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# SYNTHESIS OF NEW 2′,3′-DIDEOXY-2′,3′-α-FUSED-HETEROCYCLIC URIDINES, & SOME 2′,3′-ENE-2′-SUBSTITUTED URIDINES FROM EASILY ACCESSIBLE 2′,3′-ENE-3′-PHENYLSELENONYL URIDINE#

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*Abstract : The synthetic utilities of 2′,3′-ene-3′-phenylselenones* **1** *and* **2** *as synthetic equivalent of a dication [$CH_2^+$ - $CH_2^+$ ] have been demonstrated. They act as Michael acceptors, and undergo conjugate addition reactions at C-2′ with hydrazine, 1,2-ethylenediamine, 1,3-diaminopropane, 1,2-ethanedithiol, ethanolamine, and 2-mercaptoethanol to give the intermediary adducts, 2′,3′-dideoxy-3′-phenylselenonyl-2′-substituted* xylo*furanosyl derivatives, which then undergo a facile intramolecular $S_N2$ type displacement reaction at C-3′ by the neighbouring 2′-substituent to give a variety of hitherto unreported 2′,3′-dideoxy-2′,3′-α-fused-heterocyclic derivatives of uridine such as 2′,3′-dideoxy-2′,3′-α-biimino uridine* **5** *and* **8**, *2′,3′-dideoxy-2′,3′-α-(2-iminoimidazolidino)uridine* **9** *and* **10**, *2′,3′-dideoxy-2′,3′-N-α-(1,2-ethylene)uridine* **11** *and* **12**, *and 2′,3′-dideoxy-2′,3′-S-α-(1,2-ethylene)uridine* **20** *and* **21**. *Anions of ethanedithiol, 2-aminoethanol, methylthioglycolate, imidazole and triazole, on the other hand, undergo conjugate nucleophilic addition reactions at C-2′ to give the intermediary adducts, 2′,3′-dideoxy-3′-phenylselenonyl-2′-substituted* xylo*furanosyl derivatives, which then suffer a cis-elimination of phenylselenic acid to give various 1-(2′,3′-dideoxy-2′-substituted-β-D-*glycero-*pent-2′-eno-furanosyl)uracil such as* **18**, **26**, **32**, **34** *and* **35**. *The 2′,3′-ene-3′-phenylselenones* **3** *and* **4** *also react as dienophiles in Diels-Alder or 1,3-cycloaddition reaction to give unique 2′,3′-dideoxy-2′,3′-fused-uridine derivatives such as* **45**, **46**, **49** *or* **50**. *The methodology described herein, along with our earlier published works described in refs. 21-23 and 41, provide a general approach to fuctionalize the 2′- and 3′-carbons of β-D-nucleosides simultaneously.*

Human Immunodeficiency Virus (HIV) is the causative agent of the Acquired Immune Deficiency Syndrome (AIDS). Several 2′,3′-dideoxynucleosides[1-7] [such as 2′,3′-dideoxycytidine[1], 2′,3′-dideoxyadenosine[1], 2′,3′-dideoxy-2,6-diaminopurine ribonucleoside[2], 3′-azidothymidine[3,5], 2′,3′-dideoxythymidine[4], 3′-fluorothymidine[5], 2′,3′-dideoxy-2′,3′-didehydrothymidine and inosine[6,7]] have shown promising results as chemotherapeutic agents because of their ability to inhibit selectively the HIV specific reverse transcriptase[1-20] which results in suppression of the replication of HIV in the AIDS-patients. The mechanism of action[1-20] of these active compounds suggests that the 2′,3′-dideoxy-2′ and/or 3′-substituted-β-D-nucleosides with a free 5′-hydroxyl group are of interest due to their potential ability for specific chain termination of the cDNA synthesis on the HIV-RNA template promoted by the HIV-specific reverse transcriptase. Development of synthetic methods to produce new types of 2′,3′-dideoxynucleosides with a free 5′-hydroxyl group are therefore of considerable importance in order to devise improved therapy against AIDS.

We have shown recently that simple Michael addition reactions with an appropriately 5′-O-protected-2′,3′-ene-3′-sulfone[21] or 2′,3′-ene-3′-nitrile[22] derivatives of β-D-nucleosides gave access to various new types of 2′,3′-

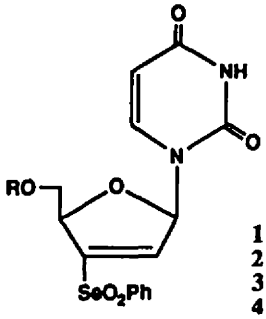
*# Dedicated to Professor C. B. Reese, F. R. S. on the occasion of his 60th Birthday*

dideoxy-2′,3′-disubstituted- or 2′-substituted nucleosides in high overall yields[21,22]. These nucleophilic addition reactions take place exclusively from the α-face of C-2′ of the 2′,3′-enesulfone[21], or 2′,3′-ene-nitrile[22] to give mainly *trans*-2′,3′-disubstituted adducts owing to the stereoelectronic factors controlling the stabilization of the intermediary chiral α-sulfonyl-3′-carbanion[21] or α-nitrile-3′-carbanion[22] at the α-face. Recently, we have also successfully exploited 2′,3′-ene-3′-phenylselenonyl nucleosides as substrates for Michael addition reactions as a means to simultaneously functionalize both the 2′- and 3′-carbons of nucleosides by amines and carbon-nucleophiles[23,41]. This is due to the fact that the 3′-selenonyl group being connected to the 2′,3′-double bond, is a strong electron-withdrawing group and therefore activates the 2′,3′-double bond towards the addition of nucleophiles at the C-2′ [24-28]. The resulting intermediary 2′-substituted-3′-selenonyl nucleosides were found to be very unstable due to the leaving group character of the 3′-selenonyl substitutent, it suffered a subsequent nucleophilic attack from the neighbouring 2′-substituent giving 2′,3′-α-fused cyclic nucleosides[23,41]. This in practice makes the 2′,3′-ene-3′-selenones, such as **1** and **2**, synthetically equivalent to the dication $CH_2^+ - CH_2^+$. The synthetic utilities of 2′,3′-ene-3′-selenones **1** and **2** have been demonstrated from the fact that they acted 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-α-aziridino uridines[23]. Dimethylamine, pyrrolidine, and morpholine, on the other hand, upon reaction with **1** or **2** gave 2,2′-O-anhydro-3′-deoxy-3′-amino or -alkylamino substituted uridines[23]. The reaction of **1** or **2** with carbon-nucleophiles such as sodio methyl malonate and conjugate bases of nitromethane and acetophenone also provided a convenient access to 2′,3′-dideoxy-2′,3′-α-cyclopropyl-[3.1.0]-uridines[23,41].

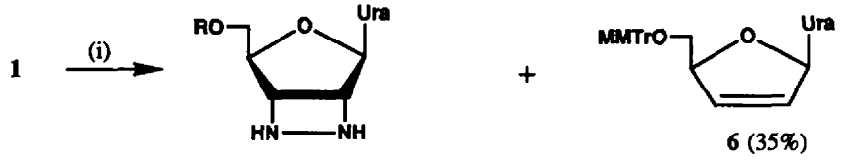
We herein report our further studies on the reaction of various nucleophiles to 2′,3′-ene-3′-phenylselenones of uridine **1** and **2** to show that these ene-selenones are indeed useful synthetic intermediates for functionalization of 2′- and 3′-carbons simultaneously to give either a variety of novel 2′,3′-dideoxy-2′,3′-fused-heterocyclic-β-D-nucleosides, or 2′,3′-dideoxy-2′,3′-ene-2′-substituted-nucleosides. We also report herein our studies of reactions of **3** and **4** as dienophiles which undergo Diels-Alder or 1,3-cycloaddition reaction, to give 2′,3′-dideoxy-2′,3′-fused-β-D-nucleosides.

***Reaction with hydrazine.***

Reaction of 2′,3′-ene-3′-phenylselenone **1** with hydrazine (3 equiv.) in dichloromethane for ~15 h at ~20 °C gave the new 1-(5′-O-(4-monomethoxytrityl) [MMTr]-2′,3′-dideoxy-2′,3′-biimino-β-D-*ribo*furanosyl)uracil **5** (60%) along with the 1-(5′-O-MMTr-2′,3′-dideoxy-β-D-*glycero*-pent-2′-eno-furanosyl)uracil **6** (35%). On the other hand, when the reaction was performed in dry THF at ~40 °C, 1-(5′-O-MMTr-2′,3′-dideoxy-2′-ulose hydrazone-β-D-*erythro*-pentofuranosyl)uracil **7c** (32%) was obtained along with the 2′,3′-dideoxy-α-fused-2′,3′-biimino uridine **5** (30%), and olefin **6** (17%). Presumably, hydrazone **7c** was formed from the isomerization of 2′,3′-ene-2′-hydrazino derivative **7b** which in turn was formed as a transient product due to the *cis*-elimination of phenylselenic acid from **7a**. The 5′-O-MMTr group from **5** could not be deprotected successfully. Therefore, **2** was directly reacted with hydrazine under the latter condition to obtain 1-(2′,3′-dideoxy-2′,3′-biimino-β-D-*ribo*furanosyl)uracil **8** in 62% yield. No hydrazone was detectable in the latter reaction.

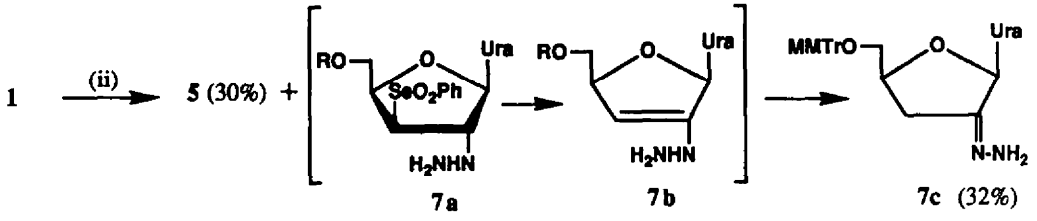


1 : R = MMTr
2 : R = H
3 : R = *p*-toluoyl (Tol)
4 : R = *t*-butyldimethylsilyl (TBDMS)



5 : R = MMTr (60%)

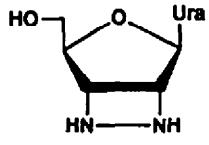
6 (35%)



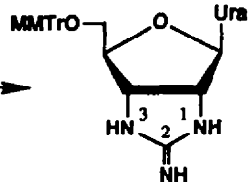
7a

7b

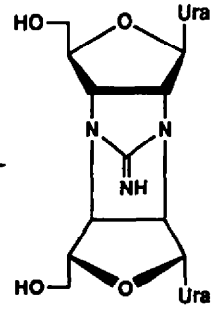
7c (32%)



8 (62%)



9 (54%)



10 (35%)

Ura = 1-Uracilyl

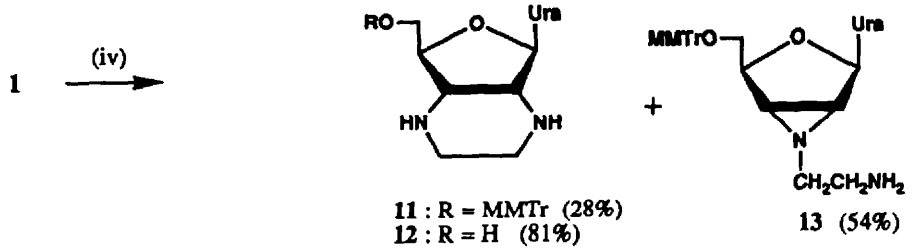
*(i) hydrazine in $CH_2Cl_2$ at ~20 °C; (ii) hydrazine in THF at ~40 °C;*
*(iii) guanindine hydrochloride, NaH in DMF at ~20 °C*

***Reaction with guanidine.***

Reaction of 2′,3′-ene-3′-phenylselenone **1** with guanidine hydrochloride in presence of sodium hydride in dry DMF at ~20 °C gave the new 1-(5′-O-MMTr-2′,3′-dideoxy-2′,3′-(2-iminoimidazolidino)-β-D-*ribo*furanosyl)uracil **9** in 54% yield. The 5′-O-MMTr group however could not be easily removed from **9** presumably because of rapid acidic hydrolysis of the fused imidazoline moiety; the reaction of guanidine was therefore performed on **2**, under identical conditions to that described for **9**, to give the unique dimeric $N^1$, $N^3$, α-fused-(2-iminoimidazolidine)-uridine **10** in 35% yield. The structure of the dimer **10** was elucidated from its high resolution mass spectra and detailed $^1$H- and $^{13}$C-NMR spectral data. It showed a molecular ion [(M-H)$^+$] at m/e 474.1397 (expected m/e for the dimer: 474.1373) in the negative Fast Atom Bombardment mass spectroscopy. The symmetrical structure of the dimer **10** was clear from the fact that it showed only one set of pentose-sugar and uracil absorptions in its $^1$H- and $^{13}$C-NMR spectra which were very similar to those of **9** (experimental). Any unsymmetrical structure for **10** would mean that both sets of sugar and the uracil residues must reside in different magnetic environments. It may be noted that other symmetrical dimers such as **16**, **19**, **22**, **23** *(vide infra)* also showed one set of sugar and uracil absorptions, only their accurate mass measurements have been able to clearly ascertain their dimeric structures (see experimental). Spectroscopic support for the 2′,3′-α-fused guanidine structure for both **9** and **10** comes from the following observations: H-2′ and H-3′ in **9** and **10** absorb at δ ~4.6 compared to δ ~3.5 in **11** and **12**. The relative downfield shift of H-2′ and H-3′ in **9** and **10** is clearly due to the inductive effect of the 2′,3′-fused guanidine moiety [compare the $\delta_{Me}$ ($CDCl_3$) of $N^1$, $N^1$, $N^3$, $N^3$-tetramethylguanidine of 2.8 ppm with that of 2.1 ppm for $N^1$, $N^1$, $N^2$, $N^2$-tetramethyldiaminoethane]. A similar downfield shift of C-2′ and C-3′ in **9** [~6 ppm] and **10** [~8 ppm], compared to their shifts in **11** and **12**, show the effect of the presence of the electron-withdrawing 2′,3′-fused guanidino group in the former. Furthermore, almost identical chemical shift of H-2′ and H-3′ in **9** and **10** as in **11** and **12** suggest that both nitrogens at C-2′ and C-3′ should be of a similar hybridization state. A comparison of difference $\delta^{13}$C between C-2′ and C-3′ in **11** [Δδ 7.3 ppm] and **12** [Δδ 6.5 ppm] with those in **9** [Δδ 5.4 ppm] and **10** [Δδ 5.9 ppm] also suggest that both C-2′ and C-3′ nitrogen substituents in these two pairs [**11**, **12** & **9**, **10**] are of similar hybridization state [*i.e* $sp^3$]. This should be also evident from the comparison of $^1J_{CH}$ of C-2′ and C-3′, which should reflect the effect of electronegativity of the α-substituent [$sp^3$ versus $sp^2$ hybridized nitrogen]. Thus the $^1J_{CH}$ of 150 - 160 Hz for both C-2′ and C-3′ suggest again that their substituents are identical.

