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INTRAMOLECULAR CYCLIZATION-TRAPPING OF CARBON RADICALS BY OLEFINS AS MEANS TO FUNCTIONALIZE 2′- AND 3′-CARBONS IN β-D-NUCLEOSIDES

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Summary : *Intramolecular free-radical addition-cyclization reactions of 1-(5′-O-(MMTr)-3′-deoxy-3′-phenylseleno-2′-O-allyl- or 2′-O-alkynyl-β-D-arabinofuranosyl)uracils* ***6a - 6d****, 1-(5′-O-(MMTr)-2′-deoxy-2′-phenylseleno-3′-O-allyl- or 3′-O-alkynyl-β-D-xylofuranosyl)uracils* ***10 - 10d****, 1-(5′-O-(MMTr)-2′-O-allyl-3′-O-phenoxythiocarbonyl-β-D-arabinofuranosyl)uracil* ***25*** *and 1-(5′-O-(MMTr)-3′-O-allyl-2′-O-phenoxythio carbonyl-β-D-xylofuranosyl)uracil* ***28*** *were found to be diastereospecific, and gave pure [3.3.0]-β-fused-bis-furano products such as 1-(3′-deoxy-3′-C, 2′-O-((1-alkyl)ethylene)-β-D-lyxofuranosyl)uracils* ***7a - 7d****, 1-(2′-deoxy-2′-C, 3′-O-((1-alkyl) ethylene)-β-D-lyxofuranosyl)uracils* ***11a - 11d****, respectively, in 65 - 92 % yields. On the other hand, 5′-O-(MMTr)-2′-deoxy-2′-phenylseleno-3′-O-allyl- or 3′-O-alkynyl-uridines* ***14a - 14d****, 1-(5′-O-(MMTr)-3′-deoxy-3′-phenylseleno-2′-O-allyl-β-D-xylofuranosyl)uracil* ***20a****, 5′-O-(MMTr)-3′-O-phen oxythiocarbonyl-2′-O-allyl-uridine* ***20b*** *gave diastereomeric mixture of [3.3.0]-α-fused-bis-furano products such as 2′-deoxy-2′-C, 3′-O-((1-alkyl)ethylene)uridines* ***15a - 15d*** *and 3′-deoxy-3′-C, 2′-O-((1-alkyl)ethylene)uridine* ***21****. The 5′-O-MMTr groups from* ***7a - 7d, 11a - 11d,15a - 15d,*** *and* ***21*** *were then removed by a brief acid treatment to give* ***8a - 8d, 12a - 12d, 16a - 16d,*** *and* ***22*** *in 80 - 90% yields.*

Human Immunodeficiency Virus type 1 (HIV-1) and type 2 (HIV-2) target themselves to the human immunological system causing highly lethal Acquired Immune Deficiency Syndrome (AIDS) including several opportunistic infections causing death to the HIV-infected patients. In recent years several 2′,3′-dideoxy- and 2′,3′-didehydro-2′,3′-dideoxy-β-D-nucleosides have been found to be extremely potent antiviral agents against HIV. These include 3′-azidothymidine (AZT)[1], 3′-azido-2′-deoxy-uridine (AZDU)[2,3], 2′,3′-dideoxyadenosine (DDA)[4], N^6-methyl-DDA[9], N^6-methyl-2′-fluoro-ara-DDA[9], 2′,3′-dideoxycytidine (DDC)[4], 2′,3′-dideoxyinosine (DDI)[4], 2′,3′-didehydro-2′,3′-dideoxythymidine (D4T)[5-8], 3′-fluorothymidine[9] etc. 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, which have potentials to suppress the HIV-reverse transcriptase promoted chain termination of the cDNA synthesis on the viral RNA template.

Untill recently, synthetic methodologies to prepare 2′- or 3′-substituted nucleosides were restricted to direct nucleophilic (S_N2) displacement[11-18], or nucleophilic addition to appropriately protected 2′- or 3′-keto nucleosides[19-28], or procedures involving rearrangements[29-39]. The use of the 2′,3′-double bond of a β-D-

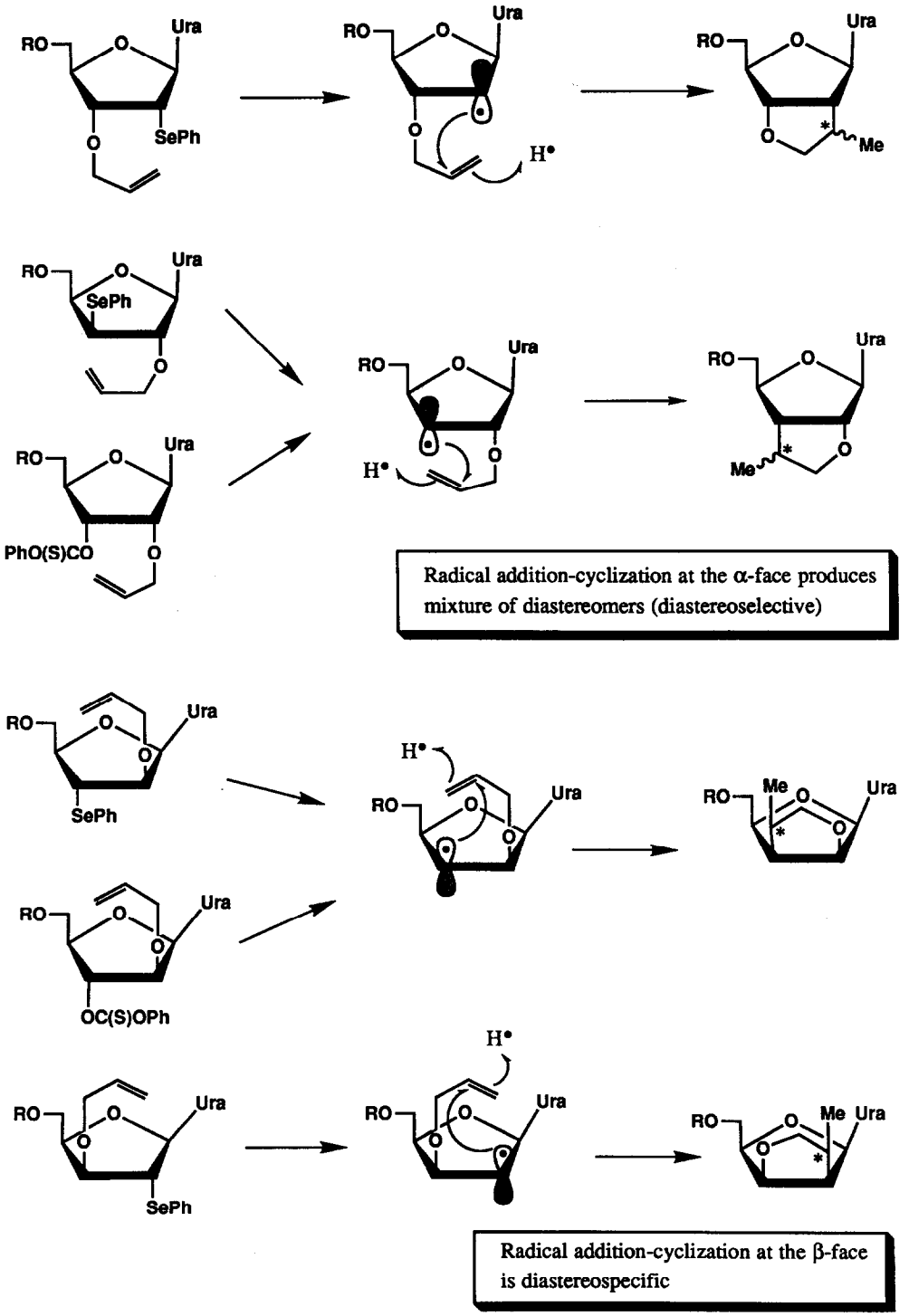
nucleoside as a substrate for electrophilic addition reactions for functionalization of the 2′ and / or 3′ carbons has been demonstrated first by us[35] through preparation of various 2′ / 3′-β-chlorosulfide analogs of nucleosides. Reversal of the polarity of the 2′,3′-double bond in a β-D-nucleoside by a 3′-electron-withdrawing substituent such as 5′-O-protected-2′,3′-ene-3′-sulfone[40] or 2′,3′-ene-3′-nitrile[41] derivatives allowed us to demonstrate unique Michael-type addition reactions to functionalize the 2′- and 3′-carbons in various manner with sulfur, nitrogen, oxygen and carbon nucleophiles. Recently, we have also shown that 2′,3′-ene-3′-phenylselenonyl[42-44] and 2′,3′-ene-2′-phenylselenonyl[45] nucleosides act as substrates for Michael addition reactions. This allows functionalization of both 2′- and 3′-carbons of nucleosides by double nucleophilic attack [synthetic equivalents of the dication: CH_2^+ - CH_2^+] by ammonia and primary amines and carbon-nucleophiles giving access to various 2′,3′-α-fused cyclic nucleosides[42-44] 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. Further studies on 2′,3′-ene-3′-phenylselenones of uridine have shown that they are indeed useful synthon to produce a variety of 2′,3′-dideoxy-2′,3′-ene-2′-substituted-nucleosides, they also act as reactive dienophile in Diels-Alder or 1,3-cycloaddition reactions giving access to various 2′,3′-dideoxy-2′,3′-fused-β-D-nucleosides[44].

We have been subsequently interested to employ free-radical methodologies for modifications at C-2′ and C-3′ of β-D-nucleosides. The generation and subsequent intermolecular reaction of acyl radicals with alkenes has been pioneered by Kharasch[46] which is recognized as a potentially useful method of carbon-carbon bond formation[47-48]. Recently described intramolecular radical cyclization-trapping methodologies allow in a single step to add two differentiated carbon-functional appendages which results into formation of two new carbon-carbon bonds with virtually complete regio- and stereochemical control[49-51]. The factors affecting the rate of intramolecular cyclization and the stereochemical outcome of substituted hexenyl radicals are well understood[52,53]. The success of a radical reaction as a synthetic tool is dependent on the controlled generation of the radical itself[54]. It is well recognized[55-57] that the success of free-radical reactions for synthetic application requires that the radical is generated at a specific site, and the radical has sufficient lifetime to undergo chemical reaction to give the desired stable products. Many free radical precursors[55-57] are used in the tin hydride methodologies, amongst which some of the most reactive ones are: I, Br, SePh, xanthate esters and tertiary nitro groups. Reactions involving intermolecular carbon-carbon bond formation have been reported in order to functionalize the 3′- and 5′-carbons of nucleosides[58-62]. Intramolecular cyclization of $C^{5'}$ and C^6 in pyrimidine and $C^{5'}$ and C^8 in purine nucleosides have been also reported[63-65].

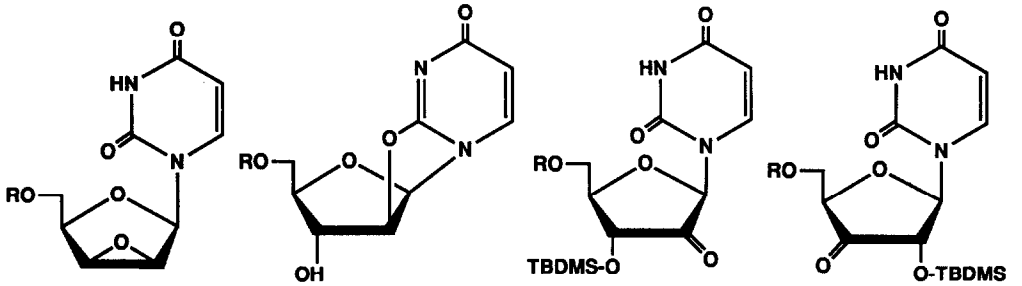
We herein show, for the first time, the scope of intramolecular free-radical trapping reactions as means to functionalize both 2′,3′-carbons of β-D-nucleoside (Scheme 1) and demonstrate the applicability of the methodology for preparation of several *new types* of 2′,3′-α-fused-[3.3.0]- and 2′,3′-β-fused-[3.3.0]-furano-nucleosides **7a-7d**, **11a-11d**, **15a-15d** & **21**, and their 5′-hydroxy derivatives **8a-8d**, **12a-12d**, **16a-16d** & **22** which were not hithertofore available by any known procedures.

Preparation of Free-radical precursors. 1-(5′-O-(4-monomethoxytrityl) [MMTr]-3′-deoxy-3′-phenylseleno-β-D-arabinofuranosyl)uracil **5** and 1-(5′-O-(MMTr)-2′-deoxy-2′-phenylseleno-β-D-xylofuranosyl)uracil **9** were prepared in 55% and 26% yields, respectively, by the nucleophilic attack of the $PhSe^-$ ion on 1-(5′-O-(MMTr)-2′,3′-O-anhydro-lyxofuranosyl)uracil **1**. Compounds **5** and **9** were subsequently alkylated with different allyl-, or propargyl bromides in tetrahydrofuran in presence of sodium hydride at room temperature to give various 3′-

SCHEME 1


RO
Ura
SePh
H•
Me
PhO(S)CO
OC(S)OPh
Radical addition-cyclization at the α-face produces mixture of diastereomers (diastereoselective)
Radical addition-cyclization at the β-face is diastereospecific

phenylseleno-2′-O-allyl ethers **6a** - **6d** and 2′-phenylseleno-3′-O-allyl ethers **10a** - **10d**, respectively, in 70 - 80% yields.



1 **2** **3** **4**

R = MMTr

5′-O-(MMTr)-2′-deoxy-2′-phenylseleno-uridine **13** was prepared by opening of 1-(5′-O-(MMTr)-2,2′-O-anhydro-β-D-arabinofuranosyl)uracil **2** by $PhSe^-$ ion in THF at ~50 °C in 93 % yield[45], which was converted to the corresponding 3′-O-allyl or 3′-O-propargyl derivatives using the condition described for **5** and **9**.

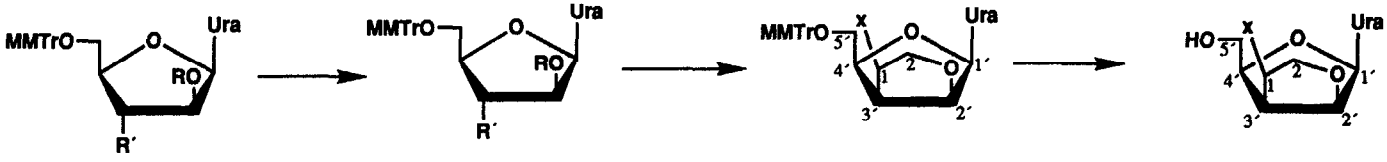
1-(5′-O-(MMTr)-3′-deoxy-3′-phenylseleno-2′-O-allyl-β-D-xylofuranosyl)uracil **20a** was prepared from 5′-O-(MMTr)-3′-O-(t-butyldimethylsilyl) [TBDMS] uridine **17** [from **17** →**18** →**19** → **20a**] in the following manner: Allylation of **17**, followed by deprotection of 3′-O-TBDMS group from the product by fluoride ion gave **18** (72%) which was then mesylated at 3′-OH to give **19**. The 3′-O-mesylate in **19** was subsequently displaced by $PhSe^-$ ion to give **20a** in 77 % overall yield in two steps [**18** →**19** → **20a**]. 5′-O-(MMTr)-3′-O-phenoxythiocarbonyl-2′-O-allyl-uridine **20b** was prepared in 90 % yield from 5′-O-(MMTr)-2′-O-allyl-uridine **18** by treatment of phenoxythiocarbonyl chloride in dry acetonitrile in presence of N,N-dimethylaminopyridine at room temperature overnight.

