

Table A. NMR Resonance Assignments^a of hU-II(4-11) in SDS-d₂₅ 200mM solution.

residue	NH (³ J _{αN} , exc, -Δδ/ΔT) ^b	C ^α H (C ^α)	C ^β H	Others
Asp 4		4.41 (52.8)	2.81	
Cys 5	8.57 (8.6, f, 6.5)	5.43 (56.5)	3.01, 2.93	
Phe 6	9.01 (7.9, ms, 2.7)	4.61 (57.5)	3.11, 3.00	7.23(δ); 7.27(ε)
Trp 7	8.64 (4.9, f, 7.0)	4.30 (58.2)	3.72, 3.00	7.27 (δ); 10.17,7.62 (ε); 7.55,7.18 (ζ); 7.24(η)
Lys 8	6.48 (6.1, ms, -0.8)	3.98 (56.4)	1.15, 0.87	0.18,-0.16(γ); 1.07,1.00 (δ); 2.54,2.45 (ε);
Tyr 9	8.02 (8.1, s, 2.5)	4.74 (57.7)	3.10, 2.90	7.13(δ); 6.73(ε)
Cys 10	8.33 (8.5, f, 6.8)	5.24 (55.9)	2.99, 2.92	
Val 11	8.32 (7.5, f, 3.4)	4.37 (61.6)	2.25	1.01(γ)

^aObtained at 300K, pH = 5.5, with TSP (δ 0.00 ppm) as reference shift. Chemical shifts are accurate to ±0.02 ppm for ¹H NMR and to ±0.1 ppm for ¹³C NMR resonances. ^b ³J_{αN} coupling constants in Hz. exc = NH exchange rate (f, fast; ms, moderately slow; s, slow; vs, very slow). -Δδ/ΔT = temperature coefficients (ppb/K).

Table B. ^1H NMR Resonance Assignments^a of Peptide hU-II,^b in SDS-d₂s 200mM solution.

residue	NH ($^3J_{\alpha\text{N}}$, exc, $-\Delta\delta/\Delta T$) ^c	C ^{α} H	C ^{β} H	Others
Glu 1		4.16	2.15	2.54(γ)
Thr 2	8.62 (7.2, f, 7.1)	4.61	4.11	1.28(γ)
Pro 3		4.46	2.29,1.90	2.00(γ); 3.83,3.68(δ)
Asp 4	8.27 (6.1, f, 7.2)	4.67	2.90	
Cys 5	7.84 (8.5, f, 5.8)	5.43	2.94	
Phe 6	8.95 (7.9, ms, 2.7)	4.60	3.08, 2.98	7.22(δ); 7.26(ϵ)
Trp 7	8.60 (4.7, f, 6.9)	4.29	3.70, 2.96	7.25(δ); 10.17,7.60(ϵ); 7.55,7.18(ζ); 7.25(η)
Lys 8	6.47 (6.3, ms, -0.9)	4.00	1.14, 0.86	0.12,-0.23(γ); 1.04,0.98(δ); 2.51,2.42(ϵ); 7.24(ζ)
Tyr 9	8.05 (8.1, s, 2.5)	4.76	3.06,2.87	7.12(δ); 6.73(ϵ)
Cys 10	8.27 (8.5, f, 6.8)	5.34	2.92	
Val 11	8.50 (7.5, f, 3.5)	4.35	2.30	1.05(γ)

^a Obtained at 300K, pH = 5.5, with TSP (δ 0.00 ppm) as reference shift. Chemical shifts are accurate to ± 0.02 ppm. ^b Most populated conformer. ^c $^3J_{\alpha\text{N}}$ coupling constants in Hz. exc = NH exchange rate (f, fast; ms, moderately slow; s, slow; vs, very slow). $-\Delta\delta/\Delta T$ = temperature coefficients (ppb/K).

