

reported [9]. The diastereoisomeric sulfoxides, ($MIC^1 \geq 100$) 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.

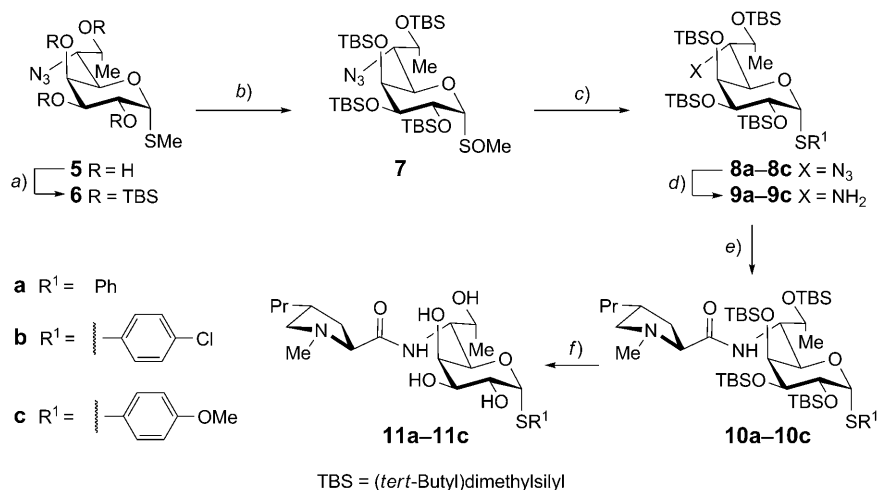
Results and Discussion. – We first aimed at a few representative *S*-aryl and *S*-arylalkyl analogues of lincomycin. The *S*-aryl analogues **11a–11c** of lincomycin were synthesized by *S*-glycosylation of the sulfoxides **7**. These were obtained as a 2 : 1 mixture of diastereoisomers³) by a high-yielding *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%.

¹) MIC = Minimal inhibitory concentration ($\mu g/ml$)

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



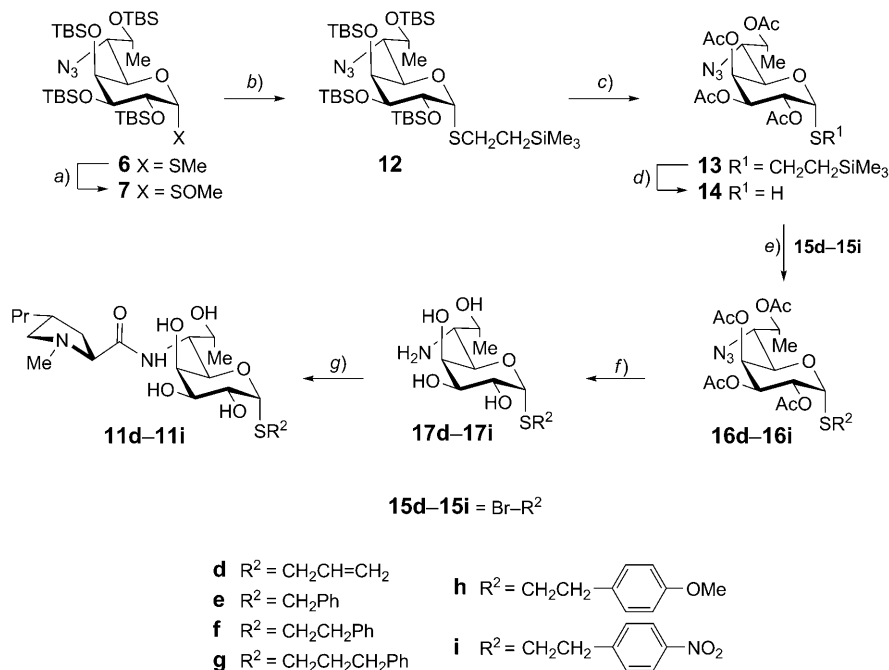
a) TBSOTf (Tf = trifluoromethylsulfonyl), pyridine, 100°; 90%. b) *m*-Chloroperbenzoic acid (*m*CPBA), CH_2Cl_2 , –30°. c) $\text{R}^1\text{-SH}$, Tf_2O , 2,6-di-(*tert*-butyl)-4-methylpyridine, 4-Å mol. sieves, CH_2Cl_2 , –78°; 70% of **8a**, 65% of **8b**, 60% of **8c**. d) Me_3P , NaOH, THF, 50°. 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) $\text{Bu}_4\text{NF} \cdot 3 \text{H}_2\text{O}$, 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 $\text{Bu}_4\text{NF} \cdot 3 \text{H}_2\text{O}$ and acetylated to provide 80% of the tetraacetate **13**. Removal of the 2-(trimethylsilyl)ethyl group required treating **13** with a 1M solution of $\text{Bu}_4\text{NF} \cdot 3 \text{H}_2\text{O}$ 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 $J(1,2) = 4.8\text{--}5.7$ Hz (see Tables 3 and 5 in the *Exper. Part*). A comparison of the ^1H -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 $^4\text{C}_1$ 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 $\text{C}(1)^4$. 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

TBS = (*tert*-Butyl)dimethylsilyl

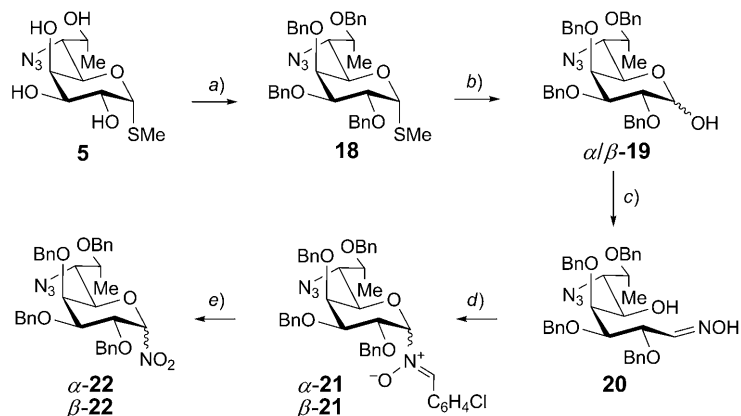
a) *m*CPBA, CH₂Cl₂, –30°. b) Me₃SiCH₂CH₂SH, Tf₂O, 2,6-di-(*tert*-butyl)-4-methylpyridine, 4-Å mol. sieves, CH₂Cl₂, –78°; 70% from **6**. c) i. Bu₄NF·3 H₂O, THF; ii. Ac₂O, 4-(Dimethylamino)pyridine (DMAP), Et₃N, CH₂Cl₂; 80%. d) 1M Bu₄NF in THF. e) **15d–15i**, THF; 90% of **16d**, 80% of **16e**, 60% of **16f**, 75% of **16g**, 75% of **16h**, 75% of **16i**. f) i. MeONa, MeOH; ii. Me₃P, 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 CD₃OD 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 Ag₂CO₃ 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].

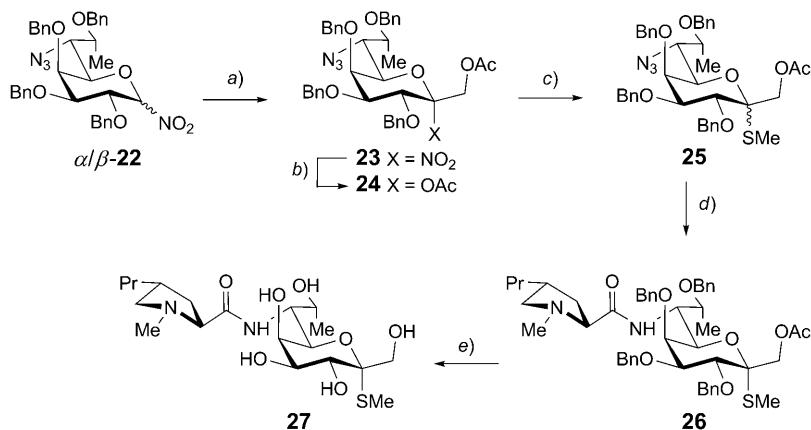
Henry reaction of the nitro aldoses α -**22**/β-**22** with paraformaldehyde gave the nitro acetate **23** (Scheme 4), which was partially hydrolysed during workup, and completely

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) $\text{NH}_2\text{OH} \cdot \text{HCl}$, 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

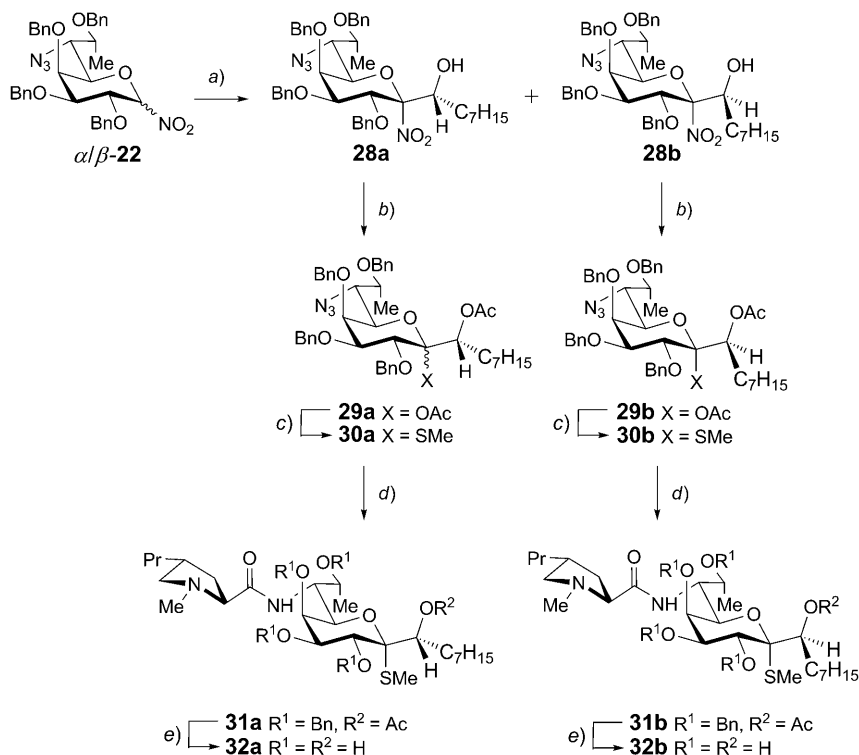


a) $(\text{CH}_2\text{O})_n$, 1M Bu_4NF in THF, CH_2Cl_2 . b) i. 7M HCl, 50° ; ii. Ac_2O , DMAP, Et_3N , CH_2Cl_2 , 50° ; 80% of **24** from **22**. c) MeSH, 4-Å mol. sieves, $\text{BF}_3 \cdot \text{OEt}_2$, CH_2Cl_2 , -30° ; 57% of α -**25** and 27% of α -**25**/ β -**25** 1:1. d) i. Me_3P , NaOH, 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 Et₄NOH, 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 NO₂ 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 BF₃·OEt₂, TMSOTf, ZnCl₂, Zn(OTf)₂, and FeCl₃ were unsuccessful.

Scheme 5

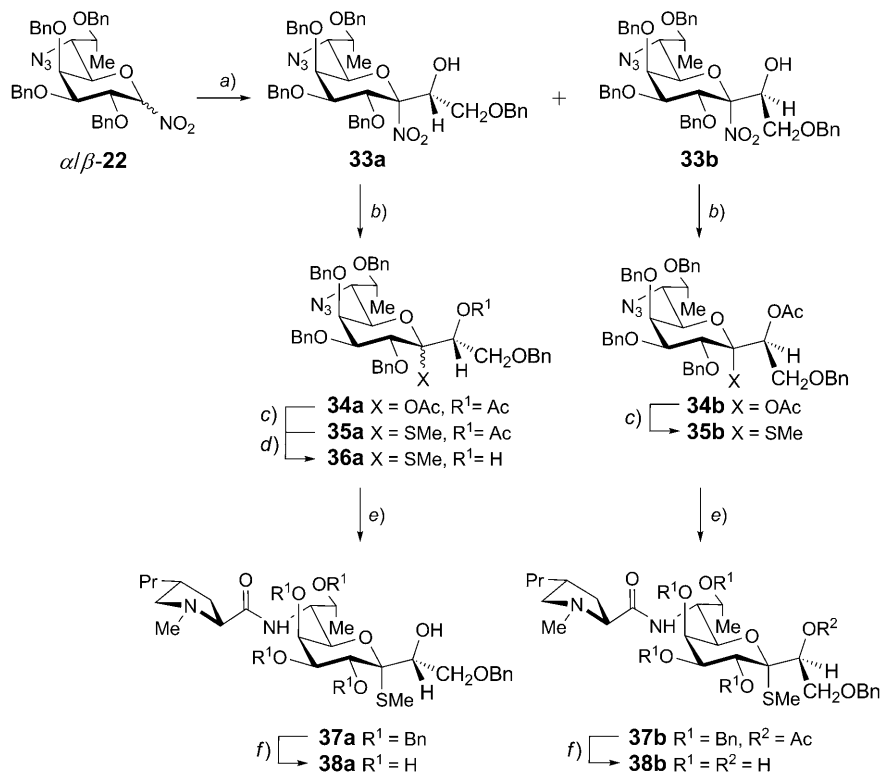


a) Octanal, Et₄NOH, DMF; 53% of **28a** and 15% of **28b**. *b)* i. 7M HCl, 50°; ii. Ac₂O, DMAP, Et₃N, CH₂Cl₂, 50°; 86% of α -**29a**, 87% of **29b**. *c)* MeSH, 4-Å mol. sieves, BF₃·OEt₂, CH₂Cl₂, –30°; 46% of α -**30a** and 23% of β -**30a**; 80% of **30b**. *d)* i. Me₃P, NaOH, THF, 50°; ii. PHA, EtOCOCl, Et₃N, CH₂Cl₂; 80% of **31a** from α -**30a**, 70% of **31b**. *e)* Na, NH₃, 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 BF₃·OEt₂. 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

