Electronic Supplementary Material (ESI) for CrystEngComm.
This journal is © The Royal Society of Chemistry 2014

Supporting Information

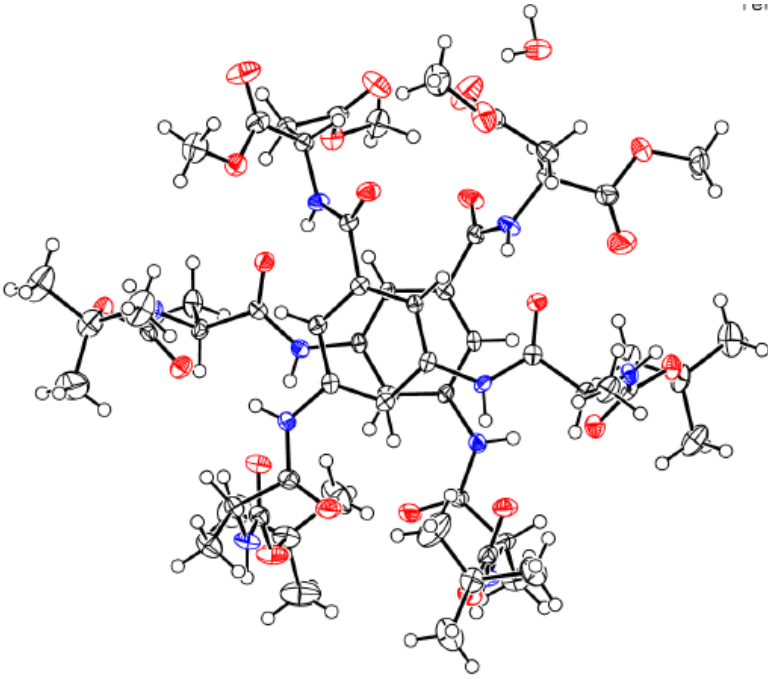
Photoelectrochemical properties of CdSe quantum dots doped disk-like tripeptide capsule†

Santu Bera, Suman Kumar Maity and Debasish Haldar*

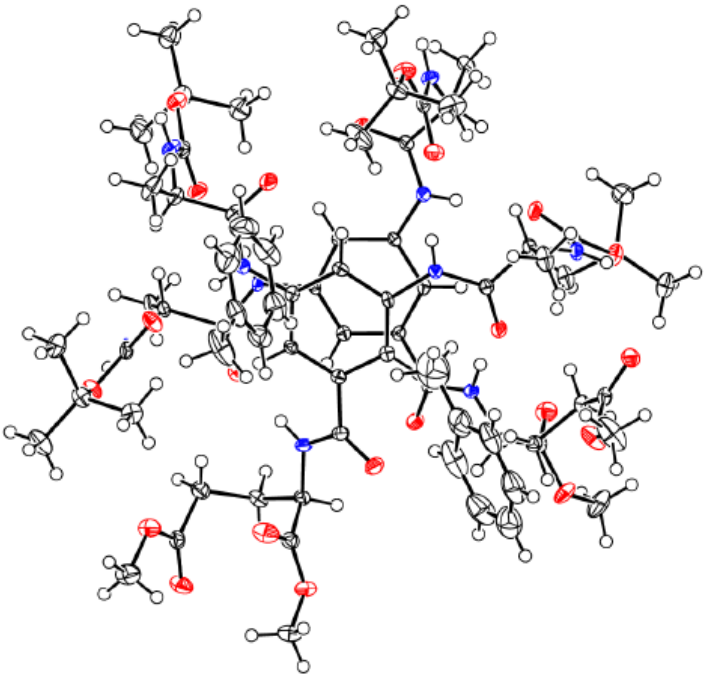
Department of Chemical Sciences, Indian Institute of Science Education and Research –Kolkata, Mohanpur, West Bengal- 741252, India.

E-mail: deba_h76@yahoo.com ; deba_h76@iiserkol.ac.in

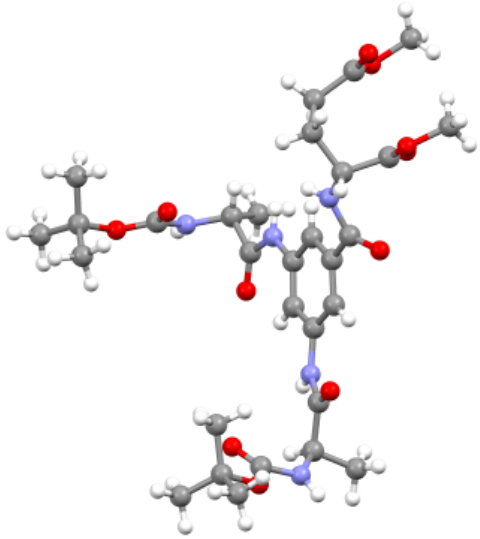
Table of contents



ESI Fig.1: The ORTEP diagram of of discotic tripeptide **1**. Ellipsoids are drawn at the 50% probability level.



ESI Fig.2: The ORTEP diagram of of discotic tripeptide **2**. Ellipsoids are drawn at the 50% probability level.



ESI Fig. 3: Molecule B of peptide **2** where the bulky glutamic acid group is on the opposite side of the central benzene ring with respect to the Boc protected alanine restudies.

Peptide synthesis:

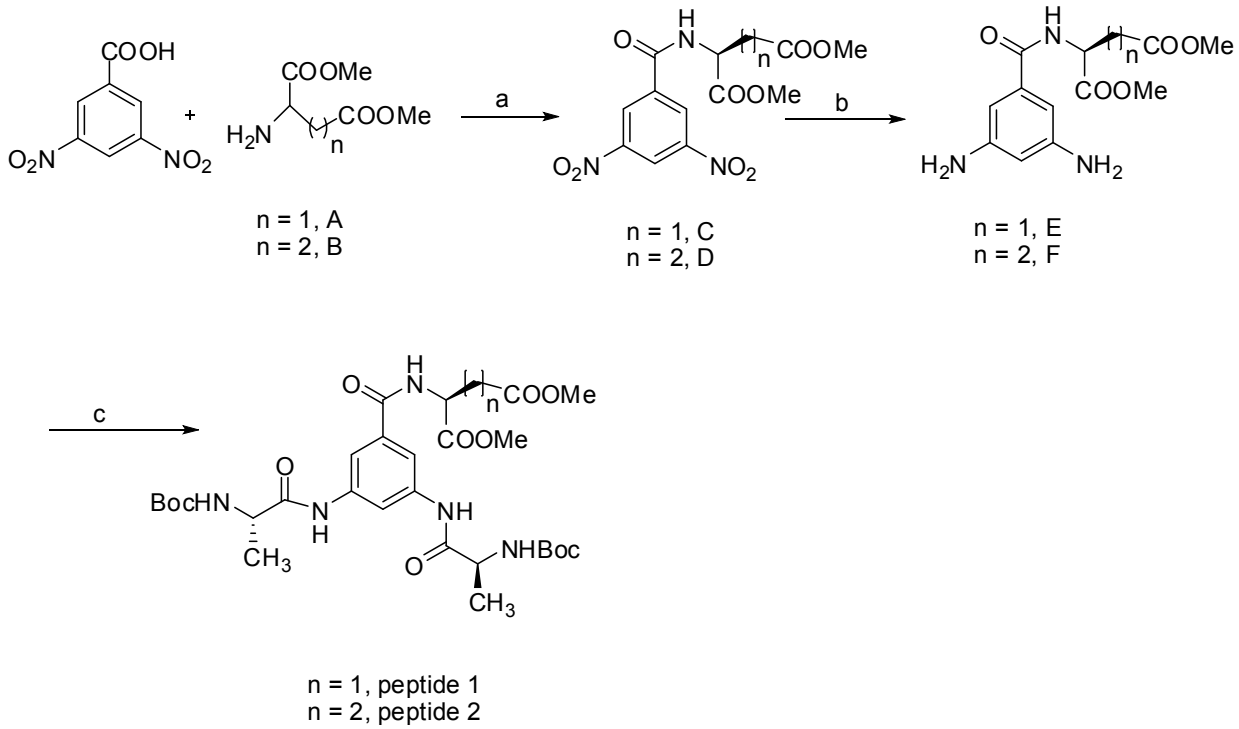


Figure S1: Schematic presentation of **s**ynthesis of peptide **1** and **2**. Reagent and condition: (a) DCC, HOBt, DCM, 0°C (b) H_2/Pd-C, MeOH (c) Boc-Ala-OH, DCC, HOBt, DCM, 0°C.

