126. Nucleosides

Part LIX[1])

The 2-(4-Nitrophenyl)ethylsulfonyl (Npes) Group: A New Type of Protection in Nucleoside Chemistry

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Dedicated to my colleague Prof. Dr. *R. R. Schmidt* on the occasion of his 60th birthday

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The 2-(4-nitrophenyl)ethylsulfonyl (npes) group is developed as a new sugar OH-blocking group in the ribonucleoside series. Its cleavage can be performed in a β-eliminating process under aprotic conditions using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as the most effective base. Since sulfonates do not show acyl migration, partial protection of 1,2-*cis*-diol moieties is possible leading to new types of oligonucleotide building blocks. A series of *Markiewicz*-protected ribonucleosides **1–10** is converted into their 2′-*O*-[2-(4-nitrophenyl)ethylsulfonyl] derivatives **29–38** in which the 5′-O–Si bond can be cleaved by acid hydrolysis forming **39–45**. Subsequent monomethoxytritylation leads to **46–50**, and desilylation affords the 5′-*O*-(monomethoxytrityl)-2′-*O*-[2-(4-nitrophenyl)ethylsulfonyl]ribonucleosides **51–55**. Acid treatment to remove trityl groups do also not harm the npes group (→ **56–58**). Unambiguous syntheses of fully blocked 2′-*O*-[2-(4-nitrophenyl)ethylsulfonyl]ribonucleosides **96–102** are achieved from the corresponding 3′-*O*-(*tert*-butyl)dimethylsilyl derivatives. Furthermore, various base-protected 5′-*O*-(monomethoxytrityl)- and 5′-*O*-(dimethoxytrityl)ribonucleosides, *i.e.* **59–77**, are treated directly with 2-(4-nitrophenyl)ethylsulfonyl chloride forming in all cases a mixture of the 2′,3′-di-*O*- and the two possible 2′- and 3′-*O*-monosulfonates **107–148** which can be separated into the pure components by chromatographic methods. The npes group is more labile towards DBU cleavage than the corresponding base-protecting 2-(4-nitrophenyl)ethyl (npe) and 2-(4-nitrophenyl)ethoxycarbonyl (npeoc) groups allowing selective deblocking which is of great synthetic potential.

1. Introduction. – The chemical synthesis of oligonucleotides was tremendously improved in recent years by the development of the phosphoramidite approach which allows an automated build-up of oligodeoxyribonucleotides in a very efficient manner on different types of solid-support materials [2–7]. More efforts, however, were put into the solution of an analogous methodology for the synthesis of oligoribonucleotides which gain more and more attention as antisense probes, modified ribozymes, and models for RNA-protein interactions as well as RNA structural studies. The additional 2′-OH group in the ribonucleoside series is responsible for the complexity of the applied strategy, since a special so-called permanent protecting group is needed which is, on one hand, stable enough to tolerate the manipulations during the synthetic cycles in assembling the

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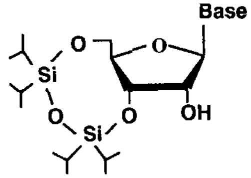
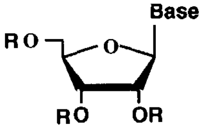
oligonucleotide chains but, on the other hand, also easily cleavable at the end of the synthesis under such mild conditions that no isomerization or breakage of the internucleotidic linkages takes place.

Various types of protecting-group combinations for the 2′- and 5′-OH functions were applied to solve the crucial problem of oligoribonucleotide synthesis. So far the best but still not the perfect solution of automated oligoribonucleotide synthesis was described by *Ogilvie et al.* [8] using the 2′-*O*-(*tert*-butyl)dimethylsilyl group in combination with the dimethoxytrityl group for 5′-*O*-protection. The use of the photolabile 2-nitrobenzyl group allowed the anticipated chemically inert 2′-*O*-protection, but the photolytic cleavage of this group was problematic [9] [10]. Acid-labile acetal and ketal groups were varied structurally to a large extent to block the 2′-OH function. However, the tetrahydro-2*H*-pyranyl [11–13], the tetrahydro-4-methoxy-2*H*-pyran-4-yl [14–16], and the more simple 1-(ethoxy)ethyl and 1-(2-chloroethoxy)ethyl group [17] required an alternative protection in place of the traditional 5′-*O*-trityl blocking groups due to unsatisfactory compatability [10–20]. Some improvements were recently achieved by applying the 1-(2-chloro-4-methylphenyl)- [21–23] and 1-(2-fluorophenyl)-4-methoxypiperidin-4-yl (Ctmp and Fmpm, resp.) protecting groups [24–27] in combination with the more acid-sensitive pixyl group. An early version of protection was seen in the use of acyl groups [28–30], but its easy intramolecular 2′→3′-*O*-migration excludes this possibility from practial application.

Since we have developed a universal blocking-group strategy [31] on the basis of β-eliminating protecting groups applying the 2-(4-nitrophenyl)ethyl (npe) and 2-(4-nitrophenyl)ethoxycarbonyl (npeoc) group for base, phosphate, and sugar protection [32–34], it was obvious to look for a new type of acyl function which does not show any tendency for the unfavorable migration in the 1,2-*cis*-diol moiety but will be cleaved by a β-elimination process. Sulfonates fullfil the first criterium [35], and combination with the npe residue leading to the 2-(4-nitrophenyl)ethylsulfonyl (npes) group [36] will meet the second one. To our knowledge, there is no indication in literature that sulfonates are prone to β-eliminations forming in the first step sulfite monoesters which then extrude SO_2 analogously to the decomposition of monoalkyl carbonates. The npes group is, therefore, a new versatile blocking group which has been studied regarding OH protection at the sugar moiety of nucleosides.

