

Synthesis of Some Novel Condensed Pyridine-2(1*H*)-thiones and Related Glycosides

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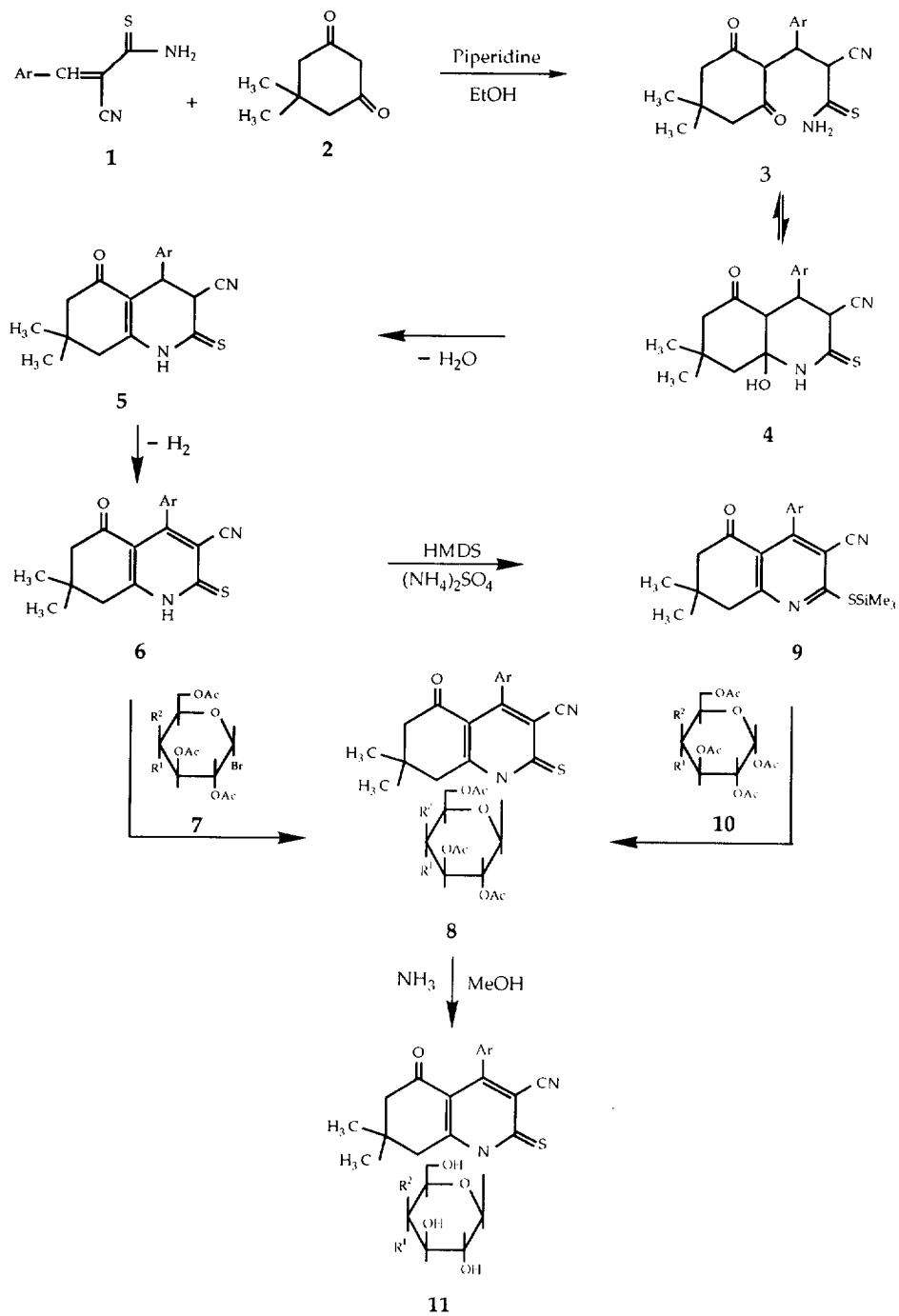
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Abstract: A novel synthesis of condensed pyridine-2(1*H*)-thiones and 3-deazapyrimidine glycosides is described utilizing arylmethylenecyanothioacetamides and dimedone as starting components.

