SUPPORTING INFORMATION

A Stabilizing Capping Motif for β Hairpins and Sheets

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References

1. Bai, Y., Milne, J.S., Mayne, L. and Englander, S.W. Primary structure effects on peptide group hydrogen exchange. *Proteins* **17**, 75-86 (1993).

2. Kier, B.L. & Andersen, N.H. Probing the lower size limit for fold protein-like fold stability: ten-residue microproteins with specific, rigid structures in water. *J. Am. Chem. Soc.* **130** 14675-14683 (2008).

3. Espinosa, J.F., Syud, F.A. & Gellman, S.H. Analysis of the factors that stabilize a designed two-stranded antiparallel β-sheet. *Prot. Sci.* **11**, 1492-1505 (2002).

Supporting Information Item 1: EtF W/W pairs flip to FtE

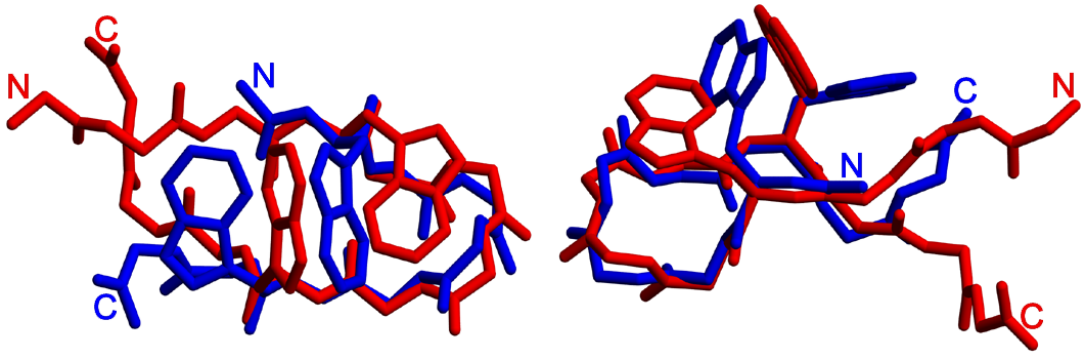


Figure S1A: EtF (Edge-to-Face) vs FtE (Face-to-Edge) Trp/Trp pairs. Two views of the overlays of lowest-energy structures for peptides WP (blue, Ac-WINGKWTG-NH_2) and HP6Va (KYVWINGKWTVE) are shown, with the N and C termini labeled. The Trp/Trp pair of peptide HP6Va (red) adopts an EtF interaction: the **N**-terminal Trp is "edge" (its sidechain displays significant ring current shifts) and it interacts with the amide units of the turn. The Trp/Trp pair of the WP peptide (blue) adopts a FtE interaction: the **C**-terminal Trp is "edge" (its sidechain displays significant ring current shifts) and it interacts with the amide unit of the C-terminal i+2 glycine.

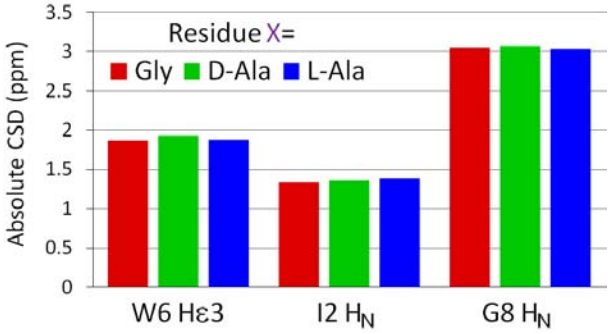


Figure S1B: Ac-WI**p**XKWTG-NH_2 Comparisons (**p** = D-Pro). NMR CSD (Chemical Shift Deviation, from expected random coil values) data at 280K.

This illustrates the lack of interplay between turn type and W/W orientation even in turn-flanking FtE interactions.

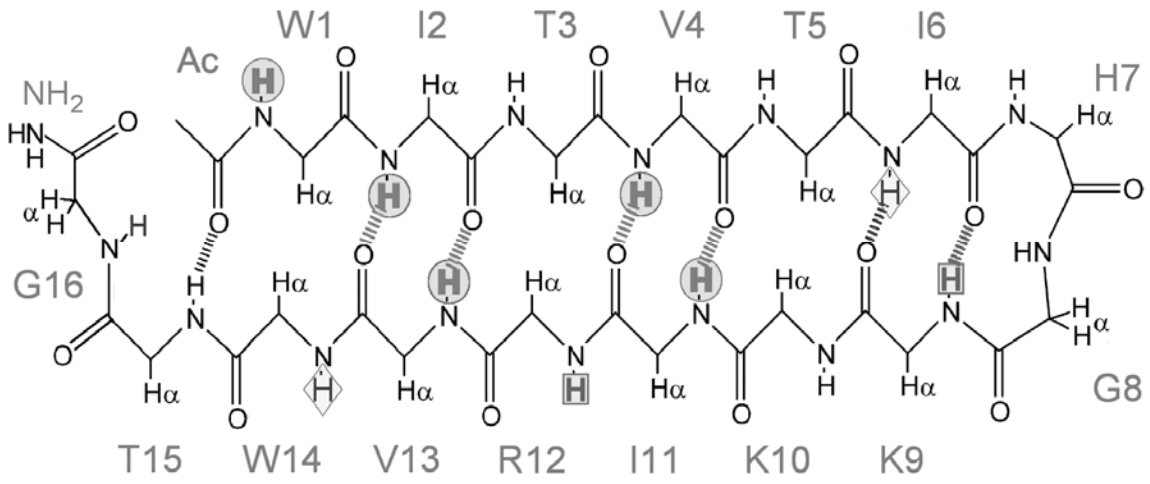
Supporting Information Item 2: Amide Exchange Data for Peptides Ac-WITVTIHGKKIRVWTG-NH_2 and Ac-WVTIpGKKIWTG-NH_2.

Table S2A: Ac-WITVTIHGKKIRVWTG-NH_2 Amide Exchange Data						
Residue	Rates		ProtFact		ΔG_u	
	k_{exp}	k_{RC}*	(k_{RC}/k_{exp})	%fold	kJ/mol	
Trp1	0.00685	0.7041	103	99.04%	10.79	best
Ile2	0.00314	0.2616	83	98.81%	10.30	best
Val4	0.0057	0.5723	100	99.01%	10.73	best
Ile6	0.02418	0.5341	22	95.67%	7.21	less
Lys9	0.0496	2.441	49	98.01%	9.07	moderate
Ile11	0.00451	0.4442	99	98.99%	10.69	best
Arg12	0.02128	1.281	60	98.37%	9.54	moderate
Val13	0.00653	0.5993	92	98.92%	10.52	best
Trp14	0.02459	0.5101	21	95.40%	7.06	less

*Random Coil Value determined using Molday Factors[1] (pD=5.89)

The kinetic plots, ln(peak integral) vs time, appear in Figure S2A (next page).

The protection factors are plotted on to a depiction of the hairpin geometry below:



Protection factors for amide hydrogens in Ac-WITVTIHGKKIRVWTG-NH_2 at 280K, pD 5.89. Circled: highly protected (Protection factors of 83x-103x) Boxed: well protected (49x-60x) Diamonds: some protection (21x-22x) Plain: no evidence for protection. In the case of highly shifted G16H_N, measuring the exchange rate was complicated by overlap with Hα protons.

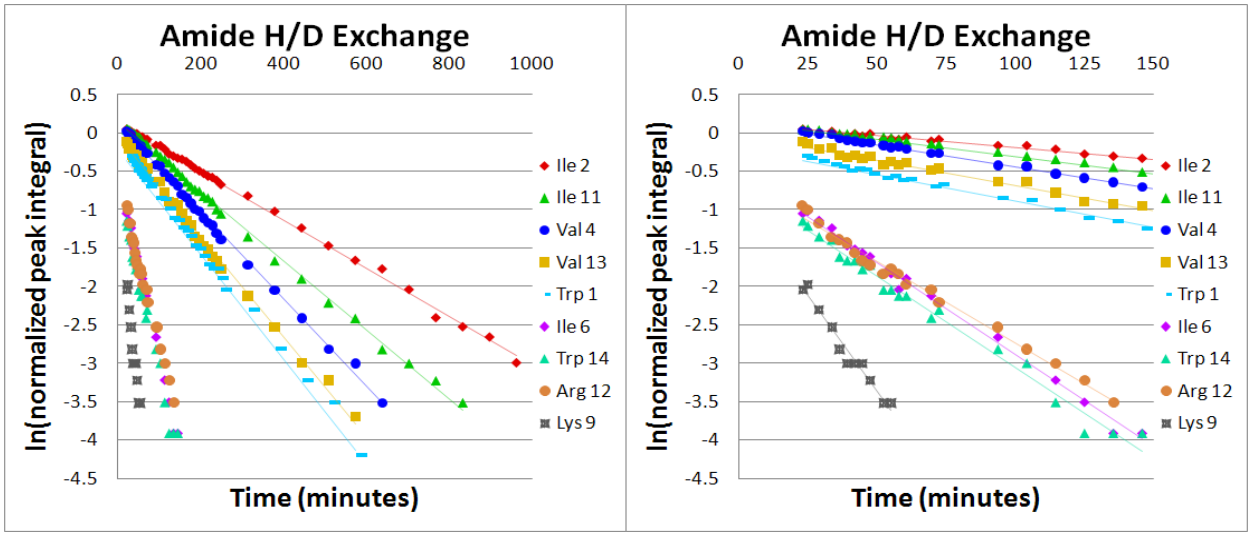


Figure S2A: Raw exchange data plotted for peptide Ac-WITVTIHGKKIRVWTG-NH_2 (blow-up of fast exchange domain on right.)

