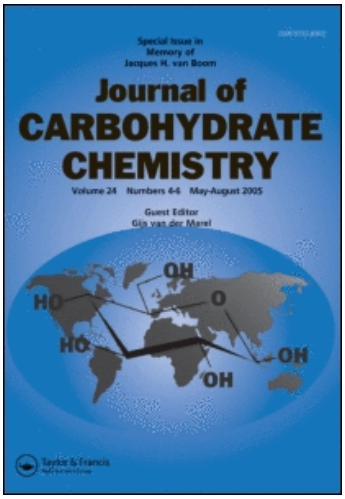

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FIRST GLYCOSIDE SYNTHESIS VIA PIPERIDINIUM SALTS OF HETEROCYCLIC NITROGEN BASES: THE SYNTHESIS OF A NEW CLASS OF DIHYDROPYRIDINE THIOGLYCOSIDES

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ABSTRACT

A first reported method for preparation of a new class of thioglycosides via reaction of piperidinium salts of dihydropyridinethiones with 2,3,4,6-tetra-*O*-acetyl-α-D-gluco- and galactopyranosyl bromides has been studied. Comparison with the products obtained from silylated thiopyridines is made.

INTRODUCTION

There is an increasing interest in the synthesis of nucleoside analogues and their incorporation into DNA sequences for the study of ligand–DNA and protein–DNA interactions. In recent reports from our laboratory, we described the preparation of different novel functionalized pyridinethione glycosides, which revealed antagonistic activity against human carcinoma cells and HIV-virus.[1–4] In an earlier brief communication we had reported the use of dihydropyridinethione glycosides as P-glycoprotein (Pgp) substrates or inhibitors in the protein glycosylation process.[5] These common features, encouraged us to develop a new straightforward route for the synthesis of these compounds. In the present report, we describe the synthesis of dihydropyridine

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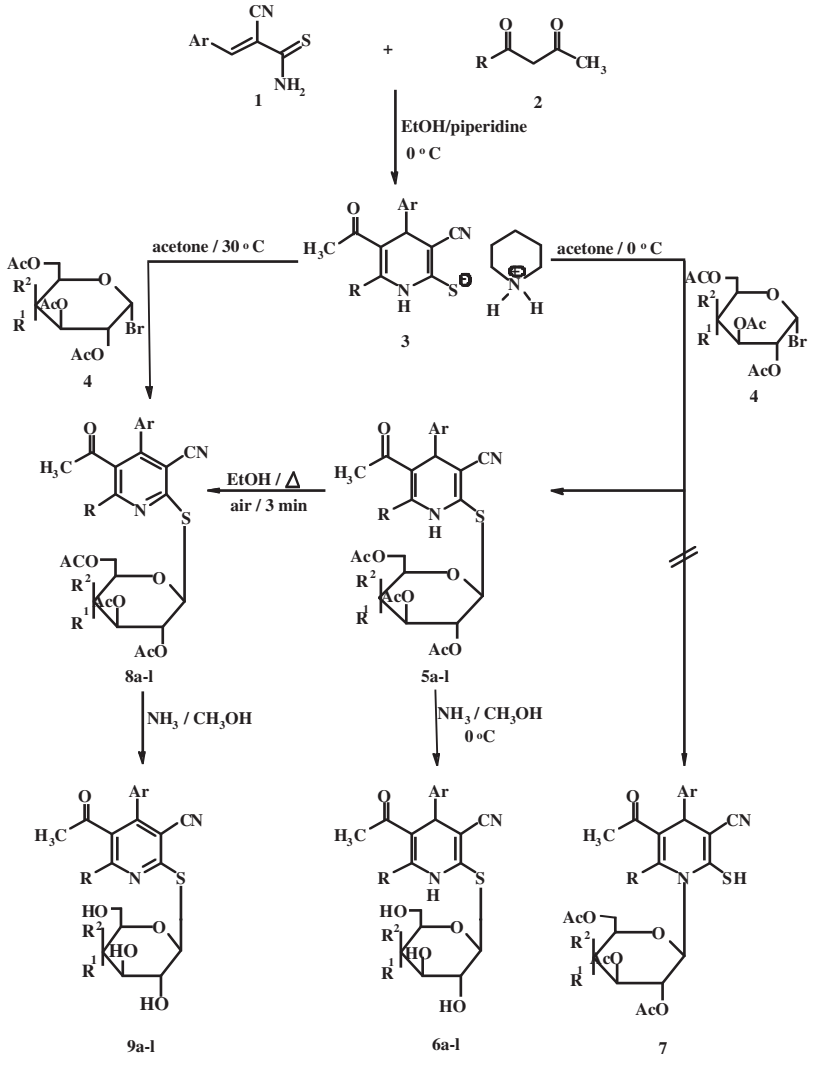
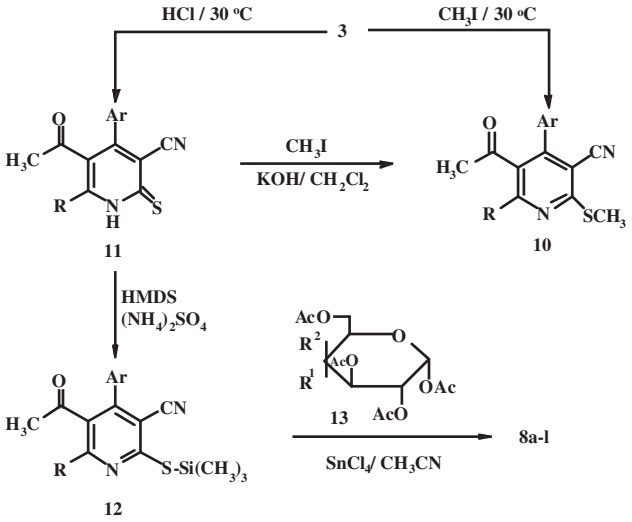
thioglycosides through reaction of piperidinium salts of dihydropyridinethiolates with δ-acetylated α-glycosyl halides. As far as we know this is the first coupling reaction of this type to be reported for glycoside formation. Thus, it has been found that arylmethylidenecyanothioacetamide **1** reacted with 1,3-diketones **2** in ethanol containing piperidine at 0°C to give the corresponding piperidinium salts of 1,4-dihydropyridine-2-thiones **3** (Scheme 1). The structure of **3** was established on the basis of their elemental analysis and spectral data. Compound **3** reacted with 2,3,4,6-tetra-*O*-acetyl-α-D-gluco- and galactopyranosyl bromides in acetone at 0°C to give in a high yield the corresponding *S*-glucosides **5a–f** or *S*-galactosides **5g–l** , respectively.



Scheme 1.

The structure of the reaction products **5a–l** were established by their elemental analyses and spectral data (MS, IR, UV, ^{1}H NMR, ^{13}C NMR). As an example, the analytical data for **5a** indicated a molecular formula $C_{29}H_{31}ClN_2SO_{10}$ ($m/z = 634/636$). The ^{1}H NMR spectrum showed the anomeric proton as a doublet at δ 5.68 ppm. The coupling constant $J_{1',2'} = 9.8$ Hz indicated H-1′ to be *trans*-diaxial to H-2′. The other six glucose protons resonated at 4.05–4.98 ppm and the four acetyl groups appeared as singlets at δ 1.86–2.11 ppm. The ^{13}C NMR spectrum of **5a** contained a signal at δ 82.5 corresponding to the C-1′ atom and five signals appearing at δ 60.7, 68.1, 71.8, 73.8 and 75.5 that were assigned to C-6′, C-4′, C-2′, C-3′ and C-5′, respectively. After deprotection of compounds **5a–l** with a saturated solution of ammonia in methanol at 0°C (Scheme 1) the final glycosides **6a–l** were obtained in almost quantitative yields, the structures of which have been established on the basis of elemental analyses and spectral data. Thus, the analytical data for **6a** revealed a molecular formula $C_{21}H_{23}ClN_2SO_6$ ($m/z = 466/468$). The ^{1}H NMR spectrum showed the anomeric proton as a doublet at δ 5.78 ppm ($J_{1',2'} = 9.8$ Hz) indicating a β-D-configuration. The signals of the other six glucose protons appeared as a multiplet at $\delta = 3.21–3.98$ ppm, while the signals that disappear on rapid exchange with D_2O and are observed at δ 4.69–5.08 ppm were assigned as the four hydroxyl groups, the ^{13}C NMR spectrum of **6a** is characterized by a signal at $\delta = 84.6$ ppm corresponding to the C-1′ and five other signals at δ 61.2, 69.4, 72.7, 77.7 and 81.2 ppm that are assigned to C-6′, C-4′, C-2′, C-3′ and C-5′, respectively. In another experiment, the piperidinium salts **3** reacted with 2,3,4,6-tetra-*O*-acetyl-α-D-gluco- and galactopyranosyl bromides in acetone at 30°C (Scheme 1) to afford the corresponding aromatized pyridine thioglucosides **8a–f** and thiogalactosides **8g–l**. Compounds **8** could also be prepared by heating dihydro thioglycosides **5** in ethanol for 3 minutes, which underwent spontaneous auto-oxidation to afford the aromatized thioglycosides **8**. The structures of the reaction products **8a–l** were established and confirmed on the basis of their elemental analyses and spectral data (MS, IR, UV, ^{1}H NMR, ^{13}C NMR). The formation of *S*-glycosides **8** and not the corresponding *N*-glycosides **7** (Scheme 1) were proved using ^{13}C NMR spectroscopy which revealed the absence of the thione carbon at δ 178 ppm and the appearance of a signal at δ 160 ppm corresponding to the C-2 carbon, whose chemical shift is the same as that of the corresponding *S*-methyl derivative.[6,7] When glycosides **8** were treated with methanolic ammonia at room temperature, the free glycoside derivatives **9a–l** were obtained, the structures of which were established on the basis of elemental analysis and spectral data. Encouraged by these results, we decided to synthesize the pyridine thioglycosides **8** using the silylation method and comparing the resulting products for stereochemical considerations. Thus, in a simple experimental procedure (Scheme 2) treatment of the piperidinium salts **3** with dilute hydrochloric acid at 30°C converted it to the corresponding pyridine-2(1*H*)thiones **11**. The latter compounds were reacted with hexamethyldisilazane (HMDS) in the presence of ammonium sulfate to give the corresponding 2-trimethylsilylthiopyridine **12**, which was subsequently treated with peracetylated sugars **13** in the presence of redistilled $SnCl_4$ to afford the *S*-glycosyl compounds **8**. The latter were shown to be the same as those obtained from the reaction of **3** with **4** by comparison of their melting points and spectral data. In summary, we have achieved a novel synthesis of interesting nonclassical dihydropyridine thioglycosides and their corresponding aromatized forms by the reaction of the piperidinium salts of dihydropyridinethiones with δ-acetylated α-glycosyl halides, the



