Supplemental Information

Solid-Phase Synthesis of Peptoid-like Oligomers Containing Diverse Diketopiperazine Units

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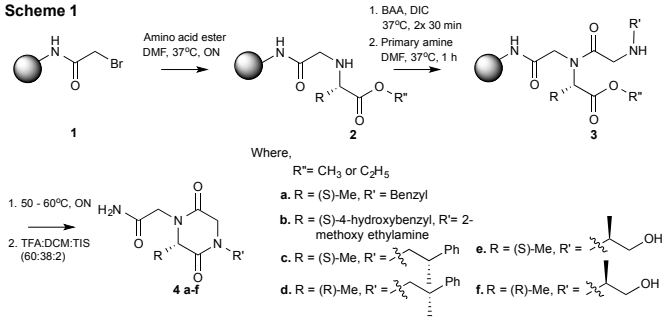
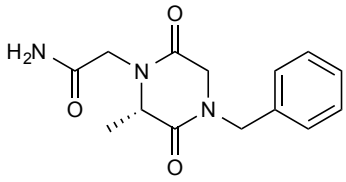
Materials and Instruments:

Amino acid esters were purchased from either from Aldrich, Acros, Advanced chemtech and Astatech. (S) and (R)-2-bromo-propionic acid were purchased from Aldrich. Mono-N-tboc-ethylenediamine was bought from Astatech Inc. Primay amines were purchased from Advanced Chemtech, Aldrich, Acros, TCI. Rest of the other chemicals and reagents were purchased either from Aldrich or Fisher Scientific. Rink amide MBHA resin (0.5 mmol/g) and Tentagel macrobead-NH_2 (160 µg, 0.4 mmol/g) resin were obtained from Chemprep and rapp-polymere, respectively. Disposable fritted columns (5 mL, 50 mL) for peptoid syntheses were bought from Intavis AG. Microwave assisted peptoid syntheses were accomplished utilizing 10% of 1550 W household microwave (GE model JE 1860 BH04). HPLC purification of crude peptoids after acid cleavage from Rink amide resin was carried out in Water 1525 binary HPLC pumps and a 2487 dual absorbance detector, or a 2998 photodiode array detector. Buffer A (H_2O with 5% CH_3CN and 0.1% trifluoroacetic acid (TFA) and buffer B (5m, 250 x 4.6 mm, Alltech) and Apollo C-18 5µ preparative column. Purities of the compounds were assessed by analytical HPLC under UV (214), otherwise mentioned in description of the spectrum. MS and MS/MS were recorded in MALDI -TOF (4800 Proteomics Analyser, Applied Biosystems) or ESI-MS (Waters). In MS/MS, the signal-to-noise ratio threshold set to 10. Cyano-4-hydroxycinnamic acid (HCCA) or charcoal was used as MALDI matrices (Aldrich). ^1H and ^{13}C NMR spectra were recorded in Bruker 400 instrument operating at 400 MHz for ^1H and 100 MHz for ^{13}C NMR using Deuterated-methanol (CD_3OD) or Deuterated-Dimethylsulfoxide (DMSO) (Cambridge) as a solvent.

Synthesis of 2, 5-DKP (4 a-f)





4a

Rink amide MBHA resin (1 g, 0.7 mmol) was swelled in DMF. Fmoc group was deprotected with 20% piperidine in DMF (2X, 15 mins). The resultant primary amine was coupled with bromoacetic acid (BAA, 2M) activated with diisopropylcarbodiimide (DIC, 2 M) in N,N'-dimethylformamide (DMF). Subsequently, the bromide was displaced with desired HCl salt of amine acid ester in DMF (2 M) along with DIEA (1.5X with respect to ester). The secondary amine was further coupled with bromoacetic acid (2M), activated with DIC (3M), 37°C (2X, 15 min). The bromide was displaced with a solution of desired primary amine (viz benzyl amine in this case) in DMF at 37°C, 1 h. At this stage, the reaction mixture further incubated at 50°C overnight so that the secondary amine thus generated after SN2 reaction undergo addition elimination at the ester thus generating six-membered 2,5 diketopiperazine. Finally, the solid support was washed with DMF, DCM and ethanol, and subjected to cleave with 50% TFA in DCM along with 2% triisopropylsilane. A crude DKP obtained after the solvent was evaporated under Argon and ether precipitation. A crude dried compound finally was subjected to NMR study without further HPLC purification by dissolving in d-methanol. ^{1}HNMR (400 MHZ, D_6-DMSO) δ 7.4-7.3 (m, 5H), 4.7 (d, 1H, J=14.7), 4.5 (d, 1H, J=14.7), 4.3 (d, 1H, J=16.7), 4.12 (q, 1H), 4.0 (d, 1H, J=17.7), 3.9 (d, 1H, J=16.7), 3.82 (d, 1H, J= 17.5), 1.5 (d, 3H, Me, J=7.2); ^{13}CNMR (100 MHz, DMSO) δ 172.3, 169.2, 166.5, 136.8, 129.9, 59.19, 50.3, 49.7, 47.8, 18.1; MALDI-TOF MS (Obs.=MNa^{+}) 298.0681 (298.1270 expected).

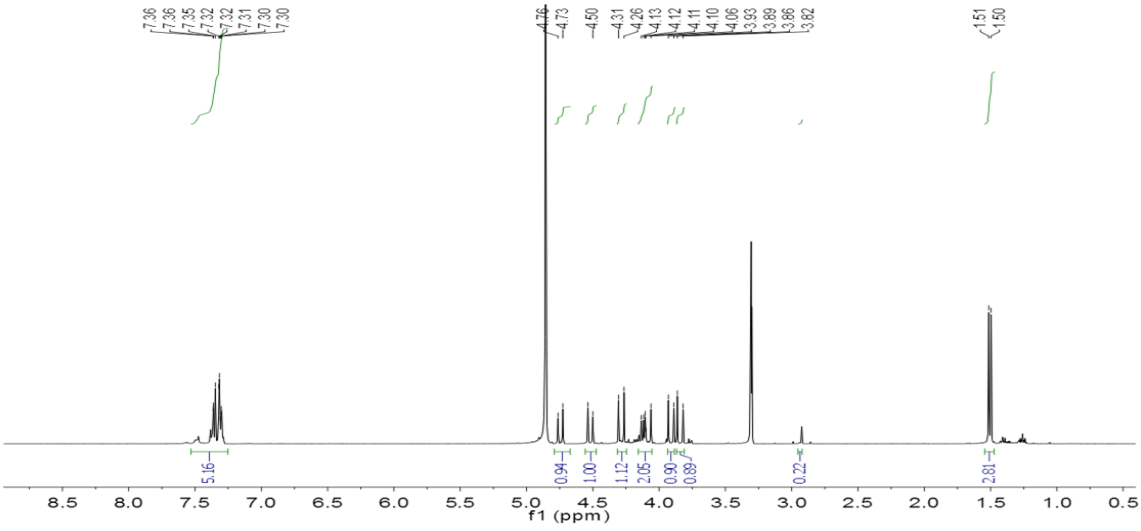


Figure S1: ^{1}HNMR of compound **4a**

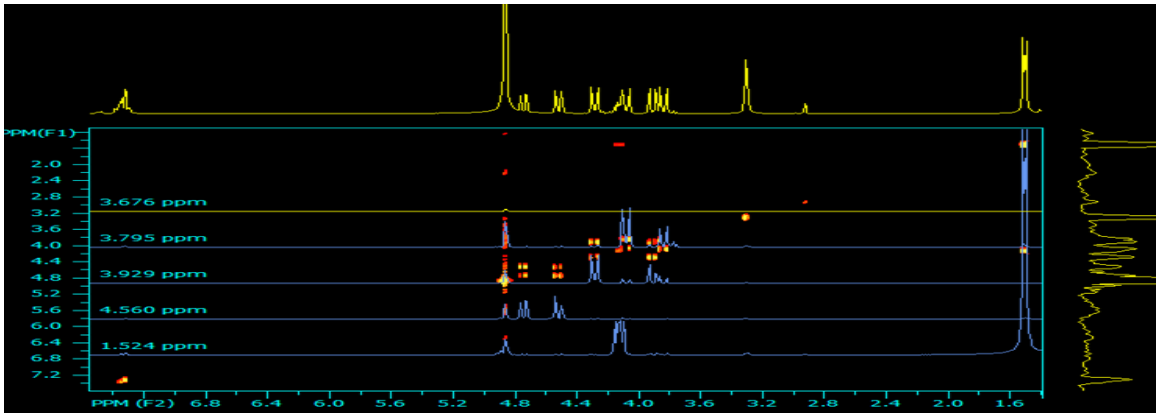


Figure S2: COSY of **4a**

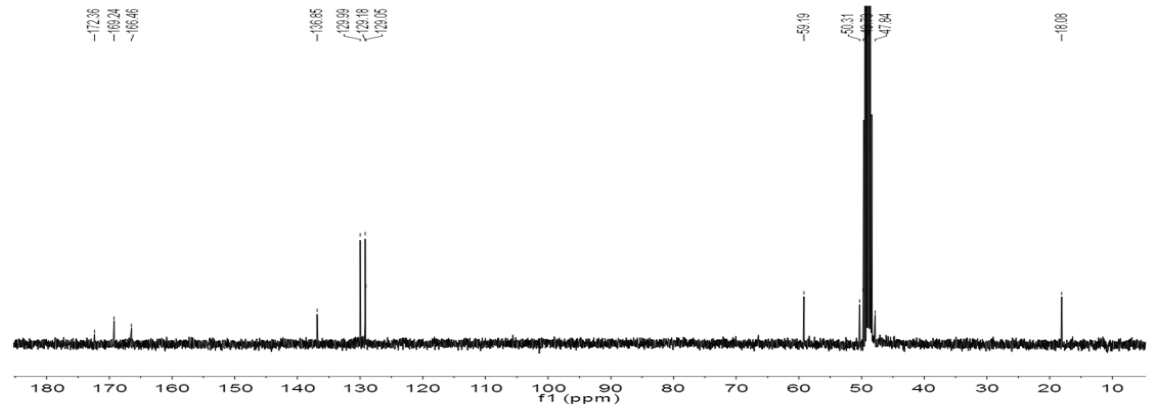


Figure S3: ^{13}CNMR of **4a**

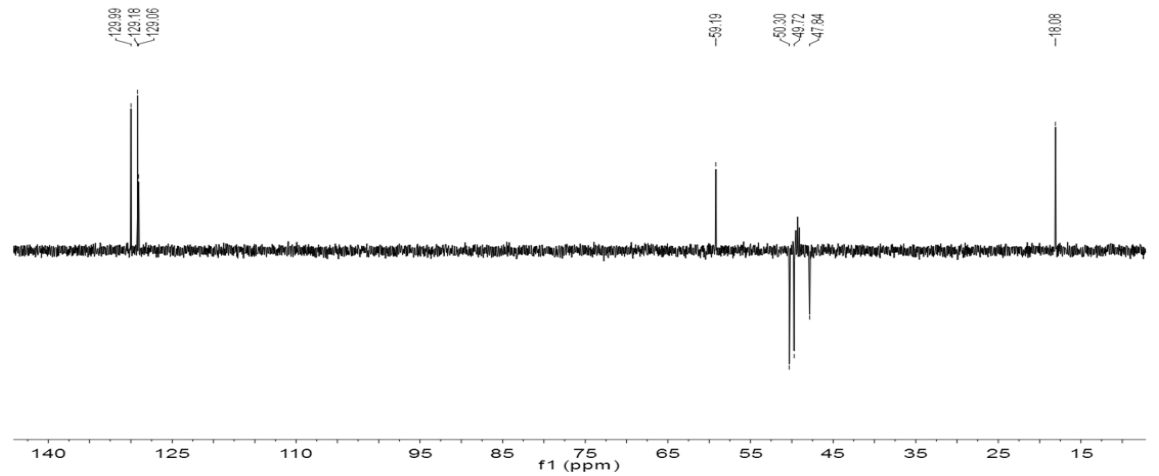


Figure S4: Dept of **4a**

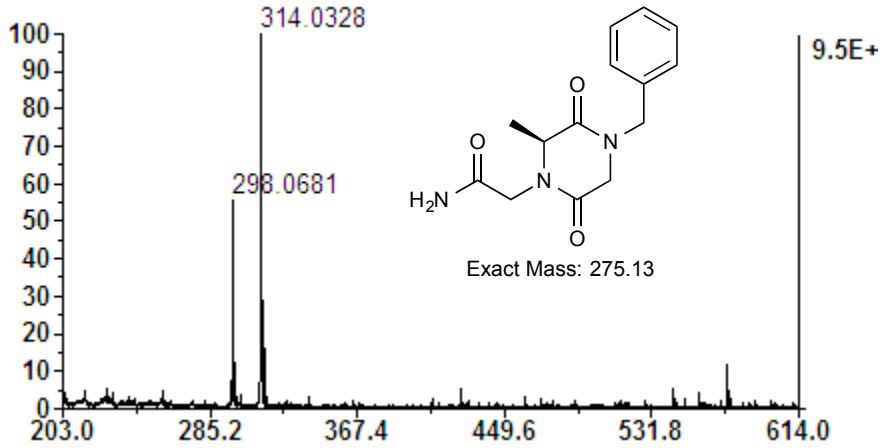
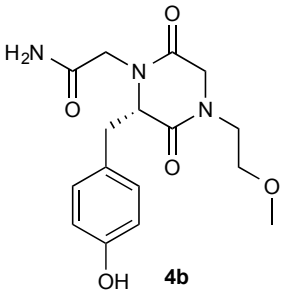


Fig S5: MALDI-MS of compound **4a**



Spectral data for compound 4b:

A crude dried compound was dissolved in in d-DMSO. ^{1}HNMR (400 MHZ, D_6-DMSO) δ 6.83 (d, 2H, J=8.3), 6.66 (d, 2H, J=8.3) 4.35 (d, 1H, J=16.4), 4.15 (t, 1H), 3.6 (d, 1H, J=16.4), 3.32 (m, 1H, J=17.1), 3.5 (d, 1H), 3.35 (m, 1H), 3.3 (m, 1H), 3.2 (s, 3H), 3.15 (m, 1H), 3.0 (dd, 1H, J=14), 2.9 (dd, 1H, J=14), 2.6 (d, 1H, J=17.1); ^{13}CNMR (100 MHz, DMSO) δ 169.2, 165.3, 164.0, 156.5, 130.7, 124.9, 115.0, 69.2, 61.7, 57.8, 49.5, 45.8, 44.9, 35.5; ESI-MS(Obs. MNa^{+}) =358.1398 (Expected=358.1481).

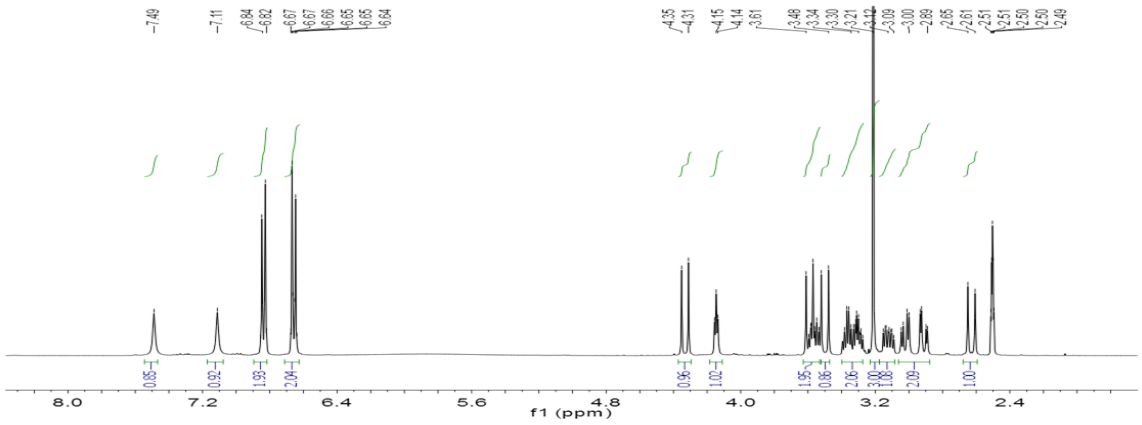


Figure S6: ^{1}HNMR of **4b**

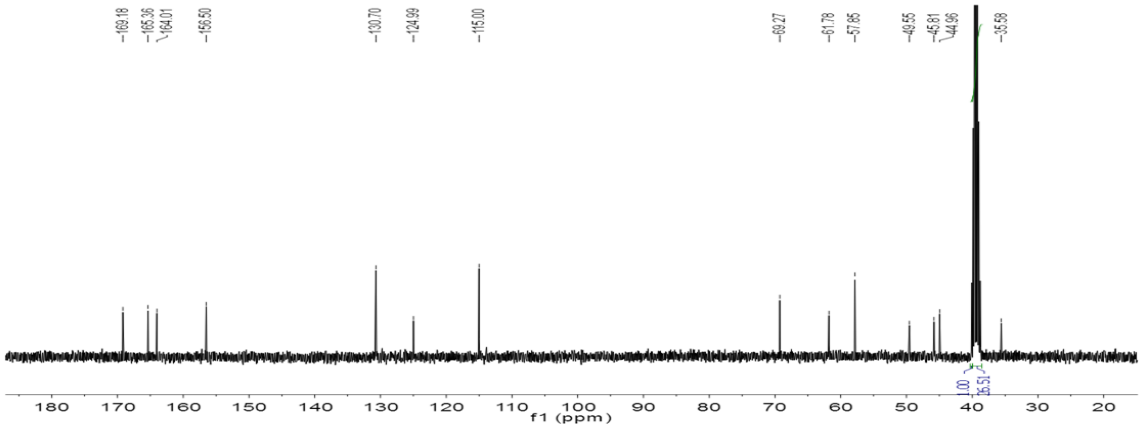


Figure S7: ^{13}CNMR of compound **4b**

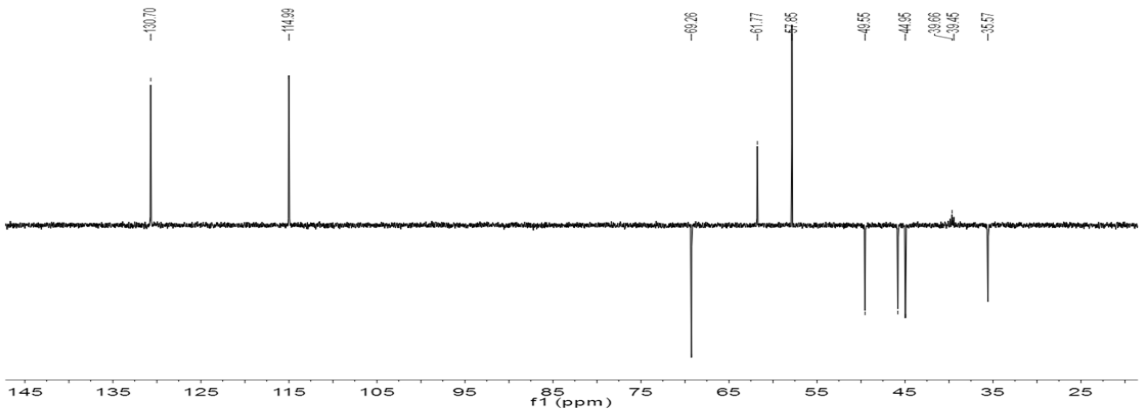


Figure S8: ^{13}C-DEPT of compound **4b**

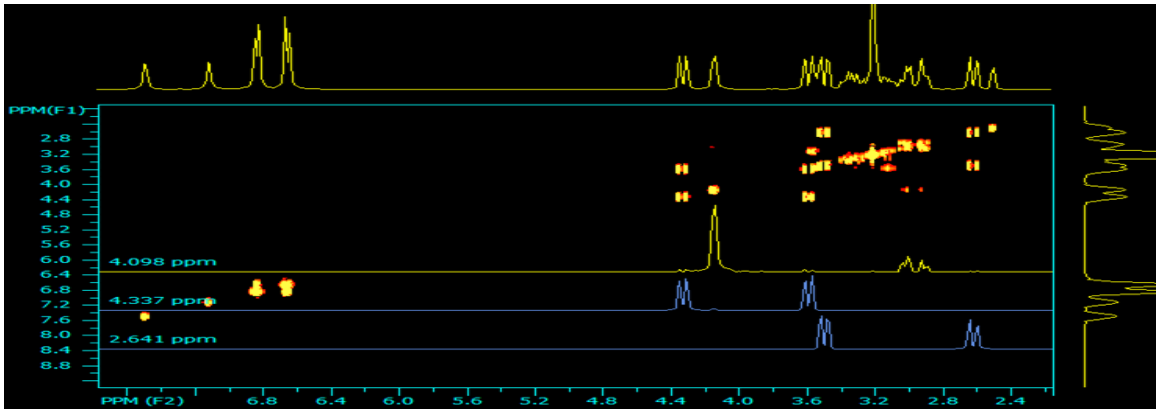


Figure S9: COSY of compound **4b**

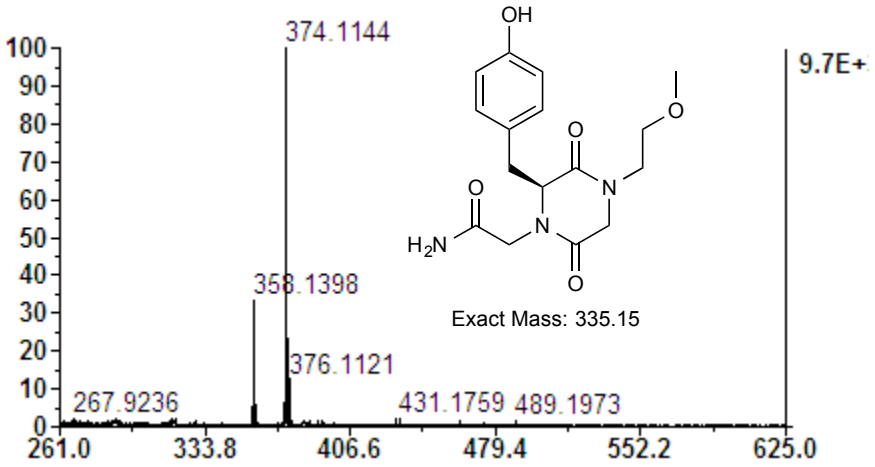


Fig S10: MALDI-MS of compound **4b**

Spectral data for compound 4c and 4d:

For compound 4d:

A HPLC purified compound was dissolved in in d-chloroform. ^{1}HNMR (400 MHZ) δ 7.3-7.2 (m, 5H), 4.03-3.97 (m, 2H), 3.90 (d, 1H), 3.60 (d, 1H), 3.35 (d, 1H), 3.23 (m, 1H), 3.02 (m, 1H), 1.45 (d, 3H), 1.29 (d, 3H); ^{13}CNMR (100 MHz, DMSO) δ 172.6,169.6, 166.9, 63.1, 59.2, 52.3, 47.7, 45.5, 17.7, 13.4; MALDI-TOF MS (Obs. MNa^{+}) 326.0962 (Expected = 326.1304 expected).

For compound 4c:

A HPLC purified compound was dissolved in in d-chloroform. ^{1}HNMR (400 MHZ) δ 7.3-7.2 (m, 5H), 4.0 (d, 1H), 3.95-3.84 (m, 3H), 3.83 (d, 1H), 3.61 (d, 1H), 3.40-3.35 (m, 1H), 3.15-310 (m, 1H), 1.3 (d, 3H), 1.2 (d, 3H); MALDI-TOF MS (Obs. MNa^{+}) 326.0962 (Expected = 326.1304 expected).

