44. Nucleotides

Part XLII[1])

The 2-Dansylethoxycarbonyl (= 2-{[5-(Dimethylamino)naphthalen-1-yl]sulfonyl}ethoxycarbonyl; Dnseoc) Group for Protection of the 5′-Hydroxy Function in Oligoribonucleotide Synthesis

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The 2-dansylethoxycarbonyl (Dnseoc) group was employed for protection of the 5′-hydroxy function in oligoribonucleotide synthesis by the phosphoramidite approach using the acid-labile tetrahydro-4-methoxy-2*H*-pyran-4-yl (Thmp) group for 2′-protection. The syntheses of monomeric building blocks, both phosphoramidites and nucleoside-functionalized supports, are described for the four common nucleosides adenosine, guanosine, cytidine, and uridine, and for the two modified minor nucleosides ribothymidine (= ribosylthymine) and pseudouridine.

1. Introduction. – The growing need of synthetic oligoribonucleotides, *e.g.* for the study of RNA structure, catalytic RNA, and of RNA-protein interactions or for antisense chemistry, requires the development of more and more efficient methods for oligoribonucleotide synthesis.

In recent years, great progress has been made in oligonucleotide synthesis by the development of the phosphoramidite method using a solid support [2–7]. The synthesis of oligoribonucleotides, however, is still difficult compared with the deoxy series, because the additional 2′-OH function must be properly protected. The 2′-protecting group should be completely stable under the conditions required for the removal of the 5′-protecting group during oligoribonucleotide synthesis and of the base- and phosphate-protecting groups at the end of synthesis as well as during the cleavage from the support. On the other hand, it should be removable under mild conditions causing no isomerization or cleavage of the formed phosphodiester linkages. In contrast to this, the 5′-protecting group must be removed selectively and quantitatively before every chain elongation step. The cleaved protecting group should, furthermore, be easily detectable to enable the determination of coupling efficiency.

The synthesis of a partially modified, 77-mer *t*-RNA with (*tert*-butyl)dimethylsilyl as 2′-protecting group in combination with dimethoxytrityl for 5′-protection was described by *Ogilvie et al.* [8]. The combination of the photolabile 2-nitrobenzyl and dimethoxytrityl for 2′- and 5′-protection was suggested by *Tanaka et al.* [9] [10]. Acid-labile acetal and ketal groups were also used for the protection of the 2′-OH function bearing

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the advantage of mild cleavage without harming the phosphodiester linkage. Unfortunately, these protecting groups are not completely compatible with the traditional 5′-dimethoxytrityl or 9-phenylxanthen-9-yl groups [11–13], and so only the syntheses of short oligoribonucleotides were described by this approach. There are two alternatives to overcome this problem. *Reese* and coworkers investigated the use of the more stable 1-(2-chloro-4-methylphenyl)-4-methoxypiperidin-4-yl (Ctmp) and 1-(2-fluorophenyl)-4-methoxypiperidin-4-yl (Fpmp) 2′-protecting groups [14–17]. On the other hand, compatibility can be achieved by the use of base-labile 5′-protecting groups. Oligoribonucleotide syntheses with 5′-levulinyl [18] and 5′-(9-fluorenylmethoxycarbonyl) groups [19] were also accomplished.

Recently, we described the successful use of the 2-dansylethoxycarbonyl (= 2-{[5-(dimethylamino)naphthalen-1-yl]sulfonyl}ethoxycarbonyl; Dnseoc) group [1] in oligodeoxyribonucleotide synthesis. The good features of the 5′-Dnseoc group prompted us to develop a new strategy in oligoribonucleotide synthesis in which the base-labile 5′-Dnseoc group is combined with the achiral acid-labile tetrahydro-4-methoxy-2*H*-pyran-4-yl (Thmp) group developed by *Reese* and coworkers [20–22]. In this paper, we wish to report the synthesis of protected phosphoramidite building blocks and of corresponding nucleoside-functionalized supports which enables an efficient oligoribonucleotide synthesis.

2. Syntheses. – At the beginning of an oligonucleotide synthesis, the protection of the functional groups of the aglycon must be carried out normally. For this purpose, the 2-(4-nitrophenyl)ethyl (npe) and 2-(4-nitrophenyl)ethoxycarbonyl (npeoc) protecting-group strategy was used to protect the adenosine, cytidine, and guanosine derivatives [23–25]. Adenosine was also protected with benzoyl as example for an acyl blocking group [26]. Uridine, ribothymidine (= ribosylthymine), and pseudouridine derivatives were commonly used unprotected at the aglycon moiety. Later, we will also describe protected building blocks for uridine and pseudouridine.

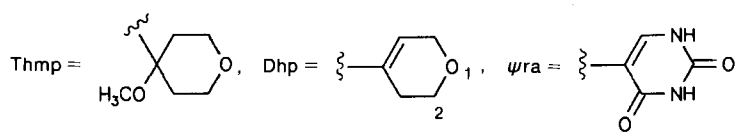
To achieve a selective high-yielding introduction of the 2′-Thmp protecting group, the 3′- and 5′-OH functions of the nucleosides **1**–**7** were intermediarily blocked with the bifunctional 1,1,3,3-tetraisopropyldisiloxane-1,3-diyl (tipds) group of *Markiewicz* [27] by reaction with a slight excess of 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane in abs. pyridine at room temperature for 12–18 h (*Scheme 1*). After workup and purification by chromatography or crystallization, 83–92% of 3′,5′-*O*-tipds-protected nucleosides **8**–**14** were obtained. The yields are mostly higher than described previously [27–31]. The ribothymidine derivative **13** has not as yet been isolated. The 2′-*O*-Thmp-nucleosides **23**–**29** were prepared by reaction of the 3′,5′-*O*-tipds-nucleosides **8**–**14** with excess (7.5–12 equiv.) of 3,6-dihydro-4-methoxy-2*H*-pyran which was synthesized by a procedure according to *Reese* and coworkers [22] [32] [33] and a catalytic amount of toluene-4-sulfonic acid (TsOH; 0.1–1 equiv.) in dioxane or CH_2Cl_2 at room temperature (→ **15**–**21**) followed by treatment with Bu_4NF (2.5 equiv.) in THF to remove the tipds group. In the case of nucleosides containing npe/npeoc groups, addition of AcOH (5 equiv.) was necessary to deactivate the F^- ions and, therefore, avoid cleavage of the npe and npeoc groups. Workup and purification by chromatography and partial crystallization led to the 2′-*O*-Thmp-nucleosides **23**–**28** in 70–93% yield. The yield of 2′-*O*-Thmp-pseudouridine (**29**) was only 42% because of the formation of a by-product by elimination of MeOH from the Thmp group of the intermediate **21** to give 2′-*O*-(3,6-dihydro-2*H*-pyran-4-yl)-3′,5′-

O-tipds-pseudouridine (**22**) which was deprotected to **30**. Compounds **15–20** were isolated for characterization despite the fact that the syntheses of **23–28** were usually achieved by a two-step procedure directly from **8** to **14**. Nucleoside **27** was already synthesized *via* 3′,5′-di-*O*-acetyluridine in 82% yield by *Reese* and coworkers [20] [22] and in 73% yield by *Gait* and coworkers [19]. *Chattopadhyaya* and coworkers [28] achieved the synthesis of **23** in 51% and of **27** in 43% yield *via* the corresponding 3′,5′-*O*-tipds-nucleosides, and *Gait* and coworkers [19] synthesized **23** analogously in 67% yield. Nucleosides **28** and **29** were synthesized according to [34] with reproducible yields. Our 2′-*O*-Thmp-pseudouridine (**29**) had the same m.p. as reported [34], but is polluted with *ca.* 5% of **30** (see above) as determined by ^{1}H-NMR spectroscopy. *Reese* and coworkers [34] attributed the low yield of **29** to difficult isolation, but did not mention the presence of a by-product which could not be separated completely by chromatographical means. Preparation of **29** from purified **21** led to a material which had a m.p. 20° higher in comparison with the product obtained by the one-pot synthesis according to [34]. The by-product **30** was also isolated in pure form by desilylation of pure **22** with Bu_4NF in THF in 62% yield.

Scheme 1

Base		Base	R	R¹	R²	Base	R	R¹	R²
1	Ade^{bz}	**8**	Ade^{bz}	tipds	H	**20** Thy		tipds	Thmp
2	Ade^{npeoc}	**9**	Ade^{npeoc}	tipds	H	**21** ψra		tipds	Thmp
3	Gua^{npe}_{npeoc}	**10**	Gua^{npe}_{npeoc}	tipds	H	**22** ψra		tipds	Dhp
4	Cyt^{npeoc}	**11**	Cyt^{npeoc}	tipds	H	**23** Ade^{bz}	H	H	Thmp
5	Ura	**12**	Ura	tipds	H	**24** Ade^{npeoc}	H	H	Thmp
6	Thy	**13**	Thy	tipds	H	**25** Gua^{npe}_{npeoc}	H	H	Thmp
7	ψra	**14**	ψra	tipds	H	**26** Cyt^{npeoc}	H	H	Thmp
		15	Ade^{bz}	tipds	Thmp	**27** Ura	H	H	Thmp
		16	Ade^{npeoc}	tipds	Thmp	**28** Thy	H	H	Thmp
		17	Gua^{npe}_{npeoc}	tipds	Thmp	**29** ψra	H	H	Thmp
		18	Cyt^{npeoc}	tipds	Thmp	**30** ψra	H	H	Dhp
		19	Ura	tipds	Thmp				

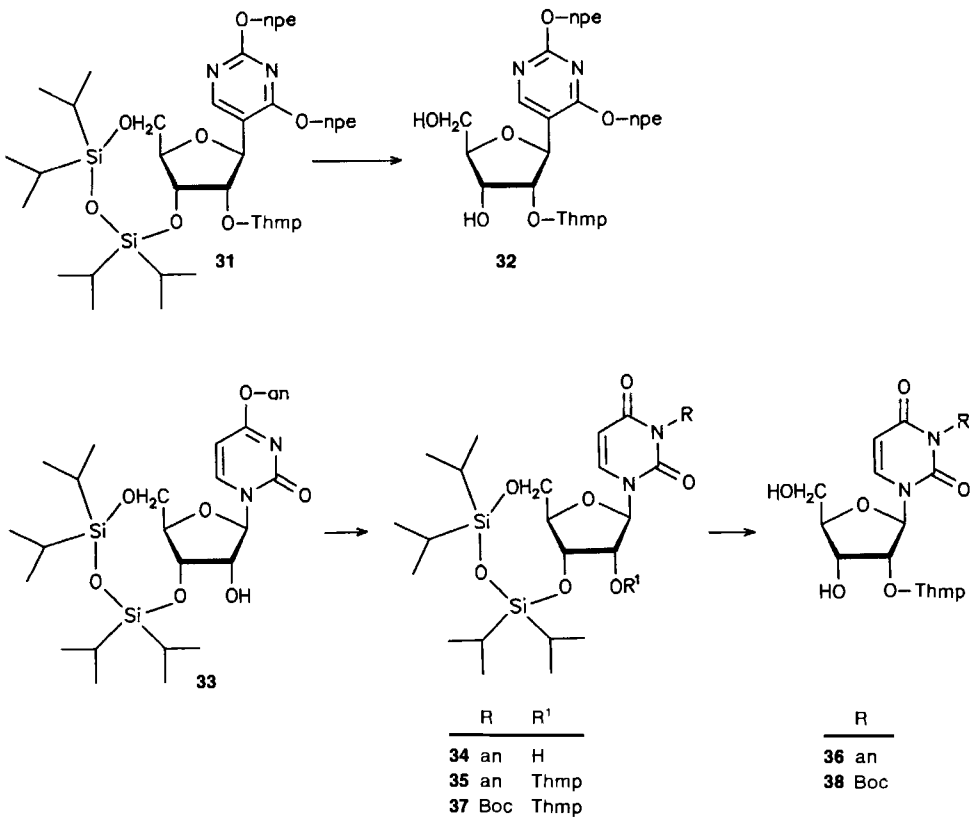
bz = PhCO, npe = 4-$NO_2C_6H_4CH_2CH_2$, npeoc = 4-$NO_2C_6H_4CH_2CH_2OCO$, tipds = $Si(i\text{-}Pr)_2OSi(i\text{-}Pr)_2$



To complete the set of nucleoside building blocks, base-protected pseudouridine and uridine derivatives were also synthesized. Both lactam functions of pseudouridine were blocked with npe according to a former procedure [35] by refluxing **21** with Ag_2CO_3 in toluene and then reaction with 2-(4-nitrophenyl)ethyl iodide to give the O^2,O^4-dialkyl-

ated product **31** in 55% yield. Desilylation of **31** with Bu_4NF/AcOH in THF led to 2′-*O*-Thmp-O^2,O^4-bis(npe)pseudouridine (**32**) in 88% yield (*Scheme 2*). On the other hand, uridine was protected both with an anisoyl (an) and a (*tert*-butyloxy)carbonyl (Boc) group, according to a procedure of *Sekine* [36] whereby **12** reacted with anisoyl chloride (2 equiv.) under basic phase-transfer conditions to a mixture of O^4- (**33**) and N^3-acylated product (**34**) with the former one in favour. However, **33** could be thermally transformed into the thermodynamically more stable N^3-acylated product **34** *via Chapman* rearrangement. Direct reaction of **34** with 3,6-dihydro-4-methoxy-2*H*-pyran under catalysis with CF_3COOH (→ **35**) followed by tipds cleavage with KF/Et_4NBr in MeCN/H_2O [37] led to N^3-an-2′-*O*-Thmp-uridine (**36**) with an overall yield of 42%. The reversed reaction sequence **12** → **19** → **35** → **36** applying the acylation conditions of *Hata* and coworkers [38] gave **36** in 61% yield. The boc protecting group could be introduced into the N^3-position in a similar manner reacting **19** with di(*tert*-butyl) dicarbonate and 4-(dimethylamino)pyridine in pyridine to **37** followed by tipds cleavage with Bu_4NF/AcOH in THF leading to N^3-boc-2′-*O*-Thmp-uridine (**38**) in 74% yield.

Scheme 2



an = 4-$MeOC_6H_4CO$, Boc = *t*-BuOCO

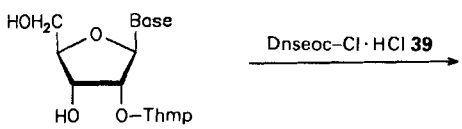
The introduction of the Dnseoc group into **23**–**29**, **32**, **36**, and **38** was best carried out by adding a slight excess (1.3 equiv.) of solid 2-dansylethyl chloroformate hydrochloride (**39**) [1] at 0° to a pyridine solution of the 2′-*O*-Thmp-nucleosides (*Scheme 3*). The reaction was complete within 1 h, and after workup and flash chromatography, the desired 5′-*O*-Dnseoc-substituted nucleosides **40**, **42**, **44**, **46**, **49**, **51**, **53**, **55**, **56**, and **59** were obtained in 61–77% yield, except the base-protected uridine derivatives **36** and **38** giving only 48%. The 5′-*O*-substitution was favoured due to higher reactivity of the primary 5′-OH function and steric hindrance of the 3′-OH function, but still 9–19% of the 3′,5′-di-*O*-substituted products **41**, **43**, **45**, **48**, **50**, **52**, **58**, and **61** were formed as by-products. Furthermore, in the case of the base-protected uridine and cytidine derivatives, the 3′-*O*-monosubstituted derivatives **47**, **57**, and **60** could also be isolated in 12–13% yield. A special case is the reaction of 2′-*O*-Thmp-pseudouridine (**29**) with **39** since a 1.3 equiv. excess afforded only a small turnover, whereas the best results were achieved by use of 2.5 equiv. of **39** and shortening of the reaction time to 15 min to suppress N^1,5′-*O*-disubstitution to **54**. The N^1-Dnseoc residue, the site of which was proven by ^{1}H-NMR spectroscopy, is, however, rather labile and is selectively cleavable by nucleophiles. It should also be mentioned that all dansylethoxycarbonylation reactions are associated with the formation of bis(2-dansylethyl) carbonate [1] in substantial amounts which could be separated by chromatography and consecutive crystallization from CH_2Cl_2/MeOH.

The 3′-phosphoramidites **64**–**75** were synthesized in 60–84% yield by phosphitylation using mostly chloro(diethylamino)[2-(4-nitrophenyl)ethoxy]phosphine (**63**) and sometimes chloro(diisopropylamino)[2-(4-nitrophenyl)ethoxy]phosphine (**62**) [1].

As a second series of building blocks for solid-phase synthesis, the 3′-*O*-succinoylnucleosides **76**–**79** of the four common bases were synthesized by reaction of 5′-*O*-Dnseoc-substituted nucleosides with succinic anhydride and 4-(dimethylamino)pyridine in CH_2Cl_2 [39]. The yields were almost quantitative. The 3′-*O*-succinoyl-nucleosides **76**–**79** were then reacted with LCAMA-CPG (= (long-chain-alkyl)methylamine controlled-pore glass) [1] using the coupling reagent *O*-{[cyano(ethoxycarbonyl)methylidene]-amino}-1,1,3,3-tetramethyluronium tetrafluoroborate (TOTU) and *N*-methylmorpholine in MeCN followed by a capping process with Ac_2O and 4-(dimethylamino)pyridine in pyridine as described recently [1]. Loadings of 15–19 μmol/g were obtained with a 500Å-CPG material. A 1000Å-CPG material was only reacted with the 3′-*O*-succinoyl-adenosine derivative **76** giving loadings of 14 μmol/g.

3. Physical Data. – The synthesized compounds were characterized by elemental analysis, UV and ^{1}H-NMR and, if possible, ^{31}P-NMR spectroscopy. The UV spectra of **8**–**38** are similar to those of the corresponding starting nucleosides **1**–**7**. The Dnseoc-substituted nucleosides and nucleotides **40**–**61** and **64**–**79** have their corresponding counterparts in the 2′-deoxyribonucleoside series [1] showing a new bathochromic absorption at 340 nm resulting from the dansyl chromophore. According to the grade of substitution, the ^{1}H-NMR spectra become more and more complex. The ^{1}H-NMR spectra of the phosphoramidites **64**–**75** which are isolated as a diastereoisomeric mixture are of most complex nature and in addition characterized by ^{31}P-NMR spectra showing two chemical shifts of *ca.* 150 ppm.

