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SYNTHESIS OF NEW 2′, 3′-MODIFIED URIDINE DERIVATIVES FROM 2′,3′-ENE-2′-PHENYLSELENONYL URIDINE BY MICHAEL ADDITION REACTIONS**

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Abstract : The synthetic utilities of 2′,3′-ene-2′-phenylselenones **12** *and* **13** *as synthetic equivalent of a dication [CH_2^+ - CH_2^+]* **5** *have been demonstrated. They act as Michael acceptors, and undergo conjugate addition reactions at C-3′ with various sulfur, nitrogen, oxygen and carbon nucleophiles giving various C-3′ substituted-2,2′-O-anhydro-, or 2′,3′-ene-3′-substituted, or 2′,3′-fused nucleoside derivatives. Easy access to these 3′-substituted nucleosides from 2′,3′-ene-2′-phenylselenones* **12** *and* **13** *make them powerful complement to the corresponding 2′-substituted derivatives obtainable from 2′,3′-ene-3′-phenylselenonyl nucleoside* **4** *(ref. 72-74).*

The availability of various types of 2′,3′-dideoxy-2′- and/or 3′-substituted-β-D-nucleosides[1-20] with a free 5′-hydroxyl group are of potential chemotherapeutic interest for the design of a suitable inhibitor of Human Immunodeficiency Virus (HIV). Owing to the lack of 3′-hydroxyl group, compounds such 3′-azidothymidine (AZT), 2′,3′-dideoxyadenosine (DDA), N^6-methyl-2′-fluoro-ara-DDA, 2′,3′-dideoxycytidine (DDC), 2′,3′-dideoxyinosine (DDI), 2′,3′-didehydro-2′,3′-dideoxythymidine (D4T), 3′-fluorothymidine have been shown to be able to specifically chain-terminate the cDNA synthesis of HIV which is promoted by its reverse transcriptase on its own RNA template. The mechanism of biochemical action of these active compounds clearly suggest that new synthetic methodologies should be developed to prepare *new types* of 5′-hydroxy-2′,3′-dideoxy-2′- and/or -3′-substituted-β-D-nucleosides in order to design effective inhibitors against 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′-*O-ribo-* or *lyxo*-anhydro-purine nucleosides or 2′,3′-O-*lyxo*-anhydro-pyrimidine nucleosides[18-43], (iii) ring-opening reactions of 2,2′-O- or 2,3′-O-anhydro-pyrimidine nucleosides or 8,2′-O- or 8,3′-O-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 nucleosides[49-58], or other procedures involving rearrangements[59-67, 68 & 69].

Electrophilic addition to the 2′,3′-double bond of a β-D-nucleoside as a means to functionalize the 2′ and / or 3′ carbons has been demonstrated first by us through the reactions of arene or alkane sulfenyl chloride with 9-(2′,3′-dideoxy-β-D-*glycero*-pent-2-enofuranosyl)adenine[65] to give various 2′ / 3′-β-chlorosulfide analogs of

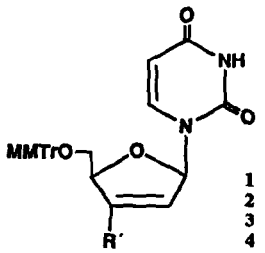
** *Dedicated to Professor Ivar Ugi on the occasion of his 60th Birthday*

nucleosides. Attempted addition reactions to this 2′,3′-double bond in β-D-nucleosides with IN_3, BrN_3, INO_2, IOCN, $PhSeNO_2$, $PhSeN_3$ were however found to be unsuccessful in our hands.

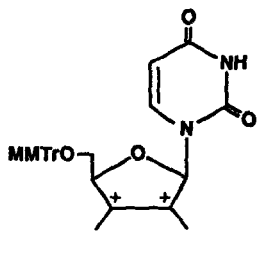
Reversal of the polarity of the 2′,3′-double bond in a β-D-nucleoside, as in **1**, by a 3′-electron-withdrawing substituent however made it amenable to unique Michael-type addition reactions which allowed us to functionalize the 2′- and 3′-carbons in various manner with sulfur, nitrogen, oxygen and carbon nucleophiles. We have thus recently shown that simple Michael addition reactions with an appropriately 5′-O-protected-2′,3′-ene-3′-sulfone[70] **3** or 2′,3′-ene-3′-nitrile[71] **2** derivatives of β-D-nucleosides gave access to various new types of 2′,3′-dideoxy-2′,3′-disubstituted- or 2′-substituted nucleosides in high overall yields[70,71]. These nucleophilic addition reactions take place exclusively from the α-face of C-2′ of the 2′,3′-ene-3′-tolylsulfone[21], or 2′,3′-ene-3′-nitrile[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[21] or α-nitrile-3′-carbanion[71] and subsequent protonation from the α-face. Recently, we have successfully shown the synthetic utilities of 2′,3′-ene-3′-phenylselenonyl nucleoside **4** as a substrate for Michael addition reactions, which allow facile functionalization at both 2′- and 3′-carbons of nucleosides simultaneously by double nucleophilic attack by ammonia and primary amines and carbon-nucleophiles giving access to various unique 2′,3′-α-fused cyclic nucleosides[72,73,74] such as 2′,3′-aziridine, 2′,3′-cyclopropane, 2′,3′-biimine, 2′,3′-(2-iminoimidazolidines), 2′,3′-N-α-(1,2-ethylene) and 2′,3′-S-α-(1,2-ethylene)uridine derivatives. On the other hand, Dimethylamine, pyrrolidine, and morpholine upon reaction with **4** gave 2,2′-O-anhydro-3′-deoxy-3′-amino or 3′-alkylamino substituted uridines[72]. The fact that 2′,3′-ene-3′-phenylselenonyl nucleoside such as **4** act as a substrate for double nucleophilc attack, first at C-2′ and then at C-3′ intramolecularly, makes it synthetically equivalent to the dication CH_2^+ - CH_2^+ **5**. Further studies on the reaction of various nucleophiles to 2′,3′-ene-3′-phenylselenone **4** have also shown that they are indeed useful synthetic intermediates to give either a variety of 2′,3′-dideoxy-2′,3′-ene-2′-substituted-nucleosides. 2′,3′-ene-3′-phenylselenone **4** also reacted as a dienophile in Diels-Alder or 1,3-cycloaddition reactions giving 2′,3′-dideoxy-2′,3′-fused-β-D-nucleosides[74].

In this paper, we show the synthetic utilities of 2′,3′-ene-2′-phenylselenonyl nucleosides **12** and **13** as substrates for Michael addition reactions, which give various C-3′ substituted derivatives upon reactions with various sulfur, nitrogen, oxygen and carbon nucleophiles. The easy access to these unique C-3′ substituted derivatives from **12** and **13** clearly show their versatile reactivity toward Michael addition reactions, which provide powerful means to functionalize the secondary carbons of the pentose moiety in β-D-nucleosides.

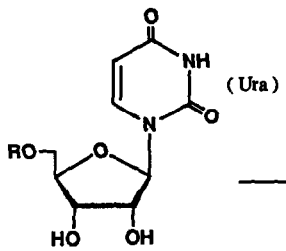
Synthesis of 2′,3′-ene-2′-phenylselenones 12 & 13 : Reaction of 5′-O-monomethoxytrityl (MMTr)-uridine with thiocarbonyl-bis-imidazole gave pure 5′-O-MMTr-2,2′-O-anhydro-uridine **8** in ~85% yield[75]. Compound **8** was reacted with a mixture of diphenyl diselenide and lithium aluminium hydride in THF at 50 °C overnight to give 5′-O-MMTr-2′-deoxy-2′-phenylseleno-uridine **9** in 93% yield. Compound **9** was mesylated to give the corresponding 3′-O-mesyl derivative **10** in 95% yield. 5′-O-MMTr-2′-deoxy-2′-phenylseleno-3′-O-mesyl-uridine **10**, upon treatment with potassium-t-butoxide at 0 °C for 1 h and at ~20 °C for 2 h followed by a standard work-up and purification step, gave 1-[5′-O-MMTr-2′,3′-dideoxy-2′-phenylseleno-β-D-*glycero*-pent-2′-enofuranosyl]uracil **11** in 86% yield. Finally, a treatment of **11** with m-chloroperoxybenzoic acid in methanol overnight gave 1-[5′-O-MMTr-2′,3′-dideoxy-2′-phenylselenonyl-β-D-*glycero*-pent-2′-enofuranosyl] uracil **12** in 97% yield (experimental section). Since the nucleophilic attack at C-3′ of 2′, 3′-ene-2′-



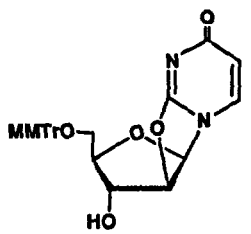
1 : R′ = H
2 : R′ = CN
3 : R′ = SO_2Tol
4 : R′ = SeO_2Ph



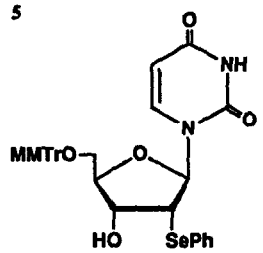
5



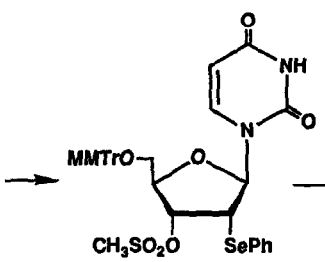
6 : R = H
7 : R = MMTr



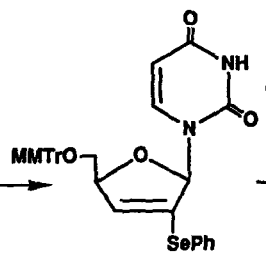
8 (85 %)



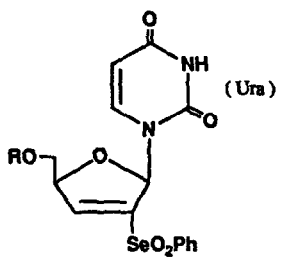
9 (93 %)



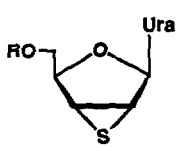
10 (95 %)



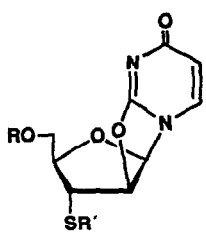
11 (86 %)



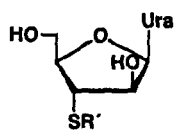
12 : R = MMTr (97 %)
13 : R = H (88 %)



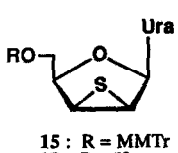
14 : R = MMTr
16 : R = H



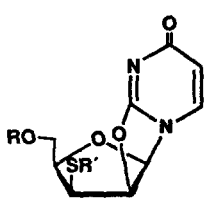
18 : R = MMTr, R′ = Et
20 : R = H, R′ = Et
22 : R = MMTr, R′ = Ph
24 : R = H, R′ = Ph
26 : R = MMTr, R′ = CH_2CO_2Me
28 : R = H, R′ = CH_2CO_2Me



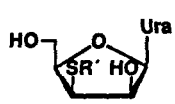
30 : R′ = Et
32 : R′ = Ph
34 : R′ = CH_2CO_2Me



15 : R = MMTr
17 : R = H



19 : R = MMTr, R′ = Et
21 : R = H, R′ = Et
23 : R = MMTr, R′ = Ph
25 : R = H, R′ = Ph
27 : R = MMTr, R′ = CH_2CO_2Me
29 : R = H, R′ = CH_2CO_2Me



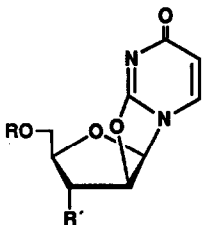
31 : R′ = Et
33 : R′ = Ph

phenylselenone can take place from its either α or β-face, it was anticipated that selectivity of α versus β attack at C-3′ can be steered by the presence or absence of sterically bulky 5′-O-MMTr group. We have therefore removed the 5′-O-MMTr group from **12** by a brief treatment with 80% aqueous acetic acid to give 1-[2′,3′-dideoxy-2′-phenylselenonyl-β-D-*glycero*-pent-2′-enofuranosyl]uracil **13**, and performed most of the reactions reported in this paper on both 5′-O-MMTr-2′, 3′-ene-2′-phenylselenone **12** and 5′-hydroxy-2′, 3′-ene-2′-phenylselenone **13**.

Reaction with hydrogen sulfide. Reaction of 5′-O-MMTr-2′, 3′-ene-2′-phenylselenone **12** with 0.2% hydrogen sulfide solution in THF (w/v, 10 equiv) in presence of triethylamine (20 equiv) at ~20 °C overnight gave a mixture of 1-[5′-O-MMTr-2′,3′-dideoxy-2′,3′-epithio-β-D-*ribo*-furanosyl]uracil **14** and 1-[5′-O-MMTr-2′,3′-dideoxy-2′,3′-epithio-β-D-*lyxo*-furanosyl]uracil **15** in 89 % yield. ^{1}H-NMR examination of this inseparable mixture showed that the 2′,3′-*ribo*-epithio nucleoside **14** ($J_{1',2'}$ = 0 Hz), and 2′,3′-*lyxo*-epithio nucleoside **15** ($J_{1',2'}$ = 2.4 Hz) were formed in 5 : 7 ratio (integration of anomeric and H-5 protons). The 5′-O-MMTr groups from **14** and **15** in the isomeric mixture were removed by a brief treatment with 80% aqueous acetic acid overnight to give the corresponding mixture of parent isomers **16** and **17**. From this mixture, only 2′,3′-*ribo*-epithio nucleoside **16** was isolated pure in ~25% yield, and 2′,3′-*lyxo*-epithio isomer **17** could be isolated in ~95% purity (contaminated with ~5% of **16**) in 37 % yield after eight flash chromatographic purifications. 2′,3′-*lyxo*-epithio isomer **17** was subsequently 5′-O-acetylated to give 5′-O-acetyl-2′,3′-dideoxy-2′,3′-epithio-β-D-*lyxo*-furanosyl]uracil which was spectroscopically identical to the authentic 2′,3′-*lyxo*-episulfide obtained by Ueda et al.[76] 2′,3′-*ribo*-epithio nucleoside **16** was found, as expected, to be relatively more unstable than the 2′,3′-*lyxo*-epithio nucleoside **17** because of the ring-opening reaction by the neighbouring C^2 = O of uracil. Fresh sample of 2′,3′-*ribo*-epithio nucleoside **16** was however found to be sufficiently stable for all spectroscopic studies (experimental). This report constitutes the first synthesis of 2′,3′-*ribo*-epithio nucleoside **16**.

Reaction with ethanethiol. Reaction of 5′-O-MMTr-2′,3′-ene-2′-phenylselenone **12** with ethanethiol (4 equiv) in presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (2 equiv) in THF at ~20 °C overnight gave 1-[5′-O-MMTr-3′-deoxy-3′-ethylthio-2,2′-O-anhydro-β-D-*arabino*-furanosyl]uracil **18** (51 %) and 1-[5′-O-MMTr-3′-deoxy-3′-ethylthio-2,2′-O-anhydro-β-D-*lyxo*-furanosyl]uracil **19** (44 %). In order to examine the steric effect of 5′-O-MMTr group on the Michael addition reaction at C-3′, the reaction of 5′-hydroxy-2′,3′-ene-2′-phenylselenone **13** with ethanthiol (6 equiv) in presence of NaH (2 equiv) in DMF was performed to give 1-[3′-deoxy-3′-ethylthio-2,2′-O-anhydro-β-D-*arabino*-furanosyl]uracil **20** (29 %) and 1-[3′-deoxy-3′-ethylthio-2,2′-O-anhydro-β-D-*lyxo*-furanosyl]uracil **21** (25 %). The ratio of products (**18** & **19** versus **20** and **21**) shows almost negligible steric effect by the 5′-O-MMTr group in the nucleophilic addition at C-3′.

