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D-Glucosamine Propanedithioacetal, an Efficient Chiral Auxiliary in β-Lactam Chemistry†

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Abstract—The synthesis of some monocyclic β-lactams (monobactams) by the Staudinger reaction using D-glucosamine propanedithioacetal as chiral auxiliary is reported. The influence of several radicals at C_3, C_4, and $C_{1'}$ (sugar moiety) as well as other structural aspects are considered in relation to the antielastase activity.

Introduction

For the last few years we have been developing an enantioselective approach to the synthesis of β-lactams,[1] which relies on the use of 3,4;5,6-di-*O*-isopropylidene-D-glucosamine propanedithioacetal (**1**)[2] as chiral auxiliary in the Staudinger reaction.[3] This methodology let us obtain the monocyclic azetidin-2-ones (monobactams I) required to prepare bicyclic β-lactam antibiotics.

The discovery that monocyclic azetidin-2-ones with appropriate substituents at 1, 3, and 4 positions are inhibitors of human leukocyte elastase[4] (HLE) prompted us to study the inhibitory activity of the monobactams I, II, and III, showed in Scheme 1,[5] against three different elastases: pancreatic porcine, rat leukocyte and human leukocyte, in order to design potent and specific HLE inhibitors.

We found[5] that all the 3,4-disubstituted 2-azetidinones (monobactams II) do not show elastase inhibition; in contrast, the introduction of an acyl group on the nitrogen atom (monobactams III) activates the β-lactam ring and shows non-selective antielastase activity; however, some monobactams I that have a butyl or a methoxy group at C-3 and a styryl or α-methylstyryl group at C-4, give selective inhibition to HLE.

Encouraged by this promising results, we turned our attention to the preparation of new monobactams I with modifications at C-3 and C-4 on the 2-azetidinone ring and at C-1 and C-2 on the sugar moiety, in order to clarify the relationship between the structure and the inhibition of HLE by these monocyclic β-lactams.

In this article, we wish to give a full account of the enantioselective preparation of compounds **1**–**28** (Scheme 1) extended by the synthesis of compounds **29**–**45** (Schemes 2–4), as well as discuss their inhibitory activities to HLE.

Results and Discussion

Chemistry

As shown in Scheme 1, the synthesis of monobactams I started from 3,4;5,6-di-*O*-isopropylidene-D-glucosamine propane dithioacetal (**1**) which was available from D-glucosamine in two steps. Condensation of **1** with various aldehydes (see Experimental) yielded the chiral Schiff-bases **2**. These crude reaction products were used without further purification in the Staudinger reaction by using triethylamine as a base and toluene as solvent. The *cis*-monobactams **3**, **4**, **5**, and **6** (3α,4α + 3β,4β diastereomers) were obtained by cycloaddition of **2** with methoxyacetyl chloride at room temperature, in a short reaction time and with good yields. From this reaction mixture the pure diastereomers could be easily separated by column chromatography or by recrystallization. In contrast, when the imines **2** were reacted with caproyl chloride no reaction was observed even after 24 h at room temperature but in refluxing toluene the *cis*-monobactams **7**–**10** were the only diastereomers obtained.

Key words: β-Lactams; synthesis; structure/circular dichroism; antielastase activity.
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† Dedicated to Professor Sir Derek H. R. Barton.

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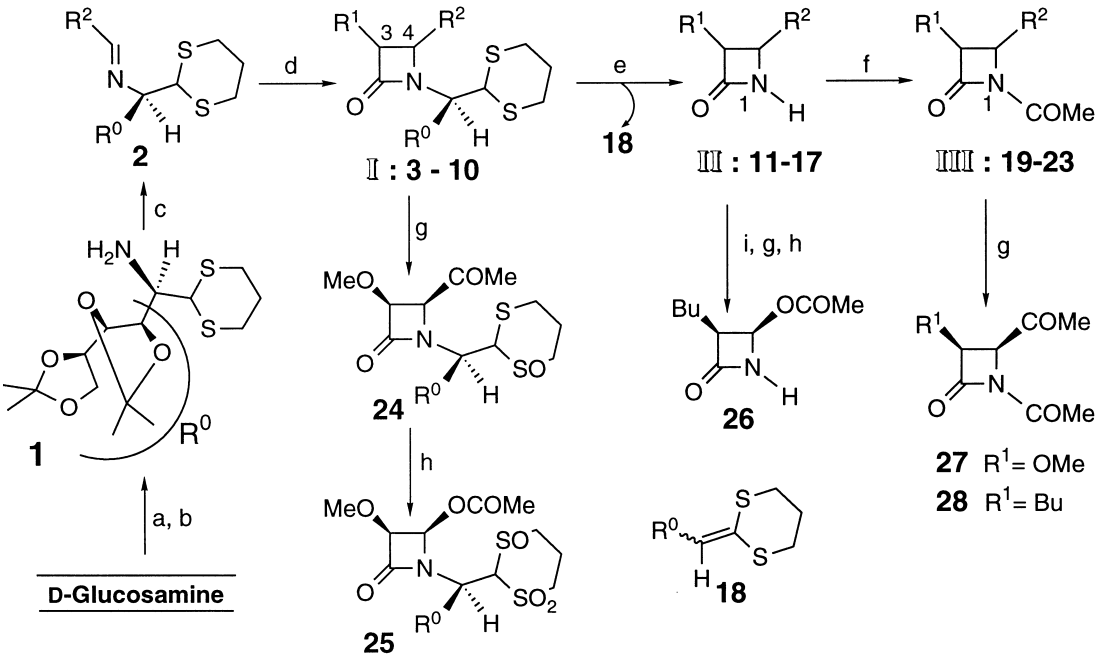


Ⅱ	Ⅲ	ⅢⅠ	R^1	R^2
3a (3α, 4α) **3b** (3β, 4β)	**11a** (3α, 4α) **11b** (3β, 4β)	**19a** (3α, 4α) **19b** (3β, 4β)	- OMe	- CH=CH-Ph
4a (3α, 4α) **4b** (3β, 4β)	**12a** (3α, 4α) **12b** (3β, 4β)	**20** (3β, 4β)	- OMe	- $C(CH_3)$=CHPh
5a (3α, 4α) **5b** (3β, 4β)	**13a** (3α, 4α) **13b** (3β, 4β)	**21** (3β, 4β)	- OMe	- Ph
6a (3α, 4α) **6b** (3β, 4β)			- OMe	- Ph(*p*-OMe)
7 (3β, 4β)	**14** (3β, 4β)		- *n*-Bu	- Ph
8 (3β, 4β)	**15** (3β, 4β)	**22** (3β, 4β)	- *n*-Bu	- CH=CH-Ph
9 (3β, 4β) **10** (3β, 4β)[1]	**16** (3β, 4β) **17** (3β, 4β)[1]	**23** (3β, 4β)	- *n*-Bu	- $C(CH_3)$=CHPh

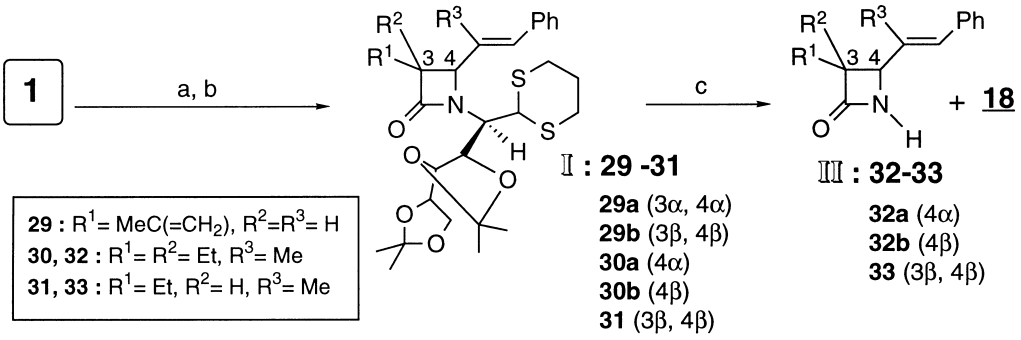
[1] *cis*-α-methylstyryl

Scheme 1. Reagents: (a) HCl (g), 1,3-propanedithiol, HCl, 60 °C; (b) 2,2-dimethoxypropane, *p*-TsOH, 60 °C, 30 cmHg; (c) R^2CHO, toluene, reflux; (d) TEA, R^1CH_2COCl, toluene, 70 °C or reflux; (e) *n*-BuLi, THF, −40 °C; (f) CH_3COCl, $Et(iPr)_2N$, DMAP, CH_3CN, rt; (g) O_3, CH_2Cl_2, −78 °C; Me_2S, rt; (h) *m*-CPBA, CH_2Cl_2, rt; (i) *t*$BuMe_2SiCl$, $Et(iPr)_2N$, CH_2Cl_2, rt.

The *N*-unsubstituted monobactams Ⅲ, **11**–**17**, were prepared in very good yields and in a short reaction time (20–40 min) by treatment of monobactams Ⅱ with 2.2 equiv of *n*-butyllithium in tetrahydrofurane at −40 °C. The *cis*-relationship of the C-3 and C-4 substituents in compounds **3a**–**17** was deduced from the vicinal coupling constants of the hydrogen atoms H-3 and H-4 ($J_{3,4} \geq 4.8$ Hz) and the absolute configuration at C-3 and C-4 was deduced from the $[\alpha]_D$ data, the CD curves (Table 1) and the X-ray crystal structure of compounds **3b** and **10**.[6]

The absolute configuration of monobactams **3b** and **10** was established as 3β,4β (3*S*,4*R* for **3b** and 3*S*,4*S* for **10**), according to the X-ray data. These monobactams have negative $[\alpha]_D$, which suggests the 3β,4β configuration for the remaining levorotatory monobactams **4b**–**6b**, **7**, **8**, and **9** (major diastereomeric reaction products) and the 3α,4α configuration for the monobactams **3a**–**6a**.

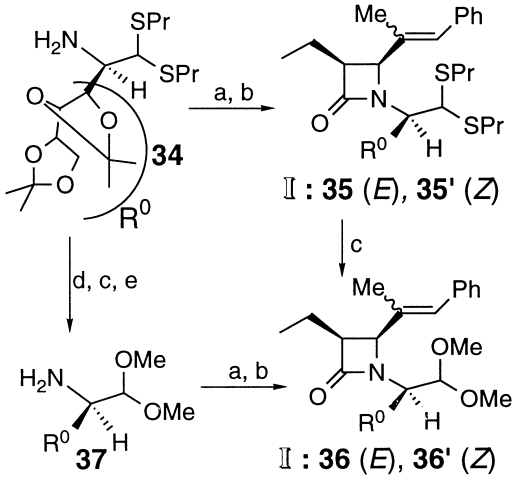
The CD measurements also confirm this absolute configuration. Two empirical rules have been proposed by Ogura et al. (lactam rule)[7] and by Schellman et al. (amide quadrant rule)[8] to correlate the Cotton effect with the absolute configuration of the lactams. There are nevertheless some exceptions and the predictions are not always in agreement.[9] In our case, the lactam rule



Scheme 2. Reagents: (a) PhCH=C(R^3)CHO, toluene, reflux; (b) TEA, R^1R^2CHCOCl, toluene (or CH_2Cl_2), reflux; (c) *n*-BuLi, THF, −40 °C.

applied to 2-azetidinones predict a negative Cotton effect for the 3β,4β isomers, which is consistent with the sign of the experimental curves. However, in the case of monobactams Ⅰ the CD curves are more complex because of the presence of an aromatic chromophore which could be responsible for the strong Cotton effects observed. The aromatic ^1L_b absorption band (220–230 nm) and the n–π* amide bands (ca. 210 and/or 220 nm) can overlap and produce an exciton coupling of both chromophores that give rise to a Davidoff splitting.[10] The intensity of the coupling depends on the degree of overlapping, the intensity of the excitons and the orientation of the chromophores: in the case of monobactams Ⅰ, the splitting reaches the maximum amplitude in **6b** ($\Delta\Delta\varepsilon_{210/230} = 35$) but the exciton splitting is not so clear in other monobactams.

According to the exciton chirality rule,[10] a positive splitting (positive first and negative second Cotton effects) is related to a positive chirality of the transition moments in the chromophores. The compounds **3a**–**6a** show positive splitting which corresponds to the 4α configuration (positive dihedral angle) while the remaining compounds display a negative splitting and should have 4β configuration.



Scheme 3. Reagents: (a) PhCH=C(Me)CHO, toluene, reflux; (b) TEA, $CH_3(CH_2)_2COCl$, toluene, reflux; (c) $PhI(COCF_3)_2$, MeOH, rt; (d) CBZ, MeOH, Na_2CO_3, rt; (e) H_2/Pd-C(5%), EtOH, rt.

The *N*-unsubstituted monobactams Ⅱ does not show the same regularity in the optical rotation as their parent monobactams (Table 1). However, the CD curves show a negative first Cotton effect for compounds 3β,4β and positive for 3α,4α, which also confirm the proposed absolute configurations.

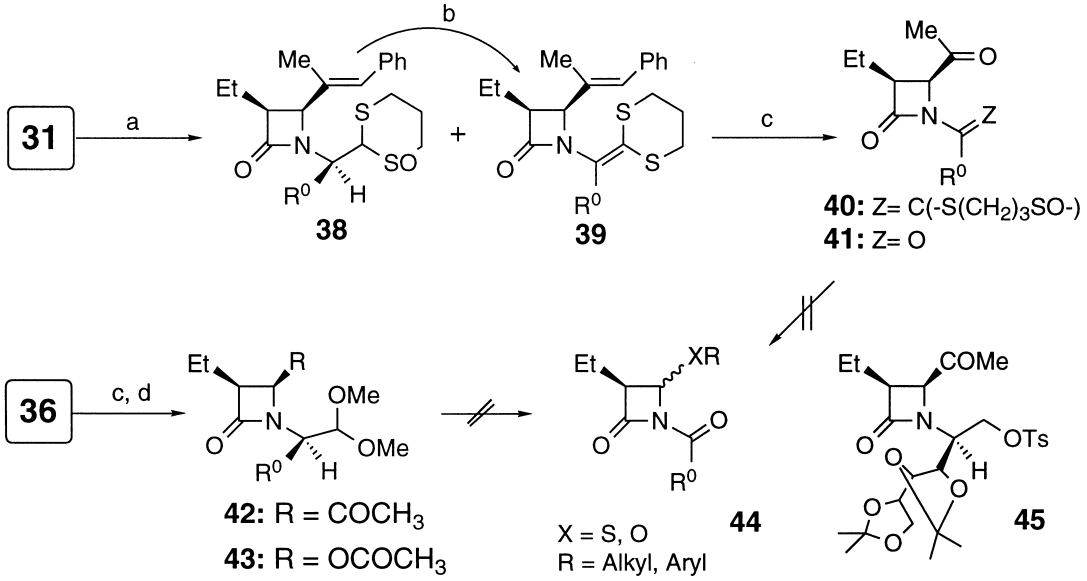
Compounds **19**–**23** (monobactams Ⅲ) were prepared by acylation of the respective monobactams Ⅱ with acetyl chloride in acetonitrile using diisopropylethylamine and 4-dimethylaminopyridine as base.

Conversion of the monobactams Ⅰ, Ⅱ and Ⅲ into the respective derivatives **24**–**28** was carried out by usual chemical manipulations. Ozonolysis of compound **4b** gave the 4β-acetyl derivative **24**, which was transformed into the 4β-acetoxyazetidinone **25** by Baeyer–Villiger reaction. On the other hand, silylation of **16** followed by ozonolysis and treatment with *m*-chloroperbenzoic acid gave **26**. Finally, the compounds **27** and **28** were obtained by ozonolysis of monobactams **20** and **23**, respectively.

Monobactams **29**–**31**, which have different alkyl groups at C-3, were prepared as shown in Scheme 2. Condensation of **1** with *trans*-cinnamaldehyde or *trans*-α-methylcinnamaldehyde, followed by treatment of β,β-dimethylacryloyl chloride or 2-ethylbutyroyl chloride in the presence of triethylamine, provided two *cis*-monobactams **29** or **30** as a diastereomeric mixture. In contrast, the Staudinger reaction between butyroyl chloride and the condensation product of amine **1** and *trans*-α-methylcinnamaldehyde yielded exclusively the monobactam **31**.

The *cis*-orientation of the substituents at C-3 and C-4 in compounds **29** and **31** was also evident from the NMR data ($J_{4,3} \geq 5.5$ Hz) and the absolute configuration was deduced from the $[\alpha]_D$ and the X-ray crystal structure of compound **10**.[6] Moreover, the structures of monobactams **30** were rigorously established on the basis of the NMR spectra and confirmed by CD-curve analysis of the *N*-unsubstituted monobactams **32a** and **32b**, which were prepared by treatment with *n*-butyllithium from **30a** and **30b**, respectively.

In order to clarify the role played by the dithianyl group in the HLE inhibition, we have also prepared the



Scheme 4. Reagents: (a) $PhICl_2$, CH_2Cl_2, −40 °C; (b) O_3, CH_2Cl_2, −78 °C; Me_2S, rt; (c) *m*-CPBA, CH_2Cl_2, rt.

monobactams **35** and **36** (Scheme 3) which have on the sugar moiety at C-1 an open chain thioacetal and acetal, respectively.