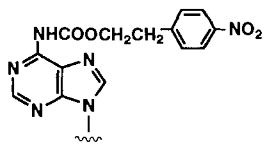
2. Syntheses. – Our first efforts in synthesizing 2′-*O*-[2-(4-nitrophenyl)ethylsulfonyl]ribonucleosides were concerned with sulfonation reactions of the corresponding free or base-protected 3′,5′-*O*-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl) (tipds) derivatives **1**–**10** by 2-(4-nitrophenyl)ethylsulfonyl chloride (Npes-Cl). The starting compounds **1**–**5** were already described in the literature, but **6**–**10** had to be prepared by different routes. *O*^{2},*O*^{4}-Bis[2-(4-nitrophenyl)ethyl]-3′,5′-*O*-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)-pseudouridine (**6**) was obtained from 2′,3′,5′-tri-*O*-acetylpseudouridine (**11**) [37] by alkylation with 2-(4-nitrophenyl)ethyl iodide in presence of Ag_2CO_3 (→ **12**, 79% yield), deacetylation with NH_3/MeOH (→ to **13**, 92%) and finally reaction with the *Markiewicz* reagent 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane (59% yield). The 5,6-dihydrouridine (**14**) was converted in a similar silylation reaction into compound **7** which was, however, not purified but used directly for the next step forming 5,6-dihydro-2′-*O*-[2-(4-nitrophenyl)ethylsulfonyl]-3′,5′-*O*-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)uridine (**35**,



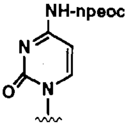


	Base		Base
1	Ade$^{\text{npeoc}}$	**6**	Ψra$^{(\text{npe})_2^{2,4}}$
2	Cyt$^{\text{npeoc}}$	**7**	h$_2^{5,6}$Ura
3	Gua$^{\text{npe}}_{\text{npeoc}}$	**8**	s^{4}Ura$^{\text{npe}^4}$
4	Ura	**9**	Ura$^{\text{me}^4}$
5	Ψra	**10**	Ura$^{\text{npe}^4}$

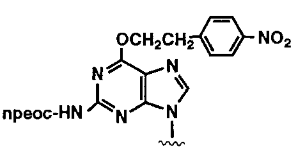
	Base	R		Base	R
11	Ψra	ac	**20**	Ura$^{\text{npe}^4}$	ac
12	Ψra$^{(\text{npe})_2^{2,4}}$	ac	**21**	Ura$^{\text{npe}^4}$	H
13	Ψra$^{(\text{npe})_2^{2,4}}$	H	**22**	Ura$^{\text{cpe}^4}$	H
14	h$_2^{5,6}$Ura	H	**23**	Thy	H
15	s^{4}Ura	bz	**24**	Thy	ac
16	s^{4}Ura$^{\text{npe}^4}$	bz	**25**	Thy$^{\text{tips}^4}$	ac
17	s^{4}Ura$^{\text{npe}^4}$	H	**26**	Thy$^{\text{cpe}^4}$	H
18	Ura	ac	**27**	Thy$^{\text{npe}^4}$	H
19	Ura$^{\text{me}^4}$	H	**28**	Gua$^{\text{npe}}_{\text{npeoc}}$	H