Table S2B: Ac-WVTIpGKKIWTG-NH_2 amide exchange data						
Residue	Rates		ProtFact	%fold	ΔG_u	
	k_{exp}	k_{RC}*	(k_{RC}/k_{exp})		kJ/mol	
Trp1	0.007987	0.8457	106	99.06%	10.85	best
Val2	0.007239	0.3367	47	97.90%	8.94	
Ile4	0.00554	0.6415	116	99.14%	11.06	best
Lys7	0.0197	2.932	149	99.33%	11.65	best
Lys8	0.0437	2.613	60	98.36%	9.52	
Ile9	0.006336	0.5336	84	98.83%	10.32	best

*Random Coil Value determined using Molday Factors (pD=5.97)

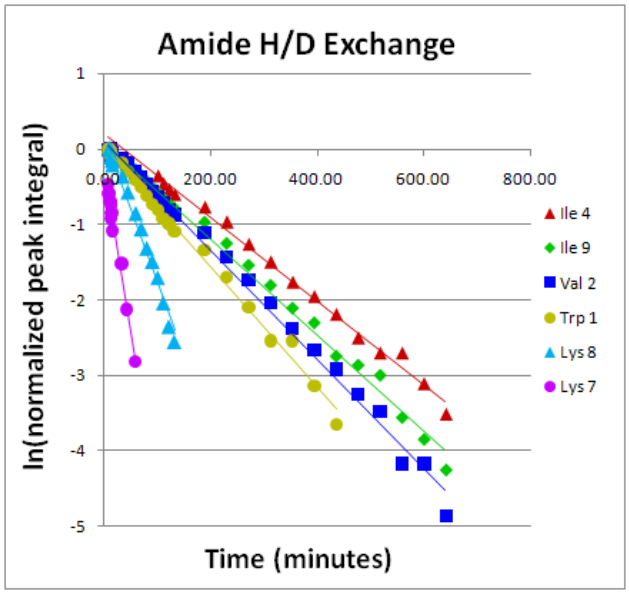


Figure S2B: Raw exchange data plotted for peptide Ac-WVTI**p**GKKIWTG-NH_2

Supporting Information Item 3: Mutants of Ac-WITVTIHGKKIRVWTG-NH_2 Illustrating the Cap's Specificity, Anti-Fraying Characteristics, and Significant Contribution to Fold Stability

Note the significant fraying not only for +WITVTIHGKKIRVWTG-NH_2 (highlighted in the main text; see Fig. 4) but also Ac-TIWVTIHGKKIWVRTG-NH_2; a peptide isomeric with Ac-WITVTIHGKKIRVWTG-NH_2 but with the Trp pair "swapped in" to a non-H-bonded position nearer to the turn. It is not just frayed, but displays lower core fold population (79%) and lacks a specific W/W conformation (no EtF or FtE) suggesting that the W/W interaction alone is not responsible for the cap. Also note that the Ac- extension is preferred over peptidic extensions (eg. mutating AT to Ac- is worth roughly 5.2 kJ/mol; Ac-GG to Ac- is worth 4.3.)

Table S3 [a]	χ_F turn[b]	χ_F mid[c]	χ_F ends[d]	χ_F W_{Cterm}[e]	$\Delta\Delta G$[f]
Ac-WITVTIHGKKIRVWTG-NH_2	0.99	0.99	0.99	0.99	0
Ac-WITVTIHGKKIRVWTG-NH_2	*0.95*	*1.02*	*0.96*	*0.88*	*~0*
+WITVTIHGKKIRVWTG-NH_2	0.76	0.74	0.51	0.11	8.3
Ac-TIWVTIHGKKIWVRTG-NH_2	0.79	0.79	0.29	0.24	7.7
+TIWVTIHGKKIWVRTG-NH_2	0.59	0.64	0.17	0.15	9.4
Ac-TITVTIHGKKIRVTTG-NH_2	0.38	0.38	0.27	NA	11.8
Ac-WITATIHGKKARVWTG-NH_2	0.77	0.65	0.72	0.71	9.2
+WITATIHGKKARVWTG-NH_2	0.13	0.09	0.00	0.00	16+
+ATWITVTIHGKKIRVWTG-NH_2	0.95	0.91	0.82	0.72	5.2
GGWITVTIHGKKIRVWTG-NH_2	0.97	0.94	0.95	0.94	4.3

[a] All data for 280K, except italicized entry (320K). Ac-WITVTIHGKKIRVWTG-NH_2 established as 99% folded at 280K by amide H/D exchange studies. (Including amides near the termini; see Table S2A and Figure S2A.) [b-e] fold diagnostics employed: [b] H7 H_N, G8 $\Delta H\alpha$, K9 H_N; [c] H_N: 4-6 & 10-11; $H\alpha$: 4-6 & 9-11; [d] H_N & $H\alpha$ of I2 & V13; [e] $H\beta3$ and $H\varepsilon3$ of W14/W12. [f] in kJ/mol; vs. Ac-WITVTIHGKKIRVWTG-NH_2, calculated from the mid-strand value (which uses many diagnostic shifts, and has minimal interference from ring current effects.)

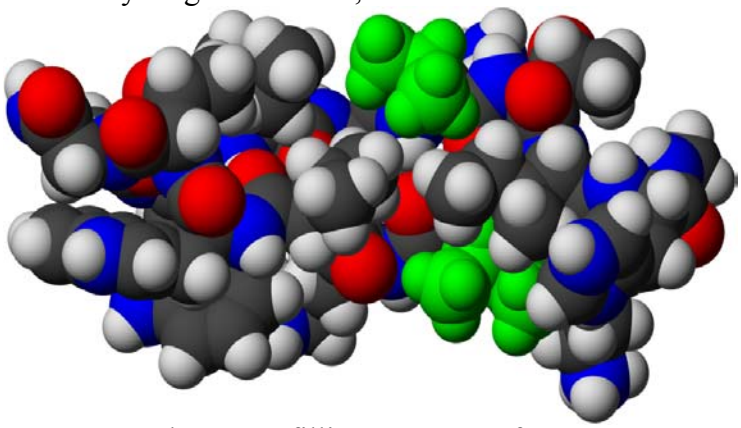


Figure S3: The space-filling structure of Ac-WITVTIHGKKIRVWTG-NH_2 with V4 and I11 highlighted in green illustrates why the $\Delta\Delta G$ of this mutation can be as high as 9.2 kJ/mol (as calculated from strand site shift changes upon mutations); greater even than loss of the cap. Due to the significant twist of the hairpin, V4 and I11 interact more strongly with the sidechains of I2, I6, and V13 than each other. The double alanine mutation doesn't just disrupt a single cross-strand interaction, but an entire hydrophobic core. (Also, removing two beta branched residues significantly lowers the beta propensities of the strands.)

Supporting Item 4: Applying the β-cap to a hairpin reported from the Gellman laboratory

Table S4	Y4H$_N$	V5H$_N$	F9H$_N$	T10H$_N$	Q3Hα	Y4Hα	K8Hα	G16 H$_N$	Gly ΔHα	χ_F [b]
cyc(RWQYVpGKFTVQpG) [a]	0.92	0.75	0.63	0.64	0.519	0.539	0.453		n.a.	0.99
RWQYVNGKFTVQ-NH$_2$ [a]	0.32	0.17	0.19	0.14	0.099	0.139	0.163		0.28	0.28 [c]
RWQYVpGKFTVQ-NH$_2$ [a]	0.43	0.54	0.36	0.21	0.169	0.409	0.283		n.a.	0.54 [c]
RWQYVNGKFTPQ-NH$_2$	0.225	0.17	0.288	0.245	-0.01	0.134	0.181		0.272	0.26
AcWRWQYVNGKFTPQWTG-NH$_2$	0.838	0.422	0.669	0.839	0.421	0.258	0.361	-2.19	0.488	0.84
WRWQYVNGKFTPQWTG-NH$_2$	0.42	0.238	0.363	0.397	0.125	0.203	0.194	-1.00	0.362	0.42
AcTRWQYVNGKFTPQWTG-NH$_2$	0.331	0.168	0.297	0.328	0.071	0.199	0.161	-1.03	0.314	0.33 [d]
TRWQYVNGKFTPQWTG-NH$_2$	0.368	0.193	0.312	0.358	0.098	0.188	0.156	-1.02	0.312	0.36 [d]

a Data from Espinosa et. al.[22]; 276 K (all other data: 280K)

b Calculated by summing the 8 largest mid-strand CSDs and setting cyc(RWQYVpGKFTVQpG) values to 99%. The fraction folded estimates given for the 2nd and 3rd differ somewhat from the estimates of Gellman and co-workers[c] which relied on the Hα CSDs at 4 H-bonded sites (Q3, V5, K8, and T10) rather than the largest CSDs.

c The fraction folded values reported by in Gellman paper were 0.61 (pG) and 0.41 (NG).

d These two peptides correspond to T1W mutants; Thr is generally viewed as having nearly the same 'β-propensity' as Trp. Thus the folding increment (χ_F 0.33 vs 0.84) provides another measure of the capping effect (ΔΔG = 5.7 kJ/mol). The absence of fold destabilization on deacetylation validates deacetylation as a measure of the capping effect in Ac-WRWQYVNGKFTPQWTG-NH$_2$.

