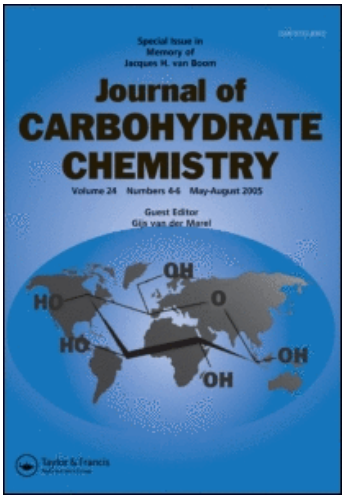

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A Practical One-Pot Synthesis of New *S*-Glycosyl Amino Acid Building Blocks for Combinatorial Neoglycopeptide Synthesis

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A Practical One-Pot Synthesis of New *S*-Glycosyl Amino Acid Building Blocks for Combinatorial Neoglycopeptide Synthesis

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S-Glycosyl L-aspartic acid building blocks were synthesized starting from 1-thiosugars by reaction with 5-aminopentanol and suitably protected L-aspartic acid pentafluorophenyl ester in a one-pot procedure under Mitsunobu conditions using 1,1′-azodicarbonyl dipiperidine and trimethyl phosphine. The method allowed for the preparation of *S*-glycosyl amino acid building blocks in one step without protection of the amino function for the Mitsunobu condensation. Alternatively, the title compounds were prepared by a stepwise approach via 5-aminopentyl 1-thioglycosides.

Keywords Thio-glycosides, Amino acids, Glycoconjugate, Mitsunobu reaction

INTRODUCTION

Highly diverse glycopeptide libraries have been shown to provide interesting targets capable of mimicking specific saccharide-protein interactions. Recently, Wong,[1] Meldal,[2] and Arya[4] have used *O*-, *N*-, and *C*-glycosyl amino acid building blocks for solid-phase synthesis of such glycopeptides. The replacement of the anomeric oxygen in such building blocks by sulphur leads to *S*-linked glycopeptides[3] with enhanced stability toward chemical[5] and enzymatic degradation,[6] which were tolerated by most biologic systems and thus, make S-linked glycopeptides interesting targets for glycopeptidomimetics.[7]

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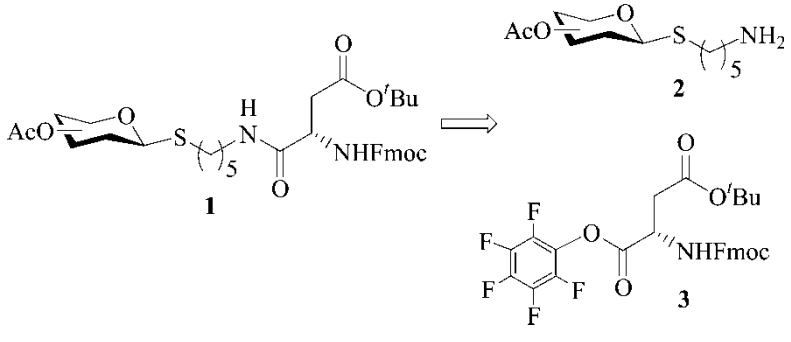
This paper is dedicated to Joseph Lloyd Stiles.
Address correspondence to Thomas Ziegler, Institute of Organic Chemistry, University of Tuebingen, Auf der Morgenstelle 18, 72076, Tuebingen, Germany. E-mail: thomas.ziegler@uni-tuebingen.de

Ongoing efforts in our group toward the efficient combinatorial solid-phase synthesis of highly glycosylated peptides as mimics for complex oligosaccharide structures[8] led us to prepare some Fmoc-protected *S*-glycosyl amino acid building blocks of general structure **1**. Previously, we have shown that similar *O*-glycosyl amino acid building blocks are suitable for automated solid-phase synthesis, either on beads[8] or via SPOT synthesis, which enabled the synthesis of large arrays of highly glycosylated peptide libraries for screening for biologic activities.[3,9] The building blocks were constructed in such a way that β-peptides were formed. β-Peptides are known to be resistant to enzymatic degradation and often form stable secondary structures like helices.[10] In order to further increase the diversity of such highly glycosylated combinatorial β-peptide libraries, we needed *S*-linked glycosyl amino acid building blocks of general structure **1**.

Envisaging the retrosynthesis for those *S*-glycosyl amino acid building blocks **1**, as outlined in Sch. 1, we needed the 5-aminopentyl-1-thioglycosides **2**, which could be condensed with suitably protected L-aspartic acid pentafluorophenyl ester derivative **3**.[8]

RESULTS AND DISCUSSION

Recently, Toth and coworkers[11a] prepared alkyl 1-thioglycosides from the respective 1-thiosugars by using N-protected serine and threonine amino acids with free hydroxyl groups under modified Mitsunobu conditions. Toth's procedure for the preparation of 1-thioglycosides appeared to us to be superior to other methods (i.e., alkylation reaction of the thiol group of 1-thiosugars), since it provides for direct condensation of suitably protected building blocks. Thus, reaction of 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranose[12] (**4a**) with 5-(9-fluorenylmethoxycarbonyl)aminopentanol[13] **9** was investigated first. Mitsunobu condensation of the latter under Toth's conditions (1,1′-(azodicarbonyl)dipiperidine/trimethylphosphine/THF)[11a] afforded the



Scheme 1: Retrosynthetic analysis of the *S*-glycosyl amino acid building blocks.

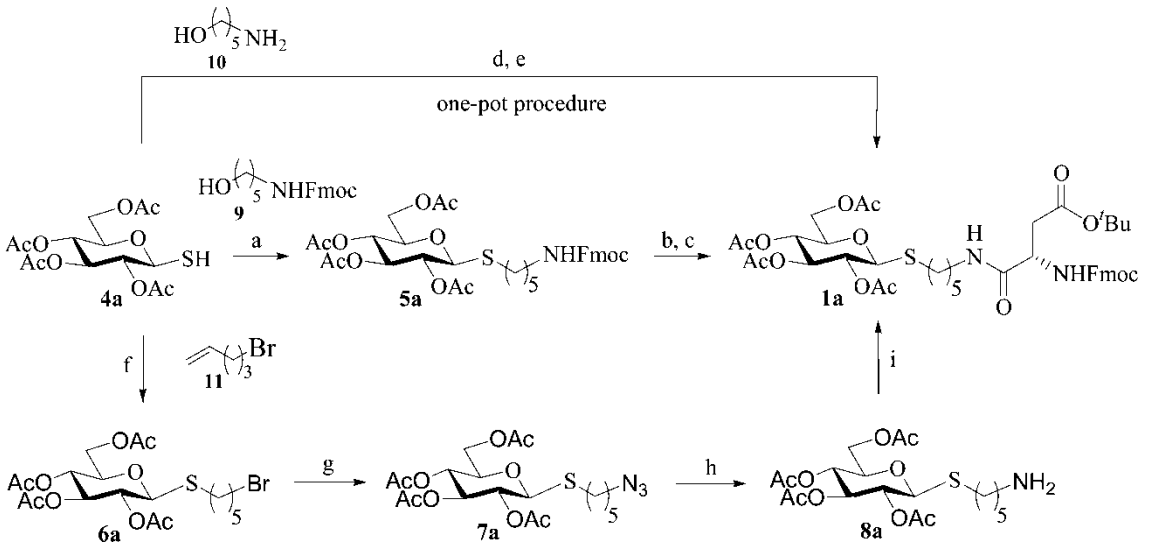
corresponding alkylated 1-thioglucoside **5a** in 38% yield. Compound **5a** was then N-deprotected with 20% piperidine/DMF, and the intermediate was immediately condensed without further purification with amino acid derivative **3** to afford the glycosyl amino acid building block **1a** in 85% yield. This three-step procedure gave an overall yield of 32% **1a** starting from **4a** (Sch. 2a–c).

