Electronic Supplementary Material (ESI) for RSC Advances.


## Supplementary Information

# Photo-responsive modulation of hybrid peptide assembly, charge transfer complex formation and gelation†

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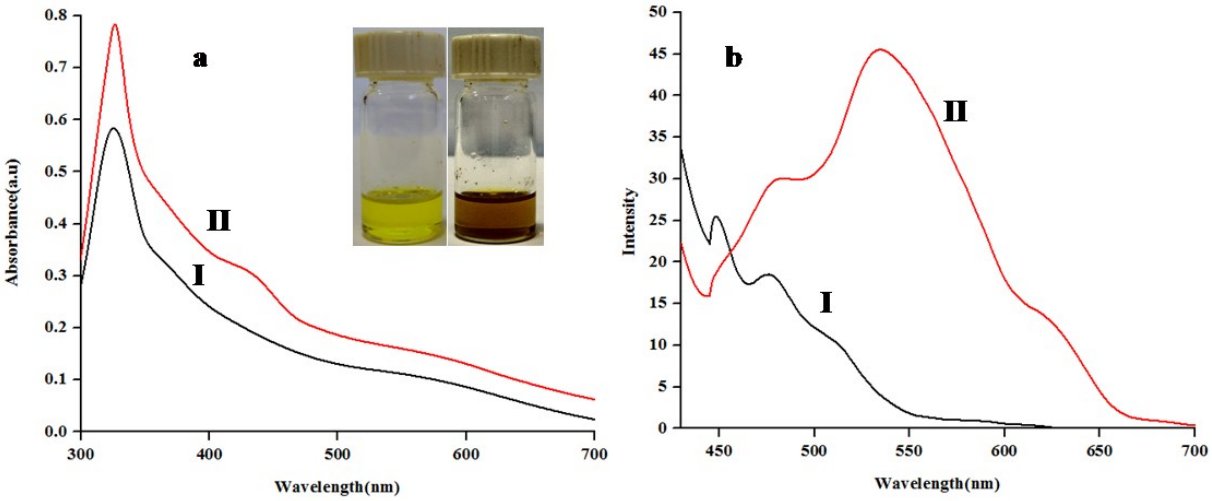
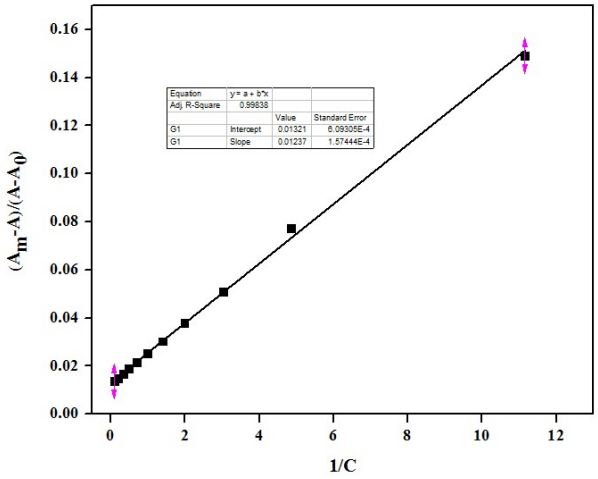
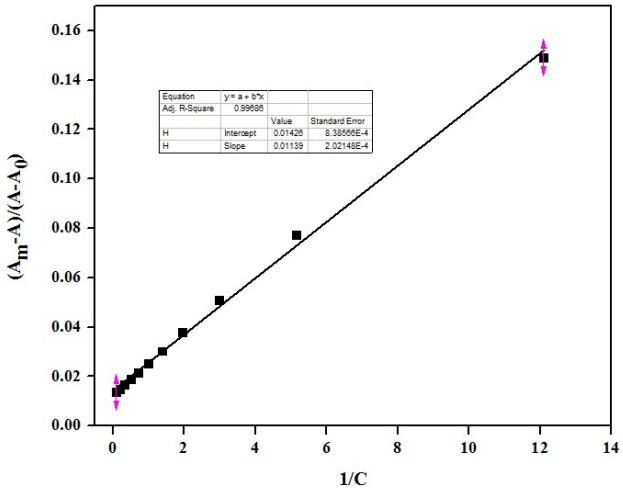


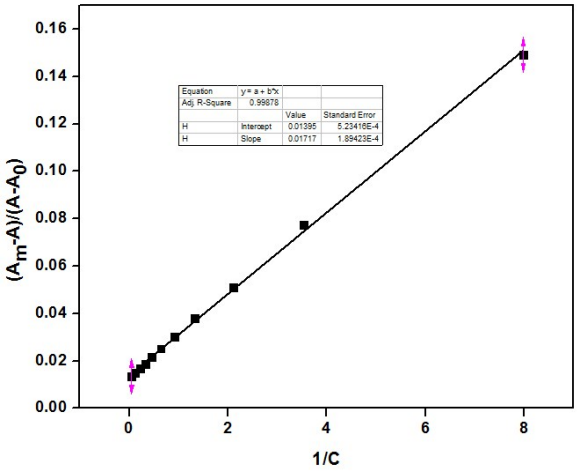

ESI Figure S1: (a) UV spectra of peptide 1 with picric acid in 1,2-dichlorobenzene (I) before UV light (II) after UV light. (b) Fluorescence spectra of peptide 1 with picric acid in 1,2-dichlorobenzene (I) before UV light (II) after UV light (ex. 420 nm).



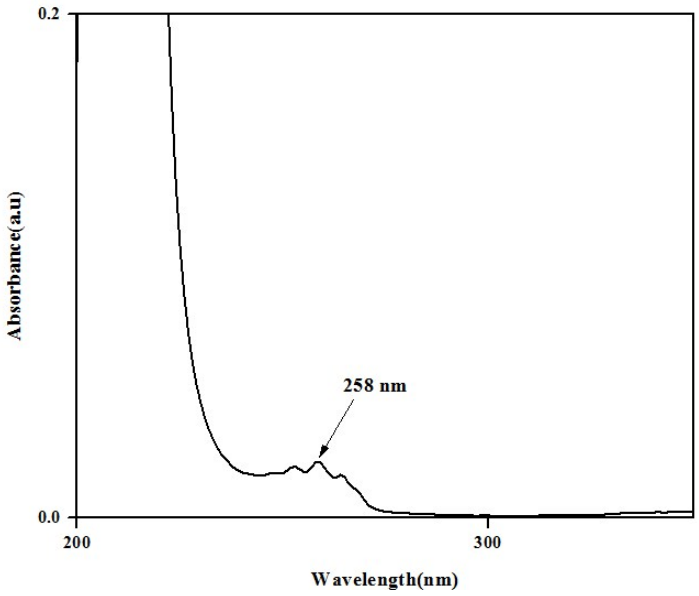

ESI figure S 2a: A plot of Benesi Hildebrand equation from UV/Vis spectroscopy of peptide 1. Absorbance is measured with increasing concentration of picric acid at a constant concentration of peptide 1 ($10^{-5}$ M). The plot shows that maximum at a 1:1 molar ratio of peptide 1 and picric acid and binding const. is 8.08 x $10^{10}M^{-1}$.



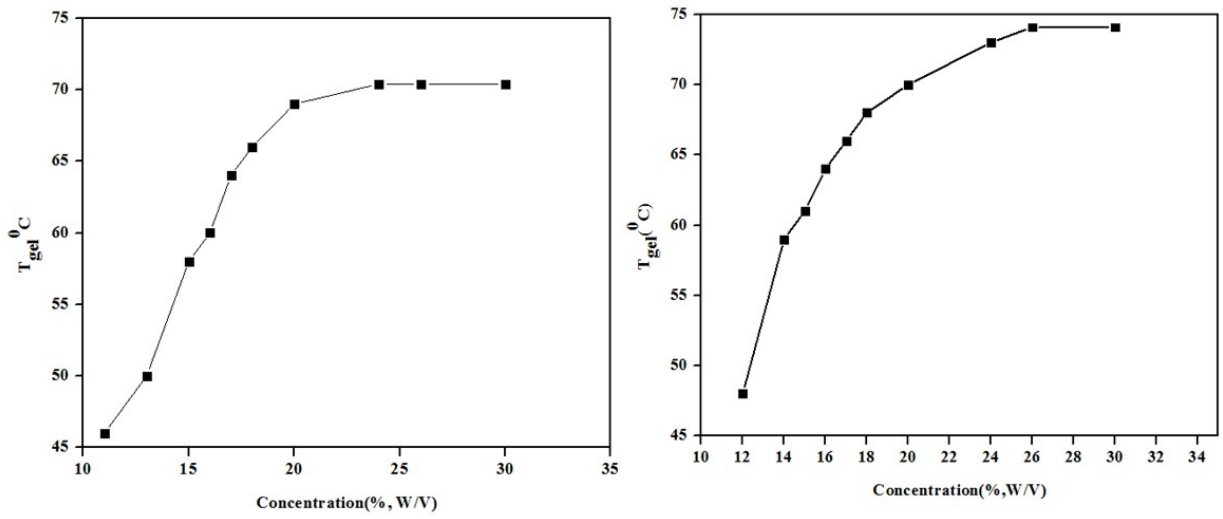

ESI figure S 2b: A plot of Benesi Hildebrand equation from UV/Vis spectroscopy of peptide 2. Absorbance is measured with increasing concentration of picric acid at a constant concentration of peptide 1 ($10^{-5}$ M). The plot shows that maximum at a 1:1 molar ratio of peptide 1 and picric acid and binding const. is 8.78 x $10^{10}M^{-1}$.




ESI figure S 2c: A plot of Benesi Hildebrand equation from UV/Vis spectroscopy of peptide 3. Absorbance is measured with increasing concentration of picric acid at a constant concentration of peptide 1 ($10^{-5}$ M). The plot shows that maximum at a 1:1 molar ratio of peptide 1 and picric acid and binding const. is 5.82 x $10^{10}M^{-1}$.




ESI figure S3: UV/visible absorption of peptide 2 in methanol ($10^{-5}$ M).




ESI figure S4 : The change of Tgel with increasing concentration of organogel obtained from (a) peptide 2 (MGC 11 mg/mL) and (b) peptide 3 (MGC 12 mg/mL) in 1,2-dichlorobenzene.

**Experimental:**

**Synthesis of peptide 1:**

**(a) Boc–Phe(1)–OH :** A solution of L-phenylalanine (3.30 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. Di-tert-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 ice-water bath, covered with a layer of ethyl acetate (about 50 mL) and acidified with a dilute solution of $KHSO_4$ 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 under vacuum. The pure material was obtained as a waxy solid.

Yield: 4.87 g, (18.35 mmol, 91.78%).

$^1$H NMR (DMSO-$d_6$, 500 MHz, $\delta$ in ppm); 12.75 (br, 1H, COOH); 7.28–7.09 (m, 5H, Ph-ring -H); 7.11–7.09 (m, Phe NH); 4.09–4.01 (m, 1H, C$^{\alpha}$H Phe); 3.02–2.87 (m, 2H, C$^{\beta}$H Phe), 1.36 (s, 9H, Boc). $^{13}$C NMR (DMSO-$d_6$, 125 MHz, $\delta$ in ppm): 173.57, 155.41, 138.00, 129.05, 128.09, 126.27, 80.24, 55.10, 36.39, 20.73.

**(b) Boc-Phe(1)-Gly(2)-OMe .** 1.5 g (5.65 mmol) of Boc-Phe-OH was dissolved in 20 mL DCM in an ice-water bath. H-Gly-OMe was isolated from 1.44 g (11.5 mmol) of the corresponding methyl ester hydrochloride by neutralization and 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 1.16 g (5.65 mmol) dicyclohexylcarbodiimide (DCC) and 764 mg (5.65 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 (50 mL) and dicyclohexylurea (DCU) was filtered off. The organic layer was washed with 2M HCl (3x50 mL), brine (2x50 mL), 1(M) sodium carbonate (3x50 mL) and brine (2x50 mL) and dried over anhydrous sodium sulfate. It was evaporated under vacuum to yield Boc-Phe-Gly-OMe as a white solid.

