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MICHAEL ADDITION REACTIONS OF α, β-ENE-3′-PHENYLSELENONE OF URIDINE. NEW SYNTHESIS OF 2′,3′-DIDEOXY-*ribo*-AZIRIDINO-, 2′,3′-DIDEOXY-2′ ,3′-*ribo*-CYCLOPROPYL- & 2,2′-*O*-ANHYDRO-3′-DEOXY-3′-AMINO URIDINE DERIVATIVES **

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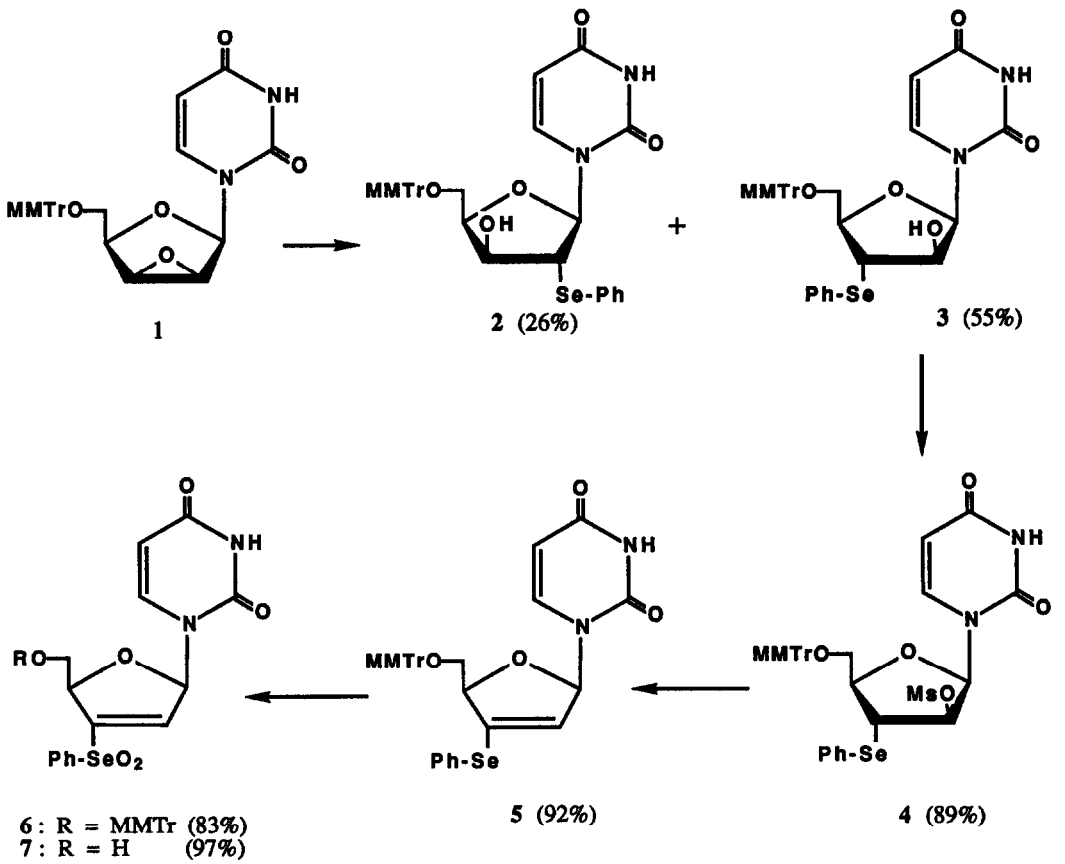
*Abstract: A high-yielding synthesis of 1-[5′-O-(4-monomethoxytrityl)-2′,3′-dideoxy-3′-phenylselenonyl-β-D-*glycero*pent-2′-enofuranosyl]uracil (6) is described starting from 5′-0-(4-monomethoxytrityl)-2′,3′-0-anhydro-β-D-lyxofuranosyl uracil 1. The α, β-ene-3′-phenylselenone 6 can be easily deprotected to give 7. The synthetic utilities of 6 and 7 as synthetic equivalent of a dication [* CH_2^+ - CH_2^+ *] have been demonstrated from the fact that they act as Michael acceptors and undergo conjugate addition reactions at C-2′ with ammonia, methylamine, benzylamine and glycine methyl ester, followed by a direct intramolecular S_N2 type displacement reaction at C-3′ in the adduct, to give various 2′,3′-dideoxy-*ribo*-aziridino uridines 8a - d or 13a - c, while dimethylamine, pyrrolidine, and morpholine give 2,2′-O-anhydro-3′-deoxy-3′-substituted-aminouridines 10a - c. Carbon-nucleophiles such as sodium methyl malonate and conjugate bases of nitromethane and acetophenone upon reaction with 6 provides a convenient access to 2′,3′-dideoxy-2′,3′-cyclopropyl(bicyclo[3.1.0] system) derivatives of uridine 14 - 16, while a reaction of 6 with methylacetoacetate gives an unusual 2′,3′-fused furano(bicyclo[3.3.0] system) derivative 19. Compounds 8a - c, 10a - c, 14, 15 and 19 were deprotected with 80% aqueous acetic acid to give various 5′-hydroxy derivatives 9a - d, 11a - c, 17, 18 and 20. 2′,3′-Dideoxy-*ribo*-aziridines 13a - c were, however, obtained by direct reactions of 7 with ammonia, methylamine and benzylamine. The methodology described herein constitute a new general approach to fuctionalize the 2′- and 3′-carbons of β-D-nucleosides simultaneously. All new 2′,3′-disubstituted nucleosides with free 5′-hydroxyl group are potential inhibitors of HIV-specific reverse transcriptase.*

Human Immunodeficiency Virus (HIV) is the causative agent of the Acquired Immune Deficiency Syndrome (AIDS). Since the discovery of AIDS, several 2′,3′-dideoxynucleosides[14-17] [2′,3′-dideoxycytidine[14], 2′,3′-dideoxythymidine[17], 2′,3′-dideoxyadenosine[14], 2′,3′-dideoxy-2,6-diaminopurine ribonucleoside[15]], its 3′-substituted derivatives [3′-azidothymidine, 3′-fluorothymidine][18], and its didehydro-analogues [2′,3′-dideoxy-2′,3′-didehydrothymidine and inosine][19,20] have been successfully employed as chemotherapeutic agents due to their abilities for selective inhibition of HIV specific reverse transcriptase[1-20] which results into suppression of the replication of HIV in the patients. These active compounds and their mechanism of action[1-20] suggest that the 2′,3′-dideoxy-2′ and 3′-substituted-β-D-nucleosides with free 5′-hydroxyl group are of potential interest for the HIV-reverse transcriptase promoted chain termination of the cDNA synthesis. New synthetic methods should therefore be developed to prepare new types of 2′,3′-dideoxynucleosides with potentials to suppress the replication of HIV. Synthetic procedures to prepare the 2′- or 3′-substituted nucleosides involve one of the following procedures: (i) direct nucleophilic (S_N2) displacement of a leaving group[21-28], (ii) nucleophilic ring-opening reactions of 2′,3′-0-*ribo*- or *lyxo*-anhydro-purine nucleosides or 2′,3′-0-*lyxo*-anhydro-pyrimidine nucleosides[18-32], (iii) ring-opening reactions of 2,2′-0- or 2,3′-0-anhydro-pyrimidine nucleosides or 8,2′-0- or 8,3′-0-anhydro-purine nucleosides[44-46], (iv) substitution through the displacement of 2′,3′-carboxonium ion[47,48], and (v) nucleophilic addition to appropriately protected 2′- or 3′-keto

** *Dedicated to Professor Sir Derek Barton on the occasion of his 70th Birthday*

nucleosides[49-58], or other procedures involving addition to the 2′,3′-double bond[65] and/or rearrangements[59-67]. The synthesis of β-D-nucleoside derivatives such as 2′,3′-dideoxy-2′,3′-epimino (aziridine), its N-substituted derivatives, 2′,3′-dideoxy- 2′,3′-cyclopropyl and its C-substituted cyclopropyl derivatives and other 2′-deoxy-2′,3′-fused cyclic β-D-nucleoside derivatives are more complex and challenging. Two examples of synthesis of 2′,3′-deoxy-*ribo*- and *lyxo*-aziridine nucleosides involve lengthy and laborious transformations using 9-(3′-deoxy-3′-azido-2′-O-tosyl-β-D-arabinofuranosyl)adenine[68], 9-(3′-deoxy-3′-azido-2′-O-mesyl-β-D-xylofuranosyl)adenine[68] and 1-(2′-deoxy-2,2′-phenylimino-β-D-arabinofuranosyl)uracil[69].

We have recently reported that simple Michael addition reactions to an appropriately 5′-O-protected-2′,3′-ene-3′-sulfone[70] or 2′,3′-ene-3′-nitrile[71] derivatives of β-D-nucleosides constitute convenient access to different 2′,3′-deoxy-2′,3′-disubstituted- or 2′-substituted nucleosides in high overall yield[70,71]. These nucleophilic addition reactions take place exclusively from the α-face of C-2′ of the 2′,3′-enesulfone[70], or 2′,3′-enenitrile[71] to give mainly *trans*-2′,3′-disubstituted adducts owing to the stereoelectronic factors controlling the stabilization of the intermediary chiral α-sulfonyl-3′-carbanion[70] or α-nitrile-3′-carbanion[71] at the α-face.



1

2 (26%)

3 (55%)

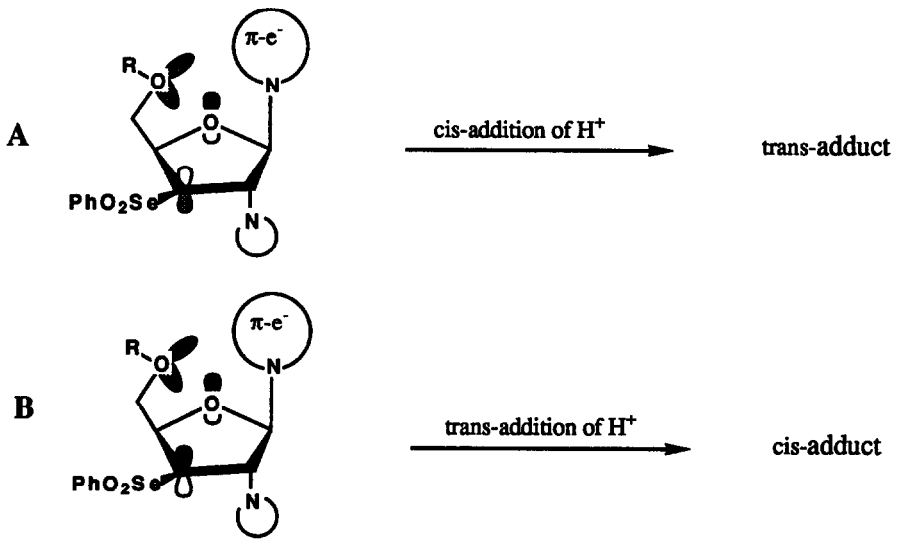
4 (89%)

5 (92%)

6 : R = MMTr (83%)
7 : R = H (97%)

We have subsequently considered 2′,3′-vinyl selenoxides and 2′,3′-vinyl selenones of 5′-protected nucleosides as substrates to exploit these powerful Michael addition reactions as a means to functionalize both

the 2′- and 3′-carbons of nucleosides simultaneously. It is well documented that the seleninyl and selenonyl groups, when connected to a double bond, are strong-electron withdrawing groups and therefore activate the α,β-double bond towards addition of nucleophiles at the β-carbon[72-76]. It was also quite clear at the outset that the α-seleninyl or selenonyl carbanion, formed upon a nucleophilic addition at C-2′, will be very unstable as a result of the leaving group character of the seleninyl or selenonyl substitutent. We however wished to base our initial studies on the 2′,3′-vinylic-3′-selenone of a nucleoside because of the pronounced electron-withdrawing effect which combined with the leaving group character of the selenonyl substituent makes the 2′,3′-vinylic-3′-selenone synthetically equivalent to the dication $CH_2^+ - CH_2^+$ [72-76].