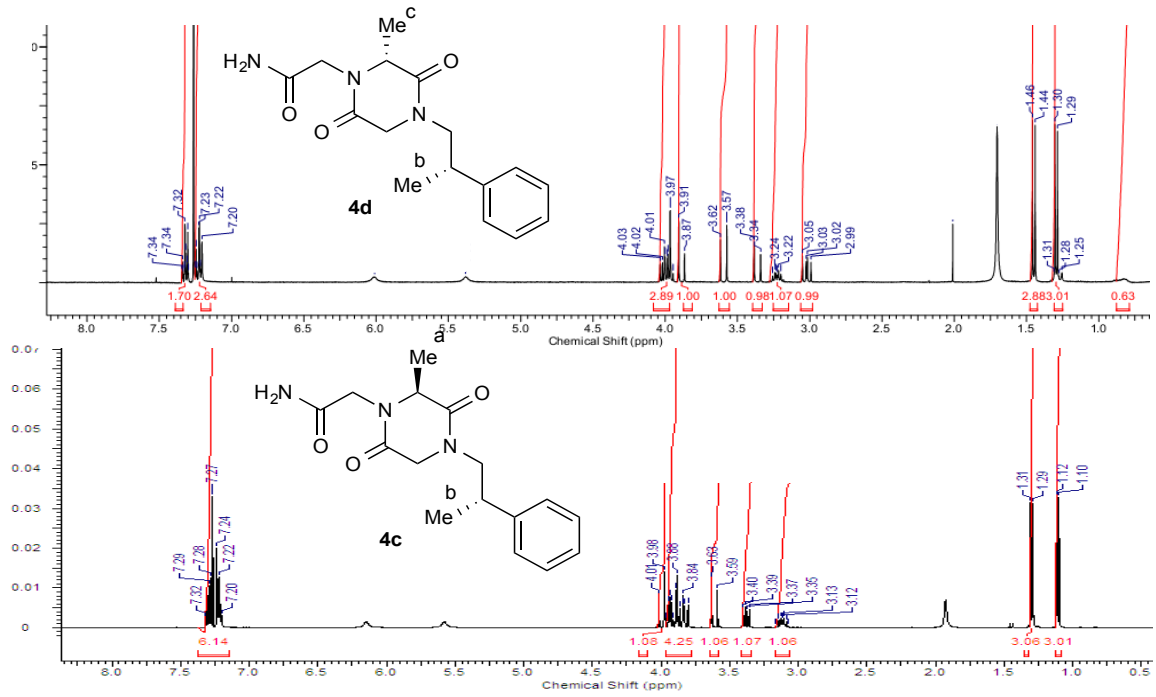


Figure S11: [1]HNMR of compound **4c and 4d**

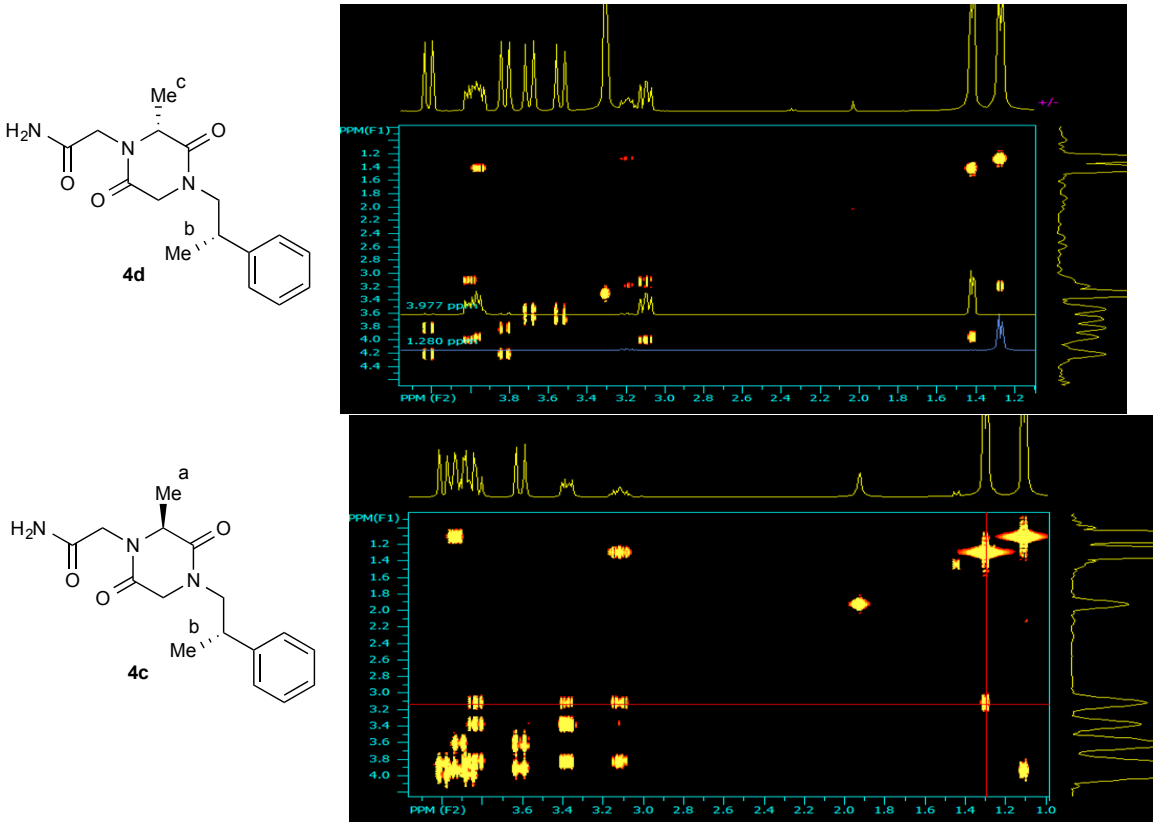


Figure S12: [13]CNMR of compound **4c and 4d**

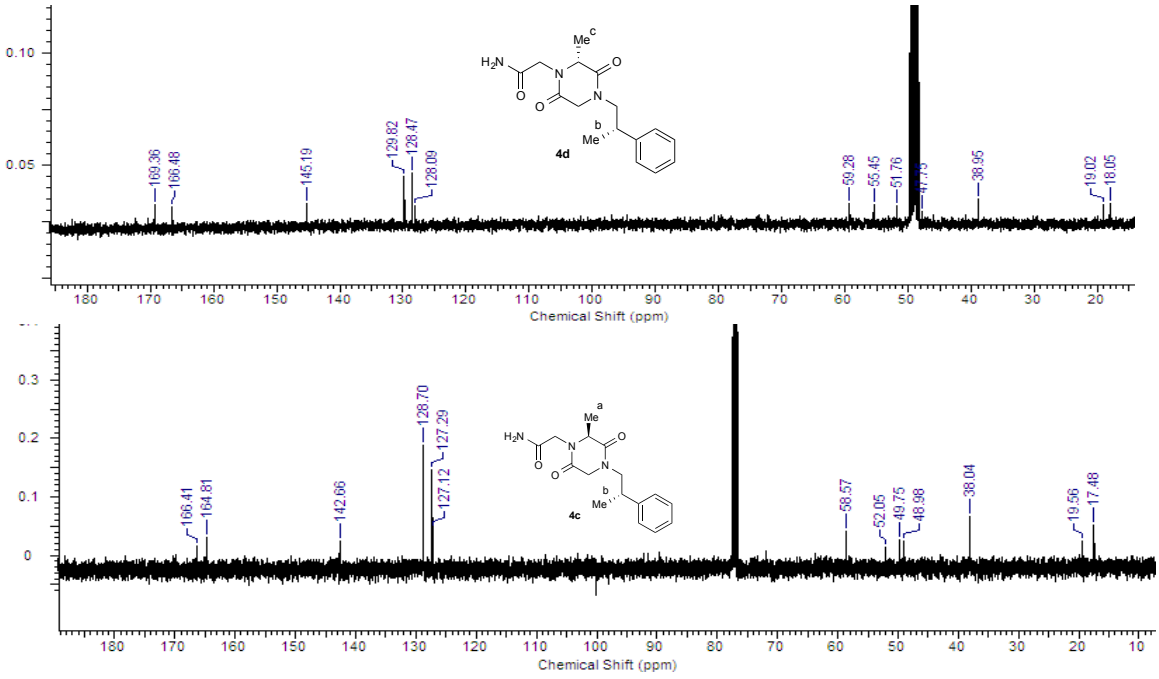


Figure S13: ^{13}CNMR of compound **4c and 4d**

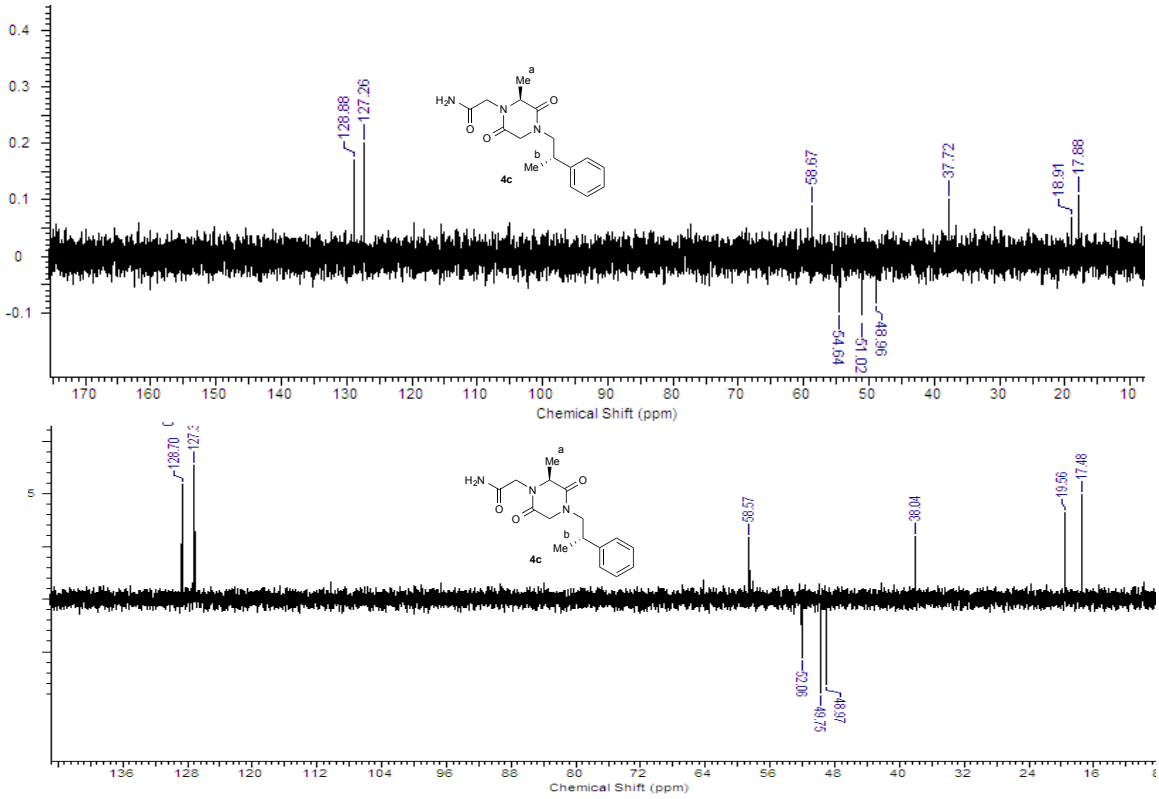


Figure S14: ^{13}CNMR of compound **4c and 4d**

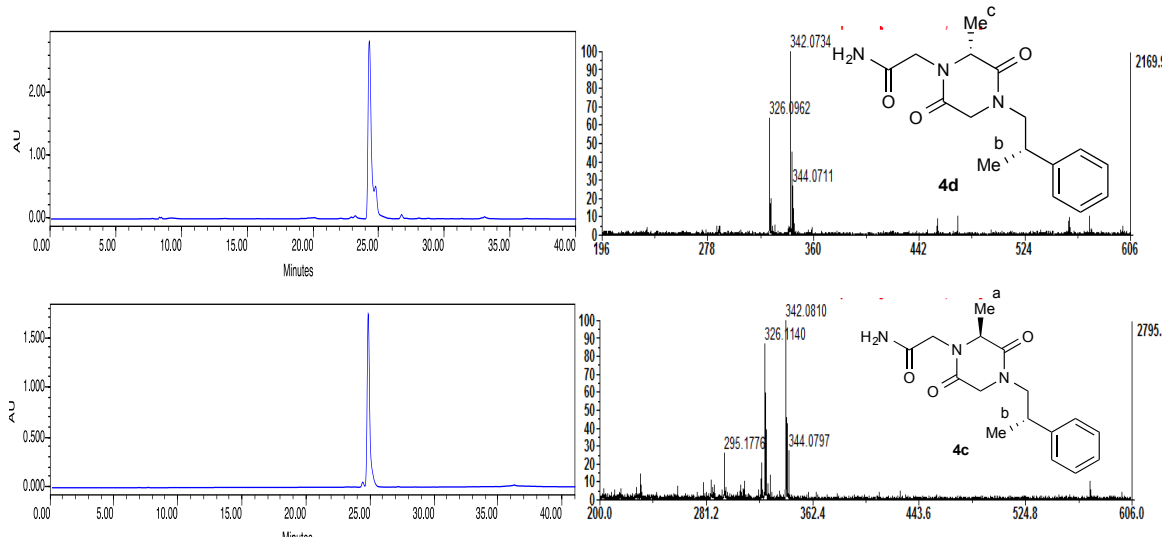
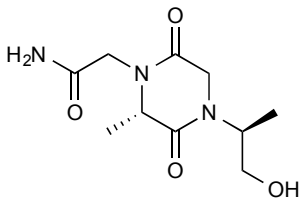


Figure S15: HPLC and ESI-MS of compound **4c and 4d**



Spectral data for compound 4e:

A crude dried compound was dissolved in in d4-methanol. ^{1}HNMR (400 MHZ, D_4-MeOH) 4.6 (m, 1H), 4.3 (d, 1H), 4.14 (d, 1H), 4.06 (q, 1H), 4.02 (d, 1H), 3.9 (d, 1H), 3.64 (m, 1H), 1.49 (d, 1H), 1.18 (d, 1H); ^{13}CNMR (100 MHz, DMSO) δ 172.6,169.6, 166.9, 63.1, 59.2, 52.3, 47.7, 45.5, 17.7, 13.4; MALDI-TOF MS (Obs. MNa^{+}) 266.0499 (Expected =266.1219).

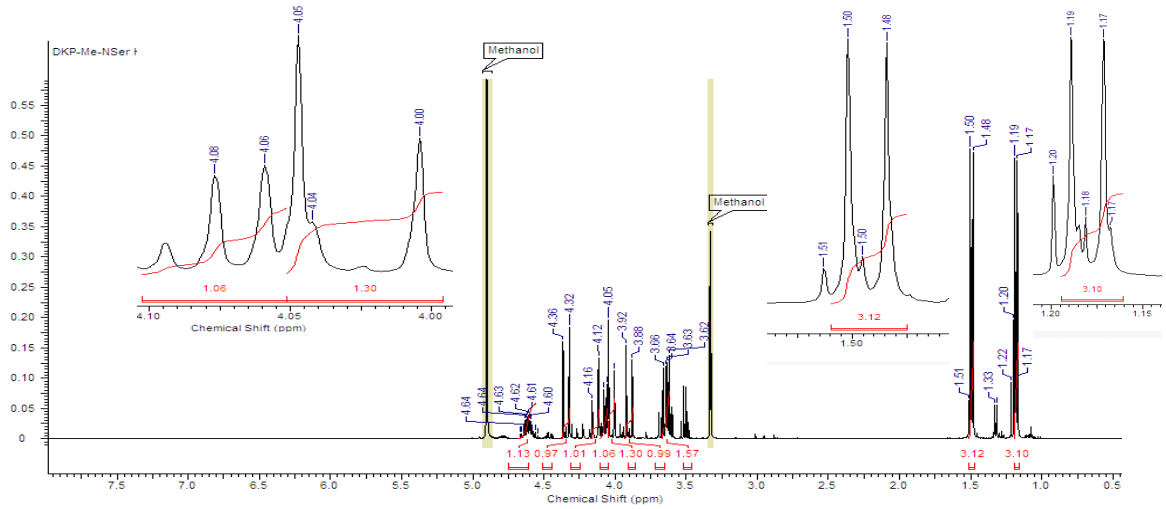


Figure S16: ^{1}HNMR of compound **4e**

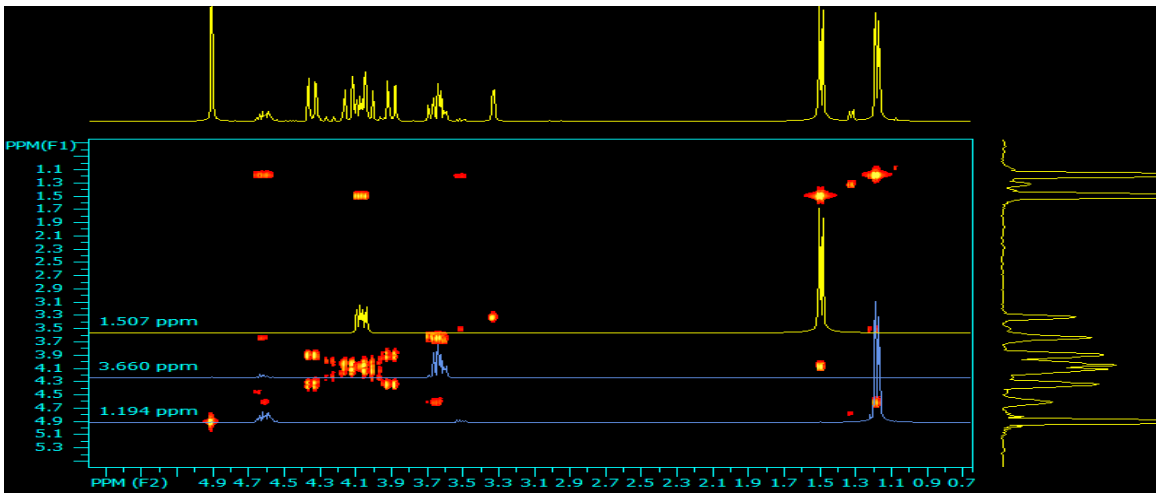


Figure S17: Cosy of compound **4e**

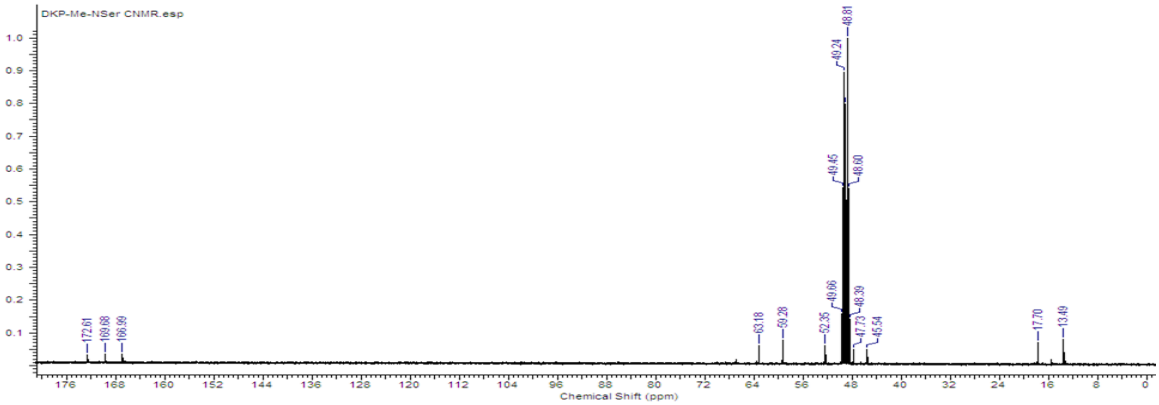


Figure S18: ^{13}CNMR of compound **4e**

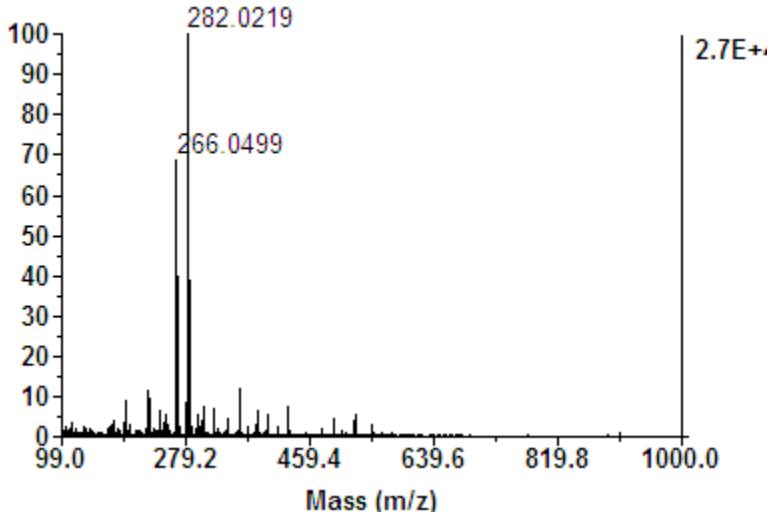
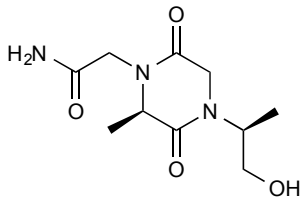


Fig S19: MALDI-MS of compound 4e



4f

Spectral data for compound 4f:

A crude dried compound was dissolved in D6-DMSO. ^{1}HNMR (400 MHZ, D_6-DMSO) 4.6 (m, 1H), 4.3 (d, 1H), 4.14 (d, 1H), 4.06 (q, 1H), 4.02 (d, 1H), 3.9 (d, 1H), 3.64 (m, 1H), 1.49 (d, 1H), 1.18 (d, 1H); ^{13}CNMR (100 MHz, DMSO) δ 169.3, 166.8, 164.2, 61.6, 59.7, 43.8, 40.0, 45.5, 17.2, 13.1; MALDI-TOF MS (Obs. MNa^{+}) 266.0122 (266.1219 expected).