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We have recently reported approaches for the synthesis of 2-oxo- and 2-thio-pyridines *via* reaction of α,β -unsaturated nitriles with active methylene reagents.¹⁻⁴ The importance of such compounds, as intermediates for the synthesis of the biologically active deazafolic acid and 3-deazapyrimidine nucleosides ring systems⁵⁻⁷ prompted our interest in the synthesis and chemistry of this class of compounds. We now report the novel reaction of 5,5-dimethyl-1,3-cyclohexadione **1** with arylmethylenecyanothioacetamides **2** in refluxing ethanol containing a catalytic amount of piperidine for 3 h to produce the condensed 3-cyanopyridine-2(1*H*)-thiones **6**. The structure of **6** could be established for the reaction products on the basis of their elemental analysis and spectral data. The formation of **6** from **1** and **2** is assumed to proceed *via* addition of an active methylene group of dimedone **2** to the double bond of **1** to give an intermediate **3**. This Michael adduct then cyclizes to give the intermediate dihydropyridine derivatives **5** which is oxidised under the reaction conditions to yield **6**. Compounds **6** were found useful for the synthesis of 3-deazapyrimidine glycosides. Thus, **6** reacted with tetra-*O*-acetyl- α -D-glucopyranosyl bromides in the presence of aqueous potassium hydroxide to give the corresponding condensed pyridinethione glycosides **8**. Although the coupling of **6** with glycosyl halides could also give the corresponding thioglycosides, the formation of **8** was proved chemically. Reaction of **6** with hexamethyldisilazane (HMDS) in the presence of ammonium sulfate⁸ gave the corresponding 2-trimethylsilylthiopyridines **7**, which were subsequently treated with peracetylated sugars in the presence of SnCl₄ according to the method of Vorbruggen *et al*⁹⁻¹² to afford the corresponding *N*-glycosides **8**. The chemical formula and molecular structure of the glycosides **8** were identified using elemental analyses and spectral data. The ¹H-NMR spectrum of **8a** showed a doublet at δ 5.98 ppm (*J* 8.39 Hz)



	Ar	Ar	R ¹	R ²		Ar	R ¹	R ²
6 a	4-ClC ₆ H ₄	8 a 4-ClC ₆ H ₄	OAc	H	11 a	4-ClC ₆ H ₄	OH	H
b	4-CH ₃ C ₆ H ₄	b 4-CH ₃ C ₆ H ₄	OAc	H	b	4-CH ₃ C ₆ H ₄	OH	H
c	4-CH ₃ OC ₆ H ₄	c 4-CH ₃ OC ₆ H ₄	OAc	H	c	4-CH ₃ OC ₆ H ₄	OH	H
d	2-furanyl	d 2-furanyl	OAc	H	d	2-furanyl	OH	H
e	2-thienyl	e 2-thienyl	OAc	H	e	2-thienyl	OH	H
f	1-naphthyl	f 1-naphthyl	OAc	H	f	1-naphthyl	OH	H
		g 4-ClC ₆ H ₄	H	OAc	g	4-ClC ₆ H ₄	H	OH
		h 4-CH ₃ C ₆ H ₄	H	OAc	h	4-CH ₃ C ₆ H ₄	H	OH
		i 4-CH ₃ OC ₆ H ₄	H	OAc	i	4-CH ₃ OC ₆ H ₄	H	OH
		j 2-furanyl	H	OAc	j	2-furanyl	H	OH
		k 2-thienyl	H	OAc	k	2-thienyl	H	OH
		l 1-naphthyl	H	OAc	l	1-naphthyl	H	OH

assigned to the anomeric proton of the glucose moiety with a diaxial orientation of H-1' and H-2' indicating the β -configuration and ⁴C₁(D) conformation. The other protons of the glucopyranose ring resonate at 4.11-4.95 ppm, while the four acetoxy groups appear as four singlets in the 1.95-2.02 ppm region providing further verification of the ⁴C₁(D) conformation with β -configuration, since these signals lie within the range expected for equatorial secondary acetoxy groups. The UV spectrum of **8c** proved that the reaction had led selectively to the formation of *N*-glucosyl derivatives and excluded substitution at the sulfur atom. Thus whereas the *S*-methyl derivative of **6c** showed two maxima at 295 and 342 nm, its *N*-glucosyl derivative exhibited three maxima at 285, 334 and 362 nm. Preparation of highly crystalline 1-(β -D-glycopyranosyl)-3-cyanopyridine-2-thiones **11** was achieved by removal of the acetyl groups on treatment with methanolic ammonia at 0 °C. TLC of the free glycosides **11** showed that a single compound was produced, and their structures were further confirmed by elemental analyses and spectral data. The ¹H-NMR spectrum of **11h** showed the anomeric proton as a doublet at δ 5.68 ppm (*J* 8.96 Hz), indicating the presence of only the β -D-galactopyranose.

