Supporting Information

Design and Synthesis of *trans* 3-Aminopyran-2-Carboxylic Acid (APyC) and α/β-Peptides with 9/11-helix

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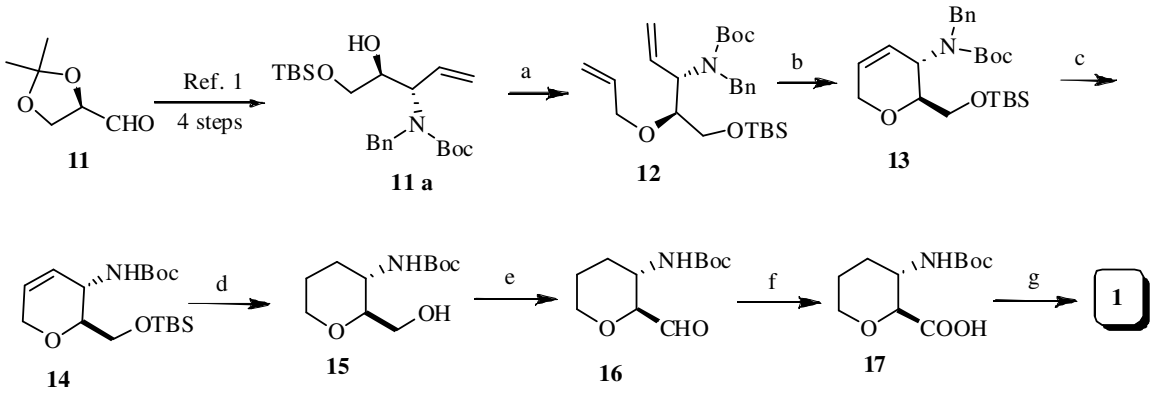
Synthesis of *trans* APyC monomer (1):

The new pyran β-amino acid (**1**) was synthesized from the known compound **11a** which was derived from (*R*)-2,3-*O*-isopropylidene-D-glyceraldehyde **11**[1].

[1] a) R. Badorrey, C. Cativiela, M. D. Diaz-de-villegas, J. A. Galvez, *Synthesis* **1997**, 747-749; b) R. Badorrey, C. Cativiela, M. D. Diaz-de-villegas, J. A. Galvez, *Tetrahedron* **1997**, *53*, 1411-1416; c) A. Madan, B. V. Rao, *Tetrahedron Letters* **2005**, *46*, 323-324.



Reagents and conditions: a) Allyl bromide, NaH, DMF, 0 °C - rt, 4 h; b) Grubb's-I catalyst, Toluene, Reflux, 8 h; c) Li, Liq NH_3, THF, -78 °C, 1 h; d) 10% Pd-C, MeOH, H_2, 6 h; e) $(COCl)_2$, DMSO, CH_2Cl_2, -78 °C; f) $NaClO_2$, 30% H_2O_2, t-BuOH: H_2O (7:3); g) CH_2N_2, ether, 1 h.

***tert.*-Butyl (3*S*,4*S*)-4-(allyloxy)-5- (*tert.*-butyldimethylsilyloxy) pent-1-en-3-yl(benzyl) carbamate (12) :**

To a stirred solution of alcohol **11a** (5.1 g, 12.6 mmol) in dry DMF (15 mL), allyl bromide (1.23 mL, 14.5 mmol) was added followed by NaH (0.64 g, 26.7 mmol), at 0 ºC stirring was continued at room temperature for 2 h. It was, quenched with sat. NH_4Cl (10 mL) and extracted with EtOAc (2 x 25 mL). The combined organic layers were washed with brine (50 mL), dried (Na_2SO_4) and evaporated in vacuum. The crude residue was purified by column chromatography (60-120 mesh Silica gel, 2% ethyl acetate in pet. ether) to afford **12** (4.4 g, 79%) as a colorless liquid. $[\alpha]_D$ = +77.2 (*c* 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.19 (m, 5H, Ar-H), 6.08-5.69 (m, 2H, olefin), 5.16-5.02 (m, 4H, olefin), 4.43 (s, 2H, -N-CH_2-Ph), 4.25-3.99 (m, 2H, -OCH_2), 3.93-3.65 (m, 2H, -OCH_2), 3.61-3.29 (m, 2H, -OCH, -NCH), 1.39 (s, 9H, Boc), 0.90 (s, 9H, Si-*t*-Bu), 0.10 (s, 6H, 2 x Si-CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.6, 139.0, 138.0, 135.0-132.0 (4C), 128.0, 127.0, 118.0, 117.0, 80.7, 80.3, 72.2, 62.8, 60.6, 28.2 (3C), 25.8 (3C), -5.5 (2C); IR (KBr): 3438, 3079, 2930, 2858, 1694, 1457, 1404, 1365, 1252, 1166, 998, 926, 838,

776, 700 cm^{-1}; HRMS (ESI): *m/z* calculated for $C_{26}H_{43}NO_4SiNa$ $[M+Na]^+$ 484.2859, found 484.2872.

***tert.*-Butyl benzyl [(2*S*,3*S*)-2-(*tert.*-butyldimethylsilyloxy)methyl)-3,6-dihydro-2H-pyran-3-yl] carbamate (13) :**

Bis olefin **12** (2.2 g, 0.32 mmol) dissolved in freshly distilled degassed anhydrous toluene, was treated with Grubbs' catalyst I (0.07 g, 5 mol %) and heated at reflux for 8 h. Most of the solvent was then distilled off and the concentrated solution left to stir at room temperature for 2 h under air bubbling in order to decompose the catalyst. Reaction mixture was evaporated to dryness to give a brown residue, which was purified by column chromatography (60-120 mesh Silica gel, 2.5% ethyl acetate in pet. ether) to afford **13** (1.65 g, 80%) as a pale brown liquid; $[\alpha]_D$ = +93.5 (*c* 0.5, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz): δ 7.28 (m, 5H, Ar-H), 5.79 (m, 1H, olefin), 5.55 (m, 1H, olefin), 4.71 (m, 1H, -OCH), 4.48 (m, 1H, -OCH), 4.25 (m, 1H, -NCH), 4.14 (s, 2H, -N-CH_2-Ph), 3.81-3.66 (m, 3H, -OCH_2, -OCH), 1.33 (s, 9H, Boc), 0.91 (s, 9H, Si-*t*-Bu), 0.07 (s, 6H, 2 x Si-CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.8, 139.7, 139.2, 128.3 (2C), 127.1 (4C), 80.3, 64.8, 63.9, 52.2, 51.2, 48.8, 28.3 (3C), 25.9 (3C), -5.23 (2C); IR (KBr): 3435, 3068, 2935, 2852, 1694, 1457, 1365, 1252, 1166, 838, 776, 700 cm^{-1}; HRMS (ESI): *m/z* calculated for $C_{24}H_{39}NO_4SiNa$ $[M+Na]^+$ 456.2546, found 456.2563.

***tert.*-Butyl (2*S*,3*S*)-2-[(*tert.*-butyldimethylsilyloxy)methyl]-3,6-dihydro-2H-pyran-3-ylcarbamate (14) :**

To a solution of liq NH_3 (25 mL) in dry THF (10 mL) under nitrogen atmosphere, lithium metal (0.16 g, 23.3 mmol) was added carefully at -78 ºC and stirred for 30 min at the same temperature. A solution of **13** (2.5 g, 5.88 mmol) in THF (15 mL) was added dropwise and stirred for additional 1 h. It was treated with sat. NH_4Cl (50 mL) drop wise and extracted with EtOAc (2 x 50 mL). The organic layers were washed with brine (25 mL), dried (Na_2SO_4) and evaporated in vacuum. The crude residue purified by column chromatography (60-120 mesh Silica gel, 20% ethyl acetate in pet. ether) to afford **14** (1.3 g, 68%) as a colorless liquid; $[\alpha]_D$ = +23.2 (*c* 0.5, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz): δ 5.86 (dq, 1H, *J* = 10.6, 2.3 Hz, olefin), 5.70 (dq, 1H, *J* = 10.6, 2.3 Hz, olefin), 4.59 (d, 1H, *J* = 8.3 Hz, -NH), 4.15 (m, 2H, *J* = 2.3 Hz, -OCH_2), 4.06 (m, 1H, -OCH), 3.81 (dd, 1H, *J* = 11.3, 3.0 Hz, -OCH), 3.74 (dd, 1H, *J* = 11.3, 6.8 Hz, -NCH), 3.34 (m,

1H, -OCH), 1.44 (s, 9H, Boc), 0.90 (s, 9H, Si-*t*-Bu), 0.08 (s, 6H, 2 x Si-CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): 156.2, 128.8, 126.1, 80.4, 78.9, 65.4, 62.4, 44.7, 28.3 (3C), 26.0 (3C), 18.0, -6.0 (2C); IR (KBr): 3345, 2931, 2857, 1693, 1523, 1452, 1458, 1368, 1312, 1251, 1169, 1093, 838, 777, 688 cm^{-1}; HRMS (ESI): *m/z* calculated for $C_{17}H_{33}NO_4SiNa$ $[M+Na]^+$ 366.2077, found 366.2091.

***tert.*-Butyl (2*S*,3*S*)-2-(hydroxymethyl)-tetrahydro-2H-pyran-3-ylcarbamate (15) :**

To a stirred solution of **14** (4.9 g, 8.33 mmol) in MeOH (15 mL), catalytic amount of 10% Pd-C (0.1 g) was added and stirred at room temperature for 6 h under hydrogen atmosphere. The reaction mixture was filtered on ceilite pad with ethyl acetate (3 x 20 mL), organic layer was evaporated and the residue purified by column chromatography (60-120 mesh Silica gel, 25% ethyl acetate in pet. ether) to furnish **15** (4.6 g, 93%) as a white solid; M.p. 75 °C; $[\alpha]_D$ = -14.93 (*c* 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 200 MHz): δ 4.46 (d, 1H, *J* = 8.0 Hz, NH), 4.01 (m, 1H, -OCH), 3.62-3.44 (m, 4H, 2 x -OCH_2), 3.31 (dt, 1H, *J* = 11.7, 3.7 Hz, -NCH), 2.86 (d, 1H, *J* = 9.5 Hz, Cγ*H*), 2.10 (m, 1H, Cγ'H), 1.70 (m, 2H, Cδ*H*), 1.44 (s, 9H, Boc); ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.4, 82.7, 80.3, 67.7, 62.3, 46.1, 30.3, 28.2 (3C), 25.5; IR (KBr): 3526, 3365, 2981, 2935, 2856, 2760, 1680, 1525, 1372, 1311, 1245, 1172, 1076, 981, 844, 778 cm^{-1}; HRMS (ESI): *m/z* calculated for $C_{11}H_{21}NO_4Na$ $[M+Na]^+$ 254.1368, found 254.1382.

(2*S*,3*S*)-Methyl 3-(*tert.*-butoxycarbonylamino)-tetrahydro-2H-pyran-2-carboxylate (1) :

To a stirred solution of oxalyl chloride (0.68 mL, 7.8 mmol) in CH_2Cl_2 (20 mL) at -78 ºC, DMSO (1.1 mL, 15.6 mmol) was added drop wise followed by a solution **15** (1.46 g, 7.0 mmol) in CH_2Cl_2 (20 mL). The reaction mixture was stirred for 1.5 h at -78 ºC and treated with Et_3N (6.0 mL, 42.8 mmol) at the same temperature. Reaction mixture was stirred at room temperature for 1 h and extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were washed with brine (20 mL), dried (Na_2SO_4) and evaporated in vacuum to afford *tert.-butyl (2S,3S)-2-formyl-tetrahydro-2H-pyran-3-ylcarbamate* **16** as a colorless liquid. This was used as such for further reaction.

To a stirred solution of **16** (1.5 g, 3.76 mmol) in *tert.*butanol:water (7:3, 10 mL), sodium chlorite (0.51 g, 5.65 mmol) and H_2O_2 (2.1 mL, 18.84 mmol, 30% aqueous solution) were added and stirred at room temperature for 6 h. The reaction mixture was

concentrated, residue dissolved in ethyl acetate (10 mL), washed with water (5 mL), brine (5 mL), dried (Na_2SO_4) and evaporated under reduced pressure to give *(2S,3S)-3-(tert.-butoxycarbonylamino)-tetrahydro-2H-pyran-2-carboxylic acid* **17**. The crude product was used as such for further reaction.

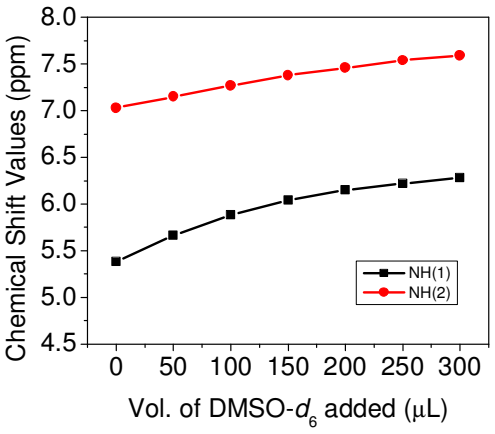
A solution of **17** (1.55 g, 4.89 mmol) in Et_2O (15 mL) was treated with ethereal diazomethane [prepared from 1.91 g of N-nitrosomethyl urea and 50% KOH (30 mL)]. The reaction mixture was stirred at 0 °C for 1 h, solvent was evaporated and purified the residue by column chromatography (60-120 mesh Silica gel, 20% ethyl acetate in pet. ether) to give **1** (1.30 g, 79%, over all 3 steps) as a white solid; M.p. 142 °C; $[\alpha]_D$ = +76.9 (*c* 0.25, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, 293 K): δ 4.65 (d, 1H, *J* = 7.3 Hz, NH), 4.02 (dt, 1H, *J* = 11.6, 4.1 Hz, CεH), 3.80 (m, 1H, CβH), 3.77 (m, 1H, CαH), 3.76 (s, 3H, $COOCH_3$), 3.46 (dt, 1H, *J* = 3.0, 11.6 Hz, Cε'H), 2.07 (m, 1H, CγH), 1.77 (m, 1H, CδH), 1.72 (m, 1H, Cδ'H), 1.47 (dq, 1H, *J* = 4.2, 12.2 Hz, Cγ'H), 1.43 (s, 9H, Boc); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 170.1, 154.9, 80.3, 79.8, 66.9, 52.7, 48.2, 29.4, 28.3 (3C), 24.0; IR (KBr): 3292, 2978, 2937, 1754, 1706, 1543, 1445, 1370, 1291, 1207, 1172, 1117, 1091, 1063, 689 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{12}H_{21}NO_5Na$: 282.1317 $[M+Na]^+$; found: 282.1319.

NMR spectroscopy: NMR spectra were recorded with 3-5mM solution of $CDCl_3$ on 600 MHz at 278-303°K using tetramethylsilane (TMS) as internal standard and the chemical shifts are shown in δ scales. The coupling constants were measured with resolution enhanced 1D spectrum and multiplicities of NMR signals are designated as s (singlet), d (doublet), t (triplet), q (quartet), br (broad), dt (doublet of triplet), dddd (doublet of doublet of doublet of doublet), dq (doublet of quartet) and m (multiplet) for unresolved lines) etc. The resonance assignment of individual residues was done using two-dimensional total correlation spectroscopy (TOCSY) experiments. The TOCSY experiments were performed with the spin locking fields of about 10 kHz and a mixing time of 0.08 s. To obtain the spatial proximity of the protons, rotating frame Overhauser effect spectroscopy (ROESY) experiment was used. The ROESY experiments were performed with mixing time of 0.2-0.3 s and a spinlocking field of about 2.5 kHz was used. All the experiments were carried out in the phase sensitive mode. The spectra were acquired with 2 × 256 or 2 × 192 free induction decays (FID) containing 8-16 transients with relaxation delays of 2 s. The two-dimensional data were processed with Gaussian apodization in both the dimensions.

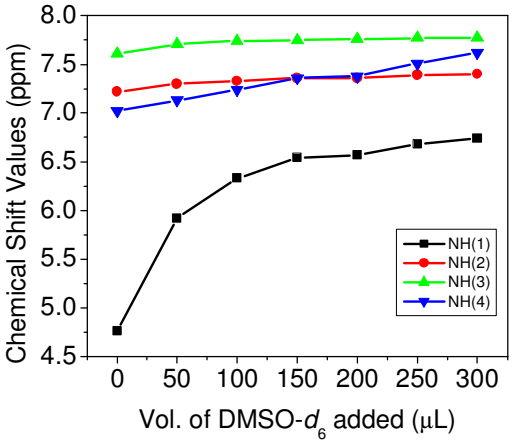
Solvent titration studies:

Solvent titration was carried out by sequentially adding up to 33% (v/v) of DMSO-d_6 (up to 300 μL) to 600 μL of $CDCl_3$ solutions of the peptides. Small changes in amide proton chemical shift (Δδ) have been used as indication for H-bonding. The spectra are illustrated in the Supporting Figure 1

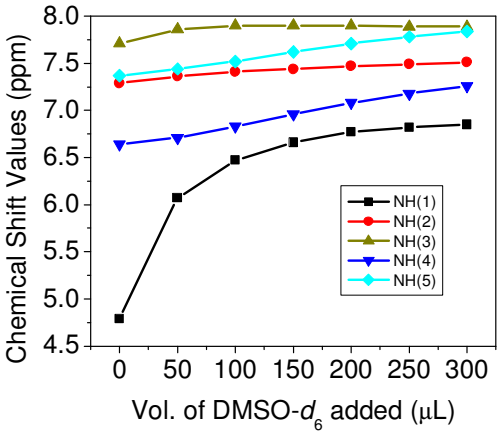
Supporting Figure 1. Solvent titration plots for peptides 3-10.