(a) Synthesis of compound C and D: 2.0 g (9.43 mmol) of 3,5-dinitro benzoic acid was dissolved in 25 mL dry DCM in an ice-water bath. H-Asp-OMe (**A**) was isolated from 1.826 g (9.43 mmol) of the corresponding methyl ester hydrochloride by neutralization, subsequent extraction with ethyl acetate and the ethyl acetate extract was concentrated to 10 mL. It was then added to the reaction mixture, followed immediately by 1.946 g (9.43 mmol) dicyclohexylcarbodiimide (DCC) and 1.274 g (9.43 mmol) of HOBt. The reaction mixture was allowed to come to room temperature and stirred for 48 h. DCM was evaporated and the residue was dissolved in ethyl acetate (60 mL) and the dicyclohexylurea (DCU) was filtered off. The organic layer was washed with 2 M HCl (3 x 50 mL), brine (2 x 50 mL), 1 M sodium carbonate (3 x 50 mL) and brine (2 x 50 mL) and dried over anhydrous sodium sulphate; and

evaporated in a vacuum to yield compound **C** as a white solid. The product was purified by silica gel (100–200 mesh) using n-hexane–ethyl acetate (3: 1) as eluent. Yield: 2.48 g (6.99 mmol, 74.22%). Compound **D** was synthesised in the similar way using H-Glu-OMe (**B**) instead of H-Asp-OMe (**A**) (Yield: 6.25 mmol, 66.27%).

For compound **C**: ^{1}H NMR (400 MHz, $CDCl_3$, δ (ppm)): 9.203-8.977 [s, 3H, aromatic protons], 7.553[s,1H NH], 5.087-5.067[m, 1H, C^{α} Asp], 3.841 [s, 3H, OMe], 3.748 [s, 3H, OMe], 3.197-3.186 [m, 1H, C^{β} Asp], 3.047-3.035[m, 1H, C^{β} Asp]. ^{13}C NMR (100 MHz, CDCl3, δ(ppm)): 168.68, 167.84, 159.82, 145.84, 134.24, 124.73, 118.61, 50.47, 49.54, 46.68, 32.88.

For compound **D**: ^{1}H NMR (400 MHz, $CDCl_3$, δ (ppm)): 9.186-9.046 [s, 3H, aromatic protons], 8.145-8.130[d,1H, J= 6, NH], 4.760-4.744[m, 1H, C^{α} Asp], 3.851 [s, 3H, OMe], 3.766 [s, 3H, OMe], 2.596-2.578 [m, 1H, C^{β} Asp], 2.320-2.256[m, 1H, C^{β} Asp]. ^{13}C NMR (100 MHz, CDCl3, δ(ppm)): 174.34,171.83, 162.63, 148.49, 136.87, 127.56, 121.18, 52.98, 52.77, 52.21, 30.20, 26.12.

(b) Synthesis of compound E and F: A dilute solution of compound **C** (1 g, 2.815 mmol) (**D** in case of compound **F**) in MeOH (200 mL) was passed through the flow hydrogenation assembly fitted with Pd-C cartridge at room temperature and normal pressure of hydrogen. After completion, as evidence from TLC (DCM – MeOH; 6:1), the solvent were evaporated under reduced pressure. And required column was done to separate the pure product by silica gel (100-200 mesh) using DCM – MeOH (10:1) as eluent. Yield 0.702 g, (2.41 mmol, 85.63%).

For compound **E**: ^{1}H NMR (400 MHz, $CDCl_3$, δ (ppm)): 8.381-8.361[d, 1H, J=8, NH], 6.206-5.946[s, 3H, aromatic protons], 4.879 [s, 4H, NH_2], 4.781-4.766[m, 1H, C^{α} Asp], 3.632

[s, 3H, OMe], 3.610 [s, 3H, OMe], 2.911-2.901 [m, 1H, C^{β} Asp], 2.852-2.833 [m, 1H, C^{β} Asp]. ^{13}C NMR (100 MHz, CDCl3, δ(ppm)): 168.68, 167.84, 159.82, 145.83, 134.24, 105.65, 97.23, 50.45, 49.54, 46.68, 32.88.

For compound **F**: ^{1}H NMR (400 MHz, $CDCl_3$, δ (ppm)): 8.315-8.297 [d, 1H, J=7.2, NH], 6.231-5.947[s, 3H, aromatic protons], 4.880 [s, 4H, NH_2], 4.376-4.362 [m, 1H, C^{α} Asp], 3.624 [s, 3H, OMe], 3.584 [s, 3H, OMe], 2.401-2.399 [m, 1H, C^{β} Asp], 2.079-2.059 [m, 1H, C^{β} Asp]. ^{13}C NMR (100 MHz, CDCl3, δ(ppm)): 174.64,170.99, 162.25, 148.49, 135.89, 105.23, 102.36, 53.25, 52.98, 52.54, 30.83, 25.93.

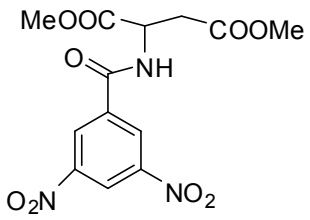
(c) Boc-Ala-OH : A solution of L-Alanine (1.78 g, 20 mmol) in a mixture of dioxane (40 mL), water (20 mL) and 1 M NaOH (20 mL) was stirred and cooled in an ice-water bath. Ditert- butylpyrocarbonate (4.8 g, 22 mmol) was added and stirring was continued at room temperature for 6 h. Then the solution was concentrated in vacuum to about 20–30 mL, cooled in an icewater bath, covered with a layer of ethyl acetate (about 50 mL) and acidified with a dilute solution of KHSO4 to pH 2–3 (Congo red). The aqueous phase was extracted with ethyl acetate and this operation was done repeatedly. The ethyl acetate extracts were pooled, washed with water and dried over anhydrous Na_2SO_4 and evaporated in a vacuum. The pure material was obtained as a waxy solid. Yield: 2.93 g (15.51 mmol, 82.0%).
1H NMR (400 MHz, $CDCl_3$, δ (ppm)): 7.78[s, 1H, NH], 5.08[s, 1H, C^{α} Ala], 2.11 [s, 9H, Boc], 2.11 [s, 3H, CH_3].13C NMR (125 MHz, CDCl3, δ(ppm)):171.44, 155.48, 80.03, 49.09, 28.25, 18.31.

(d) Synthesis of peptide 1 and 2: 1.62 g (8.56 mmol) Boc-Ala-OH was dissolved in 15 mL DCM in an icewater bath. 1 g (3.43 mmol) of compound **E** was added to the reaction mixture, followed immediately by 1.77 g (8.56 mmol) dicyclohexylcarbodiimide (DCC) and 1.16 g

(8.56 mmol) HOBt. The reaction mixture was allowed to come to room temperature and stirred for 72 h. The residue was taken into 30 mL ethyl acetate and dicyclohexylurea (DCU) was filtered off. The organic layer was washed with 2 M HCL (3 x 50 mL), brine (2 x 50 mL), then 1 M sodium carbonate (3 x 30 mL) and brine (2 x 30 mL) and dried over anhydrous sodium sulphate and evaporated under vacuum to yield the peptide **1** as a white solid. Purification was done by silicagel column (100–200 mesh size) and ethyl acetate and hexane (1: 3) as eluent. Yield: 1.67 g (2.62 mmol, 76.52%). Peptide **2** was synthesized in similar procedure using compound **F** instead of compound **E (**Yield 73.25%).

For peptide **1**: ^{1}H NMR (400 MHz, $CDCl_3$, δ (ppm)):9.119 [s, 2H, NH],7.820 [s, 1H, Asp NH], 7.817-7.785[m, 2H, aromatic protons], 7.121[s, 1H, aromatic proton], 5.492 [s, 2H, BOC NH], 5.144-5.11[m, 1H, C^{α} Asp], 4.484 [s, 2H, C^{α} Ala], 3.785[s, 3H, OMe], 3.751 [s, 3H, OMe], 3.142-3.125 [d, 2H, J=6.8 C^{β} Asp], 1.432 [s, 18H, BOC], 1.254 [s, 6H, C^{β} Ala]. ^{13}C NMR (100 MHz, CDCl3, δ(ppm)): 172.46, 171.43, 167.63, 156.28, 138.39, 138.19, 132.03, 130.77, 128.68, 80.54, 52.08, 52.01, 38.63, 28.80, 28.26, 23.63, 18.22.

