

Synthesis of C-glycosides from 1,6-Diamino-4-Phenylpyridine Derivatives

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Abstract Diamino 3a and 3b derivatives which obtained by Michael reaction were coupled with aldoses in the presence of acetic acid and I_2 with stirring at room temperature gave 4, 5 and 6 respectively. Acetylation of compound 4 and 5 gave compound 7 and 8 respectively. Coupling of fructose with 3a and 3b in the presence or not of Con HCl gave compound 9 and 11 respectively. Acetylation of compound 9 with acetic anhydride and Pyridine gave compound 10. Some of the synthesized compounds have been screened as antibacterial and antifungal. The structures of the synthesized compounds have been deduced from their elemental analysis and spectral (IR, 1H -NMR) data.

Keywords C-glycosides, Cyanoacetohydrazide, Arylidinemalononitrile

1. Introduction

C-glycosides, wherein a carbon atom replaces the glycosidic oxygen have attracted considerable attention in carbohydrate and biological chemistry because of their stability [1] towards enzymatic acidic hydrolysis. In particular hexapyranosyl nucleosides as well as C-glycoconjugates bearing carbon linked nitrogen heterocycles have given rise to numerous synthetic and biological studies [2], due to their potential antiviral and antitumor activities. Various approaches to C-glycosides have been developed [3-5]. The reaction of C-centered nucleophiles with an activated and electrophilic C-glycosyl donor or glycal represents by far the most common approach, although anomeric nucleophiles [6] and radical have also been used to generate such compounds.

Generally C-glycosyl heteroaromatics were prepared from glycosyl donors such as glycosyl halides [7], hydroxides or O-glycosyl trichloroacetimidates using either the hetero aryl compounds in presence of Lewis acids [8, 9].

2. Experimental

2.1. Instrumentation

All reagents and solvents were purified either by recrystallization or distillation, unless otherwise. Thin layer chromatography was carried out using indicating silica gel. Infrared spectra were recorded as potassium bromide discs on a Perkin-Elmer 383 spectrometer. 1H NMR spectra were obtained on a Bruker AC 200F instrument at r.t in the solvent indicated chemical shifts are reported in ppm from TMS as the internal standard. The type of signals was indicated by the following letters. Also 1HNMR spectra were measured on a Varian spectrophotometer at 300MHz using DMSO- d_6 or $CDCl_3$ as solvent at chemistry department faculty of science, Bardouex University-France. Mass spectra were determined at 70 or 15 electron volt by using AE / MS 30 mass spectrometer. Analytical data were performed by the microanalytical data unit at chemistry department faculty of science, Bardouex University – France and Cairo University, Egypt. All melting points were recorded using thermal melting point apparatus and were uncorrected

2.1.1. 1,6-Diamino-2-oxo-4-phenyl-1,2-dihydropyridine-3,5-dicarbonitrile(3a):

A mixture of cyanoacetohydrazide (1) (0.01 mol, 1.09 g) and benzylidene malononitrile (2a) (0.01mol, 1.54 g) in ethanol 15 ml and few drops of piperidine was refluxed for 3 hours. The solid thus formed was collected by filtration and recrystallized from methanol gave 3a as a pale yellow powder in 80% yield, m.p. 260-262°C. The 1H -NMR (DMSO- d_6) δ : 5.66 (s, 2H, NH_2), 7.49 (s, 2H, $2H_{ar}$), 7.54 (s, 3H, $3H_{ar}$) and 8.48 (s, 2H, NH_2) ppm. Anal. Calcd for ($C_{13}H_9N_5O$,

M. W.: 251.24): C, 62.15; H, 3.61; N, 27.87. Found: C, 61.98; H, 3.53; N, 27.53

2.1.2.

1,6-Diamino-4-(1,3-diphenyl-1H-pyrazol-4-yl)-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (3b):

A mixture of cyanoacetohydrazide (1) (0.01 mol, 1.09 g) and pyrazolidine malononitrile (2b) (0.01mol, 2.96 g) in ethanol (15 ml) and few drops of piperidine was refluxed for

3 hrs. The solid was formed and collected by filtration and recrystallized from methanol gave 3b as a pale yellow powder in 80% yield, m.p. 240-242°C. ¹H-NMR(CDCl₃) δ: 4.70 (s, 1H, NH₂), 7.48 (m, 8H, H_{ar.}), 7.80 (d, 2H, H_{ar.}) and 8.26 (s, 1H, H_{pyrazole}) ppm. Anal. Calcd for (C₂₂H₁₅N₇O, M.W. 393.40): C, 67.17; H, 3.84; N, 24.92. Found: C, 67.14; H, 3.80; N, 24.90.

