

Regioselective Synthesis of Chiral Six- and Seven-Membered N-Heterocycles from N-Allyl Carbohydrate Nitrones: Tuning of Regioselectivity by N-Substitution

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Abstract: The intramolecular cycloaddition of N-allyl carbohydrate nitrones leads to enantiomerically pure six- and seven-membered nitrogen heterocycles and the regio-selectivity of the cycloaddition was controlled by changing the substituent on the nitrogen atom of the N-allyl moiety. © 1999 Elsevier Science Ltd. All rights reserved.

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Introduction

Nitrogen heterocycles constitute the largest class of biologically active compounds,^{1,2} and several of these compounds are characterized by the presence of chiral piperidine or azepane ring systems. Synthesis of chiral six- and seven-membered nitrogen heterocycles thus forms a task of great interest. An expedient approach to the construction of chiral oxygen heterocycles involving *O*-allyl carbohydrate nitrone cycloaddition has recently gained much importance.³⁻⁹ Recently a similar strategy involving *N*-allyl carbohydrate nitrone cycloaddition for the synthesis of chiral nitrogen heterocycles from carbohydrate derivatives has been reported by us in a preliminary account.¹⁰ We detail herein the study leading to the synthesis of chiral six- and seven-membered nitrogen heterocycles from 3-*N*-allyl carbohydrate nitrones, demonstrating an interesting control of regioselectivity of

the cycloaddition by changing the substituent on the nitrogen atom of the *N*-allyl moiety.

The strategy is depicted in Scheme 1, in which the nitrone 1 derived from an N-allyl R^2 carbohydrate derivative can afford a fused isoxazolidine 2 or its bridged counterpart 3 or



both, depending upon the regioselectivity of the cycloaddition. It is clear that both 2 and 3 incorporate a nitrogen heterocycle besides the isoxazolidine ring, and the ring size of the nitrogen heterocycles in the bridged isomer 3 is one carbon atom larger than in the fused isomer 2. Moreover both 2 and 3 contain two more chiral centers than the precursor nitrone 1. An interesting possibility in the Scheme 1 was whether the regioselectivity of the cycloaddition could be controlled by changing the substituent on the nitrogen atom. The desired control could indeed be realised as described below.

Results and Discussion

The different substituted N-allyl carbohydrate derivatives required for this study were prepared from known amines 4^{11} and 5^{12} (Scheme 2). Allylation of 4 or 5 with a stoichiometric amount of allyl bromide in the presence of anhydrous K_2CO_3 in dry acetone gives a mixture of 6a / 6b or 6g / 6h. Tosylation of 4 or 5 with TsCl in pyridine followed by allylation with allyl bromide in the presence of anhydrous K₂CO₃ in acetone afforded the 3-(N-allyl-p-toluenesulphonamido)-1,2:5,6-di-O-isopropylidene carbohydrate derivatives 6f or 6i, respectively. The allylamino derivative 6a could also be obtained from the well known ketone 7^{13} via the formation of the corresponding N-allylimine 8 through reaction with allylamine followed by reduction by NaBH₄. The β-orientation of the 3-H is expected because similar stereochemistry was observed in the reaction of the ketone 7 or similar systems with NaBH₄.¹⁴ CH₃MgI,¹⁵ and LAH.¹¹ The assigned stereochemistry of the allylamino group in the compound obtained from N-allylimine 8 was also established by the fact that it was identical with the product obtained from 4 by mono allylation. The allylamino derivative 6a was utilised for the synthesis of other substituted allylamino derivatives by alkylation or acylation according to Scheme 2. The 5,6-O-isopropylidene group in 6a-i was selectively removed by using either 75% AcOH in water¹⁵ or 2N H₂SO₄ in methanol¹⁶ to furnish the 1,2-O-isopropylidene derivatives 9a-i. Oxidative cleavage¹⁷ of the diol moiety in 9a-i with sodium metaperiodate in aqueous methanol led to the aldehydes 10a-i, which were used without purification for the generation of the nitrones 11a-i by treatment with N-benzyl hydroxylamine¹⁸ in benzene at room temperature.

The **Table 1** shows the results of the cycloaddition of the nitrones **11a-f** with α -*N*-allyl moiety. Thus, the treatment of the aldehyde **10a** with *N*-benzylhydroxylamine afforded, *via* the cycloaddition of the nitrone **11a**, the azepane derivative **12a** exclusively in 80 % yield (Table 1). The gross structure of **12a** was easily established on the basis of the ¹³C NMR structure which exhibited the 5-C as a high field triplet at δ 29.9. The stereochemistry of the bridge methylene was assigned on the basis of analogy with an oxepane derivative obtained by the cycloaddition of the corresponding *O*-allyl



a 1.5 eq. allyl bromide, anhydrous K_2CO_3 , acetone; b TsCl, Py; c allyl bromide, anhydrous K_2CO_3 , acetone; d allylamine, 3A MS, benzene, reflux; e NaBH₄, MeOH; f BnBr, anhydrous K_2CO_3 , acetone; g Ac₂O, Py; h PivCl, Py; i 75 % AcOH (aq.); j 2N H₂SO₄ in MeOH; k NaIO₄ in aq. MeOH; l BnNHOH, C₆H₆, 3A MS

Scheme 2

nitrone.⁶ However, a change in the regioselectivity was observed in the cycloaddition of the *N*, *N*-diallyl nitrone 11b, which led to the formation of a mixture (78 %) of the piperidine 13b and theazepane 12b in a ratio of 2:1. The structure of 13b was established by the ¹H and ¹³C NMR spectral data. The appearance of a one-proton multiplet at δ 3.08 in the ¹H NMR spectrum and a doublet at δ 40.3 in the ¹³C NMR spectrum clearly indicated the presence of the piperidino-isoxazolidine ring in 13b. The structure and stereochemistry of 12b was secured by its identity with the product obtained by allylation of 12a (Scheme 3). Similarly, the *N*-allyl-*N*-benzyl nitrone 11e afforded a mixture (70 %) of the piperidine 13c and the azepane 12c which was found to be identical with the product obtained by benzylation of 12a (Scheme 3), in a ratio of 3:1 as evident from the ¹H NMR spectrum of the mixture. Formation of a seven-membered ring was drastically reduced when the nitrogen atom of the *N*-allyl-*N*-acetyl nitrone 11d, which afforded a mixture of products, the ¹H NMR spectrum of which indicated the formation of the piperidine 13d and the azepane 12d in a ratio of



 Table 1: Cycloaddition of α-N-allyl Carbohydrate

 Nitrones 11a-f

Nitrones	Product(s)	Yield (%)	Bridge -CH2-
11a, R = H	1 2a	80	β
11b, R = allyl	12b + 13b	78	β
11c, R = Bn	12c + 13c	70	β
11 d , R = Ac	12d + 13d	70	α
11e, R = Piv	12e + 13e	65	α
11 f , R = Ts	1 3f	85	-

ref. 19

13f, 2-βH

15i. 2-αH

AcO



 Table 2: Cycloaddition of β-N-allyl Carbohydrate Nitrones 11g-i

Nitrones	Product(s)	Yield (%)	Bridge -CH 2
11g, R = H	14g	80	β
11h, R = allyl	1 5h	78	-
11i, R = Ts	15i	70	-





12:1. A mixture (1:1) enriched in 12d along with a sample of 13d could, however, be obtained by repeated flash chromatography. The ¹H NMR spectrum of the enriched mixture exhibited the bridged methylene protons in 12d as a one-proton multiplet at δ 2.34 and a one-proton doublet at δ 2.18 (J_{gem} = 13.0 Hz). Surprisingly 12d was not found to be identical with 18 (Scheme 3), which was prepared from 12a by acetylation, because the ¹H NMR spectrum of 18 exhibited a one-proton multiplet at δ 2.56 and a one-proton doublet at δ 1.99 (J_{gem} = 12.2 Hz) although other features of the ¹H NMR spectra of 12d and 18 were similar. The only reason for the discrepancy in the chemical shifts of 12d and 18 is that they are diastereomeric, differing only in the stereochemistry of the bridge methylene. It is conceivable that the seven-membered transition state, through which 12a is

formed, becomes less probable for the formation of 12d due to the planar geometry of the amide bond. The alternative approach of the olefinic bond and nitrone dipole leads to 12d with 8-orientation unlike 12a. Similarly, the N-allyl-N-pivaloyl nitrone 11e afforded an inseparable mixture of the piperidine 13e and the azepane 12e in a ratio of 15:1 as apparent from the ¹H NMR spectrum of the mixture. However, sufficient information about their structures could be obtained from the ¹H and ¹³C NMR spectrum of this mixture. The 5-H of the piperidine 13e was indicated by a one-proton multiplet at δ 2.91, whereas the bridge methylene protons viz the $5-H_A$ and $5-H_B$ of the azepane 12e were indicated by a one-proton multiplet at δ 2.35 and a one-proton doublet at δ 2.22 respectively in the ¹H NMR spectrum of the mixture. In contrast, the product 19 obtained by pivaloylation of 12a was found to be different from 12e, because the ¹H NMR spectrum of 19 exhibited the bridge methylene protons 5-H_A and 5-H_B as a one-proton multiplet at δ 2.52 and a one-proton doublet at δ 1.97 respectively and hence, the bridge methylene in 12e was assigned the β -orientation. A more dramatic change in the regioselectivity was observed when piperidine 13f was formed exclusively in 85 % yield via the cycloaddition of the N-allyl-N-p-toluenesulphonyl nitrone 11f. The stereochemistry of the newly formed chiral centers *i.e.* 4-C and 5-C in 13f was established from the relevant ${}^{1}H$. ${}^{1}H$ coupling constants viz. $J_{3,4}$, $J_{4,5}$ and $J_{6B,5}$ in 16, which was prepared in 44 % yield by the reductive cleavage of isoxazolidine ring in 13f by transfer hydrogenation¹⁹ using cyclohexene and Pd-C followed by acetylation. The $J_{4,3} = J_{4,5} = 8.5$, $J_{6B,5} = 2.7$ and $J_{6A,5} = 2.3$ Hz in the ¹H NMR spectrum of 16 were consistent with the assigned stereochemistry of 16, and hence 13f was assigned the stereochemistry as shown. Interestingly, although no N-Ts azepane derivative was obtained from the cycloaddition, an N-Ts azepane 20 could indeed be prepared by tosylation of 12a (Scheme 3).

