Suplementary information

4-Methylpseudoproline derived from α-methylserine – synthesis and conformational studies

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Figure S10. Packing diagram with hydrogen bonds indicated with dashed lines.

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Table S2 Intra- and Intermolecular Hydrogen Bond Parameters for the Fmoc-Ala-(*R*)-(αMeSer)(ΨPro)-Ala-OBu^t **(6a).** Distances and angles are in (Å) and (^{o}), respectively.

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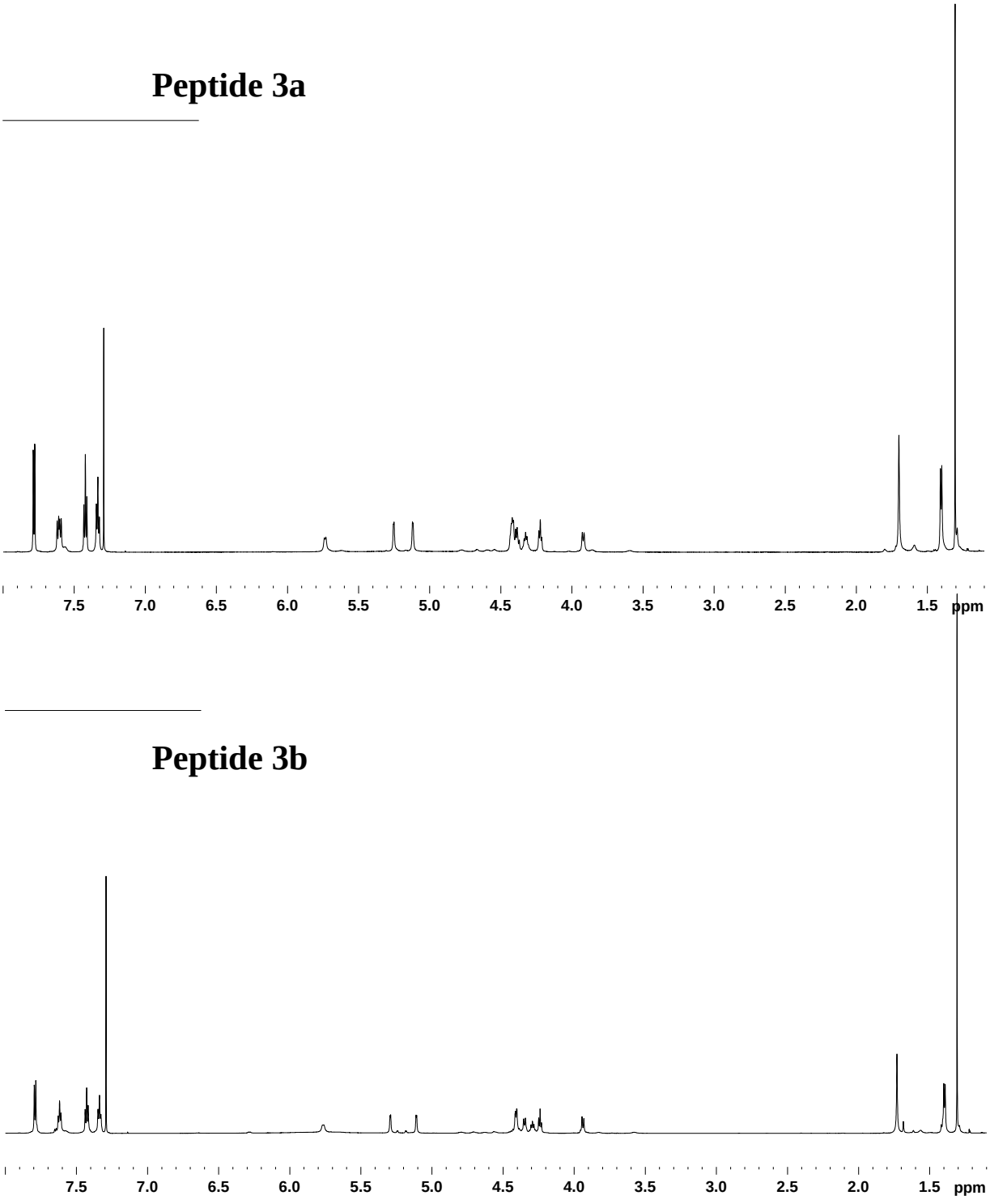

Figure S1. ^{1}H NMR spectra of dipeptides **3a** and **3b** recorded in $CDCl_3$ at 700 MHz.

