Synthesis and Evaluation of *S*- and *C(1)*-Substituted Analogues of Lincomycin

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New thioglycosides and *C(1)*-alkylated thioglycosides (*S*-ulosides) of lincomycin were synthesized, and their antibiotic activities were determined. The *S*-aryl and *S*-arylalkyl analogues **11a**–**11i** were obtained by *S*-glycosylation of the sulfoxides **7** with arenethiols, or by *S*-alkylation of the thiol **14** with alkyl bromides. Lincomycin derivatives **27**, **32a**, **32b**, **38a**, **38b**, **44**, and **47** were prepared *via Henry* reaction or *Michael* addition of the lincosamine-derived 1-deoxy-1-nitropyranoses **22**. The *S*-alkyl derivatives showed a similar activity and specificity as lincomycin. Lipophilic *S*-uloside analogues were two- to fourfold less active than the parent antibiotic, whilst the hydrophilic analogues were inactive.

Introduction. – Lincomycin (**1**; *Fig. 1*), an antibiotic isolated from S*treptomyces lincolnensis* and active against most *Gram*-positive bacteria [1], inhibits peptide-bond formation by selectively binding to bacterial 23S rRNA [2][3]. Lincomycin and clindamycin (=(7*S*)-7-chloro-7-deoxylincomycin; **2**) [4] are in clinical use [5]. Some analogues of lincomycin, such as celesticetin (**3**) [6] and desalicetin (**4**) [7] (*Fig. 1*) were isolated from the culture broth of several microorganisms [8], and many were synthesized [8].

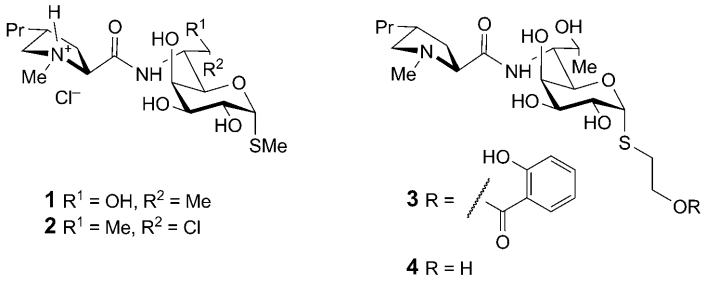

Fig. 1. *Lincomycin* (**1**), *clindamycin* (**2**), *celesticetin* (**3**), *and desalicetin* (**4**)

The known lincomycin analogues may be categorised into three groups, according to whether the glycosyl, the prolinyl, or the amide moiety is modified. Glycosyl analogues were prepared by modifying the substituents, and/or the configuration at C(1–4) and at C(7). The hemiacetal resulting from formal hydrolysis of the thioglycoside and several *O*-glycosides are known, but no biological data were

reported [9]. The diastereoisomeric sulfoxides, (*MIC*[1]) ≥ 100) and the sulfone (*MIC* 50) proved less active against *Staphylococcus aureus* KB 210 than lincomycin (*MIC* 0.78). A few *S*-alkyl analogues of lincomycin were isolated, or synthesized [10]. Celesticetin (**3**) showed a similar antibacterial activity against *S. aureus* UC 80 as lincomycin (*MIC* 1.6 and 0.8, resp.), while desalicetin (**4**), the *O*-deacylation product of celesticetin, proved less active (*MIC* 64). The α-D-thioethyl analogue of lincomycin is as active as lincomycin *in vitro* and *in vivo*. The β-D-thioethyl analogue, one of the very few β-D-configured analogues, was less active against *S. aureus* UC 76, with a *MIC* value of 3.2 that compares to *MIC* of 0.2 for the α-D-anomer and *MIC* of 0.4 for lincomycin. The activity of these analogues shows that both the nature of the substituent at C(1) and the configuration affect the biological activity.

Examination of the crystal structure of the 50S ribosomal subunit of the eubacterium *Deinococcus radiodurans* in complex with clindamycin [4] revealed a cavity around C(1)[2]). This cavity should allow to replace the thiomethyl substituent at C(1) by larger groups that may lead to additional favourable interactions with the nucleobases in the peptidyl transferase cavity, suggesting to synthesize new thioalkyl or thioaryl derivatives. Molecular modelling suggested that both hydrophilic and hydrophobic substituents at C(1) should be considered, with the prospect of forming additional H-bonds and/or hydrophobic interactions with the ribosome.

Ulose analogues of lincomycin, *i.e.,* analogues with two substituents at the anomeric centre, are not known, but may also display a higher activity. Ulose derivatives were prepared from aldoses under mild conditions by *Michael* addition or *Henry* reaction of 1-deoxy-1-nitroaldoses [11]. It appeared of interest to investigate the application of this methodology to lincomycin, and to prepare lincosamine-derived 1-deoxy-1-nitropyranoses. Solvolysis of tertiary nitro ethers was reported [11], and we planned to explore the so far unknown solvolytic cleavage of nitropyranoses by thiols to obtain lincosamine derived *S*-ulosides.

Results and Discussion. – We first aimed at a few representative *S*-aryl and *S*-arylalkyl analogues of lincomycin. The *S*-aryl analogues **11a**–**11c** of lincomycin were synthesized by *S*-glycosylation of the sulfoxides **7**. These were obtained as a 2 : 1 mixture of diastereoisomers[3]) by a high-yielding *O*-silylation of the known azido derivative **5** [12] to **6** (*Scheme 1*) and oxidation of **6** with *m*CPBA at −30°. Glycosylation of arenethiols with **7**, promoted by triflic anhydride and 2,6-di-(*tert*-butyl)-4-methylpyridine [13] gave the desired α-D-thioglycosides **8a**–**8c** as single anomers in yields of 60 to 70% from **6**. The azides **8a**–**8c** were reduced to the amines **9a**–**9c** by a *Staudinger* reaction, followed by hydrolysis [14]. Coupling of the amines with a mixed anhydride derived from propylhygric acid hydrochloride (PHA) [15] led in 60 to 75% yield to the protected amides **10a**–**10c** that were desilylated with $Bu_4NF \cdot 3\ H_2O$ in THF to afford the lincomycin analogues **11a**–**11c** in yields of 70 to 85%.

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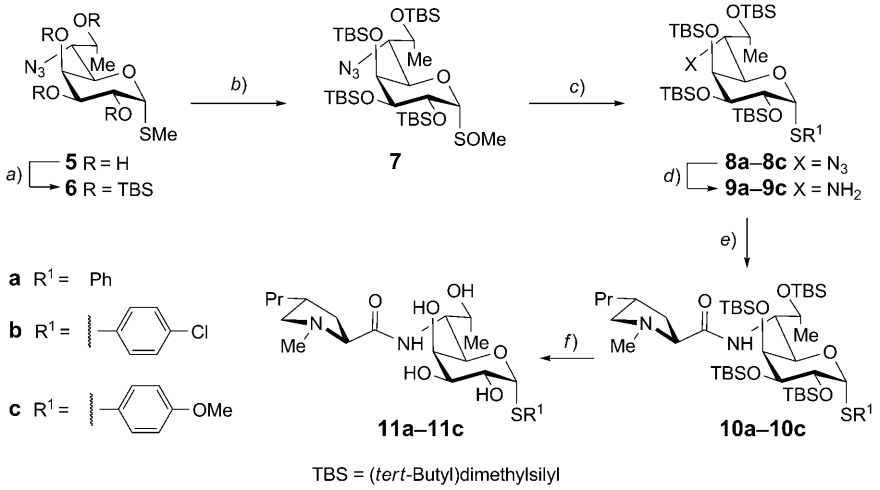
[1]) *MIC* = Minimal inhibitory concentration (μg/ml)

[2]) Molecular modelling was performed with the *Moloc* programme. We thank *Paul Gerber*, *Gerber Molecular Design*, for access to the programme.

[3]) Their configurations were not determined.

Scheme 1



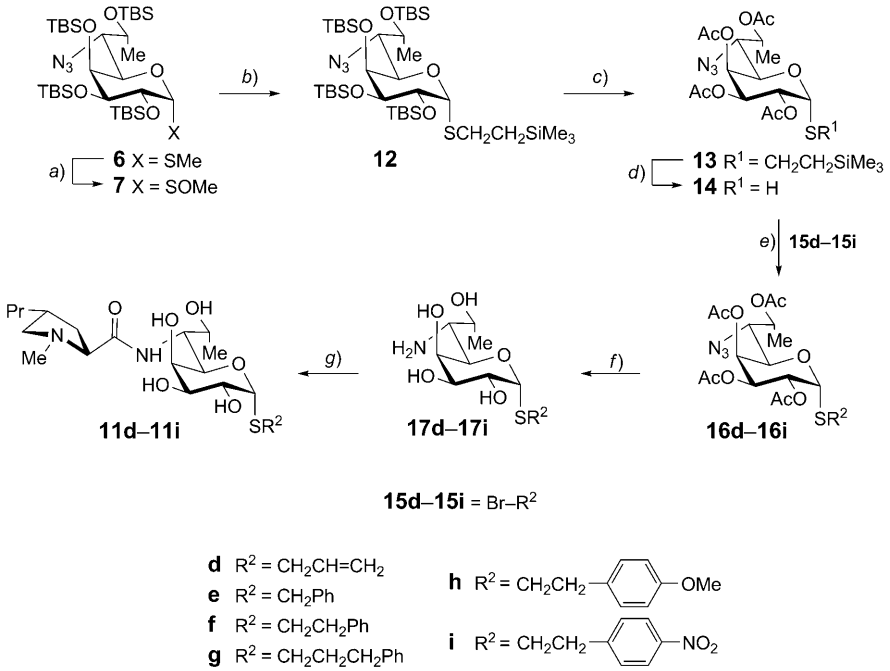
a) TBSOTf (Tf = trifluoromethylsulfonyl), pyridine, 100°; 90%. *b*) *m*-Chloroperbenzoic acid (*m*CPBA), CH_2Cl_2, −30°. *c*) R^1–SH, Tf_2O, 2,6-di-(*tert*-butyl)-4-methylpyridine, 4-Å mol. sieves, CH_2Cl_2, −78°; 70% of **8a**, 65% of **8b**, 60% of **8c**. *d*) Me_3P, NaOH, THF, 50°. *e*) 4-Propylhygric acid (= 1-Methyl-4-propyl-L-proline; PHA) hydrochloride, ClCOOEt, NEt_3, CH_2Cl_2; 75% of **10a**, 70% of **10b**, 60% of **10c** (two steps). *f*) $Bu_4NF \cdot 3\ H_2O$, THF; 67% of **11a**, 85% of **11b**, 80% of **11c**.

The *S*-arylalkyl analogues **11d**–**11i** (*Scheme 2*) were synthesized by *S*-alkylation of the thiol **14**. This intermediate was generated *via* the *S*-glycoside **12**, obtained by glycosylating 2-(trimethylsilyl)ethanethiol with the sulfoxides **7**, to yield 70% of the α-D-thioglycoside **12**. It was selectively *O*-desilylated by treatment with $Bu_4NF \cdot 3\ H_2O$ and acetylated to provide 80% of the tetraacetate **13**. Removal of the 2-(trimethylsilyl)ethyl group required treating **13** with a 1M solution of $Bu_4NF \cdot 3\ H_2O$ in THF that was dried over 4-Å molecular sieves. The resulting thiolate anion was alkylated by the alkyl bromides **15d**–**15i** to yield 75–90% of the α-D-thioglycosides **16d**–**16i**. We chose arylalkyl bromides with different chain lengths and substituted with either an electron-donating or an electron-withdrawing group. We also used this procedure to prepare the *S*-allyl glycoside. Deacetylation and reduction of the N_3 group led to the amines **17d**–**17i** that were treated with PHA methyl ester [16] to afford the lincomycin analogues **11d**–**11i** in yields of 20–35%.

The α-D-configuration of **8a**–**8c**, **12**, and **16d**–**16i** is evidenced by $J(1,2) = 4.8$–5.7 Hz (see *Tables 3* and *5* in the *Exper. Part*). A comparison of the ^{1}H-NMR spectra of the silylated azides and of the acetylated azides (in $CDCl_3$), and of the lincomycin analogues (in CD_3OD) showed that the pyranose ring adopts approximately the expected $^4C_1$ conformation (see *Table 3*–*5* in the *Exper. Part*), $J(1,2)$ of 4.8–5.7 Hz suggesting that the pyranose ring is slightly flattened around C(1)[4]). The conformation of the side chain of the silylated derivatives **6**, **8a**–**8c**, **18**, and **10a**–**10c** and of the acetylated analogues **13** and **16d**–**16i** in $CDCl_3$ solution is evidenced by a large $J(5,6)$

[4]) Typical $J(1,2)$ values for α-D-configured galactopyranosides are ≤ 4 Hz [17].

Scheme 2



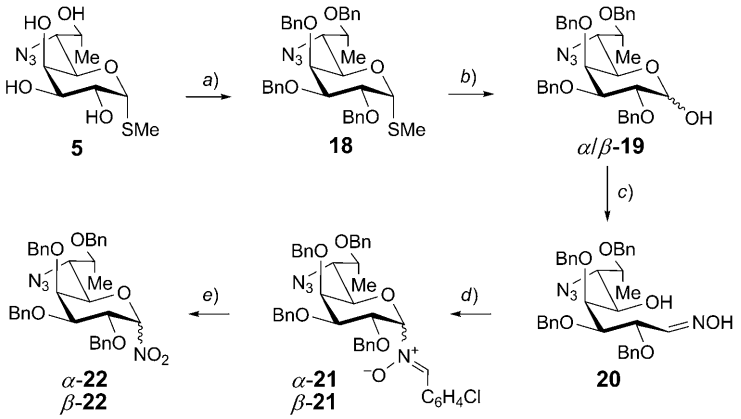
a) *m*CPBA, CH_2Cl_2, $-30°$. *b*) $Me_3SiCH_2CH_2SH$, Tf_2O, 2,6-di-(*tert*-butyl)-4-methylpyridine, 4-Å mol. sieves, CH_2Cl_2, $-78°$; 70% from **6**. *c*) i. $Bu_4NF \cdot 3\,H_2O$, THF; ii. Ac_2O, 4-(Dimethylamino)pyridine (DMAP), Et_3N, CH_2Cl_2; 80%. *d*) 1M Bu_4NF in THF. *e*) **15d**–**15i**, THF; 90% of **16d**, 80% of **16e**, 60% of **16f**, 75% of **16g**, 75% of **16h**, 75% of **16i**. *f*) i. MeONa, MeOH; ii. Me_3P, NaOH, THF, 50°. *g*) PHA methyl ester, MeONa, MeOH, 60°; 35% of **11d**, 36% of **11e**, 20% of **11f**, 27 of **11g**, 20% of **11h**, 20% of **11i** (over three steps).

value of 10.2–10.5 Hz and a small $J(6,7)$ value of 2.1–3.3 Hz as mainly *tg* about C(5)–C(6) and *gt* about C(6)–C(7) [12]. $J(5,6) = 6.6–7.2$ and $J(6,7) = 6.0–6.6$ Hz of the analogues **11a**–**11i** in CD_3OD evidence a *ca.* 1:1 equilibrium of the (5,6)*tg*/(6,7)*gt* and (5,6)*gg*/(6,7)*tg* conformers [12].

To prepare ulose analogues of lincomycin, we aimed at the protected lincosamine-derived 1-deoxy-1-nitropyranoses α-**22**/β-**22**. These anomers were prepared according to a known method [18–20] from the azide **5** that was benzylated to **18** (*Scheme 3*), and subjected to bromolysis [21–23], followed by Ag_2CO_3 promoted hydrolysis of the resulting glycosyl bromide to yield 94% of the hemiacetals **19** (94%) [21–24]. The corresponding oximes (*E*/*Z*)-**20** reacted *via* their hydroxylamine tautomers with 4-chlorobenzaldehyde to give the anomeric glycosyl nitrones α-**21**/β-**21** (α/β 1:3; 84%). Ozonolysis of **21** yielded 84% of the desired 1-deoxy-1-nitropyranoses α-**22**/β-**22** [20].

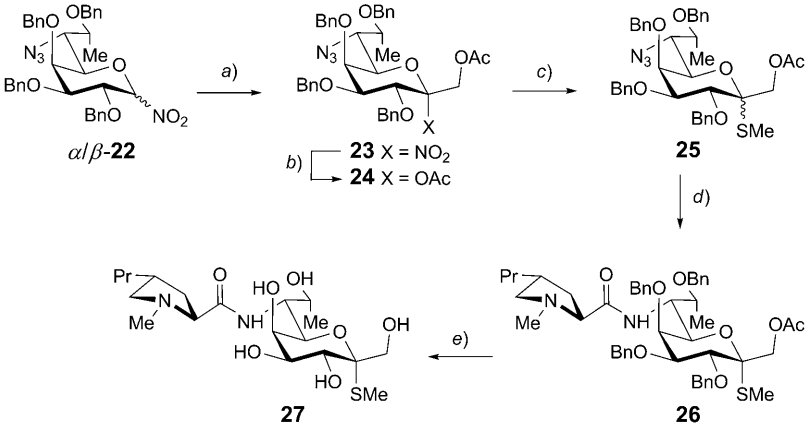
Henry reaction of the nitro aldoses α-**22**/β-**22** with paraformaldehyde gave the nitro acetate **23** (*Scheme 4*), which was partially hydrolysed during workup, and completely

Scheme 3



a) $PhCH_2Br$ (BnBr) NaH, Bu_4NI, DMF; 80%. *b*) i. Br_2, CH_2Cl_2; ii. Ag_2CO_3, acetone; 94%. *c*) $NH_2OH \cdot HCl$, EtONa, EtOH, 60°; 95%. *d*) 4-Chlorobenzaldehyde, CH_2Cl_2, 40°; 24% of α-**21** and 60% of β-**21**. *e*) O_3, CH_2Cl_2, −78°; 18% of α-**22** and 75% of β-**22**.

Scheme 4

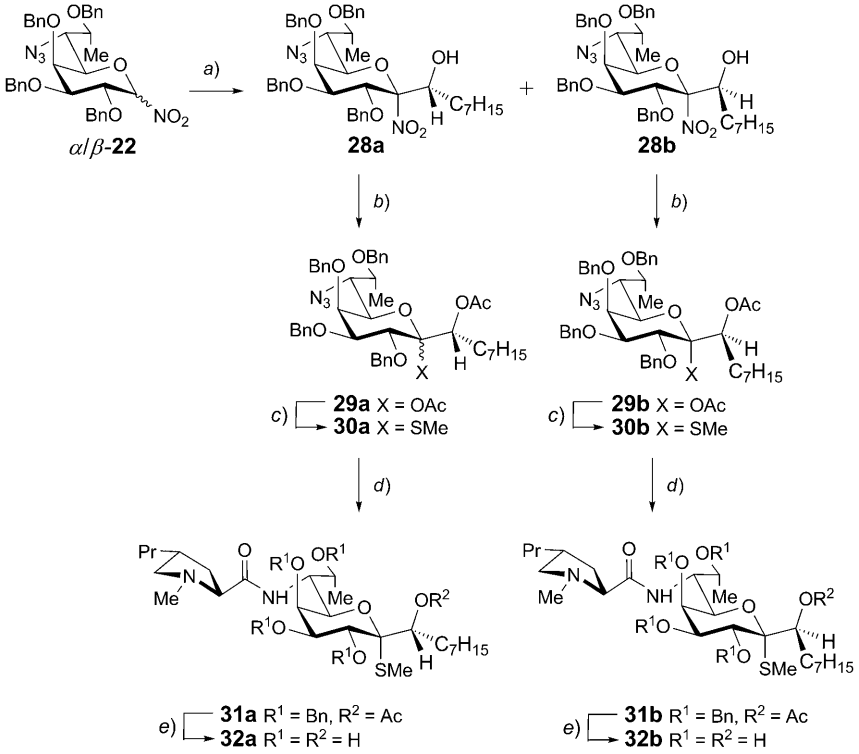


a) $(CH_2O)_n$, 1M Bu_4NF in THF, CH_2Cl_2. *b*) i. 7M HCl, 50°; ii. Ac_2O, DMAP, Et_3N, CH_2Cl_2, 50°; 80% of **24** from **22**. *c*) MeSH, 4-Å mol. sieves, $BF_3 \cdot OEt_2$, CH_2Cl_2, −30°; 57% of α-**25** and 27% of α-**25**/β-**25** 1:1. *d*) i. Me_3P, NaOH, THF, 50°; ii. PHA, EtOCOCl, Et_3N, CH_2Cl_2; 70% of **26**. *e*) Na, NH_3, THF, −78°; 65% of **27**.

hydrolysed by treatment with 7N HCl. The resulting single dihydroxy compound was acetylated to the diacetate **24** (80% from α-**22**/β-**22**). Thioglycosylation of MeSH with **24** afforded a mixture of anomers **25** (α/β 4:1; 84%). *Staudinger* reduction/hydrolysis of α-**25** and coupling with PHA afforded the protected analogue **26** (70%) [25] that was deprotected under *Birch* conditions [26] to **27** (65%).

The analogues **32a**, **32b**, **38a**, and **38b** of lincomycin were synthesised similarly, by deprotonating the nitro ethers α-**22**/β-**22** in DMF with Et_4NOH, and treating the nitronate anions with octanaldehyde or (benzyloxy)acetaldehyde to afford two diastereoisomers each of the nitro alcohols, *viz.* **28a** and **28b**, and **33a** and **33b**, column chromatography providing the pure diastereoisomers (*Scheme 5* and *6*). Unfortunately, all attempts to substitute the NO_2 group of **28a** and **28b** with MeSH, or its derivatives and analogues, such as TMS–SMe, thioacetic acid, and (4-methoxyphenyl)methanethiol, or activating the nitro ether with *Lewis* acids such as $BF_3 \cdot OEt_2$, TMSOTf, $ZnCl_2$, $Zn(OTf)_2$, and $FeCl_3$ were unsuccessful.

Scheme 5

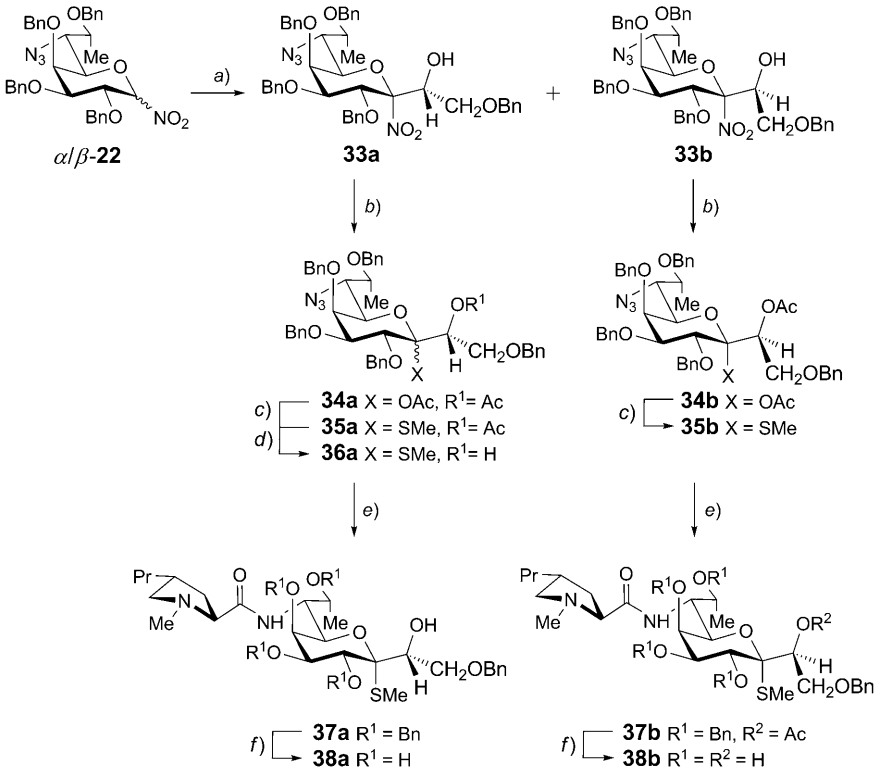


a) Octanal, Et_4NOH, DMF; 53% of **28a** and 15% of **28b**. *b*) i. 7M HCl, 50°; ii. Ac_2O, DMAP, Et_3N, CH_2Cl_2, 50°; 86% of α-**29a**, 87% of **29b**. *c*) MeSH, 4-Å mol. sieves, $BF_3 \cdot OEt_2$, CH_2Cl_2, –30°; 46% of α-**30a** and 23% of β-**30a**; 80% of **30b**. *d*) i. Me_3P, NaOH, THF, 50°; ii. PHA, EtOCOCl, Et_3N, CH_2Cl_2; 80% of **31a** from α-**30a**, 70% of **31b**. *e*) Na, NH_3, THF, –78°; 50% of **32a**, 60% of **32b**.

The nitro alcohols **28a**, **28b**, **33a**, and **33b** were hydrolysed with aqueous HCl to the corresponding diols that were acetylated to the diacetates α-**29a**, **29b**, β-L-**34a**, and **34b**, respectively. The diacetates were transformed into the thioglycosides **30a**, **30b**, **35a**, and **35b** by treatment with MeSH in the presence of $BF_3 \cdot OEt_2$. Thioglycosylation of the acetates α-**29a** and β-L-**34a** gave a mixture of the anomeric thioglycosides **30a** and **35a**, whereas the diastereoisomeric acetates **29b** and **34b** led only to the axial anomer. The

anomers **35a** were deacetylated, and the resulting alcohols **36a** were separated by column chromatography. Reduction of the N_3 group of the thioglycosides α-**30a**, **30b**, **35b**, and β-L-**36a**, and coupling of the resulting amine with PHA led to the protected amides **31a**, **31b**, **37a**, and **37b** that were deprotected to the *C(1)*-disubstituted lincomycin analogues **32a**, **32b**, **38a**, and **38b**.

Scheme 6

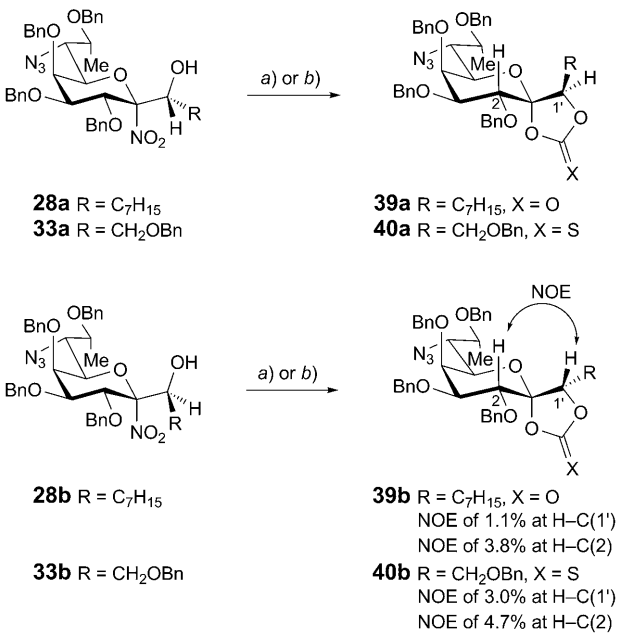


a) 2-(Benzyloxy)acetaldehyde, Et_4NOH, DMF; 70% of **33a** and 20% of **33b**. *b*) i. 7M HCl, 50°; ii. Ac_2O, DMAP, Et_3N, CH_2Cl_2, 50°; 75% of β-L-**34a**, 75% of **34b**. *c*) MeSH, 4-Å mol. sieves, $BF_3 \cdot OEt_2$, CH_2Cl_2, −30°; 65% of **35b**. *d*) MeONa, MeOH; 37% of β-L-**36a** and 30% of α-L-**36a** from β-L-**34a**. *e*) i. Me_3P, NaOH, THF, 50°; ii. PHA, EtOCOCl, Et_3N, CH_2Cl_2; 86% of **37a**, 65% of **37b**. *f*) Na, NH_3, THF, −78°; 55% of **38a**, 60% of **38b**.

To determine the configuration of the nitro alcohols **28a**, **28b**, **33a**, and **33b**, we transformed them into cyclic derivatives (*Scheme 7*). For this, we hydrolyzed the tertiary nitro ethers **28a** and **28b**, and treated the resulting dihydroxy compounds with 1,1′-carbonyldiimidazole to obtain the cyclocarbonates **39a** and **39b**, respectively. As these derivatives did not crystallize, we transformed the dihydroxy compounds resulting from hydrolysis of the nitro ethers **33a** and **33b** into the cyclothiocarbonates **40a** and **40b**, respectively. To our disappointment, the cyclothiocarbonates did not crystallize either. However, NOEs between H−C(2) and H−C(1′) of one of the

diastereoisomers each, **39b** and **40b**, evidenced the (*S*)-configuration at C(1′)[5]). There were no NOEs between H–C(2) and H–C(1′) for **39a** and **40a**, in agreement with the (*R*)-configuration of C(1′).

Scheme 7



a) for **28a** and **28b**: i. 7N HCl, 50°; ii. 1,1′-Carbonyldiimidazole, CH_2Cl_2, 50°; 77% of **39a**; 73% of **39b**. *b*) for **33a** and **33b**: i. 7M HCl, 50°; ii. 1,1′-Thiocarbonyldiimidazole, CH_2Cl_2, 50°; 75% of **40a**, 80% of **40b**.

Michael addition of the nitro ethers α-**22**/β-**22** to acrylonitrile (*Scheme 8*), followed by hydrolysis of the product in a 2M $LiClO_4$ solution in MeCN/H_2O and acetylation of the resulting hemiacetal gave the chain-elongated glycosyl acetate **41** (56%). In agreement with the literature [11], these tertiary nitro ethers were solvolyzed more readily than the products of the *Henry* reaction. Thioglycosylation of **41** with MeSH in the presence of $BF_3 \cdot OEt_2$ afforded the thioglycoside **42** (80%) as a single anomer. Azide reduction, coupling with PHA to the amide **43**, and debenzylation yielded 60% of the lincomycin analogue **44**. *Michael* addition of the nitro ethers α-**22**/β-**22** to methyl acrylate (1M Bu_4NF in THF) proceeded similarly, to afford the expected tertiary nitro ether that was directly subjected to thioglycosylation with MeSH/$BF_3 \cdot OEt_2$ to yield 85% of **45** (*Scheme 8*)[6]). Reduction of the N_3 group of **45**, coupling with PHA to the amide **46**, and debenzylation led to the lincomycin analogue **47** (40%).