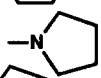
Reaction with thiophenol. Reaction of 5′-O-MMTr-2′, 3′-ene-2′-phenylselenone **12** with thiophenol (4 equiv) in presence of DBU (2 equiv) in THF at ~20 °C overnight gave 1-[5′-O-MMTr-3′-deoxy-3′-phenylthio-2,2′-O-anhydro-β-D-*arabino*-furanosyl]uracil **22** (52 %) and 1-[5′-O-MMTr-3′-deoxy-3′-phenylthio-2, 2′-O-anhydro-β-D-*lyxo*-furanosyl]uracil **23** (24 %). On the other hand, the reaction of 5′-hydroxy-2′,3′-ene-2′-phenylselenone **13** with thiophenol (4 equiv) in presence of DBU (2 equiv) in DMF at ~0 °C overnight gave 1-[3′-deoxy-3′-phenylthio-2,2′-O-anhydro-β-D-*arabino*-furanosyl]uracil **24** (32 %) and 1-[3′-deoxy-3′-phenylthio-2,2′-O-anhydro-β-D-*lyxo*-furanosyl]uracil **25** (21 %). The 3′-up (*lyxo*) products **23** or **25** were



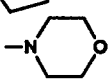
35 : R = H, R′ = NH_2
37 : R = H, R′ = NHMe
39 : R = MMTr, R′ = NMe_2
41 : R = H, R′ = NMe_2

42 : R = MMTr, R′ = 

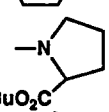
43 : R = H, R′ = 

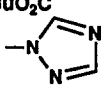
44 : R = MMTr, R′ = 

45 : R = H, R′ = 

46 : R = MMTr, R′ = 

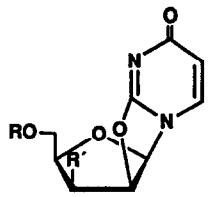
47 : R = H, R′ = 

48 : R = MMTr, R′ = 

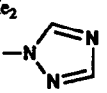
49 : R = MMTr, R′ = 

51 : R = H, R′ = 

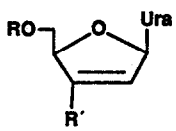
53 : R = MMTr, R′ = OCH_3
54 : R = H, R′ = OCH_3



36 : R = H, R′ = NH_2
38 : R = H, R = NHMe
40 : R = H, R′ = NMe_2

50 : R = MMTr, R′ = 

52 : R = H, R′ = 



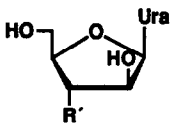
55 : R = MMTr, R′ = 

56 : R = H, R′ = 

57 : R = MMTr, R′ = 

58 : R = H, R′ = 

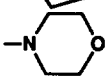
63 : R = MMTr, R′ = -C(Me)$(CO_2Me)_2$
65 : R = H, R′ = -C(Me)$(CO_2Me)_2$



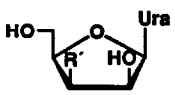
66 : R′ = NH_2
67 : R′ = NHMe
68 : R′ = -NMe_2

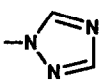
69 : R′ = 

70 : R′ = 

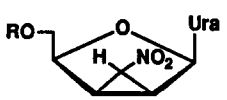
71 : R′ = 

73 : R′ = OCH_3

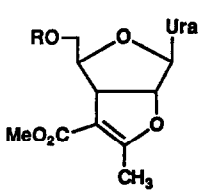


72 : R′ = 

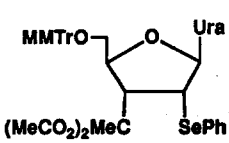
74 : R′ = -NMe_2



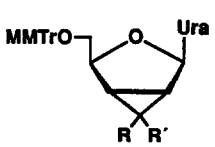
59 : R = MMTr
60 : R = H



61 : R = MMTr
62 : R = H



64



75 : R = R′ = -CO_2Me
76 : R = $CO_2CH_2CH(CH_3)_2$, R′ = CN
77 : R = PhCO, R′ = H
78 : R = R′ = -SO_2Ph

formed in both cases irrespective of whether the 5′-hydroxy group of the enselenone was protected or not. The ratio of 3′-'up' (*lyxo*) [**23** or **25**] to 3′-'down' (*arabino*) [**22** or **24**] changed however from 1:2 to 2:3 by employing 5′-hydroxy-2′,3′-ene-phenylselenone **13** instead of **12** as substrate for Michael addition reaction.

Reaction with methyl thioglycolate. Reaction of 5′-O-MMTr-2′,3′-ene-2′-phenylselenone **12** with methyl thioglycolate (3 equiv) in presence of DBU (1.5 equiv) in THF at ~20 °C gave both 1-[5′-O-MMTr-3′-deoxy-3′-S-(methoxycarbonylmethylene)-2,2′-O-anhydro-β-D-*arabino*-furanosyl] uracil **26** (35 %) and 1-[5′-O-MMTr-3′-deoxy-3′-S-(methoxycarbonylmethylene)-2,2′-O-anhydro-β-D-*lyxo*-furanosyl]uracil **27** (22 %). When this reaction was conducted with 5′-hydroxy-2′,3′-ene-2′-phenylselenone **13** in DMF, it give 1-[3′-deoxy-3′-S-(methoxycarbonylmethylene)-2,2′-O-anhydro-β-D-*arabino*-furanosyl]uracil **28** (36 %) and 1-[3′-deoxy-3′-S(methoxycarbonyl methylene)-2,2′-O-anhydro-β-D-*lyxo*-furanosyl]uracil **29** (21 %).

Reaction with ammonia. Reaction of 5′-hydroxy-2′,3′-ene-2′-phenylselenone **13** with aqueous ammonia (30%, 20 equiv) in DMF at 0 °C for 1 h gave both 1-[3′-deoxy-3′-amino-2,2′-O-anhydro-β-D-*arabino*-furanosyl]uracil **35** (37 %) and 1-[3′-deoxy-3′-amino-2,2′-O-anhydro-β-D-*lyxo*-furanosyl]uracil **36** (6 %). No 2′,3′-*ribo*- or *lyxo*-epimino nucleoside was isolated. The absence of 2′,3′-*ribo*-epimino nucleoside in this reaction, compared to a similar reaction with that of **4**, is due to the nucleophilc α-attack at C-3′ of **13**, subsequent protonation of the resulting 2′-carbanion from the β-face forces the 2′-phenylselenonyl group to the sterically less hindered α-face giving the transient 2′,3′-dideoxy-3′-amino-2′-phenylselenonyl-uridine. The result of formation of the transient 2′,3′-dideoxy-3′-amino-2′-phenylselenonyl-uridine is that the nucleophilic S_N2 displacement by the neighbouring $C^2 = O$ of uracil takes place at C-2′ giving the final 2,2′-O-anhydro-uridine derivatives **35**. Such neighbouring nucleophilic S_N2 displacement by the $C^2 = O$ of uracil also takes place preferentially in the transient 2′,3′-dideoxy-3′-amino-2′-phenylselenonyl-β-D-*arabino*-furanosyl]uracil to give **36**; this is because the conformation of the sugar ring in this transient species is presumably 2′-*endo* (South) with the bulky 2′-phenylselenonyl group in the equatorial position which prevents the neighbouring nucleophilic attack at C-2′ by the 3′-β-amine.

Reaction with methylamine. Reaction of 5′-hydroxy-2′,3′-ene-2′-phenylselenone **13** with aqueous methylamine (40 %, 20 equiv) at 0 °C for 1 h gave 1-[3′-deoxy-3′-methylamino-2,2′-O-anhydro-β-D-*arabino*-furanosyl]uracil **37** (41 %) and 1-[3′-deoxy-3′-methylamino-2,2′-O-anhydro-β-D-*lyxo*-furanosyl]uracil **38** (5 %).

Reaction with secondary amines. Reaction of 5′-O-MMTr-2′,3′-ene-2′-phenylselenone **12** with aqueous dimethylamine, piperidine, pyrrolidine, morpholine at 0 °C, and proline in presence of triethylamine at 40 °C gave the corresponding 3′-(alkylamino-substituted)-2,2′-O-anhydro uridines **39** (51 %), **42** (72 %), **44** (74 %), **46** (48 %) and **48** (48 %), respectively. In none of these reactions 3′-substituted *lyxo*-product was formed. The reactions of 5′-hydroxy-2′-ene-2′-phenylselenone **13** with these secondary amines were therefore carried out. For piperidine, pyrrolidine and morpholine, the reaction gave only *arabino*-products such as **43** (44 %), **45** (53 %), and **47** (36 %), while the reactions with dimethylamine gave both of 3′-substituted *arabino*-nucleoside **41** (42 %) and *lyxo*-nucleoside **40** (10 %).

Reaction with triazole. Reaction of 5'-O-MMTr-2',3'-ene-2'-phenylselenone **12** with 1,2,3-triazole (5 equiv) in presence of potassium carbonate (5 equiv) in THF at ~20 °C gave 1-[5'-O-MMTr-3'-deoxy-3'-triazolyl-2,2'-O-anhydro-β-D-*arabino*-furanosyl]uracil **49** (20 %) and 1-[5'-O-MMTr-3'-deoxy-3'-triazolyl-2,2'-O-anhydro-β-D-*lyxo*-furanosyl]uracil **50** (27 %). Compounds **49** and **50** were treated with sodium tert.-butoxide (1.5 equiv) in THF at ~20 °C to give 1-[5'-O-MMTr-2',3'-dideoxy-3'-triazolyl-β-D-*glycero*-pent-2-eno-furanosyl]uracil **57** in ~83 % yield. Reaction of 5'-hydroxy-2',3'-ene-2'-phenylselenone **13** with triazole (4 equiv) in DMF in presence of NaH gave also expected products: 1-[3'-deoxy-3'-triazolyl-2,2'-anhydro-β-D-*arabino*-furanosyl]uracil **51** (8 %) and 1-[3'-deoxy-3'-triazolyl-2,2'-anhydro-β-D-*lyxo*-furanosyl]uracil **52** (24 %). Both **51** and **52** upon treatment with potassium t-butoxide (1.5 eq) in DMF gave the olefin **58** (54 %).

Reaction with imidazole. Reaction of 5'-O-MMTr-2',3'-ene-2'-phenylselenone **12** with imidazole (10 equiv) in THF at 40 °C overnight gave however 1-[5'-O-MMTr-2',3'-dideoxy-3'-imidazolyl-β-D-*glycero*-pent-2-eno-furanosyl]uracil **55** (43 %) directly. No 2,2'-O-anhydro-nucleoside was found to have formed in this reaction. An identical reaction with 5'-hydroxy-2',3'-ene-2'-phenenylselenone **13** gave also expected 1-[2',3'-dideoxy-3'-imidazolyl-β-D-*glycero*-pent-2-eno-furanosyl]uracil **56** (38 %).

Reaction with sodium methoxide. Reaction of 5'-O-MMTr-2',3'-ene-2'-phenylselenone **12** with sodium methoxide (3 equiv) in methanol at ~20 °C for 2 h gave 1-[5'-O-MMTr-3'-deoxy-3'-methoxy-2,2'-O-anhydro-β-D-*arabino*-furanosyl]uracil **53** (88 %), which was deprotected with 80 % aqueous acetic acid at ~20 °C to give 1-[3'-deoxy-3'-methoxy-2,2'-O-anhydro-β-D-*arabino*-furanosyl]uracil **54** (86 %).

Reaction with nitromethane. Reaction of 5'-O-MMTr-2',3'-ene-2'-phenylselenone **12** with nitromethyl anion gave only 1-[5'-O-MMTr-2',3'-dideoxy-2',3'-[(1-nitro)cyclopropane]-β-D-*lyxo*-furanosyl]uracil **59** (25 %). No corresponding *ribo*-[(1-nitro)cyclopropane] nucleoside was found in this reaction. The reaction with 5'-hydroxy-2',3'-ene-2'-phenylselenone **13** with conjugate base of nitromethane in DMF also gave the product, 1-[2',3'-dideoxy-2',3'-[(1-nitro)cyclopropane]-β-D-*lyxo*-furanosyl]uracil **60**, but in a poor yield (19 %). It should be noted that the reaction of 2',3'-ene-3'-phenylselenone **4**, on the other hand, gave exclusively 1-[5'-O-MMTr-2',3'-dideoxy-2',3'-[(1-nitro)cyclopropane]-β-D-*ribo*-furanosyl]uracil[73].

Reaction with methyl acetoacetate. Reaction of 5'-O-MMTr-2',3'-ene-2'-phenylselenone **12** with methyl acetoacetate in dry THF (1 : 3, (v/v)) in presence of NaH (2 equiv) gave 1-[5'-O-MMTr-3'-deoxy-3'-C,2'-O-[(1-methoxycarbonyl-2-methyl)vinylene]uridine **61** (32 %). Compound **61** was deprotected with 80 % aqueous acetic acid to give the corresponding parent bicyclo[3.3.0] nucleoside **62** (95 %). Both **61** and **62** are isomers of the reported 2'-deoxy-2'-C,3'-O-[(1-methoxycarbonyl-2-methyl)vinylene]uridine which was synthezised in this laboratory by the reaction of 5'-O-MMTr-2',3'-ene-3'phenylselenonyl uridine **4**[73] with methyl acetoacetate in presence of potassium *tert*-butoxide.

Reaction with dimethyl methylmalonate. Reaction of 5'-O-MMTr-2',3'-ene-2'-phenylselenone **12** with dimethyl methylmalonate (1.5 equiv) in dry THF in presence of NaH (3 equiv) at -10 °C for 7 h and then at ~20 °C overnight gave 1-[5'-O-MMTr-2',3'-dideoxy-3'-[(1,1-dimethoxycarbonyl)ethyl]-β-D-*glycero*-pent-2'-enofuranosyl]uracil **63** (64 %) and 1-[5'-O-MMTr-2',3'-deoxy-2'-phenylseleno-3'-[(1,1-dimethoxycarbonyl) ethyl]-β-D-*ribo*-furanosyl]uracil **64** (10 %). When 5.5 equiv of NaH along with 0.5 equiv $LiAlH_4$ was used

in the reaction of **12** with dimethyl methyl malonate, compound **64** (34 %) was formed as the major product along with a small amount of **63** (4 %). In the latter reaction, the reduced product **64** was formed as the major product because the transient 1-[5′-O-MMTr-2′,3′-deoxy-2′-phenylselenonyl-3′-[(1,1-dimethoxy carbonyl)ethyl]-β-D-*ribo*-furanosyl]uracil became preferentially reduced before the S_N2 attack at C-2′ by the neighbouring $C^2 = O$ of uracil could take place. Compound **63** was deprotected with 80 % aqueous acetic acid to give the corresponding 5′-hydroxy derivative **65** (89 %). A similar attempt to remove 5′-O-MMTr group from **64** caused the cleavage of glycosidic bond which was accelerated owing to the stabilization of episelenium ion by the neighbouring 2′-phenylselenyl group[77].

Reaction with secondary carbon nucleophiles with two acidic protons. Reaction of 5′-O-MMTr-2′,3′-ene-2′-phenylselenone **12** with anions of dimethylmalonate, isobutylcyanoacetate, acetophenone and bis(phenylsulfonyl)methane in dry THF gave 2′,3′-dideoxy-2′,3′-*ribo*-cyclopropane nucleosides **75** - **78** (30 - 50 %), respectively, which were identical to the compounds prepared from 2′,3′-ene-3′-phenylselenonyl uridine **4**[72-74]. It is interesting to note that *lyxo*-cyclopropane nucleoside was found to be completely absent in all of the above reactions except for the conjugate addition reaction with nitromethyl anion that gave the corresponding *lyxo*-cyclopropane nucleoside **60** (vide supra).

Hydrolysis of 2,2′-O-anhydro compounds. Acidic hydrolysis of either of the *arabino*-2,2′-O-anhydro-nucleosides **35**, **37**, **41**, **42**, **44**, **52**, **54**, or *lyxo*-2,2′-O-anhydro nucleoside **40**, upon treatment with 0.1 N sulphuric acid at 90 °C for 1h, gave corresponding 3′-substituted-β-D-*arabino*-furanosyl]uracils **66**, **67**, **68**, **69**, **70**, **71**, **72**, and **73**, or **74**, respectively.

Deprotection of 5′-O-MMTr group. Deprotection of 5′-O-MMTr group from compounds **14**, **15**, **18**, **19**, **22**, **23**, **26**, **27**, **39**, **42**, **44**, **46**, **49**, **50**, **53**, **55**, **57**, **59**, **61** and **63** with 80 % aqueous acetic acid at room temperature gave parent nucleosides **16** (24 %), **17** (37 %), **20** (82 %), **21** (86 %), **24** (81 %), **25** (84 %), **28** (76 %), **29** (79 %), **41** (81 %), **43** (75 %), **45** (79 %), **47** (93 %), **51** (83 %), **52** (75 %), **54** (86 %), **56** (87 %), **58** (83 %), **60** (67 %), **62** (95 %), and **65** (89 %), respectively.

In conclusion, we have demonstrated in this paper that both 1-[5′-O-MMTr-2′,3′-dideoxy-2′-phenylselenonyl-β-D-*glycero*-pent-2′-enofuranosyl]uracil (**12**) and 1-(2′,3′-dideoxy-2′-phenylselenonyl-β-D-*glycero*-pent-2′-enofuranosyl]uracil (**13**) are easily available in gram quantities, and they can be conveniently used in the preparations of 2′,3′-*ribo*- and *lyxo*-episulfides, 3′-*heteroatom* substituted-2,2′-O-anhydro-β-D-*arabino*-furanosyl]uracils, 3′-*heteroatom* substituted-2,2′-O-anhydro-β-D-*lyxo*-furanosyl]uracils, 2′,3′-ene-3′-*heteroatom* substituted uridines and 2′,3′-cyclopropyl uridines and other unique [3.3.0]-α-fused-bis-furano-uridine, which are not accessible by simple S_N2 type reactions. Thus the chemical reactivities **12** and **13** show that they act as the synthetic equivalent of the dication CH_2^+ - CH_2^+ **5** as was the case with 2′,3′-ene-3′-phenylselenonyl nucleoside **4**[72-74]. Clearly, the present use of 2′,3′-ene-2′-phenylselenones **12** and **13** for accessing various 3′-substituted nucleosides is a powerful synthetic complement to the nucleophilic addition reactions of 2′,3′-ene-3′-phenylselenonyl nucleoside **4**[72-74] which provide easy access to several unique 2′-substituted nucleosides.