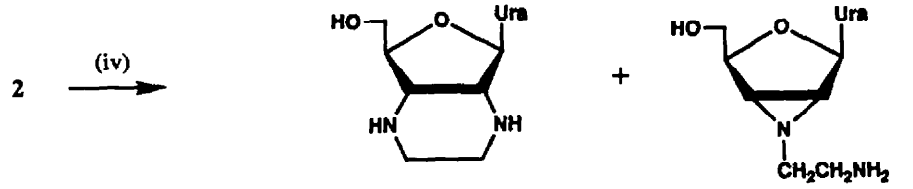
***Reaction with 1,2-ethylenediamine and 1,3-diaminopropane.***

Reaction of 2′,3′-ene-3′-phenylselenone **1** with 1,2-ethylenediamine in THF at ~20 °C gave a mixture of hitherto unreported 1-(5′-O-MMTr-2′,3′-dideoxy-2′,3′-*N*-(1,2-ethylene)-β-D-*ribo*furanosyl)uracil **11** (28%) and 1-(5′-O-MMTr-2′,3′-dideoxy-2′,3′-[N-(2-aminoethyl)]epimino-β-D-*ribo*furanosyl)uracil **13** (54%). This shows that the second nucleophilic attack at C-3′ by a more basic 2′-secondary amino group is more favoured than the β-amino group in the C-2′-substituted adduct. Proximity of the 2′-secondary amino group also perhaps contributes in its facile attack at the C-3′. The removal of 5′-O-MMTr group from **11** gave the 1-(2′,3′-dideoxy-2′,3′-*N*-(1,2-ethylene)-β-D-*ribo*furanosyl)uracil **12** in 81% yield. The 5′-O-MMTr group from the aziridine derivative **13** could not be removed because of the protonation of the aziridine ring under the acidic deprotection condition[23] and its subsequent conversion into 2,2′-O-anhydro-3′-deoxy-3′-amino substituted nucleosides. Reaction with **2** was therefore performed to give a direct access to fully deprotected nucleosides **12** and **14** in 34 and 38% yield, respectively. Reaction of **1** with 1,3-diaminopropane however



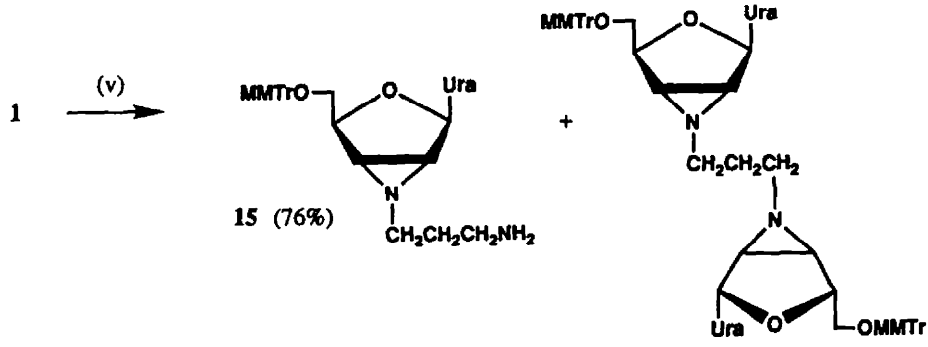

11 : R = MMTr (28%)
12 : R = H (81%)

13 (54%)




12 (34%)

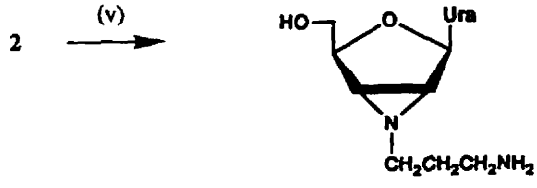
14 (38%)




15 (76%)

1 + 15 ⟶ 16 (15%)

16 (21%)




17 (76%)

*(iv)* $H_2NCH_2CH_2NH_2$ *in THF at ~0 °C; (v)* $H_2NCH_2CH_2CH_2NH_2$ *in THF at ~0 °C*

took a slightly different course in that the major product isolated was 1-(5′-O-MMTr-2′,3′-dideoxy-2′,3′-[N-(3-aminopropyl)]epimino-β-D-*ribo*furanosyl)uracil **15** (76%) along with a bis-aziridine-dimer **16** (21%). The structure of the bis-aziridine-dimer **16** was proved conclusively, independently by its synthesis through the condensation of **1** and **15**. It may be noted that the reaction of **2** with 1,3-diaminopropane gave only α-aziridine nucleoside **17** (76%) with no trace of the dimer such as **16** with free 5′-hydroxyl function.

***Reaction with 1,2-ethanedithiol.***

Reaction of 2′,3′-ene-3′-phenylselenone **1** with 1,2-ethanedithiol in THF in presence of triethylamine at ~20 °C gave only 1-(5′-O-MMTr-2′,3′-dideoxy-2′-*S*-(2-mercaptoethyl)-β-D-*glycero*-pent-2′-eno-furanosyl)uracil **18** (43%) and the 1-(5′-O-MMTr-2′,3′-dideoxy-β-D-*glycero*-pent-2′-eno-furanosyl)uracil **6** (21%). The formation of **18** is probably due to the *cis*-elimination of phenylselenic acid from the transient 1-(2′,3′-dideoxy-2′-(2-mercaptoethylthio)-3′-phenylselenonyl-*xylo*furanosyl)uracil derivative. The 5′-O-MMTr group from **18** was easily removed, but the isolated product turned out to be a disulfide **19** (79%) which was evident particularly from its high resolution mass spectral data (see experimental). The reaction of 2′,3′-ene-3′-phenylselenone **1** with 1,2-ethanedithiol in presence of a stronger base such as 1,8-diazabicyclo-[5.4.0]-undec-7-ene (DBU) in THF at ~20 °C, on the other hand, gave the new 1-(5′-O-MMTr-2′,3′-dideoxy-2′,3′-*S*-(1,2-ethylene)-β-D-*ribo*furanosyl)uracil **20** (64% ), which was easily deprotected to give the 1-(2′,3′-dideoxy-2′,3′-*S*-(1,2-ethylene)-β-D-*ribo*furanosyl)uracil **21** (63%). It may be of interest to note that the reaction of **1** with **18** gave the unique protected dimer **22** (62%) which was also smoothly deprotected to the corresponding dimer with free hydroxyl function **23** (84%). The stronger nucleophilicity of the 2′-terminal-β-thiol group in **18** with $C_2$ chain was apparently long enough to overcome the steric crowding met in its nucleophilic addition reaction with **1**, compared to a poorer reactivity of the β-amino function in **13** in an attempted reaction with **1**.

***Reaction with 2-aminoethanol.***

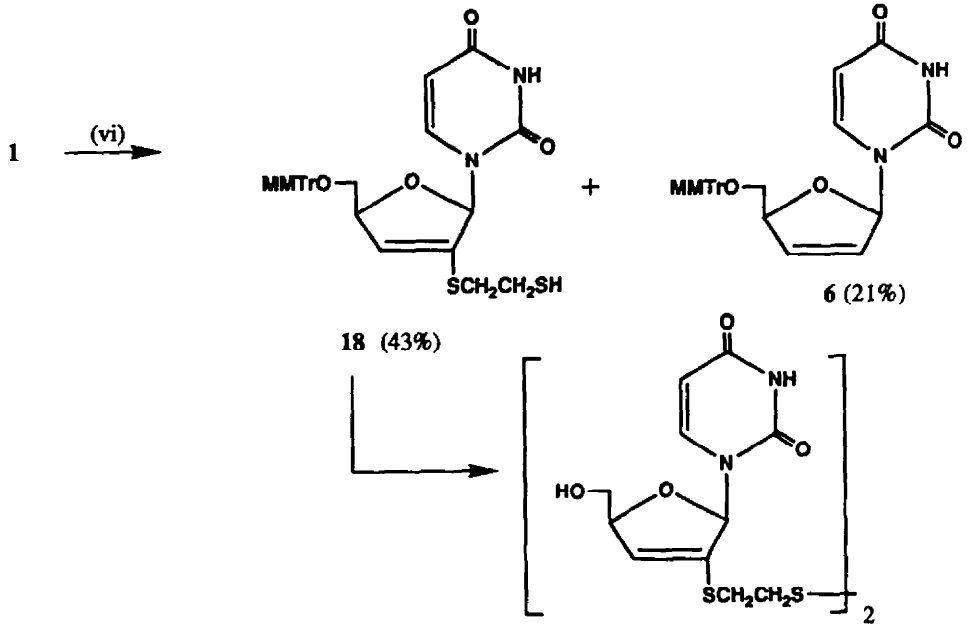
Reaction of 2′,3′-ene-3′-phenylselenone **1** with 2-ethanolamine in THF in presence of DBU gave 1-(5′-O-MMTr-2′,3′-dideoxy-2′,3′-[N-(2-hydroxyethyl)]epimino-β-D-*ribo*furanosyl)uracil **24** (54%) which, as has been said before, could not be deprotected under acidic condition because of the side reaction due to the protonation of the aziridine moiety. The reaction of **2** with ethanolamine was therefore performed to obtain 1-(2′,3′-dideoxy-2′,3′-[N-(2-hydroxyethyl)]epimino-β-D-*ribo*furanosyl)uracil **25** in 64% yield.

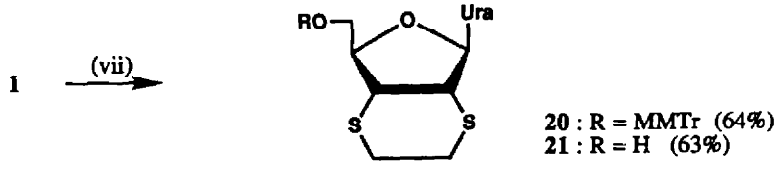
***Reaction with 2-aminoethanethiol.***

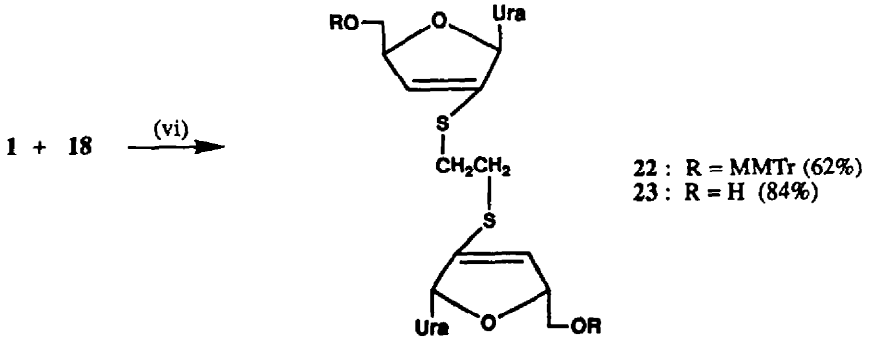
Reaction of 2′,3′-ene-3′-phenylselenone **1** with 2-aminoethanethiol hydrochloride in THF in presence of DBU at ~20 °C gave the 1-(5′-O-MMTr-2′,3′-dideoxy-2′-S-(2-aminoethyl)-β-D-*glycero*-pent-2′-eno-furanosyl)uracil **26** (53%) which was deprotected to give 1-(2′,3′-dideoxy-2′-S-(2-aminoethyl)-β-D-*glycero*-pent-2′-eno-furanosyl)uracil **27** (61%). Surprisingly, 1-(5′-O-MMTr-2′,3′-dideoxy-2′,3′-(1,4-thiazino)-β-D-*ribo*furanosyl)uracil was completely absent as one of the reaction products.

***Reaction with 2-mercaptoethanol.***

Reaction of 2′,3′-ene-3′-phenylselenone **1** with 2-mercaptoethanol gave 1-(5′-O-MMTr-2′,3′-dideoxy-2′-S-(2-hydroxyethyl)-β-D-*glycero*-pent-2′-eno-furanosyl)uracil **28** (21%) along with 1-(5′-O-MMTr-2,2′-O-anhydro-3′-*S*-(2-hydroxyethyl)-β-D-*arabino*furanosyl)uracil **30c** (17%). The **30c** was probably formed




*(vi) $HSCH_2CH_2SH$ / $Et_3N$ in THF at ~20 °C; (vii) $HSCH_2CH_2SH$ / DBU in THF at ~20 °C*

through the intermediates **30a** → **30b**. Both **28** and **30c** were deprotected to give the corresponding parent nucleoside **29** and **31** in 74 and 82% yield respectively. It is not clear to us why a thiirenium ion intermediate such as **30b** should not have formed in the reaction of **1** or **2** with 1,2-ethanedithiol and 2-aminoethanethiol to give a corresponding 2,2′-O-anhydro-3′-*S*-substituted nucleoside.

***Reaction with thioglycolic acid methyl ester.***

When 2′,3′-ene-3′-phenylselenone **1** was reacted with thioglycolic acid methyl ester in presence of either triethylamine or DBU, it gave exclusively 1-(5′-O-MMTr-2′,3′-dideoxy-2′-S-(methoxycarbonylmethyl)-β-D-*glycero*-pent-2′-eno-furanosyl)uracil **32** (64%). Compound **32** was subsequently deprotected to obtain the corresponding 5′-hydroxy derivative **33** (65%). In an anticipation that thioglycolic acid methyl ester under the influence of a strong base may generate a carbanion sandwiched between the thio and ester function, and thus may act as a bifunctional reagent in its reaction with **1**, they were therefore treated in presence of potassium t-butoxide, but the eneselenone **1** broke down under such a strong basic condition.

***Reaction with imidazole and triazole.***

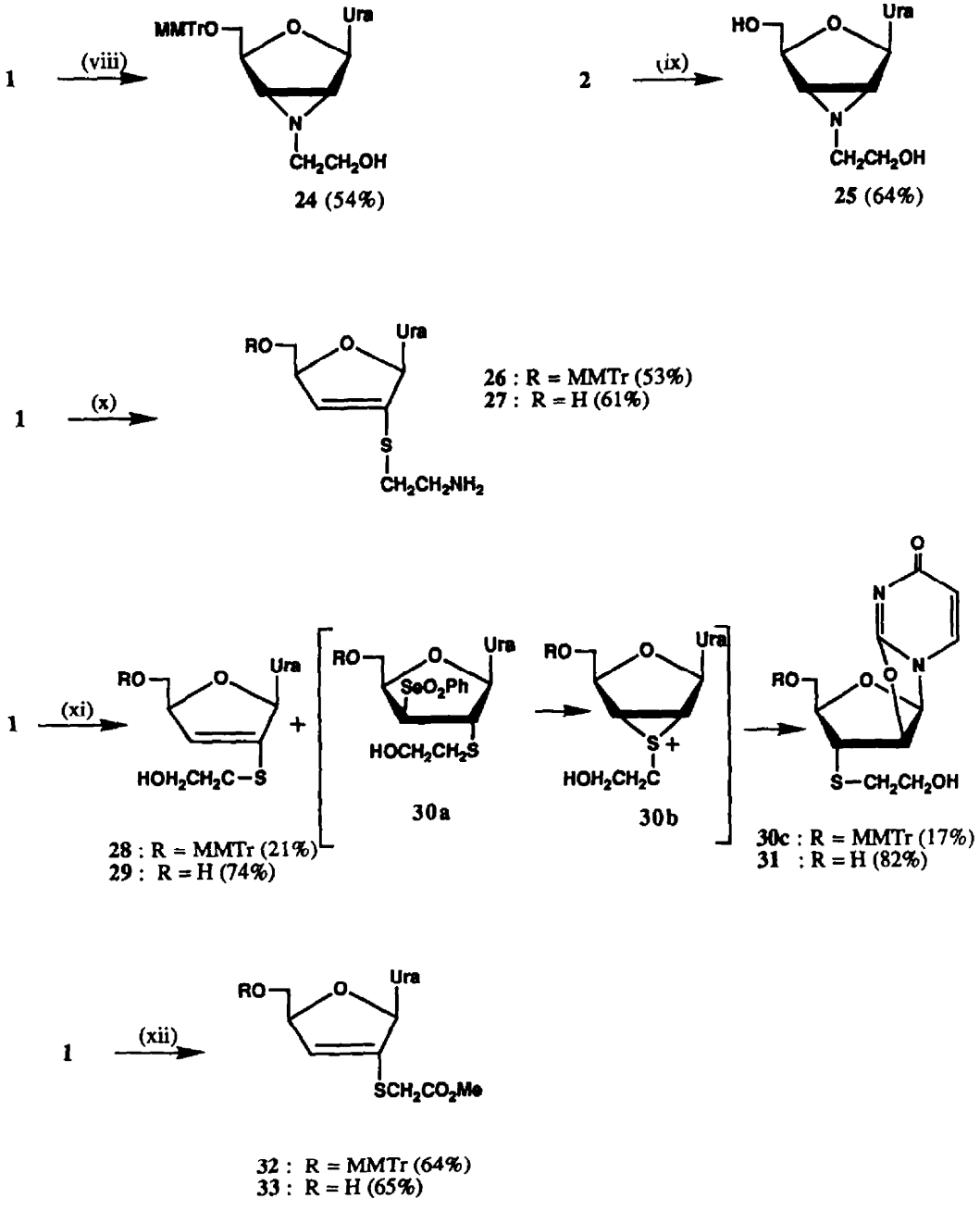
When 2′,3′-ene-3′-phenylselenone **2** was reacted with the conjugate anion of imidazole or 1,2,4-triazole in THF, in presence of potassium carbonate, 1-(2′,3′-dideoxy-2′-imidazolyl-β-D-*glycero*-pent-2-eno-furanosyl)uracil **34** (80%) or 1-(2′,3′-dideoxy-2′-(1,2,4-triazolyl)-β-D-glyceropentofuranosyl)uracil **35** (74%), respectively, were formed.

***Reaction with alcohol.***

When the 2′,3′-ene-3′-phenylselenone **1** was treated with methanol in presence of potassium carbonate at room temperature, 1-(5′-O-MMTr-2′-O-methyl-3′-phenylselenonyl-*ribo*furanosyl)uracil **36** (88%) was formed which was deprotected to give 1-(2′-O-methyl-3′-phenylselenonyl-*ribo*furanosyl)uracil **37** (77%) in the usual manner. Similarly, **1** upon reaction with ethanol under identical conditions, as described for methanol, gave 1-(5′-O-MMTr-2′-O-ethyl-3′-phenylselenonyl-*ribo*furanosyl)uracil **38** (73%) which was deprotected to give 1-(2′-O-ethyl-3′-phenylselenonyl-*ribo*furanosyl)uracil **39** (77%). The presence of 3′-phenylselenonyl group in the *ribo* configuration in **36** - **39** was evident through the analysis of $J_{4',5'}$ and $J_{4',5''}$ couplings in their $^1$H-NMR spectra which gave the estimation of γ+ population across their exocyclic C-4′ and C-5′ bond[31-43]. The population of rotamers $p^{(\gamma+)}$ about the exocyclic C-4′ and C-5′ bond has been estimated from the "sum rule" using the $J_{4',5'}$ and $J_{4',5''}$ coupling constants using the equation[39,40]:

$$p^{(\gamma+)} = \frac{13.3 - \Sigma J_{4',5'} + J_{4',5''}}{9.7}$$

The γ+ population for **36** - **39** were found to be around 100%, suggesting the *ribo* configuration in these compounds. If the 3′-phenylselenonyl group were in the "up" configuration, the γ+ population would be expected to be lower than 30%[31,32,37,9]. Although the electronegativity of the C-3′ substituent has a drastic effect on the γ+ population[14-16, 36,38], still the γ+ rule has been found to be a valid spectroscopic procedure to determine the configuration of the C-3′substitutent[14-16,21-23,31-40]. The 3′-substituent in the "down" configuration produces a high γ+ poulation (>50%), whereas the 3′-substituent in the "up" configuration produces a shift of γ+ population to <30% [14-16,21-23,31-40]. The unusual stability of **36** - **39** toward an elimination reaction is presumably due to the *cis* orientation of 3′-phenylselenonyl group with respect to 2′-O-




*(viii) 2-aminoethanol + DBU in THF at ~20°C; (ix) 2-aminoethanol in THF at ~20°C; (x) 2-aminoethanethiol hydrochloride + DBU in THF ~20°C ; (xi) 2-mercaptoethanol + NaH in THF at ~20°C; (xii) thioglycolic acid methyl ester + NaH in THF at ~20°C*

methyl group. The *trans* orientation of the 3′-phenylselenonyl group with respect to the acidic H-2′ in **36** - **39** clearly produces an unfavourable stereochemical feature for the *cis*-elimination of phenylselenic acid to give the olefin[24-28].