Yield: 1.4 g (4.16 mmol, 73.66%).

$^{1}$H NMR (500 MHz, $CDCl_3$,$\delta$ in ppm): 7.26–7.24 (d , 2 H, Phe ring -H), 7.19–7.17 (m, 3H, Ph ring -H), 6.69-6.67 (m, 1 H, Gly(2) NH), 5.17-5.16 (m, 1H, Phe-NH), 4.40-4.39 (br, 1 H, Phe $C^{\alpha}$ H), 4.01-3.94 (m, 2H, Gly $C^{\alpha}$ H), 3.69 (s, 3H,–$OCH_3$), 3.16-3.14 (m, 2 H, Phe $C^{\beta}$H), 1.36-1.34 (s, 9H, Boc -$CH_3$). $^{13}$C NMR (125 MHz,$CDCl_3$,$\delta$ in ppm): 174.17, 170.44, 156.31, 136.86, 129.54, 128.26, 126.95, 80.2, 56.43, 56.4, 52.65, 38.54, 28.32, 24.76

**(c) Boc-Phe(1)-Gly(2)-OH .** To 1.1 g (3.26 mmol) of Boc-Phe-Gly-OMe, 15 mL MeOH and 2(M) 4.5 mL NaOH were added and the progress of saponification was monitored by thin layer chromatography (TLC). The reaction mixture was stirred. After10 h, methanol was removed under vacuum; the residue was dissolved in 50 mL of water and washed with diethyl ether (2x50 mL). Then the pH of the aqueous layer was adjusted to 2 using 1M HCl and it was extracted with ethyl acetate (3x50 mL). The extracts were pooled, dried over anhydrous sodium sulfate, and evaporated under vacuum to obtained compound as a waxy solid.

Yield: 1 g (3.1 mmol, 96.9 %).

$^{1}$H NMR (500 MHz, DMSO-$d_6$, $\delta$ in ppm): 12.53-12.51 (br, 1 H, –COOH), 8.29-8.26 (m, 1 H, Gly(2) -NH), 7.26–7.19 (m, 5H, Ph ring -H) 6.89-6.88 (m, 1H, Phe-NH), 4.21-4.19 (m, 1 H, Phe $C^{\alpha}$ H), 3.80 (m, 2H, Phe $C^{\beta}$ H), 3.02-2.99 (m, 1H, Gly $C^{\alpha}$H), 2.55-2.51 (m, 1H, Gly $C^{\alpha}$H), 1.31 (s, 9H, Boc- $CH_3$). $^{13}$C NMR (125 MHz, $CDCl_3$, $\delta$ in ppm): 174.20, 170.42, 156.29, 136.86, 129.54, 128.26, 126.95, 80.2, 56.43, 52.67, 38.54, 28.32, 24.72.

**(d) Boc-Phe(1)-Gly(2)-Phe(3)-OMe.** 1 g (3.1 mmol) Boc-Phe-Gly–OH was dissolved in 5 mL of DMF in an ice–water bath. H-Phe-OMe 1.1 g (6.2 mmol) was isolated from the corresponding methyl ester hydrochloride by neutralization and subsequent extraction with ethyl acetate and the ethyl acetate extract was concentrated to 7 mL. Then it was added to the reaction mixture, followed immediately by 640 mg (3.1 mmol) of dicyclohexylcarbodiimide (DCC) and 419 mg (3.1 mmol) of HOBt. The reaction mixture was allowed to come to room temperature and then stirred for 72 h. The residue was taken in 30 mL ethyl acetate and dicyclohexylurea (DCU) was filtered off. The organic layer was washed with 2(M) HCL (3x50 mL), brine (2x50 mL), then 1 (M) sodium carbonate (3x30 mL) and brine (2x30 mL) and dried over anhydrous sodium sulfate and evaporated under vacuum to yield the tripeptide

**1** as a white solid. Purification was done by silica gel column (100–200 mesh size) with an ethyl acetate and hexane mixture 1 : 2 as the eluent.

Yield: 1.2 g (2.73 mmol, 88%).

$^{1}$H NMR (500 MHz, $CDCl_3$, $\delta$ in ppm): 7.23–7.15 (m, 10H, Ph ring -H), 7.15-7.13 (m,1H, Phe-NH and 1H, Gly-NH), 5.42 (br, 1H, Phe-NH), 4.80-4.77 (m, 1H, Phe $C^{\alpha}$ H), 4.01-3.95 (m, 1H, Phe $C^{\alpha}$ H), 3.94-3.90 (m, 2H, Gly $C^{\alpha}$H), 3.63 (s, 3 H,-$OCH_3$), 3.10-3.08 (m, 2 H, Phe $C^{\beta}$H) 3.03-3.00 (m, 2 H, Phe $C^{\beta}$ H), 1.34 (s, 9 H, Boc-$CH_3$),
$^{13}$CNMR (125 MHz, $CDCl_3$, $\delta$ in ppm): 172.02, 171.74, 168.47, 156.24, 136.71, 129.56, 129.02, 127.39, 126.67, 79.89, 60.24, 55.62, 53.41, 52.14, 42.78, 38.26, 37.68, 29.51, 25.10, 14.02. ESIMS: *m/z* 484.26, $[M+H]^+$ ; $M_{calcd}$ 483.23 .

**Synthesis of peptide 2:**

**(b) Boc-Phe(1)-β-Ala(2)-OMe .** 1.5 g (5.67 mmol) of Boc-Phe-OH was dissolved in 15 mL DCM in an ice-water bath. H-β-Ala-OMe was isolated from 1.17 g (11.34 mmol) of the corresponding methyl ester hydrochloride by neutralization and 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 1.17 g (5.67 mmol) dicyclohexylcarbodiimide (DCC) and 766.1 m g (5.67 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 dicyclohexylurea (DCU) was filtered off. The organic layer was washed with 2M HCl (3x50 mL), brine (2x50 mL), 1(M) sodium carbonate (3x50 mL) and brine (2x50 mL) and dried over anhydrous sodium sulfate. It was evaporated under vacuum to yield Boc-Phe-Gly-OMe as a white solid.

Yield: 1.3 g (3.71 mmol, 65.43%).

$^{1}$H NMR (500 MHz, $CDCl_3$,$\delta$ in ppm): 7.24-7.19 (m, 2H, Ph ring -H), 7.16–7.12 (m, 3H, Ph ring -H), 6.69-6.67 (m, 1H, β-Ala -NH), 5.39-5.37 (m, 1H, Phe-NH), 4.30-4.27 (br, 1H, Phe $C^{\alpha}$ H), 3.58-3.56 (s, 3 H,–$OCH_3$), 3.45-3.41 (m, 2H, β-Ala $C^{\alpha}$ H), 2.97-2.96 (m, 2 H, Phe $C^{\beta}$ H), 2.42-2.25 (m, 2H, β-Ala $C^{\beta}$ H) 1.33 (s, 9H, Boc-$CH_3$).

$^{13}$C NMR (125 MHz, $CDCl_3$, $\delta$ in ppm): 172.76, 171.75, 156.31, 137.13, 129.57, 129.79, 127.06, 80.20, 56.17, 51.90, 39.13, 35.06, 33.85, 29.55.

**(c) Boc-Phe(1)-β-Ala(2)-OH .** To 1.24 g (3.5 mmol) of Boc-Phe-β-Ala-OMe, 15 mL MeOH and 2(M) 4.65 mL NaOH were added and the progress of saponification was monitored by thin layer chromatography (TLC). The reaction mixture was stirred. After10 h, methanol was removed under vacuum; the residue was dissolved in 50 mL of water and washed with diethyl ether (2x50 mL). Then the pH of the aqueous layer was adjusted to 2 using 1M HCl and it was extracted with ethyl acetate (3x50 mL). The extracts were pooled, dried over anhydrous sodium sulfate, and evaporated under vacuum to obtained compound as a waxy solid.

Yield: 1.11 g (3.29 mmol, 93.42%).

$^{1}$H NMR (500 MHz, DMSO-$d_6$, $\delta$ in ppm): 12.22-12.19 (br, 1 H, –COOH), 7.94-7.91 (br, 1H, β-Ala(2) -NH), 7.27–7.22 (m, 5H, Phe ring -H ) 6.86-6.84 (d, 1H, Phe-NH), 4.01-3.99 (m, 1 H, Phe $C^{\alpha}$ H), 3.33-3.28 (m, 2H, Phe $C^{\beta}$-H), 2.91-2.89 (m, 1H, β-Ala $C^{\alpha}$H), 2.74-2.70 (m, 1H, β-Ala $C^{\alpha}$H), 2.35-2.32 (m, 2H, β-Ala $C^{\beta}$ H) 1.29 (s, 9H, BOC-$CH_3$). $^{13}$C NMR (125 MHz, $CDCl_3$, δ in ppm): 172.84, 170.42, 154.94, 137.93, 131.24, 129.13, 127.94, 126.95, 77.64, 56.43, 52.67, 38.54, 28.32.

**(d) Boc-Phe(1)-β-Ala(2)-Phe(3)-OMe .** 1.1 g (3.3 mmol) Boc-Phe-β-Ala–OH was dissolved in 5 mL of DMF in an ice–water bath. H-Phe-OMe 1.18 g (6.6 mmol) was isolated from the corresponding methyl ester hydrochloride by neutralization and subsequent extraction with ethyl acetate and the ethyl acetate extract was concentrated to 7 mL. Then it was added to the reaction mixture, followed immediately by 681 mg (3.3 mmol) of dicyclohexylcarbodiimide (DCC) and 446 mg (3.3 mmol) of HOBt. The reaction mixture was allowed to come to room temperature and then stirred for 72 h. The residue was taken in 30 mL ethyl acetate and dicyclohexylurea (DCU) was filtered off.The organic layer was washed with 2(M) HCL (3x50 mL), brine (2x50 mL), then 1 (M) sodium carbonate (3x30 mL) and brine (2x30 mL) and dried over anhydrous sodium sulfate and evaporated under vacuum to yield the tripeptide **1** as a white solid. Purification was done by silica gel column (100–200 mesh size) with an ethyl acetate and hexane mixture 1:2 as the eluent.

Yield : 1 g (2 mmol, 61%).

$^{1}$H NMR (500MHz, $CDCl_3$, δ in ppm): 7.23–7.14 (m, 10H, 2 phenyl ring protons and 1H, Phe-NH), 6.84-6.83 (br, 1H, β-ala -NH), 6.51-6.49 (br, 1H, Phe-NH), 5.25-5.23 (m, 1H, Phe –NH), 4.82-4.79 (m, 1H, Phe $C^{\alpha}$ H), 4.28 (br, 1H, Phe $C^{\alpha}$ H), 3.74 (s, 3H,-$OCH_3$), 3.22-3.15 (m, 2H, β-ala $C^{\alpha}$H), 3.14-2.96 (m, 2H, Phe $C^{\beta}$H) 2.95-2.84 (m, 1H, Phe $C^{\beta}$H) 2.38-2.24 (m, 1H, Phe $C^{\beta}$ H),2.22-2.15 (m, 1H, β-Ala $C^{\beta}$ H),2.00-1.98(m,1H, β-Ala $C^{\beta}$H), 1.37 (s, 9 H, Boc-$CH_3$).
$^{13}$CNMR (125 MHz, $CDCl_3$, *δ* in ppm): 173.01, 171.84, 172.37, 156.65, 137.62, 136.56, 129.05, 128.79, 128.47, 127.22, 127.01, 79.96, 57.25, 55.60, 53.36, 52.14, 39.42, 38.22, 37.81,30.78, 29.27. ESIMS: *m/z* 498.13, 498.18; $[M+H]^+$ ; $M_{calcd}$ 497.25 .

