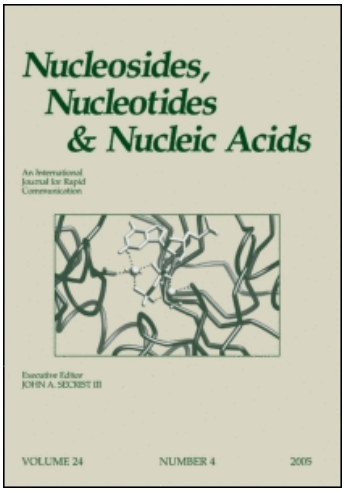

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Synthesis of 2',3'-Dideoxy-3'-nitro-2',3'-didehydrothymidine. Its Use as a General Intermediate for the Preparation of Various 2',3'-Substituted Nucleosides

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SYNTHESIS OF 2',3'-DIDEOXY-3'-NITRO-2',3'-DIDEHYDROTHYMIDINE. ITS USE AS A GENERAL INTERMEDIATE FOR THE PREPARATION OF VARIOUS 2',3'-SUBSTITUTED NUCLEOSIDES

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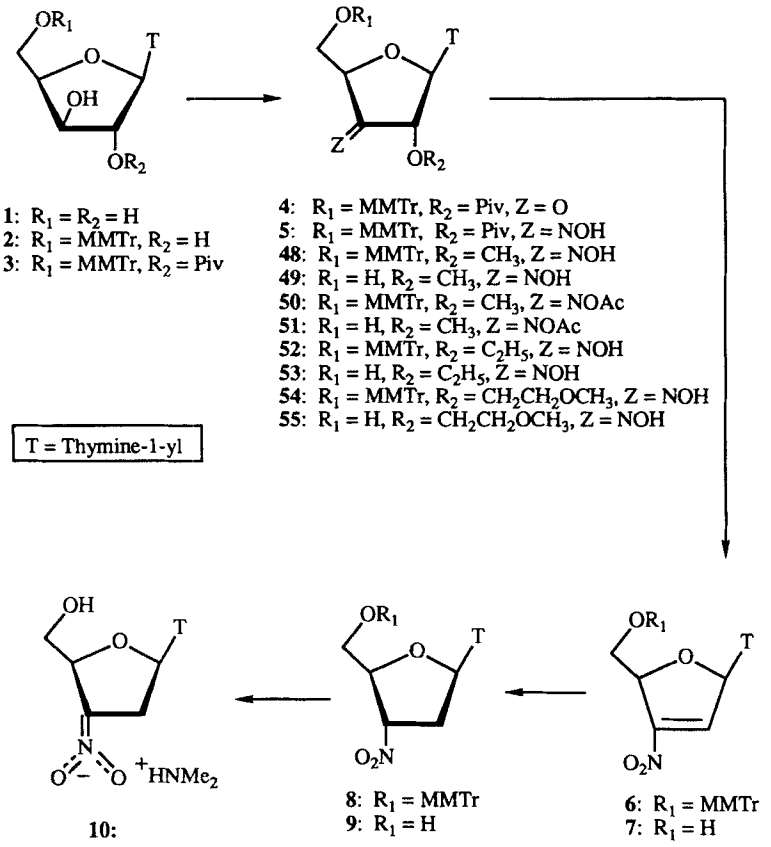
Abstract: The first synthesis of 1-(2,3-dideoxy-3-nitro-β-D-*glycero*-pent-2-enofuranosyl)thymine (**7**), is reported starting directly from 1-(β-D-*xylo*furanosyl)thymine (**1**). We also report a stereospecific conversion of (**6**) to 3'-nitro-2',3'-dideoxythymidine (**9**). Detailed NMR studies have shown that the solution conformation of 3'-nitro-2',3'-dideoxythymidine (**9**) is very similar to 3'-fluoro-2',3'-dideoxythymidine but the former is almost 100 fold less active than the later against HIV reverse transcriptase. Subsequently, the synthetic utilities of 1-(2,3-dideoxy-3-nitro-β-D-*glycero*-pent-2-enofuranosyl) thymine, (**6**) and (**7**), in the preparation of various 2'- and 3'-modified nucleosides have been established through Michael addition reactions with various oxygen, nitrogen and carbon nucleophiles.

Several 2',3'-dideoxy-3'-substituted nucleosides have been found to date which are effective inhibitors of HIV-reverse transcriptase (RT). Amongst these 3'-modified nucleosides, the first FDA approved drug for the treatment of AIDS is 3'-azidothymidine (AZT);[1,2] the others are 2',3'-dideoxyinosine (ddI)[3] and 2',3'-dideoxycytidine (ddC)[3,4]. 3'-Fluorothymidine (FLT),[2] which is also an effective inhibitor of HIV-RT, is presently undergoing the second phase of clinical trial. These results have prompted us to devise a synthesis of 2',3'-dideoxy-3'-nitro-thymidine (**9**), and its didehydro analogue **7**, as potential anti-AIDS substance. Derivatives of 3-nitro-pentofuranoses have been earlier reported by two groups of workers[5-7] which involve the oxidation of the 2,5-bis-protected



Scheme 1

pentofuranoses to the 3-keto derivative, followed by oximination and oxidation to the epimeric 3-deoxy-3-nitrosugars. To the best of our knowledge, no synthesis of the corresponding nucleosides have appeared in the literature. We herein report the first synthesis of 2',3'-dideoxy-3'-nitrothymidine (**9**) starting directly from 1-(β-D-*xylo*furanosyl)thymine (**1**). We also report the synthesis 1-(2,3-dideoxy-3-nitro-β-D-*glycero*-pent-2-enofuranosyl)thymine (**6**) and (**7**) and their applications in the preparation of various 2'- and 3'-modified nucleosides through the Michael addition reactions as potential anti-HIV substances.

*Preparation of 1-[5-O-(MMTr)-2,3-dideoxy-3-nitro-β-D-glycero-pent-2-enofuranosyl]thymine (**6**) and its conversion to 3'-nitro-2',3'-dideoxythymidine (**8**).* Following points were taken into considerations (Scheme 1) for designing the synthesis of 3'-nitro-olefin (**6**): (1) A stable 5'-protecting group was required to deal with the chemistry of the 3'-nitro-olefin for performing 2'- and 3'-modifications under basic conditions at later stages, and it should be therefore an acid-labile group. (2) A suitable 2'-group was required which should be able to act both as a protecting group for the 2'-hydroxyl function in the oxidation steps and also be able to act as a departing group under a mild basic condition to give the 3'-nitro-olefin. (3) The 2'-protecting group should be moderately bulky which should help in the preparation of 2',5'-O-bis-protected derivative selectively over the 3',5'-O-bis-protected derivative, yet its presence should not interfere with the oxidation of the 3'-oxime to the 3'-nitro derivative. These considerations prompted us to use 5'-O-MMTr and 2'-O-pivaloyl (piv) protected[8,9] derivatives of 1-(β-D-*xylo*furanosyl)thymine (**1**) for the synthesis of the corresponding 3'-nitro-olefin (**6**) (Scheme 1). 1-(5-O-MMTr-2-O-pivaloyl-β-D-*xylo*furanosyl)thymine (**3**) was then subjected to the oxidation in the presence of pyridine dichromate (PDC) and acetic anhydride in CH_2Cl_2 at 40 °C for 2 h to give 3'-ketothymidine[10] **4** (95%) (Scheme 1). Treatment of **4** with hydroxylamine hydrochloride in pyridine at room temperature overnight gave 3'-oximino derivative **5** (80%). Finally, oxidation[5,7,11] of **5** with trifluoroperacetic acid in presence of urea and an excess of Na_2HPO_4 in acetonitrile at ~0 °C for 3 h gave 3'-nitro-olefin **6** (76%). Nitro-olefin **6** was reduced in a stereospecific manner to the corresponding 3'-nitro-2',3'-dideoxythymidine **8** (68%) by a brief treatnent of $NaBH_4$ in ethanol. Both 3'-nitro-olefin **6** and 3'-nitro-2',3'-dideoxythymidine **8** were subsequently deprotected to give **7** (94%) and **9** (98%), respectively. The *erythro* configuration of 3'-nitro group in **8** and **9** was supported by the fact that the staggered conformers across its 4',5' bond were predominantly populated with γ+ conformers (53-59%)[12] *(vide infra).* The second line of evidence for the *erythro* configuration of 3'-nitro group in **9** emerged from its unequivocal synthesis from the direct oxidation of 1-[5-O-(p-toluoyl)-3-amino-2,3-dideoxy-β-D-*erythro*-pentofuranosyl]thymine with trifluoroperacetic acid in acidic condition (see experimental). The third piece of evidence for the *erythro* configuration of 3'-nitro group in **9** came from its synthesis by the glycosylation of 2,4-bis(trimethylsilyl)thymine with 1-chloro-2,3-dideoxy-3-nitro-5-O-(p-toluoyl)-α/β-D-*erythro*-pentofuranose, prepared from authentic methyl 2,3-dideoxy-3-nitro-5-O-(p-toluoyl)-β-D-*erythro*-pentofuranoside[5], in the presence of $SnCl_4$ in anhydrous dichloroethane. The product **9** was isolated along with its α-anomer in 1:1 ratio after deprotection of the reaction mixture with sodium methoxide. The *erythro* configuration of 3'-nitro-2',3'-dideoxythymidine **9** during the above two synthesis was clear from its stability both under basic and acidic conditions used in the above reactions.

Treatment of 3'-nitro-2',3'-dideoxythymidine (**9**) with an aqueous solution of dimethylamine at room temperature gave a quantitative conversion to the corresponding nitronic acid salt **10.** The structure of **10** was corroborated by the absence of H-3' in its ^{1}H-NMR spectra and a more downfield shift of H2' and H2" by ~0.25 ppm compared to the parent nucleoside **9**. Further evidence regarding the sp^2 character of C3' in the nitronic acid salt **10** emerged from the four-bond H2' and H2" and H4' coupling ("W-coupling" pathway) due to the planar nature of all three substituents at C3'. On the other hand, a brief treatment of nitronic acid salt **10** with CH_3CO_2D at room temperature immidiately regenerated 3'-nitro-2',3'-dideoxythymidine (**9**) in a quantitative manner. Compound **9** was also found to be stable for 24 h at pH 3. This suggests that the 3'-*threo*-nitro-2',3'-dideoxythymidine is thermodynamically very unstable, and indeed there is no evidence to the best of our knowledge, that it is isolable as 2,3-dideoxy-3-*threo*-nitro-pentofuranoside derivative. Mosher and coworkers have also provided evidence to this end by their observation that the $NaBH_4$ promoted reduction of methyl 2,3-didehydro-2,3-dideoxy-3-nitro-5-O-trimethylacetyl-α- or -β-pentofuranoside[5,6] gave only 3-*erythro*-nitro-pentofuranoside. In view of the above findings, it is clear that the 3'-*erythro*-nitro configuration in **9** could not be possibly epimerized to 3'-*threo* configuration under any of the above reaction conditions such as oxidation in acidic media, chlorination with HCl in glacial acetic acid or in glycosylation of chlorosugar under the influence of $SnCl_4$ *(vide supra).*

Assessment of the 3'-nitro configuration using ^{1}H-NMR spectroscopy. The configuration of the 3'-nitro group in **9** as the *erythro* was also evident from a comparison[13] of chemical shifts and coupling constants with 3'-fluoro-2',3'-dideoxythymidine and 3'-azido-2',3'-dideoxythymidine (Tables 1 and 2). It is clear from the comparison of H-3' chemical shifts in **9** and 3'-fluoro-2',3'-dideoxythymidine that the electronegativities of 3'-nitro in **9** and 3'-fluoro substituent in 3'-fluoro-2',3'-dideoxythymidine are indeed comparable while the electronegativity of 3'-azido group in 3'-azido-2',3'-dideoxythymidine is much smaller. Vicinal $^3J_{HH}$ coupling constants are known to be much more sensitive on the electronegativities of substituents and are therefore much more complex to compare particularly amongst the endocyclic couplings. We have however performed a pseudorotational analysis of all endocyclic $^3J_{HH}$ coupling constants in 3'-nitro-2',3'-dideoxythymidine **9** using PSEUROT programme[12,14] considering that the 3'-nitro-2',3'-dideoxypentose moiety in **9** exists in a two-state north (2'-*exo*, 3'-*endo*) $\rightleftarrows$ south (2'-*endo*, 3'-*exo*) equillibrium. These PSEUROT calculations with the phase angle (P) and puckering amplitude (Ψ_m) of the north sugar being constrained at 9.5° and 35°, respectively, have shown that the percentage of south pseudorotamer population in the two state north (N) $\rightleftarrows$

Table 1: Chemical shifts* of 3'-nitro-2',3'-dideoxynucleosides and their comparison with 3'-fluorothymidine, 3'-azidothymidine and 3'-aminothymidine at ambient temperature.

Compound	Chemical shift (δ)									
	H1'	H2'	H2"	H3'	H4'	H5'	H5"	Me	H5	H6
9	6.32	2.60	3.08	5.33	4.58	3.84	3.82	1.83	---	7.60
10	6.28	2.85	3.24	---	4.50	4.04	3.84	1.82	---	7.72
3'-Fluorothymidine	6.29	2.32	2.58	5.28	4.32	3.76	3.74	1.83	---	7.60
3'-Azidothymidine	6.20	2.56	2.56	4.36	4.01	3.87	3.79	1.89	---	7.64
3'-Aminothymidine	6.22	2.40	2.27	3.58	3.85	3.91	3.79	1.88	---	7.68

*The ^{1}H NMR spectra were recorded in D_2O for compounds **9** & **10** using acetonitrile (δ = 2.00 ppm) as internal standard.

Table 2: Coupling constants* of 3'-nitro-2',3'-dideoxynucleosides and their comparison with other reference compounds.

Compound	Coupling constants (Hz)								
	$J_{1'2'}$	$J_{1'2"}$	$J_{2'3'}$	$J_{2"3'}$	$J_{2'2"}$	$J_{3'4'}$	$J_{4'5'}$	$J_{4'5'}$	$J_{5',5"}$
9	7.6	6.5	8.1	3.5	15.1	4.0	3.6	4.1	12.6
10**	7.6	6.8	---	---	18.4	---	3.7	2.6	12.4
3'-Fluorothymidine	9.1	5.7	5.3	1.5	14.9	1.5	4.3	4.3	12.0
3'-Azidothymidine	6.4	6.4	6.9	6.9	0	5.4	3.5	4.6	12.6
3'-Aminothymidine	4.7	7.2	7.8	7.4	14.1	6.4	2.1	3.8	11.2

* Solvents: D_2O for compounds **9** & **10**. Acetonitrile was used as internal standard (δ = 2.00 ppm) in D_2O.
**$J_{2',4'}$ = 3.1; $J_{2",4'}$ =1.6 Hz

south (S) equillibrium, overwhelmingly predominates (77-79% S). The P_S and Ψ_m of the South conformer were found to be -154° and 30°, respectively. Results of these calculations and their comparison with those of 3'-fluoro-2',3'-dideoxythymidine and 3'-azido-2',3'-dideoxythymidine are shown in Table 3. Table 3 also shows that the relative distribution of γ^+, γ^t and γ^- populations around the staggered exocyclic C4'-C5' bond in 3'-nitro-2',3'-dideoxythymidine (**9**) were also in favour of γ^+ populations (53-59%) which is also comparable to those of 3'-fluoro-2',3'-dideoxythymidine (49%) and 3'-azido-2',3'-dideoxythymidine (54%). The rotational preference around C1'-N1 bond [*syn* ⇄ *anti* orientation (χ)] in **9** was probed via the vicinal ^{13}C-^1H coupling constants, $^3J_{H1',C2}$ and

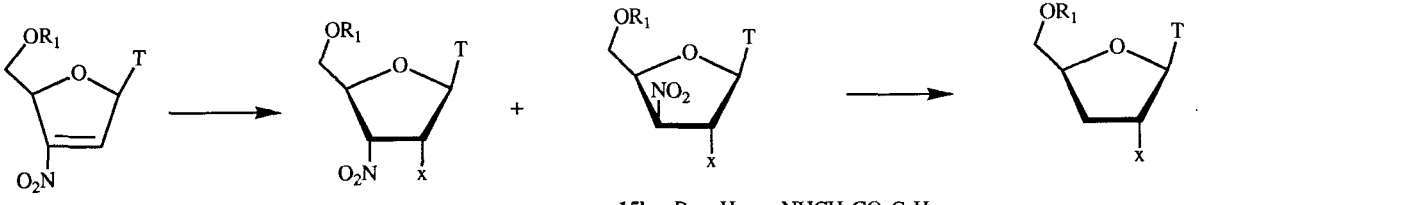
Table 3: Conformational parameters of 3'-nitro-2',3'-dideoxynucleosides in comparison with other reference compounds

Compound	% S	γ^+ %	γ^- %	γ^t %	P_N	Ψ_m (N)	P_S	Ψ_m (S)	χ
9	77	59	14	27	9.5*	35.0*	156	30	-160^0
3'-fluorothymidine	90	49	24	27	-14.0#	40.5#	151	34	$-154^{0\#}$
3'-azidothymidine	50	55	13	32	21.6#	40.0#	160	35.5	$-159^{0\#}$

* were constrained in the PSEUROT calculations as described in ref. 12; # taken from ref. 13

$^3J_{H1',C6}$, using the Karplus equation as proposed by Lemieux[15] and Davies[16] : [$^3J_{H1',C2}$ = 6.7 $\cos^2\phi$-1.3 $\cos\phi$]. The translation of the experimental coupling constants for $^3J_{H1',C2}$ = 2.4 Hz and $^3J_{H1',C6}$ = 4.6 Hz in **9** gives χ values of either -166° or -240°. This means that thymine base in **9** adopts *anti* orientation which is normal for pyrimidine nucleosides. The comparison of these data show that although the global conformation of 3'-nitro-2',3'-dideoxythymidine (**9**) and 3'-fluoro-2',3'-dideoxythymidine are quite remarkably similar, but their abilities to inhibit the HIV production in MT4 cell culture is distinctly different: **9** is almost 100 fold less active than 3'-fluoro-2',3'-dideoxythymidine[17].