Table 2 shows the results obtained in the cycloaddition of the nitrones 11g-i in which the *N*-allyl moiety has β -orientation. The nitrone 11g derived from the aldehyde 10g underwent cycloaddition affording the azepane derivative 14g as the exclusive product in 43 % yield. The stereochemistry of the bridge methylene in 14g was established by its analogy with the oxepane derivative obtained from the cycloaddition of the corresponding 3-O-allyl nitrone.⁴ However, in contrast to the behavior of 11b (Table 1), the cycloaddition of the nitrone 11h furnished exclusively a piperidine derivative 15h in 71 % yield (Table 2). The *N*-allyl-*N*-*p*-toluenesulphonyl nitrone 11i gave on cycloaddition the piperidine derivative 15i in 78 % yield, indicating that when the nitrogen atom is substituted by a *p*-toluenesulphonyl group, a six-membered ring is obtained irrespective of the stereochemistry at 3-C. The stereochemistry of 15i was established by correlation with that of 17, which was obtained in 61 % yield by the reductive cleavage of the N-O bond in 15i followed by acetylation. The $J_{4,3} = 5.2$, $J_{4,5} = 4.9$, $J_{6A,5} = 6.4$, $J_{6B,5} = 6.2$ Hz in the ¹H NMR spectrum of 17 indicated the assigned stereochemistry of 17, thus establishing also the stereochemistry of 15i. Thus, it is evident that the cycloaddition of 3-*NH* allyl nitrones 11a and 11g with the nitrogen atom bearing no substituent was observed to show the same regioselectivity as found in the cases of the corresponding *O*-allyl nitrone cycloadditions.³⁻⁶ The exclusive formation of the fused isoxazolidines 13f, 15h and 15i from the nitrones 11f, 11h and 11i was conspicuous, because the corresponding *O*-allyl-*N*-benzyl nitrones^{4,6} or the *O*-allyl-*N*-methyl nitrones⁵ were reported to give bridged isoxazolidines on cycloaddition.

The above results suggest that a seven-membered transition state leading to a bridged isoxazolidine is probable only in the cases of -NH allyl nitrones 11a and 11g, whereas in the other cases this transition state is destabilised by the steric interaction between the N-substituent and the developing isoxazolidine ring or the bridge methylene group. In conclusion, it was demonstrated that N-allyl carbohydrate nitrone cycloaddition is an important strategy for the synthesis of six- and seven-membered nitrogen heterocycles. An interesting and useful aspect of this cycloaddition is the control of the regioselectivity by substitution at the nitrogen atom. This tuning of regioselectivity will be potentially useful for the preferential synthesis of six- and seven-membered nitrogen heterocycles from carbohydrate derivatives.

EXPERIMENTAL

Melting points are uncorrected. ¹H and ¹³C NMR spectra were measured in CDCl₃ solutions at 300 and 75 MHz, respectively. Mass spectra were recorded on a JEOL AX-500 and JEOL D-300 instrument using electron impact (70 eV) as the ionisation technique. Reactions were monitored by thin layer chromatography using Merck 60 F_{254} precoated silica gel plate (No. 5554). Silica gel of mesh size 60-120 (SRL, India) was used for column chromatography. Organic extracts were dried over anhydrous Na₂SO₄. Solvents were removed in a rotary evaporator under reduced pressure.

General procedure for the preparation of 6a, 6b, 6g and 6h: A mixture of 3-deoxy-3amino-1,2:5,6-di-O-isopropylidene- α -D-allofuranose 4¹¹or 3-deoxy-3-amino-1,2:5,6-di-O-isopropylidene- α -D-glucofuranose 5¹² (18.5 mmol), anhydrous K₂CO₃ (3.85 g), allyl bromide (1.8 ml, 20.7 mmol) and acetone (50 ml), was stirred at 25^oC for 16 h. TLC of the crude reaction mixture indicates two distinct spots for the products. Filtration followed by evaporation of the solvent from the filtrate gave a yellowish syrup which on chromatography over silica gel, using hexane-ethyl acetate (19:1 to 4:1) as eluent gave diallyl and monoallyl amino derivatives. 3-Deoxy-3-allylamino-1:2,5:6-di-O-isopropylidene- α -D-allofuranose (6a): Yield 67%; [α]_D^{26.4} + 83.6 (c 0.67, CHCl₃); IR (neat): 3338, 1643, 1377 cm⁻¹; ¹H NMR: δ 5.88 (m, 1H), 5.79 (d, J = 3.8 Hz, 1H), 5.20 (dd, J = 17.2, 1.5 Hz, 1H), 5.10 (dd, J = 10.2, 1.4 Hz, 1H), 4.61(t, J = 4.2 Hz, 1H), 4.34 (dt, J = 6.9, 3.7 Hz, 1H), 4.16 (t, J = 7.9 Hz, 1H), 3.99 (dd, J = 8.0, 6.8 Hz, 1H), 3.81 (dd, J = 9.5, 3.7 Hz, 1H), 3.40 (dd, J = 14.4, 4.6 Hz, 1H), 3.24 (dd, J = 14.9, 4.9 Hz, 1H), 3.05 (dd, J = 9.5, 4.6 Hz, 1H), 1.53 (s, 3H), 1.44 (s, 3H), 1.37 (s, 3H), 1.35 (s, 3H); ¹³C NMR: δ 137.1, 116.0, 111.9, 109.4, 104.3, 79.0, 78.1, 75.8, 65.1, 61.4, 50.8, 26.7, 26.4, 26.2, 25.3; MS (EI) *m/z* 299 (M⁺), 284.

3-Deoxy-3-diallylamino-1:2,5:6-di-O-isopropylidene-α-D-allofuranose (6b): Yield 20%; [α]_D³⁰ + 89.8 (c 0.65, CHCl₃); IR (neat): 1640, 1375 cm⁻¹; ¹H NMR: δ 5.82 (m, 2H), 5.69 (d, J = 3.8 Hz, 1H), 5.20 (dd, J = 17.2, 1.4 Hz, 2H), 5.10 (bd, J = 10.2 Hz, 2H), 4.65 (t, J = 4.0 Hz, 1H), 4.30 m, 2H), 3.98 (m, 2H), 3.48 (dd, J = 14.6, 5.2 Hz, 2H), 3.28 (dd, J = 14.6, 7.3 Hz, 2H), 3.06 (dd, J = 9.6, 3.9 Hz, 1H), 1.54 (s, 3H), 1.45 (s, 3H), 1.38 (s, 3H), 1.31 (s, 3H); ¹³C NMR: δ 136.2 (2C), 115.9 (2C), 111.5, 108.5, 103.0, 78.8, 75.1, 73.9, 64.0, 62.7, 53.8 (2C), 25.9, 25.6, 25.4, 24.6; MS (EI) m / z 339 (M⁺), 324 (M⁺ - 15).

3-Deoxy-3-allylamino-1:2,5:6-di-O-isopropylidene-α-D-glucofuranose (6g): Yield 35% $[\alpha]_D^{26}$ -29.0 (c 0.8, CHCl₃); IR (neat): 3344, 1643, 1377 cm⁻¹; ¹H NMR: δ 5.86 (m, 2H), 5.24 (dd, J = 17.2, 1.6 Hz,1H), 5.13 (dd, J = 10.8, 1.4 Hz,1H), 4.53 (d, J = 3.7 Hz, 1H), 4.16 (m, 3H), 3.97 (dd, J = 8.3, 5.0 Hz, 1H), 3.40 (ddt, J = 14.4, 5.4 Hz, 1H), 3.33 (bd, J = 3.5 Hz, 1H), 3.29 (ddt, J = 14.4, 6.0 Hz, 1H), 1.50 (s, 3H), 1.42 (s, 3H), 1.35 (s, 3H), 1.31 (s, 3H); ¹³C NMR: δ 136.0, 115.9, 111.1, 109.1, 104.7, 83.2, 80.8, 72.5, 67.8, 62.9, 49.8, 26.5 (2C), 25.9, 25.0; MS (EI) *m/z* 299 (M⁺), 284 (M⁺-15).

