Supplementary Material

# Supplementary Data

**Supplementary Table 1.** Physico-chemical characteristics of synthesized substrates.

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| Substrate | Amino Acid Analysis1 | TLC2,  R*f* | HPLC7,  tR,min | Mr8 (calc./discov.) | NMR1H, DMSO-D6, δ, ppm9 |
| Glp-Phe-Gln-pNA | Glu:Phe 1.98:1 | 0.153  0.474 | 16.7 | 524.5/524.5 | 1.93 – 2.06 (m, 4H, Gln-СН2, Glp-СН2); 2.13 – 2.25 (m, 4H Gln-СН2, Glp-СН2); 2.83 (dd, *J* = 13.5, 10.4 Hz, 1H, Phe-СН2); 3.13 (dd, *J* = 9.9, 3.5 Hz, 1H, Phe-СН2); 3.98 (dd, *J* = 8.5, 5.1 Hz, 1H, Glp-СН); 4.39 (q, *J* = 7.1 Hz, 1H, Gln-СН); 4.50 – 4.59 (m, 1H, Phe-СН); 6.84 (d, *J* = 6.7 Hz, 1H, Phe-NH); 7.21 (t, *J* = 7.2 Hz, 2H, Gln-CONH2); 7.28 – 7.64 (m, 5H, Phe-C6H5); 7.96 (d, *J* = 9.2 Hz, 2H, pNA-CH); 8.22 (d, *J* = 9.2 Hz, 2H, pNA-CH); 8.38 (d, *J* = 8.6 Hz, 1H, Glp-NH); 9.09 (d, *J* = 6.7 Hz, 1H, Gln-NH); 11.32 (s, 1H, pNA-NH). |
| Glp-Phe-Gln-AMC | Glu:Phe 2.1:1 | 0.775  0.856 | 13.5 | 561.5/561.4 | 1.81 (s, 3H, AMC-СН3); 1.90 – 2.04 (m, 4H, Gln-СН2, Glp-СН2); 2.11 – 2.24 (m, 4H Gln-СН2, Glp-СН2); 2.85 (dd, *J* = 13.2, 10.2 Hz, 1H, Phe-СН2); 3.14 (dd, *J* = 10.1, 3.6 Hz, 1H, Phe-СН2); 4.01 (dd, *J* = 8.4, 5.0 Hz, 1H, Glp-СН); 4.42 (q, *J* = 7.1 Hz, 1H, Gln-СН); 4.52 – 4.62 (m, 1H, Phe-СН); 6.18 (s, 1H, AMC-СНCO);6.91 (d, *J* = 6.8 Hz, 1H, Phe-NH); 7.15 (d, *J* = 9.1 Hz, 1H, AMC-CH); 7.24 (t, *J* = 7.3 Hz, 2H, Gln-CONH2); 7.30 – 7.65 (m, 5H, Phe-C6H5); 7.71 (s, 1H, AMC-СН);8.09 (d, *J* = 9.1 Hz, 1H, AMC-CH); 8.27 (d, *J* = 8.7 Hz, 1H, Glp-NH); 8.98 (d, *J* = 6.6 Hz, 1H, Gln-NH); 10.45 (s, 1 H, AMC-NH). |

1The molar ratio of amino acid residues. Amino acid analyses were performed on a Hitachi 835 (Japan) automatic amino acid analyzer after acidic hydrolysis of samples with 5.7 M HCl at 105°C in evacuated ampoules for 24 and 48 h. 2TLC spots were detected with UV lamp and chlorine – tolidine reagent. 3In chloroform – methanol – acetic acid (45:5:1). 4In chloroform – methanol – acetic acid – water (75:15:5:2).5In *n*-butanol-water-acetic acid (4:1:1). 6In *n*-butanol-pyridine-water-acetic acid (15:12:10:3). 7HPLC chromatography was carried out with an Milichrom model A-02 chromatograph (EkoNova Russia) using a ProntoSil 120-5C18AQ (2.0 × 75 mm) column eluted with a linear gradient of 0-80 % MeCN (for HPLC, Lekbiofarm (Russia)) in water for 35 min at a flow rate 1 ml/min. The eluent contained 0.1% TFA (Fluka AG). The elution profile was monitored at 214, 280 or 350 nm. 8Mass spectra were obtained by a Finnigan LCQ-IOnTrap (Thermo Electron, USA) instrument using an electrospray ionization method. 9NMR spectra were obtained in DMSO-D6 by a "Bruker АС-300" (Germany) spectrometer at the frequency of 400 Mhz. Chemical shifts were in parts per million (δ, ppm) towards the inner standard of tetramethylsilane.