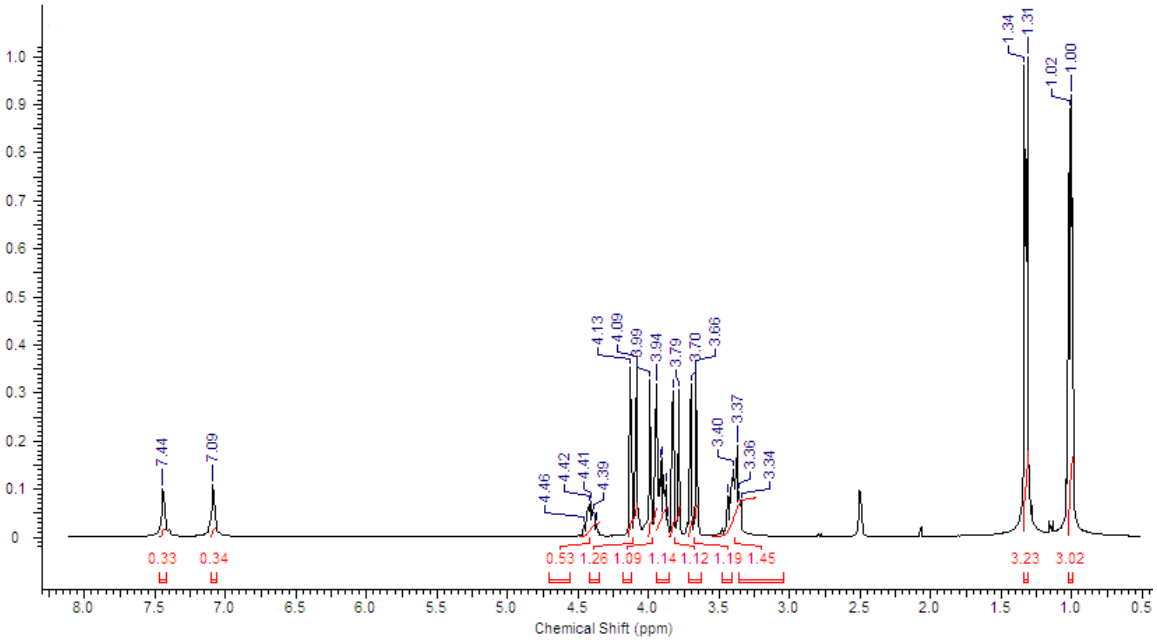


Figure S20: ^{1}H NMR of compound **4f**

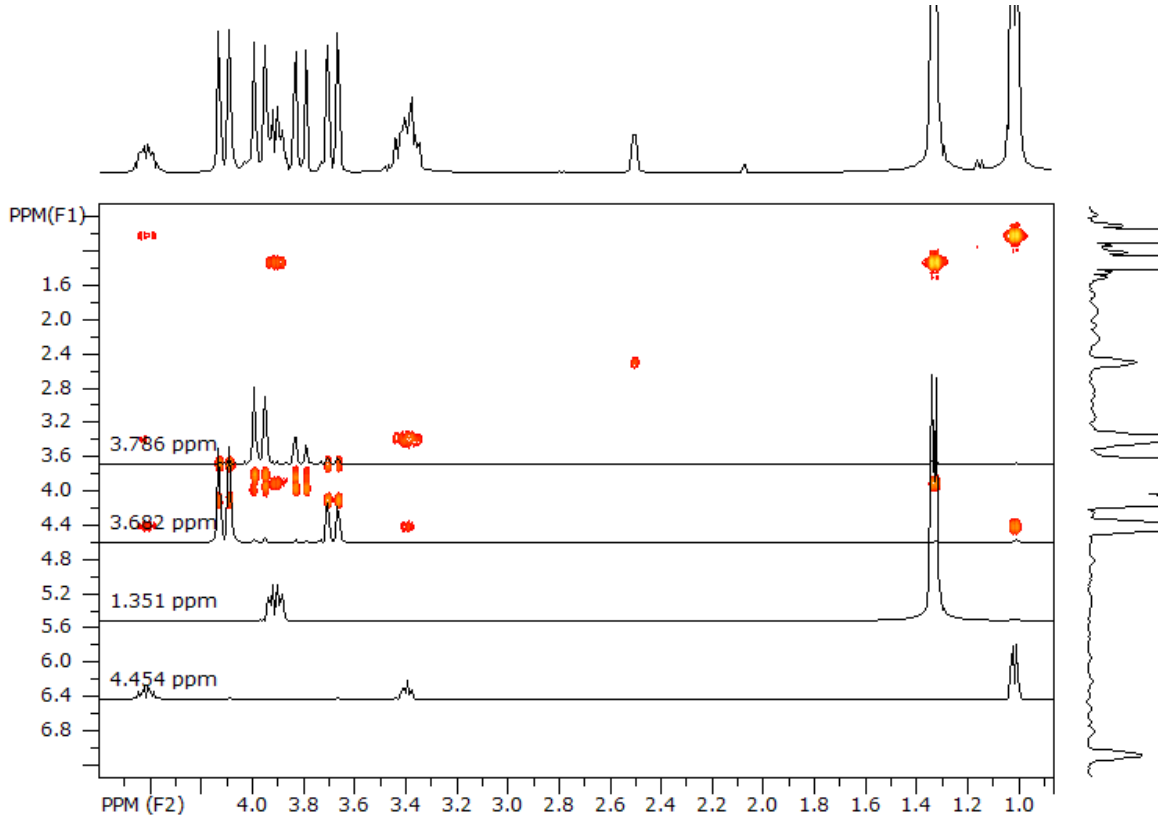


Figure S21: COSY of compound **4f**

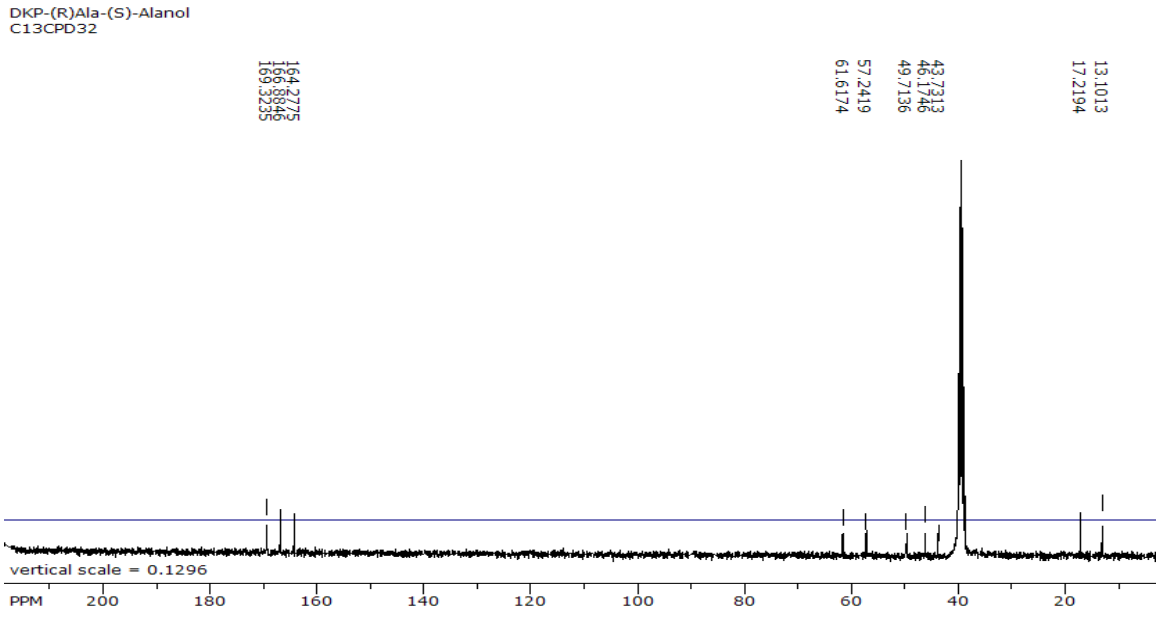


Figure S22: ^{13}C NMR of compound **4f**

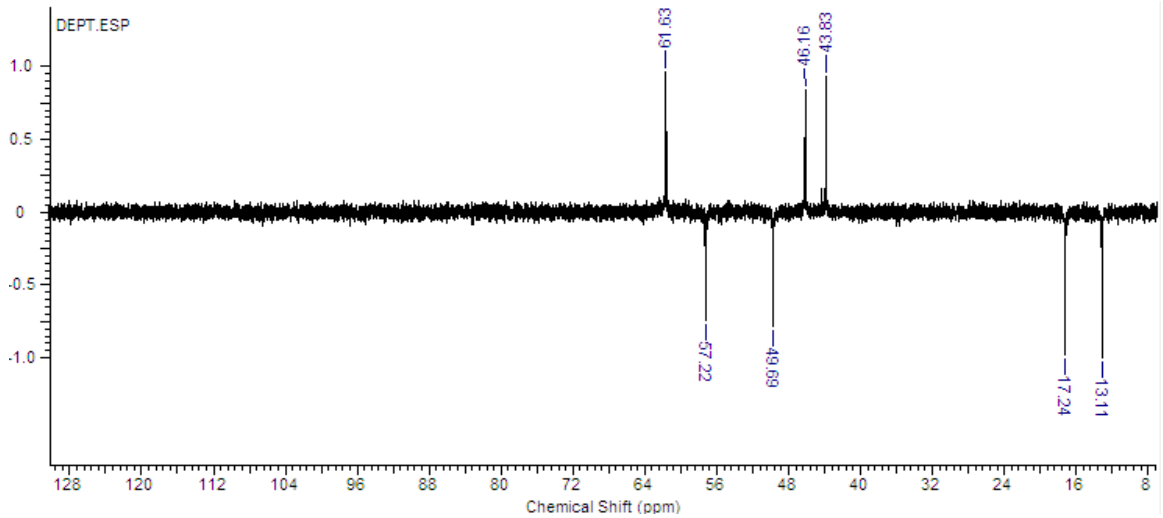


Figure S23: DEPT of compound **4f**

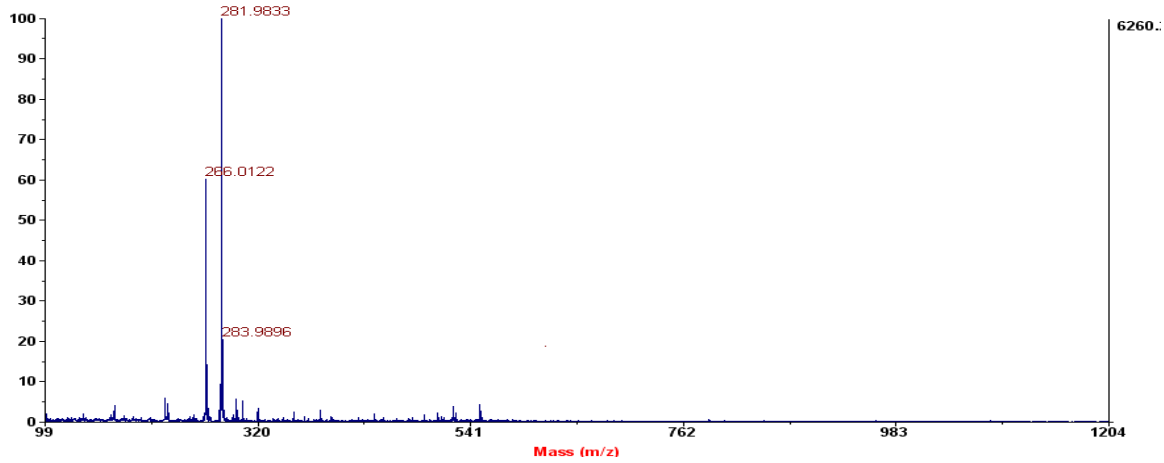


Figure S24: MALDI-TOF MS of compound **4f**

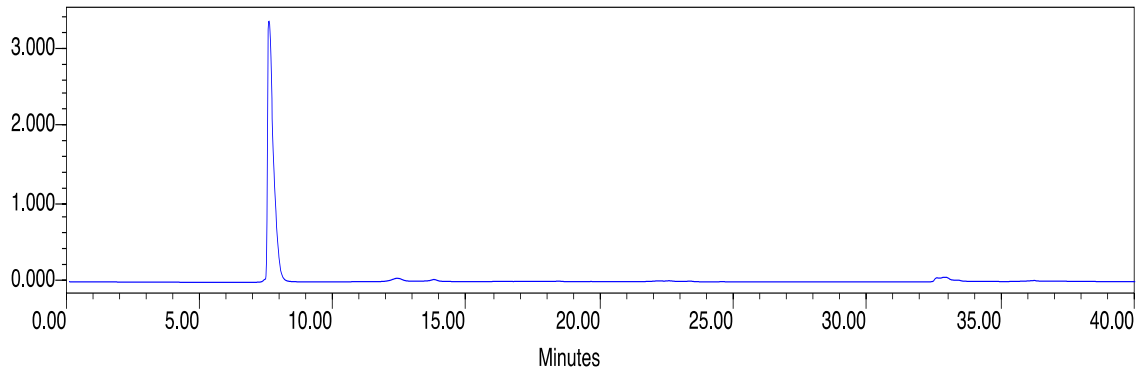
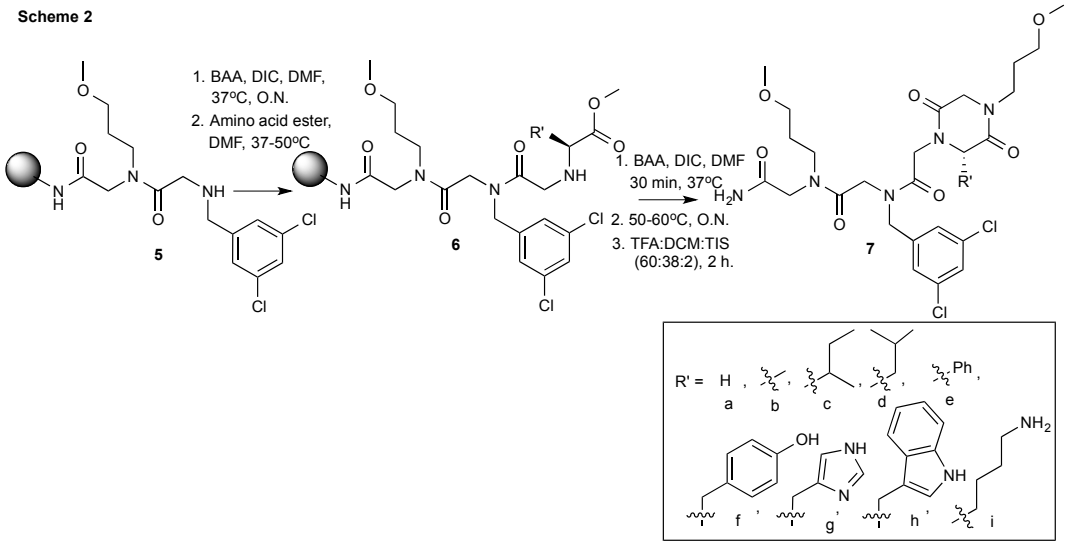


Figure S25: HPLC of compound **4f**

Solid phase synthesis protocol for 2,5-DKP containing analog utilized for purity test:



Rink amide MBHA resin (100 mg, 0.07 mmol) was swelled in DMF. After the fmoc group deprotection with 20% piperidine in DMF (2X, 15 mins), a dimer peptoid was synthesized by conventional peptoid synthesis protocol. Onto the resultant dimer additional bromoacetic acid was added and bromide was displaced by amino acid ester. The secondary amine was further coupled with DIC activated bromoacetic acid at 37°C (2X, 15 min). The bromide was displaced primary amine (2 M) in DMF at 37°C, 1 h. To afford DKP, the reaction mixture was further incubated at 50°C overnight. Completion of the reaction was confirmed by Chloranil test. The compound thus obtained was further attempted for chain extension with DIC activated BAA followed by displacement with primary amine. At this stage, the bead was acid-cleaved and subjected for HPLC to test the purity of DKP formation. HPLC fractions were subjected for MALDI-TOF analysis to confirm the presence of desired molecule.

DKP-Gly:

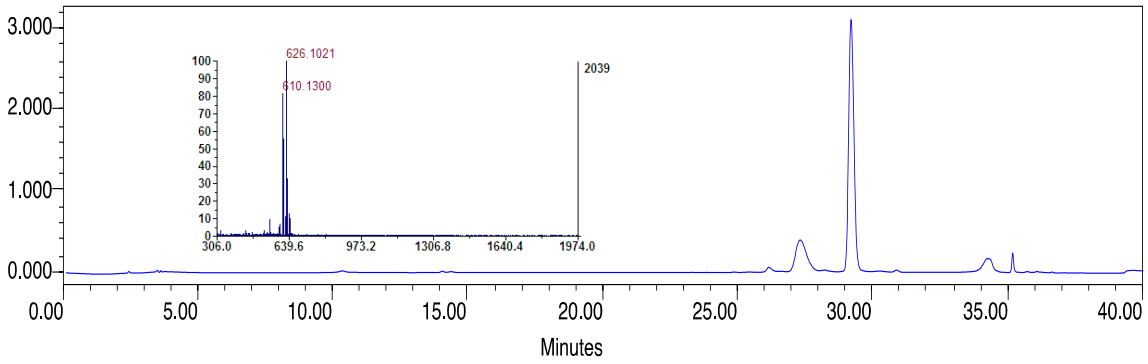


Figure S26: HPLC of **7a** showing retention time at 5 min. with MALDI-TOF (in the middle) showing the molecular mass after the purification.

DKP-Ala:

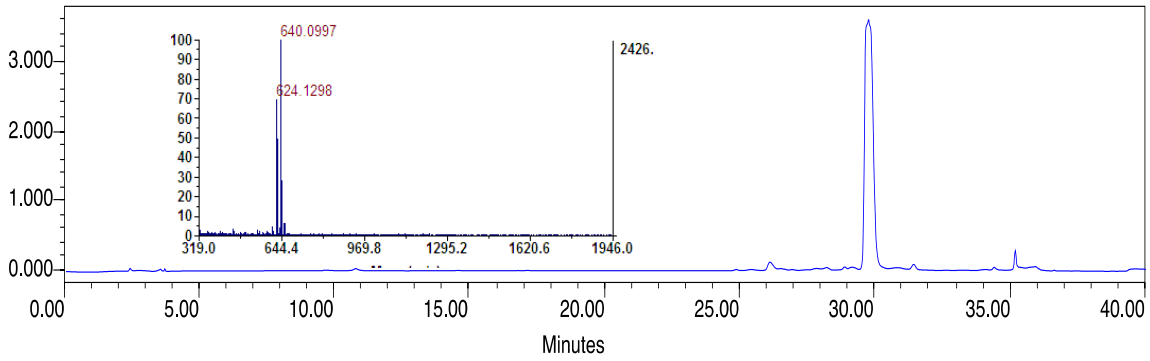


Figure S27: HPLC of **7b** showing retention time at 5 min. with MALDI-TOF (in the middle) showing the molecular mass after the purification.

DKP-Ileu:

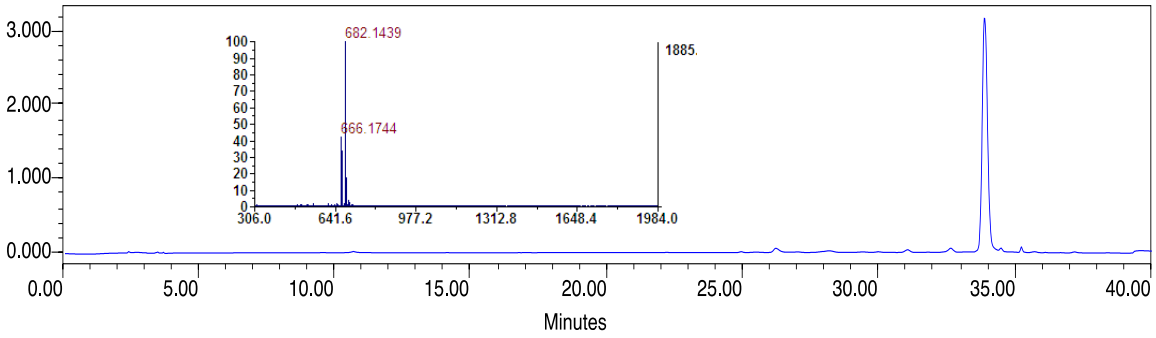


Figure S28: HPLC of **7c** showing retention time at 5 min. with MALDI-TOF (in the middle) showing the molecular mass after the purification.

DKP-Leu:

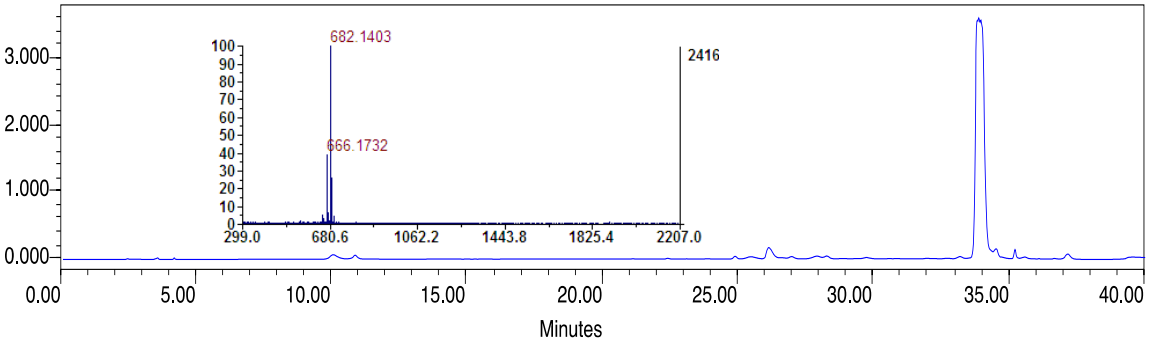


Figure S29: HPLC of **7d** showing retention time at 5 min. with MALDI-TOF (in the middle) showing the molecular mass after the purification.

DKP-PhGly:

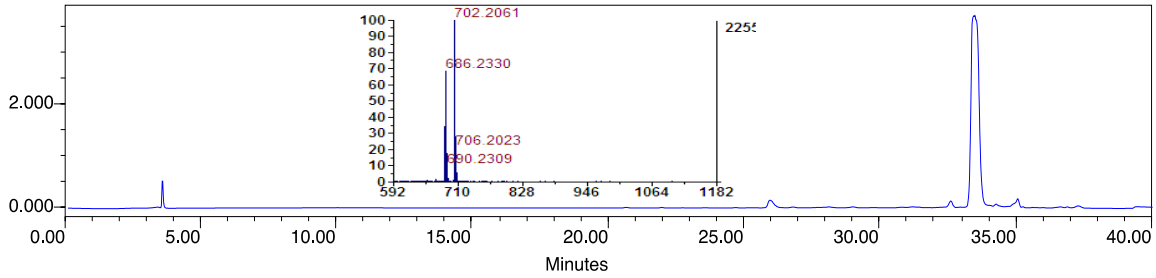


Figure S30: HPLC of **7e** showing retention time at 35 min. with MALDI-TOF (in the middle) showing the molecular mass after the purification.

DKP-Tyr:

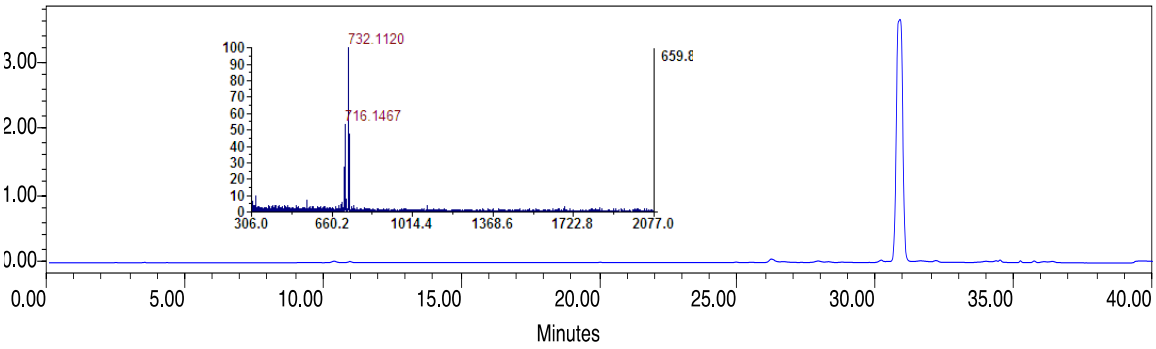


Figure S31: HPLC of **7f** showing retention time at 5 min. with MALDI-TOF (in the middle) showing the molecular mass after the purification.

DKP-His:

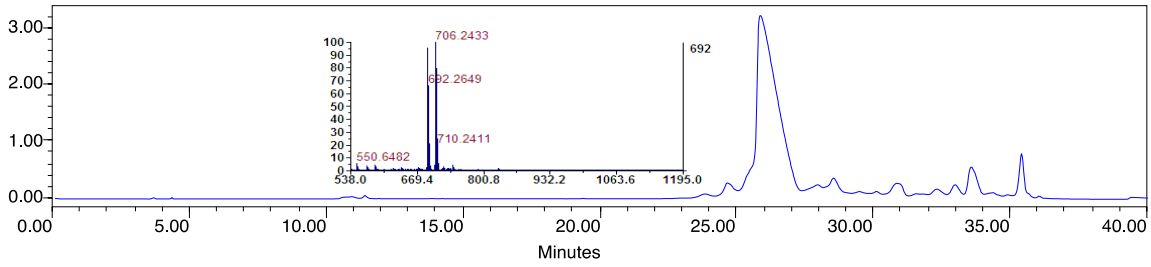


Figure S32: HPLC of **7g** showing retention time at 26 min. with MALDI-TOF (in the middle) showing the molecular mass after the purification.

DKP-Trp

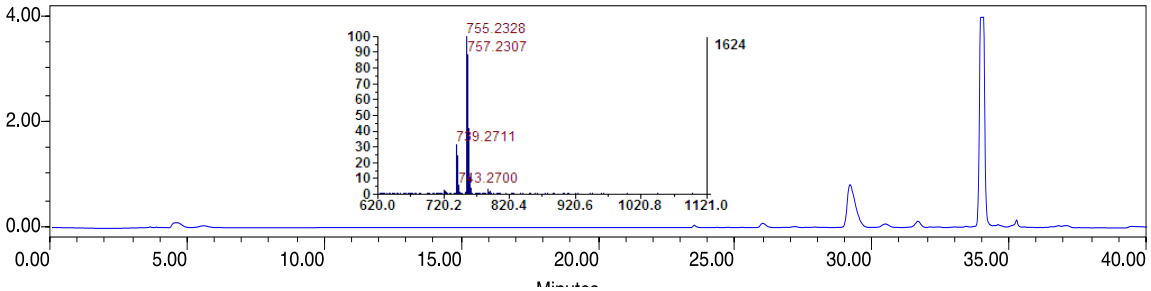


Figure S33: HPLC of **7h** showing retention time at 35 min. with MALDI-TOF (in the middle) showing the molecular mass after the purification

DKP-Lys

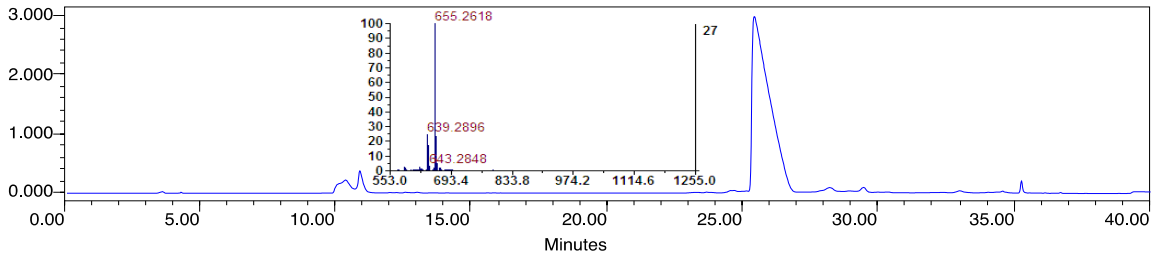


Figure S34: HPLC of **7i** showing retention time at 26 min. with MALDI-TOF (in the middle) showing the molecular mass after the purification.

HPLC and MALD-TOF with MS/MS data of few compounds that are used to test the feasibility and purity for chain extension purpose. In these particular examples alloc group was utilized as a protecting group instead of tboc- group. The alloc-group was deprotected as explained in our previous paper (*Org. Biomol. Chem.*, 2013, **11**, 2088-209**).**

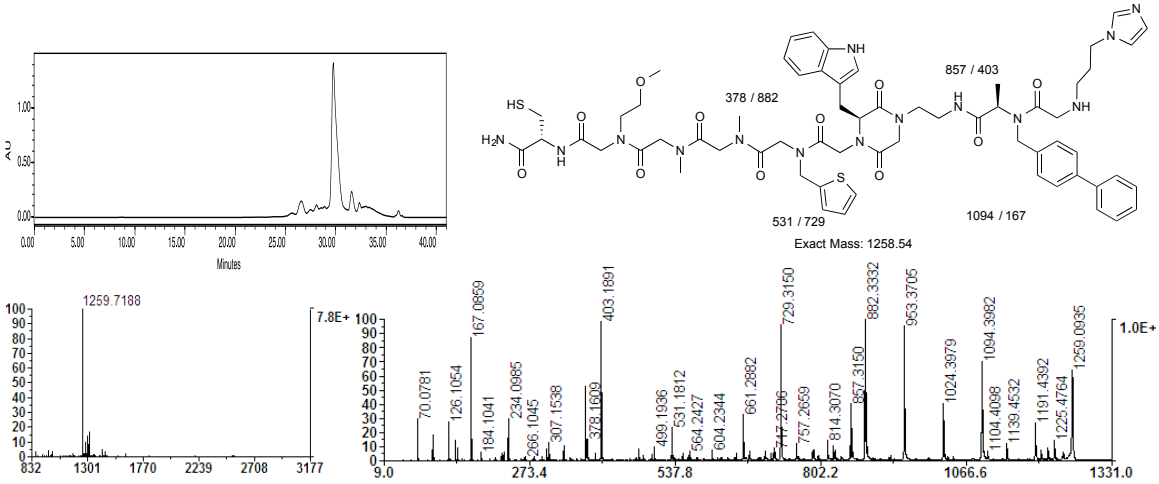


Figure S35: Top: MALDI-MS data showing parent peak (left) of peptoid (right). Bottom: MALDI-TOF MS/MS of the compound.

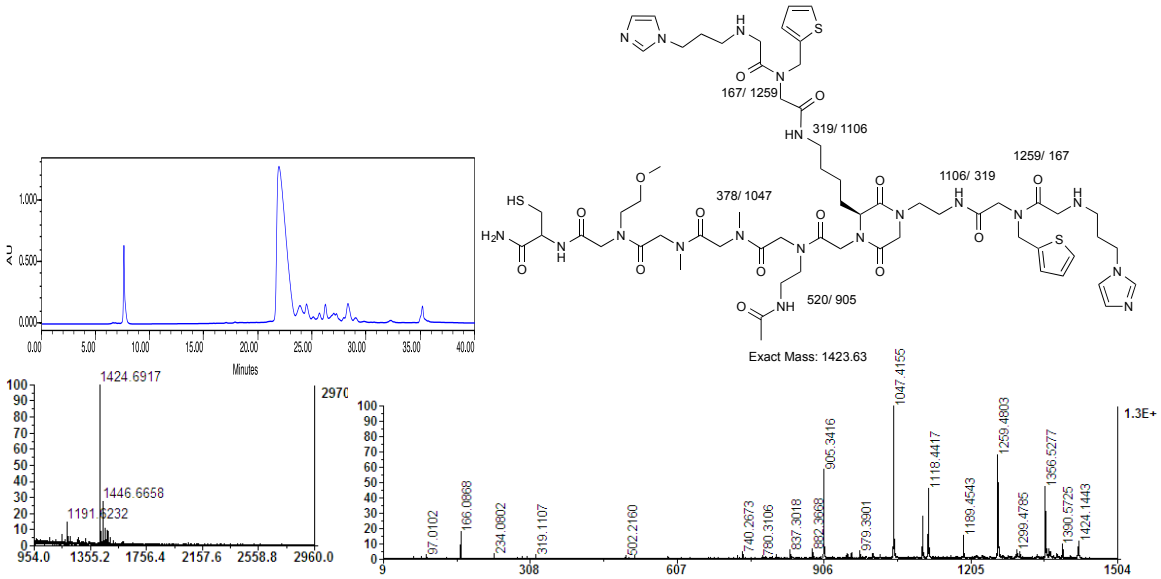


Figure S36: Top: MALDI-MS data showing parent peak (left) of peptoid (right). Bottom: MALDI-TOF MS/MS of the compound.