1-(5′-O-(MMTr)-2′-O-allyl-3′-O-phenoxythiocarbonyl-β-D-arabinofuranosyl)uracil **25** [from **23** →**24** →**25**] and 1-(5′-O-(MMTr)-3′-O-allyl-2′-O-phenoxythiocarbonyl-β-D-xylofuranosyl)uracil **28** [from **26** →**27** →**28**] were prepared[66] by allylation of 1-(5′-O-(MMTr)-3′-O-TBDMS-β-D-arabinofuranosyl)uracil **23** and 1-(5′-O-(MMTr)-2′-O-TBDMS-β-D-xylofuranosyl)uracil **26**, deprotection of the TBDMS group to give **24** (71 %) and **27** (72 %), followed by treatment of phenoxythiocarbonyl chloride in a dry basic condition (see experimentals).

Free-radical generation, addition and cyclization. The radical intermediates have been generated at the carbons bearing phenylseleno or phenylthiocarbonate group by a brief treatment of precursors **6a-6d**, **10a-10d**, **14a-14d**, **20a**, **20b**, **25**, **28** with tri-n-butyltin hydride in presence of AIBN in boiling benzene under an atmosphere of argon.

Specific stereoelectronic environments at the α- and β-face of pentofuranose ring of the β-D-nucleoside played crucial roles in the trapping of the prochiral free-radical by the olefin strategically positioned at the vicinal

Diastereospecific scavenging of radicals by olefins at the β-face of nucleosides



5: R= H; R′ = -SePh

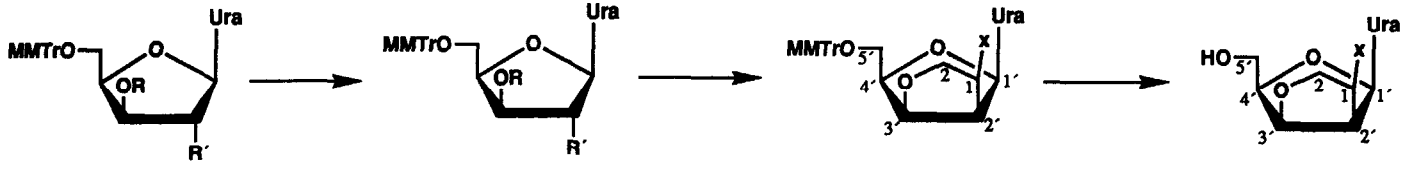
23: R= H; R′= -O-TBDMS
24: R= -$CH_2CH{=}CH_2$; R′ = -OH

6a: R = -$CH_2CH{=}CH_2$; R′= -SePh (72%)
6b: R = -$CH_2CH{=}C(Me)_2$; R′= -SePh (69%)
6c: R = -$CH_2CH{=}CH(Et)$; R′= -SePh (65%)
6d: R = -$CH_2C{\equiv}CH$; R′= -SePh (81%)

25: R = -$CH_2CH{=}CH_2$; R′= -OC(S)OPh (74%)

7a: x = -CH_3 (79 %)
7b: x = -$CH(Me)_2$ (72 %)
7c: x = -$CH_2CH_2CH_3$ (89 %)
7d: x = [=CH_2] (16 %)

8a: x = -CH_3 (79 %)
8b: x = -$CH(Me)_2$ (87 %)
8c: x = -$CH_2CH_2CH_3$ (88 %)
8d: x = [=CH_2] (81 %)



9: R= H; R′ = -SePh

26: R= H; R′= -O-TBDMS
27: R= -$CH_2CH{=}CH_2$; R′ = -OH

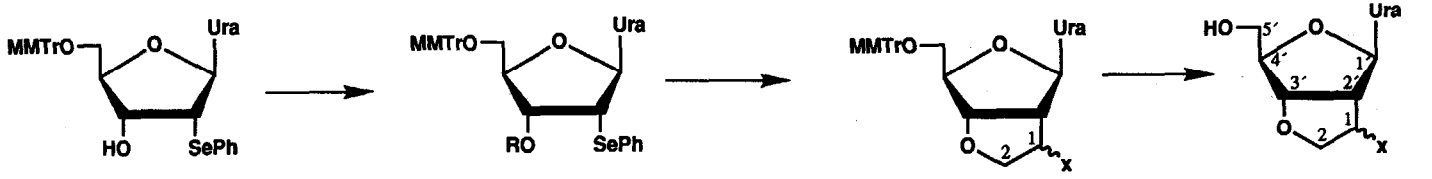
10a: R = -$CH_2CH{=}CH_2$; R′= -SePh (75%)
10b: R = -$CH_2CH{=}C(Me)_2$; R′= -SePh (92%)
10c: R = -$CH_2CH{=}CH(Et)$; R′= -SePh (73%)
10d: R = -$CH_2C{\equiv}CH$; R′= -SePh (91%)

28: R = -$CH_2CH{=}CH_2$; R′= -OC(S)OPh (77%)

11a: x = -CH_3 (95 %)
11b: x = -$CH(Me)_2$ (79 %)
11c: x = -$CH_2CH_2CH_3$ (95 %)
11d: x = [=CH_2] (52 %)

12a: x = -CH_3 (85 %)
12b: x = -$CH(Me)_2$ (94 %)
12c: x = -$CH_2CH_2CH_3$ (88 %)
12d: x = [=CH_2] (69 %)

Diastereoselective scavenging of radicals by olefins at the α-face of nucleosides

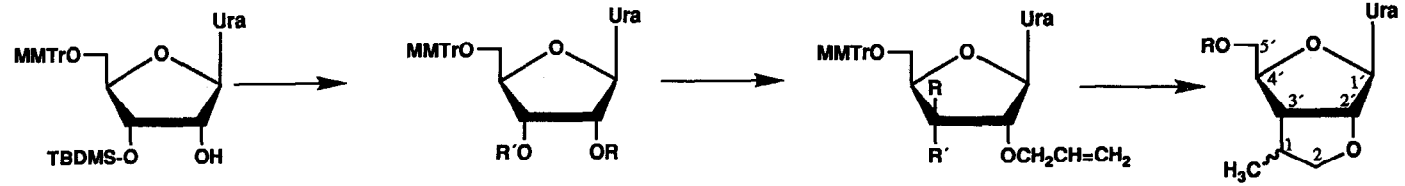


13

14a: R = $-CH_2CH{=}CH_2$; R′ = -SePh (72%)
14b: R = $-CH_2CH{=}C(Me)_2$; R′ = -SePh (76%)
14c: R = $-CH_2CH{=}CH(Et)$; R′ = -SePh (85%)
14d: R = $-CH_2C{\equiv}CH$; R′ = -SePh (82%)

15a: x = $-CH_3$ (92 %)
15b: x = $-CH(Me)_2$ (85 %)
15c: x = $-CH_2CH_2CH_3$ (94 %)
15d: x = [$=CH_2$] (65%)

16a: x = $-CH_3$ (92 %)
16b: x = $-CH(Me)_2$ (89 %)
16c: x = $-CH_2CH_2CH_3$ (88 %)
16d: x = [$=CH_2$] (76%)



17

18: R = $-CH_2CH{=}CH_2$; R′ = H (72 %)
19: R = $-CH_2CH{=}CH_2$; R′ = $-SO_2Me$

20a: R = -SePh; R′ = H (77 %)

20b: R = H; R′ = -OC(S)OPh (90 %)

21: R = MMTr (92 %)
22: R = H (82 %)

carbon. When the prochiral radical generated at the 2′- or at the 3′-carbon was trapped by the double bond of the allyl ethers as in **6a** - **6c** or the triple bond in propargyl ether as in **6d** at the β-face, these cyclization reactions produced single diastereospecific product in each case containing the cis-fused five-membered ring as in **7a-7d** & **11a-11d** in high yields. In contrast, when the radical generated at the 2′- or at the 3′-carbon was trapped by the double bond of the allyl ethers **14a** - **14c**, **20a**, **20b**, or the triple bond in propargyl ether **14d** at the α-face, it produced an inseparable diastereomeric mixture of products containing the cis-fused five-membered rings as in **15a** - **15d** & **21** (see experimentals).

Following points may be noted as the stereochemical outcome of the above free-radical addition-cyclization procedure: (1) The configuration of the alkenyl or alkynyl ether at the α- or β-face dictated the *ribo* or *lyxo* configuration, respectively, of the resultant cis-fused five-membered rings. (2) Radical-trapping cyclizations gave exclusively 5-*exo* ring-closure products, no trace of 6-*endo* ring-closure products was formed. For example, the cyclization of free-radical precursors **6a** or **25**, **10a** or **28**, **14a**, **20a** or **20b** gave cyclized *exo*-methyl pentofuranoid derivatives **7a**, **11a**, **15a** and **21** in high yields. This implies that the radical cyclizations were kinetically controlled, and preferred formation of less stable primary radical is due to chair-like transition state[67] which regiospecifically produce five-membered rings. This is consistent with other observations on the radical cyclizations in the literature[52-57]. (3) The stereochemistry of the above nucleophilic free-radical attack to the olefin was however dependent on different stereoelectronic environments at the α- and the β-face of the pentofuranose ring, which produced different degree of the stereoelectronic hindrance to the π-faces of the olefin. Thus the alkenyl group at the β-face of the pentofuranose ring presumably has a restricted rotation, and is forced to take up a specific conformation due to the streoelectronic effects of the aglycone, $O^{4'}$-lonepair, and 4′-alkoxymethylene group. It is therefore conceivable that the radical attacks the alkenyl group at the β-face at the least sterically and electronically hindered π-face to give the stereospecific reaction product. On the other hand, the alkenyl group at the α-face of the pentofuranose ring can take up two different reactive conformations, and the radical-attack therefore takes place at both π-faces albeit with a different degree of steric and electronic control to produce two possible diastereomers in different ratio. (4) The isolated yields of different free-radical addition-cyclized products suggest that the efficiency of the radical-trapping reactions by olefins were independent of either the location of the radical at C-2′ or C-3′ or the configuration of the alkenyl ether group, or the alkyl substituent on the alkene. (5) The type of the free-radical precursor (phenylseleno versus phenylthiocarbonate) did not influence the above stereospecificity of the radical-trapping on the β-face or the ratio of diastereoisomers formed at the α-face.

These radical cyclization-trapping methodologies should provide an easy access to many other new types of the cis-fused cyclopentanoids or cyclohaxanoids simply by changing the position of the double bond in the alkene or triple bond in the alkyne chain at the α- or β-face of the C-2′ or C-3′ in the free-radical precursor. Starting materials (free-radical precursors) for such intramolecular addition-cyclization reactions of unsaturated radicals are easily prepared as demonstrated in this paper, these reactions should therefore find wide applications in the synthetic manipulation of nucleosides. Our preliminary results suggest that the free-radical precursor containing 2′- or 3′-O-acrylate or -crotonate gives corresponding 2′,3′-fused-lactone[3.3.0] derivative of nucleoside. Results of these studies will be reported elsewhere. Studies on the cyclization involving other polarized multiple bonds (e.g., C≡N, C=O) are also now in progress 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. 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}H- & ^{13}C-NMR assignments of 2′/3′-O-allyl, 2′/3′-O-alkynyl chain protons and carbons are indicated by H-a (-OCH_2), H-b and H-c, or C-a, C-b and C-c and so on from 2′/3′-O- direction.

1-(5′-O-(MMTr)-3′-O-(allyl)-2′-deoxy-2′-phenylseleno-β-D-xylofuranosyl)uracil (10a) *General procedure of alkylation :* To a solution of compound **9** (982 mg, 1.5 mmol) in dry tetrahydrofuran (15 ml) was added sodium hydride (80 %, 112.5 mg, 3.75 mmol) and the mixture was stirred ultrasonically for 15 min under argon. Allyl bromide (317 µl, 3.75 mmol) was then added to the mixture and stirring was continued for 5 h. The reaction mixture was poured into a saturated solution of ammonium chloride (100 ml), which was extacted with ethyl acetate (2 x 100 ml). The combined extracts were washed with water (50 ml) and dried over $MgSO_4$. All volatile matters were removed in vacuo and residue was purified on a silica gel column to give compound **10a** (780 mg, 75 %). ^{1}H-NMR ($CDCl_3$): 9.71 (br.s, 1H) NH; 7.67 - 6.82 (m, 20H) H-6, arom.; 6.17 (d, $J_{1',2'}$ = 3.6 Hz, 1H) H-1′; 5.71 - 5.30 (m, 2H) H-5, H-b; 5.03 - 4.75 (m, 2H) H-c; 4.53 (dt, $J_{3',4'}$ = 4.6 Hz, 1H) H-4′; 3.91 (dd, $J_{2',3'}$ = 1.7 Hz, 1H) H-3′; 3.79 (s, 3H) OCH_3; 3.66 - 3.22 (m, 5H) H-2′, H-5′, H-5", H-a. ^{13}C-NMR ($CDCl_3$): 117.7 (t) C-c; 101.0 (d, J_{CH} = 175.2 Hz) C-5′; 89.4 (d, J_{CH} = 171.6 Hz) C-1′; 86.6 (s) MMTr; 81.4 (d, J_{CH} = 156.1 Hz) C-3′; 80.7 (d, J_{CH} = 146.0 Hz) C-4′; 70.1 (t, J_{CH} = 142.7 Hz) C-a; 61.6 (t, J_{CH} = 143.8 Hz) C-5′; 55.0 (q) OCH_3; 49.1 (d, J_{CH} = 147.2 Hz) C-2′. MS (FAB$^-$): calc. for (M-H)$^-$ 695.1663, found 695.1675.