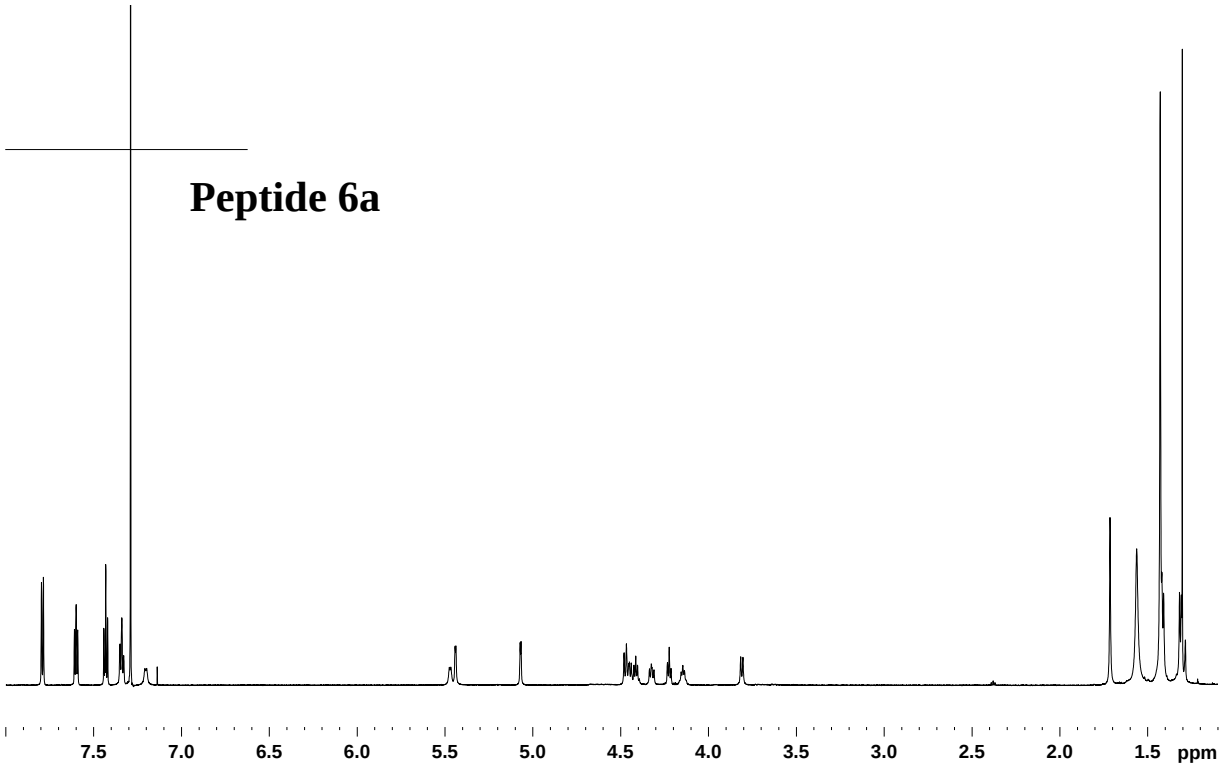

Figure S2. ^{1}H NMR spectrum of tripeptide **6a** recorded in $CDCl_3$ at 700 MHz.