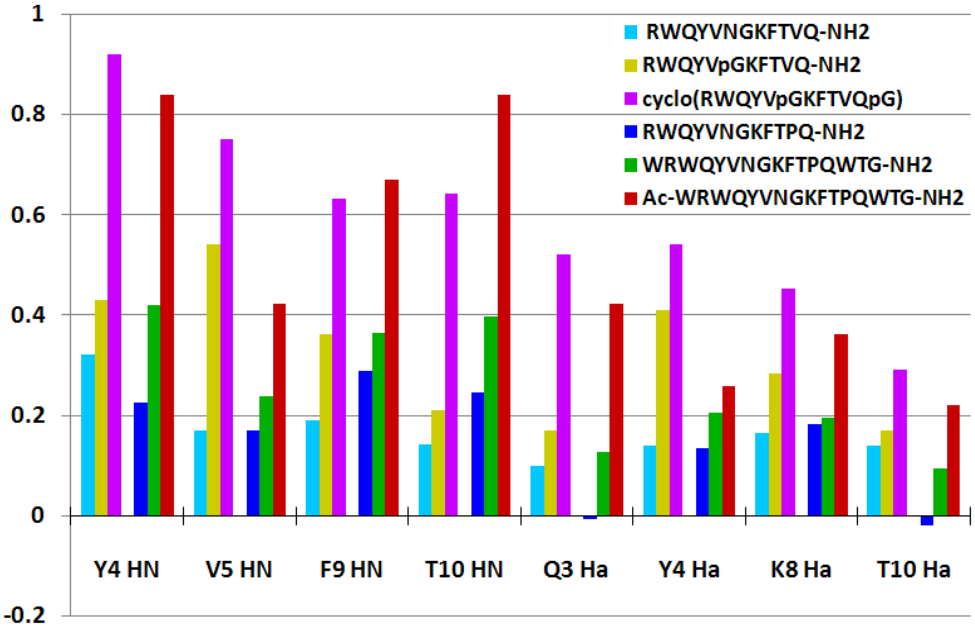


Figure S4: Visual representation of CSDs used, including the smaller shifts at T10 Hα.

From Fig. S4, the CSDs for **Ac-WRWQYVNGKFTPQWTG-NH$_2$** are 85±3 % of those observed for Gellman's cyclic 100% folded reference.

Supporting Information Item 5: Mutations of the Key W/W Pair

Only the most conservative of W→X mutations result in still-viable β-capping motifs. W→Y and W→F mutations were investigated for both the "face" (N-terminal) and "edge" (C-terminal) tryptophans in two different hairpins. Peptides with the "edge" tryptphans mutated to other aromatic residues were only modestly affected, but even the most conservative mutations of the "face" Trp (to Y, F) were significantly destabilizing. (Potential changes in ring current shifts for the 100% CSD values of various W→X mutants makes these values approximate, especially for the shorter system.)

Shaded italics data at 320K, all other data at 280K.

Table S5A	**C-term G H_N[a]**	**I2 H_N[b]**	**χ_F strand[c]**	**$\Delta\Delta G$[d]**
Pr-**W**I**p**GI**W**TGPS[e]	-3.679	1.457	0.98	(neg.)
Ac-**W**I**p**GK**W**T**G**-NH_2	-3.056	1.344	0.92	0
Ac-**Y**I**p**GK**W**T**G**-NH_2	-1.933	.738	~0.51	~5.6
Ac-**W**I**p**GK**Y**T**G**-NH_2	-1.776	1.248	~0.85	~1.6
Table S5B	**C-term G H_N[a]**	**I4 H_N[b]**	**χ_F strand[f]**	**$\Delta\Delta G$[g]**
Ac-**W**VTI**p**GKKI**W**T**G**-NH_2[h]	-2.944	0.935	0.99	0
*Ac-**W**VTI**p**GKKI**W**T**G**-NH_2*	*-2.415*	*0.901*	*0.96*	*1.9*
Ac-**F**VTI**p**GKKI**W**T**G**-NH_2	-1.655	0.803	0.71	8.6
*Ac-**F**VTI**p**GKKI**W**T**G**-NH_2*	*-1.374*	*0.730*	*0.66*	*8.9*
Ac-**W**VTI**p**GKKI**F**T**G**-NH_2	-1.777	0.906	0.93	4.7
*Ac-**W**VTI**p**GKKI**F**T**G**-NH_2*	*-1.554*	*0.851*	*0.88*	*5.3*
Ac-**W**VTI**p**GKAI**F**T**G**-NH_2	-1.990	0.804	0.88	5.9
Ac-**W**VTI**p**GKAI**L**T**G**-NH_2	0.053	0.674	0.63	9.4
Ac-**W**VTI**p**GKAI**H**T**G**-NH_2 (H^+)	0.120	0.713	0.67	9.0
*Ac-**W**VTI**p**GKAI**H**T**G**-NH_2 (H^+)*	*0.126*	*0.619*	*0.58*	*9.8*
Ac-**W**VTI**p**GKAI**H**T**G**-NH_2 (H^0)	-0.071	0.697	0.64	9.3

[a]Not a precise diagnostic of fold population; 100% folded value varies with changing i-2 residues. "Unfolded" value of Ac-WTG-NH_2 is ~1.2 ppm.

[b]A large positive **I4 H_N** CSD is indicative of cross-strand H-bond formation; it is a good turn/strand diagnostic free of ring current effects. **I/V2** and **I9** are similar, but with minor interference from ring current effects.

[c] Calculated from the **I2 H_N** value (significant changes in ring current shifts expected.)

[d]versus Ac-WI**p**GKWTG-NH_2

[e]Determined to be 98% folded by amide exchange experiments at 280K [2]

[f]Calculated from the five strand protons with the largest chemical shift deviations: **V2 H_N, T3 Hα, I4 H_N, K8 Hα, and I9 H_N** (modest changes in ring current shifts expected)

[g]versus Ac-WVTI**p**GKKIWTG-NH_2

[h]Determined to be 99% folded by amide exchange experiments at 280K (see figure and table S2B, above.)

Supporting Information Item 6: Structural Data: NMR-derived representative structures of Ac-WVTIpGKHIFTG-NH_2 and Ac-WITVTIHGKKIRVWTG-NH_2, and distance constraints for Ac-WITVTIHGKKIRVWTG-NH_2

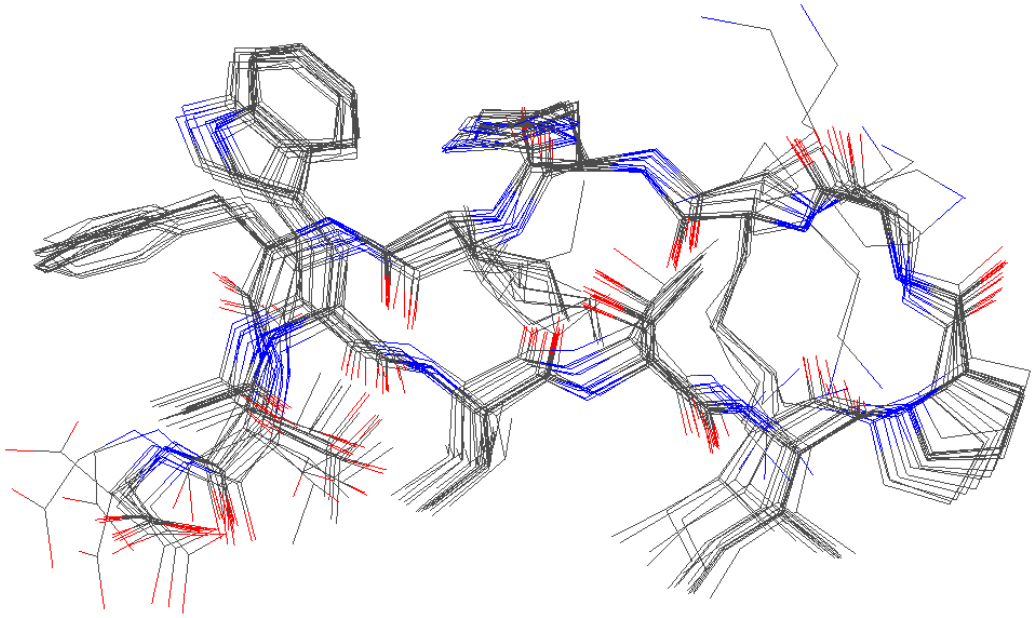


Figure S6A: (above) Preliminary NOE-derived Structure Ensemble of Ac-WVTI**p**GKHIFTG-NH_2, illustrating similar geometry in the W/F capping interaction vs. the W/W. (Better NOE data was obtained for the K8H mutant.)

