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Synthesis of octyl S-glycosides of tri- to pentasaccharide fragments related to the GPI anchor of *Trypanosoma brucei*

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ABSTRACT

The three oligosaccharide octyl-S-glycosides Man-α1,6-Man-α1,4-GlcNH$_2$-α1,*S*-Octyl (**19**), Man-α1,6-(Gal-α1,3)Man-α1,4-GlcNH$_2$-α1,*S*-Octyl (**27**) and Man-α1,2-Man-α1,6-(Gal-α1,3)Man-α1,4-GlcNH$_2$-α1,*S*-Octyl (**37**), related to the GPI anchor of *Trypanosoma brucei* were prepared by a stepwise and block-wise approach from octyl 2-azido-2-deoxy-3,6-di-*O*-benzyl-1-thio-α-D-glucopyranoside (**8**) and octyl 2-*O*-benzoyl-4,6-*O*-(1,1,3,3-tetraisopropyl-1,3-disiloxane-1,3-diyl)-1-thio-α-D-mannopyransoside (**9**). Glucosamine derivative **8** was obtained from 1,3,4,6-tetra-*O*-acetyl-2-azido-2-desoxy-β-D-glucopyranose (**1**) in five steps. Mannoside **9** was converted into the corresponding imidate **12** and coupled with **8** to give disaccharide octyl-S-glycoside **13** which was further mannosylated to afford trisaccharide **19** upon deprotection. Likewise, mannoside **9** was galactosylated, converted into the corresponding imidate and coupled with **8** to give trisaccharide **25**. Mannosylation of the latter afforded tetrasaccharide **27** upon deprotection. Condensation of **25** with disaccharide imidate **35** gave, upon deprotection of the intermediates, the corresponding pentasaccharide octyl-S-glycoside **37**. Saccharides **19**, **27** and **37** are suitable substrates for studying the enzymatic glycosylation pattern of the GPI anchor of *T. brucei*.

1. Introduction

The pathogenic organism of the often deadly sleeping sickness in humans (trypanosomiasis) and in cattle (animal trypanosomiasis or Nagana) is the tsetse fly-transmitted protozoan *Trypanosoma brucei*. This pathogenic parasite belongs to the class *Kinetoplastidae*, suborder *Flagellae*, and lives in the blood stream of its host causing strong sleeping disorders. In advanced stages of the disease the protozoan invade the central nervous system causing severe sleep-like unconsciousness, coma and death. The parasites are usually destroyed efficiently by the immune system of the host. However, some trypanosomes evade the immune system and finally exhaust the host's defense through antigenic variation. This variation is achieved by the protozoan by constantly modifying its antigenic surface structures due to a highly variant surface glycoprotein (VSG) whose presence on the cell surface can well exceed 10^7 copies.[1–3]

Despite the highly variant structure of the VSG of *Trypanosoma*, Ferguson et al.[4] could show that the variable proteins are anchored in the cell membrane of the parasites by a unique invariable glycan-phosphatidyl-inositol (GPI-anchor). GPI anchors are constructed out of a conserved 6-phosphatidyl-Man-α1,2-Man-α1,6-Man-α1,4-GlcNH$_2$-α1,6-myo-inositol-1-phosphate core structure (**ABCDE**, Fig. 1) with modifications at the mannose residues depending on the respective parasite or source of the GPI-anchor. In case of the VSG-GPI anchor of *T. brucei* the side-chains could be identified as the VSG-Protein attached to the ethanolaminophosphate residue and a branched α-glactosyl-residue of variable length (**F**, Fig. 1) attached to the first mannosyl residue of the core.

Formerly, great efforts were taken for the total synthesis of diverse GPI-anchors.[5,6] Examples of partial syntheses of this structure were published too.[7–12] Previously, we have introduced a new efficient synthetic strategy for the chemical synthesis of diverse GPI-anchor fragments of *T. brucei* using a highly flexible silicon based protecting group strategy.[9,12] The 1,1,3,3-tetraisopropyl-1,3-disiloxan-1,3-diyl (TIPS) group was therein applied as a temporary protecting group which lead to a strategy for the preparation of GPI-anchor fragments requiring less protecting group manipulations but offering more synthetic flexibility. Furthermore, we could show that the octyl-O- and S-glycosides of such fragments were suitable substrates for studying in vitro the enzymatic glycosylation patterns of GPI-anchor fragments with trypanosomal membrane fractions, and that octyl-S-glycosides were better substrates for such enzymes.[9] So far we have prepared octyl-O- and S-glycosides related to GPI-anchor fragments **CD** and **CDE**[9] (Fig. 1) and to fragments **CF**, **C(F)D** and **C(F)DE**,[12] respectively. Here we present our results for the similar chemical synthesis of a series of tri- through pentasaccharide octyl-S-glycosides related to the GPI-anchor fragments **BCD**, **BC(F)D** and **BC(F)DE** of *T. brucei* (Fig. 1) which we intend to use as substrates for further studying

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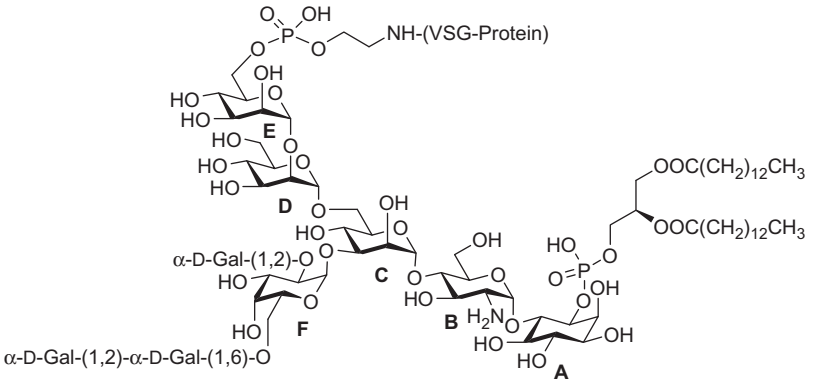


Figure 1. VSG-GPI anchor of *Trypanosoma brucei*.

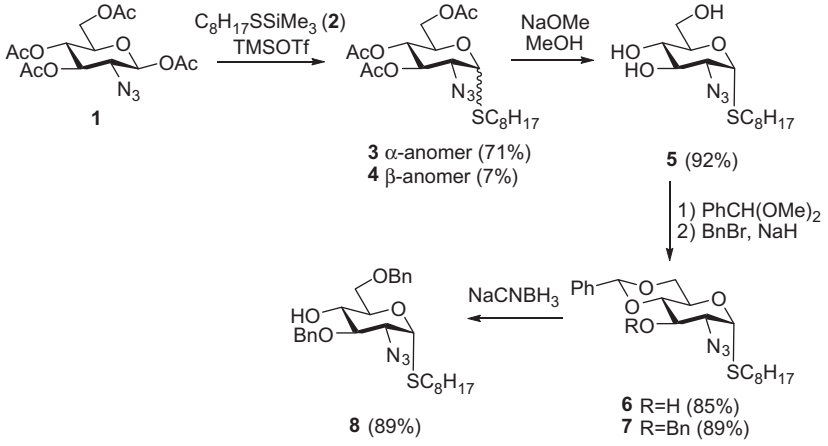
the glycosylation patterns of trypanosomal GPI-anchor fragments. Octyl-S-glycosides were chosen not only because they had been previously shown to be better substrates for that purpose but also because they could be easily converted into glycosyl donors and thus, enabling straightforward strategies for their synthesis.

2. Results and discussion

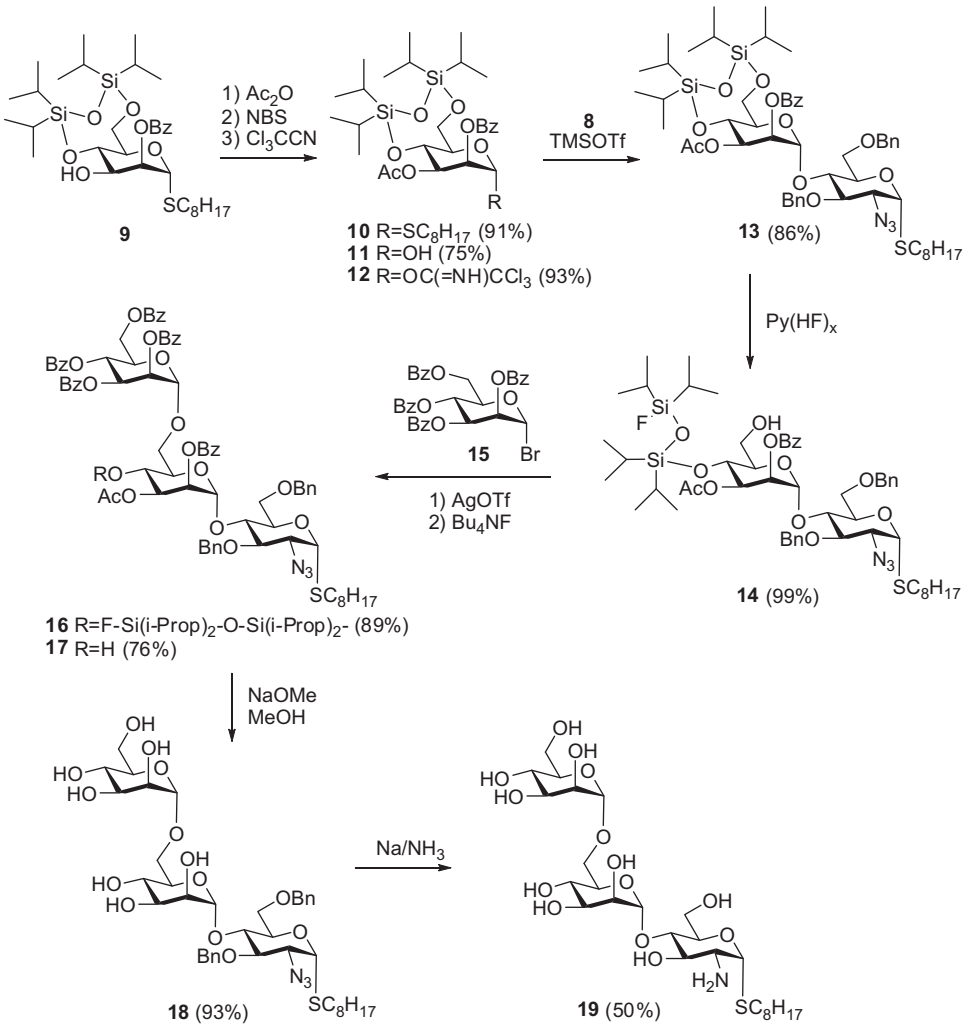
For the synthesis of the trisaccharide octyl-S-glycoside fragment Man-α1,6-Man-α1,4-GlcNH$_2$-αS-octyl (**19**) (**BCD**) we chose a stepwise approach starting from octyl 2-azido-3,6-di-*O*-benzyl-2-deoxy-1-thio-α-D-glucopyranoside (**8**). The latter was prepared in five steps as follows. First, 1,3,4,6-tetra-*O*-acetyl-2-azido-2-deoxy-β-D-glucopyranose (**1**), easily accessible from pentaacetyl mannose in two step using Kovac's carefully optimized procedure,[13,14] was reacted with octylthiotrimethylsilane (**2**) and trimethylsilyl triflate (TMSOTf) according to Glaudemans' procedure[15] to afford the octyl α-D-glucopyranoside **3** in 71% yield. A small amount (7%) of the corresponding β-D-glucopyranoside **4** was also obtained but could be easily separated by a single chromatography. The anomeric configurations of both **3** and **4** were evident from their NMR spectra which showed vicinal coupling constants for H-1 and signals for C-1 at $J_{1,2}$ = 5.5 Hz and 83.3 ppm for **3**, and $J_{1,2}$ = 10.2 Hz and 84.6 ppm for **4**, respectively. Likewise, the α-anomer **3** had a specific rotation of +147.2 while that of the β-anomer **4** was −27.9. Next, compound **3** was Zemplén deacetylated to give intermediate **5** (92%) which afforded the 4,6-*O*-benzylidene protected glucoside **6** (85%) upon treatment with benzaldehyde dimethyl acetal and camphorsulfonic acid. Compound **5** was then benzylated at position 3 with benzyl bromide and sodium hydride to afford **7** in 89%. Finally, the benzylidene group in glycoside **7** was regioselectively reduced with sodium cyanoborohydride using Garegg's[16] and Nilsson's procedure[17] to afford **8** in 89% (Scheme 1).

Previously, we have efficiently used 1,1,3,3-tetraisopropyl-1,3-disiloxane-1,3-diyl- (TIPS) protected glycosyl donors and acceptors for the synthesis of various oligosaccharides applying the flexible glycodesilylation strategy.[9,12,18–22] Therefore, we also chose the TIPS-protected imidate **12** for glycosylation of monosaccharide **8** here. Glycosyl donor **12**, bearing a 4,6-*O*-TIPS group for allowing the extension of the sugar chain at position 6, was prepared from the known TIPS-protected octyl 1-thio-glucoside **9**.[12] The latter was first acetylated to give **10** (91%), followed by selective hydrolysis of the thioether moiety with *N*-bromosuccinimide (NBS) in aqueous acetone[23] to give the mannose derivative **11** (75%), followed by treatment with trichloroacetonitrile and sodium carbonate[24] to afford imidate **12** in 93% yield (Scheme 2).

Coupling of imidate **12** with glucosyl acceptor **8** proceeded smoothly with TMSOTf in diethylether to afford disaccharide **13** in 86% yield. Next, the TIPS-group in **13** was regioselectively opened with pyridine–HF complex[18–20] giving disaccharide acceptor **14** in a virtually quantitative yield. Mannosylation of the latter with benzobromomannose **15** under Koenigs–Knorr conditions gave **16** in 89% yield which was subsequently desilylated with Bu_4NF to afford trisaccharide **17** in 76% yield. The deprotection of saccharide **17** was performed in two steps. First, compound **17** was Zemplén deprotected (NaOMe in MeOH) to give **18** (93%). Difficulties were encountered, however, when **18** was hydrogenated with various types of Pd-catalysts under various conditions (Pd on charcoal, Pearlman's catalyst, Pd-black, EtOH/AcOH/H_2O,



Scheme 1. Preparation of glucosyl acceptor **8**.



Scheme 2. Preparation of trisaccharide fragment **BCD** (**19**).

1000–100,000 hPa). In all cases, hydrogenation was either incomplete or not reproducible, or the formation of side products (namely de-aminated and acetylated side products) was observed. Reduction of the azido group and reductive debenzylation of **18** could finally be achieved under carefully optimized Birch reduction conditions with sodium in THF and liquid ammonia[25] (30 mol-equiv Na, workup with NH_4Cl) giving trisaccharide octyl-S-glycoside **19** in 50% yield. The moderate yield for the deprotection step was due to the fact that three chromatographies on silica gel, Biogel P2 and RP-C18 silica gel were required in order to obtain pure **19** (Scheme 2).