The reaction of 2′,3′-ene-3′-phenylselenone **1** with sodium methoxide, on the other hand, gave $O^2$-Methyl-1-(5′-O-MMTr-2′-O-methyl-*xylo*furanosyl)uracil **41** (82%) which was deprotected in the usual manner to give $O^2$-Methyl-1-(2′-O-methyl-*xylo*furanosyl)uracil **42**. Clearly, **41** was formed by the attack of the methoxide ion at C-2 of 2,3′-O-anhydro nucleoside **40**, which in turn was formed owing to nucleophilic displacement of 3′-phenylselenonyl group by the $C^2$=O of the uracil moiety in **36** under a strongly basic condition. The *xylo* configuration in **41** was again attributed on the basis of a low γ+ population (~30%) about its C4′-C5′ bond.

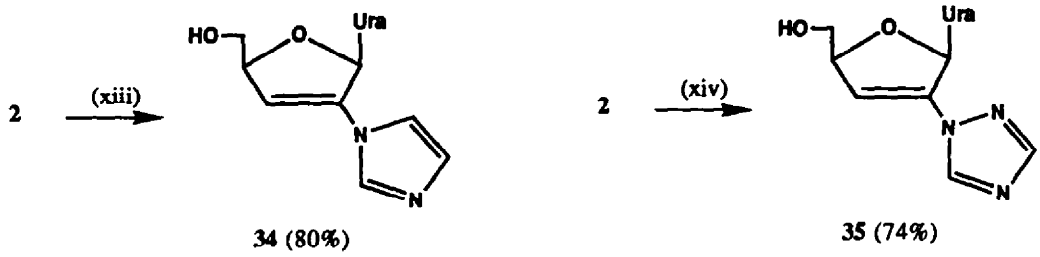
***Reaction with N-methylhydroxylamine.***

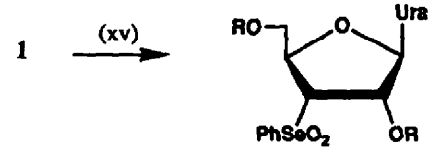
Reaction of 2′,3′-ene-3′-phenylselenone **1** with N-methylhydroxylamine in tetrahydrofuran in presence of triethylamine at ~20 °C gave 1-(2′,3′-dideoxy-2′-(N-methylhydroxyl)amino-3′-phenylselenonyl-*ribo*furanosyl)uracil **43a** in a poor yield, which turned out to be quite unstable upon storage. Therefore, when the formation of **43a** was found to be complete on Tlc, promptly ethanethiol and DBU was added and the temperature of the reaction mixture was raised to ~40 °C in order to convert **43a** to a presumably stable 1-(2′,3′-dideoxy-2′-(N-methylhydroxyl)amino-3′-ethylthio-*ribo*furanosyl)uracil derivative, but the isolated compound from the reaction mixture turned out to be 1-(5′-O-MMTr-2′,3′-dideoxy-2′-(N-methylhydroxyl)amino-3′-phenylselenyl-*ribo*furanosyl)uracil **43b** (45%) which was aparently formed by a reduction of **43a** promoted by ethanethiol. The 5′-O-MMTr group of 2′-(N-methylhydroxyl)amino-3′-phenylselenyl uridine **43b** was deprotected by a brief treatment of 80% aqueous acetic in the usual manner to give 1-(2′,3′-dideoxy-2′-(N-methylhydroxyl)amino-3′-phenylselenyl-*ribo*furanosyl)uracil **44** (76%). The population of rotamers $p^{(\gamma+)}$ about the exocyclic C-4′ and C-5′ bond for **44** was found to be ~90% which suggested *(vide supra)* that the 3′-phenylselenyl substituent must be on the α-face, *cis* to the vicinal 2′-substitutent.

It is thus clear from the above reactions that the nucleophilicity of the 2′-substituent (Nu) in the adduct (A) actually controls the outcome of the reaction summarized in the Scheme 1. The fused adduct (B) is formed only when 2′-Nu is sufficiently nucleophilic for a neighbouring $S_N2$ attack in the thermodynamically prefered *xylo*-intermediate (A) which is generated from the chiral-3′-carbanion (C). If the 2′-Nu can not act as an internal nucleophile, then the carbanion (D) is formed under the basic reaction condition which is immidiately protonated to give the kinetic product (E) which may eventually undergo a neighbouring $S_N2$ attack by $C^2$=O. If, however, the 2′-Nu in (A) is non-nucleophilic, and the reaction condition does not promote the formation of (D), then the adduct (A) suffers the *cis*-elimination of phenylselenic acid to give 2′,3′-dideoxy-2′,3′-ene-2′-substituted product (F).

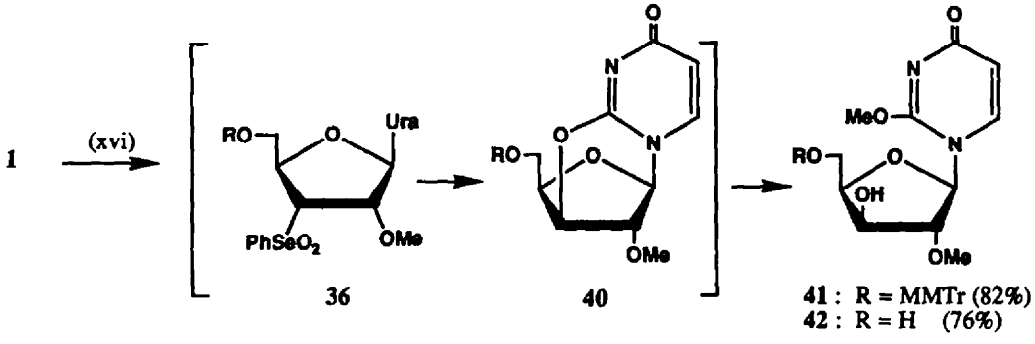
***Reaction with sodium azide.***

Reaction of sodium azide with 2′,3′-ene-3′-phenylselenone **3** in dimethylsulfoxide at ~20 °C provides a convenient access to the hitherto unreported 1-(5′-O-(*p*-toluoyl)-2′,3′-dideoxy-2′,3′-(2*H*-1,2,3-triazolo)-β-D-*glycero*-pent-2′-eno-furanosyl)uracil **45** in 64% yield through a [2 + 3] dipolar cycloaddition reaction, followed by a concerted *cis*-elimination of phenylselenic acid. The dimer **46** was also formed in the later

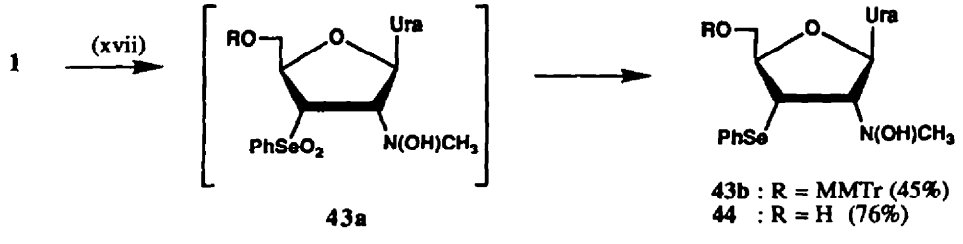



**36** : R = MMTr ; R′ = Me (88%)
**37** : R = H ; R′ = Me (77%)
**38** : R = MMTr ; R′ = Et (73%)
**39** : R = H ; R′ = Et (94%)




**41** : R = MMTr (82%)
**42** : R = H (76%)



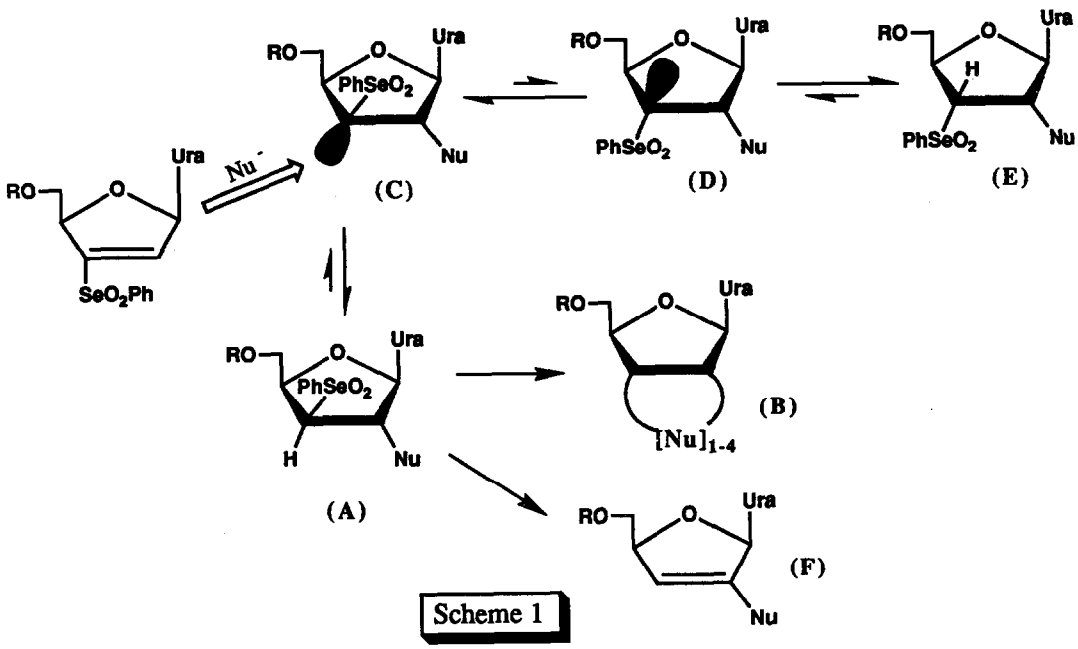

**43b** : R = MMTr (45%)
**44** : R = H (76%)

*(xiii) Imidazole and potassium carbonate in THF at ~20 °C; (xiv) 1,2,4-triazole and potassium carbonate in THF at ~20 °C; (xv) $K_2CO_3$ in methanol or ethanol at ~20 °C; (xvi) Sodium methoxide in methanol ~20 °C; (xvii) N-Hydroxymethylamine and $Et_3N$ in THF at ~20 °C, followed by ethanethiol and DBU at ~20 °C.*

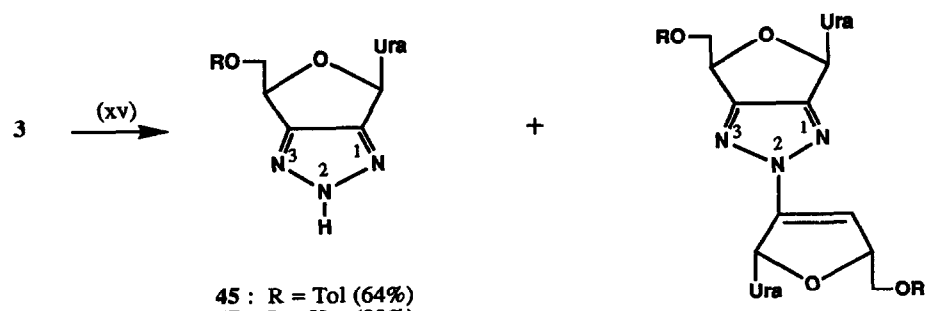
reaction in 33% yield owing to the nucleophilic attack of the N-2 of the initially formed triazolyl moiety of **45** to the eneselenone **3**. Both **45** and **46** were easily deprotected by a brief aqueous ammonia treatment for a day at ~20 °C to give 1-(2′,3′-dideoxy-2′,3′-(2*H*-1,2,3-triazolo)-β-D-*glycero*-pent-2′-eno-furanosyl)uracil **47** (88%) and the deprotected-dimer **48** (81%), respectively. It is interesting to note that the 2′,3′-fused-triazolo nucleosides **45-48** were very sensitive to both acid and fluoride ion, therefore, toluoyl group in **3** was a 5′-hydroxyl protecting group of choice in order to give the 2′,3′-fused [3.3.0]-1,2,3-triazolo nucleoside **47** and **48** with free 5′-hydroxyl function. Structures of compounds **45** and **46** were arrived from the elucidation of structures **47** and **48**. Structures of compound **47**, as the 2*H*-1,2,3-triazolyl derivative, and compound **48**, as its N-2 substituted derivative, were assigned from their $^{13}$C-NMR spectra which could not be unambiguously performed for their precursors **45** and **46**, respectively, due to the presence of additional aromatic carbon absorptions from the 5′-O-toluoyl group. A systematic $^{13}$C-NMR study [29,30] has shown a equivalence of C-4 and C-5 [δ $^{13}$C (DMSO) = 130.3] in 1,2,3-triazole which points to its symmetrical 2*H*-form. This is further substantiated by the equivalence of C-4 and C-5 in 2-methyl-1,2,3-triazole [δ $^{13}$C (DMSO) = 133.2], and their nonequivalence in 1-methyl-1,2,3-triazole [δ $^{13}$C (DMSO) = 132.6 (C-4), 124.8 (C-5), Δδ = 7.8 ppm][29,30]. The $^{13}$C NMR spectrum of **47** shows the absorptions for C-2′ and C-3′ at δ 154.09 and 153.0, respectively, with Δδ = 1.09 ppm. Similarly, the $^{13}$C NMR spectrum of **48** shows the absorptions for C-2′ and C-3′ at δ 151.5 and 150.5, respectively, with Δδ = 1.0 ppm. A comparison of Δδ for **47** and **48** (~1 ppm) with those of Δδ for 2-methyl-1,2,3-triazole [ Δδ = 0 ppm] and 1-methyl-1,2,3-triazole [Δδ = 7.8 ppm] suggests the symmetrical 2*H*-form for **47** (and to its precursor **45**), and for its N-2 substituted derivative **48** (and to its precursor **46**).

***Diels-Alder reaction.***

Our early attempts to carry out Diels-Alder reactions with a nucleoside-olefin such as **6** and a diene was completely unsuccessful. Attempts with activated olefins such as in 5′-O-protected-2′,3′-ene-3′-sulfone[21] or 2′,3′-ene-3′-nitrile[22] were also unsuccessful. The stronger electron-withdrawing character of the $PhSeO_2$ group in 2′,3′-ene-3′-phenylselenone in **1** or **4** than in 2′,3′-ene-3′-sulfone[21] or 2′,3′-ene-3′-nitrile[22] prompted us to investigate the Diels-Alder reaction of **1** or **4** with cyclopentadiene. Thus the solution of 2′,3′-ene-3′-phenylselenone **1** or **4** and freshly distilled cyclopentadiene was heated at ~ 60 °C for 4 days, the cycloadduct **49** or **50** was isolated in 75 and 64% yields, respectively, along with starting material (~20%). The reactions were found to be quite sluggish, and they did not go to completion even upon addition of an excess of diene or prolonging the reaction time, or upon addition of anhydrous $AlCl_3$ as a catalyst in the reaction of cyclopentadiene with **4**. The structures of **49** and **50** were clearly corroborated by $^1$H- and $^{13}$C-NMR (experimental). Clearly, the cycloadducts **49** and **50** were formed by a two-step mechanism involving first cycloaddition which is followed by a *cis*-elimination of phenylselenic acid. In view of the severe steric and electronic crowding on the β-face, it is likely that the cyclopentadiene approaches the 2′,3′-double bond of the sugar ring from the α-face. The adducts **49** and **50** were found to be very unstable in acid. Thus attempts to remove the 5′-O-MMTr group from **49** by a brief treatment with 80% aqueous acetic acid at room temperature gave uracil as the sole product. It was however possible to remove the 5′-O-TBDMS group from **50** by a short treatment with tetrabutylammonium fluoride in dry THF (0.1 M) for 2 h at room temperature which gave 1-(2′,3′-dideoxy-2′,3′-*C*-(2-cyclopentene-1,4-ylene)-β-D-*glycero*-pent-2′-eno-furanosyl) uracil (**51**) in 80% yield.