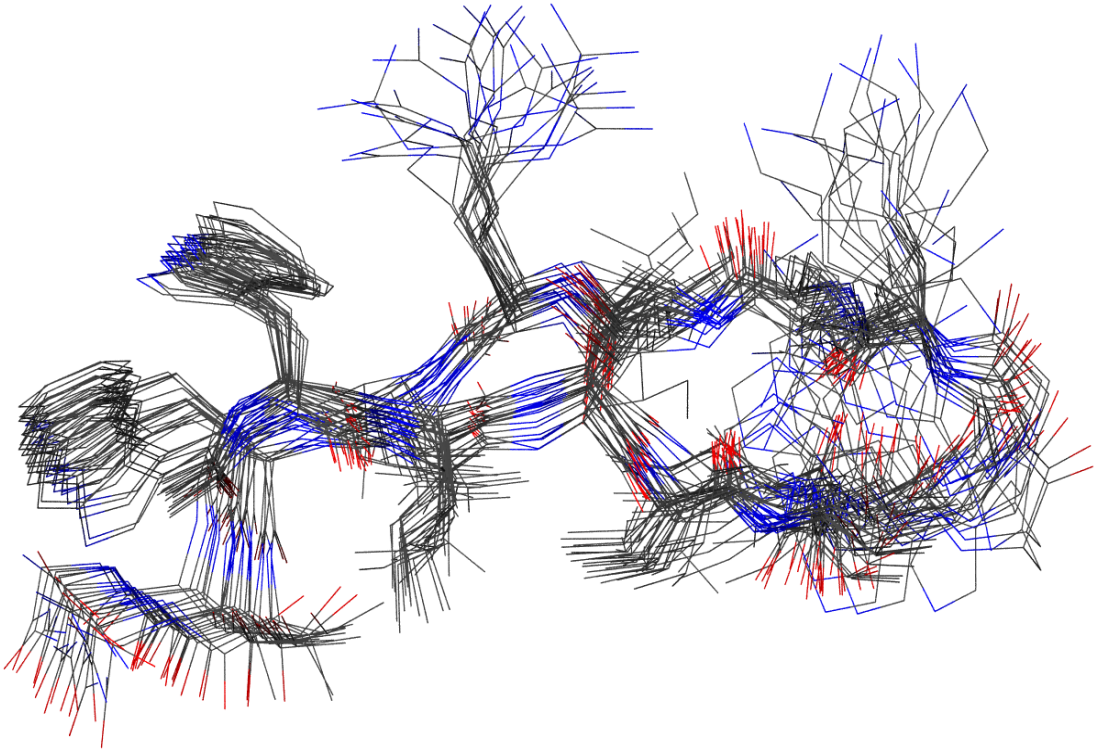


Figure S6B: 36/50 lowest energy structures of Ac-WITVTIHGKKIRVWTG-NH_2

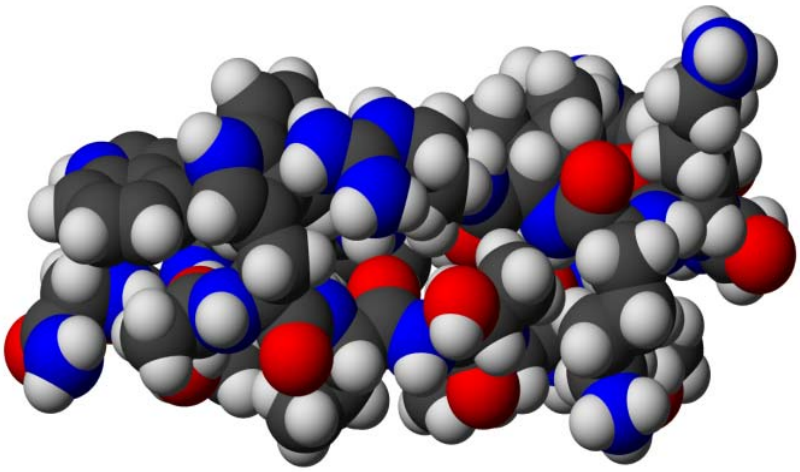


Figure S6C: Space-filling model of the lowest energy structure from above. (The opposite face of the same structure is shown as Figure S3.)

Table S6: Distance Constraints for the NMR Structure of Ac-WITVTIHGKKIRVWTG-NH_2
Long-range constraints (|i-j|>5) in **bold.**
Intra-residue constraints in *italics.* (N-term Ac- counted as part of W1)
#denotes shift-coincident methyl or germinal methylene protons
*denotes stereotopically ambiguous methylene protons

10	*hb2*	*10*	*hn*	*2.56*	*0.29*	*0.25*
10	*ha*	*10*	*hn*	*2.80*	*0.51*	*0.46*
10	*hb1*	*10*	*ha*	*2.72*	*0.35*	*0.28*
10	*hg2*	*10*	*hn*	*3.24*	*0.51*	*0.41*
10	ha	11	hn	2.13	0.16	0.18
10	ha	6	hn	3.11	0.47	0.37
11	*ha*	*11*	*hn*	*2.84*	*0.38*	*0.31*
11	*hb*	*11*	*hn*	*2.94*	*0.41*	*0.33*
11	*ha*	*11*	*hb*	*2.99*	*0.43*	*0.34*
11	*hg11*	*11*	*hn*	*3.16*	*0.48*	*0.39*
11	*hg12*	*11*	*hn*	*3.29*	*0.52*	*0.43*
11	*ha*	*11*	*hg2#*	*3.36*	*0.64*	*0.56*
11	*ha*	*11*	*hd1#*	*3.58*	*0.51*	*0.41*
11	*hg2#*	*11*	*hn*	*3.97*	*0.64*	*0.52*
11	ha	12	hn	2.12	0.15	0.18
11	hg2#	12	hn	3.47	0.68	0.38
12	*hb**	*12*	*hn*	*2.65*	*0.32*	*0.27*
12	*hg**	*12*	*hn*	*2.73*	*0.35*	*0.28*
12	*ha*	*12*	*hn*	*2.91*	*0.40*	*0.32*
12	*ha*	*12*	*hg**	*3.06*	*0.50*	*0.50*
12	*ha*	*12*	*hb**	*3.06*	*0.50*	*0.50*

12	*hg**	*12*	*he*	*3.02*	*0.44*	*0.35*
12	*hd2*	*12*	*he*	*3.10*	*0.47*	*0.37*
12	*hd1*	*12*	*he*	*3.20*	*0.50*	*0.40*
12	ha	13	hn	2.19	0.18	0.19
12	hb*	13	hn	3.25	0.51	0.42
12	**hb***	**1**	**he3**	**2.82**	**0.38**	**0.50**
12	**hg***	**1**	**he3**	**2.95**	**0.42**	**0.53**
12	**hg***	**3**	**ha**	**3.60**	**1.00**	**1.00**
12	**hg***	**3**	**hg2#**	**3.60**	**1.00**	**1.00**
12	**ha**	**3**	**hg2#**	**3.60**	**1.00**	**1.00**
12	**ha**	**4**	**hn**	**3.16**	**0.49**	**0.39**
13	*ha*	*13*	*hn*	*2.85*	*0.39*	*0.31*
13	*hb*	*13*	*hn*	*2.89*	*0.60*	*0.52*
13	*ha*	*13*	*hb*	*2.98*	*0.43*	*0.34*
13	*hg2#*	*13*	*hn*	*3.58*	*0.81*	*0.71*
13	*hg1#*	*13*	*hn*	*4.01*	*0.65*	*0.53*
13	ha	14	hn	2.09	0.15	0.18
13	hb	14	hn	3.16	0.48	0.39
13	hg1#	14	hn	3.52	0.49	0.39
13	**ha**	**1**	**hz3**	**3.04**	**0.45**	**0.56**
14	*he1*	*14*	*hd1*	*2.14*	*0.16*	*0.58*
14	*hb1*	*14*	*hn*	*2.45*	*0.26*	*0.23*
14	*hb1*	*14*	*hd1*	*2.57*	*0.30*	*0.45*
14	*ha*	*14*	*hn*	*2.92*	*0.41*	*0.33*
14	*ha*	*14*	*hb2*	*2.81*	*0.44*	*0.35*
14	*he3*	*14*	*ha*	*3.25*	*0.51*	*0.61*
14	*he3*	*14*	*hb2*	*2.85*	*0.51*	*0.61*
14	*ha*	*14*	*hd1*	*3.61*	*0.53*	*0.93*
14	ha	15	hn	2.30	0.21	0.21
14	he3	15	hn	3.25	0.58	0.68
14	**hz3**	**1**	**hd1**	**2.72**	**0.35**	**0.68**
14	**he3**	**1**	**hd1**	**3.19**	**0.49**	**0.80**
14	**he3**	**1**	**he1**	**3.40**	**1.00**	**1.00**
14	**hb2**	**1**	**hz3**	**3.30**	**0.53**	**0.63**
14	**hb2**	**1**	**hh2**	**3.60**	**1.00**	**1.00**
14	**ha**	**1**	**he3**	**3.35**	**0.54**	**0.65**
14	**ha**	**2**	**hn**	**3.52**	**0.60**	**0.51**
15	ha	13	hg1#	3.92	0.92	0.80
15	*ha*	*15*	*hn*	*2.81*	*0.37*	*0.30*
15	*ha*	*15*	*hg2#*	*2.93*	*0.31*	*0.28*
15	*hb*	*15*	*hn*	*3.40*	*0.46*	*0.67*
15	*hg2#*	*15*	*hn*	*3.41*	*0.76*	*0.67*
15	**hg2#**	**2**	**hd1#**	**2.80**	**0.80**	**0.65**
15	**hg2#**	**2**	**hg1***	**2.80**	**0.80**	**0.65**
15	hg2#	16	hn	3.60	0.30	1.50
16	ha*	14	he1	2.93	0.41	0.53
16	ha*	14	hz2	2.98	0.43	0.54
16	ha*	14	hd1	3.43	0.57	0.67
16	hn	15	hn	2.53	0.29	0.25
16	hn	15	ha	3.32	0.53	0.44
16	*hn*	*16*	*ha**	*2.26*	*0.20*	*0.20*
16	**ha***	**1**	**ha#**	**2.86**	**0.39**	**0.31**