For peptide **2**: ^{1}H NMR (400 MHz, $CDCl_3$, δ (ppm)):9.361 [s, 2H, NH],7.820[s, 1H, Asp NH], 7.813-7.773[m, 2H, aromatic protons], 7.028 [s, 2H, aromatic proton], 5.883 [s, 2H, BOC NH], 4.653-4.622[m, 1H, C^{α} Asp], 4.533-4.499 [m, 2H, C^{α} Ala], 3.719 [s, 3H, OMe], 3.704 [s, 3H, OMe], 2.773-2.752 [m, 1H, C^{β} Asp], 2.510-2.499 [m, 1H, C^{β} Asp], 2.375-2.310[m, 2H, C^{β} Asp] 1.445 [s, 18H, BOC], 1.225 [s, 6H, C^{β} Ala]. ^{13}C NMR (100 MHz, CDCl3, δ(ppm)): 173.88, 172.61, 172.11, 168.11, 156.65, 138.39, 135.40, 113.51, 112.87, 80.51, 52.33, 51.77, 50.84, 30.14, 28.35, 26.62, 18.04.



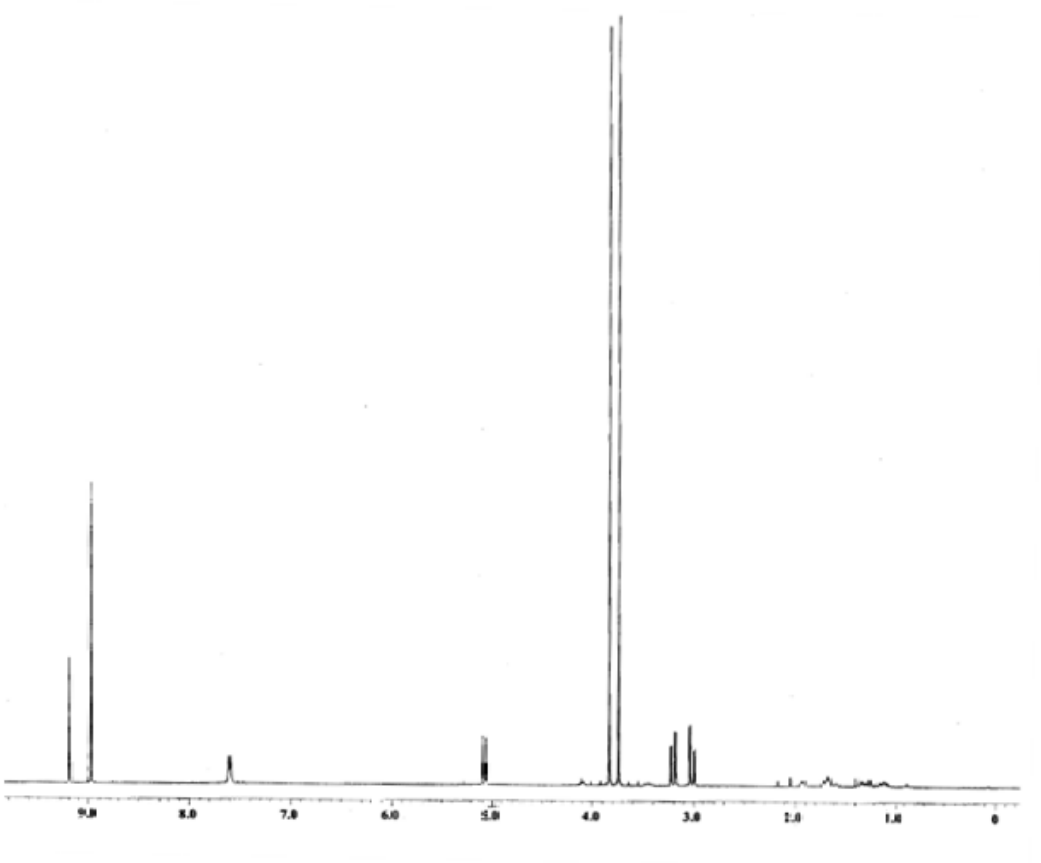
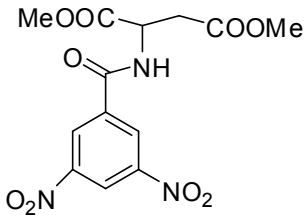


