

## Supporting information

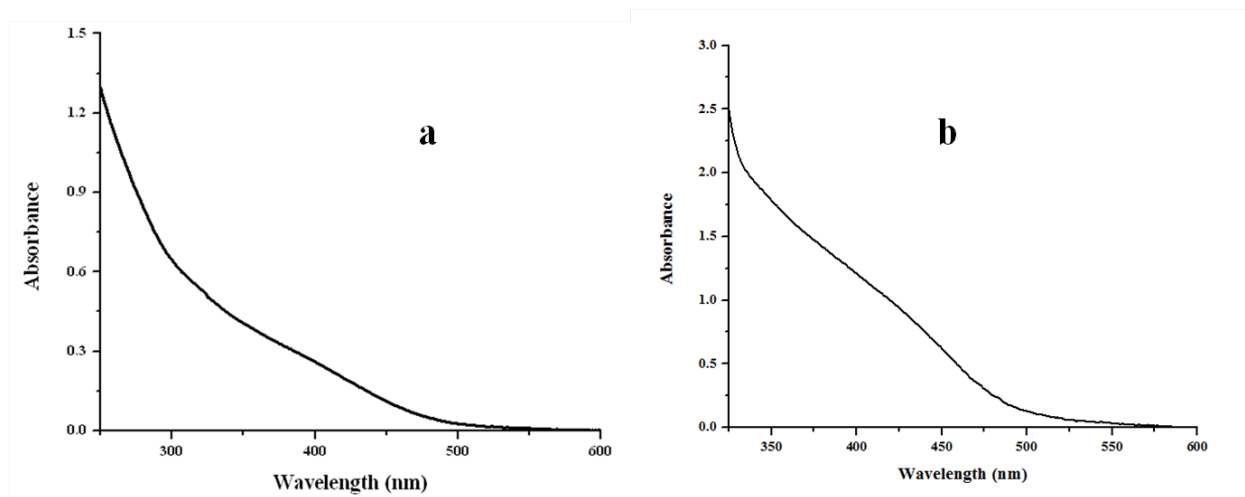
# CdS quantum dots doped peptide matrix: structural and photoelectrochemical properties

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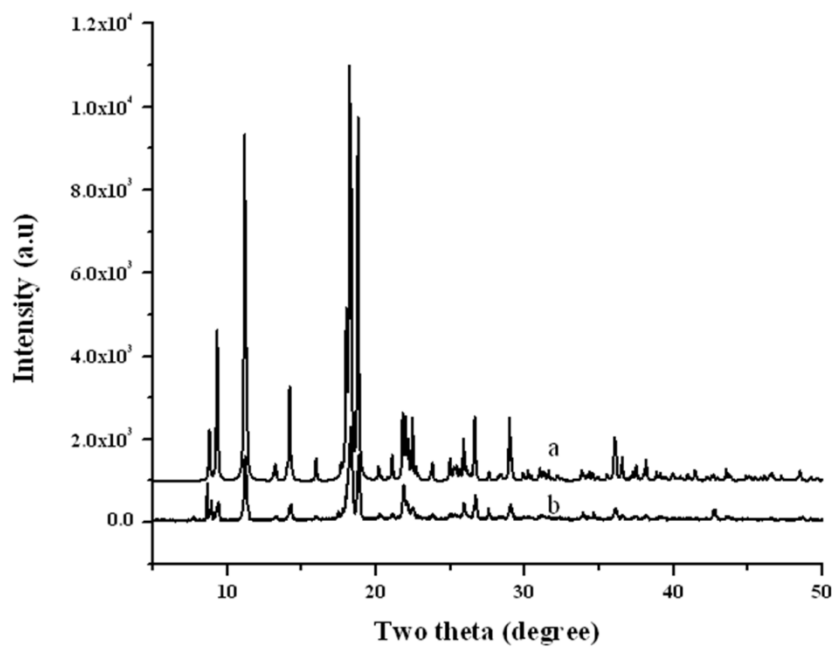
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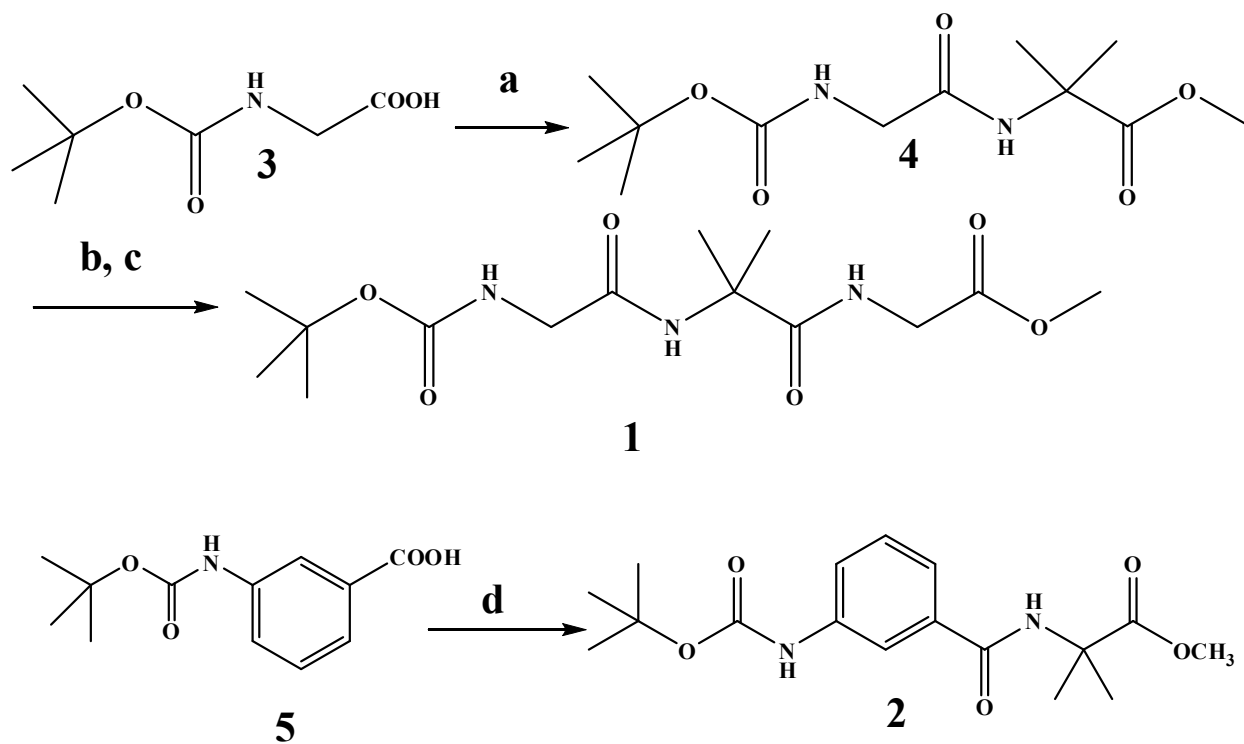
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**ESI Fig. 1:** UV spectra of (a) peptide 1-CdS, (b) peptide 2-CdS conjugates.



**ESI Fig. 2:** (a) Wide angle PXRD pattern of peptide 2 matrix from MeOH and (b) X-ray powder pattern from single crystal data of peptide 2.



**Scheme 1:** Reactions and conditions: a) dry DCM, H-Aib-OMe, DCC, HOBT, 0°C 83%, b) NaOH, MeOH, HCl, c) dry DCM, H-Gly-OMe, DCC, HOBT, 0°C, 74%, d) dry DCM, H-Maba-OMe, DCC, HOBT, 0°C, 71%.

**Figure S1:** Schematic presentation of synthesis of peptide 1, 2.

### Peptide synthesis:

**(a) Boc-Gly-OH 3:** A solution of glycine (1.5 g, 20 mmol) in a mixture of dioxan (40 mL), water (20 mL), and 1N 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 under vacuum to about 30-40 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<sub>4</sub> 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, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and evaporated under vacuum. The pure material was obtained. Yield: 3.15 g (18 mmol, 90%).

<sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>, δppm): 12.47 [1H, b, s, COOH], 7.04-7.06 [1H, t, *J* = 6 Hz, Gly(1) NH], 3.56-3.57 [2H, d, *J* = 6 Hz, Gly(1) C<sup>α</sup>H], 1.37 [s, 9H, Boc]. <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>, δppm): 171.75, 155.80, 78.00, 41.78, 28.17. Anal. Calcd for C<sub>7</sub>H<sub>13</sub>NO<sub>4</sub> (175.08): C, 47.99; H, 7.48; N, 8.00. Found: C, 47.98; H, 7.49; N, 8.02.

**(b) Boc-Gly(1)-Aib(2)-OMe 4:** A 2.41 g (14 mmol) sample of Boc-gly-OH was dissolved in a mixture of 30 mL of dichloromethane (DCM) in an ice-water bath. H-Aib-OMe was isolated from 4.60 g (30 mmol) of the corresponding methyl ester hydrochloride by neutralization, subsequent extraction with ethyl acetate, and concentration (10 mL), and this was added to the reaction mixture, followed immediately by 3.09 g (15 mmol) of dicyclohexylcarbodiimide (DCC). The reaction mixture was allowed to come to room temperature and stirred for 24 h. DCM was evaporated, and the residue was taken in ethyl acetate (60 mL); dicyclohexylurea (DCU) was filtered off. The organic layer was washed with 2 N HCl (3 × 50 mL), brine, 1 M sodium carbonate (3 × 50 mL), and brine (2 × 50 mL), dried over anhydrous sodium sulfate, and evaporated under vacuum to yield dipeptide **4** as a white solid. Purification was done on a silica gel column (100-200 mesh) using ethyl acetate: hexane (3:1) as the eluent. Yield: 3.2 g (11.6 mM, 83%).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, δppm): 6.75 [1H, s, Aib(2) NH], 5.22 [1H, t, Gly NH(1)], 3.74 [2H, d, Gly(1) C<sup>α</sup>H], 3.73 [3H, s, OCH<sub>3</sub>], 1.54 [6H, s, Aib(2) C<sup>β</sup>H], 1.44 [9H, s, Boc CH<sub>3</sub>]. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, δppm): 174.81, 168.70, 156.54, 80.03, 56.48, 52.66, 44.48, 28.24, 24.68. Anal. Calcd for C<sub>12</sub>H<sub>22</sub>N<sub>2</sub>O<sub>5</sub> (274.15): C, 52.54; H, 8.08; N, 10.21. Found: C, 52.58; H, 8.10; N, 10.12.