1-(5′-O-(MMTr)-3′-O-(2-pentenyl)-2′-deoxy-2′-phenylseleno-β-D-xylofuranosyl)uracil (10b): The general procedure for alkylation was followed using compound **9** (655 mg, 1 mmol), NaH (80%, 75 mg, 2.5 mmol) and 4-bromo-2-methyl-2-butene (250 µl, 2.5 mmol) in dry tetrahydrofuran (12 ml) to give compound **10b** (670 mg, 92%). ^{1}H-NMR ($CDCl_3$) : 9.20 (br.s. 1H) NH; 7,72 - 6.78 (m, 20H) arom., H-6; 6.17 (d, $J_{1',2'}$ = 2.7 Hz, 1H) H-1′; 5.47 (d, $J_{5,6}$ = 8.1 Hz, 1H) H-5; 4.93 (m, 1H) H-b; 4.48 (m, 1H) H-4′; 3.88 (m, 1H) H-3′; 3.79 (s, 3H) OCH_3; 3.73 - 3.16 (m, 5H) H-2′, H-5′, H-5", H-a; 1.60 (s, 3H) H-d; 1.38 (s, 3H) H-d′. ^{13}C-NMR ($CDCl_3$) : 140.6 (d, J_{CH} = 186.5 Hz) C-6; 119.7 (s) C-c; 101.3 (d, J_{CH} = 178.6 Hz) C-5; 89.7 (d, J_{CH} = 171.8 Hz) C-1′; 86.7 (s) MMTr; 81.8 (d, J_{CH} = 153.9 Hz) C-3′; C-4′; 65.8 (t, J_{CH} = 141.0 Hz) C-a; 61.9 (t, J_{CH} = 143.2 Hz) C-5′; 55.1 (q) OCH_3; 49.3 (d, J_{CH} = 152.8 Hz) C-2′; 25.5 and 17.8 (2 x q) C-d, C-d′. MS (FAB$^-$): calc. for (M-H)$^-$ 723.1978, found 723.1982.

1-(5′-O-(MMTr)-3′-O-(3-methyl-2-butenyl)-2′-deoxy-2′-phenylseleno-β-D-xylofuranosyl) uracil (10c): The general procedure for alkylation was followed using compound **9** (260 mg, 0.4 mmol), NaH (80%, 59.6 mg, 2.0 mmol) and 1-bromo-2-pentene (222 µl, 2.0 mmol) in dry tetrahydrofuran (10 ml) to give compound **10c** (210 mg, 73 %). ^{1}H-NMR ($CDCl_3$) : 9.23 (br.s, 1H) NH; 7.75 - 6.78 (m, 20H) arom., H-6; 6.17 (d, $J_{1',2'}$ = 2.7 Hz, 1H) H-1′; 5.51 - 5.04 (m, 3H) H-5, H-b, H-c; 4.47 (m, 1H) H-4′; 3.89 (dd, $J_{2',3'}$ = 3.7 Hz, $J_{3',4'}$ = 2.0 Hz, 1H) H-3′; 3.79 (s, 3H) OCH_3; 3.73 (m, 3H) H-2, H-a; 3.56 (dd, $J_{4',5'}$ = 6.1 Hz, $J_{5',5"}$ = 10.0 Hz, 1H) H-5′; 3.25 (dd, $J_{4',5"}$ = 4.6 Hz, 1H) H-5"; 1.81 (m, 2H) H-d; 0.84 (t, 3H) H-e. ^{13}C-NMR ($CDCl_3$) : 140.4 (d, J_{CH} = 180.8 Hz) C-6; 101.4 (d, J_{CH} = 180.8 Hz) C-5; 89.6 (d, J_{CH} = 173.0 Hz) C-1′; 86.7 (s) MMTr; 82.2 (d, J_{CH} = 147.2 Hz) C-4′; 81.6 (d, J_{CH} = 151.7 Hz) C-3′; 64.9 (t, J_{CH} = 142.1 Hz) C-a; 61.8 (t, J_{CH} = 142.6 Hz) C-5′; 55.1 (q) OCH_3; 49.3 (d, J_{CH} = 152.8 Hz) C-2′; 20.6 (t, J_{CH} = 125.2 Hz) C-d; 14.0 (q, J_{CH} = 125.8 Hz) C-e. MS (FAB$^-$): calc. for (M-H)$^-$ 723.1978, found 723.1985.

1-(5′-O-(MMTr)-3′-O-(2-propynyl)-2′-deoxy-2′-phenylseleno-β-D-xylofuranosyl)uracil (10d): The general procedure for alkylation was followed using compound **9** (320 mg, 0.489 mmol), NaH (80%, 73 mg, 2.45 mmol) and propargyl bromide (218 µl, 2.45 mmol) in dry tetrahydrofuran (10 ml) to give compound **10d** (308 mg, 91 %). ^{1}H-NMR ($CDCl_3$) : 9.27 (br.s, 1H) NH; 7.78 - 6.79 (m, 20H) arom., H-6; 6.16 (d, $J_{1',2'}$ = 2.7 Hz, 1H) H-1′; 5.51 (d, $J_{5,6}$ = 8.0 Hz, 1H) H-5; 4.53 (m, 1H) H-4′; 4.11 (m, 1H) H-3′; 3.86 (d, $J_{a,c}$ = 2.2 Hz, 2H) H-a; 3.79 (s, 3H) MMTr; 3.85 - 3.78 (m, 1H) H-2′; 3.57 (dd, $J_{4',5'}$ = 5.9 Hz, $J_{5',5"}$ = 10.2 Hz, 1H) H-5′; 3.28 (dd, $J_{4',5"}$ = 4.2 Hz, 1H) H-5"; 2.21 (t, 1H) H-c. ^{13}C-NMR ($CDCl_3$) : 140.2 (d, J_{CH} = 184.3 Hz) C-6; 101.5 (d, J_{CH} = 177.5 Hz) C-5; 85.6 (d, J_{CH} = 178.6 Hz) C-1′; 82.6 (d, J_{CH}

= 156.1 Hz) C-3′; 81.4 (d, J_{CH} =142.7 Hz) C-4′; 75.3 (d, J_{CH} = 133.0 Hz) C-c; 61.5 (t, J_{CH} = 142.7 Hz) C-5′; 57.1 (t, J_{CH} = 148.8 Hz) C-a; 55.1 (q) OCH_3; 48.8 (d, J_{CH} = 151.6 Hz) C-2′.MS (FAB^-): calc. for $(M-H)^-$ 693.1508, found 693.1476.

1-(5′-O-(MMTr)-2′-O-(allyl)-3′-deoxy-3′-phenylseleno-β-D-arabinofuranosyl)uracil (6a): The general procedure for alkylation was followed using compound **5** (1.11 g, 1.69 mmol), NaH (80 %, 127 mg, 4.23 mmol) and allyl bromide (357.5 µl, 4.23 mmol) in tetrahydrofuran (10 ml) to give compound **6a** (850 mg, 72 %). ^{1}H-NMR ($CDCl_3$): 9.11 (br.s, 1H) NH; 7.85 (d, $J_{5,6}$ = 8.1 Hz, 1H) H-6; 7.60 - 6.84 (m, 19H) arom.; 6.17 (d, $J_{1',2'}$ = 5.6 Hz, 1H) H-1′; 6.05 - 5.63 (m, 1H) H-b; 5.34 - 5.02 (m, 3H) H-5, H-c; 4.13 (dd, $J_{2',3'}$ = 6.3 Hz, 1H) H-2′; 3.91 - 3.67 (m, 4H) H-3′, H-4′, H-a; 3.79 (s, 3H) OCH_3; 3.49 (m, 2H) H-5′, H-5". ^{13}C-NMR ($CDCl_3$): 117.0 (d) C-c; 101.1 (d, J_{CH} = 176.3 Hz) C-5; 86.7 (s) MMTr; 83.3 (d, J_{CH} = 172.9 Hz) C-1′; 82.7 (d, J_{CH} = 147.1 Hz) C-4′; 80.9 (d, J_{CH} = 151.6 Hz) C-2′; 72.0 (t, J_{CH} = 146.0 Hz) C-a; 61.3 (t, J_{CH} = 145.7 Hz) C-5′; 54.9 (q) OCH_3; 43.2 (d, J_{CH} = 147.1 Hz) C-3′. MS (FAB^-): calc. for $(M-H)^-$ 695.1663, found 695.1702.

1-(5′-O-(MMTr)-2′-O-(3-methyl-2-butenyl)-3′-deoxy-3′-phenylseleno-β-D-arabinofuranosyl) uracil (6b): The general procedure for alkylation was followed using compound **5** (327 mg, 0.5 mmol), NaH (80 %, 75 mg, 2.5 mmol) and 4-bromo-2-methyl-2-butene (89 µl, 0.75 mmol) in tetrahydrofuran (10 ml) to give compound **6b** (250 mg, 69 %). ^{1}H-NMR ($CDCl_3$): 9.00 (br.s, 1H) NH; 7.85 (d, $J_{5,6}$ = 8.3 Hz, 1H) H-6; 7.61 - 6.82 (m, 19H) arom.; 6.19 (d, $J_{1',2'}$ = 5.4 Hz, 1H) H-1′; 5.29 (d, 1H) H-5; 5.19 (m, 1H) H-b; 4.17 - 3.59 (m, 5H) H-2′, H-3′, H-4′, H-a; 3.80 (s, 3H) OCH_3; 3.50 (d, $J_{4',5'}$ = 2.4 Hz, 2H) H-5′, H-5"; 1.71 and 1.56 (2 x s, 6H) H-d, H-d′. ^{13}C-NMR ($CDCl_3$): 142.0 (d, J_{CH} = 184.2 Hz) C-6; 119.9 (s) C-c; 101.1 (d, J_{CH} = 180.9 Hz) C-5; 86.5 (s) MMTr; 83.5 (d, J_{CH} = 168.5 Hz) C-1′; 82.6 (d, J_{CH} = 152.2 Hz) C-2′; 81.1 (d, J_{CH} = 148.3 Hz) C-4′; 68.1 (t) C-a; 61.5 (t, J_{CH} = 143.8 Hz) C-5′; 55.1 (q, J_{CH} = 143.8 Hz) OCH_3; 43.5 (d, J_{CH} = 149.4 Hz) C-3′; 25.7 (q, J_{CH} = 126.9 Hz) C-d; 17.9 (q, J_{CH} = 125.8 Hz) C-d. MS (FAB^-): calc. for $(M-H)^-$ 723.1978, found 723.1928.

1-(5′-O-(MMTr)-2′-O-(2-pentenyl)-3′-deoxy-3′-phenylseleno-β-D-arabinofuranosyl)uracil (6c): The general procedure for alkylation was followed using compound **5** (327 mg, 0.5 mmol), NaH (80 %, 75 mg, 2.5 mmol) and 1-bromo-2-pentene (94 µl, 0.75 mmol) in tetrahydrofuran (10 ml) to give compound **6c** (235 mg, 65 %). ^{1}H-NMR ($CDCl_3$): 8.82 (br.s, 1H) NH; 7.87 (d, $J_{5,6}$ = 8.1 Hz, 1H) H-6; 7.62 - 6.83 (m, 19H) arom.; 6.19 (d, $J_{1',2'}$ = 5.4 Hz, 1H) H-1′; 5.70 - 5.24 (m, 3H) H-b, H-c, H-5; 4.19 - 3.60 (m, 5H) H-2′, H-3′, H-4′, H-a; 3.80 (s, 3H) OCH_3; 3.50 (d, $J_{4',5'}$ = 2.7 Hz, 2H) H-5′, H-5"; 1.96 (m, 2H) H-d; 0.92 (t, 3H) H-e. ^{13}C-NMR ($CDCl_3$): 141.9 (d, J_{CH} = 184.2 Hz) C-6; 101.1 (d, J_{CH} = 176.4 Hz) C-5; 85.4 (s) MMTr; 83.5 (d, J_{CH} = 170.7 Hz) C-1′; 83.0 (d, J_{CH} = 147.2 Hz) C-4′; 81.1 (d, J_{CH} = 151.7 Hz) C-2′; 67.0 (t, J_{CH} = 141.5 Hz) C-a, 61.5 (t, J_{CH} = 142.7 Hz) C-5′; 55.1 (q, J_{CH} = 143.8 Hz) OCH_3; 43.5 (d, J_{CH} = 148.3 Hz) C-3′; 20.8 (t) C-d; 14.1 (q) C-e. MS (FAB^-): calc. for $(M-H)^-$ 723.1978, found 723.2015.

1-(5′-O-(MMTr)-2′-O-(2-propynyl)-3′-deoxy-3′-phenylseleno-β-D-arabinofuranosyl)uracil (6d): The general procedure for alkylation was followed using compound **5** (327 mg, 0.5 mmol), NaH (80 %, 75 mg, 2.5 mmol) and propargyl bromide (84 µl, 0.75 mmol) in tetrahydrofuran (10 ml) to give compound **6d** (282 mg, 81 %). ^{1}H-NMR ($CDCl_3$): 9.21 (br.s, 1H) NH; 7.85 (d, $J_{5,6}$ = 8.3 Hz, 1H) H-6; 7.65 - 6.82 (m, 19H) arom.; 6.19 (d, $J_{1',2'}$ = 5.4 Hz, 1H) H-1′; 5.28 (d, 1H) H-5; 4.39 - 4.25 (m, 1H) H-4′; 4.11 (d, $J_{a,c}$ = 2.4 Hz, 2H) H-a; 4.01 - 3.62 (m, 2H) H-2′, H-3′; 3.80 (s, 3H) OCH_3; 3.51 (m, 2H) H-5′, H-5"; 2.44 (t, 2H) H-c. ^{13}C-NMR ($CDCl_3$): 141.6 (d, J_{CH} = 183.1 Hz) C-6; 101.3 (d, J_{CH} = 178.6 Hz) C-5; 86.9 (s) MMTr; 83.3 (d, J_{CH} = 171.9 Hz) C-1′; 82.7 (d, J_{CH} = 167.7 Hz) C-2′; 81.1 (d, J_{CH} = 155.0 Hz) C-4′; 61.4 (t, J_{CH} = 141.5 Hz) C-5′; 58.8 (t, J_{CH} = 151.1 Hz) C-a; 55.1 (q, J_{CH} = 143.8 Hz) OCH_3; 43.1 (d, J_{CH} = 151.6 Hz) C-3′. MS (FAB^-): calc. for $(M-H)^-$ 693.1508, found 693.1473.

5′-O-(MMTr)-2′-deoxy-2′-phenylseleno-3′-O-(allyl)uridine (14a): The general procedure for alkylation was followed using compound **13** (982 mg, 1.5 mmol), NaH (80 %, 112.5 mg, 3.75 mmol) and allyl bromide (317 µl, 3.75 mmol) in tetrahydrofuran (15 ml) to give compound **14a** (750 mg, 72 %). ^{1}H-NMR ($CDCl_3$): 8.71 (br.s, 1H) NH; 7.57 - 6.83 (m, 20H) H-6, arom.; 6.51 (d, $J_{1',2'}$ = 8.5 Hz, 1H) H-1′; 6.10 - 5.67 (m, 1H) H-b; 5.37 - 5.17 (m, 2H) H-c; 5.01 (d, $J_{5,6}$ = 8.2 Hz, 1H) H-5; 4.35 (dd, $J_{2',3'}$ = 2.2 Hz, $J_{3',4'}$ = 5.6 Hz, 1H) H-3′; 4.06 (m, 1H) H-4′; 3.96 (m, 2H) H-a; 3.88 (dd, 1H) H-2′; 3.80 (s, 3H) OCH_3; 3.40 (d, 2H) H-5′, H-5". ^{13}C-NMR ($CDCl_3$): 117.8 (t) C-c; 102.1 (d, J_{CH} = 176.3 Hz) C-5; 90.2 (d, J_{CH} = 173.1 Hz) C-1′; 87.1 (s) MMTr; 82.4 (d, J_{CH} = 148.3 Hz) C-4′; 80.0 (d, J_{CH} = 151.7 Hz) C-3′; 70.8 (t, J_{CH} =

145.4 Hz) C-a; 63.7 (t, J_{CH} = 143.8 Hz) C-5′; 54.9 (q) OCH_3; 49.3 (d, J_{CH} = 145.0 Hz) C-2′. MS (FAB^-): calc. for $(M-H)^-$ 695.1663, found 695.1710.