From the proposed mechanism for the Mitsunobu condensation step[11b] we concluded that direct condensation of **4a** with unprotected 5-aminopentanol **10** should also be possible and thus, should enable us to perform a very efficient one-pot synthesis of the desired building block **1a** without the necessity to protect the amino function first. Indeed, when **4a** was reacted with 5-aminopentanol **10** for 20 min under optimized Mitsunobu conditions (see below) followed by addition of **3**, the glycosyl amino acid building block **1a** was obtained in 56% yield (Sch. 2d–e, one-pot procedure).

The proper choice of the azo and phosphine component for the Mitsunobu step appears to be decisive though, since using diethyl azodicarboxylate (DEAD) or diisopropyl azodicarboxylate (DIAD) in combination with triphenyl phosphine (standard Mitsunobu conditions[11d]) did not result in **1a** at all. Obviously, triphenyl phosphine is not basic enough to deprotonate the thiol group in **4a**. This deprotonation, however, is thought to be the initial step in Mitsunobu condensations.[11e] Therefore, when using trimethyl phosphine in combination with DIAD under otherwise identical conditions, the reaction proceeded smoothly according to TLC analysis and gave the condensation product **1a** in 37% yield. Better results were obtained under further optimized reaction conditions by substituting DIAD for 1,1′-(azodicarbonyl)dipiperidinec[11b] (ADDP). Thus, **1a** was obtained in 56% yield, although removal of the formed hydrazine dicarboxylate byproduct by chromatography still lowered the yield. Nevertheless, careful inspection of the TLC of the crude reaction mixture revealed a clean "spot-to-spot" conversion under these conditions. Using the alternative redox system ADDP/trimethyl phosphine, a considerable improvement of the Mitsunobu reaction with enhancement of the reactivity was observed. Unlike triphenyl phosphine oxide, the trimethyl analog can easily be removed by simple aqueous workup.

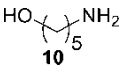
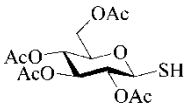
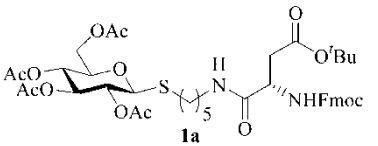
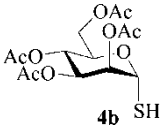
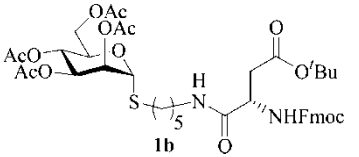
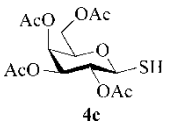
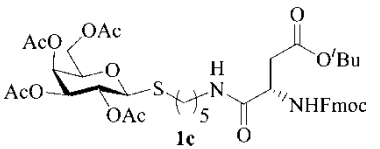
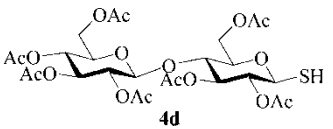
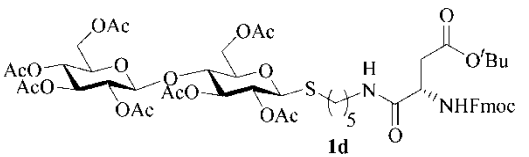
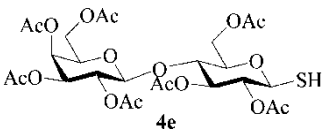
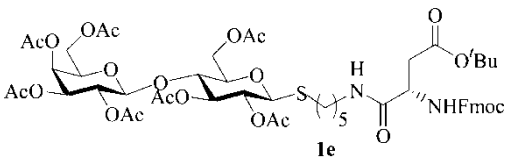
The broad applicability of this one-pot procedure to other sugars and aminoalcohols was further demonstrated by condensation of several 1-thiosugars **4a–f** with aminoalcohols **10**, **12**, and **13**, respectively, to afford the *S*-glycosyl amino acid building blocks **1a–h** (Table 1). The increased yield for disaccharide building blocks **1d–f** is due to an easier chromatographic removal of the byproducts from the initial Mitsunobu step.

For *S*-monoglycosyl L-aspartic acid building blocks **1a–c** where the overall yields for the Mitsunobu protocol was rather medium due to difficulties to remove the byproducts formed from the condensing reagents, we also used a stepwise approach for the glucose derivative **4a** as outlined in Sch. 2. For this purpose, **4a** was first reacted with 5-bromo-1-pentene **11** in the presence



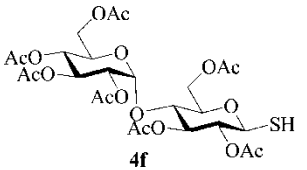
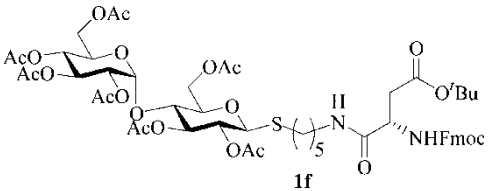
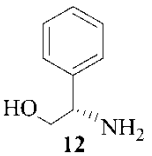
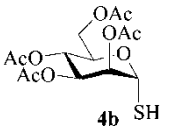
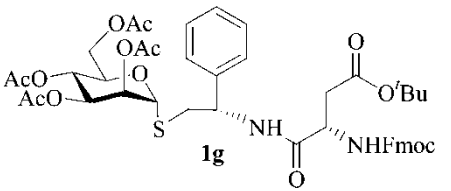
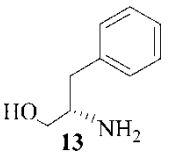
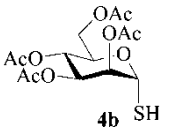
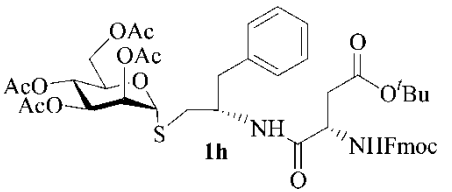
Sch. 2: Reagents and conditions: a) 5-(9-Fluorenylmethoxycarbonyl)aminopentanol **9**, Me_3P, ADDP, THF, 2 h, 20°C, 38%; b) 20% Piperidine in DMF; c) t-Butyl L-aspartic acid pentafluorophenyl ester **3**, EtOAc, 3 h, 0 → 20°C, 85% (**1a** overall yield 32%); d) 5-Aminopentanol **10**, Me_3P, ADDP, THF, 20 min, 20°C; e) t-Butyl L-aspartic acid pentafluorophenyl ester **3**, 3 h, 20°C, 56% (ADDP = 1,1′-(azodicarbonyl)dipiperidine) (**1a** overall yield 56%); f) 5-Bromo-1-pentene **11**, AIBN, 10 min, 120°C; g) NaN_3, $TBAHSO_4$, CH_2Cl_2/H_2O, 8 h, 20°C; h) H_2, Pd/C, EtOAc, 6 h, 20°C; i) t-Butyl aspartic acid pentafluorophenyl ester **3**, EtOAc, 3 h, 0 → 20°C, 66% overall yield from **4a**.

