Electronic Supplementary Material (ESI) for ChemComm.

Supporting information

Accommodation of Gly-*cis*Pro in a designed β-hairpin

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Section S1. Materials and Methods

Peptide synthesis:

All peptides were synthesized by using the standard solid-phase peptide synthesis procedure in a stepwise manner on an AAPPTEC 90II peptide synthesizer, using Fmoc chemistry. Rink amide MBHA resin (0.39 mmol/g substitution) and Fmoc-amino acids were purchased from Novabiochem while the fluorinated amino acids, Fmoc-4-*R*-fluoroproline (^{t}P) and Fmoc-4-*S*-fluoroproline (^{c}P), were purchased from BACHEM. The Fmoc-protected amino acid derivatives (5-fold excess of resin load) were coupled using PyBOP and diisopropylethylamine (DIPEA) (5- and 10-fold excess of resin substitution, respectively) in N,N-dimethylformamide (DMF). The deprotection reactions of the Fmoc group were achieved using 20% (v/v) piperidine solution in DMF. The peptides were acetylated at their N-terminal by using acetic acid, PyBOP, and DIPEA (5-, 5-, 10-fold excess of resin substitution, respectively) in DMF. The peptides were cleaved from the resin using a cleavage cocktail containing 85% TFA, 5% water, 5% phenol, 2.5% anisole and 2.5% triisopropylsilane for 1 h. TFA was removed by evaporation, and the afforded crude peptides were dissolved in methanol. Peptides were purified using reverse-phase HPLC (on Phenomenix C18 column) using a linear gradient (0 to 100% over 60 min) of H_2O/CH_3OH). The purified peptides were then lyophilized and then characterized by MALDI-TOF mass spectrometry and ^{1}H NMR spectroscopy.

CD Spectrophotometry:

Circular dichroism experiments for the peptides were carried out in methanol at two different temperatures, 298 K and 278 K respectively, on a JASCO J-1500 CD spectrophotometer. Concentrations of the peptides were maintained around 50 μM. All spectra were recorded from 260 nm to 200 nm with data interval of 1 nm. Scan speed was set to 50 nm/min and digital integration time (D.I.T) was set to 4 sec. All spectra were averaged over 3 scans. The spectra were baseline corrected manually and the ellipticity value at 260 nm for all the spectra were zero-corrected. For each peptide at least 3 independent trials were performed and the averaged data were used for analysis.

NMR Spectroscopy:

All ^{1}H NMR experiments were carried out either on a Bruker Avance III 500 MHz spectrometer equipped with a SMART probe or on a Bruker Avance III 700 MHz spectrometer equipped with an RT probe at 298 K, unless otherwise mentioned. Spectra of the peptides were obtained in CD_3OH. Resonance assignments for the amino acids within the peptides were achieved via TOCSY with 80 ms spinlock time with 2048 data points and 510 t1 increments. The sequence assignments were achieved via ROESY experiments (mixing time of 250-350 ms, 510 t1 increments, and 16 scans per t1 increment). The prolyl isomers were identified using the expected Hα–Hα and Hα–Hδ ROE cross-peaks for the *cis* and the *trans* isomers, respectively. Relative *cis*-*trans* populations were calculated from the relative integrals of appropriate well-resolved resonances (amide) from the corresponding ^{1}H NMR spectra.

Characterization of peptides by ^{1}H NMR spectroscopy

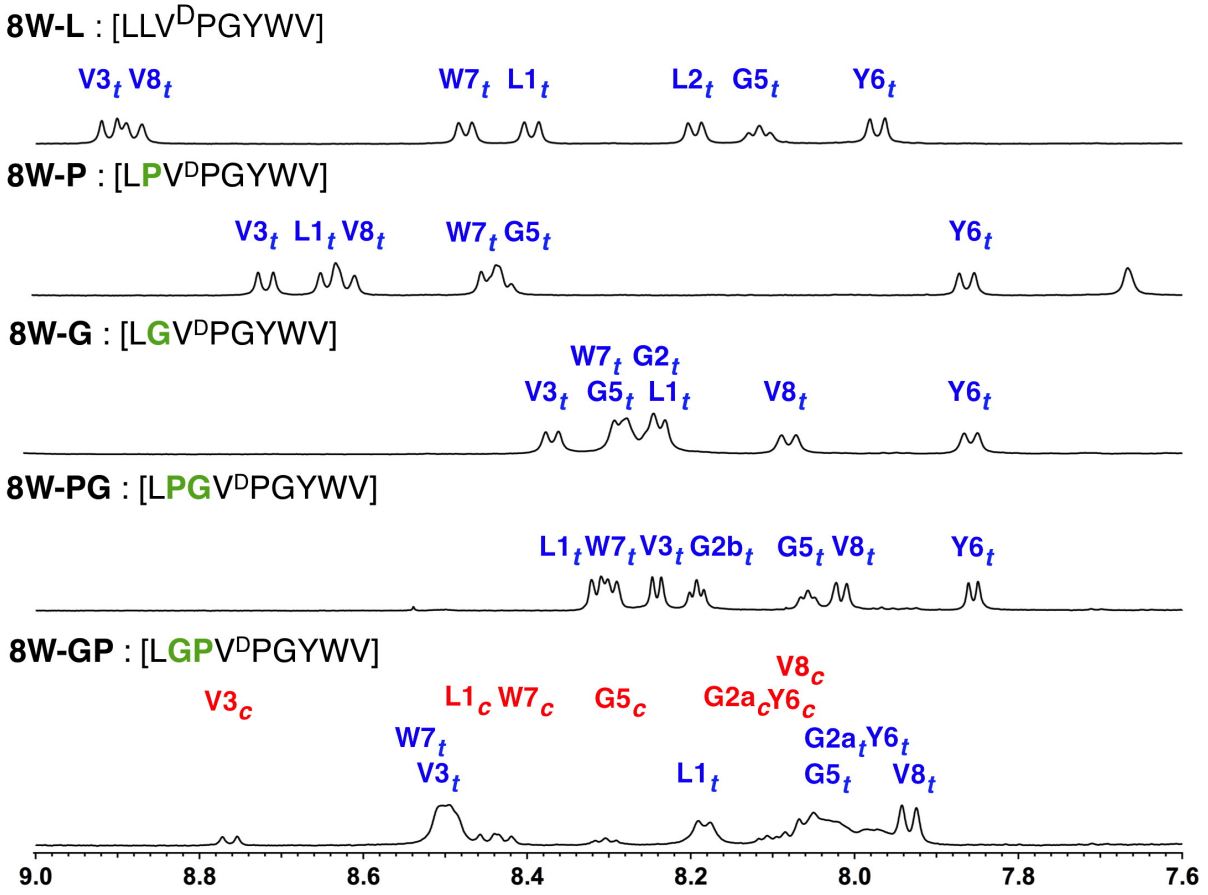

Figure S1: Comparison of the amide region in the ^{1}H NMR for the peptides 8W-L, 8W-P, 8W-G, 8W-PG, and 8W-GP in CD_3OH at 298 K.

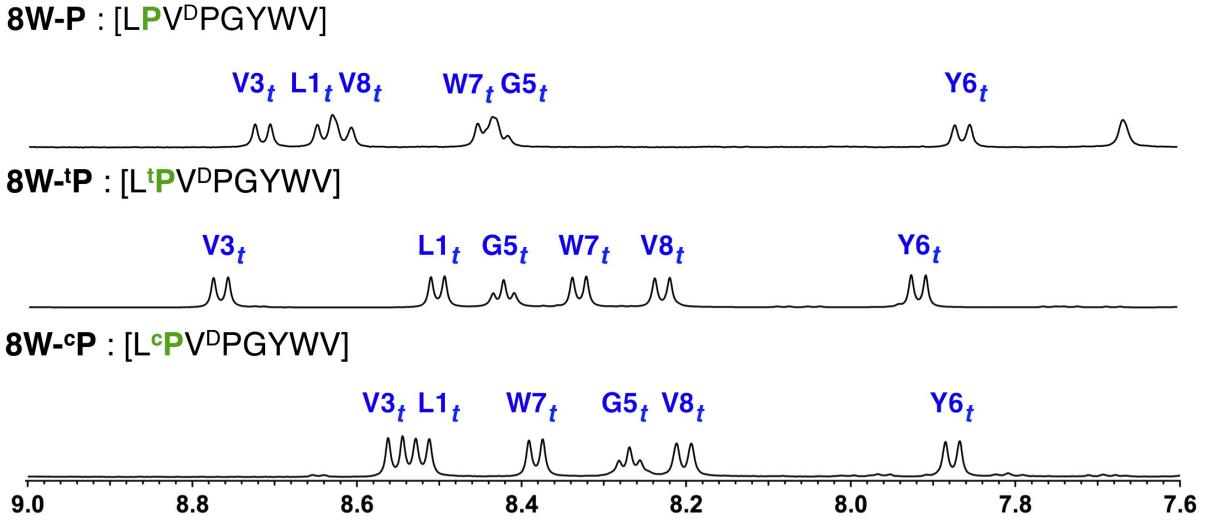

Figure S2: Comparison of the amide region in the ^{1}H NMR for the peptides 8W-P, 8W-^{t}P, and 8W-^{c}P in CD_3OH at 298 K.

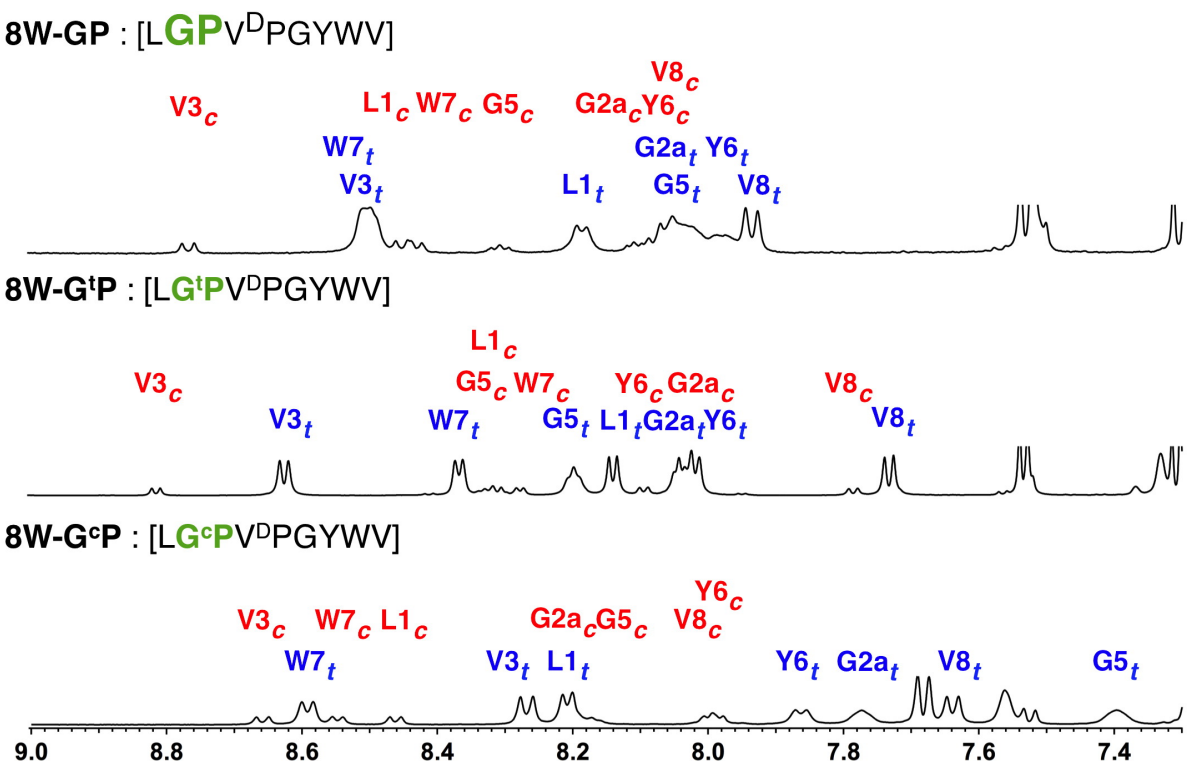

Figure S3: Comparison of the amide region in the ^{1}H NMR for the peptides 8W-GP, 8W-G^{t}P, and 8W-G^{c}P in CD_3OH at 298 K.