For the preparation of the galactosylated fragment **BC(F)D** we first contemplated to construct a suitable Gal-α1,3-Man building block through intramolecular glycosylation via prearranged glycosides.[26,27] However, previous experiments on the intramolecular glycosylation of the prearranged disaccharide as shown in Figure 2 resulted in a rearrangement of the TIPS group from positions 4 and 6 to positions 3 and 4 in the *manno*-moiety, followed by galactosylation of position 6.[28]

Since additional problems were anticipated for the TIPS-protected octyl 1-thio-mannoside building blocks which we intended to use here, we chose a classical direct α-selective galactosylation of building block **9** (Scheme 3). It has been shown previously that α1,3-galactosylation of 4,6-TIPS-protected glucosides proceeds rather sluggishly giving only medium yield of the corresponding disaccharides.[9,29] Therefore, we have tested the condensation of **9**

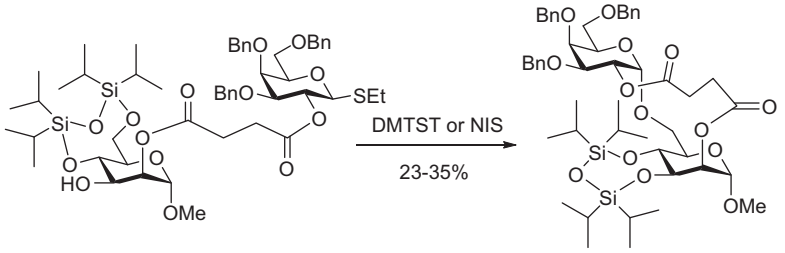
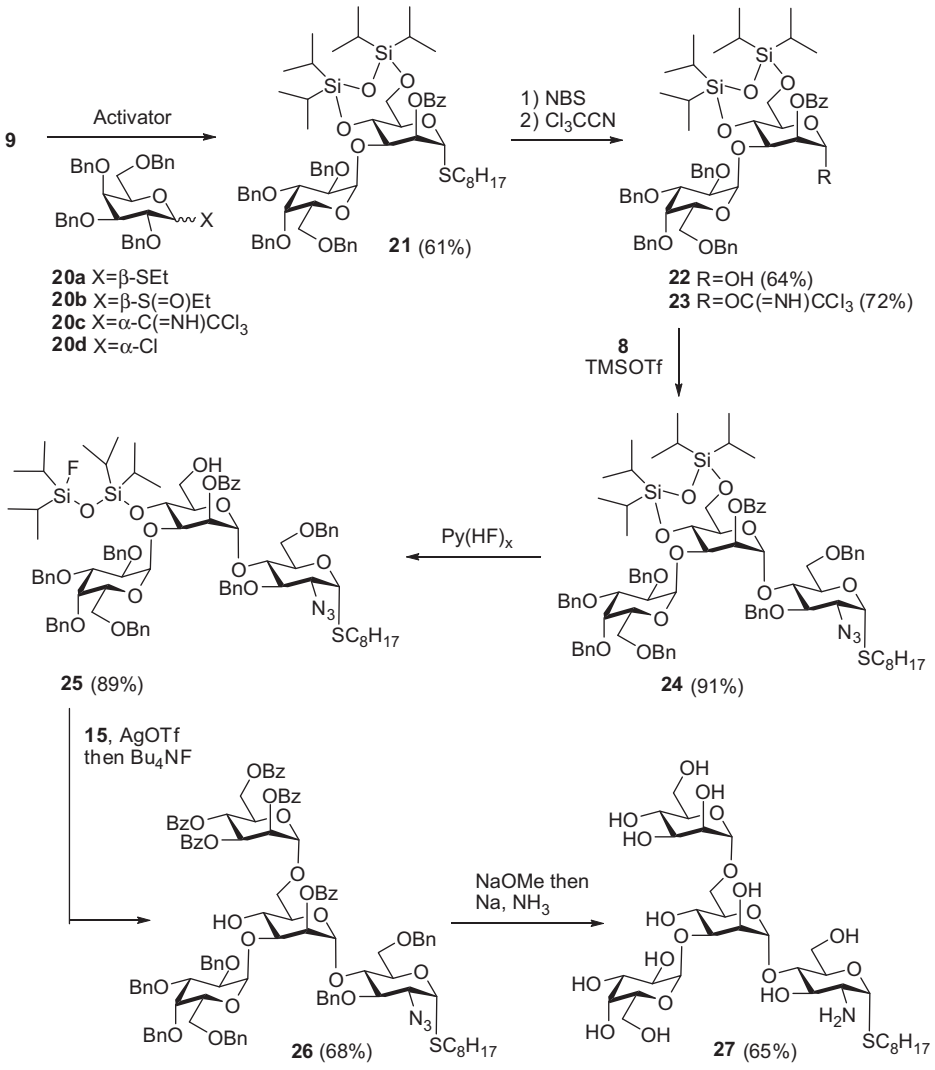


Figure 2. Intramolecular galactosylation of a 4,6-TIPS-protected methyl mannoside according to Ref. 28.



Scheme 3. Preparation of tetrasaccharide fragment **BC(F)D** (**27**).

with various fully benzyl-protected galactosyl donors (ethyl 1-thio-β-D-galactoside **20a**,[30] sulfoxide **20b**, α-trichloroacetimidate **20c**[31] and α-chloride **20d**[32]) and various activation procedures ($AgOTf/Br_2$,[33] MeOTf,[34] NIS/TMSOTf,[35] iodoniumdicollidine perchlorate (IDPC),[36] Tf_2O,[37] TMSOTf, $AgClO_4$[29]). Table 1 summarizes the results for these glycosylation reactions. Coupling with S-glycoside **20a** (Table 1, entries 1–5) either resulted in its decomposition or gave incomplete reaction and only medium yields of the desired disaccharide **21**. Sulfoxide **20b** and imidate **20c** (Table 1, entries 6 and 7) did not afford disaccharide **21** at all. Best results were obtained for the α1,3-selective galactosylation of **9** with chloride **20d** under carefully optimized reaction conditions (Table 1, entries 8 and 9) affording **21** in 61% yield (Scheme 3). The anomeric configuration was evident from the NMR spectrum of **21** which

Table 1
Condensation of **9** and **20a–d** under various conditions (see Scheme 3)

Entry	20a–d	9:20a–d[a]	Solvent	Activator	Condition	21	9[b]
1	**20a**	1:1.3	Toluol	$AgOTf/Br_2$	0 °C→rt, 2 h	46%	13%
2	**20a**	1:1.3	CH_2Cl_2	$AgOTf/Br_2$	0 °C→rt, 2 h	Decomp.	
3	**20a**	1:2.0	Et_2O	MeOTf	rt, 24 h	18%	42%
4	**20a**	1:1.3	CH_2Cl_2	NIS/TMSOTf	rt	Decomp.	
5	**20a**	1:1.3	CH_2Cl_2	IDCP[c]	rt	Decomp.	
6	**20b**	1:1	CH_2Cl_2/Tol	Tf_2O/s-Coll.	−50 °C	Decomp.	
7	**20c**	1:1	CH_2Cl_2/Et_2O	TMSOTf	−30 °C	Decomp.	
8	**20d**	1:1.2	CH_2Cl_2	$AgClO_4$ s-Coll. 2 equiv	0 °C→rt, 2 h	51%	–
9	**20d**	1:1.2	CH_2Cl_2	$AgClO_4$ s-Coll. 11 equiv	−5 °C→rt, 1.5 h	61%	–

[a] Mol-ratio.
[b] Reisolated starting material.
[c] Iodoniumdicollidine perchlorate.

showed a vicinal coupling constant $J_{1,2}$ for H-1 of the galactosyl residue of 3.5 Hz.

Disaccharide **21** was converted into the corresponding trichloroacetimidate donor **23** essentially as described above for monosaccharide donor **12**. S-Glycoside **21** was hydrolyzed with NBS to give **22** (64%) followed by treatment with trichloroacetonitrile to afford **23** in 72% yield (Scheme 3). Next, the latter was condensed with acceptor **8** to give the corresponding trisaccharide **24** in excellent 91% yield. Regioselective fluorodesilylation of the TIPS-group with pyridine–HF gave 6′-OH trisaccharide **25** (89%) which was mannosylated with benzobromomannose **15** under Koenigs–Knorr conditions and desilylated to afford tetrasaccharide **26** (68%) in two steps. Finally, sequential deprotection of the latter (Zemplén deacylation followed by reduction of the benzyl and azido groups with Na in liquid ammonia) gave the free tetrasaccharide **27** in 65% yield.

In an alternative approach to tetrasaccharide **26** we prepared a trisaccharide donor as follows. Instead of using disaccharide **21** as the donor (see Scheme 3), we now converted it into a suitable acceptor by once again regioselectively hydrolyzing the 4,6-*O*-TIPS group in **21** with the pyridine–HF complex (Scheme 4). Thus obtained disaccharide acceptor **28** (95%) was mannosylated with benzobromomannose to give trisaccharide **29** in 73% yield. Since some characteristic signals in the NMR spectra of **29** were overlapped and thus, could not get unambiguously assigned, **29** was desilylated to **30** (89%) the NMR spectra of which now could be fully interpreted. Next, **29** was converted in 95% yield into the corresponding trisaccharide imidate donor **31** by sequential hydrolysis of the aglycon with NBS followed by treatment with trichloroacetonitrile. Glycosylation of **8** with the latter proceeded somewhat sluggishly though. Tetrasaccharide **26** was only obtained in medium 44% yield. Nevertheless, both strategies as outlined in Schemes 3 and 4 are likewise suitable for the preparation of the GPI-anchor fragment **BC(F)D**.

Previously we had shown that TIPS-protected glycosides can get regioselectively glycosylated with glycosyl fluorides under catalysis of BF_3 (glycodesilylation).[19–22] Therefore, we also tested whether disaccharide **21** can be regioselectively mannosylated with benzofluoromannose **32** at position 6. Fluoride **32** was prepared in 81% from benzobromomannose **15** and KHF_2 pursuant to Thiem's procedure.[38] However, when **21** was reacted with **32** and BF_3-etherate in dichloromethane, only the galactosylated 1,6-anhydro-mannose **33** and octyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-α-D-mannopyranoside (**34**) could be isolated in 50% and 64% yield, respectively. Obviously, the intermediate mannosyl cation attacked the anomeric sulfur in **21** to give intermediates **A** and **B** (Scheme 5) which subsequently led to the products **33** and **34**. Similar intermolecular aglycon transfers had been observed upon glycosylations of thioglycosides with glycosyl imidates and halogenoses.[39–42]

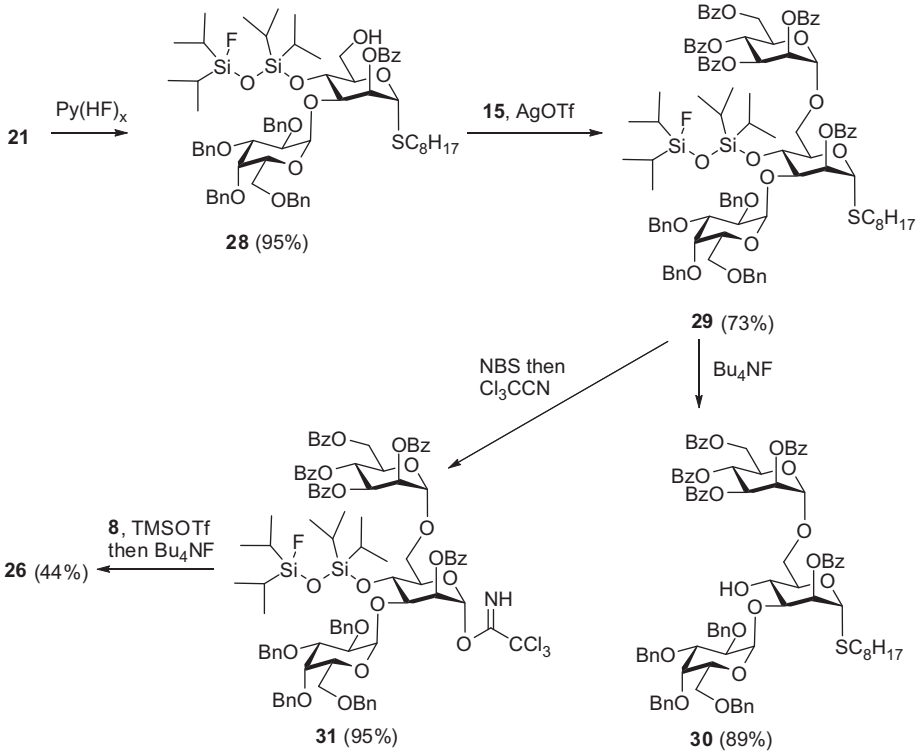
Trisaccharide **25** was also used for the preparation of the octyl S-glycoside pentasaccharide fragment related to GPI-anchor **BC(F)DE** as follows. Condensation of **25** with disaccharide imidate **35**[12] followed by fluoride-catalyzed desilylation of the intermediate afforded the pentasaccharide **36** in 86% overall yield (Scheme 6). Sequential Zemplén deprotection and Birch reduction of the latter then gave **37** in 53% yield over two steps.

In summary, we have efficiently prepared three octyl-S-glycoside tri-, tetra- and pentasaccharide fragments (**19**, **27**, **37**) related to the GPI-anchor of trypanosoma brucei using TIPS-protected glycosylacceptors. The three octyl-S-glycosides will be used as substrates for trypanosomal glycosidases and glycosyl transferases in order to further study the glycosylation pattern of trypanosoma brucei as previously described for similar GPI-anchor related octyl-S-glycosides.[9]

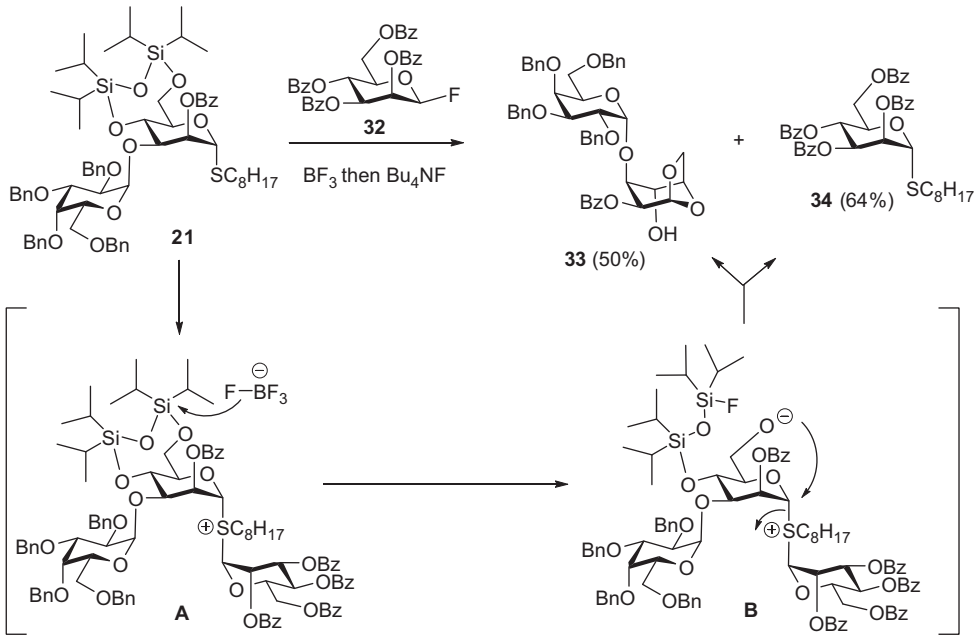
3. Experimental

3.1. General methods

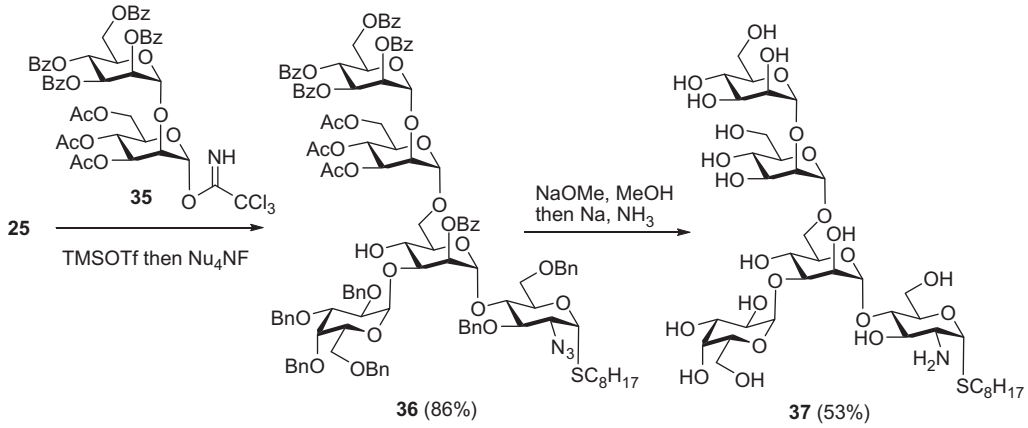
^1H and ^{13}C NMR spectra were recorded with Bruker ARX 250, Avance 400 or AMX 600 spectrometers at 250, 400 or 600 MHz



Scheme 4. Alternative preparation of tetrasaccharide fragment **BC(F)D**.