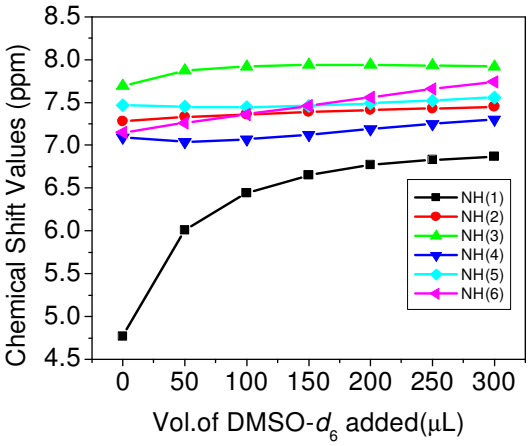
Peptide 3



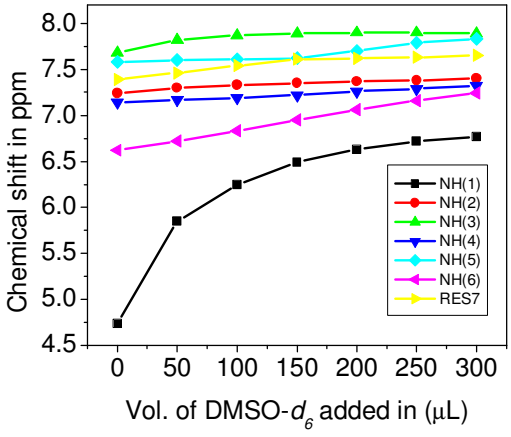
Peptide 4



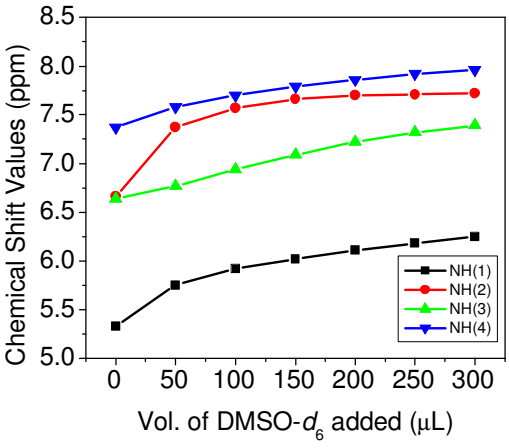
Peptide 5



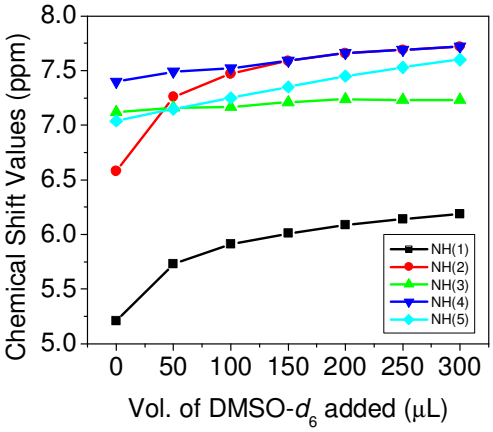
Peptide 6



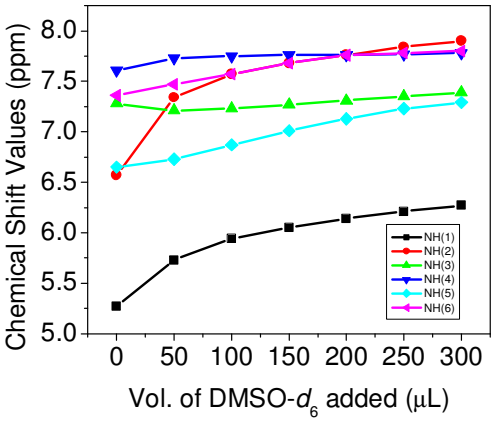
Peptide 7



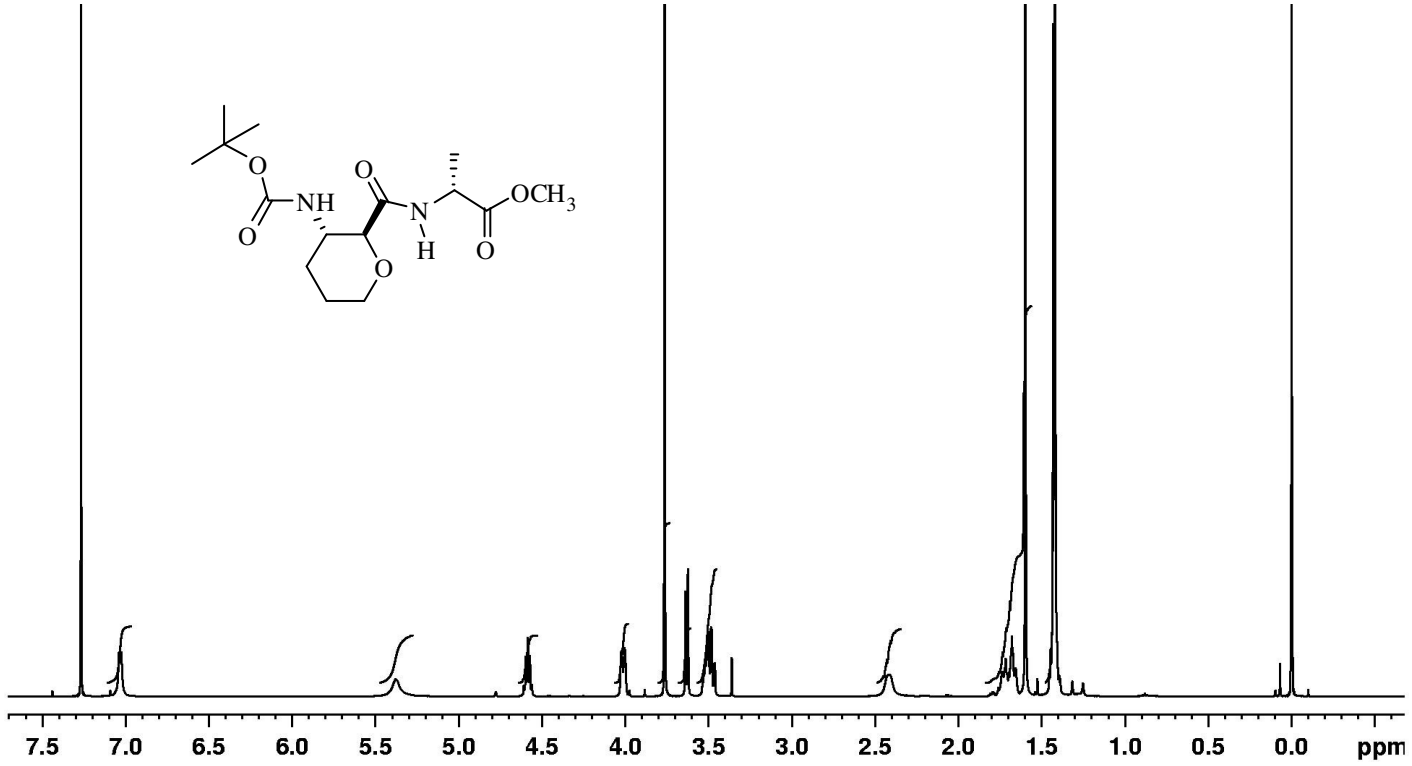
Peptide 8



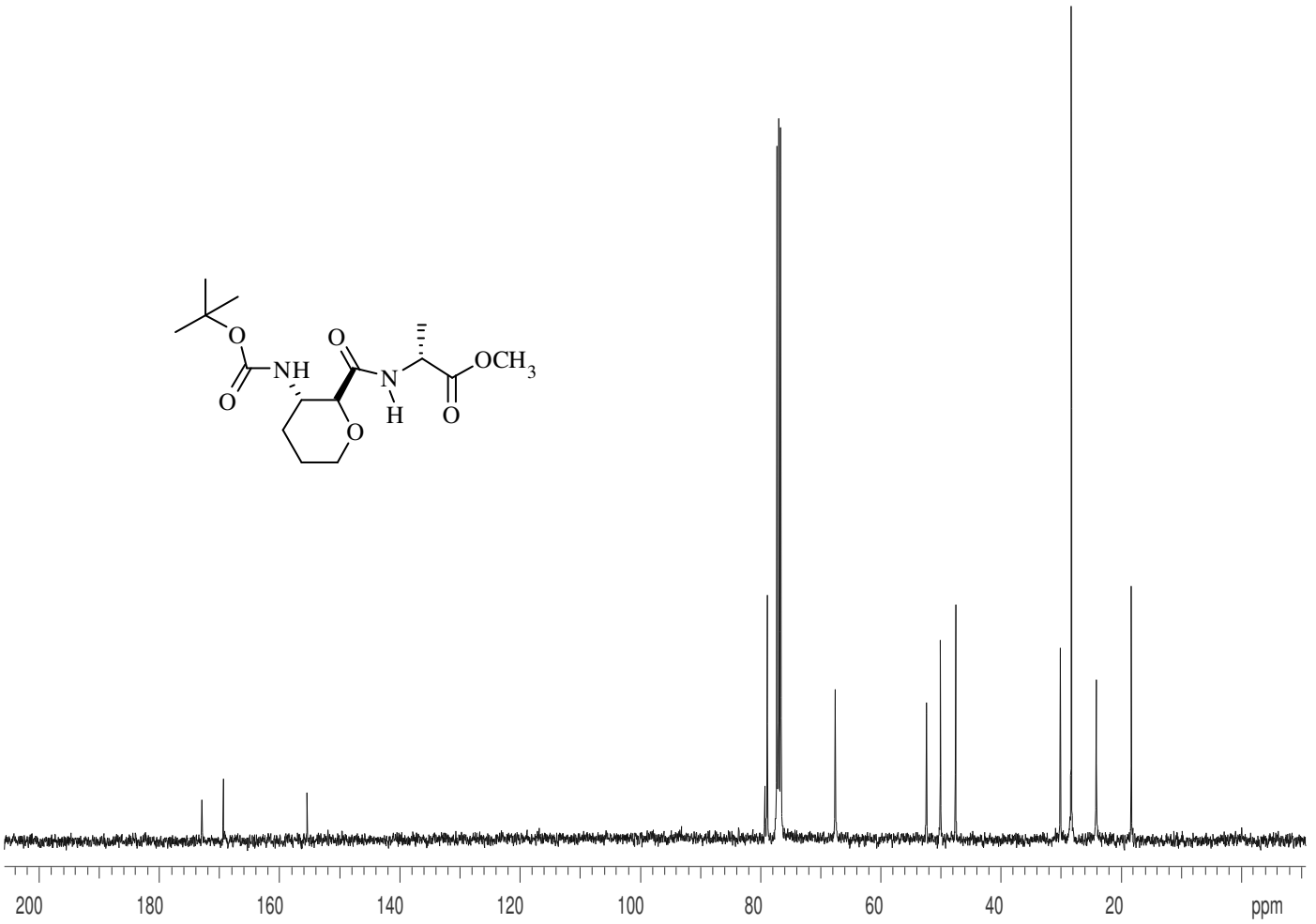
Peptide 9



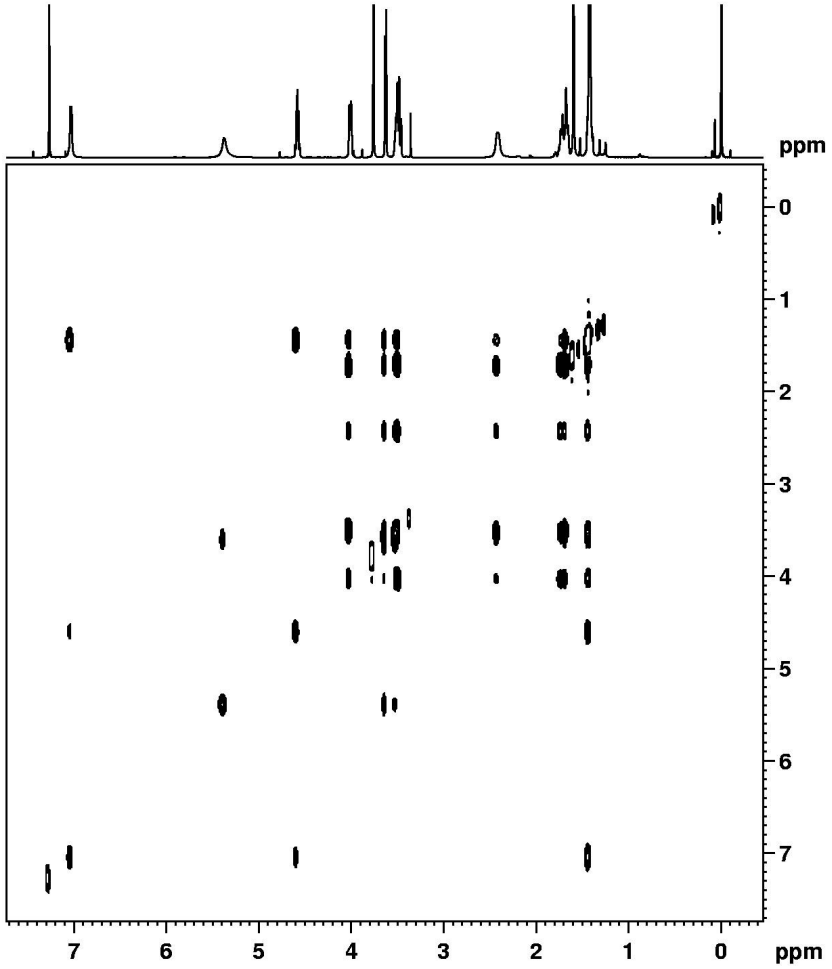
Peptide 10



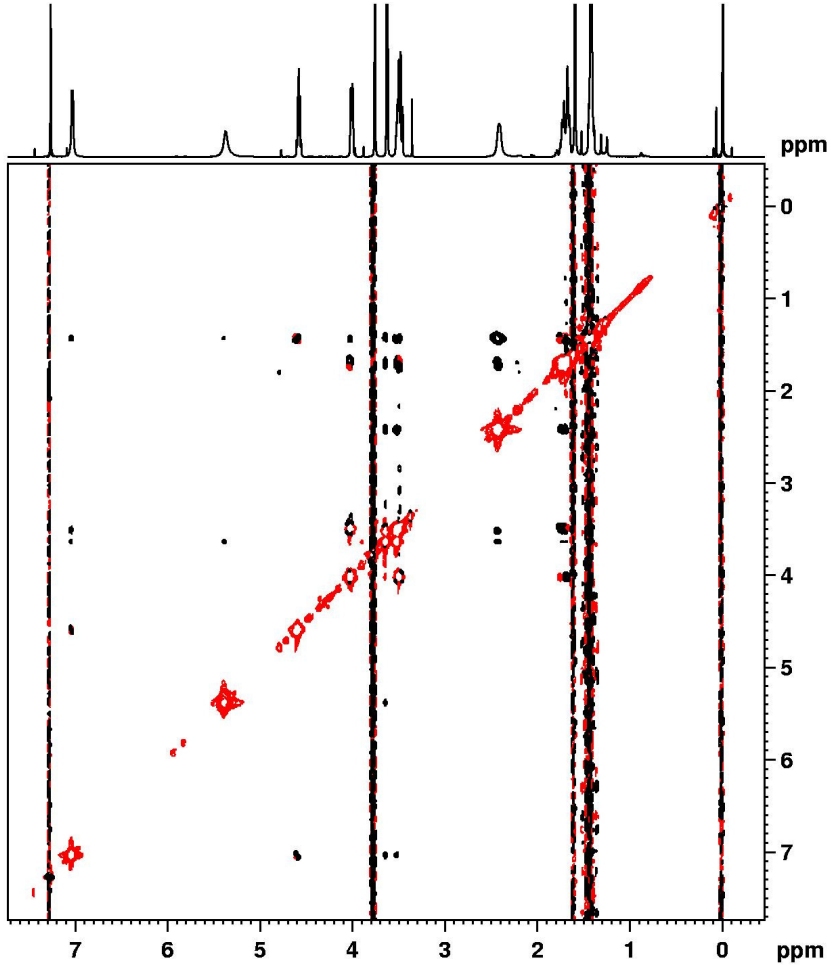
Supporting Figure 2. ^{1}H NMR spectrum of peptide 3 (600 MHz, $CDCl_3$, 298 K).



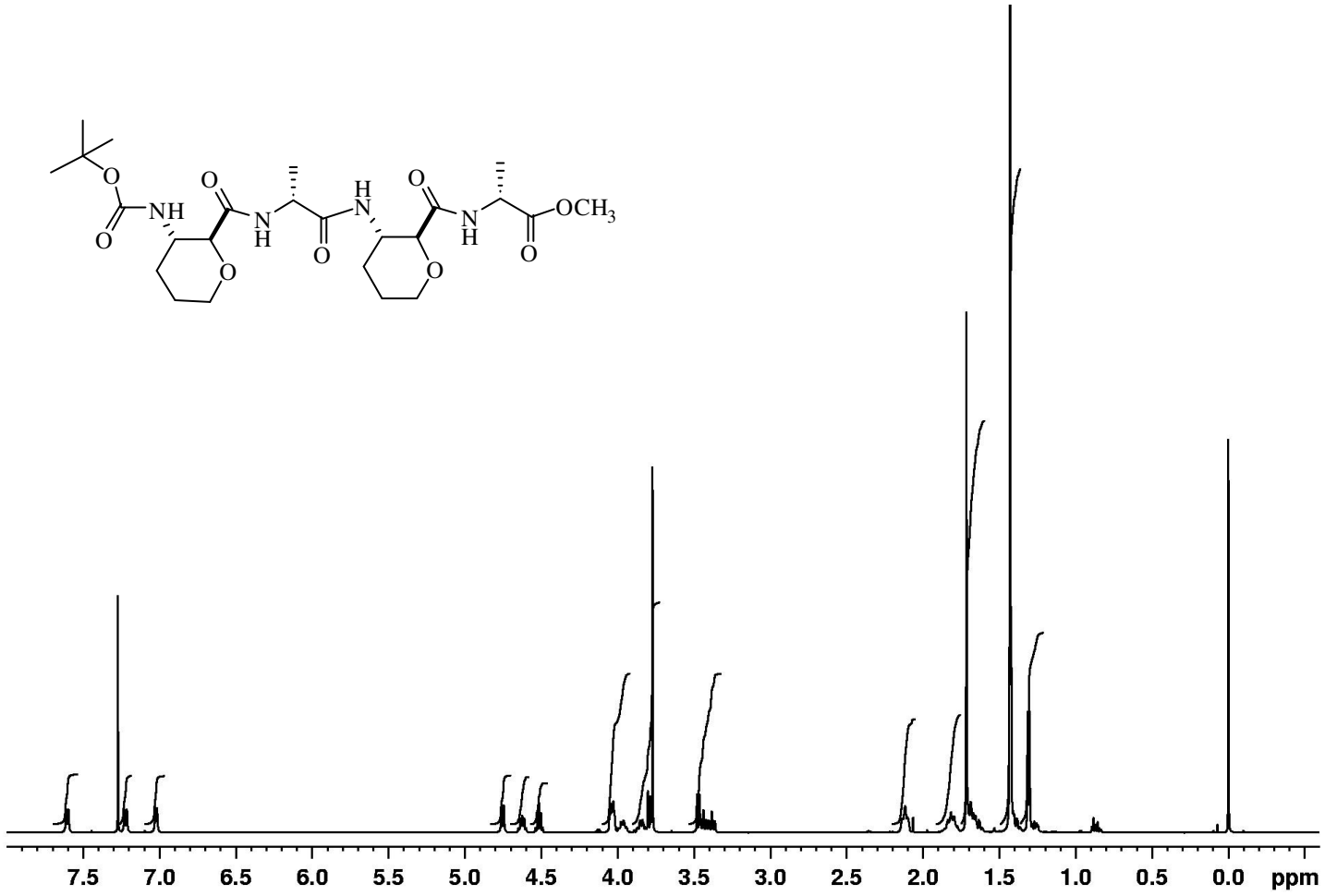
Supporting Figure 3. ^{13}C NMR spectrum of peptide 3 (100 MHz, $CDCl_3$).



