Stereoselective Synthesis of 3-Substituted and 3,4-Disubstituted Piperidine und Piperidin-2-one Derivatives

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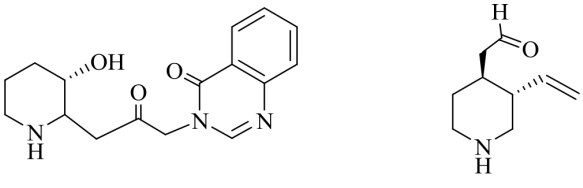
Z. Naturforsch. **2012**, *67b,* 389 – 405; received February 13, 2012

The stereoselective synthesis of 3-substituted and 3,4-disubstituted piperidine and piperidin-2-one derivatives was achieved starting from 2-pyridone. After *N*-galactosylation and subsequent *O*-silylation, nucleophilic addition of organometallic reagents proceeded with high regio- and stereoselectivity at 4-position. Substituents at position 3 were stereoselectively introduced by reaction of electrophiles with amide enolates of the *N*-galactosyl-2-piperidones.

Key words: *N*-Galactosyl Pyridone, 3-Alkyl-piperidines, 3,4-Dialkyl-piperidines, Carbohydrate Auxiliaries, Stereoselective Reactions

Introduction

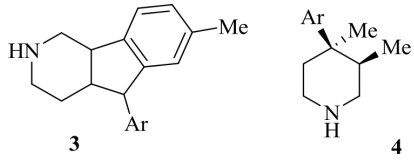
In contrast to 2- and 2,6-subsituted piperidine derivates which constitute a whole subclass of piperidine alkaloids [1], 3- and 3,4-substituted piperidines are only rarely found in Nature. Derivates of 3-hydroxypiperidine, as for example (+)-febrifugine (**1**) occurring in Chinese medicinal plants [2], or products of degradation of quinine, as for example, meroquinene or meroquinene aldehyde (**2**) [3] belong to the few exceptions (Scheme 1).



1 **2**

Scheme 1. 3-Substituted piperidine natural products.

The rare occurrence in Nature certainly is the reason that only a few syntheses of 3-alkyl and 3,4-dialkyl-piperidines lacking a 2-substituent have been reported in the literature [4], although access to these compounds through reduction of the corresponding alkyl-pyridines had been described early [5]. Optically active 3-alkyl and 3,4-dialkyl-piperidines have been obtained by separation of racemic mixtures [5c] in most cases, whereas stereoselective syntheses have rarely been reported. This is surprising since 3,4-disubstituted piperidines have been shown to exhibit attractive biological effects. For example, hexahydroindeno[1,2-*c*]pyridines **3** have been reported to act as gonadotrophic hormone-releasing hormone agonists/antagonists and integrin antagonists [6]. 4-Aryl-3,4-dimethyl-piperidines **4** obviously exhibit efficient opoid receptor antagonist activity [7] (Scheme 2).



3 **4**

Scheme 2. 3,4-Disubstituted piperidines of pharmacological interest.

We report here on stereoselective syntheses of 3-alkyl- and 3,4-dialkyl-piperidine derivatives from 2-pyridone according to the strategy of stereoselective desymmetrization induced by *N*-galactosylation [8]. *O*-Pivaloylated *N*-galactosyl-pyridin-2-one **5** [8], after activation with trialkylsilyl trifluoromethanesulfonate to afford the silyloxy-pyridinium intermediate **6**, reacted with Grignard compounds or organocuprates to afford 4-subsituted 5,6-dehydro-piperidin-2-ones **7** with complete regio- and excellent stereoselectivity [8] (Scheme 3).

In contrast to *N*-galactosyl-dehydropiperidin-4-ones obtained either by analogous reactions of *N*-galactosyl-*gamma*-pyridone [9] or by tandem-Michael-Mannich reactions [10] of *N*-glycosyl-aldimines with the Danishefsky diene, compounds of type **7** should

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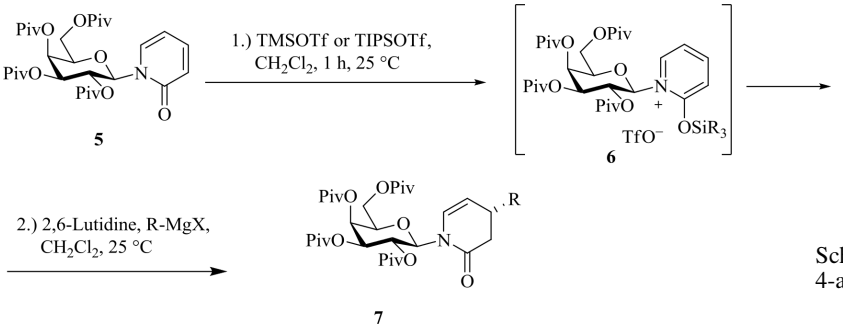
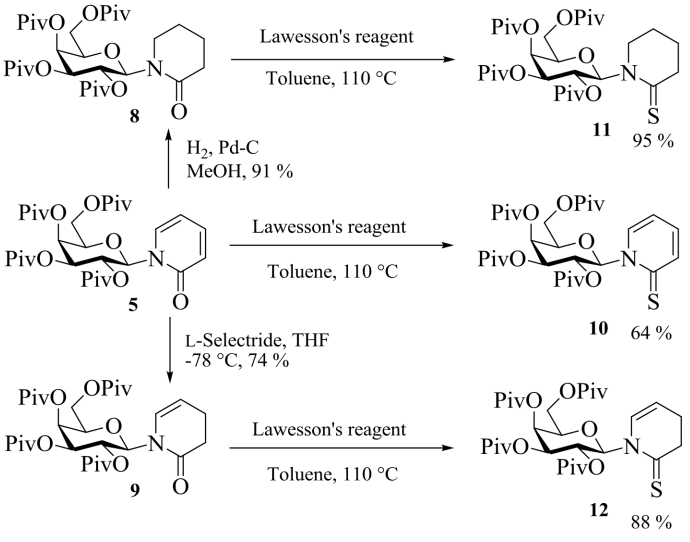
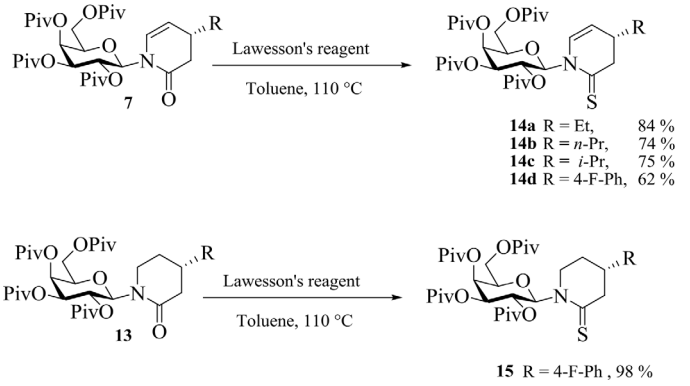


Scheme 3. Stereoselective synthesis of 4-alkyl-5,6-dihydro-piperidin-2-ones.



Scheme 4. Formation of pyridine- and piperidin-2-thiones.

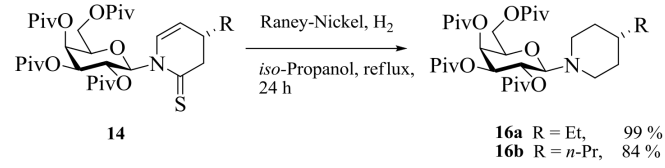


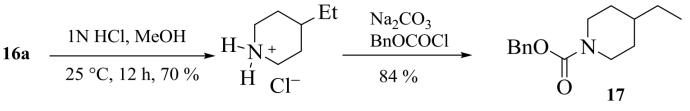
Scheme 5. Formation of 4-substituted piperidin-2-thiones.

provide stereoselective access to 3-substituted and 3,4-disubstituted piperidines which do not contain an additional substituent at 2-position.

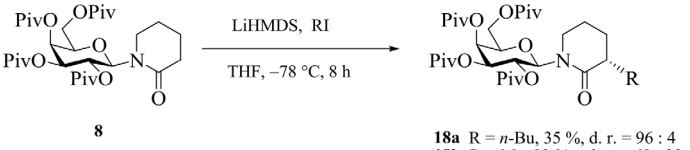
Results and Discussion

Before the introduction of a 3-substituent is outlined, the removal of the carbohydrate auxiliary should be discussed. As the *N*-glycosyl amide bond is stable towards acidic conditions, a reduction of the amide carbonyl must be achieved at first. Using *N*-galactosyl-pyrid-2-one (**5**) as the model substrate, catalytic hydrogenation gave *N*-galactosyl valerolactam (**8**), while reduction with L-Selectride® in THF at −78 °C regioselectively afforded the 5,6-dehydropiperidin-2-one **9** corresponding to compounds **7** (Scheme 4).

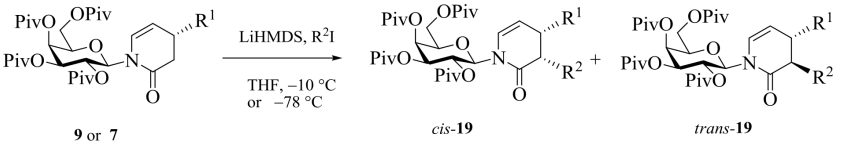




Scheme 6. Detachment of the carbohydrate auxiliary.



Scheme 7. Alkylation in 3-position; d. r. = ratio of diastereomers.



Scheme 8. 3,4-Dialkyl-piperidinones.

Educt	R^1	R^2	Temp. (°C)	Product	Yield (%)	Diastereomeric ratio *cis* : *trans*
9	H	Me	−78	**19a**	44[a]	92 : 8
9	H	*n*-Bu	−78	**19b**	27[a]	93 : 7
7b	*n*-Pr	Me	−78	**19c**	90	71 : 29
7e	*c*-Hex	Me	−10	**19d**	92	67 : 33
7b	*n*-Pr	Bu	−10	**19e**	57[a]m	58 : 42

Table 1. Alkylation of *N*-galactosyl-5,6-dehydropiperidin-2-ones.

[a] Incomplete conversion.

All three types of *N*-galactosyl amides **5**, **8** and **9** were converted to the corresponding thioamides **10**–**12** using Lawesson's reagent [11].

The same transformation was also applied to the 4-substituted dehydropiperidin-2-ones **7** and their hydrogenated analogs **13** without affecting their stereogenic centers (Scheme 5) and gave the 4-substituted thioamides **14** and **15**.

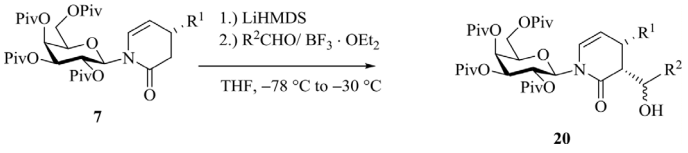
While deoxygenation of *N*-galactosyl amides **8**, **13** neither with borane nor with superhydride [12] even in the presence of BF_3 etherate [13] was successful, the thioamides **14** were readily desulfurized by hydrogenation in the presence of Raney-nickel with concomitant hydrogenation of the C=C double bond to give the *N*-galactosyl piperidines **16** (Scheme 6).

Treatment of the *N*-galactosyl piperidine **16a** with diluted hydrogen chloride in methanol smoothly cleaved the *N*-glycosidic bond to afford the free piperidine [10] which was converted to the corresponding *O*-benzyl-urethane **17** for easier characterization.

For the introduction of a 3-substituent, *N*-galactosyl-valerolactam (**8**) was deprotonated using lithium hexamethyldisilazane (LiHMDS) in tetrahydrofuran at −78 °C. The alkylation of the amide enolate proceeded slowly. However, the 3-*n*-butyl-piperidin-2-one **18a** was formed with high diastereoselectivity. The 3-methyl derivative **18b** was obtained more efficiently, but with lower diastereoselctivity (Scheme 7).

The diastereomers could not be separated by chromatography, and their configuration is not yet clarified. However, in view of the stereochemistry of compounds **7** confirmed by X-ray analysis [8] and the stereocontrol governing their formation, it can be concluded that the enolate is attacked from the (*si*)-side, and the major diastereomers **18** have (3*S*)-configuration.

Similar to **8**, the 5,6-dehydropiperidin-2-ones **7** and **9** can be alkylated after deprotonation with LiHMDS (Scheme 8).



Scheme 9. Stereoselective aldol reaction at position 3.

Table 2. Stereoselective aldol reaction of *N*-galactosyl-dehydropiperidin-2-ones **7**.

Product	R^1	R^2	Yield (%)	Diastereomeric ratio[a]
20a	*n*-Pr	Ph	81	> 99 : 1 : 0 : 0
20b	Ph	Ph	49	> 99 : 1 : 0 : 0
20c	n-Pr	5-Me-furfuryl	68	62 : 38 : 0 : 0
20d	*n*-Bu	Me_2CH	73	98 : 2 : 0 : 0
20e	Ph	Me_3C	36	91 : 6 : 3 : 0
20f	*n*-Bu	$H_2C{=}CH$[b]	78	87 : 9 : 4 : 0

[a] Determination by analyt. HPLC; [b] no activation of the acrolein with $BF_3{\cdot}OEt_2$.

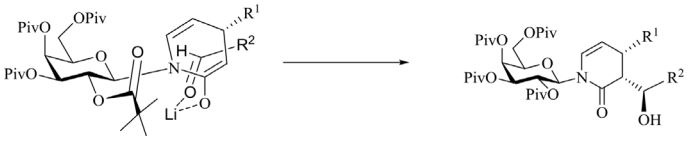
The results displayed in Table 1 show that high diastereoselectivity is achieved in these 3-alkylations at −78 °C, if no substituent is present in 4-position. The amide enolates of the 4-substituted dehydropiperidinones **7** are also alkylated, but with distinctly lower stereoselectivity. This behavior is in agreement with a stereodifferentiation during the amide enolate alkylation predominantly influenced by the shielding 2-pivaloyloxy substituent of the carbohydrate auxiliary.

Aldehydes as more reactive electrophiles also can be used for the introduction of a 3-substituent. To this end, 4-substituted dehydropiperidinones **7** were converted to their amide enolates at −78 °C. These cyclic (*E*-)amide enolates only react with aldehydes after their pre-activation with BF_3 etherate [13b] (Scheme 9, Table 2).

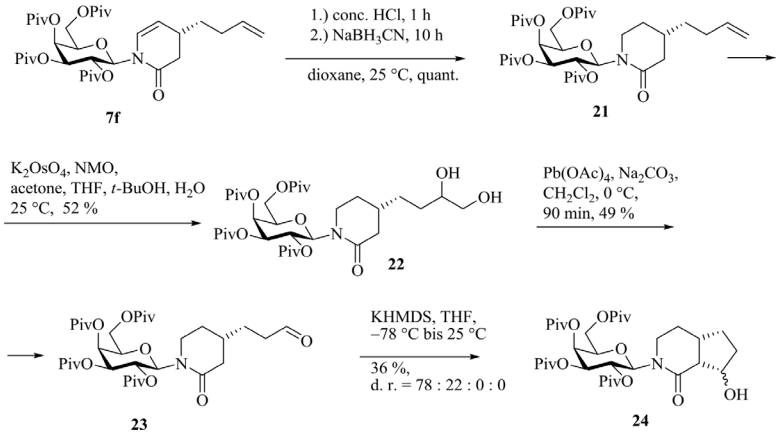
In this aldol reaction, two new stereogenic centers are formed. As a rule, only two out of four diastereomers could be detected by analytical HPLC. Both of which probably have 3,4-*cis* configuration, and one of them is generated in a high excess. These results are in agreement with a back-side (*si*-side) attack of the aldehyde at the amide enolate passing a Zimmerman-Traxler transition state [14] as is displayed in Scheme 10.

