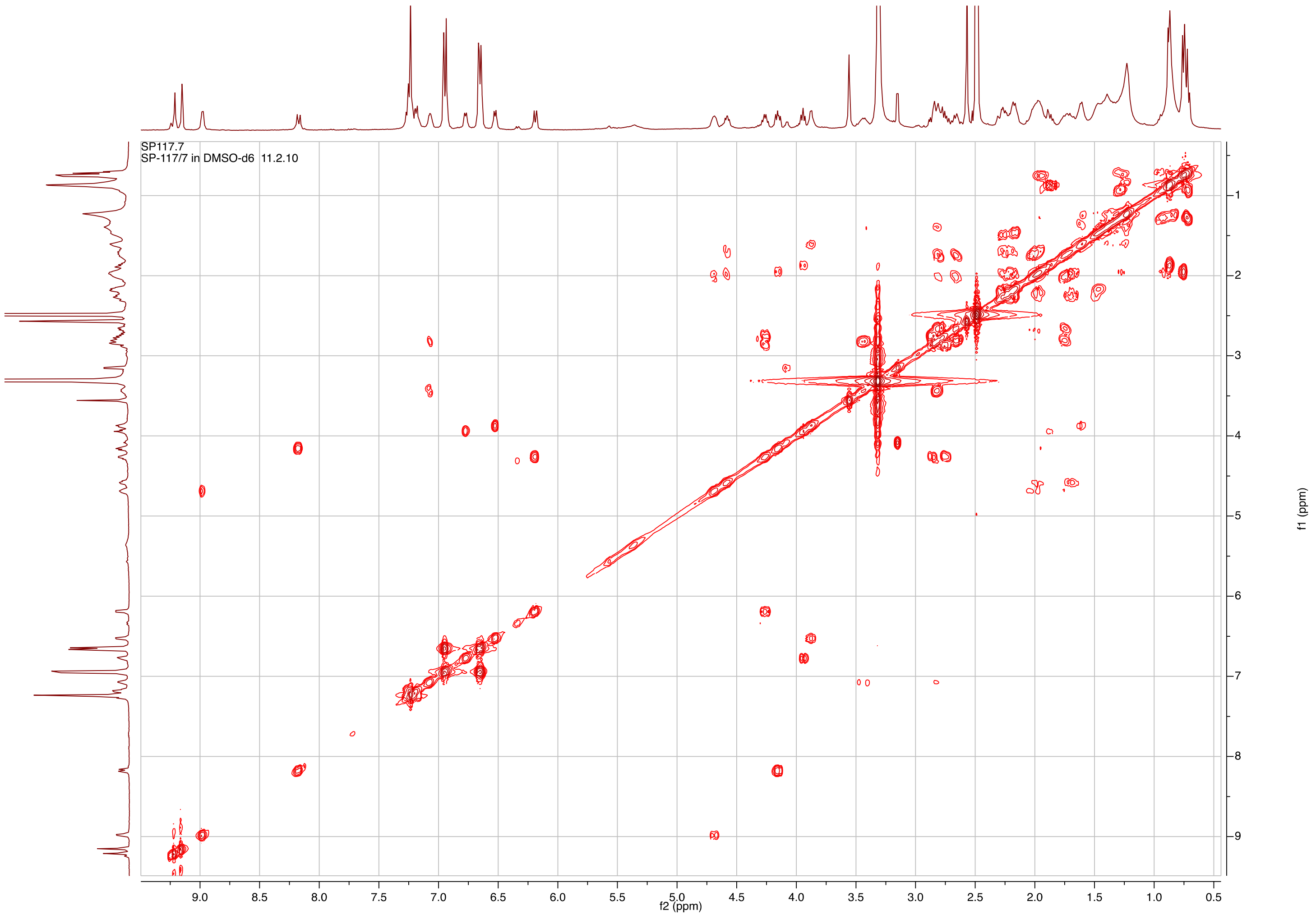


Figure S28. COSY Spectrum of Anabaenopeptin KB899 (**4**) in DMSO-d_6.

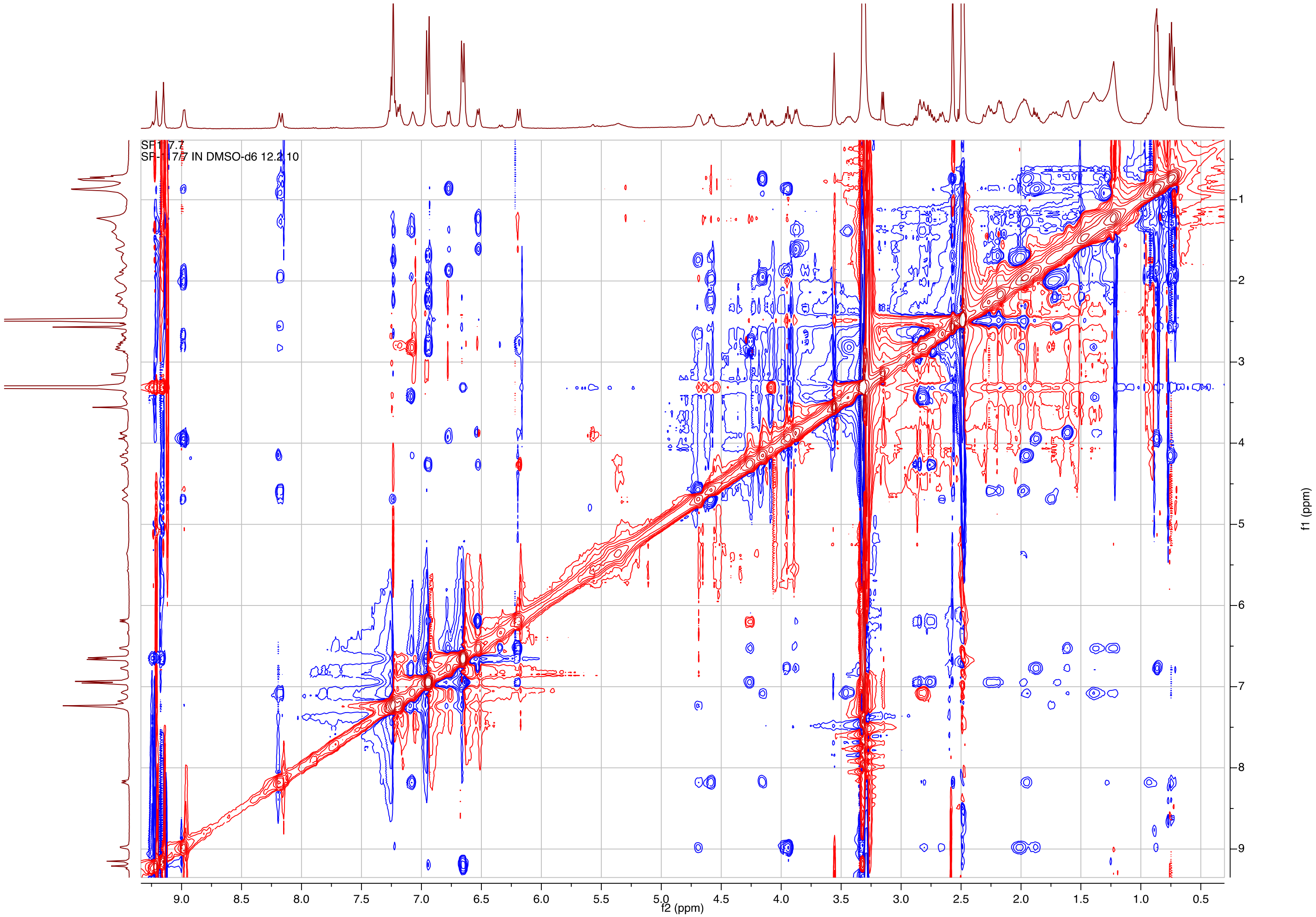


Figure S29. ROESY Spectrum of Anabaenopeptin KB899 (**4**) in DMSO-d_6 (Blue: NOE correlation).

Table S4. NMR Data of Anabaenopeptin KB899 (**4**) in DMSO-d_6.

Position	δ_C mult. [b]	δ_H mult. [b] *J* in Hz	HMBC Correlations [c]	NOE Correlations [d]
[1]Ile 1	170.7, qC	-		
2	58.1, CH	4.15, m	Ile-1,3,4,6	Ile-3,5,6,*N*H; Lys-ε-*N*H
3	35.9, CH	1.98, m		Ile-2,4a,5,6,*N*H; Lys-ε-*N*H
4 ab	24.2, CH_2	1.28, m		Ile-3,4b,5,6,*N*H
		0.93, m		Ile-4a,5,6,*N*H; *N*MeHty-*N*Me
5	11.4, CH_3	0.75, t (7.5)	Ile-2,3,4	Ile-2,3,4a,4b,*N*H; *N*MeHty-*N*Me
6	16.1, CH_3	0.76, d (7.0)	Ile-2,3,4	Ile-2,3,4a,4b,*N*H; *N*MeHty-*N*Me
*N*H	-	8.17, d (9.6)	*N*MeHty-1	Ile-2,3,4b, Lys-6b,ε-*N*H; *N*MeHty-2,3,*N*Me
[2]*N*MeHty 1	169.5, qC	-		
2	59.5, CH	4.58, t (6.0)	*N*MeHty-1,3,*N*Me; Hph-1	*N*MeHty-3a,3b,*N*Me; Hph-2, Ile-*N*H
3 ab	30.8, CH_2	1.98, m		*N*MeHty-2,3b,6,6′,*N*Me; Ile-*N*H
		1.70, m		*N*MeHty-2,3a,4b,6,6′,*N*Me
4 ab	31.4, CH_2	2.31, m	*N*MeHty-3,5,6,6′	*N*MeHty-6,6′
		2.27, m	*N*MeHty-3,5,6,6′	*N*MeHty-2,3b,6,6′,*N*Me
5	131.6, qC	-		
6,6′	129.0, CH	6.95, d (8.4)	*N*MeHty-4,7,7′,8	*N*MeHty-3a,3b,4a,4b,7,7′,*N*Me
7,7′	115.3, CH	6.66, d (8.4)	*N*MeHty-5,6,6′,8	*N*MeHty-6,6′,*O*H
8	155.7, qC	-		
*N*Me	28.6, CH_3	2.57, s	*N*MeHty-2; Hph-1	*N*MeHty-3a,3b,4b,6,6′; Ile-4b,5,6,*N*H
*O*H		9.15 s	*N*MeHty-7,7′,8	*N*MeHty-7,7′
[3]Hph 1	172.3, qC	-		
2	48.1, CH	4.69, m		Hph-3b,4b,7,7′,*N*H; *N*MeHty-2; Ile-*N*H
3 ab	33.2, CH_2	2.02, m	Hph-4,5	Hph-3b,7,7′,*N*H
		1.75, m		Hph-2,3a,7,7′,*N*H

Table S4. *Cont.*

4 ab	31.6, CH_2	2.81, m	Hph-3,6,6′	Hph-4b,8,*N*H
		2.66, m	Hph-3,5,6,6′	Hph-2,4a,7,7′,*N*H
5	141.2, qC	-		
6,6′	128.6, CH	7.25, m	Hph-4,7,7′,8	Hph-7,7′
7,7′	128.5, CH	7.23, m	Hph-6,6′,8	Hph-2,3a,3b,4a,4b; *N*MeHty-4
8	126.3, CH	7.18, m	Hph-6,6′,7,7′	Hph-4a
*N*H	-	8.98, d (4.8)	Hph-1; Val-1	Hph-2,3a,4a,4b; Val-2,3,4,5
^{4}Val	172.9, qC	-		
2	58.1, CH	3.94, dd (6.8,5.6)	Val-1,3,5	Val-3,4,5,*N*H; Hph-*N*H
3	30.1, CH	1.88, m	Val-2,5	Val-2,4,5,*N*H; Hph-*N*H
4	19.1, CH_3	0.88, d (6.7)	Val-2,3,5	Val-2,3,5,*N*H; Hph-*N*H
5	18.7, CH_3	0.87, d (6.5)	Val-2,3	Val-2,3,4,*N*H; Hph-*N*H
*N*H	-	6.78, d (5.6)	Val-1,2,3; Lys-1	Val-2,3,4,5; Lys-3,4, -*N*H
^{5}Lys 1	172.4, qC	-		
2	54.9, CH	3.85, ddd (6.4,5.6,4.6)	Lys-1,3,4	Lys-3,4a,5,α-*N*H; Val-*N*H
3	31.1, CH_2	1.61, m	Lys-1	Lys-2,4b,α-*N*H; Val-*N*H
4 ab	20.6, CH_2	1.39, m		Lys-6a,6b,α-*N*H,ε-*N*H
		1.32, m		Lys-3,α-*N*H,ε-*N*H
5	28.2, CH_2	1.40, m		Lys-2,6a,6b,α-*N*H,ε-*N*H
6 ab	38.3, CH_2	3.43, m	Lys-5	Lys-4a,5,6b,ε-*N*H
		2.81, m		Lys-4a,5,6a,ε-*N*H
α-*N*H	-	6.53, d (6.4)	Lys-1; CO	Lys-2,3,4a,4b,5; Val-*N*H; Tyr-2,α-*N*H
ε-*N*H	-	7.07, m	^{1}Ile-1	Lys-4a,4b,5,6a,6b; ^{1}Ile-2,3,*N*H
^{6}Tyr 1	173.9, qC	-		
2	54.2, CH	4.26, m	Tyr-1,3	Tyr-3a,3b,5,5′,*N*H; Lys-α-*N*H

Table S4. *Cont.*

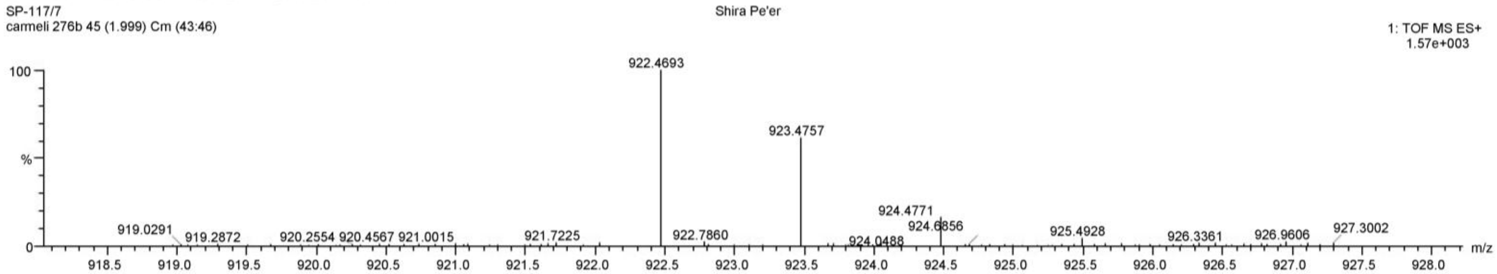
3 ab	36.9, CH_2	2.86, m	Tyr-1,2,4,5	Tyr-2,3b,5,5′,6,6′,*O*H,*N*H
		2.75, m	Tyr-1,2,4,5	Tyr-2,3a,5,5′,6,6′,*N*H
4	127.4, qC	-		
5,5	130.3, CH	6.95, d (8.4)	Tyr-3,6,6′,7	Tyr-2,3a,3b,6,6′,*O*H
6,6′	115.2, CH	6.64, d (8.4)	Tyr-4,7	Tyr-3a,3b,5,5′,*N*H
7	156.1, qC	-		
7-OH	-	9.21, s	Tyr-6,6′,7	Tyr-3a,5,5′
*N*H	-	6.19, d (8.0)	Tyr-1,2; CO	Tyr-2,3a,3b,5,5′,6,6′; Lys-α-*N*H
CO	157.2, qC	-		

[a] 100 MHz for carbons and 400 MHz for protons; [b] Multiplicity and assignment from HSQC experiment; [c] Determined from HMBC experiment, $^nJ_{CH}$ = 8 Hz, recycle time 1 s; [d] Selected NOE's from ROESY experiment.

Elemental Composition Report

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
1300 formula(e) evaluated with 27 results within limits (up to 4 best isotopic matches for each mass)
Elements Used:
C: 40-60 H: 55-80 N: 0-20 O: 0-20 Na: 0-1



		mDa	PPM	DBE
Minimum:				-1.5
Maximum:		5.0	10.0	50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
922.4693	922.4691	0.2	0.2	19.5	102.2	1.7	C48 H65 N7 O10 Na
	922.4688	0.5	0.5	23.5	102.1	1.7	C46 H60 N13 O8
	922.4701	-0.8	-0.9	28.5	101.5	1.0	C47 H56 N17 O4
	922.4704	-1.1	-1.2	24.5	101.7	1.3	C49 H61 N11 O6 Na

Figure S30. HR ESI MS data of Anabaenopeptin KB899 (**4**).

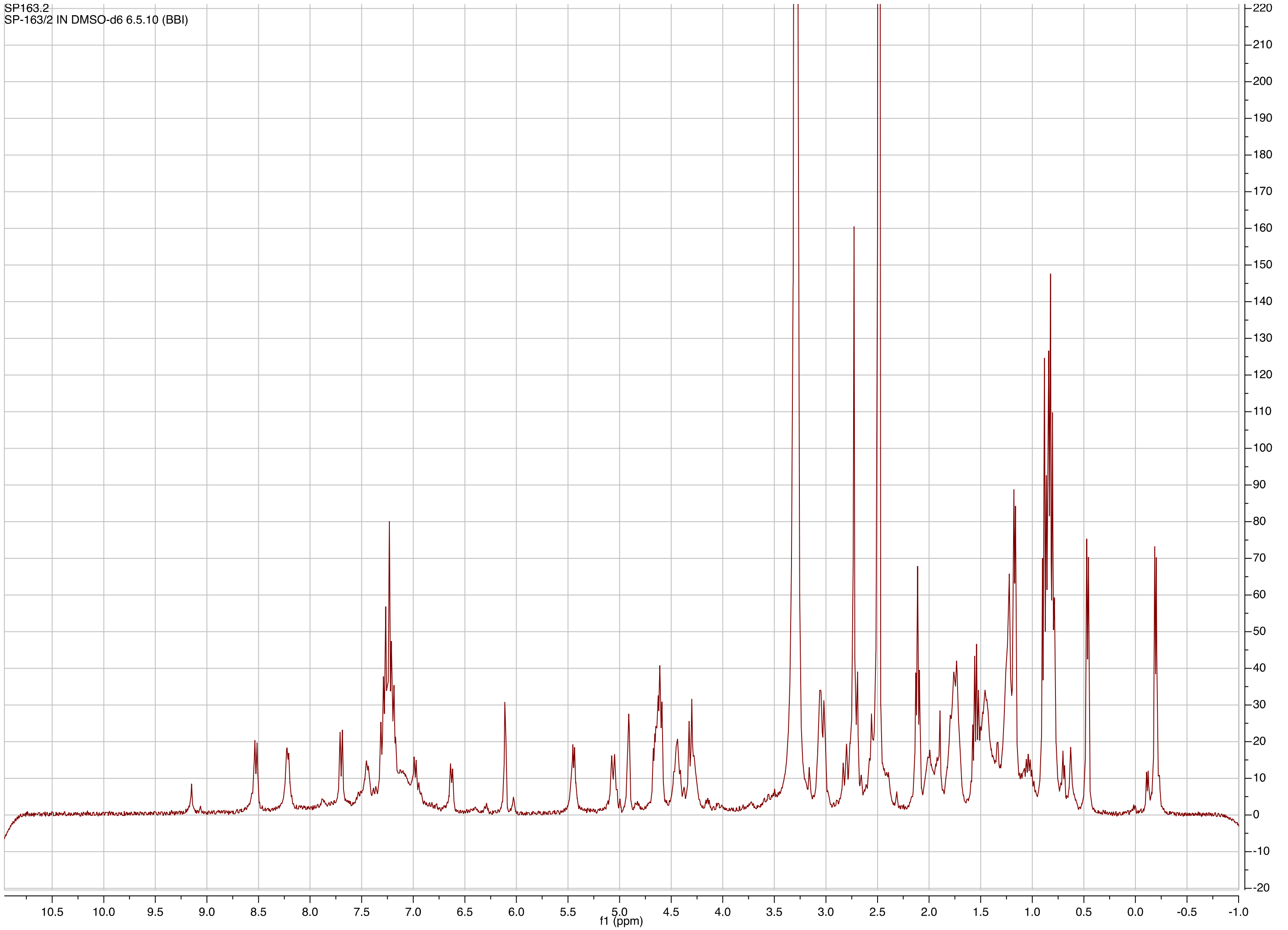


Figure S31. ^{1}H NMR Spectrum (400 MHz) of Micropeptin KB928 (**5**) in DMSO-d_6.

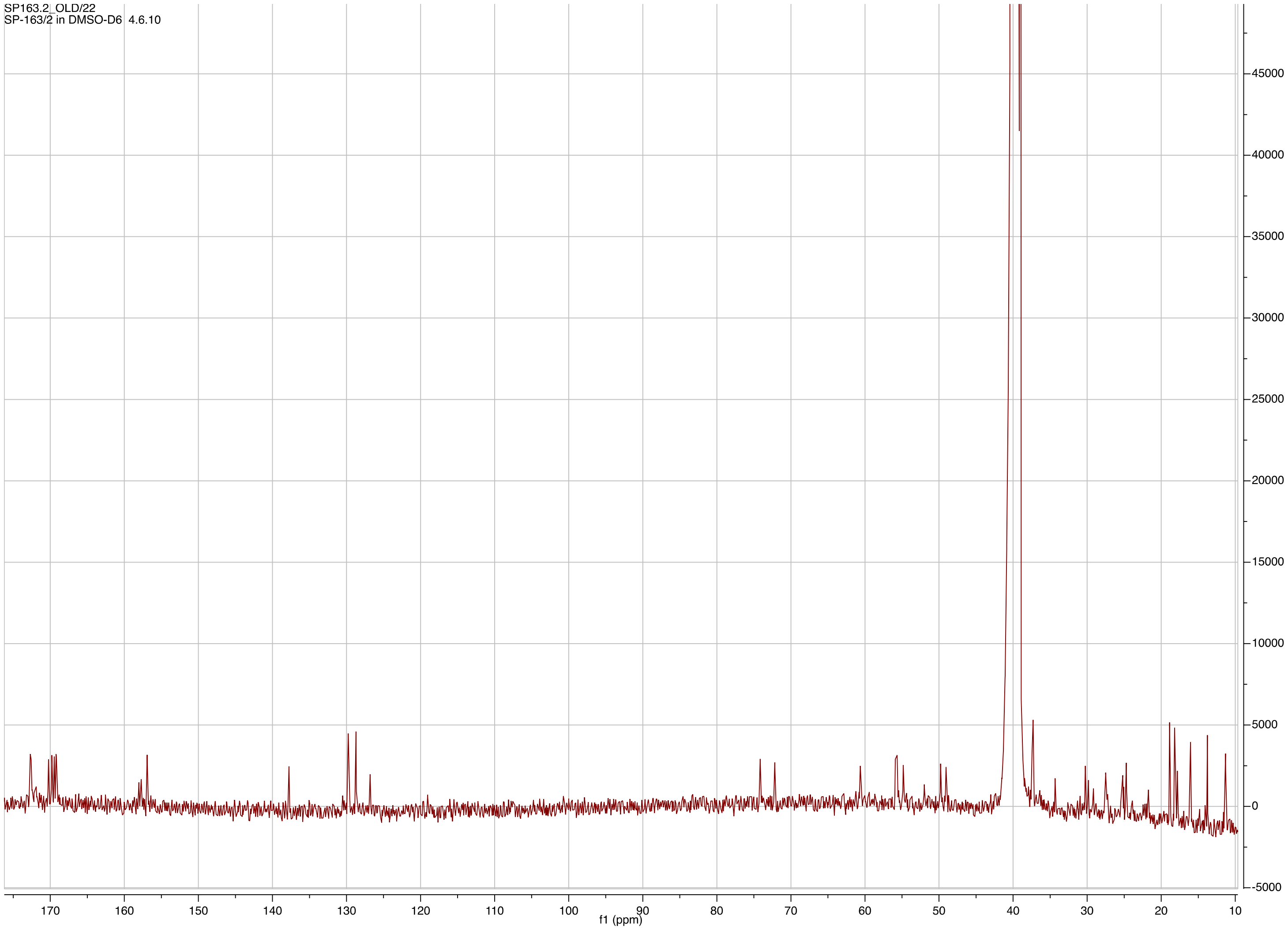


Figure S32. ^{13}C NMR Spectrum (100 MHz) of Micropeptin KB928 (**5**) in DMSO-*d*6.

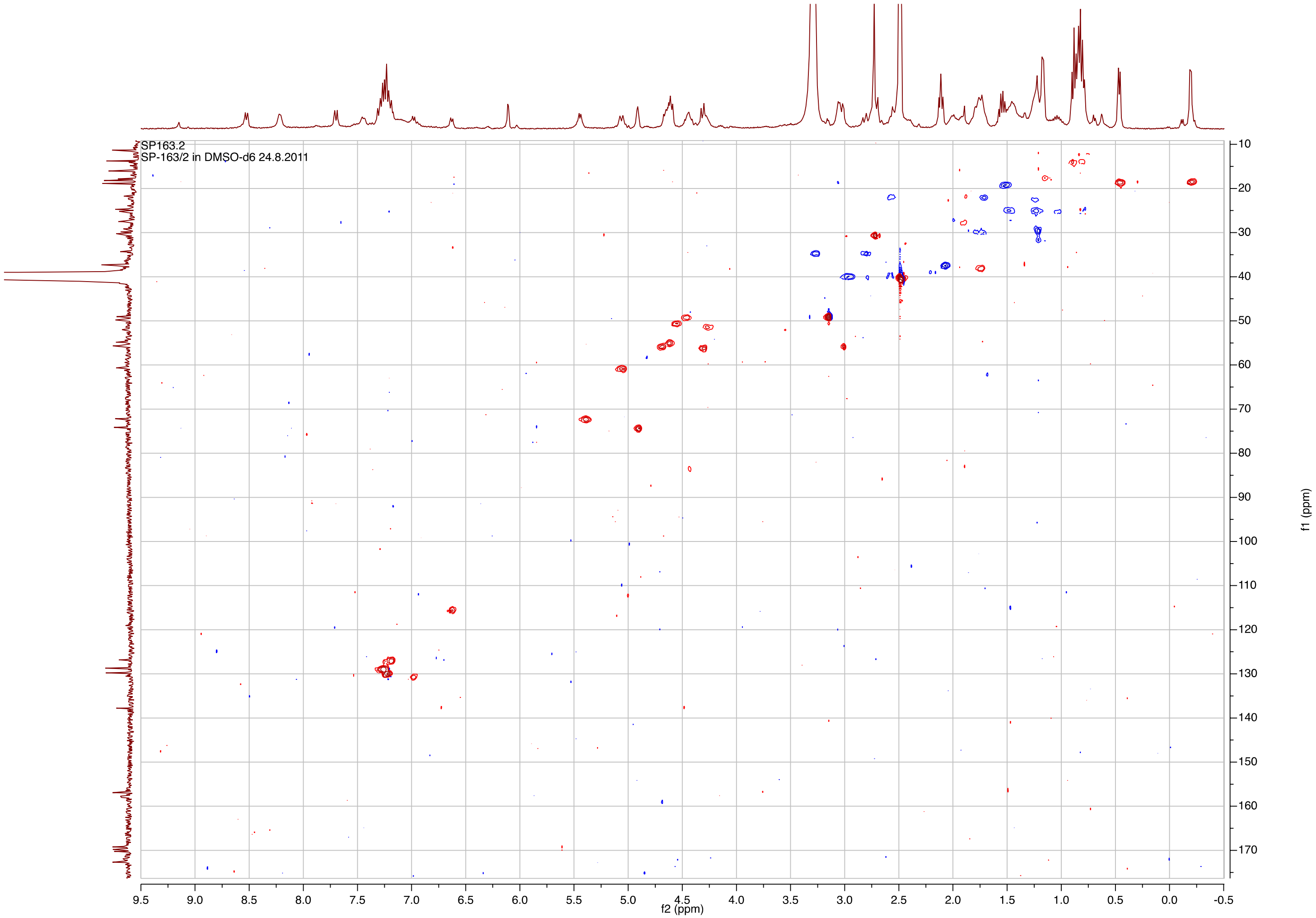


Figure S33. HSQC Spectrum of Micropeptin KB928 (**5**) in DMSO-d_6 (Red: CH, CH_3; Blue: CH_2).

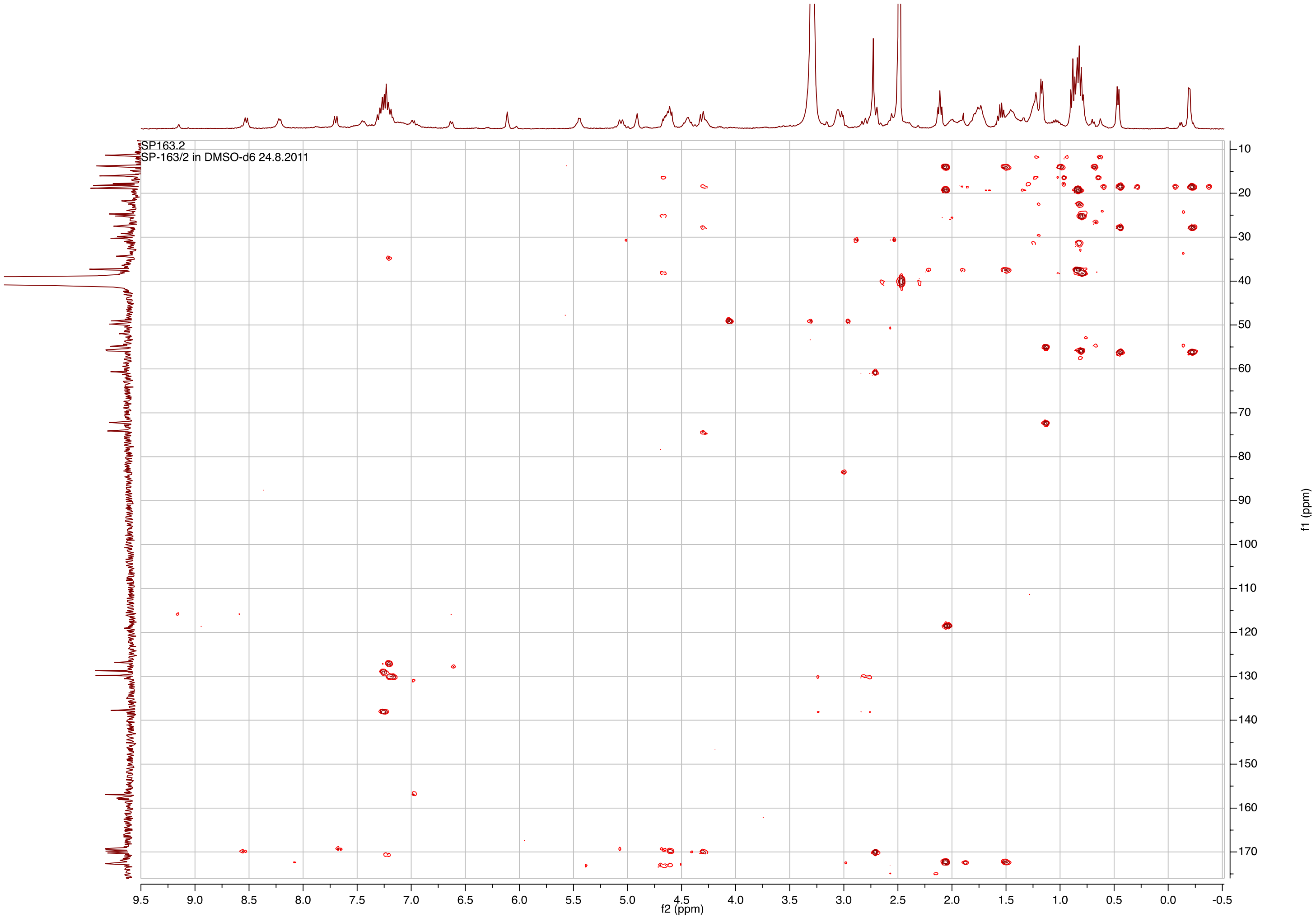


Figure S34. HMBC Spectrum of Micropeptin KB928 (**5**) in DMSO-d_6.

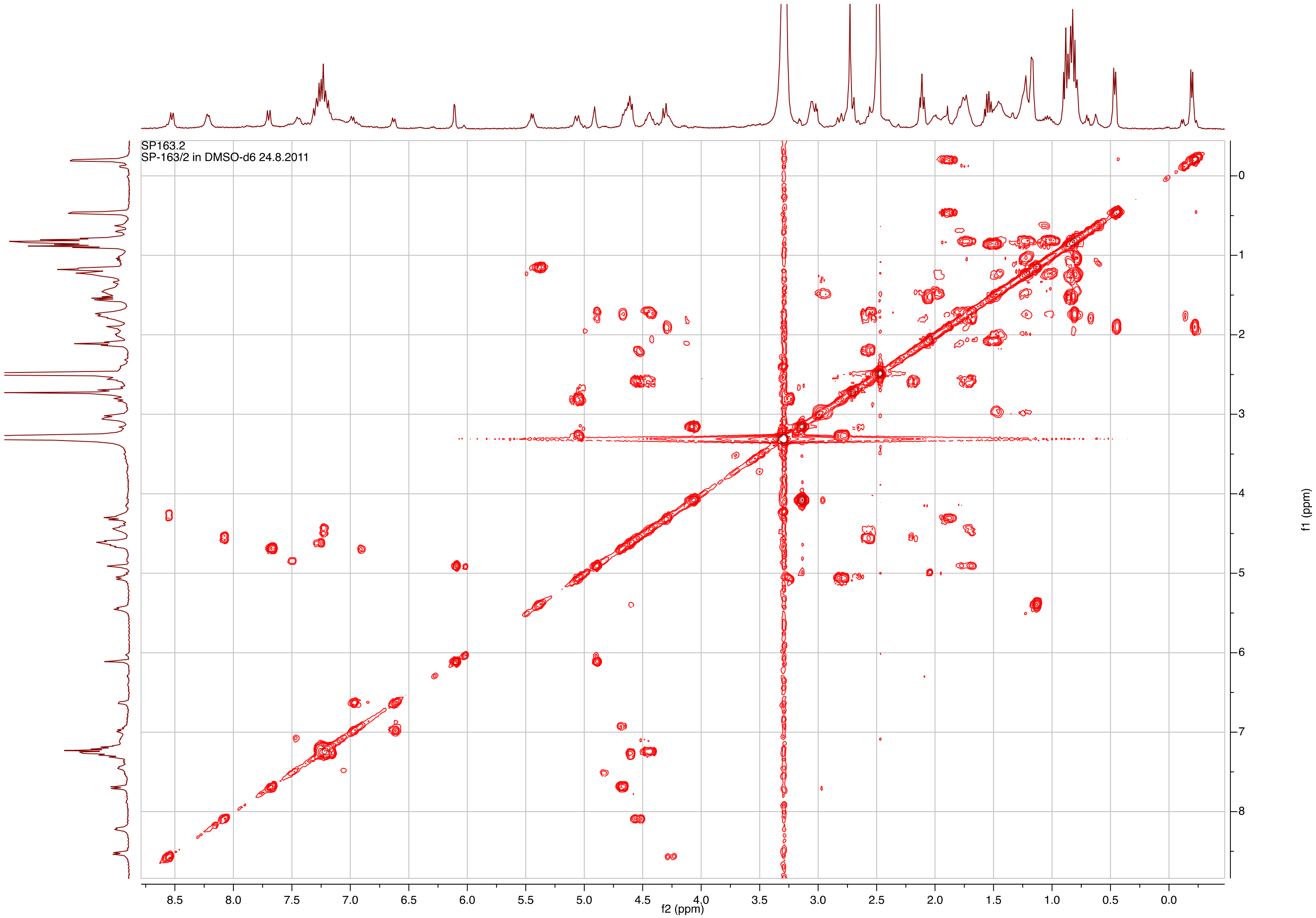


Figure S35. COSY Spectrum of Micropeptin KB928 (**5**) in DMSO-d_6.