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-(4-monomethyltrityl)(MMTr)-2'-deoxy-2'-phenylseleno-β-D-*ribo*-furanosyl]uracil (9). To a solution of diphenyldiselenide (4.68 g, 15mmol) in tetrahydrofuran (100 ml) was added lithium aluminum hydride (510 mg, 15 mmol) at ~0 °C. The mixture was stirred at room temperture for 1 h and then compound **8** (4.98 g, 10 mmol) was added. The stirring was continued at 50 °C overnight. The reaction mixture was poured into a saturated aqueous solution of ammonium chloride (200 ml) and which was extracted with dichloromethane (3 x 100 ml). The organic phase was filtered, and the filtrate was evarporated to dryness. The residue was purified on a silica gel column to give product **9** (6.1 g, 93 %). ^{1}H-NMR ($CDCl_3$): 8.27 (br, 1H) NH; 7.63-6.78 (m, 20H) arom & H-6; 6.40 (d, $J_{1',2'}$ = 9.0 Hz, 1H) H-1'; 5,18 (d, $J_{5,6}$ = 8.0 HZ, 1H) H-5; 4.48 (m, 1H) H-3'; 4.20 (m, 1H) H-4'; 3.91 (dd, $J_{2',3'}$ = 5.1 Hz, 1H) H-2'; 3.80 (s, 3H) OCH_3; 3.44 (d, $J_{4',5'}$ = 2.5 Hz, 2H) H-5',H-5". ^{13}C-NMR ($CDCl_3$): 139.6 (d, J_{CH} = 182.0 Hz) C-6; 102.6 (d, J_{CH} = 177.5 Hz) C-5; 88.3 (d, J_{CH} = 171.8 Hz) C-1'; 87.4 (s) MMTr; 84.9 (d, J_{CH} = 148.4 Hz) C-4'; 73.2 (d, J_{CH} = 157.2 Hz) C-3', 63.7 (t, J_{CH} = 144.4 Hz) C-5'; 55.1 (q) OCH_3; 53.2 (d, J_{CH} = 144.9 Hz) C-2'; Ms (FAB$^-$) calc. for $(M-H)^-$ 655.1347, found 655.1364.

1-[5'-O-MMTr-2'deoxy-2'-phenylseleno-3'-O-methanesulfonyl-β-D-*ribo*-furanosyl]uracil (10). Compound **9** (5.24 g. 8 mmol) was treated with methanesulfonyl chloride (2.74 g. 24 mmol) in dry pyridine at ~0 °C overnight and then poured into ice-water. The precipitate was collected by filtration, and was further was purified on a silica gel column to give product **10** (5.55 g, 95 %). ^{1}H-NMR ($CDCl_3$): 8.94 (br, 1H) NH; 7.59-6.83 (m, 20H) arom and H-6; 6.53 (d, $J_{1',2'}$ = 9.5 Hz, 1H) H-1'; 5.39 (d, $J_{2',3'}$ = 3.4 Hz, 1H) H-3'; 5.05 (d, $J_{5,6}$ =7.9 Hz, 1H) H-5; 4.44 (s; 1H) H-4'; 3.92 (dd, 1H) H-2'; 3.81 (s, 3H) MMTr; 3.57 (s, 2H) H-5', H-5"; 3.14 (s, 3H) Ms. ^{13}C-NMR ($CDCl_3$): 138.9 (d, J_{CH} = 180.8 Hz) C-6; 102.9 (d, J_{CH} = 178.6 Hz) C-5; 88.9 (d, J_{CH} = 171.8 Hz) C-1'; 88.0 (s) MMTr; 83.6 (d, J_{CH} = 151.7 Hz) C-4'; 82.0 (d, J_{CH} = 162.9 Hz) C-3'; 63.1 (t, J_{CH} = 144.3 Hz) C-5'; 55.2 (s) OCH_3 ;47.4 (d, J_{CH} = 143.8 Hz) C-2'; 38.7 (q, J_{CH} = 139.6 Hz) Ms.; Ms (FAB$^+$) calc. for (M^+) 734.1204, found 734.1300.

1-[5'-O-MMTr-2',3'-dideoxy-2'-phenylseleno-β-D-*glycero*-pent-2'-enofuranosyl]uracil (11). Compound **10** (3.7 g. 5 mmol) was treated with potassium tert-buthoxide (1.12 g. 10 mmol) in dry tetrahydrofuran (100 ml) at ~0 °C for 1 h and then at room temperature for 2 h. The mixture was poured into a saturated aqueous solution of ammonium chloride (100 ml) and which was extracted with dichloromethane (2 x 100 ml). The organic phase was evaporated to dryness and purified on a silica gel column to give compound **11** (2.74 g, 86 %). ^{1}H-NMR ($CDCl_3$): 9.03 (br, 1H) NH; 7.69-6.82 (m, 15H) arom and H-6; 6.93 (dd, $J_{1',3'}$=1.7 Hz, $J_{1',4'}$ = .6 Hz, 1H) H-1'; 6.11 (t, $J_{3',4'}$ = 1.7 Hz, 1H) H-3'; 4.95 (d, $J_{5,6}$ = 8.1 Hz, 1H) H-5; 4.90 (m, 1H) H-4'; 3.79 (s, 3H) OCH_3; 3.40 (d, $J_{4',5'}$ =3.0 Hz, 2H) H-5', H-5". ^{13}C-NMR ($CDCl_3$): 140.9 (d, J_{CH} = 182.0 Hz) C-6; 102.3 (d, J_{CH} = 178.6 Hz) C-5; 90.9 (d, J_{CH} = 185.4 Hz) C-1'; 87.0 (s) MMTr; 85.8 (d, J_{CH} = 149.4 Hz) C-4'; 64.2 (t, J_{CH} = 138.6 Hz) C-5'; 55.1 (q) OCH_3; Ms (FAB$^-$) calc. for $(M-H)^-$ 637.1245, found 637.1234.

1-[5'-O-MMTr-2',3'-dideoxy-2'-phenylselenonyl-β-D-*glycero*-pent-2'-enofuranosyl]uracil (12). Compound **11** (2.25 g. 3.5 mmol) was treated with m-chloroperbenzoic acid (1.73 g. 10 mmol) in dry methanol (50 ml) at room temperature overnight. The solution was poured into a saturated aqueous solution of sodium sulphite (200 ml), which was extracted with dichloromethane (2 x 150 ml). The organic phase was washed with dilute solution of sodium bicarbonate and then evaporated to dryness to give compound **12** (2.29 g, 97 %). ^{1}H-NMR ($CDCl_3$): 8.84 (br, 1H) NH; 8.01-6.86 (m, 22H) arom, H-6, H-1'and H-3'; 5.08 (m, 1H) H-4'; 4.74 (d, $J_{5,6}$ = 8.0 Hz, 1H) H-5; 3.82 (s, 3H) OCH_3; 3.62 (s, 2H) H-5'and H-5". ^{13}C-NMR: 139.9 (d, J_{CH} = 182.0 Hz) C-6; 103.0 (d, J_{CH} = 178.6 Hz) C-5; 87.8 (d, J_{CH} = 178.6 Hz) C-1'; 86.4 (s) MMTr; 85.0 (d, J_{CH} = 159.5 Hz) C-4'; 63.3 (t, J_{CH} = 146.6 H) C-5'; 55.2 (q) OCH_3; Ms (FAB$^-$) calc. for (M-Ph)$^-$ 593.0829, found 593.0815.

1-[2',3'-dideoxy-2'-phenylselenonyl-β-D-*glycero*-pent-2'-enofuranosyl]uracil (13). Compound **12** (6.7 g. 10 mmol) was treated with aqueous acetic acid (80 %, 100 ml) overnight at room temperature. The solution was evaporated and coevaporated with toluene to dryness. The residue was triturated

with dichloromethane (2 x 200 ml) and filtered to give compound **13** (3.5 g, 88 %). ^{1}H-NMR (DMSO-d_6): 7.91-7.45 (m, 7H) arom, H-6 and H-1′; 7.08 (dd, $J_{1',3'}$=1.7 Hz, $J_{3',4'}$ = 3.9 Hz, 1H) H-3′; 5.35 (d, $J_{5,6}$ = 8.1 Hz, 1H) H-5; 5.10 (m, 1H) H-4′; 3.75 (m, 2H) H-5′, H-5". ^{13}C-NMR (DMSO-d_6): 138.4 (d, J_{CH} = 181.7 Hz) C-6; 103.1 (d, J_{CH} = 175.3 Hz) C-5; 87.9 (d, J_{CH} = 179.6 Hz) C-1′; 86.7 (d, J_{CH} = 159.4 Hz) C-4′; 61.6 (d, J_{CH} = 143.5 Hz) C-5′; Ms (FAB$^-$) calc. for (M-Ph)$^-$ 320.9626, found 320.9631.

1-[5′-O-MMTr-2′3′-dideoxy-2′,3′-epithio-β-D-*ribo*-furanosyl]uracil (14) & 1-[5′-O-MMTr-2′3′-dideoxy-2′,3′-epithio-β-D-*lyxo*-furanosyl]uracil (15). To a solution of hydrogen sulfide (102 mg, 3 mmol) and triethylammine (606 mg, 6 mmol) in THF (50 ml) was added compound **12** (200 mg, 0.3 mmol) and mixture was stirred overnight at room temperture. The reaction mixture was poured into a saturated aqueous solution of ammonium chloride (100 ml), which was extracted with dichloromethane (2 x 100 ml). The organic phase was evaporated to dryness and the residue was isolated on silica gel column to give an inseparable isomeric mixture of compounds **14** and **15** (138 mg, 89.3 %). Compound **14**: ^{1}H-NMR ($CDCl_3$): 7.62 (d, $J_{5,6}$ = 8.1 Hz, 1H) H-6; 7.56-6.85 (m, 14H) arom, 6.07 (s, 1H) H-1′; 5.12 (d, 1H) H-5, 4.62 (dd, $J_{4',5'}$= 4.0 Hz, $J_{4',5"}$= 5.6 Hz, 1H) H-4′; 3.84 (d, $J_{2',3'}$= 4.8 Hz, 1H) H-2′; 3.80 (s, 3H) HHTr, 3.67 (d, 1H) H-3′; 3.42 (dd, J_{gem} = 10.5 Hz, 1H) H-5′, 3.38 (dd, 1H) H-5"; Compound **15**: ^{1}H-NMR ($CDCl_3$): 7.58 (m, 15H) H-6 and arom, 6.28 (d, $J_{1',2'}$= 2.4 Hz, 1H) H-1′, 5.63 (d, $J_{5,6}$ = 8.2 Hz, 1H) H-5, 4.44 (dt, $J_{4',5'}$= 5.4 Hz, $J_{4',5"}$= 6.0 Hz, 1H) H-4′, 3.82 (dd, $J_{2',3'}$= 5.0 Jz, 1H) H-2′, 3.65 (dd, $J_{3',4'}$= 2.5 Hz, 1H) H-3′; 3.41 (dd, J_{gem} = 9.5 Hz, 1H) H-5′, 3.27 (dd, 1H) H-5"; Ms (FAB$^-$) calc. for (M-H)$^-$ 541.1797, found 541.1772.

1-[5′-O-MMTr-3′-deoxy-3′-ethylthio-2,2′-O-anhydro-β-D-*arabino*-furansyl]uracil (18) & 1-[5′-O-MMTr-3′-deoxy-3′-ethylthio-2,2′-O-anhydro-β-D-*lyxo*-furansyl]uracil (19). To a solution of ethanthiol (75 mg, 1.2 mmol) in dry tetrahydrofuran (20 ml) was added 1,8-diazabicyclo[5.4.0]undec-7-en (91 mg, 0.60 mmol), and it was stirred for 1 h. The compound **12** (200 mg, 0.30 mmol) was added and then stirred overnight. The mixture was poured into a saturated aqueous solution of ammonium chloride (200 ml) and extracted with dichloromethane (2 x 100 ml). The organic phase was evaporated and the residue was separated on a silica gel column to give compound **18** (82 mg, 50.7 %), and compound **19** (71 mg, 43.9 %). Compound **18:** ^{1}H-NMR ($CDCl_3$): 7.26-6.80 (m, 15H) arom, H-6; 6.13 (d, $J_{1',2'}$ = 5.6 Hz, 1H) H-1′; 5.96 (d, $J_{5,6}$ = 7.9 Hz, 1H) H-5; 5.27 (m, 1H) H-2′; 4.23 (m, 1H) H-4′; 3.58 (dd, $J_{2',3'}$ =2.1 Hz, $J_{3',4'}$ = 4.8 Hz, 1H) H-3′; 3.10 (d, $J_{4',5'}$ = 5.4 Hz, 2H) H-5′, H-5"; 2.66 (q, J = 7.3 Hz, 2H) SCH_2; 1.29 (t, 3H) CH_2CH_3... ^{13}C-NMR ($CDCl_3$) 134.1 (d, J_{CH} = 185.7 Hz) C-6; 110.4 (d, J_{CH} = 174.3 Hz) C-5; 90.1 (d, J_{CH} = 180.7 Hz) C-1′; 88.9 (d, J_{CH} = 171.2 Hz) C-2′; 86.6 (s) MMTr; 86.1 (d, J_{CH} = 148.4 Hz) C-4′; 63.1 (t, J_{CH} = 142.5 Hz) C-5′; 55.2 (q) OCH_3; 48.2 (d, J_{CH} = 150.9 Hz) C-3′; 26.3 (t; J_{CH} = 140.9 Hz) SCH_2; 14.4 (q; J_{CH} =127.4 Hz) CH_2CH_3.; Ms (FAB$^-$) calc. for (M-H)$^-$ 541.1797, found 541.1812. Compound **19:** ^{1}H-NMR ($CDCl_3$): 7.36-6.77 (m, 15H) H-6 and arom, 6.17 (d, $J_{1',2'}$= 5.4 Hz, 1H) H-1′, 5.83 (d, $J_{5,6}$ = 7.4 Hz, 1H) H-5, 5.33 (t, $J_{2',3'}$= 5.8 Hz, 1H) H-2′; 4.61 (m, 1H) H-4′, 3.50 (dd, $J_{3',4'}$= 7.8 Hz, 1H) H-3′, 3.38 (dd, $J_{4',5'}$= 3.0 Hz, J_{gem} = 11.3 Hz, 1H) H-5′, 2.67 (dd, $J_{4',5"}$= 8.8 Hz, 1H) H-5", 2.48 (q, J = 7.3 Hz, 2H) CH_2CH_3, 1.14 (t, 3H) CH_2CH_3; ^{13}C-NMR ($CDCl_3$) 134.7 (d, J_{CH} = 181.9 Hz) C-6; 109.8 (d, J_{CH} = 175.2 Hz) C-5; 89.7 (d, J_{CH} = 180.9 Hz) C-1′; 83.7 (d, J_{CH} = 171.9 Hz) C-2′; 86.5 (s) MMTr; 82.9 (d, J_{CH} = 141.7 Hz) C-4′; 63.6 (t, J_{CH} = 139.9 Hz) C-5′; 55.1 (q) OCH_3; 47.9 (d, J_{CH} = 142.7 Hz) C-3′; 26.7 (t; J_{CH} = 139.3 Hz) SCH_2; 14.8 (q; J_{CH} =128.1 Hz) CH_2CH_3.; Ms (FAB$^-$) calc. for (M-H)$^-$ 541.1797, found 541.1772.

1-[3′-deoxy-3′-ethylthio-2,2′-O-anhydro-β-D-*arabino*-furanosyl]uracil (20) & 1-[3′-deoxy-3′-ethylthio-2,2′-O-anhydro-β-D-*lyxo*-furanosyl]uracil (21). Compound **13** (199 mg, 0.5 mmol) was treated with ethanthiol (186 mg, 3 mmol) and NaH (30 mg, 80 %, 1 mmol) in dimethylformamide (20 ml) for 2 h at room temperature. Acetic acid (3 ml) was added and the mixture was evaporated to dryness. The residue was separated on silica gel column to give compound **20** (40 mg, 29 %) and **21** (34 mg, 25 %). Compound **20**: ^{1}H-NMR ($CDCl_3$ + CD_3OD): 7.61 (d, $J_{5,6}$ = 7.3 Hz, 1H) H-6; 6.30 (d, $J_{1',2'}$ = 5.9 Hz,1H) H-1′; 6.07 (d, 1H) H-5; 5.39 (dd, $J_{2',3'}$ = 1.4 Hz, 1H) H-2′; 4.27 (m, 1H) H-4′; 3.73 (dd, $J_{3',4'}$ = 3.9 Hz, 1H) H-3′; 3.56 (d, $J_{4',5'}$ = 3.9 Hz, 2H) H-5′, H-5". 2.76 (q, J = 7.3 Hz, 2H) SCH_2; 1.37 (t, 3H) SCH_2CH_3. ^{13}C-NMR ($CDCl_3$ + CD_3OD): 135.9 (d, J_{CH} = 186.5 Hz) C-6; 109.0 (d, J_{CH} = 173.0 Hz) C-5; 90.6 (d, J_{CH} = 183.5 Hz) C-1′; 89.4 (d, J_{CH} = 169.6) C-2′; 88.4 (d, J_{CH} = 149.4 Hz) C-4′; 61.6 (t, J_{CH} = 142.1 Hz) C-5′; 47.9 (d, J_{CH} = 151.7 Hz) C-3′; 25.7 (t, J_{CH} = 141.0 Hz) SCH_2; 13.7 (q, J_{CH} = 125.4 hz) SCH_2CH_3 ; Ms (FAB$^-$) calc. for (M-H)$^-$ 269.0596, found 269.0594. Compound **21**: ^{1}H-NMR ($CDCl_3$ + CD_3OD): 7.69 (d, $J_{5,6}$ = 7.3 Hz, 1H) H-6; 6.27 (d, $J_{1',2'}$ = 5.6 Hz, 1H) H-1′; 6.07 (d, 1H) H-5; 5.52 (t, $J_{2',3'}$ = 6.3 Hz, 1H) H-2′; 4.55 (m, 1H) H-4′; 3.75 (dd, $J_{3',4'}$ = 8.3 Hz, 1H) H-3′; 3.58 (m, 2H) H-5′,H-5"; 2.71(q, J = 7.3 Hz, 2H) SCH_2; 1.34 (t, 3H) SCH_2CH_3. ^{13}C-NMR ($CDCl_3$ + CD_3OD): 136.2 (d, J_{CH} = 186.4 Hz) C-6; 108.4 (d, J_{CH} = 174.1 Hz) C-5; 89.4 (d, J_{CH} = 184.2 Hz) C-1′; 84.2 (d, J_{CH} = 151.7 Hz) C-4′; 83.8 (d, J_{CH} = 169.6 Hz) C-2′;

60.4 (t, J_{CH} = 141.6 Hz) C-5'; 47.3 (d, J_{CH} = 140.4 Hz) C-3'; 26.6 (t, J_{CH} = 139.3 Hz) SCH_2; 14.3 (d, J_{CH} = 126.9 Hz) SCH_2CH_3.; Ms (FAB$^-$) calc. for (M-H)$^-$ 269.0596, found 269.0582.

