SUPPORTING INFORMATION

Formation of Left-Handed Helices in Hybrid Peptide Oligomers with *cis* β-Sugar Amino Acid and L-Ala as Building Blocks

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Synthesis of alternating furanoid cis-*β*-sugar amino acid and L-Ala:

The monomer *cis*-β-FSAA(S) was synthesized from D-glucose and monomer *L-Alanine*(A) was purchased from Aldrich Inc.. Deprotection of Boc group was achieved with trifluoro acetic acid in dichloromethane (1:1) at 0 ^{o}C while esters were hydrolyzed with LiOH in THF, H_2O (3:1). The synthesis of oligomers **1**-**4** involved peptidation of monomers S and A in the requisite sequence using standard coupling reagents EDCI, HOBt and DIPEA in dry dichloromethane. All the compounds reported were purified by column chromatography over silica gel (60-120 mesh; Ethyl acetate and hexane up to tri peptides), and neutral alumina (methanol-chloroform for tetra and octa peptides). For further details please see the references **10** and **11** of the manuscript.

Circular Dichroism Spectroscopy:

CD spectroscopy is frequently used to elucidate secondary structures of α-peptides and proteins in solution. Although for β-peptides, the correlation between CD pattern and secondary structure is not yet fully established, it provides useful information when used in combination with other spectroscopic techniques. The CD spectra of the mixed peptides **1**-**4**(Figure 1) were recorded in CD_3OH (0.2 mM), which show a left-handed helical pattern with maxima (negative cotton effect) at about 205 nm with the molar ellipticity θ increasing with chain length. CD spectra were recorded on JASCO J-715 spectrometer at 25°C,using 1mm path length CD cell. All spectra represent the average of 8 scans.They are all background-corrected,Scan Range: 195-250nm: band width: 2nm.

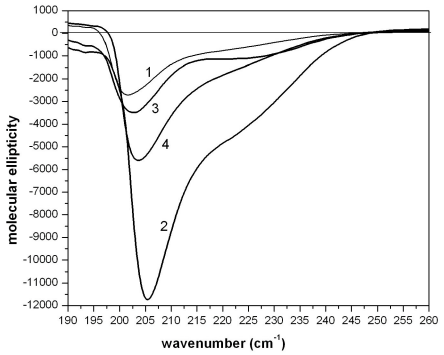
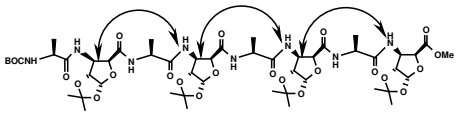
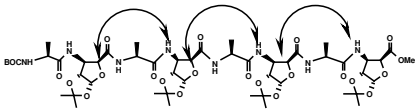
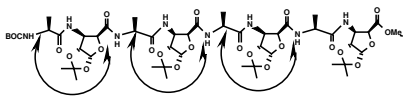
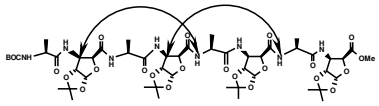
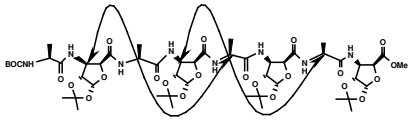
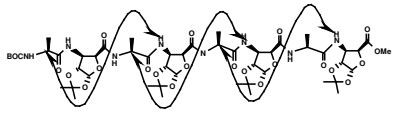
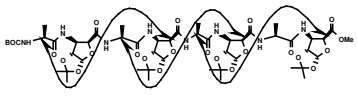
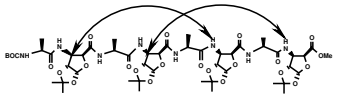
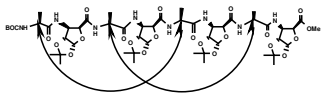


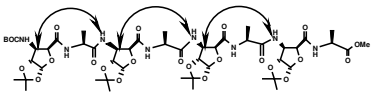
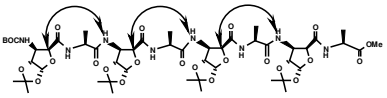
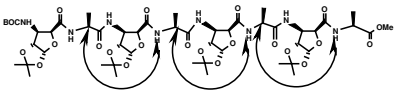
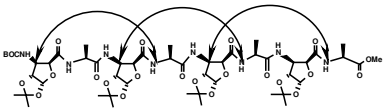
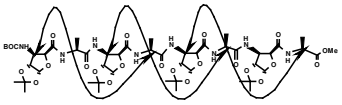
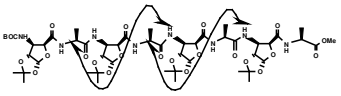
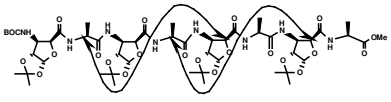
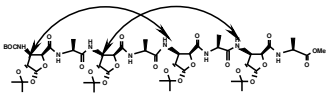
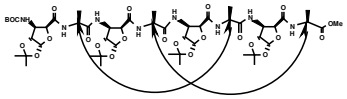
Figure 1: Circular Dichroism for **1-4**

NMR Spectroscopy

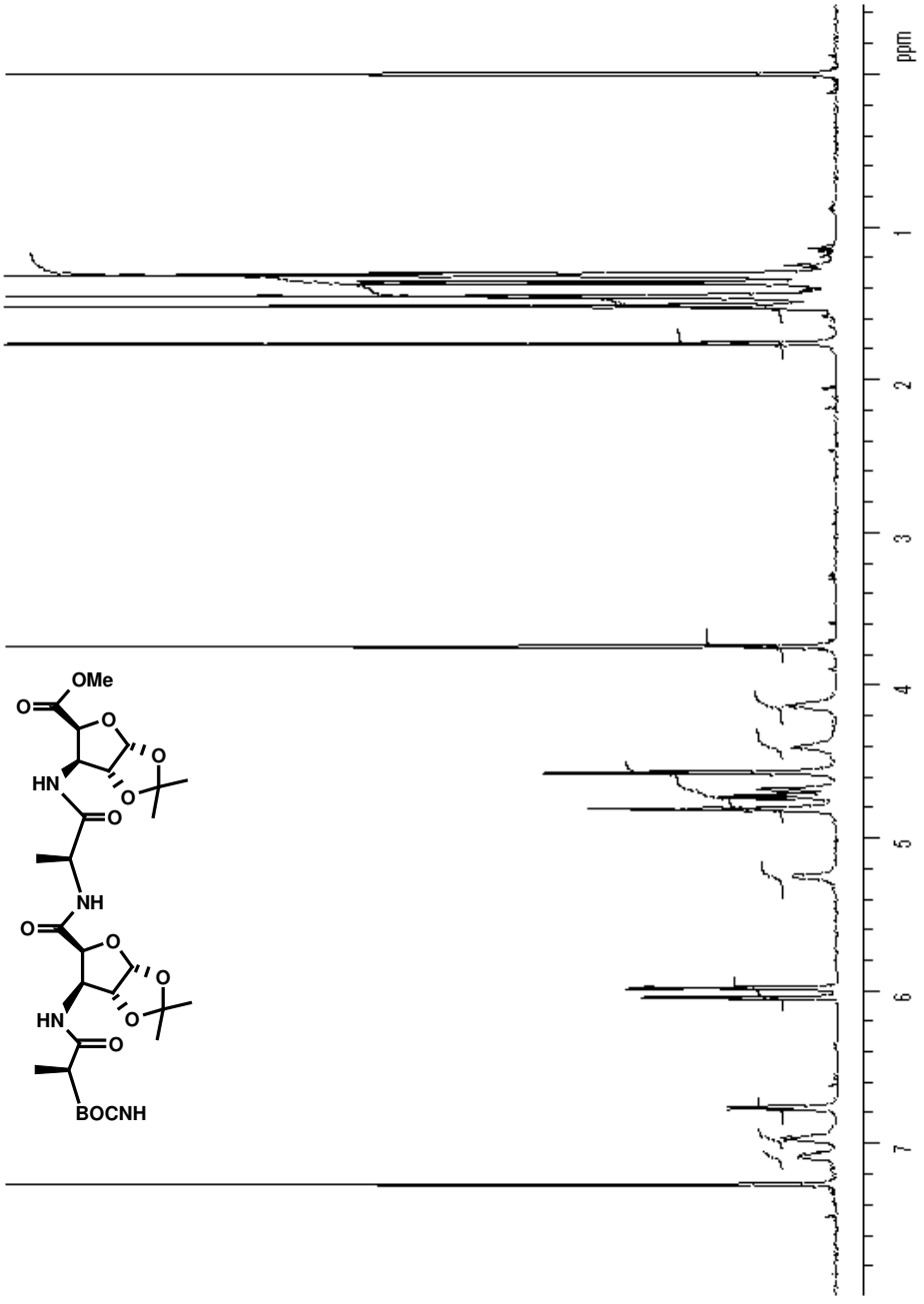
NMR spectra were recorded on Varian Unity Inova - 500 MHz and Bruker-Avance-600MHz spectrometers,in $CDCL_3$ and DMSO-d_6(7-10mM) using Tetramethylsilane as internal standard or the solvent signals as secondary standards, and the chemical shifts are shown in ppm scale. Multiplicities of NMR signals are designated as s (singlet), d (doublet), t (triplet), br (broad), m (multiplet, for unresolved lines), etc. Two dimensional (2D) total correlation spectroscopy (TOCSY), and rotating frame nuclear Overhauser effect spectroscopy (ROESY) experiments were carried out in the phase-sensitive mode. The 2D spectra were acquired with 2 x 256 or 2 x 192 free induction decays (FID) containing 8-16 transients with relaxation delays of 2.0 s. The ROESY experiments were performed with mixing time of 0.2 to 0.3 s. For ROESY experiments a spin locking field of about 2 kHz and pulsed field locking with 30° pulses were used. The TOCSY experiments were performed with the spin locking field of about 10 kHz and a mixing time of 0.08 s. The two dimensional data were processed with Gaussian apodization in both the dimensions. In these oligomers the N-terminal amide proton was easily assigned as it shows nOe with intra residue CαH proton only, whereas the other amide protons show both intra residue and inter residue NH / CαH nOe. This assignment has further supported by the nOe between the amide and Boc group. Similarly the CαH of the C- terminal residue has been identified from the presence of nOe with the intra residue NH only. The spectra (One Dimensional, TOCSY and ROESY) and solvent titration studies are illustrated in the supporting **Figures 2-24** and the chemical shifts, coupling constants are given in Supporting **Tables 1-12**.

Supporting Table-1: Possible NOE's in Octamers 2 and 4 :

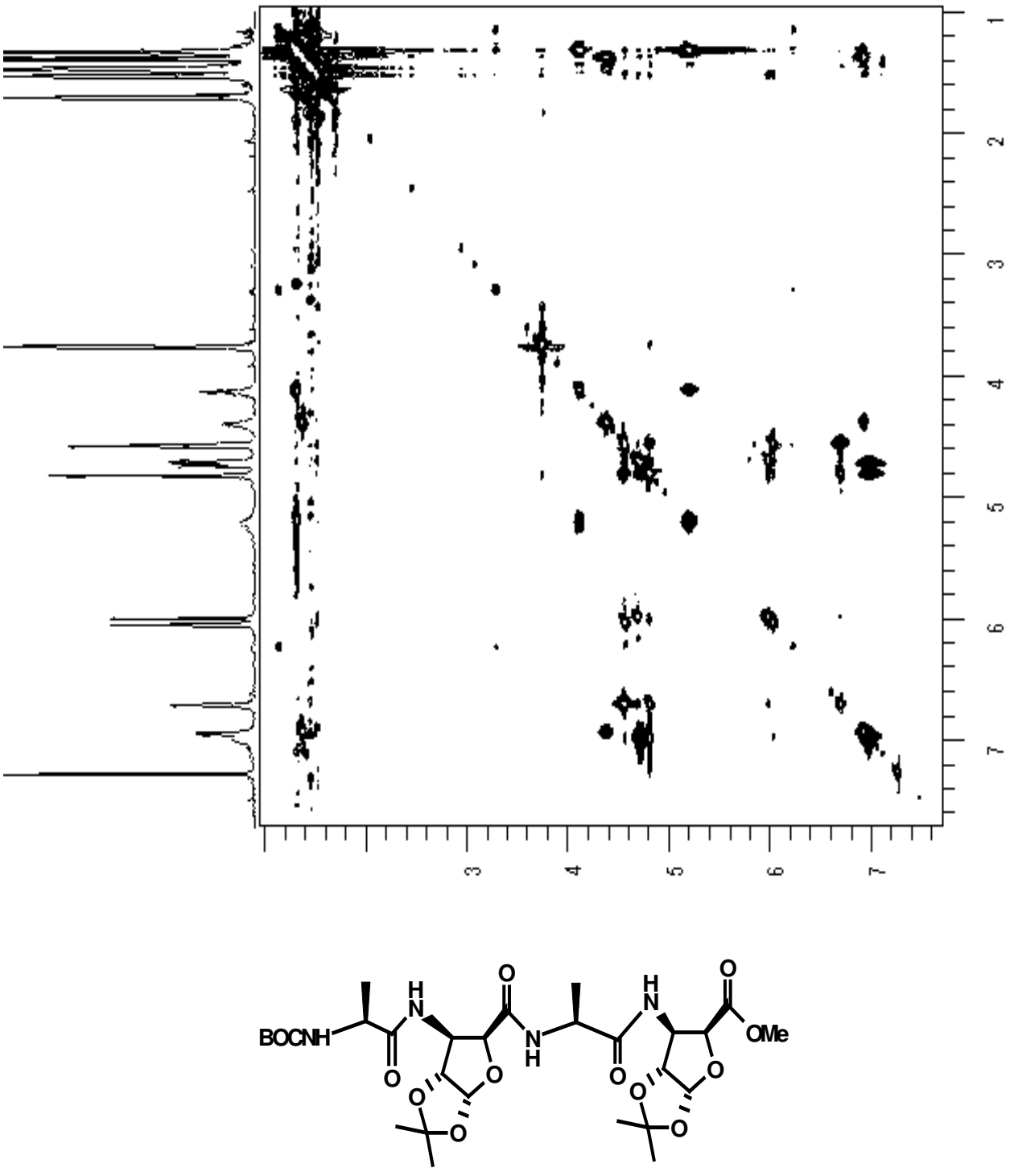
NOE type	residue
1) β–Residue Hβ (i)/β -Residue-NH (i+2): 	2-4 4-6 6-8
2) β– Residue Hα(i) /β -Residue-NH(i+2): 	2-4 4-6 6-8
3) α– Residue Hα (i)/ α-Residue-NH (i+2): 	1-3 3-5 5-7
4) β– Residue Hβ (i)/α -Residue-NH (i+3): 	2-5 4-7
5) β– Residue Hβ (i)/α -Residue-Hα(i+3): 	2-5 4-7
6) α– Residue Hα (i)/ β -Residue-NH(i+3): 	1-4 3-6 5-8
7) α– Residue Hα (i)/ β-Residue-Hα(i+3): 	1-4 3-6 5-8
8) β– Residue Hβ (i)/β -Residue-NH(i+4): 	2-6 4-8
9) α– Residue Hα(i)/ α -Residue-Hα(i+4): 	1-5 3-7