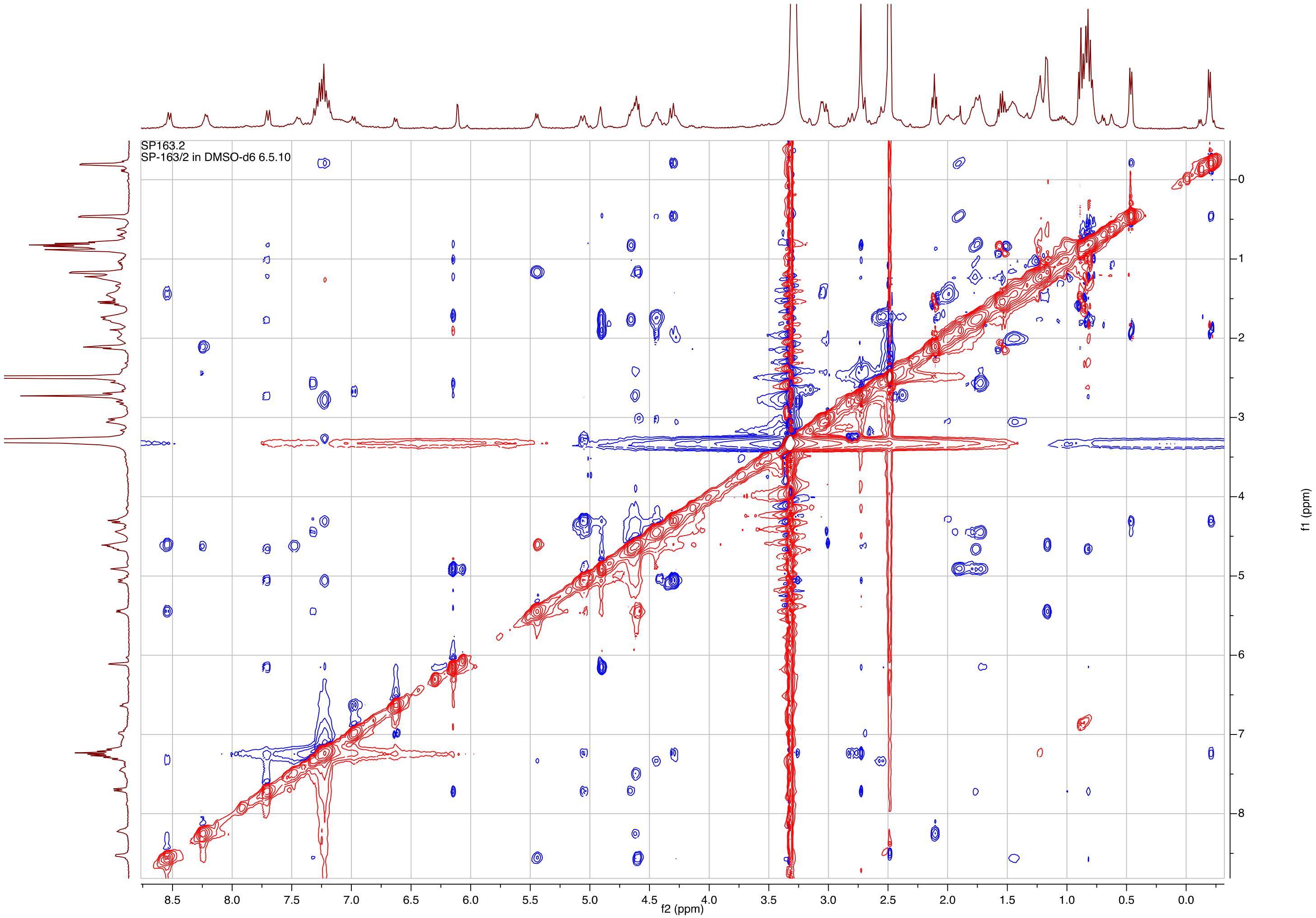


Figure S36. ROESY Spectrum of Micropeptin KB928 (**5**) in DMSO-d_6 (Blue: NOE correlation).

Table S5. NMR Data of Micropeptin KB928 (**5**) in DMSO-d_6.

Position	δ_C mult. [b]	δ_H mult.[b] *J* in Hz	HMBC Correlations [c]	NOE Correlations [d]
[1]Ba 1	172.0, qC	-		
2	37.4, CH_2	2.11, t (7.2)	Ba-1,3,4	Ba-3,4; Asp-*N*H
3	18.9, CH_2	1.53, qi (7.2)	Ba-1,2,3	Ba-2,4
4	13.8, CH_3	0.88, t (7.2)	Ba-2,3	Ba-2,3
[2]Asp 1	172.6, qC	-		
2	49.8, CH	4.55, m	Asp-1,4	Asp-3a,3b,*N*H; Thr-*N*H
3 ab	39.0, CH_2	2.58, m		Asp-2,3b,*N*H
		2.20, m		Asp-2,3a,*N*H
4	172.0, qC	-		
*N*H	-	8.09, d (8.0)	Ba-1	Asp-2,3a,3b; Ba-2, Thr-*N*H
[3]Thr 1	169.2, qC	-		
2	54.8, CH	4.62, d (9.2)	Asp-1; Thr-1	Thr-3,4,*N*H; Arg-*N*H
3	72.2, CH	5.45, q (6.8)	Thr-4; Ile-1	Thr-2,4,*N*H; Arg-*N*H; Ahp-*N*H
4	17.8, CH_3	1.17, d (6.8)	Thr-2,3	Thr-2,3
*N*H	-	7.44, brd (9.0)		Thr-2,3; Asp-2,3a,*N*H
[4]Arg 1	170.3, qC			
2	51.8, CH	4.28, m		Arg-3a,3b,4,5,*N*H; Ahp-*N*H
3 ab	27.5, CH_2	2.02, m		Arg-2,3b,4,5
		1.45,m		Arg-2,3a,5,*N*H
4	25.2, CH_2	1.45, m		Arg-2,3a,5,*N*H
5	40.1, CH_2	3.05, m		Arg-2,3a,3b,4
*N*H	-	8.57, d 8.8	Thr-1	Arg-2,3b,4; Thr-2,3; Ahp-*N*H
5-*N*H	-	7.49, brt 5.2		
6	156.9, qC	-		
6-*N*H,*N*H_2	-	7.30, brm		
		6.60, brm		

Table S5. *Cont.*

[5]Ahp 2	169.5, qC	-		
3	49.0, CH	4.44, m	Ahp-2,4	Ahp-4b,5,*N*H; Val-3,4
4	21.7, CH_2	2.55, m		Ahp-4b,*N*H,*O*H
		1.73, m		Ahp-4b,*N*H,*O*H
5	29.2, CH_2	1.70, m		Ahp-3,4b,6,*O*H
6	74.2, CH	4.91, brs		Ahp-4b,5; Val-3,4
*N*H	-	7.30, d (10.0)	Arg-1	Ahp-3,4a; Thr-3; Arg-2,*N*H
*O*H		6.11, d (3.2)		Ahp-4a,5; Val-3; *N*MePhe-*N*Me; Ile-4a,5,6,*N*H
[6]Val 1	169.8, qC	-		
2	55.7, CH	4.31, d (10.4)	Ahp-2,6; Val-1,3,4,5	Val-3,4,5; *N*MePhe-2,5,5′,6,6′
3	27.5, CH	1.90, m	Val-4,5	Val-2,4,5; Ahp-3,6,*O*H
4	18.2, CH_3	0.46, d (6.8)	Val-3,5	Val-2,3,5; Ahp-3,6; *N*MePhe-2,5,5′
5	18.1, CH_3	−0.20, d (6.4)	Val-3,4	Val-2,3,4; *N*MePhe-2,5,5′,6,6′
[7]*N*MePhe 1	169.2, qC	-		
2	60.6, CH	5.06, brd (11.2)	*N*MePhe-1,*N*Me	*N*MePhe-3a,3b,5,5′,*N*Me; Val-2,4,5; Ile-*N*H
3	34.3, CH_2	3.28, m	*N*MePhe-4,5,5′	*N*MePhe-2,3b,5,5′,*N*Me; Ile-*N*H
		2.80, m	*N*MePhe-4,5,5′	
4	137.8, qC			*N*MePhe-2,3a,5,5′,6,6′
5,5′	129.8, CH	7.23, d (7.6)	*N*MePhe-3,4,7	
6,6′	128.7, CH	7.26, t (7.6)	*N*MePhe-4	*N*MePhe-2,3a,3b,6,6′,7,*N*Me; Val-2,4,5,Ile-4a
7	126.8 CH	7.19, t (7.6)	*N*MePhe-5,5′	*N*MePhe-3b,5,5′,7; Val-2,5; Ile-4a
*N*Me	30.3, CH_3	2.73, s	Val-1; *N*MePhe-1,2	*N*MePhe-5,5′,6,6′
[8]Ile 1	172.7, qC	-		
2	55.9, CH	4.69, dd (9.2,5.2)	Ile-1,3,4,6	Ile-3,4b,5,6,*N*H
3	37.4, CH	1.78, m		Ile-2,4a,4b,5,6,*N*H

Table S5. *Cont.*

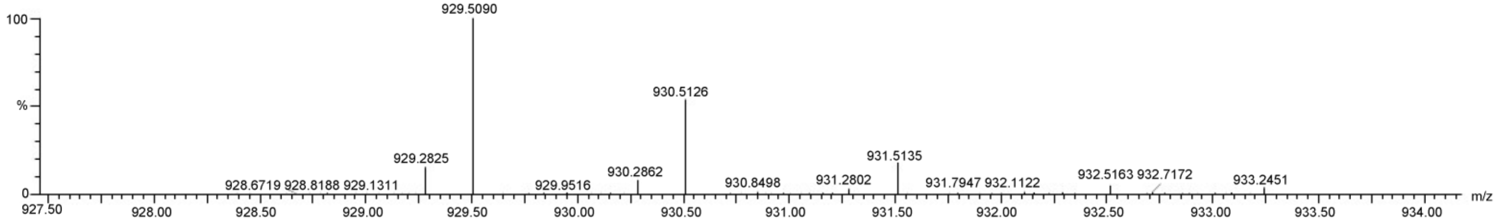
4	24.7, CH_2	1.23, m	Ile-5,6	Ile-3,4b,*N*H; Ahp-*O*H; *N*MePhe-5,6
		1.04, m	Ile-3,5,6	Ile-2,3,4a,5,6,*N*H; Ahp-*O*H
5	11.3, CH_3	0.81, t (7.2)	Ile-3,4	Ile-2,3,4b,*N*H; Ahp-*O*H; *N*MePhe-*N*Me
6	16.0, CH_3	0.83, d (7.6)	Ile-2,4	Ile-2,3,4b,*N*H, Ahp-*O*H, *N*MePhe-*N*Me
*N*H	-	7.68, d (9.6)	NMePhe-1	Ile-2,3,4a,4b,5,6; Ahp-*O*H; *N*MePhe-2,3a,*N*Me

[a] 100 MHz for carbons and 400 MHz for protons; [b] Multiplicity and assignment from HSQC experiment; [c] Determined from HMBC experiment, $^{n}J_{CH}$ = 8 Hz, recycle time 1 s; [d] Selected NOE's from ROESY experiment.

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
467 formula(e) evaluated with 9 results within limits (up to 4 best isotopic matches for each mass)
Elements Used:
C: 35-50 H: 50-80 N: 0-15 O: 0-20
SP163/2 Shira Pe'er
carmeli 255b 163 (7.172) Cm (163:169) 1: TOF MS ES+ 8.48e+003



Minimum:				-1.5			
Maximum:		5.0	10.0	50.0			

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
929.5090	929.5096	-0.6	-0.6	15.5	179.4	1.1	C44 H69 N10 O12
	929.5083	0.7	0.8	10.5	180.6	2.3	C43 H73 N6 O16
	929.5110	-2.0	-2.2	20.5	181.2	2.9	C45 H65 N14 O8
	929.5110	-2.0	-2.2	9.5	179.0	0.7	C47 H77 O18

Figure S37. HR ESI MS date of micropeptin KB928 (**5**).

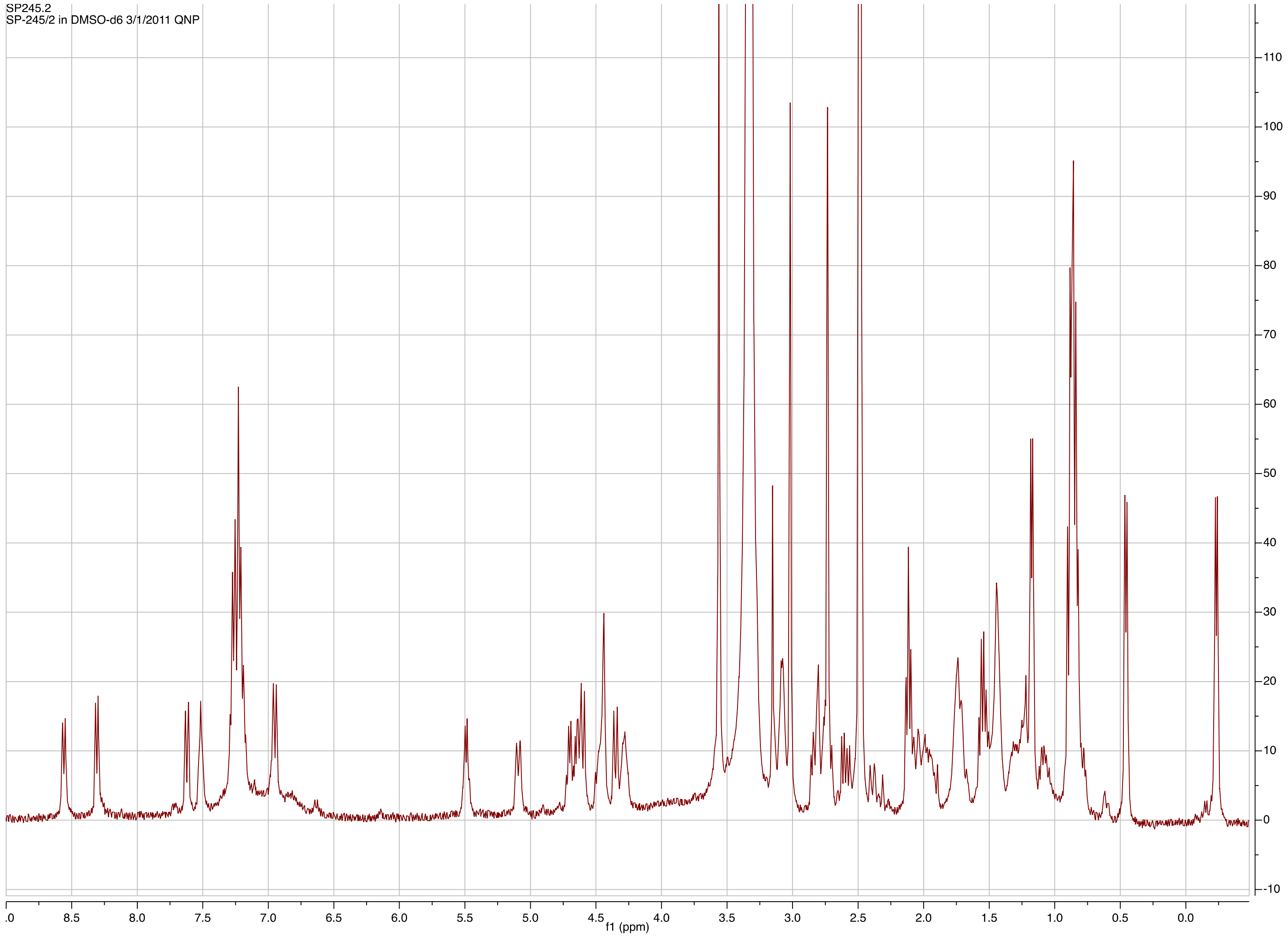


Figure S38. ^{1}H NMR Spectrum (400 MHz) of Micropeptin KB956 (**6**) in DMSO-d_6.

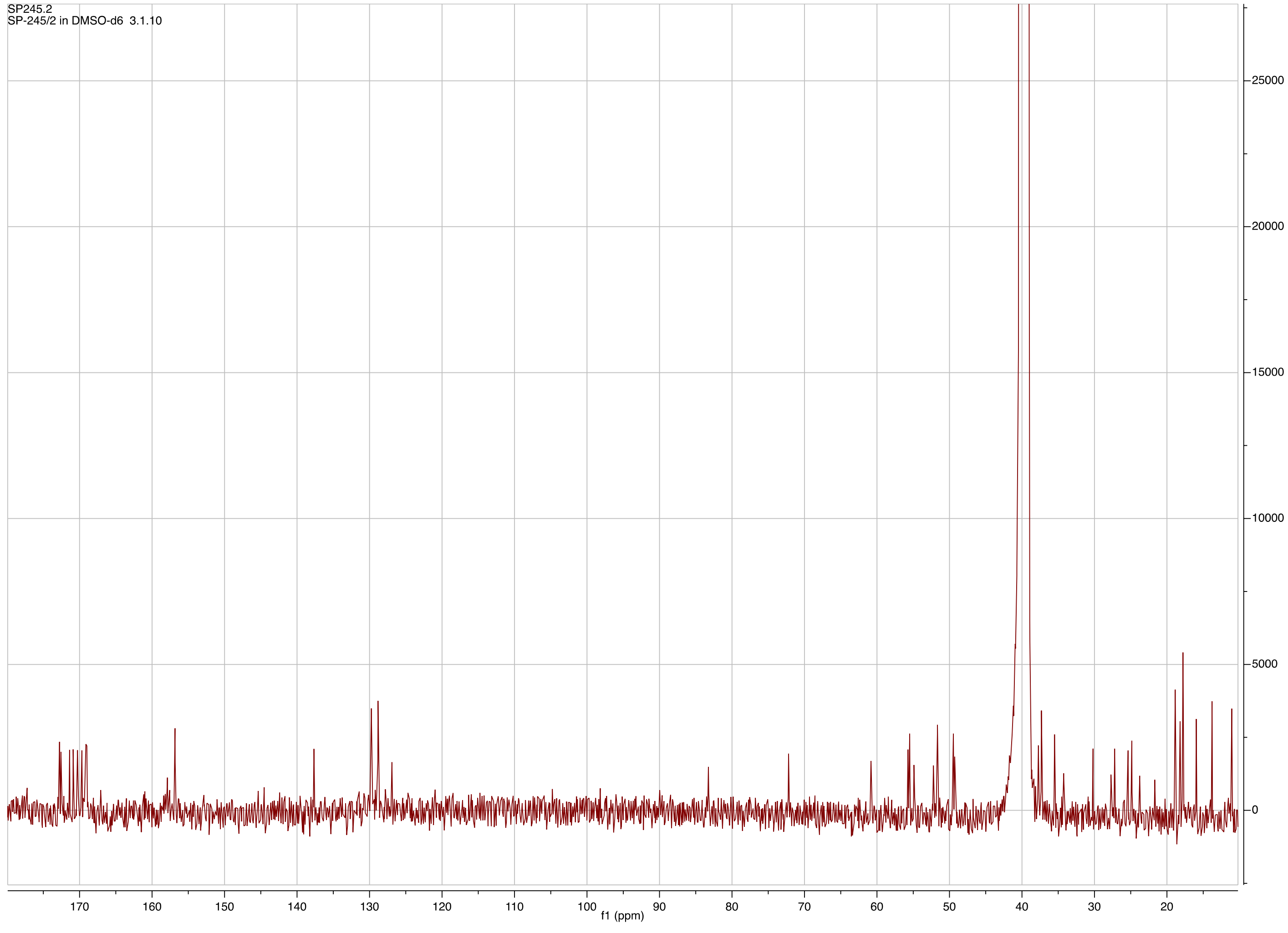


Figure S39. ^{13}C NMR Spectrum (100 MHz) of Micropeptin KB956 (**6**) in DMSO-d_6.

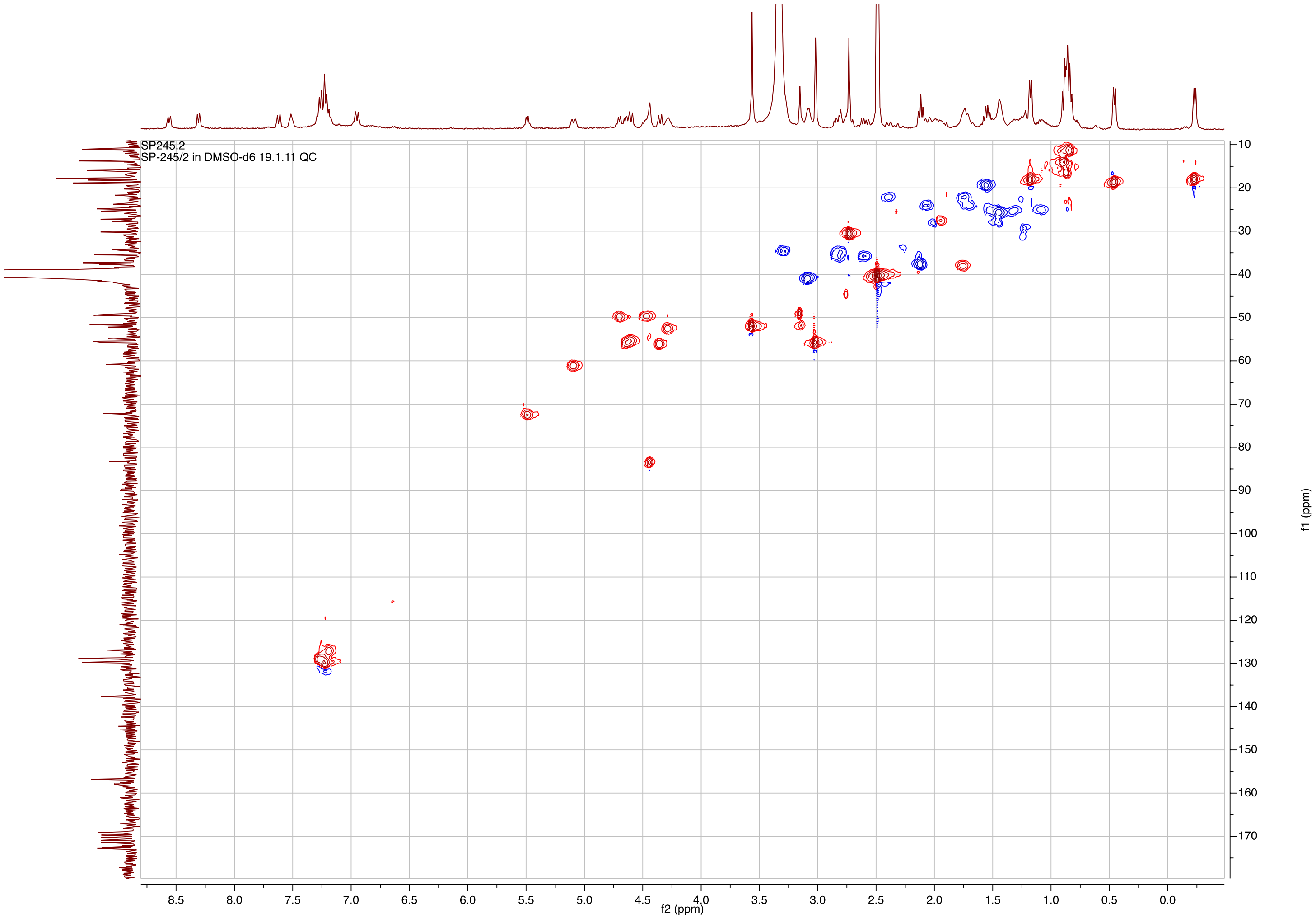


Figure S40. HSQC Spectrum of Micropeptin KB956 (**6**) in DMSO-d_6 (Red: CH, CH_3; Blue: CH_2).

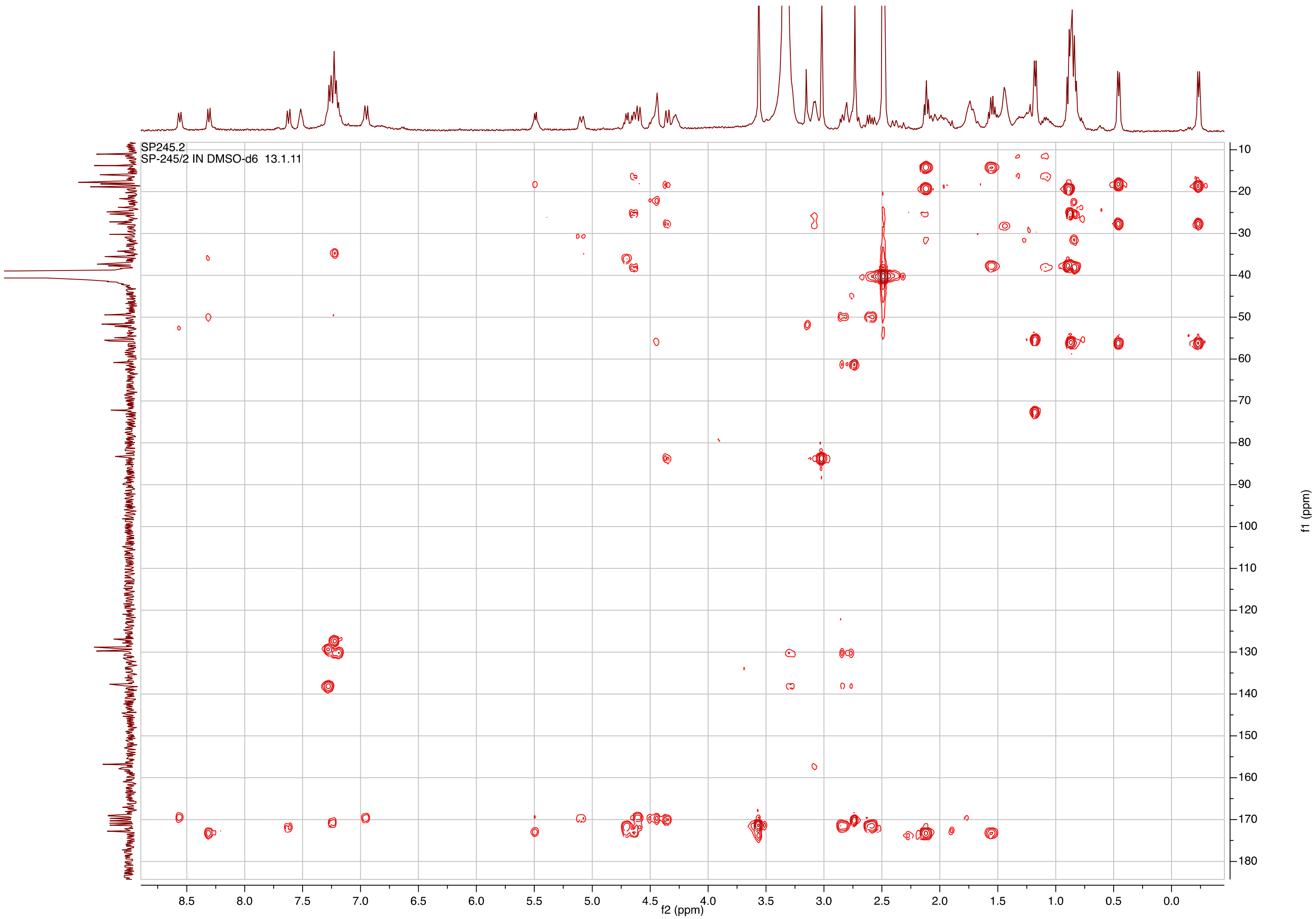


Figure S41. HMBC Spectrum of Micropeptin KB956 (**6**) in DMSO-d_6.

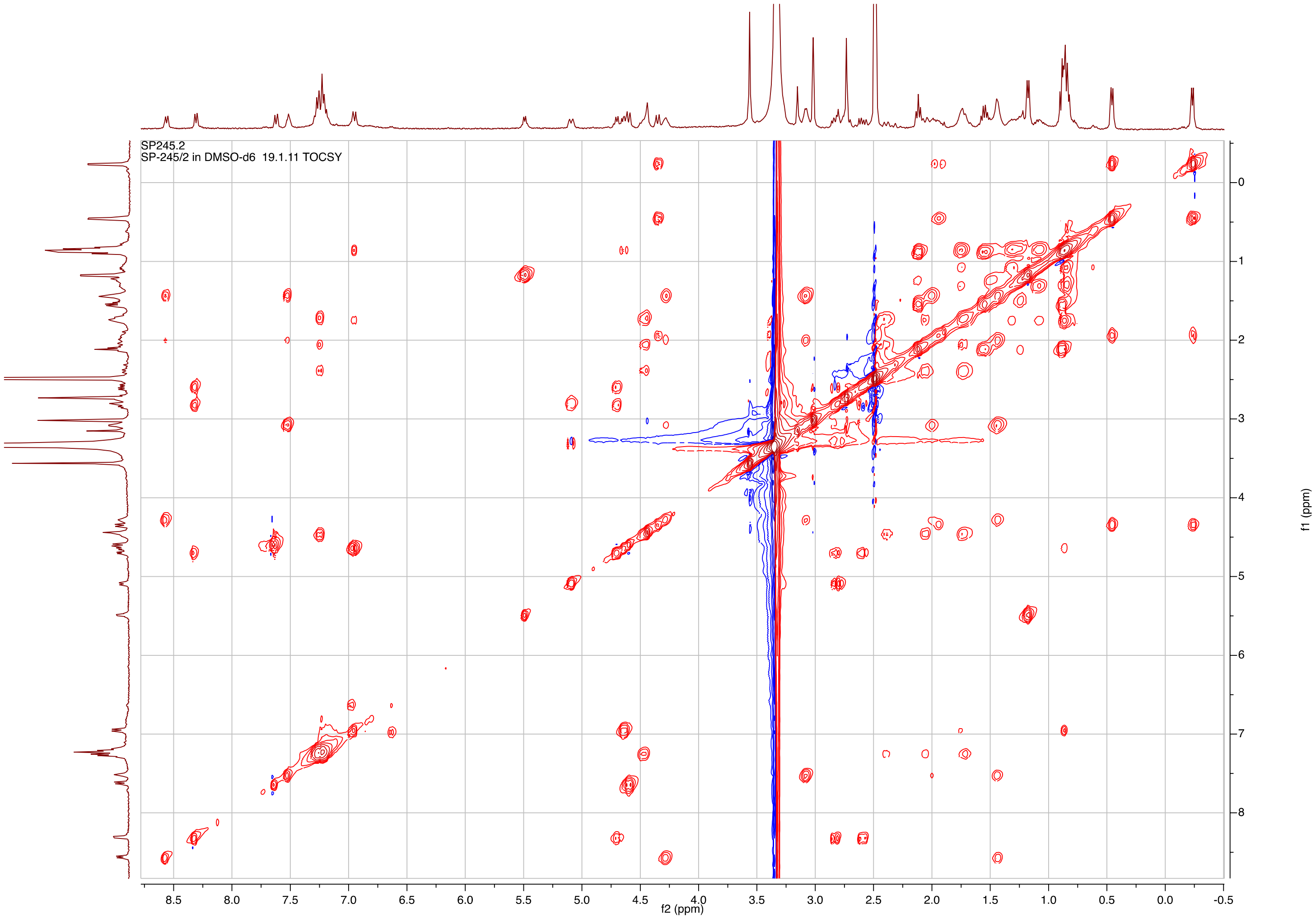


Figure S42. COSY Spectrum of Micropeptin KB956 (**6**) in DMSO-d_6.

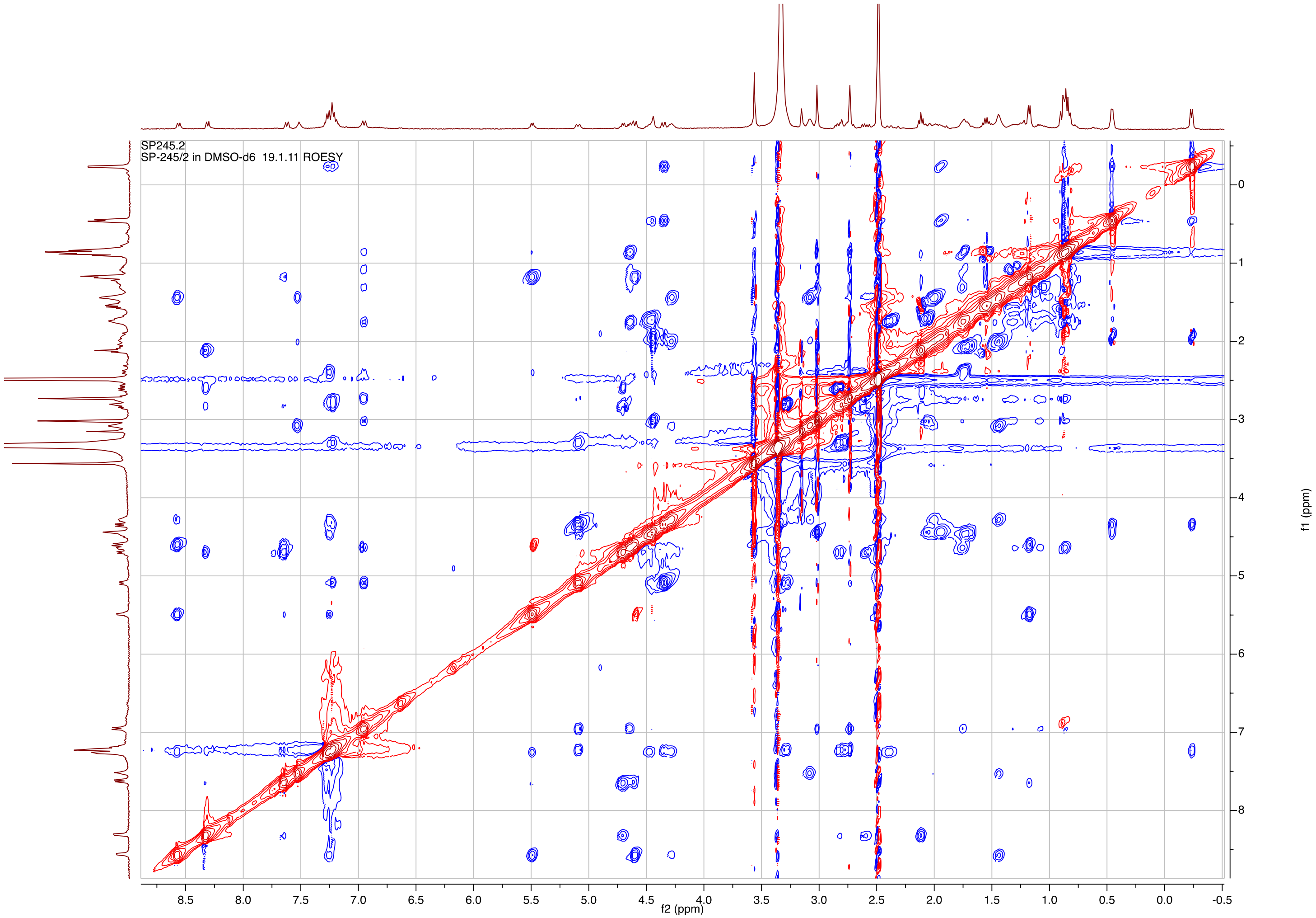


Figure S43. ROESY Spectrum of Micropeptin KB956 (**6**) in DMSO-d_6 (Blue: NOE correlation).

Table S6. NMR Data of Micropeptin KB956 (**6**) in DMSO-d_6.

Position	δ_C mult. [b]	δ_H mult.[b] *J* in Hz	HMBC Correlations [c]	NOE Correlations [d]
[1]Ba 1	172.8, qC	-		
2	37.3, CH_2	2.11, t (7.2)	Ba-1,3,4	Ba-3,4
3	18.9, CH_2	1.55, qi (7.2)	Ba-1,2,3	Ba-2,4
4	13.8, CH_3	0.88, t (7.2)	Ba-2,3	Ba-2,3
[2]Asp 1	171.4, qC	-		
2	49.5, CH	4.86, q (8.0)	Asp-1,4	Asp-3a,3b,*N*H; Thr-*N*H
3 ab	35.5, CH_2	2.80, m	Asp-2,4	Asp-2,3b,*N*H; Thr-*N*H
		2.60, dd (16.8,8.0)	Asp-2,4	Asp-2,3a,*N*H
4	170.9, qC	-		
*N*H	-	8.33, d (7.2)	Ba-1	Asp-2,3a,3b; Thr-*N*H
*O*Me	51.7, CH_3	3.56, s	Asp-4	
[3]Thr 1	169.0, qC	-		
2	54.9, CH	4.60, d (9.6)	Asp-1; Thr-1	Thr-3,4,*N*H; Arg-*N*H
3	72.2, CH	5.49, q (6.4)	Thr-4; Ile-1	Thr-2,4,*N*H; Arg-*N*H; Ahp-*N*H
4	18.2, CH_3	1.18, d (6.4)	Thr-2,3	Thr-2,3
*N*H	-	7.65, d (9.6)	Asp-1	Thr-2,3; Asp-2,3a,*N*H
[4]Arg 1	170.3, qC	-		
2	52.2, CH	4.28, m	Arg-1	Arg-3a,3b,4,5,*N*H; Amp-*N*H
3	27.7, CH_2	2.02, m	Arg-4,5	Arg-2,3b,4,5,5-*N*H
		1.45, m	Arg-4,5	Arg-2,3a,5,*N*H,5-*N*H
4	25.4, CH_2	1.45, m	Arg-3,5	Arg-2,3a,5,*N*H,5-*N*H
5	40.8, CH_2	3.08, m	Arg-6	Arg-2,3a,3b,4,5-*N*H
*N*H	-	8.57, d (7.6)	Thr-1; Arg-2	Arg-2,3b,4; Thr-2,3; Amp-*N*H
5-*N*H	-	7.53, t (5.2)	Arg-5,6	Arg-3a,3b,4,5
6	156.8, qC	-		

Table S6. *Cont.*

6-*N*H,*N*H2	-	7.30, brm 6.70, brm		
[5]Amp 2	169.2, qC	-		
3	49.3, CH	4.45, m	Amp-2,4	Amp-4b,5b,*N*H
4	21.7, CH_2	2.40, brq (12.5) 1.70, m	 Amp-2	Amp-4b,5a,*N*H Amp-3,4a
5	23.8, CH_2	2.05, m 1.75, m	Amp-6	Amp-4a,5b,6,*O*Me; *N*MePhe-*N*Me Amp-3,5a,6
6	83.3, CH	4.44, brs	Amp-4,*O*Me	Ahp-5a,5b,*O*Me; Val-3
*N*H	-	7.23, m	Arg-1	Ahp-3,4a; Thr-3; Arg-2,*N*H
*O*Me	55.5, CH_3	3.02, s	Amp-6	Amp-5a,6; Ile-*N*H
[6]Val 1	169.7, qC	-		
2	55.7, CH	4.35, d (10.4)	Amp-2,6; Val-1,3,4	Val-3,4,5; *N*MePhe-2,5,5′,6,6′
3	27.2, CH	1.95, m	Val-4,5	Val-2,4,5; Amp-6
4	18.9, CH_3	0.46, d (6.0)	Val-2,3,5	Val-2,3,5; *N*MePhe-2
5	17.8, CH_3	−0.24, d (6.0)	Val-2,3,4	Val-2,3,4; *N*MePhe-2,5,5′,6,6′
[7]*N*MePhe 1	169.1, qC	-		
2	60.8, CH	5.09, brd (11.2)	*N*MePhe-1,3,*N*Me	*N*MePhe-3a,3b,5,5′,6,6′,*N*Me; Val-2,4,5; Ile-*N*H
3	34.2, CH_2	3.25, m 2.80, m	*N*MePhe-4,5,5′ *N*MePhe-4,5,5′	*N*MePhe-2,3b,5,5′,6,6′,*N*Me *N*MePhe-2,3a,5,5′,6,6′
4	137.7, qC	-		
5,5′	129.7, CH	7.22, m	*N*MePhe-3,7	*N*MePhe-2,3a,3b,6,6′,7; Val-2,5
6,6′	128.8, CH	7.27, m	*N*MePhe-4	*N*MePhe-2,3a,3b,5,5′,7,*N*Me; Val-2.5
7	126.9, CH	7.19, m	*N*MePhe-5,5′	*N*MePhe-5,5′,6,6′
*N*Me	30.2, CH_3	2.73, s	Val-1; *N*MePhe-2	*N*MePhe-2,3a,5,5′; Ile-4a,4b,*N*H
[8]Ile 1	172.6, qC	-		

Table S6. *Cont.*

2	56.6, CH	4.64, dd (8.8,6.0)	Ile-1,3,4,6	Ile-3,5,6,*N*H
3	37.7, CH	1.74, m		Ile-2,4a,4b,5,6,*N*H
4	24.8, CH_2	1.31, m	Ile-3,5,6	Ile-3,4b,*N*H; *N*MePhe-*N*Me
		1.10, m	Ile-3,5,6	Ile-3,4a,5,6,*N*H; Amp-*O*Me;, *N*MePhe-*N*Me
5	11.1, CH_3	0.83, t (7.5)	Ile-4	Ile-2,3,4b,*N*H
6	16.0, CH_3	0.85, d (6.5)	Ile-2,3,4	Ile-2,3,4b,*N*H
*N*H	-	6.96, d (9.2)	*N*MePhe-1	Ile-2,3,4a,4b,5,6; Amp-*O*Me; *N*MePhe-2,3b,*N*Me

[a] 100 MHz for carbons and 400 MHz for protons; [b] Multiplicity and assignment from HSQC experiment; [c] Determined from HMBC experiment, $^{n}J_{CH}$ = 8 Hz, recycle time 1 s; [d] Selected NOE's from ROESY experiment.