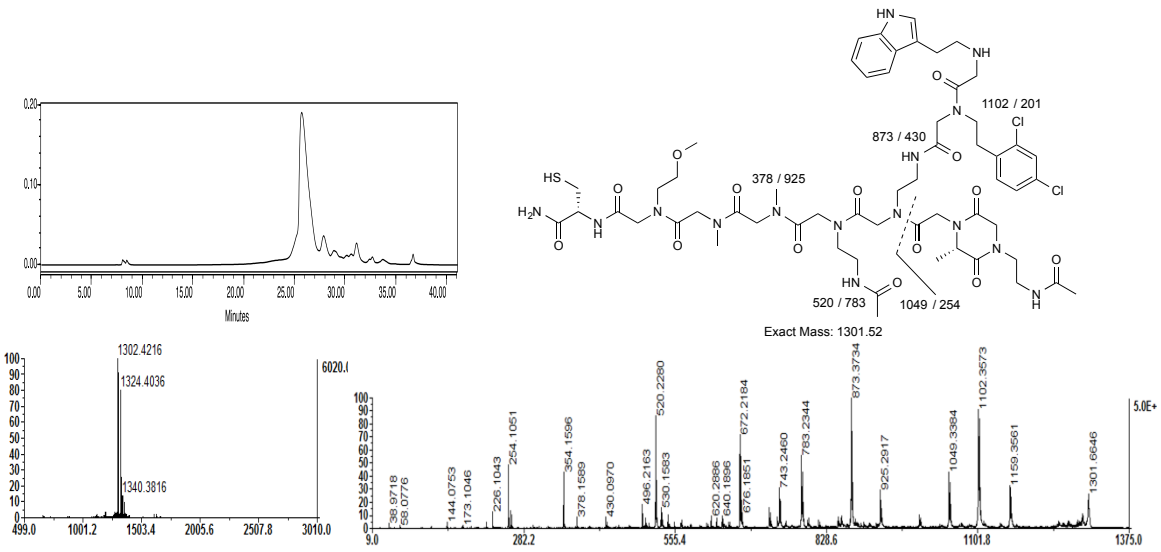


Figure S37: Top: MALDI-MS data showing parent peak (left) of peptoid (right). Bottom: MALDI-TOF MS/MS of the compound.

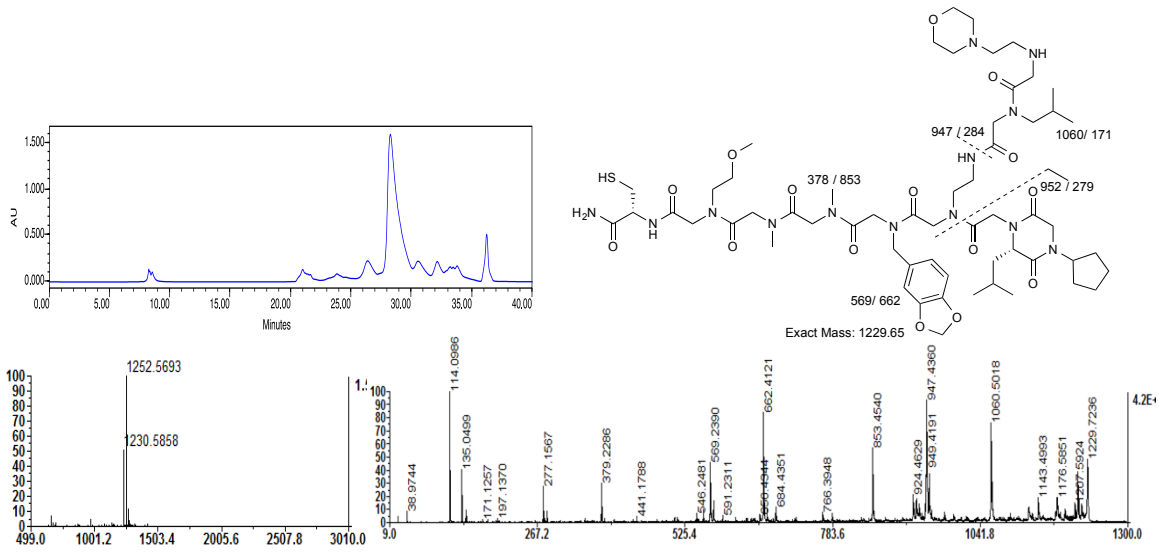


Figure S38: Top: MALDI-MS data showing parent peak (left) of peptoid (right). Bottom: MALDI-TOF MS/MS of the compound.

HPLC and MALD-TOF with MS/MS data of few compounds that resembles DKP-hybrid compound library.

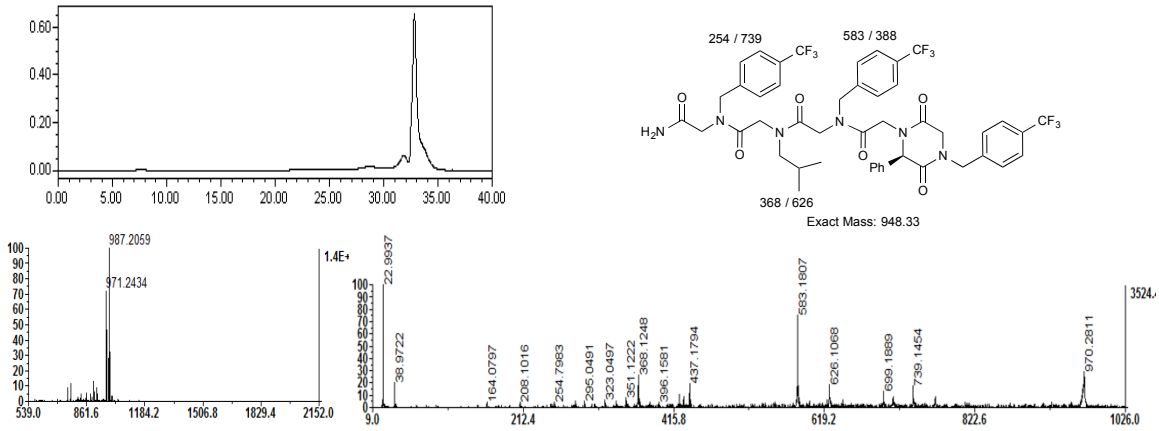


Figure S39: Top: MALDI-MS data showing parent peak (left) of peptoid (right). Bottom: MALDI-TOF MS/MS of the compound

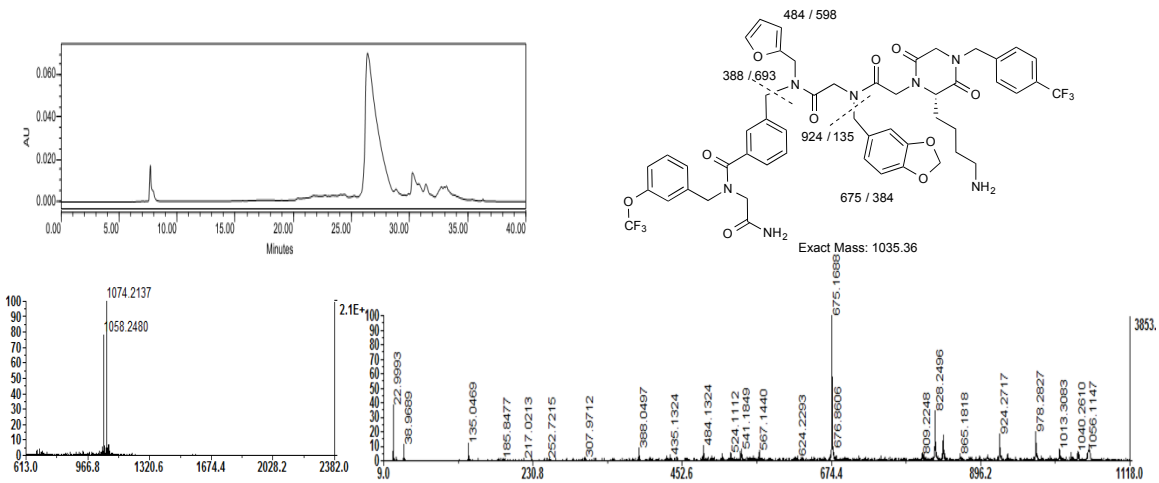


Figure S40: Top: MALDI-MS data showing parent peak (left) of peptoid (right). Bottom: MALDI-TOF MS/MS of the compound.

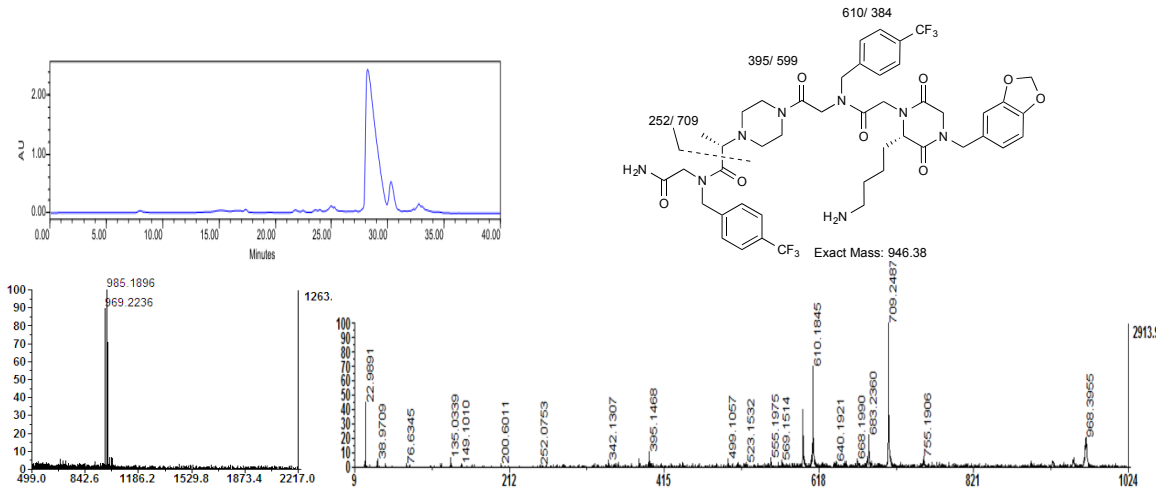


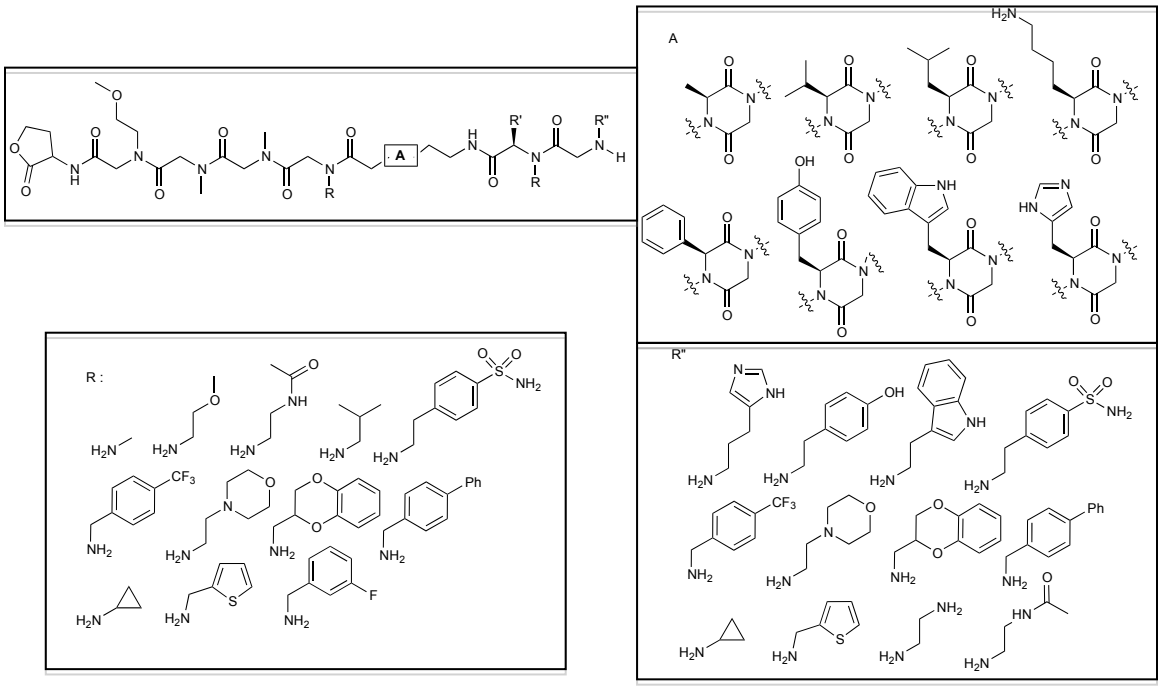
Figure S41: Top: MALDI-MS data showing parent peak (left) of peptoid (right). Bottom: MALDI-TOF MS/MS of the compound.

Protocol for peptoid library construction:

DKP-Backbone library:

Tentagel MB NH_2 (0.5 g, initial loading 0.4 mmol/g) was soaked in DMF for 30 min, RT. The beads were coupled with fmoc-methionine (5X) activated with N,N,N′,N′-Tetramethyl-O-(1H- benzotriazol-1-yl)uronium hexafluorophosphate (HBTU) (5X), N-Hydroxybenzotriazole (HOBt) (8X) and Diisopropyl ethylamine (DIEA) (10x) in DMF. Mixture was incubated 3 h at room temperature. Fmoc-group was deprotected using 20% piperidine in DMF. Resultant primary amine was treated with BAA/DIC and the bromide was displaced with methoxyethylamine under microwave condition. Likewise, methylamine was added as additional two monomers to represent a linker region. The

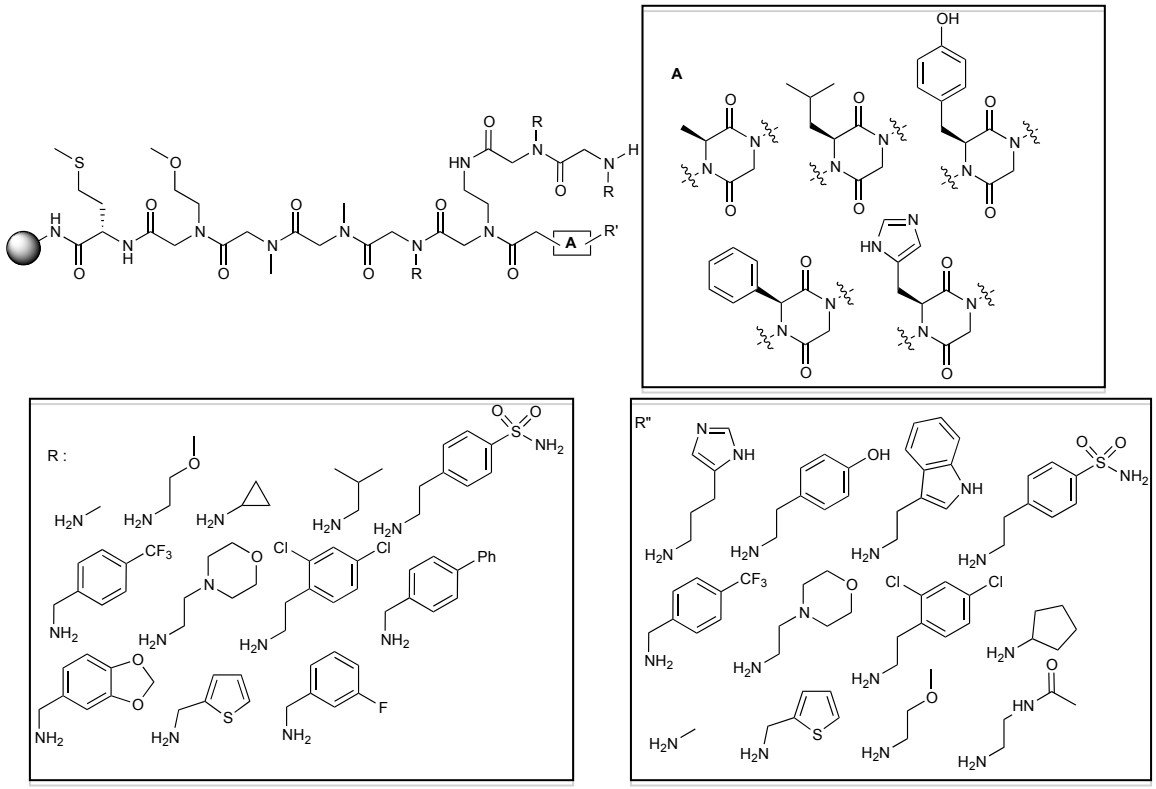
main chain 2,5-DKP containing peptoid oligomer library (~ 40 K diversity) was created utilizing 12 different commercially available primary amines along with 8 different 2,5-DKP moieties. As a first unit of peptoid library, BAA/DIC was coupled to the secondary amine from the linker. The solid support was split into 12 different fractions after the beads were washed with DMF (5X) and DCM (5X). Each portion of the beads was separately treated with different primary amines (2M) to displace the bromide under microwave condition. The beads were washed as explained above. Resultant secondary amines were pooled and coupled with BAA/DIC. The beads were washed and split into 8 different vessels and treated them separately with amino acid esters. After additional round of BAA/DIC coupling, tboc-protected ethylenediamine was used to displace the bromide. The reaction mixture was incubated 50-60^{o}C, 24h to afford 2,5-DKP formation. T-boc group was deprotected by 50% TFA in DCM. The resultant primary amine was separated into two halves and coupled with DIC-activated BAA or (S)-2-bromopropionic acid separately. The bromides were pooled and split into 12 different fractions and displaced individually by primary amines (R'). Finally a peptoid oligomer library with 2,5-DKP in the main-chain was finally completed by final round to BAA/DIC coupling and bromide displacement with different sets of 12 primary amines (R", Scheme Sch2).



DKP-Side-chain library:

The linker region and the first diversity unit in DKP-side-chain library were created as in the case of DKP-backbone library. After the first diversity element, the chain extension was carried out coupling with BAA/DIC followed by mono-N-tboc-ethylenediamine, as a later point of chain-extension as a side-chain. The secondary amine on the other hand was coupled with BAA and the solid support was split into 5 different reaction vessels. Each vessel was separately treated with amino acid ester. Beads were pooled and split into 8

fractions and treated individually with 8 different primary amines. At this stage the reaction mixture was subjected for 2,5-DKP ring formation under basic thermal condition as explained above. Once the cyclization was completed, the t-boc group was deprotected utilizing 50% TFA in DCM. Two additional peptoid monomers were added from the resultant primary amine utilizing conventional peptoid synthesis method via split and pool method.



DKP-terminated hybrid peptidomimetic library:
The linker region and the first diversity unit in DKP-side-chain library were created as in the case of DKP-backbone library. The solid support was divided into 16 different vessels. In order to incorporate variety of diversity element at the second diversity element, following processes were executed,

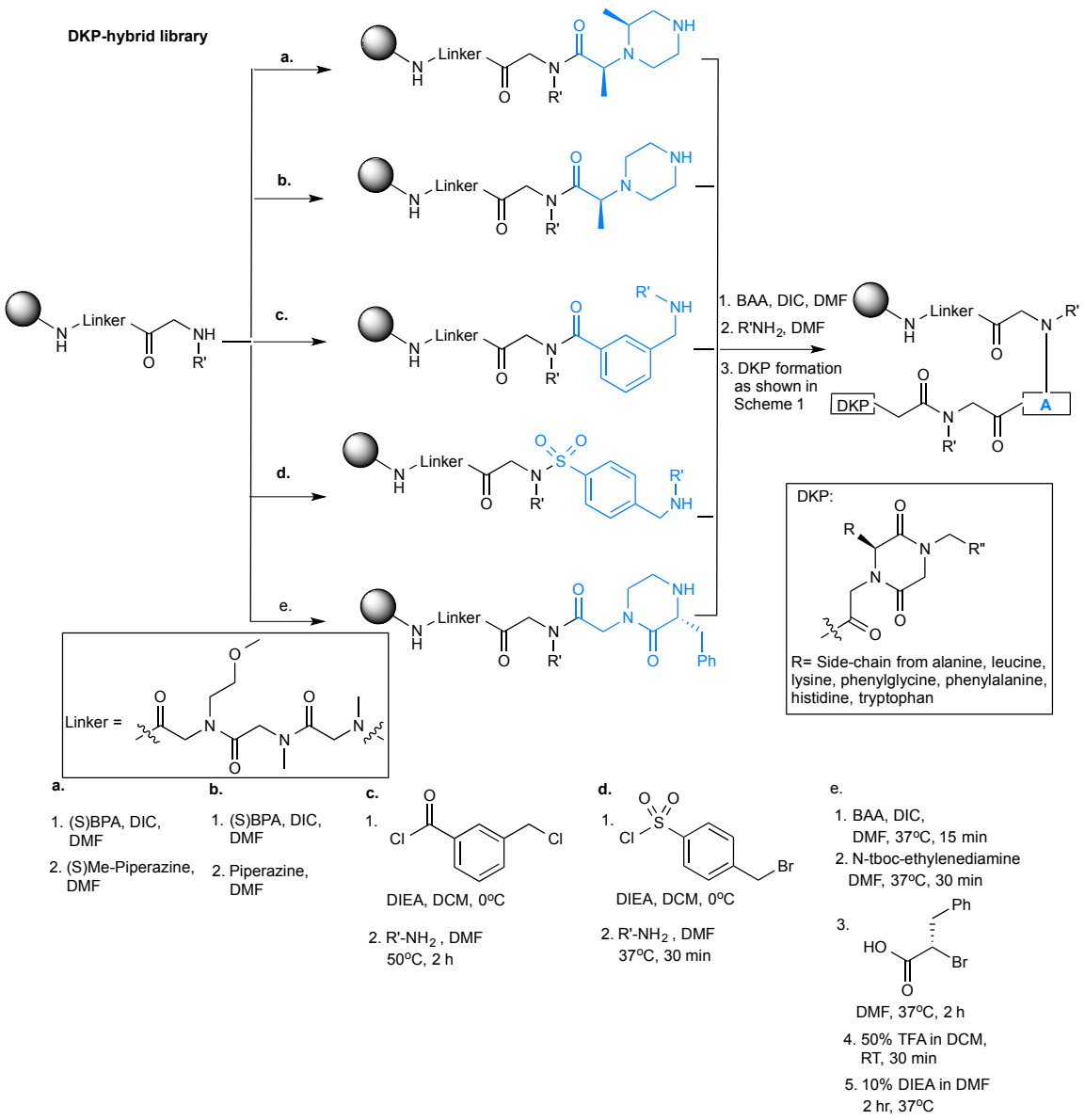
1. Out of 16, two of the fractions were separately coupled with DIC activated (S)-2-bromopropionic acid and separately treated with either mono-N-tboc-piperazine or (S)-4-N-Boc-2-methylpiperazine at 50^{o}C, O.N. The t-boc group was deprotected using 50% TFA in DCM prior to third diversity element was incorporated.

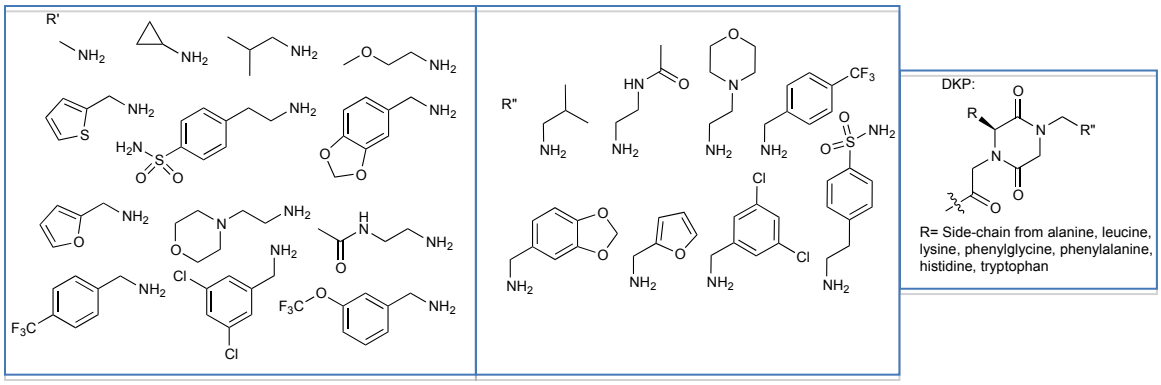
2. One portion out of remaining fractions was coupled with BAA/DIC and bromide was displaced with N-mono-t-boc-ethylenediamine. The secondary amine was coupled with DIC activated (S)-2-bromo-3-phenyl-propionic acid. t-boc group was acid-deprotected and the reaction mixture was incubated under 10% DIEA overnight to afford cyclization to afford 2-oxopiperazine unit.