The compounds described in this manuscript showed no activity against Human Immunodeficiency Virus (HIV) in MT-4 cells. They were also devoid of any activity against different types of tumor virus.

EXPERIMENTAL

Melting points are uncorrected. Aluminum-coated silica gel 60 F₂₅₄ (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 ¹³C-NMR spectra were measured in (CD₃)₂SO using SiMe₄ 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.

Condensed 4-aryl-3-cyanopyridine-2(1H)-thiones 6. General procedure:

A mixture of **1** (0.01 Mol) and **2** (0.01 Mol) was dissolved in ethanol (30 mL), a few drops of piperidine were then added. The mixture was heated under reflux for 8 h, and then allowed to stand overnight. The resulting solid product was collected by filtration and crystallized from EtOH-DMF to afford yellow crystals.

6a: Yield 61 %, mp 294 °C; IR(KBr) 3254(NH), 2222(CN), 1645(CO) cm^{-1} ; ^1H NMR(DMSO- d_6) 1.03(s,2H, CH_2), 1.12(s,2H, CH_2), 2.16(s,3H, CH_3), 2.30(s,3H, CH_3), 7.33(m,4H,Ar-H), 14.46(s,br,1H,NH) ppm; ^{13}C NMR(DMSO- d_6) 27.3(CH_3), 27.9(CH_3), 32.2(C7), 50.5(CH_2), 52.1(CH_2), 95.8(C9), 108.3(C3), 116.9(CN), 122.4-136.1(Ar-C), 150.6(C10), 155.1(C4), 160.2(CO), 192.6(CS) ppm; m/z 342(Found: C,63.31; H,4.43; N,8.29 $\text{C}_{18}\text{H}_{15}\text{ClN}_2\text{SO}$ requires C,63.06; H,4.38; N,8.17 %).

6b: Yield 60 %, mp 298 °C; IR(KBr) 3250(NH), 2228(CN), 1642(CO) cm^{-1} ; ^1H NMR(DMSO- d_6) 1.02(s,2H, CH_2), 1.15(s,2H, CH_2), 2.24(s,3H, CH_3), 2.32(s,3H, CH_3), 2.38(s,3H, CH_3), 7.12(m,4H,Ar-H), 14.39(s,br,1H,NH) ppm; ^{13}C NMR(DMSO- d_6) 21.4(CH_3), 27.9(CH_3), 28.1(CH_3), 32.2(C7), 50.9(CH_2), 52.2(CH_2), 96.9(C9), 108.3(C3), 115.9(CN), 126.4-138.3(Ar-C), 150.1(C10), 156.5(C4), 159.8(CO), 192.4(CS) ppm; m/z 322(Found: C,70.92; H,5.67; N,8.86 $\text{C}_{19}\text{H}_{18}\text{N}_2\text{SO}$ requires C,70.80; H,5.59; N,8.69 %).

6c: Yield 62 %, mp 289 °C; IR(KBr) 3254(NH), 2225(CN), 1645(CO) cm^{-1} ; ^1H NMR(DMSO- d_6) 1.03(s,2H, CH_2), 1.08(s,2H, CH_2), 2.17(s,3H, CH_3), 2.34(s,3H, CH_3), 3.84(s,3H, OCH_3), 7.09(m,4H,Ar-H), 14.33(s,br,1H,NH) ppm; ^{13}C NMR(DMSO- d_6) 27.4(CH_3), 28.2 (CH_3), 32.4(C7), 50.8(CH_2), 52.1(CH_2), 55.4(OCH_3), 96.8(C9), 107.6(C3), 114.9 (CN), 121.9-138.0(Ar-C), 150.7(C10), 156.4(C4), 159.9(CO), 193.6(CS) ppm; m/z 338(Found: C,67.71; H,5.49; N,8.50 $\text{C}_{19}\text{H}_{18}\text{N}_2\text{SO}_2$ requires C,67.45; H,5.32; N,8.28 %).

6d: Yield 59 %, mp 261 °C; IR(KBr) 3250(NH), 2226(CN), 1640(CO) cm^{-1} ; ^1H NMR(DMSO- d_6) 1.06(s,2H, CH_2), 1.16(s,2H, CH_2), 2.30(s,3H, CH_3), 2.42(s,3H, CH_3), 6.82(d,1H,furan H-4), 7.08(d,1H,furan H-3), 8.08(d,1H,furan H-5), 14.05(s,br,1H,NH) ppm; m/z 298(Found: C,64.62; H,4.76; N,9.58 $\text{C}_{16}\text{H}_{14}\text{N}_2\text{SO}_2$ requires C,64.43; H,4.69; N,9.39 %).

