Supporting Information for

Combinatorial Solid-Phase Synthesis of Multivalent Cyclic Neoglycopeptides

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Experimental Section

8: Boc-Lys(Aloc)-Orn(Ddv)-Gly-Ala-D-Lys(Ddv)-Orn(Ddv)-D-Val-Glu(OAll)-Bal-Sieber-TG (0.54 g, 70 μmol) was shaken for 16 h under argon with morpholine (77 μl, 0.88 mmol) and $Pd(PPh_3)_4$ (12 mg, 10 μmol) in DMF/DMSO (1:1) (3 mL) and subsequently washed with DMF and CH_2Cl_2. After treatment of a resin sample with the cleavage cocktail, remaining **8** was extracted with MeOH from the solid support. HPLC (20–80 % acetonitrile in water/0.1 % TFA over 30 min): retention time t_R = 18.5 min; ESI-MS ($M + H^+$): calcd. 1648.0, found 1648.6.

9: Boc-Lys-Orn(Ddv)-Gly-Ala-D-Lys(Ddv)-Orn(Ddv)-D-Val-Glu-Bal-Sieber-TG (0.3 g, 38 μmol) was treated for 6 min with a 5 % solution of HOBt in DMF and subsequently washed with DMF. A mixture of HOBt (35 mg, 228 μmol), HBTU (58 mg, 152 μmol), NMP (3 mL), and DIEA (53 μL, 304 μmol) was added and after having been shaken for 11 h at room temperature, the resin was washed with DMF and CH_2Cl_2. HPLC (20–80 % acetonitrile in water/0.1 % TFA over 30 min): t_R = 22.8 min; ESI-MS ($M + H^+$): calcd. 1630.0, found 1630.7.

11: *cyclo*[Boc-Lys-Orn(Ddv)-Gly-Ala-D-Lys(Ddv)-Orn(Ddv)-D-Val-Glu]-Bal-Sieber-TG (0.21 g, 27 μmol) was deprotected by treatment with hydrazine hydrate/DMF (4:96) (5 × 5 min) and washed with DMF. After addition of NMP (2 mL), DIEA (72 μL, 413 μmol), and **5** (240 mg, 413 μmol), the resin was shaken for 6 h at room temperature and subsequently washed with DMF and CH_2Cl_2. Cleavage from the resin was achieved by treatment with

TFA/*i*Pr_3SiH/CH_2Cl_2 (1:1:98) (5 × 5 min, each 4 mL) and thorough washing with F_3CCH_2OH/CH_2Cl_2 (1:3) and F_3CCH_2OH. The combined filtrates were neutralized with pyridine and concentrated under vacuum. Precipitation with *tert*-butyl methyl ether gave **11** (42 mg, 18 μmol, 67 %). HPLC (20–80 % acetonitrile in water/0.1 % TFA over 30 min): t_R = 10.6 min; ESI-MS ($M + H^+$): calcd. 2341.1, found 2342.1.

12: Crude neoglycopeptide **11** (18 mg, 7.7 μmol) was dissolved in $CHCl_3$/MeOH (1:1) (8 mL), a solution of NaOMe in MeOH (5.4 M) (40 μL, 216 μmol) was added, and the mixture was stirred for 3.5 h at room temperature. After neutralization with weakly acidic ion exchange resin (Amberlite IRC-86) the solvent was removed under vacuum. The remaining ion exchange resin was thoroughly washed with water and the combined filtrates were lyophilized to give deacetylated neoglycopeptide **12** (13 mg, 6.6 μmol, 86 %). The content of **12** in the crude product was 95 % (HPLC, 0–50 % acetonitrile in water/0.1 % TFA over 30 min: t_R = 17.4 min). Preparative HPLC (10–25 % acetonitrile in water/0.1 % TFA) gave 11 mg of **12**.