3-Deoxy-3-diallylamino-1,2:5,6-di-O-isopropylidene- α -D-glucofuranose (6h): Yield 60 %; $[\alpha]^{24}_{D}$ –24.6 (c 1.0, CHCl₃); IR (neat): 1642, 1376 cm⁻¹; ¹H NMR: δ 5.81 (m, 3H), 5.20 (m, 4H), 4.72 (d, J = 3.6 Hz, 1H), 4.30 (m, 1H), 4.10 (m, 2H), 3.97 (m, 1H), 3.46 (d, J = 4.8 Hz, 1H), 3.40 (bd, J = 13.2 Hz, 2H), 3.03 (dd, J = 14.7, 7.2 Hz, 2H), 1.50 (s, 3H), 1.41(s,3H), 1.36 (s, 3H), 1.31 (s, 3H); ¹³C NMR: δ 134.2 (2C), 116.2(2C), 109.8, 109.1, 103.5, 80.1, 78.8, 71.1, 66.0, 64.2, 52.6 (2C), 25.3, 25.0, 24.0, 23.7; MS (EI) m/z 339 (M⁺), 324 (M⁺- 15).

General procedure for the preparation of 6f and 6i: To a solution of 3-deoxy-3-amino-1,2:5,6-di-O-isopropylidene- α -D-allofuranose 4¹¹or 3-deoxy-3-amino-1,2:5,6-di-O-isopropylidene- α -D-glucofuranose 5¹²(6.2 mmol) in pyridine (15 ml) was added TsCl (7.5 mmol) in pyridine (15 ml), and the solution was kept at 25^oC for 16 h. It was then poured into crushed ice and the mixture was extracted with CHCl₃. The organic layer was washed with water and dried. Removal of the solvent gave a syrupy liquid. A mixture of this syrup (2 g), anhydrous K₂CO₃ (6.0 g), allyl bromide (0.85 ml, 9.0 mmol) and acetone (50 ml) was stirred at 25°C for 24 h. The mixture was filtered, and the filtrate was concentrated, diluted with water and extracted with CHCl₃. The organic layer was washed with water, dried and concentrated to gave 6f or 6i a syrupy liquid.

3-Deoxy-3-(N-allyl-p-toluenesulphonamido)-1:2,5:6-di-O-isopropylidene-a-D-allofuranose (6f): Yield 78%; $[\alpha]_D^{26.4}$ + 86.5 (c 1.1, CHCl₃); IR (neat):1638, 1375, 1339 cm⁻¹; ¹H NMR: δ 7.74 (d, J = 8.3 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 5.93 (m, 1H), 5.69 (d, J = 3.6 Hz, 1H), 5.18 (dd, J = 17.2, 1.2 Hz, 1H), 5.10 (dd, J = 10.1, 1.1 Hz, 1H), 4.49 (t, J = 4.0 Hz, 1H), 4.30 (dd, J = 9.9, 4.4 Hz, 1H), 4.23 (dd, J = 16.6, 7.2 Hz, 1H), 4.15 (dd, J = 16.6, 5.7 Hz, 1H), 4.00 (dd, J = 6.6, 4.4 Hz, 1H), 3.84 (m, 3H), 2.42 (s, 3H), 1.53 (s, 3H), 1.37 (s, 3H), 1.26 (s, 3H),1.24 (s, 3H); ¹³C NMR: δ 143.4, 137.3, 136.0, 129.5 (2C), 127.3 (2C), 117.1, 113.0, 109.4, 103.6, 80.0, 75.6, 74.8, 65.2, 60.8, 49.2, 26.5, 26.0 (2C), 25.0, 21.4; MS (EI) m / z 453 (M⁺), 438 (M⁺-15).

3-Deoxy-3-(N-allyl-p-toluenesulphonamido)-1:2,5:6-di-O-isopropylidene-α-D-glucofuranose (6i): Yield 75 %; $[\alpha]_D^{25}$ –18.3 (c 3.5, CHCl₃); IR (neat): 1639,1597,1377 cm⁻¹; ¹H NMR: δ 7.78 (d, J = 8.3 Hz, 2H), 7.28 (d, J = 8.2 Hz, 2H), 5.91 (d, J = 3.7 Hz, 1H), 5.81 (m, 1H), 5.15 (m, 2H), 4.85 (d, J = 3.6 Hz, 1H), 4.30 (d, J = 6.0 Hz, 1H), 4.04 (dd, J = 8.2, 4.4 Hz, 1H), 3.99 (m, 1H), 3.91 (m, 4H), 2.42 (s, 3H), 1.49 (s, 3H), 1.32 (s, 3H), 1.28 (s, 3H), 1.21 (s, 3H); ¹³C NMR: δ 143.4, 137.3, 134.3, 129.3 (2C), 127.8 (2C), 118.4, 111.1, 109.4, 105.0, 84.4, 80.5, 71.9, 67.5, 64.4, 50.4, 26.6, 26.4, 25.8, 25.1, 21.4; MS (EI) m/z 453 (M⁺), 438 (M⁺- 15), 298.

Preparation of 6a from the ketone 7 and allyl amine: A mixture of ketone 7^{13} (5.5 g, 19.9 mmol), activated 3A moleculer sieves (5 g) and allylamine (2 ml, 48 mmol) in C₆H₆ (40 ml), was heated under reflux for 8 h, after which the mixture was filtered and the residue was washed with MeOH (40 ml). The syrupy liquid obtained after removal of solvent from the combined filtrate and washings was taken in MeOH (25 ml), cooled to 0^{0} C and NaBH₄ (1 g) was added to this solution in portions with stirring. After addition was complete the reaction mixture was stirred for further 8 h at 0^{0} C. MeOH was removed under reduced pressure and the residue was extracted with CH₂Cl₂. The organic layer was washed with water, and dried. Removal of solvent gave a syrup, which was chromatographed over silica gel, the eluation of hexane-ethyl acetate (5:1) giving **6a** (97 %) as a colourless syrup.

Preparation of 6f from 6a: To a stirred solution of **6a** (0.5 g, 1.9 mmol) in pyridine (5 ml), TsCl (0.405 g, 2.12 mmol) was added at room temperature and the solution was kept at the same temperature for 12 h. The reaction mixture was poured into crushed ice and then extracted with CH_2Cl_2 . The organic layer was washed with water, dried, and removal of solvent furnished a syrupy liquid, which was chromatographed over silica gel to gave 6f as a colourless syrup (86 %).

Preparation of 6b from 6a: A mixture of **6a** (0.3 g, 1.0mmol), anhydrous K_2CO_3 (0.5 g, 3.6 mmol) and allyl bromide (0.1 ml, 1.2 mmol) in acetone (10 ml) was stirred at $25^{\circ}C$ f or 32 h. Filtration of the mixture and removal of solvent from the filtrate afforded a syrup, which was chromatographed over silica gel (hexane - ethyl acetate, 19:1) to gave **6b** as a syrupy liquid (91 %).

3-Deoxy-3-allyl(benzyl)amino-1:2,5:6-di-O-isopropylidene-\alpha-D-allofuranose (6c): A mixture of **6a** (0.4 g, 1.33 mmol), anhydrous K₂CO₃ (1.0 g) and benzyl bromide (0.2 ml, 2.0 mmol) in dry acetone (10 ml) was stirred at 25^oC. After completion of reaction (20 h) as revealed by TLC, the reaction mixture was filtered and the residue was washed with acetone. A syrupy liquid obtained after removal of solvent from the combined filtrate and washings chromatographed over silica gel (hexane - ethyl acetate, 9:1) giving **6c** as a colourless syrup (86%); $[\alpha]_D^{26.4}$ + 136.0 (c 0.45, CHCl₃); IR (neat): 1641, 1374 cm⁻¹; ¹H NMR: δ 7.30 (m, 5H), 5.85 (m, 1H), 5.65 (d, J = 3.7 Hz, 1H), 5.19 (m, 2H), 4.67 (t, J = 3.9 Hz, 1H), 4.37 (dd, J = 10.1, 4.0 Hz, 1H), 4.25 (m, 1H), 4.07 (d, J = 14.2 Hz, 1H), 3.86 (dd, J = 7.0, 3.5 Hz, 1H), 3.78 (d, J = 14.2 Hz, 1H), 3.50 (dd, J = 14.7, 5.1 Hz, 1H), 3.31(dd, J = 14.5, 7.4 Hz, 1H), 2.90 (dd, J = 10.0, 4.1 Hz, 1H), 1.56 (s, 3H), 1.40 (s, 3H), 1.39 (s, 3H), 1.34 (s, 3H); ¹³C NMR: δ 140.0, 137.2, 128.4 (2C), 128.2 (2C), 126.8, 116.8, 112.4, 109.2, 103.9, 79.2, 76.1, 74.8, 64.9, 63.6, 55.4, 54.8, 26.7, 26.3, 26.2, 25.4; MS (EI) *m/z* 389 (M⁺), 374 (M⁺ - 15), 298, 91.

