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## Electronic Supporting Material

### Synthesis and characterization of highly ordered self-assembled bioactive fulleropeptides

Mira Bjelaković<sup>1</sup>, Tatjana Kop<sup>1</sup>, Veselin Maslak<sup>2</sup>, Dragana Milić<sup>2\*</sup>

<sup>1</sup>*ICTM-Center for Chemistry, Belgrade, Serbia*

<sup>2</sup>*Faculty of Chemistry University of Belgrade, Serbia*

\* *dmilic@chem.bg.ac.rs*

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#### Antioxidant activity *in vitro*

##### *FOX reagent preparation* [1]

Working FOX reagent was prepared by adding 10 ml of Reagent 1 (98 mg of (NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O in 100 ml of 250 mM H<sub>2</sub>SO<sub>4</sub>) to 900 ml of Reagent 2 (95 mg of Xylenol Orange (XO) Na salt and 880 mg of 2,6-di-*t*-butyl-4-methylphenol (BHT) in 900 ml of MeOH) giving the final concentrations of 250 μM (NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>, 125 μM XO, 25 mM H<sub>2</sub>SO<sub>4</sub>, and 4 mM BHT. The complete reagent was used within 24 h or a new batch was made. The absorbance of the Fe<sup>3+</sup>-XO complex was measured at 560 nm by UV-vis spectroscopy (GBC-Cintra 40) with 90% MeOH as a zero probe.

The procedure includes preparing a standard calibration curve using increasing concentrations (0-200 μM) of TBHP incubated with a FOX reagent at room temperature for 30 min until color formation is complete. 2mM Standard solution of TBHP was prepared by dilution with MeOH.

##### *Standard probe preparation*

The standard solution of TBHP was prepared in the same manner without the sample aliquot, which was substituted with H<sub>2</sub>O. After incubation the absorbance was determined at 560 nm (A<sub>S</sub>).

##### *Blank probe preparation*

In all experiments a blank was carried out for determination of the possible activity in the absence of substrate during the incubation period. The blank contained 0.950 ml of FOX reagent and 0.050 ml of H<sub>2</sub>O instead of the sample. After incubation the absorbance was determined at 560 nm (A<sub>0</sub>).

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[1] Gao S, Miller M, Han XQ (2005) Peptide antioxidants from soy protein, EP 1 593 685 A1

Vitamin C, well-known antioxidant, was used as a positive control. The absorbance read at the spectrophotometer for each sample varies in relation to the concentration of TBHP contained in the sample being tested. All analyses were performed in triplicate and average values were taken. The direct antioxidant activity (the percentage of consumed TBHP,  $\Delta$ ) was calculated from the equation

$$\Delta = 100 \times (A - A_s) / (A_s - A_0)$$

where A,  $A_s$ , and  $A_0$  represent absorbances of the tested compound, starting (TBHP+FOX), and blank (FOX) probes, respectively. Obtained values are recalculated to the activities relative to the equimolar concentration of vitamin C according to the formula:

$$\text{Aox vs vit C} = (\Delta / \Delta_{\text{vit C}}) / (M / M_{\text{vit C}})$$

where  $\Delta$  and  $\Delta_{\text{vit C}}$  represent the direct antioxidant capacity of the tested compound and vitamin C, respectively and M and  $M_{\text{vit C}}$  their molecular weights.

### Probe preparation

Aliquots of 0.050 mL of prepared solutions of fullerosomes (0.02 mg/mL concentrated), were mixed with the 0.050 mL of the 2mM solution of peroxide and diluted with 0.900 mL of water (corresponds to mixed 0.002mg/mL of sample solution and 200 $\mu$ M standard peroxide solution in 1:1 (V/V) ratio). Mixture was then vortexed for 1 min and incubated in stoppered vial at room temperature, for 10 min. From each incubated mixture three aliquots of 0.050 mL were taken and mixed with 0.950 mL of FOX reagent. Absorbance (A) at 560 nm was measured after 80 min of incubation at room temperature, in aim to determine the percentage of consumed peroxide (direct antioxidant activity).

### Spectral data of compounds 1-12

Fullerene carbons are labelled as  $C_f$ , and pyrrolidinic nuclei as  $C/H^{\text{pyrr}}$ . The glycine moieties incorporated into the peptide backbones are labelled as Gly<sup>1</sup>, Gly<sup>2</sup> and Gly<sup>3</sup> starting from the C terminus. Corresponding GABA-fragments are labelled in the same manner as G, G' and G'' and their atoms are numbered in the order of priority. For the clarity purpose, the example of the hexapeptide **12** with schematic representation of the numbering is given below Table S1 (page S6).

**Fp-GABA-OH (Fp-G-OH) 1** (IR, UV and mass spectra were in accordance with the published data [2]).

Starting from *tert*-butyl ester (1.19 g, 1.31 mmol) in TFA/DCM (1:1, 40 mL) the acid **1** (1.10 g, 99%) was obtained. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>/CS<sub>2</sub>/CD<sub>3</sub>OH):  $\delta$ = 4.4 (CH<sub>2</sub><sup>pyrr</sup>, overlapped with CD<sub>3</sub>OH signal), 3.26 (t,  $J$ =7.0 Hz, 2H, CH<sub>2</sub><sup>4</sup>), 2.73 (t,  $J$ =7.0 Hz, 2H, CH<sub>2</sub><sup>2</sup>), 2.31 (quintet,  $J$ =7.0 Hz, 2H, CH<sub>2</sub><sup>3</sup>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>/CF<sub>3</sub>COOD):  $\delta$ = 5.84 (d,  $J$ =12.0 Hz, 2H, CH<sub>2</sub><sup>pyrr</sup>), 5.07 (d,  $J$ =12.0 Hz, 2H, CH<sub>2</sub><sup>pyrr</sup>), 4.23 (t,  $J$ =8.0 Hz, 2H, CH<sub>2</sub><sup>4</sup>), 2.94 (t,  $J$ =6.5 Hz, 2H, CH<sub>2</sub><sup>2</sup>), 2.65 (quintet,  $J$ =6.5 Hz, 2H, CH<sub>2</sub><sup>3</sup>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>/CS<sub>2</sub>/CF<sub>3</sub>COOD):  $\delta$ =179.81 (COOH), 150.07, 149.75, 148.00, 147.01, 146.91, 146.80, 146.69, 146.43, 146.27, 145.95, 145.91, 145.50, 144.98, 144.87, 144.68, 144.20, 143.33, 143.29, 142.69, 142.55, 142.54, 142.34, 141.93, 141.82, 140.86, 140.84, 136.45, 135.91, 68.00 ( $C_f$ -1, 9), 66.04 (CH<sub>2</sub><sup>pyrr</sup>), 55.39 (CH<sub>2</sub><sup>4</sup>), 30.88 (CH<sub>2</sub><sup>2</sup>), 20.77 (CH<sub>2</sub><sup>3</sup>).

### Fp-GABA<sub>2</sub>-OH (Fp-G'-G-OH) 2

Starting from *tert*-butyl ester (130 mg, 0.13 mmol) in TFA/DCM (1:1, 4 mL) the acid **2** (120 mg, 99%) was obtained. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>/CS<sub>2</sub>/CD<sub>3</sub>OH):  $\delta$ =7.58 (br.t,  $J$ =5.0 Hz, 1H, NH<sup>GABA</sup>), 4.66 (s, 4H, CH<sub>2</sub><sup>pyrr</sup>), 3.33 (t,  $J$ =6.5 Hz, 2H, CH<sub>2</sub><sup>4</sup>), 3.32 (q,  $J$ =7.0 Hz, 2H, CH<sub>2</sub><sup>4</sup>), 2.58 (t,  $J$ =7.0 Hz, 2H, CH<sub>2</sub><sup>2</sup>), 2.37 (t,  $J$ =7.0 Hz, 2H, CH<sub>2</sub><sup>2</sup>), 2.30 (quintet,  $J$ =7.0 Hz, 2H, CH<sub>2</sub><sup>3</sup>), 1.87 (quintet,  $J$ =7.0 Hz, 2H, CH<sub>2</sub><sup>3</sup>); <sup>13</sup>C NMR (125

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[2] Bjelakovic MS, Godjevac DM, Milic DR (2007) Synthesis and antioxidant properties of fullero-steroidal covalent conjugates, Carbon 45:2260-2265.

MHz, CDCl<sub>3</sub>/CS<sub>2</sub>/CD<sub>3</sub>OH):  $\delta$ =175.61 (COOH), 173.62 (CONH), 153.64 (C<sub>F</sub>-2, 5, 8, 10), 147.03 (C<sub>F</sub>-52, 60), 145.98 (C<sub>F</sub>-32, 39, 41, 48), 145.79 (C<sub>F</sub>-3, 4, 25, 26), 145.43 (C<sub>F</sub>-51, 53, 56, 59), 145.30 (C<sub>F</sub>-21, 30), 145.21 (C<sub>F</sub>-14, 19, 23, 28), 145.00 (C<sub>F</sub>-49, 50, 54, 55), 144.21 (C<sub>F</sub>-33, 38, 42, 47), 142.80 (C<sub>F</sub>-31, 40), 142.36 (C<sub>F</sub>-35, 36, 57, 58), 141.78 (C<sub>F</sub>-13, 20, 22, 29), 141.75 (C<sub>F</sub>-34, 37, 43, 46), 141.62 (C<sub>F</sub>-16, 17, 44, 45), 139.88 (C<sub>F</sub>-15, 18, 24, 27), 135.89 (C<sub>F</sub>-6, 7, 11, 12), 69.67 (C<sub>F</sub>-1, 9), 66.71 (CH<sub>2</sub><sup>pyrr</sup>), 53.93 (CH<sub>2</sub><sup>4'</sup>), 38.81 (CH<sub>2</sub><sup>4</sup>), 33.63 (CH<sub>2</sub><sup>2'</sup>), 31.30 (CH<sub>2</sub><sup>2</sup>), 24.31 (CH<sub>2</sub><sup>3</sup>), 23.55 (CH<sub>2</sub><sup>3'</sup>); IR:  $\nu$ =3438, 2928, 1672, 1429, 1186, 1137 cm<sup>-1</sup>; UV/Vis (CHCl<sub>3</sub>):  $\lambda_{\max}$  ( $\epsilon$ )=430 (3500), 324 (38000), 305 (37000), 257 nm (98000 mol<sup>-1</sup>dm<sup>3</sup>cm<sup>-1</sup>); ESI-TOF-MS:  $m/z$ : calcd for C<sub>70</sub>H<sub>19</sub>N<sub>2</sub>O<sub>3</sub>: 935.13902 [M+H]<sup>+</sup>, found 935.14058.

### Fp-GABA<sub>3</sub>-OH(Fp-G''-G'-G-OH) 3

Starting from *tert*-butyl ester (140 mg, 0.13 mmol) in TFA/DCM (1:1, 4 mL) the acid **3** (131 mg, 99%) was obtained. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>/CS<sub>2</sub>):  $\delta$ =7.72 (br.t,  $J$ =6.0 Hz, 1H, NH<sup>GABA'</sup>), 7.52 (br.t,  $J$ =5.5 Hz, 1H, NH<sup>GABA</sup>), 4.62 (s, 4H, CH<sub>2</sub><sup>pyrr</sup>), 3.31 (t,  $J$ =7.0 Hz, 2H, CH<sub>2</sub><sup>4''</sup>), 3.27 (q,  $J$ =7.0 Hz, 2H, CH<sub>2</sub><sup>4'</sup>), 3.26 (t,  $J$ =7.0 Hz, 2H, CH<sub>2</sub><sup>4</sup>), 2.57 (t,  $J$ =7.5 Hz, 2H, CH<sub>2</sub><sup>2''</sup>), 2.34 (t,  $J$ =7.0 Hz, 2H, CH<sub>2</sub><sup>2</sup>), 2.30 (quintet,  $J$ =7.0 Hz, 2H, CH<sub>2</sub><sup>3''</sup>), 2.23 (t,  $J$ =7.5 Hz, 2H, CH<sub>2</sub><sup>2'</sup>), 1.83 (quintet,  $J$ =7.0 Hz, 2H, CH<sub>2</sub><sup>3</sup>), 1.82 (quintet,  $J$ =7.0 Hz, 2H, CH<sub>2</sub><sup>3'</sup>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$ =175.71 (COOH), 173.82 (CO<sup>GABA''</sup>), 173.77 (CO<sup>GABA'</sup>), 153.85 (C<sub>F</sub>-2, 5, 8, 10), 147.09 (C<sub>F</sub>-52, 60), 146.03 (C<sub>F</sub>-32, 39, 41, 48), 145.84 (C<sub>F</sub>-3, 4, 25, 26), 145.53 (C<sub>F</sub>-51, 53, 56, 59), 145.37 (C<sub>F</sub>-21, 30), 145.25 (C<sub>F</sub>-14, 19, 23, 28), 145.06 (C<sub>F</sub>-49, 50, 54, 55), 144.28 (C<sub>F</sub>-33, 38, 42, 47), 142.86 (C<sub>F</sub>-31, 40), 142.41 (C<sub>F</sub>-35, 36, 57, 58), 141.83 (C<sub>F</sub>-13, 20, 22, 29), 141.83 (C<sub>F</sub>-34, 37, 43, 46), 141.68 (C<sub>F</sub>-16, 17, 44, 45), 139.93 (C<sub>F</sub>-15, 18, 24, 27), 135.95 (C<sub>F</sub>-6, 7, 11, 12), 69.83 (C<sub>F</sub>-1, 9), 66.91 (CH<sub>2</sub><sup>pyrr</sup>), 54.04 (CH<sub>2</sub><sup>4''</sup>), 38.82, 38.79 (CH<sub>2</sub><sup>4,4'</sup>), 33.76 (CH<sub>2</sub><sup>2</sup>), 33.32 (CH<sub>2</sub><sup>2'</sup>), 31.35 (CH<sub>2</sub><sup>2</sup>), 25.19 (CH<sub>2</sub><sup>3</sup>), 24.23 (CH<sub>2</sub><sup>3</sup>), 23.83 (CH<sub>2</sub><sup>3''</sup>); IR:  $\nu$ =3423, 3306, 3093, 2935, 1648, 1554, 1429, 1186 1137 cm<sup>-1</sup>; UV/Vis (CHCl<sub>3</sub>):  $\lambda_{\max}$  ( $\epsilon$ )=430 (3600), 322 (38000), 304 (37000), 257 nm (110000 mol<sup>-1</sup>dm<sup>3</sup>cm<sup>-1</sup>); ESI-TOF-MS:  $m/z$ : calcd for C<sub>74</sub>H<sub>26</sub>N<sub>3</sub>O<sub>4</sub>: 1020.19178 [M+H]<sup>+</sup>, found 1020.19315.

### Fp-GABA-Gly-OH(Fp-G-Gly-OH) 4

Starting from *tert*-butyl ester (125 mg, 0.13 mmol) in TFA/DCM (1:1, 4 mL) the acid **4** (117 mg, 99%) was obtained. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>/CS<sub>2</sub>/CD<sub>3</sub>OH):  $\delta$ =7.76 (br.t,  $J$ =5.5 Hz, 1H, NH<sup>Gly</sup>), 4.52 (s, 4H, CH<sub>2</sub><sup>pyrr</sup>), 3.98 (d,  $J$ =5.5 Hz, 2H, CH<sub>2</sub><sup>Gly</sup>), 3.23 (t,  $J$ =7.0 Hz, 2H, CH<sub>2</sub><sup>4</sup>), 2.64 (t,  $J$ =7.0 Hz, 2H, CH<sub>2</sub><sup>2</sup>), 2.28 (quintet,  $J$ =7.0 Hz, 2H, CH<sub>2</sub><sup>3</sup>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$ =173.72 (CONH), 171.31 (COOH), 154.15 (C<sub>F</sub>-2, 5, 8, 10), 146.82 (C<sub>F</sub>-52, 60), 145.77 (C<sub>F</sub>-32, 39, 41, 48), 145.59 (C<sub>F</sub>-3, 4, 25, 26), 145.46 (C<sub>F</sub>-51, 53, 56, 59), 145.17 (C<sub>F</sub>-21, 30), 144.98 (C<sub>F</sub>-14, 19, 23, 28), 144.81 (C<sub>F</sub>-49, 50, 54, 55), 144.06 (C<sub>F</sub>-33, 38, 42, 47), 142.62 (C<sub>F</sub>-31, 40), 142.16 (C<sub>F</sub>-35, 36, 57, 58), 141.69 (C<sub>F</sub>-13, 20, 22, 29), 141.61 (C<sub>F</sub>-34, 37, 43, 46), 141.43 (C<sub>F</sub>-16, 17, 44, 45), 139.71 (C<sub>F</sub>-15, 18, 24, 27), 135.70 (C<sub>F</sub>-6, 7, 11, 12), 69.92 (C<sub>F</sub>-1, 9), 67.04 (CH<sub>2</sub><sup>pyrr</sup>), 53.47 (CH<sub>2</sub><sup>4</sup>), 40.68 (CH<sub>2</sub><sup>Gly</sup>), 33.20 (CH<sub>2</sub><sup>2</sup>), 23.78 (CH<sub>2</sub><sup>3</sup>); IR:  $\nu$ =3428, 2925, 1656, 1638, 1545, 1187, 1138cm<sup>-1</sup>; UV/Vis (CHCl<sub>3</sub>):  $\lambda_{\max}$  ( $\epsilon$ )=430 (1900), 324 (16000), 303 (17000), 256 nm (60000 mol<sup>-1</sup>dm<sup>3</sup>cm<sup>-1</sup>); ESI-TOF-MS:  $m/z$ : calcd for C<sub>68</sub>H<sub>15</sub>N<sub>2</sub>O<sub>3</sub>: 907.10772 [M+H]<sup>+</sup>, found 907.10514.

### Fp-GABA-Gly<sub>2</sub>-OH (Fp-G-Gly<sup>2</sup>-Gly<sup>1</sup>-OH) 5

Starting from *tert*-butyl ester (133 mg, 0.13 mmol) in TFA/DCM (1:1, 4 mL) the acid **5** (124 mg, 99%) was obtained. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>/CS<sub>2</sub>/CD<sub>3</sub>OH):  $\delta$ =7.93 (br.t,  $J$ =5.0 Hz, 1H, NH<sup>Gly<sup>2</sup></sup>), 7.86 (br.t,  $J$ =5.0 Hz, 1H, NH<sup>Gly<sup>1</sup></sup>), 4.58 (s, 4H, CH<sub>2</sub><sup>pyrr</sup>), 3.95 (d,  $J$ =5.5 Hz, 2H, CH<sub>2</sub><sup>Gly<sup>2</sup></sup>), 3.94 (d,  $J$ =6.0 Hz, 2H, CH<sub>2</sub><sup>Gly<sup>1</sup></sup>), 3.28 (t,  $J$ =7.0 Hz, 2H, CH<sub>2</sub><sup>4</sup>), 2.65 (t,  $J$ =7.0 Hz, 2H, CH<sub>2</sub><sup>2</sup>), 2.29 (quintet,  $J$ =7.0 Hz, 2H, CH<sub>2</sub><sup>3</sup>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>/CS<sub>2</sub>/CD<sub>3</sub>OH):  $\delta$ =173.92 (CO<sup>GABA</sup>), 171.19 (COOH), 169.71 (CO<sup>Gly<sup>2</sup></sup>), 153.96 (C<sub>F</sub>-2, 5, 8, 10), 146.87 (C<sub>F</sub>-52, 60), 145.83 (C<sub>F</sub>-32, 39, 41, 48), 145.64 (C<sub>F</sub>-3, 4, 25, 26), 145.44 (C<sub>F</sub>-51, 53, 56, 59), 145.20 (C<sub>F</sub>-21, 30), 145.04 (C<sub>F</sub>-14, 19, 23, 28), 144.86 (C<sub>F</sub>-49, 50, 54, 55), 144.10 (C<sub>F</sub>-33, 38, 42, 47), 142.66 (C<sub>F</sub>-31, 40), 142.22 (C<sub>F</sub>-35, 36, 57, 58), 141.69 (C<sub>F</sub>-13, 20, 22, 29), 141.65 (C<sub>F</sub>-34, 37, 43, 46), 141.48 (C<sub>F</sub>-16, 17, 44, 45), 139.74 (C<sub>F</sub>-15, 18, 24, 27), 135.77 (C<sub>F</sub>-6, 7, 11, 12), 69.81 (C<sub>F</sub>-1, 9), 66.92 (CH<sub>2</sub><sup>pyrr</sup>), 53.71 (CH<sub>2</sub><sup>4</sup>), 42.20 (CH<sub>2</sub><sup>Gly<sup>2</sup></sup>), 40.55 (CH<sub>2</sub><sup>Gly<sup>1</sup></sup>), 33.22 (CH<sub>2</sub><sup>2</sup>), 23.63 (CH<sub>2</sub><sup>3</sup>); IR:  $\nu$ =3432, 2926, 1669, 1540, 1423, 1188, 1136, 1032 cm<sup>-1</sup>; UV/Vis (CHCl<sub>3</sub>):  $\lambda_{\max}$  ( $\epsilon$ )=430 (3700), 321 (38000), 305 (39000), 254 nm (110000 mol<sup>-1</sup>dm<sup>3</sup>cm<sup>-1</sup>); ESI-TOF-MS:  $m/z$ : calcd for C<sub>70</sub>H<sub>18</sub>N<sub>3</sub>O<sub>4</sub>: 964.12918 [M+H]<sup>+</sup>, found 964.13113.