5,8	Ar	R	R^1	R^2	6,9	Ar	R	R^1	R^2
a	4-ClC_6H_4	CH_3	OAc	H	a	4-ClC_6H_4	CH_3	OH	H
b	4-$CH_3OC_6H_4$	CH_3	OAc	H	b	4-$CH_3OC_6H_4$	CH_3	OH	H
c	2-furanyl	CH_3	OAc	H	c	2- furanyl	CH_3	OH	H
d	4-ClC_6H_4	C_6H_5	OAc	H	d	4-ClC_6H_4	C_6H_5	OH	H
e	4-$CH_3OC_6H_4$	C_6H_5	OAc	H	e	4-$CH_3OC_6H_4$	C_6H_5	OH	H
f	2- furanyl	C_6H_5	OAc	H	f	2- furanyl	C_6H_5	OH	H
g	4-ClC_6H_4	CH_3	H	OAc	g	4-ClC_6H_4	CH_3	H	OH
h	4-$CH_3OC_6H_4$	CH_3	H	OAc	h	4-$CH_3OC_6H_4$	CH_3	H	OH
i	2- furanyl	CH_3	H	OAc	i	2- furanyl	CH_3	H	OH
j	4-ClC_6H_4	C_6H_5	H	OAc	j	4-ClC_6H_4	C_6H_5	H	OH
k	4-$CH_3OC_6H_4$	C_6H_5	H	OAc	k	4-$CH_3OC_6H_4$	C_6H_5	H	OH
l	2- furanyl	C_6H_5	H	OAc	l	2- furanyl	C_6H_5	H	OH

Scheme 2.

nature of the products depending upon thermodynamic factors. These glycosides can be utilized as excellent starting materials for the synthesis of other carbohydrate derivatives and for further biological evaluation studies.

EXPERIMENTAL

Melting points are uncorrected. Aluminum-coated silica gel 60 F_{254} (Merck) sheets were used for thin-layer chromatography. IR spectra were collected in the transmission mode on a Pye Unicam Spectra-1000 spectrometer. ^1H and ^{13}C NMR

spectra were measured in $(CD_3)_2SO$ using $SiMe_4$ as internal reference on a Varian 400 MHz spectrometer. Mass spectra were recorded by EI on a Varian Mat 311A spectrometer and FAB on a Kratos MS 50 spectrometer.

Compounds **10** and **11** were prepared following literature procedures.[8] Yields for synthesized compounds **8a–l** are reported according to method (A).

3-Cyano-2-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-glycopyranosylthio)-1,4-dihydropyridines (5).

General coupling procedures. A mixture of **1a–l** (0.01 mol) and **2** (0.01 mol) was dissolved in dry ethanol (5 mL), and then piperidine (0.01 mol) were added. The reaction mixture was stirred at 0°C for one h and then left to stand to room temperature. The solvent was removed at reduced pressure and the resulting piperidinium salt of 1,4-dihydropyridine-2-thione (**3**) was dissolved in dry acetone (5 mL) and a solution of 2,3,4,6-tetra-*O*-acetyl-α-D-gluco- or galactopyranosyl bromide (0.01 mol) in dry acetone (20 mL) was then added at 0°C. The reaction mixture was stirred until the reaction was judged complete by TLC, using chloroform:ether 4:1 (Rf, 0.68–0.72), then concentrated under reduced pressure and the residue crystallized from chloroform–petroleum ether at 0°C to give pale yellow crystals.

5a. Yield 67%, mp 133°C, $[\alpha]_D + 22.8$; IR (KBr) 2221 (CN), 1752 (CO) cm^{-1}, ^1H NMR [$(CD_3)_2SO$, 400 MHz]: δ 1.86–2.11 (4s, 12H, $4CH_3CO$), 2.32 (s, 3H, CH_3CO), 2.30 (s, 3H, CH_3), 4.05 (m, 2H, 2H-6′), 4.16 (m, 2H, H-5′ and pyridine H-4), 4.55 (d, 1H, H-4′), 4.98 (m, 2H, H-3′ and H-2′), 5.68 (d, $J_{1'-2'}$ 9.8 Hz, 1H, H-1′), 6.90 (d, 2H, Ar–H), 7.10 (d, 2H, Ar–H), 8.32 (bs, 1H, NH); ^{13}C NMR [$(CD_3)_2SO$, 400 MHz]: δ 18.0–20.2 (5 CH_3CO), 28.7 (CH_3), 60.7 (C6′), 68.1 (C4′), 71.8 (C2′), 73.8 (C3′), 75.5 (C5′), 82.5 (C1′), 94.0 (C4), 108.8 (C3), 115.0 (CN), 128.2–139.0 (Ar–C), 137.7 (C5), 142.2 (C6), 157.0 (C2), 168.3–171.0 (4CO of glucose), 195.8 (CO of pyridine).

Anal. Calcd for $C_{29}H_{31}ClN_2SO_{10}$ (*m/z* 634): C, 54.84; H, 4.88; N, 4.41. Found: C, 55.08; H, 5.02; N, 4.62%.

5b. Yield 68%, mp 178°C, $[\alpha]_D + 30.2$; IR (KBr) 2206 (CN), 1758 (CO) cm^{-1}; ^1H NMR [$(CD_3)_2SO$, 400 MHz]: δ 1.92–2.03 (4s, 12H, $4CH_3CO$), 2.09 (s, 3H, CH_3CO), 2.32 (s, 3H, CH_3), 3.86 (s, 3H, OCH_3), 4.00 (m, 2H, 2H-6′), 4.18 (m, 2H, H-5′ and pyridine H-4), 4.62 (d, 1H, H-4′), 4.96 (m, 2H, H-3′ and H-2′), 5.88 (d, $J_{1'-2'}$ 9.6 Hz, 1H, H-1′), 6.92 (d, 2H, Ar–H), 7.15 (d, 2H, Ar–H), 8.22 (bs, 1H, NH); ^{13}C NMR [$(CD_3)_2SO$, 400 MHz]: δ 18.9–20.3 ($5CH_3CO$), 29.8 (CH_3), 55.3 (OCH_3), 61.9 (C6′), 68.1 (C4′), 70.3 (C2′), 72.8 (C3′), 75.0 (C5′), 83.5 (C1′), 94.5 (C4), 109.8 (C3), 114.4 (CN), 128.1–138.1 (Ar–C), 138.7 (C5), 144.2 (C6), 158.4 (C2), 169.2–170.0 (4CO of glucose), 196.9 (CO of pyridine).

Anal. Calcd for $C_{30}H_{34}N_2SO_{11}$ (*m/z* 630): C, 57.14; H, 5.39; N, 4.44. Found: C, 57.36; H, 5.48; N, 4.60%.

5c. Yield 66%, mp 170°C, $[\alpha]_D + 32.7$; IR (KBr) 2212(CN), 1755 (CO) cm^{-1}; ^1H NMR [$(CD_3)_2SO$, 400 MHz]: δ 1.94–2.04 (4s, 12H, $4CH_3CO$), 2.22 (s, 3H, CH_3CO), 2.30 (s, 3H, CH_3), 4.03–4.22 (m, 3H, 2H-6′ and pyridine H-4), 4.93 (m, 2H, H-5′ and H-4′), 5.39 (m, 2H, H-3′ and H-2′), 6.12 (d, $J_{1'-2'}$ 9.6 Hz, 1H, H-1′), 6.81 (s, 1H, furan H-4), 7.56 (dd, 1H, furan H-3), 8.05 (s, 1H, furan H-5), 8.88 (bs, 1H, NH); ^{13}C NMR [$(CD_3)_2SO$, 400 MHz]: δ 18.8–20.1 ($4CH_3CO$), 24.2 (CH_3CO), 29.4 (CH_3), 61.7 (C6′),

67.6 (C4′), 72.5 (C2′), 74.9 (C3′), 82.3 (C5′), 83.6 (C1′), 89.6 (C4), 105.6 (C3), 118.1 (CN), 140.0–145.0 (furan–C), 145.4 (C5), 155.5 (C6), 162.2 (C2), 168.9–169.7 (4CO of glucose), 196.1 (CO of pyridine).

Anal. Calcd for $C_{27}H_{30}N_2SO_{11}$ (*m/z* 590): C, 54.91; H, 5.08; N, 4.74. Found: C, 55.18; H, 5.20; N, 4.95%.

5d. Yield 66%, mp 128°C, $[\alpha]_D + 38.3$; IR (KBr) 2210 (CN), 1748 (CO) cm^{-1}; ^1H NMR [$(CD_3)_2SO$, 400 MHz]: δ 1.90–2.10 (4s, 12H, $4CH_3CO$), 2.24 (s, 3H, CH_3CO), 4.03–4.29 (m, 3H, 2H-6′ and pyridine H-4), 5.05 (m, 2H, H-5′ and H-4′), 5.38 (m, 2H, H-3′ and H-2′), 6.18 (d, $J_{1'-2'}$ 10.1 Hz, 1H, H-1′), 7.15–7.82 (m, 9H, Ar–H), 8.65 (bs, 1H, NH).

Anal. Calcd for $C_{34}H_{33}ClN_2SO_{10}$ (*m/z* 696): C, 58.57; H, 4.73; N, 4.02. Found: C, 58.76; H, 4.88; N, 4.32%.