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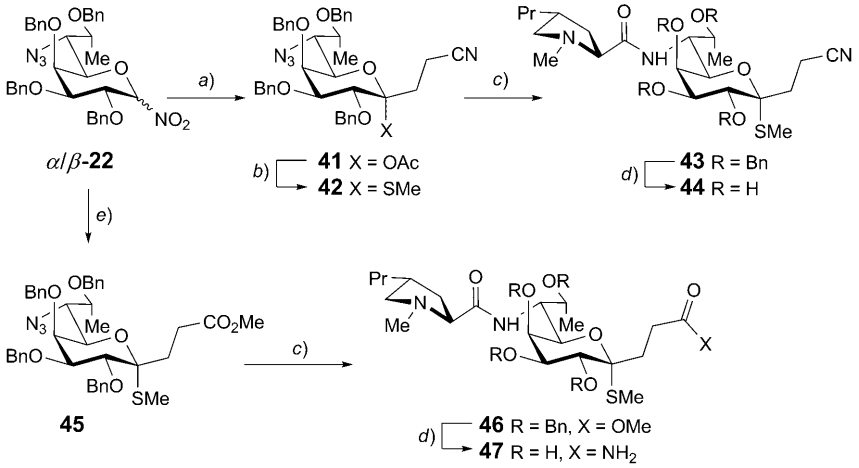
[5]) For **39b**: irradiation at H–C(2), NOE of 1.1% at H–C(1′), and irradiation at H–C(1′), NOE of 3.8% at H–C(2). For **40b**: irradiation at H–C(2), NOE of 3.0% at H–C(1′), and irradiation at H–C(1′), NOE of 4.7% at H–C(2).

[6]) Scouting experiments showed that the analogous thioglycosylation of the addition product to acrylonitrile gave a mixture of compounds.

Scheme 8



a) i. Acrylonitrile, *t*-BuONa, *t*-BuOH/CH_2Cl_2 (6:1); ii. 2M $LiClO_4$, 50°; iii. Ac_2O, DMAP, Et_3N, CH_2Cl_2, 50°; 56%. *b*) MeSH, 4-Å mol. sieves, $BF_3 \cdot OEt_2$, −30°; 80%. *c*) i. Me_3P, NaOH, THF, 50°; ii. PHA, EtOCOCl, Et_3N, CH_2Cl_2; 65% of **43**, 60% of **46**. *d*) Na, NH_3, THF, −78°; 60% of **44**, 40% of **47**. *e*) i. Methyl acrylate, 1M Bu_4NF in THF, THF; ii. MeSH, 4-Å mol. sieves, $BF_3 \cdot OEt_2$, −30°; 85%.

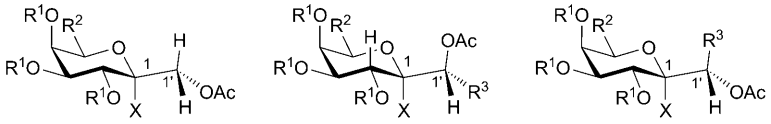
Remarkably, $J(1,2)$ of β-**22** (5.4 Hz) is smaller than $J(1,2)$ for α-**22** (6.0 Hz), due to flattening of the pyranose ring around C(1), similarly as for analogous nitropyranoses [27]. The anomeric configuration is, however, evidenced by the specific rotations that are in agreement with *Hudson*'s rule (*cf.* [27]), and the α-D-configuration is evidenced by the deshielding of H−C(3) and H−C(5) by the pseudoaxial NO_2 group (see *Table 6* in *Exper. Part*)[7]).

The coupling constants compiled in *Tables 7–11* in the *Exper. Part* confirm the $^4C_1$ conformation of the pyranose ring of the protected and unprotected lincomycin analogues in $CDCl_3$ or in CD_3OD. The ^{1}H-NMR spectra also evidence a mixture of the (5,6)*tg*/(6,7)*gt* and (5,6)*gg*/(6,7)*tg* conformers of the lincomycin analogues in $CDCl_3$ and CD_3OD, respectively, while the benzylated azides **18**–**25**, α-**29a**, **29b**, α-**30a**, **30b**, α-**34a**, **34b**, **35b**, β-L-**36a**, **41**, **42**, and **45** that cannot form a H-bond with the axial C(4)OR adopt a (5,6)*tg*/(6,7)*gt* conformation (see *Tables 7–9* in the *Exper. Part*) [12]. For the benzylated lincomycin analogues, the ratio of the two conformers is *ca.* 1:1, except for **26**, **31b**, and **37b** where the (5,6)*gg*/(6,7)*tg* conformer predominates. For the deprotected lincomycins, a 1:1 ratio of conformers is observed for **32b** and **47**, while the (5,6)*gg*/(6,7)*tg* conformer is favoured for **32a**, **38a**, and **44**, and the (5,6)*tg*/(6,7)*gt* conformation is preferred by **27** (*Table 10* in *Exper. Part*).

The substituents at C(1) of **24**–**27**, **29b**–**32b**, and **34b**–**38b** are expected to adopt the *gt* conformation about C(1′)−C(1), while a *gg* conformation is expected for the diastereoisomers α-**29a**, α-**30a**, **31a**, **32a**, α-**34a**–α-**36a**, **37a**, and **38a** (*Fig. 2*). These conformers avoid a 1,3-diaxial interaction between O−C(2), and O−C(1′) or C−C(1′),

[7]) Similar results were observed in the synthesis of 4,6-*O*-benzylidene-1-deoxy-1-nitro-α/β-D-glucopyranose [27].

and are favoured by the *gauche* effect. H–C(2) is expected to be more deshielded when O–C(1′) is *gg*-oriented, on account of the 1,5 interactions between H–C(2) and O–C(1′). However, this effect is observed only for **37a**/**37b** ($\Delta\delta = 0.14$ ppm) and **32a**/**32b** ($\Delta\delta = 0.49$ ppm). An intramolecular H-bond of HO–C(1′) to BnO–C(2) of the thioglycoside α-D-**36a** is evidenced by a 1.9 Hz *W*-coupling between HO–C(1′) and H_a–C(2′) [28][29].



24–27
gt

29a–32a
34a–38a
gg

29b–32b
34b–38b
gt

Fig. 2. *Favoured conformers of the chain at C(1) of the axial anomers*

Antibacterial Activity. – The antibacterial activity of the thioethers **11a**–**11i** was studied by determining their minimal inhibitory concentrations (*MIC*s) against both lincomycin-sensitive and lincomycin-resistant *Mycobacterium smegmatis* strains in at least three independent broth microdilution experiments, as described in [30].

Growth of wild-type *M. smegmatis* cells was completely inhibited at lincomycin concentrations of 4–8 μg/ml, while *M. smegmatis* cells with an adenine-to-guanine mutation at 23S rRNA position 2058 [31–33] were resistant to the drug (see *Table 1*). Similarly as lincomycin, all 1-de(methylsulfanyl)-1-(alkylsulfanyl)lincomycins were active against the wild type and inactive towards the mutant A2058G (see *Table 1*). The electronic nature of the substituent of the phenyl ring and the number of CH_2 groups between the S-atom and the phenyl ring has little effect on the drug's activity and specificity.

Table 1. *Antibacterial Activity of Thioether Analogues of Lincomycin*[a])

	Wild type	Mutant A2058G
Lincomycin	4–8	>512
11a	4	512
11b	4	256
11c	4	512
11d	4	512
11e	4–8	>256
11f	2–4	512
11g	8	>256
11h	4	≥256
11i	16	≥256

[a]) Antibacterial activity as minimal inhibitory concentrations (*MIC* [μg/ml]).

The hydrophilic *S*-uloside analogues, *i.e.,* **27**, **38a**, **38b**, and **47**, were inactive against the wild type (see *Table 2*). The lipophilic *S*-uloside analogues, *i.e.*, **32a**, **32b**, and **44**,

proved less active (two- to fourfold lower) than the parent antibiotic. All *S*-uloside analogues of lincomycin were inactive against A2058G mutant ribosomes. Finally, we found that the configuration at C(1′) of the analogues **32a**, **32b**, **38a**, and **38b** had a small influence on the activity towards the wild type.

Table 2. *Antibacterial Activity of* C(1)-*Substituted Analogues of Lincomycin*[a])

	Wild type	Mutant A2058G
Lincomycin	4–8	>512
27	64–128	>512
32a	8–16	128–256
32b	16	128–256
38a	128	≥512
38b	256	>256
44	16–32	≥512
47	256–512	≥512

[a]) Antibacterial activity as minimal inhibitory concentrations (*MIC* [μg/ml]).

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Experimental Part

General. Solvents were distilled: Et_2O from Na/benzophenone, MeOH, CH_2Cl_2, Et_3N from CaH_2. Reactions were carried out under N_2, unless stated otherwise. Qual. TLC: precoated silica-gel glass plates (*Merck* silica gel 60 F_{254}); detection by heating with 'mostain' (400 ml of 10% H_2SO_4 soln., 20 g of $(NH_4)_6Mo_7O_{24}\cdot 6\,H_2O$, 0.4 g of $Ce(SO_4)_2$). Flash chromatography (FC): silica gel *Merck* (0.04–0.063 mm) using distilled technical solvents as eluent. M.p.: uncorrected. Optical rotation ($[\alpha]_D^{25}$): 1-dm cell, at 589 nm and 25°; *c* concentration in g/100 ml. FT-IR Spectra: neat (ATR), absorption in cm^{-1}. ^1H- and ^{13}C-NMR spectra: chemical shifts δ in ppm rel. to TMS as external standard; coupling constants *J* in Hz. HR-MALDI-MS and HR-ESI-MS: in gentisic acid (=2,5-dihydroxybenzoic acid (DHB)) or 3-hydroxypropionaldehyde (3-PHA) matrix.

Methyl 6-Azido-2,3,4,7-tetrakis-O-*[*(tert-*butyl)dimethylsilyl]-6,8-dideoxy-1-thio*-D-erythro-α-D-galacto-*octopyranoside* (**6**). A soln. of **5** (1 g, 3.6 mmol) and DMAP (45 mg, 0.36 mmol) in pyridine (20 ml) was treated with TBDMSOTf (6.6 ml, 28.7 mmol), kept at 110° for 12 h, cooled to 25°, and evaporated. FC (hexane/CH_2Cl_2 98:2 → 4:1) gave **6** (2.38 g, 90%). Colourless oil. R_f (hexane/CH_2Cl_2 4:1) 0.53. $[\alpha]_D^{25} = +109.3$ ($c = 1.1$, $CHCl_3$). IR (ATR): 2953*w*, 2929*w*, 2887*w*, 2857*w*, 2106*m*, 1472*w*, 1463*w*, 1388*w*, 1361*w*, 1342*w*, 1321*m*, 1293*w*, 1252*m*, 1166*w*, 1137*m*, 1091*m*, 1066*m*, 1015*w*, 1005*w*, 989*w*, 962*w*, 935*w*, 887*m*, 871*m*, 858*m*, 827*s*, 810*m*, 773*s*, 726*w*, 686*w*. ^1H-NMR (300 MHz, $CDCl_3$; assignment based on selective homodecoupling experiments): see *Table 3*; additionally, 2.01 (*s*, MeS); 0.95, 0.93, 0.92, 0.89 (4*s*, 4 Me_3CSi); 0.21–0.07 (several *s*, 4 Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$; assignment based on a HSQC spectrum): see *Table 3*; additionally, 26.70, 26.37, 26.27, 25.80 (4*q*, 4 *Me*$_3$C); 18.98, 18.51, 18.48, 18.05 (4*s*, 4 Me$_3$*C*); 13.61 (*q*, MeS); −3.05 to −5.04 (several *q*, 4 Me_2Si). HR-ESI-MS: 758.4241 (100, $[M + Na]^+$, $C_{33}H_{73}N_3NaO_5SSi_4^+$; calc. 758.4240). Anal. calc. for $C_{33}H_{73}N_3O_5SSi_4$ (736.35): C 53.83, H 9.99, N 5.71; found: C 54.06, H 9.91, N 5.55.

General Procedure for Thioglycosylation (*GP 1*). At −30°, a 1M soln. of **6** in CH_2Cl_2 was treated dropwise over 4 h with 70% *m*CPBA (1 equiv.), then with Me_2S (1 equiv.) and with sat. aq. $NaHCO_3$ soln. The layers were separated, and the aq. layer was extracted with CH_2Cl_2. The combined org. layers were dried ($MgSO_4$) and evaporated, to afford the sulfoxides **7**.

Table 3. *Selected ^{1}H-NMR Chemical Shifts* [ppm] *and Coupling Constants* [Hz], *and ^{13}C-NMR Chemical Shifts* [ppm] *of the Silylated Azides* **6** *and* **8a**–**8d** *and of the Silylated Pyrrolidine-2-carboxamides* **10a**–**10c** *in $CDCl_3$*[a])

	6	**8a**	**8b**	**8c**	**12**	**10a**	**10b**	**10c**
H–C(1)	5.07	5.76	5.68	5.54	5.20	5.78	5.73	5.62
H–C(2)	4.28	4.43	4.40	4.36	4.29	4.48	4.47	4.45
H–C(3)	3.66	3.82	3.76	3.76	3.67	3.73	3.71	3.70
H–C(4)	4.05	4.10	4.07	4.05	4.04	3.96	3.96	3.96
H–C(5)	3.56	3.57	3.50	3.57	3.57	3.89	3.90	3.92
H–C(6)	3.97	3.92	3.89	3.89	3.95	4.29	4.26	4.29
H–C(7)	4.22	4.75	3.88	3.95	4.20	3.94	3.91	3.95
H_3C(8)	1.15	0.76	0.75	0.91	1.14	0.58	0.61	0.74
J(1,2)	5.1	4.8	4.8	5.1	5.1	5.7	5.4	5.4
J(2,3)	9.9	9.6	9.6	9.6	9.9	9.6	9.9	9.9
J(3,4)	2.1	1.8	1.8	1.8	1.8	1.8	1.8	1.8
J(5,6)	10.5	10.5	10.2	10.5	10.5	10.5	10.5	10.2
J(6,7)	2.1	2.1	2.4	2.1	2.4	2.7	3.0	3.3
J(7,Me)	6.0	6.3	6.0	6.3	6.0	6.0	6.3	6.3
C(1)	89.72	88.34	88.67	90.17	87.11	89.04	89.30	90.79
C(2)	69.37	69.27	69.30	69.53	69.12	69.15	69.39	69.36
C(3)	73.26	73.32	73.38	73.39	73.36	74.33	74.28	74.15
C(4)	72.43	72.19	72.19	72.27	72.44	72.20	72.16	72.15
C(5)	70.96	71.31	71.60	71.27	70.83	73.10	73.19	72.84
C(6)	64.48	64.30	64.30	64.63	64.47	52.06	52.27	52.10
C(7)	69.16	69.14	69.17	69.15	69.12	67.03	67.06	66.93
C(8)	16.48	15.85	16.11	16.50	16.50	15.86	16.12	16.11

[a]) $J(4,5) < 1.5$ Hz (line broadening).

A 1M soln. of the sulfoxides **7** in Et_2O was treated with 2,6-di(*tert*-butyl)-4-methylpyridine (2 equiv.) and 4-Å mol. sieves, stirred for 30 min at 25°, cooled to −78°, treated with Tf_2O (1.1 equiv.), and stirred for 15 min. After the addition of the thiol (2 equiv.), the mixture was warmed to 0° over 30 min, stirred for 2 h, treated with sat. aq. $NaHCO_3$ soln., and filtered over *Celite*. The layers were separated, and the aq. layer was extracted with Et_2O. The combined org. layers were dried ($MgSO_4$) and evaporated to yield the crude *S*-glycosides.

Phenyl 6-Azido-2,3,4,7-tetrakis-O-*[(*tert-*butyl)dimethylsilyl]-6,8-dideoxy-1-thio*-D-erythro-*α*-D-galacto-*octopyranoside* (**8a**). According to *GP 1*, **7** obtained from 100 mg (0.13 mmol) of **6** was treated with 17 µl (0.26 mmol) of PhSH. FC (hexane/CH_2Cl_2 98:2 → 4:1) gave **8a** (80 mg, 70%). Colourless oil. R_f (hexane/CH_2Cl_2 4:1) 0.64. $[\alpha]_D^{25} = +114.3$ ($c = 1.0$, $CHCl_3$). IR (ATR): 2953*w*, 2929*w*, 2887*w*, 2857*w*, 2107*m*, 1585*w*, 1472*w*, 1463*w*, 1439*w*, 1388*w*, 1361*w*, 1342*w*, 1253*m*, 1166*w*, 1136*m*, 1091*m*, 1068*m*, 1023*w*, 1005*w*, 990*w*, 964*m*, 936*w*, 888*s*, 870*m*, 857*m*, 827*s*, 810*m*, 774*s*, 734*s*, 687*m*. ^{1}H-NMR (300 MHz, $CDCl_3$; assignments based on selective homodecoupling experiments): see *Table 3*; additionally, 7.37–7.32 (*m*, 2 arom. H); 7.29–7.23 (*m*, 2 arom. H); 7.20–7.14 (*m*, 1 arom. H); 0.98, 0.94, 0.88 (3*s*, 4 Me_3CSi); 0.25–0.02 (several *s*, 4 Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 3*; additionally, 135.56 (*s*); 128.78 (*d*, 2 C); 128.59 (*d*, 2 C); 125.63 (*d*); 26.52, 26.16, 26.11, 25.58 (4*q*, 4 *Me*$_3$C); 18.76, 18.63, 18.16, 17.79 (4*s*, 4 Me_3*C*); −3.35 to −5.16 (several *q*, 4 Me_2Si). HR-ESI-MS: 820.4400 (100, $[M + Na]^+$, $C_{38}H_{75}N_3NaO_5SSi_4^+$; calc. 820.4397).

4-Chlorophenyl 6-Azido-2,3,4,7-tetrakis-O-*[(*tert-*butyl)dimethylsilyl]-6,8-dideoxy-1-thio*-D-erythro-*α*-D-galacto-*octopyranoside* (**8b**). According to *GP 1*, **7** obtained from 150 mg (0.20 mmol) of **6** was *S*-glycosylated with 58 mg (0.40 mmol) of 4-chlorothiophenol. FC (hexane/CH_2Cl_2 98:2 → 4:1) gave **8b** (110 mg, 65%). Colourless oil. R_f (hexane/CH_2Cl_2 4:1) 0.64. $[\alpha]_D^{25} = +99.7$ ($c = 1.1$, $CHCl_3$). IR (ATR):

2953*w*, 2929*w*, 2895*w*, 2857*w*, 2107*m*, 1472*w*, 1463*w*, 1389*w*, 1361*w*, 1342*w*, 1253*m*, 1167*w*, 1136*m*, 1092*m*, 1069*m*, 1012*w*, 990*w*, 963*m*, 936*w*, 887*s*, 869*m*, 856*m*, 827*s*, 810*s*, 773*s*, 733*m*, 684*m*, 665*m*. ^{1}H-NMR (300 MHz, $CDCl_3$; assignments based on selective homodecoupling experiments): see *Table 3*; additionally, 7.27–7.19 (*m*, 4 arom. H); 0.95, 0.91, 0.86 (3*s*, 4 *Me*$_3$C); 0.22–0.02 (several *s*, 4 Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 3*; additionally, 134.17 (*s*); 131.57 (*s*); 129.93 (*d*, 2 C); 128.69 (*d*, 2 C); 26.65, 26.29, 26.22, 25.72 (4*q*, 4 *Me*$_3$C); 18.92, 18.79, 18.32, 17.99 (4*s*, 4 Me_3C); −3.15 to −5.09 (several *q*, 4 Me_2Si). HR-ESI-MS: 854.4014 (60, $[M + Na]^+$, $C_{38}H_{75}N_3ClNaO_5SSi_4^+$; calc. 854.4007).

4-Methoxyphenyl 6-Azido-2,3,4,7-tetrakis-O-*[(*tert*-butyl)dimethylsilyl]-6,8-dideoxy-1-thio*-D-erythro-α-D-galacto-*octopyranoside* (**8c**). According to *GP 1*, **7** obtained from 150 mg (0.20 mmol) of **6** was treated with 49 µl (0.40 mmol) of 4-methoxythiophenol. FC (hexane/CH_2Cl_2 98:2 → 4:1) gave **8c** (100 mg, 60%). Colourless oil. R_f (hexane/CH_2Cl_2 4:1) 0.42. $[\alpha]_D^{25} = +94.7$ ($c = 1.0$, $CHCl_3$). IR (ATR): 2953*w*, 2929*w*, 2895*w*, 2857*w*, 2107*m*, 1594*m*, 1572*w*, 1494*w*, 1494*m*, 1471*w*, 1463*w*, 1441*w*, 1388*w*, 1361*w*, 1342*w*, 1285*w*, 1246*m*, 1168*w*, 1136*m*, 1091*m*, 1068*m*, 1036*w*, 1005*w*, 990*w*, 964*m*, 936*w*, 888*m*, 871*m*, 857*m*, 825*s*, 773*s*, 733*m*, 685*m*, 665*w*, 640*w*, 628*w*. ^{1}H-NMR (300 MHz, $CDCl_3$; assignments based on selective homodecoupling experiments): see *Table 3*; additionally, 7.28 (*m*, 2 arom. H); 6.81 (*m*, 2 arom. H); 3.78 (*s*, MeO); 0.95, 0.94, 0.93, 0.86 (4*s*, 4 Me_3CSi); 0.22 to −0.01 (several *s*, 4 Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 3*; additionally, 158.37 (*s*); 131.71 (*s*); 125.86 (*d*, 2 C); 114.31 (*d*, 2 C); 55.28 (*s*, MeO); 26.65, 26.29, 25.73 (3*q*, 4 *Me*$_3$C); 18.92, 18.80, 28.35, 17.96 (4*s*, 4 Me_3C); −3.13 to −5.12 (several *q*, 4 Me_2Si). HR-ESI-MS: 850.4499 (100, $[M + Na]^+$, $C_{39}H_{77}N_3NaO_6SSi_4^+$; calc. 850.4502).

2-(Trimethylsilyl)ethyl 6-Azido-2,3,4,7-tetrakis-O-*[(*tert*-butyl)dimethylsilyl]-6,8-dideoxy-1-thio*-D-erythro-α-D-galacto-*octopyranoside* (**12**). According to *GP 1*, **7** obtained from 1.47 g (2.01 mmol) of **6** was treated with 645 µl (4.02 mmol) of 2-(trimetrhylsilyl)ethanethiol. FC (hexane/CH_2Cl_2 98:2 → 4:1) gave **12** (1.16 g, 70%). Colourless oil. R_f (hexane/CH_2Cl_2 4:1) 0.65. $[\alpha]_D^{25} = +78.6$ ($c = 0.89$, $CHCl_3$). IR (ATR): 2953*w*, 2929*w*, 2896*w*, 2857*w*, 2107*m*, 1472*w*, 1463*w*, 1388*m*, 1361*w*, 1341*w*, 1250*m*, 1164*w*, 1136*m*, 1091*m*, 1066*m*, 1005*w*, 989*w*, 967*m*, 935*w*, 888*m*, 857*m*, 827*s*, 810*s*, 773*s*, 688*w*. ^{1}H-NMR (300 MHz, $CDCl_3$; assignments based on selective homodecoupling experiments): see *Table 3*; additionally, 2.51–2.40 (*m*, CH_2S); 0.95, 0.93, 0.89 (3*s*, 4 *Me*$_3$C); 0.90–0.70 (*m*, Me_3SiCH_2); 0.21–0.07 (several *s*, 4 Me_2Si); 0.01 (*s*, Me_3Si). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 3*; additionally, 26.66, 26.34, 26.30, 25.76 (4*q*, 4 *Me*$_3$C); 25.88 (*t*, CH_2S); 18.93, 18.81, 18.40, 17.99 (4*s*, 4 Me_3C); 17.31 (*t*, Me_3SiCH_2); −1.76 (*q*, Me_3Si); −3.13 to −5.12 (several *q*, 4 Me_2Si). HR-ESI-MS: 844.4791 (100, $[M + Na]^+$, $C_{37}H_{83}N_3NaO_5SSi_5^+$; calc. 844.4792).

General Procedure for Coupling of the Lincosamine Derivatives with Propyl Hygric Acid (*GP 2*). A 0.03M soln. of the azido derivative (1 equiv.) in THF/0.1N NaOH 4:1 was treated with 1M PMe_3 in THF (1.5 equiv.), stirred for 4–8 h at 50°, and evaporated. A soln. of the residue in CH_2Cl_2 was washed with H_2O and brine, and the org. layer was dried ($MgSO_4$) and evaporated to provide the corresponding amine.

A 0.03M suspension of PHA (1.3 equiv.) in CH_2Cl_2 was treated with Et_3N (4 equiv.), followed by ClCOOEt (1.1 equiv.), stirred at 25° for 1 h, and treated with a 0.1M soln. of the amine in CH_2Cl_2. The soln. was stirred for 1 h at 25° and evaporated to afford the crude amide.

Phenyl 2,3,4,7-Tetrakis-O-*[(*tert*-butyl)dimethylsilyl]-6,8-dideoxy-6-[(2*S*,4*R*)-1-methyl-4-propylpyrrolidine-2-carboxamido]-1-thio*-D-erythro-α-D-galacto-*octopyranoside* (**10a**). According to *GP 2,* 68 mg (0.08 mmol) of **8a** and FC of the crude amide (hexane/AcOEt 98:2 → 9:1) gave **10a** (60 mg, 75%). Colourless oil. R_f (hexane/AcOEt 95:5) 0.23. $[\alpha]_D^{25} = +98.3$ ($c = 0.62$, $CHCl_3$). IR (ATR): 2953*m,* 2928*m*, 2856*m*, 2787*w*, 1695*m*, 1510*w*, 1472*w*, 1388*w*, 1361*w*, 1303*w*, 1253*m*, 1144*m*, 1090*m*, 1069*m*, 1026*w*, 991*m*, 1005*w*, 963*m*, 890*m*, 866*m*, 835*s*, 776*s*, 737*w*, 687*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 3*; additionally, 7.38–7.10 (*m*, 5 arom. H, NH); 3.16–3.02 (*m*), 2.84 (*dd*, $J = 10.5, 5.2$) (2 H of prolinyl); 2.33 (*s*, MeN); 2.09–1.70 (*m*, 4 H); 1.32–1.23 (*m*, $MeCH_2CH_2$); 0.97, 0.93, 0.90, 0.80 (4*s*, 4 Me_3C); 0.58 (*d*, $J = 6.0$, $MeCH_2CH_2$); 0.16 to −0.03 (*m*, 4 Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 3*; additionally, 174.30 (*s*, C=O); 136.73 (*s*); 128.66 (*d*, 2 C); 127.82 (*d*, 2 C); 125.26 (*d*); 69.44 (*d*, C(2) of prolinyl); 62.85 (*t*, C(5) of prolinyl); 41.67 (*d*, MeN); 37.99 (*d*, C(4) of prolinyl); 37.55 (*t*, C(3) of prolinyl); 35.87 (*t*, $MeCH_2CH_2$); 26.54, 26.48, 26.15, 25.66 (4*q*, 4 *Me*$_3$C); 21.58 (*t*, $MeCH_2CH_2$); 18.85, 18.20, 17.85 (3*s*, 4 Me_3C); 14.37 (*q*, $MeCH_2CH_2$); −3.15 to −5.08 (several *q*, 4 Me_2Si)). HR-ESI-MS: 925.5838 (100, $[M + H]^+$, $C_{47}H_{93}N_2O_6SSi_4^+$; calc. 925.5826).

4-Chlorophenyl 2,3,4,7-Tetrakis-O-*[(*tert-*butyl)dimethylsilyl]-6,8-dideoxy-6-[(2*S*,4*R*)-1-methyl-4-propylpyrrolidine-2-carboxamido]-1-thio*-D-erythro-α-D-galacto-*octopyranoside* (**10b**). According to *GP 2*, 110 mg (0.13 mmol) of **8b** and FC of the crude amide (hexane/AcOEt 98:2 → 9:1) gave **10b** (90 mg, 70%). Colourless oil. R_f (hexane/AcOEt 95:5) 0.26. $[\alpha]_D^{25} = +185.3$ ($c = 1.6$, $CHCl_3$). IR (ATR): 2953*m*, 2928*m*, 2892*w*, 2856*m*, 2787*w*, 1651*s*, 1509*w*, 1472*s*, 1463*w*, 1389*w*, 1361*w*, 1304*w*, 1252*m*, 1144*m*, 1094*s*, 1069*m*, 1010*w*, 990*w*, 963*m*, 887*m*, 865*m*, 834*s*, 811*m*, 775*s*, 732*w*, 669*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 3*; additionally, 7.30–7.19 (*m*, 4 arom. H, NH); 3.10 (br. *dd*, *J* = 7.5, 5.1), 2.85 (*dd*, *J* = 10.5, 4.5) (2 H of prolinyl); 2.33 (*s*, MeN); 2.09–1.88 (*m*, 3 H); 1.84–1.70 (*m*, 1 H); 1.32–1.18 (*m*, $MeCH_2CH_2$); 0.97, 0.93, 0.89, 0.81 (4*s*, 4 Me_3CSi); 0.16 to −0.01 (*m*, 4 Me_2Si, $MeCH_2CH_2$). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 3*; additionally, 174.23 (*s*, C=O); 135.29 (*s*); 131.06 (*s*); 129.91 (*d*, 2 C); 128.68 (*d*, 2 C); 69.39 (*d*, C(2) of prolinyl); 62.88 (*t*, C(5) of prolinyl); 41.78 (*q*, MeN); 38.09 (*d*, C(4) of prolinyl); 37.63 (*t*, C(3) of prolinyl); 35.92 (*t*, $MeCH_2CH_2$); 26.63, 26.55, 26.22, 25.75 (4*q*, Me_3C); 21.71 (*t*, $MeCH_2CH_2$); 18.95, 18.30, 17.90 (3*s*, 4 Me_3C); 14.50 (*q*, $MeCH_2CH_2$); −3.02 to −4.92 (8*q*, 4 Me_2Si). HR-ESI-MS: 959.5436 (100, $[M + H]^+$, $C_{47}H_{92}N_2ClO_6SSi_4^+$; calc. 959.5436).

4-Methoxyphenyl 2,3,4,7-Tetrakis-O-*[(*tert-*butyl)dimethylsilyl]-6,8-dideoxy-6-[(2*S*,4*R*)-1-methyl-4-propylpyrrolidine-2-carboxamido]-1-thio*-D-erythro-α-D-galacto-*octopyranoside* (**10c**). According to *GP 2*, 100 mg (0.12 mmol) of **8c** and FC of the crude amide (hexane/AcOEt 98:2 → 9:1) gave **10c** (70 mg, 60%). Colourless oil. R_f (hexane/AcOEt 95:5) 0.20. $[\alpha]_D^{25} = +147.3$ ($c = 0.98$, $CHCl_3$). IR (ATR): 2953*m*, 2928*m*, 2856*w*, 2787*w*, 1694*m*, 1594*m*, 1509*w*, 1494*m*, 1471*m*, 1463*m*, 1388*w*, 1361*m*, 1284*w*, 1247*s*, 1173*w*, 1144*m*, 1093*m*, 1069*m*, 1034*w*, 1005*w*, 991*w*, 963*m*, 890*m*, 866*m*, 835*s*, 775*s*, 724*w*, 669*w*, 640*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 3*; additionally, 7.34–7.22 (*m*, 2 arom. H, NH); 6.84–6.78 (*m*, 2 arom. H); 3.79 (*s*, MeO); 3.11 (br. *d*, *J* = 7.5, 4.8), 2.86 (*dd*, *J* = 10.8, 4.5) (2 H of prolinyl); 2.35 (*s*, MeN); 2.05–1.99 (*m*, 3 H); 1.84–1.72 (*m*, 1 H); 1.32–1.20 (*m*, $MeCH_2CH_2$); 0.96, 0.93, 0.91, 0.81 (4*s*, 4 Me_3C); 0.16 to −0.01 (*m*, 4 Me_2Si, $MeCH_2CH_2$). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 3*; additionally, 174.21 (*s*, C=O); 157.97 (*s*); 130.13 (*s*); 127.20 (*d*, 2 C); 114.29 (*d*, 2 C); 69.36 (*d*, C(2) of prolinyl); 62.75 (*t*, C(5) of prolinyl); 55.18 (*q*, MeO); 41.60 (*q*, MeN); 37.90 (*d*, C(4) of prolinyl); 37.42 (*t*, C(3) of prolinyl); 35.75 (*t*, $MeCH_2CH_2$); 26.41, 26.35, 26.06, 25.55 (4*q*, Me_3C); 21.47 (*t*, $MeCH_2CH_2$); 18.73, 18.09, 17.75 (3*s*, 4 Me_3C); 14.26 (*q*, $MeCH_2CH_2$); −3.24 to −5.15 (several *q*, 4 Me_2Si). HR-ESI-MS: 955.5928 (100, $[M + H]^+$, $C_{48}H_{95}N_2O_7SSi_4^+$; calc. 955.5932).