6e: Yield 63 %, mp 249 °C; IR(KBr) 3260(NH), 2220(CN), 1648(CO) cm^{-1} ; m/z 314(Found: C,61.33; H,4.56; N,9.08 $\text{C}_{16}\text{H}_{14}\text{N}_2\text{S}_2\text{O}$ requires C,61.14; H,4.45; N,8.91 %).

6f: Yield 60 %, mp 306 °C; IR(KBr) 3428(NH), 2220(CN), 1620(CO) cm^{-1} ; ^1H NMR(DMSO- d_6) 1.02(s,2H, CH_2), 1.13(s,2H, CH_2), 2.25(s,3H, CH_3), 2.40(s,3H, CH_3), 7.56(m,7H,Ar-H), 14.12(s,br,1H,NH) ppm; ^{13}C NMR(DMSO- d_6) 27.9(CH_3), 29.3(CH_3), 32.2(C7), 50.8(CH_2), 51.8(CH_2), 94.9(C9), 108.3(C3), 117.8(CN), 125.7-140.3(Ar-C), 151.1(C10), 155.1(C4), 160.3(CO), 193.9(CS) ppm; m/z 358(Found: C,73.96; H,5.23; N,7.97 $\text{C}_{22}\text{H}_{18}\text{N}_2\text{SO}$ requires C,73.74; H,5.02; N,7.82 %).

3-Cyano-1-(2',3',4',6'-tetra-O-acetyl- β -D-glycopyranosyl)-pyridine-2-thiones 8.

General coupling procedures. Method A: To a solution of 3-cyanopyridine-2(1H)-thiones **6** (0.01 Mol) in aqueous KOH [0.56 g (0.01 Mol) in 6 mL of distilled water], a solution of 2,3,4,6-tetra-O-acetyl- α -D-glucor galacto-pyranosyl bromide **7** (0.011 Mol) in 30 mL acetone was added. The reaction mixture was stirred at room temperature until the reaction was judged complete by TLC (30 min to 2 h), using chloroform : ether 4:1, v/v (Rf 0.70-0.76 region), then evaporated under reduced pressure at 40 °C and the residue was washed

with distilled water to remove KBr. The product was dried prior to crystallization from EtOH to afford pale yellow needle crystals.

Method B: 3-Cyanopyridine-2(1*H*)-thiones **6** (0.01 Mol) were refluxed by stirring under anhydrous condition for 24 h with hexamethyldisilazane 60 mL and (NH₄)₂SO₄ (0.02g). The clear solution obtained was cooled and the solvent was removed *in vacuo*. The resulting trimethylsilylated pyridine **9** was dissolved in anhydrous 1,2-dichloroethane 40 mL, and a solution of α -D-glycopyranose pentaacetate **10** (0.011 Mol) in dry 1,2-dichloroethane 20 mL was then added with stirring. The mixture was cooled to -10 °C and a solution of SnCl₄ 1.6 mL in anhydrous 1,2-dichloroethane 5 mL was added dropwise and the mixture was stirred until the reaction was judged complete by TLC (2-3 h), then poured into saturated NaHCO₃ solution and extracted with CHCl₃. The organic layer was dried over MgSO₄, filtered and concentrated to give the crude nucleosides that were purified by recrystallization from EtOH to afford pale yellow needle crystals.

8a: Yield 71 %, mp 176 °C; IR(KBr) 2220(CN), 1754(CO ester), 1630(CO) cm⁻¹; ¹H NMR (DMSO-d₆) 1.03(m,4H,2CH₂), 1.95-2.02(4s,12H,4CH₃CO), 2.22(s,3H,CH₃), 2.38(s,3H,CH₃), 4.11(m,2H,H-6' and 1H,H-5'), 4.52(s,1H,H-4'), 4.94(m,2H,H-3' and H-2'), 5.98(d, J_{1'-2'} 8.39 Hz, 1H,H-1'), 7.36(m,4H,Ar-H) ppm; ¹³C NMR(DMSO-d₆) 20.1-20.5(4CH₃CO), 26.6(CH₃), 28.5(CH₃), 32.2(C7), 49.9(CH₂), 50.0(CH₂), 61.9(C6'), 67.7(C4'), 69.5(C2'), 72.7((C3'), 74.8(C5'), 83.3(C1'), 94.9(C9), 107.8(C3), 118.1(CN), 127.8-139.7(Ar-C), 143.3(C10), 149.6(C4), 169.0(CO), 169.2-169.8(4COCH₃), 194.5(CS) ppm; m/z 672(Found: C,57.32; H,5.07; N,4.29 C₃₂H₃₃ClN₂SO₁₀ requires C,57.10; H,4.90; N,4.16 %).