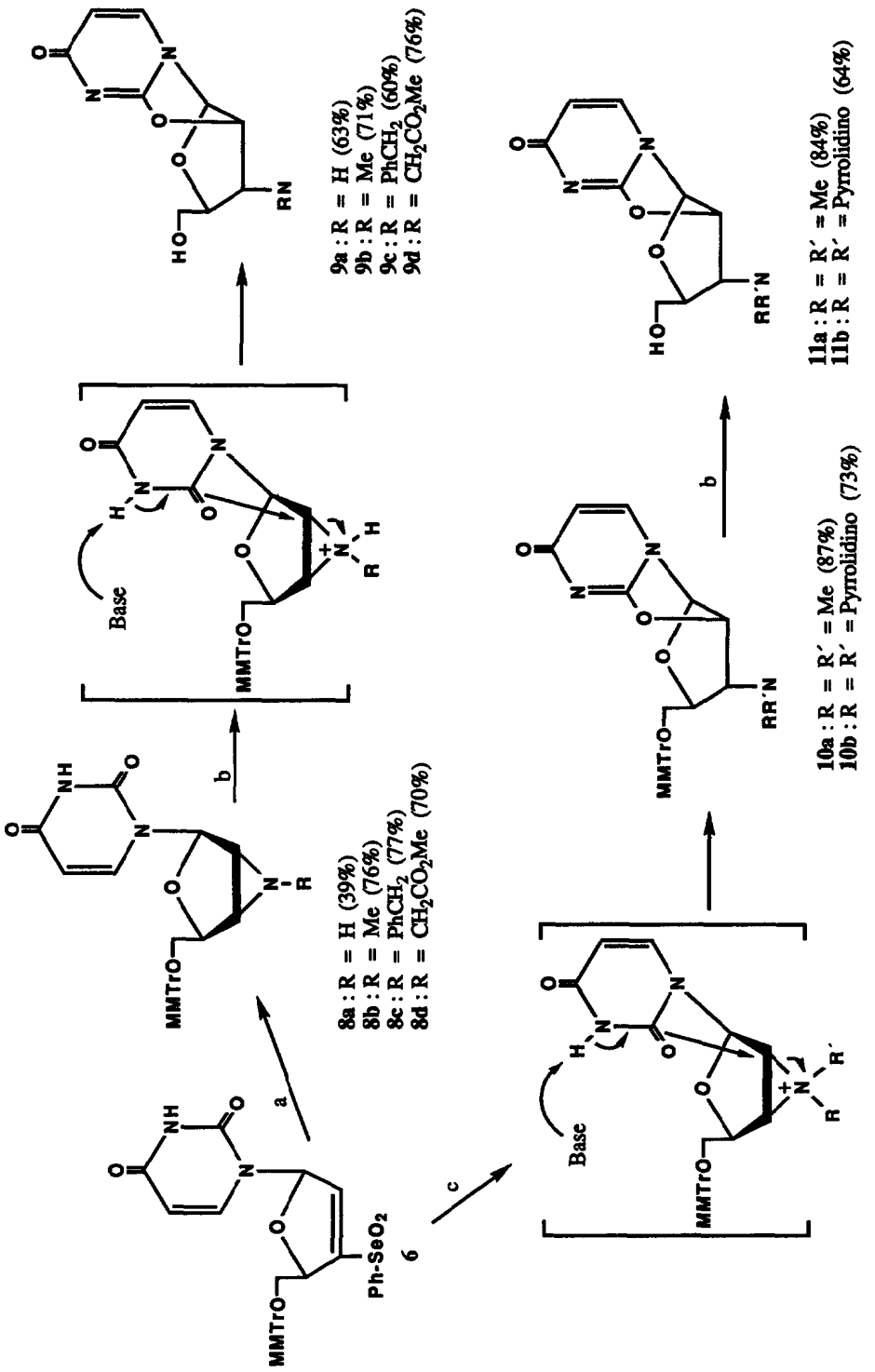


Scheme 1

We herein report a facile preparation of α,β-ene-3′-phenylselenone of uridine **6**. We also show the synthetic utilities of **6** as synthetic equivalent of a dication: (i) it undergoes conjugate addition reaction (Michael acceptor) toward ammonia, primary amines [methylamine, benzylamine and glycine methyl ester], secondary amines [dimethylamine, pyrrolidine and morpholine] and carbon-nucleophiles [such as sodium methyl malonate and conjugate bases of nitromethane, acetophenone and methylacetoacetate], and then (ii) the selenonyl group at C-3′ in the adducts act as an excellent leaving group due to an internal S_N2 attack of the neighbouring nucleophile at C-2′ to give cyclic 2′,3′-disubstituted products.

Preparation of α,β-ene-3′-phenylselenone of uridine 6

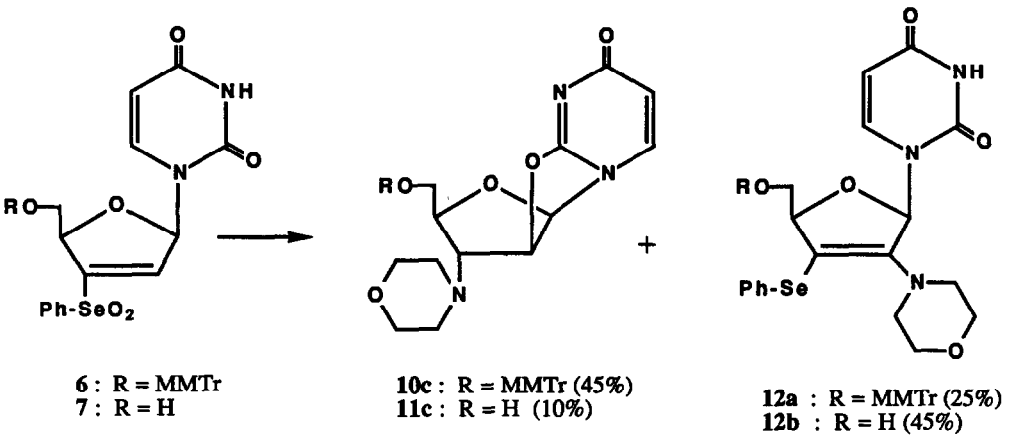
5′-0-(4-Monomethoxytrityl [MMTr])-2′,3′-O-anhydro-β-D-*lyxo*furanosyluridine was opened up by an attack of $PhSe^-$ ion [$(PhSe)_2 + LiALH_4 \rightarrow PhSe^-$] in tetrahydrofuran to give a mixture of 2′-deoxy-2′-phenylselenouridine **2** and 3′-deoxy-3′-phenylselenouridine **3** which were separated by a short column chromatography on silica gel and isolated in 26 and 55% yields respectively. The 3′-deoxy-3′-phenylseleno derivative **3** was then treated in pyridine solution with methanesulfonyl chloride to give its 2′-0-mesylate **4** in



[a] Aq. NH_3, Aq. $MeNH_2$, Benzylamine, or Glycine methyl ester, [b] 80 % aq. acetic acid at RT, [c] Aq. Me_2NH or pyrrolidine

Scheme 2

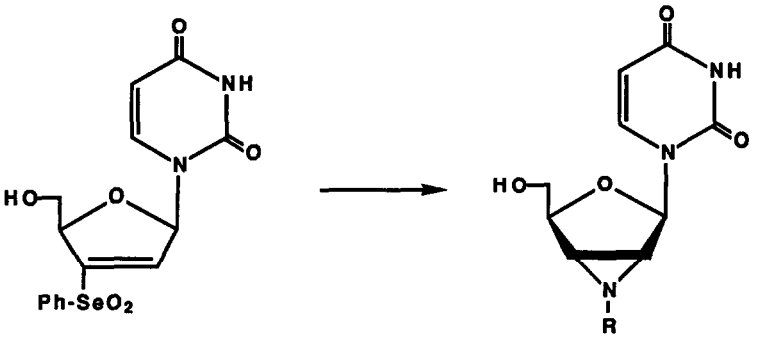
89% yield. A treatment of 2′-O-mesylate **4** with potassium tert-butoxide in dry dimethylformamide solution at 0 °C, followed by warming up to room temperature, gave α,β-ene-3′-phenylselenide **5** in 92% yield. Compound **5** was subsequently oxidised by *m*-chloroperbenzoic acid in methanolic solution to give α,β-ene-3′-phenyl-



6 : R = MMTr
7 : R = H

10c : R = MMTr (45%)
11c : R = H (10%)

12a : R = MMTr (25%)
12b : R = H (45%)



7

13a : R = H (57%)
13b : R = Me (75%)
13c : R = $PhCH_2$ (52%)

selenone **6** in 83% yield. The 3′-eneselenone **6** could be prepared easily in a 10 mmol scale in a pure form. The 5′-O-MMTr group of **6** could be also easily deprotected by a brief treatment of 80% aqueous acetic acid at room temperature to give **7** in 97% yield, which along with **6**, served as Michael acceptor in the reactions described herein.

Reaction of α,β-ene-3′-phenylselenone 6 with ammonia and primary amines.

Treatment of **6** with either an excess of aqueous ammonia in DMF, aqueous methylamine in THF, benzylamine in THF, or glycine methyl ester in DMSO gave the corresponding 2′,3′-dideoxy-2′,3′-aziridines **8a**, or their

N-substituted derivatives **8b**, **8c** and **8d** in 39, 76, 77 and 70% yields respectively. Two nucleophilic attacks explain the formation of 2′,3′-*ribo* aziridines **8a-d**. First of these nucleophilic attacks is the stereospecific nucleophilic addition to the α-face of the 2′,3′-eneselonone **6** to give the *trans*-2′,3′-addition product which instantaneously undergoes 2′-amino promoted S_N2 displacement reaction at C-3′ to give the 2′,3′-*ribo* aziridines. Clearly, the thermodynamic stability of α-selenone carbanion in **A** is overwhelmingly more pronounced than in **B** (Scheme 1), presumably due to the much reduced steric and electronic interactions with the planar α-selenone carbanion in the former than in the latter.

This is consistent with our earlier observations that the nucleophilic attack at C-2′ of 1-(5′-0-trityl-2′,3′-dideoxy-3′-(*p*-toluene)sulfonyl-β-D-*glycero*pent-2′-enofuranosyl)uracil also took place from the sterically and electronically less demanding α-face of the pento-enefuranosyl ring to give the *xylo*-addition product[70]. The 2′-keto function of appropriately protected 2′-keto-nucleosides also suffers diastereoselective nucleophilic attack from the α-face in the $NaBH_4$ promoted reduction[78,79], while the nucleophilic addition reactions by soft carbon-nucleophiles is diastereospecific[55-58], except for one example[53,54].

Reaction of α,β,-ene-3′-phenylselenone 6 with secondary amines.