Preparation of **35** was carried out starting from amine **34**[11] by condensation with *trans*-α-methylcinnamaldehyde, followed by Staudinger reaction of the intermediate imine with butyroyl chloride. A small amount of the *Z*-isomer (**35′**) was also obtained due to the presence of *cis*-α-methylcinnamaldehyde in the starting material.

In a first approach to obtain the monobactam **36**, which have an acetal group at C-1 on the sugar moiety, we used the Stork procedure.[12] Thus, treatment of compounds **31** and **35** with [bis(trifluoroacetoxy)iodo]benzene in methanol furnished the monobactam **36** in 54 and 71% yield, respectively. Alternatively, this compound was also prepared by Staudinger reaction of butyroyl chloride with the condensation product of *trans*-α-methylcinnamaldehyde and the amine **37**, which was available from **34** in a three-step sequence (i.e. carbamoylation[13] of the amine group, transacetalyzation with [bis(trifluoroacetoxy)iodo]benzene[12] and hydrogenolysis).

Table 1. Chiroptical data[a] for monobactams 𝕀 and 𝕀𝕀

𝕀	$[\alpha]_D$	$\Delta\varepsilon_{(\lambda)}$	𝕀𝕀	$[\alpha]_D$	$\Delta\varepsilon_{(\lambda)}$	C_3,C_4
3a	+115	$+29.3_{(260)}$	**11a**	−10		α,α
4a	+47		**12a**	−40		α,α
5a	+13	$+4.5_{(230)}$	**13a**	−112	$+10.2_{(226)}$	α,α
6a	+30	$+3.1_{(239)}$				α,α
3b	−102	$-17.0_{(250)}$	**11b**	+10		β,β
4b	−53		**12b**	+40		β,β
5b	−109	$-17.7_{(227)}$	**13b**	+112	$-15.4_{(226)}$	β,β
6b	−111	$-18.3_{(232)}$				β,β
7	−67	$-18.3_{(221)}$	**14**	−66	$-10.2_{(215)}$	β,β
8	−42	$-4.3_{(228)}$	**15**	+12	$-3.0_{(220)}$	β,β
9	−43	$-11.6_{(220)}$	**16**	−46	$-2.6_{(236)}$	β,β
10	−170	$-20.8_{(230)}$	**17**	−53	$-23.2_{(246)}$	β,β

[a]$[\alpha]_D$: c&1 in $CHCl_3$. $\Delta\varepsilon_{(\lambda)}$ in MeOH. See Experimental for other CD maxima.

Finally, we have carried out the preparation of compounds **38**–**43** (Scheme 4) in order to synthesise the monobactams **44** that have the sugar moiety transformed into an electron-withdrawing group and better leaving groups at C-4 of the monobactam ring. These 1,4 substituents on β-lactam ring would increase the reactivity and hence the antielastase activity of the first monobactams 𝕀,[5] since both structural requirements have been reported as important elements to design monocyclic β-lactam HLE inhibitors.[4a]

Conversion of **31** into the intermediate monobactam **41** was carried out by extended ozonolysis (45 min) of the monobactam **39**. A shorter ozonolysis time (20 min) gave the monobactam **40** only. Compound **39** along with **38**, was obtained by treatment of monobactam **31** with dichloroiodobenzene.[1c] The sulfoxide **38** was nevertheless transformed into **39** by Pummerer rearrangement.[14] The intermediate monobactam **43** was also synthesised from **36**, by ozonolysis and Baeyer–Villiger reaction.

Unfortunately, we did not succeed in the preparation of the desired monobactam **44**. Since all attempts to prepare the 4β-acetoxy derivatives from **41** or to transform the 4β-acetoxy monobactam **43** into the acylesters **44** were unproductive.

Biological properties

The antielastase activity of monobactams **29**–**31**, **35**–**36**, **39**, **41**–**43**, and the readily available 1,3,4-trisubstituted azetidin-2-one **45**[15] was evaluated in vitro.[16] It was found that only monobactams **30b**, **35**, and **45** showed significant bioactivity against HLE, whose inhibition percentage at 10^{-5} M were 27, 31, and 21%, respectively.

If we compare the structure–activity relationship of the tested β-lactams[5] and take into account that monobactams **3a** and **9** showed ca. 50% inhibition rate (IC_{50})

at 10^{-6} M, we can draw the following conclusions: (1) The *n*-butyl radical at C-3 seems to be more effective than the isopropenyl and diethyl substituents (i.e. the monobactams **29a**, **29b**, **30a**, and **30b** showed $IC_{50} \gg 270\,\mu M$). (2) The dithiane protecting group in the sugar side chain at N-1 seems to be much more effective than the dipropylthioacetal and the dimethylacetal groups (i.e. the monobactams **35** and **36** showed $IC_{50} \gg 310\,\mu M$). (3) The effect of the substituents on C-4 is not clear. The tested substances showed $IC_{50} \gg 210\,\mu M$, but they have different functionalization in the sugar moiety.

The above data suggest that the 2-deoxy-2-dithianyl-3,4;5,6-di-*O*-isopropylidene-D-2-glucosyl group may be related to the selective HLE inhibition. In conclusion, it would be interesting to synthesise a monobactam Ⅰ with the dithiane protecting group in the sugar chain at N-1, a butyl group at C-3 and a halogen, ether, sulphur, or sulphone as leaving group at C-4 in order to increase the HLE inhibition, according to the mechanism proposed by Doherty et al. for the inhibition of the L-680,833 monobactam.[17]

Experimental

General methods

Flash chromatographies were run on silica gel (Merck 60 230–400 mesh) and thin-layer chromatographies (TLC) on commercial silica gel plates (Merck F-254). Microanalyses were performed by the Analytical Department, C.N.R.S., Gif-sur-Yvette. Mass spectra (MS), were recorded on AEI MS 50 (EI) and Kratos MS 80 (FAB) spectrometers. Melting points were measured with a Reichert hot stage apparatus and are uncorrected. Optical rotations were recorded in $CHCl_3$ solution in a 1 dm cell on a Perkin–Elmer 243 polarimeter. IR spectra were recorded as neat films or in KBr pellets on a Bomem MB-100 or on a Nicolet 205 FT-IR instruments. ^1H and ^{13}C NMR spectra were obtained on Bruker instruments WP200SY, AC250 or AM 400 (200, 250, and 400 MHz, respectively) as solutions in $CDCl_3$ with tetramethylsilane as internal standard (δ, ppm). Curves of circular dichroism were obtained on Jobin Yvon Dichrograph Mark-III instrument as solutions in MeOH (HPLC), Fissons. Solvents and reagents were purified according to standard techniques.

Preparation of amines

3,4;5,6-Di-*O*-isopropylidene-1-(1′,3′-propanedithio)-D-glucosamine (1). A solution of D-glucosamine hydrochloride (25 g, 116 mmol) in hydrochloric acid (100 mL) was cooled at 0 °C and saturated with a HCl(g) flow for 2 h. 1,3-Propanedithiol (15 g, 1.2 equiv) and CH_2Cl_2 (25 mL) were added to this solution and the reaction mixture was stirred for 12 h at 60 °C. Then, the excess of dithiol was eliminated by extraction with CH_2Cl_2 and the aqueous solution was neutralized to pH 7 by addition of $PbCO_3$. Filtration through a Buchner funnel and evaporation of water under reduced pressure gave a residue which was dissolved in warm EtOH. After filtration of the solution, concentration and crystallization in EtOH, the D-glucosamine hydrochloride was isolated (27 g, 92%). A solution of this crystalline compound (24 g, 93 mmol) in 2,2-dimethoxypropane and a catalytic amount of *p*-toluenesulfonic acid (150 mL) was stirred for 3 h at 60 °C and 300 mmHg in Rotavapor®. The reaction mixture was poured over a cold saturated $NaHCO_3$ solution and extracted with hexane. The organic layers were dried (Na_2SO_4), filtered and evaporated to dryness. After crystallization in hexane the amine **1** was obtained as a white solid (29 g, 90%). MS (EI, *m*/*z*): 350 $(MH)^+$. mp: 79–80 °C (hexane). $[\alpha]_D$ +89 (c 1.3, $CHCl_3$). IR (KBr): 3393, 3323, 1228. ^1H NMR (200 MHz) δ: 1.33, 1.37, 1.41, 1.43 (4s, 12H, $C(\underline{CH_3})_2$), 1.90–2.10 (m, 2H, H9), 2.70–3.00 (m, 4H, H8), 3.16 (dd, $J_{2,1} = 8.5$ Hz, $J_{2,3} = 2.0$ Hz, 1H, H_2), 3.96 (d, $J_{2,1} = 8.5$ Hz, 1H, H_1), 4.00–4.20 (m, 4H, $H_{4\text{-}6}$), 4.50 (dd, $J_{3,2} = 2.0$ Hz, $J_{3,4} = 8.5$ Hz, 1H, H_3); ^{13}C NMR (50.3 MHz) δ: 25.1, 26.5, 26.7, 26.9 ($C(\underline{CH_3})_2$), 25.6 (C_9), 27.8, 28.2 (C_8), 51.5, 53.5 (C_1, C_2), 67,6 (C_6), 77.1, 78.0, 79.1 (C_3, C_4, C_5), 109.2, 109.3 (C_7).

3,4;5,6-Di-*O*-isopropylidene-1,1-dimethoxy-D-glucosamine (37). To a stirred solution of **34** (10 g, 25.5 mmol) in methanol (100 mL), benzyl chloroformate (5.6 g, 1.3 equiv) and sodium carbonate (3.6 g) in water (5 mL) were added. The reaction mixture was stirred at room temperature for a period of 4 h and then poured over 2 N hydrochloric acid, extracted with chloroform, washed with water, and then with a saturated sodium chloride solution. The organic layers were dried (Na_2SO_4), filtered, and evaporated to dryness. The residue was purified on a silica gel column (hexane:ethyl acetate, 9:1) to yield the carbobenzyloxy derivative of **34** (10.7 g, 80%). To a solution of this compound (2.0 g, 3.8 mmol) in dry methanol (10 mL), [bis(trifluoroacetoxy)iodo]benzene (2.5 g, 1.5 equiv) was added. The mixture was stirred at room temperature for 15 min. Once the methanol was evaporated, the residue was dissolved in ethyl acetate and the solution was washed with saturated sodium bicarbonate solution. The organic layers were dried (Na_2SO_4), filtered and evaporated to dryness. The residue was purified on a silica gel column (hexane:ethyl acetate, 8:2) to yield the carbobenzyloxy derivative of **37** (1.25 g, 75%). Next, a solution of this derivative (1.1 g, 2.4 mmol) and cyclohexene (2.4 mL, 24 mmol) was added to a stirred suspension of palladium on activated carbon (454 mg, 5%) in anhydrous ethanol (60 mL). After 1.5 h reflux under hydrogen atmosphere, the solution was filtered through a Celite pad and the filtrate was evaporated to dryness. The residue gave the amine **34** (664 mg, 91%). MS (EI, *m*/*z*): 306 $(MH)^+$. $[\alpha]_D$ +32 (c 1, $CHCl_3$). IR: 3389, 1228. ^1H NMR (200 MHz) δ: 1.30, 1.35, 1.38, 1.39 (4s, 12H, $C(\underline{CH_3})_2$), 1.50 (br s, 2H, NH_2), 2.95 (dd, $J_{2,1} = 7.8$ Hz, $J_{2,3} = 2.0$ Hz, 1H, H_2), 3.39, 3.41 (2s, 6H, OCH_3), 3.91–4.14 (m, 5H, $H_{3\text{-}6}$), 4.21 (d, $J_{1,2} = 7.8$ Hz, 1H, H_1); ^{13}C NMR (62.5 MHz) δ: 25.5, 26.7, 27.1, 27.2 (4C, $C(\underline{CH_3})_2$), 52.5 (C_2), 53.9, 54.6 (CH_3O), 67.9 (C_6), 77.5, 77.6, 79.1 (C_3, C_4, C_5), 106.5 (C_1), 109.3 (2C, C_7).

General procedure for preparation of imines. A solution of amine **1**, **34**, or **37** (1 mmol) and *trans*-cinnamaldehyde

(**A**), *trans*-1-methylcinnamaldehyde (**B**), benzaldehyde (**C**), or *p*-methoxybenzaldehyde (**D**) (1 mmol) in toluene, under the conditions showed in Table 2, yielded after solvent evaporation, the respective imines **2**(amine/aldehyde) which were used without further purification in the Staudinger reaction.

General procedure for preparation of monobactams 𝕀

To a solution of the imine **2** (1 mmol) and dry TEA (2.5 mmol) in dry toluene (10 mL), a solution of the carboxylic acid chloride (1.5 mmol) in dry toluene (8 mL) was added dropwise under argon atmosphere. The reaction mixture was stirred for the time and temperature specified in each case, until the starting material disappeared in TLC. The solution was poured into cold ammonium chloride solution, neutralised to pH 7 by addition of acetic acid and extracted with dichloromethane. The organic layers were dried (Na_2SO_4), filtered and evaporated to dryness. The residues were purified by silica gel column chromatography.

1[(1′,2′-Dideoxy-3′,4′;5′,6′-di-*O*-isopropylidene-1′(1,3-propanedithio))-D-2′-glucosyl]-3α-methoxy-4α-styryl-2-azetidinone (3a) and 1[(1′,2′-dideoxy-3′,4′;5′,6′-di-*O*-isopropylidene-1′(1,3-propanodithio))-D-2′-glucosyl]-3β-methoxy-4β-styryl-2-azetidinone (3b). They were obtained by Staudinger reaction of imine **2**(1/A) and methoxyacetyl chloride after 30 min at 25 °C, via the above general procedure, in 94% yield from **1**. The reaction mixture was purified on a silica gel column (hexane:ethyl acetate, 8:2).

3a (31%): Anal. calcd for $C_{27}H_{37}NO_6S_2$: C, 60.53; H, 6.96; N, 2.61; S, 11.97. Found: C, 60.51; H, 7.25; N, 2.53; S, 12.04. MS (IE, *m/z*): 536 $(MH)^+$. mp 156–157 °C (hexane:EtOAc). $[\alpha]_D$ +115 (c 1, $CHCl_3$). IR (KBr): 1770 (NC=O). ^1H NMR (200 MHz) δ: 1.35, 1.36, 1.49, 1.58 (4s, 12H, C($\underline{CH_3}$)$_2$), 1.93–2.13 (m, 2H, $H_{9'}$), 2.51–2.78 (m, 2H, $H_{8'ax}$), 2.93–3.26 (m, 2H, $H_{8'eq}$), 3.46 (s, 3H, OCH_3), 3.62 (t, $J_{4',3'} = J_{4',5'} = 8.0$ Hz, 1H, $H_{4'}$) 3.91–4.22 (m, 4H, $H_{1'}$, $H_{5'}$,$H_{6'}$), 4.60 (dd, $J_{2',3'} = 1.5$ Hz, $J_{2',1'} = 11.0$ Hz, 1H, $H_{2'}$), 4.69 (dd, $J_{4,3} = 5.0$ Hz, $J_{4,5} = 10.0$ Hz, 1H, H_4), 4.78 (d, $J_{3,4} = 5.0$ Hz, 1H, H_3), 4.91 (dd, $J_{3',2'} = 1.5$ Hz, $J_{3',4'} = 8.0$ Hz, 1H, $H_{3'}$), 6.61 (dd, $J_{5,4} = 10.0$ Hz, $J_{5,6} = 15.5$ Hz, 1H, H_5), 6.72 (d, $J_{6,5} = 15.5$ Hz, 1H, H_6), 7.32–7.60 (m, 5H, H_{Ph}); ^{13}C NMR (50.3 MHz), δ: 25.0 (C($\underline{CH_3}$)$_2$), 25.3($C_{9'}$), 25.6 ($C_{8'}$), 25.9 (C($\underline{CH_3}$)$_2$), 26.1 ($C_{8'}$), 26.3, 27.5 (C($\underline{CH_3}$)$_2$), 43.7 ($C_{2'}$), 51.8 (C_4), 58.6 (OCH_3), 63.0 ($C_{1'}$), 67.5 ($C_{6'}$), 77.1, 77.7, 78.5 ($C_{3'}$, $C_{4'}$, $C_{5'}$), 85.3 (C_3), 109.1, 109.4 ($C_{7'}$), 123.1, 126.6, 128.1 (5C, CH_{Ph}, C_5), 135.8 (C_6), 136.2 (C_{Ph}), 167.8 (C_2).

Table 2. Formation of imines **2**

Amine	Aldehyde	t (°C)	Time (h)	Imine
1	A	70[a]	2	**2** (1/A)
1	B	70[a]	5	**2** (1/B)
1	C	70[a]	3	**2** (1/C)
1	D	70[a]	7	**2** (1/D)
34	B	110[b]	12	**2** (34/B)
37	B	70[a]	5	**2** (37/B)

[a]Under reduced pressure (100 mmHg). Toluene was added several times.
[b]Under reflux with azeotropical removal of water.

