Supporting Information for

Metal-Directed Hierarchical Superhelices from Hybrid Peptide Foldamers

Sanjit Dey, Souvik Roy, DRGKoppalu R. Puneeth Kumar, Sachin A. Nalawade, Manjeet Singh, Sandip U. Toraskar, Souvik Panda Mahapatra, and Hosahudya N. Gopi*

Department of Chemistry, Indian Institute of Science Education and Research (IISER), Pune-411008, India. E-mail: hn.gopi@iiserpune.ac.in

Contents

[1]. ORTEP Diagrams:

A) ORTEP and Map Diagram of P1-CdI_2 Complex:

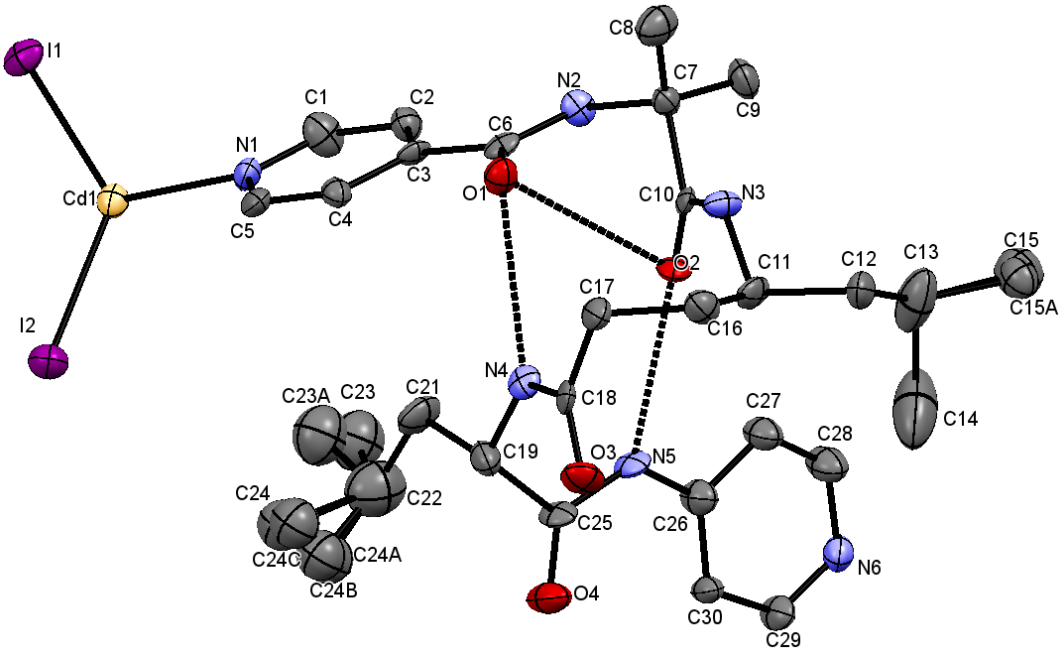
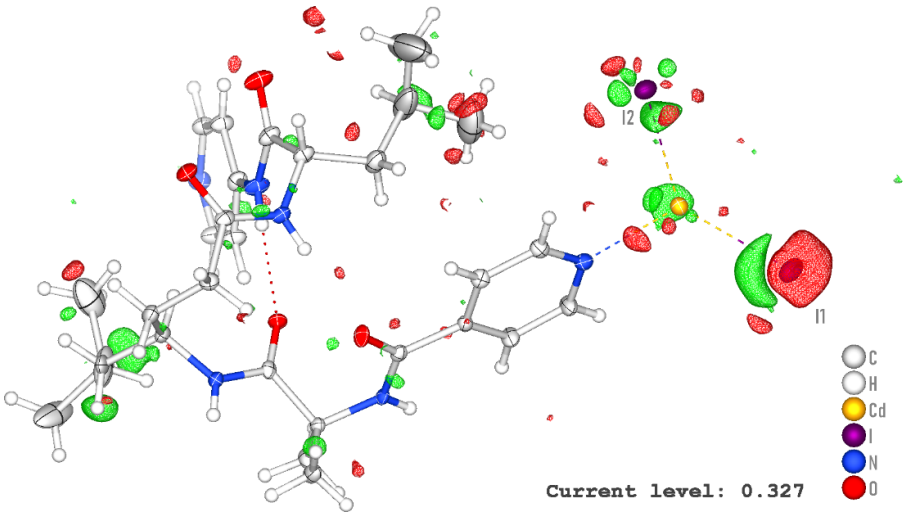


Figure S1: ORTEP diagram of **P1-CdI_2 complex (CCDC = 2103330).** H-bonds are shown in dotted lines. H-atoms are omitted for clarity. Ellipsoids are drawn at 50% probability.



Map Diagram

B) ORTEP Diagram of P2-CdI_2 Complex:

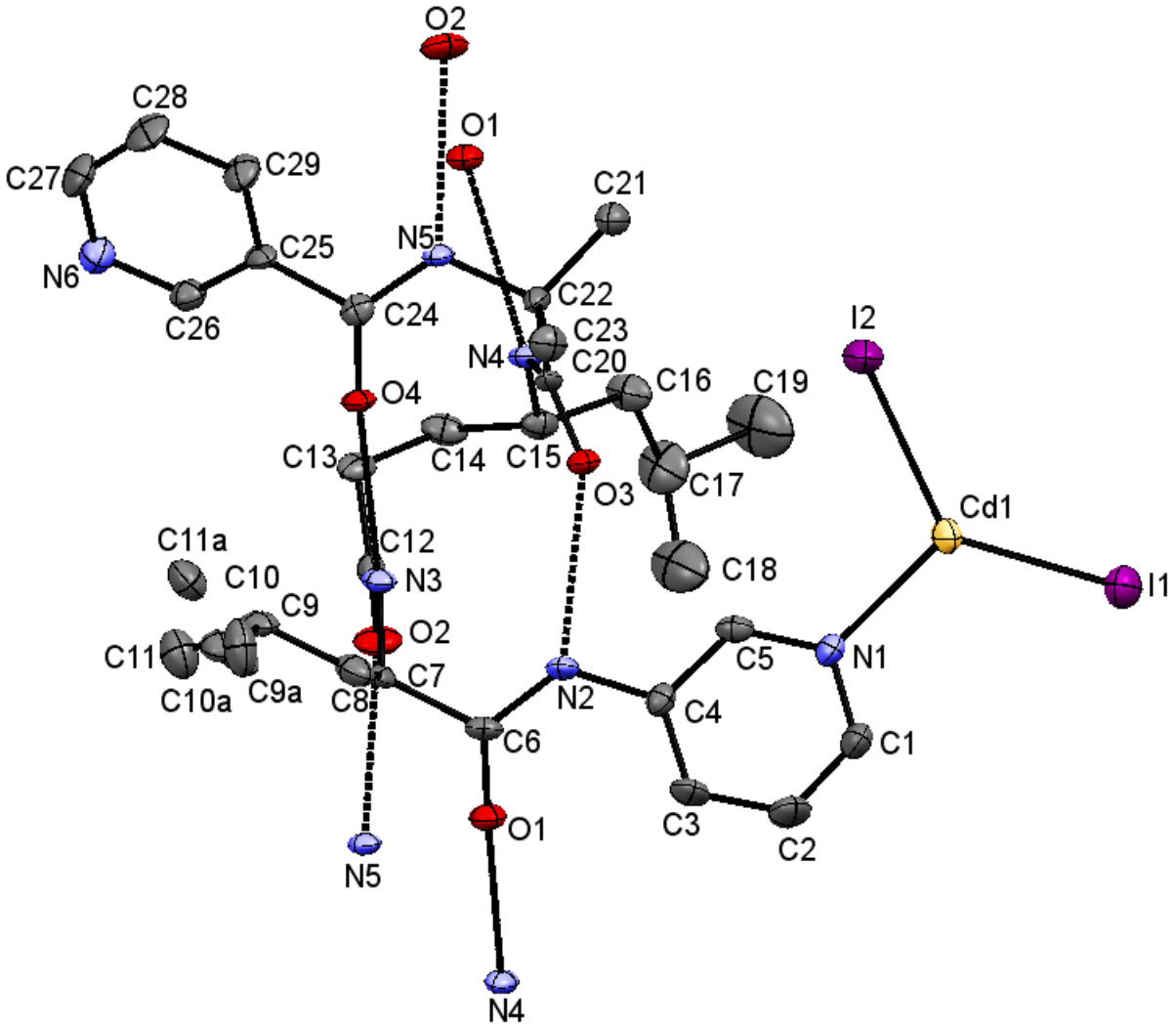


Figure S2: ORTEP diagram of **P2-CdI_2 complex (CCDC = 2172105)**. H-bonds are shown in dotted lines. H-atoms are omitted for clarity. Ellipsoids are drawn at 50% probability.

[2]. Crystal Structure Information:

A) Crystal Structure Analysis of P1-CdI_2 Complex: Crystals were grown by layering 25 mM of 500 µL solution of **P1** in methanol and 25 mM of 500 µL of aqueous solution of CdI_2 in a capped microtube. A single crystal (0.20 × 0.14 × 0.16 mm) was mounted on a loop with a small amount of the paraffin oil. The X-ray data were collected at 100K temperature on a Bruker APEX(II) DUO CCD diffractometer using MoKα radiation (λ = 0.71073Å) ω-scans (2θ = 56.898), for a total of 8900 independent reflections. Space group $P4_12_12$, a = 13.826(3), b = 13.826(3), c = 37.353(12), α, β, γ = 90, V = 7140(4)Å^3, tetragonal, Z = 8 for chemical formula C_{29} H_{31} Cd_1 I_2 N_6 O_4 with one molecule in asymmetric unit; ρcalcd = 1.663gcm^{-3}, μ = 2.380mm^{-1}, F (000) = 3464, The structure was obtained by direct methods using SHELXS-97.[1] The final R value was 0.0587 (wR2 = 0.1422) 5190 observed reflections ($F_0 \geq 4\sigma$ (|F_0|)) and 404 variables, S = 0.907

B) Crystal Structure Analysis of P2-CdI_2 Complex: Crystals were grown by complexation reaction between 25 mM of 500 µL solution of **P2** in methanol and 25 mM of 500 µL of CdI_2 in methanol. Then after 12h the clear reaction mixture left for slow evaporation. After several days later single crystal obtained. A single crystal (0.12 × 0.10 × 0.10 mm) was mounted on a loop with a small amount of the paraffin oil. The X-ray data were collected at 100K temperature on a Bruker APEX(II) DUO CCD diffractometer using MoKα radiation (λ = 0.71073Å) ω-scans (2θ = 56.816), for a total of 8997 independent reflections. Space group $Pca2_1$, a = 17.103(2), b = 8.5730(1), c = 24.367(3), α, β, γ = 90, V = 3572.8(6)Å^3, tetragonal, Z = 4 for chemical formula C_{29} H_{41} I_2 N_6 O_4 Cd_1 with one molecule in asymmetric unit; ρcalcd = 1.680gcm^{-3}, μ = 2.379mm^{-1}, F (000) = 1772. The structure was obtained by direct methods using SHELXS-97.[1] The final R value was 0.0488 (wR2 = 0.1069) 7269 observed reflections ($F_0 \geq 4\sigma$ (|F_0|)) and 385 variables, S = 1.029.

[3]. Torsion Angles and H-bond Parameters:

A) Torsion Angles:

Peptide	Residue	ϕ	θ_1	θ_2	Ψ
P1-CdI_2 complex	Aib	52(1)	-	-	-143(1)
	γLeu	-123(1)	61(1)	65(1)	-115(1)
	Leu	-77(1)	-	-	-38(2)
P2-CdI_2 complex	Aib	50.5(7)	-	-	50.3(6)
	γLeu	129.5(6)	-60.1(7)	-62.5(7)	114.0(6)
	Leu	78.6(6)	-	-	36.4(7)

Table S1: Torsion angle parameters of **P1-CdI_2,** and **P2-CdI_2** complex.

B) H-bond Parameters:

Peptide	Hydrogen Bond	C=O…H-N	C=O…N-H	∠O…H-N
		in angstroms		in degrees
P1-CdI_2 complex	Py CO↔Leu NH	2.180	3.05(1)	169.4
	Aib CO↔ NH Py	2.022	2.86(1)	158.8
P2-CdI_2 complex	Py CO↔Leu NH	1.982(6)	2.844(6)	166.3(6)
	Aib CO↔ NH Py	2.000(6)	2.829(6)	156.4(6)

Table S2: H-bond parameters of **P1-CdI_2,** and **P2- CdI_2** complex.

[4] Experimental Details:

1) Experimental details of Circular Dichroism (CD) spectroscopy:

CD spectra of the P1-CdI_2 and P1-CdI_2 (0.5mg/mL) in MeOH were recorded using JASCO(J-815) spectrometer fitted with a Peltier temperature controller set to 25 °C, using quartz cuvettes with an optical path length of 0.1 mm. The scan was performed in steps of 1 nm over a wavelength range of 190-350 nm with a spectral bandwidth of 1.0 nm and an averaging time of 3 s. The full spectrum of the sample was collected three times and averaged. The baseline was similarly recorded for MeOH and subtracted from the sample spectra.

2) Experimental details of FTIR spectroscopy:

Solution phase FTIR spectra of P1-CdI_2 and P1-CdI_2 (1.5mg/mL) in MeOH were measured at 298 K using Fourier-Transform IR spectrometer (Bruker Alpha II).

3) Experimental details of 2D NMR spectroscopies:

NMR spectra were recorded on 600 MHz Bruker spectrometer in DMSO-d_6 solvent. Nearly 5mM of both peptide and metal-peptide complex concentrations were used. Temperature was maintained at 298 K to move away residual water signal away from Cα proton signals and the water suppression power had minimal effect on nearby peptide resonances. Resonance assignments were carried by using TOCSY and ROESY spectra. All 2D spectral widths were 12 ppm with 2048 x 512-time domain points in t2 S5 and t1 domains respectively. Data set was zero filled to 2K x 1K before Fourier transformation. A mixing time of 100ms and 250ms were used for TOCSY and ROESY spectrum respectively. All NMR data were processed offline using TOPSPIN version 2.1 software. Scalar coupling (J) values were directly measured from high resolution 1D recording.

4) Experimental details of AFM and TEM Analysis:

AFM samples were prepared by deposing metal-peptide solution (4µL, 1mg/mL in MeOH) drop casted on mica, dried at room temperature and imaged. Similarly, TEM on copper grid, dried at room temperature and imaged it.

[5]. Metal-Peptide Complexation of P1 with CdI_2:

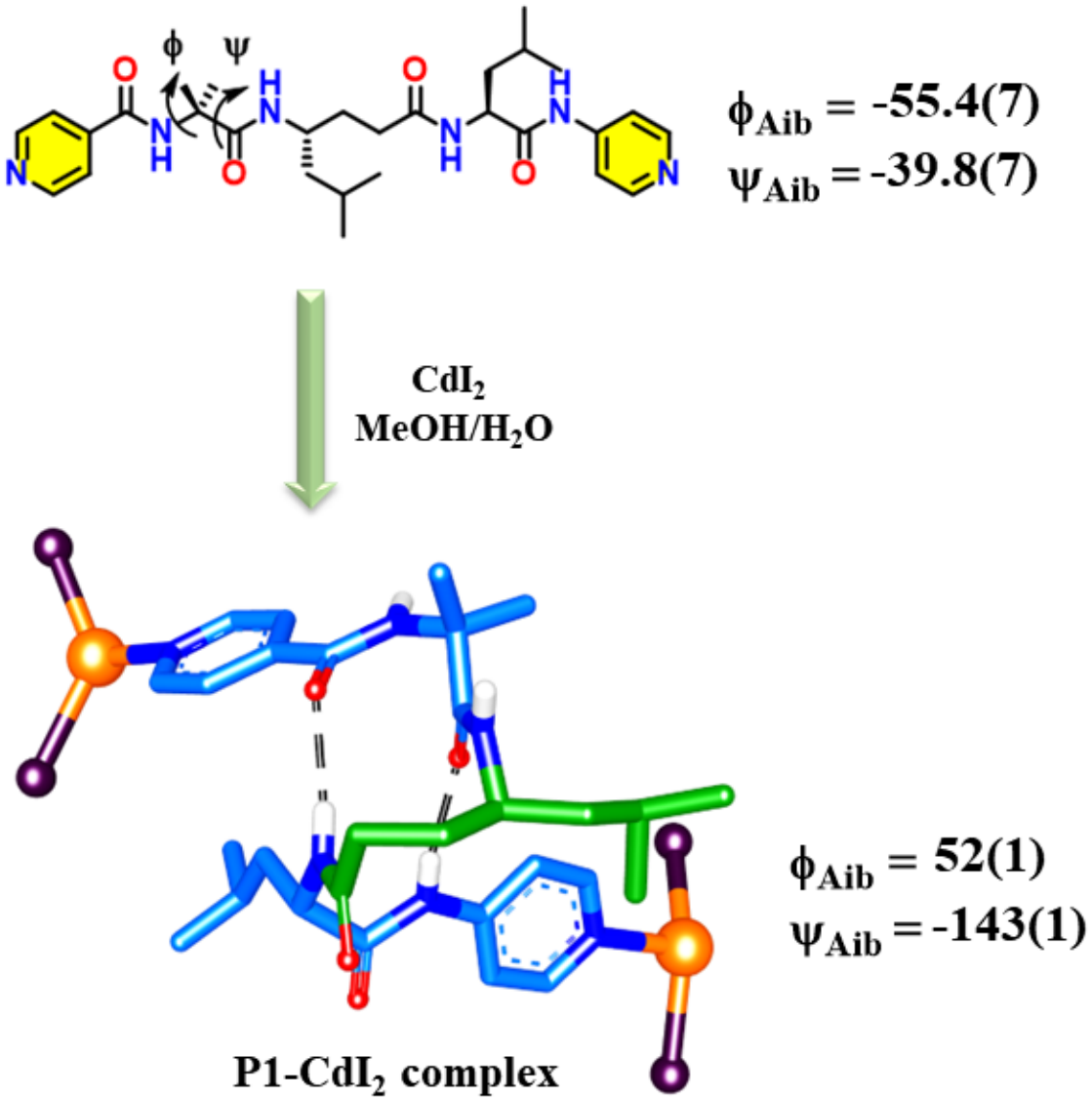
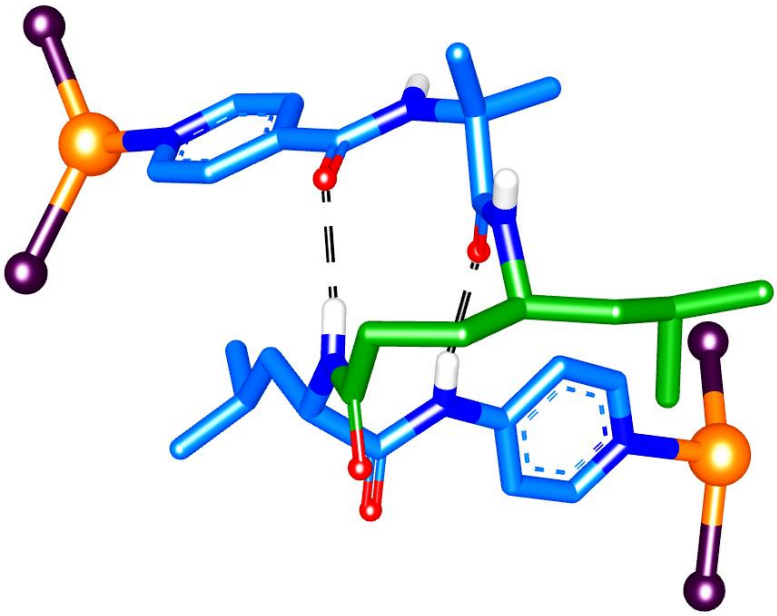
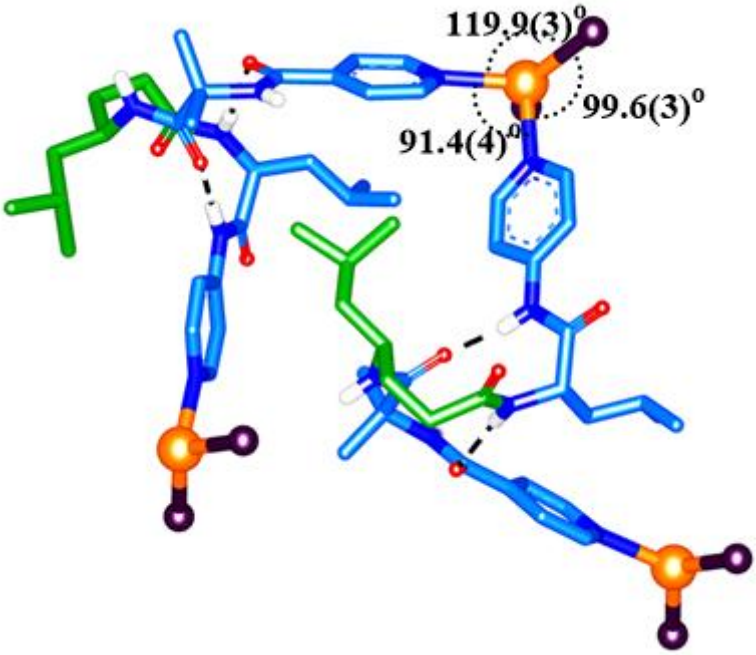


Figure S3: Metal-peptide complexation of **P1** with different metal salts. The change in the torsion angle parameters (ϕ and Ψ) of **Aib residue** before and after complexation has been shown.

[6]. Peptide(P1)-CdI_2 Crystal and Dimer Formation:

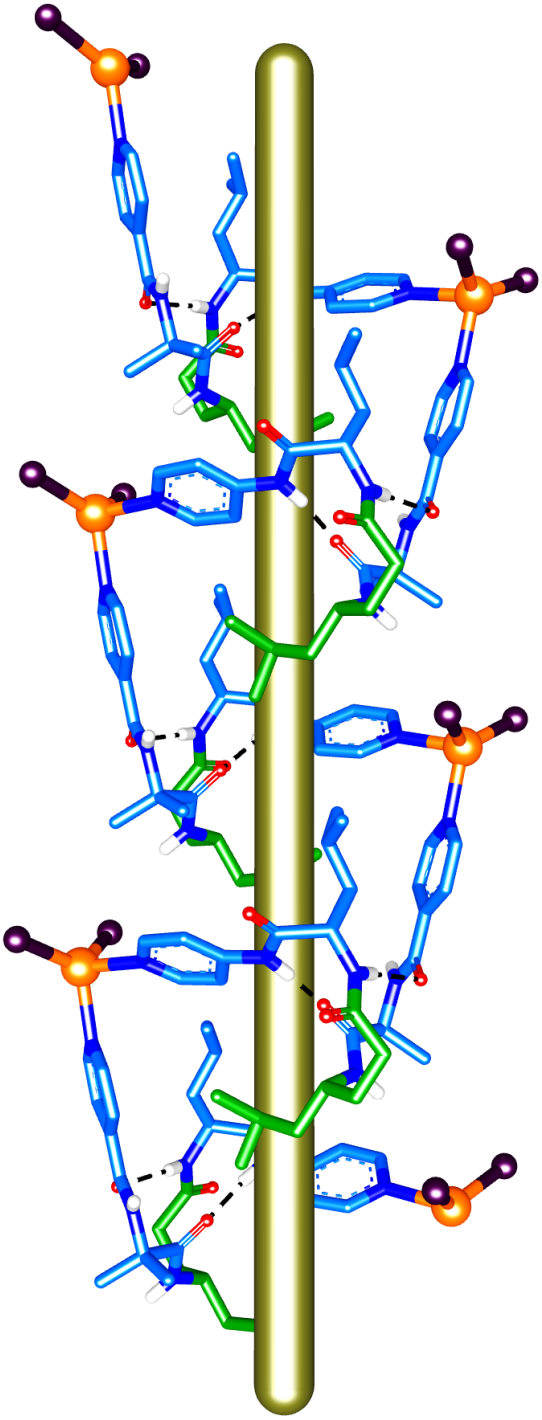




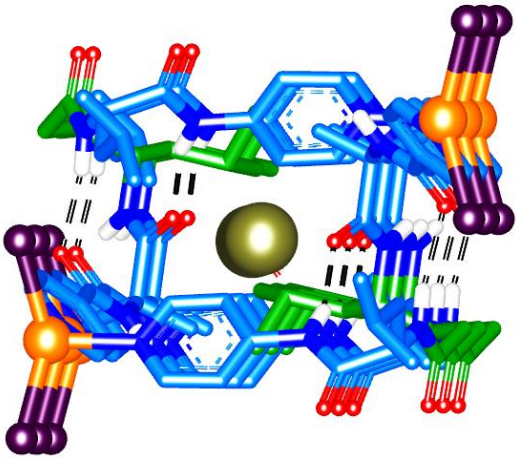
Head to Tail Metal Coordination

Figure S4: Mode of peptide (P1)-metal coordination.

[7]. Peptide (P1)-CdI_2 Coordination Polymer to Superhelix Formation:



Side view of superhelix



Top view of superhelix

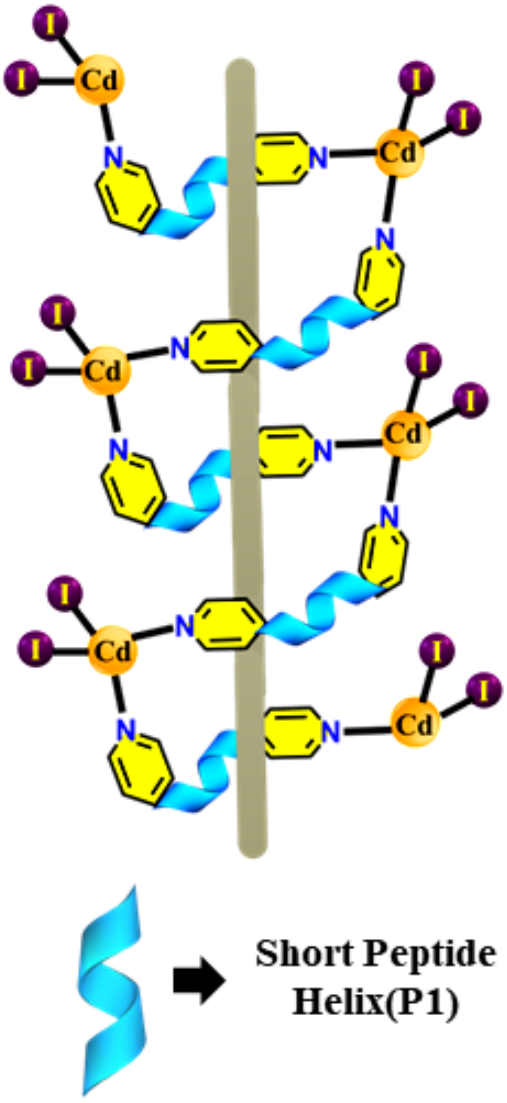


Figure S5: Peptide (P1)-CdI_2 coordinated superhelical polymer.

[8]. Packing of CdI_2-Coordinated Superhelix of Peptide (P1):

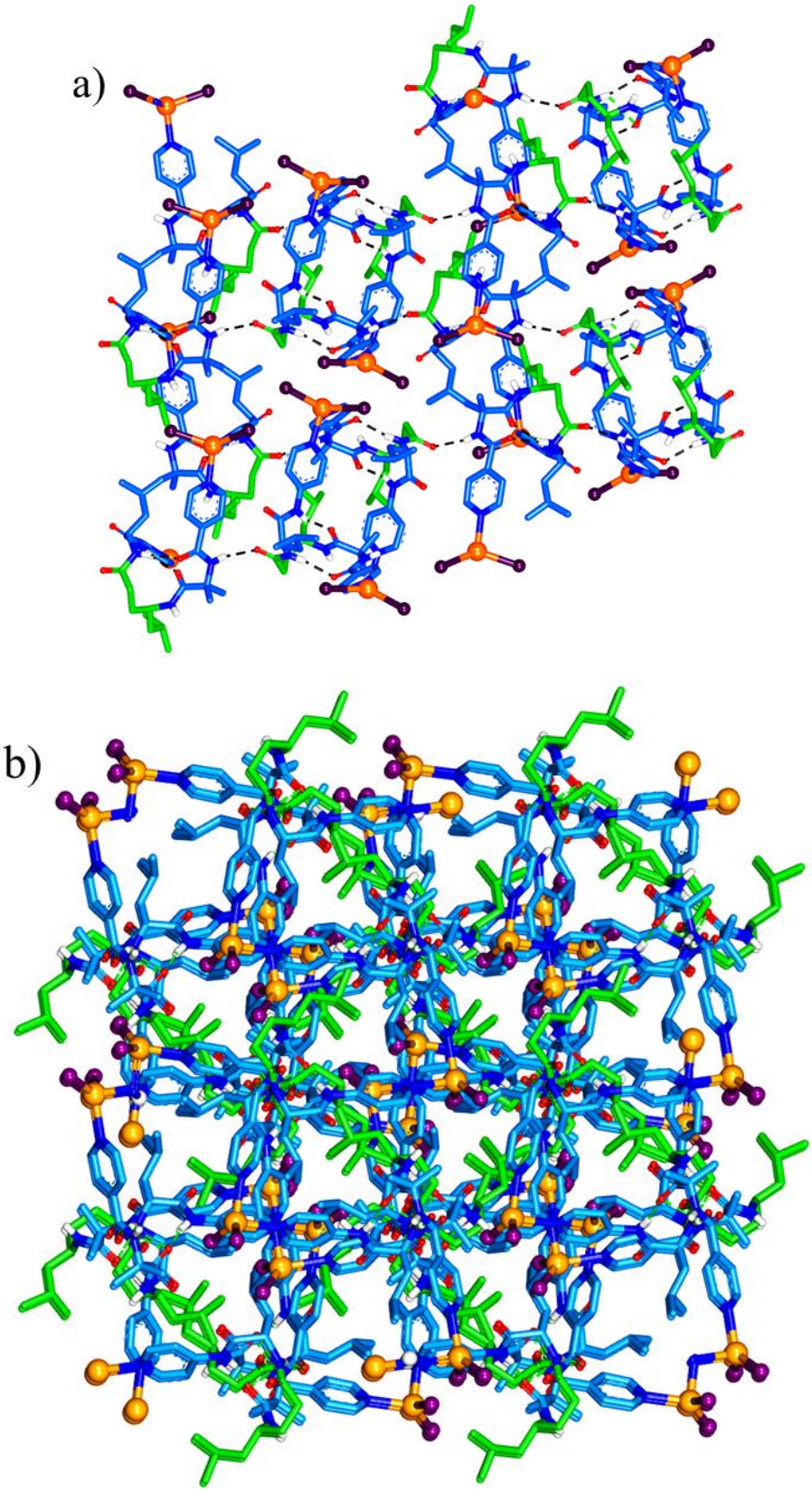


Figure S6: Packing of CdI_2-coordinated superhelix of peptide (P1).

[9]. Circular Dichroism (CD) Study of Metal-Peptide Superhelix:

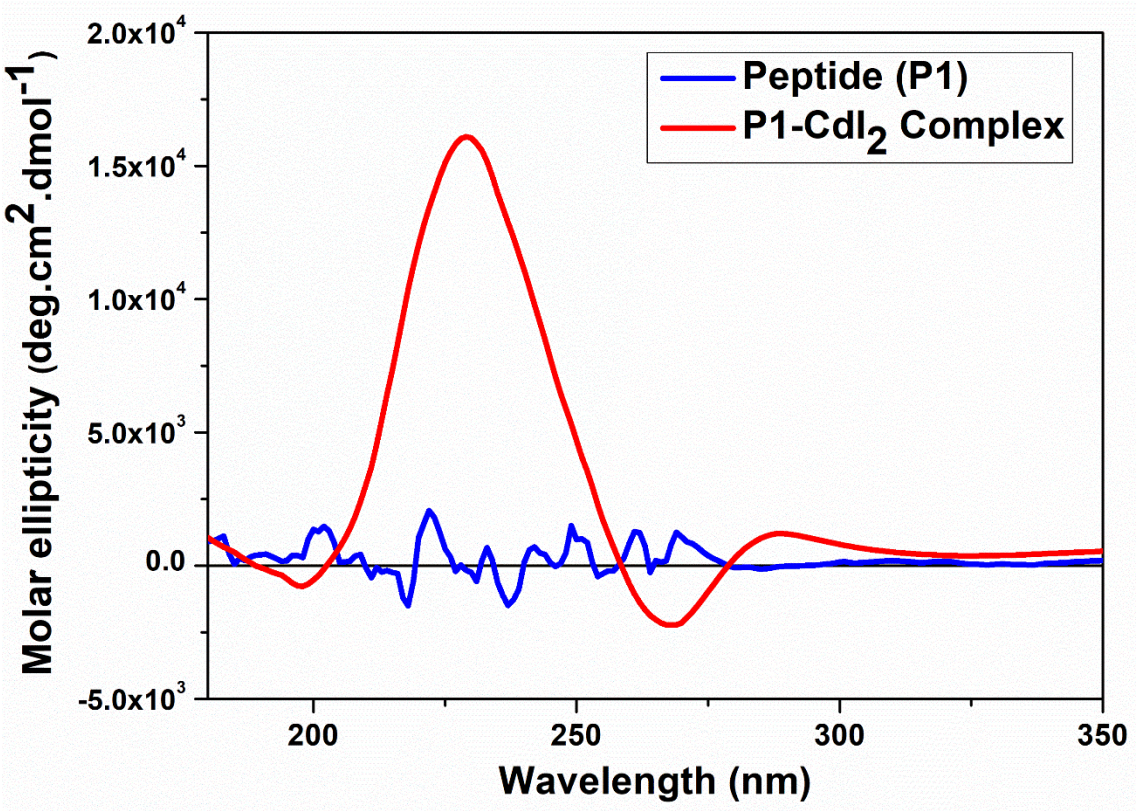


Figure S7: Circular Dichroism study of peptide and peptide-metal salts shows a strong absorption band at λ_{max} = 230 nm.