Treatment of **6** with either aqueous dimethylamine or pyrrolidine in THF gave 1-[5′-0-(MMTr)-3′-deoxy-3′-(N,N-dimethylamino-2,2′-O-anhydro-β-D-arabinofuranosyl)uracil **10a** or 1-[5′-0-(MMTr)-3′-deoxy-3′-pyrrolidino-2,2′-O-anhydro-β-D-arabinofuranosyl)uracil **10b** in 87 and 73% yield respectively. Clearly, the overall reaction course for the two nucleophilic attacks with secondary amines is similar to that suggested for ammonia or primary amines except that the 2′,3′-*ribo*-aziridinium ion is the transitional intermediate formed with the secondary amines (Scheme 2) promoting a third nucleophilic attack by the C^2-oxygen to give the stable products **10a** and **10b**. Reaction of **6** with morpholine gave the expected 3′-deoxy-3′-morpholino-2,2′-O-anhydrouridine derivative **10c** in 45% yield beside the unexpected 2′,3′-ene-2′-morpholino-3′-phenylselenide **12a** in 25% yield. The reduction of 2′,3′-ene-β-phenylselenone in **6** to 2′,3′-ene-β-phenylselenide in **12a** is evident through the comparison chemical shifts of H-4′ in **5** (δ 4.8) and **6** (δ 5.2) with that of **12a** (δ 4.8). The final structural proof of **12a** came from the exact mass measurement by the high resolution mass spectroscopy (see experimental section). The reaction mechanism for the formation of **12a** is not presently clear to us.

Removal of the 5′-0-MMTr group from 8a-d and 10a-c.

Treatment of compounds **8a-d** with 80% aqueous acetic acid at room temperature gave 2,2′-O-anhydro-3′-deoxy-3′-amines **9a-d** in 63, 71, 60 and 76% yield respectively. The formation of 2,2′-O-anhydro-3′-deoxy-3′-amines **9a-d** are easily explained by intermediary formation of the protonated 2′,3′-*ribo*-aziridinium ion which opens up due to the attack at the C-2′ by the O^2 of the uracil moiety (Scheme 2). The 5′-0-MMTr group of compounds **10a-b**, under a similar acidic treatment, gave the expected 2,2′-O-anhydro-3′-deoxy-3′-amines **11a** and **11b** in 84 and 64% yields respectively.

Since the 2′,3′-*ribo*-aziridines could not be obtained by simple deprotection of the 5′-acid labile group we turned our attention to prepare 2′,3′-*ribo*-aziridines with a free hydroxyl function by treating α,β-ene-3′-selenone **7** with ammonia and other primary amines (*vide infra*).

Reaction of α,β-ene-3′-phenylselenone 7 with ammonia and primary amines.

The Michael addition reactions of α,β-ene-3′-phenylselenone **7** with aqueous ammonia in DMF, aqueous methylamine in DMF, or benzylamine in THF in at room temperature smoothly gave 2′,3′-*ribo*-aziridine **13a** and its 2′,3′-(N-substituted)-*ribo*-aziridine derivatives **13b, c** in 57, 75 and 52% yield respectively.

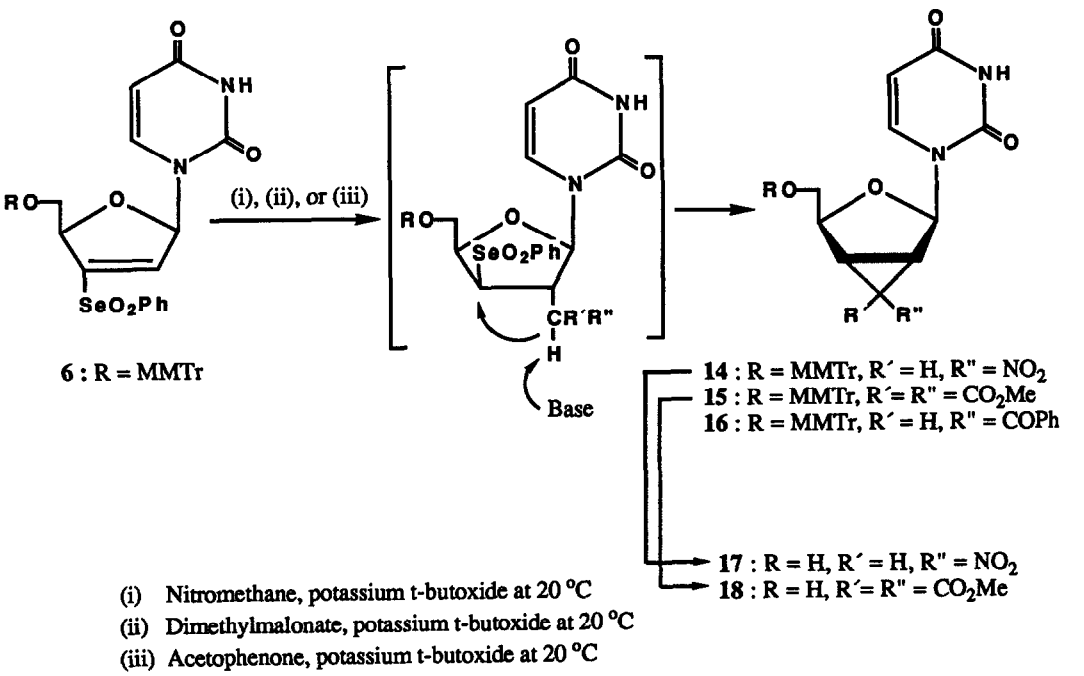
Reaction of **7** with morpholine gave the desired 3′-deoxy-3′-morpholino-2,2′-O-anhydrouridine **11c** only in 10% yield. 2′,3′-ene-2′-morpholino-3′-phenylselenide **12b** was the major product (45%) formed in this reaction. Surprisingly, the ratio of the product distribution from the reaction of morpholine and **6** was completely reverse of that with **7** (*vide supra*).

Reaction of α,β-ene-3′-phenylselenone 6 with active methylene compounds.

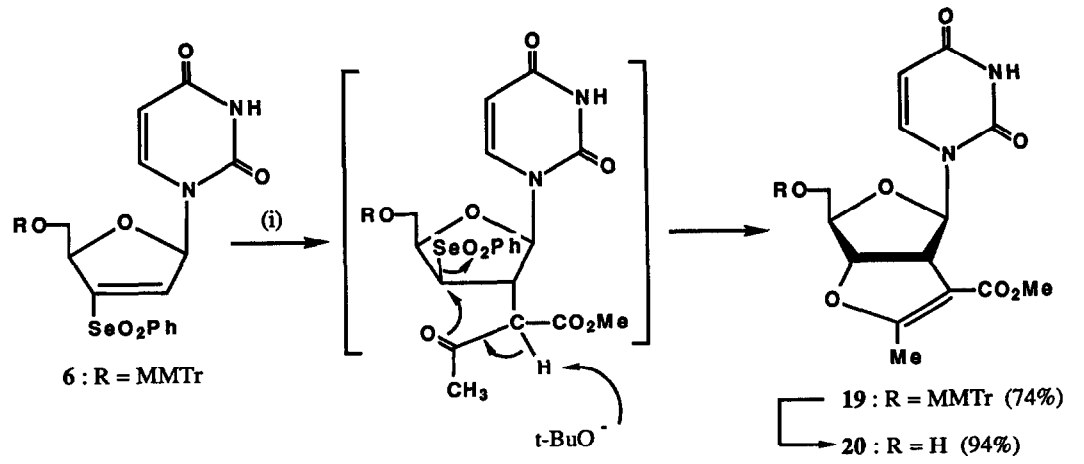
Selenonyl group activates the C = C bond in **6**, as reported for phenyl vinyl selenone[74,76], for conjugate addition of anionic species generated from active methylene compounds, such as dimethylmalonate and nitromethane, and enolate anions generated from compounds such as methyl acetoacetate or acetophenone. The 2′,3′-ene-3′-phenylselenone **6** upon a nucleophilic addition gave the *xylo*-adduct in which the selenone substitutent acts as an excellent leaving group in substitution reactions to give 2′,3′-dideoxy-2′,3′-*ribo*-carbocyclic products (Schemes 3 & 4).

Thus, a treatment of **6** with an excess of potassium salt of nitromethane or potassium dimethylmalonate gave 2′,3′-dideoxy-2′,3′-*ribo*-(1-nitro)cyclopropane **14** and 2′,3′-dideoxy-2′,3′-*ribo*-(1,1-dicarboxymethyl) cyclopropane **15** derivatives (bicyclo[3.3.1] system) of uridine in 59 and 65% yields (Scheme 3). Ambident nucleophiles, such as enolate anion of acetophenone and methylacetoacetate, have also been found to react with **6**, but in a different manner. Enolate anion of acetophenone reacts with **6** like an ordinary reactive methylene compound to give 2′,3′-*ribo*-cyclopropyl ketone **16** in only 18% yield. On the other hand, the enolate anion of methyl acetoacetate[77] reacts with **6** to give a five-membered 2′-deoxy-2′,3′-*ribo*-fused furano (bicyclo[3.3.0] system) derivative **19** in 74% yield (Scheme 4), no trace of expected 2′,3′-*ribo*-cyclopropyl derivatives was detectable in this reaction[77]. Finally, the 5′-O-MMTr group of compounds **14, 15** & **19** were deprotected using 80% aqueous acetic acid at room temperature to give the parent nucleosides **17, 18** & **20** in 77, 94 and 94% yields, respectively.

In conclusion, the addition reactions of **6** and **7** described herein constitute a new general approach to fuctionalize the 2′- and 3′-carbons of β-D-nucleosides simultaneously. Compounds **7, 9a-d, 11a-c, 12b, 13a-d, 17, 18** and **20** can not be prepared easily through any other known routes. They are all potential inhibitors of HIV-specific reverse transcriptase and they are presently undergoing *in vitro* tests for selective inhibition of HIV-specific reverse transcriptase.



Scheme 3



Scheme 4

Experimental.

^{1}H-NMR spectra were recorded (in δ scale) with Jeol 90Q spectrometer at 90 MHz, using TMS (0.0 ppm). ^{13}C-NMR were recorded at 22.5 MHz using both ^{1}H-coupled and ^{1}H-decoupled or INEPT modes. UV absorption spectra were recorded with Varian-Cary 2200 instrument. Jeol DX 303 instrument was used for recording mass spectra. TLC was carried out using Merck pre-coated silica gel F_{254} plates. The column chromatographic separations were carried out using Merck G60 silica gel.