3b (63%): Anal. calcd for $C_{27}H_{37}O_6NS_2$: C, 60.53; H, 6.96; N, 2.61; S, 11.97. Found: C, 60.41; H, 6.80; N, 2.63; S, 12.06. MS (IE, *m/z*): 536 $(MH)^+$. mp 206–207 °C (hexane:CH_2Cl_2). $[\alpha]_D$ −102 (c 1, $CHCl_3$). IR (KBr): 1768 (NC=O). ^1H NMR (200 MHz) δ: 1.20, 1.28, 1.36, 1.53 (4s, 12H, C($\underline{CH_3}$)$_2$), 1.90–2.21 (m, 2H, $H_{9'}$), 2.70–2.90 (m, 4H, $H_{8'}$), 3.46 (s, 3H, OCH_3), 3.80–4.40 (m, 7H, $H_{1'-6'}$), 4.57 (dd, $J_{4,3} = 5.0$ Hz, $J_{4,5} = 9.0$ Hz, 1H, H_4), 4.76 (d, $J_{3,4} = 5.0$ Hz, 1H, H_3), 6.45 (dd, $J_{5,4} = 9.0$ Hz, $J_{5,6} = 16.0$ Hz, 1H, H_5), 6.71 (d, $J_{6,5} = 16.0$ Hz, 1H, H_6), 7.30–7.60 (m, 5H, H_{Ph}); ^{13}C NMR (50.3 MHz) δ: 25.2 (C($\underline{CH_3}$)$_2$), 25.6 ($C_{9'}$), 26.4, 27.1, 27.2 (C($\underline{CH_3}$)$_2$), 27.3 ($C_{8'}$), 44.4 ($C_{2'}$), 54.2 (C_4), 58.7 (OCH_3), 62.4 ($C_{1'}$), 67.7 ($C_{6'}$), 76.9, 77.3, 79.0 ($C_{3'}$ $C_{4'}$, $C_{5'}$), 85.4 (C_3), 109.0, 110.0 ($C_{7'}$), 126.0, 126.9, 128.1 (5C, CH_{Ph}, C_5) 135.0 (C_6), 136.4 (C_{Ph}), 168.9 (C_2).

1[(1′,2′-Dideoxy-3′,4′;5′,6′-di-*O*-isopropylidene-1′(1,3-propanedithio))-D-2′-glucosyl]-3α-methoxy-4α-(α-methylstyryl)-2-azetidinone (4a) and 1[(1′,2′-dideoxy-3′,4′;5′,6′-di-*O*-isopropylidene-1′(1,3-propanodithio))-D-2′-glucosyl]-3β-methoxy-4β-(α-methylstyryl)-2-azetidinone (4b). They were obtained by Staudinger reaction of imine **2** (1/B) and methoxyacetyl chloride, after 2 h at 25 °C, via the general procedure in 75% yield from **1**. The reaction mixture was purified on a silica gel column (hexane: ethyl acetate, 7:3).

4a (24%): Anal. calcd for $C_{28}H_{39}NO_6S_2$: C, 61.18; H, 7.15; N, 2.55; S, 11.66. Found: C, 60.93; H, 7.03; N, 2.47; S, 11.60. MS (IE, *m/z*): 549 $(M)^+$. mp 97–99 °C (hexane:EtOAc). $[\alpha]_D$ +47 (c 1, $CHCl_3$). IR (KBr): 1758 (NC=O). ^1H NMR (250 MHz) δ: 1.50, 1.55, 1.60, 1.65 (4s, 12H, C($\underline{CH_3}$)$_2$), 1.95–2.30 (m, 2H, $H_{9'}$), 2.25 (s, 3H, CH_3), 2.88–3.10 (m, 2H, $H_{8'ax}$), 2.9–3.20 (m, 2H, $H_{8'eq.}$), 3.60 (s, 3H, OCH_3), 4.10–4.45.(m, 6H, $H_{1'-2'}$, $H_{4'-6'}$), 4.85 (d, $J_{4,3} = 4.6$ Hz, 1H, H_4), 4.90 (d, $J_{3,4} = 5.0$ Hz, 1H, H_3), 5.00 (dd, $J_{3',2'} = 3.5$ Hz, $J_{3',4'} = 8.0$ Hz, 1H, $H_{3'}$), 6.85 (s, 1H, H_6), 7.40–7.50 (m, 5H, H_{Ph}); ^{13}C NMR (62.5 MHz) δ: 16.3 (CH_3), 25.4, 25.6 (C($\underline{CH_3}$)$_2$), 26.5 ($C_{9'}$), 27.4 (2C, $C_{8'}$), 28.5, 28.7 (C($\underline{CH_3}$)$_2$), 47.0 ($C_{2'}$), 54.5 (C_4), 57.8 (OCH_3), 56.3 ($C_{1'}$), 67.9 ($C_{3'}$), 68.7 ($C_{6'}$), 76.6, 76.7, 79.3 ($C_{3'}$, $C_{4'}$, $C_{5'}$), 85.3 (C_3), 110.0 (2C, $C_{7'}$), 126.9, 128.3, 129.2 (5C, CH_{Ph}), 131.7 (C_6), 133.5 (C_{Ph}), 137.5 (C_5), 168.8 (C_2).

4b (51%): Anal. calcd for $C_{28}H_{39}NO_6S_2$: C, 61.17; H, 7.15; N, 2.55; S, 11.66. Found: C, 61.32; H, 6.99; N, 2.66; S, 11.25. MS (IE, *m/z*): 549 $(M)^+$. mp 147–149 °C (hexane:EtOAc). $[\alpha]_D$ −53 (c 1, $CHCl_3$). IR (KBr): 1757 (NC=O). ^1H NMR (400 MHz) δ: 1.16, 1.26, 1.36, 1.53 (4s, 12H, C($\underline{CH_3}$)$_2$), 2.06 (s, 3H, CH_3(C=)), 2.06–2.10 (m, 2H, $H_{9'}$), 2.58–2.78 (m, 2H, $H_{8'ax}$), 2.98–3.15 (m, 2H, $H_{8'eq}$), 3.47 (s, 3H, OCH_3), 3.82 (t, $J_{4',3'} = J_{4',5'} = 7.2$ Hz, 1H, $H_{4'}$), 3.98–4.22 (m, 4H, $H_{1'}$, $H_{5'}$, $H_{6'}$), 4.48 (d, $J_{4,3} = 5.7$ Hz, 1H, H_4), 4.65 (dd, $J_{2',1'} = 10.7$ Hz, $J_{2',3'} = 2.8$ Hz, 1H, $H_{2'}$), 4.80 (dd, $J_{3',2'} = 2.7$ Hz, $J_{3',4'} = 7.3$ Hz, 1H, $H_{3'}$), 4.83 (d, $J_{3,4} = 5.0$ Hz, 1H, H_3), 6.72 (s, 1H, H_6), 7.19–7.38 (m, 5H, H_{Ph}); ^{13}C NMR (62.5 MHz)

δ: 16.0 ($\underline{CH_3}$(C=)), 25.3 (2C, C($\underline{CH_3}$)$_2$), 25.5 ($C_{9'}$), 26.1, 26.5 (C($\underline{CH_3}$)$_2$), 26.9 ($C_{8'}$), 44.7 ($C_{2'}$), 53.9 (C_4), 58.8 (OCH_3), 66.8 ($C_{1'}$), 67.9 ($C_{3'}$), 67.6 ($C_{6'}$), 76.7, 77.2, 78.8 ($C_{3'}$, $C_{4'}$, $C_{5'}$), 85.4 (C_3), 109.0, 110.0 ($C_{7'}$), 126.8, 128.2, 129.2 (5C, CH_{Ph}), 130.4 (C_6), 134.7 (C_{Ph}), 137.4 (C_5), 171.2 (C_2).

1[(1′,2′-Deoxy-3′,4′;5′,6′-di-*O*-isopropylidene-1′(1,3-propanedithio))-D-2′-glucosyl]-3α-methoxy-4α-phenyl-2-azetidinone (5a) and 1[(1′,2′-dideoxy-3′,4′;5′,6′-di-*O*-isopropylidene-1′(1,3-propanodithio))-D-2′-glucosyl]-3β-methoxy-4β-phenyl-2-azetidinone (5b). They were obtained by Staudinger reaction of imine **2** (1/C) and methoxyacetyl chloride after 5 h at 50 °C, using dichloromethane as solvent, in 85% yield from **1**. The reaction mixture was purified on a silica gel column (hexane:ethyl acetate, 7:3).

5a (4%): Anal. calcd for $C_{25}H_{35}NO_6S_2$: C, 58.94; H, 6.88; N, 2.75; S, 12.57. Found: C, 58.65; H, 7.28; N, 2.39; S, 12.16. mp 112–114 °C (Hexane:EtOAc). $[\alpha]_D$ +13 (c 1, $CHCl_3$). IR (KBr): 1755 (NC=O). ^{1}H NMR (200 MHz) δ: 1.33, 1.35, 1.42, 1.58 (4s, 12H, C($\underline{CH_3}$)$_2$), 1.90–2.00 (m, 2H, $H_{9'}$), 2.48–2.70 (m, 2H, $H_{8'ax}$), 2.81–3.06 (m, 2H, $H_{8'eq}$), 3.12 (s, 3H, OCH_3), 3.58 (t, $J_{4',3'} = J_{4',5'} = 7.8$ Hz, 1H, $H_{4'}$), 3.71 (d, $J_{1',2'} = 9.6$ Hz, 1H, $H_{1'}$), 3.83 (dd, $J_{5',4'} = 7.8$ Hz, $J_{5',6'a} = 4.6$ Hz), 4.00–4.18 (m, 2H, $H_{6'}$), 4.30 (dd, $J_{2',3'} = 2.6$ Hz, $J_{2',1'} = 9.6$ Hz), 4.78 (d, $J_{4,3} = 4.6$ Hz, 1H, H_4), 4.81 (dd, $J_{3',2'} = 2.6$ Hz, $J_{3',4'} = 7.8$ Hz, 1H, $H_{3'}$), 5.09 (d, $J_{3,4} = 4.7$ Hz, 1H, H_3), 7.34–7.37 (m, 3H, H_{Ph}), 7.57–7.62 (m, 2H, H_{Ph}); ^{13}C NMR (62.5 MHz, C_6D_6) δ 25.3 (C($\underline{CH_3}$)$_2$), 25.6 ($C_{9'}$), 26.2, 26.9; 30.0 (C($\underline{CH_3}$)$_2$), 27.5, 27.9 ($C_{8'}$), 46.4 ($C_{2'}$), 54.5 (C_4), 57.8 (OCH_3), 64.9 ($C_{1'}$), 68.1 ($C_{6'}$), 78.1, 79.0, 79.1 ($C_{3'}$, $C_{4'}$, $C_{5'}$), 85.9 (C_3), 109.7, 110.3 ($C_{7'}$), 127.7, 130.3 (CH_{Ph}), 135.5 (C_{Ph}), 168.2 (C_2). Δε (λ): −4,17(214), +4,49(232).

5b (81%): Anal. calcd for $C_{25}H_{35}NO_6S_2$: C, 58.94; H, 6.88; N, 2.75; S, 12.57. Found: C, 58.88; H, 6.84; N, 2.72; S, 12.58. MS (IE, *m/z*): 510 $(MH)^+$. mp 175–176 °C (Hexane:CH_2Cl_2). $[\alpha]_D$ −109 (c 1, $CHCl_3$). IR (KBr): 1757 (NC=O). ^{1}H NMR (200 MHz) δ: 0.46, 1.14, 1.34, 1.50 (4s, 12H, C($\underline{CH_3}$)$_2$), 2.00–2.17 (m, 2H, $H_{9'}$), 2.53–2.73 (m, 2H, $H_{8'ax}$), 2.97 (s, 3H, OCH_3), 2.93–3.17 (m, 2H, $H_{8'eq}$), 3.72 (dd, $J_{4',3'} = 6.5$ Hz, $J_{4',5'} = 8.6$ Hz, 1H, $H_{4'}$), 3.93–4.13 (m, 4H, $H_{2'}$, $H_{5'}$, $H_{6'}$), 4.18 (d, $J_{1',2'} = 10.1$ Hz, 1H, $H_{1'}$), 4.60 (d, $J_{4,3} = 3.4$ Hz, 1H, H_4), 4.63 (dd, $J_{3',2'} = 2.3$ Hz, $J_{3',4'} = 6.4$ Hz, 1H, $H_{3'}$), 4.68 (d, $J_{4,3} = 3.4$ Hz, 1H, H_3), 7.26–7.46 (m, 5H, H_{Ph}); ^{13}C NMR (50.3 MHz) δ: 25.4 (C($\underline{CH_3}$)$_2$), 25.6 ($C_{9'}$), 26.6, 26.7 (C($\underline{CH_3}$)$_2$), 26.8, 26.9 ($C_{8'}$), 44.5 ($C_{2'}$), 54.0 (C_4), 58.0 (OCH_3), 62.7 ($C_{1'}$), 67.7 ($C_{6'}$), 76.7, 77.4, 78.9 ($C_{3'}$, $C_{4'}$, $C_{5'}$), 85.4 (C_3), 108.8, 110.1 ($C_{7'}$), 128.2, 128.5, 129.7, (CH_{Ph}), 135.6 (C_{Ph}), 170.8 (C_2). Δε (λ): +10.11 (208), −17.66 (227).

1[(1′,2′-Deoxy-3′,4′;5′,6′-di-*O*-isopropylidene-1′(1,3-propanedithio))-D-2′-glucosyl]-3α-methoxy-4α-(4-methoxyphenyl)-2-azetidinone (6a) and 1[(1′,2′-dideoxy-3′,4′;5′,6′-di-*O*-isopropylidene-1′(1,3-propanodithio))-D-2′-glucosyl]-3β-methoxy-4β-(4-methoxyphenyl)-2-azetidinone (6b). They were obtained by Staudinger reaction of imine **2** (1/D) and methoxyacetyl chloride, after 3 h at 25 °C in 70% yield, from **1**. The reaction mixture was purified on a silica gel column (hexane:ethyl acetate, 7:3).

6a (6%): Anal. Calcd for $C_{27}H_{37}NO_7S_2$: C, 57,88; H, 6,86; N, 2,60; S, 11,87. Found: C, 57.42; H, 6.92; N, 2.39; S, 11.94. mp 164–166 °C (hexane:EtOAc). $[\alpha]_D$ +30 (c 1, $CHCl_3$). IR (KBr): 1767 (NC=O). ^{1}H NMR (200 MHz) δ: 1.33, 1.36, 1.43, 1.57 (4s, 12H, C($\underline{CH_3}$)$_2$), 1.91–2.03 (m, 2H, $H_{9'}$), 2.46–2.68 (m, 2H, $H_{8'ax}$), 2.82–3.09 (m, 2H, $H_{8'eq}$), 3.15 (s, 3H, OCH_3), 3.58 (t, $J_{4',3'} = J_{4',5'} = 7.8$ Hz, 1H, $H_{4'}$), 3.64 (d, $J_{1',2'} = 10.0$ Hz, 1H, $H_{1'}$), 3.82 (s, 3H, OCH_3), 3.85 (dd, $J_{5',4'} = 7.8$ Hz, $J_{5',6'a} = 5.4$ Hz, 1H, $H_{5'}$), 4.00–4.20 (m, 2H, $H_{6'}$), 4.35 (dd, $J_{2',3'} = 2.4$ Hz, $J_{2',1'} = 9.8$ Hz, 1H, $H_{2'}$), 4.75 (d, $J_{4,3} = 4,7$ Hz, lH, H_4), 4.82 (dd, $J_{3',2'} = 2.4$ Hz, $J_{3',4'} = 7.8$ Hz, 1H, $H_{3'}$), 5.05 (d, $J_{3,4} = 5.0$ Hz, 1H, H_3), 6.88 (d, $J = 8.3$ Hz, 2H, H_{Ph}), 7.51 (d, $J = 8.7$ Hz, 2H, H_{Ph}); ^{13}C NMR (50.3 MHz) δ: 25.2, 26.1, 26.5, 27.4 (C($\underline{CH_3}$)$_2$), 25.5 ($C_{9'}$), 27.1, 27.4 ($C_{8'}$), 45.2 ($C_{2'}$), 54.2 (C_4), 55.2 (OCH_3), 58.2 (OCH_3), 64.13 ($C_{1'}$), 67.8 ($C_{6'}$), 77.3, 78.1, 78.7 ($C_{3'}$, $C_{4'}$, $C_{5'}$), 85.1 (C_3), 109.8, 110.0 ($C_{7'}$), 113.3, 126.0 (CH_{Ph}), 131.2 (C_{Ph}), 160.0 (C_{Ph}), 168.2 (C_2). Δε (λ): −14.42 (204), −3.55 (225), +3.13 (239), +2.51 (276), +2.30 (282).