### Fp-GABA-Gly<sub>3</sub>-OH (Fp-G-Gly<sup>3</sup>-Gly<sup>2</sup>-Gly<sup>1</sup>-OH) 6

Starting from *tert*-butyl ester (140 mg, 0.13 mmol) in TFA/DCM (1:1, 4 mL) the acid **6** (135 mg, 98%) was obtained.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3/\text{CS}_2/\text{CD}_3\text{OH}$ ):  $\delta$ =8.09 (br.t,  $J$ =5.5 Hz, 1H,  $\text{NH}^{\text{Gly}^3}$ ), 8.06 (br.t,  $J$ =5.0 Hz, 1H,  $\text{NH}^{\text{Gly}^2}$ ), 7.91 (br.t,  $J$ =6.0 Hz, 1H,  $\text{NH}^{\text{Gly}^1}$ ), 4.60 (s, 4H,  $\text{CH}_2^{\text{pyrr}}$ ), 3.942 (d,  $J$ =5.5 Hz, 2H,  $\text{CH}_2^{\text{Gly}^1}$ ), 3.934 (d,  $J$ =5.5 Hz, 2H,  $\text{CH}_2^{\text{Gly}^3}$ ), 3.931 (d,  $J$ =6.0 Hz, 2H,  $\text{CH}_2^{\text{Gly}^2}$ ), 3.30 (t,  $J$ =7.0 Hz, 2H,  $\text{CH}_2^4$ ), 2.66 (t,  $J$ =7.0 Hz, 2H,  $\text{CH}_2^2$ ), 2.30 (quintet,  $J$ =7.5 Hz, 2H,  $\text{CH}_2^3$ );  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3/\text{CS}_2/\text{CD}_3\text{OH}$ ):  $\delta$ =174.38 ( $\text{CO}^{\text{GABA}}$ ), 171.39 ( $\text{COOH}$ ), 170.10 ( $\text{CO}^{\text{Gly}^3}$ ), 169.82 ( $\text{CO}^{\text{Gly}^2}$ ), 153.91 ( $\text{C}_r$ -2, 5, 8, 10), 146.91 ( $\text{C}_r$ -52, 60), 145.87 ( $\text{C}_r$ -32, 39, 41, 48), 145.68 ( $\text{C}_r$ -3, 4, 25, 26), 145.44 ( $\text{C}_r$ -51, 53, 56, 59), 145.22 ( $\text{C}_r$ -21, 30), 145.08 ( $\text{C}_r$ -14, 19, 23, 28), 144.90 ( $\text{C}_r$ -49, 50, 54, 55), 144.13 ( $\text{C}_r$ -33, 38, 42, 47), 142.70 ( $\text{C}_r$ -31, 40), 142.25 ( $\text{C}_r$ -35, 36, 57, 58), 141.71 ( $\text{C}_r$ -13, 20, 22, 29), 141.68 ( $\text{C}_r$ -34, 37, 43, 46), 141.52 ( $\text{C}_r$ -16, 17, 44, 45), 139.78 ( $\text{C}_r$ -15, 18, 24, 27), 135.79 ( $\text{C}_r$ -6, 7, 11, 12), 69.80 ( $\text{C}_r$ -1, 9), 66.90 ( $\text{CH}_2^{\text{pyrr}}$ ), 53.75 ( $\text{CH}_2^4$ ), 42.62 ( $\text{CH}_2^{\text{Gly}^3}$ ), 42.05 ( $\text{CH}_2^{\text{Gly}^2}$ ), 40.55 ( $\text{CH}_2^{\text{Gly}^1}$ ), 33.18 ( $\text{CH}_2^2$ ), 23.54 ( $\text{CH}_2^3$ ); IR:  $\nu$ =3407, 2928, 1662, 1543, 1424, 1190, 1136, 1078, 1030  $\text{cm}^{-1}$ ; UV/Vis ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  ( $\epsilon$ )=430 (3500), 322 (30000), 305 (31000), 257 nm (98000  $\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$ ); ESI-TOF-MS:  $m/z$ : calcd for  $\text{C}_{72}\text{H}_{21}\text{N}_4\text{O}_5$ : 1021.15065  $[\text{M}+\text{H}]^+$ , found 1021.15062.

### Fp-GABA<sub>2</sub>-Gly-OH (Fp-G'-G-Gly-OH) 7

Starting from *tert*-butyl ester (136 mg, 0.13 mmol) in TFA/DCM (1:1, 4 mL) the acid **7** (126 mg, 98%) was obtained.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3/\text{CS}_2/\text{CD}_3\text{OH}$ ):  $\delta$ =7.76 (br.t,  $J$ =5.5 Hz, 1H,  $\text{NH}^{\text{Gly}}$ ), 7.74 (br.t,  $J$ =5.5 Hz, 1H,  $\text{NH}^{\text{GABA}}$ ), 4.70 (s, 4H,  $\text{CH}_2^{\text{pyrr}}$ ), 3.94 (d,  $J$ =5.5 Hz, 2H,  $\text{CH}_2^{\text{Gly}}$ ), 3.36 (t,  $J$ =7.5 Hz, 2H,  $\text{CH}_2^4$ ), 3.31 (q,  $J$ =6.5 Hz, 2H,  $\text{CH}_2^4$ ), 2.56 (t,  $J$ =7.0 Hz, 2H,  $\text{CH}_2^2$ ), 2.31 (t,  $J$ =7.0 Hz, 2H,  $\text{CH}_2^2$ ), 2.30 (quintet,  $J$ =7.0 Hz, 2H,  $\text{CH}_2^3$ ), 1.87 (quintet,  $J$ =7.0 Hz, 2H,  $\text{CH}_2^3$ );  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3/\text{CS}_2/\text{CD}_3\text{OH}$ ):  $\delta$ =173.98 ( $\text{CO}^{\text{GABA}}$ ), 173.74 ( $\text{CO}^{\text{GABA}}$ ), 171.69 ( $\text{COOH}$ ), 153.50 ( $\text{C}_r$ -2, 5, 8, 10), 147.04 ( $\text{C}_r$ -52, 60), 146.00 ( $\text{C}_r$ -32, 39, 41, 48), 145.80 ( $\text{C}_r$ -3, 4, 25, 26), 145.39 ( $\text{C}_r$ -51, 53, 56, 59), 145.31 ( $\text{C}_r$ -21, 30), 145.23 ( $\text{C}_r$ -14, 19, 23, 28), 145.02 ( $\text{C}_r$ -49, 50, 54, 55), 144.22 ( $\text{C}_r$ -33, 38, 42, 47), 142.81 ( $\text{C}_r$ -31, 40), 142.37 ( $\text{C}_r$ -35, 36, 57, 58), 141.79 ( $\text{C}_r$ -13, 20, 22, 29), 141.73 ( $\text{C}_r$ -34, 37, 43, 46), 141.64 ( $\text{C}_r$ -16, 17, 44, 45), 139.89 ( $\text{C}_r$ -15, 18, 24, 27), 135.93 ( $\text{C}_r$ -6, 7, 11, 12), 69.58 ( $\text{C}_r$ -1, 9), 66.61 ( $\text{CH}_2^{\text{pyrr}}$ ), 54.07 ( $\text{CH}_2^4$ ), 40.87 ( $\text{CH}_2^{\text{Gly}}$ ), 38.76 ( $\text{CH}_2^4$ ), 33.61 ( $\text{CH}_2^2$ ), 33.00 ( $\text{CH}_2^2$ ), 24.89 ( $\text{CH}_2^3$ ), 23.54 ( $\text{CH}_2^3$ ); IR:  $\nu$ =3431, 2924, 2854, 1638, 1544, 1430, 1185, 1134, 1077  $\text{cm}^{-1}$ ; UV/Vis ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  ( $\epsilon$ )=430 (3700), 323 (30000), 306 (32000), 257 nm (97000  $\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$ ); ESI-TOF-MS:  $m/z$ : calcd for  $\text{C}_{72}\text{H}_{22}\text{N}_3\text{O}_4$ : 992.16048  $[\text{M}+\text{H}]^+$ , found 992.16218.

### Fp-GABA<sub>2</sub>-Gly<sub>2</sub>-OH (Fp-G'-G-Gly<sup>2</sup>-Gly<sup>1</sup>-OH) 8

Starting from *tert*-butyl ester (144 mg, 0.13 mmol) in TFA/DCM (1:1, 4 mL) the acid **8** (133 mg, 98%) was obtained.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3/\text{CS}_2/\text{CD}_3\text{OH}$ ):  $\delta$ =7.92 (br.t,  $J$ =6.0 Hz, 1H,  $\text{NH}^{\text{Gly}^2}$ ), 7.85 (br.t,  $J$ =5.5 Hz, 1H,  $\text{NH}^{\text{Gly}^1}$ ), 7.68 (br.t,  $J$ =5.0 Hz, 1H,  $\text{NH}^{\text{GABA}}$ ), 4.50 (s, 4H,  $\text{CH}_2^{\text{pyrr}}$ ), 3.95 (d,  $J$ =5.5 Hz, 2H,  $\text{CH}_2^{\text{Gly}^1}$ ), 3.91 (d,  $J$ =5.5 Hz, 2H,  $\text{CH}_2^{\text{Gly}^2}$ ), 3.29 (q,  $J$ =6.5 Hz, 2H,  $\text{CH}_2^4$ ), 3.18 (t,  $J$ =7.0 Hz, 2H,  $\text{CH}_2^4$ ), 2.55 (t,  $J$ =7.0 Hz, 2H,  $\text{CH}_2^2$ ), 2.32 (t,  $J$ =7.0 Hz, 2H,  $\text{CH}_2^2$ ), 2.26 (quintet,  $J$ =7.0 Hz, 2H,  $\text{CH}_2^3$ ), 1.86 (quintet,  $J$ =7.0 Hz, 2H,  $\text{CH}_2^3$ );  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3/\text{CS}_2/\text{CD}_3\text{OH}$ ):  $\delta$ =174.04 ( $\text{CO}^{\text{GABA}}$ ), 173.86 ( $\text{CO}^{\text{GABA}}$ ), 171.47 ( $\text{CO}^{\text{Gly}^1}$ ), 170.04 ( $\text{CO}^{\text{Gly}^2}$ ), 154.32 ( $\text{C}_r$ -2, 5, 8, 10), 146.95 ( $\text{C}_r$ -52, 60), 145.90 ( $\text{C}_r$ -32, 39, 41, 48), 145.72 ( $\text{C}_r$ -3, 4, 25, 26), 145.60 ( $\text{C}_r$ -51, 53, 56, 59), 145.29 ( $\text{C}_r$ -21, 30), 145.10 ( $\text{C}_r$ -14, 19, 23, 28), 144.94 ( $\text{C}_r$ -49, 50, 54, 55), 144.19 ( $\text{C}_r$ -33, 38, 42, 47), 142.75 ( $\text{C}_r$ -31, 40), 142.29 ( $\text{C}_r$ -35, 36, 57, 58), 141.80 ( $\text{C}_r$ -13, 20, 22, 29), 141.72 ( $\text{C}_r$ -34, 37, 43, 46), 141.55 ( $\text{C}_r$ -16, 17, 44, 45), 139.83 ( $\text{C}_r$ -15, 18, 24, 27), 135.83 ( $\text{C}_r$ -6, 7, 11, 12), 70.09 ( $\text{C}_r$ -1, 9), 67.28 ( $\text{CH}_2^{\text{pyrr}}$ ), 53.92 ( $\text{CH}_2^4$ ), 42.28 ( $\text{CH}_2^{\text{Gly}^2}$ ), 40.73 ( $\text{CH}_2^{\text{Gly}^1}$ ), 38.41 ( $\text{CH}_2^4$ ), 33.73 ( $\text{CH}_2^2$ ), 32.71 ( $\text{CH}_2^2$ ), 24.95 ( $\text{CH}_2^3$ ), 24.14 ( $\text{CH}_2^3$ ); IR:  $\nu$ =3423, 2924, 1671, 1543, 1428, 1202, 1136  $\text{cm}^{-1}$ ; UV/Vis ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  ( $\epsilon$ )=430 (3800), 324 (30000), 307 (31000), 259 nm (90000  $\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$ ); ESI-TOF-MS:  $m/z$ : calcd for  $\text{C}_{74}\text{H}_{25}\text{N}_4\text{O}_5$ : 1049.18195  $[\text{M}+\text{H}]^+$ , found 1049.18362.

### Fp-GABA<sub>2</sub>-Gly<sub>3</sub>-OH (Fp-G'-G-Gly<sup>3</sup>-Gly<sup>2</sup>-Gly<sup>1</sup>-OH) 9

Starting from *tert*-butyl ester (151 mg, 0.13 mmol) in TFA/DCM (1:1, 4 mL) the acid **9** (142 mg, 99%) was obtained.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3/\text{CS}_2/\text{CD}_3\text{OH}$ ):  $\delta$ =8.16 (br.t,  $J$ =6.0 Hz, 1H,  $\text{NH}^{\text{Gly}^2}$ ), 8.13 (br.t,  $J$ =6.0 Hz, 1H,  $\text{NH}^{\text{Gly}^3}$ ), 7.91 (br.t,  $J$ =5.5 Hz, 1H,  $\text{NH}^{\text{Gly}^1}$ ), 7.78 (br.t,  $J$ =6.0 Hz, 1H,  $\text{NH}^{\text{GABA}}$ ), 4.53 (s, 4H,  $\text{CH}_2^{\text{pyrr}}$ ), 3.92 (d,  $J$ =5.5 Hz, 2H,  $\text{CH}_2^{\text{Gly}^1}$ ), 3.91 (d,  $J$ =5.5 Hz, 2H,  $\text{CH}_2^{\text{Gly}^2}$ ), 3.85 (d,  $J$ =6.0 Hz, 2H,  $\text{CH}_2^{\text{Gly}^3}$ ), 3.26 (q,  $J$ =6.5 Hz, 2H,  $\text{CH}_2^4$ ), 3.20 (t,  $J$ =7.0 Hz, 2H,  $\text{CH}_2^4$ ), 2.54 (t,  $J$ =7.5 Hz, 2H,  $\text{CH}_2^2$ ), 2.31 (t,  $J$ =7.0 Hz, 2H,  $\text{CH}_2^2$ ), 2.25 (quintet,  $J$ =7.5 Hz, 2H,  $\text{CH}_2^3$ ), 1.83 (quintet,  $J$ =7.0 Hz, 2H,  $\text{CH}_2^3$ );  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3/\text{CS}_2/\text{CD}_3\text{OH}$ ):  $\delta$ =174.42 ( $\text{CO}^{\text{GABA}}$ ), 173.79 ( $\text{CO}^{\text{GABA}}$ ), 171.35 ( $\text{CO}^{\text{Gly}^1}$ ), 170.26 ( $\text{CO}^{\text{Gly}^3}$ ), 169.92 ( $\text{CO}^{\text{Gly}^2}$ ), 154.11 ( $\text{C}_r$ -2, 5, 8, 10), 146.85 ( $\text{C}_r$ -52, 60), 145.80 ( $\text{C}_r$ -32, 39, 41, 48), 145.62 ( $\text{C}_r$ -3, 4, 25, 26),

145.46 (C<sub>F</sub>-51, 53, 56, 59), 145.18 (C<sub>F</sub>-21, 30), 145.01 (C<sub>F</sub>-14, 19, 23, 28), 144.84 (C<sub>F</sub>-49, 50, 54, 55), 144.09 (C<sub>F</sub>-33, 38, 42, 47), 142.65 (C<sub>F</sub>-31, 40), 142.19 (C<sub>F</sub>-35, 36, 57, 58), 141.68 (C<sub>F</sub>-13, 20, 22, 29), 141.63 (C<sub>F</sub>-34, 37, 43, 46), 141.46 (C<sub>F</sub>-16, 17, 44, 45), 139.73 (C<sub>F</sub>-15, 18, 24, 27), 135.74 (C<sub>F</sub>-6, 7, 11, 12), 69.91 (C<sub>F</sub>-1, 9), 67.09 (CH<sub>2</sub><sup>pyrr.</sup>), 53.88 (CH<sub>2</sub><sup>4'</sup>), 42.54 (CH<sub>2</sub><sup>Gly3</sup>), 41.98 (CH<sub>2</sub><sup>Gly2</sup>), 40.46 (CH<sub>2</sub><sup>Gly1</sup>), 38.23 (CH<sub>2</sub><sup>4</sup>), 33.58 (CH<sub>2</sub><sup>2'</sup>), 32.36 (CH<sub>2</sub><sup>2</sup>), 24.77 (CH<sub>2</sub><sup>3</sup>), 24.04 (CH<sub>2</sub><sup>3'</sup>); IR:  $\nu$ =3426, 2926, 1655, 1544, 1427, 1186, 1135, 1078 cm<sup>-1</sup>; UV/Vis (CHCl<sub>3</sub>):  $\lambda_{\max}$  ( $\epsilon$ )=430 (3000), 323 (27000), 305 (28000), 256 nm (90000 mol<sup>-1</sup>dm<sup>3</sup>cm<sup>-1</sup>); ESI-TOF-MS:  $m/z$ : calcd for C<sub>76</sub>H<sub>28</sub>N<sub>5</sub>O<sub>6</sub>: 1106.20341 [M+H]<sup>+</sup>, found 1106.20491.

### Fp-GABA<sub>3</sub>-Gly-OH (Fp-G''-G'-G-Gly-OH) 10

Starting from *tert*-butyl ester (147 mg, 0.13 mmol) in TFA/DCM (1:1, 4 mL) the acid **10** (138 mg, 99 %) was obtained. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>/CS<sub>2</sub>/CD<sub>3</sub>OH):  $\delta$ =7.79 (br.t,  $J$ =5.5 Hz, 1H, NH<sup>Gly</sup>), 7.72 (br.t,  $J$ =5.5 Hz, 1H, NH<sup>GABA'</sup>), 7.70 (br.t,  $J$ =5.5 Hz, 1H, NH<sup>GABA</sup>), 4.57 (s, 4H, CH<sub>2</sub><sup>pyrr.</sup>), 3.93 (d,  $J$ =5.5 Hz, 2H, CH<sub>2</sub><sup>Gly</sup>), 3.26 (q,  $J$ =6.0 Hz, 2H, CH<sub>2</sub><sup>4'</sup>), 3.25 (t,  $J$ =6.0 Hz, 2H, CH<sub>2</sub><sup>4''</sup>), 3.24 (q,  $J$ =6.5 Hz, 2H, CH<sub>2</sub><sup>4</sup>), 2.56 (t,  $J$ =7.5 Hz, 2H, CH<sub>2</sub><sup>2''</sup>), 2.28 (quintet,  $J$ =6.5 Hz, 4H, CH<sub>2</sub><sup>2</sup>, CH<sub>2</sub><sup>3''</sup>), 2.22t (t,  $J$ =7.0 Hz, 2H, CH<sub>2</sub><sup>2'</sup>), 1.82 (quintet,  $J$ =6.5 Hz, 4H, CH<sub>2</sub><sup>3,3'</sup>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>/CS<sub>2</sub>/CD<sub>3</sub>OH):  $\delta$ =173.97 (CO<sup>GABA</sup>), 173.86 (CO<sup>GABA''</sup>), 173.82 (CO<sup>GABA'</sup>), 171.70 (CO<sup>Gly</sup>), 154.02 (C<sub>F</sub>-2, 5, 8, 10), 147.01 (C<sub>F</sub>-52, 60), 145.96 (C<sub>F</sub>-32, 39, 41, 48), 145.77 (C<sub>F</sub>-3, 4, 25, 26), 145.54 (C<sub>F</sub>-51, 53, 56, 59), 145.32 (C<sub>F</sub>-21, 30), 145.17 (C<sub>F</sub>-14, 19, 23, 28), 144.99 (C<sub>F</sub>-49, 50, 54, 55), 144.22 (C<sub>F</sub>-33, 38, 42, 47), 142.80 (C<sub>F</sub>-31, 40), 142.35 (C<sub>F</sub>-35, 36, 57, 58), 141.80 (C<sub>F</sub>-13, 20, 22, 29), 141.77 (C<sub>F</sub>-34, 37, 43, 46), 141.61 (C<sub>F</sub>-16, 17, 44, 45), 139.87 (C<sub>F</sub>-15, 18, 24, 27), 135.88 (C<sub>F</sub>-6, 7, 11, 12), 69.92 (C<sub>F</sub>-1, 9), 67.06 (CH<sub>2</sub><sup>pyrr.</sup>), 53.99 (CH<sub>2</sub><sup>4'</sup>), 40.84 (CH<sub>2</sub><sup>Gly</sup>), 38.70 (CH<sub>2</sub><sup>4</sup>), 38.54 (CH<sub>2</sub><sup>4</sup>), 33.75 (CH<sub>2</sub><sup>2'</sup>), 33.18 (CH<sub>2</sub><sup>2</sup>), 32.97 (CH<sub>2</sub><sup>2</sup>), 25.14 (CH<sub>2</sub><sup>3</sup>), 24.86 (CH<sub>2</sub><sup>3</sup>), 23.97 (CH<sub>2</sub><sup>3''</sup>); IR:  $\nu$ =3427, 2928, 1646, 1544, 1430, 1187, 1136, 1077 cm<sup>-1</sup>; UV/Vis (CHCl<sub>3</sub>):  $\lambda_{\max}$  ( $\epsilon$ )=430 (3500), 323 (33000), 306 (35000), 258 nm (99000 mol<sup>-1</sup>dm<sup>3</sup>cm<sup>-1</sup>); ESI-TOF-MS:  $m/z$ : calcd for C<sub>76</sub>H<sub>29</sub>N<sub>4</sub>O<sub>5</sub>: 1077.21325 [M+H]<sup>+</sup>, found 1077.21457.