2.1.3.

3,5-Dihydro-2-(D-gluco-pentitol-1-yl)-5-oxo-7-phenyl [1,2,4]triazolo[1,5-a]pyridine-6,8-dicarbonitrile(4):

A solution of 3a (1mmol, 0.251 g) and D-glucose (1mmol, 0.180 g) were dissolved in iodine solution (1mmol, 0.254 g) in methanol (2 ml) at room temperature until the D-glucose was completely consumed as indicated by the TLC. The reaction mixture was quenched by addition of Na₂S₂O₃ (2 ml) of saturated aqueous solution, and the mixture was concentrated under reduced pressure to give crude product which was washed successively with water and methanol then recrystallized from ethanol gave 4 as yellow powder, 68% yield, m.p. 205-207°C, IR(KBr): 3395 (OH), 3236 (NH), 3195 (CH) aromatic bonds, 2949 (CH) aliphatic bonds, 2236 (C≡N), 1695 (C=O amide) and 1605, 1521, 1465 cm⁻¹ (C=N) and (C=C). MS (m/z): 412(8%), 411(34%), 393(51%), 380 (24%), 322 (20%), 321 (34%), 320 (44%), 305 (22%), 304(10%), 292 (36%), 290 (100%), 275(13%), 274 (11%), 261 (11%), 260 (42%), 234 (34%) and 77(50%).

Anal. Calcd for (C₁₉H₁₇N₅O₆, M.W. 408.41): C, 55.47; H, 4.17; N, 17.02. Found: C, 55.39; H, 4.21; N, 17.06.

2.1.4.

3,5-Dihydro-2-(D-xylo-pentitol-1-yl)-5-oxo-7-phenyl -[1,2,4]triazolo[1,5-a]pyridine-6,8-dicarbonitrile (5):

A mixture of (3a) (1mmol, 0.251 g) and D-xylose were dissolved in a solution containing acetic acid (5 ml) and water (10 ml). The mixture was stirred with a solution of iodine (1 mmol, 0.254) and by the same conditions as compound (4), the reaction was completed afforded 5 as a pale yellow powder, yield 48%. m.p. 201-203°C. IR (KBr): 3400 (OH) groups, 3232 (NH) group, 3193 (CH) aromatic bonds, 2925 (CH) aliphatic bonds, 2225 (C≡N) groups, 1672 (C=O) amide group and 1593, 1539, 1427 cm⁻¹ (C=N) and (C=C). MS (m/z): 382(13%), 381(28%), 364 (24%), 350 (13%), 322 (17%), 321 (10%), 320 (27%), 303 (19%), 302 (13%), 291 (65), 289 (17%), 288 (6%), 275 (24%), 261(17%), 260(34%), 234(20%,) and 77(100%). Anal. Calcd for

(C₁₈H₁₅N₅O₅, M.W. 408.41): C, 56.69; H, 3.96; N, 18.37. Found: C, 56.68; H, 3.93; N, 18.34.

2.1.5.

2-(D-xylo-tetritol-1-yl)-5-oxo-7-(1,3-diphenyl-1H-pyrazol-4-yl)[1,2,4]-triazolo[1,5-a]pyridine-6,8-dicarbonitrile(6):

A mixture of pyridone 3b (1mmol, 0.393 g), D-xylose (1mmol, 0.160 g) and iodine (1 mmol, 0.254 g) were

dissolved in DMF (1ml) and diluted acetic acid (5ml). The mixture was stirred with slight heating at 50°C for 10 hrs, the solvent was evaporated and the residue washed with water successively and recrystallized from methanol yielded 6 as a whitish green powder, 43% yield. m.p. 170-172°C. IR (KBr): 3400(OH), 3150 (NH), 3000 (CH) aromatic bands, 2925 (CH) aliphatic bands, 2236 (C≡N), 1666 (C=O) amide group 1600, 1593, 1504, 1410 cm⁻¹ (C=N) and (C=C). MS (m/z): 523 (34%), 492(10%), 464 (60%), 463 (76%), 462 (50%), 447 (11%), 446(13%), 445 (52%), 433 (100%), 432 (12%), 431(13%), 430 (36%), 402 (10%), 376 (9%), 375 (45%). Anal. Calcd for (C₂₇H₂₁N₇O₅, M.W. 523.50): C, 61.95; H, 4.04; N, 18.73. Found: C, 61.90; H, 4.02; N, 18.76.

2.1.6.