Elemental Composition Report

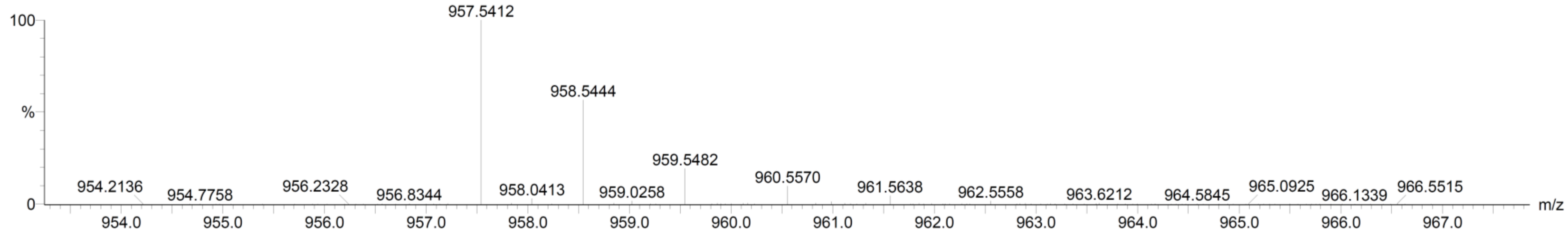
Page 1

Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
66 formula(e) evaluated with 2 results within limits (up to 4 best isotopic matches for each mass)
Elements Used:
C: 45-55 H: 70-80 N: 5-15 O: 5-15

SP-245/2 Shira Peer
carmeli 317b 64 (2.822) Cm (61:64) 1: TOF MS ES+ 1.99e+004



Minimum:				-1.5			
Maximum:		5.0	10.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
957.5412	957.5409	0.3	0.3	15.5	114.2	0.0	C46 H73 N10 O12
	957.5450	-3.8	-4.0	19.5	118.6	4.4	C51 H73 N8 O10

Figure S44. HR ESI MS data of Micropeptin KB956 (**6**).

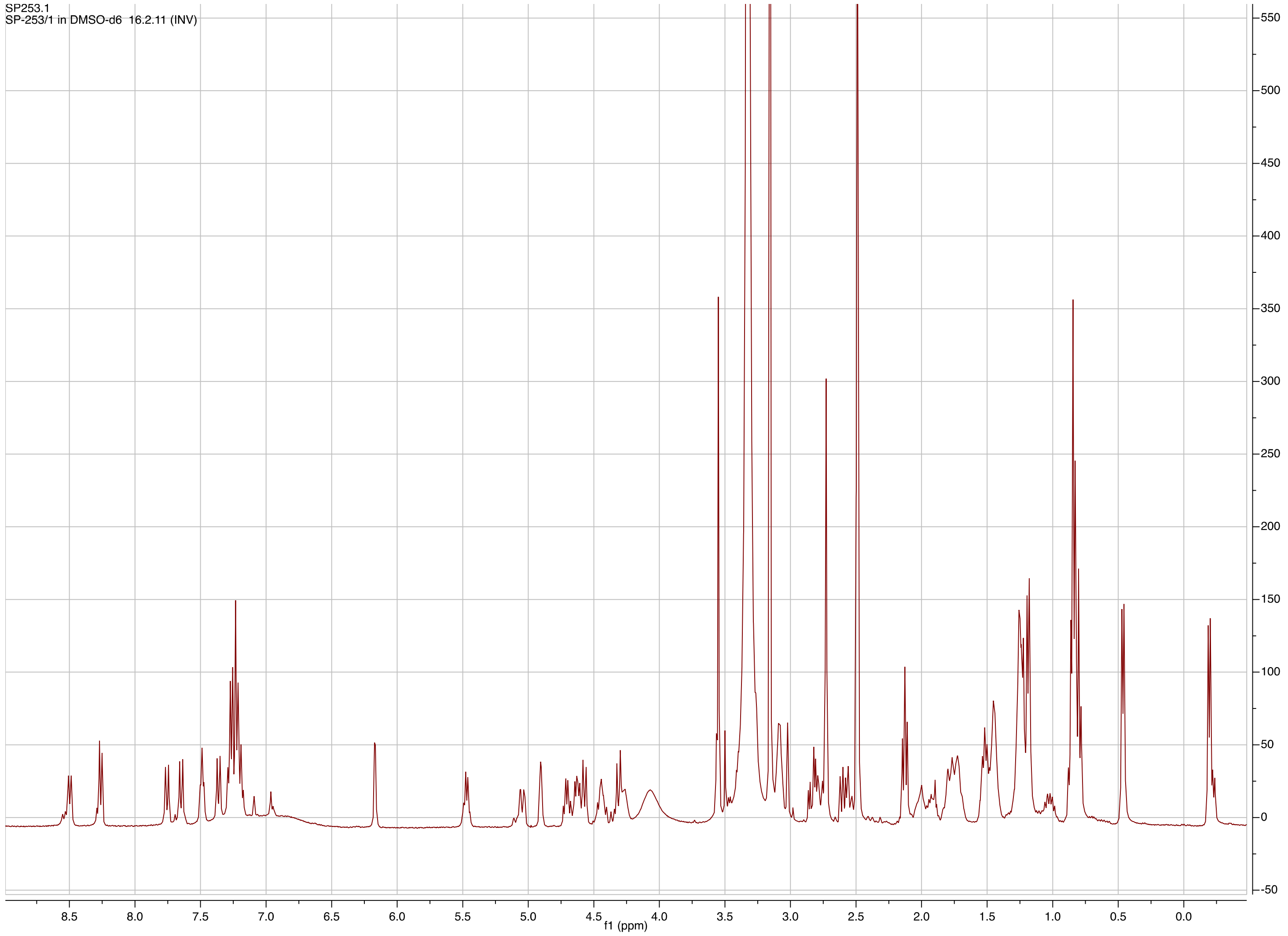


Figure S45. [1]H NMR Spectrum (400 MHz) of Micropeptin KB970A (**7**) in DMSO-d_6.

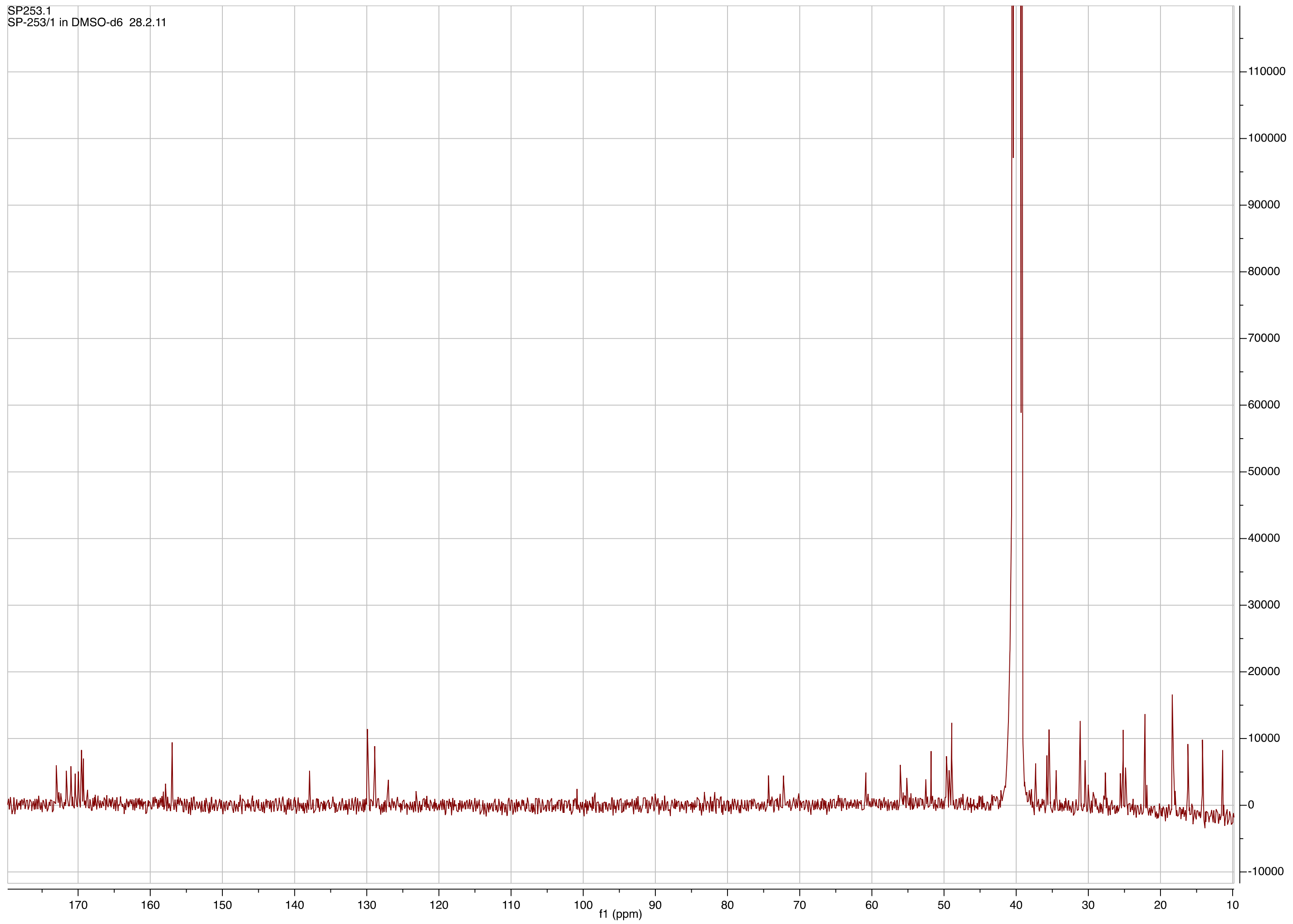


Figure S46. ^{13}C NMR Spectrum (100 MHz) of Micropeptin KB970A (**7**) in DMSO-d_6.

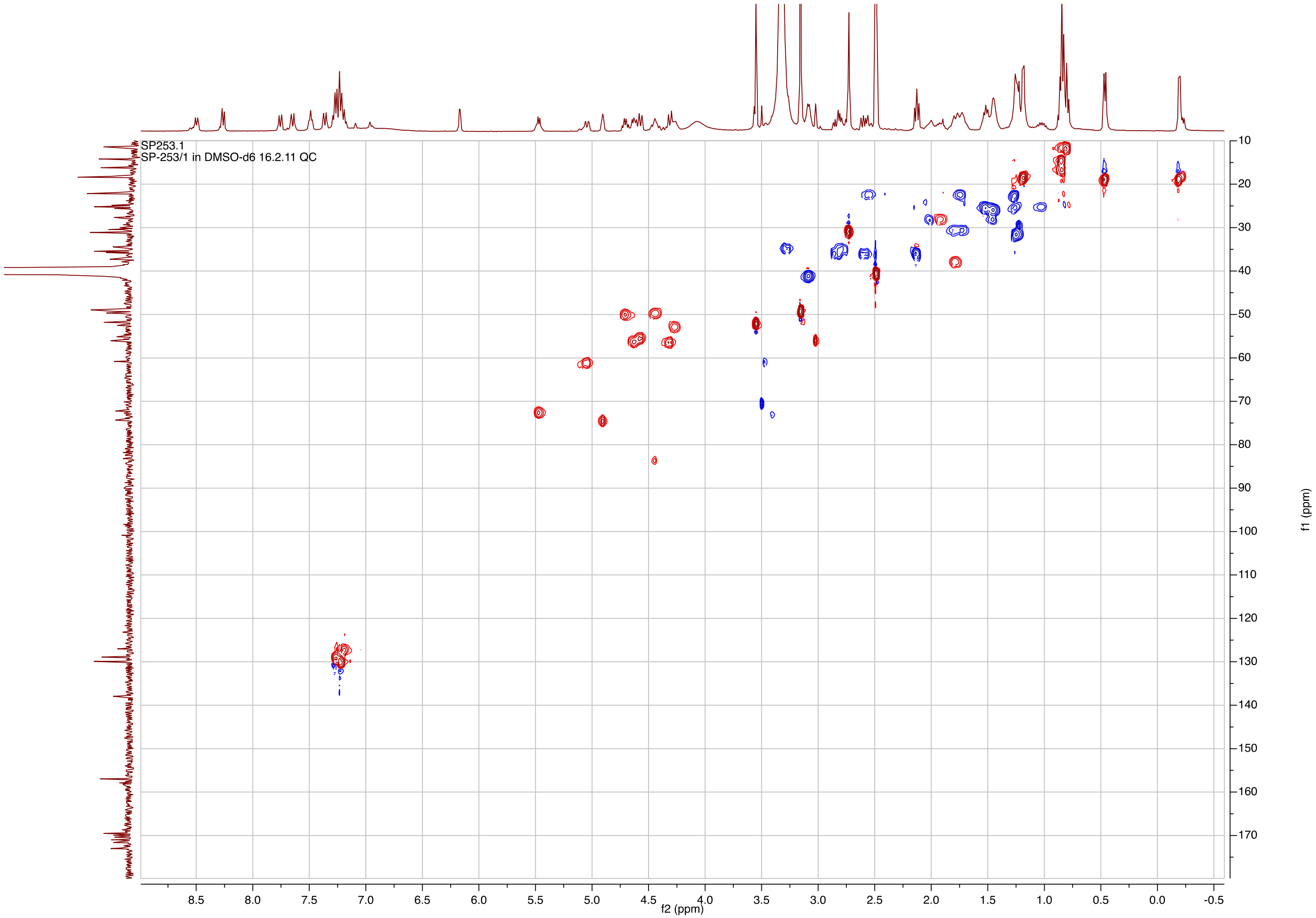


Figure S47. HSQC Spectrum of Micropeptin KB970A (**7**) in DMSO-d_6 (Red: CH, CH_3; Blue: CH_2).

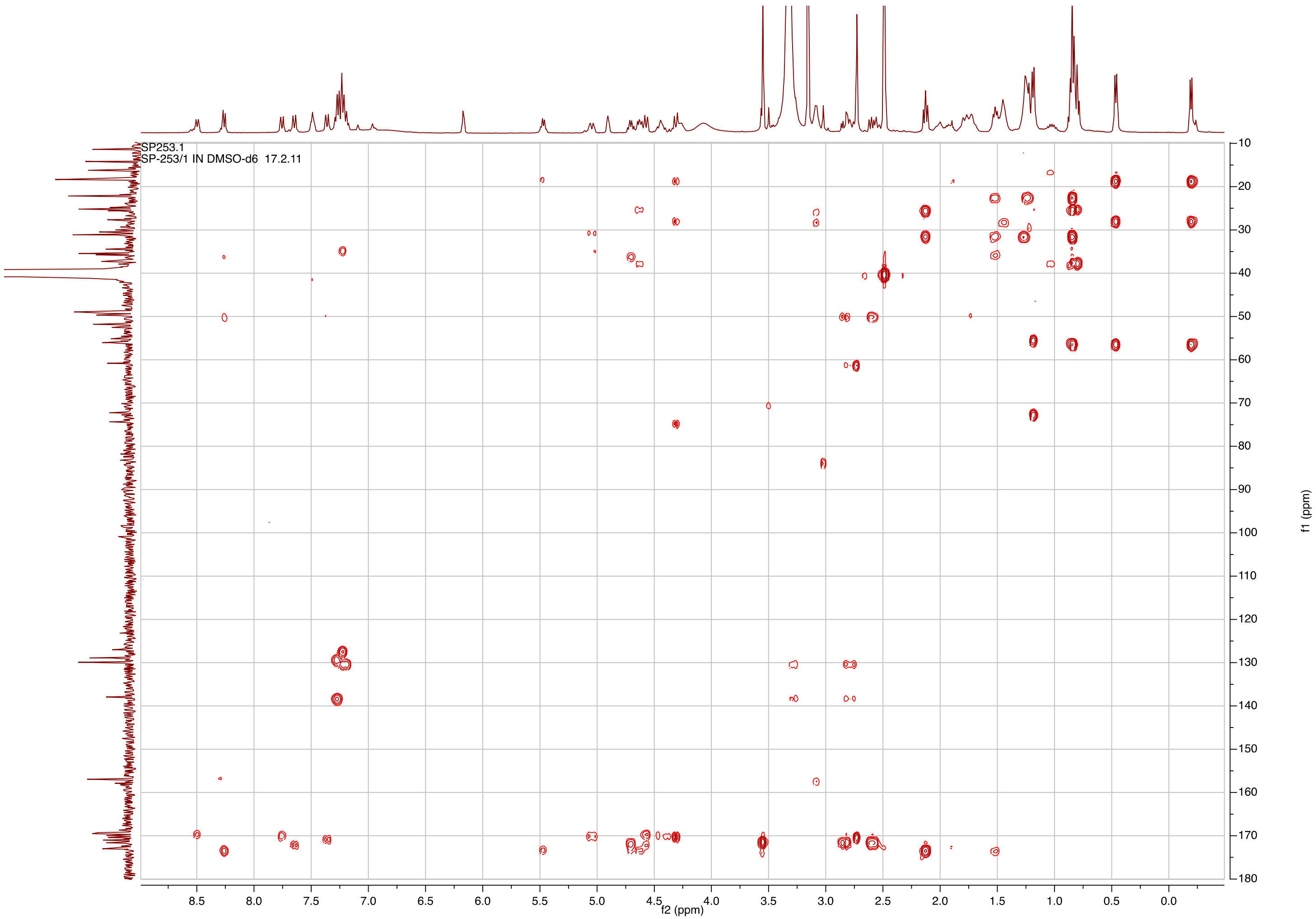


Figure S48. HMBC Spectrum of Micropeptin KB970A (**7**) in DMSO-d_6.

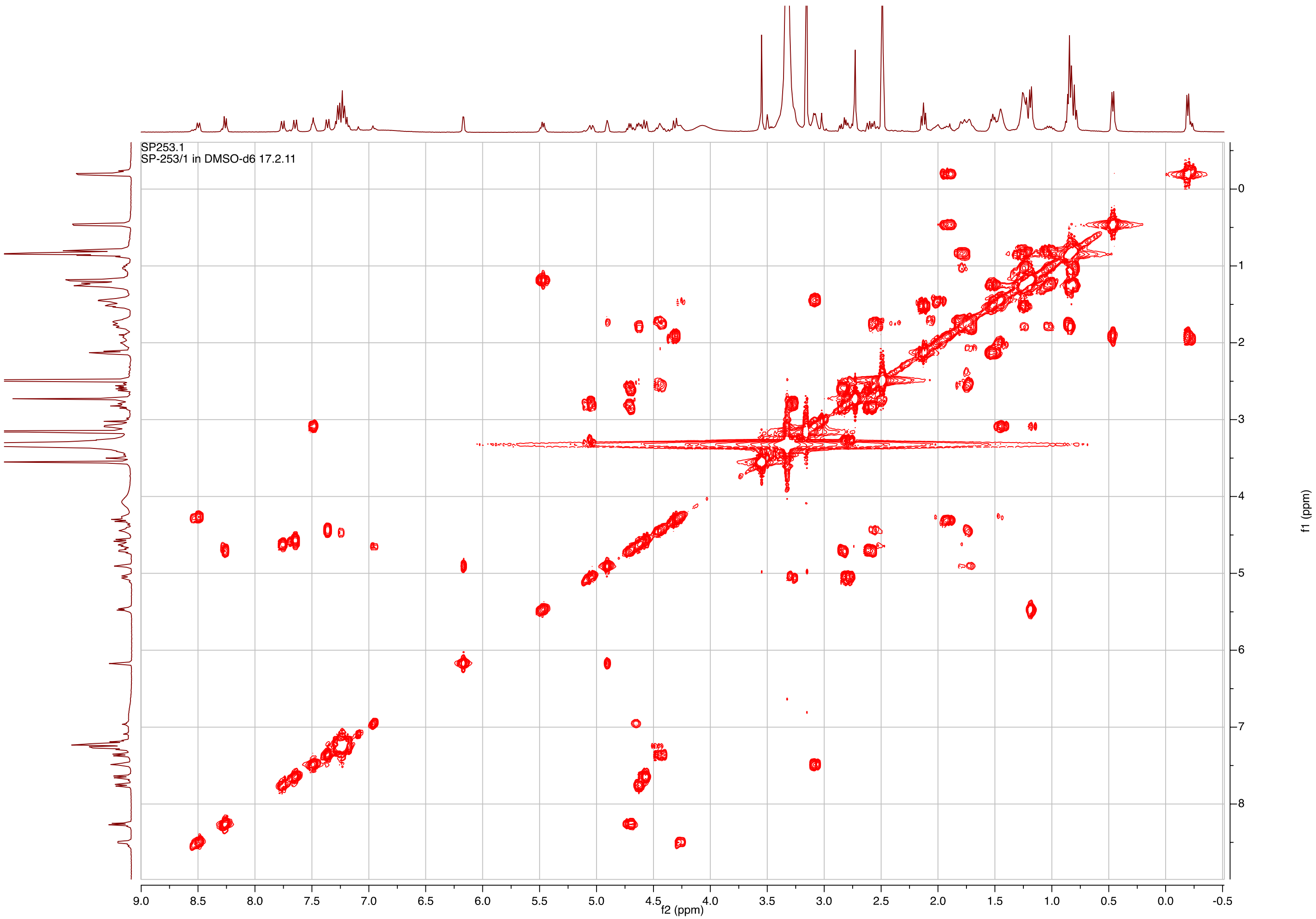


Figure S49. COSY Spectrum of Micropeptin KB970A (**7**) in DMSO-d_6.

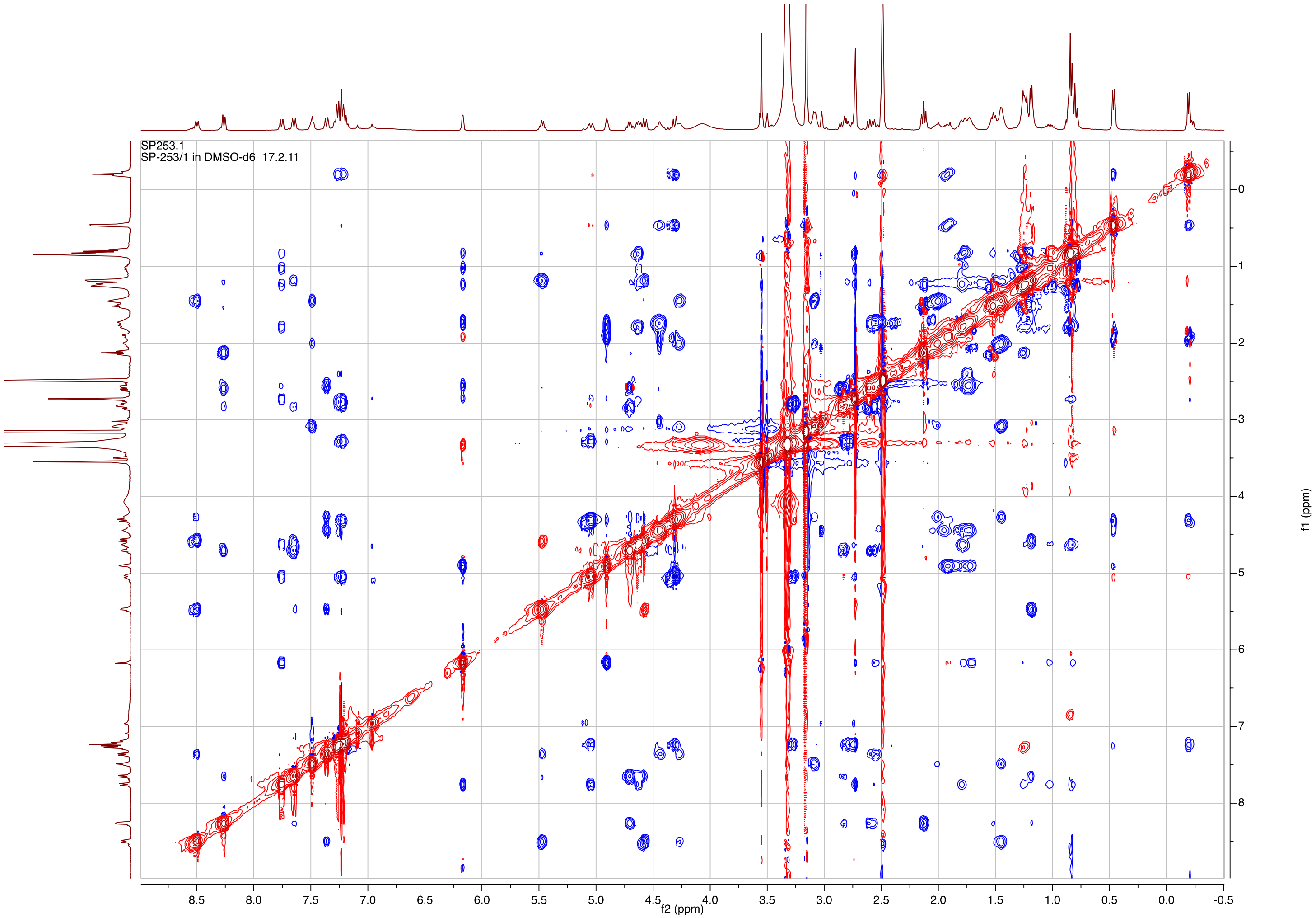


Figure S50. ROESY Spectrum of Micropeptin KB970A (**7**) in DMSO-d_6 (Blue: NOE correlation).

Table S7. NMR Data of Micropeptin KB970A (**7**) in DMSO-d_6.

Position	δ_C mult. [b]	δ_H mult.[b] *J* in Hz	HMBC Correlations [c]	NOE Correlations [d]
[1]Ha 1	173.0, qC	-		
2	35.4, CH_2	2.13, t (7.6)	Ha-1,3,4	Ha-3,4; Asp-*N*H
3	25.2, CH_2	1.52, qi (7.6)	Ha-1,2,4,5	Ha-2,4,5; Asp-*N*H
4	31.1, CH_2	1.22, m	Ha-5	Ha-2,3,5,6
5	22.1, CH_2	1.27, m	Ha-4,6	Ha-3,4,6
6	14.2, CH_3	0.84, t (6.8)	Ha-4,5	Ha-4,5
[2]Asp 1	171.6, qC	-		
2	49.7, CH	4.71, ddd (8.0,7.6,5.6)	Ha-1; Asp-1,3,4	Asp-3a,3b,*N*H; Thr-*N*H
3 ab	35.7, CH_2	2.82, dd (16.4,5.6)	Asp-2,4	Asp-2,3b,*N*H; Thr-*N*H
		2.58, dd (16.4,8.0)	Asp-2,4	Asp-2,3a,*N*H
4	171.0, qC	-		
*N*H	-	8.27, d (7.6)	Ha-1; Asp-2,3	Asp-2,3a,3b; Ha-2,3; Thr-4,*N*H
*O*Me	51.8, CH_3	3.56, s	Asp-4	
[3]Thr 1	169.3, qC	-		
2	55.1, CH	4.57, d (9.2)	Asp-1; Thr-1,3	Thr-3,4,*N*H; Arg-*N*H
3	72.2, CH	5.47, q (6.4)	Thr-4; Ile-1	Thr-2,4,*N*H; Arg-*N*H; Ahp-*N*H
4	18.2, CH_3	1.19, d (6.4)	Thr-2,3	Thr-2,3,*N*H; Asp-*N*H
*N*H	-	7.46, d (9.2)	Asp-1	Thr-2,3; Asp-2,3a,*N*H
[4]Arg 1	170.4, qC	-		
2	52.5, CH	4.26, m	Arg-1,3	Arg-3a,3b,4,5,*N*H; Ahp-*N*H
3 ab	27.6, CH_2	2.02, m		Arg-2,3b,4,5,*N*H,5-*N*H
		1.45, m		Arg-2,3a,5,*N*H,5-*N*H
4	25.8, CH_2	1.45, m	Arg-3	Arg-2,3a,5,*N*H,5-*N*H
5	41.0, CH_2	3.09, m	Arg-3,4,6	Arg-2,3a,3b,4,5-*N*H
*N*H	-	8.50, d (8.4)	Thr-1; Arg-3	Arg-2,3a,3b,4; Thr-2,3; Ahp-*N*H

Table S7. *Cont.*

5-*N*H	-	7.49, t (4.8)	Arg-4,5	Arg-3a,3b,4,5
6	157.0, qC	-		
6-*N*H,*N*H2	-	7.30, brm 6.80, brm		
[5]Ahp 2	169.5, qC	-		
3	49.3, CH	4.44, m	Ahp-2	Ahp-4b,5,*N*H; Val-2,4
4	21.9, CH_2	2.53, m		Ahp-4b,5,*O*H,*N*H; Ile-*N*H
		1.73, m	Ahp-2	Ahp-3,4a,6
5	30.0, CH_2	1.72, m	Ahp-6	Ahp-3,4a,6,*O*H
6	74.3, CH	4.91, brs	Ahp-2	Ahp-4b,5,*O*H; Val-3,4,5
*N*H	-	7.36, d (8.8)	Arg-1; Ahp-3,6	Ahp-3,4a, Thr-3; Arg-2,*N*H
*O*H	-	6.17, d (2.8)		Ahp-4a,5,6; Val-3; Ile-4a,4b,5,6,*N*H
[6]Val 1	170.0, qC	-		
2	56.1, CH	4.31, d (10.8)	Ahp-2,6; Val-1,3,4,5	Val-3,4,5; Ahp-3; *N*MePhe-2,5,5′,6,6′
3	27.8, CH	1.90, m	Val-2,4,5	Val-2,4,5; Ahp-6,*O*H
4	18.4, CH_3	0.46, d (6.4)	Val-2,3,5	Val-2,3,5; Ahp-3,6; *N*MePhe-2,5,5′,6,6′
5	18.4, CH_3	−0.19, d (6.4)	Val-2,3,4	Val-2,3,4; Ahp-6; *N*MePhe-2,5,5′,6,6′,*N*Me
[7]*N*MePhe 1	169.5, qC	-		
2	60.8, CH	5.06, brd (10.2)	*N*MePhe-1,3,*N*Me	*N*MePhe-3a,3b,5,5′,6,6′,*N*Me; Val-2,4,5; Ile-*N*H
3	34.4, CH_2	3.26, m	*N*MePhe-2,4,5,5′	*N*MePhe-2,3b,5,5′,6,6′,*N*Me
		2.80, dd (14.4,10.2)	*N*MePhe-2,4,5,5′	*N*MePhe-2,3a,5,5′,6,6′,*N*Me; Ile-*N*H
4	137.9, qC	-		
5,5′	129.9, CH	7.22, d (7.5)	*N*MePhe-3,7	*N*MePhe-2,3a,3b,6,6′,7,*N*Me; Val-2,4,5
6,6′	128.9, CH	7.27, d (7.5)	*N*MePhe-4	*N*MePhe-2,3a,3b,5,5′,7,*N*Me; Val-2,5
7	127.0, CH	7.19, d (7.5)	*N*MePhe-5,5′	*N*MePhe-5,5′,6,6′
*N*Me	30.4, CH_3	2.73, s	Val-1; *N*MePhe-2	*N*MePhe-2,3a,3b, 5,5′,6,6′; Val-4,5; Ile-4b,5,6,*N*H

Table S7. *Cont.*

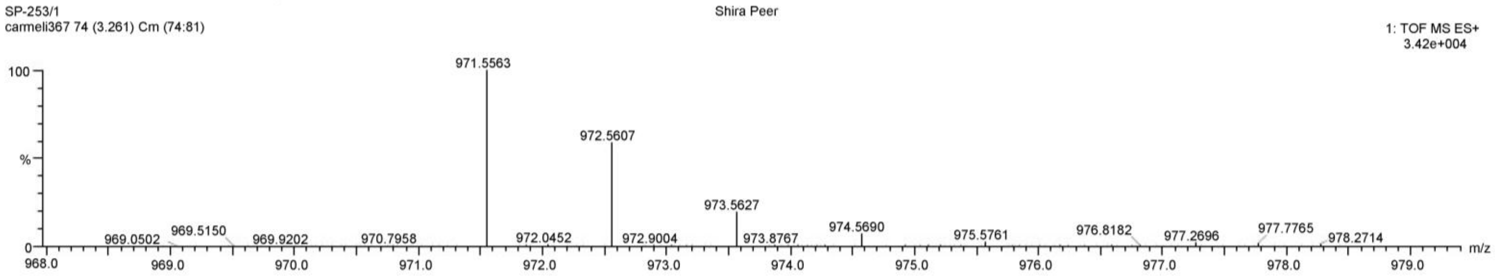
[8]Ile 1	172.9, qC	-		
2	56.0, CH	4.63, dd (9.2,6.0)	Ile-1,3,4,6	Ile-3,4b,5,6,*N*H
3	37.3, CH	1.77, m		Ile-2,4a,5,6,*N*H
4	24.8, CH_2	1.23, m	Ile-5,6	Ile-3,4b,*N*H; Ahp-*O*H; *N*MePhe-5,5′
		1.02, m	Ile-3,5,6	Ile-2,4a,5,6,*N*H; Ahp-*O*H; *N*MePhe-*N*Me
5	11.4, CH_3	0.80, t (7.3)	Ile-3,4	Ile-2,3,4b,*N*H; Ahp-*O*H; *N*MePhe-*N*Me
6	16.2, CH_3	0.84, d (6.4)	Ile-2,3,4	Ile-2,3,4b,*N*H; Ahp-*O*H; *N*MePhe-*N*Me
*N*H	-	7.76, d (9.2)	*N*MePhe-1, Ile-1	Ile-2,3,4a,4b,5,6; Ahp-4a,*O*H; *N*MePhe-2,3b

[a] 100 MHz for carbons and 400 MHz for protons; [b] Multiplicity and assignment from HSQC experiment; [c] Determined from HMBC experiment, $^{n}J_{CH}$ = 8 Hz, recycle time 1 s; [d] Selected NOE's from ROESY experiment.

Elemental Composition Report

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
212 formula(e) evaluated with 4 results within limits (up to 4 best isotopic matches for each mass)
Elements Used:
C: 40-55 H: 65-90 N: 5-15 O: 5-15



Minimum:				-1.5			
Maximum:		5.0	10.0	50.0			

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
971.5563	971.5579	-1.6	-1.6	20.5	182.8	0.5	C48 H71 N14 O8
	971.5566	-0.3	-0.3	15.5	183.2	0.9	C47 H75 N10 O12
	971.5606	-4.3	-4.4	19.5	188.9	6.6	C52 H75 N8 O10
	971.5526	3.7	3.8	11.5	191.8	9.6	C42 H75 N12 O14

Figure S51. HR ESI MS data of Micropeptin KB970A (**7**).