3. Remaining portion of the beads were divided into two fractions after pooling. Each

fraction was equilibrated in DCM and treated directly either with 3-chloromethyl benzoyl chloride (10X) or with 4-bromomethyl phenylsulfonyl chloride in DCM (5 mL). A solution of triethylamine (12X) in DCM (5 mL) was slowly added in the acid chloride solution at 0^{o}C. The reaction mixture was brought into the room temperature and allowed to stand for 3 hr. Each vessel was separately washed with DCM several times, pooled together and split into 13 different fractions. The halides were incubated with 13 different amines (R') separately at 37^{o}C, 3 hr.

After completion of above explained syntheses, all 16 vessels were pooled and coupled with BAA/DIC. The beads were further split into 13 portion and treated with 13 primary amines separately (R'), 37^{o}C, 1 h. Finally, library synthesis was accomplished by incorporating 2,5-DKP as a capping group. The formation of DKP was performed as explained above. At the terminal position, 56 different 2,5-DKPs as capping groups were generated with 7 different amino acid esters and 8 different primary amines.


DKP-hybrid library
a.
b.
c.
d.
e.
Linker
1. BAA, DIC, DMF
2. R'NH2, DMF
3. DKP formation as shown in Scheme 1
DKP
A
DKP:
R= Side-chain from alanine, leucine, lysine, phenylglycine, phenylalanine, histidine, tryptophan
Linker =
a.
1. (S)BPA, DIC, DMF
2. (S)Me-Piperazine, DMF
b.
1. (S)BPA, DIC, DMF
2. Piperazine, DMF
c.
1.
DIEA, DCM, 0°C
2. R'-NH2 , DMF 50°C, 2 h
d.
1.
DIEA, DCM, 0°C
2. R'-NH2 , DMF 37°C, 30 min
e.
1. BAA, DIC, DMF, 37°C, 15 min
2. N-tboc-ethylenediamine DMF, 37°C, 30 min
3.
DMF, 37°C, 2 h
4. 50% TFA in DCM, RT, 30 min
5. 10% DIEA in DMF 2 hr, 37°C



Following are the structures of peptoids from DKP-backbone library, identifed after CNBr mediated cleavage from the resins and subsequent MALDI – MS and MS/MS analyses. Each figure has a peptoid structure showing the mass of corresponding y and b fragments at particular substituent observed during Collision-Induced Dissociation (CID) of the parent peak:

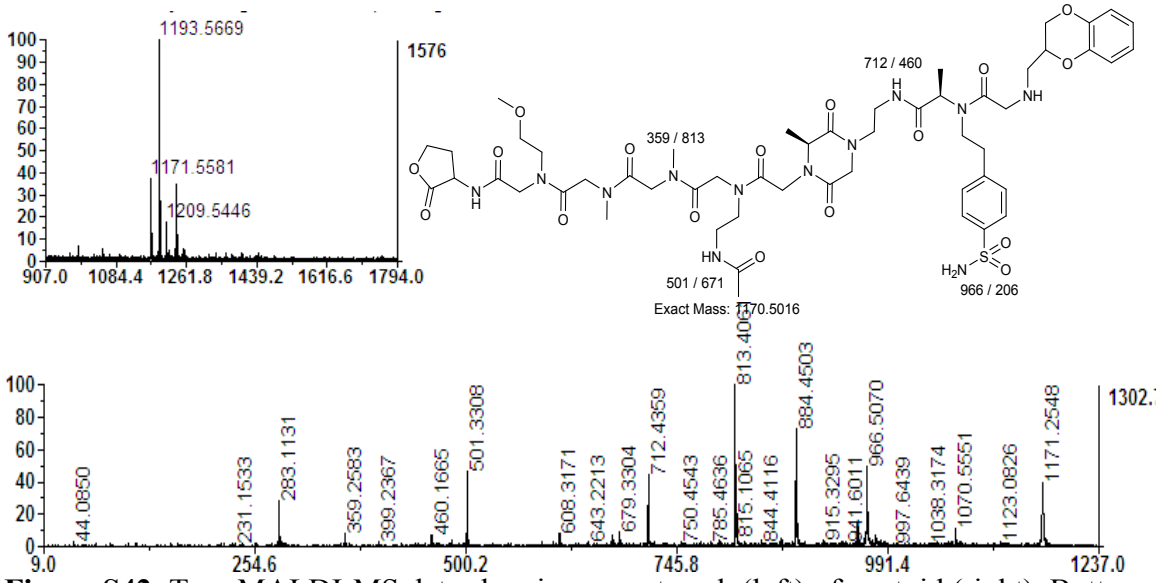


Figure S42: Top: MALDI-MS data showing parent peak (left) of peptoid (right). Bottom: MALDI-TOF MS/MS of the compound

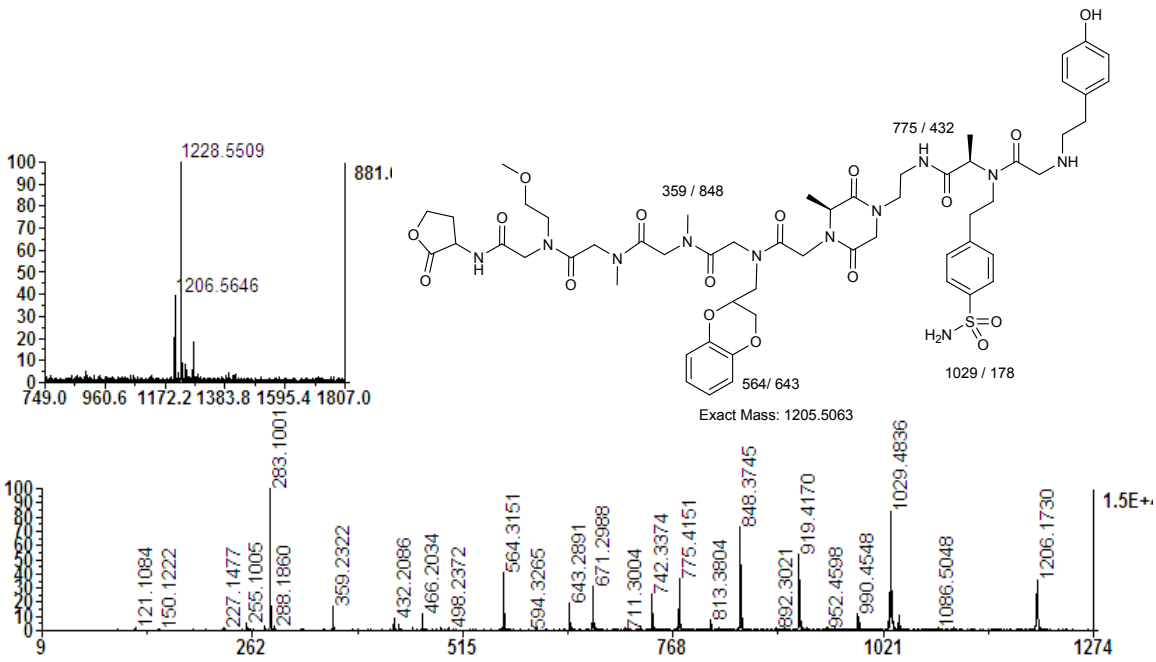


Figure S43: Top: MALDI-MS data showing parent peak (left) of peptoid (right). Bottom: MALDI-TOF MS/MS of the compound

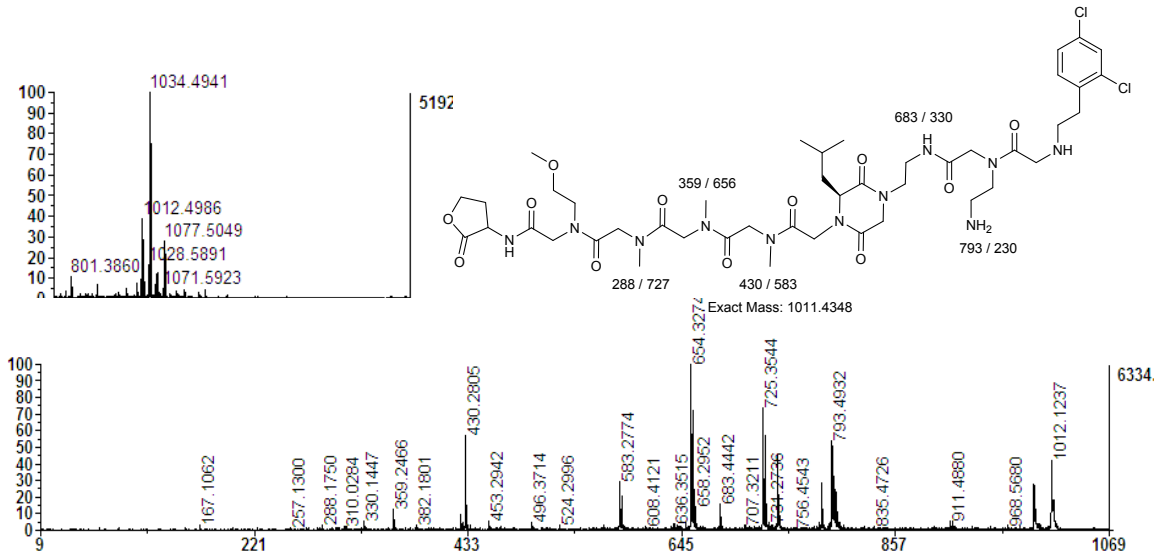


Figure S44: Top: MALDI-MS data showing parent peak (left) of peptoid (right). Bottom: MALDI-TOF MS/MS of the compound.

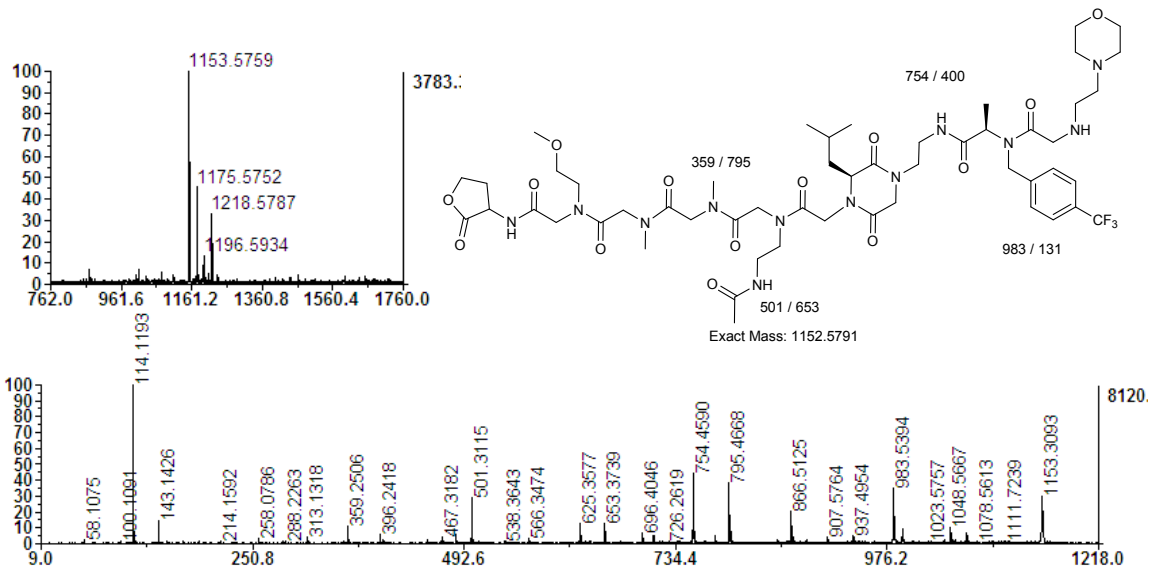


Figure S45: Top: MALDI-MS data showing parent peak (left) of peptoid (right). Bottom: MALDI-TOF MS/MS of the compound.

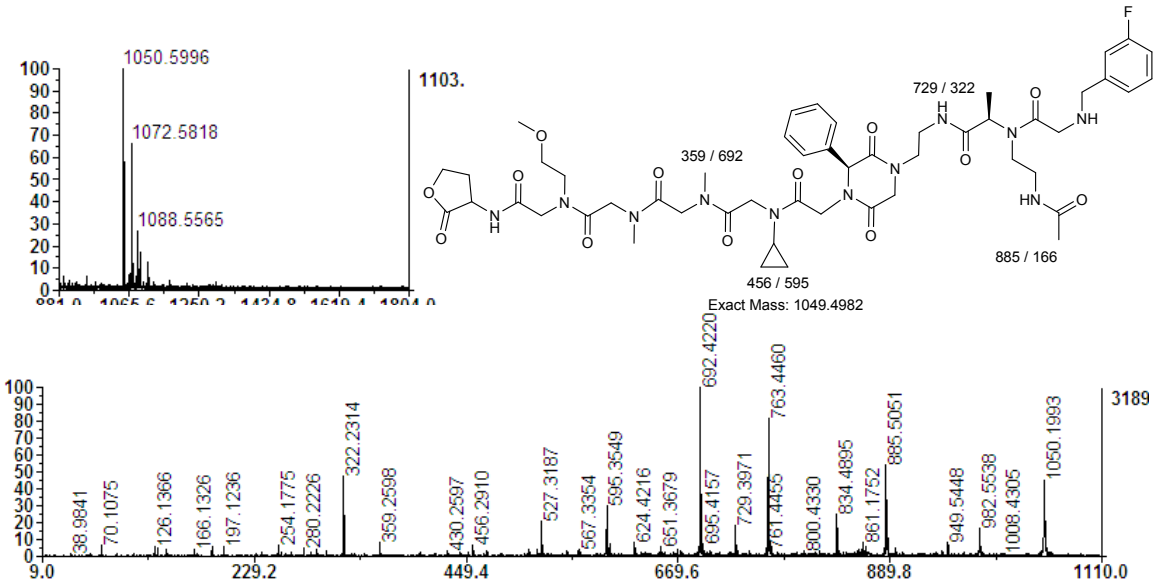


Figure S46: Top: MALDI-MS data showing parent peak (left) of peptoid (right). Bottom: MALDI-TOF MS/MS of the compound.

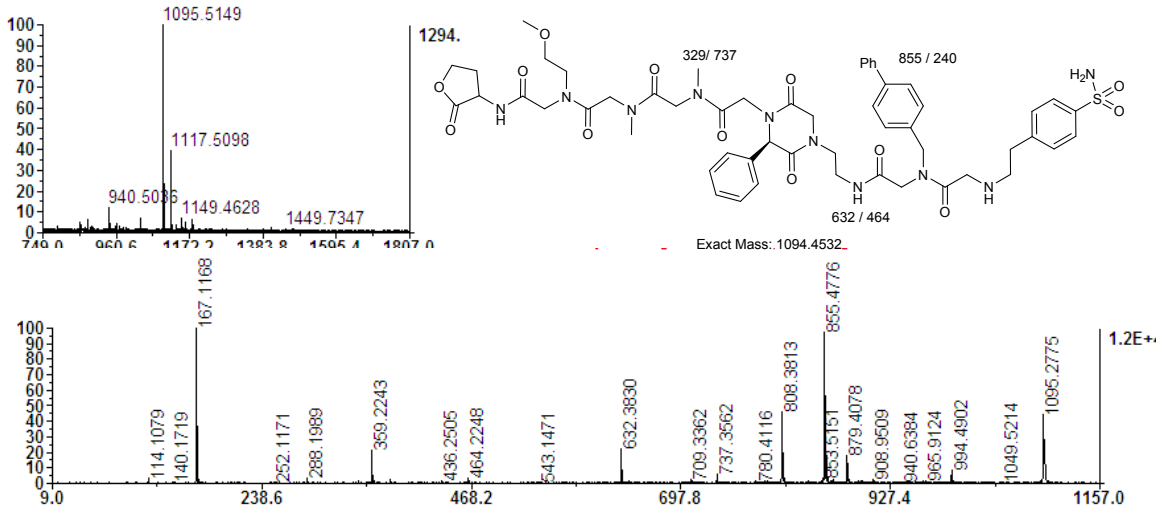


Figure S47: Top: MALDI-MS data showing parent peak (left) of peptoid (right). Bottom: MALDI-TOF MS/MS of the compound.

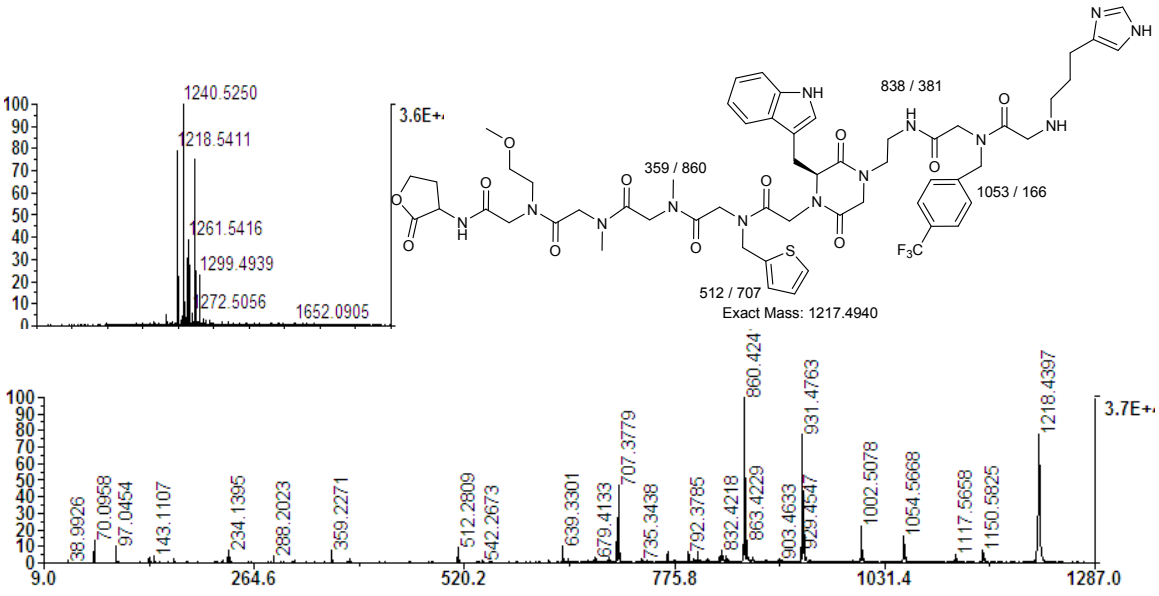


Figure S48: Top: MALDI-MS data showing parent peak (left) of peptoid (right). Bottom: MALDI-TOF MS/MS of the compound.

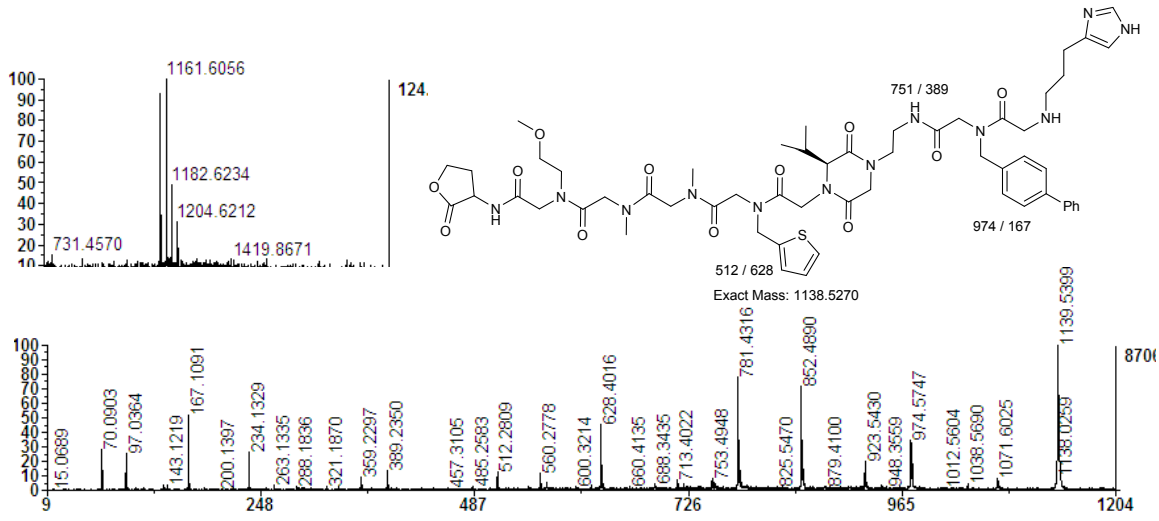


Figure S49: Top: MALDI-MS data showing parent peak (left) of peptoid (right). Bottom: MALDI-TOF MS/MS of the compound.

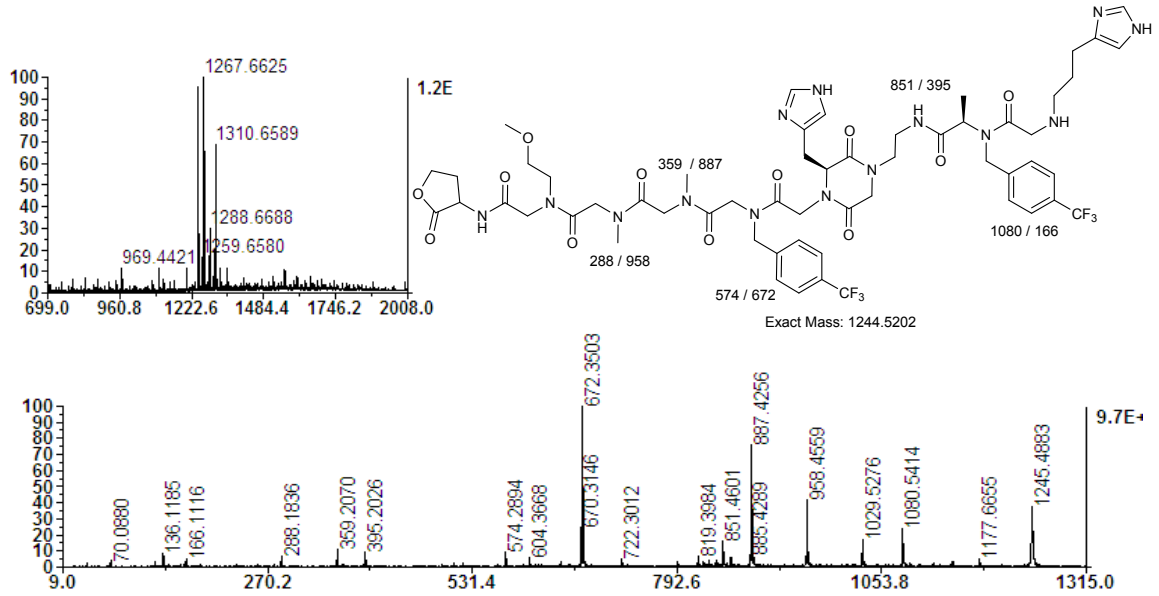


Figure S50: Top: MALDI-MS data showing parent peak (left) of peptoid (right). Bottom: MALDI-TOF MS/MS of the compound.

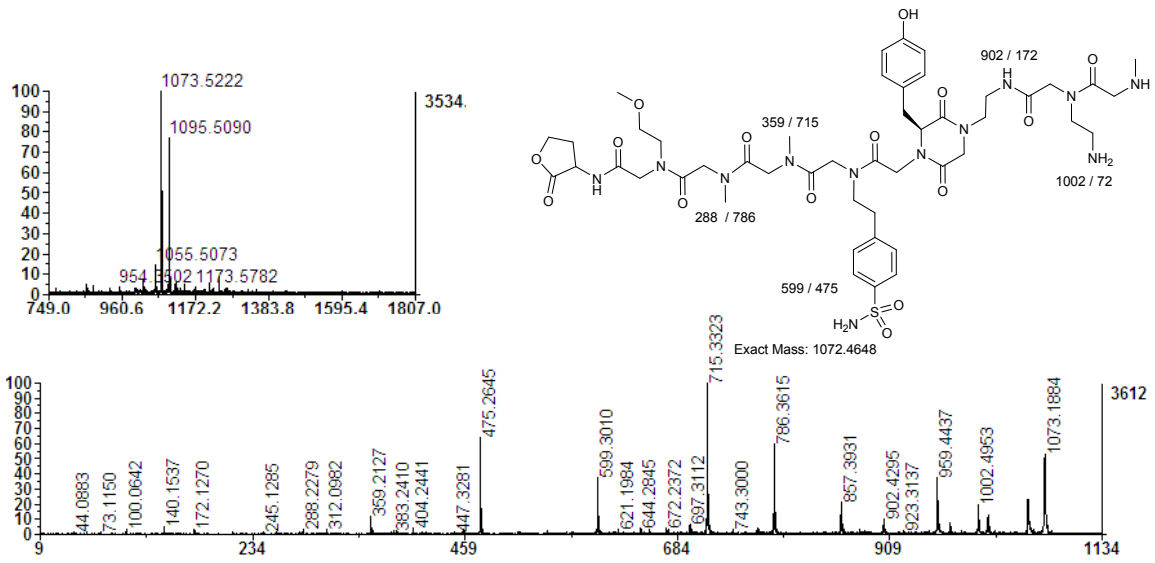


Figure S51: Top: MALDI-MS data showing parent peak (left) of peptoid (right). Bottom: MALDI-TOF MS/MS of the compound

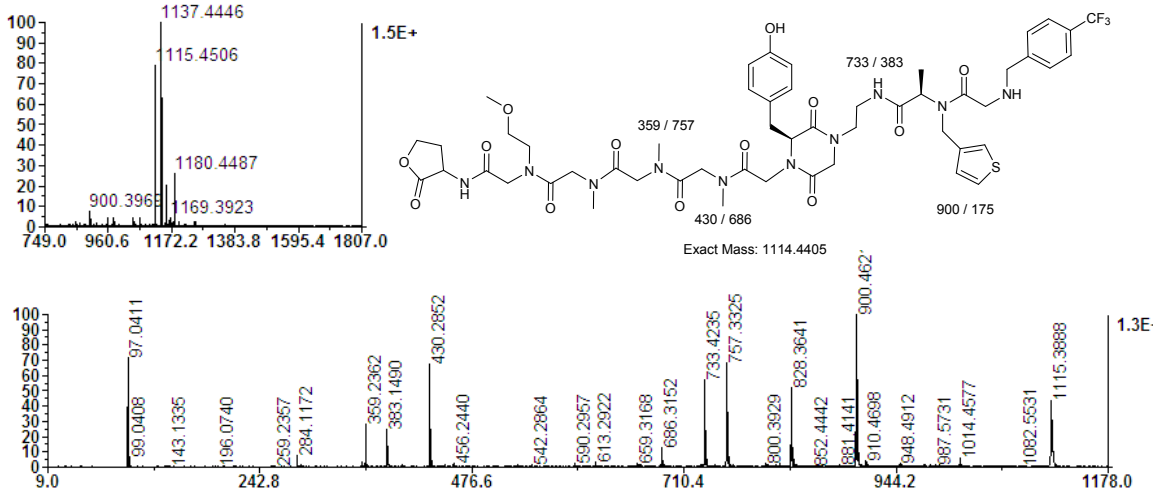


Figure S52: Top: MALDI-MS data showing parent peak (left) of peptoid (right). Bottom: MALDI-TOF MS/MS of the compound.