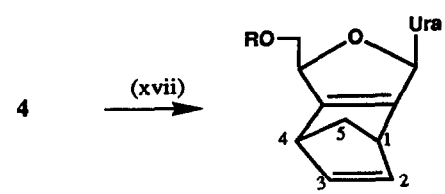



Scheme 1




**45** : R = Tol (64%)
**47** : R = H (88%)

**46** : R = Tol (33%)
**48** : R = H (81%)




**49** : R = MMTr (75 %)
**50** : R = TBDMS (64%)
**51** : R = H (88%)

*(xv) $NaN_3$ in DMSO at ~20 °C; (xvii) Cyclopentadiene in toluene at 60 °C for 4 days*

Further work to employ **1**, **3** or **4** as dienophiles in various 1,3-dipolar cycloaddition reactions and in Diels-Alder reactions as means to prepare various 2′,3′-dideoxy-2′,3′-*hypermodified*-β-D-nucleosides are currently under investigation in this laboratory.

## 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 high resolution 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′-O-*p*-Toluoyl-2′,3′-dideoxy-3′-phenylselenonyl-β-D-*glycero*-pent-2′-eno-furanosyl) uracil (3) :** To a solution of compound **2** (600 mg, 1.5 mmol) in pyridine (15 ml) was added toluoyl chloride (540 µl, 4.5 mmol) and the stirring was continued overnight. The reaction mixture was poured into saturated aqueous solution of sodium bicarbonate (100 ml), which was then extracted with chloroform (3 x 40 ml). The combined extract was evaporated and coevaporated with toluene to obtain pyridine-free residue. The residue was purified on a silica gel column to give the title compound (610 mg, 79 %). $^1$H-NMR ($CDCl_3$): 9.70 (br, 1H) NH; 8.06 -7.01 (m, 12H) H-6, H-1', H-2', arom; 5.48 (m, 1H) H-4'; 5.15 (d, $J_{5,6}$ = 8.3 Hz, 1H) H-5; 4.87 (dd, $J_{4',5'}$ = 2.4 Hz, $J_{5',5''}$ = 13.2 Hz, 1H) H-5'; 4.80 (dd, $J_{4',5''}$ = 2.6 Hz, 1H) H-5"; 2.40 (s, 3H) $CH_3$; $^{13}$C-NMR ($CDCl_3$) : 165.2 (s) carbonyl; 103.1 (d, $J_{CH}$ = 180.8 Hz) C-5; 88.2 (d, $J_{CH}$ = 165.1 Hz) C-1'; 82.9 (d, $J_{CH}$ = 150.6 Hz) C-4'; 63.9 (t, $J_{CH}$ = 148.9 Hz) C-5'; 21.5 (q) $CH_3$; MS (FAB$^-$): calc for (M-H)$^-$ 515.0358 , found 515.0372.

**1-(5′-O-*t*-butyldimethylsilyl-2′,3′-dideoxy-3′-phenylselenonyl-β-D-*glycero*-pent-2′-eno-furanosyl)uracil (4) :** To a solution of compound **2** (2.0 g, 5 mmol) in pyridine (40 ml) was added *t*-butyl-dimethylsilylchloride (1.97 g, 10.0 mmol) and the stirring was continued for 5 h. The reaction mixture was poured into saturated aqueous solution of sodium bicarbonate (200 ml), which was then extracted with dichloromethane (3 x 50 ml). The combined extract was evaporated and coevaporated with toluene to obtain pyridine-free residue. The residue was purified on a silica gel column to give the title compound (2.3 g, 90 %). $^1$H-NMR ($CDCl_3$) : 9.37 (br, 1H) NH; 8.10 -7.33 (m, 6 H) H-6, arom; 7.07 (dd, $J_{1',2'}$ = 1.7 Hz, $J_{1',4'}$ = 4.1 Hz, 1H) H-1'; 6.72 (t, $J_{2',4'}$ = 2.0 Hz, 1H) H-2'; 5.72 (d, $J_{5,6}$ = 8.1 Hz, 1H) H-5; 5.20 (m, $J_{4',5'}$ = 1.5 Hz, $J_{4',5''}$ = 1.9 Hz, 1H) H-4'; 4.29 (dd, $J_{5',5''}$ = 12.0 Hz, 1H) H-5'; 4.02 (dd, 1 H) H- 5"; 0.92, 0.13, 0.10, TBDMS. $^{13}$C-NMR ($CDCl_3$) : 103.2 (d, $J_{CH}$ =178.0 Hz) C-5; 87.5 (d, $J_{CH}$ = 176.6 Hz) C-1'; 86.0 (d, $J_{CH}$ = 147.7 Hz) C-4'; 62.9 (t, $J_{CH}$ = 144.1 Hz) C-5'; 25.9, 18.6, -5.3, -5.8, TBDMS. MS (FAB$^-$): calc. for (M-H)$^-$ 511.0804 , found 511.0834.

**1-(5′-O-MMTr-2′,3′-dideoxy-2′,3′-biimino-β-D-*ribo*furanosyl)uracil (5) & 1-(5′-O-MMTr-2′,3′-dideoxy-β-D-*glycero*-pent-2′-eno-furanosyl)uracil (6):** Compound **1** (200 mg, 0.3 mmol) was treated with anhydrous hydrazine (29 mg, 0.9 mmol) in dry dichloromethane (20 ml) at room temperature overnight. The reaction mixture was loaded on a silica gel column and eluted with hexane-dichloromethane (1:1, v/v, 100 ml ). The compounds were washed out with 2% methanol in dichloromethane (200 ml) and evaporated to dryness. The residue was separated on a silica gel column again to give compounds **6** (51 mg, 35.4%) and **5** (92 mg, 60%). $^1$H-NMR ($CDCl_3$) : 7.77 (d, $J_{5,6}$ = 8.3 Hz, 1H) H-6; 7.35-6.85 (m, 14H) arom; 5.99 (s, 1H) H-1'; 5.08 (d, 1H) H-5; 4.32 (t, $J_{4',5'}$ = 3.5 Hz, 1H) H-4'; 3.81 (s, 3H) $OCH_3$; 3.40 (m, 2H) H-5', H-5"; 3.00 (s, 2H) H-2' and H-3'. $^{13}$C-NMR ($CDCl_3$) : 140.7 (d, $J_{CH}$ = 183.1 Hz) C-6; 101.9 (d, $J_{CH}$ = 177.0 Hz) C-5; 87.1 (s) MMTr; 85.6 (d, $J_{CH}$ = 173.3 Hz) C-1'; 81.6 (d, $J_{CH}$ = 152.5 Hz) C-4'; 63.7 (t, $J_{CH}$ = 144.4 Hz) C-5'; 55.1 (q) $OCH_3$; 52.7 and 50.5 (d, $J_{CH}$ = 185.6 Hz and 183.1 Hz) C-2' and C-3'. MS (FAB$^-$) : calc. for (M-H )$^-$ 511.1982 , found 511.1989.

**1-(5′-O-MMTr-2′,3′-dideoxy-2′-ulose hydrazone-β-D-*erythro*-pentofuranosyl)uracil (7c):** Compound **1** (335 mg, 0.5 mmol) was treated with anhydrous hydrazine (96 mg, 3 mmol) in dry tetrahydrofuran (10 ml) at 40 °C for 2 h. The reaction mixture was loaded on a silica gel column and eluted with hexane-dichloromethane (1:1, v/v, 100 ml) first, and then washed with 2% methanol in dichloromethane

(250 ml). The products were concentrated in vacuum and separated on a silica gel column to give compounds **6** (42 mg, 17.2%) , **5c** (77 mg, 30.1%) and **7c** (83 mg, 32.4%). compound **5c**: $^1$H-NMR ($CDCl_3$ + $CD_3OD$) : 7.31-6.84 (m, 15H) arom and H-6; 6.40 (s, 1H) H-1'; 5.44 (d, $J_{5,6}$ = 8.0 Hz, 1H) H-5; 4.44 (m, 1H) H-4'; 3.80 (s, 3H) $OCH_3$; 3.41 (d, $J_{4',5'}$ = 3.7 Hz, 2H) H-5', H-5"; 2.64 (d, $J_{3',4'}$ = 7.8 Hz, 2H) H-3' and H-3". $^{13}$C-NMR ($CDCl_3$) : 141.6 (d, $J_{CH}$ = 180.9 Hz) C-6; 102.5 (d, $J_{CH}$ = 178.6 Hz) C-5; 86.7 (s) MMTr; 84.6 (d, $J_{CH}$ = 171.9 Hz) C-1'; 76.9 (d, $J_{CH}$ = 153.9 Hz) C-4'; 64.5 (t, $J_{CH}$ = 143.8 Hz) C-5'; 55.0 (q) $OCH_3$; 27.1 (t, $J_{CH}$ = 133.7 Hz ) C-3'. MS (FAB$^-$) : calc. for (M-H )$^-$ 511.1982, found 511.2007.

**1-(2',3'-dideoxy-2',3'-biimino-β-D-*ribo*furanosyl)uracil (8):** Compound **2** (140 mg, 0.35 mmol) was treated with hydrazine (34 mg, 1.05 mmol) in tetrahydrofuran (20 ml). The reaction mixture was stirred overnight at 40 °C, and mixture was separated on a silica gel column directly to give compound **8** (52 mg, 62%). $^1$H-NMR ($CDCl_3$) : 7.99 (d, $J_{5,6}$ = 8.2 Hz, 1H) H-6; 5.93 (s, 1H) H-1'; 5.72 (d, 1H) H-5; 4.20 (t, $J_{4',5'}$ = 4.1 Hz,1H) H-4'; 3.78 (m, 2H) H-5', H-5"; 3.01 (s, 2H) C-2' and C-3'. $^{13}$C-NMR ($CDCl_3$) : 141.3 (d, $J_{CH}$ = 179.4 Hz) C-6; 101.0 (d, $J_{CH}$ = 180.2 Hz) C-5; 85.6 (d, $J_{CH}$ = 173.4 Hz) C-1'; 82.7 (d, $J_{CH}$ = 151.4 Hz) C-4'; 61.7 (t, $J_{CH}$ = 142.9 Hz) C-5'; 51.3 and 49.3 (2 x d, $J_{CH}$ = 177.8 Hz) C-2' and C-3'. MS ( FAB$^-$) : calc. for (M-H )$^-$ 239.0780, found 239.0782.

**1-(5'-O-MMTr-2',3'-dideoxy-2',3'-(2-iminoimidazolidino)-β-D-*ribo*furanosyl)uracil (9):** To a solution of guanidinium hydrochloride (480 mg, 5 mmol) in N,N-dimethylformamide (30 ml) was added sodium hydride (150 mg, 5 mmol) and stirring was kept for 2 h at room temperature. Compound **1** (335 mg, 0.5 mmol) was added, and the stirring was continued overnight. The reaction mixture was evaporated and coevaporated with toluene to dryness. The residue was purified on silica gel column to give compound **9** ( 147 mg, 54.5 % ). $^1$H-NMR ($CDCl_3$ + $CD_3OD$) : 8.08 (d, $J_{5,6}$ = 8.0 Hz, 1H) H-6; 7.31-6.84 (m, 14H) arom; 5.73 (d, $J_{1',2'}$ = 1.7 Hz, 1H) H-1'; 5.52 (d, 1H) H-5; 4.61 (m, 2H) H-2' and H-3'; 4.44 (m, 1H) H-4'; 3.80 (s, 3H) $OCH_3$; 3.48 (m , $J_{4',5'}$ = 3.4 Hz, 2H) H-5', H-5". $^{13}$C-NMR ($CDCl_3$ + $CD_3OD$) : 140.1 (d, $J_{CH}$ = 183.1 Hz) C-6; 101.6 (d, $J_{CH}$ = 177.5 Hz) C-5; 93.9 (d, $J_{CH}$ = 170.7 Hz) C-1'; 86.9 (s) MMTr; 86.4 (d, $J_{CH}$ = 152.8 Hz) C-4'; 66.2 (d, $J_{CH}$ = 150.2 Hz) C-2'; 63.0 (t, $J_{CH}$ = 139.9 Hz) C-5'; 60.8 (d, $J_{CH}$ = 157.2 Hz) C-3'; 54.7 (q) $OCH_3$. MS (FAB$^+$) : calc. for (M+H)$^+$ 540.2247, found 540.2213.

**Dimer 10 :** To a solution of guanidinum hydrochloride (237 mg, 2.5 mmol) in dimethylformamide (15 ml) was added sodium hydride (60 mg, 2 mmol) and stirring was kept for 2 h at room temperature. Then compound **2** ( 180 mg, 0.45 mmol) was added and stirring was continued overnight. The reaction mixture was evaporated and coevaporated with toluene to dryness. The residue was separated on a silica gel column to give compound **10** (43 mg, 35%) . $^1$H-NMR ($D_2O$+$CD_3OD$) : 7.59 (d, $J_{5,6}$ = 8.1 Hz, 1H) H-6; 5.79 (d, $J_{1',2'}$ = 3.2 Hz, 1H) H-1'; 5.75 (d, 1H) H-5; 4.58-4.52 (m, 2H) H-2' and H-3'; 4.20 (m, 1H) H-4'; 3.81 (m, 2H) H-5', H-5". $^{13}$C-NMR (DMSO-$d_6$) : 140.0 (d, $J_{CH}$ = 183.1 Hz) C-6; 102.3 (d, $J_{CH}$ = 173.0 Hz) C-5; 93.5 (d, $J_{CH}$ = 167.3 Hz) C-1'; 87.8 (d, $J_{CH}$ = 146.0 Hz) C-4'; 68.5 (d, $J_{CH}$ = 153.9 Hz) C-2'; 62.6 (d, $J_{CH}$ = 151.7 Hz) C-3'; 61.8 (t, $J_{CH}$ = 141.6 Hz) C-5'. MS (FAB$^-$) : calc. for (M-H)$^-$ 474.1373, found 474.1397.

**1-(5'-O-MMTr-2',3'-dideoxy-2',3'-*N*-(1,2-ethylene)-β-D-*ribo*furanosyl)uracil (11) & 1-(5'-O-MMTr-2',3'-dideoxy-2',3'-[N-(2-aminoethyl)]epimino-β-D-*ribo*furanosyl)uracil (13):** Compound **1** (335 mg, 0.5 mmol) was treated with 1,2-ethylenediamine (90 mg, 1.5 mmol) in tetrahydrofuran (20 ml) at ~0 °C overnight. The solution was poured into a saturated solution of ammonium chloride (50 ml) and extracted with dichloromethane (3 x 30 ml). All volatile matters were removed under vacuum and the residue was separated on a silica gel column to give compounds **13** (137 mg, 54 %) and **11** (72 mg, 28 %). Compound **11.** $^1$H-NMR ($CDCl_3$) : 8.05 (d, $J_{5,6}$ = 8.2 Hz, 1H) H-6; 7.32-6.84 (m, 14H) arom; 5.86 (d, $J_{1',2'}$ = 2.5 Hz, 1H) H-1'; 5.28 (d, 1H) H-5; 4.43 (m, 1H) H-4'; 3.80 (s, 3H) $OCH_3$; 3.68-3.39 (m, 4H) H-2', H-3' and H-5', H-5"; 2.91-2.81 (m, 4H) $NCH_2CH_2N$. $^{13}$C-NMR ($CDCl_3$): 140.1 (d, $J_{CH}$ = 182.0 Hz) C-6; 101.5 (d, $J_{CH}$ = 177.4 Hz) H-5; 88.1 (d, $J_{CH}$ = 173.0 Hz) C-1'; 87.0 (s) MMTr; 79.4 (d, $J_{CH}$ = 148.2 Hz) C-4' 62.2 (t, $J_{CH}$ = 143.8 Hz) C-5'; 60.4 (d, $J_{CH}$ = 146.1 Hz) C-2'; 53.1 (d, $J_{CH}$ = 147.1 Hz) C-3'; 43.6 and 41.6 (t, $J_{CH}$ = 134.3 Hz and 136.5 Hz) $NCH_2CH_2N$. MS (FAB$^-$) calc. for (M-H)$^-$ 539.2295, found 539.2258. Compound **13.** $^1$H-NMR ($CDCl_3$) : 7.62 (d, $J_{5,6}$= 8.3 Hz, 1H) H-6; 7.32-6.84 (m, 14H) arom; 5.92 (s, 1H) H-1'; 5.13 (d, 1H) H-5; 4.35 (m, 1H) H-4'; 3.78 (s, 3H) $OCH_3$; 3.33 (d, $J_{4',5'}$ = 3.2 Hz, 2H) H-5', H-5"; 2.93-2.66 (m, 6H) H-2', H-3'and $NCH_2CH_2N$; $^{13}$C-NMR ($CDCl_3$): 140.4 (d, $J_{CH}$ = 184.8 Hz) C-6; 101.7 (d, $J_{CH}$ = 177.2 Hz) C-5; 87.0 (s) MMTr; 86.3 (d, $J_{CH}$ = 169.1 Hz) H-1'; 81.7 (d, $J_{CH}$ = 143.6 Hz) C-4'; 63.9 (t, $J_{CH}$ = 143.6 Hz) C-5'; 59.0 (t, $J_{CH}$ = 142.5 Hz) $NCH_2CH_2NH_2$; 55.1 (q) $OCH_3$; 48.4 (d,

$J_{CH}$ = 181.0 Hz) C-2'; 45.6 (d, $J_{CH}$ = 185.6 Hz) C-3'; 41.1 (t, $J_{CH}$ = 143.0 Hz) $NCH_2CH_2NH_2$. MS (FAB$^-$): calc. for (M-H)$^-$ 539.2295. found. 539.2281.

