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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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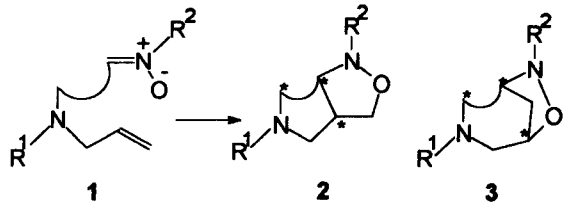
Abstract: The intramolecular cycloaddition of *N*-allyl carbohydrate nitrones leads to enantiomerically pure six- and seven-membered nitrogen heterocycles and the regioselectivity of the cycloaddition was controlled by changing the substituent on the nitrogen atom of the *N*-allyl moiety.

Keywords: *N*-heterocycles; carbohydrate; nitrone; cycloaddition; regioselectivity.

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 carbohydrate derivative can afford a fused isoxazolidine **2** or its bridged counterpart **3** or



1 **2** **3**

Scheme 1

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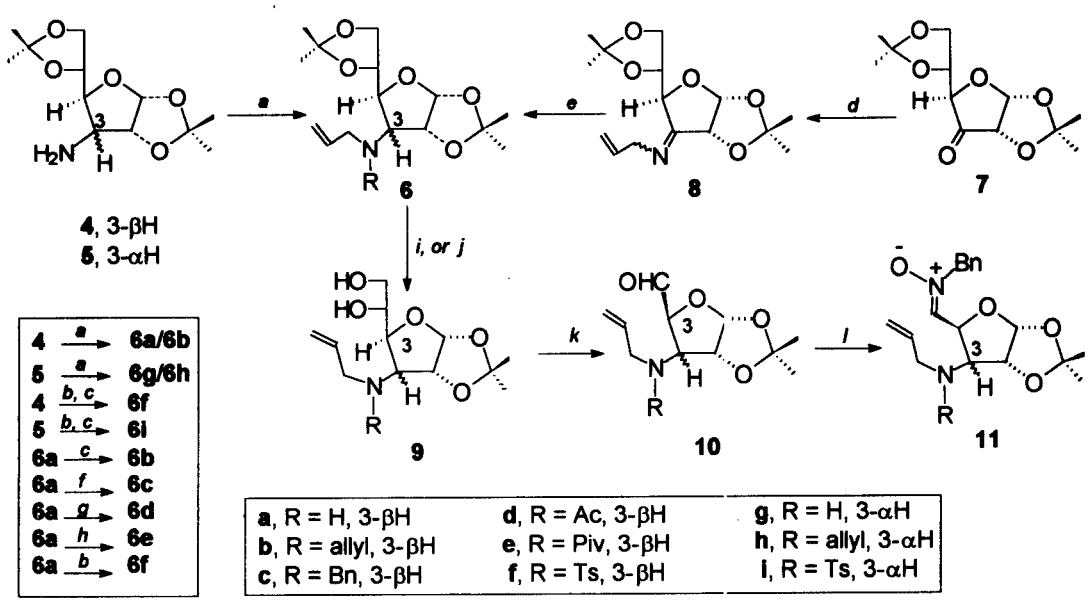
both, depending upon the regioselectivity of the cycloaddition. It is clear that both **2** and **3** incorporate a nitrogen heterocycle besides the isoxazolidine ring, and the ring size of the nitrogen heterocycles in the bridged isomer **3** is one carbon atom larger than in the fused isomer **2**. 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 K_2CO_3 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 $NaBH_4$. 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 $NaBH_4$,[14] CH_3MgI,[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 water[15] or 2N H_2SO_4 in methanol[16] to furnish the 1,2-*O*-isopropylidene derivatives **9a-i**. Oxidative cleavage[17] 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 hydroxylamine[18] in benzene at room temperature.