[10]. Metal-Peptide Complexation of P2 with CdI_2 :

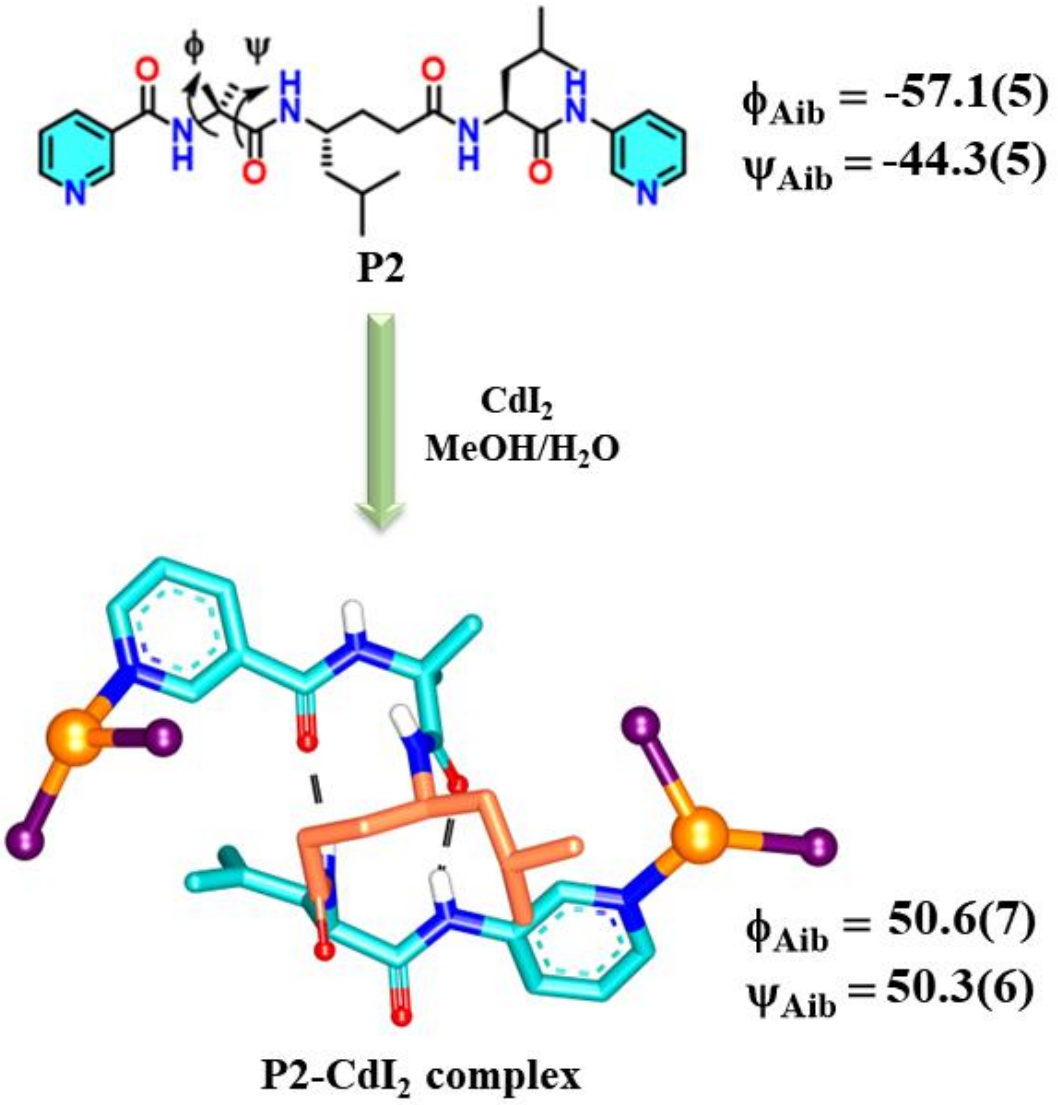
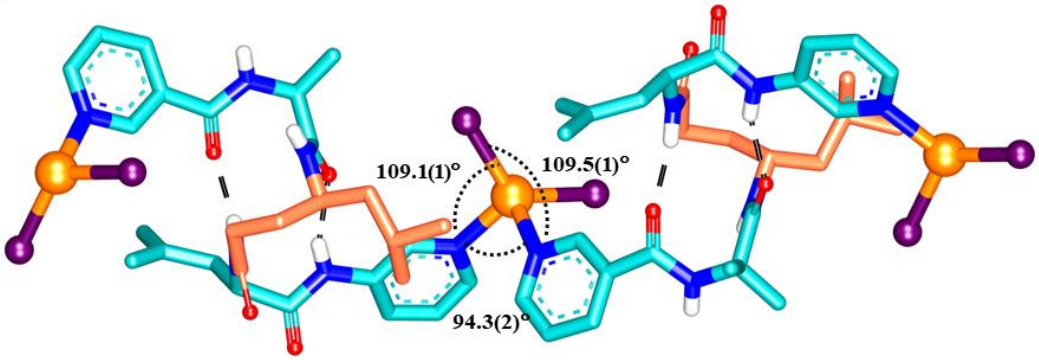


Figure S8: Metal-peptide complexation of **P2** with different metal salts. The change in the torsion angle parameters (ϕ and Ψ) of **Aib residue** before and after complexation has been shown.

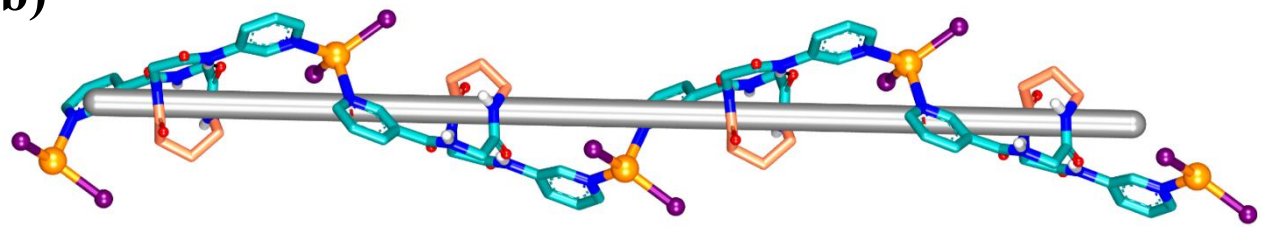
[11]. Supramolecular Assembly of P2-CdI_2 Complex:

a)



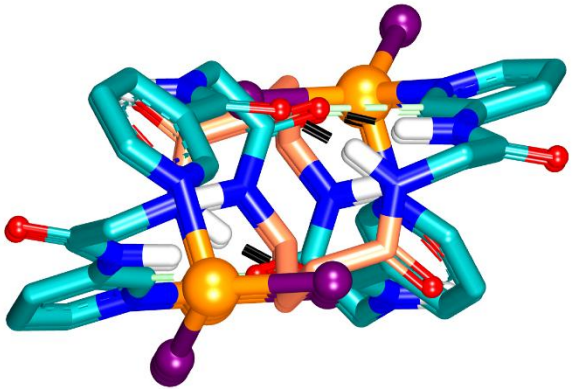
Head to Tail Metal Coordination

b)



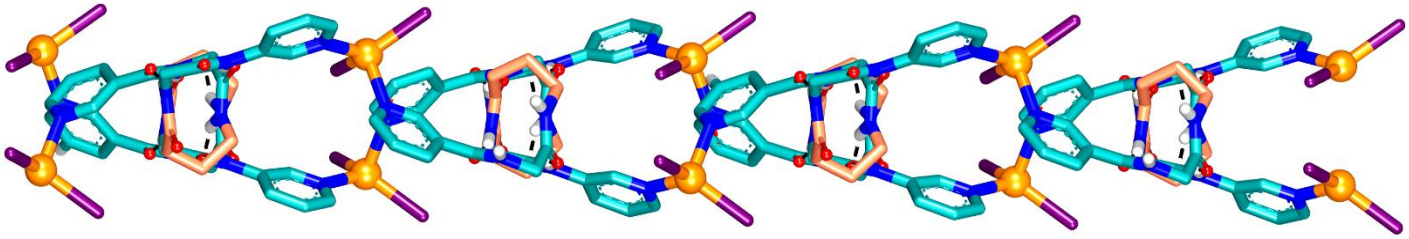
Metal coordinated superhelix (side view)

c)

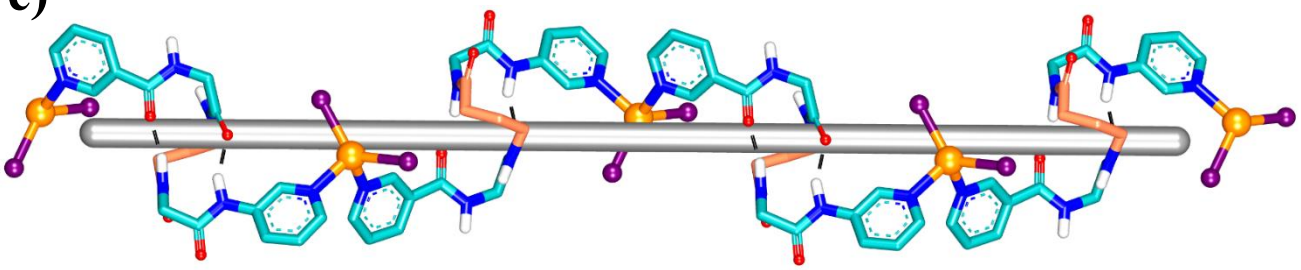


Metal coordinated superhelix (top view)

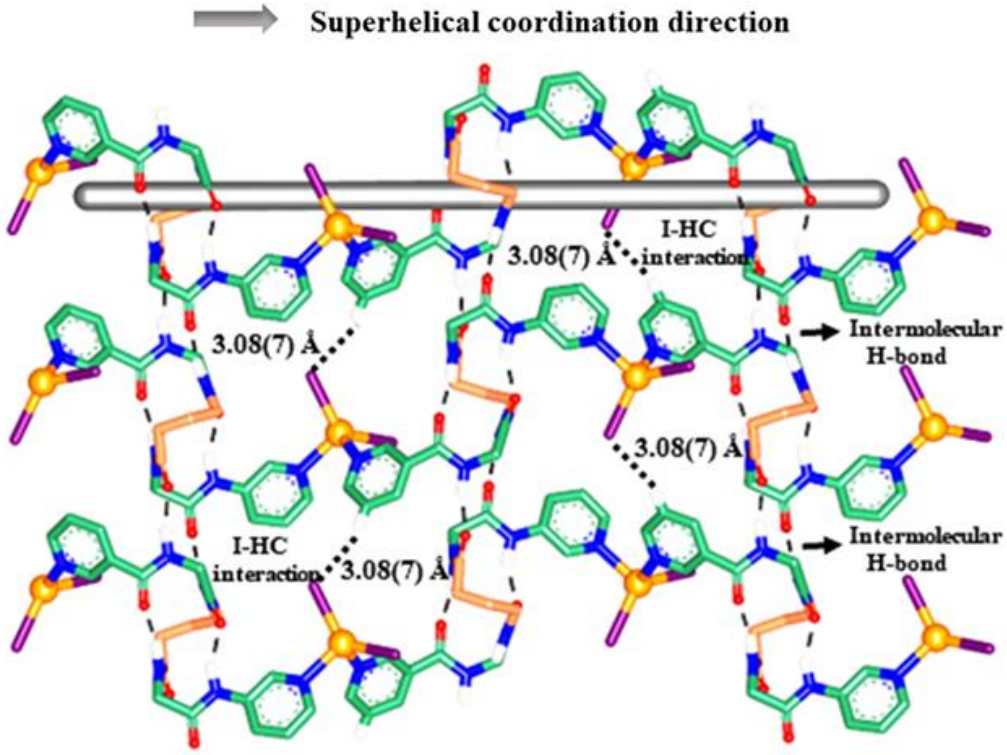
d)



e)



f)



Superhelical β-sheet assembly

g)

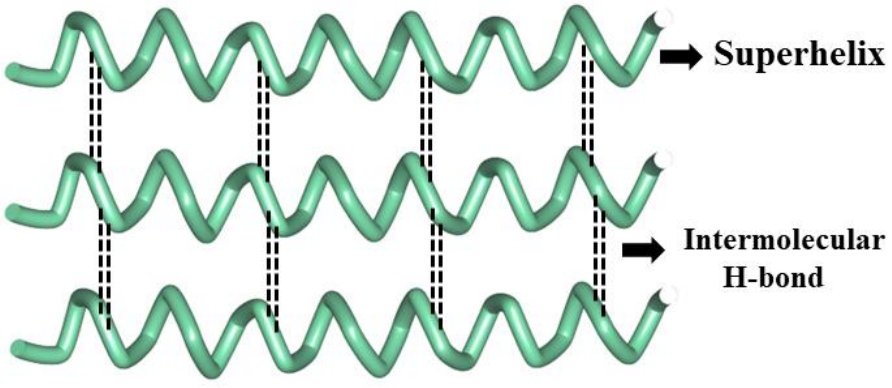


Figure S9: The X-ray diffracted structure of P2-CdI_2 complex. a) Cd^{2+} ion coordination between the two helices in a "Head-to-Tail" fashion with an angle of pyridine units observed in the crystal packing. b-e) metal coordinated superhelix. f) formation of superhelical sheet assembly by intermolecular H-bond and addition Cd-I---H-C interaction with 3.01 Å. g) A cartoon representation of superhelical β-sheet assembly.

[12] Circular Dichroism (CD) Study of Metal-Peptide (P2-CdI_2) Superhelix:

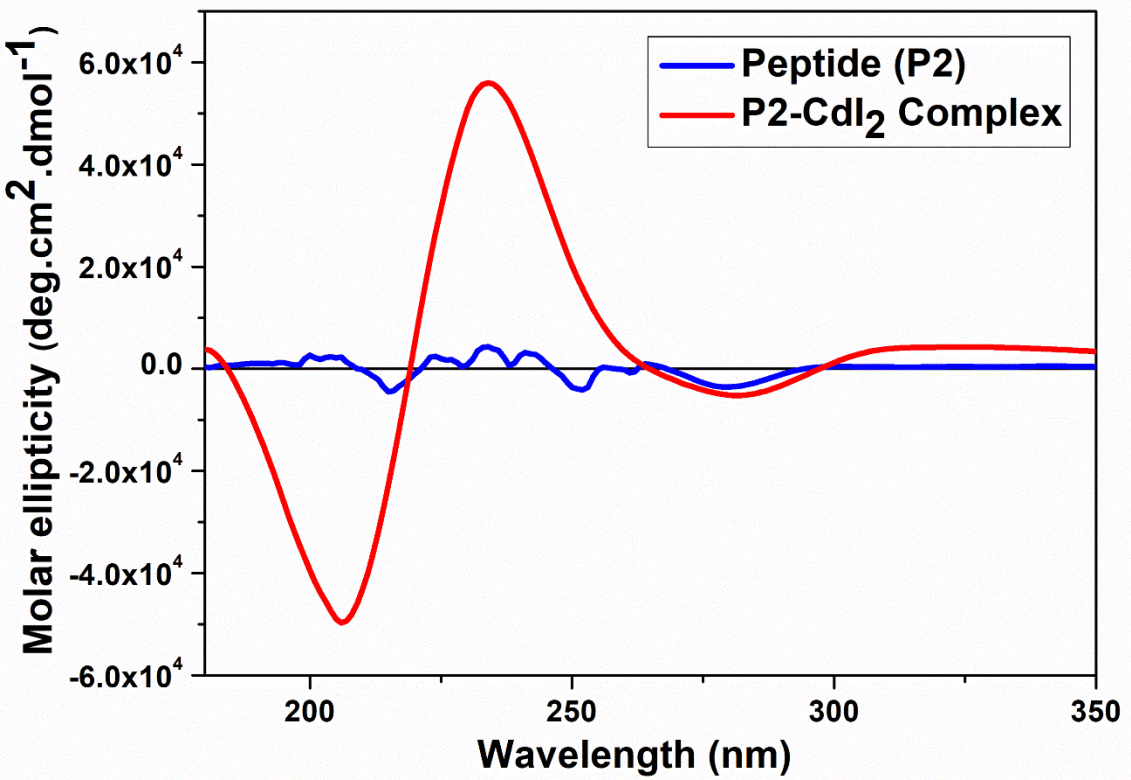
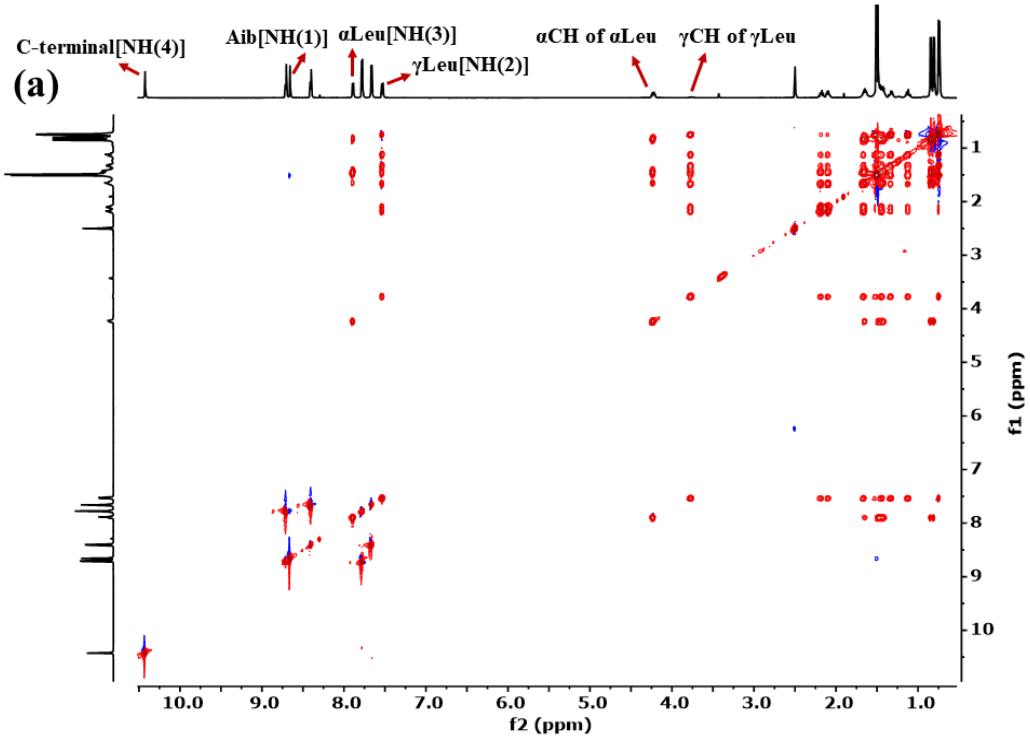
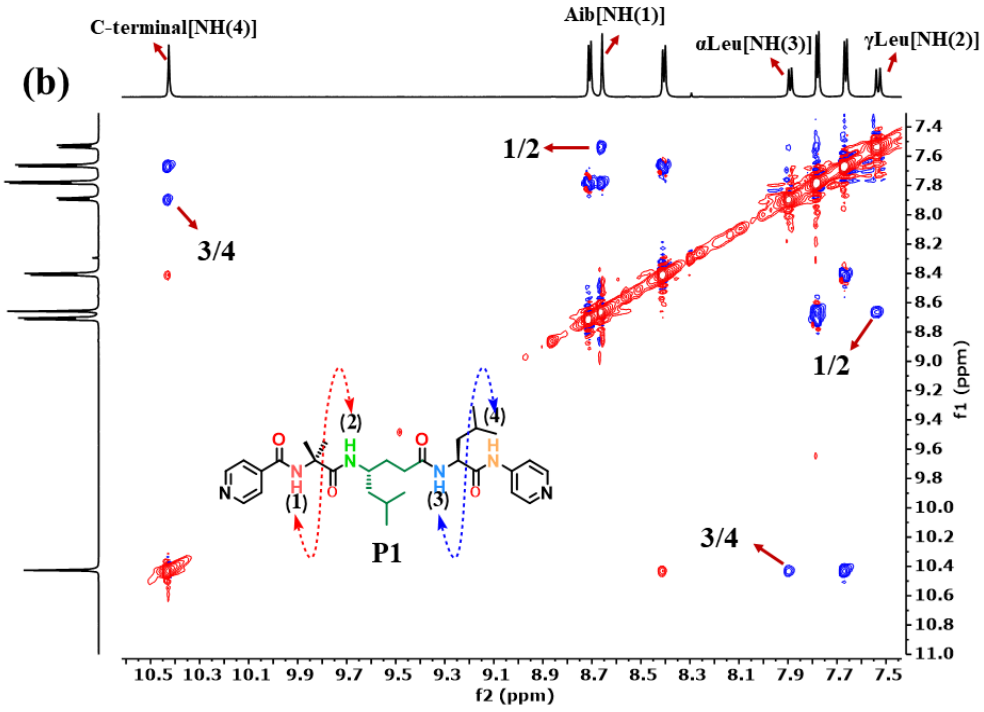