6b (64%): Anal. calcd for $C_{27}H_{37}NO_7S_2$: C, 57.88; H, 6.86; N, 2.60; S, 11.87. Found: C, 57.62; H, 6.87; N, 2.55; S, 11.75. MS (EI, *m/z*) 540 $(MH)^+$. mp 133–135 °C (hexane:EtOAc). $[\alpha]_D$ −111 (c 1, $CHCl_3$). IR (KBr): 1755 (NC=O). ^{1}H NMR (200 MHz) δ: 0.61, 1.15, 1.33, 1.50 (4s, 12H, C($\underline{CH_3}$)$_2$), 2.00–2.12 (m, 2H, $H_{9'}$), 2.55–2.74 (m, 2H, $H_{8'ax}$), 2.95–3.11 (m, 2H, $H_{8'eq}$), 3.03 (s, 3H, OCH_3), 3.72 (t, $J_{4',3'} = J_{4',5'} = 7.4$ Hz, 1H, $H_{4'}$), 3.77 (dd, $J_{2',3'} = 2.5$ Hz, $J_{2',1'} = 10.1$ Hz, 1H, $H_{2'}$), 3.82 (s, 3H, OCH_3), 3.96–4.16 (m, 3H, $H_{5'-6'}$), 4.21 (d, $J_{1',2'} = 9.8$ Hz, 1H, $H_{1'}$), 4.57 (dd, $J_{3',2'} = 2.4$ Hz, $J_{3',4'} = 7.8$ Hz, 1H, $H_{3'}$), 4.76 (d, $J_{4,3} = 4.9$ Hz, lH, H_4), 4.82 (d, $J_{3,4} = 5.0$Hz, 1H, H_3), 6.89 (d, $J = 10.0$ Hz, 2H, H_{Ph}), 7.38 (d, $J = 10.0$ Hz, 2H, H_{Ph}); ^{13}C NMR (50.3 MHz) δ: 25.5, 25.7 (C($\underline{CH_3}$)$_2$), 25.8 ($C_{9'}$), 26.4, 26.7 (C($\underline{CH_3}$)$_2$), 26.8, 27.1 ($C_{8'}$), 44.6 ($C_{2'}$), 54.2 (C_4), 55.6 (OCH_3), 58.1 (OCH_3), 62.4 ($C_{1'}$), 67.7 ($C_{6'}$), 76.7, 76.9, 79.1 ($C_{3'}$, $C_{4'}$, $C_{5'}$), 85.4 (C_3), 108.9, 110.2 ($C_{7'}$), 113.8, 127.5, 130.9 (CH_{Ph}), 160.2 (C_{Ph}), 170.8 (C_2). Δε (λ): +19.11 (206), −18.32 (232), −2.92 (275), −2.12 (282).

1[(1′,2′-Dideoxy-3′,4′;5′,6′-di-*O*-isopropylidene-1′(1,3-propanodithio))-D-2′-glucosyl]-3β-butyl-4β-phenyl-2-azetidinone (7) and *n*-(2-dideoxy-2′-dithianyl-3′,4′;5′,6′-di-*O*-isopropylidene-D-glucosyl)-hexanamide (7′). They were obtained by Staudinger reaction of imine **2** (1/C) and caproyl chloride after 40 h at 110 °C in 75% yield from **1**. The reaction mixture was purified on a silica gel column (hexane:ethyl acetate, 7:3).

7 (55%): MS (EI, *m/z*): 536 $(MH)^+$; 520 $[(MH)^+ - CH_3]$. $[\alpha]_D$ −67 (c 1, $CHCl_3$). IR: 1745 (NC=O). ^{1}H NMR (200 MHz) δ: 0.63 (t, $J_{8,7} = 6.8$ Hz, 3H, H_8), 0.76, 1.21, 1.30, 1.36 (4s, 12H, C($\underline{CH_3}$)$_2$), 0.80–1.60 (m, 6H, H_{5-7}), 1.94–2.10 (m, 2H, $H_{9'}$), 2.60–2.76 (m, 2H, $H_{8'ax}$), 2.90–3.08 (m, 2H, $H_{8'eq}$), 3.52 (dt, $J_{3,4} = 6.0$ Hz, $J_{3,5} = 6.7$ Hz, 1H, H_3), 3.78 (t, $J_{4',3'} = J_{4',5'} = 7.6$ Hz, 1H, $H_{4'}$), 3.90–4.42 (m, 5H, $H_{1'}$, $H_{2'}$, $H_{4'-6'}$), 4.55 (dd, $J_{3',2'} = 2.8$ Hz,

$J_{3',4'}=7.8$ Hz, 1H, $H_{3'}$), 4.88 (d, $J_{4,3}=6.0$ Hz, lH, H_4), 7.26–7.39 (m, 5H, H_{Ph}); ^{13}C NMR (50.3 MHz) δ: 13.5 (C_8), 22.1 (C_7), 24.5 (C_6), 25.1, 25.6, 26.2 ($C(\underline{CH_3})_2$), 25.4 (C_5), 27.0 ($C_{9'}$), 27.4, 29.1 ($C_{8'}$), 45.3 ($C_{2'}$), 54.8 (C_3), 55.3 (C_4), 59.7 ($C_{1'}$), 67.3 ($C_{6'}$), 77.0, 78.8 ($C_{3'}$, $C_{4'}$, $C_{5'}$), 108.8, 109.7 ($C_{7'}$), 127.8, 128.0, 128.4 (CH_{Ph}), 136.9 (C_{Ph}), 174.2 (C_2). Δε (λ): +9.39 (203), −6.24 (208), −18.13 (221), +0.74 (252).

7′ (20%): IR: 1730 (HNC=O). ^1H NMR (200 MHz) δ: 0.84 (t, $J=6.8$ Hz, 3H, $CH_3(CH_2)_2CH_2CH_2CO$), 1.06–1.30 (m, 4H, $CH_3(CH_2)_2CH_2CH_2CO$), 1.27, 1.31, 1.32, 1.43 (4s, 12H, $C(\underline{CH_3})_2$), 1.60–1.75 (m, 2H, $CH_3(CH_2)_2CH_2CH_2CO$), 1.87–2.09 (m, 2H, $H_{9'}$), 2.20 (t, $J=7.0$ Hz, 3H, $CH_3(CH_2)_2CH_2CH_2CO$), 2.45–2.68 (m, 2H, $H_{8'ax}$), 2.86–3.10 (m, 2H, $H_{8'eq}$), 3.52 (t, $J_{4',3'}=J_{4',5'}=7.9$ Hz, 1H, $H_{4'}$), 3.72 (d, $J_{1',2'}=8.9$ Hz, 1H, $H_{1'}$), 3.85–4.15 (m, 4H, $H_{2'}$, $H_{4'-6'}$), 4.65 (dd, $J_{3',4'}=7.8$ Hz, $J_{3',NH}=10.1$ Hz, 1H, $H_{3'}$), 5.90 (d, $J_{3',NH}=10.1$ Hz, 1H, NH).

1[(1′,2′-Dideoxy-3′,4′;5′,6′-di-*O*-isopropylidene-1′(1,3-propanedithio))-D-2′-glucosyl]-3β-butyl-4β-styryl-2-azetidinone (8). It was obtained by Staudinger reaction of imine **2** (1/A) and caproyl chloride after 30 h at 110 °C in 50% yield from **1**. The reaction product was purified on a silica gel column (hexane:ethyl acetate, 8:2) and also the amide **7′** was isolated in 15% yield. MS (EI, *m/z*): 562 $(MH)^+$; 548 $[(MH)^+ - CH_3]$. $[\alpha]_D$ −42 (c 1, $CHCl_3$). IR: 1768 (NC=O). ^1H NMR (200 MHz) δ: 0.85 (t, $J_{10,9}=6.8$ Hz, 3H, H_{10}), 1.23, 1.30, 1.34, 1.48 (4s, 12H, $C(\underline{CH_3})_2$), 1.25–1.78 (m, 6H, H_{7-9}), 2.01–2.03 (m, 2H, $H_{9'}$), 2.66–2.71 (m, 2H, $H_{8'ax}$), 2.95–3.02 (m, 2H, $H_{8'eq}$), 3.36 (dt, $J_{3,7}=6.7$ Hz, $J_{3,4}=5.5$ Hz, 1H, H_3), 3.79 (dd, $J_{4',3'}=7.2$ Hz, $J_{4',5'}=6.1$ Hz, 1H, $H_{4'}$), 4.01–4.20 (m, 3H, $H_{5'-6'}$), 4.28 (dd, $J_{2',1'}=10.1$ Hz, $J_{2',3'}=2.0$ Hz, lH, $H_{2'}$), 4.38 (d, $J_{1',2'}=10.1$ Hz, 1H, $H_{1'}$), 4.46 (dd, $J_{4,3}=5.6$ Hz, $J_{4,5}=9.5$ Hz, lH, H_4), 4.70 (dd, $J_{3',2'}=2.0$ Hz, $J_{3',4'}=7.8$ Hz, lH, $H_{3'}$), 6.34 (dd, $J_{5,6}=16.0$ Hz, $J_{5,4}=9.7$ Hz, lH, H_5), 6.60 (d, $J_{6,5}=16$ Hz, 1H, H_6), 7.24–7.39 (m, 5H, H_{Ph}); ^{13}C NMR (50.3 MHz) δ: 13.7 (C_{10}), 22.4 (C_9), 25.2, 25.5 (C_8, C_7), 25.2, 26.4, 27.0 ($C(\underline{CH_3})_2$), 27.1 ($C_{9'}$), 27.2, 29.6 ($C_{8'}$), 44.7 ($C_{2'}$), 54.2 (C_3), 54.4 (C_4), 59.0 ($C_{1'}$), 67.5 ($C_{6'}$), 76.9, 77.5, 78.9 ($C_{3'}$, $C_{4'}$, $C_{5'}$), 109.0, 109.5 ($C_{7'}$), 126.5, 127.1, 127.8 (CH_{Ph}), 128.5, 134.2 (C_5, C_6), 137.0 (C_{Ph}), 172.5 (C_2). Δε (λ): −4.33 (202), +3.07 (205), −4.29 (228), +2 (262).

1[(1′,2′-Dideoxy-3′,4′;5′,6′-di-*O*-isopropylidene-1′(1,3-propanedithio))-D-2′-glucosyl]-3β-butyl-4β-(*trans*-α-methylstyryl)-2-azetidinone (9) and 1[(1′,2′-dideoxy-3′,4′;5′,6′-di-*O*-isopropylidene-1′(1,3-propanedithio))-D-2′-glucosyl]-3β-butyl-4β-(*cis*-α-methylstyryl)-2-azetidinone (10). They were obtained by Staudinger reaction of imine **2** (1/B) and caproyl chloride after 26 h at 110 °C in 65% yield from **1**. The reaction mixture was purified on a silica gel column (hexane:ethyl acetate, 8:2). The amide **7′** was also obtained in 7% yield.

9 (59%): MS (EI, *m/z*): 575 $(M)^+$; 561 $[(M)^+ - CH_3]$. $[\alpha]_D$ −43 (c 1, $CHCl_3$). IR: 1745 (NC=O). ^1H NMR (200 MHz) δ: 0.82 (t, $J_{10,9}=6.8$ Hz, 3H, H_{10}), 1.23–1.77 (m, 6H, H_{7-9}), 1.30, 1.37, 1.47 (4s, 12H, $C(\underline{CH_3})_2$), 1.90–2.13 (m, 2H, $H_{9'}$), 1.97 (s, 3H, CH_3), 2.63–2.72 (m, 2H, $H_{8'ax}$), 2.72–3.10 (m, 2H, $H_{8'eq}$), 3.50 (dt, $J_{3,7}=6.7$ Hz, $J_{3,4}=5.3$ Hz, 1H, H_3), 3.87 (t, $J_{4',3'}=J_{4',5'}=7.0$ Hz, 1H, $H_{4'}$), 3.97–4.22 (m, 3H, $H_{5'-6'}$), 4.35 (dd, $J_{2',1'}=8.5$ Hz, $J_{2',3'}=4.6$ Hz, lH, $H_{2'}$), 4.55 (d, $J_{1',2'}=8.5$ Hz, 1H, $H_{1'}$), 4.72 (d, $J_{4,3}=5.1$ Hz, lH, H_4), 4.75 (dd, $J_{3',2'}=4.6$ Hz, $J_{3',4'}=7.2$ Hz, lH, $H_{3'}$), 6.83 (s, 1H, H_6), 7.32–7.39 (m, 5H, H_{Ph}); ^{13}C NMR (50.3 MHz) δ: 14.0 (C_{10}), 17.7 (CH_3), 22.8 (C_9), 25.0 (C_8), 25.5, 26.8, 27.0 ($C(\underline{CH_3})_2$), 27.9 (C_7), 28.3 ($C_{9'}$), 28.7, 30.4 ($C_{8'}$), 46.6 ($C_{2'}$), 54.9 (C_3), 56.3 (C_4), 63.1 ($C_{1'}$), 67.6 ($C_{6'}$), 77.3, 77.8, 79.6 ($C_{3'}$, $C_{4'}$, $C_{5'}$), 109.0, 109.9 ($C_{7'}$), 126.7, 128.3, 129.2 (CH_{Ph}), 129.3, 133.9 (C_5, C_6), 137.7 (C_{Ph}), 173.7 (C_2). Δε (λ): −7.48 (208), −1.60 (220), +1.81 (255).

10 (7%): Anal. calcd for $C_{31}H_{45}NO_5S_2$: C, 64.70; H, 7.83; N, 2.43; S, 11.13. Found: C, 64.25; H, 7.86; N, 2.38; S, 11.31. mp 118–120 °C (Hexane). $[\alpha]_D$ −170 (c 1, $CHCl_3$). IR: 1755 (NC=O). ^1H NMR (250 MHz) δ: 0.90 (t, $J_{10,9}=6.8$ Hz, 3H, H_{10}), 1.30–1.73 (m, 6H, H_{7-9}), 1.32, 1.34, 1.42, 1.53 (4s, 12H, $C(\underline{CH_3})_2$), 1.72–2.00 (m, 2H, $H_{9'}$), 2.06 (s, 3H, CH_3), 2.46–2.67 (m, 2H, $H_{8'ax}$), 2.88–3.30 (m, 2H, $H_{8'eq}$), 3.50 (dt, $J_{3,7}=8.0$ Hz, $J_{3,4}=5.0$ Hz, 1H, H_3), 3.72 (dd, $J_{4',3'}=8.0$ Hz, $J_{4',5'}=7.0$ Hz, 1H, $H_{4'}$), 3.90–4.20 (m, 3H, $H_{5'-6'}$), 4.00 (d, $J_{1',2'}=10.1$ Hz, 1H, $H_{1'}$), 4.36 (dd, $J_{2',1'}=10.1$ Hz, $J_{2',3'}=3.0$ Hz, lH, $H_{2'}$), 4.80 (d, $J_{4,3}=5.0$ Hz, lH, H_4), 4.81 (dd, $J_{3',2'}=3.0$ Hz, $J_{3',4'}=8.0$ Hz, lH, $H_{3'}$), 6.60 (s, 1H, H_6), 7.10 (d, $J=7.0$ Hz, 2H, H_{Ph}), 7.24–7.40 (m, 3H, H_{Ph}); ^{13}C NMR (62.9 MHz) δ: 13.9 (C_{10}), 21.3 (CH_3), 23.0 (C_9), 25.1 (C_8), 25.2, 26.3, 26.6 ($C(\underline{CH_3})_2$), 25.6 (C_7), 27.0 ($C_{9'}$), 27.3, 30.1 ($C_{8'}$), 45.3 ($C_{2'}$), 54.9 (C_3), 55.1 (C_4), 55.6 ($C_{1'}$), 67.7 ($C_{6'}$), 76.9, 77.4, 78.7 ($C_{3'}$, $C_{4'}$, $C_{5'}$), 109.8, 110.2 ($C_{7'}$), 126.8, 128.3, 128.6 ($5CH_{Ph}$), 131.7 (C_6), 136.0 (C_5), 137.2 (C_{Ph}), 175.4 (C_2). Δε (λ): −10.47 (207), −20.77 (230).

1[(1′,2′-Dideoxy-3′,4′;5′,6′-di-*O*-isopropylidene-1′(1,3-propanedithio))-D-2′-glucosyl]-3α-isopropenyl-4α-styryl-2-azetidinone (29a) and 1[(1′,2′-dideoxy-3′,4′;5′,6′-di-*O*-isopropylidene-1′(1,3-propanedithio))-D-2′-glucosyl]-3β-isopropenyl-4β-styryl-2-azetidinone (29b). They were obtained by Staudinger reaction of imine **2** (1/A) and β,β-dimethylacryloyl chloride after 10 h at 50 °C and dichloromethane as solvent, in 20% yield from **1**.

