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New Diastereospecific Synthesis of 2',3'-Dideoxy-2'- or 3'-C_2-branched- or 2',3'-α-fused-isoxazolidine Nucleosides Directly from the Seconucleoside

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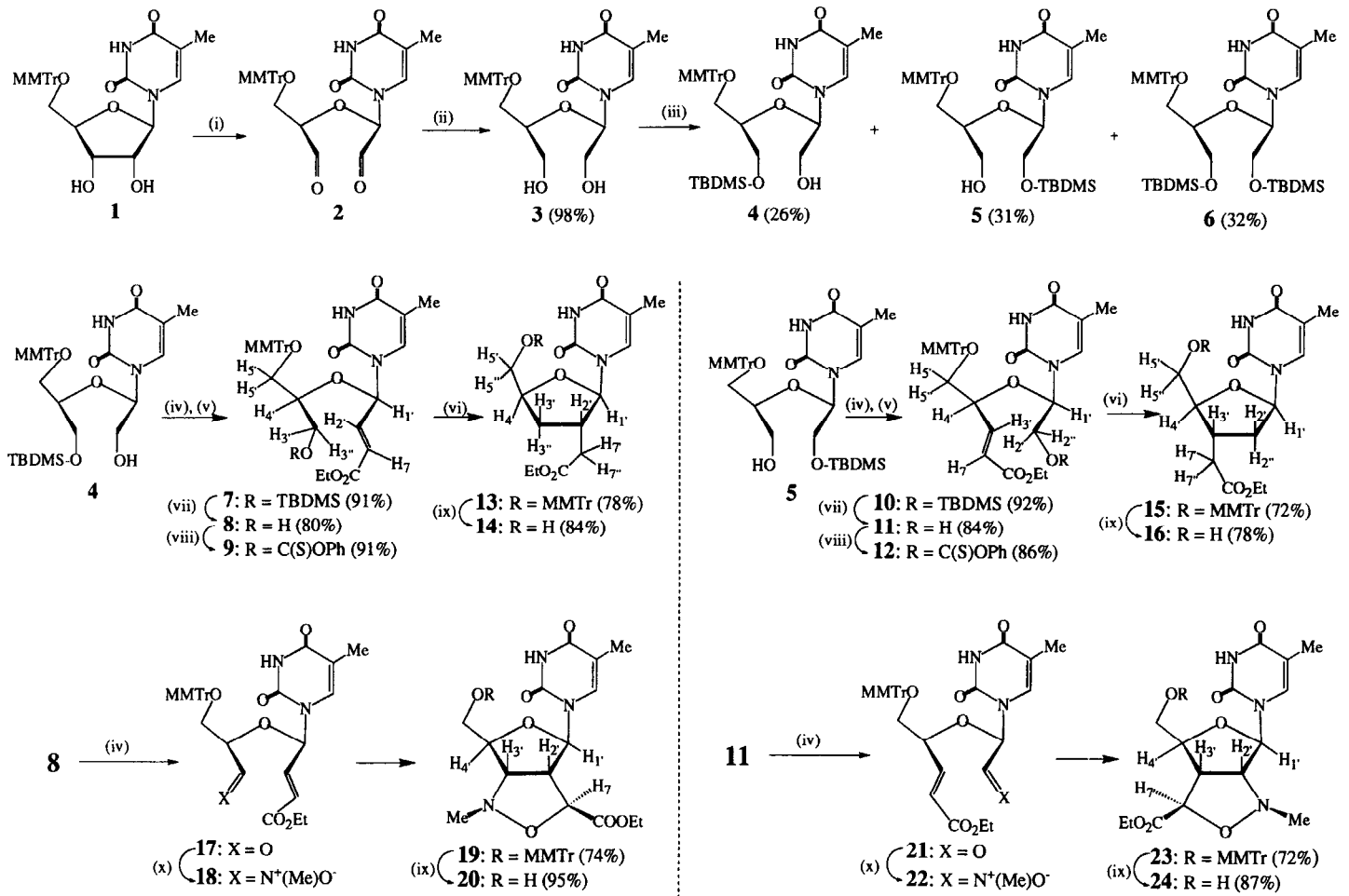
Abstract. *The first diastereospecific syntheses of [3.3.0]-α-fused-isoxazolidine nucleosides **20** or **24**, and 2'- or 3'-C_2-branched-2',3'-dideoxynucleosides **14** or **16** have been reported starting directly from 2',3'-seconucleoside **3**. The key steps involve the unsymmetrical modification of the 2'- or 3'-hydroxyl in the seconucleoside **3** to give pure **8** (**3** → **4** → **7** → **8**) or **11** (**3** → **5** → **10** → **11**) and their diastereospecific recyclisation to the furanose moiety to give the title compounds either by radical or [2+3] cycloaddition reaction.*

The discovery of various 2',3'-dideoxynucleosides as powerful selective inhibitors of HIV-reverse transcriptase[1] has led to the design and synthesis of the new types of 2',3'-modified nucleoside analogs and some of them have exhibited interesting biological property[2]. We here report the first diastereospecific synthesis of [3.3.0]-α-fused-isoxazolidine nucleosides **20** and **24**, and 2'- or 3'-C-α-branched-2',3'-dideoxynucleosides **14** and **16** starting directly from 2',3'-seconucleoside **3**. The key steps involve the selective protection of the primary hydroxyl function in **3** to the isomeric mono-*t*-butyldimethylsilyl ether (TBDMS) derivatives **4** or **5**, which upon oxidation to the corresponding aldehyde could be conveniently transformed *in situ* to the olefin **7** or **10**, respectively. Olefins **7** and **10** have been deprotected to the corresponding free alcohols **8** and **11**. These alcohols have been subsequently converted to **9** (**8** → **9**) or **12** (**11** → **12**), which have been subjected to the intramolecular radical-trapping reactions to give the furanose with diastereomerically pure 2'- or 3'-C_2-α-branching. For the preparation of the starting material for the [3+2] cycloaddition reaction, free alcohol **8** or **11** was oxidized and transformed *in situ* to their respective methylnitrone to give [3.3.0]-α-fused-isoxazolidine nucleoside **19** (**8** → **17** → **18** → **19**) or **23** (**11** → **21** → **22** → **23**). The advantages of our above synthetic protocol are that: (i) it allows the diastereospecific synthesis of 2'- or 3'-*C*-branched-2',3'-dideoxynucleoside directly from the cheap starting *ribo*nucleoside, (ii) it has the potential to give the desired carbon homologation and the functionalities of the *C*-branching depending upon the substituent pattern in the phosphonium ylide in the key Wittig reaction (*i.e.* in step **4** → **7** or **5** → **10**), (iii) it has the unique potential to give various complex furan-2',3'-fused heterocyclic nucleosides depending upon the functionalization of **4** or **5**, (iv) the cycloaddition reactions are expected *(vide infra)* to be highly diastereospecific in which the stereochemistries of four prochiral centers could be fixed in one-step (*i.e.* in step **17** → **19** or **21** → **23**), and



Reagents: (i): KIO_4/H_2O/acetone; (ii): $NaBH_4$/EtOH; (iii): TBDMS-Cl/Py; (iv): DCC/DMSO/Cl_2CHCO_2H; (v): $Ph_3P{=}CHCO_2Et$/THF; (vi): Bu_3SnH/toluene; (vii): NH_4F/MeOH; (viii): PhOCSCl/Py; (ix): 90% AcOH; (x): MeNHOH/Py

finally (v) the glycosidic bond of the acyclic aldehyde (*i.e.* in **17** or **21**) is more stable in comparison with 2'- or 3'-ketonucleoside, which should enable us to perform reactions both under strongly acidic or alkaline condition.