**1-(2',3'-dideoxy-2',3'-[N-(2-aminoethyl)]epimino-β-D-*ribo*furanosyl)uracil (14):** Compound **2** (100 mg, 0.25 mmol) was treated with 1,2-ethylenediamine (60 mg, 1 mmol) in a mixture of dry dimethylformamide (2 ml) and tetrahydrofuran (10 ml) at room temperature overnight. The volatile matters were removed in vacuum and coevaporated with toluene to dryness. The residue was separated on a silica gel column to give compounds **14** ( 25 mg, 38%) and **12** (22 mg, 34%). Compound **14.** $^1$H-NMR ($CDCl_3$ + $CD_3OD$) : 7.97 (d, $J_{5,6}$ = 8.2 Hz, 1H) H-6; 5.87 (s, 1H) H-1'; 5.69 (d, 1H) H-5; 4.21 (t, $J_{4',5'}$ = 4.4 Hz, 1H) H-4'; 3.75 (d, 2H) H-5', H-5"; 2.82-2.52 (m, 6H) H-2', H-3' and $NCH_2CH_2N$; $^{13}$C-NMR ($CDCl_3$ + $CD_3OD$) : 141.0 (d, $J_{CH}$ = 184.2 Hz) C-6; 100.7 (d, $J_{CH}$ = 176.4 Hz) C-5; 85.7 (d, $J_{CH}$ = 176.3 Hz) C-1'; 82.6 (d, $J_{CH}$ = 155.0 Hz) C-4'; 61.6 (d, $J_{CH}$ = 141.6 Hz) C-5'; 57.6 (t, $J_{CH}$ = 135.9 Hz) $NCH_2CH_2NH_2$; 47.3 and 45.5 (d, $J_{CH}$ = 179.8 and 186.5 Hz) C-2' and C-3'; 39.8 (t, $J_{CH}$ = 138.2 Hz) $NCH_2CH_2NH_2$. MS ( FAB$^-$) : calc. for (M-H )$^-$ 267.1093 , found 267.1081.

**1-(5'-O-MMTr-2',3'-dideoxy-2',3'-[N-(2-aminopropyl)]epimino-β-D-*ribo*furanosyl)uracil (15) & Dimer (16) :** To a solution of compound **1** (400 mg, 0.6 mmol) in tetrahydrofuran (10 ml) was added 1,3-diaminopropane (148 mg, 2 mmol) and the stirring was kept at ~0 °C overnight. The mixture was poured into a saturated aqueous solution of ammonium chloride (50 ml), which was extracted with dichloromethane (3 x 20 ml). The combined extract was evaporated to dryness, and the residue was separated on a silica gel column to give compounds **15** (251 mg, 76 %) and **16** (48 mg, 21 %). Compound **15**: $^1$H-NMR ($CDCl_3$): 7.59 (d, $J_{5,6}$ = 8.1 Hz, 1H) H-6; 7.31-6.84 (m, 14H) arom; 5.87 (s, 1H) H-1'; 5.12 (d, 1H) H-5; 4.33 (m, 1H) H-4'; 3.79 (s, 3H) $OCH_3$; 3.31 (d, $J_{4',5'}$ = 4.1 Hz, 2H) H-5', H-5"; 2.93 and 2.59 (m, 4H) $NCH_2CH_2CH_2N$; 2.80 and 2.59 (2 x d, $J_{2',3'}$ = 5.0 Hz, 2H) H-2' and H-3'; 1.83 (m, 2H) $CH_2CH_2CH_2$. $^{13}$C-NMR ($CDCl_3$): 143.0 (d, $J_{CH}$ = 186.5 Hz) C-6; 101.7 (d, $J_{CH}$ = 176.3 Hz) C-5; 86.8 (s) MMTr; 86.3 (d, $J_{CH}$ = 175.2 Hz) C-1'; 81.6 (d, $J_{CH}$ = 161.8 Hz) C-4'; 64.0 (t, $J_{CH}$ = 142.7 Hz) C-5'; 55.0 (q) $OCH_3$; 55.0 (t, $J_{CH}$ = 133.7 Hz) $NCH_2CH_2CH_2N$; 48.3 (d, $J_{CH}$ = 182.0 Hz) C-2'; 45.9 (d, $J_{CH}$ = 182.0 Hz) C-3'; 38.9 (t, $J_{CH}$ = 135.4 Hz) $NCH_2CH_2CH_2N$; 30.5 (t, $J_{CH}$ = 125.3 Hz) $NCH_2CH_2CH_2N$.MS (FAB$^-$) : calc. for (M-H)$^-$ 553.2451, found 553.2468. Compound **16**: $^1$H-NMR ($CDCl_3$) : 7.86-6.84 (m, 30H) H-6 and arom; 5.86 (s, 2H) H-1'; 5.10 (d, $J_{5,6}$ = 8.3 Hz, 2H) H-5; 4.28 (m, 2H) H-4'; 3.79 (s, 6H) $OCH_3$; 3.32 (d, $J_{4',5'}$ = 4.7 Hz, 4H) H-5', H-5"; 3.11 (d, $J_{2',3'}$ = 5.1 Hz, 2H) H-2'; 2.62 (m, 6H) H-3' and $NCH_2CH_2CH_2N$; 1.83 (m, 2H) $NCH_2CH_2CH_2N$. $^{13}$C-NMR ($CDCl_3$) : 140.1 (d, $J_{CH}$ = 182.0 Hz) C-6; 101.7 (d, $J_{CH}$ = 176.3 Hz) C-5; 86.9 (s) MMTr; 86.5 (d, $J_{CH}$ = 177.5 Hz) C-1'; 81.8 (d, $J_{CH}$ = 151.6 Hz) C-4'; 64.0 (t, $J_{CH}$ = 141.6 Hz) C-5'; 55.1 ( q) $OCH_3$; 53.9 (t, $J_{CH}$ = 135.9 Hz) $NCH_2$-; 48.3 (d, $J_{CH}$ = 184.2 Hz) H-2'; 46.2 (d, $J_{CH}$ = 180.8 Hz) H-3'; 29.1 (t, $J_{CH}$ = 123.6 Hz) $NCH_2CH_2CH_2N$. MS ( FAB$^-$) : calc. for (M-H )$^-$ 1033.4140, found 1033.4220.

**1-(2',3'-dideoxy-2',3'-[N-(3-aminopropyl)]epimino-β-D-*ribo*furanosyl)uracil (17) :** Compound **2** (200 mg, 0.5 mmol) was treated with 1,3-diaminopropane (90 mg, 1.5 mmol) in tetrahydrofuran (20 ml) at room temperature overnight. The reaction mixture was evaporated and coevaporated with toluene to dryness. The residue was purified on a silica gel column to give compound **17** (116 mg, 75.9% ). $^1$H-NMR ($CDCl_3$ + $CD_3OD$) : 7.90 (d, $J_{5,6}$ = 8.1 Hz, 1H) H-6; 5.85 (s, 1H) H-1'; 5.68 (d, 1H) H-5; 4.18 (t, $J_{4',5'}$ = 4.4 Hz, 1H) H-4'; 3.72 (d, 2H) H-5', H-5"; 2.80 (m, 4H) H-2', H-3' and $NCH_2CH_2CH_2NH_2$; 2.44 (m, 2H) $NCH_2CH_2CH_2NH_2$; 1.77 (m, 2H) $NCH_2CH_2CH_2NH_2$. $^{13}$C-NMR ($CDCl_3$ + $CD_3OD$) : 141.1 (d, $J_{CH}$ = 185.4 Hz) C-6; 101.0 (d, $J_{CH}$ = 177.5 Hz) C-5; 86.2 (d, $J_{CH}$ = 177.5 Hz) C-1'; 82.9 (d, $J_{CH}$ = 155.1 Hz) C-4'; 61.9 (t, $J_{CH}$ = 141.6 Hz) C-5'; 54.9 (t, $J_{CH}$ = 138.3 Hz) $NCH_2CH_2CH_2NH_2$; 47.9 and 45.9 (d, $J_{CH}$ = 186.4 Hz and 176.0 Hz) C-2' and C-3'; 38.9 (t, $J_{CH}$ = 137.1 Hz) $NCH_2CH_2CH_2NH_2$; 31.2 (t, $J_{CH}$ = 125.8 Hz) $NCH_2CH_2CH_2NH_2$. MS (FAB$^+$) : calc. for (M+H)$^+$ 283.1407, found 283.1397 .

**1-(5'-O-MMTr-2',3'-dideoxy-2'-*S*-(2-mercaptoethyl)-β-D-*glycero*-pent-2'-eno-furanosyl) uracil (18) :** To a solution of 1,2-ethanedithiol (282 mg, 3 mmol) and triethylamine (60 mg, 0.6 mmol) in tetrahydrofuran (10 ml) was added compound **1** (200 mg, 0.3 mmol) and the stirring was continued overnight at room temperature. The reaction mixture was poured into a saturated aqueous solution of ammonium chloride (50 ml), which was extracted with dichloromethane (3 x 20 ml). The combined extract was evaporated to dryness, and the residue was separated on a silica gel column to give compounds **6** (31 mg, 21.5%) and **18** (75 mg, 43.6%). Compound **18**. $^1$H-NMR ($CDCl_3$) : 7.48 (d, $J_{5,6}$ = 8.2 Hz, 1H) H-6; 7.35-6.83 (m, 14H) arom; 6.81 (m, 1H) H-1'; 5.63 (d, 1H) H-5; 5.48 (t, $J_{1',3'}$ = 1.6 Hz, $J_{3',4'}$ = 1.7 Hz, 1H) H-3'; 4.84 (m, 1H)

H-4'; 3.79 (s, 3H) $OCH_3$; 3.77 (m, 2H) H-5', H-5"; 2.57 (m, 4H) $SCH_2CH_2S$; $^{13}$C-NMR ($CDCl_3$) : 140.8 (d, $J_{CH}$ = 180.9 Hz) C-6; 102.5 (d, $J_{CH}$ = 177.4 Hz) C-5; 91.1 (d, $J_{CH}$ = 174.1 Hz) C-1'; 89.9 (d, $J_{CH}$ = 147.2 Hz) C-4'; 87.2 (s) MMTr; 63.1 (t, $J_{CH}$ = 141.6 Hz) C-5'; 55.1 ( q) $OCH_3$; 31.1 and 30.7 (t, $J_{CH}$ = 140.4 Hz) $SCH_2CH_2S$. MS ($FAB^-$) : $(M-H)^-$ calc. for 573.1518 found 573.1565.

**1-(5'-O-MMTr-2',3'-dideoxy-2',3'-*S*-(1,2-ethylene)-β-D-*ribo*furanosyl)uracil (20)** : To a solution of 1,2-ethanedithiol (235 mg, 2.5 mmol) and 1,8-diazabicyclo-(5,4,0)-undec-7-ene (152 mg, 1 mmol) in dry tetrahydrofuran (15 ml) was added compound **1** (335 mg, 0.5 mmol) and stirring was kept overnight at room temperature. The reaction mixture was poured into a saturated aqueous solution of ammonium chloride (50 ml), which was extracted with dichloromethane (3 x 20 ml). The combined organic phase was evaporated to dryness and the residue was purified on a silica gel column to give compound **20** (182 mg, 64.3%). $^1$H-NMR ($CDCl_3$) : 8.07 (d, $J_{5,6}$ = 8.2 Hz, 1H) H-6; 7.33-6.85 (m, 14H) arom; 5.89 (d, $J_{1',2'}$ = 2.6 Hz, 1H) H-1'; 5.24 (d, 1H) H-5; 4.48 (m, 1H) H-4'; 3.79 (s, 3H) $OCH_3$; 3.62 (m, 4H) H-2', H-3', H-5' and H-5"; 2.92 (m, 4H) $SCH_2CH_2S$. $^{13}$C-NMR ($CDCl_3$) : 139.9 (d, $J_{CH}$ = 180.4 Hz) C-6; 101.7 (d, $J_{CH}$ = 177.0 Hz) C-5; 87.6 (d, $J_{CH}$ = 173.3 Hz) C-1'; 87.4 (s) MMTr; 81.7 (d, $J_{CH}$ = 144.8 Hz) C-4'; 61.4 (t, $J_{CH}$ = 143.5 Hz) C-5'; 55.1 ( q) $OCH_3$; 44.7 (d, $J_{CH}$ = 151.3 Hz) C-2'; 35.8 (d, $J_{CH}$ = 136.6 Hz) C-3'; 27.5 and 25.1 (t, $J_{CH}$ = 141.6 Hz and 142.9 Hz ) $SCH_2CH_2S$. MS ( $FAB^-$) : calc. for $(M-H)^-$ 573.1518, found 573.1546.

**Dimer 22** : To a solution of compound **18** (115 mg, 0.2 mmol) in triethylamine (202 mg, 2 mmol) and tetrahydrofuran (15 ml) was added compound **1** (400 mg, 0.6 mmol). The mixture was heated under reflux for 24 h and then evaporated to dryness. The residue was separated on a silica gel column to give compound **22** (132 mg, 62.5%). $^1$H-NMR ($CDCl_3$) : 7.76 (d, $J_{5,6}$ = 7.9 Hz, 2H) H-6; 7.29-6.80 (m, 28H) arom; 6.93 (m, 2H) H-1'; 5.95 (m, 2H) H-3'; 5.07 (d, 2H) H-5; 4.98 (m, 2H) H-4'; 3.78 (s, 6H) $OCH_3$; 3.45 (s, 4H) H-5', H-5"; 3.00 (m, 4H) $SCH_2CH_2S$. $^{13}$C-NMR ($CDCl_3$) : 140.7 (d, $J_{CH}$ = 180.8 Hz) C-6; 102.9 (d, $J_{CH}$ = 178.6 Hz) C-5; 89.4 (d, $J_{CH}$ = 168.5 Hz) C-1'; 87.2 (s) MMTr; 85.7 (d, $J_{CH}$ = 165.0 Hz) C-4'; 64.3 (t, $J_{CH}$ = 143.8 Hz) C-5'; 55.2 (q) $OCH_3$; 31.1 (t, $J_{CH}$ = 143.7 Hz) $SCH_2$-. MS ($FAB^-$) : calc. for $(M-H)^-$ 1053.32, found 1053.34.

**1-(5'-O-MMTr-2',3'-dideoxy-2',3'-[N-(2-hydroxyethyl)]epimino-β-D-*ribo*furanosyl)uracil (24)** : To a solution of ethanolamine (36.6 mg, 0.6 mmol) and 1,8-diazabicyclo-(5,4,0)-undec-7-ene (136 mg, 0.9 mmol) in tetrahydrofuran (10 ml) was added compound **1** (335 mg, 0.5 mmol) and stirring was continued at room temperture overnight. The mixture was poured into a saturated aqueous of ammonium chloride (50 ml) and which was extracted with dichloromethane (3 x 20 ml) . The combined extract was evaporated to dryness, and residue was purified on silica gel column to give compound **24** (147 mg, 54%). 7.65 (d, $J_{5,6}$ = 8.1 Hz, 1H) H-6; 7.33-6.83 (m, 14H) arom; 6.01 (s, 1H) H-1'; 5.05 (d, 1H) H-5; 4.39 (t, $J_{4',5'}$ = 3.4 Hz, $J_{4',5"}$ = 4.2 Hz, 1H) H-4'; 3.79 (s+m, 5H) $OCH_3$ and $CH_2OH$; 3.35 (m, 2H) H-5', H-5", H-5"; 3.00 and 2.75 (2 x d, $J_{2',3'}$ = 4.5 Hz, 2H) H-2' and H-3'; 2.75-2.39 (m, 2H) $NCH_2$-. $^{13}$C-NMR ($CDCl_3$) : 140.8 (d, $J_{CH}$ = 182.0 Hz) C-6; 101.8 (d, $J_{CH}$ = 177.5 Hz) C-5; 87.1 (s) MMTr; 86.0 (d, $J_{CH}$ = 183.1 Hz) C-1'; 81.6 (d, $J_{CH}$ = 156.2 Hz) C-4'; 64.0 (t, $J_{CH}$ = 142.7 Hz) C-5'; 61.3 (t, $J_{CH}$ = 142.1 Hz) $OCH_2$-; 59.5 (t, $J_{CH}$ = 134.8 Hz ) $NCH_2$; 55.1 (q) $OCH_3$; 48.3 and 46.0 (d, $J_{CH}$ = 184.2 and 179.7 Hz ) H-2' and H-3'. MS ($FAB^-$) : $(M-H)^-$ calc. for 540.2134, found 540.2119.