3-(N-acetyl)-3,5-dihydro-2-(1,2,3,4,5-penta-O-acetyl-D-gluco-pentitol-1-yl)-5-oxo-7-phenyl-[1,2,4]triazolo [1,5-a]pyridine-6,8-dicarbonitrile(7):

A suspension of 4 (2mmole, 0.822 g) was boiled with acetic anhydride (10 ml) under reflux for 3 hrs. The hot solution was poured onto crushed ice and the acetate 7 was filtered off, washed with water and recrystallized from DMF and water gave white crystals, Yield 71%. m.p. 133-135°C. IR (KBr): 3059 (CH) aromatic bonds, 2920 (CH) aliphatic bonds, 2223 (C≡N) groups, 1725 (C=O) ester, 1678 (C=O) amide and 1596, 1530, 1503, 1432 cm⁻¹ (C=N) and (C=C). MS (m/z): 663 (56%), 620 (38%), 603 (12%), 561(28%), 549 (12%), 543 (12%), 530 (28%), 501 (16%), 488(29%), 387 (17%), 362 (16%), 345 (41%), 332 (100%), 316 (12%), 302 (28%), 275 (30%), 259 (12%), 246 (36%), 219(12%), 127 (36%), 77 (66%), 50 (55%). Anal. Calcd for (C₃₁H₂₉N₅O₁₂, M.W. 663.59): C, 56.11; H, 4.40; N, 10.55. Found: C, 56.14; H, 4.45; N, 10.57.

2.1.7.

3-(N-acetyl)-3,5-dihydro-2-(1,2,3,4-tetra-O-acetyl-D-xylo-tetritol-1-yl)-5-oxo-7-phenyl[1,2,4]triazolo[1,5-a]pyridine-6,8-dicarbonitrile (8):

The same procedure was repeated as compound 7 with the same conditions compound 8 obtained as a white crystals, yield 66%, m.p. 148-150°C, MS (m/z, %) 591 (33%), 531(13%), 489 (29%), 471 (25%), 458 (13%), 429 (9%), 416 (10%), 387 (7%), 345 (32%), 332 (76%), 330 (30%), 316 (8%), 302 (13%), 276 (37%), 259 (16%), 219 (9%), 127(19%), 77 (100%). Anal. Calcd for: (C₂₈H₂₅N₅O₁₀, M. wt. 591.53): C, 56.85; H, 4.26; N, 11.84. Found: C, 56.90; H, 4.29; N, 11.88

2.1.8.

3-(D-Arabetriitol-1-yl)-6-oxo-8-phenyl-6H-pyridin o[1,2-b][1,2,4]triazine-7,9-dicarbonitrile (9):

A catalytic amounts of concentrated HCl (few drops) was added to solution of pyridine 3a

(1mmol, 0.251g) and D-fructose (1mmol, 0.180 g) in ethanol (20 ml), the reaction mixture was stirred under reflux for 5 hrs. The precipitate formed by cooling was filtered off and washed with distilled water successively and

recrystallized from ethanol and water afforded **9** as a white powder, yield 67%, m.p. 270-272°C, MS (m/z %): 394 (4%, M), 363 (21%), 315(16%), 314 (39%), 303 (19%), 302(100%), 301(20%), 300 (27%), 272 (43%), 245(47%),219(21%). Anal. Calcd for: (C₁₉H₁₅N₅O₅, Mwt. 393.11): C, 58.01; H, 3.84; N, 17.80. Found: C, 58.90; H, 3.88; N, 17.79.

2.1.9.

3-(1,2,3,4-tetra-O-acetyl-D-arabino-1-yl)-6-oxo-8-phenyl-6H-pyrido[1,2-b][1,2,4]triazine-7,9-dicarbonitrile (10):

A suspension of **9** (1mmol, 0.393 g) in 3ml of acetic anhydride and pyridine 3ml was refluxed for 3 hrs. The hot solution was poured onto crushed ice the formed acetate was filtered off and washed with water and dried afforded **10** as a white crystal yield 69%, m.p.200-201°C. The IR (KBr): 3159 (CH) aromatic bonds, 2990 (CH) aliphatic bonds, 2236 (C≡N) groups, 1720 (C=O) ester, 1650 (C=O) amide and 1600 ,1523, 1500,1410 cm⁻¹ (C=N) and (C=C).MS (m/z %):562 (8%), 561(34%), 501(16%), 459 (42%), 441 (16%), 428 (13%), 386 (12%), Anal. Calcd for: (C₂₇H₂₃N₅O₉, Mwt. 561.50): C, 57.75; H, 4.13; N, 12.47. Found: C, 57.69; H, 4.10; N, 12.43.

2.1.10.

