Supporting Information

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Orthogonally Protected Sugar Diamino Acids as Novel Building Blocks for Linear and Branched Oligosaccharide Mimetics

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Experimental Section

17: β -Alanine amide **13** (27 mg, 0.067 mmol) was dissolved in dry DMF (4 mL) and treated with piperidine (1 mL). After 40 min, the solvent was removed under reduced pressure followed by co-evaporation with toluene. The residue was re-dissolved in CHCl_3 (3 mL) and **2** (44 mg, 0.081 mmol) and a solution of HBTU (31 mg, 0.081 mmol) and HOBt (19 mg, 0.121 mmol) in dry DMF (3 mL) were added. $i\text{Pr}_2\text{NEt}$ (31 μL , 0.202 mmol) was added and the mixture was stirred over night. After dilution with CHCl_3 (15 mL), the organic phase was washed with 0.1 N HCl and sat aq NaHCO_3 , dried with Na_2SO_4 and evaporated. Purification by flash chromatography (silica, EtOAc/MeOH 95/5) gave **17** (42 mg, 89 %): R_F = 0.5 (EtOAc/MeOH 9/1).

18: Peptide **17** (50 mg, 0.071 mmol) was dissolved in dry DMF (4 mL) and treated with piperidine (1 mL) for 30 min. After evaporation and co-evaporation with toluene, the remaining solid was dissolved in CHCl_3 (8 mL) and building block **1** (88 mg, 0.142 mmol), a solution of HATU (54 mg, 0.142 mmol) and HOAt (29 mg, 0.214 mmol) in DMF (8 mL), and $i\text{Pr}_2\text{NEt}$ (55 μL , 0.356 mmol) were added. After stirring over night, aqueous workup as described for **17** followed. Flash chromatography (silica, EtOAc/MeOH 95/5) gave **18** (61 mg, 79 %): R_F = 0.53 (EtOAc/MeOH 9/1).

19: To a solution of **18** (50 mg, 0.046 mmol) in THF (4 mL) PMe_3 (278 μL , 1 M in THF) and water (1 mL) were added. After 1 h, the mixture was evaporated and co-evaporated several times with toluene. The subsequent peptide coupling was carried out as described for **17** using 2 eq of **1**. Purification by flash chromatography (silica, EtOAc/MeOH 95/5) gave **19** (56 mg, 73 %): R_F = 0.48 (EtOAc/MeOH 9/1); RP-HPLC (Vydac 218TP54 C_{18} reversed-phase column, 4×250 mm, flow = 1 mL min^{-1} , 20–80 % acetonitrile in water/0.1 % TFA over 30 min): t_R = 24.0 min. HRMS (MALDI-FTICR), calcd for $\text{C}_{83}\text{H}_{110}\text{N}_8\text{O}_{27}$: 1673.73730 [$M + \text{Na}^+$], found: 1673.73587, Δm = 0.8 ppm.

20: Protected oligomer **19** (15 mg, 0.009 mmol) was dissolved in CHCl_3/THF 1 : 1 (1 mL) and stirred for 1 h. The mixture was evaporated and the remainder was dissolved in MeOH (500 μL), treated with 1 N HCl (500 μL) for 1 h, and lyophilized. Finally, stirring with 20 % piperidine in DMF (500 μL) led to complete deprotection. Purification by RP-HPLC (Vydac 218TP54 C_{18} reversed-phase column, 4×250 mm, flow = 1 mL min^{-1} , 1–100 % acetonitrile in water/0.13 % pentafluoropropionic acid over 30 min, t_R = 15.5 min) gave **20** • 4 $\text{F}_3\text{C}-\text{CF}_2-\text{CO}_2\text{H}$ (3.5 mg, 28 %). HRMS (ESI-FTICR, MeCN/ H_2O), calcd for $\text{C}_{31}\text{H}_{50}\text{N}_8\text{O}_{13}$: 743,35696 [$M + \text{H}^+$], found: 743.35563, Δm = 1.8 ppm (see Figure S-1).

Figure S-1. HRMS (ESI-FTICR, MeCN/ H_2O) of **20**.