3-Deoxy-3-allyl(acetyl)amido-1:2,5:6-di-O-isopropylidene-\alpha-D-allofuranose (6d): To a stirred solution of 6a (0.5 g, 1.9 mmol) in pyridine (2 ml), Ac₂O (1 ml) was added at room temperature and the rection mixture was kept at the same temperature for 12 h. It was then poured into crushed ice and extracted with CH₂Cl₂. The organic layer was washed with water, dried and concentrated. The residual pyridine was removed under reduced pressure by azeotropic distillation with toluene yielding a syrupy liquid, which was chromatographed over silica gel (hexane-ethyl acetate, 5:1) to give 6d as a colourless syrup (98 %); [\alpha]_D^{26.4} + 114.0 (c 0.6, CHCl₃); IR (neat): 1651, 1376 cm⁻¹; ¹H NMR: \delta 5.93 (m, 1H), 5.75 (d, J = 3.5 Hz, 1H), 5.20 (bs, 1H), 5.10 (dd, J = 9.0, 1.0 Hz, 1H), 4.83 (dd, J = 9.9, 4.4 Hz, 1H), 4.67 (t, J = 3.9 Hz, 1H), 4.23 (dd, J = 9.9, 4.6 Hz, 1H), 4.11(m, 4H), 3.91 (dd, J = 11.0, 9.0 Hz, 1H), 2.12 (s, 3H), 1.55 (s, 3H), 1.42 (s, 3H), 1.32 (s, 6H); ¹³C NMR: \delta 172.6, 135.3, 116.0, 112.7, 109.3, 103.8, 79.5, 76.3, 75.3, 65.9, 57.1, 49.0, 26.5, 26.1, 26.0, 24.9, 21.9; MS (EI) m/z 341 (M⁺), 326 (M⁺-15).

3-Deoxy-3-allyl(pivaloyl)amido-1:2,5:6-di-O-isopropylidene- α -D-allofuranose (6e): The same procedure as described above for 6d using 6a (0.7 g, 2.34 mmol), pyridine (3 ml) and (CH₃)₃CCOCl (0.5 ml, 4.0 mmol) gave 6e after chromatography over silica gel (hexane-ethyl acetate, 19 : 1) as a colourless syrup, (94.8 %); $[\alpha]_D^{26.4}$ + 92.8 (c 0.5, CHCl₃); IR (neat): 3074, 1629, 1376 cm⁻¹; ¹H NMR: δ 5.95 (m, 1H), 5.75 (d, J = 3.7 Hz, 1H), 5.11 (m, 2H), 4.73 (t, J = 3.9 Hz, 1H), 4.51 (dd, J = 9.1, 4.4 Hz, 1H), 4.40 (dd, J = 9.0, 5.2 Hz, 1H), 4.31 (bs, 2H), 4.06 (m, 2H), 3.85 (m, 1H), 1.55 (s, 3H), 1.42 (s, 3H), 1.31 (s, 15H); ¹³C NMR: δ 178.6, 137.3, 115.3, 113.0, 109.6, 103.8, 79.9, 76.6, 76.2, 66.7, 60.9, 49.0, 39.6, 28.9 (3C), 26.6, 26.2 (2C), 25.1; MS (EI) *m/z* 383 (M⁺), 368 (M⁺-15), 325.

General Procedure for the Intramolecular Nitrone Cycloaddition.

The diisopropylidene carbohydrate derivatives 6a-i were deprotected by the following methods.

Method A (for 6d, 6e, 6f and 6i): A solution of the 1,2:5,6-di-O-isopropylidene derivative (2.5 mmol) in aqueous acetic acid (75%, v/v, 10 ml) was stirred for 14 h at room temperature. The reaction mixture was then evaporated under reduced pressure and the residue was repeatedly coevaporated with dry toluene in order to remove the residual acetic acid, and dried. The residue was chromatographed over silica gel (ethyl acetate) giving the intermediate diol as a colourless syrup.

9f: Yield 83 %; $[\alpha]_D^{26}$ +126.0 (c 0.50, CHCl₃); IR (neat): 3462, 1637, 1596, 1376 cm⁻¹; ¹H NMR: δ 7.76 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 8.3 Hz, 2H), 5.91 (m, 1H), 5.65 (d, J = 3.6 Hz, 1H), 5.20 (m, 2H), 4.29 (m,3H), 4.20 (dt, J = 16.2, 5.1 Hz, 1H), 4.00 (dd, J = 10.0, 4.2 Hz, 1H), 3.75 (dd, J = 9.8, 4.8 Hz, 1H), 3.66 (m, 2H), 2.91 (d, J = 6.0 Hz, 1H), 2.44 (s, 3H), 2.15 (bs, 1H), 1.53 (s, 3H), 1.24 (s, 3H); ¹³C NMR: δ 143.8, 137.0, 135.8, 129.7 (2C), 127.3 (2C), 117.7, 113.1, 103.4, 79.5, 76.1, 71.8, 62.8, 59.2, 49.2, 26.5, 26.1, 21.5; MS (EI) m/z 398 (M⁺- 15).

9d: Yield 86 %; $[\alpha]_{D}^{24}$ + 81.0 (c 0.83, CH₃OH); IR(neat): 3400, 1624, 1378 cm⁻¹; ¹H NMR: δ 5.94 (m, 1H), 5.76 (d, J = 3.2 Hz, 1H), 5.18 (m, 2H), 4.97 (dd, J = 9.8, 4.2 Hz, 1H), 4.65 (t, J = 4.0 Hz, 1H), 4.24 (dd, J = 9.8, 4.8 Hz, 1H), 4.14 (m, 1H), 3.73 (m, 2H), 3.58 (dd, J = 11.4, 6.2 Hz, 1H), 2.13 (s, 3H), 1.55 (s, 3H), 1.26 (s, 3H); ¹³C NMR: δ 171.5, 136.2, 116.1, 111.7, 103.5, 79.6, 76.5, 72.0, 62.2, 55.0, 48.9, 26.5, 26.2, 22.2; MS (EI) m/z 301 (M⁺), 286 (M⁺-15).

9e: Yield 88 %; $[\alpha]_D^{22}$ + 87.5 (c 0.4, CHCl₃); IR (neat): 3438, 1615, 1378 cm⁻¹; ¹H NMR: δ 5.90 (m, 1H), 5.75 (d, J = 3.0 Hz, 1H), 5.19 (m, 2H), 4.70 (t, J = 3.9 Hz, 1H), 4.57 (dd, J = 9.9, 4.0 Hz, 1H), 4.50 (dd, J = 9.9, 4.3 Hz, 1H), 4.37 (m, 2H), 3.78 (m, 1H), 3.69 (dd, J = 11.4, 4.0 Hz, 1H), 3.62 (dd, J = 11.4, 6.2 Hz, 1H), 3.06 (bs, 1H), 2.28 (bs, 1H), 1.56 (s, 3H), 1.32 (s, 12H); ¹³C NMR: δ 174.4, 136.7, 116.6, 113.1, 103.3, 80.1, 76.9, 72.3, 63.4, 59.5, 49.4, 40.1, 29.0 (3C), 26.7, 26.3; MS (EI) *m/z* 343 (M⁺), 328 (M⁺ - 15), 286.

97: Yield 90 %; $[\alpha]_{D}^{24}$ +12.0 (c 0.65, CHCl₃); IR (neat): 3494, 1639, 1595, 1378 cm⁻¹; ¹H NMR: δ 7.77 (d, J = 8.3 Hz, 2H), 7.36 (d, J = 8.1 Hz, 2H), 5.77 (m, 2H), 5.16 (m, 2H), 4.41(m, 2H), 4.14 (dd, J = 9.1, 4.2 Hz, 1H), 4.04 (dd, J = 16.6, 5.9 Hz, 1H), 3.85 (m, 4H), 3.50 (bs, 1H), 2.46 (s, 3H), 2.24 (bs, 1H), 1.47 (s, 3H), 1.20 (s, 3H); ¹³C NMR: δ 144.0, 136.5, 134.0, 129.9, 127.1, 118.5, 111.4, 104.6, 82.6, 79.7, 68.3, 64.0, 63.9, 49.5, 26.1, 25.7, 21.4, 20.9, 14.0; MS (EI) *m/z* 414 (M⁺ + 1), 398 (M⁺ - 15).

Method B (for 6a-c, 6g and 6h): A solution of the 1,2:5,6-di-O-isopropylidene derivative (7.5 mmol) in a medium containing methanol (45 ml) and 2N H₂SO₄ (4 ml) was stirred at room temperature for 32 h. H₂SO₄ was neutralised by the addition of saturated aqueous NaHCO₃, and MeOH was removed under reduced pressure. The residue was diluted with water and extracted with chloroform. The organic layer was washed with water, dried and concentrated to giving a yellowish syrup which on chromatographed over silica gel (ethyl acetate) afforded the intermediate diol as a colourless syrup.

9a: Yield 83 %; $[\alpha]_D^{26}$ +110.7 (c 0.45, CHCl₃); IR (neat): 3418, 1646, 1453, 1378 cm⁻¹; ¹H NMR: δ 5.87 (m, 2H), 5.25 (dd, J = 17.1, 1.3 Hz, 1H), 5.17 (dd, J = 10.2, 1.0 Hz, 1H), 4.67 (t, J = 4.1 Hz, 1H), 4.01 (m, 1H), 3.75 (m, 2H), 3.71 (d, J = 2.8 Hz, 1H), 3.44 (ddd, J = 13.6, 6.3, 1.0 Hz, 1H), 3.22 (m, 2H), 2.06 (d, J = 1.8 Hz, 1H), 1.54 (s, 3H), 1.36 (s, 3H); ¹³C NMR: δ 135.1, 117.6, 112.3, 104.6, 81.2, 76.7, 70.6, 63.0, 59.0, 50.3, 26.6, 26.4; MS (EI) *m/z* 259 (M⁺), 258 (M⁺-1), 244.