General Procedure for the Desilylation (*GP 3*). A 1M soln. of the silyl ether in THF was treated with $Bu_4NF \cdot 3\,H_2O$ (6 equiv.), stirred at 25° for 24 h, and evaporated to afford the corresponding crude alcohol.

*Phenyl 6,8-Dideoxy-6-[(2*S*,4*R*)-1-methyl-4-propylpyrrolidine-2-carboxamido]-1-thio*-D-erythro-α-D-galacto-*octopyranoside* (**11a**). The crude alcohol, obtained from 52 mg (0.06 mmol) of **10a** according to *GP 3*, was purified by FC (AcOEt/MeOH 98:2 → 4:1) to give **11a** (19 mg, 67%). Colourless oil. R_f (AcOEt/MeOH 9:1) 0.31. $[\alpha]_D^{25} = +169.5$ ($c = 0.73$, MeOH). IR (ATR): 3320*m* (br.), 2955*w*, 2923*m*, 2871*w*, 2852*w*, 2789*w*, 1646*s*, 1584*w*, 1521*m*, 1480*w*, 1455*w*, 1438*w*, 1379*w*, 1306*w*, 1243*w*, 1209*w*, 1180*w*, 1083*s*, 1052*s*, 1026*w*, 992*m*, 907*m*, 869*w*, 805*w*, 734*s*, 690*m*, 645*w*. ^{1}H-NMR (300 MHz, CD_3OD): see *Table 4*; additionally, 7.48–7.44 (*m*, 2 arom. H); 7.33–7.18 (*m*, 3 arom. H); 3.13 (br. *d*, *J* = 8.4, 6.0), 2.90 (*dd*, *J* = 10.5, 4.8) (2 H of prolinyl); 2.34 (*s*, MeN); 2.20–1.88 (*m*, 3 H); 1.83–1.71 (*m*, 1 H); 1.31–1.26 (*m*, $MeCH_2CH_2$); 0.92–0.86 (*m*, $MeCH_2CH_2$). ^{13}C-NMR (75 MHz, CD_3OD): see *Table 4*; additionally, 177.80 (*s*, C=O); 136.15 (*s*); 131.01 (*d*, 2 C); 129.55 (*d*, 2 C); 127.18 (*d*); 69.66 (*d*, C(2) of prolinyl); 63.49 (*t*, C(5) of prolinyl); 41.53 (*q*, MeN); 38.60 (*d*, C(4) of prolinyl); 38.39 (*t*, C(3) of prolinyl); 36.63 (*t*, $MeCH_2CH_2$); 22.36 (*t*, $MeCH_2CH_2$); 14.33 (*q*, $MeCH_2CH_2$). HR-MALDI-MS: 469.2368 (100, $[M + H]^+$, $C_{23}H_{37}N_2O_6S^+$; calc. 469.2367).

*4-Chlorophenyl 6,8-Dideoxy-6-[(2*S*,4*R*)-1-methyl-4-propylpyrrolidine-2-carboxamido]-1-thio*-D-erythro-α-D-galacto-*octopyranoside* (**11b**). The crude alcohol, obtained from 89 mg (0.09 mmol) of **10b** according to *GP 3* was purified by FC (AcOEt/MeOH 98:2 → 4:1) gave **11b** (39 mg, 85%). Colourless oil. R_f (AcOEt/MeOH 9:1) 0.42. $[\alpha]_D^{25} = +255.6$ ($c = 0.96$, MeOH). IR (ATR): 3322*m* (br.), 2956*w*, 2924*w*, 2872*w*, 2789*w*, 1651*s*, 1521*m*, 1477*m*, 1455*w*, 1389*w*, 1307*w*, 1235*w*, 1206*w*, 1179*w*, 1091*s*, 1053*s*, 1011*m*, 992*w*, 906*w*, 867*w*, 811*w*, 731*m*, 691*w*. ^{1}H-NMR (300 MHz, CD_3OD): see *Table 4*; additionally, 7.47–7.41 (*m*, 2 arom. H); 7.33–7.28 (*m*, 2 arom. H); 3.13 (*dd*, *J* = 8.1, 5.7), 2.89 (*dd*, *J* = 10.5, 4.5) (2 H of prolinyl); 2.33 (*s*, MeN); 2.20–1.90 (*m*, 3 H); 1.82–1.70 (*m*, 1 H); 1.33–1.22 (*m*, $MeCH_2CH_2$); 0.92–0.86

Table 4. *Selected ^{1}H-NMR Chemical Shifts* [ppm] *and Coupling Constants* [Hz], *and ^{13}C-NMR Chemical Shifts* [ppm] *of the Lincomycin Analogues* **11a**–**11i** *in CD_3OD*

	11a	**11b**	**11c**	**11d**	**11e**	**11f**	**11g**	**11h**	**11i**
H–C(1)	5.70	5.70	5.49	5.28	5.08	5.36	5.31	5.34	5.34
H–C(2)	4.19	4.19	4.15	4.10	3.99	4.09	4.07	4.08	4.08
H–C(3)	3.64	3.64	3.63	3.58	3.61	3.57	3.57	3.56	3.56
H–C(4)	3.97	4.01	4.01	3.98	4.04	3.98	3.95	3.97	4.00
H–C(5)	4.33	4.31	4.41	4.29	4.33	4.29	4.27	4.29	4.31
H–C(6)	4.12	4.10	4.10	4.12	4.19	4.13	4.11	4.12	4.11
H–C(7)	3.89	3.88	3.90	3.97	3.95	3.99	3.94	3.98	3.93
H_3C(8)	1.00	1.00	1.10	1.19	1.23	1.17	1.13	1.16	1.17
J(1,2)	5.4	5.7	5.4	5.7	5.7	5.7	5.4	5.7	5.4
J(2,3)	10.5	10.2	10.2	10.2	9.6	10.5	9.9	10.5	10.2
J(3,4)	3.3	3.3	3.3	3.6	3.3	3.6	3.3	3.0	3.3
J(4,5)	[a])	[a])	[a])	0.9	[a])	[a])	1.2	[a])	1.2
J(5,6)	7.8	6.6	7.2	7.2	6.9	7.2	6.9	7.2	6.9
J(6,7)	6.3	6.3	6.6	6.3	6.3	6.0	6.3	6.0	6.3
J(7,Me)	6.3	6.3	6.3	6.3	6.3	6.3	6.3	6.3	6.3
C(1)	90.68	90.53	92.29	86.11	85.15	88.13	88.38	88.13	88.04
C(2)	69.16	69.10	69.23	69.25	68.79	70.07	70.06	69.49	70.15
C(3)[b])	71.67	71.62	71.56	72.19	71.69	71.91	71.94	71.93	71.88
C(4)[b])	70.23	70.19	70.30	70.34	69.66	70.69	70.56	70.52	70.33
C(5)[b])	71.08	71.04	70.70	70.66	70.30	70.50	70.68	70.73	70.70
C(6)	55.60	55.68	55.81	56.34	56.33	56.31	56.20	56.37	56.57
C(7)	67.26	67.29	67.46	68.00	67.75	67.97	67.88	67.99	68.18
C(8)	18.43	18.67	18.82	19.60	19.70	19.51	19.27	19.53	19.97

[a]) Not assigned. [b]) Assignments may be interchanged.

(*m*, *Me*CH_2CH_2). ^{13}C-NMR (75 MHz, CD_3OD): see *Table 4*; additionally, 177.80 (*s*, C=O); 135.04, 133.10 (2*s*); 132.44 (*d*, 2 C); 129.60 (*d*, 2 C); 69.68 (*d*, C(2) of prolinyl); 63.49 (*t*, C(5) of prolinyl); 41.53 (*q*, MeN); 38.60 (*d*, C(4) of prolinyl); 38.40 (*t*, C(3) of prolinyl); 36.63 (*t*, $MeCH_2CH_2$); 22.38 (*t*, $MeCH_2CH_2$); 14.34 (*q*, $MeCH_2CH_2$). HR-MALDI-MS: 503.1973 (100, $[M + H]^+$, $C_{23}H_{36}ClN_2O_6S^+$; calc. 503.1977).

*4-Methoxyphenyl 6,8-Dideoxy-6-[(2*S*,4*R*)-1-methyl-4-propylpyrrolidine-2-carboxamido]-1-thio*-D-erythro-*α*-D-galacto-*octopyranoside* (**11c**). The crude alcohol, obtained from 70 mg (0.07 mmol) of **10c** according to *GP 3*, was purified by FC (AcOEt/MeOH 98:2 → 9:1) to give **11c** (29 mg, 80%). Colourless oil. R_f (AcOEt/MeOH 9:1) 0.42. $[\alpha]_D^{25} = +255.6$ ($c = 0.96$, MeOH). IR (ATR): 3330*w* (br.), 2953*w*, 2927*w*, 2870*w*, 2788*w*, 1651*m*, 1593*w*, 1571*w*, 1522*m*, 1493*s*, 1461*w*, 1406*w*, 1379*w*, 1284*m*, 1245*s*, 1178*w*, 1153*w*, 1089*m*, 1053*m*, 1031*m*, 992*w*, 906*w*, 827*w*, 804*w*, 731*m*, 695*w*, 641*m*, 623*w*. ^{1}H-NMR (300 MHz, CD_3OD; assignments based on selective homodecoupling experiments): see *Table 4*; additionally, 7.45–7.39 (*m*, 2 arom. H); 6.90–6.85 (*m*, 2 arom. H); 3.77 (*s*, MeO); 3.14 (br. *dd*, $J = 8.1, 5.7$), 2.89 (*dd*, $J = 10.2, 4.2$) (2 H of prolinyl); 2.34 (*s*, MeN); 2.23–2.10 (*m*, 1 H); 2.04–1.90 (*m*, 2 H); 1.80–1.69 (*m*, 1 H); 1.32–1.20 (*m*, $MeCH_2CH_2$); 0.91–0.86 (*m*, *Me*CH_2CH_2). ^{13}C-NMR (75 MHz, CD_3OD): see *Table 4*; additionally, 177.88 (*s*, C=O); 160.41 (*s*); 134.45 (*d*, 2 C); 125.99 (*s*); 115.26 (*d*, 2 C); 69.63 (*d*, C(2) of prolinyl); 63.43 (*t*, C(5) of prolinyl); 55.36 (*q*, MeO); 41.43 (*q*, MeN); 38.45 (*d*, C(4) of prolinyl); 38.24 (*t*, C(3) of prolinyl); 36.48 (*t*, $MeCH_2CH_2$); 22.19 (*t*, $MeCH_2CH_2$); 14.16 (*q*, *Me*CH_2CH_2). HR-MALDI-MS: 499.2 (100, $[M + H]^+$, $C_{24}H_{39}N_2O_7S^+$; calc. 499.2472).

2-(Trimethylsilyl)ethyl 2,3,4,7-Tetra-O-acetyl-6-azido-6,8-dideoxy-1-thio-D-erythro-*α*-D-galacto-octopyranoside (**13**). A soln. of **12** (200 mg, 0.24 mmol) in THF (20 ml) was treated with $Bu_4NF \cdot 3\,H_2O$ (614 mg, 1.95 mmol), stirred for 6 h at 23°, treated with Et_3N (1 ml), Ac_2O (0.5 ml), and DMAP (13 mg,

0.10 mmol), stirred for 6 h, and evaporated. A soln. of the residue in AcOEt was washed with sat. aq. $NaHCO_3$ soln. and brine, dried ($MgSO_4$), and evaporated. FC (hexane/AcOEt 95:5 → 3:1) gave **13** (107 mg, 80%). Colourless oil. R_f (hexane/AcOEt 3:1) 0.38. $[\alpha]_D^{25} = +197.3$ ($c = 1.12$, $CHCl_3$). IR (ATR): 3005*w*, 2989*w*, 2110*w*, 1745*m*, 1370*w*, 1275*s*, 1260*s*, 1221*w*, 1162*w*, 1119*w*, 1065*w*, 1041*w*, 1007*w*, 937*w*, 911*w*, 896*w*, 859*w*, 840*w*, 763*s*, 750*s*, 706*w*, 662*w*, 623*w*. ^{1}H-NMR (300 MHz, $CDCl_3$; assignments based on selective homodecoupling experiments): see *Table 5*; additionally, 2.54 (*m*, CH_2S); 2.17, 2.07, 2.05, 1.98 (4*s*, 4 AcO); 0.94–0.69 (*m*, Me_3SiCH_2); 0.01 (*s*, Me_3Si). ^{13}C-NMR (75 MHz, $CDCl_3$; assignments based on a HSQC spectrum): see *Table 5*; additionally, 169.93, 169.61, 169.55, 169.48 (4*s*, 4 C=O); 26.75 (*t*, CH_2S); 21.06, 20.89, 20.66 (3*q*, 4 *Me*C=O); 17.04 (*t*, Me_3SiCH_2); −1.77 (*q*, Me_3Si). HR-MALDI-MS: 556.1753 (100, $[M + Na]^+$, $C_{21}H_{35}N_3NaO_6S^+$; calc. 556.1755).

Table 5. *Selected ^{1}H-NMR Chemical Shifts* [ppm] *and Coupling Constants* [Hz], *and ^{13}C-NMR Chemical Shifts* [ppm] *of the Acetylated Azides* **13** *and* **16d**–**16i** *in $CDCl_3$*

	13	**16d**	**16e**	**16f**	**16g**	**16h**	**16i**
H–C(1)	5.68	5.62	5.49	5.66	5.67	5.64	5.69
H–C(2)	5.19	5.23	5.16	5.20	5.20	5.19	5.16
H–C(3)	5.09	5.10	5.07	5.09	5.09	5.07	5.05
H–C(4)	5.55	5.56	5.55	5.55	5.54	5.53	5.53
H–C(5)	4.05	4.04	4.07	4.04	4.03	4.04	3.98
H–C(6)	3.75	3.76	3.75	3.76	3.74	3.76	3.74
H–C(7)	5.21	5.25	5.25	5.24	5.17	5.20	5.21
$H_3C(8)$	1.22	1.26	1.27	1.20	1.15	1.19	1.18
J(1,2)	5.4	5.7	5.4	5.7	5.7	5.7	5.7
J(2,3)	10.8	11.1	10.8	11.1	10.8	10.8	11.1
J(3,4)	3.3	3.0	3.0	3.0	3.0	2.4	3.0
J(4,5)	[a])	0.9	[a])	1.2	0.9	[a])	0.9
J(5,6)	9.6	10.2	9.9	10.2	9.9	9.9	10.5
J(6,7)	2.4	2.4	2.1	3.0	2.4	2.4	2.4
J(7,Me)	6.3	6.6	6.3	6.3	6.3	6.3	6.6
C(1)	82.75	81.88	82.49	83.28	83.19	83.16	82.92
C(2)	70.32	70.39	70.41	70.41	70.37	70.37	70.16
C(3)	68.20	68.39	68.29	68.12	68.10	68.08	67.90
C(4)[b])	67.84	67.86	67.96	67.88	67.84	67.83	67.62
C(5)[b])	67.30	67.43	67.33	67.62	67.50	67.53	67.62
C(6)	62.86	62.94	62.98	62.86	62.79	62.81	62.74
C(7)[b])	67.62	67.74	67.85	67.67	67.72	67.62	67.62
C(8)	13.00	13.03	13.28	12.96	12.98	12.03	12.99

[a]) $J < 1.2$ Hz (line broadening). [b]) Assignments may be interchanged.

General Procedure for the S-Alkylation (*GP 4*). A 1M soln. of **13** in THF was treated with a 1M Bu_4NF soln. in THF (5 equiv.), stirred for 1 h, treated with the corresponding alkyl bromide **15** (2 equiv.), stirred for 15 min, and poured into brine. The layers were separated, and the aq. layer was extracted with AcOEt. The combined org. layers were dried ($MgSO_4$) and evaporated to afford the crude sulfide.

Prop-2-enyl 2,3,4,7-Tetra-O-*acetyl-6-azido-6,8-dideoxy-1-thio*-D-erythro-α-D-galacto-*octopyranoside* (**16d**). According to *GP 4*, the crude sulfide, obtained from 50 mg (0.09 mmol) of **13**, was purified by FC (hexane/AcOEt 95:5 → 3:1) to give **16d** (40 mg, 90%). Colourless oil. R_f (hexane/AcOEt 3:1) 0.23. $[\alpha]_D^{25} = +211.7$ ($c = 1.0$, $CHCl_3$). IR (ATR): 2983*w*, 2109*m*, 1744*s*, 1430*w*, 1371*m*, 1219*s*, 1118*w*, 1065*m*, 1041*m*, 1008*w*, 937*w*, 911*w*, 778*w*, 739*w*, 707*w*, 623*w*. ^{1}H-NMR (300 MHz, $CDCl_3$; assignments based on selective homodecoupling experiments): see *Table 5*; additionally, 5.71 (*dddd*, $J = 15.3$, 10.5, 7.2, 6.0,

CH_2=C*H*CH_2S); 5.16 (br. *d*, *J* = 16.8), 5.13 (br. *d*, *J* = 10.8) (C*H*$_2$=CHCH$_2$S); 3.20–3.06 (*m*, CH_2=CHC*H*$_2$S); 2.18, 2.09, 2.06, 1.99 (4*s*, 4 AcO). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 5*; additionally, 170.04, 169.89, 169.78 (3*s*, 4 C=O); 132.24 (*d*, CH_2=*C*HCH$_2$S); 118.81 (*t*, *C*H$_2$=CHCH$_2$S); 33.13 (*t*, CH_2=CH*C*H$_2$S); 21.05, 20.79, 20.67, 20.62 (4*q*, 4 *Me*C=O). HR-ESI-MS: 496.1360 (100, $[M + Na]^+$, $C_{19}H_{27}N_3NaO_9S^+$; calc. 496.1360).

Benzyl 2,3,4,7-Tetra-O-*acetyl-6-azido-6,8-dideoxy-1-thio*-D-erythro-α-D-galacto-*octopyranoside* (**16e**). According to *GP 4*, the crude sulfide, obtained from 100 mg (0.18 mmol) of **13**, was purified by FC (hexane/AcOEt 95:5 → 3:1) to give **16e** (85 mg, 80%). Colourless oil. R_f (hexane/AcOEt 3:1) 0.16. $[\alpha]_D^{25} = +384.1$ (*c* = 0.67, $CHCl_3$). IR (ATR): 3059*w*, 3024*w*, 2980*w*, 2939*w*, 2109*m*, 1742*s*, 1495*w*, 1454*w*, 1430*w*, 1370*m*, 1213*s*, 1117*w*, 1065*m*, 1039*s*, 1007*m*, 988*w*, 937*w*, 910*m*, 776*w*, 729*s*, 700*m*, 647*w*, 622*w*. ^{1}H-NMR (300 MHz, $CDCl_3$; assignments based on selective homodecoupling experiments): see *Table 5*; additionally, 7.35–7.21 (*m*, 5 arom. H); 3.74, 3.65 (2*d*, *J* = 13.2, PhC*H*$_2$); 2.16, 2.09, 1.97, 1.95 (4*s*, 4 AcO). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 5*; additionally, 169.71, 169.68, 169.57 (3*s*, 4 C=O); 136.47 (*s*); 128.76 (*d*, 2 C); 128.63 (*d*, 2 C); 127.49 (*d*); 34.95 (*t*, PhC*H*$_2$); 21.18, 20.77, 20.73 (3*q*, 4 *Me*C=O). HR-MALDI-MS: 562.1259 (42, $[M + K]^+$, $C_{23}H_{29}KN_3O_9S^+$; calc. 562.1256), 546.1514 (100, $[M + Na]^+$, $C_{23}H_{29}N_3NaO_9S^+$; calc. 546.1517). Anal. calc. for $C_{23}H_{29}N_3O_9S$ (523.56): C 52.76, H 5.58, N 8.03; found: C 52.91, H 5.64, N 7.81.

2-Phenylethyl 2,3,4,7-Tetra-O-*acetyl-6-azido-6,8-dideoxy-1-thio*-D-erythro-α-D-galacto-*octopyranoside* (**16f**). According to *GP 4*, the crude sulfide, obtained from 70 mg (0.13 mmol) of **13**, was purified by FC (hexane/AcOEt 95:5 → 3:1) to give **16f** (60 mg, 60%). Colourless oil. R_f (hexane/AcOEt 3:1) 0.16. $[\alpha]_D^{25} = +185.2$ (*c* = 0.56, $CHCl_3$). IR (ATR): 3019*w*, 2993*w*, 2939*w*, 2110*m*, 1745*m*, 1497*w*, 1449*w*, 1432*w*, 1371*w*, 1222*s*, 1118*w*, 1066*m*, 1041*m*, 1008*w*, 937*w*, 911*w*, 781*w*, 699*w*, 622*w*. ^{1}H-NMR (300 MHz, $CDCl_3$; assignments based on selective homodecoupling experiments): see *Table 5*; additionally, 7.33–7.14 (*m*, 5 arom. H); 2.92–2.75 (*m*, PhC*H*$_2$C*H*$_2$); 2.19, 2.08, 2.04, 1.99 (4*s*, 4 AcO). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 5*; additionally, 170.19, 169.91, 169.75 (3*s*, 4 C=O); 139.52 (*s*); 128.60 (*d*, 2 C); 128.53 (*d*, 2 C); 126.65 (*d*); 35.70 (*t*, PhC*H*$_2$); 32.12 (*t*, CH_2S); 21.05, 20.83, 20.68, 20.62 (4*q*, 4 *Me*C=O). HR-MALDI-MS: 560.1667 (100, $[M + Na]^+$, $C_{24}H_{31}N_3NaO_9S^+$; calc. 560.1673). Anal. calc. for $C_{24}H_{31}N_3O_9S$ (537.59): C 53.62, H 5.81, N 7.82; found: C 53.49, H 5.89, N 7.64.

3-Phenylpropyl 2,3,4,7-Tetra-O-*acetyl-6-azido-6,8-dideoxy-1-thio*-D-erythro-α-D-galacto-*octopyranoside* (**16g**). According to *GP 4*, the crude sulfide, obtained from 200 mg (0.37 mmol) of **13**, was purified by FC (hexane/AcOEt 95:5 → 3:1) to give **16g** (160 mg, 75%). Colourless oil. R_f (hexane/AcOEt 3:1) 0.16. $[\alpha]_D^{25} = +123.2$ (*c* = 1.13, $CHCl_3$). IR (ATR): 3028*w*, 2938*w*, 2857*w*, 2108*m*, 1742*s*, 1603*w*, 1496*w*, 1453*w*, 1432*w*, 1370*m*, 1212*s*, 1117*w*, 1064*m*, 1039*m*, 1007*w*, 987*w*, 936*w*, 910*w*, 779*w*, 730*m*, 700*m*, 647*w*, 622*w*, 613*w*. ^{1}H-NMR (300 MHz, $CDCl_3$; assignments based on selective homodecoupling experiments): see *Table 5*; additionally, 7.30–7.24 (*m*, 2 arom. H); 7.20–7.12 (*m*, 3 arom. H); 2.75–2.36 (*m*, PhC*H*$_2$CH$_2$C*H*$_2$); 2.17, 2.07, 2.06, 1.98 (4*s*, 4 AcO); 1.97–1.82 (*m*, PhCH$_2$C*H*$_2$CH$_2$). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 5*; additionally, 169.97, 169.66, 169.53 (3*s*, 4 C=O); 140.71 (*s*); 128.36 (*d*, 2 C); 128.29 (*d*, 2 C); 125.97 (*d*); 35.65 (*t*, PhCH$_2$CH$_2$); 30.90, 30.07 (2*t*, PhCH$_2$*C*H$_2$*C*H$_2$); 21.11, 20.90, 20.74, 20.70 (4*q*, 4 *Me*C=O). HR-MALDI-MS: 590.1566 (30, $[M + K]^+$, $C_{25}H_{33}KN_3O_9S^+$; calc. 590.1569), 574.1834 (100, $[M + Na]^+$, $C_{25}H_{33}N_3NaO_9S^+$; calc. 574.1830). Anal. calc. for $C_{25}H_{33}N_3O_9S$ (551.62): C 54.44, H 6.03, N 7.53; found: C 54.57, H 6.05, N 7.53.

2-(4-Methoxyphenyl)ethyl 2,3,4,7-Tetra-O-*acetyl-6-azido-6,8-dideoxy-1-thio*-D-erythro-α-D-galacto-*octopyranoside* (**16h**). According to *GP 4*, the crude sulfide obtained from 120 mg (0.22 mmol) of **13** was purified by FC (hexane/AcOEt 95:5 → 3:1) to give **16h** (95 mg, 75%). Colourless oil. R_f (hexane/AcOEt 3:1) 0.33. $[\alpha]_D^{25} = +159.3$ (*c* = 0.88, $CHCl_3$). IR (ATR): 2938*w*, 2830*w*, 2109*m*, 1744*s*, 1611*w*, 1513*w*, 1440*w*, 1370*w*, 1301*w*, 1221*s*, 1178*w*, 1117*w*, 1065*m*, 1039*m*, 1008*w*, 937*w*, 911*w*, 895*w*, 822*w*, 756*w*, 704*w*, 623*w*. ^{1}H-NMR (300 MHz, $CDCl_3$; assignments based on selective homodecoupling experiments): see *Table 5*; additionally, 7.06–7.04 (*m*, 2 arom. H); 6.83–6.80 (*m*, 2 arom. H); 3.77 (*s*, MeO); 2.84–2.67 (*m*, CH_2CH_2S); 2.17, 2.06, 2.03, 1.97 (4*s*, 4 AcO). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 5*; additionally, 169.94, 169.67, 169.51 (3*s*, 4 C=O); 158.12 (*s*); 131.45 (*s*); 129.34 (*d*, 2 C); 113.86 (*d*, 2 C); 55.25 (*q*, MeO); 34.86 (*t*, *C*H$_2$CH$_2$S); 32.45 (*t*, CH$_2$*C*H$_2$S); 21.12, 20.91, 20.74, 20.69 (4*q*, 4 *Me*C=O). HR-MALDI-MS: 606.1539 (30, $[M + K]^+$, $C_{25}H_{33}KN_3O_{10}S^+$; calc. 606.1518), 590.1780 (100, $[M + Na]^+$, $C_{25}H_{33}N_3NaO_{10}S^+$;

calc. 590.1779). Anal. calc. for $C_{25}H_{33}N_3O_{10}S$ (567.62): C 52.90, H 5.86, N 7.40; found: C 52.85, H 5.95, N 7.33.

2-(4-Nitrophenyl)ethyl 2,3,4,7-Tetra-O-*acetyl-6-azido-6,8-dideoxy-1-thio*-D-erythro-α-D-galacto-*octopyranoside* (**16i**). According to *GP 4*, the crude sulfide, obtained from 100 mg (0.18 mmol) of **13**, was purified by FC (hexane/AcOEt 95:5 → 3:1) to give **16i** (80 mg, 75%). Colourless oil. R_f (hexane/AcOEt 3:1) 0.16. $[\alpha]_D^{25} = +184.4$ ($c = 0.56$, MeOH). IR (ATR): 2940*w*, 2109*m*, 1741*s*, 1605*w*, 1519*w*, 1431*w*, 1370*w*, 1345*w*, 1213*s*, 1111*w*, 1064*m*, 1040*m*, 1007*w*, 988*w*, 937*w*, 910*w*, 867*w*, 855*w*, 780*w*, 730*w*, 647*w*, 614*w*. ^{1}H-NMR (300 MHz, $CDCl_3$; assignments based on selective homodecoupling experiments): see *Table 5*; additionally, 8.17–8.13 (*m*, 2 arom. H); 7.35–7.30 (*m*, 2 arom. H); 3.04–2.70 (*m*, CH_2CH_2S); 2.17, 2.08, 2.02, 1.98 (4*s*, 4 AcO). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 5*; additionally, 169.90, 169.65, 169.45 (3*s*, 4 C=O); 146.78, 146.65 (2*s*); 129.27 (*d*, 2 C); 123.68 (*d*, 2 C); 35.33 (*t*, *C*H_2CH_2S); 31.12 (*t*, CH_2*C*H_2S); 21.06, 20.82, 20.67, 20.62 (4*q*, 4 *Me*C=O). HR-MALDI-MS: 621.1265 (15, $[M + K]^+$, $C_{24}H_{30}KN_4O_{11}S^+$; calc. 621.1263), 605.1521 (97, $[M + Na]^+$, $C_{24}H_{30}N_4NaO_{11}S^+$; calc. 605.1524), 600.1969 (100, $[M + NH_4]^+$, $C_{24}H_{34}N_5O_{11}S^+$; calc. 600.1976). Anal. calc. for $C_{24}H_{30}N_4O_{11}S$ (582.59): C 49.48, H 5.19, N 9.62; found: C 49.67, H 5.31, N 9.53.

General Procedure for the Deprotection and Reduction of Azides, and Coupling of the Corresponding Amines with PHA (*GP 5*). A 1M soln. of the azido tetraacetate in MeOH was treated with a 0.02N MeONa in MeOH (6 equiv.), stirred for 12 h, and neutralized with 1.2M HCl in MeOH. Evaporation gave the crude azido tetrol.

A 0.03M soln. of the crude azido tetrol in THF/0.1N NaOH 4:1 was treated with 1M PMe_3 in THF (1.5 equiv.), and stirred for 4–8 h at 50°. Evaporation gave the crude amino tetrol **17**.

A 10M soln. of the crude amino tetrol **17** in MeOH was treated with PHA methyl ester (10 equiv.) and NaOMe (1 equiv.) in MeOH, heated to 60° for 60 h, and evaporated.