1-[5'-0-(4-Monomethoxytrityl)-2'-deoxy-2'-phenylseleno-β-D-xylofuranosyl]uracil (2) & 1-[5'-0-(4-monomethoxytrityl)-3'-deoxy-3'-phenylseleno-β-D-arabinofuranosyl]uracil (3). To a solution of diphenyldiselenide (13 g, 41.6 mmol) in dry tetrahydrofuran (150 ml) was added lithium aluminium hydride (1.19 g, 31.2 mmol) in small portions under nitrogen at 0 °C. The ice-bath was removed and the mixture was allowed to stir at room temperature for 0.5 h. A solution of compound **1** (13.0 g, 26 mmol) in dry tetrahydrofuran (100 ml) was then added and the stirring was continued until no starting material was left (ca. 3 h). The reaction mixture was poured slowly with stirring into a saturated aqueous solution of ammonium chloride (200 ml), which was extracted with ethyl acetate (3 x 200 ml). The combined extract was evaporated under vacuum to give an orange oil, which was separated on a silica gel column to give compound **2** (4.4 g, 26 %) and **3** (9.3 g, 55 %) Compound **2** : ^{1}H-NMR ($CDCl_3$) : 9.38 (*br*, 1H) NH; 7.60 - 6.84 (*m*, 20 H) H-6, arom.; 6.04 (*d*, $J_{1',2'}$ = 3.1 Hz, 1H) H-1'; 5.44 (*d*, $J_{5,6}$ = 7.8 Hz, 1H) H-5; 4.30 (*m*, 2H) H-3', H-4'; 3.75 (*s*, 3H) OCH_3; 3.69 (*m*, 1H) H-2'; 3.55 (m, 2H) H-5', H-5"; ^{13}C-NMR ($CDCl_3$) : 140.9 (*d*, J_{CH} = 186.5 Hz) C-6; 101.7 (*d*, J_{CH} = 178.8 Hz) C-5; 90.4 (*d*, J_{CH} = 172.9 Hz) C-1'; 87.3 (*s*) MMTr; 78.3 (*d*, J_{CH} = 150.7 Hz) C-4'; 76.4 (*d*, J_{CH} = 159.5 Hz) C-3'; 62.1 (*t*, J_{CH} = 143.8 Hz) C-5'; 55.1 (*s*) OCH_3; 51.0 (*d*, J_{CH} = 152.8 Hz) C-2'; MS (FAB$^-$): calc. for (M-H)$^-$ 655.1347, found 655.1367. Compound **3** : ^{1}H-NMR ($CDCl_3$) : 9.92 (*br*, 1H) NH; 8.13 (*d*, $J_{5,6}$ = 7.9 Hz, 1H) H-6; 7.57 - 6.82 (*m*, 19H) arom.; 6.04 (*d*, $J_{1',2'}$ = 6.1 Hz, 1H) H-1'; 5.20 (*d*, 1H) H-5; 4.72 (*br*, 1H) OH; 4.46 (*m*, 1H) H-2'; 3.94 - 3.86 (*m*, 2H) H-3', H-4'; 3.79 (*s*, 3H) OCH_3; 3.58 (*m*, 2H) H-5', H-5"; ^{13}C-NMR ($CDCl_3$) : 101.3 (*d*, J_{CH} = 178.6 Hz) C-5; 87.1 (*s*) MMTr; 84.8 (*d*, J_{CH} = 174.1 Hz) C-1'; 81.6 (*d*, J_{CH} = 148.2 Hz) C-4'; 76.0 (*d*, J_{CH} = 148.3 Hz) C-2'; 61.2 (*t*, J_{CH} = 142.7 Hz) C-5'; 55.1 (*q*) OCH_3; 43.6 (*d*, J_{CH} = 148.2 Hz) C-3'; MS (FAB$^-$): calc. for (M-H)$^-$ 655.1347, found 655.1292.

1-[5'-0-(4-Monomethoxytrityl)-3'-deoxy-3'-phenylseleno-2'-O-methanesulfonyl-β-D-arabinofuranosyl]uracil (4). To an ice bath cold solution of compound **3** (9.3 g, 13.9 mmol) in dry pyridine (130 ml) was added methylsulfonyl chloride (4.31 ml, 55.6 nmol) and the reaction was kept at 0 °C for 20 h. Water (2 ml) was added and the mixture allowed to stand at 0 °C for another hour. The reaction mixture was poured into an ice-water solution (1500 ml) slowly with vigorous stirring. The precipitate was filtered and washed generously with cold water till it was free of pyridine. The solid was dried to give compound **4** (9.1 g, 89 %). ^{1}H-NMR ($CDCl_3$) : 9.33 (*br*, 1H) NH; 7.78 (*d*, $J_{5,6}$ = 8.2 Hz, 1H) H-6; 7.65-6.84 (*m*, 19 H) arom., 6.19 (*d*, $J_{1',2'}$ = 4.8 Hz, 1H) H-1'; 5.36 (*d*, 1H) H-5; 5.22 (t, $J_{2',3'}$ = 5.4 Hz, 1H) H-2'; 4.01-3.81 (*m*, 2H) H-3', H-4'; 3.80 (*s*, 3H) OCH_3; 3.56 (*d*, $J_{4',5'}$ = 3.0 Hz, 2H) H-5',H-5"; 2.84 (*s*, 3H) mesyl; ^{13}C-NMR ($CDCl_3$) : 101.9 (*d*, J_{CH} = 177.4 Hz) C-5; 86.9 (*s*) MMTr; 82.5 (*d*, J_{CH} = 175.2) C-1'; 82.0 (*d*, J_{CH} = 158.3 Hz) C-4'; 81.0 (*d*, J_{CH} = 153.9 Hz) C-2'; 61.2 (*t*, J_{CH} = 145.0 Hz) C-5'; 55.0 (*s*) OCH_3; 42.6 (*d*, J_{CH} = 150.5 Hz) C-3'; 38.2 (*q*) mesyl; MS (FAB$^-$): calc. for (M-H)$^-$ 733.1125, found 733.1072.

1-[5'-O-(4-Monomethoxytrityl)-2',3'-dideoxy-3'-phenylseleno-β-D-glyceropent-2'-enofuranosyl]uracil (5). Potassium tert-butoxide (3.48 g, 310 μmol) was added in portions to a solution of compound **4** (9.1 g, 12,4 mmol) in dry dimethylformamide (70 ml) at 0 °C and the stirring was continued at room temperature for 4 h. The mixture was poured into a saturated aqueous solution of ammonium chloride (200 ml) which was extracted ethyl acetate (4 x 150 ml). The combined extract was dried over $MgSO_4$, evaporated and coevaporated with toluene to dryness. The residue was then separated on a silica gel column to give compound **5** (7.3 g, 92 %). ^{1}H-NMR ($CDCl_3$) : 8.68 (*br*, 1H) NH; 7.86 (*d*, $J_{5,6}$ = 8.0 Hz, 1H) H-6; 7.56 - 6.84 (*m*, 19 H) arom.; 6.93 (*dd*, $J_{1',2'}$ = 1.5 Hz, $J_{1',4'}$ = 3.4 Hz, 1H) H-1'; 5.46 (*t*, $J_{2',4'}$ = 2.0 Hz, 1H) H-2'; 4.83 (*m*, 2H) H-5,H-4'; 3.81 (*s*, 3H) OCH_3; 3.46 (*d*, $J_{4',5'}$ = 2.7 Hz, 2H) H-5',H-5"; ^{13}C-NMR ($CDCl_3$) : 101.9 (*d*, J_{CH} = 177.1 Hz) C-5; 88.9 (*d*, J_{CH} = 173.3 Hz) C-1'; 87.4 (*d*, J_{CH} = 148.9 Hz) C-4'; 87.0 (*s*) MMTr; 62.9 (*t*, J_{CH} = 146.0 Hz) C-5'; 55.1 (*q*) OCH_3; MS (FAB$^-$): calc. for (M-H)$^-$ 637.1245, found 637.1251.

1-[5'-O-(4-Monomethoxytrityl)-2',3'-dideoxy-3'-phenylselenonyl-β-D-glyceropent-2'-enofuranosyl]uracil (6). To a solution of compound **5** (7.3 g, 11.4 mmol) in dry methanol (100 ml) was added m-chloroperbenzoic acid (6.03 g, 29.8 mmol) at 0 °C and the reaction was allowed to stir at room temperature overnight. The mixture was poured into a saturated ice cold solution of sodium bicarbonate (300 ml) with vigorous stirring. The precipitate was filtered and washed with sodium bicarbonate solution (2 x 100 ml) and then water (2 x 100 ml). The dry solid was further purified on a silica gel column to give compound **6** (6.37 g, 83 %). ^{1}H-NMR ($CDCl_3$) : 9.34 (*br*, 1H) NH; 7.68 - 6.79 (*m*, 22H) arom., H-6, H-1', H2'; 5.20 (*m*, 1H) H-4'; 4.56 (*d*, $J_{5,6}$ = 7.8 Hz, 1H) H-5; 3.82 (*m*, 2H) H-5', H-5"; 3.78 (*s*, 3H) OCH_3; ^{13}C-NMR ($CDCl_3$) : 102.6 (*d*, J_{CH} = 178.2 Hz) C-5; 88.0 (*d*, J_{CH} = 174.6 Hz) C-1'; 87.4 (*s*) MMTr; 84.4 (*d*, J_{CH} = 159.9 Hz) C-4'; 62.4 (*t*, J_{CH} = 142.8 Hz) C-5'; 55.1 (*q*) OCH_3; MS (FAB$^-$): calc. for (M-H)$^-$ 669.1140, found 669.1158.

1-(2',3'-Dideoxy-3'-phenylselenonyl-β-D-glyceropent-2'-enofuranosyl)uracil (7). Compound **6** (1.34 g, 2 mmol) was treated with 80% aqueous acetic acid (40 ml) at room temperature for 5 h. All volatile materials were removed in vacuuo. Residual acetic acid was removed by repeated coevaporations with ethanol and toluene. The residue was purified on a silica gel column to afford compound **7** (0.77 g, 97 %). ^{1}H-NMR ($CDCl_3$ + CD_3OD) : 8.10 - 7.70 (*m*, 6H) H-6, Ph; 7.05 (*dd*, $J_{1',2'}$ = 1.7 Hz, $J_{1',4'}$ = 3.9 Hz, 1H) H-1'; 6.80 (*t*, $J_{2',4'}$= 1.9 Hz, 1H) H-2'; 5.72 (*d*, $J_{5,6}$ = 8.4 Hz, 1H) H-5; 5.18 (*m*, $J_{4',5'}$ = 2.2 Hz, $J_{4',5"}$ = 2.0 Hz, 1H) H-4'; 4.12 (*dd*, $J_{5',5"}$ = 13.4 Hz, 1H) H-5'; 3.89 (*dd*, 1H) H-5"; ^{13}C-NMR ($CDCl_3$+CD_3OD) : 102.6 (*d*, J_{CH} = 179.7 Hz) C-5; 87.7 (*d*, J_{CH} = 172.7 Hz) C-1'; 86.0 (*d*, J_{CH} = 152.8 Hz) C-4'; 61.3 (*t*, J_{CH} = 144.3 Hz) C-5'; MS (FAB$^-$): calc. for (M-H)$^-$ 396.9939, found 396.9980.

1-[5'-O-(4-Monomethoxytrityl)-2',3'-dideoxy-2',3'-epimino-β-D-ribofuranosyl]uracil (8a). Compound **6** (469 mg, 0.7 mmol) was treated with aqueous ammonia (32 %, 3 ml) in dimethylformamide (3 ml) at room temperature overnight. All volatile matters were removed by evaporation and coevaporation with toluene under vacuum. The residue was then separated on a silica gel column to give compound **8a** (135 mg, 39 %). ^{1}H-NMR ($CDCl_3$) : 7.57 (*d*, $J_{5,6}$ = 8.0 Hz, 1H) H-6; 7.30 - 6.82 (*m*, 14H) arom.; 5.93 (*s*, 1H) H-1'; 5.17 (*d*, 1H) H-5; 4.37 (*t*, $J_{4',5'}$= 4.9 Hz,, 1H) H-4'; 3.31 (*t*, 2H) H-5', H-5"; 3.18, 3.11 (2 x *d*, $J_{2',3'}$ = 4.0 Hz, 2H) H-2',H-3'; ^{13}C-NMR ($CDCl_3$) : 101.8 (*d*, J_{CH} = 179.7 Hz) C-5; 86.9 (*s*) MMTr; 86.4 (*d*, J_{CH} = 175.2 Hz) C-1'; 81.8 (*d*, J_{CH} = 158.4 Hz) C-4'; 64.1 (*t*, J_{CH} = 142.1 Hz) C-5'; 55.1 (*q*) OCH_3; 39.7, 37.9 (2 x d, J_{CH} = 187.4 Hz) C-2',C-3'; MS (FAB$^-$): calc. for (M-H)$^-$ 496.1873, found 496.1837.