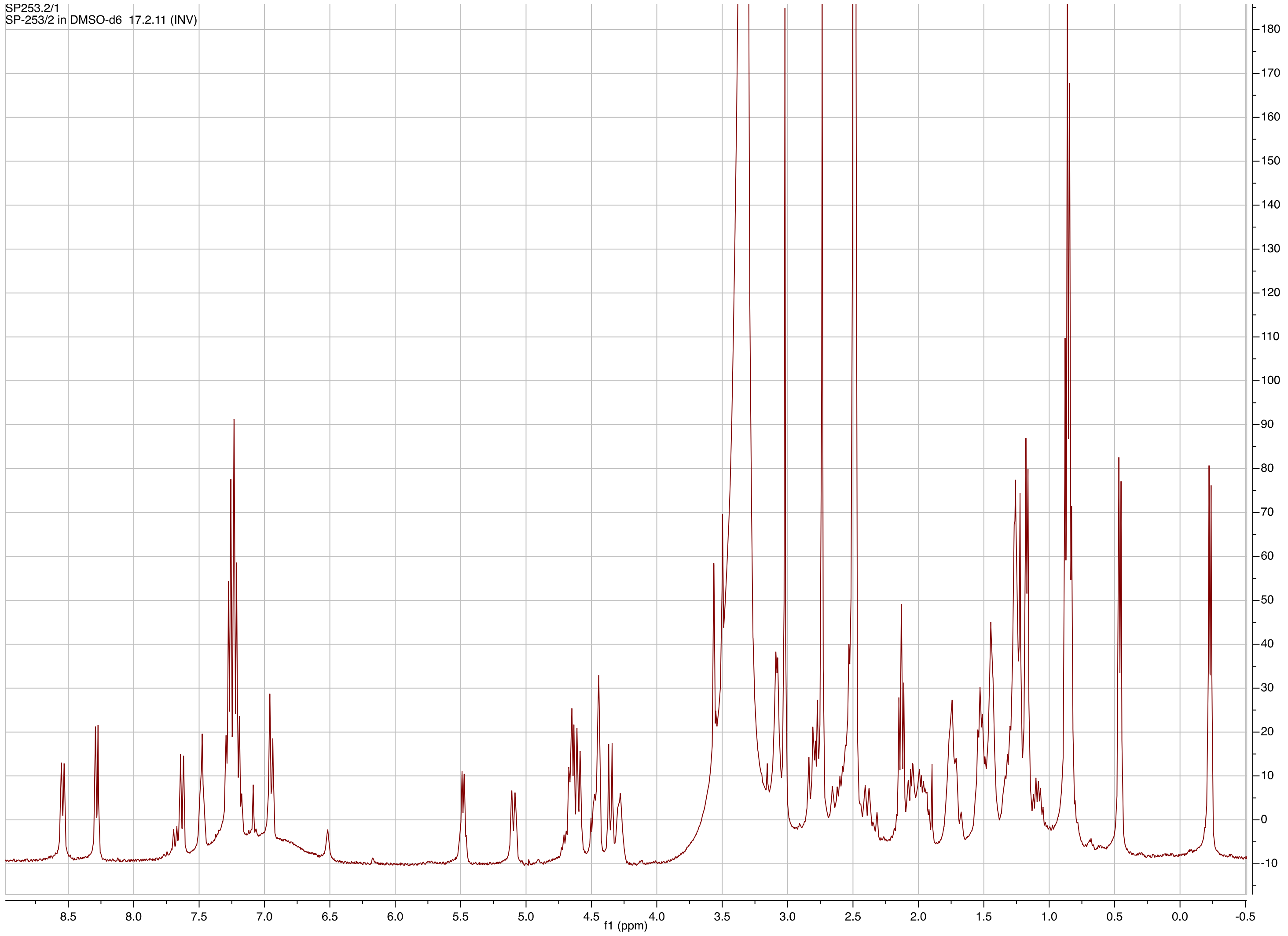


Figure S52. [1]H NMR Spectrum (500 MHz) of Micropeptin KB970B (**8**) in DMSO-d_6.

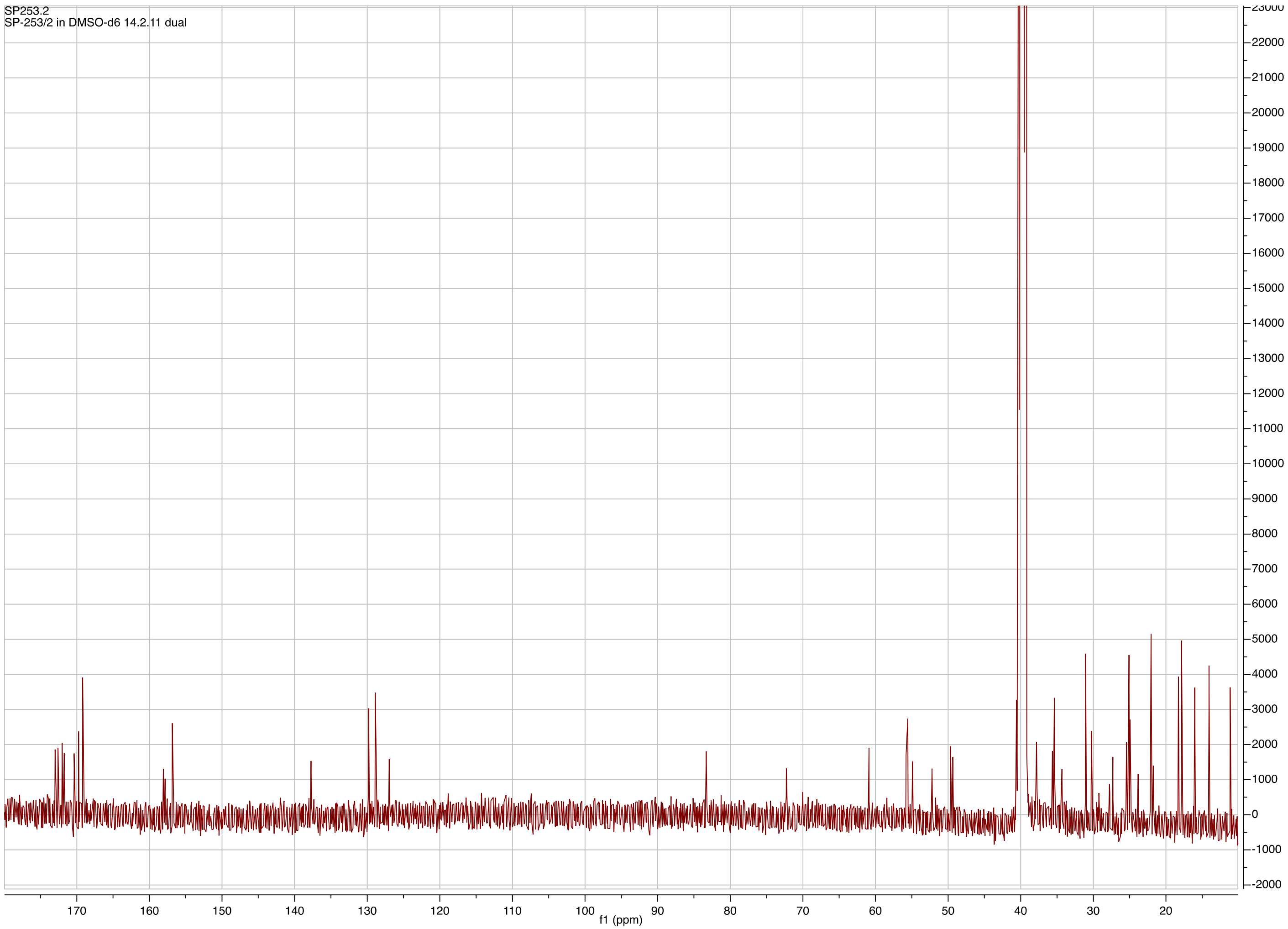


Figure S53. ^{13}C NMR Spectrum (125 MHz) of Micropeptin KB970B (**8**) in DMSO-d_6.

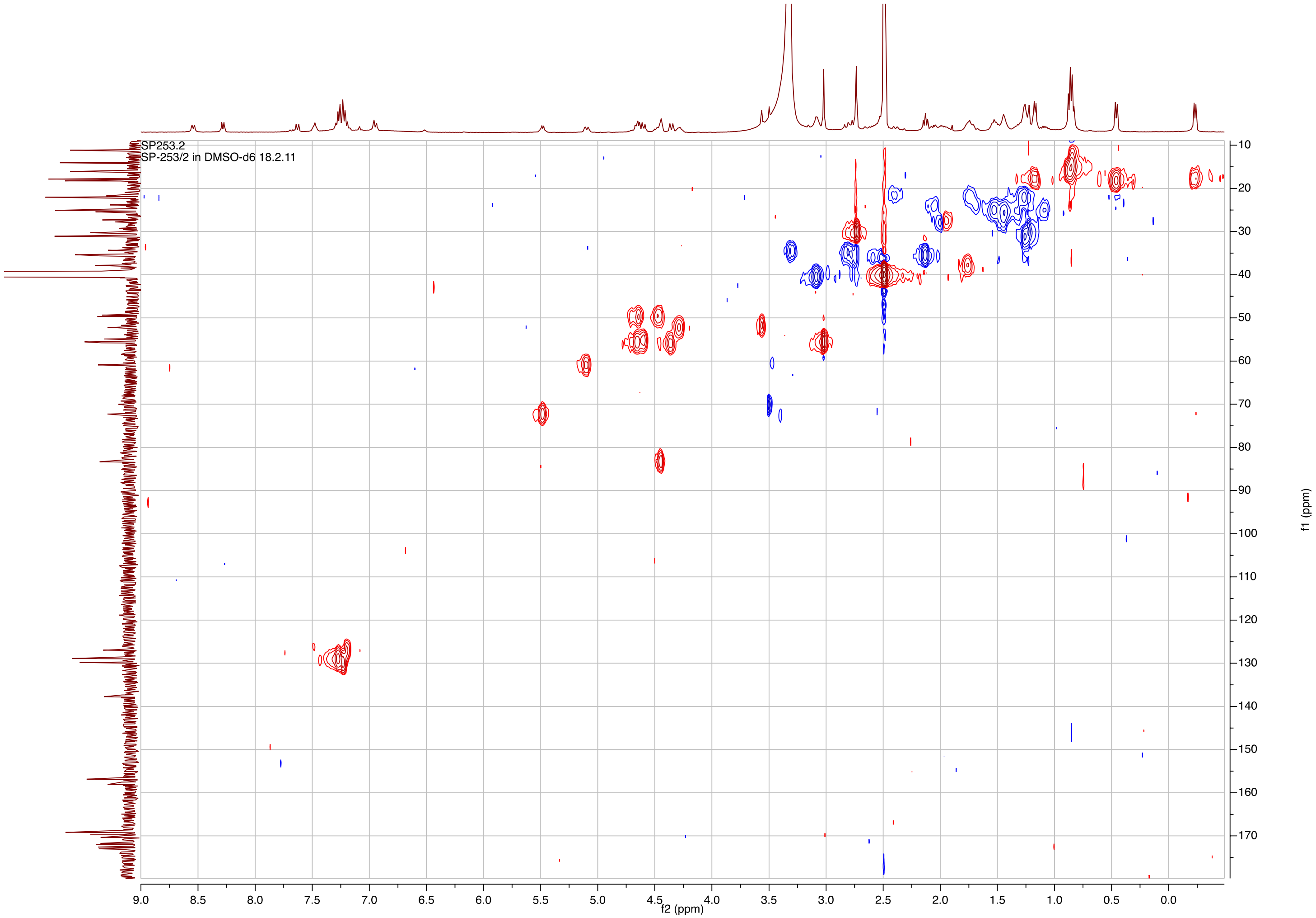


Figure S54. HSQC Spectrum of Micropeptin KB970B (**8**) in DMSO-*d*$_6$ (Red: CH, CH_3; Blue: CH_2).

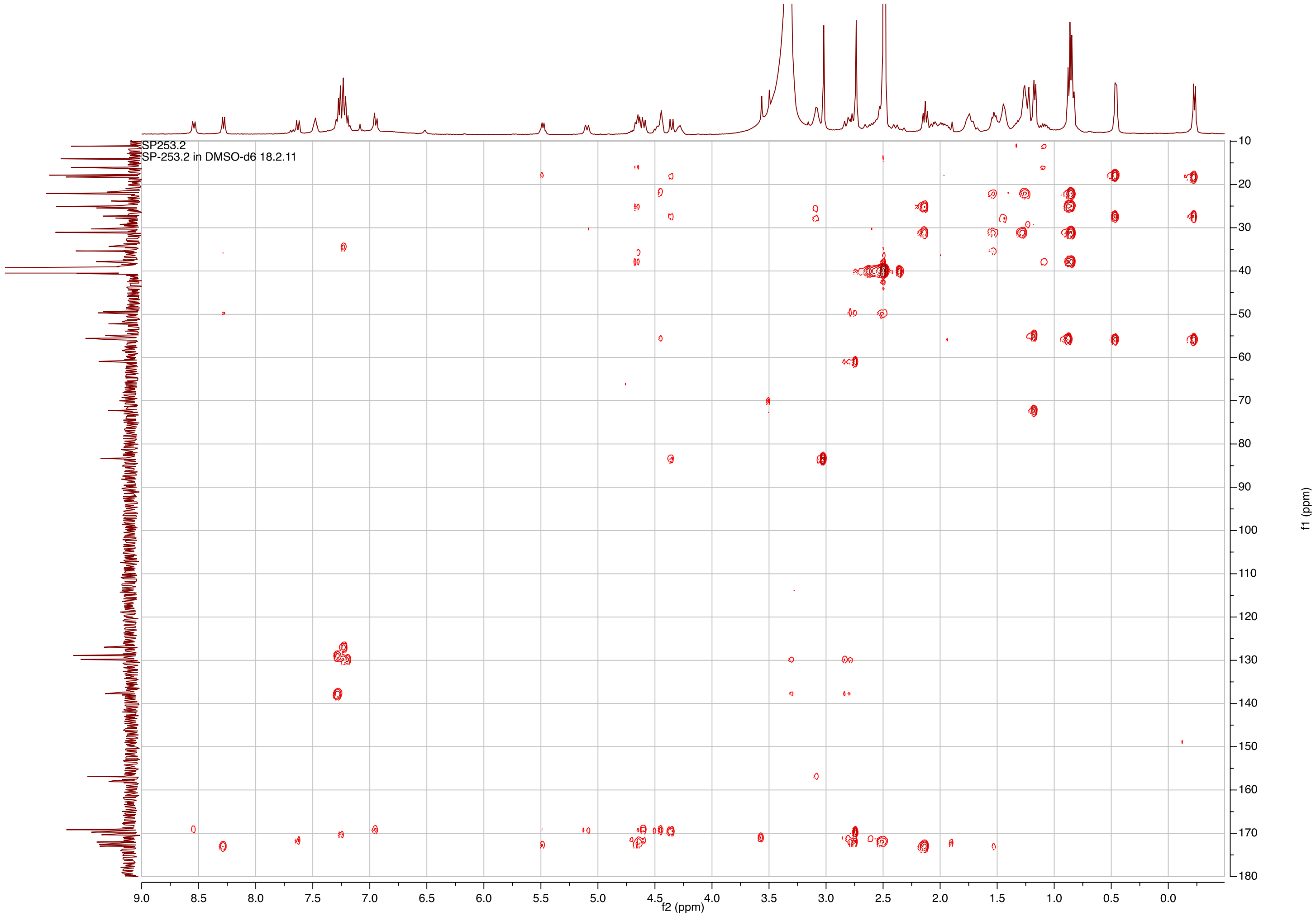


Figure S55. HMBC Spectrum of Micropeptin KB970B (**8**) in DMSO-d_6.

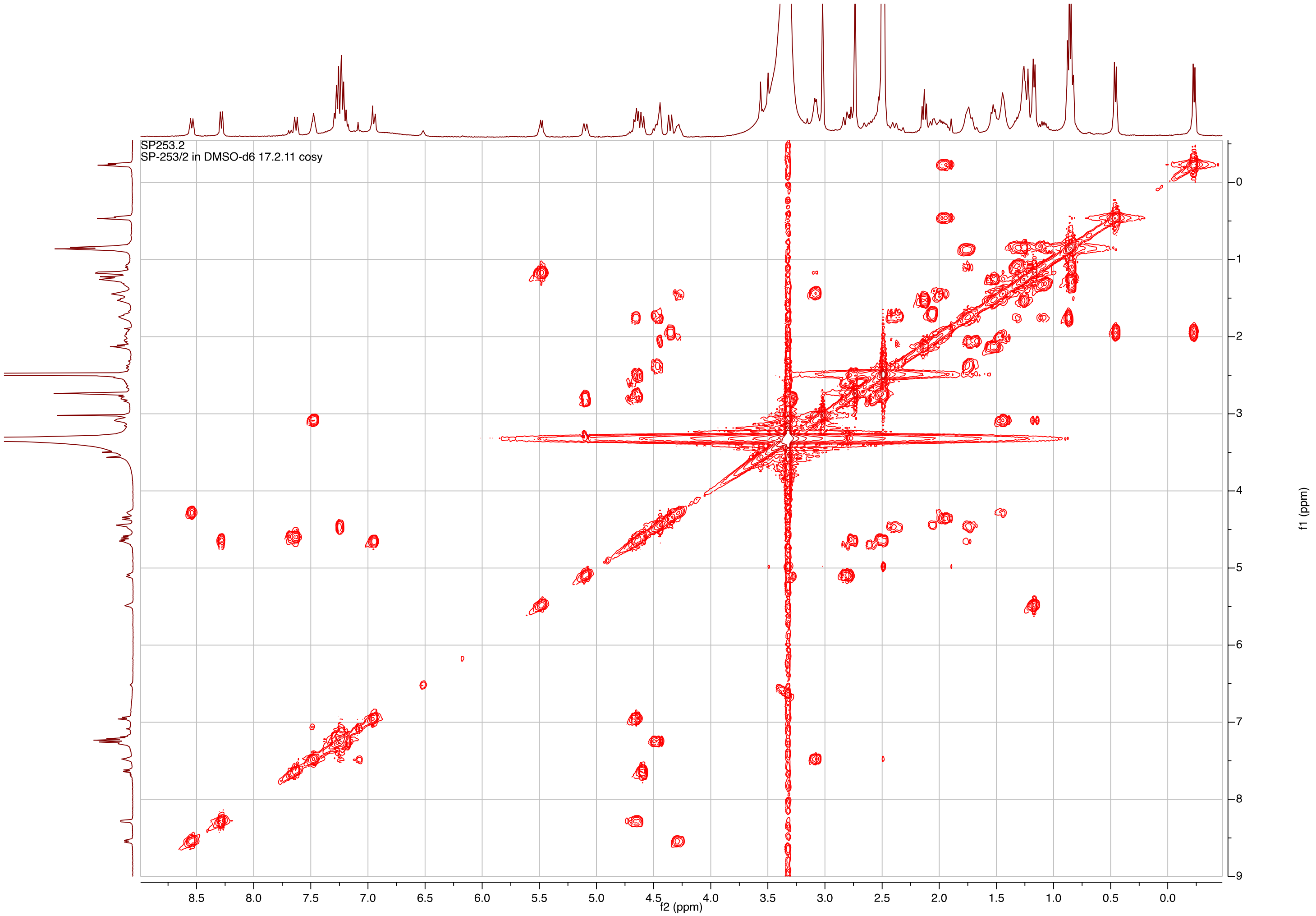


Figure S56. COSY Spectrum of Micropeptin KB970B (**8**) in DMSO-d_6.

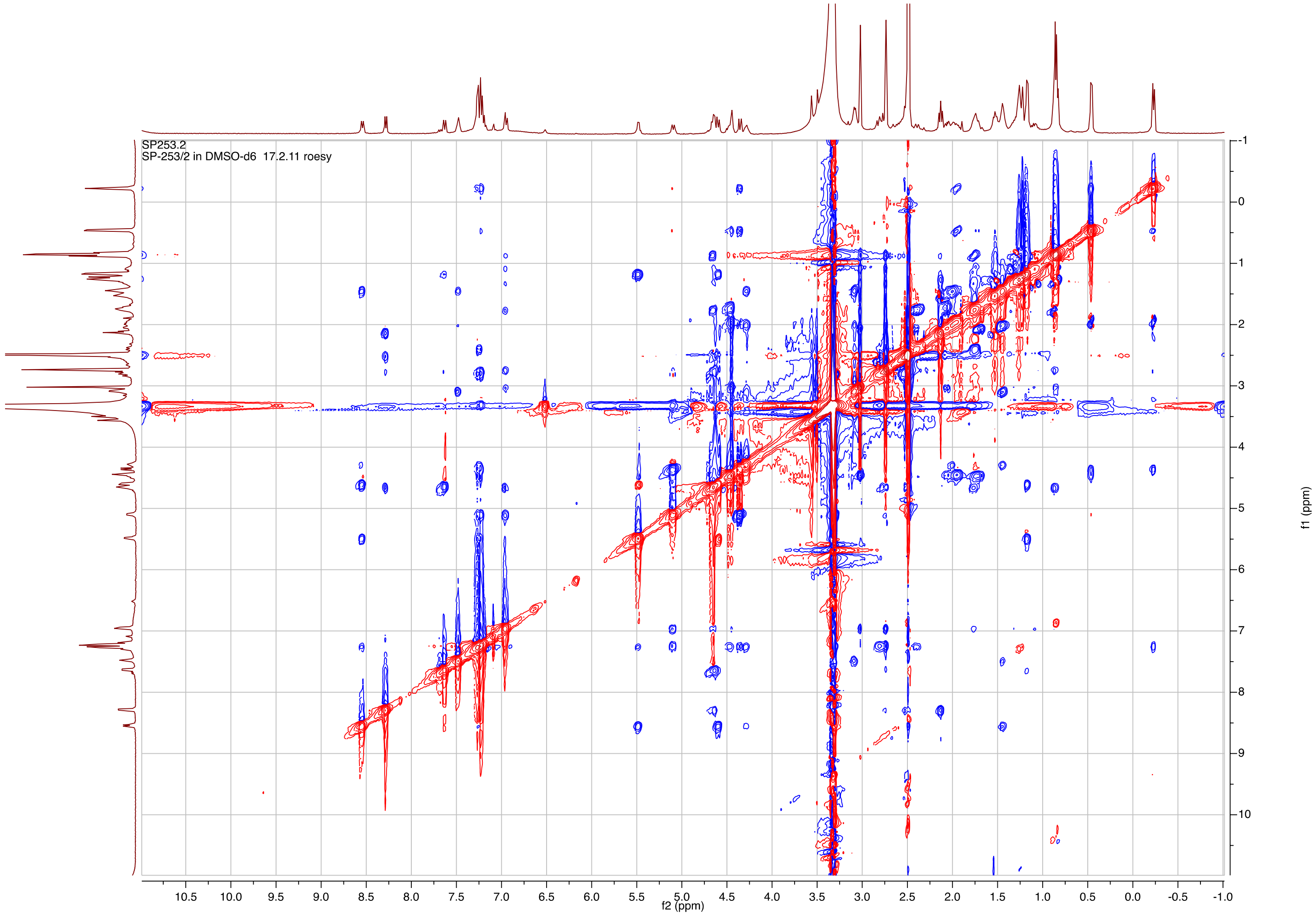


Figure S57. ROESY Spectrum of Micropeptin KB970B (**8**) in DMSO-d_6 (Blue: NOE correlation).

Table S8. NMR Data of Micropeptin KB970B (**8**) in DMSO-d_6.

Position	δ_C mult. [a]	δ_H mult.[b] *J* in Hz	HMBC Correlations [c]	NOE Correlations [d]
[1]Ha 1	173.0, qC	-		
2	35.6, CH_2	2.13, t	Ba-1,3,4	Ba-3,4; Asp-*N*H
3	25.1, CH_2	1.53, qi	Ba-1,2,3	Ba-2,4
4	31.1, CH_2	1.25, m	Ba-2,3	Ba-2,3
5	22.0, CH_2	1.27, m		
6	14.1, CH_3	0.85, t		
[2]Asp 1	171.7, qC	-		
2	49.7, CH	4.63, m	Asp-1,4	Asp-3a,3b,*N*H; Thr-*N*H
3 ab	35.4, CH_2	2.80, m		Asp-2,3b,*N*H
		2.58, m		Asp-2,3a,*N*H
4	172.0, qC	-		
*N*H	-	8.28, d	Ba-1	Asp-2,3a,3b; Ba-2; Thr-*N*H
[3]Thr 1	169.1, qC	-		
2	54.9, CH	4.60, d	Asp-1; Thr-1	Thr-3,4,*N*H; Arg-*N*H
3	72.3, CH	5.48, q	Thr-4; Ile-1	Thr-2,4,*N*H; Arg-*N*H; Ahp-*N*H
4	17.8, CH_3	1.17, d	Thr-2,3	Thr-2,3
*N*H	-	7.63, d		Thr-2,3; Asp-2,3a,*N*H
[4]Arg 1	170.4, qC	-		
2	52.2, CH	4.28, m	Arg-3	Arg-3a,3b,4,5,*N*H; Amp-*N*H
3 ab	27.8, CH_2	2.02, m		Arg-2,3b,4,5
		1.45, m	Arg-4	Arg-2,3a,5,*N*H,5-*N*H
4	25.4, CH_2	1.45, m	Arg-3	Arg-2,3a,5,*N*H,5-*N*H
5	40.2, CH_2	3.09, m	Arg-3,4,6	Arg-2,3a,3b,4,5-*N*H
*N*H	-	8.54, d (8.5)	Thr-1	Arg-2,3b,4; Thr-2,3; Amp-*N*H
5-*N*H	-	7.47, m		Arg-3a,3b,4,5
6	156.9, qC	-		

Table S8. *Cont.*

6-*N*H,*N*H_2		7.30, brm 6.77, brm		
[5]Amp 2	169.2, qC	-		
3	49.4, CH	4.47, m	Amp-2,4	Amp-4b,5b,*N*H; Val-4
4 ab	21.7, CH_2	2.40, brq (13.0) 1.75, m	 Amp-2	Amp-4b,5a,*N*H Amp-3,4a,5b,6
5 ab	23.8, CH_2	2.05, m 1.70, m		Amp-4a,5b,6,*O*Me Amp-3,4b,5a,6
6	83.3, CH	4.44, brs		Amp-5a,5b,*O*Me,*N*H; Val-3,4, Ile-*N*H
*N*H		7.24, m	Arg-1	Amp-3,4a; Thr-3; Arg-2,*N*H
*O*Me	55.6, CH_3	3.02, s	Amp-6	Amp-5a,6; Ile-*N*H
[6]Val 1	169.8, qC	-		
2	55.8, CH	4.35, d (10.5)	Amp-2,6; Val-1,3,5	Val-3,4,5; *N*MePhe-2,5,5′,6,6′
3	27.3, CH	1.95, m	Val-2,5	Val-2,4,5; Amp-6
4	18.3, CH_3	0.46, d (6.5)	Val-2,3,5	Val-2,3,5; Amp-3,6; *N*MePhe-2,5,6′,6,6′
5	17.8, CH_3	−0.23, d (6.0)	Val-2,3,4	Val-2,3,4; *N*MePhe-5,5′,6,6′
[7]*N*MePhe 1	169.2, qC	-		
2	60.9, CH	5.10, brd (11.0)	*N*MePhe-1,*N*Me	*N*MePhe-3a,3b,5,5′,6,6′,*N*Me; Val-2,4; Ile-*N*H
3 ab	34.3, CH_2	3.30, m 2.81, dd (14.2,11.0)	*N*MePhe-2,4,5,*N*Me *N*MePhe-2,4,5,*N*Me	*N*MePhe-3b,5,5′,6,6′,*N*Me *N*MePhe-2,3a,5,5′,6,6′,*N*Me
4	137.8, qC	-		
5,5′	129.8, CH	7.22, m	*N*MePhe-3	*N*MePhe-2,3a,3b,6,6′,7,*N*Me; Val-2,4,5; Ile-*N*H
6,6′	128.9, CH	7.27, m	*N*MePhe-4	*N*MePhe-2,3a,3b,5,5′,7,*N*Me; Val-2,4,5
7	127.0, CH	7.19, m	*N*MePhe-5,5′	*N*MePhe-5,5′,6,6′
*N*Me	30.3, CH_3	2.73, s	Val-1; *N*MePhe-2	*N*MePhe-2,3a,3b,5,5′,6,6′; Ile-2,5,6,*N*H
[8]Ile 1	172.6, qC	-		

Table S8. *Cont.*

2	55.6, CH	4.64, m	Ile-1,3,4,6	Ile-3,4a,4b,5,6,*N*H; *N*MePhe-*N*Me
3	37.8, CH	1.74, m		Ile-2,4a,4b,5,6,*N*H
4	24.9, CH_2	1.30, m	Ile-5,6	Ile-2,3,4b,5,6,*N*H
		1.10, m	Ile-3,5,6	Ile-2,3,4a,*N*H
5	11.2, CH_3	0.85, t	Ile-3,4	Ile-2,3,4b,*N*H; *N*MePhe-*N*Me
6	16.0, CH_3	0.87, d	Ile-2,3,4	Ile-2,3,4a,*N*H; *N*MePhe-*N*Me
*N*H	-	6.95, d	*N*MePhe-1	Ile-2,3,4a,4b,5,6; Amp-6,*O*Me; *N*MePhe-2,5,5′,*N*Me

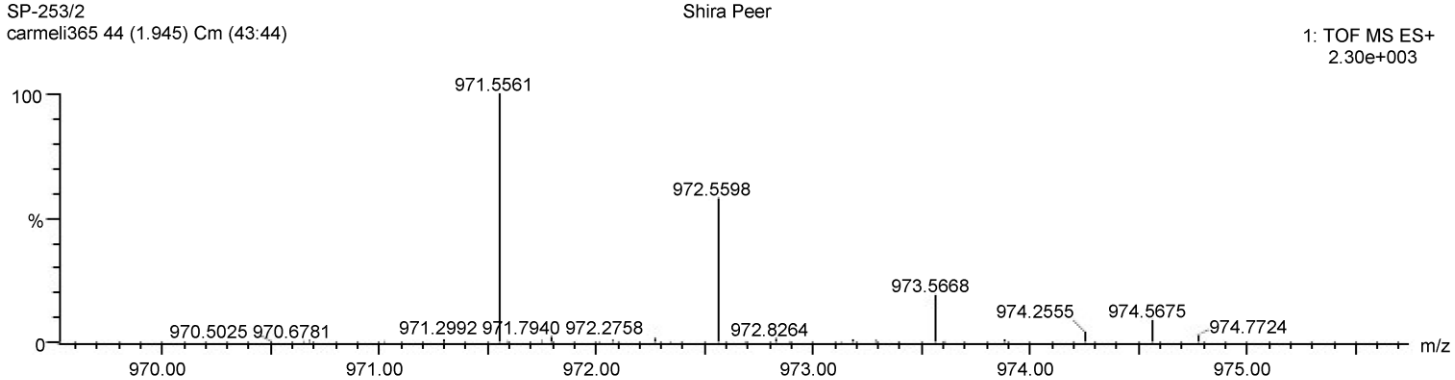
[a] 125 MHz for carbons and 500 MHz for protons; [b] Multiplicity and assignment from HSQC experiment; [c] Determined from HMBC experiment, ${}^{n}J_{CH}$ = 8 Hz, recycle time 1 s; [d] Selected NOE's from ROESY experiment.

Elemental Composition Report

Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
127 formula(e) evaluated with 4 results within limits (up to 4 best isotopic matches for each mass)
Elements Used:
C: 40-55 H: 65-80 N: 5-15 O: 5-15



Minimum:				-1.5			
Maximum:		5.0	10.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
971.5561	971.5566	-0.5	-0.5	15.5	79.6	0.5	C47 H75 N10 O12
	971.5579	-1.8	-1.9	20.5	80.1	1.0	C48 H71 N14 O8
	971.5606	-4.5	-4.6	19.5	82.9	3.8	C52 H75 N8 O10
	971.5526	3.5	3.6	11.5	84.2	5.1	C42 H75 N12 O14

Figure S58. HR ESI MS data of Micropeptin KB970B (**8**).

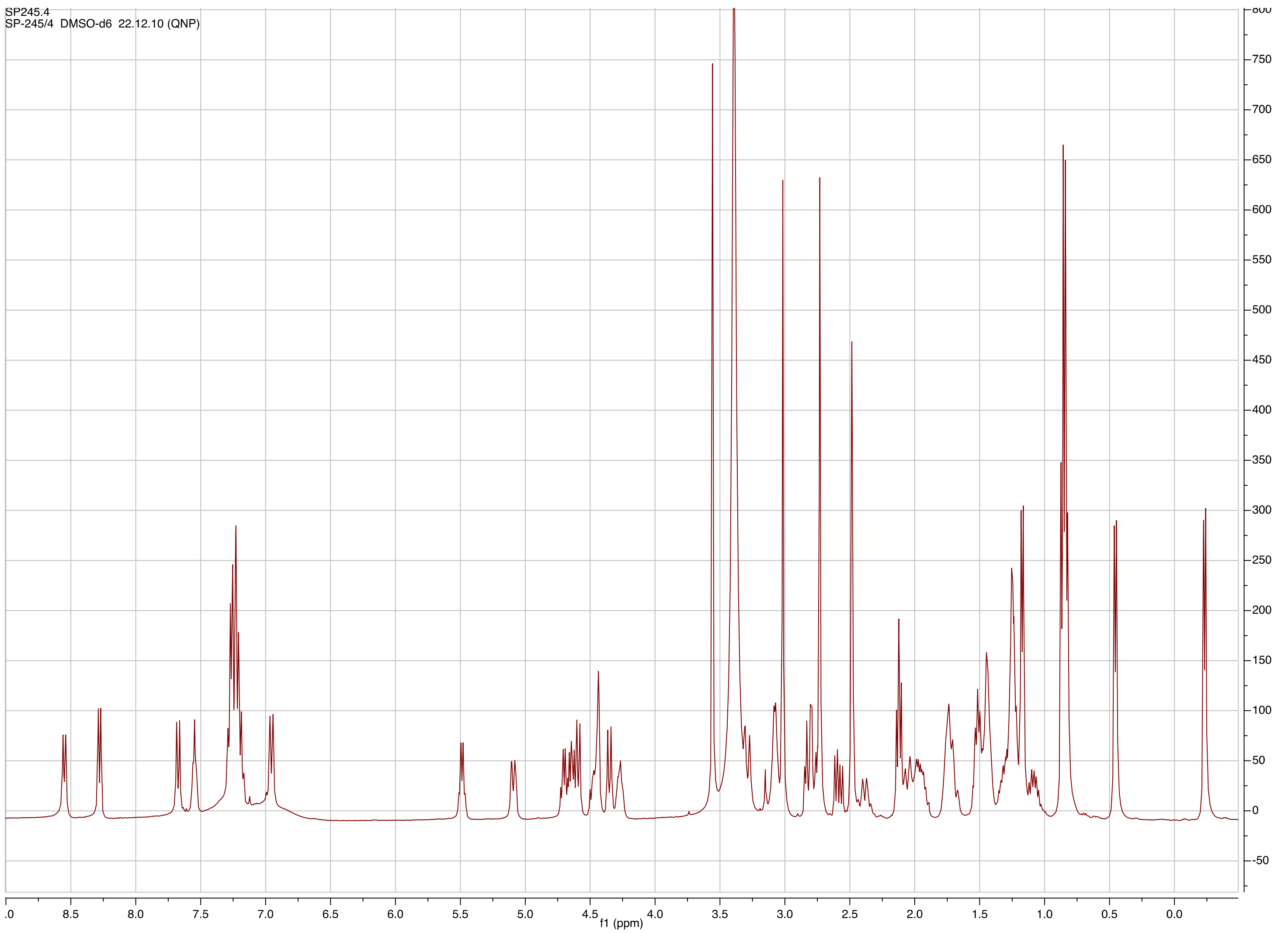


Figure S59. ^{1}H NMR Spectrum (400 MHz) of Micropeptin KB984 (**9**) in DMSO-d_6.

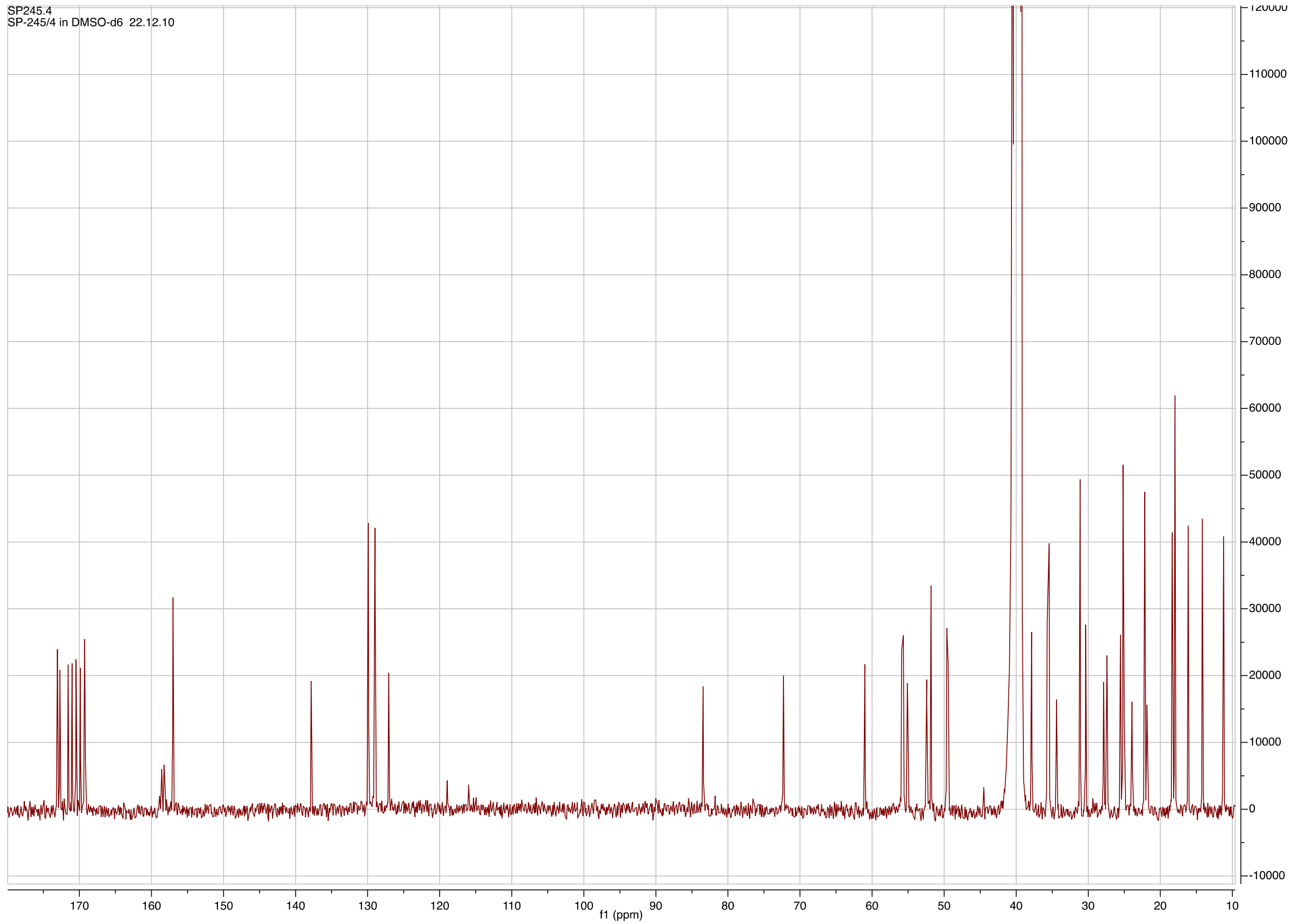


Figure S60. ^{13}C NMR Spectrum (100 MHz) of Micropeptin KB984 (**9**) in DMSO-d_6.