*Michael addition reactions of 3'-nitro-α,β-olefin **6** and **7**.* The nitro group conjugated to a double bond acts as a strong electron-withdrawing group, as in nitro-olefins [O_2N-C^{α}=C^{β}], and promote nucleophilic addition reactions at the β-carbon[18-23,46]. The unique electron-deficient character of nitro-olefins make them also powerful dienophiles which have been also exploited to give varieties of cycloaddition products under various conditions[47-50]. Herein we report the use of the *3'-nitro-olefin function* in a nucleoside for the first time, as in **6**, as a general intermediate in nucleophilic addition reactions, owing to the inherent electron-deficient character at its C-2', to give varieties of 2'-substituted-3'-nitro-nucleosides with a variety of nitrogen, oxygen and carbon nucleophiles (Scheme 2). Earlier, it has been shown from this laboratory that various 2',3'-unsaturated-nucleosides conjugated with 3'-electron-withdrawing groups, as in 2',3'-ene-3'-nitrile[24], 2',3'-ene-3'-(phenylsulfonyl)[25] and 2',3'-ene-3'-(phenylselenone)-β-D-nucleosides[26,27], provide efficient means to functionalize the 2'- and 3'- carbons as a powerful alternative to standard S_N2 type reactions. The advantage of Michael addition reactions on 3'-nitro-olefin **6**, and its 5'-hydroxy analogue **7** is that the 3'-nitro group in 2'-substituted-3'-nitro-nucleosides (Scheme 2) is easily removable to produce 3'(2')-(di)deoxy-2'-substituted-nucleosides *(vide infra)* upon treatment with tributyl tinhydride in benzene. The other advantage of the



6: R_1 = MMTr
7: R_1 = H

11: R_1 = H, x = MeNH
12: R_1 = H, x = t-BuNH
13: R_1 = MMTr, x = $PhCH_2NH$
14: R_1 = H, x = $PhCH_2NH$
15a: R_1 = H, x = $NHCH_2CO_2C_2H_5$
16: R_1 = H, x = $NHCH(CH_3)CO_2CH_3$
17: R_1 = H, x = $NHCH(CH_2Ph)CO_2CH_3$
18: R_1 = MMTr, x = OCH_3
19: R_1 = H, x = OCH_3
20: R_1 = MMTr, x = OC_2H_5
21: R_1 = H, x = OC_2H_5
22: R_1 = MMTr, x = $OCH_2CH_2OCH_3$
23: R_1 = H, x = $OCH_2CH_2OCH_3$
24: R_1 = MMTr, x = $OCH_2CH{=}CH_2$
25: R_1 = H, x = $OCH_2CH{=}CH_2$
26a: R_1 = MMTr, x = $CH(CO_2Me)_2$
27a: R_1 = H, x = $CH(CO_2Me)_2$
28: R_1 = MMTr, x = $CH(CH_3CO)_2$
29: R_1 = H, x = $CH(CH_3CO)_2$
30a: R_1 = MMTr, x = $CH(COCH_3)CO_2Me$
31a: R_1 = H, x = $CH(COCH_3)CO_2Me$
32a: R_1 = MMTr, x = 1-Cyclohexa-2-nonyl
33a: R_1 = H, x = 1-Cyclohexa-2-nonyl

15b: R_1 = H, x = $NHCH_2CO_2C_2H_5$
26b: R_1 = MMTr, x = $CH(CO_2Me)_2$
27b: R_1 = H, x = $CH(CO_2Me)_2$
30b: R_1 = MMTr, x = $CH(COCH_3)CO_2Me$
31b: R_1 = H, x = $CH(COCH_3)CO_2Me$
32b: R_1 = MMTr, x = 1-Cyclohexa-2-nonyl
33b: R_1 = H, x = 1-Cyclohexa-2-nonyl

T = Thymine-1-yl

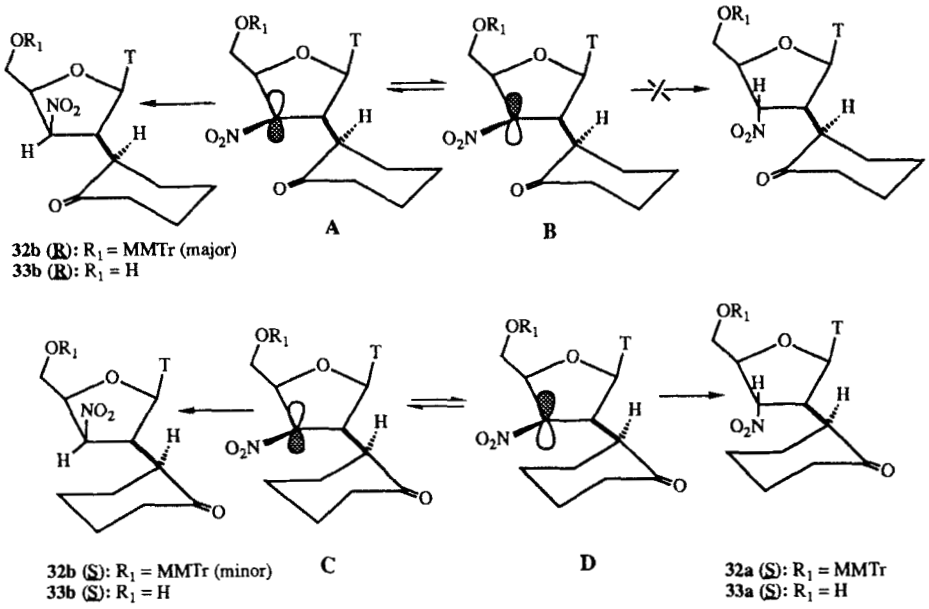
34: R_1 = MMTr, x = OC_2H_5
35: R_1 = H, x = OC_2H_5
36: R_1 = MMTr, x = OCH_3
37: R_1 = H, x = OCH_3
38: R_1 = MMTr, x = $OCH_2CH_2OCH_3$
39: R_1 = H, x = $OCH_2CH_2OCH_3$
40: R_1 = MMTr, x = $CH(CO_2Me)_2$
41: R_1 = H, x = $CH(CO_2Me)_2$
42: R_1 = MMTr, x = $CH(COCH_3)CO_2Me$
43: R_1 = H, x = $CH(COCH_3)CO_2Me$
44: R_1 = MMTr, x = 1-Cyclohexa-2-nonyl
45: R_1 = H, x = 1-Cyclohexa-2-nonyl
46: R_1 = MMTr, x = $CH(COMe)_2$
47: R_1 = H, x = $CH(COMe)_2$

Scheme 2

3'-nitro group is that it can be subsequently reduced in 2'-substituted-3'-nitro-nucleosides to introduce various other functions for structure-activity studies in medicinal chemistry.

Reaction of 3'-nitro-α,β-olefin 6 and 7 with primary amines [28]. Treatment of **7** with aqueous methylamine or t-butylamine in THF at room temperature gave the corresponding *cis*-products: 2', 3'-dideoxy-2'-(R)-methylamino-3'-(S)-nitrothymidine **11** (77%) and 2', 3'-dideoxy-2'-(R)-t-butylamino-3'-(S)-nitrothymidine **12** (91%). Treatment of **6** with benzylamine in THF also gave exclusively *cis*-addition product 2',3'-dideoxy-2'-(R)-benzylamino-3'-(S)-nitrothymidine **13** (82%).which upon treatment with 80% aqueous acetic acid at room temperature gave deprotected 2', 3'-dideoxy-2'-(R)-benzylamino-3'-(S)-nitro-thymidine **14** (77%). Treatment of **7** with L-alanine methyl ester hydrochloride or L-phenylalanine methyl ester hydrochloride in presence of triethylamine in THF gave corresponding *cis* addition product **16** (87%) and **17** (79%), respectively, but a treatment of **7** with glycine ethyl ester hydrochloride under an identical condition gave an inseparable mixture of *cis* adduct **15a** and *trans* adduct **15b** in 4 : 1 ratio (NMR) in a total yield of 81%.

Reaction of 3'-nitro-α,β-olefin 6 with Carbon nucleophiles. A treatment of 3'-nitroolefin **6** with an excess of potassium salt of dimethyl malonate gave 2',3'-dideoxy-3'-(S)-nitro-2'-(R)-(α-dimethylmalonate) **26a** (40 %) and 2',3'-dideoxy-3'-(R)-nitro-2'-(R)-(α-dimethyl malonate) **26b** (56 %). Similarly, a reaction of **6** with the conjugate base of methyl acetoacetate gave a mixture *trans* **30b** (59 %) and *cis* **30a** (37 %) derivatives, while the treatment of **6** with an excess potassium salt of acetyl acetone gave 2', 3'-dideoxy-3'-(S)-nitro-2'-(R)-(α-acetylacetone) **28** (56%) as a major product. Each of the 3'-epimeric compounds **30a** & **30b** gave an inseparable diastereomeric mixture due to the chiral centre in the 2'-substituent, $^{*}\underline{C}H(COOCH_3)COCH_3$. Removal of 3'-nitro group in **30b** gave **42** as a mixture of two diastereoisomers which was evident from two sets of anomeric sugar protons in the NMR spectra (see experimentals). The reaction of compound **6** with morpholino-1-yl cyclohexene[25,29] in THF, followed a hydrolytic workup, gave the corresponding *xylo* (**32b**) and *ribo* (**32a**) nucleosides in 53 and 17 % yield, respectively. An NMR examination of TLC pure **33a** and **33b** revealed that **33b** is still a mixture of two compounds due to the chirality of the (cyclohexanone-1-yl) moiety at C2', 2'-[$^{*}\underline{C}H$-$(CH_2)_4$-C=O], while **33a** was found to be a single diastereoisomer. Clearly, these results suggest that the protonation of chiral 3'-nitro-α-carbanion of either [A], [B], [C] or [D] (Scheme 3) is stereoelectronically controlled. When the 3'-carbanion can be protonated only at the α-face, the R stereoisomer of 2'-(cyclohexanone-1-yl) moiety in the carbanion [A] exert more stringent stereoelectronic control than the corresponding S isomer in



Scheme 3

carbanion [C] as evident in the relative distribution of *trans*-isomers : **32b**(R) (75%) versus **32b**(S) (25%). The reason for this is that the *ketone function* in the 2'-(R)-(cyclohexanone-1-yl) moiety is stereochemically located near the 3'-carbanion in [A] and therefore it can assist in the quenching of the 3'-carbanion in [A] by binding to a mole of water and delivering the proton in a thermodynamically prefered manner giving the **32b**(R)(75%) as the major product, while the 2'-(S)-(cyclohexanone-1-yl) in carbanion [C] has the ketone function sterically turned away from the 3'-carbanion and can not quench it effectively and therefore **32b**(S)(25%) is only a minor product formed. On the other hand, when the 3'-carbanion is protonated at the β-face to give the *cis* -addition product, the steric orientation (*ie*. R or S configuration) of 2'-cyclohexanonyl moiety in carbanion [B] or [D] is an important factor that contribute in the minimization of stereoelectronic repulsion between two *cis*-substituents at 2' and 3' (*i.e.* both the 3'-nitro and 2'-cyclohexanonyl groups are at the α-face). Clearly, it is the 2'-(S)-(cyclohexanone-1-yl) moiety in carbanion [D] which can only fulfil this stereoelectronic criteria, and as a result only diastereomer **32a**(S) is formed as the sole product.

Reaction of 3'-nitro-α,β-olefin **6** *with Alcohols* : Treatment of 3'-nitro-olefin **6** with alkoxides (sodium methoxide, -ethoxide, -2-methoxyethoxide and -allyloxide) at ~5 °C

gave exclusively the corresponding *cis*- adducts **18** (82 %), **20** (86 %), **22** (74 %), **24** (74 %), respectively. Treatment of **6** with methanol in presence of NaH (2 equiv) at -30 °C gave however a 2:3 mixture (NMR) of corresponding *cis* and *trans* adducts.

Removal of 3'-nitro group from 2'-Carbon- or Oxygen-substituted-3'-nitro-nucleosides ***18, 20, 22, 26b, 28, 30b and 32b:*** The displacement of a tertiary nitro group by hydrogen is well documented[30,31]. The secondary nitro group could also be normally denitrated but in some instances this denitration was not easily possible[32]. When 2'-*C*-branched *trans* isomers (**26b**, **30b**, and **32b**) were treated with tributyl tinhydride in presence of α, α' azoisobutyronitrile (AIBN) in dry benzene at 70 °C, they were readily denitrated[31] in an yield of 50-85%, while the denitration of 2'-*C*-branched *cis* isomer **28**, under the same condition, gave poorer yield (~30%). The *cis* isomers of 2'-alkoxy substituted nucleosides (**18**, **20**, **22**) could be persuaded to undergo denitration only with a large excess of tributyl tinhydride giving poor yields (5-10 %) of denitrated products (**36**, **34**, and **38**) along with several by-products. During tributyl tinhydride treatment of **18**, **20**, and **22**, the nitro group was reduced to the corresponding oximes **48** (35 %), **52** (41 %) and **54** (34 %). The structure of the oximes **48**, **52** and **54** were evident by the coupling between H2' and H4' ($^4J_{2',4'}$ = 1.4 -1.6 Hz, "W-coupling" pathway) which arises due to coplanar nature of all three substituents at the sp^2 hybridized C-3' carbon. Also note that in 5'-hydroxy analogues **49**, **53** and **55** , the C-3' absorbs at δ 155.5, 155.7 and 155.8, respectively, suggesting its sp^2 hybridized character. The structural integrity of **48**, **52** and **54** were further based on acetylation of **48**, with acetic anhydride in pyridine at room temperature over night, to give the corresponding 3'-C=N-O-acetyl derivative **50** suggesting again the presence of 3'-C=N-OH function in the parent compound **48**.

Removal of the 5'-monomethoxy trityl group from 2',3' disubstituted nucleosides: The 4-monomethoxytrityl group was deprotected by the treatment of 80 % aqueous acetic acid at room temperature overnight to give the desired nucleosides with free hydroxyl functions. When compounds **18**, **20**, **22**, **24**, **32b**, **34**, **36**, **38**, **40**, **42**, **44**, **46**, **48**, **50**, **52** and **54** were treated with 80% aqueous acetic acid at room temperature, the corresponding 5'-deprotected compounds **19** (96 %), **21** (97 %), **23** (97 %), **25** (81 %), **33b** (97 %), **35** (90 %), **37** (86 %), **39** (90 %), **41** (95 %), **43** (91 %), **45** (85 %), **47** (95 %), **49** (91 %), **51** (76 %), **53** (90 %) and **55** (89 %) were obtained, respectively. While the acetic acid treatment of compound **26a** gave an isomeric mixture (3'-nitro "up" & "down") of **27a** (69 %) & **27b** (27 %). Similarly, compounds **26b** & **32a** gave corresponding **27b** (75 %), **27a** (16 %) and **33a** (70 %), **33b** (27 %), respectively. The compounds **28**, **30b** and **30a** gave the corresponding deprotected products **29** (70 %), **31b** (77 %) and **31a** (79 %) respectively as major products.

Determination of configuration at C-3' position: The presence of 3'-nitro group in the *xylo* in **26b** and in the *ribo* configuration in **12**, **13**, **19**, **21**, **24**, **26a** & **28** was evident through the analysis of $J_{4',5'}$ and $J_{4',5''}$ couplings in their ^{1}H-NMR spectra which gave the estimation of γ+ population across their exocyclic C-4' and C-5' bond[33-41]. The populations of rotamers $p^{\gamma+}$ about the exocyclic C-4' and C-5' bond has been estimated from the "sum rule" using the $J_{4',5'}$ and $J_{4',5''}$ coupling constants using the equation[40,41] $p^{\gamma+}= [13.3-\Sigma J_{4',5'}+ J_{4',5''}] /9.7$. The γ^+ population for **12**, **13**, **19**, **21**, **24**, **26a** and **28** were found to be above 90% suggesting the presence of *ribo* configuration in these compounds while in **26b** , the γ^+ population was found to be less than 30%. If the 3'-nitro group in compounds **12**, **13**, **19**, **21**, **24**, **26a**, and **28** were in the "up" configuration, the γ^+ population would be expected to lower than 30%[33,34,38,42] as was found in compound **26b.** Although the electronegativity of the C-3' substituent has a drastic effect on the γ^+ population[37,39,43-45] still the γ^+ rule has been found to be a valid spectroscopic procedure to determine the configuration of the C-3' substituent[24-26,33-41,43-45]. The 3' substituent in the "down" configuration produces a high γ^+ population (< 50%), whereas the 3' substituent in the "up" configuration produces a shift of γ^+ population (>30%)[24-26,33-41,43-45]. Additionally, further distinction between *cis* and *trans* -adducts owing to their respective R & S configurations at C-3' was determined on the basis of the following observations in ^{1}H-NMR spectra: (1) The H-1' was always more deshielded in *cis*-isomers than in *trans*-isomers. (2) The $J_{1',2'}$ of *trans*-isomer was always smaller than corresponding *cis*-isomers. (3) In the *cis*-isomers **26a** and **32a**, the two 5'-methylene protons were well separated, compared to the *trans*-isomers **26b** and **32b**. (4) The H-6 of thymine was more deshielded in *trans* isomers **26b** and **32b** compared to the *cis* isomers **26a** and **32a**. (5) The chemical shift of H-3' in *trans*-isomers **26b**, **27b** , **30b**, **31b**, **32b** and **33b** were always more up-field than the *cis*-isomers **26a**, **27a** , **30a**, **31a**, **32a** and **33a**. (6) The $J_{2',3'}$ of *trans*-isomers **27b** and **33b** were always smaller than corresponding $J_{3',4'}$, while the $J_{2',3'}$ of *cis*-isomers **27a** and **33a** were bigger than corresponding $J_{3',4'}$.

Experimental

^{1}H-NMR spectra were recorded (in δ scale) with Jeol 90Q and JNM-GX 270 spectrometer at 90 and 270 MHz, respectively, using TMS (0.0 ppm) as reference. ^{13}C-NMR were recorded at 22.5 MHz using both ^{1}H-decoupled or INEPT modes. IR spectra were recorded with Perkin-Elmer 298 spectrometer. UV absorbtion spectra were recorded with a Varian-Carry 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 separation were carried out using Merck G60 silica gel.

1-[5-O-(MMTr)-2-O-pivaloyl-β–D-*xylo*furanosyl]thymine (3). Compound **2** (5 g, 9.4 mmol) was evaporated with pyridine, redissolved in dry pyridine (40 ml), cooled in ice-salt bath. Pivaloyl chloride (1.24 ml, 10.1 mmol) was added. The reaction mixture was stirred in the ice-salt bath for 3 h and poured slowly with stirring into ice-water, and the solid thus formed was collected by filtration, subjected to silica gel column chromatography to give **3** (5.5 g, 94 %). ^{1}H-NMR ($CDCl_3$): 7.60-6.90 (m, 15 H) arom & H-6; 5.85 (d, $J_{1',2'}$ = 1.7 Hz, 1H) H-1'; 5.11 (d, 1H) H-2'; 4.16 (m, 2H) H-3' & H-4'; 3.77 (s, 3H) OMe; 3.6 (m, 2H) H-5', H-5"; 1.77 (d, 1H) 5-CH_3; 1.20 (s , 9 H) Piv; ^{13}C-NMR ($CDCl_3$): 110.2 (s) C-5; 89.7 (d, J_{CH} = 169.6 Hz) C-1'; 87.0 (s) MMTr; 81.8 (d, J_{CH} = 158.4 Hz) C-2'; 81.6 (d, J_{CH} = 158.4 Hz) C-3'; 78.3 (d, J_{CH} = 157.3 Hz) C-4'; 61.7 (t, J_{CH} = 145.5 Hz) C-5'; 55.0 (q, J_{CH} = 143.8 Hz) OMe; 41.6 (s) C-piv; 26.7 (q, J_{CH} = 127.7 Hz) Piv; 12.2 (q, J_{CH} = 129.2 Hz) 5-CH_3. MS (FAB$^-$): cal. for (M-H)$^-$ 613.2550, found 613.2589. MS (FAB$^-$): cal. for (M-$C_5H_{10}O_2$)$^-$ 511.1869, found 511.1872. UV (EtOH): [pH 7] λ_{max} = 265 nm (ε = 10100); [pH 2] λ_{max} = 264 nm (ε = 10400); [pH 12] λ_{max} = 269 nm (ε = 8600).

1-[5-O-(MMTr)-2-O-pivaloyl-β-D-*erythro*-pentofuran-3-ulosyl]thymine (4). Compound **3** (5.5 g, 8.9 mmol) in dichloromethane (50 ml) was oxidised by heating at reflux with pyridine dichromate (PDC) (7.34 g, 19.6 mmol) and acetic anhydride (2.93 ml, 31.1 mmol) for 2 h. The reaction mixture was cooled to room temperature and diluted with ether (150 ml), filtered through a short column of silica gel. The eluents were removed by co-evaporation with toluene to give **4** (5.2 g, 95 %). ^{1}H-NMR ($CDCl_3$): 9.53 (br, 1H) NH; 7.60 (q, 1H) H-6; 7.55-6.7 (m, 14 H) arom; 6.47 (d, $J_{1',2'}$ = 7.5 Hz, 1H) H-1'; 5.33 (d, 1H) H-2'; 4.42 (m, 1H) H-4'; 3.76 (s, 3H) OMe; 3.62 (dd, $J_{4',5'}$ = 1.7 Hz, $J_{5',5"}$ = 10.5 Hz, 1H) H-5'; 3.42 (dd, $J_{4',5"}$ = 2.2 Hz, 1H) H-5"; 1.39 (d, 3H) 5-CH_3; 1.27 (s, 9 H) Piv; ^{13}C-NMR ($CDCl_3$): 109.7 (s) C-5; 86.7 (s) MMTr; 82.0 (d, J_{CH} = 168.4 Hz) C-1'; 80.5 (d, J_{CH} = 151.6 Hz) C-4'; 75.0 (d, J_{CH} = 148.3 Hz) C-2'; 63.9 (t, J_{CH} = 145.5 Hz) C-5'; 55.0 (q, J_{CH} = 143.8 Hz) OMe; 41.5 (s) C-Piv; 30.8 (q, J_{CH} = 127.7 Hz) Piv; 11.6 (q, J_{CH} = 128.4 Hz) 5-CH_3.

5'-O-(MMTr)-2'-O-pivaloyl-3'-oximinothymidine (5). Compound **4** (5.2 g, 8.4 mmol) was treated with hydroxylamine hydrochloride (875 mg, 12.6 mmol) in pyridine (100 ml). The reaction mixture was stirred at room temperature overnight, the solvent was removed in vacuo. The residue was dissolved in dichloromethane(200 ml) and washed with water (2x20 ml). The organic phase was evaporated to dryness and purified by silica gel column chromatography to give **5** (4.23 g, 80 %) as E/Z isomeric mixture (65:35 from NMR): ^{1}H-NMR ($CDCl_3$): (major isomer): 7.68-6.78 (m, 15 H) arom, H-6; 6.26 (d, $J_{1',2'}$ = 7.3 Hz, 1H) H-1'; 6.14 (dd, $J_{2',4'}$ = 1.7 Hz, 1H) H-2'; 5.08 (m, 1H) H-4'; 3.93 (dd, $J_{4',5'}$ = 1.7 Hz, $J_{5',5"}$ = 10.4 Hz, 1H) H-5'; 3.26 (dd, $J_{4',5"}$ = 1.6 Hz, 1H) H-5"; 3.76 (s, 3H) MMTr; 1.29 (d, 3H) 5-CH_3; 1.22 (s, 9H) piv. Minor isomer: 7.68-6.78 (m, 15 H) arom, H-6; 6.19 (d, $J_{1',2'}$ = 5.6 Hz, 1H) H-1'; 5.99 (dd, $J_{2',4'}$ = 1.6 Hz, 1H) H-2'; 4.95 (m, 1H) H-4'; 3.61 (dd, $J_{4',5'}$ = 3.0 Hz, $J_{5',5"}$ = 10.7 Hz, 1H) H-5'; 3.57 (dd, $J_{4',5"}$ = 2.0 Hz, 1H) H-5"; 1.41 (d, 3H) 5-CH_3; 1.22 (s, 9H) piv. MS (FAB$^-$): cal. for (M-$C_5H_{10}O_2$)$^-$ 524.1822, found 524.1840 (Piv protection from 2' end was fragmented). UV (EtOH): [pH 7] λ_{max} = 265 nm (ε = 9200); [pH 2] λ_{max} = 263 nm (ε = 9400); [pH 12] λ_{max} = 263nm (ε = 10300).