Figure S2: ^{1}H NMR (CDCl3, 400 MHz, δ_{ppm}) spectra of compound **C.**



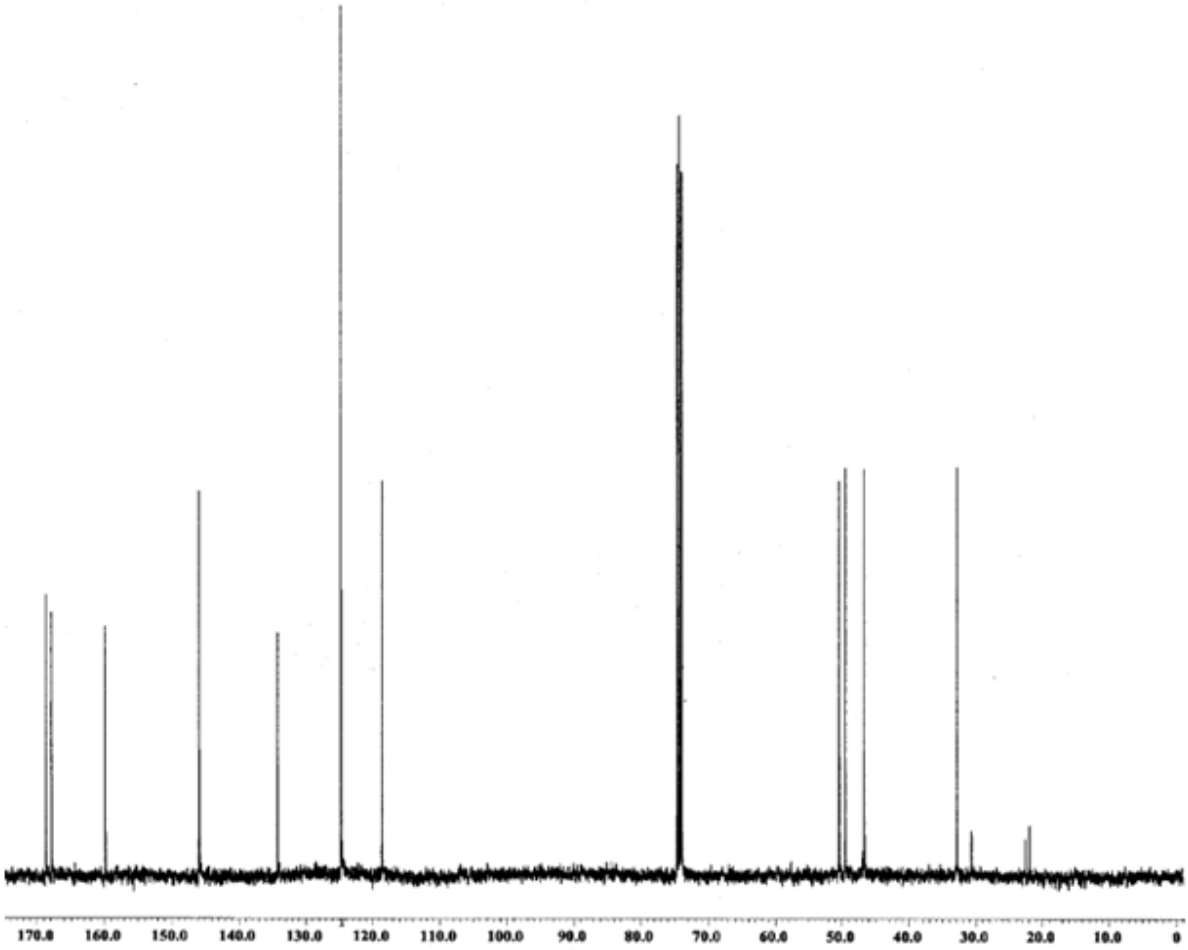


Figure S3: ^{13}C NMR ($CDCl_3$, 125 MHz, δ_{ppm}) spectra of compound **C.**

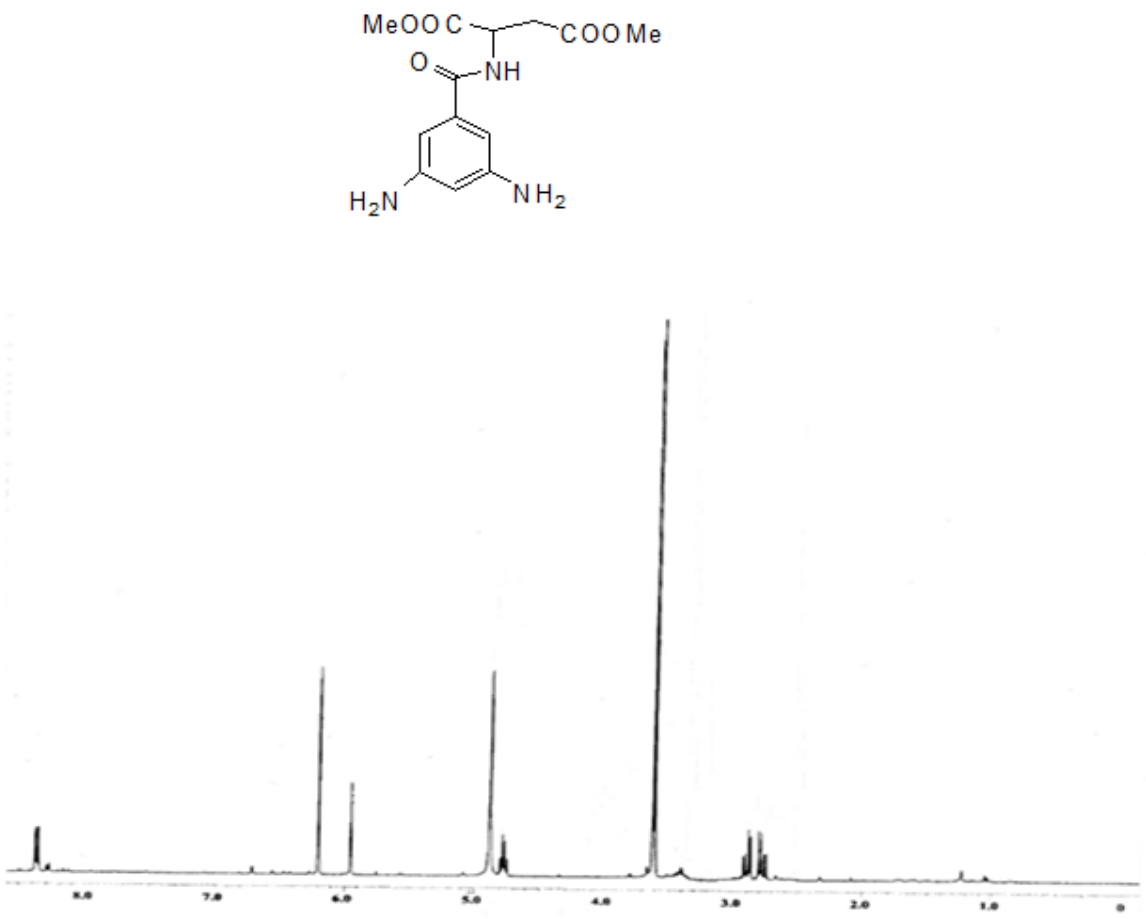


Figure S4: ^{1}H NMR (CDCl3, 400 MHz, δ_{ppm}) spectra of compound **E.**

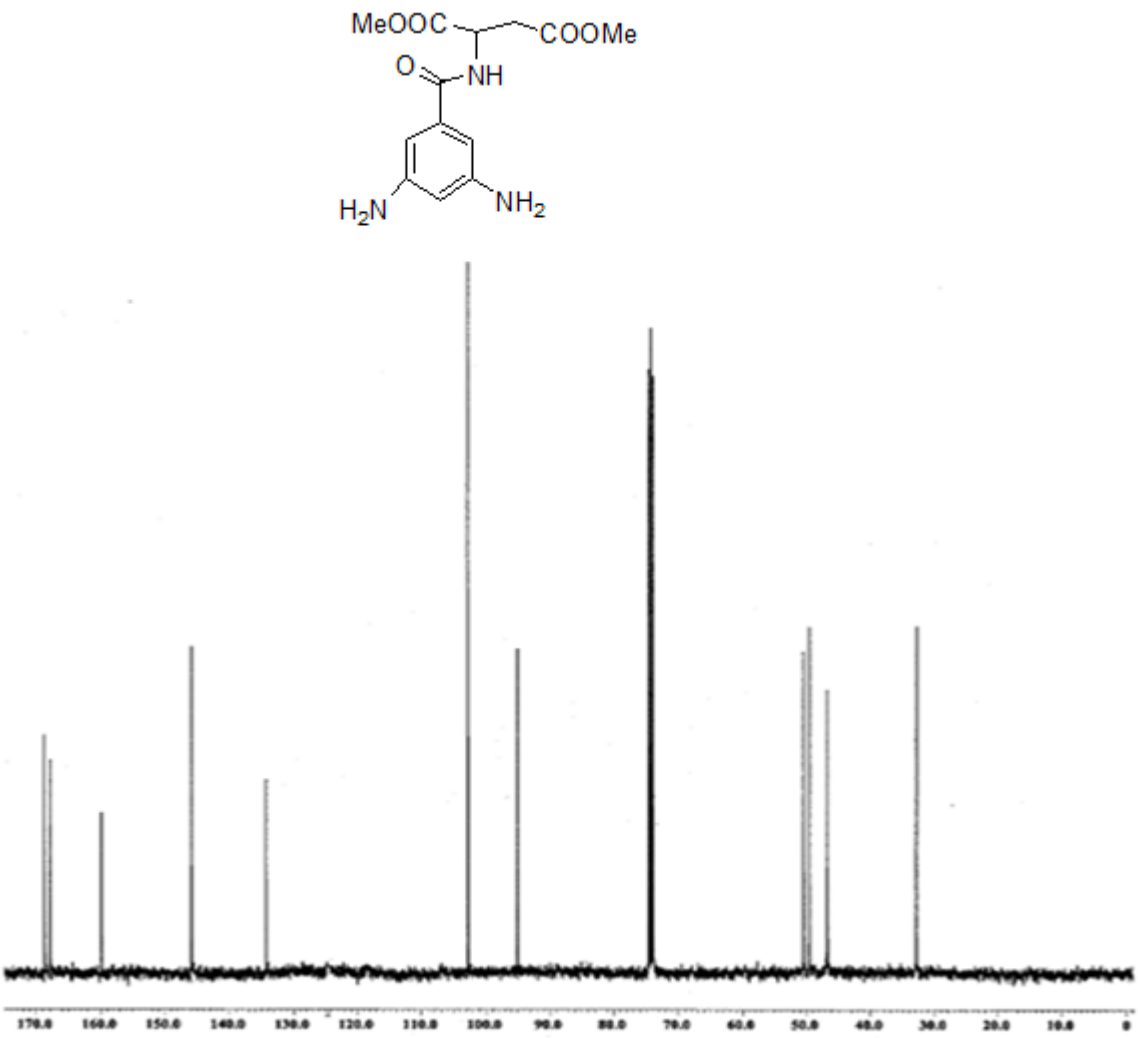


Figure S5: ^{13}C NMR ($CDCl_3$, 125 MHz, δ_{ppm}) spectra of compound **E.**