Table 1: One-pot condensation of 1-thiosugars **4a–f**.

Aminoalcohol	1-Thiosugars	*S*-Glycosyl amino acid building blocks	Yield (%)
 **10**	 **4a**	 **1a**	56%
	 **4b**	 **1b**	42%
	 **4c**	 **1c**	45%
	 **4d**	 **1d**	91%
	 **4e**	 **1e**	89%

(*continued*)

Table 1: Continued.

Aminoalcohol	1-Thiosugars	*S*-Glycosyl amino acid building blocks	Yield (%)
	 **4f**	 **1f**	61%
 **12**	 **4b**	 **1g**	40%
 **13**	 **4b**	 **1h**	38%

of AIBN to give **6a**, which was directly used in the next step without further purification. Surprisingly, the reaction proceeded quantitatively (TLC) only when it was carried out solvent free in a melt of **4a**. Performing the radical addition of **4a** to **11** in acetonitrile resulted in an incomplete reaction giving rise to only medium yields of **6a**, although similar radical additions of 1-thioglycosides to alkenes have been described to proceed smoothly in acetonitrile.[14] Subsequent treatment of crude **6a** with sodium azide under phase transfer conditions afforded **7a**, hydrogenation of which over Pd on charcoal furnished **8a** as crude product. Purification of the intermediates **6a**, **7a**, and **8a**, was not necessary since the purity (NMR, MS) of the crude products was shown to be sufficient for proceeding to the next steps. Compound **8a** was finally condensed with L-aspartic acid pentafluorophenyl ester **3** to give the desired product **1a** in 66% overall yield starting from **4a**. Although this alternative multistep procedure is more time consuming, it gave slightly better overall yield for the monosaccharide building block **1a** than the aforementioned Mitsunobu protocol.

CONCLUSIONS

The simple and easy to perform procedures presented here provide for a convenient and fast preparation of various *S*-glycosyl amino acid building blocks suitable for combinatorial solid-phase synthesis of highly glycosylated β-peptides.

EXPERIMENTAL

General Methods

^{1}H and ^{13}C NMR spectra were recorded with a Bruker spectrometer model Avance 400. Mass spectra were recorded using a TSQ 70 Finnigan spectrometer. Optical rotations were measured using a Perkin-Elmer polarimeter model 341 at 20°C. Elemental analyses were performed with a Hekatech EuroEA 3000 analysator. TLC was conducted on silica Polygram® SIL G/UV_{254} purchased from Macherey-Nagel. Flash chromatography was carried out using silica gel (0.004–0.063 nm) purchased from Macherey-Nagel. Acetone was distilled over $KMnO_4$ and K_2CO_3 under argon. THF was distilled under argon from sodium and benzophenone. All Mitsunobu reactions were performed under argon. 1-Thiosugars **4a**–**f** were synthesized according to the literature.[12]

General Procedure for One-Pot Mitsunobu Reaction for compound 1a–h

Trimethyl phosphine (8 mL, 8 mmol of a 1.0 M solution in THF) was added under argon at 0°C to a solution of ADDP (2.02 g, 8 mmol) in THF (100 mL) and

stirred for 30 min until the yellow color disappeared. Next, aminoalcohol (4 mmol) and 1-thiosugar (5.2 mmol) were added, and stirring was continued at rt for 20 min. L-Aspartic acid pentafluorophenyl ester (2.31 g, 4 mmol) was added and the mixture stirred for another 3 h. The precipitate that formed was filtered off, and the solvents were evaporated. The residue was dissolved in CH_2Cl_2 (100 mL) and the solution washed two times with water (25 mL) and saturated aqueous $NaHCO_3$ solution (25 mL), dried with $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography (ethyl acetate/petroleum ether 1:1) to afford compound **1a–h.**

(5-(*N*-Fluorenylmethoxycarbonyl)-pentyl)-2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-gluco-pyranoside (5a)

To a solution of ADDP (2.02 g, 8 mmol) in abs. THF (100 mL) was added trimethylphosphine (8 mL, 8 mmol of a 1.0 M solution in THF) under argon at 0°C and stirred for 30 min until the yellow color disappeared. Then **9** (1.30 g, 4 mmol) and **4a** (1.89 g, 5.2 mmol) were added, and stirring at rt was continued for 3 h. The precipitate was filtered off and the solution evaporated to dryness. The residue was taken up in CH_2Cl_2 (100 mL), washed with water (2 × 25 mL) and saturated aqueous $NaHCO_3$ solution (25 mL), dried with $MgSO_4$, filtered, and evaporated. The crude product was purified by column chromatography (ethyl acetate/petroleum ether 1:1) to afford compound **5a** (1.02 g, 38%) as a white amorphous solid. $[\alpha]_D - 18.7^\circ$ (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): $\delta = 7.69$, 7.52 (d, 2 H, $J = 7.3$ Hz, $J = 7.1$ Hz, Fmoc-Ar-*H*), 7.31, 7.25 (t, 2 H, $J = 7.3$ Hz, Fmoc-Ar-*H*), 5.15 (t, 1 H, $J = 9.4$ Hz, H-3), 4.97 (m, 1 H, H-4), 4.96 (m, 1 H, H-2), 4.80 (bs, 1 H, -NH-), 4.39 (d, 1 H, $J_{1\text{-}2} = 10.11$ Hz, H-1), 4.32 (d, 1 H, O-C*H*$_2$-Fmoc), 4.16 (m, 1 H, H-6a), 4.06 (m, 2 H, H-6b, H-5), 3.64 (d, 1 H, C*H*-Fmoc), 3.11 (bd, 2 H, NH-C*H*$_2$-Alkyl), 2.60 (m, 2 H, S-C*H*$_2$-Alkyl), 2.04, 2.02, 1.99, 1.97 (4 s, 12 H, C*H*$_3$-Acetyl), 1.54 (m, 2 H, C*H*$_2$-Alkyl), 1.44 (m, 2 H, C*H*$_2$-Alkyl), 1.34 (m, 2 H, C*H*$_2$-Alkyl); ^{13}C NMR ($CDCl_3$): $\delta = 171.1$, 170.7, 170.3, 169.8 (CH$_3$-*C*O), 156.8 (NH-*C*OO), 144.3, 141.7, 128.0, 127.4, 125.4, 120.4 (Fmoc-Ar-*C*), 83.8 (C-1), 76.2 (C-3), 74.3 (C-5), 70.2 (C-2), 68.6 (C-4), 66.9 (O-*C*H$_2$-Fmoc), 62.5 (C-6), 47.7 (*C*H-Fmoc), 41.2 (NH-*C*H$_2$-Alkyl), 29.9, 29.8, 29.5, 26.1 (*C*H$_2$-Alkyl), 21.4, 21.1, 21.0, 20.9 (*C*H$_3$-Acetyl). [(Positive FAB-MS) (m/z = 671.2)]: 672.2 $[M + H]^+$.