1-[5-O-(MMTr)-2, 3-dideoxy-3-nitro-β–D-*glycero*-pent-2-enofuranosyl]thymine (6). Compound **5** (2.64 g, 4.2 mmol) was dissolved in dry acetonitrile (40 ml), and then Na_2HPO_4 (11.9 g, 84 mmol) and urea (628 mg, 10.5 mmol) were added. Trifluroperacetic

acid (6.4 ml, 19.2 mmol) in acetonitrile (10 ml) was added dropwise during 30 min at 0° C and stirred for 3 h at the same temperature. The reaction mixture was poured into cold aqueous solution of $NaHCO_3$ and extracted with dichloromethane (3 x 40 ml). The organic phase was washed with H_2O (2 x 40 ml), dried over $MgSO_4$. The organic phase was evaporated and the residue was separated on a silica gel column to give **6** (1.73 g, 76 %). ^{1}H-NMR ($CDCl_3$): 9.64 (br, 1H) NH; 7.68 (d, 1H) H-6; 7.6-6.78 (m, 16 H) arom, H-1' & H-2'; 5.23 (m, 1H) H-4'; 3.79 (s, 3H) OMe; 3.7 (dd, $J_{4',5'}$ = 2.7 Hz, 1H) H-5'; 3.6 (dd, $J_{5',5''}$ = 11.1 Hz, 1H) H-5"; 1.04 (d, 3H) 5-CH_3. ^{13}C-NMR ($CDCl_3$): 112.4 (s) C-5; 87.0 (s) MMTr; 85.5 (d, J_{CH} = 180.9 Hz) C-1'; 81.0 (d, J_{CH} = 159.5 Hz) C-4'; 62.0 (t, J_{CH} = 147.2 Hz) C-5'; 54.5 (q, J_{CH} = 147.2 Hz) OMe; 10.6 (q, J_{CH} = 130 Hz) 5-CH_3. MS (FAB$^-$): cal. for (M-H)$^-$ 540.1771, found 540.1777. IR ($CHCl_3$): 1530 cm^{-1}, 1380 cm^{-1} (NO_2). UV (EtOH): [pH 7] λ_{max} = 265 nm.

1-[2, 3-Dideoxy-3-nitro-β-D-*glycero*-pent-2-enofuranosyl]thymine (7). Compound **6** (1.08 g, 2 mmol) was treated with 80% aqueous acetic acid (40 ml) at room temperature for 5 h. All volatiles were removed by co-evaporation with toluene and ethanol.The residue was purified on a silica gel column to give **7** (502 mg, 94 %) ^{1}H-NMR ($CDCl_3$+CD_3OD): 7.86 (q, $J_{CH3, H6}$ =1.1 Hz, 1H) H-6; 7.16 (ddd, $J_{1',2'}$ = 1.8 Hz, $J_{1',4'}$ =1.8 Hz, $J_{1',5''}$ = 0.5 Hz, 1H) H-1'; 7.06 (dd, $J_{2',4'}$ = 3.8 Hz, 1H) H-2'; 5.18 (m, 1H) H-4'; 4.09 (dd, $J_{4',5'}$ = 1.8 Hz, $J_{5',5''}$ = 12.7 Hz, 1H) H-5'; 3.81 (ddd, $J_{4',5''}$ = 1.8 Hz, 1H) H-5"; 1.82 (d, 3H) 5-CH_3; ^{13}C-NMR ($CDCl_3$+ CD_3OD): 138.9 (d J_{CH} = 183 Hz) C-6; 111.4 (s) C-5; 88.0 (d, J_{CH} = 177.5 Hz) C-1'; 84.5 (d) C-4'; 62.3 (t, J_{CH} = 144.9 Hz) C-5'; 12.7 (q, J_{CH} = 129 Hz) 5-CH_3. UV (EtOH): [pH 7] λ_{max} = 265 nm (ε = 12200); [pH 2] λ_{max} = 261 nm (ε = 11800); [pH 12] λ_{max} = 257 nm (ε = 16400). MS (FAB$^-$): cal. for (M-H)$^-$ 268.0570, found 268.0583.

5'-O-(MMTr)-2',3'-dideoxy-3'-nitrothymidine (8). Compound **6** (300 mg, 0.55 mmol) was treated with $NaBH_4$ (95 mg, 2.5 mmol) in ethanol (25 ml) at 0 °C for 2 h. The reaction mixture was neutralized with acetic acid, extracted with dichloromethane (2x30 ml). The organic layer was washed with water (2x15 ml), dried over $MgSO_4$, filtered and evaporated to dryness. The residue was purified on a silica gel column chromatography to give **8** (268 mg, 89 %). ^{1}HMR ($CDCl_3$): 8.23 (br, 1H) NH; 7.51 (d, $J_{CH3, H6}$ = 1.1 Hz, 1H) H-6; 7.38-6.78 (m, 14 H) arom; 6.47 (dd, $J_{1',2'}$ = 8.1 Hz, $J_{1',2''}$ = 5.9 Hz, 1H) H-1'; 5.21 (m, 1H) H-3'; 4.56 (m, 1H) H-4'; 3.79 (s, 3H) OMe; 3.67 (dd, $J_{4',5'}$= 2.8 Hz, $J_{5',5''}$ = 10.9 Hz, 1H) H-5'; 3.46 (dd, $J_{4',5''}$ = 2.7 Hz, 1H) H-5"; 3.10 (ddd, $J_{2',2''}$ = 14.7 Hz, $J_{2'',3'}$ = 2.5 Hz 1H) H-2"; 2.53 (ddd, $J_{1',2'}$ = $J_{2',3'}$= 8.1 Hz, 1H) H-2'; 1.49 (d, 3H) 5-CH_3. ^{13}C-NMR ($CDCl_3$): 163.9 (s) C-4; 150.2 (s) C-2; 134.9 (d) C-6; 111.6 (s) C-5; 87.3 (s) MMTr; 85.0, 84.9 (2xd, J_{CH} = 166.2 Hz) C-1' & C-3'; 81.8 (d, J_{CH} = 150.5 Hz) C-4'; 63.3 (t, J_{CH} = 144.4 Hz) C-5'; 55.0 (q, J_{CH} = 143.8 Hz) MMTr; 36.3 (t, J_{CH} = 136.5 Hz) C-2'; 11.6 (q, J_{CH} = 130.3 Hz) 5-CH_3. MS (FAB$^-$): cal. for (M-H)$^-$ 542.1927, found 542.1902. IR ($CHCl_3$): 1550 cm^{-1} (NO_2). UV (EtOH): [pH 7] λ_{max} = 266 nm.

2', 3'-Dideoxy-3'-nitrothymidine (9). *Method A.*: Compound **8** (50 mg, 0.09 mmol) was treated with 80 % aqueous acetic acid (1 ml) at room temperature for 6 h. All volatilematters were removed in vacuo by co-evaporation with toluene, ethanol and carbontetrachloride.The residue was purified on a silica gel column chromatography to give **9** (22 mg, 89 %). The ^{1}H-NMR data is given in Tables 1 and 2. ^{13}C-NMR (D_2O): 166.8 C-4; 152.0 (s) C-2; 137.8 (d, J_{CH} = 182.4 Hz) C-6; 112.0 (s) C-5; 86.0 (d, J_{CH} = 172.3 Hz) C-1', 85.1 (J_{CH} = 153.0 Hz) C-4'; 84.3, C-3'; 61.9 (d, J_{CH} = 143.0 Hz) C-5'; 35.4 (d, J_{CH} = 137 Hz); C-2'; 12.3 (q, J_{CH} = 126.2 Hz); 5-CH_3. MS (FAB$^-$): cal. for (M-thymine)$^-$ 147.0532, found 147.0631. UV (EtOH): [pH 7] λ_{max} = 266 nm (ε = 10800); [pH 2] λ_{max} = 265 nm (ε = 10800); [pH 12] λ_{max} = 258 nm (ε = 14900).

Method B: To the mixture containing 1-(5-O-(p-toluoyl)-3-amino-2,3-dideoxy-β-D-*erythro*-pentofuranosyl)thymine (0.6 g, 1.67 mmol), Na_2HPO_4 (0.5 g, 3 mmol) in acetonitrile (5 ml) at 0° C was added a solution of trifluoroperacetic acid (1.2 ml, 3.6 mmol) in acetonitrile during 0.5 h under stirring. The reaction mixture was allowed to warm to room temperature, after 30 min it was diluted with water (5 ml) and extracted with chloroform (3 x 10 ml). The organic layer was washed with 1 % solution of aqueous $NaHCO_3$ (10 ml) and water (10 ml), dried over $MgSO_4$ and evaporated to dryness. The residue was purified on analytical TLC plates (5 elutions, 5% of hexane in $CHCl_3$) to give 1-(5-O-(p-toluoyl)-3-nitro-2,3-dideoxy-β-D-*erythro*-pentofuranosyl)thymine (9 mg, 1.4 %). ^{1}H-NMR($CDCl_3$): 8.13 (br, 1H) NH; 7.91-7.88 (m, 2H) tol; 7.29-7.26 (m, 2H) tol; 7.1 (d, 1H) H-6; 6.28 (dd, $J_{1',2'}$ = 7.3 Hz, $J_{1',2''}$ = 6.2 Hz, 1H) H-1'; 5.33 (m, 1H) H-3'; 4.8 (m, 1H) H-4'; 4.79 (dd, $J_{4',5'}$ = 3.7 Hz, $J_{5',5''}$ = 12.1 Hz, 1H) H-5'; 4.62 (dd, $J_{4',5''}$ = 3.4 Hz, 1H) H-5''; 3.24 (ddd, $J_{2'',3'}$ = 3.2 Hz, $J_{2',2''}$ = 14.8 Hz, 1H) H-2''; 2.52 (ddd, $J_{2',3'}$ = 8.8 Hz, 1H) H-2'; 2.43 (d, 3H) tol-CH_3; 1.71 (d, 3H) 5-CH_3. ^{13}C-NMR ($CDCl_3$): 165.7 (s) C=0 of Tol; 162.8 (s) C-4; 149.5 (s) C-2; 144.8, 129.4 Tol; 135.0 (d) C-6; 111.7 (s) C-5; 86.4 (d) C-1'; 84.8 (d) C-4' ; 80.8 (d) C-3'; 63.7 (t) C-5'; 36.2 (d) C-2'; 21.6 (q) Me of Tol; 12.1 (q) 5-CH_3. This compound was subsequently deprotected using 0.1N solution of MeONa in methanol (1.0 ml) at room temperature, followed by neutralization with 50% aqueous acetic acid (0.5 ml). A standard work up and purification produced **9** (4.4 mg, 75 %).

Method C. Methyl 2, 3-didehydro-3-nitro-5-O-(p-toluoyl)-β-D-*erythro*-pentofuranoside[5] (100 mg, 0.34 mmol) was treated with 5% solution of HCl in glacial acetic acid (3 ml) and kept at 5° C overnight. The solution was evaporated, twice co-evaporated with toluene and purified on silica gel column to give anomeric mixture of 1-chloro-5-O-(p-toluoyl)-3-nitro-2,3-dideoxy-α,β-D-*erythro*-pentofuranose (α:β : 1:1) (82 mg, 80.5 %). ^{1}H-NMR ($CDCl_3$): 7.95 (d, 2H) Tol (β); 7.89 (d, 1H) Tol (α); 7.24 (m, 6H) Tol and H-6 (α and β); 6.49 (dd, $J_{1',2'}$ = 4.1 Hz; $J_{1',2''}$ = 4.1 Hz, 1H) H-1' (β); 6.39 (d, $J_{1',2'}$ = 4.5 Hz, 1H) H-1' (α) ; 5.33 (m, 1H) H-3' (β); 5.26 (m, 1H) H-3' of (α); 4.99 (m, 1H) H-4' (a); 4.91 (m, 1H) H-4' (β) ; 4.51 (m, 4H) H-5' and H-5'' (α and β); 3.08 (m, 2H) H-2'' (α and β); 2.63 (m, 2H) H-2' (α and β); 2.40 (s, 6H) Me of Tol (α and β). Then to the stirring solution of α/β-chlorosugar, 2,4-bistrimethylsilylthymine (130 µl, 0.5 mmol), in dry dichloroethane (2 ml) was added trimethylsilyl trifluoromethanesulphonate (130 µl, 0.67 mmol) and the mixture was heated at 50° C during 1h. The reaction mixture was neutralized with 3 ml of saturated solution of sodium hydrogen carbonate, evaporated to dryness, co-evaporated with toluene and extracted with $CHCl_3$ (3 x 10 ml). The combined extracts were evaporated to dryness and the residue was treated with 0.1N solution of MeONa in methanol (2.0 ml) under stirring followed by neutralization with 50% aqueous acetic acid (0.5 ml), evaporation and separation on silica gel to give **9** (9.7 mg, 13.6%) and 7.6 mg (10.2 %) of its α-anomer with more lower R_f level. Compound **9** prepared by this procedure was identical in all respects to the specimen prepared by other routes. ^{1}H-NMR of α-anomer (D_2O): 7.55 (q, 1H) H-6; 6.09 (dd, $J_{1',2'}$ = 6.5 Hz; $J_{1',2''}$ = 4.6 Hz) H-1'; 5.26 (m, $J_{2',3'}$= 7.0 Hz; $J_{2'',3}$= 4.5 Hz, 1H) H-3'; 5.05 (m, $J_{3',4'}$ = 3.9 Hz, 1H) H-4'; 3.81 (dd, $J_{4',5'}$ = 3.3 Hz, $J_{5',5''}$ = 12.6 Hz, 1H) H-5'; 3.74 (dd, $J_{4',5''}$ = 4.2 Hz, 1H)H-5''; 3.03 (m, 2H) H-2', H-2''; 1.84 (d, 3H) 5-CH_3.

1-[2,3-Dideoxy-2-methylamino-3-nitro-β–D-*ribo*furanosyl]thymine (11). Compound **7** (270 mg, 1 mmol) was treated with methylamine (40 %, 1 ml) in tetrahydrofuran (10 ml) at room temperature for 2 h. All volatile matters were removed in vacuo. The residue was separated on a silica gel column to give **11** (230 mg, 77 %). ^{1}H-NMR ($CDCl_3$+CD_3OD): 7.64 (d, 1H) H-6; 6.07(d, $J_{1',2'}$ = 8.5 Hz, 1H) H-1'; 5.47 (dd, $J_{2',3'}$ = 6.8 Hz, $J_{3',4'}$ = 2.0 Hz,

1H) H-3'; 4.66 (m, 1H) H-4'; 4.1-3.3 (m, 3H) H-2', H-5', H-5"; 2.47 (s, 3H) NCH_3; 1.92 (d, 3H) 5-CH_3. ^{13}C-NMR ($CDCl_3$+CD_3OD): 136.4 (d, J_{CH} =181 Hz) C-6; 111.5 (s) C-5; 88.3 (d, J_{CH} = 170 Hz) C-1'; 87.8 (d, J_{CH} = 159.1 Hz) C-3'; 80.7 (d, J_{CH} = 150.5 Hz) C-4' ; 65.8 (d, J_{CH} = 139.3 Hz) C-2' ; 62.4 (t, J_{CH} = 143.2 Hz) C-5'; 34.4 (q, J_{CH} = 135.2 Hz) N$\underline{C}H_3$; 12.0 (q, J_{CH} = 129 Hz) 5-CH_3. MS (FAB$^-$): cal. for $(M-H)^-$ 299.0992, found 299.0989. UV (EtOH): [pH 7] λ_{max} = 265 nm (ε = 10200); [pH 2] λ_{max} = 259 nm (ε = 9300); [pH 12] λ_{max} = 249 nm (ε = 16100).

1-[2,3-Dideoxy-2-(t-butylamino)-3-nitro-β–D-*ribo*furanosyl]thymine (12). The reaction was performed using a condition described for **11** (compound **7**, 135 mg, 0.5 mmol) to give **12** (155 mg, 91 %). ^{1}H-NMR ($CDCl_3$ + CD_3OD): 7.32 (d , 1H) H-6 ; 5.58 (d, $J_{1',2'}$ = 8.8 Hz, 1H) H-1'; 5.24 (dd, $J_{2',3'}$ = 7.2 Hz, $J_{3',4'}$ = 1.3 Hz, 1H) H-3'; 4.66 (m, 1H) H-4'; 4.33 (dd, 1H) H-2'; 4.0 (dd, $J_{4',5'}$ = 1.8 Hz, $J_{5',5''}$ = 12.5 Hz, 1H) H-5'; 3.73 (dd, $J_{4',5''}$ = 2.1 Hz, 1H) H-5"; 1.95 (d, 3H) 5-CH_3; 0.99 (s, 9H) 3 x CH_3. ^{13}C-NMR ($CDCl_3$ + CD_3OD): 136.7 (d, J_{CH} = 174.8 Hz) C-6;111.4 (s) C-5; 90.5 (d, J_{CH} =159.5 Hz) C-3'; 89.5 (d, J_{CH} = 166.2 Hz) C-1'; 81.9 (d, J_{CH} = 148.3 Hz) C-4'; 62.6 (d, J_{CH} = 139.3 Hz) C-5'; 59.5 (d, J_{CH} = 139.3 Hz) C-2'; 50.0 (s) $\underline{C}Me_3$; 29.1 (q, J_{CH} = 125.1 Hz) 3xCH_3; 12.1 (q, J_{CH} = 130.4 Hz) 5-CH_3. MS (FAB$^-$): cal. for $(M-H)^-$ 341.1461, found 341.1463. UV (EtOH): [pH 7] λ_{max} = 265 nm (ε = 9000); [pH 2] λ_{max} = 263 nm (ε = 9100); [pH 12] λ_{max} = 263 nm (ε = 9000).

1-[5-O-(MMTr)-2,3-dideoxy-2-benzylamino-3-nitro-β–D-*ribo*furanosyl] thymine (13). Compound **6** (270 mg, 0.5 mmol) was treated with benzylamine (218 µl, 2 mmol) in tetrahydrofuran (10 ml) at room temperature for 3 h. The reaction mixture was partitioned between aqueous solution of ammonium chloride (10 ml) and ethylacetate (40 ml). The organic phase was washed with water (2 x 10 ml). All volatile matters were removed in vacuo by co-evaporation with toluene, ethanol and carbon tetrachloride. The residue was separated on a silica gel column to give **13** (264 mg, 82 %) ^{1}H-NMR ($CDCl_3$): 9.38 (br, 1H) NH; 7.35-6.75 (m, 20 H) H-6, arom; 6.32 (d, $J_{1',2'}$ = 8.8 Hz, 1H) H-1'; 5.18 (dd, $J_{2',3'}$ = 7.3 Hz, $J_{3',4'}$ = 2.2 Hz, 1H) H-3'; 4.67 (m, 1H) H-4'; 3.9-3.7 (m, 3H) H-2', N$\underline{CH_2}$; 3.8(s, 3H) OMe; 3.62 (dd, $J_{4',5'}$ = 2.7 Hz, $J_{5,5''}$ = 11.4 Hz, 1H) H-5'; 3.29 (dd, $J_{4',5''}$ = 2.8 Hz) H-5"; 1.35 (d, 3H) 5-CH_3. ^{13}C-NMR ($CDCl_3$): 111.8 (s) C-5; 88.3 (d, J_{CH} = 159.5 Hz) C-3`; 87.6 (s) MMTr; 86.3 (d, J_{CH} = 170.7 Hz) C-1'; 80.0 (d, J_{CH} = 151.7 Hz) C-4'; 63.6 (t) NCH_2 ; 63.6 (t) C-5'; 55.2 (d, J_{CH} = 139.3 Hz) C-2'; 51.5 (q, J_{CH} = 143.4 Hz) OMe; 11.6 (q, J_{CH} = 128.1 Hz) 5-CH_3. MS (FAB$^-$): cal. for $(M-C_7H_7N)^-$ 542.1927, found 542.1906 (2'-benzylamine group was fragmented). UV (EtOH): [pH 7] λ_{max} = 265 nm.

1-[2,3-Dideoxy-2-benzylamino-3-nitro-β-D-*ribo*furanosyl]thymine (14). Compound **13** (162 mg, 0.25 mmol) was treated with 80% aqueous acetic acid (5 ml) at room temperature for 6 h. All volatile matters were removed in vacuo by co-evaporation with toluene and ethanol. The residue was purified on a silica gel column to give **14** (72 mg, 77 %).^{1}H-NMR ($CDCl_3$ + CD_3OD): 7.60 (m , 6H) H-6 & arom; 5.86 (d, $J_{1',2'}$ = 8.5 Hz, 1H) H-1'; 5.38 (dd, $J_{2',3'}$ = 7.1 Hz, $J_{3',4'}$ = 1.7 Hz, 1H) H-3'; 4.66 (m, 1H) H-4'; 4.1-3.6 (m, 5H) H-2', H-5', H-5", NCH_2; 1.83 (d, 3H) 5-CH_3. ^{13}C-NMR ($CDCl_3$+CD_3OD): 131.8 (d) C-6; 111.3 (s) C-5; 89.3 (d, J_{CH} = 168.5 Hz) C-1'; 88.0 (d, J_{CH} =158.4 Hz) C-3'; 81.7 (d, J_{CH} = 153.9 Hz) C-4'; 62.4 (d, J_{CH} = 143.0 Hz) C-2'; 62.4 (t, J_{CH} = 143.3 Hz) C-5'; 51.6 (t, J_{CH} = 134.2 Hz) NCH_2; 12.0 (q, J_{CH} = 130 Hz) 5-CH_3. MS (FAB$^-$): cal. for $(M-H)^-$ 375.1305, found 375.1312. UV (EtOH): [pH 7] λ_{max} = 266 nm (ε = 8200); [pH 2] λ_{max} = 262 nm (ε = 8200); [pH 12] λ_{max} = 263 nm (ε = 10900).