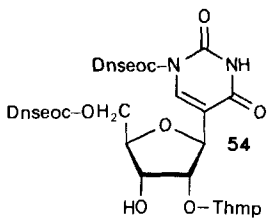
Scheme 3

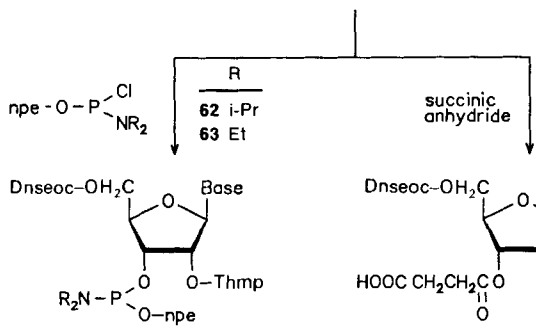


Base	Base
23 Ade^{bz}	**28** Thy
24 Ade^{npeoc}	**29** ψra
25 Gua$^{npe}_{npeoc}$	**32** ψra$^{(npe)_2}$
26 Cyt^{npeoc}	**36** Ura^{an}
27 Ura	**38** Ura^{boc}

Base	R	R^1
40 Ade^{bz}	Dnseoc	H
41 Ade^{bz}	Dnseoc	Dnseoc
42 Ade^{npeoc}	Dnseoc	H
43 Ade^{npeoc}	Dnseoc	Dnseoc
44 Gua$^{npe}_{npeoc}$	Dnseoc	H
45 Gua$^{npe}_{npeoc}$	Dnseoc	Dnseoc
46 Cyt^{npeoc}	Dnseoc	H
47 Cyt^{npeoc}	H	Dnseoc
48 Cyt^{npeoc}	Dnseoc	Dnseoc
49 Ura	Dnseoc	H
50 Ura	Dnseoc	Dnseoc

Base	R	R^1
51 Thy	Dnseoc	H
52 Thy	Dnseoc	Dnseoc
53 ψra	Dnseoc	H
55 ψra$^{(npe)_2}$	Dnseoc	H
56 Ura^{an}	Dnseoc	H
57 Ura^{an}	H	Dnseoc
58 Ura^{an}	Dnseoc	Dnseoc
59 Ura^{boc}	Dnseoc	H
60 Ura^{boc}	H	Dnseoc
61 Ura^{boc}	Dnseoc	Dnseoc

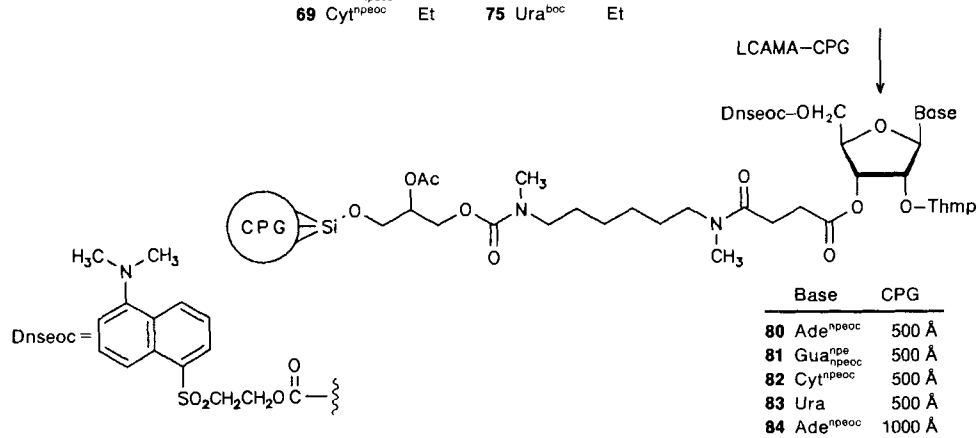




Base	R
64 Ade^{bz}	i-Pr
65 Ade^{npeoc}	i-Pr
66 Ura	i-Pr
67 Ade^{npeoc}	Et
68 Gua$^{npe}_{npeoc}$	Et
69 Cyt^{npeoc}	Et

Base	R
70 Ura	Et
71 Thy	Et
72 ψra	Et
73 ψra$^{(npe)_2}$	Et
74 Ura^{an}	Et
75 Ura^{boc}	Et

Base
76 Ade^{npeoc}
77 Gua$^{npe}_{npeoc}$
78 Cyt^{npeoc}
79 Ura



Base	CPG
80 Ade^{npeoc}	500 Å
81 Gua$^{npe}_{npeoc}$	500 Å
82 Cyt^{npeoc}	500 Å
83 Ura	500 Å
84 Ade^{npeoc}	1000 Å

Experimental Part

General. See [1]. Prep. TLC: silica gel *60 PF_{254} (Merck)*.

1. N^6-*Benzoyl-3′,5′-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)adenosine* (**8**) [28] [40]. In dry pyridine (2 × 50 ml), **1** [26] [40] (7.42 g, 20 mmol) was co-evaporated and then dissolved in dry pyridine (200 ml). Then, 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane (6.9 ml, 22 mmol) was added and the soln. stirred at r.t. for 18 h. After quenching with MeOH (10 ml), the mixture was evaporated, the residue diluted with CH_2Cl_2 (100 ml) and washed with H_2O (100 ml), the aq. phase extracted with CH_2Cl_2 (2 × 50 ml), and the combined org. phase dried (Na_2SO_4), evaporated, and co-evaporated with toluene (2 × 50 ml). Purification was achieved by FC (silica gel, 35 × 4 cm, petroleum ether/AcOEt 1:1 (600 ml) and 1:2 (300 ml) and AcOEt (800 ml)): 10.2 (83%) of **8**. Colourless foam. UV (MeOH): 203 (4.50), 228 (4.19), 279 (4.31). ^{1}H-NMR ($CDCl_3$): 9.07 (br., NH); 8.76 (*s*, H–C(2)); 8.16 (*s*, H–C(8)); 8.03 (*d*, $2H_o$ of (bz)); 7.62–7.45 (*m*, 3 H of bz); 6.05 (*s*, H–C(1′)); 5.14 (*dd*, H–C(3′)); 4.63 (*d*, H–C(2′)); 4.17–4.03 (*m*, H–C(4′), 2 H–C(5′)); 3.25 (*s*, OH–C(2′)); 1.15–1.08 (*m*, 4 i-Pr).

2. N^6-*[2-(4-Nitrophenyl)ethoxycarbonyl]-3′,5′-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)adenosine* (**9**) [29]. As described in *Exper. 1*, with **2** [23] [24] (20 g, 43.3 mmol) and 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane (15 ml, 47. 8 mmol) in dry pyridine (250 ml; 17 h at r.t.). Purification was achieved by FC (silica gel, 20 × 5.5 cm, toluene/AcOEt 1:1 (3.5 l)): 25.24 g (83%) of **9**. Colourless foam. UV (MeOH): 209 (4.51), 267 (4.44). ^{1}H-NMR ($CDCl_3$): 8.70 (*s*, H–C(2)); 8.23 (*s*, NH); 8.18 (*d*, 2 H *o* to NO_2); 8.11 (*s*, H–C(8)); 7.44 (*d*, 2 H *m* to NO_2); 6.01 (*d*, J = 1.1, H–C(1′)); 5.11 (*dd*, H–C(3′)); 4.60 (*d*, H–C(2′)); 4.54 (*t*, CH_2CH_2O); 4.16–4.02 (*m*, H–C(4′), 2 H–C(5′)); 3.22 (*d*, OH–C(2′)); 3.16 (*t*, CH_2CH_2O); 1.13–1.06 (*m*, 4 i-Pr).

3. N^2-*[2-(4-Nitrophenyl)ethoxycarbonyl]-*O^6-*[2-(4-nitrophenyl)ethyl]-3′,5′-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)guanosine* (**10**) [30]. As described in *Exper. 1*, with **3** [25] (10 g, 16 mmol) and 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane (5.51 ml, 17.6 mmol) in dry pyridine (100 ml; 12 h at r.t.). Purification was achieved by FC (silica gel, 20 × 5.5 cm, toluene/AcOEt 5:1 (0.8 l), 4:1 (1 l), and 3:1 (3.2 l)): 12.02 g (87%) of **10**. Almost colourless foam. UV (MeOH): 216 (4.63), 269 (4.56). ^{1}H-NMR ($CDCl_3$): 8.17 (*m*, 4 H *o* to NO_2); 8.00 (*s*, H–C(8)); 7.51, 7.43 (2*d*, 4 H *m* to NO_2); 7.39 (*s*, NH); 5.96 (*d*, J = 1.5, H–C(1′)); 4.81 (*t*, CH_2O(npe), H–C(3′)); 4.49 (*m*, H–C(2′)); 4.47 (*t*, CH_2O(npeoc)); 4.16–4.02 (*m*, H–C(4′), 2 H–C(5′)); 3.31 (*s*, OH–C(2′)); 3.31 (*t*, C–CH_2(npe)); 3.13 (*t*, C–CH_2(npeoc)); 1.08–1.04 (*m*, 4 i-Pr).

4. N^4-*[2-(4-Nitrophenyl)ethoxycarbonyl]-3′,5′-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)cytidine* (**11**) [29]. As described in *Exper. 1*, with **4** [23] [24] (20 g, 45.8 mmol) and 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane (15.8 ml, 50.4 mmol) in dry pyridine (250 ml; 15 h at r.t.). Purification was achieved by FC (silica gel, 20 × 5.5 cm, toluene/AcOEt 1:1 (1 l) and 1:2 (2.5 l)): 25.9 g (83%) of **11**. Colourless foam. UV (MeOH): 212 (4.43), 244 (4.25), 282 (4.17). ^{1}H-NMR ($CDCl_3$): 8.40 (br., NH); 8.17 (*m*, H–C(6), 2 H *o* to NO_2); 7.41 (*d*, 2 H *m* to NO_2); 7.17 (*d*, H–C(5)); 5.80 (*s*, H–C(1′)); 4.44 (*t*, CH_2O); 4.30–4.18 (*m*, H–C(2′), H–C(3′), H–C(4′), 1 H–C(5′)); 4.01 (*m*, 1 H–C(5′)), 3.25 (br., OH–C(2′)); 3.11 (*t*, C–CH_2); 1.10–0.92 (*m*, 4 i-Pr).

5. *3′,5′-O-(1,1,3,3-Tetraisopropyldisiloxane-1,3-diyl)uridine* (**12**) [27]. As described in *Exper. 1*, with **5** (29.3 g, 0.12 mol) and 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane (41.5 ml, 0.13 mol) in dry pyridine (1 l; 18 h at r.t.). Purification was achieved by FC (silica gel, 30 × 5.5 cm, toluene/AcOEt 2:1 (3.25 l), 1:1 (1 l), and 1:2 (0.5 l)): 53.5 g (92%) of **12**. Colourless foam. UV (MeOH): 205 (3.99), 262 (3.93). ^{1}H-NMR ($CDCl_3$): 8.90 (br., NH); 7.72 (*d*, H–C(6)); 5.74 (*s*, H–C(1′)); 5.70 (*dd*, H–C(5)); 4.36 (*m*, H–C(3′)); 4.24–4.10 (*m*, H–C(2′), H–C(4′), 1 H–C(5′)); 4.00 (*dd*, 1 H–C(5′)), 3.20 (br., OH–C(2′)); 1.10–1.02 (*m*, 4 i-Pr).

6. *3′,5′-O-(1,1,3,3-Tetraisopropyldisiloxane-1,3-diyl)ribothymidine* (**13**). As described in *Exper. 1*, with **6** (5 g, 19.4 mmol) and 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane (6.68 ml, 21.3 mmol) in dry pyridine (150 ml; 15 h at r.t.). Purification was achieved by FC (silica gel, 25 × 4 cm, toluene/AcOEt 3:1 (0.5 l) and 2:1 (0.9 l)): 8.12 g (84%) of **13**. Colourless foam. UV (MeOH): 208 (3.93), 266 (3.98). ^{1}H-NMR ($CDCl_3$): 9.50 (br., NH); 7.48 (*s*, H–C(6)); 5.72 (*s*, H–C(1′)); 4.35 (*m*, H–C(3′)); 4.24–4.12 (*m*, H–C(2′), H–C(4′), 1 H–C(5′)); 4.01 (*dd*, 1 H–C(5′)); 3.75 (br., OH–C(2′)); 1.91 (*d*, J = 0.85, Me); 1.10–1.03 (*m*, 4 i-Pr). Anal. calc. for $C_{22}H_{40}N_2O_7Si_2 \cdot 0.5\ H_2O$ (509.8): C 51.84, H 8.11, N 5.50; found: C 51.82, H 7.90, N 5.30.

7. *3′,5′-O-(1,1,3,3-Tetraisopropyldisiloxane-1,3-diyl)pseudouridine* (**14**) [31]. As described in *Exper. 1*, with a suspension of **7** (4 g, 16.4 mmol) and 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane (5.65 ml, 18 mmol) in dry pyridine (150 ml; 14 h at r.t., →soln. after 1–2 h stirring). After workup, purification was achieved by crystallization from AcOEt/hexane yielding 6.57 g of **14** as colourless crystals of m.p. 146–150° ([31]: 146–150°). Further purification of the evaporated mother liquor was achieved by FC (silica gel, 14 × 3 cm, toluene/AcOEt 1:1 (300 ml) and 1:2 (200 ml)): 0.70 g of **14** as a colourless foam. Total yield: 7.27 g (91%) of **14**. UV (MeOH): 208 (4.04), 262

(3.87). ^{1}H-NMR ($CDCl_3$): 10.22 (br. *d*, H–N(1)); 9.98 (*s*, H–N(3)); 7.55 (*d*, H–C(6)); 4.76 (*s*, H–C(1′)); 4.31 (*dd*, H–C(3′)); 4.13–3.95 (*m*, H–C(2′), H–C(4′), 2 H–C(5′)); 3.13 (*s*, OH–C(2′)); 1.05 (*m*, 4 i-Pr). Anal. calc. for $C_{21}H_{38}N_2O_7Si_2$ (486.7): C 51.82, H 7.87, N 5.76; found: C 51.76, H 7.90, N 5.16.

8. *N^6-Benzoyl-2′-O-(tetrahydro-4-methoxy-2*H*-pyran-4-yl)-3′,5′-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)adenosine* (**15**) *and* N^6-*Benzoyl-2′-O-(tetrahydro-4-methoxy-2*H*-pyran-4-yl)adenosine* (**23**). In dry 1,4-dioxane (75 ml), **8** (5 g, 8.15 mmol) and TsOH·H_2O (0.5 g, 2.63 mmol) were dissolved. Then, 73% pure 3,6-dihydro-4-methoxy-2*H*-pyran [22] [32] [33] (14.9 g, 95 mmol) was added. The mixture was stirred for 3.5 h at r.t., neutralized with a few drops of NaOMe soln. in MeOH, and evaporated to a yellowish oil. This was diluted with CH_2Cl_2 (100 ml), the soln. washed with sat. $NaHCO_3$ soln. (100 ml), the aq. phase extracted with CH_2Cl_2 (50 ml), and the combined org. phase dried (Na_2SO_4) and evaporated. The residual yellowish oil (crude **15**) was dissolved in dry THF (40 ml) and $Bu_4NF·3\ H_2O$ (6.45 g, 20.4 mmol) added. After stirring for 10 min at r.t., sat. $NaHCO_3$ soln. (30 ml) was added, the mixture extracted with CH_2Cl_2 (1 × 50 ml, 2 × 25 ml), and the combined org. phase dried (Na_2SO_4) and evaporated. Purification was achieved by FC (silica gel, 20 × 4 cm, CH_2Cl_2/MeOH gradient with 0% (500 ml), 1, 2, 3, and 4% (200 ml each), and 5% MeOH (600 ml)): 3.69 g (93%) of **23**. Colourless foam.

Isolation of **15** was possible by purification of crude **15** by FC (silica gel, 0–3% MeOH/CH_2Cl_2) and subsequent precipitation from CH_2Cl_2/hexane: 93% of colourless **15**.

15: UV (MeOH): 202 (4.49), 226 (4.16), 261 (sh, 4.10), 279 (4.30). ^{1}H-NMR ($CDCl_3$): 9.04 (br. *s*, NH); 8.78 (*s*, H–C(2)); 8.41 (*s*, H–C(8)); 8.03 (*d*, 2 H_o (bz)); 7.65 7.50 (*m*, 3 H of bz); 6.12 (*s*, H–C(1′)); 4.75–4.66 (*m*, H–C(2′), H–C(3′)); 4.31–4.22 (*m*, H–C(4′), 1 H–C(5′)); 4.04 (*dd*, 1 H–C(5′)); 3.92–3.82, 3.77–3.59 (2*m*, CH_2OCH_2); 3.38 (*s*, MeO); 2.06, 1.92 (2*m*, CH_2CCH_2); 1.14–0.90 (*m*, 4 i-Pr). Anal. calc. for $C_{35}H_{53}N_5O_8Si_2$ (728.0): C 57.74, H 7.34, N 9.62; found: C 57.45, H 7.38, N 9.30.

23: UV (MeOH): 203 (4.48), 226 (4.13), 279 (4.29). ^{1}H-NMR ($CDCl_3$): 9.10 (*s*, NH); 8.84 (*s*, H–C(2)); 8.09 (*s*, H–C(8)); 8.03 (*d*, 2 H_o (bz)); 7.67–7.52 (*m*, 3 H of bz); 6.00 (*d*, OH–C(5′)); 5.96 (*d*, J = 8, H–C(1′)); 5.36 (*dd*, H–C(2′)); 4.42 (*d*, H–C(3′)); 4.38 (*m*, H–C(4′)); 3.97 (*m*, 1 H–C(5′)); 3.80 (*m*, 1 H–C(5′)); 3.77–3.31 (3*m*, CH_2OCH_2); 2.85 (*s*, OH–C(3′)); 2.65 (*s*, MeO); 1.88 -1.39 (*m*, CH_2CCH_2). Anal. calc. for $C_{23}H_{27}N_5O_7·0.5\ H_2O$ (494.5): C 55.86, H 5.71, N 14.16; found: C 55.67, H 5.91, N 13.70.

9. *N^6-[2-(4-Nitrophenyl)ethoxycarbonyl]-2′-O-(tetrahydro-4-methoxy-2*H*-pyran-4-yl)-3′,5′-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)adenosine* (**16**) *and* N^6-*[2-(4-Nitrophenyl)ethoxycarbonyl]-2′-O-(tetrahydro-4-methoxy-2*H*-pyran-4-yl)adenosine* (**24**). In dry CH_2Cl_2 (50 ml), **9** (5 g, 7.11 mmol) and TsOH·H_2O (0.5 g, 2.63 mmol) were dissolved. After addition of 68% pure 3,6-dihydro-4-methoxy-2*H*-pyran (6 g, 35.7 mmol), the soln. was stirred for 5.5 h at r.t., diluted with CH_2Cl_2 (50 ml), and washed with sat. $NaHCO_3$ soln. (100 ml). The aq. phase was extracted with CH_2Cl_2 (50 ml), the combined org. phase dried (Na_2SO_4) and evaporated, and the residual yellow oil (crude **16**) dissolved in dry THF (40 ml) and AcOH (2 ml, 35 mmol). After addition of $Bu_4NF·3\ H_2O$ (5.6 g, 17.75 mmol), the mixture was stirred for 1.5 h at r.t., diluted with CH_2Cl_2 (100 ml), and washed with sat. $NaHCO_3$ soln. (100 ml). The aq. phase was extracted with CH_2Cl_2 (2 × 50 ml), the combined org. phase dried (Na_2SO_4) and evaporated, and the residue purified by FC (silica gel, 24 × 4 cm, CH_2Cl_2/MeOH gradient with 0, 1, 2, and 3% (0.5 l each) and 4% MeOH (1 l)): 3.74 g (92%) of **24**. Colourless foam.

Isolation of **16** was possible by purification of crude **16** by FC (silica gel, 0–1% MeOH/CH_2Cl_2) and subsequent precipitation from CH_2Cl_2/hexane: 91% of almost colourless **16**.

16: UV (MeOH): 207 (4.55), 266 (4.48), 273 (sh, 4.41). ^{1}H-NMR ($CDCl_3$): 8.71 (*s*, H–C(2)); 8.39 (*s*, H–C(8)); 8.20 (*d*, 2 H *o* to NO_2); 8.06 (br. *s*, NH); 7.45 (*d*, 2 H *m* to NO_2); 6.08 (*s*, H–C(1′)); 4.70–4.61 (*m*, H–C(2′), H–C(3′)); 4.54 (*t*, CH_2O); 4.31–4.21 (*m*, H–C(4′), 1 H–C(5′)); 4.04 (*dd*, 1 H–C(5′)); 3.90 3.80, 3.75–3.58 (2*m*, CH_2OCH_2); 3.37 (*s*, MeO); 3.16 (*t*, C–CH_2); 2.06, 1.91 (2*m*, CH_2CCH_2); 1.11–0.93 (*m*, 4 i-Pr). Anal. calc. for $C_{37}H_{56}N_6O_{11}Si_2$ (817.1): C 54.39, H 6.91, N 10.29; found: C 53.98, H 6.88, N 9.96.

