Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

β-Peptides incorporating polyhydroxylated cyclohexane β-amino acid: synthesis and conformational study

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I. MATERIALS AND INSTRUMENTATION

Specific rotations were recorded on a JASCO DIP-370 optical polarimeter. Infrared spectra were recorded on a *MIDAC Prospect FT-IR PerkinElmer Spectrum Two* spectrometer. Nuclear magnetic resonance spectra were recorded on Varian Mercury 300, Bruker Avance III 500 and Bruker NEO 750 spectrometers. Mass spectra were obtained on a Kratos MS 50 TC mass spectrometer. X-ray experiments were obtained with a Bruker Appex II apparatus. Thin layer chromatography (tlc) was performed using Merck GF-254 type 60 silica gel and ethyl EtOAc/hexane mixtures as eluents; the tlc spots were visualized with a Hanessian stain (dipping into a solution of 12.5 g of $(NH_4)_4Mo_7O_{24}\cdot 4H_2O$, 5 g of $Ce(SO_4)_2\cdot 4H_2O$ and 50 mL of H_2SO_4 in 450 mL of H_2O, and warming). Column chromatography was carried out using Merck type 9385 silica gel. Solvents were purified as in ref. (Perrin, D. D.; Armarego, W. L. F. Purification of Laboratory Chemicals; Pergamon Press: New York, 1988).

II. NMR SPECTRA OF COMPOUNDS 3, 4, 5, 6, 7, 8 AND 11

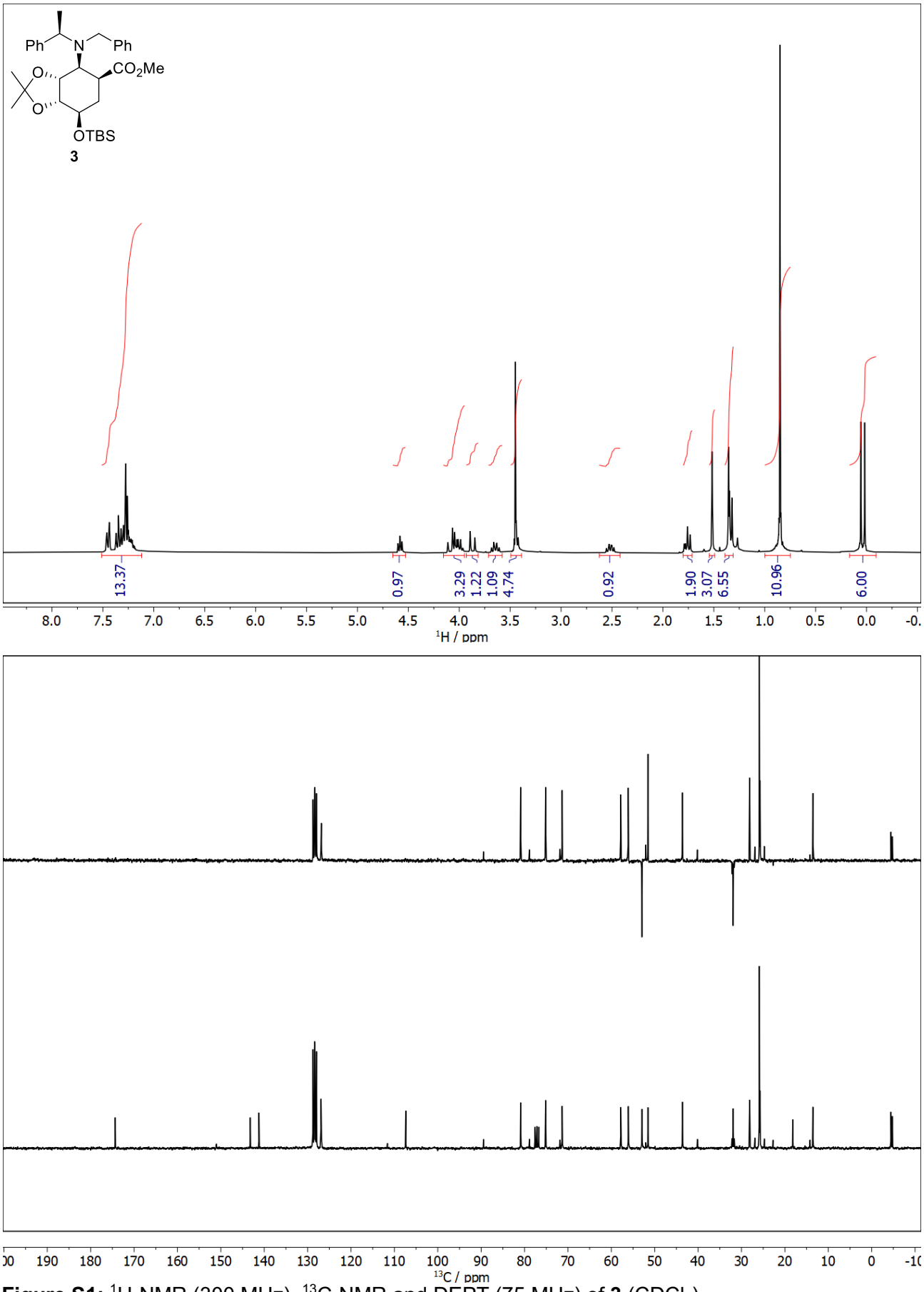


Figure S1: ^{1}H-NMR (300 MHz), ^{13}C-NMR and DEPT (75 MHz) of **3** ($CDCl_3$).

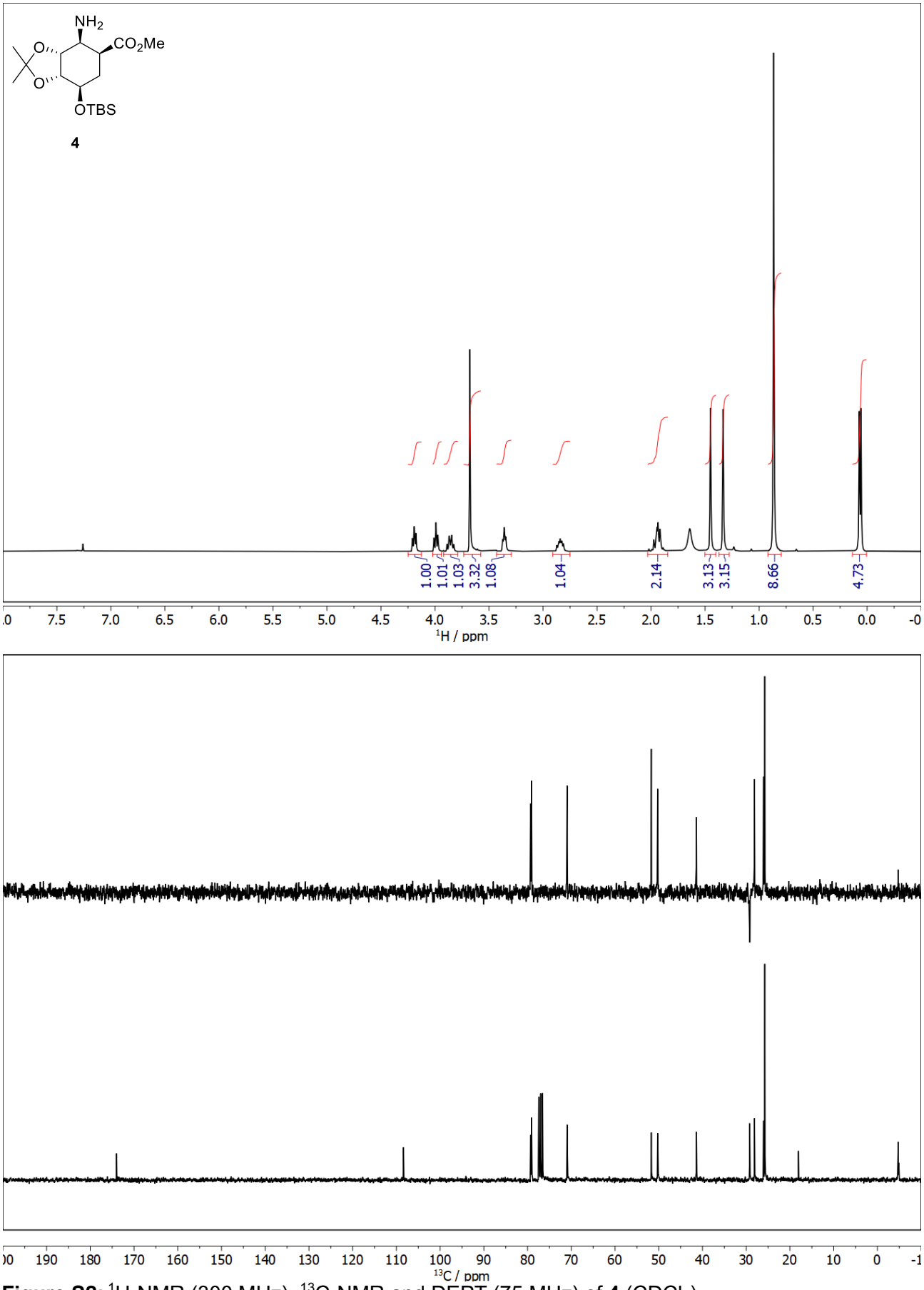


Figure S2: ^{1}H-NMR (300 MHz), ^{13}C-NMR and DEPT (75 MHz) of **4** ($CDCl_3$).

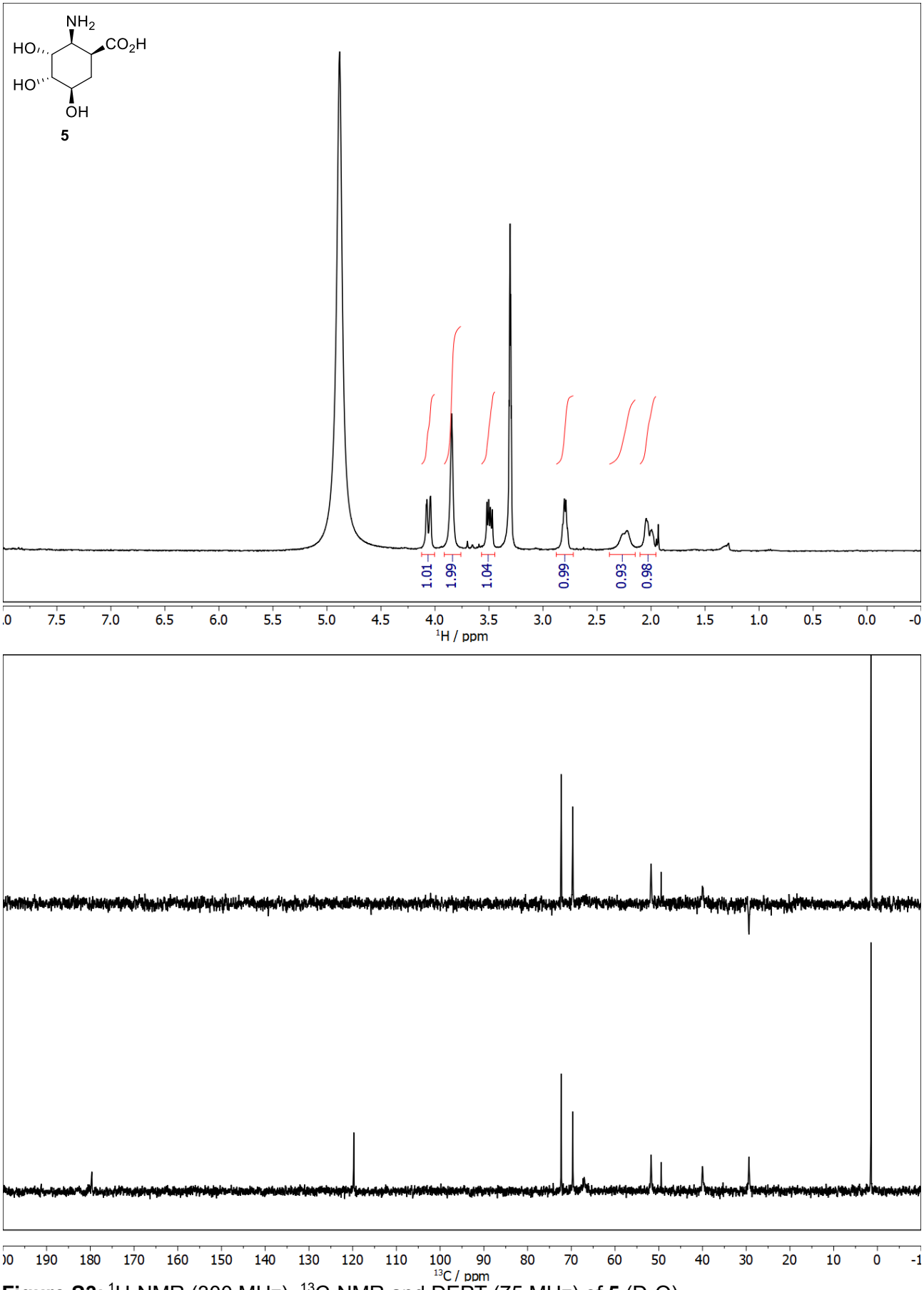


Figure S3: ^{1}H-NMR (300 MHz), ^{13}C-NMR and DEPT (75 MHz) of **5** (D_2O).

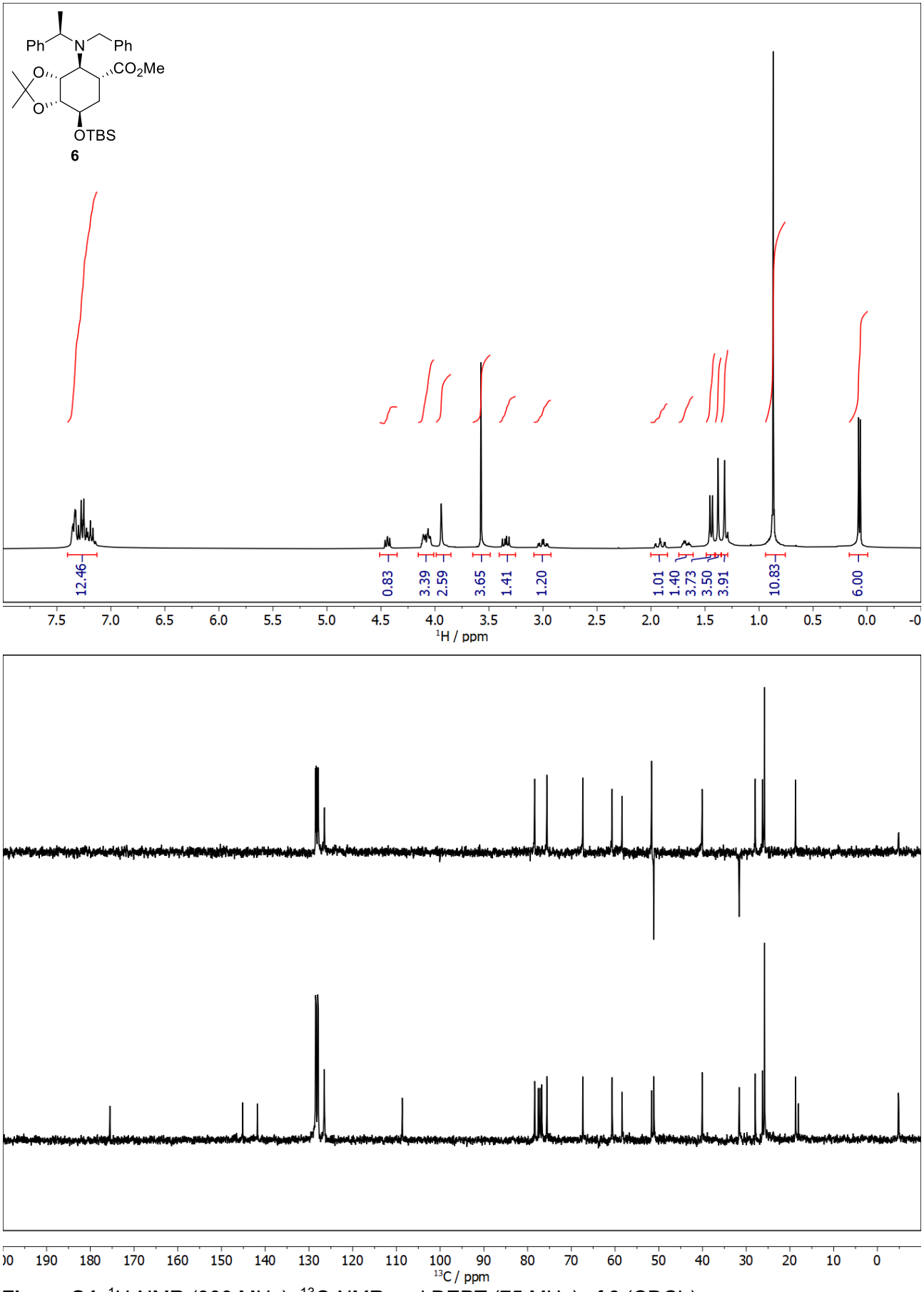


Figure S4: ^{1}H-NMR (300 MHz), ^{13}C-NMR and DEPT (75 MHz) of **6** ($CDCl_3$).

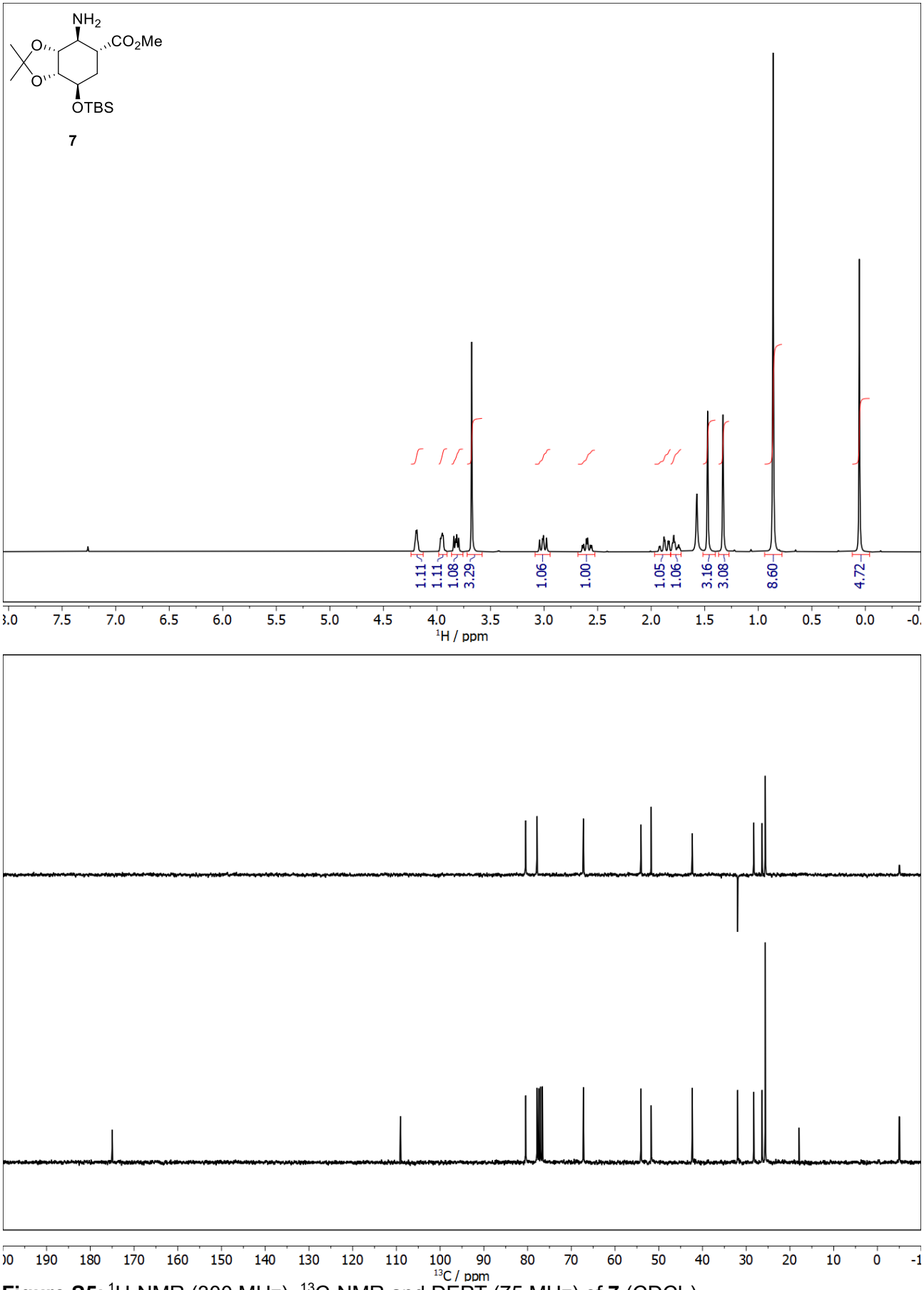


Figure S5: ^{1}H-NMR (300 MHz), ^{13}C-NMR and DEPT (75 MHz) of **7** ($CDCl_3$).

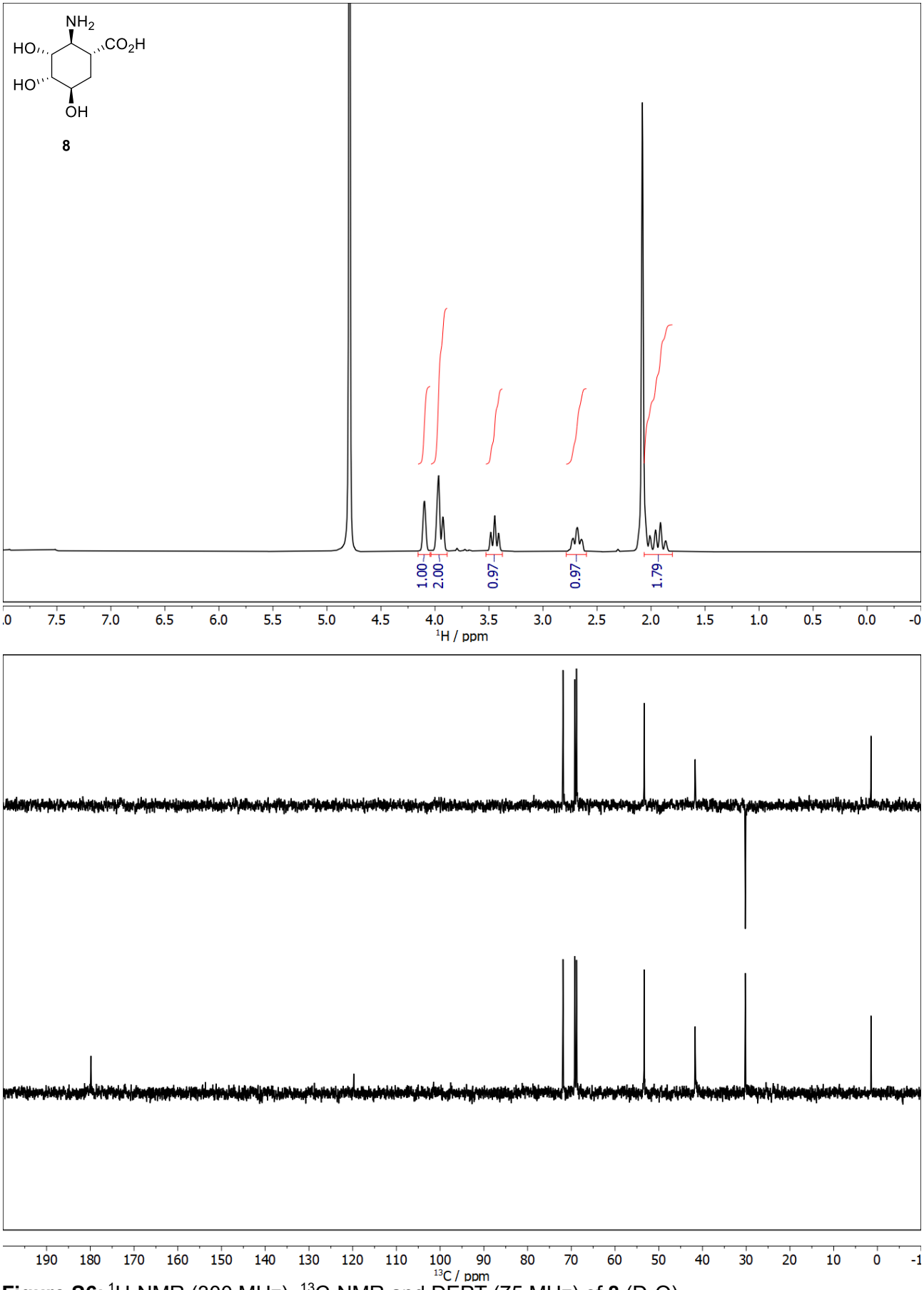


Figure S6: ^{1}H-NMR (300 MHz), ^{13}C-NMR and DEPT (75 MHz) of **8** (D_2O).

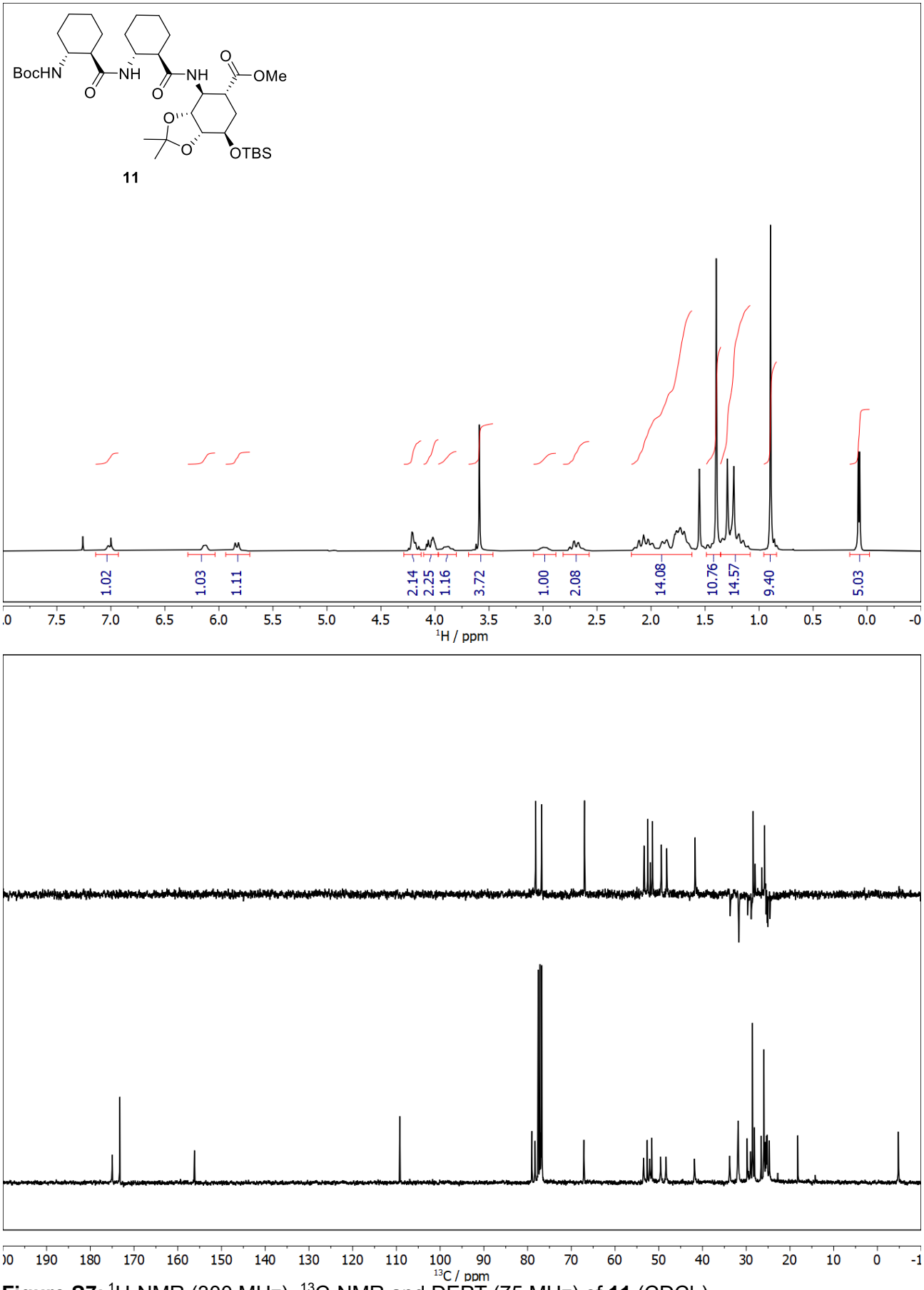


Figure S7: ^{1}H-NMR (300 MHz), ^{13}C-NMR and DEPT (75 MHz) of **11** ($CDCl_3$).

III. INFRARED SPECTROSCOPY

Table S1: Maxima (cm^{-1}) of the Amide A, Amide I, and Amide II characteristic bands for **9**, **11**, **14**, **15**, and **16**.