NOE type	residue
1) β–Residue Hβ (i)/β -Residue-NH (i+2): 	1-3 3-5 5-7
2) β– Residue Hα(i) /β -Residue-NH(i+2): 	1-3 3-5 5-7
3) α– Residue Hα (i)/ α -Residue-NH(i+2): 	2-4 4-6 6-8
4) β– Residue Hβ (i)/α -Residue-NH (i+3): 	1-4 3-6 5-8
5) β– Residue Hβ (i)/α -Residue-Hα(i+3): 	1-4 3-6 5-8
6) α– Residue Hα (i)/ β -Residue-NH(i+3): 	2-5 4-7
7) α– Residue Hα (i)/ β-Residue-Hα(i+3): 	2-5 4-7
8) β– Residue Hβ (i)/β -Residue-NH(i+4): 	1-5 3-7
9) α– Residue Hα(i)/ α -Residue-Hα(i+4): 	2-6 4-8

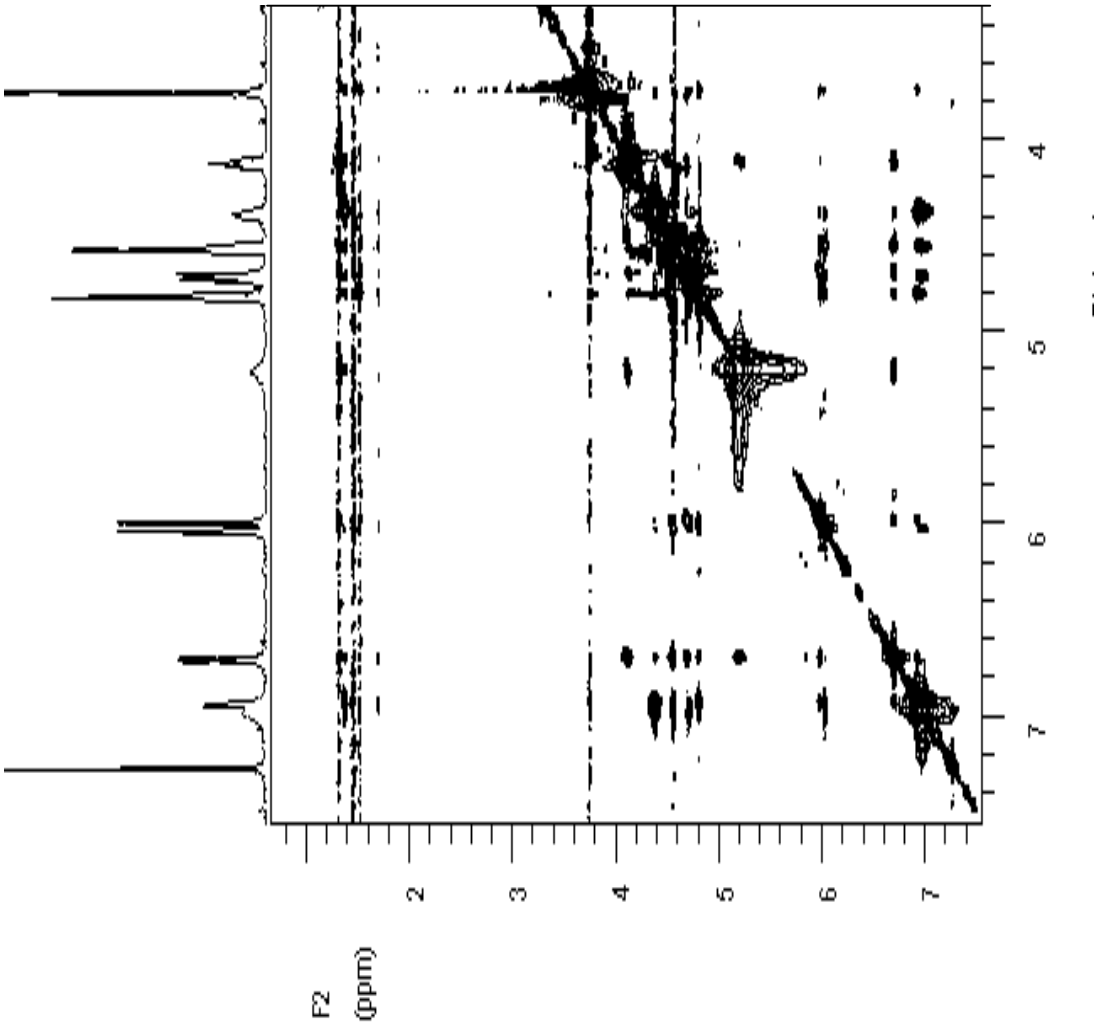
Supporting Figure-02: ^{1}H NMR spectrum of 1 [500MHz, 303K, $CDCl_3$]

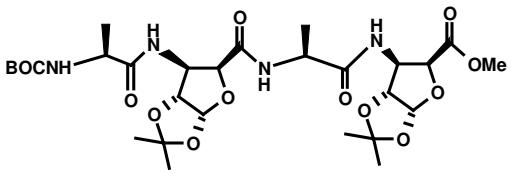


Supporting Figure-03: TOCSY spectrum of 1 [500MHz, 303K, $CDCl_3$]



Supporting Figure-04: ROESY spectrum of 1 [500MHz, 303K, $CDCl_3$]



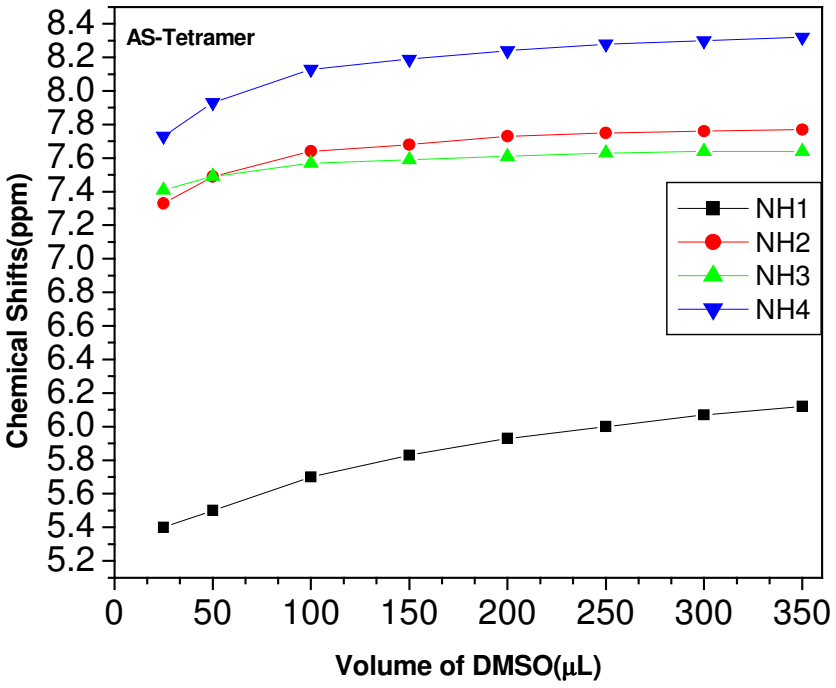


Supporting Table-02: Chemical shifts (ppm) and coupling constants (Hz) for 1 ($CDCl_3$ at 303K) *

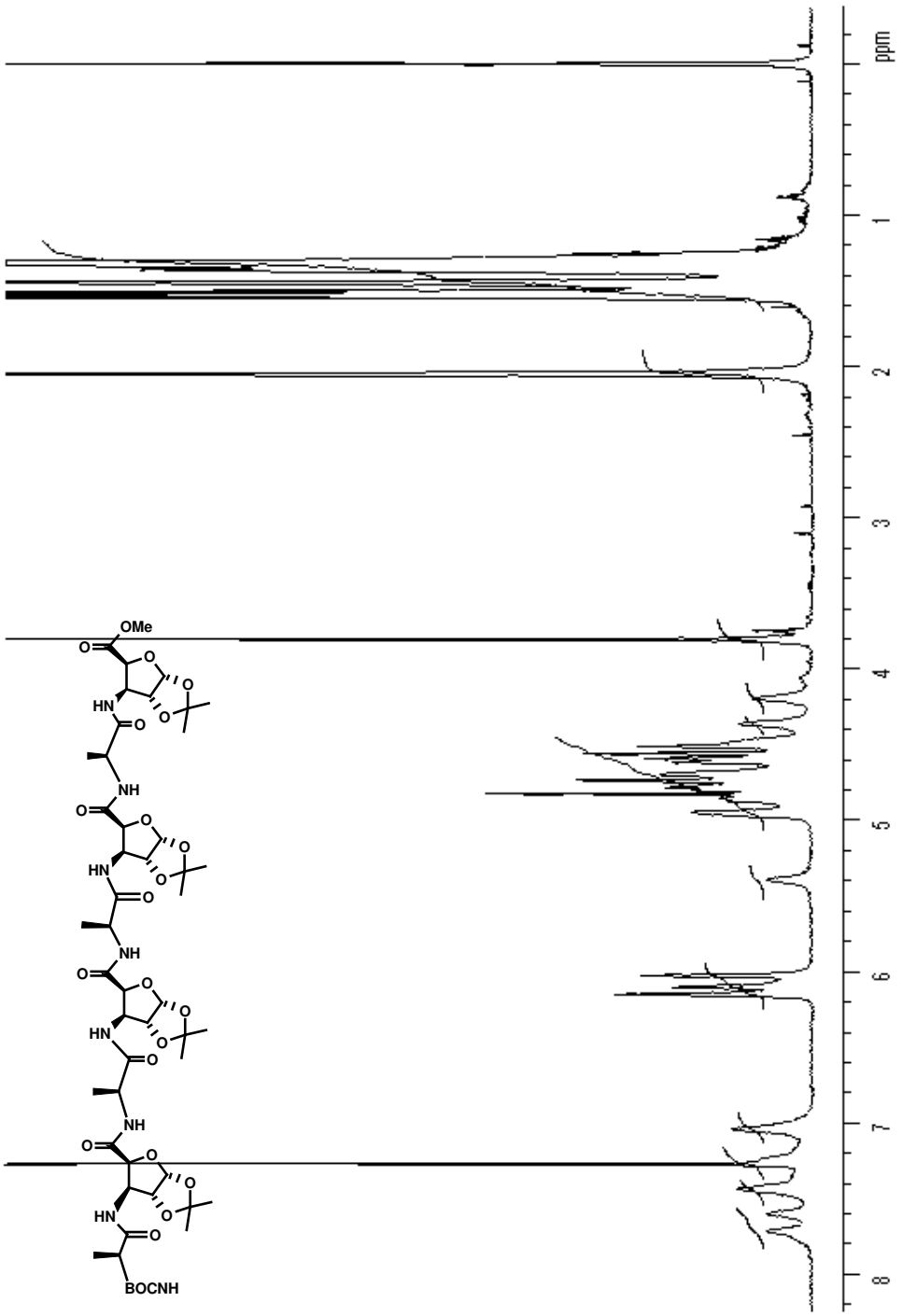
Residue	NH	CαH	CβH/CH_3	CγH	CδH
1	5.48(d) $J_{NH,\beta}$ =7.6	4.11(p) $J_{NH,\beta}$= 7.6 $J_{\alpha,\beta}$ = 7.6	1.31(d) $J_{\alpha,\beta}$ = 7.6	-	-
2	7.32(d) $J_{NH,\beta=}$8.0	4.75(d) $J_{\alpha,\beta}$ = 4.2	4.65(dd) $J_{NH,\beta=}$ 8.0 $J_{\alpha,\beta}$ = 4.2	4.57(d) $J_{\gamma,\delta}$ = 4.2	5.98(d) $J_{\gamma,\delta}$ = 4.2
3	7.42(d) $J_{NH,\beta}$ =8.0	4.43(dq) $J_{NH,\beta}$=8.0, $J_{\alpha,\beta}$ = 7.3	1.31(d) $J_{\alpha,\beta}$ = 7.3	-	-
4	7.73(d) $J_{NH,\beta=}$9.1	4.82(d) $J_{\alpha,\beta}$ = 4.2	4.76(dd) $J_{NH,\beta=}$9.1 $J_{\alpha,\beta}$ = 4.2	4.52(d) $J_{\gamma,\delta}$ = 4.2	6.04(d) $J_{\gamma,\delta}$ = 4.2