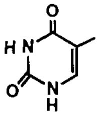
Ade$^{\text{npeoc}}$



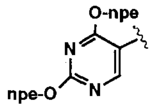
Cyt$^{\text{npeoc}}$



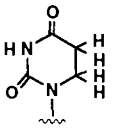
Gu$^{\text{npe}}_{\text{npeoc}}$



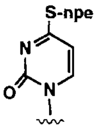
Ψra



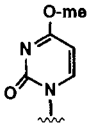
Ψra$^{(\text{npe})_2^{2,4}}$



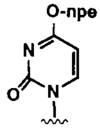
h$_2^{5,6}$Ura



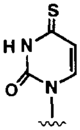
s^{4}Ura$^{\text{npe}^4}$



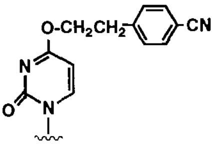
Ura$^{\text{me}^4}$



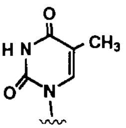
Ura$^{\text{npe}^4}$



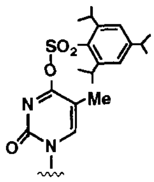
s^{4}Ura



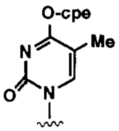
Ura$^{\text{cpe}^4}$



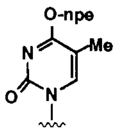
Thy



Thy$^{\text{tpbs}^4}$



Thy$^{\text{cpe}^4}$



Thy$^{\text{npe}^4}$

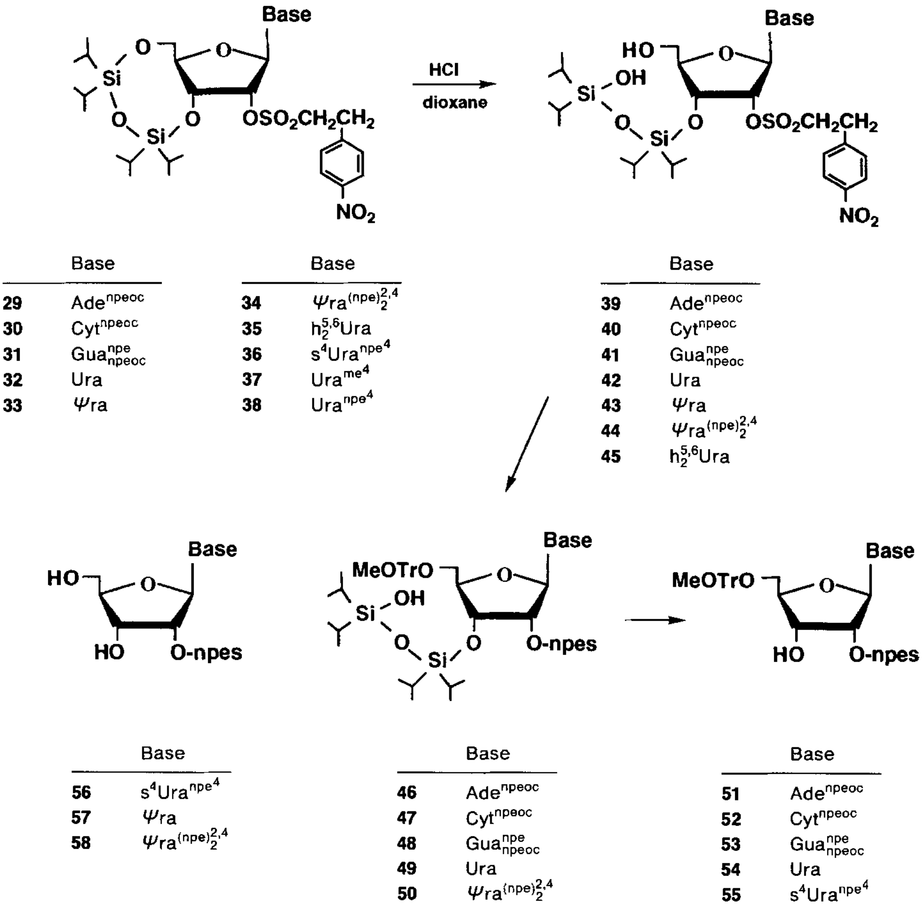
see below). Compound **8** was obtained from 2′,3′,5′-tri-*O*-benzoyl-4-thiouridine (**15**) by *S*-alkylation with 2-(4-nitrophenyl)ethyl iodide/K_2CO_3 in butan-2-one (→ **16**, 73%), debenzoylation by NH_3/MeOH (→ **17**, 85%) and silylation (79% yield). The corresponding O^4-methyl and O^4-[2-(4-nitrophenyl)ethyl] derivatives **9** and **10**, respectively, were prepared from 2′,3′,5′-tri-*O*-acetyluridine (**18**) which was converted either directly *via* the triazolide or triisopropylbenzenesulfonyl (tpbs) method into O^4-methyluridine (**19**) or *via* the *O*-alkylation procedure (→ **20**) followed by deacetylation to **21**. Subsequent silylation gave **9** and **10** in good yields. O^4-[2-(4-Cyanophenyl)ethyl]uridine (**22**) was prepared similarly by the tpbs method from **18**.

In the 'ribothymidine' (= 5-methyluridine = ribosylthymine; **23**) series, 2′,3′,5′-tri-*O*-acetylribosylthymine (**24**) was transformed into 2′,3′,5′-tri-*O*-acetyl-O^4-(1,3,5-triisopropylphenylsulfonyl)ribosylthymine (**25**) by 1,3,5-triisopropylbenzenesulfonyl chloride in CH_2Cl_2 in presence of Et_3N and 4-(dimethylamino)pyridine (DMAP) as catalyst. The activated amide function was then reacted with alcohols such as 2-(4-cyanophenyl)- or 2-(4-nitrophenyl)ethanol under the catalysis of Et_3N/1,4-diazobicylo[2.2.2]octane (DABCO) leading, after subsequent deacetylation by NH_3/MeOH, to O^4-[2-(4-cyanophenyl)ethyl]- (**26**) and O^4-[2-(4-nitrophenyl)ethyl]ribosylthymine (**27**), respectively, in 70% yield.

The doubly base-protected guanosine derivative **28** was obtained from 2′,3′,5′-tri-*O*-acetylguanosine *via* the O^6-[2-(4-nitrophenyl)ethyl] and the N^2-[2-(4-nitrophenyl)ethoxycarbonyl]-O^6-[2-(4-nitrophenyl)ethyl] derivatives after final deacetylation (see *Exper. Part*).

The partially protected ribonucleosides **1**–**10** were then sulfonated in pyridine by 2-(4-nitrophenyl)ethanesulfonyl chloride [38] which was synthesized from 2-(4-nitrophenyl)ethyl chloride [39] with sodium thiosulfate and subsequent oxidation by Cl_2. The yield of the 2′-*O*-[2-(4-nitrophenyl)ethylsulfonyl]ribonucleosides **29**–**38** were, after chro-

Scheme 1



	Base
29	Ade^{npeoc}
30	Cyt^{npeoc}
31	Gua^{npe}_{npeoc}
32	Ura
33	Ψra

	Base
34	$\Psi ra^{(npe)_2^{2,4}}$
35	$h_2^{5,6}Ura$
36	$s^4Ura^{npe^4}$
37	Ura^{me^4}
38	Ura^{npe^4}

	Base
39	Ade^{npeoc}
40	Cyt^{npeoc}
41	Gua^{npe}_{npeoc}
42	Ura
43	Ψra
44	$\Psi ra^{(npe)_2^{2,4}}$
45	$h_2^{5,6}Ura$

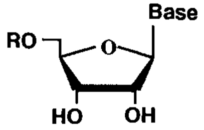
	Base
56	$s^4Ura^{npe^4}$
57	Ψra
58	$\Psi ra^{(npe)_2^{2,4}}$

	Base
46	Ade^{npeoc}
47	Cyt^{npeoc}
48	Gua^{npe}_{npeoc}
49	Ura
50	$\Psi ra^{(npe)_2^{2,4}}$

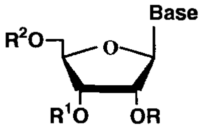
	Base
51	Ade^{npeoc}
52	Cyt^{npeoc}
53	Gua^{npe}_{npeoc}
54	Ura
55	$s^4Ura^{npe^4}$

matographic isolation on silica gel, in the range of 70–90%, except for the 5,6-dihydrouridine derivative **35** which is a quite labile compound and could only be obtained in 33% yield. It is known that *Markiewicz'* tipds blocking group can be removed by F^- ion treatment, either totally or partially by selective cleavage of the 5′-O–Si bond [40] in the eight-membered ring. An analogous regioselective ring-opening proceeds also by HCl treatment in dioxane [41] and afforded, from compounds **29–35**, the 3′-*O*-(3-hydro-1,1,3,3-tetraisopropyldisiloxan-1-yl) derivatives **39–45**. The next steps of the synthesis consisted of the monomethoxytritylation of **39–42** and **44** to the intermediates **46–50** of which compounds **46–49** were desilylation by F^- ion to give the 5′-*O*-(monomethoxytrityl)-2′-*O*-[2-(4-nitrophenyl)ethylsulfonyl]ribonucleosides **51–54**. The reaction with **49** afforded not only compound **54** but also 2,2′-anhydro-5′-*O*-(monomethoxytrityl)uridine (**150**, see below) in an intramolecular displacement under the influence of the basic F^- ion in aprotic solvents. Furthermore, **33**, **34**, and **36** were converted by prolonged acid or $(Et_3NH)F$ treatment into their 3′,5′-unprotected derivatives **56–58** of which S^4-[2-(4-nitrophenyl)ethyl]-2′-*O*-[2-(4-nitrophenyl)ethylsulfonyl]-4-thiouridine (**56**) was also monomethoxytritylated at the 5′-OH group forming **55**.