1-[5'-O-(4-Monomethoxytrityl)-2',3'-dideoxy-2',3'-(N-methyl)epimino-β-D-ribofuranosyl]-uracil (8b). Compound **6** (335 mg, 0.5 mmol) was treated with aqueous methylamine (40 %, 3 ml) in tetrahydrofuran (3 ml) at room temperature for 2 h. All volatile matters were removed under vacuum and the residue was coevaporated with toluene to dryness. The mixture was separated on a silica gel column to give compound **8b** (195 mg, 76 %). ^{1}H-NMR ($CDCl_3$): 7.70 (*d*, $J_{5,6}$ = 8.0 Hz, 1H) H-6; 7.29-6.85 (*m*, 14H) arom.; 5.90 (*s*, 1H) H-1'; 5.11 (*d*, 1H) H-5; 4.33 (*t*, $J_{4',5'}$= 4.2 Hz, $J_{4',5"}$ = 4.4 Hz, 1H) H-4'; 3.80 (*s*, 3H) OCH_3; 3.34 (*m*, 2H) H-5', H5"; 2.69, 2.55 (2 x *d*, $J_{2',3'}$ = 4.6 Hz, 2H) H-2', H-3'; 2.42 (*s*, 3H) NCH_3; ^{13}C-NMR ($CDCl_3$): 101.5 (*d*, J_{CH} = 177.0 Hz) C-5; 87.0 (*s*) MMTr; 86.2 (*d*, J_{CH} = 174.6 Hz) C-1'; 81.7 (*d*, J_{CH} = 152.7 Hz) C-4'; 64.0 (*t*, J_{CH} = 142.8 Hz) C-5'; 55.1 (*q*) OCH_3; 49.6, 47.0 (2 x *d*, J_{CH} = 183.0 Hz, J_{CH} = 181.2 Hz) C-2', C-3'; 44.3 (*q*) NCH_3; MS (FAB$^-$): calc. for (M-H)$^-$ 510.2029, found 510.2033.

1-[5'-O-(4-Monomethoxytrityl)-2',3'-dideoxy-2',3'-(N-benzyl)epimino-β-D-ribofuranosyl]-uracil (8c). Compound **6** (335 mg, 0.5 mmol) was treated with benzylamine (546 µl, 5 mmol) in tetrahydrofuran (5 ml) at room temperature for 3 h. The reaction mixture was partitioned between saturated aqueous ammonium chloride (20 ml) and ethyl acetate (50 ml). The organic phase was washed with water (2 x 20 ml) and then evaporated to dryness. The residue was separated on a silica gel column to give compound **8c** (225 mg, 77 %). ^{1}H-NMR ($CDCl_3$) : 7.68 (*d*, $J_{5,6}$ = 8.3 Hz, 1H) H-6; 7.33 - 6.83 (*m*, 14H) arom.; 5.95 (*s*, 1H) H-1'; 5.11 (*d*, 1H) H-5; 4.34 (*m*, $J_{4',5'}$ = 4.3 Hz, $J_{4',5"}$ = 4.5 Hz, 1H) H-4'; 3.80 (*s*, 3H) OCH_3; 3.58 (2 x *s*, 2H) NCH_2Ph; 3.34 (*m*, 2H) H-5', H-5"; 2.89, 2.74 (2 x *d*, $J_{2',3'}$ = 4.9 Hz, 2H) H-2',H-3'; ^{13}C-NMR ($CDCl_3$) : 101.6 (*d*, J_{CH} = 179.7 Hz) C-5; 87.0 (*s*) MMTr; 86.3 (*d*, J_{CH} = 175.2 Hz) C-1'; 81.8 (*d*, J_{CH} = 152.8 Hz) C-4'; 64.0 (*t*, J_{CH} = 142.7 Hz) C-5'; 61.0 ((*t*, J_{CH} = 137.6 Hz) NCH_2Ph; 55.1 (*q*) OCH_3; 48.7,46.2 (2 x *d*, J_{CH} = 182.0 Hz) C-2', C-3'; MS (FAB$^-$): calc. for (M-H)$^-$ 586.2342, found 586.2372.

1-[5'-O-(4-Monomethoxytrityl)-2',3'-dideoxy-2',3'-(N-glycine methyl ester)epimino-β-D-ribofuranosyl]uracil (8d). To a solution of methyl glycinate hydrochloride (125 mg, 1 mmol) and triethylamine (101 mg, 1 mmol) in dry dimethylsulfoxide (2 ml) was added compound **6** (134 mg, 0.2 mmol) and the stirring was continued for 2 h at room temperature. The reaction mixture was poured into water (50 ml). The precipitate was filtered and washed with water (50 ml). The dry solid was purified on a silica gel column to give compound **8d** (80 mg, 70 %). ^{1}H-NMR ($CDCl_3$) : 7.66 (*d*, $J_{5,6}$ = 8.1 Hz, 1H) H-6; 7.34 - 6.85 (*m*, 14H) arom.; 5.94 (*s*, 1H) H-1'; 5.10 (*d*, 1H) H-5; 4.43 (*t*, $J_{4',5'}$ = 4.0 Hz, $J_{4',5"}$ = 4.1 Hz, 1H) H-4';

3.79, 3.77 (2 x *d*, 6H) 2 x OCH_3; 3.39 (*m*, 2H) H-5', H-5"; 3.33, 3.15 (2 x *s*, 2H) $NCH_2CO_2CH_3$; 2.93, 2.76 (2 x *d*, $J_{2',3'}$ = 4.9 Hz, 2H) H-2', H-3'; ^{13}C-NMR ($CDCl_3$) : 101.7 (*d*, J_{CH} = 178.2 Hz) C-5; 87.1 (*s*) MMTr; 86.5 (*d*, J_{CH} = 179.0 Hz) C-1'; 81.8 (*d*, J_{CH} = 158.1 Hz) C-4'; 63.8 (*t*, J_{CH} = 141.5 Hz) C-5'; 57.6 (*t*, J_{CH} = 163 Hz) NCH_2COCH_3; 55.1 (*q*) OCH_3 (MMTr); 52.0 (*q*) CO_2CH_3, 48.4,46.5 (2 x *d*, J_{CH} = 181.9 Hz, J_{CH} = 175.8 Hz) C-2', C-3'; MS (FAB^-): calc. for $(M-H)^-$ 568.2084, found 568.2086.

1-[5'-O-(4-Monomethoxytrityl)-3'-deoxy-3'-(N,N-dimethylamino)-2,2'-O-anhydro-β-D-arabinofuranosyl]uracil (10a). Compound **6** (134 mg, 0.2 mmol) was treated with aqueous dimethylamine (1 ml) in tetrahydrofuran (1 ml) at room temperature for 15 min. The reaction mixture was evaporated and coevaporated with toluene to dryness. The residue was separated on a silica gel column to give compound **10a** (91 mg, 87 %). ^{1}H-NMR ($CDCl_3$) : 7.36 - 8.30 (*m*, 15 H) H-6, arom.; 6.09 (*d*, $J_{1',2'}$ = 5.9 Hz, 1H) H-1'; 5.92 (*d*, $J_{5,6}$ = 8.3 Hz, 1H) H-5; 5.30 (*dd*, $J_{2',3'}$ = 1.5 Hz, 1H) H-2'; 4.42 (*m*, $J_{3',4'}$ = 3.2 Hz, $J_{4',5'}$= 5.9 Hz, 1H) H-4'; 3.80 (*s*, 3H) OCH_3; 3.35 (*dd*, 1H) H-3'; 3.01 (*d*, 2H) H-5', H-5"; 2.28 (*s*, 6H) $N(CH_3)_2$; ^{13}C-NMR ($CDCl_3$) : 143.5 (*d*, J_{CH} = 191.0 Hz) C-6; 109.9 (*d*, J_{CH} = 173.0 Hz) C-5; 90.3 (*d*, J_{CH} = 177.5 Hz) C-1'; 86.4 (*s*) MMTr; 84.0 (*d*, J_{CH} = 165.0 Hz) C-2'; 81.9 (*d*, J_{CH} = 152.8 Hz) C-4'; ; 71.5 (*d*, J_{CH} = 141.5 Hz) C-3'; 63.8 (*t*, J_{CH} = 142.1 Hz) C-5'; 55.1 (*q*) OCH_3; 41.8 (*q*) NCH_3; MS (FAB^-): calc. for $(M-H)^-$ 524.2186, found 524.2179.

1-[5'-O-(4-Monomethoxytrityl)-3'-deoxy-3'-pyrrolidino-2,2'-O-anhydro-β-D-arabinofuranosyl]uracil (10b). Compound **6** (335 mg, 0.5 mmol) was treated with pyrrolidine (206 µl, 2.5 mmol) in tetrahydrofuran (5 ml) at room temperature for 1.5 h. The reaction mixture was evaporated to dryness. The residue was separated on a silica gel column to give compound **10b** (201 mg, 73 %). ^{1}H-NMR ($CDCl_3$) : 7.55 - 6.81 (*m*, 15H) H-6, arom.; 6.11 (*d*, $J_{1',2'}$ = 5.9 Hz, 1H) H-1'; 5.98 (*d*, $J_{5,6}$ = 7.6 Hz, 1H) H-5; 5.32 (*dd*, $J_{2',3'}$ = 1.7 Hz, 1H) H-2'; 4.43 (*m*, $J_{3',4'}$ = 3.9 Hz, $J_{4',5'}$= 5.6 Hz, 1H) H-4'; 3.80 (*s*, 3H) OCH_3; 3.34 (*dd*, 1H) H-3'; 3.07 (*d*, 2H) H-5', H-5"; 2.57 (*br*, 4H) NCH_2; 1.78 (*br*, 4H) NCH_2CH_2; ^{13}C-NMR ($CDCl_3$) : 100.0 (*d*, J_{CH} = 171.9 Hz) C-5; 90.1 (*d*, J_{CH} = 179.7 Hz) C-1'; 86.5 (*s*) MMTr; 85.7 (*d*, J_{CH} = 161.2 Hz) C-2'; 83.6 (*d*, J_{CH} = 152.8) C-4'; 69.9 (*d*, J_{CH} = 140.7) C-3'; 63.4 (*t*, J_{CH} = 138.7 Hz) C-5'; 55.1 (*q*) OCH_3; 51.3 (*t*) NCH_2; 23.1 (*t*) NCH_2CH_2; MS (FAB^+): calc. for $(M+H)^+$ 552.2499, found 552.2537.