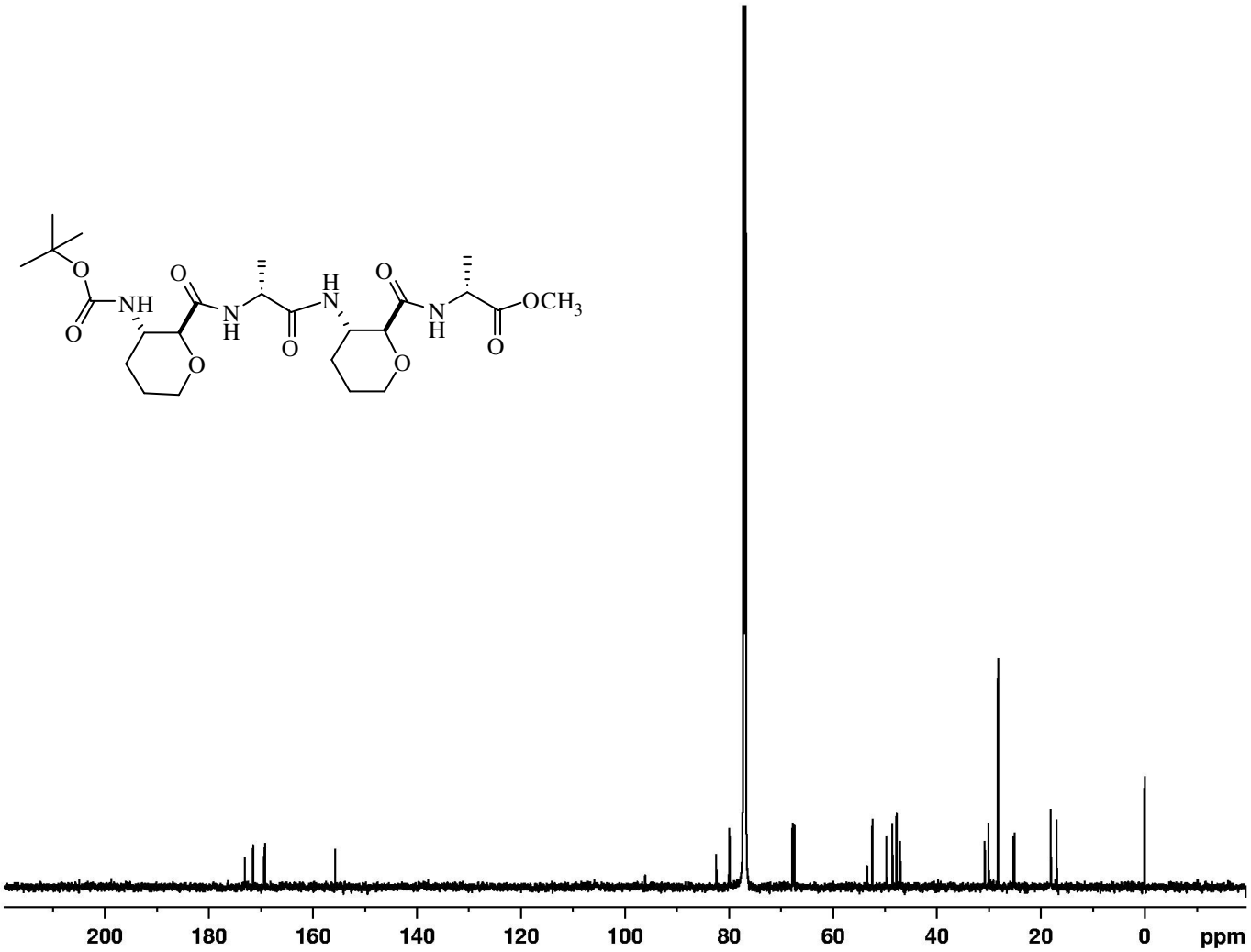
Supporting Figure 4. TOCSY spectrum of peptide 3 (600 MHz, $CDCl_3$, 298 K)



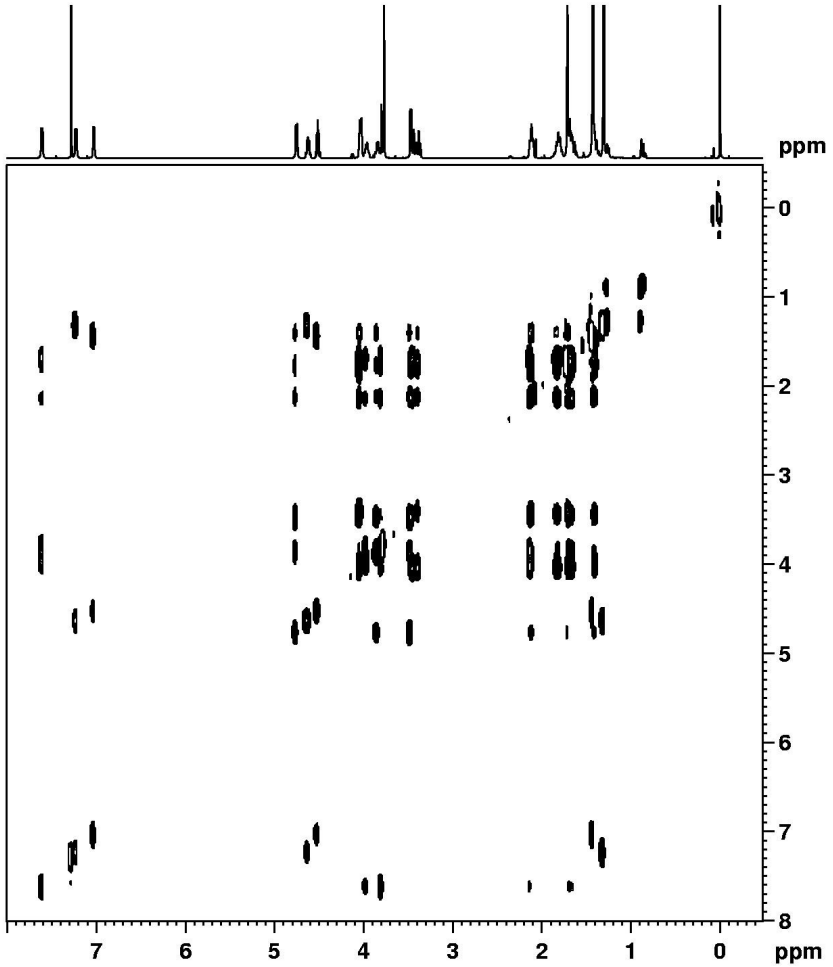
Supporting Figure 5. ROESY spectrum of peptide 3 (600 MHz, $CDCl_3$, 298 K)



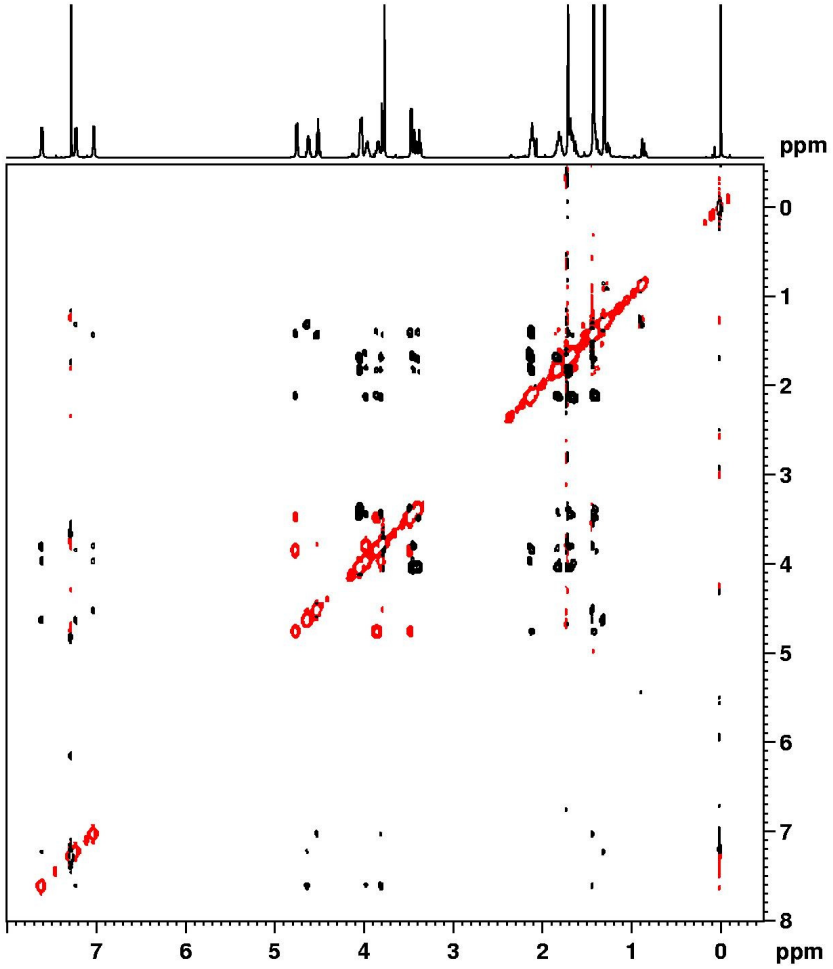
Supporting Figure 6. ^{1}H NMR spectrum of peptide 4 (600 MHz, $CDCl_3$, 278 K)



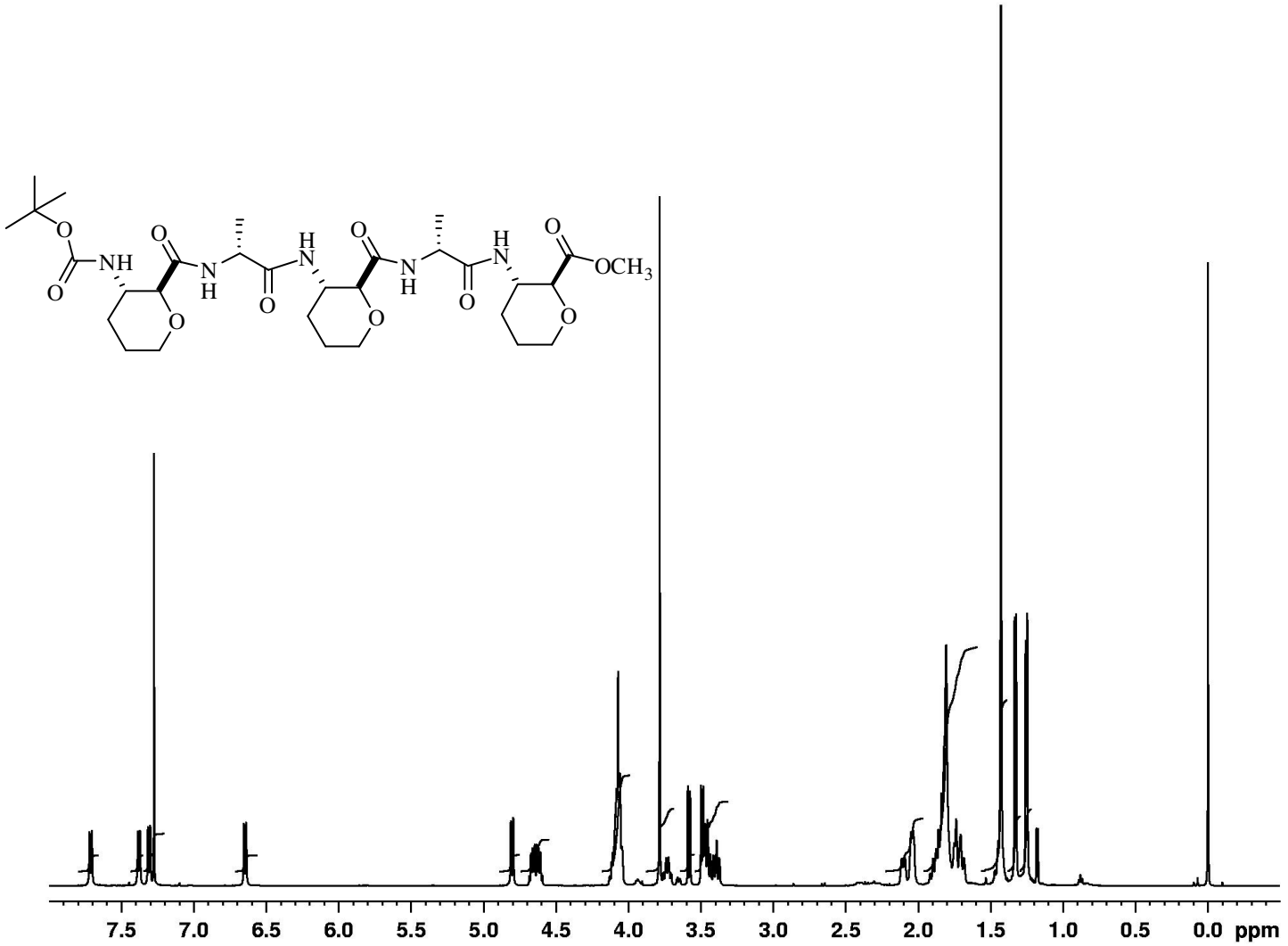
Supporting Figure 7. ^{13}C NMR spectrum of peptide 4 (150 MHz, $CDCl_3$)



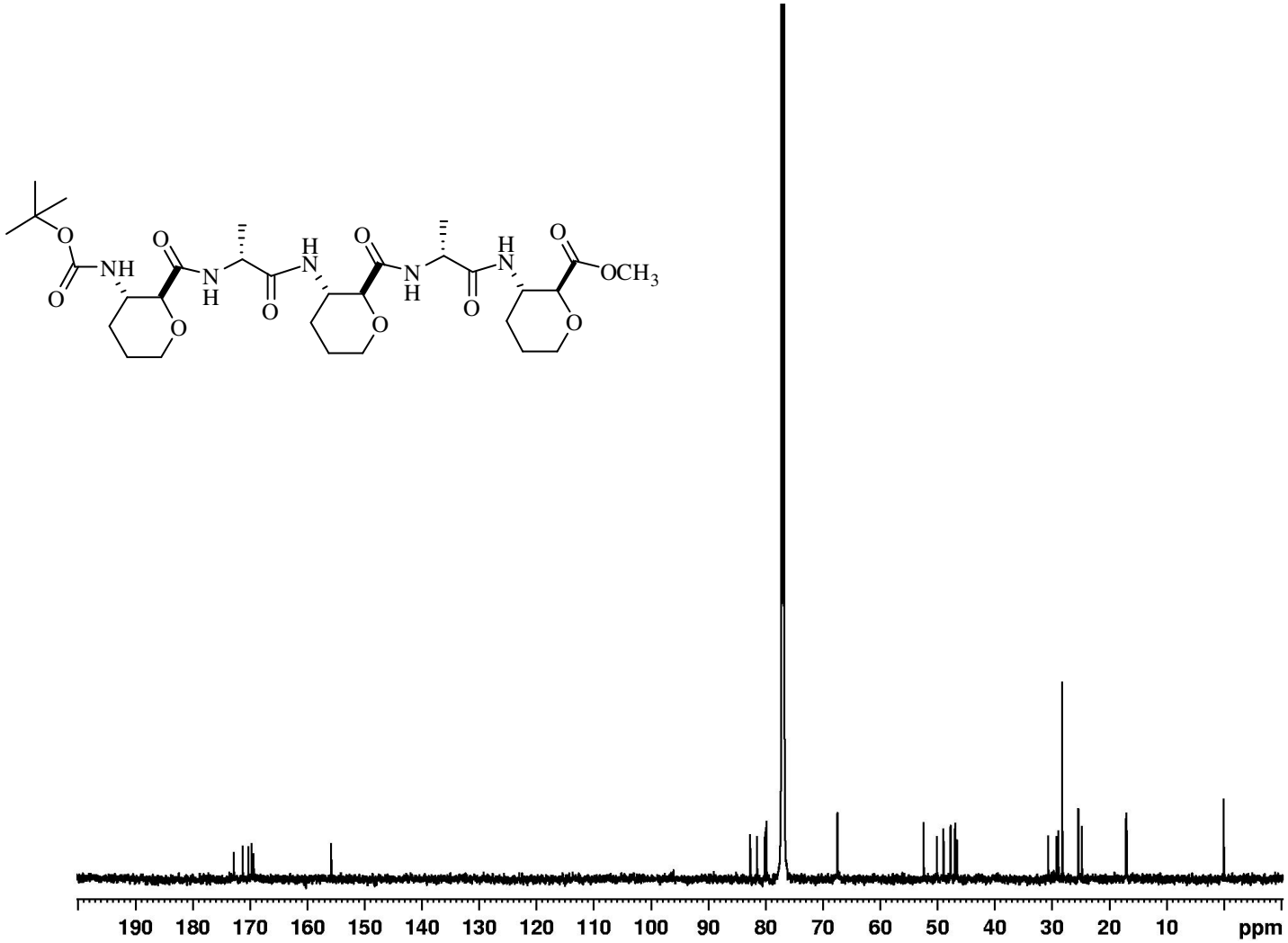
Supporting Figure 8. TOCSY spectrum of peptide 4 (600 MHz, $CDCl_3$, 278 K).



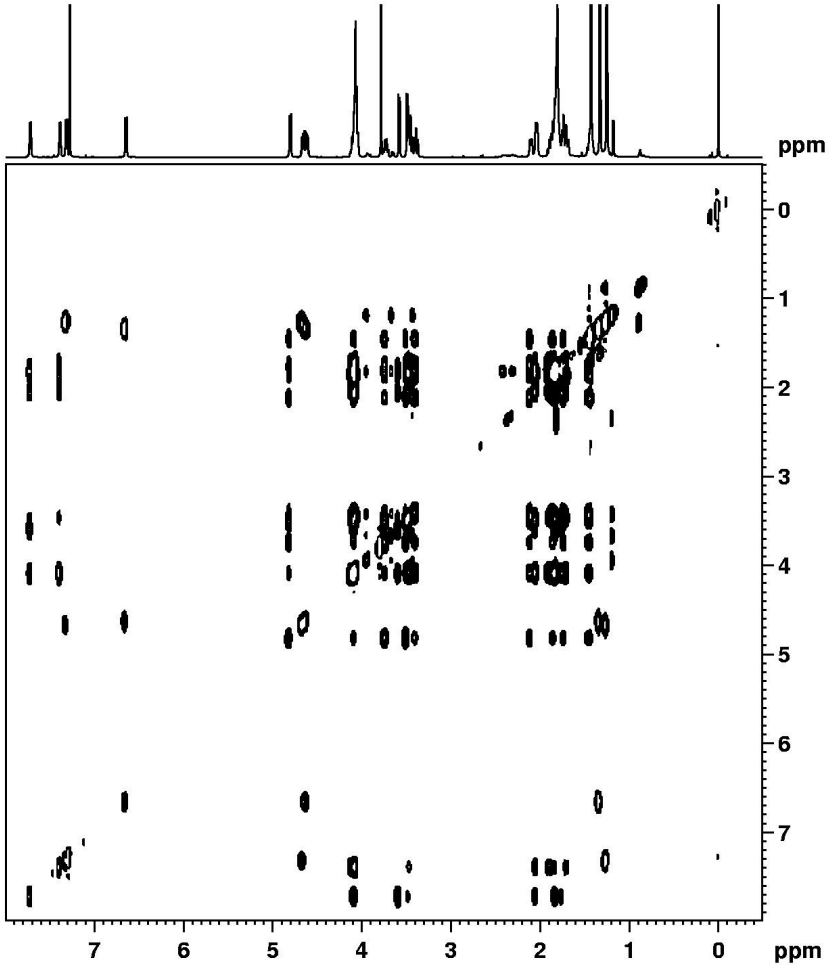
Supporting Figure 9. ROESY spectrum of peptide 4 (600 MHz, $CDCl_3$, 278 K).