16	**hn**	**1**	**ha#**	**3.18**	**0.49**	**0.39**
16	*ha**	*16*	*h1*	*3.20*	*0.50*	*0.40*
1	**he3**	**13**	**hn**	**3.17**	**0.49**	**0.59**
1	**hz3**	**14**	**hn**	**3.07**	**0.46**	**0.56**
1	**hn**	**14**	**hz3**	**3.25**	**0.51**	**0.61**
1	**ha**	**14**	**ha**	**3.26**	**0.52**	**0.42**
1	**he1**	**14**	**hz3**	**3.27**	**0.52**	**0.82**
1	**ha**	**15**	**hn**	**2.94**	**0.41**	**0.33**
1	*hb2*	*1*	*hn*	*2.58*	*0.30*	*0.25*
1	*hb2*	*1*	*hd1*	*2.61*	*0.31*	*0.46*
1	*ha*	*1*	*he3*	*2.79*	*0.37*	*0.50*
1	*hb1*	*1*	*he3*	*2.84*	*0.38*	*0.51*
1	*hd1*	*1*	*hn*	*2.90*	*0.40*	*0.52*
1	*ha*	*1*	*hn*	*2.99*	*0.43*	*0.34*
1	ha	2	hn	2.20	0.18	0.19
1	hb1	2	hn	3.19	0.49	0.40
1	he3	2	hn	3.28	0.52	0.62
1	*ha#*	*1*	*hn*	*2.28*	*0.21*	*0.20*
1	*ha#*	*1*	*hd1*	*3.23*	*0.51*	*0.41*
1	**ha#**	**14**	**hh2**	**3.28**	**0.52**	**0.42**
1	**ha#**	**14**	**hz3**	**2.87**	**0.39**	**0.31**
1	**ha#**	**15**	**hn**	**3.24**	**0.51**	**0.41**
1	**ha#**	**16**	**h1**	**3.32**	**0.53**	**0.44**
2	**hn**	**13**	**hn**	**2.83**	**0.38**	**0.31**
2	*ha*	*2*	*hb*	*2.69*	*0.33*	*0.27*
2	*ha*	*2*	*hn*	*2.87*	*0.46*	*0.39*
2	*hg1**	*2*	*hn*	*2.85*	*0.39*	*0.31*
2	*hg1**	*2*	*hn*	*3.07*	*0.46*	*0.36*
2	*hb*	*2*	*hn*	*3.25*	*0.51*	*0.41*
2	*hg2#*	*2*	*hn*	*3.78*	*0.58*	*0.46*
2	ha	3	hn	2.18	0.18	0.19
2	hb	3	hn	2.56	0.29	0.25
3	**hg2#**	**11**	**hn**	**3.71**	**0.56**	**0.44**
3	**ha**	**13**	**hn**	**3.03**	**0.44**	**0.35**
3	*hb*	*3*	*hn*	*2.53*	*0.28*	*0.24*
3	*hb*	*3*	*ha*	*3.6*	*0.4*	*1.0*
3	**hg2#**	**10**	**hb1**	**2.76**	**0.36**	**0.29**
3	**hg2#**	**10**	**ha**	**3.60**	**1.00**	**1.00**
3	*ha*	*3*	*hn*	*3.05*	*0.45*	*0.36*
3	ha	4	hn	2.13	0.16	0.18
3	hg2#	4	hn	3.46	0.48	0.38
3	hb	4	hn	3.47	0.58	0.49
3	*hg2#*	*3*	*hn*	*3.6*	*0.6*	*0.5*
4	**hn**	**11**	**hn**	**2.86**	**0.39**	**0.31**
4	*ha*	*4*	*hn*	*2.82*	*0.35*	*0.28*
4	*ha*	*4*	*hb*	*2.76*	*0.36*	*0.29*
4	*ha*	*4*	*hg1#*	*3.00*	*0.56*	*0.41*
4	*hg2#*	*4*	*hn*	*3.25*	*0.41*	*0.33*
4	*hb*	*4*	*hn*	*4.0*	*0.5*	*0.8*
4	ha	5	hn	2.17	0.17	0.19
4	hb	5	hn	2.64	0.32	0.26
5	hg2#	8	hn	3.27	0.41	0.34

5	**ha**	**11**	**hn**	**3.23**	**0.51**	**0.41**
5	*hb*	*5*	*hn*	*2.47*	*0.27*	*0.23*
5	*hb*	*5*	*ha*	*3.5*	*0.35*	*1.0*
5	*ha*	*5*	*hn*	*2.93*	*0.41*	*0.33*
5	*ha*	*5*	*hg2#*	*3.04*	*0.54*	*0.29*
5	*hg2#*	*5*	*hn*	*3.78*	*0.58*	*0.46*
5	ha	6	hn	2.19	0.18	0.14
5	hg2#	6	hn	3.46	0.47	0.38
5	hg2#	9	hn	3.77	0.57	0.46
6	*hb*	*6*	*hn*	*2.92*	*0.41*	*0.33*
6	*ha*	*6*	*hn*	*3.05*	*0.42*	*0.33*
6	*ha*	*6*	*hb*	*3.07*	*0.45*	*0.36*
6	*ha*	*6*	*hg2#*	*3.13*	*0.37*	*0.31*
6	*hg12*	*6*	*hn*	*3.27*	*0.52*	*0.42*
6	*ha*	*6*	*hd1#*	*3.60*	*0.52*	*0.41*
6	*hg2#*	*6*	*hn*	*4.21*	*0.71*	*0.60*
6	ha	7	hn	2.10	0.15	0.18
6	hg2#	7	hd2	3.38	0.45	0.60
6	hg2#	7	hn	3.40	0.46	0.37
6	hg2#	8	hn	4.14	0.69	0.57
7	hb2	6	hg2#	4.03	0.65	0.54
7	*ha*	*7*	*hn*	*2.15*	*0.16*	*0.19*
7	*ha*	*7*	*hd2*	*3.37*	*0.55*	*0.65*
7	*hb1*	*7*	*hd2*	*3.38*	*0.56*	*0.66*
7	*hb1*	*7*	*hn*	*3.39*	*0.56*	*0.46*
7	*hb2*	*7*	*hd2*	*3.42*	*0.57*	*0.67*
7	*hb2*	*7*	*hn*	*3.43*	*0.57*	*0.47*
7	*hb1*	*7*	*ha*	*3.00*	*0.6*	*0.5*
7	ha	8	hn	2.59	0.30	0.26
8	ha2	5	hg2#	3.40	0.46	0.37
8	hn	7	hn	2.97	0.42	0.34
8	*ha2*	*8*	*hn*	*2.40*	*0.24*	*0.22*
8	*ha1*	*8*	*hn*	*2.83*	*0.38*	*0.30*
8	ha2	9	hn	3.27	0.52	0.42
9	ha	10	hn	2.08	0.14	0.18
9	hb2	10	hn	3.08	0.46	0.36
9	hn	6	hn	2.76	0.36	0.29
9	hn	8	hn	2.82	0.38	0.30
9	*ha*	*9*	*hn*	*2.84*	*0.38*	*0.31*
9	*hb2*	*9*	*hn*	*2.86*	*0.39*	*0.31*
9	*hb1*	*9*	*hn*	*2.91*	*0.40*	*0.32*

Supporting Information Item 7: Chemical Shift Data for Selected Peptides at 280K (unless otherwise specified). ***Large upfield ring current shift appear in bold.***

Table S7A: Ac-WINGKWTG-NH_2

#	Res	H_N	Hα	Hβ (Hβ')	Others	^{13}Cα	^{13}Cβ
0	Ac		1.647			24.53	
1	Trp	8.810	4.930	3.156,3.113	ε1:10.230, δ1:7.420, ε3: 7.201 ζ3:7.164, η2:7.173, ζ2:7.327	57.29	29.22
2	Ile	8.975	4.323	1.722	γ:1.372,1.068,0.856, δ:0.813	60.35	39.71
3	Asn	9.573	4.448	3.077,2.757	δ:7.776,7.037	53.92	37.49
4	Gly	8.848	4.155,3.751			45.4	
5	Lys	8.025	4.782	1.821,1.771	γ:1.441,1.367, δ:1.697, ε:3.010	54.59	34.82
6	Trp	8.848	4.181	**2.826,2.044**	ε1:10.223, δ1:6.880, ε3: **6.024**, ζ3:6.900, η2:7.173, ζ2:7.385	56.71	28.56
7	Thr	7.869	4.207	4.155	γ: 1.086 (Me)	61.45	70.07
8	Gly	**5.603**	3.399,3.399		Term NH_2 cis: 7.205 trans: 7.329	44.53	