The alternative approaches towards the synthesis of base-protected 5′-*O*-(mono- or dimethoxytrityl)-2′-*O*-[2-(4-nitrophenyl)ethylsulfonyl]ribonucleosides afforded as starting materials the corresponding 5′-*O*-trityl derivatives **59–77** of which only **59–61**, **66**, and **71** were described in the literature. All other compounds were synthesized analogously to conventional tritylation procedures. In a first series of studies, 5′-*O*-(monomethoxytrityl)- and 5′-*O*-(dimethoxytrityl)-N^4-[2-(4-nitrophenyl)ethoxycarbonyl]cytidine (**61** and **62**, resp.) were treated by (*tert*-butyl)dimethylsilyl chloride (tbdms-



	Base	R
59	$\mathrm{Ade}^{\mathrm{npeoc}}$	MeOTr
60	$\mathrm{Ade}^{\mathrm{npeoc}}$	$(MeO)_2Tr$
61	$\mathrm{Cyt}^{\mathrm{npeoc}}$	MeOTr
62	$\mathrm{Cyt}^{\mathrm{npeoc}}$	$(MeO)_2Tr$
63	$\mathrm{Gua}^{\mathrm{npe}}_{\mathrm{npeoc}}$	MeOTr
64	$\mathrm{Gua}^{\mathrm{npe}}_{\mathrm{npeoc}}$	$(MeO)_2Tr$
65	$\mathrm{Gua}^{\mathrm{npe}}_{\mathrm{ib}}$	MeOTr
66	Ura	$(MeO)_2Tr$
67	$\mathrm{s^4Ura}^{\mathrm{npe}^4}$	MeOTr
68	$\mathrm{Ura}^{\mathrm{me}^4}$	$(MeO)_2Tr$
69	$\mathrm{Ura}^{\mathrm{npe}^4}$	$(MeO)_2Tr$
70	$\mathrm{Ura}^{\mathrm{cpe}^4}$	$(MeO)_2Tr$
71	$\Psi\mathrm{ra}$	MeOTr
72	$\Psi\mathrm{ra}$	$(MeO)_2Tr$
73	$\Psi\mathrm{ra}^{(\mathrm{npe})_2^{2,4}}$	MeOTr
74	$\Psi\mathrm{ra}^{(\mathrm{npe})_2^{2,4}}$	$(MeO)_2Tr$
75	Thy	MeOTr
76	$\mathrm{Thy}^{\mathrm{cpe}^4}$	MeOTr
77	$\mathrm{Thy}^{\mathrm{npe}^4}$	MeOTr

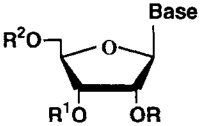


	Base	R	R^1	R^2
78	$\mathrm{Cyt}^{\mathrm{npeoc}}$	tbdms	tbdms	MeOTr
79		tbdms	H	MeOTr
80		H	tbdms	MeOTr
81	$\mathrm{Cyt}^{\mathrm{npeoc}}$	tbdms	tbdms	$(MeO)_2Tr$
82		tbdms	H	$(MeO)_2Tr$
83		H	tbdms	$(MeO)_2Tr$
84	$\mathrm{Gua}^{\mathrm{npe}}_{\mathrm{npeoc}}$	tbdms	tbdms	MeOTr
85		tbdms	H	MeOTr
86		H	tbdms	MeOTr
87	$\mathrm{Gua}^{\mathrm{npe}}_{\mathrm{npeoc}}$	tbdms	tbdms	$(MeO)_2Tr$
88		tbdms	H	$(MeO)_2Tr$
89		H	tbdms	$(MeO)_2Tr$
90	$\mathrm{Gua}^{\mathrm{npe}}_{\mathrm{ib}}$	tbdms	tbdms	MeOTr
91		tbdms	H	MeOTr
92		H	tbdms	MeOTr

	Base	R	R^1	R^2
93	$\mathrm{Ura}^{\mathrm{npe}^4}$	tbdms	tbdms	$(MeO)_2Tr$
94		tbdms	H	$(MeO)_2Tr$
95		H	tbdms	$(MeO)_2Tr$
96	$\mathrm{Ade}^{\mathrm{npeoc}}$	npes	tbdms	$(MeO)_2Tr$
97	$\mathrm{Ade}^{\mathrm{bz}}$	npes	tbdms	MeOTr
98	$\mathrm{Cyt}^{\mathrm{npeoc}}$	npes	tbdms	MeOTr
99	$\mathrm{Cyt}^{\mathrm{npeoc}}$	npes	tbdms	$(MeO)_2Tr$
100	$\mathrm{Gua}^{\mathrm{npe}}_{\mathrm{npeoc}}$	npes	tbdms	$(MeO)_2Tr$
101	$\mathrm{Gua}^{\mathrm{npe}}_{\mathrm{ib}}$	npes	tbdms	MeOTr
102	$\mathrm{Ura}^{\mathrm{npe}^4}$	npes	tbdms	$(MeO)_2Tr$
103	$\mathrm{Ade}^{\mathrm{npeoc}}$	npes	H	$(MeO)_2Tr$
104	$\mathrm{Cyt}^{\mathrm{npeoc}}$	npes	H	MeOTr
105	$\mathrm{Cyt}^{\mathrm{npeoc}}$	npes	H	$(MeO)_2Tr$
106	$\mathrm{Ade}^{\mathrm{bz}}$	npes	H	MeOTr