Anal. Calcd for $C_{34}H_{41}NO_{11}S$ (671.76): C, 60.79; H, 6.15; N, 2.09; S, 4.77. Found: C, 60.98; H, 6.16; N, 1.96; S, 4.93.

N-((5-Pentyl)-2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranosyl)-Fmoc-Asp(OtBu)-amid (1a)

A. Piperidine in DMF (20%, 10 mL) was added to compound **5a** (1.02 g, 1.52 mmol), and the mixture was stirred at rt. After TLC had indicated the

disappearance of starting material (ca. 30 min), the solvent was evaporated and coevaporated with toluene to afforded crude compound **8a** (for characterization see alternative synthesis below). Next, L-aspartic acid pentafluorophenyl ester (1.42 g, 1.48 mmol) was added at 0° C to a solution of **8a** (0.83 g, 1.48 mmol) in EtOAc (10 mL) and stirred for 3 h while warming up to 20° C. The solvent was evaporated under vacuum and the crude product purified by column chromatography (ethyl acetate/petroleum ether 1:1) to afford compound **1a** (1.06 g, 85%) as a white amorphous solid. $[\alpha]_D$ −7.4° (*c* 8.3, $CHCl_3$); ^1H NMR ($CDCl_3$): $\delta = 7.75$, 7.56 (d, 2 H, $J = 7.3$ Hz, $J = 7.1$ Hz, Fmoc-Ar-*H*), 7.39, 7.30 (t, 2 H, $J = 7.3$ Hz, Fmoc-Ar-*H*), 6.50 (bs, 1 H, N*H*-Pentyl), 5.95 (bs, 1 H, N*H*-Asp), 5.19 (t, 1 H, $J = 9.4$ Hz, H-3), 5.05 (m, 1 H, H-4), 4.99 (m, 1 H, H-2), 4.41 (m, 4 H, H-1, O-CH_2-Fmoc, C*H*-Asp), 4.19 (m, 2 H, H-6a, C*H*-Fmoc), 4.11 (m, 1 H, H-6b), 3.66 (bm, 1 H, H-5), 3.21 (bd, 2 H, NH-CH_2-Alkyl), 2.84 (m, 1 H, CH-CH_2-COO^{t}Bu), 2.62 (m, 3 H, S-CH_2-Alkyl, CH-CH_2-COO^{t}Bu), 2.04, 2.02, 1.99, 1.97 (4 s, 12 H, CH_3-Acetyl), 1.58 (m, 2 H, CH_2-Alkyl), 1.47, 1.37 (m, 13 H, [CH_3]$_3$-C, CH_2-Alkyl), 1.22 (m, 2 H, CH_2-Alkyl); ^{13}C NMR ($CDCl_3$): $\delta = 171.2$, 170.7, 170.3, 169.4 (CH_3-*C*O), 156.1 (NH-*C*OO), 144.7, 141.3, 127.8, 127.1, 125.1, 120.1 (Fmoc-Ar-*C*), 83.8 (C-1), 81.8 (*C*[CH_3]$_3$), 76.2 (C-3), 74.2 (C-5), 69.8 (C-2), 68.3 (C-4), 67.5 (O-*C*H_2-Fmoc), 62.1 (C-6), 51.2 (*C*H-Asp), 47.2 (*C*H-Fmoc), 39.4 (NH-*C*H_2-Alkyl), 37.6 (CH-*C*H_2-COO^{t}Bu), 29.6, 29.0, 25.8 (*C*H_2-Alkyl), 28.1 (C[*C*H_3]$_3$), 20.8, 20.7, 20.6, 20.5 (*C*H_3-Acetyl). [(Positive FAB-MS) (m/z = 842.3)]: 843.2 $[M + H]^+$, 865.1 $[M + Na]^+$.

Anal. Calcd for $C_{42}H_{54}N_2O_{14}S$ (842.33): C, 59.84; H, 6.46; N, 3.32; S, 3.80. Found: C, 59.82; H, 6.52; N, 3.13; S, 3.82.

B. According to the general procedure, 5-aminopentanol **10** (0.42 g, 4 mmol) and tetra-*O*-acetyl-1-thio-β-D-glucopyranose **4a** (1.89 g, 5.2 mmol) afforded **1a** (1.88 g, 56%).

C. L-Aspartic acid pentafluorophenyl ester (1.49 g, 1.55 mmol) was added to a solution of crude **8a** (0.70 g, 1.55 mmol) in EtOAc (10 mL) at 0°C, and the mixture was stirred for 3 h while warming to 20°C. The solvent was removed under vacuum, and the crude product was purified by column chromatography (ethyl acetate/petroleum ether 1:1) to afford compound **1a** (1.10 g, 66% from **6a**).

N-[(5-Pentyl)-2,3,4,6-tetra-*O*-acetyl-1-thio-α-D-mannopyranosyl)-Fmoc-Asp(OtBu)-amid (1b)

According to the general procedure, 5-aminopentanol **10** (0.42 g, 4 mmol) and tetra-*O*-acetyl-1-thio-α-D-mannopyranose **4b** (1.89 g, 5.2 mmol) afforded **1b** (1.41 g, 42%) as a colorless oil. $[\alpha]_D$+47.5° (*c* 1.5, $CHCl_3$); ^1H NMR ($CDCl_3$): $\delta = 7.74$, 7.56 (d, 2 H, $J = 7.3$ Hz, $J = 7.1$ Hz, Fmoc-Ar-*H*), 7.37, 7.28

(t, 2 H, $J = 7.3$ Hz, Fmoc-Ar-*H*), 6.49 (bs, 1 H, N*H*-Pentyl), 5.95 (bs, 1 H, N*H*-Asp), 5.40 (bd, 1 H, H-3), 5.20 (t, 1 H, $J = 9.6$ Hz, H-4), 5.03 (dd, 1 H, $J = 3.1$ Hz H-2), 4.42 (m, 4 H, H-1, O-CH_2-Fmoc, C*H*-Asp), 4.20 (m, 1 H, C*H*-Fmoc), 4.11 (m, 2 H, H-6a, H-6b), 3.89 (m, 1 H, H-5), 3.23 (bd, 2 H, NH-CH_2-Alkyl), 2.87 (m, 1 H, CH-CH_2-COO^{t}Bu), 2.64 (m, 3 H, S-CH_2-Alkyl, CH-CH_2-COO^{t}Bu), 2.15, 2.13, 2.04, 2.01 (4 s, 12 H, CH_3-Acetyl), 1.59 (m, 2 H, CH_2-Alkyl), 1.47, 1.37 (m, 13 H, [CH_3]$_3$-C, CH_2-Alkyl), 1.22 (m, 2 H, CH_2-Alkyl). ^{13}C NMR ($CDCl_3$): $\delta = 171.3$, 170.5, 170.3, 169.7 (CH_3-*C*O), 156.1 (NH-*C*OO), 143.8, 141.9, 127.9, 127.2, 125.1, 120.2 (Fmoc-Ar-*C*), 84.2 (C-1), 81.9 (*C*[CH_3]$_3$), 74.2 (C-5), 72.0 (C-3), 67.3 (C-2), 67.2 (C-4), 67.5 (O-*C*H_2-Fmoc), 61.5 (C-6), 51.2 (*C*H-Asp), 47.2 (*C*H-Fmoc) 39.5 (NH-*C*H_2-Alkyl), 37.6 (CH-*C*H_2-COO^{t}Bu), 31.0, 29.9, 25.9 (*C*H_2-Alkyl), 28.1 (C[*C*H_3]$_3$), 21.1, 20.9, 20.8, 20.6 (*C*H_3-Acetyl). [(Positive FAB-MS) (m/z = 842.3)]: 843.4 $[M + H]^+$, 865.4 $[M + Na]^+$.