Compound	Amide A	Amide I	Amide II
9	3297.27	1646.47	1533.44
11	3327.38	1679.77	1527.80
14	3281.07	1644.93	1535.61
15	3369.60	1649.42	1547.16
16	3269.40	1649.50	1546.80

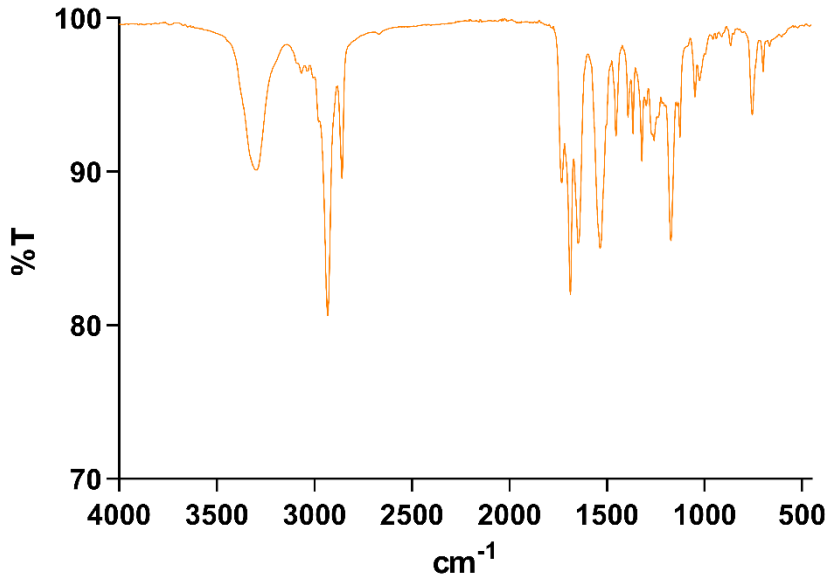


Figure S8: FTIR spectrum of **9** (Boc-*trans*-$(ACHC)_2$-OBn).

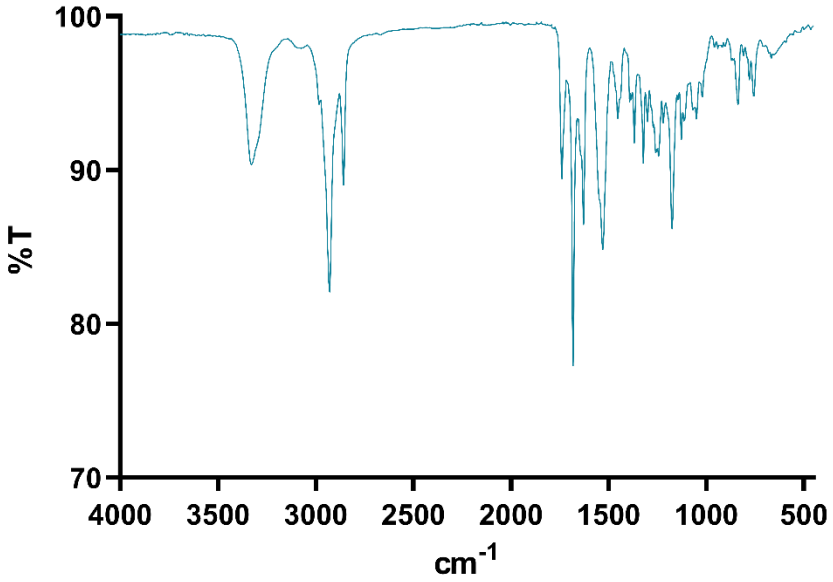


Figure S9: FTIR spectrum of **11**.

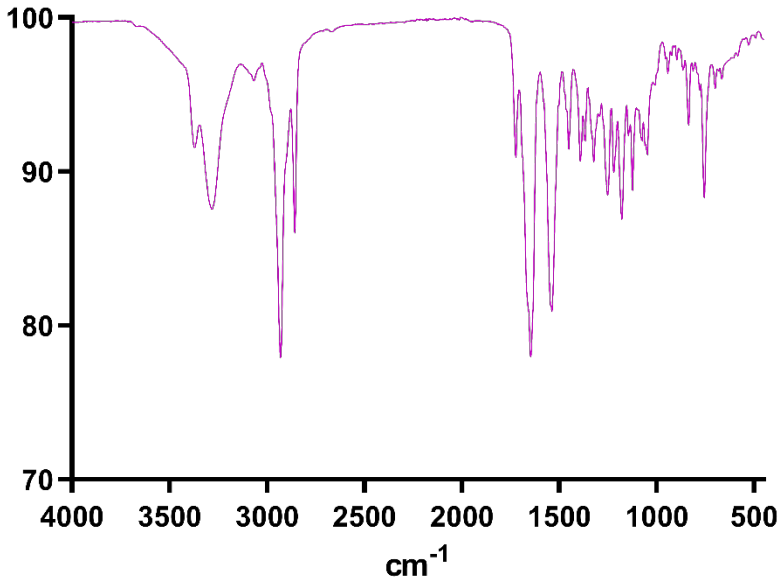


Figure S10: FTIR spectrum of **14**.

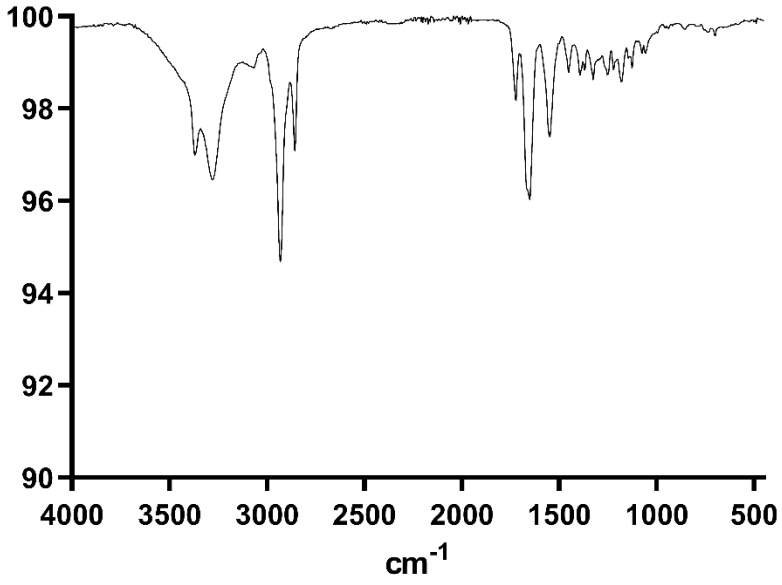


Figure S11: FTIR spectrum of **15**.

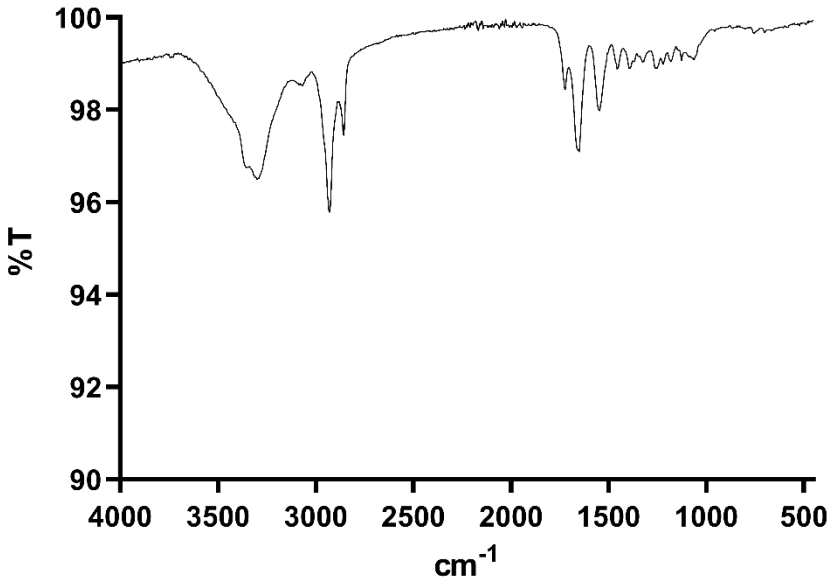


Figure S12: FTIR spectrum of **16**.

IV. CIRCULAR DICHROISM

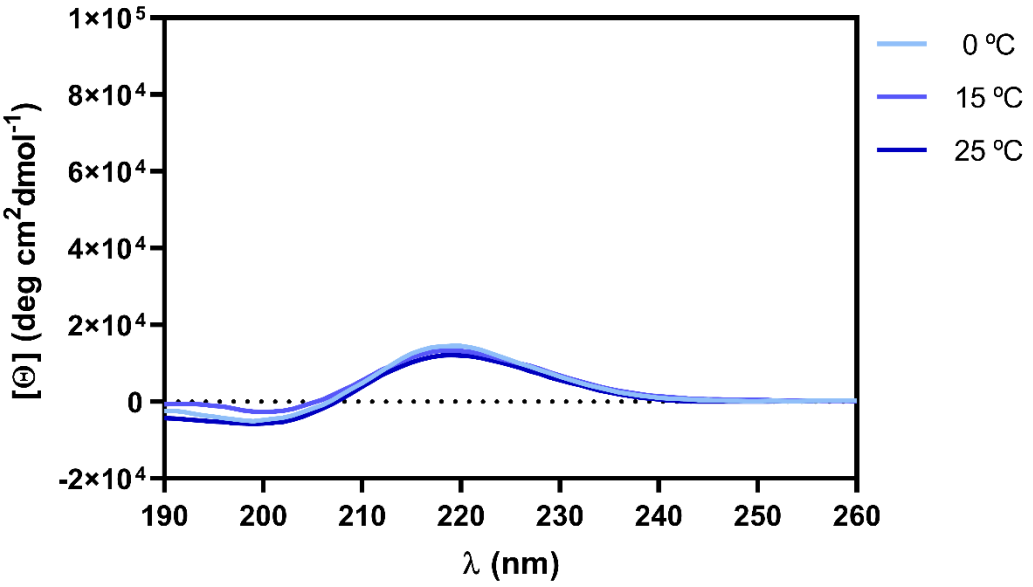


Figure S13: Circular dichroism data for **9** in methanol (c = 1 mM; T = 0, 15 and 25 °C).

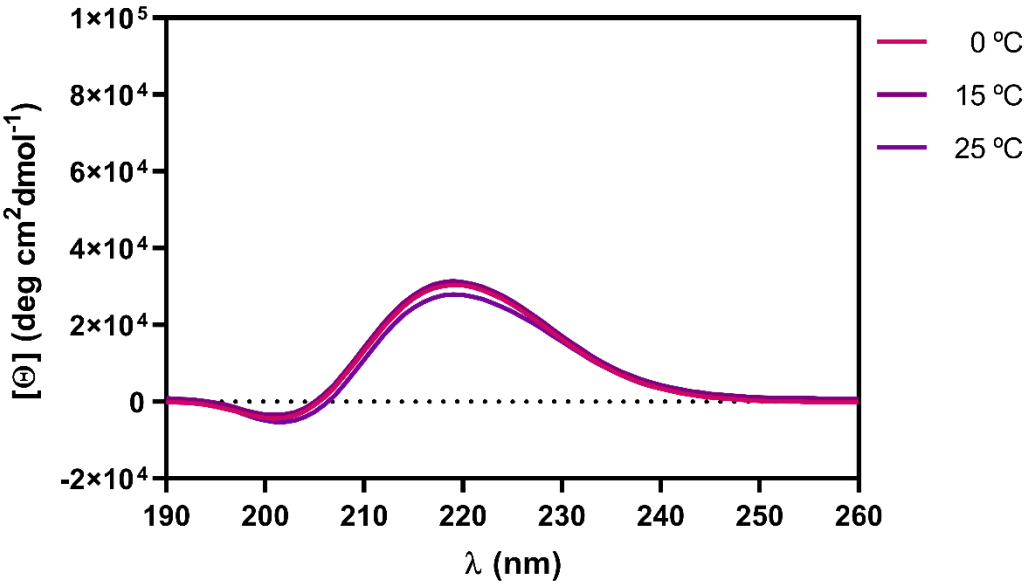


Figure S14: Circular dichroism data for **11** in methanol (c = 1 mM; T = 0, 15 and 25 °C).

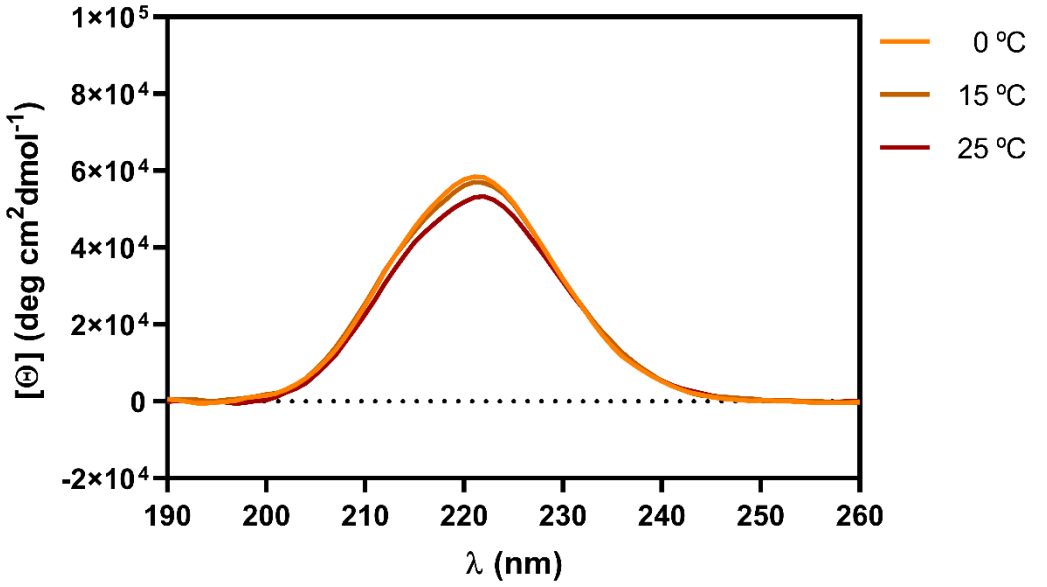


Figure S15: Circular dichroism data for **14** in methanol (c = 1 mM; T = 0, 15 and 25 °C).

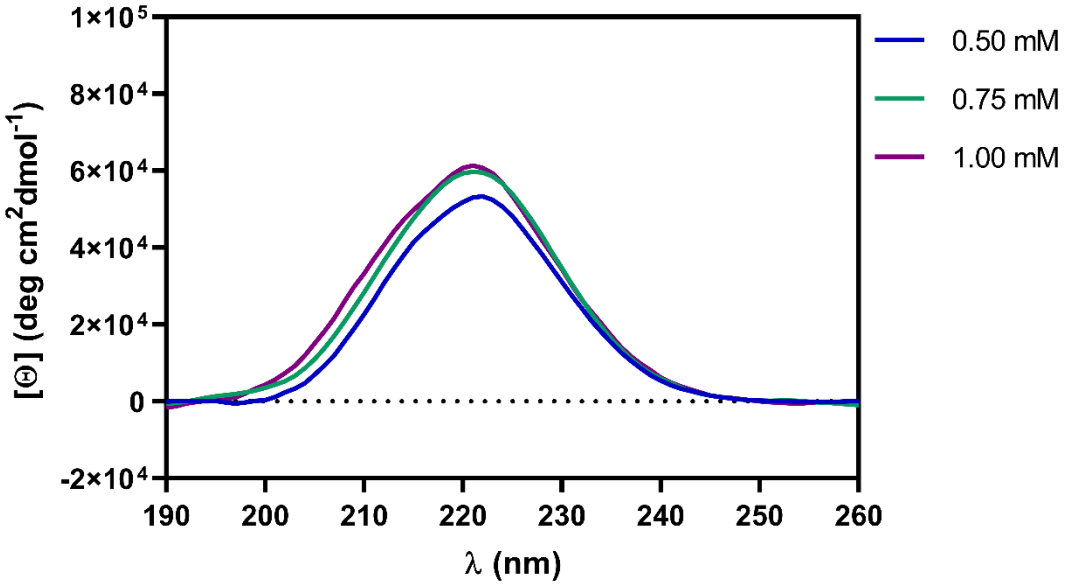


Figure S16: Circular dichroism data for **14** in methanol (c = 0.5 mM, 0.75 mM and 1 mM; T = 25 °C).

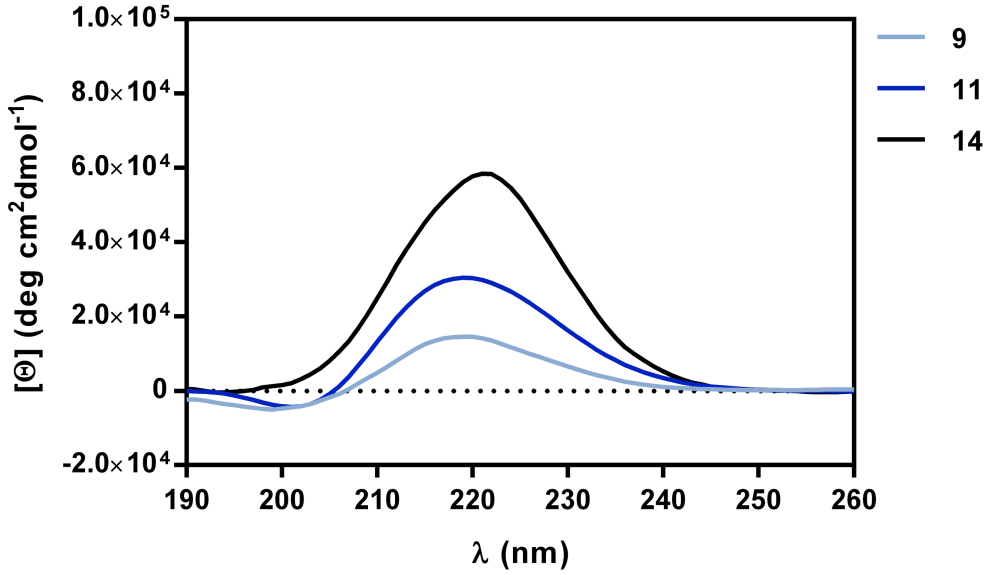


Figure S17: Circular dichroism data for **9**, **11** and **14** in methanol (c = 1 mM; T = 25 °C).

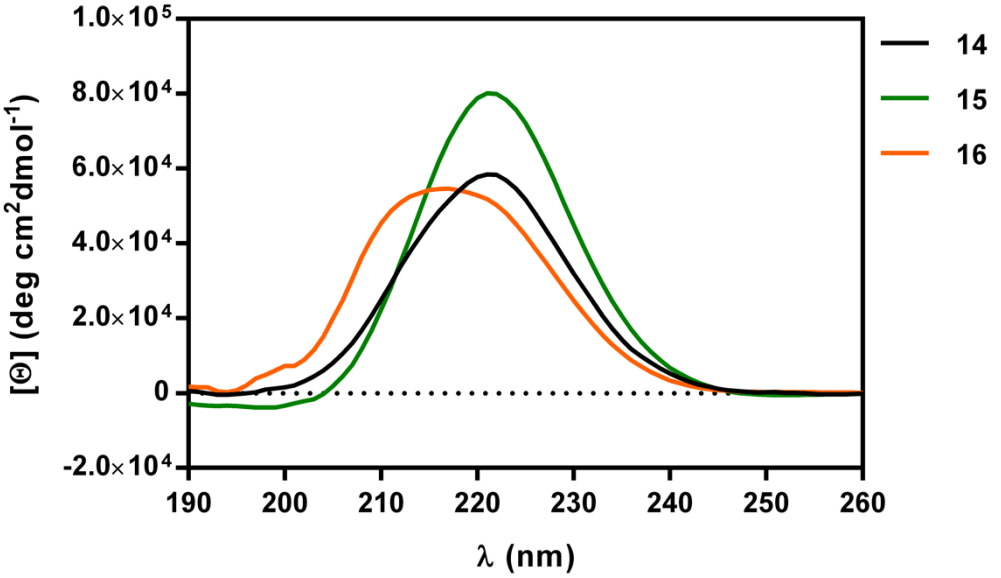
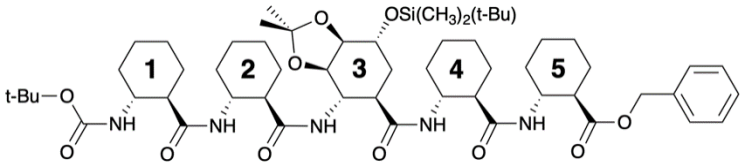


Figure S18: Circular dichroism data for peptides **14**, **15** and **16** in methanol (c = 1 mM; T = 25 °C).

V. NMR STRUCTURAL ANALYSIS OF PENTAPEPTIDES 14, 15, AND 16

V-A. Peptide 14: NMR spectroscopy in DMSO-d_6



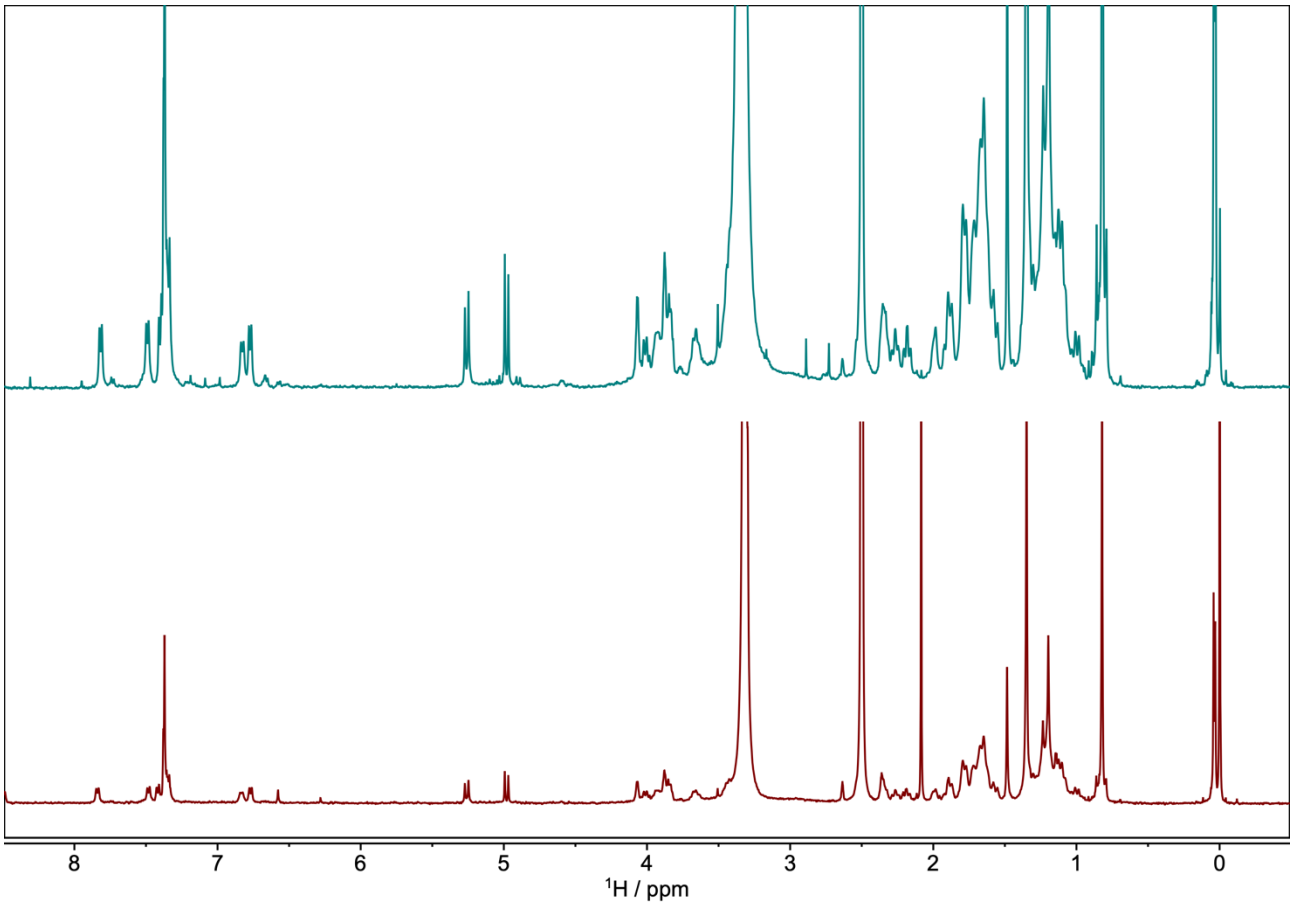


Figure S19: ^{1}H-NMR spectrum of peptide **14** at concentrations of 0.4 mM (bottom) and 1.5 mM (top). Conditions: DMSO-d_6, 500 MHz, 298 K.

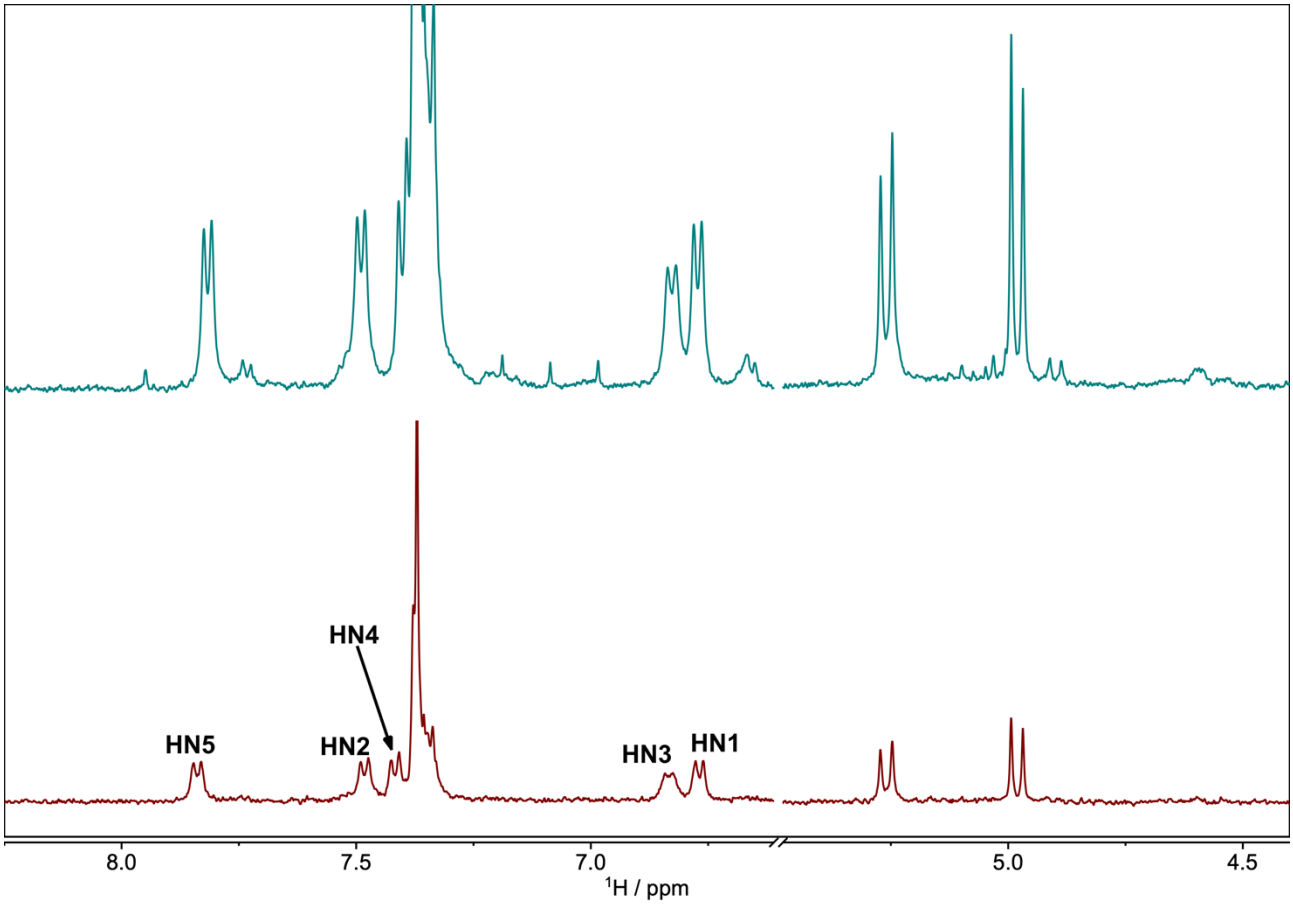


Figure S20: ^{1}H-NMR spectrum of peptide **14** at concentrations of 0.4 mM (bottom) and 1.5 mM (top): expansion of the amide and hydroxyl regions. Conditions: DMSO-d_6, 500 MHz, 298 K.