**Synthesis of peptide 3:**

**(b) Boc-Phe(1)-γ-Abu(2)-OMe.** 1.5 g (5.67 mmol) of Boc-Phe-OH was dissolved in 15 mL DCM in an ice-water bath. H-γ-Abu-OMe was isolated from 1.7 g (11.34 mmol) of the corresponding methyl ester hydrochloride by neutralization and 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 1.17 g (5.67 mmol) dicyclohexylcarbodiimide (DCC) and 766.1 m g (5.67 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 dicyclohexylurea (DCU) was filtered off. The organic layer was washed with 2M HCl (3x50 mL), brine (2x50 mL), 1(M) sodium carbonate (3x50 mL) and brine (2x50 mL) and dried over anhydrous sodium sulfate. It was evaporated in a vacuum to yield Boc-Phe-γ-Abu-OMe as a white solid.

Yield: 1.2 g (3.29 mmol, 58.07%).

$^{1}$H NMR (500 MHz, $CDCl_3$, δ in ppm): 7.26–7.16 (m, 5H, phenyl ring protons), 6.39 (br, 1H, γ-Abu(2) NH), 5.24 (s, 1H, Phe-NH), 4.25 (br, 1 H, Phe $C^{\alpha}$ H), 3.61 (s, 3H,–$OCH_3$), 3.22-3.20 (m, 2H, Phe $C^{\beta}$ H), 3.00-2.97 (br, 2H, γ-Abu $C^{\gamma}$ H), 2.17-2.15 (br, 2H, γ-Abu $C^{\alpha}$H), 1.67-1.65(br, 2H, γ-Abu $C^{\beta}$H) 1.36 (s, 9 H, Boc-$CH_3$), $^{13}$C NMR (125 MHz, $CDCl_3$, δ in

ppm): 173.96, 171.84, 155.83, 137.23, 129.69, 128.94, 127.22, 80.38, 51.98, 39.19, 34.32, 31.55, 30.04, 28.64, 26.02.

**(c) Boc-Phe(1)-γ-Abu(2)-OH.** To 1.0 g (2.74 mmol) of Boc-Phe-γ-Abu-OMe, 15 mL MeOH and 2(M) 3.70 mL NaOH were added and the progress of saponification was monitored by thin layer chromatography (TLC). The reaction mixture was stirred. After10 h, methanol was removed under vacuum; the residue was dissolved in 50 mL of water and washed with diethyl ether (2x50 mL). Then the pH of the aqueous layer was adjusted to 2 using 1(M) HCl and it was extracted with ethyl acetate (3x50 mL). The extracts were pooled, dried over anhydrous sodium sulfate, and evaporated under vacuum to obtained compound as a waxy solid.

Yield : 850 mg (2.33 mmol, 85.12%).

$^{1}$H NMR (500 MHz, DMSO-$d_6$, δ in ppm): 12.02 (br, 1H, –COOH), 7.86 (br, 1 H, γ-Abu(2) -NH), 7.25–7.23 (m, 5H, phenyl ring protons) 6.85-6.84 (d, 1H, *J*=5, Phe-NH), 4.06 (m, 1H, Phe $C^{\alpha}$ H), 3.08-2.89 (m, 2H, Phe $C^{\beta}$ H), 2.85-2.73 (m, 2H, γ-Abu $C^{\gamma}$H), 2.17-2.15 (t, 2H, γ-abu $C^{\alpha}$H), 1.61-1.59 (m, 2H, γ-Abu $C^{\beta}$H),1.30 (s, 9H, Boc -$CH_3$). $^{13}$C NMR (125 MHz, $CDCl_3$, δ in ppm): 174.18, 171.42, 155.12, 138.11, 129.12, 128.07, 126.18, 77.91, 55.78, 39.00, 37.85, 30.44, 28.32, 26.72.

**(d) Boc-Phe(1)-γ-Abu(2)-Phe(3)-OMe.** 840 mg (2.3 mmol) Boc-Phe-γ-Abu–OH was dissolved in 5 mL of DMF in an ice–water bath. H-Phe-OMe 896 mg (5 mmol) was isolated from the corresponding methyl ester hydrochloride by neutralization and subsequent extraction with ethyl acetate and the ethyl acetate extract was concentrated to 7 mL. Then it was added to the reaction mixture, followed immediately by 475 mg (2.3 mmol) of dicyclohexylcarbodiimide (DCC) and 311 mg (2.3 mmol) of HOBt. The reaction mixture was allowed to come to room temperature and then stirred for 72 h. The residue was taken in 30 mL ethyl acetate and dicyclohexylurea (DCU) was filtered off.The organic layer was washed with 2(M) HCL (3x50 mL), brine (2x50 mL), then 1 (M) sodium carbonate (3x30 mL) and brine (2x30 mL) and dried over anhydrous sodium sulfate and evaporated under vacuum to yield the tripeptide **1** as a white solid. Purification was done by silica gel column (100–200 mesh size) with an ethyl acetate and hexane mixture 1 : 2 as the eluent.

Yield : 480 mg (0.91 mmol, 39.7%).

$^{1}$H NMR (500 MHz, $CDCl_3$, δ in ppm): 7.31–7.27 (m, 10H, 2 phenyl ring protons), 6.76 (br,1 H, Phe -NH), 6.45 (br, 1H, Phe –NH), 5.18 (br, 1 H, γ-Abu -NH), 4.87 (m, 1H, Phe $C^{\alpha}$ H), 4.29 (m, 1H, Phe $C^{\alpha}$ H), 3.75 (s, 3 H,-$OCH_3$), 3.24-3.21 (m, 2 H, Phe $C^{\beta}$H), 3.20-3.16 (m, 2 H, Phe $C^{\beta}$ H), 3.12-3.06 (m, 2H, γ-Abu $C^{\gamma}$ H), 2.10-2.05 (m. 2H, γ-Abu $C^{\alpha}$H), 1.75-1.72(m, 2H, γ-Abu $C^{\beta}$H), 1.42 (s, 9H, Boc-$CH_3$).

$^{13}$CNMR (125 MHz, $CDCl_3$, *δ* in ppm): 177.79, 174.03, 172.83, 158.58, 139.36, 131.06, 130.75, 129.07, 128.13, 127.89, 126.46, 80.15, 58.29, 57.72, 39.92, 38.19, 37.97,32.48, 31.86, 29.21, 24.73, 23.44. ESIMS: *m/z* 534.19, $[M+Na]^+$ ; $M_{calcd}$ 511.26 .