Figure S10: Circular Dichroism study of peptide and peptide-metal salts shows a strong absorption band at λ_{max} = 234 nm and at λ_{min} = 207 nm.

[13]. Solution State Conformational Analysis (2D-NMR) of Peptide (P1) and Metal-Peptide Complex (P1-CdI_2 and P2-CdI_2):

A) 2D-NMR Analysis of Peptide (P1)





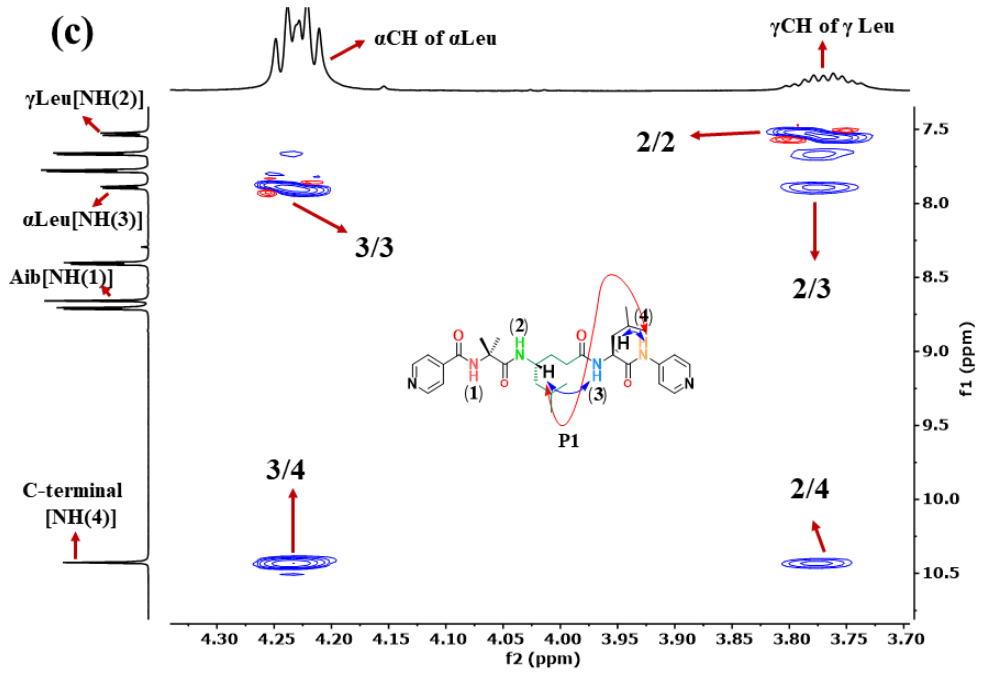
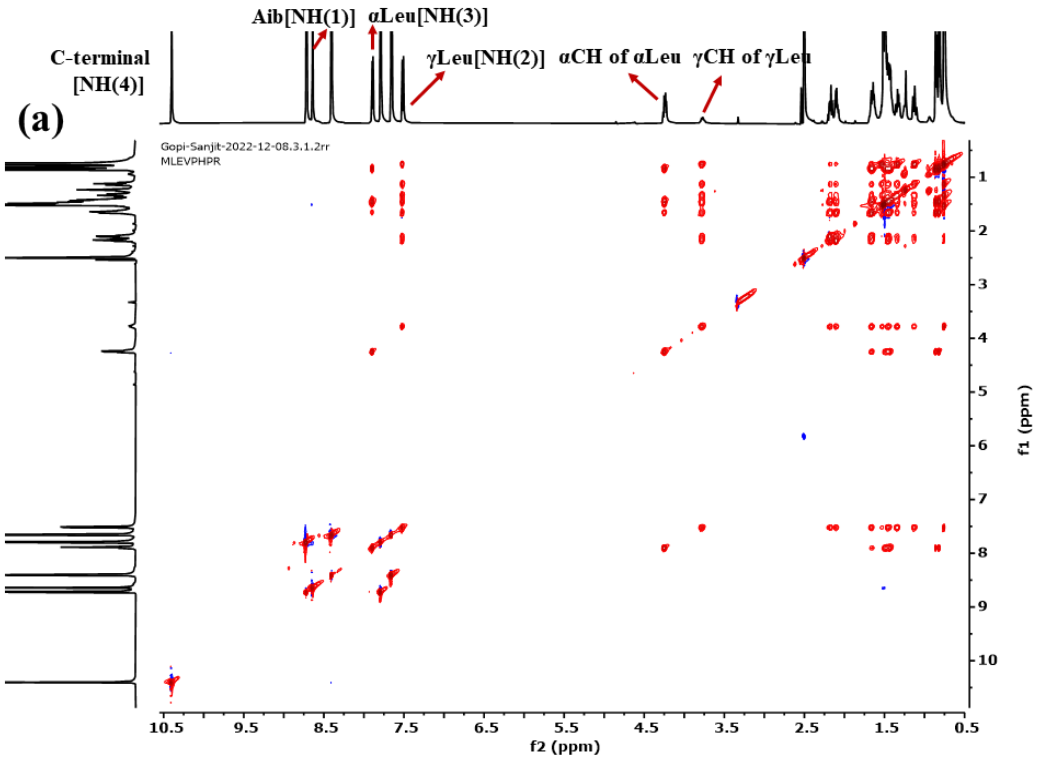


Figure S11: (a) TOCSY spectrum of peptide **P1** in DMSO-d_6. Partial ROESY spectrum of **P1** (b) showing **NH↔NH** NOEs and (c) showing **CαH↔ NH**NOEs.

B) 2D-NMR Analysis of Metal Peptide Complex (P1-CdI_2)



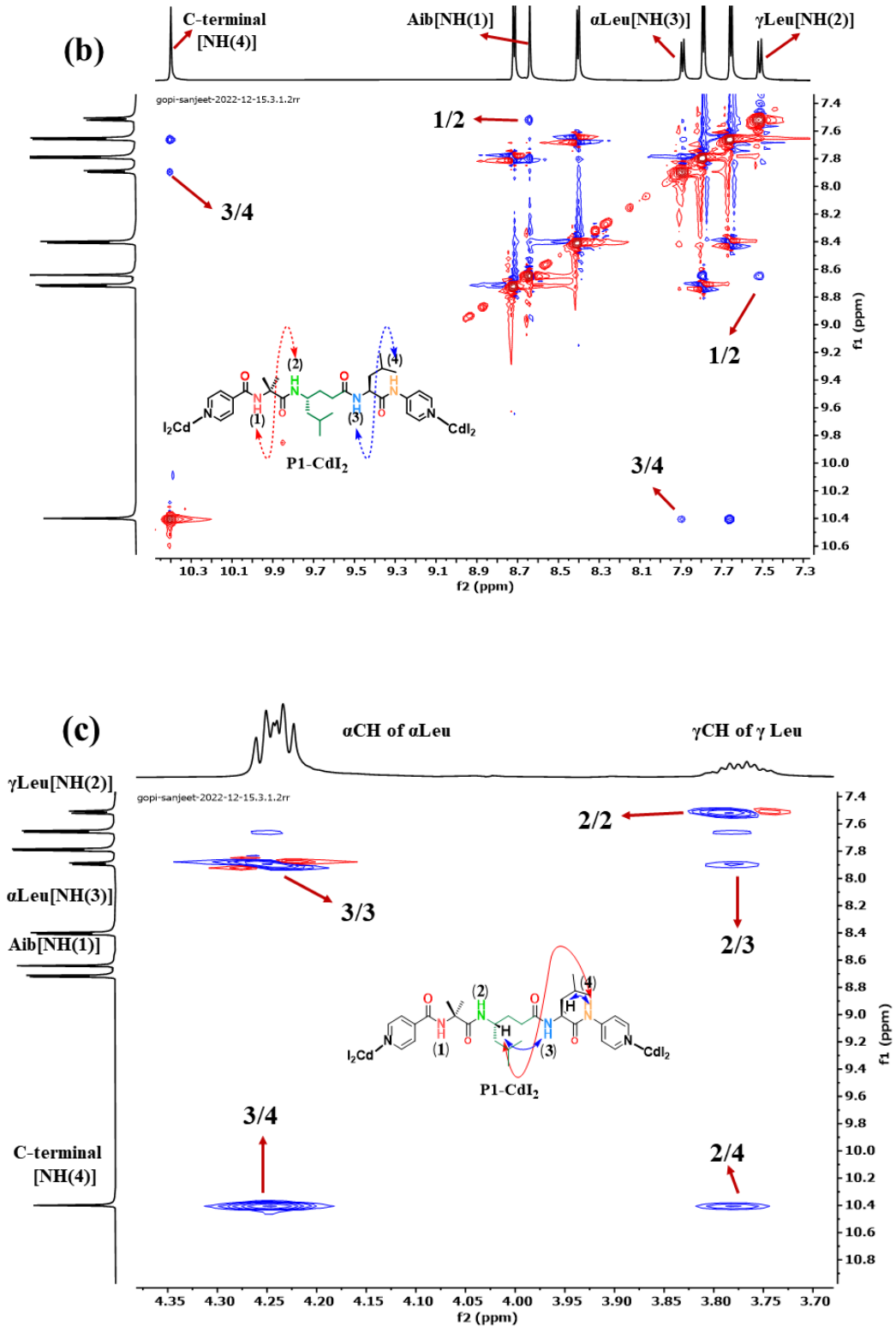
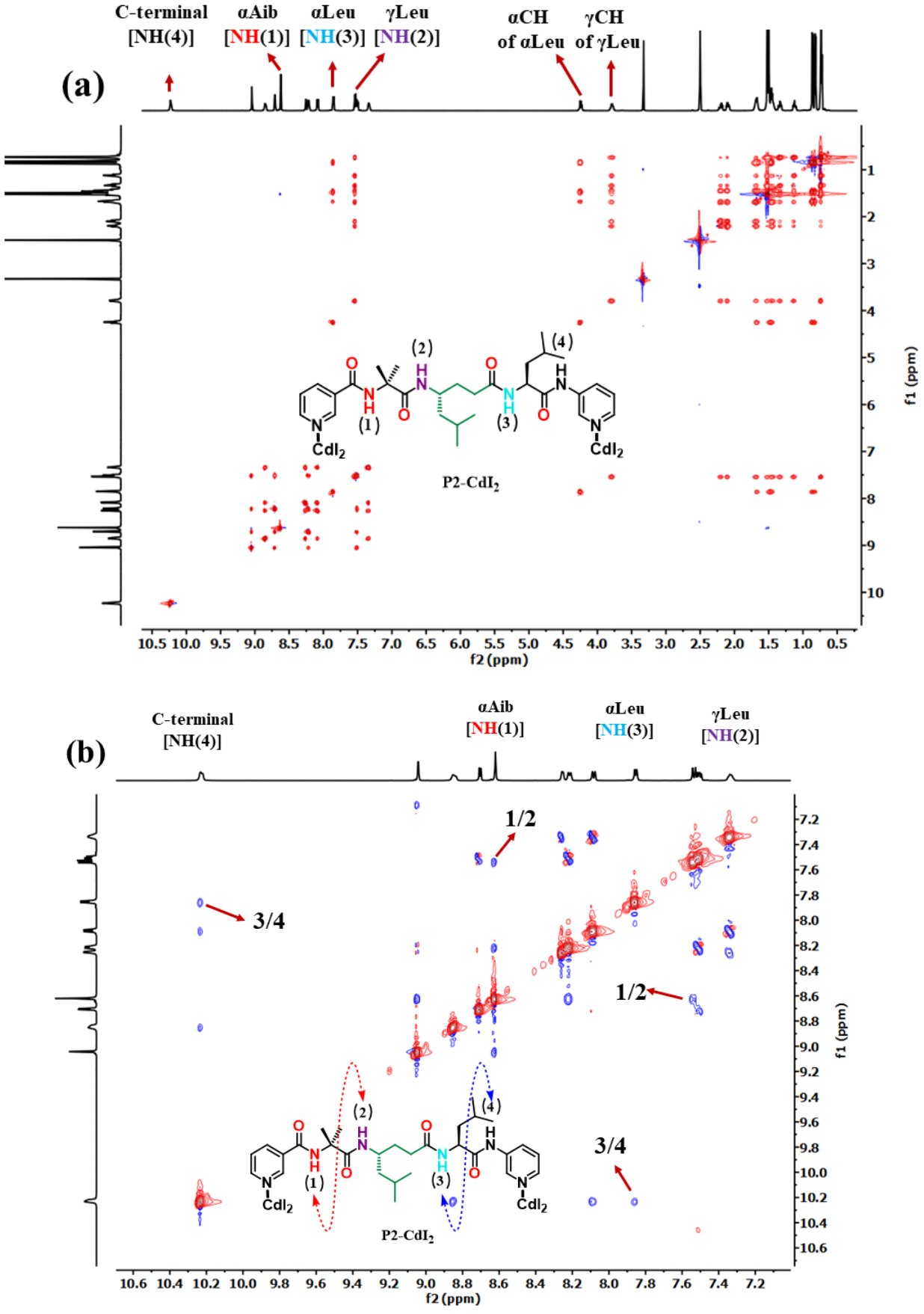


Figure S12: (a) TOCSY spectrum of **P1-CdI$_2$** complex in DMSO-d$_6$. Partial ROESY spectrum of **P1-CdI$_2$** complex (b) showing **NH↔NH** NOEs and (c) showing **CαH↔ NH**NOEs.