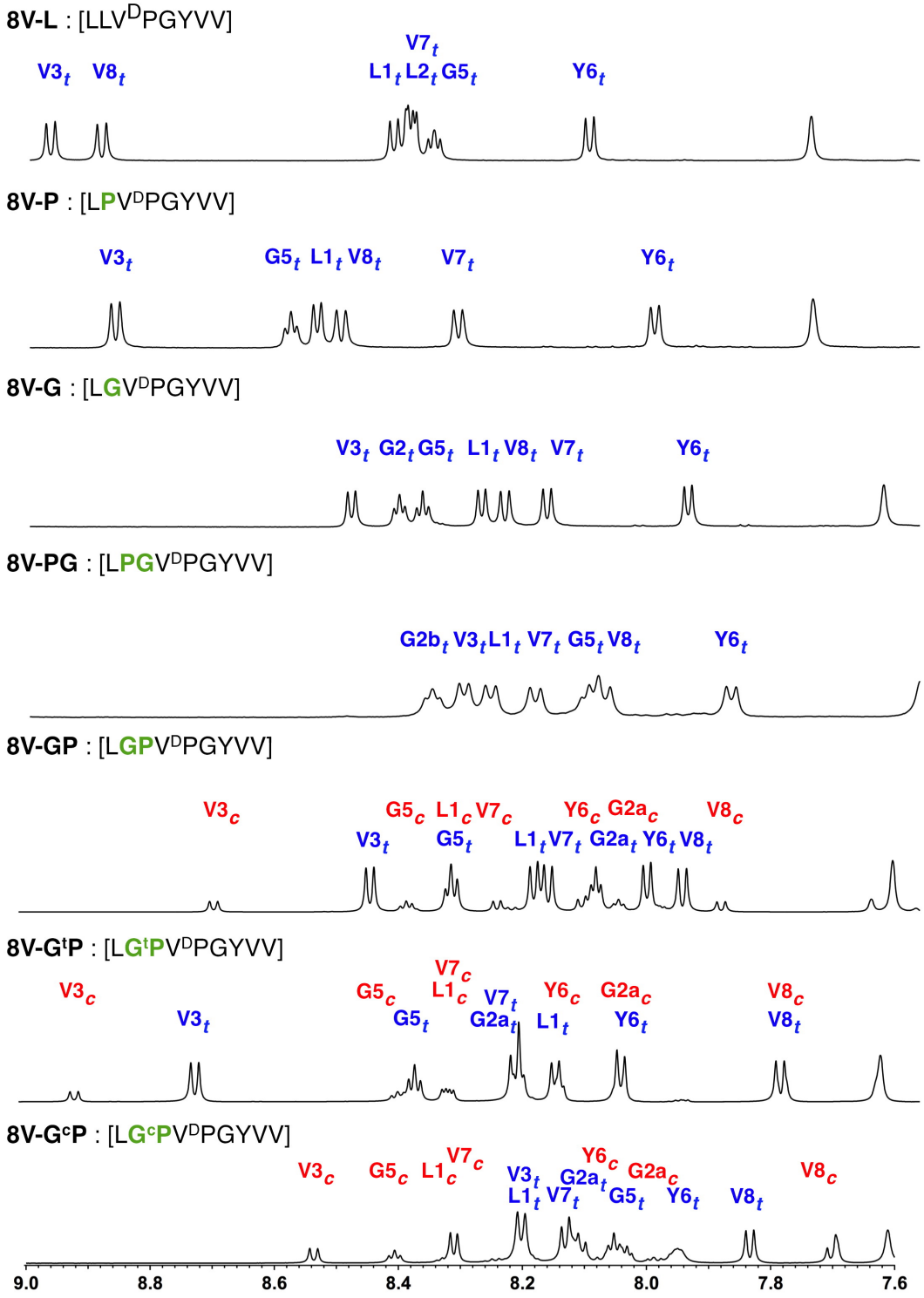

Figure S4: Comparison of the amide region in the ^{1}H NMR for the peptides in 8V series in CD_3OH at 298 K.

Assigned TOCSY spectra for all peptides

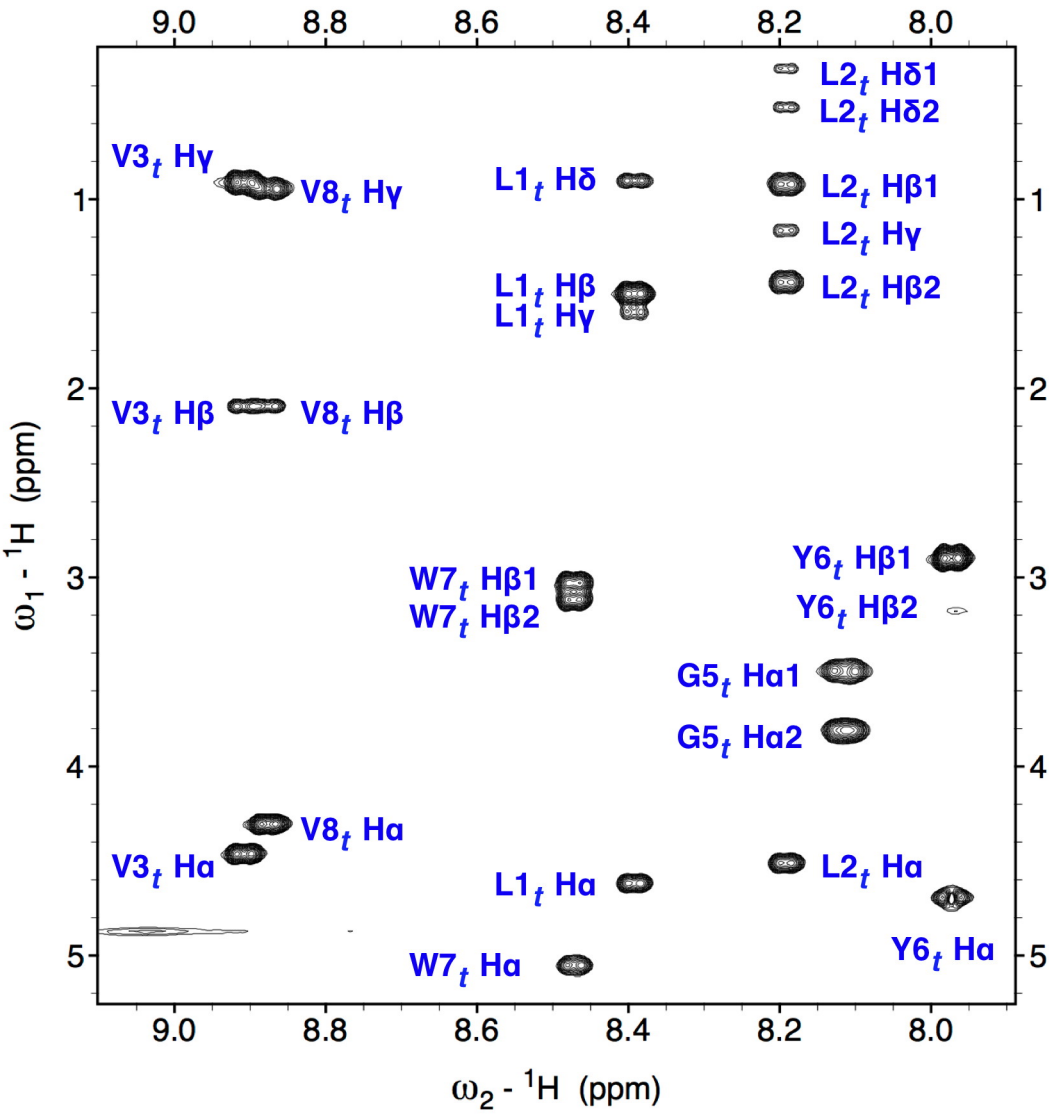

Figure S5: Amide fingerprint region from TOCSY of the peptide 8W-L in CD_3OH at 298 K.

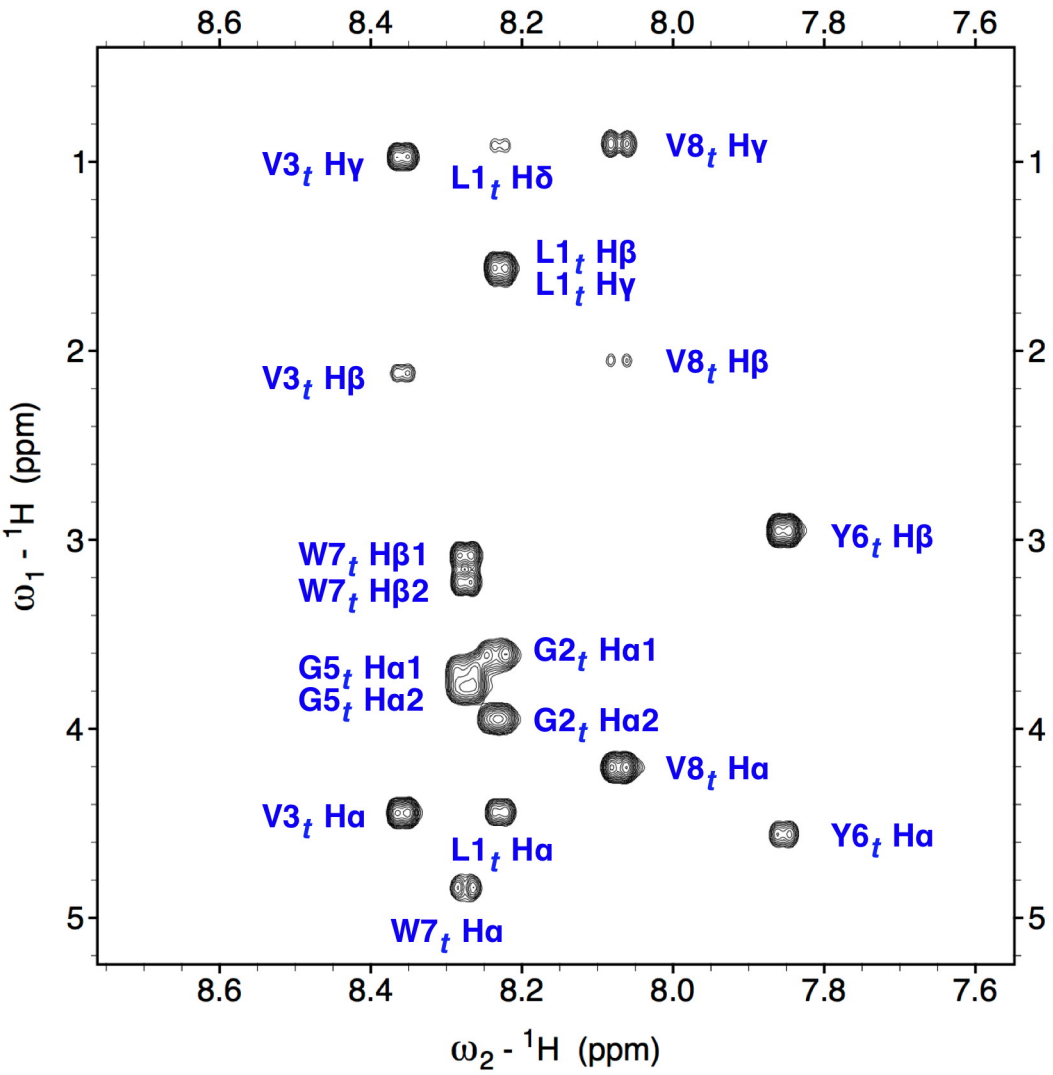

Figure S6: Amide fingerprint region from TOCSY of the peptide 8W-G in CD_3OH at 298 K.

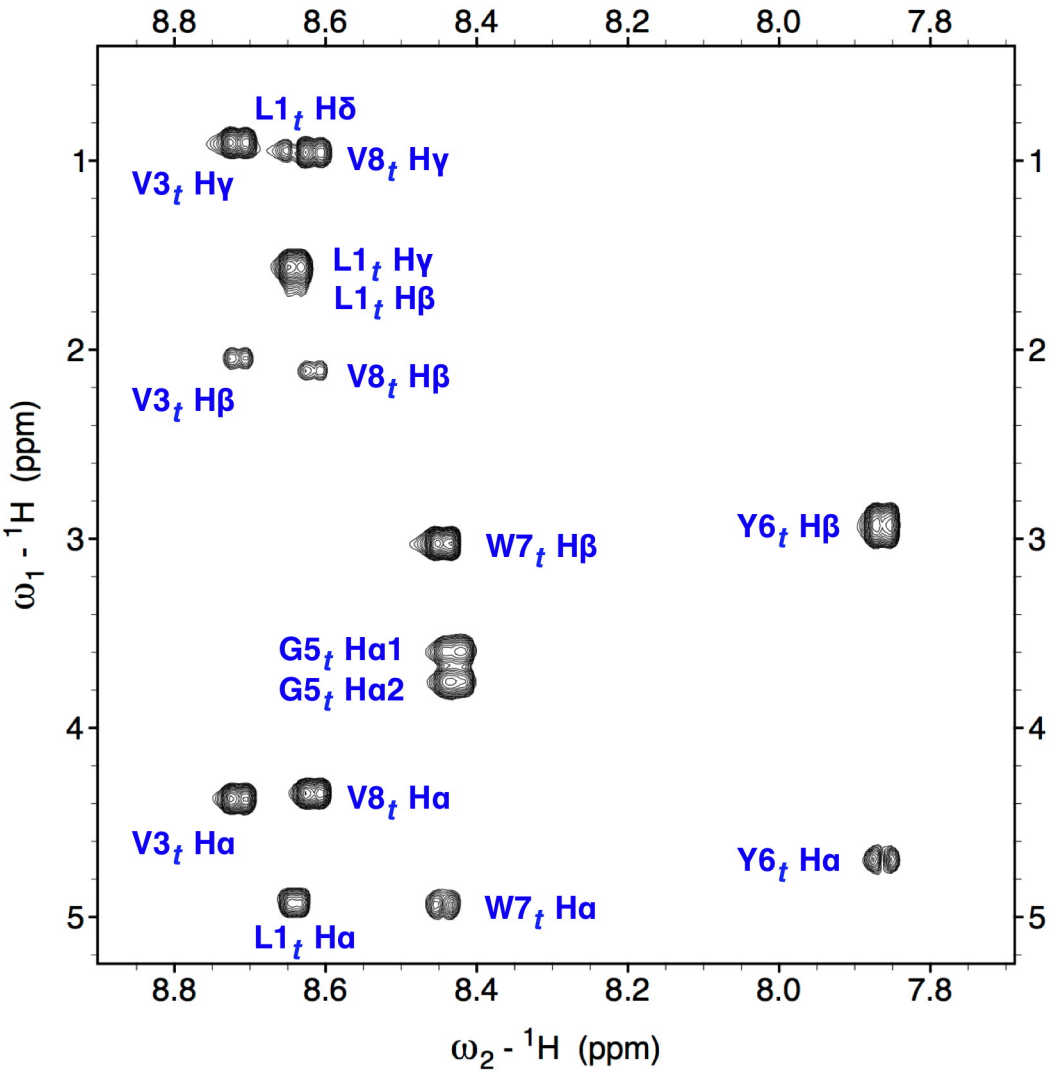

Figure S7: Amide fingerprint region from TOCSY of the peptide 8W-P in CD_3OH at 298 K.