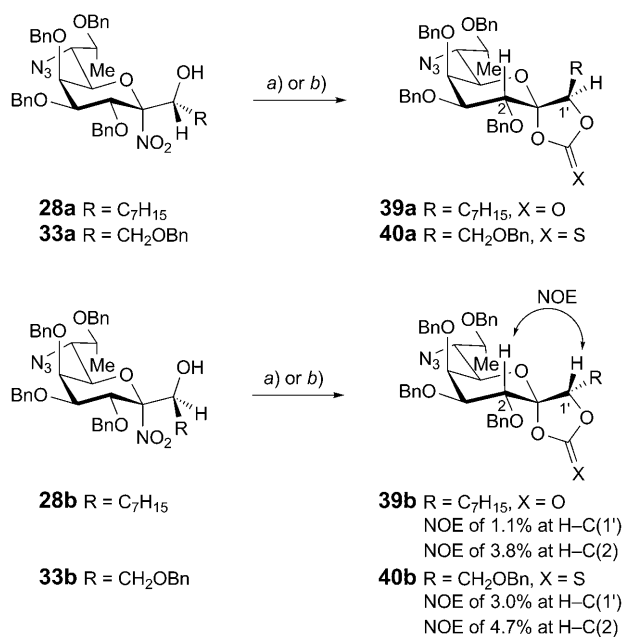


a) 2-(Benzyloxy)acetaldehyde, Et₄NOH, DMF; 70% of **33a** and 20% of **33b**. b) i. 7M HCl, 50°; ii. Ac₂O, DMAP, Et₃N, CH₂Cl₂, 50°; 75% of β -L-**34a**, 75% of **34b**. c) MeSH, 4-Å mol. sieves, BF₃·OEt₂, CH₂Cl₂, –30°; 65% of **35b**. d) MeONa, MeOH; 37% of β -L-**36a** and 30% of α -L-**36a** from β -L-**34a**. e) i. Me₃P, NaOH, THF, 50°; ii. PHA, EtOCOCl, Et₃N, CH₂Cl₂; 86% of **37a**, 65% of **37b**. f) Na, NH₃, 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



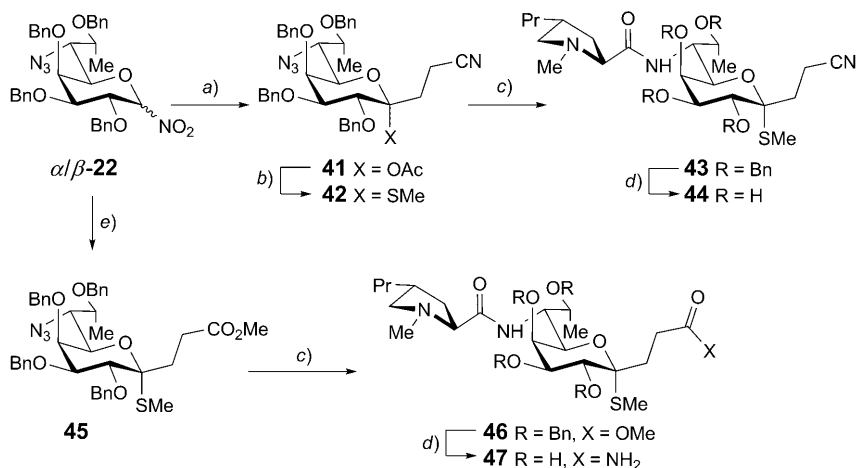
a) for **28a** and **28b**: i. 7N HCl, 50°; ii. 1,1'-Carbonyldiimidazole, CH₂Cl₂, 50°; 77% of **39a**; 73% of **39b**. b) for **33a** and **33b**: i. 7M HCl, 50°; ii. 1,1'-Thiocarbonyldiimidazole, CH₂Cl₂, 50°; 75% of **40a**, 80% of **40b**.

Michael addition of the nitro ethers α -**22**/ β -**22** to acrylonitrile (Scheme 8), followed by hydrolysis of the product in a 2M LiClO₄ solution in MeCN/H₂O 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 BF₃·OEt₂ afforded the thioglycoside **42** (80%) as a single anomer. Azide reduction, coupling with PHA to the amide **43**, and debenzoylation yielded 60% of the lincomycin analogue **44**. *Michael* addition of the nitro ethers α -**22**/ β -**22** to methyl acrylate (1M Bu₄NF in THF) proceeded similarly, to afford the expected tertiary nitro ether that was directly subjected to thioglycosylation with MeSH/BF₃·OEt₂ to yield 85% of **45** (Scheme 8)⁶⁾. Reduction of the N₃ group of **45**, coupling with PHA to the amide **46**, and debenzoylation led to the lincomycin analogue **47** (40%).

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, $\text{BF}_3 \cdot \text{OEt}_2$, -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, $\text{BF}_3 \cdot \text{OEt}_2$, -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 ^1H -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–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].

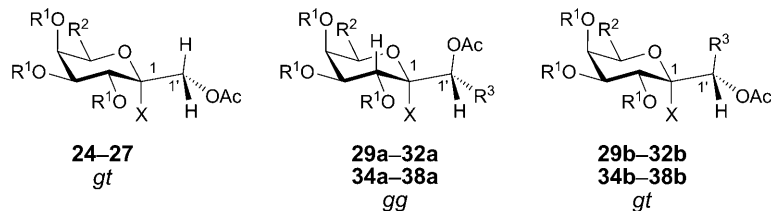


Fig. 2. Favoured conformers of the chain at C(1) of the axial anomers

Antibacterial Activity. – The antibacterial activity of the thioethers **11a–11i** was studied by determining their minimal inhibitory concentrations (*MICs*) 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 $\mu\text{g/ml}$, 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 CH₂ 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	$\geq$ 256
11i	16	$\geq$ 256

^{a)} Antibacterial activity as minimal inhibitory concentrations (*MIC* [$\mu\text{g/ml}$]).

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]).

We thank the Swiss National Science Foundation for financial support and Dr. B. Bernet for critically checking the analytical data.

Experimental Part

General. Solvents were distilled: Et₂O from Na/benzophenone, MeOH, CH₂Cl₂, Et₃N from CaH₂. Reactions were carried out under N₂, 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% H₂SO₄ soln., 20 g of (NH₄)₆Mo₇O₂₄·6 H₂O, 0.4 g of Ce(SO₄)₂). Flash chromatography (FC): silica gel Merck (0.04–0.063 mm) using distilled technical solvents as eluent. M.p.: uncorrected. Optical rotation ([α]_D²⁵): 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 ¹³C-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/CH₂Cl₂ 98:2 → 4:1) gave **6** (2.38 g, 90%). Colourless oil. *R*_f (hexane/CH₂Cl₂ 4:1) 0.53. [α]_D²⁵ = +109.3 (*c* = 1.1, CHCl₃). IR (ATR): 2953w, 2929w, 2887w, 2857w, 2106m, 1472w, 1463w, 1388w, 1361w, 1342w, 1321m, 1293w, 1252m, 1166w, 1137m, 1091m, 1066m, 1015w, 1005w, 989w, 962w, 935w, 887m, 871m, 858m, 827s, 810m, 773s, 726w, 686w. ¹H-NMR (300 MHz, CDCl₃; assignment based on selective homodecoupling experiments): see Table 3; additionally, 2.01 (s, MeS); 0.95, 0.93, 0.92, 0.89 (4s, 4 Me₃CSi); 0.21–0.07 (several s, 4 Me₂Si). ¹³C-NMR (75 MHz, CDCl₃; assignment based on a HSQC spectrum): see Table 3; additionally, 26.70, 26.37, 26.27, 25.80 (4q, 4 Me₃C); 18.98, 18.51, 18.48, 18.05 (4s, 4 Me₃C); 13.61 (q, MeS); −3.05 to −5.04 (several q, 4 Me₂Si). HR-ESI-MS: 758.4241 (100, [*M* + Na]⁺, C₃₃H₇₃N₃NaO₅SSi₄⁺; calc. 758.4240). Anal. calc. for C₃₃H₇₃N₃O₅SSi₄ (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 I). At −30°, a 1M soln. of **6** in CH₂Cl₂ was treated dropwise over 4 h with 70% *m*CPBA (1 equiv.), then with Me₂S (1 equiv.) and with sat. aq. NaHCO₃ soln. The layers were separated, and the aq. layer was extracted with CH₂Cl₂. The combined org. layers were dried (MgSO₄) and evaporated, to afford the sulfoxides **7**.

Table 3. Selected ^1H -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 ₃ C(8)	1.15	0.76	0.75	0.91	1.14	0.58	0.61	0.74
<i>J</i> (1,2)	5.1	4.8	4.8	5.1	5.1	5.7	5.4	5.4
<i>J</i> (2,3)	9.9	9.6	9.6	9.6	9.9	9.6	9.9	9.9
<i>J</i> (3,4)	2.1	1.8	1.8	1.8	1.8	1.8	1.8	1.8
<i>J</i> (5,6)	10.5	10.5	10.2	10.5	10.5	10.5	10.5	10.2
<i>J</i> (6,7)	2.1	2.1	2.4	2.1	2.4	2.7	3.0	3.3
<i>J</i> (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 Ti_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): 2953w, 2929w, 2887w, 2857w, 2107m, 1585w, 1472w, 1463w, 1439w, 1388w, 1361w, 1342w, 1253m, 1166w, 1136m, 1091m, 1068m, 1023w, 1005w, 990w, 964m, 936w, 888s, 870m, 857m, 827s, 810m, 774s, 734s, 687m. ^1H -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 (3s, 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_3C); 18.76, 18.63, 18.16, 17.79 (4s, 4 Me_3C); –3.35 to –5.16 (several *q*, 4 Me_2Si). HR-ESI-MS: 820.4400 (100, $[M + \text{Na}]^+$, $\text{C}_{38}\text{H}_{75}\text{N}_3\text{NaO}_5\text{SSi}_4^+$; 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):

2953w, 2929w, 2895w, 2857w, 2107m, 1472w, 1463w, 1389w, 1361w, 1342w, 1253m, 1167w, 1136m, 1092m, 1069m, 1012w, 990w, 963m, 936w, 887s, 869m, 856m, 827s, 810s, 773s, 733m, 684m, 665m. ¹H-NMR (300 MHz, CDCl₃; assignments based on selective homodecoupling experiments): see Table 3; additionally, 7.27–7.19 (*m*, 4 arom. H); 0.95, 0.91, 0.86 (3s, 4 Me₃C); 0.22–0.02 (several s, 4 Me₂Si). ¹³C-NMR (75 MHz, CDCl₃): 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 Me₃C); 18.92, 18.79, 18.32, 17.99 (4*s*, 4 Me₃C); –3.15 to –5.09 (several *q*, 4 Me₂Si). HR-ESI-MS: 854.4014 (60, [*M* + Na]⁺, C₃₈H₇₅N₃ClNaO₅SSi₄⁺; calc. 854.4007).

4-Methoxyphenyl 6-Azido-2,3,4,7-tetrakis-O-[(tert-butyl)dimethylsilyl]-6,8-dideoxy-1-thio- α -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 μ l (0.40 mmol) of 4-methoxythiophenol. FC (hexane/CH₂Cl₂ 98:2 $\rightarrow$ 4:1) gave **8c** (100 mg, 60%). Colourless oil. *R*_f (hexane/CH₂Cl₂ 4:1) 0.42. [α]_D²⁵ = +94.7 (*c* = 1.0, CHCl₃). IR (ATR): 2953w, 2929w, 2895w, 2857w, 2107m, 1594m, 1572w, 1494w, 1494m, 1471w, 1463w, 1441w, 1388w, 1361w, 1342w, 1285w, 1246m, 1168w, 1136m, 1091m, 1068m, 1036w, 1005w, 990w, 964m, 936w, 888m, 871m, 857m, 825s, 773s, 733m, 685m, 665w, 640w, 628w. ¹H-NMR (300 MHz, CDCl₃; 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 Me₃CSi); 0.22 to –0.01 (several *s*, 4 Me₂Si). ¹³C-NMR (75 MHz, CDCl₃): 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 Me₃C); 18.92, 18.80, 28.35, 17.96 (4*s*, 4 Me₃C); –3.13 to –5.12 (several *q*, 4 Me₂Si). HR-ESI-MS: 850.4499 (100, [*M* + Na]⁺, C₃₉H₇₇N₃NaO₆SSi₄⁺; calc. 850.4502).

2-(Trimethylsilyl)ethyl 6-Azido-2,3,4,7-tetrakis-O-[(tert-butyl)dimethylsilyl]-6,8-dideoxy-1-thio- α -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 μ l (4.02 mmol) of 2-(trimethylsilyl)ethanethiol. FC (hexane/CH₂Cl₂ 98:2 $\rightarrow$ 4:1) gave **12** (1.16 g, 70%). Colourless oil. *R*_f (hexane/CH₂Cl₂ 4:1) 0.65. [α]_D²⁵ = +78.6 (*c* = 0.89, CHCl₃). IR (ATR): 2953w, 2929w, 2896w, 2857w, 2107m, 1472w, 1463w, 1388m, 1361w, 1341w, 1250m, 1164w, 1136m, 1091m, 1066m, 1005w, 989w, 967m, 935w, 888m, 857m, 827s, 810s, 773s, 688w. ¹H-NMR (300 MHz, CDCl₃; assignments based on selective homodecoupling experiments): see Table 3; additionally, 2.51–2.40 (*m*, CH₂S); 0.95, 0.93, 0.89 (3*s*, 4 Me₃C); 0.90–0.70 (*m*, Me₃SiCH₂); 0.21–0.07 (several *s*, 4 Me₂Si); 0.01 (*s*, Me₃Si). ¹³C-NMR (75 MHz, CDCl₃): see Table 3; additionally, 26.66, 26.34, 26.30, 25.76 (4*q*, 4 Me₃C); 25.88 (*t*, CH₂S); 18.93, 18.81, 18.40, 17.99 (4*s*, 4 Me₃C); 17.31 (*t*, Me₃SiCH₂); –1.76 (*q*, Me₃Si); –3.13 to –5.12 (several *q*, 4 Me₂Si). HR-ESI-MS: 844.4791 (100, [*M* + Na]⁺, C₃₇H₈₃N₃NaO₅SSi₅⁺; calc. 844.4792).