8b: Yield 73 %, mp 141 °C; IR(KBr) 2218(CN), 1752(CO ester), 1634(CO) cm⁻¹; ¹H NMR(DMSO-d₆) 1.14(m,4H,2CH₂), 2.01-2.16(4s,12H,4CH₃CO), 2.22(s,3H,CH₃), 2.26(s,3H,CH₃), 2.38(s,3H,CH₃), 4.21(m,2H,H-6' and 1H,H-5'), 4.64(t,1H,H-4'), 5.08(m,2H,H-3' and H-2'), 6.06(d, J_{1'-2'} 8.96 Hz, 1H,H-1'), 7.17(m,4H,Ar-H) ppm; ¹³C NMR(DMSO-d₆) 20.1-20.5(4CH₃CO), 26.4(CH₃), 27.9(CH₃), 28.5(CH₃), 32.2(C7), 50.0(CH₂), 50.4(CH₂), 61.8(C6'), 67.7(C4'), 70.2(C2'), 72.8(C3'), 74.8(C5'), 83.6(C1'), 95.7(C9), 108.1(C3), 118.3(CN), 126.9-139.3(Ar-C), 141.6(C10), 149.3(C4), 167.3(CO), 169.0-169.8(4COCH₃), 194.4(CS) ppm; m/z 652(Found: C,60.82; H, 5.61; N,4.44 C₃₃H₃₆N₂SO₁₀ requires C,60.73; H,5.52; N,4.29 %).

8c: Yield 72 %, mp 168 °C; IR(KBr) 2215(CN), 1744(CO ester), 1620(CO) cm⁻¹; ¹H NMR(DMSO-d₆) 1.05(s,2H,CH₂), 1.14(s,2H,CH₂), 2.02-2.10(4s,12H,4CH₃CO), 2.27(s,3H,CH₃), 2.36(s,3H,CH₃), 3.82(s,3H,OCH₃), 4.07(s,2H,H-6'), 4.25(s,1H,H-5'), 4.64(m,2H,H-4' and H-3'), 4.98(t,1H,H-2'), 5.82(d, J_{1'-2'} 8.79 Hz, 1H,H-1'), 7.15(m,4H,Ar-H) ppm; m/z 668(Found: C,59.51; H,5.44; N,4.30 C₃₃H₃₆N₂SO₁₁ requires C,59.28; H,5.38; N,4.19 %).

8d: Yield 70 %, mp 136 °C; IR(KBr) 2218(CN), 1756(CO ester), 1640(CO) cm⁻¹; m/z 628(Found: C,57.46; H,5.18; N,4.63 C₃₀H₃₂N₂SO₁₁ requires C,57.32; H,5.09; N,4.54 %).

8e: Yield 72 %, mp 143 °C; IR(KBr) 2225(CN), 1752(CO ester), 1638(CO) cm⁻¹; m/z 644(Found: C,56.11; H,5.05; N,4.58 C₃₀H₃₂N₂S₂O₁₀ requires C,55.90; H,4.96; N,4.34 %).

8f: Yield 74 %, mp 159 °C; IR(KBr) 2216(CN), 1755(CO ester), 1640(CO) cm⁻¹; ¹H NMR(DMSO-d₆) 1.04(s,2H,CH₂), 1.18(s,2H,CH₂), 1.94-2.06(4s,12H,4CH₃CO), 2.22(s,3H,CH₃), 2.28(s,3H,CH₃), 4.19(m,2H,H-6' and 1H,H-5'), 4.70(t,1H,H-4'), 4.93(m,2H,H-3' and H-2'), 5.86(d, J_{1'-2'} 9.56 Hz, 1H,H-1'), 7.88(m,7H,Ar-H) ppm; ¹³C NMR(DMSO-d₆) 20.1-21.9(4CH₃CO), 28.5(CH₃), 30.5(CH₃), 33.8(C7), 49.8(CH₂),

50.9(CH₂), 62.8(C6'), 68.6(C4'), 70.4(C2'), 74.7(C3'), 76.7(C5'), 84.0(C1'), 96.2(C9), 108.8(C3), 117.7(CN), 126.3-142.6(Ar-C), 150.6(C10), 154.2(C4), 157.4(CO), 169.9-170.8 (4COCH₃), 195.5(CS) ppm; m/z 688(Found: C, 62.94; H, 5.48; N, 4.21 C₃₆H₃₆N₂SO₁₀ requires C, 62.79; H, 5.23; N, 4.06 %).