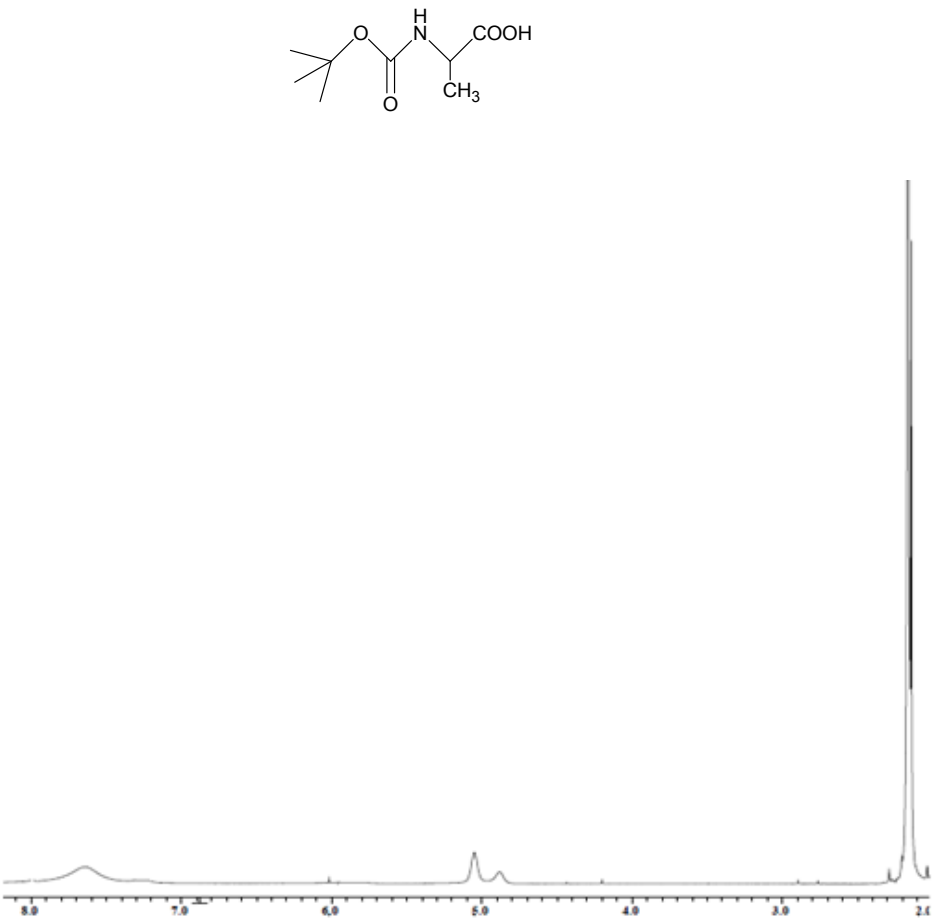


Figure S6: ^{1}H NMR (CDCl3, 400 MHz, δ_{ppm}) spectra of Boc-Ala-OH.

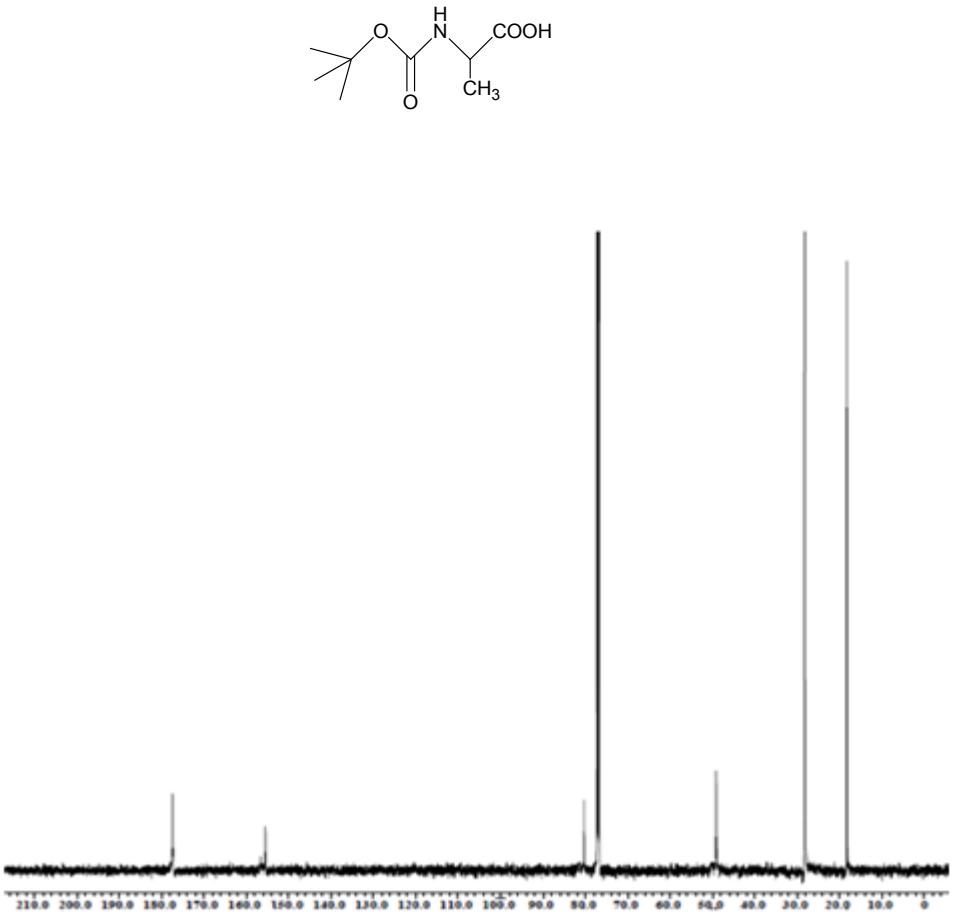
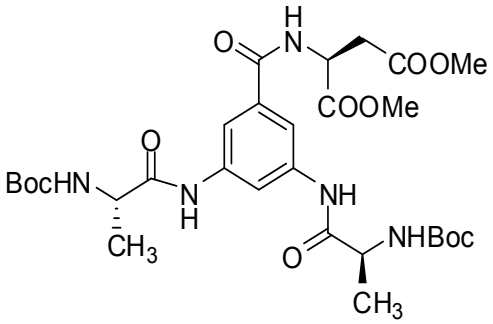


Figure S7: ^{13}C NMR ($CDCl_3$, 125 MHz, δ_{ppm}) spectra of Boc-Ala-OH.



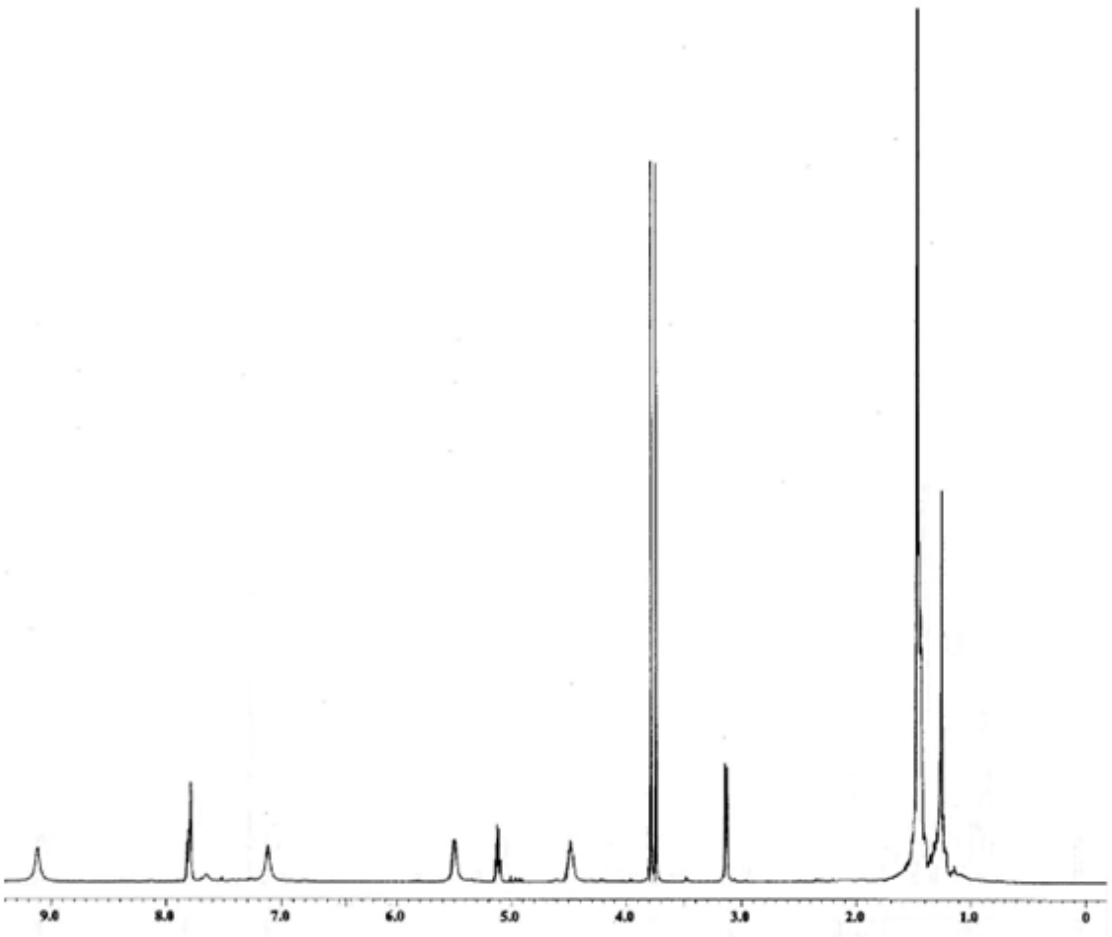
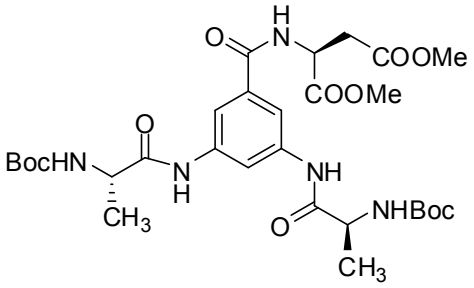


Figure S8: ^{1}H NMR (CDCl3, 400 MHz, δ_{ppm}) spectra of peptide **1**.