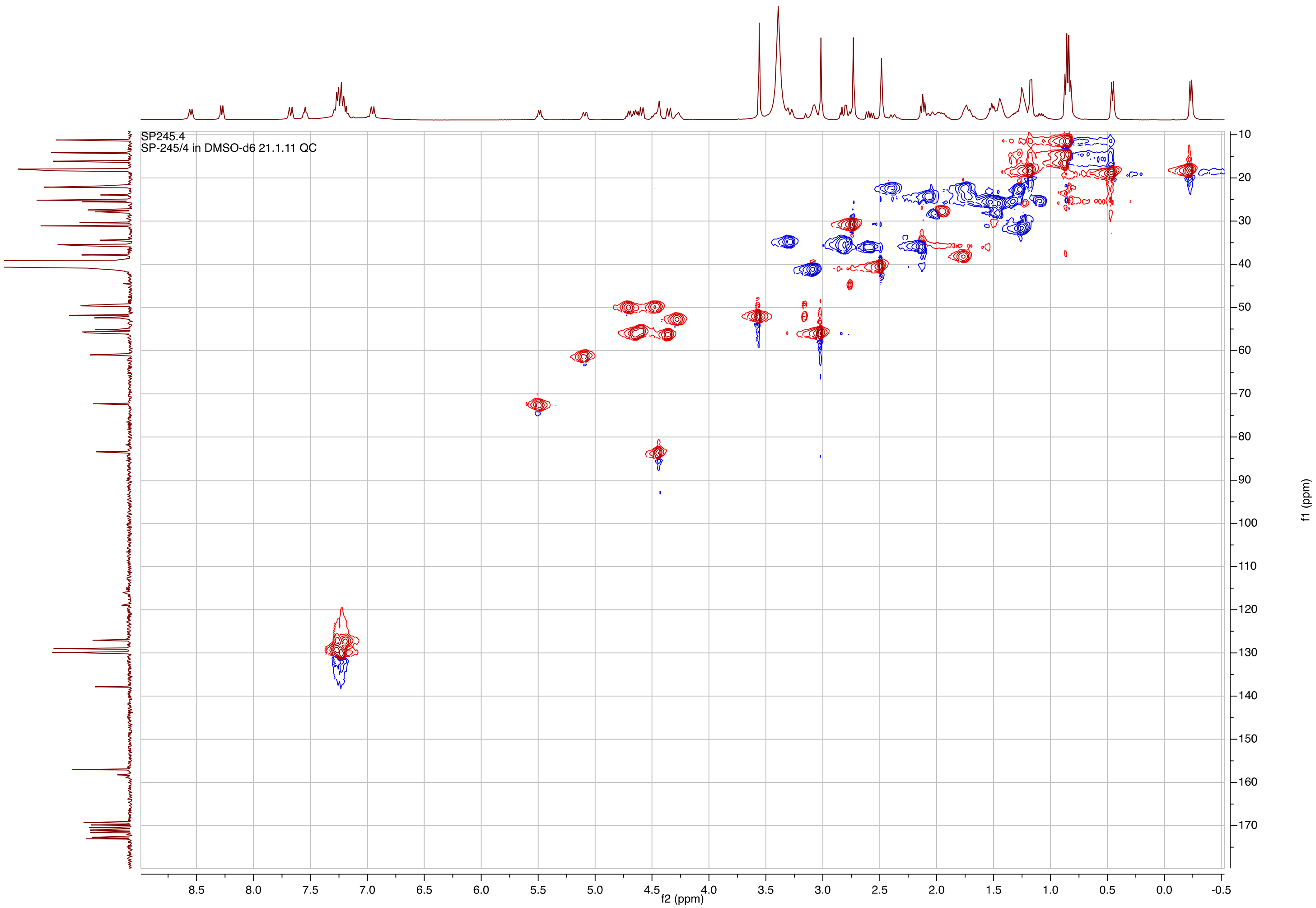


Figure S61. HSQC Spectrum of Micropeptin KB984 (**9**) in DMSO-d_6 (Red: CH, CH_3; Blue: CH_2).

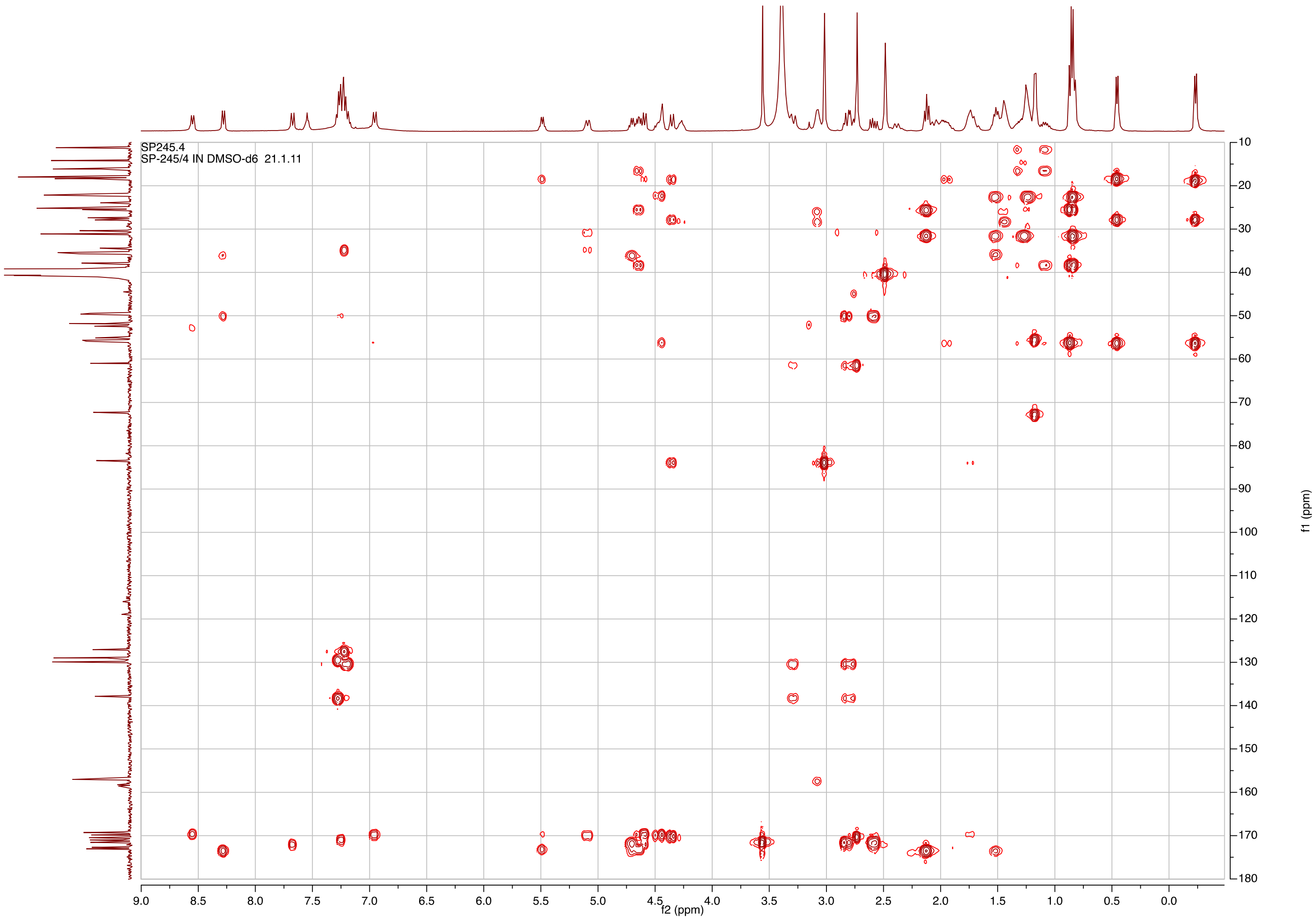


Figure S62. HMBC Spectrum of Micropeptin KB984 (**9**) in DMSO-d_6.

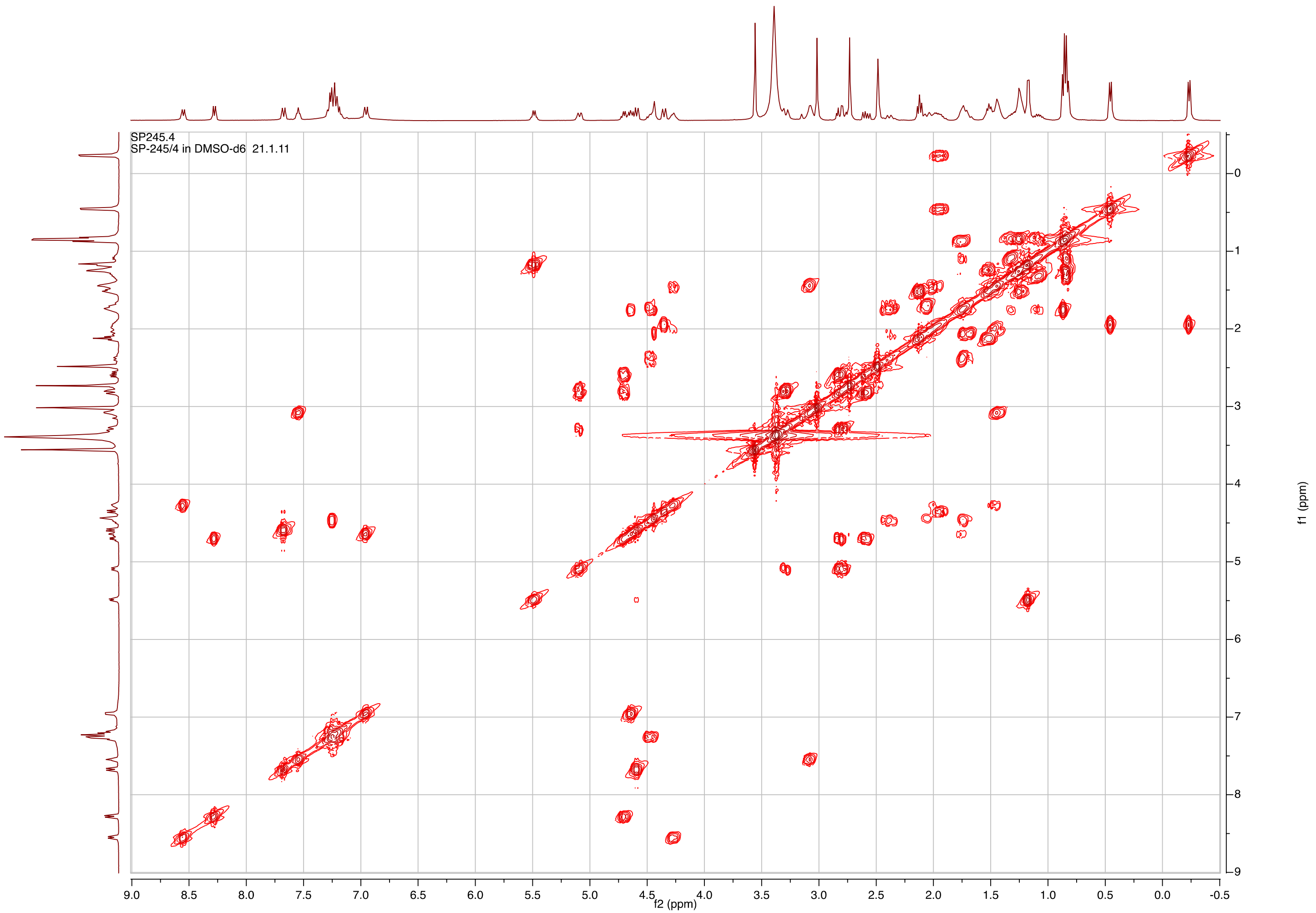


Figure S63. COSY Spectrum of Micropeptin KB984 (**9**) in DMSO-d_6.

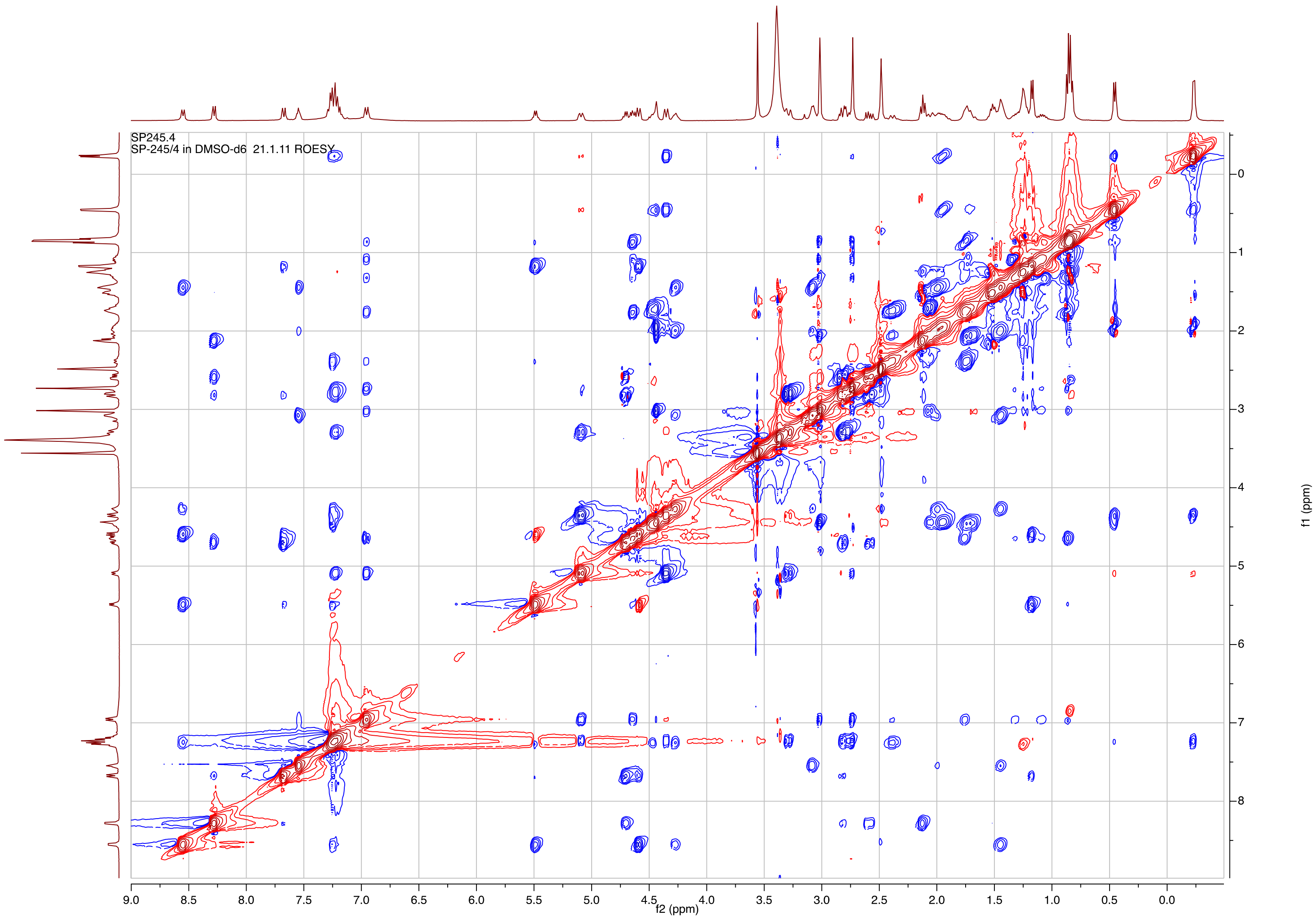


Figure S64. ROESY Spectrum of Micropeptin KB984 (**9**) in DMSO-d_6 (Blue: NOE correlation).

Table S9. NMR Data of Micropeptin KB984 (**9**) in DMSO-d_6.

Position	δ_C mult. [b]	δ_H mult.[b] *J* in Hz	HMBC Correlations [c]	NOE Correlations [d]
[1]Ha 1	173.1, qC	-		
2	35.7, CH_2	2.13, t (7.2)	Ha-1,3,4	Ha-3,4; Asp-*N*H
3	25.2, CH_2	1.51, qi (7.2)	Ha-1,2,4	Ha-2,4,5
4	31.1, CH_2	1.23, m	Ha-2,3	Ha-3,5,6
5	22.1, CH_2	1.27, m	Ha-4,6	Ha-3,4,6
6	14.2, CH_3	0.84, t (7.2)	Ha-4	Ha-4,5
[2]Asp 1	171.6, qC	-		
2	49.6, CH	4.71, dt (8.0,7.6)	Ha-1; Asp-1,4	Asp-3a,3b,*N*H; Thr-*N*H
3 ab	35.4, CH_2	2.81, m	Asp-2,4	Asp-2,3b,*N*H; Thr-*N*H
		2.58, dd (16.4,8.0)	Asp-2,4	Asp-2,3a,*N*H
4	171.0, qC	-		
*N*H	-	8.28, d (7.6)	Ha-1; Asp-2	Asp-2,3a,3b; Ha-2; Thr-*N*H
*O*Me	51.8, CH_3	3.56, s	Asp-4	
[3]Thr 1	169.2, qC	-		
2	55.1, CH	4.60, d (9.2)	Asp-1; Thr-1,3,4	Thr-3,4,*N*H; Arg-*N*H
3	72.3, CH	5.49, q (6.4)	Thr-4; Ile-1	Thr-2,4,*N*H; Arg-*N*H; Amp-*N*H
4	18.0, CH_3	1.18, d (6.4)	Thr-2,3	Thr-2,3,*N*H
*N*H	-	7.68, d (9.2)	Asp-1; Thr-2	Thr-2,3,4; Asp-2,3a,*N*H
[4]Arg 1	170.5, qC	-		
2	52.4, CH	4.27, m	Arg-1,3	Arg-3a,3b,4,5,*N*H; Amp-*N*H
3 ab	27.9, CH_2	2.02, m		Arg-2,3b,4,5,5-*N*H
		1.45, m	Arg-4,5	Arg-2,3a,5,NH,5-*N*H
4	25.5, CH_2	1.45, m	Arg-3,5	Arg-2,3a,5,NH,5-*N*H
5	40.7, CH_2	3.09, m	Arg-3,4,6	Arg-2,3a,3b,4,5-*N*H
*N*H	-	8.56, d (8.4)	Thr-1; Arg-2,3	Arg-3a,3b,4,5; Thr-2,3; Amp-*N*H
5-*N*H	-	7.56, t (5.2)	Arg-4,5,6	Arg-3a,3b,4,5

Table S9. *Cont.*

6	157.0, qC	-		
6-*N*H,*N*H2		7.30, brm		
		6.85, brm		
[5]Amp 2	169.3, qC	-		
3	49.4, CH	4.47, m	Amp-2,4	Amp-4b,5b,*N*H; Val-4
4 ab	21.9, CH_2	2.40, brq (13.2)		Amp-4b,5a,*N*H; Ile-*N*H
		1.70, m	Amp-2	Amp-3,4a
5 ab	23.9, CH_2	2.05, m		Amp-4a,5b,6,*O*Me
		1.75, m	Amp-6	Amp-3,4b,5a,6,*O*Me; *N*MePhe-*N*Me
6	83.4, CH	4.44, brs	Amp-2,4,*O*Me	Amp-5a,5b,*O*Me,*N*H; Val-3,4
*N*H		7.25, m	Arg-1	Amp-3,4a, Thr-3; Arg-2,*N*H
*O*Me	55.6, CH_3	3.02, s	Amp-6	Amp-5a,6; Ile-4a,4b,5,6,*N*H
[6]Val 1	169.9, qC	-		
2	55.9, CH	4.36, d (10.4)	Amp-2,6; Val-1,3,4,5	Val-3,4,5; *N*MePhe-2,3a,5,5′,6,6′
3	27.4, CH	1.95, m	Val-2,4,5	Val-2,4,5; Amp-6
4	18.4, CH_3	0.46, d (6.4)	Val-2,3,5	Val-2,3,5; Amp-3,6; *N*MePhe-2
5	18.0, CH_3	−0.23, d (6.4)	Val-2,3,4	Val-2,3,4; *N*MePhe-2,5,5′,6,6′,*N*Me
[7]*N*MePhe 1	169.3, qC	-		
2	61.0, CH	5.10, brd (11.0)	Val-1; *N*MePhe-1,3,*N*Me	*N*MePhe-3a,3b,5,5′,6,6′,*N*Me; Val-2,4; Ile-*N*H
3 ab	34.4, CH_2	3.29, m	*N*MePhe-2,4,5,*N*Me	*N*MePhe-2,3b,5,5,6,*N*Me; Val-2
		2.80, m	*N*MePhe-2,4,5,*N*Me	*N*MePhe-2,3a,5,6,*N*Me; Ile-*N*H
4	137.8, qC	-		
5,5′	129.9, CH	7.22, m	*N*MePhe-3,7	*N*MePhe-2,3a,3b,6,6′,*N*Me; Val-2,5
6,6′	129.0, CH	7.27, m	*N*MePhe-4	*N*MePhe-2,3a,3b,5,5′,7,*N*Me; Val-2,5
7	127.0, CH	7.19, m	*N*MePhe-5,5′	*N*MePhe-6,6′
*N*Me	30.4, CH_3	2.73, s	Val-1; *N*MePhe-2	*N*MePhe-2,3a,3b,5,5′,6,6′; Val-5; Ile-4a,4b,5,6,*N*H

Table S9. *Cont.*

[8]Ile 1	172.7, qC	-		
2	55.8, CH	4.65, dd (9.6,6.0)	Ile-1,3,4,6	Ile-3,5,6,*N*H
3	37.8, CH	1.74, m	Ile-5,6	Ile-2,4a,5,6,*N*H
4 ab	25.0, CH_2	1.30, m	Ile-3,5,6	Ile-2,3,4b,5,6,*N*H; Amp-*O*Me; *N*MePhe-*N*Me
		1.10, m	Ile-5,6	Ile-2,3,4a,*N*H; Amp-*O*Me; *N*MePhe-*N*Me
5	11.2, CH_3	0.84, t (7.2)	Ile-3,4	Ile-2,3,4b,*N*H; Amp-*O*Me; *N*MePhe-*N*Me
6	16.1, CH_3	0.87, d (6.8)	Ile-2,3,4	Ile-2,3,4a,*N*H; Amp-*O*Me; *N*MePhe-*N*Me
*N*H	-	6.96, d (9.6)	*N*MePhe-1; Ile-1,2	Ile-2,3,4a,4b,5,6; Amp-4a,*O*Me; *N*MePhe-2,3b

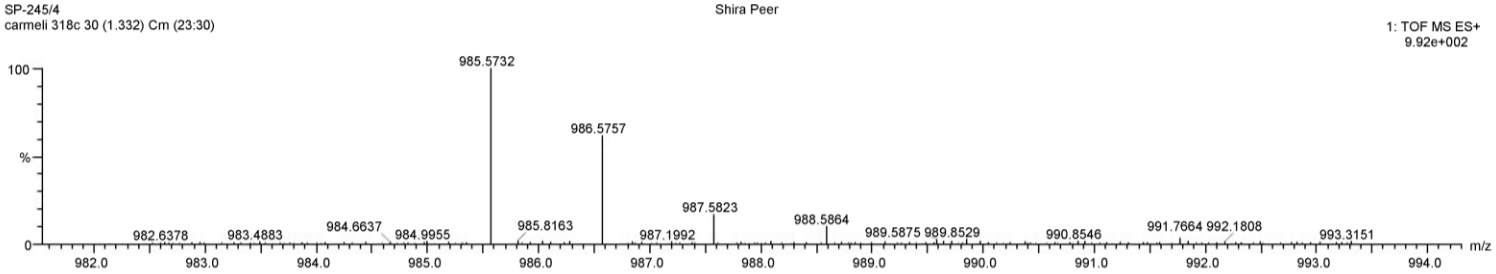
[a] 100 MHz for carbons and 400 MHz for protons; [b] Multiplicity and assignment from HSQC experiment; [c] Determined from HMBC experiment, $^{n}J_{CH}$ = 8 Hz, recycle time 1 s; [d] Selected NOE's from ROESY experiment.

Elemental Composition Report

Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
65 formula(e) evaluated with 4 results within limits (up to 4 best isotopic matches for each mass)
Elements Used:
C: 45-55 H: 70-80 N: 5-15 O: 5-15



Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
Minimum:				-1.5			
Maximum:		5.0	10.0	50.0			
985.5732	985.5736	-0.4	-0.4	20.5	115.7	0.7	C49 H73 N14 O8
	985.5722	1.0	1.0	15.5	115.7	0.8	C48 H77 N10 O12
	985.5763	-3.1	-3.1	19.5	117.8	2.9	C53 H77 N8 O10
	985.5776	-4.4	-4.5	24.5	119.1	4.1	C54 H73 N12 O6

Figure S65. HR ESI MS data of Micropeptin KB984 (**9**).

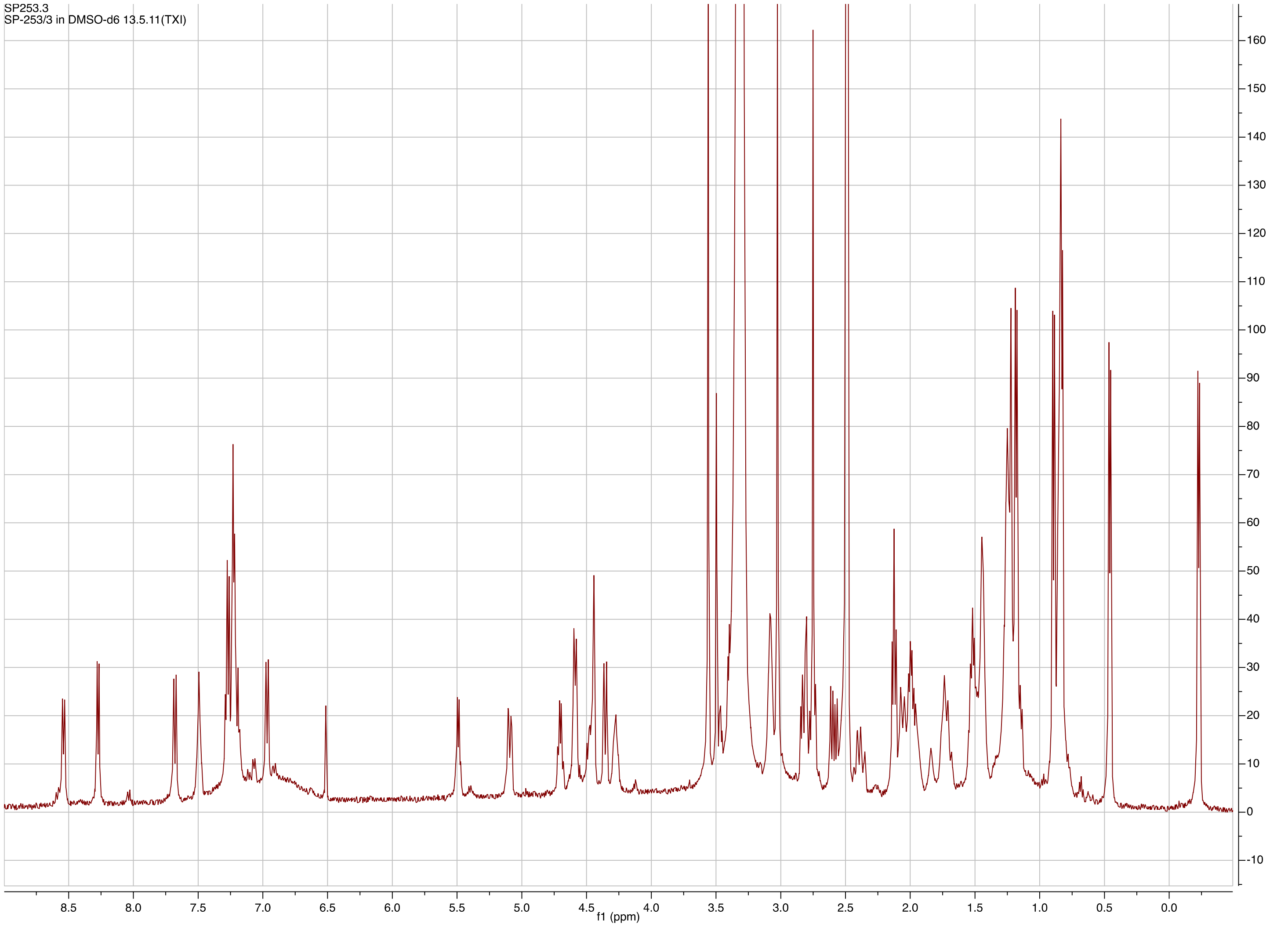


Figure S66. ^{1}H NMR Spectrum (500 MHz) of Micropeptin KB970C (**10**) in DMSO-d_6.

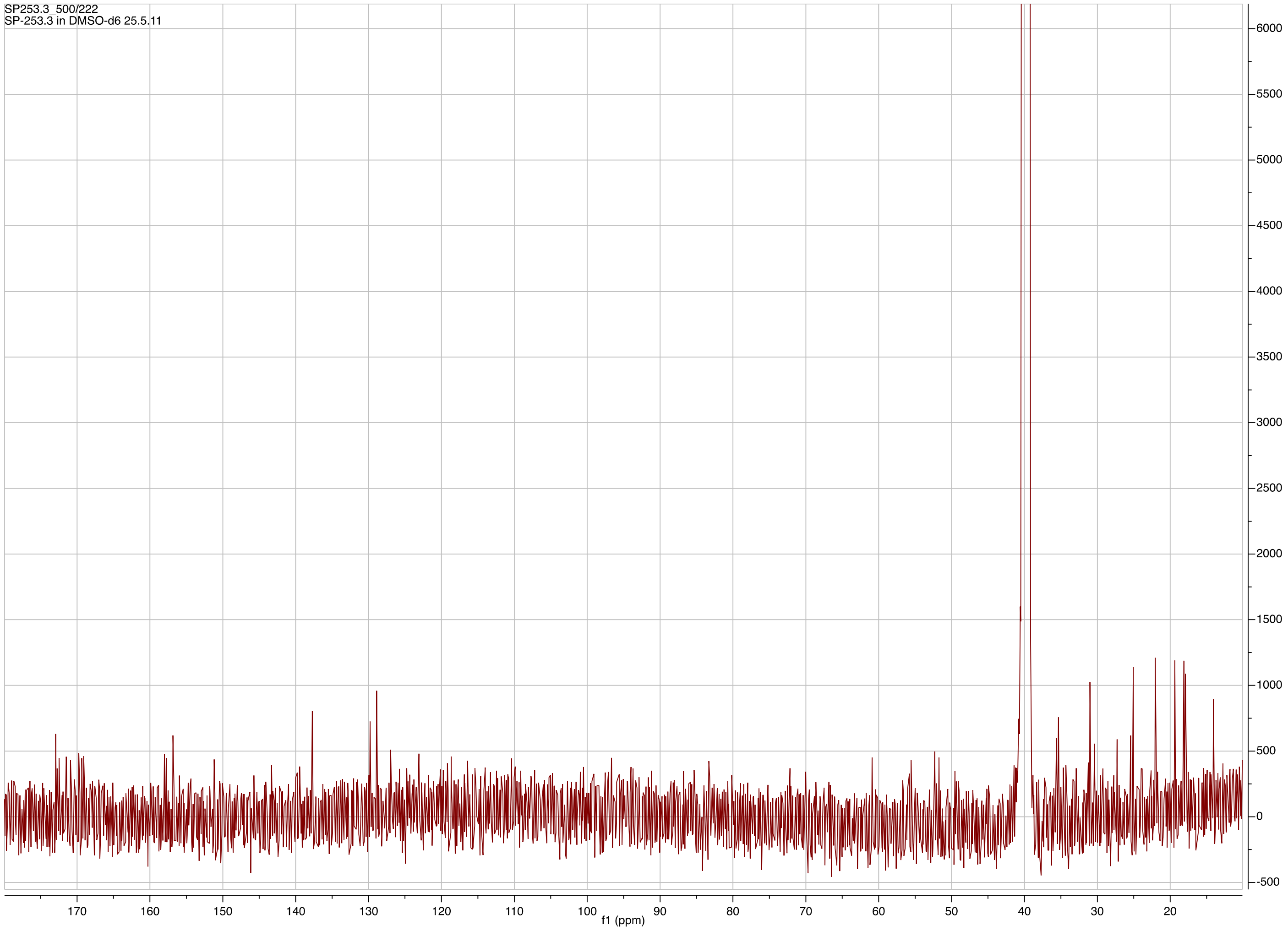


Figure S67. ^{13}C NMR Spectrum (125 MHz) of Micropeptin KB970C (**10**) in DMSO-d_6.

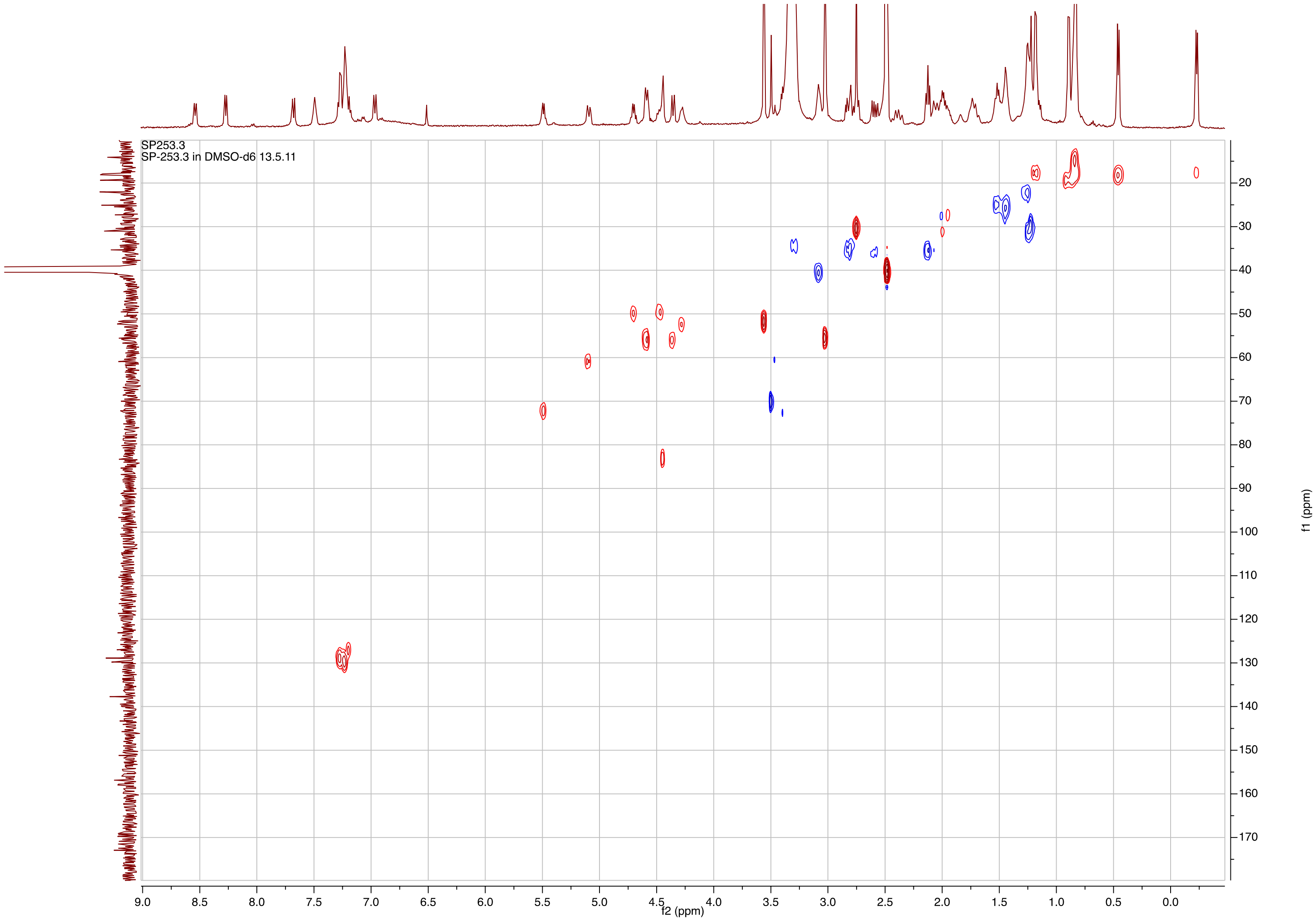


Figure S68. HSQC Spectrum of Micropeptin KB970C (**10**) in DMSO-d_6 (Red: CH, CH_3; Blue: CH_2).