9b: Yield 92 %; $[\alpha]_D^{30}$ + 97.3 (c 0.52, CHCl₃); IR (neat): 3432, 3076, 1640, 1375 cm⁻¹; ¹H NMR: δ 5.79 (m, 2H), 5.75 (d, J = 3.8 Hz, 1H), 5.21 (m, 4H), 4.73 (t, J = 3.8 Hz, 1H), 4.19 (dd, J = 10.2, 4.6 Hz, 1H), 3.90 (m, 1H), 3.76 (dd, J = 12.2, 4.2 Hz, 1H), 3.65 (m, 3H), 3.23(m, 3H), 1.55 (s,3H), 1.33 (s, 3H). ¹³C NMR: δ 134.8 (2C), 118.9 (2C), 112.8, 104.4, 77.9, 76.1, 71.7, 62.5, 61.7, 54.7 (2C), 26.7, 26.2; MS (EI) m/z 299 (M⁺), 298 (M⁺-1), 284 (M⁺- 15).

9c: Yield 82 %; $[\alpha]_D^{26.4}$ +86.0 (c 0.9, CHCl₃); IR (neat): 3430, 1642 1377 cm⁻¹; ¹H NMR: δ 7.32 (m, 5H), 5.84 (m, 1H), 5.70 (d, J = 3.6 Hz, 1H), 5.24 (m, 2H), 4.77 (t, J = 3.7 Hz, 1H), 4.25 (m, 2H), 3.70 (m, 6H), 3.27 (dd, J = 14.4, 8.8 Hz, 1H), 3.21 (dd, J = 10.1, 3.8 Hz, 1H), 1.57 (s, 3H), 1.35 (s, 3H); ¹³C NMR: δ 137.6, 135.2, 129.0 (2C),128.7 (2C), 127.7, 118.9, 112.9, 104.4, 77.8, 74.8, 72.7, 62.9, 62.8, 56.1, 55.0, 26.8, 26.3; MS (EI) *m/z* 349 (M⁺), 334 (M⁺- 15).

9h: Yield 82 %; $[\alpha]_D^{25}$ -16.0 (c 0.6, CHCl₃); IR (neat): 3446 (broad), 1643, 1378 cm⁻¹; ¹H NMR: δ 5.86 (d, J = 3.9 Hz, 1H), 5.78 (m, 2H), 5.24 (m, 4H), 4.77 (d, J = 3.9 Hz, 1H), 4.24 (m, 1H), 3.86 (m, 2H), 3.67 (m, 1H), 3.56 (d, J = 5.9 Hz, 1H), 3.40 (dd, J = 13.8, 5.4 Hz, 2H), 2.97 (dd, J = 13.8, 8.1 Hz, 2H), 1.49 (s, 3H), 1.25 (s, 3H); ¹³C NMR: δ 134.7, 119.3, 111.5, 106.1, 79.3, 71.5, 67.1, 65.0, 55.0, 27.1, 26.4; MS (EI) *m/z* 299 (M⁺), 284 (M⁺- 15).

9g: Yield 90 %; $[\alpha]_D^{24}$ -15.5 (c 0.31, CHCl₃); IR (neat): 3510, 1643, 1378 cm⁻¹; ¹H NMR: δ 5.87 (m, 2H), 5.27 (m, 2H), 4.65 (d, J = 3.4 Hz, 1H), 4.13 (t, J = 4.3 Hz, 1H), 4.04 (bs, 1H), 3.89 (m, 1H), 3.65 (dd, J = 11.5, 4.6 Hz, 1H), 3.54 (dd, J = 13.7, 5.3 Hz, 1H), 3.44 (d, J = 3.8 Hz, 1H), 3.30 (dd, J = 13.6, 6.4 Hz, 1H), 1.49 (s, 3H), 1.31 (s, 3H); ¹³C NMR: δ 134.1, 118.4, 111.6, 104.5, 82.1, 78.5, 70.5, 64.0, 63.6, 49.5, 26.5, 26.0; MS (EI) m/z 259 (M⁺), 243.

To a solution of above syrupy diol (1 mmol) in MeOH (10 ml), NaIO₄ (1.1 mmol) in water (5 ml) was added with stirring at 25° C for 2 h. The white precipitate was filtered and the residue was washed with MeOH. The residue obtained after removal of solvent from the combined filtrate and washings under reduced pressure was diluted with water and extracted with CH₂Cl₂. The organic layer was washed with water, dried and concentrated affording the intermediate aldehyde as a yellow syrup which was used immediately without any further purification; IR (neat): 10a: 1739 cm⁻¹; 10b: 1738 cm⁻¹; 10c: 1736 cm⁻¹; 10d: 1732, 1630 cm⁻¹; 10e: 1737, 1620 cm⁻¹; 10f: 1737 cm⁻¹; 10g: 1739 cm⁻¹; 10h: 1738 cm⁻¹; 10h: 1736 cm⁻¹;

A mixture of the above aldehyde (1 mmol), BnNHOH (1.2 mmol) and 3A molecular sieves (1 g) in benzene (6 ml) was stirred at 25° C till the TLC of the reaction mixture indicated the disappearance of the starting material. The reaction mixture was filtered and the residue was washed with benzene. The combined filtrate and the washings were evaporated to afford the crude product which was chromatographed over silica gel. Reaction times, chromatographic eluents and yields are shown separately for the respective compounds.

(2aR, 2bR, 4R, 5R, 5aR, 7aS)-2-benzyl-2b,4,5, 5a-tetrahydro-4,5-isopropylidenedioxy-furo [2',3':4,5]-1-oxa-2,6-diazabicyclo[4.2.1]nonane (12a): Time 16 h; eluent: ethyl acetate; yield 80 %; colourless needles; m.p104-105^oC (chloroform-hexane); $[\alpha]_D^{25}$ + 93.9 (c 0.5, CHCl₃); IR (KBr): 3350, 1454,1371 cm⁻¹; ¹H NMR: δ 7.30 (m, 5H), 5.80 (d, J = 3.6 Hz , 1H), 4.52 (m, 2H), 4.05 (d, J = 13.0 Hz, 1H), 3.85 (d, J = 13.0 Hz, 1H), 3.74 (dd, J = 7.6, 2.1Hz, 1H), 3.48 (dd, J = 9.7, 2.3 Hz, 1H), 3.39 (dd, J = 9.7, 4.3 Hz, 1H), 3.14 (d, J = 15.0 Hz, 1H), 2.71 (dd, J = 15.0, 3.0 Hz, 1H), 2.37 (m, 1H), 1.85 (d, J = 13.0 Hz, 1H), 1.50 (s, 3H), 1.30 (s, 3H); ¹³ C NMR: δ 137.4, 129.0 (2C), 128.4 (2C), 127.3, 112.0, 104.0, 81.2, 79.9, 78.6, 62.9, 61.4, 58.6, 51.5, 29.9, 26.4, 26.0. MS (EI) m / z 332 (M⁺), 317 (M⁺-15), 91; Anal. Calcd. for C₁₈H₂₄O₄N₂: N, 8.42; Found: N, 8.84.

(5aR, 6R, 7R, 8aR)-1-benzyl-5-allyl-1,3,3a,5a,6,7,8a,8b-octahydro-6,7-isopropylidenedioxy -4H-furo[2',3':5,6]pyrido[4,3-c]isoxazole (13b): Time 20 h; eluent (flash chromatography): hexanechloroform (9:1); yield (13b + 12b); 78 %; sticky material; $[\alpha]_D^{27}$ + 37.6 (c 0.51, CHCl₃); IR (KBr): 1640, 1376, 1302 cm⁻¹; ¹H NMR: δ 7.33 (m, 5H), 5.92 (m, 1H), 5.78 (d, J = 3.6 Hz, 1H), 5.21 (m, 2H), 4.62 (t, J = 3.7 Hz, 1H), 4.12 (m, 2H), 4.05 (d, J = 13.9 Hz, 1H), 3.95 (d, J = 13.6 Hz, 1H), 3.69 (t, J = 8.3 Hz, 1H), 3.49 (dd, J = 13.5, 5.8 Hz, 1H), 3.08 (m, 4H), 2.43 (dd, J = 12.4, 4.4 Hz, 1H), 2.00 (dd, J = 10.3, 3.8 Hz, 1H), 1.59 (s, 3H), 1.33 (s, 3H); ¹³C NMR: δ 137.4, 134.1, 128.9 (2C), 128.2 (2C), 127.1, 118.5, 112.9, 105.1, 77.6, 75.1, 68.5, 67.8, 66.6, 60.0, 58.2, 51.6, 40.3, 26.5, 26.2; MS (EI) *m/z* 372 (M⁺), 357 (M⁺ - 15), 91; Anal. calcd. for C₂₁H₂₈O₄N₂: N, 7.52; Found: N, 7.06.