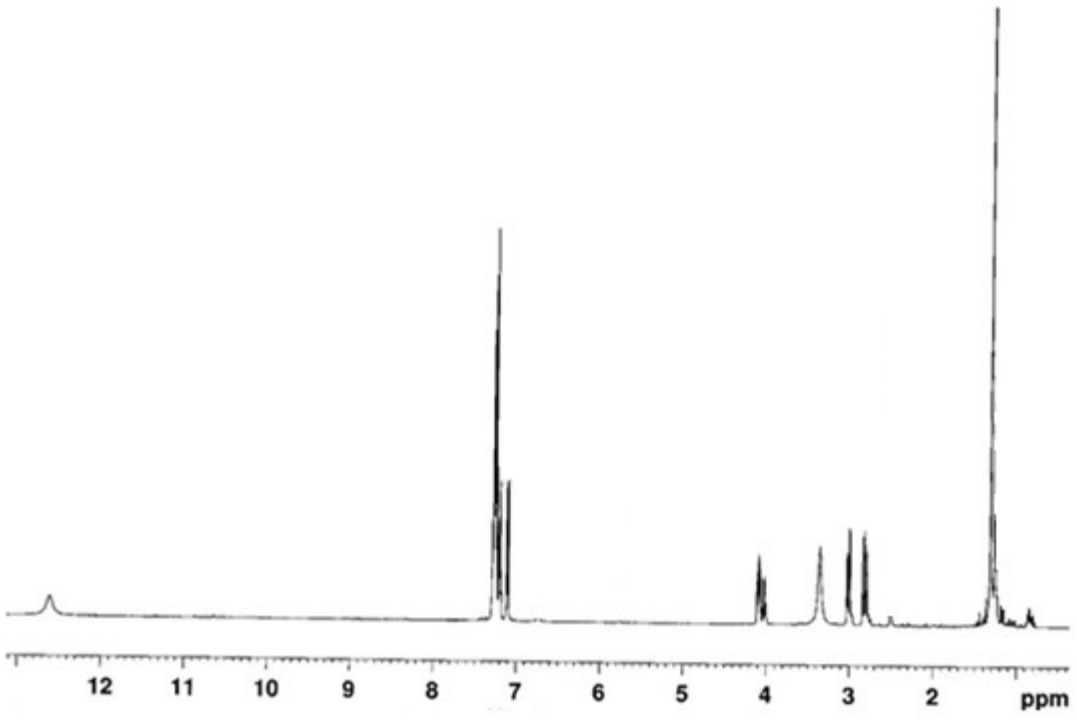



**Figure S1:** $^{1}$H NMR (500MHz, DMSO-d6) spectra of Boc-Phe-OH.

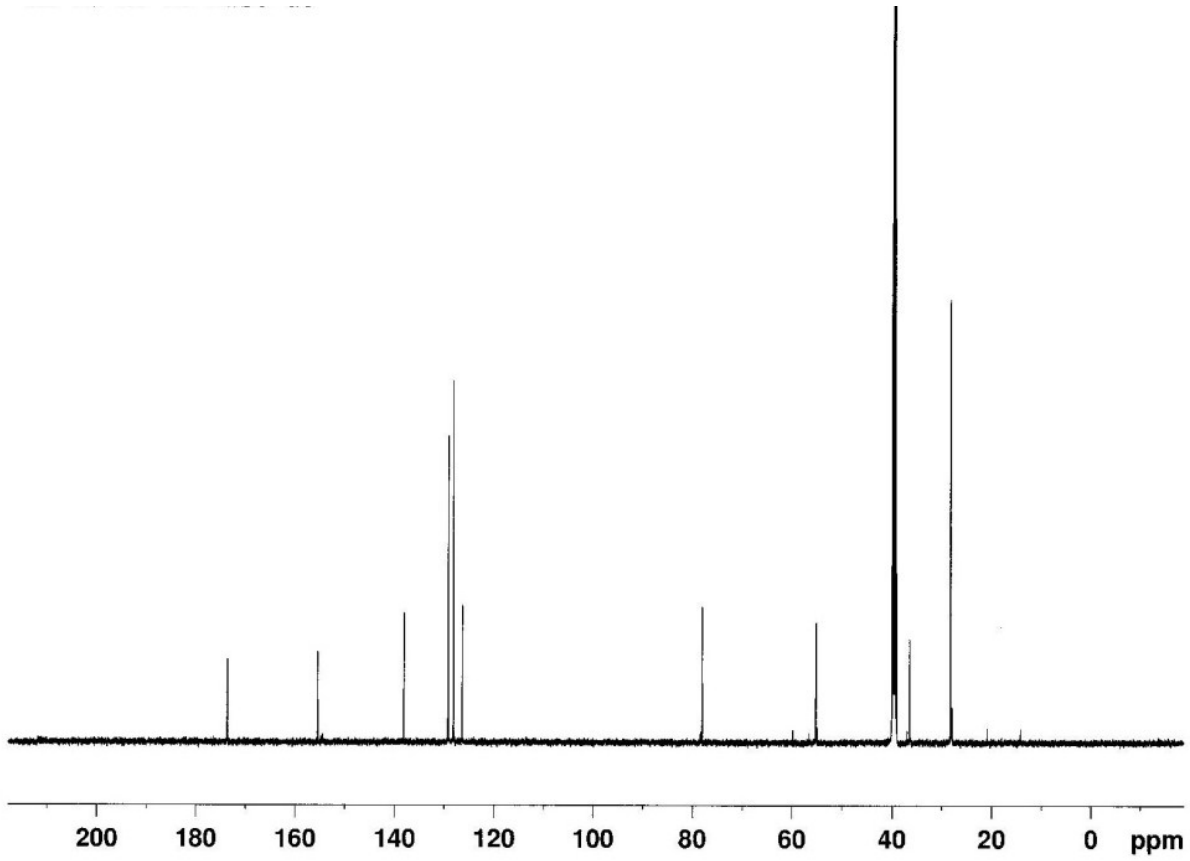



**Figure S2:** $^{13}C$ NMR (125 MHz, DMSO-$d_6$) spectra of Boc-Phe-OH.

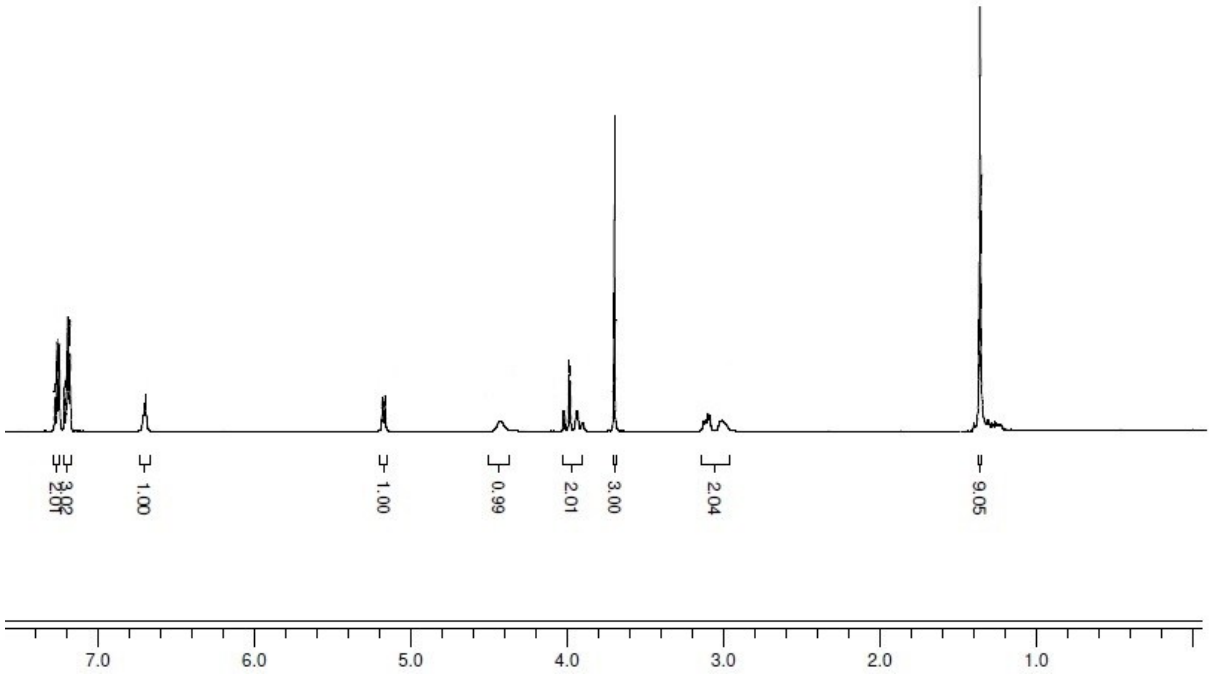



**Figure S3:** $^{1}H$ NMR(500 MHz, $CDCl_3$) of Boc-Phe-Gly-OMe.

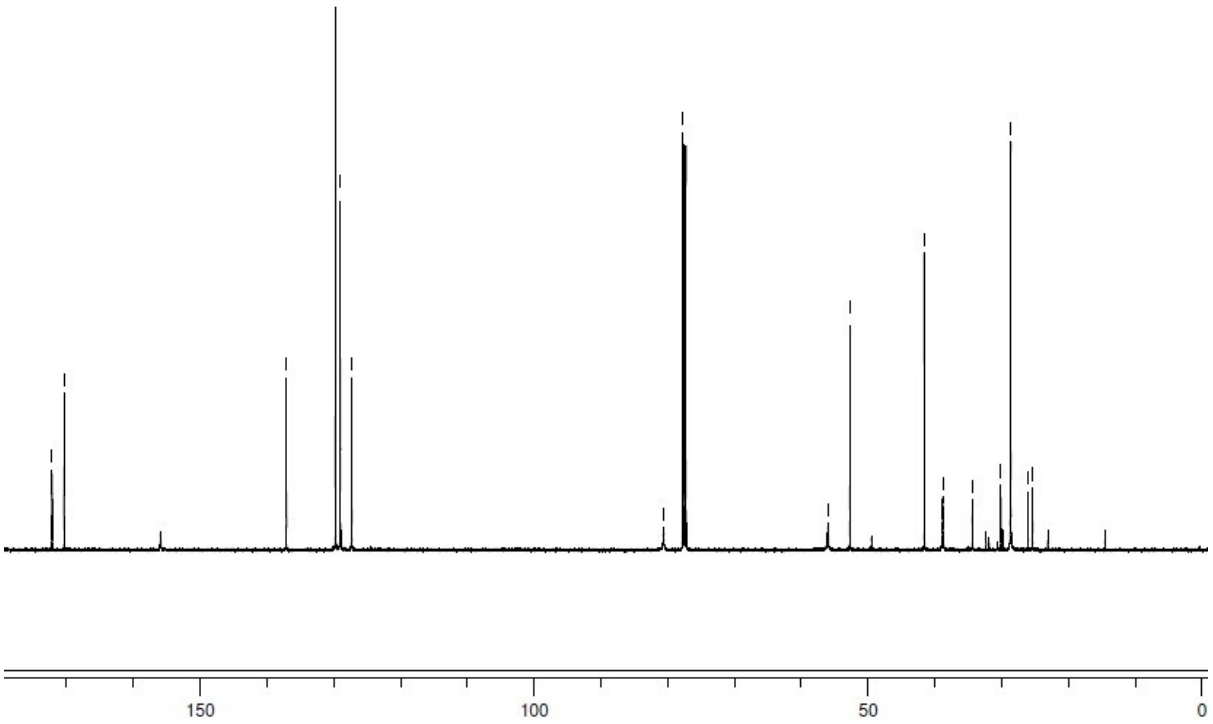



**Figure S4:** $^{13}C$ NMR(500 MHz, $CDCl_3$) of Boc-Phe-Gly-OMe.

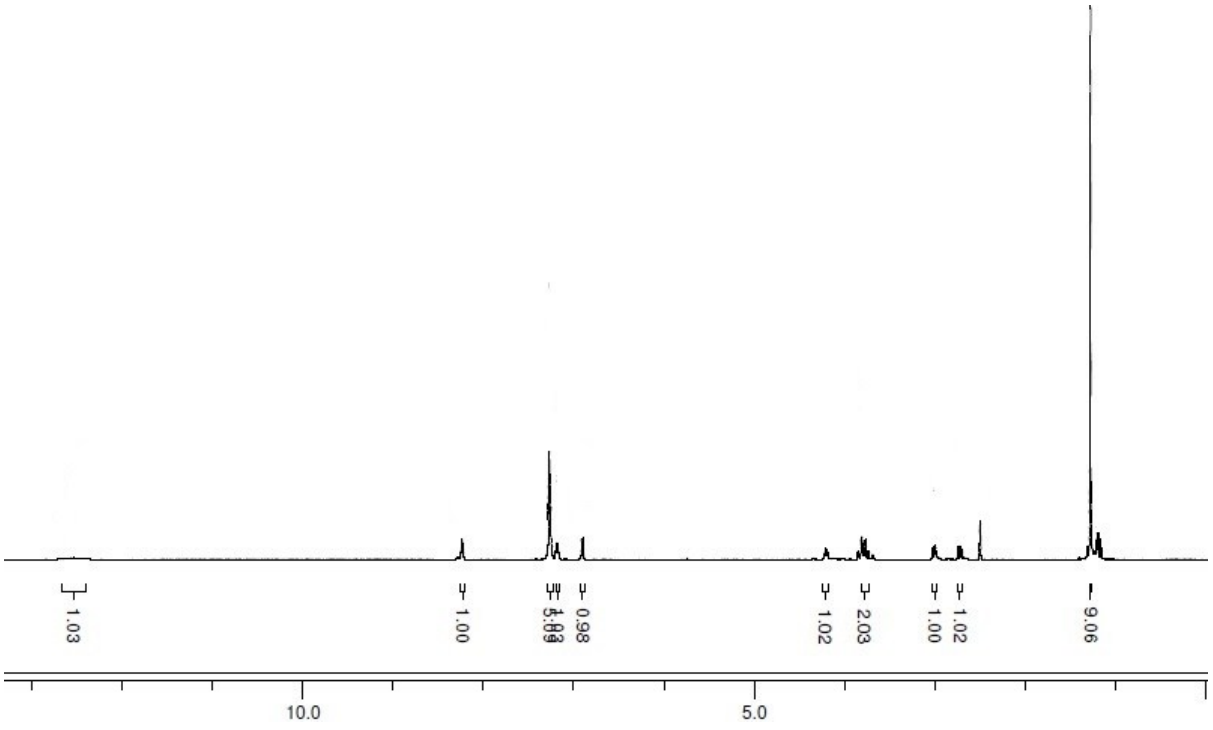