1-[5'-O-(4-Monomethoxytrityl)-3'-deoxy-3'-morpholino-2,2'-O-anhydro-β-D-arabinofuranosyl]uracil (10c) and 1-[5'-O-(4-monomethoxytrityl)-2',3'-dideoxy-2'-morpholino-3'-phenylseleno-β-D-glyceropent-2'-enofuranosyl]uracil (12a). Compound **6** (200 mg, 0.3 mmol) was treated with morpholine (260 µl, 3 mmol) in tetrahydrofuran (3 ml) at room temperature overnight. Saturated aqueous ammonium chloride solution (1 ml) was added and stirring was continued for another 0.5 h. The reaction mixture was evaporated and coevaporated with toluene, ethanol. The residue was partitioned between water (30 ml) and dichloromethane (50 ml). The organic phase was separated and evaporated to dryness. The residue was separated on a silica gel column to give compound **10c** (76 mg, 45 %).and compound **12a** (55 mg, 25 %). Compound **10c**: ^{1}H-NMR ($CDCl_3$) 7.28-6.80 (*m*, 15H) H-6, arom.; 6.08 (*d*, $J_{1',2'}$ = 6.1 Hz, 1H) H-1'; 5.90 (*d*, $J_{5,6}$ = 8.1 Hz, 1H) H-5; 5.34 (*dd*, $J_{2',3'}$ = 1.4 Hz, 1H) H-2'; 4.43 (*m*, $J_{3',4'}$ = 3.7 Hz, $J_{4',5'}$= 6.1 Hz 1H) H-4'; 3.80 (*s*, 3H) OCH_3; 3.69 (*t*, 4H) OCH_2; 3.36 (*dd*, 1H) H-3'; 3.03 (*d*, 2H) H-5', H-5"; 2.48 (*m*, 4H) NCH_2; ^{13}C-NMR ($CDCl_3$) : 110.6 (*d*, J_{CH} = 172.9 Hz) C-5; 90.2 (*d*, J_{CH} = 183.1 Hz) C-1'; 86.6 (*s*) MMTr; 84.1 (*d*, J_{CH} = 160.6 Hz) C-2'; 81.5 (*d*, J_{CH} = 149.4 Hz) C-4'; 71.5 (*d*, J_{CH} = 140.7 Hz) C-3'; 66.5 (*t*) OCH_2; 63.8 (*t*, J_{CH} = 142.1 Hz) C-5'; 55.1 (*q*) OCH_3; 49.9 (*t*) NCH_2; MS (FAB^-): calc. for $(M-H)^-$ 566.2291, found 566.2314.

Compound **12a** : ^{1}H-NMR ($CDCl_3$) 9.08 (*br*, 1H) NH; 7.94 (*d*, $J_{5,6}$ = 8.1 Hz, 1H) H-6; 7.35-6.82 (*m*, 19H) arom.; 7.07 (*d*, $J_{1',4'}$ = 2.4 Hz, 1H) H-1'; 4.91 (*d*, 1H) H-5; 4.80 (*d*, 1H) H-4'; 3.80 (*s* 3H) OCH_3; 3.48-3.28 (*m*, 10H) H-5',H-5", morpholinyl; ^{13}C-NMR ($CDCl_3$) : 102.5 (*d*, J_{CH} = 178.6 Hz) C-5; 94.4 (*s*) C-2'; 87.5 (*d*, J_{CH} = 152.8 Hz) C-4'; 86.1 (*d*, J_{CH} = 170.7 Hz) H-1'; 66.6 (*t*) OCH_2; 63.6 (*t*, J_{CH} = 143.8 Hz) C-5'; 55.1 (*q*) OCH_3; 48.3 (*t*) NCH_2; MS (FAB^-): calc. for $(M-H)^-$ 722.1769, found 722.1780.

1-[5'-O-(4-Monomethoxytrityl)-2',3'-dideoxy-2',3'-(1-nitro)cyclopropane-β-D-ribofuranosyl]uracil (14). Potassium tert-butoxide (289 mg, 2.58 mmol) was added to nitromethane (20 ml) and the stirring was continued for 15 min at room temperature. The reaction mixture was cooled in an ice-water bath and compound **6** (860 mg, 1.28 mmol) was added. After 15 min, the bath was removed and the reaction was stirred at room temperature for 2 h. The reaction mixture was poured into a saturated aqueous solution of ammonium chloride (50 ml), which was extracted with dichloromethane (2 x 50 ml). The combined extract was dried over $MgSO_4$ and evaporated to dryness. The residue was separated on a silica column to give compound **14** (450 mg, 65 %). ^{1}H-NMR ($CDCl_3$) : 9.38 (*br*, 1H) NH; 7.55 (*d*, $J_{5,6}$ = 8.1 Hz, 1H) H-6; 7.35 - 6.84 (*m*, 14H) arom.; 6.11 (*s*, 1H) H-1'; 5.18 (*d*, 1H) H-5; 4.47 (*t*, $J_{4',5'}$= 4.7 Hz, $J_{4',5''}$ = 4.9 Hz, 1H) H-4'; 4.21 (*t*, J

= 2.2 Hz, 1H) $CHNO_2$; 3.80 (*s*, 3H) OCH_3; 3.33 (*m*, $J_{5',5''}$ = 10.3 Hz, 2H) H-5',H-5"; 3.06 (*m*, $J_{2',3'}$= 7.8 Hz; 1H) H-2',H-3'; ^{13}C-NMR ($CDCl_3$) : 102.3 (*d*, J_{CH} = 177.5 Hz) C-5; 87.2 (*s*) MMTr; 86.3 (*d*, J_{CH} = 177.5 Hz) C-1'; 82.3 (*d*, J_{CH} = 153.9 Hz) C-4'; 64.4 (*t*, J_{CH} = 142.7 Hz) C-5'; 61.2 (*d*, J_{CH} = 195.5 Hz) $CHNO_2$; 55.1 (*q*) OCH_3; 33.8, 31.9 (2 x *d*, J_{CH} = 181.8 Hz, J_{CH} = 171.8 Hz) C-2', C-3'; MS (FAB$^-$): calc. for (M-H)$^-$ 540.1771, found 540.1801.

1-[5'-O-(4-Monomethoxytrityl)-2',3'-dideoxy-2',3'-(1,1-dicarboxymethyl)cyclopropane-β-D-ribofuranosyl]uracil (15). Potassium tert-butoxide (112 mg, 1 mmol) was added to dimethylmalonate (5 ml) and the stirring was continued for 15 min at room temperature. The reaction mixture was cooled in an ice-water bath and compound **6** (335 mg, 0.5 mmol) was added. The reaction was kept at 0 °C for 1.5 h and the mixture was then poured into a saturated aqueous solution of ammonium chloride (50 ml), which was extracted by dichloromethane (2 x 50 ml). The combined extract was dried over $MgSO_4$. All volatile matters were removed under vacuum. The residue was separated on a silica gel column to give compound **15** (180 mg, 59 %). ^{1}H-NMR ($CDCl_3$) : 9.01 (*br*, 1H) NH; 7.64 - 6.82 (*m*, 15H) H-6, arom.; 6.11 (*s*, 1H) H-1'; 5.18 (*d*, $J_{5,6}$ = 8.1 Hz, 1H) H-5; 4.62 (*t*, $J_{4',5'}$ = 6.6 Hz, $J_{4',5''}$ = 5.8 Hz, 1H) H-4'; 3.85, 3.80, 3.77 (3 x *s*, 9H) 3 x OCH_3; 3.21 (*m*, 2H) H-5', H-5"; 2.69 (2 x *d*, $J_{2',3'}$ = 6.3 Hz, 2H) H-2', H-3'; ^{13}C-NMR ($CDCl_3$) : 101.9 (*d*, J_{CH} = 178.2 Hz) C-5; 87.0 (*s*) MMTr; 86.0 (*d*, J_{CH} = 170.9 Hz) C-1'; 80.1 (*d*, J_{CH} = 156.7 Hz) C-4'; 64.8 (*t*, J_{CH} = 144.0 Hz) C-5'; 55.1, 53.3, 53.1 (3 x q) 3 x OCH_3; 35.8 (*s*)$C(CO_2CH_3)_2$; 34.9, 33.6 (2 x *d*, J_{CH} = 179.4 Hz, J_{CH} = 180.7 Hz) C-2', C-3'; MS (FAB$^-$): calc. for (M-H)$^-$ 611.2029, found 611.2073.

1-[5'-O-(4-Monomethoxytrityl)-2',3'-dideoxy-2',3'-(1-acetophenyl)cyclopropane-β-D-ribofuranosyl]uracil (16). Potassium tert-butoxide (112 mg, 1 mmol) was added to acetophenone (5 ml) at room temperature and the stirring was continued for 15 min. The reaction mixture was cooled in an ice-water bath and compound **6** (335 mg, 0.5 mmol) was added. After 30 min, the bath was removed and allowed the reaction to proceed at room temperature overnight. The mixture was poured into a saturated aqueous solution of ammonium chloride (50 ml) which was extracted with dichloromethane (2 x 50 ml). The combined extract ws dried over $MgSO_4$. All volatile matters were removed unded vacuum. The residue was separated on a silica gel column to give compound **16** (55 mg, 18 %). ^{1}H-NMR ($CDCl_3$) : 9.06 (*br*, 1H) NH; 8.01-6.83 (*m*, 20H) H-6,arom.; 6.24 (*s*, 1H) H-1'; 5.14 (*d*, $J_{5,6}$ = 8.1 Hz, 1H) H-5; 4.47 (*t*, $J_{4',5'}$ = 4.9 Hz, $J_{4',5''}$ = 5.1 Hz, 1H) H-4; 3.79 (*s*, 3H) OCH_3; 3.38 (*dd*, $J_{5',5''}$ = 10.4 Hz, 1H) H-5'; 3.14 (*dd*, 1H) H-5"; 2.80 - 2.53 (*m*, 3H) H-2', H-3' & *CH*COPh; ^{13}C-NMR ($CDCl_3$) : 102.1 (*d*, J_{CH} = 178.6 Hz) C-5; 87.0 (*s*) MMTr; 86.7 (*d*, J_{CH} = 174.1 Hz) C-1'; 82.8 (*d*, J_{CH} = 153.9 Hz) C-4'; 65.1 (*t*, J_{CH} = 142.7 Hz) C-5'; 55.1 (*q*) OCH_3; 33.5, 32.5 (2 x *d*, J_{CH} = 180.9 Hz, J_{CH} = 185.4 Hz) C-2', C-3'; 28.9 (*d*, J_{CH} = 168.5 Hz) *CH*COPh; MS (FAB$^-$): calc. for (M-H)$^-$ 599.2182, found 599.2183.

2'-Deoxy-2',3'-*ribo*-fused (bicyclo[3.3.0] system) furano derivative 19 Potassium tert-butoxide (112 mg, 0.5 mmol) was added to methyl acetoacetate (5 ml) and the stirring was continued for 10 min at room temperature. The reaction mixture was cooled in an ice-water bath and compound **6** (335 mg, 0.5 mmol) was added. After 0.5 h, the mixture was poured into a saturated aqueous solution of ammonium chloride (50 ml), which was extracted with dichloromthane (2 x 50 ml). The combined extract was dried over $MgSO_4$. All volatile matters were removed under vacuum. The residue was separated on a silica gel column to give compound **19** (220 mg, 74 %). ^{1}H-NMR ($CDCl_3$) : 9.12 (*br*, 1H) NH; 7.34 - 6.82 (*m*, 15H) H-6, arom.; 5.95 (*d*, $J_{1',2'}$ = 3.9 Hz, 1H) H-1'; 5.50 (*d*, $J_{5,6}$ = 7.8 Hz, 1H) H-5; 5.25 (*dd*, $J_{2',3'}$ = 4.7 Hz; $J_{3',4'}$ = 10.0 Hz, 1H)H-3'; 4.12 (dt, $J_{4',5'}$ = 4.2 Hz, 1H) H-4'; 3.93 (*m*, 1H) H-2'; 3.79,3.69 (2 x *s*, 6H) 2 x OCH_3; 3.51 (*d*, 2H) H-5', H-5"; 2.22 (*d*, $J_{2',CH3}$ = 1.2 Hz, 3H) CH_3; ^{13}C-NMR ($CDCl_3$) : 168.8 (*s*) CO_2CH_3; 102.5 (*d*, J_{CH} = 175.7 Hz) C-5; 93.1 (*d*, J_{CH} = 169.7 Hz) C-1'; 86.8 (*s*) MMTr; 85.6 (*d*, J_{CH} = 157.2 Hz) C-3'; 85.6 (*d*, J_{CH} = 157.2 Hz) C-4'; 63.3 (*t*, J_{CH} = 144.0 Hz) C-5'; 55.1 (*q*) OCH_3; 54.0 (J_{CH} = 142.8 Hz) C-2'; 51.2 (*q*) CO_2CH_3; 14.0 (*q*) CH_3; MS (FAB$^-$): calc. for (M-H)$^-$ 595.2081, found 595.2112.