(2aR, 2bR, 4R, 5R, 5aR, 7aS)-2-benzyl-6-allyl-2b,4,5,5a-tetrahydro-4,5-isopropylidenedioxy-furo[2',3':4,5]-1-oxa-2,6-diazabicyclo[4.2.1]nonane (12b): Time 20 h; eluent (flash chromatography): hexane-chloroform (9:1); yield (13b + 12b):78 %; colourless solid; m.p.118-119⁰C (chloroform-hexane); $[\alpha]_D^{27}$ + 144.8 (c 0.54, CHCl₃); IR (neat): 1640, 1377 cm⁻¹; ¹H NMR: δ 7.30 (m, 5H), 5.92 (m,1H), 5.79 (d, J = 3.4 Hz, 1H), 5.18 (m, 2H), 4.67 (t, J =3.5 Hz, 1H), 4.60 (m, 1H), 4.05 (d, J = 13.3 Hz, 1H), 3.89 (dd, J = 11.1, 2.7 Hz, 1H), 3.86 (d, J = 13.3 Hz, 1H), 3.69 (dd, J = 7.3, 2.7 Hz, 1H), 3.50 (dd, J = 6.5, 1.5 Hz, 2H), 3.12 (dd, J = 9.5, 3.8 Hz,1H), 2.74 (m, 2H), 2.30 (m,1H), 2.15 (d, J = 12.4 Hz, 1H), 1.55 (s, 3H),1.25 (s, 3H); ¹³C NMR: δ 137.0,134.8, 129.0 (2C), 128.4 (2C), 127.3, 118.0, 112.2, 103.9, 80.1, 79.4, 76.8, 63.6, 62.5, 61.3, 58.6, 56.7, 29.0, 26.7, 26.1; MS (EI) *m*/z 372 (M⁺), 371 (M⁺- 1), 357 (M⁺- 15), 91; Anal. calcd. for C₂₁H₂₈O₄N₂: N, 7.52; Found: N, 7.73.

(5aR, 6R, 7R, 8aR)-1,5-dibenzyl-1, 3,3a,5a,6,7,8a,8b-octahydro-6,7-isopropyli-denedioxy-4H-fure[2',3':5,6]pyrido[4, 3-c]isoxazole (13c): Time 20 h; eluent (flash chromatography): hexanechloroform (9:1); yield: 70 %; colourless needles; m.p.109^oC (chloroform-hexane); $[\alpha]_D^{22}$ + 48.4 (c 0.5, CHCl₃); IR (KBr): 1374 cm⁻¹; ¹H NMR: δ 7.31 (m, 10H), 5.81 (d, J = 3.5 Hz, 1H), 4.60 (bs, 1H), 4.18 (d, J = 12.8 Hz, 1H), 3.98 (m, 3H), 3.92 (d, J = 13.4 Hz, 1H), 3.63 (dd, J = 8.6, 7.5 Hz, 1H), 3.31 (d, J = 12.8 Hz, 1H), 3.19 (t, J = 8.2 Hz, 1H), 2.95 (m, 2H), 2.26 (dd, J = 12.5, 4.3 Hz, 1H), 2.03 (dd, J = 10.1, 4.0 Hz, 1H), 1.60 (s, 3H), 1.32 (s, 3H); ¹³C NMR: δ 137.9, 137.4, 129.0 (2C), 128.9 (2C), 128.2 (4C), 127.3, 127.2, 112.8, 105.3, 77.6, 68.5, 68.3, 66.3, 59.9, 58.9, 58.8, 51.6, 40.2, 26.5, 26.2; MS (EI) *m*/*z* 421 (M⁺- 1), 406 (M⁺-15), 92; Anal. calcd. for C₂₅H₃₀O₄N₂: C, 71.06; H, 7.15; N, 6.63; Found: C, 70.97; H, 6.66; N, 6.59.

(2aR, 2bR, 4R, 5R, 5aR, 7aS)-2,6-dibenzyl-2b, 4, 5, 5a-tetrahydro-4,5-isopropylidenedioxy -furo[2',3':4,5]-1-oxa-2,6-diazabicyclo[4.2.1]nonane (12c): Time 20 h; eluent (flash chromatography): hexane-chloroform (9:1); yield: 70 %; colourless needles; m.p.94-95^oC (ether); $[\alpha]_D^{22}$ + 92.5 (c 0.32, CHCl₃); IR (KBr): 1378 cm⁻¹; ¹H NMR: δ 7.32 (m,10H), 5.86(d, J = 3.4 Hz, 1H), 4.73 (t, J = 3.5 Hz, 1H), 4.51 (d, J = 12.8 Hz, 1H), 4.49 (m, 1H), 4.07 (d, J = 13.3 Hz, 1H), 3.99 (dd, J = 9.5, 2.8 Hz, 1H), 3.85 (d, J = 13.3 Hz, 1H), 3.72 (dd, J = 7.0, 2.5 Hz, 1H), 3.41 (d, J = 12.8 Hz, 1H), 3.24 (dd, J = 9.5, 3.9 Hz, 1H), 2.62 (dd, J = 13.2,4.0 Hz, 1H), 2.44 (d, J = 13.2 Hz, 1H), 2.26 (m, 1H), 2.14 (d, J = 12.2 Hz, 1H), 1.59 (s, 3H), 1.33 (s, 3H); ¹³C NMR: δ 140.3, 137.4, 129.0 (2C), 128.6 (2C), 128.3 (2C),128.1 (2C), 127.2, 126.8, 112.3, 104.5, 80.5, 79.8, 76.8, 64.8, 62.7, 61.7, 59.1, 58.3, 29.2, 26.7, 26.4; MS (EI) m / z 422 (M⁺), 407 (M⁺- 15), 91; Anal. calcd for C₂₅H₃₀O₄N₂: C, 71.06; H, 7.15; N, 6.63; Found: C, 71.27; H, 7.04; N, 6.59.

(5aR, 6R, 7R, 8aR)-1-benzyl-5-acetyl-1,3,3a,5a,6,7,8a,8b-octahydro-6,7-isopropylidenedioxy-4H-furo[2',3':5,6]pyrido[4, 3-c]isoxazole (13d): Time 24 h; eluent: ethylacetate; yield 77 %; colourless needles; m.p.86-87⁰C (chloroform-hexane); $[\alpha]_D^{26}$ + 23.3 (c 0.60, CHCl₃ ; IR (KBr): 1672, 1620, 1376 cm⁻¹; ¹H NMR: δ 7.34 (m, 5H), 5.85 (d, J = 3.5 Hz, 1H), 5.24 (t, J = 3.6 Hz, 1H), 4.33 (m, 1H), 4.30 (d, J = 14.8 Hz,1H), 4.12 (t, J = 8.4 Hz, 1H), 3.89 (d, J = 14.8 Hz,1H), 3.58 (dd, J = 13.0, 5.4 Hz, 1H), 3.45 (m, 2H), 3.24 (dd, J = 11.5, 3.7 Hz, 1H), 3.05 (t, J = 8.7 Hz, 1H), 2.95 (m, 1H), 2.12 (s, 3H), 1.54 (s, 3H),1.34 (s, 3H); ¹³C NMR: δ 170.8, 137.0, 129.0 (2C), 128.2 (2C), 127.3, 112.6, 105.6, 77.4, 75.3, 68.1, 66.5, 60.6, 59.2, 45.6, 43.0, 26.3, 26.2, 21.9; MS (EI) *m*/z 374 (M⁺), 359 (M⁺ - 15), 107, 92; Anal.calcd for C₂₀H₂₆O₅N₂: C, 64.15; H, 6.99; N, 7.48; Found C, 64.29; H, 6.72; N, 7.22.

12d: The product was a mixture of 13d and 12d present in a ratio of 1:1 (obtained by the repeated flash chromatography) as apparent from the ¹H NMR spectrum of the mixture. The spectrum of the mixture exhibit the following peaks due to 12d. ¹H NMR: δ 5.75 (d, J = 3.7 Hz, 1H), 4.95 (t, J = 3.8 Hz, 1H), 4.76 (m, 1H), 2.34 (m, 1H), 2.17 (d, J = 13.0 Hz, 1H), 2.11 (s, 3H), 1.56 (s, 3H), 1.28 (s, 3H); ¹³C NMR: δ 30.5 (CH₂)

(SaR, 6R, 7R, 8aR)-1-benzyl-5-pivaloyl-1,3,3a,5a,6,7,8a, 8b-octahydro-6,7-isopropyldenedioxy-4H-furo[2',3':5,6]pyrido[4,3-c]isoxazole (13e): The product was a mixture of 13e and 12e present in an approximate ratio of 15:1 as apparent from the ¹H NMR spectrum of the mixture. ¹H NMR (obtained from the spectrum of the mixture with 12e): δ 7.31 m, 5H), 5.83 (d, J = 3.6 Hz, 1H), 5.15 (t, J = 3.7 Hz, 1H), 4.32 (dd, J = 11.0, 9.0 Hz, 1H), 4.28 (d, J = 14.3 Hz, 1H), 4.10 (t, J = 8.5 Hz, 1H), 3.92 (dd, J = 13.0, 5.0 Hz, 1H), 3.88 (d, J = 14.3, 1H), 3.42 (dd, J = 8.6, 6.5 Hz, 1H), 3.33 (d, J = 12.9 Hz, 1H), 3.28 (dd, J = 7.1, 3.8 Hz, 1H), 3.04 (t, J = 8.2 Hz, 1H), 2.91 (m, 1H), 1.53 (s, 3H), 1.27 (m, 12H); ¹³C NMR: δ 178.5, 137.3, 129.0 (2C), 128.0 (2C), 127.1, 112.2, 105.7, 77.2, 75.0, 68.0, 66.5, 60.6, 60.4, 46.7, 44.2, 38.7, 28.0 (3C), 26.3, 26.2.