**Figure S5:** $^{1}H$ NMR (500MHz, DMSO-$d_6$) of Boc-Phe-Gly-OH.

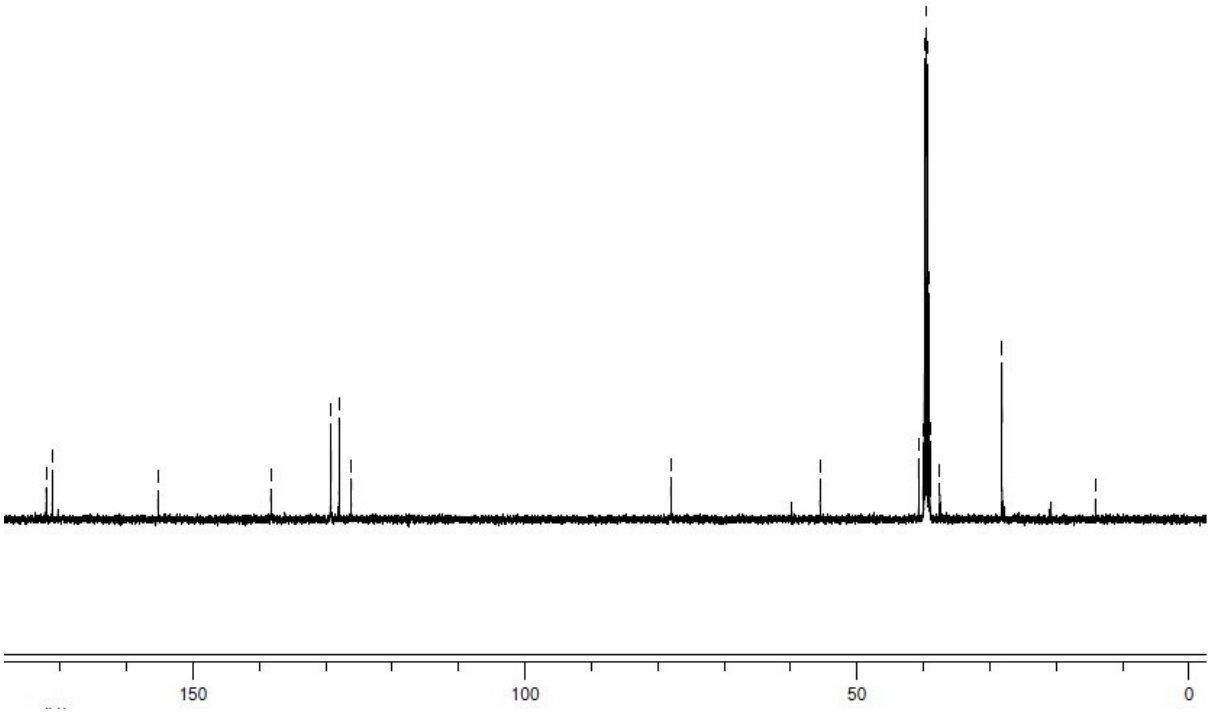



**Figure S6:** $^{13}$C NMR(125 MHz, DMSO-$d_6$) of Boc-Phe-Gly-OH.

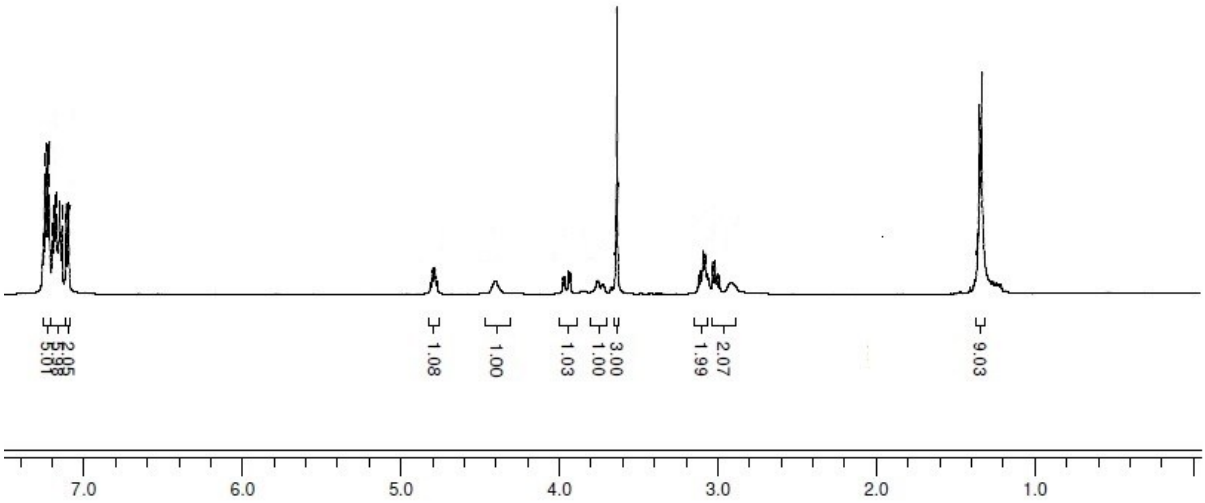



**Figure S7:** $^{1}$H NMR (500 MHz, $CDCl_3$) of Boc-Phe-Gly-Phe-OMe.

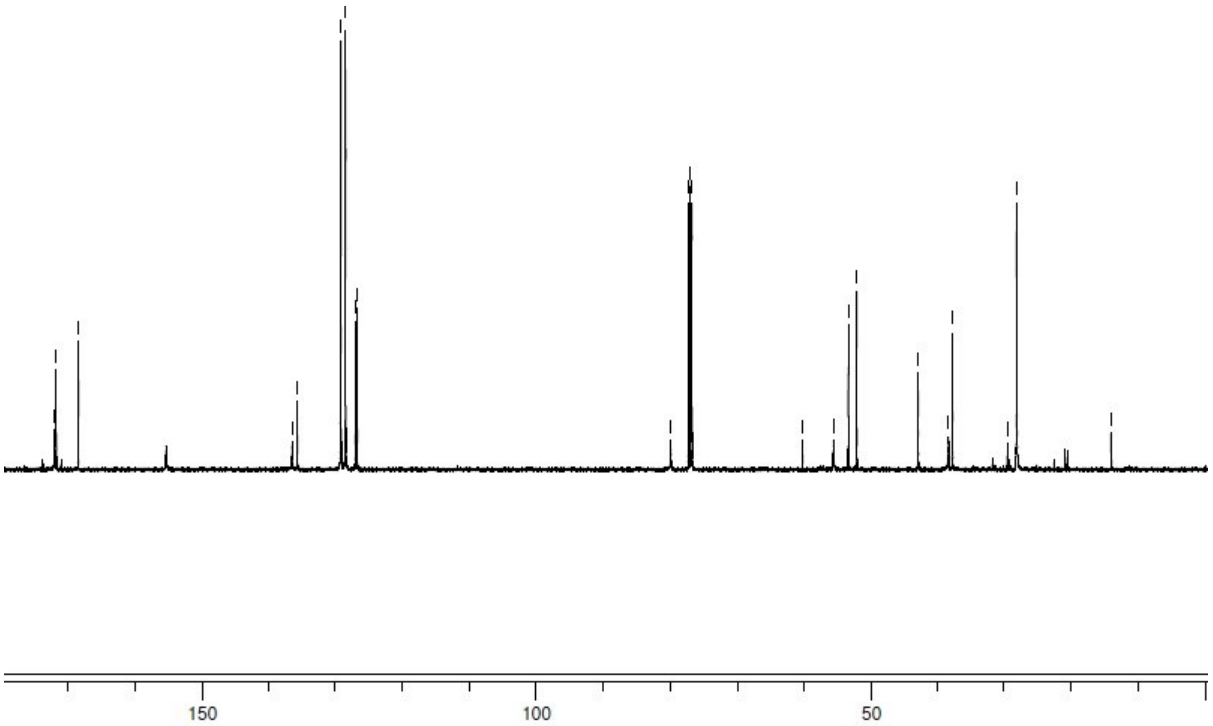



**Figure S8:** $^{13}C$ NMR(125 MHz, $CDCl_3$) of Boc-Phe-Gly-Phe-OMe.

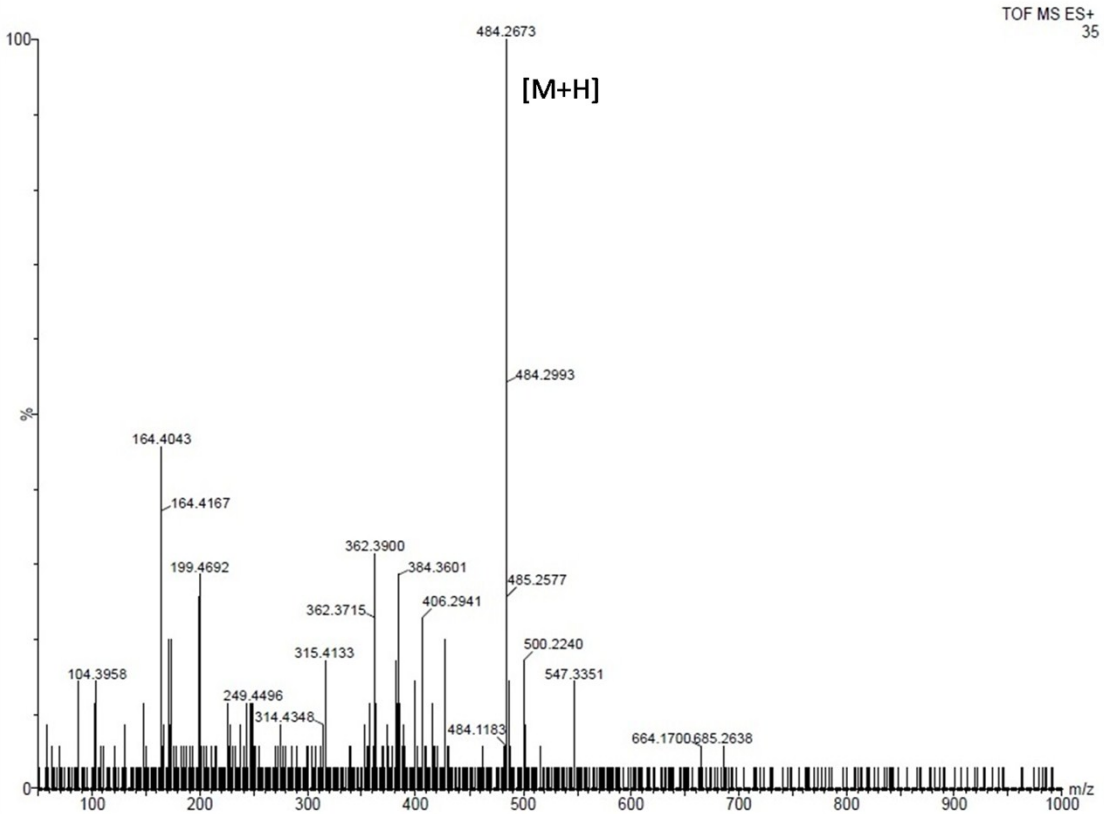



**Figure S9:** Mass Spectra of Boc-Phe-Gly-Phe-OMe.

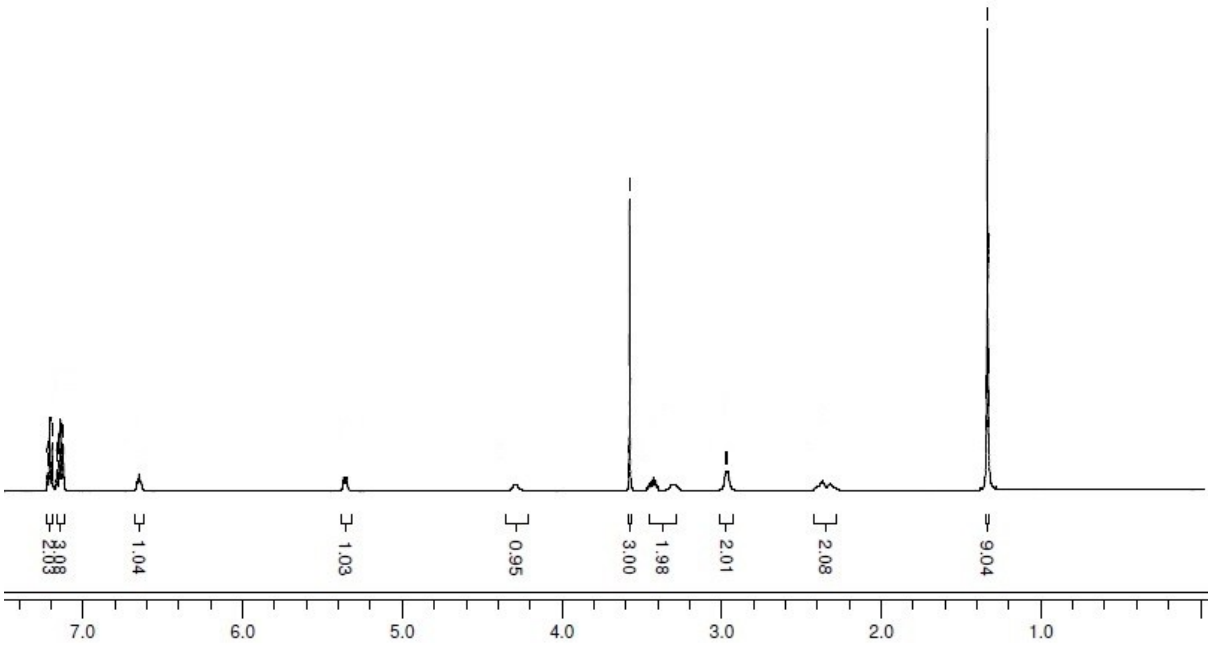