5′-O-(MMTr)-2′-deoxy-2′-phenylseleno-3′-O-(3-methyl-2-butenyl)uridine (14b): The general procedure for alkylation was followed using compound **13** (327 mg, 0.5 mmol), NaH (80 %, 75 mg, 2.5 mmol) and 4-bromo-2-methyl-2-butene (89 µl, 0.75 mmol) in tetrahydrofuran (10 ml) to give compound **14b** (274 mg, 76 %). ^{1}H-NMR ($CDCl_3$): 8.95 (br.s, 1H) NH; 7.66 - 6.85 (m, 20H) H-6, arom.; 6.52 (d, $J_{1',2'}$ = 8.6 Hz, 1H) H-1′; 5.33 (m, 1H) H-b; 4.33 - 3.87 (m, 5H) H-3′, H-4′, H-a, H-2′; 3.81 (s, 3H) OCH_3; 3.41 (t, $J_{4',5'}$ = 2.2 Hz, 2H) H-5′, H-5"; 1.70 (2 x s) H-d, H-d′. ^{13}C-NMR ($CDCl_3$): 139.5 (d, J_{CH} = 179.7 Hz) C-6; 120.0 (s) C-c; 102.2 (d, J_{CH} = 177.5 Hz) C-5; 90.4 (d, J_{CH} = 171.8 Hz) C-1′; 87.3 (s) MMTr; 82.7 (d, J_{CH} = 150.6 Hz) C-4′; 79.8 (d, J_{CH} = 157.3 Hz) C-3′; 66.6 (t, J_{CH} = 141.5 Hz) C-a; 63.8 (t, J_{CH} = 143.8 Hz) C-5′; 55.1 (q, J_{CH} = 143.8 Hz) OCH_3; 49.6 (d, J_{CH} = 143.8 Hz) C-2′; 25.7 (q, J_{CH} = 122.4 Hz) C-d; 18.0 (q, J_{CH} = 130.3 Hz) C-d′. MS (FAB^-): calc. for $(M-H)^-$ 723.1978, found 723.1981.

5′-O-(MMTr)-2′-deoxy-2′-phenylseleno-3′-O-(2-pentenyl)uridine (14c): The general procedure for alkylation was followed using compound **13** (327 mg, 0.5 mmol), NaH (80 %, 75 mg, 2.5 mmol) and 1-bromo-2-pentene (94 µl, 0.75 mmol) in tetrahydrofuran (10 ml) to give compound **14c** (308 mg, 85 %). ^{1}H-NMR ($CDCl_3$): 8.59 (br.s, 1H) NH; 7.65 - 6.84 (m, 20H) H-6, arom.; 6.49 (d, $J_{1',2'}$ = 8.8 Hz, 1H) H-1′; 5.56 (m, 2H) H-b, H-c; 5.00 (d, $J_{5,6}$ = 8.3 Hz, 1H) H-5; 4.34 - 3.86 (m, 5H) H-3′, H-4′, H-a, H-2′; 3.80 (s, 3H) OCH_3; 3.41 (t, $J_{4',5'}$ = 2.2 Hz, 2H) H-5′, H-5"; 2.02 (m, 2H) H-d; 0.96 (t, 3H) H-e. ^{13}C-NMR ($CDCl_3$): 139.5 (d, J_{CH} = 180.9 Hz) C-6; 102.2 (d, J_{CH} = 173.0 Hz) C-5; 90.4 (d, J_{CH} = 178.6 Hz) C-1′; 82.6 (d, J_{CH} = 149.4 Hz) C-4′; 80.2 (d, J_{CH} = 158.4 Hz) C-3′; 65.6 (t, J_{CH} = 139.3 Hz) C-a; 63.5 (t, J_{CH} = 142.3 Hz) C-5′; 55.1 (q, J_{CH} = 143.8 Hz) OCH_3; 49.5 (d, J_{CH} = 142.7 Hz) C-2′; 20.9 (t) C-d; 14.1 (q) C-e. MS (FAB^-): calc. for $(M-H)^-$ 723.1978, found 723.1977.

5′-O-(MMTr)-2′-deoxy-2′-phenylseleno-3′-O-(2-propynyl)uridine (14d): The general procedure for alkylation was followed using compound **13** (327 mg, 0.5 mmol), NaH (80 %, 75 mg, 2.5 mmol) and propargyl bromide (84 µl, 0.75 mmol) in tetrahydrofuran (10 ml) to give compound **14d** (284 mg, 82 %). ^{1}H-NMR ($CDCl_3$): 8.50 (br.s, 1H) NH; 7.65 - 6.84 (m, 20H) H-6, arom.; 6.47 (d, $J_{1',2'}$ = 8.8 Hz, 1H) H-1′; 5.05 (d, $J_{5,6}$ =8.3 Hz, 1H) H-5; 4.62 (dd, $J_{2',3'}$ = 5.4 Hz, $J_{3',4'}$ =1.5 Hz, 1H) H-3′; 4.28 (d, $J_{a,c}$ = 2.44 Hz, 2H) H-a; 4.16 (m, 1H) H-4′; 3.94 (m, 1H) H-2′; 3.80 (s, 3H) OCH_3; 3.46 (s, 2H) H-5′, H-5"; 2.42 (t, 1H) H-c. ^{13}C-NMR ($CDCl_3$): 139.4 (d, J_{CH} = 185.3 Hz) C-6; 102.2 (d, J_{CH} = 175.2 Hz) C-5; 90.2 (d, J_{CH} = 166.2 Hz) C-1′; 87.4 (s) MMTr; 82.5 (d, J_{CH} = 150.5 Hz) C-4′; 80.0 (d, J_{CH} = 170.4 Hz) C-3′; 63.5 (t, J_{CH} = 144.3 Hz) C-5′; 57.6 (t, J_{CH} = 147.7 Hz) C-a; 55.2 (q, J_{CH} = 143.8 Hz) OCH_3; 49.3 (d, J_{CH} = 144.9 Hz) C-2′. MS (FAB^-): calc. for $(M-H)^-$ 693.1508, found 693.1521.

5′-O-(MMTr)-2′-O-(allyl)uridine (18): The general procedure for alkylation was followed using compound **17** (840 mg, 1.33 mmol), NaH (80 %, 100 mg, 3.33 mmol) and allyl bromide (282 µl, 3.33 mmol) in tetrahydrofuran (10 ml). All volatile matters were removed in vacuo and the residue was then treated with a solution of n-Bu4NF (0.1 M, 20 ml) in tetrahydrofuran for 4 h. After removal of the solvent, the syrup was purified on a silica gel column to give compound **18** (530 mg, 72 %). ^{1}H-NMR ($CDCl_3$): 9.43 (br.s, 1H) NH; 8.03 (d, $J_{5,6}$ = 8.0 Hz, 1H) H-6; 7.45 - 6.84 (m, 14H) arom.; 6.14 - 5.72 (m, 1H) H-b; 5.97 (d, $J_{1',2'}$ = 1.5 Hz, 1H) H-1′; 5.41 - 5.21 (m, 2H) H-c; 4.39 (m, 3H) H-2′, H-3′, H-4′; 4.01 (m, 2H) H-a; 3.80 (s, 3H) OCH_3; 3.55 (d, $J_{4',5'}$ = 2.2 Hz, 2H) H-5′, H-5". ^{13}C-NMR ($CDCl_3$): 118.5 (t) C-c; 102.0 (d, J_{CH} = 175.2 Hz) C-5; 87.3 (s) MMTr; 87.3 (d, J_{CH} = 171.9 Hz) C-1′; 83.3 (d, J_{CH} = 146.1 Hz) C-4′; 81.2 (d, J_{CH} = 155.0 Hz) C-2′; 71.3 (d, J_{CH} = 151.6 Hz) C-3′; 68.3 (t, J_{CH} = 144.2 Hz) C-a; 61.2 (t, J_{CH} = 142.1 Hz) C-5′; 55.1 (q) OCH_3. MS (FAB^-): calc. for $(M-H)^-$ 555.2131, found 555.2130.

1-(5′-O-(MMTr)-2′-O-(allyl)-β-D-arabinofuranosyl)uracil (24): The general procedure for alkylation was followed using compound **23** (315 mg, 0.5 mmol), NaH (80 %, 38 mg, 1.25 mmol) and allyl bromide (106 µl, 1.25 mmol) in tetrahydrofuran (5 ml). All volatile matters were removed in vacuo and the residue was then treated with a solution of n-Bu4NF (0.1 M, 20 ml) in tetrahydrofuran for 4 h. After removal of the solvent, the syrup was purified on a silica gel column to give compound **24** (196 mg, 71 %). ^{1}H-NMR ($CDCl_3$): 9.30 (br.s, 1H) NH; 7.70 (d, $J_{5,6}$ = 8.0 Hz, 1H) H-6; 7.45 - 6.84 (m, 14H) arom.; 6.32 (d, $J_{1',2'}$ = 5.1 Hz, 1H) H-1′; 5.96 - 5.60 (m, 1H) H-b; 5.47 (d, 1H) H-5; 5.22 - 5.06 (m, 2H) H-c; 4.29 (dd, $J_{2',3'}$ = 5.6 Hz, $J_{3',4'}$ = 5.6 Hz, 1H) H-3′; 4.11 (dd, 1H) H-2′; 4.01 - 3.94 (m, 3H) H-4′, H-a; 3.80 (s, 3H) OCH_3; 3.47 (d, $J_{4',5'}$ = 4.4 Hz, 2H) H-5′, H-5"; ^{13}C-NMR ($CDCl_3$): 117.4 (t) C-c; 101.2 (d, J_{CH} = 177.5 Hz) C-5; 86.9 (s) MMTr; 83.7 (d, J_{CH} = 171.8 Hz) C-1′; 83.0 (d, J_{CH} = 149.5 Hz) C-4′; 81.5 (d, J_{CH} = 150.5 Hz) C-2′;

74.4 (d, J_{CH} = 155.0 Hz) C-3′; 71.8 (t, J_{CH} = 143.2 Hz) C-a; 61.8 (t, J_{CH} = 142.7 Hz) C-5′; 55.1 (q) OCH_3. MS (FAB⁻): calc. for (M-H)⁻ 555.2131, found 555.2104.

1-(5′-O-(MMTr)-3′-O-(allyl)-β-D-xylofuranosyl)uracil (27): The general procedure for alkylation was followed using compound **26** (315 mg, 0.5 mmol), NaH (80 %, 38 mg, 1.25 mmol) and allyl bromide (106 µl, 1.25 mmol) in tetrahydrofuran (5 ml). All volatile matters were removed in vacuo and the residue was then treated with a solution of n-Bu4NF (0.1 M, 20 ml) in tetrahydrofuran for 4 h. After removal of the solvent, the syrup was purified on a silica gel column to give compound **27** (200 mg, 72 %). ^{1}H-NMR ($CDCl_3$): 10.46 (br.s, 1H) NH; 7.45 - 6.84 (m, 15H) H-6, arom.; 5.84 (s, 1H) H-1′; 5.62 (d, $J_{5,6}$ = 8.1 Hz, 1H) H-5; 5.57 - 5.43 (m, 1H) H-b; 5.12 - 4.97 (m, 2H) H-c; 4.69 (m, 1H) H-2′; 4.37 (s, 1H) H-3′; 3.91 (m, 3H) H-4′, H-a; 3.80 (s, 3H) OCH_3; 3.51 (m, 2H) H-5′, H-5". ^{13}C-NMR ($CDCl_3$): 117.0 (t) C-c; 101.0 (d, J_{CH} = 177.8 Hz) C-5; 93.0 (d, J_{CH} = 173.0 Hz) C-1′; 86.4 (s) MMTr; 83.2 (d, J_{CH} = 152.8 Hz) C-4′; 81.4 (d, J_{CH} = 158.4 Hz) C-3′; 77.9 (d, J_{CH} = 153.9 Hz) C-2′; 70.4 (t, J_{CH} = 143.2 Hz) C-a; 61.1 (t, J_{CH} = 143.8 Hz) C-5′; 55.0 (q) OCH_3. MS (FAB⁻): calc. for (M-H)⁻ 555.2131, found 555.2147.

1-(5′-O-(MMTr)-2′-deoxy-2′-*C*, 3′-*O*-((1-methyl)ethylene)-β-D-lyxofuranosyl)uracil (11a). *General procedure of free radical cyclization:* The solution of compound **10a** (347 mg, 0.5 mmol) in dry benzene (50 ml) was degassed with a stream of argon for 10 min, to which was added dropwise under reflux a mixture of n-tributyltin hydride (213 µl, 0.75 mmol) and AIBN (12.3 mg, 0.075 mmol) in dry benzene (7 ml) during 3 h. The reaction mixture was then heated to reflux for another 2 h, cooled to room temperature and concentrated in vacuo. Chromatographic purification of the crude residue on silica gel gave compound **11a** (255 mg, 95 %). ^{1}H-NMR ($CDCl_3$): 11.0 (br.s, 1H) NH; 7.40 - 6.83 (m, 15H) H-6, arom.; 5.99 (d, $J_{1',2'}$ = 6.5 Hz, 1H) H-1′; 5.73 (d, $J_{5,6}$ = 8.1 Hz, 1H) H-5; 4.44 (dd, $J_{2',3'}$ = 6.1 Hz, $J_{3',4'}$ = 3.4 Hz, 1H) H-3′; 4.11 (m, 1H) H-4′; 3.78 (s, 3H) OCH_3; 3.66 - 3.25 (m, 4H) H-5′, H-5"; H-2; 2.91 (m, 1H) H-2′; 1.93 (m, 1H) H-1; 0.96 (d, 3H) CH_3. ^{13}C-NMR ($CDCl_3$): 101.2 (d, J_{CH} = 175.3 Hz) C-5; 86.9 (d, J_{CH} = 169.6 Hz) C-1′; 86.4 (s) MMTr; 82.5 (d, J_{CH} = 161.9 Hz) C-3′; 80.6 (d, J_{CH} = 146.0 Hz) C-4′; 76.0 (t, J_{CH} = 143.2 Hz) C-2; 62.3 (t, J_{CH} = 144.4 Hz) C-5′; 55.0 (q) OCH_3; 55.0 (d, J_{CH} = 142.6 Hz) C-2′; 35.0 (d, J_{CH} = 132.4 Hz) C-1; 18.5 (q) CH_3. MS (FAB⁻): calc. for (M-H)⁻ 539.2182, found 539.2174.