**1-(2',3'-dideoxy-2',3'-[N-(2-hydroxyethyl)]epimino-β-D-*ribo*furanosyl)uracil (25)** : Compound **2** (120 mg, 0.3 mmol) was treated with ethanolamine (183 mg, 3 mmol) in tetrahydrofuran (20 ml) and stirring was kept at room temperature overnight. The reaction mixture was evaporated and coevaporated with toluene to dryness and the residue was purified on a silica gel column to give compound **25** (52 mg, 63.7%). $^1$H-NMR ($CDCl_3$ + $CD_3OD$) : 7.12 (d, $J_{5,6}$ = 8.1 Hz, 1H) H-6; 5.90 (s, 1H) H-1'; 5.69 (d, 1H) H-5; 4.42 (m, 1H) H-4'; 3.73 (m, 4H) H-5', H-5" and $CH_2OH$; 2.85 (2 x d, $J_{2',3'}$ = 4.9 Hz) H-2' and H-3'; 2.53 (t, J = 4.8 Hz, 2H) $NCH_2$-. $^{13}$C-NMR ($CDCl_3$ + $CD_3OD$) : 141.4 (d, $J_{CH}$ = 187.6 Hz) C-6; 101.0 (d, $J_{CH}$ = 177.5 Hz) C-5; 86.1 (d, $J_{CH}$ = 176.5 Hz) C-1'; 82.6 (d, $J_{CH}$ = 162.9 Hz) C-4'; 62.0 (t, $J_{CH}$ = 141.6 Hz) C-5'; 60.6 (t, $J_{CH}$ = 141.5 Hz) $CH_2OH$; 58.8 (t, $J_{CH}$ = 134.8 Hz) $NCH_2$; 47.4 (d, $J_{CH}$ = 186.4 Hz) C-2'; 45.6 (d, $J_{CH}$ = 185.3 Hz ) C-3'. MS ( $FAB^-$) : calc. for $(M+H)^+$ 270.1090, found 270.1092.

**1-(5'-O-MMTr-2',3'-dideoxy-2'-*S*-(2-aminoethyl)-β-D-*glycero*-pent-2'-eno-furanosyl) uracil (26)** : To a solution of 2-aminoethanethiol hydrochloride (84 mg, 0.75 mmol) in tetrahydrofuran (10 ml) was added 1,8-diazabicyclo-(5,4,0)-undec-7-ene (228 mg, 1.5 mmol) and stirring was kept for 1 h at room temperature. Then **1** (335 mg, 0.5 mmol) was added and stirring was continued overnight at room temperature. The mixture was poured into a saturated aqueous solution of ammonium chloride (50 ml) and

extracted with dichloromethane (3 x 20 ml). The combined organic phase was evaporated to dryness and the residue was purified on a silica gel to give compound **26** (147 mg, 53%). $^1$H-NMR ($CDCl_3$) : 7.69 (d, $J_{5,6}$ = 8.0 Hz, 1H) H-6; 7.29-6.83 (m, 14H) arom; 6.95 (m, 1H) H-1'; 5.88 (m, 1H) H-3'; 5.09 (d,1H) H-5; 4.95 (m, 1H) H-4'; 3.79 (s, 3H) $OCH_3$; 3.41 (d, $J_{4',5'}$ = 2.9 Hz, 2H) H-5', H-5"; 2.94 (s, 4H) $SCH_2CH_2N$. $^{13}$C-NMR ($CDCl_3$) : 140.6 (d, $J_{CH}$ = 178.6 Hz) C-6; 102.7 (d, $J_{CH}$ = 179.7 Hz) C-5; 89.5 (d, $J_{CH}$ = 174.1 Hz) C-1'; 86.9 (s) MMTr; 85.6 (d, $J_{CH}$ = 160.6 Hz) C-4'; 64.4 (t, $J_{CH}$ = 144.9 Hz) C-5'; 55.0 ( q) $OCH_3$; 40.3 (t, $J_{CH}$ = 137.6 Hz) $SCH_2$-; 35.6 (t, $J_{CH}$ = 139.3 Hz) $NCH_2$-. MS (FAB$^-$) : calc. for (M-H)$^-$ 556.1906, found 556.1922.

**1-(5'-O-MMTr-2',3'-dideoxy-2'-*S*-(2-hydroxyethyl)-β-D-*glycero*-pent-2'-eno-furanosyl) uracil (28) & 1-(5'-O-MMTr-2,2'-O-anhydro-3'-*S*-(2-hydroxyethyl)-β-D-arabinofuranosyl)uracil (30c)** : To a solution of 2-mercaptoethanol (47 mg, 0.6 mmol) in tetrahydrofuran (10 ml) was added sodium hydride (16.5 mg, 0.55 mmol) and stirring was kept for 1 h at room temperature. The compound **1** (335 mg, 0.5 mmol) was added and the stirring was continued overnight. The reaction mixture was poured into a saturated aqueous solution of ammonium chloride (50 ml), and extracted with dichloromethane (3 x 20 ml). The combined extract was evaporated to dryness and the residue was separated on a silica gel column to give compounds **30c** (47 mg, 16.6%) and **28** (59 mg, 20.8%). Compound **30c**. $^1$H-NMR ($CDCl_3$) : 7.27-6.80 (m, 15H) H-6 and arom; 6.23 (d, $J_{1',2'}$ = 5.6 Hz, 1H) H-1'; 5.91 (d,1H) H-5; 5.45 ( dd, $J_{2',3'}$ = 2.0 Hz, 1H) H-2'; 4.27 (m, 1H) H-4'; 3.81 (m, 2H) -$CH_2OH$; 3.78 (s, 3H) $OCH_3$; 3.65 (dd, $J_{3',4'}$ = 4.7 Hz, 1H) H-3'; 3.08 (m, 2H) H-5', H-5"; 2.78 (m, 2H) $SCH_2$-. $^{13}$C-NMR ($CDCl_3$) : 135.0 (d, $J_{CH}$ = 185.3 Hz) C-6; 109.8 (d, $J_{CH}$ = 176.4 Hz) C-5; 90.5 (d, $J_{CH}$ = 185.3 Hz) C-1'; 89.4 (d, $J_{CH}$ = 171.9 Hz) C-2'; 86.5 (s) MMTr; 86.2 (d, $J_{CH}$ = 150.5 Hz) C-4'; 64.4 (t, $J_{CH}$ = 142.7 Hz) C-5'; 61.4 (t, $J_{CH}$ = 142.7 Hz) $CH_2OH$; 55.1 (q) $OCH_3$; 48.8 (d, $J_{CH}$ = 144.9 Hz ) C-3'; 34.4 (t, $J_{CH}$ = 137.6 Hz) $SCH_2$-. MS (FAB$^-$) : calc. for (M-H)$^-$ 557.1746, found 557.1779. compound **28**: $^1$H-NMR ($CDCl_3$) : 7.74 (d, $J_{5,6}$ = 8.1 Hz, 1H) H-6; 7.30-6.82 (m, 14H) arom; 6.97 ( dd, $J_{1',3'}$ = 1.2 Hz, $J_{1',4'}$ = 3.4 Hz, 1H) H-1'; 5.93 (t, $J_{3',4'}$ = 1.2 Hz, 1H) H-3'; 5.11 (d, 1H) H-5; 4.95 (m, 1H) H-4'; 3.86 (m, 2H) $CH_2OH$; 3.78 (s, 3H) $OCH_3$; 3.42 (d, $J_{4',5'}$ = 3.4 Hz, 2H) H-5', H-5"; 2.94 (m, 2H) $SCH_2$. $^{13}$C-NMR ($CDCl_3$) : 140.8 (d, $J_{CH}$ = 182.0 Hz) C-6; 102.6 (d, $J_{CH}$ = 179.8 Hz) C-5; 89.5 (d, $J_{CH}$ = 178.6 Hz) C-1'; 86.9 (s) MMTr; 85.6 (d, $J_{CH}$ = 150.6 Hz) C-4'; 64.5 (t, $J_{CH}$ = 143.2 Hz) C-5'; 60.1 (t, $J_{CH}$ = 142.1 Hz) $CH_2OH$; 55.0 (q) $OCH_3$; 34.5 (t, $J_{CH}$ = 139.3 Hz) $SCH_2$. MS (FAB$^-$) : calc. for (M-H)$^-$ 557.1746, found 557.1747.

**1-(5'-O-MMTr-2',3'-dideoxy-2'-*S*-(methoxycarbonylmethyl)-β-D-*glycero*-pent-2'-eno-furanosyl)uracil (32)** : To a solution of methyl thioglycolate (106 mg, 1 mmol) in tetrahydrofuran (10 ml) was added sodium hydride (18 mg, 80%, 0.6 mmol) and stirring was kept for 30 min at room temperature. **1** (200 mg, 0.3 mmol) was added and stirring was continued for 2 h. The mixture was poured into a saturated solution of ammonium chloride (50 ml), and extracted with dichloromethane (3 x 20 ml) and the combined organic phase was evaporated to dryness. The residue was purified on a silica gel column to give compound **32** (112 mg, 64% ). $^1$H-NMR ($CDCl_3$) : 7.79 (d, $J_{5,6}$ = 8.3 Hz, 1H) H-6; 7.35-6.84 (m, 14H) arom; 6.99 (dd, $J_{1',3'}$ = 1.7 Hz, $J_{1',4'}$= 3.5 Hz, 1H) H-1'; 6.01 (t, $J_{3',4'}$ = 1.7 Hz, 1H) H-3'; 5.10 (d, 1H) H-5; 4.97 (m, 1H) H-4'; 3.80 (s, 3H) $OCH_3$; 3.75 (s, 3H) $CO_2CH_3$; 3.59 (d, J = 4.7 Hz, 2H) $SCH_2CO$; 3.42 (m, $J_{4',5'}$ = 2.9 Hz, 2H) H-5', H-5". $^{13}$C-NMR ($CDCl_3$) : 140.8 (d, $J_{CH}$ = 181.8 Hz) C-6; 102.7 (d, $J_{CH}$ = 181.9 Hz) C-5; 89.3 (d, $J_{CH}$ = 173.3 Hz) C-1'; 87.0 (s) MMTr; 85.4 (d, $J_{CH}$ = 156.3 Hz) C-4'; 64.2 (t, $J_{CH}$ = 144.1 Hz) C-5'; 55.1 ( q) $OCH_3$; 52.8 (q, $J_{CH}$ = 147.7 Hz) $CO_2CH_3$; 33.7 (t, $J_{CH}$ = 151.7 Hz) $SCH_2CO$. MS (FAB$^-$) : calc. for (M-H)$^-$ 585.1695, found 585.1693.

*General procedure for the removal of 5'-O-MMTr group from compound **11, 18, 20, 22, 26, 28, 3, 32, 41 and 43.*** The compound was treated with 80% aqueous acetic acid (40 ml / mmol) at room temperature for 5 h. Acetic acid was removed by evaporation and coevaporation with toluene, and the residues were separated on a silica gel column chromatography or preparative Tlc to give compounds **12, 19, 21, 23, 27, 29, 31, 33, 42,** and **44**, respectively.

**1-(2',3'-dideoxy-2',3'-*N*-(1,2-ethylene)-β-D-*ribo*furanosyl)uracil (12)** (81.1%) : $^1$H-NMR ($CDCl_3$ + $CD_3OD$) : 8.15 (d, $J_{5,6}$ = 8.2 Hz, 1H) H-6; 6.00 (dd, $J_{1',2'}$ = 3.2 Hz, 1H) H-1'; 5.70 (d, 1H) H-5; 4.26 (m, 1H) H-4'; 3.84 (m, 2H) H-5', H-5"; 3.42 (m, 2H) H-2' and H-3'; 2.88 (m, 4H) $NCH_2CH_2N$. $^{13}$C-NMR ($CDCl_3$ + $CD_3OD$) : 140.4 (d, $J_{CH}$ = 185.3 Hz) C-6; 101.1 (d, $J_{CH}$ = 179.7 Hz) C-5; 86.8 (d, $J_{CH}$ = 169.6 Hz) C-1'; 81.7 (d, $J_{CH}$ = 146.0 Hz) C-4'; 60.7 (t, $J_{CH}$ = 142.1 Hz) C-5'; 59.4 and 52.9 (d, $J_{CH}$ =

146.0 and 140.2 Hz) C-2' and C-3'; 42.2 and 41.7 (t, $J_{CH}$ = 137.0 and 134.8 Hz) $NCH_2CH_2N$. MS ($FAB^-$) : calc. for $(M-H)^-$ 267.1093, found 267.1085.

**Dimer 19** (79.2%) : $^1$H-NMR ($CDCl_3$ + $CD_3OD$) : 7.84 (d, $J_{5,6}$ = 8.1 Hz, 1H) H-6; (dd, $J_{1',3'}$ = 1.5 Hz, $J_{1',4'}$ = 3.2 Hz, 1H) H-1'; 6.05 (t, $J_{3',4'}$ = 1.7 Hz, 1H) H-3'; 5.72 (d, 1H) H-5; 4.69 (m, 1H) H-4'; 3.77 (d, $J_{4',5'}$ = 3.1 Hz, 2H) H-5', H-5"; 3.07 (m, 4H) $SCH_2CH_2S$. $^{13}$C-NMR ($CDCl_3$ + $CD_3OD$) : 140.9 (d, $J_{CH}$ = 183.0 Hz) C-6; 132.9 (s) C-2'; 125.6 (d, $J_{CH}$ = 175.2 Hz) C-3'; 102.1 (d, $J_{CH}$ = 178.6 Hz) C-5; 89.6 (d, $J_{CH}$ = 171.9 Hz) C-1'; 87.2 (d, $J_{CH}$ = 148.3 Hz) C-4'; 62.4 (t, $J_{CH}$ = 142.1 Hz) C-5'; 36.4 and 31.0 (t, $J_{CH}$ = 141.6 Hz and 143.8 Hz) $SCH_2CH_2SH$. MS ($FAB^-$) : calc. for $(M-H)^-$ 601.0555, found 601.0571.

**1-(2',3'-dideoxy-2',3'-*S*-(1,2-ethylene)-β-D-*ribo*furanosyl)uracil (21)** (63%) : $^1$H-NMR ($CDCl_3$ + $CD_3OD$) : 8.21 (d, $J_{5,6}$ = 8.2 Hz, 1H) H-6; 6.10 (d, $J_{1',2'}$ = 4.7 Hz, 1H) H-1'; 5.71 (d, 1H) H-5; 4.29 (m, 1H) H-4'; 3.93 (t, $J_{4',5'}$ = 2.9 Hz, $J_{4',5''}$ = 2.2 Hz, 2H) H-5', H-5"; 3.66-3.46 (m, 2H) H-2' and H-3'; 2.86 (m, 4H) $SCH_2CH_2S$. $^{13}$C-NMR ($CDCl_3$ + $CD_3OD$) : 140.4 (d, $J_{CH}$ = 186.3 Hz) C-6; 101.2 (d, $J_{CH}$ = 176.4 Hz) C-5; 86.8 (d, $J_{CH}$ = 173.0 Hz) C-1'; 83.2 (d, $J_{CH}$ = 147.1 Hz) C-4'; 60.5 (t, $J_{CH}$ = 140.5 Hz) C-5'; 43.3 (d, $J_{CH}$ = 147.1 Hz) C-2'; 36.1 (d, $J_{CH}$ = 144.8 Hz ) C-3'; 25.4 (t, $J_{CH}$ = 141.0 Hz) $SCH_2CH_2S$. MS ($FAB^-$) : calc. for $(M-H)^-$ 301.0317, found 301.0343.

**Dimer 23** (84.3%) : $^1$H-NMR ($CDCl_3$ + $CD_3OD$) : 7.87 (d, $J_{5,6}$ = 8.0 Hz, 2H) H-6; 6.92 (d, $J_{1',3'}$ = 1.5 Hz, $J_{1',4'}$ = 3.4 Hz, 2H) H-1'; 6.06 (t, $J_{3',4'}$ = 1.7 Hz, 2H) H-3'; 5.73 (d, 2H) H-5; 4.96 (m, 2H) H-4'; 3.80 (d,$J_{4',5'}$ = 3.0 Hz, 4H) H-5', H-5"; 3.09 (m, 4H) $SCH_2CH_2S$. $^{13}$C-NMR ($CDCl_3$ + $CD_3OD$) : 140.8 (d, $J_{CH}$ = 183.0 Hz) C-6; 132.4 (s) C-2'; 126.8 (d, $J_{CH}$ = 175.2 Hz) C-3'; 102.5 (d, $J_{CH}$ = 180.7 Hz) C-5; 89.4 (d, $J_{CH}$ = 175.3 Hz) C-1'; 87.1 (d, $J_{CH}$ = 148.3 Hz) C-4'; 62.3 (t, $J_{CH}$ = 142.7 Hz) C-5'; 30.6 (d, $J_{CH}$ = 143.8 Hz) $SCH_2$-. MS ($FAB^-$) : calc. for $(M-H)^-$ 509.0801, found 509.0838.

**1-(2',3'-dideoxy-2'-*S*-(2-aminoethyl)-β-D-*glycero*-pent-2'-eno-furanosyl)uracil (27)** (61.0%): $^1$H-NMR ($CDCl_3$ + $CD_3OD$) : 8.0 (d, $J_{5,6}$ = 8.2 Hz, 1H) H-6; 6.99 (dd, $J_{1',3'}$ = 1.3 Hz, $J_{1',4'}$ = 3.2 Hz, 1H) H-1'; 6.18 (t, $J_{3',4'}$ = 1.7 Hz, 1H) H-3'; 5.81 (d, 1H) H-5; 5.04 (m, 1H) H-4'; 3.86 ( d, $J_{4',5'}$ = 2.9 Hz, 2H) H-5', H-5"; 3.11 (s, 4H) $SCH_2CH_2N$. $^{13}$C-NMR ($CDCl_3$ + $CD_3OD$) : 140.7 (d, $J_{CH}$ = 183.0 Hz) C-6; 132.3 (s) C-2'; 125.3 (d, $J_{CH}$ = 177.5 Hz) C-3'; 101.7 (d, $J_{CH}$ = 177.5 Hz) C-5; 89.2 (d, $J_{CH}$ = 164.0 Hz) C-1'; 87.0 (d, $J_{CH}$ = 159.5 Hz) C-4'; 61.9 (t, $J_{CH}$ = 142.1 Hz) C-5'; 38.4 (t, $J_{CH}$ = 140.2 Hz) $SCH_2CH_2NH_2$; 32.0 (t, $J_{CH}$ = 141.0 Hz) $SCH_2CH_2NH_2$. MS ($FAB^+$) : calc. for $(M+H)^+$ 286.0862, found 286.0857.