### Fp-GABA<sub>3</sub>-Gly<sub>2</sub>-OH (Fp-G''-G'-G-Gly<sup>2</sup>-Gly<sup>1</sup>-OH) 11

Starting from *tert*-butyl ester (155 mg, 0.13 mmol) in TFA/DCM (1:1, 4 mL) the acid **11** (146 mg, 99%) was obtained. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>/CS<sub>2</sub>/CD<sub>3</sub>OH):  $\delta$ =7.92 (br.t,  $J$ =5.5 Hz, 1H, NH<sup>Gly2</sup>), 7.86 (br.t,  $J$ =5.5 Hz, 1H, NH<sup>Gly1</sup>), 7.74 (br.t, 1H,  $J$ =6.0 Hz, NH<sup>GABA'</sup>), 7.69 (br.t,  $J$ =6.0 Hz, 1H, NH<sup>GABA</sup>), 4.64 (s, 4H, CH<sub>2</sub><sup>pyrr.</sup>), 3.95 (d,  $J$ =5.5 Hz, 2H, CH<sub>2</sub><sup>Gly1</sup>), 3.90 (d,  $J$ =6.0 Hz, 2H, CH<sub>2</sub><sup>Gly2</sup>), 3.31 (t,  $J$ =7.5 Hz, 2H, CH<sub>2</sub><sup>4''</sup>), 3.25 (q,  $J$ =7.0 Hz, 2H, CH<sub>2</sub><sup>4'</sup>), 3.23 (q,  $J$ =6.0 Hz, 2H, CH<sub>2</sub><sup>4</sup>), 2.56 (t,  $J$ =7.0 Hz, 2H, CH<sub>2</sub><sup>2''</sup>), 2.29 (quintet,  $J$ =7.0 Hz, 4H, CH<sub>2</sub><sup>2</sup>, CH<sub>2</sub><sup>3'</sup>), 2.22 (t,  $J$ =7.5 Hz, 2H, CH<sub>2</sub><sup>2'</sup>), 1.82 and 1.81 (2 quintets, 4H, CH<sub>2</sub><sup>3,3'</sup>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>/CS<sub>2</sub>/CD<sub>3</sub>OH):  $\delta$ =173.99 (CO<sup>GABA</sup>), 173.80 (CO<sup>GABA''</sup>), 173.78 (CO<sup>GABA'</sup>), 171.48 (CO<sup>Gly1</sup>), 170.12 (CO<sup>Gly2</sup>), 153.75 (C<sub>F</sub>-2, 5, 8, 10), 147.02 (C<sub>F</sub>-52, 60), 145.97 (C<sub>F</sub>-32, 39, 41, 48), 145.78 (C<sub>F</sub>-3, 4, 25, 26), 145.45 (C<sub>F</sub>-51, 53, 56, 59), 145.30 (C<sub>F</sub>-21, 30), 145.19 (C<sub>F</sub>-14, 19, 23, 28), 145.00 (C<sub>F</sub>-49, 50, 54, 55), 144.21 (C<sub>F</sub>-33, 38, 42, 47), 142.80 (C<sub>F</sub>-31, 40), 142.36 (C<sub>F</sub>-35, 36, 57, 58), 141.77 (C<sub>F</sub>-13, 20, 22, 29), 141.75 (C<sub>F</sub>-34, 37, 43, 46), 141.61 (C<sub>F</sub>-16, 17, 44, 45), 139.87 (C<sub>F</sub>-15, 18, 24, 27), 135.89 (C<sub>F</sub>-6, 7, 11, 12), 69.74 (C<sub>F</sub>-1, 9), 66.83 (CH<sub>2</sub><sup>pyrr.</sup>), 54.02 (CH<sub>2</sub><sup>4'</sup>), 42.34 (CH<sub>2</sub><sup>Gly2</sup>), 40.77 (CH<sub>2</sub><sup>Gly1</sup>), 38.69 (CH<sub>2</sub><sup>4'</sup>), 38.24 (CH<sub>2</sub><sup>4</sup>), 33.66 (CH<sub>2</sub><sup>2''</sup>), 33.07 (CH<sub>2</sub><sup>2'</sup>), 32.62 (CH<sub>2</sub><sup>2</sup>), 25.06 (CH<sub>2</sub><sup>3</sup>), 24.80 (CH<sub>2</sub><sup>3</sup>), 23.77 (CH<sub>2</sub><sup>3''</sup>); IR:  $\nu$ =3291, 3089, 2934, 1650, 1547, 1428, 1196, 1136, 1079 cm<sup>-1</sup>; UV/Vis (CHCl<sub>3</sub>):  $\lambda_{\max}$  ( $\epsilon$ )=430 (3000), 319 (28000), 306 (29000), 257 nm (91000 mol<sup>-1</sup>dm<sup>3</sup>cm<sup>-1</sup>); ESI-TOF-MS:  $m/z$ : calcd for C<sub>78</sub>H<sub>32</sub>N<sub>5</sub>O<sub>6</sub>: 1134.23471 [M+H]<sup>+</sup>, found 1134.23570.

### Fp-GABA<sub>3</sub>-Gly<sub>3</sub>-OH (Fp-G''-G'-G-Gly<sup>3</sup>-Gly<sup>2</sup>-Gly<sup>1</sup>-OH) 12

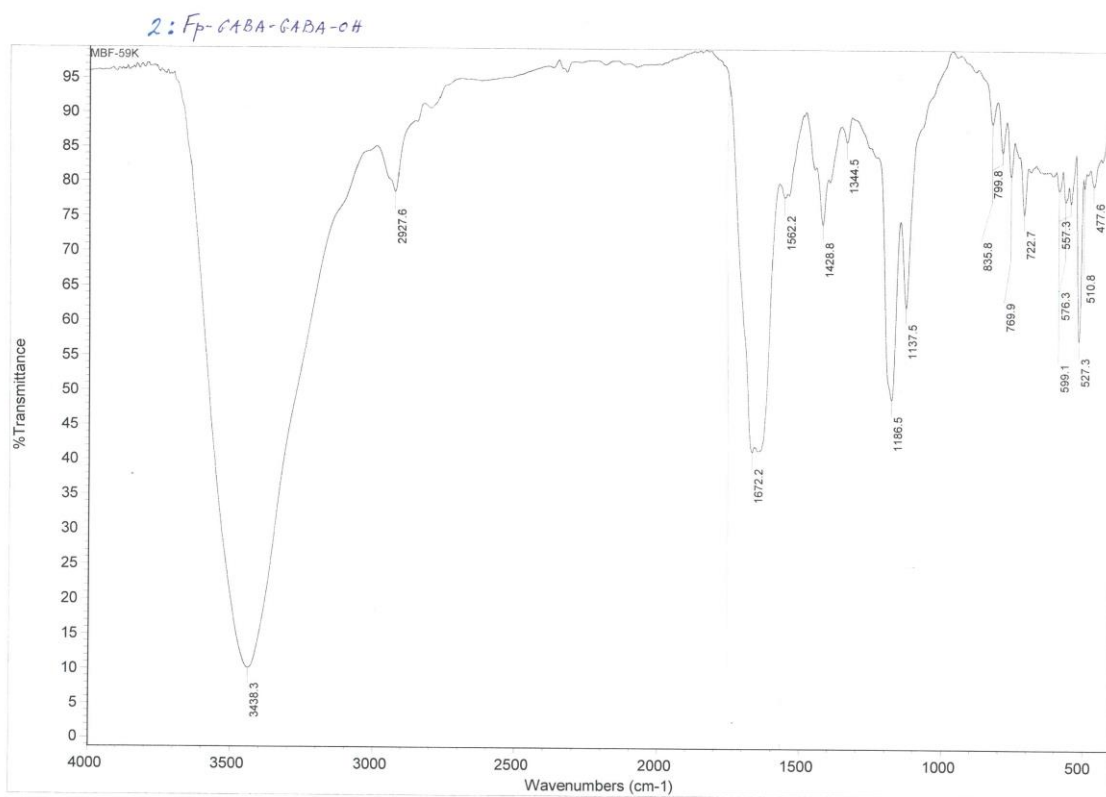
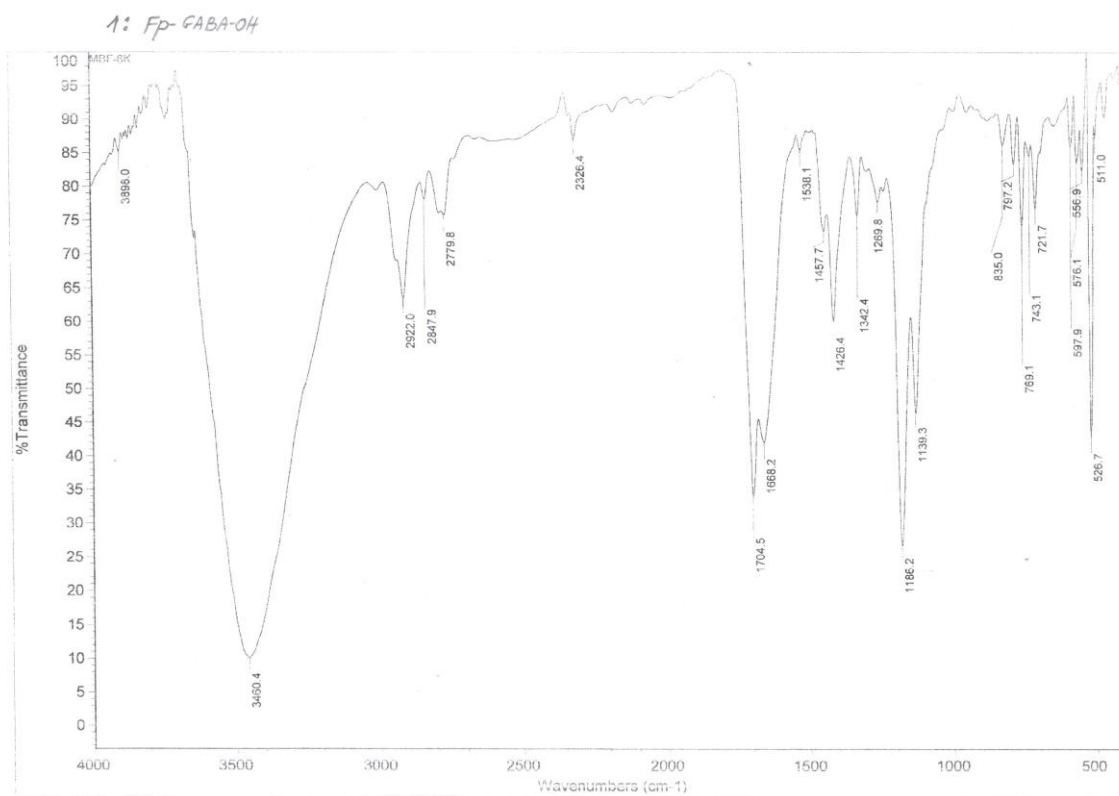
Starting from *tert*-butyl ester (162 mg, 0.13 mmol) in TFA/DCM (1:1, 4 mL) the acid **12** (154 mg, 100%) was obtained. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>/CS<sub>2</sub>/CD<sub>3</sub>OH):  $\delta$ =8.19 (br.t,  $J$ =6.0 Hz, 1H, NH<sup>Gly2</sup>), 8.12 (br.t,  $J$ =6.0 Hz, 1H, NH<sup>Gly3</sup>), 7.88 (br.t,  $J$ =5.5 Hz, 1H, NH<sup>Gly1</sup>), 7.81 (br.t, 1H,  $J$ =5.5 Hz, NH<sup>GABA</sup>), 7.71 (br.t,  $J$ =5.5 Hz, 1H, NH<sup>GABA</sup>), 4.63 (s, 4H, CH<sub>2</sub><sup>pyrr.</sup>), 3.93 (d,  $J$ =5.5 Hz, 2H, CH<sub>2</sub><sup>Gly1</sup>), 3.92 (d,  $J$ =5.0 Hz, 2H, CH<sub>2</sub><sup>Gly2</sup>), 3.86 (d,  $J$ =5.5 Hz, 2H, CH<sub>2</sub><sup>Gly3</sup>), 3.30 (t,  $J$ =7.5 Hz, 2H, CH<sub>2</sub><sup>4''</sup>), 3.25 (q,  $J$ =6.5 Hz, 2H, CH<sub>2</sub><sup>4'</sup>), 3.22 (q,  $J$ =6.5 Hz, 2H, CH<sub>2</sub><sup>4</sup>), 2.57 (t,  $J$ =7.0 Hz, 2H, CH<sub>2</sub><sup>2''</sup>), 2.29 (t,  $J$ =7.0 Hz, 2H, CH<sub>2</sub><sup>2</sup>), 2.28 (qui., 2H, CH<sub>2</sub><sup>3''</sup>), 2.22 (t,  $J$ =7.5 Hz, 2H, CH<sub>2</sub><sup>2'</sup>), 1.81 (qui.,  $J$ =6.5 Hz, 2H, CH<sub>2</sub><sup>3'</sup>), 1.80 (qui.,  $J$ =6.5 Hz, 2H, CH<sub>2</sub><sup>3</sup>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>/CS<sub>2</sub>/CD<sub>3</sub>OH):  $\delta$ =174.50 (CO<sup>GABA</sup>), 173.82 (CO<sup>GABA''</sup>), 173.80 (CO<sup>GABA'</sup>), 171.42 (CO<sup>Gly1</sup>), 170.43 (CO<sup>Gly3</sup>), 170.07 (CO<sup>Gly2</sup>), 153.74 (C<sub>F</sub>-2, 5, 8, 10), 146.97 (C<sub>F</sub>-52, 60), 145.92 (C<sub>F</sub>-32, 39, 41, 48), 145.73 (C<sub>F</sub>-3, 4, 25, 26), 145.41 (C<sub>F</sub>-51, 53, 56, 59), 145.25 (C<sub>F</sub>-21, 30), 145.14 (C<sub>F</sub>-14, 19, 23, 28), 144.95 (C<sub>F</sub>-49, 50, 54, 55), 144.16 (C<sub>F</sub>-33, 38, 42, 47), 142.76 (C<sub>F</sub>-31, 40), 142.31 (C<sub>F</sub>-35, 36, 57, 58), 141.72 (C<sub>F</sub>-13,

20, 22, 29), 141.71 (C<sub>r</sub>-34, 37, 43, 46), 141.56 (C<sub>r</sub>-16, 17, 44, 45), 139.82 (C<sub>r</sub>-15, 18, 24, 27), 135.85 (C<sub>r</sub>-6, 7, 11, 12), 69.72 (C<sub>r</sub>-1, 9), 66.82 (CH<sub>2</sub><sup>pyrr.</sup>), 54.00 (CH<sub>2</sub><sup>4''</sup>), 42.74 (CH<sub>2</sub><sup>Gly3</sup>), 42.15 (CH<sub>2</sub><sup>Gly2</sup>), 40.60 (CH<sub>2</sub><sup>Gly1</sup>), 38.63 (CH<sub>2</sub><sup>4'</sup>), 38.04 (CH<sub>2</sub><sup>4</sup>), 33.63 (CH<sub>2</sub><sup>2''</sup>), 32.99 (CH<sub>2</sub><sup>2'</sup>), 32.24 (CH<sub>2</sub><sup>2</sup>), 25.05 (CH<sub>2</sub><sup>3'</sup>), 24.70 (CH<sub>2</sub><sup>3</sup>), 23.76 (CH<sub>2</sub><sup>3''</sup>); IR:  $\nu$ =3416, 2929, 1651, 1546, 1426, 1188, 1135, 1078 cm<sup>-1</sup>; UV/Vis (CHCl<sub>3</sub>):  $\lambda_{\max}$  ( $\epsilon$ )=430 (3600), 321 (31000), 305 (32000), 257 nm (105000 mol<sup>-1</sup>dm<sup>3</sup>cm<sup>-1</sup>); ESI-TOF-MS:  $m/z$ : calcd for C<sub>80</sub>H<sub>35</sub>N<sub>6</sub>O<sub>7</sub>: 1191.25617 [M+H]<sup>+</sup>, found 1191.25671.