1-[2,3-Dideoxy-2-N-(glycine-ethylester)-3-nitro-β-D-*ribo*furanosyl]thymine (15a) and 1-[2,3-Dideoxy-2-N-(glycine-ethylester)-3-nitro-β-D-*xylo*furanosyl]thymine (15b). To a solution of glycine ethyl ester hydrochloride (34 mg, 0.24 mmol) in tetrahydrofuran (6 ml) was added triethylamine (56 µl, 0.4 mmol) and stirred for 5 min, **7** (54 mg, 0.2 mmol) was added, and the stirring continued overnight. The reaction mixture was partitioned between saturated aqueous solution of ammonium chloride (3 ml) and dichloromethane (20 ml). The organic phase was washed with water (2 x 2 ml) and then evaporated to dryness. The residue was purified on a silica gel column to give an inseparable isomeric mixture **15a** and **15b** (60 mg, 81 %). Compound **15a** ^{1}H-NMR ($CDCl_3$ + CD_3OD): 7.44 (d, 1H) H-6 ; 5.92 (d, $J_{1',2'}$ = 8.5 Hz, 1H) H-1'; 5.37 (dd, $J_{2',3'}$ = 6.8 Hz, $J_{3',4'}$ = 2.0 Hz, 1H) H-3'; 4.69 (m, 1H) H-4'; 4.3-3.6 (m, 5H) H-2', H-5', H-5", CO_2CH_2; 3.45 (s, 2H) $NHC\underline{H}_2$; 1.92 (d, 3H) 5-CH_3; 1.22 (t, 3H) $CO_2CH_2C\underline{H}_3$. ^{13}C-NMR ($CDCl_3$+ CD_3OD): 137.4 (d, J_{CH} = 180.9 Hz) C-6; 111.4 (s) C-5; 90.2 (d, J_{CH} = 169.6 Hz) C-1'; 88.0 (d, J_{CH} = 161.8 Hz) C-3'; 82.0 (d, J_{CH} = 151.6 Hz) C-4'; 63.0 (d, J_{CH} = 146.0 Hz) C-2'; 62.7 (t, J_{CH} = 144.4 Hz) C-5', 61.1 (t, J_{CH} = 150.0 Hz) $COO\underline{C}H_2CH_3$; 48.9 (t, J_{CH} = 140.0 Hz) $N\underline{C}H_2$; 13.9 (q, J_{CH} = 127.0 Hz) $CO_2CH_2\underline{C}H_3$; 12.2 (q, J_{CH} = 129.2 Hz) 5-CH_3. Compound **15b** ^{1}H-NMR ($CDCl_3$ + CD_3OD): 7.58 (d, 1H) H-6; 5.84 (d, $J_{1',2'}$ = 5.8 Hz, 1H) H-1'; 5.22 (d, $J_{2',3'}$ = 3.4 Hz, $J_{3',4'}$ = 6.6 Hz, 1H) H-3'; 4.57 (m, 1H) H-4'; 4.2-3.6 (m, 5H) H-2', $CO2C\underline{H}_2CH_3$, H-5', H-5"; 3.46 (s, 2H) NCH_2; 1.94 (d, 3H) 5-CH_3; 1.23 (t, 3H) $CO2CH_2C\underline{H}_3$. ^{13}C-NMR ($CDCl_3$+CD_3OD): 135.2 (d) C-6; 88.9 (d) C-1'; 87.4 (d) C-3'; 80.6 (d) C-4'; 64.5 (t) C-5'; 48.8 (q) NCH_2; 12.3 (q) 5-CH_3. MS (FAB$^-$): cal. for (M-H)$^-$ 371.1203, found 371.1181.

1-[2,3-Dideoxy-2-N-(alaninemethylester)-3-nitro–β-D-*ribo*furanosyl] thymine (16). The reaction was performed using a condition described for **15a** & **15b** (compound **7**, 108 mg, 0.4 mmol) to give **16** (128 mg, 87 %). ^{1}H-NMR ($CDCl_3$ + CD_3OD): 7.42 (d, 1H) H-6; 5.94 (d, $J_{1',2'}$ = 8.3 Hz, 1H) H-1'; 5.29 (dd, $J_{2',3'}$ = 7.1 Hz, $J_{3',4'}$ = 2.0 Hz, 1H) H-3'; 4.71 (m, 1H) H-4'; 4.02 (dd, 1H) H-2'; 4.10-3.60 (m, 2H) H-5'; H-5"; 3.62 (s, 3H) $CO_2C\underline{H}_3$; 3.39 (destorted t, 1H) $C\underline{H}CH_2$; 1.92 (d, 3H) 5-CH_3; 1.23 (d, $J_{CH,CH3}$ = 7.0 Hz, 3H) $CHC\underline{H}_3$. ^{13}C-NMR ($CDCl_3$+CD_3OD): 136.4 (d, J_{CH} = 179.7 Hz) C-6; 111.2 (s) C-5; 88.4 (d, J_{CH} = 166.3 Hz) C-1'; 88.4 (d) C-3'; 81.7 (d, J_{CH} = 151.6 Hz) C-4'; 62.7 (d) C-2'; 62.2 (t) C-5'; 55.1 (d, J_{CH} = 139.3 Hz) $\underline{C}HCH_3$; 51.9 (q, J_{CH} = 147.5 Hz) $CO_2\underline{C}H_3$; 18.9 (q, J_{CH} = 129.3 Hz) $CH\underline{C}H_3$; 12.1 (q, J_{CH} = 128.1 Hz) 5-CH_3. MS (FAB$^-$): cal. for (M-H)$^-$ 371.1203, found 371.1191. UV (EtOH): [pH 7] λ_{max} = 265 nm (ε = 7900); [pH 2] λ_{max} = 263 nm (ε = 7800); [pH 12] λ_{max} = 248 nm (ε = 11900).

1-[2,3-Dideoxy-2-N-(L-phenylalaninemethylester)-3-nitro-β–D-*ribo*-furanosyl] thymine (17). The reaction was performed using a condition described for **15a** & **15b** (compound **7**, 108 mg, 0.4 mmol) to give **17** (142 mg, 79 %). ^{1}H-NMR ($CDCl_3$+CD_3OD): 7.4-7.0 (m, 6H) arom, H-6; 5.73 (d, $J_{1',2'}$ = 8.3 Hz, 1H) H-1'; 5.26 (dd, $J_{2',3'}$ = 7.3 H, $J_{3',4'}$ = 1.7 Hz, 1H) H-3'; 4.65 (m, 1H) H-4'; 4.4-3.6 (m, 4 H) H-2', H-5', H-5", NHC$\underline{H}$; 3.56 (s, 3H) CO_2CH_3; 2.88 (d, $J_{CH,CH2}$ = 6.4 Hz, 2H) $C_6H_5C\underline{H}_2$; 1.90 (d, 3 H) 5-CH_3; ^{13}C-NMR ($CDCl_3$+CD_3OD): 111.3 (s) C-5; 92.7 (d, J_{CH} = 168.5 Hz) C-1'; 88.3 (d, J_{CH} = 160.6 Hz) C-3'; 82.0 (d, J_{CH} = 151.6 Hz) C-4'; 63.0 (d) NH$\underline{C}$H; 61.2 (d, J_{CH} = 143.8 Hz) C-2'; 61.2 (t, J_{CH} = 145.0 Hz) C-5' ; 52.0 (q, J_{CH} = 147.5 Hz) $COO\underline{C}H_3$; 39.3 (t, J_{CH} = 127.5 Hz) $C_6H_5\underline{C}H_2$; 12.3 (q, J_{CH} = 129.6 Hz) 5-CH_3. MS (FAB$^-$): cal. for (M-H)$^-$ 447.1516, found 447.1509. UV (EtOH): [pH 7] λ_{max} = 265 nm (ε = 10000); [pH 2] λ_{max} = 262 nm (ε = 9900); [pH 12] λ_{max} = 253 nm (ε = 15700).

1-[5-O-(MMTr)-2-O-(allyl)-3-deoxy-3-nitro-β-D-*ribo*furanosyl]thymine (24). *General procedure for nucleophilic addition of oxygen nucleophiles*: Sodium hydride (80 %, 36

mg, 1.23 mmol) was added in dry allyl alcohol and was stirred in an ultrasonic bath for 15 min. It was cooled in ice-water bath for 15 min and then **6** (225 mg, 0.41 mmol) was added. It was stirred in ice-water bath for 30 min and poured into aqueous ammonium chloride solution which was extracted with dichloromethane (3 x 25ml). The organic phase was pooled and concentrated in vacuo and was subjected to silica gel column chromatography to give **24** (200 mg, 80.0 %).^{1}H-NMR ($CDCl_3$): 8.59 (br, 1H) NH; 7.55 (d, $J_{CH3,\ H6}$ = 1.2 Hz, 1H) H-6 ; 7.39-6.78 (m, 14 H) arom ; 6.11 (d, $J_{1',\ 2'}$ = 3.9 Hz, 1H) H-1' ; 4.57 (dd, $J_{2',\ 3'}$ = 6.6 Hz, 1H) H-2' ; 5.28 (dd, $J_{3',\ 4'}$ = 5.8 Hz, 1H) H-3' ; 4.82 (m, 1H) H-4' ; 3.69 (dd, $J_{4',\ 5'}$ = 2.2 Hz, 1H)H-5'; 3.43 (dd, $J_{4',\ 5''}$ =2.2 Hz, $J_{5',\ 5''}$ =11.2 Hz, 1H) H-5" ; 4.22 (m, 2H) $OC\underline{H}_2$; 5.83 (m, 1H) $OCH_2C\underline{H}=CH_2$; 5.23 (m, 2H) $OCH_2CH=C\underline{H}_2$; 3.8 (s, 3H) $OC\underline{H}_3$; 1.41 (d, 3H) 5-CH_3. ^{13}C-NMR ($CDCl_3$): 108.7 (s) C-5; 86.7 (d, J_{CH} =173.0 Hz) C-1' ; 79.7 (d, J_{CH} = 156.1 Hz) C-2' ; 83.2 (d, J_{CH} = 156.1 Hz) C-3' ; 78.7 (d, J_{CH} = 157.1 Hz) C-4' ; 62.0 (t, J_{CH} = 144.3 Hz) C-5'; 72.0 (t, J_{CH} =143.2 Hz) $O\underline{C}H_2$; 55.0 (q, J_{CH} = 144.1 Hz) $O\underline{C}H_3$; 119 (t, J_{CH} = 159.5 Hz) $OCH_2CH=\underline{C}H_2$; 11.6 (q, J_{CH} = 129.2 Hz) 5-CH_3. MS (FAB^-): cal. for $(M-H)^-$ 598.2189, found 598.2173.

1-[2-O-allyl-3-deoxy-3-nitro-β-D-*ribo*furanosyl]thymine (25). Compound **24** (40 mg, 0.06 mmol) was treated with 80 % aqueous acetic acid (1 ml) overnight at room temperature. The solvent was removed in vacuo and co-evaporated with toluene and methanol. The residue was subjected to silica gel column chromatography to give **25** (17 mg, 81 %). ^{1}H-NMR ($CDCl_3$+CD_3OD): 7.75 (d, $J_{CH3,\ H6}$ = 1.0 Hz, 1H) H-6; 6.05 (d, $J_{1',\ 2'}$ = 4.9 Hz, 1H) H-1' ; 5.36 (dd, $J_{2',\ 3'}$ = 6.1 Hz, $J_{3',\ 4'}$ = 0.8 Hz 1H) H-3'; 4.79 (m, 1H) H-4' ; 4.57 (dd, 1H) H-2' ; 4.18 (m , 2H); $OC\underline{H}_2$; 5.79 (m, 1H) $OCH_2C\underline{H}=CH_2$; 5.21 (m, 2H) $OCH_2CH=C\underline{H}_2$; 3.9 (m, 2H) H-5',5" ; 1.91 (d, 3H) 5-CH_3. ^{13}C-NMR ($CDCl_3$+CD_3OD): 136.3 (d, J_{CH} = 185.3 Hz) C-6; 132.4 (d, J_{CH} =164.0 Hz) $OCH_2\underline{C}H=CH_2$; 118.2 (t, J_{CH} =154.4 Hz) $OCH_2CH=\underline{C}H_2$; 88.0 (d, J_{CH} =170.7 Hz) C-1' ; 80.3 (d, J_{CH} =155.0 Hz) C-3' ; 79.2 (d, J_{CH} =155.0 Hz) C-2' ; 71.8 (t, J_{CH} = 146.6 Hz) $O\underline{C}H_2$; 60.6 (t, J_{CH} =143.8 Hz) C-5'; 11.6 (q, J_{CH} =130.6 Hz) 5-CH_3. MS (FAB^-): cal. for $(M-H)^-$ 326.0988, found 326.1001.

1-[5-O-(MMTr)-2-O-ethyl-3-deoxy-3-nitro-β–D-*ribo*furanosyl]thymine (20). The general procedure for oxygen nucleophile was followed using **6** (300 mg, 0.55 mmol), NaH (48.2 mg, 1.65 mmol) in 99% ethanol (5 ml) to give **20** (280 mg, 86.0 %). ^{1}H-NMR ($CDCl_3$): 8.8 (s, 1H) NH; 7.58 (d, $J_{CH3,\ H6}$ =1.3 Hz 1H) H-6; 7.42-6.78 (m 14 H) arom; 6.03 (d, $J_{1',\ 2'}$ = 3.8 Hz, 1H) H-1'; 4.53 (dd, $J_{2',\ 3'}$ = 6.2 Hz 1H) H-2' ; 5.29 (dd, $J_{3',\ 4'}$ = 5.8 Hz, 1H) H-3' ;4.82 (m, 1H) H-4' ; 3.47 (dd, $J_{4',\ 5''}$ = 2.5 Hz, 1H) H-5' '; 3.69 (dd, $J_{5',\ 5''}$ =11.4 Hz, 1H) H-5" ; 3.8 (s, 3H) $OC\underline{H}_3$; 3.71 (m, 2H) $O\underline{C}H_2CH_3$; 1.18 (t, 3H) $OCH_2C\underline{H}_3$;1.44 (d, 3H) 5-CH_3.^{13}C-NMR ($CDCl_3$): 111.3 (s) C-5; 88 (d, J_{CH} =175.2 Hz) C-1'; 81 (d, J_{CH} = 155.0 Hz) C-2' ; 83 (d, J_{CH} = 159.5 Hz) C-3'; 78.3 (d, J_{CH} =153.9 Hz) C-4'; 61.9 (t, J_{CH} = 144.9 Hz) C-5' ; 67.5 (t, J_{CH} = 143.2 Hz) $O\underline{C}H_2CH_3$; 55 (q, J_{CH} =143.8 Hz) $O\underline{C}H_3$; 14.6 (q, J_{CH} =126.9 Hz) $OCH_2\underline{C}H_3$; 11.7 (q, J_{CH} =128.0 Hz) 5-CH_3. MS (FAB^-): cal. for $(M-H)^-$ 586.2189, found 586.2203. UV (EtOH): [pH 7] λ_{max} = 264 nm.

1-[5-O-(MMTr)-2,3-dideoxy-2-C-(α-dimethylmalonate)-β-D-*ribo*furanosyl]thymine (40). *General procedure for denitration*:. Compound **26b** (50 mg, 0.07 mmol) was dissolved in dry benzene (5 ml) and tributyl tinhydride (60 µl, 0.22 mmol) was added, followed by AIBN (12 mg, 0.07 mmol) in argon atmosphere. It was sealed with a stopper, and the reaction mixture was kept at 70° C overnight. The solvent was removed in vacuo and was purified on silica gel column chromatography to give **40** (36 mg, 78 %). ^{1}H-NMR ($CDCl_3$): 7.91 (br, 1H) NH; 7.51 (d, $J_{CH3,\ H6}$ = 1.2 Hz, 1H) H-6; 7.48-6.78 (m, 14 H) arom; 6.02 (d, $J_{1',\ 2'}$ = 7.2 Hz, 1H) H-1'; 4.28 (m, 1H) H-4'; 3.8 (s, 3H) MMTr; 3.7, 3.77 (2xs, 6H) 2x COOMe; 3.62 (d, $J_{H\alpha-2'}$ = 8.7 Hz, 1H) $C\underline{H}(COOCH_3)_2$; 3.42 (dd, $J_{4',\ 5'}$ = 2.7

Hz, $J_{5',5''}$ = 10.5 Hz, 1H) H-5'; 3.23 (dd, $J_{4',5''}$ = 3.5 Hz, 1H) H-5''; 3.18 (m, $J_{2',H\alpha}$ = 8.7 Hz, 1H) H -2'; 2.41 (m, $J_{2',3'}$ = 8.9 Hz, $J_{3',4'}$ = 5.2 Hz, $J_{3',3''}$ = 13.4 Hz, 1H) H-3'; 2.08 (m, $J_{2',3''}$ = 8.6 Hz, 1H) H-3''; 1.51 (d) 5-CH_3. ^{13}C-NMR ($CDCl_3$): 87.1 (d, J_{CH} = 165.1 Hz) C-1'; 43.2 (d) C-2'; 30.7 (t, J_{CH} = 134.2 Hz) C-3'; 77.2 (d, J_{CH} = 150.5 Hz) C-4'; 65.1 (t, J_{CH} = 143.8 Hz) C-5'; 52.8 (q, J_{CH} = 147.9 Hz) 2x$COO\underline{C}H_3$; 55.1 (q, J_{CH} = 143.8 Hz) MMTr; 52.4 (d, J_{CH} = 157.0 Hz) $\underline{C}H(COOCH_3)_2$; 11.8 (q, J_{CH} =128.7 Hz) 5-CH_3. MS (FAB^-): cal. for $(M-H)^-$ 627.2343, found 627.2334. UV (EtOH): [pH 7] λ_{max} = 266 nm.

1-[5-O-(MMTr)-2-O-ethyl-3-deoxy-β-D-*ribo*furanosyl]thymine (34). General procedure for denitration was followed using **20** (250 mg, 0.42 mmol), tributyl tinhydride (684 µl, 2.54 mmol), AIBN (69 mg, 0.42 mmol) in dry benzene (5 ml) at 70^0 C for 40 h to give **34** (20 mg, 7 %) and **52** (96 mg, 41 %). ^{1}H-NMR ($CDCl_3$): Compound **34**. 8.4 (br, 1H) NH; 7.64 (d, J_{CH_3, H_6} =1.1 Hz, 1H) H-6; 7.45-6.78 (m, 14 H) arom; 5.88 (s, 1H) H-1' ; 4.53 (m, 1H) H-4'; 3.60-3.82 (m, 2H) $OC\underline{H}_2CH_3$; 3.79 (s, 3H) $OC\underline{H}_3$; 3.51 (dd, $J_{4',5'}$ = 2.2 Hz, 1H) H-5' ; 3.31 (dd; $J_{4',5''}$ = 3.7 Hz, $J_{5',5''}$ =10.9 Hz, 1H) H-5''; 4.07 (d, $J_{2',3'}$ = 5.2 Hz, 1H) H-2'; 2.2 (ddd, $J_{3',4'}$ = 5.3 Hz, 1H) H-3'; 1.99 (dd, $J_{3'',4'}$ = 10.4 Hz, $J_{3',3''}$ = 13.4 Hz, 1H) H-3''; 1.42 (d, 3H) 5-CH_3; 1.22 (t, 3H) $OCH_2C\underline{H}_3$.^{13}C-NMR ($CDCl_3$): 110.0 (s) C-5; 90.2 (d, J_{CH} = 176.3 Hz) C-1'; 83.5 (d, J_{CH} = 152.8 Hz) C-2' ; 80.4 (d, J_{CH} = 148.3Hz) C-4' ; 65.2 (t, J_{CH} = 141.0 Hz) $O\underline{C}H_2CH_3$; 63.4 (t, J_{CH} =142.6 Hz) C-5' ; 55.1 (q, J_{CH} =143.8 Hz) OMe; 32.0 (t, J_{CH} = 130.9Hz) C-3', 15.2 (q, J_{CH} = 125.0 Hz) $OCH_2\underline{C}H_3$; 11.9 (q, J_{CH} = 129.5 Hz) 5-CH_3. MS (FAB^-): cal. for $(M-H)^-$ 541.2339, found 541.2344. UV (EtOH): [pH 7] λ_{max} = 267. ^{1}H-NMR ($CDCl_3$+CD_3OD): Compound **52**: 9.0 (br, 1H) NH; 7.64 (d, 1H) H6; 7.43-6.78 (m, 14 H) arom; 6.23 (d, $J_{1',2'}$ =7.0 Hz, 1H) H-1'; 5.01 (m, 1H) H-4'; 4.83 (d, 1H) H-2'; 3.97-3.6 (m, 3H) $OC\underline{H}_2CH_3$ & H-5'; 3.23 (d, 1H) H-5''; 3.77 (s, 3H) MMTr; 1.35-1.23 (m, 6H) $OCH_2C\underline{H}_3$ & 5-CH_3. ^{13}C-NMR ($CDCl_3$ + CD_3OD): 111.9 (s) C-5; 86.9 (d, J_{CH} = 166.2 Hz) C-1'; 85.1 (d, J_{CH} = 143.9 Hz) C-2'; 79.2 (d, J_{CH} = 156.0 Hz) C-4'; 66.2 (t, J_{CH} = 142.6 Hz) $O\underline{C}H_2CH_3$; 62.4 (t, J_{CH} = 146.6 Hz) C-5'; 54.8 (q, J_{CH} = 144.1 Hz) MMTr; 14.6 (q, J_{CH} = 126.9 Hz) $OCH_2\underline{C}H_3$; 11.8 (q, J_{CH} = 124.8 Hz) 5-CH_3. MS (FAB^-): cal. for $(M-H)^-$ 570.2240, found 570.2266. UV (EtOH): [pH 7] λ_{max} = 265 nm.