**(c) Boc-Gly(1)-Aib(2)-OH 5:** To 2.74 g (10 mmol) of **4** were added 25 mL MeOH and 15 mL of 2 N NaOH, and the progress of saponification was monitored by thin-layer chromatography (TLC). The reaction mixture was stirred. After 10 h, methanol was removed under vacuum, and the residue was taken in 50 mL of water and washed with diethyl ether (2 × 50 mL). Then, the pH of the aqueous layer was adjusted to 2 using 1 N HCl, and the aqueous layer was extracted

with ethyl acetate (3 × 50 mL). The extracts were pooled, dried over anhydrous sodium sulfate, and evaporated in vacuum to yield 2.07 g of **5**. Yield: 2.07 g, (8 mmol, 80%).

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, δppm): 12.28 [1H, s, COOH], 7.91 [1H, s, Aib(2) NH], 6.86 [1H, t, *J* = 6 Hz, Gly(1) NH], 3.50-3.50-3.52 [2H, d, *J* = 6 Hz, Gly(1) C<sup>α</sup>H], 1.37 [9H, s, Boc CH<sub>3</sub>], 1.33 [6H, s, Aib(2) C<sup>β</sup>H]. <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>, δppm): 175.52, 168.52, 155.70, 77.95, 54.83, 42.89, 28.21, 24.88. Anal. Calcd for C<sub>11</sub>H<sub>20</sub>N<sub>2</sub>O<sub>5</sub> (260.13): C, 50.76; H, 7.74; N, 10.76. Found: C, 50.74; H, 7.76; N, 10.79.

**(d) Boc-Gly(1)-Aib(2)-Gly(3)-OMe 1:** A 1.75 g (6.75 mmol) sample of Boc-Gly(1)-Aib(2)-OH in 10 mL of DMF was cooled in an ice-water bath; H-Gly-OMe was isolated from 2.5 g (20 mmol) of the corresponding methyl ester hydrochloride by neutralization, subsequent extraction with ethyl acetate, and concentration (10 mL), and it was added to the reaction mixture, followed immediately by 1.4 g (7 mmol) of DCC and 0.9 g (7 mmol) of HOBT. The reaction mixture was stirred for 3 days. The residue was taken in ethyl acetate (30 mL), and the DCU was filtered off. The organic layer was washed with 2 N HCl (3 × 50 mL), brine, 1 M sodium carbonate (3 × 50 mL), and brine (2 × 50 mL), dried over anhydrous sodium sulfate, and evaporated under vacuum to yield tripeptide **1** as a white solid. Purification was done on a silica gel column (100-200 mesh) using ethyl acetate: hexane (1:1) as the eluent. Yield: 1.65 gm (5.0 mmol, 74%). Mp: 119-120°C.

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, δppm): 8.00-8.03 [1H, t, *J* = 6 Hz Gly(3) NH], 7.94 [1H, s, Aib(2) NH], 6.95-6.98 [1H, t, *J* = 6 Hz Gly(1) NH], 3.75-3.77 [2H, d, *J* = 6 Hz, Gly(3) C<sup>α</sup>H], 3.60 [3H, s, OCH<sub>3</sub>], 3.52-3.53 [2H, d, *J* = 6 Hz Gly(1) C<sup>α</sup>H], 1.36 [6H, s, Aib(2) C<sup>β</sup>H], 1.36 [9H, s, Boc CH<sub>3</sub>]. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, δppm): 174.49, 170.33, 169.40, 156.75, 80.73, 57.25, 52.23, 45.13, 41.40, 94, 28.23, 25.23. Mass spectra: [M+Na]<sup>+</sup>: 354.16, (actual 354.09). Anal. Calcd for C<sub>14</sub>H<sub>25</sub>N<sub>3</sub>O<sub>6</sub> (331.17): C, 50.74; H, 7.60; N, 12.68. Found: C, 50.75; H, 7.55; N, 12.65.

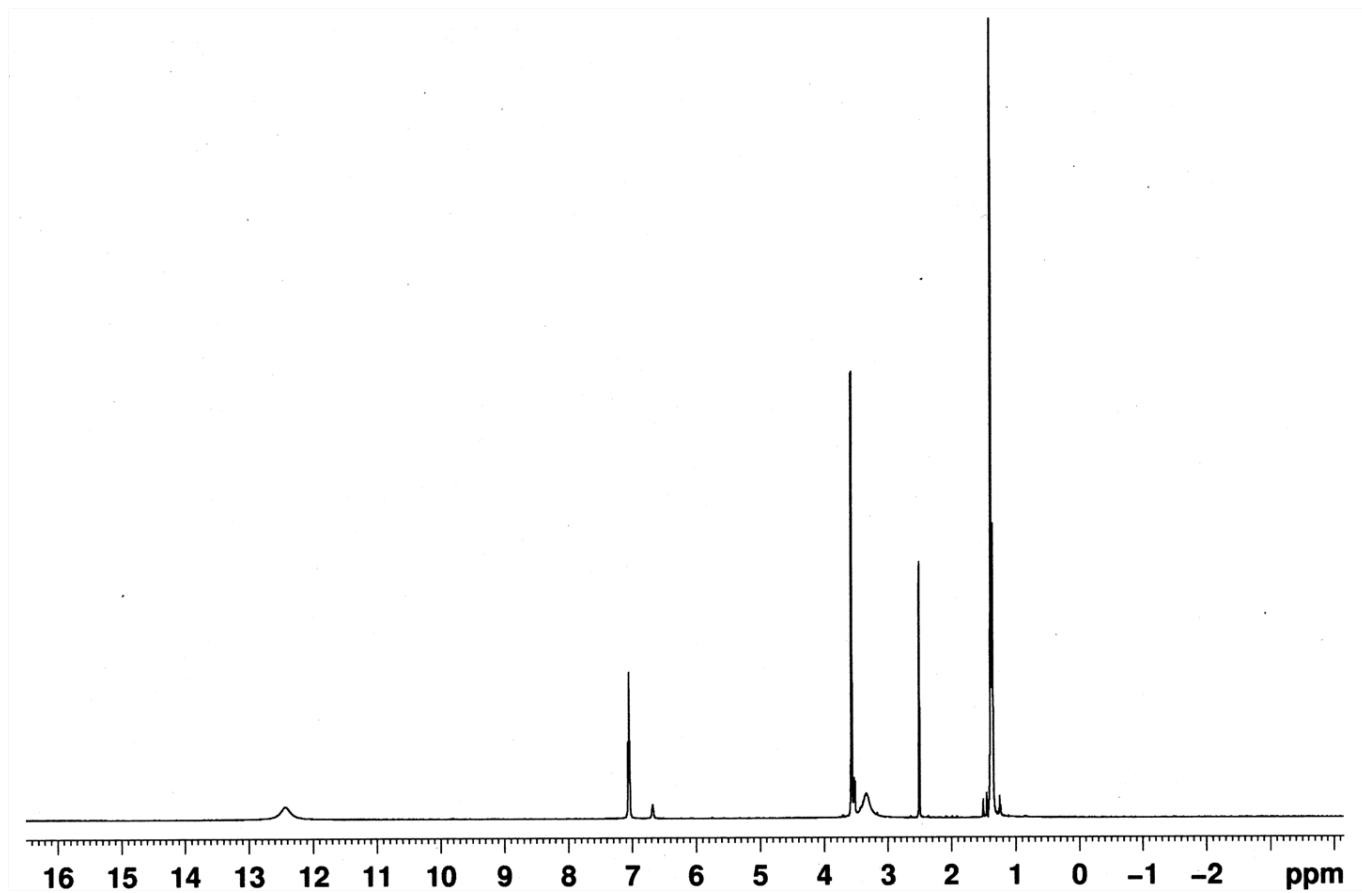
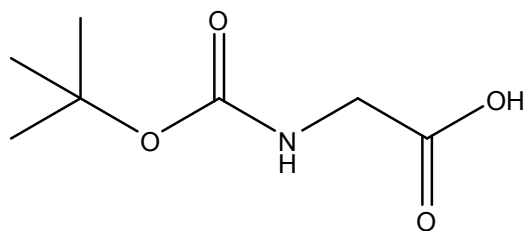
**(e) Boc-Maba-OH 6:** A solution of *m*-amino benzoic acid (2.7 g, 20 mmol) in a mixture of dioxan (40 mL), water (20 mL), and 1N NaOH (20 mL) was stirred and cooled in an ice-water bath. Di tertiarybutylpyrocarbonate (4.8 g, 22 mmol) was added, and stirring was continued at room temperature for 6 h. Then, the solution was concentrated under vacuum to about 30-40 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<sub>4</sub> 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, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and evaporated under vacuum. The pure material was obtained. Yield: 4.26 g (18 mmol, 90%).