3-(D-arabino-tetritol-1-yl)-6-oxo-8-(1,3-diphenyl-1H-pyrazol-4-yl)-6H-pyrido[1,2-b][1,2,4]triazine-7,9-dicarbonitrile (11):

Pyridone **3b** (1 mmol, 0.393 g) was added to aqueous

acetic acid (25 ml, 20% solution) and the mixture solution was stirred for 30 minutes. D-fructose (1mmol, 0.180 g) was added portion wise over 20 minutes then the mixture was heated to 100°C and stirred for 18 hours in a sealed flask. The reaction mixture was cooled to 10°C for 5 hours, the precipitate filtered off and washed with water and dried gave **11** as a whitish green powder, yield 46%, m.p. 280-281°C. MS (m/z %): 535 (26%), 517 (11%), 504 (17%), 474 (29%), 457 (22%), 456 (15%), 444 (100%), 443 (51%), 442 (15%), 414 (14%), 387 (25%), 361 (53%). Anal. Calcd for: (C₂₈H₂₁N₇O₅, M.W. 535.51): C, 62.80; H, 3.95; N, 18.31. Found: C, 62.83; H, 3.98; N, 18.34.

2. Result and Discussion

2-Amino substituted N-aminopyridones **3a, b** can be obtained by Michael addition of cyanoacetohydrazide (**1**) to arylidinemalononitrile **2a** or **2b** [10].

The ¹H-NMR spectrum of **3a** in DMSO-d₆ exhibited signals at δ 5.66 for NH₂, and 8.48 for NH₂ ppm. Also, the ¹H-NMR spectrum of **3b** in CDCl₃ showed signals at δ 4.70 for NH₂ ppm. Diverse biological activities encountered in fused heterocyclic system containing pyridine [11], triazole [12] and 1,2,4-triazole [12]. From that view, it was interested to study the condensation reaction of (**3a**) with D-glucose or/and D-xylose in the presence of methanolic iodine and diluted acetic acid at room temperature with stirring for 24 hours afforded compound **4** or/and **5** compounds respectively.