1-[5'-O-MMTr-3'-deoxy-3'-phenylthio-2,2'-O-anhydro-β-D-*arabino*-furanosyl]uracil (22) and 1-[5'-O-MMTr-3'-deoxy-3'-phenylthio-2,2'-O-anhydro-β-D-*lyxo*-furanosyl]uracil (23). To a solution of 1,8-diazabicyclo [5.4.0] undec-7-en (152 mg, 1 mmol) and thiophenol (165 mg, 1.5 mmol) in dry tetrahydrofuran (20 ml) was added compound **12** (335 mg, 0.5 mmol) and stirring was continued for 1 h. The mixture was poured into a saturated aqueous solution of ammonium chloride (100 ml) and which was extracted with dichloromethane (2 x 100 ml). The organic phase was evaporated to dryness, and residue was separated on silica gel column to give compound **22** (154 mg, 52 %) and compound **23** (72 mg, 24 %). Compound **22**: ^{1}H-NMR ($CDCl_3$): 7.38-6.80 (m, 20 H) arom, H-6; 6.08 (d, $J_{1',2'}$ = 5.7 Hz, 1H) H-1'; 5.92 (d, $J_{5,6}$ = 7.3 Hz, 1H) H-5; 5.18 (dd, $J_{2',3'}$ = 1.3 Hz, 1H) H-2'; 4.38 (m, 1H) H-4'; 3.98 (m, 1H) H-3'; 3.05(m, 2H) H-5', H-5". ^{13}C-NMR ($CDCl_3$): 134.2 (d, J_{CH} = 185.6 Hz) C-6; 110.3 (d, J_{CH} = 173.0 Hz) C-5; 90.3 (d, J_{CH} = 179.7 Hz) C-1'; 87.6 (d, J_{CH} = 175.3 Hz) C-2'; 85.6 (d, J_{CH} = 155.2 Hz) C-4'; 63.7 (t, J_{CH} = 142.7 Hz) C-5'; 55.1 (q) OCH_3; 51.3 (d, J_{CH} = 152.8 Hz) C-3'; Ms (FAB$^-$) calc. for (M-H)$^-$ 589.1797, found 589.1802. Compound **23**: ^{1}H-NMR ($CDCl_3$): 7.30-6.78 (m, 20H) arom, H-6; 6.07 (d, $J_{1',2'}$ = 5.4 Hz) H-1'; 5.93 (d, $J_{5,6}$ = 7.6 Hz, 1H) H-5; 5.31 (t, $J_{2',3'}$ = 5.7 Hz, 1H) H-2'; 4.65 (m, 1H) H-4'; 3.84 (dd, $J_{3',4'}$ = 7.8 Hz, 1H) H-3'; 3.52 (dd, $J_{4',5'}$ = 3.5 Hz, 1H) H-5'; 2.89 (dd, $J_{4',5"}$ = 8.5 Hz, 1H) H-5". ^{13}C-NMR ($CDCl_3$): 143.6 (d, J_{CH} = 181.8 Hz) C-6; 109.9 (d, J_{CH} = 174.1 Hz) C-5; 89.7 (d, J_{CH} = 178.8 Hz) C-1'; 83.4 (d, J_{CH} = 170.7 Hz) C-2'; 82.5 (d, J_{CH} = 159.0 Hz) C-4'; 63.5 (t, J_{CH} = 143.8 Hz) C-5'; 55.1 (q) OCH_3; 51.4 (d, J_{CH} = 146.0 Hz) C-3'; Ms (FAB$^-$) calc. for (M-H)$^-$ 589.1797, found 589.1802.

1-[3'-deoxy-3'-phenylthio-2,2'-O-anhydro-β-D-*arabino*-furanosyl]uracil (24) and 1-[3'-deoxy-3'-phenylthio-2,2'-O-anhydro-β-D-*lyxo*-furanosyl]uracil (25). Compound **13** (199 mg, 0.5 mmol) was treated with thiophenol (220 mg, 2 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (123 mg, 0.80 mmol) in dimethylformamide (20 ml) for 2 h at room temperature. Acetic acid (2 ml) was added and the mixture was evaporated to dryness. The residue was separated on silica gel column to give compound **24** (51 mg, 32 %) and **25** (34 mg, 21 %). Compound **24**: ^{1}H-NMR ($CDCl_3$ + CD_3OD): 7.64 (d, $J_{5,6}$ = 7.6 Hz, 1H) H-6; 7.54-7.27 (m, 5H) arom; 6.31 (d, $J_{1',2'}$ = 6.1 Hz, 1H) H-1'; 6.06 (d, 1H) H-5; 5.36 (d, 1H) H.2'; 4.36 (m, 1H) H-4'; 4.21(d, $J_{3',4'}$ = 3.7 Hz, 1H) H-3'; 3.54 (d, J4',5= 3.6 Hz, 2H) H-5'; H-5". ^{13}C-NMR ($CDCl_3$ + CD_3OD): 136.0 (d, J_{CH} = 186.1 Hz) C-6; 108.6 (d, J_{CH} = 173.7 Hz) C-5; 90.6 (d, J_{CH} = 186.6 Hz) C-1'; 88.3 (d, J_{CH} = 173.9 Hz Hz) C-2'; 87.7 (d, J_{CH} = 150.0 Hz) C-4'; 61.7 (t, J_{CH} = 142.7 Hz) C-5'; 50.3 (d, J_{CH} = 148.3 Hz) C-3'; Ms (FAB$^-$) calc. for (M-H)$^-$ 317.0596, found 317.0612. Compound **25**: ^{1}H-NMR ($CDCl_3$ + CD_3OD): 7.97 (d, $J_{5,6}$ = 7.5 Hz, 1H) H-6; 7.57-7.43 (m, 5H) arom; 6.37 (d, $J_{1',2'}$ = 5.6 Hz, 1H) H-1'; 5.96 (d, 1H) H-5; 5.69 (t, $J_{2',3'}$ = 5.6 Hz, 1H) H-2'; 5.01 (t, $J_{4',5'}$ = 4.1 Hz, $J_{4',5"}$ = 4.4 Hz, 1H) H-4'; 4.53 (d, $J_{2',3'}$ = 5.6 Hz, 1H) H-3'; 3.39 (m, 2H) H-5'; H-5". ^{13}C-NMR ($CDCl_3$ + CD_3OD): 137.0 (d, J_{CH} = 185.4 Hz) C-6; 108.6 (d, J_{CH} = 174.1 Hz) C-5; 89.5 (d, J_{CH} = 185.4 Hz) C-1'; 83.4 (d, J_{CH} = 156.2 Hz) C-4'; 183.2 (d, J_{CH} = 171.8 Hz) C-2'; 60.8 (t, J_{CH} = 139.9 Hz) C-5'; 48.8 (d, J_{CH} = 143.8 Hz) C-3'; Ms (FAB$^-$) calc. for (M-H)$^-$ 317.0596, found 317.0588.

1-[5'-O-MMTr-3'-deoxy-3'-S-(methoxycarbonylmethylene)-2,2'-O-anhydro-β-D-*arabino*-furanosyl]uracil (26) & 1-[5'-O-MMTr-3'-deoxy-3'-S-(methoxycarbonylmethylene)-2,2'-O-anhydro-β-D-*lyxo*-furanosyl]uracil (27). To the solution of methyl thioglycolate (259 mg, 1.5 mmol) in tetrahydrofuran (20 ml) was added 1,8-diazabicyclo[5.4.0]undec-7-ene (114 mg, 0.75 mmol) and was stirred for 1 h. Then compound **12** (335 mg, 0.5 mmol) was added and stirring was continued overnight at room temperature. The reaction mixture was poured into a saturated aqueous solution of ammonium chloride (100 ml) and which was extracted with dichloromethane (2 x 100 ml). The organic phase was evaporated to dryness and the residue was isolated on silica gel column to give compound **26** (104 mg, 35.5 %) and **27** (65 mg, 22 %). Compound **26**: ^{1}H-NMR ($CDCl_3$): 7.33-6.75 (m, 15 H) arom, H-6; 6.17 (d, $J_{1',2'}$ = 5.6 Hz, 1H) H-1'; 5.95 (d, $J_{5,6}$ = 7.3 Hz, 1H) H-5; 5.42 (dd, $J_{2',3'}$ = 2.0 Hz, 1H) H-2'; 4.25 (m, 1H) H-4'; 3.80 (s, 3H) MMTr; 3.71 (s, 3H) CH_3OCO; 3.38 (d, 2H) SCH_2; 3.10 (d, $J_{4',5'}$ = 5.6 Hz, 2H) H-5',H-5". ^{13}C-NMR ($CDCl_3$): 134.3 (d, J_{CH} = 185.3 Hz) C-6; 110.3 (d, J_{CH} = 176.3 Hz) C-5; 90.3 (d, J_{CH} = 185.3 Hz) C-1'; 88.4 (d, J_{CH} = 169.6 Hz) C-2'; 86.7 (s) MMTr; 85.7 (d, J_{CH} = 155.0 Hz) C-4'; 63.2 (t, J_{CH} = 143.8 Hz) C-5'; 55.2 (q) OCH_3(MMTr); 52.7 (q, J_{CH} = 146.2 Hz) CH_3OCO; 49.7 (d, J_{CH} = 148.3 Hz) C-3'; 33.4 (t, J_{CH} = 146.0 Hz) SCH_2; Ms (FAB$^-$) calc. for (M-H)$^-$ 585.1695, found 585.1678. Compound **27**: ^{1}H-NMR ($CDCl_3$): 7.28-6.77 (m, 15H) arom, H-6; 6.09 (d, $J_{1',2'}$ = 5.1 Hz, 1H) H-1'; 5.88 (d, $J_{5,6}$ = 7.3 Hz, 1H) H-5; 5.38 (t, $J_{2',3'}$ = 5.9 Hz, 1H) H-2'; 4.71 (m, 1H) H-4'; 3.81 (m, 1H) H-3'; 3.80 (s, 3H) CH_3O (MMTr); 3.70 (s, 3H) CH_3O; 3.29 (dd, $J_{4',5'}$ = 3.9 Hz, 1H) H-5'; 3.19 (d, 2H) SCH_2; 2.74 (dd, $J_{4',5"}$ = 8.8 Hz, $J_{5',5"}$ = 10.8 Hz, 1H) H-5". ^{13}C-NMR ($CDCl_3$): 134.9 (d, J_{CH} = 182.0 Hz) C-6; 109.8 (d, J_{CH} = 174.1 Hz) C-5; 89.7 (d, J_{CH} =

180.8 Hz) C-1′; 86.6 (s) MMTr; 83.2 (d, J_{CH} = 161.9 Hz) C-4′; 82.0 (d, J_{CH} = 176.4) C-2′; 63.4 (t, J_{CH} = 143.2Hz) C-5′; 55.1 (q) CH_3O(MMTr); 52.6 (q, J_{CH} = 147.5 Hz) CH_3O; 48.0 (d, J_{CH} = 143.8 Hz) C-3′; 33.2 (t, J_{CH} = 141.6 Hz) SCH_2; Ms (FAB⁻) calc. for (M-H)⁻ 585.1695, found 585.1716.

1-[3′-deoxy-3′-S-(methoxycarbonylmethylene)-2,2′-O-anhydro-β-D-*arabino*-furanosyl] uracil (28) & 1-[3′-deoxy-3′-S-(methoxycarbonylmethylene)-2,2′-O-anhydro-β-D-*lyxo*-furanosyl]uracil (29). To the solution of methyl thioglycolate (96 mg, 0.9 mmol) in dimethylformamidine (20 ml) was added 1,8-diazabicyclo[5.4.0]undec-7-ene (69 mg, 0.45 mmol) and was stirred for 1 h. Then compound **13** (120 mg, 0.3 mmol) was added and stirring was continued overnight at room temperature. After addition of acetic acid (1 ml), reaction mixture was evaporated and coevaporated to dryness and the residue was isolated on silica gel column to give compound **28** (35 mg, 36%) and **29** (20 mg, 21 %). Compound **28**: ^{1}H-NMR ($CDCl_3$ + CD_3OD): 7.76 (d, $J_{5,6}$ = 7.3 Hz, 1H) H-6; 6.38 (d, $J_{1',2'}$ = 5.9 Hz, 1H) H-1′; 6.06 (d, 1H) H-5; 5.58 (dd, $J_{2',3'}$ = 1.6 Hz, 1H) H-2′; 4.28 (m, 1H) H-4′; 3.87 (dd, $J_{3',4'}$ = 3.5 Hz, 1H) H-3′; 3.79 (s, 3H) CH_3OCO; 3.59 (s, 2H) SCH_2; 3.53 (d, $J_{4',5'}$ = 3.7 Hz, 2H) H-5′, H-5". ^{13}C-NMR ($CDCl_3$ + CD_3OD):136.2 (d, J_{CH} = 187.6 Hz) C-6; 108.0 (d, J_{CH} = 174.1 Hz) C-5; 90.3 (d, J_{CH} = 186.5 Hz) C-1′; 88.8 (d, J_{CH} = 168.5 Hz) C-2′; 87.6 (d, J_{CH} = 155.0 Hz) C-4′; 61.0 (t, J_{CH} = 142.1 Hz) C-5′; 51.4 (q, J_{CH} = 148.3 Hz) CH_3OCO; 47.4 (d, 149.4 Hz) C-3′; 32.3 (t, J_{CH} = 142.3 Hz) SCH_2; Ms (FAB⁻) calc. for (M-H)⁻ 313.0494, found 313.0503. Compound **29**: ^{1}H-NMR ($CDCl_3$ + CD_3OD): 7.80 (d, $J_{5,6}$ = 7.6 Hz, 1H) H-6; 6.30 (d, $J_{1',2'}$ = 5.9 Hz, 1H) H-1′; 6.04 (d, 1H) H-5; 5.60 (t, $J_{2',3'}$ = 6.3 Hz, 1H) H-2′; 4.59 (m, 1H) H-4′; 3.99 (dd, $J_{3',4'}$ = 8.4 Hz, 1H) H-3′; 3.57 (t, $J_{4',5'}$ = 3.4 Hz, $J_{4',5"}$ = 4.1 Hz, 2H) H-5′, H-5". ^{13}C-NMR ($CDCl_3$ + CD_3OD): 138.7 (d, J_{CH} = 187.6 Hz) C-6; 109.8 (d, J_{CH} = 173.0 Hz) C-5; 91.6 (d, J_{CH} = 186.4 Hz) C-1′; 85.8 (d, J_{CH} = 173.0 Hz) C-2′; 85.8 (d, J_{CH} = 155.0 Hz) C-4′; 62.0 (t, J_{CH} = 141.0 Hz) C-5′; 53.1 (q, J_{CH} = 147.5 Hz) CH_3OCO; 50.3 (d, J_{CH} = 151.6 Hz) C-3′; 35.4 (t, J_{CH} = 143.8 Hz) SCH_2; Ms (FAB⁻) calc. for (M-H)⁻ 313.0494, found 313.0476.