Results and Discussions

(I) Preparation of secoolefins 8 or 11. Earlier, seconucleosides have been used only for the construction of the six-membered sugar rings of the nucleosides by the *symmetrical* cyclisation of the bis-aldehyde **2** with nitromethane[3], hydroxylamine[4] and primary amines[5]. Seconucleosides have also been widely used for the synthesis of different kinds of acyclonucleosides[6,7]. The seconucleoside **3** was synthesized using a literature procedure[7] which included periodate oxidation of the *cis*-diol of 5'-*O*-MMTr-ribothymidine **1** to the bis-aldehyde **2**, followed by its reduction with $NaBH_4$ to the secodiol **3** (98%). Reaction of the secodiol **3** with TBDMS-Cl in pyridine afforded an easily separable mixture of the isomeric 3'-*O*-TBDMS ether **4** (26%) and 2'-*O*-TBDMS ether **5** (31%) and 2',3'-bis-*O*-TBDMS derivative **6** (32%). As expected, the reaction proceeded without any regioselectivity. It was however fortunate that 2',3'-bis-*O*-TBDMS ether **6** could be easily converted to the initial secodiol **3**. It was thus possible to convert secodiol **3** into **4** and **5** with a total yield of 77%. Compound **4** or **5** was oxidised (DCC, DMSO, Cl_2CHCO_2H, 2h, RT)[8] into the corresponding aldehyde (not isolated) which was treated with the Wittig reagent, (carbethoxymethylene)-triphenylphosphorane ($Ph_3P{=}CHCO_2Et$), in THF without purification to give olefin **7** (91%) or **10** (92%), respectively. During attempts to purify the aldehydes we observed considerable anomerisation at both the C1' and C4' positions (^{1}H-NMR). The NMR spectra of the crude aldehydes however helped in the unequivocal characterization of the precursors **4** and **5**: in the ^{1}H spectra of the crude 2'-aldehyde from **4**, we observed a broad singlet at δ9.36 for the aldehydic proton and two *doublets* at δ5.79 ($J_{1',2'}$ = 2.6 Hz) and δ 5.86 ($J_{1',2'}$ = 2.6 Hz) for the anomeric proton of the aldehyde and its hydrate, respectively, whereas the ^{13}C-NMR showed a doublet at δ198.3 (J_{CH} = 177.6 Hz) for the aldehydic-carbon. In the ^{1}H-spectra of the crude 3'-aldehyde from **5**, a broad singlet at δ9.62 was assigned for the aldehydic proton and two *doublet of doublets* at δ6.18 ($J_{1',2'} = J_{1',2''}$ = 5.4 Hz) and δ5.80 ($J_{1',2'} = J_{1',2''}$ = 4.8 Hz) were assigned as two anomeric protons from the aldehyde and its hydrate, whereas the ^{13}C-spectra showed a doublet at δ198.6 (J_{CH} = 178.0 Hz) for the aldehydic-carbon. *Thus the multiplicity of H1' coupling with 2'-aldehydic proton or 2'-methylene protons was the basis for the assignment of the precursor 3'-O-TBDMS ether 4 or 2'-O-TBDMS ether 5, respectively.* Both olefins **7** and **10** were assigned as the *trans*-isomers basing on the large scalar spin-spin coupling constants of $J_{2',7}$ = 15.5 Hz for **7** and $J_{3',7}$ = 15.8 Hz for **10**. Assignment of H1' in the ^{1}H spectra of **7** was also based on the 2D heteronuclear C-H correlation spectra for the deprotected **8**. Assignment of H2' and H-7 for **8** was also based on the magnitude of their coupling constant with H1' (*i.e.* $J_{1',2'}$ = 6.7 Hz and $J_{1',7}$ = 1.2 Hz). Similar reasonings were also used for the assignment of H4', H3' and H-7 in **10**.

Removal of the TBDMS protecting group in **7** or **10** was carried out using a methanolic solution of NH_4F[9] to give **8** or **11**, respectively. They were then transformed into two different types of precursors to generate the 2'- and/or 3'-functionalized furanose ring in the stereospecific manner: (i) free-radical precursor **9** or **12** was used for the radical recyclisation reaction[10] to give **13** or **15** (**8** → **9** → **13** or **11** →**12** → **15**), whereas

(ii) the corresponding aldehyde **17** or **21** was used for the [2+3] cycloaddition reaction[11] to give **19** or **23** (**8** →**17** → **19** or **11** → **21** → **23**).

(II) Free-radical cyclization to give 2'- or 3'-C_2 branched thymidines 13 or 15. For the synthesis of the radical precursor,[10b] **8** or **11** was treated with PhOC(S)Cl in pyridine to give **9** (91%) or **12** (86%). Reaction of **9** with Bu_3SnH and azobisisobutyronitrile (AIBN) in toluene at 95° for 3 h yielded stereospecifically **13** (78%), whereas the treatment of **12** under identical condition yielded stereospecifically **15** (72%). The configuration of C2' in **13** was established by 1D difference NOE experiments: saturation of H1' gives key NOE enhancements at both H7' (0.9%) and H7" (1.6%) which are consistent with C2'-(S) configuration. Removal of the 5'-O-MMTr group from **13** (90% aq. acetic acid at RT for 12 h) gave **14** (84%). The NOE experiments on **14** gave an improved picture regarding the stereochemistry of the radical-promoted ring-closure reaction: Saturation of H1' gave NOEs at H7' (3.4%), H7" (2.6%) and H3" (1.9%), wheras the saturation of H3" gives NOEs at H7' (1.1%) and H7" (3.2%) and H4' (6.8%). These NOE experiments clearly showed that H3" and the 2'-*C*-methylenecarboxyethyl group are on the α-face of the furanose ring. The configuration of C3' in **15** was again clarified by 1D difference NOE experiments: Saturation of H4' gave NOEs at H1' (1.4%), H3' (0.4%), H2' (0.2%), H7' (0.8%), H7" (1.9%) and H2" (0.5%) which are consistent with C3'-(R) configuration. Removal of 5'-*O*-MMTr group in **15** gave **16** (78%). Saturation of H4' of **16** gave NOEs at H1' (1.4%), H3' (1.9%), H7' (1.2%), H7" (1.8%) and H2" (1.3%) which show that H2" and the 3'-*C*-methylenecarboxyethyl group are on the α-face of the furanose ring.

