Table S1: ^{1}H and ^{13}C chemical shifts for cupiennin 1a in TFE/H_2O.

Residue	**Chemical shift (ppm)**				
	NH	**α-CH**	**β-CH**	**Other H**	**α-C**
Gly1	n.o*.	3.96, 3.85			42.1
Phe2	8.63	4.64	3.22, 3.11	H2, H6 7.30	58.2
				H3, H5 7.39	
				H4 7.36	
Gly3	8.57	4.03, 3.95			45.5
Ala4	8.00	4.25	1.56		53.8
Leu5	7.68	4.33	1.81	γ-CH 1.72	56.5
				δ-CH_3 1.05, 0.97	
Phe6	8.01	4.35	3.28, 3.19	H2, H6 7.29	60.0
				H3, H5 7.41	
				H4 7.37	
Lys7	7.96	4.08	2.03, 1.94	γ-CH_2 1.52, 1.42	58.4
				δ-CH_2 1.79	
				ε-CH_2 3.07	
				ε-NH_3^+ n.o.	
Phe8	7.93	4.43	3.43, 3.35	H2, H6 7.36	59.7
				H3, H5 7.40	
				H4 7.30	
Leu9	8.53	4.07	1.92, 1.69	γ-CH_2 1.96	56.9
				δ-CH_3 1.01	
Ala10	8.42	4.01	1.44		54.2
Lys11	7.70	4.13	2.06	γ-CH_2 1.62	58.0
				δ-CH_2 1.96	
				ε-CH_2 3.06	
				ε-NH_3^+ n.o.	
Lys12	7.94	4.07	2.03	γ-CH_2 1.43	58.1
				δ-CH_2 1.92	
				ε-CH_2 3.04	
				ε-NH_3^+ n.o.	
Val13	8.72	3.67	2.27	γ-CH_3 1.13, 1.02	66.1
Ala14	8.30	4.11	1.63		54.7
Lys15	8.19	4.15	2.08, 2.01	γ-CH_2 1.62	58.2
				δ-CH_2 1.79	
				ε-CH_2 3.07	
				ε-NH_3^+ n.o.	
Thr16	8.02	4.05	4.61	γ-CH_3 1.37	66.1
Val17	8.66	3.74	2.26	γ-CH_3 1.14, 1.04	65.6
Ala18	8.25	4.19	1.63		54.1

Table S1 (continued):

Residue	Chemical shift (ppm)				
	NH	**α-CH**	**β-CH**	**Other H**	**α-C**
Lys19	7.98	4.19	2.15, 2.09	γ-CH_2 1.63	58.2
				δ-CH_2 1.84	
				ε-CH_2 3.09	
				ε-NH_3^+ n.o.	
Gln20	8.13	4.26	2.36, 2.30	γ-CH_2 2.59	57.0
				δ-NH_2 7.25, 6.72	
Ala21	8.75	4.21	1.59		54.0
Ala22	8.15	4.28	1.65		53.7
Lys23	7.95	4.22	2.08	γ-CH_2 1.58	57.6
				δ-CH_2 1.83, 1.77	
				ε-CH_2 3.09	
				ε-NH_3^+ n.o.	
Gln24	8.17	4.29	2.29	γ-CH_2 2.57	56.7
				δ-NH_2 7.31, 6.74	
Gly25	8.35	4.10, 4.02			45.4
Ala26	8.03	4.28	1.58		53.6
Lys27	7.92	4.10	1.92	γ-CH_2 1.58	57.4
				δ-CH_2 1.75	
				ε-CH_2 3.06	
				ε-NH_3^+ n.o.	
Tyr28	7.86	4.46	3.35, 3.19	H2, H6 7.25	59.2
				H3, H5 6.92	
Val29	7.90	3.84	2.32	γ-CH_3 1.20, 1.06	64.3
Val30	8.20	3.90	2.20	γ-CH_3 1.14, 1.06	64.3
Asn31	8.15	4.61	2.95, 2.88	γ-NH_2 7.54, 6.73	54.6
Lys32	8.15	4.17	1.96, 1.94	γ-CH_2 1.50	57.0
				δ-CH_2 1.76	
				ε-CH_2 3.06	
				ε-NH_3^+ n.o.	
Gln33	8.31	4.27	2.28	γ-CH_2 2.53	56.8
				δ-NH_2 7.18, 6.62	
Met34	8.20	4.46	2.26	γ-CH_2 2.81, 2.68	55.7
				ε-CH_3 2.24	
Glu35	7.93	4.38	2.29, 2.19	γ-CH_2 2.68, 2.59	55.0
				$CONH_2$ 7.31, 7.00	

*n.o. indicates resonance was not observed.