According to this interpretation, the major diastereomers of the 3,4-disubsituted piperidin-2-ones **20**, which were formed almost exclusively in reactions with benzaldehyde (**20a**, **b**) and isobutyraldehyde (**20d**), should have (3*R*, α*R*)-configuration. The lower selectivity found in the reaction with 5-methyl-furfural can be traced back to a coordinating effect of the furan oxygen. The reaction of pivalaldehyde obviously is sterically more hindered, therefore, incomplete and of slightly reduced selectivity, whereas acrolein is very reactive and logically less selective. It should also be noticed that ketones, as for example acetophenone, did not undergo this aldol reaction. These findings suit with the suggested Zimmerman-Traxler mechanism (Scheme 10). The intramolecular version of the enantioselective aldol reaction should provide access to 3,4-annulated piperidine frameworks as is present, for example, in the monoterpene alkaloid α-skytanthin [15]. As a suitable starting material, 4-butenyl-5,6-dehydropiperidin-2-one **7f** [8] was selectively reduced at the enamine double bond by protonation with conc. hydrochloric acid and subsequent treatment with sodium cyanoborohydride. The quantitatively obtained *N*-galactosyl-valerolactam **21** was subjected to osmate-promoted dihydroxylation to give **22**, and its subsequent diol-cleavage using lead tetraacetate [16] led to valerolactam **23** containing an aldehyde function in the side chain (Scheme 11).

It is noteworthy, that the LiHMDS-promoted deprotonation of **23** did not induce the cyclizing aldol reaction. Obviously, the lithium ion-coordinated Zimmerman-Traxler transition state is too much strained and the lithium-coordinated amide enolate too weakly nucleophilic. Only deprotonation with potassium hexamethyldisilazane (KHMDS) producing the more nucleophilic potassium enolate resulted in the desired aldol reaction. Again, of the four possible diastereomers only the two *cis*-diastereomers have been formed. However, due to the weaker coordinating effect of the potassium ion, the stereodifferentiation of the prochiral aldehyde only amounts to 4 : 1 and cannot



Scheme 10. Hypothesis of the diastereodifferentiation.



Scheme 11. 3,4-Annulated piperidinones.

be predicted by a six-membered ring transition state. The configuration of the major diastereomer could not be confirmed so far, because the compound did not crystallize, and overlap of the crucial signals in the ^{1}H NMR spectrum rendered the interpretation difficult.

Conclusion

Although their configurations have not yet been confirmed by X-ray analyses, 3-substituted and 3,4-disubstituted piperidine derivatives have been obtained stereoselectively starting from 2-pyridone *via* *N*-galactosylation. The *N*-galactosyl auxiliary in *N*-galactosyl valerolactam (**9**), *N*-galactosyl-5,6-dehydropiperidin-2-ones **10** and their 4-substituted derivatives **7** as well as in their amide enolates obviously causes an efficient stereodifferentiation in substitution reactions at position 3 of the piperidinone ring. This holds for alkylation processes as well as for aldol reactions. In some cases of the aldol reactions, only one out of four diastereomers was obtained. The observed effects of a substituent at 4-position in substitution reactions at 3-position support the hypothesis that amide enolates of *N*-D-galactosyl-piperidin-2-ones are preferably attacked from the *si*-side due to the shielding effect of the large 2-pivaloyloxy substituent of the carbohydrate auxiliary. Model reactions have shown that the *N*-galactosyl auxiliary can be removed from the chiral piperidine products *via* conversion of the piperidinones into the corresponding thioamides, their reductive desulfurization and subsequent acidolysis of the *N*-glycosidic bond.

Experimental Section

General instrumentation

Reagents and solvents were distilled before use: Tetrahydrofuran, dioxane, and Et_2O were distilled from potassium-benzophenone ketyl. CH_2Cl_2 was distilled from CaH_2. Light petroleum refers to bp 60 – 80 °C. All reactions and distillations were carried out in flame-dried glassware under argon atmosphere.

Reversed-phase analytical HPLC was carried out using a Knauer system (Knauer MaxiStar K1000 pump and DAD2062 for diode array detection), acetonitrile-water, flow rate: 1 cm^3 min^{-1}. Column: A: Luna C8, 5 μ, 250 × 4 mm, Phenomenex; for chiral analytical HPLC: "Chiralpak AD, Daicel Chemical Industries and *n*-hexane-*iso*-propanol as eluents, flow rate: 1 cm^3 min^{-1}. Thin-layer chromatography (TLC) was performed on Merck silica gel 60$_{F254}$, flash chromatography on silica (32 – 63 μm, ICN Biochemicals). FD mass spectra were measured on a Finnigan MAT 95 spectrometer, ESI mass spectra on a ThermoQuest Navigator instrument. High-resolution ESI mass spectra were recorded on a Q-TOF Ultima 3 instrument (Waters, NaI-CsI as the internal reference). Melting points were taken on a Büchi Dr. Tottoli apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-300 or a Bruker AM-400 NMR instrument. Chemical shifts δ are given in ppm. Optical rotation values were measured with a Perkin-Elmer 241 polarimeter.

The synthesis of the 4-substituted 5,6-dehydropiperidin-2-ones **7** has been described in reference [8].

*N-Galactosyl-piperidin-2-ones **8** and **13** through hydrogenation – General procedure*

To the solution of *N*-galactosyl-2-pyridone (**5**) or *N*-galactosyl-5,6-dehydropiperidin-2-one (**7**) [8] in dry methanol palladium on charcoal (10 %, 15 mg) was added. The mixture was stirred under hydrogen atmosphere at r. t.

until monitoring by TLC showed complete conversion. Subsequently, the hydrogen was substituted by argon, the catalyst was filtered off, and the solvent was evaporated *in vacuo*. The remaining crude product was purified by flash chromatography.

*N-(2,3,4,6-Tetra-O-pivaloyl-β-D-galactopyranosyl)piperidin-2-one (**8**)*

Educt *N*-(2,3,4,6-tetra-*O*-pivaloyl-β-D-galactopyranosyl)-2-pyridone [8] (**5**): 5.00 g (8.4 mmol); reaction time: 10 h. Yield: 4.59 g (91 %), colorless amorphous solid, R_f = 0.4 (cyclohexane-ethyl acetate 2 : 1), $[alpha]_D^{25}$: 24.77 (*c* = 1.0; $CHCl_3$). – MS ((+)-ESI): m/z = 620.35 $[M+Na]^+$. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.08, 1.14, 1.23 (3s, 36H, $PivCH_3$), 1.74 (m, 4H, $NCH_2CH_2CH_2$), 2.32 (m, 2H, $COCH_2$), 3.35 (m, 2H, NCH_2), 3.88 – 4.11 (m, 3H, H-5, H-6a, H-6b), 5.22 (dd, 1H, $J_{3,4}$ = 2.9 Hz, $J_{3,2}$ = 9.9 Hz, H-3), 5.37 (m, 2H, $J_{4,3}$ = 2.9 Hz, $J_{2,1}$ = 9.2 Hz, H-4, H-2), 6.01 (d, 1H, $J_{1,2}$ = 9.2 Hz, H-1). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.61, 22.70 ($NCH_2CH_2CH_2-$), 26.87, 26.97, 27.02, 27.18 ($PivCH_3$), 32.51 ($COCH_2$), 38.68, 38.77, 39.03 ($PivC_t$), 41.15 (NCH_2), 60.73 (C-6), 65.03, 66.83, 71.51, 72.76 (C-5, C-4, C-3, C-2), 79.39 (C-1), 170.60 (NC=O), 176.47, 176.94, 177.40, 177.77 (PivC=O). – $C_{31}H_{51}NO_{10}$ (597.35): calcd. C 62.29, H 8.60, N 2.34; found C 62.22, H 8.55, N 2.23.

*(4S)-4-Ethyl-N-(2,3,4,6-tetra-O-pivaloyl-β-D-galactopyranosyl)piperidin-2-one (**13a**)*

Educt (4*R*)-4-ethyl-3,4-dihydro-*N*-(2,3,4,6-tetra-*O*-pivaloyl-β-D-galactopyranosyl)pyridine-2(1*H*)-one [8] (**7a**): 480 mg (0.77 mmol); reaction time: 10 h. – Yield: 454 mg (95 %), colorless amorphous solid, R_f = 0.47 (cyclohexane-ethyl acetate 2 : 1), $[\alpha]_D^{25}$: 15.31 (*c* = 1.0; $CHCl_3$). – MS ((+)-ESI): m/z = 648.49 $[M+Na]^+$. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, 3H, $-CH_3$), 1.10, 1.13, 1.23 (3s, 36H, $PivCH_3$), 1.38 (m, 2H, CH_2CH_3), 1.94 (m, 2H, NCH_2CH_2), 2.47 (m, 2H, $COCH_2$), 3.24 (m, 1H, CHethyl), 3.46 (m, 2H, NCH_2), 3.89 – 4.10 (m, 3H, H-5, H-6a, H-6b), 5.20 (dd, 1H, $J_{3,4}$ = 2.9 Hz, $J_{3,2}$ = 9.9 Hz, H-3), 5.41 (m, 2H, $J_{4,3}$ = 2.9 Hz, $J_{2,1}$ = 9.6 Hz, H-4, H-2), 5.98 (d, 1H, $J_{1,2}$ = 9.6 Hz, H-1). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = (signals of the major rotamer) 10.96 ($-CH_3$), 26.96, 27.03, 27.18 ($PivCH_3$), 28.43, 28.44 (CH_2CH_3, NCH_2CH_2), 33.95 (*C*Hethyl), 38.65 ($COCH_2$), 38.70, 38.77, 39.03 ($PivC_t$), 40.41 (NCH_2), 60.75 (C-6), 65.22, 66.83, 71.65, 72.65 (C-5, C-4, C-3, C-2), 79.32, (C-1), 170.54 (NC=O), 176.47, 176.97, 177.35, 177.79 (PivC=O). – $C_{33}H_{55}NO_{10}$ (625.38): calcd. C 63.34, H 8.86, N 2.24; found C 63.15, H 8.92, N 2.24.

*(4S)-4-Propyl-N-(2,3,4,6-tetra-O-pivaloyl-β-D-galactopyranosyl)piperidin-2-one (**13b**)*

Educt (4*R*)-3,4-dihydro-4-propyl-*N*-(2,3,4,6-tetra-*O*-pivaloyl-β-D-galactopyranosyl)pyridine-2(1*H*)-one [8] (**7b**): 0.45 g (0.7 mmol) **7b**; reaction time: 24 h. Yield: 0.331 g (74 %), colorless amorphous solid, R_f = 0.27 (cyclohexane-ethyl acetate 4 : 1), $[\alpha]_D^{25}$: 14.81 (*c* = 1.0, $CHCl_3$). – MS ((+)-ESI): m/z = 662.39 $[M+Na]^+$. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, 3H, $-CH_3$), 1.08, 1.14, 1.24 (3s, 36H, $PivCH_3$), 1.28 (m, 4H, $(CH_2)_2CH_3$), 1.62 (m, 2H, NCH_2CH_2), 1.95 (m, 1H, CHpropyl), 2.28, 2.46 (2m, 2H, $COCH_2$), 3.24, 3.50 (2m, 2H, NCH_2), 3.90 – 4.13 (m, 3H, H-5, H-6a, H-6b), 5.21 (dd, 1H, $J_{3,4}$ = 2.9 Hz, $J_{3,2}$ = 9.9 Hz, H-3), 5.37 (m, 2H, $J_{4,3}$ = 2.9 Hz,$J_{2,1}$ = 9.6 Hz, H-2, H-4), 5.99 (d, 1H, $J_{1,2}$ = 9.2 Hz, H-1). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 10.98 (CH_3), 26.97, 27.03, 27.18 ($PivCH_3$), 28.34, 28.44 (CH_2CH_3, NCH_2CH_2), 33.97 (CHpropyl), 38.65 (CH_2), 38.71, 38.79 ($PivC_t$), 38.54 ($COCH_2$), 39.04 ($PivC_t$), 40.12 (NCH_2), 60.76 (C-6), 65.24, 66.84, 71.65, 72.67 (C-5, C-4, C-3, C-2), 79.33 (C-1), 170.57 (NC=O), 176.49, 176.95, 177.37, 177.80 (PivC=O). – $C_{34}H_{57}NO_{10}$ (639.39): calcd. C 63.83, H 8.98, N 2.19; found C 63.10, H 9.32, N 2.24.

*(4S)-4-Isopropyl-N-(2,3,4,6-tetra-O-pivaloyl-β-D-galactopyranosyl)piperidin-2-one (**13c**)*

Educt (4*R*)−3,4-dihydro-4-isopropyl-*N*-(2,3,4,6-tetra-*O*-pivaloyl-β-D-galactopyranosyl)pyridine-2(1*H*)-one [8] (**7c**): 370 mg (0.58 mmol); reaction time: 12 h. Yield: 305 mg (82 %), colorless amorphous solid, R_f = 0.52 (cyclohexane-ethyl acetate 2 : 1), $[\alpha]_D^{25}$: 13.15 (*c* = 1.0; $CHCl_3$). – MS ((+)-ESI): m/z = 662.42 $[M+Na]^+$. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.85, 0.87 (2d, 6H, *J* = 6.3, $CH(CH_3)_2$), 1.08, 1.14, 1.24 (3s, 36H, $PivCH_3$), 1.39 (m, 1H, $CH(CH_3)_2$), 1.92, 2.13 (2m, 2H, NCH_2CH_2), 2.38 (m, 2H, $COCH_2$), 3.24 (m, 1H, CH*i*propyl), 3.44, 3.56 (2m, 2H, NCH_2), 3.96 – 4.11 (m, 3H, H-5, H-6a, H-6b), 5.20 (dd, 1H, $J_{3,4}$ = 2.9 Hz, $J_{3,2}$ = 9.9 Hz, H-3), 5.39 (m, 2H, $J_{4,3}$ = 2.9 Hz, $J_{2,1}$ = 9.6 Hz, H-4, H-2), 5.98 (d, 1H, $J_{1,2}$ = 9.6 Hz, H-1). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = (signals of the major rotamer) 19.18, 19.42 ($-CH_3$), 26.24 (NCH_2CH_2), 26.96, 27.03, 27.17 ($PivCH_3$), 31.85 (CH*i*propyl), 36.33 ($COCH_2$), 38.70, 37.79 ($PivC_t$), 38.83 ($CH(CH_3)_2$), 39.03, 39.06 ($PivC_t$), 40.42 (NCH_2), 60.75 (C-6), 65.28, 66.83, 71.63, 72.64 (C-5, C-4, C-3, C-2), 79.30 (C-1), 170.90 (NC=O), 176.49, 176.97, 177.34, 177.79 (PivC=O). – $C_{34}H_{57}NO_{10}$ (639.39): calcd. C 63.83, H 8.98, N: 2.19; found C 63.85, H 9.01, N 2.22.

*(4S)-4-(4-Fluorophenyl)-N-(2,3,4,6-tetra-O-pivaloyl-β-D-galactopyranosyl)piperidin-2-one (**13d**)*

Educt (4*S*)−3,4-dihydro-4-(4-fluorophenyl)-*N*-(2,3,4,6-tetra-*O*-pivaloyl-β-D-galactopyranosyl)pyridine-2(1*H*)-one [8] (**7d**): 2.4 g (3.48 mmol); reaction time: 24 h. Yield: 1.76 g (2.55 mmol, 73 %), colorless amorphous solid, R_f = 0.21 (cyclohexane-ethyl acetate 4 : 1), $[\alpha]_D^{25}$: 4.64 (*c* = 1.0, $CHCl_3$). – MS ((+)-ESI): m/z = 714.7 $[M+Na]^+$. – ^{1}H NMR

(300 MHz, $CDCl_3$): δ = 1.10, 1.12, 1.15, 1.24 (4s, 36H, $PivCH_3$), 1.83, 2.09 (2m, 2H, NCH_2CH_2), 2.46, 2.62 (2m, $COCH_2$), 2.88 (m, 1H, CHAr), 3.40, 3.58 (2m, 2H, NCH_2), 3.91 – 4.13 (m, 3H, H-5, H-6a, H-6b), 5.24 (dd, 1H, $J_{3,4}$ = 2.9 Hz, $J_{3,2}$ = 9.9 Hz, H-3), 5.40 (t, 1H, $J_{2,1}$ = 9.6 Hz, $J_{2,3}$ = 9.9 Hz, H-2), 5.41 (d, 1H, $J_{4,3}$ = 2.9 Hz, H-4), 6.03 (d, 1H, $J_{1,2}$ = 9.6 Hz, H-1), 6.99 (m, 2H, aryl), 7.10 (m, 2H, aryl). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 27.03, 27.18 ($PivCH_3$), 30.15 (NCH_2CH_2), 37.47 (CHaryl), 38.70, 38.73, 38.83, 39.04 ($PivC_t$), 39.75 ($COCH_2$), 40.03 (NCH_2), 60.79 (C-6), 65.34, 66.80, 71.53, 72.79 (C-5, C-4, C-3, C-2), 79.41 (C-1), 115 (d, $^2J(^{13}C,^{19}F)$ = 21 Hz, aryl), 127 (d, $^3J(^{13}C,^{19}F)$ = 8 Hz, aryl), 138.95 (*ipso*-aryl), 162 (d, $^1J(^{13}C,^{19}F)$ = 243 Hz, CF), 169.70 (NC=O), 176.46, 176.97, 177.55, 177.80 (PivC=O). – $C_{37}H_{54}FNO_{10}$ (691.37): calcd. C 64.24, H 7.87, N 2.02; found C 64.56, H 7.83, N 2.04.