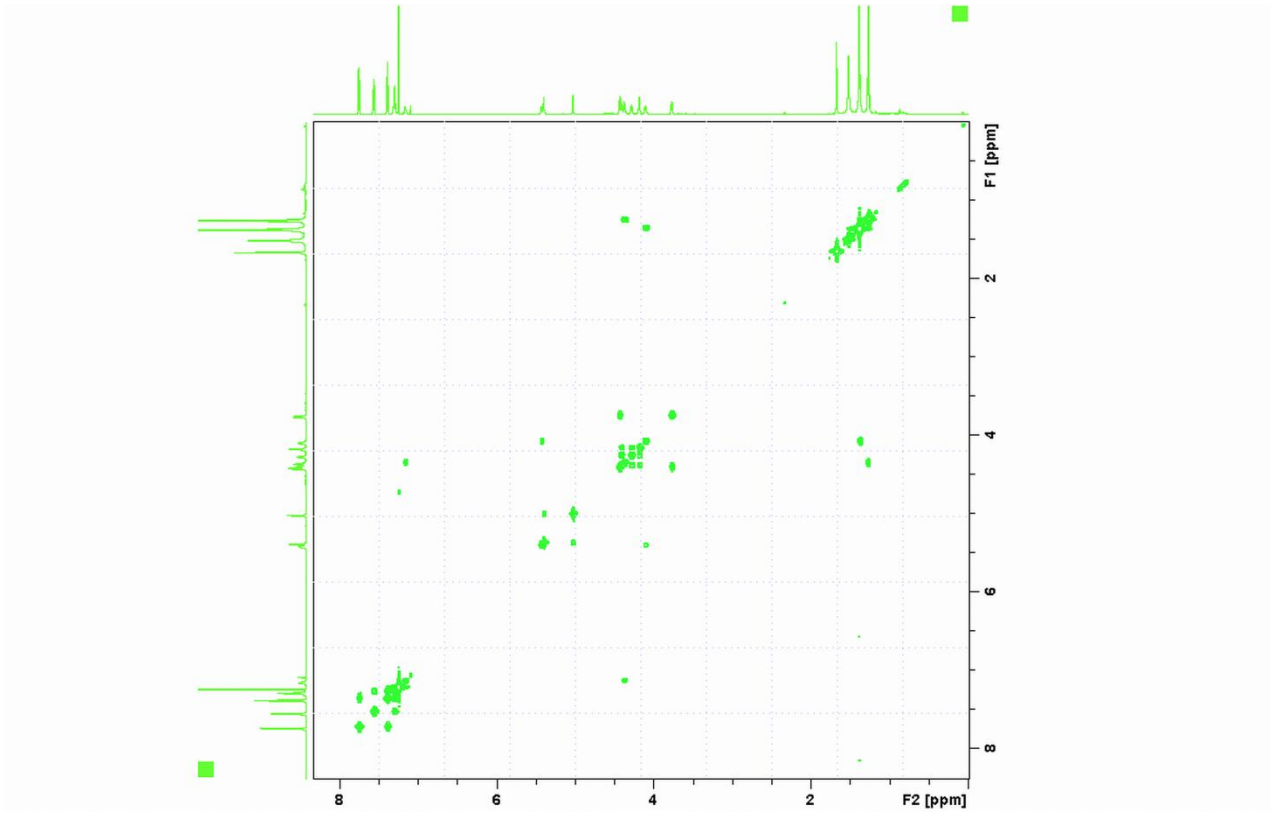

Figure S3. COSY spectrum of peptide **6a** in $CDCl_3$ (700 MHz).

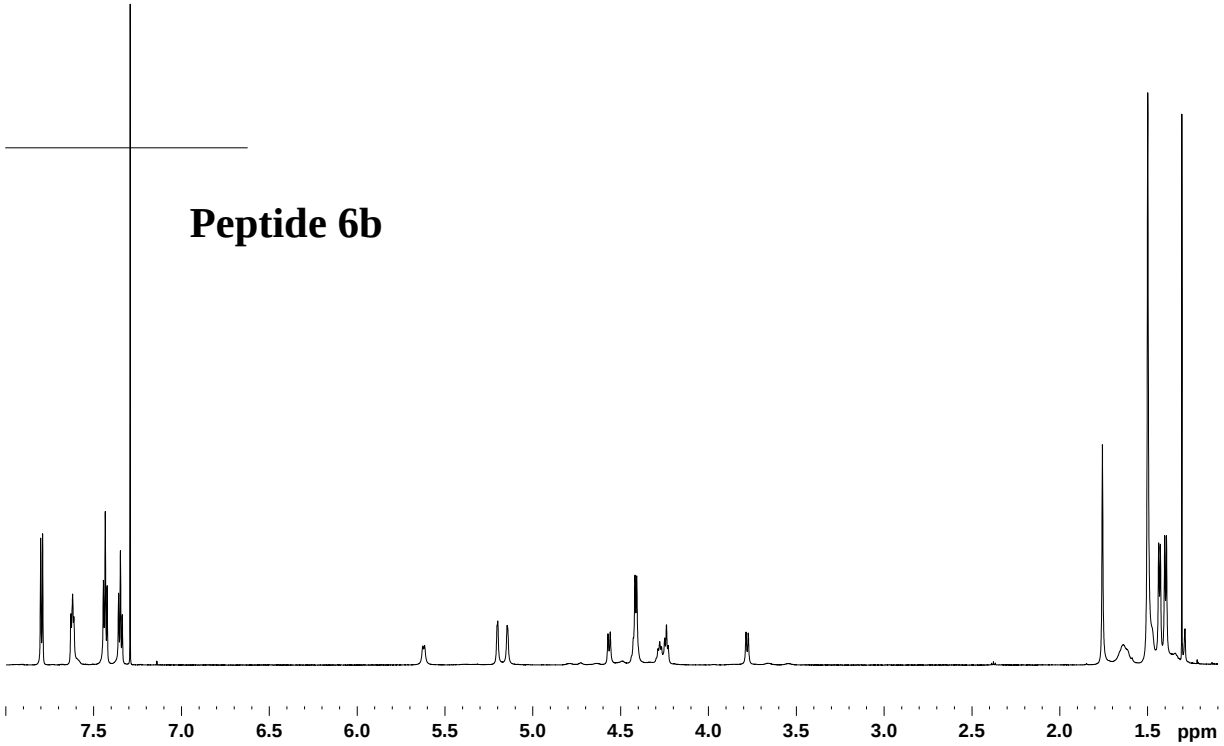

Figure S4. ^{1}H NMR spectrum of tripeptide **6b** recorded in $CDCl_3$ at 700 MHz.

