Stereoselective Synthesis of New Dihydropyrimidinone Glycoconjugates

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Stereoselective synthesis of dihydropyrimidinone glycoconjugates in high yields, from different sugar aldehydes, by a three-component coupling (Biginelli) reaction is reported. In this new method, HCl generated '*in situ*' from 2,4,6-trichloro[1,3,5]triazine (TCT; 10 mol%), was used under mild and solvent free reaction conditions.

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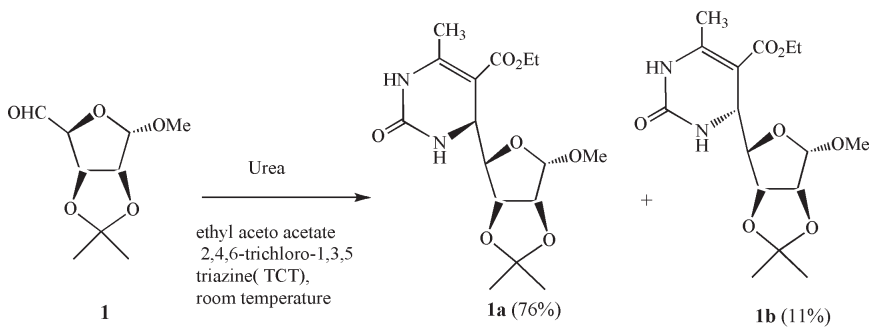
Bio-active glycoconjugates have attracted attention in chemical, medicinal and pharmaceutical research [1]. Hence, for the creation of relatively complex glycosubstances with structural diversity, which play a prominent role in the medicinal and combinatorial chemistry [2], the development of efficient methods for multicomponent reactions is an attractive strategy. The Biginelli [3] multicomponent reaction, which involves an aldehyde, urea/thiourea and a β-ketoester, with sugar-derived aldehydes would result in the synthesis of 3,4-dihydropyrimidinone (DHPM) glycoconjugates. These compounds are of vast attention to synthetic chemists due to their resemblance to C-nucleosides [4] and their pharmacological properties [5,6].

Despite the fact that many procedures [7] have been reported for the Biginelli reaction - with catalytic amount of acid either at reflux or microwave heating, TMSCl-NaI/CH_3CN [8] (equimolar/longer time) and TMSOTf [9] (strong acid) at room temperature, only one report by Dondoni *et al.* [10,11] described the synthesis of *C*-glycosylated DHPMs using CuCl (1 eq)-$BF_3.Et_2O$ (1.3 eq)-AcOH (0.2 eq) in THF at reflux as diastereomeric mixtures with moderate yields. Hence, better reaction conditions were warranted to prepare such libraries of compounds. In view of our continued studies on the synthesis of new saccharides [12] and *C*-nucleosides [13], herein, we report, the HCl, generated *in situ* from 2,4,6-trichloro[1,3,5]-triazine (TCT) [14], catalyzed efficient protocol for cyclocondensation of sugar derived aldehydes with enhanced reaction rates under solvent free Biginelli conditions at room temperature, to result the glycoconjugates in high yields (Scheme 1).

To establish the reaction conditions, 1-O-methyl 2,3-O-isopropylidene-α-D-mano-pentoaldo-1,4-furanose (**1**, Table 1) was subjected to reaction with equimolar quantities of ethyl acetoacetate and urea at room temperature in the presence of TCT (10 mol%) to furnish DHPM glycoconjugates **1a** and **1b** (Table 1), as a separable mixture of diastereoisomers in 76% and 11% yields respectively. The structures of **1a** and **1b** were unambiguously assigned from the spectral analysis.

The structures of minor and major isomers were characterized as compound **1b** and **1a** respectively by extensive nmr studies using 2D DQCOSY and NOESY experiments (Figure 1). For **1b** trans orientation of H5 (4.80, dd) with respect to H4 was evident from the large J value (J = 8.5 Hz). The NOE cross peak between CH_3(a)-H5, confirm the rotation of pyrimidine ring with respect to sugar ring. The structure was further supported by characteristic NOE between CH_3(a)-H1, CH_3(b)-H2, and CH_3(b)-H3. Similarly, for compound **1a** the characteristic small value of 1.5 Hz for $J_{4,5}$ implies restricted rotation about C4-C5

Scheme 1



1 **1a** (76%) **1b** (11%)

and the H4-C4-C5-H5 dihedral angle of about 90°. This orientation results in NOE cross peaks between CH_3(a)-NH6 and H5-H3. This fixes the configuration at C5 as "S". For the minor isomer (**1b**) conformation, on the other hand, the presence of NOE between H5-CH_3(a) and $J_{4,5}$ = 8.5 Hz corresponds to the nearly trans-disposition of H4 and H5 protons and fixes the configuration as "R" at C5.