29a (6%): IR: 1765 (NC=O). ^1H NMR (200 MHz) δ: 1.35, 1.37, 1.51, 1.59 (4s, 12H, $C(\underline{CH_3})_2$), 1.65 (s, 3H, H_8), 1.95–2.15 (m, 2H, $H_{9'}$), 2.51–2.72 (m, 2H, $H_{8'ax}$), 2.90–3.30 (m, 2H, $H_{8'eq}$), 3.70 (t, $J_{4',3'}=J_{4',5'}=7.8$ Hz, 1H, $H_{4'}$), 3.96 (d, $J_{1',2'}=9.8$ Hz, 1H, $H_{1'}$), 4.00–4.22 (m, 4H, H_3, $H_{5'}$, $H_{6'}$), 4.61 (dd, $J_{2',1'}=9.8$ Hz, $J_{2',3'}=2.3$ Hz, 1H, $H_{2'}$), 4.72 (dd, 1H, H_4, $J_{4,5}=10.0$ Hz, $J_{4,3}=5.5$ Hz), 4.91 (dd, $J_{3',2'}=2.3$ Hz, $J_{3',4'}=7.9$ Hz, 1H, $H_{3'}$), 5.08 (s, 1H, H_{9a}), 5.26 (s, 1H, H_{9b}), 6.46 (dd, $J_{5,6}=16.0$ Hz, $J_{5,4}=10.0$ Hz, 1H, H_5), 6.68 (d, $J_{6,5}=15.9$ Hz, 1H, H_6), 7.27–7.36 (m, 5H, H_{Ph}).

29b (14%): Anal. calcd for $C_{29}H_{39}NO_5S_2$: C, 63.82; H, 7.20; N, 2.57; S, 11.75. Found: C, 63.90; H, 7.31; N, 2.53; S, 11.99. $[\alpha]_D$ −109 (c 1, $CHCl_3$). IR: 1748 (NC=O). ^1H NMR (250 MHz) δ: 1.20, 1.28, 1.35, 1.50 (4s, 12H, $C(\underline{CH_3})_2$), 1.65 (s, 3H, H_8), 1.90–2.15 (m, 2H, $H_{9'}$), 2.60–2.70 (m, 2H, $H_{8'ax}$), 2.92–3.01 (m, 2H, $H_{8'eq}$),

3.82 (t, $J_{4',3'} = J_{4',5'} = 7.5$ Hz, 1H, $H_{4'}$), 4.00–4.38 (m, 6H, H_3, $H_{1'}$, $H_{2'}$, $H_{5'}$, $H_{6'}$), 4.53 (dd, $J_{4,5} = 9.5$ Hz, $J_{4,3} = 5.8$ Hz, 1H, H_4), 4.67 (dd, $J_{3',2'} = 2.2$ Hz, $J_{3',4'} = 7.7$ Hz, 1H, $H_{3'}$), 5.05 (s, 1H, H_{9a}), 5.15 (s, 1H, H_{9b}), 6.28 (dd, $J_{5,6} = 15.9$ Hz, $J_{5,4} = 9.8$ Hz, 1H, H_5), 6.61 (d, $J_{6,5} = 15.9$ Hz, 1H, H_6), 7.26–7.34 (m, 5H, H_{Ph}); ^{13}C NMR (62.5 MHz) δ: 22.2 (C_8), 25.0, 26.2, 26.3 (4C($\underline{CH_3}$)$_2$), 25.3, 26.9 (3C; $C_{8'}$, $C_{9'}$), 44.3 ($C_{2'}$), 53.9 (C_3), 59.1 (C_4), 60.5 ($C_{1'}$), 67.4 ($C_{6'}$), 76.7, 77.2, 78.9 ($C_{3'}$, $C_{4'}$, $C_{5'}$), 109.1, 109.6 ($C_{7'}$), 115.0 (C_9), 126.5 (C_5), 126.7, 127.7, 128.3 (5CH_{Ph}), 134.0 (C_6), 136.2 (C_{Ph}), 137.0 (C_7), 169.3 (C_2).

1[(1′,2′-Dideoxy-3′,4′;5′,6′-di-*O*-isopropylidene-1′(1,3-propanedithio))-D-2′-glucosyl]-3,3-diethyl-4α-(α-methylstyryl)-2-azetidinone (30a) and 1[(1′,2′-dideoxy-3′,4′;5′,6′-di-*O*-isopropylidene-1′(1,3-propanedithio))-D-2′-glucosyl]-3,3-diethyl-4β-(α-methylstyryl)-2-azetidinone (30b). They were obtained by Staudinger reaction of imine **2** (1/B) and 2-ethylbutyroyl chloride after 20 h at 50 °C, and dichloromethane as solvent, in 28% yield from **1**.

30a (11%): MS (EI, *m*/*z*): 576 $(MH)^+$. $[\alpha]_D$ −6 (c 1, $CHCl_3$). IR: 1743 (NC=O). ^{1}H NMR (250 MHz) δ: 0.94, 1.06 (2t, $J = 7.4$ Hz, 6H, H_8), 1.37, 1.46, 1.50 (3s, 12H, C($\underline{CH_3}$)$_2$), 1.70–2.00 (m, 4H, H_7), 1.91 (s, 3H, CH_3(C=)), 2.01–2.10 (m, 2H, $H_{9'}$), 2.90–3.10 (m, 4H, $H_{8'}$), 3.77 (dd, $J_{2',1'} = 7.6$ Hz, $J_{2',3'} = 3.5$ Hz, 1H, $H_{2'}$), 3.97–4.27 (m, 5H, $H_{1'}$, $H_{4'-6'}$), 4.38 (s, 1H, H_4), 5.05 (dd, $J_{3',2'} = 3.6$ Hz, $J_{3',4'} = 7.8$ Hz, 1H, $H_{3'}$), 6.84 (s, 1H, H_6), 7.20–7.38 (m, 5H, H_{Ph}); ^{13}C NMR (62.5 MHz) δ: 8.9, 9.4 (C_8), 18.1 ($\underline{CH_3}$(C=)), 20.9 (2C_7), 25.6, 26.2, 26.7, 27.4 (C($\underline{CH_3}$)$_2$), 25.8 ($C_{9'}$), 28.2, 28.6 ($C_{8'}$), 47.8 ($C_{2'}$), 55.3 (C_4), 63.5 (C_3), 67.9 ($C_{6'}$), 70.8 ($C_{1'}$), 77.6, 78.0, 79.4 ($C_{3'}$, $C_{4'}$, $C_{5'}$), 109.5, 110.2 ($C_{7'}$), 126.6, 128.3, 128.4 (5CH_{Ph}), 129.1 (C_6), 133.3 (C_5), 137.8 (C_{Ph}), 175.1 (C_2).

30b (17%): Anal. Calcd for $C_{31}H_{45}NO_5S_2$: C, 64.66; H, 7.88; N, 2.43; S, 11.14. Found: C, 64.21; H, 7.29; N, 2.02; S, 11.04. mp 156–157 °C (hexane:EtOAc). $[\alpha]_D$ −25 (c 1, $CHCl_3$). IR: 1749 (NC=O). ^{1}H NMR (250 MHz) δ: 0.94, 1.04 (2t, $J = 7.4$ Hz, 6H, H_8), 1.33, 1.34, 1.38, 1.47 (4s, 12H, C($\underline{CH_3}$)$_2$), 1.65–2.00 (m, 4H, H_7), 1.96 (s, 3H, $\underline{CH_3}$(C=)), 2.02–2.18 (m, 2H, $H_{9'}$), 2.80–2.95 (m, 4H, $H_{8'}$), 3.89 (dd, $J_{2',1'} = 7.0$ Hz, $J_{2',3'} = 3.8$ Hz, 1H, $H_{2'}$), 3.97–4.16 (m, 4H, $H_{4'-6'}$), 4.42 (s, 1H, H_4), 4.57 (t, $J_{4',3'} = J_{4',5'} = 6.8$ Hz, 1H, $H_{4'}$), 4.85 (d, 1H, $H_{1'}$, $J_{1',2'} = 6.8$ Hz), 7.00 (s, 1H, H_6), 7.15–7.32 (m, 5H, H_{Ph}); ^{13}C NMR (62.5 MHz) δ: 9.0, 9.4 (C_8), 18.2 ($\underline{CH_3}$(C=O)), 20.9, 25.3 (C_7), 25.6, 26.9, 27.2, 27.3 (C($\underline{CH_3}$)$_2$), 26.2 ($C_{9'}$), 30.4, 30.6 ($C_{8'}$), 48.1 ($C_{2'}$), 57.8 (C_4), 63.2 (C_3), 67.6 ($C_{6'}$), 70.0 ($C_{1'}$), 77.2, 78.7, 80.3 (3C; $C_{3'}$, $C_{4'}$, $C_{5'}$), 109.7 (2$C_{7'}$), 126.6, 128.4, 129.0 (5CH_{Ph}), 128.3 (C_6), 133.0 (C_5), 137.9 (C_{Ph}), 175.1 ($C_{2'}$).

1[(1′,2′-Dideoxy-3′,4′;5′,6′-di-*O*-isopropylidene-1′(1,3-propanedithio))-D-2′-glucosyl]-3β-ethyl-4β-(α-methylstyryl)-2-azetidinone (31) and *N*-(2-dideoxy-2′-dithianyl-3′,4′;5′,6′-di-*O*-isopropylidene-D-glucosyl)-butananamide (31′). They were obtained by Staudinger reaction of imine **2** (1/B) and butyroyl chloride after 20 h at room temperature in 70% yield from **1**. The reaction mixture was purified on a silica gel column (hexane:ethyl acetate, 7:3).

31 (60%): Anal. calcd for $C_{29}H_{41}NO_5S_2$: C, 63.60; H, 7.55; N, 2.56; S, 11.69. Found: C, 63.87; H, 7.44; N, 2.86; S, 11.69. MS (EI, *m*/*z*) 547 (M^+), 530 $(M^+ - CH_3)$. mp 103–105 °C (hexane:EtOAc). $[\alpha]_D$ −72 (c 1, $CHCl_3$). IR(KBr): 1742 (NC=O). ^{1}H NMR (250 MHz) δ: 0.93 (t, $J_{10,9} = 6.8$ Hz, 3H, H_8), 1.27, 1.30, 1.32, 1.41 (4s, 12H, C($\underline{CH_3}$)$_2$), 1.67–1.83 (m, 2H, H_7), 1.85–2.10 (m, 2H, $H_{9'}$), 1.94 (s, 3H, CH_3), 2.61–2.80 (m, 2H, $H_{8'ax}$), 2.85–3.03 (m, 2H, $H_{8'eq}$), 3.38 (dt, $J_{3,7} = 7.8$ Hz, $J_{3,4} = 5.8$ Hz, 1H, H_3), 3.85 (dd, $J_{4',3'} = 7.1$ Hz, $J_{4',5'} = 6.8$ Hz, 1H, $H_{4'}$), 3.94–4.13 (m, 3H, $H_{5'-6'}$), 4.27 (dd, $J_{2',1'} = 8.5$ Hz, $J_{2',3'} = 4.3$ Hz, lH, $H_{2'}$), 4.51 (d, $J_{1',2'} = 8.5$ Hz, 1H, $H_{1'}$), 4.53 (d, $J_{4,3} = 5.8$ Hz, lH, H_4), 4.63 (dd, $J_{3',2'} = 4.5$ Hz, $J_{3',4'} = 7.1$ Hz, lH, $H_{3'}$), 6.77 (s, 1H, H_6), 7.17–7.30 (m, 5H, H_{Ph}); ^{13}H NMR (50.3 MHz) δ: 13.0 (C_8), 17.9 (CH_3), 19.0 (C_7), 25.7, 27.1, 27.3 (C($\underline{CH_3}$)$_2$), 26.2 ($C_{9'}$), 28.7, 29.0 ($C_{8'}$), 46.9 ($C_{2'}$), 56.6 (C_3), 56.8 (C_4), 63.3 ($C_{1'}$), 67.9 ($C_{6'}$), 77.6, 78.2, 79.9 ($C_{3'}$, $C_{4'}$, $C_{5'}$), 110.0, 111.0 ($C_{7'}$), 127.0, 128.6 (5CH_{Ph}), 129.4 (C_6), 133.5 (C_5), 137.9 (C_{Ph}), 174.5 (C_2). Δε (λ): −14.42 (206), −11.48 (220), +2.54 (252).

31′ (10%): MS (EI, *m*/*z*) 419 (M^+), 404 $(M^+ - CH_3)$. IR: 1732 (HNC=O). ^{1}H NMR (200 MHz) δ: 0.94 (t, $J = 6.8$ Hz, 3H, $CH_3CH_2CH_2CO$), 1.33, 1.35, 1.38, 1.46 (4s, 12H, C($\underline{CH_3}$)$_2$), 1.63 (sex, $J = 6.8$ Hz, 2H, CH_3CH_2 CH_2CO), 1.90–2.10 (m, 2H, $H_{9'}$), 2.20 (t, $J = 6.8$ Hz, 2H, $CH_3CH_2CH_2CO$), 2.50–2.70 (m, 2H, $H_{8'ax}$), 2.76–3.01 (m, 2H, $H_{8'eq}$), 3.55 (t, $J_{4',3'} = J_{4',5'} = 7.9$ Hz, 1H, $H_{4'}$), 3.75 (d, $J_{1',2'} = 8.9$ Hz, 1H, $H_{1'}$), 3.90–4.15 (m, 4H, $H_{2'}$, $H_{4'-6'}$), 4.70 (dd, $J_{3',4'} = 7.8$ Hz, $J_{3',NH} = 10.1$ Hz, 1H, $H_{3'}$), 5.87 (d, $J_{3',NH} = 10.1$ Hz, 1H, NH).

1[(1′,2′-Dideoxy-3′,4′;5′,6′-di-*O*-isopropylidene-1′,1′-dipropylthio)-D-2′-glucosyl]-3β-ethyl-4β-(*trans*-α-methylstyryl)-2-azetidinone (35) and 1[(1′,2′-dideoxy-3′,4′;5′,6′-di-*O*-isopropylidene-1′,1′-dipropylthio)-D-2′-glucosyl]-3β-ethyl-4β-(*cis*-α-methylstyryl)-2-azetidinone (35′). They were obtained by Staudinger reaction of imine **2** (34/B) and butyroyl chloride after 4 h at reflux in toluene in 72% yield from **34**. The reaction mixture was purified on a silica gel column (hexane:ethyl acetate, 9:1).

35 (60%): Anal. calcd for $C_{32}H_{49}NO_5S_2$: C, 64.94; H, 8.34. Found: C, 65.01; H, 8.42. $[\alpha]_D$ −94° (c 1, $CHCl_3$). IR: 1753 (NC=O). ^{1}H NMR (200 MHz) δ: 0.92–1.02 (m, 9H, H_8, $H_{10'}$), 1.29, 1.31, 1.36, 1.38 (4s, 12H, C($\underline{CH_3}$)$_2$), 1.50–1.86 (m, 6H, H_7, $H_{9'}$), 1.95 (s, 3H, $\underline{CH_3}$(C=)), 2.60–2.80 (m, 4H, $H_{8'}$), 3.39 (dt, $J_{3,4} = 5.8$ Hz, $J_{3,7} = 7.2$ Hz, 1H, H_3), 3.80 (t, $J_{4',3'} = J_{4',5'} = 7.2$ Hz, 1H, $H_{4'}$), 3.90–4.25 (m, 4H, $H_{2'}$, $H_{5'-6'}$), 4.46 (d, $J_{1',2'} = 7.8$ Hz, 1H, $H_{1'}$), 4.56 (d, $J_{4,3} = 5.8$ Hz, 1H, H_4), 4.68 (dd, $J_{3',2'} = 2.3$ Hz, $J_{3',4'} = 6.9$ Hz, 1H, $H_{3'}$), 6.85 (s, 1H, H_6), 7.20–7.40 (m, 5H, H_{Ph}); ^{13}C NMR (62.5 MHz) δ: 12.7 (C_8), 13.7, 13.8 ($C_{10'}$), 17.7 ($\underline{CH_3}$(C=)), 18.8 (C_7), 22.5, 22.7 ($C_{9'}$), 25.6, 26.7, 27.0, 27.2 (4C($\underline{CH_3}$)$_2$), 32.7, 34.7 (2$C_{8'}$), 52.8 ($C_{2'}$), 56.4 (C_3), 57.1 (C_4), 63.4 ($C_{1'}$), 67.7 ($C_{6'}$), 77.3, 78.8, 80.0 ($C_{3'}$, $C_{4'}$, $C_{5'}$), 109.5, 110.0 (2$C_{7'}$), 126.6, 128.3, 129.1 (5CH_{Ph}), 129.0 (C_6), 133.6 (C_5), 138.1 (C_{Ph}), 173.0 (C_2).