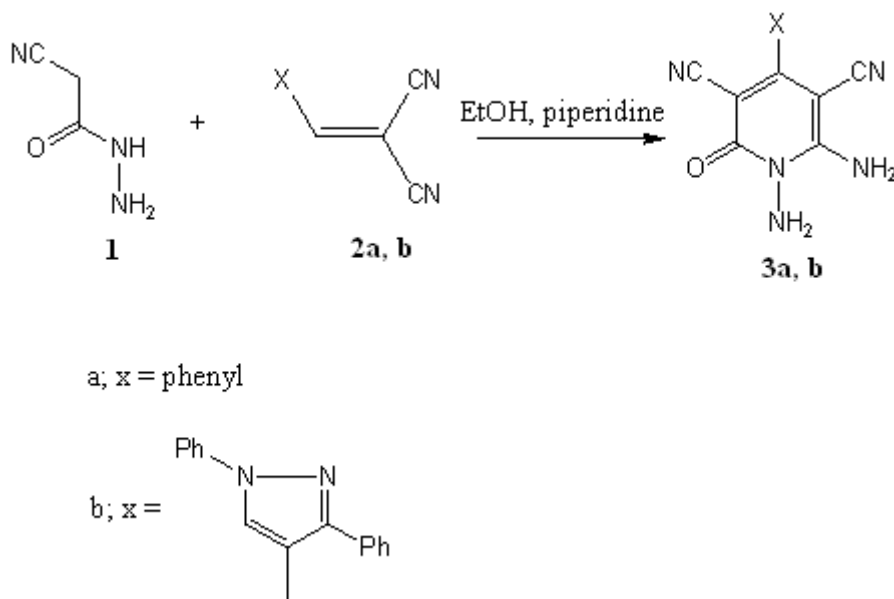


Figure 1. Synthesis of N-aminopyridones

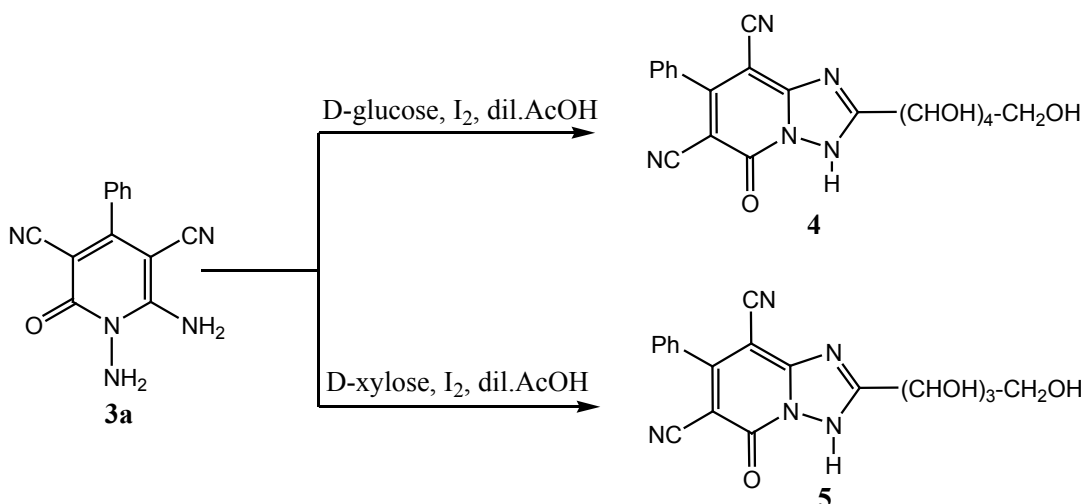


Figure 2. Synthesis of compounds 4 and 5

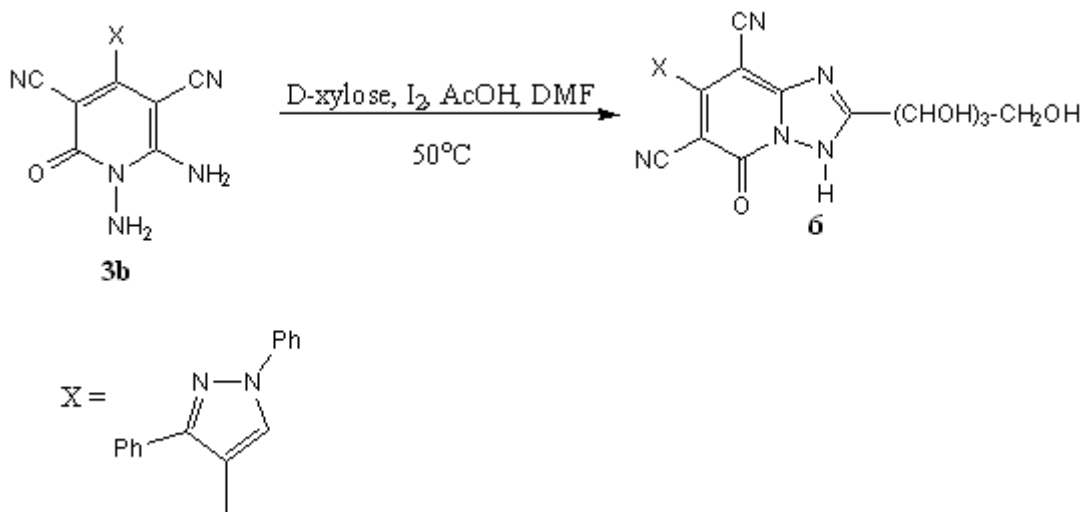


Figure 3. Coupling compound 3b with D-xylose

The chemical structure of compounds 4 and 5 were confirmed by elemental analysis and spectral data. The I.R. spectrum of 4 showed absorption bands at 3395 cm^{-1} due to (OH) groups, 3236 cm^{-1} due to (NH) group, 3195 cm^{-1} due to (CH) aromatic bonds, 2949 cm^{-1} due to (CH) aliphatic bonds, 2236 cm^{-1} due to ($\text{C}\equiv\text{N}$) groups and 1695 due to ($\text{C}=\text{O}$) amide group and 1605 , 1521 , 1465 cm^{-1} due to ($\text{C}=\text{N}$) and ($\text{C}=\text{C}$) groups. The mass spectrum of 4 showed molecular ion peaks at m/z : 412 (8 %, $\text{M}+1$), 411 (34 %, M), 393 (51 %, $\text{M}-\text{H}_2\text{O}$), 380 (24 %, $\text{M}-\text{CH}_2\text{OH}$), 322 (20 %, $\text{BH}_2\text{CHOHCHOH}$), 321 (34 %, BHCHOHCHOH), 320 (44 %, BCHOHCHOH), 305 (22 %, BH_2CHCHOH), 304 (10 %, BHCHCHOH), 292 (36 %, BHCH_2OH), 290 (100 %, BCHOH), 275 (13 %, BCH_3), 274 (11 %, BCH_2), 261 (11 %, BH), 260 (42 %, B), 234 (34 %, B-CN) and 77 (50 %, ph). Where (B) = Heterobase moiety.