* 25ul DMSO-d6 is added to $CDCl_3$, Others: Boc(1.44), acetonides: 1.29, 1.50, 1.31, 1.51

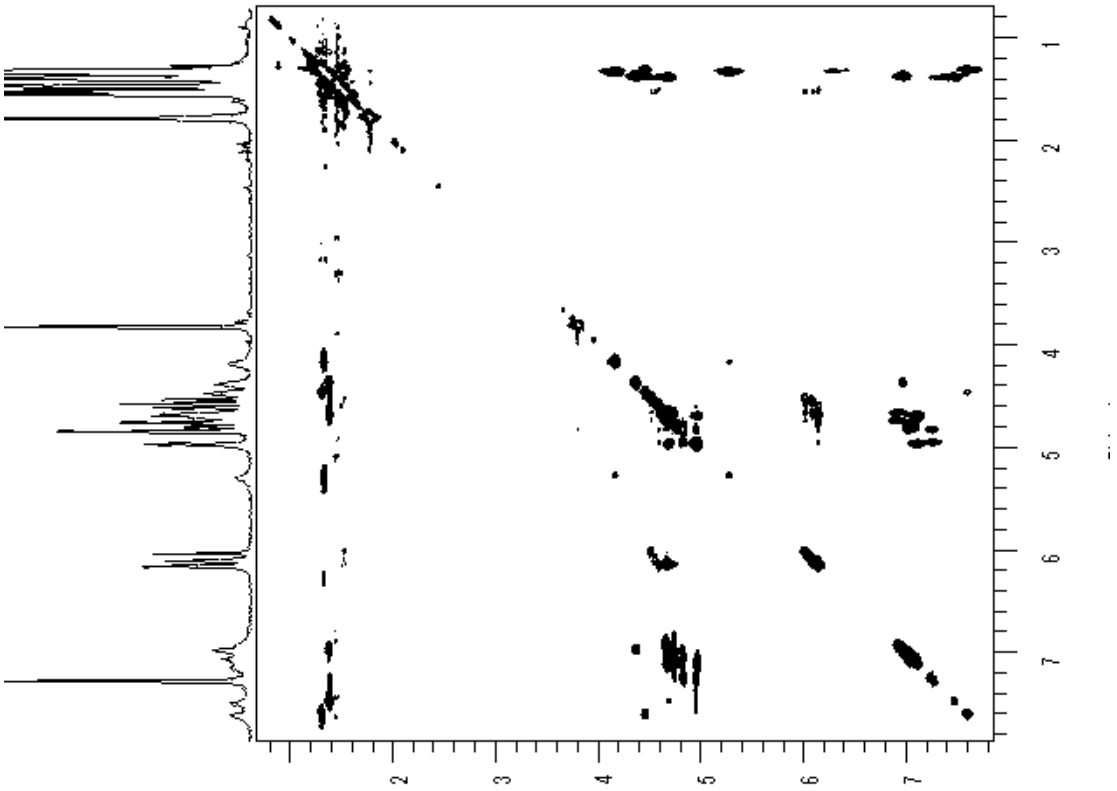
Supporting Figure-05: Solvent Titration Studies of 1

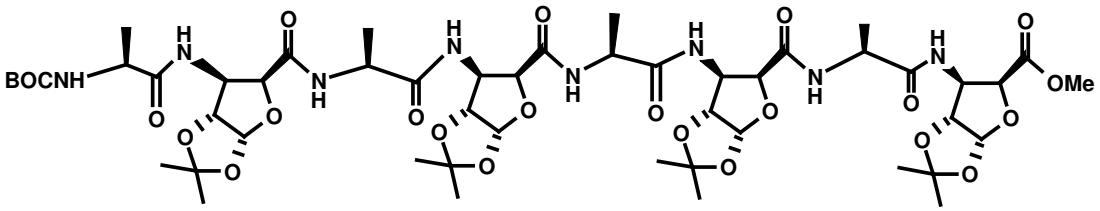


Supporting Figure-06: ^{1}H NMR spectrum of 2 [500MHz, 303K, $CDCl_3$]

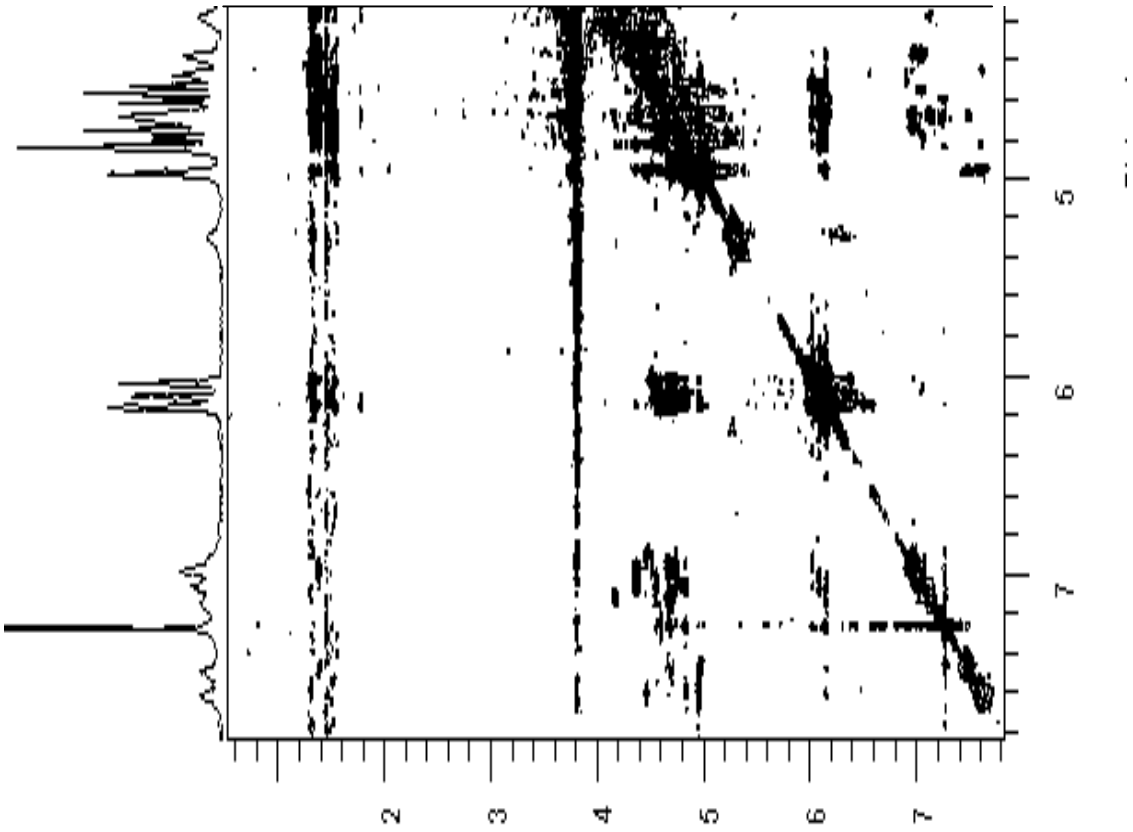


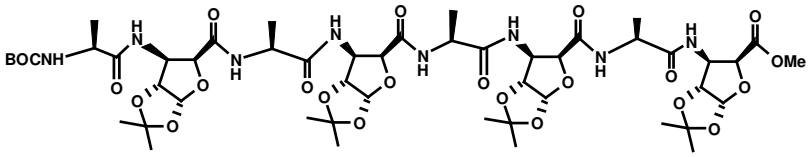
Supporting Figure-07: TOCSY spectrum of 2 [500MHz, 303K, $CDCl_3$]





Supporting Figure-08: ROESY NMR spectrum 2 [500MHz, 303K, $CDCl_3$]





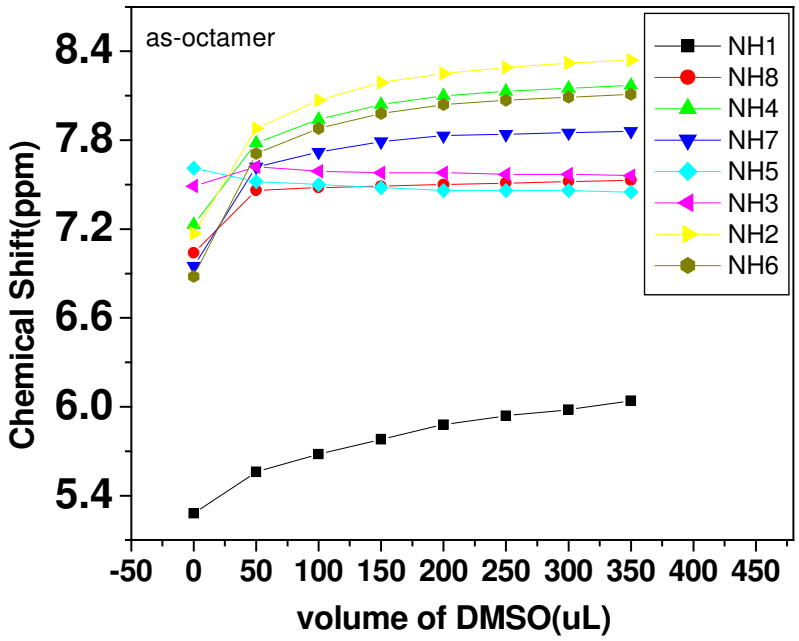
Broadened signals with unacceptable overlap of resonances due to poor-solubility, did not permit to obtain conformational details in octamer **2**. The octamers along with tetramers are studied in DMSO-d_6, which has been found to be suitable.