5e. Yield 69%, mp 151°C, $[\alpha]_D + 42.5$; IR (KBr) 2208 (CN), 1756 (CO) cm^{-1}; ^1H NMR [$(CD_3)_2SO$, 400 MHz]: δ 1.79–2.01 (4s, 12H, $4CH_3CO$), 2.06 (s, 3H, CH_3CO), 3.84 (s, 3H, OCH_3), 4.02–4.19 (m, 4H, 2H-6′, H-5′ and pyridine H-4), 4.55 (d, 1H, H-4′), 4.99 (m, 2H, H-3′ and H-2′), 5.46 (d, $J_{1'-2'}$ 10.2 Hz, 1H, H-1′), 6.88 (m, 2H, Ar–H), 7.14 (m, 2H, Ar–H), 7.48 (m, 5H, Ar–H), 8.42 (bs, 1H, NH); ^{13}C NMR [$(CD_3)_2SO$, 400 MHz]: δ 18.2–20.4 ($4CH_3$), 20.5 (CH_3), 55.5 (OCH_3), 61.9 (C6′), 67.7 (C4′), 69.5 (C2′), 72.9 (C3′), 74.9 (C5′), 83.5 (C1′), 92.6 (C4), 110.3 (C3), 114.8 (CN), 126.8–140.5 (Ar–C), 144.0 (C5), 158.4 (C6), 162.0 (C2), 169.2–169.9 (4CO of glucose), 196.3 (CO of pyridine).

Anal. Calcd for $C_{35}H_{36}N_2SO_{11}$ (*m/z* 692): C, 60.69; H, 5.20; N, 4.04. Found: C, 60.86; H, 5.38; N, 4.30%.

5f. Yield 67%, mp 180°C, $[\alpha]_D + 45.3$; IR (KBr) 2208 (CN), 1755 (CO) cm^{-1}; ^1H NMR [$(CD_3)_2SO$, 400 MHz]: δ 1.82–2.02 (4s, 12H, $4CH_3CO$), 2.08 (s, 3H, CH_3CO), 4.03–4.19 (m, 3H, 2H-6′ and pyridine H-4), 4.70 (s, 1H, H-5′), 5.06 (m, 2H, H-4′ and H-3′), 5.21 (t, 1H, H-2′), 6.08 (d, $J_{1'-2'}$ 10.6 Hz, 1H, H-1′), 6.81 (q, 1H, furan H-4), 7.62 (m, 6H, Ar–H and furan H-3), 8.05 (d, 1H, furan H-5), 8.95 (bs, 1H, NH); ^{13}C NMR [$(CD_3)_2SO$, 400 MHz]: δ 17.9–20.0 ($4CH_3$), 24.1 (CH_3), 61.6 (C6′), 68.1 (C4′), 69.3 (C2′), 73.1 (C3′), 74.9 (C5′), 82.5 (C1′), 95.5 (C4), 110.2 (C3), 115.1 (CN), 127.6–131.7 (Ar–C), 139.3–141.7 (furan–C), 154.9 (C5), 159.0 (C6), 162.1 (C2), 168.9–169.6 (4CO of glucose), 195.5 (CO of pyridine).

Anal. Calcd for $C_{32}H_{32}N_2SO_{11}$ (*m/z* 652): C, 58.89; H, 4.90; N, 4.29. Found: C, 59.14, H, 5.08; N, 4.52%.

5g. Yield 65%, mp 127°C, $[\alpha]_D + 21.6$; IR (KBr) 2216 (CN), 1748(CO) cm^{-1}; ^1H NMR [$(CD_3)_2SO$, 400 MHz]: δ 1.81–2.11 (4s, 12H, $4CH_3CO$), 2.40 (s, 3H, CH_3CO), 2.33 (s, 3H, CH_3), 4.00 (m, 2H, 2H-6′), 4.12 (m, 2H, H-5′ and pyridine H-4), 4.48 (d, 1H, H-4′), 4.77 (m, 2H, H-3′ and H-2′), 5.43 (d, $J_{1'-2'}$ 9.7 Hz, H-1′), 6.95 (d, 2H, Ar–H), 7.09 (d, 2H, Ar–H), 8.11 (bs, 1H, NH); ^{13}C NMR [$(CD_3)_2SO$, 400 MHz]: δ 18.11–21.0 (5 CH_3CO), 28.0 (CH_3), 60.0 (C6′), 68.0 (C4′), 71.4 (C2′), 73.3 (C3′), 75.0 (C5′), 81.9 (C1′), 94.7 (C4), 107.9 (C3), 116.0 (CN), 127.9–139.4 (Ar–C), 138.4 (C5), 140.9 (C6), 158.4 (C2), 168.0–172.0 (4CO of glucose), 196.0 (CO of pyridine).

Anal. Calcd for $C_{29}H_{31}ClN_2SO_{10}$ (*m/z* 634): C, 54.84; H, 4.88; N, 4.41. Found: C, 55.09; H, 5.00; N, 4.63%.

5h. Yield 66%, mp 139°C, $[\alpha]_D + 26.7$; IR (KBr) 2212(CN), 1750(CO) cm^{-1}; ^1H NMR [$(CD_3)_2SO$, 400 MHz]: δ 1.90–2.10 (4s, 12H, $4CH_3CO$), 2.34 (s, 3H, CH_3CO), 2.39 (s, 3H, CH_3), 3.99 (s, 3H, OCH_3), 4.09 (m, 2H, 2H-6′), 4.22 (m, 2H, H-5′ and

pyridine H-4), 4.62 (d, 1H, H-4′), 4.89 (m, 2H, H-3′ and H-2′), 5.67 (d, $J_{1'-2'}$ 9.7 Hz, 1H, H-1′), 6.99 (d, 2H, Ar–H), 7.19 (d, 2H, Ar–H), 8.10 (bs, 1H, NH); ^{13}C NMR [$(CD_3)_2SO$, 400 MHz]: δ 18.0–20.0 ($5CH_3CO$), 29.0 (CH_3), 56.0 (OCH_3), 61.8 (C6′), 68.0 (C4′), 71.0 (C2′), 72.6 (C3′), 74.9 (C5′), 82.9 (C1′), 95.7 (C4), 110.7 (C3), 115.6 (CN), 129.0–137.9 (Ar–C), 140.0 (C5), 145.0 (C6), 157.0 (C2), 167.0–172.6 (4CO of glucose), 195.6 (CO of pyridine).

Anal. Calcd for $C_{30}H_{34}SO_{11}$ (*m/z* 630): C, 57.14; H, 5.39; N, 4.44. Found: C, 57.38; H, 5.53; N, 4.62%.

5i. Yield 65%, mp 126°C, $[\alpha]_D$ + 23.0; IR (KBr) 2205 (CN), 1754 (CO) cm^{-1}; ^{1}H NMR [$(CD_3)_2SO$, 400 MHz]: δ 1.96–2.08 (4s, 12H, $4CH_3CO$), 2.14 (s, 3H, CH_3CO), 2.22 (s, 3H, CH_3), 4.08–4.42 (m, 2H, 2H-6′ and 1H, pyridine H-4), 4.86 (d, 1H, H-5′), 5.06 (m, 1H, H-4′), 5.36 (m, 2H, H-3′ and H-2′), 6.12 (d, $J_{1'-2'}$ 10.0 Hz, 1H, H-1′), 6.52 (d, 1H, furan H-4), 7.58 (d, 1H, furan H-3), 8.02 (d, 1H, furan H-5), 9.25 (bs, 1H, NH); ^{13}C NMR [$(CD_3)_2SO$, 400 MHz]: δ 18.9–20.4 (CH_3CO), 22.8 (CH_3CO), 29.6 (CH_3), 61.3 (C6′), 67.4(C4′), 70.7(C2′), 74.4 (C3′), 83.1 (C5′), 84.2 (C1′), 96.9 (C3), 110.4 (C4), 118.3 (CN), 140.6–146.7 (furan–C), 155.6 (C5), 157.7 (C6), 159.8 (C2), 169.1–169.8 (4CO of galactose), 196.2 (CO of pyridine).

Anal. Calcd for $C_{27}H_{39}N_2SO_{11}$ (*m/z* 590): C, 54.91; H, 5.08; N, 4.74. Found C, 55.13; H, 5.26; N, 5.04%.

5j. Yield 64%, mp 127°C, $[\alpha]_D$ + 45.0; IR (KBr) 2202 (CN), 1753 (CO) cm^{-1}; ^{1}H NMR [$(CD_3)_2SO$, 400 MHz]: δ 1.78–2.10 (4s, 12H, $4CH_3CO$), 2.18 (s, 3H, CH_3CO), 4.02–4.38 (m, 3H, 2H-6′ and pyridine H-4), 4.68 (d, 1H, H-5′), 5.08 (m, 1H, H-4′), 5.40 (m, 2H, H-3′ and H-2′), 5.82 (d, $J_{1'-2'}$ 9.8 Hz, 1H, H-1′), 7.20–7.66 (m, 9H, Ar–H), 8.47 (bs, 1H, NH); ^{13}C NMR [$(CD_3)_2SO$, 400 MHz]: δ 18.2–20.2 ($4CH_3CO$), 20.9 (CH_3CO), 61.2 (C6′), 67.5 (C4′), 70.7 (C2′), 73.9 (C3′), 74.3 (C5′), 83.9 (C1′), 91.6 (C4), 96.8 (C3), 118.4 (CN), 126.4–140.7 (Ar–C), 142.9 (C5), 158.2 (C6), 162.1 (C2), 169.2–169.8 (4CO of galactose), 196.0 (CO of pyridine).

Anal. Calcd for $C_{34}H_{33}Cl\ N_2SO_{10}$ (*m/z* 696): C, 58.57; H, 4.73; N, 4.02. Found: C, 58.86; H, 4.82; N, 4.32%.