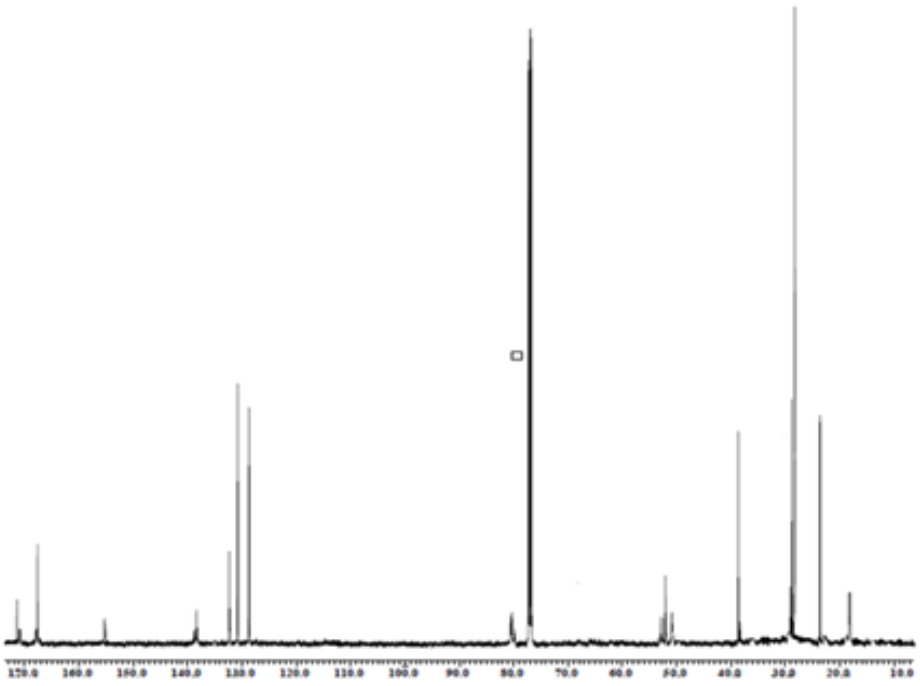


Figure S9: ^{13}C NMR ($CDCl_3$, 125 MHz, δ_{ppm}) spectra of peptide **1**.

