

Supporting information

Mueller Matrix Fluorescence Spectroscopy for Probing Self-assembled Peptide based Hybrid Supramolecular Structure and Orientation

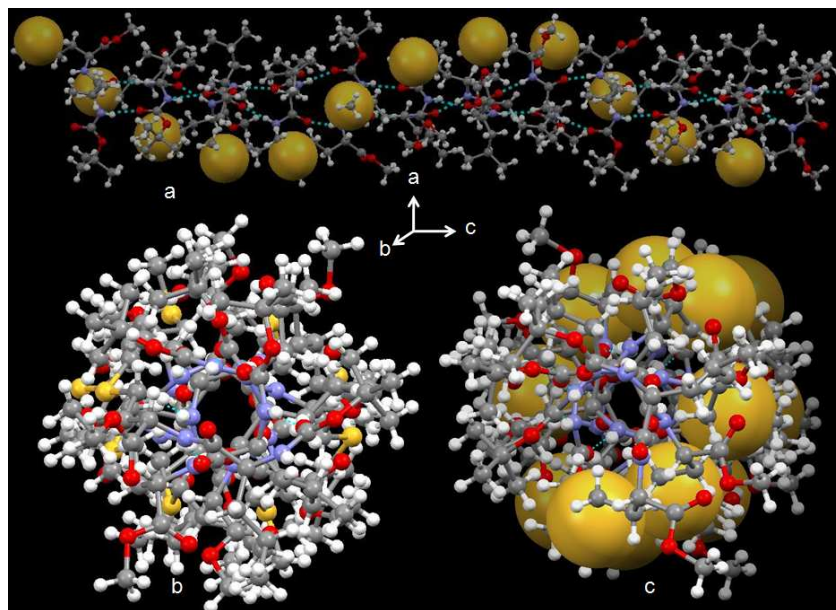
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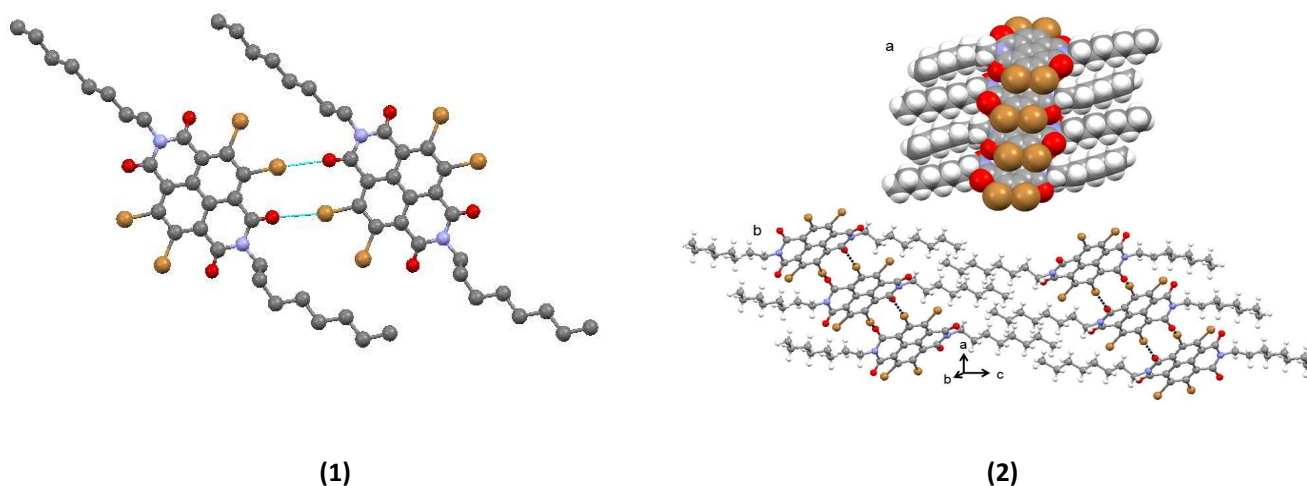
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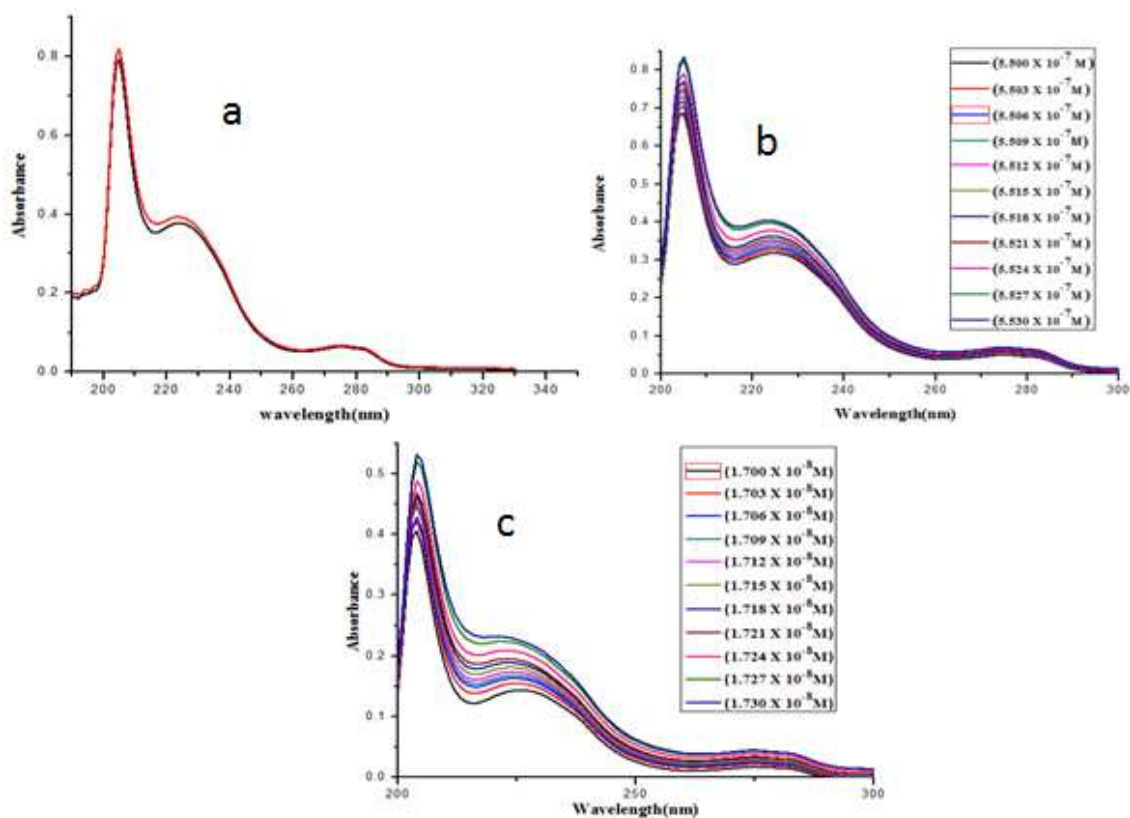
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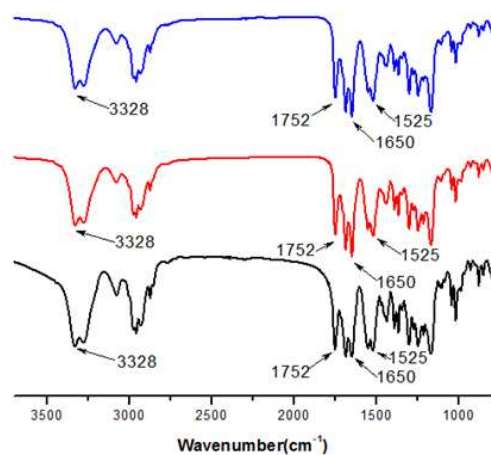
ESI Figure S1: (a) The twisted sheet like assembly of dipeptide **2** and the helical arrangement of sulfur atoms (yellow balls). The intermolecular hydrogen bonds are shown as black dotted lines. (b) and (c) The top view and packing diagram of the twisted sheet showing parallel arrangement of nanotube like structures.