Cl) in pyridine in presence of 1*H*-imidazole, leading, in analogy to former results with corresponding adenosine derivatives [42], to mixtures of 2′,3′-bis-*O*-[(*tert*-butyl)-dimethylsilyl] (**78** and **81**, resp.) as well as 2′-*O*- (**79** and **82**, resp.) and 3′-*O*-[(*tert*-butyl)-dimethylsilyl] derivatives (**80** and **83**, resp.). Separation into the three pure components was achieved by silica-gel column chromatography, and the structural assignments were based upon ^{1}H-NMR spectra. In an analogous manner reacted the 5′-*O*-(monomethoxytrityl)- (**63**), 5′-*O*-(dimethoxytrityl)-N^2-[2-(4-nitrophenyl)ethoxycarbonyl]-O^6-2-(4-nitrophenyl)ethyl- (**64**) and the 5′-*O*-(dimethoxytrityl)-N^2-isobutyryl-O^6-[2-(4-nitrophenyl)ethyl]guanosine (**65**) as well as 5′-*O*-(dimethoxytrityl)-O^4-[2-(4-nitrophenyl)ethyl]uridine (**69**) to form the (*tert*-butyl)dimethylsilyl derivatives **84**–**95**. Reaction of the resulting 3′-*O*-[(*tert*-butyl)dimethylsilyl] derivatives with 2-(nitrophenyl)ethanesulfonyl chloride afforded the corresponding 2′-*O*-sulfonates **96**–**102** which can be considered as interesting intermediates due to easy deblocking of the silyl group by F^- ion as shown by the transformation of **96**–**99** to the 3′-*O*-unprotected derivatives **103**–**106**.

Much efforts were finally invested in the direct sulfonation of the base-protected 5′-*O*-(mono- or dimethoxytrityl)ribonucleosides **59**–**77** hoping that a regioselective or at least a predominant formation of the corresponding 2′-*O*-[2-(4-nitrophenyl)ethylsulfonyl] derivatives would take place. Unfortunately, mixtures of the three possible products, the 2′,3′-di-, 2′-mono-, and 3′-monosulfonates (see **107**–**148**), were obtained, as