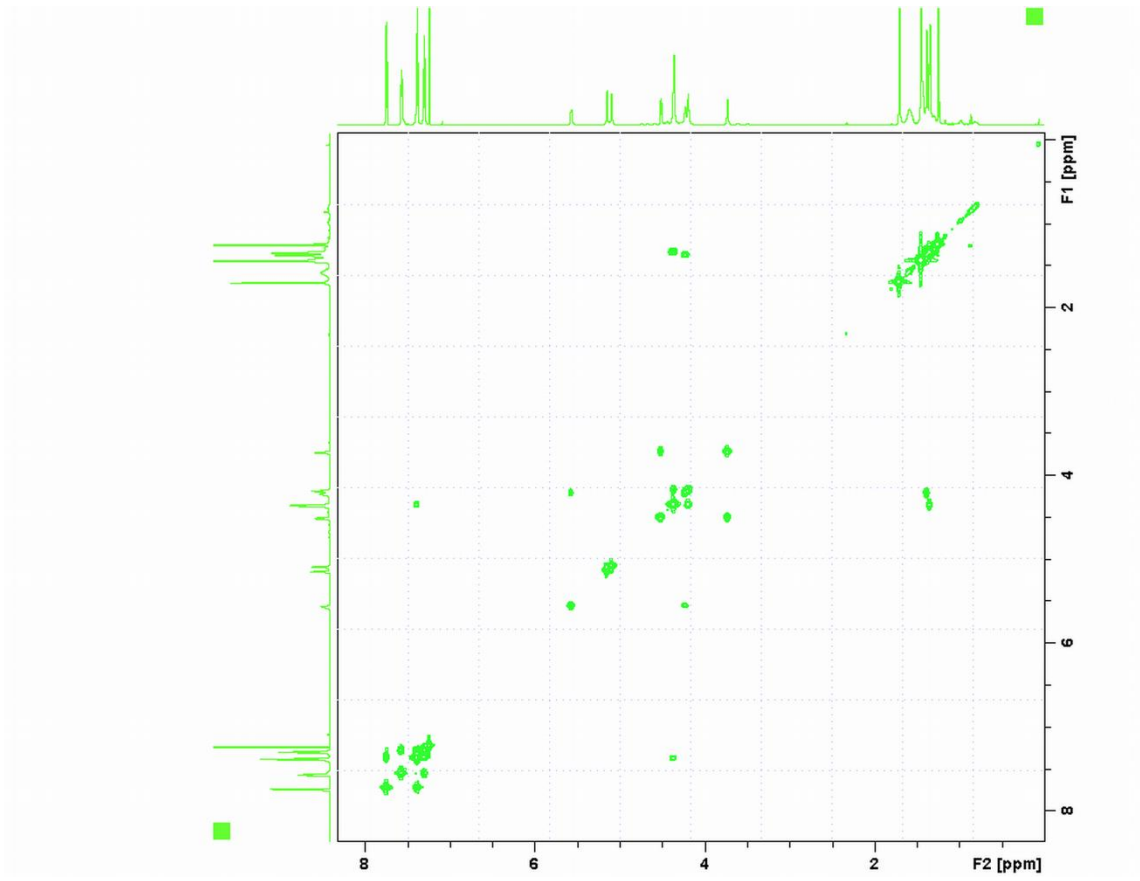

Figure S5. COSY spectrum of peptide **6b** in $CDCl_3$ (700 MHz).