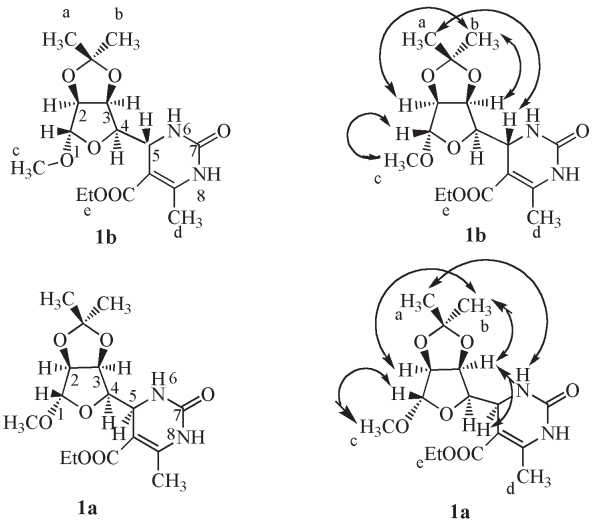


Figure 1

In a similar study, the sugar derived aldehydes, 1,2-*O*-isopropylidene-3-*O*-methyl-α-D-xylo-pentodialdo-1,4-furanose (**2**, Table 1) and 2,2,7,7-tetramethyl-(3aR,5S,5aR, 8aR,8bR)-perhydrodi[1,3]dioxolo[5,4-*b*;5,4-*d*]pyran-5-carbaldehyde (**5**, Table 1) underwent Biginelli reaction successfully to give *C*-linked DHPM glycoconjugates **2a** and **2b**; **5a** and **5b** respectively. Furthermore, the anomeric sugar aldehydes, *viz*. 2,5-anhydro-3,4:6,7-di-*O*-isopropylidene aldehydo-D-glycero-D-galacto-heptofuranose (**3**, Table 1) and 2,5-anhydro-6-*O*-*t*-butyldimethylsilyl-3,4-*O*-isopropylidene-D-allose (**4**, Table 1) furnished a new class of *C*-nucleoside glycoconjugates **3a** and **3b**; **4a** and **4b** respectively, in high yields. Both the *C*-linked as well as *C*-nucleoside glycoconjugates were very efficiently prepared under solvent free reaction conditions at room temperature with the use of *in situ* generated HCl as acid in catalytic amounts. However, reaction of **1** with 10 mol% HCl (prepared from commercial HCl) gave **1a** and **1b** in poor yields (40%).

Thus, HCl generated *in situ* from TCT (10 mol%), catalyzes the Biginelli reaction very effectively to give the new glycoconjugates. The 'incipient' moisture plays a prominent role in the generation of 'HCl' form TCT, as shown in the plausible mechanism below (Figure 2). TCT reacts with 'incipient' moisture and releases 3 moles of HCl and cyanuric acid (removable by water washing) as byproduct. The *in situ* generated HCl acts as a protic acid and activates the carbonyl oxygen and prompts the cyclo-condensation to give the product. However, attempted failure of Biginelli reaction under anhydrous reaction conditions in the presence of MS 4Å, amply indicated the significance of 'incipient' moisture for *in situ* HCl generation.