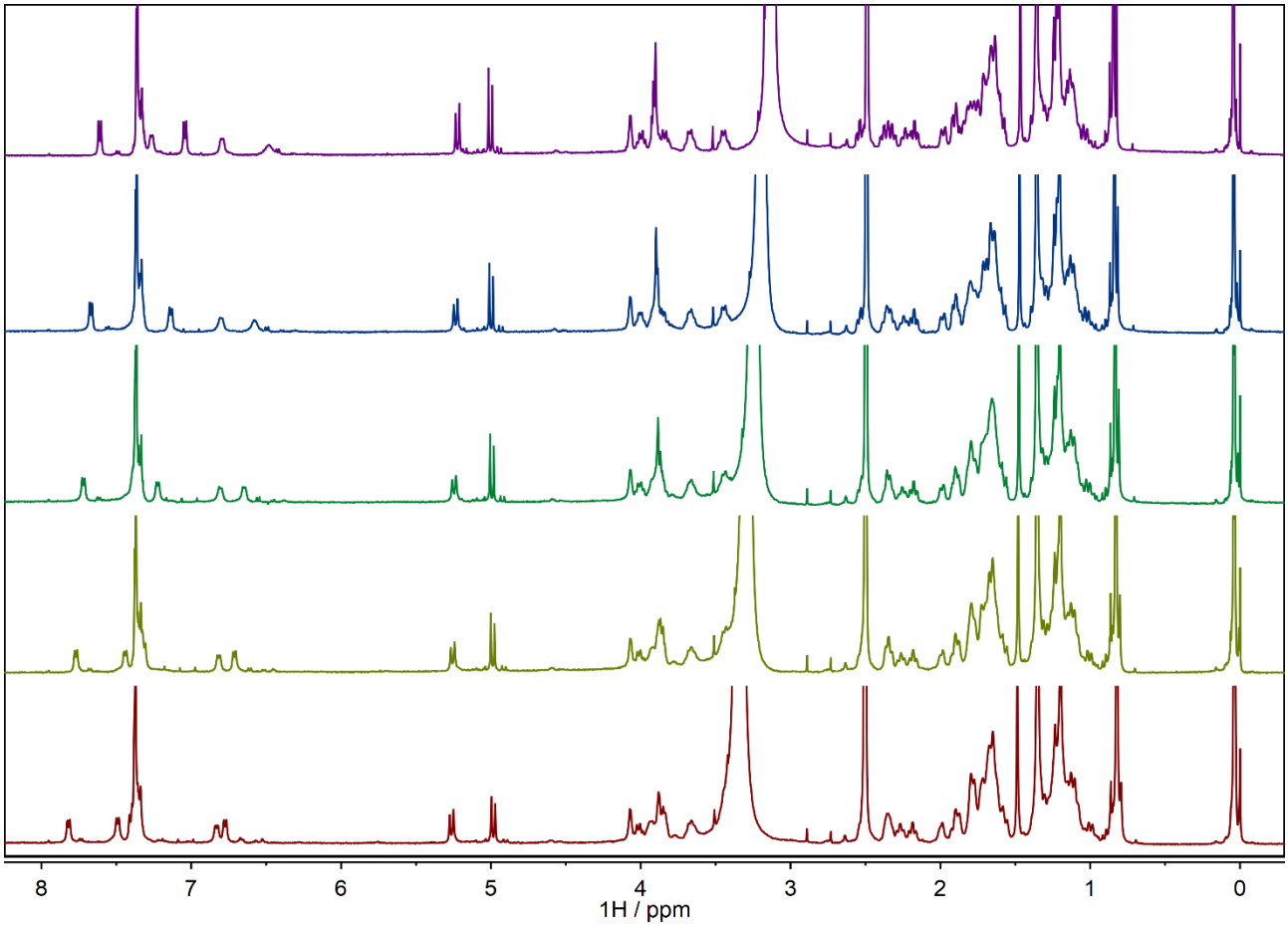


Figure S21: VT-NMR spectra of peptide **14** in DMSO-d_6 (500 MHz). Temperatures, from bottom to top: 298 to 338 K in 10 K steps.

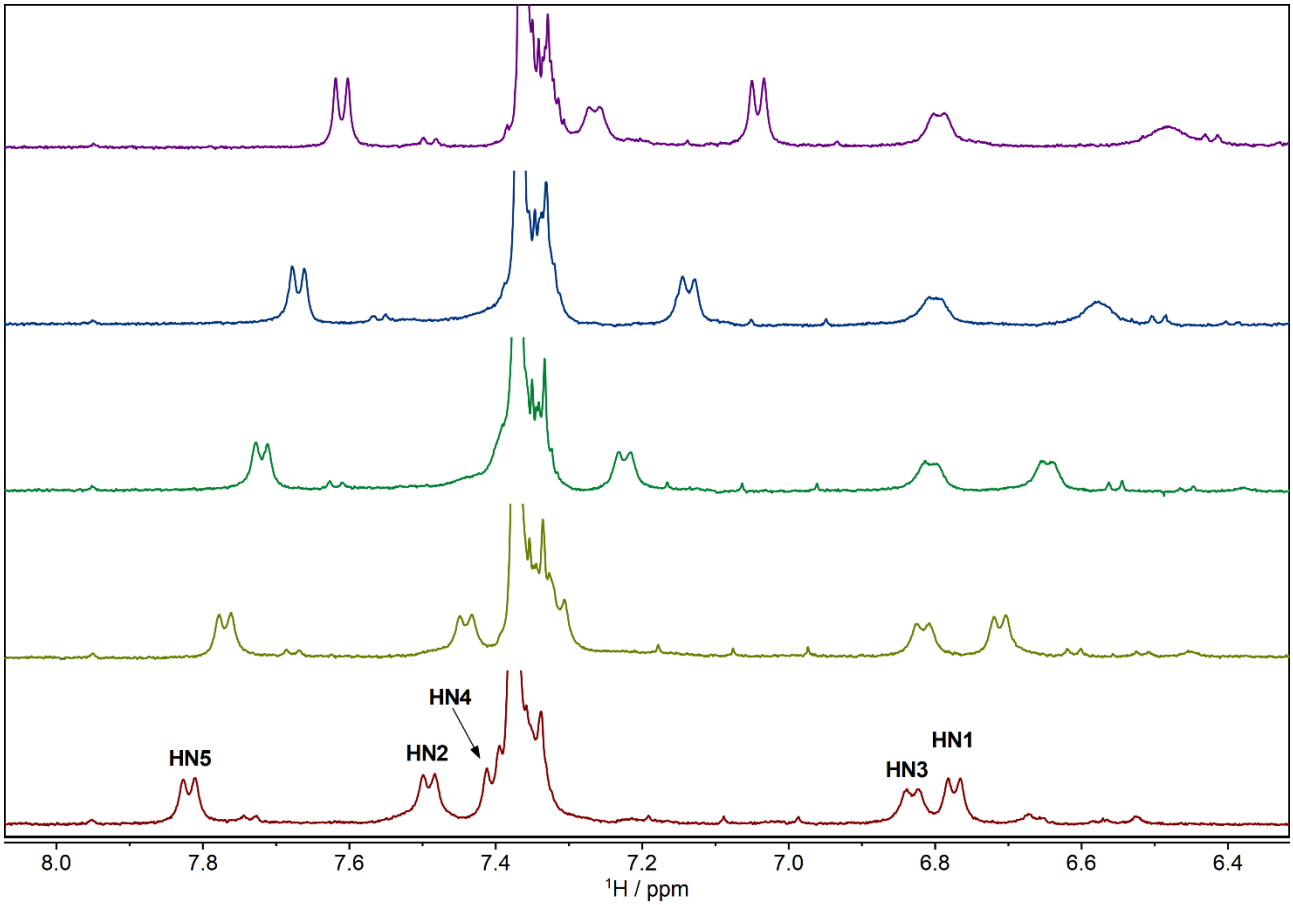


Figure S22: Expansion of the amide proton region of the VT-NMR spectra of peptide **14** in DMSO-d_6 (500 MHz). Temperatures, from bottom to top: 298 to 338 K in 10 K steps.

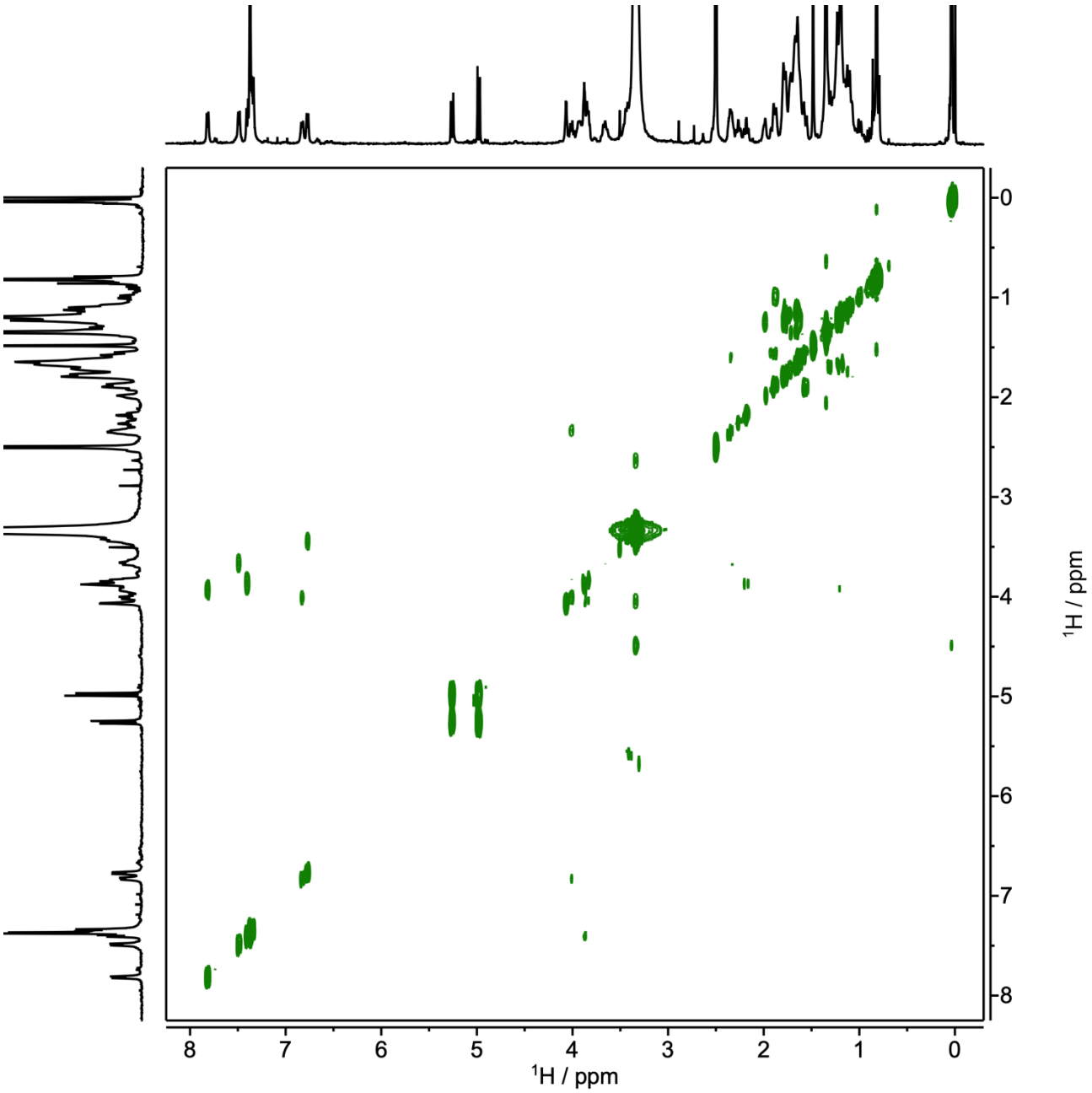


Figure S23: COSY spectrum of peptide **14** (DMSO-d_6, 500 MHz, 298 K).

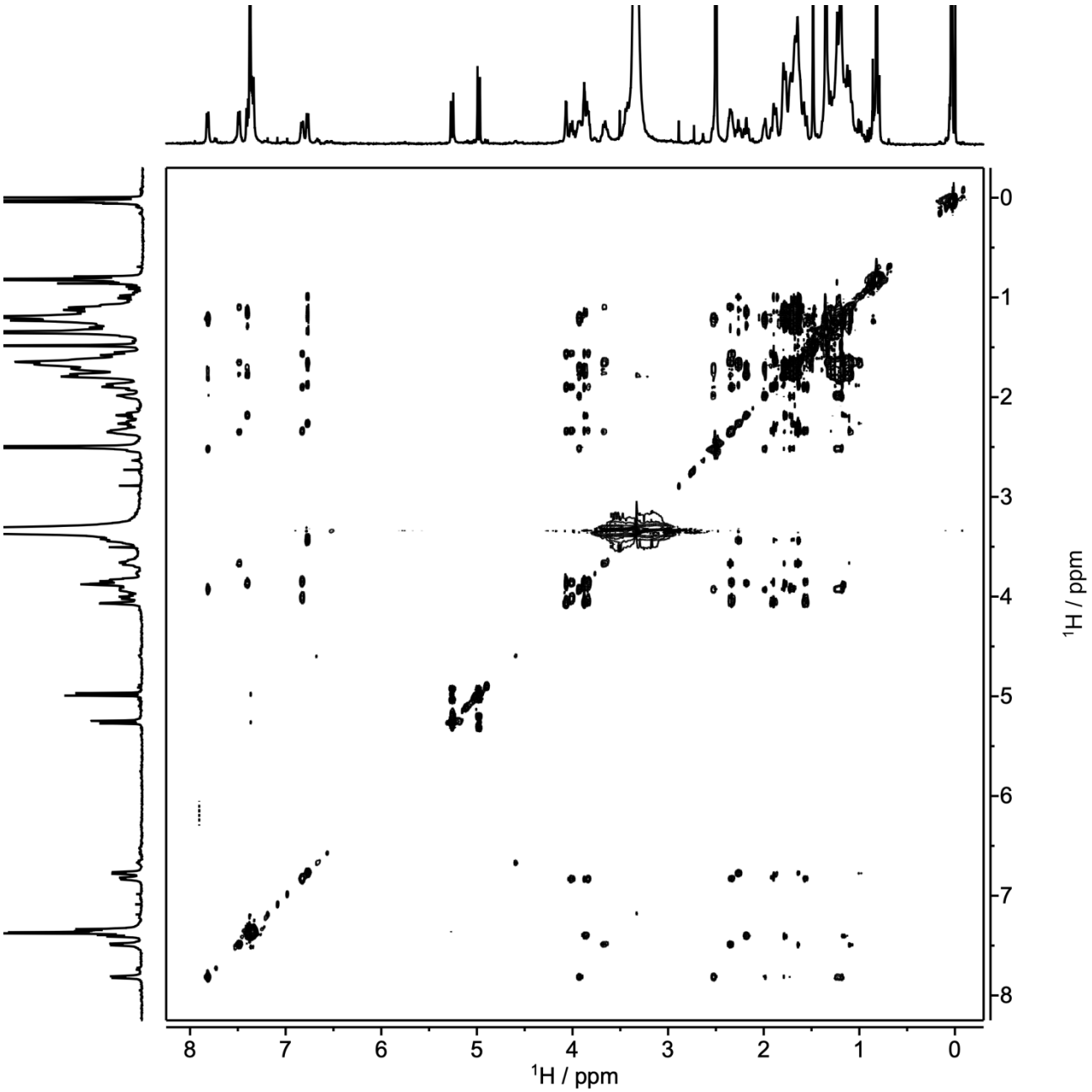


Figure S24: TOCSY spectrum of peptide **14**, t_{mix} = 70 ms (DMSO-d_6, 500 MHz, 298 K).

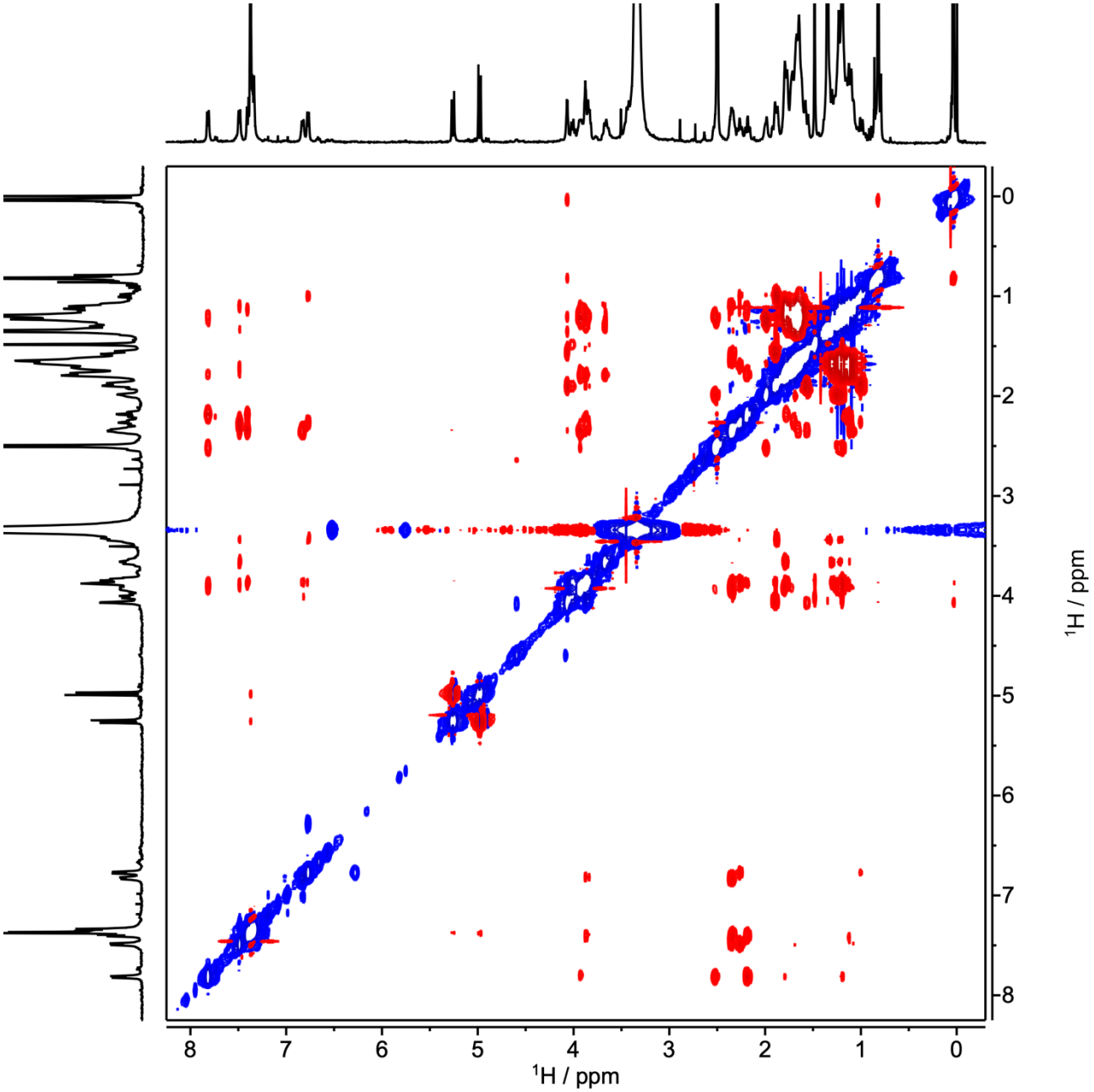


Figure S25: ROESY spectrum of peptide **14**, t_{mix} = 120 ms (DMSO-d_6, 500 MHz, 298 K).

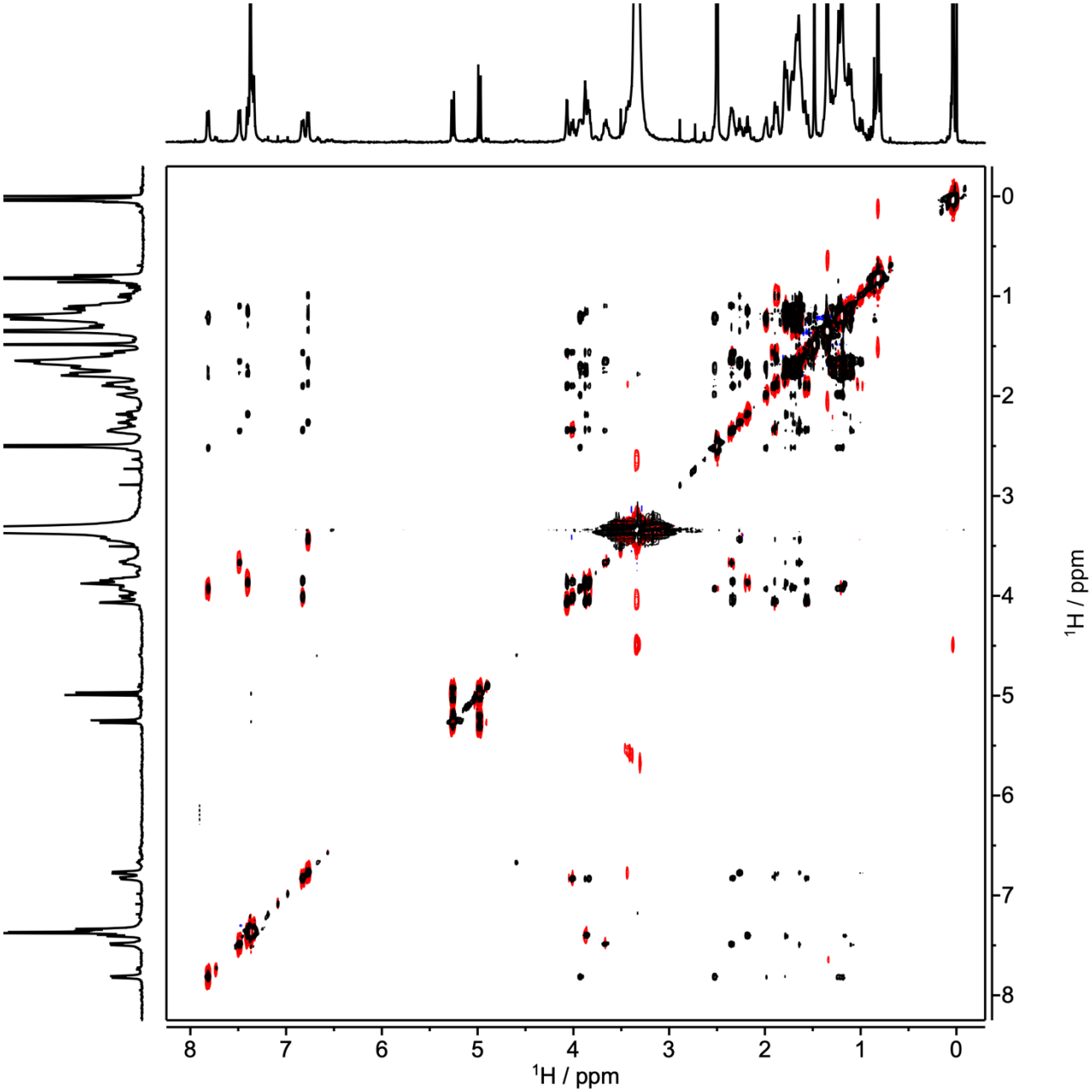


Figure S26: Overlay of the COSY (*red*) and TOCSY (*black*, t_{mix} 70 ms) spectra of peptide **14** (DMSO-d_6, 500 MHz, 298 K).

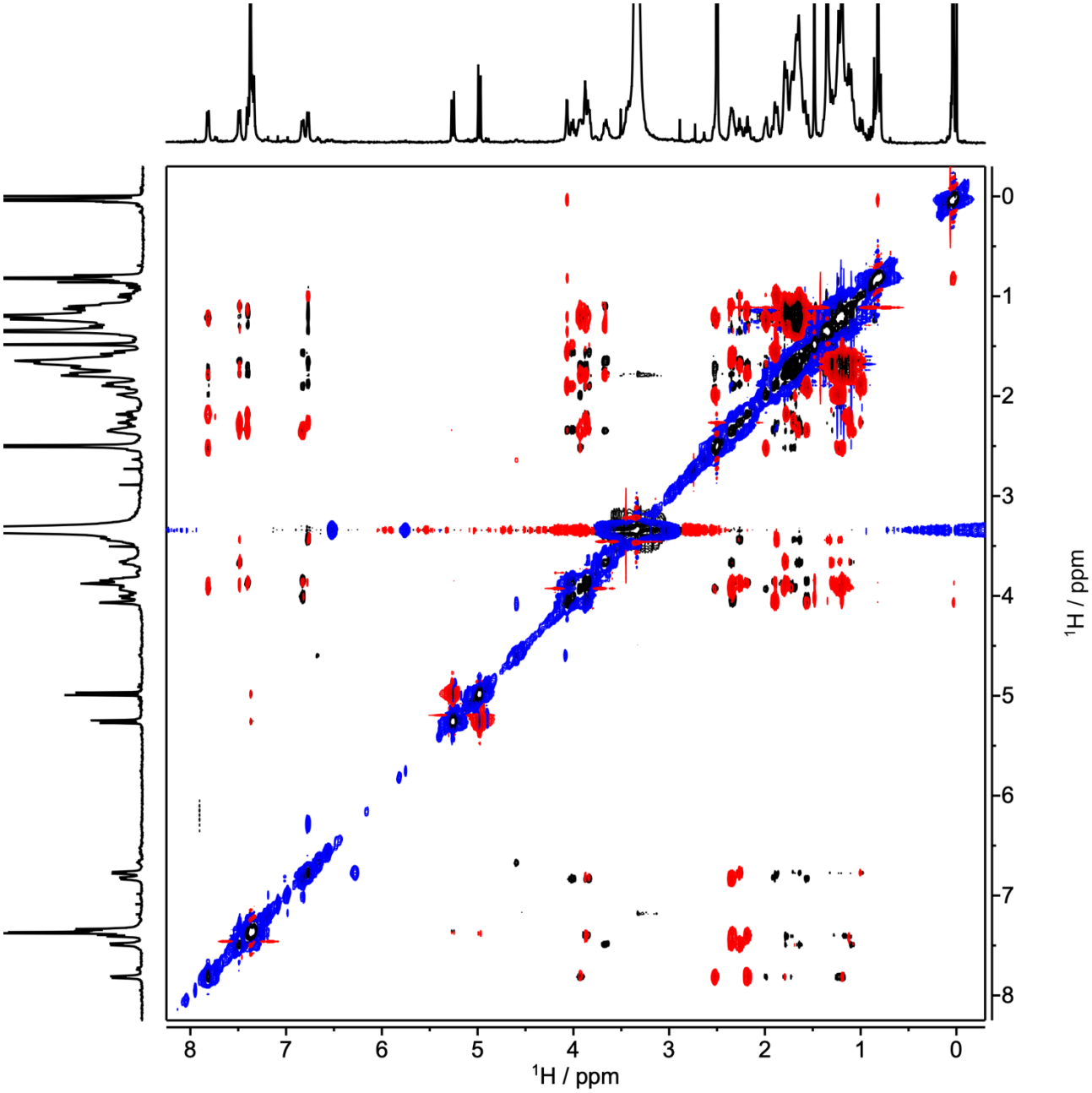


Figure S27: Overlay of the ROESY (*red/blue*, t_{mix} 120 ms) and TOCSY (*black*, t_{mix} 70 ms) spectra of peptide **14** (DMSO-d_6, 500 MHz, 298 K).

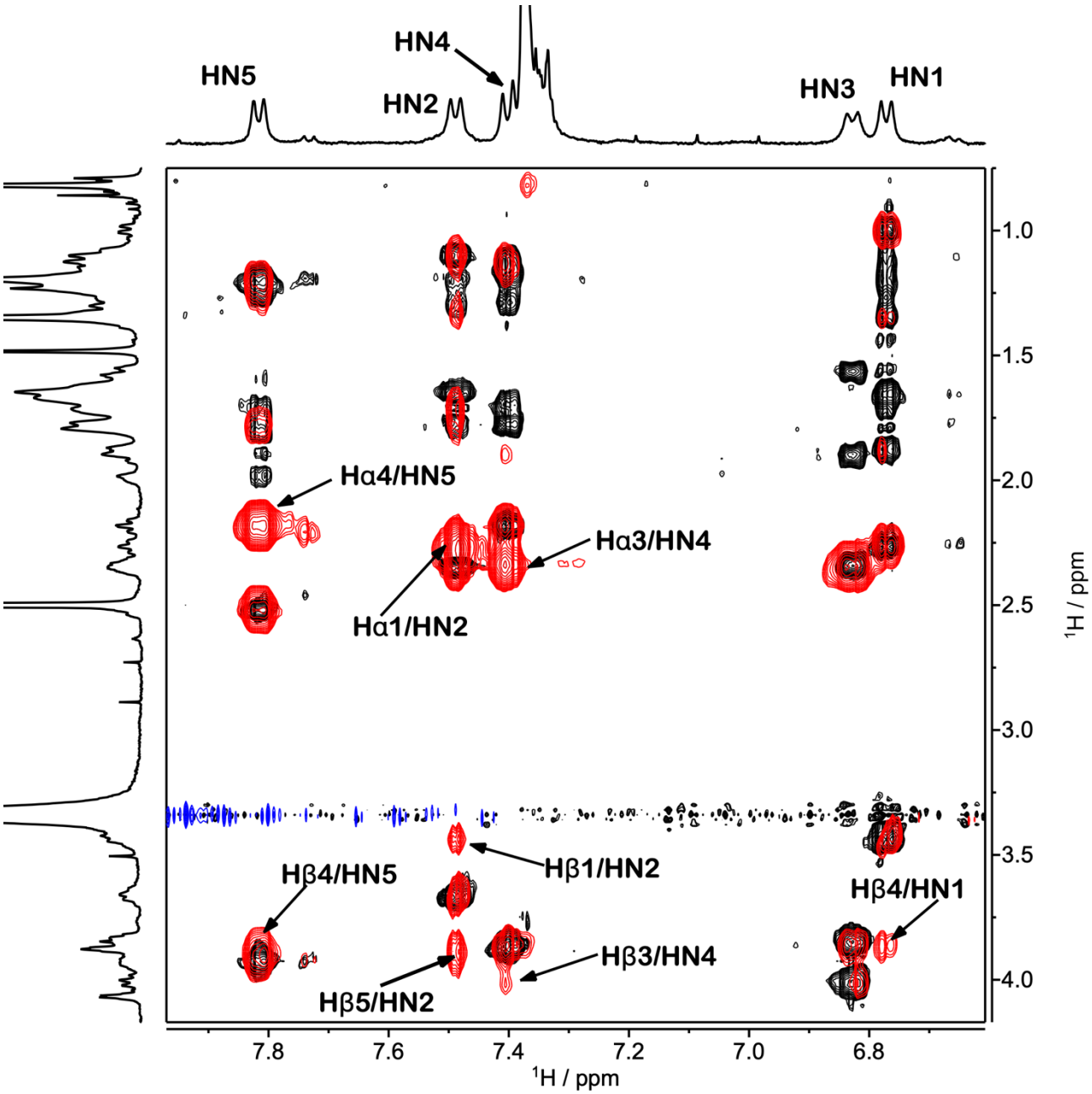


Figure S28: Overlay of the ROESY (*red/blue*, t_{mix} 120 ms) and TOCSY (*black*, t_{mix} 70 ms) spectra of peptide **14** (DMSO-d_6, 500 MHz, 298 K). Expansion of the (Hα+Hβ)/HN region.