General Procedure for Coupling of the Lincosamine Derivatives with Propyl Hygic Acid (GP 2). A 0.03M soln. of the azido derivative (1 equiv.) in THF/0.1N NaOH 4:1 was treated with 1M PMe₃ in THF (1.5 equiv.), stirred for 4–8 h at 50°, and evaporated. A soln. of the residue in CH₂Cl₂ was washed with H₂O and brine, and the org. layer was dried (MgSO₄) and evaporated to provide the corresponding amine.

A 0.03M suspension of PHA (1.3 equiv.) in CH₂Cl₂ was treated with Et₃N (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 CH₂Cl₂. 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- α -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 $\rightarrow$ 9:1) gave **10a** (60 mg, 75%). Colourless oil. *R*_f (hexane/AcOEt 95:5) 0.23. [α]_D²⁵ = +98.3 (*c* = 0.62, CHCl₃). IR (ATR): 2953m, 2928m, 2856m, 2787w, 1695m, 1510w, 1472w, 1388w, 1361w, 1303w, 1253m, 1144m, 1090m, 1069m, 1026w, 991m, 1005w, 963m, 890m, 866m, 835s, 776s, 737w, 687w. ¹H-NMR (300 MHz, CDCl₃): 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*, MeCH₂CH₂); 0.97, 0.93, 0.90, 0.80 (4*s*, 4 Me₃C); 0.58 (*d*, *J* = 6.0, MeCH₂CH₂); 0.16 to –0.03 (*m*, 4 Me₂Si). ¹³C-NMR (75 MHz, CDCl₃): 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*, MeCH₂CH₂); 26.54, 26.48, 26.15, 25.66 (4*q*, 4 Me₃C); 21.58 (*t*, MeCH₂CH₂); 18.85, 18.20, 17.85 (3*s*, 4 Me₃C); 14.37 (*q*, MeCH₂CH₂); –3.15 to –5.08 (several *q*, 4 Me₂Si). HR-ESI-MS: 925.5838 (100, [*M* + H]⁺, C₄₇H₉₃N₂O₆SSi₄⁺; calc. 925.5826).

4-Chlorophenyl 2,3,4,7-Tetrakis-O-[(tert-butyl)dimethylsilyl]-6,8-dideoxy-6-[(2S,4R)-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 $\rightarrow$ 9:1) gave **10b** (90 mg, 70%). Colourless oil. R_f (hexane/AcOEt 95:5) 0.26. $[\alpha]_D^{25} = +185.3$ ($c = 1.6$, CHCl₃). IR (ATR): 2953m, 2928m, 2892w, 2856m, 2787w, 1651s, 1509w, 1472s, 1463w, 1389w, 1361w, 1304w, 1252m, 1144m, 1094s, 1069m, 1010w, 990w, 963m, 887m, 865m, 834s, 811m, 775s, 732w, 669w. ¹H-NMR (300 MHz, CDCl₃): 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 prolanyl); 2.33 (s, MeN); 2.09–1.88 (m, 3 H); 1.84–1.70 (m, 1 H); 1.32–1.18 (m, MeCH₂CH₂); 0.97, 0.93, 0.89, 0.81 (4s, 4 Me₃CSi); 0.16 to –0.01 (m, 4 Me₂Si, MeCH₂CH₂). ¹³C-NMR (75 MHz, CDCl₃): 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 prolanyl); 62.88 (t, C(5) of prolanyl); 41.78 (q, MeN); 38.09 (d, C(4) of prolanyl); 37.63 (t, C(3) of prolanyl); 35.92 (t, MeCH₂CH₂); 26.63, 26.55, 26.22, 25.75 (4q, Me₃C); 21.71 (t, MeCH₂CH₂); 18.95, 18.30, 17.90 (3s, 4 Me₃C); 14.50 (q, MeCH₂CH₂); –3.02 to –4.92 (8q, 4 Me₂Si). HR-ESI-MS: 959.5436 (100, $[M + H]^+$, C₄₇H₆₂N₂ClO₆SSi₄⁺; calc. 959.5436).

4-Methoxyphenyl 2,3,4,7-Tetrakis-O-[(tert-butyl)dimethylsilyl]-6,8-dideoxy-6-[(2S,4R)-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 $\rightarrow$ 9:1) gave **10c** (70 mg, 60%). Colourless oil. R_f (hexane/AcOEt 95:5) 0.20. $[\alpha]_D^{25} = +147.3$ ($c = 0.98$, CHCl₃). IR (ATR): 2953m, 2928m, 2856w, 2787w, 1694m, 1594m, 1509w, 1494m, 1471m, 1463m, 1388w, 1361m, 1284w, 1247s, 1173w, 1144m, 1093m, 1069m, 1034w, 1005w, 991w, 963m, 890m, 866m, 835s, 775s, 724w, 669w, 640w. ¹H-NMR (300 MHz, CDCl₃): 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 prolanyl); 2.35 (s, MeN); 2.05–1.99 (m, 3 H); 1.84–1.72 (m, 1 H); 1.32–1.20 (m, MeCH₂CH₂); 0.96, 0.93, 0.91, 0.81 (4s, 4 Me₃C); 0.16 to –0.01 (m, 4 Me₂Si, MeCH₂CH₂). ¹³C-NMR (75 MHz, CDCl₃): 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 prolanyl); 62.75 (t, C(5) of prolanyl); 55.18 (q, MeO); 41.60 (q, MeN); 37.90 (d, C(4) of prolanyl); 37.42 (t, C(3) of prolanyl); 35.75 (t, MeCH₂CH₂); 26.41, 26.35, 26.06, 25.55 (4q, 4 Me₃C); 21.47 (t, MeCH₂CH₂); 18.73, 18.09, 17.75 (3s, 4 Me₃C); 14.26 (q, MeCH₂CH₂); –3.24 to –5.15 (several q, 4 Me₂Si). HR-ESI-MS: 955.5928 (100, $[M + H]^+$, C₄₈H₉₅N₂O₇SSi₄⁺; calc. 955.5932).

General Procedure for the Desilylation (GP 3). A 1m soln. of the silyl ether in THF was treated with Bu₄NF·3 H₂O (6 equiv.), stirred at 25° for 24 h, and evaporated to afford the corresponding crude alcohol.

Phenyl 6,8-Dideoxy-6-[(2S,4R)-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 $\rightarrow$ 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): 3320m (br.), 2955w, 2923m, 2871w, 2852w, 2789w, 1646s, 1584w, 1521m, 1480w, 1455w, 1438w, 1379w, 1306w, 1243w, 1209w, 1180w, 1083s, 1052s, 1026w, 992m, 907m, 869w, 805w, 734s, 690m, 645w. ¹H-NMR (300 MHz, CD₃OD): 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 prolanyl); 2.34 (s, MeN); 2.20–1.88 (m, 3 H); 1.83–1.71 (m, 1 H); 1.31–1.26 (m, MeCH₂CH₂); 0.92–0.86 (m, MeCH₂CH₂). ¹³C-NMR (75 MHz, CD₃OD): 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 prolanyl); 63.49 (t, C(5) of prolanyl); 41.53 (q, MeN); 38.60 (d, C(4) of prolanyl); 38.39 (t, C(3) of prolanyl); 36.63 (t, MeCH₂CH₂); 22.36 (t, MeCH₂CH₂); 14.33 (q, MeCH₂CH₂). HR-MALDI-MS: 469.2368 (100, $[M + H]^+$, C₂₃H₃₇N₂O₆S⁺; calc. 469.2367).

4-Chlorophenyl 6,8-Dideoxy-6-[(2S,4R)-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 $\rightarrow$ 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): 3322m (br.), 2956w, 2924w, 2872w, 2789w, 1651s, 1521m, 1477m, 1455w, 1389w, 1307w, 1235w, 1206w, 1179w, 1091s, 1053s, 1011m, 992w, 906w, 867w, 811w, 731m, 691w. ¹H-NMR (300 MHz, CD₃OD): see Table 4; additionally, 7.47–7.41 (m, 2 arom. H); 7.33–7.28 (m, 3 arom. H); 3.13 (dd, $J = 8.1, 5.7$), 2.89 (dd, $J = 10.5, 4.5$) (2 H of prolanyl); 2.33 (s, MeN); 2.20–1.90 (m, 3 H); 1.82–1.70 (m, 1 H); 1.33–1.22 (m, MeCH₂CH₂); 0.92–0.86

Table 4. Selected ^1H -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 ₃ C(8)	1.00	1.00	1.10	1.19	1.23	1.17	1.13	1.16	1.17
<i>J</i> (1,2)	5.4	5.7	5.4	5.7	5.7	5.7	5.4	5.7	5.4
<i>J</i> (2,3)	10.5	10.2	10.2	10.2	9.6	10.5	9.9	10.5	10.2
<i>J</i> (3,4)	3.3	3.3	3.3	3.6	3.3	3.6	3.3	3.0	3.3
<i>J</i> (4,5)	^{a)}	^{a)}	^{a)}	0.9	^{a)}	^{a)}	1.2	^{a)}	1.2
<i>J</i> (5,6)	7.8	6.6	7.2	7.2	6.9	7.2	6.9	7.2	6.9
<i>J</i> (6,7)	6.3	6.3	6.6	6.3	6.3	6.0	6.3	6.0	6.3
<i>J</i> (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*, MeCH_2CH_2). ^{13}C -NMR (75 MHz, CD_3OD): see Table 4; additionally, 177.80 (*s*, C=O); 135.04, 133.10 (*2s*); 132.44 (*d*, 2 C); 129.60 (*d*, 2 C); 69.68 (*d*, C(2) of prolanyl); 63.49 (*t*, C(5) of prolanyl); 41.53 (*q*, MeN); 38.60 (*d*, C(4) of prolanyl); 38.40 (*t*, C(3) of prolanyl); 36.63 (*t*, MeCH_2CH_2); 22.38 (*t*, MeCH_2CH_2); 14.34 (*q*, MeCH_2CH_2). HR-MALDI-MS: 503.1973 (100, $[M + \text{H}]^+$, $\text{C}_{23}\text{H}_{36}\text{ClN}_2\text{O}_6\text{S}^+$; 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 $\rightarrow$ 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): 3330w (br.), 2953w, 2927w, 2870w, 2788w, 1651m, 1593w, 1571w, 1522m, 1493s, 1461w, 1406w, 1379w, 1284m, 1245s, 1178w, 1153w, 1089m, 1053m, 1031m, 992w, 906w, 827w, 804w, 731m, 695w, 641m, 623w. ^1H -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 prolanyl); 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*, MeCH_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 prolanyl); 63.43 (*t*, C(5) of prolanyl); 55.36 (*q*, MeO); 41.43 (*q*, MeN); 38.45 (*d*, C(4) of prolanyl); 38.24 (*t*, C(3) of prolanyl); 36.48 (*t*, MeCH_2CH_2); 22.19 (*t*, MeCH_2CH_2); 14.16 (*q*, MeCH_2CH_2). HR-MALDI-MS: 499.2 (100, $[M + \text{H}]^+$, $\text{C}_{24}\text{H}_{39}\text{N}_2\text{O}_7\text{S}^+$; 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 $\text{Bu}_4\text{NF} \cdot 3 \text{H}_2\text{O}$ (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. NaHCO₃ soln. and brine, dried (MgSO₄), 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, CHCl₃). IR (ATR): 3005w, 2989w, 2110w, 1745m, 1370w, 1275s, 1260s, 1221w, 1162w, 1119w, 1065w, 1041w, 1007w, 937w, 911w, 896w, 859w, 840w, 763s, 750s, 706w, 662w, 623w. ¹H-NMR (300 MHz, CDCl₃; assignments based on selective homodecoupling experiments): see Table 5; additionally, 2.54 (*m*, CH₂S); 2.17, 2.07, 2.05, 1.98 (4s, 4 AcO); 0.94–0.69 (*m*, Me₃SiCH₂); 0.01 (*s*, Me₃Si). ¹³C-NMR (75 MHz, CDCl₃; assignments based on a HSQC spectrum): see Table 5; additionally, 169.93, 169.61, 169.55, 169.48 (4s, 4 C=O); 26.75 (*t*, CH₂S); 21.06, 20.89, 20.66 (3*q*, 4 MeC=O); 17.04 (*t*, Me₃SiCH₂); –1.77 (*q*, Me₃Si). HR-MALDI-MS: 556.1753 (100, [*M* + Na]⁺, C₂₁H₃₅N₃NaO₆S⁺; calc. 556.1755).