5k. Yield 67%, mp 143°C, $[\alpha]_D$ + 36.4; IR (KBr) 2210 (CN), 1754(CO) cm^{-1}; ^{1}H NMR [$(CD_3)_2SO$, 400 MHz]: δ 1.74–2.08 (4s, 12H, $4CH_3CO$), 2.20 (s, 3H, CH_3CO), 3.85 (s, 3H, OCH_3), 4.00–4.42 (m, 3H, 2H-6′ and pyridine H-4), 4.60 (d, 1H, H-5′), 5.32 (m, 3H, H-4′, H-3′ and H-2′), 6.02 (d, $J_{1'-2'}$ 9.6 Hz, 1H, H-1′), 6.92 (d, 2H, Ar–H), 7.15 (d, 2H, Ar–H) 7.58 (m, 5H, Ar–H), 8.77 (bs, 1H, NH); ^{13}C NMR [$(CD_3)_2SO$, 400 MHz]: δ 18.1–20.4 ($4CH_3CO$), 25.3 (CH_3CO), 55.2 (OCH_3), 61.5 (C6′), 67.5 (C4′), 70.7 (C2′), 74.3 (C3′), 79.3 (C5′), 83.9 (C1′), 96.7 (C4), 110.4 (C3), 114.9 (CN), 126.4–140.0 (Ar–C), 145.2 (C5), 158.3 (C6), 165.3 (C2), 169.2–169.9 (4 CO of galactose), 196.2 (CO of pyridine).

Anal. Calcd for $C_{35}H_{36}N_2SO_{11}$ (*m/z* 692): C, 60.69 H, 5.20; N, 4.04. Found: C, 60.92; H, 5.38; N, 4.30%.

5l. Yield 65%, mp 135°C, $[\alpha]_D$ + 36.5; IR (KBr) 2214 (CN) 1750 (CO) cm^{-1}; ^{1}H NMR [$(CD_3)_2SO$, 400 MHz]: δ 1.88–2.04 (4s, 12H, $4CH_3CO$), 2.20 (s, 3H, CH_3CO), 4.05–4.42 (m, 3H, 2H-6′ and pyridine H-4), 5.08 (m, 1H, H-5′), 5.38 (m, 3H, H-4′, H-3′ and H-2′), 6.06 (d, $J_{1'-2'}$ 10.1 Hz, 1H, H-1′), 6.35 (q, 1H, furan H-4), 7.52 (m, 6H, Ar–H and furan H-3), 8.00 (d, 1H, furan H-5), 8. 80 (bs, 1H, NH); ^{13}C NMR [$(CD_3)_2SO$, 400 MHz]: δ 18.1–20.4 ($4CH_3CO$), 25.3 (CH_3CO), 61.3 (C6′), 67.5 (C4′), 70.8 (C2′), 74.5 (C3′), 80.7 (C5′), 84.3 (C1′), 96.8 (C4), 110.5 (C3), 115.4 (CN),

128.2–140.0 (Ar–C), 141.5–147.1 (furan–C), 155.2 (C5), 159.2 (C6), 162.2 (C2), 169.2–169.9 (4CO of galactose), 195.8 (CO of pyridine).

Anal. Calcd for $C_{32}H_{32}N_2SO_{11}$ (*m/z* 652): C, 58.89; H, 4.90; N, 4.29. Found: C, 58.97; H, 5.11; N, 4.45%.

3-Cyano-2-(β-D-glycopyranosylthio)-1,4-dihydropyridines (6).

General procedure for nucleoside deacylation. Dry gaseous ammonia was passed through a solution of protected glycosides **5** (0.5 g) in 20 ml of dry methanol at 0°C for 0.5 h. The reaction mixture was stirred until completion as shown by TLC (10–12 h), using chloroform:methanol, 9:1 (Rf 0.60–0.64). The resulting mixture was then concentrated under reduced pressure to afford a solid residue that was crystallized from methanol–ether at 0°C to furnish colourless crystals.

6a. Yield 80%, mp 168°C, $[\alpha]_D + 16.9$; IR (KBr) 3660–3250 (OH), 2217 (CN) cm^{-1}; ^1H NMR [$(CD_3)_2SO$, 400 MHz]: δ 2.11 (s, 3H, CH_3CO), 2.32 (s, 3H, CH_3), 3.21–3.98 (m, 7H, 2H-6′, H-5′, H-4′, H-3′, H-2′ and pyridine H-4), 4.69 (s, 1H, 2′-OH), 5.08 (m, 3H, 3′-OH, 4′-OH and 6′-OH), 5.78 (d, $J_{1'-2'}$ 9.9 Hz, 1H, H-1′), 7.20 (d, 2H, Ar–H), 7.42 (d, 2H, Ar–H), 8. 34 (bs, 1H, NH); ^{13}C NMR [$(CD_3)_2SO$, 400 MHz]: δ 19.4 (CH_3CO), 30.1 (CH_3), 61.2 (C6′), 69.4 (C4′), 72.7 (C2′), 77.7 (C3′), 81.2 (C5′), 84.6 (C1′), 89.4 (C4), 109.8 (C3), 118.8 (CN), 128.7–142.1 (Ar–C), 144.8 (C5), 145.0 (C6), 160.4 (C2), 196.6 (CO).

Anal. Calcd for $C_{21}H_{23}ClN_2SO_6$ (*m/z* 466): C, 54.01; H, 4.93; N, 6.00. Found: C, 54.34; H, 5.16; N, 6.22%.

6b. Yield 82%, mp 218°C, $[\alpha]_D + 21.0$; IR (KBr) 3732–3209 (OH), 2229 (CN) cm^{-1}; ^1H NMR [$(CD_3)_2SO$, 400 MHz]: δ 2.13 (s, 3H, CH_3CO), 2.34 (s, 3H, CH_3), 3.24–3.98 (m, 10H, 2H-6′, H-5′, H-4′, H-3′, H-2′, OCH_3 and pyridine H-4), 4.46 (d, 1H, 2′-OH), 4.60 (s, 1H, 3′-OH), 5.04 (m, 2H, 4′-OH and 6′-OH), 5.63 (d, $J_{1'-2'}$ 9.9 Hz, 1H, H-1′), 7.13 (d, 2H, Ar–H), 7.64 (d, 2H, Ar–H), 8.66 (bs, 1H, NH); ^{13}C NMR [$(CD_3)_2SO$, 400 MHz]: δ 19.0 (CH_3CO), 24.5 (CH_3), 55.4 (OCH_3), 60.7 (C6′), 69.7 (C4′), 71.7 (C2′), 78.6 (C3′), 81.6 (C5′), 83.6 (C1′), 100.8 (C4), 110.5 (C3), 117.1 (CN), 127.4–132.0 (Ar–C), 152.9 (C5), 156.0 (C6), 161.8 (C2), 178.5 (CO).

Anal. Calcd for $C_{22}H_{26}N_2SO_7$ (*m/z* 462): C, 57.14; H, 5.62; N, 6.06. Found: C, 57.38; H, 5.81; N, 6.32%.

6c. Yield 81%, mp 203°C, $[\alpha]_D + 22.6$; IR (KBr) 3680–3240 (OH), 2209 (CN) cm^{-1}; ^1H NMR [$(CD_3)_2SO$, 400 MHz]: δ 2.22 (s, 3H, CH_3CO), 2.30 (s, 3H, CH_3), 3.11–3.78 (m, 7H, 2H-6′, H-5′, H-4′, H-3′, H-2′ pyridine H-4), 4.67 (s, 1H, 2′-OH), 5.00 (m, 3H, 3′-OH, 4′-OH and 6′-OH), 5.55 (d, $J_{1'-2'}$ 9.8 Hz, 1H, H-1′), 6.88 (q, 1H, furan H-4), 7.38 (d, 1H, furan H-3), 8.00 (d, 1H, furan H-5), 8. 34 (bs, 1H, NH); ^{13}C NMR [$(CD_3)_2SO$, 400 MHz]: δ 19.0 (CH_3CO), 30.0 (CH_3), 61.4 (C6′), 69.0 (C4′), 72.3 (C2′), 77.1 (C3′), 81.0 (C5′), 84.0 (C1′), 89.9 (C4), 109.0 (C3), 118.4 (CN), 128.3–141.0 (furan–C), 144.0 (C5), 145.5 (C6), 160.0 (C2), 196.0 (CO).

Anal. Calcd for $C_{19}H_{22}N_2SO_7$ (*m/z* 422): C, 54.02; H, 5.21: N, 6.63. Found: C, 54.34; H, 5.46; N, 6.88%.

6d. Yield 80%, mp 188°C, $[\alpha]_D + 21.9$; IR (KBr) 3630–3290 (OH), 2204 (CN) cm^{-1}; ^1H NMR [$(CD_3)_2SO$, 400 MHz]: δ 2.00 (s, 3H, CH_3CO), 3.21–4.13 (m, 7H, 2H-6′, H-5′, H-4′, H-3′, H-2′ and pyridine H-4), 4.44 (d, 1H, 2′-OH), 4.69 (m, 1H, 3′-

OH), 4.78 (d, 1H, 4′-OH), 5.13 (d, 1H, 6′-OH), 5.56 (d, $J_{1'-2'}$ 9.8 Hz, 1H, H-1′), 7.09–7.78 (m, 9H, Ar–H), 8.13 (bs, 1H, NH); ^{13}C NMR [$(CD_3)_2SO$, 400 MHz]: δ 19.1 (CH_3CO), 61.5 (C6′), 67.5 (C4′), 68.7 (C2′), 73.9 (C3′), 81.0 (C5′), 84.8 (C1′), 99.6 (C4), 108.9 (C3), 119.6 (CN), 126.9–130.7 (Ar–C), 143.9 (C5), 154.9 (C6), 160.6 (C2), 194.3 (CO).

Anal. Calcd for $C_{26}H_{25}ClN_2SO_6$ (*m/z* 528): C, 59.03; H, 4.73; N, 5.29. Found: C, 59.35; H, 4.92; N, 5.46%.