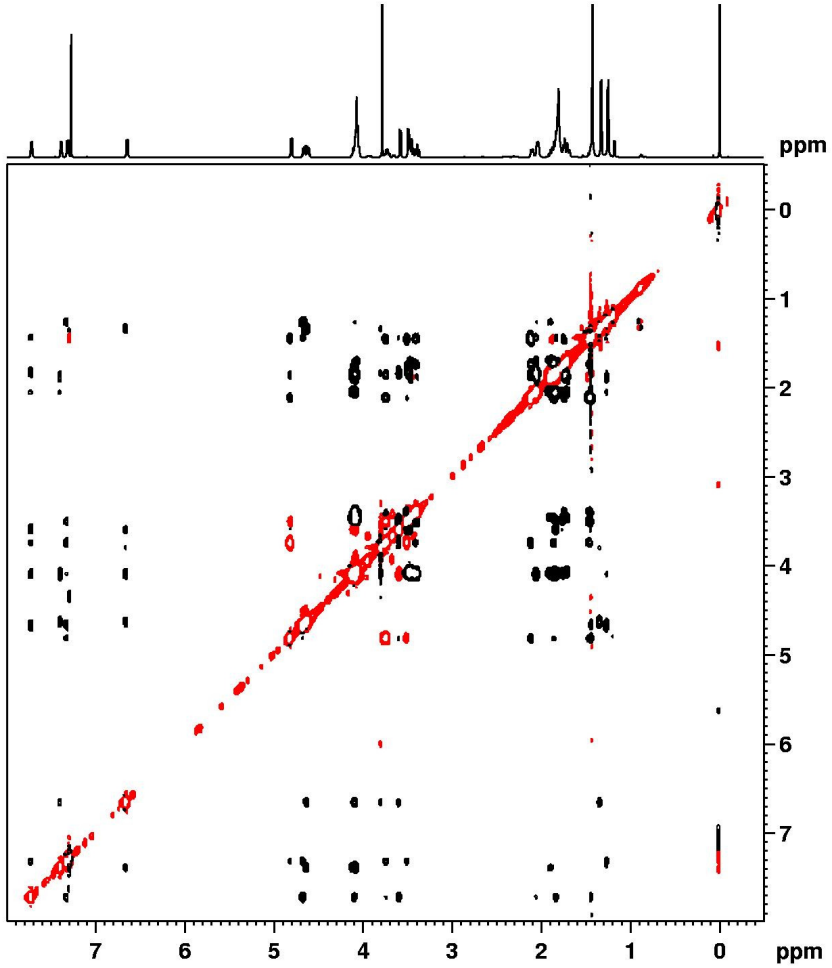
Supporting Figure 10. ^{1}H NMR spectrum of peptide 5 (600 MHz, $CDCl_3$, 288 K).



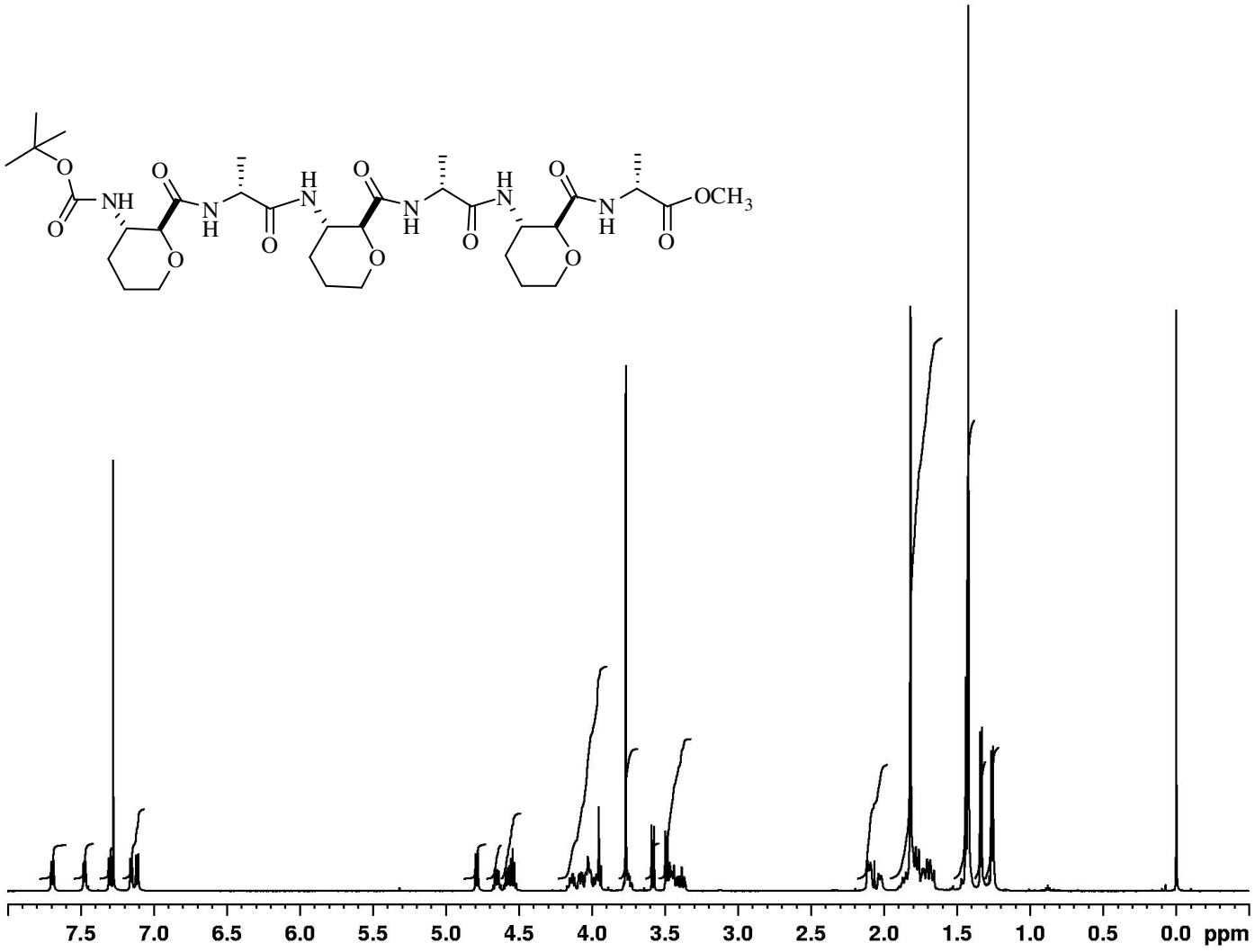
Supporting Figure 11. ^{13}C NMR spectrum of peptide 5 (150 MHz, $CDCl_3$).



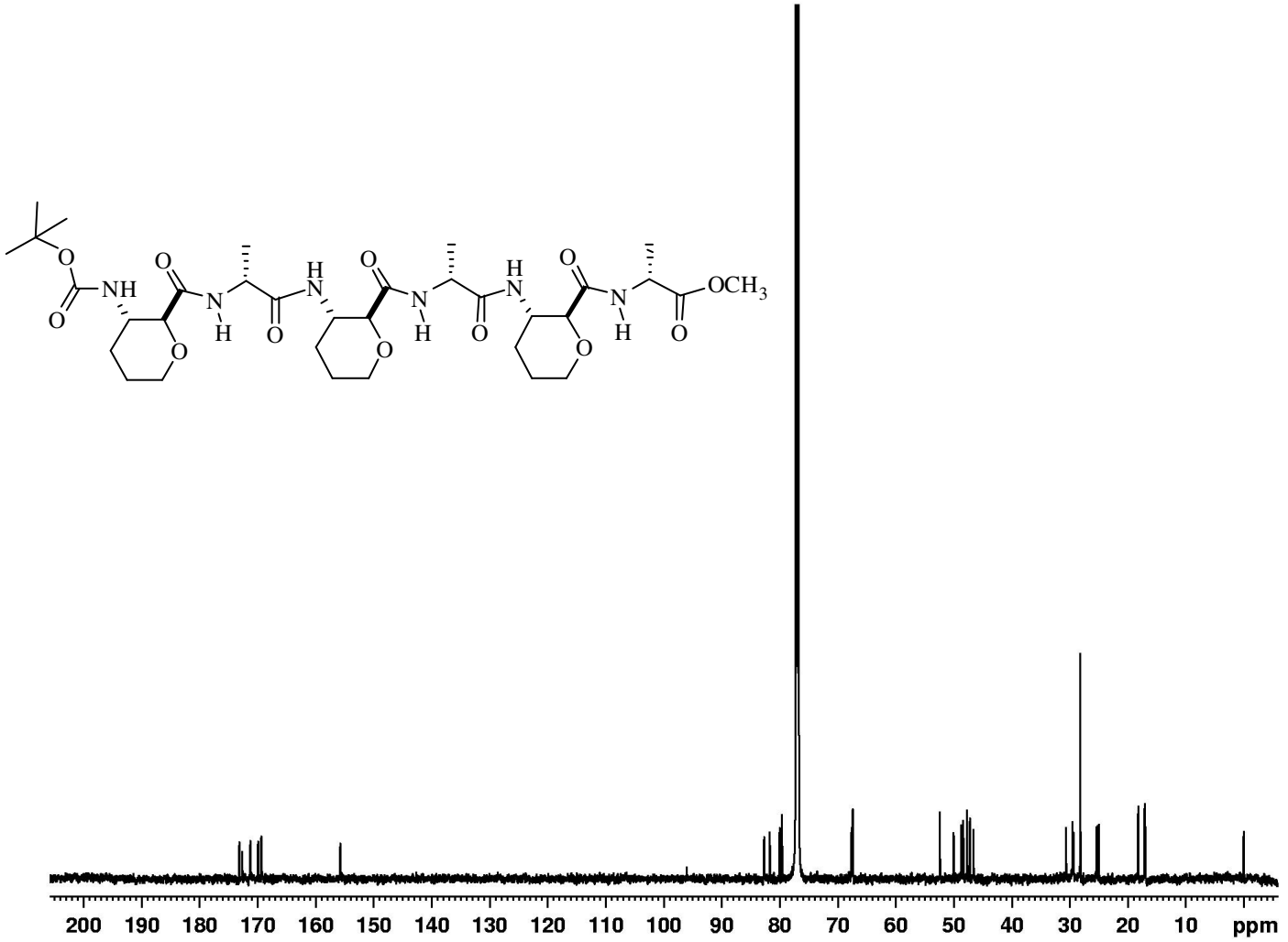
Supporting Figure 12. TOCSY spectrum of peptide 5 (600 MHz, $CDCl_3$, 288 K).



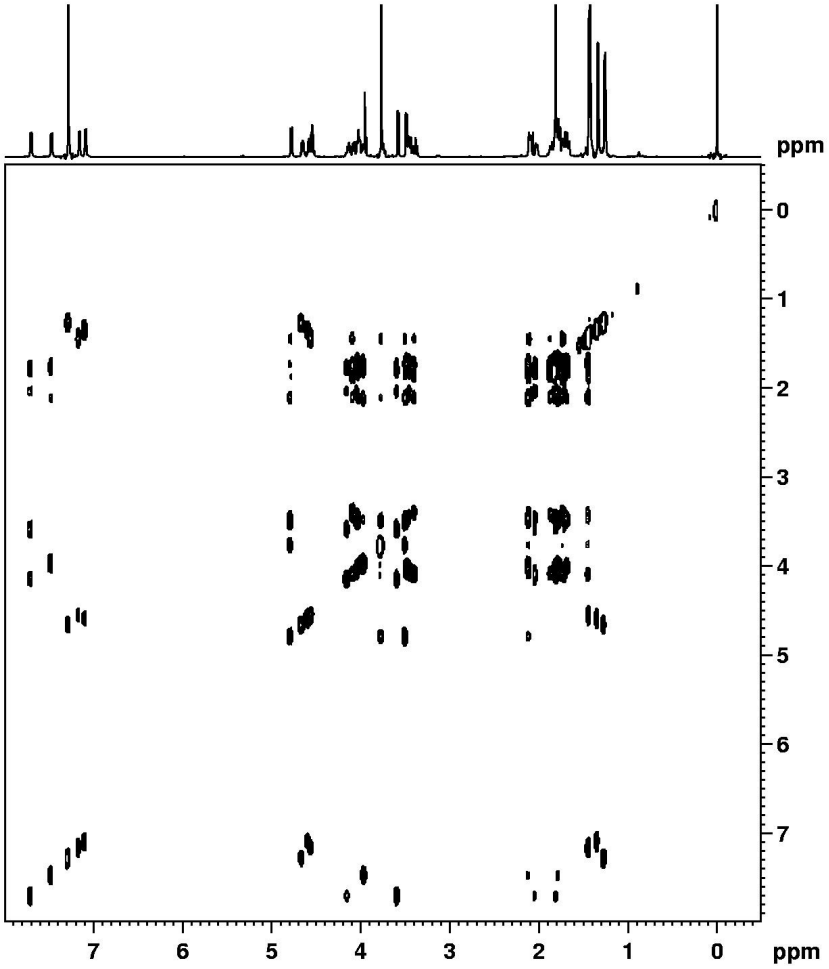
Supporting Figure 13. ROESY spectrum of peptide 5 (600 MHz, $CDCl_3$, 288 K).



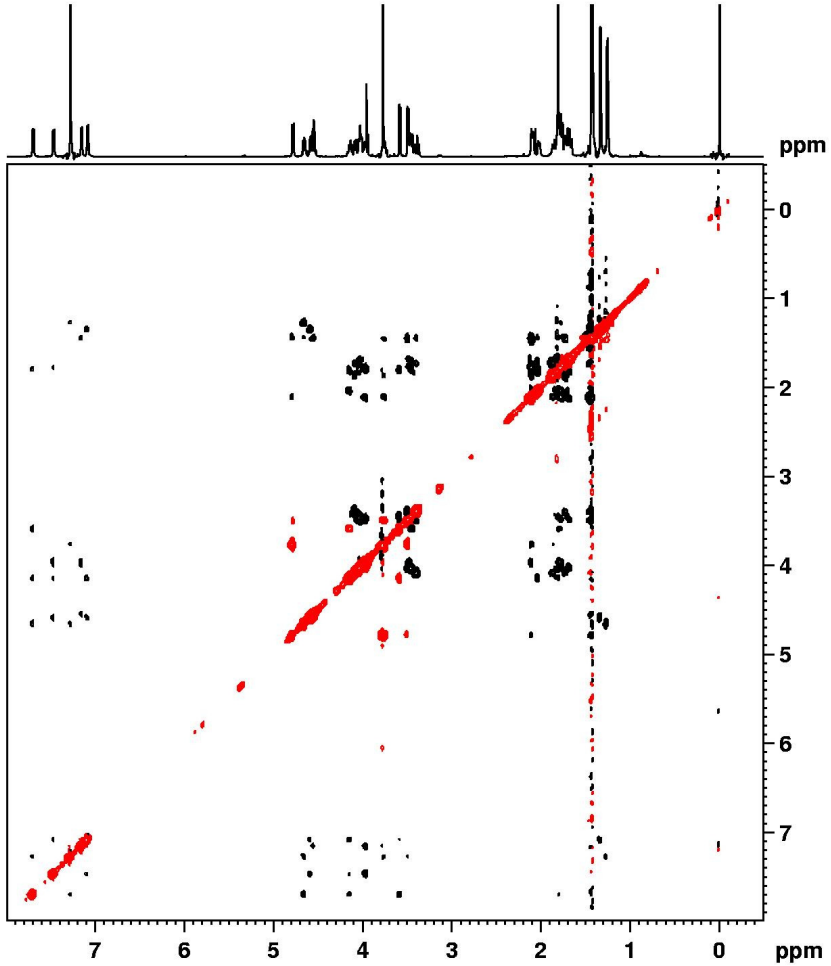
Supporting Figure 14. ^{1}H NMR spectrum of peptide 6 (600 MHz, $CDCl_3$, 278 K).



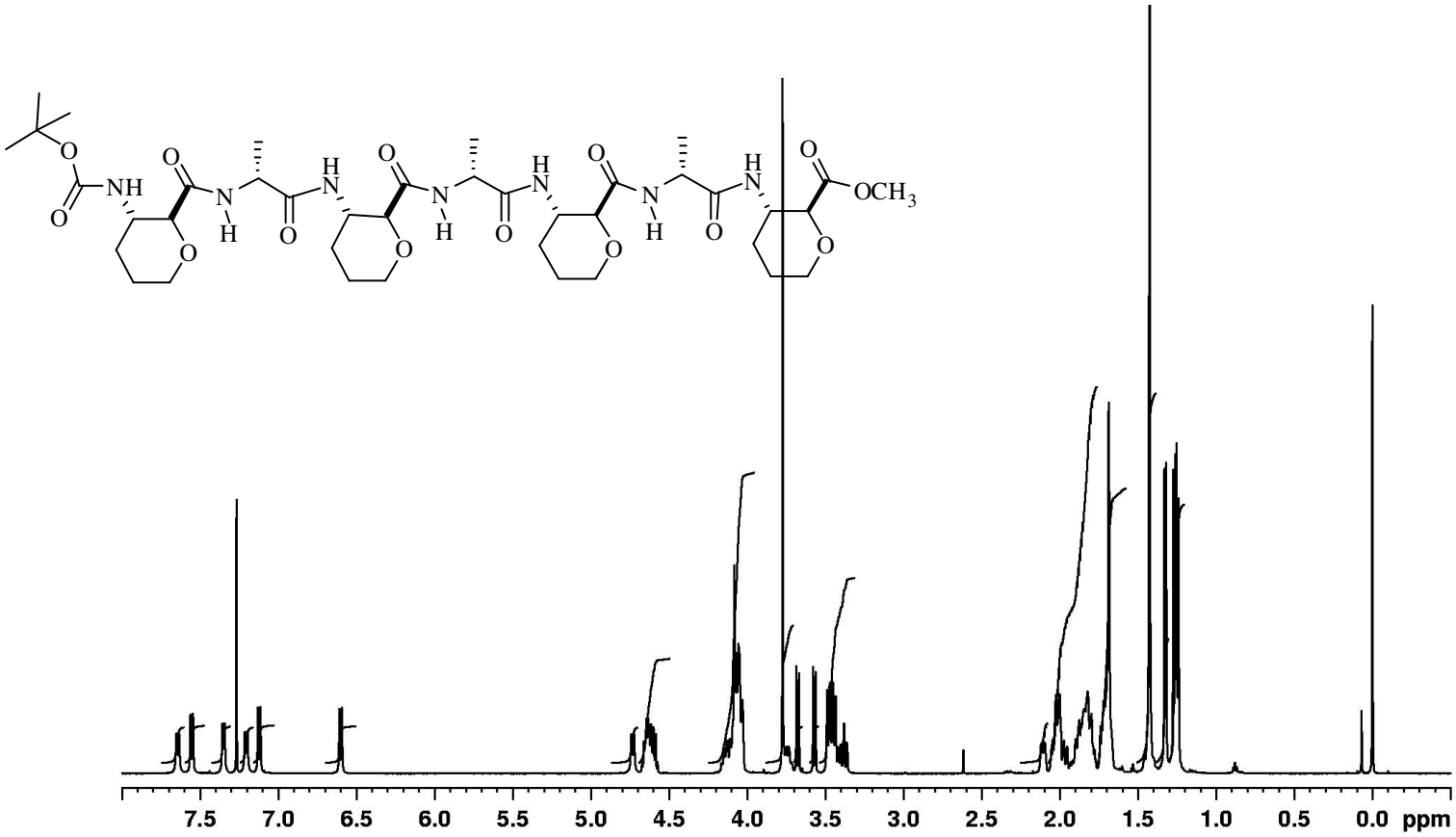
Supporting Figure 15. ^{13}C NMR spectrum of peptide 6 (150 MHz, $CDCl_3$).