The I.R. spectrum of 5 showed absorption bands at 3400 cm^{-1} due to (OH) groups, 3232 cm^{-1} due to (NH) group, 3193 cm^{-1} due to (CH) aromatic bands, 2925 cm^{-1} due to (CH) aliphatic bonds, 2225 cm^{-1} due to ($\text{C}\equiv\text{N}$) groups and 1672

due to ($\text{C}=\text{O}$) amide group and 1593 , 1539 , 1427 cm^{-1} due to ($\text{C}=\text{N}$) and ($\text{C}=\text{C}$) groups. The mass spectrum of 5 showed molecular ion peaks at m/z : 382 (13 %, $\text{M}+1$), 381 (28 %, M), 364 (24 %, $\text{M}-\text{OH}$), 350 (13 %, $\text{M}-\text{CH}_2\text{OH}$), 322 (17 %, $\text{BHCH}_2\text{OHCHOH}$), 321 (10 %, BHCHOHCHOH), 320 (27 %, BCHOHCHOH), 303 (19 %, BCHCHOH), 302 (13 %, BCHCHO), 291 (65 %, BHCH_2OH), 289 (17 %, BCHO), 288 (6 %, BCO), 275 (24 %, BCH_3), 261 (17 %, BH), 260 (34 %, B), 234 (20 %, B-CN) and 77 (100 %, ph), where B = heterocycle base.

Condensation pyridone 3b with D-xylose in a mixture of dimethyl formamide, diluted acetic acid and iodine solution with slight heating at 50°C and stirring for 10 hours gave triazolopyridone derivative (6).

The chemical structure of 6 was confirmed by elemental analysis and spectral data. The I.R. spectrum data of compound 6 showed absorption bands at 3400 cm^{-1} due to (OH) groups, 3150 cm^{-1} due to (NH) group, 3000 cm^{-1} due to (CH) aromatic bands, 2925 cm^{-1} due to (CH) aliphatic bands, 2236 cm^{-1} due to ($\text{C}\equiv\text{N}$) groups and 1666 due to ($\text{C}=\text{O}$)

amide group and 1600, 1593, 1504, 1410 cm^{-1} due to (C=N) and (C=C) groups. The mass spectrum of 6 showed molecular ion peaks at m/z : 523 (34 %, M), 492 (10 %, M-CH₂OH), 464 (60 %, BH₂CHOHCHOH), 463 (76 %, BHCHOHCHOH), 462 (50 %, BCHOHCHOH), 447 (11 %, BH₂CHCHOH), 446 (13 %, BHCHCHOH), 445 (52 %, BCHCHOH), 433 (100 %, BCH₂OH), 432 (12 %, BCHO), 431 (13 %, BCHO), 430 (36 %, BCO), 402 (10 %, B), 376 (9 %, BH-HCN), 375 (45 %, B-HCN), where (B)=heterobase moiety.

Compound 4 was heated with acetic anhydride under reflux for three hours, then poured onto crushed ice afforded acetylated compound 7.

The chemical composition of 7 was confirmed by elemental analysis, I.R and the mass spectrum.

The I.R. spectrum of compound 7 showed no absorption band for (OH) groups and appeared absorption bands at 3059 cm^{-1} due to (CH) aromatic bonds, 2920 cm^{-1} due to (CH) aliphatic bonds, 2223 cm^{-1} due to (C≡N) groups, 1725 cm^{-1} due to (C=O) ester, 1678 (C=O) amide and 1596, 1530, 1503, 1432 cm^{-1} due to (C=N) and (C=C).

the mass fragmentation showed ion peaks at m/z : 663 (56%,M), 620 (38%, CH₃CO), 603 (12%, M-AcOH), 561 (28 %, M-AcOH-CH₂CO), 549 (12%, 561-AcOH-CH₂CO), 543 (12%,M - 2AcOH), 530 (28%,M-AcOH-CH₂OAc), 501

(16 %,561-AcOH), 488 (29 %, 530-CH₂CO), 387 (17 %, BC₂H₂OAc), 362 (16 %, BHOAc), 345 (41%, BCH₂CHO), 332 (100%, BCHOH), 316 (12 %, BCH₂), 302 (28 %,B), 275 (30 %, B-HCN), 259 (12%,B-Ac), 246 (36 %), 219 (12 %), 127 (36%), 77 (66 %), 50 (55 %), where (B)= heterobase moiety.

Similarly, compound 5 was boiled with acetic anhydride as the previous conditions obtained 8.

The chemical composition of 8 was confirmed by elemental analysis and the mass spectrum.

The mass fragmentation of 8 showed ion peaks at m/z : 591 (33%,M), 531(13%,M-AcOH), 489(29%,M-AcOH-CH₂CO), 471(25%,M-2AcOH), 458(13%,M-AcOH-CH₂OAc), 429(9 %, 489 - AcOH), 416(10 %, 458 - CH₂CO), 387(7 %, B C H C H O A c), 345 %, B C H₂ C H O), 332(76%,BCHOH), 330(30%,BCO), 316(8%,BCH₂), 302(13%,B), 276(37%,B-HCN), 259(16%), 219 (9%), 127(19%), 77(100%) where (B)= heterobase moiety.