Table S7B: Ac-WVSINGKKIWTG-NH_2

#	Res	H_N	Hα	Hβ (Hβ')	Others
0	Ac		1.508		
1	Trp	8.684	5.217	3.157,3.050	Hδ:7.467,Hε:10.313,7.456,Hζ:7.351,7.148,Hη:7.227
2	Val	9.290	4.533	2.047	Hγ:0.871,0.871
3	Ser	8.633	5.231	3.735,3.631	
4	Ile	8.958	4.325	1.772	Hγ:1.458,1.089,0.881,Hδ:0.825
5	Asn	9.606	4.428	3.086,2.775	Hδ:7.037,7.753
6	Gly	8.636	4.129,3.578		
7	Lys	7.827	4.592	1.874,1.812	Hγ:1.459,1.393,Hδ:1.717,na,Hε:3.032
8	Lys	8.609	4.925	1.691,	Hγ:1.390,1.258,Hδ:1.318,na,Hε:2.515,2.439
9	Ile	9.400	4.641	1.871	Hγ:1.479,1.290,0.873,Hδ:0.833
10	Trp	8.964	4.354	**2.856,2.077**	Hδ:6.810,Hε:10.178,**5.797**,Hζ:7.351,6.744,Hη:7.128
11	Thr	7.926	4.232	4.167	Hγ: 1.067 (Me)
12	Gly	**5.604**	3.396,3.344		

Table S7C: Ac-WTVSINGKKITWTG-NH_2

#	Res	H_N	Hα	Hβ (Hβ')	Others
0	Ac		1.904		
1	Trp	8.292	4.810	3.256,3.179	(overlapped; essentially random coil)
2	Thr	8.374	4.461	4.086	Hγ: 1.105 (Me)
3	Val	8.357	4.255	2.001	Hγ: 0.932 (Me)
4	Ser	8.602	4.610	3.889,3.819	
5	Ile	8.544	4.192	1.862	Hγ:1.453,1.180,0.910,Hδ:0.878
6	Asn	8.648	4.677	2.890,2.772	Hδ:7.740,7.039
7	Gly	8.409	4.001,3.800		
8	Lys	8.025	4.354	1.818,1.759	Hγ:na, Hδ:na, Hε:2.965
9	Lys	8.492	4.426	1.706,	Hγ:1.402,1.277, Hδ:na, Hε:2.849
10	Ile	8.636	4.319	1.828	Hγ:na,1.158,0.799,Hδ:na
11	Thr	8.427	4.461	4.117	Hγ: 1.164 (Me)
12	Trp	8.600	4.744	3.179,3.058	(overlapped; essentially random coil)
13	Thr	8.157	4.216	4.158	Hγ: 1.087 (Me)
14	Gly	7.153	3.606,3.523		

Table S7D: Ac-WLSVTINGKTIKVWTG-NH_2

#	Res	H_N	Hα	Hβ (Hβ')	Others
0	Ac		1.471		
1	Trp	8.671	5.128	3.160,3.051	Hδ:7.488,Hε:10.348,7.426,Hζ:7.343,7.154,Hη:7.224
2	Leu	9.537	4.755		Hγ:1.599,Hδ:0.920,0.875
3	Ser	8.734	5.221	3.710,	
4	Val	9.155	4.471	2.022	
5	Thr	8.781	5.115	3.878	Hγ: 0.991 (Me)
6	Ile	8.937	4.314		Hγ:na,na,0.881, Hδ:na
7	Asn	9.710	4.393	3.081,2.759	Hδ:7.027,7.750
8	Gly	8.635	4.113,3.544		
9	Lys	7.851	4.704	1.854,1.795	Hγ:na, Hδ:na, Hε:3.005
10	Thr	8.906	4.967	3.909	Hγ: 1.085 (Me)
11	Ile	9.335	4.540	1.890	Hγ:na,na,0.899, Hδ:na
12	Lys	8.441	5.325	1.710,1.649	Hγ:1.385,na,Hδ:1.327,1.294,Hε:2.534,2.500
13	Val	9.465	4.679	2.071	Hγ:na,na
14	Trp	9.111	4.328	**2.853,2.135**	Hδ:6.814,Hε:10.172,**5.607**,Hζ:7.335,6.624,Hη:7.105
15	Thr	7.903	4.212	4.143	Hγ: 1.059 (Me)
16	Gly	**5.512**	3.370,		

Table S7E: Ac-WRWVKVWI**p**GKWIQVPQWTG-NH_2 (more complete data exists for 300K.)

#	Res	H_N	Hα	Hβ (Hβ')	Others
0	Ac		1.583		
1	Trp			,	Hδ:na; (essentially random coil)
2	Arg	9.132	4.712	1.798,	Hγ:1.560,1.478, Hδ:3.142,na, Hε:7.084
3	Trp	8.872	5.127	3.068,3.068	Hδ:na,Hε:na,na,Hζ:na,na,Hη:na
4	Val	9.383	4.600	2.105	Hγ:0.928,0.897
5	Lys	8.554	5.198	1.714,	Hγ:1.429 Hδ:1.303, Hε:2.430, Hζ:7.228
6	Val	9.526	4.792		Hγ:na,na
7	Trp	8.628	4.684	**2.881,1.715**	Hδ:6.701,Hε:9.972,**5.738**,Hζ:7.255,6.605,Hη:6.993
8	Ile	8.759	4.522	1.638	Hγ:na,na,0.754,Hδ:na
9	dPro		4.139	1.819,2.241	Hγ:1.957,1.959,Hδ:3.625,3.643
10	Gly		3.728,3.042		
11	Lys	6.873	4.312	1.689,1.573	Hγ:1.228, Hδ:1.608, Hε:2.934, Hζ:7.583
12	Trp	8.474	5.353	3.109,2.847	Hδ:7.415,Hε:10.202,7.338,Hζ:7.255,na,Hη:na
13	Ile	9.606	4.659	1.933	Hγ:na,na,0.922, Hδ:na
14	Gln	8.574	5.297	,	Hγ:2.331, Hε:na,na
15	Val	9.566	5.044		Hγ:na,na
16	Pro			,	Hγ:na, Hδ:na
17	Gln	9.370	4.781	,	Hγ:na, Hε:na,na
18	Trp		4.279	**2.926,2.016**	Hδ:na, Hε3: **5.950**, Hζ:7.349,6.759, Hη:7.128
19	Thr	7.864	4.181	4.093	Hγ: 0.996 (Me)
20	Gly	**5.982**	,3.395		

Table S7F: Ac-WITVTIHGKKIRVWTG-NH_2 (99% folded by amide H/D exchange)

#	Res	H_N	Hα	Hβ (Hβ')	Others	$^{13}C\alpha$	$^{13}C\beta$
0	Ac		1.495			24.7	
1	Trp	8.858	5.317	3.176,3.095	Hδ:7.495, Hε:10.235,7.471, Hζ:7.297,7.104, Hη:7.217	57.62	30.76
2	Ile	9.467	4.828	1.942	Hγ:1.307,1.153,0.877, Hδ:0.752	59.96	42.16
3	Thr	8.666	5.285	3.959	Hγ: 1.103 (Me)	61.92	69.90
4	Val	9.268	4.558	2.066	Hγ:0.898,0.878	59.80	35.21
5	Thr	8.638	5.119	3.921	Hγ: 0.945 (Me)	61.63	68.94
6	Ile	9.065	4.253	1.677	Hγ:1.365,0.935,0.738, Hδ:0.785	59.83	40.11
7	His	9.838	4.377	3.483,3.290	Hδ:7.321, Hε:8.645	55.96	27.15
8	Gly	8.672	4.154, 3.530			45.42	
9	Lys	7.843	4.644	1.848,1.823	Hγ:1.495,1.396, Hδ:1.715,na, Hε:3.034, Hζ:7.659	54.51	34.67
10	Lys	8.688	4.802	1.760,1.471	Hγ:1.296,na, Hδ:1.592,na, Hε:2.911, Hζ:7.586	56.15	32.82
11	Ile	9.424	4.490	1.852	Hγ:1.420,1.194,0.904, Hδ:0.814	59.74	41.43

12	Arg	8.580	5.369	1.838,1.690	Hγ:1.627, Hδ:2.912,2.819, Hε:6.680, Hη: 5.874,6.371	55.19	31.3
13	Val	9.611	4.644	1.975	Hγ:0.930,0.887	61.02	35.77
14	Trp	8.973	4.257	**2.726,1.753**	Hδ:6.720, Hε:10.210,**5.583**, Hζ:7.353,6.767, Hη:7.139	56.28	28.82
15	Thr	7.828	4.217	4.159	Hγ: 1.068 (Me)	61.33	70.23
16	Gly	**5.192**	3.317,			44.67	

Table S7G: Ac-WRWQYVNGKFTPQWTG-NH2 (based on a peptide by Espinosa et al[3]; Capped, V12P)

#	Res	H_N	Hα	Hβ (Hβ')	Others
0	Ac		1.608		
1	Trp	8.512	4.835	3.025,2.833	Hδ:7.340,Hε:10.137,7.217,Hζ:7.291,6.858,Hη:7.109
2	Arg	8.918	4.621	1.742,1.667	Hγ:1.445,Hδ:3.102,Hε:7.150
3	Trp	8.761	4.744	2.885,2.614	Hδ:7.092, Hε:10.121,7.002, Hζ:7.250
4	Gln	8.628	4.700	2.036,1.892	Hγ:2.176,2.136, Hε:7.410,6.904
5	Tyr	8.996	4.707	2.845,2.680	Hδ:6.623, Hε:6.623
6	Val	8.630	4.148	1.962	Hγ:0.875
7	Asn	9.456	4.382	3.020,2.719	Hδ:7.742,7.024
8	Gly	8.268	4.078,3.590		
9	Lys	7.645	4.656	1.819,1.737	Hγ:1.359, Hδ:1.691, Hε:3.012
10	Phe	9.157	4.755	3.021,2.832	Hδ:6.813, Hε:7.023, Hζ:6.983
11	Thr	9.047	4.828	4.044	Hγ: 1.221 (Me)
12	Pro		4.148	,1.625	Hδ:3.252,3.488
13	Gln	8.948	4.606	1.965,1.853	Hγ:2.244,2.166, Hε:7.431,6.925
14	Trp	8.912	4.309	2.889,2.308	Hδ:6.849,Hε:10.124,**6.081**,Hζ:7.331,6.734,Hη:7.106
15	Thr	7.892	4.198	4.108	Hγ: 0.997 (Me)
16	Gly	**6.116**	3.456,3.408		