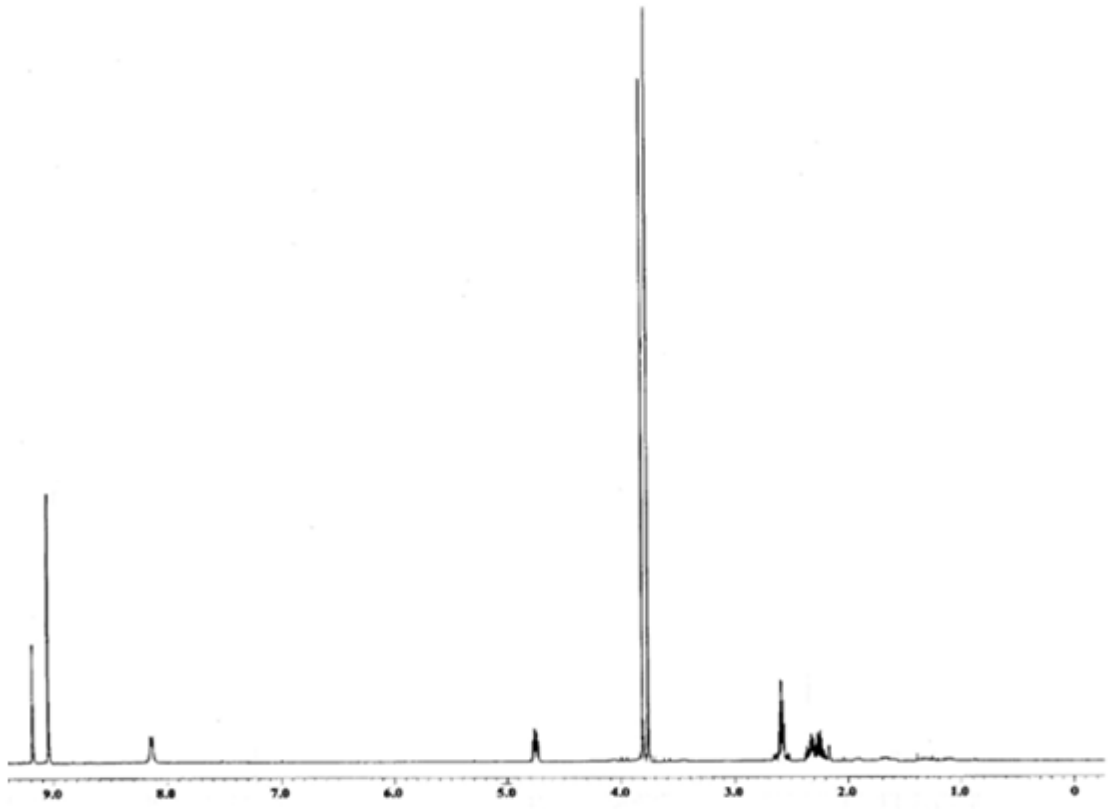


Figure S10: ^{1}H NMR (CDCl3, 400 MHz, δ_{ppm}) spectra of compound **D.**

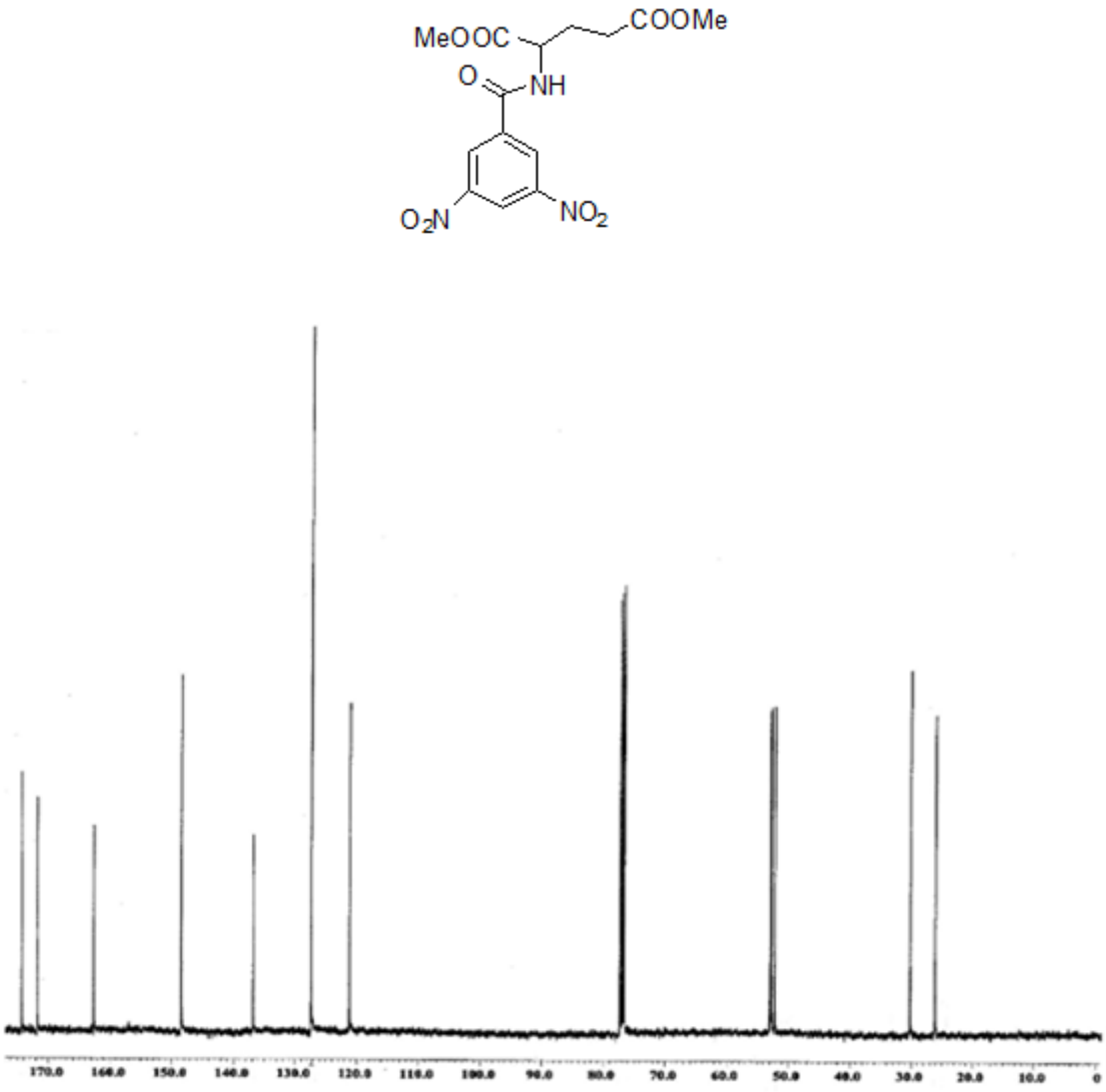


Figure S11: ^{13}C NMR ($CDCl_3$, 125 MHz, δ_{ppm}) spectra of compound **D.**

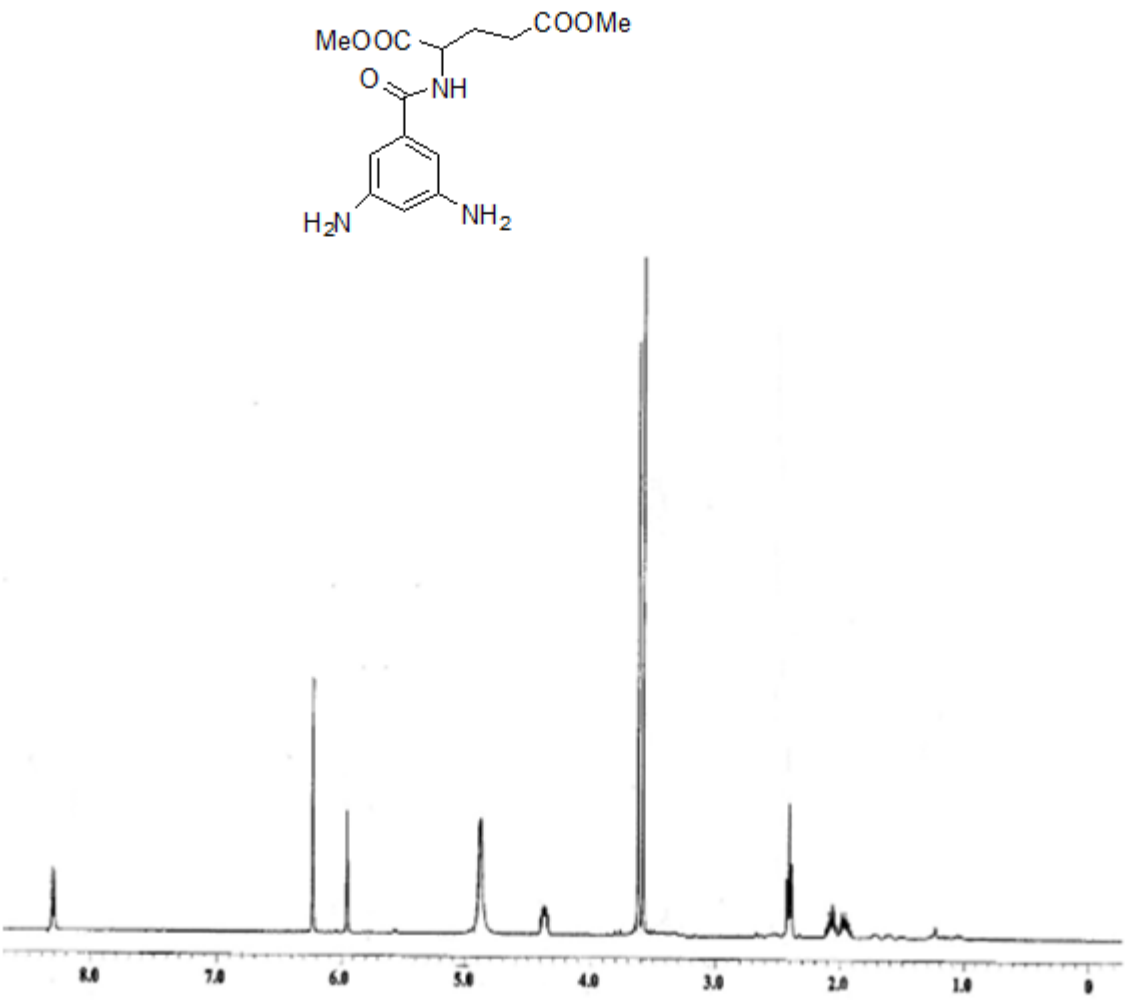


Figure S12: ^{1}H NMR (CDCl3, 400 MHz, δ_{ppm}) spectra of compound **F.**

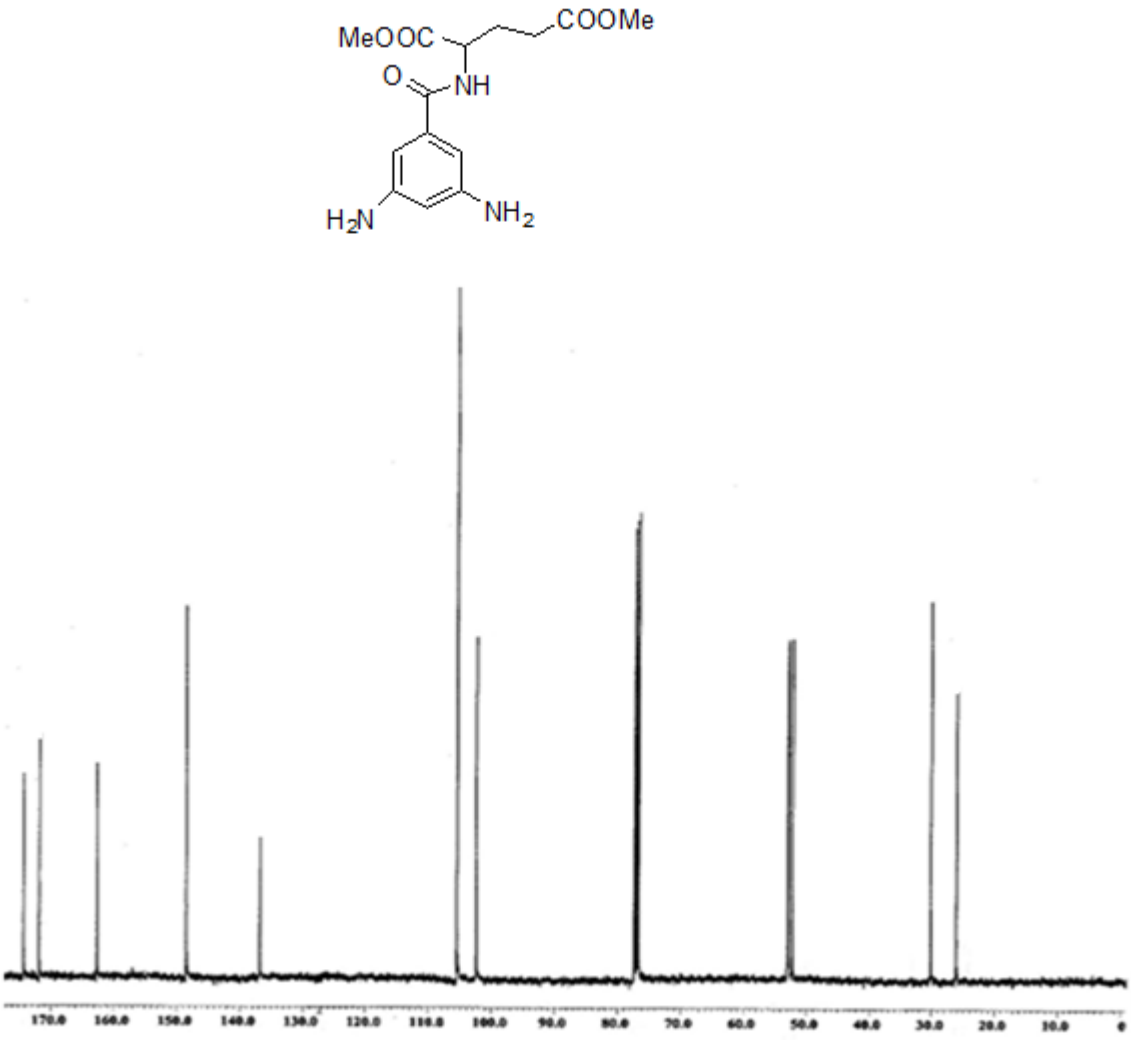
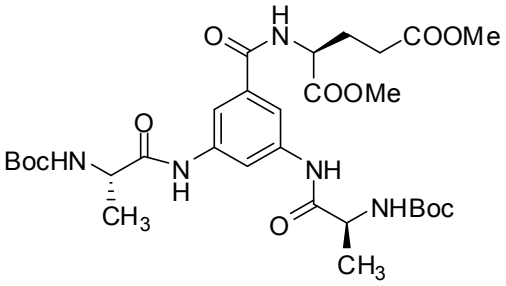