*3,4-Dihydro-N-(2,3,4,6-tetra-O-pivaloyl-β-D-galactopyranosyl)pyridine-2(1H)-one (**9**)*

To a solution of *N*-(2,3,4,6-tetra-*O*-pivaloyl-β-D-galactopyranosyl)pyridine-2(1*H*)-one [8] (**5**) (5 g, 8.4 mmol) in 100 mL of dry THF at −78 °C were dropwise added 16.8 mL of a 1.0 M solution of L-Selectride (16.8 mmol, 2 equiv.). After stirring for 2 h at this temperature, acetic acid (0.5 mL, 8.4 mmol) was added. The mixture was diluted with diethyl ether (200 mL) and washed with 50 mL of sat. NH_4Cl solution. The organic solution was dried with $MgSO_4$, and the solvents were evaporated *in vacuo*. Purification was carried out by flash chromatography. Yield: 3.71 g (6.23 mmol, 74 %), colorless amorphous solid, R_f = 0.63 (cyclohexane-ethyl acetate 2 : 1), $[\alpha]_D^{25}$: 21.57 (c = 1.0; $CHCl_3$). – MS ((+)-ESI): m/z = 618.41 $[M+Na]^+$. – HRMS ((+)-ESI): m/z = 596.3452 $[M+H]^+$ (calcd. 596.3435). – $C_{31}H_{49}NO_{10}$ (595.33): calcd. C 62.50, H 8.29, N 2.35; found C 62.67, H 8.28, N 2.27. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.07, 1.08, 1.14, 1.25 (3s, 36H, $PivCH_3$), 2.20 (m, 2H, $COCH_2CH_2$), 2.46 (m, 2H, $COCH_2CH_2$), 3.93 – 4.11 (m, 3H, H-5, H-6a, H-6b), 5.21 (dd, 1H, $J_{3,4}$ = 2.9 Hz, $J_{3,2}$ = 9.9 Hz, H-3), 5.29 (m, 2H, NCH=C*H*, H-2), 5.44 (d, 1H, $J_{4,3}$ = 2.9 Hz, H-4), 5.91 (d, 1H, $J_{1,2}$ = 9.2 Hz, H-1), 6.24 (d, J = 8.1 Hz, NCH). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 19.28 ($COCH_2$ CH_2), 26.53, 26.97, 27.54 ($PivCH_3$), 31.51 ($COCH_2$), 38.68, 38.71, 38.77, 39.03 ($PivC_t$), 60.73 (C-6), 66.23, 66.83, 71.51, 73.04 (C-5, C-4, C-3, C-2), 78.51 (C-1), 107.74 (NCH=*C*H), 123.79 (N*C*H=C), 169.60 (NC=O), 176.49, 176.70, 177.00, 177.77 (PivC=O).

Synthesis of pyridine-2- and hydropyridin-2-thiones – General procedure

To the solution of the corresponding *N*-galactosyl-dehydropiperidin-2-one or *N*-galactosyl-pyrid-2-one in dry toluene, Lawesson's reagent [9] was added. The solution was stirred and heated under reflux. After completion of the conversion (TLC monitoring) and cooling to r. t., ethyl acetate (mL) and water (50 mL) were added. The organic solution was dried with $MgSO_4$, and the solvent was evaporated *in vacuo*. The remaining residue was purified by flash chromatography.

*N-(2,3,4,6-Tetra-O-pivaloyl-β-D-galactopyranosyl)pyridine-2(1H)-thione (**10**)*

Educt *N*-(2,3,4,6-tetra-*O*-pivaloyl-β-D-galactopyranosyl)pyridine-2(1*H*)-one [8] (**5**): 0.5 g (0.84 mmol), 170 mg (0.42 mmol, 0.5 equiv.) of Lawesson's reagent; reaction time: 18 h. Yield: 0.327 g (64 %), yellow, amorphous solid, R_f = 0.52 (cyclohexane-ethyl acetate 2 : 1), $[\alpha]_D^{25}$: 170.51 (c = 1.0; $CHCl_3$). – MS ((+)-ESI): m/z = 632.34 $[M+Na]^+$. – HRMS ((+)-ESI): m/z = 632.2869 $[M+Na]^+$ (calcd.: 632.2869). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.01, 1.09, 1.14, 1.29 (4s, 36H, $PivCH_3$), 4.05 (dd, 1H, $J_{6a,5}$ = 7.7 Hz, $J_{6a,6b}$ = 11.1 Hz, H-6a), 4.14 (dd, 1H, $J_{6b,5}$ = 6.3 Hz, $J_{6b,6a}$ = 11.1 Hz, H-6b), 4.30 (t, 1H, J = 6.9 Hz, H-5), 5.39 (dd, 1H, $J_{3,4}$ = 2.9 Hz, $J_{3,2}$ = 9.9 Hz, H-3), 5.50 (m, 2H, $J_{4,3}$ = 2.9 Hz, $J_{2,1}$ = 9.6 Hz, H-4, H-2), 6.63 (dt, 1H, J = 1.1 Hz, J = 6.9 Hz, NCH=*CH*), 7.04 (dt, 1H, J = 1.5 Hz, J = 6.9 Hz, N*CH*=CH), 7.54 (d, 1H, J = 8.5 Hz, CSCH), 7.65 (bd, 2H, J = 8.8 Hz, CSCH=*CH*, H-1). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 26.99, 26.90, 27.02, 27.26 ($PivCH_3$), 38.70, 38.74, 38.86, 39.09 ($PivC_t$), 60.42 (C-6), 66.72, 68.55, 71.06, 74.24 (C-5, C-4, C-3, C-2), 84.59 (C-1), 113.19 (NCH=*CH*), 133.62 (N*CH*=CH), 135.57, 136.26 (CS*CH*, CSCH=*CH*), 176.35, 176.83, 177.25, 177.71 (PivC=O), 182.93 (C=S).

*N-(2,3,4,6-Tetra-O-pivaloyl-β-D-galactopyranosyl)piperidin-2-thione (**11**)*

Educt *N*-(2,3,4,6-tetra-*O*-pivaloyl-β-D-galactopyranosyl)-piperidin-2-one (**8**): 2 g (3.34 mmol), 1.35 g (3.34 mmol, 1 equiv.) of Lawesson's reagent; reaction time: 8 h. Yield: 1.95 g (95 %), colorless amorphous solid, R_f = 0.74 (cyclohexane-ethyl acetate 3 : 1), $[\alpha]_D^{25}$: 6.69 (c = 1.0; $CHCl_3$). – MS (FD): m/z = 614.4 $[M+H]^+$. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.09, 1.10, 1.14, 1.25 (4s, 36H, $PivCH_3$), 1.36 – 1.90 (m, 4H, $NCH_2CH_2CH_2$), 2.81 (td, 1H, J = 17.6 Hz, J = 6.9 Hz, $CSCH_2^a$), 3.03 (td, 1H, J = 17.6 Hz, J = 6.3 Hz, $CSCH_2^b$), 3.60 (m, 2H, NCH_2), 3.92 – 4.17 (m, 3H, H-5, H-6a, H-6b), 5.29 (dd, 1H, $J_{3,4}$ = 3.3 Hz, $J_{3,2}$ = 9.9 Hz, H-3), 5.42 (m, 2H, $J_{4,3}$ = 3.3 Hz, $J_{2,1}$ = 9.2 Hz, $J_{2,3}$ = 9.9 Hz, H-4, H-2), 7.13 (d, 1H, $J_{1,2}$ = 9.2 Hz, H-1). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 19.54, 22.05 ($NCH_2CH_2CH_2$), 27.03, 27.12, 27.21 ($PivCH_3$), 38.70, 38.73, 38.89, 39.04 ($PivC_t$), 42.65, 43.66 (NCH_2, $CSCH_2$), 60.49 (C-6), 66.12, 66.69, 71.27, 73.10 (C-2, C-3, C-4, C-5), 84.12 (C-1), 176.44, 176.91, 177.70, 177.74 (PivC=O), 205.95 (C=S). –

$C_{31}H_{51}NO_9S$ (613.32): calcd. C 60.66, H 8.37, N 2.28; found C 60.62, H 8.27, N 2.11.

*3,4-Dihydro-N-(2,3,4,6-tetra-O-pivaloyl-β-D-galactopyranosyl)pyridine-2(1H)-thione (**12**)*

Educt 3,4-dihydro-*N*-(2,3,4,6-tetra-*O*-pivaloyl-β-D-galactopyranosyl)pyridine-2(1*H*)-one (**9**): 2 g (3.36 mmol), 679 mg (1.68 mmol, 0.5 equiv.) of Lawesson's reagent; reaction time: 3 h. Yield: 1.81 g (88 %), colorless amorphous solid, R_f = 0.74 (cyclohexane-ethyl acetate 2 : 1), $[\alpha]_D^{25}$: 88.60 (c = 1.0; $CHCl_3$). – MS ((+)-ESI): m/z = 634.345 $[M+Na]^+$. – HRMS ((+)-ESI): m/z = 634.3044 $[M+Na]^+$ (calcd.: 634.3026). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.08, 1.14, 1.26 (3s, 36H, $PivCH_3$), 2.08 (m, 2H, $CSCH_2CH_2$), 3.02 (m, 2H, $CSCH_2$), 3.95 – 4.18 (m, 3H, H-5, H-6a, H-6b), 5.27 (dd, 1H, $J_{3,4}$ = 2.9 Hz, $J_{3,2}$ = 9.9 Hz, H-3), 5.39 (t, 1H, $J_{1,2}$ = 9.2 Hz, $J_{2,3}$ = 9.9 Hz, H-2), 5.46 (d, 1H, $J_{4,3}$ = 2.9 Hz, H-4), 5.64 (dd, 1H, J = 7.7 Hz, J = 8.5 Hz, NCH=*CH*), 6.37 (d, 1H, J = 8.1 Hz, NCH), 7.06 (d, 1H, $J_{1,2}$ = 9.2 Hz, H-1). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 18.56 ($CSCH_2CH_2$), 27.03, 27.17, 27.23 ($PivCH_3$), 38.73, 38.88, 39.06 ($PivC_t$), 41.99 ($CSCH_2$), 60.52 (C-6), 66.65, 66.93, 71.39, 73.30 (C-5, C-4, C-3, C-2), 82.82 (C-1), 112.95 (NCH=*CH*), 124.05 (N*CH*=CH), 176.46, 176.98, 177.73 (PivC=O), 202.11 (C=S). – $C_{31}H_{49}NO_9S$ (611.31): calcd. C 60.86, H 8.07, N 2.07, S 5.24; found C 60.63, H 8.11, N 2.15, S 4.78.

*(4R)-4-Ethyl-3,4-dihydro-N-(2,3,4,6-tetra-O-pivaloyl-β-D-galactopyranosyl)pyridine-2(1H)-thione (**14a**)*

Educt (4*R*)-4-ethyl-3,4-dihydro-*N*-(2,3,4,6-tetra-*O*-pivaloyl-β-D-galactopyranosyl)pyridine-2(1*H*)-one [8] (**7a**): 443 mg (0.71 mmol), 144 mg (0.36 mmol, 0.5 equiv.) of Lawesson's reagent; reaction time: 3 h. Yield: 380 mg (84 %), yellow amorphous solid, R_f = 0.6 (cyclohexane-ethyl acetate 5 : 1), $[\alpha]_D^{25}$: 68.47 (c = 1.0; $CHCl_3$). – MS ((+)-ESI): m/z = 662.37 $[M+Na]^+$. – HRMS ((+)-ESI): m/z = 662.3364 $[M+Na]^+$ (calcd.: 662.3339). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.85 (t, 3H, J = 7.3 Hz, $-CH_3$), 1.08, 1.09, 1.13, 1.26 (4s, 36H, $PivCH_3$), 1.60 (m, 2H, CH_2CH_3), 2.15 – 2.3 (m, 1H, CHethyl), 2.69 – 3.17 (m, 1H, $CSCH_2^a$), 3.10 (m, 1H, $CSCH_2^b$), 3.95 – 4.17 (m, 3H, H-5, H-6a, H-6b), 5.25 (m, 1H, H-3), 5.44 (t, 1H, $J_{2,1}$ = 9.2 Hz, $J_{2,3}$ = 9.9 Hz, H-2), 5.45 (d, 1H, $J_{4,3}$ = 2.5 Hz, H-4), 5.56 (m, 1H, NCH=*CH*), 6.34 (d, 1H, J = 7.7 Hz, N*CH*=CH), 7.02 (d, 1H, $J_{1,2}$ = 9.2 Hz, H-1). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = (signals of the major rotamer) 17.73 (CH_3), 26.50 (CH_2CH_3), 27.00, 27.03, 27.19, 27.23 ($PivCH_3$), 31.39 (CHethyl), 38.38, 38.73, 38.80, 39.06 ($PivC_{quart.}$), 47.91 ($CSCH_2$), 60.60 (C-6), 66.69, 66.92, 71.39, 73.28 (C-5, C-4, C-3, C-2), 82.78 (C-1), 116.25 (NCH=*CH*), 123.62 (N*CH*=CH), 176.48, 177.00, 177.75 (PivC=O), 202.15 (C=S).

*(4R)-3,4-Dihydro-4-propyl-N-(2,3,4,6-tetra-O-pivaloyl-β-D-galactopyranosyl)pyridine-2(1H)-thione (**14b**)*

Educt (4*R*)-3,4-dihydro-4-propyl-*N*-(2,3,4,6-tetra-*O*-pivaloyl-β-D-galactopyranosyl)pyridine-2(1*H*)-one (**7b**): 0.2 g (0.313 mmol), 65 mg (0.16 mmol, 0.5 equiv.) of Lawesson's reagent; reaction time: 16 h. Yield: 0.15 g (74 %), yellow amorphous solid, R_f = 0.35 (cyclohexane-ethyl acetate 8 : 1), $[\alpha]_D^{25}$: 86.10 (c = 1.0; $CHCl_3$). – MS ((+)-ESI): m/z = 676.50 $[M+Na]^+$. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (t, 3H, $-CH_3$), 1.07, 1.09, 1.14, 1.28 (4s, 36H, $PivCH_3$), 1.31 (m, 4H, $(CH_2)_2CH_3$), 2.18 (CHpropyl), 2.75 (dd, 1H, J = 10.6 Hz, J = 16.2 Hz, $CSCH_2^a$), 3.07 (dd, 1H, J = 5.9 Hz, J = 16.2 Hz, $CSCH_2^b$), 3.95 – 4.17 (m, 3H, H-5, H-6a, H-6b), 5.27 (dd, 1H, $J_{3,4}$ = 2.9 Hz, $J_{3,2}$ = 9.9 Hz, H-3), 5.39 (t, 1H, $J_{2,1}$ = 9.2 Hz, $J_{2,3}$ = 9.9 Hz, H-2), 5.46 (d, 1H, $J_{4,3}$ = 2.9 Hz, H-4), 5.55 (dd, 1H, J = 2.9 Hz, J = 7.7 Hz, NCH=*CH*), 6.72 (d, 1H, J = 7.7 Hz, N*CH*=CH), 7.03 (d, 1H, $J_{1,2}$ = 9.2 Hz, H-1). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = (signals of the major rotamer) 13.90 (CH_3), 19.36 (CH_2CH_3), 27.03, 27.17, 27.23 ($PivCH_3$), 29.56 (CHpropyl), 35.69 ($CH_2CH_2CH_3$), 38.70, 38.74, 38.79, 39.06 ($PivC_t$), 48.21 ($CSCH_2$), 60.61 (C-6), 66.69, 66.95, 71.39, 73.30 (C-5, -4, C-3, C-2), 82.78 (C-1), 118.18 (NCH=*CH*), 123.08 (NCH), 176.47, 177.00, 177.74 (PivC=O), 202.08 (C=S). – $C_{34}H_{55}NO_9S$ (653.35): calcd. C 62.45, H 8.48, N 2.14, S 4.90; found C 62.05, H 8.41, N 2.06, S 5.20.