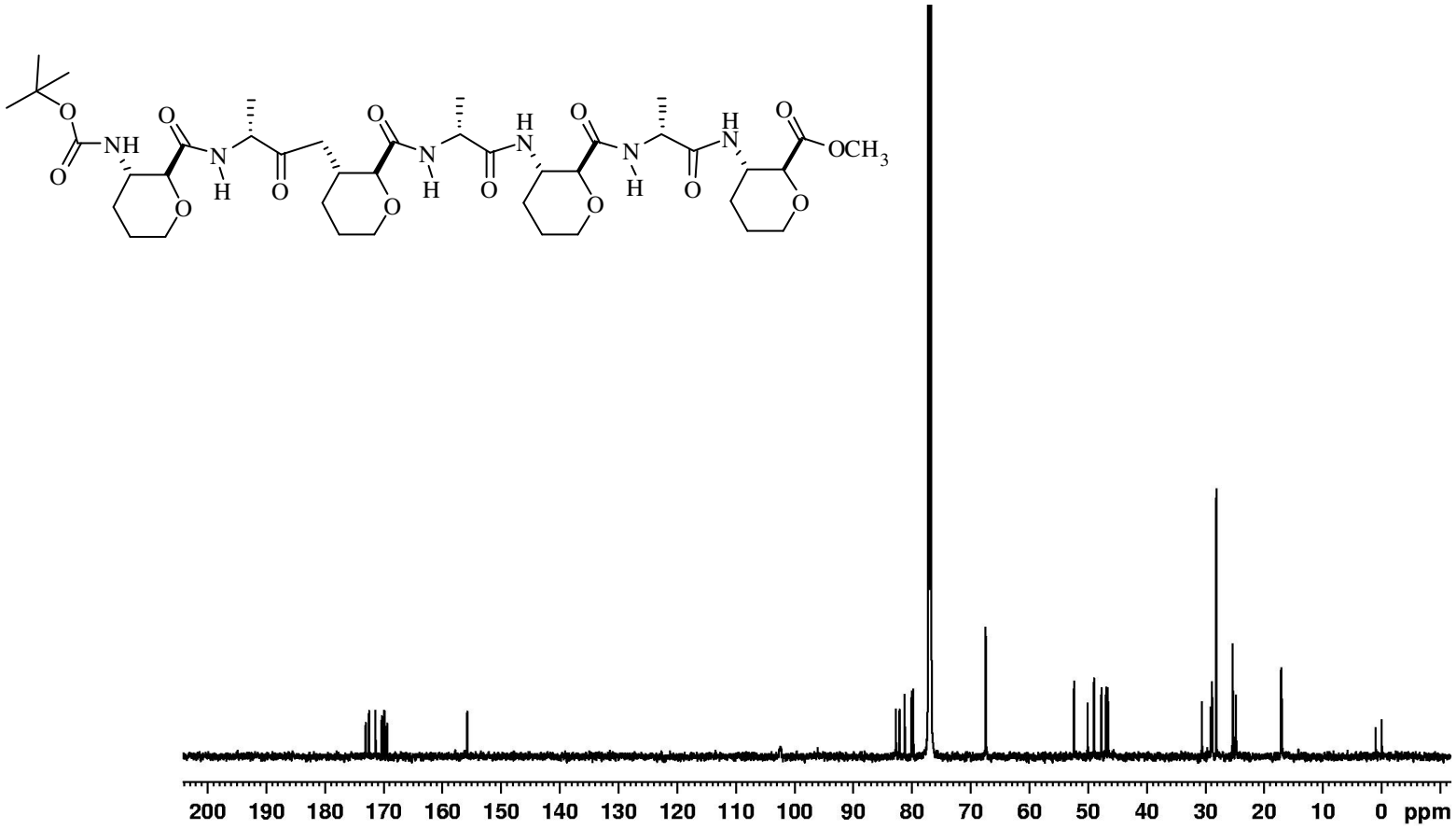
Supporting Figure 16. TOCSY spectrum of peptide 6 (600 MHz, $CDCl_3$, 278 K).



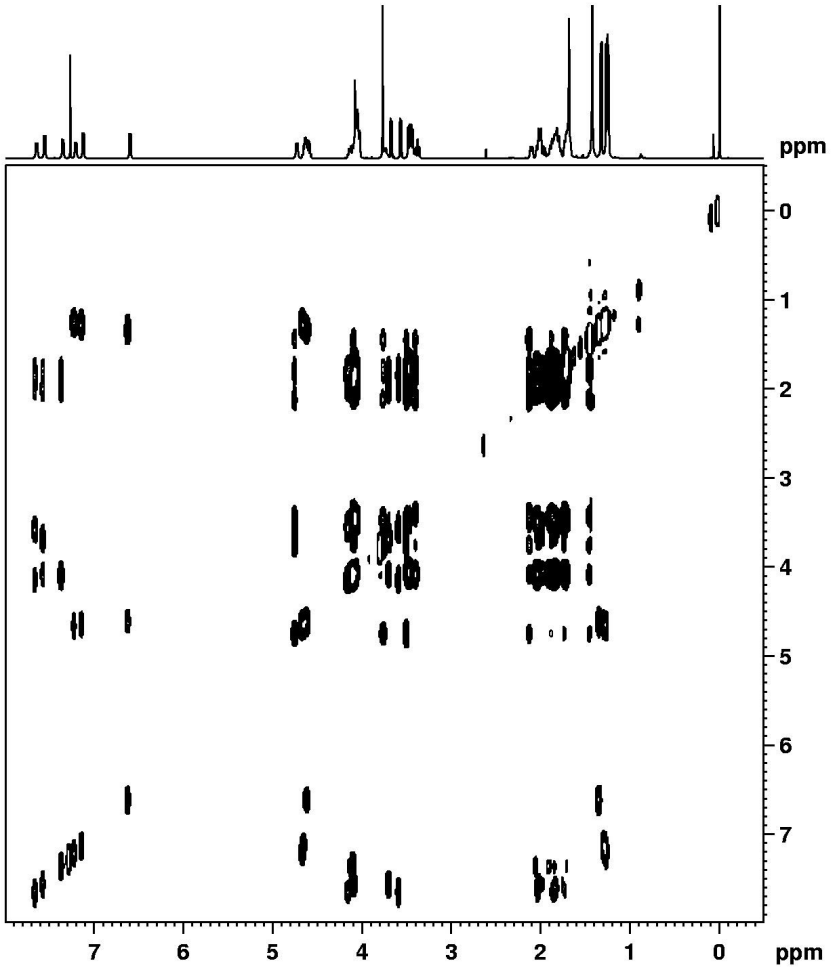
Supporting Figure 17. ROESY spectrum of peptide 6 (600 MHz, $CDCl_3$, 278 K)



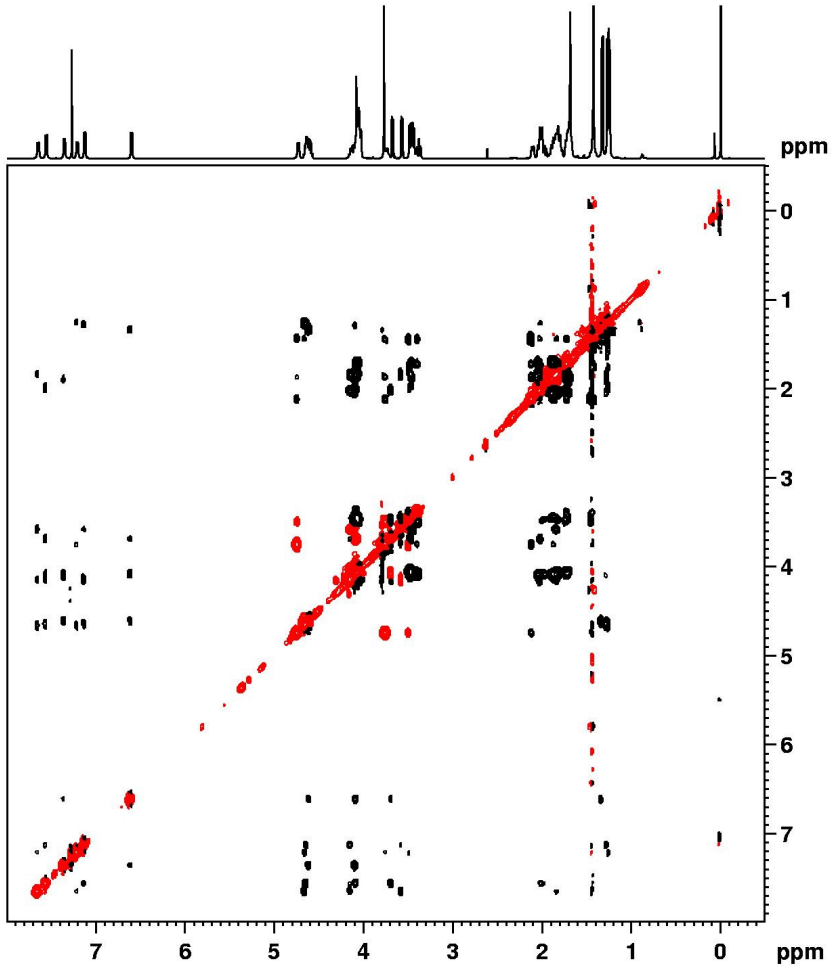
Supporting Figure 18. ^{1}H NMR spectrum of peptide 7 (600 MHz, $CDCl_3$, 288 K).



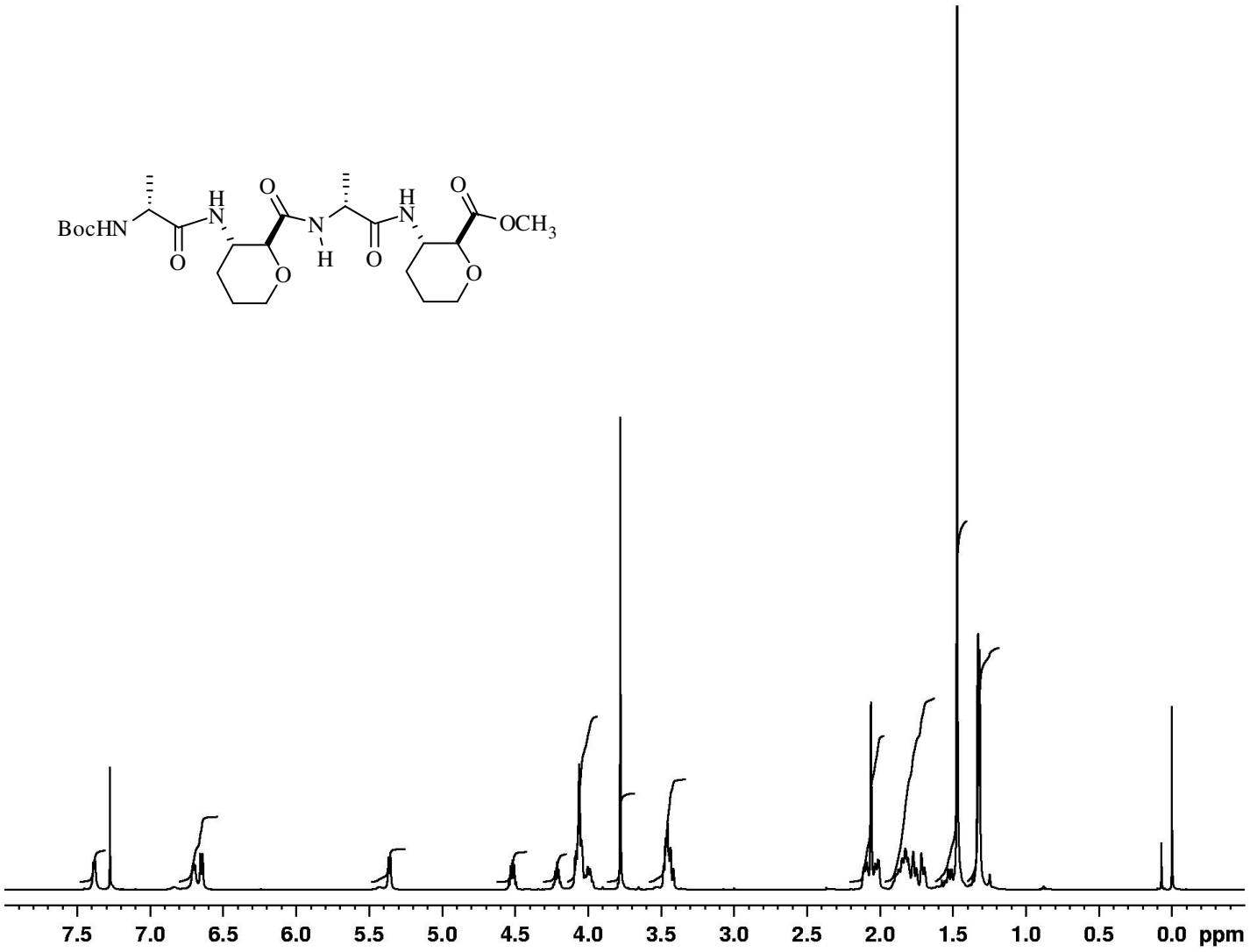
SupportingFigure 19. ^{13}C NMR spectrum of peptide 7 (150 MHz, $CDCl_3$).



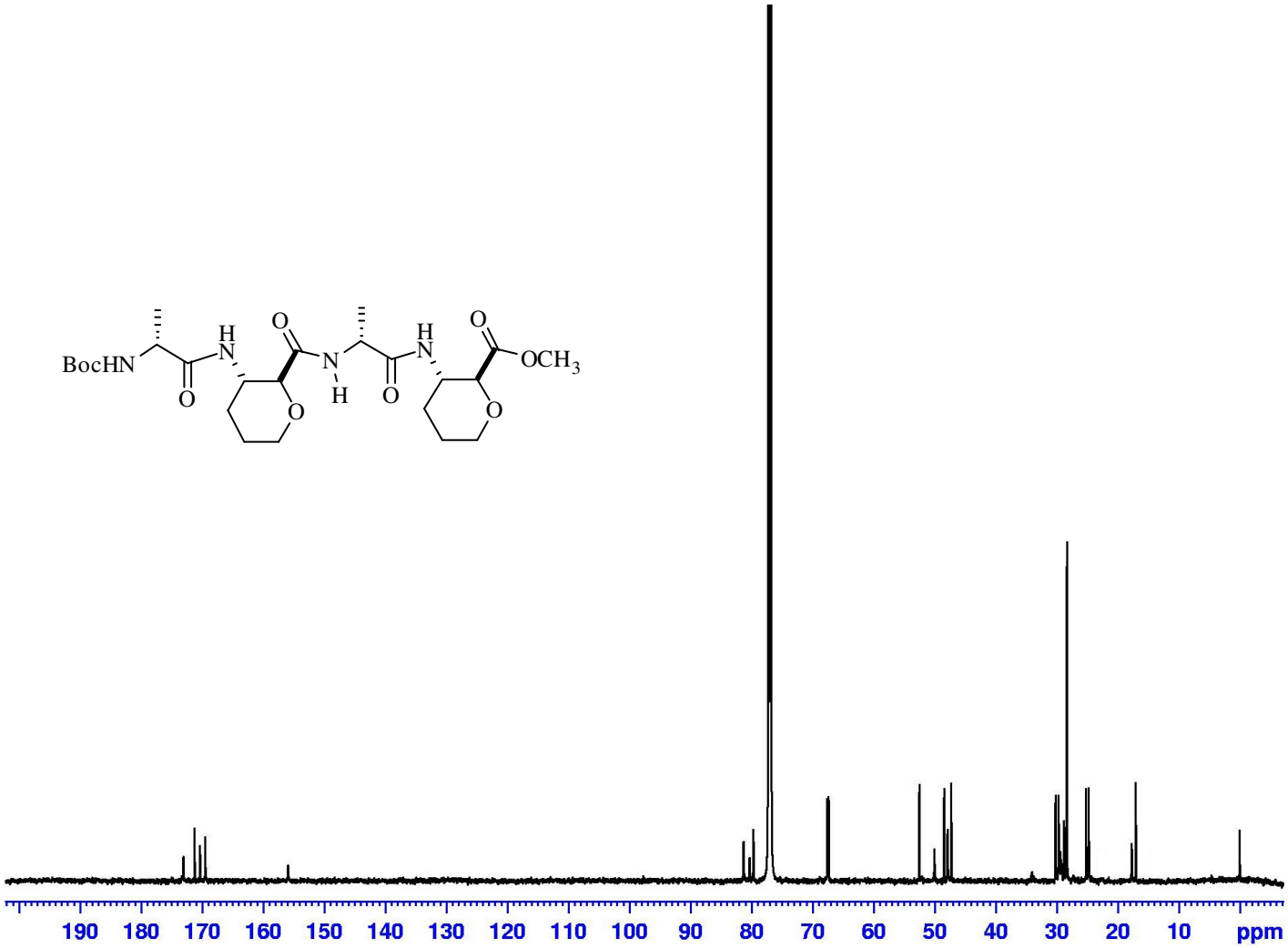
Supporting Figure 20. TOCSY spectrum of peptide 7 (600 MHz, $CDCl_3$, 288 K).



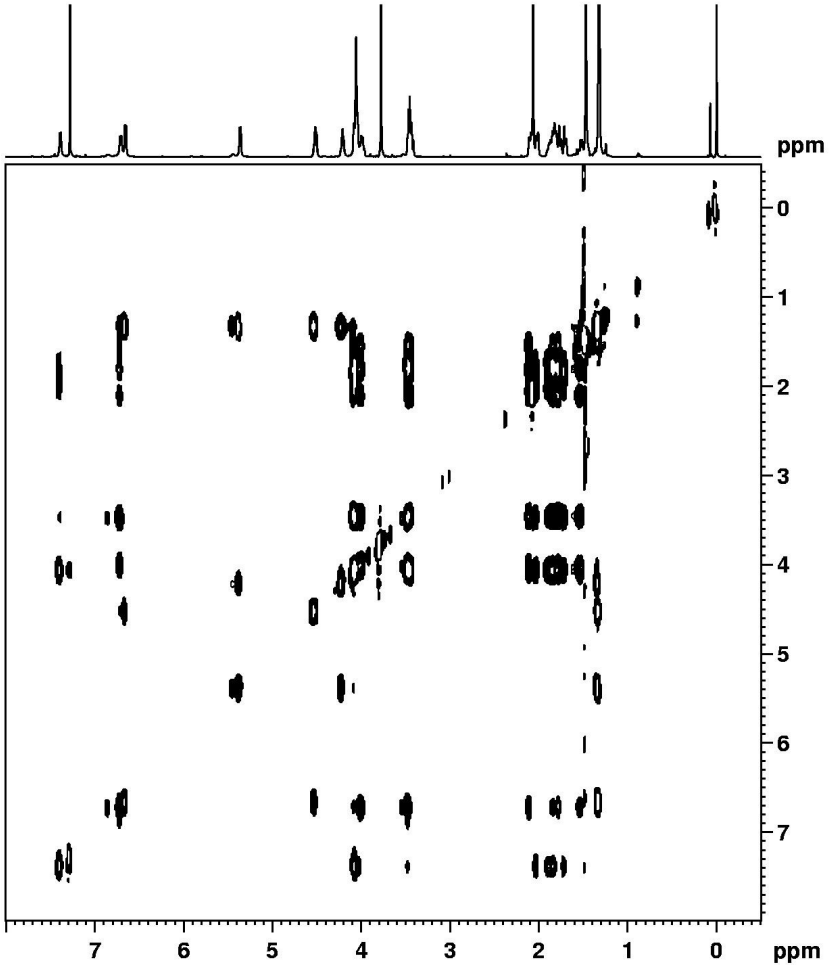
Supporting Figure 21. ROESY spectrum of peptide 7 (600 MHz, $CDCl_3$, 288 K).