\

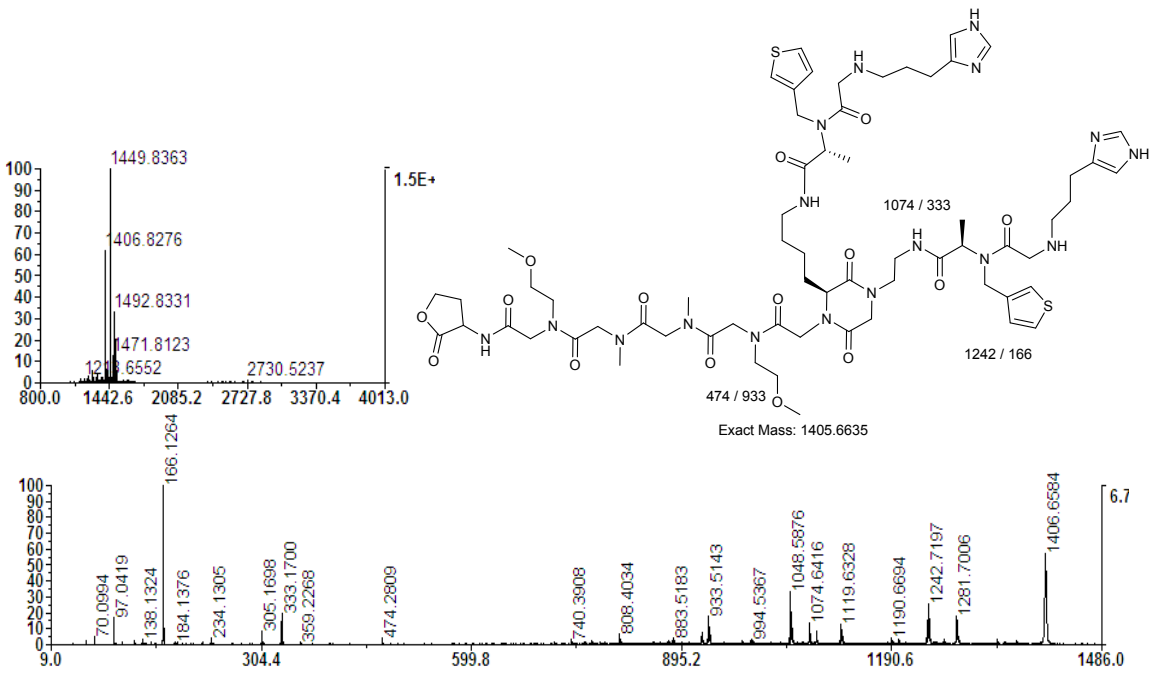


Figure S53: Top: MALDI-MS data showing parent peak (left) of peptoid (right). Bottom: MALDI-TOF MS/MS of the compound

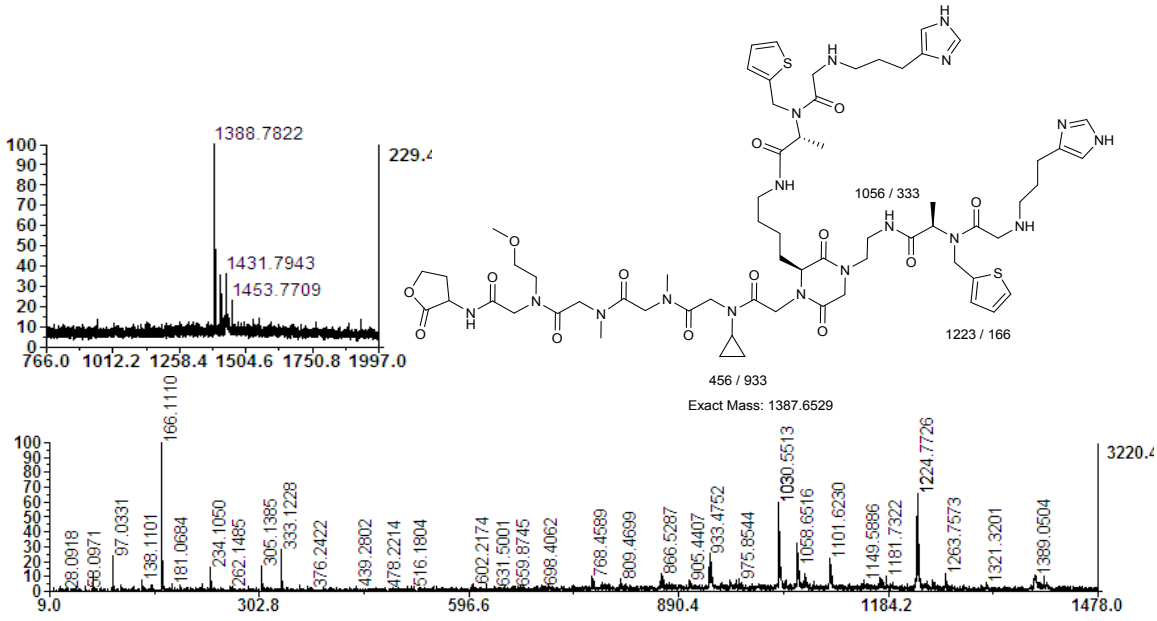


Figure S54: Top: MALDI-MS data showing parent peak (left) of peptoid (right). Bottom: MALDI-TOF MS/MS of the compound.

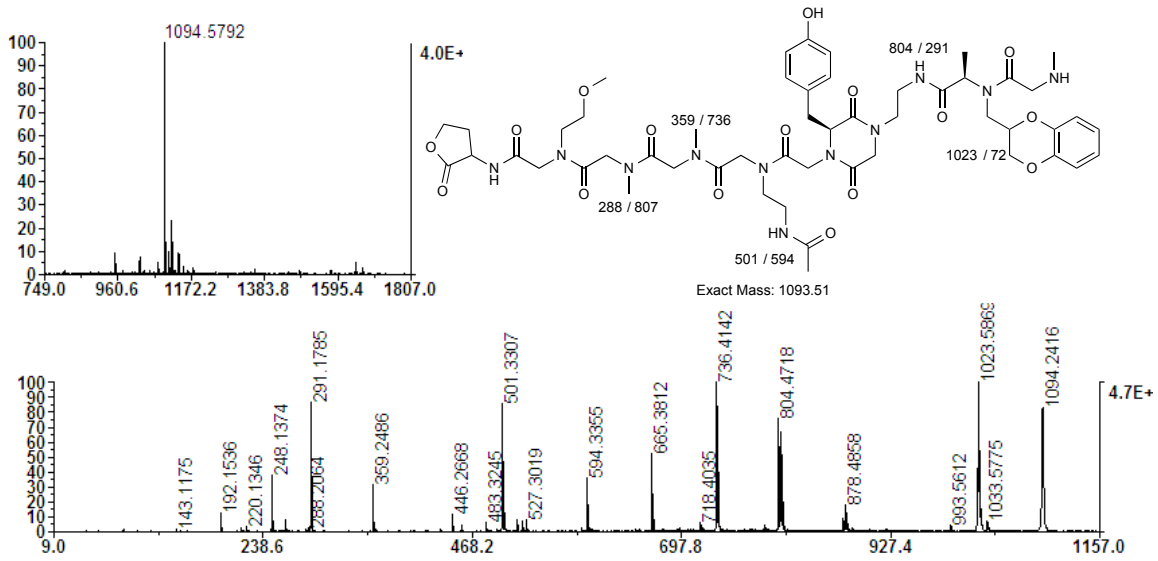


Figure S55: Top: MALDI-MS data showing parent peak (left) of peptoid (right). Bottom: MALDI-TOF MS/MS of the compound.

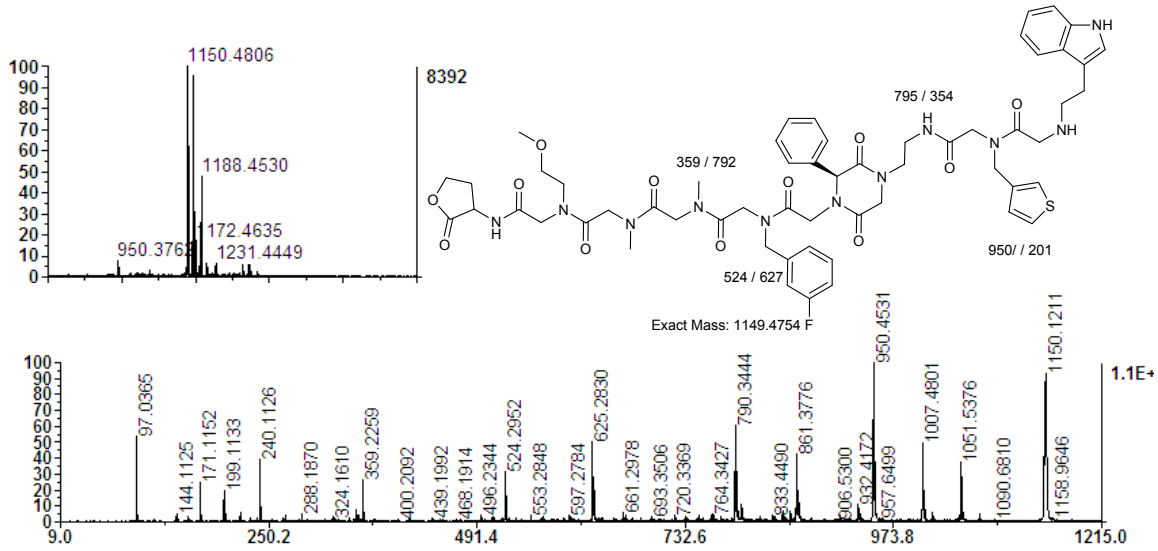


Figure S56: Top: MALDI-MS data showing parent peak (left) of peptoid (right). Bottom: MALDI-TOF MS/MS of the compound.

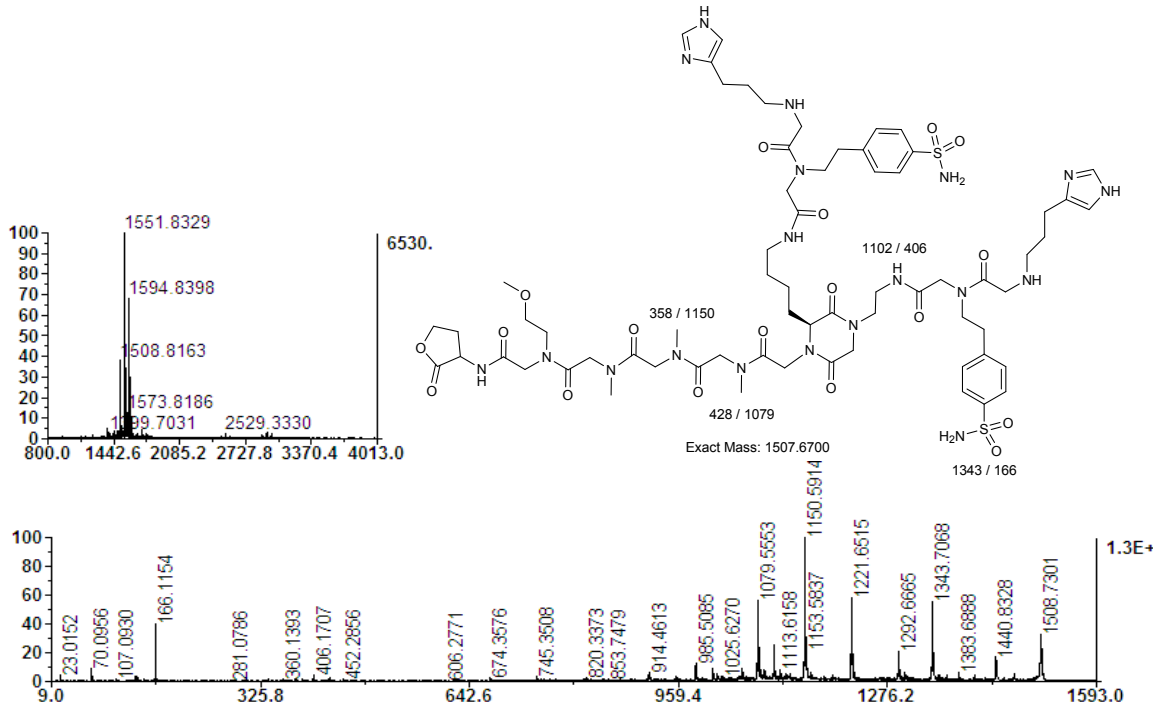


Figure S57: Top: MALDI-MS data showing parent peak (left) of peptoid (right). Bottom: MALDI-TOF MS/MS of the compound.

DKP-side chain library:

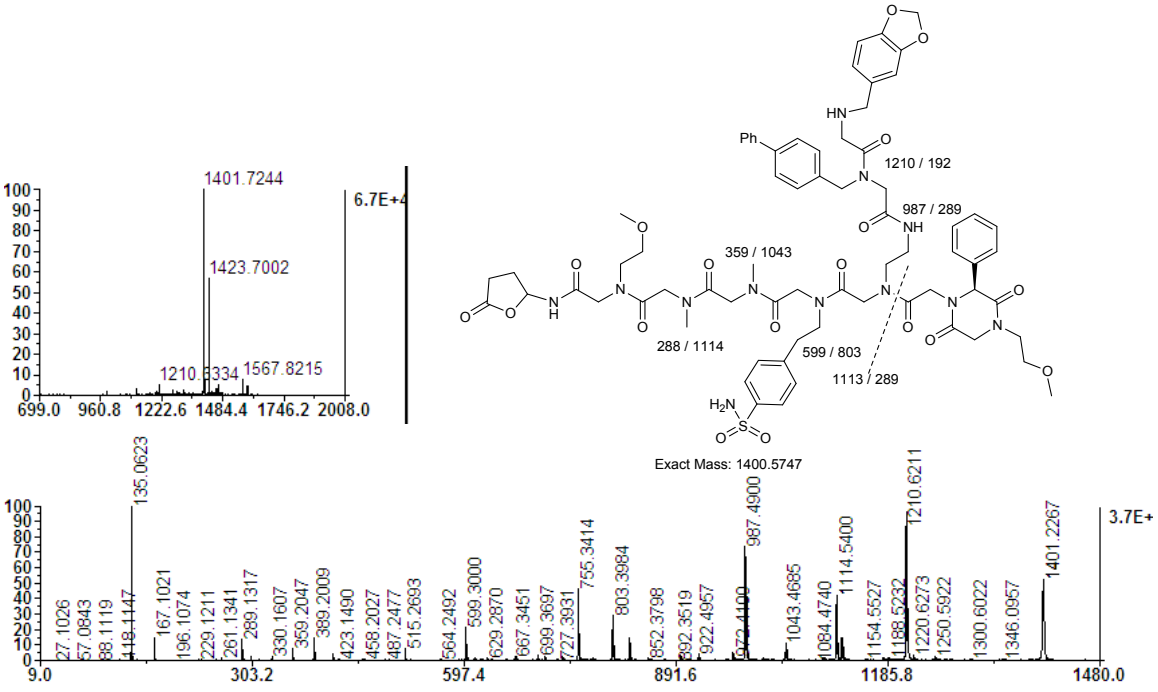


Figure S58: Top: MALDI-MS data showing parent peak (left) of peptoid (right). Bottom: MALDI-TOF MS/MS of the compound.

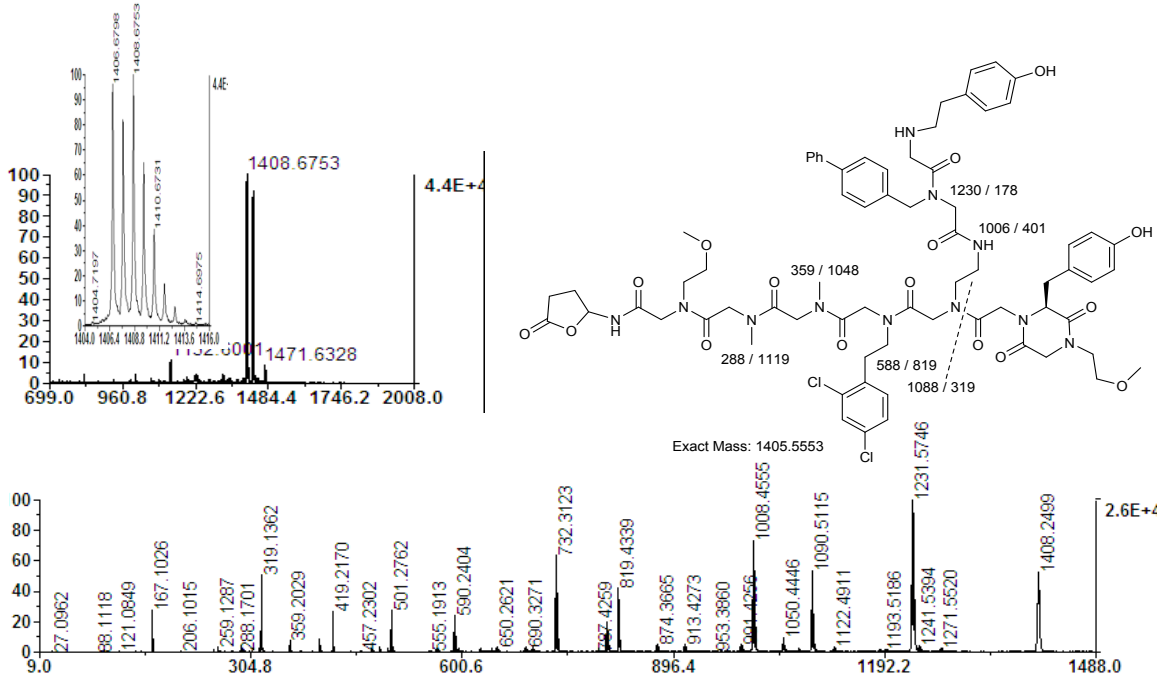


Figure S59: Top: MALDI-MS data showing parent peak (left) of peptoid (right). Bottom: MALDI-TOF MS/MS of the compound.

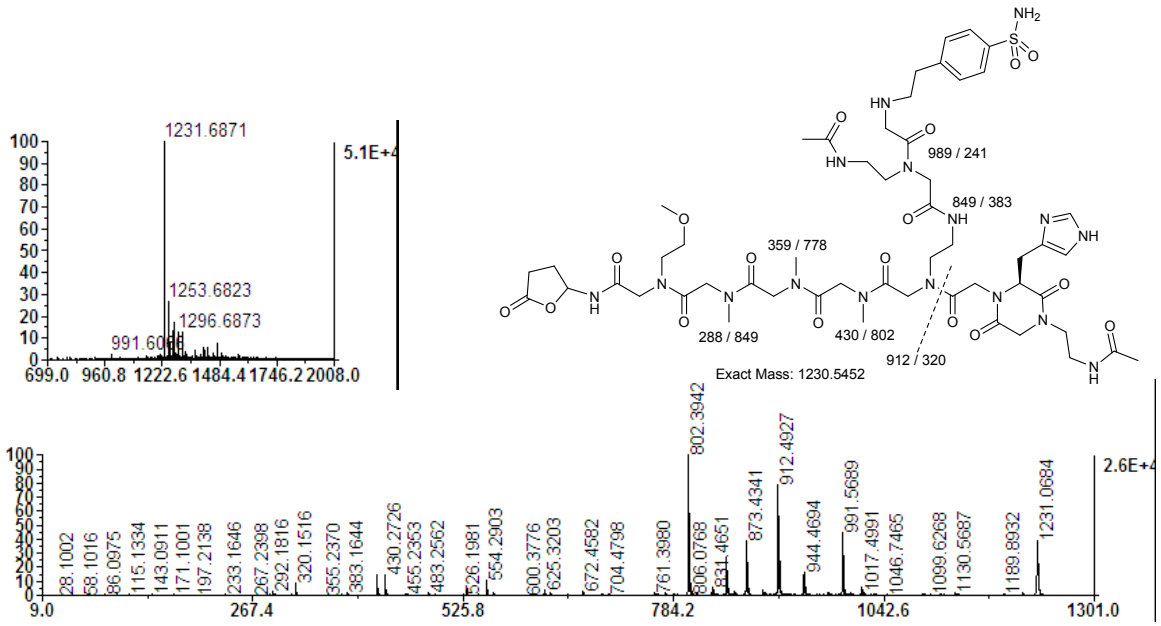


Figure S60: Top: MALDI-MS data showing parent peak (left) of peptoid (right). Bottom: MALDI-TOF MS/MS of the compound.

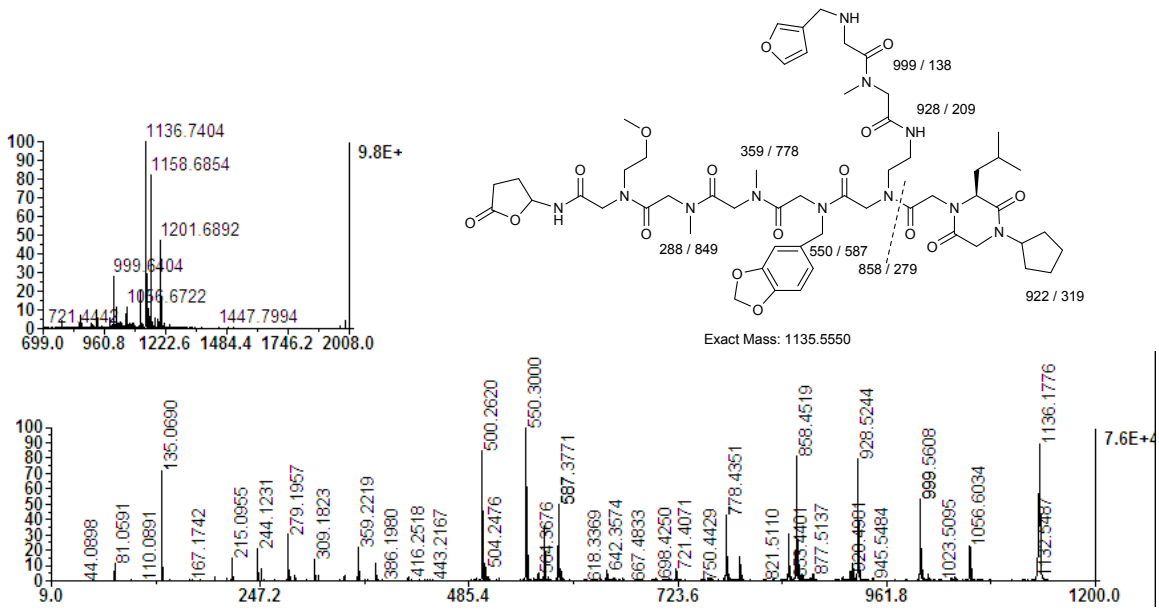


Figure S61: Top: MALDI-MS data showing parent peak (left) of peptoid (right). Bottom: MALDI-TOF MS/MS of the compound.

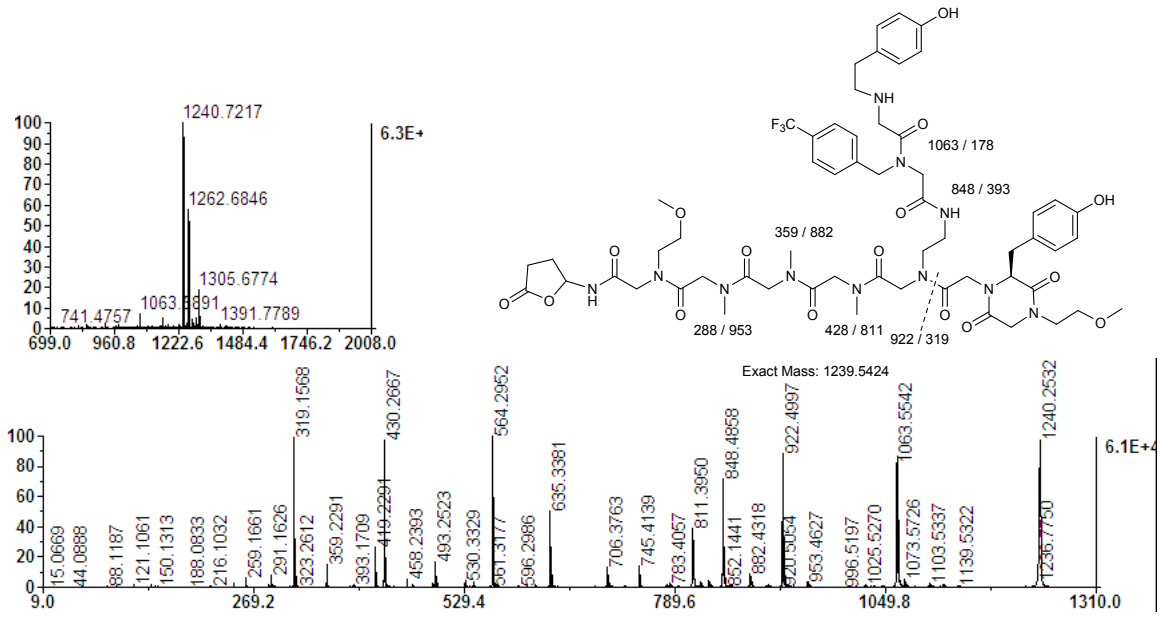


Figure S62: Top: MALDI-MS data showing parent peak (left) of peptoid (right). Bottom: MALDI-TOF MS/MS of the compound.

