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Synthesis of amino-substituted hexo- and heptopyranoses from D-galactose

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Abstract

After condensation of D-galactose with two equivalents of acetone, the last free hydroxy group was transformed into an acylated amino group by Swern oxidation, oxime formation, $LiAlH_4$ reduction and acylation. The intermediate aldehyde was homologated with the Wittig reagent, (methoxymethyl)triphenylphosphonium chloride, to afford, after careful hydrolysis, a homologous heptodialdo-1,5-pyranose. Condensation of the aldehyde with hydroxylamine and subsequent $LiAlH_4$ reduction provided a bis-*O*,*O*-isopropylidene-protected 7-amino-6,7-dideoxygalactoheptopyranose, which was acylated with various carboxylic acid derivatives. The isopropylidene protective groups were cleaved by careful hydrolysis or alcoholysis to yield 6-acylamino-6-deoxy-galactopyranoses and 7-acylamino-6,7-dideoxy-galactohepto-pyranoses.

Keywords: 6-Aminogalactopyranoses; 7-Aminoglactoheptopyranoses; Galactose; Homologation

1. Introduction

Monosaccharides with amino substituents in different ring positions are of interest as substructures of aminoglycoside antibiotics, e.g., kanamycin, gentamicin, or neomycin.[1] Moreover, pyranoses **1** with aminoalkyl substituents in position 5 will be used as starting compounds for the synthesis of selectively substituted tetrahydropyran derivatives **2** and bicyclic ring systems **3**.[2–4] In the literature only a few examples for 7-amino-7-deoxyheptopyranoses **1b** and **2b** ($n = 2$) are given.[5–7] The bicyclo[3.3.1]nonane derivative **3b** ($n = 2$) reveals structural similarity to the morphan ring system, which itself represents a substructure of the opioid analgesic morphine.[8] Following the strategy of modifying monosaccharides allows the stereoselective introduction of various substituents in different ring positions with defined stereochemistry in **2** and **3**.[9,10] The products **2** and **3** should be developed as novel ligands for receptors within the central nervous system, in particular for the class of opioid receptors.[10] (Fig. 1)

This communication deals with the synthesis of novel 6-amino-6-deoxyhexopyranoses (**1a**) ($n = 1$) and 7-amino-6,7-dideoxyheptopyranoses (**1b**) ($n = 2$), which are derived from the monosaccharide, D-galactose (**4**).

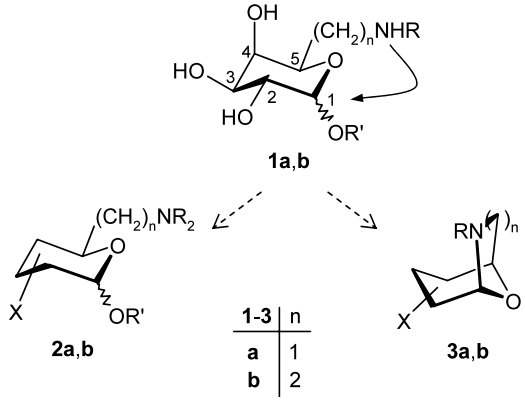

Fig. 1. Conversion of 6- or 7-amino-6- or 7-deoxy-D-*galacto*-hexo- and heptopyranoses to selectively substituted tetrahydropyrans.

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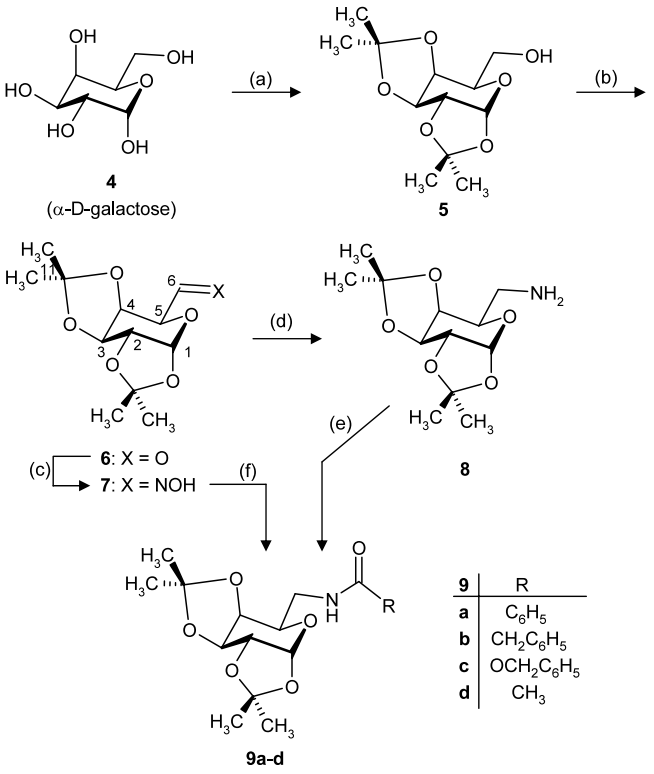


Scheme 1. Reagents and reaction conditions: (a) lit.[11]; (b) Me_2SO, $(COCl)_2$, Et_3N, CH_2Cl_2, −70 °C, 67%; (c) $H_2NOH\cdot HCl$, NaOAc, CH_3OH, rt, 76%; (d) $LiAlH_4$, Et_2O, rt, 69%; (e) RCOCl, Et_3N, CH_2Cl_2, rt, **9a**: 76%; **9b**: 85%; **9c**: 69%; (f) H_2, Raney Ni, Ac_2O, NaOAc, 70 bar, 80 °C, **9d**: 64%.

2. Results and discussion

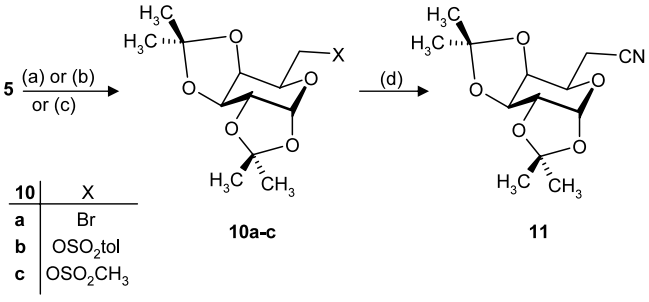
According to a literature report[11] D-galactopyranose (**4**) has been transformed with acetone, $CuSO_4$ and a catalytic amount of H_2SO_4 into the bisacetonide **5**. Swern oxidation of the bisacetonide **5** provided the aldehyde **6**,[12] which reacted with hydroxylamine to give the oxime **7**.[13] The 6-amino-6-deoxygalactopyranose derivative **8** was obtained by $LiAlH_4$ reduction of the oxime **7**. Subsequent acylation of the primary amine **8** with various carboxylic acid chlorides gave the amides **9a**–**c** in good yield. Alternatively the oxime **7** was reduced with H_2 (70 bar) and Raney nickel in the solvent, acetic anhydride, leading directly to the acetamide **9d** in 64% yield (Scheme 1).

The initial plan for the synthesis of 7-amino-6,7-dideoxy-heptopyranoses scheduled homologation of a hexopyranose derivative by introduction of a cyano group. For this purpose the free hydroxy group of **5** was activated for nucleophilic substitution. The bromide **10a** was prepared by an Appel reaction[14] of the alcohol **5** with triphenylphosphane and tetrabromomethane. The sulfonates **10b**[13,15] and **10c** were available by reaction of the alcohol **5** with *p*-toluenesulfonyl chloride and methanesulfonyl chloride, respectively. However, the reaction of **10a**–**c** with NaCN failed to give the nitrile **11**. Several modifications were investigated including variation of the CN^- source (LiCN, NaCN, KCN, TMS-CN, KCN and 18-crown-6), the CN^--amount (1 to 30 equivalents), the solvent (e.g., acetone, acetonitrile, DMF, Me_2SO, triethyleneglycol) and the reaction temperature (up to 200 °C). Finally, the isolation of a small amount of the nitrile **11** (4.2% yield) succeeded after heating the methanesulfonate **10c** with LiCN in DMF for 17 h. Obviously the nucleophilic substitution at the methylene group of **10a**–**c** is impeded by branching in the β-position. (Scheme 2)

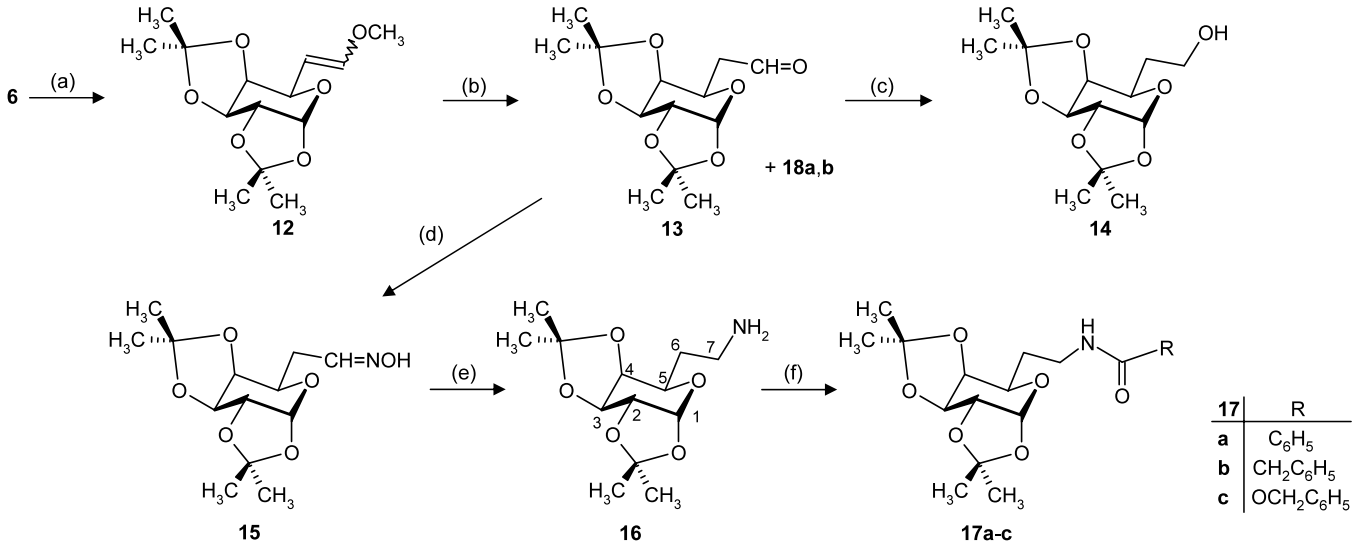
The next homologation was performed by a Wittig reaction. The aldehyde **6** was condensed with (methoxymethyl)triphenylphosphonium chloride ($Ph_3PCH_2OCH_3Cl$)[16,17] and potassium *tert*-butoxide (KO^tBu) to afford the diastereomeric enolethers (*Z*)-**12** and (*E*)-**12**[16] in the ratio 63:37. The aldehyde **13** was obtained in 90% yield after careful hydrolysis of the diastereomeric enolethers **12** with HCl in acetone. In contrast to literature reports,[16,17] addition of toxic $Hg(OAc)_2$ was not necessary. However, the formation of small amounts of the hemiacetals **18a**,**b** could not be completely suppressed even under very mild hydrolysis conditions (Scheme 3) (compare Scheme 4).