1-(5′-O-(MMTr)-2′-deoxy-2′-*C*,3′-*O*-((1-isopropyl)ethylene)-β-D-lyxofuranosyl)uracil (11b): The general procedure for free radical cyclization was followed using compound **10b** (220 mg, 0.3 mmol) in dry benzene (20 ml), n-tributyltin hydride (130 µl, 0.45 mmol) and AIBN (7.2 mg, 0.045 mmol) in dry benzene (3 ml) to give compound **11b** (134 mg, 79%). ^{1}H-NMR ($CDCl_3$): 7.51 - 6.78 (m, 15H) arom., H-6; 6.19 (d, $J_{1',2'}$ = 7.6 Hz, 1H) H-1′; 5.72 (d, $J_{5,6}$ = 8.1 Hz, 1H) H-5; 4.28 (m, 1H) H-3′; 4.12 (m, 1H) H-4′; 3.79 (s, 3H) OCH_3; 3.82 - 3.30 (m, 4H) H-2, H-5′, H-5"; 2.95 (m, 1H) H-2′; 1.53 (m, 2H) H-1, CH (1-isopropyl); 1.01 - 0.76 (m, 6H) 2 x CH_3 (1-isopropyl). ^{13}C-NMR ($CDCl_3$): 140.6 (d, J_{CH} = 188.7 Hz) C-6; 101.5 (d, J_{CH} = 177.5 Hz) C-5; 87.0 (d, J_{CH} = 170.7 Hz) C-1′; 83.2 (d, J_{CH} = 156.1 Hz) C-3′; 80.4 (d, J_{CH} = 152.8 Hz) C-4′; 73.1 (t, J_{CH} = 147.2 Hz) C-2; 62.3 (t, J_{CH} = 147.1 Hz) C-5′; 55.1 (q) OCH_3; 51.8 (d, J_{CH} = 148.1 Hz) C-2′; 47.9 (d, J_{CH} =131.2 Hz) C-1; 31.0 (d) CH (1-isopropyl); 20.8 and 20.1 (q, J_{CH} = 124.4 Hz) 2 x CH_3 (1-isopropyl). MS (FAB⁻): calc. for (M-H)⁻ 567.2495, found 567.2467.

1-(5′-O-(MMTr)-2′-deoxy-2′-*C*, 3′-*O*-((1-n-propyl)ethylene)-β-D-lyxofuranosyl)uracil (11c): The general procedure for free radical cyclization was followed using compound **10c** (200 mg, 0.28 mmol) in dry benzene (20 ml), n-tributyltin hydride (120 µl, 0.42 mmol) and AIBN (6.64 mg, 0.04 mmol) in dry benzene (3 ml) to give compound **11c** (150 mg, 95 %). ^{1}H-NMR ($CDCl_3$): 9.51 (br.s, 1H) NH; 7.53 - 6.80 (m, 15H) arom., H-6; 6.07 (d, $J_{1',2'}$ = 7.1 Hz, 1H) H-1′; 5.73 (d, $J_{5,6}$ = 8.1 Hz, 1H) H-5; 4.38 (m, 1H) H-3′; 4.11 (m, 1H) H-4′; 3.81 (s, 3H) OCH_3; 3.58 - 3.20 (m, 4H) H-5′, H-5", H-2; 2.92 (m, 1H) H-2′; 1.85 (m, 1H) H-1; 1.27 (m, 4H) 2 x CH_2 (1-n-propyl); 0.84 (m, 3H) CH_3 (1-n-propyl). ^{13}C-NMR ($CDCl_3$): 140.3 (d, J_{CH} = 187.6 Hz) C-6; 101.3 (d, J_{CH} = 176.4 Hz) C-5; 86.9 (d, J_{CH} = 168.5 Hz) C-1′; 86.4 (s) MMTr; 82.5 (d, J_{CH} = 157.3 Hz) C-3′; 80.6 (d, J_{CH} = 148.3 Hz) C-4′; 74.7 (t, J_{CH} = 146.0 Hz) C-2; 62.2 (t, J_{CH} = 141.6 Hz) C-5′; 55.1 (q) OCH_3; 53.7 (d, J_{CH} = 144.2 Hz) C-2′; 40.4 (d, J_{CH} = 131.4 Hz) C-1; 36.0 (t, J_{CH} = 127.5 Hz) CH_2 (1-n-propyl); 20.8 (t, J_{CH} = 127.8 Hz) CH_2′ (1-n-propyl); 13.8 (q, J_{CH} = 128.5 Hz) CH_3 (1-n-propyl). MS (FAB⁻): calc. for (M-H)⁻ 567.2495, found 567.2493.

1-(5′-O-(MMTr)-2′-deoxy-2′-*C*,3′-*O*-((1-methylene)ethylene)-β-D-lyxofuranosyl)uracil (11d): The general procedure for free radical cyclization was followed using compound **10d** (290 mg, 0.42

mmol) in dry benzene (20 ml), n-tributyltin hydride (170 µl, 0.63 mmol) and AIBN (10 mg, 0.06 mmol) in dry benzene (3 ml) to give compound **11d** (116 mg, 52 %). ^{1}H-NMR ($CDCl_3$): 9.69 (br.s, 1H) NH; 7.58 - 6.78 (m, 15H) arom., H-6; 6.30 (d, $J_{1',2'}$ = 7.8 Hz, 1H) H-1'; 5.66 (d, $J_{5,6}$ = 8.1 Hz, 1H) H-5; 5.02 (d, J_{gem} = 7.4 Hz, 2H) CH_2 (1-methylene) ; 4.48 (dd, $J_{2',3'}$ = 2.8 Hz, $J_{3',4'}$ = 5.4 Hz, 1H) H-3'; 4.27 - 4.15 (m, 3H) H-4'; H-2; 3.78 (s, 3H) OCH_3; 3.79 - 3.33 (m, 3H) H-2', H-5', H-5". ^{13}C-NMR ($CDCl_3$): 140.0 (d, J_{CH} = 188.4 Hz) C-6; 109.5 (t, J_{CH} = 159.5 Hz) CH_2 (1-methylene), 101.4 (d, J_{CH} = 177.5 Hz) C-5; 86.8 (d, J_{CH} = 170.7 Hz) C-1'; 83.8 (d, J_{CH} = 152.8 Hz) C-3'; 81.3 (d, J_{CH} = 146.1 Hz) C-4'; 72.5 (t, J_{CH} = 144.4 Hz) C-2; 62.0 (t, J_{CH} = 144.3 Hz) C-5'; 55.1 (q) OCH_3; 53.1 (d, J_{CH} = 140.4 Hz) C-2'. MS (FAB^-): calc. for $(M-H)^-$ 537.2026, found 537.2035.

1-(5'-O-(MMTr)-3'-deoxy-3'-*C*, 2'-*O*-((1-methyl)ethylene)-β-D-lyxofuranosyl)uracil (7a): The general procedure for free radical cyclization was followed using compound **6a** (220 mg, 0.32 mmol) in dry benzene (15 ml), n-tributyltin hydride (130 µl, 0.45 mmol) and AIBN (7.2 mg, 0.045 mmol) in dry benzene (7 ml) to give compound **7a** (134 mg, 79 %). The general procedure for free radical cyclization was followed also using compound **25** (50 mg, 0.072 mmol) in dry benzene (5 ml), n-tributyltin hydride (32 µl, 0.11 mmol) and AIBN (2.5 mg, 0.011 mmol) in dry benzene (2 ml) to give compound **7a** (37 mg, 70 %). ^{1}H-NMR ($CDCl_3$): 9.26 (br.s, 1H) NH; 7.32 - 6.84 (m, 15H) H-6, arom.; 5.79 (d, $J_{1',2'}$ = 3.9 Hz, 1H) H-1'; 5.66 (d, $J_{5,6}$ = 8.3 Hz, 1H) H-5; 4.69 (dd, $J_{2',3'}$ = 7.0 Hz, 1H) H-2'; 4.16 (dt, $J_{3',4'}$ = 5.5 Hz, 1H) H-4'; 3.80 (s, 3H) OCH_3; 3.68 - 3.16 (m, 4H) H-2, H-5', H-5"; 2.58 (dd, 1H) H-3'; 2.03 (m, 1H) H-1; 0.88 (d, 3H) CH_3. ^{13}C-NMR ($CDCl_3$): 99.3 (d, J_{CH} = 178.6 Hz) C-5; 85.2 (s) MMTr; 83.8 (d, J_{CH} = 165.1 Hz) C-1'; 80.0 (d, J_{CH} = 159.5 Hz) C-2'; 75.5 (d, J_{CH} = 148.3 Hz) C-4'; 74.9 (t, J_{CH} = 144.3 Hz) C-2; 60.8 (t, J_{CH} = 141.3 Hz) C-5'; 53.6 (q) OCH_3; 51.0 (d, J_{CH} = 152.8 Hz) C-3'; 33.7 (d, J_{CH} = 129.2 Hz) C-1; 15.5 (q) CH_3. MS (FAB^-): calc. for $(M-H)^-$ 539.2182, found 539.2195.

1-(5'-O-(MMTr)-3'-deoxy-3'-*C*, 2'-*O*-((1-isopropyl)ethylene)-β-D-lyxofuranosyl)uracil (7b): The general procedure for free radical cyclization was followed using compound **6b** (230mg, 0.32 mmol) in dry benzene (25 ml), n-tributyltin hydride (133 µl, 0.48 mmol) and AIBN (16.4 mg, 0.1 mmol) in dry benzene (10 ml) to give compound **7b** (130 mg, 72 %). ^{1}H-NMR ($CDCl_3$): 8.98 (br.s, 1H) NH; 7.52 - 6.85 (m, 15H) H-6, arom.; 5.83 (d, $J_{1',2'}$ = 3.42 Hz, 1H) H-1'; 5.67 (d, $J_{5,6}$ = 7.81 Hz, 1H) H-5; 4.67 (dd, $J_{2',3'}$ = 6.6 Hz, 1H) H-2'; 4.23 (q, $J_{4',5'}$ = 4.9 Hz, $J_{3',4'}$ = 8.3 Hz, 1H) H-4'; 3.80 (s, 3H) OCH_3; 3.71 - 3.08 (m, 4H) H-5', H-5", H-2; 2.75 (m, 1H) H-3'; 2.02 - 0.83 (m, 2H) H-1, CH (1-isopropyl); 0.78 - 0.67 (m, 6H) 2 x CH_3 (1-isopropyl). ^{13}C-NMR ($CDCl_3$): 141.6 (d, J_{CH} = 183.1 Hz) C-6; 100.6 (d, J_{CH} = 176.4 Hz) C-5; 86.5 (s) MMTr; 85.4 (d, J_{CH} = 164.0 Hz) C-1'; 81.7 (d, J_{CH} = 160.6 Hz) C-2'; 77.1 (d, J_{CH} = 150.5 Hz) C-4'; 72.7 (t, J_{CH} = 146.0 Hz) C-2; 62.5 (t, J_{CH} = 142.7 Hz) C-5'; 55.0 (q) OCH_3; 48.4 (d, J_{CH} = 139.7 Hz) C-3'; 47.1 (d, J_{CH} = 132.6 Hz) C-1; 30.4 (d, J_{CH} = 142.7 Hz) CH (1-isopropyl); 20.9 and 19.3 (2 x q, J_{CH} = 126.9 Hz) 2 x CH_3 (in 1-isopropyl). MS (FAB^-): calc. for $(M-H)^-$ 567.2495, found 567.2523.

1-(5'-O-(MMTr)-3'-deoxy-3'-*C*, 2'-*O*-((1-n-propyl)ethylene)-β-D-lyxofuranosyl)uracil (7c): The general procedure for free radical cyclization was followed using compound **6c** (173 mg, 0.24 mmol) in dry benzene (18 ml), n-tributyltin hydride (100 µl, 0.36 mmol) and AIBN (11.8 mg, 0.072 mmol) in dry benzene (7 ml) to give compound **7c** (121 mg, 89 %). ^{1}H-NMR ($CDCl_3$): 8.82 (br.s, 1H) NH; 7.52 - 6.84 (m, 15H) H-6, arom.; 5.79 (d, $J_{1',2'}$ = 3.9 Hz, 1H) H-1'; 5.66 (d, $J_{5,6}$ = 8.3 Hz, 1H) H-5; 4.63 (dd, $J_{2',3'}$ = 7.1 Hz, 1H) H-2'; 4.18 (q, $J_{4',5'}$ = 5.7 Hz, $J_{3',4'}$ = 8.1 Hz, 1H) H-4'; 3.80 (s, 3H) OCH_3; 3.71 - 3.06 (m, 4H) H-5', H-5", H-2; 2.64 (m, 1H) H-3'; 2.01 (m, 1H) H-1; 1.26 - 0.82 (m, 7H) 1-n-propyl. ^{13}C-NMR ($CDCl_3$): 98.7 (d, J_{CH} = 176.4 Hz) C-5; 85.8 (s) MMTr; 84.6 (d, J_{CH} = 161.8 Hz) C-1'; 80.8 (d, J_{CH} = 160.6 Hz) C-4'; 76.7 (d, J_{CH} = 178.6 Hz) C-2'; 75.1 (t, J_{CH} = 129.7 Hz) C-2; 63.5 (t, J_{CH} = 144.9 Hz) C-5'; 56.8 (q, J_{CH} = 143.8 Hz) OCH_3; 53.2 (d, J_{CH} = 134.8 Hz) C-3'; 43.4 (d, J_{CH} = 125.8 Hz) C-1; 38.4 (t) CH_2 (1-n-propyl); 25.5 (t) CH_2' (1-n-propyl); 18.9 (q) CH_3 (1-n-propyl). MS (FAB^-): calc. for $(M-H)^-$ 567.2495, found 567.2517.