24: UV (MeOH): 212 (4.46), 266 (4.45), 272 (sh, 4.41). ^{1}H-NMR ($CDCl_3$): 8.78 (*s*, H–C(2)); 8.23 (br. *s*, NH); 8.20 (*d*, 2 H *o* to NO_2); 8.02 (*s*, H–C(8)); 7.45 (*d*, 2 H *m* to NO_2); 5.96 (*dd*, OH–C(5′)); 5.93 (*d*, J = 7.7, H–C(1′)); 5.32 (*dd*, H–C(2′)); 4.56 (*t*, CH_2O); 4.41 (*d*, H–C(3′)); 4.38 (*m*, H–C(4′)); 3.97 (*m*, 1 H–C(5′)); 3.78 (*m*, 1 H–C(5′)); 3.76–3.30 (3*m*, CH_2OCH_2); 3.18 (*t*, C–CH_2); 2.81 (*s*, OH–C(3′)); 2.63 (*s*, MeO); 1.90–1.34 (*m*, CH_2CCH_2). Anal. calc. for $C_{25}H_{30}N_6O_{10}·1\ H_2O$ (592.6): C 50.67, H 5.44, N 14.18; found: C 50.96, H 5.46, N 14.03.

10. *N^2-[2-(4-Nitrophenyl)ethoxycarbonyl]-O^6-[2-(4-nitrophenyl)ethyl]-2′-O-(tetrahydro-4-methoxy-2*H*-pyran-4-yl)-3′,5′-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)guanosine* (**17**) *and* N^2-*[2-(4-Nitrophenyl)ethoxycarbonyl]-O^6-[2-(4-nitrophenyl)ethyl]-2′-O-(tetrahydro-4-methoxy-2*H*-pyran-4-yl)guanosine* (**25**). As described in *Exper. 9*, with **10** (3.3 g, 3.8 mmol), TsOH·H_2O (0.36 g, 1.9 mmol), 68% pure 3,6-dihydro-4-methoxy-2*H*-pyran (3.2 g (19 mmol), and after 4 h stirring additional 3.2 g (19 mmol)), dry CH_2Cl_2 (50 ml; total stirring for 6.5 h at r.t.;

workup: dilution with CH_2Cl_2 (20 ml), washing with sat. $NaHCO_3$ soln. (50 ml), extraction with CH_2Cl_2 (2 × 25 ml): crude **17** as a red-brown oil), AcOH (1.1 ml, 19 mmol), $Bu_4NF \cdot 3\ H_2O$ (3 g, 9.5 mmol), and dry THF (30 ml; stirring for 2 h at r.t.; workup: dilution with CH_2Cl_2 (100 ml), washing with sat. $NaHCO_3$ soln. (100 ml), and extraction with CH_2Cl_2 (2 × 50 ml)). Purification was achieved by FC (silica gel, 24 × 4 cm, CH_2Cl_2/MeOH gradient with 0, 1, 2, and 3% (0.5 l each) and 4% MeOH (2 l)): 2.27 g (81%) of **25**. Almost colourless foam.

Isolation of **17** was possible by purification of crude **17** by prep. TLC (2 × hexane/acetone 2:1): 42% of **17**. Almost colourless foam.

17: UV (MeOH): 204 (4.47), 216 (4.58), 268 (4.54). ^{1}H-NMR ($CDCl_3$): 8.27 (*s*, H–C(8)); 8.18 (*t*, 4 H *o* to NO_2); 7.50, 7.42 (*2d*, 4 H *m* to NO_2); 7.20 (*s*, NH); 6.06 (*s*, H–C(1′)); 4.79 (*m*, CH_2O(npe)); 4.60 (*dd*, H–C(3′)); 4.50 (*d*, H–C(2′)); 4.46 (*t*, CH_2O); 4.27 (*m*, 1 H–C(5′)); 4.11 (*m*, H–C(4′)); 4.03 (*dd*, 1 H–C(5′)); 3.92–3.80, 3.76–3.57 (*2m*, CH_2OCH_2); 3.31 (*s*, MeO); 3.31 (*t*, C–CH_2(npe)); 3.12 (*t*, C–CH_2); 2.09, 1.91 (*2t*, CH_2CCH_2); 1.14–0.94 (*m*, 4 i-Pr). Anal. calc. for $C_{45}H_{63}N_7O_{14}Si_2$ (982.2): C 55.03, H 6.47, N 9.98; found: C 54.94, H 6.65, N 9.56.

25: UV (MeOH): 203 (4.52), 215 (4.58), 268 (4.62). ^{1}H-NMR ($CDCl_3$): 8.18 (*t*, 4 H *o* to NO_2); 7.87 (*s*, H–C(8)); 7.52, 7.43 (*2d*, 4 H *m* to NO_2); 7.33 (*s*, NH); 5.86 (*d*, *J* = 7.7, H–C(1′)); 5.27–5.20 (*m*, H–C(2′), OH–C(5′)); 4.83 (*m*, CH_2O(npe)); 4.48 (*t*, CH_2O); 4.40 (*d*, H–C(3′)); 4.33 (*s*, H–C(4′)); 3.95 (*m*, 1 H–C(5′)); 3.79 (*m*, 1 H–C(5′)); 3.76–3.32 (*3m*, CH_2OCH_2); 3.32 (*t*, C–CH_2(npe)); 3.13 (*t*, C–CH_2); 2.75 (*s*, OH–C(3′)); 2.66 (*s*, MeO); 1.90–1.42 (*m*, CH_2CCH_2). Anal. calc. for $C_{33}H_{37}N_7O_{13}$ (739.7): C 53.58, H 5.04, N 13.25; found: C 53.45, H 5.32, N 12.60.

11. *N^4-[2-(4-Nitrophenyl)ethoxycarbonyl]-2′-O-(tetrahydro-4-methoxy-2H-pyran-4-yl)-3′,5′-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)cytidine* (**18**) *and* *N^4-[2-(4-Nitrophenyl)ethoxycarbonyl]-2′-O-(tetrahydro-4-methoxy-2H-pyran-4-yl)cytidine* (**26**). As described in *Exper. 9*, with **11** (5 g, 7.36 mmol), $TsOH \cdot H_2O$ (0.5 g, 2.63 mmol), and 68% pure 3,6-dihydro-4-methoxy-2*H*-pyran (6.2 g (36.9 mmol), and after 4 h stirring additional 3.1 g (18.5 mmol)), dry CH_2Cl_2 (75 ml; total stirring for 10 h at r.t.; workup: washing of the undil. mixture with sat. $NaHCO_3$ soln. (75 ml) and extraction with CH_2Cl_2 (2 × 40 ml): crude **18** as a yellow oil), AcOH (2.1 ml, 36.7 mmol), $Bu_4NF \cdot 3\ H_2O$ (5.8 g, 18.4 mmol), and dry THF (30 ml; stirring for 1.5 h at r.t.). The mixture was then shaken with CH_2Cl_2 (150 ml) and sat. $NaHCO_3$ soln. (100 ml), whereby **26** precipitated. This precipitate was then suction-filtered, washed with Et_2O, and dried over silica gel blue at 40°/high vacuum: 3 g of colourless **26**. The layers of the filtrate were separated, and the aq. phase was extracted with CH_2Cl_2 (2 × 50 ml). The combined org. phases were dried (Na_2SO_4) and evaporated. Purification was achieved by FC (silica gel, 9 × 3 cm, CH_2Cl_2/MeOH gradient with 0, 1, 2, 3, and 4% (100 ml each) and 5% MeOH (200 ml)) and the product precipitated from CH_2Cl_2/Et_2O: 0.58 g of **26**. Total yield: 3.58 g (88%) of **26**.

Isolation of **18** was possible by purification of crude **18** by FC (silica gel, 0–3% MeOH/CH_2Cl_2) and further purification of the slightly impure product by prep. TLC ($CHCl_2$/MeOH 20:1): 74% of **18**. Colourless foam.

18: UV (MeOH): 202 (4.40), 212 (4.37), 244 (4.22), 281 (4.13). ^{1}H-NMR ($CDCl_3$): 8.43 (*d*, H–C(6)); 8.18 (*d*, 2 H *o* to NO_2); 7.82 (br., NH); 7.40 (*d*, 2 H *m* to NO_2); 7.13 (*d*, H–C(5)); 5.79 (*s*, H–C(1′)); 4.44 (*m*, CH_2O, H–C(2′)); 4.31 (*m*, 1 H–C(5′)); 4.25 (*m*, H–C(4′)); 4.14 (*dd*, H–C(3′)); 4.00 (*m*, 1 H–C(5′)); 3.88–3.60 (*m*, CH_2OCH_2); 3.36 (*s*, MeO); 3.11 (*t*, C–CH_2); 2.12, 1.89 (2 *m*, CH_2CCH_2); 1.13–0.94 (*m*, 4 i-Pr). Anal. calc. for $C_{36}H_{56}N_4O_{12}Si_2$ (793.0): C 54.32, H 7.12, N 7.06; found: C 54.65, H 7.27, N 6.92.

26: M.p. 105° (sintering and browning), 185° (dec.). UV (MeOH): 203 (4.43), 211 (4.41), 245 (4.26), 275 (4.14). ^{1}H-NMR ($CDCl_3$): 8.19 (*d*, 2 H *o* to NO_2); 7.85 (*d*, H–C(6)); 7.84 (br., NH); 7.41 (*d*, 2 H *m* to NO_2); 7.22 (*d*, H–C(5)); 5.61 (*d*, *J* = 6.3, H–C(1′)); 5.14 (*t*, H–C(2′)); 4.45 (*t*, CH_2O); 4.32 (*m*, H–C(3′)); 4.24 (*m*, H–C(4′)); 3.95 (*m*, 1 H–C(5′)); 3.90–3.48 (*m*, 1 H–C(5′), CH_2OCH_2, OH–C(5′)); 3.12 (*t*, C–CH_2); 3.07 (*s*, MeO); 2.88 (*d*, OH–C(3′)); 1.85–1.60 (*m*, CH_2CCH_2). Anal. calc. for $C_{24}H_{30}N_4O_{11} \cdot 1\ H_2O$ (568.2): C 50.70, H 5.67, N 9.85; found: C 50.80, H 5.75, N 9.59.

12. *2′-O-(Tetrahydro-4-methoxy-2H-pyran-4-yl)-3′,5′-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)uridine* (**19**) *and 2′-O-(Tetrahydro-4-methoxy-2H-pyran-4-yl)uridine* (**27**) [22]. As described in *Exper. 8*, with **12** (6.5 g, 13.35 mmol), $TsOH \cdot H_2O$ (0.5 g, 2.63 mmol), 68% pure 3,6-dihydro-4-methoxy-2*H*-pyran (7.6 g (45.3 mmol), after 1 h stirring additional 7.6 g (45.3 mmol), and after 4.5 h further 1.9 g (11.3 mmol)), dry 1,4-dioxane (75 ml; total stirring for 6 h at r.t. to give, after workup, crude **19** as a red oil), $Bu_4NF \cdot 3\ H_2O$ (10.53 g, 33.4 mmol) and dry THF (50 ml). After stirring for 10 min at r.t., the mixture was evaporated and directly purified by FC (silica gel, 30 × 4 cm, CH_2Cl_2/MeOH gradient with 0, 1, 2, 3, 4, 5, 6, and 7% MeOH (0.5 l each)). After evaporation of the product fraction and addition of CH_2Cl_2 (50 ml), **27** crystallized. After suction-filtering and drying under high vacuum, **27** (2.84 g) was obtained as colourless crystals. The mother liquor was evaporated and purified by FC (silica gel, 10 × 3 cm, CH_2Cl_2/MeOH 20:1 (1.25 l)): 0.49 g of **27** as colourless foam. Total yield: 3.33 g (70%) of **27**.

Isolation of **19** was possible by purification of crude **19** by FC (silica gel, 0–3% MeOH/CH_2Cl_2): 42% of **19**. Almost colourless foam.

19: UV (MeOH): 209 (3.87), 262 (4.02). ^{1}H-NMR ($CDCl_3$): 9.39 (*s*, NH); 8.04 (*d*, H–C(6)); 5.76 (*s*, H–C(1′)); 5.67 (*dd*, H–C(5)); 4.34 (*m*, H–C(2′)); 4.28 (*m*, 1 H–C(5′)); 4.19–4.18 (*m*, H–C(3′), H–C(4′)); 3.99 (*m*, 1 H–C(5′)); 3.87–3.77, 3.71–3.58 (2*m*, CH_2OCH_2); 3.36 (*s*, MeO); 2.10–1.80 (2 *m*, CH_2CCH_2); 1.11–0.88 (*m*, 4 i-Pr). Anal. calc. for $C_{27}H_{48}N_2O_9Si_2$ (600.9): C 53.97, H 8.05, N 4.66; found: C 53.72, H 8.09, N 4.32.

27: M.p. 172–175° ([22]: 167–169° (from AcOEt)). UV (MeOH): 207 (3.91), 260 (3.99). ^{1}H-NMR ((D_6)DMSO): 11.37 (*s*, NH); 7.92 (*d*, H–C(6)); 5.99 (*d*, $J = 7.7$, H–C(1′)); 5.72 (*d*, H–C(5)); 5.24–5.17 (*m*, OH–C(3′), OH–C(5′)); 4.30 (*dd*, H–C(2′)); 3.95 (*t*, H–C(3′)); 3.89 (*m*, H–C(4′)); 3.70–3.30 (*m*, 2 H–C(5′), CH_2OCH_2); 2.94 (*s*, MeO); 1.82–1.55 (*m*, CH_2CCH_2).

13. *2′-O-(Tetrahydro-4-methoxy-2*H*-pyran-4-yl)-3′,5′-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)ribothymidine* (**20**) *and 2′-O-(Tetrahydro-4-methoxy-2*H*-pyran-4-yl)ribothymidine* (**28**) [34]. As described in *Exper. 8*, with **13** (2 g, 4 mmol), $TsOH \cdot H_2O$ (40 mg, 0.21 mmol), 80% pure 3,6-dihydro-4-methoxy-2*H*-pyran (5.7 g, 40 mmol), dry 1,4-dioxane (12 ml; stirring for 2 h at r.t.; workup: neutralization with NH_3/MeOH, evaporation, dilution with CH_2Cl_2 (50 ml), washing with $NaHCO_3$ soln. (50 ml) and extraction with CH_2Cl_2 (2 × 25 ml) to give crude **20** as an orange-coloured oil), $Bu_4NF \cdot 3\ H_2O$ (3.16 g, 10 mmol), and dry THF (15 ml). After stirring for 15 min at r.t., the mixture was evaporated and directly purified by FC (silica gel, 14 × 3 cm, CH_2Cl_2/MeOH gradient with 0% (100 ml), 1% (300 ml), 2 and 3% (400 ml each), and 4% MeOH (200 ml)). An orange impurity was removed by a further FC (silica gel, 7 × 3 cm, AcOEt (600 ml)): 1.16 g (77%) of **28**. Almost colourless foam.

Isolation of **20** was possible by purification of crude **20** by FC (silica gel, 0–2% MeOH/CH_2Cl_2) and further purification of a slightly impure product fraction by prep. TLC (CH_2Cl_2/MeOH 20:1): 66% of **20**. Colourless foam.

20: UV (MeOH): 207 (3.94), 266 (4.00). ^{1}H-NMR ($CDCl_3$): 8.52 (br. *s*, NH); 7.61 (*s*, H–C(1′)); 5.73 (*s*, H–C(1′)); 4.37 (*d*, H–C(2′)); 4.26 (*m*, H–C(3′), 1 H–C(5′)); 4.15 (*m*, H–C(4′)); 3.99 (*dd*, 1 H–C(5′)); 3.86–3.78, 3.70–3.58 (2*m*, CH_2OCH_2); 3.34 (*s*, MeO); 2.02–1.86 (2*m*, CH_2CCH_2); 1.91 (*s*, Me); 1.12–0.95 (*m*, 4 i-Pr). Anal. calc. for $C_{28}H_{50}N_2O_9Si_2 \cdot 0.5\ H_2O$ (623.9): C 53.90, H 8.24, N 4.49; found: C 54.05, H 8.17, N 4.49.

28: UV (MeOH): 209 (3.95), 264 (3.98). ^{1}H-NMR ($CDCl_3$): 8.55 (br. *s*, NH); 7.34 (*d*, $J = 1.2$, H–C(6)); 5.70 (*d*, $J = 7$, H–C(1′)); 4.88 (*dd*, H–C(2′)); 4.24 (*m*, H–C(3′)); 4.19 (*m*, H–C(4′)); 3.93 (*m*, 1 H–C(5′)); 3.82–3.49 (*m*, 1 H–C(5′), CH_2OCH_2); 3.12 (*s*, MeO); 2.99 (*m*, OH–C(5′)); 2.81 (*d*, OH–C(3′)); 1.94 (*d*, $J = 1.2$, Me); 1.92–1.67 (*m*, CH_2CCH_2). Anal. calc. for $C_{16}H_{24}N_2O_8 \cdot 1.5\ H_2O$ (399.4): C 48.12, H 6.81, N 7.01; found: C 48.28, H 6.33, N 6.78.

14. *2′-O-(Tetrahydro-4-methoxy-2*H*-pyran-4-yl)-3′,5′-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)pseudouridine* (**21**) *and 2′-O-(3,6-Dihydro-2*H*-pyran-4-yl)-3′,5′-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)pseudouridine* (**22**). In dry 1,4-dioxane (7 ml) **14** (1.95 g, 4 mmol) and $TsOH \cdot H_2O$ (76 mg, 0.4 mmol) were disolved. Then 80% pure 3,6-dihydro-4-methoxy-2*H*-pyran (2.85 g, 20 mmol) was added, the mixture stirred for 0.5 h at r.t., neutralized with NH_3/MeOH, evaporated, and co-evaporated with toluene, and the residue purified by FC (silica gel, 13 × 4 cm, toluene/AcOEt 3:1 (300 ml), 2:1 (600 ml), and 1:1 (400 ml)): 1.29 g (54%) of **21** and 0.70 g (31%) of **22** as colourless foams. By-product **22** was crystallized from AcOEt (5 ml)/hexane (15 ml) yielding hygroscopic colourless crystals. For characterization, an aliquot of **21** was further purified by prep. TLC (toluene/AcOEt 5:4).

21: UV (MeOH): 208 (3.95), 263 (3.88). ^{1}H-NMR ($CDCl_3$): 8.87 (br. 2 NH); 7.72 (*d*, $J = 4.75$, H–C(6)); 4.83 (*s*, H–C(1′)); 4.34 (*d*, H–C(2′)); 4.23–4.16 (*m*, 1 H–C(5′), H–C(3′)); 4.05 (*m*, H–C(4′)); 3.94 (*dd*, 1 H–C(5′)); 3.86–3.60 (2*m*, CH_2OCH_2); 3.35 (*s*, MeO); 2.10–1.82 (2*m*, CH_2CCH_2); 1.09–0.85 (*m*, 4 i-Pr). Anal. calc. for $C_{27}H_{48}N_2O_9Si_2 \cdot 0.5\ H_2O$ (609.9): C 53.17, H 8.10, N 4.59; found: C 53.45, H 8.01, N 4.10.

22: M.p. 186–190°. UV (MeOH): 206 (4.16), 263 (3.92). ^{1}H-NMR ($CDCl_3$). 9.19 (br., H–N(1)); 9.14 (br. *s*, H–N(3)); 7.66 (*d*, $J = 5$, H–C(6)); 5.19 (*m*, H–C(5)(Dhp)); 4.87 (*s*, H–C(1′)); 4.49 (*d*, H–C(2′)); 4.30 (*dd*, H–C(3′)); 4.21 (*m*, CH_2(6)(Dhp)); 4.15 (*m*, 1 H–C(5′)); 4.05 (*m*, H–C(4′)); 3.95 (*dd*, 1 H–C(5′)); 3.84 (*t*, CH_2(2)(Dhp)); 2.26 (*m*, CH_2(3)(Dhp)); 1.08–0.91 (*m*, 4 i-Pr). Anal. calc. for $C_{26}H_{44}N_2O_8Si_2 \cdot 0.5\ H_2O$ (577.8): C 54.04, H 7.85, N 4.85; found: C 54.22, H 7.71, N 4.38.