$NaBH_4$ reduction of the aldehyde **13** provided the bis-*O*-isopropylidene protected galactoheptopyranose derivative **14**. Condensation of **13** with hydroxylamine yielded the oxime **15**, which was reduced with $LiAlH_4$ to furnish the primary amine **16**. Acylation of the primary amine with different acyl chlorides afforded the amides **17a**–**c** in 72–79% yield.

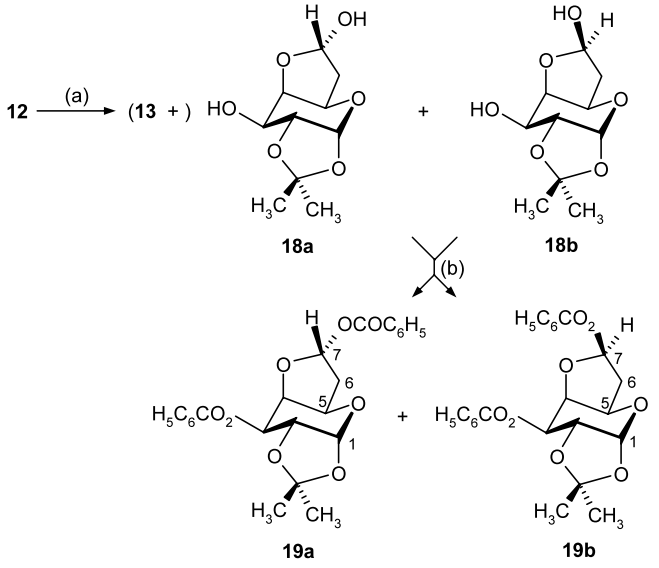
During hydrolysis of the diastereomeric enolethers **12**, formation of side products, which resulted from additional hydrolysis of the adjacent acetonide protective group, could not be completely avoided. In order to elucidate the structure of these side products, hydrolysis was performed under severe hydrolysis conditions: 2 N H_2SO_4 in acetone for 75 min at reflux temperature. Since complete purification of the hydrolysis products **18a**,**b** failed, and the product contained two isomers according to the ^1H NMR spectrum, the crude product



Scheme 2. Reagents and reaction conditions: (a) CBr_4, PPh_3, CH_2Cl_2, −60 °C, 11%; (b) *p*-TsCl, pyridine, rt, 94%; (c) MsCl, pyridine, rt, 81%; (d) **10c**, LiCN, DMF, 110 °C, 4.2%.



Scheme 3. Reagents and reaction conditions: (a) $CH_3OCH_2PPh_3Cl$, KO^{t}Bu, THF, −78 °C, 63%; (b) Me_2CO, 2 N HCl, rt, 95%; (c) $NaBH_4$, EtOH, rt, 63%; (d) $H_2NOH \cdot HCl$, NaOAc, CH_3OH, rt, 63%; (e) $LiAlH_4$, Et_2O, rt, 46%; (f) RCOCl, Et_3N, CH_2Cl_2, rt, **17a**: 72%; **17b**: 79%; **17c**: 78%.



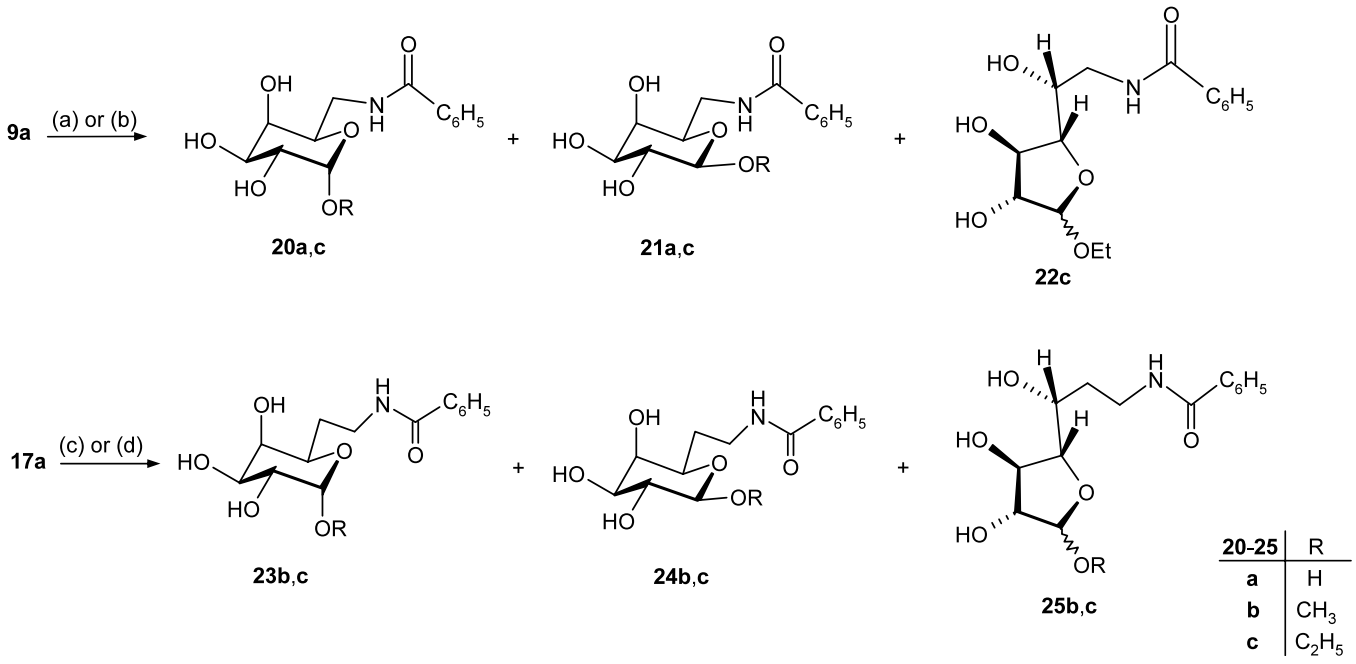
Scheme 4. Reagents and reaction conditions: (a) Me_2CO, 2 N H_2SO_4, 56 °C; (b) C_6H_5COCl, Et_3N, DMAP, CH_2Cl_2, rt, **19a**: 24%; **19b**: 47%.

was acylated with an excess of benzoyl chloride. Separation of the resulting isomeric dibenzoates **19a** and **19b** was accomplished by flash chromatography to obtain **19a** and **19b** in 24 and 47% yield, respectively.

According to the ^{1}H NMR spectra, a new five-membered acetalic moiety has been formed. We presume that the configuration of the new stereogenic center in position 7 of **19a** and **19b** is *R* and *S*, respectively. The ^{1}H NMR spectra of both diastereomers display similar doublets for the protons in position 7 (**19a**: d, $J_{6,7}$ 4.4.Hz; **19b**: d, $J_{6,7}$ 5.9 Hz), indicating coupling of 7-H with only one proton in position 6. However, the spectra of **19a** and **19b** differ significantly in the signal structure of the other 6-H revealing no coupling with 7-H: in the spectrum of **19a**, a large coupling constant between 6-H and 5-H ($J_{5,6}$ 8.1 Hz) is observed, whereas no coupling ($J_{5,6}$ 0 Hz) of these protons is seen for the diastereomer **19b**. These spectroscopic data are in accordance with the (7*R*)- and (7*S*)-configuration for **19a** and **19b**, respectively.

Hydrolysis of the 6-benzoylamino-6-deoxy-hexopyranose (**9a**) furnished a 1:1 mixture of the anomeric hemiacetals **20a** and **21a** in 79.3% yield. Cleavage of the *O*-isopropylidene protective groups of **9a** in ethanol in the presence of a strong acidic ion-exchange resin led to the ethyl glycosides **20c**, **21c** and **22c**. Whereas the α-anomer of the ethyl pyranoside **20c** could be isolated in 23.6%, yield the β-anomer **21c** and the ring-contracted diastereomeric furanoside **22c** could not be separated. Flash chromatography yielded a mixture of **21c** and **22c** (37.6%), which contained predominantly the furanosides **22c** (**21c**:**22c** = 18:82). (Scheme 5)

Similar observations were made during alcoholysis of the corresponding 7-benzoylamino-6,7-dideoxyheptopyranose (**17a**). Heating of **17a** with methanol and an acidic ion-exchange resin provided the methyl acetals **23b**, **24b** and **25b**. Flash chromatography yielded the α-anomeric methyl heptopyranoside **23b** (19.8%) and a small amount of the corresponding β-anomer **24b** (4.9%). However, an anomeric mixture of the methyl heptofuranoside **25b** (α-**25b**:β-**25b** = 65:35) was isolated as main product (67.7%). The corresponding ethyl glycosides were prepared in an analogous manner by heating of **17a** with ethanol and an acidic ion-exchange resin. Whereas the α-anomer **23c** was isolated in 25.5% yield, the β-anomer **24c** could not be separated from the



Scheme 5. Reagents and reaction conditions: (a) strong acidic ion-exchange resin, H_2O, 100 °C, 79%; (b) strong acidic ion-exchange resin, EtOH, 78 °C, **20c**: 24%; **21c**, **22c**: 38%; (c) strong acidic ion-exchange resin, CH_3OH, 65 °C, **23b**: 20%; **24b**: 4.9%; **25b**: 68%; (d) strong acidic ion-exchange resin, EtOH, 78 °C, **23c**: 26%; **24c**, **25c**: 74%.

ethyl heptofuranoside **25c**. Thus, a mixture of **24c** and **25c** (**24c**:**25c** = 10:90) was obtained in 73.6% yield.