**1-(2',3'-dideoxy-2'-*S*-(2-hydroxyethyl)-β-D-*glycero*-pent-2'-eno-furanosyl)uracil (29)** (74.2%) : $^1$H-NMR ($CDCl_3$ + $CD_3OD$) : 7.83 (d, $J_{5,6}$ = 8.1 Hz, 1H) H-6; 6.90 (dd, $J_{1',3'}$ = 1.7 Hz, $J_{1',4'}$ = 3.3 Hz, 1H) H-1'; 5.99 (t, $J_{3',4'}$ = 1.7 Hz, 1H) H-3'; 5.69 (d, 1H) H-5; 4.92 (m, 1H) H-4'; 3.78 (m, 4H) H-5', H-5" and $CH_2OH$; 3.00 (m, 2H) $SCH_2$. $^{13}$C-NMR (DMSO) : 141.1 (d, $J_{CH}$ = 183.1 Hz) C-6; 132.8 (s) C-2'; 125.6 (d, $J_{CH}$ = 173.0 Hz) C-3'; 102.5 (d, $J_{CH}$ = 177.5 Hz) C-5; 89.4 (d, $J_{CH}$ = 170.0 Hz) C-1'; 87.8 (d, $J_{CH}$ = 149.4 Hz) C-4'; 62.6 (t, $J_{CH}$ = 141.0 Hz) C-5'; 59.5 (t, $J_{CH}$ = 143.8 Hz) $CH_2OH$; 34.6 (t, $J_{CH}$ = 142.2 Hz) $SCH_2$. MS ($FAB^-$) : calc. for $(M-H)^-$ 285.0543, found 285.0550.

**1-(2,2'-O-anhydro-3'-*S*-(2-hydroxyethyl)-β-D-arabinofuranosyl)uracil (31)** (82.2%) : $^1$H-NMR ($CDCl_3$ + $CD_3OD$) : 7.71 (d, $J_{5,6}$ = 6.1 Hz, 1H) H-6; 6.35 (d, $J_{1',2'}$ = 6.0 Hz, 1H) H-1'; 6.10 (d, 1H) H-5; 5.53 (d, 1H) H-2'; 4.27 (m, 1H) H-4'; 3.84 (m, 3H) H-3' and $CH_2OH$; 3.56 (d,$J_{4',5'}$ = 4.7 Hz, 2H) H-5', H-5"; 2.82 (t, J = 5.6 and 6.9 Hz, 2H) $SCH_2$. $^{13}$C-NMR ($CDCl_3$ + $CD_3OD$) : 136.5 (d, $J_{CH}$ = 188.8 Hz) C-6; 108.6 (d, $J_{CH}$ = 174.1 Hz) C-5; 90.5 (d, $J_{CH}$ = 183.6 Hz) C-1'; 89.8 (d, $J_{CH}$ = 173.0 Hz) C-2'; 88.3 (d, $J_{CH}$ = 151.7 Hz) C-4'; 61.4 (t, $J_{CH}$ = 142.7 Hz) C-5'; 60.5 (t, $J_{CH}$ = 142.1 Hz) $CH_2OH$; 33.9 (t, $J_{CH}$ = 137.6 Hz) $SCH_2$. MS ($FAB^+$) : calc. for $(M+H)^+$ 287.0702 , found 287.0709.

**1-(2',3'-dideoxy-2'-*S*-(methoxycarbonylmethyl))-β-D-*glycero*-pent-2'-eno-furanosyl)uracil (33)** (65.4%) : $^1$H-NMR ($CDCl_3$ + $CD_3OD$) : 7.83 (d, $J_{5,6}$ = 8.0 Hz, 1H) H-6; 6.95 (dd, $J_{1',3'}$ = 1.8 Hz, $J_{1',4'}$ = 3.2 Hz, 1H) H-1'; 6.06 (t, $J_{3',4'}$ = 1.9 Hz, 1H) H-3'; 5.71 (d, 1H) H-5; 4.94 (m, 1H) H-4'; 3.78 (s) $OCH_3$; 3.76 and 3.62 (2 x bd, $J_{4',5'}$ = 1.9 Hz, 2H) H-5', H-5"; 3.37 (m, 2H) $SCH_2$. $^{13}$C-NMR ($CDCl_3$ + $CD_3OD$) : 140.9 (d, $J_{CH}$ = 183.1 Hz) C-6; 132.4 (s) C-2'; 127.1 (d, $J_{CH}$ = 180.8 Hz) C-3'; 102.3 (d, $J_{CH}$ =

179.7 Hz) C-5; 89.4 (d, $J_{CH}$ = 173.0 Hz) C-1'; 87.3 (d, $J_{CH}$ = 148.2 Hz) C-4'; 62.5 (t, $J_{CH}$ = 140.5 Hz) C-5'; 52.5 (q, $J_{CH}$ = 147.7 Hz ) $OCH_3$; 33.6 (t, $J_{CH}$ = 142.7 Hz) $SCH_2$. MS ($FAB^-$) : calc. for $(M-H)^-$ 313.0494, found 313.0502.

**1-(2',3'-dideoxy-2'-imidazolyl-β-D-*glycero*-pent-2'-eno-furanosyl)uracil (34)** : A mixture of compound **2** (80 mg, 0.2 mmol), imidazole (68 mg, 1 mmol), potassium carbonate (148 mg, 1 mmol) in tetrahydrafuran (2 ml) was stirred at room temperature overnight. Solvent was removed by evaporation and the residue was extracted with a mixture of methanol-dichloromethane (1:1, v/v). The extract was evaporated and the rsidue was separated on a preparative Tlc to give the title compound (44 mg, 80 %). $^1$H-NMR ($CDCl_3$ + $CD_3OD$) : 8.13 (d, $J_{5,6}$ = 8.1 Hz, 1H) H-6; 7.81 (t, 1H) H-2 (Im.) ; 7.40 (dd, $J_{1',3'}$ = 1.7 Hz, $J_{1'4'}$ = 3.4 Hz, 1H) H-1'; 7.22, 7.09 (m, 2H) H-4, H-5 (Im); 6.39 (t, $J_{3'4'}$ = 2.0 Hz, 1H) H-3'; 5.66 (d, 1H) H-5; 5.09 (m, $J_{4',5'}$ = 2.5 Hz, 1H) H-4'; 3.89 (d, 2H) H-5', H-5"; $^{13}$C-NMR ($CDCl_3$ + $CD_3OD$) : 102.8 (d, $J_{CH}$ = 176.4 Hz) C-5; 85.4 (d, $J_{CH}$ = 161.7 Hz) C-1'; 82.4 (d, $J_{CH}$ = 145.2 Hz) C-4'; 62.0 (t, $J_{CH}$ = 143.2 Hz) C-5'. MS ($FAB^-$): calc. for $(M-H)^-$ 275.0780, found 275.0782.

**1-(2',3'-dideoxy-2'-(1,2,4-triazolyl)-β-D-*glycero*-pent-2'-eno-furanosyl)uracil (35)** : The mixture of compound **2** (100 mg, 0.25 mmol), 1,2,4-triazole (86.2 mg, 1.25 mmol) , potassium carbonate (185 mg, 1.25 mmol) in tetrahydrafuran (3 ml) was stirred at room temperature overnight. Solvent was removed by evaporation and the residue was extracted with mixture solution of methanol-dichloromethane (1:1, v/v). The extract was evaporated and the residue was separated on preparative Tlc to give the title compound (51 mg, 74 %). $^1$H-NMR (DMSO-$d_6$) : 9.00 (s, 1H) H-3 (triazole) ; 8.16 (s, 1H) H-5 (triazole); 7.83 (d, $J_{5,6}$ = 8.1 Hz, 1H) H-6; 7.25 (dd, $J_{1',4'}$ = 3.2 Hz, $J_{1',3'}$ = 1.8 Hz, 1H) H-1'; 6.84 (t, $J_{3',4'}$ = 1.4 Hz,1H) H-3'; 5.57 (d, 1H) H-5; 5.04 (m, 1H) H-4'; 3.79 (m, 2H) H-5', H-5". $^{13}$C-NMR (DMSO-$d_6$) : 102.7 (d, $J_{CH}$ = 175.8 Hz) C-5; 86.1 (2 x d, $J_{CH}$ = 173.0 Hz, $J_{CH}$ = 161.8 Hz) C-1', C-4'; 62.6 (t, $J_{CH}$ = 143.3 Hz) C-5'. MS ($FAB^-$): calc. for $(M-H)^-$ 276.0733, found 276.0735.

**1-(5'-O-MMTr-2'-O-methyl-3'-phenylselenonyl-*ribo*furanosyl)uracil (36)** : A mixture of compound **1** (134 mg, 0.2 mmol) and potassium carbonate (82.8 mg, 0.6 mmol) in methanol (3 ml) was stirred at room temperature for 1.5 h. After the starting material was completely consumed (Tlc), the reaction mixture was poured into water (30 ml) which was then extracted with dichloromathane (2 x 30 ml). The combined extract was evaporated to dryness and purified on a silica gel column to give the title compound (124 mg, 88 %). $^1$H-NMR ($CDCl_3$): 9.78 (br, 1H) NH; 7.95-6.84 (m, 20 H) H-6, arom; 5.85 (s, 1H) H-1'; 5.05 (d, $J_{5,6}$ = 8.3 Hz, 1H) H-5; 4.73 (m, 2H) H-3', H-4'; 4.24 (d, $J_{2',3'}$ = 5.4 Hz, 1H) H-2'; 3.79 (s, 3H) $OCH_3$; 3.73 (m, 2H) H-5', H-5"; 3.40 (s, 3H) 2'-$OCH_3$; $^{13}$C-NMR ($CDCl_3$): 102.0 (d, $J_{CH}$ = 174.6 Hz) C-5; 87.8 (d, $J_{CH}$ = 175.8 Hz) C-1', MMTr; 83.8(d, $J_{CH}$ = 159.6 Hz) C-2'; 79.0 (d, $J_{CH}$ = 163.4 Hz) C-4'; 69.9 (d, $J_{CH}$ = 147.9 Hz) C-3'; 60.9 (t, $J_{CH}$ = 147.9 Hz) C-5'; 58.3 (q) 2'-$OCH_3$; 55.1 ( q) $OCH_3$. MS ($FAB^-$): calc. for $(M-H)^-$ 702.1484, found 702.1431. .

**1-(2'-O-methyl-3'-phenylselenonyl-*ribo*furanosyl)uracil (37)** (77 %): $^1$H-NMR ($CDCl_3$ + $CD_3OD$) : 8.01 (d, $J_{5,6}$ = 8.1 Hz, 1H) H-6; 7.92-7.64 (m, 5H) arom; 5.78 (d, $J_{1',2'}$ = 1.7 Hz) H-1'; 5.63 (d, 1H) H-5; 4.81 (m, $J_{3',4'}$ = 8.3 Hz, $J_{4',5'}$ = 1.5 Hz, $J_{4',5''}$ = 1.7 Hz, 1H) H-4'; 4.57 (dd, $J_{2',3'}$ = 4.9 Hz, 1H) H-3'; 4.18 (dd, 1H) H-2'; 3.94-3.80 (m, 2H) H-5', H-5"; 3.22 (s, 3H) $OCH_3$. $^{13}$C-NMR ($CDCl_3$ + $CD_3OD$) : 101.9 (d, $J_{CH}$ = 175.4 Hz) C-5; 88.6 (d, $J_{CH}$ = 175.4 Hz) C-1'; 83.1 (d, $J_{CH}$ = 160.0 Hz) C-2'; 80.0(d, $J_{CH}$ = 160.0 Hz) C-4'; 70.3 (d, $J_{CH}$ = 150.4 Hz) C-3'; 60.0 (t, $J_{CH}$ = 144.4 Hz) C-5'; 58.2(q) $OCH_3$. MS ($FAB^-$): calc. for $(M-H)^-$ 429.0201, found 429.0201.

**1-(5'-O-MMTr-2'-O-ethyl-3'-phenylselenonyl-*ribo*furanosyl)uracil (38)** : A mixture of compound **1** (200 mg, 0.3 mmol) and potassium carbonate (185 mg. 0.6 mmol) in 95 % ethanol (3 ml) was stirred at room temperature for 1.5 h .After the starting material was completely consumed (Tlc), the reaction mixture was poured into water (30 ml) which was then extracted with dichloromathane (2 x 30 ml) . The combined extract was evaporated to dryness and purified on a silica gel column to give the title compound (156 mg, 73 %). $^1$H-NMR ($CDCl_3$) : 9.81 (br, 1H) NH; 7.95-6.89 (m, 20H) H-6, arom; 5.84 (s, 1H) H-1'; 5.06 (d, $J_{5,6}$ = 8.1 Hz, 1H) H-5; 4.83 (dt, $J_{3',4'}$ = 9.2 Hz, 1H) H-4'; 4.68 (dd, $J_{2',3'}$ = 5.1 Hz, 1H) H-2'; 3.79 (s, 3H) $OCH_3$; 3.71 (s, 2H) H-5', H-5"; 3.52 (m, 2H) $OCH_2CH_3$; 1.11 (t, 3H) $CH_3$. $^{13}$C-NMR ($CDCl_3$): 102.1 (d, $J_{CH}$ = 178.6 Hz) C-5; 88.2 (d, $J_{CH}$ = 174.1 Hz) C-1'; 87.8 (s) MMTr; 81.8 (d, $J_{CH}$ = 159.6 Hz) C-2'; 78.9 (d, $J_{CH}$ = 155.0 Hz) C-4'; 70.3 (d, $J_{CH}$ = 153.8 Hz) C-3'; 66.9 (t) $OCH_2CH_3$; 61.2 (t, $J_{CH}$ = 143.3 Hz) C-5'; 55.1 (q) $OCH_3$; 14.7 (q) $OCH_2CH_3$. MS ($FAB^-$): calc. for $(M-H)^-$ 715.1558, found 715.1514.

**1-(2'-O-ethyl-3'-phenylselenonyl-*ribo*furanosyl)uracil (39)** (94 %): $^1$H-NMR ($CDCl_3$ + $CD_3OD$) : 8.13-7.79 (m, 6H) H-6, arom; 6.01 (d, $J_{1',2'}$ = 3.4 Hz) H-1'; 5.71 (d, $J_{5,6}$ = 8.0 Hz, 1H) H-5; 4.91-4.67 (m, 2H) H-3', H-4'; 4.48 (dd, $J_{2',3'}$ = 3.6 Hz, 1H) H-2'; 4.11 (dd, $J_{4',5'}$ = 1.5 Hz, $J_{5',5''}$ = 12.7 Hz, 1H) H-5'; 3.82 (dd, $J_{4',5''}$ = 1.5 Hz, 1H) H-5''; 3.69 (m, 2H) $OCH_2$; 1.02 (t, 3H) $CH_3$; $^{13}$C-NMR ($CDCl_3$): 101.4 (d, $J_{CH}$ = 178.7 Hz) C-5; 88.1 (d, $J_{CH}$ = 175.0 Hz) C-1'; 80.7 (d, $J_{CH}$ = 152.6 Hz) C-2'; 78.8 (d, $J_{CH}$ = 155.0 Hz) C-4'; 71.0 (d, $J_{CH}$ = 151.7 Hz) C-3'; 66.4 (t) $OCH_2$; 60.3 (t, $J_{CH}$ = 143.2 Hz) C-5'; 13.7 (q) $CH_3$. MS (FAB$^-$): calc. for (M-H)$^-$ 443.0358, found 443.0326.

**O$^2$-Methyl-1-(5'-O-MMTr-2'-O-methyl-*xylo*furanosyl)uracil (41)** : Compound **1** (200 mg, 0.3 mmol) was treated with sodium methoxide (54 mg, 1 mmol) in methanol (20 ml) at room temperature overnight. The solution was poured into a saturated aqueous solution of ammonium chloride (50 ml) and product was extracted with dichloromethane (3 x 20 ml). The solvent was removed on rotavapour to dryness and purified on silica gel column to give compound **41** (133 mg, 81.9 %). $^1$H-NMR ($CDCl_3$ + $CD_3OD$) : 7.71 (d, $J_{5,6}$ = 7.8 Hz, 1H) H-6; 7.30-6.82 (m, 14H) arom; 5.83 (s, 1H) H-1'; 5.71 (d, 1H) H-5; 4.46 (m, 1H) H-4'; 4.17 (d, $J_{3',4'}$ = 3.2 Hz, 1H) H-3'; 4.04 (s, 3H) C$^2$-$OCH_3$; 3.90 (s, 1H) H-2'; 3.77 (s, 3H) $OCH_3$ (MMTr); 3.50 (s, 3H) 2'-$OCH_3$. $^{13}$C-NMR ($CDCl_3$ + $CD_3OD$) : 139.1 (d, $J_{CH}$ = 186.5 Hz) C-6; 106.6 (d, $J_{CH}$ = 172.1 Hz) C-5; 90.7 (d, $J_{CH}$ = 175.0 Hz) C-1'; 89.7 (d, $J_{CH}$ = 144.1 Hz) C-2'; 86.7 (s) MMTr; 83.7 (d, $J_{CH}$ = 141.3 Hz) C-4'; 72.6 (d, $J_{CH}$ = 154.1 Hz) C-3'; 61.7 (t, $J_{CH}$ = 142.2 Hz) C-5'; 57.5 (q, $J_{CH}$ = 142.8 Hz) C$^2$-$OCH_3$; 55.6 (q, $J_{CH}$ = 148.9 Hz) 2'-$OCH_3$; 55.0 (q) MMTr-$OCH_3$. MS (FAB$^+$) : calc. for (M+H)$^+$ 545.2288, found 545.2305 .