6e. Yield 78%, mp 181°C, $[\alpha]_D$ + 25.5; IR (KBr) 3690–3340 (OH), 2204 (CN) cm^{-1}; ^{1}H NMR [$(CD_3)_2SO$, 400 MHz]: δ 1.78 (s, 3H, CH_3CO), 3.28–4.00 (m, 10H, 2H-6′, H-5′, H-4′, H-3′, H-2′, OCH_3 and pyridine H-4), 4.70 (d, 1H, 2′-OH), 5.02 (m, 3H, 3′-OH, 4′-OH and 6′-OH), 5.96 (d, $J_{1'-2'}$ 9.8 Hz, 1H, H-1′), 6.85 (d, 2H, Ar–H), 7.08 (d, 2H, Ar–H), 7.48 (m, 5H, Ar–H), 8.56 (bs, 1H, NH); ^{13}C NMR [$(CD_3)_2SO$, 400 MHz]: δ 18.4 (CH_3CO), 55.1 (OCH_3), 60.6 (C6′), 69.8 (C4′), 72.8 (C2′), 77.7 (C3′), 81.5 (C5′), 83.6 (C1′), 94.9 (C4), 110.5 (C3), 114.6 (CN,) 127.8–136.4 (Ar–C), 152.8 (C5), 158.2 (C6), 161.7 (C2), 196.2 (CO).

Anal. Calcd for $C_{27}H_{28}N_2SO_7$ (*m/z* 524): C, 61.83; H, 5.34; N, 5.34. Found: C, 62.09; H, 5.50; N, 5.58%.

6f. Yield 80%, mp 211°C, $[\alpha]_D$ + 28.4; IR (KBr) 3680–3210 (OH), 2214 (CN) cm^{-1}; ^{1}H NMR [$(CD_3)_2SO$, 400 MHz]: δ 1.96 (s, 3H, CH_3CO), 3.18–3.78 (m, 7H, 2H-6′, H-5′, H-4′, H-3′, H-2′ and pyridine H-4), 4.51–5.39 (m, 4H, 2′-OH, 3′-OH, 4′-OH and 6′-OH), 6.12 (d, $J_{1'-2'}$ 8.7 Hz, 1H, H-1′), 9.28 (d, 1H, furan H-4), 7.59–7.88 (m, 6H, Ar–H and furan H-3), 8.13 (d, 1H, furan H-5), 8.45 (bs, 1H, NH); ^{13}C NMR [$(CD_3)_2SO$, 400 MHz]: δ 17.9 (CH_3CO), 61.0 (C6′), 69.0 (C4′), 69.9 (C2′), 73.8 (C3′), 81.0 (C5′), 82.8 (C1′), 94.9 (C4), 111.4 (C3), 117.5 (CN), 126.0–138.6 (Ar–C), 140.6–148.0 (furan–C), 151.7 (C5), 154.7 (C6), 161.6 (C2), 196.4 (CO).

Anal. Calcd for $C_{24}H_{24}N_2SO_7$ (*m/z* 484): C, 59.50; H, 4.95; N, 5.78. Found: C, 59.82; H, 5.13; N, 6.04%.

6g. Yield 78%, mp 192°C, $[\alpha]_D$ + 36.4; IR (KBr) 3650–3200 (OH), 2207 (CN) cm^{-1}; ^{1}H NMR [$(CD_3)_2SO$, 400 MHz]: δ 2.23 (s, 3H, CH_3CO), 2.40 (s, 3H, CH_3), 3.18–3.77 (m, 7H, 2H-6′, H-5′, H-4′, H-3′, H-2′ and pyridine H-4), 4.72 (s, 1H, 2′-OH), 5.16 (m, 3H, 3′-OH, 4′-OH and 6′-OH), 5.65 (d, $J_{1'-2'}$ 9.6 Hz, 1H, H-1′), 7.17 (d, 2H, Ar–H), 7.34 (d, 2H, Ar–H), 8.23 (bs, 1H, NH); ^{13}C NMR [$(CD_3)_2SO$, 400 MHz]: δ 18.0 (CH_3CO), 31.5 (CH_3), 60.5 (C6′), 68.1 (C4′), 71.6 (C2′), 78.3 (C3′), 80.5 (C5′), 83.9 (C1′), 88.9 (C4), 108.3 (C3), 119.2 (CN), 127.9–142.0 (Ar–C), 143.6 (C5), 145.9 (C6), 162.5 (C2), 197.4 (CO).

Anal. Calcd for $C_{21}H_{23}ClN_2SO_6$ (*m/z* 466): C, 54.01; H, 4.93; N, 6.00. Found: C, 54.33; H, 5.14; N, 6.28%.

6h. Yield 78%, mp 177°C, $[\alpha]_D$ + 45.8; IR (KBr) 3710–3270 (OH), 2216(CN) cm^{-1}; ^{1}H NMR [$(CD_3)_2SO$, 400 MHz]: δ 1.94 (s, 3H, CH_3CO), 2.30 (s, 3H, CH_3), 3.22–4.02 (m, 10H, 2H-6′, H-5′, H-4′, H-3′, H-2′, OCH_3 and pyridine H-4), 4.66 (m, 2H, 2′-OH and 3′-OH), 4.98 (m, 1H, 4′-OH), 5.34 (d, 1H, 6′-OH), 5.58 (d, $J_{1'-2'}$ 9.6 Hz, 1H, H-1′), 7.16 (d, 2H, Ar–H), 7.38 (d, 2H, Ar–H), 8.77 (bs, 1H, NH); ^{13}C NMR [$(CD_3)_2SO$, 400 MHz]: δ 19.1 (CH_3CO), 23.1 (CH_3), 55.2 (OCH_3), 60.2 (C6′), 68.3 (C4′), 69.8 (C2′), 74.8 (C3′), 79.7 (C5′), 83.9 (C1′), 89.4 (C4), 102.4 (C3), 114.3 (CN), 127.9–138.0 (Ar–C), 156.1 (C5), 158.4 (C6), 160.5 (C2), 204.0 (CO).

Anal. Calcd for $C_{22}H_{26}N_2SO_7$ (*m/z* 462): C, 57.14; H, 5.62; N, 6.06. Found: C, 57.36; H, 5.78; N, 6.29%.

6i. Yield 77%, mp 158°C, $[\alpha]_D + 50.2$; IR (KBr) 3670–3180 (OH), 2210 (CN) cm^{-1}; ^1H NMR [$(CD_3)_2SO$, 400 MHz]: δ 2.19 (s, 3H, CH_3CO), 2.35 (s, 3H, CH_3), 3.09–3.85 (m, 7H, 2H-6′, H-5′, H-4′, H-3′, H-2′ and pyridine H-4), 4.76 (s, 1H, 2′-OH), 5.12 (m, 3H, 3′-OH, 4′-OH and 6′-OH), 5.43 (d, $J_{1'-2'}$ 9.7 Hz, 1H, H-1′), 6.45 (q, 1H, furan H-4), 7.21 (d, 1H, furan H-3), 8.13 (d, 1H, furan H-5), 8. 25 (bs, 1H, NH); ^{13}C NMR [$(CD_3)_2SO$, 400 MHz]: δ 18.9 (CH_3CO), 31.4 (CH_3), 62.2 (C6′), 68.7 (C4′), 71.7 (C2′), 78.0 (C3′), 80.6 (C5′), 83.7 (C1′), 88.6 (C4), 108.9 (C3), 119.0 (CN), 127.5–140.8 (furan–C), 145.3 (C5), 146.0 (C6), 161.4 (C2), 195.7 (CO).

Anal. Calcd for $C_{19}H_{22}N_2SO_7$ (*m/z* 422): C, 54.02; H, 5.21; N, 6.63. Found: C, 54.36; H, 5.34; N, 6.88%.

6j. Yield 78%, mp 169°C, $[\alpha]_D + 45.7$; IR (KBr) 3690–3270 (OH), 2206 (CN) cm^{-1}; ^1H NMR [$(CD_3)_2SO$, 400 MHz]: δ 1.78 (s, 3H, CH_3CO), 3.26–4.04 (m, 7H, 2H-6′, H-5′, H-4′, H-3′, H-2′ and pyridine H-4), 4.68 (d, 1H, 2′-OH), 4.76 (m, 1H, 3′-OH), 4.90 (d, 1H, 4′-OH), 5.08 (d, 1H, 6′-OH), 5.76 (d, $J_{1'-2'}$ 9.4 Hz, 1H, H-1′), 7.22–7.74 (m, 9H, Ar–H), 8.55 (bs, 1H, NH); ^{13}C NMR [$(CD_3)_2SO$, 400 MHz]: δ 18.7 (CH_3CO), 60.5 (C6′), 68.4 (C4′), 69.9 (C2′), 74.3 (C3′), 80.1 (C5′), 85.5 (C1′), 98.8 (C4), 109.8 (C3), 118.8 (CN), 127.8–131.9 (Ar–C), 144.7 (C5), 155.6 (C6), 161.8 (C2), 195.9 (CO).

Anal. Calcd for $C_{26}H_{25}ClN_2SO_6$ (*m/z* 528): C, 59.03; H, 4.73; N, 5.29. Found: C, 59.28; H, 4.95; N, 5.50%.

6k. Yield 81%, mp 208°C, $[\alpha]_D + 34.5$; IR (KBr) 3690–2930 (OH), 2201 (CN) cm^{-1}; ^1H NMR [$(CD_3)_2SO$, 400 MHz]: δ 1.80 (s, 3H, CH_3CO), 3.25–3.98 (m, 10H, 2H-6′, H-5′, H-4′, H-3′, H-2′, OCH_3 and pyridine H-4), 4.40–5.22 (m, 4H , 2′-OH, 3′-OH, 4′-OH and 6′-OH), 5.80 (d, $J_{1'-2'}$ 9.6 Hz, 1H, H-1′), 6.94–7.98 (m, 9H, Ar–H), 8.89 (bs, 1H, NH); ^{13}C NMR [$(CD_3)_2SO$, 400 MHz]: δ 18.7 (CH_3CO), 55.1 (OCH_3), 60.6 (C6′), 68.5 (C4′), 70.0 (C2′), 74.4 (C3′), 80.2 (C5′), 85.5 (C1′), 90.7 (C4), 114.1 (C3); 119.2 (CN), 128.0–140.5 (Ar–C), 154.6 (C5), 158.4 (C6), 161.9 (C2), 196.5 (CO).