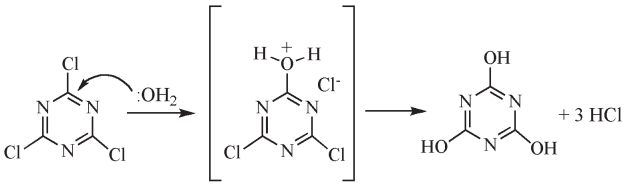


Figure 2

In summary, the present protocol, using *in situ* generated HCl from TCT (10 mol%), is very efficient for Biginelli reactions with acid sensitive sugar derived aldehydes. The notable features of this procedure are: a) use of inexpensive catalyst, b) solvent free mild reaction conditions at room temperature, amenable to large-scale synthesis and c) enhanced reaction rates with the provision for direct isolation of the products in high yields. Since the reaction conditions are consistent with sensitive sugar substrates, it provides an opportunity to synthesize a variety of DHPM glycoconjugates and C-nucleosides, which might find interesting utility in new drug discovery.

EXPERIMENTAL

General Procedure.

A mixture of aldehyde (1 mmol), ethyl acetoacetate (1 mmol), urea (1.2 mmol) and TCT (0.1 mmol) was stirred at room temperature for an appropriate time (see Table). After completion of the reaction, the mixture was diluted with water (5 mL) and the resulting solid product was filtered off and dried. In the case of syrupy products, the reaction mixture was diluted with water (5 mL), extracted with ethyl acetate (3 x 5 mL), the organic layer dried (Na_2SO_4) and evaporated under vacuum to give the product.

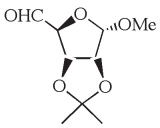
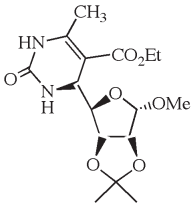
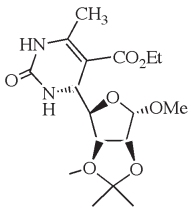
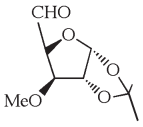
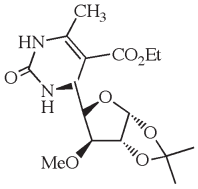
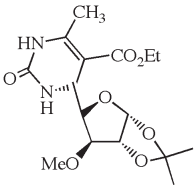
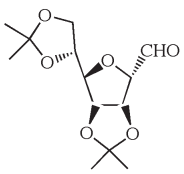
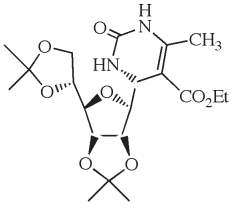
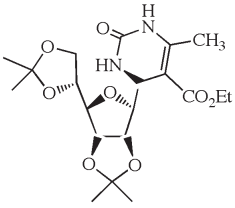
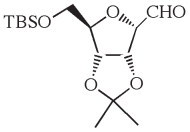
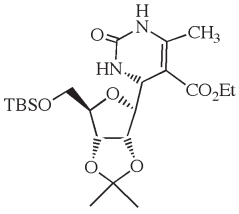
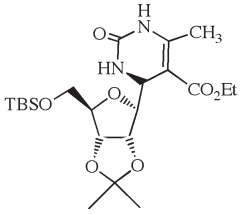
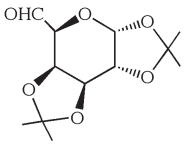
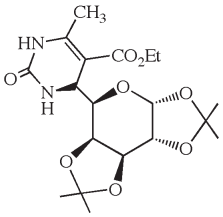
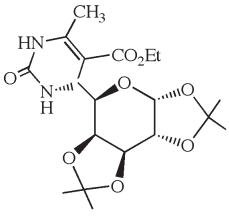
Spectroscopic Data of Selected Compounds.

Ethyl 4-[6-Methoxy-(3a*S*,4*R*,6a*S*)-perhydrofuro[3,4-*d*][1,3]-dioxol-4-yl]-6-methyl-2-oxo-(4*S*)-1,2-dihydro-5-pyrimidinecarboxylate (**1a**).