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, δppm): 12.87 [COOH, 1H, s], 9.54 [Maba NH, 1H, s], 8.14 [Maba CH, 1H, s], 7.60-7.62 [Maba CH, 1H, d], 7.52-7.54 [Maba CH, 1H, d], 7.34-7.39 [Maba CH, 1H, m], 1.48 [Boc CH<sub>3</sub>, 9H, s]. <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>, δppm): 167.25, 152.73,

139.76, 131.22, 128.77, 122.87, 122.23, 118.74, 79.28, 28.05. Anal. Calcd for C<sub>12</sub>H<sub>15</sub>NO<sub>4</sub> (237.10): C, 60.75; H, 6.37; N, 5.90. Found: C, 60.77; H, 6.34; N, 5.95;

**(f) Boc-Maba(1)-Aib(2)-OMe 2:** A 2.37 g (10 mmol) sample of Boc-Maba-OH was dissolved in a mixture of 30 mL of dichloromethane (DCM) in an ice-water bath. H-Aib-OMe was isolated from 2.34 g (20 mmol) of the corresponding methyl ester hydrochloride by neutralization, subsequent extraction with ethyl acetate, and concentration (10 mL), and this was added to the reaction mixture, followed immediately by 2.47 g (12 mmol) of dicyclohexylcarbodiimide (DCC). The reaction mixture was allowed to come to room temperature and stirred for 24 h. DCM was evaporated, and the residue was taken in ethyl acetate (60 mL); dicyclohexylurea (DCU) was filtered off. The organic layer was washed with 2 N HCl (3 × 50 mL), brine, 1 M sodium carbonate (3 × 50 mL), and brine (2 × 50 mL), dried over anhydrous sodium sulfate, and evaporated under vacuum to yield dipeptide **2** as a white solid. Purification was done on a silica gel column (100-200 mesh) using ethyl acetate: hexane (3:1) as the eluent. Yield: 2.6 g (7.1 mM, 71%). Mp: 175-176°C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, δppm): 7.71 [1H, s, Maba(1) CH], 7.57-7.59 [1H, d, J=8 Hz, Maba(1) CH], 7.40-7.42 [1H, d, J=8 Hz, Maba(1) CH], 7.30-7.33 [1H, m, Maba(1) CH], 6.83 [1H, s, Aib(2) NH], 6.76 [1H, s, Maba(1) NH], 3.76 [3H, s, OCH<sub>3</sub>], 1.65 [6H, s, Aib C<sup>β</sup>H], 1.50 [9H, s, Boc CH<sub>3</sub>]. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, δppm): 175.17, 166.32, 152.67, 138.79, 135.27, 129.27, 121.47, 121.36, 116.97, 80.78, 56.81, 52.69, 28.28, 24.77. Mass spectra: [M+Na]<sup>+</sup>: 359.15, (actual 359.07). Anal. Calcd for C<sub>17</sub>H<sub>24</sub>N<sub>2</sub>O<sub>5</sub> (336.16): C, 60.70; H, 7.19; N, 8.33. Found: C, 60.73; H, 7.16; N, 8.32.



**Figure S2:** <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 500 MHz, δ<sub>ppm</sub>) spectra of Boc-Gly-OH.

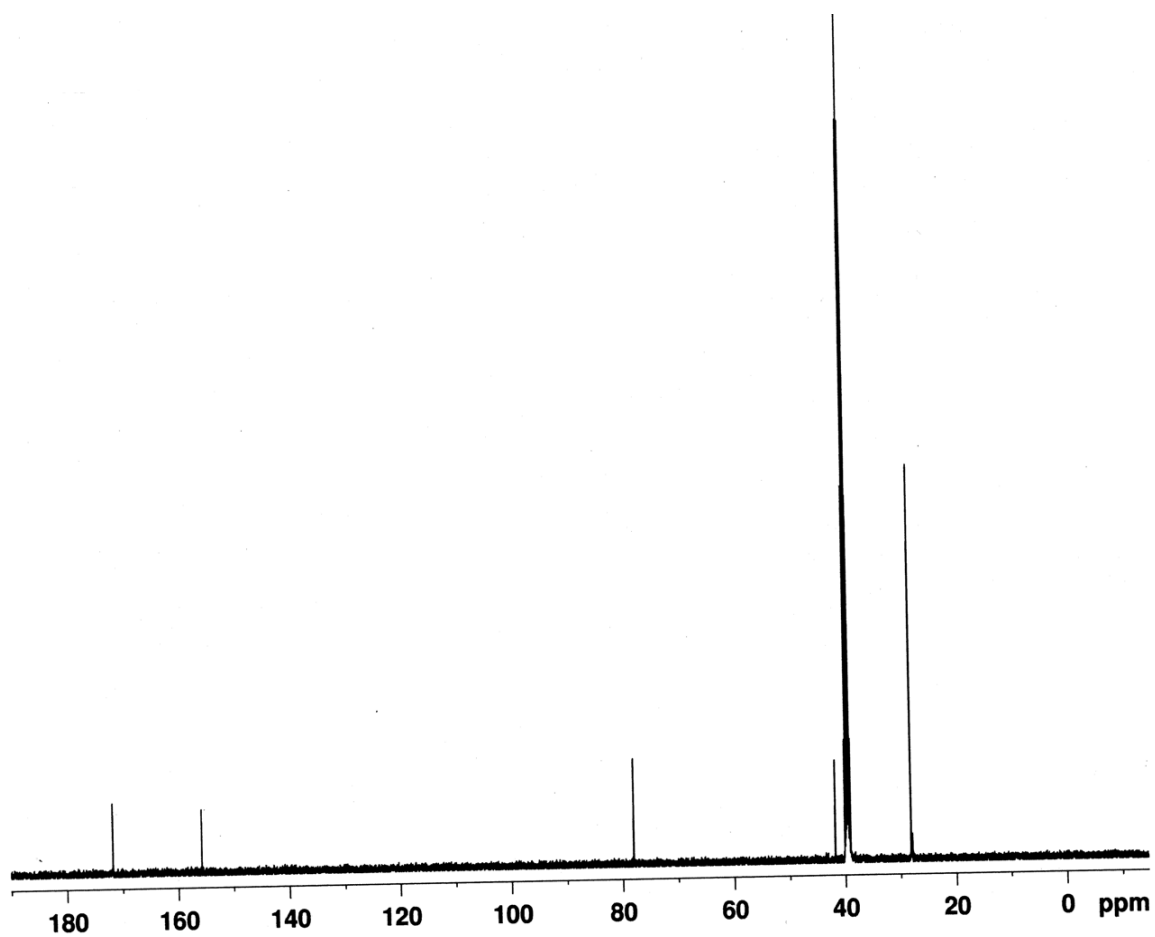
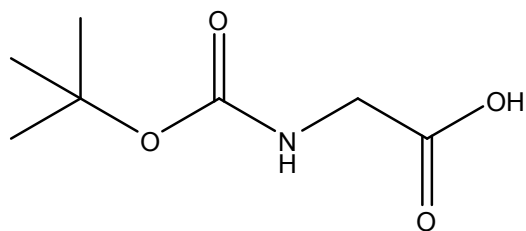
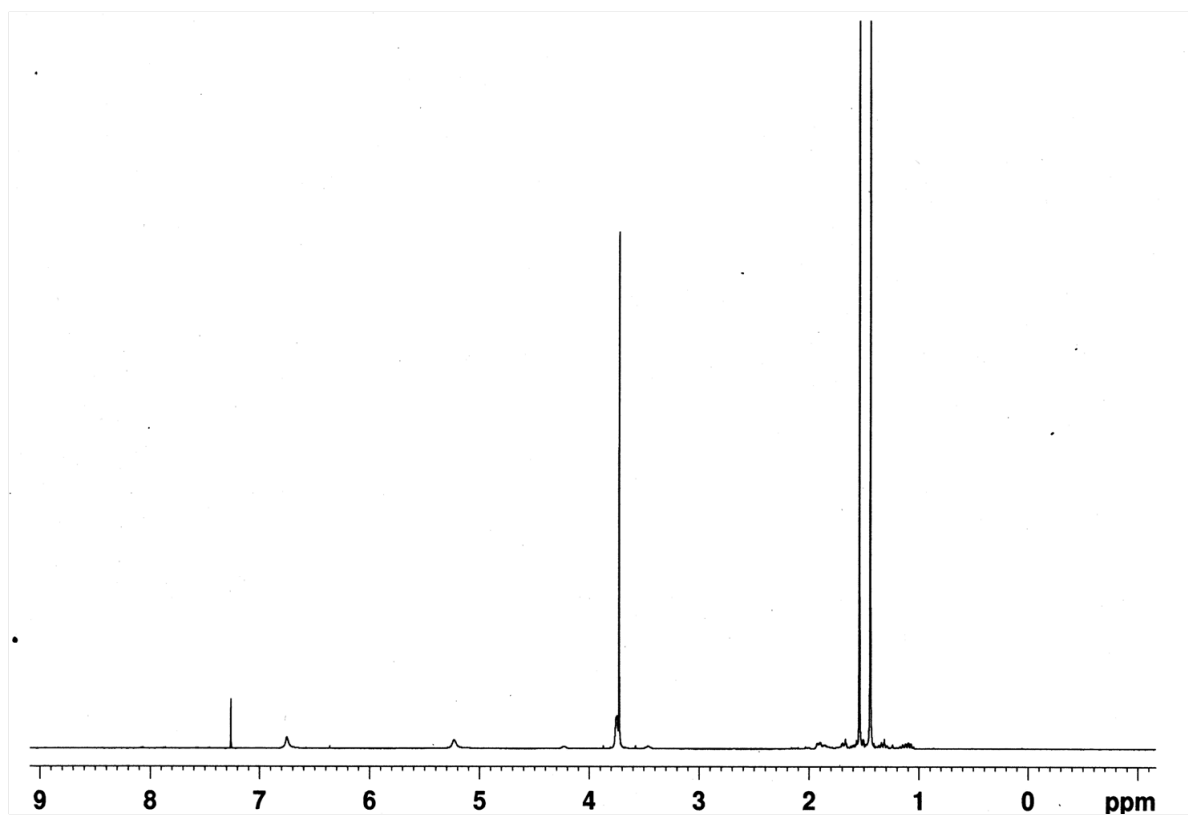
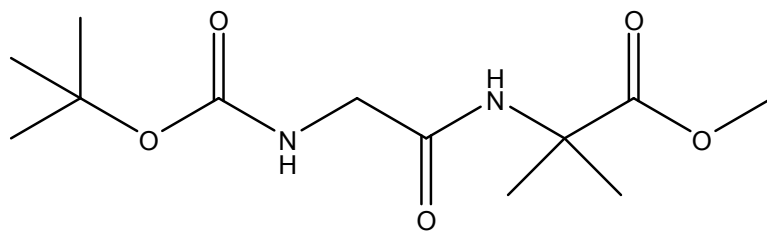
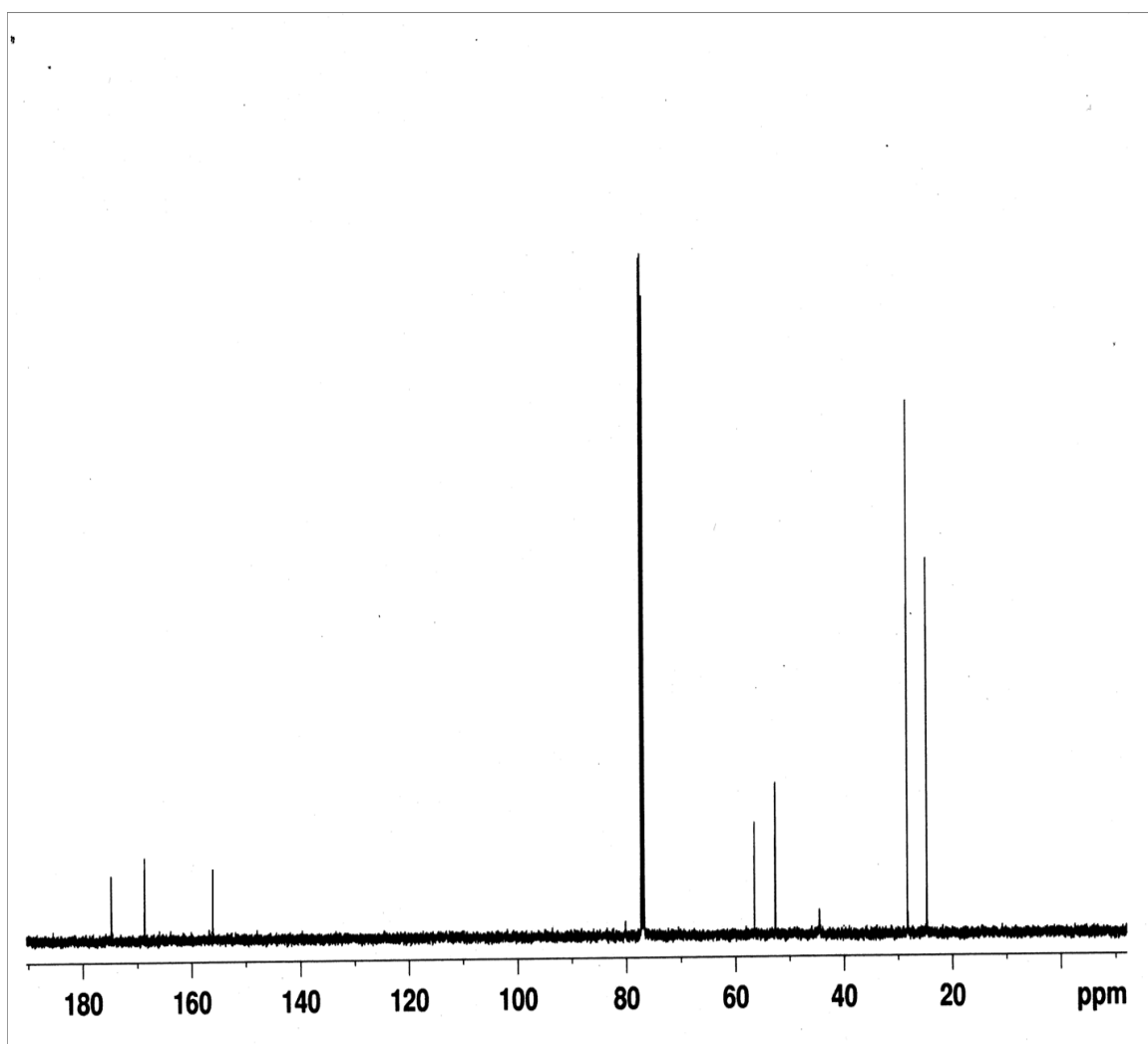
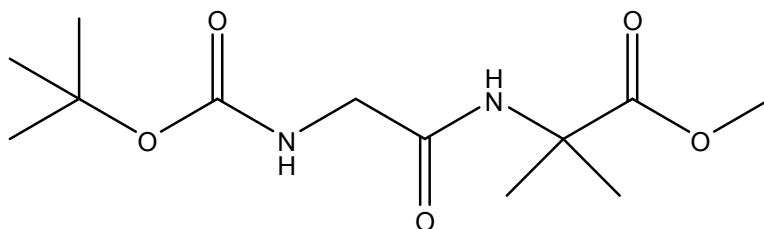