In accordance with the guidelines governing the ring closure of 2- and 4- substituted hexenyl radicals[12], high regio and stereoselectivites expected for the 5-*exo* ring closure was also observed for the free-radical ring closure of **9** or **12**[10]. Clearly, the transition state for the 5-*exo*-radical cyclization of **9** or **12** forces the bulky 1'-thyminyl and 4'-CH_2O-MMTr substituents to adopt the pseudoequatorial orientation which places the O4' in an pseudo*endo* conformation. This, in conjunction with the preferred pseudoequatorial position of the vinyl-substituent, results in the exclusive formation of α-face substituted products upon cyclisation.

(III) The [2+3] dipolar cycloaddition reaction of seco-olefin to give 19 or 23. The second approach for the diastereospecific recyclisation of the furanose ring consisted of [2+3] cycloaddition reaction[11]. Thus, the alcohol **8** was oxidised[8] to the aldehyde **17**, and was treated with N-methylhydroxylamine hydrochloride in pyridine solution to give the corresponding putative 3'-methylnitrone **18** which instantaneously cyclised *in situ* to give sugar-2',3'-α-fused-isoxazolidine **19** (74% from **8**). The configuration of the [3.3.0]-α-fused furanose-isoxazolidine ring in **19** was determined by 1D difference NOE experiments: Saturation of H1' gave NOEs at H7 (15.3%) and the saturation of H7 shows NOEs at H1' (13.9%) and H4' (1.1%) which are consistent with C2'-(S) and C7-(S) configurations, saturation of N-Me gives NOEs at H7 (0.2%), H4' (0.4%), H3' (1.0%), H2' (0.4%) which are consistent with N-Me in S configuration. Removal of 5'-*O*-MMTr group in **19** gave **20** (95%), which was also used for 1D difference NOE experiments for the reconfirmation of the structure of **19**: Saturation of H1' gave NOEs at H7 (15.3%), the saturation of H7 gave NOE at H1' (13.9%), whereas the Saturation of N-Me gave NOEs at H4' (1.0%), H3' (3.2%), H2' (0.6%), which are consistent with C2'-(S), C7-(S) and N2-(S) configurations.

A similar transformation was also performed on **11** to give **23** [**11** → **21** → **22** → **23** (72% from **11**)]. Because of the spectral overlap of H4' and H7 in **23**, it was not possible to perform 1D difference NOE experiments successfully to determine its stereochemistry except for the fact that the saturation of N-Me gave NOEs at H1' (1.6%), H7 (1.8%) and H2' (3.1%) which showed its R configuration. We therefore removed 5'-

O-MMTr group in **23** to give **24** (87%), which gave satisfactory 1D difference NOE spectra in support of [3.3.0]-α-fused furanose-isoxazolidine ring: Saturation of H7 gave NOEs at H1' (1.5%) and H4' (10.8%), saturation of N-Me gives NOEs at H1' (1.6%), H7 (0.2%), H2' (3.7%) and H3' (0.7%) and saturation of H1' gives NOEs at H7 (1.0%), H4' (1.7%), H2' (1.7%) and NMe (1.6%). These results are consistent with C2'-(R), C3'-(S), C7-(R) and N-(R) configuration for **24** which also proved the structure of the precursor **23**.

Experimental

^{1}H-NMR spectra were recorded (in δ scale) with Jeol 90Q and JNM-GX 270 spectrometer operating at 270 MHz using TMS (0.0 ppm) as reference. ^{13}C-NMR were recorded at 67.8 MHz using both in ^{1}H-decoupled or INEPT modes in the same solvent as ^{1}H-NMR. Coupling constants reported in ^{13}C-NMR part are $^3J_{CH}$. 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 flesh column chromatographic separation were carried out using Merck G60 silica gel and gradient of ethanol in dichlormethan.