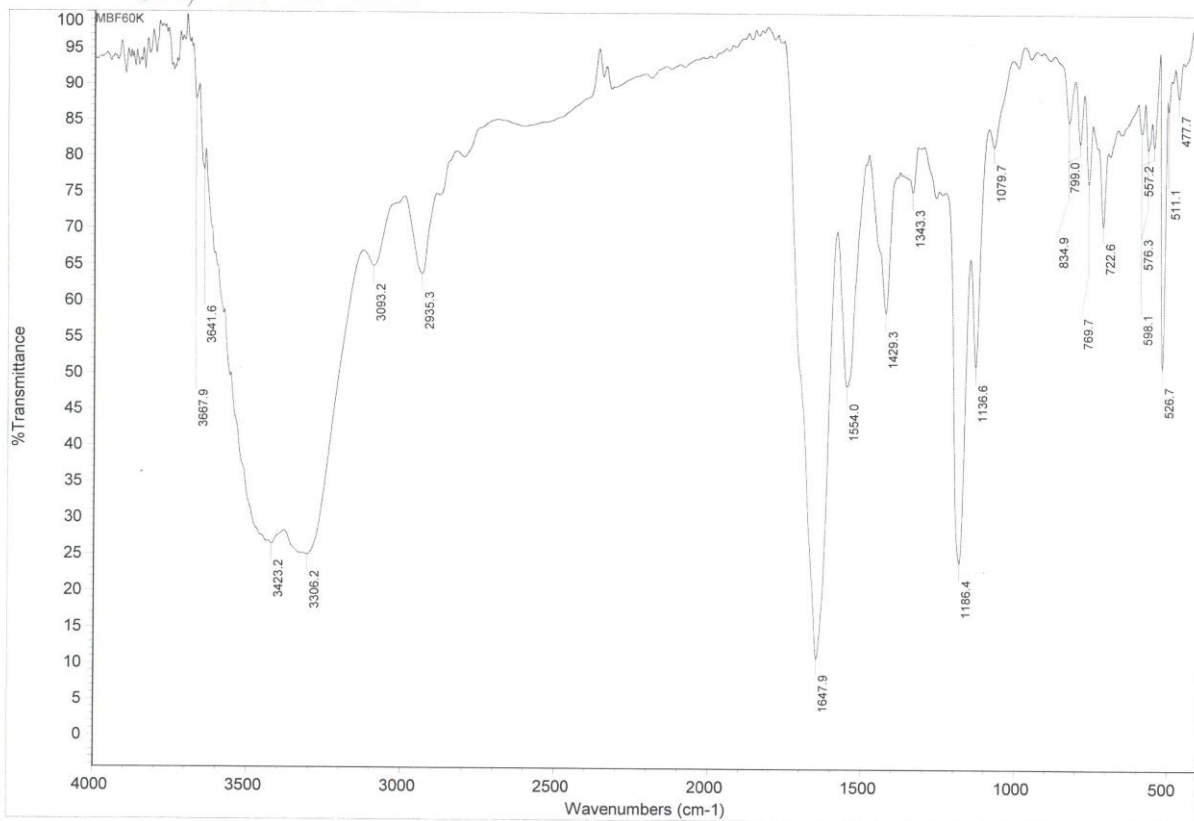




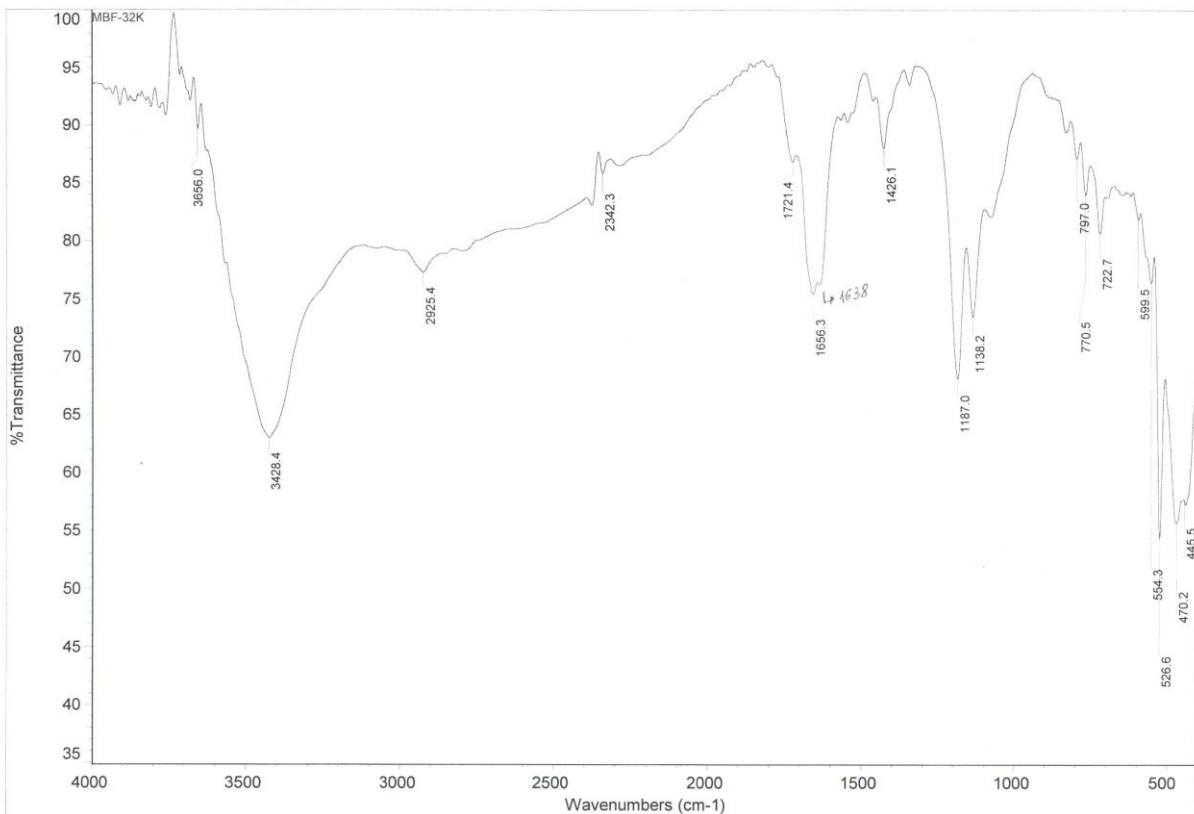
IR spectra of compounds 1-12

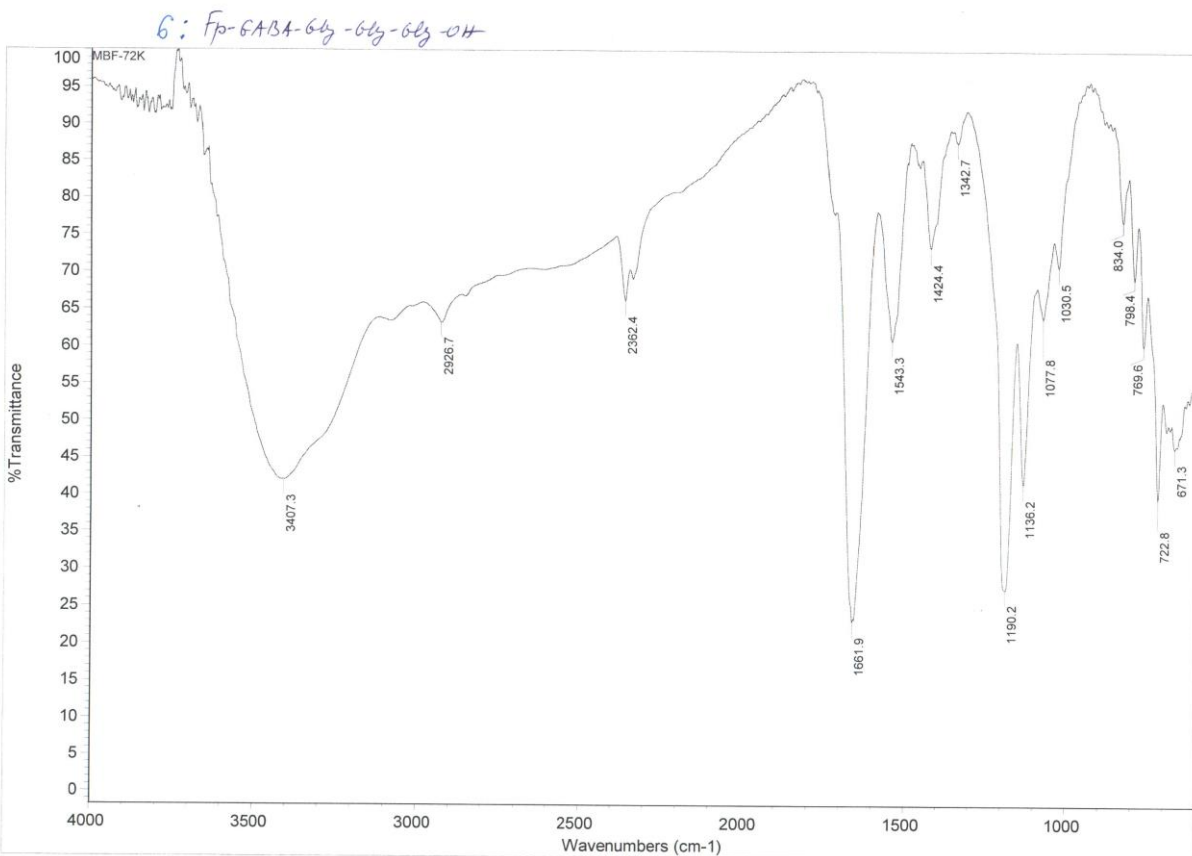
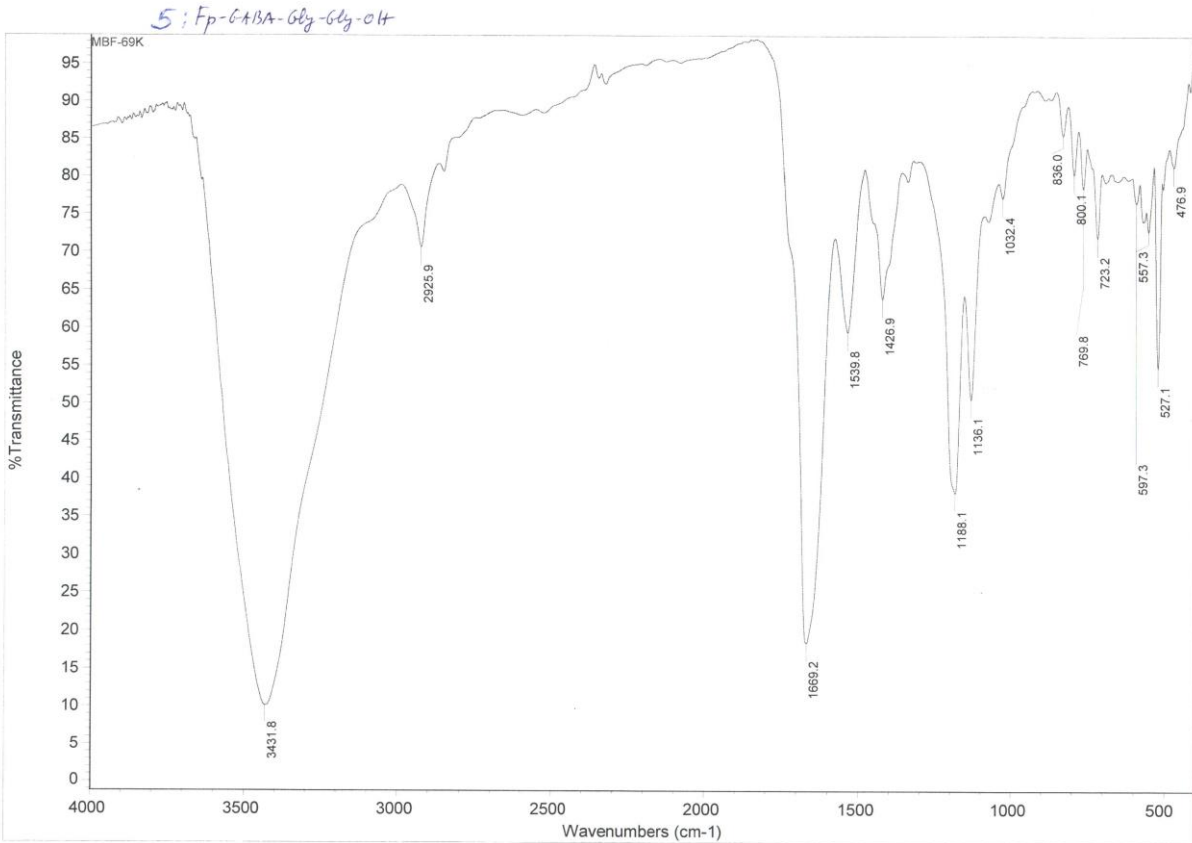