Supporting Table-03: Chemical Shifts(ppm) for 2 in $CDCl_3$ (500MHz)(lines are broad)

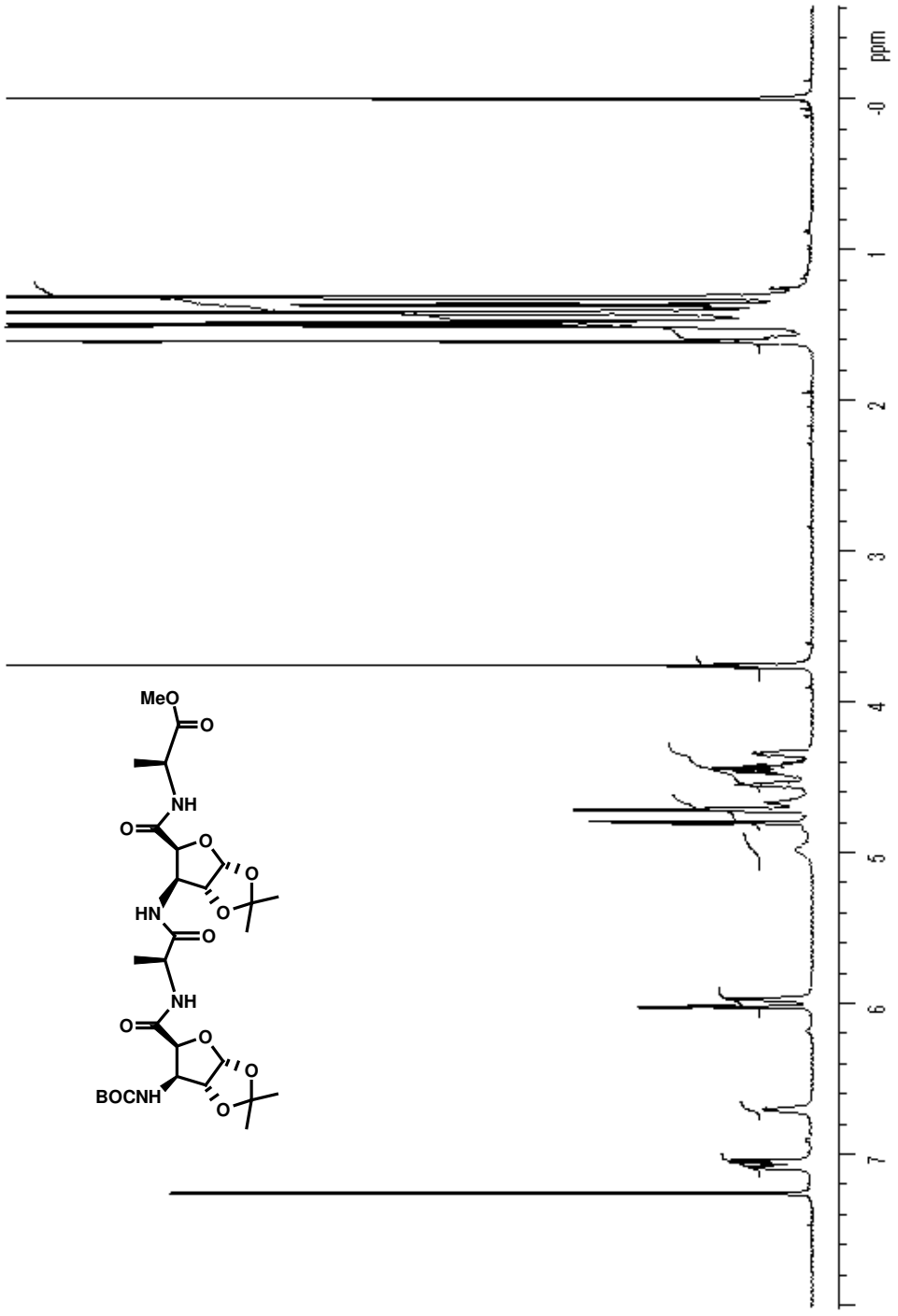
:

Residue	NH	CαH	CβH/CH_3	CγH	CδH
1	5.30	4.19	1.34	-	-
2	7.22	5.00	4.73	4.67	6.17
3	7.52	4.715	1.40	-	-
4	7.30	4.98	4.85	4.61	6.16
5	7.65	4.47	1.32	-	-
6	6.92	4.75	4.68	4.52	6.03
7	6.97	4.376	1.39	-	-
8	7.07	4.84	4.80	4.56	6.10(d)

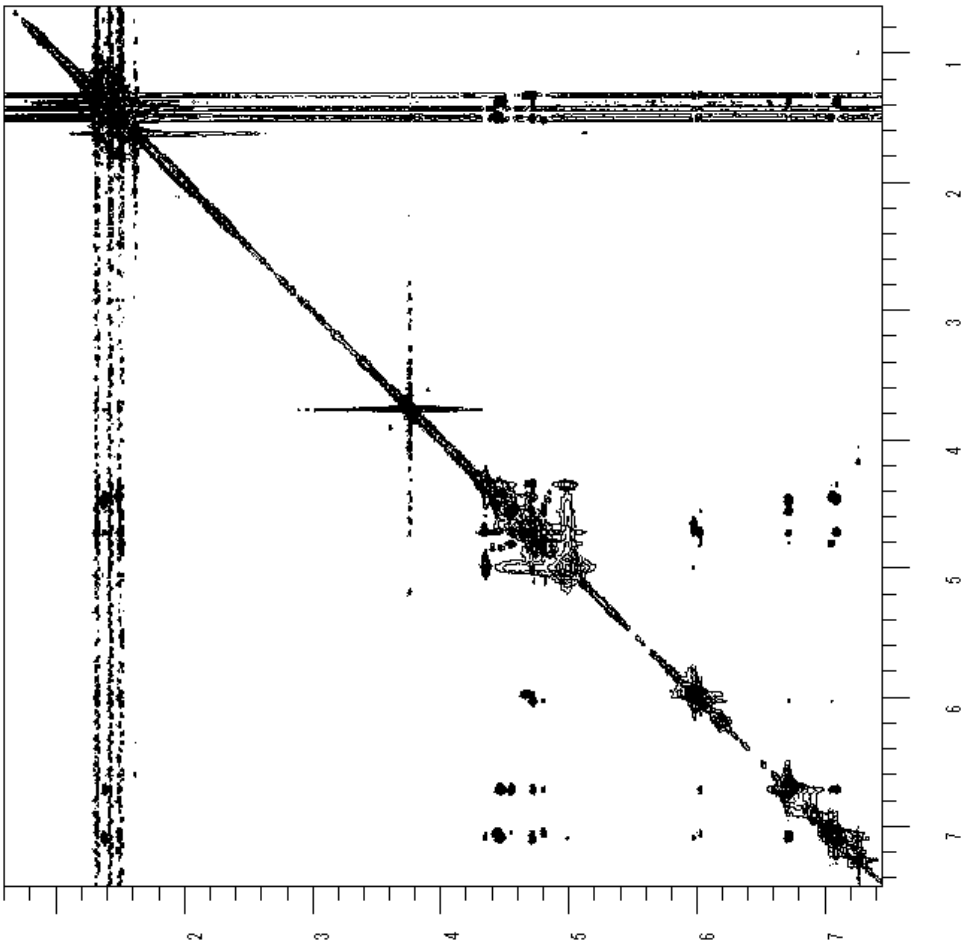
Supporting Figure-09: Solvent Titration Studies of 2

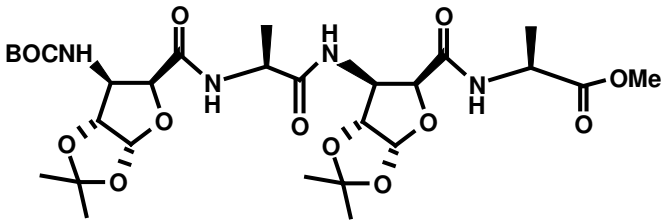


Supporting Figure-10: ^{1}H NMR spectrum of 3 [500MHz, 303K, $CDCl_3$]

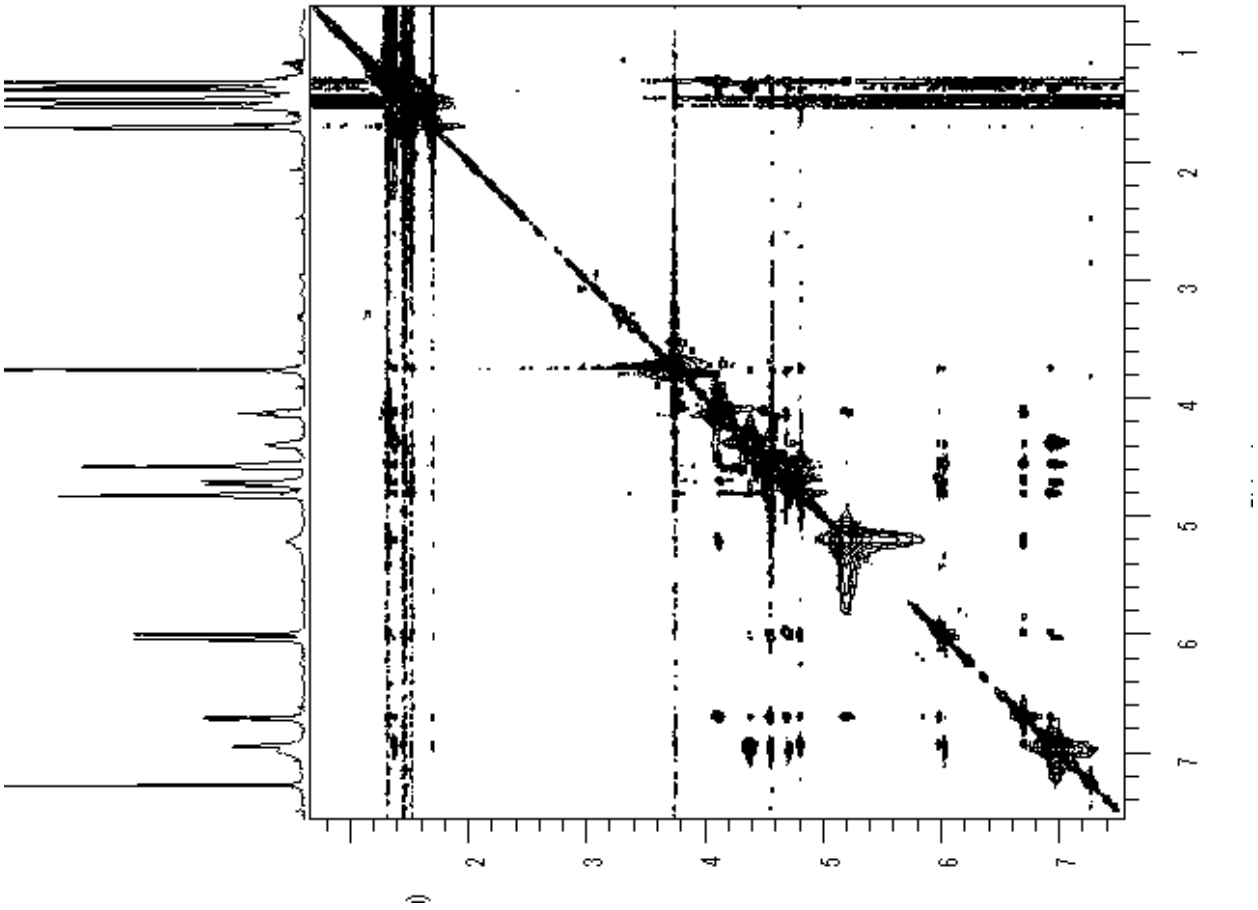


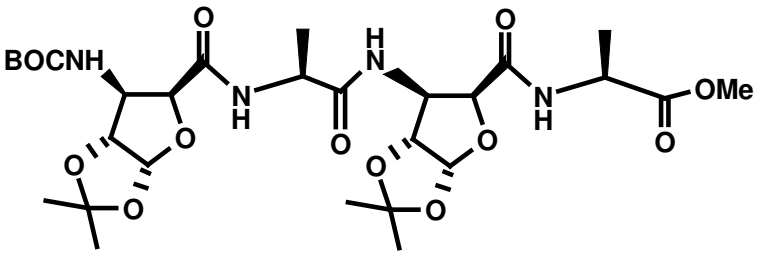
Supporting Figure-11: TOCSY NMR spectrum of 3 [500MHz, 303K, $CDCl_3$]





Supporting Figure-12: ROESY NMR spectrum of 3 [500MHz, 303K, $CDCl_3$]



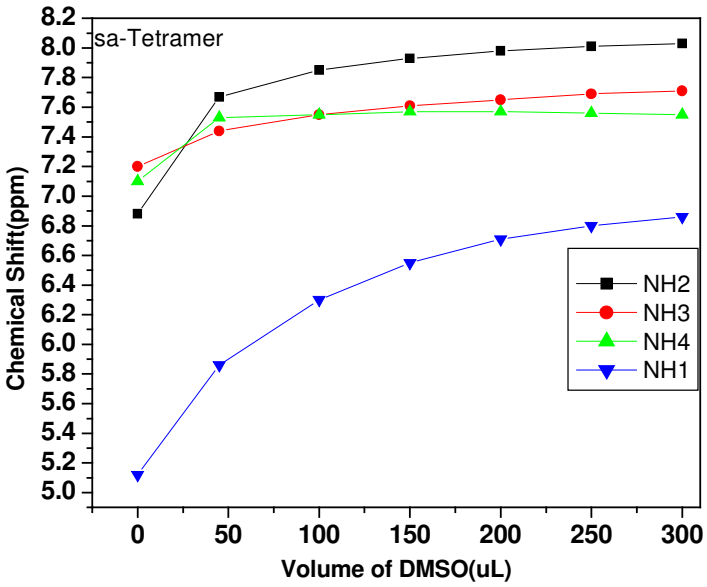


Supporting Table-04: Chemical Shifts and Coupling Constants for 3 in $CDCl_3$ (500MHz)

