

**TABLE S1 Temperature coefficients of NH resonances**

Peptide	Sequence	$-\text{d}\delta / \text{d}T$ (ppb/deg)				
		Xaa <sup>2</sup>	Xaa <sup>3</sup>	Xaa <sup>4</sup>	Xaa <sup>5</sup>	Xaa <sup>6</sup>
<b>2a</b>	c[D-PWTFFpY]	8.9	4.3	9.0	7.6	2.5
<b>2b</b>	c[D-PWTpYFF]	9.6	4.5	9.0	8.0	2.0
<b>3</b>	c[D-PpYWTFF]	10.5	2.4	6.4	10.1	3.5
<b>4a</b>	c[D-PpYTFFF]	9.3	4.4	9.6		1.5
<b>4b</b>	c[D-PpYFWFT]	10.5	4.5	9.9	9.0	0.5
<b>5*</b>	c[D-PpYTFFWF]	8.7	3.9	5.5	4.6	0.9
<b>6</b>	c[D-PpYTFFW]	11.4	4.4	9.5	9.4	3.6

\* Adams et al., 2002.

**TABLE S2 Coupling constants and  $\chi_1$  rotamer populations, 5 °C**

Residue	$^3J_{H_{\alpha}-H_{\beta r}}$ (Hz)	$^3J_{H_{\alpha}-H_{\beta s}}$ (Hz)	pI	Major rotamer	pII	pIII
<b>c[D-PWTFFPY], 2a</b>						
D-Pro <sup>1</sup>						
Trp <sup>2</sup>	9.1	4.3	0.59	$\chi_1 = -60^\circ$	0.25	0.16
Thr <sup>3</sup>	3.7					
Phe <sup>4</sup>	8.7	7.0	0.56	$\chi_1 = 180^\circ$	0.40	0.04
Phe <sup>5</sup>	10.8	4.8	0.74	$\chi_1 = -60^\circ$	0.20	0.06
pTyr <sup>6</sup>	8.5	4.8	0.54	$\chi_1 = -60^\circ$	0.26	0.20
<b>c[D-PWTpYFF], 2b</b>						
D-Pro <sup>1</sup>						
Trp <sup>2</sup>	8.8	4.6	0.57	$\chi_1 = -60^\circ$	0.25	0.18
Thr <sup>3</sup>	3.0					
pTyr <sup>4</sup>	8.3	7.3	0.52	$\chi_1 = 180^\circ$	0.43	0.05
Phe <sup>5*</sup>	10.0	4.9	0.67		0.21	0.12
Phe <sup>6*</sup>	8.6	5.0	0.55		0.23	0.22
<b>c[D-PpYWTF], 3</b>						
D-Pro <sup>1</sup>						
pTyr <sup>2</sup>	9.2	5.4	0.60	$\chi_1 = -60^\circ$	0.26	0.14
Trp <sup>3</sup>	4.9	11.7	0.83	$\chi_1 = -60^\circ$	0.21	-0.04
Thr <sup>4</sup>	6.8					
Phe <sup>5</sup>	8.7	4.9	0.56	$\chi_1 = -60^\circ$	0.23	0.21
Phe <sup>6*</sup>	8.8	5.4	0.57		0.25	0.18
<b>c[D-PpYTWFF], 4a</b>						

D-Pro <sup>1</sup>						
pTyr <sup>2</sup>	10.3	4.3	0.70	$\chi_1 = -60^\circ$	0.16	0.14
Thr <sup>3</sup>						
Trp <sup>4*</sup>	6.4	5.8	0.36		0.34	0.30
Phe <sup>5*</sup>	7.8	6.8	0.47		0.39	0.14
Phe <sup>6*</sup>	9.6	4.9	0.64		0.21	0.15

c[D-PPYFWFT], **4b**

D-Pro <sup>1</sup>						
pTyr <sup>2</sup>	11.3	4.4	0.79	$\chi_1 = -60^\circ$	0.16	0.05
Phe <sup>3</sup>	11.2	5.4	0.79	$\chi_1 = -60^\circ$	0.25	-0.04
Trp <sup>4</sup>	6.3	7.3	0.43	$\chi_1 = -60^\circ$	0.34	0.23
Phe <sup>5</sup>	7.3	5.9	0.43	$\chi_1 = -60^\circ$	0.30	0.27
Thr <sup>6</sup>	3.9					

c[D-PPYTFFW], **5**

D-Pro <sup>1</sup>						
pTyr <sup>2</sup>	10.7	4.8	0.74	$\chi_1 = -60^\circ$	0.20	0.06
Thr <sup>3</sup>						
Phe <sup>4</sup>	6.8	7.9	0.48	$\chi_1 = 180^\circ$	0.38	0.06
Trp <sup>5</sup>	10.4	4.2	0.72	$\chi_1 = -60^\circ$	0.14	0.14
Phe <sup>6</sup>	8.8	4.9	0.57	$\chi_1 = 180^\circ$	0.22	0.21

c[D-PPYTFFW], **6**

D-Pro <sup>1</sup>						
pTyr <sup>2</sup>	10.7	4.0	0.74	$\chi_1 = -60^\circ$	0.14	0.12
Thr <sup>3</sup>	3.8					

Phe <sup>4</sup>	6.8	8.8	0.56	$\chi_1 = 180^\circ$	0.39	0.05
Phe <sup>5</sup>	10.7	4.9	0.73	$\chi_1 = -60^\circ$	0.21	0.06
Trp <sup>6</sup>	8.8	4.0	0.57	$\chi_1 = 180^\circ$	0.30	0.13

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\* Stereospecificity unresolved.