Prop-2-enyl 6,8-Dideoxy-6-[(2S,4R)-1-methyl-4-propylpyrrolidine-2-carboxamido]-1-thio-D-erythro-α-D-galacto-*octopyranoside* (**11d**). The crude alcohol, obtained from 60 mg (0.12 mmol) of **16d** according to *GP 5*, was purified by FC (AcOEt/MeOH 98:2 → 4:1) to give **11d** (20 mg, 35%). Colourless oil. R_f (AcOEt/MeOH 9:1) 0.40. $[\alpha]_D^{25} = +136.3$ ($c = 1.53$, MeOH). IR (ATR): 3331*w* (br.), 2957*w*, 2921*w*, 2872*w*, 2788*w*, 1645*m*, 1521*m*, 1454*w*, 1425*w*, 1403*w*, 1379*w*, 1306*w*, 1230*w*, 1175*w*, 1157*w*, 1075*s*, 1051*s*, 989*m*, 913*w*, 865*w*, 803*w*, 750*s*, 694*w*, 664*w*, 635*w*, 611*w*. ^{1}H-NMR (300 MHz, CD_3OD): see *Table 4*; additionally, 5.88–5.73 (*dddd*, $J = 16.8$, 10.2, 8.4, 6.0, $CH_2=CHCH_2S$); 5.13 (*dq*, $J \approx 17.1$, 1.5), 5.08 (*dq*, $J = 10.2$, 1.5) ($CH_2=CHCH_2S$); 3.26–3.08 (*m*, $CH_2=CHCH_2S$, 1 H of prolinyl); 2.91 (*dd*, $J = 10.5$, 4.2, 1 H of prolinyl); 2.36 (*s*, MeN); 2.30–2.14 (*m*, 1 H); 2.09–1.90 (*m*, 2 H); 1.83–1.72 (*m*, 1 H); 1.38–1.23 (*m*, MeCH_2CH_2); 0.95–0.87 (*m*, *Me*CH_2CH_2). ^{13}C-NMR (75 MHz, CD_3OD): see *Table 4*; additionally, 178.27 (*s*, C=O); 134.93 (*d*, *C*H=CH_2); 117.76 (*t*, CH=*C*H_2); 70.05 (*d*, C(2) of prolinyl); 63.82 (*t*, C(5) of prolinyl); 41.82 (*q*, MeN); 38.92 (*d*, C(4) of prolinyl); 38.76 (*t*, C(3) of prolinyl); 36.86 (*t*, MeCH_2CH_2); 33.25 (*t*, CH_2S); 22.67 (*t*, Me*C*H_2CH_2); 14.60 (*q*, *Me*CH_2CH_2). HR-MALDI-MS: 455.2190 (8, $[M + Na]^+$, $C_{24}H_{38}N_2NaO_6S^+$; calc. 455.2186), 433.2361 (100, $[M + H]^+$, $C_{24}H_{39}N_2O_6S^+$; calc. 433.2367).

Benzyl 6,8-Dideoxy-6-[(2S,4R)-1-methyl-4-propylpyrrolidine-2-carboxamido]-1-thio-D-erythro-α-D-galacto-*octopyranoside* (**11e**). The crude alcohol, obtained from 60 mg (0.11 mmol) of **16e** according to *GP 5*, was purified by FC (AcOEt/MeOH 98:2 → 4:1) to give **11e** (20 mg, 36%). Colourless oil. R_f (AcOEt/MeOH 9:1) 0.34. $[\alpha]_D^{25} = +255.6$ ($c = 0.96$, MeOH). IR (ATR): 3331*w* (br.), 2958*w*, 2925*w*, 2873*w*, 2790*w*, 1646*m*, 1521*m*, 1495*w*, 1453*w*, 1419*w*, 1379*w*, 1309*w*, 1296*w*, 1239*w*, 1216*w*, 1180*w*, 1160*w*, 1080*w*, 1072*m*, 1050*m*, 991*m*, 943*w*, 904*w*, 859*w*, 803*w*, 749*s*, 697*m*, 664*m*, 634*w*, 604*w*. ^{1}H-NMR (300 MHz, CD_3OD): see *Table 4*; additionally, 7.35–7.16 (*m*, 5 arom. H); 3.70 (*s*, PhCH_2S); 3.15 (*dd*, $J = 7.8$, 5.7), 2.94 (*dd*, $J = 10.5$, 3.9) (2 H of prolinyl); 2.35 (*s*, MeN); 2.23–1.97 (*m*, 3 H); 1.84–1.72 (*m*, 1 H); 1.35–1.17 (*m*, MeCH_2CH_2); 0.85 (br. *t*, $J = 7.2$, *Me*CH_2CH_2). ^{13}C-NMR (75 MHz, CD_3OD): see *Table 4*; additionally, 178.06 (*s*, C=O); 138.85 (*s*); 129.93 (*d*, 2 C); 128.97 (*d*, 2 C); 127.48 (*d*); 69.53 (*d*, C(2) of prolinyl); 63.41 (*t*, C(5) of prolinyl); 41.41 (*q*, MeN); 38.54 (*d* and *t*, C(4) of prolinyl, CH_2S); 36.35 (*t*, C(3) of prolinyl); 33.73 (*t*, MeCH_2CH_2); 22.27 (*t*, Me*C*H_2CH_2); 14.16 (*q*, *Me*CH_2CH_2). HR-MALDI-MS: 521.2102 (12, $[M + K]^+$, $C_{24}H_{38}KN_2O_6S^+$; calc. 521.2188), 505.2358 (31, $[M + Na]^+$, $C_{24}H_{38}N_2NaO_6S^+$; calc. 505.2348), 483.2528 (100, $[M + H]^+$, $C_{24}H_{39}N_2O_6S^+$; calc. 483.2523).

2-Phenylethyl 6,8-Dideoxy-6-[(2S,4R)-1-methyl-4-propylpyrrolidine-2-carboxamido]-1-thio-D-erythro-α-D-galacto-*octopyranoside* (**11f**). The crude alcohol, obtained from 80 mg (0.14 mmol) of **16f**

according to *GP 5*, was purified by FC (AcOEt/MeOH 98:2 → 4:1) to give **11f** (15 mg, 20%). Colourless oil. R_f (AcOEt/MeOH 9:1) 0.42. $[\alpha]_D^{25} = +132.4$ ($c = 1.35$, MeOH). IR (ATR): 3331*w* (br.), 2956*w*, 2923*w*, 2872*w*, 2789*w*, 1646*m*, 1520*m*, 1453*m*, 1379*w*, 1307*w*, 1216*w*, 1180*w*, 1076*s*, 1049*s*, 990*w*, 904*w*, 866*w*, 804*w*, 749*s*, 696*m*, 664*w*, 635*w*, 607*w*. ^{1}H-NMR (300 MHz, CD_3OD): see *Table 4*; additionally, 7.30–7.13 (*m*, 5 arom. H); 3.15 (*dd*, $J = 8.1, 6.0$, 1 H of prolinyl); 2.94–2.69 (*m*, 1 H of prolinyl, SCH_2CH_2Ph); 2.34 (*s*, MeN); 2.21 (br. *s*, 1 H); 2.08–1.94 (*m*, 2 H); 1.84–1.72 (*m*, 1 H); 1.35–1.26 (*m*, $MeCH_2CH_2$); 0.94–0.86 (*m*, $MeCH_2CH_2$). ^{13}C-NMR (75 MHz, CD_3OD): see *Table 4*; additionally, 178.24 (*s*, C=O); 141.99 (*s*); 129.59 (*d*, 2 C); 129.45 (*d*, 2 C); 127.28 (*d*); 69.44 (*d*, C(2) of prolinyl); 63.83 (*t*, C(5) of prolinyl); 41.84 (*q*, MeN); 38.91 (*d*, C(4) of prolinyl); 38.75 (*t*, $PhCH_2$); 37.42 (*t*, C(3) of prolinyl); 36.91 (*t*, $MeCH_2CH_2$); 32.96 (*t*, $PhCH_2CH_2S$); 22.67 (*t*, $MeCH_2CH_2$); 14.62 (*q*, $MeCH_2CH_2$). HR-MALDI-MS: 535.2259 (5, $[M + K]^+$, $C_{25}H_{40}KN_2O_6S^+$; calc. 535.2244), 519.2511 (19, $[M + Na]^+$, $C_{25}H_{40}N_2NaO_6S^+$; calc. 519.2505), 497.2674 (100, $[M + H]^+$, $C_{25}H_{41}N_2O_6S^+$; calc. 497.2685).

3-Phenylpropyl 6,8-Dideoxy-6-[(2S,4R)-1-methyl-4-propylpyrrolidine-2-carboxamido]-1-thio-D-erythro-α-D-galacto-*octopyranoside* (**11g**). The crude alcohol, obtained from 80 mg (0.14 mmol) of **16g** according to *GP 5*, was purified by FC (AcOEt/MeOH 98:2 → 4:1) to give **11g** (20 mg, 27%). Colourless oil. R_f (AcOEt/MeOH 9:1) 0.42. $[\alpha]_D^{25} = +255.6$ ($c = 0.96$, MeOH). IR (ATR): 3328*m* (br.), 2924*m*, 2872*m*, 2789*w*, 1650*s*, 1522*s*, 1453*m*, 1379*w*, 1306*w*, 1254*w*, 1215*w*, 1182*w*, 1162*w*, 1077*s*, 1051*s*, 991*m*, 905*w*, 864*w*, 804*w*, 748*s*, 698*s*, 664*m*, 604*w*, 519*s*. ^{1}H-NMR (300 MHz, CD_3OD): see *Table 4*; additionally, 7.29–7.12 (*m*, 5 arom. H); 3.17 (*dd*, $J = 8.1, 6.0$), 2.91 (*dd*, $J = 10.2, 4.2$) (2 H of prolinyl); 2.72 (br. *t*, $J = 7.2$, $PhCH_2$); 2.64–2.47 (*m*, $PhCH_2CH_2$); 2.35 (*s*, MeN); 2.20 (br. *s*, 1 H); 2.06–1.88 (*m*, 2 H of prolinyl, CH_2S); 1.83–1.72 (*m*, 1 H); 1.37–1.29 (*m*, $MeCH_2CH_2$); 0.94–0.88 (*m*, $MeCH_2CH_2$). ^{13}C-NMR (75 MHz, CD_3OD): see *Table 4*; additionally, 178.32 (*s*, C=O); 142.86 (*s*); 129.53 (*d*, 2 C); 129.40 (*d*, 2 C); 126.92 (*d*); 69.43 (*d*, C(2) of prolinyl); 63.85 (*t*, C(5) of prolinyl); 41.84 (*q*, MeN); 38.91 (*d*, C(4) of prolinyl); 38.73 (*t*, $PhCH_2$); 36.92 (*t*, $PhCH_2CH_2$); 35.86 (*t*, C(3) of prolinyl); 32.63 (*t*, $MeCH_2CH_2$); 30.82 (*t*, CH_2S); 22.67 (*t*, $MeCH_2CH_2$); 14.60 (*q*, $MeCH_2CH_2$). HR-MALDI-MS: 549.2418 (2, $[M + K]^+$, $C_{26}H_{42}KN_2O_6S^+$; calc. 549.2401), 533.2668 (19, $[M + Na]^+$, $C_{26}H_{42}N_2NaO_6S^+$; calc. 533.2661), 511.2844 (100, $[M + H]^+$, $C_{26}H_{43}N_2O_6S^+$; calc. 511.2836).

2-(4-Methoxyphenyl)ethyl 6,8-Dideoxy-6-[(2S,4R)-1-methyl-4-propylpyrrolidine-2-carboxamido]-1-thio-D-erythro-α-D-galacto-*octopyranoside* (**11h**). The crude alcohol, obtained from 80 mg (0.13 mmol) of **16h** according to *GP 5*, was purified by FC (AcOEt/MeOH 98:2 → 4:1) to give **11h** (13 mg, 20%). Colourless oil. R_f (AcOEt/MeOH 9:1) 0.34. $[\alpha]_D^{25} = +122.6$ ($c = 0.86$, MeOH). IR (ATR): 3327*w* (br.), 2923*w*, 2788*w*, 1647*m*, 1611*w*, 1511*s*, 1453*w*, 1376*w*, 1300*w*, 1244*s*, 1177*m*, 1078*m*, 1047*s*, 991*m*, 942*w*, 903*w*, 850*w*, 820*w*, 805*w*, 773*w*, 691*w*. ^{1}H-NMR (300 MHz, CD_3OD): see *Table 4*; additionally, 7.19–7.12 (*m*, 2 arom. H); 6.85–6.80 (*m*, 2 arom. H); 3.75 (*s*, MeO); 3.15 (*dd*, $J = 8.4, 6.0$), 2.91 (*dd*, $J = 10.5, 5.2$) (2 H of prolinyl); 2.87–2.68 (*m*, $PhCH_2CH_2$); 2.35 (*s*, MeN); 2.28–2.12 (*m*, 1 H); 2.08–1.94 (*m*, 2 H); 1.84–1.72 (*m*, 1 H); 1.33–1.23 (*m*, $MeCH_2CH_2$); 0.93–0.87 (*m*, $MeCH_2CH_2$). ^{13}C-NMR (100 MHz, CD_3OD): see *Table 4*; additionally, 178.31 (*s*, C=O); 159.70 (*s*); 134.06 (*s*); 130.54 (*d*, 2 C); 114.87 (*d*, 2 C); 70.13 (*d*, C(2) of prolinyl); 63.86 (*t*, C(5) of prolinyl); 55.65 (*q*, MeO); 41.84 (*q*, MeN); 38.93 (*d*, C(4) of prolinyl); 38.78 (*t*, CH_2CH_2S); 36.92 (*t*, C(3) of prolinyl); 36.55 (*t*, $MeCH_2CH_2$); 33.21 (*t*, CH_2S); 22.66 (*t*, $MeCH_2CH_2$); 14.58 (*q*, $MeCH_2CH_2$). HR-MALDI-MS: 565.2350 (5, $[M + K]^+$, $C_{26}H_{42}KN_2O_7S^+$; calc. 565.2350), 549.2608 (15, $[M + Na]^+$, $C_{26}H_{42}N_2NaO_7S^+$; calc. 549.2610), 527.2783 (100, $[M + H]^+$, $C_{26}H_{43}N_2O_7S^+$; calc. 527.2785).

2-(4-Nitrophenyl)ethyl 6,8-Dideoxy-6-[(2S,4R)-1-methyl-4-propylpyrrolidine-2-carboxamido]-1-thio-D-erythro-α-D-galacto-*octopyranoside* (**11i**). The crude alcohol, obtained from 80 mg (0.13 mmol) of **16i** according to *GP 5*, was purified by FC (AcOEt/MeOH 98:2 → 4:1) to give **11i** (17 mg, 20%). Colourless oil. R_f (AcOEt/MeOH 9:1) 0.28. $[\alpha]_D^{25} = +124.6$ ($c = 0.73$, MeOH). IR (ATR): 3337*m* (br.), 2949*w*, 2925*m*, 2876*w*, 2791*w*, 1650*m*, 1604*w*, 1518*s*, 1454*w*, 1344*s*, 1095*m*, 1080*m*, 1052*m*, 992*w*, 901*w*, 855*w*, 806*w*, 749*w*, 695*w*. ^{1}H-NMR (300 MHz, CD_3OD): see *Table 4*; additionally, 8.19–8.14 (*m*, 2 arom. H); 7.53–7.49 (*m*, 2 arom. H); 3.16 (*dd*, $J = 8.1, 6.0$, 1 H of prolinyl); 3.06 (br. *t*, $J = 7.2$, CH_2CH_2S); 2.96–2.77 (*m*, 1 H of prolinyl, CH_2S); 2.35 (*s*, MeN); 2.30–2.14 (*m*, 1 H); 2.08–1.94 (*m*, 2 H); 1.84–1.73 (*m*, 1 H); 1.36–1.23 (*m*, $MeCH_2CH_2$); 0.93–0.87 (*m*, $MeCH_2CH_2$). ^{13}C-NMR (75 MHz, CD_3OD): see *Table 4*; additionally, 178.25 (*s*, C=O); 150.00, 148.05 (2*s*); 130.93 (*d*, 2 C); 124.55 (*d*, 2 C); 69.45 (*d*, C(2) of prolinyl); 63.85 (*t*, C(5) of prolinyl); 41.82 (*q*, MeN); 38.94 (*d*, C(4) of prolinyl); 38.82 (*t*, CH_2CH_2S);

37.01 (*t*, C(3) of prolinyl); 36.94 (*t*, $MeCH_2\mathit{CH}_2$); 32.04 (*t*, CH_2S); 22.70 (*t*, $Me\mathit{CH}_2CH_2$); 14.60 (*q*, $\mathit{Me}CH_2CH_2$). HR-MALDI-MS: 542.2535 (100, $[M + H]^+$, $C_{25}H_{40}N_3O_8S^+$; calc. 542.2531).

Methyl 6-Azido-2,3,4,7-tetra-O-*benzyl-6,8-dideoxy-1-thio*-D-erythro-α-D-galacto-*octopyranoside* (**18**). A soln. of **5** (3.5 g, 13 mmol) in dry DMF (50 ml) under N_2 was treated at 0° with 60% NaH in mineral oil (3.12 g, 78 mmol), BnBr (10.80 g, 63 mmol), and Bu_4NI (193 mg, 0.52 mmol), warmed to 25°, stirred for 24 h, and cautiously treated with H_2O until complete consumption of NaH. The mixture was diluted with AcOEt, washed with sat. aq. NH_4Cl soln., dried (Na_2SO_4), and evaporated. FC (hexane/AcOEt 98:2 → 9:1) gave **18** (6.64 g, 80%). Colourless oil. R_f (hexane/AcOEt 9:1) 0.69. $[\alpha]_D^{25} = +107.6$ ($c = 0.99$, $CHCl_3$). IR (ATR): 3209*w* (br.), 3031*w*, 2978*w*, 2921*w*, 2885*w*, 2110*m*, 1586*w*, 1496*w*, 1453*m*, 1388*w*, 1347*m*, 1319*w*, 1295*m*, 1264*m*, 1209*w*, 1157*w*, 1123*m*, 1079*s*, 1065*s*, 1037*s*, 1026*s*, 989*m*, 917*m*, 900*w*, 867*m*, 830*w*, 803*w*, 786*w*, 748*s*, 731*s*, 694*s*, 635*m*, 616*m*. ^{1}H-NMR (400 MHz, $CDCl_3$; assignments based on a DQFCOSY spectrum): see *Table 6*; additionally, 7.40–7.24 (*m*, 20 arom. H); 5.08 (*d*, $J = 11.0$), 4.85 (*d*, $J = 11.7$), 4.75 (*d*, $J = 11.4$, 2 H), 4.70 (*d*, $J = 11.7$), 4.65 (*d*, $J = 11.4$), 4.54 (*d*, $J = 11.7$), 4.50 (*d*, $J = 12.0$) (4 $PhC\mathit{H}_2$); 2.01 (*s*, MeS). ^{13}C-NMR (75 MHz, $CDCl_3$; assignments based on a HSQC spectrum): see *Table 6*; additionally, 138.54, 138.37, 138.34, 138.12 (4*s*); 128.66–127.49 (several *d*); 75.39, 73.63, 72.82, 70.94 (4*t*, 4 $PhC\mathit{H}_2$); 13.94 (*q*, MeS). HR-ESI-MS: 662.2661 (100, $[M + Na]^+$, $C_{37}H_{41}N_3NaO_5S^+$; calc. 662.2659). Anal. calc. for $C_{37}H_{41}N_3O_5S$ (639.81): C 69.46, H 6.46, N 6.57; found: C 69.29, H 6.29, N 6.54.

Table 6. *Selected ^{1}H-NMR Chemical Shifts* [ppm] *and Coupling Constants* [Hz], *and ^{13}C-NMR Chemical Shifts* [ppm] *of the Lincosamine Derivatives* **18**–**22** *in $CDCl_3$*

	18	α-**19**[a])	β-**19**[a])	(*E*)-**20**[a])	(*Z*)-**20**[a])	α-**21**	β-**21**	α-**22**	β-**22**
H–C(1)	5.22	5.15	4.54	7.42	6.91	4.97	4.86–4.46	5.76	5.23
H–C(2)	4.30	4.04–3.98	3.74	4.22	4.98	4.31	4.86–4.46	4.31	4.56
H–C(3)	3.71	3.82	3.52	3.91–3.84	4.05–3.99	4.80	3.65	4.06	3.66
H–C(4)	4.07	4.12–4.08	4.04–3.98	3.91–3.84	3.91–3.84	4.26	4.09	4.20	4.11–4.09
H–C(5)	3.76	3.57	3.04	3.61	3.53	4.66	3.16	4.37	3.39
H–C(6)	4.17	4.12–4.08	4.16	3.72	3.74	4.08	4.26	4.09	4.38
H–C(7)	3.91	3.95	4.04–3.98	4.05–3.99	4.05–3.99	3.88	3.97	3.88	4.12
H_3C(8)	1.20	1.18	1.17	1.16	1.18	1.13	1.15	1.16	1.19
J(1,2)	5.6	4.0	7.2	7.9	6.5	5.4	[b])	6.0	5.4
J(2,3)	10.2	9.9	9.6	4.8	3.9	9.6	9.6	10.2	9.0
J(3,4)	2.6	2.6	2.7	[b])	[b])	1.8	1.8	2.4	2.1
J(4,5)	0.3	0.3	1.1	6.3	5.7	0.9	0.3	[b])	2.1
J(5,6)	10.2	10.7	10.0	10.1	10.2	10.2	10.2	9.3	10.2
J(6,7)	2.4	2.8	2.6	2.0	2.8	2.7	2.7	2.7	2.7
J(7,Me)	6.3	6.3	6.3	6.0	6.3	6.3	6.3	6.0	6.3
C(1)	87.12	91.75	97.97	151.91	149.88	95.38	100.31	105.07	106.68
C(2)	75.90[c])	76.38	80.43	71.66	76.86	75.33	76.19	74.99	78.67
C(3)	79.91	78.98	82.30	79.67	80.95	79.57	82.47	77.76	81.71
C(4)	74.86	74.08	73.20	76.30	76.04	74.12	74.78	72.59	74.91
C(5)	69.65	69.35	73.50	70.17	69.98	74.68	72.59	73.64	72.14
C(6)	62.11	61.77	61.73	64.37	64.16	61.82	61.55	61.86	61.45
C(7)	75.48[c])	75.22	75.18	75.75	75.69	75.27	75.95	74.79	77.83
C(8)	13.61	13.23	13.67	13.54	13.90	13.32	13.58	13.20	14.08

[a]) Assignments on DQFCOSY and HSQC spectra. [b]) Not assigned. [c]) Assignments may be interchanged.

6-Azido-2,3,4,7-tetra-O-*benzyl-6,8-dideoxy*-D-erythro-α/β-D-galacto-*octopyranose* (α-**19**/β-**19**). A soln. of **18** (7.04 g, 11.02 mmol) in CH_2Cl_2 (200 ml) was treated at 0° with Br_2 (566 µl, 11.02 mmol), stirred for 15 min, and treated with sat. aq. $Na_2S_2O_5$ soln. After extraction with CH_2Cl_2, the org. layer was

dried (Na_2SO_4) and evaporated to give the corresponding galactopyranosyl bromide, which was used immediately in the next step.

A soln. of the crude galactopyranosyl bromide in acetone (200 ml) was treated at 0° with H_2O (800 µl) and Ag_2CO_3 (2.43 g, 8.82 mmol), warmed to 25°, stirred for 4 h, and filtered over *Celite*. Evaporation and FC (hexane/AcOEt 95:5 → 80:20) gave α-**19**/β-**19** (6.34 g, 94%). Colourless oil. R_f (hexane/AcOEt 3:1) 0.54. $[\alpha]_D^{25} = +31.1$ ($c = 0.76$, $CHCl_3$). IR (ATR): 3455*w* (br.), 3029*w*, 2970*w*, 2937*w*, 2104*s*, 1496*w*, 1453*m*, 1365*s*, 1269*w*, 1228*m*, 1216*s*, 1125*m*, 1058*s*, 1026*s*, 903*m*, 788*w*, 733*s*, 695*s*. ^{1}H-NMR (400 MHz, $CDCl_3$, α/β 1:1; assignments based on a DQFCOSY spectrum): see *Table 6*; additionally, 7.55–6.98 (*m*, 20 arom. H); 5.06 (*d*, $J = 11.2$, PhC*H* (β)); 5.05 (*d*, $J = 11.1$, PhC*H* (α)); 4.90–4.77 (*m*, PhCH_2, PhC*H* (α)); 4.70–4.65 (*m*, 2 PhC*H* (β), PhC*H* (α), PhC*H*); 4.52 (*s*, PhCH_2 (β)); 4.51 (*s*, PhCH_2 (α)); 2.99 (*d*, $J = 7.0$, OH (β)); 2.86 (*d*, $J = 2.0$, OH (α)). ^{13}C-NMR (75 MHz, $CDCl_3$, α/β 1:1; assignments based on a DEPT and a HSQC spectrum): see *Table 6*; additionally, 138.47–138.13 (several *s*); 128.51–127.30 (several *d*); 74.99 (*t*, PhCH_2 (α)); 74.95 (*t*, 2 PhCH_2 (β)); 73.72 (*t*, PhCH_2 (α)); 73.06 (*t*, PhCH_2 (β)); 72.94 (*t*, PhCH_2 (α)); 70.78 (*t*, PhCH_2 (β)); 70.69 (*t*, PhCH_2 (α)). HR-ESI-MS: 648.2491 (11, $[M + K]^+$, $C_{36}H_{39}KN_3O_6^+$; calc. 648.2470); 632.2721 (100, $[M + Na]^+$, $C_{36}H_{39}N_3NaO_6^+$; calc. 632.2731). Anal. calc. for $C_{36}H_{39}N_3O_6$ (609.72): C 70.92, H 6.45, N 6.89; found: C 70.79, H 6.38, N 6.92.

*(*E*)/(*Z*)-6-Azido-2,3,4,7-tetra*-O-*benzyl-6,8-dideoxy*-D-erythro-D-galacto-*octose Oxime* (**20**). A soln. of **19** (6.18 g, 0.01 mmol) in abs. EtOH (100 ml) was added to a soln. of $NH_2OH \cdot HCl$ (2.78 g, 0.041 mmol) and EtONa (1.39 g, 0.02 mmol) in abs. EtOH (150 ml). The mixture was stirred at 60° for 24 h, cooled to 25°, and evaporated. A soln. of the residue in AcOEt was washed with H_2O and brine, dried (Na_2SO_4), and evaporated to afford **20** (6.58 g, 95%). Colourless oil, which was used for the next step without further purification. R_f (hexane/AcOEt 3:1): 0.38. $[\alpha]_D^{25} = -5.6$ ($c = 0.85$, $CHCl_3$). IR (ATR): 3355*w* (br.), 3063*w*, 3029*w*, 2970*w*, 2940*w*, 2104*s*, 1586*w*, 1496*w*, 1454*m*, 1376*s*, 1304*w*, 1267*w*, 1229*m*, 1216*m*, 1065*s*, 1026*m*, 939*m*, 910*m*, 820*w*, 733*s*, 695*s*. ^{1}H-NMR (400 MHz, $CDCl_3$, (*E*)/(*Z*) 7:3; assignments based on a DQFCOSY spectrum): see *Table 6*; additionally, 7.81 (*s*, NOH (*E*)); 7.52 (*s*, NOH (*Z*)); 7.38–7.22 (*m*, 20 arom. H); 4.73–4.63 (*m*, 3 PhC*H*); 4.58–4.40 (*m*, 5 PhC*H*); 3.12 (*d*, $J = 6.0$, OH (*Z*)); 3.03 (*d*, $J = 6.3$, OH (*E*)). ^{13}C-NMR (75 MHz, $CDCl_3$; assignments based on a HSQC spectrum): see *Table 6*; additionally, 138.50–137.09 (several *s*); 128.62–127.33 (several *d*); 75.32 (*t*, PhCH_2 (*E*)); 75.25 (*t*, PhCH_2 (*Z*)); 73.43 (*t*, PhCH_2 (*E*)); 73.39 (*t*, PhCH_2 (*Z*)); 72.07 (*t*, PhCH_2 (*E*)); 71.21 (*t*, PhCH_2 (*Z*)); 70.65 (*t*, PhCH_2). HR-ESI-MS: 647.2848 (100, $[M + Na]^+$, $C_{36}H_{40}N_4NaO_6^+$; calc. 647.2840).

6-Azido-2,3,4,7-tetra-O-*benzyl*-N-*[(4-chlorophenyl)methylidene]-6,8-dideoxy*-D-erythro-α/β-D-galacto-*octopyranosylamine* N-*Oxide* (α-**21**/β-**21**). A mixture of **20** (6.58 g, 10.1 mmol) and 4-chlorobenzaldehyde (4.28 g, 30.3 mmol) in dry CH_2Cl_2 (100 ml) was refluxed for 48 h, cooled to 25°, and evaporated. FC (hexane/AcOEt 95:5 → 1:1) gave α-**21** (1.50 g, 24%) and β-**21** (4.50 g, 60%).

Data of α-**21**. Colourless powder. R_f (hexane/AcOEt 4:1) 0.42. M.p. 143–146°. $[\alpha]_D^{25} = +44.1$ ($c = 1.08$, $CHCl_3$). IR (ATR): 3085*w*, 3063*w*, 3030*w*, 2980*w*, 2927*w*, 2862*w*, 2106*m*, 1588*w*, 1573*w*, 1556*w*, 1496*w*, 1485*w*, 1453*m*, 1398*w*, 1377*w*, 1346*w*, 1331*w*, 1274*w*, 1207*w*, 1131*s*, 1088*s*, 1045*m*, 1026*m*, 1012*m*, 952*w*, 904*w*, 881*w*, 836*w*, 730*s*, 693*s*, 673*w*, 632*w*, 618*w*. ^{1}H-NMR (300 MHz, $CDCl_3$; assignments based on selective homodecoupling experiments): see *Table 6*; additionally, 8.16 (*d*, $J = 6.6$, 2 arom. H); 7.46–7.25 (*m*, 22 arom. H); 7.00 (*s*, CH=N); 5.11 (*d*, $J = 10.8$), 4.94 (*d*, $J = 12.3$), 4.92 (*d*, $J = 11.7$), 4.86 (*d*, $J = 11.7$), 4.70 (*d*, $J = 10.8$), 4.65 (*d*, $J = 12.6$) (6 PhC*H*); 4.50 (*s*, PhCH_2). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 6*; additionally, 138.42, 138.34, 138.11, 138.02, 136.07 (5*s*, 6 C); 134.45 (*d*, CH=N); 129.91–127.08 (several *d*); 75.27, 75.08, 73.29, 70.56 (4*t*, 4 PhCH_2). HR-ESI-MS: 769.2766 (100, $[M + Na]^+$, $C_{43}H_{43}ClN_4NaO_6^+$; calc. 769.2769). Anal. calc. for $C_{43}H_{43}ClN_4O_6$ (747.29): C 69.11, H 5.80, N 7.50; found: C 68.82, H 5.99, N 7.40.