Figure S13: ^{13}C NMR ($CDCl_3$, 125 MHz, δ_{ppm}) spectra of compound **F.**



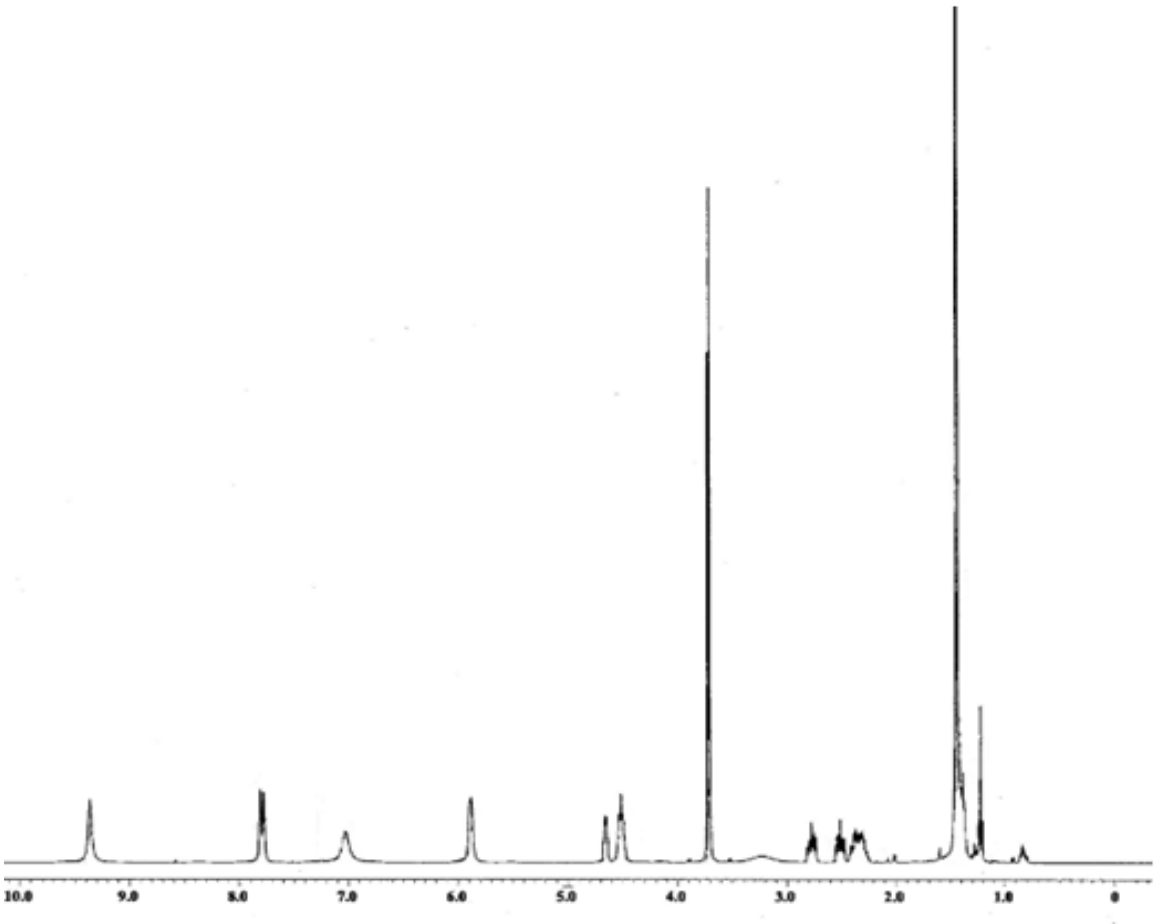
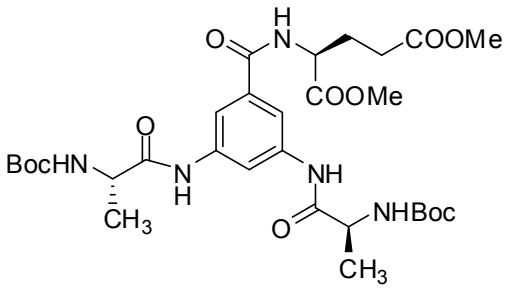


Figure S14: ^{1}H NMR (CDCl3, 400 MHz, δppm) spectra of peptide **2**.



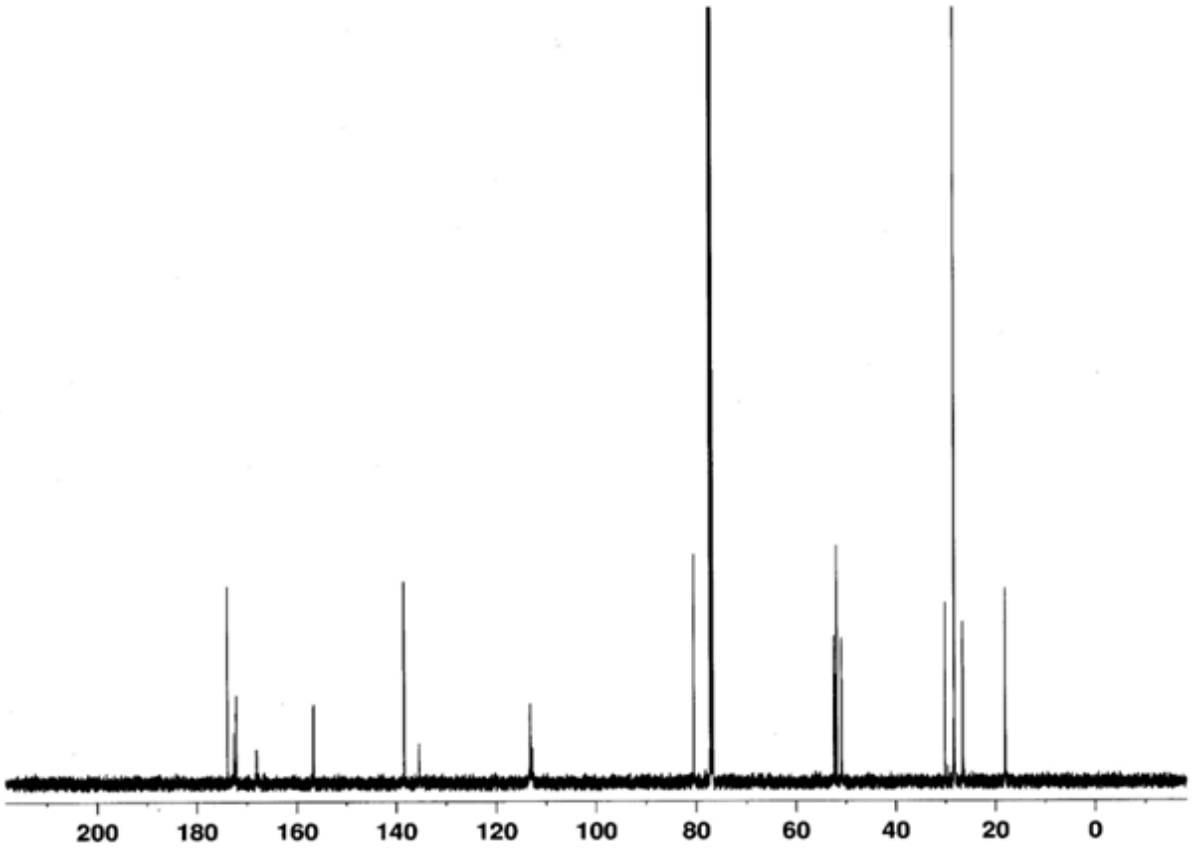


Figure S15: ^{13}C NMR ($CDCl_3$, 125 MHz, δ_{ppm}) spectra of peptide **2**.