Scheme 5. Glycosylation of disaacharide acceptor **21** with mannosyl donor **32**.



Scheme 6. Preparation of pentasaccharide fragment **BC(F)DE** (**37**).

for protons and 62.9, 100 or 151 MHz for carbons, respectively. Chemical shifts in $CDCl_3$ are reported in δ (ppm) relative to tetramethylsilane (TMS) as internal standard. Coupling constants J are reported in Hertz. Assignment of signals was made by first order inspection of the spectra and, if necessary, by $^1H^1H$-, $^{13}C^1H$-COSY, HMQC or NOESY experiments, respectively. MS spectra were recorded with Finnigan MAT TSQ 70 (EI, CI), Finnigan MAT 711 A (HRMS), Bruker Autoflex (MALDI-TOF-MS) and Bruker Apex II FT-ICR (FAB-MS, HRMS) instruments. Specific optical rotations [α] were recoded with a Perkin Elmer polarimeter Model 341 at 589 nm (Na-D) for solutions in $CHCl_3$ at 20 °C if not stated otherwise. Elemental analyses were performed with a Hekatech CHNS analysator Euro EA 3000. Melting points were determined on a Büchi B-540 instrument. TLC was performed on Macherey & Nagel silica gel SIL G/UV254 plates. Spots were detected by visual inspection of the plates under UV light, by charring with H_2SO_4 (5% in EtOH), with $KMnO_4$ (5% in water) and with I_2, respectively. Preparative column chromatography was performed by eluting compounds with various mixtures of solvents from glass columns of various sizes filled with Macherey & Nagel silica gel S (0.032–0.063 mm). Solutions in organic solvents were dried with Na_2SO_4, filtered and concentrated with a rotary evaporator. HPLC was performed on a Sykam system using a Grom Saphir Si; 5 μm; 250 × 6 mm column.

3.2. Octylthiotrimethylsilane (2)

A solution of thiooctanol (70 mL, 403 mmol) in *n*-hexane (100 mL) was dropped at rt with vigorous stirring into a slurry of Na pieces (9.34 g, 406 mmol) in *n*-hexane (100 mL), the mixture was refluxed for 2 h and cooled to rt. A solution of trimethylchlorosilane (51 mL, 403 mmol) in *n*-hexane (80 mL) was added dropwise with stirring, the mixture refluxed for another 2 h and set aside at rt without stirring for 24 h. Filtration of the mixture, concentration of the filtrate and distillation of the residue gave **2** as a colorless liquid (58.46 g, 67%). Bp 147 °C (50 hPa). ^1H NMR ($CDCl_3$): δ 2.48 (t, 2H, J = 7.2 Hz, SCH_2), 1.64–2.55 (m, 2H, CH_2), 1.40–1.27 (m, 10H, CH_2), 0.88 (t, 3H, J = 6.2 Hz, CH_3), 0.31 (br t, 9H, J = 3.3 Hz, $Si(CH_3)_3$). ^{13}C NMR ($CDCl_3$): δ 33.1, 31.8, 29.2, 29.1, 28.8, 26.4, 22.6 (CH_2), 14.1 (CH_3), 0.9 (3C, $Si(CH_3)_3$). Anal. Calcd for $C_{11}H_{26}SSi$ (218.48): C, 60.48; H, 11.99; S, 14.67. Found: C, 60.32; H, 11.94; S, 14.86.

3.3. Octyl 2-azido-3,4,6-tri-*O*-acetyl-2-deoxy-1-thio-α-D-glucopyranoside (3) and octyl 2-azido-3,4,6-tri-*O*-acetyl 2-deoxy-1-thio–D-glucopyranoside (4)

A solution of 2-azido-2-deoxy-1,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (**1**)[13] (1.0 g, 2.67 mmol), compound **2** (1.9 mL, 6.95 mmol) and a catalytic amount of TMSOTf (100 μL, 0.5 mmol) in dichloroethane (40 mL) was stirred at 70 °C for 14 d. After the mixture was cooled to rt, it was diluted with dichloromethane (40 mL), washed with saturated aq $NaHCO_3$ solution, dried, filtered and concentrated. Chromatography of the residue with 5:1 *n*-hexane/ethyl acetate gave first **3** (0.87 g, 71%) as colorless oil. $[\alpha]_D$ +147.2 (*c* 1.5, $CHCl_3$), IR λ (cm^{-1}) 2108.73 (N_3). ^1H NMR ($CDCl_3$): δ 5.42 (d, 1H, $J_{1,2}$ = 5.5 Hz, H-1), 5.29 (dd, 1H, $J_{2,3}$ = 10.5 Hz, $J_{3,4}$ = 9.2 Hz, H-3), 5.01 (dd, 1H, $J_{4,5}$ = 10.1 Hz, H-4), 4.45 (ddd, 1H, $J_{5,6a}$ = 4.4 Hz, $J_{5,6b}$ = 2.0 Hz, H-5), 4.29 (dd, 1H, $J_{6a,6b}$ = −12.3 Hz, H-6a), 4.06 (dd, 1H, H-6b), 3.98 (dd, 1H, H-2), 2.67–2.51 (m, 2H, SCH_2), 2.08 (s, 3H, CH_3), 2.07 (s, 3H, CH_3), 2.04 (s, 3H, CH_3).1.73–1.59 (m, 2H, CH_2), 1.41–1.27 (m, 10H, CH_2), 0.88 (br t, 1H, *J* = 6.7 Hz, CH_3). ^{13}C NMR ($CDCl_3$): δ 170.5, 169.8 (2C, C=O), 83.3 (C-1), 72.1 (C-3), 68.7 (C-4), 67.9 (C-5), 91.9 (C-6), 61.6 (C-2), 31.8, 30.7, 29.4, 29.1 (2C), 28.9, 22.6 (CH_2), 20.6, 20.7 (2C), 14.1 (CH_3). Anal. Calcd for $C_{20}H_{33}N_3O_4S$ (459.56): C, 52.27; H, 7.24; N, 9.14; S, 6.98. Found: C, 52.24; H, 7.29; N, 9.13; S, 7.44.

Eluted next was **4** (90 mg, 7%) as a colorless oil. $[\alpha]_D$ −27.9 (*c* 1.2, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 5.07 (t, 1H, $J_{2,3}$ = $J_{3,4}$ = 9.4 Hz, H-3), 5.01 (t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H-4), 4.37 (d, 1H, $J_{1,2}$ = 10.2 Hz, H-1), 4.25 (dd, 1H, $J_{5,6a}$ = 5.2 Hz, $J_{6a,6b}$ = −12.3 Hz, H-6a), 4.11 (dd, 1H, $J_{5,6b}$ = 2.4 Hz, H-6b), 3.67 (ddd, 1H, H-5), 3.52 (t, 1H, H-2), 2.78–2.68 (m, 2H, SCH_2), 2.10 (s, 3H, CH_3), 2.07 (s, 3H, CH_3), 2.02 (s, 3H, CH_3), 1.71–1.60 (m, 2H, CH_2), 1.42–1.27 (m, 10H, CH_2), 0.90–0.86 (m, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ = 170.5, 169.9, 169.5 (C=O), 84.6 (C-1), 75.7 (C-5), 74.4 (C-3), 68.2 (C-4), 63.6 (C-2), 62.1 (C-6), 31.7, 30.8, 29.7, 29.1, 29.0, 28.7, 22.6 (CH_2), 20.6 (2C), 20.5, 14.0 (CH_3). Anal. Calcd for $C_{20}H_{33}N_3O_7S$ (459.56): C, 52.27; H, 7.24; N, 9.14; S, 6.98. Found: C, 52.35; H, 7.23; N, 9.04; S, 7.24.

3.4. Octyl 2-azido-2-deoxy-1-thio-α-D-glucopyranoside (5)

A 1 M solution of NaOMe in MeOH (ca. 0.1 mL) was added at rt to a solution of **4** (18.5 g, 41.7 mmol) in MeOH (100 mL) and the resulting solution was stirred for 24 h. Neutralization of the solution with ion exchange resin (Dowex 50XW8, H^+ form), filtration and concentration of the filtrate gave a white crystalline solid which was recrystallized from diethylether/*n*-hexane to afford **5** (11.33 g, 82%). Mp 89–90 °C. $[\alpha]_D$ +208.9 (*c* 1.1, MeOH). ^1H NMR (MeOD-d_3): δ 5.36 (d, 1H, $J_{1,2}$ = 4.6 Hz, H-1), 3.96–3.91 (m, 1H), 3.81–3.58 (m, 4H), 3.41–3.31 (m, 1H), 2.67–2.51 (m, 2H, SCH_2), 1.67–1.53 (m, 2H, CH_2), 1.40–1.29 (m, 10H, CH_2), 0.90–0.87 (m, 3H, CH_3). ^{13}C NMR (MeOD-d_3): δ 84.9 (C-1), 74.4 (C-3), 74.1 (C-4), 71.9 (C-5), 71.7 (C-2), 62.3 (C-6), 32.9, 31.3, 30.5, 30.3, 30.2, 29.9, 23.7 (CH_2), 14.4 (CH_3). Anal. Calcd for $C_{14}H_{27}N_3O_4S$ (333.45): C, 50.43; H, 8.16; N, 12.60; S, 9.62. Found: C, 50.52; H, 8.08; N, 12.48; S, 9.62.

3.5. Octyl 2-azido-4,6-*O*-benzylidene-2-deoxy-1-thio-α-D-glucopyranoside (6)

A solution of compound **5** (2.5 g, 7.5 mmol), benzaldehyde dimethylacetal (4.2 mL, 28.0 mmol) and a catalytic amount of camphorsulfonic acid (ca. 10 mg) in MeCN (40 mL) was stirred at rt for 3 h, neutralized by the addition of Et_3N (1 mL) and concentrated. Trituation of the oily reside with *n*-hexane (50 mL) gave white crystals which were filtered off, washed with a small amount of cold *n*-hexane and dried. Recrystallization with *n*-hexane gave **6** (2.68 g, 85%). Mp 95 °C. $[\alpha]_D$ +164.4 (*c* 1.1, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 7.52–7.10 (m, 5H, PhH), 5.52 (s, 1H, PhCH), 5.32 (d, 1H, $J_{1,2}$ = 5.6 Hz, H-1), 4.28–4.19 (m, 2H), 3.96 (t, 1H, *J* = 9.6 Hz), 3.80 (dd, 1H, $J_{2,3}$ = 10.0 Hz, H-2), 3.74 (t, 1H, *J* = 11.6 Hz), 3.49 (t, 1H, *J* = 9.0 Hz), 3.03 (s, 1H, OH), 2.65–2.49 (m, 2H, SCH_2), 1.67–1.57 (m, 2H, CH_2), 1.49–1.27 (m, 10H, CH_2), 0.90–0.86 (br t, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 136.7, 129.4, 128.6, 125.7 (PhC), 102.1 (PhCH), 84.3 (C-1), 81.8 (C-4), 70.5 (C-3), 68.6 (C-6), 63.7 (C-5), 62.8 (C-2), 31.7, 30.9, 29.5, 29.1 (2C), 28.8, 22.6 (CH_2), 14.0 (CH_3). Anal. Calcd for $C_{21}H_{31}N_3O_7S$ (421.56): C, 59.83; H, 7.41; N, 9.97; S, 7.61. Found: C, 59.57, H, 7.44; N, 9.90; S, 7.76.

3.6. Octyl 2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-1-thio-α-D-glucopyranoside (7)

NaH (1.15 g, 48 mmol) was added in small portions at 0 °C to a solution of compound **6** (10.14 g, 24.1 mmol) and benzyl bromide (4.5 mL, 38 mmol) in DMF (100 mL) and stirred at rt for 1 h. Water was carefully added dropwise to destroy the excess of NaH and the resulting solution was poured into an ice/water mixture. The solid material which separated was filtered off, washed with water and dissolved in dichloromethane (100 mL). The organic solution was washed with cold 1 M aq HCl solution, dried, filtered and concentrated. Crystallization of the residue from *n*-hexane gave **7** (10.95 g, 89%) as white crystals. Mp 69 °C. $[\alpha]_D$ +63.5 (*c* 1.3, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 7.51–7.24 (m, 10H, PhH), 5.58 (s, 1H, PhCH), 5.33 (d, 1H, $J_{1,2}$ = 5.0 Hz, H-1), 4.93 (d, 1H, *J* = −10.9 Hz, $PhCH_2$), 4.78 (d, 1H, *J* = −10.9 Hz, $PhCH_2$), 4.95–4.23 (m, 2H), 3.95–3.67 (m, 4H), 2.66–2.50 (m, 2H, SCH_2), 1.67–1.57 (m, 2H, CH_2), 1.41–1.27 (m, 10H, CH_2), 0.88 (br t, 1H, *J* = 6.7 Hz, CH_3). ^{13}C NMR ($CDCl_3$): δ 137.7, 137.1, 129.0, 128.4, 128.2, 128.1, 127.9, 126.0 (PhC), 101.4 (PhCH), 84.5 (C-1), 82.8 (C-4), 77.8 (C-3), 75.1 ($PhCH_2$), 68.7 (C-6), 63.4 (C-5), 63.2 (C-2). Anal. Calcd for $C_{28}H_{37}N_3O_4S$ (511.683): C, 65.73; H, 7.29; N, 8.21; S, 6.27. Found: C, 66.04; H, 7.31; N, 8.21; S, 6.32.

3.7. Octyl 2-azido-3,6-di-*O*-benzyl-2-deoxy-1-thio-α-D-glucopyranoside (8)

A dry solution of HCl in diethylether was added dropwise with stirring at rt to a solution of **7** (5.73 g, 11.2 mmol) and $NaCNBH_3$ (4.23 g, 67.4 mmol) in THF (150 mL) until the solution became acidic toward litmus. Stirring was continued for 10 min, the resulting suspension diluted with dichloromethane (ca. 100 mL) and filtered through a layer of Celite. The filtrate was successively washed with satd aq $NaHCO_3$ solution, 1 M aq $FeCl_2$ solution and water, dried and concentrated. Chromatography of the residue with 25:1 toluene/ethyl acetate gave 8 (5.1 g, 89%) as a colorless oil. $[\alpha]_D$ +91.3 (*c* 1.1, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 7.41–7.24 (m, 10H, PhH), 5.33 (d, 1H, $J_{1,2}$ = 5.5 Hz, H-1), 4.89 (d, 1H, *J* = −11.1 Hz, $PhCH_2$), 4.78 (d, 1H, *J* = −11.1 Hz, $PhCH_2$), 4.59 (d, 1H, *J* = 12.1 Hz, $PhCH_2$), 4.51 (d, 1H, *J* = 12.0 Hz, $PhCH_2$), 4.16–4.12 (m, 1H, H-5), 3.81 (dd, 1H, $J_{2,3}$ = 9.8 Hz, H-2), 3.76–3.59 (m, 4H, H-3, H-4, H-6a,b), 2.63–2.51 (m, 2H, SCH_2), 2.35–2.14 (m, 2H, CH_2), 1.63–1.62 (m, 10H, CH_2), 0.90–0.86 (m, 3H, CH_3). ^{13}C NMR ($CHCl_3$): δ 137.9, 137.7, 128.6, 128.4, 128.1, 128.0, 127.7, 127.6 (PhC), 83.6 (C-1), 81.3 (C-3), 75.3 ($PhCH_2$), 73.6 ($PhCH_2$), 72.1 (C-4), 70.4 (C-5), 69.6 (C-6), 62.4 (C-2), 31.7, 30.6, 29.5, 29.1, 28.8, 22.6 (CH_2), 14.0 (CH_3). Anal. Calcd for $C_{28}H_{39}N_3O_4S$ (513.70): C, 65.47; H, 7.65; N, 8.18; S, 6.24. Found: C, 65.46; H, 7.57; N, 7.98; S, 6.06.