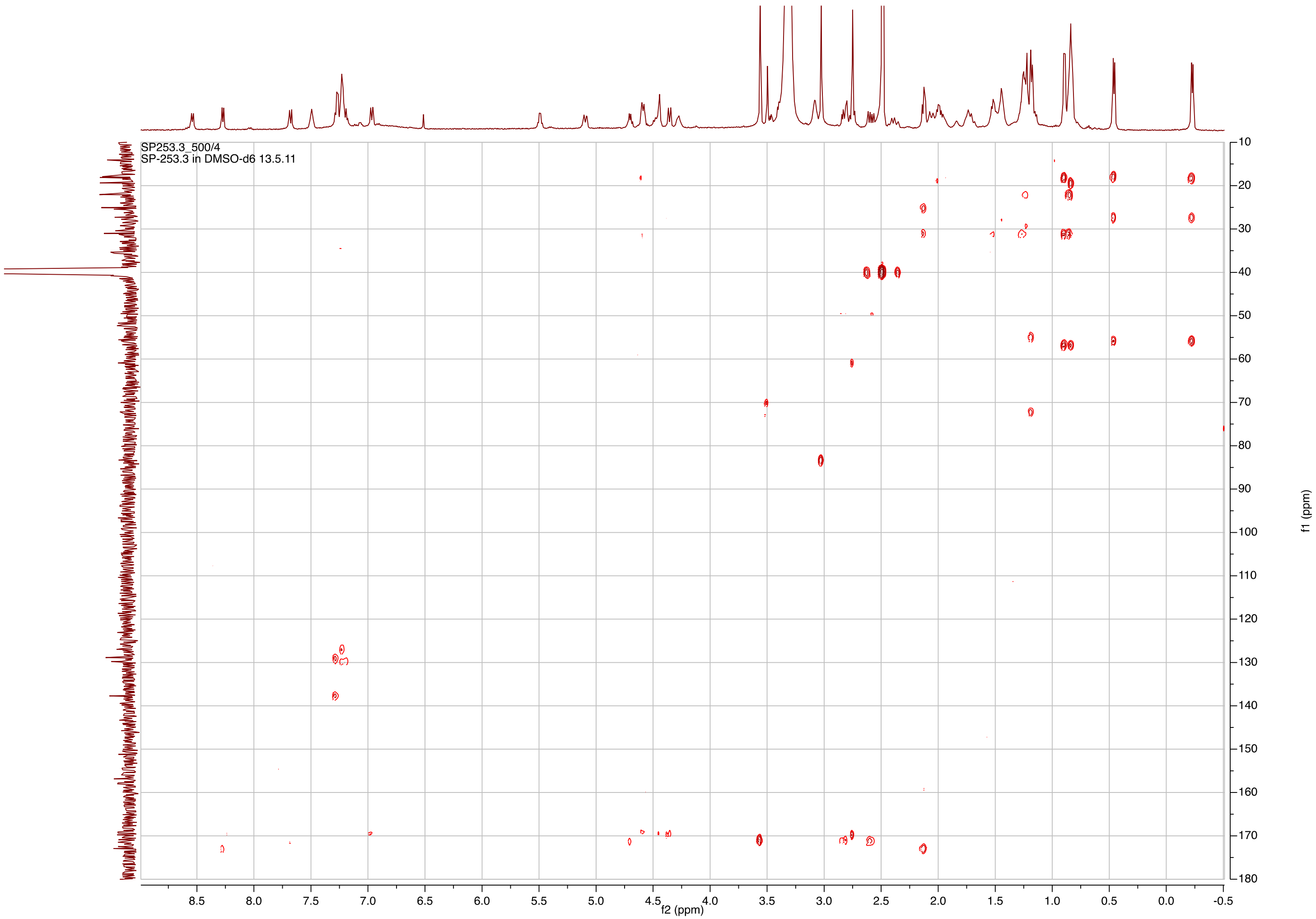


Figure S69. HMBC Spectrum of Micropeptin KB970C (**10**) in DMSO-d_6.

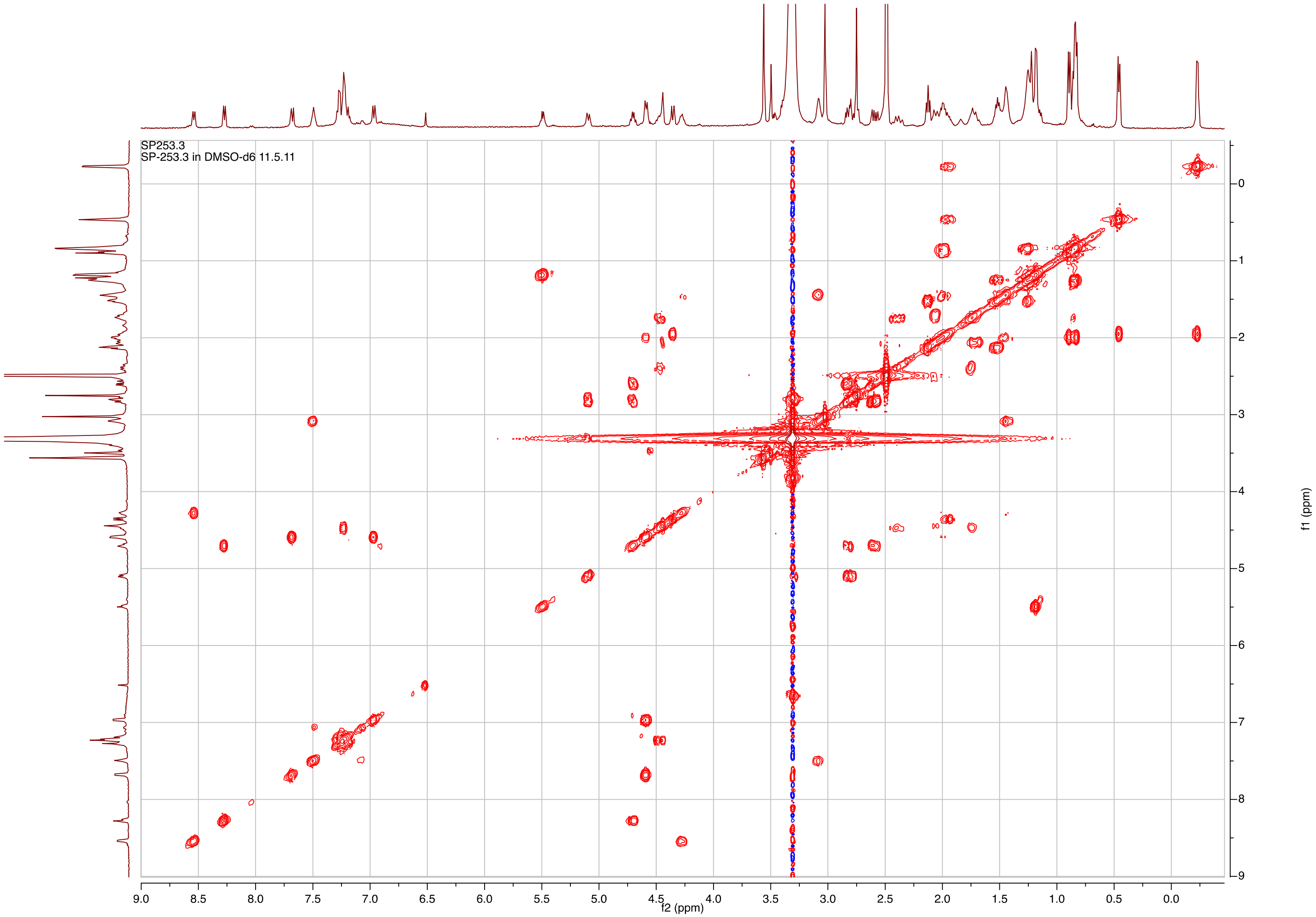


Figure S70. COSY Spectrum of Micropeptin KB970C (**10**) in DMSO-d_6.

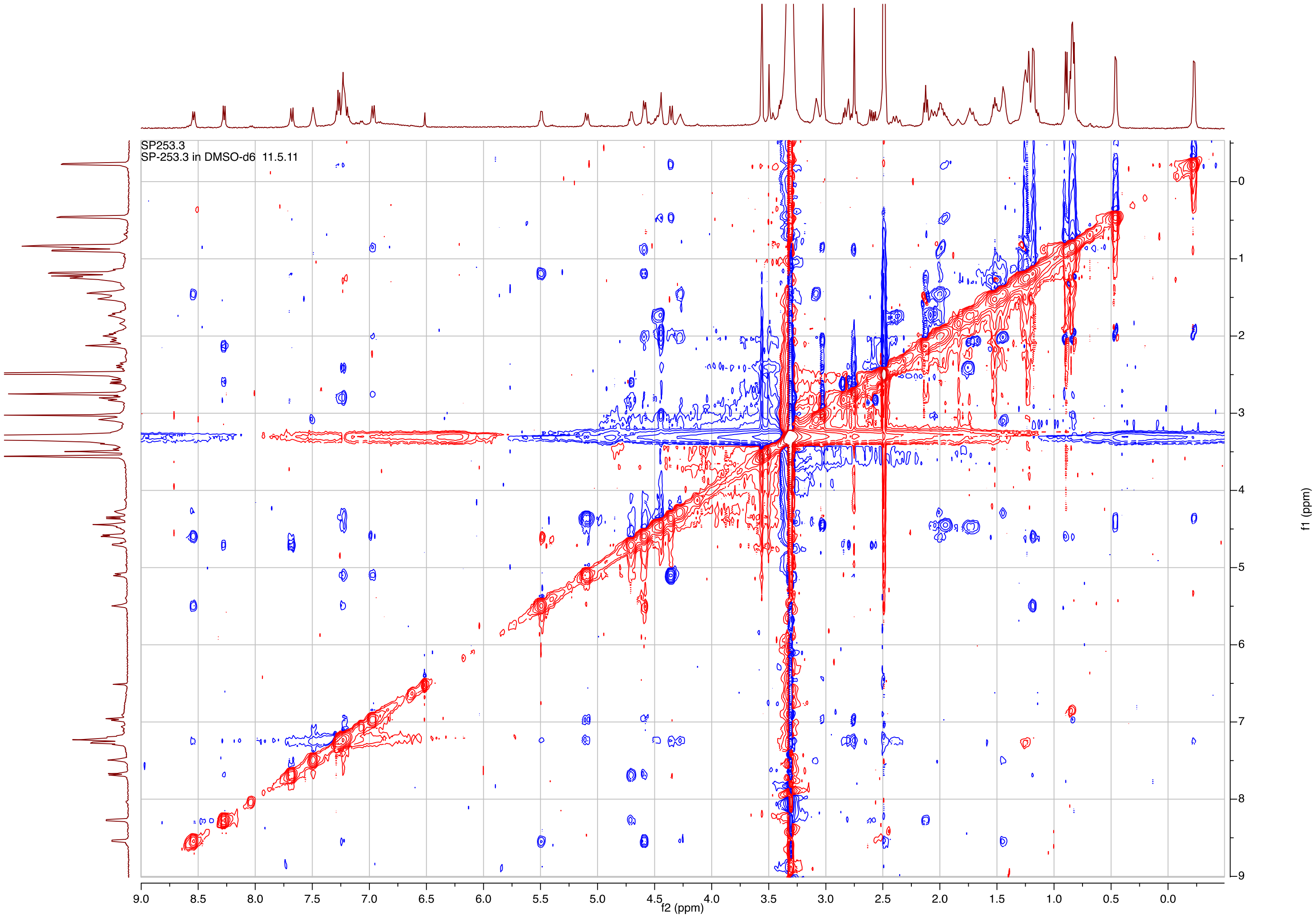


Figure S71. ROESY Spectrum of Micropeptin KB970C (**10**) in DMSO-d_6 (Blue: NOE correlation).

Table S10. NMR Data of Micropeptin KB970C (**10**) in DMSO-d_6.

Position	δ_C mult. [b]	δ_H mult.[b] *J* in Hz	HMBC Correlations [c]	NOE Correlations [d]
[1]Ha 1	172.9, qC	-		
2	35.6, CH_2	2.13, t (7.5)	Ha-1,3,4	Ha-3,4; Asp-*N*H
3	25.1, CH_2	1.52, qi (7.5)	Ha-1,2,4	Ha-2,4,5; Asp-*N*H
4	31.0, CH_2	1.25, m	Ha-2,3,5	Ha-3,5,6
5	22.1, CH_2	1.27, m	Ha-4	Ha-3,4,6
6	14.1, CH_3	0.84, t (7.2)	Ha-4,5	Ha-4,5
[2]Asp 1	171.5, qC	-		
2	49.5, CH	4.70, ddd (8.0,7.5,6.0)	Asp-1,3,4	Asp-3a,3b,*N*H; Thr-*N*H
3 ab	35.3, CH_2	2.80, m	Asp-2,4	Asp-2,3b,*N*H; Thr-*N*H
		2.58, dd (16.4,8.0)	Asp-2,4	Asp-2,3a,*N*H
4	170.8, qC	-		
*N*H	-	8.27, d (7.5)	Ha-1	Asp-2,3a,3b; Ha-2,3; Thr-*N*H
*O*Me	51.7, CH_3	3.56, s	Asp-4	
[3]Thr 1	169.1, qC	-		
2	55.0, CH	4.58, d (9.5)	Asp-1; Thr-1,2	Thr-3,4,*N*H; Arg-*N*H
3	72.2, CH	5.50, q (6.5)	Thr-4; [8]Val-1	Thr-2,4,*N*H; Arg-*N*H; Amp-*N*H
4	17.9, CH_3	1.18, d (6.5)	Thr-2,3	Thr-2,3
*N*H	-	7.68, d (9.5)	Asp-1	Thr-2,3; Asp-2,3a,*N*H
[4]Arg 1	170.4, qC	-		
2	52.2, CH	4.27, m	Arg-3	Arg-3a,3b,4,5,*N*H; Amp-*N*H
3 ab	27.8, CH_2	2.02, m		Arg-2,3b,4,5,5-*N*H
		1.45, m	Arg-4	Arg-2,3a,5,*N*H,5-*N*H
4	25.4, CH_2	1.45, m	Arg-3	Arg-2,3a,5,*N*H,5-*N*H
5	40.2, CH_2	3.09, m	Arg-4,6	Arg-2,3a,3b,4,5-*N*H
*N*H	-	8.56, d (8.5)	Thr-1	Arg-2,3b,4; Thr-2,3; Amp-*N*H

Table S10. *Cont.*

5-*N*H	-	7.56, t (5.0)	Arg-5,6	Arg-2,3b,4,5
6	156.9, qC	-		
6-*N*H,*N*H_2	-	7.30, brm 6.90, brm		
[5]Amp 2	169.2, qC	-		
3	49.4, CH	4.47 m	Amp-2	Amp-4b,5b,*N*H; Val-4
4 ab	21.7, CH_2	2.40, brq (12.5) 1.75, m		Amp-4b,5a,6,*N*H Amp-3,4a
5 ab	23.8, CH_2	2.05, m 1.70, m		Amp-4a,5b,6,*O*Me Amp-3,5a,6
6	83.3, CH	4.44, brs		Amp-5a,5b,*O*Me,*N*H; [6]Val-3,4
*N*H	-	7.24, m	Arg-1	Amp-3,4a; Thr-3; Arg-2,*N*H
*O*Me	55.6, CH_3	3.03, s	Amp-6	Amp-5a,6; [8]Val-4,5,*N*H
[6]Val 1	169.8, qC	-		
2	55.8, CH	4.36, d (10.5)	Amp-2,6; [6]Val-1,3,4	[6]Val-3,4,5, *N*MePhe-2,5,5′
3	27.3, CH	1.95, m	[6]Val-5	[6]Val-2,4,5; Amp-6
4	18.3, CH_3	0.46, d (6.5)	[6]Val-2,3,5	[6]Val-2,3,5; Amp-3,6
5	17.9, CH_3	−0.23, d (6.0)	[6]Val-2,3,4	[6]Val-2,3,4; *N*MePhe-5,5′,6,6′
[7]*N*MePhe 1	169.4, qC	-		
2	61.0, CH	5.10, brd (11.0)	*N*MePhe-1,*N*Me	*N*MePhe-3a,5,5′,6,6′,*N*Me; [6]Val-2; [8]Val-*N*H
3 ab	34.3, CH_2	3.30, m 2.80, m	*N*MePhe-5,*N*Me *N*MePhe-2,5,*N*Me	*N*MePhe-3b,5,5′,6,6′,*N*Me *N*MePhe-2,3a,5,5′,6,6′,*N*Me
4	137.7, qC	-		
5,5′	129.8, CH	7.23, d (7.5)	*N*MePhe-3,7	*N*MePhe-2,3a,3b,6,6′,*N*Me; [6]Val-2,5
6,6′	128.9, CH	7.27, t (7.5)	*N*MePhe-4,5,5′	*N*MePhe-2,3a,3b,5,5′,7,*N*Me; [6]Val-5
7	127.0, CH	7.19, t (7.5)	*N*MePhe-5,5′	*N*MePhe-6,6′
*N*Me	30.4, CH_3	2.75, s	[6]Val-1; *N*MePhe-2	*N*MePhe-2,3a,3b,5,5′,6,6′; [8]Val-4,5,*N*H

Table S10. *Cont.*

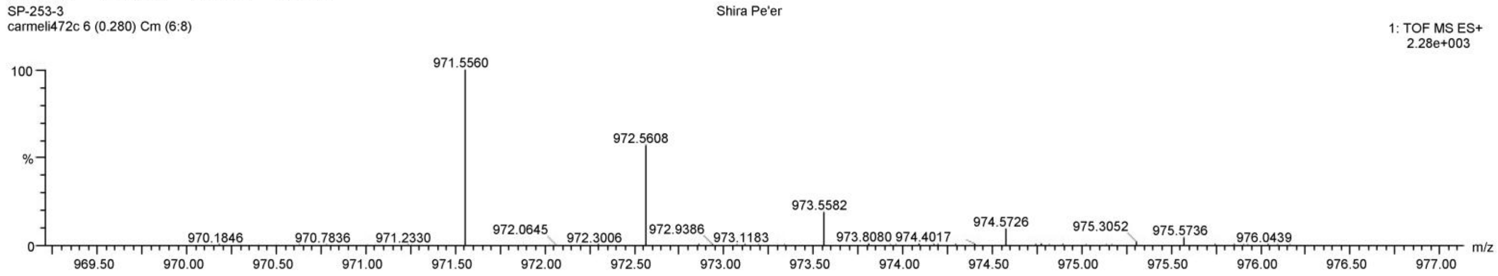
^{8}Val 1	172.5, qC	-		
2	56.7, CH	4.60, m	^{8}Val-1,3,4	^{8}Val-3,4,5,*N*H
3	31.2, CH	2.00, m	^{8}Val-4	^{8}Val-2,4,5,*N*H
4	19.4, CH_3	0.89, d (7.0)	^{8}Val-2,3,5	^{8}Val-2,3,*N*H; Amp-*O*Me; *N*MePhe-*N*Me
5	18.1, CH_3	0.83, d (6.5)	^{8}Val-2,3,4	^{8}Val-2,3,*N*H; Amp-*O*Me; *N*MePhe-*N*Me
*N*H	-	6.97, d (9.5)	*N*MePhe-1; ^{8}Val-1	^{8}Val-2,3,4,5; Amp-*O*Me; *N*MePhe-2,*N*Me

[a] 125 MHz for carbons and 500 MHz for protons; [b] Multiplicity and assignment from HSQC experiment; [c] Determined from HMBC experiment, $^{n}J_{CH}$ = 8 Hz, recycle time 1 s; [d] Selected NOE's from ROESY experiment.

Elemental Composition Report

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
58 formula(e) evaluated with 6 results within limits (up to 4 best isotopic matches for each mass)
Elements Used:
C: 42-52 H: 70-80 N: 4-14 O: 8-16



Minimum:				-1.5			
Maximum:		5.0	10.0	50.0			

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
971.5560	971.5566	-0.6	-0.6	15.5	67.0	0.8	C47 H75 N10 O12
	971.5553	0.7	0.7	10.5	67.3	1.1	C46 H79 N6 O16
	971.5579	-1.9	-2.0	20.5	67.9	1.8	C48 H71 N14 O8
	971.5593	-3.3	-3.4	14.5	69.2	3.0	C51 H79 N4 O14

Figure S72. HR ESI MS data of Micropeptin KB970C (**10**).

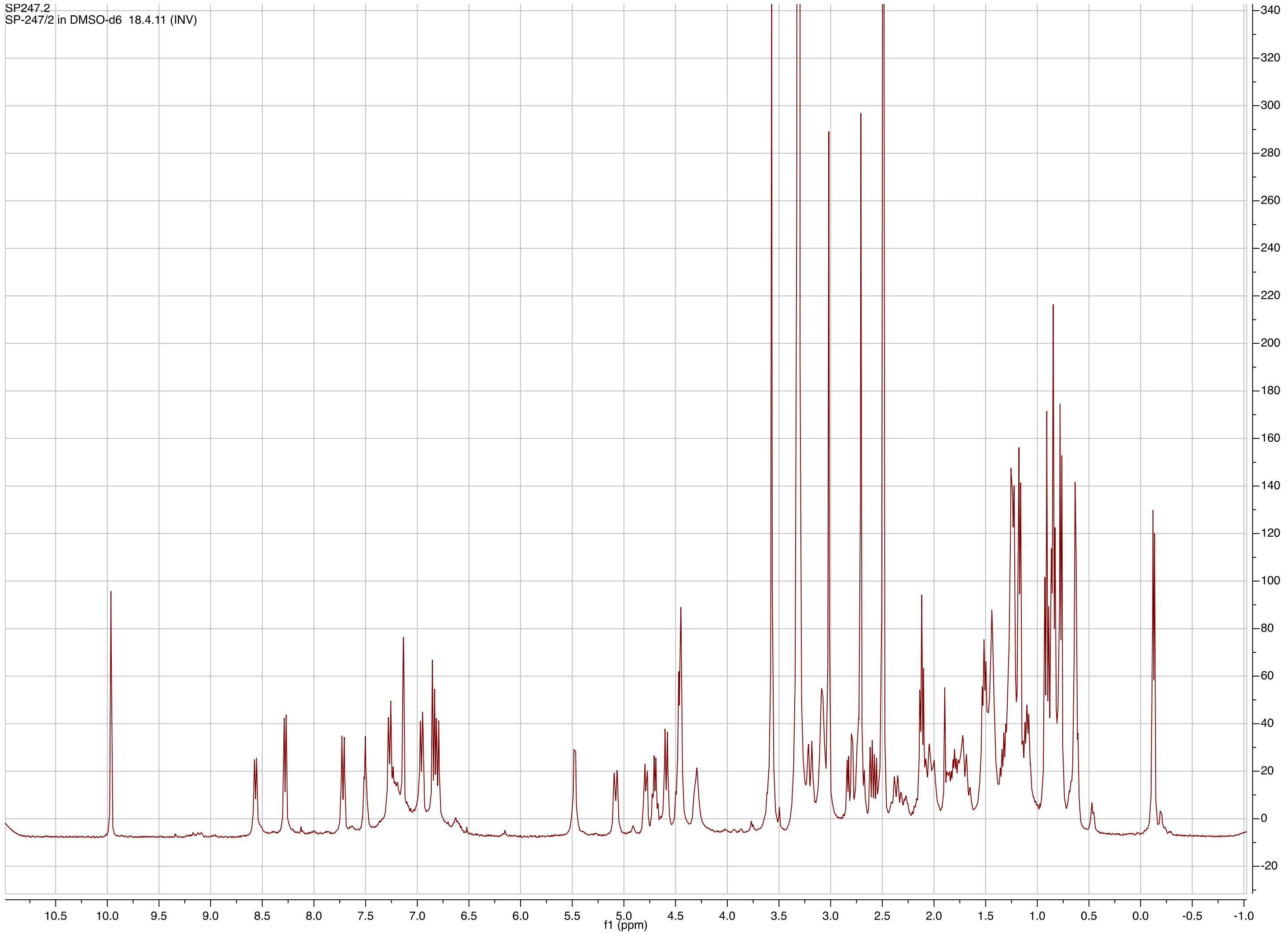


Figure S73. ^{1}H NMR Spectrum (500 MHz) of Micropeptin KB1048 (**11**) in DMSO-d_6.

Figure S74. ^{13}C NMR Spectrum (125 MHz) of Micropeptin KB1048 (**11**) in DMSO-d_6.

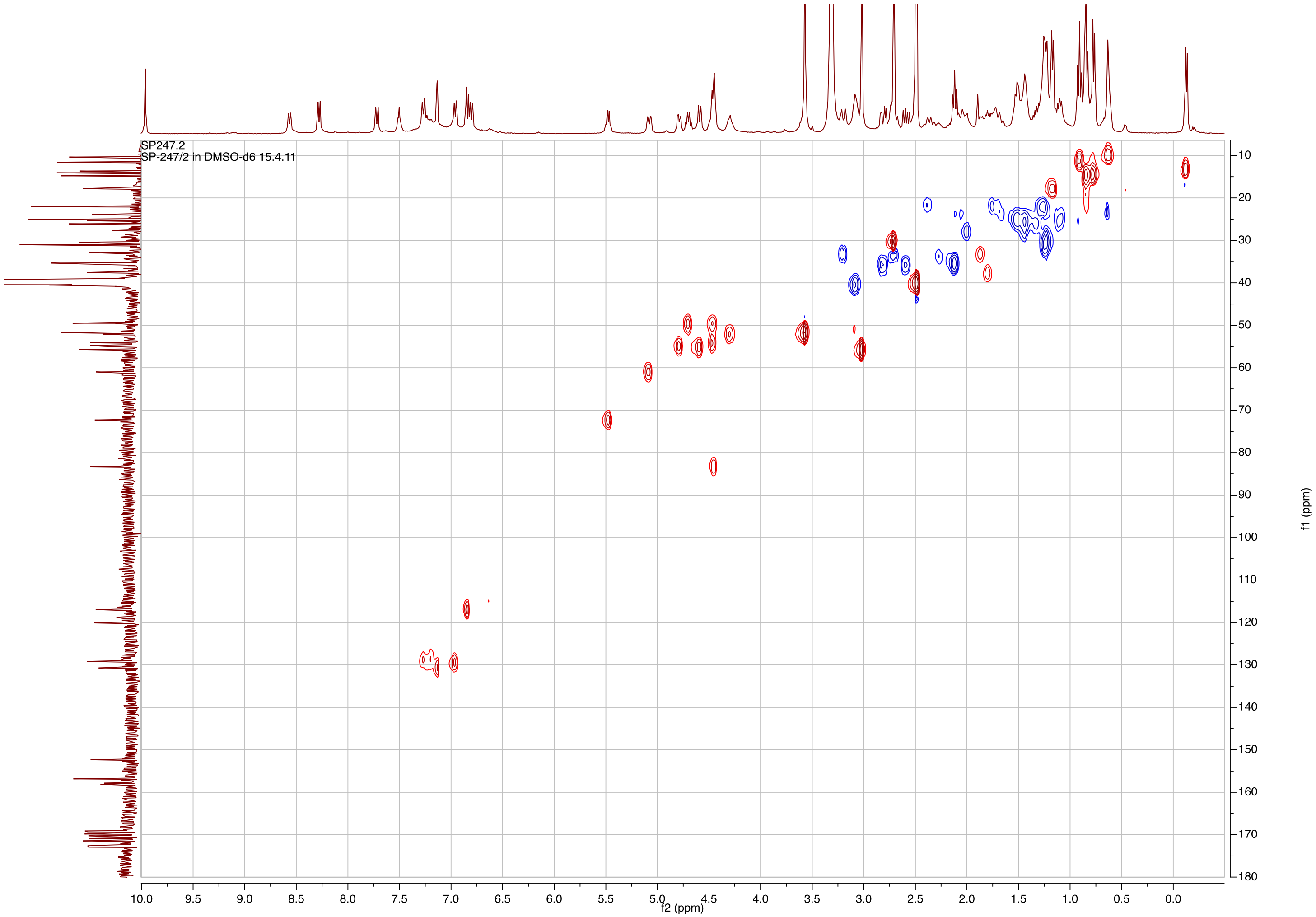


Figure S75. HSQC Spectrum of Micropeptin KB1048 (**11**) in DMSO-d_6 (Red: CH, CH_3; Blue: CH_2).

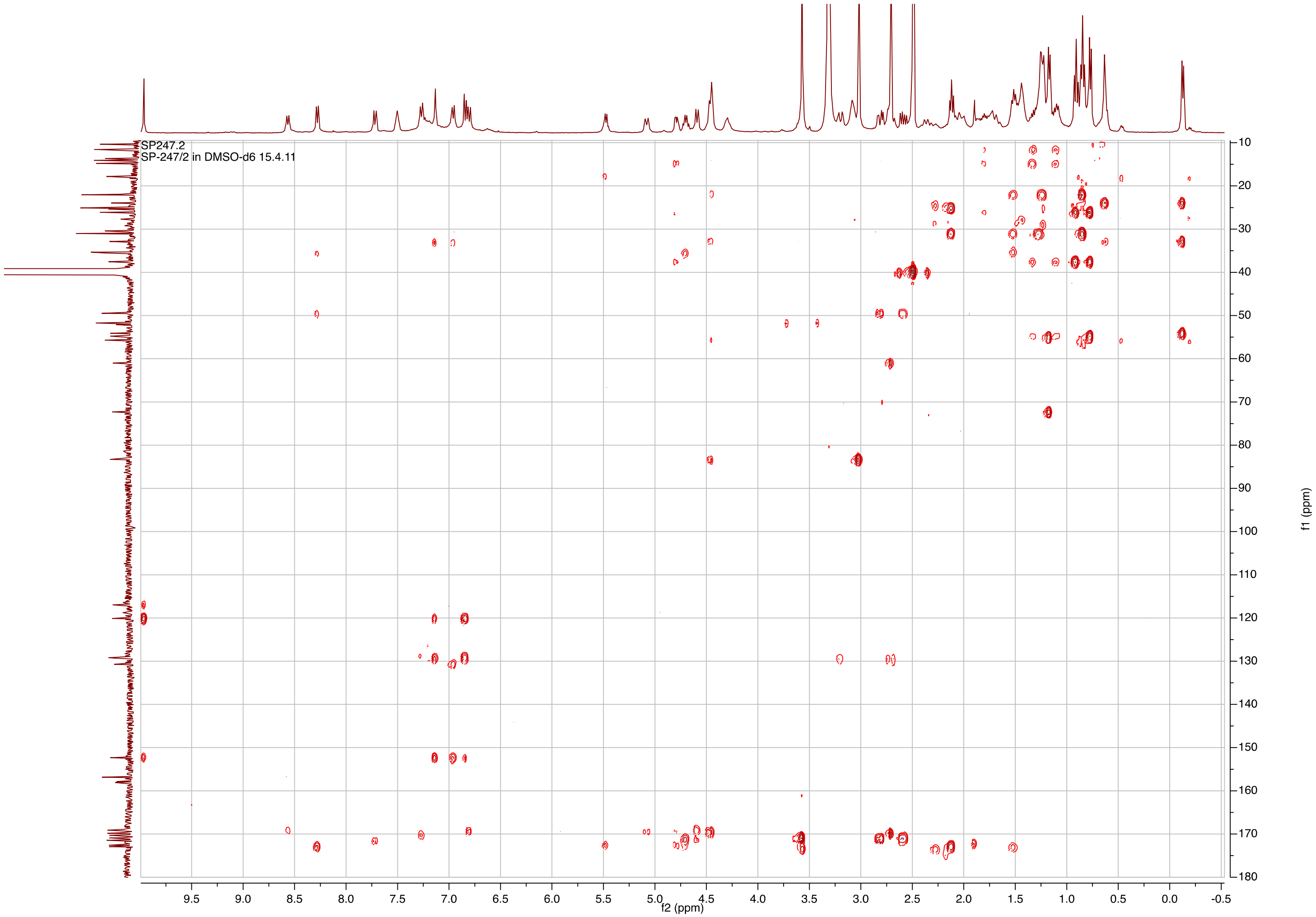


Figure S76. HMBC Spectrum of Micropeptin KB1048 (**11**) in DMSO-d_6.

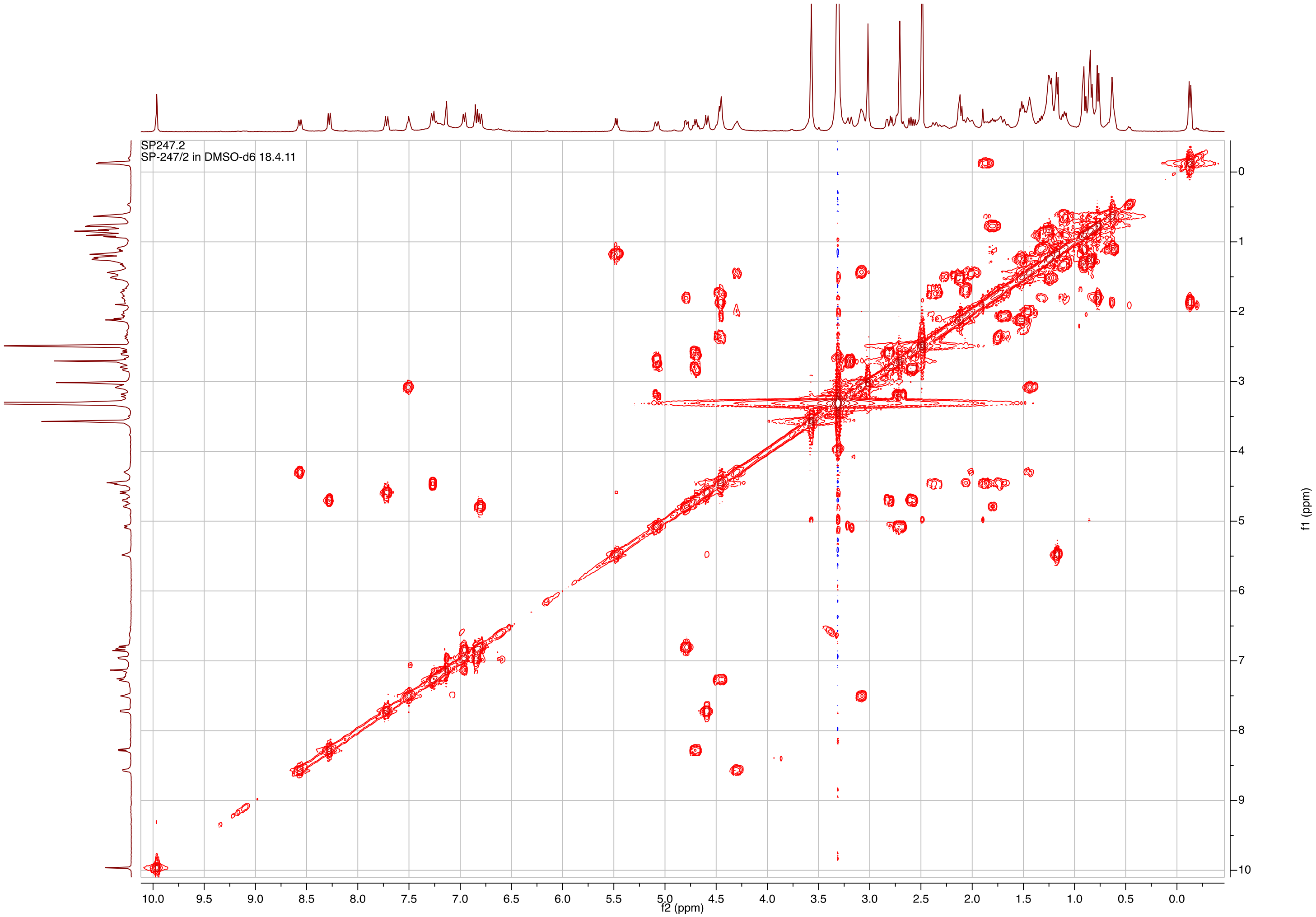


Figure S77. COSY Spectrum of Micropeptin KB1048 (**11**) in DMSO-d_6.

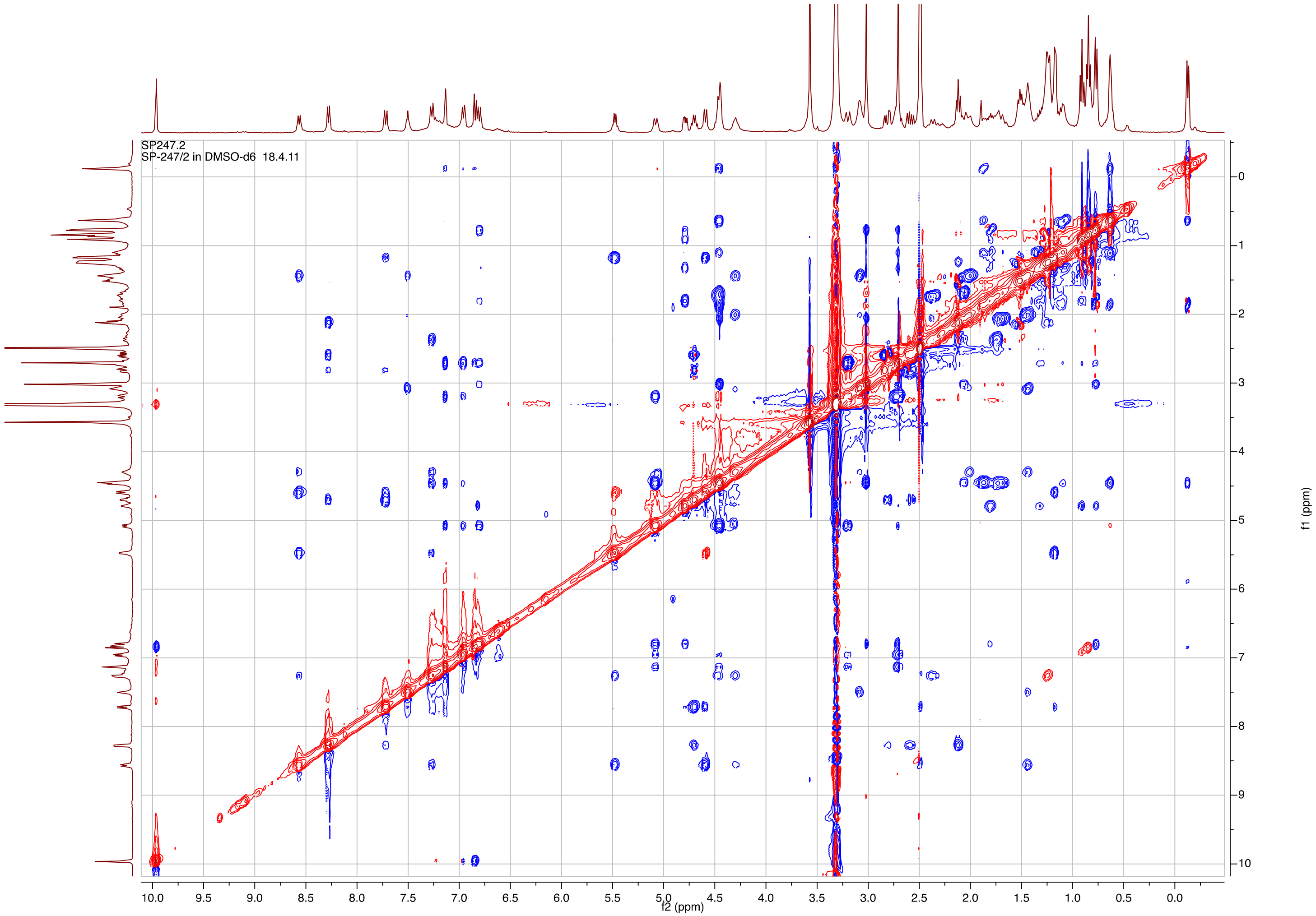


Figure S78. ROESY Spectrum of Micropeptin KB1048 (**11**) in DMSO-d_6 (Blue: NOE correlation).