Figure S3:  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 125 MHz,  $\delta_{\text{ppm}}$ ) spectra of Boc-Gly-OH.



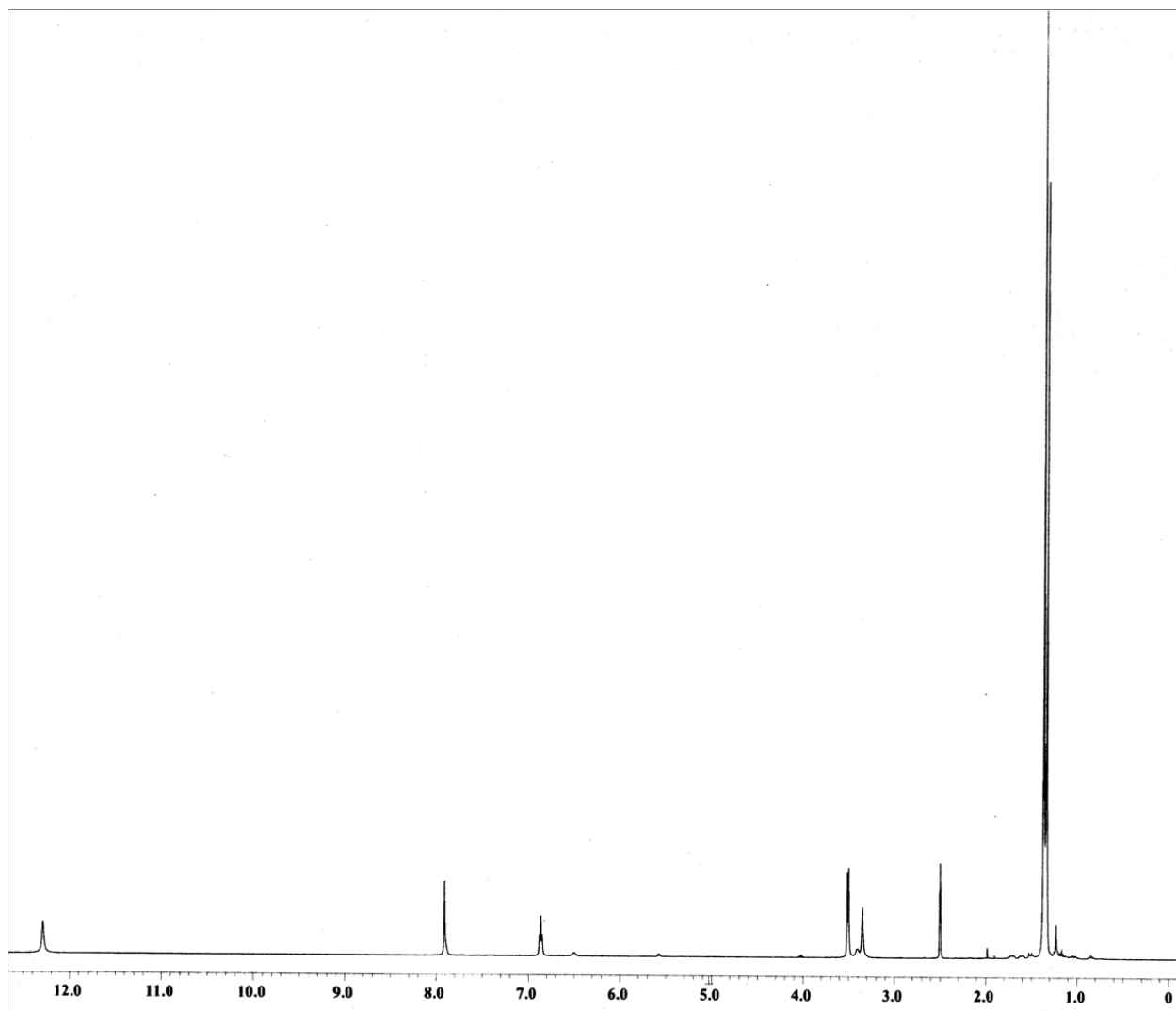
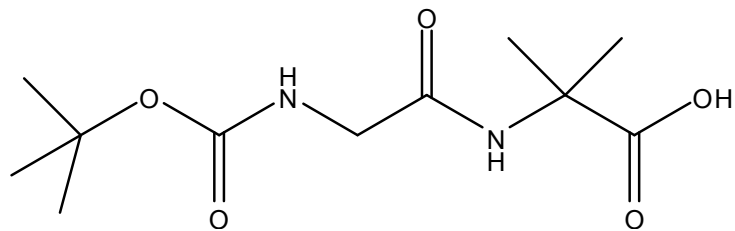