This compound was obtained as brown amorphous solid (chloroform), mp 192-194°; $[\alpha]_D$ = +22.2 (*c* 1.00, $CHCl_3$); ir (KBr): 3270, 2867, 1710, 1697 cm^{-1}; ^1H nmr ($CDCl_3$, 200 MHz): δ 1.29 (t, 3H, CH_3), 1.30 (s, 3H, CH_3), 1.58 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 3.26 (s, 3H, OCH_3), 3.88 (dd, 1H, $J_{1,2}$ = 3.7 Hz, $J_{1,3}$ = 1.5 Hz, H-4), 4.20 (q, 2H, *J* = 7.0 Hz, OCH_2), 4.53 (d, 1H, $J_{1,2,}$ = 6.0 Hz, H-2), 4.72 (dd, 1H, $J_{1,2}$ = 6.0, $J_{1,3}$ = 3.7 Hz, H-3), 4.77 (t, 1H, $J_{1,2}$ = 1.5 Hz, $J_{1,3}$ = 1.5 Hz, H-5), 4.95 (s, 1H, H-1), 5.75 (dd, 1H, $J_{1,2}$ = 2.0, $J_{1,3}$ = 1.5 Hz, H-6), 5.75 (dd, 1H, $J_{1,2}$ = 2.0, $J_{1,3}$= 1.5 Hz, H-6), 7.24 (d, 1H, *J* = 2.0 Hz, H-8); fab ms: m/z 357 (M^++1) (97), 325 (11), 279 (10), 183 (64).

Anal. Calcd. For $C_{16}H_{24}N_2O_7$: C, 53.92; H, 6.79. Found: C, 53.84; H, 6.74.

Table 1
Synthesis of new DHPM glycoconjugates catalysed by TCT (in situ HCl)

Entry	Aldehyde	Bignelli Product	
		Major	Minor
1		 **1a** 100 min 76%	 **1b** 11%
2		 **2a** 150 min 73%	 **2b** 13%
3		 **3a** 140 min 72%	 **3b** 12%
4		 **4a** 130 min 69%	 **4b** 11%
5		 **5a** 110 min 70%	 **5b** 12%

Ethyl 4-[6-Methoxy-(3a*S*,4*R*,6a*S*)-perhydrofuro[3,4-*d*][1,3]-dioxol-4-yl]-6-methyl-2-oxo-(4*R*)-1,2-di hydro-5-pyrimidinecarboxylate (**1b**).

This compound was obtained as brown solid (chloroform), mp 195-197°; $[\alpha]_D$ = -84.2 (*c* 1.00, $CHCl_3$); ir (KBr): 3345, 2915, 1750, 1645 cm^{-1}; ^1H nmr ($CDCl_3$, 200 MHz): δ 1.27 (t, 3H, *J* = 7.0 Hz, CH_3), 1.30 (s, 3H, CH_3), 1.47 (s, 3H, CH_3), 3.25 (s, 3H, OCH_3), 4.02 (dd, 1H, $J_{1,2}$ = 3.8, $J_{1,3}$ = 8.5 Hz, H-4), 4.20 (q, 2H, *J* = 7.0 Hz, OCH_2), 4.53 (d, 1H, *J* = 6.0 Hz, H-2), 4.74 (dd, 1H, $J_{1,2}$ = 6.0, $J_{1,3}$ = 3.8 Hz, H-3), 4.80 (dd, 1H, $J_{1,2}$ = 8.5, $J_{1,3}$ = 3.3 Hz, H-5), 4.85 (s,1H, H-1), 5.47 (dd, 1H, $J_{1,2}$ = 2.0, $J_{1,3}$ = 2.0 Hz, NH), 8.07 (d, 1H, *J* = 2.0 Hz, NH); fab ms: (m/z) 357 (M^++1) (68), 325 (11), 279 (10), 183 (64).

Anal. Calcd. For $C_{16}H_{24}N_2O_7$: C, 53.92; H, 6.79. Found: C, 53.88; H, 6.76.

Ethyl 4-[2,2-Dimethyl-(3a*R*,5*S*,6a*R*)-perhydrofuro[2,3-*d*][1,3]-dioxol-5-yl]-6-methyl-2-oxo-(4*S*)-1,2-dihydro-5-pyrimidinecarboxylate (**2a**).

This compound was obtained as brown amorphous solid (chloroform), mp 195-197°; $[\alpha]_D$ = +87.3 (*c* 1.00, $CHCl_3$); ir (KBr): 3345, 2887, 1765, 1665 cm^{-1}; ^1H nmr ($CDCl_3$, 200 MHz): δ 1.05-1.15 (m, 6H, 2 x CH_3), 1.35 (s, 3H, CH_3), 2.20 (s, 1H, CH_3), 3.40 (s, 3H, OCH_3), 3.70 (d, 1H, *J* = 4.46 Hz, H-3), 4.00-4.20 (m, 3H, OCH_2, H-4), 4.40 (s, 1H, H-5), 4.55 (d, 1H, *J* = 3.71 Hz, H-2), 5.40 (s,1H, NH), 5.85 (d, 1H, *J* = 3.71 Hz, H-1), 8.90 (bs, 1H, NH); fab ms: (m/z) 357 (M^++1) (100), 325 (11), 279 (10), 183 (64).