Table 5. Selected ¹H-NMR Chemical Shifts [ppm] and Coupling Constants [Hz], and ¹³C-NMR Chemical Shifts [ppm] of the Acetylated Azides **13** and **16d–16i** in CDCl₃

	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 ₃ C(8)	1.22	1.26	1.27	1.20	1.15	1.19	1.18
<i>J</i> (1,2)	5.4	5.7	5.4	5.7	5.7	5.7	5.7
<i>J</i> (2,3)	10.8	11.1	10.8	11.1	10.8	10.8	11.1
<i>J</i> (3,4)	3.3	3.0	3.0	3.0	3.0	2.4	3.0
<i>J</i> (4,5)	^{a)}	0.9	^{a)}	1.2	0.9	^{a)}	0.9
<i>J</i> (5,6)	9.6	10.2	9.9	10.2	9.9	9.9	10.5
<i>J</i> (6,7)	2.4	2.4	2.1	3.0	2.4	2.4	2.4
<i>J</i> (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 Bu₄NF 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 (MgSO₄) 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, CHCl₃). IR (ATR): 2983w, 2109m, 1744s, 1430w, 1371m, 1219s, 1118w, 1065m, 1041m, 1008w, 937w, 911w, 778w, 739w, 707w, 623w. ¹H-NMR (300 MHz, CDCl₃; assignments based on selective homodecoupling experiments): see Table 5; additionally, 5.71 (*dddd*, *J* = 15.3, 10.5, 7.2, 6.0,

$\text{CH}_2=\text{CHCH}_2\text{S}$); 5.16 (br. *d*, $J = 16.8$), 5.13 (br. *d*, $J = 10.8$) ($\text{CH}_2=\text{CHCH}_2\text{S}$); 3.20–3.06 (*m*, $\text{CH}_2=\text{CHCH}_2\text{S}$); 2.18, 2.09, 2.06, 1.99 (4s, 4 AcO). ^{13}C -NMR (75 MHz, CDCl_3): see Table 5; additionally, 170.04, 169.89, 169.78 (3s, 4 C=O); 132.24 (*d*, $\text{CH}_2=\text{CHCH}_2\text{S}$); 118.81 (*t*, $\text{CH}_2=\text{CHCH}_2\text{S}$); 33.13 (*t*, $\text{CH}_2=\text{CHCH}_2\text{S}$); 21.05, 20.79, 20.67, 20.62 (4*q*, 4 MeC=O). HR-ESI-MS: 496.1360 (100, $[M + \text{Na}]^+$, $\text{C}_{19}\text{H}_{27}\text{N}_3\text{NaO}_9\text{S}^+$; 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 $\rightarrow$ 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): 3059w, 3024w, 2980w, 2939w, 2109m, 1742s, 1495w, 1454w, 1430w, 1370m, 1213s, 1117w, 1065m, 1039s, 1007m, 988w, 937w, 910m, 776w, 729s, 700m, 647w, 622w. ^1H -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*, $J = 13.2$, PhCH_2); 2.16, 2.09, 1.97, 1.95 (4s, 4 AcO). ^{13}C -NMR (75 MHz, CDCl_3): see Table 5; additionally, 169.71, 169.68, 169.57 (3s, 4 C=O); 136.47 (*s*); 128.76 (*d*, 2 C); 128.63 (*d*, 2 C); 127.49 (*d*); 34.95 (*t*, PhCH_2); 21.18, 20.77, 20.73 (3*q*, 4 MeC=O). HR-MALDI-MS: 562.1259 (42, $[M + \text{K}]^+$, $\text{C}_{23}\text{H}_{29}\text{KN}_3\text{O}_9\text{S}^+$; calc. 562.1256), 546.1514 (100, $[M + \text{Na}]^+$, $\text{C}_{23}\text{H}_{29}\text{N}_3\text{NaO}_9\text{S}^+$; calc. 546.1517). Anal. calc. for $\text{C}_{23}\text{H}_{29}\text{N}_3\text{O}_9\text{S}$ (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 $\rightarrow$ 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): 3019w, 2993w, 2939w, 2110m, 1745m, 1497w, 1449w, 1432w, 1371w, 1222s, 1118w, 1066m, 1041m, 1008w, 937w, 911w, 781w, 699w, 622w. ^1H -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*, PhCH_2CH_2); 2.19, 2.08, 2.04, 1.99 (4s, 4 AcO). ^{13}C -NMR (75 MHz, CDCl_3): see Table 5; additionally, 170.19, 169.91, 169.75 (3s, 4 C=O); 139.52 (*s*); 128.60 (*d*, 2 C); 128.53 (*d*, 2 C); 126.65 (*d*); 35.70 (*t*, PhCH_2); 32.12 (*t*, CH_2S); 21.05, 20.83, 20.68, 20.62 (4*q*, 4 MeC=O). HR-MALDI-MS: 560.1667 (100, $[M + \text{Na}]^+$, $\text{C}_{24}\text{H}_{31}\text{N}_3\text{NaO}_9\text{S}^+$; calc. 560.1673). Anal. calc. for $\text{C}_{24}\text{H}_{31}\text{N}_3\text{O}_9\text{S}$ (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 $\rightarrow$ 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): 3028w, 2938w, 2857w, 2108m, 1742s, 1603w, 1496w, 1453w, 1432w, 1370m, 1212s, 1117w, 1064m, 1039m, 1007w, 987w, 936w, 910w, 779w, 730m, 700m, 647w, 622w, 613w. ^1H -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*, $\text{PhCH}_2\text{CH}_2\text{CH}_2$); 2.17, 2.07, 2.06, 1.98 (4s, 4 AcO); 1.97–1.82 (*m*, $\text{PhCH}_2\text{CH}_2\text{CH}_2$). ^{13}C -NMR (75 MHz, CDCl_3): see Table 5; additionally, 169.97, 169.66, 169.53 (3s, 4 C=O); 140.71 (*s*); 128.36 (*d*, 2 C); 128.29 (*d*, 2 C); 125.97 (*d*); 35.65 (*t*, PhCH_2CH_2); 30.90, 30.07 (2*t*, $\text{PhCH}_2\text{CH}_2\text{CH}_2$); 21.11, 20.90, 20.74, 20.70 (4*q*, 4 MeC=O). HR-MALDI-MS: 590.1566 (30, $[M + \text{K}]^+$, $\text{C}_{25}\text{H}_{33}\text{KN}_3\text{O}_9\text{S}^+$; calc. 590.1569), 574.1834 (100, $[M + \text{Na}]^+$, $\text{C}_{25}\text{H}_{33}\text{N}_3\text{NaO}_9\text{S}^+$; calc. 574.1830). Anal. calc. for $\text{C}_{25}\text{H}_{33}\text{N}_3\text{O}_9\text{S}$ (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 $\rightarrow$ 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): 2938w, 2830w, 2109m, 1744s, 1611w, 1513w, 1440w, 1370w, 1301w, 1221s, 1178w, 1117w, 1065m, 1039m, 1008w, 937w, 911w, 895w, 822w, 756w, 704w, 623w. ^1H -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*, $\text{CH}_2\text{CH}_2\text{S}$); 2.17, 2.06, 2.03, 1.97 (4s, 4 AcO). ^{13}C -NMR (75 MHz, CDCl_3): see Table 5; additionally, 169.94, 169.67, 169.51 (3s, 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*, $\text{CH}_2\text{CH}_2\text{S}$); 32.45 (*t*, $\text{CH}_2\text{CH}_2\text{S}$); 21.12, 20.91, 20.74, 20.69 (4*q*, 4 MeC=O). HR-MALDI-MS: 606.1539 (30, $[M + \text{K}]^+$, $\text{C}_{25}\text{H}_{33}\text{KN}_3\text{O}_{10}\text{S}^+$; calc. 606.1518), 590.1780 (100, $[M + \text{Na}]^+$, $\text{C}_{25}\text{H}_{33}\text{N}_3\text{NaO}_{10}\text{S}^+$;

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 $\rightarrow$ 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): 2940w, 2109m, 1741s, 1605w, 1519w, 1431w, 1370w, 1345w, 1213s, 1111w, 1064m, 1040m, 1007w, 988w, 937w, 910w, 867w, 855w, 780w, 730w, 647w, 614w. 1H -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 (4s, 4 AcO). ^{13}C -NMR (75 MHz, $CDCl_3$): see Table 5; additionally, 169.90, 169.65, 169.45 (3s, 4 C=O); 146.78, 146.65 (2s); 129.27 (*d*, 2 C); 123.68 (*d*, 2 C); 35.33 (*t*, CH_2CH_2S); 31.12 (*t*, CH_2CH_2S); 21.06, 20.82, 20.67, 20.62 (4*q*, 4 MeC=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-[(2*S*,4*R*)-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 $\rightarrow$ 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): 3331w (br.), 2957w, 2921w, 2872w, 2788w, 1645m, 1521m, 1454w, 1425w, 1403w, 1379w, 1306w, 1230w, 1175w, 1157w, 1075s, 1051s, 989m, 913w, 865w, 803w, 750s, 694w, 664w, 635w, 611w. 1H -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 prolanyl); 2.91 (*dd*, $J = 10.5, 4.2$, 1 H of prolanyl); 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*, $MeCH_2CH_2$). ^{13}C -NMR (75 MHz, CD_3OD): see Table 4; additionally, 178.27 (*s*, C=O); 134.93 (*d*, $CH=CH_2$); 117.76 (*t*, $CH=CH_2$); 70.05 (*d*, C(2) of prolanyl); 63.82 (*t*, C(5) of prolanyl); 41.82 (*q*, MeN); 38.92 (*d*, C(4) of prolanyl); 38.76 (*t*, C(3) of prolanyl); 36.86 (*t*, $MeCH_2CH_2$); 33.25 (*t*, CH_2S); 22.67 (*t*, $MeCH_2CH_2$); 14.60 (*q*, $MeCH_2CH_2$). 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-[(2*S*,4*R*)-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 $\rightarrow$ 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): 3331w (br.), 2958w, 2925w, 2873w, 2790w, 1646m, 1521m, 1495w, 1453w, 1419w, 1379w, 1309w, 1296w, 1239w, 1216w, 1180w, 1160w, 1080w, 1072m, 1050m, 991m, 943w, 904w, 859w, 803w, 749s, 697m, 664m, 634w, 604w. 1H -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 prolanyl); 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*, $J = 7.2$, $MeCH_2CH_2$). ^{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 prolanyl); 63.41 (*t*, C(5) of prolanyl); 41.41 (*q*, MeN); 38.54 (*d* and *t*, C(4) of prolanyl, CH_2S); 36.35 (*t*, C(3) of prolanyl); 33.73 (*t*, $MeCH_2CH_2$); 22.27 (*t*, $MeCH_2CH_2$); 14.16 (*q*, $MeCH_2CH_2$). 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-[(2*S*,4*R*)-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): 3331w (br.), 2956w, 2923w, 2872w, 2789w, 1646m, 1520m, 1453m, 1379w, 1307w, 1216w, 1180w, 1076s, 1049s, 990w, 904w, 866w, 804w, 749s, 696m, 664w, 635w, 607w. $^1\text{H-NMR}$ (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, $\text{SCH}_2\text{CH}_2\text{Ph}$); 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). $^{13}\text{C-NMR}$ (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_2); 22.67 (*t*, MeCH_2CH_2); 14.62 (*q*, MeCH_2CH_2). HR-MALDI-MS: 535.2259 (5, $[M + K]^+$, $\text{C}_{25}\text{H}_{40}\text{KN}_2\text{O}_6\text{S}^+$; calc. 535.2244), 519.2511 (19, $[M + Na]^+$, $\text{C}_{25}\text{H}_{40}\text{N}_2\text{NaO}_6\text{S}^+$; calc. 519.2505), 497.2674 (100, $[M + H]^+$, $\text{C}_{25}\text{H}_{41}\text{N}_2\text{O}_6\text{S}^+$; calc. 497.2685).

3-Phenylpropyl 6,8-Dideoxy-6-[(2*S*,4*R*)-1-methyl-4-propylpyrrolidine-2-carboxamido]-1-thio- 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): 3328m (br.), 2924m, 2872m, 2789w, 1650s, 1522s, 1453m, 1379w, 1306w, 1254w, 1215w, 1182w, 1162w, 1077s, 1051s, 991m, 905w, 864w, 804w, 748s, 698s, 664m, 604w, 519s. $^1\text{H-NMR}$ (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). $^{13}\text{C-NMR}$ (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, $[M + K]^+$, $\text{C}_{26}\text{H}_{42}\text{KN}_2\text{O}_6\text{S}^+$; calc. 549.2401), 533.2668 (19, $[M + Na]^+$, $\text{C}_{26}\text{H}_{42}\text{N}_2\text{NaO}_6\text{S}^+$; calc. 533.2661), 511.2844 (100, $[M + H]^+$, $\text{C}_{26}\text{H}_{43}\text{N}_2\text{O}_6\text{S}^+$; calc. 511.2836).

2-(4-Methoxyphenyl)ethyl 6,8-Dideoxy-6-[(2*S*,4*R*)-1-methyl-4-propylpyrrolidine-2-carboxamido]-1-thio- α -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): 3327w (br.), 2923w, 2788w, 1647m, 1611w, 1511s, 1453w, 1376w, 1300w, 1244s, 1177m, 1078m, 1047s, 991m, 942w, 903w, 850w, 820w, 805w, 773w, 691w. $^1\text{H-NMR}$ (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). $^{13}\text{C-NMR}$ (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*, $\text{CH}_2\text{CH}_2\text{S}$); 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, $[M + K]^+$, $\text{C}_{26}\text{H}_{42}\text{KN}_2\text{O}_7\text{S}^+$; calc. 565.2350), 549.2608 (15, $[M + Na]^+$, $\text{C}_{26}\text{H}_{42}\text{N}_2\text{NaO}_7\text{S}^+$; calc. 549.2610), 527.2783 (100, $[M + H]^+$, $\text{C}_{26}\text{H}_{43}\text{N}_2\text{O}_7\text{S}^+$; calc. 527.2785).