*(4S)-4-Isopropyl-N-(2,3,4,6-tetra-O-pivaloyl-β-D-galactopyranosyl)-5,6-dehydro-piperidin-2-thione (**14c**)*

Educt (4*S*)-3,4-dihydro-4-isopropyl-*N*-(2,3,4,6-tetra-*O*-pivaloyl-β-D-galactopyranosyl)pyridine-2(1*H*)-one [8] (**7c**): 2.79 g (4.37 mmol), 1.76 g (4.37 mmol, 1 equiv.) of Lawesson's reagent; reaction time: 3 h. Yield: 2.13 g (75 %), yellow amorphous solid, R_f = 0.69 (cyclohexane-ethyl acetate 3 : 1), $[\alpha]_D^{25}$: 40.59 (c = 1.0; $CHCl_3$). – MS (FD): m/z = 653.36 $[M]^+$. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (d, 6H, J = 6.6 Hz, $(CH(CH_3)_2)$, 1.08, 1.09, 1.13, 1.26 (4s, 36H, $PivCH_3$), 1.61 (m, 1H, *CH*Me_2),2.08 (m, 1H, CH*i*propyl), 2.80 – 3.12 (m, 2H, $CSCH_2$), 3.98 – 4.17 (m, 3H, H-5, H-6a, H-6b), 5.27 (dd, 1H, $J_{3,4}$ = 2.9 Hz, $J_{3,2}$ = 9.9 Hz, H-3), 5.44 (m, H-2, H-4), 5.57 (m, 1H, NCH=*CH*), 6.36 (d, 1H, J = 8.1 Hz, NCH), 7.02 (d, 1H, $J_{1,2}$ = 9.2 Hz, H-1). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = (signals of the major rotamer) 17.60, 13.39 ($CH(CH_3)_2$), 27.02, 27.12, 27.18, 27.26 ($PivCH_3$), 30.37, 36.59 (CH*i*propyl, *CH*Me_2), 38.70, 38.73, 38.80, 39.06 ($PivC_{quart.}$), 45.68 ($CSCH_2$), 60.67 (C-6), 66.56, 66.87, 71.38, 73.31 (C-5, -4, C-3, C-2), 82.82 (C-1), 116.25 (NCH=*CH*), 123.62 (N*CH*=CH), 176.47, 176.97, 177.71 (PivC=O), 202.49 (C=S). – $C_{34}H_{55}NO_9S$ (653.35): calcd. C 62.45, H 8.48, N 2.14, S 4.90; found C 62.38, H 8.59, N 2.07, S 4.84.

*(4R)-3,4-Dihydro-4-(4-fluoro-phenyl)-N-(2,3,4,6-tetra-O-pivaloyl-β-D-galactopyranosyl)pyridine-2(1H)-thione (**14d**)*

Educt (4*R*)-3,4-dihydro-4-(4-fluoro-phenyl)-*N*-(2,3,4,6-tetra-*O*-pivaloyl-β-D-galactopyranosyl)pyridine-2(1*H*)-one [8] (**7d**): 0.2 g (0.29 mmol), 59 mg (0.145 mmol, 0.5 equiv.) of Lawesson's reagent; reaction time: 5 h. Yield: 0.128 g (62 %), yellow amorphous solid, R_f = 0.4 (cyclohexane-ethyl acetate 6 : 1), $[\alpha]_D^{25}$: 95.11 (*c* = 1.0; $CHCl_3$). – MS ((+)-ESI): *m*/*z* = 728.38 $[M+Na]^+$. – HRMS ((+)-ESI): *m*/*z* = 728.3277 $[M+Na]^+$ (calcd.: 728.3277). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.10, 1.11, 1.15, 1.27 (4s, 36H, $PivCH_3$), 3.11 (dd, 1H, *J* = 9.6 Hz, *J* = 16.2 Hz, $CSCH_2^a$), 3.26 (dd, 1H, *J* = 6.6 Hz, *J* = 16.2 Hz, $CSCH_2^b$), 3.45 (m, 1H, CHaryl), 4.01 – 4.20 (m, 3H, H-5, H-6a, H-6b), 5.30 (dd, 1H, $J_{3,4}$ = 2.9 Hz, $J_{3,2}$ = 9.9 Hz, H-3), 5.43 (t, 1H, $J_{2,1}$ = 9.2 Hz, $J_{2,3}$ = 9.9 Hz, H-2), 5.49 (d, 1H, $J_{4,3}$ = 2.9 Hz, H-4), 5.70 (dd, 1H, *J* = 4.1 Hz, *J* = 8.1 Hz, NCH=*CH*), 6.52 (dd, 1H, *J* = 1.8 Hz, *J* = 8.1 Hz, NCH), 6.96 (m, 2H, aryl), 7.06 (d, 1H, $J_{1,2}$ = 9.2 Hz, H-1), 7.10 (m, 2H, aryl). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 27.02, 27.05, 27.20, 27.24 ($PivCH_3$), 35.78 (CHaryl), 38.71, 38.76, 38.94, 39.07 ($PivC_t$), 50.14 ($CSCH_2$-), 60.69 (C-6), 66.68, 67.04, 71.27, 73.40 (C-5, C-4, C-3, C-2), 82.87 (C-1), 115.20 (NCH=*CH*), 115 (d, $^2J(^{13}C,^{19}F)$ = 21 Hz, aryl), 124.17 (NCH), 128 (d, $^3J(^{13}C,^{19}F)$ = 8 Hz, aryl), 137.23 (*ipso*-aryl), 162 (d, $^1J(^{13}C,^{19}F)$ = 243 Hz, CF), 176.46, 176.97, 177.18, 177.76 (PivC=O), 200.28 (C=S).

*(4S)-4-(4-Fluorophenyl)-N-(2,3,4,6-tetra-O-pivaloyl-β-D-galactopyranosyl)piperidin-2-thione (**15**)*

Educt (4*S*)-4-(4-fluorophenyl)-*N*-(2,3,4,6-tetra-*O*-pivaloyl-β-D-galactopyranosyl)-piperidin-2-one **13d**: 0.2 g (0.29 mmol), 59 mg (0.145 mmol, 0.5 equiv.) of Lawesson's reagent; reaction time: 7 h. Yield: 0.202 g (98 %), yellow amorphous solid, R_f = 0.44 (cyclohexane-ethyl acetate 4 : 1), $[\alpha]_D^{25}$: 47.79 (*c* = 1.0; $CHCl_3$). – MS ((+)-ESI): *m*/*z* = 730.44 $[M+Na]^+$. – HRMS ((+)-ESI): *m*/*z* = 708.3586 $[M+H]^+$ calcd.: 708.3582). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.10, 1.13, 1.14, 1.25 (4s, 36H, $PivCH_3$), 1.91, 2.24 (2m, 2H, NCH_2CH_2), 2.88 (m, 1H, CHaryl), 3.07 (dd, 1H, *J* = 9.2 Hz, *J* = 18.1 Hz, $CSCH_2^a$), 3.27 (dd, 1H *J* = 5.9 Hz, *J* = 18.1 Hz, $CSCH_2^b$), 3.57, 3.74 (2m, 2H, NCH_2), 3.95 – 4.18 (m, 3H, H-5, H-6a, H-6b), 5.31 (dd, 1H, $J_{3,4}$ = 2.9 Hz, $J_{3,2}$ = 9.9 Hz, H-3), 5.46 (m, 2H, H-2, H-4), 6.97 (m, 2H, aryl), 7.11 (m, 2H, aryl), 7.19 (d, 1H, $J_{1,2}$ = 9.2 Hz, H-1). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 27.02, 27.05, 27.17, 27.20 ($PivCH_3$), 30.12 (NCH_2CH_2), 36.86 (CHaryl), 38.70, 38.74, 38.92, 39.04 ($PivC_t$), 43.49 (NCH_2), 49.63 ($CSCH_2$-), 60.55 (C-6), 66.17, 66.86, 71.29, 73.15 (C-5, C-4, C-3, C-2), 84.18 (C-1), 115 (d, $^2J(^{13}C,^{19}F)$ = 21 Hz, aryl), 128 (d, $^3J(^{13}C,^{19}F)$ = 8 Hz, aryl), 139.10 (*ipso*-aryl), 162 (d, $^1J(^{13}C,^{19}F)$ = 243 Hz, CF), 176.41, 176.91, 177.73, 177.82 (PivC=O), 204.18 (C=S). – $C_{37}H_{54}FNO_9S$ (707.35): calcd. C 62.78, H 7.69, N 1.98; found C 61.56, H 8.00, N 1.77.

Reductive Sulfurization – General procedure

To a solution of the thiolactam in dry isopropanol freshly prepared, neutrally washed Raney nickel was added. The suspension was stirred under hydrogen atmosphere at 70 °C and the conversion montored by TLC. After completion of the reaction, the catalyst was filterred off through Celite and thouroughly washed with isopropanol. The combined filtrates were evaporated to dryness *in vacuo*, and the remaining crude product was purified by flash chromatography.

*4-Ethyl-N-(2,3,4,6-tetra-O-pivaloyl-β-D-galactopyranosyl)-piperidine (**16a**)*

Educt (4*R*)-4-ethyl-3,4-dihydro-*N*-(2,3,4,6-tetra-*O*-pivaloyl-β-D-galactopyranosyl)pyridine-2(1*H*)−thione (**14a**): 0.24 g (0.377 mmol) in 20 mL of dry *iso*-propanol, 1.5 g of Ni-Al-alloy; reaction time: 3 d. Yield: 0.23 g (99 %) colorless amorphous solid, R_f = 0,6 (cyclohexane-ethyl acetate 6 : 1), $[\alpha]_D^{25}$: −6.24 (*c* = 1.0; $CHCl_3$). – MS ((+)-ESI): *m*/*z* = 634.3 $[M+Na]^+$. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.82 (t, 3H, -CH_3), 1.08, 1.12, 1.15, 1.23 (4s, 38H, CH_2CH_3, $PivCH_3$), 1.58 (m, 5H, CHethyl, 2 × NCH_2CH_2), 2.34 (t, 1H, *J* = 11.4 Hz, NCH_2^a), 2.70 (bd, 1H, *J* = 11.4 Hz, NCH_2^b), 2.74 (bt, 1H, *J* = 11.1 Hz, NCH_2^c), 3.06 (bd, 1H, *J* = 11.4 Hz, NCH_2^d), 3.82 (t, 1H, $J_{5,6a}$ = 6.9 Hz, $J_{5,6b}$ = 6.6 Hz, H-5), 3.90 (dd, 1H, $J_{6a,5}$ = 6.9 Hz, $J_{6a,6b}$ = 10.7 Hz, H-6a), 3.93 (d, 1H, $J_{1,2}$ = 9.2 Hz, H-1), 4.10 (m, 1H, $J_{6b,5}$ = 6.6 Hz, $J_{6b,6a}$ = 10.7 Hz, H-6b), 5.09 (dd, 1H, $J_{3,4}$ = 2.9 Hz, $J_{3,2}$ = 9.9 Hz, H-3), 5.34 (m, 2H, $J_{4,3}$ = 2.9 Hz, $J_{2,1}$ = 9.2 Hz, $J_{2,3}$ = 9.9 Hz, H-4, H-2). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 11.23 (-CH_3), 27.07, 27.17, 27.28 ($PivCH_3$), 31.99, 32.77 (2× NCH_2CH_2), 37.69 (CHethyl), 38.63, 38.70, 39.05 ($PivC_t$), 44.19, 52.00 (2× NCH_2), 61.38 (C-6), 65.03, 67.28, 71.67, 71.95 (C-5, C-4, C-3, C-2), 94.42 (C-1), 176.80, 176.93, 177.27, 177.91 (PivC=O).

*4-Propyl-N-(2,3,4,6-tetra-O-pivaloyl-β-D-galactopyranosyl)piperidine (**16b**)*

Educt (4*R*)-4-propyl-3,4-dihydro-*N*-(2,3,4,6-tetra-*O*-pivaloyl-β-D-galactopyranosyl)pyridine-2(1*H*)−thione (**14b**): 0.132 g (0.2 mmol) in 20 mL of dry isopropanol, 0.5 g Ni-Al alloy; reaction time: 3 d. Yield: 0.105 g (83 %) colorless oil, R_f = 0,28 (cyclohexane-ethyl acetate 20 : 1), $[\alpha]_D^{25}$: −8.94 (*c* = 1.0; $CHCl_3$). – MS ((+)-ESI): *m*/*z* = 626.44 $[M+H]^+$. – HRMS ((+)-ESI): *m*/*z* = 626.4260 $[M+H]^+$ (calcd.: 626.4268). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.83 (t, 3H, -CH_3), 1.08, 1.12, 1.15, 1.22 (4s, 40H, -$(CH_2)_2CH_3$, $PivCH_3$), 1.60 (m, 5H, CHpropyl, 2× NCH_2CH_2), 2.34 (t,

1H, J = 11.7 Hz, NCH_2^a), 2.69 (bd, 1H, J = 10.7 Hz, NCH_2^b), 2.77 (bt, 1H, J = 11.4 Hz, NCH_2^c), 3.06 (bd, 1H, J = 11.4 Hz, NCH_2^d), 3.81 (t, 1H, $J_{5,6a}$ = 6.9 Hz, $J_{5,6b}$ = 6.6 Hz, H-5), 3.90 (dd, 1H, $J_{6a,5}$ = 6.9 Hz, $J_{6a,6b}$ = 10.7 Hz, H-6a), 4.02 (d, 1H, $J_{1,2}$ = 9.2 Hz, H-1), 4.09 (m, 1H, $J_{6b,5}$ = 6.6 Hz, $J_{6b,6a}$ = 10.7 Hz, H-6b), 5.08 (dd, 1H, $J_{3,4}$ = 2.9 Hz, $J_{3,2}$ = 9.9 Hz, H-3), 5.34 (m, 2H, $J_{4,3}$ = 2.9 Hz, $J_{2,1}$ = 9.2 Hz, $J_{2,3}$ = 9.9 Hz, H-4, H-2). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.21 (-CH_3), 19.72 (CH_2CH_3), 27.00, 27.05, 27.14, 27.24 (PivCH$_3$), 32.33, 33.14 (2× NCH_2CH_2), 35.61 (CHpropyl), 38.61, 38.67, 38.95 (PivC$_t$), ($CH_2CH_2CH_3$), 39.01 (PivC$_t$), 44.17, 52.54 (2× NCH_2), 61.34 (C-6), 65.00, 67.25, 71.63, 71.93 (C-5, C-4, C-3, C-2), 94.40 (C-1), 176.77, 176.88, 177.22, 177.86 (PivC=O).

Detachment of the carbohydrate auxiliary from piperidines – General procedure

The *N*-galactosyl-piperidine (0.5 mmol) dissolved in methanol (15 mL) and 1N solution of HCl in methanol (6 mL) was stirred for 24 h. Subsequently, HCl and the solvent were removed *in vacuo*, and the remaining crude piperidinium chloride was stirred in water (50 mL) and diethyl ether (50 mL) for 5 min. The separated water solution was extracted twice with diethyl ether (50 mL). The combined ether solutions were washed with water (50 mL). The ether solution contained the tetra-*O*-pivaloyl-galactose. The combined water solutions were evaporated to dryness to give the piperidine hydrochloride.

*N-(Benzyloxycarbonyl)-4-ethyl-piperidine (**17**)*

The hydrochloride of 4-ethyl-piperidine was obtained from 4-ethyl-*N*-(2,3,4,6-tetra-*O*-pivaloyl-β-D-galactopyranosyl)piperidine (**16a**) (220 mg, 0.36 mmol) in methanol (10 mL) and 4 mL of 1 N methanolic HCl (reaction time 24 h). Yield: 37 mg (70 %), colorless amorphous solid. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 0.81 (t, 3H, -CH_3), 1.16 (q, 2H, CH_2CH_3), 1.29 (m, 3H, CHethyl, $NCH_2CH_2^a$, $NCH_2CH_2^b$), 1.71 (bd, 2H, J = 11.7 Hz, $NCH_2CH_2^c$, $NCH_2CH_2^d$), 2.75 (q, 2H, J = 11.8 Hz, NCH_2^a, NCH_2^b), 3.16 (bd, 2H, J = 12.1 Hz, NCH_2^c, NCH_2^d), 9.01, 9.24 (2 bs, NH). – ^{13}C NMR (75.5 MHz, [D$_6$]DMSO): δ = 10.93 (-CH_3), 28.02, 28.23 (CH_2CH_3, NCH_2CH_2), 34.78 (CHethyl), 43.10 (NCH_2).