Data of β-**21**. Colourless powder. R_f (hexane/AcOEt 4:1) 0.22. M.p. 191–192°. $[\alpha]_D^{25} = -35.7$ ($c = 1.0$, $CHCl_3$). IR (ATR): 3085*w*, 3063*w*, 3032*w*, 2975*w*, 2931*w*, 2856*w*, 2109*m*, 1586*w*, 1556*w*, 1496*w*, 1484*w*, 1453*m*, 1396*m*, 1378*m*, 1346*m*, 1299*m*, 1270*m*, 1213*m*, 1155*m*, 1130*s*, 1089*s*, 1046*s*, 1027*s*, 1010*m*, 960*m*, 931*m*, 912*m*, 865*m*, 832*m*, 793*w*, 731*s*, 695*s*, 674*s*, 620*w*. ^{1}H-NMR (300 MHz, $CDCl_3$; assignments based on selective homodecoupling experiments): see *Table 6*; additionally, 8.23 (*d*, $J = 8.7$, 2 arom. H); 7.45–7.09 (*m*, 22 arom. H, CH=N); 5.12 (*d*, $J = 11.7$, PhC*H*); 4.86–4.46 (*m*, 3 PhCH_2, PhC*H*). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 6*; additionally, 138.46, 138.34, 138.02, 137.78, 136.66 (5*s*, 6 C); 134.24 (*d*, *C*H=N); 130.49–127.21 (several *d*); 75.45, 74.78, 72.81, 70.75 (4*t*, 4 PhCH_2). HR-ESI-MS: 769.2770 (100,

$[M + Na]^+$, $C_{43}H_{43}ClN_4NaO_6^+$; calc. 769.2769). Anal. calc. for $C_{43}H_{43}ClN_4O_6$ (747.29): C 69.11, H 5.80, N 7.50; found: C 69.23, H 5.91, N 7.46.

6-Azido-2,3,4,7-tetra-O-*benzyl-1-6,8-trideoxy-1-nitro*-D-erythro-α/β-D-galacto-*octopyranose* (α-**22**/β-**22**). A soln. of α-**21**/β-**21** 1:3 (6.00 g, 8.03 mmol) in CH_2Cl_2 (500 ml) was cooled to $-78°$. O_3 was bubbled through the soln. until disappearance of α-**21**/β-**21**. The soln. was purged with N_2, treated with Me_2S, warmed to 25°, and evaporated. FC (hexane/AcOEt 95:5 → 3:1) gave β-**22** (3.1 g, 75%) and α-**22** (0.9 g, 18%).

Data of α-**22**. Colourless oil. R_f (hexane/AcOEt 3:1) 0.72. $[\alpha]_D^{25} = +76.5$ ($c = 1.02$, $CHCl_3$). IR (ATR): 3064*w*, 3031*w*, 2984*w*, 2940*w*, 2914*w*, 2873*w*, 2107*m*, 1557*m*, 1496*w*, 1453*m*, 1368*w*, 1347*w*, 1309*w*, 1268*m*, 1208*w*, 1091*s*, 1158*w*, 1125*m*, 1091*s*, 1045*m*, 1025*m*, 913*w*, 874*w*, 821*w*, 732*s*, 695*s*, 619*w*. ^{1}H-NMR (300 MHz, $CDCl_3$; assignments based on selective homodecoupling experiments): see *Table 6*; additionally, 7.40–7.24 (*m*, 20 arom. H); 5.05 (*d*, $J = 11.1$), 4.82 (*d*, $J = 11.7$, 2 H), 4.75 (*d*, $J = 11.7$), 4.74 (*d*, $J = 11.7$), 4.65 (*d*, $J = 10.5$), 4.55 (*d*, $J = 11.7$), 4.49 (*d*, $J = 12.0$) (8 PhC*H*). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 6*; additionally, 138.13, 137.80, 137.66, 136.73 (4*s*); 128.46–127.19 (several *d*); 75.33, 74.21, 73.51, 70.73 (4*t*, 4 Ph*C*H_2). HR-MALDI-MS: 677.2389 (59, $[M + K]^+$, $C_{36}H_{38}KN_4O_7^+$; calc. 677.2372), 661.2623 (100, $[M + Na]^+$, $C_{36}H_{38}N_4NaO_7^+$; calc. 661.2633). Anal. calc. for $C_{36}H_{38}N_4O_7$ (638.72): C 67.70, H 6.00, N 8.77; found: C 67.92, H 5.99, N 8.52.

Data of β-**22**. Colourless oil. R_f (hexane/AcOEt 3:1) 0.73. $[\alpha]_D^{25} = +45.9$ ($c = 1.12$, $CHCl_3$). IR (ATR): 3030*w*, 2970*w*, 2937*w*, 2106*m*, 1565*s*, 1496*w*, 1454*m*, 1369*m*, 1268*w*, 1229*m*, 1216*m*, 1127*m*, 1091*s*, 1047*s*, 1026*s*, 910*w*, 873*w*, 843*w*, 792*w*, 732s, 695*s*. ^{1}H-NMR (300 MHz, $CDCl_3$; assignments based on selective homodecoupling experiments): see *Table 6*; additionally, 7.42–7.26 (*m*, 20 arom. H); 5.03 (*d*, $J = 11.1$), 4.84 (*d*, $J = 10.8$), 4.78 (*d*, $J \approx 12.3$), 4.74 (*d*, $J = 11.1$), 4.72 (*d*, $J \approx 11.2$), 4.68 (*d*, $J = 11.7$) (6 PhC*H*); 4.61 (*s*, Ph*C*H_2). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 6*; additionally, 138.50, 137.72, 137.64, 137.24 (4*s*); 128.81–127.71 (several *d*); 75.08, 74.67, 72.99, 71.08 (4*t*, 4 Ph*C*H_2). ESI-MS: 661.2640 (100, $[M + Na]^+$, $C_{36}H_{38}N_4NaO_7^+$; calc. 661.2633). Anal. calc. for $C_{36}H_{38}N_4O_7$ (638.72): C 67.70, H 6.00, N 8.77; found: C 67.52, H 5.88, N 8.77.

1,2-Di-O-*acetyl-7-azido-3,4,5,8-tetra*-O-*benzyl-7,9-dideoxy*-D-erythro-α-D-galacto-*non-2-ulopyranose* (**24**). A soln. of **22** (100 mg, 0.15 mmol) and paraformaldehyde (24 mg, 0.78 mmol) in CH_2Cl_2 (2 ml) was treated with 1M Bu_4NF in THF (5 ml, 0.15 mmol), stirred for 15 min at 25°, treated with 6N HCl (3 ml), and heated to 50° for 3 h. After evaporation of THF, the aq. layer was extracted with CH_2Cl_2. The combined org. layers were washed with sat. aq. $NaHCO_3$ soln. and brine, dried ($MgSO_4$), and evaporated. A soln. of the residue in CH_2Cl_2 (5 ml) was treated with Et_3N (2 ml), DMAP (20 mg, 0.15 mmol), and Ac_2O (1 ml), stirred for 12 h, and evaporated. A soln. of the residue in AcOEt was washed with sat. aq. $NaHCO_3$ soln. and brine, dried ($MgSO_4$), and evaporated. FC (hexane/AcOEt 95:5 → 4:1) gave **24** (94 mg, 80%). R_f (hexane/AcOEt 85:15) 0.22. $[\alpha]_D^{25} = +27.9$ ($c = 1.0$, $CHCl_3$). IR (ATR): 3031*w*, 2938*w*, 2965*w*, 2107*m*, 1749*m*, 1607*w*, 1587*w*, 1496*w*, 1454*w*, 1367*w*, 1346*w*, 1265*w*, 1218*m*, 1178*w*, 1127*m*, 1094*m*, 1042*m*, 1027*m*, 1009*m*, 961*w*, 908*m*, 729*s*, 695*s*, 648*w*. ^{1}H-NMR (300 MHz, $CDCl_3$; assignments based on selective homodecoupling experiments): see *Table 7*; additionally, 7.43–7.23 (*m*, 20 arom. H); 5.14 (*d*, $J = 11.1$), 4.94 (*d*, $J = 11.1$), 4.84 (*d*, $J = 11.4$), 4.77 (*d*, $J = 11.7$), 4.69 (*d*, $J = 11.7$, 2 H), 4.58 (*d*, $J = 11.7$), 4.50 (*d*, $J = 11.4$) (4 Ph*C*H_2); 2.05, 1.92 (2*s*, 2 AcO). ^{13}C-NMR (75 MHz, $CDCl_3$; assignments based on a HSQC spectrum): see *Table 7*; additionally, 169.68, 168.26 (2*s*, 2 C=O); 138.48, 138.37, 137.90, 137.84 (4*s*); 128.43–127.30 (several *d*); 75.43, 74.56, 72.63, 70.80 (4*t*, 4 Ph*C*H_2); 21.58, 20.63 (2*q*, 2 *Me*C=O). HR-ESI-MS: 746.3047 (100, $[M + Na]^+$, $C_{41}H_{45}N_3NaO_9^+$; calc. 746.3048). Anal. calc. for $C_{41}H_{45}N_3O_9$ (723.82): C 68.03, H 6.27, N 5.81; found: C 68.26, H 6.33, N 5.80.

General Procedure for Additions of **22** *to Aldehydes* (*GP 6*). A 1M soln. of α-**22**/β-**22** in DMF was treated with the aldehyde (5 equiv.) and then in four portions, one every 30 min, with a 1.5M soln. of Et_4NOH (0.1 equiv.), stirred for 24 h at 25°, and evaporated to afford the crude ulose derivative.

Addition of **22** *to Octanal*. According to *GP 6*, 1 g (1.57 mmol) of α-**22**/β-**22** was treated with 1.23 ml (7.85 mmol) of octanal. FC (hexane/AcOEt 98:2) of the crude gave **28b** (180 mg, 15%) and **28a** (640 mg, 53%).

*(1*R*)-7-Azido-3,4,5,8-tetra*-O-*benzyl-2,7,9-trideoxy-1*-C-*heptyl-2-nitro*-D-erythro-α-D-galacto-*non-2-ulopyranose* (**28a**). R_f (hexane/AcOEt 85:15) 0.73. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.40–7.24 (*m*, 20 arom. H); 5.06 (*d*, $J = 10.8$), 4.87 (*d*, $J = 11.4$), 4.78 (*d*, $J = 11.2$), 4.75 (*d*, $J = 11.2$), 4.67 (*d*, $J = 11.4$), 4.65 (*d*,

Table 7. *Selected ^{1}H-NMR Chemical Shifts* [ppm] *and Coupling Constants* [Hz], *and ^{13}C-NMR Chemical Shifts* [ppm] *of the Acetates* **24**, *α*-**29a**, **29b**, *β*-L-**34a**, **34b**, *and* **41** *in $CDCl_3$* (numbering as for lincosamine)

	24[a])	*α*-**29a**	**29b**[a])	*β*-L-**34a**[a])	**34b**[a])	**41**
H–C(2)	4.31	4.12	4.43	4.27	4.44	3.83
H–C(3)	3.97	3.93	3.98	3.95	3.95	4.07
H–C(4)	4.17	4.13	4.13	4.17	4.14	4.13
H–C(5)	3.37	3.52	3.34	3.56	3.36	3.28
H–C(6)	4.13	4.15	4.02	4.19	4.05	3.94
H–C(7)	3.98	4.01	4.03	3.98	4.04	3.95
H_3C(8)	1.13	1.17	1.13	1.20	1.16	1.20
H_a–C(1′)	5.05	5.83	5.93	6.23	6.35	[b])
H_b–C(1′)	4.31	–	–	–	–	[b])
H_a–C(2′)	–	1.74–1.42	1.83–1.53	3.79	3.72–3.65	[b])
H_b–C(2′)	–	1.74–1.42	1.83–1.53	3.70	3.72–3.65	[b])
J(2,3)	9.9	9.3	9.9	9.6	9.9	9.6
J(3,4)	2.7	2.7	1.8	2.4	2.4	2.1
J(4,5)	0.9	[c])	[c])	0.6	[c])	[c])
J(5,6)	9.9	10.2	10.2	10.2	10.5	10.2
J(6,7)	2.4	2.4	2.1	2.4	1.8	2.4
J(7,Me)	6.3	6.3	6.0	6.3	6.3	6.0
$J(1',2'_a)$	–	3.3	10.8	3.0	7.2	[d])
$J(1',2'_b)$	–	9.3	1.5	6.9	4.5	[d])
$J(1'_a,1'_b)$	11.4	–	–	–	–	[d])
C(1)	103.41	104.43	104.76	103.82	103.93	104.10
C(2)	74.93	75.47	74.47	76.29	74.25	74.56
C(3)	80.30	81.17	81.29	81.00	81.04	80.45
C(4)	73.62	73.38	73.65	73.55	73.57	73.57
C(5)	71.78	71.94	71.80	72.24	71.79	71.74
C(6)	62.20	62.40	62.53	62.51	62.52	62.28
C(7)	75.07	74.92	75.49	75.04	75.41	74.95
C(8)	13.28	13.14	13.87	13.44	13.76	13.39
C(1′)	63.16	73.38	74.57	71.22	72.26	30.07
C(2′)	–	[d])	[d])	68.27	68.63	11.68[e])

[a]) Assignments based on a HSQC spectrum. [b]) 2.79–2.64 ppm (*m*, 1 H); 2.22–2.05 (*m*, 2 H); 1.74–1.55 (*m*, 1 H). [c]) $J < 1.5$ Hz (line broadening). [d]) Not assigned. [e]) *s* of C≡N at 119.17 ppm.

$J = 11.1$), 4.60 (*d*, $J = 12.0$), 4.47 (*d*, $J = 12.0$) (4 PhCH_2); 4.30 (*dd*, $J = 10.1$, 2.1, H–C(6)); 4.25 (*d*, $J = 9.7$, H–C(3)); 4.18 (*dd*, $J = 2.6$, 1.9, H–C(5)); 4.03 (*dd*, $J = 10.1$, 2.6, H–C(4)); 4.05–4.00 (*m*, H–C(1)); 3.88 (*dd*, $J = 9.6$, 2.2, H–C(7)); 3.77 (*qd*, $J = 6.0$, 2.2, H–C(8)); 1.99 (*d*, $J = 8.4$, OH); 1.48–1.38 (*m*, 1 H), 1.35–1.09 (*m*, 11 H) (Me(CH_2)$_6$); 1.23 (*d*, $J = 6.3$, Me); 0.88 (*t*, $J = 6.6$, *Me*(CH$_2$)$_6$).

*(1*S*)-7-Azido-3,4,5,8-tetra-*O*-benzyl-2,7,9-trideoxy-1-*C*-heptyl-2-nitro-*D*-erythro-α-*D*-galacto-non-2-ulopyranose* (**28b**). R_f (hexane/AcOEt 85:15) 0.74. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.44–7.22 (*m*, 20 arom. H); 5.10 (*d*, $J = 11.0$, PhCH), 4.87 (br. *s*, PhCH_2); 4.78 (*d*, $J = 10.0$, H–C(3)); 4.72 (*d*, $J = 11.5$), 4.67 (*d*, $J = 12.0$), 4.64 (*d*, $J = 11.0$), 4.60 (*d*, $J = 12.1$), 4.48 (*d*, $J = 12.1$) (5 PhCH); 4.36 (*dd*, $J = 10.0$, 1.3, H–C(6)); 4.17–4.14 (*m*, H–C(1), H–C(5)); 4.02 (*dd*, $J = 10.1$, 2.6, H–C(4)); 3.83 (*dd*, $J = 10.1$, 2.1, H–C(7)); 3.79 (*qd*, $J = 6.3$, 2.1, H–C(8)); 1.52–1.40 (*m*, 1 H), 1.39–1.19 (*m*, 11 H) (Me(CH_2)$_6$); 1.20 (*d*, $J = 6.3$, Me); 0.88 (*t*, $J = 6.3$, *Me*(CH$_2$)$_6$).

General Procedure for the Hydrolysis and Acetylation of the 2-Nitroaldulopyranosides (*GP 7*). A 1M soln. of the nitro compound in 7N HCl was kept at 50° for 36 h and evaporated. A soln. of the residue in CH_2Cl_2 was washed with H_2O, sat. aq. $NaHCO_3$ soln., and brine, dried ($MgSO_4$), and evaporated. A soln.

of the residue in CH_2Cl_2 (5 ml) was treated with Et_3N (2 ml), DMAP (2 equiv.), and Ac_2O (1 ml), heated for 24 h at 50°, and evaporated. A soln. of the residue in AcOEt was washed with sat. aq. $NaHCO_3$ soln. and brine, dried ($MgSO_4$), and evaporated to give the crude acetates.

*(1*R*)-1,2-Di*-O-*acetyl-7-azido-3,4,5,8-tetra*-O-*benzyl-7,9-dideoxy-1*-C-*heptyl*-D-erythro-*α*-D-galacto-*non-2-ulopyranose* (*α*-**29a**). According to *GP 7*, 300 mg (0.39 mmol) of **28a** and FC of the crude acetate (hexane/AcOEt 95:5 → 4:1) gave *α*-**29a** (280 mg, 87%). R_f (hexane/AcOEt 85:15) 0.42. $[\alpha]_D^{25} = +66.3$ ($c = 1.0$, $CHCl_3$). IR (ATR): 3031*w*, 2927*w*, 2857*w*, 2107*m*, 1743*m*, 1496*w*, 1454*m*, 1368*m*, 1225*m*, 1094*s*, 1044*s*, 1027*s*, 1008*m*, 930*m*, 840*w*, 781*w*, 733*s*, 695*s*. ^{1}H-NMR (300 MHz, $CDCl_3$; assignments based on selective homodecoupling experiments): see *Table 7*; additionally, 7.42–7.23 (*m*, 20 arom. H); 5.12 (*d*, $J = 11.1$), 4.86 (*d*, $J = 11.1$), 4.80 (*d*, $J = 11.4$), 4.79 (*d*, $J = 11.1$), 4.69 (*d*, $J = 11.4$), 4.67 (*d*, $J = 11.4$), 4.61 (*d*, $J = 12.0$), 4.52 (*d*, $J = 12.0$) (4 PhCH_2); 1.99, 1.91 (2*s*, 2 AcO); 1.74–1.42 (*m*, 2 H); 1.38–1.12 (*m*, 10 H) ((CH_2)$_6$Me); 0.88 (*t*, $J = 6.9$, (CH$_2$)$_6$*Me*). ^{13}C-NMR (75 MHz, $CDCl_3$; assignments based on a HSQC spectrum): see *Table 7*; additionally, 170.17, 168.03 (2*s*, 2 C=O); 138.60, 138.55, 138.32, 137.91 (4*s*); 128.36–127.26 (several *d*); 74.92, 74.55, 72.64, 70.64 (4*t*, 4 PhCH$_2$); 31.71, 29.54, 29.41, 29.10, 25.69, 22.56 (6*t*, Me(CH_2)$_6$); 21.90, 20.80 (2*q*, 2 *Me*C=O); 14.01 (*q*, *Me*(CH$_2$)$_6$). ESI-MS: 844.1 (100, $[M + Na]^+$). Anal. calc. for $C_{48}H_{59}N_3O_9$ (822.01): C 70.14, H 7.23, N 5.11; found: C 69.85, H 7.33, N 5.24.

*(1*S*)-1,2-Di*-O-*acetyl-7-azido-3,4,5,8-tetra*-O-*benzyl-7,9-dideoxy-1*-C-*heptyl*-D-erythro-*α*-D-galacto-*non-2-ulopyranose* (**29b**). According to *GP 7*, 79 mg (0.10 mmol) of **28b** and FC of the crude acetate (hexane/AcOEt 95:5 → 4:1) gave **29b** (73 mg, 86%). R_f (hexane/AcOEt 85:15) 0.42. $[\alpha]_D^{25} = +45.3$ ($c = 1.0$, $CHCl_3$). IR (ATR): 3031*w*, 2926*w*, 2857*w*, 2106*m*, 1753*s*, 1497*w*, 1454*w*, 1368*m*, 1346*w*, 1213*m*, 1155*w*, 1127*m*, 1090*s*, 1046*m*, 1027*m*, 1009*m*, 983*m*, 927*m*, 783*w*, 732*s*, 695*s*. ^{1}H-NMR (300 MHz, $CDCl_3$; assignments based on selective homodecoupling experiments): see *Table 7*; additionally, 7.42–7.24 (*m*, 20 arom. H); 5.12 (*d*, $J = 10.5$), 5.01 (*d*, $J = 11.4$), 4.83 (*d*, $J = 11.4$), 4.78 (*d*, $J = 11.4$), 4.73 (*d*, $J = 11.7$), 4.63 (*d*, $J = 10.8$), 4.59 (*d*, $J = 11.1$), 4.50 (*d*, $J = 11.4$) (4 PhCH_2); 2.06, 1.85 (2*s*, 2 AcO); 1.83–1.53 (*m*, 2 H), 1.28–1.14 (*m*, 10 H) (Me(CH_2)$_6$); 0.87 (*t*, $J = 7.2$, *Me*(CH$_2$)$_6$). ^{13}C-NMR (75 MHz, $CDCl_3$; assignments based on a HSQC spectrum): see *Table 7*; additionally, 169.55, 168.16 (2*s*, 2 C=O); 138.58, 138.52, 137.95, 137.91 (4*s*); 128.44–127.30 (several *d*); 74.97, 74.71, 72.66, 71.14 (4*t*, 4 PhCH$_2$); 31.86, 29.78, 29.25 (2 C), 26.32, 22.77 (5*t*, Me(CH$_2$)$_6$); 21.88, 20.95 (2*q*, 2 *Me*C=O); 14.26 (*q*, *Me*(CH$_2$)$_6$). ESI-MS: 844.2 (100, $[M + Na]^+$). Anal. calc. for $C_{48}H_{59}N_3O_9$ (822.01): C 70.14, H 7.23, N 5.11; found: C 69.87, H 7.26, N 5.26.

Addition of **22** *to (Benzyloxy)acetaldehyde.* According to *GP 6*, 800 mg (1.25 mmol) of *α*-**22**/*β*-**22** were treated with 880 µl (6.25 mmol) of (benzyloxy)acetaldehyde. FC (hexane/AcOEt 98:2 → 90:10) gave **33b** (220 mg, 22%) and **33a** (690 mg, 70%).

8-Azido-1,4,5,6,9-penta-O-*benzyl-3,8,10-trideoxy-3-nitro*-D-ribo-*β*-L-gluco-*dec-3-ulopyranose* (**33a**). R_f (hexane/AcOEt 85:15) 0.63. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.40–7.22 (*m*, 25 arom. H); 5.08 (*d*, $J =$ 11.1, PhC*H*); 4.87 (br. *s*, PhCH_2); 4.81 (*d*, $J = 10.2$, H–C(4)); 4.73–4.62 (*m*, H–C(7), PhCH_2); 4.60–4.52 (*ddd*, $J = 8.7$, 6.3, 3.6, H–C(2)); 4.46 (*d*, $J = 12.3$, PhC*H*); 4.40 (br. *s*, PhCH_2); 4.36 (*d*, $J =$ 12.0), 4.32 (*d*, $J = 10.2$) (2 PhC*H*); 4.15 (br. *s*, H–C(6)); 4.05 (*dd*, $J = 10.2$, 3.0, H–C(8)); 3.86 (*dd*, $J = 9.9$, 1.8, H–C(5)); 3.74 (*qd*, $J = 6.3$, 3.0, H–C(9)); 3.44 (*dd*, $J = 10.2$, 3.6, H_a–C(1)); 3.36 (*dd*, $J =$ 10.2, 6.6, H_b–C(1)); 2.43 (*d*, $J = 8.7$, OH); 1.16 (*d*, $J = 6.3$, Me).

8-Azido-1,4,5,6,9-penta-O-*benzyl-3,8,10-trideoxy-3-nitro*-D-ribo-*β*-L-manno-*dec-3-ulopyranose* (**33b**). R_f (hexane/AcOEt 85:15) 0.64. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.42–7.16 (*m*, 25 arom. H); 5.03 (*d*, $J = 10.5$, PhC*H*); 4.77 (br. *s*, PhCH_2); 4.72 (*d*, $J = 11.6$), 4.66 (*d*, $J = 11.6$), 4.65 (*d*, $J = 10.8$) (3 PhC*H*); 4.56–4.53 (*m*, H–C(2) overlapping with PhC*H*); 4.54 (*d*, $J = 12.0$, PhC*H*); 4.47 (*d*, $J = 9.6$, H–C(4)); 4.40 (*d*, $J = 12.0$, PhC*H*); 4.35 (br. *d*, $J = 10.2$, H–C(7)); 4.27 (*d*, $J = 11.8$), 4.20 (*d*, $J = 12.0$) (2 PhC*H*); 4.18 (br. *s*, H–C(6)); 4.04 (*dd*, $J = 10.2$, 2.7, H–C(8)); 3.86 (*dd*, $J = 9.6$, 2.4, H–C(5)); 3.85 (*qd*, $J = 6.3$, 2.4, H–C(9)); 3.42, 3.34 (2*dd*, $J = 10.2$, 5.1, 2 H–C(1)); 2.41 (*d*, $J = 7.5$, OH); 1.21 (*d*, $J = 6.3$, Me).

2,3-Di-O-*acetyl-8-azido-1,4,5,6,9-penta*-O-*benzyl-8,10-dideoxy*-D-ribo-*β*-L-gluco-*dec-3-ulopyranose* (*β*-L-**34a**). According to *GP 7*, 200 mg (0.25 mmol) of **33a** and FC of the crude acetate (hexane/AcOEt 95:5 → 4:1) gave *β*-L-**34a** (165 mg, 75%). R_f (hexane/AcOEt 85:15) 0.33. $[\alpha]_D^{25} = +75.7$ ($c = 1.0$, $CHCl_3$). IR (ATR): 3063*w*, 3030*w*, 2936*w*, 2868*w*, 2107*m*, 1748*w*, 1605*w*, 1587*w*, 1496*w*, 1453*m*, 1368*m*, 1346*w*, 1232*m*, 1216*m*, 1095*s*, 1047*m*, 1026*m*, 1008*m*, 915*m*, 781*w*, 733*s*, 695*s*. ^{1}H-NMR (300 MHz, $CDCl_3$; assignments based on selective homodecoupling experiments): see *Table 7*; additionally, 7.47–7.24 (*m*, 25

arom. H); 5.15 (*d*, *J* = 11.4, PhC*H*); 4.86 (br. *s*, PhCH_2); 4.81 (*d*, *J* = 11.4), 4.73 (*d*, *J* = 11.7), 4.72 (*d*, *J* = 11.4), 4.60 (*d*, *J* = 12.0), 4.59 (*d*, *J* = 11.7), 4.51 (*d*, *J* = 11.7), 4.43 (*d*, *J* = 11.7) (7 PhC*H*); 2.02, 1.97 (2*s*, 2 AcO). ^{13}C-NMR (75 MHz, $CDCl_3$; assignments based on a HSQC spectrum): see *Table 7*; additionally, 169.95, 168.15 (2*s*, 2 C=O); 138.65, 138.57, 138.30, 137.96 (4*s*); 128.42–127.28 (several *d*); 75.04, 74.78, 72.85, 72.83, 70.85 (5*t*, 5 PhCH_2); 22.17, 21.06 (2*q*, 2 *Me*C=O); 13.44 (*q*, Me). ESI-MS: 866.0 (100, $[M + Na]^+$). Anal. calc. for $C_{49}H_{53}N_3O_{10}$ (843.97): C 69.73, H 6.33, N 4.98; found: C 69.68, H 6.35, N 4.93.

2,3-Di-O-*acetyl-8-azido-1,4,5,6,9-penta*-O-*benzyl-8,10-dideoxy*-D-ribo-*β*-L-manno-*dec-3-ulopyranose* (**34b**). According to *GP 7*, 190 mg (0.21 mmol) of **33b** and FC of the acetate (hexane/AcOEt 95:5 → 4:1) gave **34b** (150 mg, 75%). R_f (hexane/AcOEt 85:15) 0.33. $[\alpha]_D^{25} = +46.7$ (*c* = 0.98, $CHCl_3$). IR (ATR): 3063*w*, 3031*w*, 2931*w*, 2867*w*, 2107*m*, 1753*w*, 1605*w*, 1587*w*, 1496*w*, 1453*m*, 1368*m*, 1346*w*, 1214*m*, 1126*m*, 1090*s*, 1044*m*, 1027*m*, 1009*m*, 925*m*, 851*w*, 732*s*, 695*s*. ^{1}H-NMR (300 MHz, $CDCl_3$; assignments based on selective homodecoupling experiments): see *Table 7*; additionally, 7.42–7.20 (*m*, 25 arom. H); 5.12 (*d*, *J* = 11.1), 4.86 (*d*, *J* = 10.8), 4.82 (*d*, *J* = 11.1), 4.72 (*d*, *J* = 11.4), 4.71 (*d*, *J* = 11.4), 4.65 (*d*, *J* = 10.5), 4.61 (*d*, *J* = 11.7), 4.51 (*d*, *J* = 11.7), 4.50 (*d*, *J* = 12.3), 4.38 (*d*, *J* = 12.0) (5 PhCH_2); 1.97, 1.93 (2*s*, 2 AcO). ^{13}C-NMR (75 MHz, $CDCl_3$; assignments based on a HSQC spectrum): see *Table 7*; additionally, 169.29, 168.23 (2*s*, 2 C=O); 138.67, 138.62, 138.09, 137.91 (4*s*); 128.55–127.44 (several *d*); 74.92, 74.71, 72.60, 72.09, 71.14 (5*t*, 5 PhCH_2); 21.64, 20.88 (2*q*, 2 *Me*C=O). HR-ESI-MS: 866.3620 (100, $[M + Na]^+$, $C_{49}H_{53}N_3NaO_{10}^+$; calc. 866.3623). Anal. calc. for $C_{49}H_{53}N_3O_{10}$ (843.97): C 69.73, H 6.33, N 4.98; found: C 69.68, H 6.35, N 4.93.

4-O-*Acetyl-9-azido-5,6,7,10-tetra*-O-*benzyl-2,3,9,11-tetradeoxy*-D-erythro-*α*-D-galacto-*undec-4-ulopyranosononitrile* (**41**). A soln. of *α*-**22**/*β*-**22** (200 mg, 0.31 mmol) and acrylonitrile (45 µl, 0.63 mmol) in *t*-BuOH/CH_2Cl_2 6:1 (7 ml) was treated with *t*-BuONa (31 mg, 0.31 mmol), stirred for 3 h, and evaporated. A soln. of the residue in 2M aq. $LiClO_4$ (5 ml), stirred for 48 h at 25°, and evaporated. A soln. of the residue in CH_2Cl_2 was washed with H_2O and brine, dried ($MgSO_4$), and evaporated. A soln. of the residue in CH_2Cl_2 (5 ml) was treated with Et_3N (2 ml), DMAP (39 mg, 0.31 mmol), and Ac_2O (1 ml), stirred for 12 h, and evaporated. FC (hexane/AcOEt 95:5 → 4:1) gave **41** (120 mg, 56%). R_f (hexane/AcOEt 85:15) 0.11. $[\alpha]_D^{25} = +16.5$ (*c* = 1.0, $CHCl_3$). IR (ATR): 3030*w*, 2933*w*, 2108*s*, 1748*m*, 1586*w*, 1496*w*, 1454*m*, 1367*m*, 1346*w*, 1305*w*, 1270*w*, 1212*m*, 1127*m*, 1092*s*, 1047*m*, 1026*s*, 1009*m*, 967*m*, 927*m*, 735*s*, 697*s*. ^{1}H-NMR (300 MHz, $CDCl_3$; assignments based on selective homodecoupling experiments): see *Table 7*; additionally, 7.45–7.22 (*m*, 20 arom. H); 5.07 (*d*, *J* = 11.4), 4.94 (*d*, *J* = 11.4), 4.83 (*d*, *J* = 11.4), 4.77 (*d*, *J* = 11.4), 4.75 (*d*, *J* = 11.4), 4.67 (*d*, *J* = 10.8), 4.59 (*d*, *J* = 11.7), 4.50 (*d*, *J* = 11.7) (4 PhCH_2); 2.03 (*s*, AcO). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 7*; additionally, 168.26 (*s*, C=O); 138.18, 138.63, 137.03 (4*s*); 128.93–127.47 (several *d*); 75.15, 74.95, 72.57, 70.79 (4*t*, 4 PhCH_2); 22.17 (*q*, *Me*C=O). ESI-MS: 727.1 (100, $[M + Na]^+$). Anal. calc. for $C_{41}H_{44}N_4O_7$ (704.82): C 69.87, H 6.29, N 7.95; found: C 69.89, H 6.41, N 7.88.