2-(4-Nitrophenyl)ethyl 6,8-Dideoxy-6-[(2*S*,4*R*)-1-methyl-4-propylpyrrolidine-2-carboxamido]-1-thio- α -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): 3337m (br.), 2949w, 2925m, 2876w, 2791w, 1650m, 1604w, 1518s, 1454w, 1344s, 1095m, 1080m, 1052m, 992w, 901w, 855w, 806w, 749w, 695w. $^1\text{H-NMR}$ (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*, $J = 7.2$, $\text{CH}_2\text{CH}_2\text{S}$); 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). $^{13}\text{C-NMR}$ (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*, $\text{CH}_2\text{CH}_2\text{S}$);

37.01 (*t*, C(3) of prolanyl); 36.94 (*t*, MeCH₂CH₂); 32.04 (*t*, CH₂S); 22.70 (*t*, MeCH₂CH₂); 14.60 (*q*, MeCH₂CH₂). HR-MALDI-MS: 542.2535 (100, [*M* + H]⁺, C₂₅H₄₀N₃O₈S⁺; 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 N₂ was treated at 0° with 60% NaH in mineral oil (3.12 g, 78 mmol), BnBr (10.80 g, 63 mmol), and Bu₄NI (193 mg, 0.52 mmol), warmed to 25°, stirred for 24 h, and cautiously treated with H₂O until complete consumption of NaH. The mixture was diluted with AcOEt, washed with sat. aq. NH₄Cl soln., dried (Na₂SO₄), 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. [*α*]_D²⁵ = +107.6 (*c* = 0.99, CHCl₃). 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*. ¹H-NMR (400 MHz, CDCl₃; assignments based on a DQF-COSY 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 PhCH₂); 2.01 (*s*, MeS). ¹³C-NMR (75 MHz, CDCl₃; 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 PhCH₂); 13.94 (*q*, MeS). HR-ESI-MS: 662.2661 (100, [*M* + Na]⁺, C₃₇H₄₁N₃NaO₅S⁺; calc. 662.2659). Anal. calc. for C₃₇H₄₁N₃O₅S (639.81): C 69.46, H 6.46, N 6.57; found: C 69.29, H 6.29, N 6.54.

Table 6. Selected ¹H-NMR Chemical Shifts [ppm] and Coupling Constants [Hz], and ¹³C-NMR Chemical Shifts [ppm] of the Lincosamine Derivatives **18**–**22** in CDCl₃

	18	<i>α</i> - 19 ^{a)}	<i>β</i> - 19 ^{a)}	(<i>E</i>)- 20 ^{a)}	(<i>Z</i>)- 20 ^{a)}	<i>α</i> - 21	<i>β</i> - 21	<i>α</i> - 22	<i>β</i> - 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 ₃ C(8)	1.20	1.18	1.17	1.16	1.18	1.13	1.15	1.16	1.19
<i>J</i> (1,2)	5.6	4.0	7.2	7.9	6.5	5.4	^{b)}	6.0	5.4
<i>J</i> (2,3)	10.2	9.9	9.6	4.8	3.9	9.6	9.6	10.2	9.0
<i>J</i> (3,4)	2.6	2.6	2.7	^{b)}	^{b)}	1.8	1.8	2.4	2.1
<i>J</i> (4,5)	0.3	0.3	1.1	6.3	5.7	0.9	0.3	^{b)}	2.1
<i>J</i> (5,6)	10.2	10.7	10.0	10.1	10.2	10.2	10.2	9.3	10.2
<i>J</i> (6,7)	2.4	2.8	2.6	2.0	2.8	2.7	2.7	2.7	2.7
<i>J</i> (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 DQF-COSY 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 CH₂Cl₂ (200 ml) was treated at 0° with Br₂ (566 μ l, 11.02 mmol), stirred for 15 min, and treated with sat. aq. Na₂S₂O₅ soln. After extraction with CH₂Cl₂, 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 $\rightarrow$ 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): 3455w (br.), 3029w, 2970w, 2937w, 2104s, 1496w, 1453m, 1365s, 1269w, 1228m, 1216s, 1125m, 1058s, 1026s, 903m, 788w, 733s, 695s. $^1\text{H-NMR}$ (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*, $J = 11.2$, PhCH (β)); 5.05 (*d*, $J = 11.1$, PhCH (α)); 4.90–4.77 (*m*, PhCH_2 , PhCH (α)); 4.70–4.65 (*m*, 2 PhCH (β), PhCH (α), PhCH (β)); 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)). $^{13}\text{C-NMR}$ (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, $[M + K]^+$, $\text{C}_{36}\text{H}_{39}\text{KN}_3\text{O}_6^+$; calc. 648.2470); 632.2721 (100, $[M + Na]^+$, $\text{C}_{36}\text{H}_{39}\text{N}_3\text{NaO}_6^+$; calc. 632.2731). Anal. calc. for $\text{C}_{36}\text{H}_{39}\text{N}_3\text{O}_6$ (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 $\text{NH}_2\text{OH} \cdot \text{HCl}$ (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): 3355w (br.), 3063w, 3029w, 2970w, 2940w, 2104s, 1586w, 1496w, 1454m, 1376s, 1304w, 1267w, 1229m, 1216m, 1065s, 1026m, 939m, 910m, 820w, 733s, 695s. $^1\text{H-NMR}$ (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 PhCH); 4.58–4.40 (*m*, 5 PhCH); 3.12 (*d*, $J = 6.0$, OH (*Z*)); 3.03 (*d*, $J = 6.3$, OH (*E*)). $^{13}\text{C-NMR}$ (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, $[M + Na]^+$, $\text{C}_{36}\text{H}_{40}\text{N}_3\text{NaO}_6^+$; 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 $\rightarrow$ 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. $143\text{--}146^\circ$. $[\alpha]_D^{25} = +44.1$ ($c = 1.08$, CHCl_3). IR (ATR): 3085w, 3063w, 3030w, 2980w, 2927w, 2862w, 2106m, 1588w, 1573w, 1556w, 1496w, 1485w, 1453m, 1398w, 1377w, 1346w, 1331w, 1274w, 1207w, 1131s, 1088s, 1045m, 1026m, 1012m, 952w, 904w, 881w, 836w, 730s, 693s, 673w, 632w, 618w. $^1\text{H-NMR}$ (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*, $\text{CH}=\text{N}$); 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 PhCH); 4.50 (*s*, PhCH_2). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): see Table 6; additionally, 138.42, 138.34, 138.11, 138.02, 136.07 (5s, 6 C); 134.45 (*d*, $\text{CH}=\text{N}$); 129.91–127.08 (several *d*); 75.27, 75.08, 73.29, 70.56 (4t, 4 PhCH_2). HR-ESI-MS: 769.2766 (100, $[M + Na]^+$, $\text{C}_{43}\text{H}_{43}\text{ClN}_4\text{NaO}_6^+$; calc. 769.2769). Anal. calc. for $\text{C}_{43}\text{H}_{43}\text{ClN}_4\text{O}_6$ (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. $191\text{--}192^\circ$. $[\alpha]_D^{25} = -35.7$ ($c = 1.0$, CHCl_3). IR (ATR): 3085w, 3063w, 3032w, 2975w, 2931w, 2856w, 2109m, 1586w, 1556w, 1496w, 1484w, 1453m, 1396m, 1378m, 1346m, 1299m, 1270m, 1213m, 1155m, 1130s, 1089s, 1046s, 1027s, 1010m, 960m, 931m, 912m, 865m, 832m, 793w, 731s, 695s, 674s, 620w. $^1\text{H-NMR}$ (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, $\text{CH}=\text{N}$); 5.12 (*d*, $J = 11.7$, PhCH); 4.86–4.46 (*m*, 3 PhCH_2 , PhCH). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): see Table 6; additionally, 138.46, 138.34, 138.02, 137.78, 136.66 (5s, 6 C); 134.24 (*d*, $\text{CH}=\text{N}$); 130.49–127.21 (several *d*); 75.45, 74.78, 72.81, 70.75 (4t, 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 $\rightarrow$ 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): 3064w, 3031w, 2984w, 2940w, 2914w, 2873w, 2107m, 1557m, 1496w, 1453m, 1368w, 1347w, 1309w, 1268m, 1208w, 1091s, 1158w, 1125m, 1091s, 1045m, 1025m, 913w, 874w, 821w, 732s, 695s, 619w. 1H -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 PhCH). ^{13}C -NMR (75 MHz, $CDCl_3$): see Table 6; additionally, 138.13, 137.80, 137.66, 136.73 (4s); 128.46–127.19 (several d); 75.33, 74.21, 73.51, 70.73 (4t, 4 PhCH₂). 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): 3030w, 2970w, 2937w, 2106m, 1565s, 1496w, 1454m, 1369m, 1268w, 1229m, 1216m, 1127m, 1091s, 1047s, 1026s, 910w, 873w, 843w, 792w, 732s, 695s. 1H -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 PhCH); 4.61 (s , PhCH₂). ^{13}C -NMR (75 MHz, $CDCl_3$): see Table 6; additionally, 138.50, 137.72, 137.64, 137.24 (4s); 128.81–127.71 (several d); 75.08, 74.67, 72.99, 71.08 (4t, 4 PhCH₂). 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 $\rightarrow$ 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): 3031w, 2938w, 2965w, 2107m, 1749m, 1607w, 1587w, 1496w, 1454w, 1367w, 1346w, 1265w, 1218m, 1178w, 1127m, 1094m, 1042m, 1027m, 1009m, 961w, 908m, 729s, 695s, 648w. 1H -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 PhCH₂); 2.05, 1.92 (2s, 2 AcO). ^{13}C -NMR (75 MHz, $CDCl_3$; assignments based on a HSQC spectrum): see Table 7; additionally, 169.68, 168.26 (2s, 2 C=O); 138.48, 138.37, 137.90, 137.84 (4s); 128.43–127.30 (several d); 75.43, 74.56, 72.63, 70.80 (4t, 4 PhCH₂); 21.58, 20.63 (2q, 2 MeC=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%).

(1R)-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. 1H -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 ^1H -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 ₃ C(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
$J(7,\text{Me})$	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 PhCH₂); 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(CH₂)₆); 1.23 (*d*, $J = 6.3$, Me); 0.88 (*t*, $J = 6.6$, Me(CH₂)₆).

(*1S*)-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. ^1H -NMR (300 MHz, CDCl₃): 7.44–7.22 (*m*, 20 arom. H); 5.10 (*d*, $J = 11.0$, PhCH), 4.87 (*br. s*, PhCH₂); 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(CH₂)₆); 1.20 (*d*, $J = 6.3$, Me); 0.88 (*t*, $J = 6.3$, Me(CH₂)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 CH₂Cl₂ was washed with H₂O, sat. aq. NaHCO₃ soln., and brine, dried (MgSO₄), 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.

(IR)-1,2-Di-O-acetyl-7-azido-3,4,5,8-tetra-O-benzyl-7,9-dideoxy-1-C-heptyl-D-erythro- α -D-galactono-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 $\rightarrow$ 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): 3031w, 2927w, 2857w, 2107m, 1743m, 1496w, 1454m, 1368m, 1225m, 1094s, 1044s, 1027s, 1008m, 930m, 840w, 781w, 733s, 695s. $^1\text{H-NMR}$ (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 (2s, 2 AcO); 1.74–1.42 (m, 2 H); 1.38–1.12 (m, 10 H) ($(\text{CH}_2)_6\text{Me}$); 0.88 (t, $J = 6.9$, $(\text{CH}_2)_6\text{Me}$). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3 ; assignments based on a HSQC spectrum): see Table 7; additionally, 170.17, 168.03 (2s, 2 C=O); 138.60, 138.55, 138.32, 137.91 (4s); 128.36–127.26 (several d); 74.92, 74.55, 72.64, 70.64 (4t, 4 PhCH_2); 31.71, 29.54, 29.41, 29.10, 25.69, 22.56 (6t, $\text{Me}(\text{CH}_2)_6$); 21.90, 20.80 (2q, 2 MeC=O); 14.01 (q, $\text{Me}(\text{CH}_2)_6$). ESI-MS: 844.1 (100, $[\text{M} + \text{Na}]^+$). Anal. calc. for $\text{C}_{48}\text{H}_{59}\text{N}_3\text{O}_9$ (822.01): C 70.14, H 7.23, N 5.11; found: C 69.85, H 7.33, N 5.24.