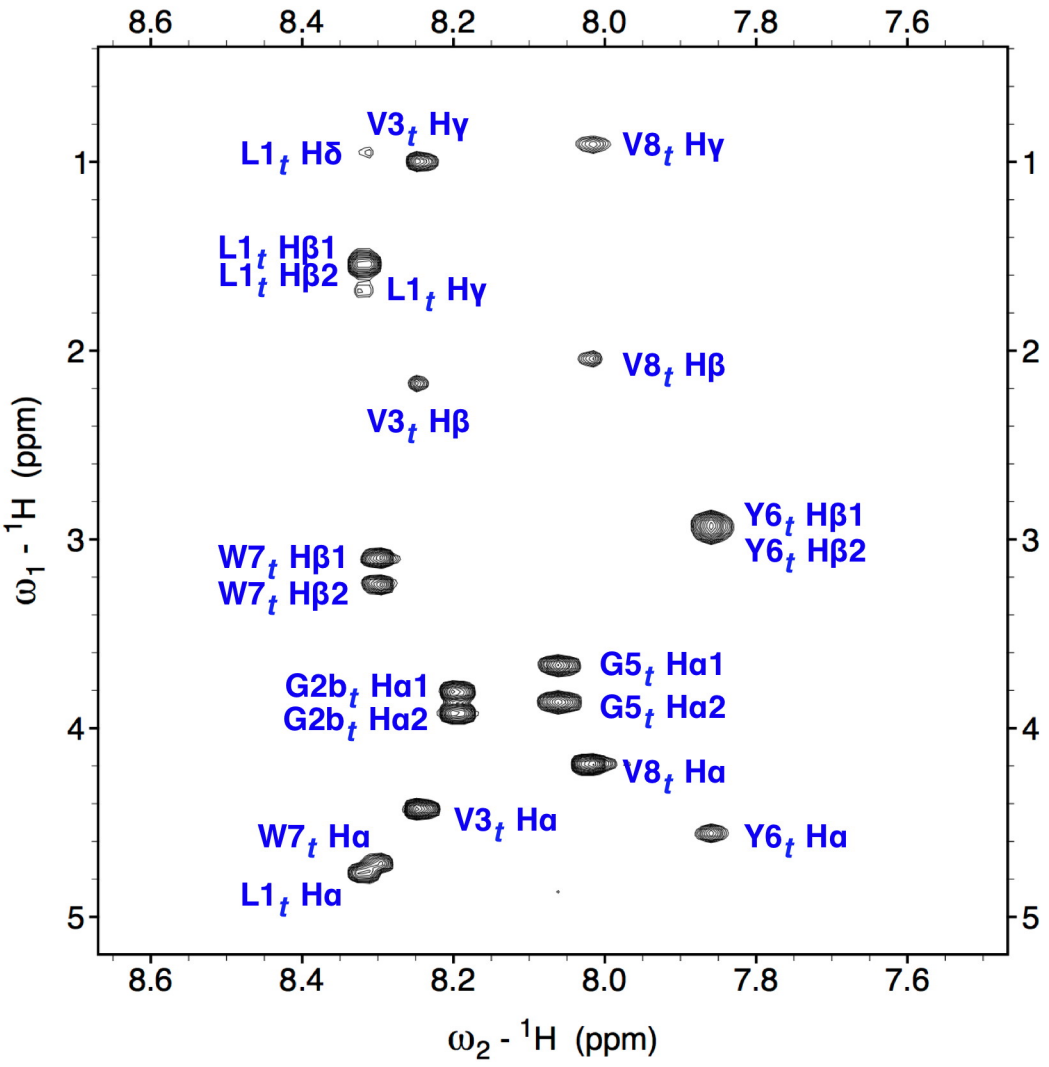

Figure S8: Amide fingerprint region from TOCSY of the peptide 8W-PG in CD_3OH at 298 K. Numbering the proline and glycine as residues with numbers as 2a and 2b, respectively, reflects the replacement of L2 with PG.

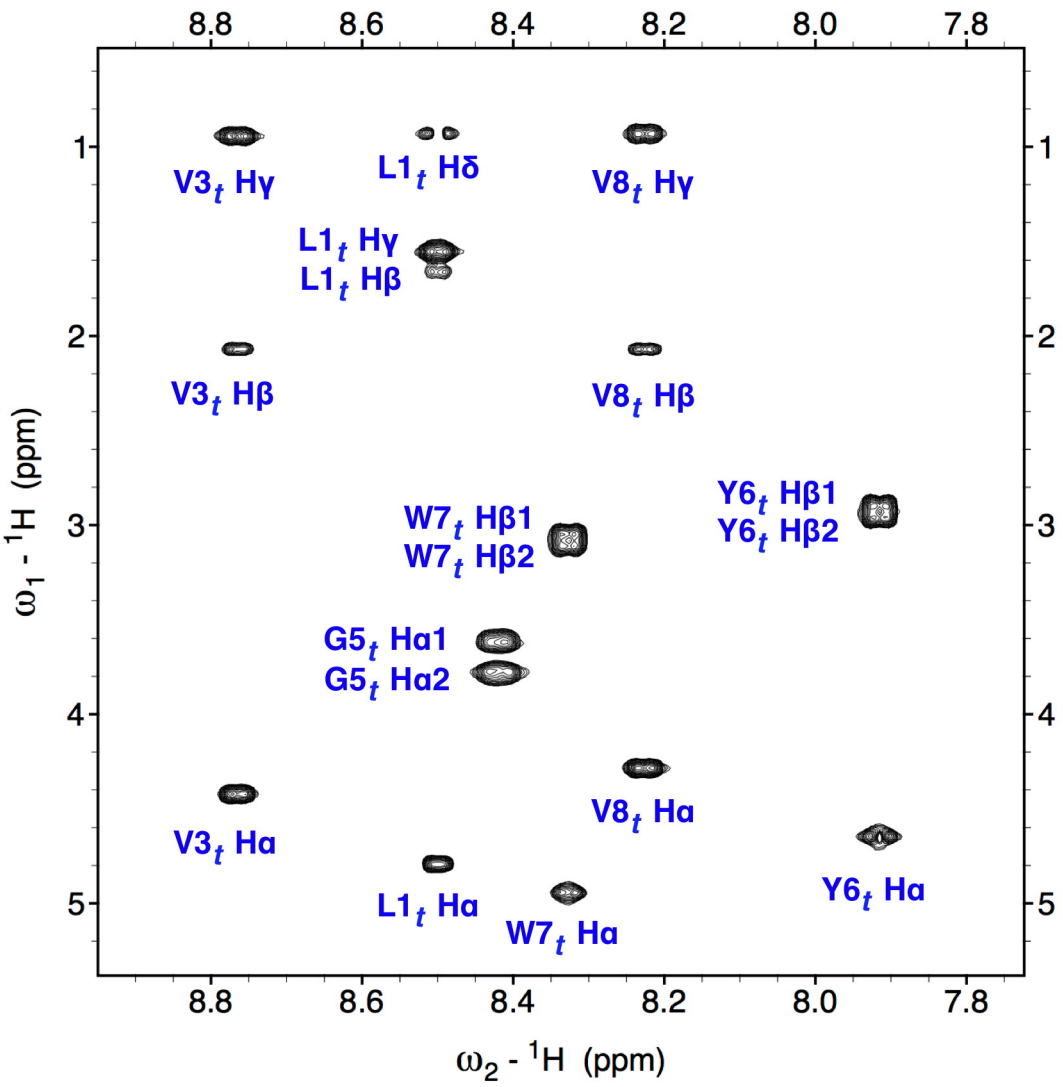

Figure S9: Amide fingerprint region from TOCSY of the peptide 8W-^{t}P in CD_3OH at 298 K.

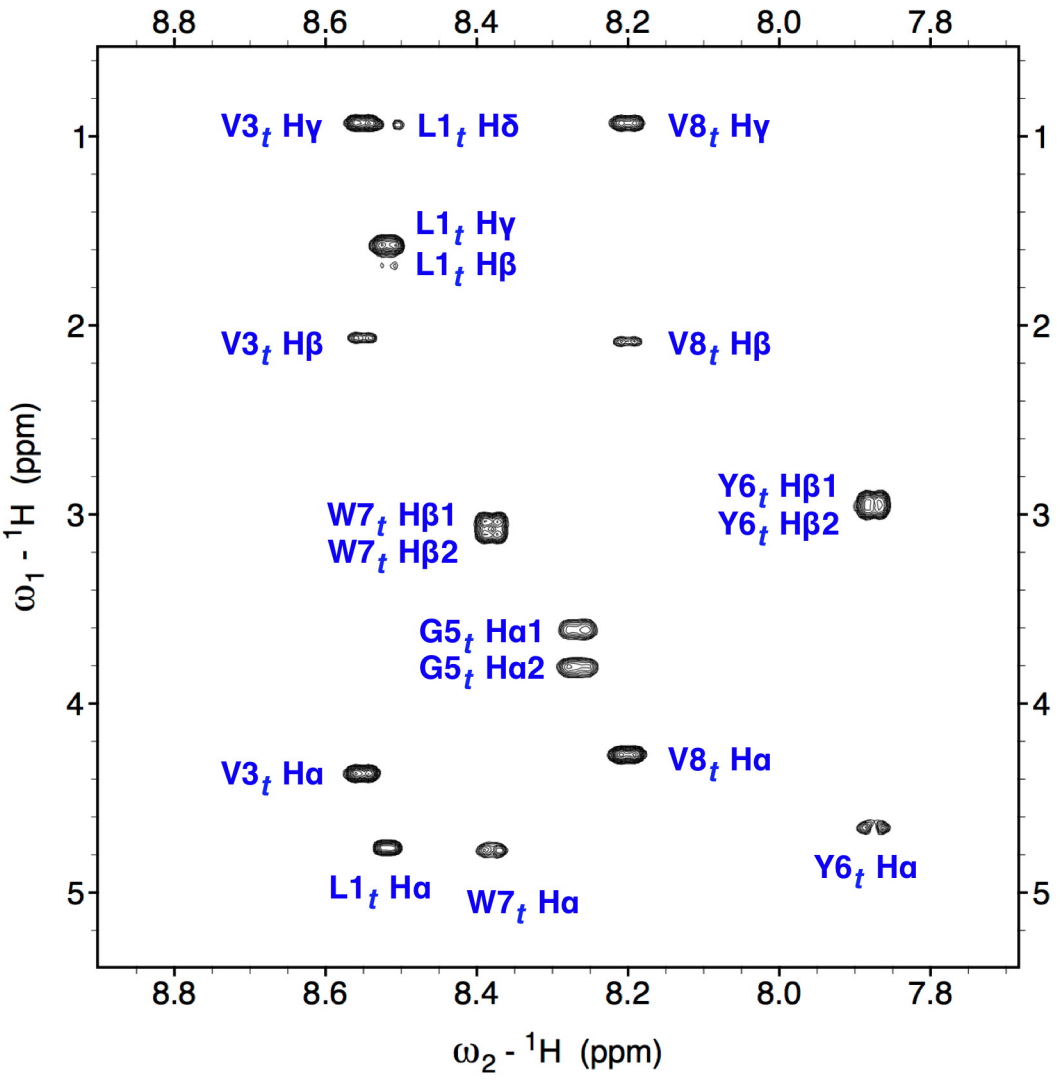

Figure S10: Amide fingerprint region from TOCSY of the peptide 8W-^{c}P in CD_3OH at 298 K.