**Figure S10:** $^{1}H$ NMR (500 MHz, $CDCl_3$) of Boc-Phe-β-Ala-OMe.

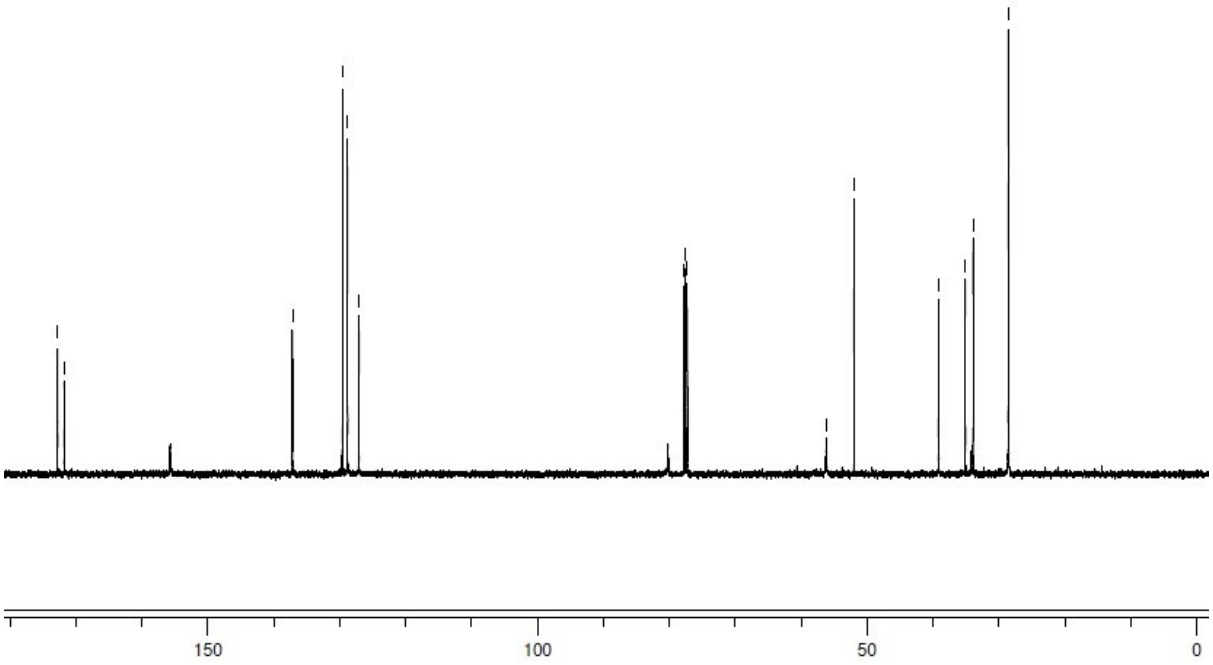



**Figure S11:** $^{13}C$ NMR(125 MHz, $CDCl_3$) of Boc-Phe-β-Ala-OMe.

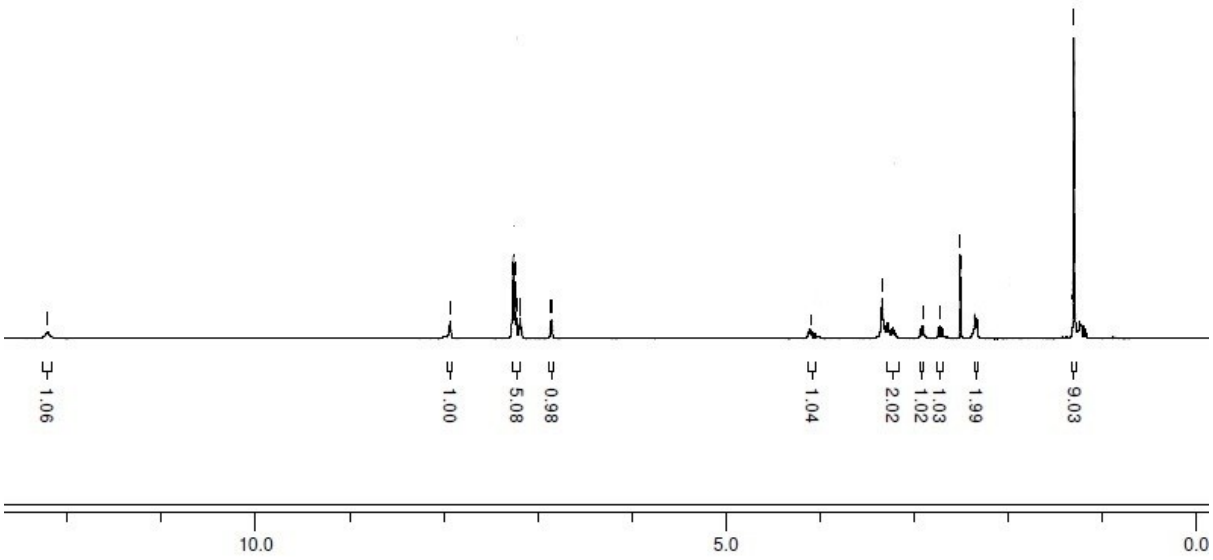



**Figure S12:** $^{1}$H NMR (500MHz, DMSO-d$_6$) of Boc-Phe-β-Ala-OH.

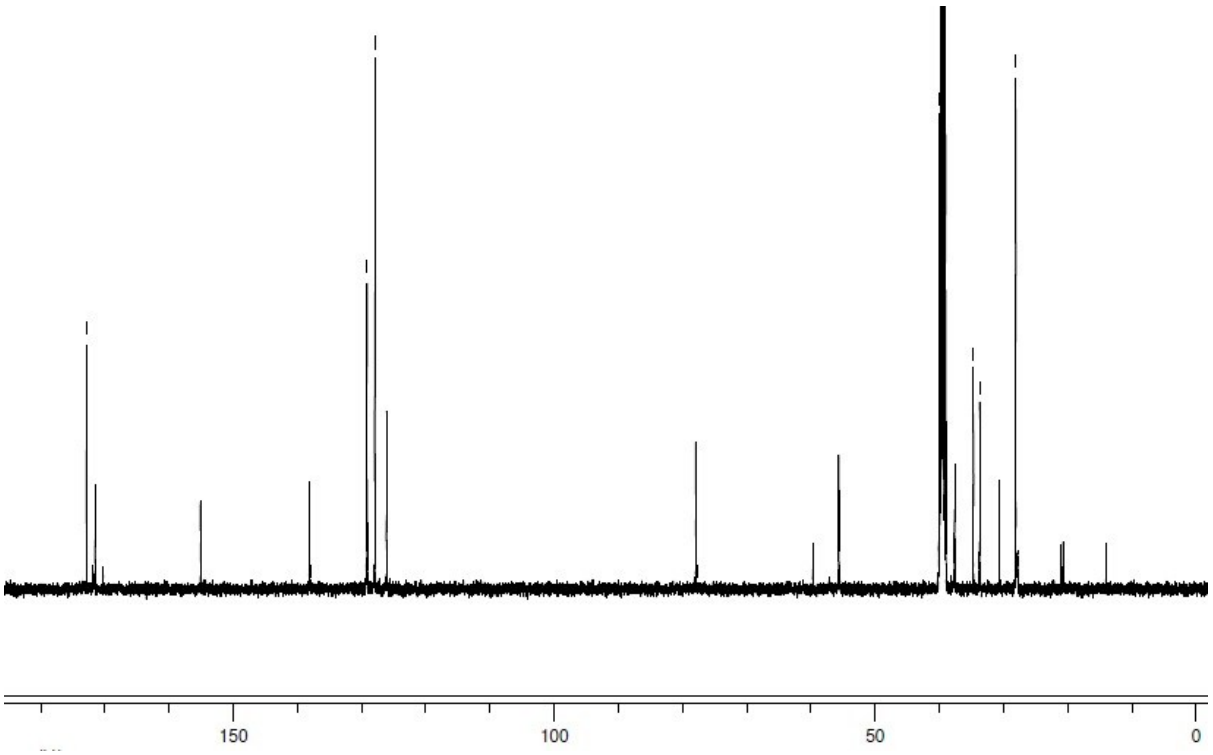



**Figure S13:** $^{13}$C NMR(125 MHz, DMSO-$d_6$) of Boc-Phe-β-Ala-OH.

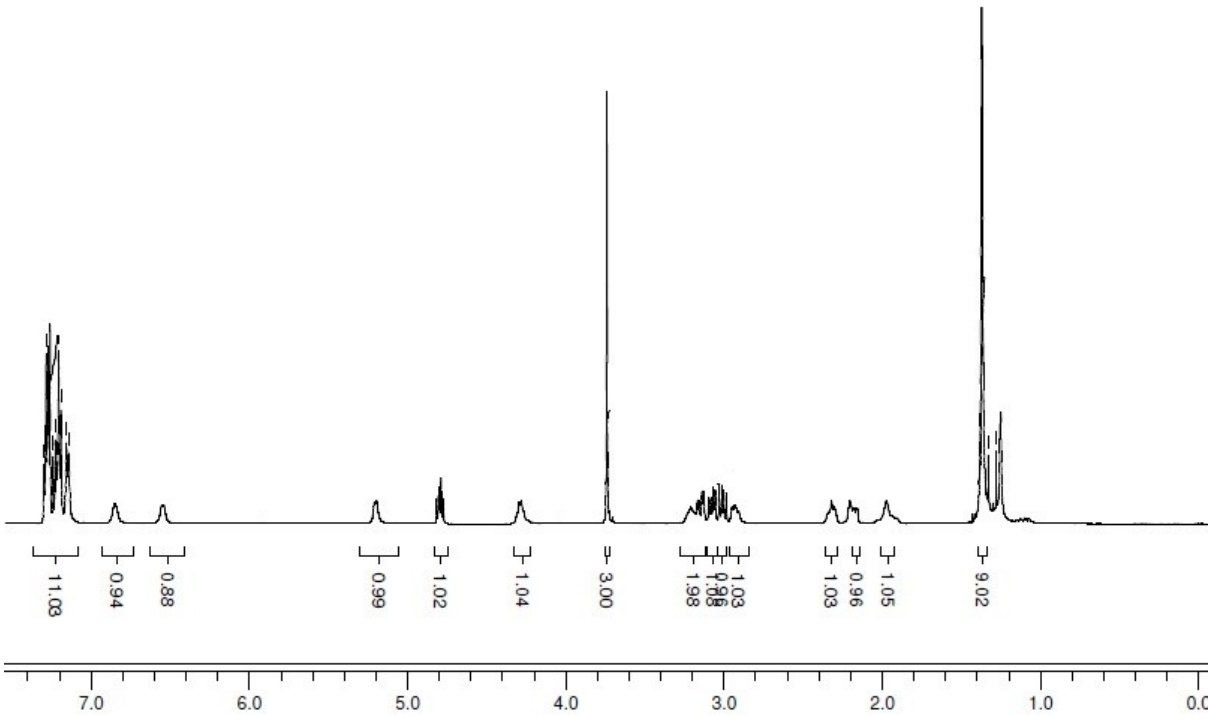