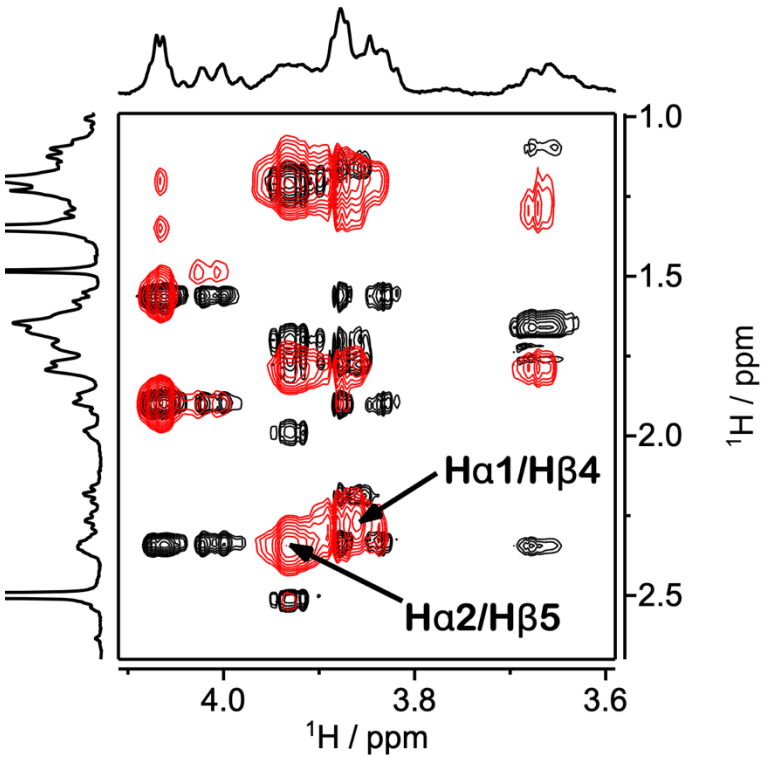
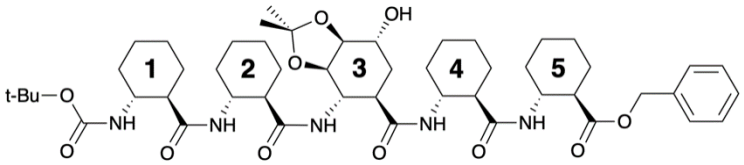


Figure S29: Overlay of the ROESY (*red/blue*, t_{mix} 120 ms) and TOCSY (*black*, t_{mix} 70 ms) spectra of peptide **14** (DMSO-d_6, 500 MHz, 298 K). Expansion of the Hα/Hβ region.

V-B. Peptide 15: NMR spectroscopy in DMSO-d_6



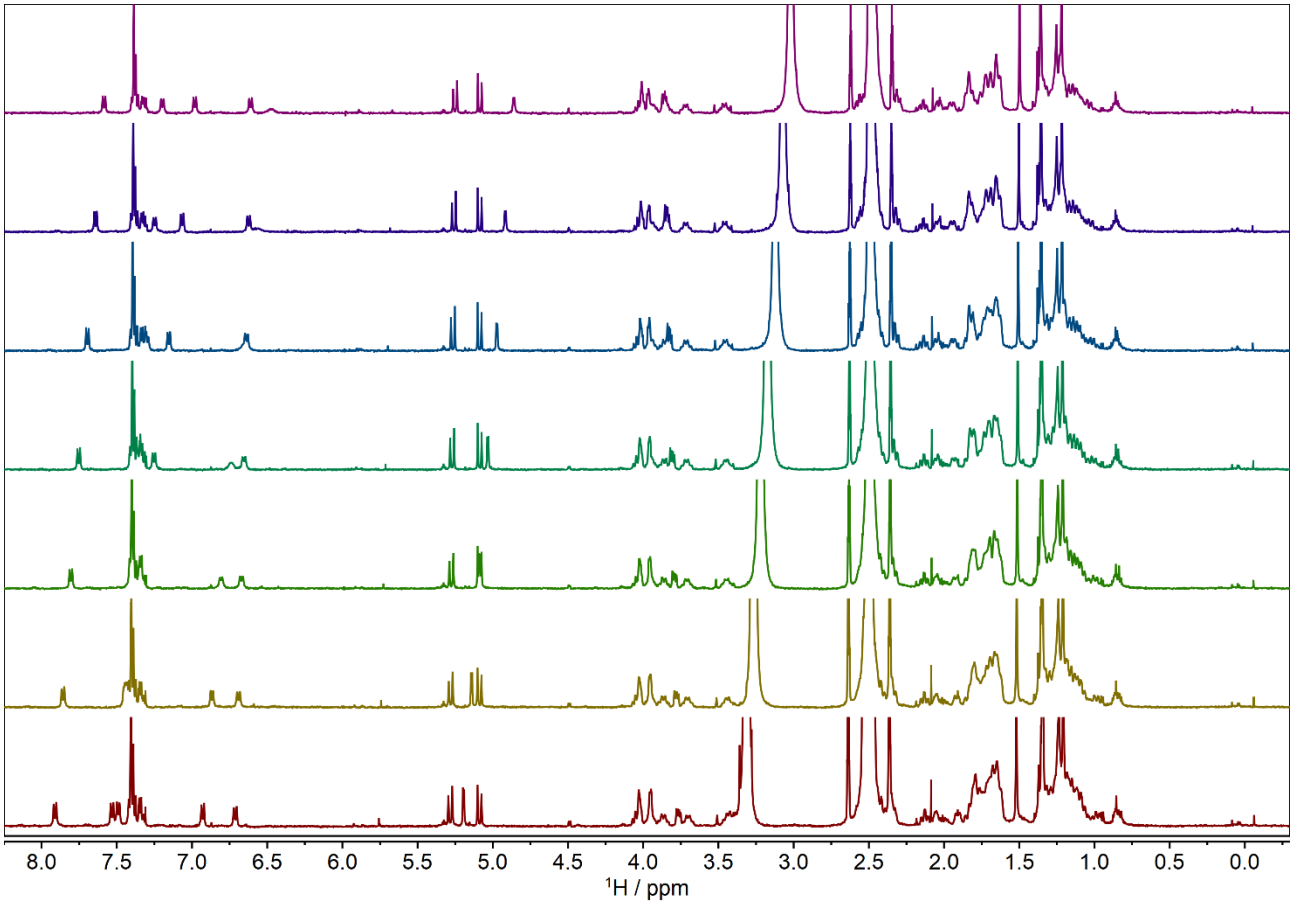


Figure S30: VT-NMR spectra of peptide **15** in DMSO-d_6 (500 MHz). Temperatures, from bottom to top: 298 to 358 K in 10 K steps.

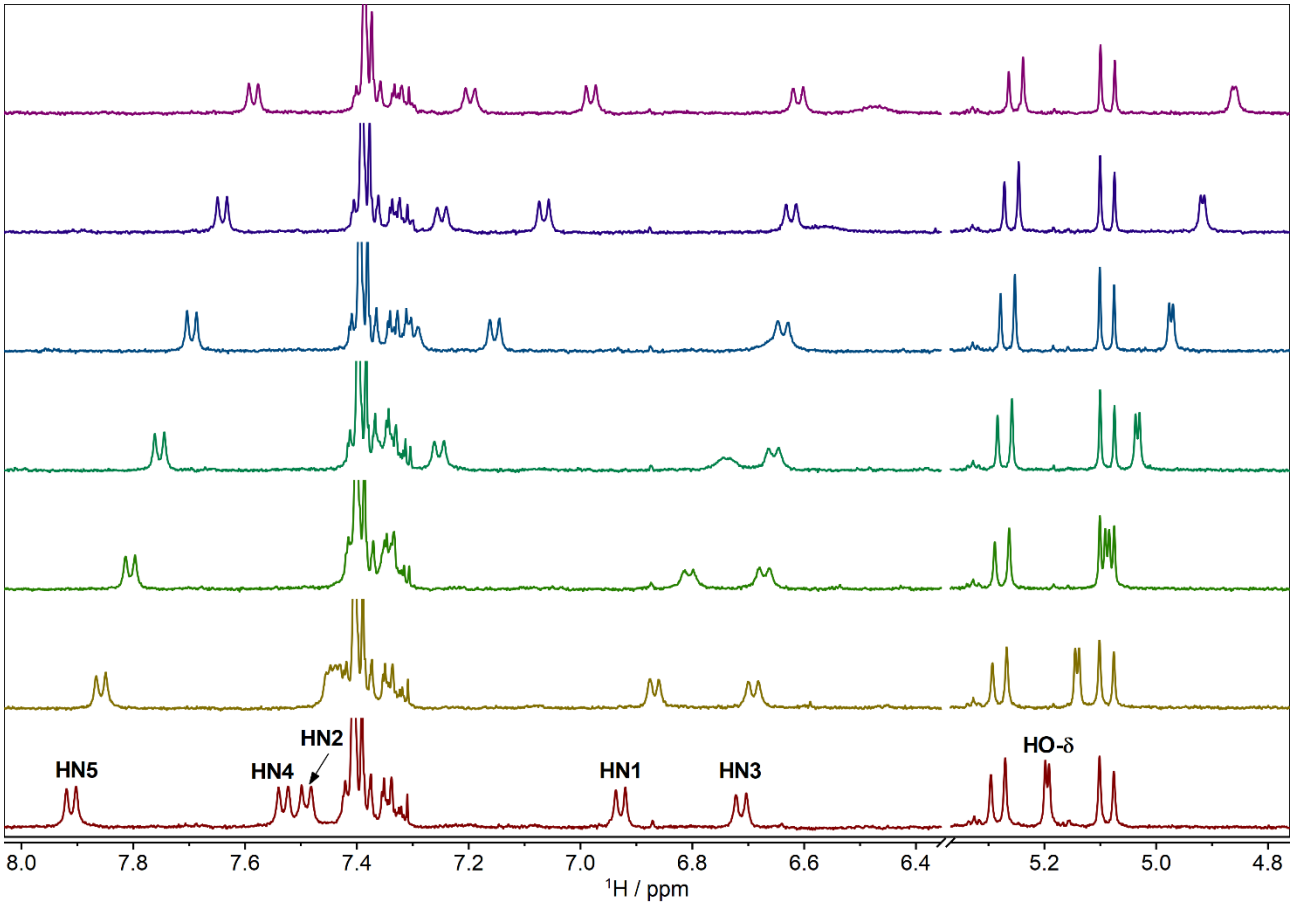


Figure S31: Expansion of the amide proton region of the VT-NMR spectra of peptide **15** in DMSO-d_6 (500 MHz). Temperatures, from bottom to top: 298 to 358 K in 10 K steps.

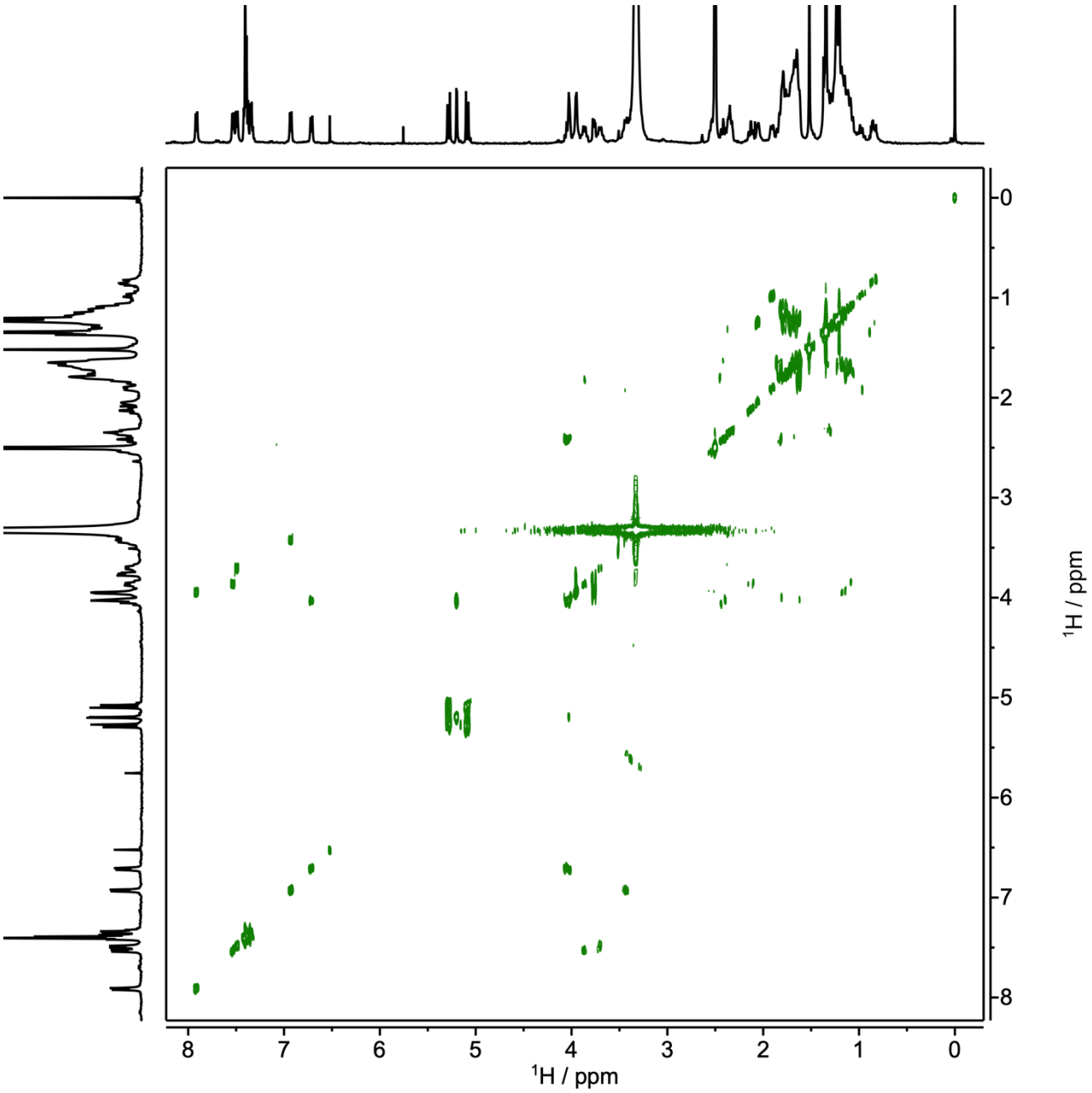


Figure S32: COSY spectrum of peptide **15** (DMSO-d_6, 500 MHz, 298 K).

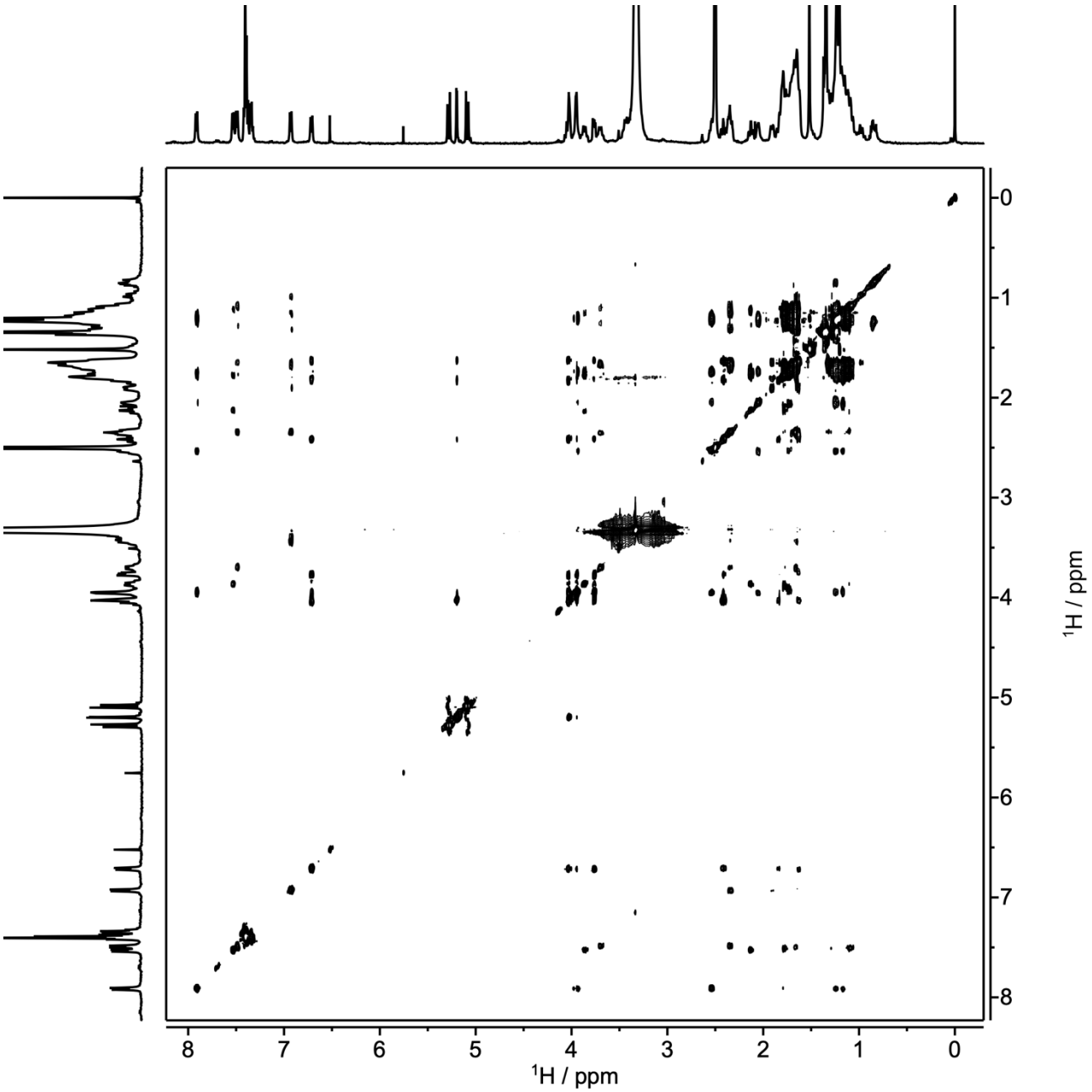


Figure S33: TOCSY spectrum of peptide **15**, t_{mix} = 70 ms (DMSO-d_6, 500 MHz, 298 K).

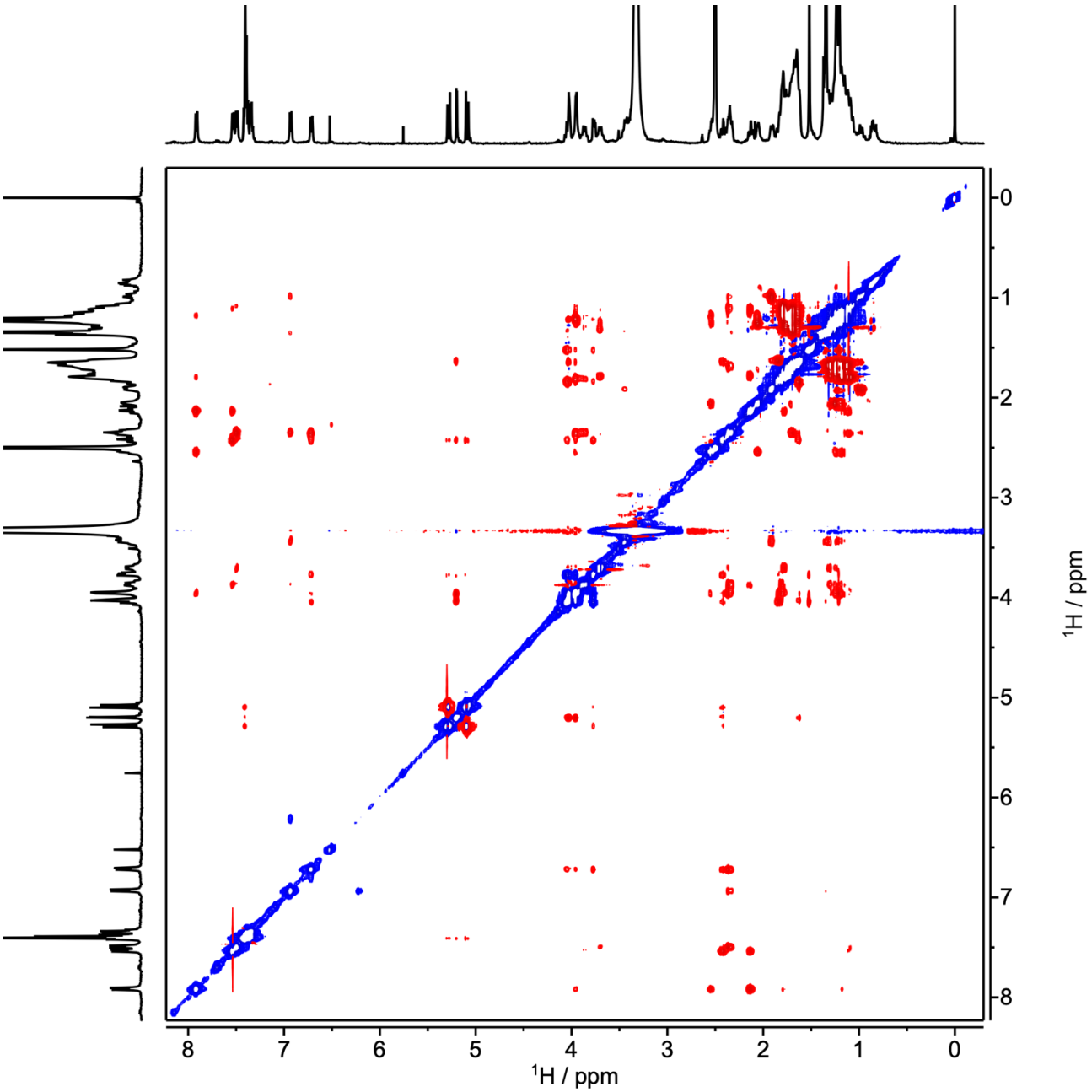


Figure S34: ROESY spectrum of peptide **15**, t_{mix} = 200 ms (DMSO-d_6, 500 MHz, 298 K).

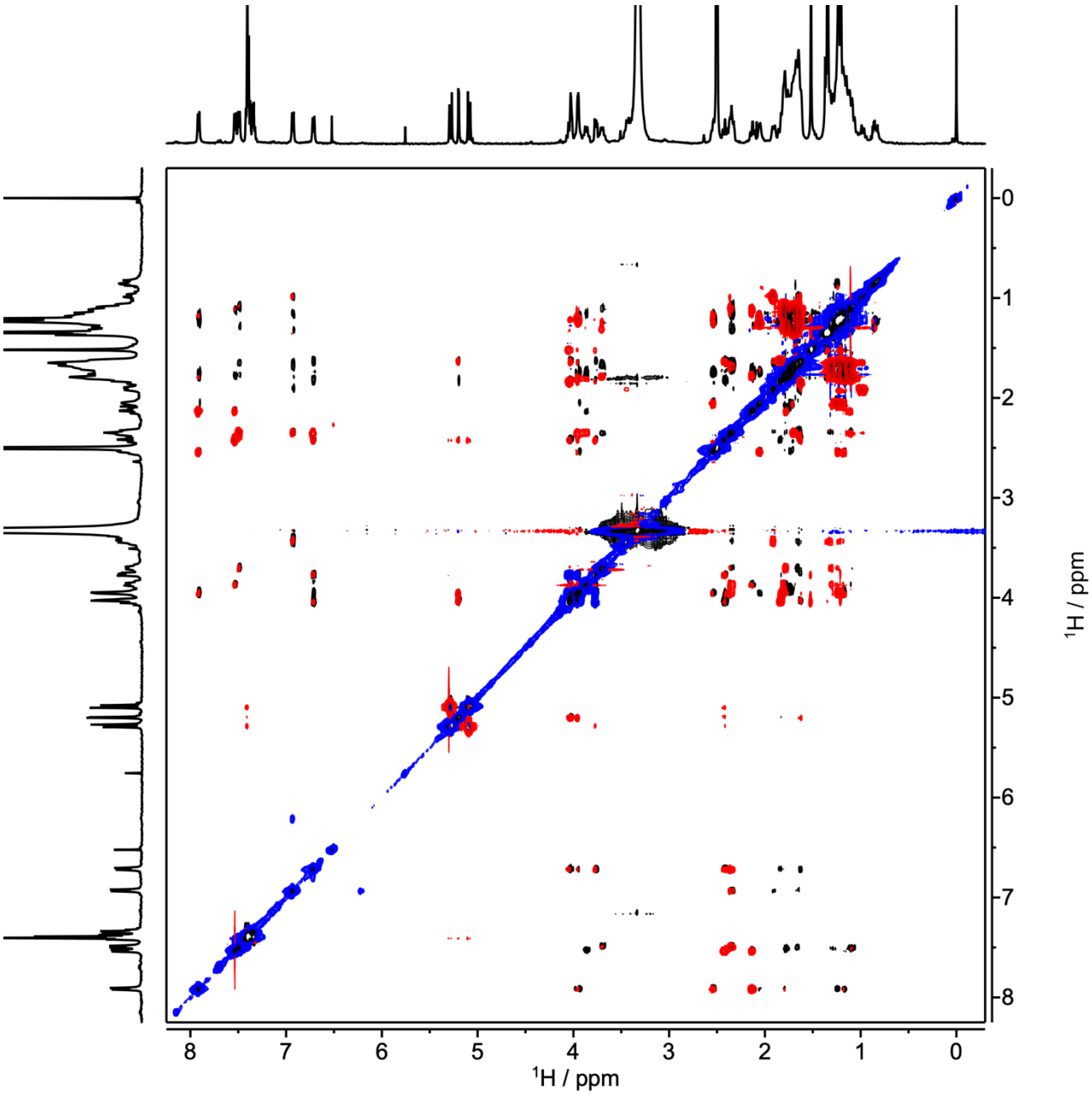


Figure S35: Overlay of the ROESY (*red/blue*, t_{mix} 200 ms) and TOCSY (*black*, t_{mix} 70 ms) spectra of peptide **15** (DMSO-d_6, 500 MHz, 298 K).

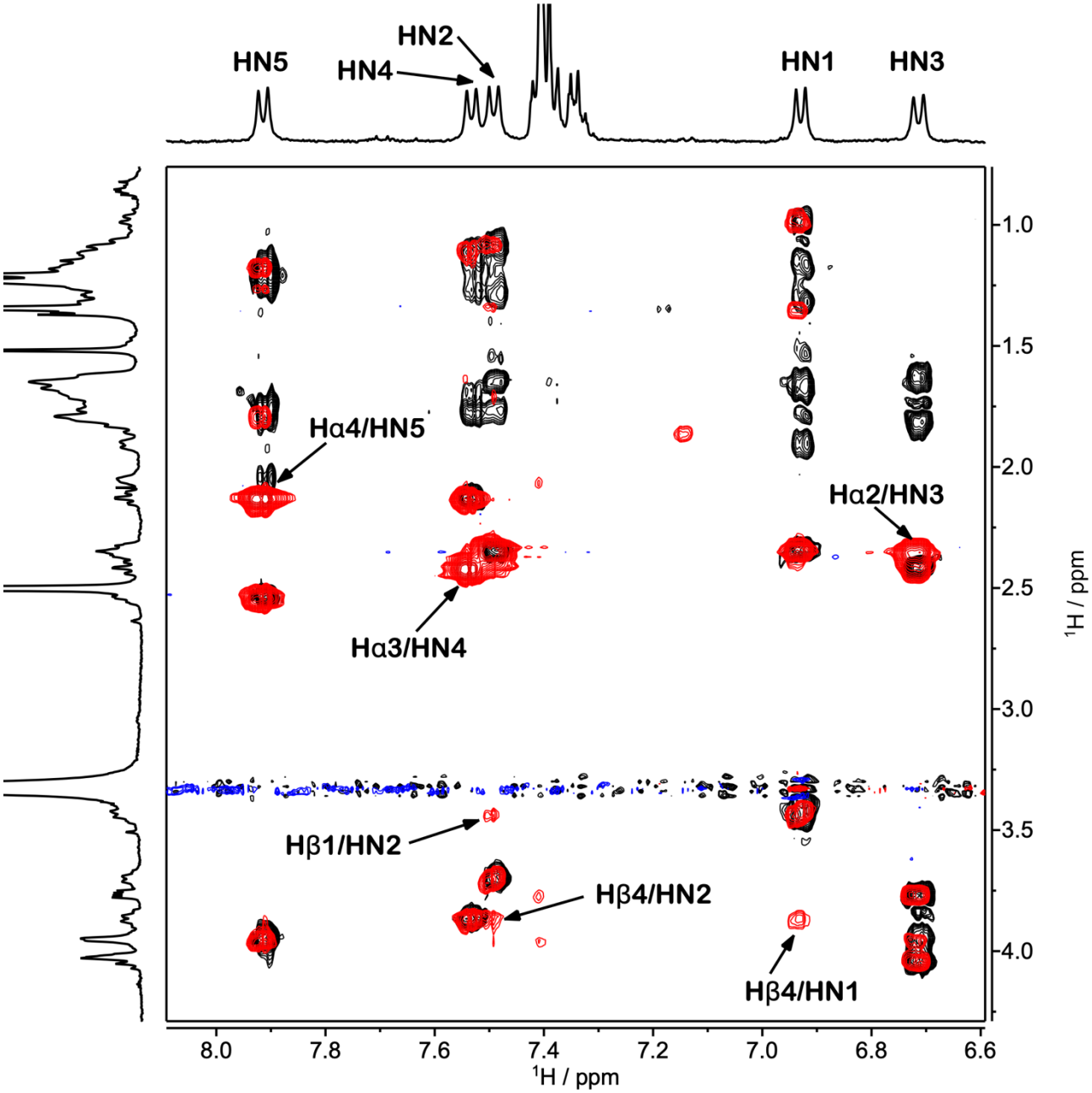


Figure S36: Overlay of the ROESY (*red/blue*, t_{mix} 200 ms) and TOCSY (*black*, t_{mix} 70 ms) spectra of peptide **15** (DMSO-d_6, 500 MHz, 298 K). Expansion of the (Hα+Hβ)/HN region.