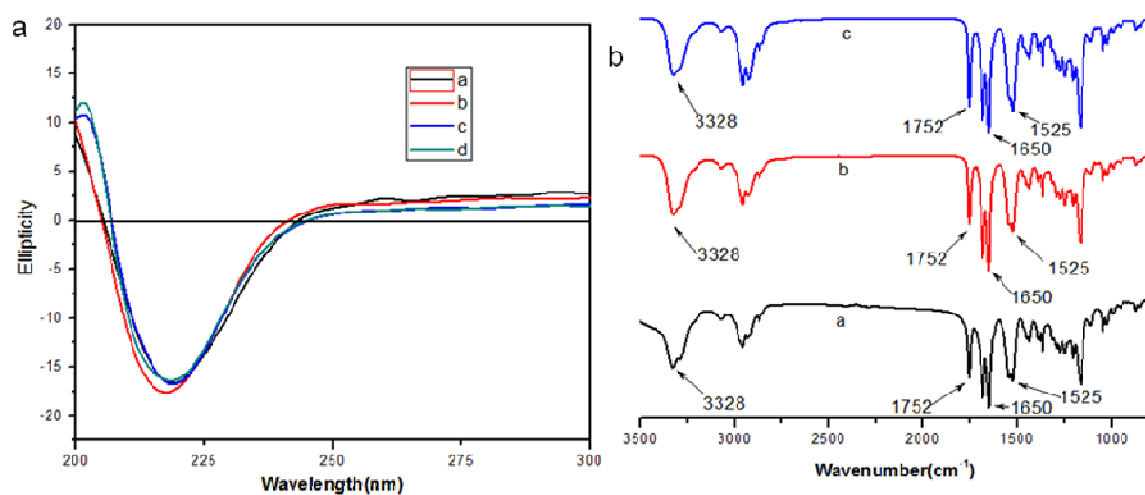
ESI Figure S2. (1) Halogen bonded dimer of TB-NDI. 2(a) Higher order packing of TB-NDI showing a column like structure through π - π stacking interactions. 2(b) The complex sheet like structure of TB-NDI through hydrophobic interactions between octyl moieties.