This hydrochloride was dissolved in 2 mL of water. After addition 2 mL of sat. Na_2CO_3 solution, the mixture was stirred for 1 h at r. t. Subsequently, benzyl chloroformate (53 μL, 0.38 mmol, 1.5 equiv.) was added and the mixture stirred for 2 h. The solution was extracted three times with diethyl ether (30 mL), the combined organic solutions were dried with $MgSO_4$, and the solvent was evaporated *in vacuo*. Purification of the crude product was performed by flash chromatography.

Yield: 52 mg (84 %) **17**, colorless oil, R_f = 0.14 (cyclohexane-ethyl acetate 4 : 1). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (t, 3H, J = 7 Hz, -CH_3), 1.06 (m, 2H, $NCH_2CH_2^a$, $NCH_2CH_2^b$), 1.22 (q, 3H, J = 7 Hz, CHethyl, CH_2CH_3), 1.64 (bd, 2H, J = 12.5 Hz, $NCH_2CH_2^c$, $NCH_2CH_2^d$), 2.72 (bt, 2H, J = 12.1 Hz, NCH_2^a, NCH_2^b), 4.12 (m, 2H, NCH_2^c, NCH_2^d), 5.09 (s, 2H, CH_2Ph), 7.33 (m, 5H, aryl). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 11.13 (-CH_3), 29.11, 31.74 (CH_2CH_3, NCH_2CH_2), 37.59 (CHethyl), 44.30 (NCH_2), 66.86 (CH_2Ph), 127.78, 127.84, 128.43 (aryl), 137.02 (*ipso*-aryl), 155.29 (NC=O).

C-3 Alkylation of N-galactosyl piperidin-2-ones - General procedure

To the solution of the *N*-galactopyranosyl-piperidin-2-one in THF at −78 °C, lithium hexamethyldisilazane (LiHMDS, 1 M solution in THF) was added. After 1 h stirring at this temperature, the alkyl iodide was added and the stirring continued for 15 h at the given temperature. The reaction was terminated by addition of sat. NH_4Cl solution (20 mL) at the low temperature. After warming to r. t., the solution was extracted three times with diethyl ether (100 mL). The combined organic solutions were dried with $MgSO_4$, the solvent was evaporated *in vacuo*, and the residue was purified by flash chromatography.

*3-Butyl-1-(2,3,4,6-tetra-O-pivaloyl-β-D-galactopyranosyl)-piperidin-2-one (**18a**)*

The reaction was carried out at −10 °C starting from piperidinone **8** (0.2 g, 0.335 mmol) dissolved in 3 mL of dry THF, treated with 0.57 mL (0.57 mmol, 1.7 equiv.) of LiHMDS solution, and using 0.114 mL (1.0 mmol, 3 equiv.) of butyl iodide. Purification was achieved by flash chromatography (20 × 1 cm, cyclohexane-ethyl acetate 6 : 1). Yield: 90 mg (41 %), colorless amorphous solid, R_f = 0.37 (cyclohexane-ethyl acetate 4 : 1). Diastereomeric ratio: 91 : 9 (^{1}H NMR after chromatography and analytical HPLC). Analytical HPLC: Chiral Pack AD; hexane-*iso*-propanol 98 : 2, isocratic, R_t (min): 4.65 (major diastereomer), 5.80 (minor diastereomer), $[\alpha]_D^{25}$: 24.59 (c = 1.0, $CHCl_3$). – MS ((+)-ESI): m/z = 676.43 $[M+Na]^+$. – HRMS ((+)-ESI): m/z = 654.4220 $[M+Na]^+$ (calcd.: 654.4217).

The reaction performed at −78 °C gave 80 mg (35 %) of **18a** as a colorless solid, R_f = 0.37 (cyclohexane: ethyl acetate 4 : 1). Diastereomeric ratio: 96 : 4 (^{1}H NMR after chromatography and analytical HPLC). Analytical HPLC: Chiral Pack AD; hexane-*iso*-propanol 98 : 2 isocratic, R_t (min): 4.70 (major diastereomer), 5.85 (minor diastereomer), $[\alpha]_D^{25}$: 30.81 (c = 0.5, $CHCl_3$). – HRMS ((+)-ESI): m/z = 654.4196 $[M+H]^+$ (calcd.: 654.4217). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = (signals of the major diastereomer): 0.88 (t, 3H, CH_3), 1.08, 1.13, 1.23 (3s, 38H, CH_2CH_3, PivCH$_3$), 1.25 (m, 4H,

*(CH$_2$)$_2$*CH$_3$), 1.86 (m, 4H, NCH$_2$*(CH$_2$)$_2$*), 2.12 (m, 1H, CO*CH*butyl), 3.32 (m, 2H, NCH$_2$), 3.90, 4.12 (2m, 3H, H-5, H-6a, H-6b), 5.18 (dd, 1H, $J_{3,4}$ = 2.9 Hz, $J_{3,2}$ = 9.9 Hz, H-3), 5.35 (t, 1H, $J_{2,1}$ = 9.2 Hz, $J_{2,3}$ = 9.9 Hz, H-2), 5.41 (d, 1H, $J_{4,3}$ = 2.9 Hz, H-4), 5.90 (d, 1H, $J_{1,2}$ = 9.2 Hz, H-1). – ^{13}C NMR (75.5 MHz, CDCl$_3$): δ = (signals of the major diastereomer): 13.99 (CH$_3$), 21.36, 22.72, 25.79 (*(CH$_2$)$_2$*CH$_3$, N(CH$_2$)$_2$*CH$_2$*), 26.017, 27.05, 27.14, 27.21 (PivCH$_3$), 29.23, 31.24 (*CH$_2$*(CH$_2$)$_2$CH$_3$, NCH$_2$*CH$_2$*), 38.68, 38.79, 39.03 (PivC$_t$), 41.17 (NCH$_2$), 41.59 (CO*CH*), 60.73 (C-6), 65.16, 66.86, 71.53, 72.76 (C-2, C-3, C-4, C-5), 79.72 (C-1), 173.82 (NC=O), 176.55, 177.00, 177.43, 177.80 (PivC=O).

*3-Methyl-N-(2,3,4,6-tetra-O-pivaloyl-β-D-galactopyranosyl)piperidin-2-one (**18b**)*

The reaction was carried out at −78 °C starting from piperidinone **8** (0.2 g, 0.335 mmol) dissolved in 3 mL of dry THF, treated with 0.57 mL (0.57 mmol, 1.7 equiv.) of LiHMDS solution, and using 63 μL (1.0 mmol, 3 equiv.) of methyl iodide. Purification was achieved by flash chromatography (20 × 1 cm, cyclohexane-ethyl acetate 5 : 1). Yield: 171 mg (83 %), colorless amorphous solid, R_f = 0.3 (cyclohexane-ethyl acetate 4 : 1). Diastereomeric ratio: 67 : 33 (^{1}H NMR after chromatography and analytical HPLC). Analytical HPLC: Chiral Pack AD; hexane-*iso*-propanol 98 : 2 isocratic, R_t (min): 4.95 (minor diastereomer), 5.77 (major diastereomer), $[\alpha]_D^{25}$: 26.50 (*c* = 1.0, CHCl$_3$). – MS ((+)-ESI): *m/z* = 634.38 [M+Na]$^+$. – HRMS ((+)-ESI): *m*/z = 634.3586 [M+Na]$^+$ (calcd.: 634.3567). – ^{1}H NMR (300 MHz, CDCl$_3$): δ = (signals of the major diastereomer) 1.07, 1.08, 1.13, 1.23 (4s, 39H, CH$_3$, PivCH$_3$), 1.69, 1.86 (2m, 4H, NCH$_2$*(CH$_2$)$_2$*), 2.24 (m, 1H, CO*CH*Me), 3.33 (m, 2H, NCH$_2$), 3.93, 4.07 (2m, 3H, H-5, H-6a, H-6b), 5.22 (dd, 1H, $J_{3,4}$ = 2.9 Hz, $J_{3,2}$ = 9.9 Hz, H-3), 5.35 (t, 1H, $J_{2,1}$ = 9.6 Hz, $J_{2,3}$ = 9.9 Hz, H-2), 5.41 (d, 1H, $J_{4,3}$ = 2.9 Hz, H-4), 5.90 (d, 1H, $J_{1,2}$ = 9.2 Hz, H-1). – ^{13}C NMR (75.5 MHz, CDCl$_3$): δ = (signals of the major diastereomer) 17.43 (CH$_3$), 21.34 (N(CH$_2$)$_2$*CH$_2$*), 26.97, 27.02, 27.08, 27.17 (PivCH$_3$), 28.78 (NCH$_2$*CH$_2$*), 36.60 (NCH$_2$), 38.67, 38.70, 38.77, 39.01 (PivC$_t$), 41.40 (CO*CH*), 60.65 (C-6), 65.19, 66.80, 71.48, 72.71 (C-2, C-3, C-4, C-5), 79.68 (C-1), 174.24 (NC=O), 176.50, 176.97, 177.41, 177.77 (PivC=O).

*3,4-Dihydro-3-methyl-N-(2,3,4,6-tetra-O-pivaloyl-β-D-galactopyranosyl)pyridine-2(1H)-one (**19a**)*

The reaction was carried out at −78 °C starting from 5,6-dehydropiperidinone **9** (0.2 g, 0.335 mmol) dissolved in 3 mL of dry THF, treated with 0.57 mL (0.57 mmol, 1.7 equiv.) of LiHMDS solution, and using 63 μL (1.0 mmol, 3 equiv.) of methyl iodide. Purification was achieved by flash chromatography (20 × 1 cm, cyclohexane-ethyl acetate 8 : 1). – Yield: 89 mg (44 %), pale-yellow amorphous solid, R_f = 0.25 (cyclohexane-ethyl acetate 4 : 1). Diastereomeric ratio: 92 : 8 (^{1}H NMR and analytical HPLC). Analytical HPLC: Luna C18, gradient: acetonitrile-water 80 : 20 to 100 : 0 within 40 min, R_t (min): 21.62 (major diastereomer), 22.53 (minor diastereomer). $[\alpha]_D^{25}$: 17.74 (*c* = 1.0, CHCl$_3$). – MS ((+)-ESI): *m/z* = 632.3 [M+Na]$^+$. – HRMS ((+)-ESI): *m/z* = 632.3391 [M+Na]$^+$ (calcd.: 632.3411). – ^{1}H NMR (400 MHz, CDCl$_3$): δ = (signals of the major diastereomer) 1.06, 1.09, 1.14, 1.25 (4s, 36 H, CH$_3$, PivCH$_3$), 2.08, 2.28, 2.44 (3m, 3H, CH$_2$, CO*CH*Me), 3.91 – 4.14 (m, 3H, H-5, H-6a, H-6b), 5.22 (m, 2H, $J_{3,4}$ = 2.9 Hz, $J_{3,2}$ = 9.9 Hz, H-3, NCH=*CH*), 5.33 (t, 1H, $J_{2,1}$ = 9.2 Hz, $J_{2,3}$ = 9.9 Hz, H-2), 5.44 (d, 1H, $J_{4,3}$ = 2.9 Hz, H-4), 5.89 (d, 1H, $J_{1,2}$ = 9.2 Hz, H-1), 6.22 (d, 1H, J_f = 6.2 Hz, N*CH*=CH). – ^{13}C NMR (100.6 MHz, CDCl$_3$): δ = (signals of the major diastereomer: 15.58 (CH$_3$), 26.94, 27.00, 27.20, 27.24 (PivCH$_3$), 27.54 (CH$_2$), 35.72 (CO*CH*Me), 38.65, 38.68 38.74, 39.03 (PivC$_t$), 60.49 (C-6), 66.20, 66.74, 71.51, 73.00 (C-2, C-3, C-4, C-5), 78.79 (C-1), 106.29 (NCH=*CH*), 123.51 (NCH), 172.59 (NC=O), 176.50, 176.80, 176.97 177.70 (PivC=O).

*3-Butyl-3,4-dihydro-N-(2,3,4,6-tetra-O-pivaloyl-β-D-galactopyranosyl)pyridine-2(1H)-one (**19b**)*

The reaction was carried out at −78 °C starting from 5,6-dehydropiperidinone **9** (0.2 g, 0.335 mmol) dissolved in 3 mL of dry THF, treated with 0.57 mL (0.57 mmol, 1.7 equiv.) of LiHMDS solution, and using 0.114 mL (1.0 mmol, 3 equiv.) of butyl iodide. Purification was achieved by flash chromatography (20 × 1 cm, cyclohexane-ethyl acetate 9 : 1). Yield: 59 mg (27 %), pale-yellow waxy solid, R_f = 0.37 (cyclohexane-ethyl acetate 4 : 1). Diastereomeric ratio: 93 : 7 (^{1}H NMR and analytical HPLC). Analytical HPLC: Luna C18, gradient: acetonitrile-water 80 : 20 to 100 : 0 within 40 min, R_t (min): 32.95 (major diastereomer), 34.65 (minor diastereomer), $[\alpha]_D^{25}$: 23.26 (*c* = 1.0, CHCl$_3$). – MS ((+)-ESI): *m/z* = 674.4 [M+Na]$^+$. – HRMS ((+)-ESI): *m/z* = 674.3859 [M+Na]$^+$ (calcd.: 674.3880). – ^{1}H NMR (300 MHz, CDCl$_3$): δ = (signals of the major diastereomer): 0.86 (t, 3H, CH$_3$), 1.06, 1.08, 1.13, 1.25 (4s, 42 H, *(CH$_2$)$_3$*, PivCH$_3$), 2.07, 2.72 (2m, 3H, CH$_2$, CO*CH*butyl), 3.91 – 4.14 (m, 3H, H-5, H-6a, H-6b), 5.20 (m, 2H, $J_{3,4}$ = 2.9 Hz, $J_{3,2}$ = 9.9 Hz, H-3, NCH=*CH*), 5.32 (t, 1H, $J_{2,1}$ = 9.2 Hz, $J_{2,3}$ = 9.9 Hz, H-2), 5.43 (d, 1H, $J_{4,3}$ = 2.9 Hz, H-4), 5.88 (d, 1H, $J_{1,2}$ = 9.2 Hz, H-1), 6.20 (d, 1H, J_f = 7.7 Hz, N*CH*=CH). – ^{13}C NMR (75.5 MHz, CDCl$_3$): δ = (signals of the major diastereomer): 13.87 (CH$_3$), 22.49, 24.76 (2× CH$_2$), 26.76, 26.85, 27.09, 27.18 (PivCH$_3$), 29.10, 29.64 (2× CH$_2$), 38.65, 38.70, 38.76, 39.03 (PivC$_t$), 40.74 (CO*CH*), 60.79 (C-6), 66.32, 66.81, 71.57, 73.04 (C-2, C-3, C-4, C-5), 78.69 (C-1), 106.24 (NCH=*CH*), 123.38 (NCH), 172.10 (NC=O), 176.52, 176.77, 176.98, 177.71 (PivC=O).