**Figure S4:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz,  $\delta_{\text{ppm}}$ ) spectra of Boc-Gly-Aib-OMe.

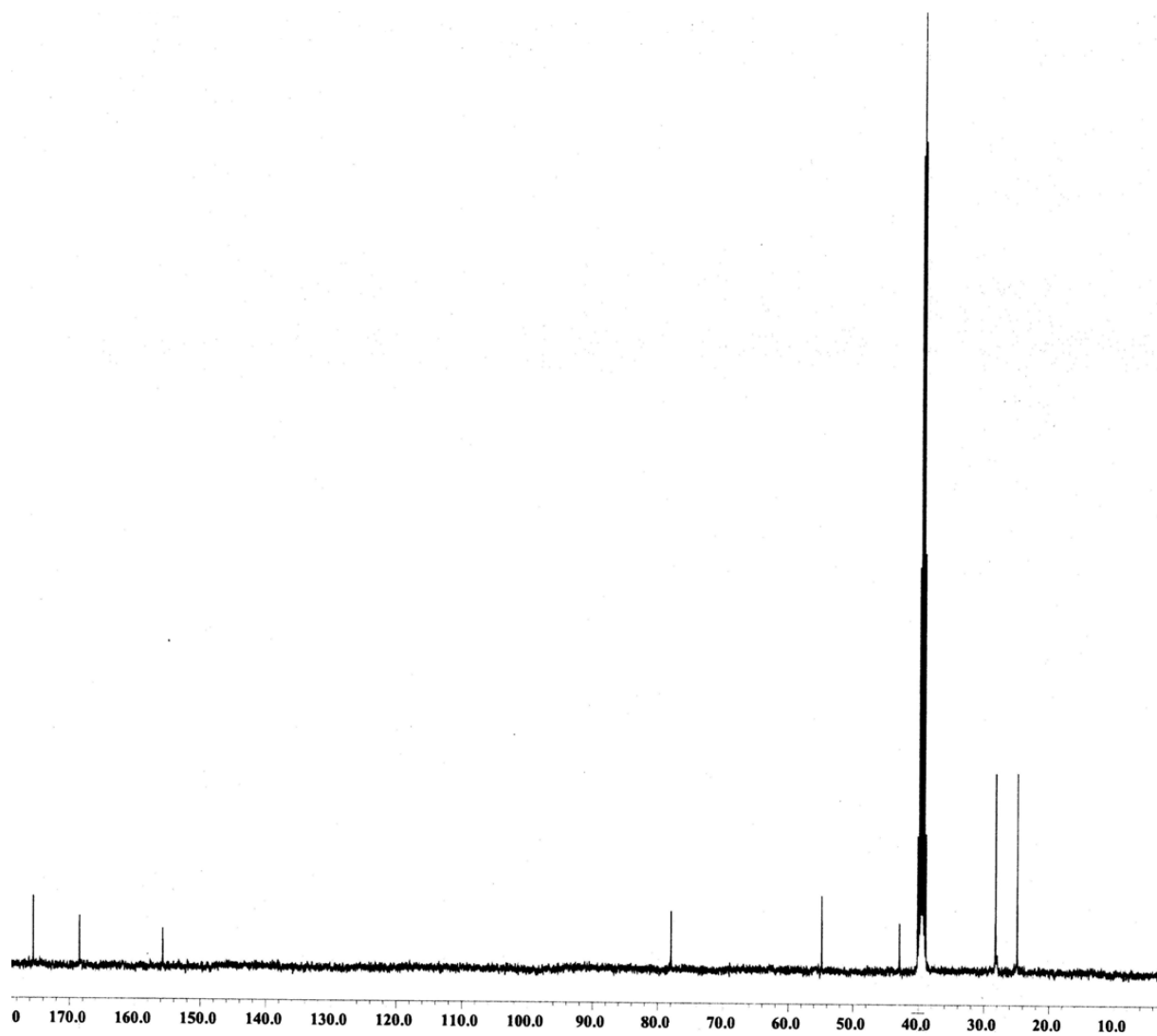
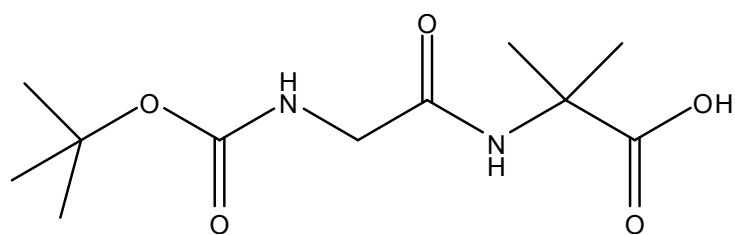