3.8. Octyl 3-*O*-acetyl-2-*O*-benzoyl-4,6-*O*-(1,1,3,3-tetraisopropyl-1,3-disiloxane-1,3-diyl)-1-thio-α-D-mannopyranoside (10)

Ac_2O (3 mL) was added at 0 °C to a solution of compound **9**[12] (0.82 g, 1.25 mmol) and a catalytic amount of DMAP (10 mg) in

pyridine (6 mL), and the mixture was stirred at rt for 16 h. The mixture was poured into ice-cold diluted aqueous HCl solution (ca. 300 mL) and extracted with dichloromethane (3 × 50 mL). The combined extracts were successively washed with diluted aqueous HCl solution, saturated $NaHCO_3$ solution, dried, filtered and concentrated. Chromatography of the residue with toluene gave 10 (0.79 g, 91%) as a colorless oil. $[\alpha]_D$ +16.9 (*c* 0.9, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 8.08–7.15 (m, 5H, PhH), 5.63 (dd, 1H, $J_{1,2}$ = 1.2 Hz, $J_{2,3}$ = 3.3 Hz, H-2), 5.40 (d, 1H, H-1), 5.28 (dd, 1H, $J_{3,4}$ = 9.9 Hz, H-3), 4.49 (t, 1H, *J* = 9.4 Hz, H-4), 4.24 (dd, 1H, $J_{5,6a}$ = 2.0 Hz, $J_{6a,6b}$ = 12.6 Hz, H-6a), 4.11 (br d, 1H, *J* = 9.4 Hz, H-5), 3.92 (dd, 1H, $J_{5,6b}$ = 0.5 Hz, H-6b), 2.60 (dddd, 2H, *J* = 29.7 Hz, *J* = 12.9 Hz, *J* = 7.3 Hz, *J* = 7.3 Hz, S-CH_2), 1.98 (s, 3H, Acetyl-CH_3), 1.64–0.83 (m, 42H, CH, CH_2, CH_3). ^{13}C NMR ($CDCl_3$): δ 170.0, 165.5 (C=O), 133.3, 129.9, 129.0, 128.3, 128.2, 125.3 (PhC), 83.1 (C-1), 73.7 (C-5), 72.4 (C-3), 72.3 (C-2), 64.8 (C-4), 61.0 (C-6), 31.8, 31.3, 29.5, 29.1 (2C), 28.8, 22.6 (CH_2), 21.0, 17.4, 17.2 (5C), 14.0, 13.5, 13.2, 12.5, 12.4 (CH, CH_3). Anal. Calcd for $C_{35}H_{60}O_8SSi_2$ (697.08): C, 60.30; H, 8.68. Found: C, 60.18; H, 8.46.

3.9. 3-*O*-Acetyl-2-*O*-benzoyl-4,6-*O*-(1,1,3,3-tetraisopropyl-1,3-disiloxane-1,3-diyl)-α-D-mannopyranose (11)

NBS (0.74 g, 4.13 mmol) was added at 0 °C with stirring to a solution of compound. **10** (1.77 g, 2.54 mmol) in a mixture of acetone (40 mL) and water (0.4 mL) and the mixture was stirred for 10 min. Saturated aqueous $NaHCO_3$ solution (1 mL) was added, the mixture was poured into diluted aqueous $NaHCO_3$ solution (100 mL) and extracted with dichloromethane (3 × 25 mL). The combined organic extracts were washed with water, dried, filtered and concentrated. Chromatography of the residue with 10/1 toluene–ethyl acetate gave **11** (1.09 g, 76%) as a colorless oil. $[\alpha]_D$ −65.4 (*c* 1.3, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 8.12–7.26 (m, 5H, PhH), 5.57 (dd, 1H, $J_{1,2}$ = 1.6 Hz, $J_{2,3}$ = 3.2 Hz, H-2), 5.41 (dd, 1H, $J_{3,4}$ = 10.0 Hz, H-3), 5.37 (dd, 1H, $J_{1,OH}$ = 3.3 Hz, H-1), 4.46 (t, 1H, *J* = 9.8 Hz, H-4), 4.21 (dd, 1H, $J_{5,6a}$ = 1.9 Hz, $J_{6a,6b}$ = 12.6 Hz, H-6a), 3.99 (br d, 1H, *J* = 9.4 Hz, H-5), 3.92 (dd, 1H, $J_{5,6b}$ = 0.9 Hz, H-6b), 3.30 (d, 1H, OH), 2.00 (s, 3H, Acetyl-CH_3), 1.15–0.97 (m, 28H, CH, CH_3). ^{13}C NMR ($CDCl_3$): δ 170.3, 165.7 (C=O), 133.3, 129.4, 128.9, 128.3 (PhC), 92.9 (C-1), 73.2 (C-5), 71.8 (C-3), 70.9 (C-2), 64.5 (C-4), 61.0 (C-6), 21.0 (CH_3), 17.4, 17.3, 17.2 (2C), 17.1 (2C),13.5, 13.2, 12.5, 12.4 (CH, CH_3). Anal. Calcd for $C_{27}H_{44}O_9Si_2$ (568.80): C, 57.01; H, 7.80. Found: C, 56.82; H, 7.79.

3.10. 3-*O*-Acetyl-2-*O*-benzoyl-4,6-*O*-(1,1,3,3-tetraisopropyl-1,3-disiloxane-1,3-diyl)-α-D-mannopyranosyl trichloroacetimidate (12)

A mixture of compound **11** (1.09 g, 1.92 mmol), K_2CO_3 (2.06 g 14.9 mmol) and trichloroacetonitrile (2.1 mL, 20.9 mmol) in dichloromethane (50 mL) was stirred at rt for 16 h, centrifugated, and the centrifugate was concentrated. Chromatography of the residue with 30/1 toluene–ethyl acetate gave **12** (1.28 g, 93%) as a yellowish oil. $[\alpha]_D$ −18.3 (*c* 0.9, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 8.70 (s,1H, NH), 8.08–7.39 (m, 5H, PhH), 6.37 (d, 1H, $J_{1,2}$ = 1.7 Hz, H-1), 5.72 (dd, 1H, $J_{2,3}$ = 3.4 Hz, H-2), 5.52 (t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.8 Hz, H-4), 5.39 (dd, 1H, H-3), 4.18 (dd, 1H, $J_{5,6a}$ = 2.1Hz, $J_{6a,6b}$ = −12.7 Hz, H-6a), 3.97 (dd, 1H, $J_{5,6b}$ = 1.1Hz, H-6b), 3.88 (br d, *J* = 9.5 Hz, H-5),1.98 (s, 3H, Acetyl-CH_3), 1.14–0.96 (m, 28H, CH, CH_3). ^{13}C NMR ($CDCl_3$): δ 170.2 (C=NH), 165.4, 160.1 (C=O), 133.6, 130.1, 129.2, 128.5 (PhC), 95.8 (C-1), 90.6 (CCl_3), 76.3 (C-5), 71.8 (C-3), 68.9 (C-2), 64.1 (C-4), 60.7 (C-6), 21.1 (CH_3), 17.6, 17.4 (2C), 17.3 (2C), 17.2, 13.6, 13.3, 12.6 (2C, CH, CH_3). Anal. Calcd for $C_{29}H_{44}Cl_3O_9Si_2$ (713.19): C, 48.84; H, 6.22; N, 1.96. Found: C, 48.86; H, 6.16; N, 1.91.

3.11. Octyl 3-*O*-acetyl-2-*O*-benzoyl-4,6-*O*-(1,1,3,3-tetraisopropyl-1,3-disiloxane-1,3-diyl)-α-D-mannopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-1-thio-α-D-glucopyranoside (13)

TMSOTf (55 μL, 0.3 mmol) was added under Ar at −15 °C to a suspension solution of compound **12** (1.28 g, 1.79 mmol), compound **8** (0.78 g, 1.52 mmol) and 4 Å molecular sieves (5.0 g) in diethylether (100 mL). The mixture was warmed to 0 °C within 1.5 h, $NaHCO_3$ (ca. 1 g) was added, and the mixture was filtered through a layer of celite. The filtrate was washed with aqueous $NaHCO_3$ solution, dried, filtered and concentrated. Chromatography of the residue with 25/1 toluene–ethyl acetate gave **13** (1.39 g, 86%) as a colorless oil. $[\alpha]_D$ +28.2 (*c* 0.5, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 7.94–6.92 (m, 15H, PhH), 5.57 (dd, 1H, $J_{1',2'}$ = 1.5 Hz, $J_{2',3'}$ = 3.2 Hz, H-2'), 5.49 (br s, 1H, H-1′), 5.41 (d, 1H, $J_{1,2}$ = 4.9 Hz, H-1), 5.26 (dd, 1H, $J_{3',4'}$ = 9.9 Hz, H-3′), 4.90 (d, 1H, *J* = −10.5 Hz, $PhCH_2$), 4.70 (d, 1H, *J* = −10.9 Hz, $PhCH_2$), 4.56 (br s, 2H, $PhCH_2$), 4.33 (t, 1H, $J_{3',4'}$ = $J_{4',5'}$ = 9.8 Hz, H-4′), 4.30–4.24 (m, 1H, H-5), 3.93 (t, 1H, $J_{3,4}$ = $J_{4,5}$ = 8.3 Hz, H-4), 3.88–3.57 (m, 7H, H-2, H-3, H-5′, H-6a,b, H-6′a,b), 2.67–2.55 (m, 2H, SCH_2), 1.97 (s, 3H, Acetyl-CH_3), 1.68–1.57 (m, 2H, CH_2), 1.38–1.27 (m, 12H, CH_2), 1.06–0.81 (m, 29H, CH, CH_3). ^{13}C NMR ($CDCl_3$): δ 170.3, 165.2 (C=O), 138.0, 137.1, 133.2, 129.9, 129.0, 128.3, 128.2, 128.1, 127.6, 127.4, 127.1 (PhC), 99.1 (C-1′), 83.5 (C-1), 82.0 (C-3), 75.2 ($PhCH_2$), 74.6 (C-4), 74.1 (C-5′), 73.4 ($PhCH_2$), 71.9 (C-3′), 70.5 (C-2′), 70.4 (C-5), 68.9 (C-6), 64.5 (C-2), 64.2 (C-4′), 60.6 (C-6′), 31.8, 30.6, 29.6, 29.1, 28.9, 22.6 (CH_2), 21.0 (Acetyl-CH_3), 17.4, 17.3, 17.2, 17.1, 17.0, 14.1, 13.4, 13.1, 12.5, 12.3 (CH, CH_3). Anal. Calcd for $C_{55}H_{81}N_3O_{12}SSi_2$ (1064.48): C, 62.02; H, 1.67; N, 3.95; S, 3.01. Found: C, 62.27; H, 7.75; N, 3.61; S, 3.07.

3.12. Octyl 3-*O*-acetyl-2-*O*-benzoyl-4-*O*-(1-fluoro-1,1,3,3-tetraisopropyl-1,3-disiloxane-3-yl)-α-D-mannopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-1-thio-α-D-glucopyranoside (14)

Pyridine hydrofluoride (70%, 127 μL, 4.45 mmol) was added at rt to a stirred solution of compound **13** (0.68 g, 0.65 mmol) in dichloromethane (20 mL) and stirring continued for 5 min. The mixture was poured into diluted aqueous $NaHCO_3$ solution (ca. 150 mL) and extracted with dichloromethane (3 × 25 mL). The combined organic extracts were dried, filtered and concentrated. Chromatography of the residue with 20/1 toluene–ethyl acetate gave **14** (0.69 g, 99%) as a colorless oil. $[\alpha]_D$ +47.7 (*c* 0.9, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 7.95–7.02 (m, 15H, PhH), 5.62 (dd, $J_{1',2'}$ = 2.0 Hz, $J_{2',3'}$ = 3.0 Hz, H-2′), 5.42 (d, 1H, H-1′), 5.41 (d, 1H, $J_{1,2}$ = 4.7 Hz, H-1), 5.19 (dd, 1H, $J_{3',4'}$ = 9.6 Hz, H-3′), 4.91 (d, 1H, *J* = −10.6 Hz, $PhCH_2$), 4.76 (d, 1H, *J* = −10.6 Hz, $PhCH_2$), 4.61 (d, 1H, *J* = −12.2 Hz, $PhCH_2$), 4.57 (d, 1H, *J* = −12.2 Hz, $PhCH_2$), 4.34 (t, 1H, $J_{3',4'}$ = $J_{4',5'}$ = 9.3 Hz, H-4′), 4.26 (br d, 1H, *J* = 8.5 Hz, H-5), 3.98 (t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.0 Hz, H-4), 3.92 (dd, 1H, $J_{6a,5}$ = 3.6 Hz, $J_{6a,6b}$ = −11.4 Hz, H-6a), 3.88–3.75 (m, 5H, H-2, H-3, H-5′, H-6a,b′), 3.69 (dd, 1H, $J_{6b,5}$ = 1.8 Hz, H-6b), 2.65–2.54 (m, 2H, SCH_2), 2.04 (t, *J* = 6.2 Hz, OH), 1.98 (s, 3H, Acetyl-CH_3), 1.69–1.60 (m, 2H, CH_2), 1.38–1.02 (m, 11H, CH_2), 1.01–0.87 (m, 31H, CH,CH_3). ^{13}C NMR ($CDCl_3$): δ 170.3, 165.1 (C=O), 138.0, 137.1, 133.3, 129.7, 129.4, 129.0, 128.4. 128.3, 128.2 (2C), 127.9, 127.6 (2C), 127.4, 125.3 (PhC), 98.9 (C-1′), 83.4 (C-1), 81.7 (C-3), 75.5 (C-4), 75.4 ($PhCH_2$), 74.3 (C-5′), 73.5 ($PhCH_2$), 72.5 (C-3′), 70.7 (C-5), 70.0 (C-2′), 68.5 (C-6), 65.6 (C-4′), 64.6 (C-2), 61.5 (C-6′), 31.8, 30.7, 29.5, 29.1 (2C), 28.9, 22.6 (CH_2), 20.9 (Acetyl-CH_3), 17.2, 17.1 (3C), 16.6, 16.5, 14.0, 13.7, 13.1, 12.5 (2C), 12.3 (2C, CH, CH_3). Anal. Calcd for $C_{55}H_{82}FN_3O_{12}SSi_2$ (1084.49): C, 60.91; H, 7.62; N, 3.87; S, 2.96. Found: C, 60.75; H, 7.56; N, 3.89; S, 2.88.

3.13. Octyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-3-*O*-acetyl-2-*O*-benzoyl-4-*O*-(1-fluoro-1,1,3,3-tetraisopropyl-1,3-disiloxane-3-yl)-α-D-mannopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-1-thio-α-D-glucopyranoside (16)

A solution of **15**[43] (237 mg, 0.36 mmol) and *sym*-collidine (35 mL, 0.26 mmol) in dichloromethane (15 mL) was slowly added at −25 °C to a stirred slurry of **14** (339 mg, 0.33 mmol), AgOTf (92 g, 0.36 mmol) and 4 Å molecular sieves (0.5 g) in dichloromethane (15 mL) and stirring was continued for 1 h. Et_3N (1.0 mL) was added and the slurry was filtered through a layer of Celite. The filtrate was successively washed with aqueous $Na_2S_2O_3$, HCl and Na_2CO_3 solutions, dried, filtered and concentrated. Chromatography of the residue with 50/1 toluene-ethyl acetate gave crude **16** which was directly used for the next step.