5'-O-MMTr-2',3'-secoribothymidine (3). **1** (9.1 g, 17.14 mmol) was treated with $NaIO_4$ (4.03 g, 18.8 mmol) in a water-acetone mixture 3/7 (900 ml, v/v) for 24 h. The reaction mixture was worked using a procedure described for corresponding secouridine[8] to give **3** (8.9 g, 98%). ^{1}H-NMR ($CDCl_3$ + D_2O): 7.35-7.17 (m, 13 H) & 6.78 (m, 2 H) arom; 5.99 (dd, $J_{1',2'} = J_{1',2''} = 5.6$ Hz, 1H) H1'; 3.76 (s, 3H) OMe; 3.73 (m, 5H) H2', H2", H3', H3", H4'; 3.15 (d, J = 4.1 Hz, 2H) H5', H5"; 1.68 (d, J = 1.0 Hz, 3H) 5-Me; ^{13}C-NMR: 163.9 (s) C4; 151.4 (s) C2; 135.6 (d, 179.6 Hz) C6; 111.0 (s) C5; 84.6 (d, 164.1 Hz) C1'; 80.3 (d, 143.9 Hz) C4'; 63.8 (t, 143.0 Hz) & 63.3 (t, 144.3 Hz) & 62.5 (t, 143.0 Hz) C2' + C5' + C3'; 55.0 (q, 143.9 Hz) OMe; 11.9 (q, 129.2 Hz) 5-Me.
5'-O-MMTr-3'-O-TBDMS-2',3'-secoribothymidine (4) & 5'-O-MMTr-2'-O-TBDMS-2',3'-secoribo thymidine (5). **3** (8.9 g, 16.7 mmol) was coevaporated with pyridine, dissolved in pyridine (100 ml) and treated with TBDMS-Cl (2.26 g, 15.0 mmol) at RT overnight. Pyridine was evaporated and the residue was purified by silica gel column chromatography to give **4** (2.1 g, 19%), **5** (2.48 g, 23%), **6** (3.1 g, 24%) and unreacted **3** (2.2 g, 25%). **4**: ^{1}H-NMR ($CDCl_3$): 8.37 (br s, 1H) NH; 7.39-7.18 (m, 13H) + 6.80 (m, 2H) arom; 5.92 (dd, $J_{1',2'} = 4.6$ Hz, $J_{1',2''} = 5.9$ Hz, 1H) H1'; 3.79 (s, 3H) OMe; 3.70 (m, 5H) H2', H2", H3', H3", H4'; 3.15 (s, 2H) H5', H5"; 2.78 (m, 1H) OH; 1.73 (d, J = 0.9 Hz, 3H) 5-Me; 0.87 (s, 9H) TBDMS; 0.05 (s, 6H) TBDMS. ^{13}C-NMR: 163.8 (s) C4; 151.0 (s) C2; 135.8 (d, 179.0 Hz) C6; 111.8 (s) C5; 83.9 (d, 162.4 Hz) C1'; 80.0 (d, 143.8 Hz) C4'; 63.5 (t, 143.3 Hz), 63.5 (t, 143.3 Hz) & 62.8 (t, 141.8 Hz) C2' + C5' + C3'; 55.1 (q, 143.8 Hz) OMe; 25.7 (q, 124.9 Hz) TBDMS; 18.1 (s) $Me_3\underline{C}$; 12.3 (q, 129.1 Hz) 5-Me; -5.6 (q, 118.3 Hz) TBDMS. **5**: ^{1}H-NMR ($CDCl_3$): 9.18 (br s, 1H) NH; 7.37-7.16 (m, 13H) + 6.80 (m, 2H) arom; 5.93 (dd, $J_{1',2'} = 4.9$ Hz, $J_{1',2''} = 5.9$ Hz, 1H) H1'; 3.77 (s, 3H) OMe; 3.72 (m, 5H) H2', H2", H3', H3", H4'; 3.17 (d J = 4.9 Hz, 2H) H5', H5"; 2.86 (m, 1H) OH; 1.72 (d, J = 0.9 Hz, 3H) 5-Me; 0.88 (s, 9H) TBDMS; 0.08 (s, 6H) TBDMS. ^{13}C-NMR: 163.8 (s) C4; 150.7 (s) C2; 135.7 (d, 178.0 Hz) C6; 110.5 (s) C5; 84.2 (d, 163.3 Hz) C1'; 80.6 (d, 141.8 Hz) C4'; 64.2 (t, 143.3 Hz), 63.5 (t, 142.8 Hz) & 62.4 (t, 143.3 Hz) C2' + C5' + C3'; 55.0 (q, 143.8 Hz) OMe; 25.6 (q, 125.2 Hz) TBDMS; 18.1 (s) $Me_3\underline{C}$; 12.2 (q, 128.8 Hz) 5-Me; -5.7 (q, 118.3 Hz) TBDMS. Compound **6**:^{1}H-NMR ($CDCl_3$): 8.80 (br s, 1H) NH; 7.39-7.18 (m, 13H) + 6.79 (m, 2H) arom; 5.97 (dd, 1H) H1'; 3.80 (dd, $J_{1',2'} = 4.2$ Hz, $J_{2',2''} = 11.1$ Hz, 1H) H2'; 3.78 (s, 3H) OMe; 3.71 (dd, $J_{1',2''} = 5.1$ Hz, 1H) H2"; 3.66 (m, 3H) H4', H3', H3"; 3.17 (dd, $J_{4',5'} = 3.2$ Hz, $J_{5',5''} = 10.2$ Hz, 1H) H5'; 3.08 (dd, $J_{4',5''} = 5.7$ Hz, 1H) H5"; 1.69 (d, J = 1.0 Hz, 3H) 5-CH_3; 0.84 & 0.83 (2 s, 18 H) TBDMS; 0.01 (m, 12H) TBDMS.
Deprotection of 6 for recycling. **6** (3.1 g, 4.08 mmol) was dissolvd in methanol (20 ml) and treated with NH_4F (0.9 g, 24 mmol) overnight. The solvent was evaporated and the residue was purified by silica gel column chromatography to give initial **3** (1.8 g, 83 %). The total conversion of the **3** into the **4** and **5** is 77 %.
5'-O-MMTr-3'-O-TBDMS-2'-deoxy-2'-*C*-(E-carbethoxymethylidene)-2',3'-secoribothymidine (7). **4** (0.50 g, 0.77 mmol) was dissolvd in DMSO (3 ml) and treated with DCC (0.48 g, 2.3 mmol) and dichloroacetic acid (46 mg, 0.35 mmol) for 2 h. Then acetic acid (0.1 ml) was added and mixture was dissolved in ethylacetate (20 ml), filtered and washed with water (4 x 50 ml). Organic phase was dried (Na_2SO_4), evaporated coevaporated with THF and dissolved in 5 ml of THF. Ph_3P=CHCOOEt (0.33 g, 0.9 mmol) was added and reaction mixture was kept overnight. The solvent was evaporated and the residue was purified by silica gel column chromatography to give **7** (0.51 g, 91 %). ^{1}H-NMR ($CDCl_3$): 8.95 (br s, 1H) NH; 7.38-7.13 (m, 12H) arom; 7.02 (q, J = 1.2 Hz, 1H) H6; 6.80 (m, 2H) arom; 6.75 (dd, $J_{1',2'} = 3.4$ Hz, $J_{2',7} = 15.5$ Hz, 1H) H2'; 6.66 (dd, $J_{1',7} = 1.7$ Hz, 1H) H1'; 6.30 (dd, 1H) H7; 4.23 (q, J = 7.2 Hz, 2H) $OC\underline{H_2}CH_3$; 3.76 (s, 3H) OMe; 3.70 (m, 2H)

H4' + H3'; 3.67 (dd, $J_{3',4'}$ = 4.1 Hz, $J_{3',3''}$ = 7.7 Hz, 1H) H3''; 3.12 (m, 2H) H5' + H5''; 1.71 (d, 3H) 5-CH_3; 1.30 (t, 3H) $OCH_2\underline{CH_3}$; 0.83 (s, 9H) TBDMS; 0.01 (s, 6H) TBDMS.

5'-O-MMTr-2'-deoxy-2'-*C*-(E-carbethoxymethylidene)-2',3'-secoribothymidine (8). The reaction on **7** (0.48 g, 0.67 mmol) was performed using a reaction condition described for **6** to give **8** (0.32 g, 80%). ^{1}H-NMR ($CDCl_3$): 9.29 (br s, 1H) NH; 7.40-7.18 (m, 13H) arom; 7.14 (dd, $J_{1',7}$ = 1.2 Hz, $J_{2',1'}$ = 6.7 Hz, 1H) H1'; 6.80 (m, 2H) arom; 6.22 (dd, $J_{2',7}$ = 11.6 Hz, 1H) H2'; 6.02 (dd, 1H) H7; 4.19 (q, J = 7.1 Hz, 2H) OCH_2CH_3; 3.77 (s, 3H) OMe; 3.71 (m, 3H) H4', H3', H3''; 3.26 (dd, $J_{4',5'}$ = 6.1 Hz, $J_{5',5''}$ = 10.3 Hz, 1H) H5'; 3.18 (dd, $J_{4',5''}$ = 4.5 Hz, 1H) H5''; 2.88 (bs, 1H) OH; 1.77 (d, 3H) 5-CH_3; 1.26 (t, 3H) OCH_2CH_3. ^{13}C-NMR: 164.9 (s) COO; 163.7 (s) C4; 150.7 (s) C2; 140.4 (d, 164.0 Hz) C2'; 135.9 (d, 177.8 Hz) C6; 123.9 (d, 166.8 Hz) C7; 111.6 (s) C5; 79.0 (d, 178.7 Hz) C1'; 78.0 (d, 143.9 Hz) C4'; 63.7 (t, 143.0 Hz) C5'; 61.5 (t, 143.0 Hz) C3'; 61.0 (t, 148.5 Hz) $O\underline{C}H_2CH_3$; 55.0 (q, 143.9 Hz) OMe; 13.8 (q, 127.1 Hz) $OCH_2\underline{C}H_3$; 12.3 (q, 129.2 Hz) 5-Me.