1-[2-O-ethyl-3-deoxy-3-nitro-β-D-*ribo*furanosyl]thymine (21). Compound **20** (90 mg, 0.15 mmol) was treated with 80 % aqueous acetic acid (3 ml) at room temperature overnight. The solvent was removed in vacuo and co-evaporated with toluene and methanol. The residue was subjected to silica gel column chromatography to give **21** (47 mg, 97 %). ^{1}H-NMR ($CDCl_3$+ CD_3OD): 7.74 (d, $J_{CH3, H6}$ = 1.2 Hz, 1H) H-6; 6.01 (d, $J_{1',2'}$ = 5.4 Hz) H-1'; 5.39 (dd, $J_{2',3'}$ = 5.8 Hz, $J_{3',4'}$ = 3.9 Hz, 1H) H-3'; 4.78 (m, 1H) H-4' ; 4.53 (dd, 1H) H-2' ; 3.98 (dd, $J_{4',5'}$ = 2.0 Hz, 1H) H-5' ; 3.82 (dd, $J_{4',5''}$ = 2.0 Hz, $J_{5',5''}$ = 12.2 Hz, 1H) H -5'' ; 3.72 (m, 2H) $OC\underline{H}_2CH_3$; 1.91 (d, 3H) 5-CH_3; 1.16 (t, 3H) $OCH_2C\underline{H}_3$.^{13}C-NMR ($CDCl_3$ + CD_3OD): 136.5 (d, J_{CH} = 180.8 Hz) C-6; 110.8 (s) C-5 ; 88.4 (d, J_{CH} = 170.7 Hz) C-1' ; 83.9 (d J_{CH} = 158.4 Hz) C -3' ; 80.2 (d, J_{CH} = 155.0 Hz) C-2'; 67.2 (t, J_{CH} = 143.2 Hz) $O\underline{C}H_2CH_3$; 80.2 (d, J_{CH} = 155.0 Hz) C -4' ; 60.7 (t, J_{CH} =143.8 Hz) C-5'; 14.3 (q, J_{CH} = 124.7 Hz) $OCH_2\underline{C}H_3$; 11.7 (q, J_{CH} =129.2 Hz) 5-CH_3. MS (FAB^-): cal. for $(M-H)^-$ 314.0988, found 314.1010. UV (EtOH): [pH 7] λ_{max} = 265 nm (ε = 7200); [pH 2] λ_{max} = 263 nm (ε = 6900); [pH 12] λ_{max} = 259 nm (ε = 11800).

1-[5-O-(MMTr)-2-O-methyl-3-deoxy-3-nitro-β-D-*ribo*furanosyl]thymine (18). The general procedure for oxygen nucleophiles was followed using **6** (400 mg, 0.74 mmol), sodium hydride (66 mg, 2.22 mmol) in dry methanol (5 ml) to give **18** (350 mg, 83 %). ^{1}H-NMR ($CDCl_3$): 8.88 (br, 1H) NH; 7.56 (d, $J_{CH3, H6}$ = 1.2 Hz, 1H) H-6; 7.41-6.78 (m, 14 H) arom; 6.05 (d, $J_{1',2'}$ = 3.9 Hz, 1H) H-1'; 5.3 (dd, $J_{2',3'}$ = 7.4 Hz, $J_{3',4'}$ = 5.2 Hz, 1H) H-3' ; 4.83 (m, 1H) H-4' ; 4.41 (dd, 1H) H-2'; 3.8 (s, 3H) MMTr ; 3.55 (m, 2H) H-5', 5'' ;

3.56 (s, 3H) $OC\underline{H}_3$; 1.44 (d, 3H) 5-CH_3. ^{13}C-NMR ($CDCl_3$): 111.5 (s) C-5; 87.7 (d, J_{CH} = 171.9 Hz) C-1'; 82.6 (d, J_{CH} = 159.5 Hz) C-2' ; 82.9 (d, J_{CH} = 159.5 Hz) C-3'; 78.6 (d, J_{CH} = 155.0 Hz) C-4'; 61.7 (t, J_{CH} = 145.9 Hz) C-5'; 59.4 (q, J_{CH} =143.8 Hz) $O\underline{C}H_3$; 55.0 (q, J_{CH} =144.5 Hz)MMTr; 11.7 (q, J_{CH} =130.3 Hz) 5-CH_3. MS (FAB$^-$): cal. for $(M-H)^-$ 572.2033, found 572.2091. UV (EtOH): [pH 7] λ_{max} = 266 nm.

1-[2-O-methyl-3-deoxy-3-nitro-β-D-*ribo*furanosyl]thymine (19). Compound **18** (50 mg, 0.09 mmol) was treated with 80 % aqueous acetic acid (1 ml) overnight at room temperature.The solvent was removed in vacuo and co-evaporated with methanol and toluene. The residue was subjected to silica gel column chromatography to give **19** (25 mg, 96 %). ^{1}H-NMR ($CDCl_3$+ CD_3OD): 7.75 (d, $J_{CH3,\ H6}$ = 1.2 Hz, 1H) H-6; 6.03 (d, $J_{1',\ 2'}$ = 4.9 Hz, 1H) H-1'; 5.42 (dd, $J_{2',\ 3'}$ = 6.5 Hz, $J_{3',\ 4'}$ = 4.5 Hz, 1H) H-3'; 4.78 (m, 1H) H-4'; 4.43 (dd, 1H) H-2'; 3.97 (dd, $J_{4',\ 5'}$ = 2.3 Hz, 1H) H-5' ; 3.78 (dd, $J_{4',\ 5''}$ = 2.0 Hz, $J_{5',\ 5''}$ =12.4 Hz, 1H) H-5''; 3.52 (s, 3H) OCH_3; 1.91 (d, 3H)5-CH_3.^{13}C-NMR ($CDCl_3$+CD_3OD): 136.4 (d, J_{CH}=180.8 Hz) C-6; 88.0 (d, J_{CH} =169.6 Hz) C-1' ; 82.0 (d, J_{CH} =159.5 Hz) C-2'; 83.7 (d, J_{CH} =159.5 Hz) C-3' ; 80.3 (d, J_{CH} =151.5 Hz) C-4' ; 60.7 (t, J_{CH} =141.5 Hz) C-5' ; 58.9 (q, J_{CH} = 132.1 Hz) OCH_3; 11.7 (q, J_{CH} = 131.4 Hz) 5-CH_3. MS (FAB$^-$): cal. for $(M-H)^-$ 300.0832, found 300.0804. UV (EtOH): [pH 7] λ_{max} = 266.

1-[5-O-(MMT)-2-O-methyl-3-deoxy-β-D-*ribo*furanosyl]thymine (36). General procedure for denitration was followed using **18** (500 mg, 0.87 mmol), tributyl tinhydride (1.05 ml, 3.9 mmol), AIBN (142 mg, 0.87 mmol) in dry benzene (10 ml) for 40 h to give **36** (50 mg, 11 %) and **48** (170 mg, 35 %). ^{1}H-NMR ($CDCl_3$): (**36**): 7.66 (d, $J_{CH3,\ H6}$ =1.2 Hz, 1H) H-6; 7.5- 6.78 (m, 14 H) arom ; 5.91 (s, 1H) H-1'; 4.5 (m, 1H) H-4'; 3.79 (s, 3H) MMTr; 3.31 (dd, $J_{4',\ 5''}$ = 4.1 Hz, $J_{5',\ 5''}$ =11.5 Hz, 1H) H-5''; 3.57 (m, 1H) H-5'; 3.52 (s, 3H) OMe; 2.41-1.76 (m, 2H) H-3', 3''; 1.4 (d, 3H) 5-CH_3. ^{13}C-NMR ($CDCl_3$): 110.2 (s) C-5; 89.7 (d, J_{CH} = 175.2 Hz) C-1' ; 85.3 (d, J_{CH} = 156.1 Hz) C-2'; 80.3 (d, J_{CH} = 148.2 Hz) C-4'; 63.3 (t, J_{CH} = 142.6 Hz) C-5' ; 57.5 (q, J_{CH} = 143.4 Hz) OMe; 55.1 (q, J_{CH} = 143.8 H) MMTr; 31.6 (t, J_{CH} = 133.1 Hz) C-3'; 11.9 (q, J_{CH} = 129.5 Hz) 5-CH_3. MS (FAB$^-$): cal. for $(M-H)^-$ 527.2182, found 527.2183. ^{1}H-NMR ($CDCl_3$): (**48**): 9.0 (br, 1H) NH; 7.6 (s, 1H) H-6; 7.5- 6.8 (m, 14 H) arom; 6.2 (d, $J_{1',\ 2'}$ = 7.3 Hz, 1H) H-1'; 5.0 (s, 1H) H-4'; 4.7 (d, 1H) H-2'; 3.9 (d, $J_{5',\ 5''}$ = 10.5 Hz) H-5'; 3.2 (d, 1H) H-5''; 3.8 (s, 3H) MMTr; 3.6 (s, 3H) OCH_3; 1.3 (s, 3H) 5-CH_3. ^{13}C-NMR ($CDCl_3$): 112.2 (s) C-5; 87.1 (s) MMTr; 85.4 (d, J_{CH} = 169.6 Hz) C-1'; 81.1 (d, J_{CH} = 150.5 Hz) C-2'; 75.9 (d, J_{CH} =152.8 Hz) C-4'; 62.5 (t, J_{CH} = 145.5 Hz) C-5'; 58.6 (q, J_{CH} = 141.5 Hz) OMe; 55.2 (q, J_{CH} = 144.1 Hz) MMTr; 11.3 (q, J_{CH} = 128.6 Hz) 5-CH_3. MS (FAB$^-$): cal. for $(M-H)^-$ 556.2084, found 556.2096. UV (EtOH): [pH 7] λ_{max} = 265 nm.

1-[2-O-methyl-3-deoxy-β-D-*ribo*furanosyl]thymine (37). Compound **36** (30 mg, 0.06 mmol) was treated with 80 % aqueous acetic acid (1 ml) at room temperature overnight. The solvent was removed in vacuo, co-evaporated with toluene and methanol. The residue was subjected to silica gel column chromatography to give **37** (12 mg, 86 %). ^{1}H-NMR ($CDCl_3$ + CD_3OD): 7.93 (d, $J_{CH3,\ H6}$ = 1.2 Hz, 1H) H-6; 5.88 (s, 1H) H-1'; 4.46 (m, 1H) H-4'; 3.97 (m, 1H) H-2'; 3.68 (dd, $J_{4',\ 5'}$ = 2.9 Hz, $J_{5',\ 5''}$ = 12.4 Hz, 1H) H-5'; 3.97 (m, 1H) H-5''; 3.49 (s, 3H) OMe; 2.31-1.95 (m, 2H) H-3', 3''; 1.88 (d, 3H) 5-CH_3. ^{13}C-NMR ($CDCl_3$+CD_3OD): 136.4 (d, J_{CH} = 191.0 Hz) C-6; 109.7 (s) C-5; 89.5 (d, J_{CH} = 169.7 Hz) C-1'; 85.3 (d, J_{CH} = 156.1Hz) C-2'; 81.2 (d, J_{CH} = 144.9 Hz) C-4'; 61.2 (t, J_{CH} = 141.5 Hz) C-5'; 57.0 (q, J_{CH} = 140.8 Hz) OMe; 30.3 (t, J_{CH} = 134.8 Hz) C-3'; 11.7 (q, J_{CH} = 128.6 Hz) 5-CH_3. MS (FAB$^-$): cal. for $(M-H)^-$ 255.0981, found 255.1002. UV (EtOH): [pH 7] λ_{max} = 267 nm.

1-[5-O-(MMTr)-2-O-methyl-3-oximinoacetyl-β-D-*ribo*furanosyl]thymine (50). Compound **48** (100 mg, 0.18 mmol) was dissolved in pyridine (2 ml), acetic anhydride

(200 µl) was added, and was kept at room temperature overnight. After usual workup it was purified through silica gel column chromatography to give **50** (80 mg, 75 %). ^{1}H-NMR ($CDCl_3$): 7.59 (d, $J_{CH3, H6}$ = 1.2 Hz, 1H) H-6; 7.41- 6.78 (m, 14 H) arom; 6.3 (d, $J_{1', 2'}$ = 7.0 Hz, 1H) H-1'; 5.02 (m, 1H) H-4'; 4.79 (dd, $J_{2', 4'}$ = 1.6 Hz, 1H) H-2'; 3.63 (m, 1H) H-5'; 3.43 (dd, $J_{4', 5''}$ = 2.0 Hz, $J_{5', 5''}$ = 10.9 Hz, 1H) H-5''; 3.79 (s, 3H) MMTr; 3.67 (s, 3H) OMe; 1.95 (s, 3H) $COCH_3$; 1.34 (d, 3H) 5-CH_3. ^{13}C-NMR ($CDCl_3$): 112.6 (s) C-5; 87.2 (s) MMTr; 85.4 (d, J_{CH} = 173.0 Hz) C-1'; 80.9 (d, J_{CH} = 148.3 Hz) C-2'; 76.6 (d, J_{CH} = 157.2 Hz) C-4'; 62.4 (t, J_{CH} = 147.9 Hz) C-5'; 58.8 (q, J_{CH} = 142.9 Hz) OMe; 55.1 (q, J_{CH} = 143.8 Hz) MMTr; 18.9 (q, J_{CH} = 130.3 Hz) $COCH_3$; 11.3 (q, J_{CH} = 129.2 Hz) 5-CH_3. MS (FAB^-): cal. for $(M-H)^-$ 598.2189, found 598.2202. UV (EtOH): [pH 7] λ_{max} = 264 nm.

1-[2-O-methyl-3-oximinoacetyl-β-D-*ribo*furanosyl]thymine (51). Compound **50** (60 mg, 0.1 mmol) was treated with 80% aqueous acetic acid (1 ml) at room temperature overnight. After removal of the solvent it was purified through silica gel column chromatography to give **51** (25 mg, 76 %). ^{1}H-NMR ($CDCl_3$): 7.3 (s, 1H) H-6; 5.64 (d, $J_{1', 2'}$ = 6.3 Hz, 1H) H-1'; 5.0 (m, 2H) H-4', & H-2'; 4.0 (dd, $J_{5', 5''}$ = 12.7 Hz, 2H) H-5', 5''; 3.61 (s, 3H) OMe; 2.21 (s, 3H) $COCH_3$; 1.93 (s, 3H) 5-CH_3. ^{13}C-NMR ($CDCl_3$): 163.6 (s) C-4; 150.5 (s) C-2; 138.0 (d, J_{CH} = 180.8 Hz) C-6; 111.9 (s) C-5; 91.2 (d, J_{CH} = 166.2 Hz) C-1'; 79.4, 79.1 (2xd, J_{CH} = 152.7 Hz) C-2' & C-4'; 61.7 (t, J_{CH} = 146.0 Hz) C-5'; 59.0 (q, J_{CH} = 143.8 Hz) OMe; 19.2 (q, J_{CH} = 130.7 Hz) $COCH_3$; 12.3 (q, J_{CH} = 129.5 Hz) 5-CH_3. MS (FAB^-): cal. for $(M-H)^-$ 326.0988, found 326.0978. UV (EtOH): [pH 7] λ_{max} = 265 nm (ε = 9300); [pH 2] λ_{max} = 263 nm (ε = 9200); [pH 12] λ_{max} = 263 nm (ε = 8000).

1-[5-O-(MMTr)-2-O-(2-methoxyethyl)-3-deoxy-3-nitro-β-D-*ribo*furanosyl]thymine (22). The general procedure for addition of oxygen nucleophiles was followed using **6** (450 mg, 0.83 mmol), NaH (75 mg, 2.49 mmol) in 2-methoxyethanol (5 ml) to give **22** (380 mg, 74 %). ^{1}H-NMR ($CDCl_3$): 8.6 (br, 1H) NH ; 7.51 (d, $J_{CH3, H6}$ = 1.2 Hz, 1H) H-6, 7.42-6.78 (m, 14 H) arom; 6.15 (d, $J_{1', 2'}$ = 5.4 Hz, 1H) H-1'; 5.38 (dd, $J_{2', 3'}$ = 6.6 Hz, $J_{3', 4'}$ = 4.4 Hz, 1H) H-3'; 4.78 (m, 1H') H-4'; 3.9-3.4 (m, 6H) $OC\underline{H}_2C\underline{H}_2OCH_3$ & H-5', 5''; 3.8 (s, 3H) MMTr; 3.31 (s , 3H) OCH_3; 1.4 (d, 3H) 5-CH_3. ^{13}C-NMR ($CDCl_3$): 108.3 (s) C-5; 87.6 (d, J_{CH} = 173.0 Hz) C-1'; 81.9 (d) C-2'; 84.4 (d, J_{CH} = 158.4 Hz) C-3'; 78.7 (d, J_{CH} = 156.2 Hz) C-4'; 62.5 (t, J_{CH} = 142.6 Hz) C-5'; 72.4 (t, J_{CH} = 143.0 Hz) OCH_2; 71.2 (d, J_{CH} = 144.9 Hz) $OCH_2\underline{C}H_2OCH_3$; 58.8 (q, J_{CH} = 141.1 Hz) OMe; 55.0 (q, J_{CH} = 143.8 Hz) MMTr; 11.6 (q, J_{CH} = 128.0 Hz) 5-CH_3. MS (FAB^-): cal. for $(M-H)^-$ 616.2295, found 616.2306. UV (EtOH): [pH 7] λ_{max} = 266 nm.

1-[2-O-(2-methoxyethyl)-3-deoxy-3-nitro-β-D-*ribo*furanosyl]thymine (23). Compound **22** (70 mg, 0.11 mmol) was treated with 80 % aqueous acetic acid (2 ml) at room temperature overnight. The solvent was removed in vacuo and co-evaporated with toluene and methanol. The residue was purified by silica gel column chromatography to give **23** (38 mg, 97 %). ^{1}H-NMR ($CDCl_3$+ CD_3OD): 7.71 (d, $J_{CH3, H6}$ = 1.2 Hz, 1H) H-6; 6.01 (d, $J_{1', 2'}$ = 5.4 Hz, 1H) H-1'; 5.41 (dd, $J_{2', 3'}$ = 6.5 Hz, $J_{3', 4'}$ = 4.8 Hz, 1H) H-3'; 4.75 (m, 2H) H-4' & H-2'; 3.84 (m, 4H) H-5',5'' and $OC\underline{H}_2CH_2OCH_3$; 3.51 (m, 2H) $OCH_2C\underline{H}_2OCH_3$; 3.31 (s, 3H) OMe; 1.91 (d, 3H) 5-CH_3. ^{13}NMR-($CDCl_3$+CD_3OD): 136.8 (d, J_{CH} = 187.6 Hz) C-6; 110.7 (s) C-5; 88.6 (d, J_{CH} = 169.6 Hz) C-1'; 83.9 (d, J_{CH} = 157.2 Hz) C-3'; 81.0 (d, J_{CH} = 155.0 Hz) C-2'; 80.3 (d, J_{CH} = 155.0 Hz) C-4'; 60.7 (t, J_{CH} = 143.2 Hz) C-5'; 71.5, 70.7 (2xt, J_{CH} = 141.5 Hz & 145.4 Hz) $O\underline{C}H_2\underline{C}H_2$; 58.4 (q, J_{CH} = 141.5 Hz) OMe; 11.7 (q, J_{CH} = 129.7 Hz) 5-CH_3. MS (FAB^-): cal. for $(M-H)^-$ 344.1094, found 344.1101. UV (EtOH): [pH 7] λ_{max} = 264 nm (ε = 12400); [pH 2] λ_{max} = 264 nm (ε = 11700); [pH 12] λ_{max} = 260 nm (ε = 18600).

