

SUPPLEMENTARY MATERIAL

The Single Disulfide-Directed β -Hairpin Fold. Role of Disulfide Bond in Folding and Effect of an Additional Disulfide Bond on Stability

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Table S1. Chemical shifts for contryphan-Vc1₁₋₂₂[Q1C, Y9C]) at pH 4.0, 313K

Residue	H ^N	H ^{α}	H ^{β}	N	other
Cys1	ND	4.42	3.40,3.54	ND	
Trp2	8.90	4.96	3.44,3.37	126.2	H ^{δ1} 7.45 H ^{ϵ1} 10.19 H ^{ϵ3} 7.80 q H ^{γ2} 7.63q H ^{γ3} 7.67 q N ^{ϵ} 129.2
Cys3	8.17	4.95	2.66,3.25	121.2	
Gln4	8.67	4.48	1.96,2.31	121.6	H ^{γ} 2.42,2.50 H ^{ϵ} 7.31,7.41 N ^{ϵ} 111.9
Pro5	-	4.57	2.55,2.09	-	H ^{γ} 2.39, 2.25; H ^{δ} 3.86, 4.03
Gly6	8.91	4.49,3.76	-	111.7	
Tyr7	8.23	5.14	2.76,3.43	120.1	H ^{δ} 6.95; H ^{ϵ} 6.94
Ala8	9.34	4.79	1.53	122.7	
Cys9	8.91	4.81	3.21,3.34	120.4	
Asn10	9.04	5.36	3.18	127.4	H ^{δ2} 7.53, 8.05 N ^{δ2} 114.9
Pro11	-	4.56	2.51	-	H ^{γ} 2.25 ; H ^{δ} 4.22,4.12
Val12	7.89	4.1	2.33	118.7	H ^{γa} 1.14; H ^{γb} 1.22
Leu13	7.47	4.57	1.81		H ^{γ} 1.66 H ^{δa} 1.09
Gly14	8.70	3.99,4.21	-	107.6	
Ile15	7.01	4.85	2.10	111.8	H ^{γ1} 1.54; H ^{γ} 1.17; H ^{δ1} 1.10
Cys16	8.86	5.42	2.96,3.17	122.1	
Thr17	9.42	5.04	4.45	117.1	H ^{γ2} 1.43
Ile18	8.63	3.89	1.65	124.9	H ^{γ1} 0.94 ; H ^{γ2} 1.34; H ^{δ1} 0.86
Thr19	8.24	4.51	4.21	119.6	H ^{γ2} 1.28
Leu20	8.32	4.56	1.78	125.6	H ^{δa} 1.06; H ^{δb} 1.04

Ser21	8.41	4.61	4.03	117.0	
Arg22	8.46	4.53	1.95,2.09	123.7	H ^γ 1.51; H ^δ 3.40; H ^ε 7.34; N ^ε 117.1
NH ₂	7.7,7.3			107.7	