(IS)-1,2-Di-O-acetyl-7-azido-3,4,5,8-tetra-O-benzyl-7,9-dideoxy-1-C-heptyl-D-erythro- α -D-galactono-2-ulopyranose (**29b**). According to GP 7, 79 mg (0.10 mmol) of **28b** and FC of the crude acetate (hexane/AcOEt 95:5 $\rightarrow$ 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): 3031w, 2926w, 2857w, 2106m, 1753s, 1497w, 1454w, 1368m, 1346w, 1213m, 1155w, 1127m, 1090s, 1046m, 1027m, 1009m, 983m, 927m, 783w, 732s, 695s. $^1\text{H-NMR}$ (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 (2s, 2 AcO); 1.83–1.53 (m, 2 H), 1.28–1.14 (m, 10 H) ($\text{Me}(\text{CH}_2)_6$); 0.87 (t, $J = 7.2$, $\text{Me}(\text{CH}_2)_6$). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3 ; assignments based on a HSQC spectrum): see Table 7; additionally, 169.55, 168.16 (2s, 2 C=O); 138.58, 138.52, 137.95, 137.91 (4s); 128.44–127.30 (several d); 74.97, 74.71, 72.66, 71.14 (4t, 4 PhCH_2); 31.86, 29.78, 29.25 (2 C), 26.32, 22.77 (5t, $\text{Me}(\text{CH}_2)_6$); 21.88, 20.95 (2q, 2 MeC=O); 14.26 (q, $\text{Me}(\text{CH}_2)_6$). ESI-MS: 844.2 (100, $[\text{M} + \text{Na}]^+$). Anal. calc. for $\text{C}_{48}\text{H}_{59}\text{N}_3\text{O}_9$ (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 $\rightarrow$ 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-glucodec-3-ulopyranose (**33a**). R_f (hexane/AcOEt 85:15) 0.63. $^1\text{H-NMR}$ (300 MHz, CDCl_3): 7.40–7.22 (m, 25 arom. H); 5.08 (d , $J = 11.1$, PhCH); 4.87 (br. s, PhCH_2); 4.81 (d , $J = 10.2$, $\text{H-C}(4)$); 4.73–4.62 (m, $\text{H-C}(7)$, PhCH_2); 4.60–4.52 (ddd, $J = 8.7$, 6.3, 3.6, $\text{H-C}(2)$); 4.46 (d , $J = 12.3$, PhCH); 4.40 (br. s, PhCH_2); 4.36 (d , $J = 12.0$), 4.32 (d , $J = 10.2$) (2 PhCH); 4.15 (br. s, $\text{H-C}(6)$); 4.05 (dd, $J = 10.2$, 3.0, $\text{H-C}(8)$); 3.86 (dd, $J = 9.9$, 1.8, $\text{H-C}(5)$); 3.74 (qd, $J = 6.3$, 3.0, $\text{H-C}(9)$); 3.44 (dd, $J = 10.2$, 3.6, $\text{H}_a\text{-C}(1)$); 3.36 (dd, $J = 10.2$, 6.6, $\text{H}_b\text{-C}(1)$); 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-mannodec-3-ulopyranose (**33b**). R_f (hexane/AcOEt 85:15) 0.64. $^1\text{H-NMR}$ (300 MHz, CDCl_3): 7.42–7.16 (m, 25 arom. H); 5.03 (d , $J = 10.5$, PhCH); 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 PhCH); 4.56–4.53 (m, $\text{H-C}(2)$ overlapping with PhCH); 4.54 (d , $J = 12.0$, PhCH); 4.47 (d , $J = 9.6$, $\text{H-C}(4)$); 4.40 (d , $J = 12.0$, PhCH); 4.35 (br. d , $J = 10.2$, $\text{H-C}(7)$); 4.27 (d , $J = 11.8$), 4.20 (d , $J = 12.0$) (2 PhCH); 4.18 (br. s, $\text{H-C}(6)$); 4.04 (dd, $J = 10.2$, 2.7, $\text{H-C}(8)$); 3.86 (dd, $J = 9.6$, 2.4, $\text{H-C}(5)$); 3.85 (qd, $J = 6.3$, 2.4, $\text{H-C}(9)$); 3.42, 3.34 (2dd, $J = 10.2$, 5.1, 2 $\text{H-C}(1)$); 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-glucodec-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 $\rightarrow$ 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): 3063w, 3030w, 2936w, 2868w, 2107m, 1748w, 1605w, 1587w, 1496w, 1453m, 1368m, 1346w, 1232m, 1216m, 1095s, 1047m, 1026m, 1008m, 915m, 781w, 733s, 695s. $^1\text{H-NMR}$ (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, PhCH); 4.86 (br. s, PhCH₂); 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 PhCH); 2.02, 1.97 (2s, 2 AcO). ¹³C-NMR (75 MHz, CDCl₃; assignments based on a HSQC spectrum): see Table 7; additionally, 169.95, 168.15 (2s, 2 C=O); 138.65, 138.57, 138.30, 137.96 (4s); 128.42–127.28 (several *d*); 75.04, 74.78, 72.85, 72.83, 70.85 (5t, 5 PhCH₂); 22.17, 21.06 (2*q*, 2 MeC=O); 13.44 (*q*, Me). ESI-MS: 866.0 (100, [*M* + Na]⁺). Anal. calc. for C₄₉H₅₃N₃O₁₀ (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. [*α*]_D²⁵ = +46.7 (*c* = 0.98, CHCl₃). IR (ATR): 3063w, 3031w, 2931w, 2867w, 2107m, 1753w, 1605w, 1587w, 1496w, 1453m, 1368m, 1346w, 1214m, 1126m, 1090s, 1044m, 1027m, 1009m, 925m, 851w, 732s, 695s. ¹H-NMR (300 MHz, CDCl₃; 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 PhCH₂); 1.97, 1.93 (2s, 2 AcO). ¹³C-NMR (75 MHz, CDCl₃; assignments based on a HSQC spectrum): see Table 7; additionally, 169.29, 168.23 (2s, 2 C=O); 138.67, 138.62, 138.09, 137.91 (4s); 128.55–127.44 (several *d*); 74.92, 74.71, 72.60, 72.09, 71.14 (5t, 5 PhCH₂); 21.64, 20.88 (2*q*, 2 MeC=O). HR-ESI-MS: 866.3620 (100, [*M* + Na]⁺, C₄₉H₅₃N₃NaO₁₀⁺; calc. 866.3623). Anal. calc. for C₄₉H₅₃N₃O₁₀ (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-tetradecoxy-D-erythro-α-D-galacto-undec-4-ulopyranosonitrile (41). A soln. of **α-22/β-22** (200 mg, 0.31 mmol) and acrylonitrile (45 μl, 0.63 mmol) in *t*-BuOH/CH₂Cl₂ 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. LiClO₄ (5 ml), stirred for 48 h at 25°, and evaporated. A soln. of the residue in CH₂Cl₂ was washed with H₂O and brine, dried (MgSO₄), and evaporated. A soln. of the residue in CH₂Cl₂ (5 ml) was treated with Et₃N (2 ml), DMAP (39 mg, 0.31 mmol), and Ac₂O (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. [*α*]_D²⁵ = +16.5 (*c* = 1.0, CHCl₃). IR (ATR): 3030w, 2933w, 2108s, 1748m, 1586w, 1496w, 1454m, 1367m, 1346w, 1305w, 1270w, 1212m, 1127m, 1092s, 1047m, 1026s, 1009m, 967m, 927m, 735s, 697s. ¹H-NMR (300 MHz, CDCl₃; 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 PhCH₂); 2.03 (*s*, AcO). ¹³C-NMR (75 MHz, CDCl₃): see Table 7; additionally, 168.26 (*s*, C=O); 138.18, 138.63, 137.03 (4s); 128.93–127.47 (several *d*); 75.15, 74.95, 72.57, 70.79 (4t, 4 PhCH₂); 22.17 (*q*, MeC=O). ESI-MS: 727.1 (100, [*M* + Na]⁺). Anal. calc. for C₄₁H₄₄N₄O₇ (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-tetradecoxy-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 Bu₄NF · 3 H₂O 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 CH₂Cl₂ (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 BF₃ · OEt₂ (22 μl, 0.24 mmol), and stirred for 1 h. The mixture was treated with sat. aq. NaHCO₃ soln. and filtered over *Celite*. The layers were separated, and the aq. layer was extracted with CH₂Cl₂. The combined org. layers were dried (MgSO₄) and evaporated. FC (hexane/AcOEt 95 : 5 → 4 : 1) gave **45** (146 mg, 85%). *R*_f (hexane/AcOEt 85 : 15) 0.36. [*α*]_D²⁵ = +42.6 (*c* = 1.0, CHCl₃). IR (ATR): 3063w, 3030w, 2925w, 2105s, 1735m, 1496w, 1453m, 1435w, 1380w, 1345w, 1268w, 1194w, 1171w, 1127m, 1086s, 1026m, 951w, 910w, 732s, 695s. ¹H-NMR (300 MHz, CDCl₃; 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 PhCH₂); 3.57 (*s*, MeO); 1.87 (*s*, MeS). ¹³C-NMR (75 MHz, CDCl₃): see Table 8; additionally, 173.64 (*s*, C=O); 138.80, 138.18, 138.06, 137.83 (4s); 128.43–127.38 (several *d*); 75.12, 74.67, 72.58, 70.76 (4t, 4 PhCH₂); 9.74 (*q*, MeS). ESI-MS: 747.9 (100, [*M* + Na]⁺). Anal. calc. for C₄₁H₄₇N₃O₇S (725.90): C 67.84, H 6.53, N 5.79; found: C 67.96, H 6.39, N 5.80.

Table 8. Selected ^1H -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 ₃ C(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
$J(7,\text{Me})$	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 $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (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): 3028w, 2970w, 2943w, 2104m, 1739s, 1496w, 1454m, 1365s, 1228s, 1216s, 1091m, 1047m, 1026m, 951w, 906w, 900w, 781w, 733m, 695m. ^1H -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 PhCH₂); 1.90 (*s*, MeS); 1.84 (*s*, AcO). ¹³C-NMR (75 MHz, CDCl₃; 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 PhCH₂); 20.75 (*q*, MeC=O); 9.30 (*q*, MeS). ESI-MS: 734.01 (100, $[M + Na]^+$). Anal. calc. for C₄₀H₄₅N₃O₇S (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*. ¹H-NMR (400 MHz, CDCl₃; 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 PhCH); 4.52 (*d*, $J = 12.8$, H_a–C(1)); 4.49 (*d*, $J = 10.8$), 4.44 (*d*, $J = 12.0$) (2 PhCH); 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). ¹³C-NMR (100 MHz, CDCl₃; 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*, PhCH₂); 74.84 (*d*, C(8)); 74.76 (*t*, PhCH₂); 73.99 (*d*, C(5)); 73.20 (*d*, C(6)); 72.76, 70.74 (2*t*, 2 PhCH₂); 64.12 (*t*, C(1)); 62.56 (*d*, C(7)); 20.81 (*q*, MeC=O); 13.37 (*q*, Me); 10.63 (*q*, MeS). ESI-MS: 750.2833 (55, $[M + K]^+$, C₄₀H₄₅KN₃O₇S⁺; calc. 750.2615); 734.2879 (100, $[M + Na]^+$, C₄₀H₄₅N₃NaO₇S⁺; calc. 734.2870).

Methyl (IR)-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, CHCl₃). 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*. ¹H-NMR (300 MHz, CDCl₃; 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 PhCH₂); 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(CH₂)₆); 0.87 (*t*, $J = 6.0$, Me(CH₂)₆). ¹³C-NMR (75 MHz, CDCl₃; 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 PhCH₂); 31.90, 30.02, 29.65, 29.26, 26.64, 22.75 (6*t*, Me(CH₂)₆); 21.14 (*q*, MeC=O); 14.41 (*q*, Me(CH₂)₆); 9.72 (*q*, MeS). ESI-MS: 832.1 (100, $[M + Na]^+$). Anal. calc. for C₄₇H₅₉N₃O₇S (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*. ¹H-NMR (300 MHz, CDCl₃; 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 PhCH₂); 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(CH₂)₆); 1.23 (*d*, $J = 6.3$, Me); 0.88 (*t*, $J = 6.6$, Me(CH₂)₆). ¹³C-NMR (75 MHz, CDCl₃; 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*, PhCH₂); 75.54 (*d*, C(5)); 74.80 (*t*, PhCH₂); 74.73 (*d*, C(8)); 73.39 (*t*, PhCH₂); 72.66 (*d*, C(6)); 70.92 (*d*, C(1)); 70.78 (*t*, PhCH₂); 63.23 (*d*, C(7)); 31.84, 30.36, 29.63, 29.33, 25.94, 22.72 (6*t*, Me(CH₂)₆); 20.87 (*q*, MeC=O); 14.41 (*q*, Me(CH₂)₆); 9.90 (*q*, MeS). HR-ESI-MS: 832.3968 (100, $[M + Na]^+$, C₄₈H₅₃N₃NaO₈S⁺; calc. 832.3966).