**Figure S5:** <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz, δ<sub>ppm</sub>) spectra of Boc-Gly-Aib-OMe.

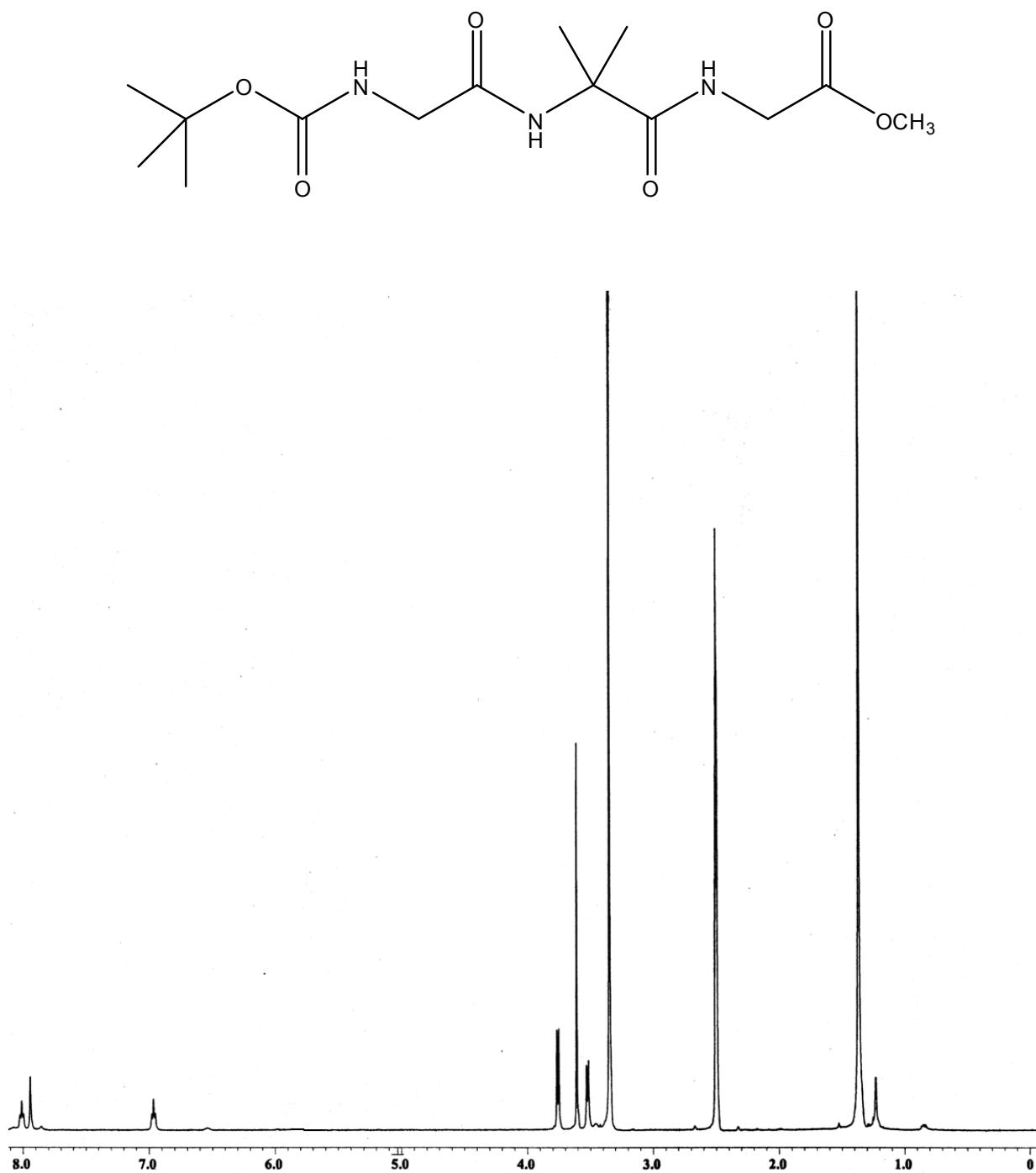




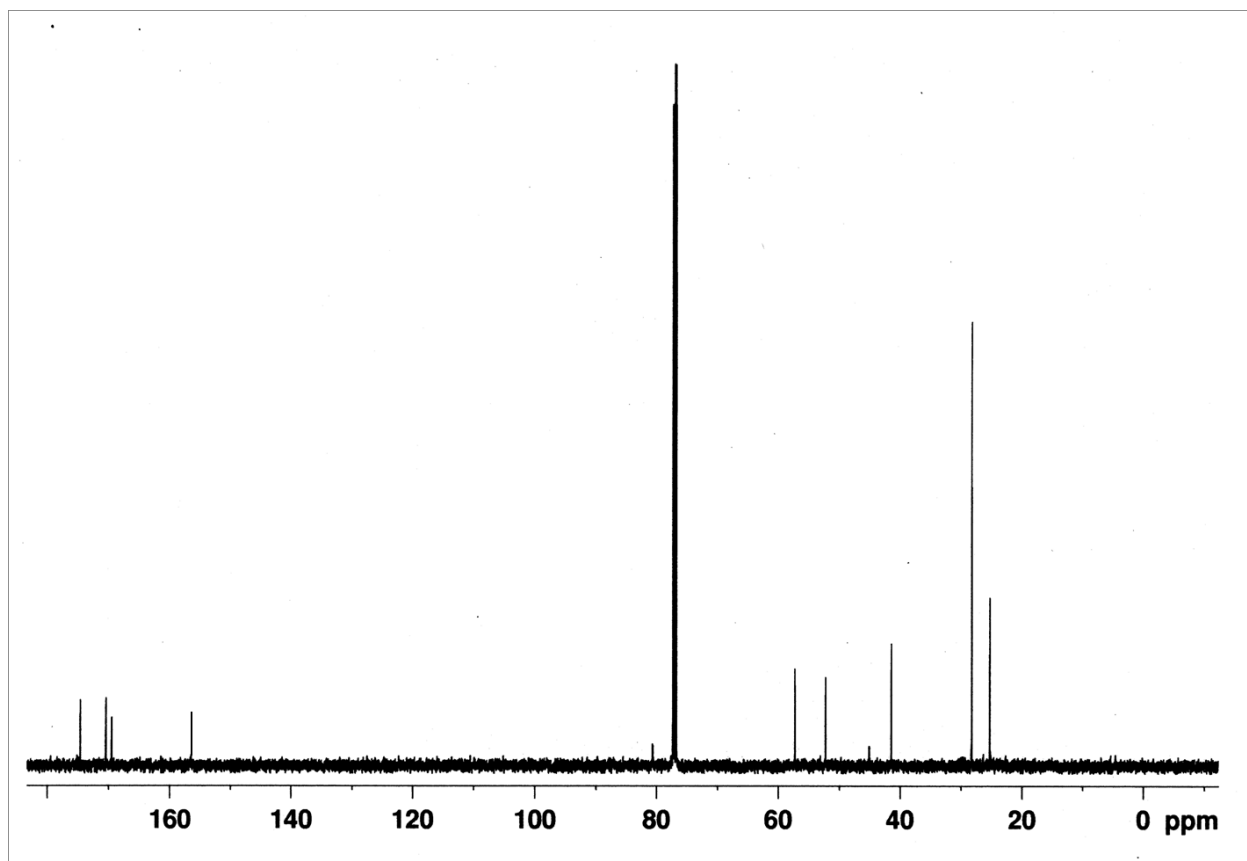
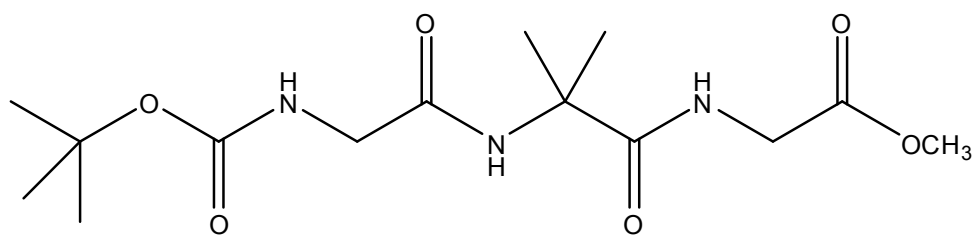
**Figure S6:**  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ , 400 MHz,  $\delta_{\text{ppm}}$ ) spectra of Boc-Gly-Aib-OH.



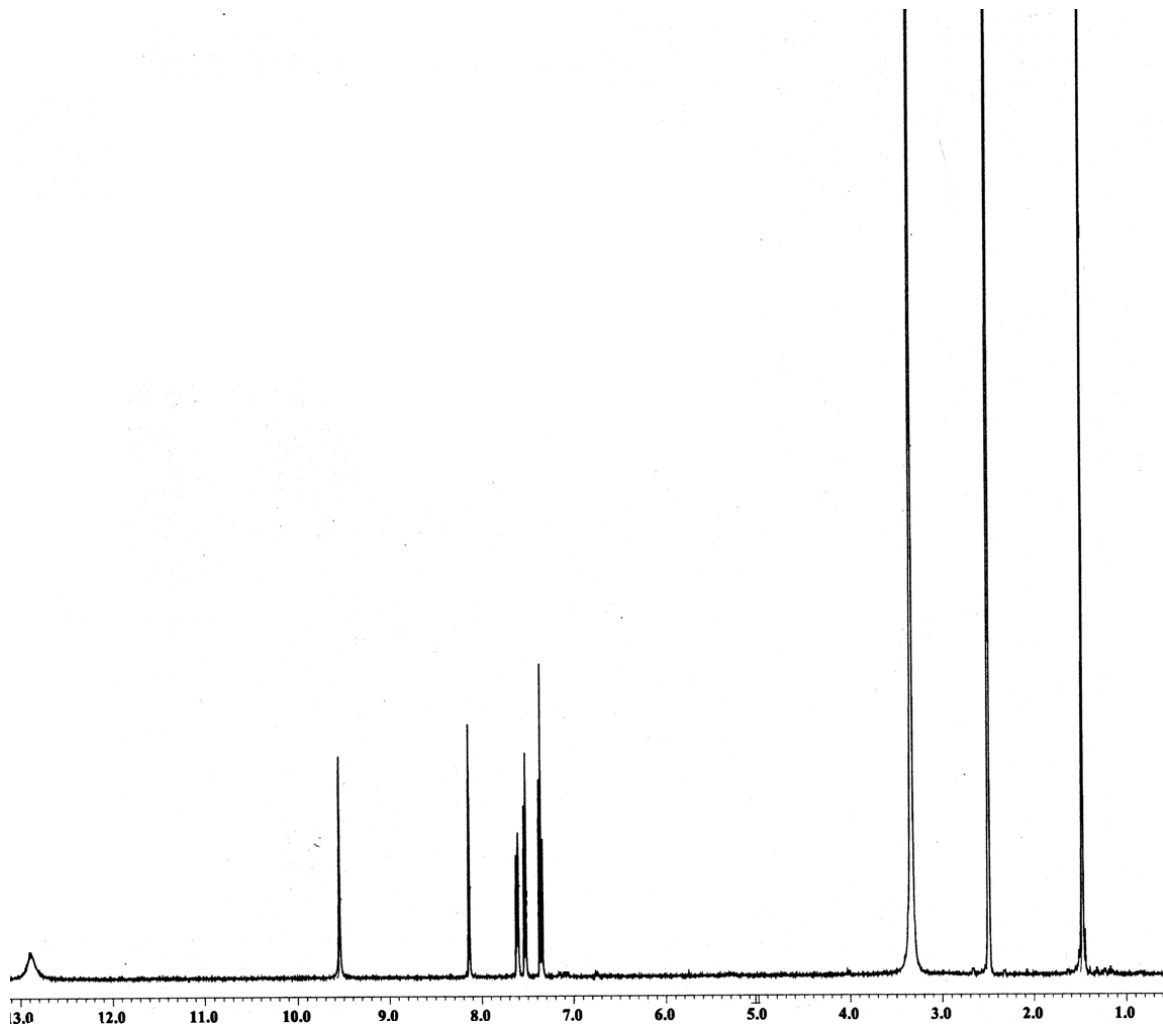
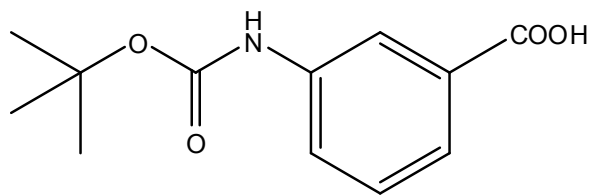
**Figure S7:**  $^{13}\text{C}$  NMR ( $\text{DMSO-}d_6$ , 100 MHz,  $\delta_{\text{ppm}}$ ) spectra of Boc-Gly-Aib-OH.



**Figure S8:** <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz, δ<sub>ppm</sub>) spectra of Boc-Gly-Aib-Gly-OMe 1.