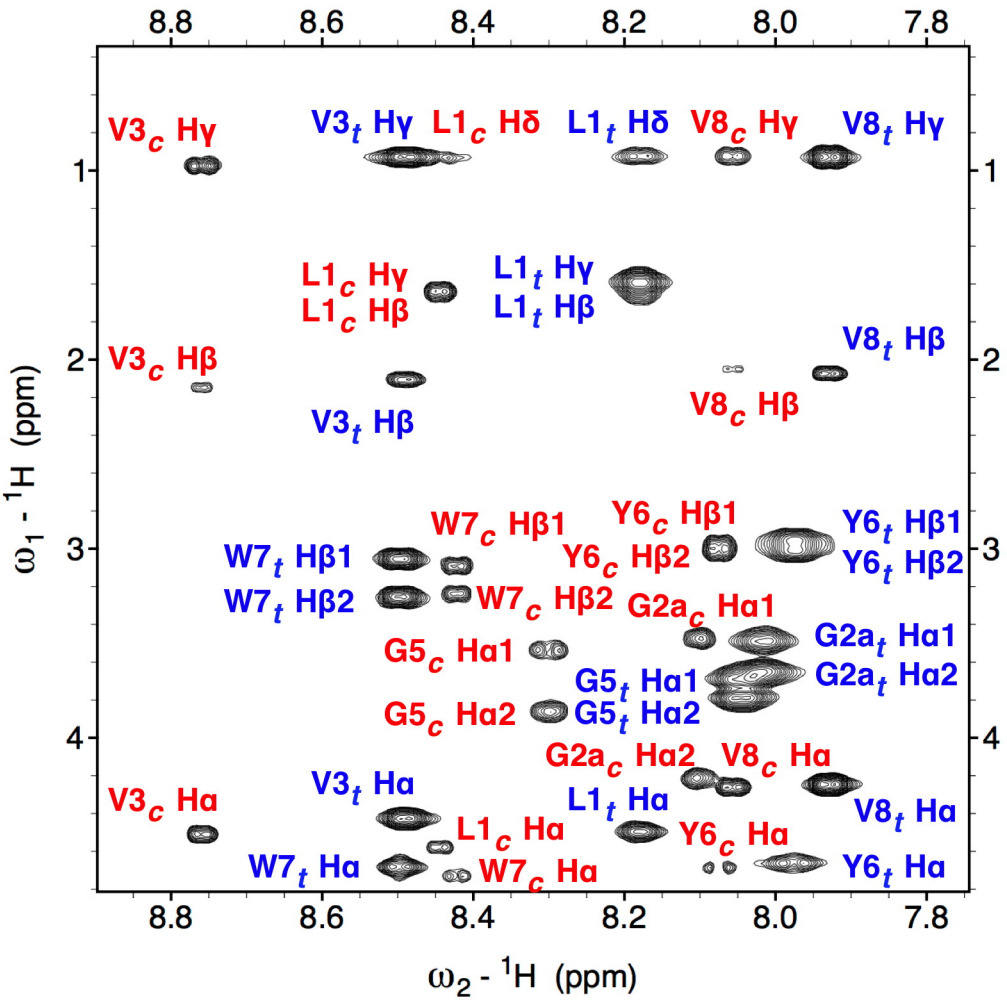

Figure S11: Amide fingerprint region from TOCSY of the peptide 8W-GP in CD_3OH at 298 K. Numbering the glycine and proline as residues with numbers as 2a and 2b, respectively, reflects the replacement of L2 with GP. The resonances corresponding to the *cis* and the *trans* isomers are labeled in red and blue, respectively.

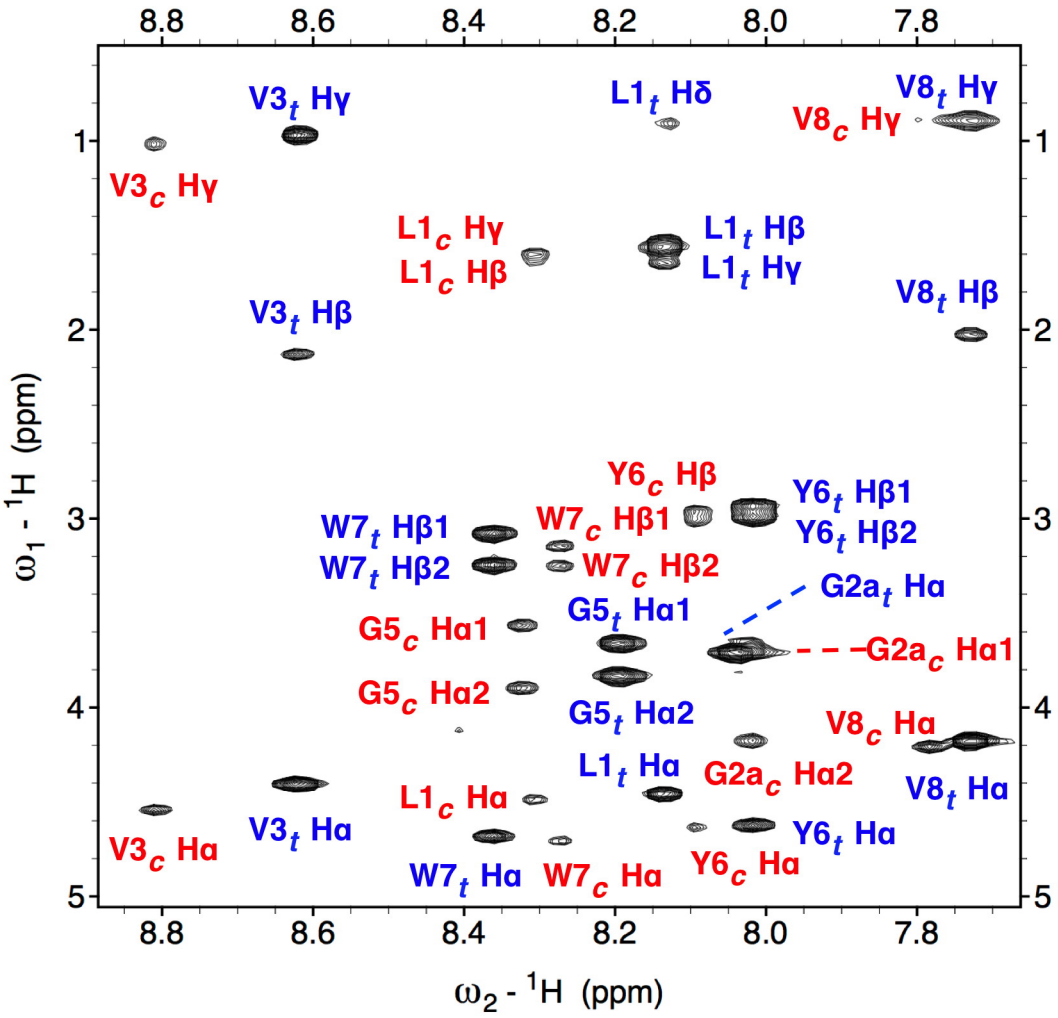

Figure S12: Amide fingerprint region from TOCSY of the peptide 8W-G^{t}P in CD_3OH at 298 K. Numbering the glycine and 4*R*-fluoroproline (^{t}P) as residues with numbers as 2a and 2b, respectively, reflects the replacement of L2 with G^{t}P. The resonances corresponding to the *cis* and the *trans* isomers are labeled in red and blue, respectively.

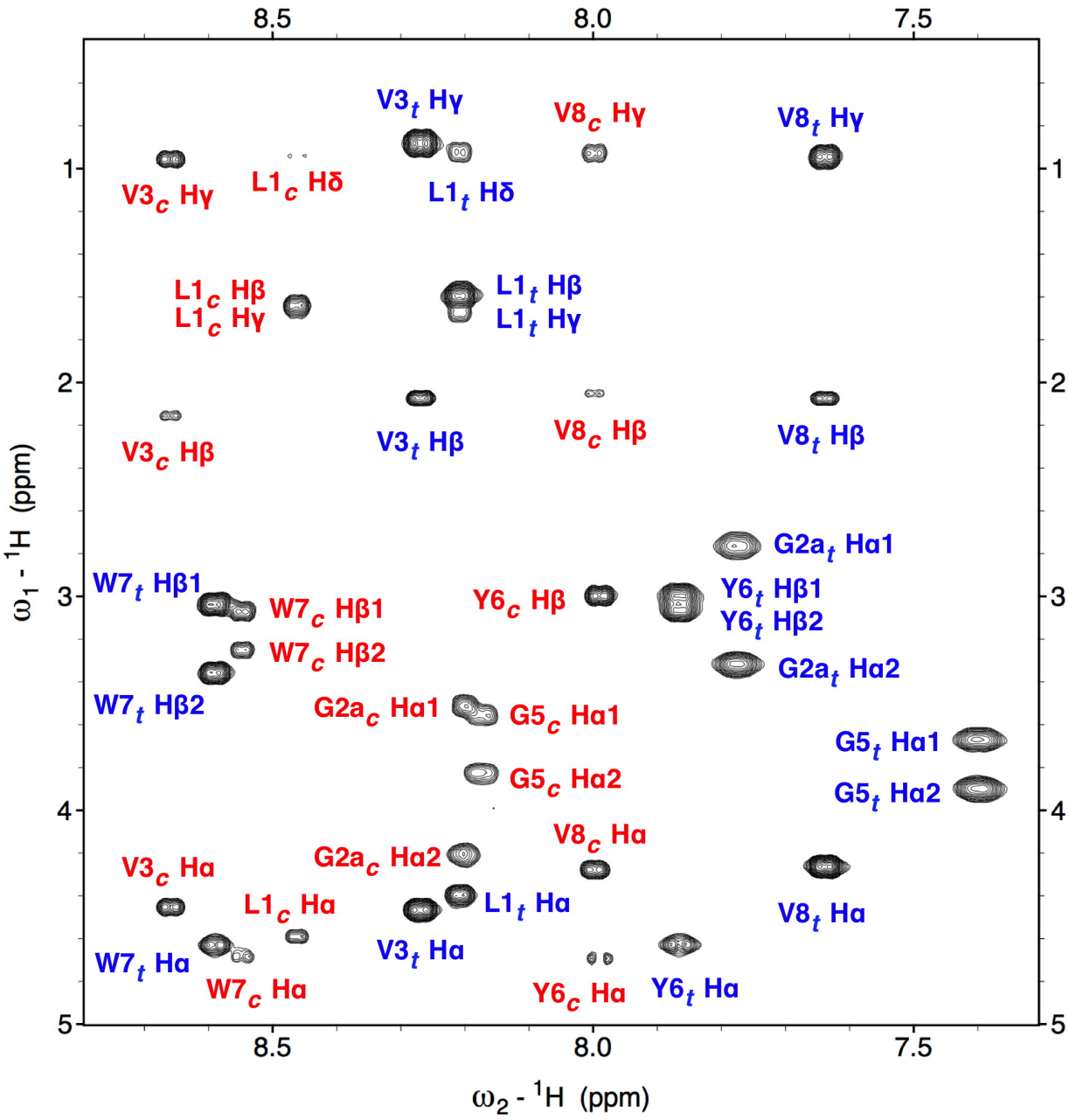

Figure S13: Amide fingerprint region from TOCSY of the peptide 8W-G^{c}P in CD_3OH at 298 K. Numbering the glycine and 4*S*-fluoroproline (^{c}P) as residues with numbers as 2a and 2b, respectively, reflects the replacement of L2 with G^{c}P. The resonances corresponding to the *cis* and the *trans* isomers are labeled in red and blue, respectively.

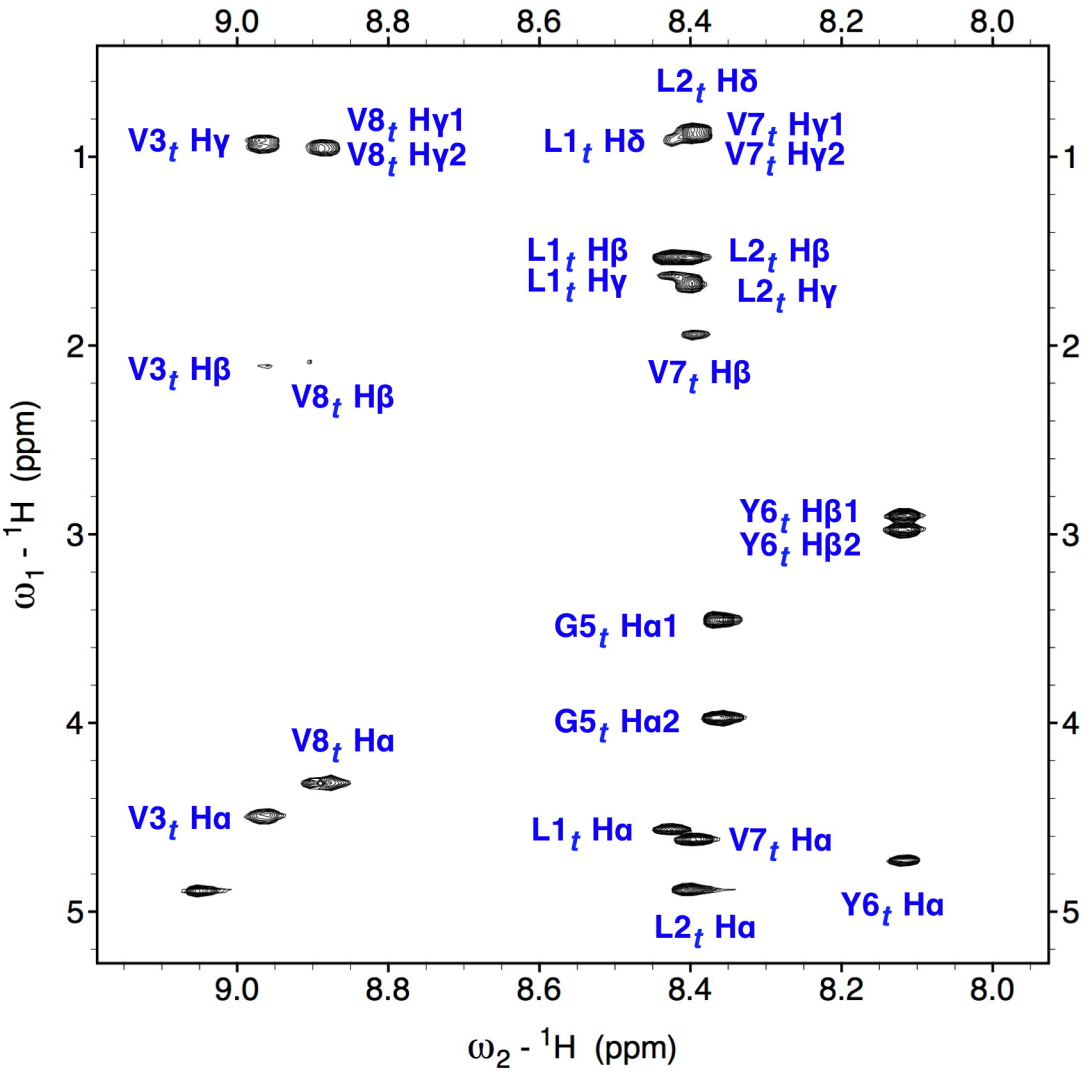

Figure S14: Amide fingerprint region from TOCSY of the peptide 8V-L in CD_3OH at 298 K.