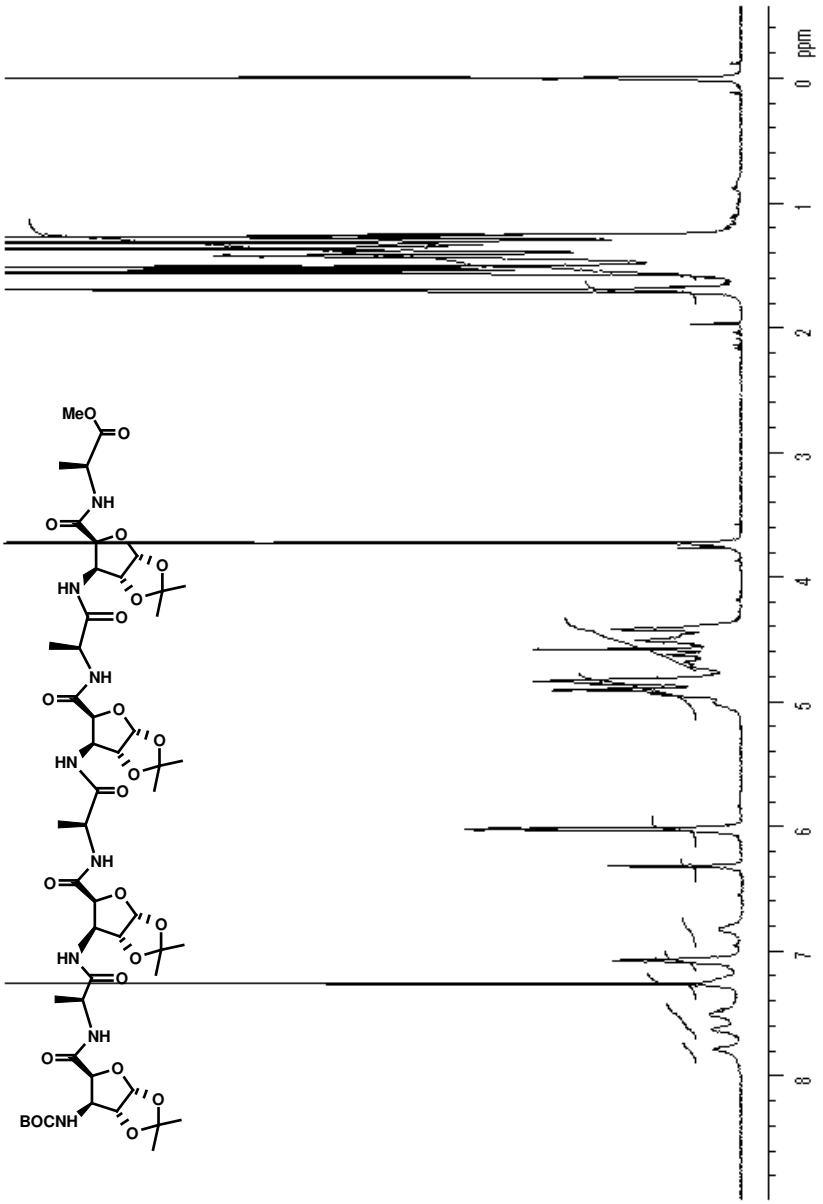
Residue	NH	CαH	CβH/CH_3	CγH	CδH
1	4.98(d) $J_{NH,\beta}$ =8.2	4.71(d) $J_{\alpha,\beta}$ = 4.2	4.35(dd) $J_{NH,\beta}$= 8.2 $J_{\alpha,\beta}$ = 4.2	4.67(d) $J_{\gamma,\delta}$ =3.7	5.99(d) $J_{\gamma,\delta}$ =3.7
2	7.10(d) $J_{NH,\beta}$ =7.7	4.48(dq) $J_{NH,\beta}$=7.7, $J_{\alpha,\beta}$ = 7.2	1.37(d) $J_{\alpha,\beta}$ = 7.2	-	-
3	6.71(d) $J_{NH,\beta=}$7.2	4.81(d) $J_{\alpha,\beta}$ = 4.6	4.55(dd) $J_{\alpha,\beta}$ = 4.6 $J_{NH,\beta=}$7.2	4.72(d) $J_{\gamma,\delta}$ =3.5	6.03(d) $J_{\gamma,\delta}$ =3.5
4	7.05(d) $J_{NH,\beta}$= 7.2	4.44(dq) $J_{NH,\beta=}$7.2 $J_{\alpha,\beta}$ = 7.0	1.48(d) $J_{\alpha,\beta}$ =7.0	-	-

Others: Boc(1.42, 1.61, 1.62), acetonides: 1.31, 1.50, 1.32, 1.51

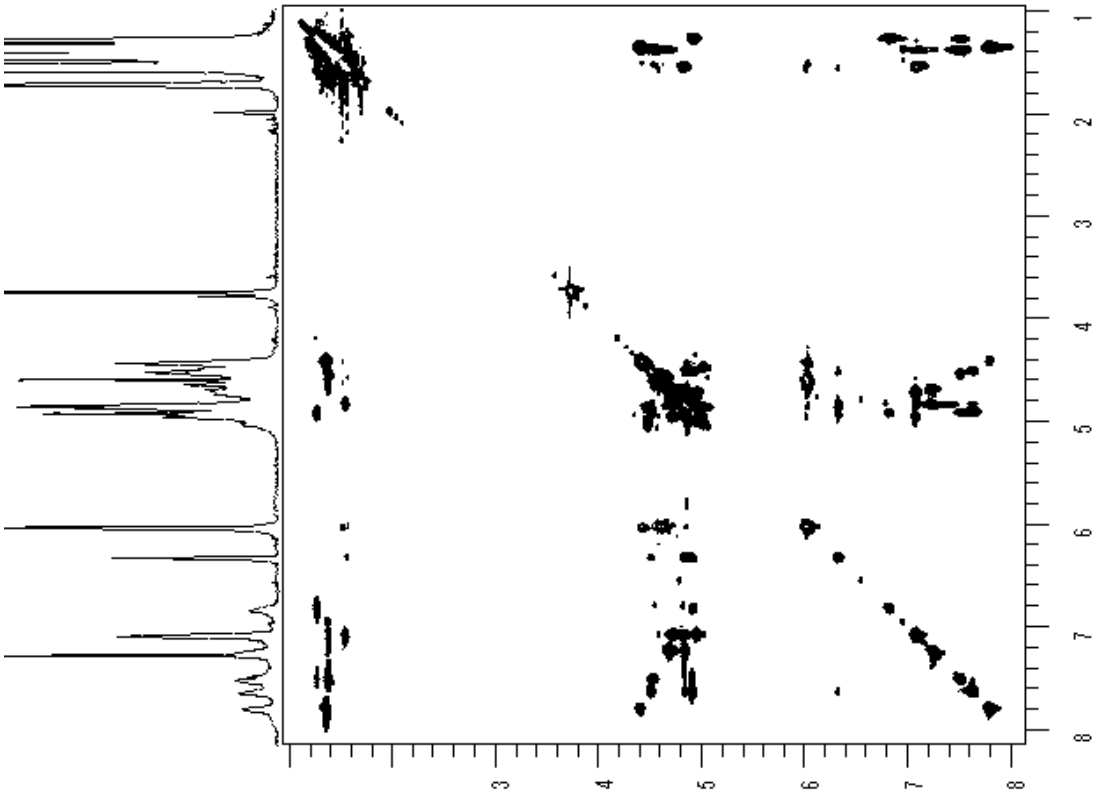
Supporting Figure-13: Solvent Titration Studies of 3

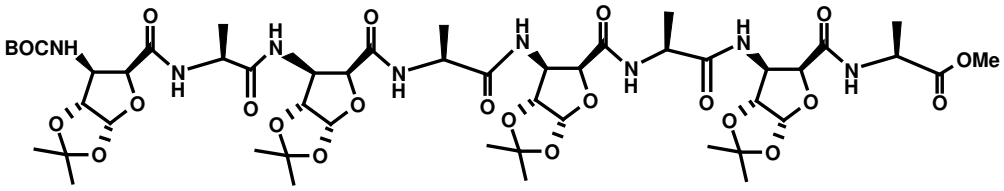


Supporting Figure-14: ^{1}H NMR spectrum of 4 [500MHz, 303K, $CDCl_3$]



Supporting Figure-15: TOCSY NMR spectrum of 4 [500MHz, 303K, $CDCl_3$]





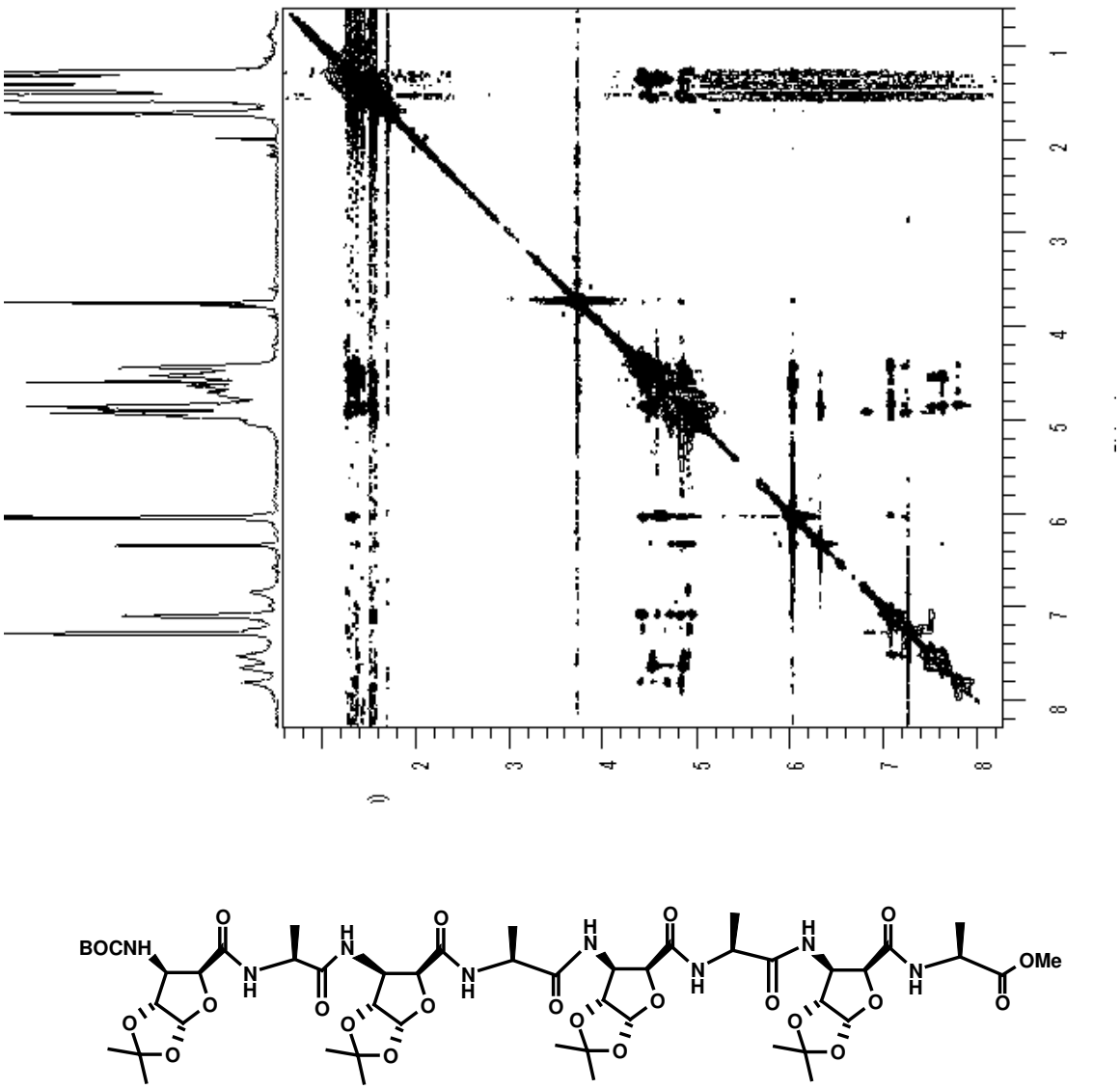
Supporting Table-05: Chemical Shifts and Coupling Constants for 4 in $CDCl_3$ (500MHz)

Residue	NH	CαH	CβH/CH_3	CγH	CδH
1	5.70(d) $J_{NH,\beta}$ =9.00	4.72(d) $J_{\alpha,\beta}$ = 3.6	4.48(dd) $J_{NH,\beta}$= 9.00 $J_{\alpha,\beta}$ = 3.6	4.57(d) $J_{\gamma,\delta}$ =3.6	6.01(d) $J_{\gamma,\delta}$ =3.6
2	7.60(d) $J_{NH,\beta}$ =8.00	4.59(dq) $J_{NH,\beta}$=8.0, $J_{\alpha,\beta}$ = 7.3	1.31(d) $J_{\alpha,\beta}$ = 7.3	-	-
3	7.90(d) $J_{NH,\beta=}$8.5	4.75(d) $J_{\alpha,\beta}$ = 3.6	4.69(dd) $J_{NH,\beta=}$8.5 $J_{\alpha,\beta}$ = 3.6	4.58(d) $J_{\gamma,\delta}$ =3.6	6.13(d) $J_{\gamma,\delta}$ =3.6
4	7.70(d) $J_{NH,\beta}$= 8.5	4.41(dq) $J_{NH,\beta=}$8.5 $J_{\alpha,\beta}$ = 7.3	1.30(d) $J_{\alpha,\beta}$ =7.3	-	-
5	7.53(d) $J_{NH,\beta=}$8.5	4.71(d) $J_{\alpha,\beta}$ = 3.6	4.52(dd) $J_{NH,\beta=}$8.5 $J_{\alpha,\beta}$ = 3.6	4.53(d) $J_{\gamma,\delta}$ =3.6	6.05(d) $J_{\gamma,\delta}$ =3.6
6	7.66(d) $J_{NH,\beta}$= 8.00	4.40(dq) $J_{NH,\beta=}$8.00 $J_{\alpha,\beta}$ = 7.3	1.30(d) $J_{\alpha,\beta}$ =7.3	-	-
7	7.80(d) $J_{NH,\beta=}$9.00	4.81(d) $J_{\alpha,\beta}$ = 3.6	4.76(dd) $J_{NH,\beta=}$9.00 $J_{\alpha,\beta}$ = 3.6	4.64(d) $J_{\gamma,\delta}$ =3.6	6.06(d) $J_{\gamma,\delta}$ =3.6
8	7.40(d) $J_{NH,\beta}$= 7.3	4.57(p) $J_{NH,\beta=}$7.3 $J_{\alpha,\beta}$ = 7.3	1.44(d) $J_{\alpha,\beta}$ =7.3	-	-