**Figure S14:** $^{1}H$ NMR (500 MHz, $CDCl_3$) of Boc-Phe-β-Ala-Phe-OMe.

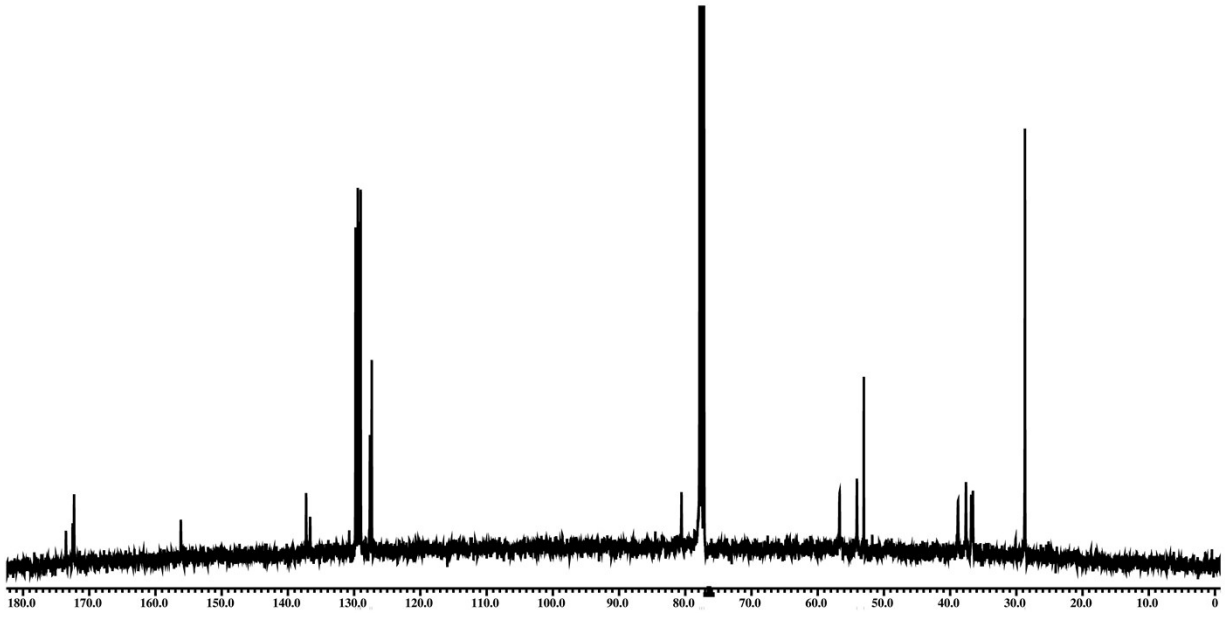



**Figure S15:** $^{13}C$ NMR(125 MHz, $CDCl_3$) of Boc-Phe-β-Ala-Phe-OMe.

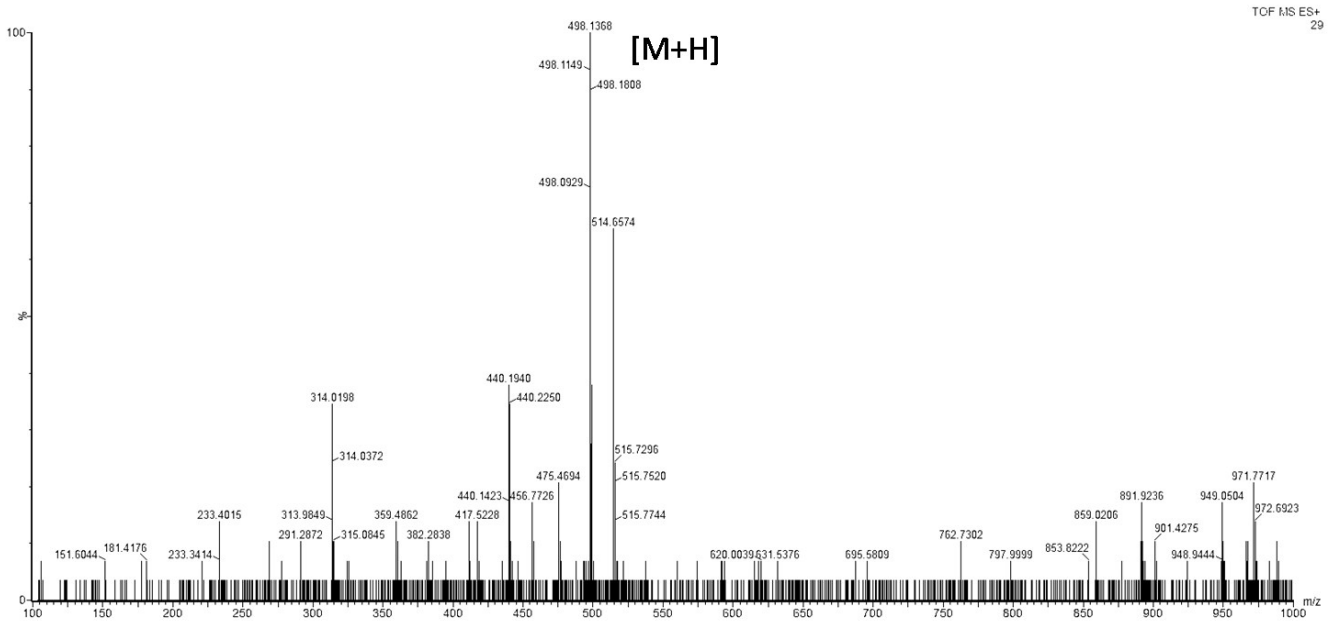



**Figure S16:** Mass spectra of Boc-Phe-β-ala-Phe-OMe.

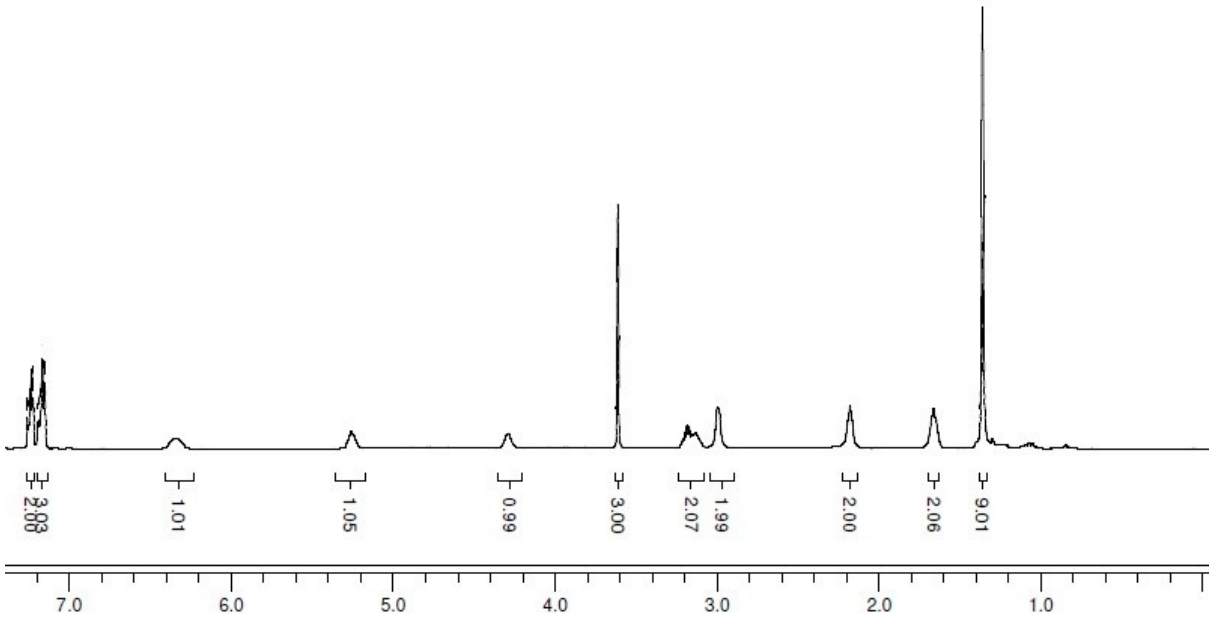



**Figure S17:** $^{1}H$ NMR(500 MHz, $CDCl_3$) of Boc-Phe-γ-Abu-OMe.

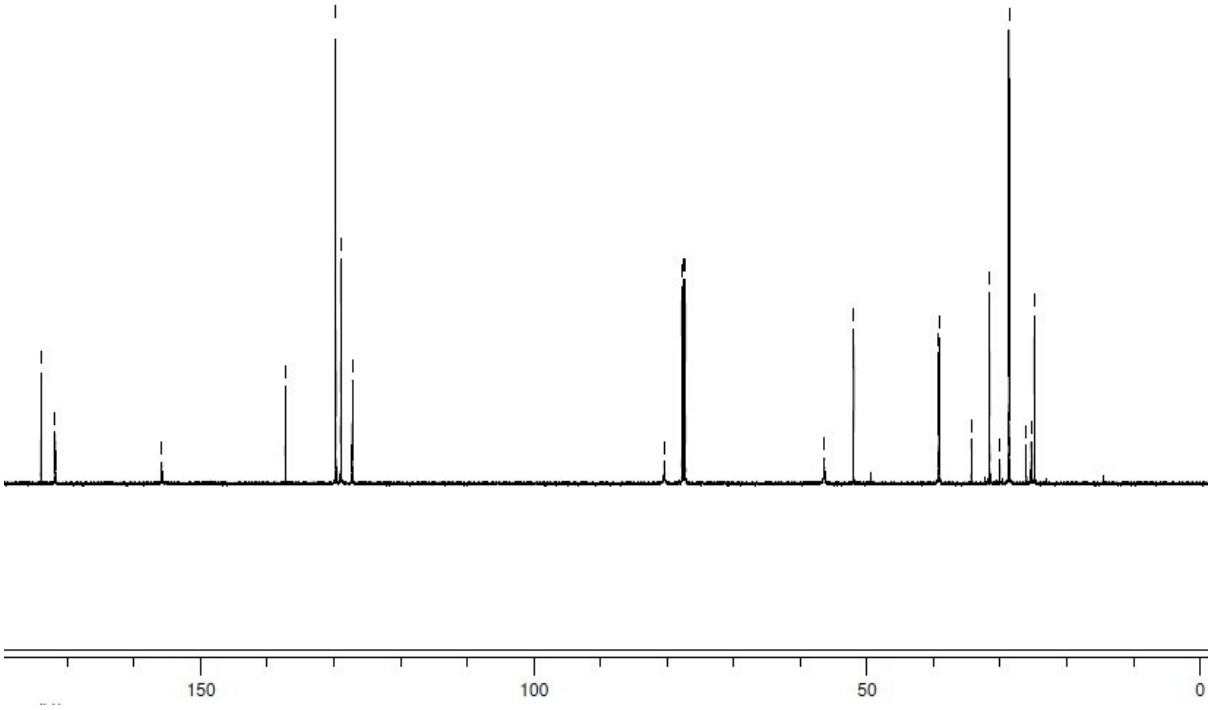



**Figure S18:** $^{13}C$ NMR (500 MHz, $CDCl_3$) of Boc-Phe-γ-Abu-OMe.

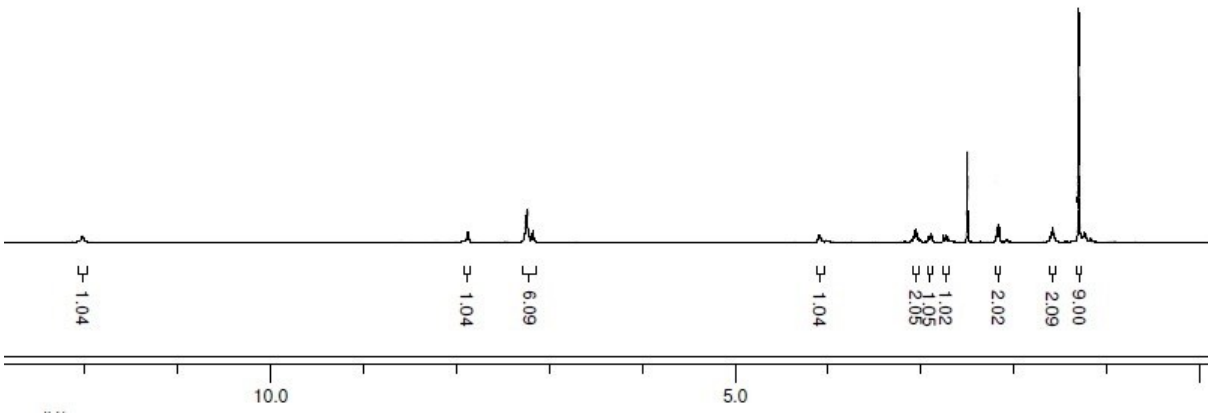