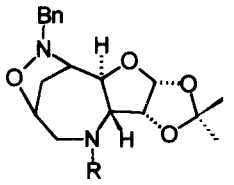
The **Table 1** shows the results of the cycloaddition of the nitrones **11a-f** with α-*N*-allyl moiety. Thus, the treatment of the aldehyde **10a** with *N*-benzylhydroxylamine afforded, *via* the cycloaddition of the nitrone **11a**, the azepane derivative **12a** exclusively in 80 % yield (Table 1). The gross structure of **12a** was easily established on the basis of the ^{13}C 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



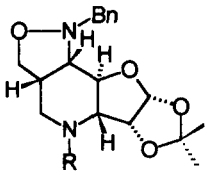
a 1.5 eq. allyl bromide, anhydrous K_2CO_3, acetone; *b* TsCl, Py; *c* allyl bromide, anhydrous K_2CO_3, acetone; *d* allylamine, 3A MS, benzene, reflux; *e* $NaBH_4$, MeOH; *f* BnBr, anhydrous K_2CO_3, acetone; *g* Ac_2O, Py; *h* PivCl, Py; *i* 75 % AcOH (aq.); *j* 2N H_2SO_4 in MeOH; *k* $NaIO_4$ in aq. MeOH; *l* BnNHOH, C_6H_6, 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 ^{13}C 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 ^{13}C 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 **11c** 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 moiety was substituted by an acetyl group. This was apparent in the cycloaddition 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



12



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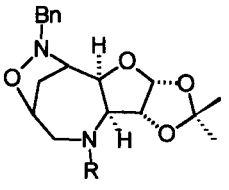

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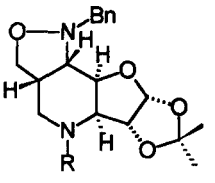


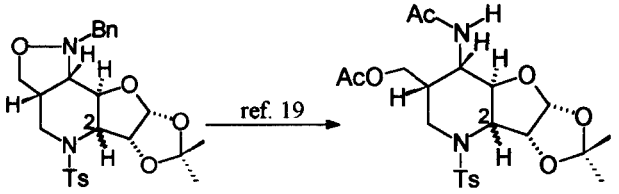
15

Table 1: Cycloaddition of α-*N*-allyl Carbohydrate Nitrones **11a-f**

Nitrones	Product(s)	Yield (%)	Bridge -CH_2-
11a, R = H	**12a**	80	β
11b, R = allyl	**12b + 13b**	78	β
11c, R = Bn	**12c + 13c**	70	β
11d, R = Ac	**12d + 13d**	70	α
11e, R = Piv	**12e + 13e**	65	α
11f, R = Ts	**13f**	85	–

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	**15h**	78	–
11i, R = Ts	**15i**	70	–