15. *2′-O-(Tetrahydro-4-methoxy-2*H*-pyran-4-yl)pseudouridine* (**29**). *Method A* [34]: As described in *Exper. 14*, with **14** (0.98 g, 2 mmol), $TsOH \cdot H_2O$ (38 mg, 0.2 mmol), 80% pure 3,6-dihydro-4-methoxy-2*H*-pyran (2.85 g, 20 mmol) and dry 1,4-dioxane (4 ml). After workup, the yellow oil was dissolved in dry THF (8 ml), $Bu_4NF \cdot 3\ H_2O$ (1.58 g, 5 mmol) added, and the mixture stirred for 15 min at r.t., evaporated, and directly purified by FC (silica gel, 11 × 3 cm, CH_2Cl_2/MeOH gradient with 100 ml 0, 1, 2, 3, 4, 5, 6, 7, 8, and 9% MeOH (100 ml each)). The combined product fractions which contained all the by-product **30** with almost identical R_f were concentrated to 100 ml, whereby **29** crystallized. These crystals were suction-filtered and crystallized from EtOH: 304 mg (42%) of **29**. Colourless crystals. M.p. 194–197° ([34]: m.p. 194–197°; 42% yield). According to ^{1}H-NMR, this **29** contained *ca.* 5% of **30**.

Method B: In dry THF (4 ml), **21** (0.5 g, 0.83 mmol) was dissolved, $Bu_4NF \cdot 3\ H_2O$ (0.66 g, 2.09 mmol) added, the mixture stirred for 15 min at r.t., evaporated, and co-evaporated with CH_2Cl_2, and the residue purified by FC (silica gel, 9 × 2 cm, CH_2Cl_2/MeOH gradient with 0, 5, 8, and 10% MeOH (50 ml each)). Evaporation and crystallization from EtOH (15 ml) gave 0.24 g (81%) of **29**. Colourless crystals. M.p. 219–220°. UV (MeOH): 207 (3.97), 263 (3.89). ^{1}H-NMR ((D$_6$)DMSO): 11.15 (br. *s*, H–N(3)); 10.99 (br., H–N(1)); 7.63 (*s*, H–C(6)); 4.82 (*dd*, OH–C(5′)); 4.70 (*d*, OH–C(3′)); 4.53 (*d*, J = 7.1, H–C(1′)); 4.34 (*dd*, H–C(2′)); 3.92 (*m*, H–C(3′)); 3.74 (*m*, H–C(4′)); 3.70–3.36 (*m*, 2 H–C(5′), CH_2OCH_2); 3.00 (*s*, MeO); 1.82–1.60 (*m*, CH_2CCH_2). Anal. calc. for $C_{15}H_{22}N_2O_8$ (358.4): C 50.28, H 6.19, N. 7.82; found: C 49.85, H 6.11, N 7.85.

16. *2′-O-(3,6-Dihydro-2*H*-pyran-4-yl)pseudouridine* (**30**). As described in *Exper. 15* (*Method B*), with **22** (150 mg, 0.26 mmol) and $Bu_4NF \cdot 3\ H_2O$ (0.21 g, 0.67 mmol; 15 min at r.t.). After evaporation, purification by FC (silica gel, 9 × 1.25 cm, CH_2Cl_2/MeOH gradient with 0, 2, 4, 6, and 8% MeOH (25 ml each)) and evaporation of the product fraction to a smaller volume yielded crystals: 53 mg (62%) of **30**. Colourless hygroscopic crystals. M.p. 236–237°. UV (MeOH): 204 (4.12), 262 (3.89). ^{1}H-NMR ((D$_6$)DMSO): 11.14, 10.96 (2 br. *s*, 2 NH); 7.66 (*s*, H–C(6)); 4.95 (*m*, H–C(5)(Dhp)); 4.90–4.86 (*m*, OH–C(5′), OH–C(3′)); 4.64 (*d*, J = 4, H–C(1′)); 4.39 (*t*, H–C(2′)); 4.13 (*m*, H–C(3′)); 4.03 (*d*, J = 1.9, CH_2(6)(Dhp)); 3.75–3.60 (*m*, H–C(4′), 1 H–C(5′)); 3.67 (*t*, CH_2(2)(Dhp)); 3.50–3.42 (*m*, 1 H–C(5′)); 2.19–1.99 (*m*, CH(3)(Dhp)). Anal. calc. for $C_{14}H_{18}N_2O_7 \cdot 0.25\ H_2O$ (330.8): C 50.83, H 5.64, N 8.47; found: C 50.87, H 5.58, N 8.47.

17. *O^2,O^4-Bis[2-(4-nitrophenyl)ethyl]-2′-O-(tetrahydro-4-methoxy-2*H*-pyran-4-yl)-3′,5′-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)pseudouridine* (**31**). In abs. toluene (30 ml), **21** (0.9 g, 1.5 mmol) and Ag_2CO_3 (1.03 g, 3.75 mmol) were refluxed for 1.5 h. After cooling, the mixture was evaporated to *ca.* 20 ml, 2-(4-nitrophenyl)ethyl iodide [41] (1.25 g, 4.5 mmol) added, and the mixture stirred for 65 h at 60° under exclusion of moisture, filtered before cooling, and evaporated. Purification was achieved by FC (silica gel, 18 × 2.5 cm, toluene (200 ml), toluene/AcOEt 20:1 (200 ml), 10:1 (200 ml), 8:1 (200 ml), and 6:1 (300 ml)) and subsequent crystallization from EtOH (10 ml). 0.74 g (55%) of **31**. Colourless crystals. M.p. 117–119°. UV (MeOH): 203 (4.44), 216 (4.40), 268 (4.42). ^{1}H-NMR ($CDCl_3$): 8.62 (*s*, H–C(6)); 8.17 (*m*, 4 H *o* to NO_2); 7.45, 7.38 (2*d*, 4 H *m* to NO_2); 4.94 (*s*, H–C(1′)); 4.78–4.59 (*m*, CH_2O); 4.58 (*t*, CH_2O); 4.31 (*dd*, H–C(3′)); 4.23–4.18 (*m*, 1 H–C(5′), H–C(2′)); 4.04 (*m*, H–C(4′)); 3.99 (*dd*, 1 H–C(5′)); 3.82–3.68, 3.59–3.49 (2*m*, CH_2OCH_2); 3.22 (*t*, C–CH_2); 3.19 (*s*, MeO); 1.85–1.74 (*m*, CH_2CCH_2); 1.10–0.86 (*m*, 4 i-Pr). Anal. calc. for $C_{43}H_{62}N_4O_{13}Si_2$ (899.2): C 57.44, H 6.95, N 6.23; found: C 57.39, H 6.94, N 6.13.

18. *O^2,O^4-Bis[2-(4-nitrophenyl)ethyl]-2′-O-(tetrahydro-4-methoxy-2*H*-pyran-4-yl)pseudouridine* (**32**). To a soln. of **31** (1 g, 1.11 mmol) in dry THF (5 ml), AcOH (0.32 ml, 5.6 mmol) and $Bu_4NF \cdot 3\ H_2O$ (0.88 g, 2.78 mmol) were added. The mixture was stirred for 2 h at r.t., then diluted with CH_2Cl_2 (20 ml) and washed with sat. $NaHCO_3$ soln. (20 ml). The aq. phase was extracted with CH_2Cl_2 (2 × 10 ml), the combined org. phase dried (Na_2SO_4) and evaporated, and the residue crystallized from EtOH (10 ml): 0.64 g (88%) of **32**. Colourless crystals. M.p. 88–92°. UV (MeOH): 203 (4.42), 216 (4.39), 268 (4.42). ^{1}H-NMR ($CDCl_3$): 8.22 (*s*, H–C(6)); 8.18 (*d*, 4 H *o* to NO_2); 7.45 (*d*, 4 H *m* to NO_2); 4.79–4.62 (*m*, CH_2O, H–C(1′)); 4.60 (*t*, CH_2O): 4.44 (*dd*, H–C(2′)); 4.09 (*m*, H–C(3′)); 4.03 (*m*, H–C(4′)); 3.83 (*m*, 1 H–C(5′)); 3.74–3.66 (*m*, 1 H–C(5′), 1 H of CH_2OCH_2); 3.58–3.29 (2*m*, 3 H of CH_2OCH_2); 3.23 (2*t*, 2 C–CH_2); 2.88 (*s*, MeO); 2.74 (*d*, OH–C(3′)); 2.18 (br., OH–C(5′)); 1.73–1.38 (*m*, CH_2CCH_2). Anal. calc. for $C_{31}H_{36}N_4O_{12}$ (656.7): C 56.70, H 5.53, N 8.53; found: C 56.51, H 5.65, N 8.32.

19. *N^3-Anisoyl-2′-O-(tetrahydro-4-methoxy-2*H*-pyran-4-yl)uridine* (**36**). *Method A*: In CH_2Cl_2/H_2O 1:1 (10 ml), **12** (0.3 g, 0.62 mmol), Na_2CO_3 (0.52 g, 4.93 mmol), and Bu_4NBr (9 mg, 0.028 mmol) were dissolved. Then anisoyl chloride (137 mg, 0.80 mmol) was added. After 1.5 h of vigorous stirring at r.t., more anisoyl chloride (74 mg, 0.43 mmol) was added and stirring continued for another 0.5 h. Then, the aq. phase was extracted with CH_2Cl_2 (2 × 5 ml) and the combined org. phase dried (Na_2SO_4) and evaporated: **33**/**34** as colourless foam. This foam was dissolved in dry 1,2-dichloroethane (10 ml) and warmed for 45 min at 60° causing a complete rearrangement of **33** to **34**. After cooling, 50% CF_3COOH/CH_2Cl_2 (0.17 ml) and 77% pure 3,6-dihydro-4-methoxy-2*H*-pyran (0.46 g, 3.1 mmol) were added. After stirring for 2 h at r.t., another portion of 77% pure 3,6-dihydro-4-methoxy-2*H*-pyran (0.46 g, 3.1 mmol) was added and stirring continued for another 2 h. Then the mixture was diluted with CH_2Cl_2 (10 ml) and washed with sat. $NaHCO_3$ soln. (20 ml), the aq. phase extracted with CH_2Cl_2 (2 × 10 ml), and the combined org. phase dried (Na_2SO_4), evaporated, and co-evaporated twice with toluene. To the brownish residue, KF (215 mg, 3.7 mmol), Et_4NBr (0.78 g, 3.7 mmol), MeCN (7.5 ml), and H_2O (0.22 ml) were added. The mixture was vigourously stirred for 2.5 h at 60°, then cooled, diluted with CH_2Cl_2 (10 ml), and washed with H_2O (20 ml). The aq. phase was extracted with CH_2Cl_2 (2 × 10 ml) and the combined org. phase dried (Na_2SO_4), evaporated, and purified by FC (silica gel, 11 × 2 cm, CH_2Cl_2/MeOH gradient with 0 (100 ml), 1 (100 ml), 2 (200 ml), 3 (300 ml),

and 5% MeOH (100 ml)). Upon evaporation of the product fraction, **36** crystallized. The crystals were suction-filtered, washed with Et_2O, and dried under high vacuum: 127 mg (42%) of **36**. Colourless crystals. M.p. 112–114°.

Method B: In dry 1,4-dioxane (75 ml), **12** (4 g, 8.22 mmol) was dissolved, and then $TsOH \cdot H_2O$ (0.30 g, 1.58 mmol) and 68% pure 3,6-dihydro-4-methoxy-2*H*-pyran (6.9 g (41 mmol), and after 2.5 h stirring another 6.9 g (41 mmol)) were added. The mixture was stirred for 5 h at r.t., neutralized with a few drops of NaOMe in MeOH, evaporated, diluted with CH_2Cl_2 (100 ml), and washed with sat. $NaHCO_3$ soln. (100 ml). The aq. phase was extracted with CH_2Cl_2 (2 × 50 ml) and the combined org. phase dried (Na_2SO_4), evaporated, and co-evaporated twice with dry pyridine. The residual red oil (crude **19**) was dissolved in dry pyridine (40 ml), and $(i\text{-}Pr)_2EtN$ (2.11 ml, 12.3 mmol) and anisoyl chloride (2.8 g, 16.4 mmol) were added. The mixture was stirred for 6 h ar r.t., diluted with CH_2Cl_2 (100 ml), and washed with H_2O (100 ml). The aq. phase was extracted with CH_2Cl_2 (2 × 50 ml), dried (Na_2SO_4), evaporated, and co-evaporated twice with toluene. The red residue (crude **35**) was dissolved in MeCN (100 ml), and then KF (2.87 g, 49.4 mmol), Et_4NBr (10.38 g, 49.4 mmol), and H_2O (2.96 ml, 0.16 mmol) were added. The mixture was vigorously stirred for 3 h at 60°, then cooled, diluted with CH_2Cl_2 (100 ml), and washed with H_2O (150 ml). The aq. phase was extracted with CH_2Cl_2 (2 × 50 ml) and the combined org. phase dried (Na_2SO_4), evaporated, and purified by FC (silica gel, 24 × 4 cm, CH_2Cl_2/MeOH gradient with 200 ml 0, 1, and 2% (200 ml each), 3% (1.2 l), 4% (200 ml), and 5% MeOH (500 ml)). After addition of CH_2Cl_2 (10 ml) to the evaporated product fraction, **36** crystallized. The crystals were suction-filtered, washed with Et_2O, and dried under high vacuum: 2.47 g (61%) of **36**. Almost colourless crystals. M.p. 112–114°. UV (MeOH): 202 (4.20), 219 (4.08), 283 (4.31). ^{1}H-NMR ((D_6)DMSO): 8.19 (*d*, H–C(6)); 7.88 (br., 2 H *m* to MeO); 7.10 (*d*, 2 H *o* to MeO); 6.03 (*d*, H–C(5)); 5.98 (*d*, J = 7.2, H–C(1′)); 5.31 (*t*, OH–C(5′)); 5.24 (*d*, OH–C(3′)); 4.38 (*m*, H–C(2′)); 4.00–3.95 (*m*, H–C(3′), H–C(4′)); 3.87 (*s*, MeO(an)); 3.72–3.52 (*m*, 2 H–C(5′), 2 H of CH_2OCH_2); 3.50–3.30 (*m*, 2 H of CH_2OCH_2); 3.05 (br. *s*, MeO(Thmp)); 1.85–1.60 (*m*, CH_2CCH_2). Anal. calc. for $C_{23}H_{28}N_2O_{10} \cdot 1\ H_2O$ (510.5): C 55.09, H 5.83, N 5.59; found: C 55.09, H 5.80, N 5.37.

20. N^3-*[(*tert*-Butyloxy)carbonyl]-2′-O-(tetrahydro-4-methoxy-2*H*-pyran-4-yl)uridine* (**38**). As described in *Exper. 19*, to obtain crude **19** as a red oil which was co-evaporated with dry pyridine (2 × 30 ml) and dissolved in dry pyridine (75 ml). To this soln., 4-(dimethylamino)pyridine (1 g, 8.2 mmol) and di(*tert*-butyl)dicarbonate (3.58 g, 16.4 mmol) were added (stirring for 0.5 h at r.t.; CO_2 evolution). The mixture was then quenched with MeOH (5 ml), evaporated, diluted with CH_2Cl_2 (100 ml), and washed with sat. $NaHCO_3$ soln. (100 ml). The aq. phase was extracted with CH_2Cl_2 (2 × 50 ml), dried (Na_2SO_4), evaporated, and co-evaporated twice with toluene and CH_2Cl_2. The red residue (crude **37**) was dissolved in dry THF (50 ml), and then AcOH (2.35 ml, 41 mmol) and $Bu_4NF \cdot 3\ H_2O$ (6.48 g, 20.5 mmol) were added. The mixture was stirred for 1.5 h at r.t., diluted with CH_2Cl_2 (100 ml) and washed with sat. $NaHCO_3$ soln. (100 ml). The aq. phase was extracted with CH_2Cl_2 (2 × 50 ml) and the combined org. phase dried (Na_2SO_4), evaporated, and taken up in CH_2Cl_2 (50 ml). The crystals were suction-filtered, washed with Et_2O, and dried under high vacuum: Et_2O 2.50 g of **38**. The mother liquor was evaporated and crystallized from CH_2Cl_2/Et_2O 1:1 (20 ml): 0.27 g of **38**. Total yield: 2.77 g (74%) of **38**. Colourless crystals. M.p. 156°. UV (MeOH): 207 (3.95), 261 (3.97). ^{1}H-NMR ((D_6)DMSO): 8.09 (*d*, H–C(6)); 5.97 (*d*, J = 8, H–C(5), H–C(1′)); 5.29 (*t*, OH–C(5′)); 5.24 (*d*, OH–C(3′)); 4.32 (*dd*, H–C(2′)); 3.99–3.95 (*m*, H–C(3′), H–C(4′)); 3.70–3.30 (*m*, 2 H–C(5′), CH_2OCH_2); 2.95 (*s*, MeO); 1.85–1.60 (*m*, CH_2CCH_2); 1.48 (*s*, t-Bu). Anal. calc. for $C_{20}H_{30}N_2O_{10} \cdot 1\ H_2O$ (476.5): C 50.42, H 6.77, N 5.88; found: C 50.60, H 6.44, N 5.72.

21. N^6-*Benzoyl-5′-O-(2-dansylethoxycarbonyl)-2′-O-(tetrahydro-4-methoxy-2*H*-pyran-4-yl)adenosine* (**40**) *and* N^6-*Benzoyl-3′,5′-O-bis(2-dansylethoxycarbonyl)-2′-O-(tetrahydro-4-methoxy-2*H*-pyran-4-yl)adenosine* (**41**). In dry pyridine (2 × 30 ml), **23** (2.43 g, 5 mmol) was co-evaporated and then taken up in dry pyridine (40 ml). After cooling in an ice-bath, **39** [1] (2.46 g, 6.5 mmol) was added in solid form. The ice-cooled mixture was stirred for 1 h and then the reaction stopped with MeOH (2 ml). After evaporation, the residue was diluted with CH_2Cl_2 (200 ml) and washed with sat. $NaHCO_3$ soln. (200 ml). The aq. phase was extracted with CH_2Cl_2 (2 × 100 ml), the combined org. phase dried (Na_2SO_4), evaporated, and co-evaporated with toluene (2 × 50 ml), AcOEt/EtOH 1:1 (50 ml), and CH_2Cl_2 (50 ml), and the residue purified by FC (silica gel, 24 × 4 cm, CH_2Cl_2/MeOH gradient with 0 (0.5 l), 1 (1 l), and 2% MeOH (1.5 l)): 2.86 g (72%) of **40** and 0.47 g (9%) of **41** as yellow foams.

40: UV (MeOH): 206 (4.81), 257 (4.42), 272 (sh, 4.38), 339 (3.65). ^{1}H-NMR ($CDCl_3$): 9.03 (br., NH); 8.81 (*s*, H–C(2)); 8.61 (*d*, H–C(2)(Dns)); 8.35–8.30 (*m*, H–C(4)(Dns), H–C(8)(Dns)); 8.23 (*s*, H–C(8)); 8.03 (*d*, 2 H_o (bz)); 7.65–7.50 (*m*, 3 H of bz, H–C(3)(Dns), H–C(7)(Dns)); 7.20 (*d*, H–C(6)(Dns)); 6.20 (*d*, J = 5.5, H–C(1′)); 5.13 (*t*, H–C(2′)); 4.52–4.32 (*m*, CH_2O, H–C(3′), H–C(4′), 2 H–C(5′)); 3.77–3.43 (*m*, CH_2OCH_2); 3.72 (*t*, SO_2CH_2); 2.90 (br., OH–C(3′)); 2.89 (*s*, Me_2N); 2.87 (*s*, MeO); 1.95–1.55 (*m*, CH_2CCH_2). Anal. calc. for $C_{38}H_{42}N_6O_{11}S \cdot 1\ H_2O$ (808.9): C 56.43, H 5.48, N 10.39; found: C 56.58, H 5.46, N 10.28.