Table S7H: Ac-WVTI**p**GKKIWTG-NH_2

#	Res	H_N	Hα	Hβ (Hβ')	Others
0	Ac		1.449		
1	Trp	8.786	5.302	3.167,3.090	over-lapped (essentially random coil)
2	Val	9.499	4.639	2.097	Hγ:0.908,0.891
3	Thr	8.709	5.244	3.976	Hγ: 1.019 (Me)
4	Ile	9.032	4.707	1.798	Hγ:1.509,1.113,0.917, Hδ:0.838
5	dPro		4.372	1.980,2.396	Hγ:2.168,2.061, Hδ:3.921,3.855
6	Gly	8.564	4.015,3.709		
7	Lys	8.020	4.657	1.875,1.834	Hγ:1.449,1.407, Hδ:1.712, Hε:3.019
8	Lys	8.649	5.044	1.728,1.672	Hγ:1.380,1.295, Hδ:1.305,1.303, Hε:2.454,2.351
9	Ile	9.629	4.690	1.868	Hγ:1.483,1.278,0.865, Hδ:1.271

10	Trp	9.023	4.319	**2.804,1.953**	Hδ:6.764,Hε:10.191,**5.557**,Hζ:7.342,6.685,Hη:7.122
11	Thr	7.910	4.239	4.169	Hγ: 5.599 (OH), 1.073 (Me)
12	Gly	**5.364**	3.359,3.318		

Table S7I: Ac-WVTI**p**GKKIFTG-NH_2

#	Res	H_N	Hα	Hβ (Hβ')	Others
0	Ac		1.842		
1	Trp	8.598	5.215	3.059,3.059	Hδ:7.384,Hε:10.325,7.421,Hζ:7.373,7.097,Hη:7.233
2	Val	9.369	4.637	2.130	Hγ:0.915,0.898
3	Thr	8.623	5.208	3.974	Hγ: 1.028 (Me)
4	Ile	9.003	4.696	1.795	Hγ:1.500,1.121,0.912, Hδ:0.836
5	dPro		4.373	1.971,2.382	Hγ:2.049,2.149, Hδ:3.855,3.900
6	Gly	8.538	4.006,3.722		
7	Lys	8.025	4.644	1.857,1.830	Hγ:1.439,1.407, Hδ:1.704, Hε:3.011
8	Lys	8.627	5.038	1.709,1.709	Hγ:1.384,1.308, Hδ:1.320,1.320, Hε:2.523,2.458
9	Ile	9.441	4.560	1.800	Hγ:1.442,1.200,0.836, Hδ:0.821
10	Phe	8.872	4.253	**2.525,1.397**	Hδ:**6.218**, Hε:7.136, Hζ:7.161
11	Thr	8.094	4.219	4.186	Hγ: 1.077 (Me)
12	Gly	**6.621**	3.649,3.586		

Table S7J: Ac-FVTI**p**GKKIWTG-NH_2

#	Res	H_N	Hα	Hβ (Hβ')	Others
0	Ac		1.690		
1	Phe	8.448	5.290	2.757,2.661	Hδ:7.149, Hε:7.415, Hζ:7.374
2	Val	9.052	4.481	2.067	Hγ:0.898,0.868
3	Thr	8.592	5.139	3.952	Hγ: 0.995 (Me)
4	Ile	8.900	4.672	1.787	Hγ:1.496,1.105,0.905, Hδ:0.838
5	dPro		4.365	1.965,2.375	Hγ:2.131,2.038, Hδ:3.877,3.869
6	Gly	8.503	4.003,3.700		
7	Lys	8.007	4.580	1.834,1.796	Hγ:1.440,1.369, Hδ:1.686, Hε:3.007
8	Lys	8.585	4.707	1.580,1.443	Hγ:1.260,1.042, Hδ:1.253,1.161, Hε:2.358,2.289
9	Ile	9.298	4.498	1.888	Hγ:1.438,1.266,0.881, Hδ:0.814
10	Trp	9.093	4.614	3.248,3.056	Hδ:6.997,Hε:10.235,**6.542**,Hζ:7.378,6.933,Hη:7.157
11	Thr	8.170	4.274	4.186	Hγ: 1.111 (Me)
12	Gly	**6.653**	3.622,3.416		

Table S7K: (Pr-WTTVCIRKWTGPK-NH_2)$_2$

#	Res	HN	Hα	Hβ (Hβ')	Others	^{13}Cα	^{13}Cβ
0	Pr		1.459, 1.881	0.392			11.19
1	Trp	8.392	5.151	3.132,3.090	Hδ:7.469,Hε:10.33,7.40,Hζ:7.38,7.127,Hη:7.228		
2	Thr	9.394	4.735	4.053	Hγ: 1.135 (Me)		71.66
3	Thr	8.824	5.117	4.003	Hγ: 1.137 (Me)		69.85
4	Val	9.085	4.381	2.001	Hγ:0.938,0.936	61.44	34.38
5	Cys	9.188	5.709	3.000,2.602	Hγ:na	55.42	
6	Ile	9.047	4.554	1.911	Hγ:1.472,1.214,0.944, Hδ:0.887	59.78	41.97
7	Arg	8.701	5.285	1.792,1.659	Hγ:1.578,1.560, Hδ:2.811,2.763, Hε:6.655, Hη:6.284, 5.853		31.60
8	Lys	9.455	4.958	1.816,1.700	Hγ:1.405,1.346, Hδ:1.678,1.639, Hε:2.910, Hζ:7.703		36.49
9	Trp	9.142	4.271	**2.774,1.949**	Hδ:6.636,Hε:9.857,**5.569**,Hζ:7.369,6.692,Hη:7.127	56.93	28.57
10	Thr	8.057	4.285	4.132	Hγ: 1.028 (Me)	61.33	69.52
11	Gly	**5.731**	3.690, 3.271			44.37	
12	Pro		4.397	1.950,2.314	Hγ:2.054,2.034, Hδ:3.540,3.610	63.12	32.20
13	Lys	8.698	4.245	1.832,1.769	Hγ:1.478,1.430, Hδ:1.666, Hε:2.964, Hζ:7.573	56.58	33.04

Table S7L: (WTTVCIRKWTGPK-NH_2)$_2$

#	Res	HN	Hα	Hβ (Hβ')	Others
1	Trp		4.461	3.232,3.192	Hδ:7.259,Hε:10.424,7.423,Hζ:7.575,7.167,Hη:7.294
2	Thr	9.017	4.622	4.113	Hγ: 1.163 (Me)
3	Thr	8.704	4.904	4.046	Hγ: 1.157 (Me)
4	Val	8.839	4.344	2.004	Hγ: 0.930
5	Cys	9.003	5.443	2.988,2.746	Hγ:na
6	Ile	8.935	4.448	1.902	Hγ:1.461,1.192,0.927, Hδ:0.869
7	Arg	8.621	4.730	1.571,	Hγ:1.442,1.306, Hδ:2.593,2.566, Hε:6.725
8	Lys	8.982	4.620	1.807,1.648	Hγ:1.394,1.365, Hδ:na, Hε:2.915
9	Trp	8.962	4.290	3.153,3.058	Hδ:7.028, Hε:10.053,7.115, Hζ:7.413,7.011, Hη:7.165
10	Thr	7.685	4.266	4.103	Hγ: 1.081 (Me)
11	Gly	7.423	3.838,3.713		
12	Pro		4.410	1.957,2.322	Hγ:2.047, Hδ:3.621,3.594
13	Lys	8.621	4.204	1.795,1.733	Hγ:1.433,1.376, Hδ:1.617, Hε:2.907

Table S7M: WTTVCIRKWTGPK-NH_2 (monomer)

#	Res	HN	Hα	Hβ (Hβ')	Others
1	Trp		4.389	3.436,3.382	Hδ:7.291, Hε:10.291,7.602, Hζ:7.515,7.149, Hη:7.248
2	Thr		4.412	4.099	Hγ: 1.161 (Me)
3	Thr	8.420	4.284	4.149	Hγ: 1.222 (Me)
4	Val	8.376	4.076	2.035	Hγ:0.935,0.920
5	Cys	8.624	4.477	2.834,2.834	Hγ:na
6	Ile	8.521	4.142	1.849	Hγ:1.468,1.199,0.889, Hδ:0.858
7	Arg	8.540	4.289	1.709,1.709	Hγ:1.562,1.516, Hδ:3.098, Hε:7.184, Hη:6.170, 7.142
8	Lys	8.508	4.301	1.744,1.685	Hγ:1.398,1.354, Hδ:1.658, Hε:2.955
9	Trp	8.604	4.713	3.267,3.267	Hδ:7.244, Hε:10.168,7.634, Hζ:7.488,7.153, Hη:7.244
10	Thr	8.068	4.274	4.142	Hγ: 1.114 (Me)
11	Gly	7.351	3.861,3.706		
12	Pro		4.419	1.955,2.330	Hγ:2.058,2.058, Hδ:3.625,3.625
13	Lys	8.619	4.223	1.807,1.746	Hγ:1.435,1.376, Hδ:1.628, Hε:2.927