C) 2D-NMR Analysis of Metal Peptide Complex (P2-CdI_2)



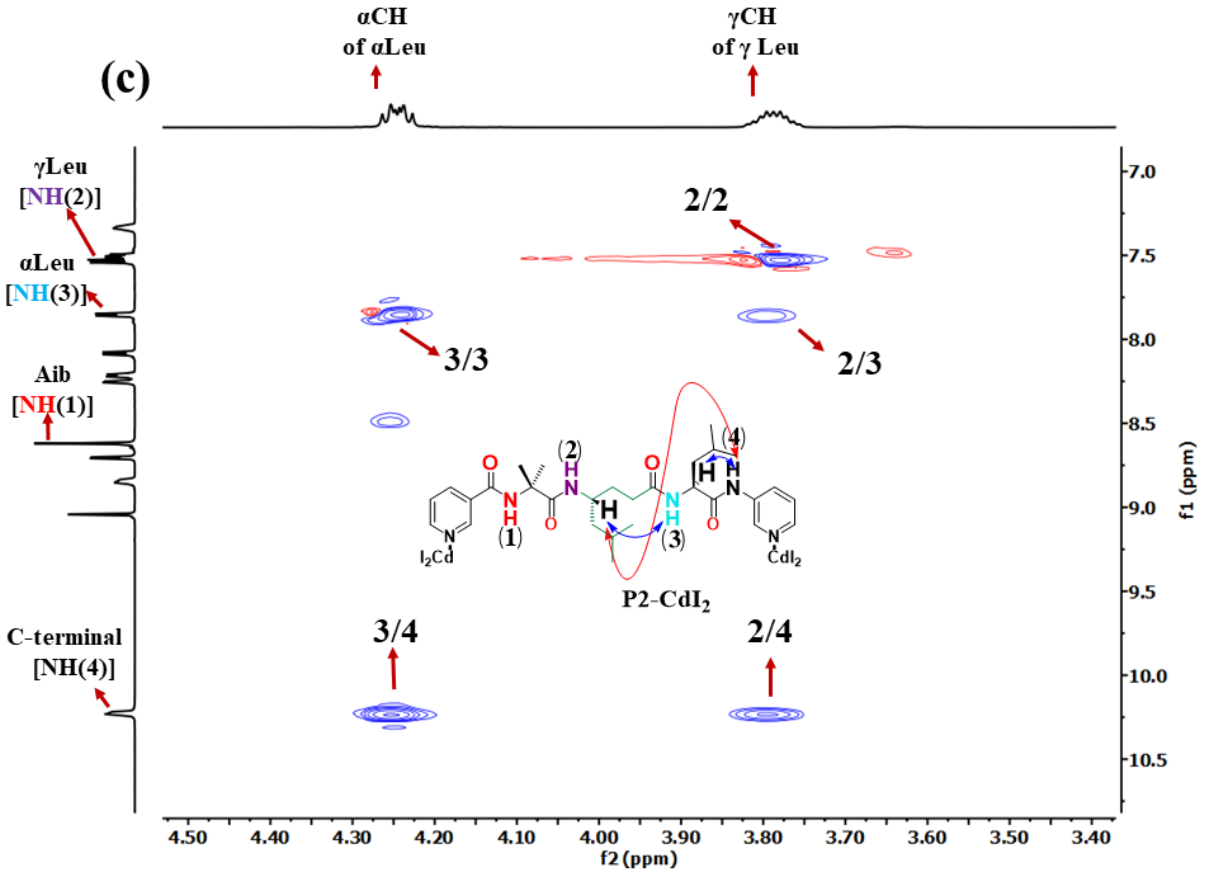


Figure S13: (a) TOCSY spectrum of **P2-CdI$_2$** complex in DMSO-d$_6$. Partial ROESY spectrum of **P2-CdI$_2$** complex (b) showing **NH↔NH** NOEs and (c) showing **CαH↔ NH**NOEs.

D) Temperature Dependent NMR Analysis and Correlation of Coupling Constant with Torsion Angle of Metal-Peptide Complex (P2-CdI_2):

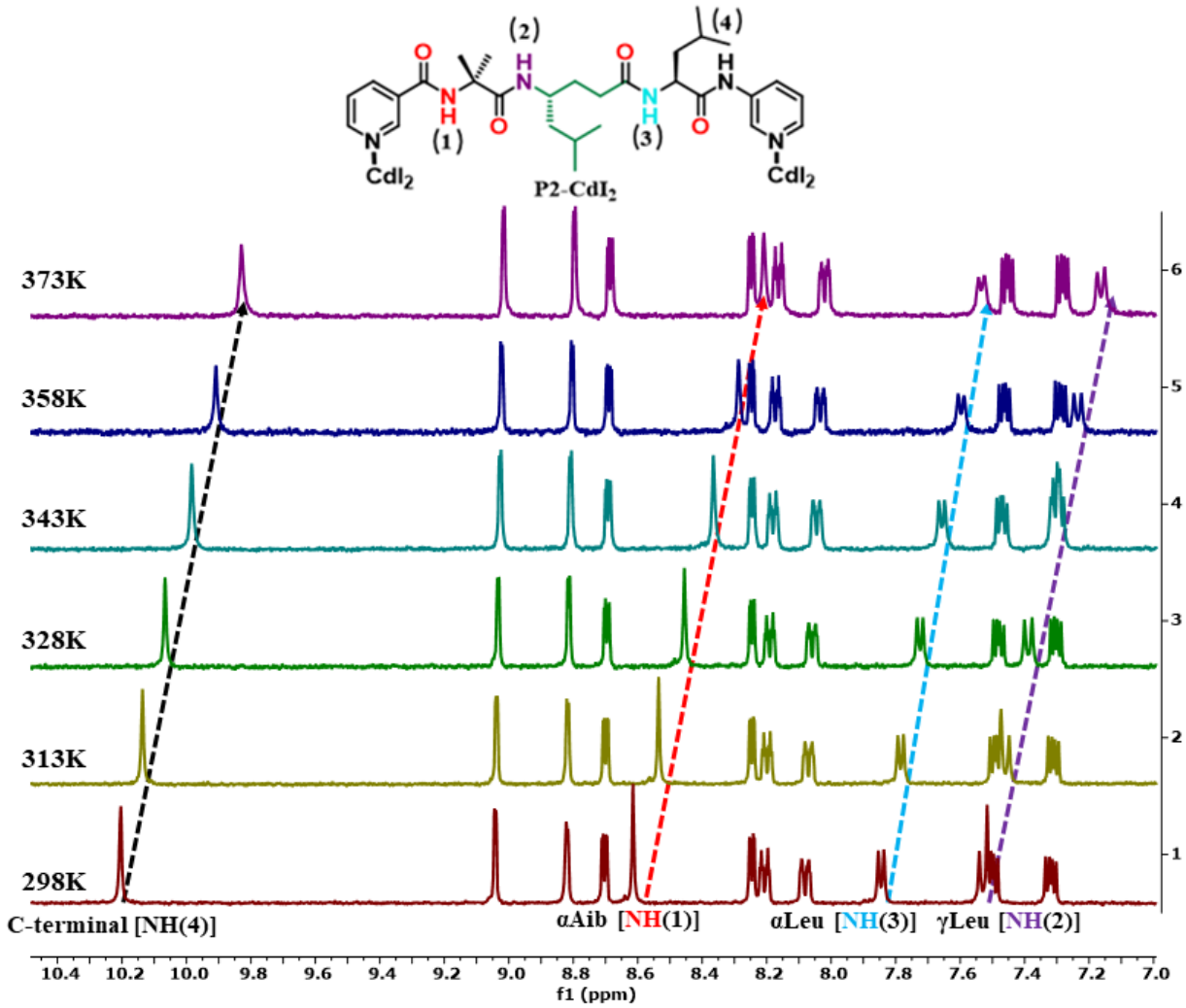


Figure S14: Partial ^{1}H-NMR spectrum of **P2-CdI_2** complex at different temperatures.

Temp(K)	Chemical Shift (δ_{ppm}) for P2-CdI_2 complex			
	C terminal-NH	αAib-NH	αLeu-NH	γLeu-NH
298	10.20	8.62	7.85	7.53
313	10.14	8.54	7.78	7.46
328	10.07	8.46	7.73	7.39
343	9.98	8.37	7.66	7.31
358	9.91	8.29	7.60	7.24
373	9.83	8.21	7.53	7.16
$\Delta\delta/\Delta T$ (ppb K^{-1})	**-5.01**	**-5.5**	**-4.21**	**-4.93**

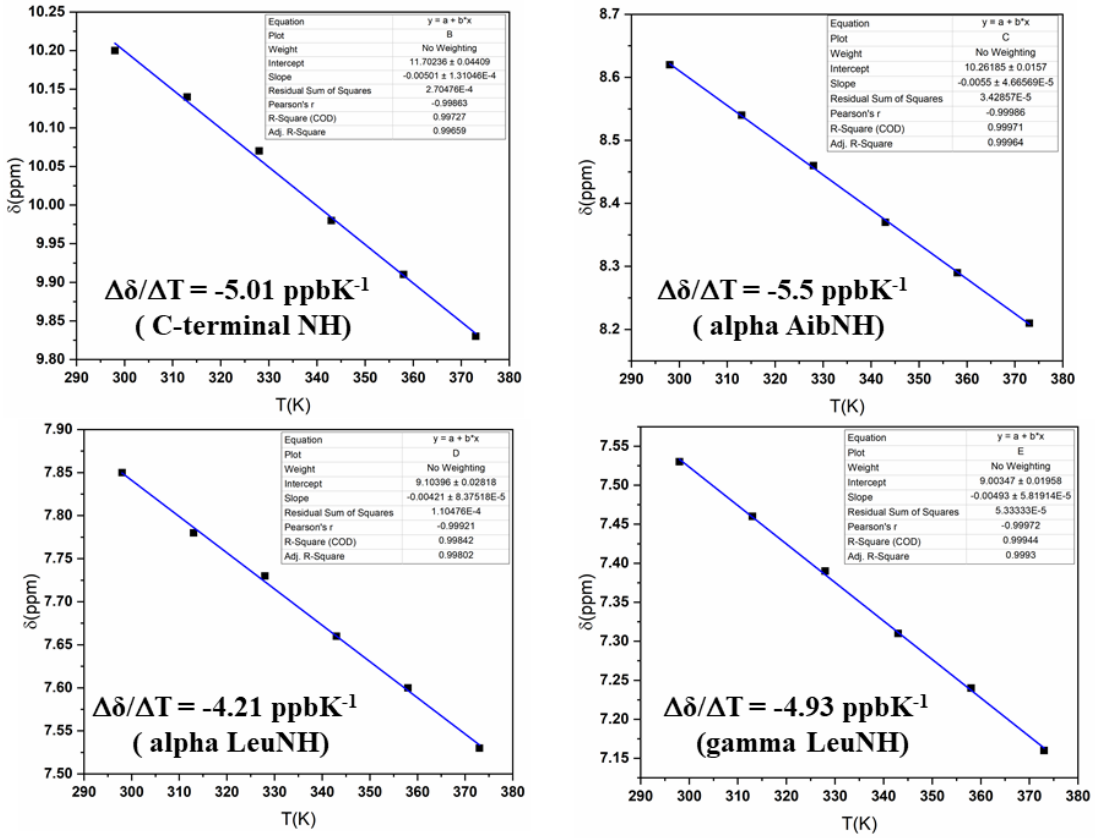


Figure S15: Temperature dependent ^{1}H-NMR analysis of CONH signals and $\Delta\delta/\Delta T$ of P2-CdI_2 complex in DMSO-d_6.

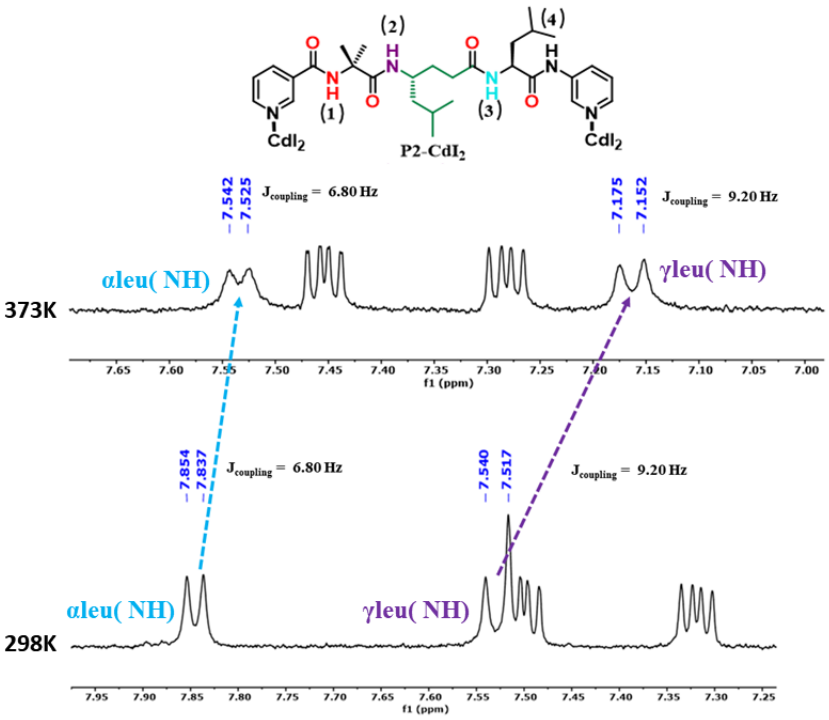


Figure S16: Partial ^{1}H-NMR spectrum of **P2-CdI$_2$** complex and coupling constants.

[14]. PXRD of P2-CdI$_2$ complex:

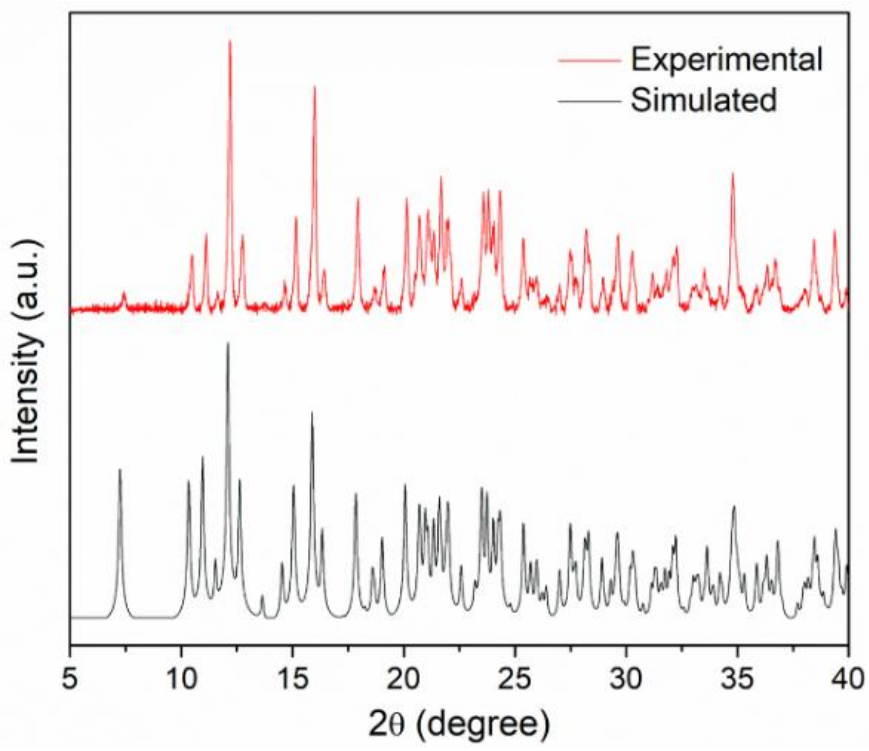


Figure S17: PXRD of **P2-CdI$_2$** complex

[15]. Structural Correlation of P1-CdI_2 and P2-CdI_2 Complexes in Solution and Single Crystals:

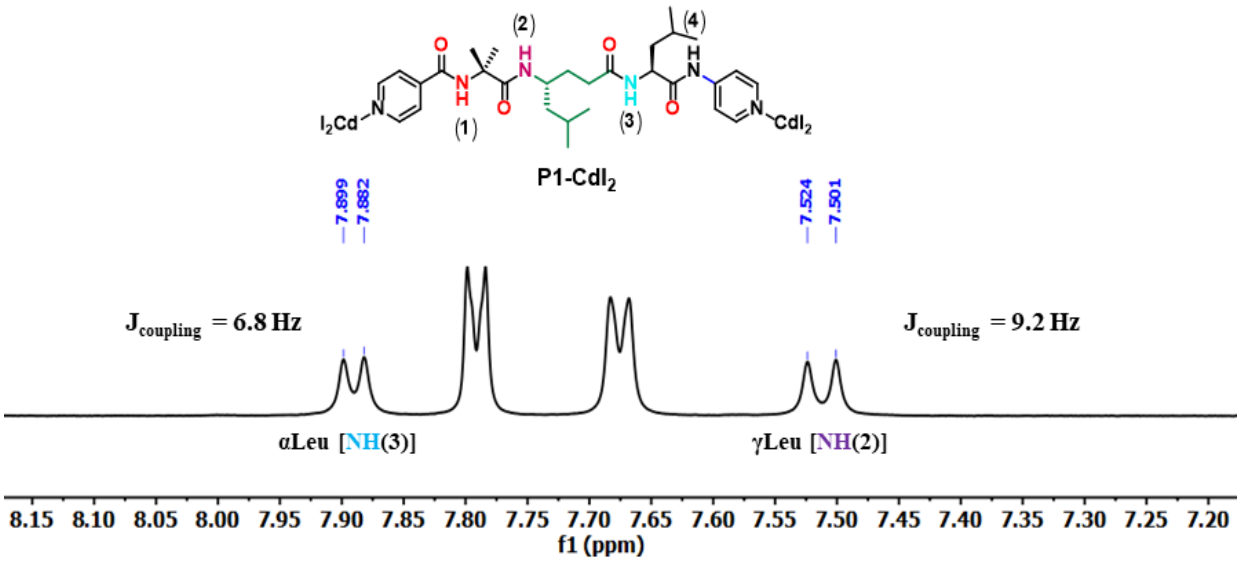


Figure S18: Partial ^{1}H-NMR spectra for the analysis of coupling constant of P1-CdI_2 complex in DMSO-d_6.