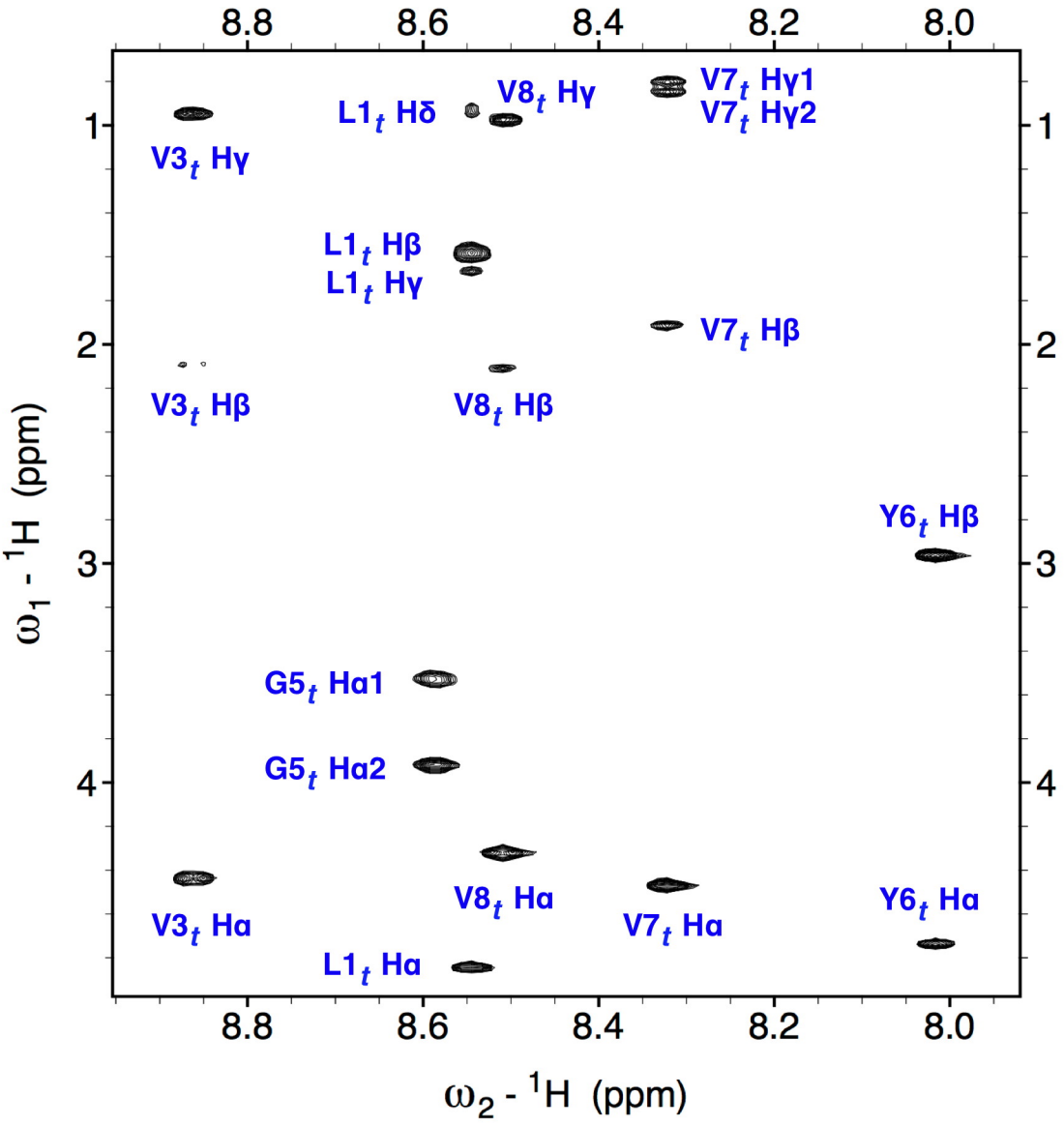

Figure S15: Amide fingerprint region from TOCSY of the peptide 8V-P in CD_3OH at 298 K.

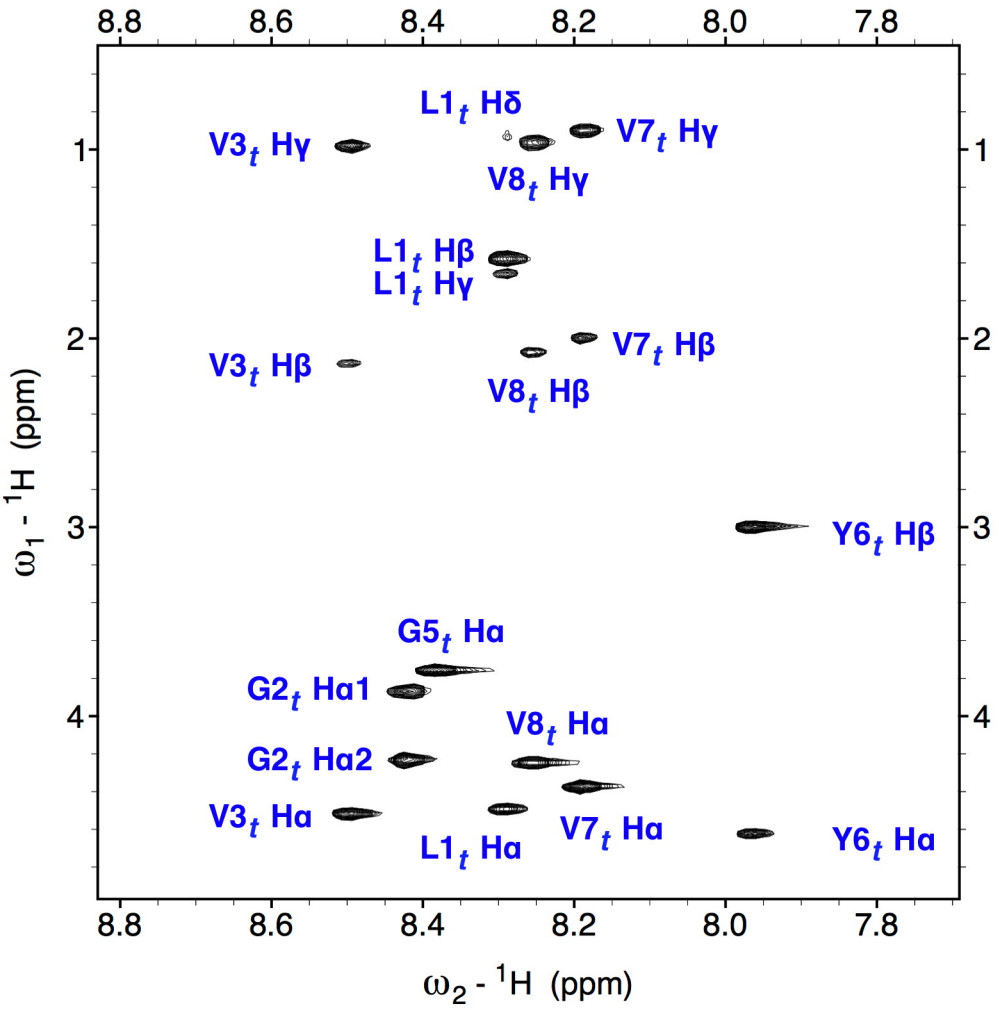

Figure S16: Amide fingerprint region from TOCSY of the peptide 8V-G in CD_3OH at 298 K.

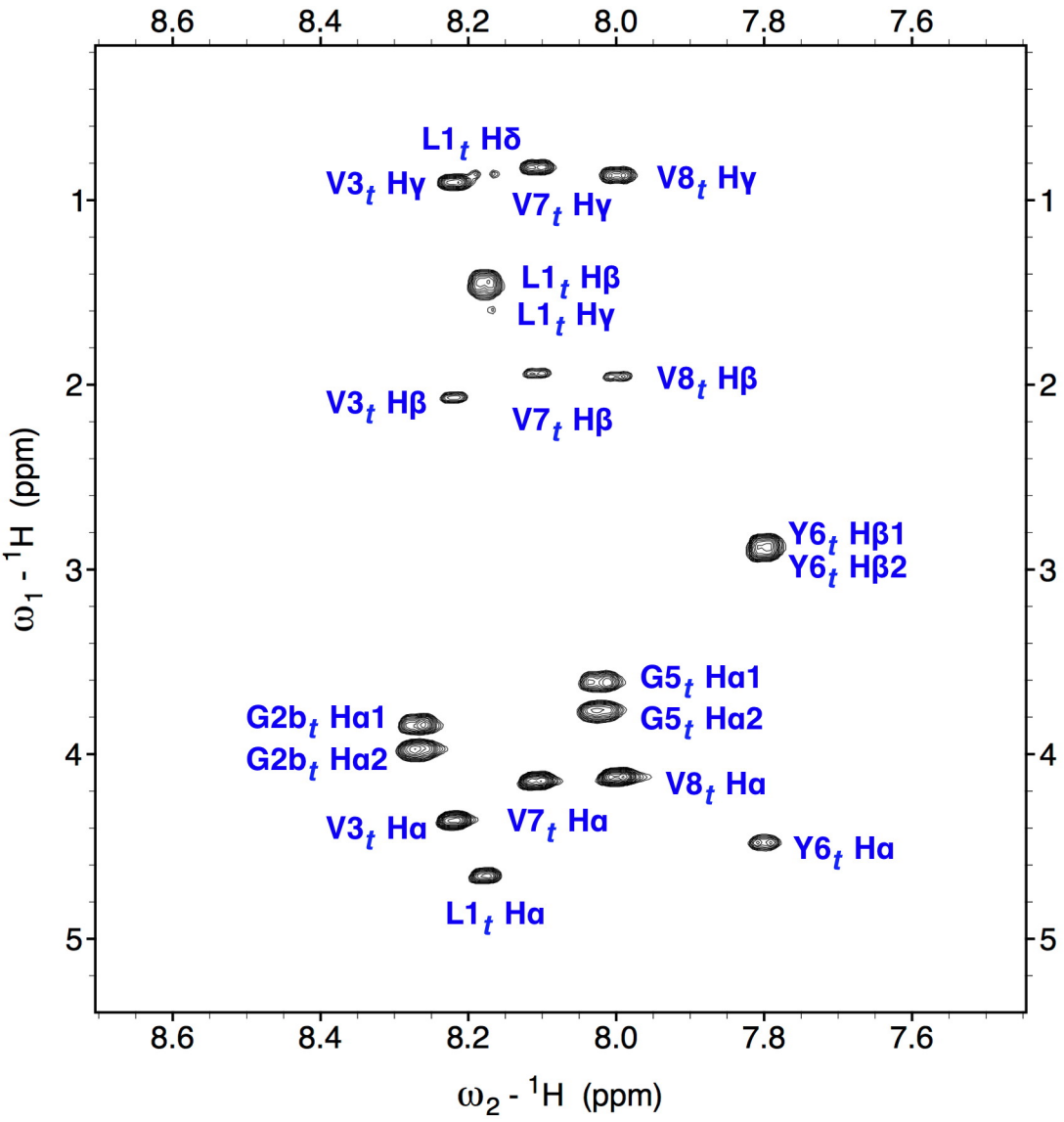

Figure S17: Amide fingerprint region from TOCSY of the peptide 8V-PG in CD_3OH at 298 K. Numbering the proline and glycine as residues with numbers as 2a and 2b, respectively, reflects the replacement of L2 with PG.