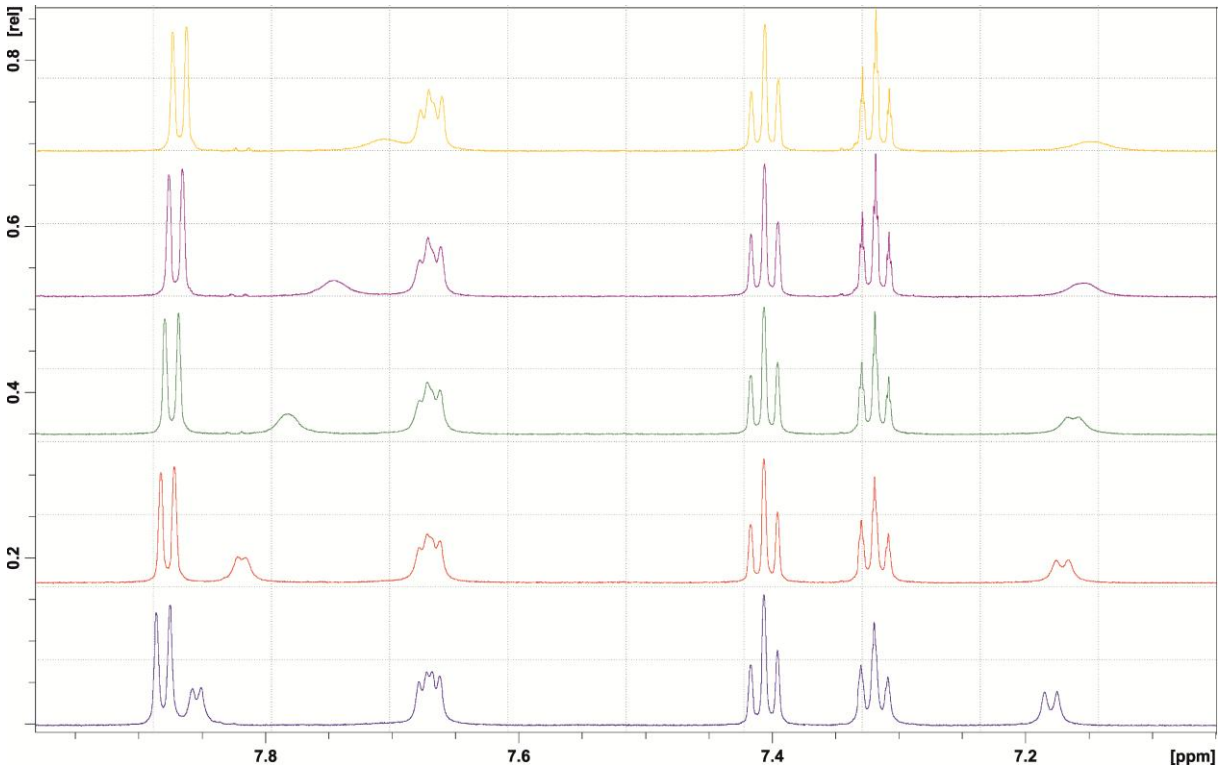

Figure S6. Temperature effect on NH chemical shifts for peptide **6a**. Spectra were recorded at 5 K intervals from 300 K (bottom) to 320 K (top).

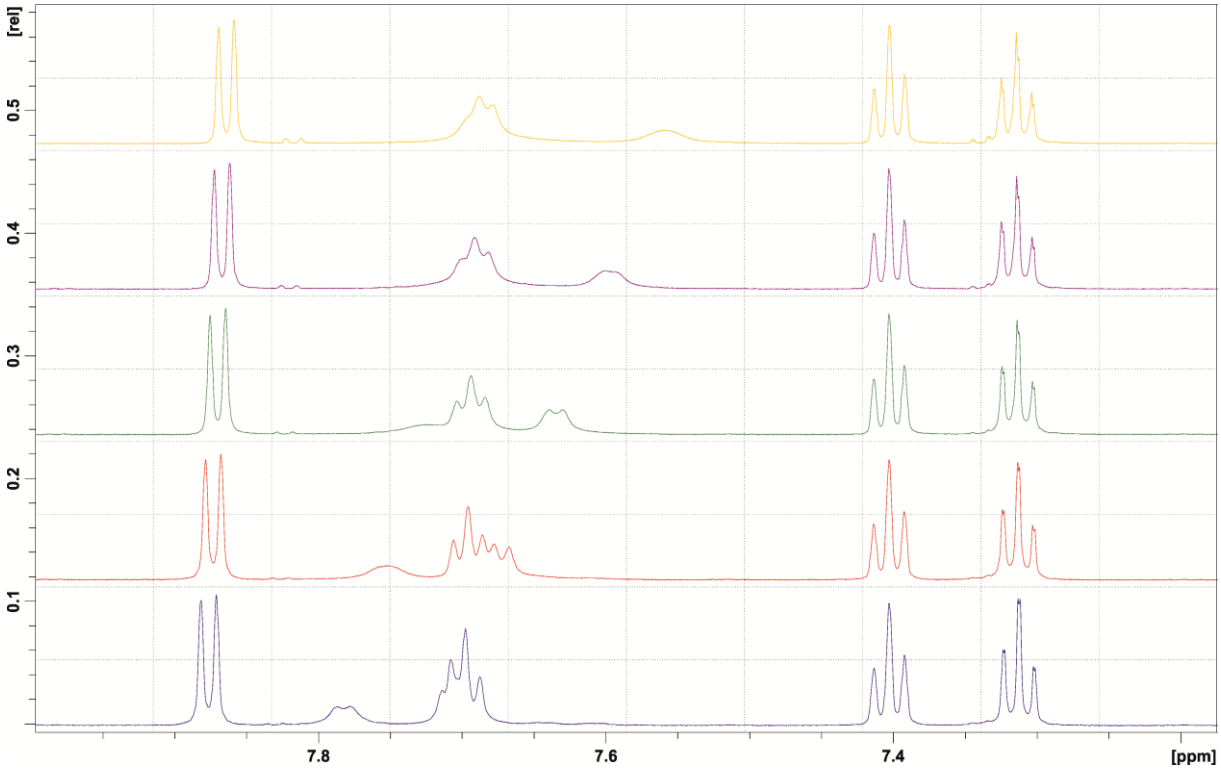

Figure S7. Temperature effect on NH chemical shifts for peptide **6b**. Spectra were recorded at 5K intervals from 300 K (bottom) to 320 K (bottom).