Anal. Calcd. For $C_{16}H_{24}N_2O_7$: C, 53.92; H, 6.79. Found: C, 53.87; H, 6.74.

Ethyl 4-[2,2-Dimethyl-(3a*R*,5*S*,6a*R*)-perhydrofuro[2,3-*d*][1,3]-dioxol-5-yl]-6-methyl-2-oxo-(4*R*)-1,2-dihydro-5-pyrimidinecarboxylate (**2b**).

This compound was obtained as brown solid $[\alpha]_D$ = -22.1 (*c* 1.00, $CHCl_3$); mp 195-197°; ir (KBr): 3320, 2987, 1745, 1685 cm^{-1}; ^1H nmr ($CDCl_3$+DMSO-d_6, 400 MHz): δ 1.00-1.15 (m, 6H, 2 x CH_3), 1.40 (s, 3H, CH_3), 2.15 (s, 1H, CH_3), 3.35 (s, 3H, OCH_3), 3.60 (d, 1H, *J* = 3.71 Hz, H-3), 4.00-4.20 (m, 3H, OCH_2, H-4), 4.40 (d, 1H, *J* = 3.71 Hz, H-2), 4.60 (dd, 1H, $J_{1,2}$ = 1.51, $J_{1,3}$ = 6.92 Hz, H-5), 5.60 (s,1H, NH), 5.75 (d, 1H, *J* = 3.71 Hz, H-1), 8.90 (bs, 1H, NH); fab ms (m/z): 357 (M^++1) (100), 325 (11), 279 (10), 183 (47).

Anal. Calcd. For $C_{16}H_{24}N_2O_7$: C, 53.92; H, 6.79. Found: C, 53.88; H, 6.75; N, 7.84.

Methyloxycarbonylmethyl-4-[6-[2,2-dimethyl-(4*R*)-1,3-dioxolan-4-yl]-2,2-dimethyl-(3a*R*,6*R*,6a*S*)-perhydrofuro[3,4-*d*][1,3]-dioxol-4-yl]-5-methyl-2-oxo-(4*R*)-1,2-dihydro-6-pyrimidinecarboxylate **(3a**).

This compound was obtained as white crystalline solid (methanol), mp 150-153°; $[\alpha]_D$ = +132.2 (*c* 1.0, MeOH); ir (KBr): 3315, 2990, 1745, 1680 cm^{-1}; ^1H nmr ($CDCl_3$, 400 MHz): δ 1.20-1.60 (m, 15H), 2.25 (s, 3H, CH_3), 3.50 (d, 1H, *J* = 3.5 Hz, CH_2-6), 3.60 (d, 1H, *J* = 6.5 Hz, CH_2-6), 4.05 (m, 3H, -$COOCH_2$-, H-4), 4.25-4.30 (m, 1H, H-5), 4.45 (dd, 1H, $J_{1,2}$ = 3.0 Hz, $J_{1,3}$ = 5.8 Hz, H-3), 4.65-4.70 (m, 2H, H-2, -CH), 4.75 (d, 1H, *J* = 3.5 Hz, H-1), 5.70 (s, 1H, -NH), 7.90 (s, 1H, -NH); fab ms (m/z): 426 (M^+) (50), 352 (11), 279 (10), 183 (100).

Anal. Calcd. For $C_{20}H_{30}N_2O_8$: C, 56.33; H, 7.09. Found: C, 56.35; H, 7.10.

Methyloxycarbonylmethyl-4-[6-[2,2-dimethyl-(4*R*)-1,3-dioxolan-4-yl]-2,2-dimethyl-(3a*R*,6*R*,6a*S*)-perhydrofuro[3,4-*d*][1,3]dioxol-4-yl]-5-methyl-2-oxo-(4*S*)-1,2-dihydro-6-pyrimidinecarboxylate (**3b**).