ESI Figure S3. (a) UV Spectra of the dipeptides **1** (black) and **2** (red) at concentration 5.47×10^{-7} M. (b) Concentration dependent UV Spectra of Boc-Val-Met-OMe **1**. (c) Concentration dependent UV Spectra of Boc-Leu-Met-OMe **2**.



ESI Figure S4. FT-IR spectra of Peptide **1** in solid state (Black), Peptide **1** in methanol (red), Peptide **1** with TB-NDI in methanol (blue).



ESI Figure S5 (a) CD spectra of dipeptide **2** and TB-NDI hybrid. Black - peptide **2** in solid state, red – peptide **2** and TB-NDI in solid state, blue- only peptide **2** in methanol, green - peptide **2** with TB-NDI in methanol. (b) FT-IR spectra of peptide **2** in solid state (black), peptide **2** in methanol solution (red), peptide **2** with TB-NDI in methanol solution (blue).

ESI Table 1. Selected Backbone Torsional Angles (deg) of dipeptides **1** and **2**.

	$\phi 1$	$\psi 1$	$\phi 2$	$\psi 2$
Peptide 1				
Mol-1	174.26	-100.00	-62.58	140.92
Mol-2	-172.16	-109.73	-63.80	151.33
Mol-3	-177.57	-118.59	-81.33	-5.11
Mol-4	-79.91	145.40	-65.56	149.03
Peptide 2				
Mol-1	-110.61	124.02	-53.52	134.69
Mol-2	-97.37	144.20	-55.28	141.43
Mol-3	-86.16	125.21	-64.44	158.69
Mol-4	-100.23	131.27	-64.39	147.84

ESI Table 2. Hydrogen bonding parameters of dipeptides **1** and **2**.

	D-H....A	D..H(Å)	H..A(Å)	D..A(Å)	D-H..A(°)
1	N5-H5....O69	0.860(3)	2.267(3)	2.938(3)	134.9(2)
	N8-H8....O41	0.860(3)	1.986(2)	2.831(2)	167.1(2)
	N29-H29....O89 ^a	0.860(3)	1.975(2)	2.831(2)	173.4(2)
	N32-H32...O22	0.860(3)	2.082(3)	2.887(3)	155.5(3)
	N52-H52...O93	0.860(3)	2.032(3)	2.868(3)	164.1(2)
	N55-H55...O18	0.860(3)	2.024(2)	2.857(2)	162.8(2)
	N76-H76...O45 ^b	0.860(3)	2.039(3)	2.884(3)	167.2(2)
	N79-H79...O65	0.860(3)	1.969(3)	2.819(3)	169.5(2)
2	N1-H1....O17 ^c	0.8600	2.1500	3.003(11)	172.00
	N2-H2....O8 ^d	0.8600	1.9600	2.818(11)	177.00
	N3-H3....O2 ^e	0.8600	2.1400	2.927(11)	152.00
	N4-H4...O13	0.8600	1.9400	2.799(11)	176.00
	N5-H5...O7	0.8600	2.1200	2.957(11)	165.00
	N6-H6A...O18	0.8600	1.9500	2.809(11)	178.00
	N7-H7...O12	0.8600	2.1000	2.942(11)	168.00

^aSymmetry equivalent $a = 3/2-x, 1-y, 1/2+z$, $b = 3/2-x, 1-y, -1/2+z$, $c = 3/2-x, 1-y, -1/2+z$, $d = x, -1+y, z$, $e = x, 1+y, z$.