3: Fp-GABA-GABA-GABA-OH

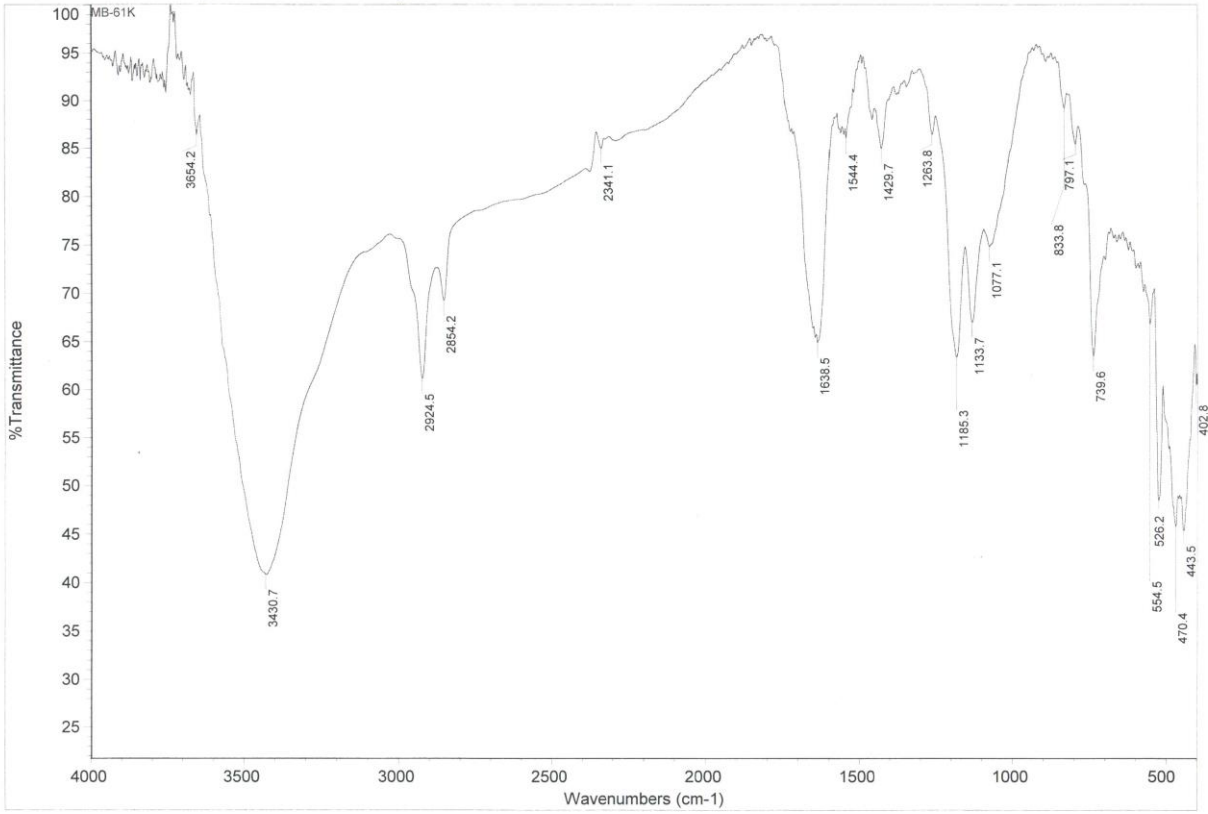


4: Fp-GABA-EGy-OH

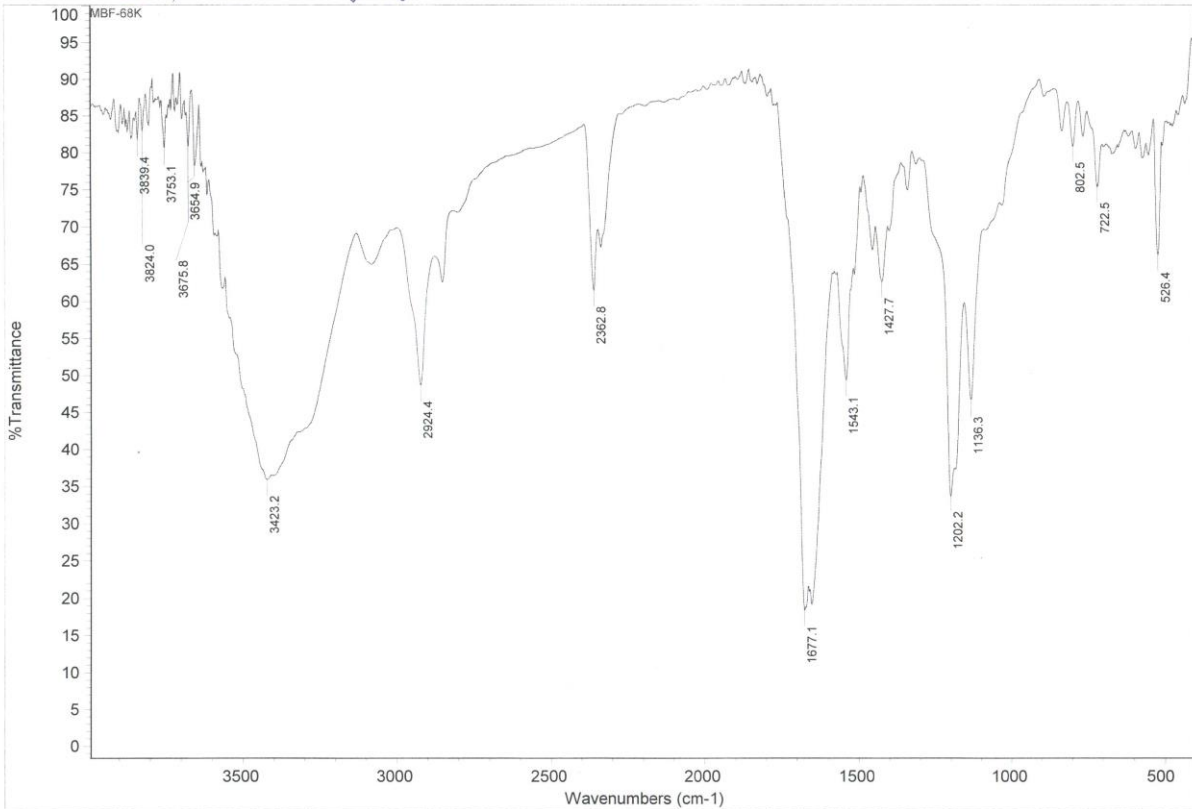




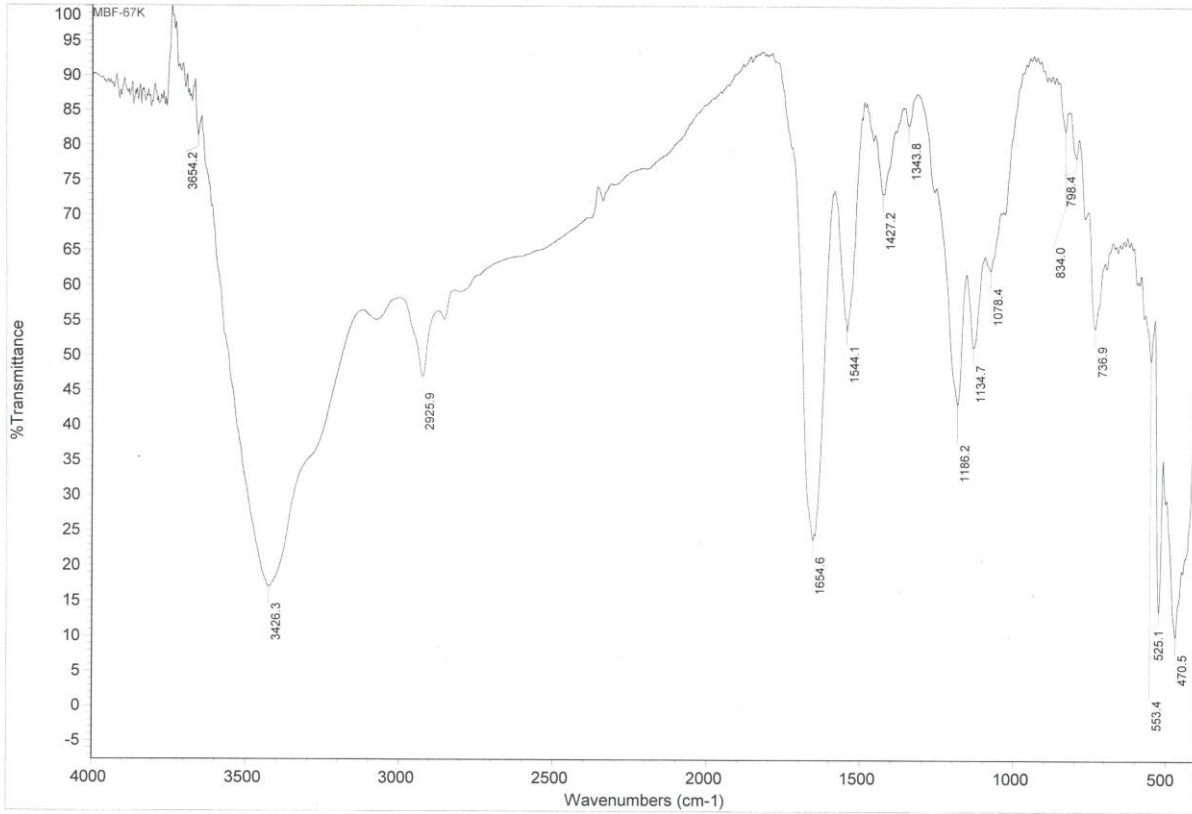
7: Fp-GABA-GABA-Gly-OH



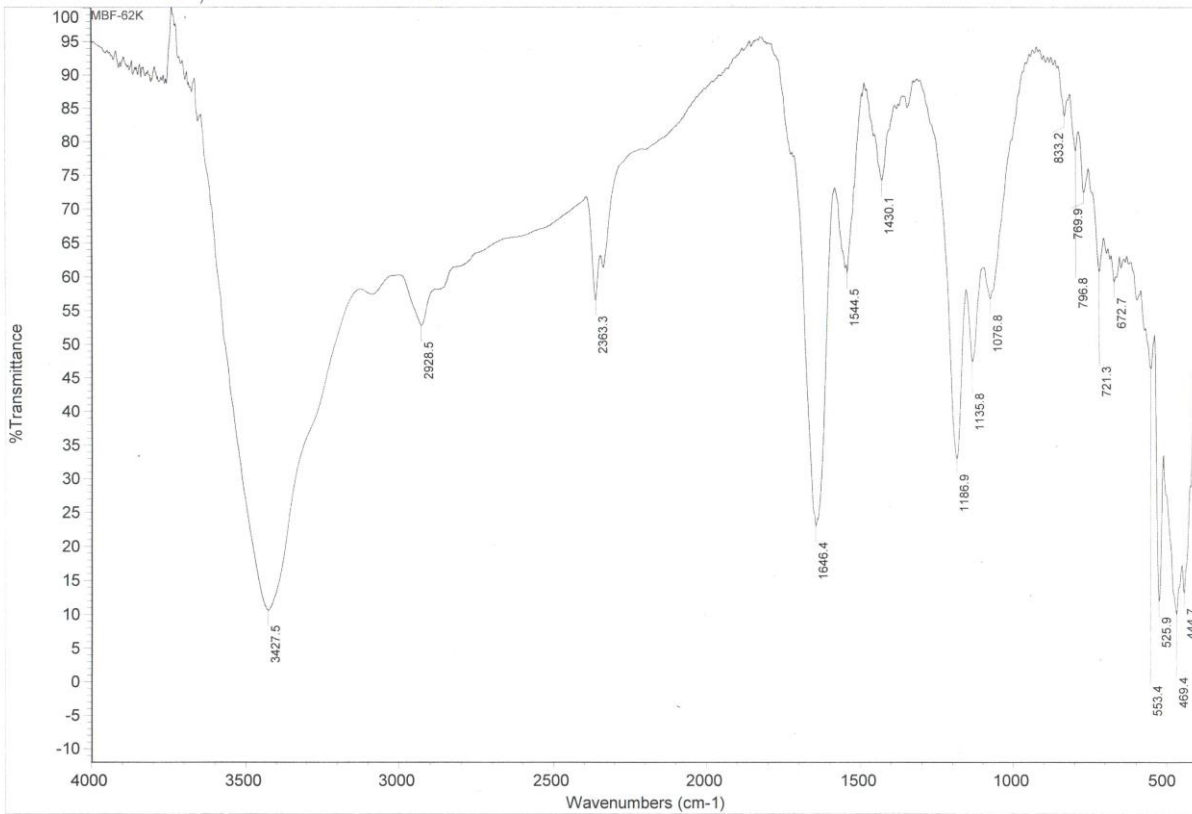
8: Fp-GABA-GABA-Gly-Gly-OH

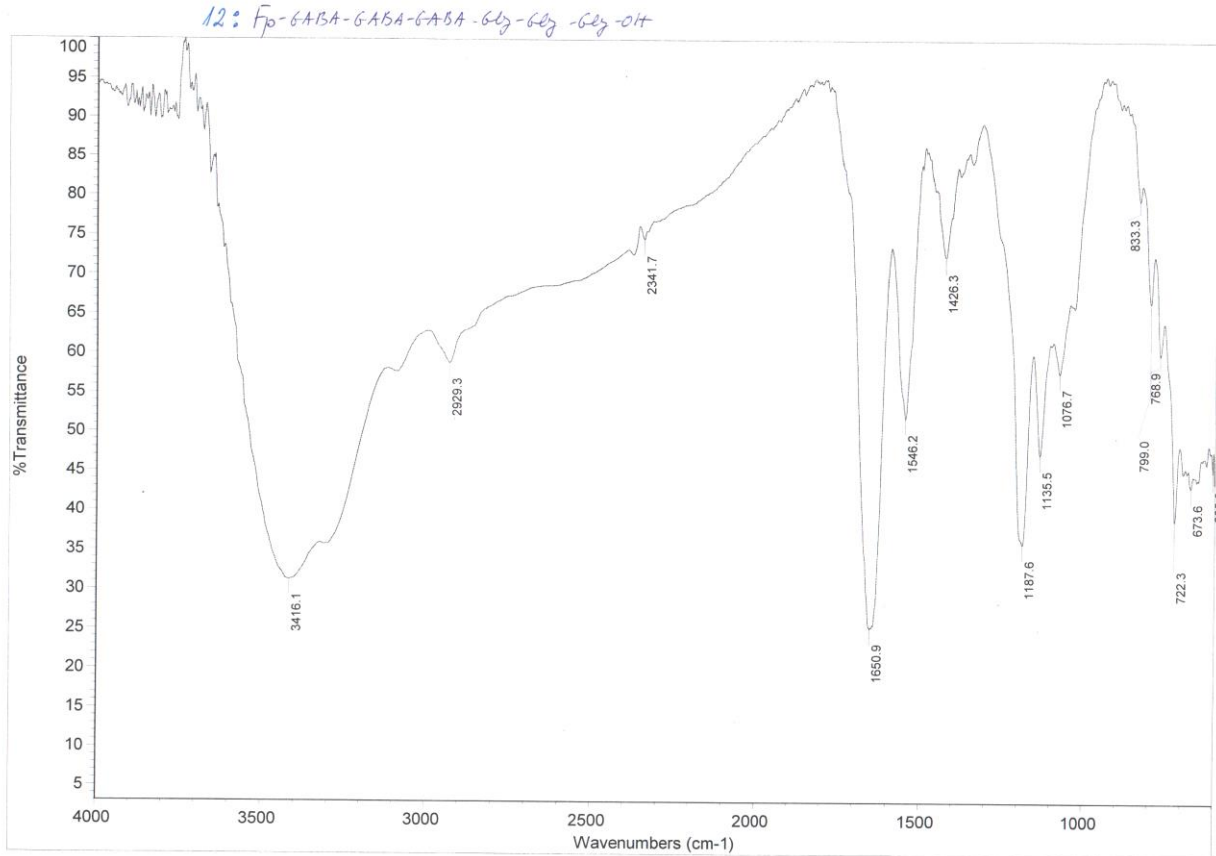
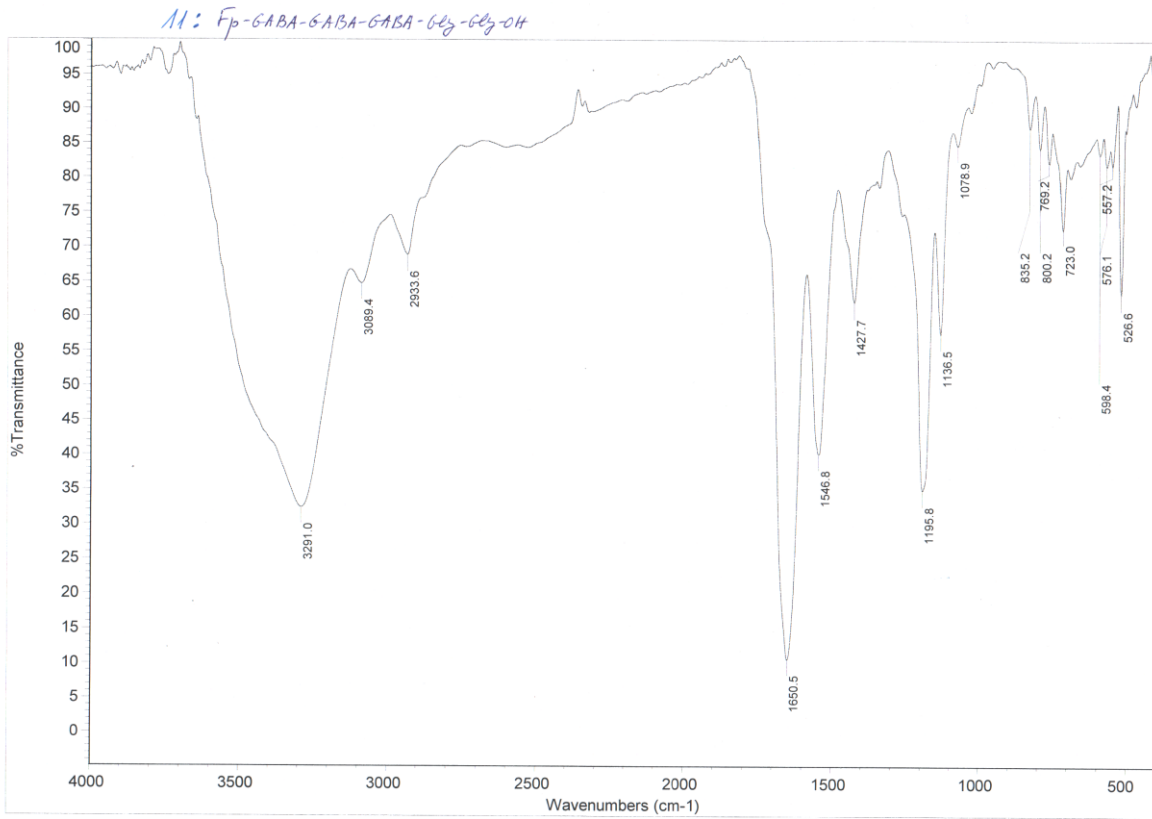


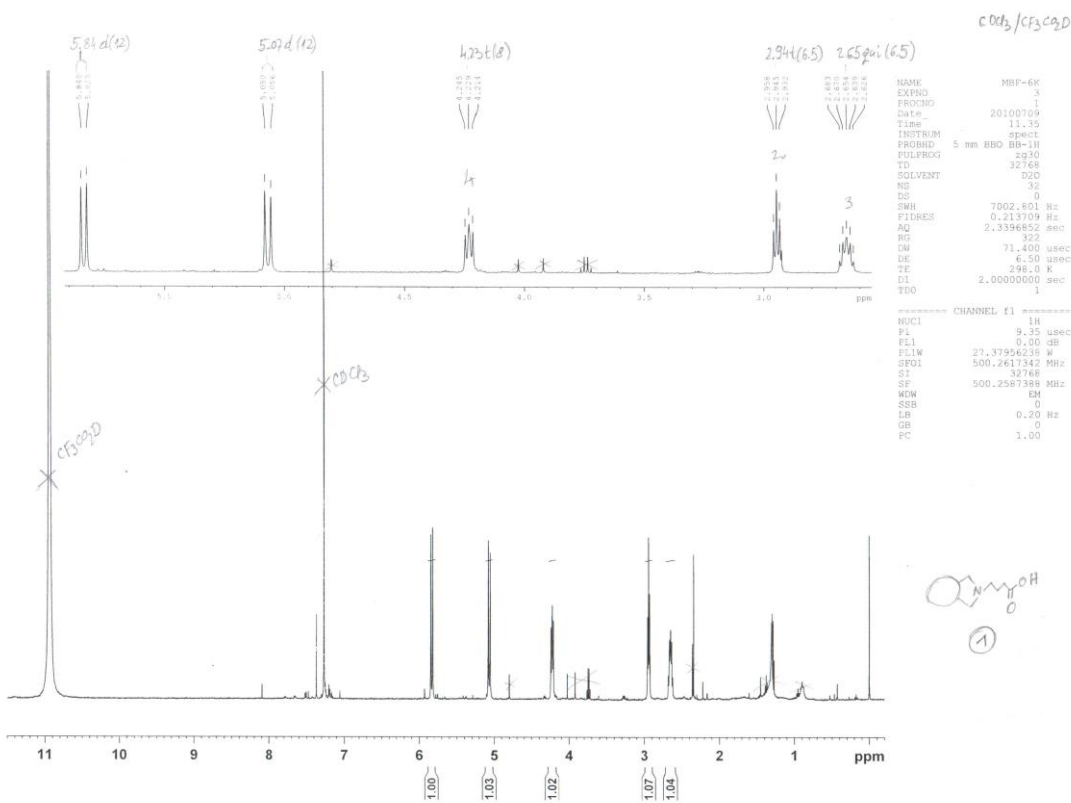
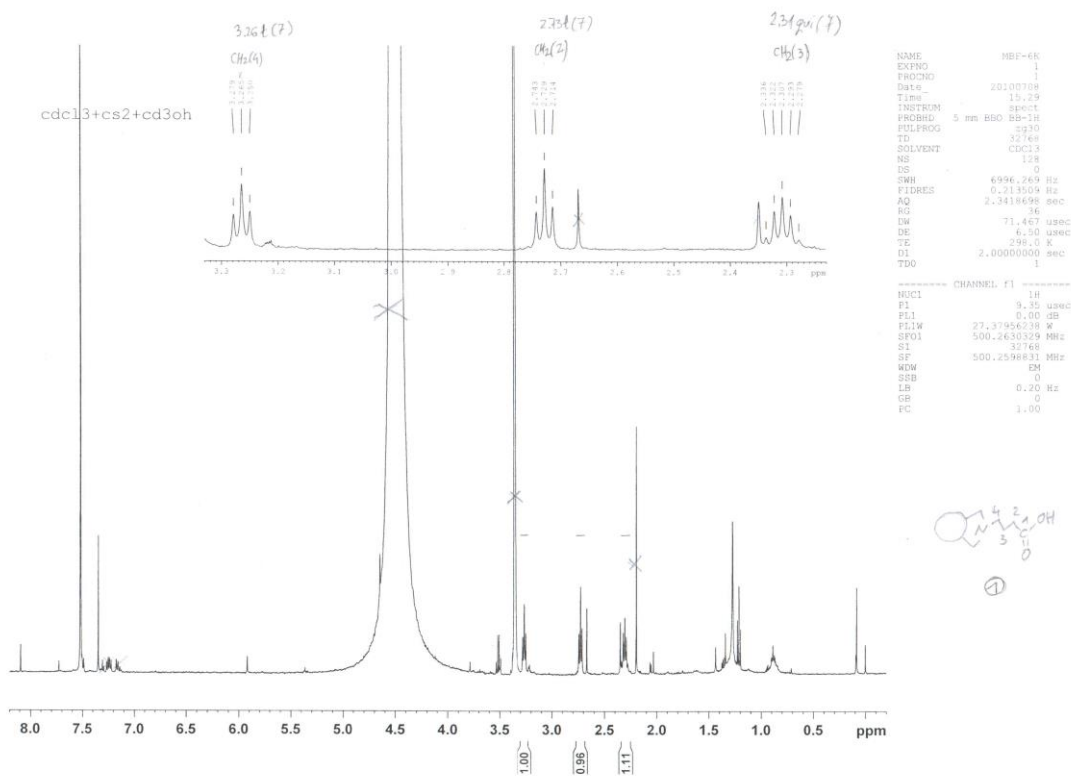
9:  $F_p$ -GABA-GABA-Gly-Gly-Gly-OH

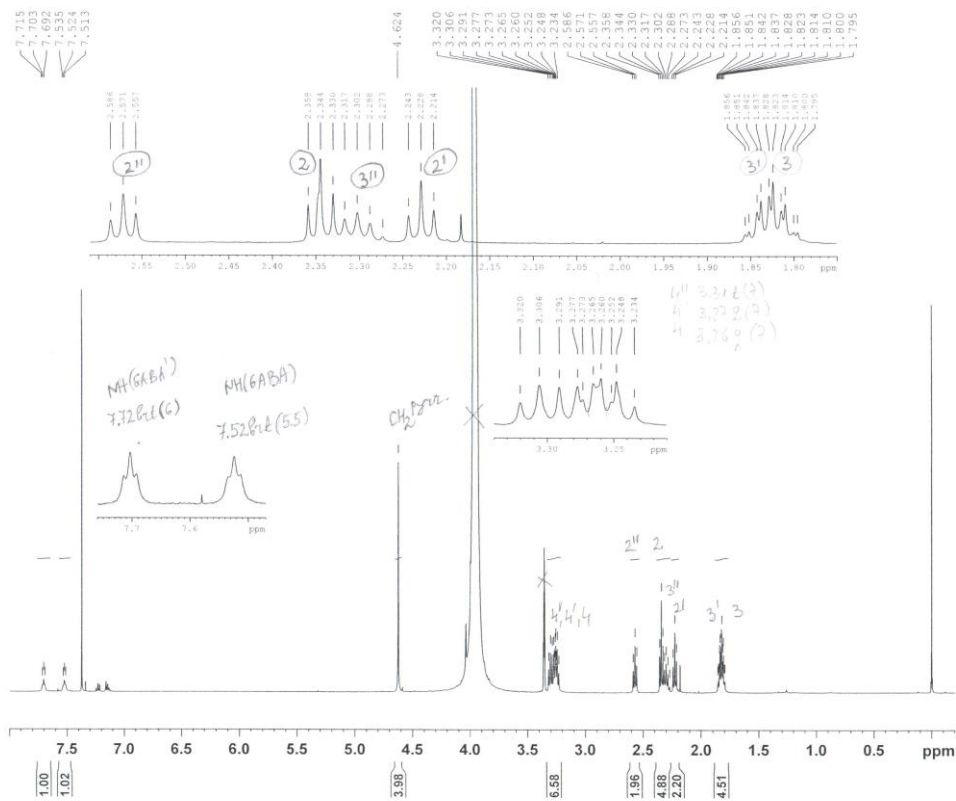
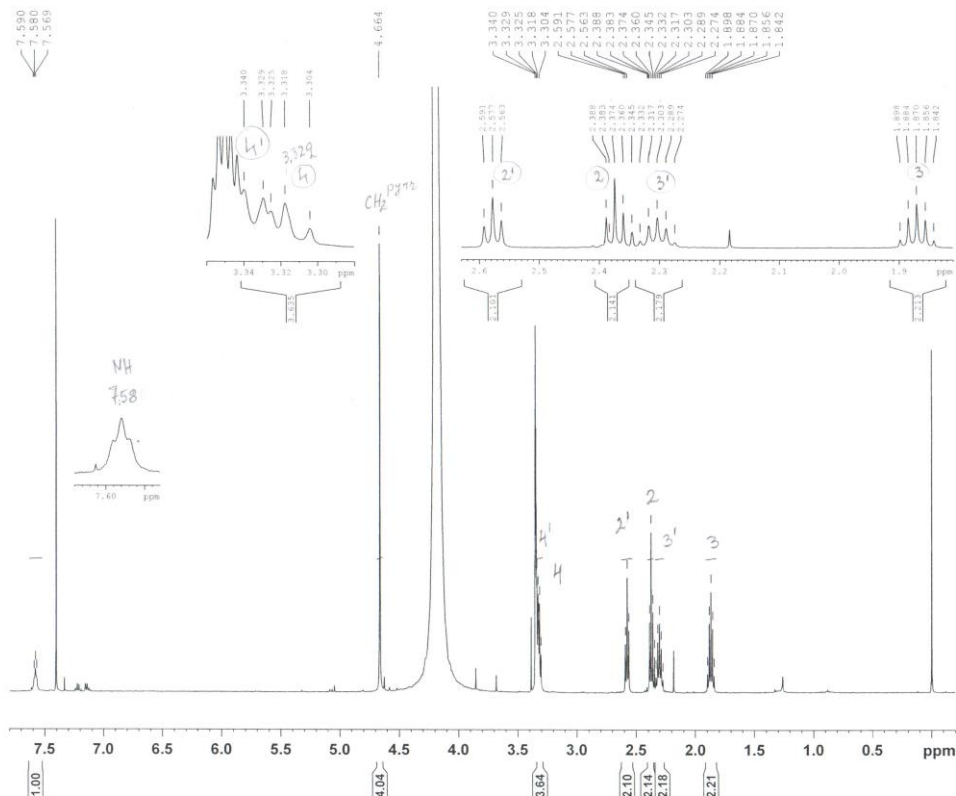


10:  $F_p$ -GABA-GABA-GABA-Gly-OH

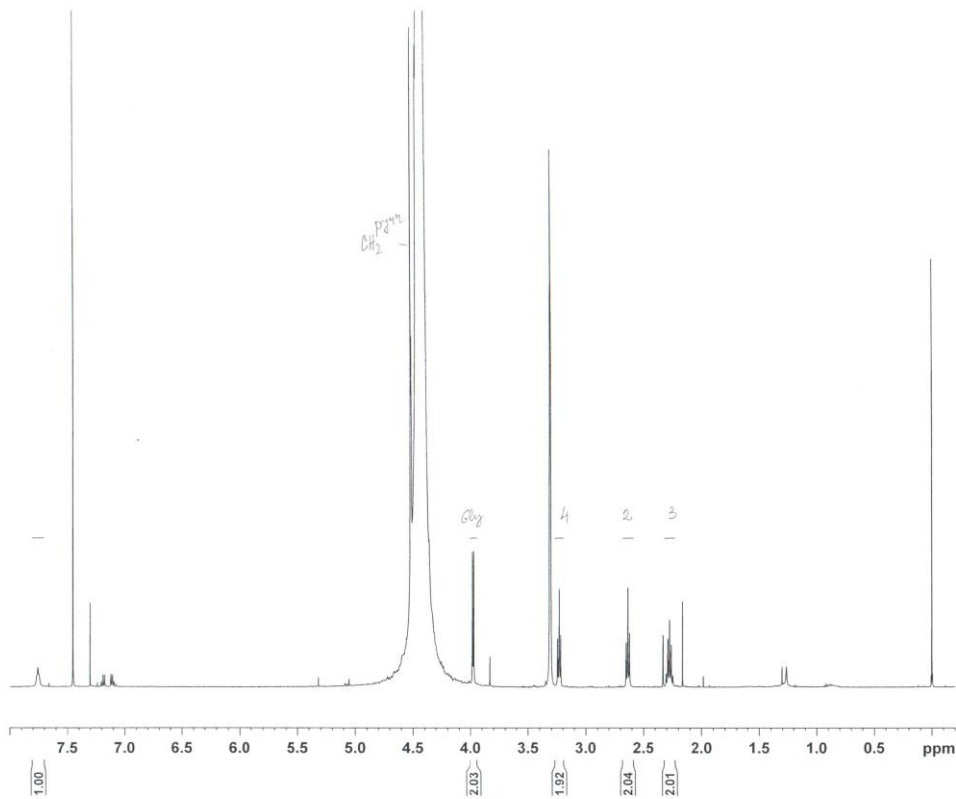




<sup>1</sup>H NMR spectra of compounds 1-12





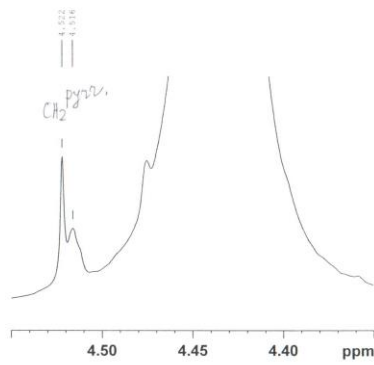
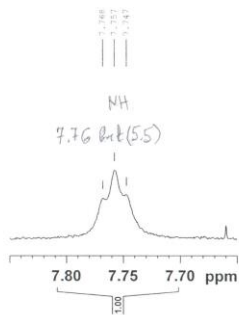
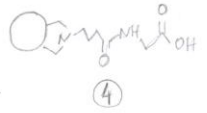


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EXPNO         1
PROCNO        1
Date_         20100715
Time          15.29
INSTRUM       spect
PROBHD        5 mm BBO BB-1H
PULPROG       zg30
TD            32768
SOLVENT       CDCl3
NS            64
DS            0
SWH           4746.835 Hz
FIDRES        0.144862 Hz
AQ            3.4516127 sec
RG            71.8
DW            105.333 usec
DE            6.50 usec
TE            298.0 K
D1            2.00000000 sec
TDO           1
    
```

```

===== CHANNEL f1 =====
NUC1          1H
P1            9.35 usec
PL1           0.00 dB
PL1W          27.37956238 W
SF01          500.2617955 MHz
SI            32768
SF            500.2599178 MHz
WDW           EM
SSB           0
LB            0.20 Hz
GB            0
PC            1.00
    