In summary, the synthesis of various 6-amino substituted hexopyranoses **8**, **9a**–**d** and 7-amino-substituted heptopyranoses **16**, **17a**–**c** starting from α-D-galactose is presented. Preliminary investigations demonstrate, that removal of the *O*,*O*-isopropylidene protective groups succeeds with water, methanol and ethanol to afford the corresponding deprotected monosaccharides **20**–**25**. The described amino substituted hexo- and heptopyranose derivatives should allow the regio- and stereoselective introduction of pharmacophoric substituents into the pyran moiety (compare lead structure **2**) and the construction of novel morphan analogues (compare lead structure **3**).

3. Experimental

3.1. General methods

Unless otherwise noted, moisture-sensitive reactions were conducted under dry nitrogen. Thin-layer chromatography (TLC) was carried out on silica gel 60 F_{254} plates (E. Merck), and flash chromatography (FC)[18] on silica gel 60, 0.040–0.063 mm (E. Merck); parentheses include diameter of the column (cm), eluent, fraction size (mL), and R_f. Melting points (mp) were determined on a melting point apparatus of Dr Tottoli (Büchi), and the mps are uncorrected. Optical rotations were measured on a Perkin–Elmer model 241 spectropolarimeter using a 1.0-dm tube; concentration *c* (g/100 mL); temperature 20 °C. Elemental analyses (CHN) were determined on a Rapid (Heraeus) and on a Perkin–Elmer Elemental Analyzer, model 240. Mass spectra were measured on a Hewlett–Packard 5989A instrument in either the electron-impact (EI) or chemical-ionization (CI) mode. FTIR spectra were determined on Perkin–Elmer model 1600 and 2000 FTIR instruments. ^{1}H NMR (400 MHz) were determined on GSX FT NMR spectrometer (JEOL) using TMS as the internal standard δ-values (in ppm) and coupling constants (in Hz) are given with 0.5 Hz resolution.

3.2. (−)-1,2:3,4-Di-*O*-isopropylidene-α-D-galactodialdo-1,5-pyranose (6)[12]

A solution of oxalyl chloride (23.6 g, 185.4 mmol) in THF (15 mL) and CH_2Cl_2 (20 mL) was cooled to −70 °C. Then, a solution of Me_2SO (29.0 g, 370.8 mmol) in CH_2Cl_2 (20 mL) was slowly added at −70 °C, and the mixture was stirred for 10 min at −70 °C. A solution of **5** (20.0 g, 76.9 mmol) in CH_2Cl_2 (20 mL) was added within 5 min, and the mixture was stirred for 10 min at −60 °C. The mixture was cooled to −70 °C, and a solution of Et_3N (75.0 g, 741.6 mmol) in CH_2Cl_2 (20 mL) was added within 15 min. After stirring at −60 °C for 30 min, the reaction mixture was warmed to room temperature (rt) and H_2O (100 mL) was added. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 100 mL). The organic extracts were dried (Na_2SO_4), the solvent was evapo-

rated in vacuo, and the residue was purified by FC (8 cm, 70:30 petroleum ether–EtOAc, fractions 50 mL). Colorless oil, yield 12.9 g (67%), lit.[12] 82%; $[\alpha]_D$ −131.3° (*c* 1.13, $CHCl_3$); lit.[13] $[\alpha]_D$ −131° (*c* 0.9, $CHCl_3$).

3.3. 1,2:3,4-Di-*O*-isopropylidene-α-D-galactodialdo-1,5-pyranose-6-oxime (7)[13]

A solution of **6** (1.65 g, 6.35 mmol), $NH_2OH \cdot HCl$ (1.32 g, 19.1 mmol), NaOAc (0.825 g, 13.2 mmol) in H_2O (8.25 mL) and CH_3OH (80 mL) was stirred at rt for 24 h. The mixture was concentrated in vacuo, and the residual aqueous layer was extracted with Et_2O (2 × 60 mL). The concentrated Et_2O layer (50 mL) was extracted with 1 M NaOH (3 × 50 mL), then 1 N HCl (pH 4–5) was added to the NaOH layer, and the aqueous layer was extracted with Et_2O (3 × 70 mL). The Et_2O layer was dried ($MgSO_4$), concentrated in vacuo and the residual solid was recrystalized. Colorless solid (2-Pr_2O), mp 114–115 °C, lit.[13] mp 107–108 °C, yield 1.31 g (76%), lit.[13] 66%. The ratio of (*E*)-**7**:(*Z*)-**7** varied in the range from 1:1 to 2:1.

3.4. (−)-6-Amino-6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (8)

A mixture of **7** (1.95 g, 7.14 mmol), $LiAlH_4$ (0.74 g, 20 mmol) and Et_2O (17 mL) was stirred for 2 h at rt. A small amount of H_2O was carefully added. Then, $MgSO_4$ was added, the mixture was filtered, and the filtrate was concentrated in vacuo. The residue was purified by FC [3 cm, fractions 15 mL, at first the solvent was 96:4 CH_2Cl_2–CH_3OH (225 mL)], then 90:10 CH_2Cl_2–CH_3OH (200 mL), R_f 0.16 96:4 (CH_2Cl_2–CH_3OH). Colorless oil, yield 1.27 g (69%); $[\alpha]_D$ −53.1° (*c* 1.03, $CHCl_3$); IR (film): $\nu = 3676$ (NH), 3378 (NH), 1383 (C–N), 1256 (C–O), 1212 (C–O), 1168 (C–O); 1069 cm^{-1} (C–O); ^1H NMR ($CDCl_3$): δ 1.27 (s, 6 H, CH_3), 1.39 (s, 3 H, CH_3), 1.47 (s, 3 H, CH_3), 1.89 (s, broad, 2 H, NH_2), 2.80 (dd, *J* 13.2/5.1 Hz, 1 H, CH_2NH$_2$), 2.93 (dd, *J* 13.2/8.1 Hz, 1 H, CH_2NH$_2$), 3.67 (ddd, *J* 8.8/5.1/1.5 Hz, 1 H, 5-H), 4.17 (dd, *J* 8.1/1.5 Hz, 1 H, 4-H), 4.26 (dd, *J* 5.1/2.2 Hz, 1 H, 2-H), 4.54 (dd, *J* 8.1/2.2 Hz, 1 H, 3-H), 5.50 (d, *J* 5.1 Hz, 1 H, 1-H); ^{13}C NMR ($CDCl_3$): δ 24.29 (CH_3), 24.88 (CH_3), 25.92 (CH_3), 26.01 (CH_3), 42.09 (CH_2), 69.06 (C-5), 70.32 (C-3), 70.74 (C-4), 71.71 (C-2), 96.33 (C-1), 108.46 [*C*(CH_3)$_2$], 109.19 [*C*(CH_3)$_2$]; CIMS: *m*/*z* 260 (MH^+), 244 ($M^+ - CH_3$); Anal. Calcd for $C_{12}H_{21}NO_5$ (259.2): C, 55.6; H, 8.17; N, 5.40. Found: C, 55.3; H, 8.24; N, 5.38.

Data for **8**·HCl: colorless solid (EtOAc), mp 215 °C; $[\alpha]_D$ −50.1° (*c* 1.06, CH_3OH); IR (KBr): $\nu = 3172$ (broad, NH_3^+), 1599 (NH_3^+), 1257 (C–O), 1215 (C–O), 1168 (C–O), 1060 cm^{-1} (C–O); ^1H NMR (CD_3OD): δ 1.32 (s, 3 H, CH_3), 1.32 (s, 3 H, CH_3), 1.44 (s, 3 H, CH_3), 1.65 (s, 3 H, CH_3), 3.22–3.29 (m, 2 H, CH_2), 4.20 (m, 1 H, 5-H), 4.25 (d, *J* 8.1 Hz, 1 H, 4-H), 4.35 (dd, *J* 5.1/2.2 Hz, 1 H, 2-H), 4.63 (dd, *J* 8.1/2.2 Hz, 1 H, 3-H), 5.58 (d, *J* 5.1 Hz, 1 H, 1-H), 8.34 (s, broad, 3 H, NH_3^+); EIMS: *m*/*z* 260 ($M^+ - Cl$); Anal. Calcd for $C_{12}H_{22}ClNO_5$ (295.8): C, 48.8; H, 7.50; N, 4.73. Found: C, 48.6; H, 7.42; N, 4.45.

3.5. (−)-6-Benzoylamino-6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactoyranose (9a)

A solution of **8** (9.31 g, 35.9 mmol), Et_3N (4.72 g, 46.7 mmol) and benzoyl chloride (6.56 g, 46.7 mmol) in CH_2Cl_2 (50 mL) was stirred for 30 min at rt. The organic layer was washed with 1 N HCl (3 × 50 mL), and a satd solution of $NaHCO_3$ (3 × 50 mL), dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by FC (8 cm, 70:30 petroleum ether–EtOAc fractions 50 mL, R_f 0.24). Colorless solid (2-Pr_2O), mp 132 °C, yield 9.86 g (76%); $[\alpha]_D$ −39.7° (*c* 1.02, $CHCl_3$); IR (KBr): $\nu =$ 3354 (N–H), 1646 (C=O), 1525 (amide-II), 1254 (C–O), 1215 (C–O), 1159 (C–O), 1071 cm^{-1} (C–O); ^1H NMR ($CDCl_3$): δ 17 (s, 3 H, CH_3), 1.22 (s, 3 H, CH_3), 1.33 (s, 3 H, CH_3), 1.34 (s, 3 H, CH_3), 3.27 (ddd, *J* 13.9/4.4/3.7 Hz, 1 H, CH_2NHCO), 3.83 (ddd, *J* 13.9/8.1/3.7 Hz, 1 H, CH_2NHCO), 3.89 (ddd, *J* 8.8/4.4/2.2 Hz, 1 H, 5-H), 4.14 (dd, *J* 8.1/2.2 Hz, 1 H, 4-H), 4.18 (dd, *J* 5.1/2.2 Hz, 1 H, 2-H), 4.49 (dd, *J* 8.1/2.2 Hz, 1 H, 3-H), 5.40 (d, *J* 5.1 Hz, 1 H, 1-H), 6.47 (t, *J* 3.7 Hz, 1 H, NH), 7.28 (t, *J* 7.3 Hz, 2 H, H-arom.), 7.33–7.37 (m, 1 H, H-arom.), 7.61 (d, *J* 7.3 Hz, 2 H, H-arom.); CIMS: *m*/*z* 364 (MH^+), 348 ($M^+ - CH_3$); Anal. Calcd for $C_{19}H_{25}NO_6$ (363.4): C, 62.8; H, 6.93; N, 3.85. Found: C, 62.7; H, 7.08; N, 3.81.