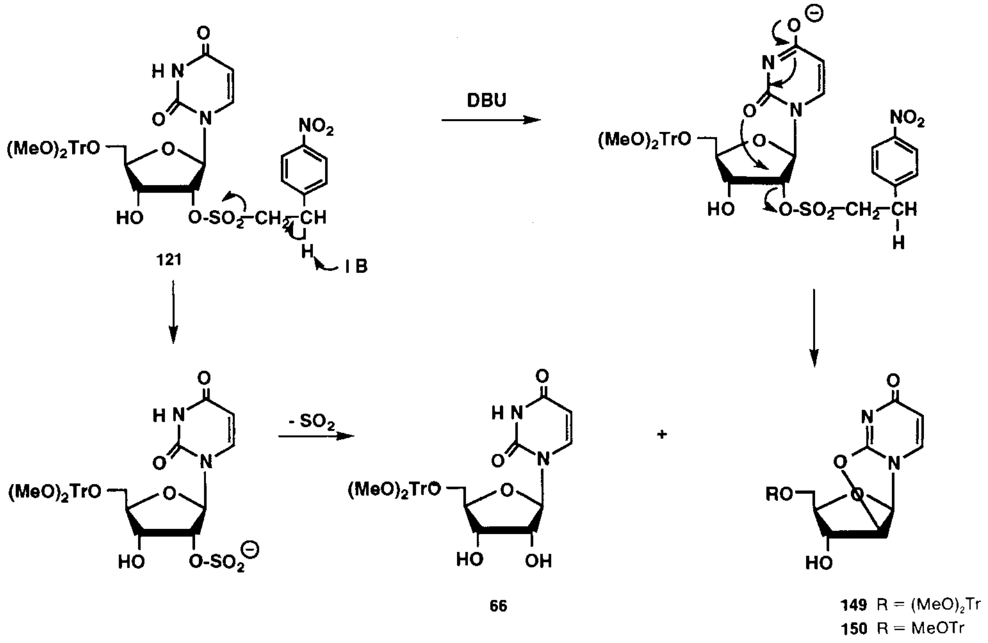


	Base	R	R¹	R²
107	$\mathrm{Ade}^{\mathrm{npeoc}}$	npes	npes	MeOTr
51		npes	H	MeOTr
108		H	npes	MeOTr
109	$\mathrm{Ade}^{\mathrm{npeoc}}$	npes	npes	$(\mathrm{MeO})_2\mathrm{Tr}$
103		npes	H	$(\mathrm{MeO})_2\mathrm{Tr}$
110		H	npes	$(\mathrm{MeO})_2\mathrm{Tr}$
111	$\mathrm{Cyt}^{\mathrm{npeoc}}$	npes	npes	$(\mathrm{MeO})_2\mathrm{Tr}$
112		npes	H	$(\mathrm{MeO})_2\mathrm{Tr}$
113		H	npes	$(\mathrm{MeO})_2\mathrm{Tr}$
114	$\mathrm{Cyt}^{\mathrm{bz}}$	npes	npes	MeOTr
115		npes	H	MeOTr
116		H	npes	MeOTr
117	$\mathrm{Cyt}^{\mathrm{bz}}$	npes	npes	$(\mathrm{MeO})_2\mathrm{Tr}$
118		npes	H	$(\mathrm{MeO})_2\mathrm{Tr}$
119		H	npes	$(\mathrm{MeO})_2\mathrm{Tr}$
120	Ura	npes	npes	$(\mathrm{MeO})_2\mathrm{Tr}$
121		npes	H	$(\mathrm{MeO})_2\mathrm{Tr}$
122		H	npes	$(\mathrm{MeO})_2\mathrm{Tr}$
123	$\mathrm{Ura}^{\mathrm{me}^4}$	npes	npes	$(\mathrm{MeO})_2\mathrm{Tr}$
124		npes	H	$(\mathrm{MeO})_2\mathrm{Tr}$
125		H	npes	$(\mathrm{MeO})_2\mathrm{Tr}$
126	$\mathrm{Ura}^{\mathrm{npe}^4}$	npes	npes	$(\mathrm{MeO})_2\mathrm{Tr}$
127		npes	H	$(\mathrm{MeO})_2\mathrm{Tr}$
128		H	npes	$(\mathrm{MeO})_2\mathrm{Tr}$
129	$\mathrm{Ura}^{\mathrm{cep}^4}$	npes	npes	$(\mathrm{MeO})_2\mathrm{Tr}$
130		npes	H	$(\mathrm{MeO})_2\mathrm{Tr}$
131		H	npes	$(\mathrm{MeO})_2\mathrm{Tr}$
132	$\Psi\mathrm{ra}$	npes	npes	MeOTr
133		npes	H	MeOTr
134		H	npes	MeOTr
135	$\Psi\mathrm{ra}$	npes	npes	$(\mathrm{MeO})_2\mathrm{Tr}$
136		npes	H	$(\mathrm{MeO})_2\mathrm{Tr}$
137		H	npes	$(\mathrm{MeO})_2\mathrm{Tr}$
138	$\Psi\mathrm{ra}^{(\mathrm{npe})_2^{2,4}}$	npes	npes	MeOTr
139		npes	H	MeOTr
140		H	npes	MeOTr
141	$\Psi\mathrm{ra}^{(\mathrm{npe})_2^{2,4}}$	npes	npes	$(\mathrm{MeO})_2\mathrm{Tr}$
142		npes	H	$(\mathrm{MeO})_2\mathrm{Tr}$
143		H	npes	$(\mathrm{MeO})_2\mathrm{Tr}$
144	Thy	npes	npes	MeOTr
145		npes	H	MeOTr
146	$\mathrm{Thy}^{\mathrm{cpe}^4}$	npes	npes	MeOTr
147		npes	H	MeOTr
148		H	npes	MeOTr

found already in former studies with N^6-benzoyl-5′-*O*-(dimethoxytrityl)adenosine [43]. The separation into the pure components by chromatographic methods was mostly a very tedious procedure and was paid with loss of material. Variation of the reaction conditions, especially of the temperature between −20° and room temperature, changed the isomeric ratio of the monosulfonates of *ca.* 1:1 only slightly. The partially protected guanosine derivatives **63**–**65** and 5′-*O*-(monomethoxytrityl)-S^4-[2-(4-nitrophenyl)ethyl]-4-thiouridine (**67**) led to very complex mixtures which could not be separated successfully. In the uridine series, we also tried the method of *Moffatt* and coworkers [44] who could achieve, in the presence of dibutyltin oxide, a selective 2′-*O*-tosylation with uridine. The same reaction did not give any sulfonation with 2-(4-nitrophenyl)ethanesulfonyl chloride under the reported conditions, but a recent modification by *Groullier et al.* [45] using dibutyltin oxide in combination with tetrahexylammonium chloride worked with 5′-*O*-(dimethoxytrityl)- (**66**) and 5′-*O*-(dimethoxytrityl)-O^4-[2-(4-nitrophenyl)ethyl]uridine (**69**). However, again mixtures of the 2′- and 3′-monosulfonates were obtained with the latter one in excess. Since the isolation of the anticipated products was even more tedious because of difficulties in separation from the tin and tetraalkylammonium compounds, this route is not recommended.

The cleavage of the npes protecting group could be achieved even by 0.1M 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in MeCN and proceeded even faster than the removal of the npe and npeoc groups from the aglycone moieties. It was a very clean reaction in the cytidine (**52**), adenosine (**51**), and guanosine (**53**) series and was finished in *ca.* 2 h, but uridine derivatives showed, unfortunately, 2,2′-anhydronucleoside formation (**121** → **149**; *Scheme 2*) as a critical side reaction. Since the sulfonate function is a good

Scheme 2



leaving group, this finding is not surprising due to the fact that the intramolecular displacement reaction seems to be of similar rate as the bond cleavage by β-elimation ($\rightarrow$ **66**).

The value of the 2-(4-nitrophenyl)ethylsulfonyl group for sugar-OH protection in oligonucleotide synthesis was already demonstrated [42] [43] and may be an interesting alternative for special, multifunctional syntheses.

Experimental Part

General. Products were dried under high vacuum or in a desiccator over P_4O_{10}. TLC: Precoated silica gel thin-layer sheets *F 1500 LS 254* from *Schleicher & Schüll* or *60 F$_{254}$* from *Merck*. Flash column chromatography (FC): silica gel, *Baker* (30–60 mm), 0.2 bar. Column chromatography (CC): silica gel *60*, *Merck 60* (0.063–0.2 mesh). M.p.: *Gallenkamp* or *Büchi*, model Dr. *Tottoli* melting-point apparatus; no corrections. UV/VIS: *Perkin-Elmer Lambda 5*; λ_{max} in nm (log ε). ^{1}H-NMR: *Bruker WM 250, AC 250, Jeol JM GX-400*; in ppm rel. to $SiMe_4$, $CDCl_3$, or (D_6)DMSO as internal standard.