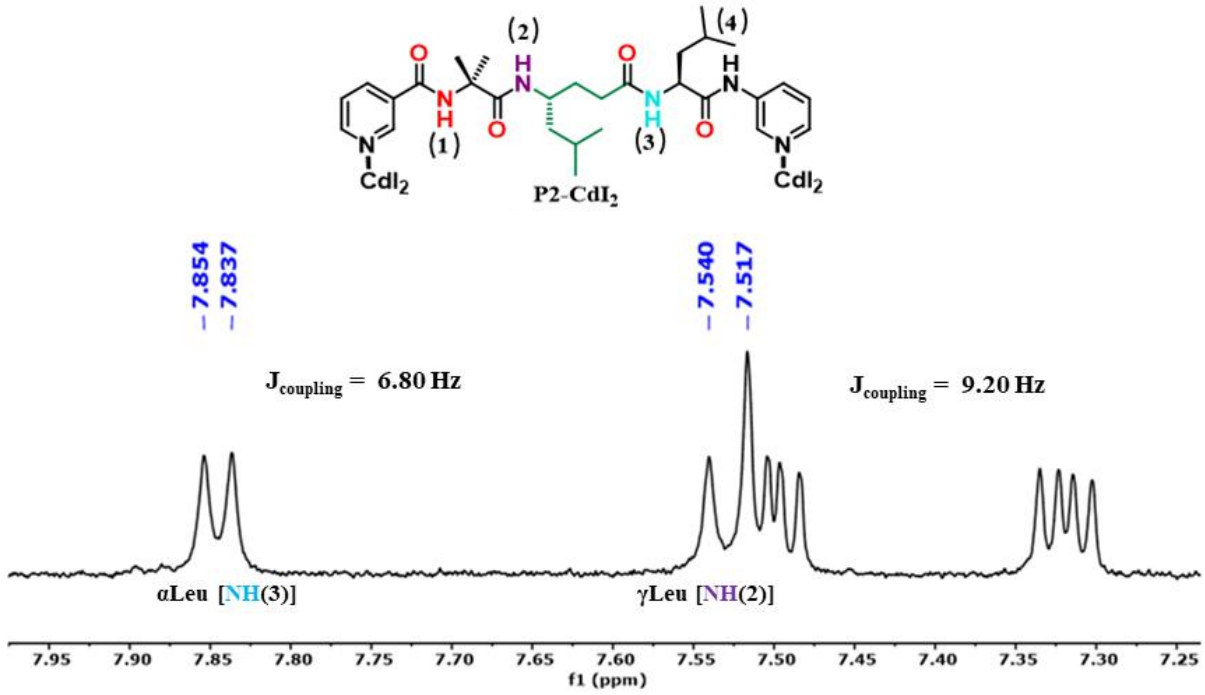


Figure S19: Partial ^{1}H-NMR spectra for the analysis of coupling constant of P2-CdI_2 complex in DMSO-d_6.

Calculation of phi angle from Coefficients of Karplus Equations, $^{3}J_{HNH\alpha} = A\cos^{2}(\phi + \theta) + B\cos(\phi + \theta) + C$

[Where, $^{3}J_{HNH\alpha} = 6.8$, $\theta = -60°$, A = +6.98, B = -1.38, and C = +1.72].

Metal Peptide Complex	Phi(ϕ) of alpha Leu	
	NMR	XRD
P1-CdI_2	76.7	-77.0
P2-CdI_2	76.7	78.6

These results strongly indicate almost similar helical conformations of peptides in both solution and in single crystals.

[16]. Morphology Investigation of Peptide-Metal Complexes:

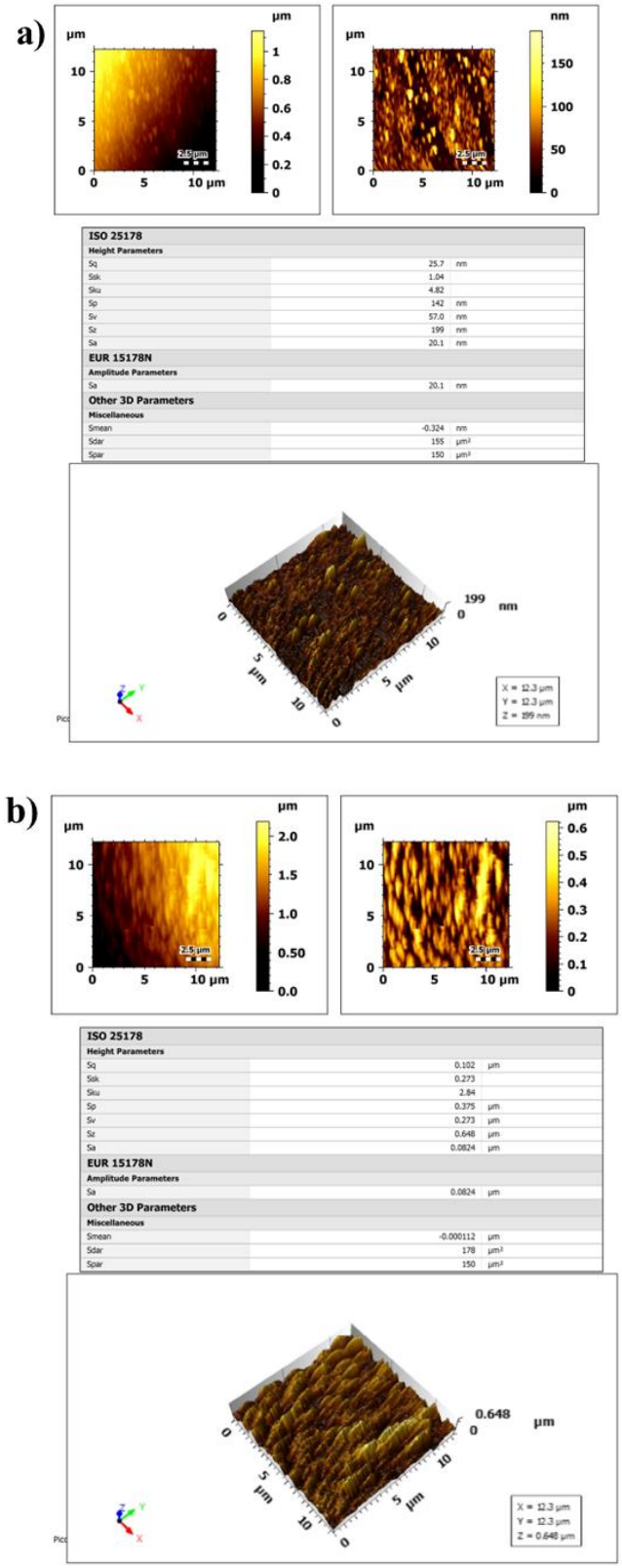


Figure S20: AFM images of a) P1-CdI_2 and b) P2-CdI_2 complexes

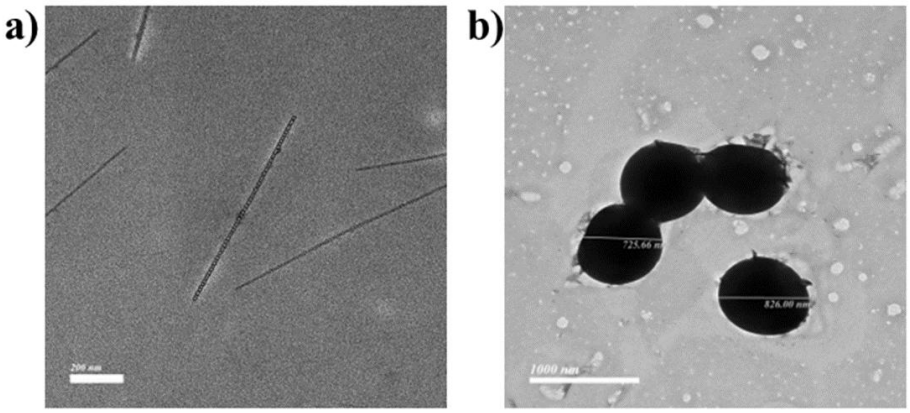


Figure S21: TEM images of a) P1-CdI_2 and b) P2-CdI_2 complexes

[17]. Comparison of Torsion Angle Parameters of Peptide and Peptide-Metal Complexes:

Complex	Residue	ϕ	θ_1	θ_2	Ψ
Ligand Peptide P1	Aib	-55.4(7)	-	-	-39.8(7)
	γLeu	-133.3(6)	55.2(6)	60.1(6)	-112.6(5)
	Leu	-60.1(6)	-	-	-41(6)
P1-CdI_2 complex	Aib	52(1)	-	-	-143(1)
	γLeu	-123(1)	61(1)	65(1)	-115(1)
	Leu	-77(1)	-	-	-38(2)
Ligand Peptide P2	Aib	-57.1(5)	-	-	-44.3(5)
	γLeu	-122.0(4)	48.3(5)	69.1(5)	-116.8(4)
	Leu	-88.0(5)	-	-	-19.6(6)
P2-CdI_2 complex	Aib	50.5(7)	-	-	50.3(6)
	γLeu	129.5(6)	-60.1(7)	-62.5(7)	114.0(6)
	Leu	78.6(6)	-	-	36.4(7)

Table S3: Torsion angle parameters of P1, P2 and Peptide-CdI_2 complexes.

[18]. Effect of Aib Residue and Comparision of Superhelix and Superhelical Sheet:

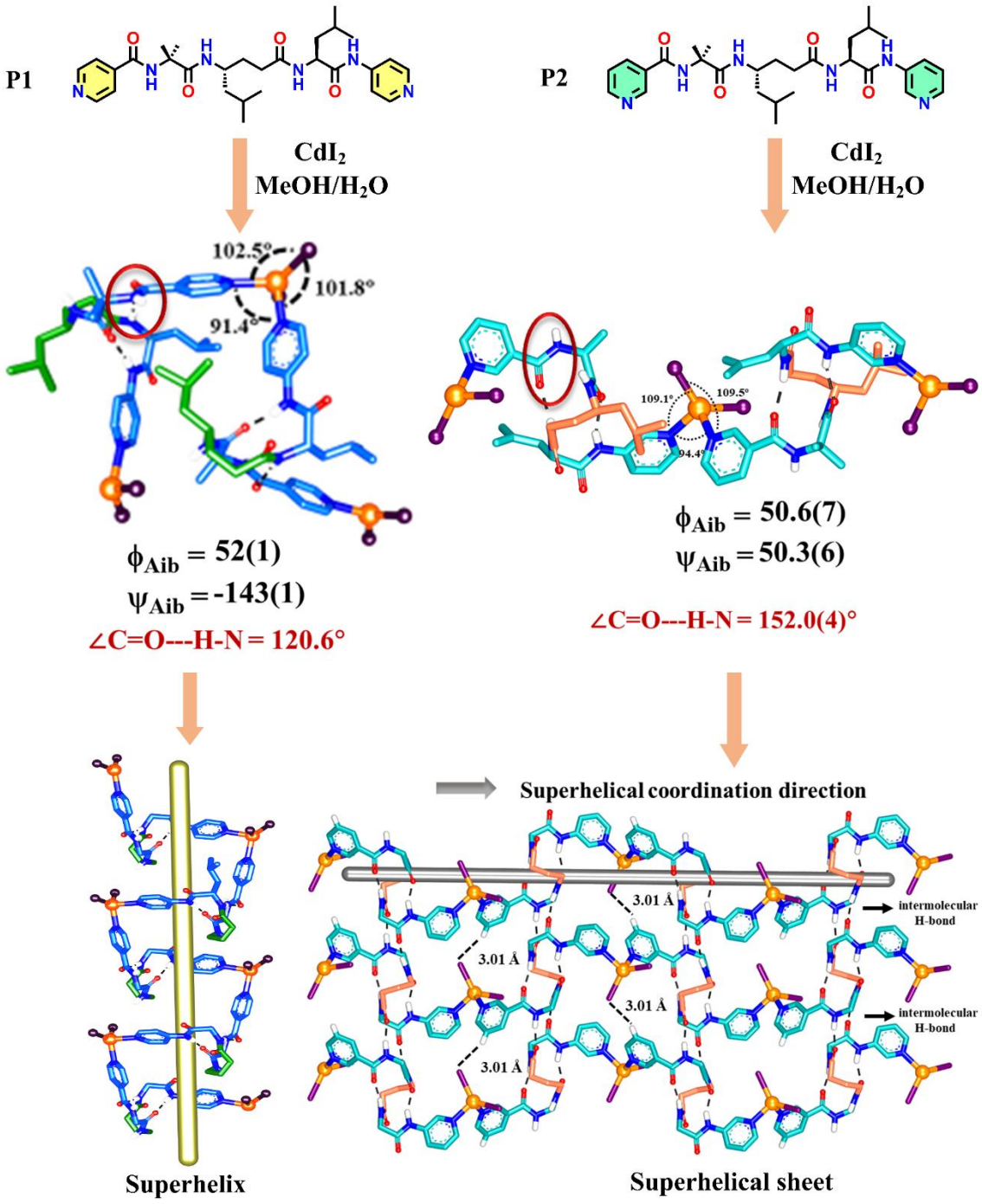
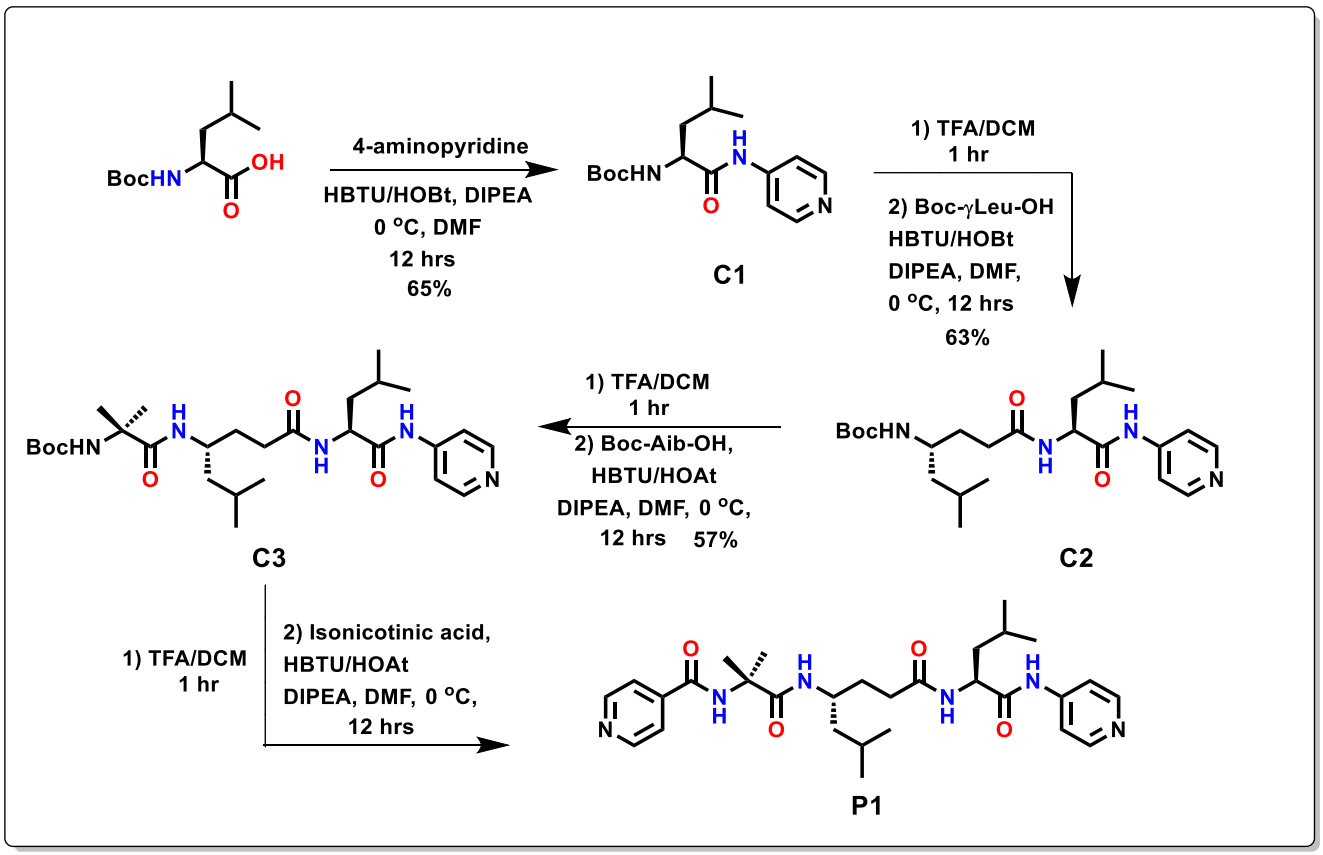


Figure S22: Effect of Aib Residue and Comparision of Superhelix and Superhelical Sheet.

[19]. Materials and Methods:

All the amino acids, HBTU, HOAt, CdI_2, and NMR solvents, THF, DCM, DMF, methanol, ethanol, chloroform, EtOAc, 4-aminopyridine, isonicotinic acid, di-tert-butyl dicarbonate, TFA, ethyl bromoacetate, triphenyl phosphine, oxone, DIPEA, $NaBH_4$, DCC and HOBt were obtained from commercial sources and used without further purification. Column chromatography was performed on silica gel (120–200 mesh). The ^1H NMR spectra were recorded on 400 MHz (or 100 MHz for ^{13}C NMR) / spectrometer using residual solvent signals as an internal reference ($CDCl_3$ ^1H-7.26 ppm, ^{13}C- 77.16 ppm). The chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz.