8g: Yield 73 % , mp 137 °C; IR(KBr) 2228(CN), 1752(CO ester), 1638(CO) cm⁻¹; ¹H NMR(DMSO-d₆) 1.44(s, 2H, CH₂), 1.52(s, 2H, CH₂), 1.91-2.02(4s, 12H, 4CH₃CO), 2.23(s, 3H, CH₃), 2.38(s, 3H, CH₃), 4.05(m, 2H, H-6' and 1H, H-5'), 4.93(d, 1H, H-4'), 5.37(m, 2H, H-3' and H-2'), 6.14(d, J₁₋₂ 10.25 Hz, 1H, H-1'), 7.35(m, 4H, Ar-H) ppm; ¹³C NMR(DMSO-d₆) 20.2-20.4(4CH₃CO), 26.5(CH₃), 28.8(CH₃), 31.9(C7), 49.9(CH₂), 52.3(CH₂), 61.1(C6'), 66.2(C4'), 67.6(C2'), 70.9(C3'), 74.3(C5'), 84.2(C1'), 95.2(C9), 107.8(C3), 113.8(CN), 122.3-143.8(Ar-C), 149.8(C10), 153.6(C4), 161.5(CO), 169.3-169.9 (4COCH₃), 195.3(CS) ppm; m/z 672(Found: C, 57.34; H, 5.02; N, 4.37 C₃₂H₃₃ClN₂SO₁₀ requires C, 57.10; H, 4.90; N, 4.16 %).

8h: Yield 71 % , mp 117 °C; IR(KBr) 2216(CN), 1750(CO ester), 1635(CO) cm⁻¹; ¹H NMR(DMSO-d₆) 1.08(s, 2H, CH₂), 1.58(s, 2H, CH₂), 1.94-2.12(4s, 12H, 4CH₃CO), 2.25(s, 3H, CH₃), 2.30(s, 3H, CH₃), 2.42(s, 3H, CH₃), 4.14(m, 2H, H-6' and 1H, H-5'), 4.83(d, 1H, H-4'), 5.28(m, 2H, H-3' and H-2'), 5.88(d, J₁₋₂ 8.39 Hz, 1H, H-1'), 7.53(m, 4H, Ar-H) ppm; ¹³C NMR(DMSO-d₆) 20.2-20.5(4CH₃CO), 26.2(CH₃), 26.4(CH₃), 28.9(CH₃), 31.9(C7), 50.0(CH₂), 50.9(CH₂), 61.5(C6'), 67.6(C4'), 70.6(C2'), 73.8(C3'), 74.3(C5'), 84.2 (C1'), 94.8(C9), 118.3(CN), 126.8-139.7(Ar-C), 141.8(C10), 149.5(C4), 166.2(CO), 169.3-169.8(4COCH₃), 194.5 (CS) ppm; m/z 652(Found: C, 60.91; H, 5.58; N, 4.40 C₃₃H₃₆N₂SO₁₀ requires C, 60.73; H, 5.52; N, 4.29 %).

8i: Yield 72 % , mp 128 °C; IR(KBr) 2214(CN), 1752(CO ester), 1638(CO) cm⁻¹; ¹H NMR(DMSO-d₆) 1.12(s, 2H, CH₂), 1.62(s, 2H, CH₂), 1.98-2.12(4s, 12H, 4CH₃CO), 2.22(s, 3H, CH₃), 2.38(s, 3H, CH₃), 3.86(s, 3H, OCH₃), 4.17(m, 2H, H-6' and 1H, H-5'), 4.92(t, 1H, H-4'), 5.24(m, 2H, H-3' and H-2'), 6.05(d, J₁₋₂ 8.76 Hz, 1H, H-1'), 7.18(d, 2H, Ar-H), 7.64(d, 2H, Ar-H) ppm; m/z 668(Found: C, 59.47; H, 5.50; N, 4.36 C₃₃H₃₆N₂SO₁₁ requires C, 59.28; H, 5.38; N, 4.19 %).