3.6. (−)-6-Deoxy-1,2:3,4-di-*O*-isopropylidene-6-(phenylacetylamino)-α-D-galactopyranose (9b)

A solution of **8** (0.42 g, 1.62 mmol), Et_3N (0.20 g, 1.94 mmol) and phenylacetyl chloride (0.30 g, 1.94 mmol) in CH_2Cl_2 (10 mL) was stirred for 30 min at rt. The mixture was washed with 1 N HCl (2 × 5 mL), and a satd solution of $NaHCO_3$ (3 × 5 mL), dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by FC (2 cm, 90:10 petroleum ether–EtOAc, R_f 0.06, then 75:25 petroleum ether–EtOAc fractions 13–15 mL, R_f 0.15). Colorless solid (2-Pr_2O), mp 72 °C, yield 520 mg (85%); $[\alpha]_D$ −17.2° (*c* 0.97, $CHCl_3$); IR (KBr): $\nu = 3323$ (N–H), 1644 (C=O), 1556 (amide-II), 1253 (C–O), 1212 (C–O), 1167 (C–O), 1069 cm^{-1} (C–O); ^1H NMR ($CDCl_3$): δ 1.23 (s, 3 H, CH_3), 1.25 (s, 3 H, CH_3), 1.32 (s, 3 H, CH_3), 1.38 (s, 3 H, CH_3), 3.08 (ddd, *J* 13.2/4.4/3.7 Hz, 1 H, CH_2NHCO), 3.49 (s, 2 H, phenyl–CH_2), 3.63 (ddd, *J* 13.2/8.1/3.7 Hz, 1 H, CH_2NHCO), 3.79 (ddd, *J* 8.1/5.1/1.5 Hz, 1 H, 5-H), 4.07 (dd, *J* 8.1/1.5 Hz, 1 H, 4-H), 4.20 (dd, *J* 4.7/2.2 Hz, 1 H, 2-H), 4.49 (dd, *J* 8.1/2.2 Hz, 1 H, 3-H), 5.38 (d, *J* 5.1 Hz, 1 H,

1-H), 5.80 (t, *J* 3.7 Hz, 1 H, NH), 7.19–7.29 (m, 5 H, H-arom.); CIMS: *m/z* 378 (MH^+), 362 ($M^+ - CH_3$); Anal. Calcd for $C_{20}H_{27}NO_6$ (377.4): C, 63.6; H, 7.21; N, 3.71. Found: C, 63.7; H, 7.18; N, 3.67.

3.7. (−)-6-(Benzyloxycarbonylamino)-6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (9c)

A solution of **8** (1.00 g, 3.86 mmol), Et_3N (0.78 g, 7.72 mmol) and benzyl chloroformate (0.99 g, 5.79 mmol) in CH_2Cl_2 (20 mL) was stirred for 19 h at rt. The mixture was washed with 1 N HCl (3 × 10 mL) and a satd solution of $NaHCO_3$ (3 × 10 mL), dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by FC (3 cm, 90:10 petroleum ether–EtOAc, R_f 0.21, then 70:30 petroleum ether–EtOAc, R_f 0.39 fractions 20 mL). Colorless oil, yield 1.05 g (69%); $[\alpha]_D$ −30.3° (*c* 0.96, $CHCl_3$); IR (film): $\nu = 3384$ (N–H), 1723 (C=O), 1526 (amide-II), 1254 (C–O), 1211 (C–O), 1071 (C–O), 1011 cm^{-1} (C–O); ^1H NMR ($CDCl_3$): δ 1.38 (s, 3 H, CH_3), 1.46 (s, 3 H, CH_3), 1.49 (s, 3 H, CH_3), 1.52 (s, 3 H, CH_3), 3.37 (ddd, *J* 12.5/5.9/3.7 Hz, 1 H, CH_2NH), 3.56 (ddd, *J* 12.9/8.1/3.7 Hz, 1 H, CH_2NH), 3.97 (ddd, *J* 7.7/5.9/1.5 Hz, 1 H, 5-H), 4.25 (dd, *J* 8.1/1.5 Hz, 1 H, 4-H), 4.35 (dd, *J* 5.1/2.2 Hz, 1 H, 2-H), 4.65 (dd, *J* 8.1/2.2 Hz, 1 H, 3-H), 5.12–5.19 (m, 3 H, CH_2Ph, NH), 5.55 (d, *J* 5.1 Hz, 1 H, 1-H), 7.31–7.41 (m, 5 H, arom.); CIMS: *m/z* 394 (MH^+), 378 ($M^+ - CH_3$); Anal. Calcd for $C_{20}H_{27}NO_7$ (393.4): C, 61.0; H, 6.92; N, 3.56. Found: C, 61.2; H, 7.14; N, 3.39.

3.8. (−)-6-(Acetylamino)-6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (9d)

NaOAc (9.3 mg, 0.11 mmol) and Raney Ni (15.6 mg) were added to a solution of **7** (90 mg, 0.33 mmol) in Ac_2O (0.25 mL, 0.27 g, 2.01 mmol). The mixture was hydrogenated with 70 bar of H_2 pressure at 80 °C for 16 h. It was filtered, and the filtrate was concentrated in vacuo. The residue was dissolved in CH_2Cl_2 (5 mL), and the solution was washed with 1 N HCl (3 × 5 mL) and a satd solution of $NaHCO_3$ (3 × 5 mL), dried ($MgSO_4$) and concentrated in vacuo. Colorless oil, yield 63 mg (64%), R_f 0.24 (75:25 petroleum ether–EtOAc); $[\alpha]_D$ −27.3° (*c* 1.03, $CHCl_3$); IR (film): $\nu = 3318$ (N–H), 1654 (C=O), 1542 (amide-II), 1256 (C–O), 1213 (C–O), 1167 (C–O), 1069 cm^{-1} (C–O); ^1H NMR ($CDCl_3$): δ 1.26 (s, 3 H, CH_3), 1.27 (s, 3 H, CH_3), 1.38 (s, 3 H, CH_3), 1.42 (s, 3 H, CH_3), 1.94 (s, 3 H, CH_3–C=O), 3.12 (ddd, *J* 13.9/9.5/3.7 Hz, 1 H, CH_2), 3.67 (ddd, *J* 13.9/8.1/3.7 Hz, 1 H, CH_2), 3.83 (ddd, *J* 9.5/7.3/1.5 Hz, 1 H, 5-H), 4.15 (dd, *J* 7.7/1.5 Hz, 1 H, 4-H), 4.25 (dd, *J* 5.1/2.9 Hz, 1 H, 2-H), 4.53 (dd, *J* 8.1/2.2 Hz, 1 H, 3-H), 5.45 (d, *J* 5.1 Hz, 1 H, 1-H), 6.08 (t, *J* 3.7 Hz, 1 H, NH); CIMS: *m/z* 302 (MH^+), 286 ($M^+ - CH_3$); Anal. Calcd for $C_{14}H_{23}NO_6$ (301.3): C, 55.8; H, 7.69; N, 4.65. Found: C, 55.6; H, 7.9; N, 4.87.

3.9. (−)-6-Bromo-6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (10a)

Under N_2 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**5**) (3.50 g, 11.5 mmol) and CBr_4 (3.81 g, 11.5 mmol) were dissolved in CH_2Cl_2 (15 mL). The solution was cooled to −60 °C. Then, a solution of PPh_3 (3.01 g, 11.5 mmol) in CH_2Cl_2 (15 mL) was added, and the mixture was stirred for 2 h at −60 °C and 24 h at rt. The solvent was evaporated in vacuo, and the residue was purified by FC (5 cm, 75:25 petroleum ether–EtOAc, fractions 20 mL, R_f 0.10). Colorless solid, mp 46 °C, yield 400 mg (11%); $[\alpha]_D$ −49.3° (*c* 1.01, $CHCl_3$); IR (KBr): $\nu = 1255$ (C–O), 1212 (C–O), 1165 (C–O), 1070 cm^{-1} (C–O); ^1H NMR ($CDCl_3$): δ 1.34 (s, 3 H, CH_3), 1.36 (s, 3 H, CH_3), 1.45 (s, 3 H, CH_3), 1.55 (s, 3 H, CH_3), 3.42 (dd, *J* 10.3/6.6 Hz, 1 H, –CH_2Br), 3.52 (dd, *J* 10.3/6.6 Hz, 1 H, –CH_2Br), 3.97 (td, *J* 6.6/1.5 Hz, 1 H, 5-H), 4.32 (dd, *J* 5.1/2.2 Hz, 1 H, 2-H), 4.38 (dd, *J* 8.1/1.5 Hz, 1 H, 4-H), 4.64 (dd, *J* 8.1/2.2 Hz, 1 H, 3-H), 5.54 (d, *J* 5.1 Hz, 1 H, 1-H); ^{13}C NMR ($CDCl_3$): δ 24.42 (CH_3), 24.86 (CH_3), 25.90 (CH_3), 25.99 (CH_3), 29.69 (*C*H_2Br), 68.37 (C-3), 70.47 (C-4), 70.87 (C-5), 71.00 (C-2), 96.59 (C-1), 108.86 [*C*(CH_3)$_2$], 109.55 [*C*(CH_3)$_2$]; CIMS: *m/z* 325, 323 (MH^+); Anal. Calcd for $C_{12}H_{19}BrO_5$ (323.1): C, 44.6; H, 5.93. Found: C, 44.8; H, 5.83.

3.10. (−)-1,2:3,4-Di-*O*-isopropylidene-6-*O*-(4-methylphenylsulfonyl)-α-D-galactopyranose (10b)[13,15]

At 0 °C a solution of **2** (2.00 g, 7.69 mmol) in Py (5 mL) was added dropwise to a solution of *p*-TsCl (4.40 g, 23.07 mmol) in Py (5 mL). The reaction mixture was stirred for 12 h at rt and for 2 h at 60 °C. Then water (20 mL) and Et_2O (20 mL) were added, and the aqueous layer was separated and extracted with Et_2O (2 × 20 mL). The organic layer was dried ($MgSO_4$) and evaporated in vacuo. Colorless solid (2-Pr_2O), mp 88–89 °C, lit.[15] mp 87–89 °C, yield 3.00 g (94%), lit.[15] 87%.