Table S7N: Ac-WI**p**GKWTGP-KG-KTWNPATGKWTE at 290K *[1]

#	Res	HN	Hα	Hβ (Hβ')	Others
1	Trp	8.718	5.010	3.309,3.102	Hδ:7.463,Hε:10.072,7.315,Hζ:7.181,7.119,Hη:7.372
2	Ile	9.136	4.736	1.822	Hγ:1.417,1.099,0891,Hδ:0816
3	dPro		4.422	2.373,2.148	Hγ:2.064,1.985,Hδ:3.895,3.849
4	Gly	8.762	4.021,3.931		
5	Lys	8.145	4.801	1.894,1.799	Hγ:1.337,Hδ:1.685,Hε:2.985
6	Trp	8.816	4.187	**2.744,1.929**	Hδ:6.735,Hε:9.788,**5.688**,Hζ:7.375,6.798,Hη:7.175
7	Thr	7.765	4.239	4.127	Hγ: 1.043 (Me)
8	Gly	**5.178**	3.618,3.099		
9	Pro		4.330	2.233	Hγ:1.907,1.832,Hδ:3.323
10	Lys	8.559	4.238	1.772,1.730	Hγ:1.425,1.376,Hδ:1.633,Hε:2.930
11	Gly	8.366	3.945		
12	Lys	8.143	4.664	1.956	Hγ:1.404,1.304,Hδ:1.493,1.407,Hε:2.711
13	Thr	8.905	4.750	4.061	Hγ: 1.135 (Me)
14	Trp	8.898	4.109	**2.685,1.964**	Hδ:6.640,Hε:9.999,**5.547**,Hζ:7.265,6.432,Hη:6.915
15	Asn	7.555	4.895	3.079,2.357	Hδ:7.240,5.934
16	Pro		3.756	2.373	Hγ:2.021,1.977,Hδ:3.671
17	Ala	7.785	4.148	1.392	
18	Thr	6.903	4.261	4.121	Hγ: 1.002 (Me)
19	Gly	8.004	3.744,3.249		
20	Lys	6.680	4.442	1.763,1.646	Hγ:1.413,1.241,Hδ:1.565,Hε:2.960
21	Trp	8.528	5.069	3.175,	Hδ:7.487,Hε:10.154,7.381,Hζ:7.161,7.069,Hη:7.373
22	Thr	9.248	4.567	4.317	Hγ: 1.215 (Me)
23	Glu	8.293	4.251	2.101,1.942	Hγ:2.269

KTWNPATGKWTE isolated at 290K *[1]

#	Res	HN	Hα	Hβ (Hβ')	Others
1	Lys		4.451	2.080, 1.901	Hγ:1.418,Hδ:1.258,Hε:2.484,2.391
2	Thr	9.239	4.870	4.043	Hγ: 1.243 (Me)
3	Trp	9.049	4.091	**2.648, 1.840**	Hδ:6.631,Hε:10.002,**5.425**,Hζ:7.274,6.430,Hη:6.910
4	Asn	7.457	4.920	3.059,2.373	Hδ:7.19,7.22
5	Pro		3.736	2.391,1.987	Hγ:2.037,Hδ:3.796,3.665
6	Ala	7.796	4.138	1.397	
7	Thr	6.864	4.262	4.116	Hγ: 0.997 (Me)
8	Gly	7.970	3.734,3.215		
9	Lys	6.621	4.496	1.767,1.420	Hγ:1.256,Hδ:1.671,1.572Hε:2.978
10	Trp	8.671	5.139	3.178	Hδ:7.564,Hε:10.361,7.375,Hζ:7.154,7.181Hη:7.286
11	Thr	9.402	4.645	4.330	Hγ: 1.222 (Me)
12	Glu	8.452	4.145	2.119,1.952	Hγ:2.317,Hε:na

Ac-WIpGKWTGPS isolated at 290K *[1]

#	Res	HN	Hα	Hβ (Hβ')	Others
1	Trp	8.860	5.049	3.341,3.141	Hδ:7.513,Hε:10.216,7.339,Hζ:7.287,7.159,Hη:7.205
2	Ile	9.245	4.764	1.858	Hγ:1.446,1.117,0.906,Hδ:0.834
3	dPro		4.438	2.001,2.392	Hγ:2.171,2.082,Hδ:3.864,3.935
4	Gly	8.900	4.034,3.965		
5	Lys	8.207	4.844	1.936,1.811	Hγ:1.434,1.342,Hδ:1.700,Hε:2.995
6	Trp	8.939	4.135	**2.712,1.838**	Hδ:6.739,Hε:9.879,**5.570**,Hζ:7.414,6.813,Hη:7.182
7	Thr	7.749	4.237	4.136	Hγ: 5.519 (OH), 1.056 (Me)
8	Gly	**5.041**	3.737,3.189		
9	Pro		4.479	2.055,2.330	Hγ:2.091,2.039,Hδ:3.526,3.617
10	Ser	8.320	4.348	3.891,3.866	Hγ:na

Table S7O: Ac-WI**p**GKWTGPK-GG-WI**p**GKWTGPK-NH_2 at 290K *[1]

#	Res	HN	Hα	Hβ (Hβ')	Others
1	Trp	8.727	5.028	3.321,3.112	Hδ:7.471,Hε:10.054,7.341,Hζ:7.166,7.141,Hη:7.265
2	Ile	9.175	4.739	1.837	Hγ:1.424,1.105,0.896,Hδ:0.822
3	dPro		4.421	2.372,2.010	Hγ:2.145,2.068,Hδ:3.909,3.845
4	Gly	8.775	4.016,3.923		
5	Lys	8.172	4.812	1.896,1.806	Hγ:1.424,1.349,Hδ:1.681,Hε:2.980
6	Trp	8.851	4.182	**2.725,1.918**	Hδ:6.722,Hε:9.821,**5.595**,Hζ:7.327,6.764,Hη:7.128
7	Thr	7.772	4.259	4.141	Hγ:1.043
8	Gly	**4.968**	3.757,3.176		
9	Pro		4.405	2.315	Hγ:2.023,1.946,Hδ:3.576,3.512
10	Lys	8.613	4.307	1.811,1.761	Hγ:1.505,1.444,Hδ:1.665,Hε:2.978

11	Gly	8.210	3.672		
12	Gly	7.547	3.654,3.381		
13	Trp	8.465	4.932	3.218,3.050	Hδ:7.355,Hε:10.176,7.266,Hζ:7.292,7.165,Hη:na
14	Ile	9.002	4.641	1.774	Hγ:1.336,0.999,0.811,Hδ:0.747
15	dPro		4.415	2.373,1.974	Hγ:2.132,2.048,Hδ:3.828
16	Gly	8.705	4.012,3.910		
17	Lys	8.114	4.809	1.877,1.809	Hγ:1.418,1.338,Hδ:1.662,Hε:2.973
18	Trp	8.836	4.141	**2.741,1.986**	Hδ:6.698,Hε:9.781,**5.791**,Hζ:7.280,6.739,Hη:7.052
19	Thr	7.837	4.202	3.948	Hγ: 0.960 (Me)
20	Gly	**6.293**	3.559		
21	Pro		4.306	2.165	Hγ:1.952,1.873,Hδ:3.450,3.367
22	Lys	8.520	4.191	1.773,1.703	Hγ:1.423,1.340,Hδ:1.604,Hε:2.914

Table S7P: Ac-WITVTI-$G_4K_2G_4$-KKIRVWTG-NH_2

#	Res	HN	Hα	Hβ (Hβ')	Others
1	Trp	8.634	5.101	3.169,3.145	Hδ:7.395,Hε:10.198,7.514,Hζ:7.364,7.125,Hη:7.226
2	Ile	9.110	4.628	1.862	Hγ:1.350,1.127,0.858,Hδ:0.763
3	Thr	8.545	4.943	4.021	Hγ: 1.141 (Me)
4	Val	8.979	4.397	2.046	Hγ:na,0.897
5	Thr	8.564	4.726	4.024	Hγ: 1.095 (Me)
6	Ile	8.906	4.332	1.887	Hγ:na,1.210,0.920,Hδ:0.829
7	Gly	8.817	4.052,3.959		
16	Gly	8.415	,3.908		
17	Lys	8.382	4.442	1.795,1.758	Hγ:1.414,1.382,Hδ:1.682,1.682, Hε:na
18	Lys	8.541	4.866	1.695,1.586	Hγ:1.446,1.358,Hδ:1.603,1.603,Hε:na, Hζ:7.556
19	Ile	8.919	4.477		Hγ:na,na,0.894,Hδ:0.828
20	Arg	8.541	5.084	1.789,1.677	Hγ:1.555,1.553,Hδ:2.929,2.893, Hε:6.791
21	Val	9.220	4.484	1.979	Hγ:0.917,0.895
22	Trp	8.884	4.421	**2.914,2.235**	Hδ:6.899,Hε:10.203,**6.255**,Hζ:7.387,6.887,Hη:7.160
23	Thr	7.909	4.214	4.170	Hγ: 1.074 (Me)
24	Gly	**5.859**	3.383,3.435		

*[1] CSDs reported for these species in the article text are from the more limited data obtained at 280K. Complete assignments, as reported herein, were obtained at 290K.