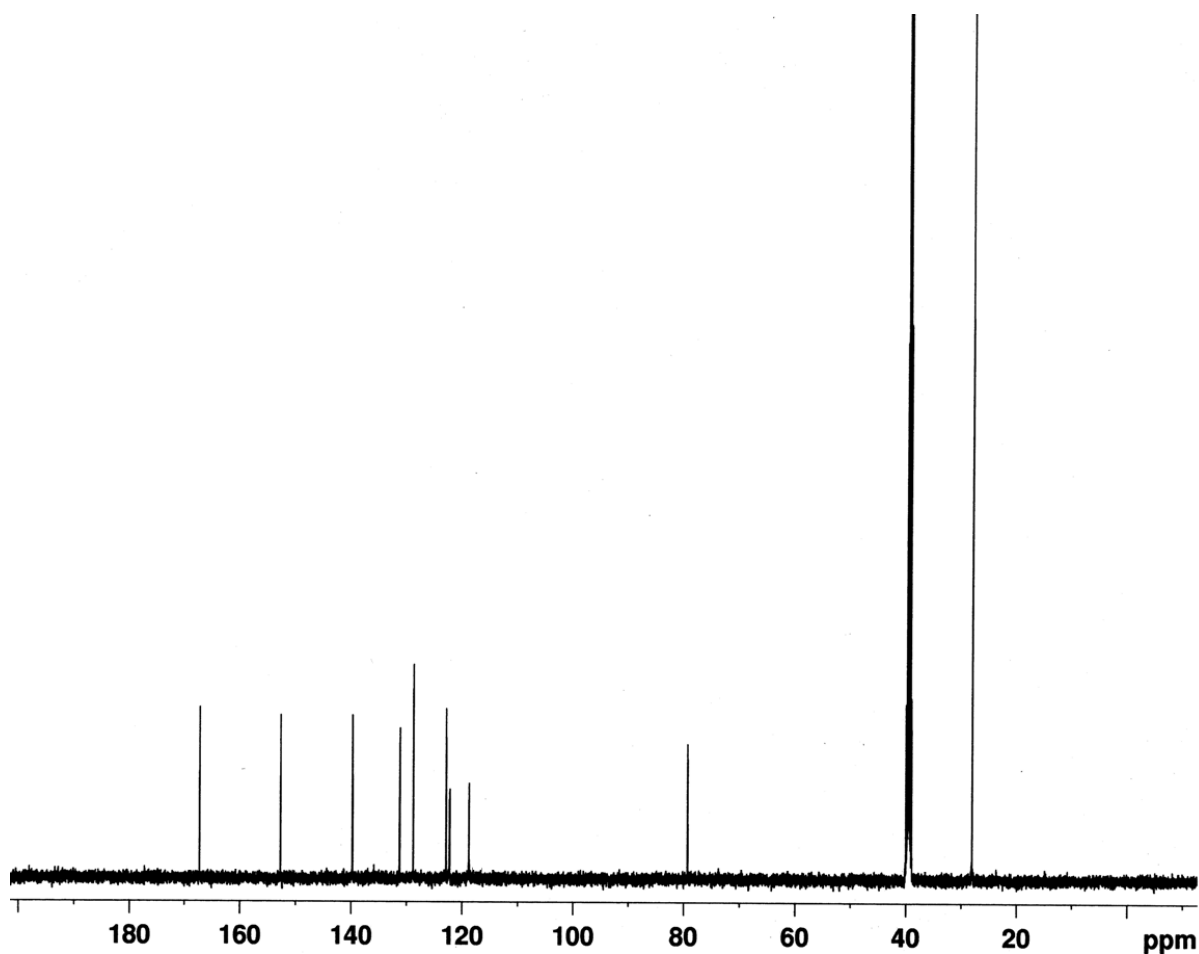
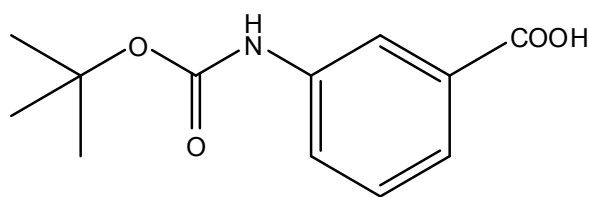


**Figure S9:** <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz, δ<sub>ppm</sub>) spectra of Boc-Gly-Aib-Gly-OMe 1.

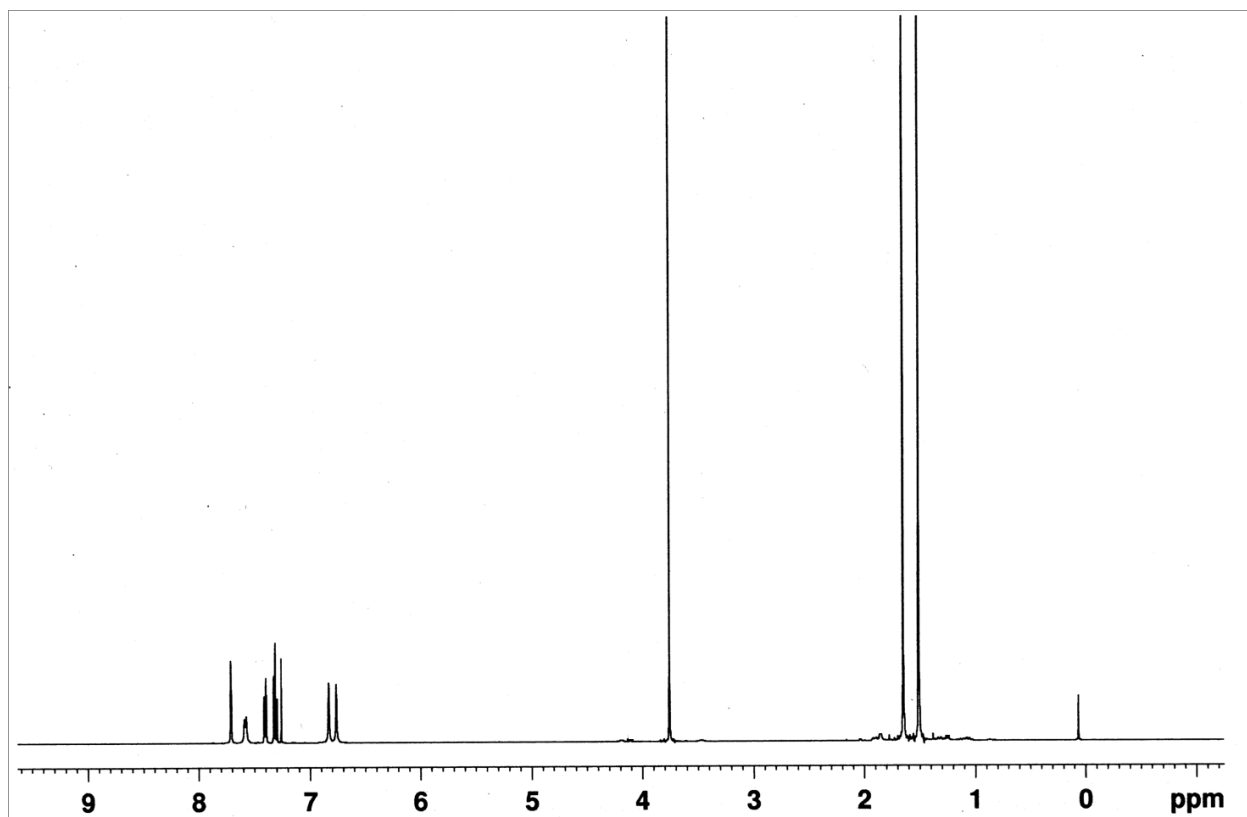
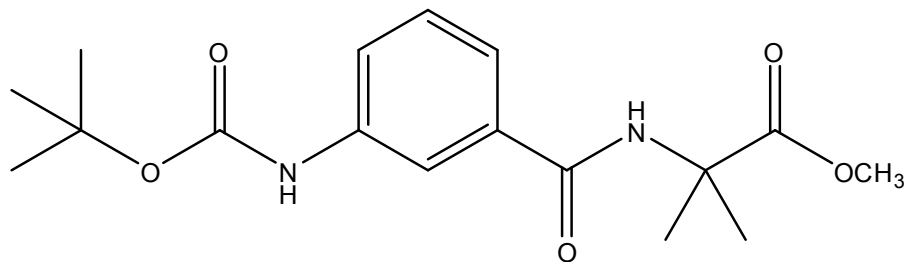


**Figure S10:**  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ , 400 MHz,  $\delta_{\text{ppm}}$ ) spectra of Boc-Maba-OH.

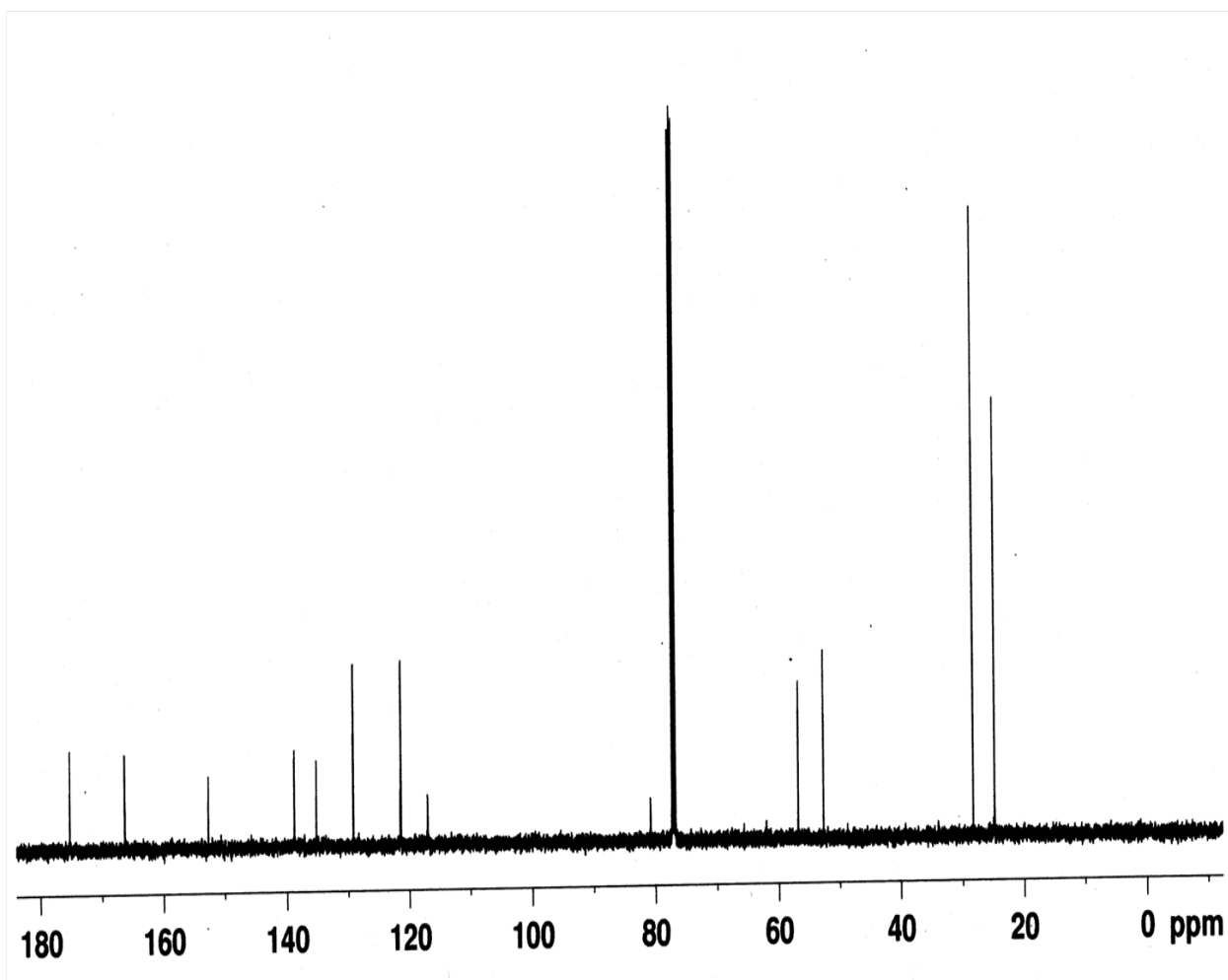
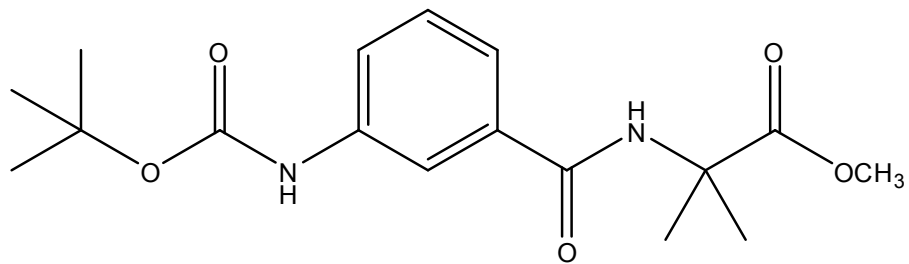