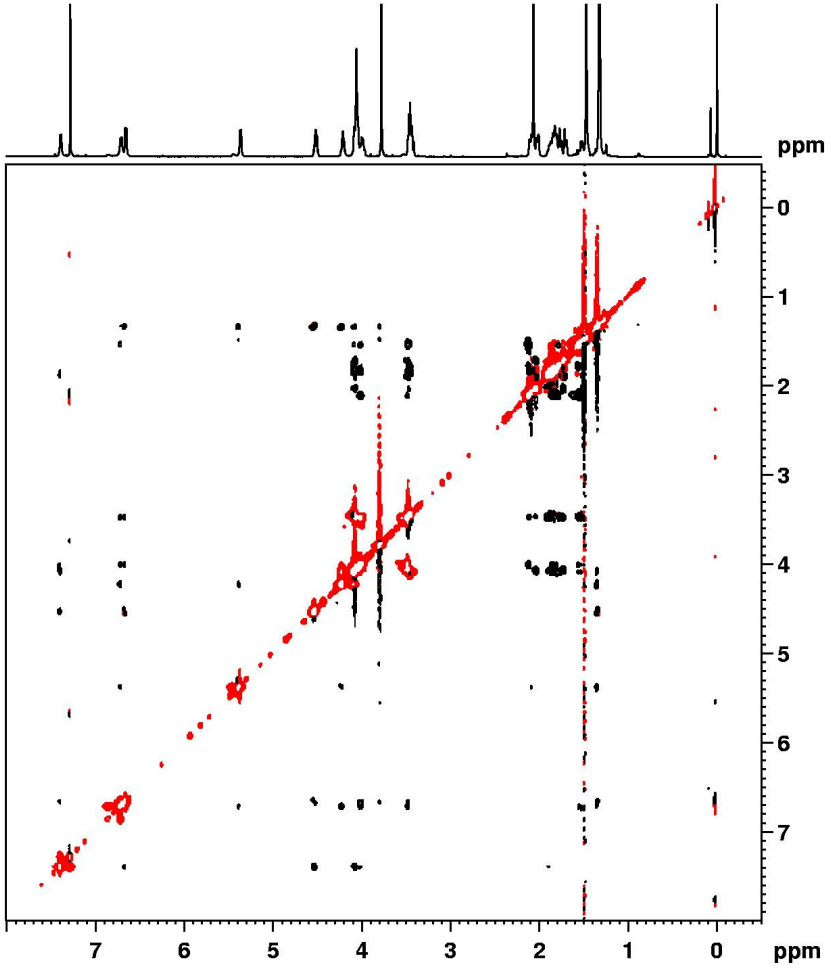
Supporting Figure 22. ^{1}H NMR spectrum of peptide 8 (600 MHz, $CDCl_3$, 278 K).



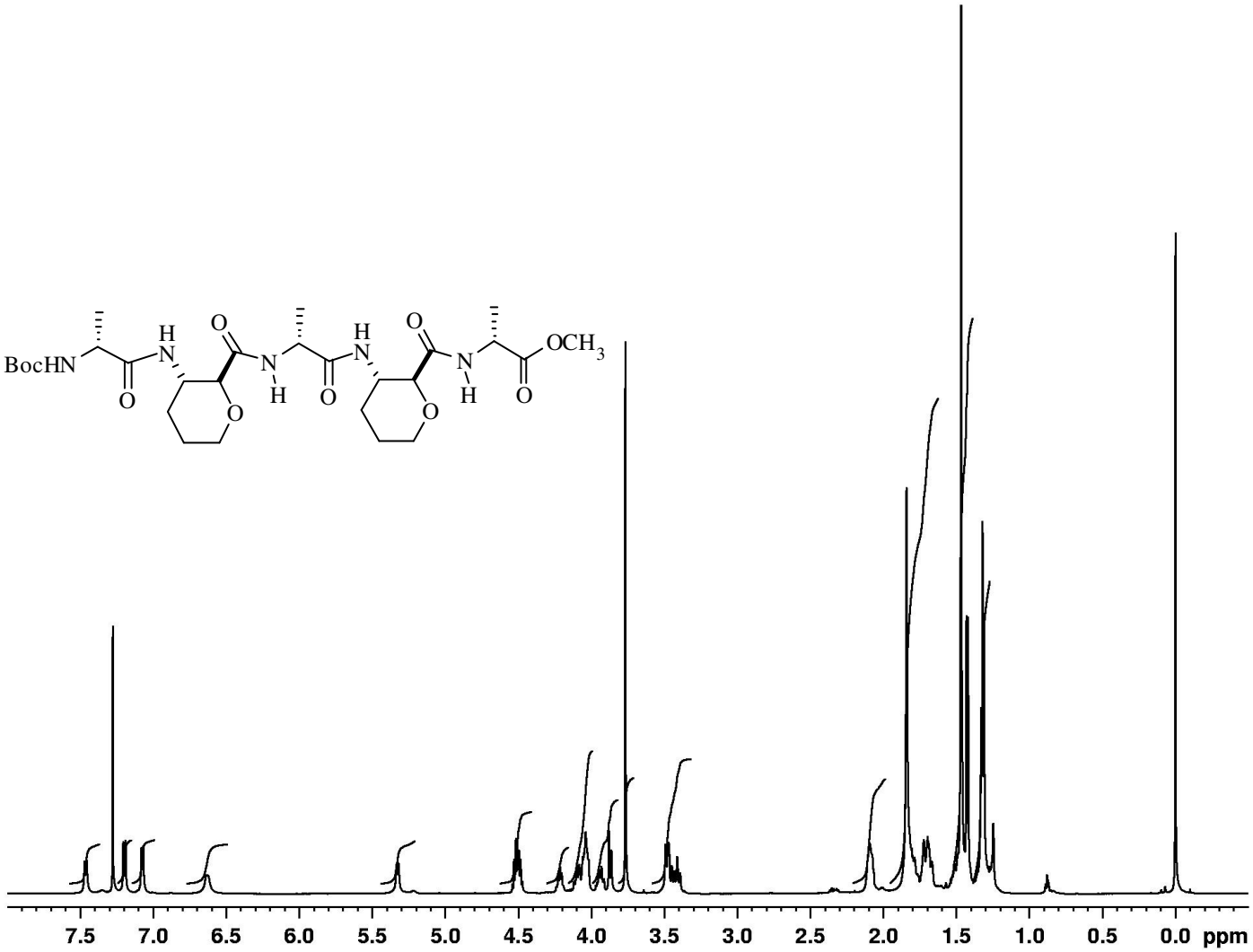
Supporting Figure 23. ^{13}C NMR spectrum of peptide 8 (150 MHz, $CDCl_3$).



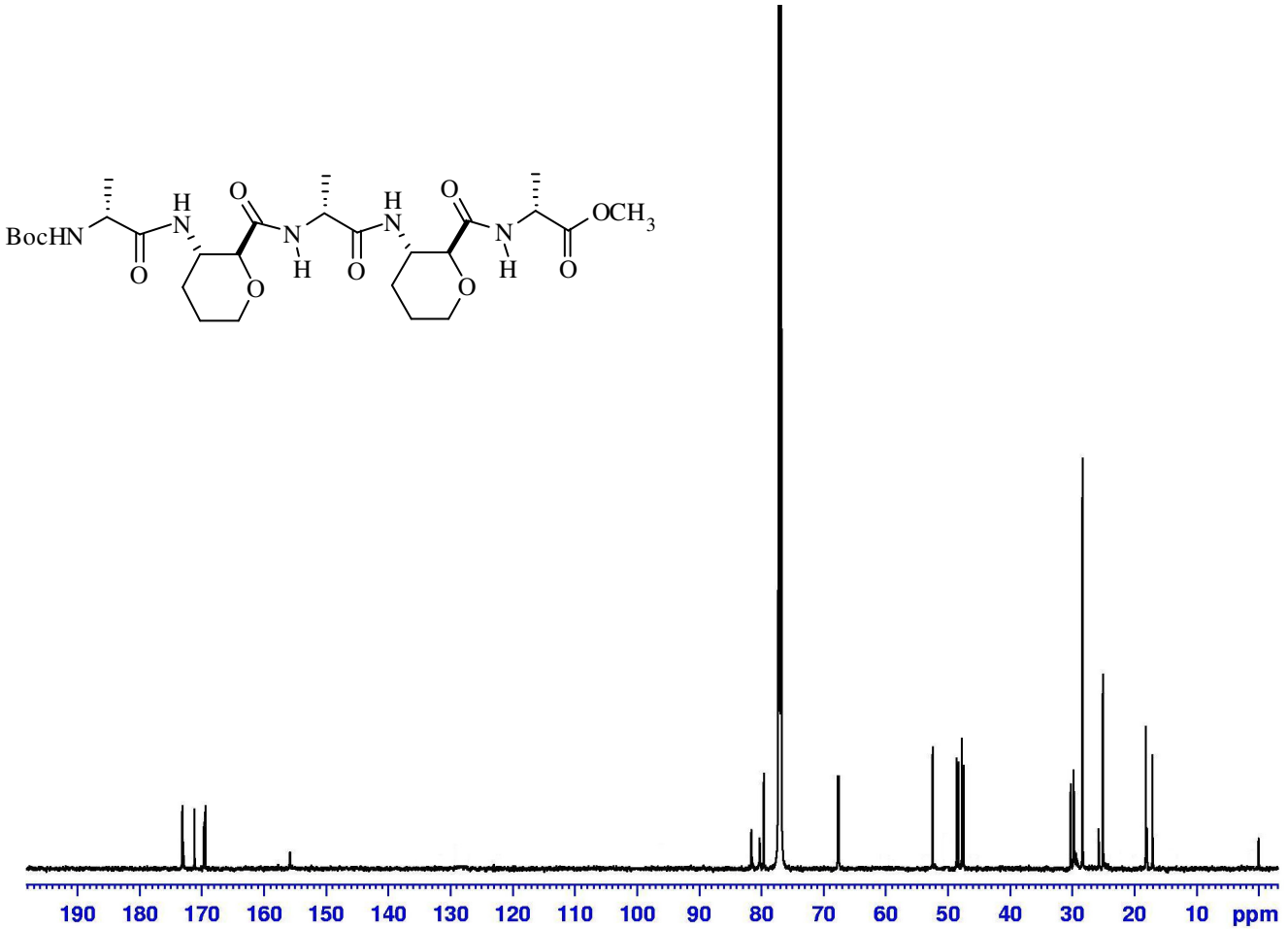
Supporting Figure 24. TOCSY spectrum of peptide 8 (600 MHz, $CDCl_3$, 278 K).



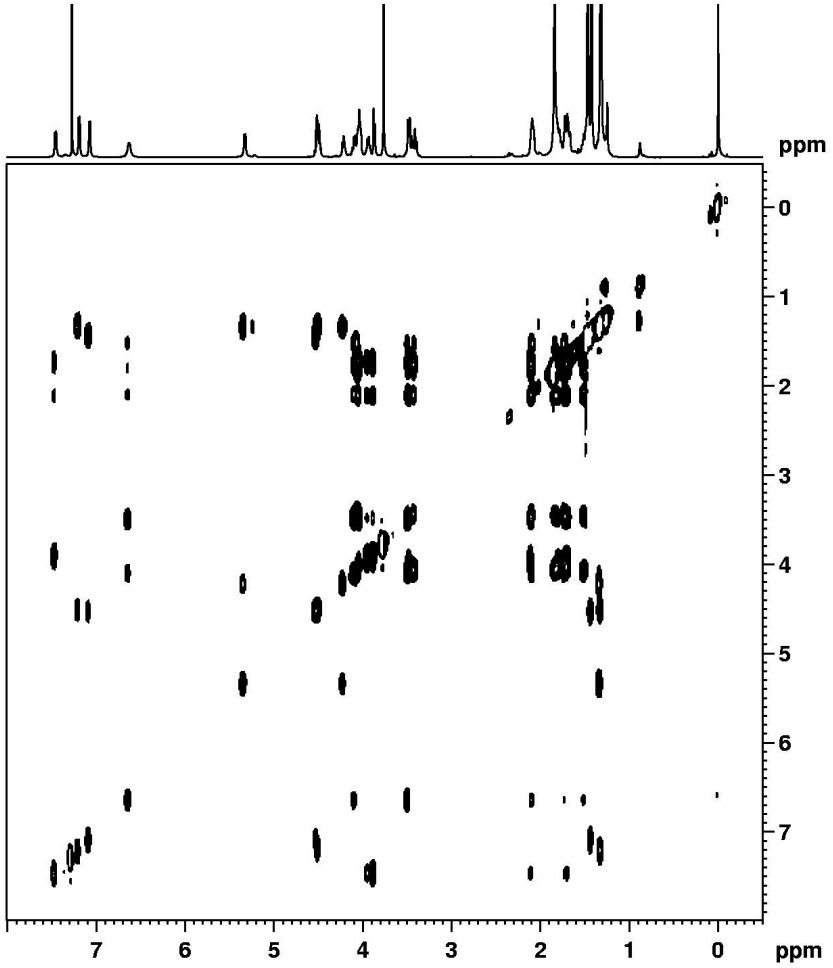
Supporting Figure 25. ROESY spectrum of peptide 8 (600 MHz, $CDCl_3$, 278 K).



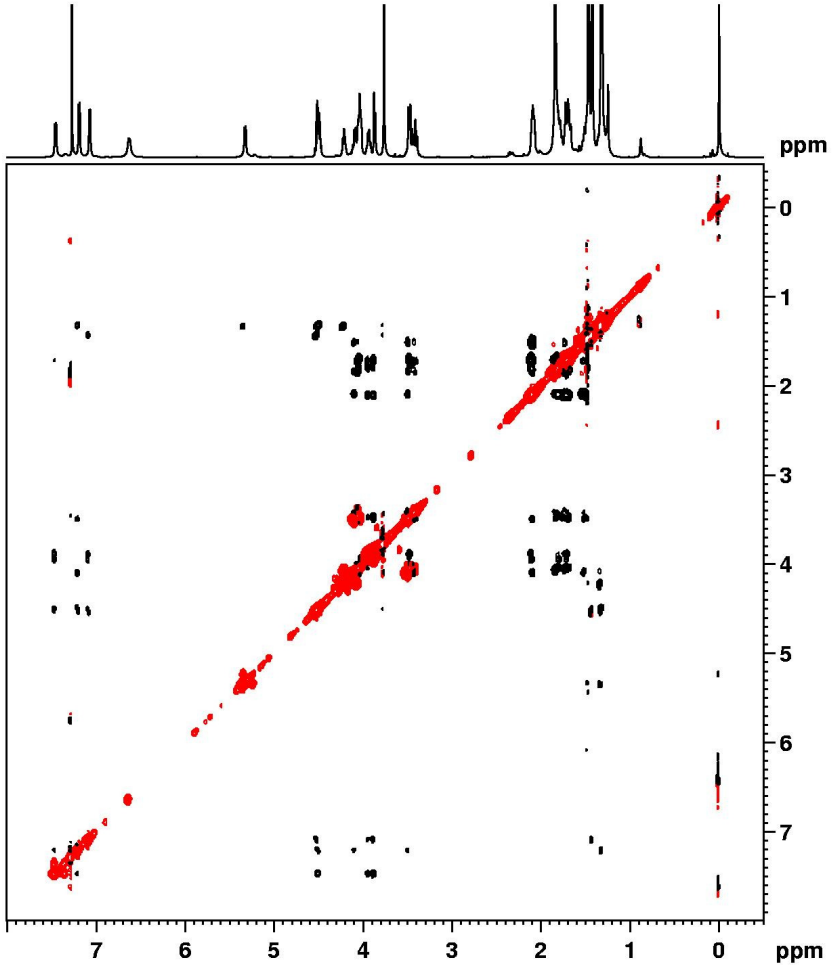
Supporting Figure 26. ^{1}H NMR spectrum of peptide 9 (600 MHz, $CDCl_3$, 278 K).



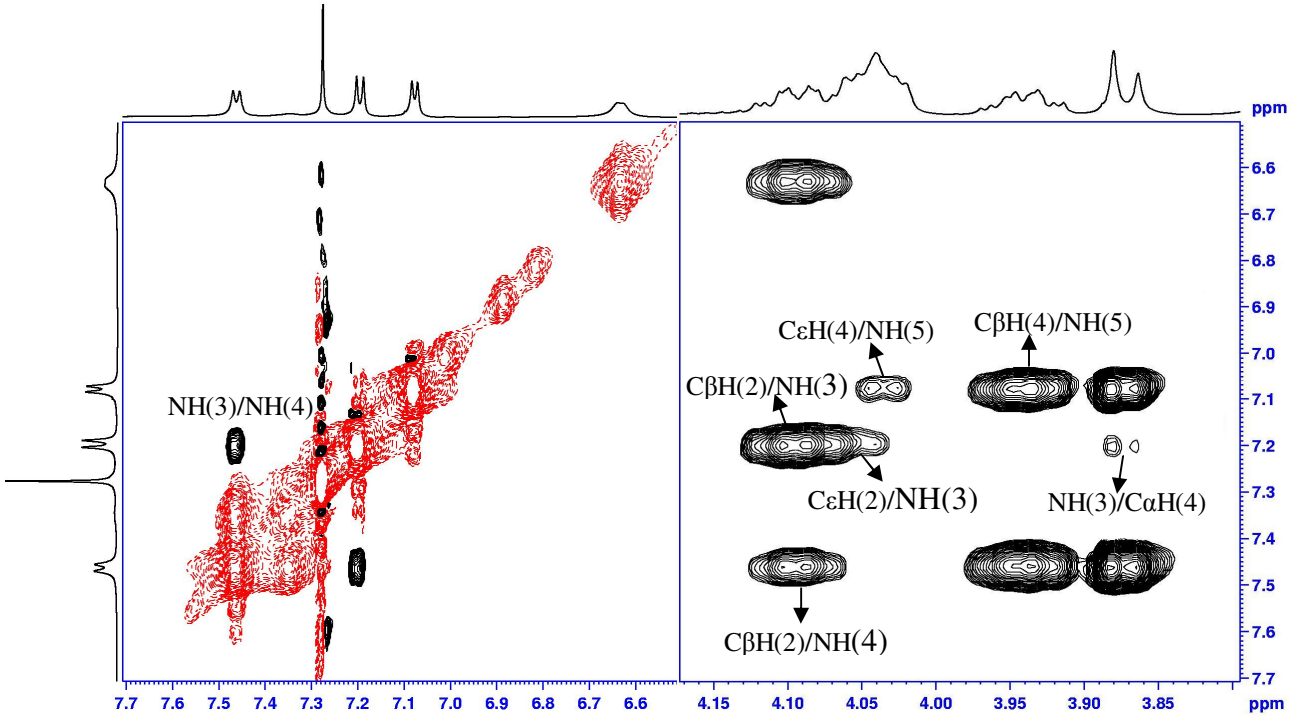
Supporting Figure 27. ^{13}C NMR spectrum of peptide 9 (150 MHz, $CDCl_3$).