35′ (12%): $[\alpha]_D$ −103 (c 1.5, $CHCl_3$). IR: 1758 (NC=O). ^{1}H NMR (200 MHz) δ: 0.88, 0.95 (2t, 6H, $H_{10'}$,

$J = 7.4$ Hz), 1.12 (t, 3H, H_9, $J = 7.4$ Hz), 1.32, 1.37, 1.42, 1.47 (4s, 12H, C($\underline{CH_3}$)$_2$), 1.35–1.92 (m, 6H, H_7, $H_{9'}$), 2.04 (s, 3H, $\underline{CH_3}$(C=)), 2.35–2.70 (m, 4H, $H_{8'}$), 3.42 (dd, $J_{3,4} = 6.2$ Hz, $J_{3,7} = 7.0$ Hz, 1H, H_3), 3.70 (t, $J_{4',3'} = J_{4',5'} = 7.9$ Hz, 1H, $H_{4'}$), 3.88–4.14 (m, 5H, $H_{1'}$, $H_{2'}$, $H_{5'-6'}$), 4.85 (d, $J_{4,3} = 6.2$ Hz, 1H, H_4), 4.87 (dd, $J_{3',2'} = 2.2$ Hz, $J_{3',4'} = 7.9$ Hz, 1H, $H_{3'}$), 6.57 (s, 1H, H_6), 7.13 (d, $J = 9.0$ Hz, 2H, H_{Ph}), 7.26–7.32 (m, 3H, H_{Ph}); ^{13}C NMR (62.5 MHz) δ: 13.1 (C_8), 13.8, 14.2 (2C, $C_{10'}$), 18.9 (C_7), 21.4 ($\underline{CH_3}$(C=)), 22.4, 22.5 ($C_{9'}$), 25.3, 26.3, 26.4, 26.6 (4C($\underline{CH_3}$)$_2$), 31.5, 33.3 (2$C_{8'}$), 53.6 ($C_{2'}$), 55.8 (C_3), 56.4 (C_4), 57.0 ($C_{1'}$), 67.9 ($C_{6'}$), 77.7, 78.5 (3C; $C_{3'}$, $C_{4'}$, $C_{5'}$), 109.5, 110.0 (2$C_{7'}$), 126.8, 128.3, 128.7 (5CH_{Ph}), 131.5 (C_6), 135.9 (C_5), 137.5 (C_{Ph}), 174.8 (C_2).

1[(1′,2′-Dideoxy-3′,4′;5′,6′-di-*O*-isopropylidene-1′,1′-dimethoxy)-D-2′-glucosyl]-3β-ethyl-4β-(*trans*-α-methylstyryl)-2-azetidinone (36) and 1[(1′,2′-dideoxy-3′,4′;5′,6′-di-*O*-isopropylidene-1′,1′-dimethoxy)-D-2′-glucosyl]-3β-ethyl-4β-(*cis*-α-methylstyryl)-2-azetidinone (36′). They were obtained by Staudinger reaction of imine **2** (37/ B) and butyroyl chloride after 12 h at reflux in toluene, in 70% yield from **37**. The reaction mixture was purified on a silica gel column (hexane:ethyl acetate, 8:2). The monobactam **36** was also obtained by reaction of **31** or **35** with [bis(trifluoroacetoxy)iodo]benzene in methanol according to the procedure reported by Stork et al.[12] in 54 and 71% yield, respectively.

36 (58%): Anal. calcd for $C_{28}H_{41}NO_7$: C, 66.77; H, 8.20; N, 2.78 . Found: C, 66.11; H, 8.58; N, 3.01. $[\alpha]_D$ −130 (c 1.9, $CHCl_3$). IR: 1755 (NC=O). ^{1}H NMR (200 MHz) δ: 0.99 (t, $J_{8,7} = 7.4$ Hz, 3H, H_8), 1.29, 1.32, 1.36, 1.40 (4s, 12H, C($\underline{CH_3}$)$_2$), 1.45–1.80 (m, 2H, H_7), 1.69 (s, 3H, $\underline{CH_3}$(C=)), 3.27 (ddd, $J_{3,4} = J_{3,7a} = 5.6$ Hz, $J_{3,7b} = 8.6$ Hz, 1H, H_3), 3.44, 3.53 (2s, 6H, OCH_3), 3.65 (dd, 1H, $H_{2'}$, $J_{2',1'} = 7.8$ Hz, $J_{2',3'} = 3.4$ Hz), 3.86 (t, $J_{4',3'} = J_{4',5'} = 7.4$ Hz, 1H, $H_{4'}$), 3.91–4.18 (m, 3H, $H_{5'-6'}$), 4.25 (dd, $J_{3',2'} = 3.2$ Hz, $J_{3',4'} = 7.4$ Hz, 1H, $H_{3'}$), 4.40 (d, $J_{4,3} = 5.6$ Hz, 1H, H_4), 5.20 (d, $J_{1',2'} = 7.8$ Hz, 1H, $H_{1'}$), 6.90 (s, 1H, H_6), 7.20–7.31 (m, 5H, H_{Ph}); ^{13}C NMR (50.3 MHz) δ: 12.6 (C_8), 17.3 ($\underline{CH_3}$(C=)), 18.6 (C_7), 25.3, 26.7, 27.3, 27.4 (4C($\underline{CH_3}$)$_2$), 54.2, 56.0 (2OCH_3), 56.2 (C_3), 57.1 (C_4), 63.6 ($C_{2'}$), 67.7 ($C_{6'}$), 77.3, 78.8, 79.5 ($C_{3'}$, $C_{4'}$, $C_{5'}$), 102.6 ($C_{1'}$), 109.8, 109.9 (2$C_{7'}$), 126.6, 128.3, 129.1 (5CH_{Ph}), 129.0 (C_6), 132.6 (C_5), 137.8 (C_{Ph}), 171.5 (C_2).

36′ (12%): IR: 1755 (NC=O). ^{1}H NMR (250 MHz) δ: 1.09 (t, $J_{8,7} = 7.2$ Hz, 3H, H_8), 1.28, 1.30, 1.38 (3s, 12H, C($\underline{CH_3}$)$_2$), 1.50–2.00 (m, 2H, H_7), 2.03 (s, 3H, $\underline{CH_3}$(C=)), 3.22 (ddd, $J_{3,4} = J_{3,7a} = 6.0$ Hz, $J_{3,7b} = 8.2$ Hz, 1H, H_3), 3.32, 3.35 (2s, 6H, OCH_3), 3.59 (dd, $J_{2',1'} = 7.7$ Hz, $J_{2',3'} = 3.6$ Hz, 1H, $H_{2'}$), 3.65–3.80 (m, 2H, $H_{4'-5'}$), 3.92–4.10 (m, 2H, $H_{6'}$), 4.16 (dd, $J_{3',2'} = 3.6$ Hz, $J_{3',4'} = 7.5$ Hz, 1H, $H_{3'}$), 4.83 (d, $J_{4,3} = 6.0$ Hz, 1H, H_4), 4.87 (d, $J_{1',2'} = 7.7$ Hz, 1H, $H_{1'}$), 6.63 (s, 1H, H_6), 7.12 (d, $J = 7.0$ Hz, 2H, H_{Ph}), 7.20–7.40 (m, 3H, H_{Ph}); ^{13}C NMR (62.5 MHz) δ: 12.9 (C_8), 19.0 (C_7), 20.9 ($\underline{CH_3}$(C=)), 25.3, 26.5, 26.9 (4C($\underline{CH_3}$)$_2$), 53.8, 55.5 ($O\underline{CH_3}$), 56.6 (2C; C_3, $C_{2'}$), 57.2 (C_4), 67.3 ($C_{6'}$), 77.2, 78.1, 78.5 ($C_{3'}$, $C_{4'}$, $C_{5'}$), 102.2 ($C_{1'}$), 109.7 (2$C_{7'}$), 126.9, 128.3, 128.6 (5CH_{Ph}), 131.9 (C_6), 135.4 (C_5), 137.0 (C_{Ph}), 172.8 (C_2).

General procedure for preparation of monobactams II

To a solution of monobactam I (1 mmol) in dry THF (25 mL) a 1.6 M solution of *n*-butyllithium (1.5 mL, 2.2 equiv) in hexane was slowly added under an inert atmosphere at −40 °C. The mixture was stirred for 20–40 min, poured into cold ammonium chloride solution and extracted with dichloromethane. The organic layers were dried (Na_2SO_4), filtered, and evaporated to dryness. After purification by silica gel column chromatography (hexane:ethyl acetate, 9:1), the compound **18** was obtained as a brown oil in 95–100% yield, ^{1}H NMR (200 MHz) δ: 1.01, 1.50 (2s, 12H, C($\underline{CH_3}$)$_2$), 2.20–2.45 (m, 2H, H_9), 2.80–3.00 (m, 4H, H_8), 3.90–4.20 (m, 3H, H_{5-6}), 4.85 (dd, $J_{3,2} = 8.8$ Hz, $J_{3,4} = 7.8$ Hz, 1H, H_3), 5.84 (d, $J_{2,3} = 8.8$ Hz, 1H, H_2).

3α-Methoxy-4α-styryl-2-azetidinone (11a) and 3β-methoxy-4β-styryl-2-azetidinone (11b). They were obtained from **3a** (3 mmol) and **3b** (4.8 mmol) via the above general procedure in 85 and 90% yield, respectively, after chromatography on silica gel (hexane:ethyl acetate, 7:3).

Anal. calcd for $C_{12}H_{13}O_2N$: C, 70.91; H, 6.45; O, 15.75; N, 6.89. Found: C, 70.66; H, 6.20; O, 15.82 for **11a** and C, 70.87; H, 6.35; N, 6.57 for **11b**. mp 125–127 °C (heptane:CH_2Cl_2). $[\alpha]_D$ −10 (c 1, $CHCl_3$) for **11a** and $[\alpha]_D$ +10 (c 1, $CHCl_3$) for **11b**. IR(KBr): 1768 (NC=O). ^{1}H NMR (200 MHz) δ: 3.44 (s, 3H, OCH_3), 4.38 (dd, $J_{4,3} = 4.8$ Hz, $J_{4,5} = 8.3$ Hz, 1H, H_4), 4.64 (dd, $J_{3,4} = 4.8$ Hz, $J_{3,1} = 2.0$ Hz, 1H, H_3), 6.26 (dd, $J_{5,4} = 8.3$ Hz, $J_{5,6} = 16.0$ Hz, 1H, H_5), 6.56 (br.s, 1H, NH), 6.65 (d, $J_{6,5} = 16.0$ Hz, 1H, H_6), 7.20–7.50 (m, 5H, H_{Ph}). ^{13}C NMR (50.3 MHz) δ: 56.9 (C_4), 58.5 (OCH_3), 86.8 (C_3), 125.0 (C_6), 126.7, 128.1, 128.7 (5CH_{Ph}), 134.8 (C_5), 136.4 (C_{Ph}), 168.0 (C_2). Δε (λ): +53 (226) for **11a** and −101.6 (226) for **11b**.

3α-Methoxy-4α-(*trans*-α-methylstyryl)-2-azetidinone (12a) and 3β-methoxy-4β-(*trans*-α-methylstyryl)-2-azetidinone (12b). They were obtained from **4a** (1 mmol) and **4b** (1 mmol) via the general procedure above in 97 and 95% yield, respectively, after chromatography on silica gel (hexane:ethyl acetate, 7:3). Anal. Calcd for $C_{13}H_{15}O_2N$: C, 71.86; H, 6.96; N, 6.44. Found: C, 71.64; H, 6.80; N, 6.23 for **12a** and C, 71.52; H, 6.98; N, 6.33 for **12b**. MS (EI, *m*/*z*): 217 (M^+), 402 ($M^+ - CH_3$). mp 91–93 °C (heptane:CH_2Cl_2). $[\alpha]_D$ −40 (c 1, $CHCl_3$) for **12a** and $[\alpha]_D$ +40 (c 1, $CHCl_3$) for **12b**. IR(KBr): 1756 (NC=O). ^{1}H NMR (250 MHz) δ: 3.44 (s, 3H, OCH_3), 4.38 (dd, $J_{4,3} = 4.8$ Hz, $J_{4,5} = 8.3$ Hz, 1H, H_4), 4.64 (dd, $J_{3,4} = 4.8$ Hz, $J_{3,1} = 2.0$ Hz, 1H, H_3), 6.26 (dd, $J_{5,4} = 8.3$ Hz, $J_{5,6} = 16.0$ Hz, 1H, H_5), 6.56 (br.s, 1H, NH), 6.65 (d, $J_{6,5} = 16.0$ Hz, 1H, H_6), 7.20–7.50 (m, 5H, H_{Ph}); ^{13}C NMR (62.5 MHz) δ: 15.5 ($\underline{CH_3}$(C=)), 58.9 (OCH_3), 61.3 (C_4), 86.6 (C_3), 127.2, 128.5, 129.5 (5CH_{Ph}), 134.7 (C_6), 137.1 (2C, C5, C_{Ph}), 169.1 (C_2).

3α-Methoxy-4α-phenyl-2-azetidinone (13a) and 3β-methoxy-4β-phenyl-2-azetidinone (13b). They were obtained from **5a** (0.2 mmol) and **5b** (2.3 mmol) according to the general procedure in 80 and 87% yield,

respectively, after chromatography on silica gel (hexane: ethyl acetate, 7:3). Anal. calcd for $C_{10}H_{11}O_2N$: C, 67.80; H, 6.21; N, 7.91. Found: C, 67.55; H, 6.27; N, 8.11 for **13b**. mp 46–48 °C (hexane:EtOAc). $[\alpha]_D$ −112 (c 1, $CHCl_3$) for **13a** and $[\alpha]_D$ +112 (c 1, $CHCl_3$) for **13b**. IR(KBr): 1765 (NC=O). ^{1}H NMR (200 MHz) δ: 3.15 (s, 3H, OCH_3), 4.73 (br.s, 1H, H_4), 4.83 (d, $J_{3,4}$ = 4.3 Hz, 1H, H_3), 6.56 (br.s, 1H, NH), 7.37 (br.s, 5H, H_{Ph}); ^{13}C NMR (50.3 MHz) δ: 58.2 (2C, C_4, OCH_3), 86.8 (C_3), 127.7, 128.4 (5C, CH_{Ph}), 135.8 (C_{Ph}), 169.1 (C_2). Δε (λ): −4.87 (209), +10.18 (226) for **13a** and +4.60 (211), −15.40 (226) for **13b**.

3β-Butyl-4β-phenyl-2-azetidinone (14). It was obtained from **7** (2.3 mmol) in 70% yield after chromatography on silica gel (hexane:ethyl acetate, 8:2). MS (EI, *m*/*z*): 203 (M^+), 175 (M^+ −CO).$[\alpha]_D$ −66 (c 1, $CHCl_3$). IR: 1756 (NC=O). ^{1}H NMR (200 MHz) δ: 0.70 (t, $J_{8,7}$ = 4.6 Hz, 3H, H_8), 1.02–1.38 (m, 6H, H_{5-7}), 3.43–3.47 (m, 1H, H_3), 4.86 (d, $J_{4,3}$ = 5.4 Hz, 1H, H_4), 6.02 (br.s, 1H, NH), 7.29–7.37 (m, 5H, H_{Ph}); ^{13}C NMR (50.3 MHz) δ: 13.5 (C_8), 22.2 (C_7), 25.2 (C_6), 29.0 (C_5), 54.9 (C_3), 56.2 (C_4), 126.3, 127.9, 128.3 (5C, CH_{Ph}), 137.4 (C_{Ph}), 171.5 (C_2). Δε (λ): −7.82 (207), −10.15 (215).

3β-Butyl-4β-styryl-2-azetidinone (15). It was obtained from **8** (0.35 mmol) in 85% yield after chromatography on silica gel (hexane:ethyl acetate, 8:2). MS (EI, *m*/*z*): 229 (M^+), 201 (M^+ −CO). mp 77–79 °C (heptane: CH_2Cl_2). $[\alpha]_D$ +12 (c 1, $CHCl_3$). IR (KBr): 1755 (NC=O). ^{1}H NMR (200 MHz) δ: 0.93 (t, $J_{10,9}$ = 6.8 Hz, 3H, H_{10}), 1.30–1.82 (m, 6H, H_{7-9}), 3.41 (m, 1H, H_3), 4.45 (dd, $J_{4,3}$ = 5.4 Hz, $J_{4,5}$ = 7.5 Hz, 1H, H_4), 5.95 (br.s, 1H, NH), 6.29 (dd, $J_{5,4}$ = 7.4 Hz, $J_{5,6}$ = 15.9 Hz, 1H, H_5), 6.69 (d, $J_{6,5}$ = 16.0 Hz, 1H, H_6), 7.33–7.47 (m, 5H, H_{Ph}); ^{13}C NMR (50.3 MHz) δ: 13.9 (C_{10}), 22.6 (C_9), 25.2 (C_8), 29.7 (C_7), 53.5 (C_3), 55.9 (C_4), 126.2, 126.6, 128.1 (5C, CH_{Ph}), 128.8 (C_6), 133.7 (C_5), 136.3 (C_{Ph}), 17.15 (C_2). Δε (λ): +4.01 (212), −3.89 (215), −2.98 (220), −2.12 (242).

3β-Butyl-4β-(*trans*-α-methylstyryl)-2-azetidinone (16). It was obtained from **9** (13 mmol) in 95% yield after chromatography on silica gel (hexane:ethyl acetate, 8:2). Anal. calcd for $C_{16}H_{21}ON$: C, 79.01; H, 8.64; N, 5.76. Found: C, 79.00; H, 8.59; N, 5.45. $[\alpha]_D$ −46 (c 1, $CHCl_3$). IR: 1754 (NC=O). ^{1}H NMR (200 MHz) δ: 0.90 (t, $J_{10,9}$ = 6.8 Hz, 3H, H_{10}), 1.27–1.70 (m, 6H, H_{7-9}), 1.90 (s, 3H, CH_3), 3.38 (m, 1H, H_3), 4.30 (d, $J_{4,3}$ = 5.4 Hz, 1H, H_4), 6.30 (br.s, 1H, NH), 6.58 (s, 1H, H_6), 7.23–7.43 (m, 5H, H_{Ph}); ^{13}C NMR (50.3 MHz) δ: 13.9 (C_{10}), 16.9 (CH_3), 22.8 (C_9), 25.1 (C_8), 29.9 (C_7), 53.4 (C_3), 57.4 (C_4), 126.7, 128.3, (5C, CH_{Ph}), 128.9 (C_6), 134.5 (C_5), 137.3 (C_{Ph}), 171.5 (C_2). Δε (λ): −8.20 (210), −4.98 (215), −2.55 (236).