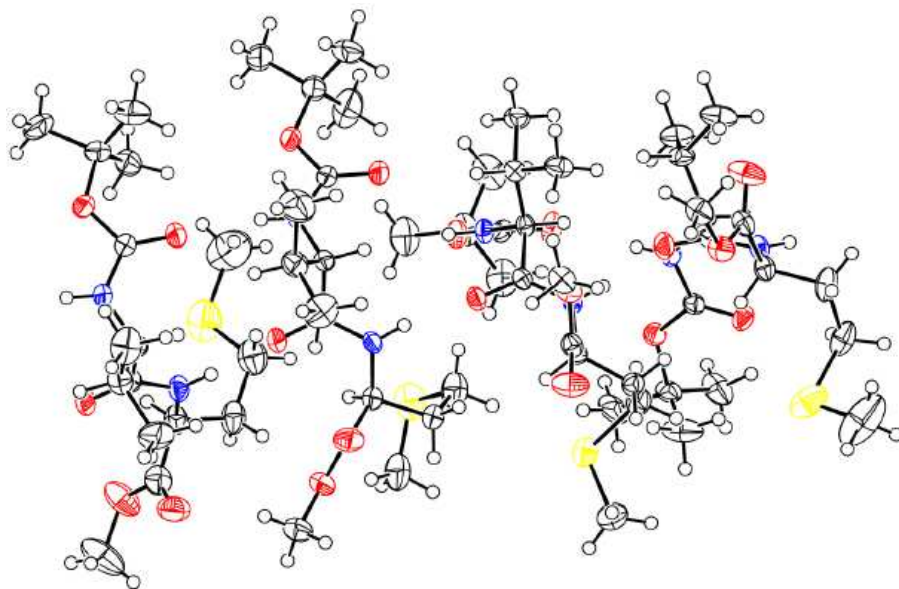


Figure S6: ORTEP diagram of peptide **1** showing the atomic numbering scheme. Ellipsoids are drawn at the 50 % probability level.

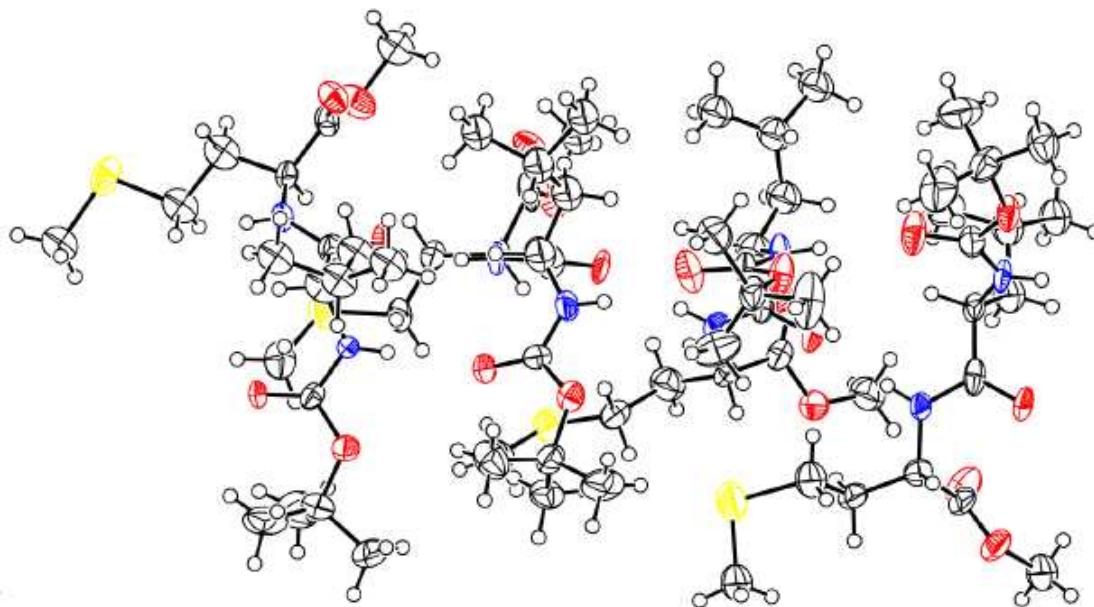
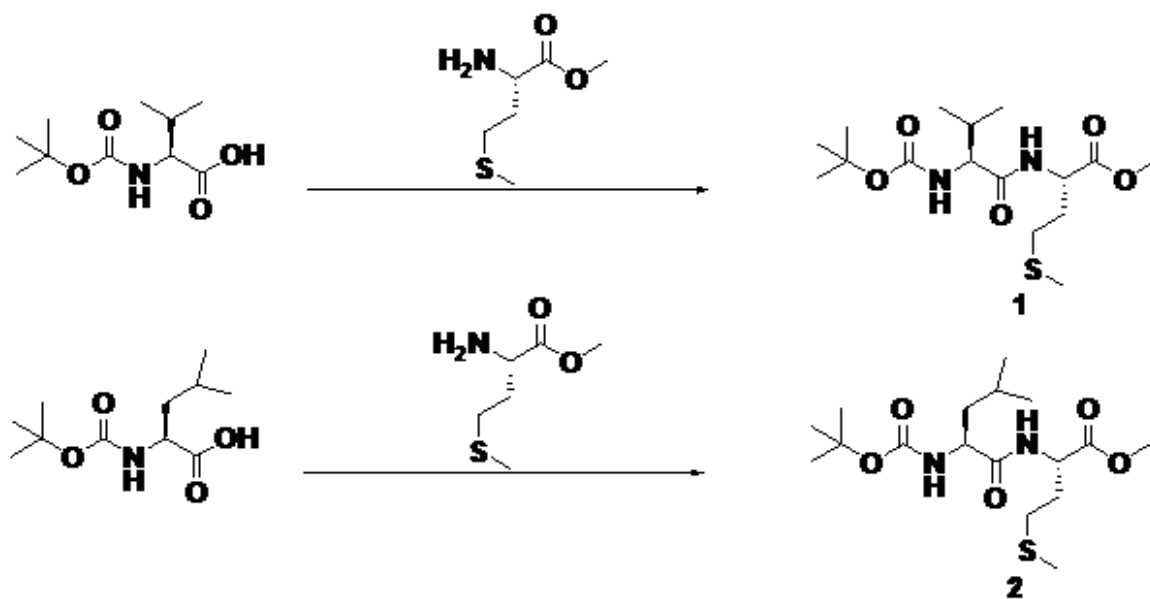