Anal. Calcd for $C_{27}H_{28}N_2SO_7$ (*m/z* 524): C, 61.83; H, 5.34; N, 5.34. Found: C, 62.14; H, 5.60; N, 5.64%.

6l. Yield 80%, mp 206°C, $[\alpha]_D + 33.9$; IR (KBr) 3600–3220 (OH), 2208 (CN) cm^{-1}; ^1H NMR [$(CD_3)_2SO$, 400 MHz]: δ 1.82 (s, 3H, CH_3CO), 3.22–3.96 (m, 7H, 2H-6′, H-5′, H-4′, H-3′, H-2′ and pyridine H-4), 4.68–5.44 (m, 4H, 2′-OH, 3′-OH, 4′-OH and 6′-OH), 6.08 (d, $J_{1'-2'}$ 8.7 Hz, 1H, H-1′), 9.36 (d, 1H, furan H-4), 7.68 (m, 6H, Ar–H and furan H-3), 8.08 (d, 1H, furan H-5), 8.37 (bs, 1H, NH); ^{13}C NMR [$(CD_3)_2SO$, 400 MHz]: δ 18.4 (CH_3CO), 60.4 (C6′), 68.3 (C4′), 69.8 (C2′), 74.2 (C3′), 80.1 (C5′), 83.5 (C1′), 95.6 (C4), 110.4 (C3), 118.8 (CN), 127.8–139.9 (Ar–C), 141.8–147.2 (furan–C), 152.8 (C5), 155.4 (C6), 162.0 (C2), 195.8 (CO).

Anal. Calcd for $C_{24}H_{24}N_2SO_7$ (*m/z* 484): C, 59.50; H, 4.95; N, 5.78. Found: C, 59.82; H, 5.16; N, 6.08%.

3-Cyano-2-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-glycopyranosylthio)-pyridines (8). General coupling procedures.

Method (A). The piperidinium salt of dihydropyridinethiones **3** (0.01 mol) was dissolved in dry acetone (5 mL) and a solution of 2,3,4,6-tetra-*O*-acetyl-α-D-gluco- or galactopyranosyl bromide (0.01 mol) in dry acetone (20 mL) was then added at 30°C. The reaction mixture was stirred until the reaction was judged complete by TLC, using

chloroform: petroleum ether 9:1 (Rf, 0.62–0.66), then concentrated under reduced pressure at 40°C. The resulting product was crystallized from ethanol to afford pale yellow crystals.

Method (B). A mixture of pyridine-2(1*H*)-thiones **11** (0.01 mol), hexamethyldisilazane (25 mL) and ammonium sulphate (0.02 g) were boiled under reflux, with stirring for 48 h. The excess of hexamethyldisilazane was removed under diminished pressure, providing the silylated bases **12** as a colorless oil. The latter was added to a solution of 1,2,3,4,6-penta-*O*-acetyl-α-D-gluco- or galactopyranose (0.011 mol) in dry acetonitrile (20 mL) and $SnCl_4$ (1.6 mL). The reaction mixture was stirred at room temperature for (6 h), poured into saturated $NaHCO_3$ solution and then extracted with $CHCl_3$. The organic layers were dried over $MgSO_4$, filtered and then concentrated to give the crude nucleosides which were purified by recrystallization from ethanol.

Method (C). A suspension of pyridine thioglycosides 5 (0.01 mol) in ethanol were refluxed with stirring for 3 min. The resulting products were collected by filtration and crystallized from ethanol.

8a. Yield 68%, mp 139°C, $[\alpha]_D + 26.4$; IR (KBr) 2218 (CN), 1748 (CO) cm^{-1}; ^1H NMR [$(CD_3)_2SO$, 400 MHz]: δ 1.88–2.10 (5s, 15H, $5CH_3CO$), 2.35 (s, 3H, CH_3), 4.09 (m, 3H, 2H-6′ and H-5′), 5.00 (t, 1H, H-4′), 5.16 (t, 1H, H-3′), 5.49 (t, 1H, H-2′), 6.11 (d, $J_{1'-2'}$ 9.0 Hz, 1H, H-1′), 7.09 (d, 2H, Ar–H), 7.44 (d, 2H, Ar–H); ^{13}C NMR [$(CD_3)_2SO$, 400 MHz]: δ 21.0–21.9 ($4CH_3CO$), 23.0 (CH_3CO), 30.0 (CH_3), 60.9 (C6′), 67.1 (C4′), 67.6 (C2′), 74.0 (C3′), 75.7 (C5′), 81.2 (C1′), 107.6 (C3), 114.0 (CN), 126.9–134.0 (Ar–C), 152.0 (C4), 156.0 (C5), 159.3 (C6), 163.0 (C2), 166.0–168.2 (4CO of glucose), 200.0 (CO of pyridine).

Anal. Calcd for $C_{29}H_{29}ClN_2SO_{10}$ (*m/z* 632): C, 55.01; H, 4.58; N, 4.42. Found: C, 55.42; H, 4.80; N, 4.73%.

8b. Yield 70%, mp 143°C, $[\alpha]_D + 33.6$; IR (KBr) 2222 (CN), 1754 (CO) cm^{-1}; ^1H NMR [$(CD_3)_2SO$, 400 MHz]: δ 1.94–2.04 (5s, 15H, $5CH_3CO$), 2.58 (s, 3H, CH_3), 3.88 (s, 3H, OCH_3), 4.16 (m, 3H, 2H-6′ and H-5′), 5.04 (t, 1H, H-4′), 5.18 (t, 1H, H-3′), 5.56 (t, 1H, H-2′), 6.18 (d, $J_{1'-2'}$ 10.5 Hz, 1H, H-1′), 7.12 (d, 2H, Ar–H), 7.34 (d, 2H, Ar–H); ^{13}C NMR [$(CD_3)_2SO$, 400 MHz]: δ 20.2–20.3($4CH_3CO$), 22.9 (CH_3CO), 31.2 (CH_3), 55.3 (OCH_3), 61.7 (C6′), 68.1 (C4′), 68.8 (C2′), 73.1 (C3′), 75.0 (C5′), 80.1 (C1′), 105.0 (C3), 114.4 (CN), 125.5–133.5 (Ar–C), 150.2 (C4), 157.2 (C5), 158.0 (C6), 160.6 (C2), 169.1–169.8 (4CO of glucose), 202.8 (CO of pyridine).

Anal. Calcd for $C_{30}H_{32}N_2SO_{11}$ (*m/z* 628): C, 57.32; H, 5.09; N, 4.45. Found: C, 57.66; H, 5.28; N, 4.73%.

8c. Yield 66%, mp 129°C, $[\alpha]_D + 30.0$; IR (KBr) 2210 (CN), 1752 (CO) cm^{-1} ^1H NMR [$(CD_3)_2SO$, 400 MHz]: δ 1.90–2.12 (5s, 15H, $5CH_3CO$), 2.38 (s, 3H, CH_3), 4.14 (m, 3H, 2H-6′ and H-5′), 5.20 (m, 2H, H-4′, H-3′), 5.68 (d, 1H, H-2′), 6.15 (d, $J_{1'-2'}$ 10.6 Hz, 1H, H-1′), 6.94 (m, 1H, furan H-4), 7.34 (d, 1H, furan H-3), 8.08 (d, 1H, furan H-5).

Anal. Calcd for $C_{27}H_{28}N_2SO_{11}$ (*m/z* 588): C, 55.10; H, 4.76; N, 4.76. Found: C, 55.37; H, 4.92; N, 5.05%.

8d. Yield 68%, mp 161°C, $[\alpha]_D + 20.6$; IR(KBr) 2215(CN), 1752 (CO) cm^{-1}; ^1H NMR [$(CD_3)_2SO$, 400 MHz]: δ 1.88–2.12 (5s, 15H, $5CH_3CO$), 4.14 (m, 3H, 2H-6′ and H-5′), 5.18 (m, 2H, H-4′ and H-3′), 5.62 (t, 1H, H-2′), 6.20 (d, $J_{1'-2'}$ 10.1 Hz, 1H, H-1′), 7.66 (m, 9H, Ar–H).

Anal. Calcd for $C_{34}H_{31}Cl\ N_2SO_{10}$ (*m/z* 494): C, 58.74; H, 4.46; N, 4.03. Found: C, 59.12; H, 4.60; N, 4.35%.

8e. Yield 70%, mp 171°C, $[\alpha]_D + 40.5$; IR (KBr) 2218 (CN) 1748 (CO) cm^{-1}; ^1H NMR [$(CD_3)_2SO$, 400 MHz]: δ 1.94–2.08 (4s, 12H, $4CH_3CO$), 2.28 (s, 3H, CH_3CO), 3.82 (s, 3H, OCH_3), 4.20 (m, 3H, 2H-6′ and H-5′), 5.08 (t, 1H, H-4′), 5.26 (t, 1H, H-3′), 5.64 (t, 1H, H-2′), 6.26 (d, $J_{1'-2'}$ 10.8 Hz, 1H, H-1′), 6.85 (d, 2H, Ar–H), 7.18 (d, 2H, Ar–H), 7.62 (m, 5H, Ar–H); ^{13}C NMR [$(CD_3)_2SO$, 400 MHz]: δ 17.7–20.3 (4 CH_3CO), 23.0 (CH_3CO), 55.0 (OCH_3), 61.8 (C6′), 68.1 (C4′), 68.7 (C2′), 73.0 (C3′), 75.0 (C5′), 80.1 (C1′), 105.58 (C3), 114.6 (CN), 124.2–136.3 (Ar–C), 151.1 (C4), 154.4 (C5), 158.5 (C6), 160.1 (C2), 169.2–169.8 (4 CO of glucose), 195.0 (CO of pyridine).

Anal. Calcd for $C_{35}H_{34}N_2SO_{11}$ (*m/z* 690): C, 60.86; H, 4.92; N, 4.05. Found: C, 61.12; H, 5.08; N, 4.34%.