3.14. Octyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-3-*O*-acetyl-2-*O*-benzoyl-α-D-mannopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-1-thio-α-D-glucopyranoside (17)

A solution of crude **16** and Bu_4NF trihydrate (100 mg) in THF was stirred at rt for 1 h and worked up as described for the preparation of compound. **14**. Chromatography with 10/1 toluene–ethyl acetate gave **17** (353 mg, 76% in rel. to **14**) as colorless oil. $[\alpha]_D$ +32.5 (*c* 1.1, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 8.13–6.96 (m, 35H, PhH), 6.14 (t, 1H, $J_{3'',4''} = J_{4'',5''}$ = 10.0 Hz, H-4″), 5.90 (dd, 1H, $J_{2'',3''}$ = 3.2 Hz, H-3″), 5.82 (dd, 1H, $J_{1'',2''}$ = 1.7 Hz, H-2″), 5.61 (dd, 1H, $J_{1',2'}$ = 2.9 Hz, H-2′), 5.50 (d, 1H, H-1′), 5.44 (d, 1H, $J_{1,2}$ = 5.3 Hz, H-1), 5.23 (dd, $J_{3',4'}$ = 5.2 Hz, H-3′), 5.08 (d, 1H, H-1″), 4.94 (d, 1H, *J* = −10.6 Hz, $PhCH_2$), 4.77 (d, 1H, *J* = −10.7 Hz, $PhCH_2$), 4.71–4.63 (m, 1H, H-6a″), 4.61 (s, 2H, $PhCH_2$), 4.46–4.41 (m, 2H, H-6b″, H-5″), 4.31–4.22 (m, 2H, H-4′, H-5), 4.03–3.60 (m, 9H, H-2, H-3, H-4′, H-5′, H-5″, H-6, H-6″), 2.71–2.55 (m, 2H, SCH_2), 2.49 (d, 1H, *J* = 4.9 Hz, OH), 2.08 (s, 3H, Acetyl-CH_3), 1.68–1.61 (m, 2H, CH_2), 1.39–1.03 (m, 10H, CH_2), 0.90–0.83 (m, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 171.2, 166.2, 165.3 (2C), 165.2, 164.9 (C═O), 137.8, 136.9, 133.4, 133.3, 133.2, 133.1, 129.8, 19.7, 129.6 (2C), 129.1, 129.0 (2C), 128.9, 128.6 (2C), 128.5, 128.3, 128.2 (2C), 127.7, 127.6 (3C), 127.4, 125.2 (PhC), 98.9 ($J_{C1',H1'}$ = 174.7 Hz, C-1′), 97.9 ($J_{C1'',H1''}$ = 175.3 Hz, C-1″), 83.2 ($J_{C1,H1}$ = 166.4 Hz, C-1), 81.6 (C-3), 75.2 ($PhCH_2$), 75.1 (C-4), 73.2 ($PhCH_2$), 72.4 (2C, C-5′, C-3′), 70.4 (C-5), 70.0 (C-3″), 69.8 (2C, C-2′, C-2″), 68.7 (C-6), 68.5 (C-5″), 66.5 (C-4″), 65.8 (C-6′), 65.1 (C-4′), 64.2 (C-2), 62.6 (C-6″), 31.8, 30.5, 29.5, 29.1 (2C), 28.9, 22.6 (CH_2), 21.0 (Acetyl-CH_3), 14.1 (CH_3). Anal. Calcd for $C_{77}H_{81}N_3O_{20}S$ (1400.54): C, 66.03; H, 5.83; N, 3.00; S, 2.29. Found: C, 66.36; H, 5.94; N, 2.88; S, 2.33.

3.15. Octyl α-D-mannopyranosyl-(1→6)-α-D-mannopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-1-thio-α-D-glucopyranoside (18)

A solution of **17** (336 mg, 0.24 mmol) and 1 M NaOMe in MeOH (ca. 1 μL) in MeOH (10 mL) was stirred at rt for 16 h. Work up as described for the preparation of compound **5** and lyophilization of the residue gave **18** (188 mg, 93%) as white foam. $[\alpha]_D$ +119.4 (*c* 0.8, MeOH). ^1H NMR (MeOD-d_4): δ 7.44–7.25 (m, 10H, PhH), 5.46 (d, 1H, $J_{1Glc,2Glc}$ = 5.4 Hz, H-1_{Glc}), 5.24 (d, 1H, $J_{1',2'}$ = 1.62 Hz, H-1′), 4.91–4.78 (m, 18H, Bn, OH), 4.76 (d, 1H, $J_{1'',2''}$ = 1.62 Hz, H-1″), 4.73 (d, 1H, *J* = −10.6 Hz, $PhCH_2$), 4.61 (d, 1H, *J* = 11.8 Hz, $PhCH_2$), 4.55 (d, 1H, *J* = 11.8 Hz, $PhCH_2$), 4.19 (dt, 1H, $J_{4Glc,5Glc}$ = 9.2 Hz, $J_{5Glc,6aGlc} = J_{5Glc,6bGlc}$ = 3.8 Hz, H-5_{Glc}), 3.96 (dd, 1H, $J_{2Glc,3Glc}$ = 9.8 Hz, H-2), 3.90–3.59 (m, 16H, H-3_{Glc}, H-4_{Glc}, H-6a,b_{Glc}, H-2′, H-3′, H-4′, H-5′, H-6a,b′, H-2″, H-3″, H-4″, H-5″, H-6a,b″), 2.67–2.53 (m, 2H, SCH_2), 1.65–1.57 (m, 2H, CH_2), 1.37–1.28 (m, 10H, CH_2), 0.89 (d, 1H, *J* = 6.7 Hz, CH_3). ^{13}C NMR (MeOD-d_4): δ 139.7, 139.0, 129.4 (3C), 128.9, 128.8, 128.6 (PhC), 103.3 (C-1′), 101.6 (C-1), 84.2 (C-1_{Glc}), 82.8 (C-3_{Glc}), 77.5 (C-4_{Glc}), 76.1 ($PhCH_2$), 74.4 ($PhCH_2$), 74.4, 74.3, 72.6 (2C), 72.4, 72.2, 72.0 (C-5_{Glc}, C-2′, C-3′, C-5′, C-2″, C-3″, C-4″), 70.9 (C-6_{Glc}), 68.6 (C-5″), 68.2 (C-4′), 67.4 (C-6′), 65.2 (C-2_{Glc}), 62.8 (C-6″), 33.0, 31.1, 30.6, 30.3, 30.2, 30.0, 23.7 (CH_2), 14.5 (CH_3). HRMS ESI: Calcd for $C_{40}H_{59}N_3NaO_{14}S$ (M+Na^+): *m/z* 860.3616; Found: *m/z* 860.3618.

3.16. Octyl α-D-mannopyranosyl-(1→6)-α-D-mannopyranosyl-(1→4)-2-amino-2-deoxy-1-thio-α-D-glucopyranoside (19)

Sodium (75 mg, 0.11 mmol) was added in three portions within 10 minutes at −78 °C to a stirred solution of **18** (90 mg, 0.11 mmol) in THF (5 mL) and liquid NH_3 (15 mL). Stirring was continued for 15 minutes, NH_4Cl (0.25 g) was added to the mixture in one portion and the solvent was removed at rt in a stream of Ar. Successive chromatography of the residue with 10/2/1/3 *n*-butanol–ethanol–ammonia–water on silica gel and with water on Biogel P2, followed by filtration through a Sulpelco RP C18 Superclean cartridge with a 1/1 water–methanol mixture and lyophyilization gave pure **19** (34 mg, 51%) as a white foam. $[\alpha]_D$ +119 (*c* 0.1, MeOH). ^1H NMR (MeOD-d_4): δ 5.26 (d, 1H, $J_{1Glc,2Glc}$ = 5.3 Hz, H-1_{Glc}), 5.25 (d, 1H, $J_{1,2}$ = 1.8 Hz, H-1), 4.82 (H-1′), 4.00 (ddd, 1H, $J_{4Glc,5Glc}$ = 9.4 Hz, $J_{5Glc,6aGlc}$ = 4.0 Hz, $J_{5Glc,6bGlc}$ = 3.0 Hz, H-5_{Glc}), 3.95 (dd, 1H, $J_{2,3}$ = 2.8 Hz, H-2), 3.89 (H-6a), 3.87 (H-2′), 3.80 (H-6a′, H-6a$_{Glc}$, H-6b$_{Glc}$), 3.78 (H-3′), 3.77 (H-5), 3.75 (H-6b), 3.71 (H-6b′), 3.67 (H-3), 3.66 (H-5′), 3.65 (H-4), 3.62 (H-4′), 3.52 (t, 1H, $J_{3Glc,4Glc}$ = 8.8 Hz, H-4_{Glc}), 3.44 (dd, 1H, $J_{2Glc,3Glc}$ = 9.8 Hz, H-3_{Glc}), 2.90 (dd, 1H, H-2_{Glc}), 2.69–2.69 (m, 2H, CH_2), 1.60–1.21 (m, 12H, CH_2), 0.89 (t, 3H, *J* = 6.2 Hz, CH_3). ^{13}C NMR (MeOD-d_4): δ 102.8 (C-1), 101.5 (C-1′), 88.0 (C-1_{Glc}), 78.7 (C-4_{Glc}), 76.6 (C-3_{Glc}), 74.4 (C-5′), 74.1 (C-5), 73.3 (C-5_{Glc}), 72.5 (2C, C-3, C-3′), 72.2 (C-2), 72.0 (C-2′), 68.6 (C-4′), 68.5 (C-4), 67.9 (C-6), 62.9 (C-6′), 62.7 (C-6_{Glc}), 57.4 (C-2_{Glc}), 33.0, 32.1, 30.9, 30.4, 30.3, 30.0, 23.7 (CH_2), 14.4 (CH_3). HRMS ESI: Calcd for $C_{26}H_{49}NO_{14}S$ (M+H^+): *m/z* 632.295; Found: *m/z* 632.293.

3.17. Ethyl 2,3,4,6-tetra-*O*-benzyl-1-sulfinyl-β-D-galactopyransoside (20b)

m-Chloroperbenzoic acid (50%, 967 mg, 2.8 mmol) was added at −25 °C to a stirred solution of **20a**[30] (1.50 g, 2.55 mmol) in dichloromethane (110 mL). The mixture is warmed to rt, washed with aqueous $NaHCO_3$ solution, dried, filtered and concentrated. Chromatography of the residue with 5/1 toluene–ethyl acetate gave **20b** (1.52 g, 99%) as a white amorphous solid. $[\alpha]_D$ −40.9 (*c* 1, $CHCl_3$). ^{13}C-NMR ($CDCl_3$): δ 138.4, 138.0, 137.9, 137.7, 128.6, 128.5, 128.4 (2C), 128.2, 128.1, 127.9, 127.8, 127.5, 127.4 (PhC), 89.6 (C-1), 84.1 (C-5), 78.7 (C-2), 75.9 ($PhCH_2$), 74.4 ($PhCH_2$), 73.6 ($PhCH_2$), 73.0 (2C, C-3, C-4), 72.5 ($PhCH_2$), 68.9 (C-6), 40.7 (SCH_2), 7.4 (CH_3). Anal. Calcd for $C_{36}H_{40}O_6S$ (600.77): C, 71.97; H, 6.71; S, 5.34. Found: C, 71.92; H, 6.69, S, 5.43.

3.18. Octyl 2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-(1,1,3,3-tetraisopropyl-1,3-disiloxane-1,3-diyl)-1-thio-α-D-mannopyranoside (21)

(a) Bromine (12 μL, 0.23 mmol) was added with syringe at 0 °C to a stirred slurry of **9** (188 mg, 0.29 mmol), **20a** (212 mg, 0.36 mmol), 4 Å molecular sieves (0.5 g), AgOTf (154 mg, 0.60 mmol) and tetramethyl urea (72 μL, 0.60 mmol) in toluene (6 mL), and stirring was continued for 2 h while the mixture was gradually allowed to warm to rt. Et_3N (0.12 mL) was added, the mixture filtered through a layer of Celite, and the filtrate washed successively with aqueous $Na_2S_2O_3$ and $NaHCO_3$ solutions, dried and concentrated. Chromatography of the residue with 1/3 *n*-hexane–dichloromethane gave first **21** (156 mg, 46%) as a white

amorphous solid. $[\alpha]_D$ +25.9 (*c* 0.9, $CHCl_3$). ^1H NMR ($CDCl_3$): δ8.05–6.98 (m, 25H, PhH), 5.51 (br s, 2H, H-1, H-2), 4.91 (d, 1H, $J_{1Gal,2Gal}$ = 3.5 Hz, H-1_{Gal}), 4.82 (d, 1H, *J* = −11.3 Hz, $PhCH_2$), 4.77 (d, 1H, *J* = −12.6 Hz, $PhCH_2$), 4.75 (d, 1H, *J* = −11.6 Hz, $PhCH_2$), 4.66 (d, 1H, *J* = −11.6 Hz, $PhCH_2$), 4.65 (t, 1H, $J_{3,4} = J_{4,5}$ = 9.1 Hz, H-4), 4.63 (d, 1H, *J* = −12.5 Hz, $PhCH_2$), 4.34 (dd, 1H, $J_{5,6a}$ = 1.5 Hz, $J_{6a,6b}$ = −12.6 Hz, H-6a), 4.03–3.82 (m, 10H, H-3, H-5, H-6b, H-2_{Gal}, H-3_{Gal}, H-4_{Gal}, H-5_{Gal}, $PhCH_2$), 3.50 (t, 1H, *J* = 8.9 Hz, H-$6a_{Gal}$), 3.16 (dd, 1H, $J_{5Gal,6bGal}$ = 4.7 Hz, $J_{6aGal,6bGal}$ = 8.4 Hz, H-$6b_{Gal}$), 2.67–2.54 (m, 2H, SCH_2), 1.64–1.59 (m, 2H, CH_2), 1.37–0.91 (m, 41H, CH, CH_2, CH_3), 0.90–0.86 (m, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 165.9 (C═O), 139.0, 138.9, 137.9, 133.2, 129.9, 129.7, 129.0, 128.4, 128.3, 128.2, 128.1 (2C), 127.9, 127.8, 127.7, 127.5, 127.4, 127.3 (2C), 127.2 (PhC), 100.9 (C-1_{Gal}), 82.8 (C-1), 81.0 (C-3), 78.9 (C-3_{Gal}), 76.6 (C-2_{Gal}), 75.3 (C-5), 74.8 ($PhCH_2$), 74.7 (C-4_{Gal}), 74.4 (C-2), 73.2 ($PhCH_2$), 73.1 ($PhCH_2$), 72.9 ($PhCH_2$), 69.9 (C-5_{Gal}), 67.7 (C-6_{Gal}), 66.2 (C-4), 61.1 (C-6), 31.8 (2C), 29.8, 29.2, 29.1, 28.8, 22.7 (CH_2), 17.9, 17.8, 17.6, 17.4 (3C), 17.3, 17.1, 14.1, 13.3, 13.0, 12.9, 12.7 (CH, CH_3). Anal. Calcd for $C_{87}H_{92}O_{12}SSi_2$ (1177.683): C, 68.33; H, 7.86. Found: C, 68.12; H, 7.72.

Eluted next was not consumed starting material **9** (25 mg, 13%).

(b) Performing the reaction as described under (a) but in dichloromethane instead of toluene resulted in a complex inseperable mixture of unidentified products.