Table C. ^1H NMR Resonance Assignments^a of Peptide **hU-II**,^b in SDS-d₂₅ 200mM solution.

residue	NH ($^3J_{\alpha\text{N}}$, exc, $-\Delta\delta/\Delta T$) ^c	C $^{\alpha}$ H	C $^{\beta}$ H	Others
Glu 1		4.19	2.15	2.52(γ)
Thr 2	8.49 (7.3, f, 7.1)	4.55	4.18	1.27(γ)
Pro 3		4.46	2.33,1.90	2.05(γ); 3.80,3.55(δ)
Asp 4	8.42 (7.4, f, 7.3)	4.53	2.82	
Cys 5	7.81 (7.1, f, 6.4)	4.35	2.82	
Phe 6	7.68 (7.4, f, 6.2)	4.46	3.05, 2.97	7.17(δ); 7.25(ϵ)
Trp 7	7.38 (6.7, f, 7.0)	4.60	3.26, 3.15	7.22(δ); 9.96,7.47(ϵ); 7.44,7.06(ζ); 7.14(η)
Lys 8	7.34 (6.5, f, 6.0)	4.00	1.36, 1.28	0.81(γ); 1.44(δ); 2.82(ϵ); 7.32(ζ)
Tyr 9	7.13 (7.2, f, 5.9)	4.46	3.03,2.59	6.94(δ); 6.74(ϵ)
Cys 10	8.32 (7.2, f, 7.9)	5.36	2.92	
Val 11	8.58 (7.3, f, 5.5)	4.36	2.30	1.09(γ)

^aObtained at 300K, pH = 5.5, with TSP (δ 0.00 ppm) as reference shift. Chemical shifts are accurate to ± 0.02 ppm. ^b Less populated conformer. ^c $^3J_{\alpha\text{N}}$ coupling constants in Hz. exc = NH exchange rate (f, fast; ms, moderately slow; s, slow; vs, very slow). $-\Delta\delta/\Delta T$ = temperature coefficients (ppb/K).

Table D. ^1H NMR Resonance Assignments^a of Peptide **hU-II**, in $\text{H}_2\text{O}/\text{D}_2\text{O}$ 90:10 solution.

residue	NH ($^3J_{\alpha\text{N}}$, exc, $-\Delta\delta/\Delta T$) ^b	C^αH	C^βH	Others
Glu 1		4.16	2.15	2.50(γ)
Thr 2	8.75 (6.9, f, 6.8)	4.65	4.17	1.28(γ)
Pro 3		4.36	2.30	2.01,1.90(γ); 3.87,3.73(δ)
Asp 4	8.49 (7.1, f, 6.5)	4.51	2.82,2.76	
Cys 5	7.96 (7.6, f, 6.6)	4.50	3.15,2.87	
Phe 6	7.94 (7.2, f, 6.8)	4.53	2.90, 2.69	6.99(δ); 7.23(ϵ)
Trp 7	7.50 (7.4, f, 6.0)	4.73	3.33, 3.10	7.21(δ); 10.25,7.59(ϵ); 7.54,7.21(ζ); 7.30(η)
Lys 8	7.75 (6.0, f, 6.7)	3.94	1.51	0.99,0.90(γ); 1.48(δ); 2.85(ϵ);
Tyr 9	7.60 (7.2, f, 6.9)	4.64	3.13,3.00	7.12(δ); 6.81(ϵ)
Cys 10	7.90 (7.6, f, 6.1)	4.55	3.21,3.02	
Val 11	Not observed ^c	4.16	2.16	0.94(γ)

^aObtained at 300K, pH = 5.5, with TSP (δ 0.00 ppm) as reference shift. Chemical shifts are accurate to ± 0.02 ppm. ^b $^3J_{\alpha\text{N}}$ coupling constants in Hz. exc = NH exchange rate (f, fast; ms, moderately slow; s, slow; vs, very slow). $-\Delta\delta/\Delta T$ = temperature coefficients (ppb/K). ^cThis signal was not observed probably due to chemical exchange.

Table E. NMR Resonance Assignments^a of Peptide **PSU**, in SDS-d₂₅ 200mM solution.

residue	NH (³ J _{αN} , exc, -Δδ/ΔT) ^b	C ^α H	C ^β H	Others
Asp 4		4.42 (52.2)	2.66	
Pen 5	8.47 (9.2, f, 6.2)	5.05 (61.9)		1.23, 1.08(γ)
Phe 6	9.18 (8.2, s, 2.5)	4.65 (56.6)	3.10, 3.01	7.21(δ); 7.25(ε)
Trp 7	8.80 (4.6, f, 6.4)	4.25 (59.2)	3.81, 3.14	7.26(δ); 10.13, 7.62(ε); 7.54, 7.17(ζ); 7.24(η)
Lys 8	6.60 (6.0, f, -1.0)	4.06 (55.8)	1.19, 0.82	0.25, -0.15(γ); 1.08, 1.00(δ); 2.53, 2.41(ε); 7.23(ζ)
Tyr 9	8.15 (8.4, s, 2.4)	4.82 (57.6)	3.08, 2.96	7.17(δ); 6.76(ε)
Cys 10	8.50 (8.6, f, 7.1)	5.48 (55.4)	2.92	
Val 11	8.35 (8.2, ms, 3.3)	4.44 (61.0)	2.27	1.02(γ)