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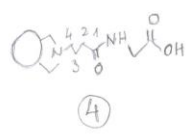
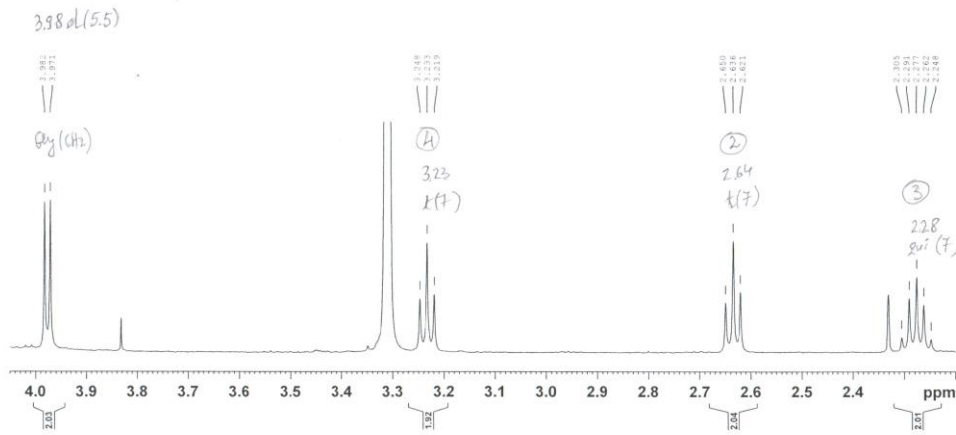


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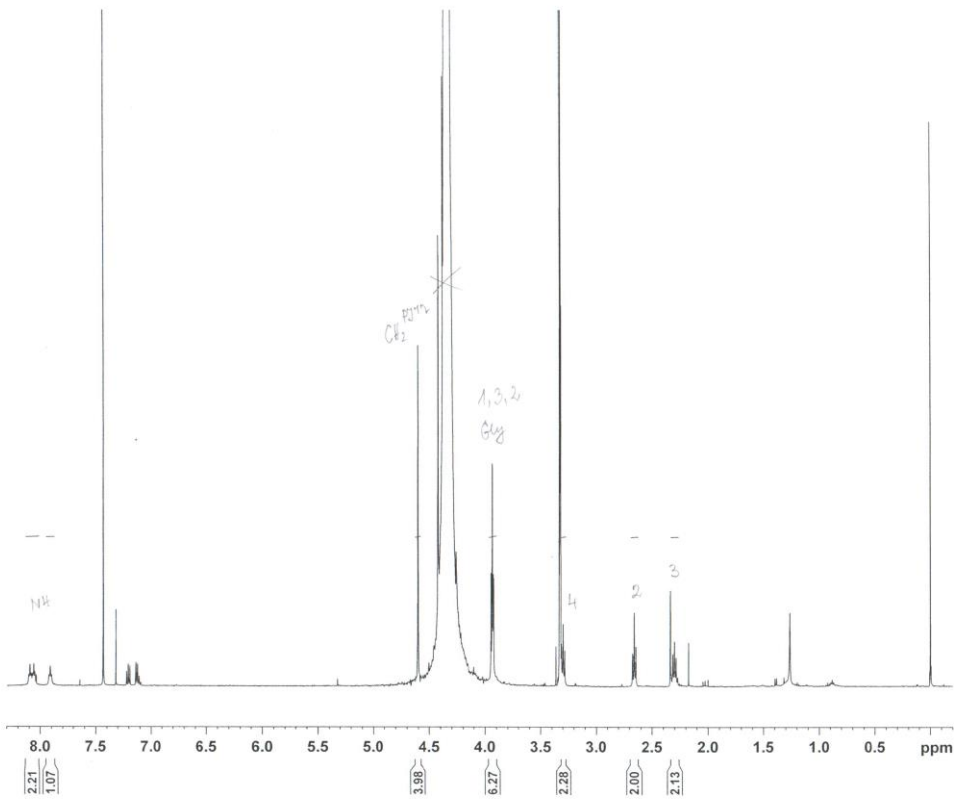
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EXPNO         1
PROCNO        1
Date_         20100715
Time          15.29
INSTRUM       spect
PROBHD        5 mm BBO BB-1H
PULPROG       zg30
TD            32768
SOLVENT       CDCl3
NS            64
DS            0
SWH           4746.835 Hz
FIDRES        0.144862 Hz
AQ            3.4516127 sec
RG            71.8
DW            105.333 usec
DE            6.50 usec
TE            298.0 K
D1            2.00000000 sec
TDO           1
    
```

```

===== CHANNEL f1 =====
NUC1          1H
P1            9.35 usec
PL1           0.00 dB
PL1W          27.37956238 W
SF01          500.2617955 MHz
SI            32768
SF            500.2599178 MHz
WDW           EM
SSB           0
LB            0.20 Hz
GB            0
PC            1.00
    
```



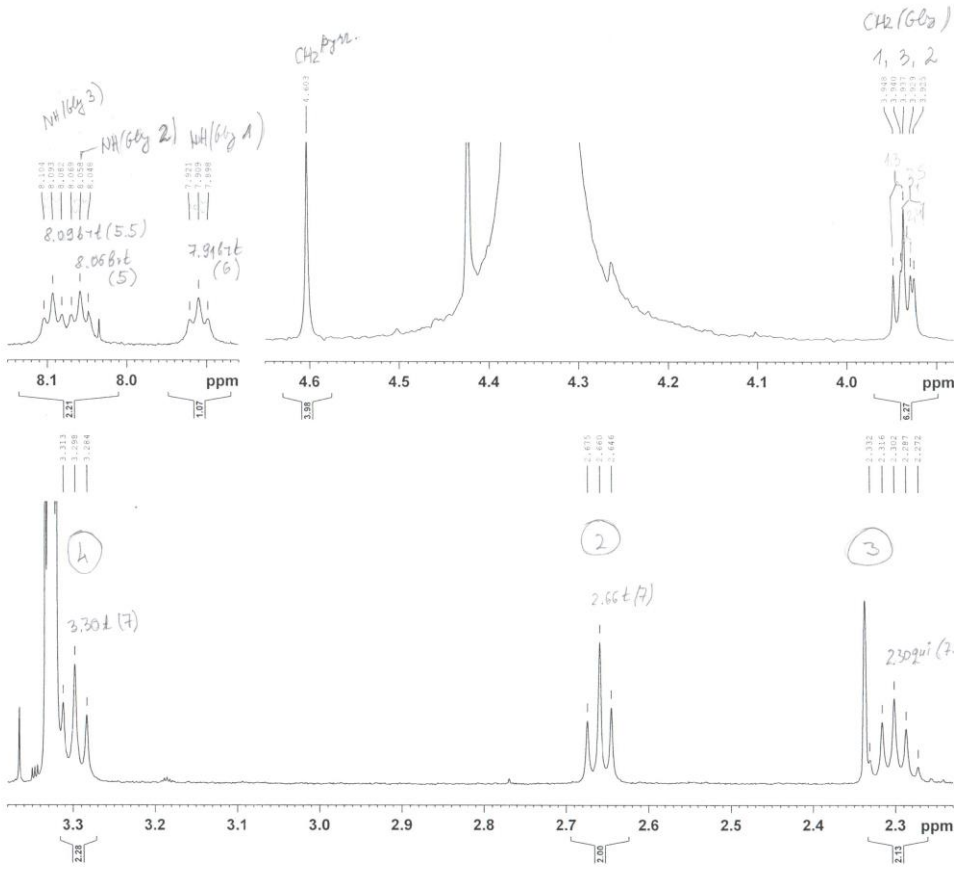




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NAME      MBF-72K
EXPNO    1
PROCNO   1
Date_    20100722
Time     16.40
INSTRUM  spect
PROBHD   5 mm BBO BB-1H
PULPROG  zg30
TD        32768
SOLVENT  CDCl3
NS        64
DS        0
SWH       4854.369 Hz
FIDRES   0.148144 Hz
AQ        3.3751540 sec
RG        71.8
DW        103.000 usec
DE        6.50 usec
TE        298.0 K
D1        2.00000000 sec
TD0       1

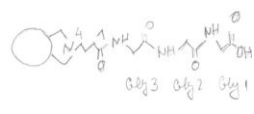
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NUC1     1H
P1       9.35 usec
PL1     0.00 dB
PL1W    27.37956238 W
SFO1    500.2618634 MHz
SI       32768
SF       500.2599270 MHz
WDW      EM
SSB      0
LB       0.20 Hz
GB       0
PC       1.00
    
```

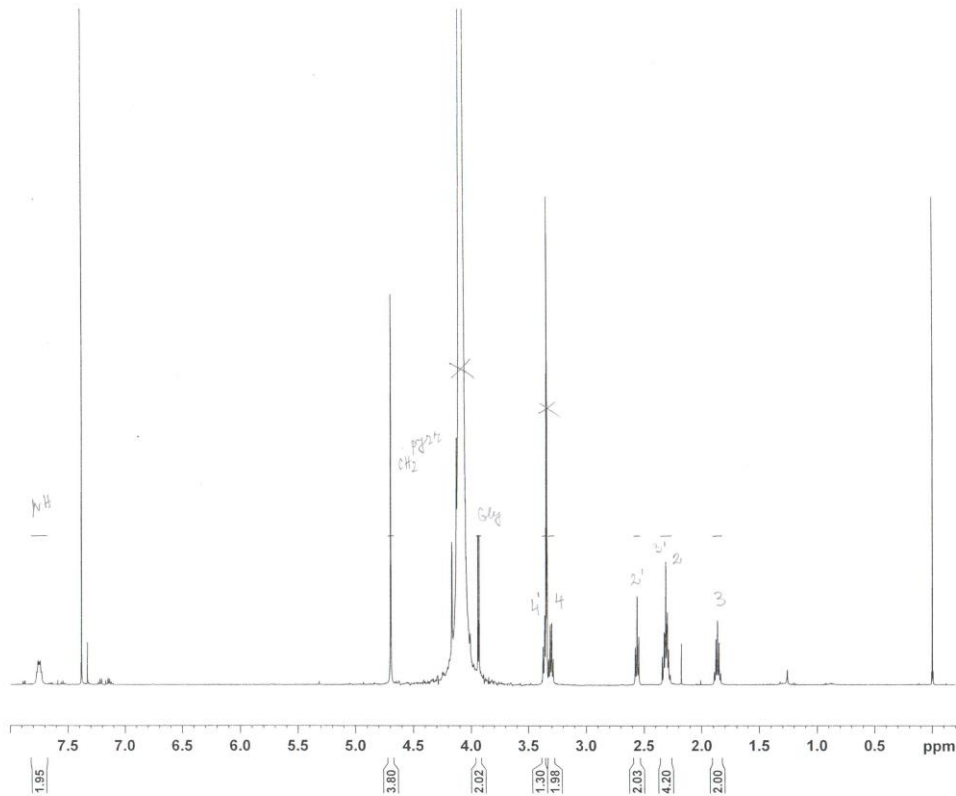


```

NAME      MBF-72K
EXPNO    1
PROCNO   1
Date_    20100722
Time     16.40
INSTRUM  spect
PROBHD   5 mm BBO BB-1H
PULPROG  zg30
TD        32768
SOLVENT  CDCl3
NS        64
DS        0
SWH       4854.369 Hz
FIDRES   0.148144 Hz
AQ        3.3751540 sec
RG        71.8
DW        103.000 usec
DE        6.50 usec
TE        298.0 K
D1        2.00000000 sec
TD0       1

===== CHANNEL f1 =====
NUC1     1H
P1       9.35 usec
PL1     0.00 dB
PL1W    27.37956238 W
SFO1    500.2618634 MHz
SI       32768
SF       500.2599270 MHz
WDW      EM
SSB      0
LB       0.20 Hz
GB       0
PC       1.00
    
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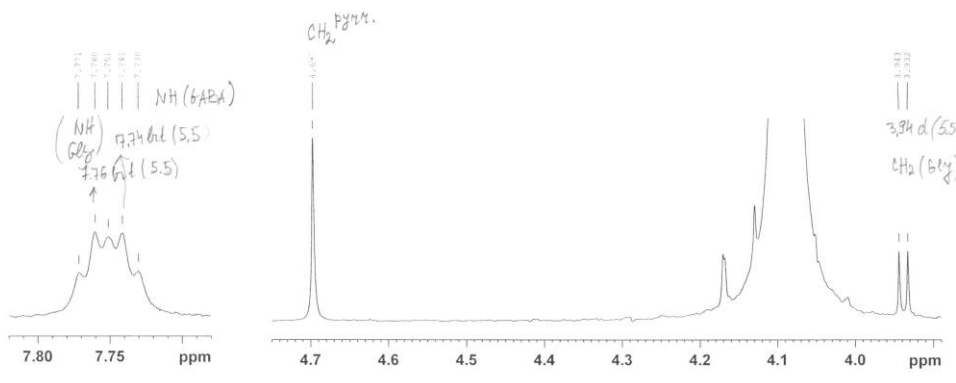


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NAME      MBF-61K
EXPNO    1
PROCNO   1
Date_    20100726
Time     16.42
INSTRUM  spect
PROBHD   5 mm BBO BB-1H
PULPROG  zg30
TD        32768
SOLVENT  CDCl3
NS        32
DS        0
SWH       5000.000 Hz
FIDRES   0.152588 Hz
AQ        3.2768500 sec
RG        71.8
DW        100.000 usec
DE        6.50 usec
TE        298.0 K
D1        2.00000000 sec
TDO       1
    
```

```

----- CHANNEL f1 -----
NUC1      1H
P1        9.35 usec
PL1       0.00 dB
PL1W      27.37956238 W
SFO1      500.2618270 MHz
SI        32768
SF        500.2599527 MHz
WDW       EM
SSB       0
LB        0.20 Hz
GB        0
PC        1.00
    
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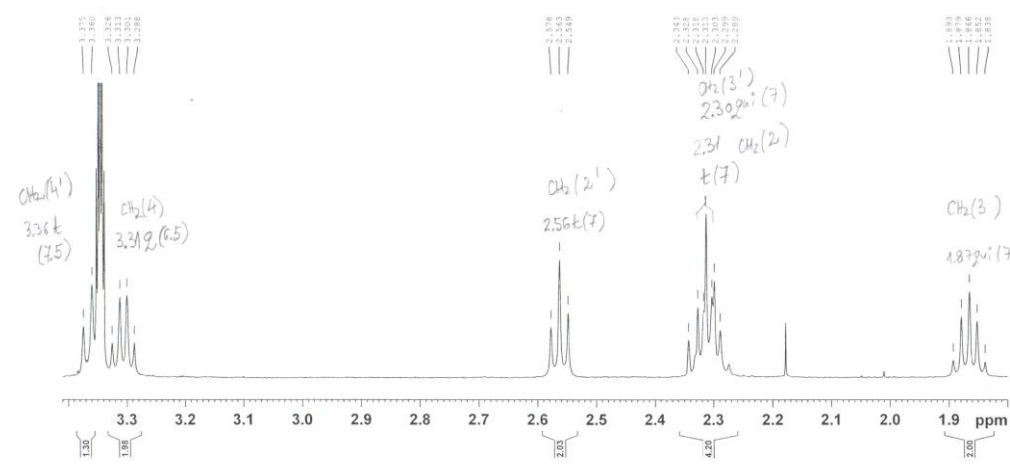
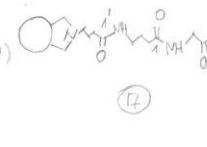


```

NAME      MBF-61K
EXPNO    1
PROCNO   1
Date_    20100726
Time     16.42
INSTRUM  spect
PROBHD   5 mm BBO BB-1H
PULPROG  zg30
TD        32768
SOLVENT  CDCl3
NS        32
DS        0
SWH       5000.000 Hz
FIDRES   0.152588 Hz
AQ        3.2768500 sec
RG        71.8
DW        100.000 usec
DE        6.50 usec
TE        298.0 K
D1        2.00000000 sec
TDO       1
    
```

```

----- CHANNEL f1 -----
NUC1      1H
P1        9.35 usec
PL1       0.00 dB
PL1W      27.37956238 W
SFO1      500.2618270 MHz
SI        32768
SF        500.2599527 MHz
WDW       EM
SSB       0
LB        0.20 Hz
GB        0
PC        1.00
    
```

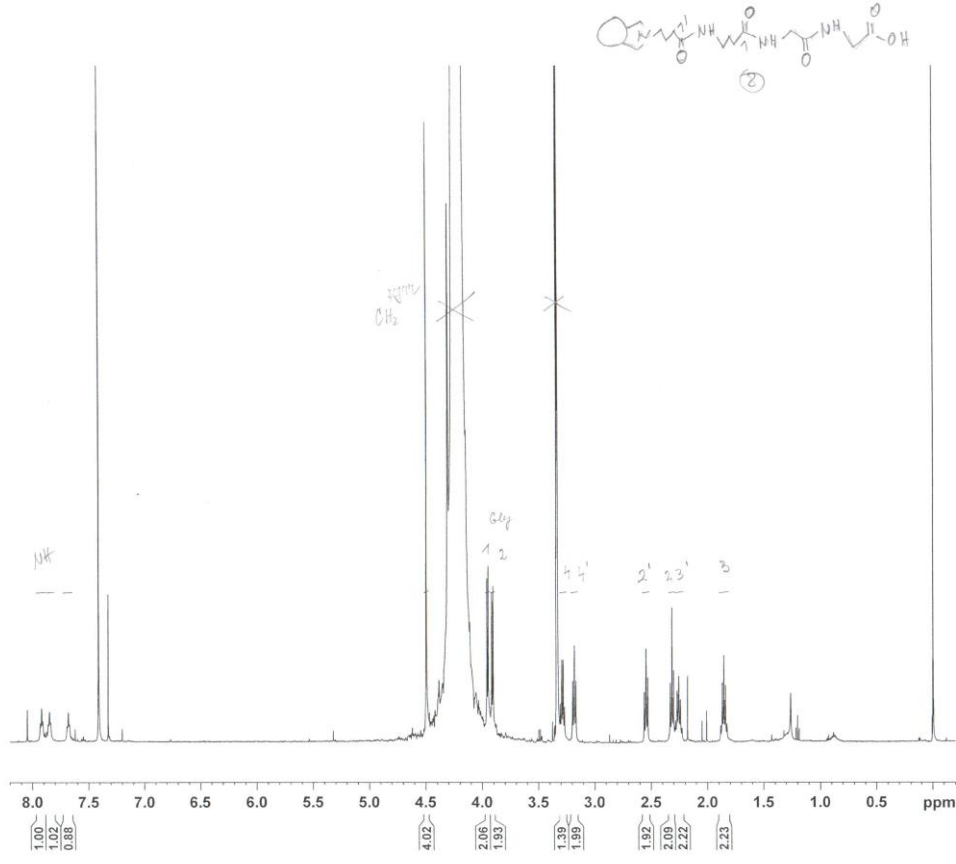


```

NAME      MBF-61K
EXPNO    1
PROCNO   1
Date_    20100726
Time     16.42
INSTRUM  spect
PROBHD   5 mm BBO BB-1H
PULPROG  zg30
TD        32768
SOLVENT  CDCl3
NS        32
DS        0
SWH       5000.000 Hz
FIDRES   0.152588 Hz
AQ        3.2768500 sec
RG        71.8
DW        100.000 usec
DE        6.50 usec
TE        298.0 K
D1        2.00000000 sec
TDO       1
    
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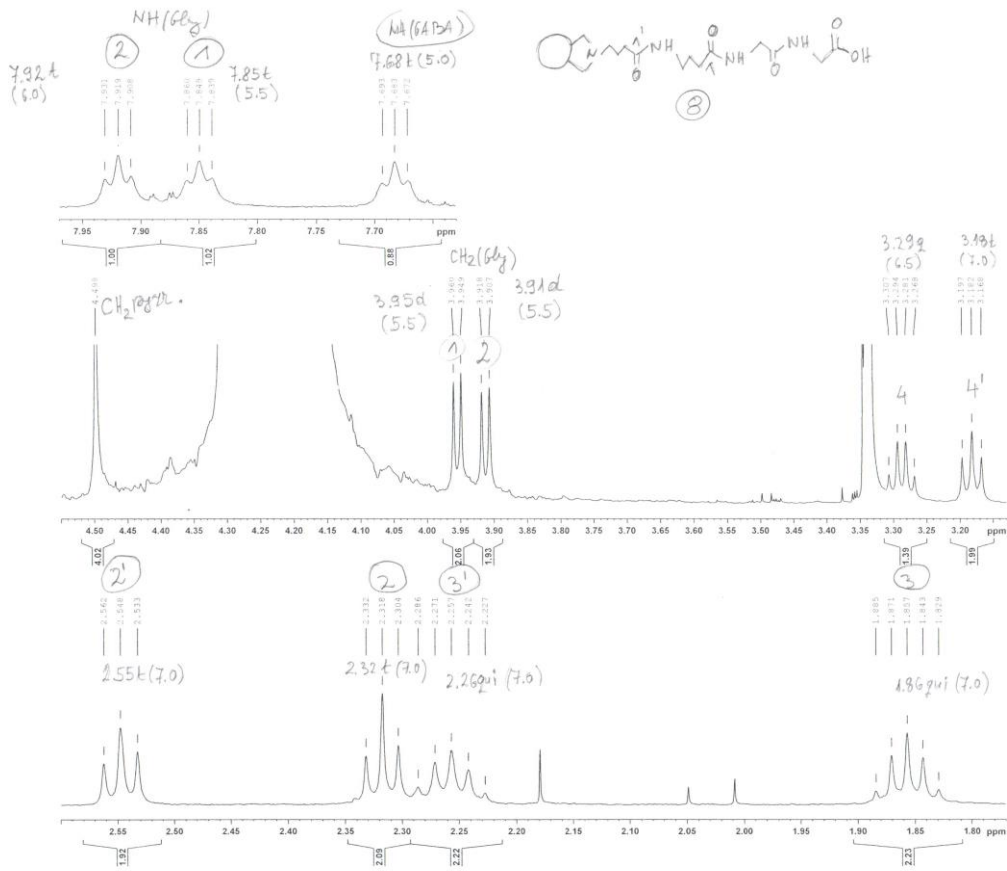
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----- CHANNEL f1 -----
NUC1      1H
P1        9.35 usec
PL1       0.00 dB
PL1W      27.37956238 W
SFO1      500.2618270 MHz
SI        32768
SF        500.2599527 MHz
WDW       EM
SSB       0
LB        0.20 Hz
GB        0
PC        1.00
    