12e: The ¹ HNMR spectrum of the mixture exhibited the following discernible peaks due to 12e; $\delta 5.71$ (d, J = 3.8 Hz, 1H), 4.95 (t, J = 3.8 Hz, 1H), 2.35 (m, 1H), 2.22 (d, J = 12.2 Hz, 1H).

(5aR, 6R, 7R, 8aR)-1-benzyl-5-allyl-1,3,3a,5a,6,7,8a,8b-octahydro-6,7-isopropylidenedioxy -4H-fure[2',3':5,6]pyride[4,3-c]isoxazole (13f): Time 16 h; eluent: hexane-ethyl acetate (5:1); yield 85 %; colourless needles; m.p 110-111⁰C (ether-hexane); $[\alpha]_D^{30}+21.1$ (c 0.664, CHCl₃); IR (KBr): 1598, 1376, 1346 cm⁻¹; ¹H NMR: δ 7.78 (d, J = 8.3 Hz, 2H), 7.30 (m, 7H), 5.85 (d, J = 3.6 Hz, 1H), 4.96 (t, J = 3.6 Hz, 1H), 4.26 (dd, J = 11.0, 8.7 Hz, 1H), 4.23 (d, J = 14.5 Hz, 1H), 3.94 (t, J = 8.5Hz, 1H), 3.80 (d, J = 14.5 Hz, 1H), 3.55 (dd, J = 14.4, 5.3 Hz, 1H), 3.28 (dd, J = 8.8, 5.5 Hz, 1H), 3.18 (dd, J = 14.4, 12.9 Hz, 1H), 3.05 (dd, J = 11.0, 3.7 Hz, 1H), 2.81 (t, J = 9.1 Hz, 1H), 2.48 (s, 3H), 2.45 (m, 1H), 1.57 (s, 3H), 1.38 (s, 3H); ¹³C NMR: δ 144.2, 136.8, 135.0, 129.8, 128.9, 128.1, 127.6, 122.2, 112.9, 105.5, 78.5, 75.7, 68.0, 66.6, 60.4, 59.4, 45.4, 41.6, 26.4, 26.3, 21.5; MS (EI) *m*/z 486 (M⁺), 471 (M⁺ - 15), 91; Anal. calcd for C₂₃H₃₀N₂O₆S: N, 5.76; Found: N, 5.49.

(2aS, 2bR, 4R, 5R, 5aS, 7aR)-2-benzyl-2b,4,5,5a-tetrahydro-4,5-isopropylidenedioxy-fure [2',3':4,5]-1-oxa-2,6-diazabicyclo[4.2.1]nonane (14g): Time 16 h; eluent: ethyl acetate; colourless needles; Yield 43%; m.p.119-120^oC (ether-hexane); $[\alpha]_D^{25}$ - 57.3 (c 0.3, CHCl₃); IR (KBr): 3432, 1377 cm⁻¹; ¹H NMR: δ 7.35 (m, 5H), 5.81 (d, J = 3.7 Hz, 1H), 4.62 (dd, J = 8.5, 3.4 Hz, 1H), 4.25 (d, J = 3.7 Hz, 1H), 4.08 (d, J = 12.6 Hz, 1H), 4.05 (d, J = 4.1 Hz, 1H), 3.73 (d, J = 12.6 Hz, 1H), 3.69 (dd, J = 6.3, 3.7 Hz, 1H), 3.37 (d, J = 2.3 Hz, 1H), 2.92 (d, J = 14.3 Hz,1H), 2.76 (dd, J = 14.3, 3.7 Hz,1H), 2.52 (d, J = 12.6 Hz, 1H), 2.33 (m, 1H), 1.47 (s, 3H), 1.27 (s, 3H); ¹³C NMR: δ 136.9, 129.2, 128.5, 127.6, 111.4, 103.7, 86.4, 79.3, 78.5, 63.3, 62.5, 51.4, 26.8, 26.5, 26.0; MS (EI) *m/z* 332 (M⁺), 91; Anal. calcd for C₁₈H₂₄O₄N₂: C, 65.04; H, 7.27; N, 8.42; Found: C, 65.20; H, 6.87; N, 8.37.

(5aS, 6R, 7R, 8aR)-1-benzyl-5-allyl-1,3,3a,5a,6,7,8a,8b-octahydro-6,7-isopropylidenedioxy-4H-furo[2',3':5,6]pyrido[4, 3-c]isoxazole (15h): Time 18 h; eluent: hexane-ethyl acetate (5:1); yield 71 %; sticky material; $[\alpha]_D^{25}$ - 210.0 (c 0.2, CHCl₃); IR (neat): 1640, 1377 cm⁻¹; ¹H NMR: δ 7.32 (m, 5H), 5.80 (m, 2H), 5.20 (m, 2H), 4.62 (d, J = 3.8 Hz, 1H), 4.03 (m, 4H), 3.60 (d, J = 7.8 Hz, 1H), 3.52 (td, J = 14.5, 4.5, 2.4 Hz, 1H), 3.23 (bd, J = 4.8 Hz, 1H), 2.84 (d, J = 3.6 Hz, 1H), 2.78 (m, 3H), 2.25 (bt, 1H), 1.38 (s, 3H), 1.30 (s, 3H); ¹³C NMR: δ 137.4, 134.9, 129.4 (2C), 128.8 (2C), 127.8, 118.4, 111.4, 104.2, 82.9, 75.5, 69.6, 65.5, 64.4, 62.9, 58.2, 51.1, 40.9, 27.0, 26.5; MS(EI) *m/z* 372 (M⁺), 355 (M⁺- 15), 91; Anal. calcld. for C₂₁H₂₈O₄N₂: N, 7.52; Found: N, 7.12.

(5aS, 6R, 7R, 8a)-1-benzyl-5-*p*-toluenesulphonyl-1,3,3a,5a,6,7,8a,8b-octahydro-6,7-isopropylidenedioxy-4H-furo[2',3':5,6]pyrido[4,3-c]isoxazole (15i): Time 16 h; eluent: hexane-ethyl acetate (5:1); Yield 78 %; sticky material; $[\alpha]_D^{30}$ - 102.5 (c 0.4, CHCl₃); IR (neat): 1598, 1376, 1340 cm⁻¹; ¹H NMR: 8 7.77 (d, J = 8.2 Hz, 2H), 7.30 (m, 7H), 5.77 (d, J = 3.7 Hz, 1H), 4.84 (d, J = 3.7 Hz, 1H), 4.15 (s, 2H), 3.97 - 3.66 (m, 3H), 3.43 (d, J = 14.0 Hz, 1H), 3.23 (m, 2H), 3.09 (t, J = 8.4 Hz, 1H), 2.78 (m, 1H), 2.42 (s, 3H), 1.42 (s, 3H), 1.27 (s, 3H); ¹³CNMR: δ 143.8, 138.9, 138.7, 129.7, 128.4 (2C), 128.3 (2C), 27.5 (2C), 127.4 (2C), 111.8, 103.8, 85.4, 73.5, 68.8, 61.6, 61.2, 59.4, 40.6, 39.9, 29.5, 26.1, 21.5; MS (EI) *m*/*z* 486 (M⁺), 471 (M⁺ - 15), 106, 91; HRMS calcd for C₂₅H₃₀O₆ N₂S: 486.182459; M⁺ found 486.182821.

(2aR, 2bR, 4R, 5R, 5aR, 7aS)-2-benzyl-6-*p*-toluenesulphonyl-2b,4,5,5a-tetrahydro-4,5-isopropylidenedioxy-furo [2',3':4,5]-1-oxa-2,6-diazabicyclo [4.2.1]nonane (20): It was prepared by the procedure, described for 6f from 6a. Yield 70 %; colourless needles; m.p.139^oC (ether); $[\alpha]_D^{26}$ + 170.5 (c 0.4, CHCl₃); IR (KBr): 1622, 1368 cm⁻¹; ¹H NMR: δ 7.68 (d, J = 7.0 Hz, 2H), 7.28 (m, 5H), 7.18 (d, J = 7.5 Hz, 2H), 5.71 (d, J = 3.6 Hz, 1H), 4.73 (t, J = 3.3 Hz, 1H), 4.66 (m, 1H), 4.06 (dd, J= 10.1, 3.3 Hz, 1H), 3.96 (d, J = 13.4 Hz, 1H), 3.89 (d, J = 3.69 Hz, 1H), 3.81 (d, J = 13.4 Hz, 1H), 3.77 (dd, J = 10.0, 3.5 Hz, 1H), 3.64 (dd, J = 7.3, 2.3 Hz, 1H), 3.62 (dd, J = 14.9, 2.6 Hz, 1H), 2.42 (m, 1H), 2.37 (s, 2H), 2.05 (d, J = 12.9 Hz, 1H), 1.30 (s, 3H), 1.19 (s, 3H); ¹³C NMR: δ 143.1, 139.5, 137.2, 129.3 (2C), 129.2 (2C), 128.8 (2C), 127.8, 127.7 (2C), 113.0, 104.4, 79.5, 78.2, 75.8, 63.2, 62.0, 61.4, 55.4, 31.8, 26.8, 26.7, 21.9; MS (EI) *m*/z 486 (M⁺), 472 (M⁺- 15), 91; Anal. calcd for C₂₅H₃₀O₆N₂S: N, 5.76; Found: N, 5.93