Heating compound 3a with D-fructose and few drops of conc. hydrochloric acid in ethanol with reflux in a sealed flask for 5 hours gave compound 9 [13], which acetylated with acetic anhydride in the presence of pyridine for 24 hours at room temperature gave compound 10.

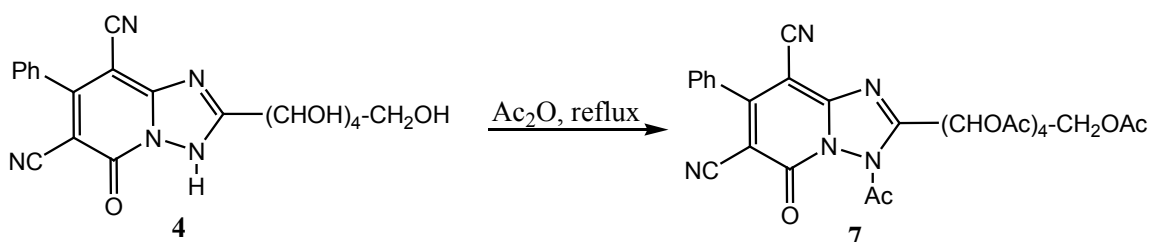


Figure 4. Acetylation of compound 4

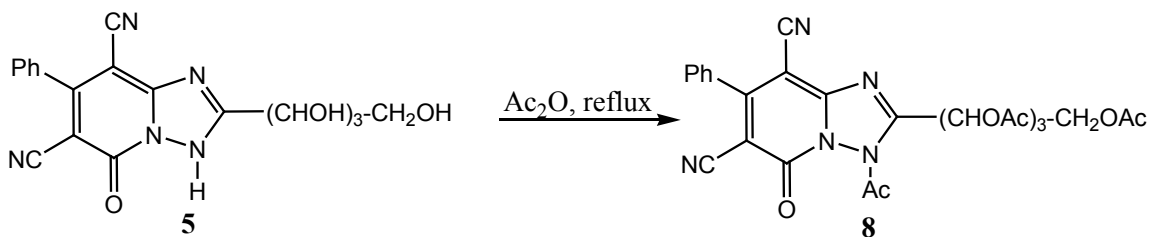


Figure 5. Acetylation of compound 5

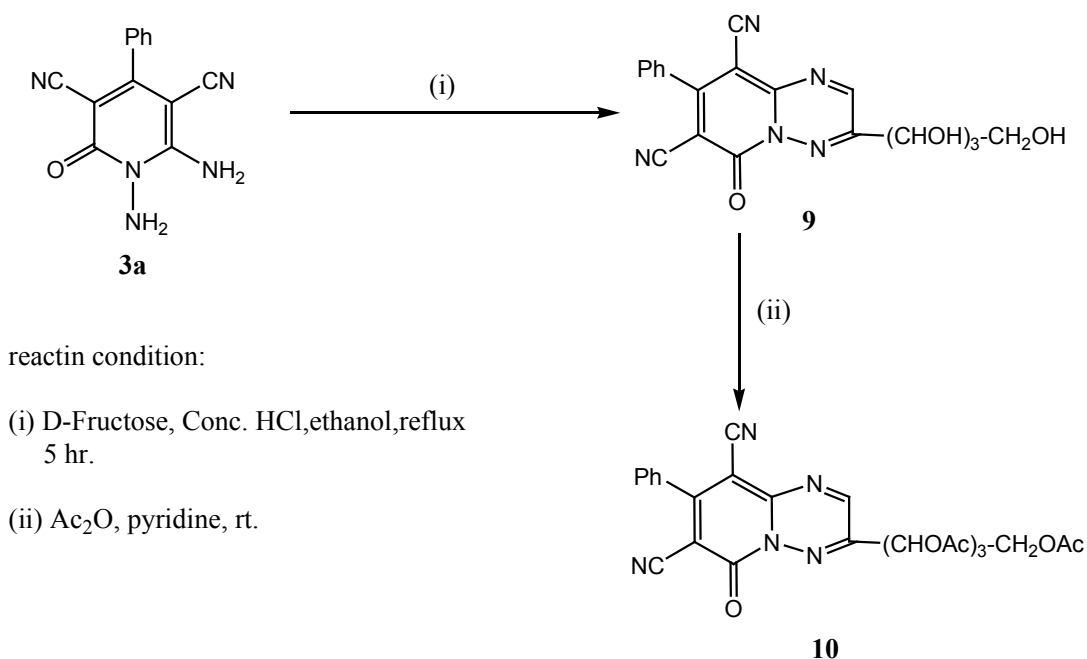
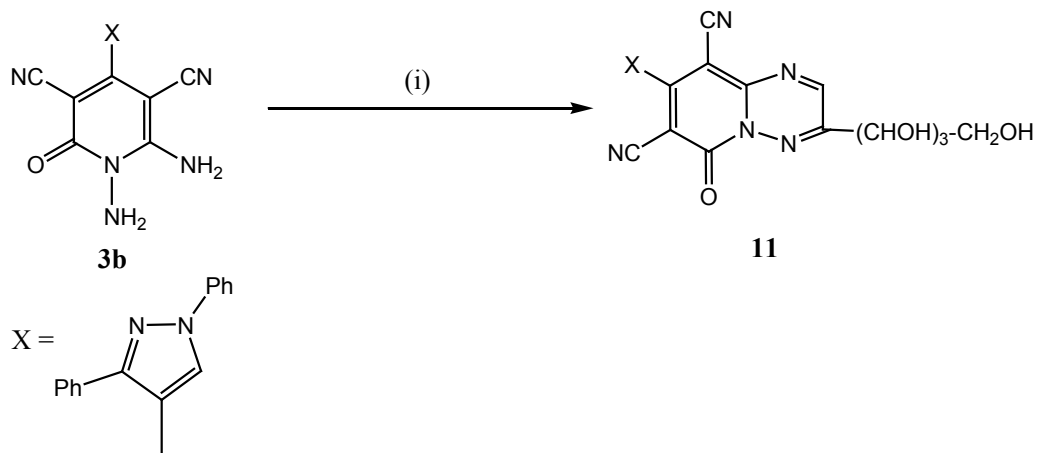