Figure S7: ORTEP diagram of peptide **2** showing the atomic numbering scheme. Ellipsoids are drawn at the 50 % probability level.



Scheme 1: Reactions and conditions: (a) Dry DCM, DCC, HOBT, 0°C, 48h.

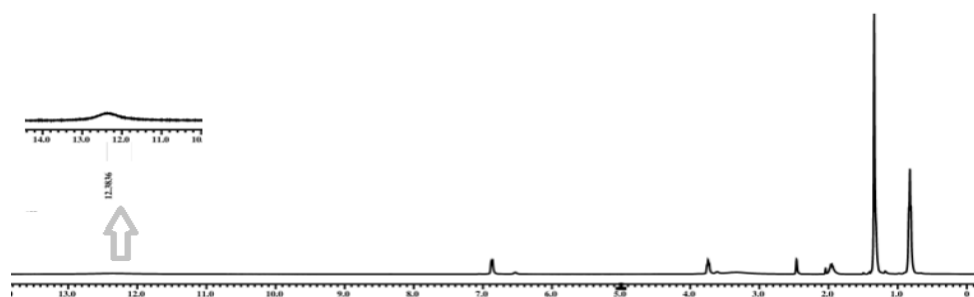


Figure S8: ¹H NMR Spectra of (400 MHz, DMSO-*d*₆, δ in ppm) Boc-Val-OH.

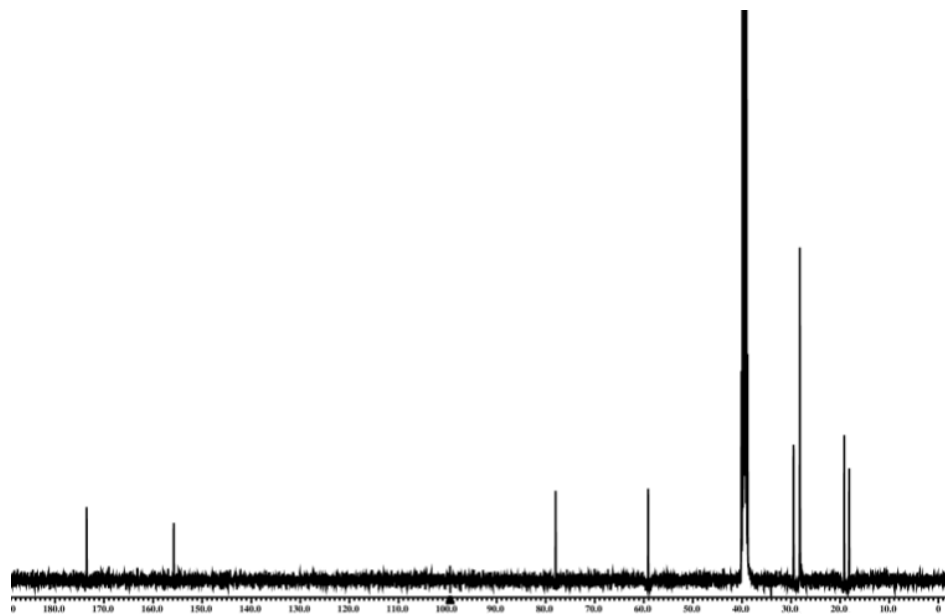


Figure S9: ^{13}C NMR Spectra of (100 MHz, $\text{DMSO-}d_6$, δ in ppm) Boc-Val-OH.