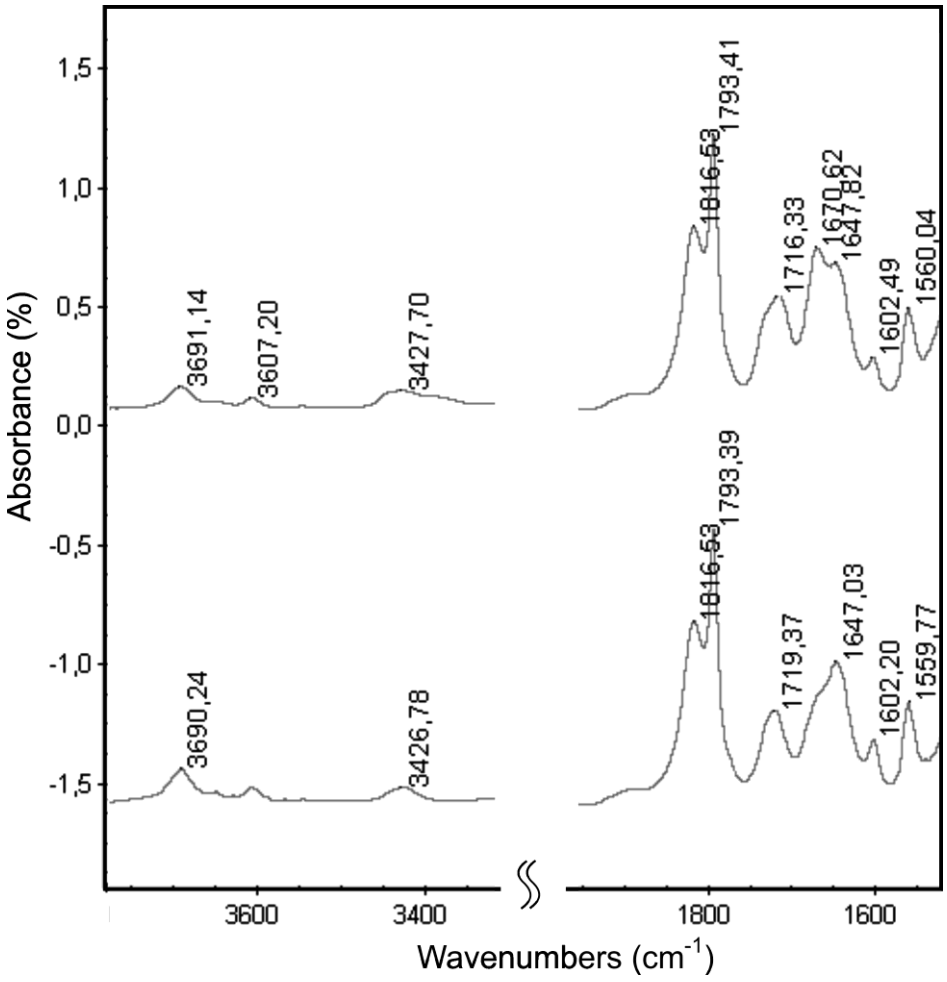

Figure S8. FTIR absorption spectra in the NH stretching region (3600 – 3300 cm^{-1}) and in the CO stretching region (1850 – 1600 cm-1) for 2 mM samples of **6a** (top) and **6b** (bottom) in $CDCl_3$.