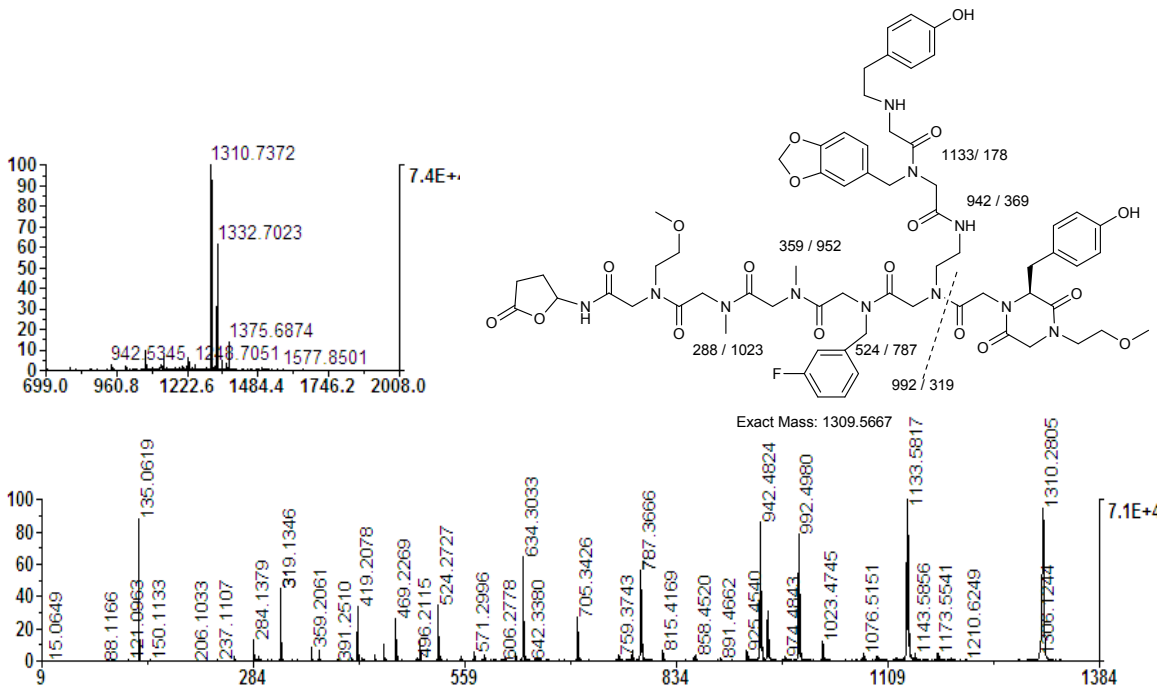


Figure S63: Top: MALDI-MS data showing parent peak (left) of peptoid (right). Bottom: MALDI-TOF MS/MS of the compound.

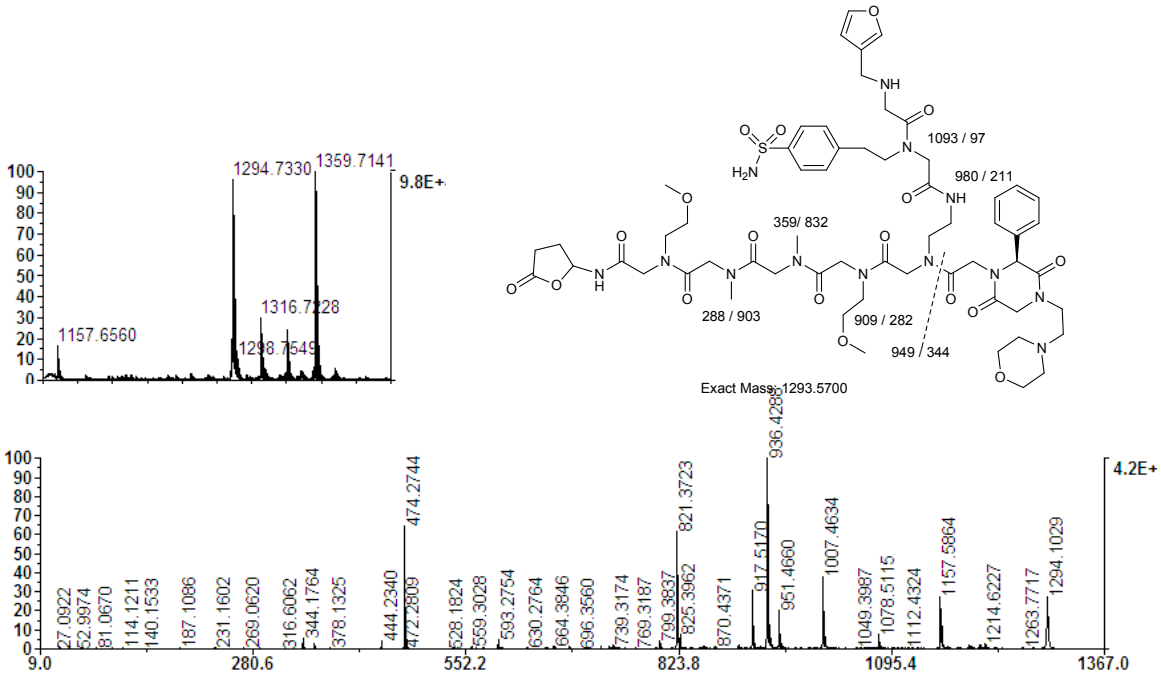


Figure S64: Top: MALDI-MS data showing parent peak (left) of peptoid (right). Bottom: MALDI-TOF MS/MS of the compound.

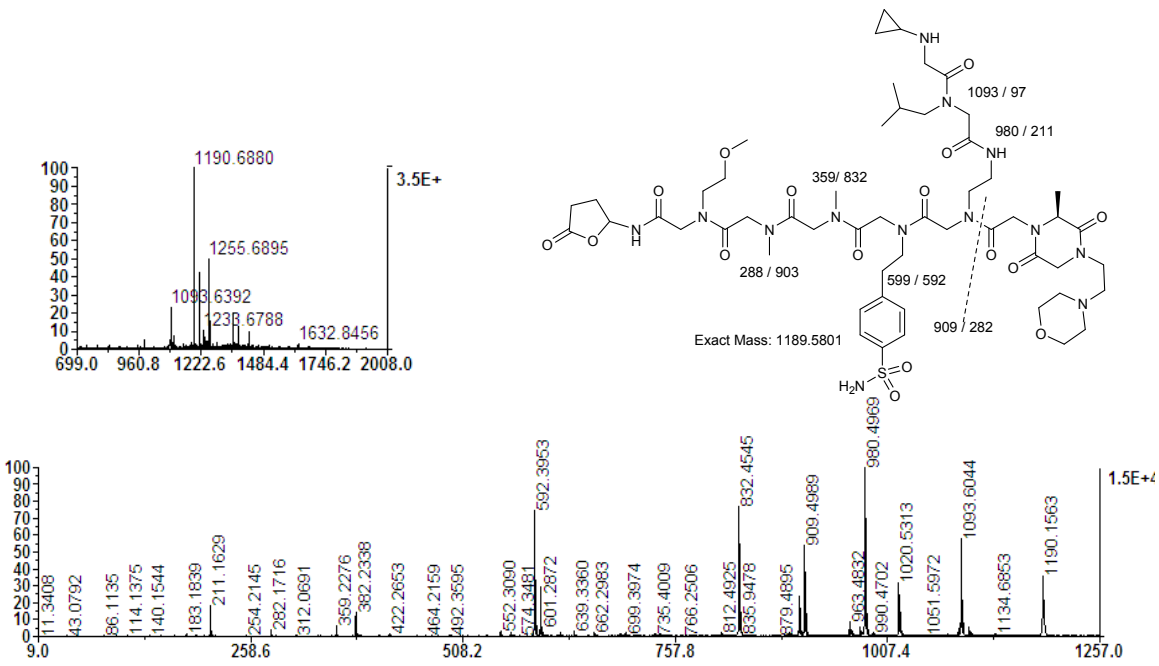


Figure S65: Top: MALDI-MS data showing parent peak (left) of peptoid (right). Bottom: MALDI-TOF MS/MS of the compound.

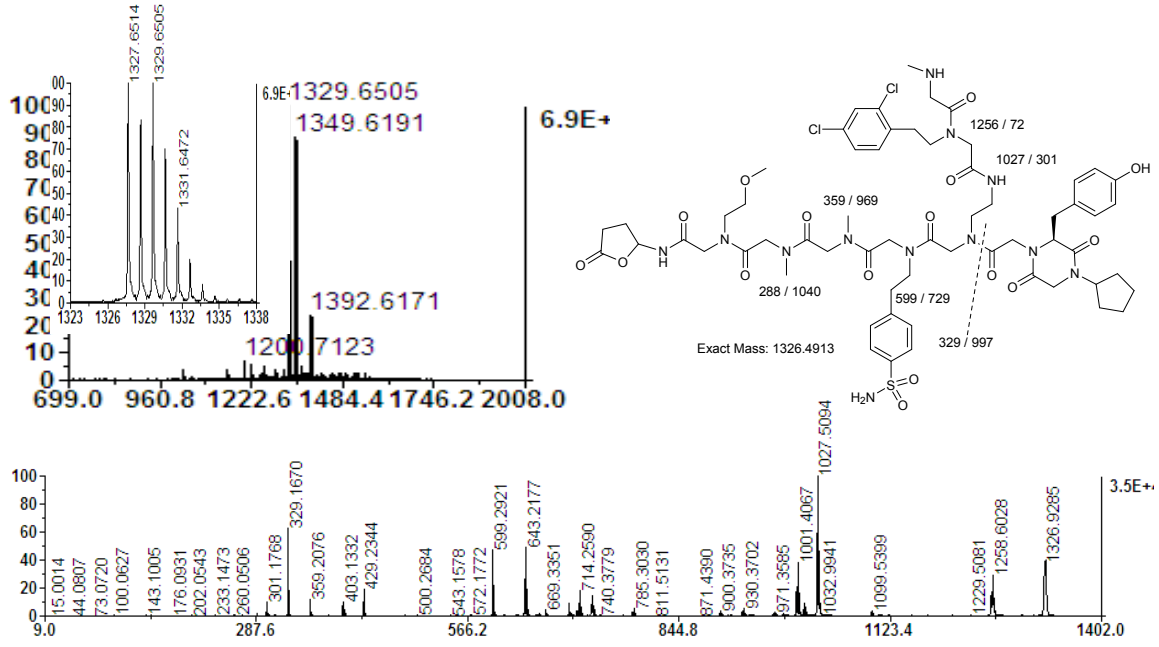


Figure S66: Top: MALDI-MS data showing parent peak (left) of peptoid (right). Bottom: MALDI-TOF MS/MS of the compound.

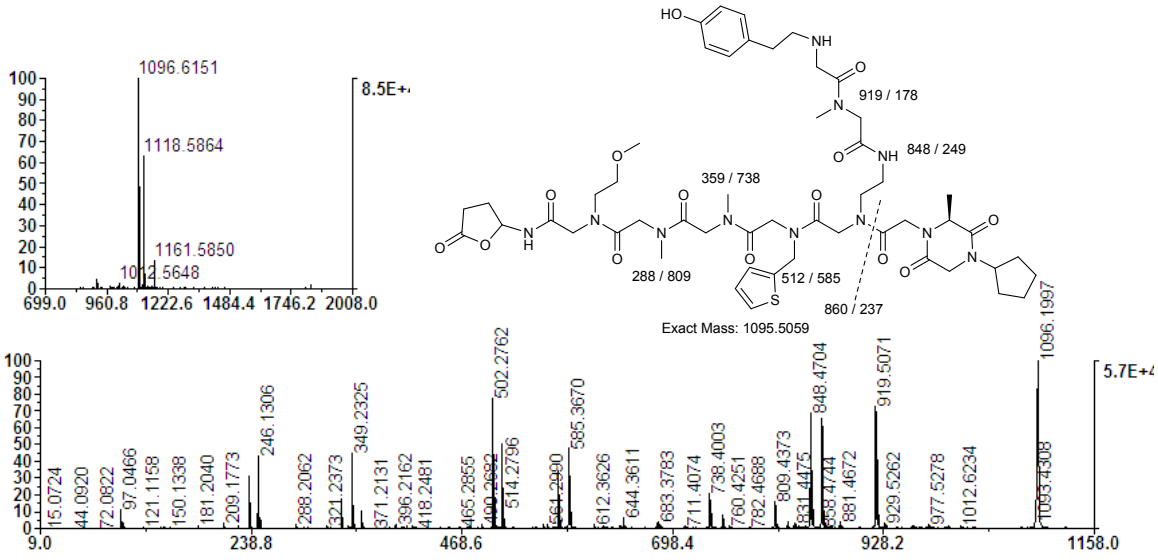


Figure S67: Top: MALDI-MS data showing parent peak (left) of peptoid (right). Bottom: MALDI-TOF MS/MS of the compound.

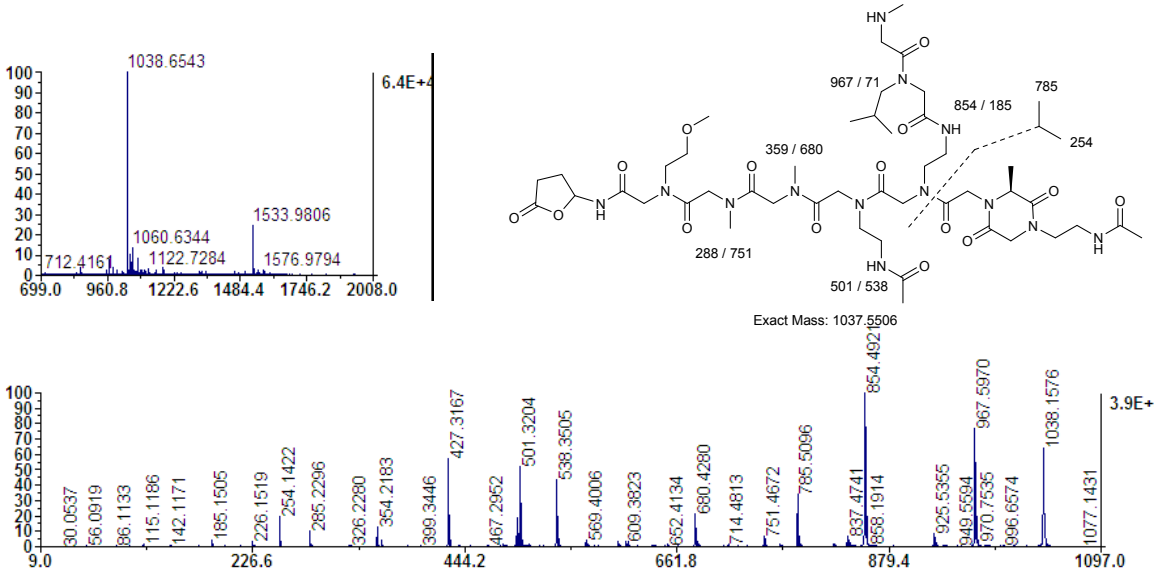


Figure S68: Top: MALDI-MS data showing parent peak (left) of peptoid (right). Bottom: MALDI-TOF MS/MS of the compound.

Hybrid DKP-capped library:

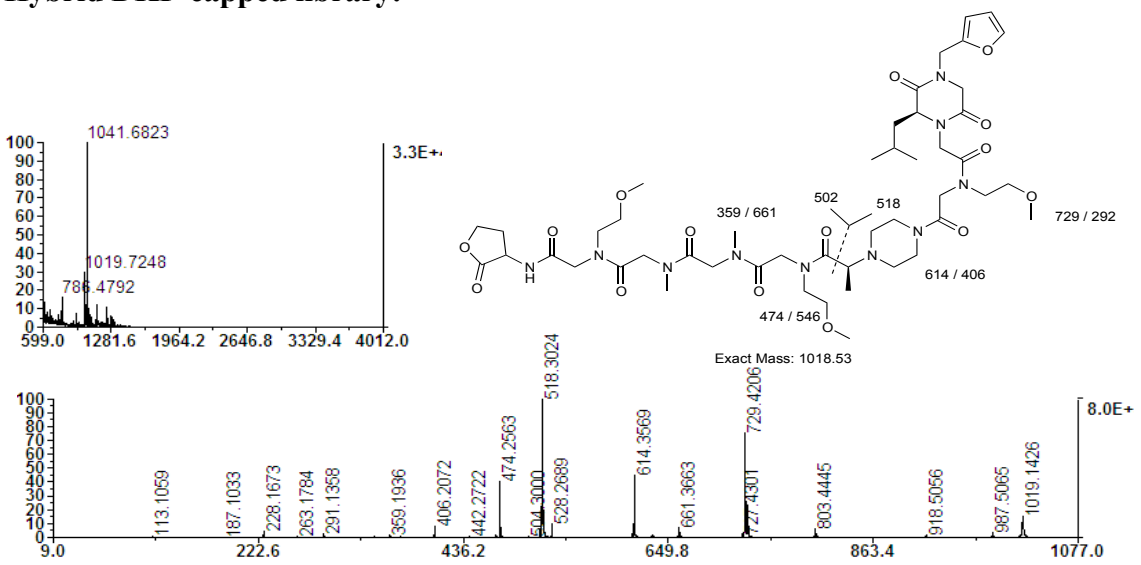


Figure S69: Top: MALDI-MS data showing parent peak (left) of peptoid (right). Bottom: MALDI-TOF MS/MS of the compound.

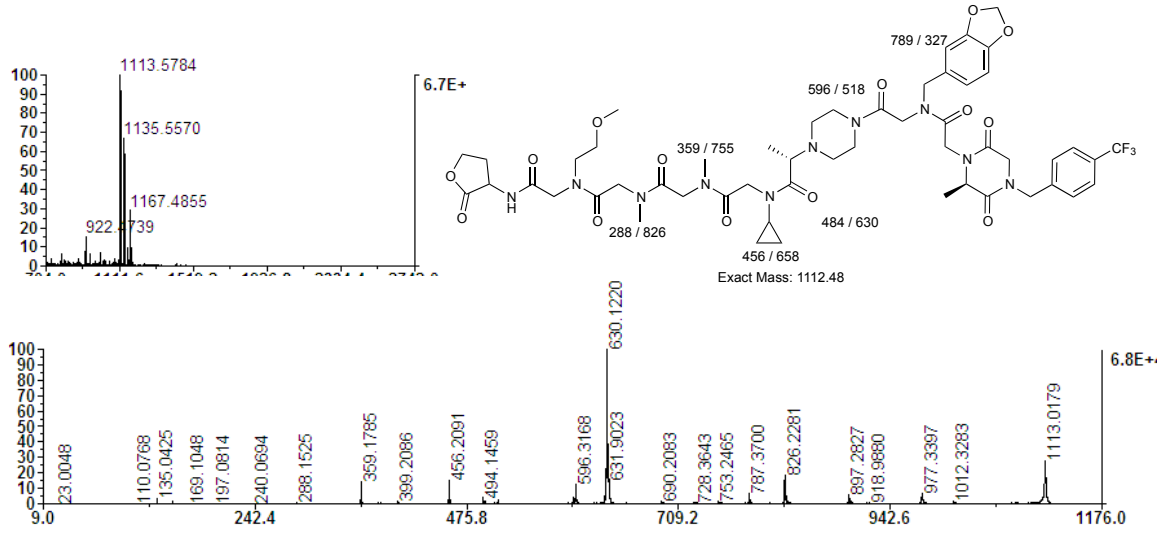


Figure S70: Top: MALDI-MS data showing parent peak (left) of peptoid (right). Bottom: MALDI-TOF MS/MS of the compound.

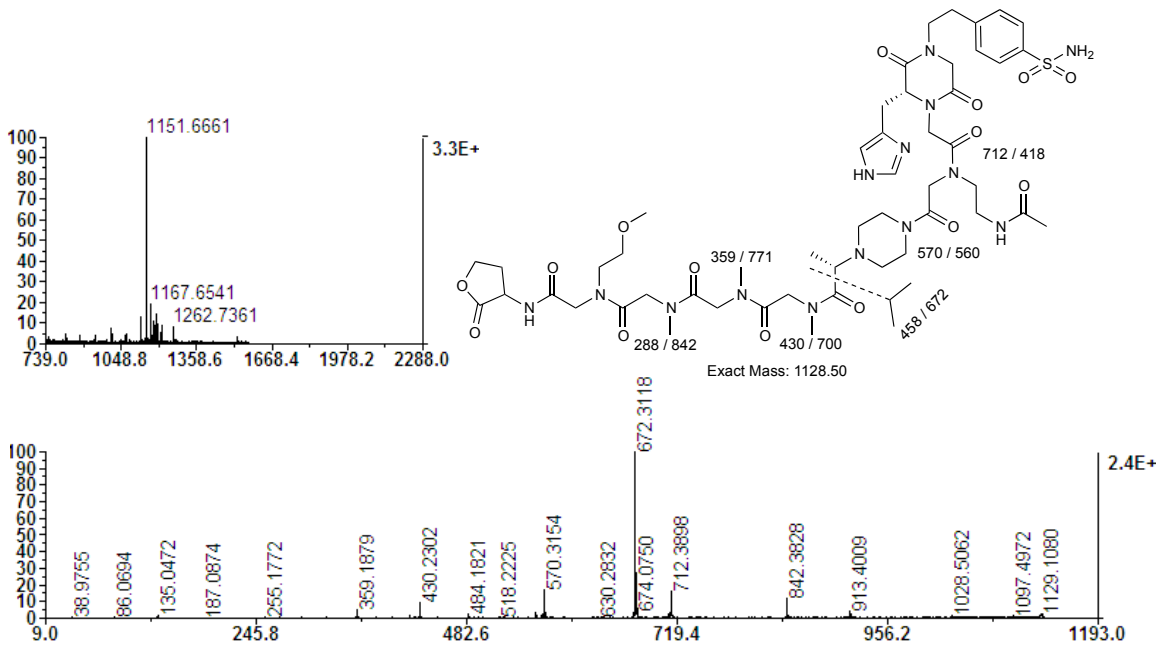


Figure S71: Top: MALDI-MS data showing parent peak (left) of peptoid (right). Bottom: MALDI-TOF MS/MS of the compound.

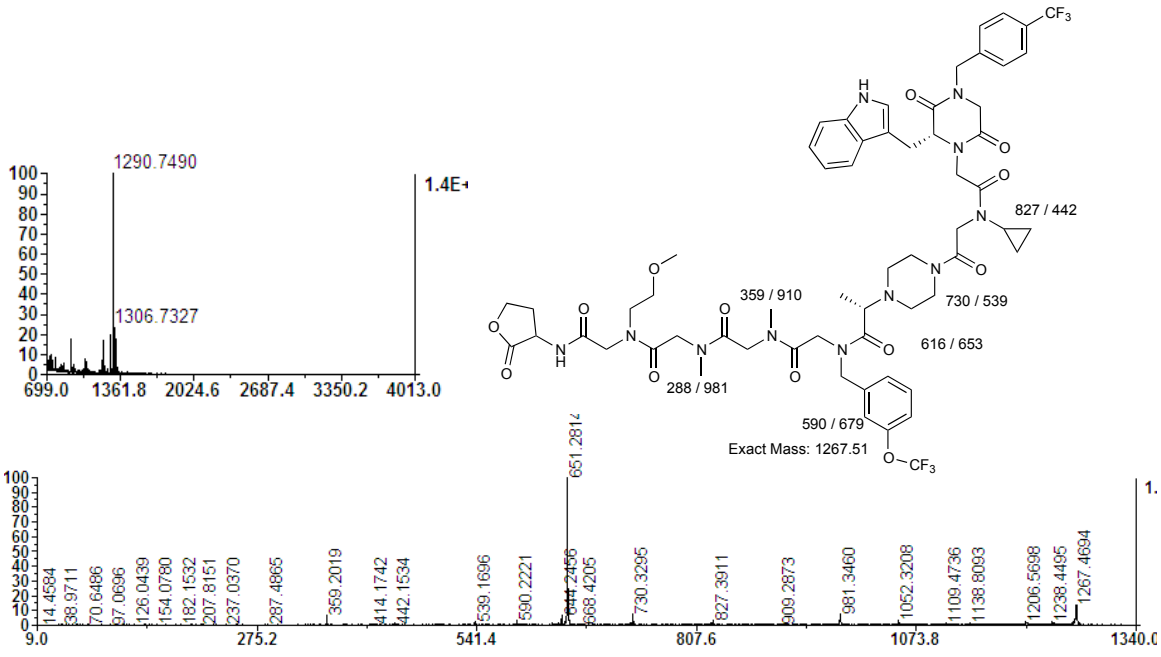


Figure S72: Top: MALDI-MS data showing parent peak (left) of peptoid (right). Bottom: MALDI-TOF MS/MS of the compound.