Figure S1: Partial TOCSY and NOESY spectra of cupiennin 1a in TFE/H_2O. Vertical lines connect resonances of the same spin system. NOEs between sequential amide protons are indicated in the NOESY spectrum.

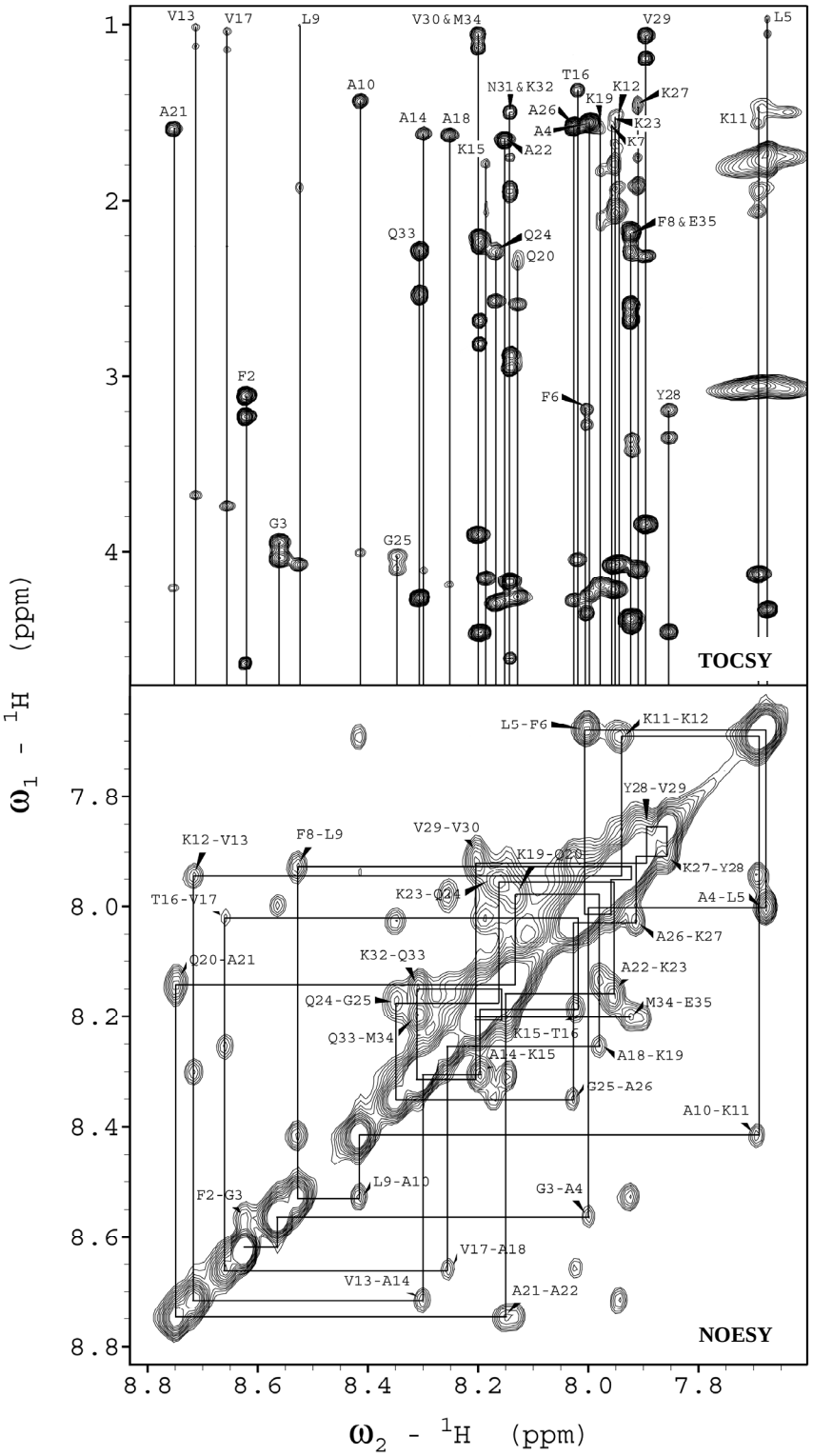


Figure S2: αH-αC region of the HSQC spectrum of cupiennin 1a in TFE/H_2O.