Methyl (IS)-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 (**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, CHCl₃). 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*,

785w, 732s, 696s. $^1\text{H-NMR}$ (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) ($\text{Me}(\text{CH}_2)_6$); 1.91 (*s*, MeS); 1.77 (*s*, AcO); 0.85 (*t*, $J = 6.9$, $\text{Me}(\text{CH}_2)_6$). $^{13}\text{C-NMR}$ (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 (4s); 128.41–126.90 (several *d*); 74.86, 74.51, 72.45, 71.08 (4t, 4 PhCH_2); 31.89, 30.02, 29.26, 29.20, 26.77, 22.74 (6t, $\text{Me}(\text{CH}_2)_6$); 20.91 (*q*, MeC=O); 14.42 (*q*, $\text{Me}(\text{CH}_2)_6$); 9.19 (*q*, MeS). ESI-MS: 832.2 (100, $[M + \text{Na}]^+$). Anal. calc. for $\text{C}_{47}\text{H}_{59}\text{N}_3\text{O}_7\text{S}$ (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-glucopyranoside (β-L-36/α-L-36a). According to *GP 8*, 140 mg of $\beta\text{-L-34a}$ (0.16 mmol) gave a mixture of epimeric acetates $\alpha\text{-L-35}/\beta\text{-L-35a}$ which could not be separated. A soln. of the crude acetates $\alpha\text{-L-35}/\beta\text{-L-35a}$ in $\text{CH}_2\text{Cl}_2/\text{MeOH}$ 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 $\alpha\text{-L-36a}$ (37 mg, 30%) and $\beta\text{-L-36a}$ (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): 3506w (br.), 3063w, 3030w, 2866w, 2105m, 1496w, 1453m, 1380w, 1345w, 1304w, 1271w, 1208w, 1088s, 1072s, 1026m, 910w, 732s, 695s. $^1\text{H-NMR}$ (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). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3 ; assignments based on a HSQC spectrum): see *Table 8*; additionally, 138.61, 138.13, 137.97 (2 C), 137.90 (4s); 128.39–127.40 (several *d*); 75.03, 74.72, 73.68, 72.66, 70.74 (5t, 5 PhCH_2); 9.42 (*q*, MeS). HR-ESI-MS: 828.3305 (33, $[M + \text{K}]^+$, $\text{C}_{46}\text{H}_{51}\text{KN}_3\text{O}_7\text{S}^+$; calc. 828.3079), 812.3340 (100, $[M + \text{Na}]^+$, $\text{C}_{46}\text{H}_{51}\text{N}_3\text{NaO}_7\text{S}^+$; calc. 812.3340). Anal. calc. for $\text{C}_{46}\text{H}_{51}\text{N}_3\text{O}_7\text{S}$ (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): 3467w (br.), 3063w, 3030w, 2923w, 2869w, 2106m, 1496w, 1453m, 1381w, 1345w, 1273w, 1209w, 1088s, 1066s, 1027m, 960w, 911w, 733s, 696s. $^1\text{H-NMR}$ (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, $\text{H}_a\text{–C}(1)$); 3.54 (*dd*, $J = 10.4$, 7.5, $\text{H}_b\text{–C}(1)$); 3.67 (*dd*, $J = 9.6$, 1.0, H–C(7)); 1.91 (*s*, MeS); 1.02 (*d*, $J = 6.3$, Me). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3 ; assignments based on a HSQC spectrum): 138.68, 138.23, 138.10, 137.80, 137.16 (5s); 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 (2t, 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, $[M + \text{Na}]^+$, $\text{C}_{46}\text{H}_{51}\text{NaN}_3\text{O}_7\text{S}^+$; 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%). Colourless oil. R_f (hexane/AcOEt 85:15) 0.42. $[\alpha]_D^{25} = +59.3$ ($c = 1.09$, CHCl_3). IR (ATR): 3063w, 3030w, 2927w, 2864w, 2104m, 1747m, 1496w, 1453m, 1369m, 1346w, 1300w, 1270w, 1225m, 1124m, 1073s, 1042m, 1026m, 985m, 947m, 905w, 731s, 695s. $^1\text{H-NMR}$ (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*, MeC=O). $^{13}\text{C-NMR}$ (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 (5s); 128.41–126.74 (several *d*); 74.73, 74.48, 72.50, 72.21, 70.98 (5t, 5 PhCH_2); 20.73 (*q*, MeC=O); 9.00 (*q*, MeS). HR-ESI-MS: 870.3435 (33, $[M + \text{K}]^+$, $\text{C}_{48}\text{H}_{53}\text{KN}_3\text{O}_8\text{S}^+$; 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-tetradecoxy-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 $\rightarrow$ 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): 3063w, 3030w, 2926w, 2105s, 1496w, 1453m, 1380w, 1346m, 1304w, 1267w, 1209w, 1128m, 1085s, 1026s, 951m, 910m, 733s, 696s. 1H -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 (4s); 129.04–127.46 (several d); 119.74 (s , CN); 74.55, 73.57, 72.37, 70.68 (4t, 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-[(2S,4R)-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 $\rightarrow$ 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): 3030w, 2926w, 2870w, 2784w, 1742m, 1676m, 1497m, 1453m, 1375m, 1305w, 1223m, 1089s, 1027s, 949w, 909w, 732s, 696s. 1H -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 $PhCH_2$); 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 $PhCH$); 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 ($br. t$, $J = 6.6$, $MeCH_2CH_2$). ^{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 (4s); 128.35–127.13 (several d); 75.07, 73.44, 72.53, 70.65 (4t, 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 , MeC=O); 14.20 (q , $MeCH_2CH_2$); 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 (1R)-1-O-Acetyl-3,4,5,8-tetra-O-benzyl-7,9-dideoxy-1-C-heptyl-7-[(2S,4R)-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 $\rightarrow$ 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): 3356w ($br.$), 3030w, 2958w, 2925m, 2856w, 2781w, 1739m, 1674m, 1497m, 1453m, 1369w, 1305m, 1233s, 1179w, 1087s, 1027s, 912w, 820w, 732s, 695s. 1H -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 , $J = 11.4$, $PhCH$); 4.83, 4.63 (2s, 2 $PhCH_2$); 4.58 (d , $J = 11.4$), 4.50 (d , $J = 11.4$), 4.32 (d , $J = 11.4$) (3 $PhCH$); 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 , $Me(CH_2)_5CH_2$); 1.90 (s , MeS); 1.89 (s , AcO); 1.38–1.18 (m , $MeCH_2CH_2$, $Me(CH_2)_5CH_2$); 0.92–0.85 (m , $Me(CH_2)_6$, $MeCH_2CH_2$). ^{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) (3s); 128.30–126.95 (several d); 74.46, 73.21, 72.96, 70.86 (4t, 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 (6t, $Me(CH_2)_6$); 21.74 (t ,

Table 9. Selected ^1H -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 ₃ C(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
<i>J</i> (2,3)	8.8	9.3	9.3	9.3	9.6	9.9	^{e)}
<i>J</i> (3,4)	2.4	2.1	2.1	2.1	2.4	2.4	^{e)}
<i>J</i> (5,6)	6.8	6.0	8.4	6.3	8.4	6.3	6.0
<i>J</i> (6,7)	4.4	6.3	3.3	6.3	3.2	6.0	5.7
<i>J</i> (7,Me)	6.4	6.3	6.3	6.3	6.4	6.3	6.0
<i>J</i> (6,NH)	9.6	9.3	9.9	9.9	10.0	9.6	9.6
<i>J</i> (1',2' _a)	–	1.5 ^{f)}	1.5 ^{f)}	2.4	2.8	^{e)}	^{e)}
<i>J</i> (1',2' _b)	–	10.2 ^{f)}	8.1 ^{f)}	6.9	8.8	^{e)}	^{e)}
<i>J</i> (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 DQF-COSY and HSQC spectra. ^{d)} See *Exper. Part.* ^{e)} Not assigned. ^{f)} Can be interchanged. ^{g)} *J*(2'_a,2'_b).

MeCH_2CH_2); 21.14 (*q*, $\text{MeC}=\text{O}$); 14.48 (*q*, MeCH_2CH_2); 14.24 (*q*, $\text{Me}(\text{CH}_2)_6$); 9.84 (*q*, MeS). ESI-MS: 937.4 (100, $[M + H]^+$). Anal. calc. for $\text{C}_{56}\text{H}_{76}\text{N}_2\text{O}_8\text{S}$ (937.29): C 71.76, H 8.17, N 2.99; found: C 71.67, H 8.11, N 2.98.

Methyl (1S)-1-O-Acetyl-3,4,5,8-tetra-O-benzyl-7,9-dideoxy-1-C-heptyl-7-[(2S,4R)-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): 3346w (br.), 3030w, 2953w, 2924w, 2855w, 2785w, 1743m, 1681m, 1497m, 1453m, 1369w, 1304m, 1229m, 1122m, 1086s, 1027m, 946w, 910w, 822w, 787w, 731s, 695s. ^1H -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* ≈ 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 PhCH); 4.47 (br. *s*, PhCH₂); 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(CH₂)₅CH₂); 1.96 (*s*, MeS); 1.71 (*s*, AcO); 1.63–1.49 (*m*, 1 H of prolinyl); 1.35–1.02 (*m*, MeCH₂CH₂, Me(CH₂)₅CH₂); 0.92–0.82 (*m*, Me(CH₂)₆, MeCH₂CH₂). ¹³C-NMR (75 MHz, CDCl₃): 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 PhCH₂); 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*, MeCH₂CH₂); 31.70, 29.88, 29.25, 29.09, 26.51, 22.53 (6*t*, Me(CH₂)₆); 21.56 (*t*, MeCH₂CH₂); 20.53 (*q*, MeC=O); 14.17 (*q*, MeCH₂CH₂); 14.00 (*q*, Me(CH₂)₆); 9.28 (*q*, MeS). HR-ESI-MS: 959.5226 (17, [M + Na]⁺, C₅₆H₇₆N₂O₈S⁺; calc. 959.5215), 937.5394 (100, [M + H]⁺, C₅₆H₇₇N₂O₈S⁺; calc. 937.5395). Anal. calc. for C₅₆H₇₆N₂O₈S (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-[(2S,4R)-1-methyl-4-propylpyrrolidine-2-carboxamido]-3-thio-D-ribo-β-L-glucopyranoside (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. [α]_D²⁵ = +57.5 (*c* = 1.0, CHCl₃). 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*. ¹H-NMR (300 MHz, CDCl₃; 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 PhCH₂); 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*, MeCH₂CH₂); 0.92–0.85 (*m*, MeCH₂CH₂). ¹³C-NMR (75 MHz, CDCl₃; 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 PhCH₂); 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*, MeCH₂CH₂); 21.54 (*t*, MeCH₂CH₂); 14.26 (*q*, MeCH₂CH₂); 9.45 (*q*, MeS). ESI-MS: 939.4 (100, [M + Na]⁺). Anal. calc. for C₅₅H₆₈N₂O₈S (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-[(2S,4R)-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. [α]_D²⁵ = +33.4 (*c* = 0.51, CHCl₃). 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*. ¹H-NMR (400 MHz, CDCl₃; assignments based on a DQF-COSY 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 PhCH₂); 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*, MeCH₂CH₂); 0.78 (*t*, *J* = 6.6, MeCH₂CH₂). ¹³C-NMR (75 MHz, CDCl₃; 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 PhCH₂); 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*, MeCH₂CH₂); 21.67 (*t*, MeCH₂CH₂); 20.71 (*q*, MeC=O); 14.29 (*q*, MeCH₂CH₂); 9.66 (*q*, MeS). HR-ESI-MS: 981.4704 (100, [M + Na]⁺, C₅₇H₇₀N₂NaO₉S⁺; calc. 981.4694), 959.4884 (43, [M + H]⁺, C₅₇H₇₁N₂O₉S; calc. 959.4875).

Methyl 5,6,7,10-Tetra-O-benzyl-2,3,9,11-tetradecoxy-9-[(2S,4R)-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. [α]_D²⁵ = +17.7 (*c* = 1.0, CHCl₃). 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*. ¹H-NMR (300 MHz, CDCl₃; 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 PhCH₂); 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 , MeCH₂CH₂); 0.97–0.85 (m , MeCH₂CH₂). ¹³C-NMR (75 MHz, CDCl₃; 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 PhCH₂); 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 , MeCH₂CH₂); 21.74 (t , MeCH₂CH₂); 14.33 (q , MeCH₂CH₂); 9.36 (q , MeS). HR-ESI-MS: 820.4356 (100, $[M + H]^+$, C₄₀H₆₂N₃O₆S⁺; 820.4354).

Methyl {Methyl 5,6,7,10-Tetra-O-benzyl-2,3,9,11-tetradecoxy-9-[(2S,4R)-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. $[\alpha]_D^{25} = +23.95$ ($c = 1.0$, CHCl₃). IR (ATR): 3030w, 2925w, 2870w, 2781w, 1736m, 1670m, 1497m, 1453m, 1376w, 1304w, 1171w, 1086s, 1026m, 909m, 731s, 696s. ¹H-NMR (300 MHz, CDCl₃; 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 PhCH₂); 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 , MeCH₂CH₂); 0.92–0.86 (m , MeCH₂CH₂). ¹³C-NMR (75 MHz, CDCl₃; 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 PhCH₂); 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 , MeCH₂CH₂); 21.84 (t , MeCH₂CH₂); 14.56 (q , MeCH₂CH₂); 9.64 (q , MeS). ESI-MS: 853.1 (100, $[M + H]^+$). Anal. calc. for C₅₀H₆₄N₂O₈S (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). NH₃ 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-[(2S,4R)-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. $[\alpha]_D^{25} = +58.0$ ($c = 1.13$, CHCl₃). IR (ATR): 3321m (br.), 2958m, 2927m, 2872w, 2789w, 1646m, 1522m, 1454w, 1403w, 1379w, 1235w, 1076s, 945w, 863w, 750s, 701w, 664w. ¹H-NMR (300 MHz, CD₃OD; 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 , MeCH₂CH₂); 0.85 (br. $t, J = 6.9$, MeCH₂CH₂). ¹³C-NMR (75 MHz, CD₃OD; 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 , MeCH₂CH₂); 20.80 (t , MeCH₂CH₂); 13.45 (t , MeCH₂CH₂); 8.10 (q , MeS). ESI-MS: 437.23 (100, $[M + H]^+$).

Methyl (IR)-7,9-Dideoxy-1-C-heptyl-7-[(2S,4R)-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. $[\alpha]_D^{25} = +73.6$ ($c = 1.3$, CHCl₃). IR (ATR): 3334w (br.), 2956w, 2924m, 2855w, 2790w, 1645m, 1522m, 1455w, 1378w, 1303w, 1215w, 1077m, 1059s, 980w, 943w, 879w, 751s, 664w. ¹H-NMR (400 MHz, CD₃OD; assignments based on a DQF-COSY 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 , CH₂(CH₂)₅Me); 1.44–1.22 (m , MeCH₂CH₂, Me(CH₂)₅CH₂); 0.98–0.85 (m , Me(CH₂)₆, MeCH₂CH₂). ¹³C-NMR (100 MHz, CD₃OD; 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 , MeCH₂CH₂); 32.78, 31.59, 30.54, 30.46, 27.67, 23.47 (6t, Me(CH₂)₆); 22.45 (t , MeCH₂CH₂); 14.40 (q , MeCH₂CH₂); 14.16 (q , Me(CH₂)₆); 8.31 (q , MeS). HR-MALDI-MS: 573.2995 (6, $[M + K]^+$,

Table 10. Selected ^1H -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 ₃ C(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)}
<i>J</i> (2,3)	9.6	9.6	9.6	9.5	9.6	^{c)}	9.6
<i>J</i> (3,4)	3.0	3.3	3.9	3.4	3.3	1.8	3.3
<i>J</i> (4,5)	^{d)}	^{d)}	^{d)}	1.2	^{d)}	1.5	^{d)}
<i>J</i> (5,6)	8.7	5.7	6.6	6.0	^{c)}	6.0	6.6
<i>J</i> (6,7)	4.8	7.8	6.3	8.1	^{c)}	7.8	6.6
<i>J</i> (7,Me)	6.3	6.3	6.6	6.3	6.3	6.6	6.6
<i>J</i> (1',2' _a)	–	9.9 ^{e)}	10.5 ^{e)}	4.0	^{c)}	^{c)}	^{c)}
<i>J</i> (1',2' _b)	–	1.5 ^{e)}	1.5 ^{e)}	7.0	^{c)}	^{c)}	^{c)}
<i>J</i> (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 DQF-COSY and HSQC spectra. ^{b)} See *Exper. Part.* ^{c)} Not assigned. ^{d)} $J < 1.5$ Hz (line broadening). ^{e)} Assignments may be interchanged. ^{f)} $J(2'_a, 2'_b)$.