1-(5'-O-(MMTr)-3'-deoxy-3'-*C*,2'-*O*-((1-methylene)ethylene)-β-D-lyxofuranosyl)uracil (7d): The general procedure for free radical cyclization was followed using compound **6d** (285 mg, 0.41 mmol) in dry benzene (30 ml), n-tributyltin hydride (172 µl, 0.62 mmol) and AIBN (20 mg, 0.12 mmol) in dry benzene (15 ml) to give compound **7d** (35 mg, 16 %). ^{1}H-NMR ($CDCl_3$): 9.48 (br.s, 1H) NH; 7.53 - 6.83 (m, 15H) arom., H-6; 5.89 (d, $J_{1',2'}$ = 2.9 Hz, 1H) H-1'; 5.70 (d, $J_{5,6}$ = 8.3, 1H) H-5; 4.86 (m, 2H) CH_2 (1-methylene); 4.75 (dd, $J_{2',3'}$ = 6.10 Hz, 1H) H-2'; 4.28 (m, 1H) H-4'; 4.16 (s, 2H) H-2; 3.80 (s, 3H) OCH_3; 3.52 - 3.21 (m, 3H) H-3', H-5', H-5". ^{13}C-NMR ($CDCl_3$): 100.8 (d, J_{CH} = 176.4 Hz) C-5; 86.7 (s) MMTr;

86.0 (d, J_{CH} = 167.4 Hz) C-1′; 82.4 (d, J_{CH} = 162.9 Hz) C-2′; 77.4 (d, J_{CH} = 144.9 Hz) C-4′; 73.0 (t, J_{CH} = 160.1 Hz) C-2; 63.4 (t, J_{CH} = 142.1 Hz) C-5′; 55.1 (q) OCH_3; 49.5 (d, J_{CH} = 141.5 Hz) C-3′. MS (FAB^-): calc. for $(M-H)^-$ 537.2026, found 537.1993.

5′-O-(MMTr)-2′-deoxy-2′-*C*, 3′-*O*-((1-methyl)ethylene)uridine (15a): The general procedure for free radical cyclization was followed using compound **14a** (346 mg, 0.5 mmol) in dry benzene (50 ml), n-tributyltin hydride (213 µl, 0.75 mmol) and AIBN (12.3 mg, 0.075 mmol) in dry benzene (7 ml) to give an inseparable diastereomeric mixture (8:1 ratio) of compound **15a** (247 mg, 92 %). *Major Diasteromer # 1* : ^{1}H-NMR ($CDCl_3$): 9.96 (br.s, 1H) NH; 7.78 (d, $J_{5,6}$ = 8.1 Hz, 1H) H-6; 7.34 - 6.83 (m, 14H) arom.; 6.27 (d, $J_{1',2'}$ = 6.8 Hz, 1H) H-1′; 5.30 (d, 1H) H-5; 4.87 (dd, $J_{2',3'}$ = 2.4 Hz, $J_{3',4'}$ = 6.8 Hz, 1H) H-3′; 4.11 - 4.04 (m, 2H) H-4′, H-2a; 3.78 (s, 3H) OCH_3; 3.60 (m, 1H) H-2b; 3.41 (d, $J_{4',5'}$ = 2.7 Hz, 2H) H-5′, H-5"; 2.90 (dd, 1H) H-2′; 2.65 (m, 1H) H-1; 1.12 (d, 3H) CH_3. ^{13}C-NMR ($CDCl_3$): 102.9 (d, J_{CH} = 177.4 Hz) C-5; 86.9 (s) MMTr; 85.2 (d, J_{CH} = 157.5 Hz) C-3′; 84.3 (2 x d, J_{CH} = 151.7 Hz, J_{CH} = 160.6 Hz) C-1′, C-4′; 72.9 (t, J_{CH} = 144.2 Hz) C-2; 63.4 (t, J_{CH} = 142.1 Hz) C-5′; 55.0 (q) OCH_3; 53.9 (d, J_{CH} = 143.8 Hz) C-2′; 35.9 (d, J_{CH} = 128.1 Hz) C-1; 11.0 (q) CH_3. *Minor Diasteromer # 2* : ^{1}H-NMR ($CDCl_3$): 7.82 (d, $J_{5,6}$ = 8.3 Hz) H-6; 5.92 (d, $J_{1',2'}$ = 5.4 Hz) H-1′; 5.39 (d) H-5. ^{13}C-NMR ($CDCl_3$): 101.2; 83.6; 61.0; 37.6; 18.3. MS (FAB^-): calc. for $(M-H)^-$ 539.2182, found 539.2165.

5′-O-(MMTr)-2′-deoxy-2′-*C*, 3′-*O*-((1-isopropyl)ethylene)uridine (15b): The general procedure for free radical cyclization was followed using compound **14b** (485 mg, 0.67 mmol) in dry benzene (55 ml), n-tributyltin hydride (312 µl, 1.12 mmol) and AIBN (3.7 mg, 0.022 mmol) in dry benzene (20 ml) to give an inseparable diastereomeric mixture (3:2 ratio) of compound **15b** (323 mg, 85 %) which were not distinguishable by ^{1}H-NMR spectroscopy. ^{1}H-NMR ($CDCl_3$, mixture of diastereomers): 8.75 (br.s, 1H) NH; 7.87 (d, $J_{5,6}$ = 8.1 Hz, 0.6H) H-6(A); 7.76 (d, $J_{5,6}$ = 8.1 Hz, 0.4H) H-6(B); 7.51 - 6.85 (m, 14H) arom.; 6.28 (d, $J_{1',2'}$ = 7.3 Hz, 0.6H) H-1′(A); 6.08 (d, $J_{1',2'}$ = 6.4 Hz, 0.4H) H-1′(B); 5.33 (m, 1H) H-5; 4.85 (d, $J_{2',3'}$ = 6.3 Hz, 0.6H) H-3′(A); 4.63 (d, $J_{2',3'}$ = 6.5 Hz, 0.4H) H-3′(B); 4.25 - 4.0 (m, 1H) H-4′; 3.80 (s, 3H) OCH_3; 3.63 - 3.42 (m, 4H) H-5′, H-5", H-2; 3.00 (m, 0.6H) H-2′(A); 2.65 (m, 0.4H) H-2′(B); 1.30 (m, 2H) H-1, CH (1-isopropyl); 0.92 - 0.75 (m, 6H) 2 x CH_3. ^{13}C-NMR ($CDCl_3$, mixture of diastereomers): 103.1; 102.5; 90.3; 87.0; 85.9; 84.9; 83.8; 72.8; 70.7; 64.0; 54.9; 51.9; 50.2; 30.4; 21.9; 20.5; 20.1. MS (FAB^-): calc. for $(M-H)^-$ 567.2495, found 567.2523.

5′-O-(MMTr)-2′-deoxy-2′-*C*, 3′-*O*-((1-n-propyl)ethylene)uridine (15c): The general procedure for free radical cyclization was followed using compound **14c** (272 mg, 0.37 mmol) in dry benzene (30 ml), n-tributyltin hydride (156 µl, 0.56 mmol) and AIBN (25 mg, 0.15 mmol) in dry benzene (10 ml) to give an inseparable diastereomeric mixture (4:1 ratio) of compound **15c** (201 mg, 94 %). ^{1}H-NMR ($CDCl_3$, mixture of diastereomers): 9.07(br.s, 1H) NH; 7.82 (d, $J_{5,6}$ = 8.1 Hz, 0.8H) H-6(A); 7.75 (d, 0.2H) H-6(B); 7.44 - 6.84 (m, 14H) arom.; 6.26 (d, $J_{1',2'}$ = 7.6 Hz, 0.8H) H-1′(A); 6.00 (d, $J_{1',2'}$ = 6.1 Hz, 0.2H) H-1′(B); 5.38 - 5.12 (m, 1H) H-5; 4.84 - 4.67 (m, 1H) H-3′; 4.25 - 3.99 (m, 2H) H-4′, H-2a; 3.80 (s, 3H) OCH_3; 3.76 - 3.40 (m, 3H) H-5′,H-5", H-2b; 2.95 (m, 0.8H) H-2′(A); 2.53 (m, 0.2H) H-2′(B); 1.40 (m, 5H) H-1,2 x CH_2 (1-n-propyl); 0.89 (m, 3H) CH_3. ^{13}C-NMR ($CDCl_3$, mixture of diastereomers): 103.0; 86.9; 85.3; 84.2; 84.0; 83.8; 75.5; 71.5; 64.1; 57.2; 55.0; 52.6; 41.8; 28.4; 22.0; 13.8. MS (FAB^-): calc. for $(M-H)^-$ 567.2495, found 567.2523.

5′-O-(MMTr)-2′-deoxy-2′-*C*, 3′-*O*-((1-methylene)ethylene)uridine (15d): The general procedure for free radical cyclization was followed using compound **14d** (565 mg, 0.81 mmol) in dry benzene (60 ml), n-tributyltin hydride (339 µl, 1.22 mmol) and AIBN (4 mg, 0.025 mmol) in dry benzene (20 ml) to give compound **15d** (285 mg, 65 %). ^{1}H-NMR ($CDCl_3$): 9.17 (br.s, 1H) NH; 7.85 (d, $J_{5,6}$ = 8.30 Hz, 1H) H-6; 7.41 - 6.84 (m, 14H) arom.; 6.14 (d, $J_{1',2'}$ = 5.1 Hz, 1H) H-1′; 5.34 - 5.17 (m, 3H) H-5, CH_2 (1-methylene); 4.93 (dd, $J_{3',4'}$ = 3.4 Hz, $J_{2',3'}$ = 7.1 Hz, 1H) H-3′; 4.52 (m, 2H) H-2; 4.23 (m, 1H) H-4′; 3.80 (s, 3H) OCH_3; 3.47 (m, 3H) H-5′, H-5", H-2′. ^{13}C-NMR ($CDCl_3$): 102.6 (d, J_{CH} = 175.2 Hz) C-5; 89.7 (d, J_{CH} = 171.9 Hz) C-1′; 87.1 (s) MMTr; 84.8 (d, J_{CH} = 161.8) C-3′; 83.6 (d, J_{CH} = 147.2 Hz) C-4′; 71.6 (t, J_{CH} = 150.0 Hz) C-2; 63.3 (t, J_{CH} = 143.8 Hz) C-5′; 55.3 (d, J_{CH} = 144.9 Hz) C-2′; 55.1 (q) OCH_3. MS (FAB^-): calc. for $(M-H)^-$ 537.2026, found 537.2001.

5′-O-(MMTr)-3′-deoxy-3′-*C*, 2′-*O*-((1-methyl)ethylene)uridine (21): The general procedure for free radical cyclization was followed using compound **20a** (104 mg, 0.15 mmol) in dry benzene (15 ml), n-tributyltin hydride (65 µl, 0.23 mmol) and AIBN (6 mg, 0.037 mmol) in dry benzene (2.5 ml) to give an inseparable diastereomeric mixture (7:3 ratio) of compound **21** (74 mg, 92 %). The general procedure for free radical cyclization was followed also using compound **20b** (260 mg, 0.37 mmol) in dry benzene (40 ml), n-

tributyltin hydride (164 µl, 0.56 mmol) and AIBN (9.8 mg, 0.06 mmol) in dry benzene (7 ml) to give compound **21** (190 mg, 94 %). ^{1}H-NMR ($CDCl_3$, mixture of diastereomers): 9.13 (br.s, 1H) NH; 7.81 (d, $J_{5,6}$ = 8.1 Hz, 0.7H) H-6(A); 7.64 (d, $J_{5,6}$ = 8.1 Hz, 0.3H) H-6(B); 7.60 - 6.84 (m, 14H) arom.; 5.92 (d, $J_{1',2'}$ = 1 Hz, 1H) H-1'; 5.41 (2 x d, 1H) H-5; 4.60 (dd, $J_{2',3'}$ = 5.8 Hz, 1H) H-2'; 4.19 - 3.99 (m, 3H) H-4', H-2; 3.80 (s, 3H) OCH_3; 3.65 - 3.45 (m, 2H) H-5', H-5"; 3.10 (m, 1H) H-3'; 2.65 (m, 1H) H-1; 1.05 (d, 0.9H) CH_3(B); 0.83 (d, 2.1H) CH_3(A). ^{13}C-NMR ($CDCl_3$): 101.8; 91.7; 90.3; 88.4; 86.9; 84.8; 80.3; 75.3; 73.2; 63.7; 60.3; 55.1; 52.2; 46.6; 37.4; 35.6; 18.9; 10.7. MS (FAB$^-$): calc. for (M-H)$^-$539.2182, found 539.2200.

1-(3'-deoxy-3'-*C*, 2'-*O*-((1-methyl)ethylene)-β-D-lyxofuranosyl)uracil (8a): *General Procedure for Removal of 5'-O-MMTr Group :* Compound **7a** (80 mg, 0.15 mmol) was treated with 80 % aqueous AcOH (6 ml) at room temperature for 5 h. All volatile matters were removed in vacuo and the residue was purified on a preparative TLC plate to give compound **8a** (31 mg, 79 %). ^{1}H-NMR ($CDCl_3$+CD_3OD): 7.58 (d, $J_{5,6}$ = 8.1 Hz, 1H) H-6; 5.74 (d, $J_{1',2'}$ = 4.0 Hz, 1H) H-1'; 5.67 (d, 1H) H-5; 4.72 (dd, $J_{2',3'}$ = 7.2 Hz, 1H) H-2'; 4.01 - 3.82(m, 4H) H-4', H-5', H-5", H-2a; 3.37 (dd, J_{gem} = 8.3 Hz, $J_{1,2}$ = 7.0 Hz, 1H) H-2b; 2.62 (ddd, $J_{3',4'}$ = 6.3 Hz, $J_{3',1}$ = 5.2 Hz, 1H) H-3'; 2.35 (m, 1H) H-1; 1.08 (d, 3H) CH_3. ^{13}C-NMR ($CDCl_3$+CD_3OD): 141.7 (d, J_{CH} = 187.6 Hz) C-6; 99.8 (d, J_{CH} = 175.1 Hz) C-5; 85.1 (d, J_{CH} = 171.8 Hz) C-1'; 81.2 (d, J_{CH} = 164.0 Hz) C-2'; 78.1 (d, J_{CH} = 149.9 Hz) C-4'; 76.1 (t, J_{CH} = 146.6 Hz) C-2; 59.9 (t, J_{CH} = 141.5 Hz) C-5'; 51.8 (d, J_{CH} = 143.8 Hz) C-3'; 34.5 (d, J_{CH} = 133.7 Hz) C-1; 16.4 (q, J_{CH} = 125.7 Hz) CH_3. MS (FAB$^-$): calc. for (M-H)$^-$ 267.0981, found 267.0983.