^aObtained at 300K, pH = 5.5, with TSP (δ 0.00 ppm) as reference shift. Chemical shifts are accurate to ±0.02 ppm for ¹H NMR and to ±0.1 ppm for ¹³C NMR resonances. ^b³J_{αN} coupling constants in Hz. exc = NH exchange rate (f, fast; ms, moderately slow; s, slow; vs, very slow). -Δδ/ΔT = temperature coefficients (ppb/K).

Table F. NMR Resonance Assignments^a of Peptide 1 in SDS-d₂₅ 200mM solution.

residue	NH (³ J _{αN} , exc, -Δδ/ΔT) ^b	C ^α H	C ^β H	Others
Asp 4		4.44 (51.8)	2.66, 2.60	
Pen 5	8.53 (8.8, f, 6.8)	5.28 (62.0)		1.25, 1.06(γ)
Phe 6	9.26 (8.5, s, 2.2)	4.68 (55.9)	3.05, 3.01	7.16(δ); 7.20(ε)
Trp 7	8.97 (4.5, f, 6.1)	4.25 (59.1)	3.82, 3.23	7.28(δ); 10.14, 7.62(ε); 7.53, 7.22(ζ); 7.16(η)
Lys 8	6.52 (5.9, f, 2.8)	4.11 (55.2)	1.21, 0.92	0.24, -0.15(γ); 1.08, 1.03(δ); 2.52, 2.42(ε); 7.22(ζ)
Tyr 9	8.33 (8.4, vs, -1.1)	4.89 (57.2)	3.02	7.22(δ); 6.79(ε)
Pen 10	8.48 (8.7, f, 6.7)	5.12 (61.3)		1.37, 1.27(γ)
Val 11	8.56 (8.6, s, 3.0)	4.51 (59.9)	2.31	1.04, 1.00(γ)

^aObtained at 300K, pH = 5.5, with TSP (δ 0.00 ppm) as reference shift. Chemical shifts are accurate to ±0.02 ppm for ¹H NMR and to ±0.1 ppm for ¹³C NMR resonances. ^b³J_{αN} coupling constants in Hz. exc = NH exchange rate (f, fast; ms, moderately slow; s, slow; vs, very slow). -Δδ/ΔT = temperature coefficients (ppb/K).

Table G. NMR Resonance Assignments^a of Peptide **2** in SDS-d₂₅ 200mM solution.

residue	NH (³ J _{αN} , exc, -Δδ/ΔT) ^b	C ^α H	C ^β H	Others
Asp 4		4.44 (52.1)	2.79	
Cys 5	8.58 (8.5, f, 7.0)	5.57 (56.5)	3.00, 2.89	
Phe 6	9.01 (8.1, s, 2.8)	4.62 (56.5)	3.03, 2.99	7.17(δ); 7.25(ε)
Trp 7	8.78 (4.9, f, 6.2)	4.27 (57.9)	3.74, 3.07	7.27(δ); 10.16, 7.60(ε); 7.53, 7.18(ζ); 7.24(η)
Lys 8	6.44 (5.2, s, -1.0)	4.05 (55.7)	1.17, 0.98	0.12, -0.23(γ); 1.03(δ); 2.51, 2.42(ε); 7.21(ζ)
Tyr 9	8.20 (7.8, s, 2.8)	4.82 (57.3)	3.03, 2.91	7.17(δ); 6.76(ε)
Pen 10	8.36 (8.6, f, 6.4)	4.94 (61.4)		1.31, 1.29(γ)
Val 11	8.44 (8.2, ms, 3.2)	4.43 (60.4)	2.30	1.02(γ)

^aObtained at 300K, pH = 5.5, with TSP (δ 0.00 ppm) as reference shift. Chemical shifts are accurate to ±0.02 ppm for ¹H NMR and to ±0.1 ppm for ¹³C NMR resonances. ^b³J_{αN} coupling constants in Hz. exc = NH exchange rate (f, fast; ms, moderately slow; s, slow; vs very slow). -Δδ/ΔT = temperature coefficients (ppb/K).