General procedure for the removal of 5'-O-MMTr group from 8a-d, 10a-c, 14, 15 and 19. Compounds **8a-d, 10a-c, 14, 15** and **19** were treated with 80% aqueous acetic acid (ca. 30 ml / mmol) at room temperature. The reaction was followed by TLC [**8a-d** and **10a-b** took ca. 20 h while **14, 15** and **19** took ca 5 h for completion). All volatile matters were removed in vacuum. Residual acetic acid was removed by repeated coevaporations with ethanol and toluene. The residue was separated by silica gel column chromatography or by preparative TLC to give compound **9a-d, 11a-c, 17, 18** and **20**, respectively.

Compound **9a** (yield 63 %). ^{1}H-NMR (CD_3OD) : 7.83 (*d*, $J_{5,6}$ = 8.3 Hz, 1H) H-6; 6.36 (*d*, $J_{1',2'}$ = 5.7 Hz, 1H) H-1'; 6.03 (*d*, 1H) H-5; 5.21 (*dd*, $J_{2',3'}$= 1.0 Hz, 1H) H-2'; 4.10 (*m*, $J_{3',4'}$ = 2.9 Hz, $J_{4',5'}$ = 4.2 Hz, 1H) H-4'; 3.80 (*dd*, 1H) H-3'; 3.48 (*d*, 2H) H-5', H-5"; ^{13}C-NMR (CD_3OD) : 139.1 (*d*, J_{CH} = 193.2 Hz) C-6; 110.0 (*d*, J_{CH} = 176.3 Hz) C-5; 92.7 (*d*, J_{CH} = 187.5 Hz) C-1'; 92.2 (*d*, J_{CH} = 167.3 Hz) C-2'; 91.8 (*d*, J_{CH} = 148.2 Hz) C-4'; 63.2 (*t*, J_{CH} = 141.5 Hz) C-5'; 59.7 (*d*, J_{CH} = 147.1 Hz) C-3'; UV (H_2O): λ_{max} 223, 252 nm

(pH 2), 223, 252 nm (pH 7), 223, 252 nm (pH 12); MS (FAB^+): calc. for $(M+H)^+$ 226.0828, found 226.0834.

Compound **9b** (yield 71 %). ^{1}H-NMR (DMSO-d_6) : 7.83 (*d*, $J_{5,6}$ = 7.8 Hz, 1H) H-6; 6.25 (*d*, $J_{1',2'}$ = 5.6 Hz, 1H) H-1'; 5.84 (*d*, 1H) H-5; 5.21 (*d*, 1H) H-2'; 4.02 (*m*, 1H) H-4'; 3.31 (*br*, 5H) H-3',H-5', H5", NH, OH; 2.35 (*s*, 3H) NCH_3; ^{13}C-NMR (DMSO-d_6) : 137.0 (*d*, J_{CH} = 187.6 Hz) C-6; 108.6 (*d*, J_{CH} = 171.9 Hz) C-5; 90.3 (*d*, J_{CH} = 176.4 Hz) C-1'; 87.3 (*d*, J_{CH} = 170.8 Hz) C-2'; 86.9 (*d*, J_{CH} = 152.1 Hz) C-4'; 66.5 (*d*, J_{CH} = 139.3 Hz) C-3'; 61.8 (*t*, J_{CH} = 141.0 Hz) C-5'; 34.1 (*q*) NCH_3; UV (H_2O): λ_{max} 223, 252 nm (pH 2), 223, 252 nm (pH 7), 223, 252 nm (pH 12); MS (FAB^+): calc. for $(M+H)^+$ 240.0984, found 240.0984.

Compound **9c** (yield 60 %). ^{1}H-NMR (DMSO-d_6) : 7.95 (*d*, $J_{5,6}$ = 7.6 Hz,, 1H) H-6; 7.46 (*m*, 5H) Ph; 6.39 (*d*, $J_{1',2'}$ = 5.9 Hz, 1H) H-1'; 5.96 (*d*, 1H) H-5; 5.41 (*d*, 1H) H-2'; 5.06 (*t*, 1H) OH; 4.24 (*m*, 1H) H-4'; 3.91 (*s*, 2H) CH_2Ph; 3.49 - 3.27 (*m*, 4H) H-3', H-5', H-5", NH; ^{13}C-NMR (DMSO-d_6) : 137.5 (*d*, J_{CH} = 187.6 Hz) C-6; 108.9 (*d*, J_{CH} = 176.6 Hz) C-5; 90.7 (*d*, J_{CH} = 183.1 Hz) C-1'; 87.7 (2 x *d*, J_{CH} = 145.7 Hz, J_{CH} 157.3 Hz) C-2', C-4'; 64.1 (*d*, J_{CH} = 143.7 Hz) C-3'; 61.9 (*t*, J_{CH} = 139.9 Hz) C-5'; 51.1 (*t*) NCH_2Ph; UV (H_2O): λ_{max} 223 (sh), 249 nm (pH 2), 223 (sh), 251 nm (pH 7), 223 (sh), 252 nm (pH 12); MS (FAB^-): calc. for $(M-H)^-$ 314.1141, found 314.1101.

Compound **9d** (yield 76 %). ^{1}H-NMR (CD_3OD + $CDCl_3$) : 7.70 (*d*, $J_{5,6}$ = 7.8 Hz, 1H) H-6; 6.25 (*d*, $J_{1',2'}$ = 6.0 Hz, 1H) H-1'; 5.96 (*d*, 1H) H-5; 5.27 (*d*, 1H) H-2'; 4.10 (*m*, 1H) H-4'; 3.66 (*s*, 3H) CO_2CH_3; 3.53 - 3.26 (*m*, 5H) H-3', H-5', H-5", NCH_2; ^{13}C-NMR (CD_3OD + $CDCl_3$) : 138.6 (*d*, J_{CH} = 187.9 Hz) C-6; 109.9 (*d*, J_{CH} = 175.6 Hz) C-5; 92.4 (*d*, J_{CH} = 186.7 Hz) C-1'; 89.6, 89.4 (2 x *d*, J_{CH} = 163.6 Hz, J_{CH} = 152.6 Hz) C-2',C-4'; 66.0 (*d*, J_{CH} = 138.0 Hz) C-3'; 63.1 (*t*, J_{CH} = 141.5 Hz) C-5'; 52.7 (*q*) CO_2CH_3; 49.0 (*t*) $CNCH_2CO_2CH_3$; UV (H_2O): λ_{max} 223, 251 nm (pH 2), 223, 252 nm (pH 7), 223, 252 nm (pH 12); MS (FAB^-): calc. for $(M-H)^-$ 296.0883, found 296.0863.

Compound **11a** (yield 84 %). ^{1}H-NMR (D_2O) : 7.91 (*d*, $J_{5,6}$ = 7.6 Hz, 1H) H-6; 6.53 (*d*, $J_{1',2'}$ = 6.1 Hz, 1H) H-1'; 6.20 (*d*, 1H) H-5; 5.76 (*d*, 1H) H-2'; 4.60 (*m*, $J_{3',4'}$ = 2.6 Hz, $J_{4',5'}$ = 2.4 Hz,1H) H-4'; 3.85 (*d*, 1H) H-3', 3.59 (*t*, 2H) H-5', H-5"; 2.50 (*s*, 6H) $N(CH_3)_2$; ^{13}C-NMR (D_2O) : 139.7 (*d*, J_{CH} = 189.9 Hz) C-6; 110.3 (*d*, J_{CH} = 178.6 Hz) C-5; 93.0 (*d*, J_{CH} = 186.5 Hz) C-1'; 85.9 (*d*, J_{CH} = 168.4 Hz) C-4'; 85.6 (*d*, J_{CH} = 174.1 Hz) C-2'; 72.4 (*d*, J_{CH} = 147.1 Hz) C-3'; 63.5 (*t*, J_{CH} = 143.3 Hz) C-5'; 41.8 (*q*) NCH_3; UV (H_2O): λ_{max} 223, 250 nm (pH 2), 223, 251 nm (pH 7), 223, 251 nm (pH 12); MS (FAB^-): calc. for $(M-H)^-$ 252.0984, found 252.0970.

Compound **11b** (yield 64 %): ^{1}H-NMR (DMSO-d_6) : 7.80 (*d*, $J_{5,6}$ = 7.6 Hz, 1H) H-6; 6.27 (*d*, $J_{1',2'}$ = 6.1 Hz, 1H) H-1'; 5.85 (*d*, 1H) H-5; 5.45 (*d*, 1H) H-2'; 4.97 (*t*, 1H) OH; 4.30 (*m*, 1H) H-4'; 3.32 (*m*, 3H) H-3', H-5', H-5"; 2.56 (*br*, 4H) NCH_2; 1.72 (*br*, 4H) NCH_2CH_2; ^{13}C-NMR (DMSO-d_6) : 136.8 (*d*, J_{CH} = 186.5 Hz) C-6; 108.7 (*d*, J_{CH} = 171.9 Hz) C-5; 90.3 (*d*, J_{CH} = 183.1 Hz) C-1'; 85.4 (*d*, J_{CH} = 172.0 Hz)C-2'; 84.8 (*d*, J_{CH} = 148.3 Hz) C-4'; 68.9 (*d*, J_{CH} = 143.8 Hz) C-3'; 62.0 (*t*, J_{CH} = 139.3 Hz) C-5'; 50.4 , 23.1 (2 x *t*) pyrrolidinyl; UV (H_2O): λ_{max} 222, 252 nm (pH 2), 222, 252 nm (pH 7), 222, 252 nm (pH 12); MS (FAB^-): calc. for $(M-H)^-$ 278.1141, found 278.1131.

Compound **11c** (yield 73 %). ^{1}H-NMR (CD_3OD + D_2O) : 7.86 (*d*, $J_{5,6}$ = 7.6 Hz, 1H) H-6; 6.42 (*d*, $J_{1',2'}$ = 6.1 Hz, 1H) H-1'; 6.14 (*d*, 1H) H-5; 5.71 (*d*, 1H) H-2'; 4.53 (*m*, 1H) H-4'; 3.78 (*t*, 4H) OCH_2; 3.64 (*m*, 1H) H-3'; 3.54 (*m*, 2H) H-5',H-5"; 2.70 (*br*, 4H) NCH_2; ^{13}C-NMR (CD_3OD + D_2O) : 139.2 (*d*, J_{CH} = 188.7 Hz) C-6; 109.9 (*d*, J_{CH} = 178.6 Hz) C-5; 92.7 (*d*, J_{CH} = 167.4 Hz) C-1'; 86.0 (*d*, J_{CH} = 166.3 Hz) C-2'; 85.4 (*d*, J_{CH} = 160.0 Hz) C-4'; 72.4 (*d*, J_{CH} = 152.7 Hz) C-3'; 67.6 (*t*) OCH_2; 63.6 (*t*, J_{CH} = 144.3 Hz) C-5'; 50.2 (*t*) NCH_2; UV (H_2O): λ_{max} 225, 252 nm (pH 2), 225, 252 nm (pH 7), 224, 252 nm (pH 12); MS (FAB^-): calc. for $(M-H)^-$ 294.1090, found 294.1066.