*(4R)-3,4-Dihydro-3-methyl-4-propyl-N-(2,3,4,6-tetra-O-pivaloyl-β-D-galactopyranosyl)pyridine-2(1H)-one (**19c**)*

The reaction was carried out at −78 °C starting from 4-propyl-5,6-dehydropiperidin-2-one (**7b**) (0.1 g, 0.157 mmol) dissolved in 3 mL of dry THF, treated with 0.27 mL (0.27 mmol, 1.7 equiv.) of LiHMDS solution, and using 0.03 mL (0.47 mmol, 3 equiv.) of methyl iodide. Purification was performed by flash chromatography (20 × 1 cm, light petroleum-ether acetate 8 : 1). Yield: 92 mg (90 %), colorless amorphous solid, R_f = 0.48 (light petroleum-ethyl acetate 8 : 1). Diastereomeric ratio: 71 : 29 (^{1}H NMR and analytical HPLC). Analytical HPLC: Luna C18, gradient: acetonitrile-water 90 : 10 to 100 : 0 within 40 min, R_t (min): 17.39 (major diastereomer), 17.69 (minor diastereomer), $[\alpha]_D^{29}$: 57.42 (c = 1.0, $CHCl_3$). – MS ((+)-ESI): m/z = 674.4 $[M+Na]^+$. – HRMS ((+)-ESI): m/z = 674.3873 $[M+Na]^+$ (calcd.: 674.3880). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = (signals of the major diastereomer) 0.86 (m, 6H, -CH_3); 1.06, 1.07, 1.14, 1.25 (4s, 36H, PivCH_3), 1.38 – 1.28 (m, 4H, $(CH_2)_2CH_3$), 2.25 – 2.38 (m, 1H, *CH*propyl), 3.47 – 3.42 (m, 1H, CO*CH*), 3.91 – 4.02 (m, 1H, H-5), 4.04 – 4.12 (m, 2H, H-6a, H-6b), 5.15 – 5.22 (m, 2H, H-3, NCH=*CH*), 5.31 (dd, 1H, $J_{2,1}$ = 9.2 Hz, H-2), 5.42 (d, 1H, $J_{4,3}$ = 2.7 Hz, H-4), 5.85 (d, 1H, $J_{1,2}$ = 9.2 Hz, H-1), 6.20 (d, 1H, J_f = 6.7 Hz, J_l = 1.6 Hz, N*CH*=CH). – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = (signals of the major diastereomer) 14.12 (propylCH_3), 15.19 (COCH*CH_3*), 19.00 (CH_2CH_3), 27.05, 27.10, 27.21 (PivCH_3), 35.43 (*CH_2*Et), 37.81 (CHPropyl), 38.72, 39.05 (PivC_t), 40.92 (CO*CH*Me), 60.89 (C-6), 66.03, 66.76, 71.67, 72.84 (C-2, C-3, C-4, C-5), 78.63 (C-1), 111.53 (NCH=*CH*), 122.11 (NCH), 172.78 (NC=O), 176.57, 176.77, 177.82 (PivC=O).

*(4S)-4-Cyclohexyl-3,4-dihydro-3-methyl-N-(2,3,4,6-tetra-O-pivaloyl-β-D-galacto-pyranosyl)pyridine-2(1H)-one (**19d**)*

The reaction was carried out at −10 °C starting from 4-cyclohexyl-5,6-dehydropiperidin-2-one [8] (**7e**) (0.2 g, 0.295 mmol) dissolved in 3 mL of dry THF, treated with 0.5 mL (0.501 mmol, 1.7 equiv.) of LiHMDS solution, and using 50 μL (0.885 mmol, 3 equiv.) of methyl iodide. Purification was carried out by flash chromatography (20 × 1 cm, light petroleum-ethyl acetate 8 : 1). Yield: 0.188 g (92 %), colorless amorphous solid, R_f = 0.4 (light petroleum-ethyl acetate 8 : 1). Diastereomeric ratio: 67 : 33 (^{1}H NMR and analytical HPLC). Analytical HPLC: Luna C18, gradient: acetonitrile-water 90 : 10 to 100 : 0 within 40 min, R_t (min): 26.70 und 27.30. $[\alpha]_D^{20}$: 36.38 (c = 1.0 g mL^{-1}, $CHCl_3$). – MS ((+)-ESI): m/z = 714.6 $[M+Na]^+$. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = (signals of the major diastereomer) 0.86 (m, 3H, CH_3), 1.07, 1.16, 1.18, 1.23 (4s, 36 H, PivCH_3), 1.35 (m, 5 H, *CH*cyclohexyl, 2× CH_2), 1.59 – 1.79 (m, 6H, 3× CH_2), 1.94 – 1.96 (m, 1H, *CH*cyclohexyl), 2.59 – 2.63 (m, 1H, CO*CH*Me), 4.06 – 4.19 (m, 3H, H-5, H-6a, H-6b), 5.23 – 5.32 (m, 2H, H-3, NCH=*CH*), 5.46 (dd, 1H, $J_{2,1}$ = 9.4 Hz, H-2), 5.52 (d, 1H, $J_{4,3}$ = 2.7 Hz, H-4), 5.95 (d, 1H, $J_{1,2}$ = 9.4 Hz, H-1), 6.32 (d, 1H, J_f = 8.2 Hz, N*CH*=CH). – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = (signals of the major diastereomer) 17.09 (CH_3), 26.51 (C-4cyclohexyl), 26.36 (C-3cyclohexyl, C-5cyclohexy$_l$), 27.02, 27.05, 27.13, 27.24 (PivCH_3), 28.18 (C-2cyclohexyl, C-6cyclohexyl), 29.35 (*CH*cyclohexy$_l$), 38.73, 39.02 (PivC_t), 41.05 (*CH*cyclohexyl), 44.56 (*CH*Me), 61.01 (C-6), 65.80, 66.79, 71.72, 72.79 (C-2, C-3, C-4, C-5), 78.59 (C-1), 108.59 (NCH=*CH*), 122.54 (NCH), 173.32 (NC=O), 176.57, 176.77, 177.82 (PivC=O).

*(4R)-3-Butyl-3,4-dihydro-4-propyl-1-(2,3,4,6-tetra-O-pivaloyl-β-D-galactopyranosyl)pyridine-2(1H)-one (**19e**)*

The reaction was carried out at −10 °C starting from 4-propyl-5,6-dehydropiperidin-2-one (**7b**) (0.2 g, 0.314 mmol) dissolved 3 mL of dry THF, treated with 0.53 mL (0.53 mmol, 1.7 equiv.) of LiHMDS solution, and using 0.11 mL (0.942 mmol, 3 equiv.) of butyl iodide. Purification was carried out by flash chromatography (20 × 1 cm, light petroleum-ethyl acetate 15 : 1). Yield: 0.124 g (57 %), colorless, amorphous soid, R_f = 0.17 (cyclohexane-ethyl acetate 15 : 1). Diastereomeric ratio: 58 : 42 (^{1}H NMR and analytical HPLC). Analytical HPLC: Luna C18, gradient: acetonitrile-water 80 : 20 to 100 : 0 within 60 min, R_t (min): 42.32 and 42.93. $[\alpha]_D^{20}$: 32.55 (c = 1.0, $CHCl_3$). – MS ((+)-ESI): m/z = 716.7 $[M+Na]^+$. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = (signals of the major diastereomer) 0.95 (m, 6H, 2× -CH_3), 1.15, 1.17, 1.18, 1.23 (4s, 36 H, PivCH_3), 1.35 (m, 10 H, 5× -CH_2-), 2.24 (m, 1H, CHpropyl), 2.38 – 2.42 (m, 1H, CO*CH*), 4.03 – 4.18 (m, 3H, H-5, H-6a, H-6b), 5.27 – 5.49 (m, 3H, H-3, NCH=*CH*, H-2), 5.51 (d, 1H, $J_{4,3}$ = 3.1 Hz, H-4), 5.95 (m, 1H, $J_{1,2}$ = 9.4 Hz, H-1), 6.26 (d, 1H, J_f = 8.2 Hz, J_l = 2.4 Hz, N*CH*=CH). – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = (signals of the major diastereomer) 13.92, 14.07 (2× CH_3), 19.38, 19.76, 22.61 (3× CH_2), 27.02, 27.07, 27.12, 27.22 (PivCH_3), 29.24, 29.53 (2× CH_2), 34.76 (CH-propyl), 38.67, 39.05 (PivC_t), 46.85 (CO*CH*butyl), 60.96 (C-6), 65.38, 66.82, 71.90, 72.78 (C-2, C-3, C-4, C-5), 78.59 (C-1), 110.08 (NCH=*CH*), 122.07 (NCH), 172.61 (NC=O), 176.60, 177.07, 177.82 (PivC=O).

Aldol addition reaction at N-galactosylpiperidin-2-ones – General procedure

To the solution of the *N*-galactosyl-piperidin-2-one (**7**) in dry THF at −78 °C, 1.0 M LiHMDS solution was added. After stirring at this temperature for 15 min, a solution of the aldedyde and $BF_3 \cdot OEt_2$, stirred for some time (see: individual compounds) was added. The mixture was stirred at r. t. for 12 h. Subsequently, sat. NH_4Cl solution was added

and the solution extracted three times with diethyl ether. The combined organic solutions were dried with $MgSO_4$ and evaporated *in vacuo*. Purification was carried out by flash chromatography using cyclohexane-ethyl acetate containing 1 % (v/v) of NEt_3 as the eluent.

*(4R)-3-(α-Hydroxy-phenyl-methyl)-3,4-dihydro-4-propyl-1-(2,3,4,6-tetra-O-pivaloyl-β-D-galactopyranosyl)pyridine-2(1H)-one (**20a**)*

The reaction was carried out starting from 4-propyl-5,6-dehydropiperidin-2-one (**7b**) (0.2 g, 0.314 mmol), treated with 0.345 mL (0.345 mmol, 1.1 equiv.) of LiHMDS solution, and using 48 μL (0.471 mmol, 1.5 equiv.) of freshly distilled benzaldehyde pre-activated by stirring with 60 μL (0.471 mmol, 1.5 equiv.) of $BF_3 \cdot OEt_2$ for 30 min. Yield: 190 mg (81 %), colorless oil, R_f = 0.24 (cyclohexane-ethyl acetate 3 : 1). Diastereoselectivity: Only one diastereomer was detected by ^{1}H NMR and analytical HPLC). Analytical HPLC: Luna C18, gradient: acetonitrile-water 80 : 20 to 100 : 0 within 40 min, R_t (min): 27.78, $[\alpha]_D^{25}$: 38.42 (c = 1.0, $CHCl_3$). – MS ((+)-ESI): m/z = 744.49 $[M+H]^+$. – HRMS ((+)-ESI): m/z = 766.4141 $[M+Na]^+$ (calcd.: 766.4142). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.67 (t, 3H, -CH_3), 1.10, 1.12, 1.13 1.26 (4s, 40H, *C*H_2*C*$H_2$$CH_3$, Piv$CH_3$), 1.77 (m, 1H, CHpropyl), 2.67 (bd, 1H, J = 9.6 Hz, CO*CH*), 2.81 (d, 1H, J = 3.3 Hz, CH*OH*), 3.92 – 4.12 (m, 3H, H-5, H-6a, H-6b), 4.56 (dd, 1H, J = 3.3 Hz, J = 9.6 Hz, *CH*OH), 5.18 (dd, 1H, J = 6.9 Hz, J = 7.0 Hz, NCH=*CH*), 5.25 (dd, 1H, $J_{3,4}$ = 2.9 Hz, $J_{2,3}$ = 9.9 Hz, H-3), 5.42 (m, 2H, H-2, H-4), 5.93 (d, 1H $J_{1,2}$ = 9.2 Hz, H-1), 6.25 (d, 1H, J = 7.0 Hz, NCH), 7.29 (m, 5H, aryl). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 13.70 (-CH_3), 18.96 (*C*$H_2$$CH_3$), 27.02, 27.06, 27.23 (PivCH_3), 33.28 (CHpropyl), 36.09 (*C*$H_2$$CH_2$$CH_3$), 38.67, 38.76, 38.89, 39.06 (PivC_t), 54.60 (CO*CH*), 60.94 (C-6), 65.46, 66.72, 71.80 (C-5, C-4, C-3), 72.85 (CHOH), 73.24 (C-2), 78.81 (C-1), 110.06 NCH=*CH*), 122.39 (NCH), 126.73, 128.26, 128.64 (aryl), 141.28 (*ipso*-aryl), 170.90 (NC=O), 176.56, 177.07, 177.41, 177.79 (PivC=O).

*(4R)-3-(α-Hydroxy-phenyl-methyl)-3,4-dihydro-4-phenyl-1-(2,3,4,6-tetra-O-pivaloyl-β-D-galactopyranosyl)pyridine-2(1H)-one (**20b**)*

The reaction was carried out starting from 4-phenyl-5,6-dehydropiperidin-2-one [8] (**7f**) (0.3 g, 0.446 mmol), treated with 0.67 mL (0.67 mmol, 1.5 equiv.) of LiHMDS solution, and using 0.227 mL (2.23 mmol, 5 equiv.) of freshly distilled benzaldehyde pre-activated by stirring with 0.284 mL (2.23 mmol, 5 equiv.) of $BF_3 \cdot OEt_2$ for 30 min. Yield: 170 mg (49 %), colorless oil, R_f = 0.16 (cyclohexane-ethyl acetate 5 : 1). Diastereoselectivity: Only one diastereomer was detected by ^{1}H NMR and analytical HPLC). Analytical HPLC: Luna C18, gradient: acetonitrile-water 80 : 20 to 100 : 0 within 40 min, R_t (min): 29.58, $[\alpha]_D^{25}$: 68.86 (c = 1.0, $CHCl_3$). – MS ((+)-ESI): m/z = 800.29 $[M+Na]^+$. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.11, 1.14, 1.16, 1.27 (4s, 36H, PivCH_3), 3.02 (m, 1H, CHphenyl), 3.31 (dd, 1H, J = 5.5 Hz, J = 5.2 Hz, CO*CH*), 4.06 (m, 3H, H-5, H-6a, H-6b), 4.58 (d, 1H, J = 6.9 Hz, *CH*OH), 5.25 (dd, 1H, $J_{3,4}$ = 2.9 Hz, $J_{3,2}$ = 9.9 Hz, H-3), 5.34 (dd, 1H, J = 4.8 Hz, J = 8.0 Hz, NCH=*CH*), 5.47 (m, 2H, $J_{4,3}$ = 2.9 Hz, $J_{2,1}$ = 9.6 Hz, H-2, H-4), 5.92 (d, 1H, $J_{1,2}$ = 9.6 Hz, H-1), 6.47 (d, 1H, J = 8.0 Hz, NCH), 6.98 (m, 3H, aryl), 7.31 (m, 7H, aryl). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 27.05, 27.09, 27.15, 27.26 (PivCH_3), 40.56 (CHphenyl), 38.70, 38.77, 38.92, 39.07 (PivC_t), 56.55 (CO*CH*), 60.76 (C-6), 65.82, 66.65, 71.66, (C-5, C-4, C-3), 72.86 (*CH*OH), 72.94 (C-2), 78.82 (C-1), 110.72 (NCH=*CH*), 123.47 (NCH), 1226.28, 127.26, 127.44, 127.95, 128.58, 128.93 (aryl), 141.22, 141.89 (*ipso*-aryl), 170.11 (NC=O), 176.52, 177.07, 177.31, 177.79 (PivC=O). – $C_{44}H_{59}NO_{11}$ (777.40): calcd. C 67.93, H 7.64, N 1.80; found C 67.80, H 7.57, N 1.84.

*(4R)-4-Benzyl-3-(α-hydroxy-pyridine-4-yl-methyl)-3,4-dihydro-1-(2,3,4,6-tetra-O-pivaloyl-β-D-galactopyranosyl)-pyridine-2(1H)-one (**20g**)*

The reaction was carried out starting from 4-benzyl-5,6-dehydropiperidin-2-one [8] (**7g**) (0.225 g, 0.328 mmol), 0.49 mL (0.49 mmol, 1.5 equiv.) of LiHMDS solution, and using 31 μL (1.64 mmol, 5 equiv.) pyridine-4-carbaldehyde (freshly distilled). Yield : 81 mg (31 %) **20g**, 47 mg (18 %) **20g'**, 47 mg (18 %) **20g"**. Diastereomeric ratio: 44 : 36 : 17 : 1 (analytical HPLC). Analytcal HPLC: Luna C18, gradient: acetonitrile-water 80 : 20 to 100 : 0 within 40 min, R_t (min): 16.98 (44 %), 18.13 (1 %), 18.77 (17 %), 20.58 (36 %), separated through preparative HPLC (Luna C8, gradient: acetonitrile-water 80 : 20 to 100 : 0 within 120 min).