```



```

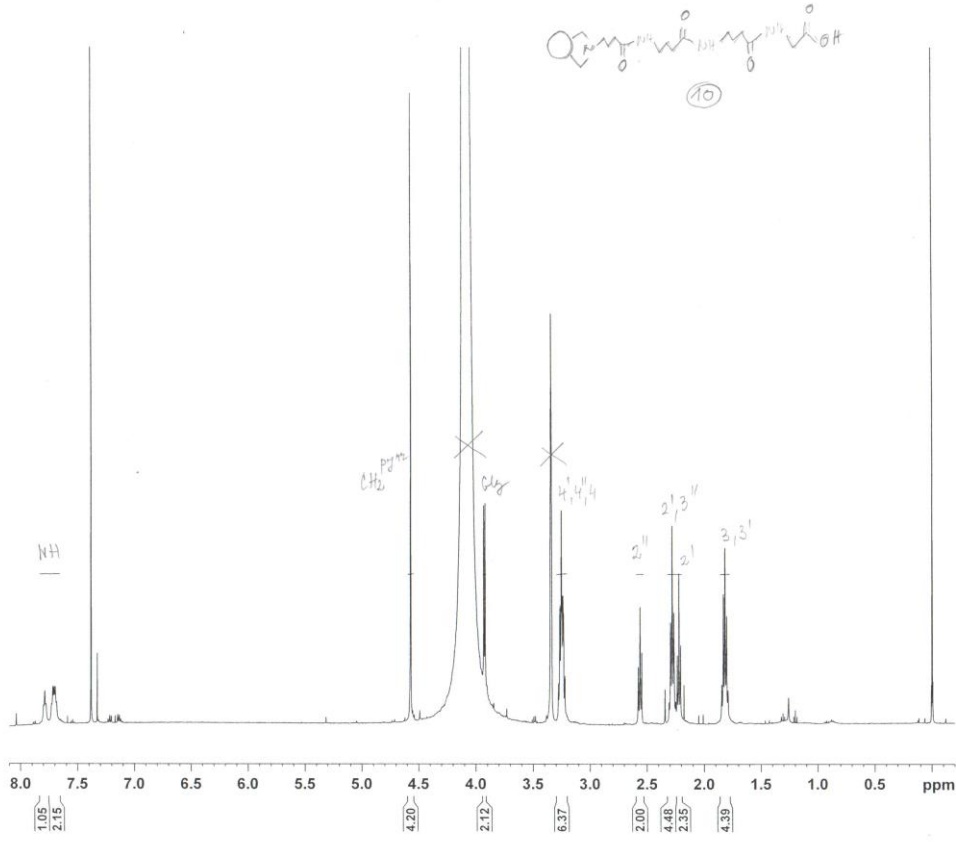
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EXPNO    1
PROCNO   1
Date_    20100811
Time     13.33
INSTRUM  spect
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PULPROG  zg30
TD       32768
SOLVENT  CDCl3
NS       163
DS       0
SWH      4807.692 Hz
FIDRES   0.146719 Hz
AQ       3.4079220 sec
RG       71.8
DW       104.000 usec
DE       6.50 usec
TE       298.0 K
D1       2.00000000 sec
TD0      1
===== CHANNEL f1 =====
NUC1     1H
P1       9.35 usec
PL1     0.00 dB
PL1W    27.37956238 W
SF01    500.2618050 MHz
SI       32768
SF       500.2599369 MHz
WDW      EM
SSB      0
LB       0.20 Hz
GB       0
PC       1.00
    
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```

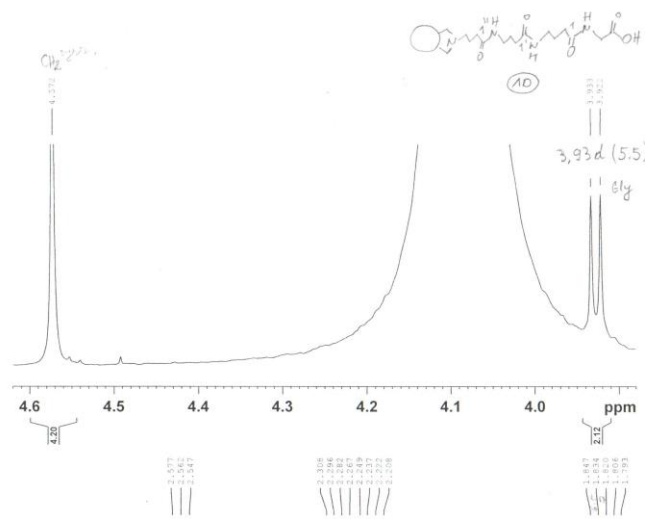
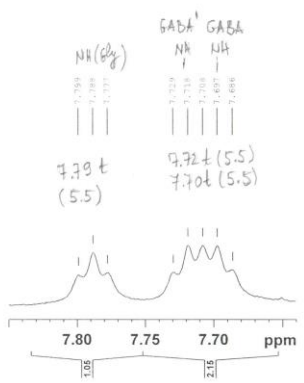
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EXPNO    1
PROCNO   1
Date_    20100811
Time     13.33
INSTRUM  spect
PROBHD   5 mm BBO BB-1H
PULPROG  zg30
TD       32768
SOLVENT  CDCl3
NS       163
DS       0
SWH      4807.692 Hz
FIDRES   0.146719 Hz
AQ       3.4079220 sec
RG       71.8
DW       104.000 usec
DE       6.50 usec
TE       298.0 K
D1       2.00000000 sec
TD0      1
===== CHANNEL f1 =====
NUC1     1H
P1       9.35 usec
PL1     0.00 dB
PL1W    27.37956238 W
SF01    500.2618050 MHz
SI       32768
SF       500.2599369 MHz
WDW      EM
SSB      0
LB       0.20 Hz
GB       0
PC       1.00
    
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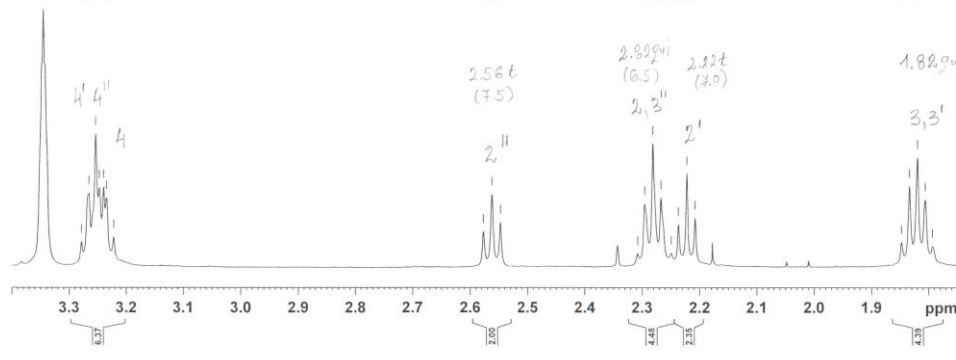
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 PULPROG zg30  
 TD 32768  
 SOLVENT MeOD  
 NS 128  
 DS 0  
 SWH 4573.171 Hz  
 FIDRES 0.139562 Hz  
 AQ 3.5826848 sec  
 RG 71.8  
 DW 109.333 usec  
 DE 6.50 usec  
 TE 298.0 K  
 DI 2.0000000 sec  
 TDO 1

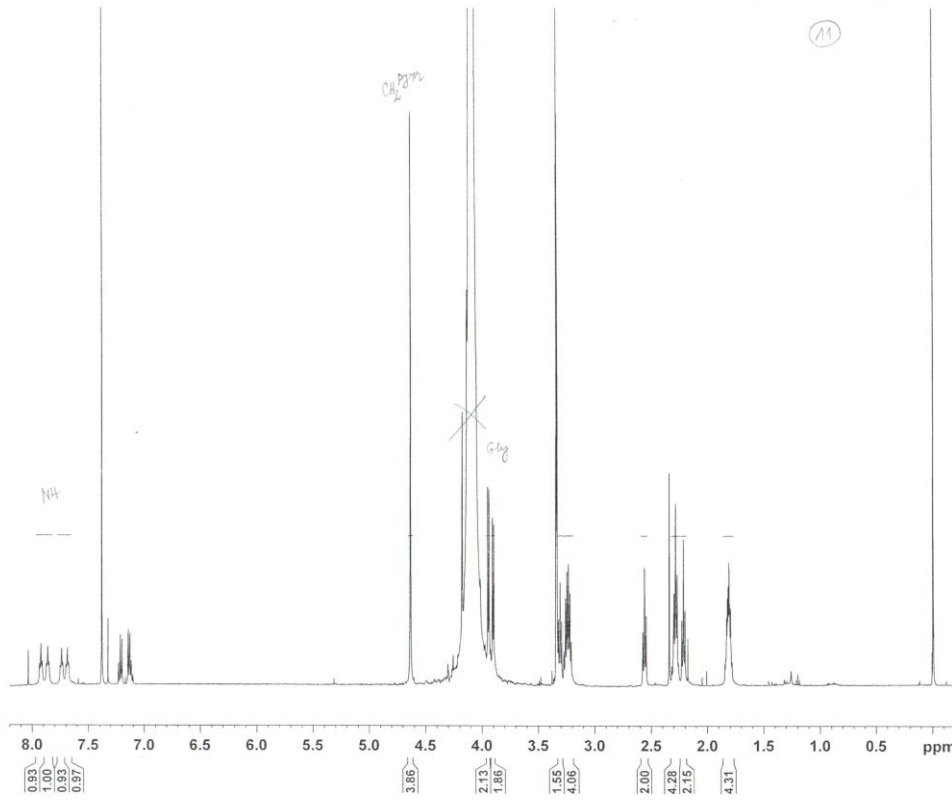
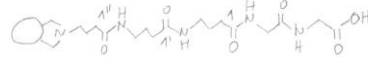
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 P1 9.35 usec  
 PL1 0.00 dB  
 PL1W 27.37956238 W  
 SFO1 500.2618319 MHz  
 SI 32768  
 SF 500.2599941 MHz  
 WDW EM  
 SSB 0  
 LB 0.20 Hz  
 GB 0  
 PC 1.00



NAME MRF-62K  
 EXPNO 1  
 PROCNO 1  
 Date\_ 20100816  
 Time\_ 16.48  
 INSTRUM spect  
 PROBHD 5 mm BBO BB-1H  
 PULPROG zg30  
 TD 32768  
 SOLVENT MeOD  
 NS 128  
 DS 0  
 SWH 4573.171 Hz  
 FIDRES 0.139562 Hz  
 AQ 3.5826848 sec  
 RG 71.8  
 DW 109.333 usec  
 DE 6.50 usec  
 TE 298.0 K  
 DI 2.0000000 sec  
 TDO 1

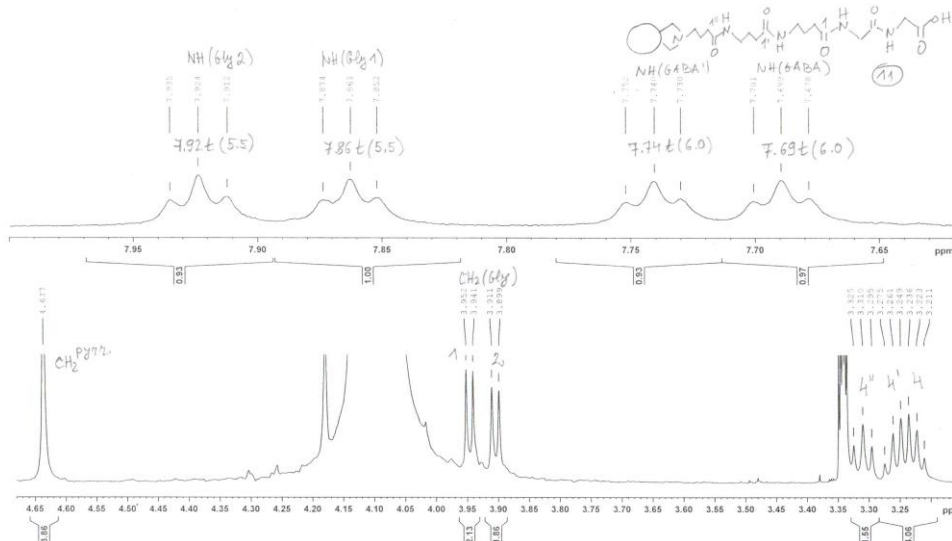
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 PL1 0.00 dB  
 PL1W 27.37956238 W  
 SFO1 500.2618319 MHz  
 SI 32768  
 SF 500.2599941 MHz  
 WDW EM  
 SSB 0  
 LB 0.20 Hz  
 GB 0  
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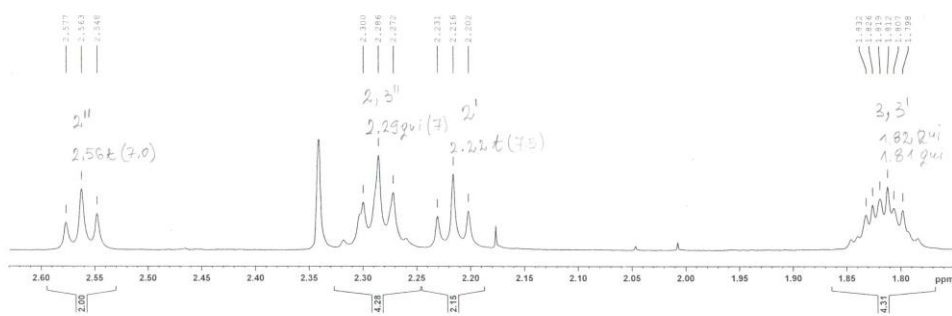
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 FIDRES 0.148721 Hz  
 AQ 3.3620467 sec  
 RG 71.8  
 DW 102.600 usec  
 DE 6.50 usec  
 TE 298.0 K  
 D1 2.0000000 sec  
 TDO 1

CHANNEL f1  
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 P1 9.35 usec  
 PL1 0.00 dB  
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 LB 0.20 Hz  
 GB 0  
 PC 1.00



NAME MB-71-k1a  
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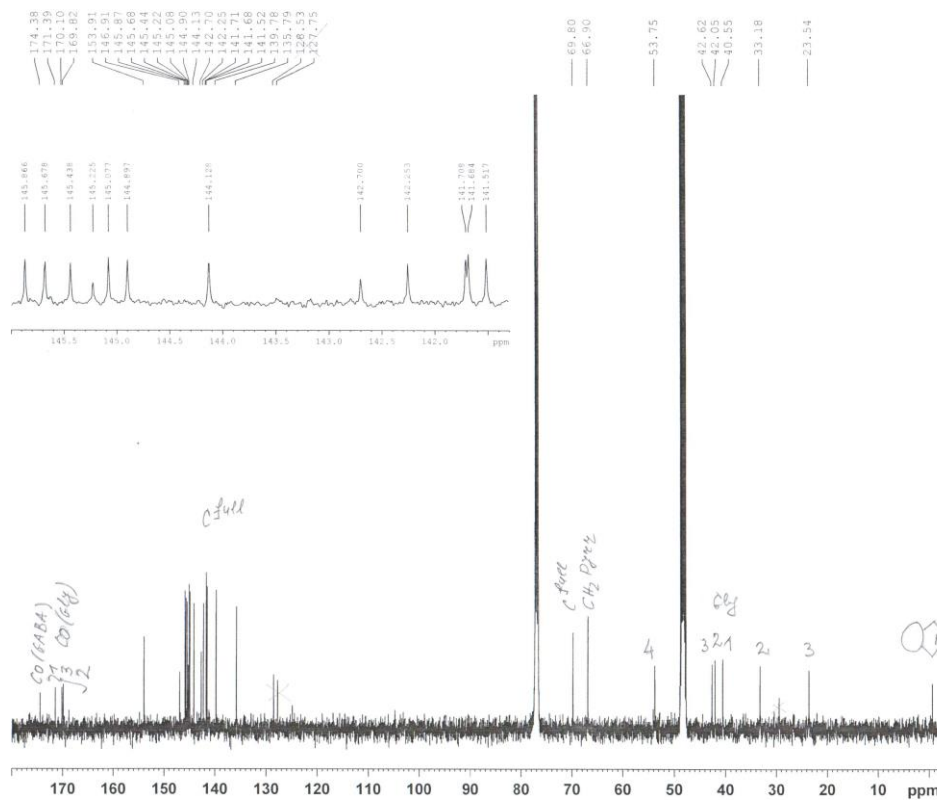
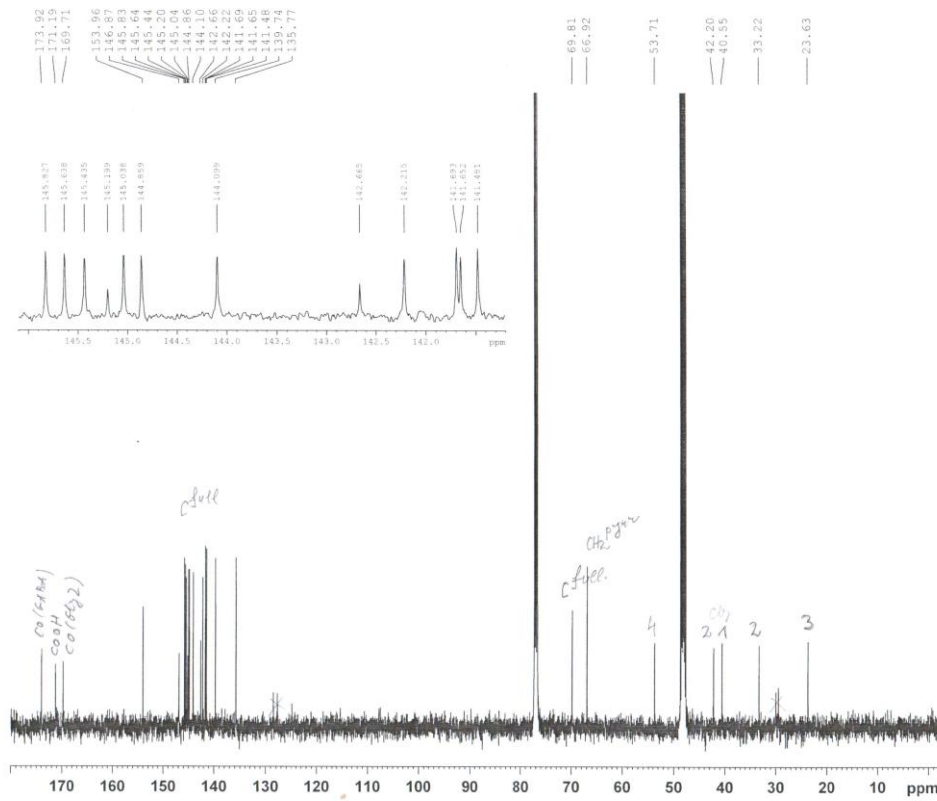
$4'' = 3.31 t (7.5)$   
 $4' = 3.25 t (7.0)$   
 $4 = 3.23 t (6.0)$