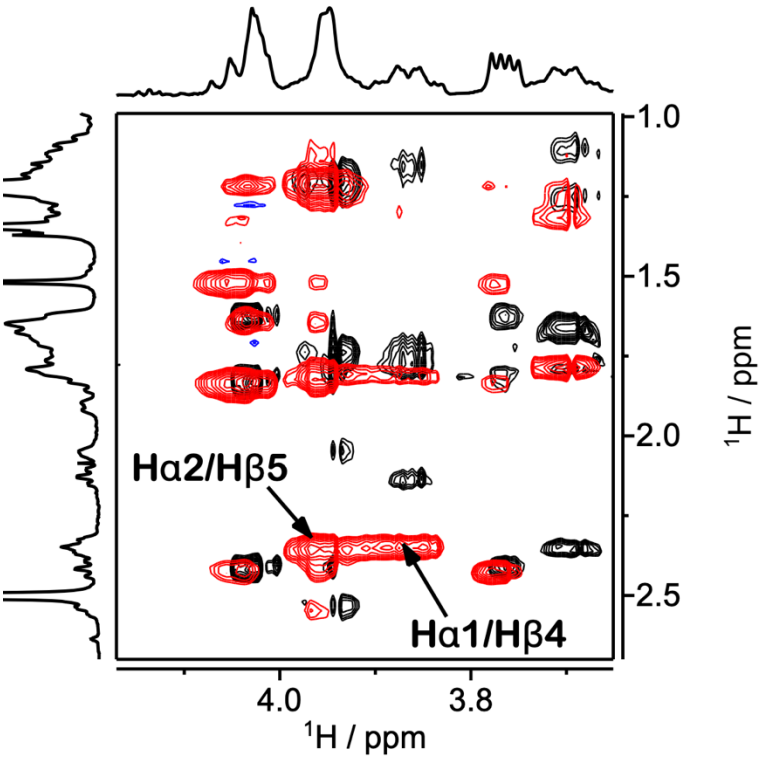
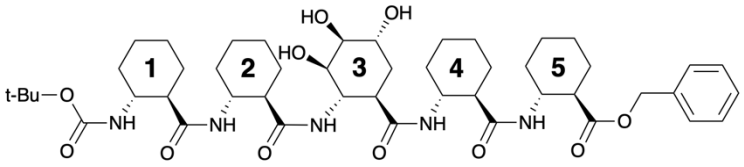


Figure S37: Overlay of the ROESY (*red/blue*, t_{mix} 200 ms) and TOCSY (*black*, t_{mix} 70 ms) spectra of peptide **15** (DMSO-d_6, 500 MHz, 298 K). Expansion of the Hα/Hβ region.

V-C. Peptide 16: NMR spectroscopy in DMSO-d_6



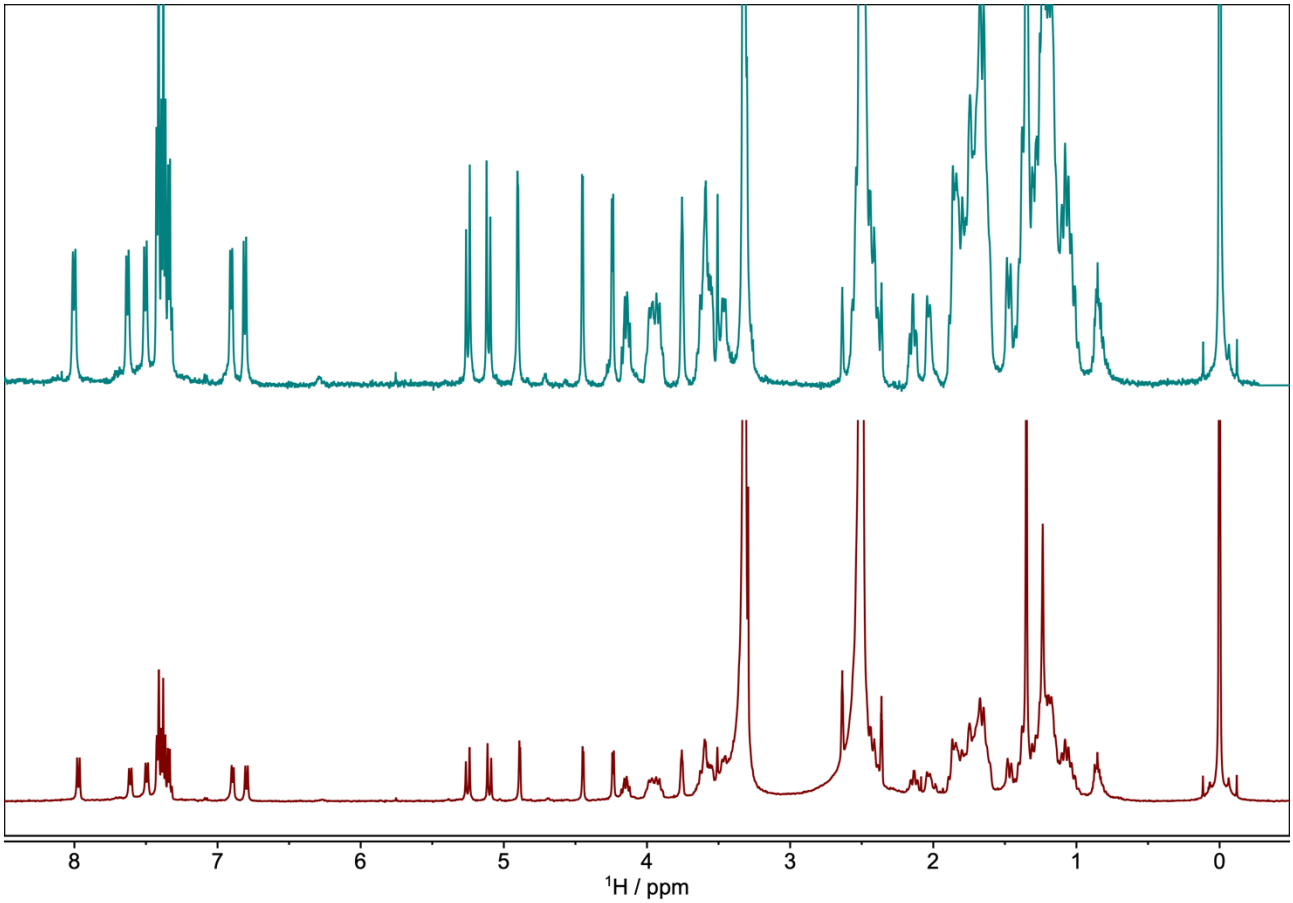


Figure S38: ^{1}H-NMR spectrum of peptide **16** at concentrations of 1.8 mM (bottom) and 10 mM (top). Conditions: DMSO-d_6, 500 MHz, 298 K.

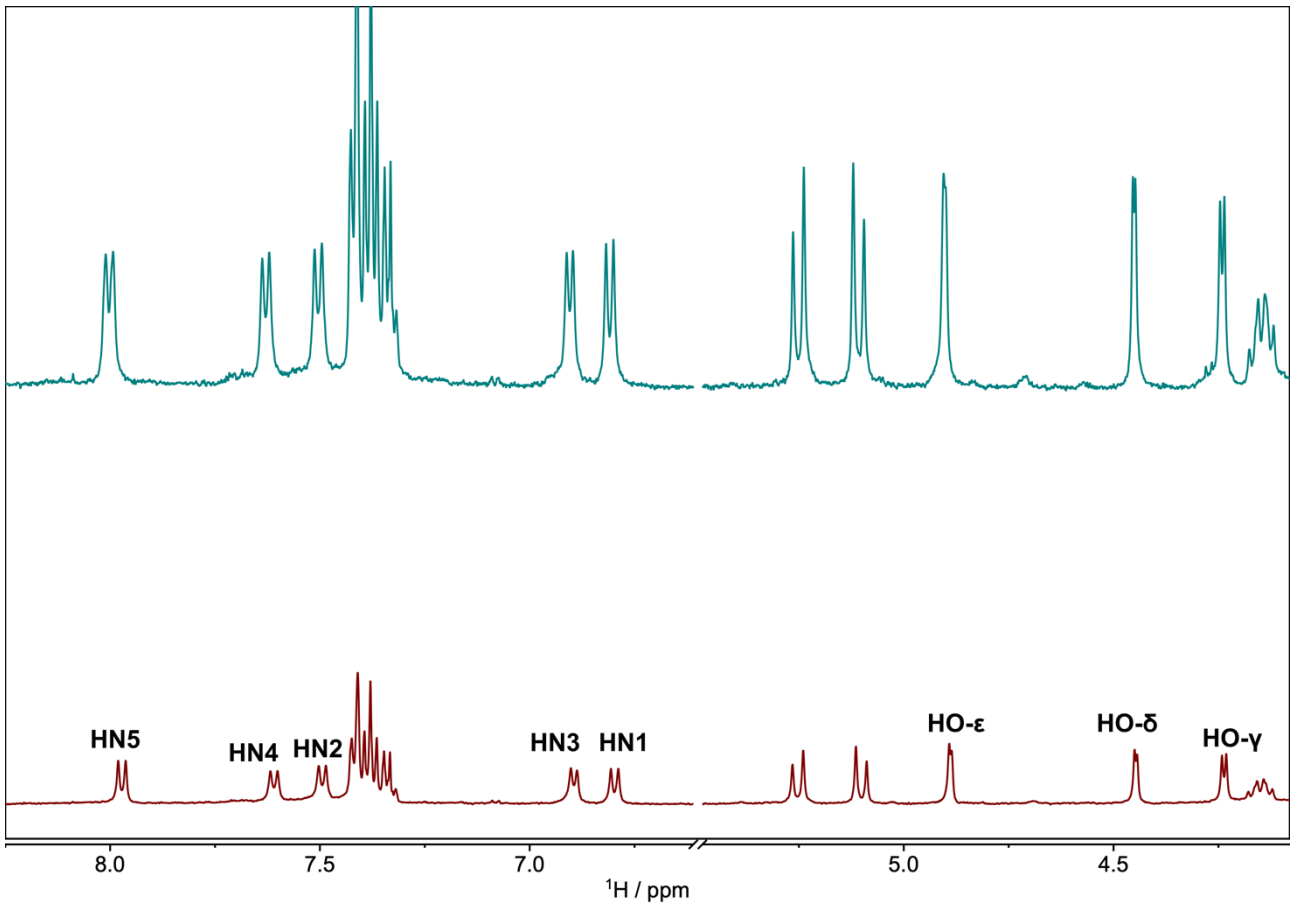


Figure S39: ^{1}H-NMR spectrum of peptide **16** at concentrations of 1.8 mM (bottom) and 10 mM (top): expansion of the amide and hydroxyl regions. Conditions: DMSO-d_6, 500 MHz, 298 K.

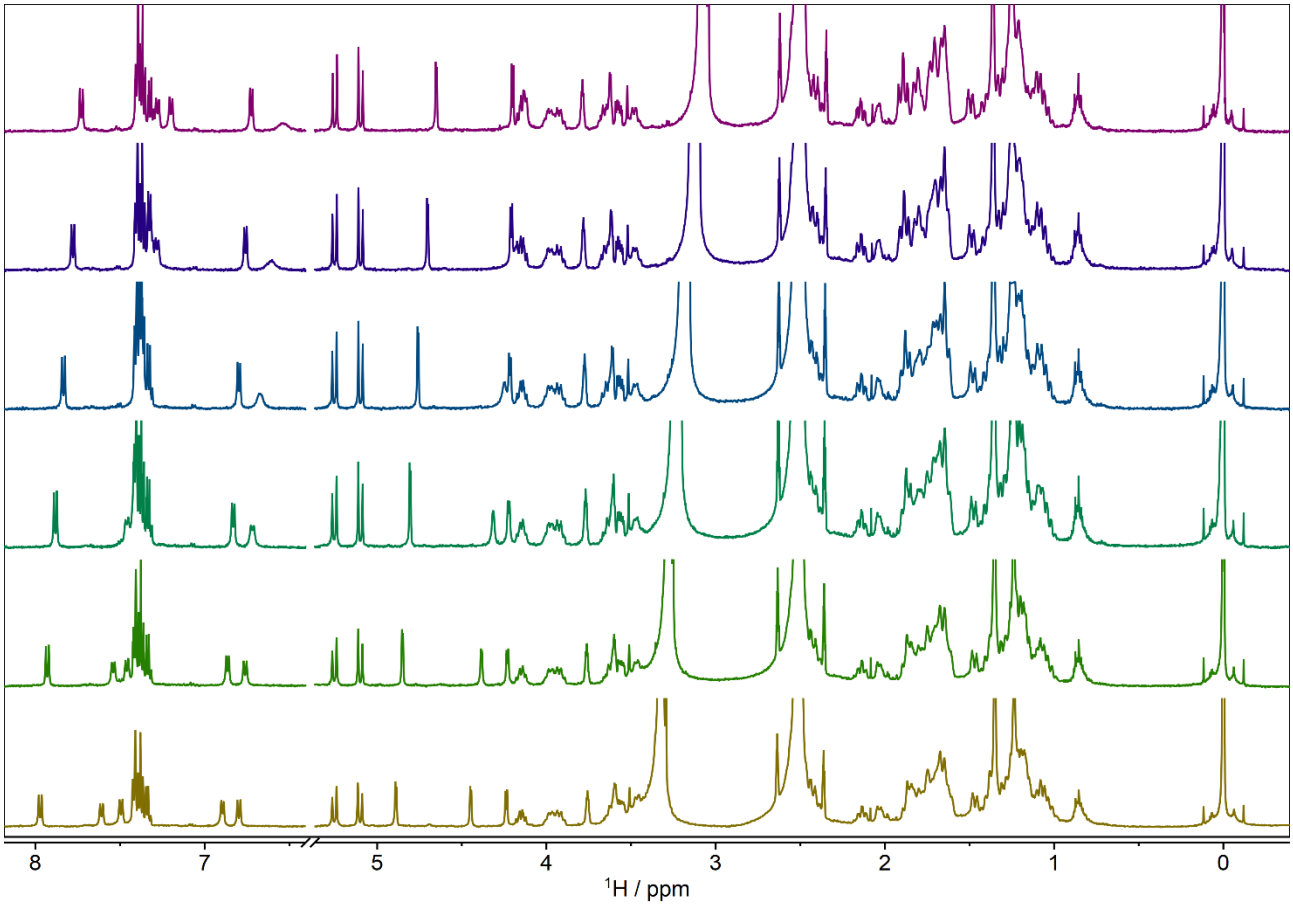


Figure S40: VT-NMR spectra of peptide **16** in DMSO-d_6 (500 MHz). Temperatures, from bottom to top: 298 to 348 K in 10 K steps.

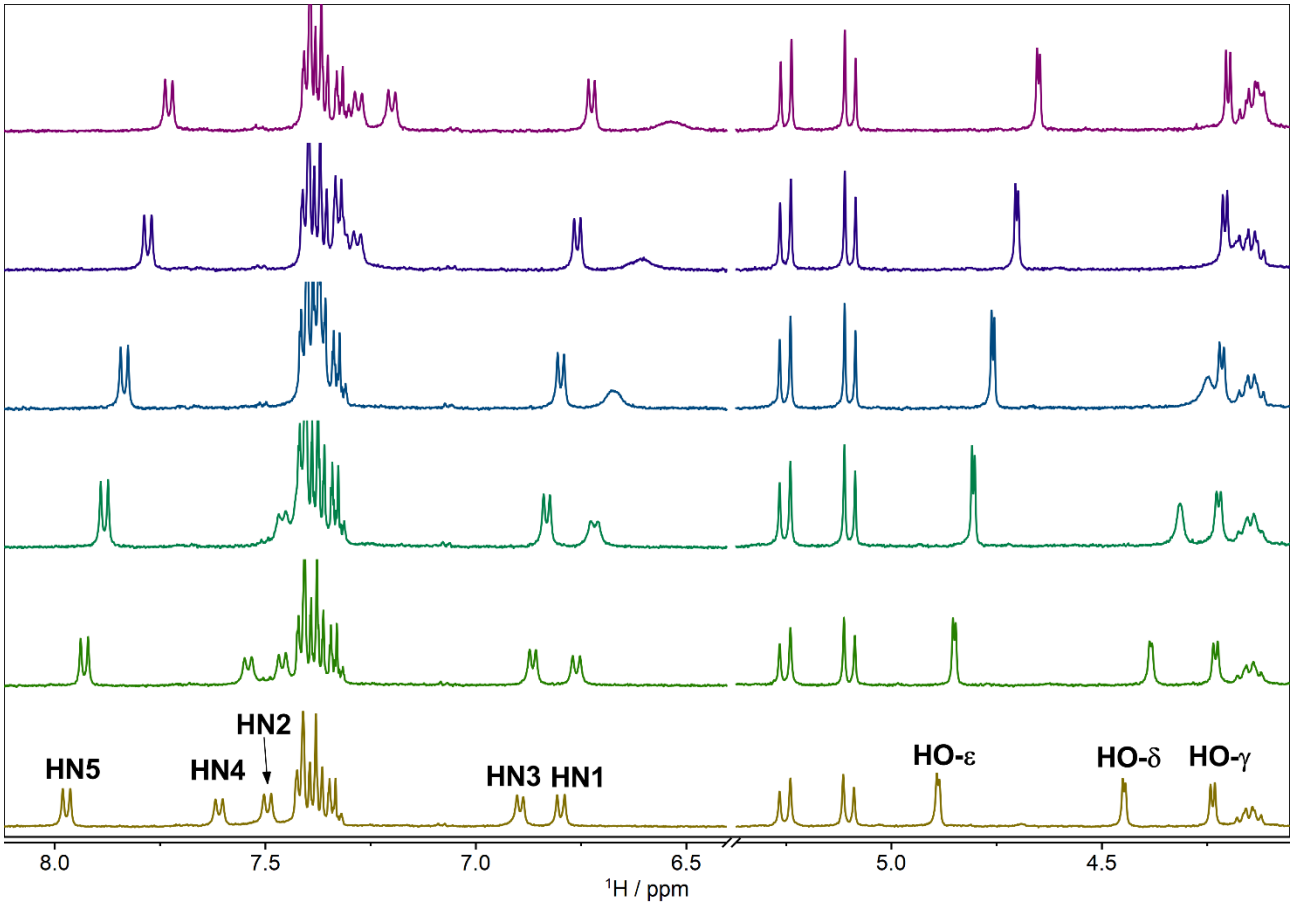


Figure S41: Expansion of the amide proton region of the VT-NMR spectra of peptide **16** in DMSO-d_6 (500 MHz). Temperatures, from bottom to top: 298 to 348 K in 10 K steps.

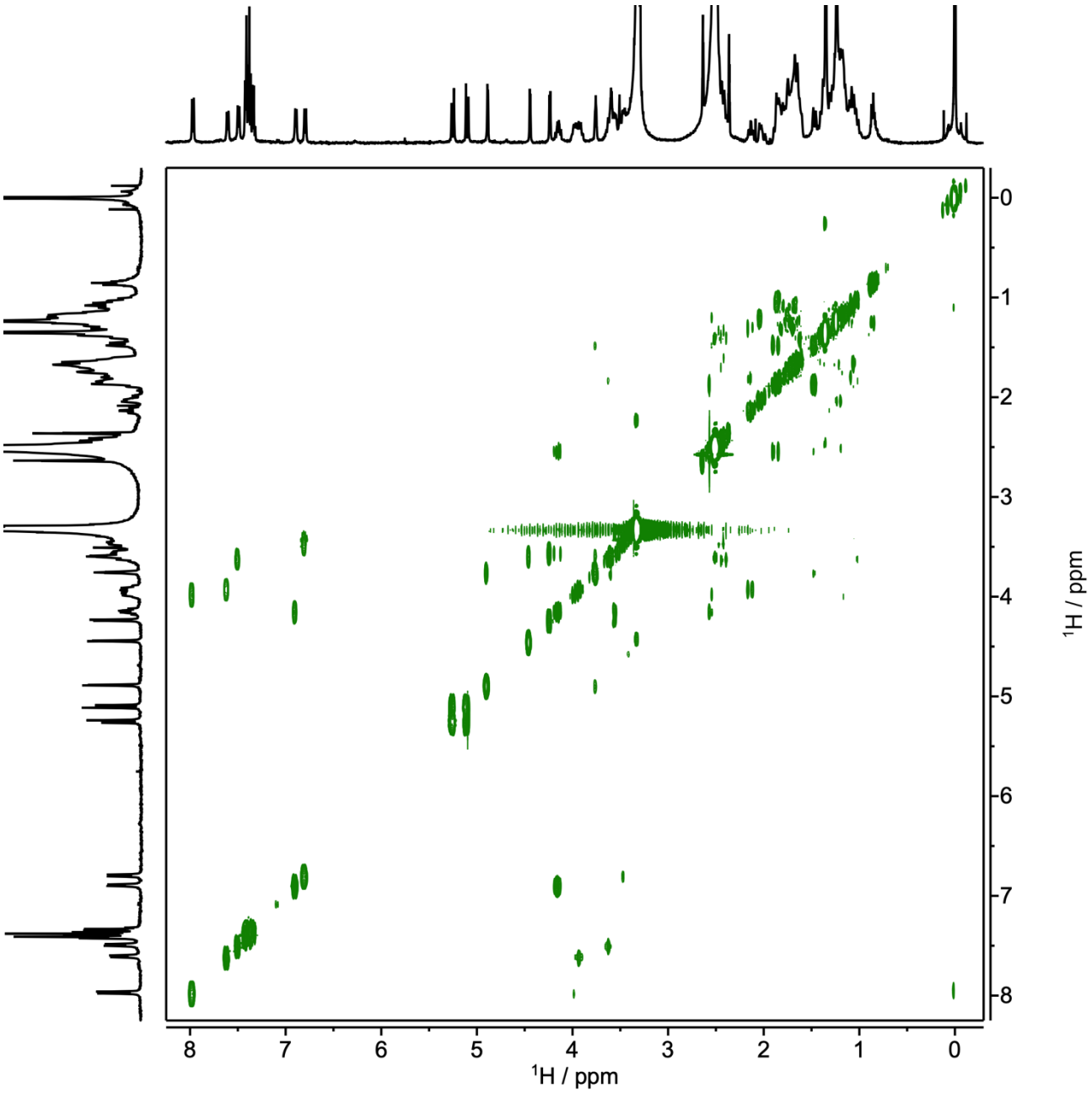


Figure S42: COSY spectrum of peptide **16** (DMSO-d_6, 500 MHz, 298 K).

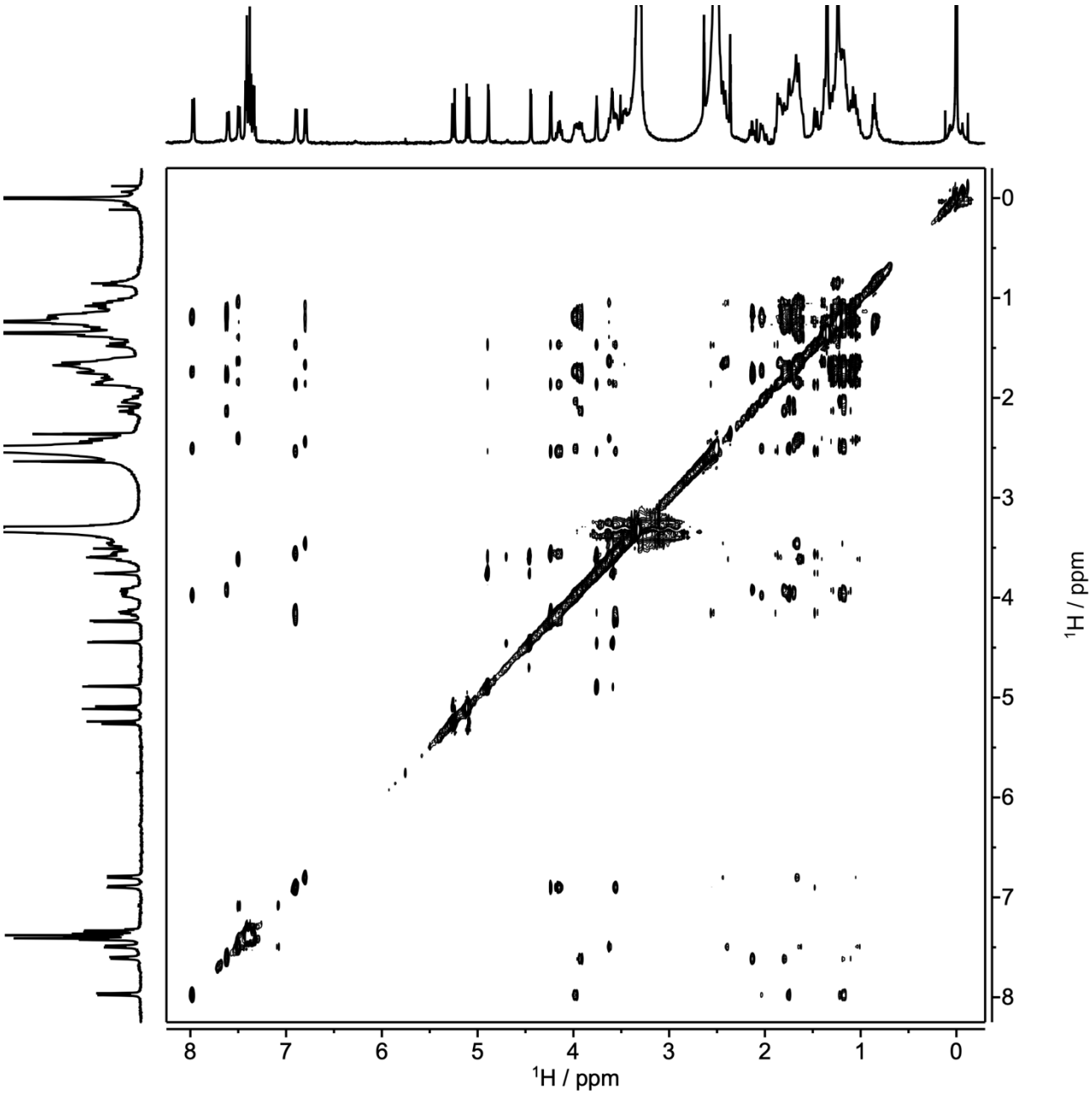


Figure S43: TOCSY spectrum of peptide **16**, t_{mix} = 80 ms (DMSO-d_6, 500 MHz, 298 K).