3β-Butyl-4β-(*cis*-α-methylstyryl)-2-azetidinone (17). It was obtained from **10** (1.4 mmol) in 88% yield after chromatography on silica gel (hexane:ethyl acetate, 8:2). MS (EI, *m*/*z*): 243 (M^+). mp 121–123 °C (heptane). $[\alpha]_D$ −53 (c 1, $CHCl_3$). IR (KBr): 1747 (NC=O). ^{1}H NMR (200 MHz) δ: 0.90 (t, $J_{10,9}$ = 6.8 Hz, 3H, H_{10}), 1.30–1.73 (m, 6H, H_{7-9}), 1.97 (s, 3H, CH_3), 3.42 (m, 1H, H_3), 4.70 (d, $J_{4,3}$ = 5.6 Hz, 1H, H_4), 6.28 (br.s, 1H, NH), 6.60 (s, 1H, H_6), 7.08–7.13 (m, 2H, H_{Ph}), 7.23–7.38 (m, 3H, H_{Ph}); ^{13}C NMR (50.3 MHz) δ: 13.7 (C_{10}), 21.7 (CH_3), 22.5 (C_9), 25.2 (C_8), 29.9 (C_7), 52.3 (C_3), 56.4 (C_4), 126.7, 128.2, (5C, CH_{Ph}), 129.9 (C_6), 134.9 (C_5), 136.5 (C_{Ph}), 171.9 (C_2). Δε (λ): −15.07 (210), −23.33 (246).

3,3-Diethyl-4α-(*trans*-α-methylstyryl)-2-azetidinone (32a) and 3,3-diethyl-4β-(*trans*-α-methylstyryl)-2-azetidinone (32b). They were obtained from **30a** (0.5 mmol) and **30b** (0.8 mmol) in 84 and 85% yield, respectively, after chromatography on silica gel (hexane:ethyl acetate, 6:4). MS (EI, *m*/*z*): 243 (M^+), 215 (M^+ −CO) for **32a**. $[\alpha]_D$ +47° (c 1, $CHCl_3$) for **32a** and $[\alpha]_D$ −47 (c 1, $CHCl_3$) for **32b**. IR: 1766 (NC=O). ^{1}H NMR (200 MHz) δ: 0.92 (t, $J_{7,8}$ = 6.8 Hz, 3H, H_8), 1.41–1.65 (m, 2H, H_7), 1.78 (s, 3H, CH_3), 3.90 (s, 1H, H_4), 6.18 (br.s, 1H, NH), 6.44 (s, 1H, H_6), 7.24–7.40 (m, 5H, H_{Ph}). Δε (λ): +1.3 (220) for **32a** and −1.4 (220) for **32b**.

3β-Ethyl-4β-(*trans*-α-methylstyryl)-2-azetidinone (33). It was obtained from **31** (0.65 mmol) in 87% yield after chromatography on silica gel (hexane:ethyl acetate, 8/2). mp 78–80 °C (Hexane:ether). $[\alpha]_D$ −11 (c 1, $CHCl_3$). IR (KBr): 1755 (NC=O). ^{1}H NMR (200 MHz) δ: 1.07 (t, $J_{7,8}$ = 6.8 Hz, 3H, H_8), 1.46–1.80 (m, 2H, H_7), 1.90 (s, 3H, CH_3), 3.34 (m, 1H, H_3), 4.32 (d, $J_{4,3}$ = 5.0 Hz, 1H, H_4), 5.94 (br.s, 1H, NH), 6.56 (s, 1H, H_6), 7.25–7.41 (m, 5H, H_{Ph}); ^{13}C NMR (50.3 MHz) δ: 12.1 (C_8), 16.8 (CH_3), 18.7 (C_7), 56.7 (C_3), 57.2 (C_4), 126.4, 126.6, 128.2 (5C, CH_{Ph}), 128.8 (C_6), 134.3 (C_5), 137.1 (C_{Ph}), 171.5 (C_2). Δε (λ): −4.05 (198), −7.59 (215), −4.04 (237).

General procedure for preparation of monobactams III

To a solution of monobactam II (1 mmol), *N*,*N*′-diisopropylethylamine (2.2 mmol) and a catalytic amount of 4-dimethylaminopyridine in dry acetonitrile (5 mL), acetyl chloride (2.2 mmol) at 25 °C was added under inert atmosphere. The mixture was stirred at room temperature overnight, poured into cold ammonium chloride solution and extracted with dichloromethane. The organic layers were dried (Na_2SO_4), filtered and evaporated to dryness. After purification by silica gel column chromatography some starting material was recovered, as well as the pure compounds **19**–**23** (hexane:ethyl acetate, 9:1).

1-Acetyl-3α-methoxy-4α-styryl-2-azetidinone (19a) and 1-acetyl-3β-methoxy-4β-styryl-2-azetidinone (19b). They were obtained from **11a** (1 mmol) and **11b** (1.5 mmol) via the general procedure above in 45% and 50% yield, respectively. Anal. calcd for $C_{14}H_{15}NO_3$: C, 68.55; H, 6.16; N, 5.71. Found: C, 68.42; H, 6.06; N, 5.71 for **19a** and C, 68.21; H, 6.14; N, 5.82 for **19b**. MS (EI, *m*/*z*): 245 (M^+), 202 [(M^+)− CO–CH_3]. mp 121–123 °C (heptane:CH_2Cl_2). $[\alpha]_D$ +103 (c 1, $CHCl_3$) for **19a** and $[\alpha]_D$ −103° (c 1, $CHCl_3$) for **19b**. IR (KBr): 1805 (CO–N), 1709 (N-CO-CH_3). ^{1}H NMR (250 MHz) δ: 2.45 (s, 3H, CH_3CO), 3.55 (s, 3H, OCH_3), 4.60 (d, $J_{3,4}$ = 4.8 Hz, 1H, H_3), 4.85 (dd, $J_{4,3}$ = 4.8 Hz, $J_{4,5}$ = 8.2 Hz, 1H, H_4), 6.25 (dd, $J_{5,4}$ = 8.2 Hz, $J_{5,6}$ = 16.0 Hz, 1H, H_5), 6.85 (d,

$J_{6,5}$ = 16.0 Hz, 1H, H_6), 7.25–7.50 (m, 5H, H_{Ph}); ^{13}C NMR (62.5 MHz) δ: 24.4 ($\underline{CH_3}CO$), 59.0 (C4), 59.3 (OCH_3), 84.4 (C_3), 121.1 ($\underline{C_5}$), 126.9, 128.4, 128.6 ($5CH_{Ph}$), 136.1 (C_6), 137.0 (C_{Ph}), 164.8 ($CH_3\underline{CO}$), 168.0 (C_2).

1-Acetyl-3β-methoxy-4β-(*trans*-α-methylstyryl)-2-azetidinone (20). It was obtained from **12b** (2.5 mmol) via the above general procedure in 55% yield. Anal. calcd for $C_{15}H_{15}NO_3$: C, 69.91; H, 6.69; N, 5.40. Found: C, 69.50; H, 6.62; N, 5.32. MS (EI, *m*/*z*): 259 (M^+). mp 51–53 °C (pentane:ether). $[\alpha]_D$ −134 (c 1, $CHCl_3$). IR (KBr): 1795 ($\underline{CO}$-N), 1700 ($\underline{CO}$-CH_3). ^1H NMR (200 MHz) δ: 1.90 (s, 3H, $\underline{CH_3}(C=)$), 2.50 (s, 3H, $\underline{CH_3}CO$), 3.60 (s, 3H, OCH_3), 4.70 (d, $J_{4,3}$ = 6.0 Hz, 1H, $\underline{H_4}$), 4.80 (d, $J_{3,4}$ = 6.0 Hz, 1H, H_3), 6.50 (s, 1H, H_6), 7.30–7.50 (m, 5H, H_{Ph}); ^{13}C NMR (50.3 MHz) δ: 15.1 ($CH_3(C=)$), 24.2 ($\underline{CH_3}CO$), 59.6 (OCH_3), 63.5 (C_4), 84.7 (C_3), 127.0, 128.3, 129.2, 130.0 ($5CH_{Ph}$), 131.2 (C_6), 136.0 (2C; C5, C_{Ph}), 165.3 ($CH_3\underline{CO}$), 168.2 (C_2).

1-Acetyl-3β-methoxy-4β-phenyl-2-azetidinone (21). It was obtained from **13b** (0.13 mmol) in 53% yield. Anal. calcd for $C_{15}H_{15}NO_3$: C, 65.75; H, 5.94; N, 6.39. Found: C, 65.75; H, 5.85; N, 6.30. mp 83–84 °C (Hexane). IR (KBr): 1796 ($\underline{CO}$-N), 1713 ($\underline{CO}$-CH_3). ^1H NMR (200 MHz) δ: 2.47 (s, 3H, $\underline{CH_3}CO$), 3.23 (s, 3H, OCH_3), 4.80 (d, $J_{4,3}$ = 5.0 Hz, 1H, $\underline{H_4}$), 5.20 (d, $J_{3,4}$ = 5.1 Hz, 1H, H_3), 7.27–7.40 (m, 5H, H_{Ph}); ^{13}C NMR (50.3 MHz) δ: 24.4 ($\underline{CH_3}CO$), 58.0 (OCH_3), 60.1 (C_4), 84.5 (C_3), 127.7, 128.6 ($5CH_{Ph}$), 133.0 (C_{Ph}), 170.1 ($CH_3\underline{CO}$), 172.0 (C_2).

1-Acetyl-3β-butyl-4β-styryl-2-azetidinone (22). It was obtained from **15** (0.5 mmol) in 20% yield. IR: 1796 ($\underline{CO}$-N), 1720 ($\underline{CO}$-CH_3). ^1H NMR (200 MHz) δ: 0.81 (t, $J_{10,9}$ = 6.8 Hz, 3H, H_{10}), 1.17–1.69 (m, 6H, H_{7-9}), 2.38 (s, 3H, $\underline{CH_3}CO$), 3.22–3.31 (m, 1H, H_3), 4.25 (dd, $J_{4,3}$ = 6.0 Hz, $J_{4,5}$ = 6.3 Hz, 1H, H_4), 6.06 (dd, $J_{5,4}$ = 6.3 Hz, $J_{5,6}$ = 16.2 Hz, 1H, H_5), 6.81 (d, $J_{6,5}$ = 16.3 Hz, 1H, H_6), 7.09–7.28 (m, 5H, H_{Ph}).

1-Acetyl-3β-butyl-4β-(*trans*-α-methylstyryl)-2-azetidinone (23). It was obtained from **17** (4.7 mmol) in 25% yield. Anal. calcd for $C_{18}H_{23}NO_2$: C, 75.79; H, 8.07; N, 4.91. Found: C, 75.50; H, 8.26; N, 5.16. MS (EI, *m*/*z*): 285 (M^+), 243 [(M^+)-CO-CH_3]. IR: 1782 ($\underline{CO}$-N), 1709 ($\underline{CO}$-CH_3). ^1H NMR (200 MHz) δ: 0.89 (t, $J_{10,9}$ = 6.8 Hz, 3H, H_{10}), 1.24–1.74 (m, 6H, H_{7-9}), 1.88 (s, 3H, $CH_3(C=)$), 2.46 (s, 3H, $\underline{CH_3}CO$), 3.45 (m, 1H, H_3), 4.68 (d, $J_{4,3}$ = 6.0 Hz, 1H, H_4), 6.40 (s, 1H, H_6), 7.23–7.40 (m, 5H, H_{Ph}); ^{13}C NMR (50.3 MHz) δ: 13.9 (C_{10}), 16.4 ($CH_3(C=)$), 22.7 (C_9), 24.1 ($\underline{CH_3}CO$), 24.5 (C_8), 30.1 (C_7), 53.9 (C_3), 59.6 (C_4), 126.9, 128.1, 128.3 ($5CH_{Ph}$), 129.1 (C_6), 131.6 (C_5), 137.0 (C_{Ph}), 168.5 ($CH_3\underline{CO}$), 168.9 (C_2).

General procedure for ozonolysis

A solution of diene (1 mmol) in dichloromethane (20 mL) was cooled to −78 °C and a ozone current was bubbled through it until permanent blue coloration of the solution. Dimethyl sulfide (2 mmol) was added and the solution was brought to room temperature and stirred for 30 min. Evaporation of solvent under reduced pressure gave a crude product which was purified by silica gel column chromatography using hexane:ethyl acetate mixtures as eluents.

4β-Acetyl-3β-methoxy-1[(1′,2′-dideoxy-3′,4′;5′,6′-di-*O*-isopropylidene-1′(1-sulfinyl-3-thiopropane))-D-2′-glucosyl]-2-azetidinone (24). It was obtained from **4a** (3 mmol) in 70% yield (hexane:ethyl acetate, 3:7). Anal. calcd for $C_{21}H_{33}O_8NS_2$: C, 51.33; H, 6.77; N, 2.85; S, 13.07. Found: C, 51.17; H, 6.61; N, 2.86; S, 13.21. MS (EI, *m*/*z*): 491 (M^+), 486 [(M^+) -CH_3]. mp 76–78 °C (heptane:EtOAc). $[\alpha]_D$ +47 (c 1, $CHCl_3$). IR (KBr): 1768 ($\underline{CO}$-N), 1735 ($\underline{CO}$-CH_3). ^1H NMR (400 MHz) δ: 1.30, 1.45 (2s, 12H, $C(\underline{CH_3})_2$), 1.95–2.37 (m, 1H, $H_{10'a}$), 2.25 (s, 3H, $\underline{CH_3}CO$), 2.50–2.80 (m, 4H, $H_{8'a}$, $H_{9'}$, $H_{10'b}$), 3.10–3.60 (m, 1H, $H_{8'b}$), 3.50 (s, 3H, OCH_3), 3.85–4.05 (m, 2H, $H_{6'}$), 4.10 (dd, $J_{5',4'}$ = 8.0 Hz, $J_{5',6'a}$ = 6.0 Hz, 1H, $H_{5'}$), 4.15 (dd, $J_{4',3'}$ = 6 Hz, $J_{4',5'}$ = 8.0 Hz, 1H, $H_{4'}$), 4.25 (d, $J_{1',2'}$ = 6 Hz, 1H, $H_{1'}$), 4.50 (d, $J_{4,3}$ = 6.0 Hz, 1H, H_4), 4.51–4.70 (m, 2H, $H_{2'}$, $H_{3'}$), 4.80 (d, $J_{3,4}$ = 6.0 Hz, 1H, H_3); ^{13}C NMR (62.5 MHz) δ: 22.3, 25.3 ($4C(\underline{CH_3})_2$), 26.2 ($C_{10'}$), 27.4 ($C_{9'}$), 28.0 ($\underline{CH_3}CO$), 28.5 ($C_{8'}$), 51.5 (OCH_3), 53.1 ($C_{2'}$), 64.5 ($C_{1'}$), 66.5 (C_4), 67.7 ($C_{6'}$), 76.6, 77.9, 79.0 ($C_{3'}$, $C_{4'}$, $C_{5'}$), 85.3 (C_3), 107.4, 109.9 ($C_{7'}$), 168.3 (C_2), 203.5 ($CH_3\underline{CO}$).

1,4-Diacetyl-3β-methoxy-2-azetidinone (27). It was obtained from **20** (3 mmol) in 62% yield (hexane:ethyl acetate, 7:3). Anal. Calcd for $C_8H_{11}NO_4$: C, 51.88; H, 6.15; N, 7.49. Found: C, 51.88; H, 5.98; N, 7.56. $[\alpha]_D$ = −197 (c = 1, $CHCl_3$). IR (KBr): 1805 ($\underline{CO}$-N), 1714 ($\underline{CO}$-CH_3). ^1H NMR (250 MHz) δ: 2.25 (s, 3H, $\underline{CH_3}CO$), 2.50 ($NCO\underline{CH_3}$), 3.60 (OCH_3), 4.75 (d, $J_{4,3}$ = 6.0 Hz, 1H, H_4), 4.80 (d, $J_{3,4}$ = 6.0 Hz, 1H, H_3); ^{13}C NMR (62.5 MHz) δ: 24.0 ($NCO\underline{CH_3}$), 28.1 ($\underline{CH_3}CO$), 59.9 (OCH_3), 62.1 (C_4), 83.5 (C_3), 163.5 (2C; C_2, $N\underline{C}OCH_3$), 200.2 ($COCH_3$).