5'-O-MMTr-2'-O-TBDMS-3'-deoxy-3'-*C*-(E-carbethoxymethylidene)-2',3'-secoribothymidine (10). The reaction on **5** (0.65 g, 1.0 mmol) was performed using a reaction condition described for **7** to give **10** (0.66 g, 92%). ^{1}H-NMR ($CDCl_3$): 8.78 (br s, 1H) NH; 7.45-7.20 (m, 13H) + 6.80 (m, 2H) arom; 6.65 (dd, $J_{3',4'}$ = 6.2 Hz, $J_{3',7}$ = 15.8 Hz, 1H) H3'; 6.04 (dd, $J_{7,4'}$ = 1.0 Hz, 1H) H7; 5.69 (dd, 1H) H1'; 4.18 (q, J = 7.2 Hz, 2H) OCH_2CH_3; 3.91 (m, 1H) H4'; 3.81 (dd, $J_{1',2'}$ = 5.1 Hz, $J_{2',2''}$ = 11.0 Hz, 1H) H2'; 3.79 (s, 3H) OMe; 3.73 (dd, $J_{1',2''}$ = 4.8 Hz, 1H) H2''; 3.33 (dd, $J_{4',5'}$ = 7.5 Hz, $J_{5',5''}$ = 10.8 Hz, 1H) H5'; 3.15 (dd, $J_{4',5''}$ = 3.4 Hz, 1H) H5''; 1.73 (d, J = 1.0 Hz, 3H) 5-CH_3; 1.28 (t, 3H) $OCH_2\underline{CH_3}$; 0.86 (s, 9H) TBDMS; 0.06 (s, 3H) TBDMS; 0.04 (s, 3H) TBDMS.

5'-O-MMTr-3'-deoxy-3'-*C*-(E-carbethoxymethylidene)-2',3'-secoribothymidine (11). The deprotection of TBDMS from **10** (0.66 g, 0.92 mmol) was performed using a reaction condition described for **6** to give **11** (0.46 g, 84%). ^{1}H-NMR ($CDCl_3$): 9.56 (br s, 1H) NH; 7.40-7.17 (m, 13H) + 6.80 (m, 2H) arom; 6.66 (dd, $J_{3',4'}$ = 6.5 Hz, $J_{3',7}$ = 15.7 Hz, 1H) H3'; 6.01 (dd, $J_{7,4'}$ = 1.1 Hz, 1H) H7; 5.74 (dd, $J_{1',2'}$ = 4.9 Hz, $J_{1',2''}$ = 5.9 Hz, 1H) H1'; 4.16 (q, J = 7.1 Hz, 2H) OCH_2CH_3; 3.92 (m, 1H) H4'; 3.86 (dd, $J_{2',2''}$ = 12.2 Hz, 1H) H2'; 3.78 (s, 3H) OMe; 3.71 (dd, 1H) H2''; 3.33 (dd, $J_{4',5'}$ = 7.4 Hz, $J_{5',5''}$ = 10.8 Hz, 1H) H5'; 3.17 (dd, $J_{4',5''}$ = 3.5 Hz, 1H) H5''; 1.68 (d, J = 0.9 Hz, 3H) 5-CH_3; 1.26 (t, 3H) $OCH_2\underline{CH_3}$. ^{13}C-NMR: 165.5 (s) COO; 164.1 (s) C4; 151.6 (s) C2; 142.2 (d, 159.5 Hz) C3'; 135.8 (d, 175.9 Hz) C6; 124.5 (d) C7; 111.8 (s) C5; 82.3 (d, 162.2 Hz) C1'; 77.0 (d, 146.6 Hz) C4'; 65.5 (t, 143.4 Hz) C5'; 62.9 (t, 144.3 Hz) C2'; 60.5 (t, 148.9 Hz) $O\underline{C}H_2CH_3$; 55.0 (q, 143.9 Hz) OMe; 14.0 (q, 126.5 Hz) $OCH_2\underline{C}H_3$; 12.2 (q, 129.2 Hz) 5-Me.

5'-O-MMTr-2',3'-dideoxy-3'-*N*-2'-*C*-(N-(S)-methyl-5-(S)-ethoxycarbonyl-1,2-isoxazolidine)-ribo thymidine (19). **8** (0.2 g, 0.33 mmol) was dissolvd in DMSO (1 ml) and treated with DCC (0.14 g, 0.66 mmol) and dichloroacetic acid (30 mg, 0.23 mmol) for 1 h. Then acetic acid (0.05 ml) was added and mixture was dissolved in ethylacetate (20 ml) and washed with water (4 x 50 ml). Organic phase was dried (Na_2SO_4), evaporated, coevaporated with toluene and dissolved in 5 ml of pyridine. N-methylhydroxylamine hydrochloride (40 mg, 0.4 mmol) was added and reaction mixture was kept overnight. The solvent was evaporated and the residue was purified by silica gel column chromatography to give **19** (0.155 g, 74 %). ^{1}H-NMR ($CDCl_3$): 9.30 (br s, 1H) NH; 7.56 (q, J = 1.0 Hz, 1H) H6; 7.45-7.21 (m, 12H) + 6.85 (m, 2H) arom; 6.14 (d, $J_{1',2'}$ = 4.8 Hz, 1H) H1'; 4.77 (d, $J_{7,2'}$ = 3.3 Hz, 1H) H7; 4.24 (q, J = 7.1 Hz, 2H) OCH_2CH_3; 4.10 (m, 1H) H4'; 3.85 (dd, $J_{2',3'}$ = 8.4 Hz, $J_{3',4'}$ = 3.7 Hz, 1H) H3'; 3.79 (s, 3H) OMe; 3.73 (ddd, 1H) H2'; 3.56 (dd, $J_{4',5'}$ = 2.8 Hz, $J_{5',5''}$ = 10.6 Hz, 1H) H5'; 3.31 (dd, $J_{4',5''}$ = 3.2 Hz, 1H) H5''; 2.63 (s, 3H) NMe; 1.63 (d, 3H) 5-CH_3; 1.29 (t, 3H) $OCH_2\underline{CH_3}$. ^{13}C-NMR: 170.2 (s) COO; 163.8 (s) C4; 150.2 (s) C2; 134.8 (d, 183.3 Hz) C6; 111.1 (s) C5; 89.7 (d, 167.7 Hz) C1'; 81.3 (d, 145.7 Hz) C4'; 80.6 (d, 152.1 Hz) C7; 73.4 (d, 139.3 Hz) C3'; 62.8 (t, 143.0 Hz) C5'; 61.7 (t, 148.5 Hz) $O\underline{C}H_2CH_3$; 58.4 (d, 143.0 Hz) C2'; 55.0 (q, 143.6 Hz) OMe; 44.7 (q, 137.6 Hz) NMe; 13.8 (q, 127.4 Hz) $OCH_2\underline{C}H_3$; 11.9 (q, 128.6 Hz) 5-Me.