Methyl (Methyl 9-Azido-5,6,7,10-tetra-O-*benzyl-2,3,9,11-tetradeoxy-4-thio*-D-erythro-*α*-D-galacto-*undec-4-ulopyranosid)onate* (**45**). A soln. of *α*-**22**/*β*-**22** (150 mg, 0.24 mmol) and methyl acrylate (43 µl, 0.48 mmol) in THF (5 ml) was treated with a 1M $Bu_4NF \cdot 3\,H_2O$ soln. in THF (24 µl, 0.24 mmol), stirred for 30 min, and evaporated. A suspension of the residue and 4-Å mol. sieves in CH_2Cl_2 (5 ml) was stirred for 30 min at 25°, cooled to −78°, and treated with bubbling MeSH for 2 min, warmed to −30°, treated with $BF_3 \cdot OEt_2$ (22 µl, 0.24 mmol), and stirred for 1 h. The mixture was treated with sat. aq. $NaHCO_3$ soln. and filtered over *Celite*. The layers were separated, and the aq. layer was extracted with CH_2Cl_2. The combined org. layers were dried ($MgSO_4$) and evaporated. FC (hexane/AcOEt 95:5 → 4:1) gave **45** (146 mg, 85%). R_f (hexane/AcOEt 85:15) 0.36. $[\alpha]_D^{25} = +42.6$ (*c* = 1.0, $CHCl_3$). IR (ATR): 3063*w*, 3030*w*, 2925*w*, 2105*s*, 1735*m*, 1496*w*, 1453*m*, 1435*w*, 1380*w*, 1345*w*, 1268*w*, 1194*w*, 1171*w*, 1127*m*, 1086*s*, 1026*m*, 951*w*, 910*w*, 732*s*, 695*s*. ^{1}H-NMR (300 MHz, $CDCl_3$; assignments based on selective homodecoupling experiments): see *Table 8*; additionally, 7.41–7.20 (*m*, 20 arom. H); 5.10 (*d*, *J* = 11.1), 4.94 (*d*, *J* = 11.7), 4.78 (*d*, *J* = 11.4), 4.73 (*d*, *J* = 11.4), 4.71 (*d*, *J* = 11.4), 4.64 (*d*, *J* = 11.4), 4.56 (*d*, *J* = 11.7), 4.48 (*d*, *J* = 11.7) (4 PhCH_2); 3.57 (*s*, MeO); 1.87 (*s*, MeS). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 8*; additionally, 173.64 (*s*, C=O); 138.80, 138.18, 138.06, 137.83 (4*s*); 128.43–127.38 (several *d*); 75.12, 74.67, 72.58, 70.76 (4*t*, 4 PhCH_2); 9.74 (*q*, MeS). ESI-MS: 747.9 (100, $[M + Na]^+$). Anal. calc. for $C_{41}H_{47}N_3O_7S$ (725.90): C 67.84, H 6.53, N 5.79; found: C 67.96, H 6.39, N 5.80.

Table 8. *Selected ^{1}H-NMR Chemical Shifts* [ppm] *and Coupling Constants* [Hz], *and ^{13}C-NMR Chemical Shifts* [ppm] *of the Thioglycosides* α-**25**, α-**30a**, **30b**, β-L-**36a**, **35b**, **42**, *and* **45** *in $CDCl_3$* (numbering as for lincosamine)

	α-**25**[a])	α-**30a**[a])	**30b**[a])	β-L-**36a**[a])	**35b**[a])	**42**[a])	**45**
H–C(2)	4.43	4.29	4.43	4.46	4.44	3.95	4.09–4.03
H–C(3)	4.02	3.99	3.98	3.99	3.99–3.94	4.07	4.09–4.03
H–C(4)	4.12	4.08	4.09	4.09	4.10	4.11	4.09–4.03
H–C(5)	3.66	3.64	3.59	3.67	3.63	3.63	3.62
H–C(6)	4.10	4.10	4.10	4.07	4.09	4.08	4.09–4.03
H–C(7)	3.91	3.90	3.96	3.88–3.80	3.99–3.94	3.88	3.86
H_3C(8)	1.21	1.25	1.21	1.20	1.21	1.21	1.19
H_a–C(1′)	4.64	5.07	5.16	3.88–3.80	5.51	[b])	[c])
H_b–C(1′)	4.00	–	–	–	–	[b])	[c])
H_a–C(2′)	–	[b])	[b])	3.88–3.80	4.21	[b])	[c])
H_b–C(2′)	–	[b])	[b])	3.60	3.53	[b])	[c])
J(2,3)	9.9	9.3	9.6	9.6	9.9	9.6	[d])
J(3,4)	2.4	2.7	2.1	2.4	[e])	2.4	[d])
J(4,5)	[e])	[e])	0.9	[e])	0.9	[e])	[e])
J(5,6)	9.9	9.6	9.9	9.6	9.9	9.9	9.9
J(6,7)	1.8	2.7	2.4	2.4	2.1	2.1	2.1
J(7,Me)	6.6	6.0	6.3	6.3	6.3	6.3	6.6
$J(1',2'_a)$	–	2.1	1.5	[d])	2.1	[d])	[d])
$J(1',2'_b)$	–	9.9	11.4	6.6	9.3	[d])	[d])
$J(1'_a,1'_b)$	10.8	–	–	10.5[f])	11.4[f])	[d])	[d])
C(1)	83.93	92.53	92.84	92.79	91.14	89.89	91.13
C(2)	74.50	76.21	74.86	76.95	74.39	73.54	73.32
C(3)	81.20	82.10	82.75	81.80	82.19	81.57	81.75
C(4)	74.15	73.92	73.81	73.91	73.67	73.92	74.95
C(5)	71.20	70.98	70.63	71.61	70.50	71.20	71.06
C(6)	62.96	63.23	62.80	62.81	62.65	62.59	63.04
C(7)	75.09	74.78	75.51	72.87	75.32	74.40	75.96
C(8)	14.44	14.24	14.24	14.25	14.73	13.91	13.97
C(1′)	64.04	73.77	75.74	74.72	74.39	32.40	32.02
C(2′)	–	[b])	–	70.94	69.46	11.09	28.28

[a]) Assignments based on a HSQC spectrum. [b]) See *Exper. Part.* [c]) 2.32–2.19 (*m*, 2 H); 2.17–2.01 (*m*, 1 H); 1.99–1.89 (*m*, 5 H). [d]) Not assigned. [e]) <1.5 Hz (line broadening). [f]) $J(2'_a,2'_b)$.

General Procedure for Thioglycosylation of Aldulopyranosyl Acetates (*GP 8*). A 1M soln. of the acetate in CH_2Cl_2 was treated with 4-Å mol. sieves, stirred for 30 min at 25°, and cooled to $-78°$. MeSH was passed through the mixture for 2 min. The mixture was warmed to $-30°$, treated with $BF_3 \cdot Et_2O$ (1 equiv.), stirred for 1 h, diluted with sat. aq. $NaHCO_3$ soln., and filtered over *Celite*. The layers were separated, and the aq. layer was extracted with CH_2Cl_2. The combined org. layers were dried ($MgSO_4$) and evaporated.

Methyl 1-O-*Acetyl-7-azido-3,4,5,8-tetra*-O-*benzyl-7,9-dideoxy-2-thio*-D-erythro-α/β-D-galacto-*non-2-ulopyranoside* (α-**25**/β-**25**). According to *GP 8*, 100 mg (0.14 mmol) of **24** and FC of the crude thioglycoside (hexane/AcOEt 95:5 → 4:1) gave α-**25** (57 mg, 57%) and α-**25**/β-**25** 1:1 (27 mg, 27%). FC of α-**25**/β-**25** 1:1 afforded an anal. sample of β-**25**.

Data of α-**25**. Colourless oil. R_f (hexane/AcOEt 85:15) 0.45. $[\alpha]_D^{25} = +48.9$ ($c = 1.0$, $CHCl_3$). IR (ATR): 3028*w*, 2970*w*, 2943*w*, 2104*m*, 1739*s*, 1496*w*, 1454*m*, 1365*s*, 1228*s*, 1216*s*, 1091*m*, 1047*m*, 1026*m*, 951*w*, 906*w*, 900*w*, 781*w*, 733*m*, 695*m*. ^{1}H-NMR (300 MHz, $CDCl_3$; assignments based on selective

homodecoupling experiments): see *Table 8*; additionally, 7.43–7.23 (*m*, 20 arom. H); 5.15 (*d*, *J* = 11.4), 4.95 (*d*, *J* = 11.7), 4.81 (*d*, *J* = 11.4), 4.75 (*d*, *J* = 11.4), 4.74 (*d*, *J* = 11.4), 4.61 (*d*, *J* = 11.4), 4.55 (*d*, *J* = 11.4), 4.49 (*d*, *J* = 11.4) (4 PhC*H*$_2$); 1.90 (*s*, MeS); 1.84 (*s*, AcO). ^{13}C-NMR (75 MHz, $CDCl_3$; assignments based on a HSQC spectrum): see *Table 8*; additionally, 170.12 (*s*, C=O); 138.82, 138.17, 138.02, 137.91 (4*s*); 128.37–127.33 (several *d*); 75.34, 74.43, 72.59, 70.85 (4*t*, 4 Ph*C*H$_2$); 20.75 (*q*, *Me*C=O); 9.30 (*q*, MeS). ESI-MS: 734.01 (100, $[M + Na]^+$). Anal. calc. for $C_{40}H_{45}N_3O_7S$ (711.98): C 67.49, H 6.37, N 5.90; found: C 67.54, H 6.40, N 5.86.

*Data of β-***25**. R_f (hexane/AcOEt 85:15) 0.44. Colourless oil. IR (ATR): 3030*w*, 2926*w*, 2865*w*, 2107*s*, 1744*m*, 1496*w*, 1453*m*, 1378*m*, 1346*w*, 1269*w*, 1227*s*, 1090*s*, 1054*m*, 1027*m*, 909*w*, 781*w*, 734*m*, 697*m*. ^{1}H-NMR (400 MHz, $CDCl_3$; assignments based on selective homodecoupling experiments): 7.31–7.14 (*m*, 20 arom. H); 5.05 (*d*, *J* = 11.2), 4.86 (*d*, *J* = 10.8), 4.78 (*d*, *J* = 10.4), 4.68 (*d*, *J* = 11.6, 2 H), 4.59 (*d*, *J* = 11.2) (6 PhC*H*); 4.52 (*d*, *J* = 12.8, H$_a$–C(1)); 4.49 (*d*, *J* = 10.8), 4.44 (*d*, *J* = 12.0) (2 PhC*H*); 4.19 (*d*, *J* = 12.4, H$_b$–C(1)); 4.17 (*d*, *J* = 9.6, H–C(3)); 4.02 (*dd*, *J* = 9.6, 2.8, H–C(7)); 3.98 (*dd*, *J* = 2.4, 0.8, H–C(5)); 3.91 (*qd*, *J* = 6.4, 2.4, H–C(8)); 3.72 (*dd*, *J* = 10.0, 2.4, H–C(4)); 3.28 (*dd*, *J* = 9.6, 0.8, H–C(6)); 2.00 (*s*, MeS); 1.86 (*s*, AcO); 1.10 (*d*, *J* = 6.4, Me). ^{13}C-NMR (100 MHz, $CDCl_3$; assignments based on a HSQC spectrum): 170.14 (*s*, C=O); 138.62, 138.28, 138.20, 138.06 (4*s*); 128.57–127.49 (several *d*); 86.80 (*s*, C(2)); 80.85, (*d*, C(4)); 78.09 (*d*, C(3)); 76.26 (*t*, Ph*C*H$_2$); 74.84 (*d*, C(8)); 74.76 (*t*, Ph*C*H$_2$); 73.99 (*d*, C(5)); 73.20 (*d*, C(6)); 72.76, 70.74 (2*t*, 2 Ph*C*H$_2$); 64.12 (*t*, C(1)); 62.56 (*d*, C(7)); 20.81 (*q*, *Me*C=O); 13.37 (*q*, Me); 10.63 (*q*, MeS). ESI-MS: 750.2833 (55, $[M + K]^+$, $C_{40}H_{45}KN_3O_7S^+$; calc. 750.2615); 734.2879 (100, $[M + Na]^+$, $C_{40}H_{45}N_3NaO_7S^+$; calc. 734.2870).

*Methyl (1*R*)-1-*O*-Acetyl-7-azido-3,4,5,8-tetra*-O*-benzyl-7,9-dideoxy-1-*C*-heptyl-2-thio*-D-erythro-*α*/*β*-D-galacto-*non*-2-ulopyranoside* (**30a**). According to *GP 8*, 165 mg (0.20 mmol) of *α*-**29a** and FC of the crude thioglycoside (hexane/AcOEt 95:5 → 4:1) gave *β*-**30a** (37 mg, 23%) and *α*-**30a** (73 mg, 46%).

*Data of α-***30a**. Colourless oil. R_f (hexane/AcOEt 85:15) 0.64. $[\alpha]_D^{25} = +97.5$ (*c* = 1.0, $CHCl_3$). IR (ATR): 3030*w*, 2926*w*, 2857*w*, 2105*m*, 1739*m*, 1496*w*, 1453*w*, 1370*w*, 1346*w*, 1303*w*, 1232*s*, 1088*s*, 1046*s*, 1027*s*, 979*w*, 909*w*, 820*w*, 783*w*, 731*s*, 695*s*. ^{1}H-NMR (300 MHz, $CDCl_3$; assignments based on selective homodecoupling experiments): see *Table 8*; additionally, 7.41–7.22 (*m*, 20 arom. H); 5.15 (*d*, *J* = 11.4), 4.89 (*d*, *J* = 11.4), 4.86 (*d*, *J* = 11.4), 4.75 (*d*, *J* = 11.7), 4.68 (*d*, *J* = 11.4), 4.65 (*d*, *J* = 11.4), 4.57 (*d*, *J* = 11.7), 4.50 (*d*, *J* = 11.7) (4 PhC*H*$_2$); 1.90 (*s*, MeS); 1.82 (*s*, AcO); 1.98–1.88 (*m*, 1 H), 1.66–1.48 (*m*, 1 H), 1.38–1.25 (*m*, 10 H) (Me(C*H*$_2$)$_6$); 0.87 (*t*, *J* = 6.0, *Me*(CH$_2$)$_6$). ^{13}C-NMR (75 MHz, $CDCl_3$; assignments based on a HSQC spectrum): see *Table 8*; additionally, 170.35 (*s*, C=O); 138.83, 138.75, 138.07, 137.93 (4*s*); 128.29–126.83 (several *d*); 74.48, 74.34, 72.86, 70.68 (4*t*, 4 Ph*C*H$_2$); 31.90, 30.02, 29.65, 29.26, 26.64, 22.75 (6*t*, Me(*C*H$_2$)$_6$); 21.14 (*q*, *Me*C=O); 14.41 (*q*, *Me*(CH$_2$)$_6$); 9.72 (*q*, MeS). ESI-MS: 832.1 (100, $[M + Na]^+$). Anal. calc. for $C_{47}H_{59}N_3O_7S$ (810.07): C 69.69, H 7.34, N 5.19; found: C 69.70, H 7.44, N 5.21.

*Data of β-***30a**. Colourless oil. R_f (hexane/AcOEt 85:15) 0.65. IR (ATR): 3031*w*, 2924*w*, 2856*w*, 2105*m*, 1739*m*, 1496*w*, 1454*w*, 1369*w*, 1345*w*, 1232*s*, 1092*s*, 1057*s*, 1027*s*, 961*w*, 924*w*, 732*s*, 696*s*. ^{1}H-NMR (300 MHz, $CDCl_3$; assignments based on selective homodecoupling experiments): 7.45–7.24 (*m*, 20 arom. H); 5.56 (*dd*, *J* = 10.5, 1.2, H–C(1)); 5.19 (*d*, *J* = 11.1), 4.91 (*d*, *J* = 11.7), 4.82 (br. *s*, 2 H), 4.80 (*d*, *J* = 12.6), 4.64 (*d*, *J* = 11.4), 4.57 (*d*, *J* = 11.4), 4.53 (*d*, *J* = 11.7) (4 PhC*H*$_2$); 4.31 (*d*, *J* = 10.2, H–C(3)); 4.12 (*dd*, *J* = 10.5, 2.7, H–C(4)); 4.09 (*dd*, *J* = 9.6, 2.1, H–C(7)); 4.05 (*dd*, *J* = 2.4, 1.2, H–C(5)); 4.01 (*qd*, *J* = 6.3, 1.8, H–C(8)); 3.39 (*dd*, *J* = 9.9, 1.2, H–C(6)); 2.08 (*s*, MeS); 1.51 (*s*, AcO); 1.85–1.54 (*m*, 2 H), 1.32–1.20 (*m*, 10 H) (Me(C*H*$_2$)$_6$); 1.23 (*d*, *J* = 6.3, Me); 0.88 (*t*, *J* = 6.6, *Me*(CH$_2$)$_6$). ^{13}C-NMR (75 MHz, $CDCl_3$; assignments based on a HSQC spectrum): 170.64 (*s*, C=O); 138.79, 138.53, 138.17, 138.03 (4*s*); 128.75–127.38 (several *d*); 88.68 (*s*, C(2)); 79.89 (*d*, C(4)); 78.30 (*d*, C(3)); 76.69 (*t*, Ph*C*H$_2$); 75.54 (*d*, C(5)); 74.80 (*t*, Ph*C*H$_2$); 74.73 (*d*, C(8)); 73.39 (*t*, Ph*C*H$_2$); 72.66 (*d*, C(6)); 70.92 (*d*, C(1)); 70.78 (*t*, Ph*C*H$_2$); 63.23 (*d*, C(7)); 31.84, 30.36, 29.63, 29.33, 25.94, 22.72 (6*t*, Me(*C*H$_2$)$_6$); 20.87 (*q*, *Me*C=O); 14.41 (*q*, *Me*(CH$_2$)$_6$); 9.90 (*q*, MeS). HR-ESI-MS: 832.3968 (100, $[M + Na]^+$, $C_{48}H_{53}N_3NaO_8S^+$; calc. 832.3966).

*Methyl (1*S*)-1-*O*-Acetyl-7-azido-3,4,5,8-tetra*-O*-benzyl-7,9-dideoxy-1-*C*-heptyl-2-thio*-D-erythro-*α*-D-galacto-*non*-2-ulopyranoside* (**30b**). According to *GP 8*, 90 mg (0.11 mmol) of **29b** and FC of the crude thioglycoside (hexane/AcOEt 95:5 → 4:1) gave **30b** (74 mg, 80%). Colourless oil. R_f (hexane/AcOEt 85:15) 0.58. $[\alpha]_D^{25} = +62.1$ (*c* = 1.0, $CHCl_3$). IR (ATR): 3064*w*, 3031*w*, 2925*w*, 2856*w*, 2104*s*, 1743*m*, 1496*w*, 1454*m*, 1370*m*, 1347*w*, 1264*w*, 1228*s*, 1124*m*, 1090*s*, 1072*s*, 1045*m*, 1027*s*, 983*w*, 945*w*, 909*w*, 822*w*,

785*w*, 732*s*, 696*s*. ^{1}H-NMR (300 MHz, $CDCl_3$; assignments based on selective homodecoupling experiments): see *Table 8*; additionally, 7.43–7.23 (*m*, 20 arom. H); 5.12 (*d*, *J* = 10.5, 2 H), 4.79 (*d*, *J* = 11.4), 4.72 (*d*, *J* = 11.8), 4.66 (*d*, *J* = 11.4), 4.59 (*d*, *J* = 10.5), 4.56 (*d*, *J* = 11.7), 4.52 (*d*, *J* = 12.0) (4 PhCH_2); 2.22–2.02 (*m*, 1 H), 1.65–1.55 (*m*, 1 H), 1.28–1.15 (*m*, 10 H) (Me(CH_2)$_6$); 1.91 (*s*, MeS); 1.77 (*s*, AcO); 0.85 (*t*, *J* = 6.9, *Me*(CH_2)$_6$). ^{13}C-NMR (75 MHz, $CDCl_3$; assignment based on a HSQC spectrum): see *Table 8*; additionally, 170.61 (*s*, C=O); 138.57, 138.48, 138.35, 137.85 (4*s*); 128.41–126.90 (several *d*); 74.86, 74.51, 72.45, 71.08 (4*t*, 4 PhCH_2); 31.89, 30.02, 29.26, 29.20, 26.77, 22.74 (6*t*, Me(CH_2)$_6$); 20.91 (*q*, *Me*C=O); 14.42 (*q*, *Me*(CH_2)$_6$); 9.19 (*q*, MeS). ESI-MS: 832.2 (100, $[M + Na]^+$). Anal. calc. for $C_{47}H_{59}N_3O_7S$ (810.07): C 69.69, H 7.34, N 5.19; found: C 69.60, H 7.37, N 5.19.

Methyl 8-Azido-1,4,5,6,9-penta-O-*benzyl-8,10-dideoxy-3-thio*-D-ribo-*β*/*α*-L-gluco-*dec-3-ulopyranoside* (*β*-L-**36**/*α*-L-**36a**). According to *GP 8*, 140 mg of *β*-L-**34a** (0.16 mmol) gave a mixture of epimeric acetates *α*-L-**35**/*β*-L-**35a** which could not be separated. A soln. of the crude acetates *α*-L-**35**/*β*-L-**35a** in CH_2Cl_2/MeOH 1:1 (10 ml) was treated with MeONa (100 mg, 1.66 mmol), stirred for 48 h at 25°, and evaporated. A soln. of the residue in AcOEt was washed with H_2O and brine, and dried ($MgSO_4$), and evaporated. FC (hexane/AcOEt 95:5 → 4:1) gave *α*-L-**36a** (37 mg, 30%) and *β*-L-**36a** (47 mg, 37%).

Data of β-L-**36a**. Colourless oil. R_f (hexane/AcOEt 85:15) 0.32. $[\alpha]_D^{25} = +48.7$ (*c* = 1.0, $CHCl_3$). IR (ATR): 3506*w* (br.), 3063*w*, 3030*w*, 2866*w*, 2105*m*, 1496*w*, 1453*m*, 1380*w*, 1345*w*, 1304*w*, 1271*w*, 1208*w*, 1088*s*, 1072*s*, 1026*m*, 910*w*, 732*s*, 695*s*. ^{1}H-NMR (300 MHz, $CDCl_3$; assignments based on selective homodecoupling experiments): see *Table 8*; additionally, 7.95–7.22 (*m*, 25 arom. H); 5.11 (*d*, *J* = 11.1), 4.87 (*d*, *J* = 10.8), 4.80 (*d*, *J* = 10.8), 4.77 (*d*, *J* = 11.7), 4.70 (*d*, *J* = 11.7), 4.65 (*d*, *J* = 11.1), 4.57 (*d*, *J* = 11.7), 4.49 (*d*, *J* = 11.7, 2 H), 4.43 (*d*, *J* = 11.7) (5 PhCH_2); 3.03 (*d*, *J* = 4.5, OH); 1.86 (*s*, MeS). ^{13}C-NMR (75 MHz, $CDCl_3$; assignments based on a HSQC spectrum): see *Table 8*; additionally, 138.61, 138.13, 137.97 (2 C), 137.90 (4*s*); 128.39–127.40 (several *d*); 75.03, 74.72, 73.68, 72.66, 70.74 (5*t*, 5 PhCH_2); 9.42 (*q*, MeS). HR-ESI-MS: 828.3305 (33, $[M + K]^+$, $C_{46}H_{51}KN_3O_7S^+$; calc. 828.3079), 812.3340 (100, $[M + Na]^+$, $C_{46}H_{51}N_3NaO_7S^+$; calc. 812.3340). Anal. calc. for $C_{46}H_{51}N_3O_7S$ (789.99): C 69.94, H 6.51, N 5.32; found: C 69.84, H 6.46, N 5.26.

Data of α-L-**36a**. Colourless oil. R_f (hexane/AcOEt 85:15) 0.33. IR (ATR): 3467*w* (br.), 3063*w*, 3030*w*, 2923*w*, 2869*w*, 2106*m*, 1496*w*, 1453*m*, 1381*w*, 1345*w*, 1273*w*, 1209*w*, 1088*s*, 1066*s*, 1027*m*, 960*w*, 911*w*, 733*s*, 696*s*. ^{1}H-NMR (400 MHz, $CDCl_3$; assignments based on selective homodecoupling experiments): 7.42–7.24 (*m*, 25 arom. H); 5.04 (*d*, *J* = 11.1), 4.81 (*d*, *J* = 10.0, 2 H), 4.70 (*d*, *J* = 11.9, 2 H), 4.56 (*d*, *J* = 11.2), 4.47 (*d*, *J* = 11.9), 4.43 (*d*, *J* = 11.9), 4.39 (*d*, *J* = 11.9), 4.31 (*d*, *J* = 11.8) (5 PhCH_2); 4.32–4.29 (*m*, H–C(2) overlapping with PhCH); 4.26 (*d*, *J* = 10.1, H–C(4)); 3.99–3.97 (*m*, H–C(6), OH); 3.93 (*dd*, *J* = 9.6, 2.2, H–C(8)); 3.84 (*dd*, *J* = 10.8, 2.4, H–C(5)); 3.82 (*qd*, *J* = 6.3, 2.2, H–C(9)); 3.65 (*dt*, *J* = 10.4, 1.9, H_a–C(1)); 3.54 (*dd*, *J* = 10.4, 7.5, H_b–C(1)); 3.67 (*dd*, *J* = 9.6, 1.0, H–C(7)); 1.91 (*s*, MeS); 1.02 (*d*, *J* = 6.3, Me). ^{13}C-NMR (100 MHz, $CDCl_3$; assignments based on a HSQC spectrum): 138.68, 138.23, 138.10, 137.80, 137.16 (5*s*); 128.63–127.45 (several *d*); 88.12 (*s*, C(3)); 80.69 (*d*, C(5)); 79.25 (*d*, C(4)); 77.14, 74.81 (2*t*, 2 PhCH_2); 74.76 (*d*, C(9)); 74.60 (*d*, C(6)); 73.54 (*t*, PhCH_2); 73.40 (*d*, C(2)); 73.10 (*d*, C(7)); 72.90 (*t*, PhCH_2); 72.03 (*t*, C(1)); 70.77 (*t*, PhCH_2); 63.25 (*d*, C(8)); 13.73 (*q*, Me); 9.35 (*q*, MeS). HR-ESI-MS: 812.3341 (100, $[M + Na]^+$, $C_{46}H_{51}NaN_3O_7S^+$; calc. 812.3340).

Methyl 2-O-*Acetyl-8-azido-1,4,5,6,9-penta*-O-*benzyl-8,10-dideoxy-3-thio*-D-ribo-*β*-L-manno-*dec-3-ulopyranoside* (**35b**). According to *GP 8*, 127 mg (0.15 mmol) of **34b** and FC the crude thioglycoside (hexane/AcOEt 95:5 → 4:1) gave **35b** (80 mg, 65%). Colouress oil. R_f (hexane/AcOEt 85:15) 0.42. $[\alpha]_D^{25} = +59.3$ (*c* = 1.09, $CHCl_3$). IR (ATR): 3063*w*, 3030*w*, 2927*w*, 2864*w*, 2104*m*, 1747*m*, 1496*w*, 1453*m*, 1369*m*, 1346*w*, 1300*w*, 1270*w*, 1225*m*, 1124*m*, 1073*s*, 1042*m*, 1026*m*, 985*m*, 947*m*, 905*w*, 731*s*, 695*s*. ^{1}H-NMR (300 MHz, $CDCl_3$; assignments based on selective homodecoupling experiments): see *Table 8*; additionally, 7.41–7.16 (*m*, 25 arom. H); 5.12 (*d*, *J* = 10.8), 4.78 (*d*, *J* = 11.4), 4.64 (*d*, *J* = 11.7), 4.60 (*d*, *J* = 11.4), 4.57 (*d*, *J* = 11.4), 4.56 (*d*, *J* = 11.3), 4.52 (*d*, *J* = 11.7), 4.51 (*d*, *J* = 11.7), 4.43 (*d*, *J* = 11.7), 4.34 (*d*, *J* = 12.3) (5 PhCH_2); 1.93 (*s*, MeS); 1.86 (*s*, *Me*C=O). ^{13}C-NMR (75 MHz, $CDCl_3$; assignments based on a HSQC spectrum): see *Table 8*; additionally, 170.10 (*s*, C=O); 138.57, 138.39, 138.16, 137.96, 137.71 (5*s*); 128.41–126.74 (several *d*); 74.73, 74.48, 72.50, 72.21, 70.98 (5*t*, 5 PhCH_2); 20.73 (*q*, *Me*C=O); 9.00 (*q*, MeS). HR-ESI-MS: 870.3435 (33, $[M + K]^+$, $C_{48}H_{53}KN_3O_8S^+$; calc. 870.3185), 854.3444 (100,

$[M + Na]^+$, $C_{48}H_{53}N_3NaO_8S^+$; calc. 854.3446). Anal. calc. for $C_{48}H_{53}N_3O_8S$ (832.03): C 69.29, H 6.42, N 5.05; found: C 69.38, H 6.43, N 4.95.

Methyl 9-Azido-5,6,7,10-tetra-O-*benzyl-2,3,9,11-tetradeoxy-4-thio*-D-erythro-α-D-galacto-*undec-4-ulopyranosidonitrile* (**42**). According to *GP 8*, 110 mg (0.15 mmol) of **41** and FC the crude thioglycoside (hexane/AcOEt 95:5 → 4:1) gave **42** (90 mg, 80%). Colourless oil. R_f (hexane/AcOEt 85:15) 0.35. $[\alpha]_D^{25} = +17.7$ ($c = 1.0$, $CHCl_3$). IR (ATR): 3063*w*, 3030*w*, 2926*w*, 2105*s*, 1496*w*, 1453*m*, 1380*w*, 1346*m*, 1304*w*, 1267*w*, 1209*w*, 1128*m*, 1085*s*, 1026*s*, 951*m*, 910*m*, 733*s*, 696*s*. ^{1}H-NMR (300 MHz, $CDCl_3$; assignments based on selective homodecoupling experiments): see *Table 8*; additionally, 7.46–7.24 (*m*, 20 arom. H); 5.08 (*d*, $J = 11.1$), 4.95 (*d*, $J = 11.7$), 4.83 (*d*, $J = 11.4$), 4.79 (*d*, $J = 12.3$), 4.75 (*d*, $J = 11.7$), 4.67 (*d*, $J = 11.1$), 4.59 (*d*, $J = 11.7$), 4.52 (*d*, $J = 12.0$) (4 PhCH_2); 2.09–2.00 (*m*, 2 H); 1.99–1.92 (*m*, 1 H); 1.84 (*s*, MeS); 1.52–1.41 (*m*, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$; assignments based on a HSQC spectrum): see *Table 8*; additionally, 138.50, 138.05, 137.78, 137.16 (4*s*); 129.04–127.46 (several *d*); 119.74 (*s*, CN); 74.55, 73.57, 72.37, 70.68 (4*t*, 4 PhCH_2); 9.31 (*q*, MeS). ESI-MS: 715.0 (100, $[M + Na]^+$). Anal. calc. for $C_{37}H_{41}N_3O_5S$ (692.88): C 69.34, H 6.40, N 8.09; found: C 69.29, H 6.43, N 7.98.