1-[5-O-(MMTr)-2-O-(2-methoxyethyl)-3-deoxy-β-D-*ribo*furanosyl]thymine (38). General procedure for denitration was followed using **22** (380 mg, 0.61 mmol), tributyl tinhydride (990 µl, 3.6 mmol), AIBN (101 mg, 0.61 mmol) in dry benzene (7 ml) for 40 h at 70^0 C to give **38** (25 mg, 7 %) and **54** (125 mg, 34 %). ^{1}H-NMR ($CDCl_3$): 8.98 (br, 1H) NH; 7.66 (s, 1H) H-6; 7.5-6.78 (m, 14 H) arom; 5.89 (s, 1H) H-1'; 4.56 (m, 1H) H-4'; 4.13 (m, 1H) H-2'; 3.93-3.21 (m, 6H) H-5', 5", & OCH_2CH_2; 3.79 (s, 3H) MMTr; 3.38 (s, 3H) OMe; 2.12 (m, 2H) H-3', 3"; 1.42 (s, 3H) 5-CH_3. ^{13}C-NMR ($CDCl_3$): 90.0 (d, J_{CH} = 173.0 Hz) C-1'; 86.7, MMTr; 84.2 (d, J_{CH} = 152.8 Hz) C-2'; 80.5 (d, J_{CH} = 149.4 Hz) C-4'; 71.8 (t, J_{CH} = 144.3 Hz) OCH_2CH_2; 68.9 (t, J_{CH} = 143.2 Hz) OCH_2CH_2; 63.3 (t, J_{CH} = 142.1 Hz) C-5'; 58.9 (q, J_{CH} = 140.8 Hz) OMe; 55.1 (q, J_{CH} = 143.8 Hz) MMTr; 31.8 (t, J_{CH} = 133.7 Hz) C-3'; 11.9 (q, J_{CH} = 129.2 Hz) 5-CH_3. MS (FAB$^-$): cal. for $(M-H)^-$ 571.2444, found 571.2462. UV (EtOH): [pH 7] λ_{max} = 267 nm. ^{1}H-NMR ($CDCl_3$): **(54):** 9.5 (br, 1H) NH; 7.6 (s, 1H) H-6; 7.5-6.77 (m, 14 H) arom; 6.23 (d, $J_{1',2'}$ = 7.0 Hz, 1H) H-1'; 5.01 (m, 2H) H-2' & H-4'; 4.0-3.16 (m, 6H) H-5', 5" and $OCH_2CH_2OCH_3$; 3.28 (s, 3H) OMe; 1.28 (s, 3H) 5-CH_3. ^{13}C-NMR ($CDCl_3$): 111.8 (s) C-5; 87.0 (s) MMTr; 85.3 (d, J_{CH} = 172.9 Hz) C-1'; 80.0 (d, J_{CH} = 148.2 Hz) C-2'; 75.8 (d, J_{CH} = 151.6 Hz) C-4'; 72.5 (t, J_{CH} = 137.0 Hz) OCH_2CH_2; 69.8 (t, J_{CH} = 144.3 Hz) $OCH_2CH_2OCH_3$; 62.6 (t, J_{CH} = 146.6 Hz) C-5'; 58.8 (q, J_{CH} = 141.2 Hz) OMe; 55.0 (q, J_{CH} = 143.8 Hz) MMTr; 11.2 (q, J_{CH} = 129.7 Hz) 5-CH_3. MS (FAB$^-$): cal. for $(M-H)^-$ 600.2346, found 600.2311. UV (EtOH): [pH 7] λ_{max} = 265.

1-[2-O-(2-methoxyethyl)-3-deoxy-β-D-*ribo*furanosyl]thymine (39). Compound **38** (20 mg, 0.03 mmol) was treated with 80 % aqueous acetic acid (1ml) at room temperature overnight. The solvent was removed in vacuo, co-evaporated with toluene and methanol. The residue was purified through silica gel column chromatography to give **39** (9 mg, 90 %). ^{1}H-NMR ($CDCl_3$): 8.7 (br, 1H) NH; 7.61 (d, $J_{CH3,\ H6}$= 1.1 Hz) H-6; 5.8 (d, $J_{1',2'}$ = 1.4 Hz) H-1'; 4.5 (m, 1H) H-4'; 4.17 (m, 1H) H-2'; 4.07 (dd, $J_{4',5'}$ = 2.0 Hz, $J_{5',5''}$ = 12.3 Hz) H-5'; 3.9-3.67 (m, 3H) H-5" and OCH_2CH_2; 3.53 (m, 2H) OCH_2CH_2; 3.37 (s, 3H) OMe; 2.27-2.16 (m, $J_{3',4'}$ = 9.9 Hz, $J_{2',3'}$ = 5.8 Hz, 1H) H-3'; 2.06-1.98 (m, $J_{3'',4'}$ = 5.7 Hz, $J_{3',3''}$ = 13.4 Hz, 1H) H-3"; 1.9 (d, 3H) 5-CH_3. ^{13}C-NMR ($CDCl_3$): 136.8 (d, J_{CH} = 183.3 Hz) C-6; 110.2 (s) C-5; 91.5 (d, J_{CH} = 169.5 Hz) C-1'; 83.9 (d, J_{CH} = 151.2 Hz) C-2'; 81.0 (d, J_{CH} = 146.6 Hz) C-4'; 71.8 (t, J_{CH} = 138.3 Hz) OCH_2CH_2; 69.1 (t, J_{CH} = 142.0 Hz) OCH_2CH_2; 62.5 (t, J_{CH} = 142.0 Hz)C-5'; 58.9 (q, J_{CH} = 140.5 Hz) OMe; 31.3 (t, J_{CH} = 132.9 Hz) C-3'; 12.4 (q, J_{CH} = 129.5 Hz) 5-CH_3. MS (FAB$^-$): cal. for $(M-H)^-$ 299.1243, found 299.1265. UV (EtOH): [pH 7] λ_{max} = 268 nm (ε = 8800); [pH 2] λ_{max} = 267 nm (ε = 8800); [pH 12] λ_{max} = 267 nm (ε = 6800).

1-[3-deoxy-2-O-ethyl-β-D-*ribo*furanosyl]thymine (35). Compound **34** (20 mg, 0.03 mmol) was treated with 80% aqueous acetic acid (1 ml) at room temperature overnight. After removal of the solvent, the residue was purified by silica gel column chromatography to give **35** (9 mg, 90 %). ^{1}H-NMR ($CDCl_3$): 8.6 (br, 1H) NH; 7.6 (d, $J_{CH3,H6}$ = 1.2 Hz) H-6; 5.8 (d, $J_{1',2'}$ = 1.5 Hz, 1H) H-1'; 4.5 (m, 1H) H-4'; 4.1 (m, 2H) H-5' & H-2'; 3.8 (m, $J_{5',5''}$ =12.3 Hz, 2H) H-5", OCH_2; 3.5 (m, 1H) OCH_2CH_3; 2.3 (m, $J_{2',3''}$ =5.4 Hz, $J_{3',4'}$ =9.9 Hz, 1H) H-3'; 2.0 (m, $J_{3'',4'}$ = 5.7 Hz, $J_{3',3''}$ = 13.1 Hz, 1H) H-3"; 1.9 (d, 3H) 5-CH_3; 1.2 (t, 3H) OCH_2CH_3. ^{13}C-NMR ($CDCl_3$): 136.7 (d, J_{CH} = 184.2 Hz) C-6; 110.2 (s) C-5; 91.5 (d, J_{CH} = 170.4 Hz) C-1'; 83.2 (d, J_{CH} = 151.0 Hz) C-2'; 80.9 (d, J_{CH} = 145.7 Hz) C-4'; 65.2 (t, J_{CH} = 141.1 Hz) OCH_2CH_3; 62.5 (t, J_{CH} = 143.9 Hz) C-5'; 31.3 (t, J_{CH} = 131.0 Hz) C-3'; 15.2 (q, J_{CH} = 126.2 Hz) OCH_2CH_3; 12.4 (q, J_{CH} = 129.2 Hz) 5-CH_3. MS (FAB$^-$): cal. for $(M-H)^-$ 269.1138, found 269.1149. UV (EtOH): [pH 7] λ_{max} = 267 nm (ε = 7300); [pH 2] λ_{max} = 267 nm (ε = 7100); [pH 12] λ_{max} = 266 nm (ε = 6700).

1-[2-O-methyl-3-oximino-β-D-*ribo*furanosyl]thymine (49). Compound **48** (30 mg, 0.05 mmol) was treated with 80% aqueous acetic acid (1 ml) at room temperature overnight. After removal of the solvent it was purified by silica gel column chromatography to give **49** (14 mg, 91 %). ^{1}H-NMR ($CDCl_3$+CD_3OD): 7.7 (s, 1H) H-6; 5.9 (d, $J_{1',2'}$ = 5.6 Hz, 1H) H-1'; 4.96 (s, 1H) H-4'; 4.53 (d, $J_{2',4'}$ = 1.4 Hz, 1H) H-2'; 4.1 (m, 2H) H-5', 5"; 3.5 (s, 3H) OMe; 1.92 (s, 3H) 5-CH_3. ^{13}C-NMR ($CDCl_3$+CD_3OD): 136.8 (d, J_{CH} = 179.8 Hz) C-6; 88.0 (d, J_{CH} = 167.4 Hz) C-1'; 80.5 (d, J_{CH} = 148.6 Hz) C-2'; 78.5 (d, J_{CH} = 151.7 Hz) C-4'; 60.9 (t, J_{CH} = 144.9 Hz) C-5'; 58.0 (q, J_{CH} = 141.5 Hz) OMe; 155.5 (s) C-3'; 11.9 (q, J_{CH} = 129.1 Hz) 5-CH_3. MS (FAB$^-$): cal. for $(M-H)^-$ 284.0883, found 284.0890. UV (EtOH): [pH 7] λ_{max} = 265 nm (ε = 9900); [pH 2] λ_{max} = 265 nm (ε = 9900); [pH 12] λ_{max} = 265 nm (ε = 8300).

1-[2-O-(2-methoxyethyl)-3-oximino-β-D-*ribo*furanosyl]thymine (55). Compound **54** (80 mg, 0.13 mmol) was treated with 80% aqueous acetic acid (2 ml) at room temperature overnight. After removal of the solvent it was purified through silica gel column to give **55** (39 mg, 89 %). ^{1}H-NMR ($CDCl_3$+CD_3OD): 7.6 (s, 1H) H-6; 5.9 (d, $J_{1',2'}$ = 6.1 Hz, 1H) H-1'; 4.9 (s, 1H) H-4'; 4.8 (dd, $J_{2',4'}$ = 1.4 Hz, 1H) H-2'; 4.2 (d, $J_{5',5"}$ = 12.0 Hz, 1H) H-5'; 3.7 (m, 5H) H-5", & $OCH_2CH_2OCH_3$; 3.3 (s, 3H) OMe; 1.9 (s, 3H) 5-CH_3. ^{13}C-NMR ($CDCl_3$+CD_3OD): 164.3 (s) C-4; 155.8 (s) C-3'; 150.7 (s) C-2; 137.3 (d, J_{CH} = 187.6 Hz) C-6; 111.3 (s) C-5; 88.6 (d, J_{CH} = 167.4 Hz) C-1'; 79.3 , 78.6 (2xd, J_{CH} = 147.1 Hz, J_{CH} = 153.9 Hz) C-2' & C-4'; 71.6 (t, J_{CH} = 142.6 Hz) $OCH_2CH_2OCH_3$; 69.4 (t) $OCH_2CH_2OCH_3$; 60.7 (t, J_{CH} = 145.5 Hz) C-5'; 58.5 (q, JCH = 141.5 Hz) $OCH_2CH_2OCH_3$; 11.9 (q, J_{CH} = 129.2 Hz) 5-CH_3. MS (FAB$^-$): cal. for $(M-H)^-$ 328.1145, found 328.1127. UV (EtOH): [pH 7] λ_{max} = 265 nm (ε = 11100); [pH 2] λ_{max} = 264 nm (ε = 11000); [pH 12] λ_{max} = 260 nm (ε = 9600).

1-[2-O-ethyl-3-oximino-β-D-*ribo*furanosyl]thymine (53). Compound **52** (30 mg, 0.05 mmol) was treated with 80% aqueous acetic acid (1 ml) at room temperature overnight. After removal of the solvent it was purified through silica gel column chromatography to give **53** (14 mg, 90 %). (isomeric mixture 1: 4, from NMR, 270 MHz). ^{1}H-NMR ($CDCl_3$ + CD_3OD): (major isomer): 7.62 (d, $J_{CH3,H6}$ = 1.2 Hz) H-6; 5.88 (d, $J_{1',2'}$ = 6.2 Hz) H-1'; 4.95 (m) H-4'; 4.63 (dd, $J_{2',4'}$ = 1.6 Hz)H-2'; 4.21 (dd, $J_{4',5'}$ = 2.3 Hz) H-5'; 4.84 (dd, $J_{5',5"}$ = 121.1 Hz) H-5"; 3.8- 3.5 (m) OCH_2CH_3; 1.93 (d) 5-CH_3; 1.2 (t) OCH_2CH_3. ^{13}C-NMR ($CDCl_3$+CD_3OD): 164.2 (s) C-4; 150.6 (s) C-2; 136.8 (d, J_{CH} = 186.9 Hz) C-6; 111.4 (s) C-5; 88.2 (d, J_{CH} = 168.6 Hz) C-1'; 79.0, 78.4 (2xd, J_{CH} = 149.4 & 155.8 Hz) C-2' & C-4'; 155.7 (s) C-3'; 66.0 (t, J_{CH} = 142.5 Hz) OCH_2CH_3; 60.7 (t, J_{CH} = 145.2 Hz) C-5'; 14.6 (q, J_{CH} = 127.4 Hz) OCH_2CH_3; 11.8 (q, J_{CH} = 129.2 Hz) 5-CH_3. ^{1}H-NMR ($CDCl_3$ + CD_3OD): (minor isomer): 7.4 (d, $J_{CH3,H6}$ = 1.2 Hz) H-6; 5.89 (s) H-1'; 4.82 (s) H-2'; 4.72 (t) H-4'; 3.96 (m, $J_{4',5'}$ = 2.9 Hz, $J_{4',5"}$ = 3.3 Hz, $J_{5',5"}$ = 12.3 Hz) H-5', 5"; 3.8-3.5 (m) OCH_2CH_3; 1.89 (d) 5-CH_3; 1.22 (t) OCH_2CH_3. ^{13}C-NMR ($CDCl_3$+CD_3OD): 90.4 (d) C-1'; 66.4 (t) OCH_2CH_3; 61.0 (t) C-5'. MS (FAB$^-$): cal. for $(M-H)^-$ 298.1039, found 298.1041. UV (EtOH): [pH 7] λ_{max} = 265 nm (ε = 8100); [pH 2] λ_{max} = 265 nm (ε = 8100); [pH 12] λ_{max} = 263 nm (ε = 7300).

1-[5-O-(MMTr)-2,3-dideoxy-3-nitro-2-C-(α-dimethylmalonate)-β-D-*ribo*furanosyl] thymine (26a) & 1-[5-O-(MMTr)-2,3-dideoxy-3-nitro-2-C-(α-dimethylmalonate)-β-D-*xylo*furanosyl]thymine (26b). *General procedure for nucleophilic addition by carbon nucleophiles*: Potassium t-butoxide (82 mg, 0.74 mmol) was added to dimethyl malonate and kept at room temperature for 30 min. It was cooled in an ice-water bath for 15 min and **6** (200 mg, 0.37 mmol) was added and kept stirring for 2 h in ice water bath. The reaction mixture was poured into aqueous ammonium chloride solution which was extracted with

dichloromethane (3x 20 ml). The organic phase was separated and concentrated in vacuo. The residue was subjected to silica gel column chromatography to give **26a** (100mg, 40.0 %) and **26b** (140 mg, 56.0 %). ^{1}H-NMR ($CDCl_3$): **26a** 7.92 (br, 1H) NH, 7.51-6.78 (m, 15 H) arom, and H-6; 6.51 (d, $J_{1',2'}$ = 9.6 Hz, 1H) H-1'; 5.56 (dd $J_{2',3'}$ = 6.7 Hz, $J_{3',4'}$ = 1.1Hz, 1H) H-3'; 4.57 (m, 1H) H-4'; 3.8 (m, 1H) H -2'; 3.72 (d, $J_{2',H\alpha}$ = 5.3 Hz, 1H) C<u>H</u>($COOCH_3$)$_2$; 3.64 (dd, $J_{4',5'}$ = 2.7 Hz, $J_{5',5''}$ = 10.6 Hz, 1H) H-5'; 3.46 (dd, $J_{4',5''}$ = 2.1 Hz, 1H) H-5"; 3.79 MMTr; 3.81, 3.62 (2xs, 6H) 2x$COOCH_3$; 1.23 (d, $J_{CH3,H6}$ =1.2 Hz, 3H) 5-CH_3 ^{13}C-NMR ($CDCl_3$): 111.9 (s)-C-5, 87.0 (s) MMTr; 88.9 (d, J_{CH} = 165.1 Hz) C-3'; 45.2 (d, J_{CH} = 143.0 Hz) C-2'; 80.1 (d, J_{CH} = 156.1 Hz) C-4'; 85.4 (d, J_{CH} = 174.1 Hz) C-1'; 64.2 (t, J_{CH} = 142.0 Hz) C-5'; 55.2 (q, J_{CH} = 143.8 Hz) OCH_3; 53.4 (q, J_{CH} = 148.3 Hz) $COOCH_3$; 48.7 (d) C<u>H</u>($COOCH_3$)$_2$; 11.3 (q) 5-CH_3. MS (FAB$^-$): cal. for (M-NO2)$^-$ 626.2264, found 626.2229. UV (EtOH): [pH 7] λ_{max} = 266 nm. **26b:** ^{1}H-NMR ($CDCl_3$): 9.01 (br, 1H) NH; 7.58 (d, $J_{CH3,H6}$ = 1.2 Hz) H-6; 7.44-6.78 (m, 14 H) arom; 6.12 (d, $J_{1',2'}$ = 7.2 Hz, 1H) H-1'; 5.41 (dd, $J_{2',3'}$ = 3.8 Hz, $J_{3',4'}$ = 6.4 Hz, 1H) H-3'; 4.51 (m, 1H) H-4' 3.95 (d, $J_{H\alpha,2'}$ = 5.3 Hz, 1H) C<u>H</u>($COOCH_3$)$_2$; 3.82, 3.72 (2xs, 6H) 2x$COOCH_3$; 3.8 (s, 3H) MMTr; 3.48 (dd, $J_{4',5'}$ = 5.7 Hz, 1H) H-5'; 3.37 (dd, $J_{4',5''}$ = 5.3 Hz, 1H) H-5"; 3.44 (m, 1H) H-2'; 1.91 (d, $J_{CH3,H6}$ = 1.2 Hz, 3H) 5-CH_3. ^{13}C-NMR ($CDCl_3$): 112.4 (s) C-5, 88.5 (d) C-3'; 49.6 (d, J_{CH} = 135.9 Hz) C-2'; 78.7 (d) C-4'; 85.0 (d, J_{CH} = 165.1 Hz) C-1'; 61.1 (t, J_{CH} = 142.6 Hz) C-5'; 55.1 (q, J_{CH} = 143.8 Hz) MMTr; 53.3 (q, J_{CH} = 148.3 Hz) $COOCH_3$; 49.6 (d, J_{CH} = 135.9 Hz) C<u>H</u>($COOCH_3$)$_2$; 12.5 (q, J_{CH} = 129.2 Hz) 5-CH_3. MS (FAB$^-$): cal. for (M-H)$^-$ 672.2194, found 672.2208.

1-[2,3-dideoxy-2-<u>C</u>-(α-dimethylmalonate)-β-D-*ribo*furanosyl]thymine (41). Compound **40** (18 mg, 0.03 mmol) was treated with 80% aqueous acetic acid (2 ml) overnight at room temperature. The solvent was removed in vacuo with co-evaporation with toluene. The residue was subjected to silica gel column chromatography to give **41** (9.5 mg, 95 %). ^{1}H-NMR ($CDCl_3$): 8.4 (br, 1H) NH ; 7.5 (d, $J_{CH3,H6}$ = 1.0 Hz, 1H) H-6; 5.9 (d, $J_{1',2'}$ = 6.9 Hz, 1H) H-1' ; 4.2 (m, 1H) H-4'; 3.1(m, 1H) H-2'; 2.35 (m, $J_{3',4'}$ = 5.8 Hz, $J_{3',3''}$ = 12.9 Hz , $J_{2',3'}$ = 9.0 Hz) H-3'; 1.95 (m, $J_{3'',4'}$ = 7.9 Hz, $J_{2',3''}$ = 7.7 Hz, 1H) H-3"; 3.55 (d, $J_{H\alpha,2'}$ = 8.8 Hz, 1H) C<u>H</u>($COOCH_3$)$_2$; 3.7, 3.75 (2xs, 6H) 2x$COOCH_3$; 1.95 (d, $J_{CH3,H6}$ = 1.0 Hz, 3H) 5-CH_3 . ^{13}C-NMR ($CDCl_3$): 110.5 (s) C-5; 89.0 (d, J_{CH} = 170.7 Hz) C-1', 42.6 (d, J_{CH} = 137.0 Hz) C-2'; 30.0 (t, J_{CH} = 134.2 Hz) C-3'; 75.4 (d, J_{CH} = 160.6 Hz) C-4'; 64.1 (t, J_{CH} = 142.1 Hz) C-5'; 42.6 (d, J_{CH} = 137.0 Hz) C<u>H</u>($COOCH_3$)$_2$; 52.9 (q, J_{CH} = 148.2 Hz) 2x$COOCH_3$; 12.5 (q) 5-CH_3. MS (FAB$^-$): cal. for (M-H)$^-$ 355.1142, found 355.1151. UV (EtOH): [pH 7] λ_{max} = 266 nm.