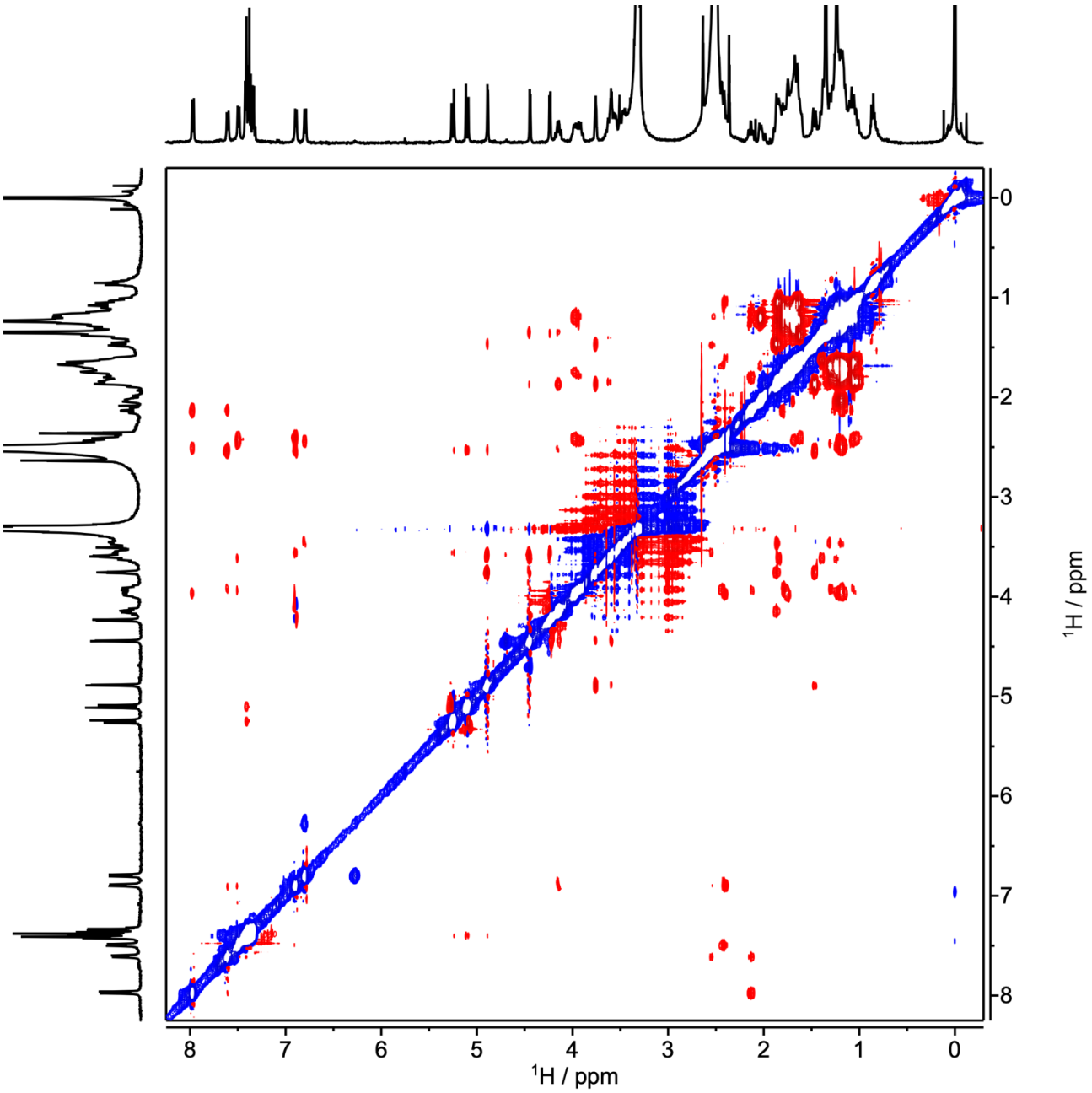


Figure S44: ROESY spectrum of peptide **16**, t_{mix} = 200 ms (DMSO-d_6, 500 MHz, 298 K).

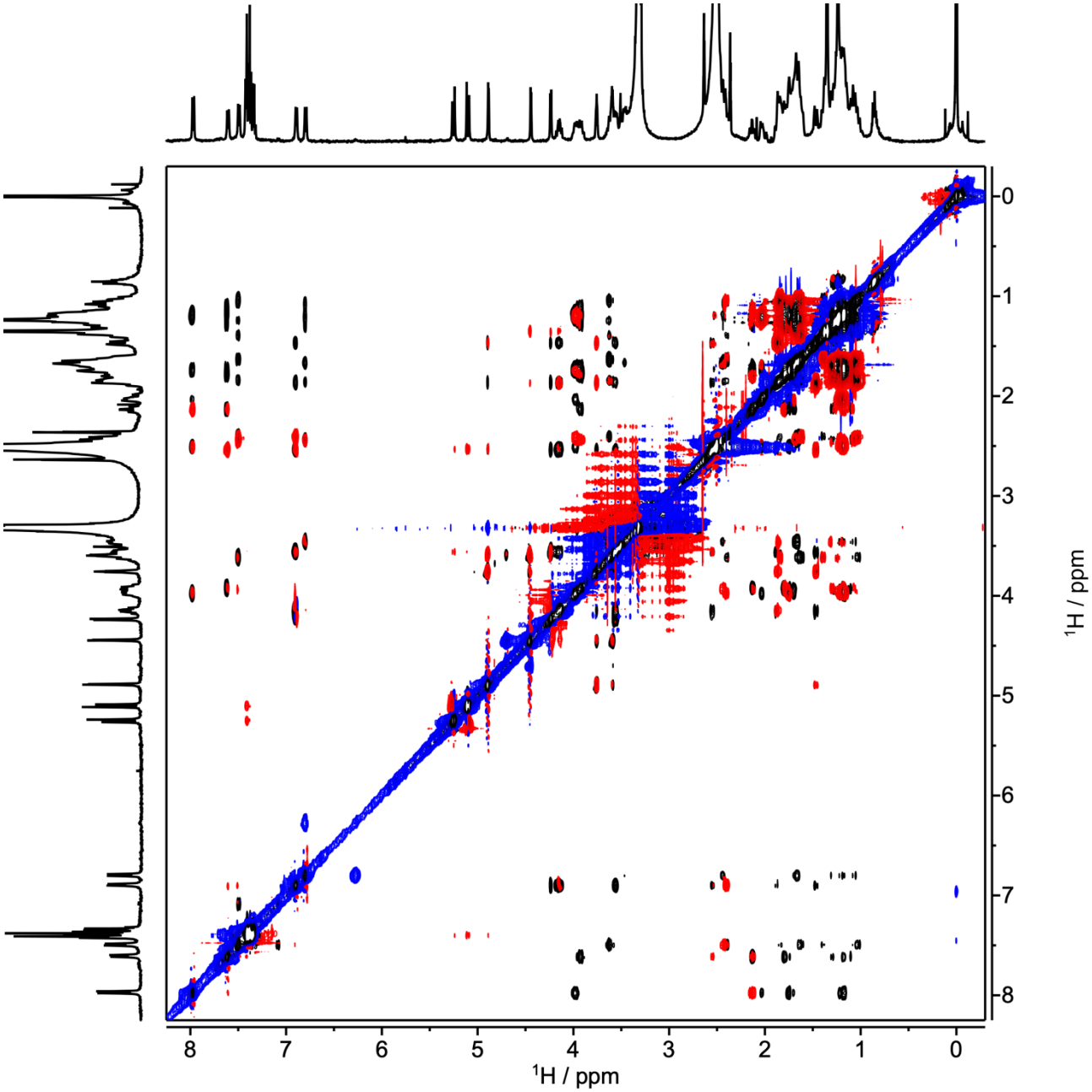


Figure S45: Overlay of the ROESY (*red/blue*, t_{mix} 200 ms) and TOCSY (*black*, t_{mix} 80 ms) spectra of peptide **16** (DMSO-d_6, 500 MHz, 298 K).

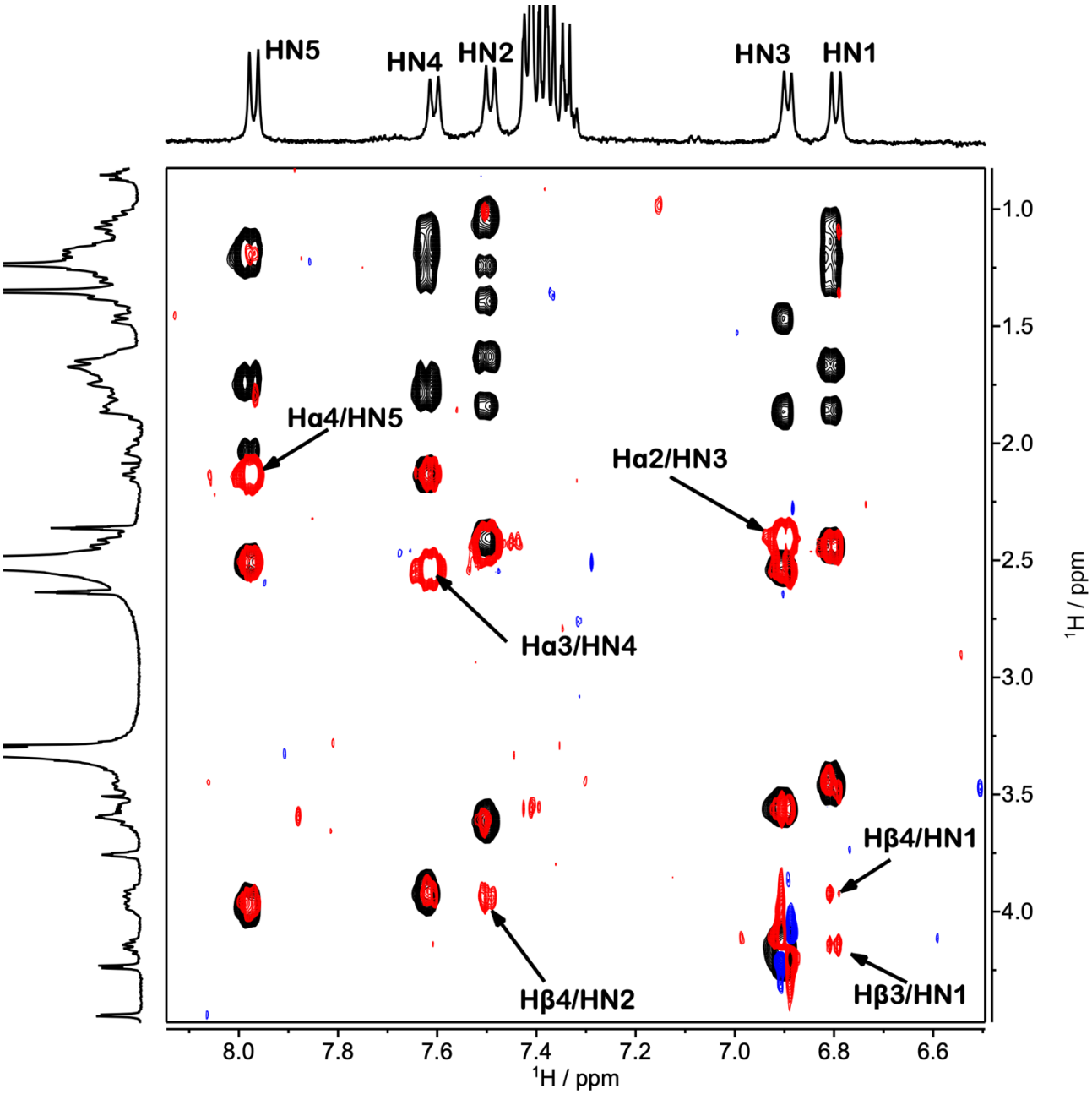


Figure S46: Overlay of the ROESY (*red/blue*, t_{mix} 200 ms) and TOCSY (*black*, t_{mix} 80 ms) spectra of peptide **16** (DMSO-d_6, 500 MHz, 298 K). Expansion of the (Hα+Hβ)/HN region.

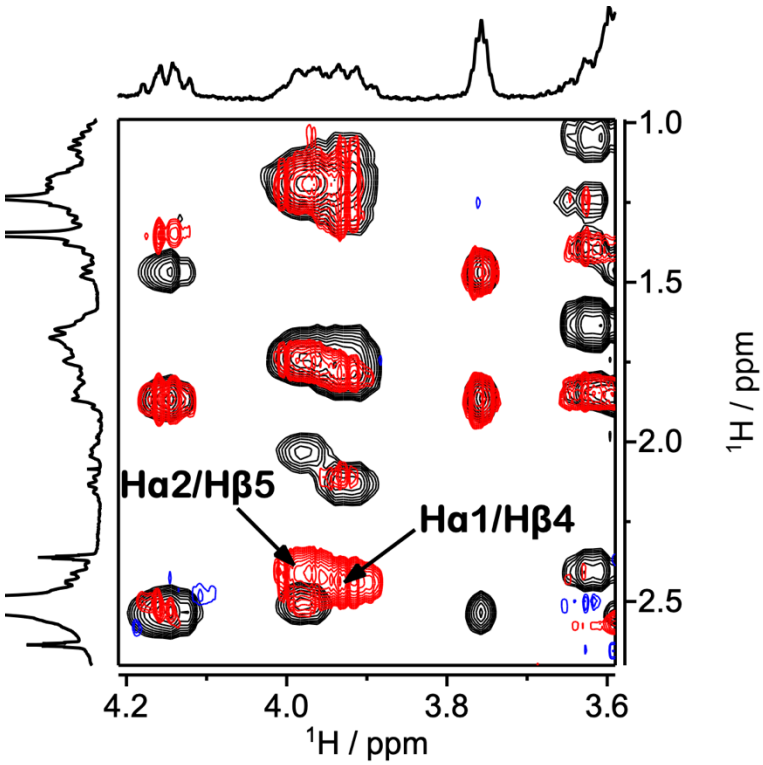
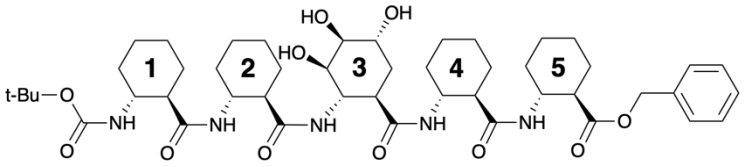


Figure S47: Overlay of the ROESY (*red/blue*, t_{mix} 200 ms) and TOCSY (*black*, t_{mix} 80 ms) spectra of peptide **16** (DMSO-d_6, 500 MHz, 298 K). Expansion of the Hα/Hβ region.

V-D. Peptide 16: NMR spectroscopy in methanol-d_3



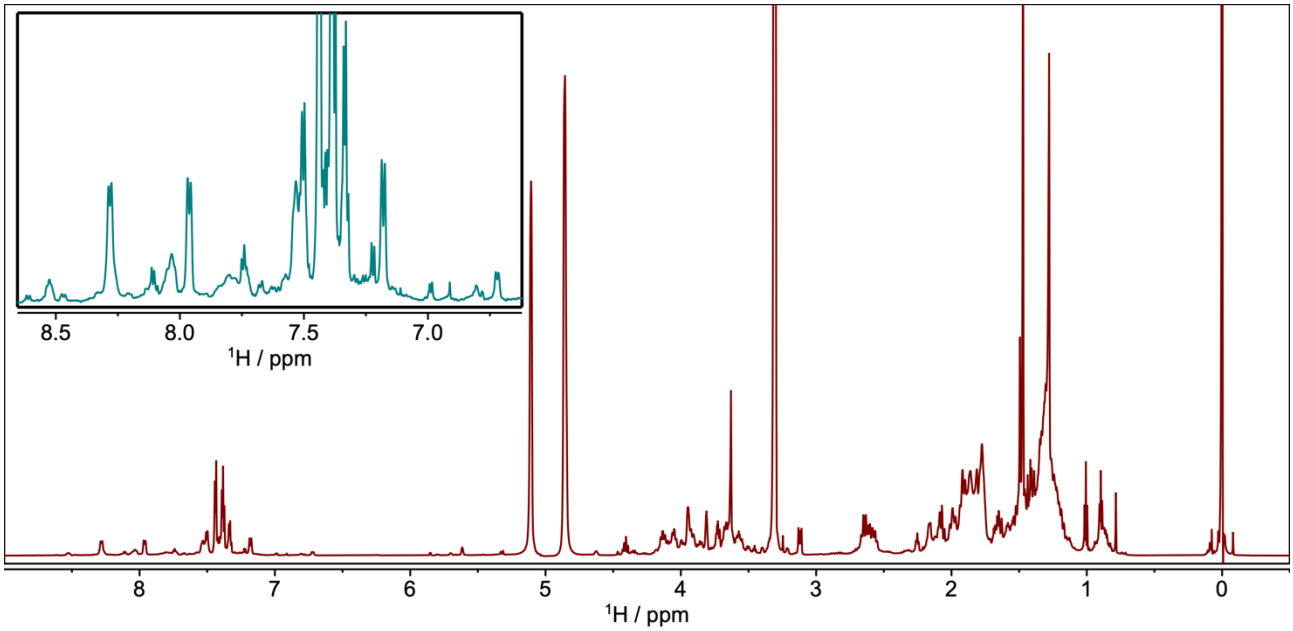


Figure S48: ^{1}H-NMR spectrum of peptide **16** at 1 mM concentration (methanol-d_3, 500 MHz, 298 K).

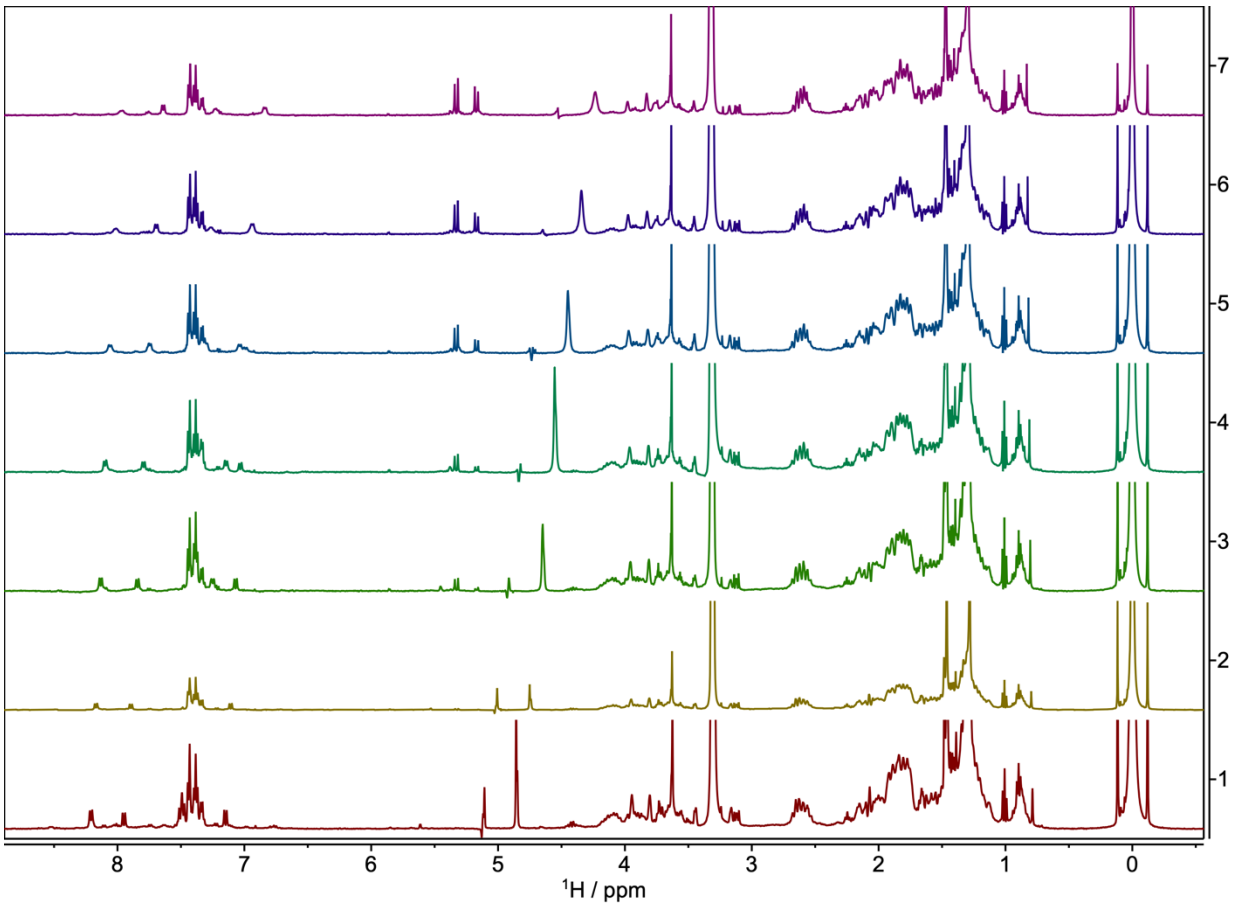


Figure S49: VT-NMR spectra of peptide **16** in methanol-d_3 (500 MHz). Temperatures, from bottom to top: 273 to 333 K in 10 K steps. The *zggpw5* pulse program was used to suppress the strong HO signal.

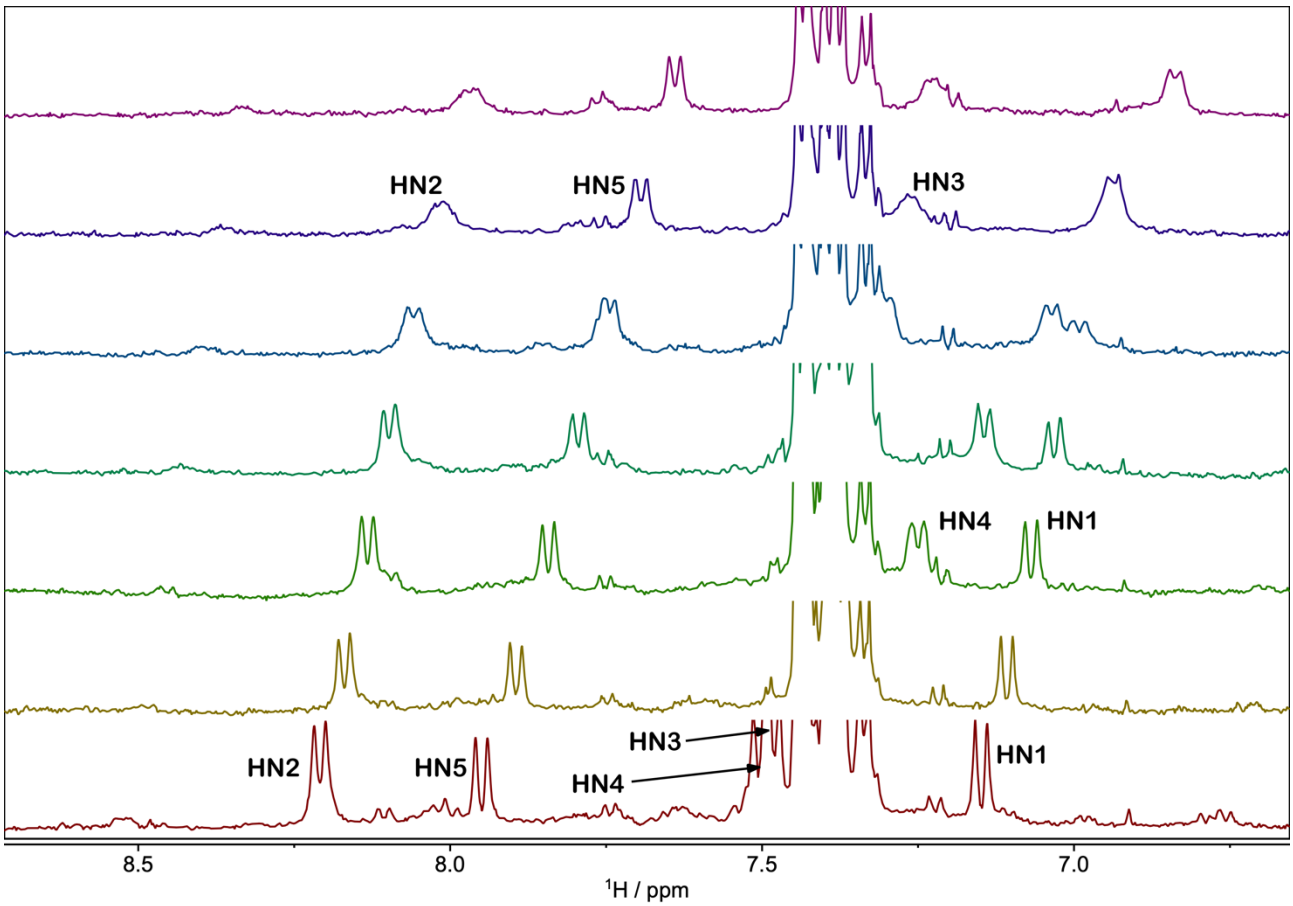


Figure S50: Expansion of the amide proton region of the VT-NMR spectra of peptide **16** in methanol-d_3 (500 MHz). Temperatures, from bottom to top: 273 to 333 K in 10 K steps.

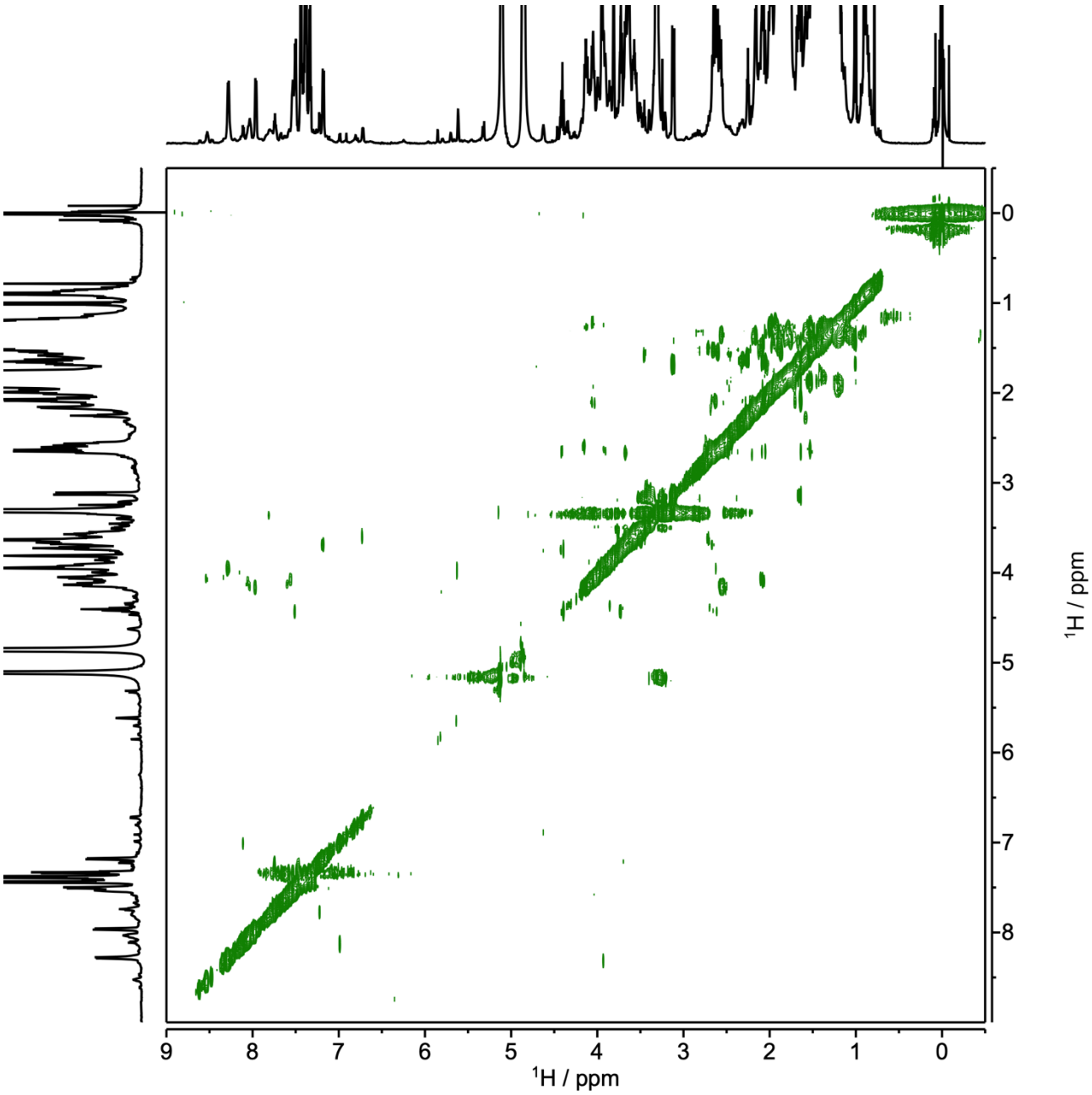


Figure S51: CLIP-COSY spectrum of peptide **16** (methanol-d_3, 750 MHz, 273 K).