**O$^2$-Methyl-1-(2'-O-methyl-*xylo*furanosyl)uracil (42)** (76.4%). $^1$H-NMR ($CDCl_3$ + $CD_3OD$) : 8.04 (d, $J_{5,6}$ = 8.0 Hz, 1H) H-6; 6.00 (d, 1H) H-5; 5.83 (s, 1H) H-1'; 4.26 (m, 2H) H-3' and H-4'; 4.08 (s, 3H) C$^2$-$OCH_3$; 4.03 (m, 2H) H-5', H-5''; 3.79 (s, 1H) H-2'; 3.51 (s, 3H) 2'-$OCH_3$. $^{13}$C-NMR ($CDCl_3$ + $CD_3OD$) : 139.4 (d, $J_{CH}$ = 187.6 Hz) C-6; 106.5 (d, $J_{CH}$ = 174.1 Hz) C-5; 90.4 (d, $J_{CH}$ = 175.2 Hz) C-1'; 90.2 (d, $J_{CH}$ = 158.3 Hz) C-2'; 83.3 (d, $J_{CH}$ = 142.7 Hz) C-4'; 72.7 (d, $J_{CH}$ = 153.9 Hz) C-3'; 59.5 (t, $J_{CH}$ = 143.2 Hz) C-5'; 57.5 (q, $J_{CH}$ = 143.8 Hz) $OCH_3$-2; 55.4 ( q, $J_{CH}$ = 149.4 Hz) 2'-$OCH_3$. MS (FAB$^-$) : calc. for (M-H)$^-$ 271.0930, found 271.0924.

**1-(5'-O-MMTr-2',3'-dideoxy-2'-(N-methylhydroxyl)amino-3'-phenylselenyl-*ribo*furanosyl) uracil (43b)** : To a solution of compound **1** (200 mg. 0.3 mmol) in tetrahydrofuran (10 ml) was added N-hydroxymethylamine (126 mg, 1.5 mmol) and triethylamine (303 mg, 3 mmol) and the mixture was stirred at room temperature overnight when Tlc showed the formation of **43a** was complete [compound **43a**. $^1$H-NMR ($CDCl_3$) : 8.14-6.78 (m, 20 H) arom, H-6; 6.47 (d, $J_{1',2'}$ = 5.1 Hz, 1H) H-1'; 5.90 (d, $J_{5,6}$ = 8.3 Hz, 1H) H-5; 4.60 (m, 1H) H-3'; 4.20 (d, 1H) H-2'; 3.97 (m, 1H) H-4'; 3.75 (s, 3H) MMTr; 3.79-3.37 (m, 2H) H-5'; 2.53 (s, 3H) $NCH_3$. $^{13}$C-NMR ($CDCl_3$): 141.6, C-6; 103.9, C-5; 85.0, C-1'; 80.0, C-4'; 73.2 and 70.1, C-2' and C-3'; 62.9, C-5'; 46.6, $NCH_3$]. Then ethanethiol (186 mg, 3 mmol) and 1,8-diazabicyclo-(5,4,0)-undec-7-ene (93 mg, 0.6 mmol) was added. The mixture was heated in an oil bath to 40 °C, and stirring was continued for 48 h. The mixture was poured into a saturated aqueous solution of ammonium chloride (50 ml) and the product was extracted with dichloromethane (3 x 20 ml) . The organic solution was evaporated to dryness and purified on silica gel column to give compound **43b** (92 mg, 45%). $^1$H-NMR ($CDCl_3$) : 7.94 (d, $J_{5,6}$ = 8.0 Hz, 1H) H-6; 7.46-6.80 (m, 19H) arom; 6.50 (d, $J_{1',2'}$ = 3.7 Hz, 1H) H-1'; 5.18 (d, 1H) H-5; 4.45 (m, 1H) H-4'; 4.05 (t, $J_{2',3'}$ = 7.0 Hz, $J_{3',4'}$ = 7.0 Hz, 1H) H-3'; 3.80 (s, 3H) $OCH_3$; 3.51-3.16 (m, 3H) H-2', H-5' and H-5''; 2.89 (s, 3H) $NCH_3$. $^{13}$C-NMR ($CDCl_3$) : 140.5 (d, $J_{CH}$ = 180.8 Hz) C-6; 102.4 (d, $J_{CH}$ = 177.5 Hz) C-5; 86.3 (s) MMTr; 86.3 (d, $J_{CH}$ = 175.2 Hz) C-1'; 85.3 (d, $J_{CH}$ = 153.9 Hz) C-4'; 75.0 (d, $J_{CH}$ = 146.0 Hz) C-2'; 63.3 (t, $J_{CH}$ = 142.1 Hz) C-5'; 55.1 ( q) $OCH_3$; 47.2 ( q, $J_{CH}$ = 136.7 Hz) $NCH_3$; 44.1 (d, $J_{CH}$ = 147.2 Hz) C-3'. MS (FAB$^-$) : calc. for (M-H)$^-$ 684.1616, found 684.1636.

**1-(2',3'-dideoxy-2'-(N-methylhydroxyl)amino-3'-phenylselenyl-*ribo*furanosyl)uracil (44)** (76 %): $^1$H-NMR ($CDCl_3$ + $CD_3OD$) : 7.99 (d, H5,6 = 8.2 Hz, 1H) H-6; 7.59-7.33 (m, 5H) PhSe; 6.39 (d, $J_{1',2'}$ = 4.9 Hz, 1H) H-1'; 5.73 (d, 1H) H-5; 4.36 (m, 1H) H-4'; 4.08 (dd, $J_{2',3'}$ = 5.7 Hz, $J_{3',4'}$ = 7.4 Hz, 1H) H-3'; 3.80-3.19 (m, 3H) H-2', H-5' and H-5''; 2.84 (s, 3H) $NCH_3$. $^{13}$C-NMR ($CDCl_3$ + $CD_3OD$) : 141.6 (d, $J_{CH}$ = 183.1 Hz) C-6; 102.2 (d, $J_{CH}$ = 177.5 Hz) C-5; 87.1 (d, $J_{CH}$ = 169.6 Hz) C-1'; 86.7 (d, $J_{CH}$ = 150.5 Hz) C-4'; 73.8 (d, $J_{CH}$ = 142.7 Hz) C-2'; 62.5 (t, $J_{CH}$ = 142.7 Hz) C-5'; 47.2 (q, $J_{CH}$ = 135.9 Hz) $CH_3N$; 43.4 (d, $J_{CH}$ = 149.2 Hz) C-3'. MS (FAB$^-$) : calc. for (M-H)$^-$ 414.0569, found 414.0556.

**1-(5′-O-*p*-toluoyl-2′,3′-dideoxy-2′,3′-(2*H*-1,2,3-triazolo)-β-D-*glycero*-pent-2′-eno-furanosyl)uracil (45) & Dimer (46) :** Compound **3** (230 mg, 0.44 mmol) was treated with sodium azide (289 mg, 4.4 mmol) in dimethyl sulfoxide (4 ml) and water (0.4 ml) for 5 h at room temperature. The reaction mixture was poured into saturated aqueous solution of ammonium chloride (70 ml) and the precipitate was filtered and washed with water. The solid was purified on a silica gel column to give the title compound **45** (103 mg, 64 %) and **46** (51 mg, 33 %). Compound **45** : $^1$H-NMR ($CDCl_3$ + $CD_3OD$) : 7.74, 7.22 (2 x d, J = 8.2 Hz, 4H) arom; 7.28 (s, 1H) H-1'; 6.99 (d, $J_{5,6}$ = 8.0 Hz, 1H) H-6; 5.51 (m, $J_{4',5'}$ = 3.0 Hz, $J_{4',5''}$ = 4.4 Hz, 1H) H-4; 5.28 (d, 1H) H-5; 4.75 (2 x d, 2H) H-5', H-5"; 2.41 (s, 3H) $CH_3$; $^{13}$C-NMR ($CDCl_3$ + $CD_3OD$) : 102.4 (d, $J_{CH}$ = 177.5 Hz) C-5; 79.3 (d, $J_{CH}$ = 178.6 Hz) C-1'; 73.8 (d, $J_{CH}$ = 147.2 Hz) C-4'; 63.8 (t, $J_{CH}$ = 150.6 Hz) C-5'; 21.1 (q) $CH_3$. MS ($FAB^-$): calc. for $(M-H)^-$ 368.0995, found 368.1005. Compound **46**: $^1$H-NMR ($CDCl_3$ + $CD_3OD$) : 7.94-7.26 (m, 11H) arom, H-6 (U2), 2 x H-1'; 7.01 (d, $J_{5,6}$ = 8.1 Hz, 1H) H-6 (U1); 6.85 (m, 1H) 2 x H-3' (U2); 5.51-5.26 (m, 4H) 2 x H-4', H-5; 4.72 (m, 4H) 2 x (H-5', H-5"); 2.42 (s, 6H) 2 x $CH_3$; $^{13}$C-NMR ($CDCl_3$ + $CD_3OD$) : 103.3 (d, $J_{CH}$ = 177.5 Hz) C-5; 85.9 (d, $J_{CH}$ = 174.2 Hz) C-1'(U2) ; 82.5 (d, $J_{CH}$ = 159.4 Hz) C-4' (U2) ; 79.9 (d, $J_{CH}$ = 174.1 Hz) C-1' (U1) ; 74.1 (d, $J_{CH}$ = 157.3 Hz) C-4'(U1) ; 64.2 & 63.4 (2 x t, $J_{CH}$ = 140.4 Hz) 2 x C-5'; 21.3 (q) $CH_3$. MS ($FAB^-$): calc. for $(M-H)^-$ 694.1898, found 694.1993.

**1-(2′,3′-dideoxy-2′,3′-(2*H*-1,2,3-triazolo)-β-D-*glycero*-pent-2′-eno-furanosyl)uracil (47) :** Compound **45** (80 mg, 0.22 mmol) was treated with aqueous ammonia (32 %, 5 ml) for one day at room temperature. All volatile matters were removed by evaporation and the residue was crystallized from a mixture of methanol-dichloromethane to give the title compound (30 mg). The mother liquor was separated on a preparative Tlc to give second lot of the title compound (18 mg), [total yield 48 mg, 88 %]. $^1$H-NMR ($CD_3OD$) : 7.52 (d, $J_{5,6}$ = 8.1 Hz, 1H) H-6; 7.36 (d, $J_{1',4'}$ = 1.0 Hz, 1H) H-1'; 5.69 (d, 1H) H-5; 5.29 (m, $J_{4',5'}$ = 3.7 Hz, 1H) H-4'; 4.01 (d, 2H) H-5', H-5"; $^{13}$C-NMR ($CD_3OD$) : 103.1 (d, $J_{CH}$ = 176.3 Hz) C-5; 81.4 (d, $J_{CH}$ = 174.1 Hz) C-1'; 79.3 (d, $J_{CH}$ = 152.7 Hz) C-4'; 64.4 (t, $J_{CH}$ = 142.7 Hz) C-5'. MS ($FAB^-$) : calc. for $(M-H)^-$ 250.0576, found, 250.0580.

**Dimer 48 :** Compound **46** (60 mg, 0.087 mmol) was treated with aqueous ammonia (32 %, 6 ml) for one day at room temperature. All volatile matters were removed by evaporation and the residue was crystallized from methanol to give the title compound (32 mg, 81 %). $^1$H-NMR (DMSO-$d_6$) : 7.99 (d, $J_{5,6}$ = 7.9 Hz, 1H) H-6 (U2); 7.57 (d, $J_{5,6}$ = 8.4 Hz, 1H) H-6 (U1) ; 7.40 (2 x d, 1H) H-1' (U2) ; 7.32 (s, 1H) H-1' (U1) ; 6.98 (t, 1H) H-3' (U2); 5.72 (2 x d, 2H) H-5; 5.36 (m, 1H) H-4' (U2) ; 5.15 (m, 1H) H-4' (U1) ; 3.86 (m, 4H) H-5', H-5". $^{13}$C-NMR (DMSO-$d_6$) : 102.7 (d, $J_{CH}$ = 181.0 Hz) C-5; 86.0 (2 x d, $J_{CH}$ = 164.0 Hz) C-1', C-4' (U2) ; 79.4 (d, $J_{CH}$ = 174.1 Hz) C-1 (U1) ; 77.3 (d, $J_{CH}$ = 152.8 Hz) C-4' (U1) ; 62.4 (t, $J_{CH}$ = 142.1 Hz) C-5'. MS ($FAB^-$): calc. for $(M-H)^-$ 458.1060, found 458.1075.

**1-(5′-O-(*t*-butyldimethylsilyl)-2′,3′-dideoxy-2′,3′-*C*-(2-cyclopentene-1,4-ylene)-β-D-*glycero*-pent-2′-eno-furanosyl)uracil (50) :** The solution of compound **4** (205 mg, 0.4 mmol) and fresh distilled cyclopentadiene (0.5 ml) in dry toluene (3 ml) was heated at 60 °C for 4 days. All volatile matters were removed by evaporation with oil pump and the syrup was separated on a silica gel column to give the title compound (99 mg, 64 %) and the recovered starting material (54 mg, 26 %). $^1$H-NMR ($CDCl_3$) [see the numbering in **50** for assignments] : 9.18 (br, 1H) NH; 7.92 (d, $J_{5,6}$ = 8.1 Hz, 1H) H-6 ; 6.91 (m, 2H) H-2, H-3 (cyclopentene); 6.73 (d, $J_{1',4'}$ = 4.2 Hz, 1H) H-1'; 5.73 (d, 1H) H-4'; 4.57 (m, $J_{4',5'}$ = 2.7 Hz, 1H) H-5; 3.94 (d, 2H) H-5', H-5"; 3.60 - 3.53 (m, 2H) H-1, H-4 (cyclopentene); 2.47 (m, 2H) H-5 (cyclopentene) ; 0.94, 0.11 (15H) TBDMS. $^{13}$C-NMR ($CDCl_3$) : 102.4 (d, $J_{CH}$ = 178.6 Hz) C-5 (Ura); 85.9 (d, $J_{CH}$ = 169.6 Hz) C-1'; 83.1 (d, $J_{CH}$ = 144.9 Hz) C-4'; 75.2 (t, $J_{CH}$ = 137.1 Hz) C-5 (cyclopentadiene); 63.7 (t, $J_{CH}$ = 141.6 Hz) C-5'; 47.6, 46.9 (2 x d, $J_{CH}$ = 167.4 Hz) C-1, C-4 (cyclopentene); 25.8, -5.5, TBDMS. MS ($FAB^-$): calc. for $(M-H)^-$ 387.1740, found 387.1755.

**1-(2′,3′-dideoxy-2′,3′-*C*-(2-cyclopentene-1,4-ylene)-β-D-*glycero*-pent-2′-eno-furanosyl) uracil (51) :** Compound **50** was treated with a solution of tetrabutylammonium fluoride (5 ml, 0.1 M in tetrahydrafuran) for 2 h. The reaction mixture was evaporated and the residue was separated on a silica gel column to give the title compound (45 mg, 88 %). $^1$H-NMR ($CDCl_3$) [see the numbering in **51** for assignments] : 9.19 (br, 1H) NH; 7.69 (d, $J_{5,6}$ = 8.0 Hz, 1H) H-6 (Ura); 6.91 (m, 2H) H-2, H-3 (cyclopentene); 6.72 (d, $J_{1',4'}$ = 4.2 Hz, 1H) H-1'; 5.71 (d, 1H) H-5 (Ura); 4.59 (dt, $J_{4',5'}$ = 3 Hz, 1H) H-4'; 3.91 (m, 2H) H-5', H-5"; 3.66 & 3.49 ( 2 x m, 2H) H-1, H-4 (cyclopentene); 2.52 (t, J = 1.3 Hz, 2H) H-5 (cyclopentene). $^{13}$C-NMR ($CDCl_3$) : 102.4 (d, $J_{CH}$ = 176.4 Hz) C-5 (Ura); 86.5 (d, $J_{CH}$ = 171.9 Hz) C-1';

83.3 (d, $J_{CH}$ = 148.3 Hz) C-4'; 75.0 (t, $J_{CH}$ = 137.1 Hz) C-5 (cyclopentene); 62.9 (t, $J_{CH}$ = 144.3 Hz) C-5'; 47.8, 47.1 (2 x d, $J_{CH}$ = 160.6 Hz) C-1, C-4 (cyclopentene). MS ($FAB^-$): calc. for $(M-H)^-$ 273.0876, found 273.0874.

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