2',3'-dideoxy-3'-*N*-2'-*C*-(N-(S)-methyl-5-(S)-ethoxycarbonyl-1,2-isoxazolidine)-ribothymidine (20). The reaction on **19** (145 mg, 0.23 mmol) was performed using a reaction condition described for **24** to give **20** (78 mg, 95%). ^{1}H-NMR ($CDCl_3$ + CD_3OD): 7.63 (q, J = 1.1 Hz, 1H) H6; 6.07 (d, $J_{1',2'}$ = 4.4 Hz, 1H) H1'; 4.73 (d, $J_{7,2'}$ = 3.8 Hz, 1H) H7; 4.24 (q, J = 7.2 Hz, 2H) OCH_2CH_3; 4.02 (m, 1H) H4'; 3.92 (m, 1H) H3'; 3.93 (dd, $J_{4',5'}$ = 2.7 Hz, $J_{5',5''}$ = 12.5 Hz, 1H) H5'; 3.75 (dd, $J_{4',5''}$ = 2.8 Hz, 1H) H5''; 3.73 (ddd, $J_{2',3'}$ = 8.2 Hz, 1H) H2'; 2.73 (s, 3H) NMe; 1.92 (d, 3H) 5-CH_3; 1.29 (t, 3H) $OCH_2\underline{CH_3}$. ^{13}C-NMR: 170.4 (s) COO; 164.1 (s) C4; 150.3 (s) C2; 136.1 (d, 180.5 Hz) C6; 111.8 (s) C5; 90.5 (d, 169.6 Hz) C1'; 82.8 (d, 145.7 Hz) C4'; 80.8 (d, 152.1 Hz) C7; 72.8 (d, 149.4 Hz) C3'; 61.8 (t, 150.3 Hz) $O\underline{C}H_2CH_3$; 61.3 (t, 142.5 Hz) C5'; 57.8 (d, 143.9 Hz) C2'; 45.0 (q, 133.8 Hz) NMe; 13.7 (q, 127.1 Hz) $OCH_2\underline{C}H_3$; 12.0 (q, 129.5 Hz) 5-Me. λ_{max} = 266 nm. HRMS (FAB^-): calcd. for $(M-H)^-$ 354.1301, found 354.1322.

5'-O-MMTr-2',3'-dideoxy-3'-*C*-2'-*N*-(N-(R)-methyl-5-(R)-ethoxycarbonyl-1,2-isoxazolidine)ribo thymidine (23) The reaction on **11** (0.20 g, 0.33 mmol) was performed using a reaction condition described for **19** to give **23** (150 mg, 72%). ^{1}H-NMR ($CDCl_3$): 8.89 (br s, 1H) NH; 7.57 (q, J = 1.1 Hz, 1H) H6; 7.44-7.24 (m, 12H) + 6.84 (m, 2H) arom; 5.95 (d, $J_{1',2'}$ = 1.8 Hz, 1H) H1'; 4.42 (m, 1H) H4'; 4.39 (d, $J_{7,3'}$ = 3.0 Hz, 1H)

H7; 4.19 (q, J = 7.0 Hz, 2H) OCH_2CH_3; 3.81 (m, 1H) H3'; 3.80 (s, 3H) OMe; 3.62 (dd, $J_{2',3'}$ = 7.8 Hz, 1H) H2'; 3.55 (dd, $J_{4',5'}$ = 2.8 Hz, $J_{5',5''}$ = 10.7 Hz, 1H) H5'; 3.42 (dd, $J_{4',5''}$ = 3.4 Hz, 1H) H5''; 2.93 (s, 3H) NMe; 1.47 (d, 3H) 5-CH_3; 1.21 (t, 3H) OCH_2CH_3. ^{13}C-NMR: 169.6 (s) COO; 164.0 (s) C4; 150.1 (s) C2; 135.1 (d, 182.4 Hz) C6; 111.8 (s) C5; 87.7 (d, 172.3 Hz) C1'; 84.3 (d, 150.3 Hz) C7; 79.2 (d, 153.0 Hz) C4'; 78.8 (d, 149.4 Hz) C2'; 62.5 (t, 143.0 Hz) C5'; 61.5 (t, 148.5 Hz) OCH_2CH_3; 55.0 (q, 143.9 Hz) OMe; 53.2 (d, 143.9 Hz) C3'; 44.5 (q, 136.5 Hz) NMe; 13.9 (q, 127.1 Hz) OCH_2CH_3; 11.7 (q, 128.9 Hz) 5-Me.

2',3'-dideoxy-3'-*C*-2'-*N*-(N-(R)-methyl-5-(R)-ethoxycarbonyl-1,2-isoxazolidine)ribothymidine (24). **23** (0.13 g, 0.21 mmol) was treated with 90 % aqueous acetic acid (3 ml) at RT overnight. The solvent was removed in vacuo and residue was purified by silica gel column chromatography to give **24** (64 mg, 87%). ^{1}H-NMR ($CDCl_3$ + CD_3OD): 7.63 (br s, 1H) H6; 5.78 (d, $J_{1',2'}$ = 3.0 Hz, 1H) H1'; 4.47 (d, $J_{7,3'}$ = 3.5 Hz, 1H) H7; 4.35 (m, $J_{4',3'}$ = 4.9 Hz, 1H) H4'; 4.26 (q, J = 7.2 Hz, 2H) OCH_2CH_3; 3.96 (dd, $J_{4',5'}$ = 2.1 Hz, $J_{5',5''}$ = 12.3 Hz, 1H) H5'; 3.81 (dd, $J_{2',3'}$ = 7.9 Hz, 1H) H2'; 3.73 (m, 2H) H3' + H5''; 2.84 (s, 3H) NMe; 1.90 (br s, 3H) 5-CH_3; 1.32 (t, 3H) OCH_2CH_3. ^{13}C-NMR: 170.3 (s) COO; 164.2 (s) C4; 150.3 (s) C2; 137.0 (d, 179.6 Hz) C6; 110.6 (s) C5; 89.3 (d, 169.5 Hz) C1'; 85.6 (d, 149.4 Hz) C4'; 80.3 (d, 146.6 Hz) C7; 77.8 (d, 154.0 Hz) C2'; 61.7 (t, 142.0 Hz) C5'; 61.7 (t, 146.3 Hz) OCH_2CH_3; 52.1 (q, 143.9 Hz) C3'; 44.7 (q, 135.0 Hz) NMe; 13.6 (q, 126.5 Hz) OCH_2CH_3; 11.8 (q, 125.9 Hz) 5-Me. λ_{max} = 266 nm. HRMS (FAB^-): calcd. for $(M-H)^-$ 354.1301, found 354.1324.