8j: Yield 70 % , mp 116 °C; IR(KBr) 2220(CN), 1752(CO ester), 1644(CO) cm⁻¹; ¹H NMR(DMSO-d₆) 1.18(m, 4H, 2CH₂), 1.96-2.10(4s, 12H, 4CH₃CO), 2.25(s, 3H, CH₃), 2.34(s, 3H, CH₃), 4.06(m, 2H, H-6' and 1H, H-5'), 4.68(t, 1H, H-4'), 5.02(t, 1H, H-3'), 5.38(m, 1H, H-2'), 6.08(d, J₁₋₂ 10.51 Hz, 1H, H-1'), 6.72(q, 1H, furan H-4), 6.98(dd, 1H, furan H-3), 7.88(m, 1H, furan H-5) ppm; ¹³C NMR(DMSO-d₆) 20.2-20.4(4CH₃CO), 26.1(CH₃), 28.9(CH₃), 32.3(C7), 50.0(CH₂), 52.3(CH₂), 61.4(C6'), 66.2(C4'), 67.6(C2'), 70.9(C3'), 74.3(C5'), 84.5(C1'), 94.9(C9), 107.6(C3), 114.0(CN), 118.1(furan C4), 122.4 (furan C3), 142.1(C10), 146.0(C4), 150.4(furan C5), 155.5 (furan C2), 166.1(CO), 169.3-169.9(4COCH₃), 194.8(CS) ppm; m/z 628(Found: C, 57.57; H, 5.13; N, 4.61 C₃₀H₃₂N₂SO₁₁ requires C, 57.32; H, 5.09; N, 4.45 %).

8k: Yield 70 % , mp 126 °C; IR(KBr) 2224(CN), 1748(CO ester), 1642(CO) cm⁻¹; ¹H NMR(DMSO-d₆) 1.26(m, 4H, 2CH₂), 1.92-2.08(4s, 12H, 4CH₃CO), 2.15(s, 3H, CH₃), 2.24(s, 3H, CH₃), 4.05(m, 2H, H-6' and 1H, H-5'), 4.48(t, 1H, H-4'), 5.12(m, 1H, H-3'), 5.36(m, 1H, H-2'), 6.14(d, J₁₋₂ 10.51 Hz, 1H, H-1'), 6.94(m, 1H, thiophene H-4), 7.16(m, 1H, thiophene H-3), 7.78(d, 1H, thiophene H-5) ppm; ¹³C NMR(DMSO-d₆) 20.3-20.8(4CH₃CO), 26.2(CH₃), 27.8(CH₃), 31.9(C7), 49.9(CH₂), 52.5(CH₂), 61.5(C6'), 66.2(C4'), 67.3(C2'), 70.6(C3'), 74.3(C5'), 84.2(C1'), 94.4(C9), 108.5(C3), 113.7(CN), 118.2(thiophene C4), 122.7(thiophene C3), 147.7(C10), 148.0(C4), 149.6(thiophene C5), 161.6(thiophene C2), 166.0(CO), 169.3-169.7(4COCH₃), 195.0(CS) ppm; m/z 644(Found: C, 56.21; H, 5.07; N, 4.58 C₃₀H₃₂N₂S₂O₁₀ requires C, 55.90; H, 4.96; N, 4.34 %).

8l: Yield 73 %, 136 °C; IR(KBr) 2222(CN), 1755(CO ester), 1648(CO) cm^{-1} ; ^1H NMR(DMSO- d_6) 1.12(m,4H,2CH₂), 1.93-2.12(4s,12H,4CH₃CO), 2.17(s,3H,CH₃), 2.31(s,3H,CH₃), 4.06(m,2H,H-6' and 1H,H-5'), 4.38(t,1H,H-4'), 4.72(d,1H,H-3'), 5.06(t,1H,H-2'), 5.88(d, $J_{1,2}$ 7.98 Hz, 1H,H-1'), 7.33-7.90 (m,7H,Ar-H) ppm; m/z 688(Found: C,62.96; H,5.32; N,4.23 C₃₆H₃₆N₂SO₁₀ requires C,62.79; H,5.23; N,4.06 %).

3-Cyano-1-(β -D-glycopyranosyl)-pyridine-2-thiones **11. General Procedure for Nucleoside Deacylation:**

Dry ammonia gas was passed into a solution of protected nucleosides **8** (0.5 g) in 20 mL of dry MeOH at 0 °C for 0.5 h. The reaction mixture was stirred until completion as shown by TLC (8-12 h), using chloroform :Methanol 9:1, v:v, (R_f 0.62-0.64 region). The resulting mixture was then concentrated under reduced pressure at 40 °C to afford a solid residue that was crystallized from MeOH to furnish colorless crystals.

11a: Yield 80 %, mp 207 °C; IR(KBr) 3620-3280(OH), 2222(CN), 1656(CO) cm^{-1} ; m/z 504(Found: C,57.22; H,5.08; N,5.71 C₂₄H₂₅N₂ClSO₆ requires C,57.08; H,4.95; N, 5.55 %).