Figure 6. Synthesis of compounds 9 and 10



reactin condition:

(i) D-fructose, aq. AcOH,
heat, 18 hr.

Figure 7. Synthesis of compound 11

The chemical structure of compound **9** was confirmed by elemental analysis and the mass spectra. The mass spectrum of compound **9** showed ion peaks at m/z : 394 (4 %, M+1), 363 (21%, M-CHOH), 315(16 %, BCHCHOH), 314 (39%, BCHCHO), 303 (19%, BHCHOH), 302 (100 %, BCHOH), 301(20 %, BCHO), 300 (27 %, BCO), 272 (43%, B), 245(47 %, B-HCN), 219(21 %, B-HCN-CN), where (B) = Heterobase moiety.

The chemical structure of compound **10** was confirmed by elemental analysis, I.R and the mass spectra. The I.R. spectrum of compound **10** showed no absorption band for

(OH) groups and appeared absorption bands at 3159 cm^{-1} due to (CH) aromatic bonds, 2990 cm^{-1} due to (CH) aliphatic bonds, 2236 cm^{-1} due to (C≡N) groups, 1720 cm^{-1} due to (C=O) ester, 1650 cm^{-1} (C=O) amide and $1600, 1523, 1500, 1410\text{ cm}^{-1}$ due to (C=N) and (C=C). The mass spectrum of compound **10** showed ion peaks at m/z : 562 (8%, M+1), 561(34%, M), 501(16%, M-AcOH), 459 (42%, M-AcOH-CH₂CO), 441 (16%, M- 2AcOH), 428 (13%, M-AcOH- CH₂OAc), 386 (12%, 428-CH₂CO), 382 (41%, M-AcOH- CH₂CO- AcOH), 357 (33%, M- CHOAc-CH₂OAc- AcO), 344(9%,BCHOAc), 340(19%,382-CH₂C

O), 327(9%,BCH₂CHO), 302(13%,BCHOH), 301(58%,BCHO), 298 (20%, BCH₂), 245 (36%), 219 (22%) and 72 (100%).

A solution of D-fructose in aqueous acetic acid was heated with compound 3b in a sealed flask at 100°C for 18 hours gave pyridotriazine derivative 11.

The chemical structure of compound 11 was confirmed by elemental analysis and the mass spectra. The mass spectrum of compound 11 showed ion peaks at m/z:

535 (26%, M), 517 (11%, M-H₂O), 504 (17%, M-CH₂OH), 474 (29%, BCHOHCHOH), 457 (22%, BCHCHOH), 456 (15%, BCHCHO), 444 (100%, BCHOH), 443 (51%, BCHO), 442 (15%, BCO), 414 (14%, B), 387 (25%, B-HCN), 361 (53%, B-HCN-CN).

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