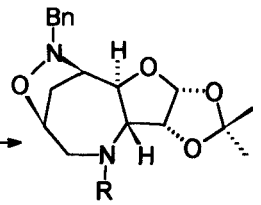


13f, 2-βH
15i, 2-αH

ref. 19

16, 2-βH
17, 2-αH

12a →



12b, R = Allyl
12c, R = Bn
18, R = Ac
19, R = Piv
20, R = Ts

Scheme 3

12:1. A mixture (1:1) enriched in **12d** along with a sample of **13d** could, however, be obtained by repeated flash chromatography. The ^{1}H 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 ^{1}H 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 ^{1}H 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 β-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 ^{1}H NMR spectrum of the mixture. However, sufficient information about their structures could be obtained from the ^{1}H and ^{13}C 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 ^{1}H NMR spectrum of the mixture. In contrast, the product **19** obtained by pivaloylation of **12a** was found to be different from **12e**, because the ^{1}H 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 hydrogenation[19] 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 ^{1}H 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 ^{1}H 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 nitrones[5] 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. ^{1}H and ^{13}C NMR spectra were measured in $CDCl_3$ 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 Na_2SO_4. 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-3-amino-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose **4**[11]or 3-deoxy-3-amino-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose **5**[12] (18.5 mmol), anhydrous K_2CO_3 (3.85 g), allyl bromide (1.8 ml, 20.7 mmol) and acetone (50 ml), was stirred at 25^{0}C 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%; $[\alpha]_D^{26.4}$ + 83.6 (c 0.67, $CHCl_3$); 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); ^{13}C 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%; $[\alpha]_D^{30}$ + 89.8 (c 0.65, $CHCl_3$); 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); ^{13}C 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, $CHCl_3$); 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); ^{13}C 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, $CHCl_3$); 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); ^{13}C 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 **4**[11]or 3-deoxy-3-amino-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose **5** [12] (6.2 mmol) in pyridine (15 ml) was added TsCl (7.5 mmol) in pyridine (15 ml), and the solution was kept at 25°C for 16 h. It was then poured into crushed ice and the mixture was extracted with $CHCl_3$. 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 K_2CO_3 (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 $CHCl_3$. 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-α-D-allofuranose (6f): Yield 78%; $[\alpha]_D^{26.4}$ + 86.5 (c 1.1, $CHCl_3$); 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); ^{13}C 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, $CHCl_3$); 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); ^{13}C 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 C_6H_6 (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°C and $NaBH_4$ (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°C. MeOH was removed under reduced pressure and the residue was extracted with CH_2Cl_2. 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^{0}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-α-D-allofuranose (6c): A mixture of **6a** (0.4 g, 1.33 mmol), anhydrous K_2CO_3 (1.0 g) and benzyl bromide (0.2 ml, 2.0 mmol) in dry acetone (10 ml) was stirred at 25^{0}C. 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, $CHCl_3$); IR (neat): 1641, 1374 cm^{-1}; ^{1}H 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); ^{13}C 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-α-D-allofuranose (6d): To a stirred solution of **6a** (0.5 g,1.9 mmol) in pyridine (2 ml), Ac_2O (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 CH_2Cl_2. 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, $CHCl_3$); IR (neat): 1651, 1376 cm^{-1}; ^{1}H NMR: δ 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); ^{13}C NMR: δ 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 $(CH_3)_3CCOCl$ (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, $CHCl_3$); 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); ^{13}C 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, $CHCl_3$); 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); ^{13}C 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, CH_3OH); 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); ^{13}C 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, $CHCl_3$); 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); ^{13}C 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.

9i: Yield 90 %; $[\alpha]_D^{24}$+12.0 (c 0.65, $CHCl_3$); 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); ^{13}C 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 H_2SO_4 (4 ml) was stirred at room temperature for 32 h. H_2SO_4 was neutralised by the addition of saturated aqueous $NaHCO_3$, 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, $CHCl_3$); 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); ^{13}C 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, $CHCl_3$); 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). ^{13}C 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, $CHCl_3$); 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); ^{13}C 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, $CHCl_3$); 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); ^{13}C 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, $CHCl_3$); IR (neat): 3510, 1643, 1378 cm^{-1}; ^{1}H 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); ^{13}C 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), $NaIO_4$ (1.1 mmol) in water (5 ml) was added with stirring at 25^{0}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 CH_2Cl_2. 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}; **10i**: 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^{0}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^{0}C (chloroform-hexane); $[\alpha]_D^{25}$ + 93.9 (c 0.5, $CHCl_3$); IR (KBr): 3350, 1454,1371 cm^{-1}; ^{1}H 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 $C_{18}H_{24}O_4N_2$: 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): hexane-

chloroform (9:1); yield (**13b** + **12b**); 78 %; sticky material; $[\alpha]_D^{27}$ + 37.6 (c 0.51, $CHCl_3$); 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); ^{13}C 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 $C_{21}H_{28}O_4N_2$: 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.118-119^{0}C (chloroform-hexane); $[\alpha]_D^{27}$ + 144.8 (c 0.54, $CHCl_3$); 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); ^{13}C 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 $C_{21}H_{28}O_4N_2$: 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-furo[2',3':5,6]pyrido[4, 3-c]isoxazole (13c): Time 20 h; eluent (flash chromatography): hexane-chloroform (9:1); yield: 70 %; colourless needles; m.p.109^{0}C (chloroform-hexane); $[\alpha]_D^{22}$ + 48.4 (c 0.5, $CHCl_3$); 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); ^{13}C 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 $C_{25}H_{30}O_4N_2$: 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^{0}C (ether); $[\alpha]_D^{22}$ + 92.5 (c 0.32, $CHCl_3$); 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); ^{13}C 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 $C_{25}H_{30}O_4N_2$: 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.86-87^{0}C (chloroform-hexane); $[\alpha]_D^{26}$ + 23.3 (c 0.60, $CHCl_3$; IR (KBr): 1672, 1620, 1376 cm^{-1}; ^{1}H 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); ^{13}C 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 $C_{20}H_{26}O_5N_2$: 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 ^{1}H NMR spectrum of the mixture. The spectrum of the mixture exhibit the following peaks due to **12d**. ^{1}H 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); ^{13}C NMR: δ 30.5 (CH_2)