1-[2,3-dideoxy-3-nitro-2-<u>C</u>-(α-dimethylmalonate)-β-D-*ribo*furanosyl]thymine (27a). Compound **26a** (50 mg, 0.07 mmol) was treated with 80 % aqueous acetic acid (3 ml) overnight at room temperature. The solvent was removed in vacuo, and co-evaporated with toluene and methanol. The residue was subjected to silica gel column chromatography to give **27a** (20 mg, 70 %) and **27b** (8 mg, 27 %). ^{1}H-NMR ($CDCl_3$): 8.4 (br, 1H) NH; 7.33 (d, $J_{CH3,H6}$ = 1.2 Hz, 1H) H-6 ; 6.11(d, $J_{1',2'}$ = 8.8 Hz, 1H) H-1' ; 5.61 (dd, $J_{2',3'}$ = 6.1 Hz, $J_{3',4'}$ = 1.5 Hz, 1H) H-3' ; 4.57 (m, 1H) H-4'; 3.98-3.83 (m, 4H) H-2', H-5', H-5" & C<u>H</u>($COOCH_3$)$_2$; 3.62 (s, 3H) $COOCH_3$; 3.76 (s, 3H) $COOCH_3$; 1.95 (d, 3H) 5-CH_3. ^{13}C-NMR ($CDCl_3$): 137.6 (d) C-6; 111.6 (s) C-5; 90.4 (d, J_{CH} = 166.2 Hz) C-3'; 43.7 (d, J_{CH} = 137.0 Hz) C-2'; 88.5 (d) C-1'; 82.2 (d) C-4'; 63.4 (t, J_{CH} = 145.4 Hz) C-5'; 48.9 (d, J_{CH} = 137.0 Hz) C<u>H</u>($COOCH_3$)$_2$; 53.4, 53.3 (2xq, J_{CH} = 147.9 Hz) $COOCH_3$; 12.8 (q, J_{CH} = 129.2 Hz)5-CH_3. MS (FAB$^-$): cal. for (M-H)$^-$ 400.0992, found 400.0970. UV (EtOH): [pH 7] λ_{max} = 265 nm (ε = 5500); [pH 2] λ_{max} = 262 nm (ε = 5500); [pH 12] λ_{max} = 260 nm (ε = 12900)

1-[2,3-dideoxy-3-nitro-2-<u>C</u>-(α–dimethylmalonate)-β–D-*xylo*furanosyl]thymine (27b). Compound **26b** (40 mg, 0.05 mmol) was treated with 80 % aqueous acetic acid (3 ml)

overnight at room temperature. The solvent was removed in vacuo, co-evaporated with toluene and methanol. The residue was subjected to silica gel column chromatography to give an isomeric mixture of *xylo* and *ribo* products of **27b** (18 mg, 75 %) and **27a** (4 mg, 16 %). ^{1}H-NMR ($CDCl_3$): 9.0 (br, 1H) NH; 7.55 (d, $J_{CH3,H6}$ = 1.2 Hz, 1H) H-6; 6.14 (d, $J_{1',2'}$ = 7.3 Hz, 1H) H-1'; 5.47 (dd, $J_{2',3'}$ = 3.7, Hz, $J_{3',4'}$ = 6.3 Hz, 1H) H-3'; 4.56 (m, 1H) H-4'; 3.84- 3.68 (m, 2H) H-5', 5"; 3.93 (d, $J_{H\alpha,2'}$ = 5.6 Hz, 1H) C<u>H</u>$(COOCH_3)_2$; 3.51 (m, 1H) H-2'; 3.83, 3.74 (2xs, 6H) 2xCOOC<u>H</u>$_3$; 1.98 (d, $J_{CH3,H6}$ =1.2 Hz, 3H) 5-CH_3. ^{13}C-NMR ($CDCl_3$): 134.6 (d, J_{CH} = 186.0 Hz) C-6; 112.6 (s) C-5; 88.5 (d, J_{CH} = 160.6) C-3'; 48.8 (d, J_{CH} = 139.3 Hz) C-2'; 79.5 (d, J_{CH} = 146.0 Hz) C4'; 84.7 (d, J_{CH} = 175.2 Hz) C-1'; 60.5 (t, J_{CH} = 142.6 Hz) C-5'; 53.5 (q, J_{CH} = 148.6 Hz) 2xCOO<u>C</u>H_3; 49.5 (d, J_{CH} = 133.6 Hz) <u>C</u>H$(COOCH_3)_2$; 12.6 (q, J_{CH} = 127.3 Hz) 5-CH_3. MS (FAB$^-$): cal. for (M-H)$^-$ 400.0992, found 400.1007. UV (EtOH): [pH 7] λ_{max} = 265 nm (ε = 7600); [pH 2] λ_{max} = 263 nm (ε = 7600); [pH 12] λ_{max} = 260 nm (ε = 16500).

1-[5-O-(MMTr)-2,3-dideoxy-3-nitro-2-<u>C</u>-(α-methylacetoacetate)-β-D-*xylo* furanosyl]thymine (30b) & 1-[5-O-(MMTr)-2,3-dideoxy-3-nitro-2-<u>C</u>-(α-methylacetoacetate)-β-D-*ribo*furanosyl]thymine (30a). The general procedure for addition of carbon nucleophiles was followed using **6** (200 mg, 0.37 mmol), potassium t-butoxide (123 mg, 1.1 mmol) in methyl acetoacetate (5 ml) to give **30b** (144 mg, 59 %) and **30a** (90 mg, 37 %) respectively. Each of the compounds **30b** and **30a** is an inseparable isomeric mixture due to chiral center in <u>C</u>H$(COOCH_3)COCH_3$ atom. **30b** (minor isomer): ^{1}H-NMR($CDCl_3$): 7.8 (d, $J_{CH3,H6}$ = 1.0 Hz) H-6; 7.48-6.78 (m) arom; 6.03 (d, $J_{1',2'}$ = 6.9 Hz) H-1'; 3.45 (m, $J_{2',3'}$ = 3.3 Hz, $J_{2',H\alpha}$= 5.4 Hz) H-2'; 5.26 (dd, $J_{3',4'}$ = 6.1 Hz) H-3'; 4.44 (m) H-4'; 4.12 (d) C<u>H</u>$(COOCH_3)COCH_3$; 3.45-3.34 (m) H-5', 5", 3.8 (s) MMTr; 3.84 (s), $COOCH_3$; 2.34 (s) $COCH_3$; 1.92 (d) 5-CH_3 ^{1}H-NMR ($CDCl_3$): (major isomer) 8.4 (br) NH; 7.7 (d, $J_{CH3,H6}$ = 1.0 Hz) H-6; 7.48-6.78 (m) arom; 5.92 (d, $J_{1',2'}$ = 7.4 Hz) H-1'; 3.34 (m, $J_{2',3'}$ = 3.7 Hz, $J_{H\alpha,2'}$ = 4.6 Hz) H-2'; 5.42 (dd, $J_{3',4'}$ = 5.5 Hz) H-3'; 4.64 (m) H-4'; 3.45-3.34 (m) H-5', 5"; 4.15 (d) C<u>H</u>$(COOCH_3)COCH_3$; 1.92 (d) 5-CH_3; 3.79 (s) MMTr; 3.73 (s) $COOCH_3$; 2.44 (s) $COCH_3$. ^{13}C-NMR ($CDCl_3$): 111.3 (s) C-5; 88.9 (d, J_{CH} = 164.0 Hz) C-3' ; 50.1 (d) C-2'; 78.8 (d, J_{CH} = 156.1 Hz) C-4' ; 85.3, 84.8 (2xd, J_{CH} = 172.9 Hz) 2xC-1' ; 61.3 (t, J_{CH} = 144.3 Hz) C-5'; 53.3 (q, J_{CH} = 148.6 Hz) $COOCH_3$; 30.9, 30.0 (2xq, J_{CH} = 128.8 Hz) 2x$COCH_3$; 57.4 (d) <u>C</u>H$(COOCH_3)COCH_3$; 55.1 (q, J_{CH} = 143.8 Hz) MMTr; 12.5 (q, J_{CH} = 128.8 Hz) 5-CH_3. MS (FAB$^-$): cal. for (M-H)$^-$ 656.2244, found 656.2262. UV (EtOH): [pH 7] λ_{max} = 264 nm. **30a:** ^{1}H-NMR ($CDCl_3$): 8.2 (br, 1H) NH; 7.55, 7.5 (2xd, 1H) H6; 7.45-6.78 (m, 14 H) arom; 6.41 (d, $J_{1',2'}$ = 9.4 Hz) H-1' (minor isomer); 6.39 (d, $J_{1',2'}$ = 9.1 Hz) H-1' (major isomer); 5.55 (m, 1H) H-3'; 4.6 (m, 1H) H-4'; 4.05-3.8 (m, 2H) H-2' and C<u>H</u>$(COCH_3)COOCH_3$; 3.65-3.4 (m, 2H) H-5', 5"; 3.8 (s) $COOC\underline{H}_3$; 3.65 (s) $COOC\underline{H}_3$; 3.79 (s, 3H) MMTr; 2.3, 2.35 (2xs, 3H) 2x$COCH_3$; 1.4, 1.34 (2xd, 3H) 2x5-CH_3.^{13}C-NMR ($CDCl_3$): 112.1, 111.8 (2xs) 2xC-5; 89.5, 88.6 (2xd, J_{CH} = 161.Hz) 2xC-3'; 86.0 (d, J_{CH} = 165.4Hz) C-1'; 85.5 (d, J_{CH} = 170.4 Hz) C-1'; 80.3 (d, J_{CH} = 148.4 Hz) C-4'; 79.7 (d, J_{CH} = 156.7 Hz) C-4'; 64.2, 64.1 (2xd, J_{CH} = 144.3 Hz) 2xC-5'; 56.9 (d, J_{CH} = 142.7 Hz) <u>C</u>H$(COOCH_3)COCH_3$; 55.9 (d, J_{CH} = 141.1Hz) <u>C</u>H$(COOCH_3)COCH_3$; 55.2 (q, J_{CH} = 143.9 Hz) MMTr; 53.3, 53.2 (2xq, J_{CH} = 148.4 Hz) 2xCOO<u>C</u>H_3; 45.0, 44.9 (2xd, J_{CH} = 139.3 Hz) 2xC-2'; 30.6, 29.6 (2xq, J_{CH} = 129.2 Hz) 2xCO<u>C</u>H_3; 11.5, 11.4 (2xq, J_{CH} = 129.2 Hz) 2x5-CH_3. MS (FAB$^-$): cal. for (M-H)$^-$ 656.2244, found 656.2265. UV (EtOH): [pH 7] λ_{max} = 264 nm.

1-[2,3-dideoxy-3-nitro-2-<u>C</u>-(α-methylacetoacetate)-β-D-*ribo*furanosyl]thymine (31a). Compound **30a** (50 mg, 0.07 mmol) was treated with 80% aqueous acetic acid (1 ml) at room temperature overnight. After removal of the solvent the residue was purified through silica gel column chromatography to give **31a** (23 mg, 79 %) as a major product. ^{1}H-NMR ($CDCl_3$): [isomeric mixture due to the chiral center <u>C</u>H$(COOCH_3)COCH_3$

atom]. 7.63 (d, $J_{CH3, H6}$ = 1.2 Hz) H-6; 7.54 (d, $J_{CH3, H6}$ = 1.0 Hz) H-6; 6.29 (d, $J_{1', 2'}$ = 9.3 Hz) H-1'; 6.18 (d, $J_{1', 2'}$ = 8.7 Hz) H-1'; 5.54 (m, 1H) H-3'; 4.59 (m, 1H) H-4'; 4.06-3.65 (m, 4H) H-5', 5", H-2' and C<u>H</u>(COOCH$_3$)COCH$_3$; 3.76, 3.64 (2xs, 3H) 2xCOOCH$_3$; 2.31, 2.25 (2xs, 3H) 2xCOC<u>H</u>$_3$; 1.94 (2xd, 3H) 2x5-CH$_3$. ^{13}C-NMR ($CDCl_3$): 136.7, 135.8 (2xd) 2xC-6; 111.8, 111.6 (2xs) 2xC-5; 89.2 (d, J_{CH} = 168.6 Hz) C-1'; 87.4 (d, J_{CH} = 166.8 Hz) C-1'; 88.3 (d, J_{CH} = 164.6 Hz) C-3'; 81.8 (d, J_{CH} = 148.5 Hz) C-4'; 81.5 (d, J_{CH} = 151.2 Hz) C-4'; 63.2 (t, J_{CH} = 144.3 Hz) C-5'; 57.2 (d, J_{CH} = 136.5 Hz) <u>C</u>H(COOCH$_3$)COCH$_3$; 56.1 (d, J_{CH} = 133.8 Hz) <u>C</u>H(COOCH$_3$)COCH$_3$; 53.4 (q, J_{CH} = 148.5 Hz) COO<u>C</u>H$_3$; 53.3 (q, J_{CH} = 148.8 Hz) COO<u>C</u>H$_3$; 44.6 (d, J_{CH} = 133.8 Hz) C-2'; 44.3 (d, J_{CH} = 136.5 Hz) C-2'; 30.5 (q, J_{CH} = 128.9 Hz) CO<u>C</u>H$_3$; 29.4 (q, J_{CH} = 129.2 Hz) CO<u>C</u>H$_3$; 12.5 (q, J_{CH} = 129.5 Hz) 5-CH$_3$. MS (FAB$^-$): cal. for (M-H)$^-$ 384.1043, found 384.1035. UV (EtOH): [pH 7] λ_{max} = 264 nm (ε = 10200); [pH 2] λ_{max} = 264 nm (ε = 10200); [pH 12] λ_{max} = 270 nm (ε = 22200).

1-[2,3-dideoxy-3-nitro-2-<u>C</u>-(α-methylacetoacetate)-β-D-*xylo*furanosyl]thymine (31b). Compound **30b** (100 mg, 0.15 mmol) was treated with 80% aqueous acetic acid (2 ml) at room temperature overnight. The solvent was removed in vacuo and was purified on silica gel column chromatography to give **31b** (45 mg, 77 %) as a major product. ^{1}H-NMR ($CDCl_3$): 9.85 (br, 1H) NH; 7.57 (s, 1H) H-6; 6.07 (d, $J_{1', 2'}$ = 6.8 Hz) H-1'(minor isomer); 5.95 (d, $J_{1', 2'}$ = 7.8 Hz) H-1' (major isomer); 5.44 (m, 1H) H-3'; 4.61 (m, 1H) H-4'; 4.2 (m, 1H) C<u>H</u>(COOCH$_3$)COCH$_3$; 3.75 (m, 2 H) H-5', 5"; 3.47 (m, 1H) H-2'; 3.83, 3.74 (2xs, 3H) 2xCOOC<u>H</u>$_3$; 2.43, 2.35 (2xs, 3H) 2xCOC<u>H</u>$_3$; 1.95 (s, 3H) 5-CH$_3$. ^{13}C-NMR ($CDCl_3$): 134.0 (d, J_{CH} = 186.5 Hz) C-6; 112.4 (s) C-5; 88.9 (d, J_{CH} = 161.7 Hz) C-3'; 84.8, 84.5 (2xd, J_{CH} = 167.4 Hz) 2xC-1'; 79.5 (d, J_{CH} = 152.8 Hz) C-4'; 60.3 (t, J_{CH} = 145.0 Hz) C-5'; 57.2, 56.4 (2xd) 2x<u>C</u>H(COOCH$_3$)CO<u>C</u>H$_3$; 53.3 (q, J_{CH} = 148.6 Hz) 2xCOO<u>C</u>H$_3$; 49.2 (d, J_{CH} = 132.5 Hz) C-2'; 48.0 (d, J_{CH} = 135.9 Hz) C-2'; 30.6, 30.0 (2xq, J_{CH} = 129.2 Hz) 2xCO<u>C</u>H$_3$; 12.5 (q, J_{CH} = 129.9 Hz) 5-CH$_3$. MS (FAB$^-$): cal. for (M-H)$^-$ 384.1043, found 384.1047. UV (EtOH): [pH 7] λ_{max} = 265 nm (ε = 8900); [pH 2] λ_{max} = 260 nm (ε = 8700); [pH 12] λ_{max} = 270 nm (ε = 17000)

1-[5-O-(MMTr)-2,3-dideoxy-2-<u>C</u>-(α-methylacetoacetate)-β-D-*ribo*furanosyl]thymine (42). The general procedure for denitration was followed using **30b** (90 mg, 0.13 mmol), tributyl tinhydride (110 µl, 0.41 mmol), AIBN (22 mg, 0.13 mmol) in dry benzene (7 ml) to give **42** (70 mg, 84 %). ^{1}H-NMR ($CDCl_3$): 8.21 (s, 1H) NH; 7.53-6.78 (m, 15 H) arom & H-6 ; 5.96 (d, $J_{1', 2'}$ = 7.5 Hz) H-1'(one of the isomers) 5.89 (d, $J_{1', 2'}$ = 7.6 Hz) H-1' (other isomer, both are 1:1 ratio, only H-1' separated); 4.25 (m, 1H) H-4'; 3.75 (d) C<u>H</u>(COOCH$_3$)COCH$_3$; 3.39 (m, 1H) H-5' ; 3.22 (m, 2H) H-5" &H-2' ; 2.36 (m, 1H) H-3'; 1.97 (m, 1H) H-3"; 3.8 (s, 3H) MMTr; 3.76, 3.69 (2xs, 3H) 2xCOOC<u>H</u>$_3$; 2.28, 2.26 (2xs, 3H) 2xCOC<u>H</u>$_3$; 1.53, 1.51 (2xd, $J_{CH3\ H6}$=1.1 Hz) 2x5-CH$_3$. ^{13}C-NMR ($CDCl_3$): 111.3 (s) C-5 ; 87.5 (d, J_{CH} = 163.4 Hz) C-1' ;42.8 (d) C-2' ; 30.9 (t, J_{CH} = 134.8 Hz) C-3'; 78.8 (d, J_{CH} = 148.2 Hz) C-4'; 65.4 (t, J_{CH} = 143.2 Hz) C-5'; 60.2 (d, J_{CH} = 122.4 Hz) <u>C</u>H(COOCH$_3$)COCH$_3$; 52.7 (q, J_{CH} = 149.0 Hz) COO<u>C</u>H$_3$; 29.8 (q,J_{CH} = 128.4 Hz) CO<u>C</u>H$_3$; 55.1 (q, J_{CH} = 143.8 Hz) MMTr; 11.9 (q, J_{CH} = 129.5 Hz) 5-CH$_3$. MS (FAB$^-$): cal. for (M-H)$^-$ 611.2394, found 611.2401.

1-[2,3-dideoxy-2-<u>C</u>-(α-methylacetoacetate)-β-D-*ribo*furanosyl]thymine (43). The compound **42** (40 mg, 0.06 mmol) was treated with 80 % aqueous acetic acid (3 ml) at room temperature overnight. The solvent was removed in vacuo and was co-evaporated with methanol and toluene. The residue was subjected to silica gel column chromatography to give **43** (20 mg, 91 %). ^{1}H-NMR ($CDCl_3$): 8.8 (br, 1H) NH; 7.41(d, $J_{CH3, H6}$ = 1.2 Hz) H-6, (minor isomer); 7.39 (d, $J_{CH3,H6}$=1.2 Hz) H-6 (major isomer); 5.86 (d, $J_{1', 2'}$ = 7.2 Hz) H-1' (minor isomer); 5.81 (d, $J_{1', 2'}$ = 7.3 Hz) H-1' (major isomer); 4.2 (m, 1H) H-4'; 3.74 (m, 3H) H-5', 5" &C<u>H</u>(COOCH$_3$)COCH$_3$; 3.09 (m, 1H) H-2'; 3.76,

3.69 (2xs, 3H) 2xCOOC$\underline{H}_3$; 2.27, 2.25 (2xs, 3H) 2xCOC$\underline{H}_3$; 2.3 (m, 1H) H-3'; 1.9 (m, 1H) H-3"; 1.93 (d, 1H) 5-CH_3. ^{13}C-NMR ($CDCl_3$): (isomeric mixture): 136.5, 136.0 (2xd, J_{CH} = 186.0 Hz, & 178.7 Hz) 2x C-6; 111.3 (s) C-5; 88.6, 88.5 (2xd, J_{CH} = 166.8 Hz) 2x C-1'; 78.2, 78.1 (2xd, J_{CH} = 150.3 Hz) 2x C-4' ; 64.4, 64.2 (2xt, J_{CH} = 140.7 Hz) 2xC-5'; 60.7, 60.5 (2xd) 2xCOO$\underline{C}H_3$; 52.9, 52.8 (2xd) 2 x$\underline{C}H(COOCH_3)COCH_3$; 42.2, 41.8 (2Xd) 2 x C-2'; 30.2, 30.0 (2x t) 2xC-3'; 29.8, 29.6 (2xq) 2xCO$\underline{C}H_3$; 12.5 (q, J_{CH} = 127.4 Hz) 5-CH_3.MS (FAB$^-$): cal. for (M-H)$^-$ 339.1192, found 339.1178. UV (EtOH): [pH 7] λ_{max} = 266 nm.