1-[3′-deoxy-3′-amino-2,2′-O-anhydro-β-D-*arabino*-furanosyl]uracil (35) and 1-[3′-deoxy-3′-amino-2,2′-O-anhydro-β-D-*lyxo*-furanosyl]uracil (36). Compound **13** (199 mg, 0.5 mmol) was treated with aqueous ammonia (30 %, 0.57 ml, 10 mmol) in dimethylformamide (10 ml) for 4 h at 0 °C. The solution was evaporated to dryness and the residue was separated on a silica gel column to give compound **35** (42 mg. 37 %) and compound **36** (7 mg, 6 %). Compound **35**: ^{1}H-NMR (D_2O): 7.85 (d, $J_{5,6}$ = 7.4 Hz, 1H) H-6; 6.42 (d, $J_{1',2'}$ =5.8 Hz, 1H) H-1′; 6.11 (d, 1H) H-5; 5.29 (d, 1H) H-2′; 4.17 (m, 1H) H-4′; 3.80 (d, $J_{3',4'}$ = 2.0 Hz, 1H) H-3′′; 3.49 (m, 2H) H-5′; H-5". ^{13}C-NMR (D_2O): 138.8 (d, J_{CH} = 189.8 Hz) C-6; 109.1 (d, J_{CH} = 177.5 Hz) C-5; 91.4 (d, J_{CH} = 189.8 Hz) C-1′; 90.7 (d, J_{CH} = 166.2 Hz) C-2′; 90.3 (d, J_{CH} = 149.4 Hz) C-4′; 61.8 (t, J_{CH} = 143.2 Hz) C-5′; 58.1 (d, J_{CH} = 146.0 Hz) C-3′; Ms (FAB⁻) calc. for (M-H)⁻ 224.0671, found 224.0676. Compound **36**: ^{1}H-NMR (D_2O): 7.72 (d, $J_{5,6}$ = 7.6 Hz, 1H) H-6; 6.26 (d, $J_{1',2'}$ = 6.3 Hz, 1H) H-1′; 6.09 (d, 1H) H-5; 5.06 (d, 1H) H-2′; 4.27 (m, 1H) H-4′; 3.53 (m, 1H) H-3′; 3.38 (m, 2H) H-5′, H-5"; Ms (FAB⁻) calc. for (M-H)⁻ 224.0671, found 224.0675.

1-[3′-deoxy-3′-methylamino-2,2′-O-anhydro-β-D-*arabino*-furanosyl]uracil (37) and 1-[3′-deoxy-3′-methylamino-2,2′-O-anhydro-β-D-*lyxo*-furanosyl]uracil (38). Compound **13** (199 mg, 0.5 mmol) was treated with a aqueous methylamine (40 %, 0.78 ml, 10 mmol) in dimethylformamide (10 ml) for 4 h at 0 °C. The solution was evaporated and coevaporated with toluene (3 x 20 ml) to dryness and the residue was separated on a silica gel column to give compound **37** (49 mg, 41 %) and **38** (6 mg, 5 %). Compound **37**: ^{1}H-NMR ($CDCl_3$ + CD_3OD): 7.61 (d, $J_{5,6}$ = 7.5 Hz, 1H) H-6; 6.31 (d, $J_{1',2'}$ = 5.6 Hz, 1H) H-1′; 6.06 (d, 1H) H-5; 5.27 (d, 1H) H-2′; 4.18 (m, 1H) H-4′; 3.52 (m, 3H) H-3′, H-5′; H-5". ^{13}C-NMR ($CDCl_3$ + CD_3OD): 136.1 (d, J_{CH} = 187.6 Hz) C-6; 108.9 (d, J_{CH} = 173.0 Hz) C-5; 90.5 (d, J_{CH} = 183.1 Hz) C-1′; 87.7 (d, J_{CH} = 147.2 Hz) C-4′; 87.0 (d, J_{CH} = 170.8 Hz) C-2′; 66.4 (d, J_{CH} = 142.7 Hz) C-3′; 61.7 (t, J_{CH} = 143.8 Hz) C-5′; 33.6 (q, J_{CH} = 133.3 Hz) NCH_3; Ms (FAB⁺) calc. for (M+H)⁺ 240.0984, found 240.0979. Compound **38**: ^{1}H-NMR ($CDCl_3$ + CD_3OD): 7.39 (d, $J_{5,6}$ = 7.6 Hz, 1H) H-6; 6.16 (d, $J_{1',2'}$ = 6.1 Hz, 1H) H-1′; 6.05 (d, 1H) H-5; 4.25 (m, 1H) H-4′; 3.52-3.34 (m, 3H) H-3′, H-5′; H-5"; Ms (FAB⁺) calc. for (M+H)⁺ 240.0984, found 240.0982.

1-[5′-O-MMTr-3′-deoxy-3′-dimethylamino-2,2′-O-anhydro-β-D-*arabino*-furanosyl]uracil (39). Compound **12** (335 mg, 0.5 mmol) was treated with a aqueous solution of dimethylamine (0.56 ml, 40 %, 10 mmol) and in tetrahydrofuran (20 ml) at 0 °C for 1h, and stirring was continued for 4 h at room temperature. The reaction mixture was the evaporated to dryness and the residue was separated on silica gel column to give compound **39** (175 mg, 51%)

1-[3'-deoxy-3'-dimethylamino-2,2'-O-anhydro-β-D-*arabino*-furanosyl]uracil (41) and 1-[3'-deoxy-3'-dimethylamino-2,2'-O-anhydro-β-D-*lyxo*-furanosyl]uracil (40). Compound **13** (199 mg, 0.5 mmol) was treated with a aqueous methylamine (40 %,1.15 ml, 10 mmol) in dimethylformamide (10 ml) for 4 4 h at 0 °C. The solution was evaporated and coevaporated with toluene to dryness and the residue was separated on a silica gel column to give compound **41** (49 mg. 42 %) and compound **40** (12 mg, 10 %). Compound **40**: ^{1}H-HMR ($CDCl_3$ + CD_3OD): 7.62 (d, $J_{5,6}$ = 7.6 Hz, 1H) H-6; 6.21 (d, $J_{1',2'}$ =5.6 Hz,1H) H-1'; 6.09 (d, 1H) H-5; 5.34 (t, $J_{2',3'}$= 5.6 Hz, 1H) H-2'; 4.50 (m, 1H) H-4'; 3.56 (dd, $J_{4',5'}$ = 3.2 Hz, $J_{5',5''}$ = 7.3 Hz, 2H) H-5', H-5"; 3.04 (dd, $J_{3',4'}$= 7.3 Hz, 1H) H-3'. ^{13}C-NMR ($CDCl_3$): 135.7 (d, J_{CH} = 184.5 Hz) C-6, 109.2 (d, J_{CH} = 173.0 Hz) C-5; 89.2 (d, J_{CH} = 180.9 Hz) C-1'; 83.7 (d, J_{CH} = 147.1 Hz) C-4'; 81.7 (d, J_{CH} = 164.0 Hz) C-2'; 70.0 (d, J_{CH} = 146.2 Hz)C-3'; 60.7 (t, J_{CH} = 141.0 Hz) C-5'; 44.9 (q, J_{CH} = 131.8 Hz) NCH_3; Ms (FAB$^-$) calc. for (M-H)$^-$ 252.0984, found 252.0970.

1-[5'-O-MMTr-3'-deoxy-3'-piperidinyl-2,2'-O-anhydro-β-D-*arabino*-furanosyl]uracil (42). Compound **12** (335 mg, 0.5 mmol) was treated with piperidine (127.5 mg, 1.5 mmol) in dry tetrahydrofuran (20 ml) at 0 °C for 1h and stirring was continued for 4 h at room temperature. The reaction mixture was poured into a saturated solution of ammonium chloride (100 ml) and extracted with dichloromethane (2 x 100 ml). The organic phase was pooled and evaporated to dryness. The residue was then separated on silica gel column to give compound **42** (204 mg, 72%). ^{1}H-($CDCl_3$): 7.39-6.80 (m, 15H) arom, H-6; 6.05 (d, $J_{1',2'}$=5.9Hz, 1H) H-1'; 5.93 (d, $J_{5,6}$ = 7.6 Hz, 1H) H-5; 5.34 (dd, $J_{2',3'}$ = 1.2 Hz, 1H) H-2'; 4.45 (m, 1H) H-4'; 3.80 (s, 3H) OCH_3; 3.35 (dd, $J_{3',4'}$ = 3.4 Hz, 1H) H-3'; 3.03 (d, $J_{4',5'}$ =6.1 Hz, 2H) H-5',H-5"; 2.42 (m, 4H) H-2 and H-6 (piperidine); 1.53 (m, 6H) H-3, H-4, and H-5 (piperidine). ^{13}C-NMR ($CDCl_3$): 134.5 (d, J_{CH} = 184.4 Hz) C-6; 109.7 (d, J_{CH} = 173.0 Hz) C-5; 90.2 (d, J_{CH} = 183.0 Hz) C-1'; 86.3 (s) MMTr; 84.4 (d, J_{CH} = 167.4 Hz) C-2'; 81.6 (d, J_{CH} = 151.6 Hz) C-4'; 71.8 (d, J_{CH} = 143.8 Hz) C-3'; 64.0 (t, J_{CH} = 142.1 Hz) C-5'; 55.0 (q) OCH_3; 50.6 (t, J_{CH} = 130.9 Hz) C-2 and C-6 (piperidine); 25.5 (t, J_{CH} = 125.8 Hz) C-3 and C-5 (piperidine); 23.6 (t, J_{CH} = 126.9 Hz) C-4 (piperidine); Ms (FAB$^-$) calc. for (M-H)$^-$ 564.2499, found 564.2535.

1-[3'-deoxy-3'-piperidinyl-2,2'-O-anhydro-β-D-*arabino*-furanosyl]uracil (43). Compound **13** (199 mg, 0.5 mmol) was treated with piperidine (128 mg, 1.5 mmol) in dimethylformamide (10 ml) at 0 °C overnight and acetic acid (2 ml) was added. The mixture was evaporated to dryness and the residue was separated on silica gel column to give compound **43** (66 mg, 44 %). ^{1}H-NMR ($CDCl_3$ + CD_3OD): 7.66 (d, $J_{5,6}$ = 7.4 Hz, 1H) H-6; 6.27 (d, $J_{1',2'}$ = 6.1 Hz, 1H) H-1'; 6.08 (d, 1H) H-5; 5.54 (d, 1H) H-2'; 4.44 (m, 1H) H-4'; 3.65 (m, 1H) H-3'; 3.52 (d, $J_{4',5'}$ = 3.4 Hz, 2H) H-5', H-5". ^{13}C-NMR ($CDCl_3$ + CD_3OD): 136.0 (d, J_{CH} = 186.4 Hz) C-6; 108.8 (d, J_{CH} = 174.1 Hz) C-5; 90.6 (d, J_{CH} = 183.1 Hz) C-1'; 83.9 (d, J_{CH} = 165.1 Hz) C-2'; 83.8 (d, J_{CH} = 150.5 Hz) C-4'; 71.4 (d, J_{CH} = 147.2 Hz) C-3'; 62.1 (t, J_{CH} = 141.6 Hz) C-5'; 49.7 (t, J_{CH} = 130.9 Hz) C-2, C-6 (piperidine) 25.0 (t, J_{CH} = 127.5 Hz) C-3, C-5 (piperidine) 23.2 (t, J_{CH} = 128.6 Hz) C-4 (piperidine); Ms (FAB$^-$) calc. for (M-H)$^-$ 292.1297, found 292.1313.

1-[5'-O-MMTr-3'-deoxy-3'-pyrrolidinyl-2,2'-O-anhydro-β-D-*arabino*-furanosyl]uracil (44). Compound **12** (335 mg, 0.5 mmol) was treated with pyrrolidine (106.5 mg, 1.5 mmol) in dry tetrahydrofuran (20 ml) at 0 °C for 1 h and stirring was continued for 4 h at room temperature. The reaction mixture was poured into a saturated solution of ammonium chloride (100 ml) and which was extracted with dichloromethane (2 x 100 ml). The organic phase was evaporated and the residue separated on silica gel column to give compound **44** (204 mg, 74%) .

1-[3'-deoxy-3'-pyrrolidinyl-2,2'-O-anhydro-β-D-*arabino*-furanosyl]uracil (45). Compound **13** (199 mg, 0.5 mmol) was treated with pyrrolidine (106.5 mg, 1.5 mmol) in dry dimethylforamide (10 ml) at 0 °C for 4 h. The reaction mixture was evaporated and the residue was separated on silica gel column to give compound **45** (75 mg, 53 %).

1-[5'-O-MMTr-3'-deoxy-3'-morpholinyl-2,2'-O-anhydro-β-D-*arabino*-furanosyl]uracil (46). Compound **5** (335 mg, 0.5 mmol) was treated with morpholine (435 mg, 5 mmol) in dry tetrahydrofuran (20 ml) at 0 °C for 1 h and stirring was continued for 4 h at room temperature. The reaction mixture was poured into a saturated solution of ammonium chloride (100 ml), which was extracted with dichloromethane (2 x 100 ml). The organic phase was pooled and was separated on silica gel column to give compound **46** (137 mg, 48%)

1-[3'-deoxy-3'-morpholinyl-2,2'-O-anhydro-β-D-*arabino*-furanosyl]uracil (47). Compound **13** (119 mg, 0.5 mmol) was treated with morpholine (435 mg, 5 mmol) in dry dimethylforamide (10 ml) at 0 °C for 4 h. The reaction mixture was evaporated and the residue separated on silica gel column to give compound **47** (53 mg, 36 %).

1-[5′-O-MMTr-3′-deoxy-3′-(proline-1yl)-2,2′-O-anhydro-β-D-*arabino*-furanosyl]uracil (48). Compound **12** (335 mg, 0.5 mmol) was treated with proline (342 mg, 2 mmol) and triethylamine (202 mg, 2 mmol) in dry tetrahydrofuran (20 ml) at 60 °C for 1 h, and stirring was continued for 4 h at room temperature. The reaction mixture was poured into a saturated solution of ammonium chloride (100 ml) and extracted with dichloromethane (2 x 100 ml). The organic phase was evaporated to dryness and the residue was separated on silica gel column to give compound **48** (156 mg, 48%). ^{1}H-NMR ($CDCl_3$): 7.32-6.75 (m, 15H) arom, H-6′; 6.10 (d, $J_{1',2'}$ = 5.8 Hz, 1H) H-1′; 5.98 (d, $J_{5,6}$ = 7.3 Hz, 1H) H-5; 5.42 (dd, $J_{2',3'}$ = 1.7 Hz, 1H) H-2′; 4.43 (m, 1H) H-4′; 3.81 (s) MMTr; 3.74 (m, 1H) H-3′; 3.17-2.95 (m, 5H) H-5″, H-5", H-2 (proline), H-5 (proline); 2.20-1.77 (m, 4H) H-3, H-4 (proline); 1.47 (s, 12H) tert-Bu. ^{13}C-NMR ($CDCl_3$): 134.3 (d, J_{CH} = 184.5 Hz) C-6; 110.2 (d, J_{CH} = 173.7 Hz) C-5; 90.0 (d, J_{CH} = 183.1 Hz) C-1′; 86.4 (s) MMTr; 86.2 (d, J_{CH} = 169.6 Hz) C-2′; 83.0 (d, J_{CH} = 153.9 Hz) C-4′; 68.0 (d, J_{CH} = 141.5 Hz) C-3′; 63.6 (d, J_{CH} = 142.7 Hz) C-2 (proline); 63.6 (t, J_{CH} = 142.7 Hz) C-5′;55.1 (q) OCH_3; 49.9 (t, J_{CH} = 135.3 Hz) C-5 (proline); 29.8 (t, J_{CH} = 140.4 Hz) C-3, C-4 (proline); 27.9 (q, J_{CH} = 126.9 Hz) tert-Bu; Ms (FAB$^-$) calc. for (M-H)$^-$ 650.2866, found 650.2840.

1-[5′-O-MMTr-3′-deoxy-3′-triazolo-2,2′-O-anhydro-β-D-*arabino*-furanosyl]uracil (49) & 1-[5′-O-MMTr-3′-deoxy-3′-triazolo-2,2′-O-anhydro-β-D-*lyxo*-furanosyl]uracil (50). To a suspension of potassium carbonate (345 mg, 2.5 mmol) and 1,2,3-triazole (172.5 mg, 2.5 mmol) in tetrahydrofuran was added compound **12** (335 mg, 0.5 mmol) and stirring was continued overnight. The reaction mixture was poured into a saturated aqueous solution of ammonium chloride (100 ml) and which was extracted with dichloromethane (2 x 50 ml). The organic phase was evaporated to dryness and separated on silica gel column to give compound **49** (56 mg, 20 %) and compound **50** (76 mg, 27 %). Compound **49**: ^{1}H-NMR ($CDCl_3$): 8.32 (s, 1H) H-3(triazole); 7.87 (s, 1H) H-5 (triazole); 7.35-6.76 (m, 15H) arom, H-6; 6.41 (d, $J_{1',2'}$ = 4.9 Hz, 1H) H-1′; 5.98 (d, $J_{5,6}$ = 7.4 Hz, 1H) H-5; 5.51 (t, $J_{2',3'}$ = 6.1 Hz, 1H) H-2′; 5.30 (dd, $J_{3',4'}$ = 2.7 Hz, 1H) H-3′; 4.68 (m, 1H) H-4′; 3.75 (s, 3H) OCH_3; 3.56 (dd, $J_{4',5'}$ = 2.6 Hz, $J_{5',5''}$ = 11.1 Hz, 1H) H-5′; 3.18 (dd, $J_{4',5''}$ = 3.2 Hz, 1H) H-5". ^{13}C-NMR ($CDCl_3$): 151.0 (d, J_{CH} = 210.0 Hz) C-3 (triazole);143.2 (d, J_{CH} = 213.4 Hz) C-5 (triazole); 135.8 (d, J_{CH} = 182.5 Hz) C-6; 109.5 (d, J_{CH} = 173.0 Hz) C-5; 89.3 (d, J_{CH} = 174.1 Hz) C-1′; 80.6 (d, J_{CH} = 174.1 Hz) C-2′; 79.1 (d, J_{CH} = 140.0 Hz) C-4′; 60.4 (t, J_{CH} = 143.8 Hz) C-5′; 60.3 (d, J_{CH} = 150.5 Hz) C-3′; 54.7 (q) CH_3O; Ms (FAB$^-$) calc. for (M-H)$^-$ 548.1934, found 548.1915. Compound **50**: ^{1}H-NMR ($CDCl_3$): 8.01 (s, 1H) H-3 (triazole); 7.98 (s, 1H) H-5 (triazole); 7.34-6.80 (m, 15H) arom, H-6; 6.35 (d, $J_{1',2'}$ = 5.6 Hz, 1H) H-1′; 6.05 (d, $J_{5,6}$ = 7.6 Hz, 1H) H-5; 5.61 (dd, $J_{2',3'}$ = 2.1 Hz, 1H) H-2′; 5.21 (m, 1H) H-3′; 4.34 (m, 1H) H-4′; 3.80 (s, 3H) OCH_3; 3.24 (d, $J_{4',5'}$ = 5.4 Hz, 2H) H-5′,H-5". ^{13}C-NMR ($CDCl_3$): 153.3 (d, J_{CH} = 210.0 Hz) C-3 (triazole); 143.3 (d, J_{CH} = 204.4 Hz) C-5 (triazole); 134.3 (d, J_{CH} = 190.8 Hz) C-6; 110.6 (d, J_{CH} = 170.8 Hz) C-5; 90.2 (d, J_{CH} = 196.2 Hz) C-1′; 87.1 (s) MMTr; 86.3 (d, J_{CH} = 169.6 Hz) C-2′; 84.4 (d, J_{CH} = 153.9 Hz) C-4′; 64.1 (d, J_{CH} = 147.2 Hz) C-3′; 61.7 (t, J_{CH} = 143.8 Hz) C-5′; 55.2 (q) CH_3O; Ms (FAB$^-$) calc. for (M-H)$^-$ 548.1934, found 548.1929.