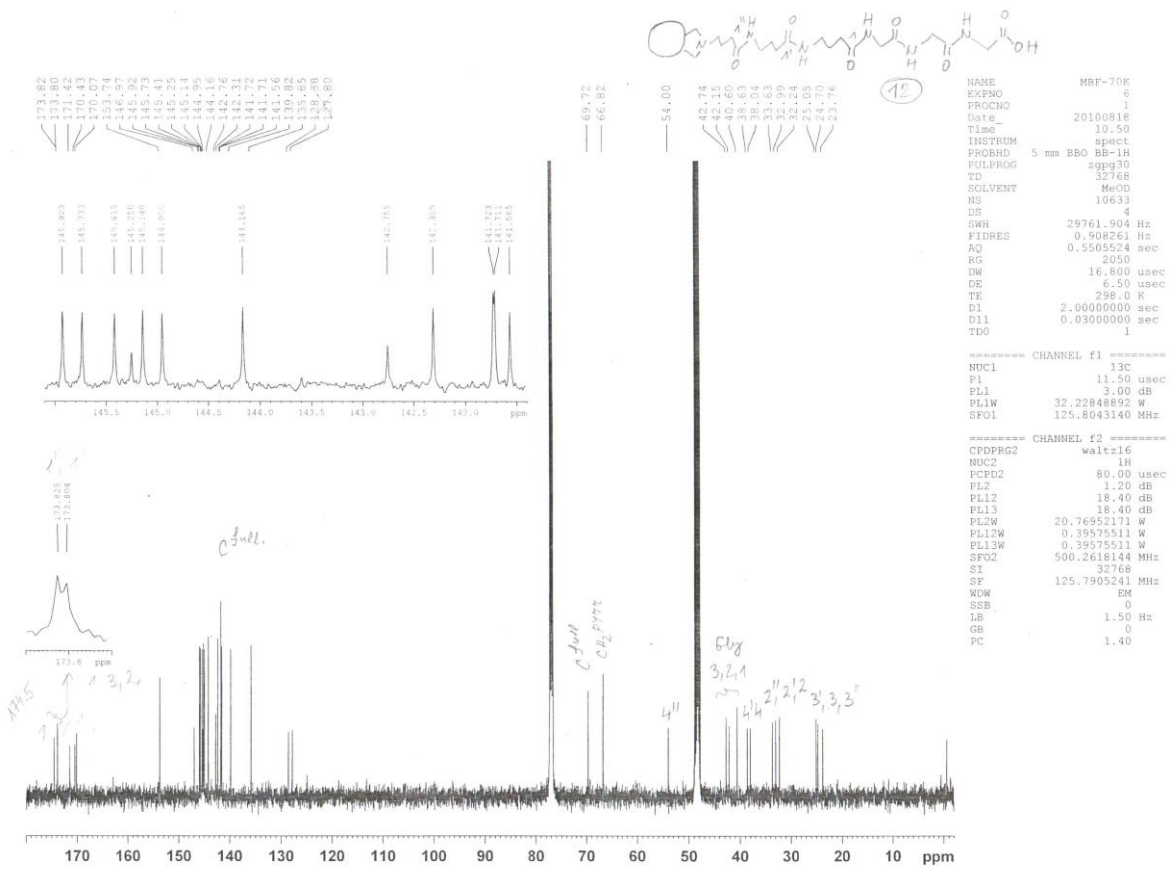
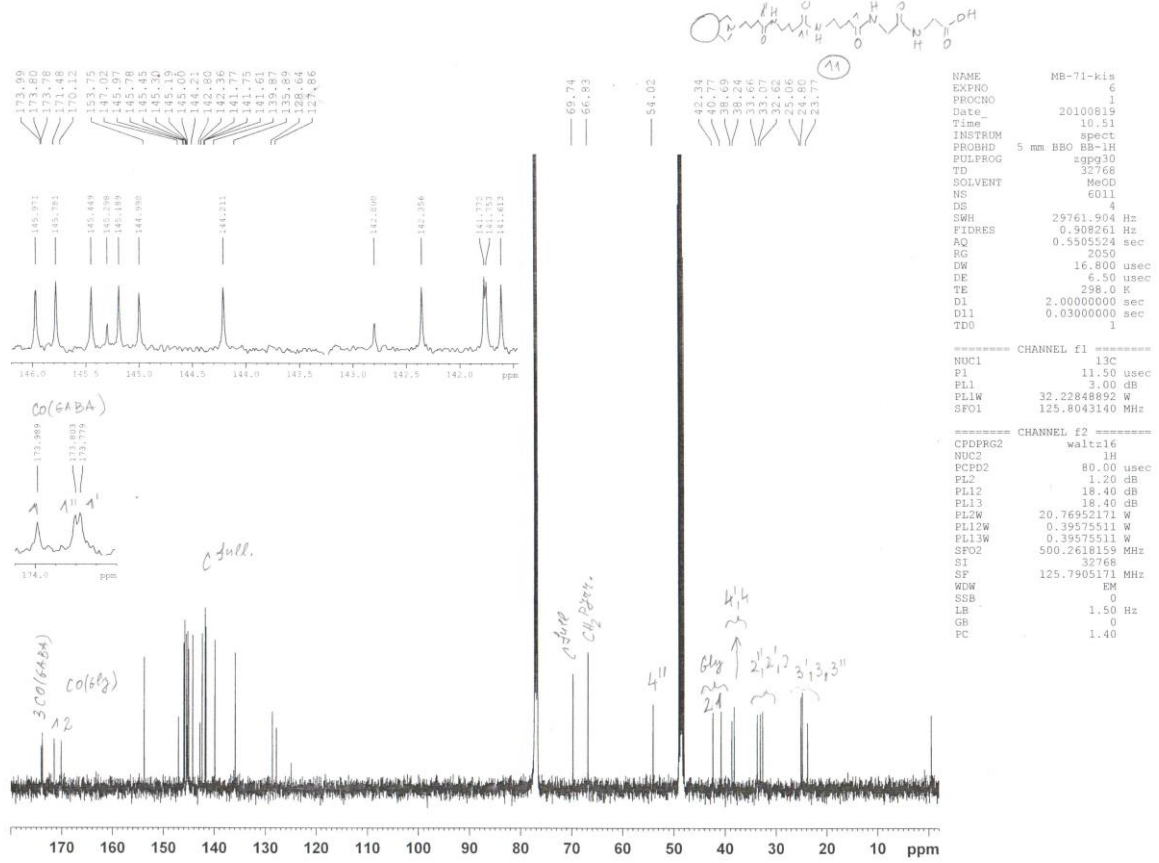




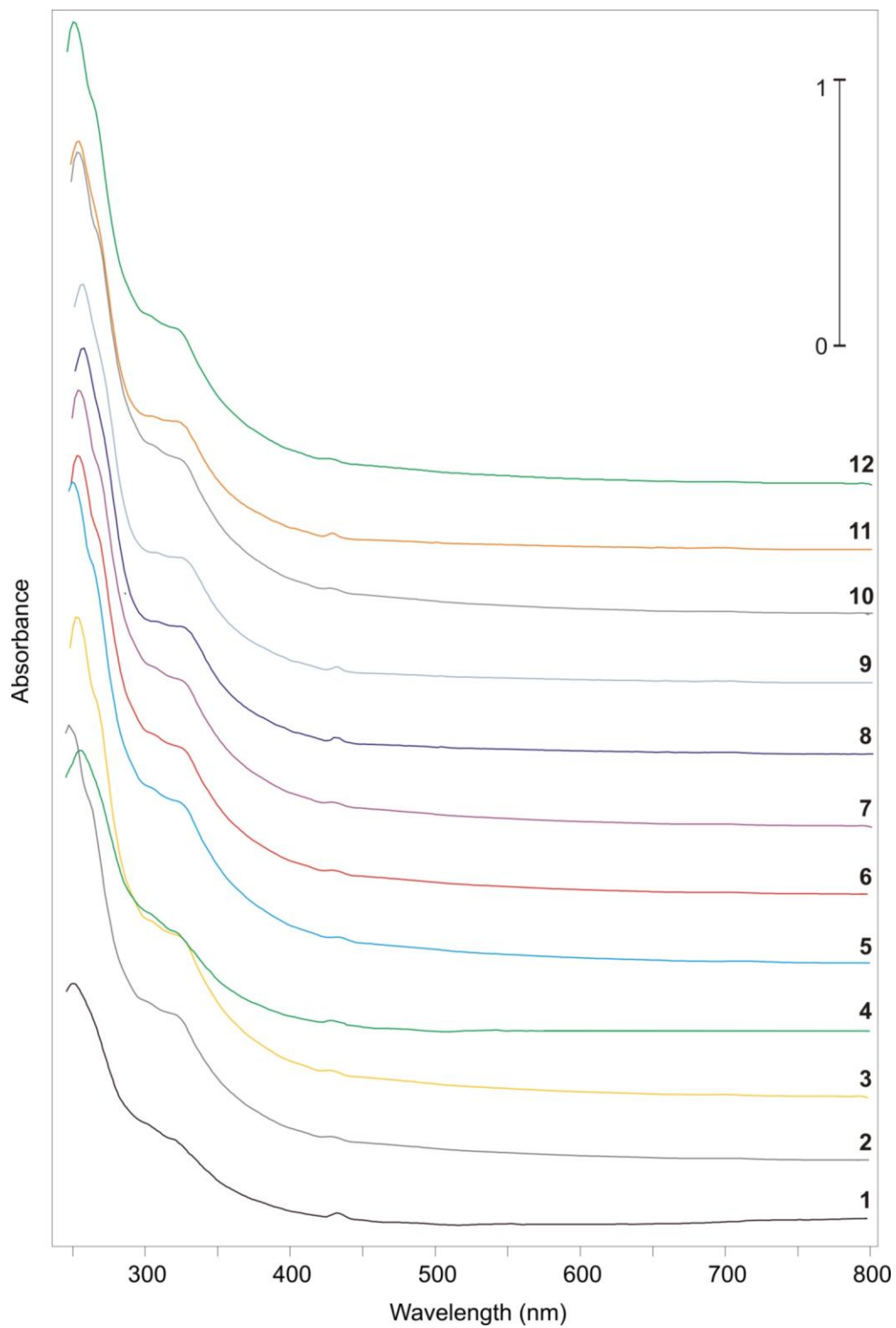






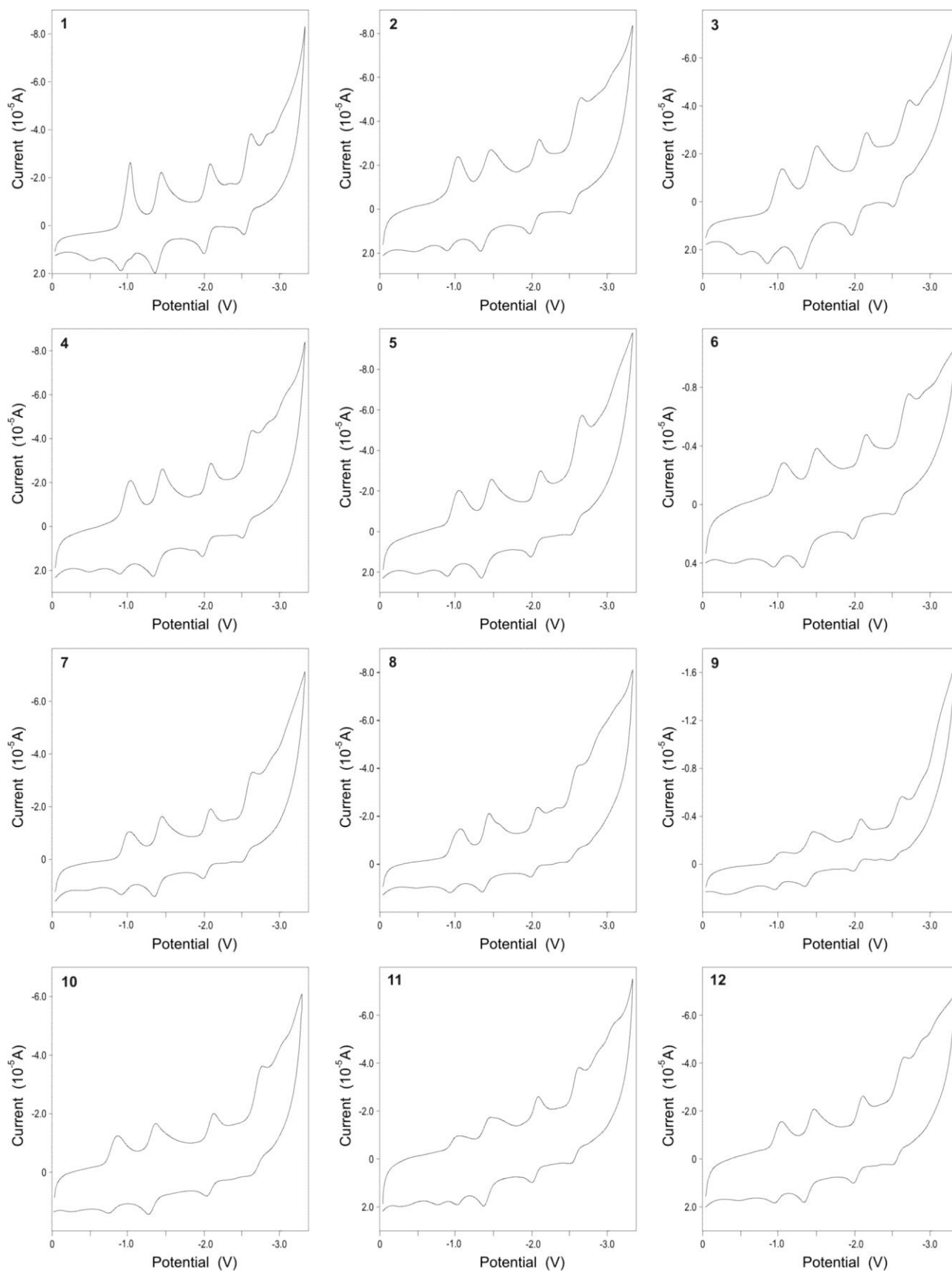


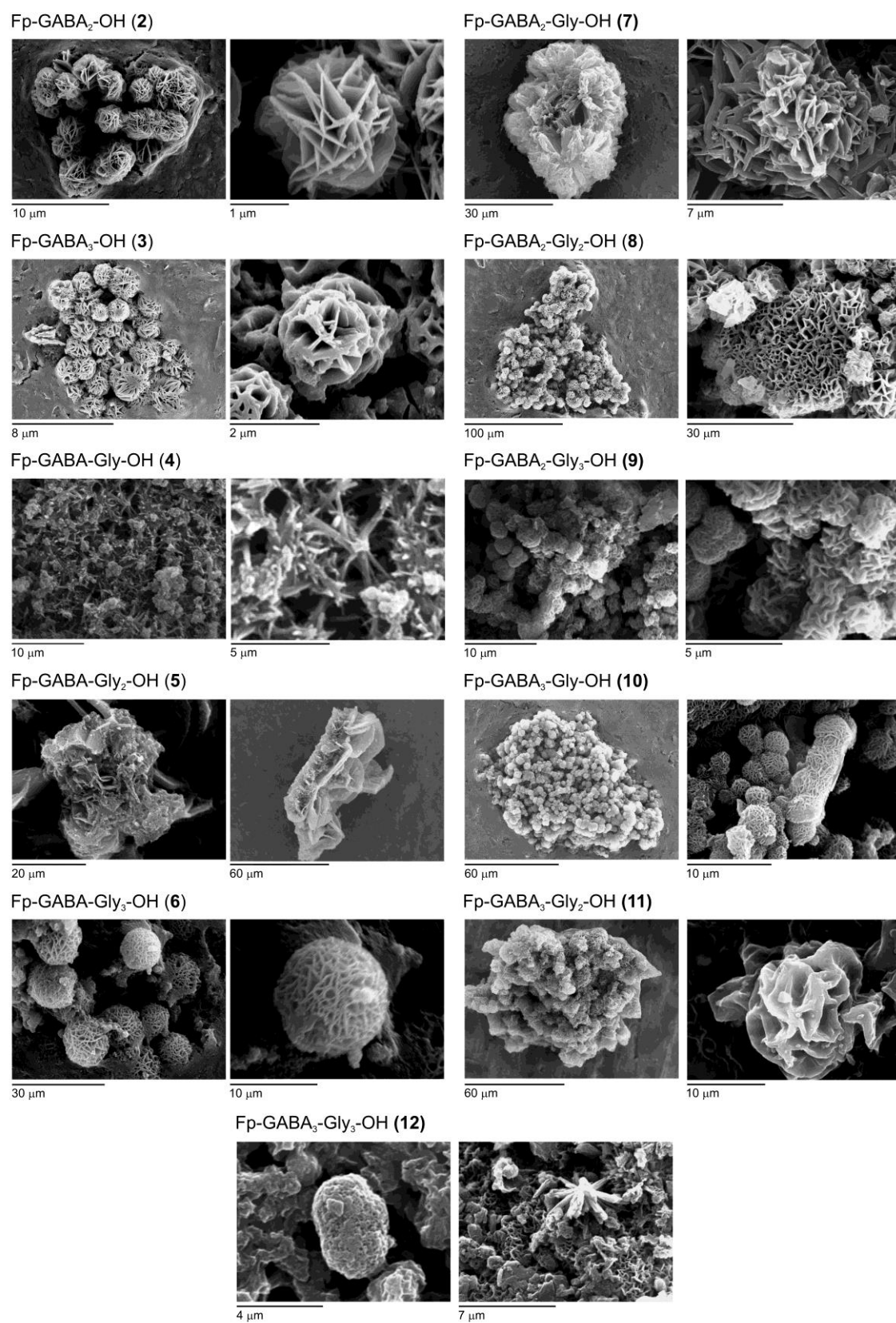
## UV spectra of compounds 1-12



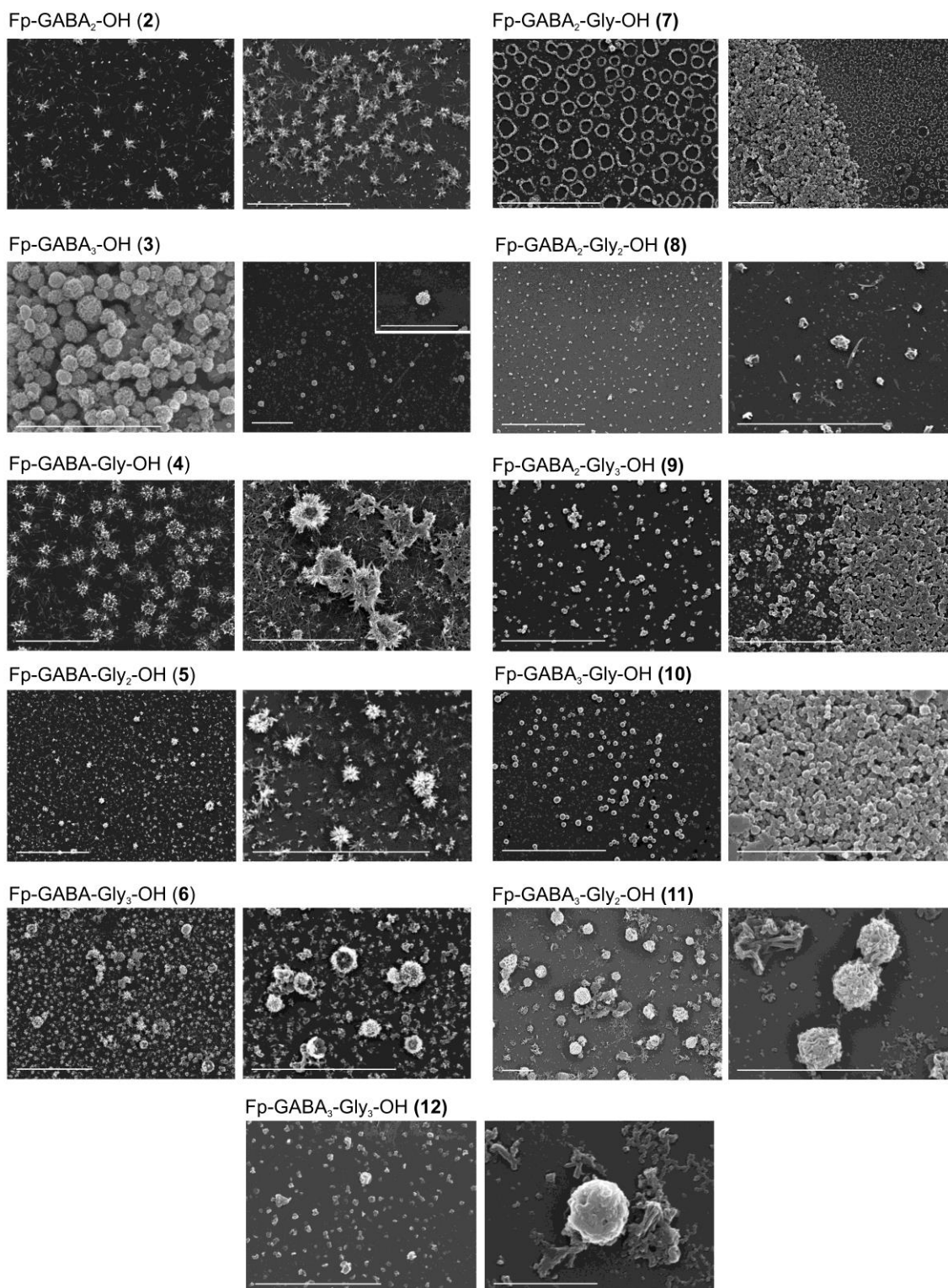


## Cyclic voltammograms of compounds 1-12





**Figure S1** SEM images of fulleropeptide acids 2-12 deposited on a brass substrate after precipitation with MeOH



**Figure S2** SEM images of compounds **2-12** prepared from PhMe/MeOH (5/1, v/v) mixture on a Si substrate upon evaporation of 10  $\mu$ L of 1mM solution at room temperature; inset on **3**: 10  $\mu$ L of 0.1mM solution; **9** and **10**, right, 30  $\mu$ L of 1mM solution.