ND- not determined

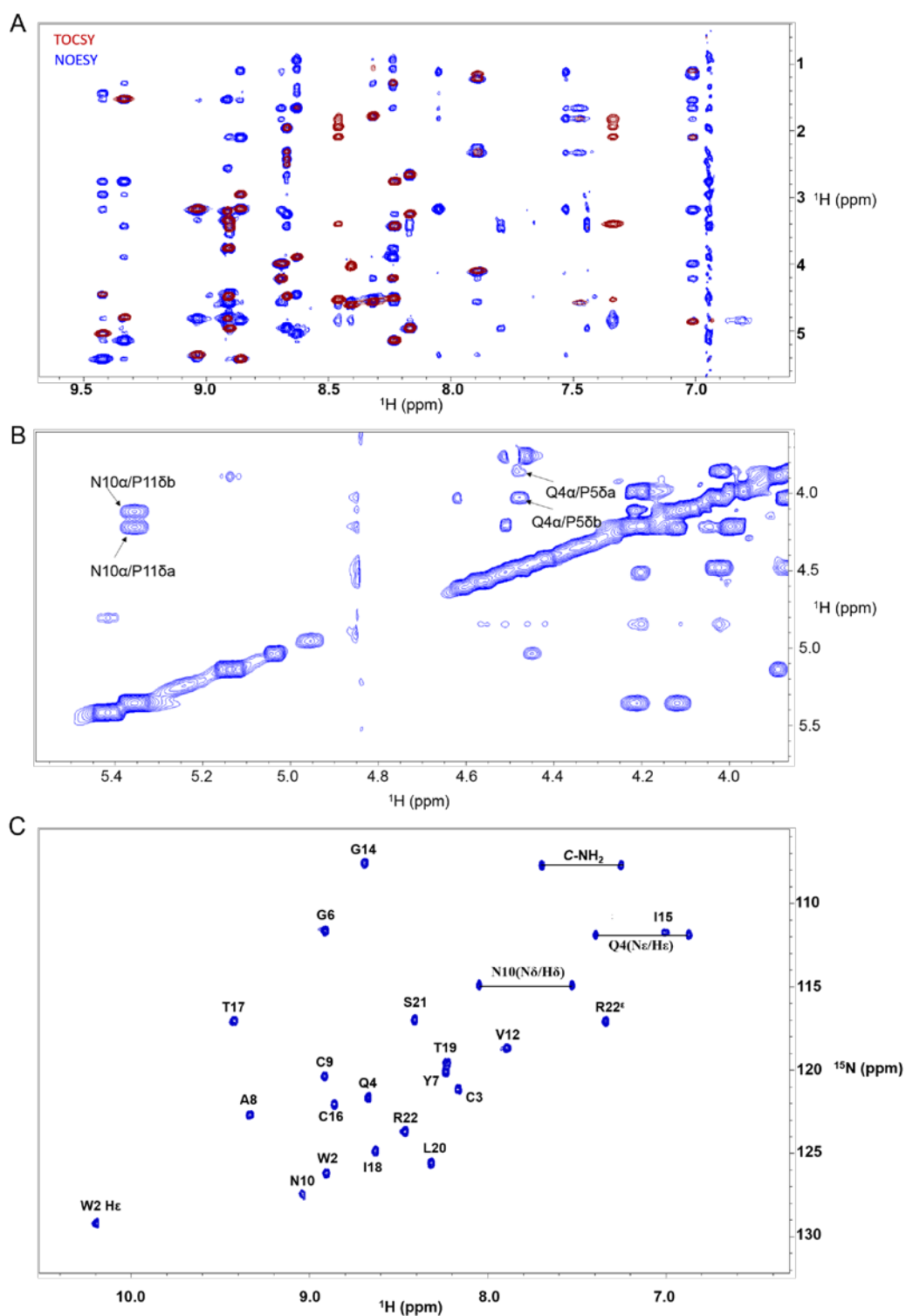


Figure S1 **A.** Overlay of two-dimensional ^1H NMR spectra TOCSY and NOESY of contryphan-Vc1₁₋₂₂[Q1C, Y9C] recorded at 40°C. **B.** Region of two-dimensional NOESY spectra showing Gln4 $^\alpha$ - Pro5 $^\delta$ and Asn10 $^\alpha$ - Pro11 $^\delta$ cross peaks, suggesting that both prolines are in the *trans* conformation. **C.** ^{15}N -HSQC spectra of 1 mM contryphan-Vc1₁₋₂₂[Q1C, Y9C] at pH 4.0 and 40°C in water containing 7% $^2\text{H}_2\text{O}$.

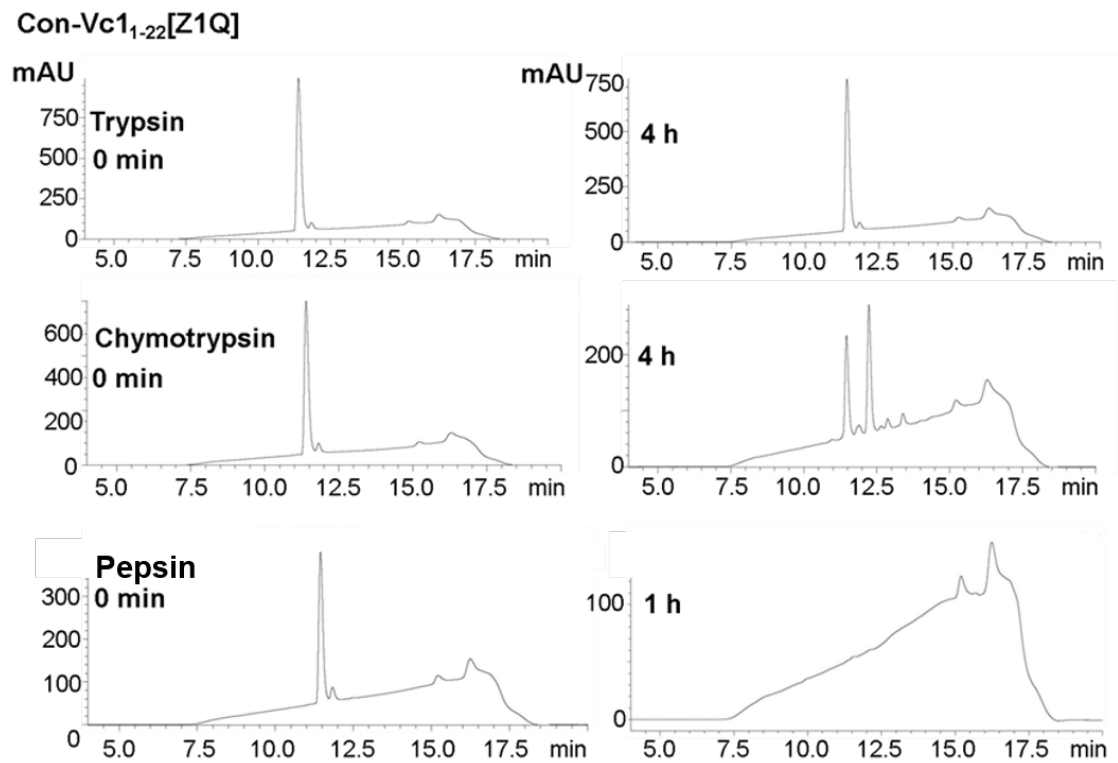


Figure S2 Reversed-phase HPLC analyses of rCon-Vc1₁₋₂₂[Z1Q] treated with trypsin, α -chymotrypsin and pepsin. Details are given under Proteolysis Assays in the Experimental.