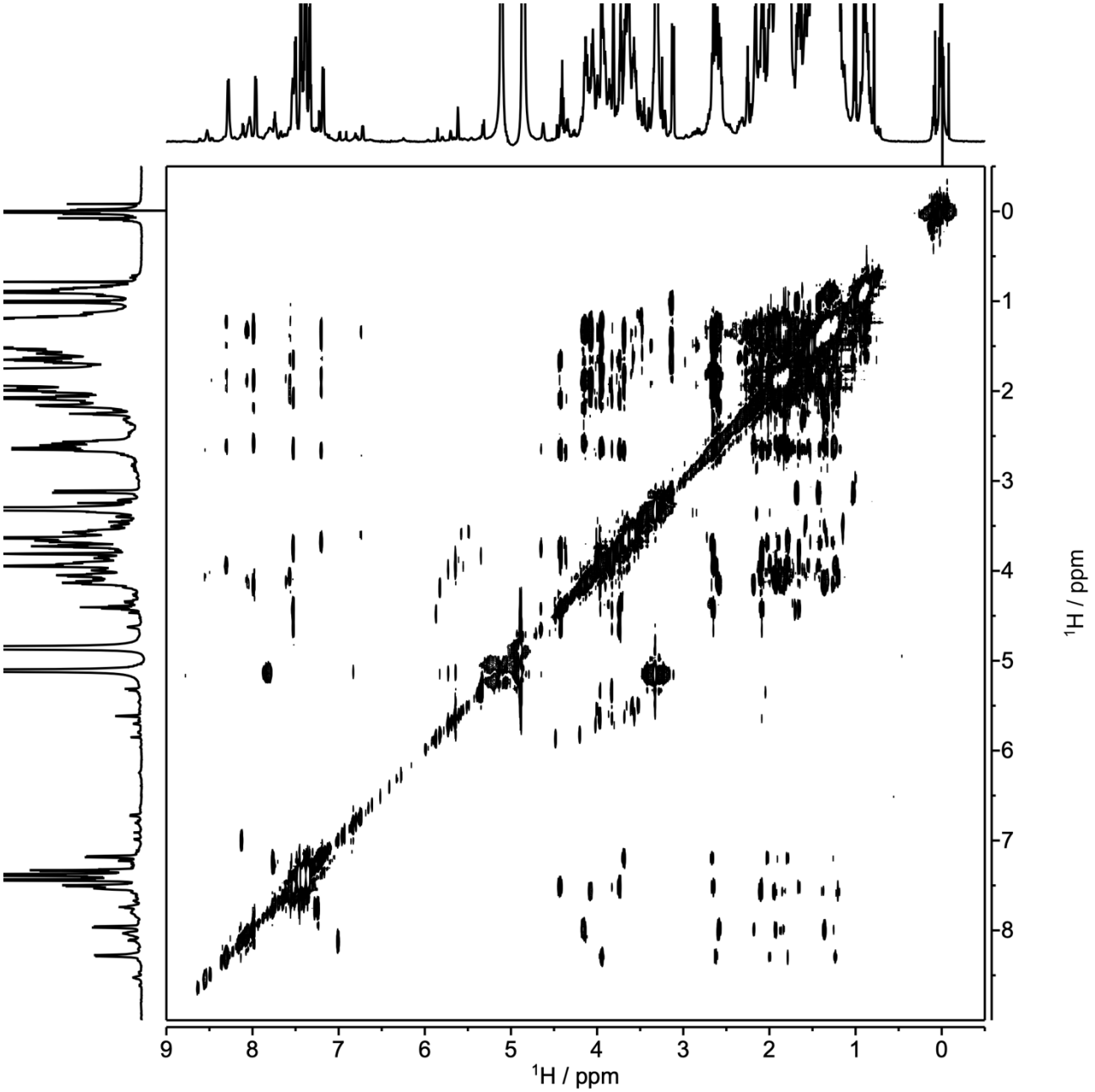


Figure S52: TOCSY spectrum of peptide **16**, t_{mix} = 80 ms (methanol-d_3, 750 MHz, 273 K).

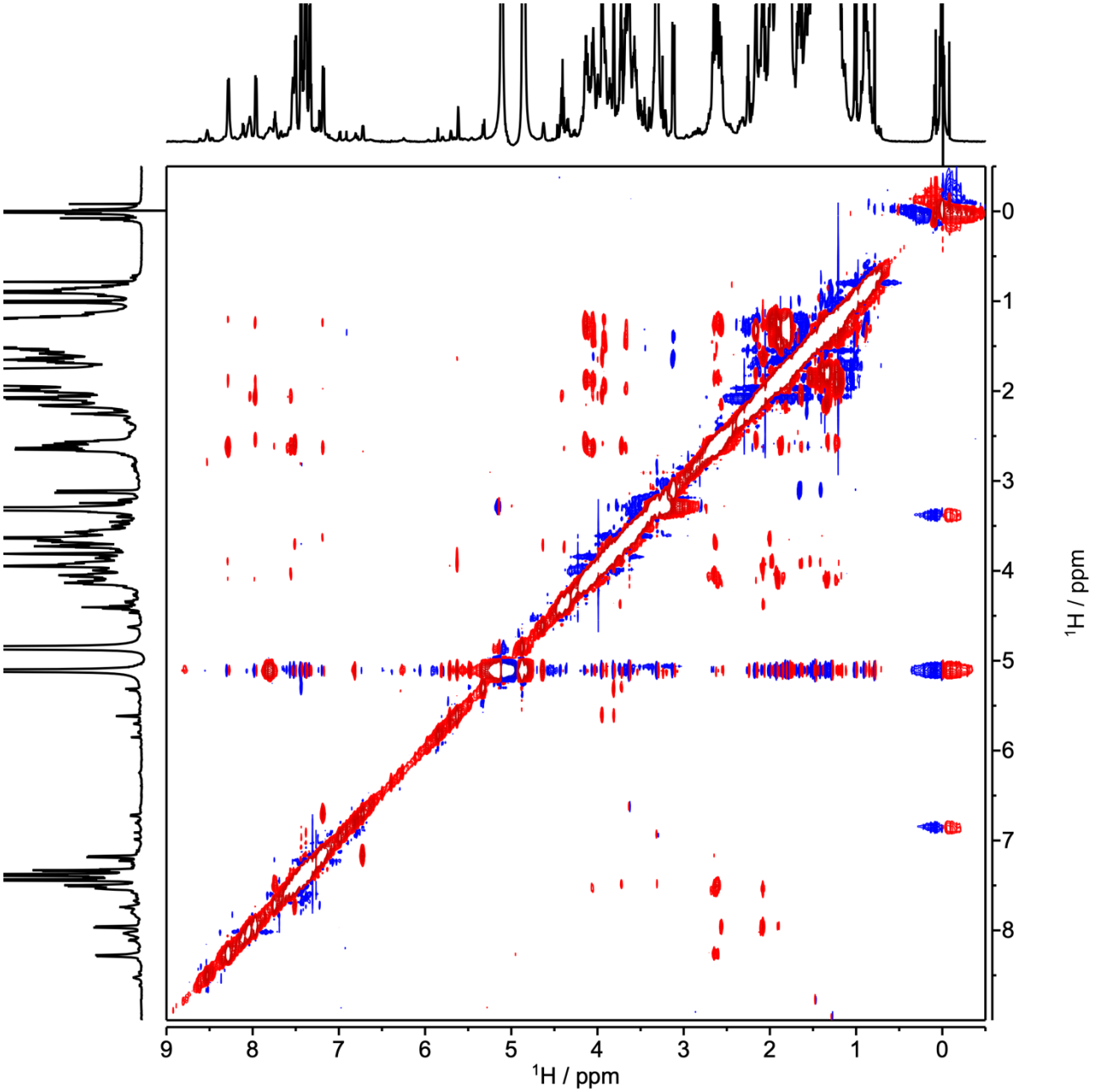


Figure S53: NOESY spectrum of peptide **16**, t_{mix} = 500 ms (methanol-d_3, 750 MHz, 273 K).

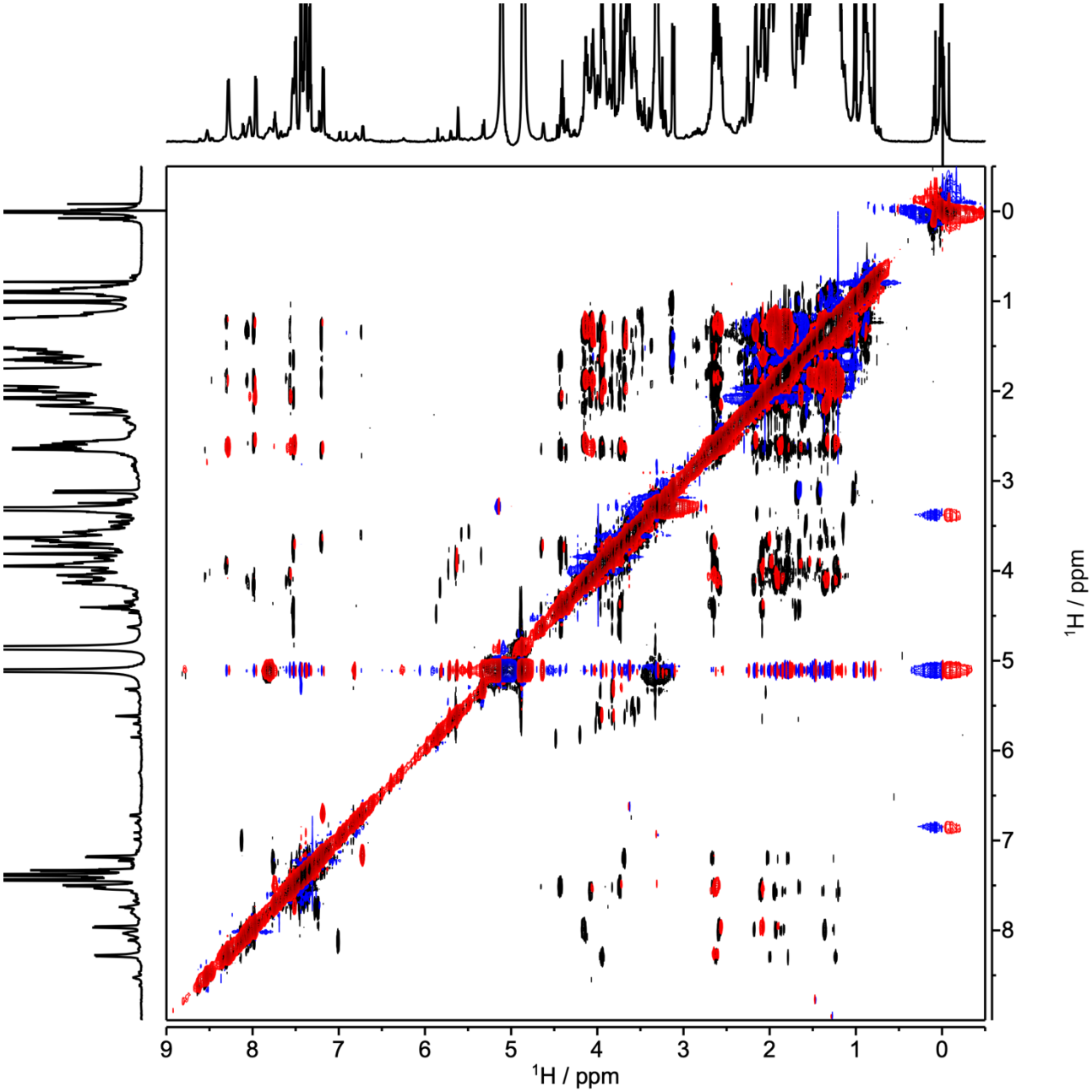


Figure S54: Overlay of the NOESY (*red/blue*, t_{mix} 500 ms) and TOCSY (*black*, t_{mix} 80 ms) spectra of peptide **16** (methanol-d_3, 750 MHz, 273 K).

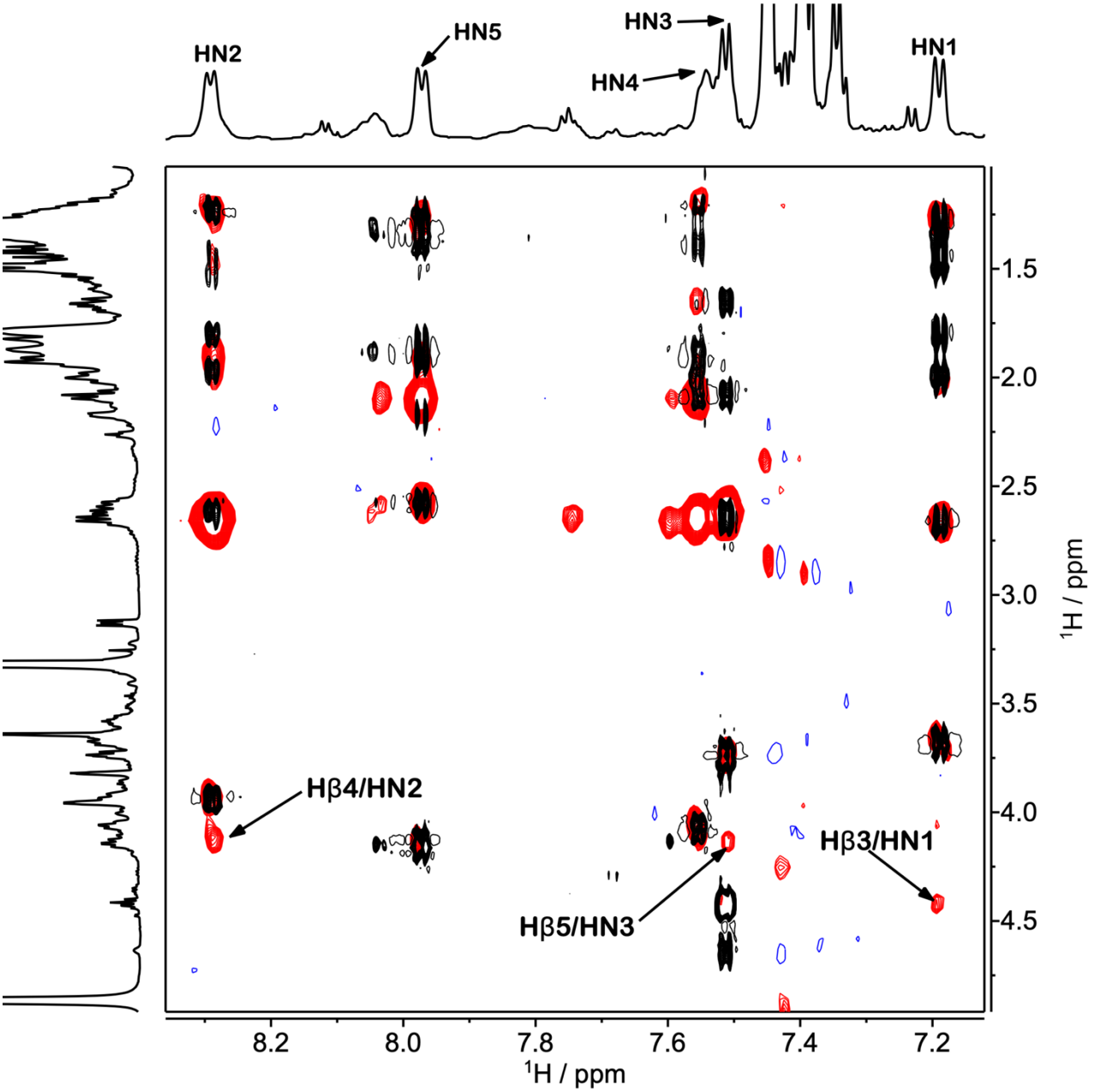


Figure S55: Overlay of the NOESY (*red/blue*, t_{mix} 500 ms) and TOCSY (*black*, t_{mix} 80 ms) spectra of peptide **16** (methanol-d_3, 750 MHz, 273 K). Expansion of the (Hα+Hβ)/HN region. Assignment of the HN peaks of the major conformer is shown.

V-E. NMR SPECTROSCOPY - TABLES

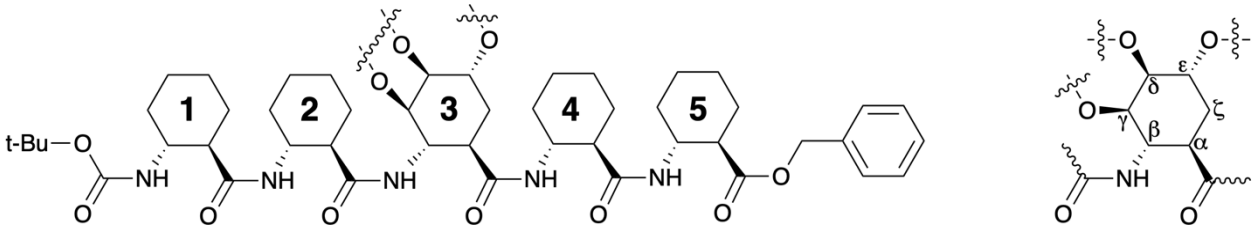


Figure S56: Residue and atom naming used in the following tables.

Table S2: Assignment of pentapeptide **14** in DMSO-d_6 (T = 298 K). Spectra were referenced to the resonance of TMS (δ = 0.00 ppm).

residue	HN	Hβ	Hα	Other
t-Bu	—	—	—	1.35
1	6.77	3.45	2.27	0.98, 1.01, 1.11, 1.20, 1.31, 1.34, 1.43, 1.65, 1.86
2	7.49	3.67	2.35	1.07, 1.10, 1.12, 1.14, 1.21, 1.30, 1.64, 1.67, 1.77, 1.80
3	6.83	4.02	2.34	0.03 (Si-CH_3), 0.04 (Si-CH_3), 0.08 (Si-*t*Bu), 1.20 (CH_3), 1.48 (CH_3), 1.57 and 1.89 (Hζ*), 3.83-3.87 (Hγ, Hδ, Hε)
4	7.40	3.87	2.18	1.10, 1.12, 1.16, 1.30, 1.71, 1.76, 1.78
5	7.82	3.93	2.52	1.19, 1.21, 1.23, 1.68, 1.72, 1.79, 1.88, 1.98
-O-CH_2-Ph	—	—	—	4.98 and 5.26 (CH_2), 7.32-7.39 (Ph)

Table S3: Assignment of pentapeptide **15** in DMSO-d_6 (T = 298 K). Spectra were referenced to the resonance of TMS (δ = 0.00 ppm).

residue	HN	Hβ	Hα	other
t-Bu	—	—	—	1.35
1	6.92	3.44	2.35	0.99, 1.32, 1.66, 1.91
2	7.49	3.70	2.36	1.09, 1.27, 1.65, 1.76
3	6.72	4.05	2.44	1.21 (CH_3), 1.52 (CH_3), 1.63 and 1.83 (Hζ*), 3.77 (Hγ), 3.96 (Hδ), 4.02 (Hε), 5.20 (HO-ε)
4	7.53	3.87	2.13	1.12, 1.26, 1.79
5	7.91	3.95	2.54	1.17, 1.24, 1.80
-O-CH_2-Ph	—	—	—	5.09 and 5.28 (CH_2), 7.29-7.44 (Ph)

Table S4: Assignment of pentapeptide **16** in DMSO-d_6 (T = 298 K). Spectra were referenced to the resonance of TMS (δ = 0.00 ppm).

residue	HN	Hβ	Hα	other
t-Bu	—	—	—	1.35
1	6.80	3.46	2.44	1.06, 1.19, 1.32, 1.67, 1.86
2	7.49	3.62	2.41	1.03, 1.08, 1.24, 1.38, 1.62, 1.85
3	6.89	4.19	2.54	1.47 and 1.88 (Hζ*), 3.56 (Hγ), 3.60 (Hδ), 3.76 (Hε), 4.25 (HO-γ), 4.47 (HO-δ), 4.89 (HO-ε)
4	7.61	3.93	2.13	1.09, 1.10, 1.19, 1.30, 1.73, 1.80
5	7.97	3.97	2.50	1.18, 1.21, 1.71, 1.75
-O-CH_2-Ph	—	—	—	5.10 and 5.25 (CH_2), 7.31-7.44 (Ph)

Table S5: Properties of amide HN protons (DMSO-d_6, 500 MHz). Chemical shifts and scalar couplings were determined at 298 K. Temperature coefficients in –ppb/K units.

	δ_H (ppm)			$^3J_{HN\text{-}H\beta}$ (Hz)			T-coef (–ppb/K)		
	14	**15**	**16**	**14**	**15**	**16**	**14**	**15**	**16**
HN1	6.77	6.92	6.80	8.3	8.5	8.8	7.3	7.5	5.2
HN2	7.49	7.49	7.49	7.9	8.3	8.6	5.6	4.9	4.3
HN3	6.83	6.71	6.89	8.3	9.2	7.3	0.9	1.7	3.4
HN4	7.40	7.53	7.61	8.4	8.6	8.6	9.0	9.2	8.2
HN5	7.82	7.91	7.97	7.9	8.6	8.9	5.2	5.4	4.9

Table S6: Properties of hydroxyl HO protons of residue 3 (DMSO-d_6, 500 MHz). Chemical shifts and scalar couplings were determined at 298 K. Temperature coefficients in –ppb/K units.

	δ_H (ppm)			$^3J_{HN\text{-}H\beta}$ (Hz)			T-coef (–ppb/K)		
	14	**15**	**16**	**14**	**15**	**16**	**14**	**15**	**16**
HO-γ	—	—	4.24	—	—	5.1	—	—	0.7
HO-δ	—	—	4.45	—	—	3.1	—	—	6.4
HO-ε	—	5.20	4.89	—	3.3	2.9	—	5.6	4.8

V-F. TABLES OF NOEs

Table S7: Summary of backbone NOE intensities from the ROESY spectra of pentapeptides **14**, **15** and **16** (DMSO-d_6, 500 MHz, 298 K). Classification of NOE intensities: ***S*** strong, ***M*** medium, ***W*** weak, ***X*** overlapped. The dash (—) indicates absence of cross-peak.

proton (residue)	proton (residue)	14	15	16
Intra-residual: HN(i) / Hα(i)				
HN (1)	Hα (1)	S	S	S
HN (2)	Hα (2)	S	S	S
HN (3)	Hα (3)	S	S	S
HN (4)	Hα (4)	S	S	S
HN (5)	Hα (5)	S	S	S
Intra-residual: HN(i) / Hβ(i)				
HN (1)	Hβ (1)	M	M	M
HN (2)	Hβ (2)	M	M	M
HN (3)	Hβ (3)	M	M	M
HN (4)	Hβ (4)	M	M	M
HN (5)	Hβ (5)	M	M	M
Inter-residual: HN(i) / Hα(i–1)				
HN (2)	Hα (1)	S	S	S
HN (3)	Hα (2)	S	S	S
HN (4)	Hα (3)	S	S	S
HN (5)	Hα (4)	S	S	S
Inter-residual: HN(i) / Hβ(i–1)				
HN (2)	Hβ (1)	W	W	—
HN (3)	Hβ (2)	—	—	*X*
HN (4)	Hβ (3)	W	—	—
HN (5)	Hβ (4)	*X*	—	*X*
Inter-residual: HN(i) / Hβ(i+2)				
HN (1)	Hβ (3)	—	—	M
HN (2)	Hβ (4)	*X*	M	M
HN (3)	Hβ (5)	*X*	*X*	*X*
Inter-residual: HN(i) / Hβ(i+3)				
HN (1)	Hβ (4)	M	M	W
HN (2)	Hβ (5)	M	—	—
Inter-residual: Hα(i) / Hβ(i+3)				
Hα (1)	Hβ (4)	S	S	S
Hα (2)	Hβ (5)	S	S	S
Inter-residual: HN / HN				
HN (3)	HN (2)	—	—	M
HN (3)	HN (4)	—	—	W

Table S8: Summary of inter-residual NOE contacts of residue 3 with the *N*-terminal *t*-Bu group and the *C*-terminal OBn group, determined from the ROESY spectra of pentapeptides **14**, **15** and **16** (DMSO-d_6, 500 MHz, 298 K). Classification of NOE intensities: ***S*** strong, ***M*** medium, ***W*** weak, ***X*** overlapped. The dash (—) indicates absence of cross-peak.

proton (residue)	**proton (residue)**	**14**	**15**	**16**
Inter-residual: t-Bu				
t-Bu (1)	Hα (3)	—	—	—
t-Bu (1)	Hβ (3)	W	W[b*]	W
t-Bu (1)	Hγ (3)	—	—	—
t-Bu (1)	Hδ (3)	—	—	—
t-Bu (1)	Hε (3)	—	W[b*]	—
t-Bu (1)	HO-γ (3)	*n.e.*	*n.e.*	W
t-Bu (1)	HO-δ (3)	*n.e.*	*n.e.*	M
t-Bu (1)	HO-ε (3)	*n.e.*	—	—
Inter-residual: Benzylic CH_2				
OCH_2–a (5)	HN (3)	—	W	W
OCH_2–b (5)	HN (3)	—	W	—
OCH_2–a (5)	Hα (3)	W	M	M
OCH_2–b (5)	Hα (3)	W	M	M
OCH_2–a (5)	Hγ (3)	W[a*]	M	M[c*]
OCH_2–b (5)	Hγ (3)	W[a*]	W	W[c*]
OCH_2–a (5)	Hδ (3)	W[a*]	—	M[c*]
OCH_2–b (5)	Hδ (3)	W[a*]	—	W[c*]
OCH_2–a (5)	Hε (3)	W[a*]	—	—
OCH_2–b (5)	Hε (3)	W[a*]	—	—
OCH_2–a (5)	HO-ε (3)	*n.e.*	—	—
OCH_2–b (5)	HO-ε (3)	*n.e.*	—	—
Inter-residual: Benzylic Ph				
Ph (5)	HO-γ (3)	*n.e.*	*n.e.*	—
Ph (5)	HO-δ (3)	*n.e.*	*n.e.*	—
Ph (5)	HO-ε (3)	*n.e.*	W	W
Ph (5)	Hγ (3)	—	W	W[c*]
Ph (5)	Hδ (3)	—	W	W[c*]
Ph (5)	Hε (3)	—	—	—

O-CH_2*. The two diastereotopic benzylic protons give separate peaks but were not assigned stereospecifically. Labels 'a' and 'b' refer to the most deshielded and most shielded resonances, respectively.

n.e.: not existing, *i.e.* one or two of the H atoms do not exist in this compound.

[a*] Hγ(3), Hδ(3) and Hε(3) overlap in **14**.

[b*] Hβ(3) and Hε(3) overlap in **15**.

[c*] Hγ(3) and Hδ(3) overlap in **16**.

Table S9: Summary of intra-residual NOE contacts of residue 3 in the ROESY spectra of pentapeptides **14**, **15** and **16** (DMSO-d_6, 500 MHz, 298 K). Classification of NOE intensities: ***S*** strong, ***M*** medium, ***W*** weak, ***X*** overlapped. The dash (—) indicates absence of cross-peak.

proton (residue)	proton (residue)	14	15	16
Intra-residual: hydroxyls				
HO-ε (3)	Hα (3)	*n.e.*	M	W
HO-ε (3)	Hβ (3)	*n.e.*	W	—
HO-ε (3)	Hγ (3)	*n.e.*	W	—
HO-ε (3)	Hδ (3)	*n.e.*	M	M
HO-ε (3)	Hε (3)	*n.e.*	M	S
Intra-residual: acetonide				
Me-a (3)	Hα (3)	—	—	*n.e.*
Me-b (3)	Hα (3)	—	—	*n.e.*
Me-a (3)	Hβ (3)	S	S[b*]	*n.e.*
Me-b (3)	Hβ (3)	W	M[b*]	*n.e.*
Me-a (3)	Hγ (3)	*X*[a*]	W	*n.e.*
Me-b (3)	Hγ (3)	*X*[a*]	M	*n.e.*
Me-a (3)	Hδ (3)	*X*[a*]	W	*n.e.*
Me-b (3)	Hδ (3)	*X*[a*]	S	*n.e.*
Me-a (3)	Hε (3)	*X*[a*]	S[b*]	*n.e.*
Me-b (3)	Hε (3)	*X*[a*]	M[b*]	*n.e.*
Me-a (3)	HO-ε (3)	*n.e.*	W	*n.e.*
Me-b (3)	HO-ε (3)	*n.e.*	M	*n.e.*

Me-a and *Me-b* refer to the methyl groups of the acetonide protecting group of residue 3. The two diastereotopic methyl groups give separate peaks but were not assigned stereospecifically. Labels 'a' and 'b' refer to the most deshielded and most shielded methyl resonances, respectively.

n.e.: not existing, *i.e.* one or two of the H atoms do not exist in this compound.

[a*] Hγ(3), Hδ(3) and Hε(3) resonances overlap in **14**.

[b*] Hβ(3) and Hε(3) resonances overlap in **15**.

Table S10: Assignment of pentapeptide **16** in CD_3-OH (T = 273 K, 750 MHz). Spectra were referenced to the resonance of TMS (δ = 0.00 ppm).

residue	HN	Hβ	Hα	other
t-Bu	—	—	—	1.47
1	7.19	3.68	2.66	1.31, 1.46, 1.81, 1.99
2	8.29	3.94	2.60	1.25, 1.51, 1.80, 1.96
3	7.51	4.42	2.63	3.73 and 4.63 (Hγ, Hδ and Hε); 1.65, 2.08
4	7.56	4.06	2.08	1.22, 1.42, 1.87
5	7.97	4.15	2.57	1.31, 1.89, 2.19
-O-CH_2-Ph	—	—	—	7.31-7.46 (Ph)

Table S11: Properties of the amide HN protons of pentapeptide **16** in CD_3-OH (T = 273 K, 750 MHz). Scalar couplings were determined at 273 K and 750 MHz.

	$^3J_{HN\text{-}H\beta}$ (Hz)	T-coef (–ppb/K)
HN1	9.2	5.2
HN2	8.3	4.0
HN3	8.2	4.2
HN4	8.6	11.0
HN5	9.2	5.2

VI. CARTESIAN COORDINATES OF PENTAPEPTIDES 14-16

Cartesian coordinates (Å) of conformations optimized at the M052X/6-31G(d) level.