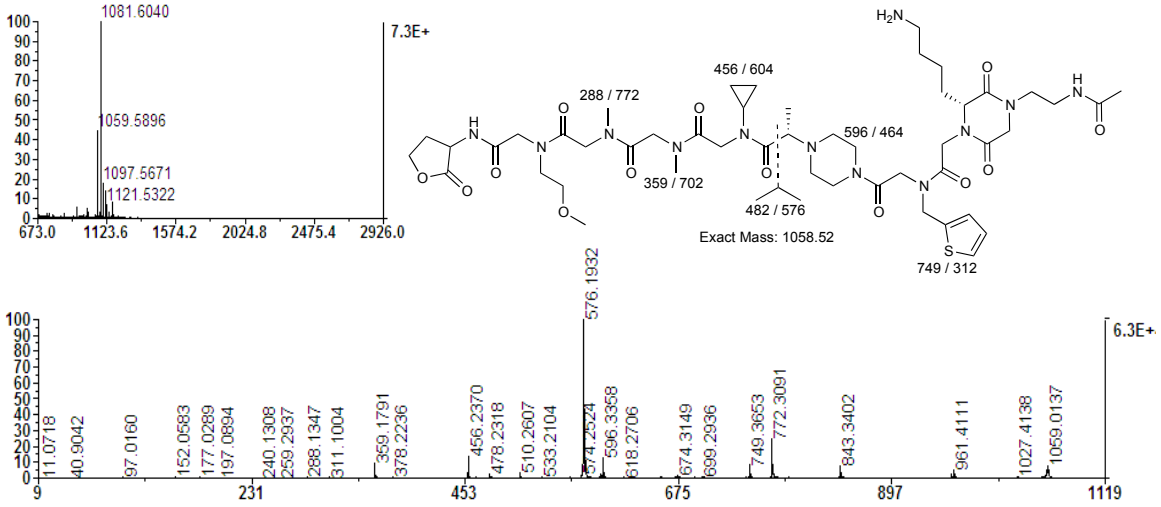


Figure S73: Top: MALDI-MS data showing parent peak (left) of peptoid (right). Bottom: MALDI-TOF MS/MS of the compound.

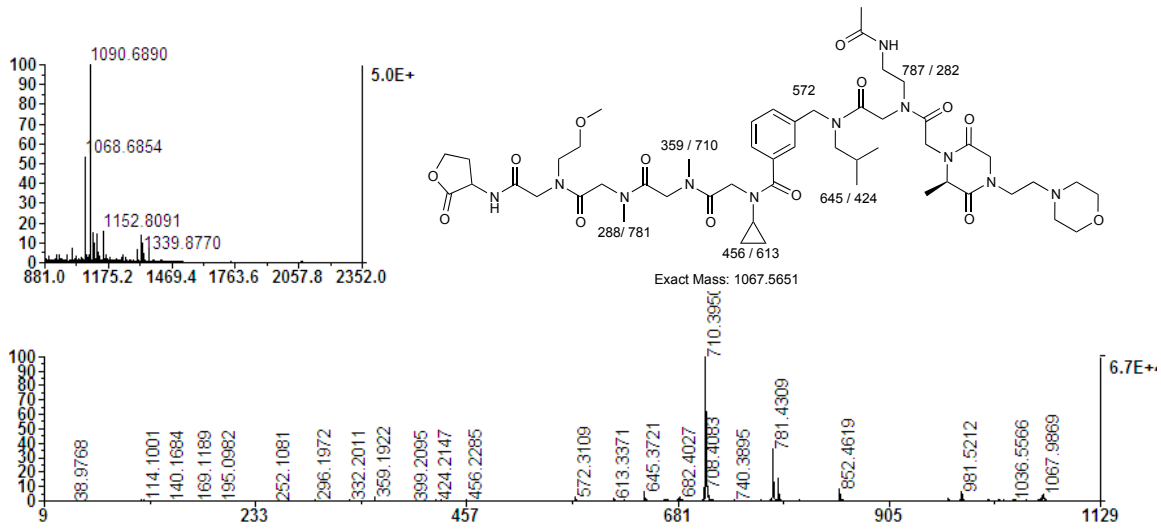


Figure S74: Top: MALDI-MS data showing parent peak (left) of peptoid (right). Bottom: MALDI-TOF MS/MS of the compound.

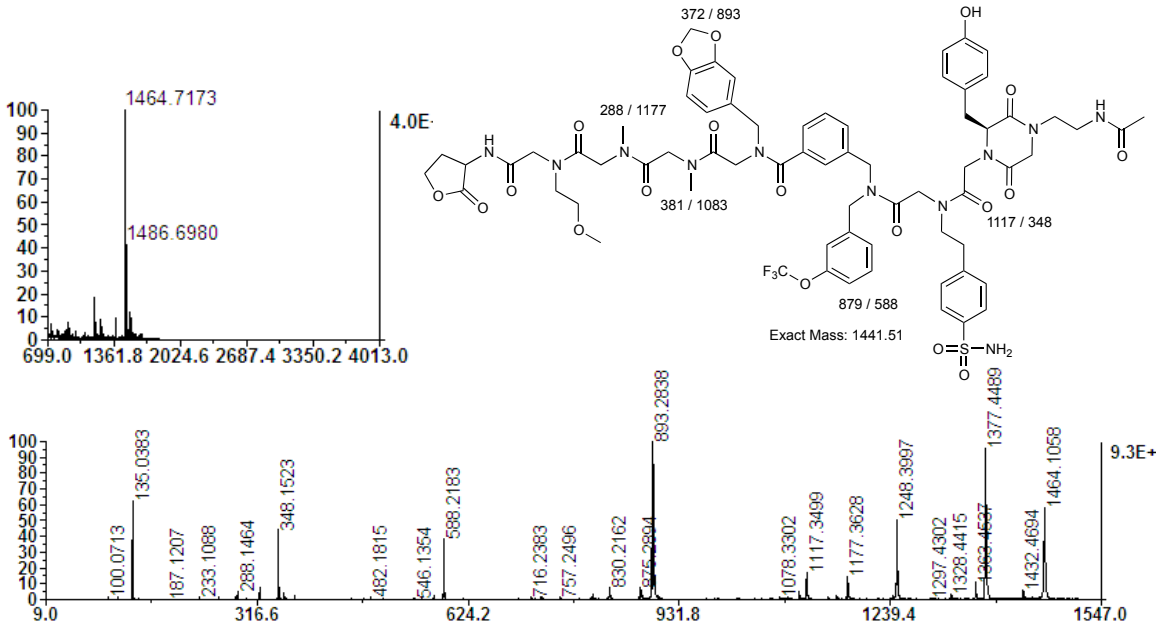


Figure S75: Top: MALDI-MS data showing parent peak (left) of peptoid (right). Bottom: MALDI-TOF MS/MS of the compound.

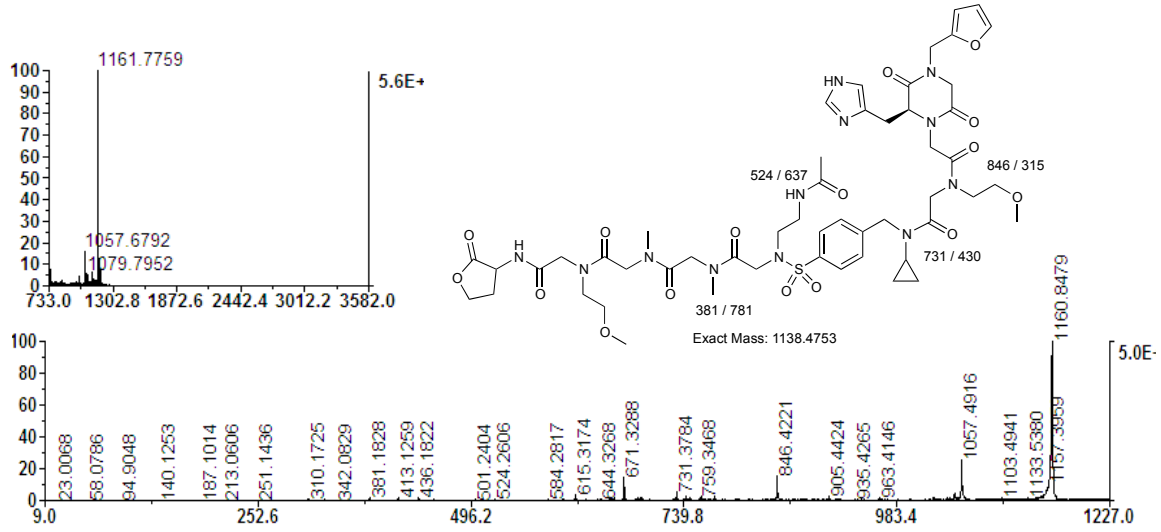


Figure S76: Top: MALDI-MS data showing parent peak (left) of peptoid (right). Bottom: MALDI-TOF MS/MS of the compound.

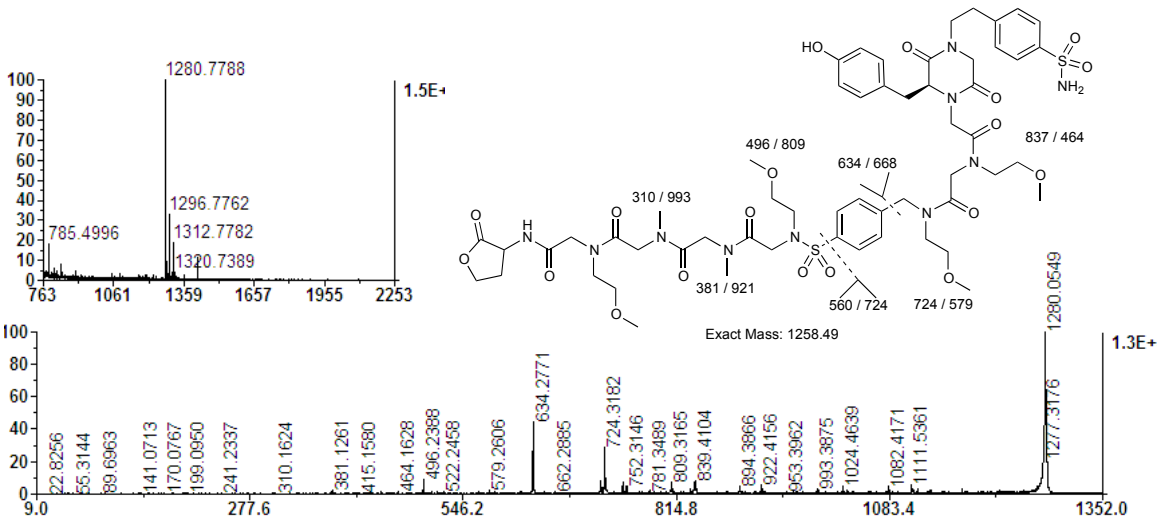


Figure S77: Top: MALDI-MS data showing parent peak (left) of peptoid (right). Bottom: MALDI-TOF MS/MS of the compound.

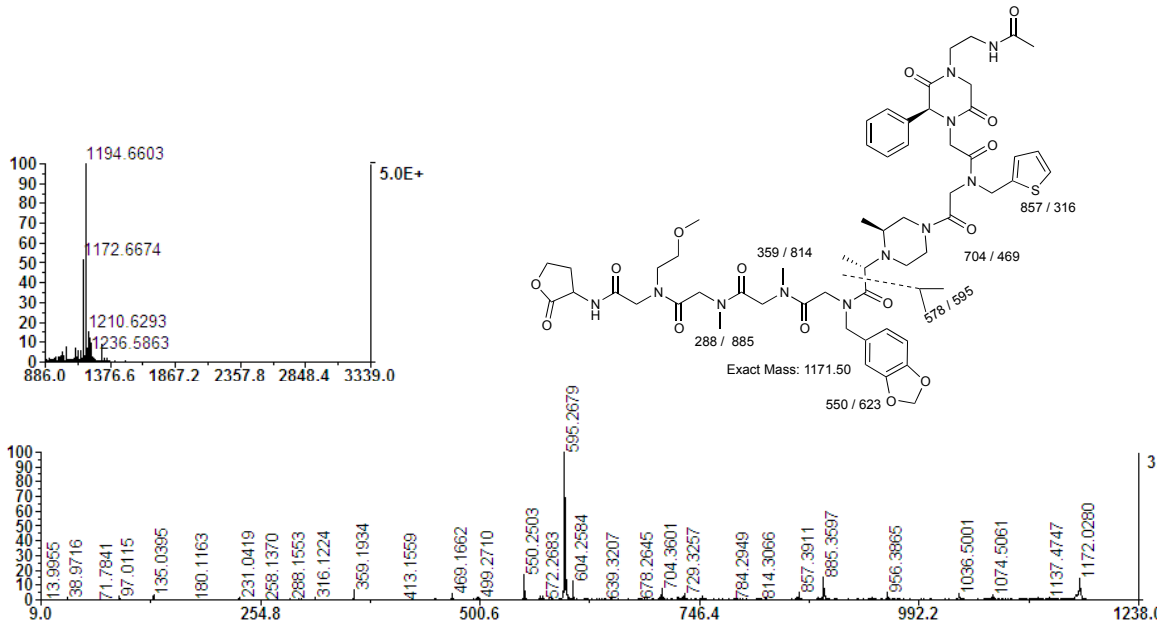


Figure S78: Top: MALDI-MS data showing parent peak (left) of peptoid (right). Bottom: MALDI-TOF MS/MS of the compound.

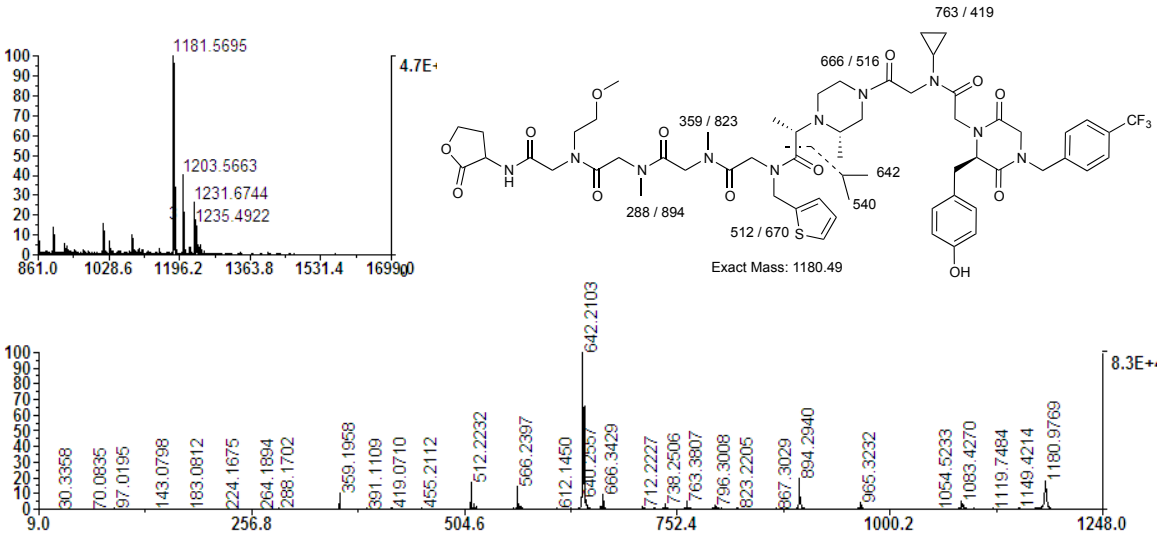


Figure S79: Top: MALDI-MS data showing parent peak (left) of peptoid (right). Bottom: MALDI-TOF MS/MS of the compound.

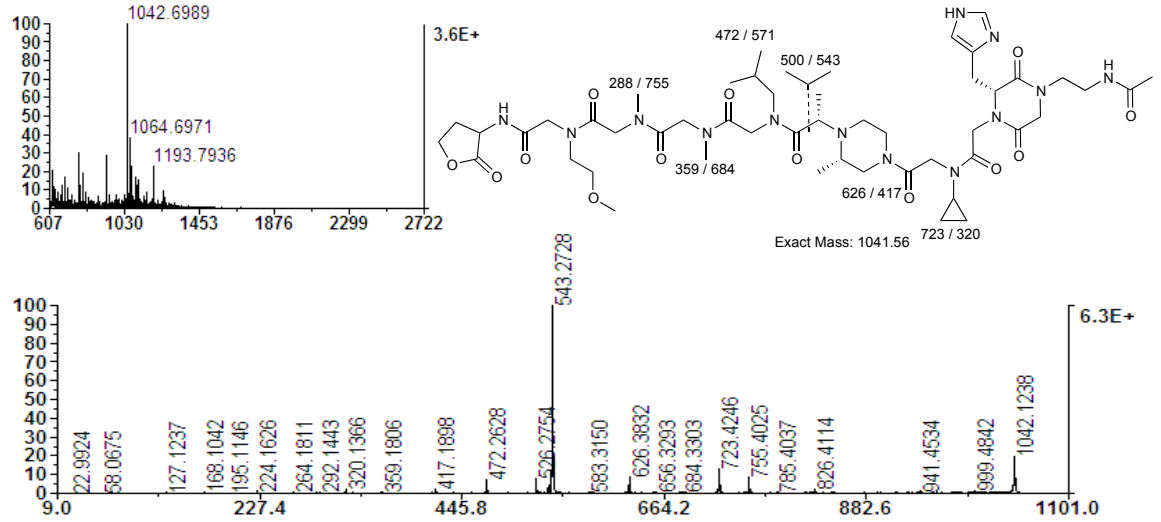


Figure S80: Top: MALDI-MS data showing parent peak (left) of peptoid (right). Bottom: MALDI-TOF MS/MS of the compound.

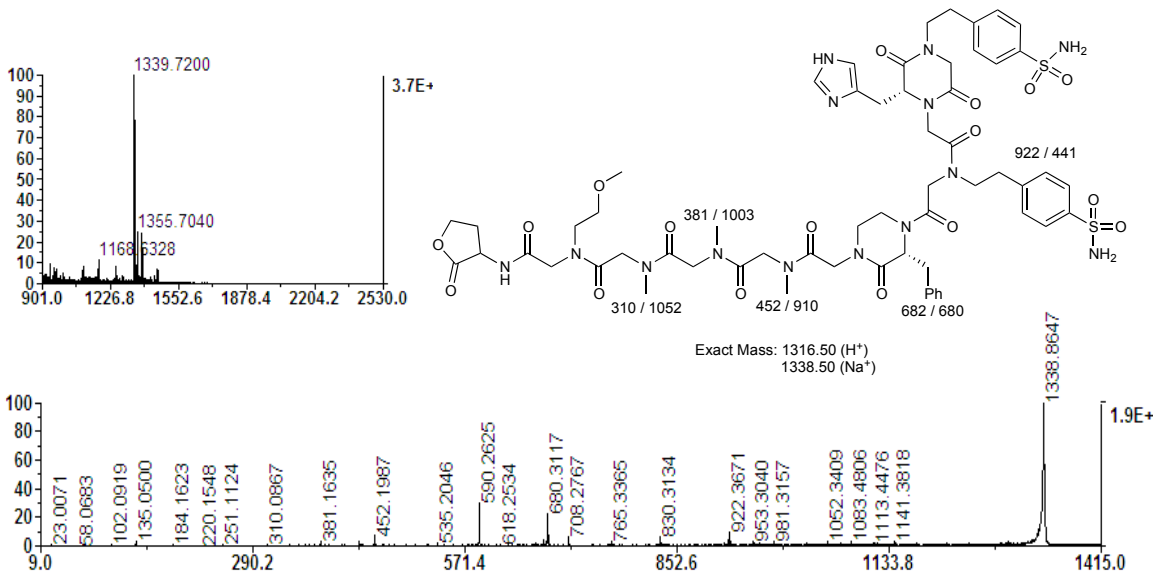


Figure S81: Top: MALDI-MS data showing parent peak (left) of peptoid (right). Bottom: MALDI-TOF MS/MS of the compound

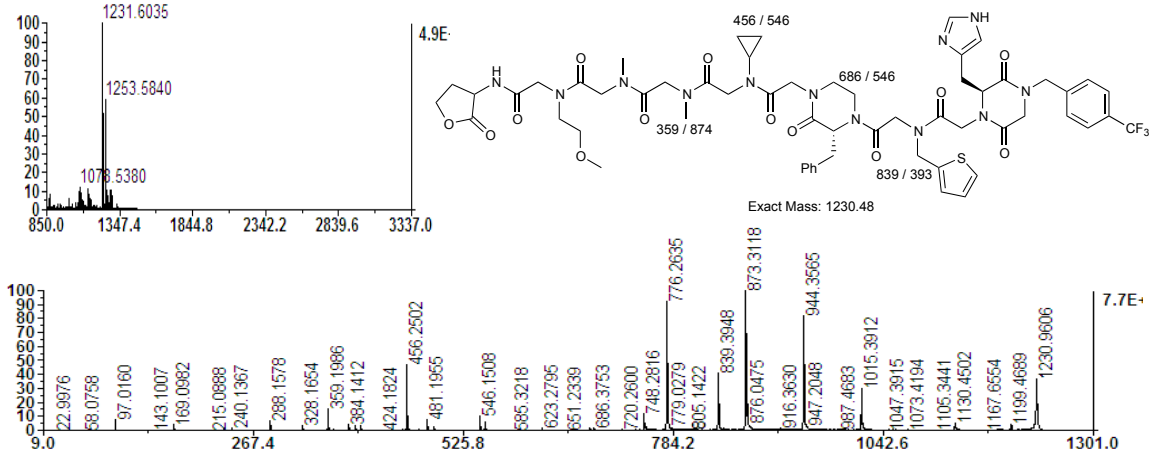


Figure S82: Top: MALDI-MS data showing parent peak (left) of peptoid (right). Bottom: MALDI-TOF MS/MS of the compound.

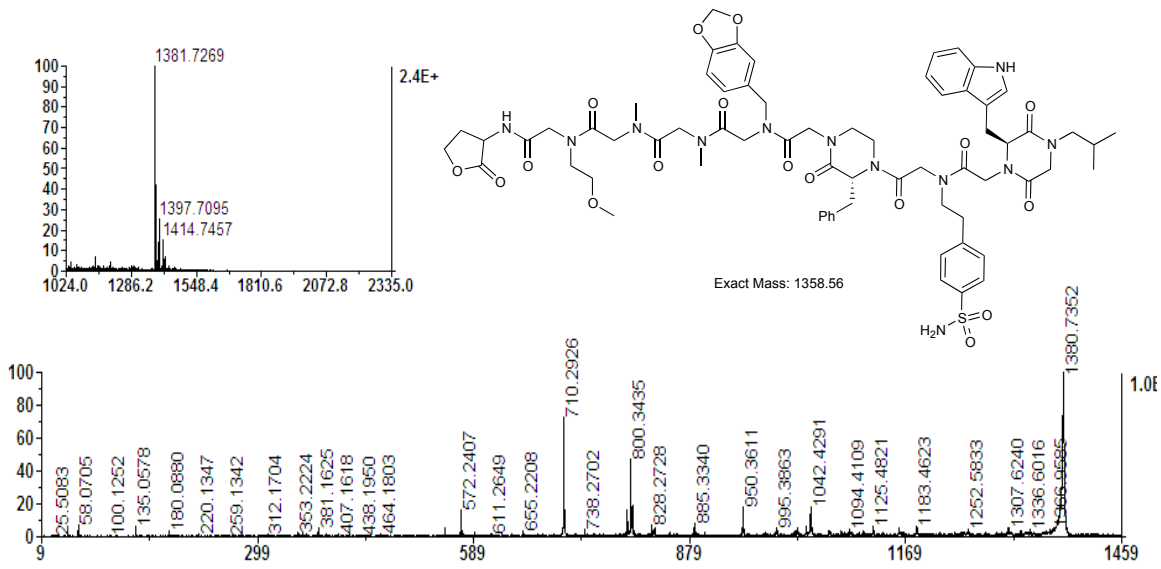


Figure S83: Top: MALDI-MS data showing parent peak (left) of peptoid (right). Bottom: MALDI-TOF MS/MS of the compound.

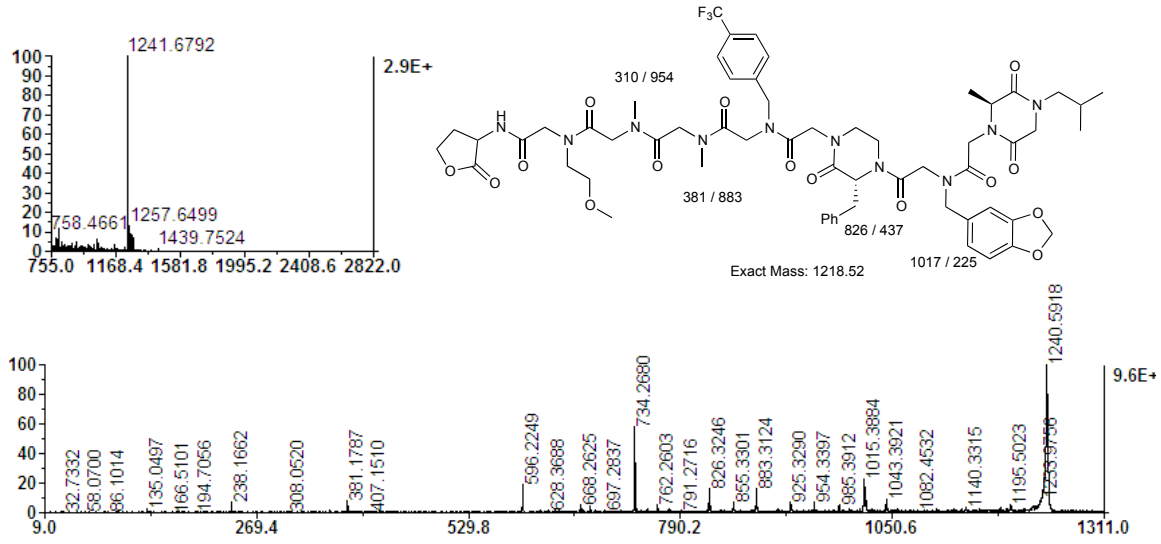


Figure S84: Top: MALDI-MS data showing parent peak (left) of peptoid (right). Bottom: MALDI-TOF MS/MS of the compound.