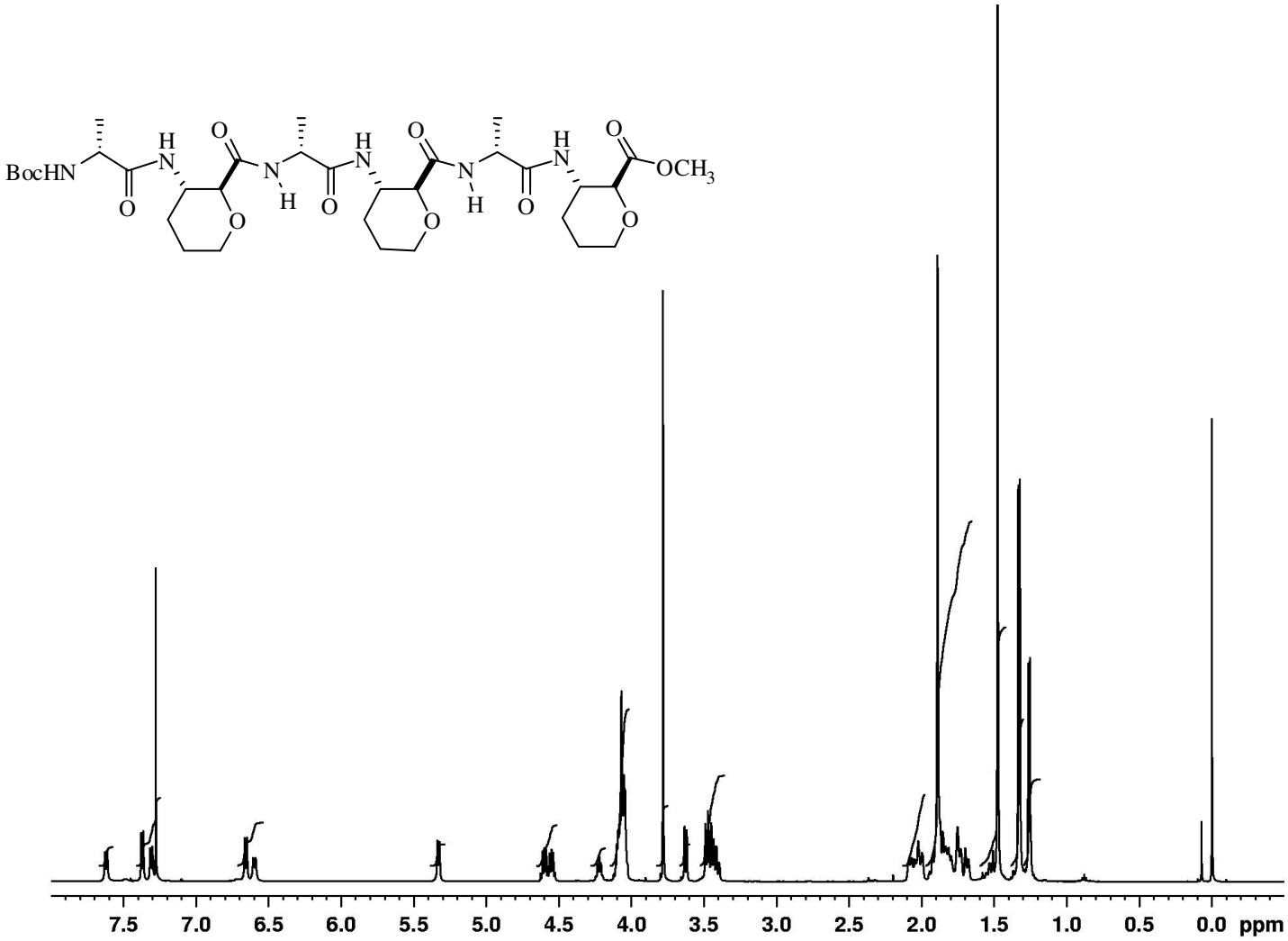
Supporting Figure 28. TOCSY spectrum of peptide 9 (600 MHz, $CDCl_3$, 278 K).



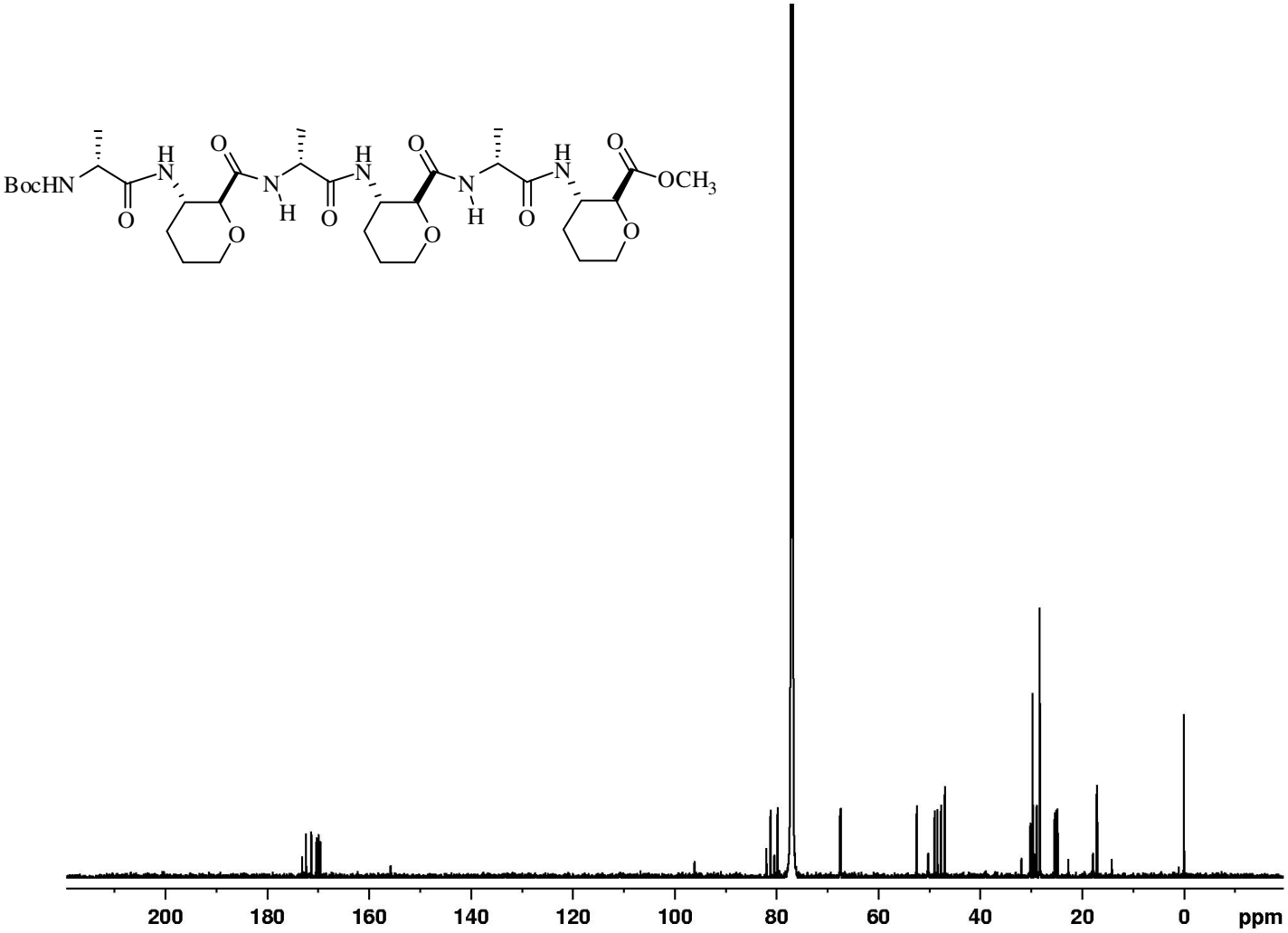
Supporting Figure 29. ROESY spectrum of peptide 9 (600 MHz, $CDCl_3$, 278 K).



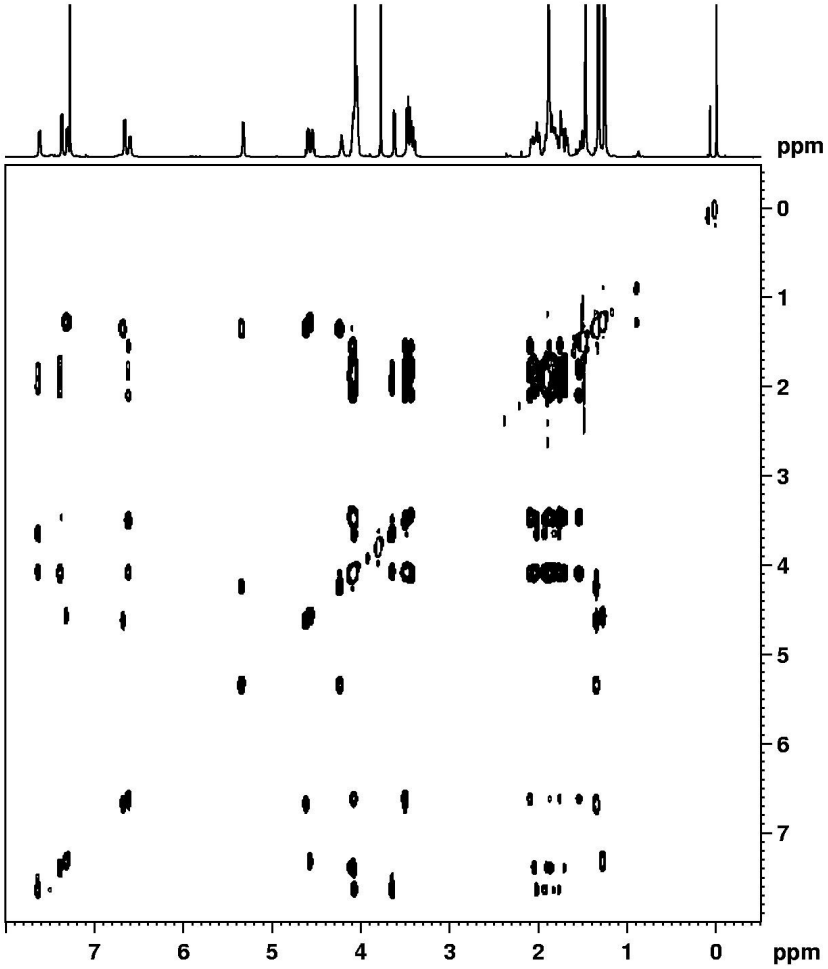
Supporting Figure 30. Expanded ROESY spectrum of peptide 9



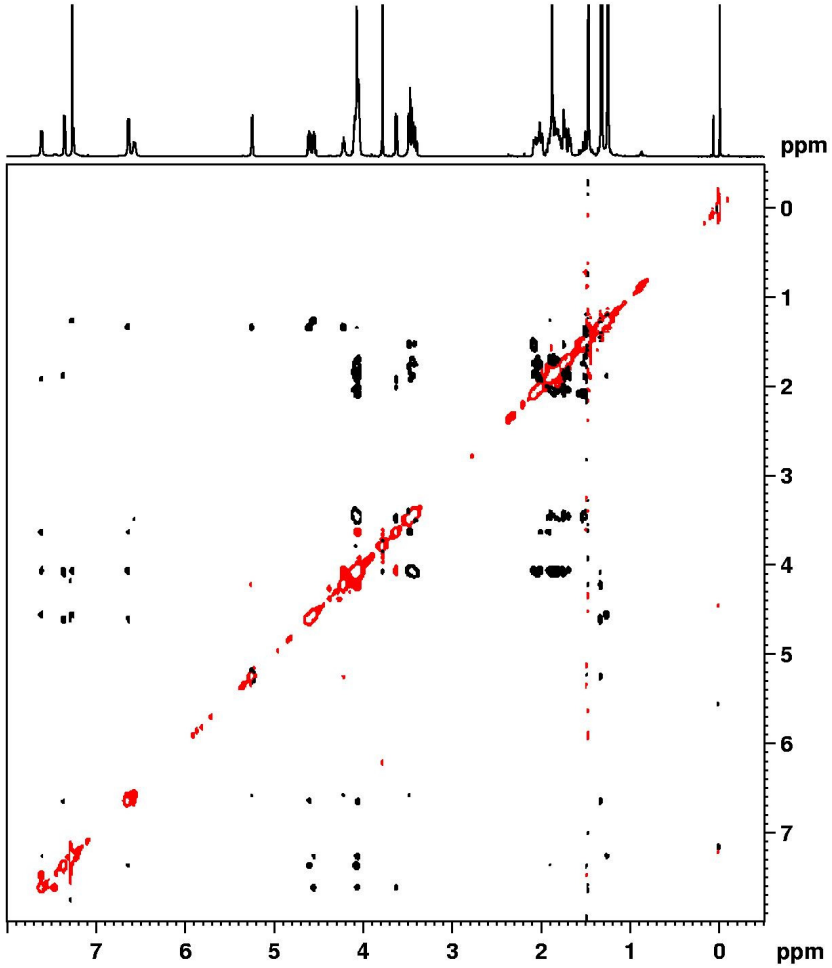
Supporting Figure 31. ^{1}H NMR spectrum of peptide 10 (600 MHz, $CDCl_3$, 278 K).



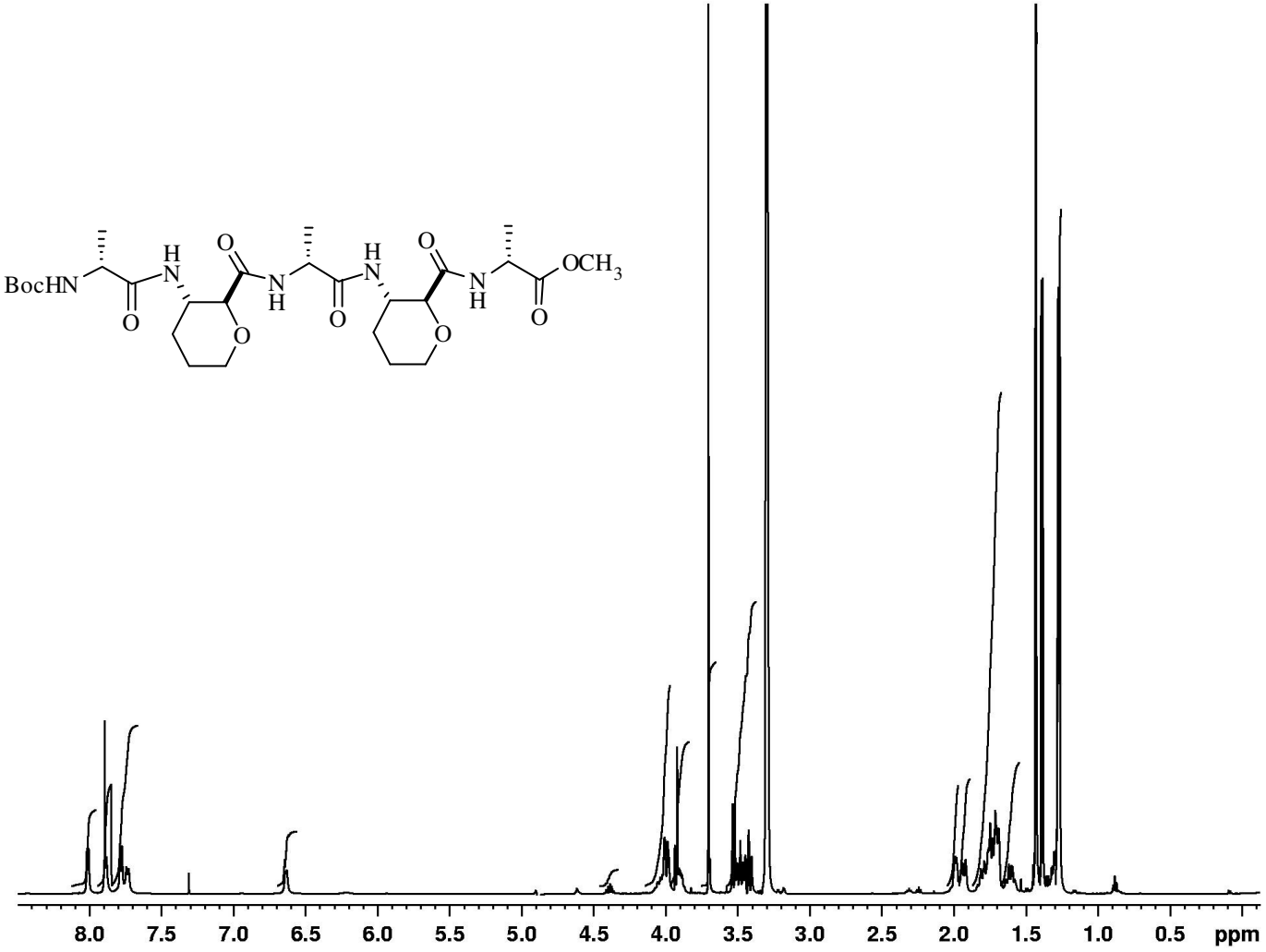
Supporting Figure 32. ^{13}C NMR spectrum of peptide 10 (150 MHz, $CDCl_3$).



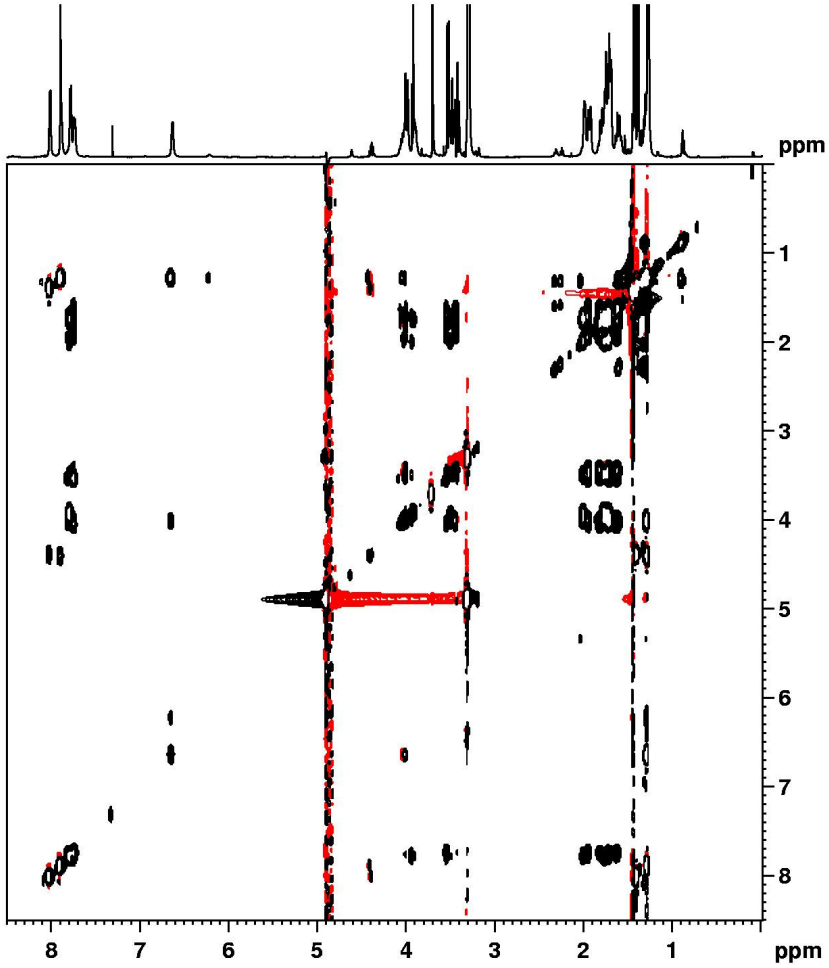
Supporting Figure 33. TOCSY spectrum of peptide 10 (600 MHz, $CDCl_3$, 278 K).