Table S11. NMR Data of Micropeptin KB1048 (**11**) in DMSO-d_6.

Position	δ_C mult. [b]	δ_H mult.[b] *J* in Hz	HMBC Correlations [c]	NOE Correlations [d]
[1]Ha 1	173.0, qC	-		
2	35.3, CH_2	2.17, t (7.0)	Ha-1,3,4	Ha-3,4; Asp-*N*H
3	25.1, CH_2	1.51, qi (7.0)	Ha-1,2,4	Ha-2,4,5
4	31.0, CH_2	1.22, m	Ha-2,3,5	Ha-3,5,6
5	22.1, CH_2	1.24, m	Ha-4,6	Ha-3,4,6
6	14.8, CH_3	0.85, t (7.3)	Ha-4,5	Ha-4,5
[2]Asp 1	171.5, qC	-		
2	49.5, CH	4.70, ddd (8.0,7.5,6.0)	Ha-1; Asp-1,3,4	Asp-3a,3b,*N*H; Thr-*N*H
3 ab	35.5, CH_2	2.81, dd (16.5,6.0) 2.59, dd (16.5,8.0)	Asp-2,4 Asp-2,4	Asp-2,3b,*N*H; Thr-*N*H Asp-2,3a,*N*H
4	170.9, qC	-		
*N*H	-	8.28, d (7.5)	Ha-1	Asp-2,3a,3b; Ha-2; Thr-*N*H
*O*Me	51.7, CH_3	3.57, s	Asp-4	
[3]Thr 1	169.1, qC	-		
2	55.0, CH	4.59, d (9.5)	Asp-1; Thr-1,2	Thr-3,4,*N*H; Arg-*N*H
3	72.3, CH	5.47, q (6.5)	Thr-4; [8]Ile-1	Thr-2,4,*N*H; Arg-*N*H; Amp-*N*H
4	17.8, CH_3	1.17, d (6.5)	Thr-2,3	Thr-2,3,*N*H
*N*H	-	7.71, d (9.5)	Asp-1	Thr-2,3,4; Asp-2,3a,*N*H
[4]Arg 1	170.3, qC	-		
2	52.1, CH	4.29, m	Arg-1	Arg-3a,3b,4,5,*N*H; Amp-*N*H
3 ab	27.7, CH_2	2.00, m 1.45, m	Arg-4	Arg-2,3b,4,5,5-*N*H Arg-2,3a,5,*N*H,5-*N*H
4	25.4, CH_2	1.45, m		Arg-2,3a,5,*N*H,5-*N*H
5	40.1, CH_2	3.08, m	Arg-4,6	Arg-2,3a,3b,4,5-*N*H
*N*H	-	8.56, d (8.5)	Thr-1; Arg-2	Arg-2,3b,4; Thr-2,3; Amp-*N*H

Table S11. *Cont.*

5-*N*H	-	7.50, t (5.2)	Arg-5,6	Arg-2,3b,4,5
6	156.9, qC	-		
6-*N*H,*N*H_2	-	7.30, brm 6.90, brm		
^{5}Amp 2	169.3, qC	-		
3	49.4, CH	4.46 m	Amp-2,4	Amp-4b,5b,*N*H
4 ab	21.9, CH_2	2.40, brq (12.8) 1.75, m		Amp-4b,5a,*N*H Amp-3,4a,6
5 ab	23.9, CH_2	2.06, brd (13.4) 1.70, m		Amp-4a,5b,6,*O*Me Amp-3,5a,6,*O*Me
6	83.3, CH	4.46, brs		Amp-4b,5a,5b,*O*Me,*N*H; ^{6}Ile-3,4a
*N*H	-	7.26, d (9.6)	Arg-1	Amp-3,4a,6; Thr-3; Arg-2,*N*H
*O*Me	55.7, CH_3	3.02, s	Amp-6	Amp-5a,5b,6; ^{8}Ile-4a,4b,5,6,*N*H
^{6}Ile 1	169.9, qC	-		
2	54.1, CH	4.46, m	Amp-2,6; ^{6}Ile -1,3,6	^{6}Ile-3,4a,4b,5,6; Cl-*N*MeTyr-2,5,9
3	33.1, CH	1.86, m		^{6}Ile-2,3,4b,5; Amp-6
4 ab	23.9, CH_2	1.10, m 0.63, m	^{6}Ile-3,4,5	^{6}Ile-2,3,5; Amp-6 ^{6}Ile-2,3,6; Cl-*N*MeTyr-2,5
5	10.4, CH_3	0.63, m	^{6}Ile-3,4	^{6}Ile-2,3,6; Cl-*N*MeTyr-2,5
6	13.7, CH_3	−0.13, d (6.5)	^{6}Ile-2,3,4	^{6}Ile-2,3,4a,4b,5; Cl-*N*MeTyr-2,5,8,9, *N*Me
^{7}Cl-*N*MeTyr 1	169.3, qC	-		
2	61.0, CH	5.08, brd (11.0)	Cl-*N*MeTyr-1,3,*N*Me	Cl-*N*MeTyr-3a,5,9,*N*Me; ^{6}Ile-2,4b,5,6; ^{8}Ile-*N*H
3 ab	32.9, CH_2	3.20, brd (14.4) 2.71, m	Cl-*N*MeTyr-4,5,*N*Me Cl-*N*MeTyr-2,4,5,*N*Me	Cl-*N*MeTyr-2,3b,5,9,*N*Me; ^{6}Ile-2 Cl-*N*MeTyr-3a,5,8,9,*N*Me; ^{6}Ile-2
4	129.3, qC	-		
5	130.7, CH	7.13, s	Cl-*N*MeTyr -3,6,7,9	Cl-*N*MeTyr-2,3a,3b,*N*Me; ^{6}Ile-2,4b,5,6

Table S11. *Cont.*

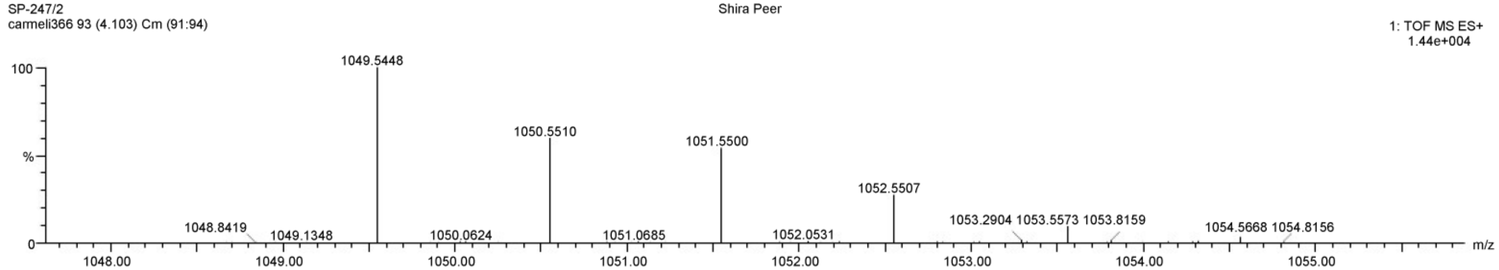
6	120.1, qC			
7	152.3, qC			
8	117.0, CH	6.84 d, (8.2)	Cl-*N*MeTyr-4,6,7	Cl-*N*MeTyr-3b,9,*N*Me; [6]Ile-6
9	129.6, CH	6.96, d (8.2)	Cl-*N*MeTyr-3,5,7,8	Cl-*N*MeTyr-2,3a,3b,8,*N*Me; [6]Ile-2,6
*N*Me	30.4, CH_3	2.71, s	[6]Val-1; Cl-*N*MeTyr-2	Cl-*N*MeTyr-2,3a,5,9; [8]Ile-4a,4b,5,6,*N*H
*O*H		9.96, s	Cl-*N*MeTyr-6,7,8	
[8]Ile 1	172.6, qC	-		
2	58.4, CH	4.79, dd (9.5,4.5)	[8]Ile-1,3,4,6	[8]Ile-3,4a,4b,5,6,*N*H
3	37.6, CH	1.80, m	[8]Ile-4,5,6	[8]Ile-2,4b,5,6,*N*H
4 ab	26.0, CH_2	1.32, m	[8]Ile-3,5,6	[8]Ile-2,4b,5,*N*H; Amp-*O*Me; Cl-*N*MeTyr-*N*Me
		1.10, m	[8]Ile-3,5,6	[8]Ile-2,3,4a,*N*H; Amp-*O*Me; Cl-*N*MeTyr-*N*Me
5	11.6, CH_3	0.91, t (7.3)	[8]Ile-2,3,4	[8]Ile-2,3,4a; Amp-*O*Me; Cl-*N*MeTyr-*N*Me
6	14.1, CH_3	0.77, d (7.0)	[8]Ile-2,3,4	[8]Ile-2,3,*N*H; Amp-*O*Me; Cl-*N*MeTyr-*N*Me
*N*H	-	6.80, d (9.5)	Cl-*N*MeTyr-1	[8]Ile-2,3,4a,4b,6; Amp-*O*Me; Cl-*N*MeTyr-2,3b,*N*Me

[a] 125 MHz for carbons and 500 MHz for protons; [b] Multiplicity and assignment from HSQC experiment; [c] Determined from HMBC experiment, ${}^{n}J_{CH}$ = 8 Hz, recycle time 1 s; [d] Selected NOE's from ROESY experiment.

Elemental Composition Report

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
935 formula(e) evaluated with 21 results within limits (up to 5 best isotopic matches for each mass)
Elements Used:
C: 40-55 H: 65-90 N: 5-15 O: 5-15 Cl: 0-4



		mDa	PPM	DBE			
Minimum:				-1.5			
Maximum:		5.0	10.0	50.0			

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
1049.5448	1049.5452	-0.4	-0.4	20.5	100.0	1.8	C50 H74 N14 O9 Cl
	1049.5438	1.0	1.0	15.5	98.5	0.3	C49 H78 N10 O13 Cl
	1049.5479	-3.1	-3.0	19.5	100.9	2.6	C54 H78 N8 O11 Cl
	1049.5492	-4.4	-4.2	24.5	102.6	4.4	C55 H74 N12 O7 Cl
	1049.5398	5.0	4.8	11.5	103.6	5.4	C44 H78 N12 O15 Cl

Figure S79. HR ESI MS data of Micropeptin KB1048 (**11**).

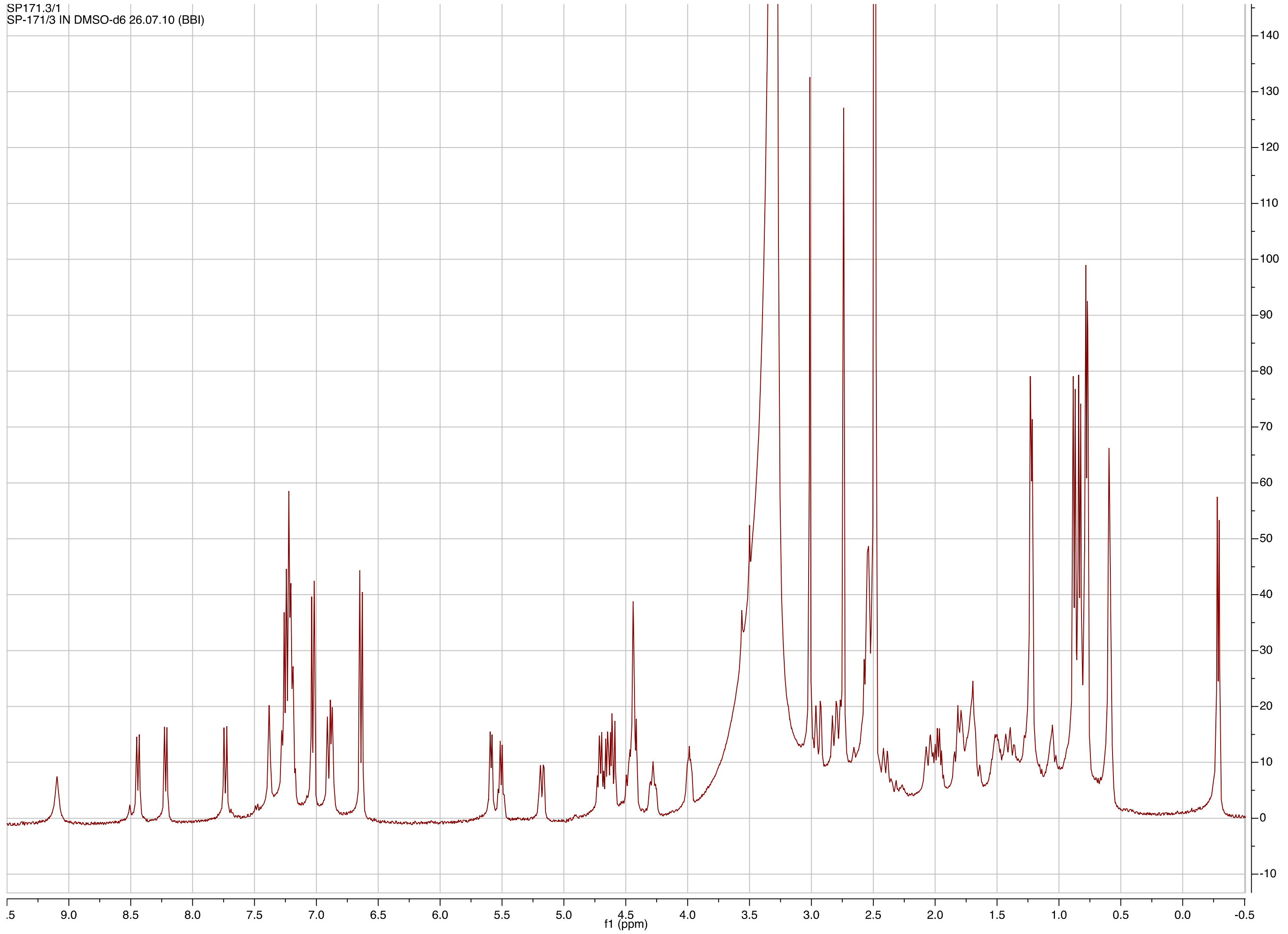


Figure S80. ^{1}H NMR Spectrum (500 MHz) of Micropeptin KB992 (**12**) in DMSO-d_6.

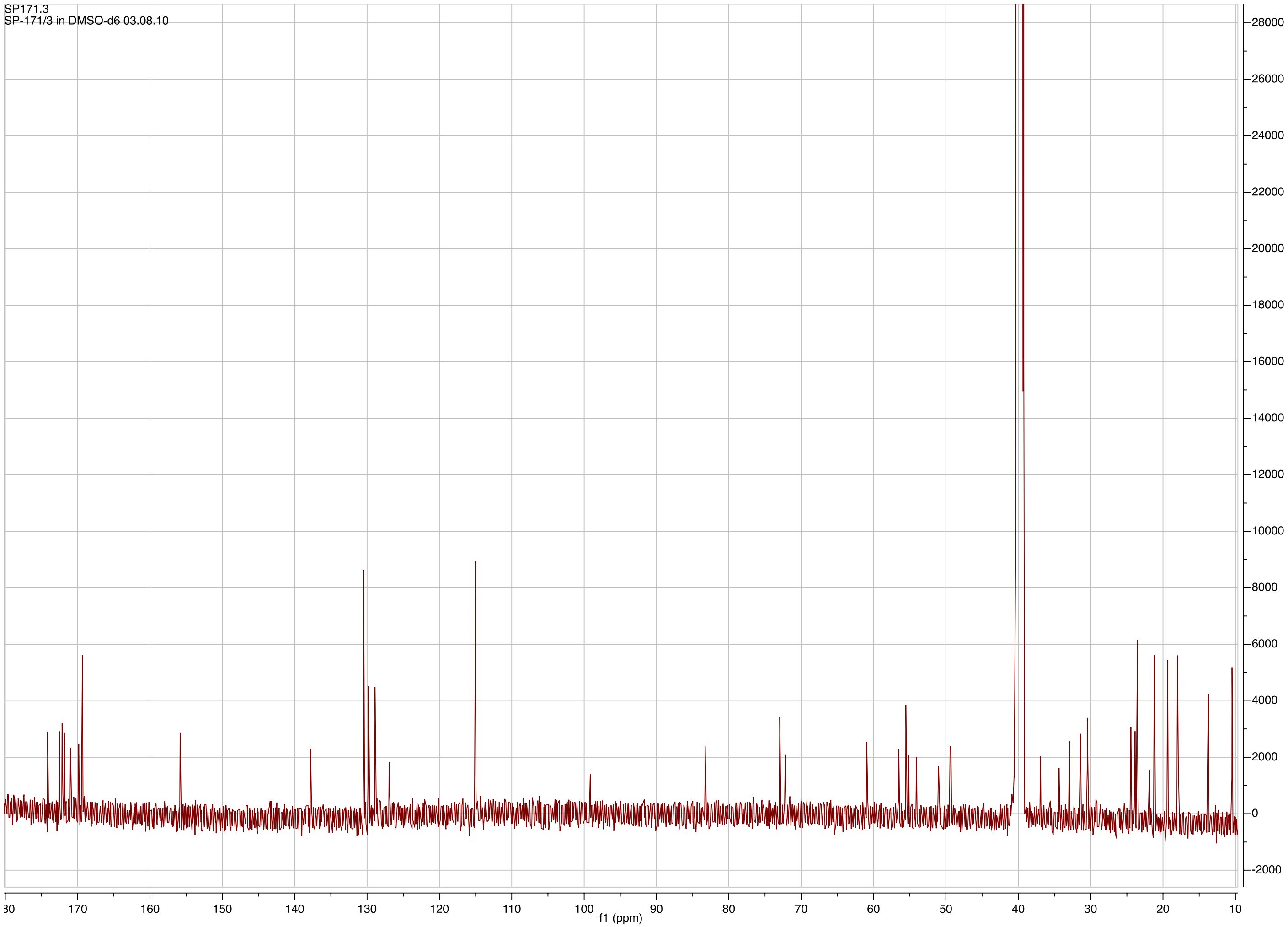


Figure S81. ^{13}C NMR Spectrum (125 MHz) of Micropeptin KB992 (**12**) in DMSO-d_6.

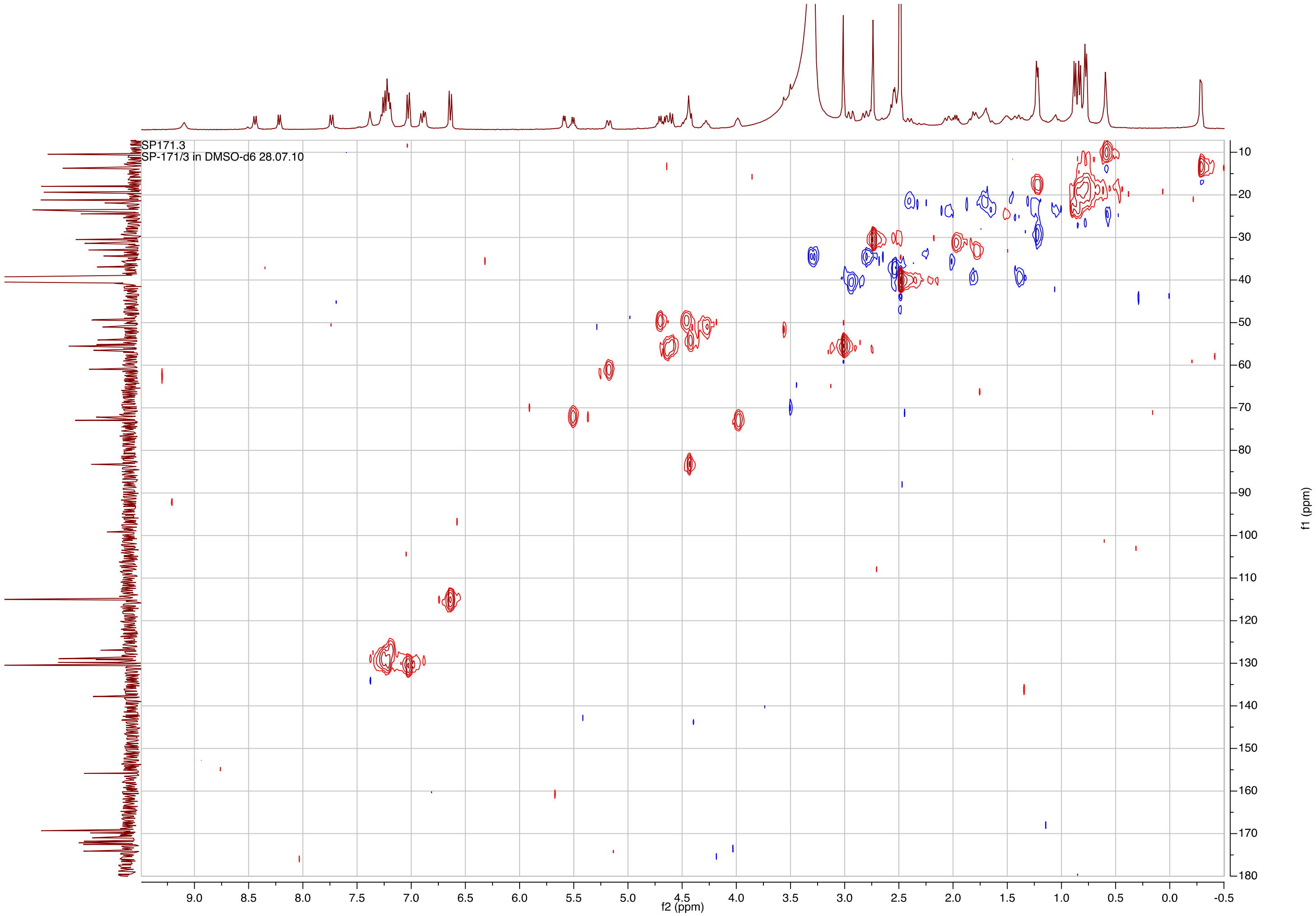


Figure S82. HSQC Spectrum of Micropeptin KB992 (**12**) in DMSO-d_6 (Red: CH, CH_3; Blue: CH_2).

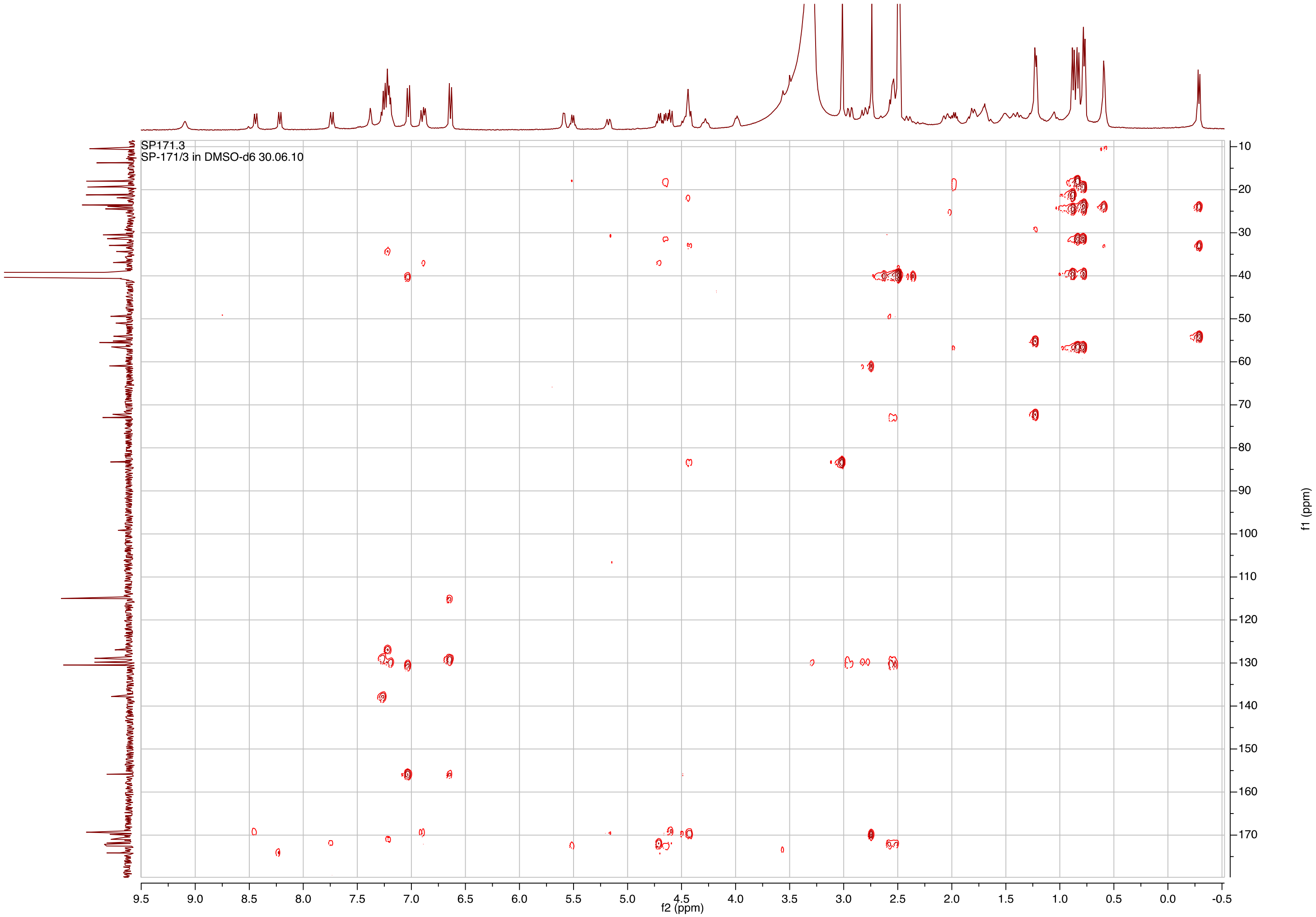


Figure S83. HMBC Spectrum of Micropeptin KB992 (**12**) in DMSO-d_6.

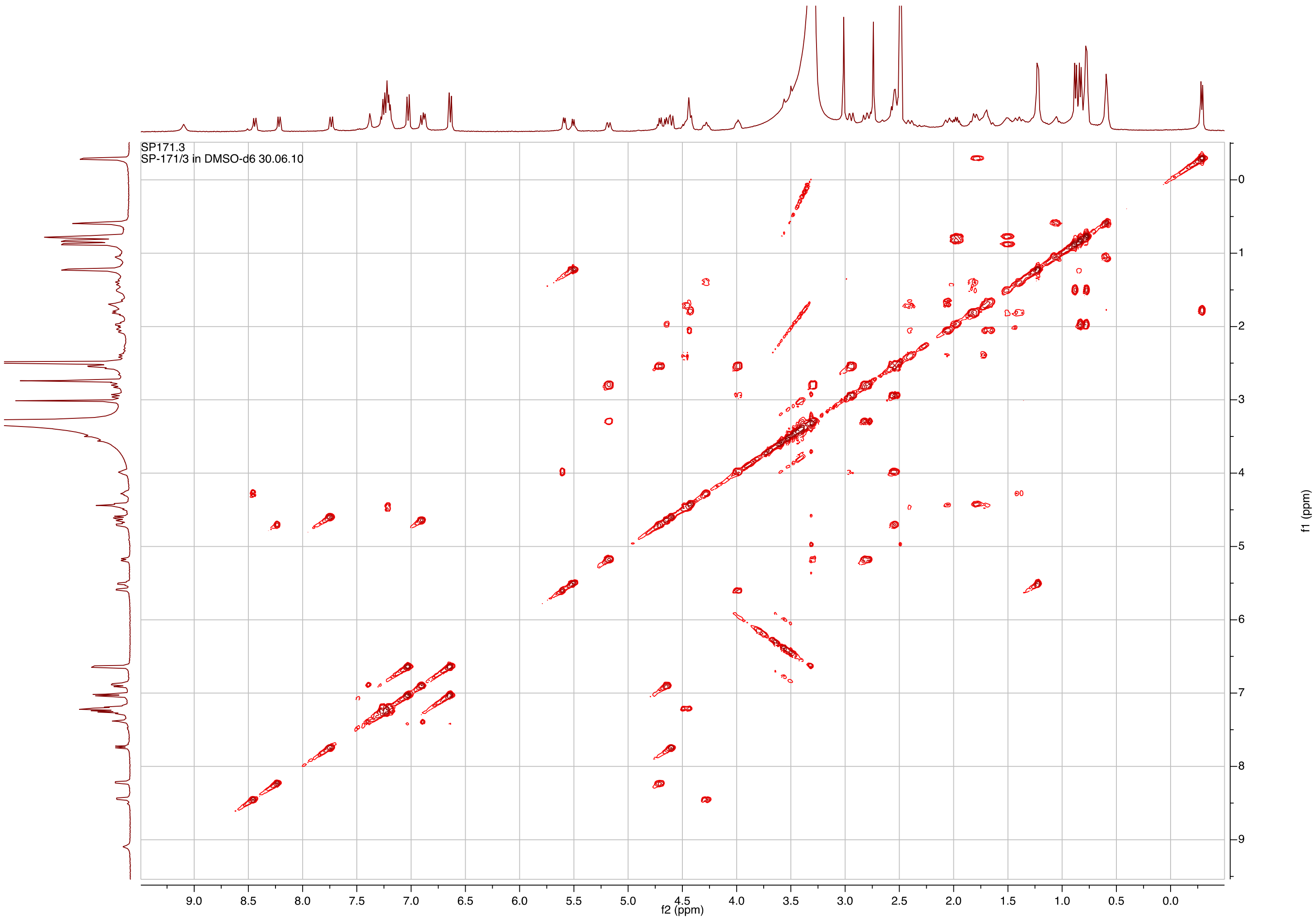


Figure S84. COSY Spectrum of Micropeptin KB992 (**12**) in DMSO-d_6.

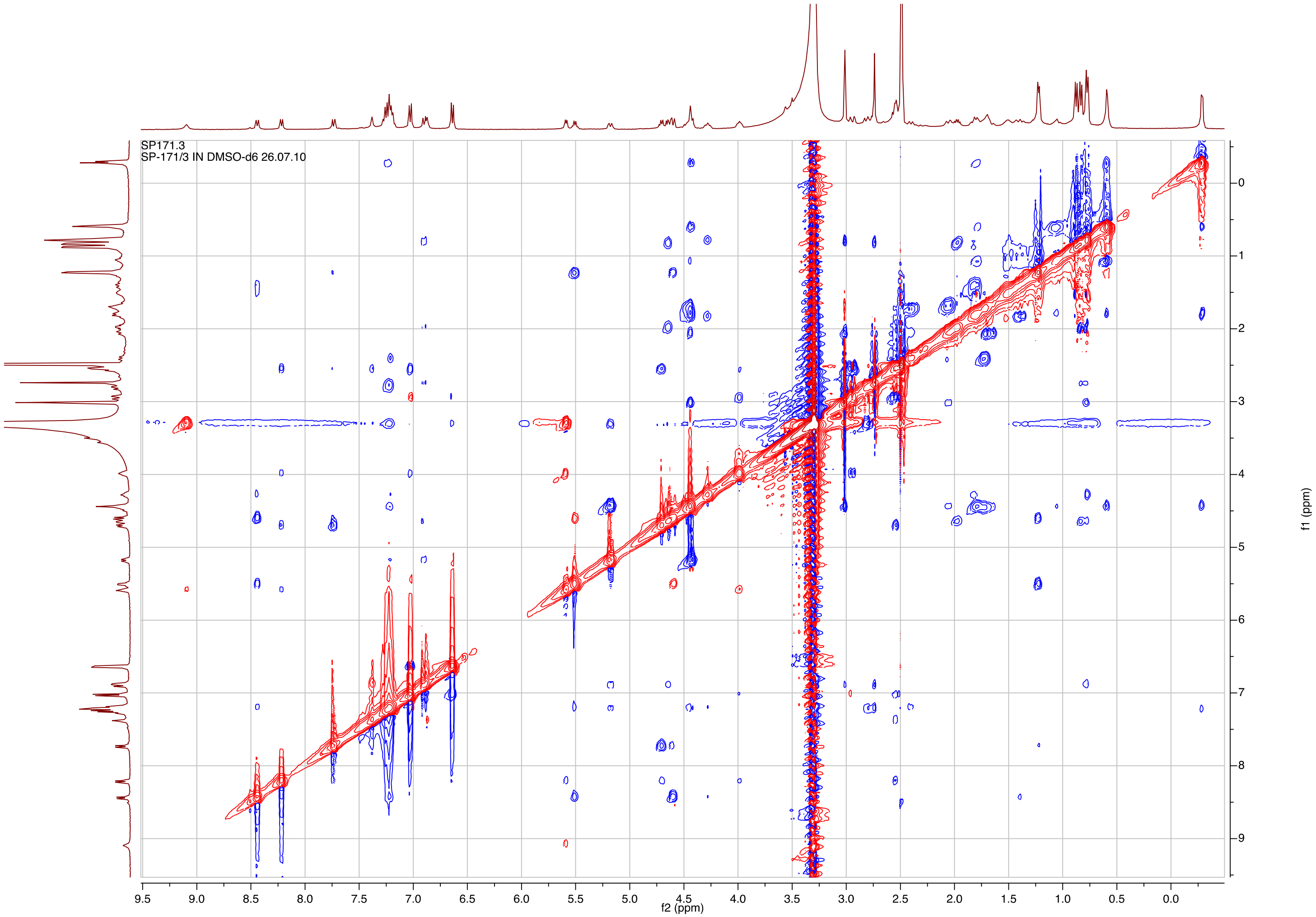


Figure S85. ROESY Spectrum of Micropeptin KB992 (**12**) in DMSO-d_6 (Blue: NOE correlation).

Table S12. NMR Data of Micropeptin KB992 (**12**) in DMSO-d_6.