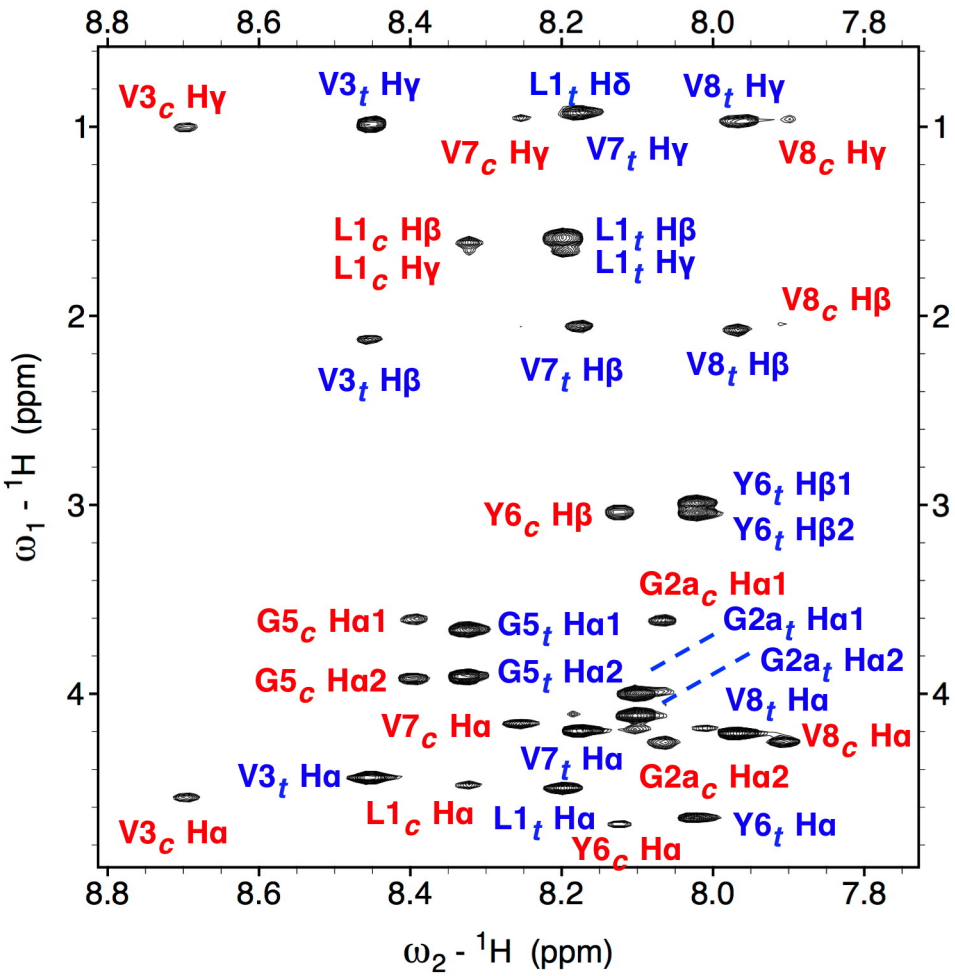

Figure S18: Amide fingerprint region from TOCSY of the peptide 8V-GP in CD_3OH at 298 K. Numbering the glycine and proline as residues with numbers as 2a and 2b, respectively, reflects the replacement of L2 with GP. The resonances corresponding to the *cis* and the *trans* isomers are labeled in red and blue, respectively.

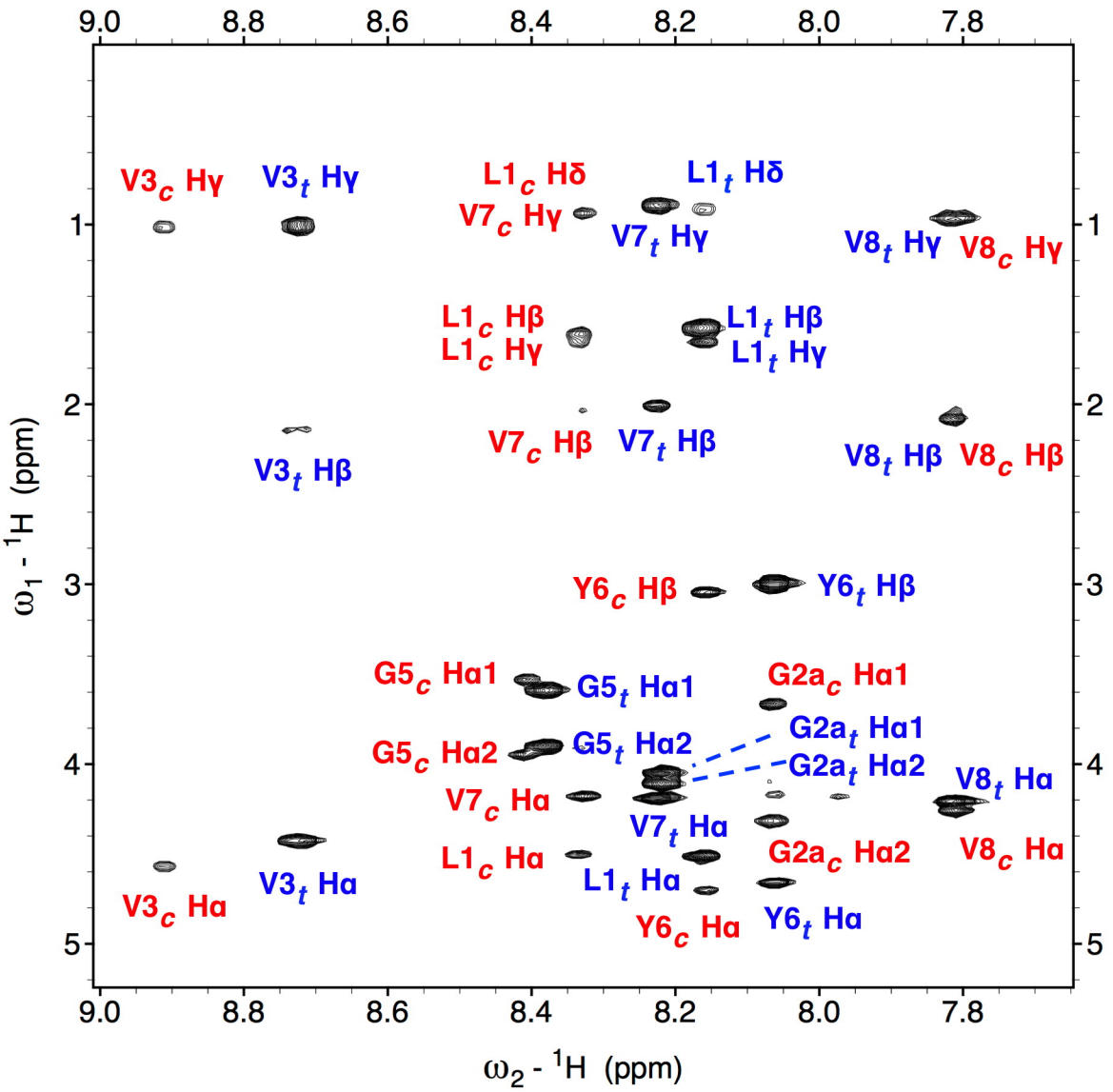

Figure S19: Amide fingerprint region from TOCSY of the peptide 8V-G^{t}P in CD_3OH at 298 K. Numbering the glycine and 4*R*-fluoroproline (^{t}P) as residues with numbers as 2a and 2b, respectively, reflects the replacement of L2 with G^{t}P. The resonances corresponding to the *cis* and the *trans* isomers are labeled in red and blue, respectively.

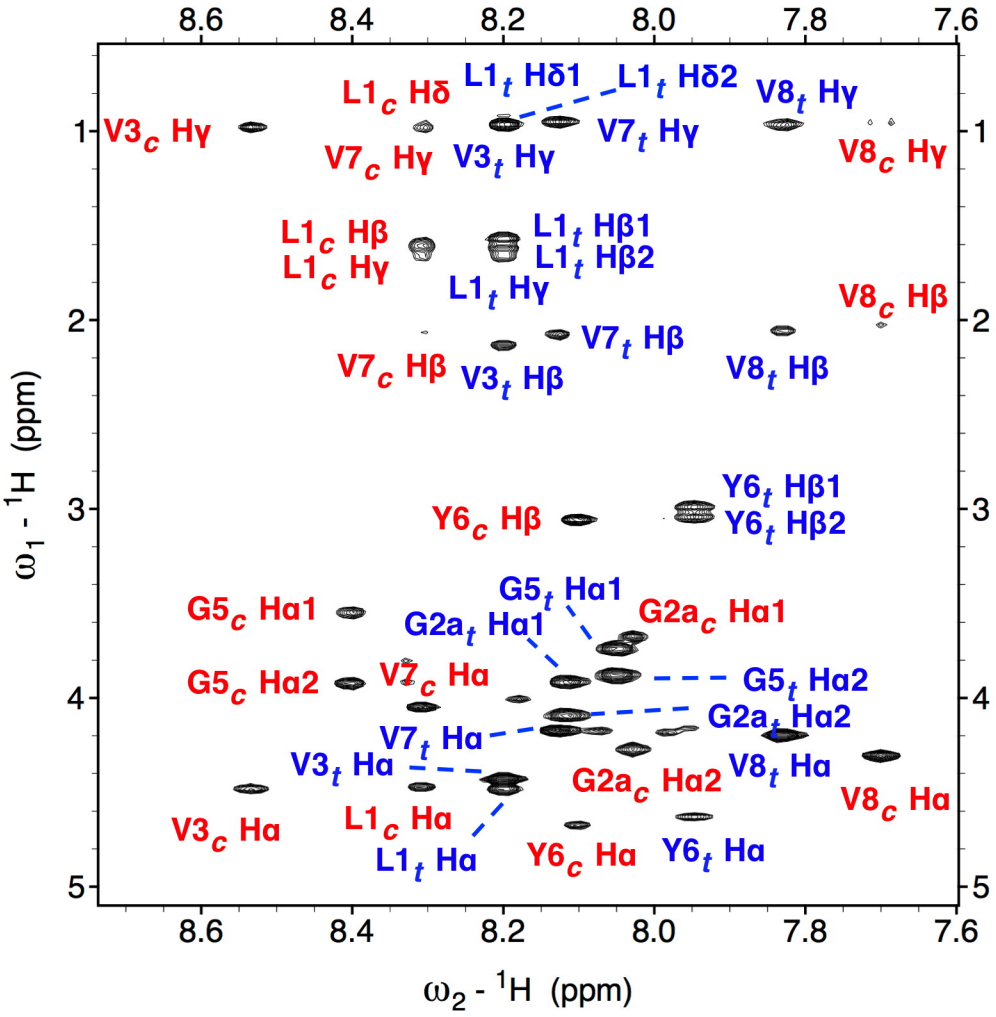

Figure S20: Amide fingerprint region from TOCSY of the peptide 8V-G^{c}P in CD_3OH at 298 K. Numbering the glycine and 4*S*-fluoroproline (^{c}P) as residues with numbers as 2a and 2b, respectively, reflects the replacement of L2 with G^{c}P. The resonances corresponding to the *cis* and the *trans* isomers are labeled in red and blue, respectively.

Key ROESY spectra from the peptides in the 8W series

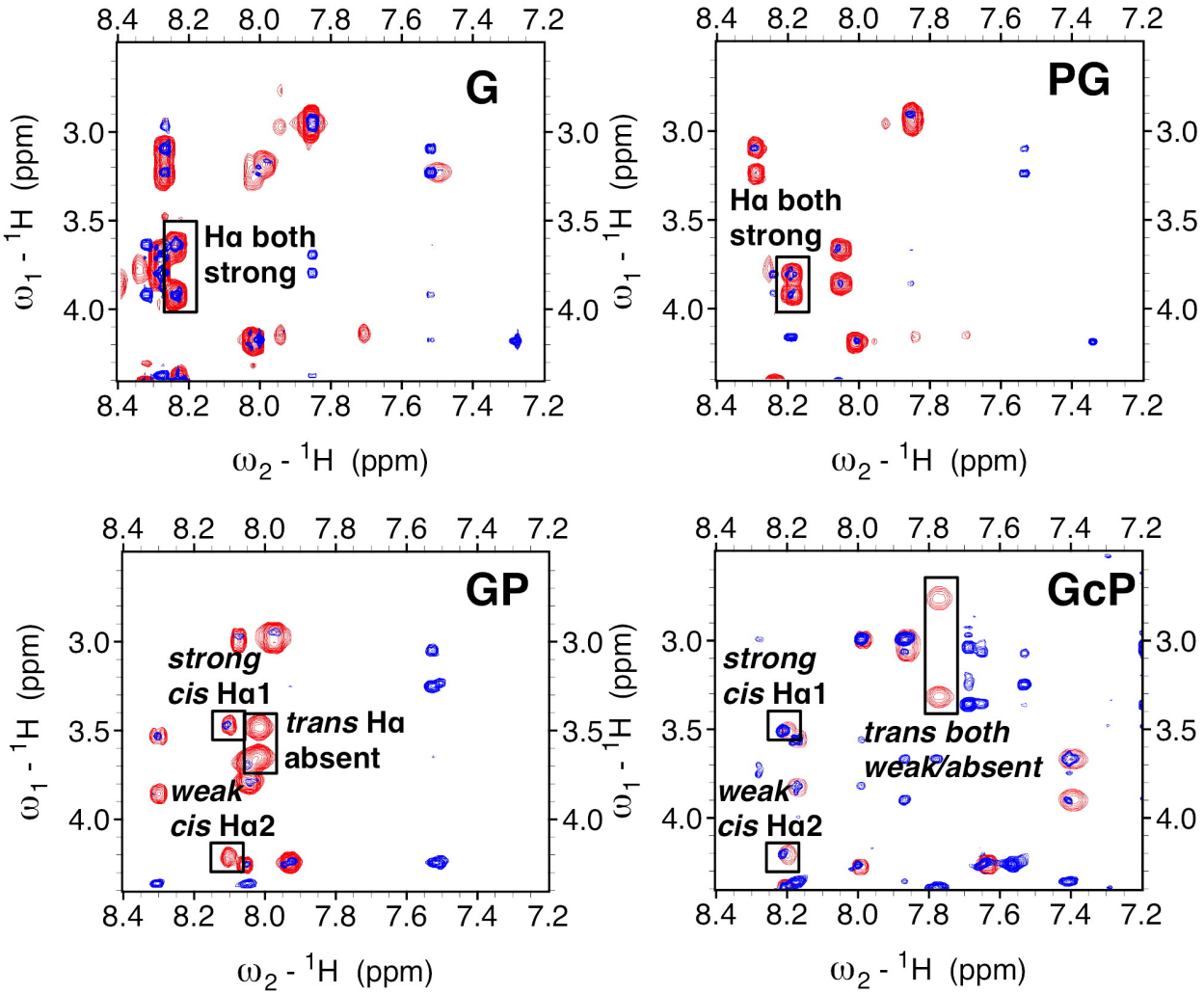

Figure S21: Superimposed TOCSY (red) and ROESY (blue) of 8W-G, 8W-PG, 8W-GP, and 8W-G^{c}P. The relative intensities of the HN-Hα crosspeaks corresponding to the Gly residue occupying either the 2nd or the 2a or the 2b (whichever is applicable) are boxed.