Compound **17** (yield 94 %). ^{1}H-NMR (DMSO-d_6) : 8.07 (*d*, $J_{5,6}$ = 8.1 Hz, 1H) H-6; 6.24 (*s*, 1H) H-1'; 5.73 (*d*, 1H) H-5; 5.30 (*br*, 1H) OH; 4.83 (*t*, J = 2.2 Hz, 1H) $CHNO_2$; 4.32 (*t*, $J_{4',5'}$= 4.4 Hz, $J_{4',5"}$ = 4.6 Hz, 1H) H-4'; 3.64 (*d*, 2H) H-5', H-5"; 3.34 - 3.19 (2 x *dd*, $J_{2',3'}$ = 7.7 Hz, 2H) H-2',H-3'; ^{13}C-NMR (DMSO-d_6) : 141.3 (*d*, J_{CH} = 182.0 Hz) C-6; 101.6 (*d*, J_{CH} = 176.3 Hz) C-5; 85.6 (*d*, J_{CH} = 176.4 Hz) C-1'; 83.6 (*d*, J_{CH} = 156.1 Hz) C-4'; 62.8 (*t*, J_{CH} = 142.1 Hz) C-5'; 61.4 (*d*, J_{CH} = 202.2 Hz) $CHNO_2$; 33.9,33.0 (2 x *d*, J_{CH} = 183.2 Hz, J_{CH} =184.3 Hz) C-2', C-3'; MS (FAB^-): calc. for $(M-H)^-$ 268.0569, found 268.0548.

Compound **18** (yield 77 %). ^{1}H-NMR (D_2O) : 7.99 (*d*, $J_{5,6}$ = 8.1 Hz, 1H) H-6; 6.16 (*s*, 1H) H-1'; 5.86 (*d*, 1H) H-5; 4.38 (*t*, $J_{4',5'}$ = 4.3 Hz, $J_{4',5"}$ = 4.6 Hz, 1H) H-4'; 3.87, 3.79 (2 x s, 6H) 2 x OCH_3; 3.65 (2 x *d*, 2H) H-5', H-5"; 3.01, 2.89 (2 x *d*, $J_{2',3'}$ = 6.8 Hz, 2H) H-2', H-3'; ^{13}C-NMR (D_2O) : 141.8 (*d*, J_{CH} = 187.6) C-6; 100.8 (*d*, J_{CH} = 182.0 Hz) C-5; 84.6 (*d*, J_{CH} = 174.1 Hz) C-1'; 80.9 (*d*, J_{CH} = 155.1 Hz) C-4'; 62.0 (*t*,

J_{CH} = 141.6 Hz) C-5'; 53.1, 53.0 (2 x q) 2 x OCH_3; 35.1 (*s*) $C(CO_2CH_3)$ 32.5, 32.2 (2 x *d*, J_{CH} = 181.3 Hz) C-2', C-3'; MS (FAB^-): calc. for $(M-H)^-$ 339.0829, found 339.0868.

Compound **20** (yield 94 %). ^{1}H-NMR ($CDCl_3$) : 7.32 (*d*, $J_{5,6}$ = 8.1 Hz, 1H) H-6: 5.75 (*d*, 1H) H-5; 5.62 (*d*, $J_{1',2'}$ = 3.6 Hz, 1H) H-1'; 5.35 (*dd*, 1H) H-3'; 4.10-3.92 (*m*, 4H) H-2', H-4', H-5', H-5"; 3.70 (*s*, 3H) CO_2CH_3; 2.24 (*d*, $J_{2',CH3}$ = 1.5 Hz, 3H) CH_3; ^{13}C-NMR ($CDCl_3$) : 169.0; 143.1 (*d*, J_{CH} = 180.8 Hz) H-6; 102.3 (*d*, J_{CH} = 177.5 Hz) C-5; 96.3 (*d*, J_{CH} = 168.5 Hz) C-1'; 87.1 (*d*, J_{CH} = 152.7 Hz) C-4'; 84.3 (*d*, J_{CH} = 156.0 Hz) C-3'; 61.7 (*t*, J_{CH} = 144.4 Hz) C-5'; 53.7 (*d*, J_{CH} = 139.2 Hz) C-2'; 51.2 (*q*) CO_2CH_3; 14.3 (*q*) CH_3; MS (FAB^-): calc. for $(M-H)^-$ 323.0879, found 323.0898.

1-(2',3'-Dideoxy-2',3'-epimino-β-D-ribofuranosyl)uracil (13a). Compound **7** (120 mg, 0.30 mmol) was treated with aqueous ammonia (32 %, 2 ml) in dimethylformamide (2 ml) at room temperature overnight. All volatile matters were removed by evaporation and coevaporations with toluene. The residue was separated by preparative TLC to give compound **13a** (31 mg, 57 %). ^{1}H-NMR (CD_3OD + D_2O) : 7.98 (*d*, $J_{5,6}$ = 8.0 Hz, 1H) H-6; 5.91 (*s*, 1H) H-1'; 5.74 (*d*, 1H) H-5; 4.16 (*t*, $J_{4',5'}$ = 5.1 Hz, $J_{4',5"}$ = 4.6 Hz, 1H) H-4'; 3.69 (*d*, 2H) H-5', H-5"; 3.25, 3.15 (2 x *d*, $J_{2',3'}$ = 4.1 Hz, 2H) H-2', H-3'; ^{13}C-NMR (CD_3OD + D_2O) : 143.8 (*d*, J_{CH} = 183.0 Hz) C-6; 102.5 (*d*, J_{CH} = 178.3 Hz) C-5; 87.7 (*d*, J_{CH} = 175.3 Hz) C-1'; 84.5 (*d*, J_{CH} = 156.1 Hz) C-4'; 63.8 (*t*, J_{CH} = 142.1 Hz) C-5'; 40.1,39.1 (2 x *d*, J_{CH} = 186.5 Hz, J_{CH} = 179.7 Hz) C-2', C-3'; MS (FAB^+): calc. for $(M+H)^+$ 226.0828, found 226.0815.

1-(2',3'-Dideoxy-2',3'-(N-methyl)epimino-β-D-ribofuranosyl)uracil (13b). Compound **7** (80 mg, 0.2 mmol) was treated with aqueous methylamine (40 %, 2 ml) in dimethylformamide (2 ml) in the same way as descrived for the preparation of compound **13a** to give compound 13b (36 mg, 75 %). ^{1}H-NMR (CD_3OD + D_2O) : 7.97 (*d*, $J_{5,6}$ = 8.1 Hz, 1H) H-6; 5.89 (*s*, 1H) H-1'; 5.69 (*d*, 1H) H-5; 4.20 (*t*, $J_{4',5'}$ = 4.4 Hz, $J_{4',5"}$ = 4.2 Hz, 1H) H-4'; 3.73 (*d*, 2H) H-5', H-5"; 2.81,2.70 (2 x *d*, $J_{2',3'}$ = 4.6 Hz, 2H) H-2',H-3'; 2.43 (*s*, 3H) NCH_3; ^{13}C-NMR (CD_3OD + D_2O) : 140.6 (*d*, J_{CH} = 184.3 Hz) C-6; 101.6 (*d*, J_{CH} = 177.5 Hz) C-5; 85.1 (*d*, J_{CH} = 174.1 Hz) C-1'; 82.1 (*d*, J_{CH} = 151.2 Hz) C-4'; 62.9 (*t*, J_{CH} = 141.6 Hz) C-5'; 51.0, 49.2 (2 x *d*, J_{CH} = 184.3 Hz, J_{CH} = 182.0 Hz) C-2',C-3'; 45.7 (*q*) NCH_3; MS (FAB^+): calc. for $(M+H)^+$ 240.0984, found 240.0992.

1-(2',3'-Dideoxy-2',3'-(N-benzyl)epimino-β-D-ribofuranosyl)uracil (13c). Compound **7** (100 mg, 0.25 mmol) was treated with benzylamine (273 µl, 2.5 mmol) in tetrahydrofuran (5 ml) at room temperature for 5 h. All volatile matters were removed under vacuum. The residue was separated on a silica gel column to give compound **13c** (41 mg, 52 %). ^{1}H-NMR ($CDCl_3$ + CD_3OD) : 7.89 (*d*, $J_{5,6}$ = 8.0 Hz, 1H) H-6; 7.33 (*s*, 5H) Ph; 5.90 (*s*, 1H) H-1'; 5.67 (*d*, 1H) H-5; 4.21 (*t*, $J_{4',5'}$ = 4.2 Hz, $J_{4',5"}$ = 3.7 Hz, 1H) H-4'; 3.74 (*d*, 2H) H-5', H-5"; 3.59 (2 x s, 2H) CH_2Ph; 2.93, 2.82 (2 x *d*, $J_{2',3'}$ = 5.1 Hz, 2H) H-2', H-3'; ^{13}C-NMR ($CDCl_3$ + CD_3OD) : 141.6 (*d*, J_{CH} = 187.6 Hz) C-6; 101.3 (*d*, J_{CH} = 179.7 Hz) C-5; 86.6 (*d*, J_{CH} = 173.0 Hz) C-1'; 83.1 (*d*, J_{CH} = 161.8 Hz) C-4'; 62.4 (*t*, J_{CH} = 142.1 Hz) C-5'; 60.8 (*t*) CH_2Ph; 48.4,46.2 (2 x *d*, J_{CH} = 183.2 Hz, J_{CH} = 180.8 Hz) C-2', C-3'; MS (FAB^-): calc. for $(M-H)^-$ 314.1141, found 314.1107.

1-(3'-Deoxy-3'-morpholino-2,2'-O-anhydro-β-D-arabinofuranosyl)uracil (11c) & 1-(2',3'-dideoxy-2'-morpholino-3'-phenylseleno-β-D-glyceropent-2'-enofuranosyl]uracil (12b) To a solution of compound **7** (100 mg, 0.25 mmol) in dimethylformamide (1 ml) was added morpholine (217 µl, 2.5 mmol) and the reaction was stirred at room temperature overnight. All volatile matters were removed by evaporation and coevaporation with toluene and ethanol. The residue was separated on a silica gil column to give compound **12b** (51 mg, 45 %) and **11c** (7 mg, 10 %) Compound **12b** :^{1}H-NMR ($CDCl_3$) 9.43 (*br*, 1H) NH; 7.77 (*d*, $J_{5,6}$ = 8.0 Hz, 1H) H-6; 7.45 - 7.30 (*m*, 5H) Ph; 7.08 (*d*, $J_{1',4'}$ = 2.2 Hz, 1H) H-1'; 5.74 (*d*, 1H) H-5; 4.69 (*m*, 1H) H-4'; 3.79 (*br*, 2H) H-5',H-5"; 3.51 (*br*, 4H) OCH_2; 3.34 (*br*, 4H) NCH_2; 2.55 (*br*, 1H) OH; ^{13}C-NMR ($CDCl_3$) : 141.4 (*d*, J_{CH} = 182.0 Hz) C-6; 102.7 (*d*, J_{CH} = 178.6 Hz) C-5; 94.4 (*s*) C-2'; 89.1 (*d*, J_{CH} = 149.4 Hz) C-4'; 86.4 (*d*, J_{CH} = 171.9 Hz) C-1'; 66.5 (*t*) OCH_2; 62.5 (*t*, J_{CH} = 143.8 Hz) C-5'; 48.3 (*t*) NCH_2; MS (FAB^-): calc. for $(M-H)^-$ 450.0568, found 450.0522.

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