1-[3′-deoxy-3′-triazolo-2,2′-O-anhydro-β-D-*arabino*-furanosyl]uracil (51) and 1-[3′-deoxy-3′-triazolo-2,2′-O-anhydro-β-D-*lyxo*-furanosyl]uracil (52). To a solution of triazole (138 mg, 2 mmol) in dimethylformamide (10 ml) was added sodium hydride (24 mg, 0.8 mmol) and stirred for 2 h. Then **13** (199 mg, 0.5 mmol) was added and stirred was contiued for 3 h at room temperature. The reaction mixture was evaporated and the residue was separated on silica gel column to give compound **51** (11 mg, 8 %) and compound **52** (34 mg, 24 %). Compound **51**: ^{1}H-NMR ($CDCl_3$ + CD_3OD): 8.73 (s, 1H) H-3 (triazole); 8.03 (s, 1H) H-5 (triazole); 7.85 (d, $J_{5,6}$ = 7.3 Hz, 1H) H-1′; 6.53 (d, $J_{1',2'}$ = 5.9 Hz, 1H) H-1′; 5.63 (m, 1H) H-2′; 4.37 (m,1H) H-4′; 3.53-3.26 (m 3H) H-3′, H-5′; H-5". ^{13}C-NMR (DMSO): 150.8 (d, J_{CH} = 210.1 Hz) C-3 (triazole); 144.9 (d, J_{CH} = 210.1 Hz) C-5 (triazole); 142.4 (d, J_{CH} = 187.6 Hz) C-6; 100.8 (d, J_{CH} = 176.3 Hz) C-5; 84.1 (d, J_{CH} = 168.4 Hz) C-1′; 80.1 (d, J_{CH} = 152.7 Hz) C-4′; 74.2 (d, J_{CH} = 144.9 Hz) C-2′; 64.1 (d, J_{CH} = 142.7 Hz) C-3′; 59.8 (t, J_{CH} = 142.2 Hz) C-5′; Ms (FAB$^-$) calc. for (M-H)$^-$ 276.0733, found 276.0740. Compound **52**: ^{1}H-NMR ($CDCl_3$ + CD_3OD): 8.56 (s, 1H) H-3 (triazole); 7.99 (s, 1H) H-5 (triazole); 7.73 (d, $J_{5,6}$ = 7.5 Hz, 1H) H-6; 6.48 (d, $J_{1',2'}$ = 5.2 Hz, 1H) H-1′; 6.13 (d, 1H) H-5; 5.67 (t, $J_{2',3'}$ = 6.8 Hz, 1H) H-2′; 5.38 (dd, $J_{3',4'}$ = 9.0 Hz, 1H) H-3′; 4.70 (dt, $J_{4',5'}$ = 2.1 Hz, $J_{4',5''}$ = 2.6 Hz, 1H) H-4′; 3.95 (dd, $J_{5',5''}$ = 13 Hz, 1H) H-5′; 3.61 (dd, 1H) H-5". ^{13}C-NMR ($CDCl_3$ + CD_3OD): 151.0 (d, J_{CH} = 197.7 Hz) C-3 (triazole); 144.1 (d, J_{CH} = 216.8 Hz) C-5 (triazole); 135.7 (d, J_{CH} = 187.6 Hz) C-6; 109.5 (d, J_{CH} = 174.1 Hz) C-5; 89.7 (d, J_{CH} = 185.3 Hz) C-1′; 80.7 (d, J_{CH} = 176.3 Hz) C-2′; 79.0 (d, J_{CH} = 157.2 Hz) C-4′; 58.7 (d, J_{CH} = 158.5 Hz) C-3′; 58.2 (t, J_{CH} = 143.3 Hz) C-5′; Ms (FAB$^-$) calc. for (M-H)$^-$ 276.0733, found 276.0738.

1-[5′-O-MMTr-2′,3′-dideoxy-3′-imidazolo-β-D-*glycero*-pent-2′-enofuranosyl]uracil (55). Compound **12** (335 mg, 0.5 mmol) was treated with imidazole (340 mg, 5 mmol) in tetrahydrofuran (20 ml) at

40 °C overnight. The mixture was poured into a saturated aqueous solution of ammonium chloride (100 ml) and extracted with dichloromethane (2 x 100 ml). The combined organic phase was evaporated and the residue was separated on silica gel column to give compound **55** (118 mg, 43 %). ^{1}H-NMR ($CDCl_3$): 9.64 (br) NH; 8.12 (d, $J_{5,6}$ = 8.1 Hz, 1H) H-6; 7.77 (s, 1H) imidazole; 7.30-6.78 (m, 18 H) arom H-6, H-1', 2H (imidazole); 5.92 (t, $J_{1',2'}$ = 1.4 Hz, $J_{2',4'}$ = 1.7 Hz, 1H) H-2'; 5.25 (m, 1H) H-4'; 4.89 (d, $J_{5,6}$ = 8.1 Hz, 1H) H-5; 3.78 (s, 3H) OCH_3; 3.54 (m, 2H) H-5', H-5". ^{13}C-NMR ($CDCl_3$): 141.0 (d, J_{CH} = 183.1 Hz) H-6; 111.4 (d, J_{CH} = 179.7 Hz) C-2'; 102.3 (d, J_{CH} = 179.7 Hz) H-5; 87.3 (d, J_{CH} = 171.8 Hz) H-1'; 87.2 (s) MMTr; 82.4 (d, J_{CH} = 147.1 Hz) C-4'; 62.4 (t, J_{CH} = 144.9 Hz) H-5'; 55.0 (q) OCH_3; Ms (FAB$^-$) calc. for (M-H)$^-$ 547.1982, found 547.2010.

1-[2',3'-dideoxy-3'-imidazolo-β-D-*glycero*-pent-2'-enofuranosyl]uracil (56). Compound **13** (120 mg, 0.3 mmol) was treated with imidazole (204 mg, 3 mmol) in dimethylformamide (10 ml) at 40 °C. The reaction mixture was evaporated to dryness and the residue was separated on silica gel column to give compound **56** (32 mg, 38 %). ^{1}H-NMR (D_2O+CD_3OD): 8.09 (s, 1H) H-2 (imidazole) 8.06 (d, $J_{5,6}$ = 8.0 Hz, 1H) H-6; 7.51 (s, 1H) H-5 (imidazole) 7.19 (s, 1H) H-4 (imidazole); 7.07 (t, $J_{1',2'}$ = 1.9 Hz, $J_{1',4'}$ 2.5 Hz, 1H) H-1'; 6.13 (t, $J_{2',4'}$ = 1.7 Hz, 1H) H-3'; 5.81 (d, 1H) H-5; 5.41 (m, 1H) H-4'; 3.90 (d, $J_{4',5'}$ = 2.2 Hz, 2H) H-5', H-5". ^{13}C-NMR (D_2O+CD_3OD): 141.4 (d, J_{CH} = 183.1 Hz) C-6; 111.5 (d, J_{CH} = 180.9 Hz) C-2'; 103.1 (d, J_{CH} = 177.5 Hz) C-5; 90.3 (d, J_{CH} = 176.4 Hz) C-1'; 85.6 (d, J_{CH} = 151.6 Hz) C-4'; 62.5 (t, J_{CH} = 142.7 Hz) C-5'; Ms (FAB$^-$) calc. for (M-H)$^-$ 275.0780, found 275.0788.

1-[5'-O-MMTr-3'-O-methyl-2,2'-O-anhydro-β-D-*arabino*-furanosyl]uracil (53): Compound **12** (335 mg, 0.5 mmol) was treated with sodium methoxide (81 mg, 1.5 mmol) in methanol (20 ml) at room temperature for 2 h. The reaction mixture was poured into a saturated solution of ammonium chloride (100 ml) and extracted with dichloromethane (2 x 100 ml). The organic phase was evaporated to dryness and the residue was separated on silica gel column to give compound **53** (226 mg, 88%). ^{1}H-NMR ($CDCl_3$): 7.33-6.80 (m, 15H) arom, H-6; 6.11 (d, $J_{1',2'}$ = 6.4 Hz, 1H) H-1'; 5.89 (d, $J_{5,6}$ = 7.6 Hz, 1H) H-5; 5.17 (d, 1H) H-2'; 4.35 (m, 1H) H-4'; 4.04 (d, $J_{3',4'}$ = 2.7 Hz, 1H) H-3'; 3.79 (s, 3H) MMTr; 3.41 (s, 3H) OCH_3; 3.31-2.97 (m, 2H) H-5'. H-5". ^{13}C-NMR ($CDCl_3$): 134.4 (d, J_{CH} = 186.5 Hz) C-6; 110.1 (d, J_{CH} = 173.0 Hz) C-5; 89.8 (d, J_{CH} = 183.1 Hz) C-1'; 85.9 (d, J_{CH} = 169.6 Hz) C-2'; 84.8 and 84.5 (d, J_{CH} = 150.5) C-3', C-4'; 62.3 (t, J_{CH} = 142.1 Hz) C-5'; 57.8 (q, J_{CH} = 142.3) CH_3O; 55.0 (q) OCH_3 (MMTr); Ms (FAB$^-$) calc. for (M-H)$^-$ 511.1869, found 511.1880.

1-[5'-O-MMTr-2',3'-dideoxy-2',3'-(1-nitro)cyclopropano-β-D-*lyxo*-furanosyl]uracil (59). To a solution of nitromethane (10 ml) in tetrahydrofuran (10 ml) was added sodium hydride (30 mg, 80 %, 1 mmol) and stirred for 1h. The compound 12 (200 mg 0.3 mmol) was added and stirring was continued overnight at room temperture. The mixture was poured into a saturated aqueous solution of ammonium chloride and extracted with dichloromethane (2 x 50 ml). The solvent was evaporated and the residue was separated on silica gel column to give compound **59** (41 mg, 25 %). ^{1}H-NMR ($CDCl_3$): 9.27 (br, 1H) NH; 7.39-6.84 (m, 15 H) arom, H-6; 6.08 (d. $J_{1',2'}$ = 2.9 Hz, 1H) H-1'; 5.69 (d, $J_{5,6}$ = 8.3 Hz, 1H) H-5; 4.48 (m 1H) H-4'; 4.38 (t, $J_{CHNO2,2'}$ = 1.9 Hz, $J_{CHNO2,3}$ = 2.0 Hz, 1H) $CHNO_2$; 3.44 (d, $J_{4',5'}$ = 4.8 Hz, 2H) H-5', H-5"; 3.26 (dt, $J_{2',3'}$ = 8.5 Hz, 1H) H-2'; 2.85 (dt, $J_{3',4'}$ = 2.6 Hz, 1H) H-3'. ^{13}C-NMR ($CDCl_3$): 143.5 (d, J_{CH} = 185.4 Hz) C-6; 102.4 (d, J_{CH} = 180.1 Hz) C-5; 87.1 (s) MMTr; 85.4 (d, J_{CH} = 171.9 Hz) C-1'; 78.6 (d, J_{CH} = 148.2 Hz) C-4'; 62.5 (t, J_{CH} = 141.7 Hz) C-5'; 56.2 (d, J_{CH} = 193.2 Hz) CNO_2; 55.1 (q) OCH_3; 31.2 and 30.5 (d J_{CH} = 185.4 and 183.1 Hz) C-2'and C-3'; Ms (FAB$^-$) calc. for (M-H)$^-$ 540.1771, found 540.1761.

1-[2',3'-dideoxy-2',3'-(1-nitro)cyclopropane-β-D-*lyxo*-furanosyl]uracil (60). To a solution of nitromethane (10 ml) in dimethylformamide (10 ml) was added sodium hydride (36 mg, 80 %, 1.2 mmol) and stirred for 2h. Then compound **13** (120 mg, 0.3 mmol) was added and stirring was kept for overnight at room temperture. Acetic acid (2 ml) was added, the reaction mixture was evaporated to dryness and residue was separated on silica gel column to give compound **60** (15 mg, 19 %). ^{1}H-NMR ($CDCl_3$): 7.68 (d, $J_{5,6}$ = 8.3 Hz, 1H) H-6; 6.08 (d, $J_{1',2'}$ =2.7 Hz, 1H) H-1'; 5.76 (d, 1H) H-5; 4.68 (m, 1H) $CHNO_2$; 4.37 (m, 1H) H-4'; 3.88 (d, $J_{4',5'}$ = 4.1 Hz, 2H) H-5', H-5", 3.16 (m, 1H) H-2'; 2.87 (m 1H) H-3'. ^{13}C-NMR ($CDCl_3$): 139.1 (d, J_{CH} = 185.4 Hz) C-6; 101.4 (d, J_{CH} = 177.5 Hz) C-5; 85.1 (d, J_{CH} = 173.0 Hz) C-1'; 79.6 (d, 150.5 Hz) C-4'; 60.5 (t, J_{CH} = 143.7 Hz) C-5'; 55.7 (d, J_{CH} = 148.2 Hz) $CHNO_2$; 30.7 and 29.8 (d, J_{CH} = 184.3 Hz and 184.2 Hz) C-2'and C-3'; Ms (FAB$^-$) calc. for (M-H)$^-$ 268.0569, found 268.0569.

1-[5'-MMTr-3'-C,2'-O-(1-methoxycarbonyl-2-methyl)vinylene]uracil (61). A mixture of sodium hydride (27 mg, 80 %, 0.9 mmol) and methyl acetoacetate (5 ml) in dry tetrahydrofuran (15 ml) was stirred for 30 min at room temperature. It was then chilled to -10 °C and compound **12** (300 mg, 0.45 mmol) was added to this and stirring was continued overnight at the same temperature. 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 organic phase was evaporated to dryness and the residue was separated on a silica gel

column to give compound **61** (85 mg, 32 %). ^{1}H-NMR ($CDCl_3$): 8.68 (br, 1H) NH; 7.68 (d, $J_{5,6}$ = 8.3 Hz, 1H) H-6; 7.32-6.84 (m, 14H) arom; 6.07 (d, $J_{1',2'}$ = 2.9 Hz, 1H) H-1'; 5.35 (d, 1H) H-5; 5.14 (dd, $J_{2',3'}$ = 10 Hz, 1H) H-2'; 4.11 (m, 1H) H-4'; 4.02 (m, 1H) H-3'; 3.79 (s, 3H) CH_3O (MMTr); 3.55 (s, 3H) CH_3OCO; 3.50 (m, 2H) H-5', H-5"; 2.26 (s, 3H) CH_3. ^{13}C-NMR ($CDCl_3$): 140.2 (d, J_{CH} = 180.0 Hz, 102.6 (d, J_{CH} = 178.6 Hz) C-5; 92.0 (d, J_{CH} = 170.7 Hz) C-1'; 90.4 (d, J_{CH} = 160.6 Hz) C-4'; 88.1 (d, J_{CH} = 153.9 Hz) C-2'; 64.2 (t, J_{CH} = 145.5 Hz) C-5'; 55.1 (q) OCH_3; 50.8 (q, J_{CH} = 146.0 Hz) CH_3OCO; 47.8 (d, J_{CH} = 142.7 Hz) C-3'; 13.9 (q, J_{CH} = 130.3 Hz) CH_3; Ms (FAB$^-$) calc. for (M-H)$^-$ 595.2081, found 595.2081.