Others: Boc(1.44), acetonides: 1.30, 1.50, 1.31, 1.52

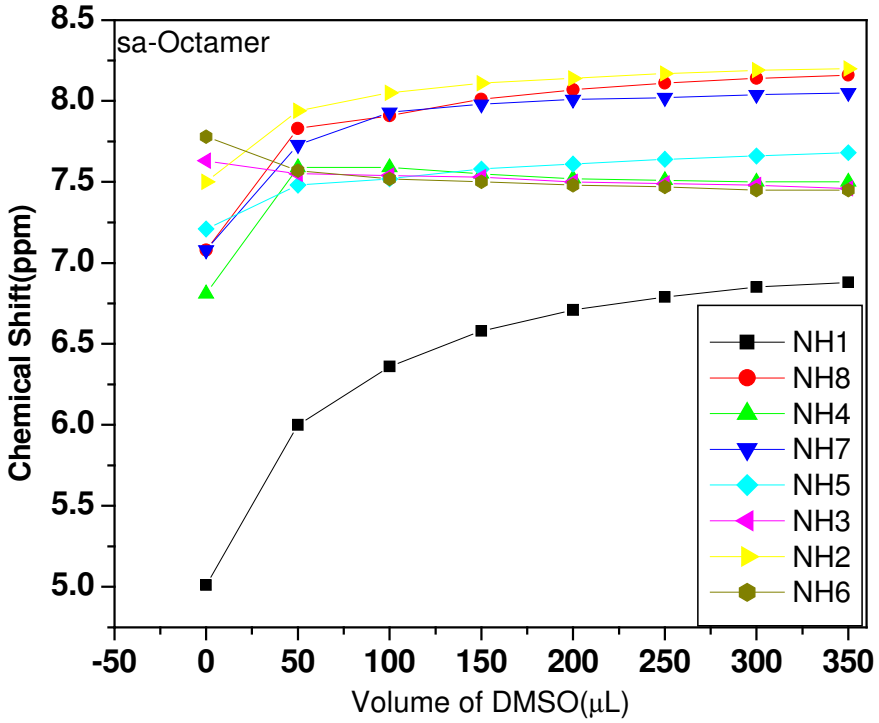
The observed coupling constants in CD_3OH are closely comparable with those observed in DMSO-d_6. The results suggest that these oligomers adopt similar helical conformation in both the solvents. However,due to the overlapped resonances detailed spatial correlation (ROESY) could not be established.

Supporting Figure-16: ROESY NMR spectrum of 4 [500MHz, 303K, $CDCl_3$]



Broadened signals with unacceptable overlap of resonances due to poor-solubility, did not permit to obtain conformational details in octamer **4**. The octamers along with tetramers are studied in DMSO-d_6, which has been found to be suitable

Supporting Figure-17: Solvent Titration Studies of 4



Supporting Table-06: Chemical shifts (ppm) and coupling constants (Hz) for 4 (METHANOL-at 281K)-600MHz.

Residue	NH	CαH	CβH/CH_3	CγH	CδH
1	7.21(d) $J_{NH,\beta}$ =10.3	4.62(d) $J_{\alpha,\beta}$ = 4.0	4.46(dd) $J_{NH,\beta}$= 10.3 $J_{\alpha,\beta}$ = 4.0	4.53(d) $J_{\gamma,\delta}$ =3.3	5.97(d) $J_{\gamma,\delta}$ =3.3
2	7.70(d) $J_{NH,\beta}$ =8.1	4.51(p) $J_{NH,\beta}$=8.1 $J_{\alpha,\beta}$ = 8.1	1.34(d) $J_{\alpha,\beta}$ =8.1	-	-
3	8.34(d) $J_{NH,\beta=}$9.5	4.67(d) $J_{\alpha,\beta}$ = 4.0	4.7558(dd) $J_{NH,\beta=}$9.5 $J_{\alpha,\beta}$ = 4.0	4.57(d) $J_{\gamma,\delta}$ =3.6	6.08(d) $J_{\gamma,\delta}$ =3.6
4	8.15(d) $J_{NH,\beta}$=7.3	4.48(p) $J_{NH,\beta=}$7.3 $J_{\alpha,\beta}$ = 7.3	1.40(d) $J_{\alpha,\beta}$ =7.3	-	-
5	8.20(d) $J_{NH,\beta=}$8.8	4.76(d) $J_{\alpha,\beta}$ = 4.0	4.7518(dd) $J_{NH,\beta=}$8.8	4.57(d) $J_{\gamma,\delta}$ =3.6	6.06(d) $J_{\gamma,\delta}$ =3.6
6	7.862(d) $J_{NH,\beta}$= 7.7	4.38(p) $J_{NH,\beta=}$7.7 $J_{\alpha,\beta}$ = 7.7	1.29(d) $J_{\alpha,\beta}$ =7.7	-	-
7	8.17(d) $J_{NH,\beta=}$8.0	4.71(d) $J_{\alpha,\beta}$ = 4.0	4.70(dd) $J_{NH,\beta=}$ 8.0 $J_{\alpha,\beta}$ = 4.0	4.58(d) $J_{\gamma,\delta}$ =3.6	6.04(d) $J_{\gamma,\delta}$ =3.6
8	7.868(d) $J_{NH,\beta}$= 7.7	4.34(p) $J_{NH,\beta=}$7.7 $J_{\alpha,\beta}$ = 7.7	1.31(d) $J_{\alpha,\beta}$ =7.7	-	-

Others: Boc(1.42), acetonides: 1.30, 1.51, 1.31, 1.52

The observed coupling constants in CD_3OH are closely comparable with those observed in DMSO-d_6. The results suggest that these oligomers adopt similar helical conformation in both the solvents.However,due to the overlapped resonances detailed spatial correlation(ROESY) could not be established.

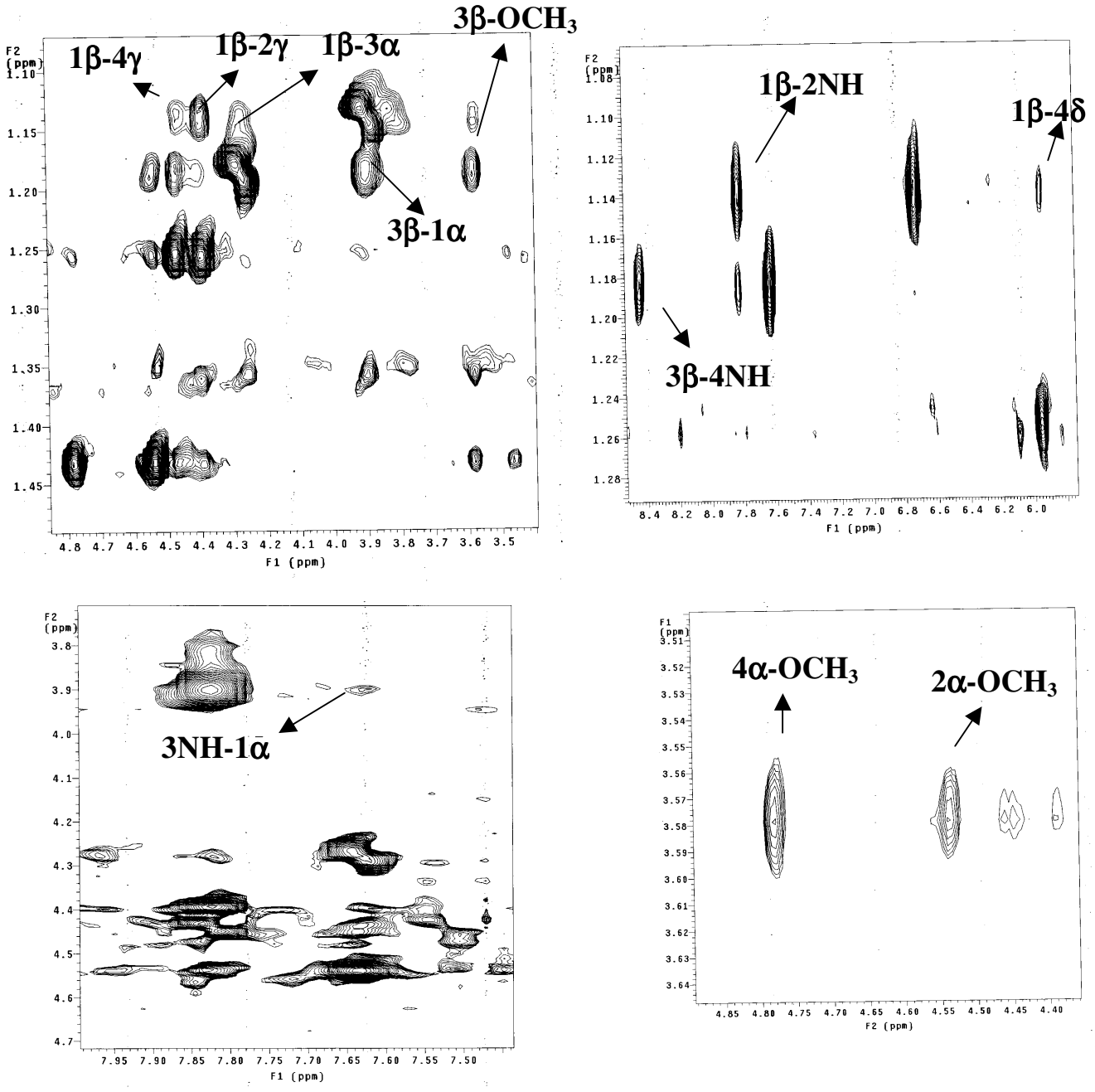
NMR STUDIES IN DMSO-d_6

Supporting Table-07: Chemical shifts (ppm) and coupling constants (Hz) for 1 (DMSO-d6 at 298K) 500-MHz

Residue	NH	CαH	CβH/CH_3	CγH	CδH
1	6.73(d) $J_{NH,\beta}$ =7.6 Hz	3.89(p) $J_{NH,\beta}$=7.6 $J_{\alpha\beta}$ = 7.6	1.13(d) $J_{\alpha\beta}$ = 7.6	-	-
2	7.83(d) $J_{NH,\beta=}$9.2 Hz	4.53(d) $J_{\alpha\beta}$ = 4.4 Hz	4.43(dd) $J_{NH,\beta=}$4.4 hz $J_{\alpha\beta}$ = 4.4 Hz	4.39(d) $J_{\gamma,\delta}$ = 3.9	5.94(d) $J_{\gamma,\delta}$ = 3.9
3	7.63(d) $J_{NH,\beta}$ =8.0 Hz	4.27(dq) $J_{NH,\beta}$=8.0, $J_{\alpha\beta}$ = 8.0	1.17(d) $J_{\alpha\beta}$ = 8.0	-	-
4	8.44(d) $J_{NH,\beta=}$9.2 Hz	4.77(d) $J_{\alpha\beta}$ = 4.5 Hz	4.55(dd) $J_{NH,\beta=}$9.2 Hz $J_{\alpha\beta}$ = 4.5 Hz	4.47(d) $J_{\gamma,\delta}$ = 3.7 Hz	5.96(d) $J_{\gamma,\delta}$ = 3.7 Hz

Others: Boc(1.43), acetonides :1.25,1.36,1.41,1.43.