O^2,O^4-Bis[2-(4-nitrophenyl)ethyl]-3′,5′-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)pseudouridine (**6**). In dry pyridine (3 × 20 ml), **13** (0.5, 0.92 mmol) was co-evaporated and dissolved in pyridine (10 ml), and 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane (0.32 ml, 1.01 mmol) was added. The yellow mixture was stirred at r.t. for 4 h and then evaporated and co-evaporated several times with toluene. The residue was taken up in Et_2O, the soln. washed with sat. NaCl soln. (3 × 20 ml), dried (Na_2SO_4), and evaporated, and the crude product purified by CC (20 g of silica gel, *d* 3.5 cm; $CHCl_3$ (140 ml)): 0.6 g (83%) of **6**. Colorless foam. TLC ($CHCl_3$): R_f 0.40. UV (MeOH): 203 (4.47), 215 (4.42), 269 (4.41). ^{1}H-NMR ($CDCl_3$): 8.39 (*s*, H–C(6)); 8.16 (*d*, 4 H *o* to NO_2 (npe)); 7.49 (2*d*, 4 H *m* to NO_2 (npe)); 4.94 (*d*, H–C(1′)); 4.57 (*t*, 4 H, OCH_2CH_2 (npe)); 4.23 (*m*, H–C(3′)); 4.15–3.82 (*m*, H–C(2′), H–C(4′), 2 H–C(5′)); 3.21 (*t*, 4 H, OCH_2CH_2 (npe)); 2.82 (*d*, OH–C(2′)); 1.03 (*m*, 4 Me_2CH). Anal. calc. for $C_{37}H_{52}N_4O_{11}Si_2$ (785.0): C 56.61, H 6.68, N 7.14; found: C 56.48, H 6.68, N 7.10.

5,6-Dihydro-3′,5′-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)uridine (**7**). In dry pyridine (2 × 15 ml), 5,6-dihydrouridine (**14**) [46] (3.17 g, 12.8 mmol) was co-evaporated, taken up in pyridine (75 ml), and under ice-cooling, 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane (4.45 ml, 14.2 mmol) was added. After 20 h stirring at r.t., the solvent was evaporated, the residue taken up in CH_2Cl_2/0.5N HCl (200 ml each), and the org. phase washed with 0.25N $NaHCO_3$, dried (Na_2SO_4), and evaporated. Final evaporations were done with toluene. The crude product which crystallized from hexane/Et_2O 4:1 at −18° (M.p. 113–115°) was used directly for the synthesis of **35**.

S^4-[2-(4-Nitrophenyl)ethyl]-3′,5′-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)-4-thiouridine (**8**). As described for **7**, with pyridine (3 × 20 ml), **17** (4.1 g, 10 mmol), pyridine (150 ml), and 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane (3.3 ml, 10.5 mmol). The crude product was purified by FC (250 g of silica gel, toluene/AcOEt 4:1 (500 ml), 3:1 (1 l), and 3:2 (1 l)): 5.1 g (79%) of pure **8**. Colorless foam. TLC (toluene/AcOEt 1:1): R_f 0.60. UV (MeOH): 280 (sh, 4.28), 301 (4.29), 316 (sh, 4.11). ^{1}H-NMR ($CDCl_3$): 8.15 (*d*, 2 H *o* to NO_2 (npe)); 7.45 (*d*, 2 H *m* to NO_2 (npe)); 5.75 (*d*, H–C(1′)); 4.20 (*m*, H–C(2′), H–C(3′), H–C(4′), 2 H–C(5′)); 3.45 (*t*, 2 H, OCH_2CH_2 (npe)); 3.15 (*m*, 2 H, OCH_2CH_2 (npe)). Anal. calc. for $C_{29}H_{45}N_3O_8SSi_2 \cdot 0.25$ toluene (652.0): C 54.96, H 7.03, N 6.15; found: C 55.06, H 7.02, N 6.15.

O^4-Methyl-3′,5′-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)uridine (**9**). In dry pyridine (2 × 20 ml), **19** (0.9 g, 3.5 mmol) was co-evaporated and dissolved in pyridine (30 ml), and then 1,3-dichloro-1,1,3,3-tetraisopropyl-1,3-disiloxane (1.2 ml, 3.85 mmol) was added. The mixture was stirred at r.t. for 3 h, treated with MeOH, and after 15 min evaporated. The residue was taken up in $CHCl_3$ (80 ml), the soln. washed with H_2O (2 × 40 ml), dried (Na_2SO_4), and evaporated, the residue co-evaporated with toluene, and the crude product purified by CC (silica gel, 13 × 3.5 cm, toluene/AcOEt 2:1 (600 ml) and 1:1 (200 ml): 1.23 g (70%) of pure **9**. Colorless foam. TLC (toluene/AcOEt 1:1): R_f 0.29. UV (MeOH): 205 (4.09), 218 (sh, 3.95), 275 (3.81). ^{1}H-NMR ($CDCl_3$): 7.99 (*d*, H–C(6)); 5.88 (*d*, H–C(5)); 5.78 (*d*, H–C(1′)); 4.21 (*m*, H–C(2′), H–C(3′), H–C(4′), 2 H–C(5′)); 3.96 (*s*, MeO); 3.05 (*d*, OH–C(2′)); 1.02 (*m*, 4 Me_2CH). Anal. calc. for $C_{22}H_{40}N_2O_7Si_2$ (500.7): C 52.77, H 8.05, N 5.59; found: C 52.53, H 8.27, N 5.50.

O^4-[2-(4-Nitrophenyl)ethyl]-3′,5′-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)uridine (**10**). As described for **9**, with pyridine (2 × 20 ml), **21** (0.59 g, 1.5 mmol), pyridine (15 ml), and 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane (0.52 ml, 1.65 mmol; 5 h at r.t.). CC (40 g of silica gel, 14 × 3 cm, toluene/AcOEt 7:3 (800 ml)) gave 0.56 g (59%) of pure **10**. Colorless foam. TLC (toluene/AcOEt 1:1): R_f 0.65. UV (MeOH): 204 (4.43), 217 (sh, 4.26), 274

(4.22). ^{1}H-NMR ($CDCl_3$): 8.17 (*d*, 2 H *o* to NO_2 (npe)); 7.97 (*d*, H–C(6)); 7.41 (*d*, 2 H *m* to NO_2 (npe)); 5.82 (*d*, H–C(5)); 5.77 (*d*, H–C(1′)); 4.65 (*m*, 2 H, OCH_2CH_2 (npe)); 4.26 (*m*, H–C(2′), H–C(3′), H–C(4′), 1 H–C(5′)); 4.00 (*m*, H–C(5′)); 3.17 (*t*, 2 H, OCH_2CH_2 (npe)); 2.88 (*d*, OH–C(2′)); 1.00 (*m*, 4 Me_2CH). Anal. calc. for $C_{29}H_{45}N_3O_9Si_2$ (653.9): C 54.78, H 7.13, N 6.61; found: C 54.72, H 7.14, N 6.37.