General Procedure for the Reduction of the Azides and Coupling with Propylhygric Acid (*GP 9*). A 1M soln. of the azido compound in THF/0.1N NaOH 4:1 was treated with 1M PMe_3 in THF (1.5 equiv.), stirred for 6 h at 50°, and evaporated. A soln. of the residue in CH_2Cl_2 was washed with H_2O and brine. The org. layer was dried ($MgSO_4$) and evaporated to afford the corresponding amine.

A 2M suspension of PHA (2 equiv.) in CH_2Cl_2 was treated with Et_3N (6 equiv.), followed by ClCOOEt (2 equiv.), and stirred at 25° for 1 h. After addition of a 2M soln. of the crude amine in CH_2Cl_2, the mixture was stirred for 1 h at 25° and evaporated.

Methyl 1-O-*Acetyl-3,4,5,8-tetra*-O-*benzyl-7,9-dideoxy-7-[(2*S,*4*R*)-1-methyl-4-propylpyrrolidine-2-carboxamido]-2-thio*-D-erythro-α-D-galacto-*non-2-ulopyranoside* (**26**). According to *GP 9*, 120 mg (0.16 mmol) of α-**25** and FC of the crude amide (amino phase gel, hexane/AcOEt 4:1 → 1:1) gave **26** (100 mg, 70%). Colourless oil. R_f (amino phase TLC, hexane/AcOEt 3:2) 0.50. $[\alpha]_D^{25} = +17.9$ ($c = 1.0$, $CHCl_3$). IR (ATR): 3030*w*, 2926*w*, 2870*w*, 2784*w*, 1742*m*, 1676*m*, 1497*m*, 1453*m*, 1375*m*, 1305*w*, 1223*m*, 1089*s*, 1027*s*, 949*w*, 909*w*, 732*s*, 696*s*. ^{1}H-NMR (300 MHz, $CDCl_3$; assignments based on selective homodecoupling experiments): see *Table 9*; additionally, 7.77 (*d*, $J = 9.6$, NH); 7.31–7.17 (*m*, 20 arom. H); 4.84 (*d*, $J = 10.4$), 4.80 (*d*, $J = 11.6$), 4.63 (*d*, $J = 11.1$) (3 PhC*H*); 4.61 (br. *s*, PhCH_2), 4.43 (*d*, $J = 11.6$), 4.43 (*d*, $J = 10.4$), 4.30 (*d*, $J = 11.2$) (3 PhC*H*); 2.81 (*dd*, $J = 8.4, 6.0$), 2.77 (*dd*, $J = 10.4, 5.2$) (2 H of prolinyl); 2.11 (*s*, MeN); 1.86 (*s*, MeS); 1.96–1.72 (*m*, 4 H); 1.71 (*s*, AcO); 1.28–1.20 (*m*, MeCH_2CH_2); 0.89 (br. *t*, $J = 6.6$, *Me*CH_2CH_2). ^{13}C-NMR (75 MHz, $CDCl_3$; assignments based on a HSQC spectrum): see *Table 9*; additionally, 174.23 (*s*, NC=O); 170.23 (*s*, OC=O); 139.05, 138.33, 138.15, 137.93 (4*s*); 128.35–127.13 (several *d*); 75.07, 73.44, 72.53, 70.65 (4*t*, 4 PhCH_2); 68.99 (*d*, C(2) of prolinyl); 62.62 (*t*, C(5) of prolinyl); 41.46 (*q*, MeN); 37.57 (*d*, C(4) of prolinyl); 37.46 (*t*, C(3) of prolinyl); 36.10 (*t*, MeCH_2CH_2); 21.49 (*t*, MeCH_2CH_2); 20.43 (*q*, *Me*C=O); 14.20 (*q*, *Me*CH_2CH_2); 9.28 (*q*, MeS). ESI-MS: 839.4 (100, $[M + Na]^+$). Anal. calc. for $C_{49}H_{62}N_2O_8S$ (839.10): C 70.14, H 7.45, N 3.34; found: C 70.43, H 7.62, N 3.39.

*Methyl (1*R*)-1*-O-*Acetyl-3,4,5,8-tetra*-O-*benzyl-7,9-dideoxy-1*-C-*heptyl-7-[(2*S,*4*R*)-1-methyl-4-propylpyrrolidine-2-carboxamido]-2-thio*-D-erythro-α-D-galacto-*non-2-ulopyranoside* (**31a**). According to *GP 9*, 200 mg (0.25 mmol) of α-**30a** and FC of the crude amide (amino phase gel, hexane/AcOEt 4:1 → 1:1) gave **31a** (185 mg, 80%). Colourless oil. R_f (amino phase TLC, hexane/AcOEt 3:2) 0.56. $[\alpha]_D^{25} = +60.4$ ($c = 1.0$, $CHCl_3$). IR (ATR): 3356*w* (br.), 3030*w*, 2958*w*, 2925*m*, 2856*w*, 2781*w*, 1739*m*, 1674*m*, 1497*m*, 1453*m*, 1369*w*, 1305*m*, 1233*s*, 1179*w*, 1087*s*, 1027*s*, 912*w*, 820*w*, 732*s*, 695*s*. ^{1}H-NMR (300 MHz, $CDCl_3$; assignments based on selective homodecoupling experiments): see *Table 9*; additionally, 8.02 (*d*, $J = 9.3$, NH); 7.39–7.21 (*m*, 20 arom. H); 4.92 (*d*, $J = 11.4$, PhC*H*); 4.83, 4.63 (2*s*, 2 PhCH_2); 4.58 (*d*, $J = 11.4$), 4.50 (*d*, $J = 11.4$), 4.32 (*d*, $J = 11.4$) (3 PhC*H*); 2.82 (*dd*, $J = 10.8, 5.4$), 2.81–2.75 (*m*) (2 H of prolinyl); 2.13 (*s*, MeN); 2.04–1.52 (*m*, Me(CH_2)$_5$CH_2); 1.90 (*s*, MeS); 1.89 (*s*, AcO); 1.38–1.18 (*m*, MeCH_2CH_2, Me(CH_2)$_5$CH_2); 0.92–0.85 (*m*, *Me*(CH$_2$)$_6$, *Me*CH_2CH_2). ^{13}C-NMR (75 MHz, $CDCl_3$; assignments based on a HSQC spectrum): see *Table 9*; additionally, 174.10 (*s*, NC=O); 170.33 (*s*, OC=O); 138.99, 138.73, 138.13 (2 C) (3*s*); 128.30–126.95 (several *d*); 74.46, 73.21, 72.96, 70.86 (4*t*, 4 PhCH_2); 69.13 (*d*, C(2) of prolinyl); 62.71 (*t*, C(5) of prolinyl); 41.53 (*q*, MeN); 37.59 (*d* and *t*, C(3) and C(4) of prolinyl); 36.56 (*t*, MeCH_2CH_2); 31.92, 29.77, 29.67, 29.46, 26.60, 22.78 (6*t*, *Me*(CH_2)$_6$); 21.74 (*t*,

Table 9. *Selected ^{1}H-NMR Chemical Shifts* [ppm] *and Coupling Constants* [Hz], *and ^{13}C-NMR Chemical Shifts* [ppm] *of the Protected Lincomycin Analogues* **26**, **31a**, **31b**, **37a**, **37b**, **43**, *and* **46** *in $CDCl_3$* (numbering as for lincosamine)[a])

	26[b])	**31a**[b])	**31b**	**37a**[b])	**37b**[c])	**43**[b])	**46**[b])
H–C(2)	4.29	4.26	4.36	4.50	4.36	3.92	4.05–3.98
H–C(3)	3.93	3.99	4.00	3.99	3.90	4.04	4.05–3.98
H–C(4)	3.91	4.07	3.94	3.96	3.84	3.99	4.05–3.98
H–C(5)	3.97	4.08	3.90	4.07	3.87	4.06	4.10
H–C(6)	4.42–4.40	4.42	4.64–4.58	4.42	4.57–4.53	4.36	4.37
H–C(7)	3.60	3.67	3.82	3.45	3.72	3.52	3.53
H_3C(8)	1.14	1.27	1.22	1.20	1.14	1.21	1.22
H_a–C(1′)	4.36	5.15	5.19	3.92–3.96	5.46	[d])	[d])
H_b–C(1′)	4.05	–	–	–	–	[d])	[d])
H_a–C(2′)	–	[d])	[d])	3.87	4.06	[d])	[d])
H_b–C(2′)	–	[d])	[d])	3.63	3.44	[d])	[d])
NH	7.77	8.02	7.77	7.97	7.67	7.99	8.07
J(2,3)	8.8	9.3	9.3	9.3	9.6	9.9	[e])
J(3,4)	2.4	2.1	2.1	2.1	2.4	2.4	[e])
J(5,6)	6.8	6.0	8.4	6.3	8.4	6.3	6.0
J(6,7)	4.4	6.3	3.3	6.3	3.2	6.0	5.7
J(7,Me)	6.4	6.3	6.3	6.3	6.4	6.3	6.0
J(6,NH)	9.6	9.3	9.9	9.9	10.0	9.6	9.6
J(1′,2′$_a$)	–	1.5[f])	1.5[f])	2.4	2.8	[e])	[e])
J(1′,2′$_b$)	–	10.2[f])	8.1[f])	6.9	8.8	[e])	[e])
J(1′$_a$,1′$_b$)	11.6	–	–	9.9[g])	11.6[g])	[e])	[e])
C(1)	89.46	92.29	92.67	91.96	91.36	89.53	90.83
C(2)	74.40	76.47	76.35	77.23	75.43	74.66	76.54
C(3)	81.88	82.78	83.10	82.31	82.81	82.43	82.62
C(4)	74.91	74.46	73.91	74.11	74.03	74.41	75.02
C(5)	70.89	69.99	70.79	70.64	71.12	70.21	70.07
C(6)	51.67	53.05	50.39	52.56	50.52	52.69	53.10
C(7)	75.37	75.44	75.21	74.91	75.57	75.08	75.34
C(8)	16.01	16.46	15.66	16.13	15.90	16.21	16.35
C(1′)	65.07	74.26	75.29	74.11	75.11	33.60	33.17
C(2′)	–	[d])	[d])	70.64	70.90	11.15	28.27

[a]) $J(4,5) < 1.5$ Hz (line broadening). [b]) Assignments based on a HSQC spectrum. [c]) Assignments based on DQFCOSY and HSQC spectra. [d]) See *Exper. Part.* [e]) Not assigned. [f]) Can be interchanged. [g]) $J(2'_a,2'_b)$.

Me*C*H$_2$CH$_2$); 21.14 (*q*, *Me*C=O); 14.48 (*q*, *Me*CH$_2$CH$_2$); 14.24 (*q*, *Me*(CH$_2$)$_6$); 9.84 (*q*, MeS). ESI-MS: 937.4 (100, $[M + H]^+$). Anal. calc. for $C_{56}H_{76}N_2O_8S$ (937.29): C 71.76, H 8.17, N 2.99; found: C 71.67, H 8.11, N 2.98.

*Methyl (1*S*)-1-*O*-Acetyl-3,4,5,8-tetra*-O*-benzyl-7,9-dideoxy-1-*C*-heptyl-7-[(2*S*,4*R*)-1-methyl-4-propylpyrrolidine-2-carboxamido]-2-thio*-D-erythro-*α*-D-galacto-*non-2-ulopyranoside* (**31b**). According to *GP 9*, 100 mg (0.12 mmol) of **30b** and FC of the crude amide (amino phase gel, hexane/AcOEt 4:1 → 1:1) gave **31b** (82 mg, 70%). Colourless oil. R_f (amino phase TLC, hexane/AcOEt 3:2) 0.56. $[\alpha]_D^{25} = +23.8$ ($c = 1.0$, $CHCl_3$). IR (ATR): 3346*w* (br.), 3030*w*, 2953*w*, 2924*w*, 2855*w*, 2785*w*, 1743*m*, 1681*m*, 1497*m*, 1453*m*, 1369*w*, 1304*m*, 1229*m*, 1122*m*, 1086*s*, 1027*m*, 946*w*, 910*w*, 822*w*, 787*w*, 731*s*, 695*s*. ^{1}H-NMR (300 MHz, $CDCl_3$; assignments based on selective homodecoupling experiments): see *Table 9*; additionally, 7.77 (*d*, $J = 9.9$, NH); 7.48–7.21 (*m*, 20 arom. H); 5.03 (*d*, $J = 11.7$), 4.89 (*d*, $J \approx 9.9$), 4.72 (*d*, $J =$

12.0), 4.70 (*d*, *J* = 11.4), 4.65 (*d*, *J* = 11.4), 4.52 (*d*, *J* ≈ 9.6) (6 PhC*H*); 4.47 (br. *s*, PhCH_2); 2.96 (br. *dd*, *J* = 13.8, 2.1), 2.91 (*dd*, *J* = 9.9, 5.1) (2 H of prolinyl); 2.24 (*s*, MeN); 2.14–1.75 (*m*, 3 H of prolinyl, Me$(CH_2)_5CH_2$); 1.96 (*s*, MeS); 1.71 (*s*, AcO); 1.63–1.49 (*m*, 1 H of prolinyl); 1.35–1.02 (*m*, MeCH_2CH_2, Me$(CH_2)_5CH_2$); 0.92–0.82 (*m*, *Me*$(CH_2)_6$, *Me*CH_2CH_2). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 9*; additionally, 174.17 (*s*, NC=O); 170.67 (*s*, OC=O); 138.94, 138.57, 138.20, 138.03 (4*s*); 128.33–127.22 (several *d*); 74.51, 73.91, 72.19, 70.79 (4*t*, 4 PhCH_2); 68.92 (*d*, C(2) of prolinyl); 62.65 (*t*, C(5) of prolinyl); 41.59 (*q*, MeN); 37.78 (*d*, C(4) of prolinyl); 37.54 (*t*, C(3) of prolinyl); 35.97 (*t*, MeCH_2CH_2); 31.70, 29.88, 29.25, 29.09, 26.51, 22.53 (6*t*, Me$(CH_2)_6$); 21.56 (*t*, MeCH_2CH_2); 20.53 (*q*, *Me*C=O); 14.17 (*q*, *Me*CH_2CH_2); 14.00 (*q*, *Me*$(CH_2)_6$); 9.28 (*q*, MeS). HR-ESI-MS: 959.5226 (17, $[M + Na]^+$, $C_{56}H_{76}N_2NaO_8S^+$; calc. 959.5215), 937.5394 (100, $[M + H]^+$, $C_{56}H_{77}N_2O_8S^+$; calc. 937.5395). Anal. calc. for $C_{56}H_{76}N_2O_8S$ (937.29): C 71.76, H 8.17, N 2.99; found: C 71.68, H 8.37, N 3.02.

Methyl 1,4,5,6,9-Penta-O-*benzyl-8,10-dideoxy-8-[(2*S*,4*R*)-1-methyl-4-propylpyrrolidine-2-carboxamido]-3-thio*-D-ribo-*β*-L-gluco-*dec-3-ulopyranoside* (**37a**). According to *GP 9*, 70 mg (0.089 mmol) of *β*-L-**36a** and FC of the crude amide (amino phase gel, hexane/AcOEt 4:1 → 1:1) gave **37a** (70 mg, 86%). Colourless oil. R_f (amino phase TLC, hexane/AcOEt 3:2) 0.26. $[\alpha]_D^{25} = +57.5$ (*c* = 1.0, $CHCl_3$). IR (ATR): 3347*w* (br.), 3062*w*, 3029*w*, 2926*w*, 2869*w*, 2782*w*, 1671*m*, 1496*m*, 1453*m*, 1377*w*, 1361*w*, 1306*w*, 1208*w*, 1089*s*, 1026*s*, 958*w*, 911*w*, 821*w*, 732*s*, 695*s*. ^{1}H-NMR (300 MHz, $CDCl_3$; assignments based on selective homodecoupling experiments): see *Table 9*; additionally, 7.97 (*d*, *J* = 9.9, NH); 7.39–7.22 (*m*, 25 arom. H); 4.90 (*d*, *J* = 10.5), 4.83 (*d*, *J* = 11.4), 4.77 (*d*, *J* = 11.4), 4.67 (*d*, *J* = 12.0), 4.61 (*d*, *J* = 11.7), 4.55 (*d*, *J* = 12.0), 4.55 (*d*, *J* = 11.4), 4.49 (*d*, *J* = 10.8), 4.47 (*d*, *J* = 11.7), 4.28 (*d*, *J* = 11.4) (5 PhCH_2); 2.94 (*d*, *J* = 4.5, OH); 2.85 (*dd*, *J* = 10.8, 4.8), 2.76 (*dd*, *J* = 8.4, 6.0) (2 H of prolinyl); 2.14 (*s*, MeN); 2.12–1.70 (*m*, 4 H); 1.90 (*s*, MeS); 1.30–1.13 (*m*, MeCH_2CH_2); 0.92–0.85 (*m*, *Me*CH_2CH_2). ^{13}C-NMR (75 MHz, $CDCl_3$; assignments based on a HSQC spectrum): see *Table 9*; additionally, 174.61 (s, C=O); 138.64, 138.33, 138.15, 138.10, 138.07 (5*s*); 128.38–127.24 (several *d*); 74.91, 73.56, 73.43, 72.85, 70.47 (5*t*, 5 PhCH_2); 68.91 (*d*, C(2) of prolinyl); 62.53 (*t*, C(5) of prolinyl); 41.47 (*q*, MeN); 37.67 (*d*, C(4) of prolinyl); 37.57 (*t*, C(3) of prolinyl); 36.00 (*t*, MeCH_2CH_2); 21.54 (*t*, MeCH_2CH_2); 14.26 (*q*, *Me*CH_2CH_2); 9.45 (*q*, MeS). ESI-MS: 939.4 (100, $[M + Na]^+$). Anal. calc. for $C_{55}H_{68}N_2O_8S$ (917.22): C 72.02, H 7.47, N 3.05; found: C 71.98, H 7.55, N 3.07.

Methyl 2-O-*Acetyl-1,4,5,6,9-penta*-O-*benzyl-8,10-dideoxy-8-[(2*S*,4*R*)-1-methyl-4-propylpyrrolidine-2-carboxamido]-3-thio*-D-ribo-*β*-L-manno-*dec-3-ulopyranoside* (**37b**). According to *GP 9*, 70 mg (0.08 mmol) of **37b** and FC of the crude amide (amino phase gel, hexane/AcOEt 4:1 → 1:1) gave **35b** (50 mg, 65%). Colourless oil. R_f (amino phase TLC, hexane/AcOEt 3:1) 0.14. $[\alpha]_D^{25} = +33.4$ (*c* = 0.51, $CHCl_3$). IR (ATR): 3030*w*, 2926*w*, 2870*w*, 2785*w*, 1747*m*, 1678*m*, 1497*m*, 1453*m*, 1369*m*, 1305*w*, 1227*s*, 1177*w*, 1087*s*, 1045*s*, 1027*s*, 948*w*, 909*w*, 732*s*, 696*s*. ^{1}H-NMR (400 MHz, $CDCl_3$; assignments based on a DQFCOSY spectrum): see *Table 9*; additionally, 7.67 (*d*, *J* = 10.0, NH); 7.39–7.09 (*m*, 25 arom. H); 4.94 (*d*, *J* = 11.7), 4.81 (*d*, *J* = 9.6), 4.59 (*d*, *J* = 11.6), 4.55 (*d*, *J* = 11.6), 4.53 (*d*, *J* = 11.6), 4.45 (*d*, *J* = 10.0), 4.41 (*d*, *J* = 11.2), 4.38 (*d*, *J* = 11.2), 4.33 (*d*, *J* = 12.0), 4.23 (*d*, *J* = 12.0) (5 PhCH_2); 2.93 (*dd*, *J* = 8.4, 6.0), 2.84 (*dd*, *J* = 10.4, 5.2) (2 H of prolinyl); 2.17 (*s*, MeN); 2.08–1.72 (*m*, 4 H); 1.89 (*s*, MeS); 1.68 (*s*, AcO); 1.26–1.14 (*m*, MeCH_2CH_2); 0.78 (*t*, *J* = 6.6, *Me*CH_2CH_2). ^{13}C-NMR (75 MHz, $CDCl_3$; assignments based on a HSQC spectrum): see *Table 9*; additionally, 174.28 (*s*, NC=O); 170.18 (*s*, OC=O); 139.09, 138.63, 138.33, 138.17, 138.06 (5*s*); 128.47–127.11 (several *d*); 74.64, 74.16, 72.56, 72.27, 69.81 (5*t*, 5 PhCH_2); 69.04 (*d*, C(2) of prolinyl); 62.81 (*t*, C(5) of prolinyl); 41.76 (*q*, MeN); 37.99 (*d*, C(4) of prolinyl); 37.69 (*t*, C(3) of prolinyl); 36.00 (*t*, MeCH_2CH_2); 21.67 (*t*, MeCH_2CH_2); 20.71 (*q*, *Me*C=O); 14.29 (*q*, *Me*CH_2CH_2); 9.66 (*q*, MeS). HR-ESI-MS: 981.4704 (100, $[M + Na]^+$, $C_{57}H_{70}N_2NaO_9S^+$; calc. 981.4694), 959.4884 (43, $[M + H]^+$, $C_{57}H_{71}N_2O_9S$; calc. 959.4875).

Methyl 5,6,7,10-Tetra-O-*benzyl-2,3,9,11-tetradeoxy-9-[(2*S*,4*R*)-1-methyl-4-propylpyrrolidine-2-carboxamido]-3-thio*-D-erythro-*α*-D-galacto-*undec-4-ulopyranosidonitrile* (**43**). According to *GP 9*, 165 mg (0.23 mmol) of **42** and FC of the crude amide (amino phase gel, hexane/AcOEt 4:1 → 1:1) gave **43** (125 mg, 65%). Colourless oil. R_f (amino phase TLC, hexane/AcOEt 3:2) 0.36. $[\alpha]_D^{25} = +17.7$ (*c* = 1.0, $CHCl_3$). IR (ATR): 3030*w*, 2926*w*, 2871*w*, 2783*w*, 1668*m*, 1497*m*, 1453*m*, 1377*w*, 1349*m*, 1306*w*, 1267*w*, 1208*w*, 1086*s*, 1026*m*, 909*m*, 729*s*, 696*s*. ^{1}H-NMR (300 MHz, $CDCl_3$; assignments based on selective homodecoupling experiments): see *Table 9*; additionally, 7.99 (*d*, *J* = 9.6, NH); 7.41–7.23 (*m*, 20 arom. H); 4.92 (*d*, *J* = 11.7), 4.81 (*d*, *J* = 10.8), 4.76 (*d*, *J* = 12.0), 4.70 (*d*, *J* = 11.7), 4.65 (*d*, *J* = 11.7), 4.58 (*d*,

$J = 11.4$), 4.48 (d, $J = 10.5$), 4.31 (d, $J = 11.1$) (4 PhCH_2); 2.84 (dd, $J = 9.9, 5.1$), 2.64–2.60 (m) (2 H of prolinyl); 2.12 (s, MeN); 2.11–2.02 (m, 3 H); 1.88 (s, MeS); 1.85–1.73 (m, 4 H); 1.50–1.39 (m, 1 H); 1.25–1.15 (m, MeCH_2CH_2); 0.97–0.85 (m, *Me*CH_2CH_2). ^{13}C-NMR (75 MHz, $CDCl_3$; based on a HSQC spectrum): see *Table 9*; additionally, 174.56 (s, C=O); 138.75, 138.19, 137.96, 137.34 (4s); 129.00–127.47 (several d); 119.54 (s, CN); 74.61, 73.75, 72.74, 70.75 (4t, 4 PhCH_2); 68.83 (d, C(2) of prolinyl); 62.41 (t, C(5) of prolinyl); 41.46 (q, MeN); 38.03 (d, C(4) of prolinyl); 37.82 (t, C(3) of prolinyl); 35.73 (t, MeCH_2CH_2); 21.74 (t, MeCH_2CH_2); 14.33 (q, *Me*CH_2CH_2); 9.36 (q, MeS). HR-ESI-MS: 820.4356 (100, $[M + H]^+$, $C_{49}H_{62}N_3O_6S^+$; 820.4354).

Methyl {Methyl 5,6,7,10-Tetra-O-*benzyl-2,3,9,11-tetradeoxy-9-[(2*S*,4*R*)-1-methyl-4-propylpyrrolidine-2-carboxamido]*-D-erythro-*α*-D-galacto-*undec-4-ulopyranosid}onate* (**46**). According to *GP 9*, 180 mg (0.25 mmol) of **45** and FC of the crude amide (amino phase gel, hexane/AcOEt 4:1 → 1:1) gave **46** (120 mg, 60%). Colourless oil. R_f (amino phase TLC, hexane/AcOEt 3:2) 0.33. $[\alpha]_D^{25} = +23.95$ ($c = 1.0$, $CHCl_3$). IR (ATR): 3030w, 2925w, 2870w, 2781w, 1736m, 1670m, 1497m, 1453m, 1376w, 1304w, 1171w, 1086s, 1026m, 909m, 731s, 696s. ^{1}H-NMR (300 MHz, $CDCl_3$; assignments based on selective homodecoupling experiments): see *Table 9*; additionally, 8.07 (d, $J = 9.6$, NH); 7.40–7.22 (m, 20 arom. H); 4.90 (d, $J = 12.0$), 4.84 (d, $J = 11.1$), 4.73 (d, $J = 12.0$), 4.69 (d, $J = 11.7$), 4.63 (d, $J = 11.4$), 4.57 (d, $J = 11.7$), 4.50 (d, $J = 10.8$), 4.33 (d, $J = 11.7$) (4 PhCH_2); 3.58 (s, MeO); 2.84 (dd, $J = 7.5, 4.5$), 2.68–2.60 (m) (2 H of prolinyl); 2.39–2.12 (m, 5 H); 2.11 (s, MeN); 2.01–1.66 (m, 3 H); 1.91 (s, MeS); 1.29–1.23 (m, MeCH_2CH_2); 0.92–0.86 (m, *Me*CH_2CH_2). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 9*; additionally, 174.56 (s, NC=O); 174.56 (s, OC=O); 139.13, 138.49, 138.40, 138.08 (4s); 128.62–127.45 (several d); 75.10, 73.74, 72.95, 70.89 (4t, 4 PhCH_2); 69.09 (d, C(2) of prolinyl); 62.61 (t, C(5) of prolinyl); 41.60 (q, MeN); 38.01 (d, C(4) of prolinyl); 37.90 (t, C(3) of prolinyl); 36.07 (t, MeCH_2CH_2); 21.84 (t, MeCH_2CH_2); 14.56 (q, *Me*CH_2CH_2); 9.64 (q, MeS). ESI-MS: 853.1 (100, $[M + H]^+$). Anal. calc. for $C_{50}H_{64}N_2O_8S$ (853.13): C 70.39, H 7.56, N 3.28; found: C 70.23, H 7.66, N 3.37.

General Procedure for the Debenzylation (*GP 10*). NH_3 was condensed in a cold (−78°) 5M soln. of the benzyl ether in THF. The mixture was treated with Na (20 equiv.), stirred for 8 h, treated dropwise with MeOH until the blue color disappeared, warmed to 25°, and evaporated.

*Methyl 7,9-Dideoxy-7-[(2*S*,4*R*)-1-methyl-4-propylpyrrolidine-2-carboxamido]-2-thio-*D-erythro-*α*-D-galacto-*non-2-ulopyranoside* (**27**). According to *GP 10*, debenzylation of 60 mg (0.07 mmol) of **26**, followed by FC (amino phase gel, AcOEt/MeOH 98:2 → 4:1), gave **27** (20 mg, 65%). R_f (amino phase TLC, AcOEt/MeOH 9:1) 0.69. $[\alpha]_D^{25} = +58.0$ ($c = 1.13$, $CHCl_3$). IR (ATR): 3321m (br.), 2958m, 2927m, 2872w, 2789w, 1646m, 1522m, 1454w, 1403w, 1379w, 1235w, 1076s, 945w, 863w, 750s, 701w, 664w. ^{1}H-NMR (300 MHz, CD_3OD; assignments based on selective homodecoupling experiments): see *Table 10*; additionally, 3.15 (dd, $J = 8.4, 6.6$), 3.03 (dd, $J = 9.6, 6.0$) (2 H of prolinyl); 2.31 (s, MeN); 2.21–2.12 (m, 1 H); 2.05 (br. t, $J = 9.3$, 1 H); 1.97 (s, MeS); 1.94–1.76 (m, 2 H); 1.38–1.22 (m, MeCH_2CH_2); 0.85 (br. t, $J = 6.9$, *Me*CH_2CH_2). ^{13}C-NMR (75 MHz, CD_3OD): see *Table 10*; additionally, 176.45 (s, C=O); 67.56 (d, C(2) of prolinyl); 62.15 (t, C(5) of prolinyl); 40.46 (q, MeN); 37.75 (d, C(4) of prolinyl); 36.49 (t, C(3) of prolinyl); 35.59 (t, MeCH_2CH_2); 20.80 (t, MeCH_2CH_2); 13.45 (t, *Me*CH_2CH_2); 8.10 (q, MeS). ESI-MS: 437.23 (100, $[M + H]^+$).