3β-Butyl-1,4-diacetyl-2-azetidinone (28). It was obtained from **23** (3 mmol) in 89% (hexane:ethyl acetate, 8:2). Anal. calcd for $C_{11}H_{17}NO_3$: C, 62.56; H, 8.06; N, 6.64. Found: C, 62.56; H, 7.94; N, 6.20. IR: 1800 ($\underline{CO}$-N), 1727 ($N\underline{CO}$-CH_3), 1710 ($\underline{CO}$-CH_3). ^1H NMR (200 MHz) δ: 0.64 (t, J_{7-8} = 6.8 Hz, 3H, H_8), 1.07–1.39 (m, 6H, H_{5-7}), 2.01, 2.15 (2s, 6H, CH_3CO), 3.25 (t, 1H, $J_{3,7}$ = $J_{3,4}$ = 6.5 Hz, H_3), 4.36 (d, $J_{4,3}$ = 6.5 Hz, 1H, H_4); ^{13}C NMR (62.5 MHz) δ: 13.8 (C_8), 22.4 (C_9), 23.7 (CH_3CO), 24.8 (C_8), 29.1 (CH_3CO), 29.7 (C_7), 52.5 (C_3), 58.5 (C_4), 168.2 ($N\underline{C}OCH_3$), 169.0 (C_2), 202.4 ($\underline{C}OCH_3$).

4β-Acetyl-3β-ethyl-1[(1′,2′-dideoxy-3′,4′;5′,6′-di-*O*-isopropylidene-1′(1-sulfinyl-3-thiopropane))-D-2′-glucosyl]-2-azetidinone (40). It was obtained from **39** (3 mmol) in 70% yield (hexane:ethyl acetate, 3:7), after 20 min ozonolysis. Anal. Calcd for $C_{22}H_{35}NO_7S_2$: C, 53.98; H, 7.20; N, 2.86; S, 13.07. Found: C, 54.02; H, 7.02; N, 2.83. mp 58–60 °C (hexane:MeOH). IR (KBr): 1770 ($\underline{CO}$-N), 1720 ($\underline{CO}$-CH_3). ^1H NMR (200 MHz) δ: 1.07 (t, J = 7 Hz, 3H, H_8), 1.21, 1.29, 1.36, 1.51 (4s, 12H, $C(\underline{CH_3})_2$), 1.63 (m, 2H, H_7), 2.03 (s, 3H, H_6), 2.15 (m, 2H, $H_{10'}$), 2.61 (m, 2H, $H_{9'}$), 3.12 (m, 2H, $H_{8'}$), 3.42–4.20

(m, 5H, H3, $H_{4'-6'}$), 4.72 (m, 4H, $H_{4'-6'}$), 4.72 (d, $J_{4,3}$ = 6.6 Hz, 1H, H_4), 5.24 (d, $J_{3',4'}$ = 8 Hz, 1H, $H_{3'}$); ^{13}C NMR (50.3 MHz) δ 12.0 (C_8), 16.0 ($C_{10'}$), 19.6 (C_7), 25.2, 27.3, 28.6 (C($\underline{CH_3}$)$_2$), 29.0 (C_6), 31.2 ($C_{9'}$), 48.3 ($C_{8'}$), 56.5 (C_3), 63.5 (C_4), 67.7 ($C_{6'}$), 76.5, 77.8; 80.0 ($C_{3'}$, $C_{4'}$, $C_{5'}$), 109.5; 110.8 ($C_{7'}$), 133.4 ($C_{1'}$), 137.2 ($C_{2'}$), 169.3 (C_2), 205.4 (C_5).

4β-Acetyl-1[(2′,3′;4′,5′-di-*O*-isopropylidene)-D-1′-arabinosyl)]-3β-ethyl-2-azetidinone (41). It was obtained from **39** (3 mmol) in 60% yield (hexane:ethyl acetate, 7:3) after 45 min ozonolysis. MS (FAB, *m/z*): 376 $(M + Li)^+$, 370 $(MH)^+$. IR: 1800 (CO-N), 1732 (NCO-CH_3), 1713 (CO-CH_3). ^{1}H NMR (200 MHz) δ: 1.07 (t, *J* = 7 Hz, 3H, H_8), 1.34, 1.39, 1.46 (3s, 12H, C($\underline{CH_3}$)$_2$), 1.61 (m, 2H, H_7), 2.26 (s, 3H, H_6), 3.30–3.55 (m, 2H, H_3, $H_{5'a}$), 4.10–4.40 (m, 3H, $H_{3'-4'}$, $H_{5'b}$), 4.62 (d, $J_{2',3'}$ = 7.2 Hz, 1H, $H_{2'}$), 5.09 (d, $J_{4,3}$ = 6.6 Hz, 1H, H_4).

4β-Acetyl-1[(2′-didesoxi-3′,4′;5′,6′-di-*O*-isopropylidene-1′,1′-dimethoxy)-D-2(-glucosyl]-3β-ethyl-2-azetidinone (42). It was obtained from **36** (0.5 mmol) in 80% yield (hexane:ethyl acetate, 6:4). IR: 1770 (CO-N), 1726 (CO-CH_3). ^{1}H NMR (200 MHz) δ: 0.97 (t, *J* = 7.5 Hz, 3H, H_8), 1.30, 1.33, 1.34, 1.43 (4s, 12H, C($\underline{CH_3}$)$_2$), 1.50–1.70 (m, 2H, H_7), 2.21 (s, 3H, H_6), 3.36, 3.41 (2s, 6H, CH_3O), 3.30–3.50 (m, 1H, H_3), 3.93–4.13 (m, 6H, $H_{2'-6'}$), 4.40 (d, $J_{4,3}$ = 6.3 Hz, 1H, H_4), 4.75 (d, $J_{1',2'}$ = 7.2 Hz, 1H, $H_{1'}$). ^{13}C NMR (62.5 MHz) δ: 12.2 (C_8), 18.8 (C_7), 25.3, 26.3, 26.4, 26.7 (4C, C(CH_3)$_2$), 29.5 (C_6), 53.2, 54.0 (2C, CH_3O), 55.0 (C_3), 56.2 ($C_{2'}$), 61.6 (C_4), 67.6 ($C_{6'}$), 77.3, 77.9 (3C; $C_{3'}$, $C_{4'}$, $C_{5'}$), 101.3 ($C_{1'}$), 109.1, 110.0 (2C, $C_{7'}$), 171.4 (C_2), 205.1 (C_5).

4β-Acetoxy-3β-methoxy-1[(1′,2′-dideoxy-3′,4′;5′,6′-di-*O*-isopropylidene-1′(3-sulfinyl-1-sulfonyl))-D-2′-glucosyl]-2-azetidinone (25). A solution of **24** (442 mg, 0.9 mmol) in dry dichloromethane (10 mL) containing *m*-CPBA (1.2 equiv) was stirred under argon atmosphere at room temperature overnight. The reaction mixture was diluted with dichloromethane, washed with a solution of sodium bicarbonate and water. The organic layers were dried (Na_2SO_4), filtered and evaporated to dryness. Column chromatography (hexane:ethyl acetate, 4:6) gave **25** as a white solid (377 mg, 77%). Anal. calcd for $C_{21}H_{33}NO_{11}S_2 + 2/3\ H_2O$: C, 45.72; H, 6.27; N, 2.54; S, 11.63. Found: C, 45.51; H, 6.34; N, 2.27; S, 11.41. MS (EI, *m/z*): $(M)^+$ 539. mp 186–220 °C (EtOAc). $[\alpha]_D$ −22 (c 1, $CHCl_3$). IR (KBr): 1795 (NC=O), 1735 (OCO-CH_3). ^{1}H NMR (250 MHz) δ: 1.20, 1.45 (2s, 12H, C($\underline{CH_3}$)$_2$), 2.25 (s, 3H, $\underline{CH_3}$CO), 2.55–2.70 (m, 2H, $H_{10'}$), 2.85–3.20 (m, 2H, $H_{8'ax}$, $H_{9'ax}$), 3.25–3.75 (m, 2H, $H_{8'eq}$, $H_{9'eq}$), 3.45 (s, 3H, OCH_3), 3.85–4.25 (m, 4H, $H_{4'-6'}$), 4.65–5.40 (m, 5H, $H_{1'-3'}$, H_{3-4}); ^{13}C NMR (62.5 MHz) δ: 26.5, 26.7 (4C($\underline{CH_3}$)$_2$), 27.4 ($\underline{CH_3}$CO), 28.2 ($C_{10'}$), 49.5 ($C_{9'}$), 51.5 ($\underline{OCH_3}$), 52.4 ($\underline{C_{8'}}$), 52.5 ($C_{2'}$), 67.4 ($C_{1'}$), 68.1 ($C_{6'}$), 78.7, 79.1, 79.2 ($C_{3'}$, $C_{4'}$ $C_{5'}$), 84.4 (2C; C_3, C_4), 109.7, 110.3 ($C_{7'}$), 168.2 (C_2), 205.4 ($O\underline{C}OCH_3$).

4β-Acetoxy-1[(2′-dideoxy-3′,4′;5′,6′-di-*O*-isopropylidene-1′,1′-dimethoxy)-D-2′-glucosyl]-3β-ethyl-2-azetidinone (43). This compound was prepared in 30% from **42** (0.5 mmol) according to the procedure reported for **25**. MS (EI, *m/z*): $(M)^+$ 449. $[\alpha]_D$ −52 (c 1, $CHCl_3$). IR: 1760 (NC=O), 1745 ($\underline{CO}$-CH_3). ^{1}H NMR (200 MHz) δ: 1.03 (t, $J_{6,7}$ = 7.2 Hz, 3H, H_7), 1.32, 1.41, 1.48 (3s, 12H, C($\underline{CH_3}$)$_2$), 1.62–1.85 (m, 2H, H_6), 3.20–3.85 (m, 2H, H_3), 3.38, 3.40 (2s, 6H, OCH_3), 3.80–4.20 (m, 6H, $H_{2'-6'}$), 4.78 (d, $J_{1'-2'}$ = 8.5 Hz, 1H, $H_{1'}$), 6.24 (d, $J_{6,7}$ = 4.5 Hz, 1H, H_4).

4β-Acetoxy-3β-butyl-2-azetidinone (26). A solution of monobactam **16** (587 mg, 2.4 mmol), *N*,*N*′-diisopropylethylamine (1.3 mL, 7.6 mmol) and *tert*-butyldimethylsilyl chloride (1.18 g, 3.7 mmol) in dichloromethane (20 mL) was stirred at room temperature for 19 h and then poured into cold ammonium chloride solution and extracted with dichloromethane. The organic layers were dried (Na_2SO_4), filtered and evaporated to dryness. Column chromatography (hexane:ethyl acetate, 8/2) gave the silyl derivative of **16** (462 mg, 54%): IR: 1755 (NC=O). ^{1}H NMR (200 MHz) δ: 0.10, 0.32 (2s, 6H, $\underline{CH_3}$Si), 0.89 (t, $J_{10,9}$ = 6.8 Hz, 3H, H_{10}), 0.99 (s, 9H, $\underline{CH_3}$^{t}Bu), 1.18–1.68 (m, 6H, H_{7-9}), 1.87 (s, 3H, CH_3 (C=O)), 3.44 (c, $J_{3,4}$ = $J_{3,7}$ = 6.2 Hz, 1H, H_3), 4.20 (d, $J_{4,3}$ = 6.0 Hz, 1H, H_4), 6.54 (s, 1H, H_6), 7.23–7.40 (m, 5H, H_{Ph}). This compound (462 mg, 1.3 mmol) gave by ozonolysis a residue which was diluted with dry dichloromethane (6 mL) and *m*-CPBA (420 mg, 2.4 mmol) was added. The mixture was stirred under argon atmosphere for 10 h at room temperature and then diluted with dichloromethane, washed with a solution of sodium bicarbonate and with water. The organic layers were dried (Na_2SO_4), filtered, and evaporated to dryness. The residue was diluted with methanol (15 mL) and with a 0.5 N HCl (10 mL) solution . This solution was stirred for 5 h at room temperature and then neutralised with IRA-68 resin and filtered. The filtrate was evaporated to dryness and the residue was diluted in ethyl acetate and washed with water. The organic layers were dried (Na_2SO_4), filtered and evaporated to dryness. Column chromatography (hexane:ethyl acetate, 1:1) on Florisil® yielded **26** as an oil (84 mg, 35%): Anal. calcd for $C_9H_{15}O_3N$: C, 58.36; H, 8.16; N, 7.56. Found: C, 58.20; H, 8.11; N, 7.86. MS (IE, *m/z*): 186 $(MH)^+$; 170 $[(MH)^+ - CH_3)$. $[\alpha]_D$ −35 (c 1, $CHCl_3$). IR: 3200 (NH), 1773 (N-C=O), 1727 (O$\underline{OC}$-CH_3). ^{1}H NMR (200 MHz) δ: 0.89 (t, $J_{10,9}$ = 6.8 Hz, 3H, H_{10}), 1.26–1.56 (m, 6H, H_{7-9}), 2.23 (s, 3H, $\underline{CH_3}$CO), 3.56 (dd, $J_{3,7}$ = 6.4 Hz, $J_{3,4}$ = 6.0 Hz, 1H, H_3), 4.32 (d, $J_{4,3}$ = 6.0 Hz, 1H, H_4), 6.80 (br.s, 1H, NH); ^{13}C NMR (50.3 MHz) δ: 13.8 (C_{10}), 22.7 (C_9), 25.9 (C_8), 28.2 (CH_3CO), 29.5 (C_7), 56.1 (C_3), 58.7 (C_4), 171.0 (CO), 172.1 (C_2).

1[(1′,2′-Dideoxy-3′,4′;5′,6′-di-*O*-isopropylidene-1′-(1-sulfinyl-3-thiopropane))-D-2′-glucosyl]-3β-ethyl-4β-(*trans*-α-methylstyryl)-2-azetidinone (38) and 1[(1′,2′-dehydro-1′,2′-dideoxy-3′,4′;5′,6′-di-*O*-isopropylidene-1′-(1,3-propanedithio)-D-2(-glucosyl]-3β-ethyl-4β(*trans*-α-methylstyryl)-2-azetidinone (39). To a solution of **31** (547 mg, 1 mmol) in dry dichloromethane (2 mL) cooled to −40 °C, a solution of iodobenzene dichloride (1.2 equiv) and dry pyridine (3.5 equiv) in dry dichloromethane (2 mL) was added. The reaction mixture was stirred for 1 h and brought to room temperature. After 30 min the

mixture was poured into cold ammonium chloride solution and extracted with dichloromethane. The organic layers were dried (Na_2SO_4), filtered and evaporated to dryness. Column chromatography (hexane:ethyl acetate, 1:1) gave the compounds **39** (54 mg, 10%) and **38** (338 mg, 60%). Monobactam **39** was also obtained in 65% yield by treatment of **38** (300 mg, 0.53 mmol) with trifluoroacetic anhydride (1.7 equiv) and dry TEA (3 mmol) in dry dichloromethane (30 mL) for 6 h.

(**38**): MS (IE, *m*/*z*): 563 $(M)^+$. IR: 1763 (NC=O). ^1H NMR (200 MHz) δ: 0.98 (t, $J=7$ Hz, 3H, H_8), 1.33, 1.37, 1.43, 1.45 (4s, 12H, $C(\underline{CH_3})_2$), 1.70–1.82 (m, 3H, H_7), 1.92 (s, 3H, $\underline{CH_3}(C=)$), 2.21–2.40 (m, 2H, $H_{10'}$), 2.50–2.72 (m, 2H, $H_{9'}$), 3.21–3.40 (m, 2H, $H_{8'}$), 3.41–3.51 (m, 1H, H_3), 3.81–4.20 (m, 5H, $H_{2'}$, $H_{4'-6'}$), 4.35 (d, $J_{1',2'}=12$ Hz, 1H, $H_{1'}$), 4.40 (d, $J_{4,3}=5.9$ Hz, 1H, H_4), 4.84 (dd, $J_{3',2'}=2$ Hz, $J_{3',4'}=8.8$ Hz, 1H, $H_{3'}$), 6.82 (s, 1H, H_6), 7.35–7.50 (m, 5H, H_{Ph}).

(**39**): MS (IE, *m*/*z*): 545 $(M)^+$. IR: 1752 (NC=O). ^1H NMR (200 MHz) δ: 1.06 (t, $J=7$ Hz, 3H, H_8), 1.18, 1.29, 1.38, 1.51 (4s, 12H, $C(\underline{CH_3})_2$), 1.65–1.70 (m, 2H, H_7), 1.90 (s, 3H, $\underline{CH_3}(C=)$), 2.05–2.12 (m, 1H, $H_{9'ax}$), 2.70–2.85 (m, 1H, $H_{9'eq}$), 3.05–3.36 (m, 5H, $H_{8'}$, H_3), 3.80–4.11 (m, 4H, $H_{4'-6'}$), 4.74 (d, $J_{4,3}=5.7$ Hz 1H, H_4), 5.20 (d, $J_{3',4'}=8$ Hz, 1H, $H_{3'}$), 6.72 (s, 1H, H_6), 7.25–7.30 (m, 5H, H_{Ph}).

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