5'-O-MMTr-3'-O-phenoxythiocarbonyl-2'-deoxy-2'-*C*-(E-carbethoxymethylidene)-2',3'-secoribo thymidine (9). Compound **8** (110 mg, 0.18 mmol) with DMAP (44 mg, 0.36 mmol) was coevaporated with pyridine, dissolved in acetonitrile (3 ml) and treated with PhOC(S)Cl (40 mg, 0.23 mmol) for 30 min. The solvent was removed in vacuo. The residue was purified by silica gel column chromatografy to give **9** (123 mg, 91%). ^{1}H-NMR ($CDCl_3$): 8.92 (br s, 1H) NH; 7.44-7.18 (m, 15H) + 7.09 (m, 2H) + 6.82 (m, 2H) arom; 6.95 (q, J = 1.1 Hz, 1H) H6; 6.71 (dd, $J_{2',7}$ = 15.6 Hz, $J_{2',1'}$ = 3.4 Hz, 1H) H2'; 6.57 (dd, $J_{1',7}$ = 1.7 Hz, 1H) H1'; 6.31 (dd, 1H) H7; 4.82 (dd, $J_{4',3'}$ = 3.2 Hz, $J_{3',3''}$ = 11.8 Hz, 1H) H3'; 4.59 (dd, $J_{4',3''}$ = 6.6 Hz, 1H) H3''; 4.23 (q, J = 7.1 Hz, 2H) OCH_2CH_3; 4.09 (m, 1H) H4', 3.79 (s, 3H) OMe; 3.26 (dd, $J_{4',5'}$ = 5.6 Hz, $J_{5',5''}$ = 10.4 Hz, 1H) H5'; 3.19 (dd, $J_{4',5''}$ = 5.2 Hz, 1H) H5''; 1.76 (d, 3H) 5-CH_3; 1.30 (t, 3H) OCH_2CH_3. ^{13}C-NMR: 194.4 (s) CS; 165.0 (s) COO; 163.5 (s) C4; 150.7 (s) C2; 140.6 (d, 160.1 Hz) C2'; 134.7 (d, 178.2 Hz) C6; 125.4 (d, 163.7 Hz) C7; 112.2 (s) C5; 80.8 (d, 164.8 Hz) C1'; 76.0 (d, 146.0 Hz) C4'; 72.7 (t, 150.5 Hz) C3'; 62.9 (t, 142.5 Hz) C5'; 60.8 (t, 145.0 Hz) OCH_2CH_3; 55.1 (q, 143.9 Hz) OMe; 13.9 (q, 127.1 Hz) OCH_2CH_3; 12.1 (q, 130.7 Hz) 5-Me.

5'-O-MMTr-2',3'-dideoxy-2'-*C*-carbethoxymethylene-ribothymidine (13). **9** (110 mg, 0.15 mmol) was treated with Bu_3SnH (100 mg, 0.35 mmol) in toluene (10 ml) at 95°C for 3 h.The solvent was evaporated. The residue was purified by column chromatografy to give **13** (68 mg, 78%) & **8** (5 mg, 6%). ^{1}H-NMR ($CDCl_3$): 8.71 (bs, 1H) NH; 7.59 (q, J = 1.2 Hz, 1H) H6; 7.47-7.22 (m, 12H) + 6.85 (m, 2H) arom; 5.86 (d, $J_{1',2'}$ = 6.6 Hz, 1H) H1'; 4.31 (m, 1H) H4'; 4.13 (m, 2H) OCH_2CH_3; 3.79 (s, 3H) OMe; 3.43 (dd, $J_{4',5'}$ = 2.7 Hz, $J_{5',5''}$ = 10.4 Hz, 1H) H5'; 3.24 (dd, $J_{4',5''}$ = 3.5 Hz, 1H) H5''; 2.88 (m, 1H) H2'; 2.68 (dd, $J_{7',2'}$ = 5.3 Hz, $J_{7',7''}$ = 16.3 Hz, 1H) H7'; 2.46 (dd, $J_{7'',2'}$ = 9.2 Hz, 1H) H7''; 2.43 (ddd, $J_{2',3'}$ = 8.5 Hz, $J_{3',3''}$ = 12.4 Hz, $J_{4',3'}$ = 5.1 Hz, 1H) H3'; 1.91 (ddd, $J_{2',3''}$ = $J_{4',3''}$ = 8.0 Hz, 1H) H3''; 1.48 (d, 3H) 5-CH_3; 1.24 (t, 3H) OCH_2CH_3. ^{13}C-NMR: 171.2 (s) COO; 163.7 (s) C4; 150.6 (s) C2; 135.5 (d, 182.4 Hz) C6; 110.9 (s) C5; 88.9 (d, 167.7 Hz) C1'; 77.7 (d, 149.4 Hz) C4'; 65.2 (t, 142.1 Hz) C5'; 60.7 (t, 147.5 Hz) OCH_2CH_3; 55.1 (q, 143.9 Hz) OMe; 41.0 (d, 132.0 Hz) C2'; 35.6 (t, 129.2 Hz) C7; 32.4 (t, 132.0 Hz) C3'; 14.0 (q, 127.4 Hz) OCH_2CH_3; 11.7 (q, 129.2 Hz) 5-Me.

2',3'-dideoxy-2'-*C*-carbethoxymethylene-ribothymidine (14). Compound **13** (60 mg, 0.10 mmol) was treated 90% acetic acid (5 ml) at RT for 12 h. The solvent was removed in vacuo. The residue was purified by silica gel column chromatografy to give **14** (26 mg, 84%) ^{1}H-NMR ($CDCl_3$ + CD_3OD): 7.72 (q, J = 1.2 Hz, 1H) H6; 5.80 (d, $J_{1',2'}$ = 6.3 Hz, 1H) H1'; 4.25 (m, 1H) H4'; 4.12 (dq, J = 1.0 Hz, J = 7.1 Hz, 2H) OCH_2CH_3; 3.86 (dd, $J_{4',5'}$ = 2.9 Hz, $J_{5',5''}$ = 12.0 Hz, 1H) H5'; 3.65 (dd, $J_{4',5''}$ = 3.6 Hz, 1H) H5''; 2.74 (m, 1H) H2'; 2.63 (dd, $J_{7',2'}$ = 5.7 Hz, $J_{7',7''}$ = 16.1 Hz, 1H) H7'; 2.47 (dd, $J_{7'',2'}$ = 8.7 Hz, 1H) H7''; 2.31 (ddd, $J_{2',3'}$ = 8.2 Hz, $J_{3',3''}$ = 13.1 Hz, $J_{4',3'}$ = 5.6 Hz, 1H) H3'; 1.92 (d, 3H) 5-CH_3; 1.84 (ddd, $J_{2',3''}$ = $J_{4',3''}$ = 7.6 Hz, 1H) H3''; 1.25 (t, 3H) OCH_2CH_3. ^{13}C-NMR: 171.6 (s) COO; 164.3 (s) C4; 150.8 (s) C2; 136.2 (d, 181.5 Hz) C6; 110.5 (s) C5; 89.2 (d, 172,3 Hz) C1'; 78.9 (d, 145.6 Hz) C4'; 63.4 (t, 142.1 Hz) C5'; 60.7 (t, 147.5 Hz) OCH_2CH_3; 40.6 (d, 132.9 Hz) C2'; 35.6 (t, 126.0 Hz) C7; 31.5 (t, 133.3 Hz) C3'; 13.6 (q, 127.1 Hz) OCH_2CH_3; 11.9 (q, 124.9 Hz) 5-Me. λ_{max} = 266 nm. HRMS (FAB^-): calcd. for $(M-H)^-$ 311.1243, found 311.1223.