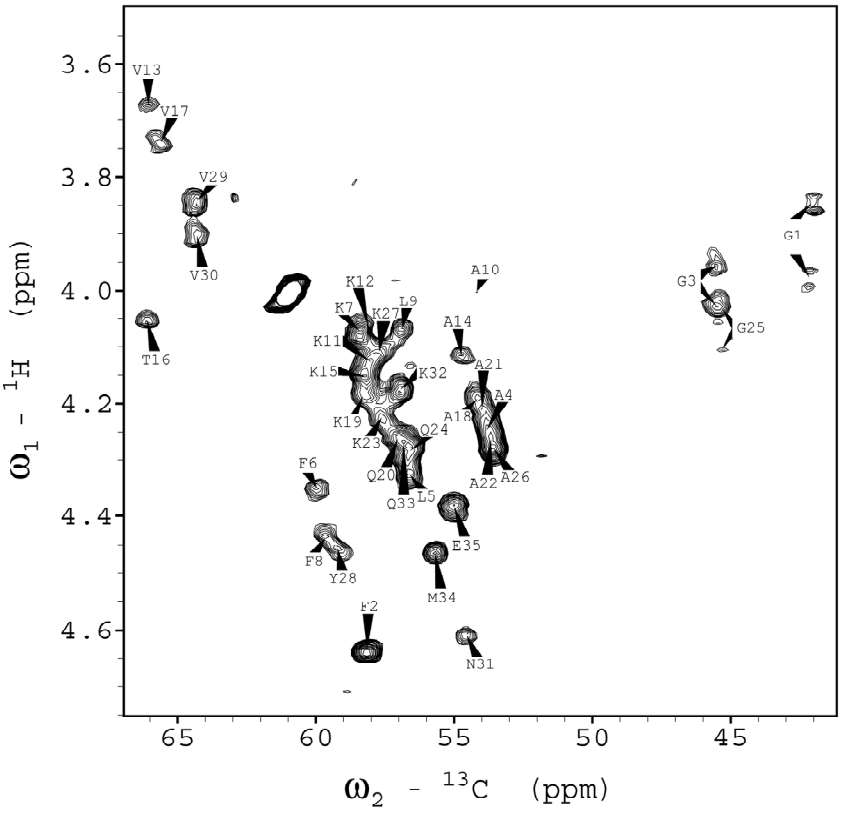


Figure S3: Ramachandran plot for cupiennin 1a in TFE/H_2O (1:1 v/v). Favourable regions for α-helices are labelled A, allowable and generous regions are labelled a and ~a, respectively. Gly residues are indicated by ▲, remaining residues are indicated by ●, and well-defined residues are indicated by filled symbols.

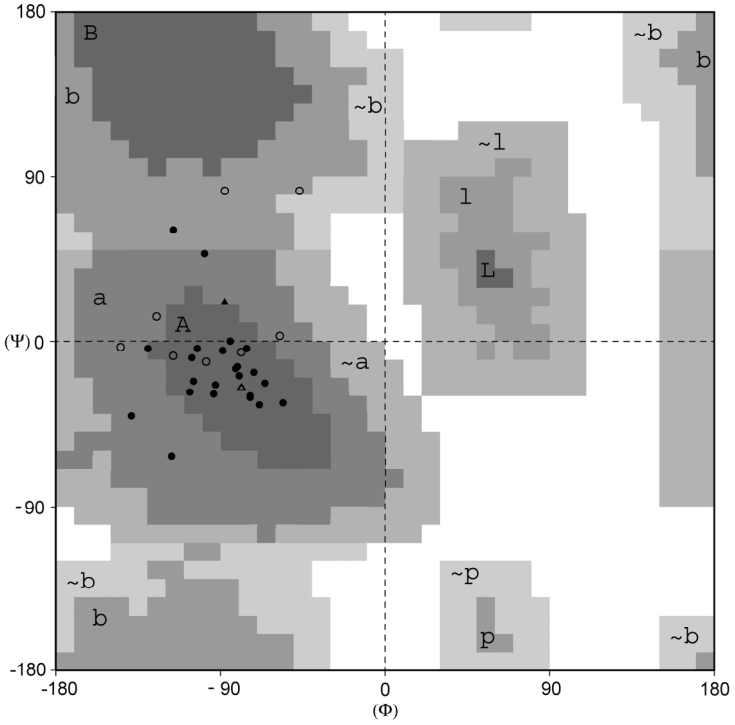


Figure S4: Plot of the angular order parameters Sϕ (black) and Sψ (grey) for the individual residues of cupiennin 1a in TFE/H_2O (1:1 v/v).