$\text{C}_{26}\text{H}_{50}\text{KN}_2\text{O}_7\text{S}^+$; calc. 573.2970), 557.3224 (29, $[\text{M} + \text{Na}]^+$, $\text{C}_{26}\text{H}_{50}\text{N}_2\text{NaO}_7\text{S}^+$; calc. 557.3231), 535.3403 (100, $[\text{M} + \text{H}]^+$, $\text{C}_{26}\text{H}_{51}\text{N}_2\text{O}_7\text{S}^+$; calc. 535.3411).

Methyl (1S)-7,9-Dideoxy-1-C-heptyl-3-[(2S,4R)-1-methyl-4-propylpyrrolidine-2-carboxamido]-2-thio-D-erythro-α-D-galacto-non-2-ulopyranoside (32b). According to *GP 10*, debenzoylation 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): 3330m (br.), 2955m, 2923m, 2854w, 2787w, 1645m, 1523m, 1455w, 1403w, 1378w, 1303w, 1232w, 1082s, 1059s, 996w, 945m, 908w, 893w, 875w, 793w, 753s, 725w, 702w, 663w, 636w. ^1H -NMR (300 MHz, CD_3OD ; assignments based on a DQF-COSY 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, $\text{Me}(\text{CH}_2)_5\text{CH}_2$); 1.40–1.22 (m, MeCH_2CH_2 , $\text{Me}(\text{CH}_2)_5\text{CH}_2$); 0.98–0.85 (m, $\text{Me}(\text{CH}_2)_6$, 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 (6t,

Me(CH₂)₆); 22.48 (*t*, MeCH₂CH₂); 14.44 (*t*, MeCH₂CH₂); 14.20 (*t*, Me(CH₂)₆); 10.14 (*q*, MeS). HR-MALDI-MS: 573.2949 (16, [*M* + K]⁺, C₂₆H₅₀KN₂O₇S⁺; calc. 573.2970), 557.3220 (59, [*M* + Na]⁺, C₂₆H₅₀N₂NaO₇S⁺; calc. 557.3231), 535.3400 (100, [*M* + H]⁺, C₂₆H₅₁N₂O₇S⁺; calc. 535.3411).

Methyl 8,10-Dideoxy-8-[(2S,4R)-1-methyl-4-propylpyrrolidine-2-carboxamido]-3-thio-D-ribo-β-L-glucopyranoside (38a). According to *GP 10*, debenzoylation 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. [*α*]_D²⁵ = +75.3 (*c* = 1.06, CHCl₃). 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*. ¹H-NMR (300 MHz, CD₃OD; 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*, MeCH₂CH₂); 0.92 (*t*, *J* = 6.0, MeCH₂CH₂). ¹³C-NMR (75 MHz, CD₃OD; 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*, MeCH₂CH₂); 22.59 (*t*, MeCH₂CH₂); 14.65 (*q*, MeCH₂CH₂); 9.11 (*q*, MeS). HR-MALDI-MS: 489.2252 (100, [*M* + Na]⁺, C₂₀H₃₈NaN₂O₇S⁺; calc. 489.2241); 467.2423 (100, [*M* + H]⁺, C₂₀H₃₉N₂O₇S⁺; calc. 467.2422).

Methyl 8,10-Dideoxy-8-[(2S,4R)-1-methyl-4-propylpyrrolidine-2-carboxamido]-3-thio-D-ribo-β-L-manno-dec-3-ulopyranoside (38b). According to *GP 10*, debenzoylation 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. [*α*]_D²⁵ = +75.3 (*c* = 1.06, CHCl₃). 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*. ¹H-NMR (400 MHz, CD₃OD; 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*, MeCH₂CH₂); 0.90 (*t*, *J* = 6.8, MeCH₂CH₂). ¹³C-NMR (100 MHz, CD₃OD; 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*, MeCH₂CH₂); 22.62 (*t*, MeCH₂CH₂); 14.69 (*q*, MeCH₂CH₂); 9.32 (*q*, MeS). HR-MALDI-MS: 489.2252 (100, [*M* + Na]⁺, C₂₀H₃₈NaN₂O₇S⁺; calc. 489.2241), 467.2423 (100, [*M* + H]⁺, C₂₀H₃₉N₂O₇S⁺; calc. 467.2422).

Methyl 2,3,9,11-Tetradecoxy-9-[(2S,4R)-1-methyl-4-propylpyrrolidine-2-carboxamido]-4-thio-D-erythro-α-D-galacto-undec-4-ulopyranosidonitrile (44). According to *GP 10*, debenzoylation 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. [*α*]_D²⁵ = +61.6 (*c* = 0.99, CHCl₃). 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*. ¹H-NMR (300 MHz, CD₃OD; 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, CH₂CH₂CN); 2.35 (*s*, MeN); 1.99–1.82 (*m*, 4 H of prolinyl, CH₂CH₂CN); 1.93 (*s*, MeS); 1.36–1.24 (*m*, MeCH₂CH₂); 0.92 (*t*, *J* = 6.6, MeCH₂CH₂). ¹³C-NMR (75 MHz, CD₃OD; 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*, MeCH₂CH₂); 22.55 (*t*, MeCH₂CH₂); 14.45 (*q*, MeCH₂CH₂); 8.75 (*q*, MeS). HR-MALDI-MS: 482.2300 (20, [*M* + Na]⁺, C₂₁H₃₇N₃NaO₆S⁺; calc. 482.2295), 460.2478 (100, [*M* + H]⁺, C₂₁H₃₈N₃O₆S⁺; calc. 460.2476).

Methyl 2,3,9,11-Tetradecoxy-9-[(2S,4R)-1-Methyl-4-propylpyrrolidine-2-carboxamido]-4-thio-D-erythro-α-D-galacto-undec-4-ulopyranosidonamide (47). According to *GP 10*, debenzoylation 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. [*α*]_D²⁵ = +28.8 (*c* = 1.0, CHCl₃). 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*. ¹H-NMR (300 MHz, CD₃OD): 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, CH₂CH₂CONH₂); 1.93 (*s*, MeS); 1.38–1.24 (*m*, MeCH₂CH₂); 0.90 (*t*, *J* = 6.9, MeCH₂CH₂). ¹³C-NMR (75 MHz, CD₃OD): 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*, MeCH₂CH₂); 22.35 (*t*, MeCH₂CH₂); 14.42

(*q*, MeCH₂CH₂); 8.77 (*q*, MeS). HR-MALDI-MS: 479.2422 (100, [*M* – NH₂ + H₂O]⁺, C₂₁H₃₈N₃O₇S⁺; calc. 479.2422).

(IR)-7-Azido-3,4,5,8-tetra-O-benzyl-1,2-O-carbonyl-7,9-dideoxy-1-C-heptyl-D-erythro- α -D-galactono-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 CH₂Cl₂ was washed with H₂O, sat. aq. NaHCO₃ soln., and brine, dried (MgSO₄), and evaporated. A soln. of the residue in CH₂Cl₂ (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 **39a** (38 mg, 73%). *R*_f (hexane/AcOEt 85:15) 0.48. [α]_D²⁵ = +74.8 (*c* = 1.0, CHCl₃). IR (ATR): 3031w, 2926w, 2857w, 2108m, 1810m, 1602w, 1560w, 1496w, 1453w, 1362w, 1266m, 1213m, 1094s, 1047s, 1026s, 914w, 849w, 733s, 695s. ¹H-NMR (300 MHz, CDCl₃; 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 PhCH₂); 4.25 (*dd*, *J* = 10.2, 3.9, irradi. at 4.12 → no NOE, H–C(1)); 4.12 (*d*, *J* = 9.9, irradi. 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 ¹H-NMR Chemical Shifts [ppm] and Coupling Constants [Hz], and ¹³C-NMR Chemical Shifts [ppm] of the Lincomsamine Derivatives **39a**, **39b**, **40a**, and **40b** in CDCl₃ (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 ₃ C(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
<i>J</i> (2,3)	9.6	9.9	9.7	9.9
<i>J</i> (3,4)	2.1	2.1	2.4	2.4
<i>J</i> (4,5)	0.9	^{d)}	1.1	1.2
<i>J</i> (5,6)	10.2	9.9	10.2	10.5
<i>J</i> (6,7)	3.0	2.4	2.7	2.9
<i>J</i> (7,Me)	6.3	6.6	6.3	6.5
<i>J</i> (1',2' _a)	10.2	8.7	7.4	8.6
<i>J</i> (1',2' _b)	3.9	6.6	5.6	2.4
<i>J</i> (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 DQF-COSY and HSQC spectra.

^{c)} See *Exper. Part*. ^{d)} Not assigned.

9 H) ($\text{Me}(\text{CH}_2)_6$); 0.85 (*t*, $J = 6.9$, $\text{Me}(\text{CH}_2)_6$). ^{13}C -NMR (75 MHz, CDCl_3 ; assignments based on a HSQC spectrum): see Table 11; additionally, 152.25 (*s*, $\text{C}=\text{O}$); 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*, $\text{Me}(\text{CH}_2)_6$); 14.05 (*q*, $\text{Me}(\text{CH}_2)_6$). HR-ESI-MS: 802.3473 (20, $[M + K]^+$, $\text{C}_{45}\text{H}_{53}\text{KN}_3\text{O}_8^+$; calc. 802.3464), 786.3733 (100, $[M + Na]^+$, $\text{C}_{45}\text{H}_{53}\text{N}_3\text{NaO}_8^+$; 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-galactono-2-ulopyranose (**39b**). A soln. of **28b** (50 mg, 0.065 mmol) in 7*N* 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 $\rightarrow$ 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*. ^1H -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, irradi. at 3.89 $\rightarrow$ NOE of 1.1%, $\text{H}-\text{C}(1)$); 3.89 (*d*, $J = 9.9$, irradi. at 4.19 $\rightarrow$ NOE of 3.8%, $\text{H}-\text{C}(3)$); 1.45–1.56 (*m*, $\text{Me}(\text{CH}_2)_6$); 0.88 (*t*, $J = 6.6$, $\text{Me}(\text{CH}_2)_6$). ^{13}C -NMR (75 MHz, CDCl_3 ; assignments based on a HSQC spectrum): see Table 11; additionally, 152.53 (*s*, $\text{C}=\text{O}$); 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*, $\text{Me}(\text{CH}_2)_6$); 14.08 (*q*, $\text{Me}(\text{CH}_2)_6$). HR-ESI-MS: 802.3475 (20, $[M + K]^+$, $\text{C}_{45}\text{H}_{53}\text{KN}_3\text{O}_8^+$; calc. 802.3464), 786.3735 (100, $[M + Na]^+$, $\text{C}_{45}\text{H}_{53}\text{N}_3\text{NaO}_8^+$; 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-ulopyranose (**40a**). A soln. of **33a** (80 mg, 0.10 mmol) in 7*N* 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 $\rightarrow$ 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*. ^1H -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 PhCH); 4.70 (*dd*, $J = 7.4$, 5.6, irradi. at 4.24 $\rightarrow$ no NOE, $\text{H}-\text{C}(2)$); 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 PhCH); 4.24 (*d*, $J = 9.7$, irradi. at 4.70 $\rightarrow$ no NOE, $\text{H}-\text{C}(4)$). ^{13}C -NMR (100 MHz, CDCl_3 ; assignments based on a HSQC spectrum): see Table 11; additionally, 189.16 (*s*, $\text{C}=\text{S}$); 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, $[M + K]^+$, $\text{C}_{46}\text{H}_{47}\text{KN}_3\text{O}_8\text{S}^+$; calc. 840.2715), 824.2974 (100, $[M + Na]^+$, $\text{C}_{46}\text{H}_{47}\text{N}_3\text{NaO}_8\text{S}^+$; calc. 824.2976).

8-Azido-1,4,5,6,9-penta-O-benzyl-8,10-dideoxy-2,3-O-(thiocarbonyl)-D-ribo- β -L-glucodec-3-ulopyranoside (**40b**). A soln. of **33b** (80 mg, 0.10 mmol) in 7*N* 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 $\rightarrow$ 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*. ^1H -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 PhCH); 4.66 (*dd*, $J = 8.6$, 2.4, irradi. at 4.10 $\rightarrow$ NOE of 3.0%, $\text{H}-\text{C}(2)$); 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 PhCH); 4.10 (*d*, $J = 9.9$, irradi. at 4.66 $\rightarrow$ NOE of 4.7%, $\text{H}-\text{C}(4)$). ^{13}C -NMR (100 MHz, CDCl_3 ; assignments based on a HSQC spectrum): see Table 11; additionally, 189.32 (*s*, $\text{C}=\text{S}$); 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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