1-[5'-O-MMTr-2',3'-dideoxy-3'-(1,1-dimethoxydicarbonylethylene)-β-D-*glycero*-pent-2'-enofuranosyl]uracil (63) & 1-[5'-O-MMTr-2',3'-deoxy-2'-phenylseleno-3'-(1,1-dimethoxydicarbonylethylene)-β-D-*ribo*-furanosyl]uracil (64). The mixture of NaH (40.5 mg, 80 %, 1.35 mmol) and dimethyl methylmalonate (99 mg, 0.68 mmol) in dry tetrahydrofuran (20 ml) was stirred for 30 min at 0 °C. The compound **12** (300 mg, 0.45 mmol) was added after cooling to -10 °C and stirring was continued for 7 h and then overnight at room temperature. 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 organic phase was evaporated to dryness and the residue was separated on a silica gel column to give compound **63** (180 mg, 64 %) and **64** (36 mg, 10 %). Compound **63**: ^{1}H-NMR ($CDCl_3$): 7.61 (d, $J_{5,6}$ = 8.0 Hz, 1H) H-6; 7.32-6.80 (m, 14 H) arom; 7.02 (dd, $J_{1',2'}$ = 1.5 Hz, $J_{1',4'}$ 2.9 Hz, 1H) H-1'; 5.79 (t, $J_{2',3'}$ = 2.0 Hz, 1H) H-2'; 5.20 (m, 2H) H-5, H-4'; 3.79 (s, 3H) CH_3O (MMTr); 3.65 and 3.58 (2 x s, 6H) CH_3O; 3.42-3.22 (m, 2H) H-5', H-5"; 1.58 (s, 3H) CH_3. ^{13}C-NMR ($CDCl_3$):140.6 (d, J_{CH} = 182.0 Hz) C-6; 125.1 (d, J_{CH} = 174.1 Hz) C-2'; 102.9 (d, J_{CH} = 177.5 Hz) C-5; 88.4 (d, J_{CH} = 173.0 Hz) C-1'; 87.1 (s) MMTr; 85.9 (d, J_{CH} = 161.8 Hz) C-4'; 64.7 (t, J_{CH} = 144.9 Hz) C-5'; 55.1 (q) OCH_3 (MMTr); 53.1 (q, J_{CH} = 148.3 Hz) CH_3OCO; 21.2 (q, J_{CH} = 132.5 Hz) CH_3; Ms (FAB$^-$) calc. for (M-H)$^-$ 625.2186, found 625.2177. Compound **64**: ^{1}H-NMR ($CDCl_3$): 9.23 (br, 1H) NH; 7.67 (d, $J_{5,6}$ = 8.3 Hz, 1H) H-6; 7.40-6.83 (m, 19H) arom; 5.81 (d, 1H) H-5; 5.32 (d, $J_{1',2'}$ = 2.7 Hz, 1H) H-1'; 4.76 (m, 1H) H-4'; 3.78 (s, 3H) CH_3O (MMTr); 3.68 and 3.58 (2 x s; 6H) CH_3OCO; 3.53 (m, 3H) H-2', H-5', H-5"; 3.26 (d, $J_{3',4'}$ = 4.9 Hz, 1H) H-3'; 1.43 (s, 3H) CH_3. ^{13}C-NMR ($CDCl_3$): 139.5 (d, J_{CH} = 191.0 Hz) C-6; 102.4 (d, J_{CH} = 180.9 Hz) C-5; 88.2 (d, J_{CH} = 192.1 Hz) C-1'; 86.2 (s) MMTr; 81.5 (d, J_{CH} = 156.1 Hz) C-4'; 65.9 (t, J_{CH} = 142.7 Hz) C-5'; 56.4 C-2'; 55.1 (q) CH_3O (MMTr); 52.6 (d, J_{CH} = 148.3 Hz) CH_3OCO; 50.1 (d, J_{CH} = 141.5 Hz) C-3'; 16.7 (q, J_{CH} = 134.8 Hz) CH_3; Ms (FAB$^-$) calc. for (M-SePh)$^-$ 625.2186, found 625.2217.

1-[5'-O-MMTr-2',3'-dideoxy-3'-triazolo-β-D-*glycero*-pent-2'-enofuranosyl]uracil (57). The mixture of compounds **49** and **50** (88 mg 0.16 mmol) was treated with potassium t-butoxide (22.4 mg, 0.2 mmol) in dry tetrahydrofuran (20 ml) for 4 h at room temperture and the reaction mixture was poured into a saturated aqueous solution of ammonium chloride (100 ml), which was extracted with dichloromethane (2 x 100 ml) and the organic phase was evaporated to dryness. The residue was separated on silica gel column to give compound **57** (73 mg, 83%). ^{1}H-NMR ($CDCl_3$): 9.13 (br, 1H) NH; 8.32 (s, 1H) H-3 (triazole); 7.92 (s, 1H) H-5 (triazole); 7.33-6.77 (m, 16H) arom, H-6, H-1'; 6.16 (s, 1H) H-2'; 5.79 (d, $J_{5,6}$ = 8.3 Hz, 1H) H-5; 5.56 (m, 1H) H-4'; 3.78 (s, 3H) CH_3O; 3.66 (dd, $J_{4',5'}$ = 2.5 Hz, $J_{5',5"}$ = 10.6 Hz, 1H) H-5'; 3.34 (dd, $J_{4',5"}$ = 2.6 Hz,1H) H-5". ^{13}C-NMR ($CDCl_3$): 152.5 (d, J_{CH} = 211.1 Hz) C-3 (triazole); 143.5 (d, J_{CH} = 213.5 Hz) C-5 (triazole); 139.1 (d, J_{CH} = 179.7 Hz) C-6; 110.3 (d, J_{CH} = 177.4 Hz) C-2'; 103.1 (d, J_{CH} = 177.5 Hz) C-5; 89.5 (d, J_{CH} = 175.2 Hz) C-1'; 86.3 (s) MMTr; 82.9 (d, J_{CH} = 158.4 Hz) C-4'; 62.8 (t, J_{CH} = 145.5 Hz) C-5'; 55.1 (q) CH_3O; Ms (FAB$^-$) calc. for (M-H)$^-$ 548.1934, found 548.1909.

1-[2',3'-dideoxy-3'-triazolo-β-D-*glycero*-pent-2'-enofuranosyl]uracil (58). The mixture of compounds **51** and **52** (55 mg 0.2 mmol) was treated with potassium t-butoxide (28 mg, 0.25 mmol) in dry dimethylformamide (20 ml) for 4 h at room temperture and then acetic acid (2 ml) was added. The reaction mixture was evaporated, and coevaporated with toluene (3 x 10 ml) to dryness and the residue was separated on silica gel column to give compound **58** (30 mg, 54 %). ^{1}H-NMR ($CDCl_3$ + CD_3OD): 8.75 (s, 1H) H-3 (triazole); 8.08 (s, 1H) H-5 (triazole); 7.37 (d, $J_{5,6}$ = 8.2 Hz, 1H) H-6; 7.16 (dd, $J_{1',2'}$ = 1.7 Hz, $J_{1',4'}$ 5.2 Hz, 1H) H-1'; 6.20 (t, $J_{2',4'}$ = 1.7 Hz, 1H) H-2'; 5.76 (d, 1H) H-5; 5.54 (m, 1H) H-4'; 3.97 (d, $J_{4',5'}$ = 2.5 Hz, 2H) H-5', H-5". ^{13}C-NMR ($CDCl_3$ + CD_3OD): 152.0 (d, J_{CH} = 211.1 Hz) C-3 (triazole); 143.2 (d, J_{CH} = 218.6 Hz) C-5 (triazole); 139.5 (d, J_{CH} = 179.7 Hz) C-6; 139.0 (s) C-3'; 110.4 (d, J_{CH} = 179.7 Hz) C-2'; 102.8 (d, J_{CH} = 175.2 Hz) C-5; 89.1 (d, J_{CH} = 183.1 Hz) C-1'; 84.1 (d, J_{CH} = 150.6 Hz) C-4'; 61.8 (t, J_{CH} = 144.3 Hz) C-5; Ms (FAB$^-$) calc. for (M-H)$^-$ 276.0733, found 276.0728.

General procedure for the removal of 5'-O-MMTr group from compound **14, 15, 53, 61** and **63**. Compound **53, 61** or **63**. was treated with 80 % aqueous acetic acid (50 ml / mmol) at room temperature overnight. Acetic acid was removed by evaporation and coevaporation with toluene, and the residue was separated on a silica gel column or preparative TLC to give compounds **54, 62** and **65**, respectively. The inseparable mixture of

compounds **14** and **15** was deprotected directly with 80 % aqueous acetic acid. The deprotected mixture was than separated on a silica gel column to give pure **16** (24 %), and compound **17** was isolated in 37 % yield in 95 % purity, along with a mixture of **16** and **17** (21 %). **Compound 16** (24 %), ^{1}H-NMR (DMSO): 7.89 (d, $J_{5,6}$ = 8.0 Hz, 1H) H-6; 5.98 (s, 1H) H-1'; 5.53 (d, 1H) H-5; 4.30 (t, $J_{4',5'}$ = 4.8 Hz, 1H) H-4'; 3.87 (d, $J_{2',3'}$= 4.9 Hz, 1H) H-2', 3.75 (d, 1H) H-3', 3.63 (d, 2H) H-5', H-5"; ^{13}C-NMR ($CDCl_3$ + CD_3OD): 141.8 (d, J_{CH} = 179.7 Hz) C-6; 101.1 (d, J_{CH} = 170.8 Hz) C-5; 88.5 (d, J_{CH} = 168.6 Hz) C-1'; 85.8 (d, J_{CH} = 151.7 Hz) C-4'; 62.9 (t, J_{CH} = 142.5 Hz) C-5'; 41.8 and 40.5 (d, J_{CH} = 182.2 Hz and 180.6 Hz) C-2', C-3'; Ms (FAB$^-$) calc. for (M-H)$^-$ 241.0283, found 241.0272. **Compound 17** (37 %), ^{1}H-NMR ($CDCl_3$ + CD_3OD): 7.49 (d, $J_{5,6}$ = 8.2 Hz, 1H) H-6; 6.11 (d, $J_{1',2'}$= 2.3 Hz, 1H) H-1'; 5.55 (d, 1H) H-5; 4.28 (dt, $J_{3',4'}$= 2.5 Hz, $J_{4',5'}$ = 5.7 Hz, $J_{4',5"}$= 6.2 Hz, 1H) H-4'; 3.74 (dd, $J_{2',3'}$= 5.0 Hz, 1H) H-2', 3.67 (dd, Jgem = 11.3 Hz, 1H) H-5', 3.65 (dd, 1H) H-5", 3.58 (dd, 1H) H-3'; ^{13}C-NMR ($CDCl_3$ + CD_3OD): 140.1 (d, J_{CH} = 191.0 Hz) C-6; 100.7 (d, J_{CH} = 176.3 Hz) C-5; 82.7 (d, J_{CH} = 168.5 Hz) C-1'; 77.8 (d, J_{CH} = 152.8 Hz) C-4'; 62.8 (t, J_{CH} = 142.1 Hz) C-5'; 40.1 and 39.2 (d, J_{CH} = 188.8 Hz and 187.6 Hz) C-2', C-3'; Ms (FAB$^-$) calc. for (M-H)$^-$ 241.0283, found 241.0284. **Compound 54** (86 %), ^{1}H-NMR ($CDCl_3$ + CD_3OD): 7.66 (d, $J_{5,6}$ = 7.3 Hz, 1H) H-6; 6.34 (d, $J_{1',2'}$ = 6.1 Hz, 1H) H-1'; 6.07 (d, 1H) H-5; 5.38 (d, 1H) H-2'; 4.35 (m, 1H) H-4'; 4.23 (d, $J_{3',4'}$ = 1.9 Hz, 1H) H-3'; 3.53 (d, $J_{4',5'}$ = 6.0 Hz, 2H) H-5', H-5"; 3.49 (s, 3H) CH_3O. ^{13}C-NMR ($CDCl_3$ + CD_3OD): 136.0 (d, J_{CH} = 186.5Hz) C-6; 108.6 (d, J_{CH} =176.3 Hz) C-5; 90.3 (d, J_{CH} = 178.7 Hz) C-1'; 87.2 (d, J_{CH} = 150.5 Hz) C-4'; 86.2 (d, J_{CH} = 167.3 Hz) C-2'; 84.8 (d, J_{CH} = 141.5 Hz) C-3'; 61.0 (t, J_{CH} = 141.6Hz) C-5'; 56.9 (q, J_{CH} = 147.1 Hz) CH_3O; Ms (FAB$^-$) calc. for (M-H)$^-$ 239.0668, found 239.0664. **Compound 62** (95 %), ^{1}H-NMR (DMSO-d_6): 7.95 (d, $J_{5,6}$ = 8.1 Hz, 1H) H-6; 6.02 (d, $J_{1',2'}$ = 3.4 Hz, 1H) H-1'; 5.81 (d, 1H) H-5; 5.43 (dd, $J_{2',3'}$ = 10.0 Hz, 1H) H-2'; 5.16 (br, 1H) OH; 4.18 (m, 1H) H-4'; 3.90 (m, 1H) H-3'; 3.77 (s, 3H) CH_3OCO; 3.51 (m, 2H) H-5', H-5"; 2.31 (s, 3H) CH_3. ^{13}C-NMR (DMSO-d_6): 141.6 (d, J_{CH} = 184.2 Hz) C-6; 102.1 (d, J_{CH} = 176.4 Hz) C-5; 91.5 (d, J_{CH} = 162.9 Hz) C-1'; 89.3 (d, J_{CH} = 164.0 Hz) C-4'; 89.0 (d, J_{CH} = 150.5 Hz) C-2'; 62.5 (t, J_{CH} = 144.3 Hz) C-5'; 51.1 (q, J_{CH} = 147.2 Hz) OCH_3; 47.2 (d, J_{CH} = 144.9 Hz) C-3'; 14.0 (q, J_{CH} = 129.2 Hz) CH_3; Ms (FAB$^-$) calc. for (M-H)$^-$ 323.0879, found 323.0882. **Compound 65** (89 %), ^{1}H-NMR ($CDCl_3$): 8.05 (d, $J_{5,6}$ = 8.1 Hz, 1H) H-6; 6.92 (dd, $J_{1',2'}$ = 1.5 Hz, $J_{1',4'}$ 3.2 Hz, 1H) H-1'; 5.94 (t, $J_{2',4'}$ = 1.5 Hz, 1H) H-2'; 5.72 (d, 1H) H-5; 4.96 (m, 1H) H-4'; 3.82 (m, 8H) 2 x CH_3O, H-5', H-5"; 1.77 (s, 3H) CH_3. ^{13}C-NMR ($CDCl_3$): 143.2 (s) C-3'; 140.9 (d, J_{CH} = 183.1 Hz) C-6; 127.1 (d, J_{CH} = 175.2 Hz) C-2'; 102.1 (d, J_{CH} = 176.4 Hz) C-5; 88.4 (d, J_{CH} = 182.0 Hz) C-1'; 87.6 (d, J_{CH} = 151.7 Hz) C-4'; 62.0 (t, J_{CH} = 143.2 Hz) C-5'; 54.9 (s) α-C (malonate); 53.5 and 53.3 (q, J_{CH} = 148.3 Hz) CH_3OCO; 21.4 (q, J_{CH} = 132.6 Hz) CH_3; Ms (FAB$^-$) calc. for (M-H)$^-$ 353.0985, found 353.0993.