Anal. Calcd for $C_{42}H_{54}N_2O_{14}S$ (842.33): C, 59.84; H, 6.46; N, 3.32; S, 3.80. Found: C, 59.82; H, 6.51; N, 3.21; S, 3.73.

N-[(5-Pentyl)-2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-galactopyranosyl)-Fmoc-Asp(OtBu)-amid (1c)

According to the general procedure, 5-aminopentanol **10** (0.42 g, 4 mmol) and tetra-*O*-acetyl-1-thio-β-D-galactopyranose **4c** (1.89 g, 5.2 mmol) afforded **1c** (1.51 g, 45%) as a white amorphous solid. $[\alpha]_D - 4.2^\circ$ (*c* 4.3, $CHCl_3$); ^{1}H NMR ($CDCl_3$): $\delta = 7.73$, 7.55 (d, 2 H, $J = 7.1$ Hz, Fmoc-Ar-*H*), 7.37, 7.28 (t, 2 H, $J = 7.3$ Hz, Fmoc-Ar-*H*), 6.50 (bs, 1 H, N*H*-Pentyl), 5.95 (bd, 1 H, $J = 6.6$ Hz, N*H*-Asp), 5.39 (s, 1 H, H-4), 5.19 (t, 1 H, $J = 9.9$ Hz, H-2), 5.01 (m, 1 H, H-3), 4.40 (m, 4 H, H-1, O-CH_2-Fmoc, C*H*-Asp), 4.19 (m, 1 H, C*H*-Fmoc), 4.09 (m, 2 H, H-6b, H-6a), 3.89 (m, 1 H, H-5), 3.20 (bd, 2 H, NH-CH_2-Alkyl), 2.85 (bm, 1 H, CH-CH_2-COO^{t}Bu), 2.62 (m, 3 H, S-CH_2-Alkyl, CH-CH_2-COO^{t}Bu), 2.11, 2.02, 2.00, 1.95 (4 s, 12 H, CH_3-Acetyl), 1.58 (m, 2 H, CH_2-Alkyl), 1.47, 1.41 (m, 13 H, [CH_3]$_3$-C, CH_2-Alkyl), 1.22 (m, 2 H, CH_2-Alkyl). ^{13}C NMR ($CDCl_3$): $\delta = 171.3$, 170.4, 170.1, 169.4 (CH_3-*C*O), 156.1 (NH-*C*OO), 143.7, 141.3, 127.8, 127.1, 125.1, 120.1 (Fmoc-Ar-*C*), 84.1 (C-1), 81.9 (*C*[CH_3]$_3$), 74.4 (C-3), 71.9 (C-5), 67.3 (C-2), 67.2 (C-4), 67.5 (O-*C*H_2-Fmoc), 62.5 (C-6), 51.2 (*C*H-Asp), 47.2 (*C*H-Fmoc) 39.4 (NH-*C*H_2-Alkyl), 37.6 (CH-*C*H_2-COO^{t}Bu), 29.9, 29.1, 25.9 (*C*H_2-Alkyl), 28.1 (C[*C*H_3]$_3$), 22.9, 22.4, 20.9, 20.7 (*C*H_3-Acetyl). [(Positive FAB-MS) (m/z = 842.3)]: 843.9 $[M + H]^+$, 865.9 $[M + Na]^+$.

Anal. Calcd for $C_{42}H_{54}N_2O_{14}S$ (842.33): C, 59.84; H, 6.46; N, 3.32; S, 3.80. Found: C, 59.46; H, 6.52; N, 2.98; S, 3.76.

N-((Pentyl)-2′,3′,4′,6′-tetra-*O*-acetyl-β-D-glucopyranosyl(1 → 4)-2,3,6-tri-*O*-acetyl-1-thio-β-D-glucopyranosyl)-Fmoc-Asp(OtBu)-amid (1d)

According to the general procedure, 5-aminopentanol **10** (0.42 g, 4 mmol) and hepta-*O*-acetyl-1-thio-*β*-D-cellobiose **4d** (3.39 g, 5.2 mmol) afforded **1d** (5.26 g, 91%) as a white amorphous solid. $[\alpha]_D - 15.3^\circ$ (*c* 3.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$): $\delta = 7.75$, 7.56 (d, Fmoc-Ar-*H*), 7.37, 7.28 (m, Fmoc-Ar-*H*), 6.48 (bs, 1 H, N*H*-Pentyl), 5.93 (bs, 1 H, N*H*-Asp), 5.14 (m, 2 H, H-3, H-3′), 5.05 (m, 1 H, H-4′), 4.89 (m, 2 H, H-2′, H-2), 4.48, 4.41, 4.34 (bm, 7 H, H-1′, H-1, H-6a, H-6a′, O-CH_2-Fmoc, C*H*-Asp), 4.20 (m, 1 H, H-6b), 4.08, 4.04 (m, 2 H, H-6b′, C*H*-Fmoc), 3.74 (t, 1 H,$J = 10.0$ H-4), 3.63 (bd, 1 H, H-5), 3.58 (bs, 1 H, H-5′) 3.21 (bs, 2 H, NH-CH_2-Alkyl), 2.85 (d, 1 H, CH-CH_2-COO^{t}Bu), 2.59 (m, 3 H, S-CH_2-Alkyl, CH-CH_2-COO^{t}Bu), 2.09, 2.06, 2.02, 2.00, 1.99, 1.96 (7 s, 21 H, CH_3-Acetyl), 1.57 (m, 2 H, CH_2-Alkyl), 1.55, 1.43 (m, 13 H, [CH_3]$_3$-C, CH_2-Alkyl), 1.37, 1.24 (m, 2 H, CH_2-Alkyl). ^{13}C NMR ($CDCl_3$): $\delta = 171.0$, 170.2, 170.0, 169.5, 169.4, 169.1, 168.8 (CH_3-*C*O), 155.8 (NH-*C*OO), 143.4, 141.1, 127.5, 126.8, 124.8, 119.8 (Fmoc-Ar-*C*), 100.6 (C-1′), 83.2 (C-1), 81.6 (*C*[CH_3]$_3$), 76.2 (C-4), 73.2 (C-5), 72.7 (C-3′), 71.7 (C-5′), 71.3 (2 C, C-3, C-2′), 69.9 (C-2), 67.5 (O-*C*H_2-Fmoc), 66.9 (C-4′), 61.8 (C-6), 61.2 (C-6′), 50.9 (*C*H-Asp), 46.9 (*C*H-Fmoc),39.1 (NH-*C*H_2-Alkyl), 37.3 (CH-*C*H_2-COO^{t}Bu), 29.6, 28.8, 25.5 (*C*H_2-Alkyl), 27.9 (C[*C*H_3]$_3$), 20.6, 20.5, 20.4, 20.3 (1 C, 1 C, 1 C, 4 C, *C*H_3-Acetyl). [(Positive FAB-MS) (m/z = 1130.4)]: 1131,1 $[M + H]^+$, 1153,1 $[M + Na]^+$.