3.11. (−)-1,2:3,4-Di-*O*-isopropylidene-6-*O*-(4-methylsulfonyl)-α-D-galactopyranose (10c)

A solution of **2** (2.00 g, 7.69 mmol) in Py (5 mL) was slowly added at 0 °C to a solution of CH_3SO_2Cl (1.76 g, 15.4 mmol) in Py (5 mL). After stirring for 12 h at rt, water (20 mL) and Et_2O (20 mL) were added. The aqueous layer was separated and extracted with Et_2O (2 × 20 mL). The Et_2O layer was dried ($MgSO_4$) and concentrated in vacuo. Colorless solid (2-Pr_2O), mp 118 °C, yield 2.10 g (81%), R_f 0.35 (75:25 petroleum ether–EtOAc); $[\alpha]_D$ −117.1° (*c* 0.99, $CHCl_3$); IR (KBr): $\nu = 1348$ (R–SO_2OR'), 1239 (C–O), 1216 (C–O), 1174

(R–SO_2OR'), 1163 (C–O), 1075 cm^{-1} (C–O); ^1H NMR ($CDCl_3$): δ 1.33 (s, 6 H, CH_3), 1.49 (s, 3 H, CH_3), 1.58 (s, 3 H, CH_3), 3.08 (s, 3 H, –O–SO_2–CH_3), 4.11 (ddd, *J* 6.6/5.1/1.5 Hz, 1 H, 5-H), 4.24 (dd, *J* 8.1/1.5 Hz, 1 H, 4-H), 4.35 (dd, *J* 5.1/2.6 Hz, 1 H, 2-H), 4.36–4.40 (m, 2 H, –CH_2–O–SO_2), 4.64 (dd, *J* 8.1/2.6 Hz, 1 H, 3-H), 5.54 (d, *J* 5.1 Hz, 1 H, 1-H); ^{13}C NMR ($CDCl_3$): δ 24.33 (CH_3), 24.84 (CH_3), 25.87 (CH_3), 25.90 (CH_3), 37.86 (CH_3SO_3), 66.28 (C-5), 69.05 (C-3), 69.06 (CH_2OSO_2–), 70.34 (C-4), 70.58 (C-2), 96.15 (C-1), 108.99 [$C(CH_3)_2$], 109.79 [$C(CH_3)_2$]; CIMS: *m*/*z* 339 (MH^+), 323 ($M^+ - CH_3$); Anal. Calcd for $C_{13}H_{22}O_8S$ (338.4): C, 46.1; H, 6.55. Found: C, 46.1; H, 6.59.

3.12. (−)-6-Cyano-6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (11)

Methanesulfonate **10c** (600 mg, 1.77 mmol) was dissolved in a solution of LiCN in DMF (1 M, 13 mL) and heated to 110 °C for 17 h. Then, H_2O (5 mL) and petroleum ether (10 mL) were added, the organic layer was separated, and the aqueous layer was extracted with petroleum ether (3 × 10 mL). The combined petroleum ether layers were dried ($MgSO_4$), concentrated in vacuo and the residue (70 mg) was purified by FC (2 cm, 85:15 petroleum ether–EtAOc, fractions 10 mL, R_f 0.38). Colorless oil, yield 20.2 mg (4.2%); $[\alpha]_D$ −52.3° (*c* 0.57, $CHCl_3$); IR (film): ν = 2255 (CN), 1256 (C–O), 1213 (C–O), 1165 (C–O), 1070 cm^{-1} (C–O); ^1H NMR ($CDCl_3$): δ 1.27 (s, 3 H, CH_3), 1.29 (s, 3 H, CH_3), 1.38 (s, 3 H, CH_3), 1.47 (s, 3 H, CH_3), 2.58 (dd, *J* 16.9/7.0 Hz, 1 H, CH_2CN), 2.64 (dd, *J* 16.9/7.0 Hz, 1 H, CH_2CN), 3.98 (t, *J* 7.0 Hz, 1 H, 5-H), 4.18 (d, *J* 7.3 Hz, 1 H, 4-H), 4.27 (dd, *J* 5.1/2.2 Hz, 1 H, 2-H), 4.59 (dd, *J* 7.3/2.2 Hz, 1 H, 3-H), 5.44 (d, *J* 5.1 Hz, 1 H, 1-H); CIMS: *m*/*z* 270 (MH^+); Anal. Calcd for $C_{13}H_{19}NO_5$ (269.1): C, 58.0; H, 7.12; N, 5.20. Found: C, 58.3; H, 7.18; N, 4.97.

3.13. (*E*)- and (*Z*)-6-Deoxy-1,2:3,4-di-*O*-isopropylidene-7-*O*-methyl-α-D-*galacto*-hepto-6-enopyranose (12)

At −78 °C KO^{t}Bu (0.90 g, 7.99 mmol) was slowly added to a solution of (methoxymethyl)triphenylphosphonium chloride (2.29 g, 6.66 mmol) in THF (10 mL). Then a solution of aldehyde **6** (0.86 g, 3.33 mmol) in Et_2O (10 mL) was added dropwise. The mixture was stirred for 10 min at −78 °C, then the cooling bath was removed, and the mixture was stirred for 5 h at rt. Subsequently, H_2O (10 mL) was added, and the aqueous layer was separated and extracted with Et_2O (3 × 20 mL). The organic layer was dried ($MgSO_4$) and concentrated in vacuo, and the residue was purified by FC (4 cm, 90:10 petroleum ether–EtOAc, fractions 15 mL, R_f 0.29). Colorless oil, yield 0.60 g (63%); IR (film): ν = 1659 (C=C), 1252 (C–O), 1213 (C–O), 1162 (C–O), 1060 cm^{-1} (C–O); ^1H NMR ($CDCl_3$): δ 1.34 (s, 6 H, CH_3), 1.36 (s, 3 H, CH_3), 1.48 (s, 3 H, CH_3), 3.59 (s, 3 × 0.37 H, OCH_3), 3.62 (s, 3 × 0.63 H, OCH_3), 4.13 (dd, *J* 8.8/1.5 Hz, 0.37 H, 4-H), 4.19 (dd, *J* 8.8/1.5 Hz, 1 H, 3-H), 4.20 (dd, *J* 8.8/1.5 Hz, 0.63 H, 4-H), 4.29 (dd, *J* 5.1/2.2 Hz, 1 H, 2-H), 4.60 (dd, *J* 8.1/1.5 Hz, 0.37 H, 5-H), 4.66 (dd, *J* 8.8/5.9 Hz, 0.63 H, (*Z*)-C*H*=CH–OCH_3), 4.86 (dd, *J* 8.8/1.5 Hz, 0.63 H, 5-H), 4.97 (dd, *J* 13.2/8.8 Hz, 0.37 H, (*E*)-C*H*=CH–OCH_3), 5.54 (d, *J* 5.1 Hz, 1 H, 1-H), 6.05 (d, *J* 5.9 Hz, 0.63 H, (*Z*)-CH=C*H*–OCH_3), 6.64 (d, *J* 13.2 Hz, 0.37 H, (*E*)-CH=C*H*–OCH_3). The ratio (*Z*)-**12**:(*E*)-**12** is 63:37; CIMS: *m*/*z* 287 (MH^+); Anal. Calcd for $C_{14}H_{22}O_6$ (286.2): C, 58.8; H, 7.75. Found: C, 58.6; H, 7.87.

3.14. (−)-6-Deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*galacto*-heptodialdo-1,5-pyranose (13)

A solution of **12** (100 mg, 0.35 mmol) and 2 N HCl (0.30 mL, ca. 0.60 mmol HCl) in $(CH_3)_2CO$ (3 mL) was stirred for 15 min at rt. Then, a solution of Na_2CO_3 (64 mg, 0.60 mmol) in H_2O (5 mL) was added (pH 7) and the mixture was extracted with Et_2O (3 × 5 mL). The Et_2O layer was dried ($MgSO_4$) and concentrated in vacuo, and the residue was purified by FC (2 cm, 90:10, petroleum ether–EtOAc, fractions 10–15 mL, R_f 0.16). Colorless oil, yield 90 mg (95%); $[\alpha]_D$ −64.9° (*c* 1.01, $CHCl_3$); IR (film): ν = 1727 (C=O), 1257 (C–O), 1213 (C–O), 1168 (C–O), 1070 cm^{-1} (C–O); ^1H NMR ($CDCl_3$): δ 1.27 (s, 6 H, CH_3), 1.39 (s, 3 H, CH_3), 1.49 (s, 3 H, CH_3), 2.72 (ddd, *J* 17.4/7.0/1.8 Hz, 1 H, CH_2–CHO), 2.64 (ddd, *J* 17.4/5.9/1.8 Hz, 1 H, CH_2–CHO), 4.15 (dd, *J* 8.1/2.2 Hz, 1 H, 4-H), 4.23 (ddd, *J* 7.0/5.9/2.2 Hz, 1 H, 5-H), 4.26 (dd, *J* 5.1/2.2 Hz, 1 H, 2-H), 4.56 (dd, *J* 8.1/2.2 Hz, 1 H, 3-H), 5.44 (d, *J* 5.1 Hz, 1 H, 1-H), 9.73 (t, *J* 1.8 Hz, 1 H, CH_2–C*H*=O); CIMS: *m*/*z* 257 ($M^+ - CH_3$); Anal. Calcd for $C_{13}H_{20}O_6$ (272.2): C, 57.4; H, 7.41. Found: C, 57.6; H, 7.12.

3.15. (−)-6-Deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*galacto*-heptopyranose (14)

$NaBH_4$ (13.9 mg, 0.37 mmol) was carefully added at 0 °C to a solution of **13** (100 mg, 0.37 mmol) in C_2H_5OH (7 mL). The mixture was stirred for 4 h at rt. H_2O (4 mL) and 2 N HCl (1 mL) were added, the mixture was concentrated in vacuo, and the residual aqueous layer was extracted with EtOAc (3 × 10 mL). The organic extract was dried ($MgSO_4$) and evaporated in vacuo, and the residue was purified by FC (2 cm, 70:30 petroleum ether–EtOAc, fractions 30 mL, R_f 0.31). Colourless oil, yield 63 mg (63%); $[\alpha]_D$ −62.7° (*c* 0.98, $CHCl_3$); IR (film): ν = 3448 (O–H), 1255 (C–O), 1212 (C–O), 1167 (C–O), 1069 cm^{-1} (C–O); ^1H NMR ($CDCl_3$): δ 1.34 (s, 3 H, CH_3), 1.35 (s, 3 H, CH_3), 1.47 (s, 3 H, CH_3), 1.54 (s, 3 H, CH_3), 1.72–1.80 (m, 1

H, CH_2CH$_2$OH), 1.93–2.01 (m, 1 H, CH_2CH$_2$OH), 2.09 (s, broad, 1 H, OH), 3.75–3.80 (m, 2 H, CH$_2$CH_2OH), 4.01 (ddd, *J* 8.1/5.9/2.2 Hz, 1 H, 5-H), 4.15 (dd, *J* 8.1/2.2 Hz, 1 H, 4-H), 4.31 (dd, *J* 5.1/2.2 Hz, 1 H, 2-H), 4.61 (dd, *J* 8.1/2.2 Hz, 1 H, 3-H), 5.54 (d, *J* 5.1 Hz, 1 H, 1-H); EIMS: *m/z* 274 (M^+), 259 ($M^+ - CH_3$); Anal. Calcd for $C_{13}H_{22}O_6$ (274.3): C, 56.9; H, 8.08. Found: C, 56.9; H, 8.09.