Supporting Figure-18: ROESY expansions of 1 :

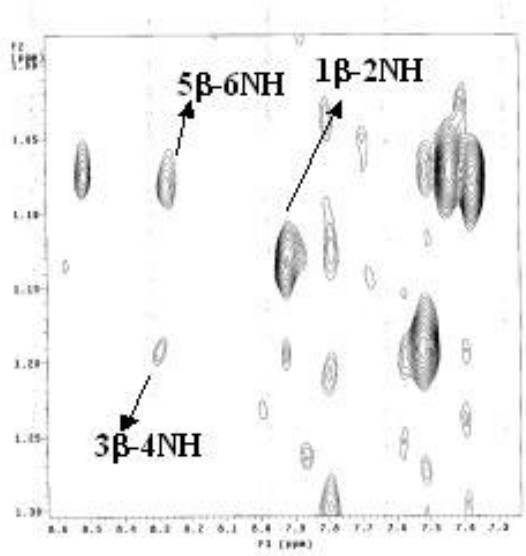


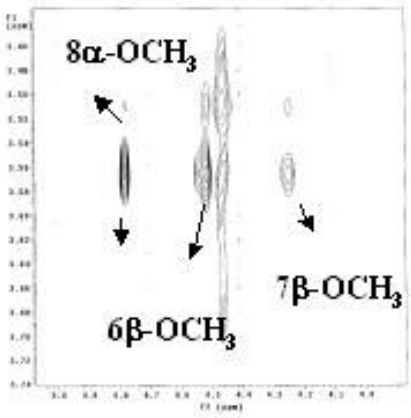
Supporting Table-08: Chemical shifts (ppm) and coupling constants (Hz) for 2 (DMSO-d6 at 298K)

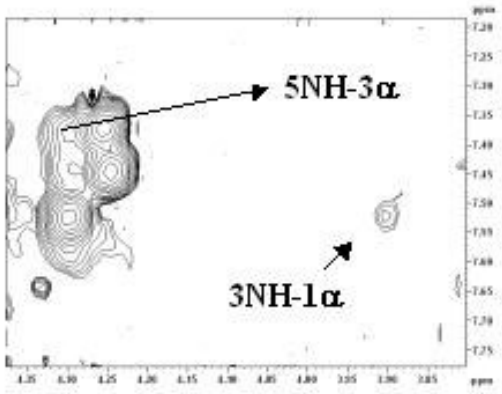
Residue	NH	CαH	CβH/CH_3	CγH	CδH
1	6.75(d) $J_{NH,\beta}$ =7.7	3.90(dq) $J_{NH,\beta}$= 7.7 $J_{\alpha\beta}$ = 7.3	1.12(d) $J_{\alpha\beta}$ = 7.3	-	-
2	7.92(d) $J_{NH,\beta=}$8.3	4.53(d) overlapped	4.44(dd) $J_{NH,\beta=}$8.3	4.43(d) $J_{\gamma,\delta}$ = 3.8	5.96(d) $J_{\gamma,\delta}$ = 3.8
3	7.52(d) $J_{NH,\beta}$ =8.3	4.29(dq) $J_{NH,\beta}$=8.3, $J_{\alpha\beta}$ = 7.3	1.18(d) $J_{\alpha\beta}$ = 7.3	-	-
4	8.30(d) $J_{NH,\beta=}$9.80	4.51(d) overlapped	4.51(dd) $J_{NH,\beta=}$9.80 overlapped	4.48(d) $J_{\gamma,\delta}$ = 3.8	5.98(d) $J_{\gamma,\delta}$ = 3.8
5	7.37(d) $J_{NH,\beta}$ =8.3	4.25(dq) $J_{NH,\beta}$=8.3, $J_{\alpha\beta}$ = 7.3	1.06(d) $J_{\alpha\beta}$ = 7.3	-	-
6	8.28(d) $J_{NH,\beta=}$10.1	4.51(d) overlapped	4.51(dd) $J_{NH,\beta=}$10.1 overlapped	4.46(d) $J_{\gamma,\delta}$ = 3.8	5.98(d) $J_{\gamma,\delta}$ =3.8
7	7.44(d) $J_{NH,\beta}$ =8.0	4.24(dq) $J_{NH,\beta}$=8.0, $J_{\alpha\beta}$ = 7.3	1.06(d) $J_{\alpha\beta}$ = 7.3	-	-
8	8.52(d) $J_{NH,\beta=}$9.40	4.78(d) $J_{\alpha\beta}$ = 4.5	4.53(dd) $J_{NH,\beta=}$9.40 $J_{\alpha\beta}$ = 4.5	4.37(d) $J_{\gamma,\delta}$ =3.8	5.45(d) $J_{\gamma,\delta}$ =3.8

Others: Boc(1.35), acetonides: 1.30, 1.50, 1.31, 1.52

Supporting Figure-19 :ROESY expansions of 2 : (DMSO-d_6)





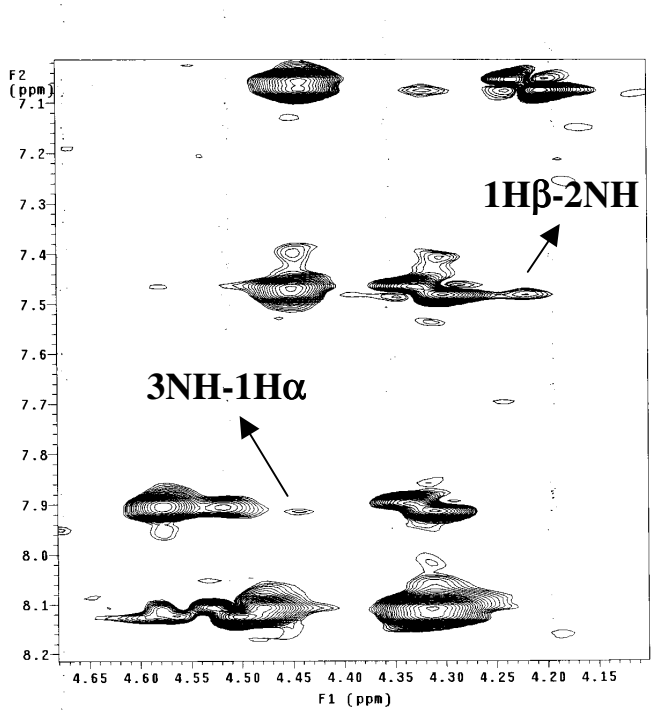


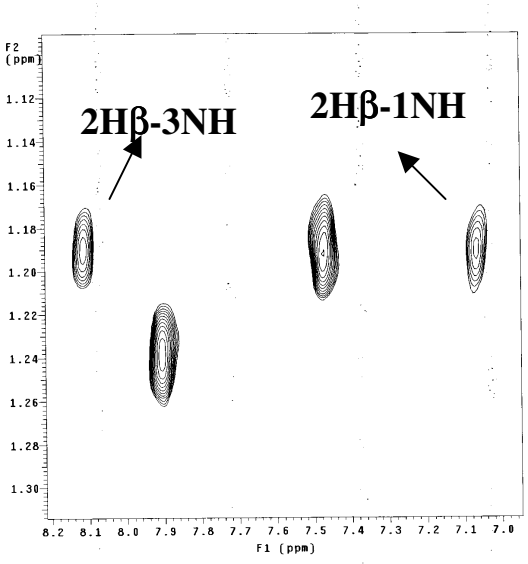
Supporting Table-09 :Chemical shifts (ppm) and coupling constants (Hz) for 3 (DMSO-d6 at 298K)

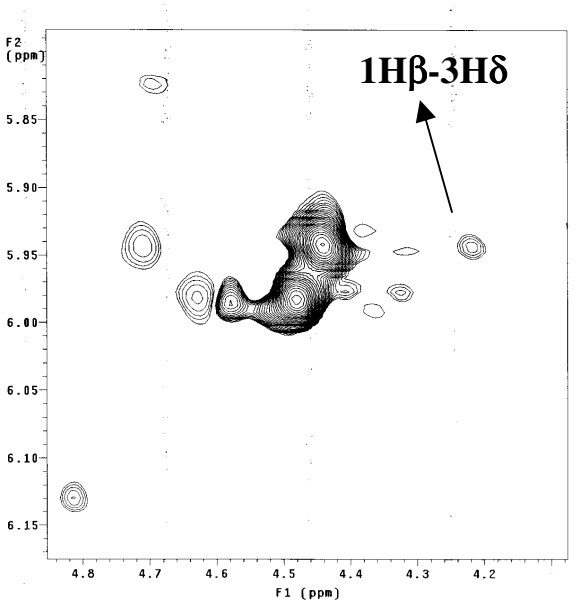
Residue	NH	CαH	CβH/CH_3	CγH	CδH
1	7.07(d) $J_{NH,\beta}$=9.8	4.45(d) $J_{\alpha\beta}$ = 4.5	4.22(dd) $J_{NH,\beta}$=9.8 $J_{\alpha\beta}$ = 4.5	4.44(d) $J_{\gamma,\delta}$ =3.8	5.94(d) $J_{\gamma,\delta}$ =3.8
2	7.47(d) $J_{NH,\beta}$=8.2	4.31(dq) $J_{NH,\beta}$=8.2 $J_{\alpha\beta}$ = 7.0	1.19(d) $J_{\alpha\beta}$ = 7.0	-	-
3	8.12(d) $J_{NH,\beta}$=9.5	4.58(d) $J_{\alpha\beta}$ = 4.5	4.52(dd) $J_{NH,\beta}$=9.5 $J_{\alpha\beta}$ = 4.5	4.48(d) $J_{\gamma,\delta}$ =3.8	5.98(d) $J_{\gamma,\delta}$ =3.8
4	7.91(d) $J_{NH,\beta}$=7.3	4.32(dq) $J_{NH,\beta}$=7.3 $J_{\alpha\beta}$ = 7.0	1.24(d) $J_{\alpha\beta}$ = 7.0	-	-

Others: Boc(1.43), acetonides: 1.25 , 1.27 , 1.40 , 1.44

Supporting Figure-20: ROESY expansions of 3 (DMS0-d_6):





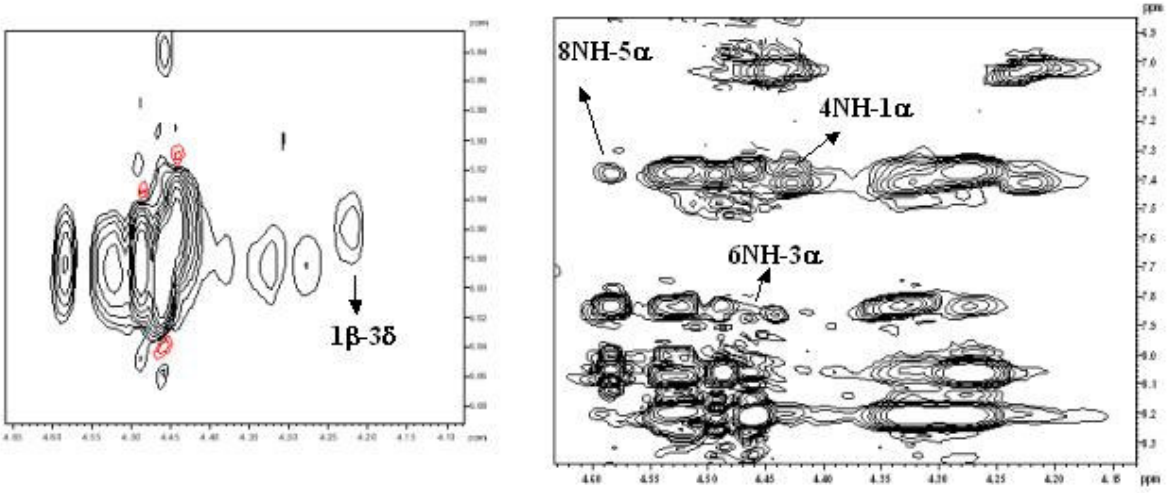


Supporting Table-10: Chemical shifts (ppm) and coupling constants (Hz) for 4 (DMSO-d6 at 298K)-600MHz