41: UV (MeOH): 213 (4.98), 254 (4.58), 278 (sh, 4.37), 343 (3.91). ^{1}H-NMR ($CDCl_3$): 9.05 (br. *s*, NH); 8.83 (*s*, H–C(2)); 8.67, 8.61 (2*d*, 2 H, H–C(2)(Dns)); 8.35–8.29 (*m*, 4 H, H–C(4)(Dns), H–C(8)(Dns)); 8.22 (*s*, H–C(8)); 8.03 (*d*, 2 H_o (bz)); 7.68–7.50 (*m*, 7 H, 3 H of bz, H–C(3)(Dns), H–C(7)(Dns)); 7.21 (*t*, (2*d*), 2 H, H–C(6)(Dns)); 6.13 (*d*, *J* = 7.3, H–C(1′)); 5.31 (*dd*, H–C(2′)); 5.12 (*m*, H–C(3′)); 4.60–4.45 (*m*, 2 CH_2O); 4.43–4.30 (*m*, 2 H–C(5′)); 4.23 (*m*, H–C(4′)); 3.80–3.25 (*m*, CH_2OCH_2); 3.72 (*t*, 2 SO_2CH_2); 2.89, 2.88 (2*s*, 2 Me_2N); 2.63 (*s*, MeO); 1.78–1.38 (*m*, CH_2CCH_2). Anal. calc. for $C_{53}H_{57}N_7O_{15}S_2$ (1096.2): C 58.07, H 5.24, N 8.94; found: C 57.87, H 5.46, N 8.67.

22. *5′-O-(2-Dansylethoxycarbonyl)-N^6-[2-(4-nitrophenyl)ethoxycarbonyl]-2′-O-(tetrahydro-4-methoxy-2H-pyran-4-yl)adenosine* (**42**) *and 3′,5′-O-Bis(2-dansylethoxycarbonyl)-N^6-[2-(4-nitrophenyl)ethoxycarbonyl]-2′-O-(tetrahydro-4-methoxy-2H-pyran-4-yl)adenosine* (**43**). As described in *Exper. 21*, with **24** (1 g, 1.74 mmol) and **39** [1] (0.85 g, 2.26 mmol) in dry pyridine (15 ml; stirring for 1 h). Purification was achieved by FC (silica gel, 14 × 3 cm, CH_2Cl_2/MeOH gradient with 0 (200 ml), 1 (400 ml), 2 (400 ml, 3 (200 ml), 4 (100 ml), and 5% MeOH (100 ml)): 0.96 g (63%) of **42** and 0.30 g (14%) of **43** as yellow foams.

42: UV (MeOH): 216 (4.78), 263 (4.57), 343 (3.64). ^{1}H-NMR ($CDCl_3$): 8.74 (*s*, H–C(2)); 8.62 (*d*, H–C(2)(Dns)); 8.34–8.30 (*m*, H–C(4)(Dns)), H–C(8)(Dns)); 8.20–8.16 (*m*, NH, 2 H *o* to NO_2); 8.17 (*s*, H–C(8)); 7.64–7.56 (*m*, H–C(3)(Dns), H–C(7)Dns)); 7.44 (*d*, 2 H *m* to NO_2); 7.21 (*d*, H–C(6)(Dns)); 6.16 (*d*, *J* = 5.6, H–C(1′)); 5.11 (*t*, H–C(2′)); 4.57–4.32 (*m*, 2 CH_2O, H–C(3′), H–C(4′), 2 H–C(5′)); 3.78–3.37 (3*m*, CH_2OCH_2); 3.71 (*t*, SO_2CH_2); 3.16 (*t*, C–CH_2); 2.97 (*d*, OH–C(3′)); 2.89 (*s*, Me_2N); 2.85 (*s*, MeO); 1.94–1.54 (*m*, CH_2CCH_2). Anal. calc. for $C_{40}H_{45}N_7O_{14}S \cdot 1\,H_2O$ (897.9): C 53.51, H 5.28, N 10.92; found: C 53.19, H 5.23, N 10.52.

43: UV (MeOH): 216 (4.94), 259 (4.66), 344 (3.88). ^{1}H-NMR ($CDCl_3$): 8.76 (*s*, H–C(2)); 8.67, 8.62 (2*d*, 2 H, H–C(2)(Dns)); 8.34–8.30 (*m*, 4 H, H–C(4)(Dns), H–C(8)(Dns)); 8.19 (*d*, 2 H *o* to NO_2); 8.16 (*s*, H–C(8)); 8.06 (*s*, NH); 7.68–7.56 (*m*, 4 H, H–C(3)(Dns), H–C(7)(Dns)); 7.44 (*d*, 2 H *m* to NO_2); 7.23–7.19 (*m*, 2 H, H–C(6)(Dns)); 6.10 (*d*, *J* = 7.3, H–C(1′)); 5.28 (*dd*, H–C(2′)); 5.11 (*d*, H–C(3′)); 4.57–4.47 (*m*, 3 CH_2O); 4.43–4.30 (*m*, 2 H–C(5′)); 4.23 (*m*, H–C(4′)); 3.76–3.23 (3*m*, CH_2OCH_2); 3.71 (*t*, 2 SO_2CH_2); 3.17 (*t*, C–CH_2); 2.89 (*s*, 2 MeN); 2.61 (*s*, OMe); 1.78–1.30 (*m*, CH_2CCH_2). Anal. calc. for $C_{55}H_{60}N_8O_{18}S_2$ (1185.3): C 55.74, H 5.10, N 9.45; found: C 55.46, H 5.22, N 9.00.

23. *5′-O-(2-Dansylethoxycarbonyl)-N^2-[2-(4-nitrophenyl)ethoxycarbonyl]-O^6-[2-(4-nitrophenyl)ethyl]-2′-O-(tetrahydro-4-methoxy-2H-pyran-4-yl)guanosine* (**44**) *and 3′,5′-O-Bis(2-dansylethoxycarbonyl-N^2-[2-(4-nitrophenyl)ethoxycarbonyl]-O^6-[2-(4-nitrophenyl)ethyl]-2′-O-(tetrahydro-4-methoxy-2H-pyran-4-yl)guanosine* (**45**). As described in *Exper. 21*, with **25** (0.5 g, 0.68 mmol) and **39** [1] (0.33 g, 0.88 mmol) in dry pyridine (7.5 ml; stirring for 0.5 h). Purification was achieved by FC (silica gel, 11 × 3 cm, CH_2Cl_2/MeOH gradient with 0 (250 ml), 1 (400 ml), 2 (600 ml), and 3% MeOH (200 ml)): 545 mg (77%) of **44** and 84 mg (9%) of **45** as yellow foams.

44: UV (MeOH): 215 (4.89), 262 (4.61), 342 (3.61). ^{1}H-NMR ($CDCl_3$): 8.61 (*d*, H–C(2)(Dns)); 8.33–8.27 (*m*, H–C(4)(Dns), H–C(8)(Dns)); 8.19–8.14 (*m*, 4 H *o* to NO_2); 7.90 (*s*, H–C(8)); 7.64–7.42 (*m*, H–C(3)(Dns), H–C(7)(Dns), NH, 4 H *m* to NO_2); 7.20 (*d*, H–C(6)(Dns)); 5.97 (*d*, *J* = 5,6, H–C(1′)); 5.22 (*t*, H–C(2′)); 4.79 (*t*, CH_2O (npe)); 4.50–4.40 (*m*, 2 CH_2O, H–C(3′), 2 H–C(5′)); 4.27 (*m*, H–C(4′)); 3.78–3.37 (*m*, CH_2OCH_2); 3.68 (*t*, SO_2CH_2); 3.30 (*t*, C–CH_2(npe)); 3.13 (*t*, C–CH_2); 2.89 (*s*, Me_2N); 2.88 (br., OH–C(3′)); 2.87 (*s*, MeO); 1.92–1.55 (*m*, CH_2CCH_2). Anal. calc. for $C_{48}H_{52}N_8O_{17}S$ (1045.1): C 55.17, H 5.02, N 10.72; found: C 55.15, H 5.23, N 10.25.

45: UV (MeOH): 214 (5.10), 258 (4.75), 344 (3.93). ^{1}H-NMR ($CDCl_3$): 8.67, 8.60 (2*d*, 2 H, H–C(2)(Dns)); 8.36–8.25 (*m*, 4 H, H–C(4)(Dns), H–C(8)(Dns)); 8.16 (*m*, 4 H *o* to NO_2); 7.89 (*s*, H–C(8)); 7.66–7.41 (*m*, 9 H, NH, H–C(3)(Dns), H–C(7)(Dns), 4 H *m* to NO_2); 7.21 (*t*(2*d*), 2 H, H–C(6)(Dns)); 5.88 (*d*, *J* = 7.4, H–C(1′)); 5.59 (*dd*, H–C(2′)); 5.18 (*d*, H–C(3′)); 4.80 (*t*, CH_2O(npe)); 4.62–4.40 (*m*, 3 CH_2O, 2 H–C(5′)); 4.24 (*m*, H–C(4′)); 3.77–3.60 (*m*, 2 SO_2CH_2, 1 H of CH_2OCH_2); 3.51–3.23 (2*m*, 3 H of CH_2OCH_2); 3.31 (*t*, C–CH_2(npe)); 3.12 (*t*, C–CH_2); 2.89, 2.88 (2*s*, 2 Me_2N); 2.63 (*s*, MeO); 1.80–1.38 (*m*, CH_2CCH_2). Anal. calc. for $C_{63}H_{67}N_9O_{21}S_2$ (1350.4): C 56.04, H 5.00, N 9.33; found: C 56.27, H 5.22, N 8.94.

24. *5′-O-(2-Dansylethoxycarbonyl)-N^4-[2-(4-nitrophenyl)ethoxycarbonyl]-2′-O-(tetrahydro-4-methoxy-2H-pyran-4-yl)cytidine* (**46**), *3′-O-(2-Dansylethoxycarbonyl)-N^4-[2-(4-nitrophenyl)ethoxycarbonyl]-2′-O-(tetrahydro-4-methoxy-2H-pyran-4-yl)cytidine* (**47**), *and 3′,5′-O-Bis(2-dansylethoxycarbonyl)-N^4-[2-(4-nitrophenyl)-ethoxycarbonyl]-2′-O-(tetrahydro-4-methoxy-2H-pyran-4-yl)cytidine* (**48**). As described in *Exper. 2*, with **26** (1 g, 1.82 mmol) and **39** [1] (0.89 g, 2.36 mmol), and after stirring for 1 h additional 0.14 g (0.36 mmol) in dry pyridine (40 ml; total stirring for 1.5 h). Purification was achieved by FC (silica gel, 12 × 4 cm, CH_2Cl_2/MeOH gradient with 0 (350 ml), 1 (500 ml), 2 (3 l), 3 (500 ml), and 4% MeOH (400 ml)): 1.02 g (65%) of **46**, 184 mg (12%) of **47**, and 317 mg (15%) of **48** as yellow foams.

46: UV (MeOH): 212 (4.80), 248 (4.49), 284 (sh, 4.15), 341 (3.63). ^{1}H-NMR ($CDCl_3$): 8.61 (*d*, H–C(2)(Dns)); 8.32 (*d*, H–C(4)(Dns), H–C(8)(Dns)); 8.16 (*d*, 2 H *o* to NO_2); 7.89 (br., NH); 7.87 (*d*, H–C(6)); 7.60, 7.59 (2*t*, H–C(3)(Dns), H–C(7)(Dns)); 7.39 (*d*, 2 H to NO_2); 7.23–7.19 (*m*, H–C(5), H–C(6)(Dns)); 6.06 (*d*, J = 4, H–C(1′)); 4.53–4.41 (*m*, H–C(2′), 2 CH_2O); 4.35 (*m*, 2 H–C(5′)); 4.20 (*m*, H–C(4′)); 4.06 (*m*, H–C(3′)); 3.82–3.53 (*m*, SO_2CH_2, CH_2OCH_2); 3.24 (br. *d*, OH–C(3′)); 3.16 (*s*, MeO); 3.11 (*t*, C–CH_2); 2.89 (*s*, Me_2N); 1.98–1.70 (*m*, CH_2CCH_2). Anal. calc. for $C_{39}H_{45}N_5O_{15}S$ (855.9): C 54.73, H 5.30, N 8.18; found: C 55.18, H 5.28, N 7.72.

47: UV (MeOH): 213 (4.80), 249 (4.50), 284 (sh, 4.13), 343 (3.61). ^{1}H-NMR ($CDCl_3$): 8.64 (*d*, H–C(2)(Dns)); 8.34–8.30 (*m*, H–C(4)(Dns), H–C(8)(Dns)); 8.18 (*d*, 2 H, *o* to NO_2); 7.98 (br., NH); 7.79 (*d*, H–C(6)); 7.62 (*t*, H–C(3)(Dns), H–C(7)(Dns)); 7.41 (*d*, 2 H *m* to NO_2); 7.23–7.17 (*m*, (2*d*), H–C(6)(Dns), H–C(5)); 5.49 (*d*, J = 7.4, H–C(1′)); 5.30 (*t*, H–C(2′)); 5.12 (*d*, H–C(3′)); 4.60–4.44 (*m*, CH_2O); 4.45 (*t*, CH_2O); 4.31 (br., OH–C(5′)); 4.11 (*s*, H–C(4′)); 3.87 (*m*, 1 H–C(5′)); 3.79–3.38 (*m*, 1 H–C(5′), CH_2OCH_2); 3.71 (*t*, SO_2CH_2); 3.12 (*t*, C–CH_2); 2.94 (*s*, MeO); 2.90 (*s*, Me_2N); 1.82–1.47 (*m*, CH_2CCH_2). Anal. calc. for $C_{39}H_{45}N_5O_{15}S$ (855.9): C 54.73, H 5.30, N 8.18; found: C 55.20, H 5.44, N 7.71.

48: UV (MeOH): 213 (5.01), 250 (4.65), 285 (sh, 4.18), 344 (3.92). ^{1}H-NMR ($CDCl_3$): 8.63 (*t* (2*d*), 2 H, H–C(2)(Dns)); 8.33–8.30 (*m*, 4 H, H–C(4)(Dns), H–C(8)(Dns)); 8.15 (*d*, 2 H *o* to NO_2); 7.84 (*d*, H–C(6)); 7.75 (br., NH); 7.67–7.56 (*m*, 4 H, H–C(3)(Dns), H–C(7)(Dns)); 7.37 (*d*, 2 H *m* to NO_2); 7.26 (*d*, H–C(5)); 7.21 (*d*, 2 H, H–C(6)(Dns)); 6.12 (*d*, J = 6.2, H–C(1′)); 4.92 (*t*, H–C(3′)); 4.62–4.40 (*m*, H–C(2′), 3 CH_2O); 4.30 (*m*, 2 H–C(5′)); 4.16 (*m*, H–C(4′)); 3.78–3.38 (*m*, CH_2OCH_2, 2 SO_2CH_2); 3.12 (*t*, C–CH_2); 2.99 (*s*, MeO); 2.89 (*s*, 2 Me_2N); 1.85–1.58 (*m*, CH_2CCH_2). Anal. calc. for $C_{54}H_{60}N_6O_{19}S_2$ (1161.2): C 55.85, H 5.21, N 7.24; found: C 56.13, H 5.19, N 6.79.

25. *5′-O-(2-Dansylethoxycarbonyl)-2′-O-(tetrahydro-4-methoxy-2*H*-pyran-4-yl)uridine* (**49**) *and 3′,5′-O-Bis-(2-dansylethoxycarbonyl)-2′-O-(tetrahydro-4-methoxy-2*H*-pyran-4-yl)uridine* (**50**). As described in *Exper. 21*, with **27** (1 g, 2.79 mmol) and **39** [1] (1.37 g, 3.63 mmol) in dry pyridine (25 ml; stirring for 1 h). Purification was achieved by FC (silica gel, 14 × 3 cm, CH_2Cl_2/MeOH gradient with 0 (200 ml), 1 (200 ml), 2 (200 ml), 3 (200 ml), and 4% MeOH (300 ml)): 1.40 g (76%) of **49** and 0.39 (14%) of **50** as yellow foams.

49: UV (MeOH): 213 (4.66), 255 (4.33), 344 (3.59). ^{1}H-NMR ($CDCl_3$): 8.90 (br., NH); 8.63 (*d*, H–C(2)(Dns)); 8.33–8.29 (*m*, H–C(4)(Dns), H–C(8)(Dns)); 7.66–7.57 (*m*, H–C(3)(Dns), H–C(7)(Dns)); 7.45 (*d*, H–C(6)); 7.22 (*d*, H–C(6)(Dns)); 6.06 (*d*, J = 5.9, H–C(1′)); 5.84 (*d*, H–C(5)); 4.53 (*t*, CH_2O); 4.45 (*t*, H–C(2′)); 4.32 (*m*, 2 H–C(5′)); 4.20 (*m*, H–C(4′)); 4.12 (*m*, H–C(3′)); 3.80–3.50 (*m*, SO_2CH_2, CH_2OCH_2); 3.16 (*s*, MeO); 3.03 (br., OH–C(3′)); 2.90 (*s*, Me_2N); 1.91–1.68 (*m*, CH_2CCH_2). Anal. calc. for $C_{30}H_{37}N_3O_{12}S$ (663.7): C 54.29, H 5.62, N 6.33; found: C 54.38, H 5.86, N 5.86.

50: UV (MeOH): 218 (4.88), 254 (4.57), 346 (3.91). ^{1}H-NMR ($CDCl_3$): 8.70 (br., NH); 8.67–8.61 (*m*, 2 H, H–C(2)(Dns)); 8.34–8.28 (*m*, 4 H, H–C(4)(Dns), H–C(8)(Dns)); 7.67–7.57 (*m*, 4 H, H–C(3)(Dns), H–C(7)(Dns)); 7.45 (*d*, H–C(6)); 7.21 (*d*, 2 H, H–C(6)(Dns)); 6.06 (*d*, J = 7.7, H–C(1′)); 5.87 (*d*, H–C(5)); 4.95 (*m*, H–C(3′)); 4.61–4.45 (*m*, 2 CH_2O, H–C(2′)); 4.28 (*m*, 2 H–C(5′)); 4.10 (*m*, H–C(4′)); 3.80–3.40 (*m*, 2 CH_2SO_2, CH_2OCH_2); 3.04 (*s*, MeO); 2.89 (*s*, 2 Me_2N); 1.85–1.55 (*m*, CH_2CCH_2). Anal. calc. for $C_{45}H_{52}N_4O_{16}S_2$ (969.1): C 55.78, H 5.41, N 5.78; found: C 55.62, H 5.52, N 5.54.

26. *5′-O-(2-Dansylethoxycarbonyl)-2′-O-(tetrahydro-4-methoxy-2*H*-pyran-4-yl)ribothymidine* (**51**) *and 3′,5′-O-Bis(2-dansylethoxycarbonyl)-2′-O-(tetrahydro-4-methoxy-2*H*-pyran-4-yl)ribothymidine* (**52**). As described in *Exper. 21*, with **28** (0.88 g, 2.36 mmol) and **39** [1] (1.16 g, 3.07 mmol) in dry pyridine (20 ml; stirring for 1 h). Purification was achieved by FC (silica gel, 18 × 3 cm, CH_2Cl_2/MeOH gradient with 0 (200 ml), 1 (400 ml), 2 (300 ml), and 3 MeOH (400 ml)): 0.97 g (61%) of **51** and 235 mg (10%) of **52** as yellow foams.

51: UV (MeOH): 214 (4.66), 257 (4.31), 344 (3.58). ^{1}H-NMR ($CDCl_3$): 8.92 (br., NH); 8.63 (*d*, H–C(2)(Dns)); 8.33–8.29 (*m*, H–C(4)(Dns), H–C(8)(Dns)); 7.65–7.57 (*m*, H–C(3)(Dns), H–C(7)(Dns)); 7.24 (*s*, H–C(6)); 7.22 (*d*, H–C(6)(Dns)); 6.03 (*d*, J = 5.6, H–C(1′)); 4.51 (*m*, CH_2O); 4.43 (*t*, H–C(2′)); 4.31 (*m*, 2 H–C(5′)); 4.17 (*m*, H–C(4′)); 4.11 (*m*, H–C(3′)); 3.79–3.50 (2*m*, CH_2OCH_2, SO_2CH_2); 3.14 (*s*, MeO); 3.02 (br., OH–C(3′)); 2.90 (*s*, Me_2N); 1.93–1.77 (*m*, CH_2CCH_2); 1.88 (*s*, Me). Anal. calc. for $C_{31}H_{39}N_3O_{12}S \cdot 1\ H_2O$ (695.8): C 53.52, H 5.94, N 6.04; found: C 53.04, H 5.70, N 5.54.