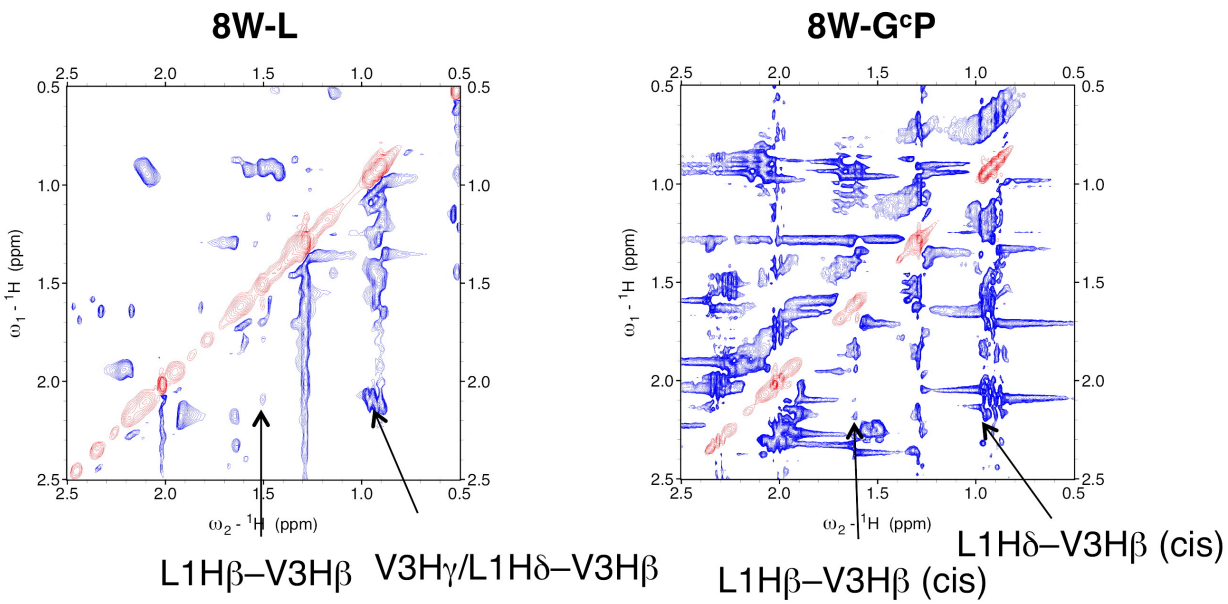

Figure S22: ROESY of 8W-L and 8W-G^{c}P. The red contours represent the diagonal, and negative cross peaks are shown in blue. The key side-chain-side-chain ROE cross peaks are shown with arrows. In 8W-L the Leu1 and Val3 side chains exhibit ROE cross peaks (***i*→*i*+2**) while in 8W-G^{c}P the Leu1 and Val3 side chains, that are separated by the united residue Gly-cisPro, exhibit (***i*→*i*+3**) ROE cross peaks.

Characterization of peptides by mass spectroscopy

Table S1: The m/z expected and observed for all peptides.

Peptides	$m_{expected}$ (Da)	$m/z_{observed}$ (Da)	
		$M+Na^+$	$M+K^+$
8W-L	987.19	1009.59	1025.57
8W-G	931.09	953.53	969.50
8W-P	971.15	993.55	1009.50
8W-^{t}P	989.15	1011.50	1027.50
8W-^{c}P	989.15	1011.60	1027.60
8W-PG	1028.20	1050.60	1066.60
8W-GP	1028.20	1050.60	1066.50
8W-G^{t}P	1046.20	1068.60	1084.50
8W-G^{c}P	1046.20	1068.60	1084.50
8V-L	900.11	922.52	938.49
8V-G	844.01	866.41	882.39
8V-P	884.07	906.44	922.42
8V-PG	941.12	963.54	979.52
8V- GP	941.12	963.50	979.48
8V- G^{t}P	959.12	981.50	997.42
8V- G^{c}P	959.12	981.45	997.42

Table S2: Resonance assignment of 8W-L in CD_3OH at 298 K

Residue	X-P amide	H^N	Hα	Hβ	Hγ	Others
Ac	*trans*	–	–	–	–	2.01
L1	*trans*	8.39	4.61	1.49	1.60	Hδ: 0.90
L2	*trans*	8.19	4.51	0.92, 1.43	1.16	Hδ: 0.31, 0.51
V3	*trans*	8.90	4.46	2.09	0.90	–
^{D}P4	*trans*	–	4.36	2.17	1.95	Hδ: 3.72
G5	*trans*	8.11	3.50, 3.81	–	–	–
Y6	*trans*	7.97	4.69	2.90, 3.17	–	Hδ: 7.11; Hε: 6.68
W7	*trans*	8.47	5.05	3.02, 3.12	–	Hδ1: 7.07, Hε1: 10.15, Hε3: 7.39, Hζ3: 7.03, Hη2: 6.96, Hζ2: 7.27
V8	*trans*	8.87	4.30	2.09	0.94	–
$CONH_2$	*trans*	6.93, 7.53	–	–	–	–

Table S3: Resonance assignment of 8W-P in CD_3OH at 298 K

Residue	X-P amide	H^N	Hα	Hβ	Hγ	Others
Ac	*trans*	–	–	–	–	2.03
L1	*trans*	8.64	4.93	1.56	1.68	Hδ: 0.94
P2	*trans*	–	4.41	1.33, 1.65	1.75, 2.10	Hδ: 3.62, 3.82
V3	*trans*	8.71	4.37	2.04	0.90	–
^{D}P4	*trans*	–	4.34	2.18	1.90	Hδ: 3.60, 3.66
G5	*trans*	8.43	3.59, 3.75	–	–	–
Y6	*trans*	7.86	4.69	2.92, 2.97	–	Hδ: 7.10; Hε: 6.67
W7	*trans*	8.44	4.94	2.97, 3.02	–	Hδ1: 7.03, Hε1: 10.20, Hε3: 7.33, Hζ3: 7.04, Hη2: 6.97, Hζ2: 7.27
V8	*trans*	8.61	4.33	2.10	0.96	–
$CONH_2$	*trans*	7.06, 7.67	–	–	–	–

Table S4: Resonance assignment of 8W-G in CD_3OH at 298 K

Residue	X-P amide	H^N	Hα	Hβ	Hγ	Others
Ac	*trans*	–	–	–	–	1.94
L1	*trans*	8.22	4.43	1.56	1.56	Hδ: 0.91
G2	*trans*	8.23	3.60, 3.95	–	–	–
V3	*trans*	8.35	4.45	2.11	0.94	–
^{D}P4	*trans*	–	4.36	2.23	2.00	Hδ: 3.70, 3.86
G5	*trans*	8.27	3.69, 3.77	–	–	–
Y6	*trans*	7.85	4.55	2.93		Hδ: 7.08; Hε: 6.65
W7	*trans*	8.27	4.84	3.06, 3.22	–	Hδ1: 7.08, Hε1: 10.18, Hε3: 7.50, Hζ3:7.05, Hη2: 6.97, Hζ2: 7.28
V8	*trans*	8.07	4.21	2.05	0.88	–
$CONH_2$	*trans*	6.91, 7.31	–	–	–	–

Table S5: Resonance assignment of 8W-PG in CD_3OH at 298 K

Residue	X-P amide	H^N	Hα	Hβ	Hγ	Others
Ac	*trans*	–	–	–	–	1.91
L1	*trans*	8.31	4.76	1.53, 1.57	1.69	Hδ: 0.95
P2a	*trans*	–	4.16	2.04	1.90	Hδ: 3.61, 3.84
G2b	*trans*	8.19	3.82, 3.91	–	–	–
V3	*trans*	8.24	4.42	2.17	0.99	–
^{D}P4	*trans*	–	4.41	2.23	2.02	Hδ: 3.71, 3.96
G5	*trans*	8.06	3.68, 3.85	–	–	–
Y6	*trans*	7.86	4.55	2.90, 2.96	–	Hδ: 7.05; Hε: 6.65
W7	*trans*	8.29	4.71	3.11, 3.23	–	Hδ1: 7.13, Hε1: 10.19, Hε3: 7.53, Hζ3: 7.05, Hη2: 6.98, Hζ2: 7.30
V8	*trans*	8.01	4.19	2.03	0.90	–
$CONH_2$	*trans*	6.95, 7.34	–	–	–	–

** For two-residue substitution at position 2, the 1st amino acid was denoted by position 2a and the 2nd amino acid was denoted by position 2b to maintain parity with one-residue substitution

Table S6: Resonance assignment of 8W-GP in CD_3OH at 298 K

Residue	X-P amide	H^N	Hα	Hβ	Hγ	Others
Ac	*cis*	–	–	–	–	2.00
	trans	–	–	–	–	1.98
L1	*cis*	8.44	4.57	1.64	1.68	Hδ: 0.93
	trans	8.17	4.50	1.59	1.66	Hδ: 0.91
G2a	*cis*	8.10	3.47, 4.21	–	–	–
	trans	8.01	3.48, 3.65	–	–	–
P2b	*cis*	–	4.48	1.85	1.46, 1.65	Hδ: 3.28, 3.44
	trans	–	4.44	1.90	1.71, 1.82	Hδ: 3.02, 3.31
V3	*cis*	8.76	4.50	2.14	0.97	–
	trans	8.49	4.43	2.10	0.93	–
^{D}P4	*cis*	–	4.36	2.22	1.95, 2.07	Hδ: 3.72
	trans	–	4.36	2.22	1.95, 2.07	Hδ: 3.72
G5	*cis*	8.3	3.54, 3.85	–	–	–
	trans	8.05	3.68, 3.78	–	–	–
Y6	*cis*	8.07	4.68	2.97, 3.01	–	Hδ: 6.96; Hε: 6.64
	trans	7.96	4.66	2.95, 3.01	–	Hδ: 7.11; Hε: 6.68
W7	*cis*	8.42	4.73	3.08, 3.23	–	Hδ1: 7.11, Hε1: 10.22, Hε3: 7.50, Hζ3: 7.05, Hη2: 6.93, Hζ2: 7.28
	trans	8.50	4.67	3.05, 3.25	–	Hδ1: 7.11, Hε1: 10.23, Hε3: 7.51, Hζ3: 7.08, Hη2: 7.00, Hζ2: 7.30
V8	*cis*	8.06	4.25	2.05	0.93	–
	trans	7.93	4.24	2.07	0.92	–
$CONH_2$	*cis*	n.d. ,7.51	–	–	–	–
	trans	6.99, 7.52	–	–	–	–

* n.d. – not identified

Table S7: Resonance assignment of 8W-^{t}P in CD_3OH at 298 K

Residue	X-P amide	H^N	Hα	Hβ	Hγ	Others
Ac	*trans*	–	–	–	–	1.92
L1	*trans*	8.50	4.79	1.66	1.55	Hδ: 0.92
^{t}P2	*trans*	–	4.76	2.07, 2.19	5.36	Hδ: 3.87, 4.26
V3	*trans*	8.76	4.42	2.07	0.94	–
^{D}P4	*trans*	–	4.35	2.2	1.95, 2.07	Hδ: 3.68
G5	*trans*	8.42	3.62, 3.77	–	–	–
Y6	*trans*	7.91	4.65	2.90, 2.96	–	Hδ: 7.08; Hε: 6.66
W7	*trans*	8.32	4.94	3.05, 3.10	–	Hδ1: 7.01, Hε1:10.12, Hε3: 7.43, Hζ3: 7.03, Hη2: 6.98, Hζ2: 7.27
V8	*trans*	8.22	4.28	2.07	0.93	–
$CONH_2$	*trans*	7.00, 7.52	–	–	–	–

Table S8: Resonance assignment of 8W-^{c}P in CD_3OH at 298 K

Residue	X-P amide	H^N	Hα	Hβ	Hγ	Others
Ac	*trans*	–	–	–	–	2.03
L1	*trans*	8.52	4.76	1.68	1.57	Hδ: 0.94
^{c}P2	*trans*	–	4.59	1.51, 2.02	4.98	Hδ: 3.76, 4.10
V3	*trans*	8.55	4.37	2.06	0.93	–
^{D}P4	*trans*	–	4.34	2.16	1.94, 2.04	Hδ: 3.66
G5	*trans*	8.26	3.60, 3.81	–	–	–
Y6	*trans*	7.87	4.66	2.93, 2.97	–	Hδ: 7.09; Hε: 6.67
W7	*trans*	8.38	4.77	3.03, 3.10	–	Hδ1: 7.08, Hε1: 10.25, Hε3: 7.40, Hζ3: 7.07, Hη2: 6.97, Hζ2: 7.31
V8	*trans*	8.2	4.27	2.08	0.92	–
$CONH_2$	*trans*	7.03, 7.53	–	–	–	–