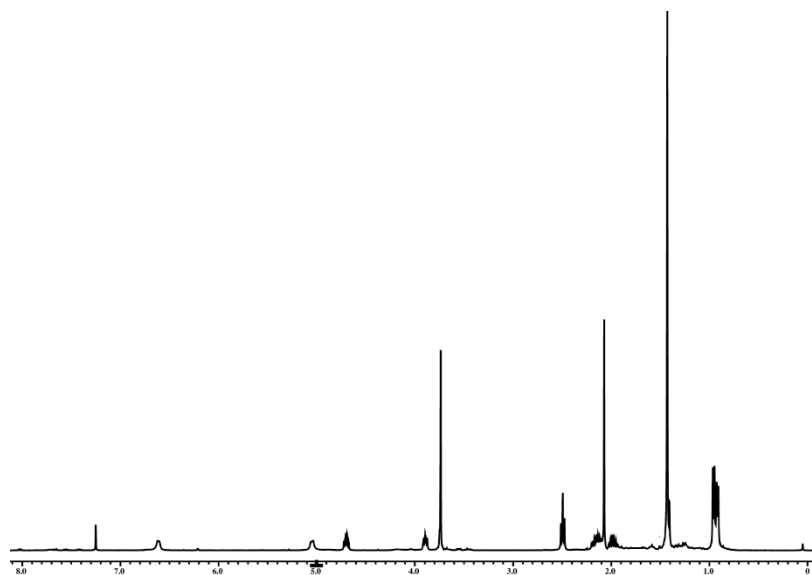


Figure S10: ^1H NMR Spectra of (400 MHz, CDCl_3 , δ in ppm) Boc-Val (1)-Met (2)-OMe **1**.

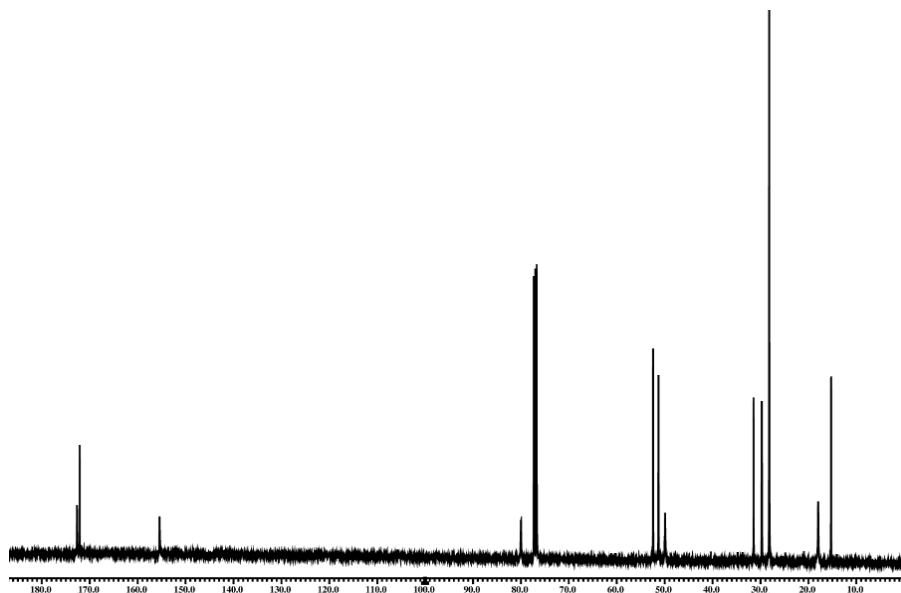


Figure S11: ^{13}C NMR Spectra (100 MHz, CDCl_3 , δ in ppm) of Boc-Val (1)-Met (2)-OMe **1**.

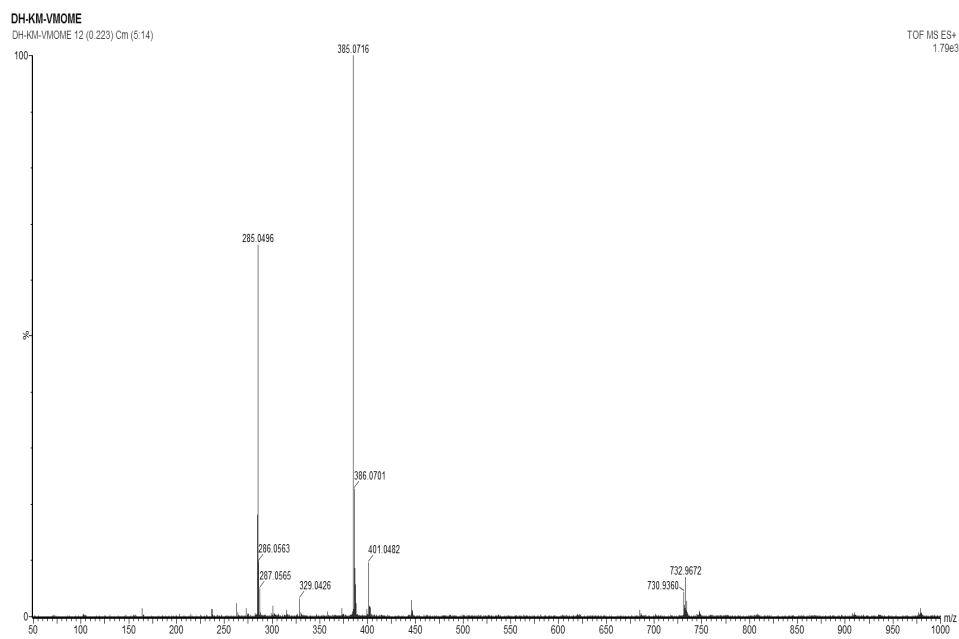


Figure S12: Mass Spectra of Boc-Val (1)-Met (2)-OMe **1**.