This compound was obtained as white crystalline solid (methanol), mp 145-147°; $[\alpha]_D$ = -56.4 (*c* 1.0, MeOH); ir (KBr): 3315, 2990, 1745, 1680 cm^{-1}; ^1H nmr ($CDCl_3$, 200 MHz): δ 1.25-1.65 (m, 15H), 2.30 (s, 3H, CH_3), 3.60 (d, 2H, *J* = 7.5 Hz, CH_2-6,), 4.02 (dd, 1H, $J_{1,2}$ = 4.2 Hz, $J_{1,3}$ = 8.5 Hz, H-4), 4.20-4.30 (m, 3H, -$COOCH_2$-, H-5), 4.60 (dd, 1H, $J_{1,2}$ = 4.0 Hz, $J_{1,3}$ = 8.0 Hz, H-3) 4.65-4.72 (m, 2H, H-2, -CH), 4.80 (dd, 1H, $J_{1,2}$ = 4.8 Hz, $J_{1,3}$ = 8.5 Hz, H-1), 5.80 (s, 1H, -NH), 8.20 (s, 1H, -NH); fab ms (m/z): 426 (M^+) (100), 352 (11), 279 (10), 183 (76).

Anal. Calcd. For $C_{20}H_{30}N_2O_8$: C, 56.33; H, 7.09. Found: C, 56.27; H, 7.04.

Ethyl 4-[6-(*tert*-Butoxy)-2,2-dimethyl-(3a*S*,4*R*,6a*S*)-perhydrofuro[3,4-*d*][1,3]dioxol-4-yl]-6-methyl-2-oxo-(4*S*)-1,2-dihydro-5-pyrimidinecarboxylate (**4a**).

This compound was obtained as white crystalline solid (methanol), mp 162-165°; $[\alpha]_D$ = +52.50 (*c* 0.50, MeOH); ir (KBr): 3324, 2897, 1740, 1675 cm^{-1}; ^1H nmr ($CDCl_3$+DMSO-d_6, 400 MHz): δ 0.00 (s, 6H, 2 x CH_3), 0.80 (s, 9H, 3 x CH_3), 1.20 (t, 3H, *J* = 4.5 Hz, CH_3), 1.30 (s, 3H, CH_3), 1.55 (s, 3H, CH_3), 2.15 (s, 3H, CH_3), 3.50 (dd, 1H, $J_{1,2}$ = 3.5 Hz, $J_{1,3}$ = 6.1 Hz, H-5), 3.70 (dd, 1H, $J_{1,2}$ = 3.3 Hz, $J_{1,3}$ = 6.0 Hz, H-5), 3.90 (dd, 1H, $J_{1,2}$ = 3.0 Hz, $J_{1,3}$ = 5.8 Hz, H-2), 4.00 (d, 1H, *J* = 4.0 Hz, H-3), 4.10-4.25 (m, 3H, OCH_2CH_3, H-4), 4.50 (dd, 1H, $J_{1,2}$ = 3.5 Hz, $J_{1,3}$ = 5.5 Hz, H-1), 4.70 (d, 1H, *J* = 2.5 Hz, H-5), 6.90 (bs, 1H, NH), 8.75 (bs, 1H, NH); fab ms: (m/z) 471 (M^++1) (67), 286 (40), 183 (100).

Anal. Calcd. For $C_{22}H_{38}N_2O_7Si$: C, 56.14; H, 8.14. Found: C, 56.09; H, 8.10.

Ethyl 4-[6-(*tert*-Butoxy)-2,2-dimethyl-(3a*S*,4*R*,6a*S*)-perhydrofuro[3,4-*d*][1,3]dioxol-4-yl]-6-methyl-2-oxo-(4*R*)-1,2-dihydro-5-pyrimidinecarboxylate (**4b**).