Peptide 14:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-4.119268	-1.871251	-0.525786
2	6	0	-4.358270	-3.114948	-0.051754
3	8	0	-5.461122	-3.624593	0.046234
4	6	0	-3.214895	-5.066523	0.841217
5	8	0	-3.189865	-3.716635	0.297608
6	6	0	-3.929915	-5.072333	2.187774
7	6	0	-3.845936	-6.042624	-0.148759
8	6	0	-1.737952	-5.396510	1.016779
9	6	0	-4.868337	0.338628	-1.252561
10	6	0	-5.176774	-1.162388	-1.228898
11	6	0	-5.350849	-1.706170	-2.650632
12	6	0	-6.437259	-0.950105	-3.414381
13	6	0	-6.116833	0.543987	-3.455752
14	6	0	-5.948777	1.095035	-2.040341
15	6	0	-4.847567	0.875355	0.170564
16	8	0	-5.809972	0.725665	0.912469
17	7	0	-3.732017	1.546672	0.543612
18	6	0	-2.138604	2.038110	2.332566
19	6	0	-3.607375	2.069479	1.892561
20	6	0	-4.184378	3.477674	2.029401
21	6	0	-4.060834	3.967802	3.473443
22	6	0	-2.605836	3.915951	3.945584
23	6	0	-2.023068	2.509656	3.786607
24	6	0	-1.641001	0.612909	2.175291
25	8	0	-2.200198	-0.314804	2.738174
26	7	0	-0.576448	0.452928	1.340379
27	6	0	0.420113	-1.028448	-0.409871
28	6	0	-0.050549	-0.860934	1.046522
29	6	0	1.140918	-1.222738	1.940690
30	6	0	1.668073	-2.631298	1.651740
31	6	0	1.679437	-3.100039	0.197037
32	8	0	0.776034	-1.314078	3.305950
33	8	0	0.763966	-3.415707	2.413789
34	6	0	0.520631	-2.691773	3.621124
35	6	0	1.505660	-3.116551	4.699015
36	6	0	-0.919833	-2.899929	4.031589
37	8	0	2.924896	-2.677262	-0.366638
38	14	0	3.982749	-3.821891	-1.004235
39	6	0	5.473721	-2.830559	-1.607293
40	6	0	4.464899	-5.043515	0.343743
41	6	0	3.136802	-4.740558	-2.412717
42	6	0	5.000636	-1.732972	-2.568546
43	6	0	6.171009	-2.188295	-0.400707
44	6	0	6.459140	-3.752226	-2.337685
45	6	0	0.547249	-2.534922	-0.655078
46	6	0	-0.538224	-0.394463	-1.395860
47	8	0	-1.628949	-0.888426	-1.669114
48	7	0	-0.108390	0.745400	-1.987322
49	6	0	-0.603130	2.989457	-2.849720
50	6	0	-1.008322	1.513933	-2.838666
51	6	0	-1.074742	0.958871	-4.260828

52	6	0	-2.071064	1.763224	-5.097892
53	6	0	-1.712158	3.250421	-5.102463
54	6	0	-1.617793	3.796031	-3.676594
55	6	0	-0.560809	3.500868	-1.421270
56	8	0	-1.435523	3.211254	-0.611599
57	7	0	0.499123	4.279229	-1.098240
58	6	0	2.270018	4.330036	0.586214
59	6	0	0.803175	4.635798	0.278933
60	6	0	0.472688	6.094402	0.595880
61	6	0	0.797082	6.419547	2.055467
62	6	0	2.261117	6.110762	2.372571
63	6	0	2.592595	4.651269	2.059301
64	6	0	2.604746	2.883875	0.302523
65	8	0	1.796167	1.980306	0.197952
66	8	0	3.917877	2.697962	0.201005
67	6	0	4.347477	1.328249	-0.024430
68	6	0	5.837301	1.338777	-0.190762
69	6	0	6.399117	1.516156	-1.454187
70	6	0	6.671478	1.169338	0.913015
71	6	0	7.780718	1.517527	-1.615857
72	6	0	8.053325	1.168333	0.755130
73	6	0	8.608513	1.340682	-0.510230
74	1	0	-3.158251	-1.636035	-0.743172
75	1	0	-4.980807	-4.822300	2.061810
76	1	0	-3.466120	-4.344586	2.856039
77	1	0	-3.846750	-6.064047	2.639077
78	1	0	-3.369163	-5.933941	-1.125619
79	1	0	-4.912701	-5.865611	-0.250477
80	1	0	-3.678333	-7.063326	0.203598
81	1	0	-1.240701	-5.416207	0.043435
82	1	0	-1.631979	-6.380004	1.479260
83	1	0	-1.244071	-4.654845	1.644278
84	1	0	-3.892342	0.477934	-1.730830
85	1	0	-6.095340	-1.309589	-0.658603
86	1	0	-5.587386	-2.770032	-2.582558
87	1	0	-4.390787	-1.608410	-3.172763
88	1	0	-7.399816	-1.097428	-2.913073
89	1	0	-6.538210	-1.349746	-4.426549
90	1	0	-6.903248	1.093630	-3.979503
91	1	0	-5.188439	0.694252	-4.020128
92	1	0	-6.888091	0.997767	-1.488592
93	1	0	-5.698786	2.160095	-2.065681
94	1	0	-2.999905	1.750248	-0.121437
95	1	0	-1.571416	2.711742	1.683709
96	1	0	-4.167480	1.384898	2.532527
97	1	0	-5.228921	3.454316	1.712727
98	1	0	-3.639920	4.147136	1.352646
99	1	0	-4.668679	3.325901	4.119628
100	1	0	-4.455198	4.982554	3.567372
101	1	0	-2.529568	4.238199	4.987163
102	1	0	-2.013769	4.619812	3.346646
103	1	0	-2.563120	1.799220	4.418662
104	1	0	-0.975174	2.488471	4.100521
105	1	0	-0.124699	1.264886	0.947930
106	1	0	1.405520	-0.564003	-0.523930
107	1	0	-0.867685	-1.559605	1.236614
108	1	0	1.906810	-0.449772	1.839702
109	1	0	2.687910	-2.737683	2.039389
110	1	0	1.610728	-4.193975	0.217458
111	1	0	1.372972	-2.489276	5.580960
112	1	0	2.530525	-3.002277	4.343587
113	1	0	1.334543	-4.158523	4.971056

114	1	0	-1.588467	-2.534676	3.255453
115	1	0	-1.122706	-2.336763	4.942859
116	1	0	-1.094467	-3.961087	4.218846
117	1	0	4.892641	-4.528720	1.206299
118	1	0	5.203160	-5.759696	-0.025263
119	1	0	3.600757	-5.614418	0.691575
120	1	0	3.776254	-5.538444	-2.797477
121	1	0	2.893475	-4.069478	-3.239025
122	1	0	2.205599	-5.201565	-2.074016
123	1	0	4.522571	-2.154636	-3.456917
124	1	0	5.854946	-1.131536	-2.899874
125	1	0	4.281637	-1.068973	-2.082715
126	1	0	5.469399	-1.597521	0.194183
127	1	0	6.972973	-1.518125	-0.731134
128	1	0	6.614016	-2.945144	0.252018
129	1	0	6.010230	-4.197309	-3.229807
130	1	0	6.810512	-4.562790	-1.692793
131	1	0	7.338620	-3.182424	-2.657960
132	1	0	0.777090	-2.747066	-1.701550
133	1	0	-0.404470	-3.013369	-0.414416
134	1	0	0.726023	1.178410	-1.619400
135	1	0	0.388912	3.083948	-3.311013
136	1	0	-2.004455	1.450432	-2.395338
137	1	0	-1.367887	-0.090273	-4.205986
138	1	0	-0.075749	1.007089	-4.709000
139	1	0	-3.074219	1.636575	-4.676884
140	1	0	-2.103205	1.376960	-6.118491
141	1	0	-2.453069	3.820956	-5.666444
142	1	0	-0.748592	3.389623	-5.605642
143	1	0	-2.590316	3.724021	-3.179762
144	1	0	-1.332681	4.851135	-3.682799
145	1	0	1.172154	4.498281	-1.814997
146	1	0	2.921628	4.946612	-0.044201
147	1	0	0.176375	3.989829	0.895476
148	1	0	-0.584381	6.262333	0.381788
149	1	0	1.052307	6.746003	-0.068496
150	1	0	0.153194	5.820675	2.708341
151	1	0	0.575027	7.467826	2.262747
152	1	0	2.475673	6.317382	3.422740
153	1	0	2.909576	6.762270	1.776739
154	1	0	1.995420	3.991998	2.698526
155	1	0	3.644813	4.437341	2.251985
156	1	0	4.032870	0.724652	0.826860
157	1	0	3.843518	0.954275	-0.915062
158	1	0	5.750722	1.639210	-2.314266
159	1	0	6.235991	1.024759	1.895117
160	1	0	8.210065	1.648807	-2.600863
161	1	0	8.695254	1.027229	1.615139
162	1	0	9.683782	1.333777	-0.635124

Peptide 15:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	4.109606	0.640959	-0.513784
2	1	0	3.156362	0.683356	-0.853039

3	6	0	4.735968	1.824021	-0.314904
4	8	0	5.935112	1.958484	-0.144679
5	6	0	4.309007	4.214450	-0.212811
6	8	0	3.835399	2.843025	-0.336408
7	6	0	3.040778	5.038160	-0.399484
8	1	0	2.272802	4.743853	0.315674
9	1	0	2.648839	4.896959	-1.409855
10	1	0	3.265830	6.097833	-0.262412
11	6	0	4.901186	4.441437	1.173736
12	1	0	5.146690	5.499270	1.294844
13	1	0	5.801756	3.845807	1.303633
14	1	0	4.174494	4.161968	1.938365
15	6	0	5.304190	4.547897	-1.321812
16	1	0	4.877124	4.280140	-2.291120
17	1	0	6.240680	4.015032	-1.184132
18	1	0	5.494576	5.623813	-1.316134
19	6	0	4.081663	-1.802069	-0.633497
20	1	0	3.167717	-1.727880	-1.234237
21	6	0	4.905545	-0.528861	-0.856193
22	1	0	5.754147	-0.551683	-0.170722
23	6	0	5.406291	-0.446549	-2.301886
24	1	0	5.999476	0.464166	-2.405717
25	1	0	4.534291	-0.356735	-2.962110
26	6	0	6.223151	-1.679451	-2.685693
27	1	0	7.113366	-1.734008	-2.049955
28	1	0	6.570358	-1.599156	-3.718798
29	6	0	5.390309	-2.946078	-2.494319
30	1	0	5.974947	-3.835450	-2.743317
31	1	0	4.537352	-2.919120	-3.182966
32	6	0	4.886160	-3.042538	-1.055055
33	1	0	5.733590	-3.130597	-0.369362
34	1	0	4.268417	-3.935718	-0.919330
35	6	0	3.747671	-1.937913	0.844718
36	8	0	4.635121	-1.938587	1.687868
37	7	0	2.440428	-2.099265	1.162047
38	1	0	1.731773	-2.158797	0.445690
39	6	0	0.655006	-1.513791	2.725044
40	1	0	-0.079711	-2.091752	2.156137
41	6	0	2.028552	-2.170214	2.553819
42	1	0	2.758021	-1.580681	3.112719
43	6	0	2.017989	-3.601598	3.087915
44	1	0	3.014044	-4.028083	2.954474
45	1	0	1.313384	-4.193656	2.491784
46	6	0	1.607983	-3.617127	4.562189
47	1	0	2.364570	-3.082979	5.146562
48	1	0	1.577871	-4.642591	4.938412
49	6	0	0.252081	-2.936108	4.762513
50	1	0	-0.015419	-2.923729	5.822126
51	1	0	-0.520741	-3.516446	4.242389
52	6	0	0.264555	-1.509588	4.207590
53	1	0	0.989902	-0.895720	4.748881
54	1	0	-0.714293	-1.037747	4.331718
55	6	0	0.749849	-0.100804	2.177625
56	8	0	1.564556	0.696753	2.612457
57	7	0	-0.101019	0.178786	1.150262
58	1	0	-0.798405	-0.500732	0.886952
59	6	0	-0.418850	1.407696	-0.991636
60	1	0	-1.489845	1.234316	-1.118258
61	6	0	-0.109664	1.476760	0.514528
62	1	0	0.890402	1.891437	0.652882
63	6	0	-1.149473	2.411271	1.148174
64	1	0	-2.114495	1.900488	1.164011

65	6	0	-1.204322	3.779624	0.466829
66	1	0	-2.143550	4.284769	0.720719
67	6	0	-1.059695	3.810165	-1.047843
68	1	0	-0.752678	4.819888	-1.336373
69	8	0	-0.813501	2.764984	2.477208
70	8	0	-0.104650	4.429660	1.080965
71	6	0	-0.113737	4.017841	2.452563
72	6	0	-0.902994	5.009343	3.292000
73	1	0	-0.997498	4.629657	4.309570
74	1	0	-1.902875	5.143882	2.877464
75	1	0	-0.391017	5.971751	3.313888
76	6	0	1.313281	3.856480	2.926924
77	1	0	1.312160	3.518890	3.963456
78	1	0	1.828693	4.816423	2.861349
79	1	0	1.830977	3.106369	2.333093
80	8	0	-2.381249	3.537573	-1.538497
81	1	0	-2.348398	3.573935	-2.502665
82	6	0	-0.075588	2.774867	-1.585970
83	1	0	-0.140082	2.755713	-2.679240
84	1	0	0.951490	3.040798	-1.327565
85	6	0	0.336565	0.284556	-1.668611
86	8	0	1.548913	0.313715	-1.856143
87	7	0	-0.425221	-0.759977	-2.076246
88	1	0	-1.374920	-0.788258	-1.733890
89	6	0	-0.765873	-3.169765	-2.331001
90	1	0	-1.630666	-3.025520	-2.992106
91	6	0	0.201734	-1.999564	-2.521878
92	1	0	1.066599	-2.181489	-1.878515
93	6	0	0.684233	-1.927000	-3.969222
94	1	0	1.367039	-1.082053	-4.063301
95	1	0	-0.175776	-1.741291	-4.622498
96	6	0	1.375003	-3.236103	-4.357328
97	1	0	2.271217	-3.362608	-3.740317
98	1	0	1.707793	-3.191988	-5.396157
99	6	0	0.447119	-4.433864	-4.145615
100	1	0	0.964053	-5.365153	-4.385988
101	1	0	-0.407410	-4.355686	-4.827194
102	6	0	-0.064093	-4.484839	-2.704330
103	1	0	0.769754	-4.631305	-2.010912
104	1	0	-0.752638	-5.322484	-2.566806
105	6	0	-1.218195	-3.197734	-0.881311
106	8	0	-0.420101	-3.048216	0.037893
107	7	0	-2.547163	-3.370571	-0.679615
108	1	0	-3.138099	-3.532152	-1.479311
109	6	0	-4.348910	-2.262536	0.560150
110	1	0	-5.122151	-2.663495	-0.106071
111	6	0	-3.163870	-3.231578	0.630052
112	1	0	-2.393557	-2.797220	1.269585
113	6	0	-3.599487	-4.575616	1.213272
114	1	0	-2.728978	-5.232501	1.257611
115	1	0	-4.329011	-5.040115	0.539024
116	6	0	-4.219670	-4.389625	2.599505
117	1	0	-3.458492	-3.996515	3.282080
118	1	0	-4.539269	-5.353885	2.998655
119	6	0	-5.399579	-3.417621	2.543530
120	1	0	-5.817113	-3.266223	3.540670
121	1	0	-6.194787	-3.845180	1.923031
122	6	0	-4.973821	-2.071111	1.957333
123	1	0	-4.229057	-1.603353	2.610080
124	1	0	-5.821797	-1.388715	1.882102
125	6	0	-3.921448	-0.922363	0.012031
126	8	0	-2.772677	-0.524648	-0.026486

127	8	0	-4.950295	-0.192635	-0.410235
128	6	0	-4.615625	1.116172	-0.924906
129	1	0	-4.085982	1.678818	-0.157733
130	1	0	-3.929134	0.986044	-1.763745
131	6	0	-5.874228	1.822007	-1.349581
132	6	0	-7.064201	1.141601	-1.594757
133	1	0	-7.112357	0.072211	-1.440897
134	6	0	-5.816198	3.204207	-1.538562
135	1	0	-4.887730	3.729709	-1.343414
136	6	0	-8.189772	1.839486	-2.025301
137	1	0	-9.113514	1.305443	-2.208735
138	6	0	-6.940031	3.895931	-1.975351
139	1	0	-6.888820	4.967973	-2.117804
140	6	0	-8.130659	3.215340	-2.218790
141	1	0	-9.007058	3.755537	-2.553460

Peptide 16:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	3.658488	-0.129033	-1.350022
2	6	0	4.757252	0.347605	-0.722475
3	8	0	5.862076	-0.164031	-0.753254
4	6	0	5.417146	2.106149	0.819583
5	8	0	4.442445	1.493607	-0.069762
6	6	0	6.638842	2.576505	0.036371
7	6	0	4.658269	3.302414	1.379080
8	6	0	5.779361	1.138846	1.941354
9	6	0	2.550524	-2.291854	-1.631861
10	6	0	3.681316	-1.364417	-2.103627
11	6	0	3.565686	-1.110298	-3.608014
12	6	0	3.580525	-2.423027	-4.393658
13	6	0	2.469361	-3.359145	-3.915195
14	6	0	2.578153	-3.610360	-2.410784
15	6	0	2.725587	-2.545490	-0.144565
16	8	0	3.696943	-3.142377	0.302636
17	7	0	1.741050	-2.043489	0.636492
18	6	0	0.796972	-1.168599	2.697505
19	6	0	1.772592	-2.177973	2.079060
20	6	0	1.426935	-3.598311	2.534073
21	6	0	1.449211	-3.706285	4.058908
22	6	0	0.493238	-2.692551	4.690119
23	6	0	0.819097	-1.271968	4.227383
24	6	0	1.174740	0.236829	2.269823
25	8	0	2.225391	0.758096	2.657281
26	7	0	0.290817	0.867560	1.478345
27	6	0	-0.427521	2.329490	-0.313860
28	6	0	0.531274	2.176315	0.871407
29	6	0	0.306807	3.310994	1.881291
30	6	0	0.368562	4.692892	1.225885
31	6	0	-0.530809	4.810767	0.008345
32	8	0	1.310979	3.337272	2.881917
33	8	0	1.687043	4.944983	0.786966
34	8	0	-1.874752	4.733947	0.482144
35	6	0	-0.233533	3.694941	-0.985124
36	6	0	-0.202479	1.236360	-1.342909
37	8	0	0.915208	0.828200	-1.635884

38	7	0	-1.323619	0.787763	-1.957566
39	6	0	-2.286996	-1.398921	-2.526375
40	6	0	-1.279221	-0.309320	-2.906996
41	6	0	-1.494365	0.148572	-4.349139
42	6	0	-1.372760	-1.036211	-5.310102
43	6	0	-2.343731	-2.156476	-4.931528
44	6	0	-2.140494	-2.597162	-3.480383
45	6	0	-2.053300	-1.827431	-1.088267
46	8	0	-0.936096	-1.835795	-0.589744
47	7	0	-3.160487	-2.206774	-0.396423
48	6	0	-4.020717	-1.693316	1.842638
49	6	0	-3.095562	-2.582547	1.006730
50	6	0	-3.412731	-4.058033	1.245543
51	6	0	-3.265752	-4.397068	2.731229
52	6	0	-4.150762	-3.497232	3.596430
53	6	0	-3.856619	-2.017757	3.339368
54	6	0	-3.705749	-0.238471	1.599313
55	8	0	-2.598594	0.211204	1.409061
56	8	0	-4.810825	0.522510	1.642926
57	6	0	-4.629074	1.933416	1.452275
58	6	0	-4.671851	2.321550	-0.006916
59	6	0	-4.718623	1.382877	-1.033741
60	6	0	-4.665812	3.681416	-0.328057
61	6	0	-4.733380	1.797699	-2.366698
62	6	0	-4.675834	4.094792	-1.656077
63	6	0	-4.701235	3.151168	-2.682391
64	1	0	2.790049	0.380922	-1.260153
65	1	0	6.324383	3.222386	-0.786355
66	1	0	7.190792	1.729882	-0.363032
67	1	0	7.288500	3.153577	0.698907
68	1	0	3.782727	2.956422	1.929406
69	1	0	4.336158	3.956044	0.565560
70	1	0	5.302292	3.867535	2.055795
71	1	0	6.326910	0.284002	1.550622
72	1	0	4.865892	0.793797	2.429047
73	1	0	6.399156	1.656344	2.677829
74	1	0	1.594836	-1.784756	-1.805271
75	1	0	4.634750	-1.845028	-1.875899
76	1	0	4.385819	-0.459272	-3.918513
77	1	0	2.629270	-0.569171	-3.794347
78	1	0	4.547354	-2.916145	-4.246236
79	1	0	3.481383	-2.226677	-5.464348
80	1	0	2.506619	-4.306209	-4.459753
81	1	0	1.495536	-2.901271	-4.134571
82	1	0	3.515907	-4.122756	-2.178147
83	1	0	1.763841	-4.255804	-2.068455
84	1	0	0.913209	-1.675309	0.192216
85	1	0	-0.212226	-1.398348	2.331268
86	1	0	2.785125	-1.930503	2.410275
87	1	0	2.141248	-4.283522	2.076696
88	1	0	0.428238	-3.848161	2.151548
89	1	0	2.465748	-3.509816	4.415662
90	1	0	1.191964	-4.720962	4.372172
91	1	0	0.539074	-2.747516	5.780429
92	1	0	-0.536747	-2.940387	4.401877
93	1	0	1.816094	-0.982321	4.568996
94	1	0	0.112137	-0.554494	4.653253
95	1	0	-0.584751	0.406569	1.275376
96	1	0	-1.455507	2.268087	0.059595
97	1	0	1.564621	2.202792	0.514709
98	1	0	-0.682711	3.170256	2.332224
99	1	0	0.053835	5.432673	1.971866

100	1	0	-0.343326	5.782813	-0.459356
101	1	0	1.743132	2.460152	2.927838
102	1	0	2.250465	4.624667	1.509935
103	1	0	-2.447950	4.653329	-0.290743
104	1	0	0.795112	3.788880	-1.337271
105	1	0	-0.898682	3.777799	-1.852654
106	1	0	-2.217407	1.158032	-1.670213
107	1	0	-3.304966	-0.996958	-2.622518
108	1	0	-0.277584	-0.730388	-2.814288
109	1	0	-0.755792	0.917584	-4.583487
110	1	0	-2.486173	0.608635	-4.439643
111	1	0	-0.347565	-1.419766	-5.270392
112	1	0	-1.551621	-0.710458	-6.336732
113	1	0	-2.216284	-3.011743	-5.598294
114	1	0	-3.373427	-1.802028	-5.057677
115	1	0	-1.136453	-3.014538	-3.350706
116	1	0	-2.854154	-3.380431	-3.210938
117	1	0	-4.040201	-2.273780	-0.883841
118	1	0	-5.064034	-1.865407	1.557562
119	1	0	-2.064495	-2.387823	1.301439
120	1	0	-2.738827	-4.666345	0.639344
121	1	0	-4.437223	-4.268498	0.914942
122	1	0	-2.218378	-4.263213	3.022596
123	1	0	-3.511925	-5.446699	2.901408
124	1	0	-3.999792	-3.722125	4.653999
125	1	0	-5.204018	-3.697590	3.372164
126	1	0	-2.827227	-1.784556	3.632968
127	1	0	-4.520350	-1.381516	3.928250
128	1	0	-5.451304	2.397791	1.993350
129	1	0	-3.682220	2.242940	1.895059
130	1	0	-4.749099	0.327027	-0.795234
131	1	0	-4.641654	4.417237	0.468688
132	1	0	-4.778606	1.059814	-3.158844
133	1	0	-4.675083	5.152276	-1.890618
134	1	0	-4.711923	3.470659	-3.716243

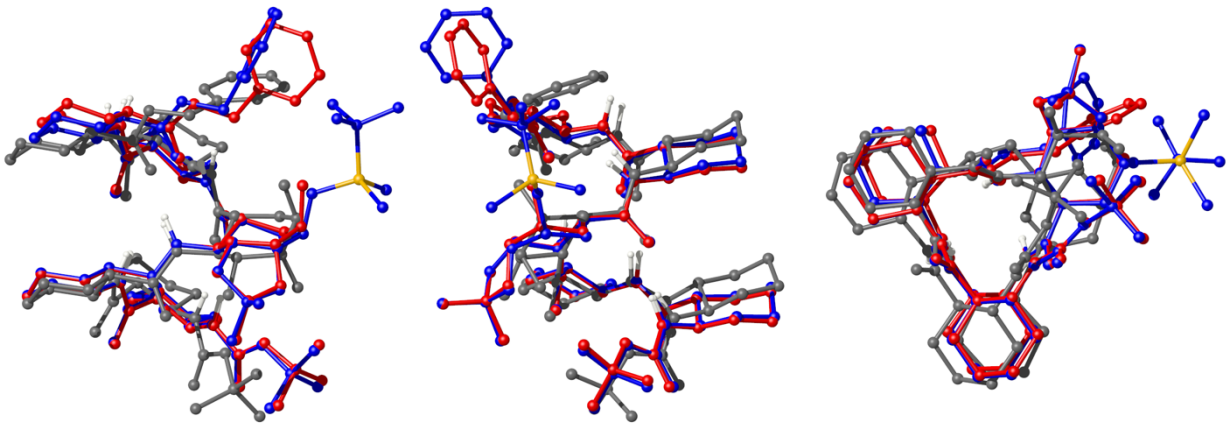


Figure S57: Alignment of the models of peptides **14**-**16** calculated from NMR data and further optimized at the M052X DFT level. Compound colours: **14** *blue*, **15** *red*, **16** *grey*. Atom colours: Si *yellow*, H^N *white*; hydrogen atoms not bound to nitrogen have been omitted for clarity. RMSD of backbone heavy atoms = 0.246 Å (carbonyl C, Cα, Cβ, N).

VII. X-RAY OF COMPOUND 3

Crystal data

$C_{32}H_{47}NO_5Si$
M_r = 553.79
Monoclinic, $P2_1$
a = 7.7332 (3) Å
b = 8.4891 (4) Å
c = 24.0949 (9) Å
β = 95.619 (2)°
V = 1574.18 (11) Å^3
Z = 2
$F(000)$ = 600
D_x = 1.168 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å Cell parameters from 9346 reflections θ = 2.6–27.4° μ = 0.11 mm^{-1}
T = 100 K
Plate, clear colourless
0.89 × 0.74 × 0.13 mm

Data collection

κ–geometry diffractometer
Radiation source: sealed x-ray tube, SIEMENS KFN MO 2K-90
Graphite monochromator
Detector resolution: 8.3333 pixels mm^{-1}
φ or ω oscillation scans
Absorption correction: multi-scan *SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction
T_{min} = 0.85, T_{max} = 0.99
25016 measured reflections
7146 independent reflections
6355 reflections with $I > 2\sigma(I)$ R_{int} = 0.035
θ_{max} = 27.6°, θ_{min} = 1.7° h = −10→10 k = −11→11 l = −31→20

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.085
S = 1.05
7146 reflections
361 parameters
1 restraint
Primary atom site location: dual
Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map H-atom parameters constrained $w = 1/[\sigma^2(F_o^2) + (0.0338P)^2 + 0.3617P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ < 0.001

Special details

$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}
Absolute structure: Flack x determined using 2459 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
Absolute structure parameter: −0.01 (5)

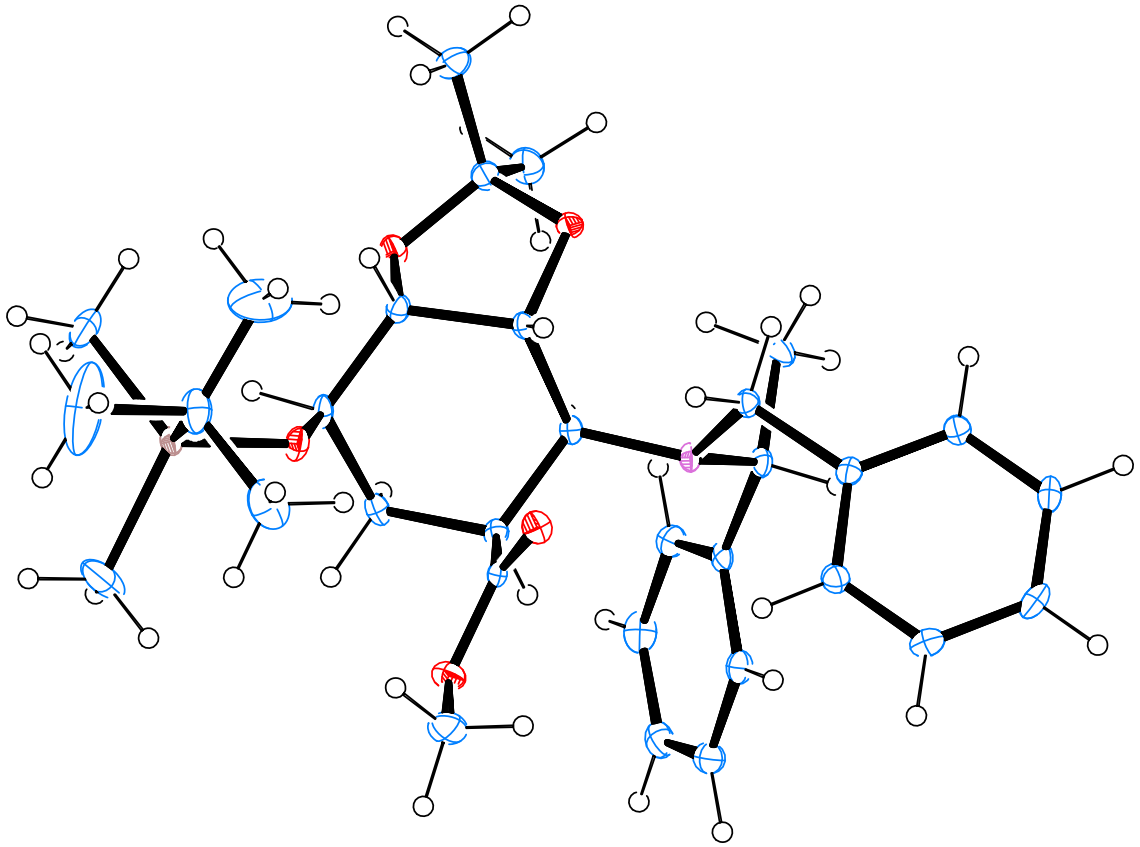


Figure S58: ORTEP diagram for compound **3**.