Anal. Calcd for $C_{54}H_{70}N_2O_{22}S$ (1130.42): C, 57.34; H, 6.24; N, 2.48; S, 2.83. Found: C, 57.33; H, 6.36; N, 2.31; S, 2.56.

N-((5-Pentyl)-2′,3′,4′,6′-tetra-*O*-acetyl-*β*-D-galactopyranosyl(1 → 4)-2,3,6-tri-*O*-acetyl-1-thio-β-D-glucopyranosyl)-Fmoc-Asp(OtBu)-amid (1e)

According to the general procedure, 5-aminopentanol **10** (0.42 g, 4 mmol) and hepta-*O*-acetyl-1-thio-*β*-D-lactose **4e** (3.39 g, 5.2 mmol) afforded **1e** (5.12 g, 89%) as a white amorphous solid. $[\alpha]_D - 2.7^\circ$ (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): $\delta = 7.75$, 7.55 (bd, Fmoc-Ar-*H*), 7.37, 7.28 (m, Fmoc-Ar-*H*), 6.56 (bs, 1 H, N*H*-Pentyl), 6.01 (bs, 1 H, N*H*-Asp), 5.32 (s, 1 H, H-4′), 5.18 (bt, 1 H, $J = 8.8$ Hz, H-2′), 5.08 (bt, 1 H, $J = 8.8$ Hz, H-3′), 4.91 (m, 2 H, H-3, H-2), 4.43 (m, 6 H, H-1, H-1′, H-6a, O-CH_2-Fmoc, C*H*-Asp), 4.19 (m, 1 H, C*H*-Fmoc), 4.07 (m, 3 H, H-6a′, H-6b, H-6b′), 3.86 (bm, 1 H, H-5′), 3.75 (bt, 1 H, $J_{3\text{-}4} = 9.4$, $J_{4\text{-}5} = 9.1$ H-4), 3.57 (m, b, 1 H, H-5), 3.19 (bs, 2 H, NH-CH_2-Alkyl), 2.81 (m, 1 H, CH-CH_2-COO^{t}Bu), 2.59 (m, 3 H, S-CH_2-Alkyl, CH-CH_2-COO^{t}Bu), 2.12, 2.07, 2.01, 1.94 (4 s, 21 H, CH_3-Acetyl), 1.55 (m, 2 H, CH_2-Alkyl), 1.42, 1.36, 1.22 (m, 13 H, [CH_3]$_3$-C, CH_2-Alkyl), 1.22 (m, 2 H, CH_2-

Alkyl). ^{13}C NMR ($CDCl_3$): $\delta = 171.0$, 170.1, 170.3, 170.1, 170.0, 169.6, 169.0 (CH_3-*C*O), 156.0 (NH-*C*OO), 143.6, 141.2, 127.7, 127.0, 125.0, 120.0 (Fmoc-Ar-*C*), 101.0 (C-1′), 83.3 (C-1), 81.6 (*C*[CH_3]$_3$), 76.6 (C-4), 76.1 (C-5), 73.7 (C-3), 70.9 (C-3′), 70.6 (C-2), 70.7 (C-5′), 67.4 (O-*C*H_2-Fmoc), 67.0 (C-2′), 66.6 (C-4′), 62.3 (C-6′), 61.2 (C-6), 51.1 (*C*H-Asp), 47.1 (*C*H-Fmoc), 39.3 (NH-*C*H_2-Alkyl), 37.5 (CH-*C*H_2-COO^{t}Bu), 29.8, 28.8, 25.7 (*C*H_2-Alkyl), 28.0 (C[*C*H_3]$_3$), 21.0, 20.8, 20.7, 20.6, 20.5, 20.4 (1 C, 1 C, 1 C, 1 C, 2 C, 1 C, *C*H_3-Acetyl). [(Positive FAB-MS) (m/z = 1130.4)]: 1131.3 $[M + H]^+$, 1153.3 $[M + Na]^+$.

Anal. Calcd for $C_{54}H_{70}N_2O_{22}S$ (1130.42): C, 57.34; H, 6.24; N, 2.48; S, 2.83. Found: C, 57.18; H, 6.30; N, 2.52; S, 2.73.

N-((5-Pentyl)-2′,3′,4′,6′-tetra-*O*-acetyl-α-D-glucopyranosyl(1 → 4)-2,3,6-tri-*O*-acetyl-1-thio-β-D-glucopyranosyl)-Fmoc-Asp(OtBu)-amid (1f)

According to the general procedure 5-aminopentanol **10** (0.42 g, 4 mmol) and hepta-*O*-acetyl-1-thio-β-D-maltose **4f** (3.39 g, 5.2 mmol) afforded **1f** (3.53 g, 61%) as a white amorphous solid. $[\alpha]_D$+19.4° (*c* 0.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$): $\delta = 7.76$, 7.57 (d, Fmoc-Ar-*H*), 7.40, 7.31 (m, Fmoc-Ar-*H*), 6.50 (bs, 1 H, N*H*-Pentyl), 5.95 (bs, 1 H, N*H*-Asp), 5.39 (d, 1 H, $J = 3.3$ Hz, H-1′), 5.35 (m, 1 H, H-3′), 5.26 (t, 1 H, $J = 9.0$ Hz H-3), 5.04 (t, 1 H, $J = 10.0$ Hz, H-4′), 4.87 (m, 1 H, H-2), 4.84 (m, 1 H, H-2′), 4.49, 4.46, 4.42 (bm, 4 H, H-1, H-6a, O-C*H*$_2$-Fmoc, C*H*-Asp), 4.25 (m, 1 H, H-6b), 4.23 (m, 1 H, H-6a′), 4.12 (m, 1 H, H-6b′), 4.06 (m, 1 H, C*H*-Fmoc), 4.02 (m, 1 H, H-4), 3.97 (m, 1 H, H-5′), 3.95 (m, 1 H, H-5), 3.22 (bs, 2 H, NH-C*H*$_2$-Alkyl), 2.87 (d, 1 H, CH-C*H*$_2$-COO^{t}Bu), 2.60 (m, 3 H, S-C*H*$_2$-Alkyl, CH-C*H*$_2$-COO^{t}Bu), 2.14, 2.12, 2.09, 2.04, 2.01 1.99 (4 s, 21 H, C*H*$_3$-Acetyl), 1.57, 1.44 (m, 13 H, [C*H*$_3$]$_3$-C, C*H*$_2$-Alkyl), 1.37, 1.24 (m, 2 H, C*H*$_2$-Alkyl). ^{13}C NMR ($CDCl_3$): $\delta = 171.4$, 170.8, 170.7, 170.4, 170.2, 170.0, 169.7 (CH_3-*C*O), 156.0 (NH-*C*OO), 143.8, 141.4, 127.9, 127.3, 125.1, 120.2 (Fmoc-Ar-*C*), 95.7 (C-1′), 83.3 (C-1), 81.9 (*C*[CH_3]$_3$), 72.8 (C-3), 70.9 (C-5), 70.1 (C-4), 69.5 (C-2), 68.6 (C-2′), 68.3 (C-3′), 68.1 (C-5′), 67.4 (O-*C*H_2-Fmoc), 67.0 (C-2′), 66.6 (C-4′), 63.1 (C-6), 61.6 (C-6′), 51.2 (*C*H-Asp), 47.3 (*C*H-Fmoc), 39.5 (NH-*C*H_2-Alkyl), 37.7 (CH-*C*H_2-COO^{t}Bu), 29.9 29.3, 25.9 (*C*H_2-Alkyl), 28.2 (C[*C*H_3]$_3$), 21.0, 20.9, 20.8, 20.7, 20.6 (1 C, 1 C, 2 C, 2 C, 1 C, *C*H_3-Acetyl). [(Positive FAB-MS) (m/z = 1130.4)]: 1131.4 $[M + H]^+$, 1153.2 $[M + Na]^+$.