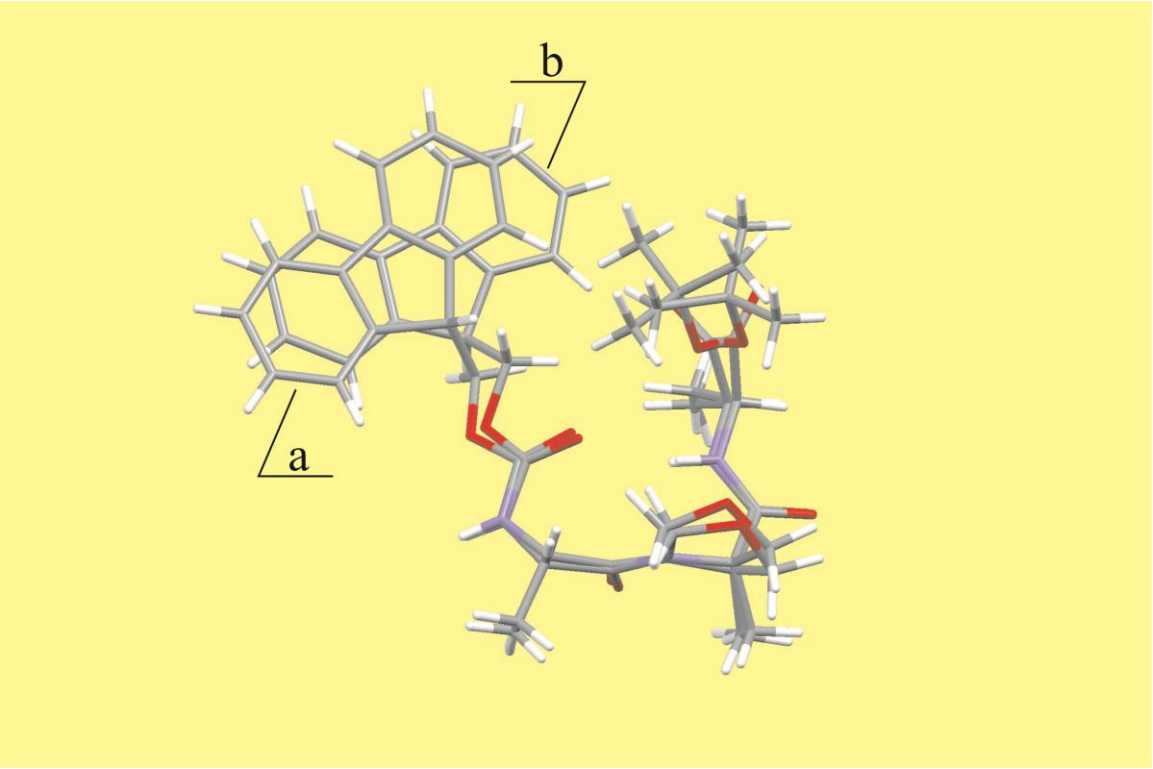

Figure S9. Superposition of the two symmetrically independent molecules **a** and **b** of the Fmoc-Ala-(*R*)-αMeSer(ΨPro)-Ala-OBu^t **(6a)**. Only distances between the respective main chain atoms were minimized. The root mean square displacement of the fit was 0.19 Å.