Position	δ_C mult. [b]	δ_H mult.[b] *J* in Hz	HMBC Correlations [c]	NOE Correlations [d]
[1]Hpla 1	174.2, qC	-		
2	73.0, CH	3.99, ddd (8.7,5.8,3.1)	Hpla-3,4	Hpla-3a,3b,5,5′,2-*O*H; Asn-2
3 ab	41.0, CH_2	2.93, dd (13.5,3.1)	Hpla-4,5,5′	Hpla-2,5,5′,6,6′,2-*O*H
		2.54, m	Hpla-1,2,4,5,5′	Hpla-2,5,5′,2-*O*H; Asn-*N*H
4	129.1, qC			
5,5′	130.5, CH	7.02, d (8.5)	Hpla-3,4,7	Hpla-2,3a,3b,6,6′
6,6′	115.0, CH	6.64, d (8.5)	Hpla-4,5,5′,7	Hpla-3a,5,5′
7	155.8, qC	-		
2-*O*H	-	5.60, d (5.8)	Hpla-2,3	Hpla-2,3a,3b; Asn-*N*H
7-*O*H	-	9.11, s		
[2]Asn 1	171.8, qC	-		
2	49.3, CH	4.70, dt (8.0,7.5)	Hpla-1; Asn-1,3,4	Asn-3,*N*H; Thr-*N*H
3	36.9, CH_2	2.54, m	Asn-1,2,4	Asn-2,*N*H,*N*H_2(a); Thr-*N*H
4	172.2, qC	-		
*N*H		8.23, d (8.0)	Hpla-1; Asn-2	Asn-2,3; Hpla-2,3b,2-*O*H
NH_2 ab	-	7.39, s	Asn-3,4	Asn-*N*H_2(b)
		6.89, s		Asn-*N*H_2(a)
[3]Thr 1	169.2, qC	-		
2	55.1, CH	4.60, d (9.0)	Asn-1; Thr-1	Thr-3,4,*N*H; Arg-*N*H
3	72.2, CH	5.50, q (6.3)	Thr-4; [8]Val-1	Thr-2,4,*N*H; Arg-*N*H; Ahp-*N*H
4	17.9, CH_3	1.22, d (6.3)	Thr-2,3	Thr-2,3
*N*H		7.74, δ (9.0)	Asn-1	Thr-2,3; Asp-2,3a,*N*H
[4]Leu 1	171.0, qC	-		
2	51.0, CH	4.28, ddd (9.0,8.5,3.2)		Leu-3a,3b,4,6,*N*H; Amp-*N*H
3 ab	39.0, CH_2	1.80, m		Leu-2,3b,4,5
		1.39, m		Leu-2,3a,5,*N*H

Table S12. *Cont.*

4	24.4, CH	1.50, m		Leu-3a,5,*N*H
5	23.9, CH_3	0.87, d (6.6)	Leu-3,4,6	Leu-2,5
6	21.2, CH_3	0.78, d (7.0)	Leu-3,4,5	Leu-2,3b,4; Thr-2,3; Amp-*N*H
*N*H		8.45, d (8.5)	Thr-1	Arg-2,3b,4,5
^{5}Amp 2	169.3, qC	-		
3	49.4, CH	4.47 m	Amp-2	Amp-4b,5b,*N*H
4 ab	21.9, CH_2	2.40, q (12.6)		Amp-4b,5a,*N*H
		1.70, m		Amp-3,4a
5 ab	23.9, CH_2	2.05, brd (14.4)		Amp-4a,5b,6,*O*Me
		1.75 m		Amp-3,5a,6
6	83.3, CH	4.43, brs		Amp-5a,5b,*O*Me
*N*H	-	7.21, m	Leu-1; Amp-*O*Me	Amp-3,4a; Thr-3; Leu-2,*N*H; ^{6}Ile-5,6
*O*Me	55.5, CH_3	3.01, s	Amp-6	Amp-5a,6; ^{8}Val-5,*N*H
^{6}Ile 1	169.8, qC	-		
2	54.1, CH	4.43, m	Amp-2,6; ^{6}Ile-1,3,4,6	^{6}Ile-3,4,5; *N*MePhe-2,5,5′
3	32.9, CH	1.78, m	^{6}Ile-5	^{6}Ile-2,4,5; Amp-6
4	23.5, CH_2	1.05, m	^{6}Ile-2,3,5	^{6}Ile-2,3,5; Amp-3,6
		0.59, m		
5	10.5, CH_3	0.59, m	^{6}Ile-2,3,4	^{6}Ile-2,3,4; *N*MePhe-5,5′,6,6′
6	13.7, CH_3	−0.30, d (6.5)	^{6}Ile-2,3,4,5	
^{7}*N*MePhe 1	169.3, qC	-		
2	60.9, CH	5.17, dd (11.0,2.1)	*N*MePhe-1,*N*Me	*N*MePhe-3a,3b,5,5′,*N*Me; ^{6}Ile-2; ^{8}Val-*N*H
3 ab	34.4, CH_2	3.30, m	*N*MePhe-4,5	*N*MePhe-2,3b,5,5′,*N*Me
		2.80, dd (14.3,11.0)	*N*MePhe-2,4,5,*N*Me	*N*MePhe-2,3a,5,5′,*N*Me
4	137.8, qC	-		
5,5′	129.8, CH	7.21, d (7.5)	*N*MePhe-3,7	*N*MePhe-2,3a,3b,6,6′,*N*Me; ^{6}Ile-2,5,6

Table S12. *Cont.*

6,6′	128.9, CH	7.25, t (7.5)	*N*MePhe-4,5,5′	*N*MePhe-3b,5,5′,7,*N*Me
7	126.9, CH	7.19, t (7.5)	*N*MePhe-5,5′	*N*MePhe-6,6′
*N*Me	30.5, CH_3	2.74, s	*N*MePhe-2,4	*N*MePhe-2,3a,5,5′,6,6′; ^{8}Val-*N*H
^{8}Val 1	172.5, qC	-		
2	56.5, CH	4.64, dd (9.5,6.0)	^{8}Val-1,3	^{8}Val-3,4,5,*N*H
3	31.4, CH	1.97, m	^{8}Val-4,5	^{8}Val-2,4,5,*N*H
4	19.5, CH_3	0.83, d (6.5)	^{8}Val-2,3,5	^{8}Val-2,3,5,*N*H,
5	18.0, CH_3	0.77, d (6.5)	^{8}Val-2,3,4	^{8}Val-2,3,*N*H; Amp-*O*Me,
*N*H	-	6.90, d (9.5)	*N*MePhe-1; ^{8}Val-1	^{8}Val-2,3,4,5; Amp-*O*Me; *N*MePhe-2,*N*Me

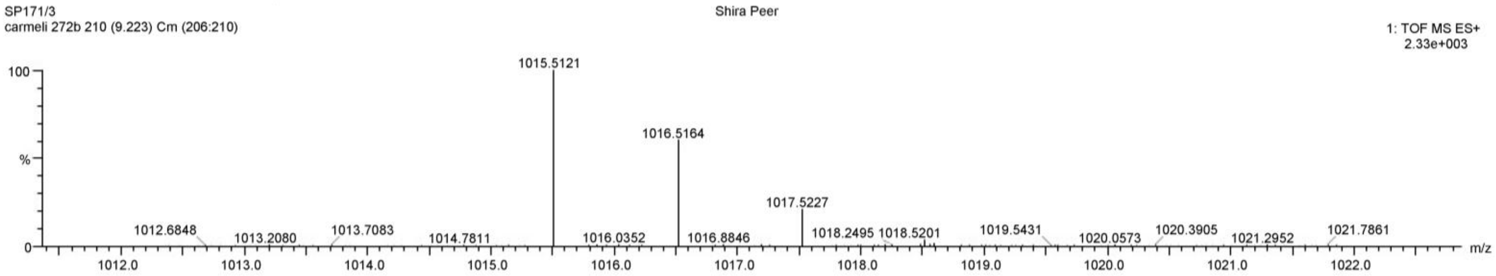
[a] 125 MHz for carbons and 500 MHz for protons; [b] Multiplicity and assignment from HSQC experiment; [c] Determined from HMBC experiment, $^{n}J_{CH}$ = 8 Hz, recycle time 1 s; [d] Selected NOE's from ROESY experiment.

Elemental Composition Report

Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
342 formula(e) evaluated with 10 results within limits (up to 4 best isotopic matches for each mass)
Elements Used:
C: 45-55 H: 60-80 N: 5-15 O: 5-20 Na: 0-1



Minimum:				-1.5			
Maximum:		5.0	10.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
1015.5121	1015.5117	0.4	0.4	18.5	98.9	1.2	C50 H72 N8 O13 Na
	1015.5141	-2.0	-2.0	21.5	99.0	1.3	C52 H71 N8 O13
	1015.5130	-0.9	-0.9	23.5	99.1	1.3	C51 H68 N12 O9 Na
	1015.5114	0.7	0.7	22.5	99.5	1.8	C48 H67 N14 O11

Figure S86. HR ESI MS data of Micropeptin KB992 (**12**).

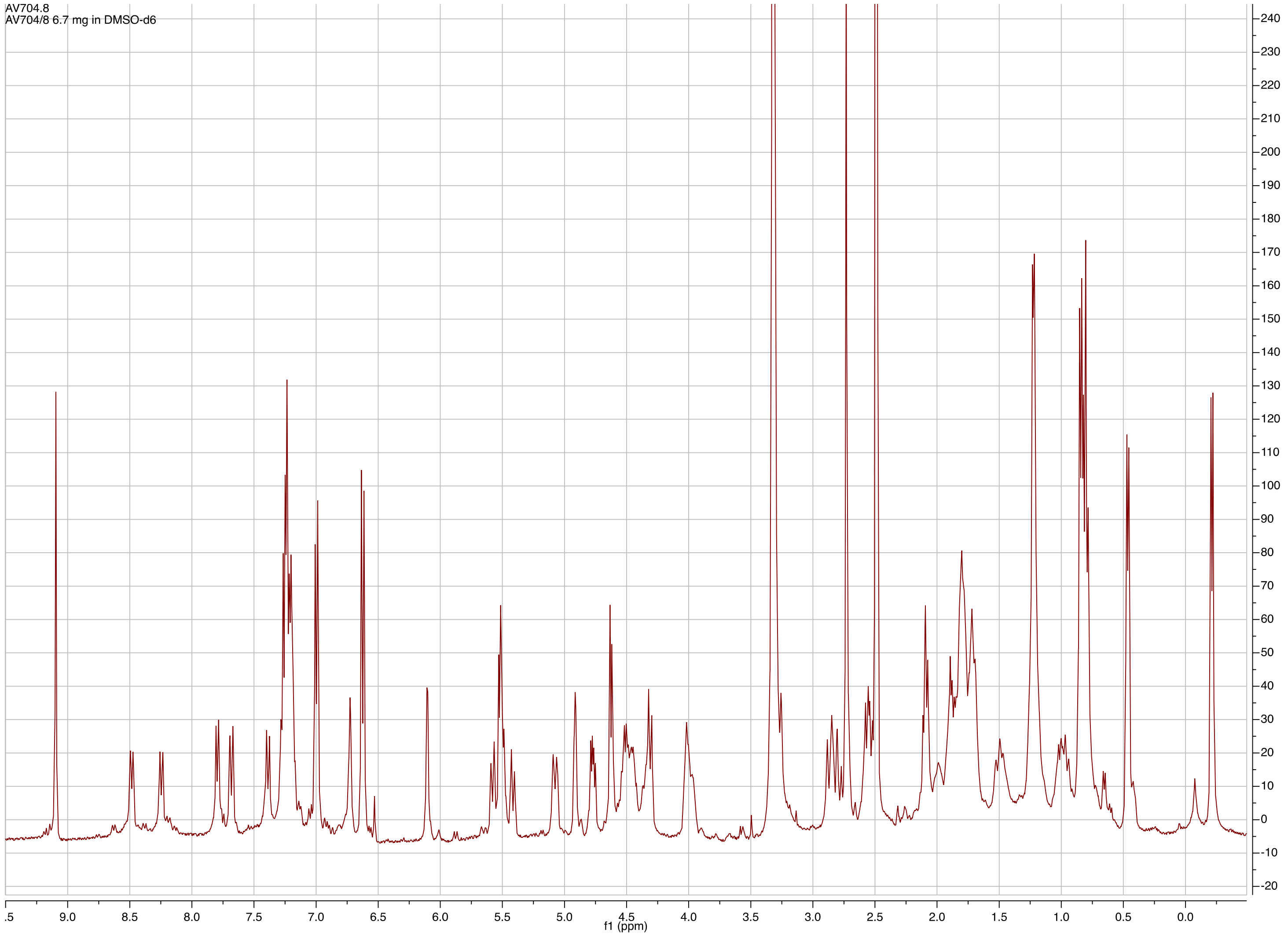


Figure S87. ^{1}H NMR Spectrum (400 MHz) of Micropeptin KB1046 (**13**) in DMSO-d_6.

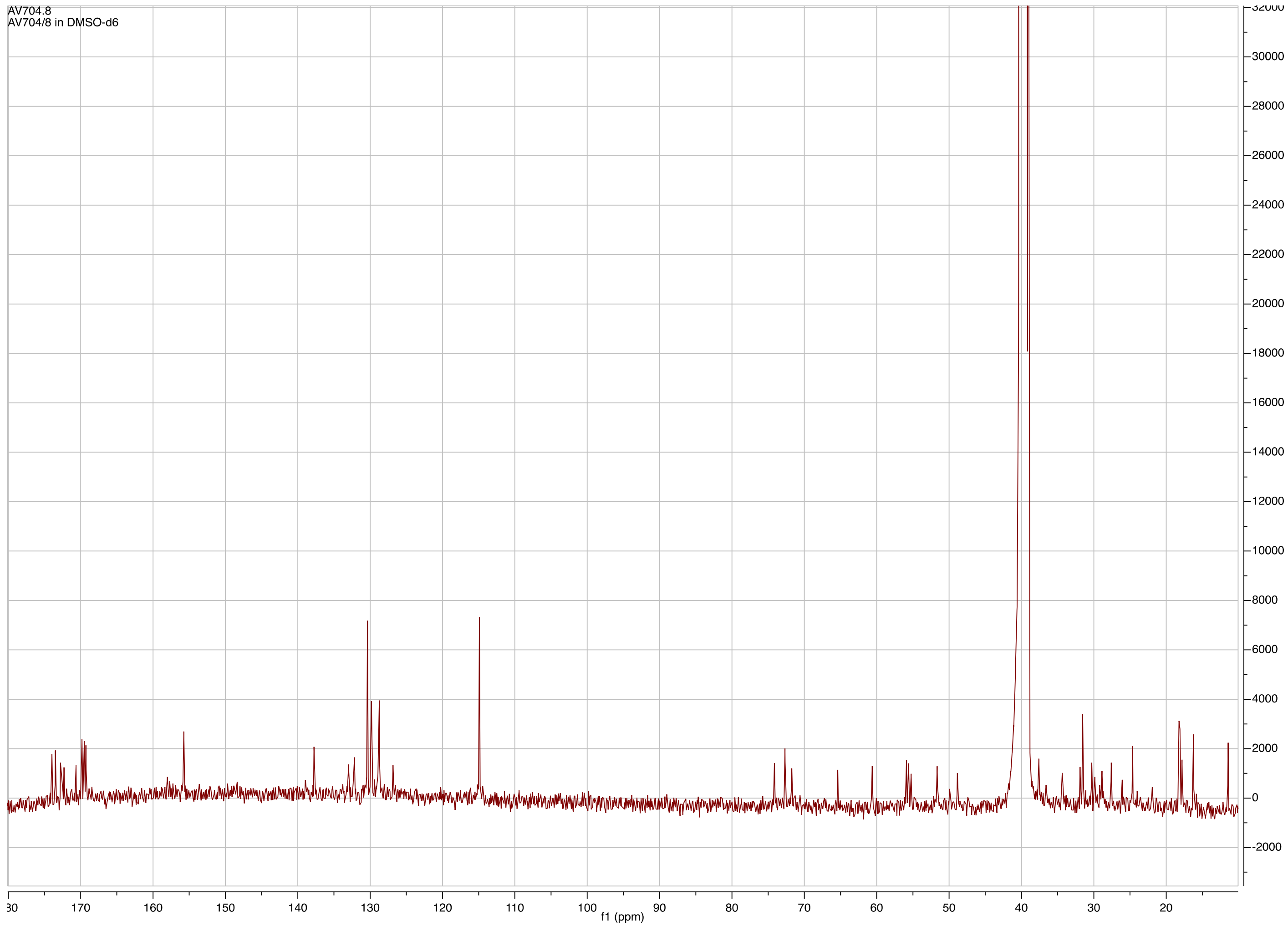


Figure S88. ^{13}C NMR Spectrum (100 MHz) of Micropeptin KB1046 (**13**) in DMSO-d_6.

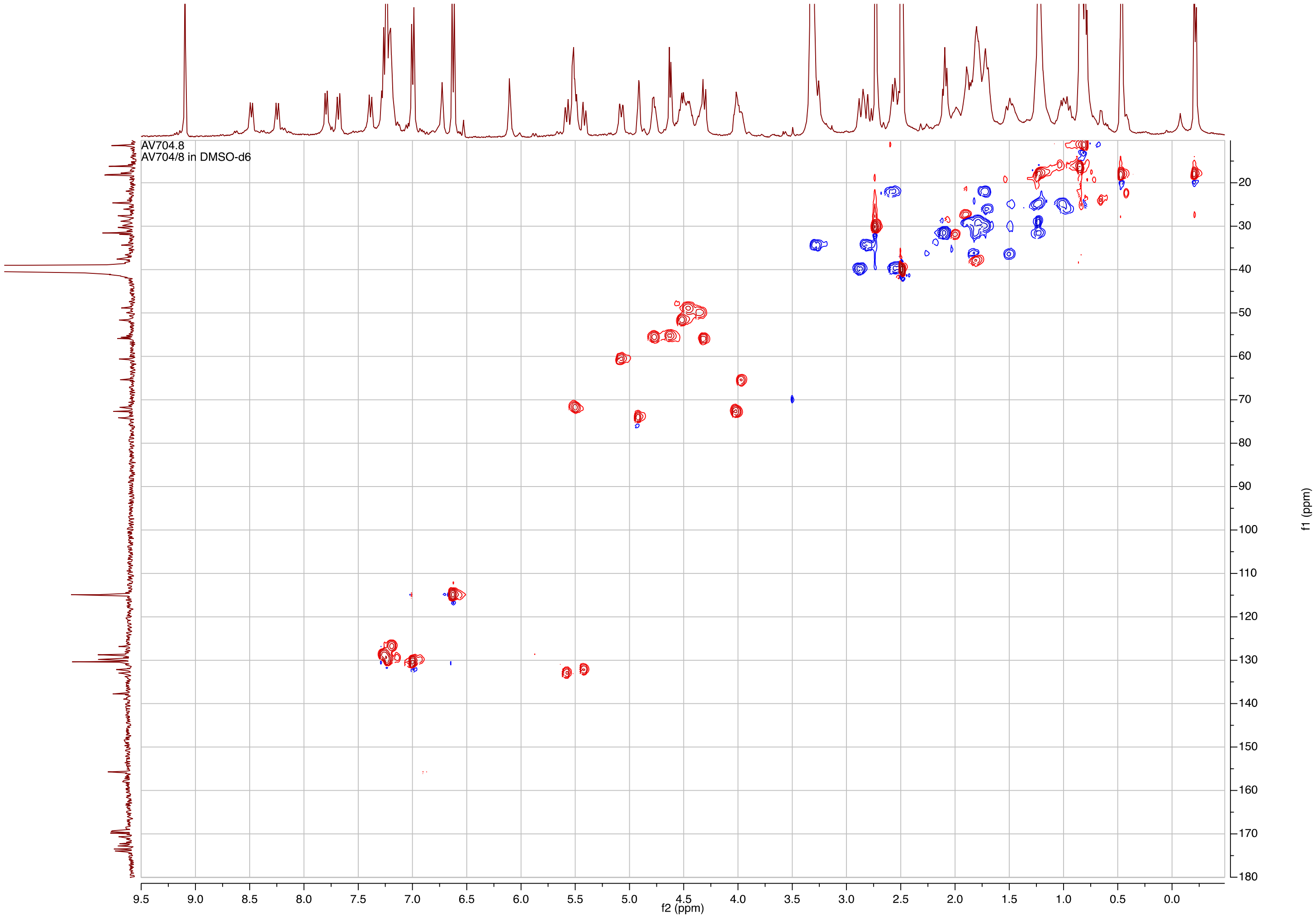


Figure S89. HSQC Spectrum of Micropeptin KB1046 (**13**) in DMSO-d_6 (Red: CH, CH_3; Blue: CH_2).

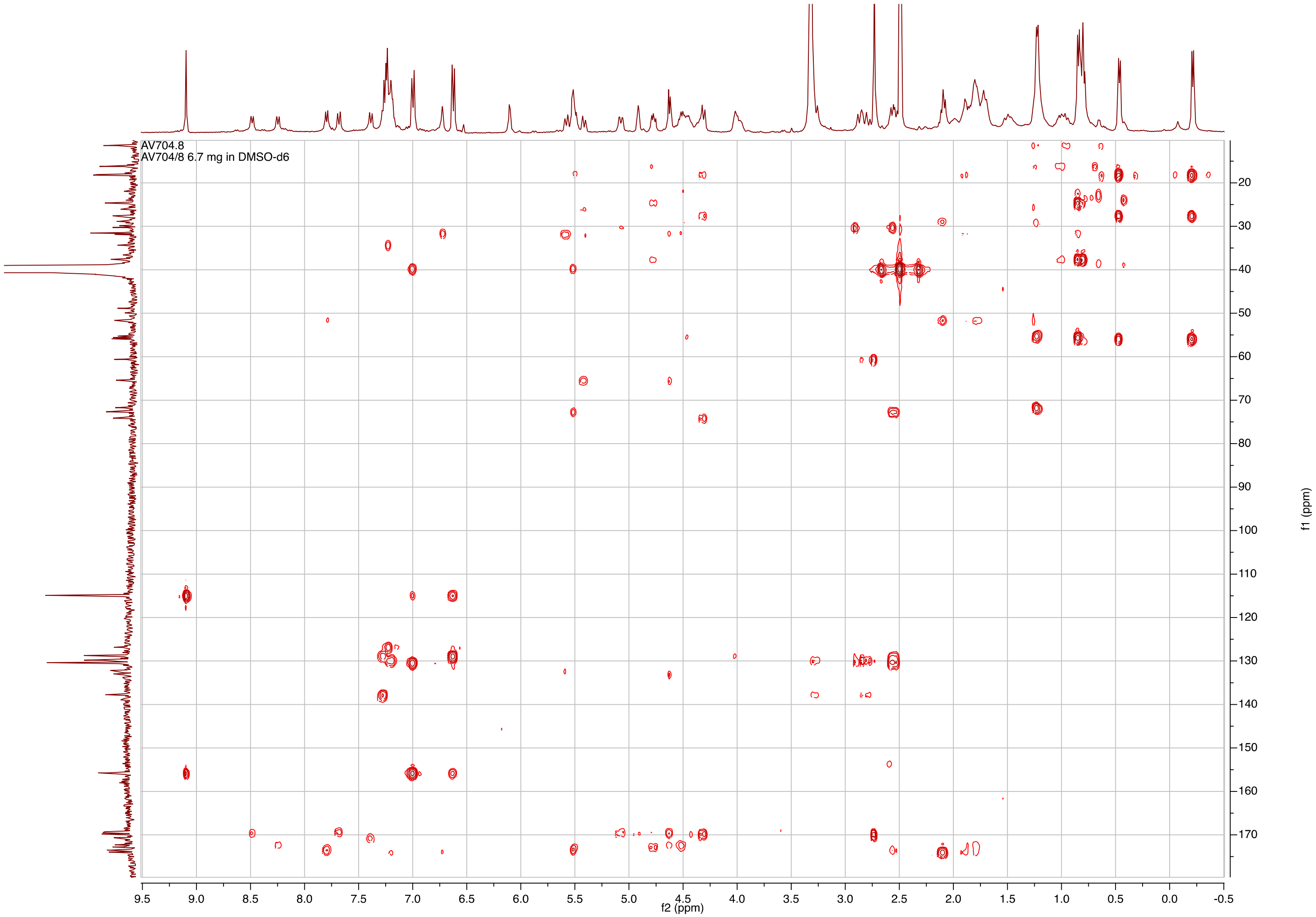


Figure S90. HMBC Spectrum of Micropeptin KB1046 (**13**) in DMSO-d_6.

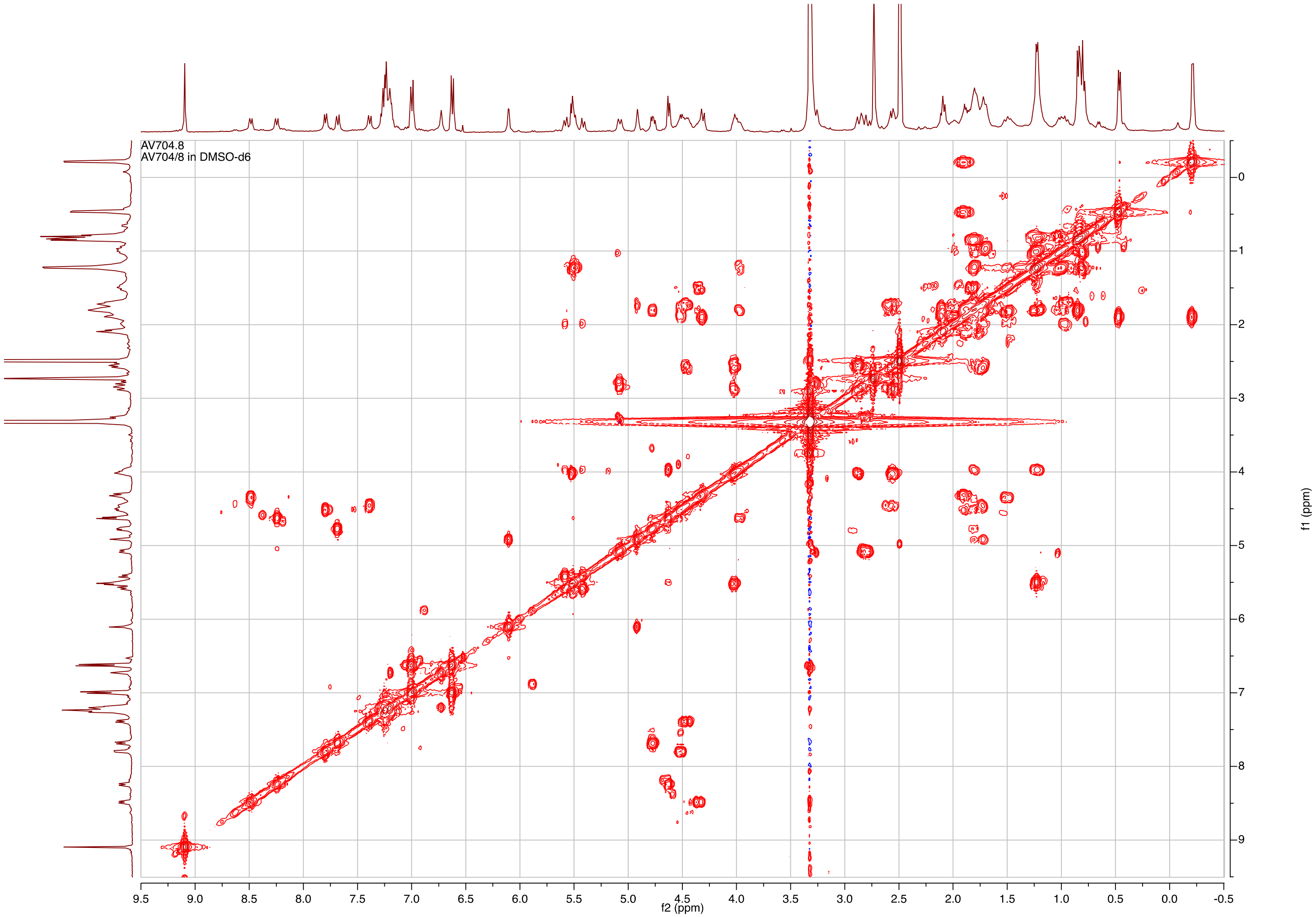


Figure S91. COSY Spectrum of Micropeptin KB1046 (**13**) in DMSO-d_6.

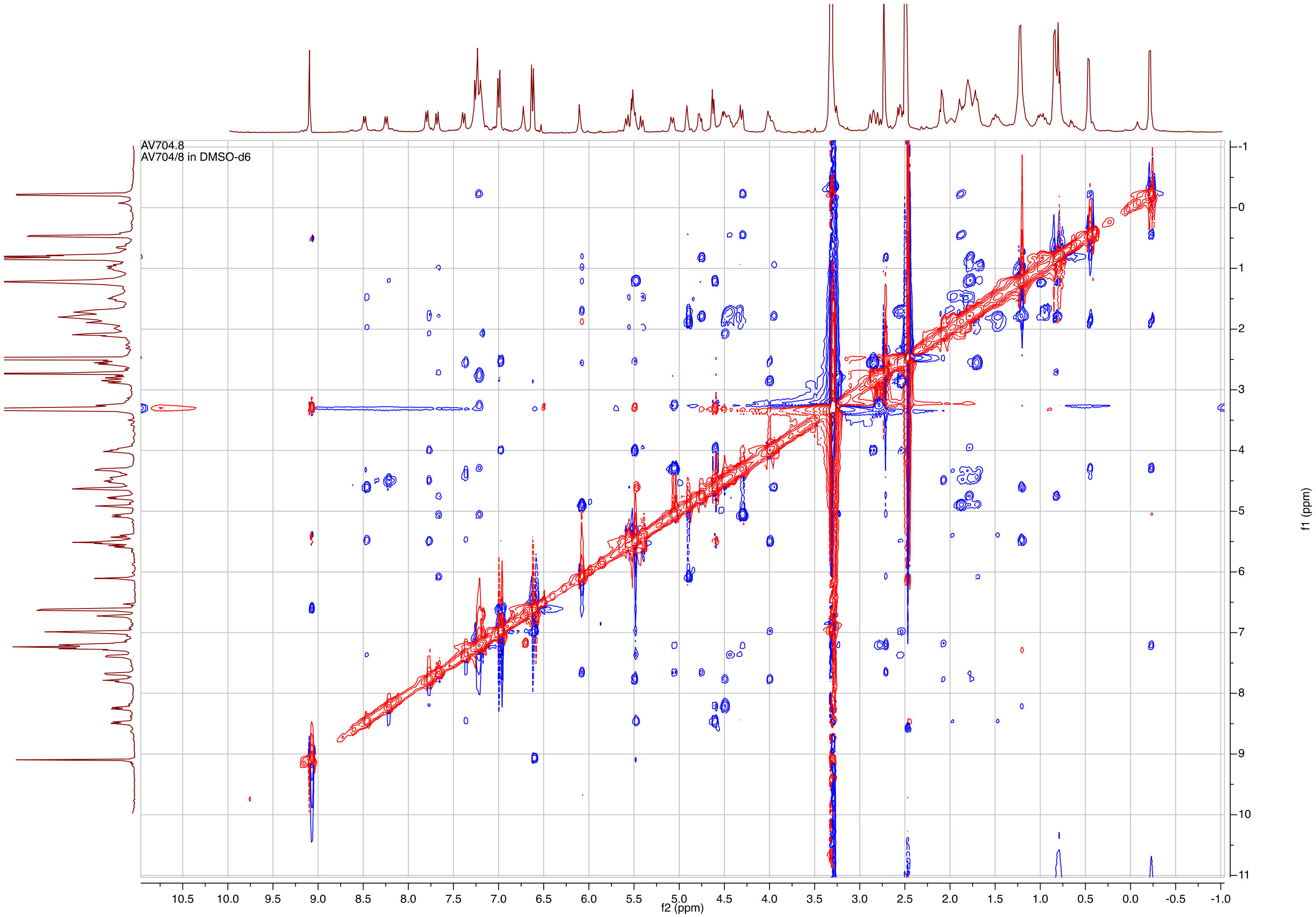


Figure S92. ROESY Spectrum of Micropeptin KB1046 (**13**) in DMSO-d_6 (Blue: NOE correlation).

Table S13. NMR Data of Micropeptin KB1046 (**13**) in DMSO-d_6.

Position	δ_C mult. [b]	δ_H mult.[b] *J* in Hz	HMBC Correlations [c]	NOE Correlations [d]
[1]Hpla 1	173.6, qC	-		
2	72.7, CH	4.01, ddd (8.7,5.6,2.4)	Hpla-1,4	Hpla-3a,3b,5,5′; Gln-*N*H, Thr-2
3 ab	39.8, CH_2	2.87, dd (13.6,2.4) 2.55, m	Hpla-4,5,5′ Hpla-1,2,4,5,5′	Hpla-2,3b,6,6′; Gln-*N*H Hpla-2,3a,5,5′; Gln-3b
4	128.8, qC			
5,5′	130.4, CH	7.00, d (7.6)	Hpla-3,6,6′,7	Hpla-2,3b,6,6′; Gln-4
6,6′	115.0, CH	6.62, d (7.6)	Hpla-4,7	Hpla-3a,3b,5,5′,7-*O*H
7	155.8, qC	-		
2-*O*H	-	5.52, d (5.6)	Hpla-1,2,3	
7-*O*H	-	9.06, s	Hpla-6,6′	Hpla-6,6′
[2]Gln 1	172.4, qC	-		
2	51.4, CH	4.51, dt (8.4,74.8)	Gln-1,3,4	Gln -3a,3b,4,*N*H; Thr-*N*H
3 ab	28.9, CH_2	1.82, m 1.75, m	Gln-5 Gln-2	Gln-2,4,*N*H Gln-2,4,*N*H; Hpla-3b; Thr-4
4	31.6, CH_2	2.10, t (5.6)	Gln-2,5	Gln-2,3a,3b,*N*H,*N*H_2(a); Hpla-5,5′
5	174.0, qC	-		
*N*H		7.78, d (8.4)	Hpla-1	Gln-2,3a,3b,4; Hpla-2,3a
NH_2 ab	-	7.18, s 6.70, s	Gln-4	Gln-4,*N*H_2(b) Gln-*N*H_2(a)
[3]Thr 1	169.1, qC	-		
2	55.0, CH	4.58, d (9.5)	Thr-1,4	Thr-4, HcAla-*N*H; [8]Ile-4a,4b,5
3	72.2, CH	5.50, q (6.5)	Thr-4; [8]Ile-1	Thr-4,*N*H; HcAla-*N*H; Ahp-*N*H; [8]Ile-5
4	17.9, CH_3	1.18, d (6.5)	Thr-2,3	Thr-3,*N*H; Hpla-6,6′
*N*H	-	7.68, d (9.5)	Gln-1	Thr-2,3,4; Gln-2,3a,3b,4

Table S13. *Cont.*

[4]HcAla 1	170.7, qC	-		
2	50.0, CH	4.33, m		HcAla-3b,4,NH; Ahp-*N*H
3 ab	36.6, CH_2	1.89, m		HcAla-3b,5,6
		1.49, m		HcAla-2,3a,4,5,6,*N*H
4	32.0, CH_2	1.99, m		HcAla-2,3b,5,6,8pax,9peq,*N*H
5	132.2, CH	5.42, brd (10.4)	HcAla-3,4,7,9	HcAla-3a,3b,4,6,7
6	133.0, CH	5.58, brd (10.4)	HcAla-4,5,8	HcAla-3a,3b,4,5,7,*O*H
7	65.5 CH	3.97, m		HcAla-5,6,8peq,9pax,*O*H
8 peq pax	31.6 CH_2	1.80, m		HcAla-7,8pax,9pax
		1.20, m		HcAla-4,8peq,9peq,*O*H
9 peq pax	26.2 CH_2	1.70, m		HcAla-4,8pax,9pax
		0.96, m		HcAla-7,8peq,9peq
*N*H		8.47, d (8.4)	Thr-1	HcAla-2,3b,4; Thr-3; Ahp-*N*H
*O*H		4.63, d (5.6)	HcAla-6,7,8	HcAla-6,7,8pax
[5]Ahp 2	169.6, qC	-		
3	48.9, CH	4.45 m	Ahp-2	Ahp-5,*N*H
4 ab	22.0, CH_2	2.55, m		Ahp-4b,*N*H,*O*H
		1.72, m		Ahp-4a,6
5	29.9, CH_2	1.71, m		Ahp-3,6
6	74.2, CH	4.92, brs		Ahp-4b,5,*O*H; [6]Val-3,4
*N*H	-	7.37, d (9.2)	HcAla-1	Ahp-3,4a; Thr-3; HcAla-2,*N*H
*O*H	55.6, CH_3	6.07, brs	Ahp-6	Ahp-4a,5
[6]Val 1	169.9, qC	-		
2	56.0, CH	4.32, d (10.4)	Ahp-2,6; [6]Val-1,3,4,5	[6]Val-3,4,5; *N*MePhe-2,5,5′
3	27.7, CH	1.90, m	[6]Val-2,5	[6]Val-2,4,5; Ahp-3,6
4	18.3, CH_3	0.46, d (6.0)	[6]Val-2,3,5	[6]Val-2,3,5; Ahp-3,6; *N*MePhe-2
5	18.2, CH_3	-0.21, d (6.0)	[6]Val-2,3,4	[6]Val-2,3,4; *N*MePhe-2,5,5′

Table S13. *Cont.*

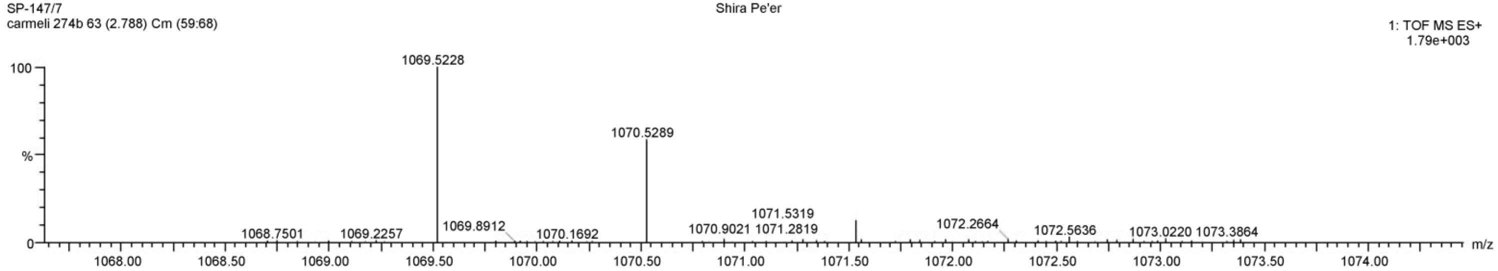
[7]*N*MePhe 1	169.3, qC	-		
2	60.7, CH	5.08, brd (11.2)	*N*MePhe-1,*N*Me	*N*MePhe-3a,3b,5,5′,*N*Me; [6]Val-2; [8]Ile-*N*H
3 ab	34.4, CH_2	3.28, m	*N*MePhe-4,5,*N*Me	*N*MePhe-2,3b,5,5′
		2.80, m	*N*MePhe-2,4,5,*N*Me	*N*MePhe-2,3a,5,5′
4	137.8, qC	-		
5,5′	129.9, CH	7.22, m	*N*MePhe-3,7	*N*MePhe-2,3a,3b,6,6′,*N*Me; [6]Val-2
6,6′	128.8, CH	7.26, m	*N*MePhe-4,5,5′	*N*MePhe-5,5′,7,*N*Me; [6]Val-5
7	126.7, CH	7.19, m	*N*MePhe-5,5′	*N*MePhe-6,6′; [6]Val-5
*N*Me	30.3, CH_3	2.73, s	[6]Val-1, *N*MePhe-2	*N*MePhe-2,5,5′; [8]Ile-6,*N*H
[8]Ile 1	172.9, qC	-		
2	55.7, CH	4.77, dt (9.2,4.8)	[8]Ile-1,3,4,6	[8]Ile-3,5,6,*N*H
3	37.7, CH	1.80, m		[8]Ile-2,4a,4b,,5,*N*H
4	24.7, CH	1.26, m	[8]Ile-2,5,6	[8]Ile-3; Thr-2
		1.00, m	[8]Ile-5,6	[8]Ile-3,5; Thr-2
5	11.5, CH_3	0.80, t (7.2)	[8]Ile-3,4	[8]Ile-2,3,4a; Thr-2,3
6	16.3 CH_3	0.83, d (6.8)	[8]Ile-2,3,4a	[8]Ile-2; *N*MePhe-*N*Me
*N*H	-	7.67, d (9.2)	*N*MePhe-1	[8]Ile-2,3; Thr-2; *N*MePhe-2,*N*Me

[a] 100 MHz for carbons and 400 MHz for protons; [b] Multiplicity and assignment from HSQC experiment; [c] Determined from HMBC experiment, $^{n}J_{CH}$ = 8 Hz, recycle time 1 s; [d] Selected NOE's from ROESY experiment.

Elemental Composition Report

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
437 formula(e) evaluated with 11 results within limits (up to 4 best isotopic matches for each mass)
Elements Used:
C: 50-60 H: 60-80 N: 0-20 O: 10-20 23Na: 0-1



Minimum:				-1.5			
Maximum:		5.0	10.0	50.0			

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
1069.5228	1069.5233	-0.5	-0.5	18.5	153.0	1.3	C54 H77 N4 O18
	1069.5236	-0.8	-0.7	25.5	153.1	1.4	C54 H70 N12 O10 23Na
	1069.5222	0.6	0.6	20.5	153.1	1.4	C53 H74 N8 O14 23Na
	1069.5246	-1.8	-1.7	23.5	153.2	1.5	C55 H73 N8 O14

Figure S93. HR ESI MS data of Micropeptin KB1046 (**13**).