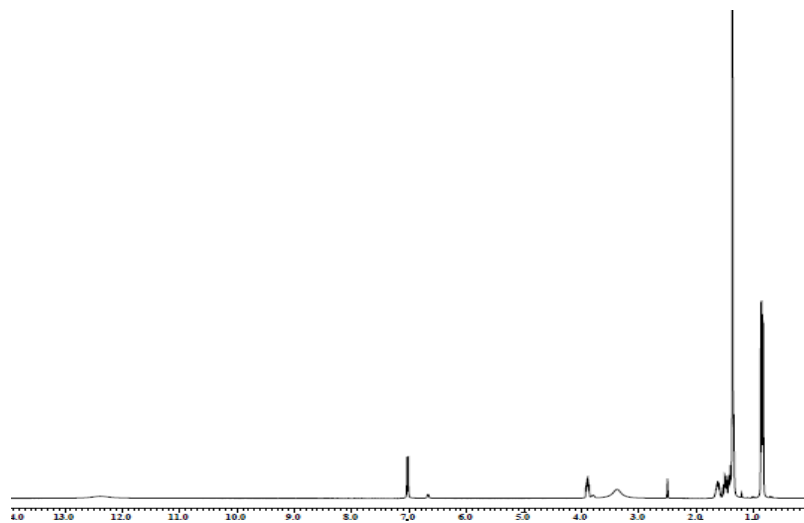


Figure S13: ^1H NMR Spectra (400 MHz, $\text{DMSO-}d_6$, δ in ppm) of Boc-Leu (1)-OH.

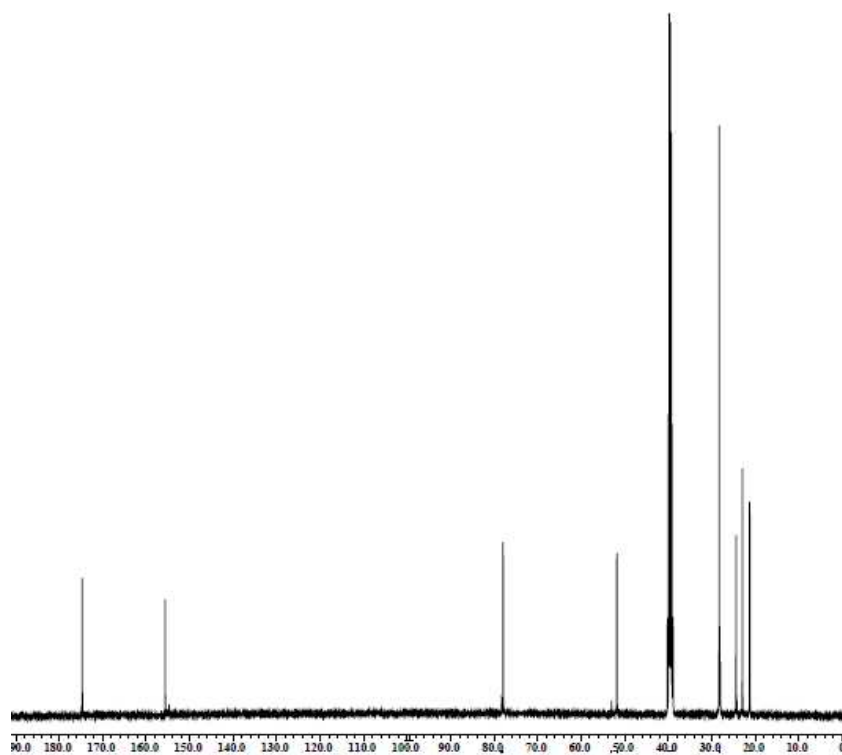


Figure S14: ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$, δ in ppm) spectra of Boc-Leu (1)-OH.