52: UV (MeOH): 214 (4.93), 255 (4.54), 347 (3.90). ^{1}H-NMR ($CDCl_3$): 8.66–8.61 (*m*, 2 H, H–C(2)(Dns)); 8.57 (br., NH); 8.34–8.28 (*m*, 4 H, H–C(4)(Dns), H–C(8)(Dns)); 7.67–7.56 (*m*, 4 H, H–C(3)(Dns), H–C(7)(Dns)); 7.23 (*s*, H–C(6)); 7.21 (*d*, 2 H, H–C(6)(Dns)); 6.02 (*d*, J = 7.4, H–C(1′)); 4.94 (*dd*, H–C(3′)); 4.58–4.45 (*m*, H–C(2′), 2 CH_2O); 4.34–4.20 (*m*, 2 H–C(5′)); 4.09 (*m*, H–C(4′)); 3.78–3.40 (2*m*, CH_2OCH_2); 3.70 (*m*, 2 SO_2CH_2); 3.02 (*s*, MeO); 2.89 (*s*, 2 Me_2N); 1.89 (*d*, J = 0.7, Me); 1.82–1.54 (*m*, CH_2CCH_2). Anal. calc. for $C_{46}H_{54}N_4O_{16}S_2 \cdot 1\ H_2O$ (1001.1): C 55.19, H 5.64, N 5.60; found: C 55.45, H 5.50, N 5.17.

27. *5′-O-(2-Dansylethoxycarbonyl)-2′-O-(tetrahydro-4-methoxy-2H-pyran-4-yl)pseudouridine* (**53**) *and* N^1,*5′-O-Bis(2-dansylethoxycarbonyl)-2′-O-(tetrahydro-4-methoxy-2H-pyran-4-yl)pseudouridine* (**54**). In hot dry pyridine (20 ml), **29** (150 mg, 0.42 mmol) was dissolved. After cooling, the soln. was evaporated to an oil which was taken up in dry pyridine (4 ml). After cooling in an ice-bath, **39** [1] (0.40 g, 1.06 mmol) was added in solid form, the ice-cooled mixture stirred for 15 min, and then the reaction stopped with MeOH (3 ml). After evaporation, the residue was diluted with CH_2Cl_2 (20 ml) and washed vigorously with sat. $NaHCO_3$ soln. (20 ml). The aq. phase was extracted with CH_2Cl_2 (2 × 10 ml), the combined org. phase dried (Na_2SO_4), evaporated, and co-evaporated with toluene (2 × 50 ml), AcOEt/EtOH 1:1 (50 ml), and CH_2Cl_2 (50 ml), and the residue purified by FC (silica gel, 11 × 2 cm, CH_2Cl_2/MeOH gradient with 0 (100 ml), 1 (100 ml), 2 (200 ml), and 3% MeOH (450 ml)): 171 mg (62%) of **53** and 84 mg (21%) of **54** as yellow foams.

53: UV (MeOH): 215 (4.56), 251 (4.08), 343 (3.60). ^{1}H-NMR ($CDCl_3$): 9.83 (br. *d*, *J* = 5.1, H–N(1)); 9.55 (*s*, H–N(3)); 8.62 (*d*, H–C(2)(Dns)); 8.31, 8.26 (2*d*, H–C(4)(Dns), H–C(8)(Dns)); 7.68 (*d*, *J* = 6, H–C(6)); 7.61 (2*t*, H–C(3)(Dns), H–C(7)(Dns)); 7.21 (*d*, H–C(6)(Dns)); 4.96 (*d*, *J* = 1.5, H–C(1′)); 4.70–4.61 (*m*, 1 H of CH_2O); 5.51 (*dd*, 1 H–C(5′)); 4.48–4.42 (*m*, 1 H of CH_2O, H–C(2′)); 4.27 (*dd*, 1 H–C(5′)); 4.11 (*m*, H–C(3′)); 4.03 (*m*, H–C(4′)); 3.82–3.63 (*m*, CH_2OCH_2, SO_2CH_2); 3.27 (*s*, MeO); 3.01 (br., OH–C(3′)); 2.89 (*s*, Me_2N); 2.11–1.80 (*m*, CH_2CCH_2). Anal. calc. for $C_{30}H_{37}N_3O_{12}S \cdot 1\,H_2O$ (681.7): C 52.86, H 5.77, N 6.16; found: C 52.51, H 5.54, N 5.85.

54: UV (MeOH): 216 (4.84), 249 (4.38), 347 (3.91). ^{1}H-NMR ((D$_6$)DMSO): 11.56 (*s*, H–N(3)); 8.53 (*t*, 2 H, H–C(2)(Dns)); 8.19 (*t*, 4 H, H–C(4)(Dns), H–C(8)(Dns)); 7.71–7.59 (*m*, 5 H, H–C(3)(Dns), H–C(7)(Dns), H–C(6)); 7.25 (*t*, 2 H, H–C(6)(Dns)); 5.04 (*d*, OH–C(3′)); 4.52 (*m*, CH_2O, H–C(1′)); 4.34 (*m*, CH_2O, H–C(2′)); 4.12 (*m*, 1 H–C(5′)); 3.97–3.82 (2*m*, 2 SO_2CH_2, H–C(3′), H–C(4′), 1 H–C(5′)); 3.70–3.28 (*m*, CH_2OCH_2); 3.06 (*s*, MeO); 2.82, 2.79 (2*s*, 2 MeN); 1.80–1.64 (*m*, CH_2CCH_2). Anal. calc. for $C_{45}H_{52}N_4O_{16}S_2 \cdot 1\,H_2O$ (987.1): C 54.76, H 5.51, N 5.68; found: C 54.75, H 5.45, N 5.16.

28. *5′-O-(2-Dansylethoxycarbonyl)-*O^2,O^4*-bis[2-(4-nitrophenyl)ethyl]-2′-O-(tetrahydro-4-methoxy-2H-pyran-4-yl)pseudouridine* (**55**). As described in *Exper. 21*, with **32** (220 mg, 0.33 mmol) and **39** [1] (190 mg, 0.5 mmol) in dry pyridine (5 ml; for 0.5 h). Purification was achieved by FC (silica gel, 13 × 2 cm, CH_2Cl_2/MeOH gradient with 0 (200 ml), 1 (200 ml), and 2% MeOH (100 ml)): 217 mg (68%) of **55** as yellow foam. The 3′,5′-*O*-disubstituted derivative was not isolated. UV (MeOH): 214 (4.85), 2.62 (4.58), 343 (3.67). ^{1}H-NMR ($CDCl_3$): 8.61 (*d*, H–C(2)(Dns)); 8.33–8.27 (*m*, H–C(4)(Dns), H–C(8)(Dns)); 8.18 (*s*, H–C(6)); 8.16 (*d*, 4 H *o* to NO_2); 7.63–7.55 (*m*, H–C(3)(Dns), H–C(7)(Dns)); 7.44, 7.43 (2*d*, 4 H *m* to NO_2); 7.20 (*d*, H–C(6)(Dns)); 4.79–4.60 (*m*, CH_2O); 4.74 (*d*, *J* = 5.8, H–C(1′)); 4.58, 4.46 (2*t*, 2 CH_2O); 4.31 (*t*, H–C(2′)); 4.29 (*dd*, 1 H–C(5′)); 4.13 (*dd*, 1 H–C(5′)); 3.97–3.91 (*m*, H–C(3′), H–C(4′)); 3.74–3.34 (*m*, CH_2OCH_2); 3.68 (*t*, SO_2CH_2); 3.22 (*m*, 2 C–CH_2); 2.97 (*s*, MeO); 2.89 (*s*, Me_2N); 2.77 (*d*, OH–C(3′)); 1.79–1.40 (*m*, CH_2CCH_2). Anal. calc. for $C_{46}H_{51}N_5O_{16}S$ (962.0): C 57.43, H 5.34, N 7.28; found: C 57.33, H 5.36, N 7.34.

29. N^3*-Anisoyl-5′-O-(2-dansylethoxycarbonyl)-2′-O-(tetrahydro-4-methoxy-2H-pyran-4-yl)uridine* (**56**), N^3*-Anisoyl-3′-O-(2-dansylethoxycarbonyl)-2′-O-(tetrahydro-4-methoxy-2H-pyran-4-yl)uridine* (**57**), *and* N^3*-Anisoyl-3′,5′-O-bis(2-dansylethoxycarbonyl)-2′-O-(tetrahydro-4-methoxy-2H-pyran-4-yl)uridine* (**58**). As described in *Exper. 21*, with **36** (200 mg, 0.41 mmol) and **39** [1] (200 mg, 0.53 mmol) in dry pyridine (4 ml; stirring for 1 h). Purification was achieved by FC (silica gel, 11 × 2 cm, CH_2Cl_2/MeOH gradient with 0 (100 ml), 1 (200 ml), 2 (200 ml), and 3% MeOH (100 ml)). A fraction containing **56**/**57** was evaporated separately, purified once more by prep. TLC (CH_2Cl_2/MeOH 100:6), and combined with the corresponding pure product fractions to give 154 mg (48%) of **56**, 43 mg (13%) of **57**, and 87 mg (19%) of **58** as yellow foams. For characterization, **57** was purified by prep. TLC (CH_2Cl_2/MeOH 100:6) again.

56: UV (MeOH): 215 (4.68), 262 (4.38), 284 (sh, 4.31), 345 (3.59). ^{1}H-NMR ($CDCl_3$): 8.63 (*d*, H–C(2)(Dns)); 8.31 (2*d*, H–C(4)(Dns), H–C(8)(Dns)); 7.87 (*d*, 2 H *m* to MeO); 7.66–7.54 (*m*, H–C(3)(Dns), H–C(7)(Dns), H–C(6)); 7.22 (*d*, H–C(6)(Dns)); 6.94 (*d*, 2 H *o* to MeO); 6.03 (br. *d*, H–C(1′)); 5.93 (*d*, H–C(5)); 4.54 (*t*, CH_2O); 4.49 (*t*, H–C(2′)); 4.34 (*m*, 2 H–C(5′)); 4.20 (*m*, H–C(4′)); 4.12 (*m*, H–C(3′)); 3.87 (*s*, MeO (an)); 3.80–3.52 (*m*, SO_2CH_2, CH_2OCH_2); 3.21 (*s*, MeO(Thmp)); 2.96 (br., OH–C(3′)); 2.90 (*s*, Me_2N); 1.95–1.62 (*m*, CH_2CCH_2). Anal. calc. for $C_{38}H_{43}N_3O_{14}S$ (797.8): C 57.21, H 5.43, N 5.37; found: C 57.20, H 5.53, N 4.92.

57: UV (MeOH): 215 (4.68), 263 (4.41), 285 (sh, 4.31), 344 (3.60). ^{1}H-NMR ($CDCl_3$): 8.63 (*d*, H–C(2)(Dns)); 8.31 (2*d*, H–C(4)(Dns), H–C(8)(Dns)); 7.88 (*d*, 2 H *m* to MeO); 7.67 (*d*, H–C(6)); 7.62 (*t*, H–C(3)(Dns), H–C(7)(Dns)); 7.21 (*d*, H–C(6)(Dns)); 6.95 (*d*, 2 H *o* to MeO); 5.88 (*d*, H–C(5)); 5.72 (br. *d*, *J* = 6.8, H–C(1′)); 5.06 (*d*, H–C(3′)); 4.92 (*t*, H–C(2′)); 4.60–4.42 (*m*, CH_2O); 4.06 (*s*, H–C(4′)); 3.88 (*s*, MeO (an)); 3.82–3.40 (*m*, SO_2CH_2, CH_2OCH_2, 2 H–C(5′)); 3.12 (*s*, MeO(Thmp)); 3.07 (br., OH–C(5′)); 2.89 (*s*, Me_2N); 1.90–1.55 (*m*, CH_2CCH_2). Anal. calc. for $C_{38}H_{43}N_3O_{14}S$ (797.8): C 57.21, H 5.43, N 5.27; found: C 57.66, H 5.55, N 4.70.

58: UV (MeOH): 215 (4.97), 258 (4.60), 285 (sh, 4.37), 344 (3.92). ^{1}H-NMR ($CDCl_3$): 8.63 (*d*, 2 H, H–C(2)(Dns)); 8.30 (2*d*, 4 H, H–C(4)(Dns), H–C(8)(Dns)); 7.87 (*d*, 2 H *m* to MeO); 7.66–7.57 (*m*, 4 H, H–C(3)(Dns), H–C(7)(Dns)); 7.54 (*d*, H–C(6)); 7.23–7.18 (*m*, 2 H–C(6)(Dns)); 6.94 (*d*, 2 H *o* to MeO); 6.02 (br. *d*, H–C(1′)); 5.98 (*d*, H–C(5)); 4.95 (*dd*, H–C(3′)); 4.62–4.42 (*m*, H–C(2′), 2 CH_2O); 4.29 (*m*, 2 H–C(5′)); 4.08 (*m*, H–C(4′)); 3.87 (*s*, MeO (an)); 3.80–3.60 (*m*, SO_2CH_2, CH_2OCH_2); 3.12 (*s*, MeO(Thmp)); 2.90, 2.88 (2*s*, 2 Me_2N); 1.88–1.56 (*m*, CH_2CCH_2). Anal. calc. for $C_{53}H_{58}N_4O_{18}S_2$ (1103.2): C 57.70, H 5.30, N 5.08; found: C 57.81, H 5.38, N 4.80.

30. *N^3-[(*tert*-Butyloxy)carbonyl]-5′-O-(2-dansylethoxycarbonyl)-2′-O-(tetrahydro-4-methoxy-2*H*-pyran-4-yl)uridine* (**59**), *N^3-[(*tert*-Butyloxy)carbonyl]-3′-O-(2-dansylethoxycarbonyl)-2′-O-(tetrahyro-4-methoxy-2*H*-pyran-4-yl)uridine* (**60**), *and N^3-[(*tert*-Butyloxy)carbonyl]-3′,5′-O-bis(2-dansylethoxycarbonyl)-2′-O-(tetrahydro-4-methoxy-2*H*-pyran-4-yl)uridine* (**61**). As described in *Exper. 21*, with **38** (200 mg, 0.44 mmol) and **39** [1] (215 mg, 0.57 mmol) in dry pyridine (4 ml; stirring for 1 h). Purification was achieved by FC (silica gel, 11 × 2 cm, CH_2Cl_2/MeOH gradient with 0 (200 ml), 1 (300 ml), 2 (300 ml), and 3% MeOH (100 ml)): 159 mg (48%) of **59**, 41 mg (12%) of **60**, and 74 mg (16%) of **61** as yellow foams. For characterization, **60** was purified by prep. TLC (CH_2Cl_2/MeOH 100:6) once more.

59: UV (MeOH): 214 (4.68), 256 (4.33), 347 (3.59). ^{1}H-NMR ($CDCl_3$): 8.63 (*d*, H–C(2(Dns)); 8.30 (2*d*, H–C(4)(Dns), H–C(8)(Dns)); 7.66–7.57 (*m*, H–C(3)(Dns), H–C(7)(Dns)); 7.43 (*d*, H–C(6)); 7.22 (*d*, H–C(6)(Dns)); 6.05 (*d*, *J* = 5.9, H–C(1′)); 5.84 (*d*, H–C(5)); 4.53 (*t*, CH_2O); 4.42 (*t*, H–C(2′)); 4.22 (*m*, 2 H–C(5′)); 4.21 (*m*, H–C(4′)); 4.10 (*m*, H–C(3′)); 3.80–3.51 (*m*, CH_2OCH_2, SO_2CH_2); 3.16 (*s*, MeO); 2.90 (*s*, Me_2N, OH–C(3′)); 1.95–1.60 (*m*, CH_2CCH_2); 1.59 (*s*, *t*-Bu). Anal. calc. for $C_{35}H_{45}N_3O_{14}S$ (763.8): C 55.04, H 5.94, N 5.50; found: C 55.23, H 6.06, N 5.22.

60: UV (MeOH): 213 (4.67), 256 (4.36), 348 (3.63). ^{1}H-NMR ($CDCl_3$): 8.64 (*d*, H–C(2)(Dns)); 8.34–8.30 (*m*, H–C(4)(Dns), H–C(8)(Dns)); 7.63 (*t*, H–C(3)(Dns), H–C(7)(Dns)); 7.53 (*d*, H–C(6)); 7.22 (*d*, H–C(6)(Dns)); 5.80 (*d*, H–C(5)); 5.67 (*d*, *J* = 7.8, H–C(1′)); 5.04 (*d*, H–C(3′)); 4.90 (*dd*, H–C(2′)); 4.60–4.42 (*m*, CH_2O); 4.04 (*m*, H–C(4′)); 3.87 (*m*, 1 H–C(5′)); 3.80–3.40 (2*m*, 1 H–C(5′), SO_2CH_2, CH_2OCH_2); 3.04 (*s*, MeO); 2.92 (br., OH–C(5′)); 2.90 (*s*, Me_2N); 1.85–1.48 (*m*, CH_2CCH_2); 1.59 (*s*, *t*-Bu). Anal. calc. for $C_{35}H_{45}N_3O_{14}S$ (763.8): C 55.04, H 5.94, N 5.50; found: C 55.44, H 5.87, N 5.00.

61: UV (MeOH): 214 (4.91), 255 (4.53), 345 (3.89). ^{1}H-NMR ($CDCl_3$): 8.64 (*t* (2*d*), 2 H, H–C(2)(Dns)); 8.33–8.28 (*m*, 4 H, H–C(4)(Dns), H–C(8)(Dns)); 7.67–7.57 (*m*, 4 H, H–C(3)(Dns), H–C(7)(Dns)); 7.41 (*d*, H–C(6)); 7.21 (*d*, 2 H, H–C(6)(Dns)); 6.04 (*d*, *J* = 7.7, H–C(1′)); 5.89 (*d*, H–C(5)); 4.92 (*d*, H–C(3′)); 4.61–4.42 (*m*, H–C(2′), 2 CH_2CH_2O); 4.26 (*m*, 2 H–C(5′)); 4.05 (*m*, H–C(4′)); 3.80–3.40 (2*m*, $SO_2CH_2CH_2O$, CH_2OCH_2); 3.05 (*s*, MeO); 2.90 (*s*, Me_2N); 1.90–1.52 (*m*, CH_2CCH_2); 1.59 (*s*, *t*-Bu). Anal. calc. for $C_{50}H_{60}N_4O_{18}S_2$ (1069.2): C 56.17, H 5.66, N 5.24; found: C 56.56, H 5.70, N 4.89.