General Procedure for the Synthesis of Peptide P1:



N-Boc protected Leucine (10 mmol, 2.31 g) was dissolved in 10 mL of DMF and was cooled down to 0 ^{o}C under N_2 atmosphere. To this, HBTU (10 mmol, 3.79 g) and HOBt (10 mmol, 1.36 g) were added and the reaction mixture was stirred for 10 minutes. This was followed by the addition of 4-aminopyridine (12 mmol, 1.13 g). The reaction mixture was stirred for overnight and the progress was monitored by TLC. Upon completion, the reaction mixture was diluted with 150 mL EtOAc and was washed with water (100 mL X 2), 10% Na_2CO_3 (100 mL X 3) and finally with brine solution (100 mL X 2). The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give a crude powder which was then purified by column chromatography (60% EtOAc in Hexane) to get a white crystalline product Compound 1 (Yield- 2.5 g, 82%).
Compound C1(5.2 mmol, 1.6 g) was subjected to Boc deprotection using 50% TFA in DCM (5 mL TFA in 5 mL DCM). Upon completion, the reaction mixture was evaporated several times with DCM to remove the residual TFA. The resulting TFA salt of amine was dissolved in 2 mL DMF and was quenched with DIPEA (15 mmol, 2.7 mL) to get the free amine of compound C1.

N-Boc protected γ-leucine (5 mmol, 1.30 g) was dissolved in 3 mL of DMF and this solution was then cooled to 0 ^{o}C using an ice bath in N_2 atmosphere. To this, HBTU (5 mmol, 1.90 g), HOBt (5 mmol, 0.68 g), and DIPEA (10 mmol, 1.8 ml) were added and the reaction mixture was stirred for 10 mins. This was followed by the addition of amine cocktail of compound C1 and the reaction mixture was further stirred for overnight at room temperature. Upon completion, the reaction mixture was diluted with 150 mL of EtOAc and was washed with water (100 mL X 2), 10% Na_2CO_3 solution (100 mL X 3) and finally with brine (100 mL X 2). The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give a crude peptide which was then purified by column chromatography (75% EtOAc in Hexane) to get pure compound C2 (Yield- 1.7 g, 73%).

Compound C2 (3.79 mmol, 1.7 g) was then subjected to Boc deprotection using 50% TFA in DCM (4 mL TFA in 4 mL DCM). Upon completion, the reaction mixture was evaporated several times with DCM to remove the residual TFA. The resulting TFA salt of the amine was dissolved in 1 mL DMF and was quenched with of DIPEA (12 mmol, 2.0 mL) to get free amine of compound C2.

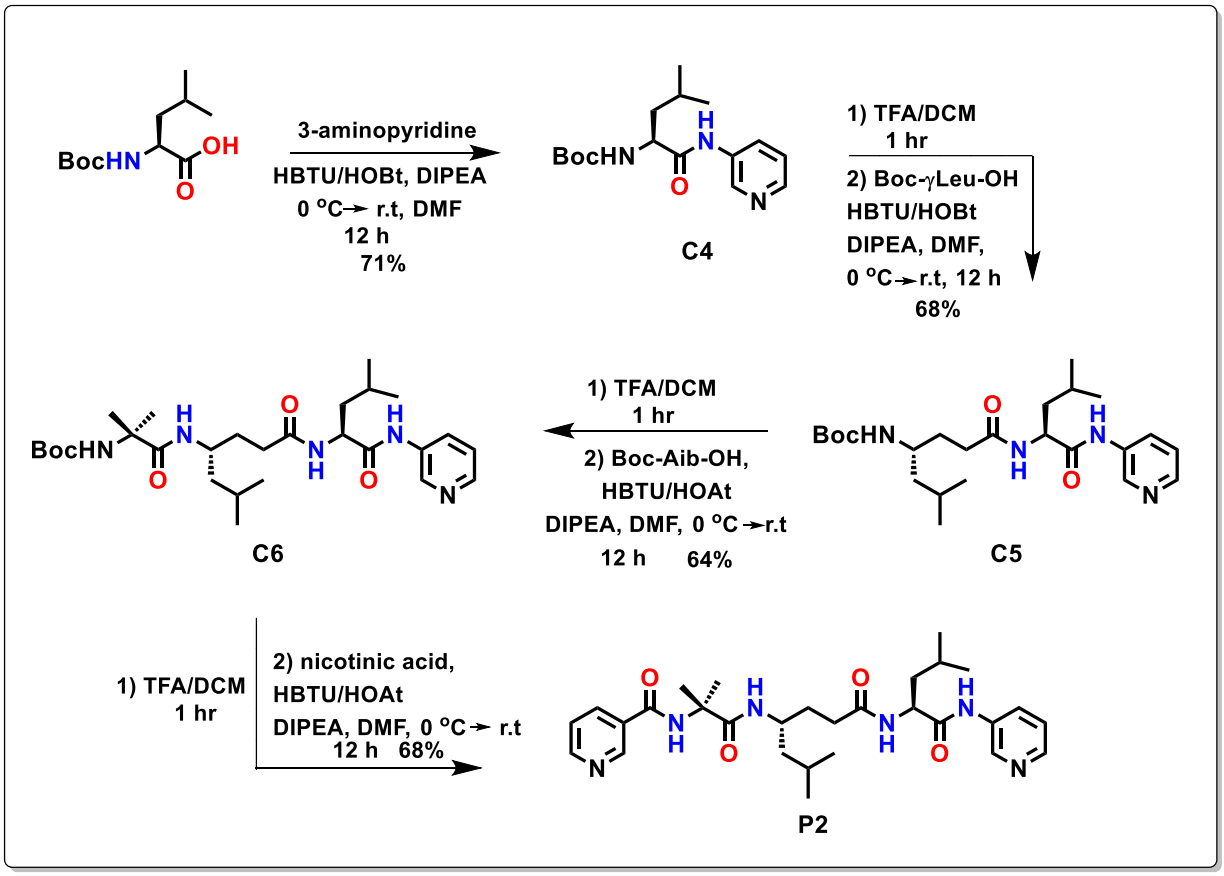
N-Boc protected 2-amino isobutyric acid (Aib) (3.7 mmol, 0.75 g) was dissolved in 3.0 mL of DMF and the solution was then cooled to 0 ^{o}C using an ice bath in N_2 atmosphere. To this, HBTU (3.7 mmol, 1.41 g), HOAt (3.7 mmol, 0.50 g) and DIPEA (7.4 mmol, 1.3 mL) were added and the reaction mixture was stirred for 10 mins. This was followed by the addition of amine cocktail of compound C2 and the reaction mixture was further stirred overnight at room temperature. Upon completion, the reaction mixture was diluted with 150 mL of EtOAc and was washed with water (100 mL X 2), 10% Na_2CO_3 solution (100 mL X 3) and finally with brine solution (100 mL X 2). The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give a crude peptide which was then purified by column chromatography (EtOAc) to get pure compound C3 (Yield- 1.3 g, 66%).

The compound C3 (2.4 mmol, 1.3 g) was further subjected to Boc deprotection using 50% TFA in DCM (3 mL TFA in 3 mL DCM). Upon completion, the reaction mixture was evaporated several times with DCM to remove the residual TFA. The resulting TFA salt of the amine was dissolved in 1 mL DMF and was quenched with DIPEA (7.2 mmol, 1.3 mL) to get the free amine of compound C3.

Finally, 2 mL of DMF was added to isonicotinic acid (2.3 mmol, 0.283 g) and it was then cooled down to 0 ^{o}C using an ice bath in N_2 atmosphere. To this, HBTU(2.3 mmol, 0.87 g), HOAt (2.3 mmol, 0.32 g) and DIPEA (4.6 mmol 0.8 mL) were added and the reaction mixture was stirred 10 mins. This was followed by the addition of amine cocktail of compound C3 and the reaction mixture was further stirred overnight at room temperature. Upon completion, the reaction

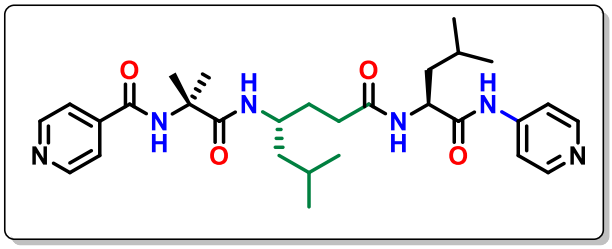
mixture was diluted with 150 mL of EtOAc and was washed with water (100 mL X 2), 10% Na_2CO_3 solution (100 mL X 3) and finally with brine solution (100 mL X 2). The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give a crude peptide which was then subjected to column chromatography (10% MeOH in DCM) to get the pure peptide, **P1** (Yield- 0.88 g, 71%).

General Procedure for the Synthesis of Peptide P2:



The synthesis of **P2** was carried out as described in the above scheme, following similar protocols as of **P1** (Yield- 0.62 g, 68%).

[20]. ^{1}H, ^{13}C NMR and Mass Spectra of Peptide:

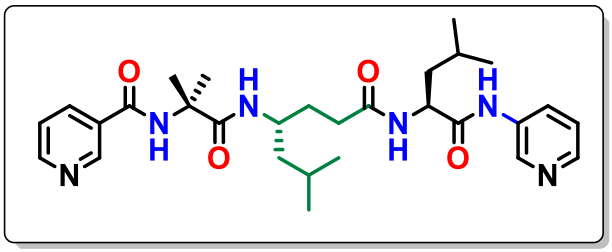


P1

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.42 (s, 1H), 8.75 – 8.68 (m, 2H), 8.65 (s, 1H), 8.45 – 8.37 (m, 2H), 7.88 (d, *J* = 6.7 Hz, 1H), 7.81 – 7.74 (m, 2H), 7.71 – 7.61 (m, 2H), 7.53 (d, *J* = 9.3 Hz, 1H), 4.23 (dt, *J* = 9.6, 6.1 Hz, 1H), 3.77 (dt, *J* = 9.0, 4.5 Hz, 1H), 2.28 – 2.13 (m, 1H), 2.09 (ddd, *J* = 13.7, 7.3, 5.0 Hz, 1H), 1.77 – 1.58 (m, 3H), 1.50 (d, *J* = 8.4 Hz, 6H), 1.45 (ddd, *J* = 11.5, 9.0, 5.6 Hz, 1H), 1.33 (dd, *J* = 9.1, 4.5 Hz, 1H), 1.12 (td, *J* = 8.9, 4.5 Hz, 1H), 0.84 (d, *J* = 6.6 Hz, 3H), 0.80 (d, *J* = 6.5 Hz, 3H), 0.74 (dd, *J* = 6.5, 1.1 Hz, 6H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 173.84, 172.99, 172.90, 164.97, 150.14, 149.90, 146.12, 141.70, 121.65, 113.68, 56.92, 53.22, 46.13, 44.02, 40.41, 31.74, 31.48, 25.32, 25.00, 24.41, 24.36, 23.14, 22.84, 22.04, 21.50.

MALDI TOF/TOF m/z calculated for $C_{29}H_{42}N_6O_4$ [M+Na] is 561.327 and observed value is 561.628



P2

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.36 (s, 1H), 9.12 (d, *J* = 2.2 Hz, 1H), 8.80 (d, *J* = 2.4 Hz, 1H), 8.49 (s, 1H), 8.43 (dd, *J* = 4.7, 1.6 Hz, 1H), 8.20 (dd, *J* = 4.7, 1.5 Hz, 1H), 8.16 (dt, *J* = 8.1, 2.0 Hz, 1H), 8.05 (s, 1H), 7.93 (dt, *J* = 8.3, 2.0 Hz, 1H), 7.44 (d, *J* = 9.7 Hz, 1H), 7.07 (dd, *J* = 8.0, 4.7 Hz, 1H), 7.00 (dd, *J* = 8.4, 4.7 Hz, 1H), 4.23 (dt, *J* = 10.0, 4.7 Hz, 1H), 4.07 (d, *J* = 13.1 Hz, 1H), 2.61 (t, *J* = 12.2 Hz, 1H), 2.32 – 2.17 (m, 2H), 1.94 (dd, *J* = 13.4, 6.8 Hz, 1H), 1.84 (s, 3H), 1.71 (s, 3H), 1.66 – 1.56 (m, 3H), 1.52 – 1.35 (m, 3H), 0.90 (dd, *J* = 13.4, 6.4 Hz, 6H), 0.80 (dd, *J* = 8.9, 6.5 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.22, 174.55, 173.46, 166.21, 152.40, 149.12, 144.51, 142.10, 135.77, 135.18, 129.02, 127.02, 122.99, 57.87, 56.36, 46.40, 41.19, 32.33, 32.03, 27.22, 25.37, 24.91, 23.97, 23.44, 23.21, 22.67, 21.73.

MALDI TOF/TOF m m/z calculated for $C_{29}H_{42}N_6O_4$ [M+Na] is 561.327 and the Observed value is 561.524

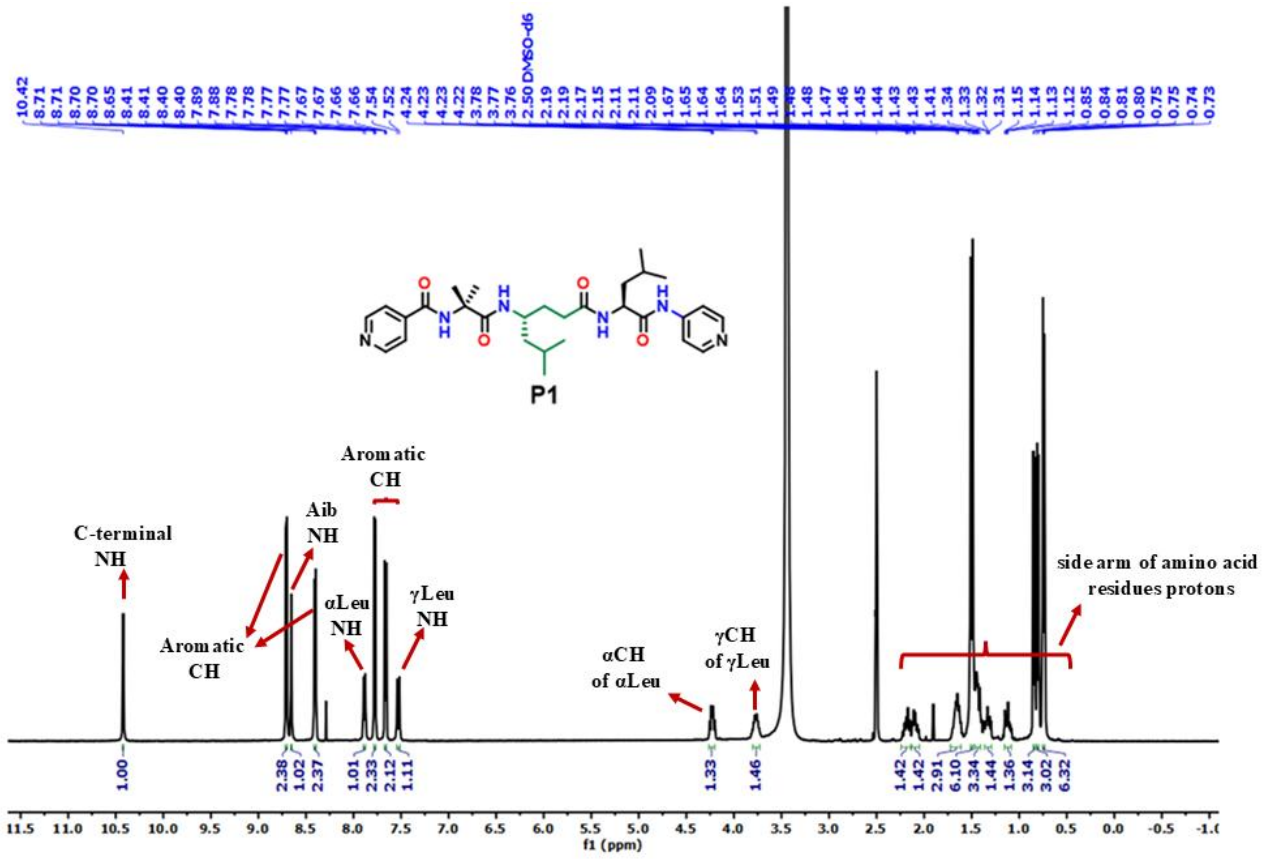


Figure S23: ^{1}H NMR spectrum of **P1** in DMSO-d_6.