**Figure S19:** $^{1}H$ NMR(500MHz, DMSO-$d_6$) of Boc-Phe-γ-Abu-OH.

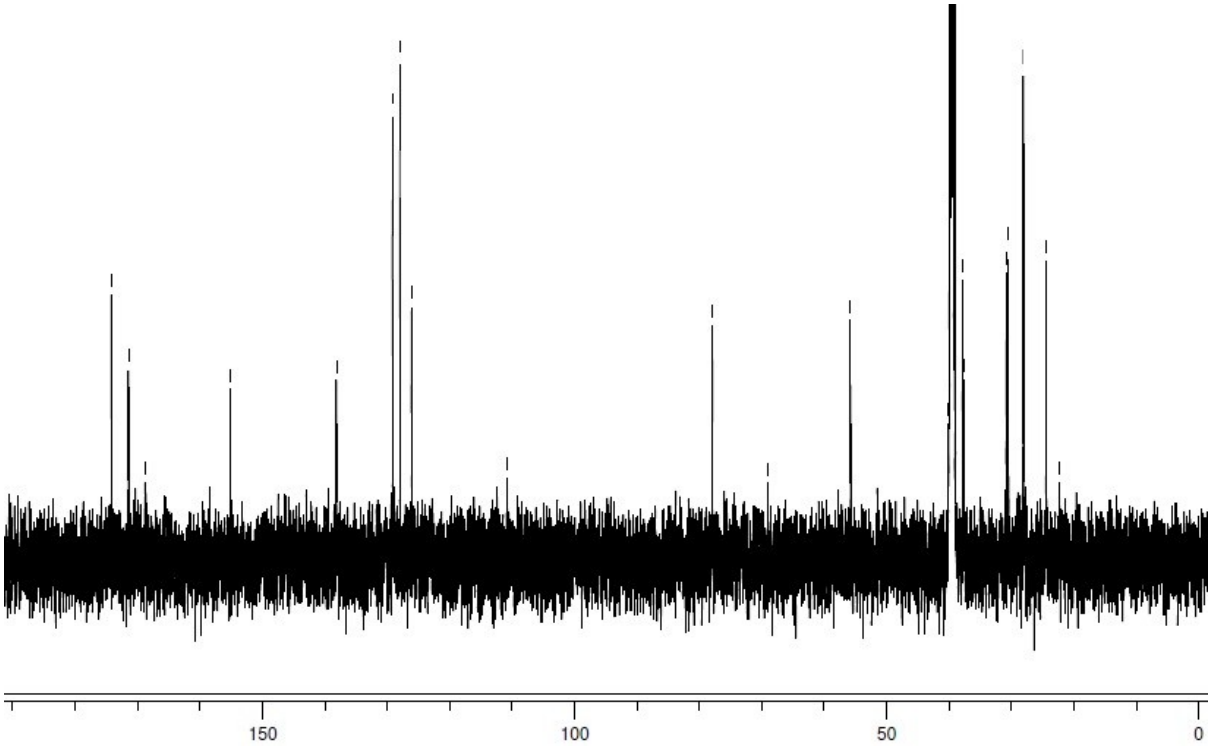



**Figure S20:** $^{13}C$ NMR(125 MHz, DMSO-$d_6$) of Boc-Phe-γ-Abu-OH.

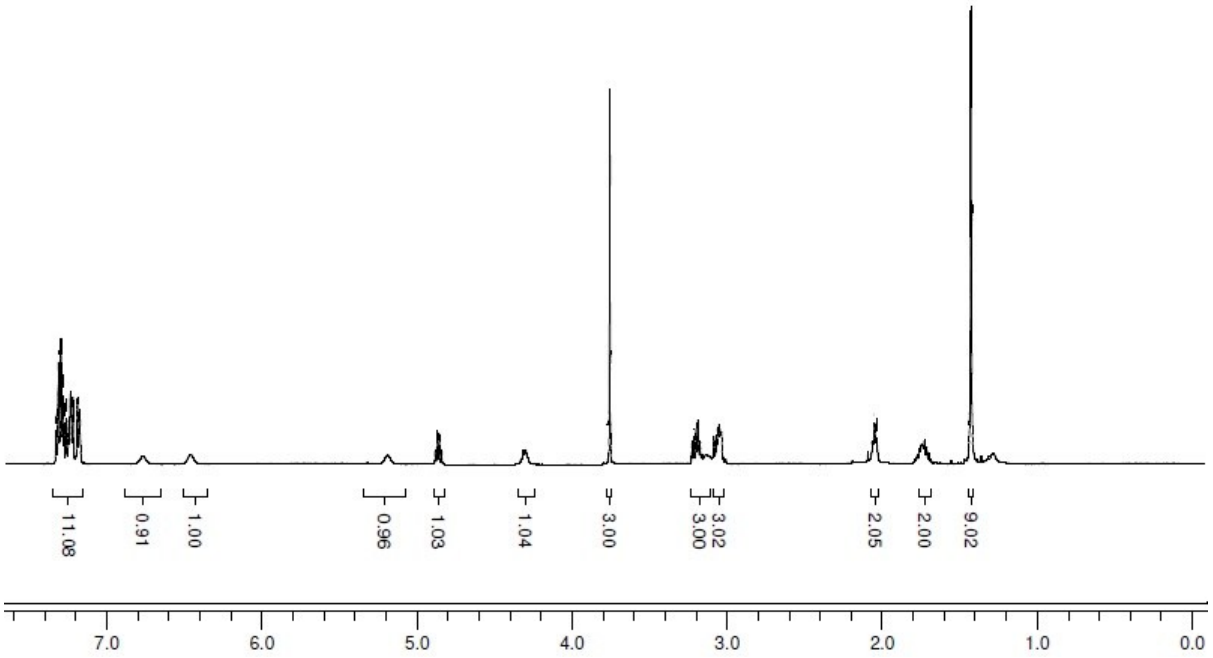



**Figure S21:** $^{1}H$ NMR (500 MHz, $CDCl_3$) of Boc-Phe-γ-Abu-Phe-OMe.

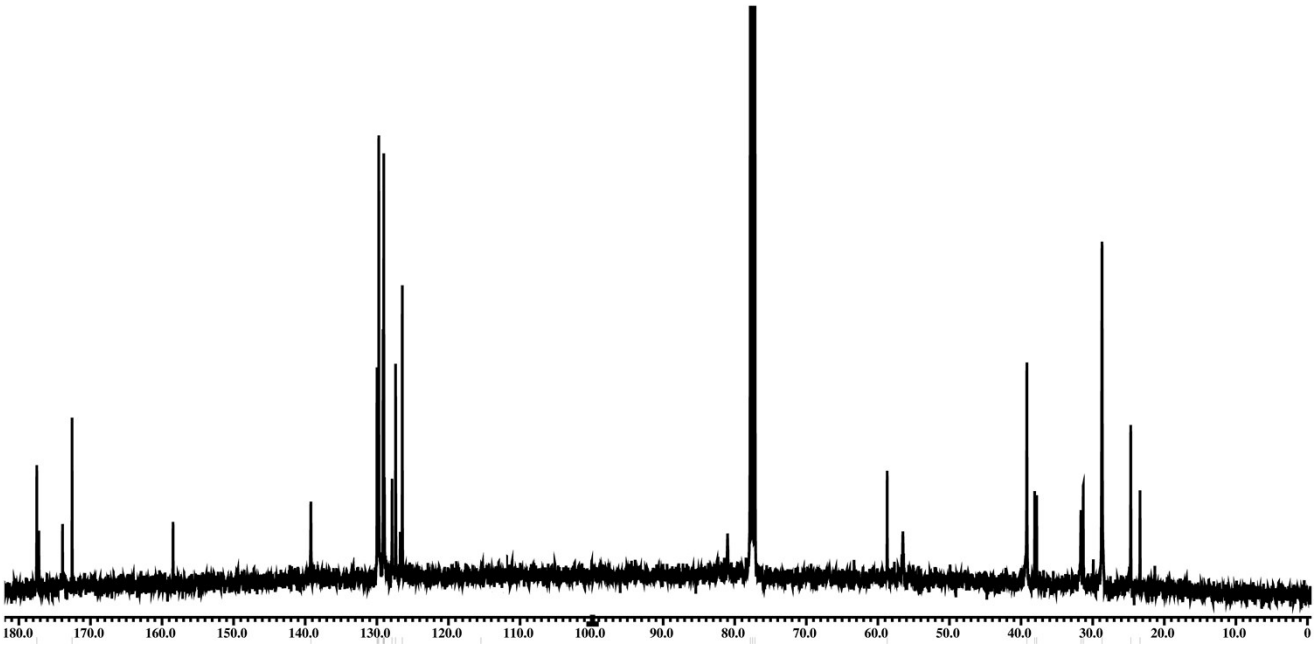



**Figure S22:** $^{13}C$ NMR(125 MHz,$CDCl_3$) of Boc-Phe-γ-Abu-Phe-OMe.

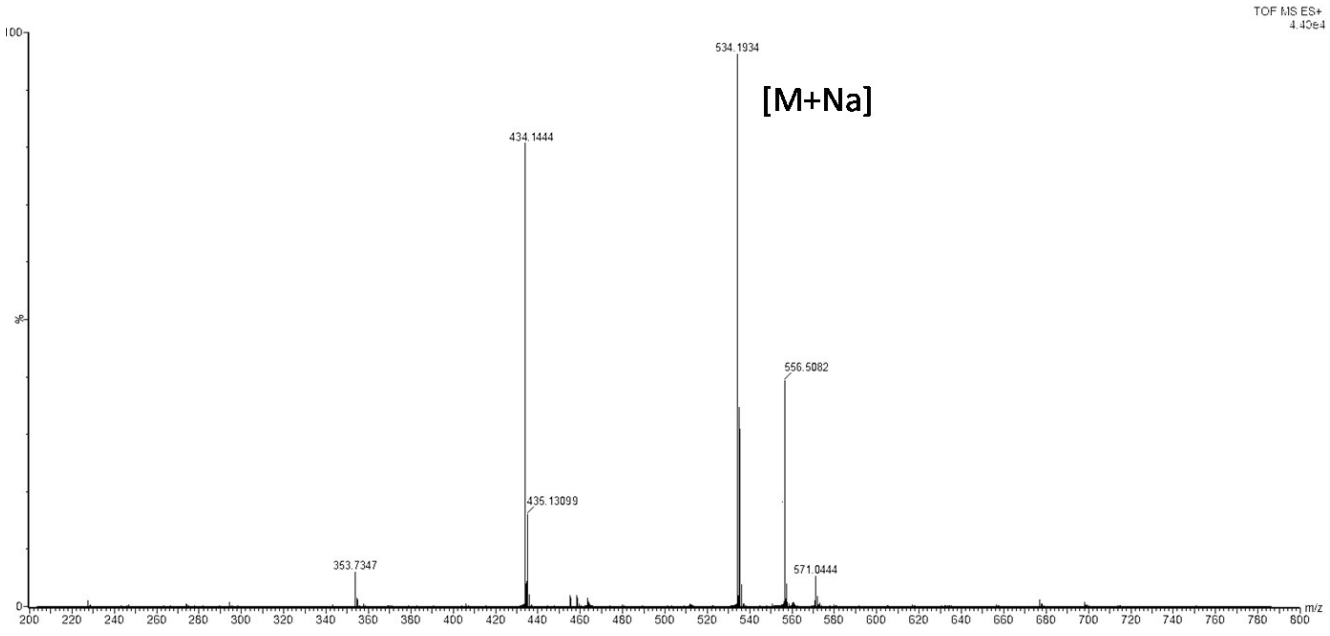



**Figure S23:** Mass spectra of Boc-Phe-γ-Abu-Phe-OMe.