(c) MeOTf (114 μL, 1.05 mmol) was added at rt to a stirred slurry of **9** (328 mg, 0.50 mmol), **20a** (585 mg, 1.0 mmol), 2,6-di-*t*-butyl pyridine (0.62 mL, 2.8 mmol) and 4 Å molecular sieves (1.0 g) in diethylether (10 mL) and the mixture was stirred at rt for 24 h. After addition of Et_3N (1.0 mL) and dichloromethane (50 mL) the mixture was worked up as described under (a). Chromatography of the residue with 50/1 toluene-ethyl acetate gave first **21** (108 mg, 18%). Eluted next was not consumed starting material **9** (136 mg, 42%).

(d) Performing the reaction as described under (a) but with N-iodosuccinimide and TMSOTf in dichloromethane instead of bromine in toluene resulted in a complex inseperable mixture of unidentified products.

(e) Performing the reaction as described under (a) but with iodoniumdicollidine perchlorate in dichloromethane instead of bromine in toluene resulted in a complex inseperable mixture of unidentified products.

(f) Tf_2O (131 μL, 0.5 mmol) was added at −50 °C to a stirred solution of **9** (328 mg, 0.50 mmol), **20b** (300 mg, 0.5 mmol), *sym*-collidine (67 μL, 0.5 mmol) in a 1:1 mixture of toluene and dichloromethane (8 mL) and the mixture was stirred at for 30 min. TLC showed the formation of a complex inseperable mixture of unidentified products.

(g) TMSOTf (10 μL) was added at −30 °C to a stirred solution of **9** (314 mg, 0.48 mmol) and **20c**[31] (411 mg, 0.60 mmol) in 1:1 dichloromethane and diethylether (7 mL) and stirring was continued for 18 h. TLC showed the formation of a complex inseperable mixture of unidentified products.

(h) A solution of 2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl chloride (**20d**)[32] (1.74 g, 3.13 mmol) in dichloromethane (30 mL) was added within 1 h at 0 °C to a stirred slurry of **9** (1.57 g, 2.5 mmol), $AgClO_4$ (1.24 g, 5.98 mmol), *sym*-collidine (0.75 mL, 5.62 mmol) and 4 Å molecular sieves (3.0 g) in dichloromethane (20 mL), and stirring was continued for 2 h while the mixture was allowed to warm up to rt. Workup as described under (a) and chromatography of the residue with 10:1 *n*-hexane–ethyl acetate gave **21** (1.51 g, 51%).

(i) A solution of **20d** (0.92 g, 1.65 mmol) in dichloromethane (20 mL) was added within 30 min at −5 °C to a stirred slurry of **9** (0.7 g, 1.12 mmol), $AgClO_4$ (1.50 g, 7.24 mmol), *sym*-collidine (1.72 mL, 12.9 mmol) and 4 Å molecular sieves (2.0 g) in dichloromethane (50 mL), and stirring was continued for 1.5 h while the mixture was allowed to warm up to 5 °C. Workup as described under (a) and chromatography of the residue with 10:1 *n*-hexane–ethyl acetate gave **21** (0.78 g, 61%).

3.19. 2,3,4,6-Tetra-*O*-benzyl-α-D-galactopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-(1,1,3,3-tetraisopropyl-1,3-disiloxane-1,3-diyl)-α-D-mannopyranose (22)

Treatment of compound. **21** (1.68 g, 1.43 mmol) with NBS (0.41 g, 2.32 mmol) in aqueous acetone (1% water content, 50 mL) as described for the preparation of compound. **11** and chromatography with 15:1 toluene–ethyl acetate gave crude **22** (0.96 g, 64%) as a colorless oil which was directly used for the next step.

3.20. 2,3,4,6-Tetra-*O*-benzyl-α-D-galactopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-(1,1,3,3-tetraisopropyl-1,3-disiloxane-1,3-diyl)-α-D-mannopyranosyl trichloroacetimidat (23)

Treatment of crude **22** (0.91 g, 0.87 mmol) with trichloroacetonitrile (0.92 ml) as described for the preparation of compound **12** and chromatography with 50:1 toluene–ethyl acetate gave **23** (0.63 g, 72%) as a colorless oil. $[\alpha]_D$ −12.0 (*c* 0.1, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 8.72 (s, 1H, C═NH), 8.07–7.00 (m, 25H, PhH), 6.53 (d, 1H, $J_{1,2}$ = 1.5 Hz, H-1), 5.55 (br t, 1H, *J* = 2.4 Hz, H-2), 4.86 (d, 1H, $J_{1Gal,2Gal}$ = 3.7 Hz, H-1_{Gal}), 4.83 (d, 1H, *J* = 11.5 Hz, $PhCH_2$), 4.78 (d, 1H, *J* = −11.6 Hz, $PhCH_2$), 7.76 (d, 1H, *J* = 11.8 Hz, $PhCH_2$), 4.74 (t, 1H, $J_{3,4} = J_{4,5}$ = 9.6 Hz, H-4), 4.71 (d, 1H, *J* = −12.9 Hz, $PhCH_2$), 4.67 (d, 1H, *J* = −11.6 Hz, $PhCH_2$), 4.59 (d, 1H, *J* = −12.6 Hz, $PhCH_2$), 4.43 (d, 1H, *J* = −11.3 Hz, $PhCH_2$), 4.20 (dd, 1H, $J_{5,6a}$ = 1.8 Hz, $J_{6a,6b}$ = −12.6 Hz, H-6a), 4.14 (dd, 1H, H-3), 4.06–3.85 (m, 5H, H-2_{Gal}, H-3_{Gal}, H-4_{Gal}, H-5_{Gal}, $PhCH_2$), 3.79 (br d, *J* = 9.4 Hz, H-6b), 3.50 (br t, 1H, *J* = 8.8 Hz, H-$6a_{Gal}$), 3.19 (dd, 1H, $J_{5Gal,6bGal}$ = 4.7 Hz, $J_{6aGal,6bGal}$ = 8.4 Hz, H-$6b_{Gal}$), 1.28–0.98 (m, 28H, CH, CH_3). ^{13}C NMR ($CDCl_3$): δ 165.7 (C═O), 159.7 (C═NH), 139.1, 139.0, 138.8, 137.8, 133.4, 129.8, 129.4, 129.0, 128.4, 128.3, 128.2, 128.1 (2C), 127.9, 127.8 (2C), 127.5, 127.3 (2C), 127.1 (PhC), 101.5 (C-1_{Gal}), 94.7 (C-1), 80.2 (C-3), 78.9 (C-3_{Gal}), 76.7 (2C, C-5, C-2_{Gal}), 74.8 ($PhCH_2$), 74.6 (C-4_{Gal}), 73.5 ($PhCH_2$), 73.2 ($PhCH_2$), 73.0 ($PhCH_2$), 71.9 (C-2), 69.9 (C-5_{Gal}), 67.5 (C-6_{Gal}), 65.5 (C-4), 60.6 (C-6_{Gal}), 17.8, 17.7, 17.5, 17.4 (3C), 17.3, 17.0, 13.2, 13.0 (2C), 12.8 (CH, CH_2). Anal. Calcd for $C_{61}H_{76}Cl_3O_{13}Si_2$ (1193.78): C, 61.37; H, 6.42; N, 1.17. Found: C, 61.34; H, 6.44; N, 1.17.

3.21. Octyl 2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-(1,1,3,3-tetraisopropyl-1,3-disiloxane-1,3-diyl)-α-D-mannopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-1-thio-α-D-glucopyranoside (24)

TMSOTf (18 μL) was added at −20 °C to a stirred slurry of **23** (667 mg, 0.56 mmol), **8** (430 mg, 0.84 mmol) and 4 Å molecular sieves (2 g) in diethylether (50 mL) and the mixture was stirred for 1.5 h. After neutralization of the mixture by addition of solid $NaHCO_3$, the mixture was filtered through a layer of Celite and the filtrate was washed with aqueous $NaHCO_3$ solution, dried and concentrated. Chromatography of the residue with 40:1 toluene–ethyl acetate gave **24** (789 mg, 91%) as a colorless oil. $[\alpha]_D$ +32.6 (*c* 1.7, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 7.95–6.97 (m, 35H, PhH), 5.53 (dd, 1H, $J_{1,2}$ = 1.6 Hz, $J_{2,3}$ = 2.8 Hz, H-2), 5.50 (d, 1H, H-1), 5.40 (d, 1H, $J_{1Glc,2Glc}$ = 5.3 Hz, H-1_{Glc}), 4.97 (d, 1H, *J* = −10.9 Hz, $PhCH_2$), 4.93 (d, 1H, $J_{1Gal,2Gal}$ = 3.2 Hz, H-1_{Gal}), 4.81 (d, 1H, *J* = −11.3 Hz, $PhCH_2$), 4.78 (d, 1H, *J* = −12.3 Hz, $PhCH_2$), 4.75 (d, 1H, *J* = −10.6 Hz, $PhCH_2$), 4.73 (d, 1H, *J* = −11.6 Hz, $PhCH_2$), 4.66–

4.53 (m, 5H, $PhCH_2$, H-4), 4.43 (d, 1H, J = −11.3 Hz, $PhCH_2$), 4.28–4.25 (br m, 1H, H-6a), 4.05–3.70 (m, 14H, H-3, H-6b, H-2_{Glc}, H-3_{Glc} H-4_{Glc}, H-5_{Glc}, H-6_{Glc}, H-2_{Gal}, H-3_{Gal}, H-4_{Gal}, H-5_{Gal}, $PhCH_2$), 3.56 (br d, 1H, J = 11.3 Hz, H-5), 3.46 (t, 1H, J = 8.9 Hz, H-$6a_{Gal}$), 3.13 (dd, 1H, $J_{6aGal,6bGal}$ = −8.5 Hz, $J_{5Gal,6bGal}$ = 4.6 Hz, H-$6b_{Gal}$), 2.69–2.53 (m, 2H, SCH_2), 1.70–1.60 (m, 2H, CH_2), 1.38–0.82 (m, 41H, CH, CH_2, CH_3). ^{13}C NMR ($CDCl_3$): δ 165.5 (C=O), 139.2, 139.0, 138.9, 138.0, 137.9, 133.0, 129.7 (2C), 129.0, 128.3, 128.2 (2C), 128.1 (2C), 128.0 (2C), 127.8 (2C), 127.6, 127.5 (2C), 127.4, 127.3, 127.3, 127.2, 127.1 (2C), 125.3 (PhC), 100.8 ($J_{C1Gal,H1-Gal}$ = 167.0 Hz, C-1_{Gal}), 98.6 ($J_{C1,H1}$ = 170.3 Hz, C-1), 83.3 ($J_{C1Glc,H1Glc}$ = 166.4 Hz, C-1_{Glc}), 81.4 (C-3_{Glc}), 79.8 (C-3), 78.9 (C-3_{Gal}), 76.7 (C-2_{Gal}), 75.9 (C-4_{Glc}), 75.2 ($PhCH_2$), 74.8 ($PhCH_2$), 74.7 (C-4_{Gal}), 73.3 ($PhCH_2$), 73.3 (3C, C-5*, C-2*, $PhCH_2$), 73.1 ($PhCH_2$), 72.8 ($PhCH_2$), 70.8 (C-5_{Glc}), 69.2 (C-5_{Gal}), 69.2 (C-6_{Glc}), 67.7 (C-6_{Gal}), 65.8 (C-4), 64.5 (C-2_{Glc}), 60.7 (C-6), 31.8, 29.5, 29.1 (2C), 29.0, 22.6 (CH_2), 17.8, 17.7, 17.4 (3C), 17.3, 17.1, 14.1 (CH_3), 13.2, 12.9 (2C), 12.7 (CH). Anal. Calcd for $C_{87}H_{113}N_3O_{16}SSi_2$ (1545.08): C, 7.63; H, 7.37; N, 2.72; S, 2.1. Found: C, 67.55; H, 7.27; N, 2.55; S, 2.1.

3.22. Octyl 2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl-(1→3)-2-*O*-benzoyl-4-*O*-(1-fluoro-1,1,3,3-tetraisopropyl-1,3-disiloxane-3-yl)-α-D-mannopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-1-thio-α-D-glucopyranoside (25)

Treatment of compound **24** (300 mg, 0.19 mmol) with HF in pyridine (70%, 38 μL) in dichloromethane (15 mL) as described for the preparation of **14** and chromatography with 20:1 toluene–ethyl acetate gave **25** (267 mg, 89%) as a colorless oil which was used for the next step without further characterization. $[\alpha]_D$ +55.0 (*c* 0.9, $CHCl_3$). Anal. Calcd for $C_{87}H_{114}FN_3O_{16}SSi_2$ (1565.08): C, 66.77; H, 7.34; N, 2.68. Found: C, 66.76; H, 7.40; N, 2.65.

3.23. Octyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-[2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl-(1→3)]-2-*O*-benzoyl-α-D-mannopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-1-thio-α-D-glucopyranoside (26)

(a) Treatment of **25** (191 mg, 0.12 mmol), AgOTf (34 mg, 0.13 mmol), 4 Å molecular sieves (1 g) in dichloromethane (10 mL) with **15** (89 mg, 0.13 mmol) and *sym*-collidine (13 μL, 0.1 mmol) in dichloromethane (5 mL) at −25 °C as described for the preparation of **16**, followed by treatment of the intermediate with Bu_4NF trihydrate (50 mg) in THF (10 mL) as described for the preparation of **17** and chromatography with 30:1 toluene–ethyl acetate gave **26** (157 mg, 68%). $[\alpha]_D$ +42.0 (*c* 0.6, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 8.13–7.02 (m, 55H, PhH), 6.13 (t, 1H, $J_{3',4'} = J_{4',5'}$ = 10 Hz, H-4′), 5.94 (dd, 1H, $J_{2',3'}$ = 3.2 Hz, H-3′), 5.78 (dd, 1H, $J_{1',2'}$ = 1.5 Hz, H-2′), 5.64 (dd, 1H, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 2.9 Hz, H-2), 5.47 (d, 1H, $J_{1,2}$ = 1.2 Hz, H-1), 5.42 (d, 1H, $J_{1Glc,2Glc}$ = 5.3 Hz, H-1_{Glc}), 5.08 (d, 1H, H-1′), 5.01 (d, 1H, $J_{1Gal,2Gal}$ = 3.7 Hz, H-1_{Gal}), 4.88 (d, 1H, J = −11.6 Hz, $PhCH_2$), 4.82 (d, 1H, J = −11.2 Hz, $PhCH_2$), 4.81 (br s, 2H, $PhCH_2$), 4.73 (d, 1H, J = −11.6 Hz, $PhCH_2$), 4.65 (H-6a′), 4.65 (2H, $PhCH_2$), 4.62 (2H, $PhCH_2$), 4.51 (d, 1H, J = −11.3 Hz, $PhCH_2$), 4.44 (H-5′), 4.39 (2H, H-6b′, $PhCH_2$-4a), 4.34 (d, 1H, J = −11.8 Hz, $PhCH_2$), 4.29 (H-5_{Glc}), 4.18 (t, 1H, $J_{3,4} = J_{4,5}$ = 9.4 Hz, H-4), 4.07 (dd, 1H, $J_{2Gal,3Gal}$ = 9.4 Hz, H-2_{Gal}), 4.00 (2H, H-6a, H-4_{Glc}), 3.98 (H-5_{Gal}), 3.96 (H-$6a_{Glc}$), 3.95 (H-5), 3.93 (H-4_{Gal}), 3.92 (H-2_{Glc}), 3.91 (2H, H-3, H-3_{Gal}), 3.84 (t, 1H, J = 9.5 Hz, H-$6b_{Glc}$), 3.79 (dd, 1H, $J_{2,3}$ = 8.9 Hz, $J_{3,4}$ = 9.8 Hz, H-3_{Glc}), 3.72 (br s, 1H, H-6b), 3.55 (t, 1H, J = 8.7 Hz, H-$6a_{Gal}$), 3.44 (dd, 1H, $J_{5Gal,6bGal}$, H-$6b_{Gal}$), 2.63 (m, 2H, SCH_2), 1.66–1.25 (m, 12H, CH_2), 0.87 (br t, J = 6.7 Hz, CH_3). ^{13}C NMR ($CDCl_3$): δ 166.2, 165.4, 165.3 (2C), 165.0 (C=O), 138.7, 138.4, 138.2, 138.1, 137.7, 137.3, 133.3, 133.1, 132.9, 130.0, 129.8, 129.7, 129.6, 129.4, 129.2, 129.0, 128.5 (2C), 128.4, 128.3 (2C), 128.2, 128.1, 128.0 (2C), 127.9, 127.7, 127.6, 127.5, 127.4, 127.3, 102.3 (C-1_{Gal}), 99.2 (C-1), 97.9 (C-1′), 83.2 (C-1_{Glc}), 81.5 (C-3_{Glc}), 81.5 (C-3), 79.6 (C-3_{Gal}), 76.3 (C-2_{Gal}), 75.4 (C-4_{Glc}), 75.1 ($PhCH_2$), 74.8 ($PhCH_2$), 74.5 ($PhCH_2$), 74.2 (C-4_{Gal}), 73.5 ($PhCH_2$), 73.1 ($PhCH_2$), 72.6 (C-5), 72.3 ($PhCH_2$), 71.8 (C-2), 70.8 (C-5_{Glc}), 70.3 (C-3′), 70.2 (C-2′), 69.6 (C-5_{Gal}), 69.2 (C-6_{Glc}), 68.7 (C-5′), 67.8 (C-6_{Gal}), 66.7 (C-4′), 66.6 (C-4), 66.5 (C-6), 64.2 (C-2_{Glc}), 62.6 (C-6′), 31.8, 30.5, 29.5, 29.2 (2C), 29.0, 22.6 (CH_2), 14.1 (CH_3). FAB-MS (pos.): *m/z* 1903.6 $[M+Na]^+$. Anal. Calcd for $C_{109}H_{113}N_3O_{24}S$ (1881.14): C, 69.59; H, 6.05; N, 2.23. Found: C, 69.39; H, 6.16; N, 2.16.