8f. Yield 67%, mp 139°C, $[\alpha]_D + 29.9$; IR (KBr) 2208 (CN), 1755 (CO) cm^{-1}; ^1H NMR [$(CD_3)_2SO$, 400 MHz]: δ 1.99–2.15 (5s, 15H, $5CH_3CO$), 2.45 (s, 3H, CH_3), 4.11 (m, 3H, 2H-6′ and H-5′), 5.12 (t, 1H, H-4′), 5.24 (t, 1H, H-3′), 5.50 (t, 1H, H-2′), 6.09 (d, $J_{1'-2'}$ 9.5 Hz, 1H, H-1′), 7.00–7.99 (m, 8H, Ar–H and furan–H,); ^{13}C NMR [$(CD_3)_2SO$, 400 MHz]: δ 22.0–22.9($4CH_3CO$), 24.5 (CH_3CO), 32.0 (CH_3), 61.9 (C6′), 67.9 (C4′), 67.9 (C2′), 74.5 (C3′), 75.9 (C5′), 81.9 (C1′), 108.6 (C3), 115.5 (CN), 127.0–136.6 (Ar–C and furan–C), 150.9 (C4), 155.6 (C5), 158.0 (C6), 165.8 (C2), 169.0–172.2 (4CO of glucose), 203.0 (CO of pyridine).

Anal. Calcd for $C_{32}H_{30}N_2SO_{11}$ (*m/z* 650): C, 59.07, H, 4.61; N, 4.30. Found: C, 59.38; H, 4.86; N, 4.58%.

8g. Yield 69%, mp 156°C, $[\alpha]_D + 25.9$; IR (KBr) 2204 (CN), 1752 (CO) cm^{-1}; ^1H NMR [$(CD_3)_2SO$, 400 MHz]: δ 1.90–2.16 (5s, 15H, $5CH_3CO$), 2.60 (s, 3H, CH_3), 4.12 (m, 3H, 2H-6′ and H-5′), 5.20 (m, 1H, H-4′), 5.52 (m, 2H, H-3′ and H-2′), 5.98 (d, $J_{1'-2'}$ 10.1 Hz, 1H, H-1′), 7.44 (m, 4H, Ar–H).

Anal. Calcd for $C_{29}H_{29}ClN_2SO_{10}$ (*m/z* 632): C, 55.01; H, 4.58; N, 4.42. Found: C, 55.40; H, 4.73; N, 4.68%.

8h. Yield 71%, mp 167°C, $[\alpha]_D + 38.9$; IR (KBr) 2220 (CN), 1752 (CO) cm^{-1}; ^1H NMR [$(CD_3)_2SO$, 400 MHz]: δ 1.94–2.05 (5s, 15H, $5CH_3CO$), 2.37 (s, 3H, CH_3), 36.84 (s, 3H, OCH_3), 4.15 (m, 3H, 2H-6′ and H-5′), 5.04 (t, 1H, H-4′), 5.22 (t, 1H, H-3′), 5.55 (t, 1H, H-2′), 6.18 (d, $J_{1'-2'}$ 10.5 Hz, 1H, H-1′), 7.12 (d, 2H, Ar–H), 7.34 (d, 2H, Ar–H); ^{13}C NMR [$(CD_3)_2SO$, 400 MHz]: δ 17.5–20.3 ($4CH_3CO$), 22.9 (CH_3CO), 31.2 (CH_3), 55.3 (OCH_3), 61.7 (C6′), 68.1 (C4′), 68.8 (C2′), 73.1 (C3′), 74.9 (C5′), 80.1 (C1′), 105.0 (C3), 114.3 (CN), 125.4–133.5 (Ar–C), 150.8 (C4), 153.4 (C5), 158.0 (C6), 160.8 (C2), 169.1–169.8 (4CO of galactose), 200.3 (CO of pyridine).

Anal. Calcd for $C_{30}H_{32}N_2SO_{11}$ (*m/z* 628): C, 57.32; H, 5.09; N, 4.45. Found: C, 57.68; H, 5.25; N, 4.72%.

8i. Yield 68%, mp 141°C, $[\alpha]_D + 27.5$; IR (KBr) 2220 (CN), 1740 (CO) cm^{-1}; ^1H NMR [$(CD_3)_2SO$, 400 MHz]: δ 1.83–2.11 (5s, 15H, $5CH_3CO$), 2.43 (s, 3H, CH_3), 4.09 (m, 3H, 2H-6′ and H-5′), 5.02 (m, 2H, H-4′, H-3′), 5.55 (d, 1H, H-2′), 6.05 (d, $J_{1'-2'}$ 10.0 Hz, 1H, H-1′), 6.90 (m, 1H, furan H-4), 7.11 (d, 1H, furan H-3), 8.00 (d, 1H, furan H-5).

Anal. Calcd for $C_{27}H_{28}N_2SO_{11}$ (*m/z* 588): C, 55.10; H, 4.76; N, 4.76. Found: C, 55.37; H, 4.98; N, 5.08%.

8j. Yield 70%, mp 196°C, $[\alpha]_D + 31.4$; IR (KBr) 2210 (CN), 1748 (CO) cm^{-1}; ^1H NMR [$(CD_3)_2SO$, 400 MHz]: δ 1.96–2.18 (5s, 15H, $5CH_3CO$), 4.10 (m, 3H, 2H-6′

and H-5′), 5.13 (m, 2H, H-4′ and H-3′), 5.40 (t, 1H, H-2′), 6.15 (d, $J_{1'-2'}$ 9.7 Hz, 1H, H-1′), 7.00–7.83 (m, 9H, Ar–H).

Anal. Calcd for $C_{34}H_{31}ClN_2SO_{10}$ (*m/z* 694): C, 58.74; H, 4.46; N, 4.03. Found: C, 59.05; H, 4.62; N, 4.30%.

8k. Yield 65%, mp 121°C, $[\alpha]_D + 22.5$; IR (KBr) 2214 (CN), 1755 (CO) cm^{-1}; ^1H NMR [$(CD_3)_2SO$, 400 MHz]: δ 1.88–2.14 (5s, 15H, $5CH_3CO$), 3.82 (s, 3H, OCH_3), 4.15 (m, 3H, 2H-6′ and H-5′), 5.44 (m, 1H, H-4′), 5.72 (m, 2H, H-3′ and H-2′), 6.00 (d, $J_{1'-2'}$ 10.3 Hz, 1H, H-1′), 6.96 (d, 2H, Ar–H), 7.12 (d, 2H, Ar–H), 7.48 (m, 5H, Ar–H) ppm.

Anal. Calcd for $C_{35}H_{34}N_2SO_{11}$ (*m/z* 690): C, 60.86; H, 4.92; N, 4.05. Found: C, 61.20; H, 5.15; N, 4.34%.

8l. Yield 70%, mp 193°C, $[\alpha]_D + 36.8$; IR (KBr) 2210 (CN), 1754 (CO) cm^{-1}; ^1H NMR [$(CD_3)_2SO$, 400 MHz]: δ 1.80–2.22 (5s, 15H, $5CH_3CO$), 2.50 (s, 3H, CH_3), 4.05 (m, 3H, 2H-6′ and H-5′), 5.20 (t, 1H, H-4′), 5.40 (t, 1H, H-3′), 5.62 (t, 1H, H-2′), 6.16 (d, $J_{1'-2'}$ 9.0 Hz, 1H, H-1′), 6.89–7.90 (m, 8H, Ar–H and furan–H); ^{13}C NMR [$(CD_3)_2SO$, 400 MHz]: δ 20.3–21.7($4CH_3CO$), 26.0 (CH_3CO), 60.2 (C6′), 68.0 (C4′), 67.5 (C2′), 75.3 (C3′), 77.4 (C5′), 80.7 (C1′), 111.0 (C3), 117.5 (CN), 124.0–138.0 (Ar–C and furan–C), 151.3 (C4), 154.6 (C5), 159.0 (C6), 166.2 (C2), 168.0–171.7 (4CO of glucose), 201.6 (CO of pyridine).

Anal. Calcd for $C_{32}H_{30}N_2SO_{11}$ (*m/z* 650): C, 59.07; H, 4.61; N, 4.30. Found: C, 59.41; H, 4.78; N, 4.62%.

3-Cyano-2-(β-D-glycopyranosylthio)-pyridines (9).

General procedure. Dry gaseous ammonia was passed through a solution of protected nucleoside **8** (0.5 g) in dry methanol (20 mL) at room temperature for 10 min. The mixture was stirred until the reaction was judged complete by TLC (10–12 h) using $CHCl_3$:MeOH, 9:1 (Rf, 0.66–0.68). The resulting mixture was then concentrated under reduced pressure to afford a solid residue that was crystallized from methanol to give crystals.

9a. Yield 78%, mp 193°C, $[\alpha]_D + 22.6$; IR (KBr) 3600–3180 (OH), 2206 (CN) cm^{-1}; ^1H NMR [$(CD_3)_2SO$, 400 MHz]: δ 2.05 (s, 3H, CH_3CO), 2.36 (s, 3H, CH_3), 3.20–3.84 (m, 6H, 2H-6′, H-5′, H-4′, H-3′ and H-2′), 4.68 (m, 2H, 2′-OH and 3′-OH), 5.52 (m, 2H, 4′-OH and 6′-OH), 5.68 (d, $J_{1'-2'} = 10.0$ Hz, 1H, H-1′), 7.42 (d, 2H, Ar–H), 7.58 (d, 2H, Ar–H).

Anal. Calcd for $C_{21}H_{21}ClN_2SO_6$ (*m/z* 464): C, 54.25; H, 4.52; N, 6.02. Found: C, 54.62; H, 4.68; N, 6.29%.

9b. Yield 82%, mp 216°C, $[\alpha]_D + 31.8$; IR (KBr) 3640–3210 (OH), 2211 (CN) cm^{-1}; ^1H NMR [$(CD_3)_2SO$, 400 MHz]: δ 2.09 (s, 3H, CH_3CO), 2.36 (s, 3H, CH_3), 3.19–3.65 (m, 6H, 2H-6′, H-5′, H-4′, H-3′ and H-2′), 3.99 (s, 3H, OCH_3), 4.33 (d, 2H, 2′-OH and 3′-OH), 4.76 (d, 1H, 4′-OH), 5.22 (d, 1H, 6′-OH), 5.99 (d, $J_{1'-2'}$ 10.0 Hz, 1H, H-1′), 7.00 (d, 2H, Ar–H), 7.36 (d, 2H, Ar–H).