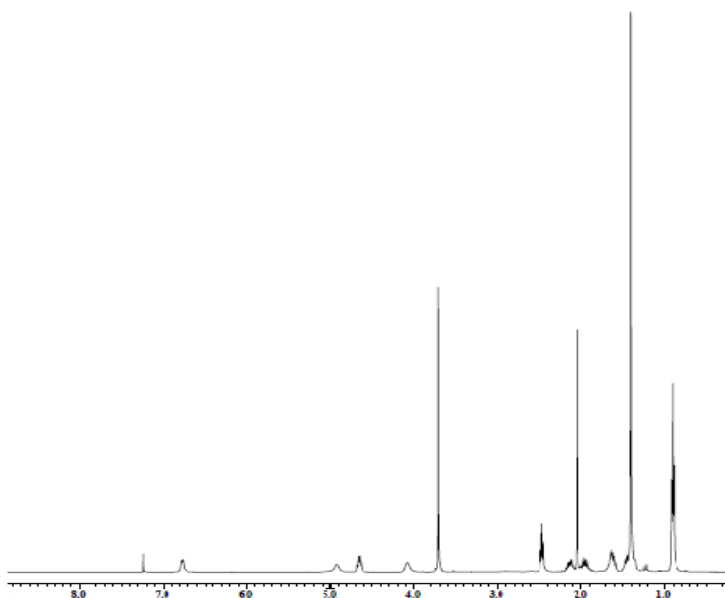


Figure S15: ^1H NMR Spectra (400 MHz, CDCl_3 , δ in ppm) of Boc-Leu (1)-Met (2)-OMe **2**.

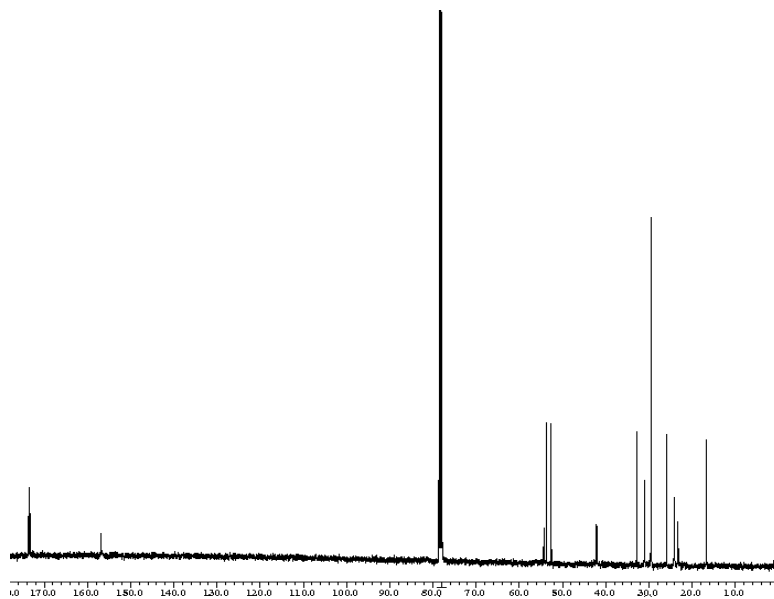


Figure S16: ^{13}C NMR Spectra (100 MHz, CDCl_3 , δ in ppm) of Boc-Leu (1)-Met (2)-OMe **2**.

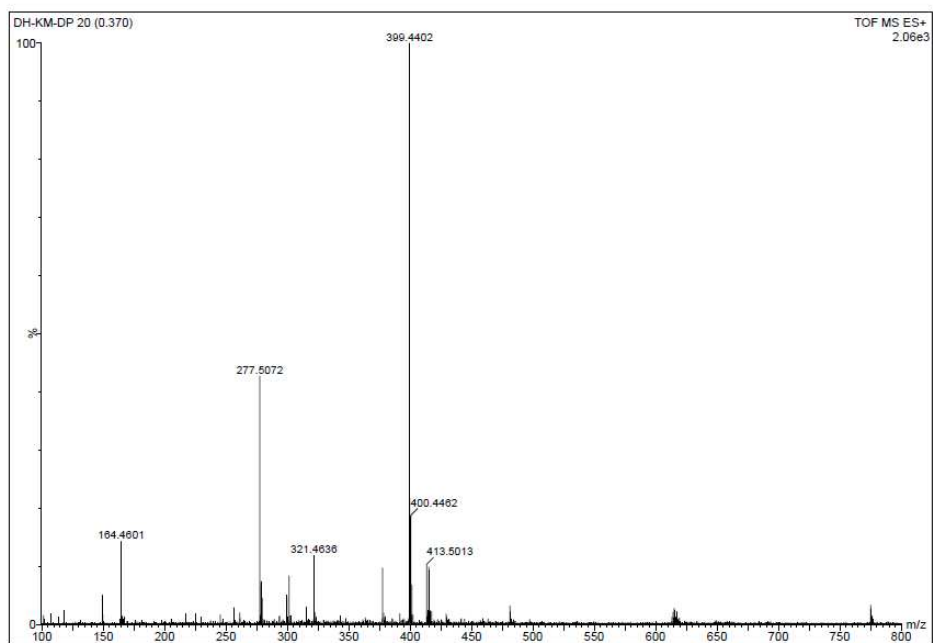


Figure S17: Mass Spectra of Boc-Leu (1)-Met (2)-OMe **2**.