1-(3'-deoxy-3'-*C*, 2'-*O*-((1-isopropyl)ethylene)-β-D-lyxofuranosyl)uracil (8b): Compound **7b** (100 mg, 0.18 mmol) was treated with 80 % aqueous AcOH (5 ml) to give compound **8b** (45 mg, 87 %). ^{1}H-NMR ($CDCl_3$+CD_3OD): 7.64 (d, $J_{5,6}$ = 8.2 Hz, 1H) H-6; 5.75 (d, $J_{1',2'}$ = 3.2 Hz, 1H) H-1'; 5.68 (d, 1H) H-5; 4.63 (dd, $J_{2',3'}$ = 6.8 Hz, 1H) H-2'; 4.12 (m, 1H) H-4'; 4.01 - 3.56 (m, 4H) H-5', H-5", H-2; 2.85 (ddd, $J_{3',4'}$ = 7.1 Hz, $J_{3',1}$ = 3.6 Hz, 1H) H-3'; 2.18 (m, 1H) H-1; 1.62 (m, 1H) CH (1-isopropyl); 0.97 and 0.90 (2 x d, 6H) 2 x CH_3. ^{13}C-NMR ($CDCl_3$+CD_3OD): 141.8 (d, J_{CH} = 185.4 Hz) C-6; 99.9(d, J_{CH} = 176.4 Hz) C-5; 85.5 (d, J_{CH} = 162.8 Hz) C-1'; 81.7 (d, J_{CH} = 157.2 Hz) C-2'; 78.6 (d, J_{CH} = 150.5 Hz) C-4'; 72.5 (t, J_{CH} = 144.9 Hz) C-2; 60.8 (t, J_{CH} = 142.1 Hz) C-5'; 48.1 (d, J_{CH} = 138.2 Hz) C-3'; 46.5 (d, J_{CH} = 135.9 Hz) C-1; 30.2 (d, J_{CH} = 137.0 Hz) CH (1-isopropyl); 20.3 and 18.8 (2 x q) 2 x CH_3. MS (FAB$^-$): calc. for (M-H)$^-$ 295.1294, found 295.1272.

1-(3'-deoxy-3'-*C*, 2'-*O*-((1-n-propyl)ethylene)-β-D-lyxofuranosyl)uracil (8c): Compound **7c** (90 mg, 0.16 mmol) was treated with 80 % aqueous AcOH (6 ml) to give compound **8c** (41 mg, 88 %). ^{1}H-NMR ($CDCl_3$+CD_3OD): 7.56 (d, $J_{5,6}$ = 8.1 Hz, 1H) H-6; 5.74 (d, $J_{1',2'}$ = 3.7 Hz, 1H) H-1'; 5.68 (d, 1H) H-5; 4.66 (dd, $J_{2',3'}$ = 7.1 Hz, 1H) H-2'; 4.11 - 3.83 (m, 4H) H-4', H-5', H-5", H-2a; 3.45 (dd, J_{gem} = 8.6 Hz, $J_{1,2}$ = 6.6 Hz, 1H) H-2b; 2.70 (ddd, 1H) H-3'; 2.27 (m, 1H) H-1; 1.35 (m, 4H) 2 x CH_2 (1-n-propyl); 0.96 (m, 3H) CH_3. ^{13}C-NMR ($CDCl_3$+CD_3OD): 141.9 (d, J_{CH} = 189.8 Hz) C-6; 100.1 (d, J_{CH} = 176.4 Hz) C-5; 85.3 (d, J_{CH} = 174.1 Hz) C-1'; 81.2 (d, J_{CH} = 157.3 Hz) C-2'; 78.3 (d, J_{CH} = 145.7 Hz) C-4'; 74.8 (t, J_{CH} = 147.2 Hz) C-2; 60.4 (t, J_{CH} = 142.1 Hz) C-5'; 50.5 (d, J_{CH} = 137.0 Hz) C-3'; 40.1 (d, J_{CH} = 129.2 Hz) C-1; 35.1 (t, J_{CH} = 124.7 Hz) CH_2 ; 20.8 (t, J_{CH} = 127.5 Hz) CH_2; 13.6 (q, J_{CH} = 125.4 Hz) CH_3. MS (FAB$^-$): calc. for (M-H)$^-$ 295.1294, found 295.1317.

1-(3'-deoxy-3'-*C*, 2'-*O*-((1-methylene)ethylene)-β-D-lyxofuranosyl)uracil (8d): Compound **7d** (70 mg, 0.13 mmol) was treated with 80 % aqueous AcOH (6 ml) to give compound **8d** (28 mg, 81 %). ^{1}H-NMR ($CDCl_3$+CD_3OD): 7.64 (d, $J_{5,6}$ = 8.3 Hz, 1H) H-6; 5.84 (d, $J_{1',2'}$ = 2.9 Hz, 1H) H-1'; 5.70 (d, 1H) H-5; 5.14 (q, 2H) H-2; 4.78 (dd, $J_{2',3'}$ = 6.1 Hz, 1H) H-2'; 4.33 (t, 2H) CH_2 (1-methylene); 4.18 (ddd, $J_{3',4'}$ = 7.6 Hz, $J_{4',5'}$ = 3.7 Hz, 1H) H-4'; 3.93 - 3.38 (m, 3H) H-3', H-5', H-5". ^{13}C-NMR ($CDCl_3$+CD_3OD): 145.3 (s) C-1; 141.8 (d, J_{CH} = 184.2 Hz) C-6; 108.6 (t, J_{CH} = 160.6 Hz) CH_2 (1-methylene); 100.5 (d, J_{CH} = 179.7 Hz) C-5; 85.9 (d, J_{CH} = 165.8 Hz) C-1'; 82.5 (d, J_{CH} = 165.1 Hz) C-2'; 78.8 (d, J_{CH} = 143.6 Hz) C-4'; 73.0 (t, J_{CH} = 152.2 Hz) C-2; 61.7 (t, J_{CH} = 143.2 Hz) C-5'; 49.2 (d, J_{CH} = 142.7 Hz) C-3'. MS (FAB$^-$): calc. for (M-H)$^-$ 265.0825, found 265.0812.

1-(2'-deoxy-2'-*C*, 3'-*O*-((1-methyl)ethylene)-β-D-lyxofuranosyl)uracil (12a): Compound **11a** (105 mg, 0.2 mmol) was treated with 80 % aqueous AcOH (6 ml) to give compound **12a** (44 mg, 85 %). ^{1}H-NMR ($CDCl_3$+CD_3OD): 7.78 (d, $J_{5,6}$ = 8.2 Hz, 1H) H-6; 5.88 (d, $J_{1',2'}$ = 6.9 Hz, 1H) H-1'; 5.74 (d, 1H)

H-5; 4.63 (dd, $J_{2',3'}$ = 6.6 Hz, $J_{3',4'}$ = 3.2 Hz, 1H) H-3'; 3.96 (m, 3H) H-4', H-5', H-5"; 3.94 (dd, J_{gem} = 8.7 Hz, 1H) H-2a; 3.33 (dd, $J_{1,2}$ = 6.5 Hz, 1H) H-2b; 2.96 (ddd, $J_{2',1}$ = 3.8 Hz, 1H) H-2'; 1.94 (m, 1H) H-1; 1.00 (d, 3H) CH_3. ^{13}C-NMR ($CDCl_3$+CD_3OD): 141.4 (d, J_{CH} = 186.5 Hz) C-6; 101.8 (d, J_{CH} = 176.3 Hz) C-5; 87.7 (d, J_{CH} = 170.8 Hz) C-1'; 83.6 (d, J_{CH} = 153.9 Hz) C-3'; 82.2 (d, J_{CH} = 150.5 Hz) C-4'; 76.9 (t, J_{CH} = 143.3 Hz) C-2; 60.9 (d, J_{CH} = 143.8 Hz) C-5'; 55.9 (d, J_{CH} = 139.3 Hz) C-2'; 36.0 (d, J_{CH} = 132.5 Hz) C-1; 18.6 (q, J_{CH} = 124.7 Hz) CH_3. MS (FAB^-): calc. for $(M-H)^-$ 267.0981, found 267.0994.

1-(2'-deoxy-2'-*C*, 3'-*O*-((1-isopropyl)ethylene)-β-D-lyxofuranosyl)uracil (12b): Compound **11b** (130 mg, 0.23 mmol) was treated with 80 % aqueous AcOH (10 ml) to give compound **12b** (63 mg, 94 %). ^{1}H-NMR ($CDCl_3$): 9.60 (br.s, 1H) NH; 7.69 (d, $J_{5,6}$ = 8.1 Hz, 1H) H-6; 6.13 (d, $J_{1',2'}$ = 7.3 Hz, 1H) H-1'; 5.77 (d, 1H) H-5; 4.52 (dd, $J_{2',3'}$ =6.1 Hz, $J_{3',4'}$ = 2.7 Hz, 1H) H-3'; 4.02 (m, 3H) H-4', H-5', H-5"; 3.96 (dd, J_{gem} = 8.9 Hz, 1H) H-2a; 3.52 (dd, $J_{1,2b}$ = 6.3 Hz, 1H) H-2b; 3.03 (ddd, $J_{2',1}$ = 2.9 Hz, 1H) H-2'; 1.62 (m, 2H) H-1, CH (1-isopropyl); 0.87 (m, 6H) 2 x CH_3. ^{13}C-NMR ($CDCl_3$): 140.3 (d, J_{CH} = 185.3 Hz) C-6; 101.7 (d, J_{CH} = 177.4 Hz) C-5; 86.6 (d, J_{CH} = 169.6 Hz) C-1'; 84.1 (d, J_{CH} = 159.4 Hz) C-3'; 80.2 (d, J_{CH} = 150.5 Hz) C-4'; 73.3 (t, J_{CH} = 147.1 Hz) C-2; 60.9 (t, J_{CH} = 143.2 Hz) C-5'; 51.9 (d, J_{CH} = 141.5 Hz) C-2'; 47.8 (d, J_{CH} = 129.2 Hz) C-1; 30.9 (d, J_{CH} = 128.1 Hz) CH (1-isopropyl); 20.7 and 20.0 (2 x q) 2 x CH_3. MS (FAB^-): calc. for $(M-H)^-$ 295.1294, found 295.1310.

1-(2'-deoxy-2'-*C*, 3'-*O*-((1-n-propyl)ethylene)-β-D-lyxofuranosyl)uracil (12c): Compound **11c** (120 mg, 0.21 mmol) was treated with 80 % aqueous AcOH (10 ml) to give compound **12c** (55 mg, 88 %). ^{1}H-NMR ($CDCl_3$): 9.87 (br.s, 1H) NH; 7.75 (d, $J_{5,6}$ = 8.3 Hz, 1H) H-6; 5.99 (d, $J_{1',2'}$ = 7.1 Hz, 1H) H-1'; 5.77 (d, 1H) H-5; 4.64 (dd, $J_{2',3'}$ = 6.1Hz, $J_{3',4'}$ = 2.6 Hz, 1H) H-3'; 4.03 (m, 3H) H-4', H-5', H-5"; 3.96 (dd, J_{gem} = 8.8 Hz, 1H) H-2a; 3.40 (dd, $J_{1,2b}$ = 6.6 Hz, 1H) H-2b; 3.00 (ddd, $J_{2',1}$ = 3.9 Hz, 1H) H-2'; 1.83 (m, 1H) H-1; 1.25 (m, 4H) 2 x CH_2 (1-n-propyl); 0.84 (m, 3H) CH_3. ^{13}C-NMR ($CDCl_3$): 140.2 (d, J_{CH} = 186 4Hz) C-6; 101.4 (d, J_{CH} = 177.5 Hz) C-5; 86.5 (d, J_{CH} = 169.6 Hz) C-1'; 83.4 (d, J_{CH} = 162.9 Hz) C-3'; 80.4 (d, J_{CH} = 143.9 Hz) C-4'; 75.0 (t, J_{CH} = 147.2 Hz) C-2; 60.7 (d, J_{CH} = 144.3 Hz) C-5'; 53.8 (d, J_{CH} = 140.4 Hz) C-2'; 40.5 (d, J_{CH} = 131.4 Hz) C-1; 35.6 (t, J_{CH} = 128.0 Hz) 1-n-propyl); 20.8 (t, J_{CH} = 124.7 Hz) 1-n-propyl); 13.7 (q, J_{CH} = 125.0 Hz) CH_3. MS (FAB^-): calc. for $(M-H)^-$ 295.1294, found 295.1295.

1-(2'-deoxy-2'-*C*, 3'-*O*-((1-methylene)ethylene)-β-D-lyxofuranosyl)uracil (12d): Compound **11d** (100 mg, 0.19 mmol) was treated with 80 % aqueous AcOH (10 ml) to give compound **12d** (34 mg, 69%). ^{1}H-NMR ($CDCl_3$+CD_3OD): 7.62 (d, $J_{5,6}$ = 8.1 Hz, 1H) H-6; 6.2 (d, $J_{1',2'}$ = 8.1 Hz, 1H) H-1'; 5.67 (d, 1H) H-5; 5.02 (m, 2H) 1-methylene; 4.64 (dd, $J_{2',3'}$ = 5.3 Hz, $J_{3',4'}$ = 2.7 Hz, 1H) H-3'; 4.28 (m, 2H) H-2; 4.14-3.80 (m, 4H) H-2', H-4', H-5', H-5". ^{13}C-NMR ($CDCl_3$+CD_3OD): 147.2 (s) C-1; 142.2 (d, J_{CH} = 186.4 Hz) C-6; 109.9 (t, J_{CH} = 145.6 Hz) 1-methylene; 102.2 (d, J_{CH} = 176.3 Hz) C-5; 88.2 (d, J_{CH} = 173.0 Hz) C-1'; 85.3 (d, J_{CH} = 156.1 Hz) C-3'; 83.9 (d, J_{CH} = 149.4 Hz) C-4'; 73.9 (t, J_{CH} = 154.1 Hz) C-2; 61.2 (t, J_{CH} = 143.8 Hz) C-5'; 54.6 (d, J_{CH} = 156.1 Hz) C-2'. MS (FAB^-): calc. for $(M-H)^-$ 265.0825, found 265.0805.

2'-deoxy-2'-*C*, 3'-*O*-((1-methyl)ethylene)uridine (16a): Compound **15a** (130 mg, 0.24 mmol) was treated with 80 % aqueous AcOH (6 ml) to give an inseparable diastereomeric mixture (8:1 ratio) of compound **16a** (59 mg, 92 %). ^{1}H-NMR ($CDCl_3$+CD_3OD, mixture of diastereomers): 7.97 (d, $J_{5,6}$ = 8.1 Hz, 1H) H-6; 6.19 (d, $J_{1',2'}$ = 7.3 Hz, 1H) H-1'; 5.79 (d, 1H) H-5; 4.71 (dd, $J_{2',3'}$ = 6.4 Hz, $J_{3',4'}$ = 2.4 Hz, 1H) H-3'; 4.05 (m, 2H) H-4', H-2a; 3.81 (m, 2H) H-5', H-5"; 3.66 (dd, J_{gem} = 10.3 Hz, 1H) H-2b; 2.92 (ddd, $J_{2',1}$ = 7.3 Hz, 1H) H-2'; 2.55 (m, 1H) H-1; 1.09 (d, 3H) CH_3. ^{13}C-NMR ($CDCl_3$+CD_3OD, mixture of diastereomers): 141.0 (d, J_{CH} = 182.0 Hz) C-6; 102.4 (d, J_{CH} = 178.6 Hz) C-5; 84.8 (d, J_{CH} = 167.4 Hz) C-1'; 84.7 (d, J_{CH} = 157.2 Hz) C-3'; 84.2 (d, J_{CH} = 148.3 Hz) C-4'; 72.4 (t, J_{CH} = 144.9 Hz) C-2; 61.7 (t, J_{CH} = 143.3 Hz) C-5'; 52.7 (d, J_{CH} = 140.5 Hz) C-2'; 35.2 (d, J_{CH} = 130.3 Hz) C-1; 10.3 (q, J_{CH} = 125.8 Hz) CH_3. MS (FAB^-): calc. for $(M-H)^-$ 267.0981, found 267.0969.