General procedure for hydrolysis of 2,2'-O-anhydro compounds. Compound **20**, **21**, **24**, **25**, **28**, **35**, **37**, **40**, **41**, **43**, **45**, **47**, **52** or **54** was treated with 0.1 N aqueous solution of sulfuric acid at 90 °C until all starting material was consumed (~ 1 - 2 h), aqueous ammonia (30 %, 10 ml) was added after cooling to room temperature and the reaction mixtures were evaporated to dryness. The residue was separated on a silica gel column or preparative TLC to give compound **30**, **31**, **32**, **33**, **34**, **66**, **67**, **74**, **68**, **69**, **70**, **71**, **72** or **73**, respectively. **Compound 30** (56 %), ^{1}H-NMR ($CDCl_3$ + CD_3OD): 7.92 (d, $J_{5,6}$ = 8.0 Hz, 1H) H-6; 6.16 (d, $J_{1',2'}$ = 4.4 Hz, 1H) H-1'; 5.68 (d, 1H) H-5; 4.29 (t, $J_{2',3'}$ = 4.0 Hz, 1H) H-2'; 4.01-3.72 (m, 3H) H-4', H-5', H-5"; 3.28 (dd, $J_{3',4'}$ = 6.7 Hz, 1H) H-3'; 2.71 (q, J = 7.4 Hz, 2H) SCH_2; 1.31 (t, 3H) CH_3. ^{13}C-NMR ($CDCl_3$ + CD_3OD): 142.0 (d, J_{CH} = 184.2 Hz) C-6; 100.0 (d, J_{CH} = 176.3 Hz) C-5; 85.6 (d, J_{CH} = 176.2 Hz) C-1'; 82.8 (d, J_{CH} = 149.4 Hz) C-4'; 75.6 (d, J_{CH} = 153.9 Hz) C-2'; 60.9 (t, J_{CH} = 142.7 Hz) C-5'; 46.3 (d, J_{CH} = 156.0 Hz) C-3'; 25.4 (t, J_{CH} = 141.0 Hz) SCH_2; 14.0 (q, J_{CH} = 126.2 Hz) CH_3; Ms (FAB$^-$) calc. for (M-H)$^-$ 287.0702, found 287.0717. **Compound 31** (52 %), ^{1}H-NMR ($CDCl_3$ + CD_3OD): 7.86 (d, $J_{5,6}$ = 8.1 Hz, 1H) H-6; 5.98 (d, $J_{1',2'}$ = 2.9 Hz, 1H) H-1'; 5.67 (d, 1H) H-5; 4.50 (dt, $J_{3',4'}$ = 9.1 Hz, $J_{4',5'}$ = 2.5 Hz, 1H) H-4'; 4.25 (dd, $J_{2',3'}$ = 4.6 Hz, 1H) H-2'; 3.84-3.69 (m, 3H) H-3', H-5'; H-5"; 2.62 (q, J = 7.3 Hz, 2H) SCH_2; 1.31 (t, 3H) CH_2CH_3.. ^{13}C-NMR ($CDCl_3$ + CD_3OD): 141.9 (d, J_{CH} = 187.7 Hz) C-6; 100.1 (d, J_{CH} = 176.3 Hz) C-5; 86.7 (d, J_{CH} = 170.7 Hz) C-1'; 80.6 (d, J_{CH} = 147.2 Hz) C-4'; 69.5 (d, J_{CH} = 154.0 Hz) C-2'; 60.7 (t, J_{CH} = 144.9 Hz) C-5'; 47.7 (t, J_{CH} = 142.7 Hz) C-3'; 26.4 (q, J_{CH} = 139.8 Hz) SCH_2; 14.4 (q, J_{CH} = 127.3 Hz) CH_3; Ms (FAB$^-$) calc. for (M-H)$^-$ 287.0702, found 287.0806. **Compound 32** (62%), ^{1}H-NMR ($CDCl_3$ + CD_3OD): 7.91 (d, $J_{5,6}$ = 8.3 Hz, 1H) H-6; 7.44-7.27 (m, 5H) arom; 6.19 (d, $J_{1',2'}$ = 4.4 Hz, 1H) H-1'; 5.67 (d, 1H) H-5; 4.28 (m, 1H) H-2'; 4.05-3.84 (m, 3H) H-4', H-5', H-5"; 3.70 (dd, $J_{2',3'}$ = 4.1 Hz, $J_{3',4'}$ = 5.5 Hz, 1H) H-3'. ^{13}C-NMR ($CDCl_3$ + CD_3OD): 142.0 (d, J_{CH} = 184.3 Hz) C-6; 100.2 (d, J_{CH} = 179.7 Hz) C-5; 85.9 (d, J_{CH} = 169.7 Hz) C-1'; 82.4 (d, J_{CH} = 147.2 Hz) C-4'; 74.5 (d, J_{CH} = 159.5 Hz) C-2'; 61.4 (t, J_{CH} = 142.7 Hz) C-5'; 51.2 (d, J_{CH} = 152.7 Hz) C-3'; Ms (FAB$^-$) calc. for (M-H)$^-$

335.0702, found 335.0708. **Compound 33** (59%), ^{1}H-NMR ($CDCl_3$ + CD_3OD): 7.91 (d, $J_{5,6}$ = 8.3 Hz, 1H) H-6; 7.45-7.27 (m, 5H) arom; 5.98 (d, $J_{1',2'}$ = 2.9 Hz, 1H) H-1'; 5.69 (d, 1H) H-5; 4.61 (dt, $J_{3',4'}$ = 8.8 Hz, $J_{4',5'}$ = 2.7 Hz, 1H) H-4'; 4.37-4.11 (m, 2H) H-2', H-3'; 3.92 (d, 2H) H-5', H-5". ^{13}C-NMR ($CDCl_3$ + CD_3OD): 141.7 (d, J_{CH} = 184.2 Hz) C-6; 99.8 (d, J_{CH} = 178.6 Hz) C-5; 86.4 (d, J_{CH} = 184.0 Hz) C-1'; 80.3 (d, J_{CH} = 156.1 Hz) C-4'; 69.8 (d, J_{CH} = 159.5 Hz) C-2'; 60.49 (t, J_{CH} = 142.0 Hz) C-5'; 52.3 (d, J_{CH} = 147.2 Hz) C-3'; Ms (FAB$^-$) calc. for (M-H)$^-$ 335.0702, found 335.0679. **Compound 34** (42%), ^{1}H-NMR ($CDCl_3$ + CD_3OD): 8.21 (d, $J_{5,6}$ = 8.3 Hz, 1H) H-6; 5.94 (d, $J_{1',2'}$ = 0.7 Hz, 1H) H-1'; 5.59 (d, 1H) H-5; 4.82 (dd, $J_{2',3'}$ = 5.1 Hz, 1H) H-2'; 4.09 (m, 1H) H-4'; 4.00 (dd, $J_{4',5'}$ = 1.8 Hz, $J_{5',5"}$ = 12.3 Hz, 1H) H-5'; 3.78 (dd, $J_{4',5"}$ = 2.2 Hz, 1H) H-5"; 3.71 (dd, $J_{3',4'}$ = 9.8 Hz, 1H) H-3'; 3.65 (s, 3H) CH_3O; 3.36 (2 x d, J = 15.2 Hz, 2H) SCH_2; Ms (FAB$^-$) calc. for (M-H)$^-$ 331.0600, found 331.0601. **Compound 66** (42%), ^{1}H-NMR (D_2O): 7.81 (d, $J_{5,6}$ = 8.2 Hz, 1H) H-6; 6.14 (d, $J_{1',2'}$ = 5.2 Hz, 1H) H-1'; 5.81 (d, 1H) H-5; 4.41 (t, $J_{2',3'}$ = 5.9 Hz, 1H) H-2'; 3.86 (m 3H) H-4', H-5', H-5"; 3.32 (m, 1H) H-3'. ^{13}C-NMR (D_2O): 143.3 (d, J_{CH} = 191.0 Hz) C-6; 101.6 (d, J_{CH} = 178.6 Hz) C-5; 85.3 (d, J_{CH} = 171.9 Hz) C-1'; 82.1 (d, J_{CH} = 151.6 Hz) C-4'; 75.8 (d, J_{CH} = 150.6 Hz) C-2'; 60.7 (t, J_{CH} = 143.8 Hz) C-5'; 56.3 (d, J_{CH} = 145.0 Hz) C-3'; Ms (FAB$^-$) calc. for (M-H)$^-$ 242.0777, found 242.0779. **Compound 67** (38%), ^{1}H-NMR ($CDCl_3$ + CD_3OD): 7.86 (d, $J_{5,6}$ = 8.3 Hz, 1H) H-6; 6.13 (d, $J_{1',2'}$ = 4.9 Hz, 1H) H-1'; 5.70 (d, 1H) H-5; 4.41 (dd, $J_{2',3'}$ = 3.6 Hz, 1H) H-2'; 3.99-3.88 (m, 3H) H-4', H-5', H-5"; 3.29 (m, 1H) H-3'; 2.60 (s, 3H) NCH_3. ^{13}C-NMR ($CDCl_3$ + CD_3OD): 142.0 (d, J_{CH} = 186.5 Hz) C-6; 100.0 (d, J_{CH} = 178.6 Hz) C-5; 85.4 (d, J_{CH} = 167.4 Hz) C-1'; 80.9 (d, J_{CH} = 144.9 Hz) C-4'; 72.8 (d, J_{CH} = 149.4 Hz) C-2'; 65.4 (d, J_{CH} = 14.9 Hz) C-3'; 60.9 (t, J_{CH} = 142.7 Hz) C-5'; 32.6 (q, J_{CH} = 136.7 Hz) NCH_3; Ms (FAB$^-$) calc. for (M-H)$^-$ 256.0934, found 256.0935. **Compound 68** (46 %), ^{1}H-NMR ($CDCl_3$ + CD_3OD): 7.84 (d, $J_{5,6}$ = 8.1 Hz, 1H) H-6; 5.98 (d, $J_{1',2'}$ = 4.2 Hz) H-1'; 5.69 (d, 1H) H-5; 4.47 (dd, $J_{2',3'}$ = 2.4 Hz, 1H) H-2'; 4.12(m, 1H) H-4'; 3.96 (dd, $J_{4',5'}$ =2.7 Hz, $J_{5',5"}$ = 11.7 Hz, 1H) H-5'; 3.72 (dd, $J_{4',5"}$ = 3.8 Hz, 1H) H-5"; 3.06 (dd, $J_{3',4'}$ = 4.9 Hz, 1H) H-3'. ^{13}C-NMR (D_2O): 143.5 (d, J_{CH} = 187.6 Hz) C-6; 101.2 (d, J_{CH} = 180.8 Hz) C-5; 86.2 (d, J_{CH} = 168.5 Hz) C-1'; 79.5 (d, J_{CH} = 147.1 Hz) C-4'; 71.8 (d, J_{CH} = 147.1 Hz) C-2'; 70.9 (d, J_{CH} = 150.5 Hz) C-3'; 62.5 (t, J_{CH} = 144.4 Hz) C-5'; 41.9 (q, J_{CH} = 135.2 Hz) NCH_3; Ms (FAB$^-$) calc. for (M-H)$^-$ 270.1090, found 270.1108. **Compound 69**: (52 %), ^{1}H-NMR ($CDCl_3$ + CD_3OD): 7.84 (d, $J_{5,6}$ = 8.0 Hz, 1H) H-6; 5.97 (d, $J_{1',2'}$ = 4.1 Hz, 1H) H-1'; 5.67 (d, 1H) H-5; 4.48 (dd, $J_{2',3'}$ = 2.1 Hz, 1H) H-2'; 4.15 (m, 1H) H-4'; 3.93 (dd, $J_{4',5'}$ = 3.0 Hz, $J_{5',5"}$ = 11.9 Hz, 1H) H-5'; 3.72 (dd, $J_{4',5"}$ = 4.3 Hz, 1H) H-5"; 3.07 (dd, $J_{3',4'}$ = 4.8 Hz, 1H) H-3'; 2.66 (m, 4H) H-2 and H-6 (piperidine); 1.57 (m, 6H) H-3, H-4 and H-5 (piperidine). ^{13}C-NMR ($CDCl_3$ + CD_3OD): 142.1 (d, J_{CH} = 189.8 Hz) C-6; 99.5 (d, J_{CH} = 176.4 Hz) C-5; 86.7 (d, J_{CH} = 176.3 Hz) C-1'; 79.7 (d, J_{CH} = 143.8 Hz) C-4'; 73.3 (d, J_{CH} = 152.8 Hz) C-2'; 69.5 (d, J_{CH} = 156.2 Hz) C-3'; 62.5 (t, J_{CH} = 143.2 Hz) C-5'; 50.9 (t, J_{CH} = 131.5 Hz) C-2 and C-6 (piperidine); 25.2 (t, J_{CH} = 128.1 Hz) C-3 and C-5 (piperidine); 23.4 (t, J_{CH} = 128.1 Hz) C-4 (piperidine); Ms (FAB$^-$) calc. for (M-H)$^-$ 310.1403, found 310.1412. **Compound 70** (49 %), ^{1}H-NMR ($CDCl_3$ + CD_3OD): 7.84 (d, $J_{5,6}$ = 8.1 Hz, 1H) H-6; 6.10 (d, $J_{1',2'}$ = 3.6 Hz, 1H) H-1'; 5.68 (d, 1H) H-5; 4.42 (dd, 1H) H-2'; 4.17 (m, 1H) H-4'; 3.84 (t, 2H) H-5', H-5"; 2.92 (dd, $J_{3',4'}$ =4.3 Hz, 1H) H-3'; 2.72 (m, 4H) H-2 and H-5 (pirrolidine); 1.86 (m, 4H) H-3 and H-4 (pirrolidine). ^{13}C-NMR ($CDCl_3$ + CD_3OD): 142.1 (d, J_{CH} = 186.5 Hz) C-6; 99.5 (d, J_{CH} = 178.6 Hz) C-5; 85.7 (d, J_{CH} = 166.2 Hz) C-1'; 81.1 (d, J_{CH} = 147.2 Hz) C-4'; 72.4 (d, J_{CH} = 150.5 Hz) C-2'; 71.4 (d, J_{CH} = 148.1 Hz) C-3'; 61.8 (t, J_{CH} = 140.5 Hz) C-5'; 51.5 (t, J_{CH} = 135.9 Hz) C-2 and C-5 (pirrolidine); 22.2 (t, J_{CH} = 133.1 Hz) C-3 and C-4 (pirrolidine);Ms (FAB$^-$) calc. for (M-H)$^-$ 196.1247, found 296.1247. **Compound 71** (61 %), ^{1}H-NMR ($CDCl_3$ + CD_3OD): 7.87 (d, $J_{5,6}$ = 8.1 Hz, 1H) H-6; 5.98 (d, $J_{1',2'}$ = 4.4 Hz, 1H) H-1'; 5.67 (d, 1H) H-5; 4.49 (dd, $J_{2',3'}$ = 3.1 Hz, 1H) H-2'; 4.08 (m, 1H) H-4'; 3.86-3.69 (m, 6H) $O(CH_2)_2$ (morpholine), H-5', H-5"; 2.99 (dd, $J_{3',4'}$ = 5.8 Hz, 1H) H-3'; 2.68 (m, 4H) $N(CH_2)_2$ (morpholine). ^{13}C-NMR (D_2O): 144.3 (d, J_{CH} = 185.3 Hz) C-6; 102.0 (d, J_{CH} = 177.5 Hz) C-5; 87.0 (d, J_{CH} = 169.6 Hz) C-1'; 80.1 (d, J_{CH} = 148.3 Hz) C-4'; 72.9 (d, J_{CH} = 156.2 Hz) C-2'; 72.2 (d, J_{CH} = 156.2 Hz) C-3'; 67.1 (t, J_{CH} = 145.4 Hz) $O(CH_2)_2$ (morpholine); 63.4 (t, J_{CH} = 132.5 Hz) C-5'; 51.6 (t, J_{CH} = 134.8 Hz) $N(CH_2)_2$ (morpholine); Ms (FAB$^-$) calc. for (M-H)$^-$ 312.1196, found 312.1207. **Compound 72** (54 %), ^{1}H-NMR ($CDCl_3$ + CD_3OD): 8.60 (s, 1H) H-3 (triazole); 7.98 (s, 1H) H-5 (triazole); 7.74 (d, $J_{5,6}$ = 8.0 Hz, 1H) H-6; 6.30 (d, $J_{1',2'}$ = 3.4 Hz, 1H) H-1'; 5.71 (d, 1H) H-5; 5.30 (dd, $J_{2',3'}$ = 4.4 Hz, $J_{3',4'}$ = 9.9 Hz, 1H) H-3'; 4.90-4.60 (m, 2H) H-2', H-4'; 3.95 (dd, $J_{4',5'}$ = 2.3 Hz, $J_{5',5"}$ = 11.8 Hz, 1H) H-5'; 3.60 (dd, $J_{4',5"}$ = 3.1 Hz, 1H) H-5". ^{13}C-NMR ($CDCl_3$ + CD_3OD): 149.8 (d, J_{CH} = 208.8 Hz) C-3 (triazole) 143.4 (d, J_{CH} = 210.6 Hz) C-5 (triazole); 141.8 (d, J_{CH} = 184.2 Hz) C-6; 99.6 (d, J_{CH} = 176.4 Hz) C-5; 86.5 (d, J_{CH} = 168.5 Hz) C-4; 80.2 (d, J_{CH} = 153.9 Hz) C-4'; 69.7 (d, J_{CH} = 156.1 Hz) C-2'; 60.3 (d, J_{CH} = 143.8 Hz) C-3'; 59.6 (d, J_{CH} = 143.8 Hz) C-5'; Ms (FAB$^-$) calc. for (M-H)$^-$ 294.0839, found 294.0848. **Compound 73** (81 %), ^{1}H-NMR ($CDCl_3$ + CD_3OD): 7.72 (d, $J_{5,6}$ = 8.1 Hz, 1H) H-6; 6.06 (d, $J_{1',2'}$ = 3.8 Hz, 1H) H-1'; 5.67 (d,

1H) H-5; 4.28 (dd, $J_{2',3'}$ = 1.7 Hz, 1H) H-2'; 4.05 (m, 1H) H-4'; 3.83 (m, 3H) H-3', H-5', H-5"; 3.47 (s, 3H) OCH_3. ^{13}C-NMR ($CDCl_3$ + CD_3OD): 142.1 (d, J_{CH} = 185.3 Hz) C-6; 99.7 (d, J_{CH} = 176.3 Hz) C-5; 86.1 (d, J_{CH} = 165.1 Hz) C-1'; 85.9 (d, J_{CH} = 153.2 Hz) C-3'; 82.8 (d, J_{CH} = 148.3 Hz) C-4'; 71.8 (d, J_{CH} = 153.9 Hz) C-2'; 61.2 (t, J_{CH} = 142.7 Hz) C-5'; 56.7 (q, J_{CH} =143.4 Hz) OCH_3; Ms (FAB$^-$) calc. for (M-H)$^-$ 257.0774, found 257.0784. **Compound 74** (43%), ^{1}H-NMR ($CDCl_3$ + CD_3OD): 7.92 (d, $J_{5,6}$ = 8.3 Hz, 1H) H-6; 5.98 (d, J_{CH} = 3.2 Hz, 1H) H-1'; 5.69 (d, 1H) H-5; 4.41 (dt, $J_{3',4'}$ = 8.3 Hz, $J_{4',5'}$ = 2.4 Hz, 1H) H-4'; 4.24 (dd, $J_{2',3'}$ = 4.2 Hz, 1H) H-2'; 3.86 (d, 2H) H-5', H-5"; 2.99 (dd, 1H) H-3'; Ms (FAB$^-$) calc. for (M-H)$^-$ 270.1090, found 270.1090.

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