1-[5-O-(MMTr)-2,3-dideoxy-3-nitro-2-$\underline{C}$-(α-acetylacetone)-β-D-*ribo*furanosyl] thymine (28). General procedure for addition of carbon nucleophiles was followed using **6** (100 mg, 0.18 mmol), potassium t-butoxide (61.5 mg, 0.55 mmol) in distilled acetyl acetone (3 ml) to give **28** (66 mg, 56 %). ^{1}H-NMR ($CDCl_3$): 8.44 (br, 1H) NH; 7.52 (d, $J_{CH3,\ H6}$ = 1.2 Hz, 1H) H-6; 7.53-6.78 (m, 14 H) arom; 6.36 (d, $J_{1',\ 2'}$ = 9.0 Hz, 1H) H-1'; 5.38 (dd, $J_{2',\ 3'}$ = 5.8 Hz, $J_{3',\ 4'}$ = 1.2 Hz, 1H) H-3'; 4.59 (m, 1H) H-4'; 3.39 (dd, $J_{4',\ 5"}$ = 1.4 Hz, 1H) H-5"; 3.6 (dd, $J_{4',\ 5'}$ = 2.4 Hz, $J_{5',\ 5"}$ = 10.6 Hz, 1H) H-5'; 4.17 (d, 1H) $C\underline{H}(COCH_3)_2$; 4.07 (m, 1H) H-2'; 3.81 (s, 3H) MMTr; 2.32, 2.35 (2xs, 6H) 2xCOC$\underline{H}_3$; 1.32 (d, 3H) 5-CH_3. ^{13}C-NMR ($CDCl_3$): 109.5 (s) C-5; 88.9 (d, J_{CH} = 165.1 Hz) C-3'; 85.3 (d, J_{CH} = 174.1 Hz) C-1'; 79.6 (d, J_{CH} = 151.6 Hz) C-4'; 64.9 (t, J_{CH} = 142.6 Hz) C-5'; 45.8 (d, J_{CH} = 139.3 Hz) C-2'; 64.0 (d, J_{CH} = 136.9 Hz) $\underline{C}H(COCH_3)_2$; 55.0 (q, J_{CH} = 144.1 Hz) MMTr 31.5, 30.7 (2xq, J_{CH} = 128.7 Hz, 128.0 Hz) 2xCO$\underline{C}H_3$; 11.4 (q, J_{CH} = 128.0 Hz) 5-CH_3. MS (FAB$^-$): cal. for (M-H)$^-$ 640.2295, found 640.2287. UV (EtOH): [pH 7] λ_{max} = 267 nm.

1-[2,3-dideoxy-3-nitro-2-$\underline{C}$-(α–acetylacetone)-β-D-*ribo*furanosyl]thymine (29). Compound **28** (25 mg, 0.03 mmol) was treated with 80% aqueous acetic acid (1.5 ml) at room temperature overnight. The solvent was removed in vacuo and co-evaporated with methanol and toluene.The residue was subjected to silica gel column chromatography to give **29** (10 mg, 70 %). ^{1}H-NMR ($CDCl_3$): 8.18 (s, 1H) NH; 7.48 (d) H-6, 6.19 (d, $J_{1',\ 2'}$ = 9.4 Hz, 1H) H-1'; 5.4 (dd, $J_{2',\ 3'}$ = 7.0 Hz, $J_{3',\ 4'}$ = 1.4 Hz, 1H) H-3'; 4.6 (m, 1H) H-4'; 4.1-3.84 (m, 2H) H-5', 5"; 4.18 (d, $J_{2',\ H\alpha}$ = 10.7 Hz, 1H) $C\underline{H}(COCH_3)_2$; 3.8 (m, 1H) H-2'; 2.28, 2.3 (2xs, 2x3H) 2xCOC$\underline{H}_3$; 1.95 (d, 3H) 5-CH_3. ^{13}C-NMR ($CDCl_3$): 88.7 (d, J_{CH} = 163.1 Hz) C-3'; 87.5 (d, J_{CH} = 171.4 Hz) C-1'; 81.1 (d, J_{CH} = 152.1 Hz) C-4'; 63.3 (t, J_{CH} = 144.3 Hz) C-5'; 45.3 (d, J_{CH} = 136.6 Hz) C-2'; 65.7 (d, J_{CH} = 134.7 Hz) $\underline{C}H(COCH_3)_2$; 135.7 (d, J_{CH} = 175.9 Hz) C-6; 31.0, 30.7 (2xq, J_{CH} = 128.9 Hz) 2xCO$\underline{C}H_3$; 12.6 (q, J_{CH} = 129.5 Hz) 5-CH_3. MS (FAB$^-$): cal. for (M-H)$^-$ 368.1094, found 368.1053. UV (EtOH): [pH 7] λ_{max} = 265 nm (ε = 9500); [pH 2] λ_{max} = 263 nm (ε = 9500).

1-[5-O-(MMTr)-2,3-dideoxy-3-nitro-2-$\underline{C}$-(α–cyclohexanonyl)-β–D-*ribo*furanosyl] thymine (32a) and 1-[5-O-(MMTr)-2,3-dideoxy-3-nitro-2-$\underline{C}$-(α–cyclohexanonyl)-β-D-*xylo*furanosyl]thymine (32b). Compound **6** (540 mg, 1 mmol) was dissolved in dry THF (5 ml) and morpholino-1-yl cyclohexene (1.67 ml, 10 mmol) was added, stirred at room temperature for 3 h under an argon atmosphere. Then the reaction mixture was kept at 70^0 C for 90 min. To that reaction mixture water (2 ml) was added and continued for another 90 min. The solvent was removed in vacuo, co-evaporated with toluene to give a foam which was subjected to silica gel column chromatography to give **32a** (110 mg, 17 %) & **32b** (340 mg, 53 %). ^{1}H-NMR ($CDCl_3$): **32a:** 7.55-6.8 (m, 15 H) H-6 & arom; 6.54 (d, $J_{1',\ 2'}$ =9.7 Hz, 1H) H-1'; 5.7 (m, 1H) H-3'; 4.59 (m, 1H) H-4'; 3.7-3.27 (m, 4H) H-5', 5", H-2', & $C\underline{H}C$=O; 3.81 (s, 3H) MMTr; 2.46-1.37 (m, 8H) $COCH_2CH_2CH_2CH_2$; 1.23 (d, $J_{CH3,\ H6}$=1.2 Hz, 3H) 5-CH_3. ^{13}C-NMR ($CDCl_3$): 112.1 (s) C-5; 90.2 (d, J_{CH} = 162.9 Hz) C-3'; 85.3 (d, J_{CH} = 168.5 Hz) C-1'; 79.8 (d, J_{CH} = 152.7 Hz) C-4'; 64.1 (t, J_{CH} = 144.9 Hz) C-5'; 45.7 (d, J_{CH} = 131.4 Hz) C-2'; 48.3 (d, J_{CH} = 128.0 Hz) $\underline{C}HC$=O; 55.0 (q, J_{CH} =144.1 Hz) MMTr; 41.9, 36.6, 28.2, 24.8 for $COCH_2CH_2CH_2CH_2$; 11.0 (q, J_{CH}=128.8

Hz) 5-CH_3. MS (FAB^-): cal. for $(M-H)^-$ 638.2502, found 638.2476. UV (EtOH): [pH 7] λ_{max} = 266 nm. Compound **32b**: ^{1}H-NMR ($CDCl_3$): 8.91 (br, 1H) NH; 7.62 (d) H-6; 7.5-6.78 (m, 14 H) arom; 6.12 (d, $J_{1',2'}$ = 6.1 Hz, 1H) H-1'; 5.0 (m, 1H) H-3'; 4.6 (m, 1H) H-4', 3.4 (m, 2H) H-5', 5''; 2.77 (m, 2H) H-2', C<u>H</u>C=O; 3.8 (s, 3H) MMTr; 2.44-1.25 (m, 8H) $COCH_2CH_2CH_2CH_2$; 1.92 (d) 5-CH_3. ^{13}C-NMR ($CDCl_3$): 112.3 (s) C-5; 89.9 (d, J_{CH} = 159.5 Hz) C-3'; 85.2 (d, J_{CH} = 174.1 Hz) C-1'; 78.0 (d) C-4'; 61.2 (t, J_{CH} = 144.3 Hz) C-5'; 49.8 (d, J_{CH} = 138.1 Hz) C-2'; 52.0 (d, J_{CH} = 134.8 Hz) <u>C</u>HC=O; 55.0 (q, J_{CH} = 143.8 Hz) MMTr; 42.0, 32.5, 27.6, 24.9 for $COCH_2CH_2CH_2CH_2CH_2$; 12.5 (q, J_{CH} = 129.2 Hz) 5-CH_3. MS (FAB^-): cal. for $(M-H)^-$ 638.2502, found 638.2498. UV (EtOH): [pH 7] λ_{max} = 265 nm.

1-[5-O-(MMTr)-2,3-dideoxy-2-<u>C</u>-(α-cyclohexanonyl)-β-D-*ribo*furanosyl]thymine (44). The general procedure for denitration was followed using **32b** (150 mg, 0.23 mmol), tributyl tinhydride (188 µl 0.7 mmol), AIBN (38 mg, 0.23 mmol) in dry benzene (10 ml) to give **44** (77 mg, 55 %). ^{1}H-NMR ($CDCl_3$): 8.99 (br, 1H) NH; 7.56 (d, $J_{CH3,\ H6}$=1.2 Hz, 1H) H-6; 7.47-6.78 (m, 14 H) arom; 6.07 (d, $J_{1',2'}$ = 6.6 Hz, 1H) H-1'; 4.26 (m, 1H) H-4'; 3.22 (dd, $J_{4',5''}$ =3.5 Hz, 1H) H-5''; 3.39 (dd, $J_{4',5'}$ =2.7 Hz, $J_{5',5''}$=10.4 Hz, 1H) H-5'; 2.58 (m, 2H) H-2', C<u>H</u>C=O; 1.8 (m, 2H) H-3', 3''; 3.79 (s, 3H) MMTr; 2.4-1.25 (m, 8H) $COCH_2CH_2CH_2CH_2$; 1.48 (d, 3H) 5-CH_3. ^{13}C-NMR ($CDCl_3$): 111.0 (s) C-5; 86.8 (d, J_{CH} = 168.5 Hz) C-1'; 77.4 (d, J_{CH} = 149.4 Hz) C-4'; 65.3 (t, J_{CH} = 141.5 Hz) C-5'; 43.8 (d, J_{CH} = 133.7 Hz) C-2'; 31.6 (t, J_{CH} = 132.5 Hz) C-3'; 55.0 (q, J_{CH} = 143.8 Hz) MMTr; 52.2 (d, J_{CH} = 126.9 Hz) <u>C</u>HC=O; 42.3, 31.8, 27.9, and 24.8 for $COCH_2CH_2CH_2CH_2$; 11.7 (q, J_{CH} =129.2 Hz) 5-CH_3. MS (FAB^-): cal. for $(M-H)^-$ 593.2652, found 593.2632. UV (EtOH): [pH 7] λ_{max} = 266 nm.

1-[2, 3-dideoxy-2-<u>C</u>-(α-cyclohexanonyl)-β-D-*ribo*furanosyl]thymine (45). Compound **44** (35 mg, 0.06 mmol) was treated with 80 % aqueous acetic acid (1 ml) at room temperature overnight. The solvent was removed in vacuo and co-evaporated with toluene and methanol. The residue was purified through silica gel column chromatography to give **45** (16 mg, 85 %). ^{1}H-NMR ($CDCl_3$ + CD_3OD): 7.71 (d, $J_{CH3,\ H6}$ = 1.2 Hz, 1H) H-6; 5.99 (d, $J_{1',2'}$ = 6.1 Hz, 1H) H-1'; 4.17 (m, 1H) H-4'; 3.55 (m, 1H) H-5'; 3.8 (dd, $J_{4',5''}$ = 3.0 Hz, $J_{5',5''}$ = 11.8 Hz, 1H) H-5''; 2.66-1.26 (m, 12H) H-2', H-3',3'', and $CHCOCH_2CH_2CH_2CH_2$; 1.92 (d, 3H) 5-CH_3. ^{13}C-NMR ($CDCl_3$+ CD_3OD): 136.6 (d, J_{CH} = 184.2 Hz) C-6; 110.9 (s) C-5; 87.1 (d, J_{CH} = 166.2 Hz) C-1'; 78.7 (d, J_{CH} = 147.2 Hz) C-4'; 63.7 (t, J_{CH} = 142.6 Hz) C-5'; 52.2 (d, J_{CH} = 130.3 Hz) <u>C</u>HC=O; 43.6 (d, J_{CH} = 131.4 Hz) C-2'; 31.5 (d) C-3'; 42.2, 30.8, 27.7 and 24.3 for $COCH_2CH_2CH_2CH_2$; 12.0 (q, J_{CH} = 130.3 Hz) 5-CH_3. MS (FAB^-): cal. for $(M-H)^-$ 321.1451, found 321.1443. UV (EtOH): [pH 7] λ_{max} = 267 nm (ε = 7500); [pH 2] λ_{max} = 267 nm (ε = 7700); [pH 12] λ_{max} = 265 nm (ε = 6000)

1-[2,3-dideoxy-3-nitro-2-<u>C</u>-(α-cyclohexanonyl)-β-D-*xylo*furanosyl]thymine (33b). Compound **32b** (70 mg, 0.1 mmol) was treated with 80 % aqueous acetic acid (2 ml) at room temperature overnight. The solvent was removed in vacuo, co-evaporated with toluene and methanol. The residue was subjected to silica gel column chromatography to give an inseparable isomeric mixture (<u>R</u> and <u>S</u>) of **33b** (39 mg, 97 %). ^{1}H-NMR ($CDCl_3$+CD_3OD): 7.72 (d, $J_{CH3,\ H6}$ = 1.2 Hz, 1H) H-6; 6.18 (d, $J_{1',2'}$ = 7.1 Hz) H-1' (minor isomer); 6.13 (d, $J_{1',2'}$ = 7.0 Hz) H-1' (major isomer); 5.04 (dd, $J_{2',3'}$ = 2.8 Hz, $J_{3',4'}$ = 6.2 Hz, 1H) H-3'; 4.5 (m, 1H) H-4'; 3.76 (d, 2H) H-5', 5''; 2.96 (m, 2H) H-2' and C<u>H</u>C=O; 2.43-1.26 (m, 8H) $COCH_2CH_2CH_2CH_2$; 1.96 (d, 3H) 5-CH_3. ^{13}C-NMR ($CDCl_3$ + CD_3OD): 135.4 (d, J_{CH} =180.8 Hz) C-6; 112.0 (s) C-5; 89.8 (d, J_{CH} =158.4 Hz) C-3'; 84.6 (d, J_{CH} = 173.0 Hz) C-1'; 78.7 (d, J_{CH} =155.0 Hz) C-4'; 59.5 (t, J_{CH} =141.5 Hz) C-5'; 49.4 (d, J_{CH} =130.3 Hz) C-2'; 50.6 (d, J_{CH} =137.0 Hz) <u>C</u>HC=O; 41.7, 32.0, 27.4, and 24.4 for $COCH_2CH_2CH_2CH_2$; 12.1 (q, J_{CH} =129.2 Hz) 5-CH_3. MS (FAB^-): cal. for $(M-H)^-$

366.1301, found 366.1297. UV (EtOH): [pH 7] λ_{max} = 265 nm (ε = 8100); [pH 2] λ_{max} = 263 nm (ε = 8000); [pH 12] λ_{max} = 246 nm (ε = 10500).

1-[2,3-dideoxy-3-nitro-2-C-(α-cyclohexanonyl)-β-D-*ribo*furanosyl]thymine (33a). Compound **32a** (70 mg, 0.1 mmol) was treated with 80 % aqueous acetic acid (2 ml) overnight at room temperature. The solvent was removed in vacuo, co-evaporated with toluene and methanol. The residue was purified through silica gel column chromatography to give **33a** (28 mg, 70 %) and **33b** (11 mg, 27 %). ^{1}H-NMR ($CDCl_3$+CD_3OD): **33a:** 7.9 (s, 1H) H-6; 6.42 (d, $J_{1',2'}$ = 9.5 Hz) H-1'; 5.67 (d, $J_{2',3'}$ = 6.7 Hz, 1H) H-3'; 4.51 (m, 1H) H-4'; 3.87 (s, 2H) H-5', 5''; 3.1 (m, 1H) H-2'; 2.68-1.27 (m, 9H) $CHCOCH_2CH_2CH_2CH_2$; 1.92 (s, 3H) 5-CH_3. ^{13}C-NMR ($CDCl_3$+CD_3OD): 136.0 (d, J_{CH} = 185.3 Hz) C-6; 111.7 (s) C-5; 89.9 (d, J_{CH} = 166.2 Hz) C-3'; 85.9 (d, J_{CH} = 169.6 Hz) C-1'; 81.4 (d, J_{CH} = 151.6 Hz) C-4'; 62.5 (t, J_{CH} = 142.7 Hz) C-5'; 48.4 (d, J_{CH} = 132.5 Hz) CHC=O; 45.8 (d, J_{CH} = 134.8 Hz) C-2'; 41.7, 31.3, 27.9, 24.5 for $COCH_2CH_2CH_2CH_2$; 11.9 (q, J_{CH} = 129.7 Hz) 5-CH_3. MS (FAB$^-$): cal. for (M-H)$^-$ 366.1301, found 366.1273. UV (EtOH): [pH 7] λ_{max} = 266 nm.

1-[5-O-(MMTr)-2,3-dideoxy-2-C-(α-acetylacetone)-β-D-*ribo*furanosyl]thymine (46). The general procedure for denitration was followed using **28** (70 mg, 0.1 mmol), tributyl tinhydride (87 µl, 0.3 mmol), AIBN (16 mg, 0.1 mmol) in dry benzene (8 ml) overnight to give compound **46** (20 mg, 31 %). ^{1}H-NMR ($CDCl_3$): 7.61 (s, 1H) H-6; 7.53-6.78 (m. 14 H) arom; 5.84 (d, $J_{1',2'}$ =7.5 Hz , 1H) H-1'; 4.26 (m, 1H) H-4'; 3.93 (d, $J_{H\alpha,2'}$ = 10.0 Hz, 1H) CH$(COCH_3)_2$; 3.8 (s, 3H) MMTr; 3.32 (m, 3H) H-5', 5'' and H-2'; 2.2 (m, 2H) H-3', 3''; 2.21 (s, 6H) 2x$COCH_3$; 1.53 (s, 3H) 5-CH_3. ^{13}C-NMR ($CDCl_3$): 111.6 (s) C-5; 87.5 (d, J_{CH} = 166.2 Hz) C-1'; 76.6 (d, J_{CH} = 147.2 Hz) C-4'; 69.9 (d, J_{CH} = 133.7 Hz) CH$(COCH_3)_2$; 65.5 (t, J_{CH} = 141.5 Hz) C-5'; 55.2 (q, J_{CH} = 143.8 Hz) MMTr; 42.5 (d) C-2'; 30.6 (t, J_{CH} = 130.3 Hz) C-3'; 30.3, 28.8 (q, J_{CH} = 128.0 Hz) 2x$COCH_3$; 11.9 (q, J_{CH} = 129.2 Hz) 5-CH_3. MS (FAB$^-$): cal. for (M-H)$^-$ 595.2444, found 595.2480. UV (EtOH): [pH 7] λ_{max} = 266 nm.

1-[2,3-dideoxy-2-C-(α-acetylacetone)-β-D-*ribo*furanosyl]thymine (47). Compound **46** (35 mg, 0.06 mmol) was treated with 80 % aqueous acetic acid (1 ml) at room temperature overnight. The solvent was removed in vacuo, co-evaporated with toluene and methanol. The residue was purified through silica gel column chromatography to give **47** (18 mg, 95 %). ^{1}H-NMR ($CDCl_3$): 7.46 (s, 1H) H-6; 5.77 (d, $J_{1',2'}$ = 7.3 Hz, 1H) H-1'; 4.24 (m, $J_{4',5'}$ = 3.2 Hz, 1H) H-4'; 3.99-3.57 (m , 3H) CH$(COCH_3)_2$ & H-5', 5''; 3.16 (m , 1H) H-2'; 2.36-1.77 (m, 2H) H-3', 3''; 2.21 (s, 6H) 2x$COCH_3$; 1.94 (s, 3H) 5-CH_3. ^{13}C-NMR ($CDCl_3$): 135.9 (d, J_{CH} = 189.8 Hz) C-6; 111.4 (s) C-5; 88.4 (d, J_{CH} = 168.5 Hz) C-1'; 77.9 (d, J_{CH} = 149.4 Hz) C-4'; 70.2 (d, J_{CH} = 126.9 Hz) CH$(COCH_3)_2$; 64.4 (t, J_{CH} = 142.6 Hz) C-5'; 42.2 (d, J_{CH} = 130.3 Hz) C-2'; 30.3 (t, J_{CH} = 130.0 Hz) C-3'; 29.8, 29.2 (2xq, J_{CH} = 128.2 Hz) 2x$COCH_3$; 12.5 (q, J_{CH} =129.2 Hz) 5-CH_3. MS (FAB$^-$): cal. for (M-H)$^-$ 323.1243, found 323.1252. UV (EtOH): [pH 7] λ_{max} = 265 nm (ε = 6500); [pH 2] λ_{max} = 265 nm (ε = 6300).

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