(2aR, 2bR, 4R, 5R, 5aR, 7aS)-2-benzyl-6-acetyl-2b,4,5,5a-tetrahydro-4,5-isopropylidenedioxy-fure[2',3':4,5]-1-oxa-2,6-diazabicyclo[4.2.1]nonane (18): It was prepared by the procedure, described for 6d from 6a. Yield 93 %; colourless needles; m.p.126⁰C (chloroform); $[\alpha]_D^{26}$ + 198.7 (c 0.9, CHCl₃); IR (KBr): 1638, 1377 cm⁻¹; ¹H NMR: δ 7.27 (m, 5H), 5.73 (d, J = 3.7 Hz, 1H), 5.17 (t, J =3.7 Hz, 1H), 4.57 (dt, J = 8.2,1.8 Hz, 1H), 4.41 (dd, J =10.5, 3.7 Hz,1H), 4.06 (d, J = 10.5 Hz, 1H), 4.03 (d, J = 13.6 Hz, 1H), 3.95 (dd, J = 15.1, 8.1 Hz, 1H), 3.79 (d, J = 13.6 Hz, 1H), 3.69 (d, J = 6.1 Hz, 1H), 3.15 (dd, J = 15.1, 1.8 Hz, 1H), 2.55 (m, 1H), 2.01 (s, 3H), 1.99 (d, J = 12.2 Hz, 1H), 1.77 (s, 3H), 1.30 (s, 3H); ¹³C NMR: δ 173.4,137.8, 129.2 (2C), 129.0 (2C), 128.0, 112.4, 104.5, 79.7, 79.0, 72.5, 63.7, 62.0, 61.4, 52.7, 39.6, 27.0, 26.7, 23.4; MS (EI) *m*/z 374 (M⁺), 359 (M⁺- 15), 106, 91; Anal. calcd. for C₂₀H₂₆O₅N₂: C, 64.15; H, 6.99; N, 7.48; Found: C, 64.30; H, 6.71; N, 7.52.

(2aR, 2bR, 4R, 5R, 5aR, 7aS)-2-benzyl-6-pivaloyl-2b,4,5,5a-tetrahydro-4,5-isopropylidenedioxy-furo[2',3':4,5]-1-oxa-2,6-diazabicyclo[4.2.1]nonane (19): It was prepared by the procedure, described for 6e from 6a. Yield 73 %; colourless needles; m.p. 152^{0} C (ether); $[\alpha]_{D}^{26}$ + 171.0 (c 0.4, CHCl₃); IR (KBr): 1620, 1373 cm⁻¹; ¹H NMR: δ 7.27 (m, 5H), 5.70 (d, J = 3.9 Hz, 1H), 5.16 (t, J = 3.7 Hz, 1H), 4.54 (dt, J = 7.4, 2.1Hz, 1H), 4.30 (dd, J = 10.5, 3.7 Hz, 1H), 4.15 (dd, J = 14.9, 7.5 Hz, 1H), 4.08 (d, J = 13.7 Hz, 1H), 4.03 (d, J = 10.5 Hz, 1H), 3.76 (d, J = 13.6 Hz, 1H), 3.68 (d, J = 6.1 Hz, 1H), 3.14 (dd, J = 14.9, 2.2 Hz, 1H), 2.52 (m, 1H), 1.97 (d, J = 12.1 Hz, 1H), 1.46 (s, 3H), 1.28

12173

(s, 12H); ¹³C NMR: δ 181.1, 137.8, 129.3 (2C), 129.0 (2C), 127.9, 112.1, 104.3, 79.5, 78.8, 73.2, 63.5, 62.6, 61.9, 52.7, 40.0, 38.5, 29.5 (3C), 27.0, 26.8; MS (EI) *m/z* 416 (M⁺), 401 (M⁺- 15), 91; Anal. cald. for C₂₃H₃₂O₅N₂: N, 6.72; Found: N, 6.86.

(2R, 3R, 3aR, 6R, 7S, 7aR)-4-p-toluenesulphonyl-6-acetoxy-7-N-acetylamino-2,3,3a,6,7,7ahexahydro-2,3-isopropylidenedioxy-5H-furo[3,2-b]pyridine (16): To a solution of 13f (0.4 g. 0.82 mmol) in ethanol (24 ml), palladium-charcoal (10%) (0.5 g) and cyclohexene (3 ml) were added and the mixture was reflux under nitrogen atmosphere for 10 h. After cooling the reaction mixture was filtered and the residue was washed with hot ethanol repeatedly. The combined filtrate and the washings were evaporated under reduced pressure and an oily residue was obtained. The materials was dissolved in pyridine (5 ml) and acetic anhydride (3.5 ml) was added at 0° C. The reaction mixture was allowed to warm up to 25°C and left 12 h. It was then poured into ice-water (20 ml) and extracted with CH₂Cl₂. The organic layer was washed with water and dried. Removal of solvent to afforded a solid (0.35 g) which was washed thoroughly with ether and crystallised from ether-hexane to furnish **16 as colourless needles (61.7%);** m.p.120 -123⁰C; $[\alpha]_D^{28}$ + 80.8 (c 0.50, CHCl₃); IR (KBr): 3326, 1720, 1648, 1377 cm⁻¹; ¹H NMR: δ 7.71 (d, J = 8.2 Hz, 2H), 7.36 (d, J = 7.8 Hz, 2H), 6.17 (d, J = 5.2Hz, 1H), 5.76 (d, J = 3.2 Hz, 1H), 5.11 (t, J = 3.3 Hz, 1H), 4.25 (dd, J = 10.9, 3.6 Hz, 1H), 3.99 (m, 2H), 3.90 (dt, $J_{43} = J_{45} = 8.5$ Hz, $J_{4NH} = 5.1$ Hz, 1H, 4-H), 3.80 (dd, J = 12.5, 2.3 Hz, 1H), 2.62 (m, 1H, 5-H), 2.54 (dd, J = 12.5, 2.7 Hz, 1H), 2.46 (s, 3H), 2.28 (dd, J = 8.4, 4.2 Hz, 1H), 2.01 (s, 3H), 1.97(s, 3H), 1.56 (s, 3H), 1.39 (s, 3H); ¹³C NMR: δ 170.8, 170.6, 144.5, 132.3, 129.7 (2C), 128.2 (2C), 113.2, 104.4, 79.0, 73.1, 64.1, 60.7, 52.1, 49.5, 36.4, 26.2, 26.0, 23.1, 21.5, 20.7; MS (FAB) m/z 483 (M⁺ + 1), 467 (M⁺ - 15), 107; Anal. calcd for C₂₂H₃₀O₈N₂S: N, 5.80; Found: N, 5.89.

(2R, 3R, 3aS, 6R, 7S, 7aR)-4-*p*-toluenesulphonyl-6-acetoxy-7-*N*-acetylamino-2,3,3a,6,7,7ahexahydro-2,3-isopropylidenedioxy-5H-furo[3,2-b]pyridine (17): The same procedure as described above for 13f furnished 17. Yield: 75 %; colourless needles; m.p. 83-85⁰C (ether-hexane); $[\alpha]_D^{28}$ - 9.8 (c 0.45, CHCl₃); IR (KBr): 3326, 1720, 1648, 1378 cm⁻¹; ¹H NMR: δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 7.8 Hz, 2H), 5.81 (d, *J* = 3.8 Hz, 1H), 5.55 (d, *J* = 9.5 Hz, 1H), 4.66 (d, *J* = 3.8 Hz, 1H), 4.62 (dt, *J*_{4.5} = *J*_{4.NH} = 9.6 Hz, *J*_{4.3} = 5.2 Hz, 1H), 4.42 (t, *J* = 5.2 Hz, 1H), 4.15 (m, 2H), 3.90 (dd, *J* = 11.2, 7.5 Hz, 1H), 3.19 (dd, *J* = 13.4, 6.2 Hz, 1H), 3.13 (dd, *J* = 13.4, 6.2 Hz, 1H), 2.54 (m, 1H), 2.44 (s, 3H), 2.04 (s, 3H), 1.84 (s, 3H), 1.52 (s, 3H), 1.30 (s, 3H); ¹³C NMR: δ 170.0, 169.9, 144.6, 134.7, 130.1 (2C), 127.5 (2C), 112.2, 104.9, 85.3, 75.7, 62.9, 60.1, 43.9, 41.3, 32.3, 26.9, 26.5, 23.1,21.6, 20.8; MS (FAB) *m/z* 483 (M⁺+ 1), 467, 107; Anal.calcd.for C₂₂H₃₀O₈N₂S: N, 5.80; Found: N, 5.75.

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