Table S9: Resonance assignment of 8W-G^{t}P in CD_3OH at 298 K

Residue	X-P amide	H^N	Hα	Hβ	Hγ	Others
Ac	*cis*	–	–	–	–	1.99
	trans	–	–	–	–	1.97
L1	*cis*	8.30	4.49	1.65	1.60	Hδ: 0.92
	trans	8.13	4.46	1.56	1.64	Hδ: 0.90
G2a	*cis*	8.01	3.69, 4.17	–	–	–
	trans	8.03	3.71	–	–	–
^{t}P2b	*cis*	–	4.81	2.16, 2.54	5.12	Hδ: 3.53, 4.00
	trans	–	4.70	2.03, 2.38	5.23	Hδ: 3.66
V3	*cis*	8.81	4.54	2.17	1.02	–
	trans	8.62	4.40	2.13	0.97	–
^{D}P4	*cis*	–	4.38	2.16	1.94	Hδ: 3.73, 3.81
	trans	–	4.38	2.22	1.97, 2.08	Hδ: 3.69, 3.78
G5	*cis*	8.32	3.56, 3.90	–	–	–
	trans	8.19	3.65, 3.83	–	–	–
Y6	*cis*	8.09	4.63	2.96	–	Hδ: 7.07; Hε: 6.66
	trans	8.01	4.62	2.93, 2.98	–	Hδ: 7.09; Hε: 6.67
W7	*cis*	8.27	4.70	3.14, 3.25	–	Hδ1: 7.10, Hε1: 10.21, Hε3:7.53, Hζ3: 7.05, Hη2: 6.97, Hζ2: 7.29
	trans	8.36	4.68	3.08, 3.24	–	Hδ1: 7.09, Hε1: 10.22, Hε3: 7.54, Hζ3: 7.08, Hη2: 7.02, Hζ2: 7.31
V8	*cis*	7.78	4.20	2.00	0.89	–
	trans	7.72	4.18	2.02	0.89	–
$CONH_2$	*cis*	6.92, 7.37	–	–	–	–
	trans	6.86, 7.33	–	–	–	–

Table S10: Resonance assignment of 8W-G^{c}P in CD_3OH at 298 K

Residue	X-P amide	H^N	Hα	Hβ	Hγ	Others
Ac	*cis*	–	–	–	–	1.98
	trans	–	–	–	–	2.01
L1	*cis*	8.46	4.59	1.64	1.69	Hδ: 0.94
	trans	8.21	4.40	1.60	1.68	Hδ: 0.93
G2a	*cis*	8.20	3.51, 4.21	–	–	–
	trans	7.77	2.76, 3.31	–	–	–
^{c}P2b	*cis*	–	4.64	1.53, 2.24	4.77	Hδ: 3.47, 3.65
	trans	–	4.49	2.02, 2.31	5.03	Hδ: 2.98, 3.21
V3	*cis*	8.66	4.45	2.15	0.96	–
	trans	8.27	4.47	2.07	0.88	–
^{D}P4	*cis*	–	4.36	2.05	1.92, 2.16	Hδ: 3.63, 3.70
	trans	–	4.36	2.03	1.94, 2.26	Hδ: 3.70, 3.74
G5	*cis*	8.17	3.55, 3.82	–	–	–
	trans	7.40	3.67, 3.90	–	–	–
Y6	*cis*	7.99	4.69	3.00	–	Hδ: 7.12; Hε: 6.68
	trans	7.86	4.63	3.00, 3.06	–	Hδ: 7.14; Hε: 6.69
W7	*cis*	8.55	4.68	3.07, 3.25	–	Hδ1: 7.14, Hε1: 10.25, Hε3: 7.52, Hζ3: 7.05, Hη2: 6.92, Hζ2: 7.29
	trans	8.59	4.63	3.04, 3.36	–	Hδ1: 7.19, Hε1: 10.21, Hε3: 7.68, Hζ3: 7.09, Hη2: 7.05, Hζ2: 7.28
V8	*cis*	8.00	4.28	2.05	0.92	–
	trans	7.64	4.27	2.07	0.94	–
$CONH_2$	*cis*	n.d.	–	–	–	–
	trans	7.03, 7.56	–	–	–	–

* n.d. – not identified

Table S11: Resonance assignment of 8V-L in CD_3OH at 298 K

Residue	X-P amide	H^N	Hα	Hβ	Hγ	Others
Ac	*trans*	–	–	–	–	1.93
L1	*trans*	8.42	4.56	1.53	1.62	Hδ: 0.92
L2	*trans*	8.39	4.88	1.53	1.67	Hδ: 0.85
V3	*trans*	8.97	4.49	2.11	0.91, 0.95	–
^{D}P4	*trans*	–	4.39	2.19	1.98	Hδ: 3.72
G5	*trans*	8.36	3.45, 3.97	–	–	–
Y6	*trans*	8.12	4.73	2.90, 2.97	–	Hδ: 7.14; Hε: 6.69
V7	*trans*	8.39	4.61	1.94	0.85, 0.89	–
V8	*trans*	8.88	4.32	2.08	0.94, 0.96	–
$CONH_2$	*trans*	7.07, 7.77	–	–	–	–

Table S12: Resonance assignment of 8V-P in CD_3OH at 298 K

Residue	X-P amide	H^N	Hα	Hβ	Hγ	Others
Ac	*trans*	–	–	–	–	1.91
L1	*trans*	8.54	4.84	1.58	1.66	Hδ: 0.91, 0.94
P2	*trans*	–	4.04	2.15, 2.27	1.98	Hδ: 3.71
V3	*trans*	8.86	4.44	2.09	0.94	–
^{D}P4	*trans*	–	4.39	2.15, 2.21	1.98	Hδ: 3.66, 3.73
G5	*trans*	8.59	3.53, 3.92	–	–	–
Y6	*trans*	8.01	4.73	2.96	–	Hδ: 7.13; Hε: 6.68
V7	*trans*	8.32	4.47	1.91	0.80, 0.85	–
V8	*trans*	8.50	4.32	2.11	0.97	–
$CONH_2$	*trans*	7.11, 7.77	–	–	–	–

Table S13: Resonance assignment of 8V-G in CD_3OH at 298 K

Residue	X-P amide	H^N	Hα	Hβ	Hγ	Others
Ac	*trans*	–	–	–	–	1.96
L1	*trans*	8.29	4.49	1.57	1.65	Hδ: 0.93
G2	*trans*	8.42	3.87, 4.23	–	–	–
V3	*trans*	8.49	4.51	2.13	0.98	–
^{D}P4	*trans*	–	4.37	2.24	1.98, 2.08	Hδ: 3.73, 3.84
G5	*trans*	8.38	3.76	–	–	–
Y6	*trans*	7.96	4.62	2.99	–	Hδ: 7.12; Hε: 6.67
V7	*trans*	8.19	4.37	1.99	0.90	–
V8	*trans*	8.25	4.24	2.07	0.96	–
$CONH_2$	*trans*	7.04, 7.65	–	–	–	–

Table S14: Resonance assignment of 8V-PG in CD_3OH at 298 K

Residue	X-P amide	H^N	Hα	Hβ	Hγ	Others
Ac	*trans*	–	–	–	–	1.90
L1	*trans*	8.27	4.75	1.55	1.69	Hδ: 0.95
P2a	*trans*	–	4.32	2.16	1.98	Hδ: 3.64, 3.91
G2b	*trans*	8.36	3.93, 4.07	–	–	–
V3	*trans*	8.31	4.46	2.16	0.99	–
^{D}P4	*trans*	–	4.38	2.23	2.02	Hδ: 3.72, 3.96
G5	*trans*	8.12	3.70, 3.86	–	–	–
Y6	*trans*	7.89	4.57	2.96, 3.01	–	Hδ: 7.09; Hε: 6.66
V7	*trans*	8.20	4.24	2.03	0.92	–
V8	*trans*	8.09	4.22	2.05	0.96	–
$CONH_2$	*trans*	7.02, 7.60	–	–	–	–

Table S15: Resonance assignment of 8V-GP in CD_3OH at 298 K

Residue	X-P amide	H^N	Hα	Hβ	Hγ	Others
Ac	*cis*	–	–	–	–	2.00
	trans	–	–	–	–	1.99
L1	*cis*	8.32	4.48	1.61	1.65	Hδ: 0.94
	trans	8.19	4.50	1.58	1.66	Hδ: 0.92
G2a	*cis*	8.06	3.61, 4.26	–	–	–
	trans	8.10	4.00, 4.12	–	–	–
P2b	*cis*	–	4.74	2.26	1.88, 2.16	Hδ: 3.58, 3.63
	trans	–	4.65	2.16	1.99, 2.08	Hδ: 3.60, 3.66
V3	*cis*	8.70	4.55	2.16	1.00	–
	trans	8.45	4.44	2.13	0.99	–
^{D}P4	*cis*	–	4.38	2.21	1.98, 2.10	Hδ: 3.75, 3.79
	trans	–	4.38	2.21	1.98, 2.09	Hδ: 3.70, 3.79
G5	*cis*	8.39	3.60, 3.92	–	–	–
	trans	8.32	3.66, 3.91	–	–	–
Y6	*cis*	8.12	4.69	3.04	–	Hδ: 7.13; Hε: 6.69
	trans	8.02	4.65	2.99, 3.04		Hδ: 7.12; Hε: 6.70
V7	*cis*	8.25	4.16	2.05	0.95	–
	trans	8.17	4.19	2.05	0.93	–
V8	*cis*	7.90	4.26	2.04	0.95	–
	trans	7.96	4.20	2.07	0.96	–
$CONH_2$	*cis*	7.01, 7.68	–	–	–	–
	trans	7.01, 7.64	–	–	–	–

Table S16: Resonance assignment of 8V_G^{t}P in CD_3OH at 298 K

Residue	X-P amide	H^N	Hα	Hβ	Hγ	Others
Ac	*cis*	–	–	–	–	1.99
	trans	–	–	–	–	1.97
L1	*cis*	8.33	4.50	1.60	1.65	Hδ: 0.93
	trans	8.16	4.51	1.57	1.65	Hδ: 0.92
G2a	*cis*	8.07	3.66, 4.31	–	–	–
	trans	8.22	4.05, 4.10	–	–	–
^{t}P2b	*cis*	–	4.96	2.25, 2.69	5.24	Hδ: 3.57, 4.12
	trans	–	4.86	2.14, 2.56	5.35	Hδ: 3.82, 3.96
V3	*cis*	8.91	4.57	2.17	1.02	–
	trans	8.72	4.43	2.14	0.98, 1.02	–
^{D}P4	*cis*	–	4.37	2.20	1.97, 2.10	Hδ: 3.75, 3.77
	trans	–	4.37	2.21	1.97, 2.10	Hδ: 3.71, 3.76
G5	*cis*	8.41	3.53, 3.94	–	–	–
	trans	8.38	3.59, 3.90	–	–	–
Y6	*cis*	8.15	4.70	3.04	–	Hδ: 7.14; Hε: 6.69
	trans	8.06	4.66	2.99	–	Hδ: 7.12; Hε: 6.68
V7	*cis*	8.33	4.18	2.03	0.94	–
	trans	8.22	4.19	2.00	0.89	–
V8	*cis*	7.81	4.26	2.03	0.93, 0.95	–
	trans	7.81	4.20	2.08	0.97	–
$CONH_2$	*cis*	7.02, 7.66	–	–	–	–
	trans	7.03, 7.66	–	–	–	–

Table S17: Resonance assignment of 8V_G^{c}P in CD_3OH at 298 K

Residue	X-P amide	H^N	Hα	Hβ	Hγ	Others
Ac	*cis*	–	–	–	–	1.99
	trans	–	–	–	–	1.97
L1	*cis*	8.31	4.47	1.61	1.66	Hδ: 0.92
	trans	8.20	4.48	1.57, 1.62	1.67	Hδ: 0.90, 0.93
G2a	*cis*	8.03	3.67, 4.27	–	–	–
	trans	8.11	3.91, 4.09	–	–	–
^{c}P2b	*cis*	–	4.86	2.54, 2.69	5.24	Hδ: 3.81, 3.86
	trans	–	4.73	2.45	5.34	Hδ: 3.90, 3.97
V3	*cis*	8.53	4.48	2.19	0.98	–
	trans	8.20	4.43	2.13	0.96	–
^{D}P4	*cis*	–	4.37	2.16	1.95, 2.09	Hδ: 3.67, 3.75
	trans	–	4.37	2.18	1.96, 2.04	Hδ: 3.65, 3.81
G5	*cis*	8.39	3.55, 3.92	–	–	–
	trans	8.05	3.74, 3.87	–	–	–
Y6	*cis*	8.10	4.68	3.05	–	Hδ: 7.16; Hε: 6.69
	trans	7.94	4.63	2.99, 3.04	–	Hδ: 7.12; Hε: 6.68
V7	*cis*	8.30	4.05	2.06	0.98	–
	trans	8.12	4.17	2.07	0.95	–
V8	*cis*	7.70	4.30	2.02	0.95	–
	trans	7.83	4.19	2.06	0.96	–
$CONH_2$	*cis*	7.01, 7.69	–	–	–	–
	trans	7.01, 7.60	–	–	–	–