*Analytical data of **20g***: colorless amorphous solid, $[\alpha]_D^{25}$: 20.59 (c = 1.0, $CHCl_3$). - MS ((+)-ESI): m/z = 815.44 $[M+Na]^+$. - HRMS ((+)-ESI): m/z = 793.4250 $[M+H]^+$ (calcd.: 793.4275). - ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.08, 1.09, 1.11, 1.25 (4s, 36H, PivCH_3), 2.23 (m, 1H, CHbenzyl), 2.53 – 2.71 (m, 3H, CH_2Ph, CO *CH*), 3.78 (bs, 1H, CH*OH*), 3.93 – 4.11 (m, 3H, H-5, H-6a, H-6b), 4.69 (d, 1H, J = 7.7 Hz, *CH*OH), 5.23 (m, 2H, $J_{3,4}$ = 2.9 Hz, $J_{3,2}$ = 9.6 Hz, H-3, NCH=*CH*), 5.40 (m, 2H, $J_{2,1} = J_{2,3}$ = 9.6 Hz, H-2, H-4), 5.84 (bs, 1H, H-1), 6.29 (d, 1H, J = 8.0 Hz, NCH), 6.89 (m, 2H, aryl), 7.18 (m, 7H, aryl). - ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 26.78, 26.99, 27.02, 27.21 (PivCH_3), 35.06 (CHbenzyl), 38.67, 38.74, 38.85, 39.04 (PivC_t), 39.15 (CH_2Ph), 52.31 (CO*CH*), 60.78 (C-6), 65.78, 66.57 (C-5, C-4), 71.21 (CHOH), 71.60, 72.94 (C-3, C-2), 78.87 (C-1), 110.48 (NCH=*CH*), 123.05 (NCH), 126.69 (*para*-phenyl), 128.59, 129.10 (*ortho*-phenyl, *meta*-phenyl), 138.16 (*ipso*-phenyl), 147.84, 153 (pyridyl), 169.48 (NC=O), 176.50, 177.07, 177.32, 177.77 (PivC=O).

Analytical data of ***20g'***: colorless amorphous solid, $[\alpha]_D^{25}$: 75.00 (c = 1.0, $CHCl_3$). - MS ((+)-ESI): m/z = 815.45 $[M+Na]^+$. - HRMS ((+)-ESI): m/z = 793.4288 $[M+H]^+$ (calcd.: 793.4275). - ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.99, 1.08, 1.14, 1.25 (4s, 36H, $PivCH_3$), 2.34 (d, 1H, J = 12.0 Hz,CH_2^aPh), 2.39 (m, 1H, CHbenzyl), 2.84 (t, 1H, J = 5.5 Hz, COCH), 3.21 (dd, 1H, J = 2.6 Hz, J = 12.0 Hz, CH_2^bPh), 3.96 – 4.18 (m, 4H, CH*OH*, H-5, H-6a, H-6b), 5.07 (dd, J = 8.0 Hz, J = 6.3 Hz, NCH=*CH*), 5.24 (dd, 1H, $J_{3,4}$ = 2.9 Hz, $J_{3,2}$ = 10.3 Hz, H-3), 5.33 (t, 1H, $J_{2,1}$ = 9.2 Hz, $J_{2,3}$ = 10.3 Hz, H-2), 5.40 (d, 1H, J = 5.5 Hz, *CH*OH), 5.46 (d, 1H, $J_{4,3}$ = 2.9 Hz, H-4), 5.89 (d, 1H, $J_{1,2}$ = 9.2 Hz, H-1), 6.15 (d, 1H, J = 8.0 Hz, NCH), 6.91 (d, 2H, J = 6.3 Hz, aryl), 7.18 (m, 5H, aryl), 7.42 (m, 2H, aryl). - ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 26.84, 27.02, 27.20 ($PivCH_3$), 33.64 (CHbenzyl), 35.73 (CH_2Ph), 38.70, 38.73, 39.06 ($PivC_t$), 51.25 (CO*CH*), 60.94 (C-6), 65.73, 66.71 (C-5, C-4), 69.73 (CHOH), 71.24, 73.28 (C-3, C-2), 78.76 (C-1), 113.78 (NCH=*CH*), 122.69 (NCH), 126.16 (*para*-phenyl), 128.19, 128.93 (*ortho*-phenyl, *meta*-phenyl), 139.22 (*ipso*-phenyl), 149.23, 151.62 (pyridyl), 170.36 (NC=O), 176.52, 176.95, 177.03, 177.79 (PivC=O).

Analytical data of ***20g''***: colorless amorphous solid, $[\alpha]_D^{25}$: 23.13 (c = 1.0, $CHCl_3$). – MS ((+)-ESI): m/z = 793.48 $[M+H]^+$. – HRMS ((+)-ESI): m/z = 793.4296 $[M+H]^+$ calcd.: 793.4275). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.10, 1.15, 1.25 (3s, 36H, $PivCH_3$), 2.01 (m, 1H, CHbenzyl), 2.35 (m, 1H, J = 12.0 Hz, CH_2^aPh), 2.76 (dd, 1H, J = 5.5 Hz, J = 9.2 Hz, COCH), 2.84 (dd, 1H, J = 3.7 Hz, J = 12.0 Hz, CH_2^bPh), 3.96 – 4.20 (m, 4H, CH*OH*, H-5, H-6a, H-6b), 5.02 (dd, J = 8.0 Hz, J = 7.0 Hz, NCH=*CH*), 5.15 (d, 1H, J = 9.2 Hz, *CH*OH), 5.27 (dd, 1H, $J_{3,4}$ = 2.9 Hz, $J_{3,2}$ = 9.9 Hz, H-3), 5.35 (t, 1H, $J_{2,1}$ = 9.2 Hz, $J_{2,3}$ = 9.9 Hz, H-2), 5.48 (d, 1H, $J_{4,3}$ = 2.9 Hz, H-4), 5.94 (d, 1H, $J_{1,2}$ = 9.2 Hz, H-1), 6.18 (d, 1H, J = 8.0 Hz, NCH), 6.86 (d, 2H, J = 5.9 Hz, aryl), 7.17 (m, 5H, aryl), 7.42 (m, 2H, aryl). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 26.84, 27.02, 27.20 ($PivCH_3$), 33.64 (CHbenzyl), 35.73 (CH_2Ph), 38.70, 38.73, 39.06 ($PivC_t$), 51.25 (CO*CH*), 60.94 (C-6), 65.73, 66.71 (C-5, C-4), 69.73 (CHOH), 71.24, 73.28 (C-3, C-2), 78.76 (C-1), 113.78 (NCH=*CH*), 122.69 (NCH), 126.16 (*para*-phenyl), 128.19, 128.93 (*ortho*-phenyl, *meta*-phenyl), 139.22 (*ipso*-phenyl), 149.23, 151.62 (pyridyl), 170.36 (NC=O), 176.52, 176.95, 177.03, 177.79 (PivC=O).

*(4R)-3-[α-Hydroxy-(5-methyl-furfuryl)-methyl]-3,4-dihydro-4-propyl-1-(2,3,4,6-tetra-O-pivaloyl-β-D-galactopyranosyl)pyridine-2(1H)-one (**20c**)*

The reaction was carried out starting from 4-propyl-5,6-dehydropiperidin-2-one (**7b**) 0.23 g (0.36 mmol), 0.54 mL (0.54 mmol, 1.5 equiv.) of LiHMDS solution, and using 0.179 mL (1.8 mmol, 5 equiv.) of freshly distilled 5-methylfurfural pre-activated by stirring with 0.230 mL (1.8 mmol, 5 equiv.) of $BF_3 \cdot OEt_2$ for 30 min. Yield: 113 mg (42 %) **20c**, 70 mg (26 %) **20c'**. Diastereomeric ratio: 67 : 33 (analytical HPLC). Analytical HPLC: Luna C18, gradient: acetonitrile-water 80 : 20 to 100 : 0 within 40 min, R_t (min): 28.23 (major diastereomer), 29.651 min (minor diastereomer), separated by flash chromatography:

Analytcal data of ***20c***: colorless oil, R_f = 0.37 (cyclohexane-ethyl acetate 4 : 1), $[\alpha]_D^{25}$: 26.38 (c = 1.0, $CHCl_3$). – MS ((+)-ESI): m/z = 770.40 $[M+Na]^+$, 730.47 $[M-H_2O+H]^+$. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.76 (t, 3H, -$(CH_2)_2CH_3$), 1.08, 1.10, 1.12, 1.24 (4s, 40H, $CH_2CH_2CH_3$, $PivCH_3$), 1.95 (m, 1H, CHpropyl), 2.22 (s, 3H, -CH_3), 2.79 (d, 1H, J = 6.6 Hz, CH*OH*), 2.90 (dd, 1H, J = 8.8 Hz, J = 3.3 Hz, CO*CH*), 3.89 – 4.06 (m, 3H, H-5, H-6a, H-6b), 4.56 (dd, 1H, J = 6.9 Hz, J = 8.8 Hz, *CH*OH), 5.17 (m, 2H, $J_{3,4}$ = 2.9 Hz, $J_{3,2}$ = 9.9 Hz, J = 8.0 Hz, H-3, NCH=*CH*), 5.36 (t, 1H, $J_{2,1}$ = 9.6 Hz, $J_{2,3}$ = 9.9 Hz, H-2), 5.42 (d, 1H, $J_{3,4}$ = 2.9 Hz, H-4), 5.86 (m, 2H, H-1, CH_3-C=*CH*), 6.11 (d, 1H, J = 2.9 Hz, R-C=*CH*), 6.21 (d, 1H, J = 8.0 Hz, NCH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 13.49, 13.73 (-CH_3), 18.93 (CH_2CH_3), 27.00, 27.06, 27.21 ($PivCH_3$), 33.55 (CHpropyl), 35.75 ($CH_2CH_2CH_3$), 38.67, 38.73, 38.86, 39.04 ($PivC_t$), 51.69 (CO*CH*), 60.88 (C-6), 65.49 (CHOH), 66.47, 66.68, 71.77, 72.80 (C-5, C-4, C-3, C-2), 78.79 (C-1), 106.15 (R-C=CH), 108.94 (CH_3-C=*CH*), 111.02 (NCH=*CH*), 122.11 (NCH), 151.85, 152.16 (*ipso*-aryl), 170.29 (NC=O), 176.53, 177.06, 177.37, 177.76 (PivC=O). – $C_{40}H_{61}NO_{12}$ (747.42): calcd. C 64.24, H 8.22, N 1.87; found C 63.99, H 8.24, N 1.79.

Analytcal data of ***20c'***: colorless oil, R_f = 0.12 (cyclohexane-ethyl acetate 4 : 1), $[\alpha]_D^{25}$: −10.30 (c = 1.0, $CHCl_3$). – MS ((+)-ESI): m/z = 770.47 $[M+Na]^+$, 730.47 $[M-H_2O+H]^+$. – HRMS ((+)-ESI): m/z = 770.4109 $[M+Na]^+$ (calcd.: 770.4091). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.76 (t, 3H, -$(CH_2)_2CH_3$), 1.08, 1.14 1.25 (3s, 40H, $CH_2CH_2CH_3$, $PivCH_3$), 1.91 (m, 1H, CHpropyl), 2.23 (s, 3H, -CH_3), 2.82 (bs, 1H, CH*OH*), 2.89 (d, 1H, J = 9.4 Hz, CO*CH*), 3.93 – 4.13 (m, 3H, H-5, H-6a, H-6b), 4.71 (d, 1H, J = 9.4 Hz, *CH*OH), 5.17 (m, 2H, $J_{3,4}$ = 2.9 Hz, $J_{3,2}$ = 9.6 Hz, H-3, NCH=*CH*), 5.31 (t, 1H, $J_{2,1}$ = 9.2 Hz, $J_{2,3}$ = 9.6 Hz, H-2), 5.43 (d, 1H, $J_{3,4}$ = 2.9 Hz, H-4), 5.85 (m, 2H, H-1, CH_3-C=*CH*), 6.13 (d, 1H, J = 2.9 Hz, R-C=*CH*), 6.22 (d, 1H, J = 7.7 Hz, NCH). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 13.51, 13.58 (-CH_3), 19.41 (CH_2CH_3), 27.00, 27.03, 27.09, 27.23 ($PivCH_3$), 33.25 (CHpropyl), 35.78 ($CH_2CH_2CH_3$), 38.68, 38.73, 39.04 ($PivC_t$), 51.67 (CO*CH*), 60.70 (C-6), 66.53 (CHOH), 66.56, 66.86, 71.66, 72.85 (C-5, C-4, C-3, C-2), 78.79 (C-1), 106.11 (R-C=*CH*), 109.37 (CH_3-C=*CH*), 110.53 (NCH=*CH*), 121.21 (NCH), 151.30, 152.30 (*ipso*-aryl), 169.94 (NC=O), 176.52, 176.58, 177.03, 177.77 (PivC=O).

*(4R)-4-Benzyl-3-(1-hydroxy-2-methyl-propyl)-3,4-dihydro-1-(2,3,4,6-tetra-O-pivaloyl-β-D-galactopyranosyl)pyridine-2(1H)-one (**20d**)*

The reaction was carried out starting from 4-benzyl-5,6-dehydropiperidin-2-one [8] (**7g**) (0.22 g, 0.328 mmol), treated with 0.49 mL (0.49 mmol, 1.5 equiv.) of LiHMDS solution, and using 0.148 mL (1.64 mmol, 5 equiv.) of freshly distilled isobutyraldehyde pre-activated by stirring with 0.210 mL (1.64 mmol, 5 equiv.) $BF_3 \cdot OEt_2$ for 5 min. Yield: 182 mg (73 %), colorless oil, $R_f = 0.54$ (cyclohexane-ethyl acetate 3 : 1). Diastereomeric ratio: 98 : 2 (analytical HPLC). Analytical HPLC: Luna C18, gradient: acetonitrile-water 80 : 20 to 100 : 0 within 40 min, R_t (min): 32.72 (minor diastereomer), 33.08 (major diastereomer), $[\alpha]_D^{25}$: 23.41 (c = 1.0, $CHCl_3$). – MS ((+)-ESI): m/z = 780.46 $[M+Na]^+$. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.60, 0.83 (2d, 6H, J = 6.6 Hz, CH(*C*H_3)$_2$), 1.08, 1.09, 1.13, 1.25 (4s, 36H, PivCH_3), 1.79 (m, 1H, *C*H(CH_3)$_2$), 1.95 (d, 1H, J = 6.9 Hz, CH*OH*), 2.43 – 2.63 (m, 4H, CH_2Ph, CHbenzyl, CO*CH*), 3.39 (dd, 1H, J = 6.9 Hz, J = 11.7 Hz, *CH*OH), 3.92 – 4.14 (m, 3H, H-5, H-6a, H-6b), 5.19 (m, 1H, J = 2.9 Hz, J = 7.7 Hz, NCH=*CH*), 5.23 (dd, 1H, $J_{3,4}$ = 2.9 Hz, $J_{3,2}$ = 9.9 Hz, H-3), 5.37 (t, 1H, $J_{2,1}$ = 9.6 Hz, $J_{2,3}$ = 9.9 Hz, H-2) 5.44 (d, 1H, $J_{4,3}$ = 2.9 Hz, H-4), 5.91 (d, 1H $J_{1,2}$ = 9.6 Hz, H-1), 6.22 (d, 1H, J = 8.0 Hz, NCH), 7.18 (m, 5H, aryl). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.93, 19.87 (CH(*C*H_3)$_2$), 26.97, 27.03, 27.08, 27.23 (PivCH_3), 30.67 (*C*H(CH_3)$_2$), 35.75 (CHbenzyl), 38.68, 38.74, 38.82, 39.04 (PivC$_t$), 39.76 (CH_2Ph), 49.80 (CO*CH*), 60.89 (C-6), 65.37, 66.72, 71.78, 72.88 (C-5, C-4, C-3, C-2), 74.21 (CHOH), 78.66 (C-1), 110.48 (NCH=*CH*), 122.91 (NCH), 126.49 (*para*-aryl), 128.50, 129.28 (*ortho*-aryl, *meta*-aryl), 138.33 (*ipso*-aryl), 170.81 (NC=O), 176.55, 177.09, 177.25, 177.77 (PivC=O). – $C_{42}H_{63}NO_{11}$ (757.44): calcd. C 66.55, H 8.38, N 1.85; found C 66.52, H 8.39, N 1.70.