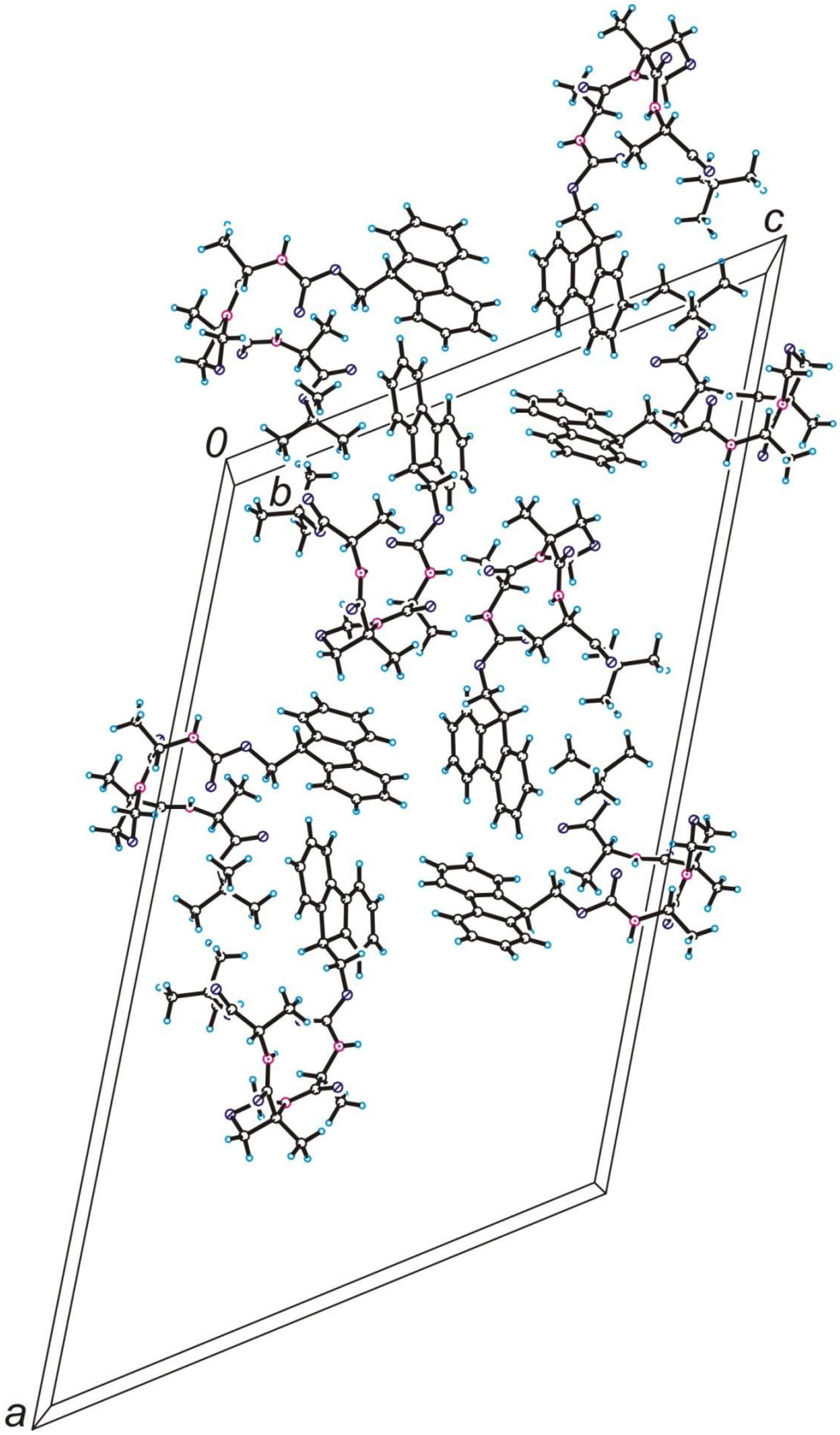

Figure S10. Packing diagram of Fmoc-Ala-(*R*)-αMeSer(ΨPro)-Ala-OBu^t **(6a)** with hydrogen bonds indicated with dashed lines.

Table S1. Main chain torsion angles (°) defining the peptide conformation of the two symmetrically independent molecules **a** (first entry) and **b** (second entry) of Fmoc-Ala-(*R*)-(αMe)Ser(ΨPro)-Ala-OBu^t **(6a)**.

ϕ(1)	C(15)-N(1)-C(16)-C(18)	-57.4(3)
	C(45)-N(4)-C(46)-C(48)	-58.8(3)
ψ(1)	N(1)-C(16)-C(18)-N(2)	139.5(2)
	N(4)-C(46)-C(48)-N(5)	129.1(2)
ω(1)	O(1)-C(15)-N(1)-C(16)	179.0(3)
	O(8)-C(45)-N(4)-C(46)	-179.6(3)
ϕ(2)	C(18)-N(2)-C(21)-C(23)	78.8(3)
	C(48)-N(5)-C(51)-C(53)	69.6(3)
ψ(2)	N(2)-C(21)-C(23)-N(3)	1.4(3)
	N(5)-C(51)-C(53)-N(6)	10.4(3)
ω(2)	C(16)-C(18)-N(2)-C(21)	176.0(2)
	C(46)-C(48)-N(5)-C(51)	178.2(2)
ϕ(3)	C(23)-N(3)-C(24)-C(26)	-124.5(3)
	C(53)-N(6)-C(54)-C(56)	-131.9(3)
ψ(3)	N(3)-C(24)-C(26)-O(6)	-16.8(4)
	N(6)-C(54)-C(56)-O(14)	59.5(3)
ω(3)	C(21)-C(23)-N(3)-C(24)	177.6(2)
	C(51)-C(53)-N(6)-C(54)	171.9(2)

Table S2 Intra- and Intermolecular Hydrogen Bond Parameters for the Fmoc-Ala-(*R*)-(αMeSer)(ΨPro)-Ala-OBu^t **(6a).** Distances and angles are in (Å) and (^{o}), respectively.

D-H···A	**D-H**	**H···A**	**D···A**	**D-H···A**	**Symmetry code**
N(1)-H(1)··· O(3)	0.88	1.96	2.841(4)	177	3/2-*x*,1/2+*y*,1-*z*
N(3)-H(31)···O(2)	0.88	2.29	3.095(4)	152	*x*,*y*,*z*
N(4)-H(4)···O(10)	0.88	2.03	2.897(4)	169	1/2-*x*,y-1/2,-*z*
N(6)-H(6)···O(9)	0.88	2.06	2.903(4)	161	*x*,*y*,*z*

Table S3 Endocyclic 1,3-oxazolidine torsion angles (°) for each symmetrically independent molecule **A** (upper section) and **B** (lower section) of Fmoc-Ala-(*R*)-αMeSer(ΨPro)-Ala-OBu^t **(6a)** accompanied by the three lowest asymmetry parameters (°).

Independent molecule	**Torsion angle (°)**	
A	O(4)-C(19)-N(2)-C(21)	4.7(3)
	C(19)-N(2)-C(21)-C(20)	18.1(3)
	N(2)-C(21)-C(20)-O(4)	-34.9(3)
	C(21)-C(20)-O(4)-C(19)	40.8(3)
	C(20)-O(4)-C(19)-N(2)	-28.1(3)
	$\Delta C_s^{C(20)}$=8.2(3) $\Delta C_2^{N(2)}$=10.6(3) $\Delta C_s^{O(4)}$=23.2(3)	
B	O(11)-C(49)-N(5)-C(51)	14.1(3)
	C(49)-N(5)-C(51)-C(50)	10.7(3)
	N(5)-C(51)-C(50)-O(11)	-32.1(3)
	C(51)-C(50)-O(11)-C(49)	43.4(3)
	C(50)-O(11)-C(49)-N(5)	-35.4(3)
	$\Delta C_2^{N(5)}$=3.3(3) $\Delta C_s^{O(11)}$=14.0(3) $\Delta C_s^{C(50)}$=23.2(3)	