(b) TMSOTf (5 μL) was added at −20 °C to a stirred slurry of compound **31** (280 mg, 0.16 mmol), compound **8** (120 mg, 0.23 mmol) and 4 Å molecular sieves (0.5 g) in diethylether (20 mL) and stirring was continued for 1.5 h. Workup as described for the preparation of compound **13** followed by treatment of the intermediate with Bu_4NF trihydrate (50 mg) in THF (10 mL) as described for the preparation of **17** and chromatography with 30:1 toluene–ethyl acetate gave **26** (128 mg, 44%).

3.24. Octyl α-D-mannopyranosyl-(1→6)-[α-D-galactopyranosyl-(1→3)]-α-D-mannopyranosyl-(1→4)-2-amino-2-deoxy-1-thio-α-D-glucopyranoside (27)

Compound **26** (105 mg, 0.06 mmol) was deprotected with a catalytic amount of NaOMe in MeOH as described for the preparation of compound **18** followed by treatment of the intermediate with Na (71 mg, 3.09 mmol) in THF (5 mL) and liquid NH_3 (15 mL) as described for the preparation of compound **19**. Purification as described for the preparation of compound **19** gave pure **27** (29 mg, 64%). $[\alpha]_D$ +222 (*c* 0.1, MeOH). ^{1}H NMR (MeOD-d_4): δ 5.37 (d, 1H, $J_{1Glc,2Glc}$ = 5.0 Hz, H-1_{Glc}), 5.22 (d, 1H, $J_{1,2}$ = 1.6 Hz, H-1), 5.15 (d, 1H, $J_{1Gal,2Gal}$ = 3.2 Hz, H-1_{Gal}), 4.83 (d, 1H, $J_{1',2'}$ = 1.4 Hz, H-1′), 4.25 (br s, 1H, H-2), 4.10 (dd, 1H, J = 7.7 Hz, J = 4.0 Hz, H-5_{Gal}), 4.02 (dt, $J_{4Glc,5Glc}$ = 9.0 Hz, $J_{5Glc,\ 6aGlc} = J_{5Glc,6bGlc}$ = 3.2 Hz, H-5_{Glc}), 3.91 (H-6a), 3.87 (2H, H-2′, H-4_{Gal}), 3.86 (H-4), 3.83 (H-5), 3.82 (2H, H-$6a_{Glc}$, H-$6b_{Glc}$), 3.81 (2H, H-6a′, H-3_{Gal}), 3.79 (H-$6a_{Gal}$), 3.78 (3H, H-3′, H-3, H-2_{Gal}), 3.76 (H-6b), 3.75 (H-6b′), 3.70 (H-$6b_{Gal}$), 3.65 (3H, H-4′, H-5′, H-3_{Glc}), 3.57 (t, 1H, $J_{3Glc,4Glc}$ = 9.2 Hz, H-4_{Glc}), 3.20 (dd, 1H, $J_{2glc,3Glc}$ = 9.8 Hz, H-2_{Glc}), 2.67 (t, 2H, J = 7.2 Hz, SCH_2), 1.68–1.63 (m, 2H, CH_2), 1.40–1.28 (m, 10H, CH_2), 0.89 (t, 3H, J = 6.9 Hz, CH_3). ^{13}C NMR (MeOD-d_4): δ 103.2 (C-1), 102.3 (C-1_{Gal}), 102.0 (C-1′), 86.0 (C-1_{Glc}), 81.5 (C-3), 78.7 (C-4_{Glc}), 74.4 (C-5′), 74,2 (C-5), 74.1 (C-3_{Glc}), 73.5 (C-5_{Glc}), 73.0 (C-5_{Gal}), 72.5 (C-3′), 72.0 (C-2′), 71.5 (C-3_{Gal}), 71.3 (2C, C-2, C-4_{Gal}), 70.8 (C-2_{Gal}), 68.6 (C-4′), 67.7 (C-6), 67.2 (C-4), 63.2 (C-6_{Gal}), 62.8 (C-6′), 62.3 (C-6_{Glc}), 56.5 (C-2_{Glc}), 33.0, 32.6, 30.9, 30.4, 30.3, 29.9, 23.7 (CH_2), 14.4 (CH_3). HRMS ESI Calcd for ($C_{32}H_{60}NO_{19}S$) ($M+H^+$): *m/z* 794.348; Found: *m/z* 794.348.

3.25. Octyl 2,3,4,6-Tetra-*O*-benzyl-α-D-galactopyranosyl-(1→3)-2-*O*-benzoyl-4-*O*-(3-fluoro-1,1,3,3-tetraisopropyl-1,3-disiloxane-1-yl)-1-thio-α-D-mannopyranoside (28)

Treatment of compound **21** (565 mg, 0.48 mmol) with HF in pyridine (70%, 50 μL) in dichloromethane (20 mL) as described for the preparation of **14** and chromatography with 70:1 toluene–ethyl acetate gave **28** (544 mg, 95%) as a colorless oil. $[\alpha]_D$ +47.5 (*c* 1.5, $CHCl_3$). ^{1}H NMR: ($CDCl_3$) δ 8.01–7.02 (m, 25H, PhH), 5.49 (dd, 1H, J = 6.1 Hz, J = 2.9 Hz, H-2), 5.30 (br d, 1H, J = 6 Hz, H-1), 4.91 (d, 1H, J = 3.5 Hz, H-1), 4.80 (d, 1H, J = 11.3 Hz, $PhCH_2$), 4.78 (d, 1H, J = 12.2 Hz, $PhCH_2$), 4.72–4.66 (m, 3H), 4.47–4.39 (m,

2H), 4.18 (dd, 1H, J = 6.0 Hz, J = 2.9 Hz), 4.06–3.80 (m, 10H), 3.37 (t, 1H, J = 3.4 Hz), 2.91 (dd, 1H, J = 8.5 Hz, J = 5.1 Hz), 2.73–2.56 (m, 2H, SCH_2), 1.62–1.57 (m, 2H, CH_2), 1.37–1.04 (m, 40H, CH, CH_2, CH_3), 0.87 (t, 3H, J = 6.4 Hz, CH_3). ^{13}C NMR ($CDCl_3$): δ 165.5 (C═O), 139.0, 138.7, 138.2, 133.0, 130.4, 129.8, 128.5, 129.4 (2C), 128.3, 128.2, 128.1, 127.8, 127.7, 127.6, 127.5, 127.3 (PhC), 99.4 (C-1), 79.1, 78.7, 76.7, 75.9, 75.1, 74.8 ($PhCH_2$), 74.1 ($PhCH_2$), 73, 1 ($PhCH_2$), 72.9 ($PhCH_2$), 70.1, 68.0, 67.8 (C-6), 61.4 (C-6), 31.8, 29.9,.29.1, 28.9, 22.6 (CH_2), 17.4, 17.3, 17.1, 16.8, 16.7, 14.0 , 13.1, 12.9, 12.8, 12.7 (CH, CH_3). Anal. Calcd for $C_{67}H_{93}O_{12}SSi_2$ (1197.70): C, 67.19; H, 7.83; S, 2.68. Found: C, 67.10; H, 7.61; S, 2.80.

3.26. Octyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-[2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl-(1→3)]-2-*O*-benzoyl-4-*O*-(1-fluoro-1,1,3,3-tetraisopropyl-1,3-disiloxane-3-yl)-1-thio-α-D-mannopyranoside (29)

Treatment of **28** (681 mg, 0.57 mmol), AgOTf (161 mg, 0.27 mmol), 4 Å molecular sieves (1 g) in dichloromethane (10 mL) with **15** (435 mg, 0.66 mmol) and *sym*-collidine (61 μL, 0.46 mmol) in dichloromethane (5 mL) at −25 °C as described for the preparation of **16** and chromatography with 5:1 *n*-hexane–ethyl acetate gave **29** (741 mg, 73%) as a colorless glassy material. $[\alpha]_D$ +25.3 (c 1.3, $CHCl_3$). ^1H NMR: ($CDCl_3$): not assignable due to extensive overlapping of signals. ^{13}C NMR ($CDCl_3$): δ 166.1, 165.7, 165.3, 164.9 (C═O), 138.8, 137.9, 133.2, 133.1, 132.9, 132.8, 130.1, 130.0, 129.8, 129.7, 129.6, 129.3, 129.2, 128.5, 128.4, 128.3 (2C), 128.2, 128.1, 128.0, 127.8, 127.6, 127.4, 127.3, 127.1 (PhC), 79.2, 77.2, 76.0, 74.9, 74.8 ($PhCH_2$), 73.1 ($PhCH_2$), 72.9 ($PhCH_2$), 70.3, 70.2, 68.5, 67.6 (C-6), 66.7, 62.7 (C-6), 31.7,28.9, 22.6 (CH_2), 17.9, 17.7, 17.2, 17.1, 17.0, 16.8, 16.7, 14.0, 12.7, 12.5 (CH, CH_3). Anal. Calcd for $C_{101}H_{119}FO_{21}SSi_2$ (1776.25): C, 68.29; H, 6.75; S, 1.81. Found: C, 68.15, H, 6.75, S, 1.9.

3.27. Octyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-[2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl-(1→3)]-2-*O*-benzoyl-1-thio-α-D-mannopyranoside (30)

Treatment of **29** (60 mg, 0.03 mmol) with Bu_4NF trihydrate (10 mg) in THF (5 mL) as described for the preparation of **17** and chromatography with 30:1 toluene–ethyl acetate gave **30** (46 mg, 89%) as a colorless oil. $[\alpha]_D$ +22.9 (c 0.7, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 8.14–7.18 (m, 45H, PhH), 6.16 (t, 1H, $J_{3',4'}$ = 10.1 Hz, H-4′), 5.96 (dd, 1H, $J_{2',3'}$ = 3.2 Hz, H-3′), 5.80 (dd, 1H, $J_{1',2'}$ = 1.8 Hz, H-1′), 5.59 (dd, 1H, $J_{1,2}$ = 1.2 Hz, $J_{2,3}$ = 3.2 Hz, H-2), 5.41 (s, 1H, H-1), 5.21 (d, 1H, H-1′), 4.99 (d, 1H, $J_{1g,2g}$ = 3.8 Hz, H-1_g), 4.87 (d, 1H, J = –11.6 Hz, $PhCH_2$), 4.83 (d, 1H, J = −11.5 Hz, $PhCH_2$), 4.72–4.66 (m, 4H, $PhCH_2$, H-6a′), 4.55–4.45 (m, 2H, J_{PhCH2} = −10.3 Hz, H-5′,$PhCH_2$), 4.45 (dd, 1H, $J_{6a',6b'}$ = −11.8 Hz, $J_{5,6b'}$ = 7.4 Hz, H-6b′), 4.40–4.29 (m, 3H, J_{PhCH2} = −11.8 Hz, J_{PhCH2} = −11.7 Hz, $PhCH_2$, H-5), 4.22 (t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.8 Hz, H-4), 4.16 (dd, 1H, $J_{5,6a}$ = 5.6 Hz, $J_{6a,6b}$ = −11.3 Hz, H-6a), 4.06 (dd, 1H, $J_{2g,3g}$ = 10.4 Hz, H-2_g), 3.96–3.89 (m, 5H, H-3, H-3_g, H-4_g, H-5_g, H-6b), 3.57 (t, 1H, J = 8.9 Hz, H-$6a_g$), 3.44 (dd, 1H, $J_{6ag,6bg}$ = −8.8 Hz, $J_{5g,6bg}$ = 5.3 Hz, H-$6b_g$), 2.80–2.64 (m, 2H, SCH_2), 1.73–1.63 (m, 2H, CH_2), 1.25–1.20 (m, 10H, CH_2), 0.83–0.78 (m, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 166.2, 165.7, 165.4, 165.3, 165.1 (C═O), 138.7, 138.4, 138.2, 137.7, 133.3, 133.2, 133.1, 132.9, 129.9, 129.8, 129.7 (2C), 129.4, 129.2, 129.0, 128.6, 128.5 (3C), 128.4 (2C), 128.3 (2C), 128.2, 128.1, 128.0, 127.9, 127.7, 127.5, 127.4, 127.3 (PhC), 101.9 (C-1_g), 97.6 (C-1′), 82.6 (C-1), 81.9 (C-3), 79.5 (C-3_g), 76.3 (C-2_g), 74.7 ($PhCH_2$), 74.4 ($PhCH_2$), 74.2 (C-5_g), 73.5 (C-2), 73.2 ($PhCH_2$), 72.4 ($PhCH_2$), 71.7 (C-5), 70.3 (C-2′), 70.2 (C-3′), 69.7 (C-4_g), 68.7 (C-5′), 67.9 (C-6_g), 67.1 (C-4), 66.7 (C-4′), 66.5 (C-6), 62.7 (C-6′), 31.7, 31.3, 29.3, 29.2 (2C), 28.8, 22.6 (CH_2), 14.0 (CH_3). Anal. Calcd for $C_{89}H_{92}O_{20}S$ (1513.74): C, 70.62; H, 6.13. Found: C, 70.54; H, 6.15.

3.28. 2,3,4,6-Tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-[2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl-(1→3)]-2-*O*-benzoyl-4-*O*-(1-fluoro-1,1,3,3-tetraisopropyl-1,3-disiloxane-3-yl)-1-thio-α-D-mannopyranosyl trichloroacetimidate (31)

Treatment of compound **29** (355 mg, 0.2 mmol) with NBS (53 mg, 0.3 mmol) in aqueous acetone (1% water content, 10 mL) as described for the preparation of compound **11** and chromatography with 15:1 toluene–ethyl acetate gave a colorless intermediate which was treated with trichloroacetonitrile (0.5 ml) and K_2CO_3 (0.5 g) in dichloromethane (10 mL) as described for the preparation of compound **12** and chromatography with 30:1 toluene–ethyl acetate gave **31** (334 mg, 95%) as a colorless oil which was used for the next step without further characterization. $[\alpha]_D$ +8.8 (c 0.4, $CHCl_3$). Anal. Calcd for $C_{95}H_{103}Cl_3FNO_{22}Si_2$ (1792.36): C, 63.66; H, 5.79; N, 0.78. Found: C, 63.55; H, 5.74; N, 0.80.