**Figure S11:**  $^{13}\text{C}$  NMR ( $\text{DMSO-}d_6$ , 100 MHz,  $\delta_{\text{ppm}}$ ) spectra of Boc-Maba-OH.



**Figure S12:** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, δ<sub>ppm</sub>) spectra of Boc-Maba-Aib-OMe 2.



**Figure S13:**  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz,  $\delta_{\text{ppm}}$ ) spectra of Boc-Maba-Aib-OMe 2.

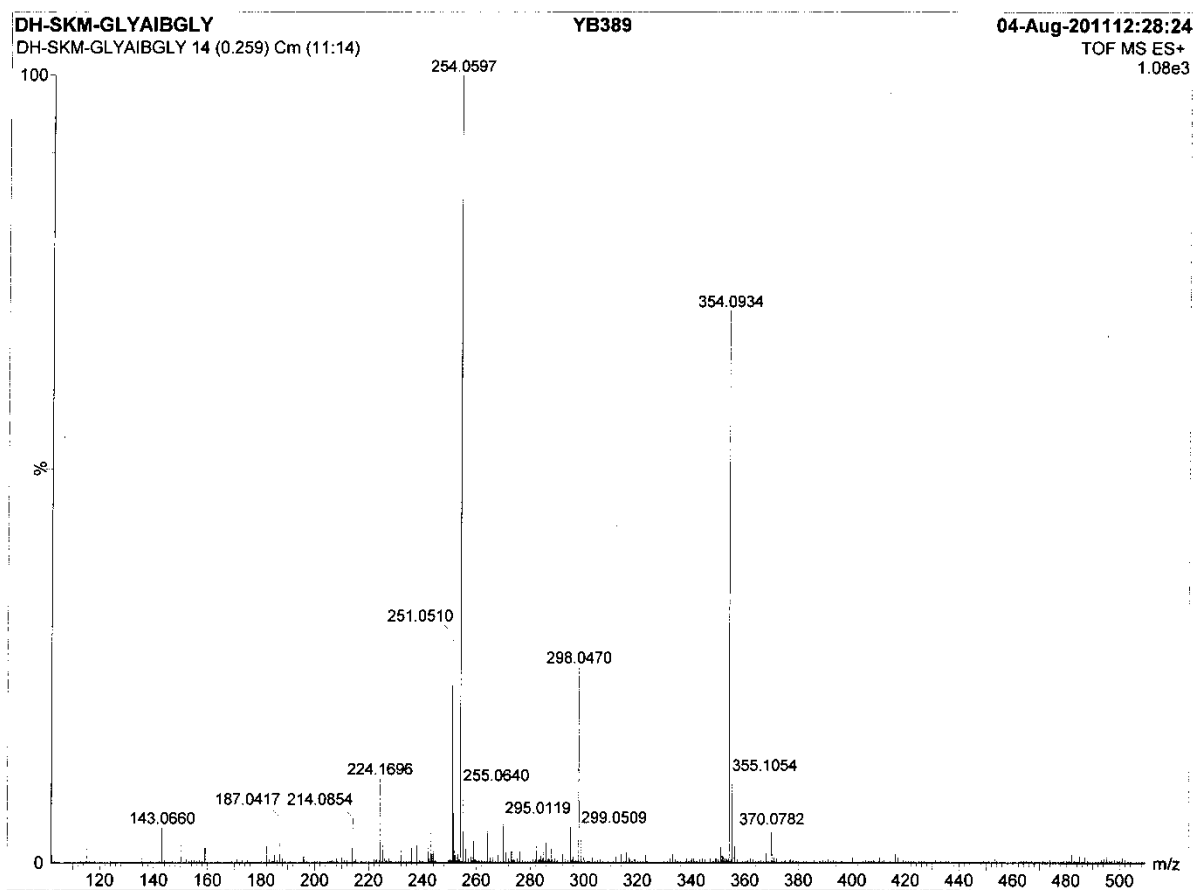
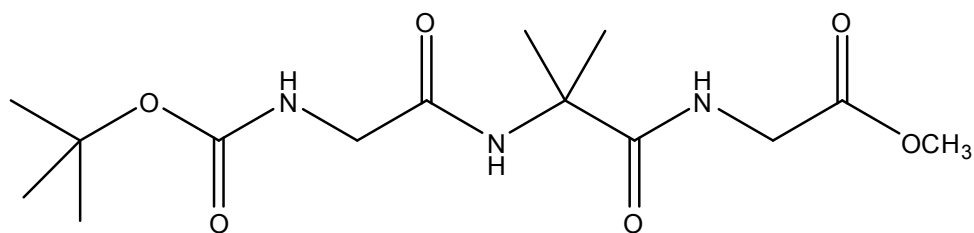


Figure S14: Mass spectra of tripeptide 1.

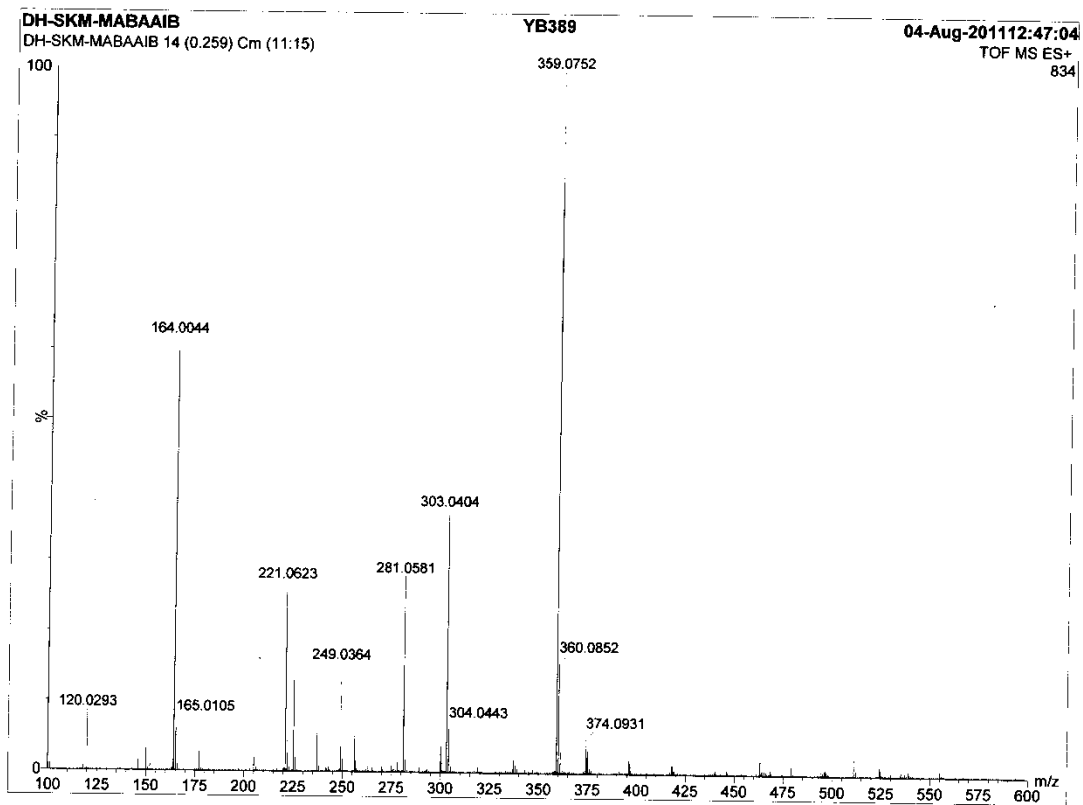
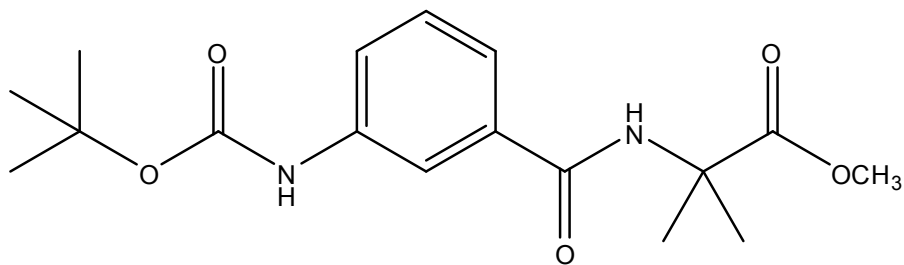


Figure S15: Mass spectra of dipeptide 2.