31. *N^6-Benzoyl-5′-O-(2-dansylethoxycarbonyl)-2′-O-(tetrahydro-4-methoxy-2*H*-pyran-4-yl)adenosine 3′-[2-(4-Nitrophenyl)ethyl* N,N-*Diisopropylphosphoramidite]* (**64**). In dry CH_2Cl_2 (6 ml), **40** (1 g; 1.26 mmol) was dissolved. Then, abs. (i-Pr)$_2$EtN (0.86 ml, 5.02 mmol) and **62** [1] (0.84 g, 2.53 mmol) were added. The mixture was stirred at r.t. for 1.25 h under Ar in the dark. After addition of more **62** (0.42 g, 1.26 mmol), stirring was continued for further 1.25 h. The mixture was diluted with CH_2Cl_2 (75 ml) and washed with phosphate buffer pH 7 (7.5 ml). The aq. phase was extracted with CH_2Cl_2 (2 × 40 ml), the combined org. phase dried (Na_2SO_4) and evaporated, and the residue quickly purified by FC (silica gel, 12 × 3 cm, CH_2Cl_2 (250 ml), CH_2Cl_2/AcOEt 100:1, 100:2, 100:3, 100:5, 100:7, and 9:1 (100 ml each), CH_2Cl_2/AcOEt 4:1 (350 ml), CH_2Cl_2/AcOEt 2:1, 1:1, and 1:2 (100 ml each), and AcOEt (100 ml)): 0.96 (70%) of **64**. Yellow foam. UV (MeOH): 205 (4.85), 261 (4.50), 340 (3.64). ^{1}H-NMR ($CDCl_3$): 9.07 (br., NH); 8.83, 8.82 (2*s*, H–C(2)); 8.61 (*d*, H–C(2)(Dns)); 8.35–8.29 (*m*, H–C(4)(Dns), H–C(8)(Dns)); 8.24, 8.22 (2*s*, H–C(8)); 8.18–8.13 (2*d*, 2 H *o* to NO_2); 8.03 (*d*, 2 H_o (bz)); 7.64–7.49 (*m*, 3 H of bz, H–C(3)(Dns), H–C(7)(Dns)); 7.45–7.38 (2*d*, 2 H *m* to NO_2); 7.19 (*d*, H–C(6)(Dns)); 6.23, 6.15 (2*d*, *J* = 7.1, 6.8, H–C(1′)); 5.20, 5.11 (2*dd*, H–C(2′)); 4.48 (*t*, CH_2OCO); 4.44–4.18 (*m*, H–C(3′), H–C(4′), 2 H–C(5′)); 4.10–3.88 (*m*, CH_2OP); 3.84–3.25 (*m*, 2 Me_2CHN, CH_2OCH_2); 3.71 (*t*, SO_2CH_2); 3.06 (*t*, C–CH_2); 2.88 (*s*, Me_2N); 2.66, 2.61 (2*s*, MeO); 2.00–1.40 (*m*, CH_2CCH_2); 1.26–1.12 (*m*, 2 Me_2CHN). ^{31}P-NMR ($CDCl_3$): 151.34, 149.47. Anal. calc. for $C_{52}H_{63}N_8O_{14}PS$ (1087.2): C 57.45, H 5.84, N 10.31; found: C 57.08, H 5.87, N 10.29.

32. *5′-O-(2-Dansylethoxycarbonyl)-N^6-[2-(4-nitrophenyl)ethoxycarbonyl]-2′-O-(tetrahydro-4-methoxy-2*H*-pyran-4-yl)adenosine 3′-[2-(4-Nitrophenyl)ethyl* N,N-*Diisopropylphosphoramidite]* (**65**). In dry CH_2Cl_2 (0.7 ml), **42** (200 mg, 0.23 mmol) was dissolved. Then, abs. (i-Pr)$_2$EtN (0.16 ml, 0.91 mmol) and **62** [1] (151 mg, 0.45 mmol) were added. The mixture was stirred at r.t. for 1 h under Ar in the dark. After addition of more **62** (76 mg, 0.23 mmol), stirring was continued for further 1.5 h. The mixture was then quenched with 0.5 ml of abs. i-PrOH, stirred for 30 min at r.t., diluted with CH_2Cl_2 (10 ml), and washed with phosphate puffer pH 7 (10 ml). The aq.

phase was extracted with CH_2Cl_2 (2 × 10 ml) and the combined org. phase dried (Na_2SO_4), evaporated, and quickly purified by FC (silica gel, 9 × 2 cm, CH_2Cl_2 (100 ml), CH_2Cl_2/AcOEt 100:2, 100:4, 100:6, 100:8, 9:1, 4:1, 2:1, and 1:1 (50 ml each), and AcOEt (30 ml) with addition of 1% pyridine, resp.). Evaporation of the combined product fractions and co-evaporation with toluene (2×) and CH_2Cl_2 (2×) gave 149 mg (56%) of **65**. Yellow foam. UV (MeOH): 210 (4.89), 264 (4.67), 341 (3.67). ^{1}H-NMR ($CDCl_3$): 8.74, 8.73 (2*s*, H–C(2)); 8.60 (*d*, H–C(2(Dns)); 8.47 (br. *s*, NH); 8.32–8.27 (*m*, H–C(4)(Dns), H–C(8)(Dns)); 8.19–8.11 (*m*, H–C(8), 4 H *o* to NO_2); 7.62–7.54 (*m*, H–C(3)(Dns), H–C(7)(Dns)); 7.43–7.35 (*m*, 4 H *m* to NO_2); 7.18 (*d*, H–C(6)(Dns)); 6.18, 6.10 (2*d*, *J* = 7.2, 6.9, H–C(1′)); 5.18, 5.15 (2*dd*, H–C(2′)); 4.55–4.36 (*m*, 2 CH_2OCO); 4.31–4.15 (*m*, H–C(3′), H–C(4′), 2 H–C(5′)); 4.08–3.85 (2*m*, CH_2OP); 3.77–3.23 (*m*, CH_2OCH_2, 2 Me_2CHN); 3.68 (*t*, SO_2CH_2); 3.14 (*t*, C–CH_2(npeoc)); 3.02 (*m*, C–CH_2(npe)); 2.87 (*s*, Me_2N); 2.61, 2.55 (2*s*, MeO); 1.92–1.35 (*m*, CH_2CCH_2); 1.23–1.10 (*m*, 2 Me_2CHN). ^{31}P-NMR ($CDCl_3$): 151.37, 149.47. Anal. calc. for $C_{54}H_{66}N_9O_{17}PS$ (1176.2): C 55.14, H 5.66, N 10.72; found: C 54.90, H 5.71, N 10.28.

33. *5′-O-(2-Dansylethoxycarbonyl)-2′-O-(tetrahydro-4-methoxy-2*H*-pyran-4-yl)uridine 3′-[2-(4-Nitrophenyl)ethyl* N,N-*Diisopropylphosphoramidite]* (**6**). As described in *Exper. 32*, with **49** (200 mg, 0.30 mmol), abs. (i-Pr)$_2$EtN (0.21 ml, 1.23 mmol) and **62** (0.2 g (0.60 mmol), and after stirring for 1 h additional 0.1 g (0.30 mmol)) in dry CH_2Cl_2 (0.8 ml). Purification was achieved by prep. TLC (toluene/AcOEt 1:3 containing 1% pyridine). Elution of the product band with CH_2Cl_2/MeOH 100:5 (150 ml), drying (Na_2SO_4), evaporation, and co-evaporation with toluene (2×) and CH_2Cl_2 (2×) gave 173 mg (60%) of **66** as yellow foam. It is recommendable to purify **6** of a larger-scale synthesis by FC according to *Exper. 32*. UV (MeOH): 212 (4.74), 258 (4.47), 343 (3.65). ^{1}H-NMR ($CDCl_3$): NH not visible; 8.62 (*d*, H–C(2)(Dns)); 8.32–8.27 (*m*, H–C(4)(Dns), H–C(8)(Dns)); 8.13 (*d*, 2 H *o* to NO_2); 7.64–7.56 (*m*, H–C(3)(Dns), H–C(7)(Dns)); 7.50–7.35 (*m*, 2 H *m* to NO_2, H–C(6)); 7.21 (*d*, H–C(6)(Dns)); 6.19, 6.07 (2*d*, *J* = 7.9, 7.5, H–C(1′)); 5.85, 5.83 (2*d*, H–C(5)); 4.60–4.45 (*m*, CH_2OCO); 4.42–3.37 (*m*, CH_2OP, H–C(2′), H–C(3′), H–C(4′), 2 H–C(5′), CH_2OCH_2, 2 Me_2CHN); 3.67 (*t*, SO_2CH_2); 3.04, 3.03 (2*s*, MeO); 3.00 (*t*, C–CH_2); 2.89 (*s*, Me_2N); 1.95–1.55 (*m*, CH_2CCH_2); 1.25–1.09 (*m*, 2 Me_2CHN). ^{31}P-NMR ($CDCl_3$): 151.40, 149.13. Anal. calc. for $C_{44}H_{58}N_5O_{15}PS$ (960.0): C 55.05, H 6.09, N 7.30; found: C 54.99, H 6.13, N 7.03.

34. *5′-O-(2-Dansylethoxycarbonyl)-*N^6*-[2-(4-nitrophenyl)ethoxycarbonyl]-2′-O-(tetrahydro-4-methoxy-2*H*-pyran-4-yl)adenosine 3′-[2-(4-Nitrophenyl)ethyl* N,N-*Diethylphosphoramidite]* (**67**). In dry THF (8 ml) **42** (0.88 g, 1 mmol) was dissolved. Then, abs. (i-Pr)EtN (1.04 ml, 6 mmol) and **63** [1] (0.61 g, 2 mmol) were added. The mixture was stirred at r.t. for 1.5 h under Ar in the dark and then quenched with abs. i-PrOH (200 µl). The mixture was stirred for further 15 min and then poured on CH_2Cl_2/phosphate buffer pH 7 1:1 (50 ml). The aq. layer was extracted with CH_2Cl_2 (20 ml), the combined org. phase dried (Na_2SO_4) and evaporated, and the residue dried under high vacuum for 1 h and purified by FC (silica gel, 11 × 2 cm, soln. in CH_2Cl_2/petroleum ether 2:1, then quickly petroleum ether/acetone 2:1 (200 ml) and 1:1 (100 ml)): 887 mg (77%) of **67**. Yellow foam. UV (MeOH): 211 (4.87), 264 (4.65), 343 (3.62). ^{1}H-NMR (CD_3CN): NH not visible; 8.59, 8.57 (2*s*, H–C(2)); 8.54 (*d*, H–C(2)(Dns)); 8.28–8.06 (*m*, H–C(4)(Dns), H–C(8)(Dns), 4 H *o* to NO_2, H–C(8)); 7.62–7.42 (*m*, H–C(3)(Dns), H–C(7)(Dns), 4 H *m* to NO_2); 7.21, 7.20 (2*d*, H–C(6)(Dns)); 6.07, 6.03 (2*d*, *J* = 7.45, 7, H–C(1′)); 5.11, 5.03 (2*dd*, H–C(2′)); 4.46–3.17 (*m*, 2 CH_2OCO, CH_2OP, H–C(3′), H–C(4′), 2 H–C(5′), CH_2OCH_2); 3.69 (*t*, SO_2CH_2); 3.12–2.89 (*m*, 2 C–CH_2, 2 MeCH_2N); 2.81, 2.80 (2*s*, Me_2N); 2.52, 2.47 (2*s*, MeO); 1.72–1.18 (*m*, CH_2CCH_2); 1.07–0.94 (*m*, 2 *Me*CH_2N). ^{31}P-NMR (CD_3CN): 150.66, 149.70. Anal. calc. for $C_{52}H_{62}N_9O_{17}PS$ (1148.2): C 54.40, H 5.44, N 10.98; found: C 53.65, H 5.44, N 10.54.

35. *5′-O-(2-Dansylethoxycarbonyl)-*N^2*-[2-(4-nitrophenyl)ethoxycarbonyl]-*O^6*-[2-(4-nitrophenyl)ethyl]-2′-O-(tetrahydro-4-methoxy-2*H*-pyran-4-yl)guanosine 3′-[2-(4-Nitrophenyl)ethyl* N,N-*Diethylphosphoramidite]* (**68**). As described in *Exper. 34*, with **44** (1.05 g, 1 mmol). Purification was achieved by FC (silica gel, 11 × 2 cm, soln. in CH_2Cl_2/petroleum ether 2:1, then quickly petroleum ether/acetone 7:3 (200 ml) and 6:4 (200 ml)): 998 mg (76%) of **68**. Yellow foam. UV (MeOH): 214 (4.91), 264 (4.68), 341 (3.66). ^{1}H-NMR (CD_3CN): 8.51 (*d*, H–C(2)(Dns)); 8.35 (br., NH); 8.24–8.07 (*m*, H–C(4)(Dns), H–C(8)(Dns), 6 H *o* to NO_2); 8.00, 7.98 (2*s*, H–C(8)); 7.61–7.42 (*m*, H–C(3)(Dns), H–C(7)(Dns), 6 H *m* to NO_2); 7.20, 7.19 (2*d*, H–C(6)(Dns)); 5.91, 5.87 (2*d*, *J* = 7.6, H–C(1′)); 5.39–5.28 (2*dd*, H–C(2′)); 4.77 (2*t*, CH_2O(npe)); 4.41–3.17 (*m*, 2 CH_2OCO, CH_2OP, H–C(3′), H–C(4′), 2 H–C(5′), CH_2OCH_2); 3.66 (*t*, SO_2CH_2); 3.27 (*t*, C–CH_2); 3.10–2.96 (*m*, 2 CCH_2, 2 MeCH_2N); 2.79 (*s*, Me_2N); 2.53, 2.50 (2*s*, MeO); 1.75–1.30 (*m*, CH_2CCH_2); 1.06–0.95 (*m*, 2 *Me*CH_2N). ^{31}P-NMR (CD_3CN): 151.52, 150.64. Anal. calc. for $C_{60}H_{69}N_{10}O_{20}PS$ (1313.3): C 54.87, H 5.30, N 10.67; found: C 54.45, H 5.38, N 10.24.

36. *5′-O-(2-Dansylethoxycarbonyl)-*N^4*-[2-(4-nitrophenyl)ethoxycarbonyl]-2′-O-(tetrahydro-4-methoxy-2*H*-pyran-4-yl)cytidine 3′-[2-(4-Nitrophenyl)ethyl* N,N-*Diethylphosphoramidite]* (**69**). As described in *Exper. 34*, with **46** (856 mg, 1 mmol). Purification was achieved by FC (silica gel, 11 × 2 cm, soln. in CH_2Cl_2/petroleum ether 1:1, then quickly petroleum ether/acetone 2:1 (200 ml) and 1:1 (100 ml)): 798 mg (71%) of **69**. Yellow foam. UV

(MeOH): 212 (4.84), 252 (4.55), 282 (sh, 4.36), 342 (3.65). ^{1}H-NMR (CD_3CN): NH not visible; 8.59 (*d*, H–C(2)(Dns)); 8.28–8.21 (*m*, H–C(4)(Dns), H–C(8)(Dns)); 8.15–8.08 (*m*, 4 H *o* to NO_2); 7.81–7.76 (2*d*, H–C(6)); 7.61 (*t*, H–C(3)(Dns), H–C(7)(Dns)); 6.50–7.42 (*m*, 4 H *m* to NO_2); 7.24 (*d*, H–C(6)(Dns)); 7.10 (br., H–C(5)); 6.10, 6.01 (2*d*, J = 7.3, 6.7, H–C(1′)); 4.47–4.33 (*m*, 2 CH_2OCO, H–C(2′)); 4.20–3.25 (*m*, CH_2OP, H–C(3′), H–C(4′), 2 H–C(5′), CH_2OCH_2); 3.70 (*t*, SO_2CH_2); 3.10–2.93 (*m*, 2 C–CH_2, 2 MeCH_2N); 2.89, 2.88 (2*s*, MeO); 2.83 (2*s*, Me_2N); 1.80–1.40 (*m*, CH_2CCH_2); 1.03–0.94 (*m*, 2 *Me*CH_2N). ^{31}P-NMR (CD_3CN): 151.37, 150.55. Anal. calc. for $C_{51}H_{62}N_7O_{18}PS$ (1124.1): C 54.49, H 5.56, N 8.72; found: C 53.99, H 5.69, N 8.29.

37. *5′-O-(2-Dansylethoxycarbonyl)-2′-O-(tetrahydro-4-methoxy-2*H*-pyran-4-yl)uridine 3′-[2-(4-Nitrophenyl)ethyl* N,N-*Diethylphosphoramidite]* (**70**). As described in *Exper. 34*, with **49** (664 mg, 1 mmol). Purification was achieved by FC (silica gel, 11 × 2 cm, soln. in CH_2Cl_2/petroleum ether 1:1, then quickly petroleum ether/acetone 7:3 (200 ml) and 6:4 (100 ml)): 677 mg (73%) of **70**. Yellow foam. UV (MeOH): 212 (4.72), 258 (4.44), 343 (3.60). ^{1}H-NMR (CD_3CN): NH not visible; 8.61 (*d*, H–C(2)(Dns)); 8.28–8.21 (*m*, H–C(4)(Dns), H–C(8)(Dns)); 8.15–8.09 (*m*, 2 H *o* to NO_2); 7.66–7.60 (*m*, H–C(3)(Dns), H–C(7)(Dns)); 7.51–7.40 (*m*, 2 H *m* to NO_2, H–C(6)); 7.26 (*d*, H–C(6)(Dns)); 5.99–5.91 (2*d*, J = 8, 7.5, H–C(1′)); 5.71–5.65 (2*d*, H–C(5)); 4.55–3.26 (*m*, CH_2OCO, CH_2OP, H–C(2′), H–C(3′), H–C(4′), 2 H–C(5′), CH_2OCH_2); 3.71 (*t*, SO_2CH_2); 3.17–2.90 (*m*, C–CH_2, 2 MeCH_2N); 2.97 (*s*, MeO); 2.85 (*s*, Me_2N); 1.82–1.42 (*m*, CH_2CCH_2); 1.18–0.94 (*t* and *m*, 2 *Me*CH_2N). ^{31}P-NMR (CD_3CN): 151.54, 150.53. Anal. calc. for $C_{42}H_{54}N_5O_{15}PS$ (932.0): C 54.13, H 5.84, N 7.51; found: C 54.01, H 5.92, N 7.05.

38. *5′-O-(2-Dansylethoxycarbonyl)-2′-O-(tetrahydro-4-methoxy-2*H*-pyran-4-yl)ribothymidine 3′-[2-(4-Nitrophenyl)ethyl* N,N-*Diethylphosphoramidite]* (**71**). As described in *Exper. 34*, with **51** (170 mg, 0.25 mmol), (i-Pr)$_2$EtN (0.26 ml, 1.5 mmol) and **63** (0.15 g, 0.5 mmol) in dry THF (2 ml). Purification was achieved by FC (silica gel, 7 × 2 cm, soln. in CH_2Cl_2/petroleum ether 2:1, then quickly petroleum ether/acetone 7:3 (150 ml) and 6:4 (100 ml)): 183 mg (77%) of **71**. Yellow foam. UV (MeOH): 213 (4.73), 260 (4.45), 340 (3.59). ^{1}H-NMR (CD_3CN): 9.10 (br., NH); 8.61 (*d*, H–C(2)(Dns)); 8.29–8.22 (*m*, H–C(4)(Dns), H–C(8)(Dns)); 8.17–8.10 (*m*, 2 H *o* to NO_2); 7.63 (*t*, H–C(3)(Dns), H–C(7)(Dns)); 7.50, 7.45 (2*d*, 2 H *m* to NO_2); 7.27 (*d*, H–C(6)(Dns)); 5.99, 5.91 (2*d*, J = 8, 7.6, H–C(1′)); 4.42, 4.41 (2*t*, CH_2OCO); 4.37, 4.30 (2*dd*, H–C(2′)); 4.19–3.28 (*m*, CH_2OP, H–C(3′), H–C(4′), 2 H–C(5′), CH_2OCH_2); 3.72 (*t*, SO_2CH_2); 3.07–2.93 (*m*, C–CH_2, 2 MeCH_2); 2.96 (*s*, MeO); 2.86 (*s*, Me_2N); 1.80, 1.78 (2*d*, J = 1, Me); 1.76–1.40 (*m*, CH_2CCH_2); 1.05–0.95 (*m*, 2 *Me*CH_2N). ^{31}P-NMR (CD_3CN): 150.50, 149.50. Anal. calc. for $C_{43}H_{56}N_5O_{15}PS$ (946.0): C 54.60, H 5.97, N 7.40; found: C 54.27, H 6.11, N 6.96.