3.29. 2,3,4,6-Tetra-O-benzyl-α-D-galactopyranosyl-(1→3)-1,6-anhydro-2-O-benzoyl-β-D-mannopyranoside (33) and octyl 2,3,4,6-tetra-O-benzoyl-1-thio-α-D-mannopyranoside (34)

BF_3 etherate (0.2 mL, 1.6 mmol) was added at rt to a solution of **21** (1.2 g, 1.02 mmol) and **32**[12] (0.61 g, 1.02 mmol) and the mixture was stirred for 1.5 h, poured into water, and extracted with dichloromethane (3 × 50 mL). The combined extracts were washed with aqueous $NaHCO_3$ solution, dried and concentrated. Treatment of the residue with Bu_4NF trihydrate (50 mg) in THF (10 mL) as described for the preparation of compound **17** and chromatography with a 70:1–5:1 gradient toluene–ethyl acetate gave first **34** (476 mg, 64%). $[\alpha]_D$ −2.5 (c 0.8, $CHCl_3$). ^1H NMR ($CDCl_3$) δ 8.11–7.19 (m, 20H, PhH), 6.14 (t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.8 Hz, H-4), 5.85 (dd, 1H, $J_{2,3}$ = 3.2 Hz, H-3), 5.81 (dd, 1H, $J_{1,2}$ = 1.5 Hz, H-2), 5.55 (d, 1H, H-1), 4.84 (ddd, 1H, $J_{5,6a}$ = 2.5 Hz, $J_{5,6b}$ = 4.5 Hz, H-5), 4.68 (dd, 1H, $J_{6a,6b}$ = −12.2 Hz, H-6a), 4.53 (dd, 1H, H-6b), 2.80–2.62 (m, 2H, SCH_2), 1.72–1.61 (m, 2H, CH_2), 1.38–1.12 (m, 10H, CH_2), 0.88 (t, 3H, J = 6.8 Hz, CH_3). ^{13}C NMR ($CDCl_3$): δ 166.1, 165.4 (2C), 165.3 (C═O), 133.4 (2C), 133.2, 133.0, 129.8, 129.7, 129.3, 128.9 (2C), 128.6, 128.4 (2C), 128.3 (PhC), 82.5 (C-1), 72.1 (C-2), 70.5 (C-3), 69.2 (C-5), 67.1 (C-4), 62.9 (C-6), 31.7, 31.4, 29.5, 29.1, 29.0, 28.8, 22.6 (CH_2), 14.1 (CH_3). Anal. Calcd for $C_{42}H_{44}O_9S$ (724.86): C, 69.59; H, 6.12. Found: C, 69.43; H, 6.12.

Eluted next was **33** (408 mg, 51%). $[\alpha]_D$ +15.3 (c 0.6, $CHCl_3$). ^1H NMR ($CDCl_3$): δ8.08–7.04 (m, 25H, PhH), 5.50 (br s, 1H, H-1), 5.09 (dd, 1H, $J_{1,2}$ = 2.0 Hz, $J_{2,3}$ = 5.3 Hz, H-2), 4.88 (d, 1H, J = −11.9 Hz, $PhCH_2$), 4.88 (d, 1H, $J_{1gal,2gal}$ = 3.4 Hz, H-1_{gal}), 4.84 (d, 1H, J = −11.5 Hz, $PhCH_2$), 4.75 (br s, 2H, $PhCH_2$), 4.61 (d, 1H, J = −11.3 Hz, $PhCH_2$), 4.51 (d, J = 7.4 Hz, H-6a), 4.45 (d, 1H, J = −11.2 Hz, $PhCH_2$), 4.35 (br d, 1H, J = 5.4 Hz, H-5), 4.20–4.18 (m, 1H, H-3), 4.06–3.92 (m, 6H, H-2′, H-3′, H-4′, H-5′, $PhCH_2$), 3.83 (br d, 1H, J = 8.5 Hz, H-4), 3.59 (dd, 1H, $J_{6a,6b}$ = 6.9 Hz, $J_{6b,5}$ = 6.3 Hz, H-6), 3.32 (t, $J_{5',6a'}$ = $J_{6a',6b'}$ = 8.6 Hz, H-6a′), 2.88 (dd, 1H, $J_{5',6b'}$ = 5.4 Hz, H-6b′), 2.61 (d, 1H, J = 8.7 Hz, OH). ^{13}C NMR ($CDCl_3$): δ 165.7 (C═O), 138.7, 138.6, 138.3, 137.9, 133.2, 129.8, 129.4, 129.0, 128.4 (2C), 128.3, 128.2, 128.1 (2C), 127.9 (2C), 127.8, 127.5 (2C), 127.4 (2C), 125.3 (PhC), 99.6 (C-1), 99.0 (C-1_{gal}), 78.8 (C-2_{gal}), 76.9 (C-3), 76.5 (C-5), 76.4 (C-3_{gal}), 74.8 ($PhCH_2$), 74.6 (C-4_{gal}), 74.3 ($PhCH_2$), 72.9 ($PhCH_2$), 72.3 ($PhCH_2$), 70.1 (C-4), 69.6 (C-5_{gal}), 69.4 (C-2), 67.6 (C-6_{gal}), 65.1 (C-6). Anal. Calcd for $C_{47}H_{48}O_{11}$ (788.88): C, 71.56; H, 6.13. Found: C, 71.20; H, 6.16.

3.30. Octyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→6)-[2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl-(1→3)]-2-*O*-benzoyl-α-D-mannopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-1-thio-α-D-glucopyranosid (36)

TMSOTf (5 μL) was added at −20 °C to a solution of **25** (270 mg, 0.17 mmol) and **35**[12] (196 mg, 0.19 mmol) in diethylethylether (10 mL). After 45 min an additional amount of **35** (50 mg, 0.05 mmol) was added and stirring at −20 °C continued for 1.5 h. Workup as described for the preparation of compound **13** followed by treatment of the intermediate (252 mg, 60%) with Bu_4NF trihydrate (50 mg) in THF (10 mL) as described for the preparation of **17** and chromatography with 5:1 toluene-ethyl acetate gave **36** (192 mg, 51%). $[\alpha]_D$ +23.5 (*c* 0.4, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 8.09–7.04 (m, 55H, PhH), 6.11 (t, 1H, $J_{3'',4''} = J_{4'',5''}$ = 10.0 Hz, H-4″), 5.94 (dd, 1H, $J_{2'',3''}$ = 3.2 Hz, H-3″), 5.68 (dd, 1H, $J_{1'',2''}$ = 1.9 Hz, H-2″), 5.54 (dd, 1H, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 2.9 Hz, H-2), 5.47 (d, 1H, H-1), 5.46 (t, 1H, $J_{3',4'} = J_{4',5'}$ = 9.6 Hz, H-4′), 5.40 (d, 1H, $J_{1glc,2glc}$ = 5.4 Hz, H-1_{glc}), 5.39 (dd, $J_{2',3'}$ = 2.9 Hz, H-3′), 5.03 (d, 1H, $J_{1',2'}$ = 1.2 Hz, H-1′), 5.01 (d, 1H, H-1″), 4.97 (d, 1H, $J_{1gal,\ 2gal}$ = 3.8 Hz, H-1_{gal}), 4.87 (d, 1H, *J* = 11.6 Hz, $PhCH_2$), 4.82 (d, 1H, *J* = 10.7 Hz, $PhCH_2$), 4.80 (d, 1H, *J* = 11.5 Hz, $PhCH_2$), 4.76 (d, 1H, *J* = 11.3 Hz, $PhCH_2$), 4.72 (d, 1H, *J* = 11.6 Hz, $PhCH_2$), 4.62 (s, 2H, $PhCH_2$), 4.56 (H-6a″), 4.55 (2H, $PhCH_2$), 4.52 (H-5″), 4.48 (d, 1H, *J* = 11.3 Hz, $PhCH_2$), 4.40 (H-6b″), 4.31 (d, 1H, *J* = 11.8 Hz, $PhCH_2$),4.27 (d, 1H, *J* = 11.8 Hz, $PhCH_2$), 4.25 (H-5_{glc}), 4.25 (H-5_{glc}), 4.21 (H-6a′), 4.08 (H-6b′), 4.06 (H-5′), 4.04 (H-2_{Gal}), 4.03 (H-2′), 4.02 (H-4), 3.92 (H-4_{Glc}), 3.90 (H-5_{Gal}), 3.89 (H-5, H-2_{Glc}), 3.88 (H-4_{Gal}), 3.87 (H-3_{Gal}), 3.85 (H-3), 3.84 (H-$6a_{Glc}$), 3.81 (H-6a), 3.77 (H-$6b_{Glc}$), 3.74 (H-3_{Glc}), 3.61 (br d, 1H, *J* = 9.8 Hz, H-6b), 3.51 (t, 1H, $J_{5Gal,\ 6aGal} = J_{6agal,\ 6bGal}$ = 8.7 Hz, H-$6a_{Gal}$), 3.37 (dd, 1H, $J_{5Gal,6bGal}$ = 5.3 Hz, H-$6b_{Gal}$), 2.59 (m, 2H, SCH_2), 2.15 (s, 3H, CH_3), 2.10 (s, 3H, CH_3), 1.92 (s, 3H, CH_3), 1.63–1.25 (m, 12H, CH_2), 0.86 (br t, 3H, *J* = 7.0 Hz, CH_3). ^{13}C NMR ($CDCl_3$): δ 171.0, 170.3, 169.5, 165.7, 165.6, 165.2 (2C), 165.0 (C═O), 138.7, 138.4, 138.2 (2C), 137.7, 137.5, 133.5, 133.4, 133.2, 133.1, 132.9, 129.8 (2C), 129.7 (2C), 129.6, 129.3, 129.2, 129.0 (2C), 128.6, 128.5, 128.4 (3C), 128.3 (2C), 128.2 (2C), 128.1 (4C), 128.0, 127.9 (2C), 127.7, 127.5 (3C), 127.4 (2C), 127.3 (PhC), 102.1 (C-1_{Gal}), 99.3 (C-1″), 98.7 (C-1), 98.3 (C-1′), 83.3 (C-1_{Glc}), 81.5 (C-3_{Glc}), 81.3 (C-3), 79.5 (C-3_{Gal}), 77.4 (C-2′), 76.3 (C-2_{Gal}), 75.0 (C-4_{Glc}), 74.9 ($PhCH_2$), 74.2 (C-4_{Gal}), 73.4 ($PhCH_2$), 73.1 ($PhCH_2$), 72.3 (2C, C-5, $PhCH_2$), 71.9 (C-2), 70.8 (C-5_{Glc}), 70.7 (C-2″), 70.4 (C-3′), 69.6 (C-5_{Gal}), 69.4 (2C, C-3″, C-5″), 69.3 (C-6_{Glc}), 68.4 (C-5′), 67.8 (C-6_{Gal}), 67.0 (C-4″), 66.6 (C-4), 66.4 (C-6), 66.2 (C-4′), 64.2 (C-2_{Glc}), 62.8 (C-6″), 62.1 (C-6′), 31.8, 30.5, 29.6, 29.2 (2C), 29.0, 22.7 (CH_2), 14.1 (CH_3). Anal. Calcd for $C_{121}H_{129}N_3O_{32}S$ (2169.39): C, 66.99; H, 5.99; N, 1.94. Found: C, 66.89; H, 6.23; N, 1.81.

3.31. Octyl α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→6)-[α-D-galactopyranosyl-(1→3)]-α-D-mannopyranosyl-(1→4)-2-amino-2-deoxy-1-thio-α-D-glucopyranoside (37)

Compound **36** (150 mg, 0.07 mmol) was deprotected with a catalytic amount of NaOMe in MeOH as described for the preparation of compound **18** followed by treatment of the intermediate with Na (81 mg, 3.52 mmol) in THF (5 mL) and liquid NH_3 (15 mL) as described for the preparation of compound **19**. Purification as described for the preparation of compound **19** gave pure **37** (35 mg, 54%). $[\alpha]_D$ +131 (*c* 0.1, MeOH). ^1H NMR (MeOD-d_4): δ 5.38 (d, 1H, $J_{1Glc,2Glc}$ = 5.1 Hz, H-1_{Glc}), 5.23 (d, 1H, $J_{1,2}$ = 1.5 Hz, H-1), 5.15 (d, 1H, $J_{1Gal,2Gal}$ = 3.7 Hz, H-1_{Gal}), 5.13 (d, 1H, $J_{1',2'}$ = 1.4 Hz, H-1′), 4.98 (d, 1H, $J_{1'',2''}$ = 1.4 Hz, H-1″), 4.25 (br t, 1H, *J* =2.3 Hz, H-2), 4.10 (dd, 1H, *J* = 7.9 Hz, *J* = 4.2 Hz, H-5_{Gal}), 4.02 (ddd, 1H, $J_{4Glc,5Glc}$ = 9.6 Hz, $J_{5,6a}$ = 4.2 Hz, $J_{5,6b}$ = 2.6 Hz, H-5_{Glc}), 3.98 (dd, 1H, $J_{2'',3''}$ = 3.1 Hz, H-2″), 3.93 (H-2′), 3.92 (H-6a), 3.90 (H-3′), 3.87 (2H, H-4, H-4_{Gal}), 3.84 (2H, H-6a″, H-6a′), 3.81 (4H, H-5, H-$6a_{Glc}$, H-$6b_{Glc}$, H-3_{Gal}), 3.78 (2H, H-3, H-2_{Gal}), 3.77 (H-$6a_{Gal}$), 3.76 (H-6b), 3.71 (2H, H-3″, H-5″), 3.68 (3H, H-6b′, H-6b″, H-$6b_{Gal}$), 3.66 (H-3_{Glc}), 3.63 (H-5′), 3.62 (H-4′), 3.58 (2H, H-4″, H-4_{Glc}), 3.23 (dd, 1H, $J_{2Glc,3Glc}$ = 10.4 Hz, H-2_{Glc}), 2.68 (t, 2H, *J* = 7.3 Hz, SCH_2), 1.68–1.62 (m, 2H, CH_2), 1.45–1.36 (m, 2H, CH_2), 1.30–1.29 (m, 8H, CH_2), 0.89 (t, 3H, *J* = 6.9 Hz, CH_3). ^{13}C NMR (MeOD-d_4): δ 104.1 (C-1″), 103.2 (C-1), 102.4 (C-1_{Gal}), 100.1 (C-1′), 85.9 (C-1_{Glc}), 81.5 (C-3), 80.4 (C-2′), 78.6 (C-4_{Glc}), 74.9 (C-5″), 74.5 (C-5′), 74.3 (C-5), 74.0 (C-3_{Glc}), 73.5 (C-5_{Glc}), 73.0 (C-5_{Gal}), 72.4 (C-3″), 72.1 (C-3′), 71.9 (C-2″), 71.5 (C-3_{Gal}), 71.3 (C-4_{Gal}), 71.2 (C-2), 70.8 (C-2_{Gal}), 69.0 (C-4′), 68.8 (C-4″), 67.8 (C-6), 67.2 (C-4), 63.1 (C-6_{Gal}), 63.0 (C-6′), 62.9 (C-6″), 62.4 (C-6_{Glc}), 56.4 (C-2_{Glc}), 33.0, 32.6, 30.9, 30.4, 30.3, 29.9, 23.7 (CH_2), 14.5 (CH_3). HRMS ESI Calcd for $C_{38}H_{70}NO_{24}S$ ($M+H^+$): *m/z* 956.393; Found: *m/z* 956.397.

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