3.16. (*E*)- and (*Z*)-6-Deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*galacto*-heptodialdo-1,5-pyranose-7-oxime (15)

A solution of **13** (240 mg, 0.88 mmol), NH$_2$OH·HCl (184 mg, 2.65 mmol), NaOAc (145 mg, 1.76 mmol), H$_2$O (1.6 mL) and CH$_3$OH (16 mL) were stirred for 24 h at rt. The solvent was evaporated in vacuo. The residue was dissolved in H$_2$O (5 mL) and extracted with Et$_2$O (2 × 10 mL). The organic layer was dried (MgSO$_4$) and concentrated in vacuo. Colorless oil, yield 160 mg (63%), R_f 0.29 (80:20 petroleum ether–EtOAc); IR (film): ν = 3412 (OH), 1652 (C=N), 1256 (C–O), 1212 (C–O), 1167 cm^{-1} (C–O); ^{1}H NMR (CDCl$_3$): δ 1.33 (s, 3 H, CH$_3$), 1.35 (s, 3 H, CH$_3$), 1.47 (s, 3 H, CH$_3$), 1.52 (s, 3 H, CH$_3$), 2.54 (m, 1 H, CH_2–CH=NOH), 2.69 (m, 1 H, CH_2–CH=NOH), 3.98 (ddd, *J* 7.3/5.9/2.2 Hz, 1 H, 5-H), 4.17 (dd, *J* 8.1/2.2 Hz, 1 H, 4-H), 4.32 (dd, *J* 5.1/2.2 Hz, 1 H, 2-H), 4.62 (dd, *J* 8.1/2.2 Hz, 1 H, 3-H), 5.52 (d, *J* 5.1 Hz, 1 H, 1-H), 6.90 (t, *J* 5.1 Hz, 0.5 H, CH$_2$–C*H*=NOH), 7.51 (t, *J* 6.2 Hz, 0.5 H, CH$_2$–C*H*=NOH). A signal for the =N–O*H* proton could not be found; CIMS: *m/z* 288 (MH^+), 272 ($M^+ - CH_3$); Anal. Calcd for $C_{13}H_{21}NO_6$ (287.3): C, 54.3; H, 7.37; N, 4.87. Found: C, 54.1; H, 7.59; N, 4.65.

3.17. (−)-7-Amino-6,7-dideoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*galacto*-heptopyranose (16)

A solution of **15** (160 mg, 0.56 mmol) in Et$_2$O (1.5 mL) was slowly added to a suspension of LiAlH$_4$ (42.3 mg, 1.11 mmol) in Et$_2$O (1.5 mL). The suspension was stirred for 5 h at rt, then a solution of LiAlH$_4$ (1 mL, 1 M in Et$_2$O) was added, and the mixture was stirred for further 12 h at rt. A small amount of H$_2$O was carefully added, and the suspension was dried (MgSO$_4$), filtered and concentrated in vacuo. The residue was purified by FC (2 cm, 96:4, CH$_2$Cl$_2$–CH$_3$OH, fractions 7 mL, R_f 0.19). Colorless oil, yield 70 mg (46%); $[\alpha]_D$ −48.4° (*c* 1.02, CHCl$_3$); IR (film): ν = 3462 (NH), 3369 (NH), 1289 (C–N), 1231 (C–O), 1099 cm^{-1} (C–O); ^{1}H NMR (CDCl$_3$): δ 1.30 (s, 3 H, CH$_3$), 1.33 (s, 3 H, CH$_3$), 1.46 (s, 3 H, CH$_3$), 1.49 (s, broad, 2 H, NH$_2$), 1.52 (s, 3 H, CH$_3$), 1.60–1.67 (m, 1 H, CH_2–CH$_2$–NH$_2$), 1.82–1.88 (m, 1 H, CH_2–CH$_2$–NH$_2$), 2.83–2.89 (m, 2 H, CH$_2$–CH_2–NH$_2$), 3.87 (ddd, *J* 7.3/5.9/1.5 Hz, 1 H, 5-H), 4.12 (dd, *J* 8.1/2.2 Hz, 1 H, 4-H), 4.30 (dd, *J* 5.1/2.2 Hz, 1 H, 2-H), 4.59 (dd, *J* 8.1/2.2 Hz, 1 H, 3-H), 5.53 (d, *J* 5.1 Hz, 1 H, 1-H); CIMS: *m/z* 274 (MH^+), 258 ($M^+ - CH_3$); Anal. Calcd for $C_{13}H_{23}NO_5$ (273.3): C, 57.1; H, 8.48; N, 5.12. Found: C, 56.9; H, 8.19; N, 4.84.

3.18. (−)-7-(Benzoylamino)-6,7-dideoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*galacto*-hepto-pyranose (17a)

Et$_3$N (0.85 g, 8.42 mmol) and benzoyl chloride (1.18 g, 8.42 mmol) were added at 0 °C to a solution of **16** (1.92 g, 7.02 mmol) in CH$_2$Cl$_2$ (20 mL). After stirring for 30 min at rt, the mixture was washed with 1 N HCl (3 × 20 mL) and a saturated solution of NaHCO$_3$ (3 × 20 mL). The organic layer was dried (MgSO$_4$) and concentrated in vacuo. Colorless solid (2-Pr$_2$O), mp 120 °C, yield 1.90 g (72%), R_f 0.14 (75:25 petroleum ether–EtOAc); $[\alpha]_D$ −62.5° (*c* 1.00, CHCl$_3$); IR (KBr): ν = 3369 (N–H), 1639 (C=O), 1533 (amide-II), 1260 (C–O), 1212 (C–O), 1166 (C–O), 1069 cm^{-1} (C–O); ^{1}H NMR (CDCl$_3$): δ 1.37 (s, 3 H, CH$_3$), 1.40 (s, 3 H, CH$_3$), 1.41 (s, 3 H, CH$_3$), 1.52 (s, 3 H, CH$_3$), 1.98–2.07 (m, 2 H, CH_2–CH$_2$–NH), 3.67–3.69 (m, 2 H, CH$_2$–CH_2–NH), 3.94 (ddd, *J* 7.3/4.4/2.2 Hz, 1 H, 5-H), 4.21 (dd, *J* 8.1/2.2 Hz, 1 H, 4-H), 4.37 (dd, *J* 5.1/2.2 Hz, 1 H, 2-H), 4.65 (dd, *J* 8.1/2.2 Hz, 1 H, 3-H), 5.63 (d, *J* 5.1 Hz, 1 H, 1-H), 6.86 (s, broad, 1 H, NH), 7.47 (t, *J* 7.3 Hz, 2 H, arom.), 7.53 (t, *J* 7.0 Hz, 1 H, arom.), 7.84 (d, *J* 7.3 Hz, 2 H, arom.); EIMS: *m/z* 377 (M^+), 362 ($M^+ - CH_3$); Anal. Calcd for $C_{20}H_{27}NO_6$ (377.4): C, 63.6; H, 7.21; N, 3.71. Found: C, 63.8; H, 7.23; N, 3.51.

3.19. (−)-6,7-Dideoxy-1,2:3,4-di-*O*-isopropylidene-7-(phenylacetylamino)-α-D-*galacto*-hepto-pyranose (17b)

Et$_3$N (31 mg, 0.31 mmol) and phenylacetyl chloride (47.5 mg, 0.31 mmol) were added at 0 °C to a solution of **16** (70 mg, 0.26 mmol) in CH$_2$Cl$_2$ (2 mL). After stirring for 45 min at rt, the mixture was washed with 1 N HCl (2 × 5 mL) and a satd solution of NaHCO$_3$ (3 × 5 mL). The organic extract was dried (MgSO$_4$) and concentrated in vacuo. The residue was purified by FC (2 cm, 70:30 petroleum ether–EtOAc, fractions 15 mL, R_f 0.19). Colorless solid (2-Pr$_2$O), mp 62 °C, yield 79.2 mg (79%); $[\alpha]_D$ −38.4° (*c* 1.00, CHCl$_3$); IR (KBr): ν = 3339 (N–H), 1640 (C=O), 1535 (amide-II), 1261 (C–O), 1213 (C–O), 1165 (C–O), 1070 cm^{-1} (C–O); ^{1}H NMR (CDCl$_3$): δ 1.24 (s, 3 H, CH$_3$), 1.25 (s, 3 H, CH$_3$), 1.33 (s, 3 H, CH$_3$), 1.38 (s, 3 H, CH$_3$), 1.63–1.73 (m, 2 H, CH_2–CH$_2$–NH), 3.17–3.24 (m, 1 H, CH$_2$–CH_2–NH), 3.37–3.42 (m, 1 H, CH$_2$–CH_2–NH), 3.49 (s, 2 H, phenyl–CH_2), 3.65 (ddd, *J* 6.6/4.6/2.2 Hz, 1 H, 5-H), 3.99 (dd, *J* 8.1/2.2 Hz, 1 H, 4-H), 4.19 (dd, *J* 5.1/2.2 Hz, 1 H, 2-H), 4.48 (dd, *J* 8.1/2.2 Hz, 1 H, 3-H), 5.29 (d, *J* 5.1 Hz, 1 H, 1-H), 5.91 (s broad, 1 H, NH), 7.20–7.30 (m, 5 H, arom.); CIMS: *m/z* 392 (MH^+), 376 ($M^+ - CH_3$); Anal. Calcd for $C_{21}H_{29}NO_6$ (391.5): C, 64.4; H, 7.47; N, 3.58. Found: C, 64.6; H, 7.54; N, 3.39.