2'-deoxy-2'-*C*, 3'-*O*-((1-isopropyl)ethylene)uridine (16b): Compound **15b** (224 mg, 0.39 mmol) was treated with 80 % aqueous AcOH (15 ml) to give an inseparable diastereomeric mixture (3:2 ratio) of compound **16b** (103 mg, 89 %) which were not distinguishable by ^{1}H-NMR spectroscopy. ^{1}H-NMR ($CDCl_3$+CD_3OD, mixture of diastereomers): 8.09 (d, $J_{5,6}$ = 8.3 Hz, 1H) H-6; 6.24 (d, $J_{1',2'}$ = 8.0 Hz, 1H) H-1'; 5.81 (d, 1H) H-5; 4.69 (dd, $J_{2',3'}$ = 5.8 Hz, $J_{3',4'}$ = 1.5 Hz, 1H) H-3'; 4.22 - 3.66 (m, 5H) H-4', H-5', H-5", H-2; 3.01 (ddd, $J_{3',1}$ = 6.2 Hz, 1H) H-2'; 2.18 (m, 1H) H-1, 1.70 (m, 1H) 1-isopropyl, 0.86 (m, 6H) 2 x CH_3. ^{13}C-NMR ($CDCl_3$+CD_3OD, mixture of diastereomers): 140.9; 140.7; 102.7; 102.1; 85.7; 84.7; 84.0;

72.6; 70.2; 61.9; 61.6; 54.3; 51.0; 49.7; 30.2; 26.4; 21.4 and 21.3. MS (FAB$^-$): calc. for (M-H)$^-$ 295.1294, found 295.1322.

2′-deoxy-2′-*C*, 3′-*O*-((1-n-propyl)ethylene)uridine (16c): Compound **15c** (181 mg, 0.32 mmol) was treated with 80 % aqueous AcOH (10 ml) to give an inseparable diastereomeric mixture (4:1 ratio) of compound **16c** (83 mg, 88 %). ^{1}H-NMR ($CDCl_3$+CD_3OD, mixture of diastereomers): 8.00 (d, $J_{5,6}$ = 8.1 Hz, 1H) H-6; 6.20 (d, $J_{1',2'}$ = 7.6 Hz, 1H) H-1′; 5.81 (d, 1H) H-5; 4.69 (dd, $J_{2',3'}$ = 6.3 Hz, $J_{3',4'}$ = 1.9 Hz, 1H) H-3′; 4.17 - 4.00 (m, 2H) H-4′; H-2a; 3.78 (d, $J_{4',5'}$ = 2.7 Hz, 2H) H-5′, H-5"; 3.66 (dd, J_{gem} = 10.7 Hz, 1H) H-2b; 2.96 (ddd, $J_{2',1}$ = 6.9 Hz, 1H) H-2′; 2.51 (m, 1H) H-1; 1.36 (m, 4H) 1-n-propyl; 0.89 (m, 3H) CH_3. ^{13}C-NMR ($CDCl_3$+CD_3OD, mixture of diastereomers): 141.0; 102.7; 85.0; 84.7; 84.1; 71.2; 61.9; 51.6; 41.2; 28.2; 21.6; 13.3. MS (FAB$^-$): calc. for (M-H)$^-$ 295.1294, found 295.1317.

2′-deoxy-2′-*C*, 3′-*O*-((1-methylene)ethylene)uridine (16d): Compound **15d** (250 mg, 0.46 mmol) was treated with 80 % aqueous AcOH (15 ml) to give compound **16d** (94 mg, 76 %). ^{1}H-NMR ($CDCl_3$+CD_3OD): 8.01 (d, $J_{5,6}$ = 8.1 Hz, 1H) H-6; 6.05 (d, $J_{1',2'}$ = 6.9 Hz, 1H) H-1′; 5.78 (d, 1H) H-5; 5.16 (m, 2H) 1-methylene; 4.78 (dd, $J_{2',3'}$ = 6.5 Hz, $J_{3',4'}$ = 2.5 Hz, 1H) H-3′; 4.57 - 4.44 (m, 2H) H-2; 4.20 (dd, 1H) H-4′; 3.82 (m, 2H) H-5′, H-5"; 3.40 (m, 1H) H-2′; ^{13}C-NMR ($CDCl_3$+CD_3OD): 145.2 (s) C-1; 140.9 (d, J_{CH} = 183.1 Hz) C-6; 107.5 (t, J_{CH} = 159.5 Hz) 1-methylene; 102.0 (d, J_{CH} = 177.5 Hz) C-5; 90.0 (d, J_{CH} = 170.7 Hz) C-1′; 84.8 (d, J_{CH} = 164.0 Hz) C-3′; 84.3 (d, J_{CH} = 149.4 Hz) C-4′; 71.0 (t, J_{CH} = 150.0 Hz) C-2; 61.3 (t, J_{CH} = 142.1 Hz) C-5′; 54.3 (d, J_{CH} = 143.8 Hz) C-2′. MS (FAB$^-$): calc. for (M-H)$^-$ 265.0825, found 265.0825.

3′-deoxy-3′-*C*, 2′-*O*-((1-methyl)ethylene)uridine (22): Compound **21** (160 mg, 0.3 mmol) was treated with 80 % aqueous AcOH (10 ml) to give an inseparable diastereomeric mixture (2:1 ratio) of compound **22** (65 mg, 82 %). ^{1}H-NMR ($CDCl_3$+CD_3OD): 7.72 (d, $J_{5,6}$ = 8.1 Hz, 1H) H-6; 5.75 (d, $J_{1',2'}$ = 1.5 Hz, 1H) H-1′; 5.65 (d, 1H) H-5; 4.58 (dd, $J_{2',3'}$ = 6.6 Hz, 1H) H-2′; 4.10 - 3.58 (m, 5H) H-4′, H-5′, H-5", H-2; 2.92 (ddd, 1H) H-3′; 2.52 (m, 1H) H-1; 1.02 (d, 3H) CH_3. ^{13}C-NMR ($CDCl_3$+CD_3OD): 141.3; 101.3; 92.0; 89.7; 87.9; 85.7; 81.0; 72.8; 62.1; 62.0; 45.9; 37.1; 35.2; 18.1; 10.1. MS (FAB$^-$): calc. for (M-H)$^-$ 267.0981, found 267.0977.

1-(5′-O-(MMTr)-2′-O-(allyl)-3′-deoxy-3′-phenylseleno-β-D-xylofuranosyl)uracil (20a): To a solution of compound **18** (380 mg, 0.68 mmol) in dry pyridine (10 ml) was added methylsulfonyl chloride (159 µl, 2.05 mmol) and the reaction was kept at room temperature for 3 h. The reaction mixture was poured into ice water with vigorous stirring. Precipitate was filtered and washed with water till free of pyridine, which was dried over magnesium sulfate to give the pure mesylate derivative (372 mg). To a solution of diphenyldiselenide (131 mg, 0.42 mmol) in dry dioxane (10 ml) was added $LiAlH_4$ (12 mg, 0.32 mmol) and the mixture was stirred 2 h. The mesylate (164 mg, 0.26 mmol) was then added and the reaction was heated under reflux for 5 h. The mixture was poured into a saturated solution of ammonium chloride(50 ml), which was extracted with ethylacetate(3 x 50 ml). All volatile matters were removed in vacuo and the residue was purified on a silica gel column to give compound **20a** (160 mg, 77 %). ^{1}H-NMR ($CDCl_3$): 11.0 (br.s, 1H) NH; 7.86 (d, $J_{5,6}$ = 8.0 Hz, 1H) H-6; 7.61 - 6.84 (m, 19H) arom.; 5.97 (d, $J_{1',2'}$ = 1.9 Hz, 1H) H-1′; 5.89 - 5.59 (m, 2H) H-5, H-b; 5.23-5.04 (m, 2H) H-c; 4.80 (dt, $J_{3',4'}$ = 4.3 Hz, $J_{4',5'}$ = 5.1 Hz, 1H) H-4′; 4.18 (dd, $J_{2',3'}$ = 1.7 Hz, 1H) H-2′; 4.06 (m, 2H) H-a; 3.80 (s, 3H) OCH_3; 3.78 (dd, 1H) H-3′; 3.56 (m, 2H) H-5′, H-5". ^{13}C-NMR ($CDCl_3$): 117.5 (t) C-c; 101.3 (d, J_{CH} = 175.2 Hz) C-5; 90.1 (d, J_{CH} = 173.0 Hz) C-1′; 87.3 (s) MMTr; 87.3 (d, J_{CH} = 156.1 Hz) C-2′; 81.3 (d, J_{CH} = 147.2 Hz) C-4′; 70.7 (t, J_{CH} = 142.7 Hz) C-a; 64.2 (t, J_{CH} = 143.2 Hz) C-5′; 55.0 (q) OCH_3; 46.8 (d, J_{CH} = 150.6 Hz) C-3′. MS (FAB$^-$): calc. for (M-H)$^-$ 695.1663, found 695.1675.

5′-O-(MMTr)-2′-O-(allyl)-3′-O-(phenoxythiocarbonyl)uridine (20b): The mixture of compound **18** (150 mg, 0.27 mmol), 4-N,N-dimethylaminopyridine (DMAP) (67.5 mg, 0.76 mmol) and phenoxythiocarbonyl chloride (PTC-Cl) (55 µl, 0.30 mmol) was stirred at room temperature overnight. Solvent was evaporated and the residue was partitioned between ethylacetate (50 ml) and water (50 ml). Organic phase was evaporated and the residue was purified on a silica gel column to give compound **20b** (168 mg, 90 %). ^{1}H-NMR ($CDCl_3$): 9.48 (br.s, 1H) NH; 7.88 (d, $J_{5,6}$ = 8.3 Hz, 1H) H-6; 7.40 - 6.83 (m, 19H) arom.; 6.17 (d, $J_{1',2'}$ = 4.1 Hz, 1H) H-1′; 5.97 - 5.71 (m, 2H) H-5, H-b; 5.43-5.21 (m, 3H) H-3′, H-c; 4.43 (m, 2H) H-2′, H-4′; 4.24 (m, 2H) H-a; 3.80 (s, 3H) OCH_3; 3.57 (d, $J_{4',5'}$ = 2.5 Hz, 2H) H-5′, H-5". ^{13}C-NMR ($CDCl_3$): 118.4 (t) C-c; 102.6 (d, J_{CH} = 177.0 Hz) C-5; 90.4 (d, J_{CH} = 174.1 Hz) C-1′; 87.3 (s) MMTr; 87.3 (d, J_{CH} = 150.5 Hz) C-3′; 80.8 (d, J_{CH} = 151.6 Hz) C-4′; 78.4 (d, J_{CH} = 153.4 Hz) C-2′; 71.9 (t, J_{CH} = 141.6 Hz) C-a; 61.9 (t, J_{CH} = 143.2 Hz) C-5′; 55.1 (q) OCH_3.

1-(5′-O-(MMTr)-2′-O-(allyl)-3′-O-phenoxythiocarbonyl-β-D-arabinofuranosyl)uracil (25): The mixture of compound **24** (80 mg, 0.14 mmol), 4-N,N-dimethylaminopyridine (DMAP) (35 mg, 0.29 mmol) and phenoxythiocarbonyl chloride (PTC-Cl) (29 µl, 0.16 mmol) was stirred at room temperature overnight. Solvent was evaporated and the residue was partitioned between ethylacetate (50 ml) and water (50 ml). Organic phase was evaporated and the residue was purified on a silica gel column to give compound **25** (74 mg, 74 %). ^{1}H-NMR ($CDCl_3$): 9.80 (br.s, 1H) NH; 7.40 - 6.84 (m, 20H) arom., H-6; 6.83 (d, $J_{1',2'}$ = 3.9 Hz, 1H) H-1′; 5.68 - 5.51 (m, 3H) H-5, H-3′, H-b; 5.14 - 4.94 (m, 2H) H-c; 4.45 (m, 1H) H-4′; 4.26 (d, 1H) H-2′; 4.01 (m, 2H) H-a; 3.80 (s, 3H) OCH_3; 3.48 (d, $J_{4',5'}$ = 5.9 Hz, 2H) H-5′, H-5". ^{13}C-NMR ($CDCl_3$): 117.9 (t) C-c; 100.8 (d, J_{CH} = 177.5 Hz) C-5; 86.5 (s) MMTr; 85.6 (d, J_{CH} = 167.4 Hz) C-1′; 84.8 (d, J_{CH} = 165.1 Hz) C-3′; 81.5 (d, J_{CH} = 151.6 Hz) C-4′; 79.6 (d, J_{CH} = 156.2 Hz) C-2′; 71.6 (t, J_{CH} = 142.1 Hz) C-a; 62.8 (t, J_{CH} = 142.1 Hz) C-5′; 55.0 (q) OCH_3.

1-(5′-O-(MMTr)-3′-O-(allyl)-2′-O-phenoxythiocarbonyl-β-D-xylofuranosyl)uracil (28): The mixture of compound **27** (130 mg, 0.23 mmol), 4-N,N-dimethylaminopyridine (DMAP) (57.5 mg, 0.47 mmol) and phenoxythiocarbonyl chloride (PTC-Cl) (47 µl, 0.26 mmol) was stirred at room temperature overnight. Solvent was evaporated and the residue was partitioned between ethylacetate (50 ml) and water (50 ml). Organic phase was evaporated and the residue was purified on a silica gel column to give compound **28** (123 mg, 77 %). ^{1}H-NMR ($CDCl_3$): 9.27 (br.s, 1H) NH; 7.42 - 6.84 (m, 20H) arom., H-6; 6.25 (d, $J_{1',2'}$ = 1.0 Hz, 1H) H-1′; 5.85 - 5.59 (m, 3H) H-5, H-2′, H-b; 5.19 - 5.05 (m, 2H) H-c; 4.47 (m, 1H) H-4′; 4.17 - 4.05 (m, 3H) H-3′, H-a; 3.80 (s, 3H) OCH_3; 3.57 - 3.42 (m, 2H) H-5′, H-5". ^{13}C-NMR ($CDCl_3$): 118.0 (t) C-c; 101.8 (d, J_{CH} = 176.4 Hz) C-5; 88.1 (d, J_{CH} = 171.9 Hz) C-1′; 86.6 (d, J_{CH} = 161.8 Hz) C-2′; 81.9 (d, J_{CH} = 149.0 Hz) C-4′; 78.9 (d, J_{CH} = 157.2 Hz) C-3′; 70.7 (t, J_{CH} = 144.3 Hz) C-a; 60.8 (t, J_{CH} = 143.2 Hz) C-5′; 55.0 (q) OCH_3.

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