Anal. Calcd for $C_{22}H_{24}N_2SO_7$ (*m/z* 460): C, 57.39; H, 5.21; N, 6.08. Found: C, 57.65; H, 5.32; N, 6.34%.

9c. Yield 81%, mp 215°C, $[\alpha]_D + 32.1$; IR (KBr) 3610–3190 (OH), 2214 (CN) cm^{-1}; ^1H NMR [$(CD_3)_2SO$, 400 MHz]: δ 2.10 (s, 3H, CH_3CO), 2.32 (s, 3H, CH_3), 3.28–3.78 (m, 6H, 2H-6′, H-5′, H-4′, H-3′ and H-2′), 4.60 (m, 2H, 2′-OH and 3′-OH),

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5.28 (m, 2H, 4′-OH and 6′-OH), 5.62 (d, $J_{1'-2'}$ 10.0 Hz, 1H, H-1′), 6.92 (q, 1H, furan H-4), 7.44 (d, 1H, furan H-3), 8.06 (d, 1H, furan H-5).

Anal. Calcd for $C_{19}H_{20}N_2SO_7$ (*m/z* 420): C, 54.28; H, 4.76; N, 6.66. Found: C, 54.46; H, 4.88; N, 6.92%.

9d. Yield 80%, mp 211°C, $[\alpha]_D$ +45.0; IR (KBr) 3650–3220 (OH), 2215 (CN) cm^{-1}; ^1H NMR [$(CD_3)_2SO$, 400 MHz]: δ 2.13 (s, 3H, CH_3CO), 3.18–3.82 (m, 6H, 2H-6′, H-5′, H-4′, H-3′ and H-2′), 4.42(m, 2H, 2′-OH and 3′-OH), 5.58 (m, 2H, 4′-OH and 6′-OH), 5.78 (d, $J_{1'-2'}$ 9.9 Hz, 1H, H-1′), 7.55 (m, 9H, Ar–H).

Anal. Calcd for $C_{26}H_{23}ClN_2SO_6$ (*m/z* 526): C, 59.25; H, 4.36; N, 5.31. Found: C, 59.66; H, 4.49; N, 5.50%.

9e. Yield 79%, mp 207°C, $[\alpha]_D$ +29.9; IR (KBr) 3680–3260 (OH), 2217 (CN) cm^{-1}; ^1H NMR [$(CD_3)_2SO$, 400 MHz]: δ 2.12 (s, 3H, CH_3CO), 3.09–3.88 (m, 6H, 2H-6′, H-5′, H-4′, H-3′ and H-2′), 4.04 (s, 3H, OCH_3), 4.30 (d, 2H, 2′-OH and 3′-OH), 4.65 (d, 1H, 4′-OH), 5.17 (d, 1H, 6′-OH), 6.09 (d, $J_{1'-2'}$ 10.7 Hz, 1H, H-1′), 7.10–7.86 (m, 9H, Ar–H).

Anal. Calcd for $C_{27}H_{26}N_2SO_7$ (*m/z* 522): C, 62.06; H, 4.98; N, 5.36. Found: C, 62.39; H, 5.17; N, 5.62%.

9f. Yield 79%, mp 205°C, $[\alpha]_D$ 19.9; IR (KBr) 3640–3280 (OH), 2212 (CN) cm^{-1}; ^1H NMR [$(CD_3)_2SO$, 400 MHz]: δ 2.14 (s, 3H, CH_3CO), 3.10–3.88 (m, 6H, 2H-6′, H-5′, H-4′, H-3′ and H-2′), 4.23 (d, 2H, 2′-OH and 3′-OH), 5.00 (d, 1H, 4′-OH), 5.44 (d, 1H, 6′-OH), 5.67 (d, $J_{1'-2'}$ 10.0 Hz, 1H, H-1′), 7.00–7.98 (m, 8H, Ar–H and furan–H).

Anal. Calcd for $C_{24}H_{22}N_2SO_7$ (*m/z* 482): C, 59.75; H, 4.56; N, 5.80. Found: C, 60.12; H, 4.70; N, 6.05%.

9g. Yield 80%, mp 199°C, $[\alpha]_D$ +48.8; IR (KBr) 3610–3230 (OH), 2216 (CN) cm^{-1}; ^1H NMR [$(CD_3)_2SO$, 400 MHz]: δ 2.02 (s, 3H, CH_3CO), 2.34 (s, 3H, CH_3), 3.16–3.80 (m, 6H, 2H-6′, H-5′, H-4′, H-3′ and H-2′), 4.52 (d, 2H, 2′-OH and 3′-OH), 5.00 (d, 1H, 4′-OH), 5.42 (d, 1H, 6′-OH), 5.58 (d, $J_{1'-2'}$ 10.4 Hz, 1H, H-1′), 7.40 (d, 2H, Ar–H), 7.68 (d, 2H, Ar–H).

Anal. Calcd for $C_{21}H_{21}ClN_2SO_6$ (*m/z* 464): C, 54.25; H, 4.52; N, 6.02. Found: C, 54.46; H, 4.70; N, 6.23%.

9h. Yield 81%, mp 217°C, $[\alpha]_D$ +30.0; IR (KBr) 3620–3190 (OH), 2208 (CN) cm^{-1}; ^1H NMR [$(CD_3)_2SO$, 400 MHz]: δ 1.98 (s, 3H, CH_3CO), 2.38 (s, 3H, CH_3), 3.20–3.78 (m, 6H, 2H-6′, H-5′, H-4′, H-3′ and H-2′), 3.92 (s, 3H, OCH_3), 4.55 (d, 2H, 2′-OH and 3′-OH), 4.98 (d, 1H, 4′-OH), 5.48 (d, 1H, 6′-OH), 5.70 (d, $J_{1'-2'}$ 10.2 Hz, 1H, H-1′), 7.12 (d, 2H, Ar–H), 7.40 (d, 2H, Ar–H).

Anal. Calcd for $C_{22}H_{24}N_2SO_7$ (*m/z* 460): C, 57.39; H, 5.21; N, 6.08. Found: C, 57.70; H, 5.43; N, 6.39%.

9i. Yield 83%, mp 220°C, $[\alpha]_D$ +28.9; IR (KBr) 3640–3250 (OH), 2213 (CN) cm^{-1}; ^1H NMR [$(CD_3)_2SO$, 400 MHz]: δ 2.12 (s, 3H, CH_3CO), 2.40 (s, 3H, CH_3), 3.12–3.74 (m, 6H, 2H-6′, H-5′, H-4′, H-3′ and H-2′), 4.50 (d, 2H, 2′-OH and 3′-OH), 4.92 (d, 1H, 4′-OH), 5.44 (d, 1H, 6′-OH), 5.68 (d, $J_{1'-2'}$ 10.3 Hz, 1H, H-1′), 6.84 (q, 1H, furan H-4), 7.36 (d, 1H, furan H-3), 8.00 (d, 1H, furan H-5).

Anal. Calcd for $C_{19}H_{20}N_2SO_7$ (*m/z* 420): C, 54.28; H, 4.76; N, 6.66. Found: C, 54.55; H, 4.98; N, 6.93%.

9j. Yield 81%, mp 206°C, $[\alpha]_D$ 24.4; IR (KBr) 3680–3210 (OH), 2210 (CN) cm^{-1}; ^1H NMR [$(CD_3)_2SO$, 400 MHz]: δ 1.78 (s, 3H, CH_3CO), 3.18–3.85 (m, 6H,

2H-6′, H-5′, H-4′, H-3′ and H-2′), 4.52 (d, 2H, 2′-OH and 3′-OH), 5.02 (d, 1H, 4′-OH), 5.48 (d, 1H, 6′-OH), 5.74 (d, $J_{1'-2'}$ 10.2 Hz, 1H, H-1′), 7.58 (m, 9H, Ar–H).

Anal. Calcd for $C_{26}H_{23}ClN_2SO_6$ (*m/z* 526): C, 59.25; H, 4.36; N, 5.31. Found: C, 59.63; H, 4.52; N, 5.65%.

9k. Yield 80%, mp 202°C, $[\alpha]_D + 30.8$; IR (KBr) 3680–3260 (OH), 2212 (CN) cm^{-1}; ^1H NMR [$(CD_3)_2SO$, 400 MHz]: δ 2.19 (s, 3H, CH_3CO), 3.09–3.93 (m, 6H, 2H-6′, H-5′, H-4′, H-3′ and H-2′), 3.99 (s, 3H, OCH_3), 4.34 (d, 2H, 2′-OH and 3′-OH), 5.00 (d, 1H, 4′-OH), 5.52 (d, 1H, 6′-OH), 5.99 (d, $J_{1'-2'}$ 9.7Hz, 1H, H-1′), 7.13–7.90 (m, 9H, Ar–H).

Anal. Calcd for $C_{27}H_{26}N_2SO_7$ (*m/z* 522): C, 62.06; H, 4.98; N, 5.36. Found: C, 62.39; H, 5.22; N, 5.64%.

9l. Yield 81%, mp 207°C, $[\alpha]_D + 43.9$; IR (KBr) 3640–3190 (OH), 2215 (CN) cm^{-1}; ^1H NMR [$(CD_3)_2SO$, 400 MHz]: δ 2.00 (s, 3H, CH_3CO), 3.19–3.97 (m, 6H, 2H-6′, H-5′, H-4′, H-3′ and H-2′), 4.54 (d, 2H, 2′-OH and 3′-OH), 5.28 (d, 1H, 4′-OH), 5.53 (d, 1H, 6′-OH), 5.99 (d, $J_{1'-2'}$ 9.6 Hz, 1H, H-1′), 6.78–7.77 (m, 8H, Ar–H and furan–H).

Anal. Calcd. for $C_{24}H_{22}N_2SO_7$ (*m/z* 482): C, 59.75; H, 4.56; N, 5.80. Found: C, 60.12; H, 4.80; N, 6.08%.

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