39. *5′-O-(2-Dansylethoxycarbonyl)-2′-O-(tetrahydro-4-methoxy-2*H*-pyran-4-yl)pseudouridine 3′-[2-(4-Nitrophenyl)ethyl* N,N-*Diethylphosphoramidite]* (**72**). As described in *Exper. 34*, with **53** (332 mg, 0.5 mmol), (i-Pr)$_2$EtN (0.52 ml, 3 mmol), and **63** (0.31 g, 1 mmol) in dry THF (4 ml). Purification was achieved by FC (silica gel, 7 × 2 cm, soln. in CH_2Cl_2/petroleum ether 2:1, then quickly petroleum ether/acetone 2:1 (150 ml) and 1:1 (100 ml)): 328 mg (70%) of **72**. Yellow foam. UV (MeOH): 212 (4.73), 259 (4.43), 344 (3.60). ^{1}H-NMR (CD_3CN): 8.61 (*d*, H–C(2)(Dns)); 8.25 (*t*, H–C(4)(Dns), H–C(8)(Dns)); 8.15 (br., NH); 8.11 (*t*, 2 H *o* to NO_2); 7.63 (*t*, H–C(3)(Dns), H–C(7)(Dns)); 7.51 (br., NH); 7.45 (*t*, 2 H *m* to NO_2); 7.38 (*s*, H–C(6)); 7.27 (*d*, H–C(6)(Dns)); 4.59 (*m*, H–C(1′)); 4.50–3.32 (*m*, CH_2OCO, CH_2OP, H–C(2′), H–C(3′), H–C(4′), 2 H–C(5′), CH_2OCH_2); 3.73, 3.72 (2*t*, SO_2CH_2); 3.06, 3.03 (2*s*, MeO); 3.06–2.92 (*m*, C–CH_2, 2 MeCH_2N); 2.86 (*s*, Me_2N); 1.85–1.50 (*m*, CH_2CCH_2); 1.03–0.93 (*m*, 2 *Me*CH_2N). ^{31}P-NMR (CD_3CN): 149.87, 149.41. Anal. calc. for $C_{42}H_{54}N_5O_{15}PS$ (932.0): C 54.13, H 5.84, N 7.51; found: C 53.60, H 5.86, N 7.00.

40. *5′-O-(Dansylethoxycarbonyl)-*O^2,O^4*-bis[2-(4-nitrophenyl)ethyl]-2′-O-(tetrahydro-4-methoxy-2*H*-pyran-4-yl)pseudouridine 3′-[2-(4-Nitrophenyl)ethyl* N,N-*Diethylphosphoramidite]* (**73**). As described in *Exper. 34*, with **55** (400 mg, 0.41 mmol), (i-Pr)$_2$EtN (0.43 ml, 2.48 mmol), and **63** (0.25 g, 0.83 mmol) in dry THF (3.5 ml). Purification was achieved by FC (silica gel, 7 × 2 cm, soln. in CH_2Cl_2/petroleum ether 1:1, then quickly petroleum ether/acetone 3:1 (100 ml) and 2:1 (100 ml)): 404 mg (79%) of **73**. Yellow foam. UV (MeOH): 214 (4.83), 264 (4.62), 340 (3.64). ^{1}H-NMR (CD_3CN): 8.58 (*d*, H–C(2)(Dns)); 8.27–8.16 (*m*, H–C(4)(Dns), H–C(8)(Dns), H–C(6)); 8.14–8.07 (*m*, 6 H *o* to NO_2); 7.64–7.56 (*m*, H–C(3)(Dns), H–C(7)(Dns)); 7.51–7.42 (*m*, 6 H *m* to NO_2); 7.24, 7.23 (2*d*, H–C(6)(Dns)); 4.79, 4.74 (2*d*, J = 8.5, 7.8, H–C(1′)); 4.64–4.56 (*m*, 2 CH_2OCO); 4.40, 4.39 (2*t*, CH_2OCO); 4.30–3.22 (*m*, CH_2OP, H–C(2′), H–C(3′), H–C(4′), 2 H–C(5′), CH_2OCH_2); 3.71 (*t*, SO_2CH_2); 3.19 (*t*, 2 C–CH_2); 3.10–2.87 (*m*, C–CH_2, 2 MeCH_2N); 2.83 (*s*, Me_2N); 2.66, 2.64 (2*s*, MeO); 1.75–1.28 (*m*, CH_2CCH_2); 0.96–0.92 (*m*, 2 *Me*CH_2N). ^{31}P-NMR (CD_3CN): 150.04, 149.53. Anal. calc. for $C_{58}H_{68}N_7O_{19}PS$ (1230.3): C 56.63, H 5.57, N 7.97; found: C 55.88, H 5.91, N 7.99.

41. N^3*-Anisoyl-5′-O-(2-dansylethoxycarbonyl)-2′-O-(tetrahydro-4-methoxy-2*H*-pyran-4-yl)uridine 3′-[2-(4-Nitrophenyl)ethyl* N,N-*Diethylphosphoramidite]* (**74**). As described in *Exper. 34*, with **56** (399 mg, 0.5 mmol), (i-Pr)$_2$EtN (0.52 ml, 3 mmol), and **63** (0.31 g, 1 mmol) in dry THF (4 ml). Purification was achieved by FC (silica

gel, 9 × 2 cm, soln. in CH_2Cl_2/petroleum ether, then quickly petroleum ether/acetone 3:1 (100 ml) and 2:1 (150 ml)): 345 mg (84%) of **74**. Yellow foam. UV (MeOH): 214 (4.77), 266 (4.57), 284 (sh, 4.49), 341 (3.60). ^{1}H-NMR (CD_3CN): 8.63 (*d*, H–C(2)(Dns)); 8.30–8.23 (*m*, H–C(4)(Dns), H–C(8)(Dns)); 8.17–8.08 (*m*, 2 H *o* to NO_2); 7.89 (br. *d*, 2 H *m* to MeO); 7.68–7.60 (*m*, H–C(3)(Dns), H–C(7)(Dns), H–C(6)); 7.52–7.43 (*m*, 2 H *m* to NO_2); 7.28 (*d*, H–C(6)(Dns)); 7.06–7.01 (*m*, 2 H *o* to MeO); 5.99, 5.91 (2*d*, H–C(1′)); 5.90, 5.87 (2*d*, H–C(5)); 4.52–4.35 (*m*, CH_2OCO, H–C(2′)); 4.25–3.35 (*m*, CH_2OP, H–C(3′), H–C(4′), 2 H–C(5′), CH_2OCH_2); 3.88 (2*s*, MeO of an); 3.73 (*t*, SO_2CH_2); 3.09 (*s*, MeO(Thmp)); 3.09–2.88 (*m*, C–CH_2, 2 MeCH_2N); 2.86 (*s*, Me_2N); 1.88–1.49 (*m*, CH_2CCH_2); 1.04–0.95 (*m*, 2 *Me*CH_2N). ^{31}P-NMR (CD_3CN): 150.52, 149.62. Anal. calc. for $C_{50}H_{60}N_5O_{17}PS$ (1066.1): C 56.33, H 5.67, N 6.57; found: C 55.55, H 6.33, N 6.66.

42. N^3-*[(*tert*-Butyloxy)carbonyl]-5′*-O-*(2-dansylethoxycarbonyl)-2′*-O-*(tetrahydro-4-methoxy-2*H*-pyran-4-yl)uridine 3′-[2-(4-Nitrophenyl)ethyl* N,N-*Diethylphosphoramidite]* (**75**). As described in *Exper. 34*, with **59** (260 mg, 0.34 mmol) (i-Pr)$_2$EtN (0.35 ml, 2 mmol), and **63** (0.21 g, 0.68 mmol) in dry THF (3 ml). Purification was achieved by FC (silica gel, 6 × 2 cm, soln. in CH_2Cl_2/petroleum ether, then quickly petroleum ether/AcOEt 3:1 (50 ml), and 1:1 (100 ml): 225 mg (64%) of **75**. Yellow foam. UV (MeOH): 205 (4.75), 259 (4.48), 340 (3.63). ^{1}H-NMR (CD_3CN): 8.62 (*d*, H–C(2)(Dns)); 8.29–8.22 (*m*, H–C(4)(Dns), H–C(8)(Dns)); 8.18–8.07 (*m*, 2 H *o* to NO_2); 7.64 (*t*, H–C(3)(Dns), H–C(7)(Dns)); 7.52–7.44 (*m*, 2 H *m* to NO_2, H–C(6)); 7.27 (*d*, H–C(6)(Dns)); 5.99, 5.91 (2*d*, *J* = 7.9, 7.2, H–C(1′)); 5.80, 5.77 (2*d*, H–C(5)); 4.52–3.30 (*m*, CH_2OCO, CH_2OP, H–C(2′), H–C(3′), H–C(4′), 2 H–C(5′), CH_2OCH_2); 3.72 (*t*, SO_2CH_2); 3.12–2.90 (*m*, C–CH_2, 2 MeCH_2N); 3.00 (*s*, MeO); 2.86 (*s*, Me_2N); 1.82–1.47 (*m*, CH_2CCH_2); 1.54, 1.53 (2*s*, *t*-Bu); 1.07–0.96 (*m*, 2 *Me*CH_2N). ^{31}P-NMR (CD_3CN): 150.53, 149.47. Anal. calc. for $C_{47}H_{62}N_5O_{17}PS$ (1032.1): C 54.70, H 6.06, N 6.79; found: C 54.08 H 6.34, N 6.62.

43. *5′*-O-*(2-Dansylethoxycarbonyl)*-N^6-*[2-(4-nitrophenyl)ethoxycarbonyl]-3′*-O-*succinoyl-2′*-O-*(tetrahydro-4-methoxy-2*H*-pyran-4-yl)adenosine* (**76**). In dry CH_2Cl_2 (5 ml), **42** (0.88 g, 1 mmol), succinic anhydride (0.2 g, 2 mmol), and 4-(dimethylamino)pyridine (0.16 g, 1.3 mmol) were stirred at r.t. for 2 h. Then, the mixture was diluted with CH_2Cl_2 (50 ml) and washed with sat. $NaHCO_3$ soln. (50 ml). The aq. phase was extracted with CH_2Cl_2 (2 × 25 ml), the combined org. phase washed with 10% citric acid (50 ml), the aq. phase re-extracted with CH_2Cl_2 (25 ml), and the combined org. phase dried (Na_2SO_4) and evaporated: 975 mg (99.5%) of **76** as a yellow amorphous solid which was used for reaction with the support. For anal. characterization, **76** (100 mg) was purified first by prep. TLC (CH_2Cl_2/MeOH 10:1), then by FC (silica gel, 2 × 2 cm, 0–10% MeOH/CH_2Cl_2), and then by precipitation from CH_2Cl_2/hexane: yellow powder. UV (MeOH): 211 (4.86), 263 (4.59), 342 (3.68). ^{1}H-NMR ((D_6)DMSO): 12.35 (br., COOH); 10.67 (br. *s*, NH); 8.72, 8.64 (2*s*, H–C(2), H–C(8)); 8.48 (*d*, H–C(2)(Dns)); 8.16 (*t*, H–C(4)(Dns), H–C(8)(Dns)); 8.15 (*d*, 2 H *o* to NO_2); 7.67–7.59 (*m*, H–C(3)(Dns), H–C(7)(Dns)); 7.61 (*d*, 2 H *m* to NO_2); 7.24 (*d*, H–C(6)(Dns)); 6.16 (*d*, *J* = 7.6, H–C(1′)); 5.39 (*dd*, H–C(2′)); 5.31 (*d*, H–C(3′)); 4.41–4.31 (*m*, 2 CH_2O, 2 H–C(5′)); 4.23 (*m*, H–C(4′)); 3.84 (*t*, SO_2CH_2); 3.60–3.10 (*m*, CH_2OCH_2); 3.10 (*t*, C–CH_2); 2.78 (*s*, Me_2N); 2.66, 2.55 (2*m*, $C(O)CH_2CH_2C(O)$); 2.39 (*s*, MeO); 1.75–1.30 (*m*, CH_2CCH_2). Anal. calc. for $C_{44}H_{49}N_7O_{17}S$ (980.0): C 53.93, H 5.04, N 10.00; found: C 53.44, H 5.08, N 9.53.

44. *5′*-O-*(2-Dansylethoxycarbonyl)*-N^2-*[2-(4-nitrophenyl)ethoxycarbonyl]*-O^6-*[2-(4-nitrophenyl)ethyl]-3′*-O-*succinoyl-2′*-O-*(tetrahydro-4-methoxy-2*H*-pyran-4-yl)guanosine* (**77**). As described in *Exper. 43*, with **44** (1.05 g, 1 mmol). Workup yielded **77** (1.12 g, 98%) as a yellow amorphous solid which was used for reaction with the support. For anal. characterization **77** (100 mg) was purified as described in *Exper. 43*: yellow powder. UV (MeOH): 214 (4.90), 262 (4.63), 340 (3.66). ^{1}H-NMR ((D_6)DMSO): 12.30 (br., COOH); 10.40 (*s*, NH); 8.46 (*d*, H–C(2)(Dns)); 8.45 (*s*, H–C(8)); 8.17 (*t*, H–C(4)(Dns), H–C(8)(Dns)); 8.15 (*d*, 4 H *o* to NO_2); 7.61 (*t*, H–C(3)(Dns), H–C(7)(Dns), 2 H *m* to NO_2); 7.23 (*d*, H–C(6)(Dns)); 6.05 (*d*, *J* = 7.8, H–C(1′)); 5.62 (*dd*, H–C(2′)); 5.25 (*d*, H–C(3′)); 4.76 (*t*, CH_2O(npe)); 4.45–4.28 (*m*, 2 CH_2O, 2 H–C(5′)); 4.18 (*t*, H–C(4′)); 3.83 (*t*, SO_2CH_2); 3.58–3.08 (*m*, CH_2OCH_2, C–CH_2(npe)); 3.06 (*t*, C–CH_2); 2.77 (*s*, Me_2N); 2.64, 2.54 (2*m*, $C(O)CH_2CH_2C(O)$); 2.45 (*s*, MeO); 1.75–1.30 (*m*, CH_2CCH_2). Anal. calc. for $C_{52}H_{56}N_8O_{20}S$ (1145.1): C 54.54, H 4.93, N 9.79; found: C 54.18, H 5.06, N 9.63.

45. *5′*-O-*(2-Dansylethoxycarbonyl)*-N^4-*[2-(4-nitrophenyl)ethoxycarbonyl]-3′*-O-*succinoyl-2′*-O-*(tetrahydro-4-methoxy-2*H*-pyran-4-yl)cytidine* (**78**). As described in *Exper. 43*, with **46** (856 mg, 1 mmol). Workup yielded **78** (936 mg, 98%) as a yellow amorphous solid which was used for reaction with the support. For anal. characterization, **78** (100 mg) was purified as described in *Exper. 43*: yellow powder. UV (MeOH): 212 (4.79), 248 (4.49), 282 (sh, 4.16), 341 (3.63). ^{1}H-NMR ((D_6)DMSO): 12.30 (br., COOH); 10.90 (br., NH); 8.53 (*d*, H–C(2)(Dns)); 8.22–8.12 (*m*, H–C(4)(Dns), H–C(8)(Dns)); 8.15 (*d*, 2 H *o* to NO_2); 8.06 (*d*, H–C(6)); 7.70–7.57 (*m*, H–C(3)(Dns), H–C(7)(Dns)); 7.59 (*d*, 2 H *m* to NO_2); 7.26 (*d*, H–C(6)(Dns)); 7.05 (*d*, H–C(5)); 6.03 (*d*, *J* = 7.55, H–C(1′)); 5.11 (*dd*, H–C(3′)); 4.73 (*dd*, H–C(2′)); 4.41–4.33 (*m*, 2 CH_2O); 4.21 (*m*, 2 H–C(5′)); 4.12 (*m*, H–C(4′)); 3.85 (*t*,

SO_2CH_2); 3.62–3.22 (*m*, CH_2OCH_2); 3.07 (*t*, C–CH_2); 2.81 (*s*, Me_2N); 2.80 (*s*, MeO); 2.62, 2.52 (2*m*, $C(O)CH_2CH_2C(O)$); 1.75–1.40 (2*m*, CH_2CCH_2). Anal. calc. for $C_{43}H_{49}N_5O_{18}S$ (956.0): C 54.03, H 5.17, N 7.33; found: C 53.57, H 5.30, N 7.09.

46. *5′-O-(2-Dansylethoxycarbonyl)-3′-O-succinoyl-2′-O-(tetrahydro-4-methoxy-2H-pyran-4-yl)uridine* (**79**). As described in *Exper. 43*, with **49** (664 mg, 1 mmol). To obtain complete phase separation on washing with sat. $NaHCO_3$ soln., 10% citric acid was added. Further workup yielded 724 mg (95%) of **79** as a yellow amorphous solid which was used for reaction with the support. For anal. characterization, **79** (100 mg) was purified as described in *Exper. 43*: yellow powder. UV (MeOH): 211 (4.72), 255 (4.37), 344 (3.63). ^{1}H-NMR ((D_6)DMSO): 12.30 (br., COOH); 11.52 (*s*, NH); 8.54 (*d*, H–C(2)(Dns)); 8.19–8.15 (*m*, H–C(4)(Dns), H–C(8)(Dns)); 7.71–7.62 (*m*, H–C(3)(Dns), H–C(7)(Dns), H–C(6)); 7.28 (*d*, H–C(6)(Dns)); 5.94 (*d*, J = 8.15, H–C(1′)); 5.76 (*d*, H–C(5)); 5.07 (*d*, H–C(3′)); 4.64 (*dd*, H–C(2′)); 4.39 (*m*, CH_2O); 4.20 (*m*, 2 H–C(5′)); 4.09 (*t*, H–C(4′)); 3.86 (*t*, SO_2CH_2); 3.62–3.20 (*m*, CH_2OCH_2); 2.90 (*s*, MeO); 2.82 (*s*, Me_2N); 2.62, 2.53 (2*m*, $C(O)CH_2CH_2C(O)$); 1.80–1.42 (2*m*, CH_2CCH_2). Anal. calc. for $C_{34}H_{41}N_3O_{15}S$ (763.8): C 53.47, H 5.41, N 5.50; found: C 53.32, H 5.50, N 5.22.

47. *Reaction of LCAMA-CPG 500 Å with 5′-O-(2-Dansylethoxycarbonyl)-3′-O-succinoyl-nucleosides* **76**–**79**. To a mixture of 200 mg of LCAMA-CPG 500 Å [1] (200 mg), 45 µmol of **76** (44 mg), **77** (52 mg), **78** (43 mg), or **79** (34 mg), and TOTU (30 mg, 91.4 µmol), abs. MeCN (3 ml) and *N*-methylmorpholine (19 µl, 180 µmol) were added. After a short ultrasonic treatment (30 s) and 2 h standing in the dark at r.t., the CPG material was collected in a glass-frit suction funnel and washed with MeOH, DMF, MeOH, and Et_2O. Capping-procedure: The nucleoside-substituted CPG, 4-(dimethylamino)pyridine (50 mg, 0.41 mmol), abs. pyridine (10 ml), and Ac_2O (1 ml, 10.6 mmol) were kept in the dark for 45 min at r.t. Thereafter, the nucleoside-substituted CPG (see **80**–**83**) was collected in a glass-frit suction funnel and washed with MeOH, DMF, MeOH, and Et_2O. Determination of loading: A defined amount of **80**, **81**, **82**, or **83** (5–10 mg) was weighed in a 1-ml micro cuvette (d = 1 cm). Then 0.1M 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in MeCN (500 µl) was added. After 1 min, the soln. was neutralized with 0.1M AcOH in MeCN (500 µl). Then, the absorbance at 345 nm was measured against a 0.05M DBU-acetate soln. in MeCN. By considering log ε = 3.63 of the formed 5-(dimethylamino)naphthalene-1-yl vinyl sulfone, the loading was calculated by the formula L [µmol/g] = 234.75 · A/m (L = loading, A = absorbance at 345 nm; m = weighed CPG **80**–**83** in mg): **80**, L = 18 µmol/g; **81**, L = 15–16 µmol/g; **82**, L = 19 µmol/g; **83**, L = 17 µmol/g.

48. *Reaction of LCAMA-CPG 1000 Å with 5′-O-(2-Dansylethoxycarbonyl)-3′-O-succinoyladenosine* **76**. As described in *Exper. 47*, with LCAMA-CPG 1000 Å (200 mg; synthesized by the same procedure as 500Å CPG [1]), **76** (10 mg, 10.2 µmol), TOTU (7 mg, 21.3 µmol), and *N*-methylmorpholine (5 µl, 47 µmol) in abs. MeCN (3 ml): **84** of L = 14 µmol/g.

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