Anal. Calcd for $C_{54}H_{70}N_2O_{22}S$ (1130.42): C, 57.34; H, 6.24; N, 2.48; S, 2.83. Found: C, 57.14; H, 6.23; N, 2.24; S, 2.55.

N-((L-α-phenylglycinyl)-2,3,4,6-tetra-*O*-acetyl-1-thio-α-D-mannopyranosyl)-Fmoc-Asp(OtBu)-amid (1g)

According to the general procedure, L-(+)-α-phenylglycionol **12** (0.55 g, 4 mmol) and tetra-*O*-acetyl-1-thio-α-D-mannopyranose **4b** (1.89 g, 5.2 mmol)

afforded **1 g** (1.40 g, 40%) as a colorless oil. $[\alpha]_D$+0.32° (*c* 1, $CHCl_3$); ^1H NMR ($CDCl_3$): $\delta = 7.75$, 7.64 (m, 2 H, Fmoc-Ar-*H*), 7.59, 7.57 (m, 2 H, Fmoc-Ar-*H*), 7.41, 7.39 (m, 2 H, Fmoc-Ar-*H*), 7.36, 7.33 (m, 2 H, Fmoc-Ar-*H*), 7.36, 7.34 (m, 2 H, CH_2-Ar-*H*), 7.32, 7.31, 7.29 (m, 3 H, CH_2-Ar-*H*), 5.98 (m, 1 H, N*H*-Asp), 5.89 (s, 1 H, N*H*-CH), 5.37 (m, 1 H, H-3), 5.34 (m, 1 H, H-4), 5.16 (m, 1 H, $J = 3.1$ Hz H-2), 4.69 (m, 1 H, C*H*-CH_2-Ar), 4.59 (m, 1 H, H-1), 4.44 (m, 1 H, C*H*-Fmoc), 4.27 (m, 3 H, H-6a, O-CH_2-Fmoc), 4.09 (m, 1 H, H-6b), 3.99 (m, 1 H, C*H*-Asp), 3.80 (m, 1 H, H-5), 3.05 (dd, 1 H, CH-CH_2-COO^{t}Bu), 2.68 (dd, 1 H, CH-CH_2-COO^{t}Bu), 2.18 (m, 2 H, S-CH_2), 2.10, 2.08, 2.04, 1.99 (4 s, 12 H, CH_3-Acetyl), 1.43 (s, 9 H, [CH_3]$_3$-C). ^{13}C NMR ($CDCl_3$): $\delta = 195.9$ (NH-*C*O), 170.8 (Asp-*C*O-CH), 170.1, 170.0, 169.9, 169.7 (CH_3-*C*O), 156.0 (NH-*C*OO), 143.9, 141.6, 128.1, 127.5, 125.4, 120.3 (Fmoc-Ar-*C*), 143.6, 141.4, 127.4, 125.2 (CH_2-Ar-*C*), 82.6 (*C*[CH_3]$_3$), 80.8 (C-1), 79.7 (C-5), 77.4 (C-3), 72.6 (C-2), 71.3 (C-4), 68.0 (O-*C*H_2-Fmoc), 62.5 (C-6), 57.8 (*C*H-Asp), 47.4 (*C*H-Fmoc), 47.3 (*C*H-Ar), 37.8 (*C*H_2-Asp), 37.6 (CH-*C*H_2-COO^{t}Bu), 28.4 (C[*C*H_3]$_3$), 21.3, 21.1, 21.0, 20.9 (*C*H_3-Acetyl). [FAB (m/z = 876.9)]: 899.3 $[M + Na]^+$.

N-((L-α-phenylalaninyl)-2,3,4,6-tetra-*O*-acetyl-1-thio-α-D-mannopyranosyl)-Fmoc-Asp(OtBu)-amid (1h)

According to the general procedure, L-(+)-α-phenylalaninol **13** (0.61 g, 4 mmol) and tetra-*O*-acetyl-1-thio-α-D-mannopyranose **4b** (1.89 g, 5.2 mmol) afforded **1 h** (1.35 g, 38%) as a colorless oil. $[\alpha]_D$+0.40° (*c* 1, $CHCl_3$); ^1H NMR ($CDCl_3$): $\delta = 7.70$, 7.57 (m, 2 H, Fmoc-Ar-*H*), 7.56, 7.51 (m, 2 H, Fmoc-Ar-*H*), 7.34, 7.33 (m, 2 H, Fmoc-Ar-*H*), 7.27, 7.25 (m, 2 H, Fmoc-Ar-*H*), 7.18, 7.17 (m, 2 H, CH_2-Ar-*H*), 7.10, 7.08, 7.06 (m, 3 H, CH_2-Ar-*H*), 5.98 (m, 1 H, N*H*-Asp), 5.89 (s, 1 H, N*H*-CH), 5.35 (m, 1 H, H-3), 5.32 (m, 1 H, H-4), 5.17 (m, 1 H, $J = 3.1$ Hz H-2), 4.72 (m, 1 H, C*H*-CH_2-Ar), 4.58 (m, 1 H, H-1), 4.41 (m, 1 H, C*H*-Fmoc), 4.20 (m, 3 H, H-6a, O-CH_2-Fmoc), 4.04 (m, 1 H, H-6b), 3.96 (m, 1 H, C*H*-Asp), 3.79 (m, 1 H, H-5), 3.04 (dd, 1 H, CH-CH_2-COO^{t}Bu), 2.66 (dd, 1 H, CH-CH_2-COO^{t}Bu), 2.18 (m, 2 H, S-CH_2, Ar-CH_2), 2.09, 2.08, 2.07, 2.04 (4 s, 12 H, CH_3-Acetyl), 1.43 (s, 9 H, [CH_3]$_3$-C). ^{13}C NMR ($CDCl_3$): $\delta = 195.9$ (NH-*C*O), 170.8 (Asp-*C*O-CH), 170.1, 170.0, 169.9, 169.7 (CH_3-*C*O), 156.0 (NH-*C*OO), 143.8, 141.4, 127.9, 127.2, 125.1, 120.1 (Fmoc-Ar-*C*), 143.6, 141.4, 127.4, 125.2 (CH_2-Ar-*C*), 82.6 (*C*[CH_3]$_3$), 80.4 (C-1), 79.6 (C-5), 77.4 (C-3), 72.3 (C-2), 71.0 (C-4), 68.0 (O-*C*H_2-Fmoc), 62.4 (C-6), 57.8 (*C*H-Asp), 47.2 (*C*H-Fmoc), 47.1 (*C*H-CH_2-Ar), 37.5 (CH-*C*H_2-Ar), 37.4 (*C*H_2-Asp), 37.3 (CH-*C*H_2-COO^{t}Bu), 28.1 (C[*C*H_3]$_3$), 20.9, 20.8, 20.7, 20.6 (*C*H_3-Acetyl). [FAB (m/z = 890.9)]: 913.3 $[M + Na]^+$.