11b: Yield 81 %, mp 223 °C; IR(KBr) 3680-3210(OH), 2218(CN), 1632(CO) cm^{-1} ; ^1H NMR(DMSO- d_6) 1.16(m,4H,2CH₂), 2.22(s,3H,CH₃), 2.30(s,3H,CH₃), 2.38(s,3H,CH₃), 3.12-3.56(m,6H,2H-6',H-5',H-4',H-3' and H-2'), 4.42(d,2H,2'-OH and 3'-OH), 4.82(s,1H,4'-OH), 5.23(s,1H,6'-OH), 5.69(d, $J_{1,2}$ 8.84 Hz, 1H,H-1'), 7.38(m,4H,Ar-H) ppm; m/z 484(Found: C,62.17; H,5.88; N,5.90 C₂₅H₂₈N₂SO₆ requires C,61.98; H,5.78; N,5.78 %).

11c: Yield 82 %, mp 215 °C; IR(KBr) 3640-3260(OH), 2214(CN), 1636(CO) cm^{-1} ; m/z 500(Found: C,60.21; H,5.68; N,5.76 C₂₅H₂₈N₂SO₇ requires C,60.00; H,5.60; N,5.60 %).

11d: Yield 79 %, mp 191 °C; IR(KBr) 3580-3190(OH), 2218(CN), 1640(CO) cm^{-1} ; m/z 460(Found: C,57.61; H,5.30; N,6.17 C₂₂H₂₄N₂SO₇ requires C,57.39; H,5.22; N,6.08 %).

11e: Yield 81 %, mp 196 °C; IR(KBr) 3610-3280(OH), 2223(CN), 1648(CO) cm^{-1} ; m/z 476(Found: C,55.65; H,5.15; N,5.99 C₂₂H₂₄N₂S₂O₆ requires C,55.46; H,5.04; N,5.88 %).

11f: Yield 83 %, mp 186 °C; IR(KBr) 3640-3200(OH), 2216(CN), 1635(CO) cm^{-1} ; ^1H NMR(DMSO- d_6) 1.18(m,4H,2CH₂), 2.20(s,3H,CH₃), 2.34(s,3H,CH₃), 3.12-3.82(m,6H,2H-6',H-5',H-4',H-3' and H-2'), 4.66(d,2H,2'-OH and 3'-OH), 5.05(s,1H,4'-OH), 5.28(s,1H,6'-OH), 5.70(d, $J_{1,2}$ 8.92 Hz, 1H,H-1'), 7.56(m,7H,Ar-H) ppm; m/z 520(Found: C, 64.80; H,5.46; N,5.52 C₂₈H₂₈N₂SO₆ requires C,64.61; H,5.38; N,5.38 %).

11g: Yield 82 %, mp 218 °C; IR(KBr) 3580-3345(OH), 2225(CN), 1660(CO) cm^{-1} ; ^1H NMR (DMSO- d_6) 1.15(m,4H,2CH₂), 2.24(s,3H,CH₃), 2.38(s,3H,CH₃), 3.35-3.74(m,6H,2H-6', H-5',H-4',H-3' and H-2'), 4.42(d,1H,2'-OH), 4.82(t,2H,3'-OH and 4'-OH), 4.94(d,1H,6'-OH), 5.78(d, $J_{1,2}$ 9.56 Hz, 1H,H-1'), 7.36(m,4H,Ar-H) ppm; ^{13}C NMR(DMSO- d_6) 26.5(CH₃), 28.8(CH₃), 31.9(C7), 50.0(CH₂), 52.3(CH₂), 60.4(C6'), 68.1(C4'), 69.7 (C2'), 74.2(C3'), 79.9(C5'), 85.4(C1'), 96.7(C9), 107.6(C3), 113.6(CN),121.2-144.2(Ar-C), 149.5(C10), 156.3(C4), 167.1(CO), 194.4(CS) ppm; m/z 504(Found: C,57.21; H,5.08; N,5.76 C₂₄H₂₅N₂ClSO₆ requires C,57.08; H,4.95; N,5.55 %).

11h: Yield 80 %, mp 201 °C; IR(KBr), 3640-3310(OH), 2214(CN), 1654(CO) cm^{-1} ; ^1H NMR(DMSO- d_6) 1.14(s,2H,CH₂), 1.21(s,2H,CH₂), 2.18(s,3H,CH₃), 2.26(s,3H,CH₃), 2.34(s,3H,CH₃), 3.12-3.88(m,6H,2H-6',H-

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