This compound was obtained as colorless syrup. $[\alpha]_D$ = -32.30 (*c* 0.50, MeOH); ir (KBr): 3317, 2920, 1745, 1680, 1456 cm^{-1}; ^1H nmr ($CDCl_3$+DMSO-d_6, 200 MHz): δ 0.10 (s, 6H, 2 x CH_3), 0.80 (s, 9H, 3 x CH_3), 1.15 (t, 3H, *J* = 3.5 Hz, CH_3), 1.25 (s, 3H, CH_3), 1.40 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 3.40 (dd, 1H, $J_{1,2}$ = 2.8 Hz, $J_{1,3}$ = 5.5 Hz, H-5), 3.55 (dd, 1H $J_{1,2}$ = 3.0 Hz, $J_{1,3}$ = 5.0 Hz, H-5), 3.85 (d, 1H, *J* = 4.2 Hz, H-3), 4.05 (d, 1H, *J* = 4.0 Hz, H-2), 4.10-4.20 (q, 3H, OCH_2CH_3), 4.25 (dd, 1H, *J* = 5.5 Hz, 7.0 Hz, H-4), 4.40 (d, 1H, *J* = 5.0 Hz, H-1), 4.55 (dd, 1H, $J_{1,2}$ = 5.0 Hz, $J_{1,3}$ = 9.6 Hz, H-5), 6.00 (bs, 1H, NH), 7.85 (bs, 1H, NH); fab ms: (m/z) 471 (M^++1) (45), 286 (32), 183 (100).

Anal. Calcd. For $C_{22}H_{38}N_2O_7Si$: C, 56.14; H, 8.14. Found: C, 56.09; H, 8.09.

Ethyl 6-Methyl-2-oxo-4-[2,2,7,7-tetramethyl-(3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-perhydrodi[1,3]dioxolo[5,4-*b*:5,4-*d*]pyran-5-yl]-(4*R*)-1,2-dihydro-5-pyrimidinecarboxylate (**5a**).

This compound was obtained as a yellow crystalline solid (methanol), mp 192-194°; $[\alpha]_D$ = +38.50 (*c* 1.00, MeOH); ir (KBr): 3320, 2987, 1745, 1685, 1465 cm^{-1}; ^1H nmr ($CDCl_3$+DMSO-d_6, 200 MHz): δ 1.10 (m, 12H, 4 x CH_3), 1.45 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 3.60 (bs, 1H, H-5), 4.00-4.10 (m, 2H, OCH_2), 4.20-4.30 (m, 2H, H-2, H-4), 4.42 (bs, 1H, CH) 4.50 (dd, 1H, $J_{1,2}$ = 1.45 Hz, $J_{1,3}$ = 6.45 Hz, H-3), 5.42 (d, 1H, *J* = 5.23 Hz, H-1), 5.80 (bs, 1H, NH), 8.90 (bs, 1H, NH); fab ms: (m/z) 413 (M^++1) (18), 325 (11), 279 (10), 183 (100).

Anal. Calcd. For $C_{19}H_{28}N_2O_8$: C, 55.33; H, 6.84. Found: C, 55.29; H, 6.78.

Ethyl 6-Methyl-2-oxo-4-[2,2,7,7-tetramethyl-(3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-perhydrodi[1,3]dioxolo[5,4-*b*:5,4-*d*]pyran-5-yl]-(4*R*)-1,2-dihydro-5-pyrimidinecarboxylate (**5b**).

This compound was obtained as a yellow crystalline solid (methanol), mp 175-177°; $[\alpha]_D$ = -55.40 (*c* 1.00, MeOH); ir (KBr): 3240, 2980, 1756, 1667 cm^{-1}; ^1H nmr ($CDCl_3$+DMSO-d_6, 200 MHz): δ 1.10-1.40 (m, 15H, 5 x CH_3), 2.25 (s, 3H, CH_3),

3.80 (dd, 1H, $J_{1,2}$ = 1.65 Hz, $J_{1,3}$ = 6.62 Hz, H-5), 4.00-4.10 (q, 2H, OCH_2), 4.20-4.30 (m, 2H, H-2, H-4), 4.50-4.65 (m, 2H, CH, H-3), 5.49 (d, 1H, J = 4.96 Hz, H-1), 5.85 (bs, 1H, NH), 8.65 (bs, 1H, NH); fab ms: (m/z) 413 (M^++1) (27), 325 (19), 279 (30), 183 (100).

Anal. Calcd. For $C_{19}H_{28}N_2O_8$: C, 55.33; H, 6.84. Found: C, 55.28; H, 6.79.

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