5-Bromopentyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (6a)

Tetra-*O*-acetyl-1-thio-β-D-glucopyranose **4a** (0.73 g, 2 mmol) was heated to 120°C until the solid had melted and 5-bromo-1-pentene **8** (237 μL, 2 mmol) and AIBN (33 mg, 0.2 mmol) were added under stirring. After 10 min, the reaction was cooled to rt to afford crude **6a** (0.97 g). ^{1}H NMR ($CDCl_3$): δ(ppm) = 5.20 (t, 1 H, J = 9.4 Hz, H-3), 5.04 (m, 2 H, H-4, H-2), 4.46 (d, 1 H, J = 9.8 Hz, H-1), 4.23 (m, 1 H, H-6a), 4.11 (m, 1 H, H-6b), 3.69 (bm, 1 H, H-5), 3.32 (t, 2 H, J = 6.8 Hz, Br-CH_2-Alkyl), 2.63 (m, 2 H, S-CH_2-Alkyl), 2.07, 2.06, 2.01, 1.99 (4 s, 12 H, CH_3-Acetyl), 1.82 (t, 2 H, Br-CH_2-CH_2-Alkyl), 1.61 (bm, 2 H, S-CH_2-CH_2-Alkyl), 1.48 (m, 2 H, CH_2-CH_2-CH_2-CH_2-CH_2). ^{13}C NMR ($CDCl_3$): δ (ppm) = 170.7, 170.3, 169.5, 169.5 (CH_3-*C*O), 83.6 (C-1), 76.0 (C-5), 74.0 (C-3), 69.9 (C-4), 68.4 (C-2), 62.2 (C-6), 33.5 (Br-*C*H_2-CH_2), 33.2 (Br-CH_2-*C*H_2), 29.7 (S-*C*H_2), 29.6 (CH_2- CH_2 -CH_2- CH_2- CH_2), 28.6 (S-CH_2-*C*H_2), 20.9, 20.8, 20.7, 20.6 (*C*H_3-Acetyl). [FAB (m/z = 513.40)]: 536.20 $[M + Na]^+$.

5-Azidopentyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (7a)

A solution of tetrabutyl ammonium hydrogen sulfate (0.64 g, 1.89 mmol) in aqueous saturated $NaHCO_3$ (10 mL) was added to a solution of crude **6a** (0.97 g) in dichloromethane (10 mL). Then, NaN_3 (0.49 g, 7.56 mmol) was added under vigorous stirring. The reaction was stirred for 8 h and diluted with EtOAc (100 mL). The organic layer was separated; washed with aqueous saturated $NaHCO_3$ (2 × 20 mL), H_2O (2 × 20 mL), and aqueous saturated NaCl solution (20 mL); dried (Na_2SO_4); filtered and concentrated under reduced pressure to afford crude **7a** (0.86 g). ^{1}H NMR ($CDCl_3$): δ(ppm) = 5.20 (t, 1 H, J = 9.4 Hz, H-3), 5.04 (m, 2 H, H-4, H-2), 4.46 (d, 1 H, J = 9.8 Hz, H-1), 4.22 (m, 1 H, H-6a), 4.11 (m, 1 H, H-6b), 3.68 (bm, 1 H, H-5), 3.25 (t, 2 H, J = 7.0 Hz, N_3-CH_2-Alkyl), 2.66 (m, 2 H, S-CH_2-Alkyl), 2.06, 2.04, 2.00, 1.99 (4 s, 12 H, CH_3-Acetyl), 1.57 (bm, 4 H, N_3-CH_2-CH_2-Alkyl, S-CH_2-CH_2-Alkyl), 1.46 (m, 2 H, CH_2-CH_2-CH_2-CH_2-CH_2). ^{13}C NMR ($CDCl_3$): δ (ppm) = 170.7, 170.3, 169.5, 169.5 (CH_3-*C*O), 83.6 (C-1), 76.0 (C-5), 74.0 (C-3), 69.8 (C-4), 68.4 (C-2), 62.2 (C-6), 51.3 (N_3-*C*H_2-CH_2), 29.6 (S-*C*H_2), 29.2 (CH_2- CH_2 -CH_2- CH_2- CH_2), 28.5 (S-CH_2-*C*H_2), 25.9 (N_3-CH_2-*C*H_2), 20.9, 20.8, 20.7, 20.6 (*C*H_3-Acetyl). [(Positive FAB-MS) (m/z = 560.4)]: 583.0 $[M + Na]^+$.

5-Aminopentyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (8a)

A solution of crude **7a** (0.86 g) in EtOAc (10 mL) was hydrogenolyzed over a catalytic amount of Pd on charcoal (ca. 10 mg). When TLC indicated the disappearance of all starting material, the mixture was filtered through a layer of

Celite. Concentration of the filtrate under reduced pressure afforded crude **8a** (0.70 g). ^{1}H NMR ($CDCl_3$): δ (ppm) = 5.21 (t, 1 H, J = 9.4 Hz, H-3), 5.04 (m, 2 H, H-4, H-2), 4.47 (d, 1 H, J = 9.8 Hz, H-1), 4.22 (m, 1 H, H-6a), 4.13 (m, 1 H, H-6b), 3.68 (bm, 1 H, H-5), 2.87 (t, 2 H, J = 7.3 Hz, NH_2-CH_2-Alkyl), 2.66 (m, 2 H, S-CH_2-Alkyl), 2.07, 2.05, 2.01, 1.99 (4 s, 12 H, CH_3-Acetyl), 1.63 (bm, 4 H, NH_2-CH_2-CH_2-Alkyl, S-CH_2-CH_2-Alkyl), 1.43 (m, 2 H, CH_2-CH_2-CH_2-CH_2-CH_2). ^{13}C NMR ($CDCl_3$): δ (ppm) = 171.1, 170.6, 170.0, 169.8 (CH_3-*C*O), 84.0 (C-1), 76.3 (C-5), 74.2 (C-3), 70.3 (C-4), 68.7 (C-2), 62.5 (C-6), 58.8 (NH_2-*C*H_2-CH_2), 29.8 (S-*C*H_2), 29.3 (CH_2- CH_2 -CH_2- CH_2- CH_2), 28.1 (S-CH_2-*C*H_2), 25.9 (NH_2-CH_2-*C*H_2), 21.2, 21.1, 21.0, 21.0 (*C*H_3-Acetyl). [(Positive FAB-MS) (m/z = 560.4)]: 583.0 [M + Na] + .

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