*(4R)-3-(1-Hydroxy-2,2-dimethyl-propyl)-3,4-dihydro-4-phenyl-1-(2,3,4,6-tetra-O-pivaloyl-β-D-galactopyranosyl)-pyridine-2(1H)-one (**20e**)*

The reaction was carried out starting from 4-phenyl-5,6-dehydropiperidin-2-one [8] (**7f**) (0.215 g, 0.319 mmol), 0.479 mL (0.479 mmol, 1.5 equiv.) of LiHMDS solution, and using 0.17 mL (1.6 mmol, 5 equiv.) of freshly distilled pivalaldehyde pre-activated by stirring with 0.204 mL (1.6 mmol, 5 equiv.) $BF_3 \cdot OEt_2$ for 30 min. Yield: 90 mg (36 %), colorless oil, R_f = 0.64 (cyclohexane-ethyl acetate 3 : 1). Diastereomeric ratio: 90 : 6 : 3 : 0 (analytical HPLC). Analytical HPLC: Luna C18, gradient: acetonitrile-water 80 : 20 to 100 : 0 within 40 min, R_t (min): 30.03 (minor diastereomer), 34.27 (minor diastereomer), 36.267 (major diastereome), $[\alpha]_D^{25}$: 68.46 (c = 1.0, $CHCl_3$). – MS ((+)-ESI): m/z = 780.52 $[M+Na]^+$. – HRMS ((+)-ESI): m/z = 758.4484 $[M+H]^+$ (calcd.: 758.4479). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.63 (s, 9H, (*t*BuCH_3), 1.09, 1.13, 1.15, 1.25 (4s, 36H, PivCH_3), 2.78 (d, 1H, J = 11.7 Hz, CHphenyl), 3.17 (d, 1H, J = 11.7 Hz, CO*CH*), 3.53 (bd, 1H, J = 12.1 Hz, CH*OH*), 3.75 (d, 1H, J = 12.1 Hz, *CH*OH), 3.96 – 4.16 (m, 3H, H-5, H-6a, H-6b), 5.22 (dd, 1H, $J_{3,4}$ = 2.9 Hz, $J_{2,3}$ = 9.9 Hz, H-3), 5.37 (m, 2H, J = 2.6 Hz, J = 7.7 Hz, $J_{2,1}$ = 9.2 Hz, H-2, NCH=*CH*), 5.46 (d, 1H, $J_{4,3}$ = 2.9 Hz, H-4), 5.92 (d, 1H $J_{1,2}$ = 9.2 Hz, H-1), 6.37 (dd, 1H, J_1 = 2.2 Hz, J_f = 7.7 Hz, NCH), 7.23 (m, 5H, aryl). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 26.36 (*t*BuCH_3), 27.03, 27.14, 27.21 (PivCH_3), 35.79 (*t*BuC$_t$), 38.70, 38.73, 38.89, 39.06 (PivC$_t$), 43.57 (CHphenyl), 47.57 (CO*CH*), 60.61 (C-6), 66.23, 66.59, 71.62, 72.95 (C-5, C-4, C-3, C-2), 78.42 (CHOH), 78.61 (C-1), 113.87 (NCH=*CH*), 122.97 (NCH), 127.33 (*para*-aryl), 128.65, 128.76 (*ortho*-aryl, *meta*-aryl), 141.89 (*ipso*-aryl), 170.66 (NC=O), 176.49, 177.07, 177.18, 177.74 (PivC=O).

*(4R)-4-Benzyl-3-(1-hydroxy-allyl)-3,4-dihydro-1-(2,3,4,6-tetra-O-pivaloyl-β-D-galactopyranosyl)pyridine-2(1H)-one (**20f**)*

The reaction was carried out starting from 4-benzyl-5,6-dehydropiperidin-2-one [8] (**7g**) (0.2 g, 0.291 mmol), 0.44 mL (0.44 mmol, 1.5 equiv.) of LiHMDS solution, and using 20 μL (1.45 mmol, 5 equiv.) freshly distilled acrolein. Yield: 166 mg (78 %), colorless oil, R_f = 0.35 (cyclohexane-ethyl acetate 3 : 1). Diastereomeric ratio: 87 : 9 : 4 : 0 (^{1}H NMR and analytical HPLC). Analytical HPLC: Luna C18, gradient: acetonitrile-water 80 : 20 to 100 : 0 within 40 min, R_t (min): 23.77 (minor diastereomer), 24.67 (major diastereomer), 26.18 (minor diastereomer), $[\alpha]_D^{25}$: 38.57 (c = 1.0, $CHCl_3$). – MS ((+)-ESI): m/z = 764.49 $[M+Na]^+$. – HRMS ((+)-ESI): m/z = 764.3981 $[M+Na]^+$ (calcd.: 764.3986). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.08, 1.13, 1.24 (3s, 36H, PivCH_3), 2.40, 2.57, 2.63 (3m, 5H, CH_2Ph, CHbenzyl, CH*OH*, CO*CH*), 3.91 – 4.17 (m, 4H, *CH*OH, H-5, H-6a, H-6b), 5.17 (m, 4H, $J_{3,4}$ = 2.9 Hz, H-3, CH=*C*H_2, NCH=*CH*), 5.36 (t, 1H, $J_{2,1} = J_{2,3}$ = 9.6 Hz, H-2) 5.66 (m, 1H, *C*H=CH_2), 5.89 (d, 1H $J_{1,2}$ = 9.6 Hz, H-1), 6.21 (d, 1H, J = 8.1 Hz, NCH), 7.07, 7.21 (2m, 5H, aryl). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 26.78, 27.05, 27.21 (PivCH_3), 35.19 (CHbenzyl), 38.68, 38.73, 38.82, 39.04 (PivC$_t$), 39.67 (CH_2Ph), 52.09 (CO*CH*), 60.86 (C-6), 65.45, 66.68, 71.78 (C-5, C-4, C-3), 71.92 (CHOH), 72.86 (C-2), 78.79 (C-1), 110.53 (NCH=CH), 117.64 (CH=*C*H_2), 122.67 (NCH), 126.45 (para-aryl), 128.44, 129.22 (*ortho*-aryl, *meta*-aryl), 138.16 (*ipso*-aryl), 138.56 (*C*H=CH_2), 170.00 (NC=O), 176.53, 177.09, 177.25, 177.77 (PivC=O).

*(4S)-4-(3-Butenyl)-N-(2,3,4,6-tetra-O-pivaloyl-β-D-galacto-pyranosyl)piperidin-2-one (**21**)*

To a solution of (4*R*)-(3-butenyl)-5,6-dehydropiperidin-2-one [8] (**7h**) (0.382 g, 0.58 mmol) in 20 mL of dioxane 2 mL of conc. HCl was added. The mixture was stirred at r. t. for 1 h. Then, $NaCNBH_3$ was cautiously added (fume hood!) until evolution of gas did no longer occur. The mixture was stirred for 12 h. It is then adjusted to weakly basic conditions by addition of diluted NaOH solution. After addition of diethyl ether (100 mL) the solution was washed with sat. NaCl solution. After separation, the aqueous layer was extracted once more with diethyl ether (100 mL). The combined organic solutions were dried with $MgSO_4$, and the solvent was evaporated to dryness. The purification of the remaining residue was achieved by flash chromatography. Yield: 0.377 g (quant.), colorless amorphous solid, $R_f = 0.26$ (cyclohexane-ethyl acetate 4 : 1), $[\alpha]_D^{27}$: 9.64 (c = 1.0; $CHCl_3$). – MS ((+)-ESI): m/z = 674.38 $[M+Na]^+$. – HRMS ((+)-ESI): m/z = 674.3854 $[M+Na]^+$ (calcd.: 674.3880). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.08, 1.14, 1.23 (3s, 36H, $PivCH_3$), 1.37 (m, 2H, $CH_2CH_2CH{=}CH_2$), 1.61 (m, 1H, CHR), 1.81 – 2.10 (m, 5H, NCH_2CH_2, $COCH_2^a$, $CH_2CH{=}CH_2$), 2.46 (dd, 1H, ^3J= 3.3 Hz, ^2J= 18.1 Hz, $COCH_2^b$), 3.24, 3.52 (2m, 2H, NCH_2), 3.89 – 4.11 (m, 3H, H-5, H-6a, H-6b), 4.95 (m, 2H, $CH{=}CH_2$), 5.20 (dd, 1H, $J_{3,4}$ = 2.9 Hz, $J_{3,2}$ = 9.9 Hz, H-3), 5.42 (m, 2H, $J_{2,3}$ = 9.9 Hz, $J_{4,3}$ = 2.9 Hz, H-2, H-4), 5.73 (m, 1H, $CH{=}CH_2$), 5.98 (d, 1H, $J_{1,2}$ = 9.2 Hz, H-1). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 26.96, 27.03, 27.18 ($PivCH_3$), 28.69, 30.60 ($CH_2CH_2CH{=}CH_2$, NCH_2CH_2), 31.50 (CHR), 34.69 ($CH_2CH{=}CH_2$), 38.68, 38.71, 38.77, 38.98 ($PivC_t$), 39.03 ($COCH_2$), 40.05 (NCH_2), 60.75 (C-6), 65.24, 66.84, 71.63, 72.70, (C-5, C-4, C-3, C-2), 79.33 (C-1), 115.07 ($CH{=}CH_2$), 137.91 ($CH{=}CH_2$), 170.33 (NC=O), 176.47, 176.97, 177.37, 177.79 (PivC=O).

*(4S)-4-(3-Oxo-propyl)-1-(2,3,4,6-tetra-O-pivaloyl-β-D-galactopyranosyl)piperidin-2-one (**23**)*

To a solution of *N*-methylmorpholine-1-oxide (NMO, 128 mg (0.95 mmol), 1.1 equiv.) in water (5.7 mL), acetone (3.7 mL), *tert*-butanol (3.7 mL) and THF (3.7 mL) catalytic amouts of potassium osmate(VI)-dihydrate (about 1 mol-%) were added. A solution of (4*S*)−4-(3-butenyl)-*N*-(2,3,4,6-tetra-*O*-pivaloyl-β-D-galactopyranosyl)-piperidin-2-one (**21**) (0.562 mg, 0.863 mmol) in 3 mL of acetone was added dropwise. All solvents had been carefully degassed under ultrasound. The mixture was stirred at r. t. until monitoring by TLC indicated complete conversion (about 2 d). Subsequently, 5 g of talkum (magnesium silicate hydrate) and 20 mL of a 10 % solution of sodium dithionite in water were added, and the mixture was stirred for 15 min and filtered. The residue was thouroughly washed with ethyl acetate. The combined filtrates were extracted with 10 mL of 1N HCl. The aqueous layer was extracted twice with ethyl acetate (2 × 10 mL). The combined organic solutions were washed with sat. $NaHCO_3$ solution, and the aqueous layer again extracted with ethyl acetate. The combined organic solutions were dried with $MgSO_4$, and the solvent was evaporated *in vacuo* to give the crude diol **22**. Yield: 310 mg (52 %), colorless oil. – MS ((+)-ESI): m/z = 685.4 $[M]^+$.

This product **22** (0.310 g, 0.452 mmol) was directly subjected to glycol cleavage: It was dissolved in dry dichloromethane (20 mL). Na_2CO_3 (96 mg, 0.904 mmol, 2 equiv.) was added, and the mixture was cooled to 0 °C. Under argon atmosphere lead tetraacetate (242 mg, 0.542 mmol, 1.2 equiv.) was added. The lemon-yellow solution was stirred for 90 min. Addition of water (50 mL) terminated the reaction. After filtration and separation, the residue was washed with dichloromethane, and the aqueous layer was extracted with dichloromethane (3 × 30 mL). The combined organic solutions were dried with $MgSO_4$, and the solvent was evaporated *in vacuo*. Purification was carried out by flash chromatography. Yield: 144 mg (49 %) **23**, colorless amorphous solid, R_f = 0.52 (cyclohexane-ethyl acetate 1 : 1), $[\alpha]_D^{25}$: 8.92 (c = 1.0, $CHCl_3$). – MS ((+)-ESI): m/z = 676.37 $[M+Na]^+$. – HRMS ((+)-ESI): m/z = 676.3693 $[M+Na]^+$ (calcd.: 676.3673). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.08, 1.09, 1.14, 1.23 (4s, 36H, $PivCH_3$), 1.67 (m, 4H, NCH_2CH_2, CH_2CH_2CHO), 1.95 (m, 2H, CH_2CHO) 2.46 (m, 3H, $COCH_2$, CHR), 3.27, 3.54 (2m, 2H, NCH_2), 3.90 – 4.19 (m, 3H, H-5, H-6a, H-6b), 5.20 (dd, 1H, $J_{3,4}$ = 2.9 Hz, $J_{2,3}$ = 9.9 Hz, H-3), 5.35 (t, 1H, $J_{2,1}$ = 9.6 Hz, $J_{2,3}$ = 9.9 Hz, H-2), 5.42 (d, 1H, $J_{4,3}$ = 2.9 Hz, H-4), 5.97 (d, 1H $J_{1,2}$ = 9.6 Hz, H-1), 9.76 (s, 1H, CHO). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 26.96, 27.03, 27.18 ($PivCH_3$), 27.54 (NCH_2CH_2), 28.52 (CH_2CH_2CHO), 31.78 (CHR), 38.58 ($COCH_2$), 38.67, 38.71, 39.03 ($PivC_t$), 39.93 (CH_2CHO), 40.89 (NCH_2), 60.75 (C-6), 65.27, 66.80, 71.56, 72.71 (C-5, C-4, C-3, C-2), 79.33 (C-1), 169.72 (NC=O), 176.46, 176.97, 177.43, 177.79 (PivC=O), 201.10 (CHO).

*(6S)-9-Hydroxy-N-(2,3,4,6-tetra-O-pivaloyl-β-D-galacto-pyranosyl)-3-aza-bicyclo[4.3.0]nonan-2-one (**24**)*

To potassium hexamethyldisilazane [KHMDS, 23 mg (0.115 mmol, 1.5 equiv.)] in 2 mL of dry THF at −78 °C a solution of (4*S*)-4-(3-oxo-propyl)-*N*-(2,3,4,6-tetra-*O*-pivaloyl-β-D-galactopyranosyl)piperidin-2-one (**23**) (50 mg, 0.0765 mmol) in 2 mL of dry THF was added dropwise. The solution was stirred for 12 h while warming to r. t.. After addition of 5 mL sat. aqueous NH_4Cl, the solution was extracted with diethyl ether (3 × 20 mL). The combined organic solutions were dried with $MgSO_4$, and the solvents were evaporated to dryness. Purification of the crude product was carried out by flash chromatography. Yield: 18 mg (36 %) **24**, pale-yellow amorphous solid, R_f = 0.05 (cyclo-

hexane-ethyl acetate 3 : 1). Diastereomeric ratio: 78 : 22 : 0 : 0 (analytical HPLC). Analytcal HPLC: Luna C18, gradient: acetonitrile-water 80 : 20 to 100 : 0 within 40 min, R_t (min): 13.78 (minor diastereomer), 14.30 (major diastereomer), $[\alpha]_D^{25}$: 3.02 (c = 1.0, $CHCl_3$). – MS ((+)-ESI): m/z = 676.42 $[M+Na]^+$. – HRMS ((+)-ESI): m/z = 676.3699 $[M+Na]^+$ (calcd.: 676.3673). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.08, 1.13 1.23 (3s, 36H, $PivCH_3$), 1.32, 1.63 (2m, 4H, $CHOHCH_2CH_2$), 1.95 (m, 2H, NCH_2CH_2), 2.47 (m, 2H, COCH, CHR), 3.28, 3.54 (2m, 2H, NCH_2), 3.90 – 4.19 (m, 4H, H-5, H-6a, H-6b, *CH*OH), 5.20 (dd, 1H, $J_{3,4}$ = 2.9 Hz, $J_{3,2}$ = 9.9 Hz, H-3), 5.35 (t, 1H, $J_{2,1}$ = 9.6 Hz, $J_{2,3}$ = 9.9 Hz, H-2), 5.41 (d, 1H, $J_{4,3}$ = 2.9 Hz, H-4), 5.97 (d, 1H, $J_{1,2}$ = 9.6 Hz, H-1). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 26.99, 27.03, 27.18 ($PivCH_3$), 28.49 (NCH_2CH_2), 29.65, 30.28 (CH_2CH_2CHOH), 32.11 (CHR), 38.71 (CO*CH*), 38.80, 38.86, 39.04 ($PivC_t$), 40.05 (NCH_2), 60.72 (C-6), 65.30, 66.78, 71.56, 72.70 (C-5, C-4, C-3, C-2), 79.32 (C-1), 82.82 (CHOH), 170.03 (NC=O), 176.46, 176.97, 177.46, 177.80 (PivC=O).

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