3.20. (−)-7-(Benzyloxycarbonylamino)-6,7-dideoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*galacto*-hepto-pyranose (17c)

Et_3N (340 mg, 3.36 mmol) and benzyl chloroformate (287 mg, 1.68 mmol) were added at 0 °C to a solution of **16** (460 mg, 1.68 mmol) in CH_2Cl_2 (10 mL). After stirring for 16 h at rt, the mixture was washed with 1 N HCl (3 × 10 mL) and a satd solution of $NaHCO_3$ (3 × 10 mL). The organic extract was dried ($MgSO_4$) and concentrated in vacuo. Colorless solid (1:1 hexane–2-Pr_2O), mp 94 °C, yield 534 mg (78%), R_f 0.22 (80:20 petroleum ether–EtOAc); $[\alpha]_D$ −28.6° (*c* 1.00, $CHCl_3$); IR (KBr): $\nu = 3357$ (NH), 1716 (C=O), 1533 (amide-II), 1255 (C–O), 1211 (C–O), 1167 (C–O), 1071 cm^{-1} (C–O); ^1H NMR ($CDCl_3$): δ 1.32 (s, 3 H, CH_3), 1.35 (s, 3 H, CH_3), 1.46 (s, 3 H, CH_3), 1.59 (s, 3 H, CH_3), 1.80–1.91 (m, 2 H, CH_2–CH_2–NH), 3.30–3.50 (m, 2 H, CH_2–CH_2–NH), 3.81–3.84 (m, 1 H, 5-H), 4.12 (dd, *J* 6.6/2.2 Hz, 1 H, 4-H), 4.31 (dd, *J* 5.1/2.2 Hz, 1 H, 2-H), 4.59 (dd, *J* 8.1/2.2 Hz, 1 H, 3-H), 5.09–5.13 (m, 3 H, CH_2Ph, NH), 5.53 (d, *J* 5.1 Hz, 1 H, 1-H), 7.30–7.53 (m, 5 H, arom.); CIMS: *m*/*z* 408 (MH^+); Anal. Calcd for $C_{21}H_{29}NO_7$ (407.5): C, 61.9; H, 7.17; N, 3.44. Found: C, 61.7; H, 7.30; N, 3.47.

3.21. (+)-(7*R*)-3,7-di-*O*-Benzoyl-6-deoxy-1,2-*O*-isopropylidene-α-D-*galacto*-heptodialdo-1,5-pyranose-4,7-furanose (19a) and (+)-(7*S*)-3,7-di-*O*-benzoyl-6-deoxy-1,2-*O*-isopropylidene-α-D-*galacto*-heptodialdo-1,5-pyranose-4,7-furanose (19b)

A solution of **12** (200 mg, 0.70 mmol) and 2 N H_2SO_4 (0.30 mL) in $(CH_3)_2CO$ (6 mL) was heated to reflux for 75 min. The solution was neutralized with 2 N NaOH (0.3 mL) and concentrated in vacuo. The residue was purified by FC (2 cm, 96:4 CH_2Cl_2–CH_3OH, fractions 30 mL) to yield **18a** and **18b** colorless oils, yield 57 mg (35%).

Et_3N (0.46 g, 4.5 mmol), benzoyl chloride (0.56 g, 4.0 mmol) and DMAP (100 mg, 0.8 mmol) were added at 0 °C to a solution of **18a/18b** (105 mg, 0.45 mmol, **18a**:**18b** = 1:2) CH_2Cl_2 (10 mL). After stirring for 48 h at rt, the mixture was extracted with 1 N HCl (2 × 10 mL) and a satd solution of $NaHCO_3$ (2 × 10 mL). The organic layer was dried ($MgSO_4$) and concentrated in vacuo, and the residue was purified by FC (2 cm, 85:15 petroleum ether–EtOAc, fractions 20 mL). Fractions 7 and 8 contained the isomer **19a**, and fractions 13–21 contained the isomer **19b**.

Data for **19a** (R_f 0.35): colorless solid (2-Pr_2O), mp 144 °C, yield 47.4 mg (24%); $[\alpha]_D$ +18.0° (*c* 0.25, $CHCl_3$); IR (KBr): $\nu = 1725$ (C=O), 1268 (C–O), 1114 (C–O), 1078 cm^{-1} (C–O); ^1H NMR ($CDCl_3$): δ 1.38 (s, 3 H, CH_{3exo}), 1.58 (s, 3 H, CH_{3endo}), 2.47 (dt, *J* 14.7/5.1 Hz, 1 H, 6-H), 2.63 (ddd, *J* 14.7/8.1/1.5 Hz, 1 H, 6-H), 4.50 (t, *J* 4.8 Hz, 1 H, 2-H), 4.64 (dd, *J* 6.9/4.4 Hz, 1 H, 4-H), 4.88 (dt, *J* 8.1/5.5 Hz, 1 H, 5-H), 5.58 (d, *J* 5.1 Hz, 1 H, 1-H), 5.79 (t, *J* 4.4 Hz, 1 H, 3-H), 6.62 (d, *J* 4.4 Hz, 1 H, 7-H1), 7.39–7.45 (m, 4 H, arom.), 7.52–7.95 (m, 2 H, arom.), 7.96 (dd, *J* 8.1/1.5 Hz, 2 H, arom.), 8.05 (dd, *J* 7.3/1.5 Hz, 2 H, arom.); EIMS: *m*/*z* 319 [M^+ − $PhCO_2$]; Anal. Calcd for $C_{24}H_{24}O_8$ (440.5): C, 65.4; H, 5.49. Found: C, 65.3; H, 5.60.

Data for **19b** (R_f 0.15): colorless solid (2-Pr_2O), mp 155 °C, yield 92.8 mg (47%); $[\alpha]_D$ +16.6° (*c* 0.25, $CHCl_3$); IR (KBr): $\nu = 1732$ (C=O), 1276 (C–O), 1120 (C–O), 1076 cm^{-1} (C–O); ^1H NMR ($CDCl_3$): δ 1.38 (s, 3 H, CH_{3exo}), 1.62 (s, 3 H, CH_{3endo}), 2.45 (d, *J* 15.4 Hz, 1 H, 6-H), 2.61 (dt, *J* 15.4/5.9 Hz, 1 H, 6-H), 4.47 (t, *J* 4.4 Hz, 1 H, 2-H), 4.55 (t, *J* 5.9 Hz, 1 H, 4-H), 4.67 (t, *J* 5.9 Hz, 1 H, 5-H), 5.77 (d, *J* 5.1 Hz, 1 H, 1-H), 5.91 (dd, *J* 6.6/4.4 Hz, 1 H, 3-H), 6.48 (d, *J* 5.9 Hz, 1 H, 7-H), 6.94 (t, *J* 7.3 Hz, 2 H, arom.), 7.22–7.27 (m, 3 H, arom.), 7.47 (dd, *J* 7.3/1.5 Hz, 1 H, arom.), 7.73 (dd, *J* 7.3/1.5 Hz, 2 H, arom.), 7.86 (dd, *J* 6.6/1.5 Hz, 2 H, arom.); ^{13}C NMR ($CDCl_3$): δ 25.17 (CH_{3exo}), 25.96 (CH_{3endo}), 38.89 (C-6), 64.60 (C-3), 68.51 (C-5), 72.32 (C-2), 77.58 (C-4), 97.01 (C-1), 98.95 (C-7), 110.14 [$C(CH_3)_2$], 127.86 (2 × C-arom.), 128.06 (2 × C-arom.), 128.95 (C-arom.), 129.69 (4 × C-arom.), 129.83 (C-arom.), 132.70 (C-arom.), 132.81 (C-arom.), 165.70 (2 × C=O). The signals were assigned by a ^1H,^{13}C HETCOR spectrum; EIMS: *m*/*z* 319 [M^+ − $PhCO_2$]; Anal. Calcd for $C_{24}H_{24}O_8$ (440.5): C, 65.4; H, 5.49. Found: C, 65.4; H, 5.58.

3.22. 6-(Benzoylamino)-6-deoxy-α- and β-D-galactopyranose (20a and 21a)

A mixture of **9a** (40 mg, 0.11 mmol), a strong acidic ion-exchange resin (40 mg), $(CH_3)_2CO$ (7 mL) and H_2O (1 mL) was heated to reflux for 25 h. Then the mixture was filtered, the solvent was evaporated in vacuo, and the residue was purified by FC (2 cm, 80:20 CH_2Cl_2–CH_3OH, fractions 10 mL, R_f 0.49). Colorless oil, yield 24.7 mg (79%); IR (film): $\nu = 3363$ (O–H, N–H), 1634 (C=O), 1546 cm^{-1} (amide-II); ^1H NMR (CD_3OD): δ 3.35–3.76 (m, 5 H, 3-H, 4-H, 5-H, 6-H), 4.10 [t, *J* 6.6 Hz, 0.5 H, 2-H (**21a**)], 4.33 [td, *J* 7.3/4.4 Hz, 0.5 H, 2-H (**20a**)], 5.05 [d, *J* 3.7 Hz, 0.5 H, 1-H (**20a**)], 7.35 (t, *J* 7.3 Hz, 2 H, arom.), 7.43 (td, *J* 7.3/1.5 Hz, 1 H, arom.), 7.73 (dd, *J* 7.3/1.5 Hz, 2 H, arom.). The signal of H-1 of the anomer **21a** was hidden under the HCD_2OD signal (4.70–4.85 ppm) of the solvent. The signals of the OH- and NH-protons are not seen in the solvent CD_3OD. The ratio of anomers **20a**:**21a** is 1:1; EIMS: *m*/*z* 266 (M^+ − OH); Anal. Calcd for $C_{13}H_{17}NO_6$ (283.3): C, 55.1; H, 6.05; N, 4.94. Found: C, 54.9; H, 6.09; N, 5.09.

3.23. (−)-Ethyl 6-(benzoylamino)-6-deoxy-α-D-galactopyranoside (20c) (−)-ethyl 6-(benzoylamino)-6-deoxy-β-D-galactopyranoside (21c), and ethyl 6-(benzoylamino)-6-deoxy-α- and β-D-galactofuranoside (22c)

A mixture of **9a** (40 mg, 0.11 mmol), a strong acidic ion-exchange resin (40 mg) and C_2H_5OH (8 mL) was heated to reflux for 69 h. Then, the mixture was filtered and concentrated in vacuo, and the residue was purified by FC (2 cm, 98:2 EtOAc–CH_3OH, fractions 10 mL).