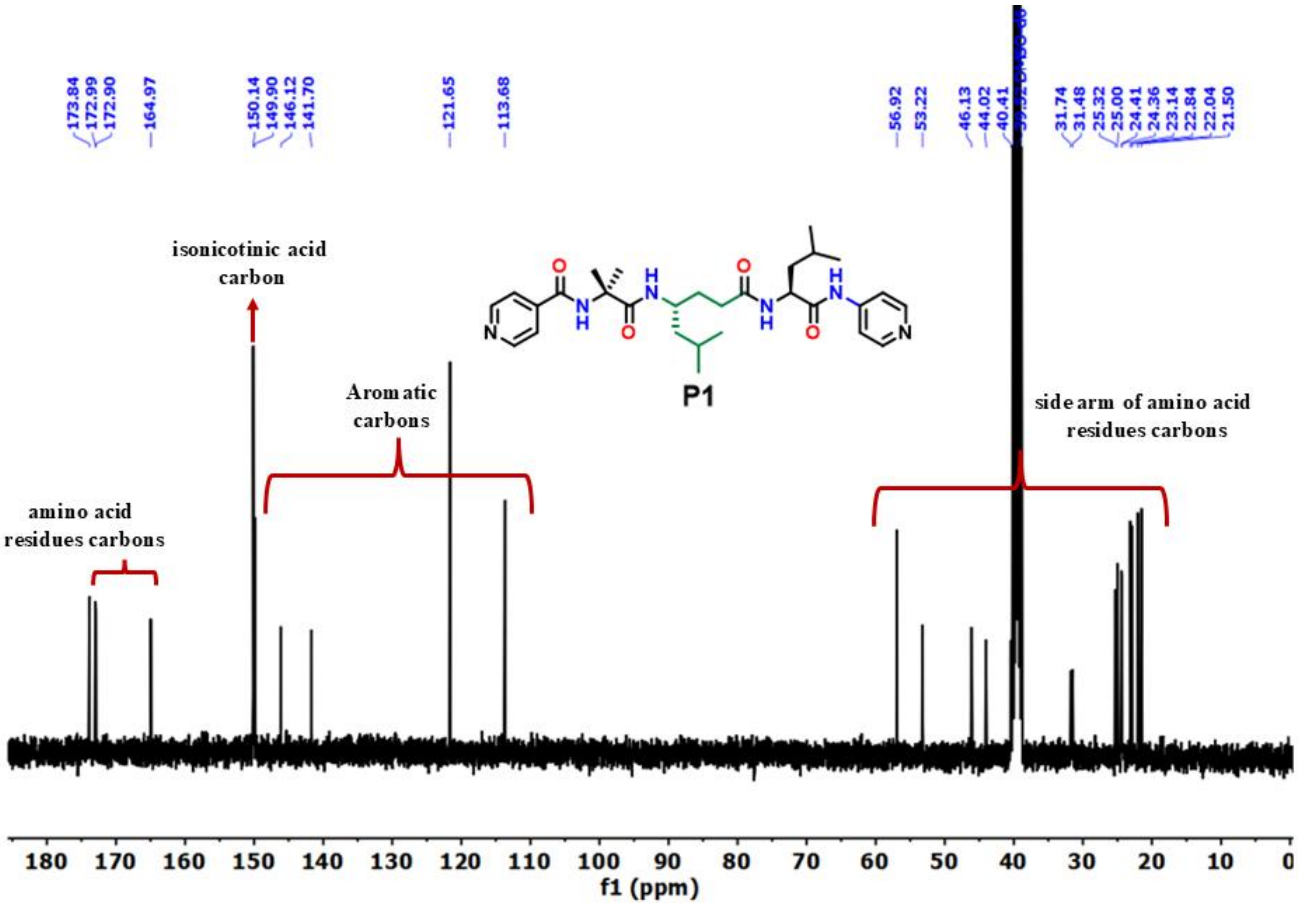


Figure S24: ^{13}C NMR spectrum of **P1** in DMSO-d_6.

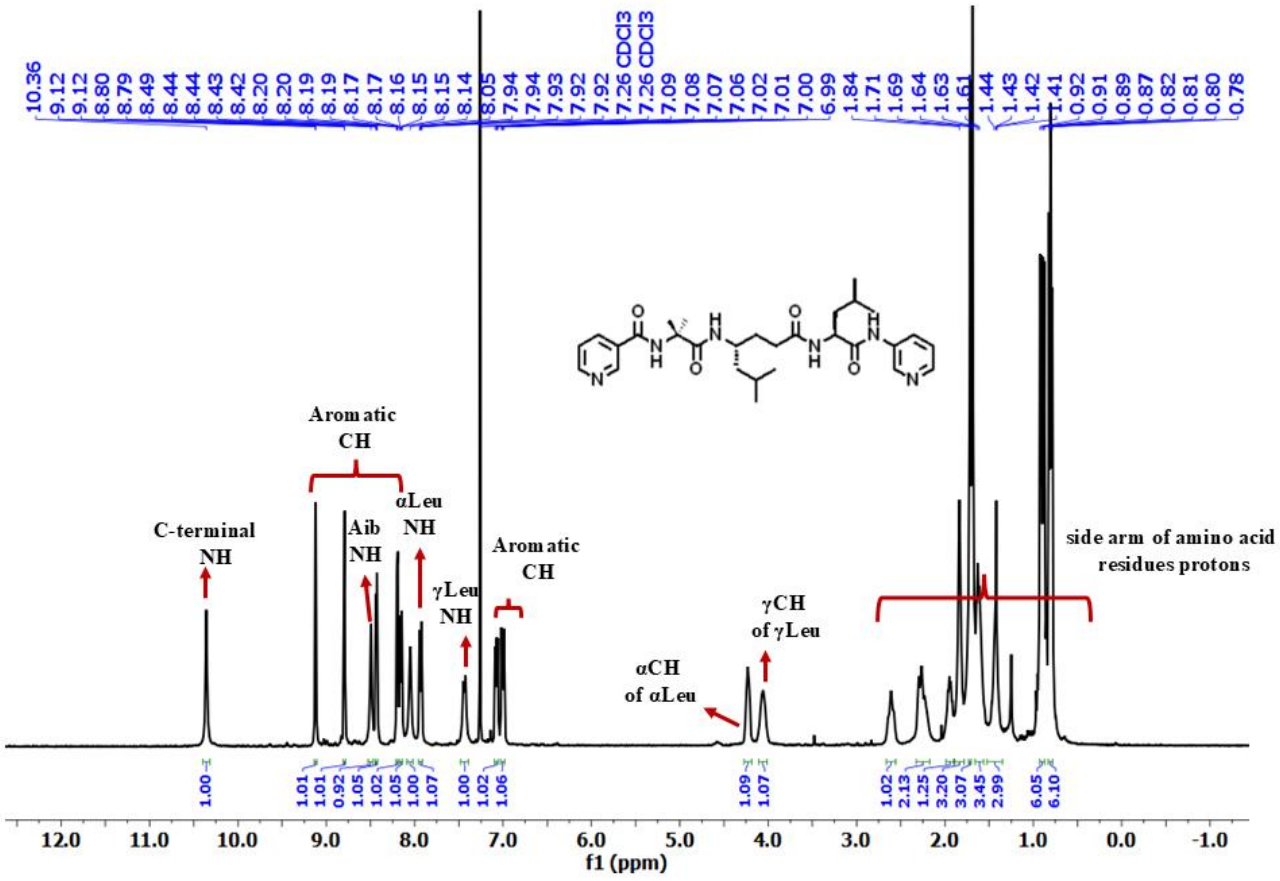


Figure S25: ^{1}H NMR spectrum of **P2** in $CDCl_3$

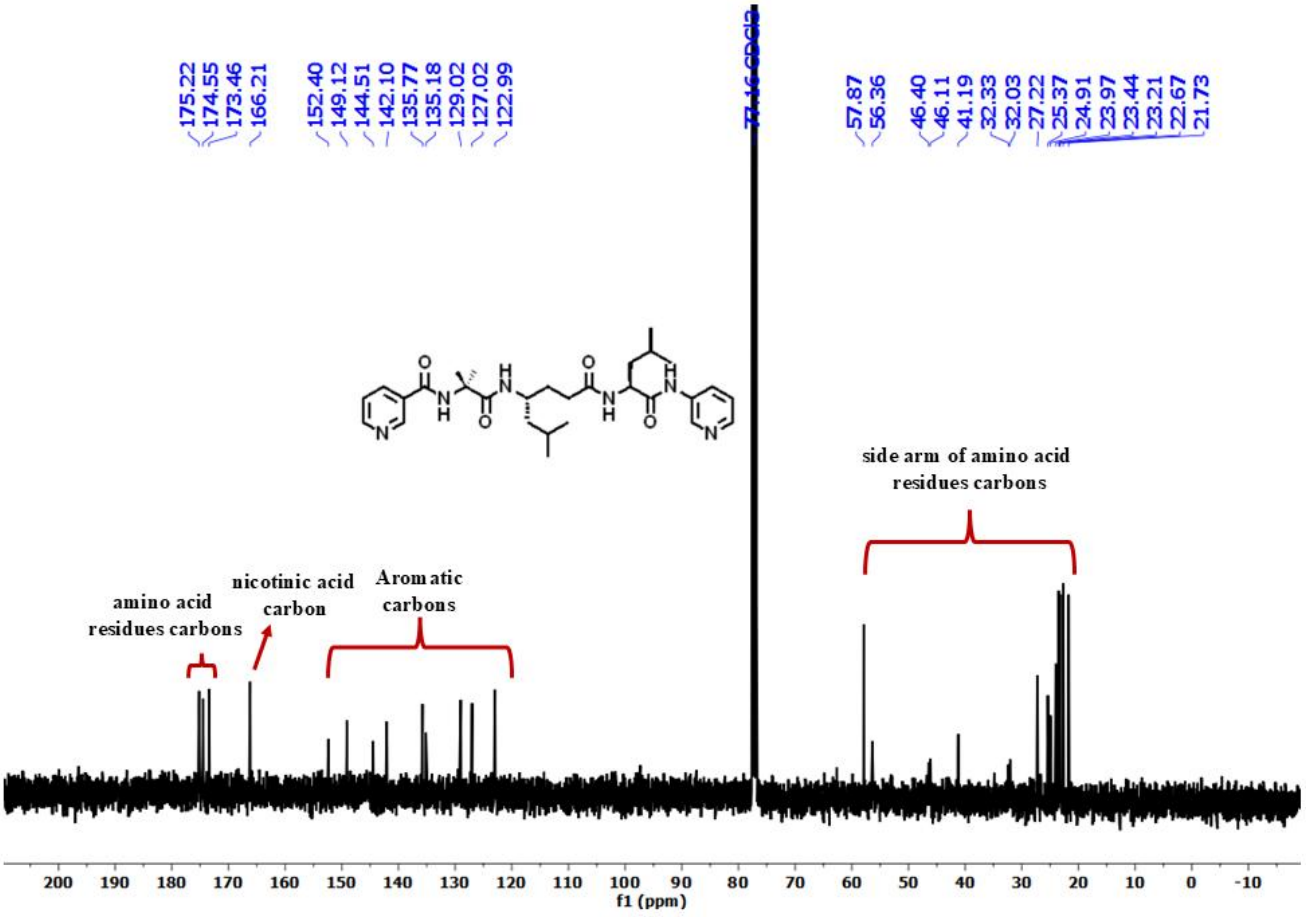


Figure S26: ^{13}C NMR spectrum of **P2** in $CDCl_3$.

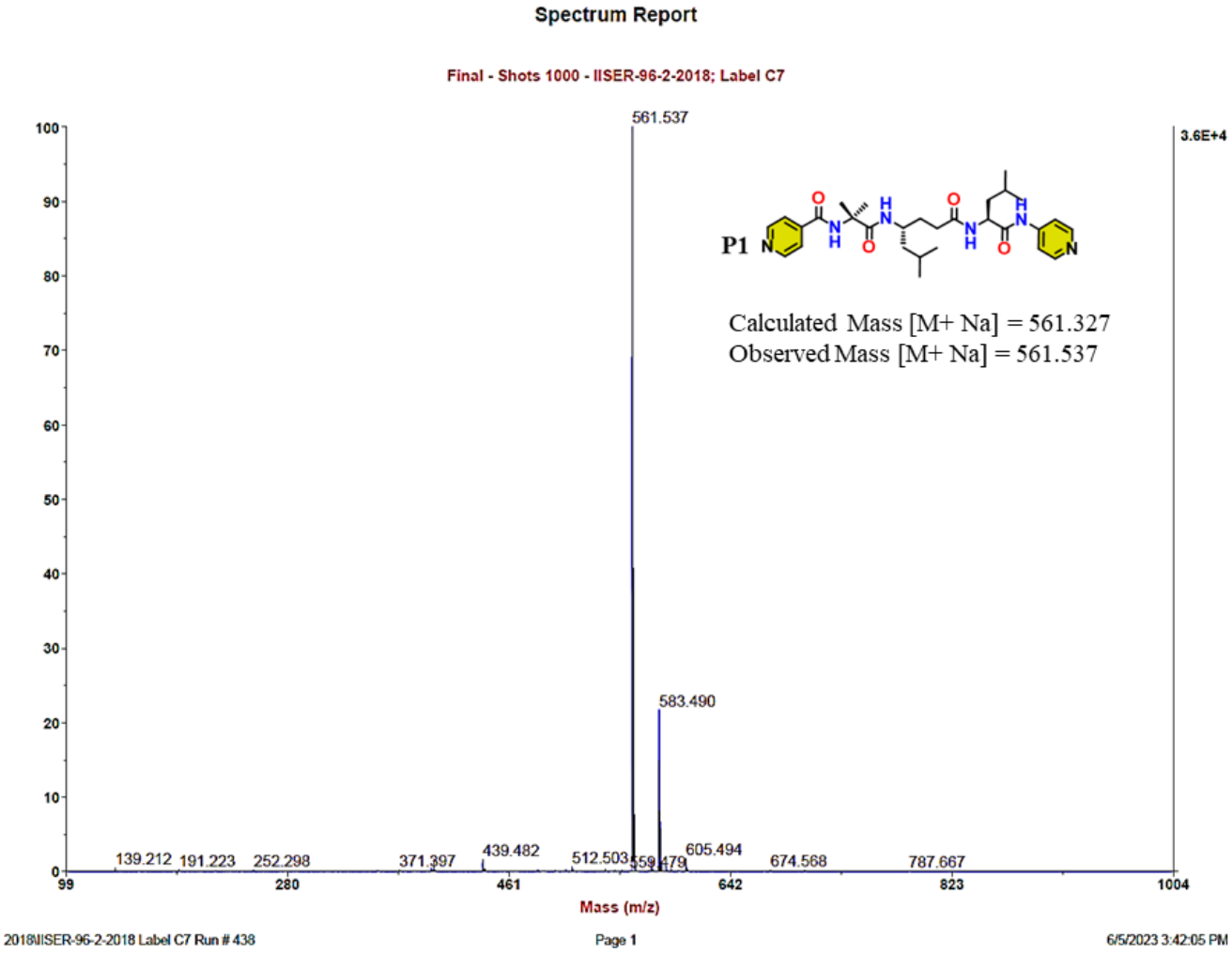


Figure S27: MALDI-TOF/TOF mass spectrum of **P1**.

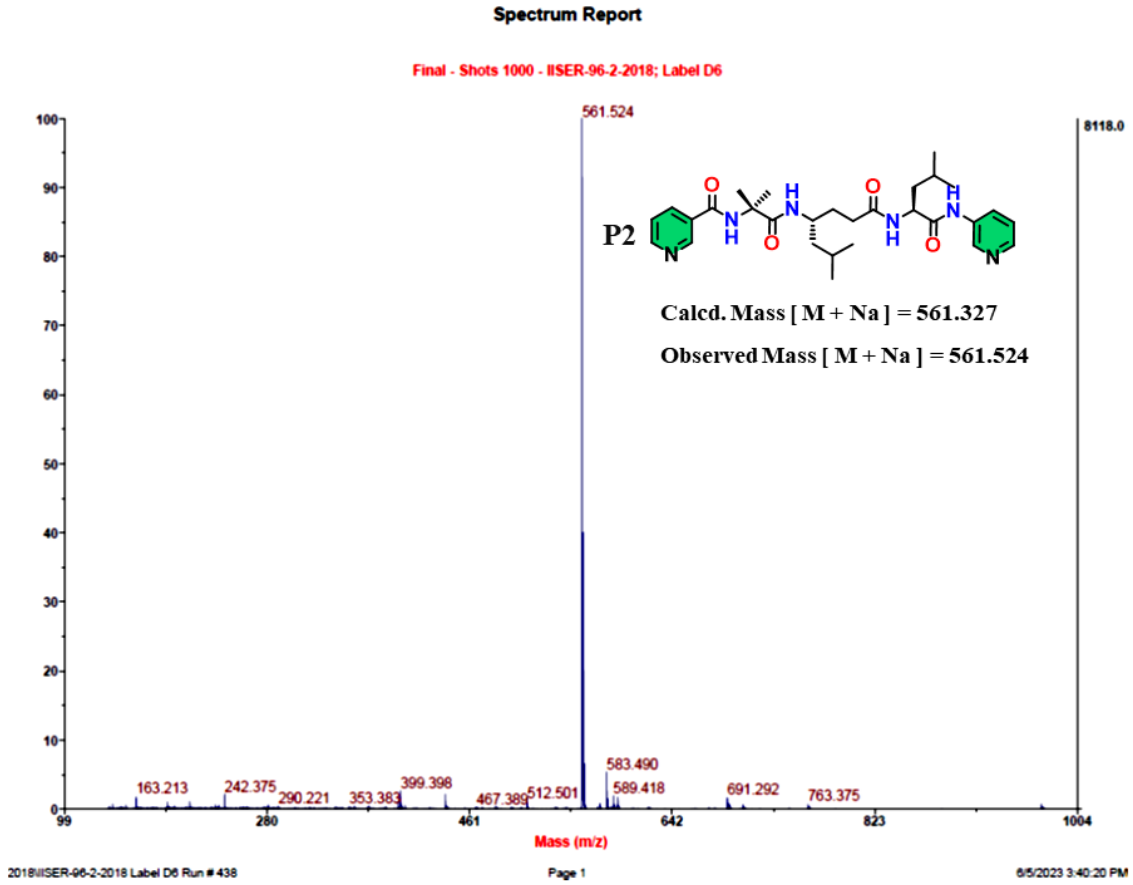


Figure S28: MALDI-TOF/TOF mass spectrum of **P2**.

[21] References:

1. Sheldrick, G. M. *Acta Crystallography. Sect A*. 1990, **46**, 467.
2. Spek, A. L. *Acta Crystallogr*. 1990, **A46**, C34.