(5aR, 6R, 7R, 8aR)-1-benzyl-5-pivaloyl-1,3,3a,5a,6,7,8a, 8b-octahydro-6,7-isopropylidenedioxy-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 ^{1}H NMR spectrum of the mixture. ^{1}H 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); ^{13}C 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**; δ 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-furo[2',3':5,6]pyrido[4,3-c]isoxazole (13f): Time 16 h; eluent: hexane-ethyl acetate (5:1); yield 85 %; colourless needles; m.p 110-111^{0}C (ether-hexane); $[\alpha]_D^{30}$+21.1 (c 0.664, $CHCl_3$); IR (KBr): 1598, 1376, 1346 cm^{-1}; ^{1}H 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* = 8.5 Hz, 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); ^{13}C 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 $C_{25}H_{30}N_2O_6S$: N, 5.76; Found: N, 5.49.

(2aS, 2bR, 4R, 5R, 5aS, 7aR)-2-benzyl-2b,4,5,5a-tetrahydro-4,5-isopropylidenedioxy-furo [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^{0}C (ether-hexane); $[\alpha]_D^{25}$ - 57.3 (c 0.3, $CHCl_3$); IR (KBr): 3432, 1377 cm^{-1}; ^{1}H 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); ^{13}C 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 $C_{18}H_{24}O_4N_2$: 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, $CHCl_3$); IR (neat): 1640, 1377 cm^{-1}; ^{1}H 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); ^{13}C 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 $C_{21}H_{28}O_4N_2$: 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, $CHCl_3$); IR (neat): 1598, 1376, 1340 cm^{-1}; ^{1}H NMR: δ 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); ^{13}CNMR: 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 $C_{25}H_{30}O_6N_2S$: 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^{0}C (ether); $[\alpha]_D^{26}$ + 170.5 (c 0.4, $CHCl_3$); IR (KBr): 1622, 1368 cm^{-1}; ^{1}H 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); ^{13}C 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 $C_{25}H_{30}O_6N_2S$: 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-furo[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.126^{0}C (chloroform); $[\alpha]_D^{26}$ + 198.7 (c 0.9, $CHCl_3$); IR (KBr): 1638, 1377 cm^{-1}; ^{1}H 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); ^{13}C 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 $C_{20}H_{26}O_5N_2$: 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, $CHCl_3$); IR (KBr): 1620, 1373 cm^{-1}; ^{1}H 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

(s, 12H); ^{13}C 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 $C_{23}H_{32}O_5N_2$: N, 6.72; Found: N, 6.86.

(2R, 3R, 3aR, 6R, 7S, 7aR)-4-*p*-toluenesulphonyl-6-acetoxy-7-*N*-acetylamino-2,3,3a,6,7,7a-hexahydro-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 0^0C. The reaction mixture was allowed to warm up to 25^0C and left 12 h. It was then poured into ice-water (20 ml) and extracted with CH_2Cl_2. 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 -123^{0}C; $[\alpha]_D^{28}$ + 80.8 (c 0.50, $CHCl_3$); 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 = 5.2 Hz, 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, $J_{4,3} = J_{4,5}$ = 8.5 Hz, $J_{4,NH}$ = 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); ^{13}C 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 $C_{22}H_{30}O_8N_2S$: N, 5.80; Found: N, 5.89.

(2R, 3R, 3aS, 6R, 7S, 7aR)-4-*p*-toluenesulphonyl-6-acetoxy-7-*N*-acetylamino-2,3,3a,6,7,7a-hexahydro-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. 83-85^{0}C (ether-hexane); $[\alpha]_D^{28}$ - 9.8 (c 0.45, $CHCl_3$); 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); ^{13}C 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 $C_{22}H_{30}O_8N_2S$: N, 5.80; Found: N, 5.75.

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