Table H. NMR Resonance Assignments^a of Peptide 3 in SDS-d₂₅ 200mM solution.

residue	NH (³ J _{αN} , exc, -Δδ/ΔT) ^b	C ^α H	C ^β H	Others
Asp 4		4.24 (53.0)	2.81,2.74	
Cys 5	8.56 (6.4, f, 6.4)	4.78 (54.9)	3.25,2.83	
Phe 6	8.46 (6.8, f, 6.0)	4.58 (58.0)	3.04	7.19(δ); 7.26(ε)
Trp 7	8.21 (7.2, f, 6.6)	4.59 (57.3)	3.50, 3.17	7.34(δ); 10.12,7.59(ε); 7.52,7.10(ζ); 7.17(η)
Lys 8	6.98 (7.1, f, 6.4)	3.87 (57.6)	1.22, 1.15	0.42,0.23(γ); 1.25(δ); 2.66(ε); 7.31(ζ)
Tyr 9	7.34 (6.8, f, 6.1)	4.55 (57.7)	3.05,2.62	6.98(δ); 6.73(ε)
Hcys 10	7.94 (7.0, f, 6.0)	4.77 (54.8)	2.84,2.76	2.07(γ)
Val 11	7.94 (7.2, f, 6.9)	4.19 (62.1)	2.20	1.00(γ)

^aObtained at 300K, pH = 5.5, with TSP (δ 0.00 ppm) as reference shift. Chemical shifts are accurate to ±0.02 ppm for ¹H NMR and to ±0.1 ppm for ¹³C NMR resonances. ^b³J_{αN} coupling constants in Hz. exc = NH exchange rate (f, fast; ms, moderately slow; s, slow; vs very slow). -Δδ/ΔT = temperature coefficients (ppb/K).

Table I. RMS deviations (Å) of the best 20 calculated structures of studied peptides.

peptide	Cyclic bb ^a	All bb	Cyclic heavy	All heavy
hU-II(4-11)	0.22	0.40	0.46	0.90
PSU	0.18	0.24	0.32	0.70
1	0.11	0.15	0.19	0.50
2	0.21	0.30	0.50	0.64
3	1.02	1.17	1.66	1.88

^a Backbone heavy atoms of the cyclic portion (Cyclic bb);
Backbone heavy atoms of all the molecule (All bb)
All heavy atoms of the cyclic portion (Cyclic heavy);
All heavy atoms of the molecule (All heavy).

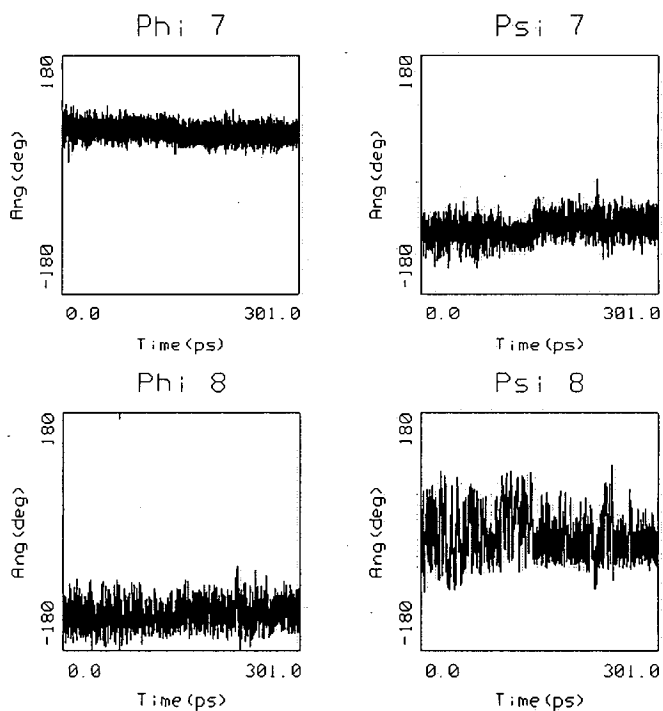


Figure A. ϕ and ψ backbone torsion angles of residues Trp⁷ and Lys⁸ of P5U during a 300 ps time course of molecular dynamics at 300K starting from minimized NMR structures. Angle values are recorded every picosecond including 1 ps of equilibration period. hU-II(4-11), and peptides 1-2 turn dihedral angles show very similar behavior. Canonical ϕ and ψ angles of a type II' β -turn are: $\phi_{i+1} = +60$ and $\psi_{i+1} = -120$, and $\phi_{i+2} = -80$ and $\psi_{i+2} = 0$ degrees.