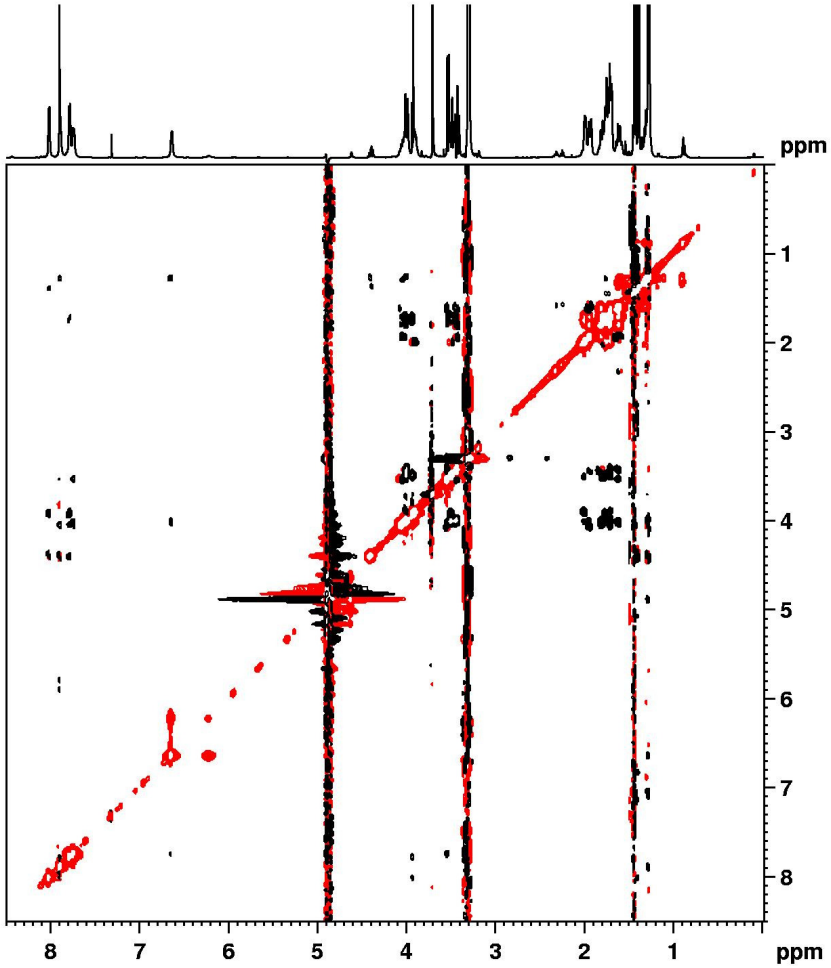
Supporting Figure 34. ROESY spectrum of peptide 10 (600 MHz, $CDCl_3$, 278 K).



Supporting Figure 35. ^{1}H NMR spectrum of peptide 9 (600 MHz, CD_3OH, 298 K).



Supporting Figure 36. TOCSY spectrum of peptide 9 (600 MHz, CD_3OH, 298 K).



Supporting Figure 37. ROESY spectrum of peptide 9 (600 MHz, CD_3OH, 298 K)

Molecular dynamics (MD) studies: Model building and molecular dynamics simulations were carried out using Insight II (97.0) / Discover1 program on a Silicon Graphics Octane and Fuel workstations using IRIX64 (6.5) operating system. The cvff force field with default parameters was used throughout the simulations. The initial minimizations were done with constraints, first with steepest decent, followed by conjugate gradient methods for a maximum of 1000 iterations each or RMS deviation of 0.001 kcal/mol, whichever was earlier. The energy-minimized structures were then subjected to MD simulations. The inter-atomic distances were obtained from the volume integrals of the ROESY spectra using two-spin approximation and the distance between the geminal protons at CεH of 1.80 Å. The upper and lower bound of the distance constraints have been obtained by enhancing and reducing the derived distance by 10%. The distance constraints were used as restraints in the MD runs. For MD runs, a temperature of 300 K was used. The molecules were initially equilibrated for 50 ps and subsequently subjected to a 1 ns dynamics with a step size of 1 fs, sampling the trajectory at equal intervals of 10 ps. In this trajectory, 100 samples were generated and were again energy minimized without constraints, by using the above-mentioned protocol. Twenty of the lowest energy structures were selected to superimpose for display.

Supporting Table 1: Distance constraints used in MD calculations for peptide 4, derived from ROESY experiment in $CDCl_3$.

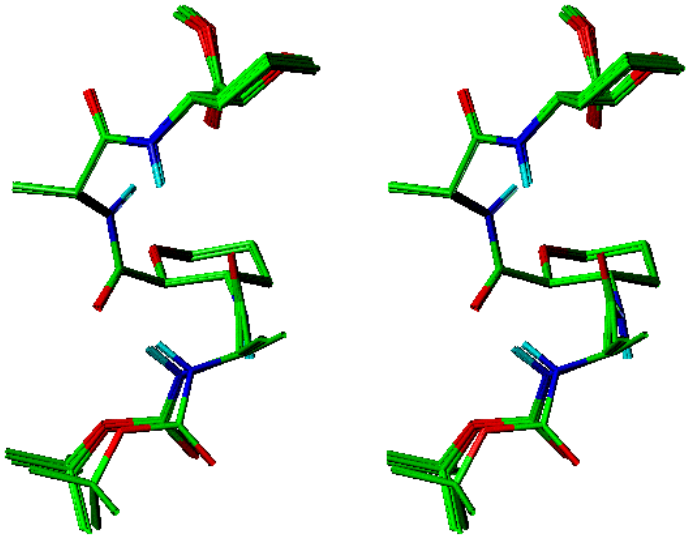
RESIDUE	ATOM	RESIDUE	ATOM	UPPERBOND	LOWERBOND
1	NH	1	CαH	2.62	2.14
1	NH	1	Cγ'H	2.94	2.41
1	CβH	2	NH	3.39	2.78
1	CβH	3	NH	3.55	2.90
1	CεH	2	NH	4.32	3.53
2	NH	3	NH	3.43	2.81
2	NH	3	CαH	4.62	3.78
2	NH	4	CαH	5.33	4.36
2	CαH	3	NH	3.01	2.46
3	NH	3	CαH	3.05	2.50
3	NH	3	Cγ'H	3.44	2.82
3	CβH	4	NH	3.31	2.71
3	CεH	4	NH	4.41	3.61

Supporting Table 2: Distance constraints used in MD calculations for peptide 6, derived from ROESY experiment in $CDCl_3$.

RESIDUE	PROTON	RESIDUE	PROTON	UPPERBOND	LOWERBOND
1	NH	1	CαH	3.24	2.65
1	NH	1	Cγ'H	3.00	2.46
1	CβH	2	NH	3.11	2.54
1	CβH	3	NH	3.50	2.87
1	CβH	3	CαH	2.87	2.35
1	CεH	2	NH	4.24	3.47
2	NH	3	CαH	3.76	3.08
2	NH	3	NH	3.40	2.78
2	NH	4	NH	4.34	3.55
2	CαH	3	NH	2.83	2.31
3	NH	3	CαH	2.91	2.38
3	NH	3	Cγ'H	3.83	3.13
3	CβH	4	NH	3.00	2.45
3	CβH	5	NH	3.22	2.64
3	CβH	5	CαH	3.52	2.88
3	CεH	4	NH	3.97	3.24
4	NH	5	CαH	3.83	3.13
4	NH	5	NH	3.30	2.70
4	CαH	5	NH	2.88	2.35
5	NH	5	CαH	2.82	2.31
5	NH	5	Cγ'H	3.08	2.52
5	CβH	6	NH	2.89	2.36
5	CεH	6	NH	4.22	3.45

Supporting Table 3: Distance constraints used in MD calculations for peptide 8, derived from ROESY experiment in $CDCl_3$.

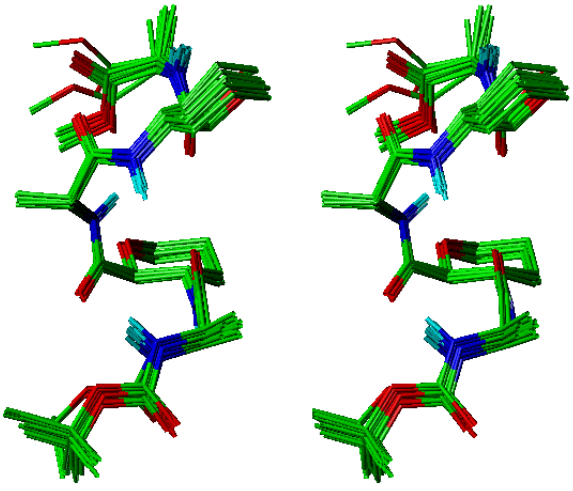
RESIDUE	ATOM	RESIDUE	ATOM	UPPERBOND	LOWERBOND
1	NH	2	NH	3.48	2.85
1	NH	2	CαH	5.01	4.10
1	CαH	2	NH	3.11	2.55
2	NH	2	CαH	3.19	2.61
2	NH	2	Cγ'H	3.31	2.71
2	CαH	3	NH	3.52	2.88
2	CβH	3	NH	3.32	2.71
2	CβH	4	NH	3.59	2.94
2	CεH	3	NH	4.14	3.39
3	NH	4	NH	3.54	2.90
3	NH	4	CαH	4.24	3.47
3	CαH	4	NH	3.02	2.47
4	NH	4	CαH	2.81	2.30
4	NH	4	Cγ'H	3.87	3.17



Supporting Figure 38. Stereo view of twenty superimposed structures of peptide 8 (hydrogens are removed for clarity)

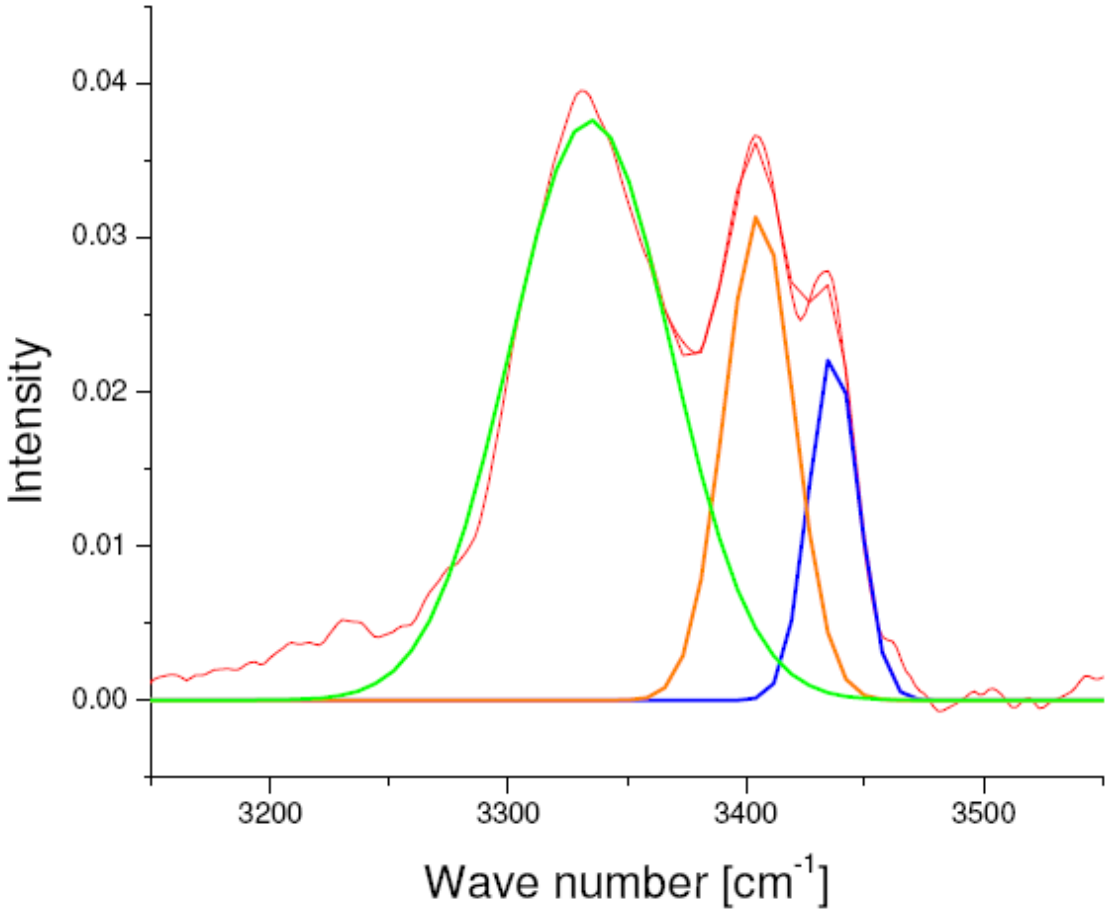
Supporting Table 4: Distance constraints used in MD calculations for peptide 9, derived from ROESY experiment in $CDCl_3$

RESIDUE	ATOM	RESIDUE	ATOM	UPPERBOND	LOWERBOND
1	NH	2	NH	4.15	3.39
1	NH	2	CαH	5.01	4.10
1	CαH	2	NH	3.54	2.90
2	NH	2	CαH	3.67	3.00
2	NH	2	Cγ'H	3.31	2.71
2	CβH	3	NH	3.26	2.66
2	CβH	4	NH	3.76	3.08
2	CβH	4	CαH	4.15	3.39
2	CεH	3	NH	4.48	3.66
3	NH	4	NH	3.61	2.96
3	NH	4	NH	4.15	3.39
3	CαH	4	NH	3.02	2.47
4	NH	4	CαH	2.81	2.30
4	NH	4	Cγ'H	3.87	3.17
4	CβH	5	NH	3.28	2.69
4	CεH	5	NH	4.49	3.68

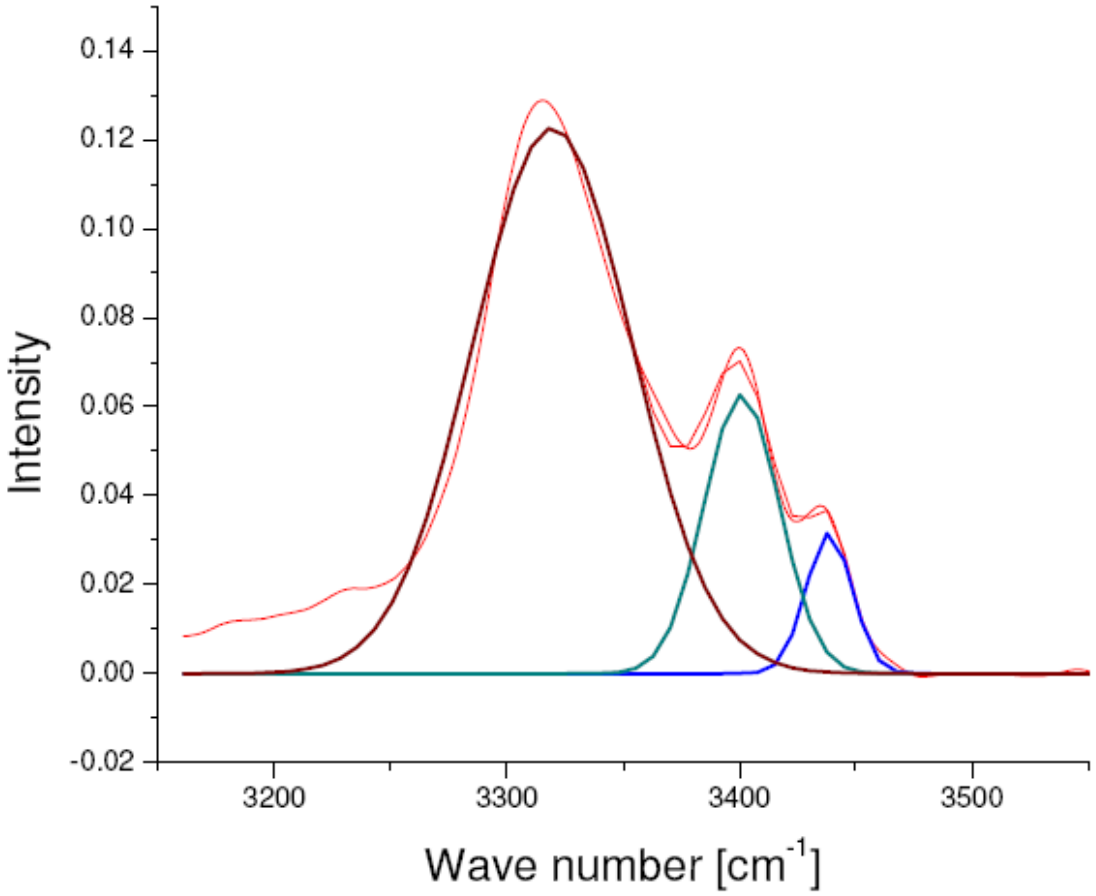


Supporting Figure 39. Stereo view of twenty superimposed structures of peptide 9 (hydrogens are removed for clarity)

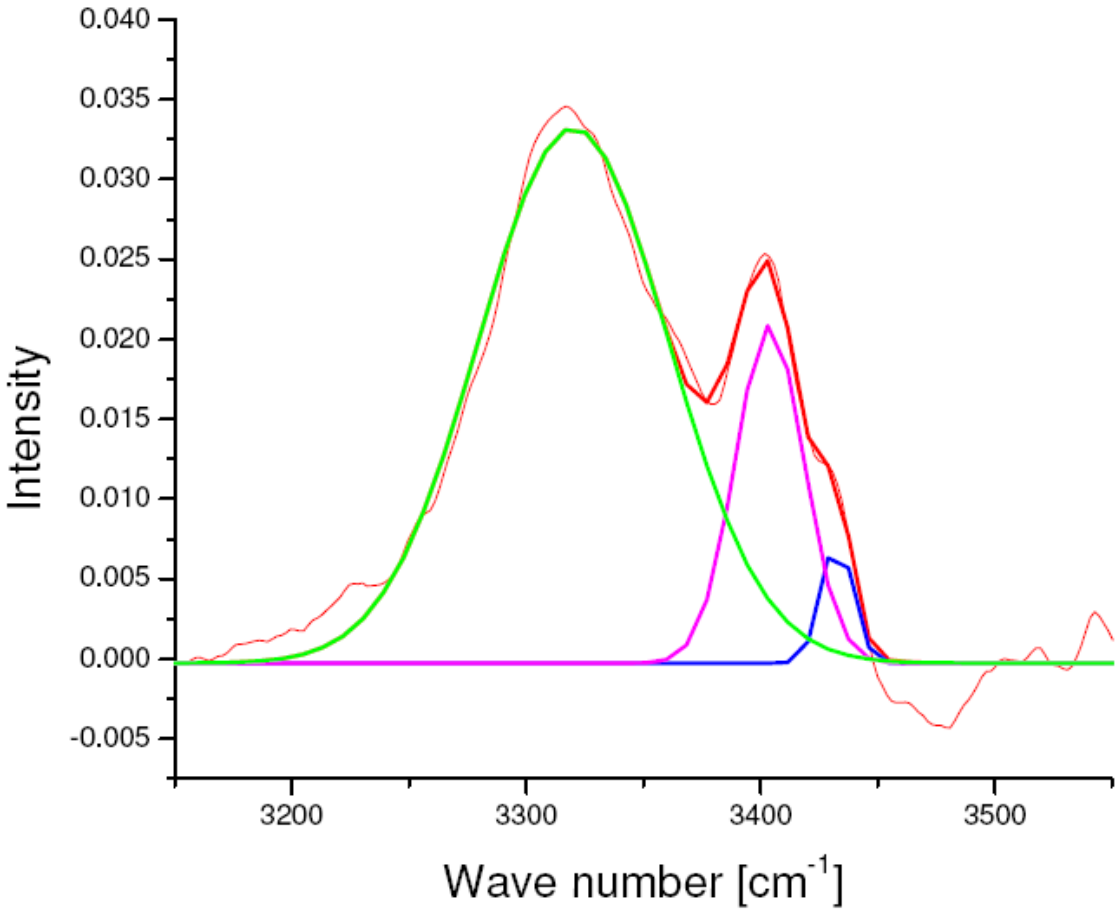
IR STUDIES



Supporting Figure 40: Deconvoluted IR spectrum of peptide 4



Supporting Figure 41: Deconvoluted IR spectrum of peptide 5



Supporting Figure 42: Deconvoluted IR spectrum of peptide 6