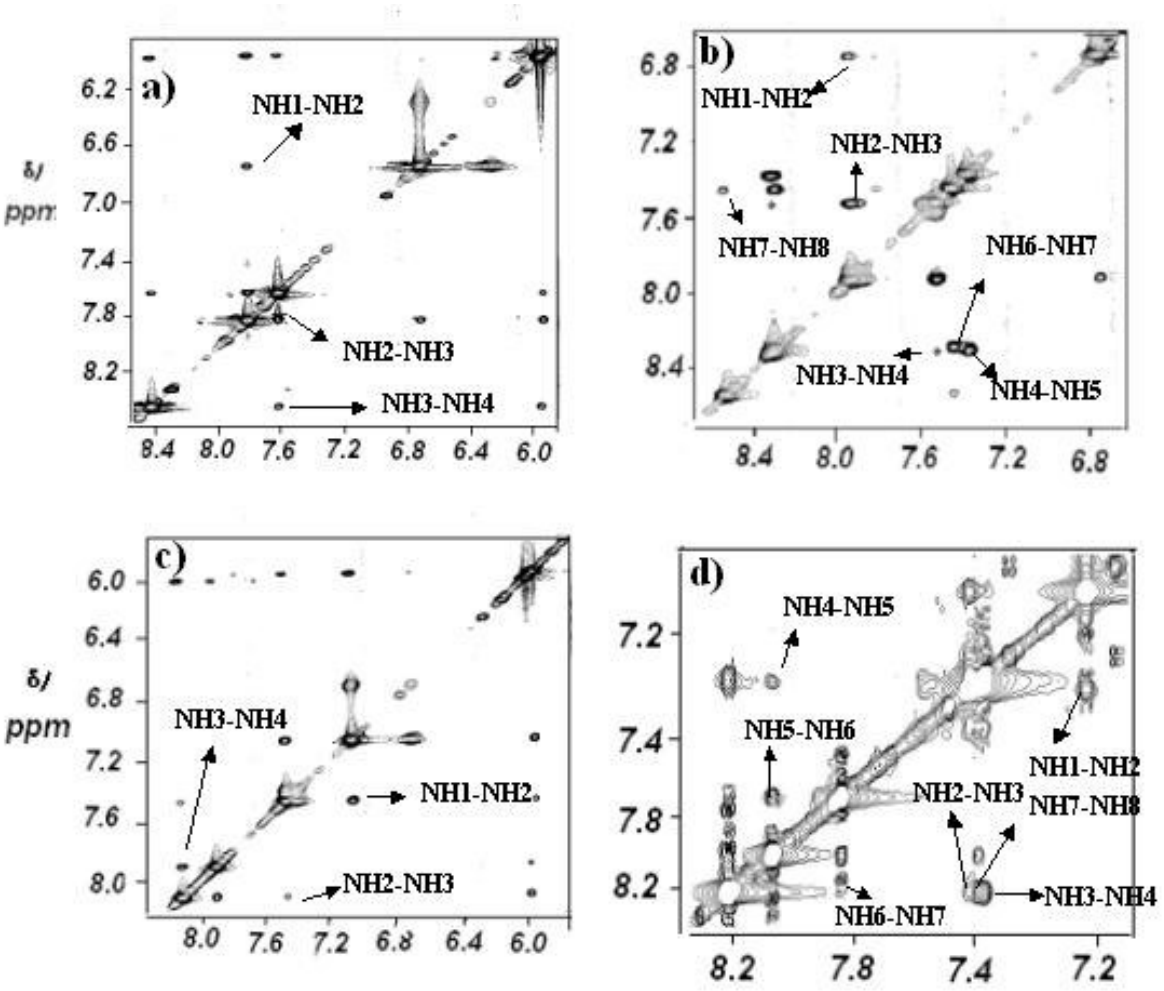
Residue	NH	CαH	CβH	CγH	CδH
1	7.03(d) $J_{NH,\beta}$ =9.80	4.42(d) $J_{\alpha\beta}$ = 4.2	4.22(dd) $J_{NH,\beta}$= 9.80 $J_{\alpha\beta}$ = 4.2	4.44(d) $J_{\gamma,\delta}$ =8.5	5.95(d) $J_{\gamma,\delta}$ =3.5
2	7.41(d) $J_{NH,\beta}$ =8.30	4.29(dq) $J_{NH,\beta}$=8.3, $J_{\alpha\beta}$ = 8.3	1.48(d) $J_{\alpha\beta}$ = 8.3	-	-
3	8.20(d) $J_{NH,\beta=}$9.6	5.20(d) $J_{\alpha\beta}$ = 4.4	5.149(dd) $J_{NH,\beta=}$8.5 $J_{\alpha\beta}$ = 4.4	4.95(d) $J_{\gamma,\delta}$ =3.5	6.34(d) $J_{\gamma,\delta}$ =3.5
4	7.36(d) $J_{NH,\beta}$=8.30	4.27(dq) $J_{NH,\beta=}$8.3 $J_{\alpha\beta}$ = 8.3	1.10(d) $J_{\alpha\beta}$ =8.3	-	-
5	8.06(d) $J_{NH,\beta=}$9.3	4.585(d) $J_{\alpha\beta}$ = 4.3	4.5293(dd) $J_{NH,\beta=}$9.3 $J_{\alpha\beta}$ = 4.3	4.44(d) $J_{\gamma,\delta}$ =3.5	5.97(d) $J_{\gamma,\delta}$ =3.5
6	7.83(d) $J_{NH,\beta}$= 7.4	4.33(dq) $J_{NH,\beta=}$7.4 $J_{\alpha\beta}$ = 7.4	1.23(d) $J_{\alpha\beta}$ =7.4	-	-
7	8.2(d) $J_{NH,\beta=}$9.6	4.49(d) $J_{\alpha\beta}$ = 3.5	4.5211(dd) $J_{NH,\beta=}$9.6 $J_{\alpha\beta}$ = 3.5	4.48(d) $J_{\gamma,\delta}$ =3.5	5.98(d) $J_{\gamma,\delta}$ =3.5
8	7.38(d) $J_{NH,\beta}$= 8.1	4.32(p) $J_{NH,\beta=}$8.1 $J_{\alpha\beta}$ = 8.1	1.10(d) $J_{\alpha\beta}$ =8.1	-	-

Others: Boc(1.42), acetonides: 1.30, 1.50, 1.31, 1.52

Supporting Figure-21 : ROESY expansions of 4



Supporting Figure-22 : ROESY expansions showing NH-NH sequensial NOE's 1-4 (DMSO)



FT-IR STUDIES

FT-IR investigations were carried out on Nicholet 670 spectrometer. About 4mM concentrated compounds in $CHCl_3$ in liquid cell, and also on KBr pellet were studied. IR data exhibited a characteristic NH-stretching band at ~3300 cm^{-1} (Dan Yang *et al*., *J. Am. Chem.Soc*, 2004, *126*, 6956 ; Claridge, T.D.W *et al*., *Tetrahedron.Lett*, 2001, *42*, 4251) and amide-I band at ~1670 cm^{-1} (Ricci. M *et al*., *AAPS PharmsSciTech*, 2000, *1*, 1; Martneck . T.A *et al*., *Angew. Chem. Int. Ed*. 2002, *41*, 1718; Hetenyi *et al*., *J. Am. Chem. Soc*. 2005, *127*, 547), which show the possibility of strong inter-residue NH-CO H-bonding. Wherever necessary, the IR spectra were deconvoluted (assuming Gaussian shapes) to estimate the *relative* intensities of the strongly and weakly H-bonded/non-bonded amide groups. There could be some acceptable error in the intensities and widths of the fitted curves due to smearing of lines and shoulders. The purpose of this exercise was mainly to show the variation of relative intensities of H-bonded peaks with respect to the chain length of the oligomers. These findings are in accordance with the CD and NMR observations.

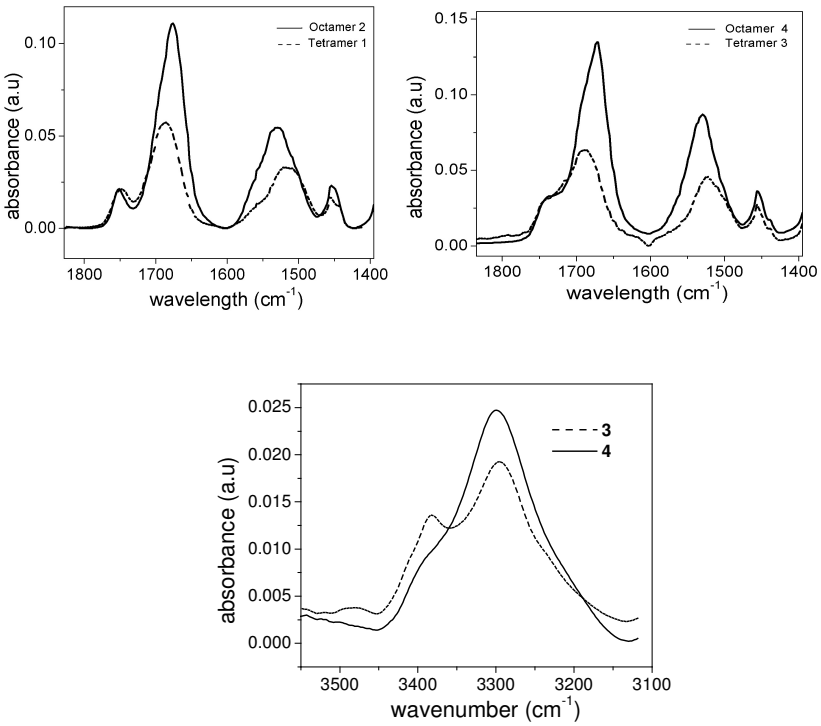
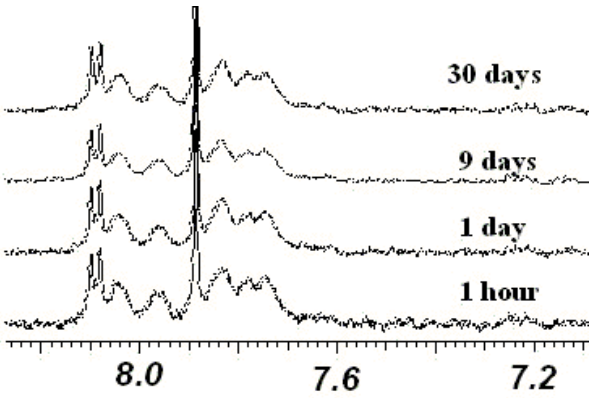


Figure 23: FT-IR bands of Amide-I and NH region: Signatures of H-bonding in **1**-**4**

^{1}H NMR NH/ND exchange studies in Methanol-d_4 :

Representative spectra of NH/ND exchange: The shielding of the hydrogen bonded NH-protons has been assessed by NH/ND exchange(Hetenyi *et al*., *J. Am. Chem. Soc*. 2005, *127*, 547) measurements in Methanol-d_4. These experiments were carried out for 30 days. Most of the NH protons did not exchange rapidly in this period for **2**.



Molecular Dynamics

All molecular dynamics calculations were carried out by using Sybyl (6.7) program on a Silicon Graphics O_2 workstation. The Tripos force-field with default parameters was used throughout the simulations. Minimizations were carried out first with steepest decent, followed by conjugate gradient method until the convergence was attained. The convergence was defined as attaining of low gradient. The minimized structures were then subjected to MD simulations for duration of 550ps (50 cycles, each of 11ps period, of the simulated annealing protocol). The atomic velocities were applied following Boltzmann distribution about the center of mass to obtain a starting temperature of 1000K. After simulating for 1ps at this high temperature, the system temperature was reduced stepwise over 10ps period to reach a final temperature of 300K. Resulting structures were sampled after every 11ps (one cycle), leading to an ensemble of total 50 structures. The samples were minimized using the above mentioned energy minimization protocol, compared and superimposed as shown in figure 5. NOE distances and torsional angles obtained from NMR data were used as restraints in the minimization as well as MD runs. Supporting Figure 23 illustrate the top view and side view of peptides **2** and **4** . For the sake of clarity, in some of the compounds the protons and acetonide groups have been removed.

Supporting Table-11: Distance constraints used in MD calculations for 2 derived from ROESY experiment

Residue	Atom	Residue	Atom	Intensity
1	NH	2	NH	M
2	NH	1	CαH	M
2	NH	2	CδH	M
2	NH	3	NH	M
2	NH	1	CβH	M
2	NH	2	CγH	M
3	NH	2	CαH	M
3	NH	4	NH	M
3	CαH	5	NH	W
3	NH	1	CαH	VW
4	NH	4	CδH	M
4	NH	5	NH	M
4	NH	3	CβH	
4	NH	3	CαH	M
4	NH	4	CγH	M
5	NH	4	CαH	M
5	CαH	7	NH	W
5	CαH	8	NH	W
5	NH	3	CαH	VW
5	CβH	7	CαH	W
6	NH	5	CαH	M
6	NH	7	NH	M
6	NH	6	CγH	M
6	NH	6	CδH	M
6	NH	5	CβH	M
7	NH	6	CαH	M
7	NH	8	NH	M
8	NH	7	CαH	M
8	NH	8	CδH	M
8	NH	8	CγH	M-
-	OCH_3	6	CβH	W
-	OCH_3	6	CαH	M
-	OCH_3	7	CβH	M
-	OCH_3	8	CαH	M

Supporting Table-12: Distance constraints used in MD calculations for 4 derived from ROESY experiment

Residue	Atom	Residue	Atom	Intensity
1	CβH	3	NH	W
1	NH	2	NH	M
1	CβH	5	NH	W
1	NH	1	CγH	M
1	NH	1	CδH	M
1	CβH	3	CδH	VW
2	NH	3	NH	M
2	NH	1	CαH	M
3	NH	3	CγH	M
3	NH	4	NH	M
3	NH	2	CαH	M
3	NH	3	CδH	W
4	NH	3	CαH	M
4	NH	5	NH	M
5	NH	6	NH	M
5	NH	5	CδH	W
5	CβH	8	NH	M
5	NH	4	CαH	M
5	NH	5	CγH	M
6	NH	7	NH	M
6	NH	5	CαH	M
7	NH	8	NH	M
7	NH	7	CδH	W
7	NH	7	CγH	M-
7	NH	6	CαH	M
8	NH	5	CαH	VW
8	NH	7	CαH	M

Supporting Figure-24: Five Superimposed minimum energy structures a)side view b) top view for 2 c)side view for 4