*Methyl (1*R*)-7,9-Dideoxy-1-*C*-heptyl-7-[(2*S*,4*R*)-1-methyl-4-propylpyrrolidine-2-carboxamido]-2-thio-*D-erythro-*α*-D-galacto-*non-2-ulopyranoside* (**32a**). According to *GP 10*, debenzylation of 100 mg (0.10 mmol) of **31a**, followed by FC (amino phase gel, AcOEt/MeOH 98:2 → 4:1), gave **32a** (30 mg, 50%). R_f (amino phase TLC, AcOEt/MeOH 9:1) 0.69. $[\alpha]_D^{25} = +73.6$ ($c = 1.3$, $CHCl_3$). IR (ATR): 3334w (br.), 2956w, 2924m, 2855w, 2790w, 1645m, 1522m, 1455w, 1378w, 1303w, 1215w, 1077m, 1059s, 980w, 943w, 879w, 751s, 664w. ^{1}H-NMR (400 MHz, CD_3OD; assignments based on a DQFCOSY spectrum): see *Table 10*; additionally, 3.23 (dd, $J = 7.5, 5.4$), 2.97 (dd, $J = 10.2, 5.1$) (2 H of prolinyl); 2.37 (s, MeN); 2.26–1.72 (m, 4 H); 1.91 (s, MeS); 1.62–1.44 (m, CH_2(CH_2)$_5$Me); 1.44–1.22 (m, MeCH_2CH_2, Me(CH_2)$_5$CH_2); 0.98–0.85 (m, *Me*(CH$_2$)$_6$, *Me*CH_2CH_2). ^{13}C-NMR (100 MHz, CD_3OD; assignments based on a HSQC spectrum): see *Table 10*; additionally, 174.73 (s, C=O); 69.76 (d, C(2) of prolinyl); 63.55 (t, C(5) of prolinyl); 41.63 (q, MeN); 38.53 (d, C(4) of prolinyl); 38.33 (t, C(3) of prolinyl); 37.08 (t, MeCH_2CH_2); 32.78, 31.59, 30.54, 30.46, 27.67, 23.47 (6t, Me(CH_2)$_6$); 22.45 (t, MeCH_2CH_2); 14.40 (q, *Me*CH_2CH_2); 14.16 (q, *Me*(CH$_2$)$_6$); 8.31 (q, MeS). HR-MALDI-MS: 573.2995 (6, $[M + K]^+$,

Table 10. *Selected ^{1}H-NMR Chemical Shifts* [ppm] *and Coupling Constants* [Hz], *and ^{13}C-NMR Chemical Shifts* [ppm] *of* **27**, **32a**, **32b**, **38a**, **38b**, **44**, *and* **47** *in CD_3OD* (numbering as for lincosamine)

	27	**32a**[a])	**32b**[a])	**38a**[a])	**38b**[a])	**44**[a])	**47**
H–C(2)	4.09	4.50	4.01	4.06	4.17	3.86–3.80	3.90
H–C(3)	3.87	3.84	3.84	3.83	3.80	3.86–3.80	3.83
H–C(4)	3.95	4.06	4.08	4.05	3.99	4.08	4.00
H–C(5)	4.13	4.24	4.13	4.23	4.19–4.15	4.18	4.08
H–C(6)	4.29	4.09	4.13	4.07	4.19–4.15	4.09	4.13
H–C(7)	4.18	3.87	3.89	3.86	4.03–3.96	3.86	3.86
H_3C(8)	1.17	1.19	1.19	1.19	1.20	1.19	1.18
H–C(1′)	3.86–3.78	3.71	3.74	3.82	3.95–3.85	[b])	[b])
H_a–C(2′)	–	[b])	[b])	3.92	3.95–3.85	[b])	[b])
H_b–C(2′)	–	[b])	[b])	3.72	3.95–3.85	[b])	[b])
J(2,3)	9.6	9.6	9.6	9.5	9.6	[c])	9.6
J(3,4)	3.0	3.3	3.9	3.4	3.3	1.8	3.3
J(4,5)	[d])	[d])	[d])	1.2	[d])	1.5	[d])
J(5,6)	8.7	5.7	6.6	6.0	[c])	6.0	6.6
J(6,7)	4.8	7.8	6.3	8.1	[c])	7.8	6.6
J(7,Me)	6.3	6.3	6.6	6.3	6.3	6.6	6.6
$J(1',2'_a)$	–	9.9[e])	10.5[e])	4.0	[c])	[c])	[c])
$J(1',2'_b)$	–	1.5[e])	1.5[e])	7.0	[c])	[c])	[c])
$J(1'_a,1'_b)$	12.3	–	–	11.4[f])	–	[c])	[c])
C(1)	91.00	93.63	93.20	93.35	94.03	90.90	92.79
C(2)	70.53	70.47	71.96	71.43	68.77	71.49	71.48
C(3)	70.82	72.42	72.51	72.49	72.77	71.94	71.78
C(4)	68.58	69.90	69.94	70.17	70.33	70.18	70.31
C(5)	68.58	71.08	71.11	71.66	71.78	71.05	71.00
C(6)	53.51	56.98	56.88	57.11	56.52	56.84	56.58
C(7)	66.63	68.26	68.03	68.50	68.40	68.00	67.80
C(8)	16.48	20.31	20.33	20.60	19.90	20.27	19.68
C(1′)	63.81	75.28	80.21	77.49	77.81	35.14	35.26
C(2′)	–	[b])	[b])	64.03	63.69	12.50	32.19

[a]) Assignments based on DFQCOSY and HSQC spectra. [b]) See *Exper. Part.* [c]) Not assigned. [d]) $J <$ 1.5 Hz (line broadening). [e]) Assignments may be interchanged. [f]) $J(2'_a,2'_b)$.

$C_{26}H_{50}KN_2O_7S^+$; calc. 573.2970), 557.3224 (29, $[M + Na]^+$, $C_{26}H_{50}N_2NaO_7S^+$; calc. 557.3231), 535.3403 (100, $[M + H]^+$, $C_{26}H_{51}N_2O_7S^+$; calc. 535.3411).

*Methyl (1*S*)-7,9-Dideoxy-1-*C*-heptyl-3-[(2*S*,4*R*)-1-methyl-4-propylpyrrolidine-2-carboxamido]-2-thio-*D*-erythro-α-*D*-galacto-non-2-ulopyranoside* (**32b**). According to *GP 10*, debenzylation of 60 mg (0.06 mmol) of **31b**, followed by FC (amino phase gel, AcOEt/MeOH 98:2 → 4:1), gave **32b** (20 mg, 60%). R_f (amino phase TLC, AcOEt/MeOH 9:1) 0.69. $[\alpha]_D^{25} = +40.0$ ($c = 0.86$, $CHCl_3$). IR (ATR): 3330*m* (br.), 2955*m*, 2923*m*, 2854*w*, 2787*w*, 1645*m*, 1523*m*, 1455*w*, 1403*w*, 1378*w*, 1303*w*, 1232*w*, 1082*s*, 1059*s*, 996*w*, 945*m*, 908*w*, 893*w*, 875*w*, 793*w*, 753*s*, 725*w*, 702*w*, 663*w*, 636*w*. ^{1}H-NMR (300 MHz, CD_3OD; assignments based on a DQFCOSY spectrum): see *Table 10*; additionally, 3.20 (*dd*, $J = 7.5, 5.7$), 2.96 (*dd*, $J = 10.2$, 4.5) (2 H of prolinyl); 2.36 (*s*, MeN); 2.26–1.74 (*m*, 4 H); 1.97 (*s*, MeS); 1.64–1.42 (*m*, $Me(CH_2)_5CH_2$); 1.40–1.22 (*m*, $MeCH_2CH_2$, $Me(CH_2)_5CH_2$); 0.98–0.85 (*m*, $Me(CH_2)_6$, $MeCH_2CH_2$). ^{13}C-NMR (75 MHz, CD_3OD; assignments based on a HSQC spectrum): see *Table 10*; additionally, 176.99 (*s*, C=O); 69.66 (*d*, C(2) of prolinyl); 63.44 (*t*, C(5) of prolinyl); 41.57 (*q*, MeN); 38.61 (*d*, C(4) of prolinyl); 38.39 (*t*, C(3) of prolinyl); 36.89 (*t*, $MeCH_2CH_2$); 32.77, 32.47, 30.58, 30.34, 27.91, 23.48 (6*t*,

Me(CH_2)$_6$); 22.48 (*t*, MeCH_2CH$_2$); 14.44 (*t*, *Me*CH_2CH$_2$); 14.20 (*t*, *Me*(CH_2)$_6$); 10.14 (*q*, MeS). HR-MALDI-MS: 573.2949 (16, $[M + K]^+$, $C_{26}H_{50}KN_2O_7S^+$; calc. 573.2970), 557.3220 (59, $[M + Na]^+$, $C_{26}H_{50}N_2NaO_7S^+$; calc. 557.3231), 535.3400 (100, $[M + H]^+$, $C_{26}H_{51}N_2O_7S^+$; calc. 535.3411).

*Methyl 8,10-Dideoxy-8-[(2*S*,4*R*)-1-methyl-4-propylpyrrolidine-2-carboxamido]-3-thio*-D-ribo-*β*-L-gluco-*dec-3-ulopyranoside* (**38a**). According to *GP 10*, debenzylation of 90 mg (0.99 mmol) of **37a**, followed by FC (amino phase gel, AcOEt/MeOH 98 : 2 → 4 : 1), gave **38a** (25 mg, 55%). R_f (amino phase TLC, AcOEt/MeOH 4 : 1) 0.21. $[\alpha]_D^{25} = +75.3$ ($c = 1.06$, $CHCl_3$). IR (ATR): 3316*m* (br.), 2926*m*, 2789*w*, 1646*m*, 1523*m*, 1454*m*, 1408*m*, 1375*m*, 1306*w*, 1215*w*, 1077*s*, 959*w*, 915*w*, 881*w*, 751*s*, 698*w*, 663*w*. ^{1}H-NMR (300 MHz, CD_3OD; assignments based on a DQFCOSY spectrum): see *Table 10*; additionally, 3.18 (*dd*, $J = 8.4, 6.2$), 2.90 (*dd*, $J = 10.7, 4.6$) (2 H of prolinyl); 2.34 (*s*, MeN); 2.33–1.97 (*m*, 3 H); 1.95 (*s*, MeS); 1.84–1.78 (*m*, 1 H); 1.36–1.20 (*m*, MeCH_2CH_2); 0.92 (*t*, $J = 6.0$, *Me*CH_2CH_2). ^{13}C-NMR (75 MHz, CD_3OD; assignments based on a HSQC spectrum): see *Table 10*; additionally, 177.82 (*s*, C=O); 70.08 (*d*, C(2) of prolinyl); 63.82 (*t*, C(5) of prolinyl); 41.94 (*q*, MeN); 38.97 (*d*, C(4) of prolinyl); 38.64 (*t*, C(3) of prolinyl); 37.05 (*t*, MeCH_2CH_2); 22.59 (*t*, MeCH_2CH_2); 14.65 (*q*, *Me*CH_2CH_2); 9.11 (*q*, MeS). HR-MALDI-MS: 489.2252 (100, $[M + Na]^+$, $C_{20}H_{38}NaN_2O_7S^+$; calc. 489.2241); 467.2423 (100, $[M + H]^+$, $C_{20}H_{39}N_2O_7S^+$; calc. 467.2422).

*Methyl 8,10-Dideoxy-8-[(2*S*,4*R*)-1-methyl-4-propylpyrrolidine-2-carboxamido]-3-thio*-D-ribo-*β*-L-manno-*dec-3-ulopyranoside* (**38b**). According to *GP 10*, debenzylation of 40 mg (0.04 mmol) of **37b**, followed by FC (amino phase gel, AcOEt/MeOH 98 : 2 → 4 : 1) gave **38b** (12 mg, 60%). R_f (amino phase TLC, AcOEt/MeOH 4 : 1) 0.21. $[\alpha]_D^{25} = +75.3$ ($c = 1.06$, $CHCl_3$). IR (ATR): 3308*m* (br.), 2958*m*, 2925*m*, 2865*m*, 1645*m*, 1522*m*, 1454*m*, 1379*m*, 1306*w*, 1067*s*, 952*w*, 894*w*, 751*s*, 664*w*. ^{1}H-NMR (400 MHz, CD_3OD; assignments based on a DQFCOSY spectrum): see *Table 10*; additionally, 3.18 (*dd*, $J = 8.1, 6.0$), 2.91 (*dd*, $J = 10.5, 4.8$) (2 H of prolinyl); 2.35 (*s*, MeN); 2.28–1.95 (*m*, 3 H); 1.95 (*s*, MeS); 1.90–1.74 (*m*, 1 H); 1.35–1.24 (*m*, MeCH_2CH_2); 0.90 (*t*, $J = 6.8$, *Me*CH_2CH_2). ^{13}C-NMR (100 MHz, CD_3OD; assignments based on a HSQC spectrum): see *Table 10*; additionally, 177.96 (*s*, C=O); 70.09 (*d*, C(2) of prolinyl); 63.95 (*t*, C(5) of prolinyl); 42.06 (*q*, MeN); 39.01 (*d*, C(4) of prolinyl); 38.60 (*t*, C(3) of prolinyl); 37.18 (*t*, MeCH_2CH_2); 22.62 (*t*, MeCH_2CH_2); 14.69 (*q*, *Me*CH_2CH_2); 9.32 (*q*, MeS). HR-MALDI-MS: 489.2252 (100, $[M + Na]^+$, $C_{20}H_{38}NaN_2O_7S^+$; calc. 489.2241), 467.2423 (100, $[M + H]^+$, $C_{20}H_{39}N_2O_7S^+$; calc. 467.2422).

*Methyl 2,3,9,11-Tetradeoxy-9-[(2*S*,4*R*)-1-methyl-4-propylpyrrolidine-2-carboxamido]-4-thio*-D-erythro-*α*-D-galacto-*undec-4-ulopyranosidonitrile* (**44**). According to *GP 10*, debenzylation of 80 mg (0.10 mmol) of **43**, followed by FC (amino phase gel, AcOEt/MeOH 98 : 2 → 4 : 1), gave **44** (25 mg, 60%). R_f (amino phase TLC, AcOEt/MeOH 9 : 1) 0.69. $[\alpha]_D^{25} = +61.6$ ($c = 0.99$, $CHCl_3$). IR (ATR): 3322*w* (br.), 2953*w*, 2926*w*, 2872*w*, 2790*w*, 1645*m*, 1524*m*, 1454*w*, 1379*w*, 1216*w*, 1082*s*, 1022*m*, 947*w*, 920*w*, 870*m*, 750*s*, 664*w*, 629*w*. ^{1}H-NMR (300 MHz, CD_3OD; assignments based on a DQFCOSY spectrum): see *Table 10*; additionally, 3.18 (*dd*, $J = 8.1, 5.4$), 2.95 (*dd*, $J = 7.5, 4.5$); 2.63 (*t*, $J = 7.5$, CH_2CH_2CN); 2.35 (*s*, MeN); 1.99–1.82 (*m*, 4 H of prolinyl, CH_2CH_2CN); 1.93 (*s*, MeS); 1.36–1.24 (*m*, MeCH_2CH_2); 0.92 (*t*, $J = 6.6$, *Me*CH_2CH_2). ^{13}C-NMR (75 MHz, CD_3OD; assignments based on a HSQC spectrum): see *Table 10*; additionally, 177.14 (*s*, C=O); 120.74 (*s*, CN); 69.55 (*d*, C(2) of prolinyl); 63.37 (*t*, C(5) of prolinyl); 41.58 (*q*, MeN); 38.91 (*d*, C(4) of prolinyl); 38.45 (*t*, C(3) of prolinyl); 36.61 (*t*, MeCH_2CH_2); 22.55 (*t*, MeCH_2CH_2); 14.45 (*q*, *Me*CH_2CH_2); 8.75 (*q*, MeS). HR-MALDI-MS: 482.2300 (20, $[M + Na]^+$, $C_{21}H_{37}N_3NaO_6S^+$; calc. 482.2295), 460.2478 (100, $[M + H]^+$, $C_{21}H_{38}N_3O_6S^+$; calc. 460.2476).

*Methyl 2,3,9,11-Tetradeoxy-9-[(2*S*,4*R*)-1-Methyl-4-propylpyrrolidine-2-carboxamido]-4-thio*-D-erythro-*α*-D-galacto-*undec-4-ulopyranosidonamide* (**47**). According to *GP 10*, debenzylation of 100 mg (0.11 mmol) of **46**, followed by FC (amino phase gel, AcOEt/MeOH 98 : 2 → 4 : 1), gave **47** (20 mg, 40%). R_f (amino phase TLC, AcOEt/MeOH 9 : 1) 0.69. $[\alpha]_D^{25} = +28.8$ ($c = 1.0$, $CHCl_3$). IR (ATR): 3318*m* (br.), 2958*m*, 2926*m*, 1649*m*, 1564*s*, 1528*m*, 1455*m*, 1400*m*, 1305*m*, 1257*w*, 1217*w*, 1074*s*, 940*w*, 873*w*, 751*s*, 663*w*. ^{1}H-NMR (300 MHz, CD_3OD): see *Table 10*; additionally, 3.21 (*dd*, $J = 8.4, 6.0$), 2.97 (*dd*, $J = 10.5, 4.8$) (2 H of prolinyl); 2.37 (*s*, MeN); 2.48–1.78 (*m*, 4 H of prolinyl, $CH_2CH_2CONH_2$); 1.93 (*s*, MeS); 1.38–1.24 (*m*, MeCH_2CH_2); 0.90 (*t*, $J = 6.9$, *Me*CH_2CH_2). ^{13}C-NMR (75 MHz, CD_3OD): see *Table 10*; additionally, 177.14 (*s*, 2 C=O); 69.65 (*d*, C(2) of prolinyl); 63.38 (*t*, C(5) of prolinyl); 41.57 (*q*, MeN); 38.60 (*d*, C(4) of prolinyl); 38.25 (*t*, C(3) of prolinyl); 36.79 (*t*, MeCH_2CH_2); 22.35 (*t*, MeCH_2CH_2); 14.42

(*q*, *Me*CH_2CH_2); 8.77 (*q*, MeS). HR-MALDI-MS: 479.2422 (100, $[M - NH_2 + H_2O]^+$, $C_{21}H_{38}N_3O_7S^+$; calc. 479.2422).

*(1*R*)-7-Azido-3,4,5,8-tetra*-O-*benzyl-1,2*-O-*carbonyl-7,9-dideoxy-1*-C-*heptyl*-D-erythro-*α*-D-galacto-*non-2-ulopyranose* (**39a**). A soln. of **28a** (50 mg, 0.065 mmol) in 7N HCl (2 ml) was kept at 50° for 36 h and evaporated. A soln. of the residue in CH_2Cl_2 was washed with H_2O, sat. aq. $NaHCO_3$ soln., and brine, dried ($MgSO_4$), and evaporated. A soln. of the residue in CH_2Cl_2 (2ml) was treated with 1,1′-carbonyldiimidazole (53 mg, 0.32 mmol), kept at 50° for 18 h, and evaporated. FC (hexane/AcOEt 95 :5 → 4 :1) gave **39a** (38 mg, 73%). R_f (hexane/AcOEt 85 :15) 0.48. $[\alpha]_D^{25} = +74.8$ (*c* = 1.0, $CHCl_3$). IR (ATR): 3031*w*, 2926*w*, 2857*w*, 2108*m*, 1810*m*, 1602*w*, 1560*w*, 1496*w*, 1453*w*, 1362*w*, 1266*m*, 1213*m*, 1094*s*, 1047*s*, 1026*s*, 914*w*, 849*w*, 733*s*, 695*s*. ^{1}H-NMR (300 MHz, $CDCl_3$; assignments based on selective homodecoupling experiments): see *Table 11*; additionally, 7.41 – 7.20 (*m*, 20 arom. H); 5.18 (*d*, *J* = 11.7), 5.07 (*d*, *J* = 11.1), 4.79 (*d*, *J* = 11.4), 4.67 (*d*, *J* = 11.1), 4.65 (*d*, *J* = 11.4, 2 H), 4.59 (*d*, *J* = 11.7), 4.50 (*d*, *J* = 11.7) (4 PhCH_2); 4.25 (*dd*, *J* = 10.2, 3.9, irrad. at 4.12 → no NOE, H–C(1)); 4.12 (*d*, *J* = 9.9, irrad. at 4.25 → no NOE, H–C(3)); 1.83 – 1.74 (*m*, 1 H), 1.68 – 1.59 (*m*, 1 H), 1.56 – 1.42 (*m*, 1 H), 1.38 – 1.22 (*m*,

Table 11. *Selected ^{1}H-NMR Chemical Shifts* [ppm] *and Coupling Constants* [Hz]*, and ^{13}C-NMR Chemical Shifts* [ppm] *of the Lincomsamine Derivatives* **39a**, **39b**, **40a**, *and* **40b** *in $CDCl_3$* (numbering as for lincosamine)

	39a	**39b**[a])	**40a**[b])	**40b**[b])
H–C(2)	4.12	3.89	4.24	4.10
H–C(3)	4.03	3.99	4.07	4.03
H–C(4)	4.13	4.13	4.17	4.16
H–C(5)	3.53	3.53	3.65	3.60
H–C(6)	4.09	4.05	4.10	4.04
H–C(7)	3.88	3.77	3.88	3.90
H_3C(8)	1.20	1.14	1.19	1.18
H–C(1′)	4.25	4.19	4.70	4.66
H_a–C(2′)	[c])	[c])	3.73	3.51
H_b–C(2′)	[c])	[c])	3.66	3.44
J(2,3)	9.6	9.9	9.7	9.9
J(3,4)	2.1	2.1	2.4	2.4
J(4,5)	0.9	[d])	1.1	1.2
J(5,6)	10.2	9.9	10.2	10.5
J(6,7)	3.0	2.4	2.7	2.9
J(7,Me)	6.3	6.6	6.3	6.5
$J(1',2'_a)$	10.2	8.7	7.4	8.6
$J(1',2'_b)$	3.9	6.6	5.6	2.4
$J(2'_a,2'_b)$	[d])	[d])	10.3	10.7
C(1)	106.57	105.16	110.45	109.71
C(2)	74.29	73.11	73.57	73.37
C(3)	81.84	80.95	81.73	80.77
C(4)	73.03	73.59	72.95	73.63
C(5)	73.66	72.82	73.54	73.21
C(6)	61.69	61.84	61.48	61.65
C(7)	74.82	74.53	74.91	74.53
C(8)	13.20	13.05	13.23	12.85
C(1′)	85.76	80.62	87.51	82.23
C(2′)	[c])	[c])	66.48	65.09

[a]) Assignments based on a HSQC spectrum. [b]) Assignments based on DQFCOSY and HSQC spectra. [c]) See *Exper. Part.* [d]) Not assigned.

9 H) (Me(CH_2)$_6$); 0.85 (*t*, *J* = 6.9, *Me*(CH$_2$)$_6$). ^{13}C-NMR (75 MHz, $CDCl_3$; assignments based on a HSQC spectrum): see *Table 11*; additionally, 152.25 (*s*, C=O); 138.21, 138.03, 137.72, 137.28 (4*s*); 128.65–126.64 (several *d*); 75.11, 74.29, 72.75, 70.75 (4*t*, 4 PhCH_2); 31.65, 29.11, 28.95, 28.45, 26.02, 22.56 (6*t*, Me(CH_2)$_6$); 14.05 (*q*, *Me*(CH$_2$)$_6$). HR-ESI-MS: 802.3473 (20, $[M + K]^+$, $C_{45}H_{53}KN_3O_8^+$; calc. 802.3464), 786.3733 (100, $[M + Na]^+$, $C_{45}H_{53}N_3NaO_8^+$; calc. 786.3725).

*(1*S*)-7-Azido-3,4,5,8-tetra*-O-*benzyl-1,2*-O-*carbonyl-7,9-dideoxy-1*-C-*heptyl*-D-erythro-*α*-D-galacto-*non-2-ulopyranose* (**39b**). A soln. of **28b** (50 mg, 0.065 mmol) in 7N HCl (2 ml) was kept at 50° for 36 h and evaporated. A soln. of the residue in CH_2Cl_2 was washed with H_2O, sat. aq. $NaHCO_3$ soln., and brine, dried ($MgSO_4$), and evaporated. A soln. of the residue in CH_2Cl_2 (2 ml) was treated with 1,1′-carbonyldiimidazole (53 mg, 0.32 mmol), kept at 50° for 18 h, and evaporated. FC (hexane/AcOEt 95:5 → 4:1) gave **39b** (40 mg, 77%). R_f (hexane/AcOEt 85:15) 0.48. $[\alpha]_D^{25} = -2.4$ (*c* = 0.83, $CHCl_3$). IR (ATR): 3031*w*, 2927*w*, 2857*w*, 2108*m*, 1809*m*, 1496*w*, 1454*w*, 1381*w*, 1366*w*, 1347*w*, 1266*m*, 1210*m*, 1127*m*, 1092*s*, 1046*s*, 1026*s*, 1002*m*, 946*w*, 914*w*, 733*s*, 696*s*. ^{1}H-NMR (300 MHz, $CDCl_3$; assignments based on selective homodecoupling experiments): see *Table 11*; additionally, 7.42–7.22 (*m*, 20 arom. H); 5.07 (*d*, *J* = 11.1), 4.98 (*d*, *J* = 12.0), 4.82 (*d*, *J* = 11.4), 4.75 (*d*, *J* = 12.3), 4.67 (*d*, *J* = 11.7), 4.56 (*d*, *J* = 11.7), 4.46 (*d*, *J* = 12.0), 4.50 (*d*, *J* = 11.7) (4 PhCH_2); 4.19 (*dd*, *J* = 8.7, 6.6, irrad. at 3.89 → NOE of 1.1%, H–C(1)); 3.89 (*d*, *J* = 9.9, irrad. at 4.19 → NOE of 3.8%, H–C(3)); 1.45–1.56 (*m*, Me(CH_2)$_6$); 0.88 (*t*, *J* = 6.6, *Me*(CH$_2$)$_6$). ^{13}C-NMR (75 MHz, $CDCl_3$; assignments based on a HSQC spectrum): see *Table 11*; additionally, 152.53 (*s*, C=O); 138.24, 138.06, 137.53, 136.97 (4*s*); 128.75–127.36 (several *d*); 75.09, 74.97, 72.89, 70.66 (4*t*, 4 PhCH_2); 31.68, 29.29, 29.07, 27.74, 25.05, 22.62 (6*t*, Me(CH_2)$_6$); 14.08 (*q*, *Me*(CH$_2$)$_6$). HR-ESI-MS: 802.3475 (20, $[M + K]^+$, $C_{45}H_{53}KN_3O_8^+$; calc. 802.3464), 786.3735 (100, $[M + Na]^+$, $C_{45}H_{53}N_3NaO_8^+$; calc. 786.3725).

8-Azido-1,4,5,6,9-penta-O-*benzyl-8,10-dideoxy-2,3*-O-*(thiocarbonyl)*-D-ribo-*β*-L-manno-*dec-3-ulo-pyranose* (**40a**). A soln. of **33a** (80 mg, 0.10 mmol) in 7N HCl (2 ml) was kept at 50° for 36 h and evaporated. A soln. of the residue in CH_2Cl_2 was washed with H_2O, sat. aq. $NaHCO_3$ soln., and brine, dried ($MgSO_4$), and evaporated. A soln. of the residue in CH_2Cl_2 (2 ml) was treated with 1,1′-thiocarbonyldiimidazole (89 mg, 0.5 mmol), kept at 50° for 18 h, and evaporated. FC (hexane/AcOEt 95:5 → 4:1) gave **40a** (60 mg, 75%). R_f (hexane/AcOEt 85:15) 0.48. $[\alpha]_D^{25} = +75.2$ (*c* = 0.86, $CHCl_3$). IR (ATR): 3063*w*, 3030*w*, 2927*w*, 2869*w*, 2108*m*, 1815*m*, 1496*w*, 1453*m*, 1385*w*, 1316*s*, 1213*m*, 1299*s*, 1233*m*, 1210*m*, 1126*s*, 1094*s*, 1045*m*, 1027*m*, 999*m*, 917*w*, 735*s*, 696*s*. ^{1}H-NMR (300 MHz, $CDCl_3$; assignments based on a DQFCOSY spectrum): see *Table 11*; additionally, 7.40–7.14 (*m*, 25 arom. H); 5.10 (*d*, *J* = 12.0), 5.03 (*d*, *J* = 11.2), 4.76 (*d*, *J* = 11.2) (3 PhC*H*); 4.70 (*dd*, *J* = 7.4, 5.6, irrad. at 4.24 → no NOE, H–C(2)); 4.66 (*d*, *J* = 11.2), 4.62 (*d*, *J* = 11.2), 4.57 (*d*, *J* = 11.9), 4.49 (*d*, *J* = 12.0, 2 H), 4.43 (*d*, *J* = 11.9), 4.36 (*d*, *J* = 11.8) (7 PhC*H*); 4.24 (*d*, *J* = 9.7, irrad. at 4.70 → no NOE, H–C(4)). ^{13}C-NMR (100 MHz, $CDCl_3$; assignments based on a HSQC spectrum): see *Table 11*; additionally, 189.16 (*s*, C=S); 138.18, 137.92, 137.58, 137.14, 136.90 (5*s*); 128.64–126.50 (several *d*); 75.22, 73.97, 73.66, 72.70, 70.83 (5*t*, 5 PhCH_2). HR-ESI-MS: 840.2717 (30, $[M + K]^+$, $C_{46}H_{47}KN_3O_8S^+$; calc. 840.2715), 824.2974 (100, $[M + Na]^+$, $C_{46}H_{47}N_3NaO_8S^+$; calc. 824.2976).

8-Azido-1,4,5,6,9-penta-O-*benzyl-8,10-dideoxy-2,3*-O-*(thiocarbonyl)*-D-ribo-*β*-L-gluco-*dec-3-ulopyr-anoside* (**40b**). A soln. of **33b** (80 mg, 0.10 mmol) in 7N HCl (2 ml) was kept at 50° for 36 h and evaporated. A soln. of the residue in CH_2Cl_2 was washed with H_2O, sat. aq. $NaHCO_3$ soln., and brine, dried ($MgSO_4$), and evaporated. A soln. of the residue in CH_2Cl_2 (2 ml) was treated with 1,1′-thiocarbonyldiimidazole (89 mg, 0.5 mmol), kept at 50° for 18 h, and evaporated. FC (hexane/AcOEt 95:5 → 4:1) gave **40b** (65 mg, 80%). R_f (hexane/AcOEt 85:15) 0.69. IR (ATR): 3031*w*, 2869*w*, 2108*m*, 1814*m*, 1605*w*, 1496*w*, 1386*w*, 1316*m*, 1298*m*, 1264*m*, 1233*m*, 1209*m*, 1123*m*, 1091*s*, 1043*m*, 1026*m*, 999*m*, 947*w*, 915*w*, 731*s*, 695*s*. ^{1}H-NMR (400 MHz, $CDCl_3$; assignments based on a DQFCOSY spectrum): see *Table 11;* additionally, 7.40–7.19 (*m*, 25 arom. H); 5.06 (*d*, *J* = 11.0), 4.98 (*d*, *J* = 11.6), 4.80 (*d*, *J* = 11.5), 4.75 (*d*, *J* = 11.4), 4.69 (*d*, *J* = 11.7), 4.67 (*d*, *J* = 11.8) (6 PhC*H*); 4.66 (*dd*, *J* = 8.6, 2.4, irrad. at 4.10 → NOE of 3.0%, H–C(2)); 4.46 (*d*, *J* = 12.1), 4.39 (*d*, *J* = 11.7), 4.34 (*d*, *J* = 12.1), 4.29 (*d*, *J* = 11.8) (4 PhC*H*); 4.10 (*d*, *J* = 9.9, irrad. at 4.66 → NOE of 4.7%, H–C(4)). ^{13}C-NMR (100 MHz, $CDCl_3$; assignments based on a HSQC spectrum): see *Table 11*; additionally, 189.32 (*s*, C=S); 138.16, 138.08, 137.51, 137.19, 136.96 (5*s*); 128.71–126.51 (several *d*); 75.39, 75.26, 73.67, 73.07, 70.54 (5*t*, 5 PhCH_2). HR-

ESI-MS: 840.2708 (37, $[M + K]^+$, $C_{46}H_{47}KN_3O_8S^+$; calc. 840.2715), 824.2977 (100, $[M + Na]^+$, $C_{46}H_{47}N_3NaO_8S^+$; calc. 824.2976).

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