5'-O-MMTr-2'-O-phenoxythiocarbonyl-3'-deoxy-3'-*C*-(E-carbethoxymethylidene)-2',3'-secoribo thymidine (12). The reaction on **11** (0.17 g, 0.28 mmol) was performed using a reaction condition described for **9** to give **12** (179 mg, 86%). ^{1}H-NMR ($CDCl_3$): 8.36 (br s, 1H) NH; 7.45-7.21 (m, 16 H) + 7.07 (m, 2H) + 6.82 (m, 2H) arom; 6.67 (dd, $J_{3',4'}$ = 6.4 Hz, $J_{3',7}$ = 15.8 Hz, 1H) H3'; 6.05 (dd, $J_{7,4'}$ = 1.1 Hz, 1H) H7; 6.04 (dd, $J_{1',2'}$ = $J_{1',2''}$ = 5.3 Hz, 1H) H1'; 4.78 (dd, $J_{2',2''}$ = 11.6 Hz, 1H) H2'; 4.57 (dd, 1H) H2''; 4.18 (q, J = 7.1 Hz, 2H) OCH_2CH_3; 3.95 (m, 1H) H4'; 3.79 (s, 3H) OMe; 3.38 (dd, $J_{4',5'}$ = 7.5 Hz, $J_{5',5''}$ = 11.0 Hz, 1H) H5';

3.21 (dd, $J_{4',5''}$ = 3.3 Hz, 1H) H5"; 1.74 (d, J = 1.1 Hz, 3H) 5-CH_3; 1.26 (t, 3H) $OCH_2\underline{C}H_3$. ^{13}C-NMR: 194.1 (s) CS; 165.2 (s) COO; 163.7 (s) C4; 150.7 (s) C2; 141.3 (d, 160.4 Hz) C3'; 134.7 (d, 178.7 Hz) C6; 124.9 (d, 164.0 Hz) C7; 111.7 (s) C5; 79.0 (d, 165.0 Hz) C1'; 77.4 (d, 146.6 Hz) C4'; 71.6 (t, 151.1 Hz) C2'; 65.5 (t, 142.5 Hz) C5'; 60.5 (t, 145.7 Hz) $O\underline{C}H_2CH_3$; 55.0 (q, 143.9 Hz) OMe; 13.9 (q, 127.1 Hz) $OCH_2\underline{C}H_3$; 12.2 (q, 130.1 Hz) 5-Me.

5'-O-MMTr-2',3'-dideoxy-3'-*C*-carbethoxymethylene-ribothymidine (15). The reaction on **12** (160 g, 0.22 mmol) was performed using a reaction condition described for **13** to give **15** (91 mg, 72%). ^{1}H-NMR ($CDCl_3$): 8.40 (br s, 1H) NH; 7.61 (q, J = 1.2 Hz, 1H) H6; 7.47-7.21 (m, 12H) + 6.84 (m, 2H) arom; 6.14 (dd, $J_{1',2'}$ = 3.9 Hz, $J_{1',2''}$ = 6.8 Hz, 1H) H1'; 4.07 (dq, J = 1 Hz, J = 7.2 Hz, 2H) OCH_2CH_3; 3.85 (ddd, $J_{4',5'}$ = 2.7 Hz, $J_{4',5''}$ = 3.7 Hz, $J_{4',3'}$ = 8.2 Hz, 1H) H4'; 3.80 (s, 3H) OMe; 3.52 (dd, $J_{5',5''}$ = 10.8 Hz, 1H) H5'; 3.29 (dd, 1H) H5"; 2.82 (m, 1H) H3'; 2.42 (ddd, $J_{2',3'}$ = 8.2 Hz, $J_{2',2''}$ = 13.7 Hz, 1H) H2'; 2.39 (dd, $J_{7',3'}$ = 5.4 Hz, $J_{7',7''}$ = 15.8 Hz, 1H) H7'; 2.25 (dd, $J_{7'',3'}$ = 8.7 Hz, 1H) H7"; 2.18 (ddd, $J_{2'',3'}$ = 8.8 Hz, 1H) H2"; 1.52 (d, 3H) 5-CH_3; 1.22 (t, 3H) $OCH_2\underline{C}H_3$. ^{13}C-NMR ($CDCl_3$): 171.2 (s) COO; 163.8 (s) C4; 150.3 (s) C2; 135.4 (d, 183.3 Hz) C6; 110.5 (s) C5; 84.7 (d, 171.4 Hz) C1'; 84.2 (d, 146.6 Hz) C4'; 63.0 (t, 142.0 Hz) C5'; 60.6 (t, 149.8 Hz) $O\underline{C}H_2CH_3$; 55.1 (q, 143.9 Hz) OMe; 38.8 (t, 133.3 Hz) C2'; 36.4 (t, 128.3 Hz) C7; 34.7 (d, 133.8Hz) C3'; 14.0 (q, 127.1 Hz) $OCH_2\underline{C}H_3$; 11.9 (q, 129.2 Hz) 5-Me.

2',3'-dideoxy-3'-*C*-carbethoxymethylene-ribothymidine (16). **15** (80 mg, 0.13 mmol) was treated 90% acetic acid (5 ml) at RT for 12 h. The solvent was removed in vacuo. The residue was purified by silica gel column chromatografy to give **16** (32 mg, 78%) ^{1}H-NMR ($CDCl_3$ + CD_3OD): 7.93 (q, J = 1.2 Hz, 1H) H6; 6.10 (dd, $J_{1',2'}$ = 3.5 Hz, $J_{1',2''}$ = 6.8 Hz, 1H) H1'; 4.17 (q, J = 7.1 Hz, 2H) OCH_2CH_3; 3.95 (dd, $J_{4',5'}$ = 2.3 Hz, $J_{5',5''}$ = 12.1 Hz, 1H) H5'; 3.79 (m, 1H) H4'; 3.72 (dd, $J_{4',5''}$ = 3.3 Hz, 1H) H5"; 2.72 (m, 1H) H3'; 2.59 (dd, $J_{7',3'}$ = 5.6 Hz, $J_{7',7''}$ = 16.0 Hz, 1H) H7'; 2.35 (ddd, $J_{2',3'}$ = 7.8 Hz, $J_{2',2''}$ = 13.7 Hz, 1H) H2'; 2.39 (dd, $J_{7'',3'}$ = 8.4 Hz, 1H) H7"; 2.19 (ddd, $J_{2'',3'}$ = 9.4 Hz, 1H) H2"; 1.91 (d, 3H) 5-CH_3; 1.28 (t, 3H) $OCH_2\underline{C}H_3$. ^{13}C-NMR: 171.7 (s) COO; 164.5 (s) C4; 150.3 (s) C2; 136.2 (d, 183.3 Hz) C6; 109.5 (s) C5; 85.3 (d, 146.6 Hz) C4'; 84.3 (d, 172.3 Hz) C1'; 60.4 (t, 144.3 Hz) and 60.3 (t, 149.4 Hz) $O\underline{C}H_2CH_3$ and C5'; 38.3 (t, 134.3 Hz) C2'; 35.6 (t, 128.3 Hz) C7; 33.0 (d, 133.9 Hz) C3'; 13.2 (q, 126.5 Hz) $OCH_2\underline{C}H_3$; 11.3 (q, 127.7 Hz) 5-Me. $\tilde{\lambda}_{max}$ = 266 nm. HRMS (FAB^-): calcd. for $(M-H)^-$ 311.1243, found 311.1205.

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