Data for **20c** (R_f 0.24): colorless oil, yield 8.1 mg (24%); $[\alpha]_D$ −23.9° (*c* 0.34, $CHCl_3$); IR (film): $\nu = 3356$ (O–H, N–H), 1644 (C=O), 1544 cm^{-1} (amide-II); ^1H NMR ($CDCl_3$): δ 1.25 (t, *J* 7.0 Hz, 3 H, OCH_2CH_3), 3.43 (s, broad, 1 H, OH), 3.56 (dq, *J* 16.2/7.0 Hz, 1 H, OCH_2CH_3), 3.74–3.89 (m, 4 H, OCH_2CH_3, 5-H, 6-H), 4.07–4.16 (m, 4 H, 2-H, 3-H, 4-H, OH), 4.96 (s, broad, 1 H, OH), 5.09 (s, 1 H, 1-H), 7.03 (s, broad, 1 H, NH), 7.47 (t, *J* 7.7 Hz, 2 H, arom.), 7.56 (t, *J* 7.3 Hz, 1 H, arom.), 7.81 (d, *J* 6.6 Hz, 2 H, arom.); CIMS: *m*/*z* 312 (MH^+), 266 ($M^+ - C_2H_5O$); Anal. Calcd for $C_{15}H_{21}NO_6$ (311.3): C, 57.9; H, 6.80; N, 4.50. Found: C, 57.6; H, 7.05; N, 4.46.

Data for **21c** and **22c** (R_f 0.19): fractions 8–15 contained an inseparable mixture of **21c**:**22c** in a ratio of 18:82. Colorless oil, yield 12.9 mg (38%).

3.24. (−)-Methyl 7-(benzoylamino)-6,7-dideoxy-α-D-*galacto*-heptopyranoside (23b), (+)-methyl 7-(benzoylamino)-6,7-dideoxy-β-D-*galacto*-heptopyranoside (24b), and methyl 7-(benzylamino)-6,7-dideoxy-α- and β-D-*galacto*-heptofuranoside (25b)

A mixture of **17a** (160 mg, 0.42 mmol), a strong acidic ion-exchange resin (60 mg) and CH_3OH (8 mL) was heated to reflux for 48 h. Then the mixture was filtered and concentrated in vacuo, and the residue was purified by FC (2 cm, 90:10 CH_2Cl_2–CH_3OH, fractions 10 mL).

Data for **23b** (R_f 0.27): colorless oil, yield 26.1 mg (20%); $[\alpha]_D$ −10.8° (*c* 0.46, $CHCl_3$); IR (film): $\nu = 3333$ (O–H, N–H), 1637 (C=O), 1545 (amide-II), 1023 cm^{-1} (C–O); ^1H NMR ($CDCl_3$): δ 1.76–1.90 (m, 2 H, 6-H), 3.05 (s, broad, 1 H, OH), 3.49 (s, 3 H, OCH_3), 3.51–3.56 (m, 1 H, 7-H), 3.76–3.84 (m, 5 H, 2-H, 3-H, 5-H, 2 × OH), 4.08–4.13 (m, 2 H, 7-H, 4-H), 4.85 (d, *J* 2.2 Hz, 1 H, 1-H), 6.88 (s, broad, 1 H, NH), 7.42–7.45 (m, 2 H, arom.), 7.47–7.56 (m, 1 H, arom.), 7.77 (dd, *J* 8.8/1.5 Hz, 2 H, arom.); CIMS: *m*/*z* 312 (MH^+), 280 ($M^+ - CH_3O$); Anal. Calcd for $C_{15}H_{21}NO_6$ (311.3): C, 57.9; H, 6.80; N, 4.50. Found: C, 57.6; H, 7.12; N, 4.45.

Data for **24b** (R_f 0.20): colorless oil, yield 6.5 mg (4.9%); $[\alpha]_D$ +86.7° (*c* 0.21, $CHCl_3$); IR (film): $\nu = 3351$ (O–H), 1641 (C=O), 1551 (amide-II), 1029 cm^{-1} (C–O); ^1H NMR ($CDCl_3$): δ 1.60–1.71 (m, 1 H, 6-H), 2.06–2.14 (m, 1 H, 6-H), 2.88 [d, *J* 11.7 Hz, 1 H, OH (C-4)], 3.31 (ddd, *J* 13.9/9.5/4.4 Hz, 1 H, 7-H), 3.40 (s, 3 H, OCH_3), 3.82–3.85 (m, 1 H, 5-H), 3.96 (d, *J* 11.0 Hz, 1 H, 2-H), 4.01–4.07 (m, 3 H, 7-H, 3-H, 4-H), 4.88 (d, *J* 11.0 Hz, 1 H, 1-H), 4.94 (s, broad, 1 H, OH), 5.70 (s, broad, 1 H, OH), 6.51 (t, *J* 5.5 Hz, 1 H, NH), 7.47 (t, *J* 8.1 Hz, 2 H, arom.), 7.52–7.58 (m, 1 H, arom.), 7.77 (dd, *J* 8.8/1.5 Hz, 2 H, arom.); the signals were assigned by a $^1H,^{13}C$ COSY spectrum; CIMS: *m*/*z* 312 (MH^+), 280 ($M^+ - CH_3O$); Anal. Calcd for $C_{15}H_{21}NO_6$ (311.3): C, 57.9; H, 6.80; N, 4.50. Found: C, 57.6; H, 7.04; N, 4.39.

Data for **25b** (R_f 0.14): colorless oil, yield 89.3 mg (68%); IR (film): $\nu = 3344$ (O–H), 1640 (C=O), 1544 (amide-II), 1075 (C–O), 1040 cm^{-1} (C–O); ^1H NMR (CD_3OD): δ 1.78–1.96 (m, 2 H, 6-H), 3.26 (s, 3 × 0.65 H, OCH_3), 3.35–3.38 (m, 2 × 0.65 H, 7-H), 3.40 (s, 3 × 0.35 H, OCH_3), 3.44–3.50 (m, 0.65 H, 4-H, 3 × 0.35 H, 7-H, 4-H), 3.57–3.68 (m, 0.35 H, 5-H), 3.74–3.77 (m, 2 × 0.65 H, 2-H, 3-H, 2 × 0.35 H, 2-H, 3-H), 3.75 (q, *J* 4.4 Hz, 0.65 H, 5-H), 4.02 (d, *J* 7.3 Hz, 0.35 H, 1-H), 4.59 (d, *J* 2.9 Hz, 0.65 H, 1-H), 7.33–7.37 (m, 2 H, arom.), 7.41–7.43 (m, 1 H, arom.), 7.70–7.73 (m, 2 H, arom.), the signals of the OH- and NH-protons were not observed in the solvent, CD_3OD. The signals were assigned by a $^1H,^1H$ COSY spectrum. The ratio of the α- and β-anomers α-**25b**:β-**25b** was 65:35; ^{13}C NMR (CD_3OD): δ 31.37 (C-6), 31.75 (C-6), 37.97 (C-7), 38.21 (C-7), 55.73 (OCH_3), 57.25 (OCH_3), 69.46 (C-5), 70.05 (C-5), 71.49 (C-4), 72.21 (C-4), 72.41 (C-3), 72.74 (C-3), 73.96 (C-2), 75.01 (C-2), 101.54 (C-1), 105.82 (C-1), 128.2 (C-arom.), 129.5 (C-arom.), 132.6 (C-arom.), 135.7 (C-arom.), 170.3 (C=O); the signals were assigned by a $^1H,^{13}C$ HETCOR spectrum; EIMS: *m*/*z* 311 (M^+), 280 ($M^+ - CH_3O$); Anal. Calcd for $C_{15}H_{21}NO_6$ (311.3): C, 57.9; H, 6.80; N, 4.50. Found: C, 57.7; H, 7.05; N, 4.74.

3.25. (−)-Ethyl 7-(benzoylamino)-6,7-dideoxy-α-D-*galacto*-heptopyranoside (23c), ethyl 7-(benzoylamino)-6,7-dideoxy-β-D-*galacto*-heptopyranoside (24c), and ethyl 7-(benzylamino)-6,7-dideoxy-α- and β-D-*galacto*-heptofuranoside (25c)

A mixture of **17a** (40 mg, 0.11 mmol), a strong acidic ion-exchange resin (40 mg) and C_2H_5OH (8 mL) was heated to reflux for 70 h. Then the mixture was filtered and concentrated in vacuo, and the residue was purified by FC (2 cm, at first 96:4 CH_2Cl_2–CH_3OH) (ca. 100 mL) then EtOAc (200 mL), fractions 15 mL.

Data for **23c** (R_f 0.29 90:10 CH_2Cl_2–CH_3OH): colorless oil, yield 8.8 mg (26%); $[\alpha]_D$ −16.6° (*c* 0.26, $CHCl_3$); IR (film): $\nu = 3362$ (O–H), 1634 (C=O), 1538 cm^{-1} (amide-II); ^1H NMR ($CDCl_3$): δ 1.20 (t, *J* 7.0 Hz, 3 H, OCH_2CH_3), 1.64–1.70 (m, 1 H, 6-H), 2.03–2.11 (m, 1 H, 6-H), 3.04 (s, broad, 1 H, OH), 3.29–3.37 (m, 1 H, 7-H), 3.52 (dq, *J* 16.9/7.3 Hz, 1 H, OCH_2CH_3), 3.74–3.85 (m, 2 H, OCH_2CH_3, 5-H), 3.96–4.06 (m, 4 H, 2-H, 3-H,

4-H, 7-H, CH_2N), 4.95 (s, broad, 1 H, OH), 5.04 (s, 1 H, 1-H), 5.59 (s, broad, 1 H, OH), 6.61 (s, broad, 1 H, NH), 7.46 (t, *J* 7.3 Hz, 2 H, arom.), 7.54 (t, *J* 7.3 Hz, 1 H, arom.), 7.76 (dd, *J* 8.8/1.5 Hz, 2 H, arom.); CIMS: *m*/*z* 326 (MH^+), 280 ($M^+ - C_2H_5O$); Anal. Calcd for $C_{16}H_{23}NO_6$ (325.4): C, 59.1; H, 7.13; N, 4.30. Found: C, 59.1; H, 6.93; N 4.57.

Data for **24c** and **25c** (R_f 0.24, 90:10 CH_2Cl_2–CH_3OH): fractions 9–25 contained an inseparable mixture of **24c**:**25c** in a ratio of 10:90. Colorless oil, yield 25.4 mg (74%).

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