*2′,3′,5′-Tri-*O*-acetyl-*O^2*,*O^4*-bis[2-(4-nitrophenyl)ethyl]pseudouridine* (**12**). In a soln. of toluene, 2′,3′,5′-tri-*O*-acetylpseudouridine (**11**) [47] (1 g, 2.7 mmol) and Ag_2CO_3 (1.9 g, 6.75 mmol) were heated to 90° and then evaporated and co-evaporated. After cooling to 60°, 2-(4-nitrophenyl)ethyl iodide [32] (2.2 g, 8.1 mmol) was added and stirred at r.t. for 64 h. The silver salt was filtered off and the filtrate evaporated. The residue was purified by CC (50 g of silica gel, 20 × 3.5 cm, $CHCl_3$ (200 ml), then $CHCl_3$/acetone 19:1): 1.42 g (79%) of **12**. Yellowish syrup. TLC ($CHCl_3$/acetone 9:1): R_f 0.69. UV (MeOH): 215 (4.38), 268 (4.39). ^{1}H-NMR ((D_6)DMSO): 8.32 (*s*, H–C(6)); 8.15 (*m*, 4 H *o* to NO_2 (npe)); 7.58 (*m*, 4 H *m* to NO_2); 5.22 (*t*, H–C(2′)); 5.07 (*t*, H–C(3′)); 4.84 (*d*, H–C(1′)); 4.64 (*t*, 2 H, OCH_2CH_2 (npe)); 4.57 (*t*, 2 H, OCH_2CH_2 (npe)); 4.28–4.00 (*m*, H–C(4′), 2 H–C(5′)); 3.19 (*t*, 4 H, OCH_2CH_2 (npe)). Anal. calc. for $C_{31}H_{32}N_4O_{13}$ (668.6): C 55.69, H 4.82, N 8.38; found: C 55.86, H 4.94, N 8.36.

O^2*,*O^4*-Bis[2-(4-nitrophenyl)ethyl]pseudouridine* (**13**). A mixture of $MeOH/NH_3$ (20 ml), dioxane (5 ml), and **12** (2.71 g, 4.05 mmol) was stirred in a closed vessel at 60° for 24 h. After evaporation, the residue was co-evaporated with MeOH (3 × 10 ml) and the residue crystallized from EtOH: 2.02 g (92%) of **13**. Colorless needles. TLC ($CHCl_3$/MeOH, 97:3): R_f 0.32. M.p. 81–82°. UV (MeOH): 202 (4.05), 215 (4.40), 2.68 (4.41). ^{1}H-NMR ((D_6)DMSO): 8.42 (*s*, H–C(6)); 8.16 (2*d*, 4 H *o* to NO_2 (npe)); 7.60 (2*d*, 4 H *m* to NO_2); 4.97, 4.87 (2*d*, OH–C(2′), OH–C(3′)); 4.80 (*t*, OH–C(5′)); 4.67 (*d*, H–C(1′)); 4.53 (*m*, 4 H, OCH_2CH_2 (npe)); 3.83–3.81 (*m*, H–C(2′), H–C(3′), H–C(4′), 2 H–C(5′)); 3.18 (*t*, 4 H, OCH_2CH_2 (npe)). Anal. calc. for $C_{25}H_{26}N_4O_{10} \cdot 0.5\ H_2O$ (551.5): C 54.45, H 4.93, N 10.16; found: C 54.42, H 4.96, N 10.03.

*2′,3′,5′-Tri-*O*-benzoyl-*S^4*-[2-(4-nitrophenyl)ethyl]-4-thiouridine* (**16**). In dry butan-2-one (50 ml), 2′,3′,5′-tri-*O*-benzoyl-4-thiouridine (**15**) [47] (1.15 g, 2 mmol), 2-(nitrophenyl)ethyl iodide [32] (0.42 g, 3 mmol), and anh. K_2CO_3 (0.94 g, 3.35 mmol) were heated under reflux in the dark and exclusion of moisture for 2.5 h. After cooling to r.t. and filtering the undissolved material, the filtrate was evaporated and the residue crystallized from MeOH/EtOH 1:1 (75 ml): 1.05 g (73%) of **16**. Colorless crystals. TLC ($CHCl_3$/AcOEt 5:1): R_f 0.87. M.p. 145–147°. UV (MeOH): 204 (4.32), 237 (sh, 3.60), 278 (4.22), 302 (sh, 4.20). ^{1}H-NMR ($CDCl_3$): 8.16–7.33 (*m*, H–C(6), arom. H of npe, bz); 6.32 (*d*, H–C(1′)); 6.04 (*d*. H–C(5)); 5.88 (*dd*, H–C(2′)); 5.79 (*dd*, H–C(3′)); 4.88–4.64 (*m*, H–C(4′), 2 H–C(5′)); 3.44 (*t*, 2 H, OCH_2CH_2 (npe)); 3.10 (*m*, 2 H, OCH_2CH_2 (npe)). Anal. calc. for $C_{38}H_{31}N_3O_{10}S \cdot 0.75\ H_2O$ (735.2): C 62.08, H 4.35, N 5.71; found: C 62.15, H 4.27, N 5.56.

S^4*-[2-(4-Nitrophenyl)ethyl]-4-thiouridine* (**17**). A soln. of **16** (3 g, 0.138 mmol) in sat. NH_3/MeOH (100 ml) was stirred at r.t. for 20 h and then evaporated. The resulting yellow syrup crystallized on standing. The solid was treated with Et_2O (200 ml), filtered, and dried in a desiccator. The Et_2O phase was washed with H_2O (3 × 50 ml) and then the aq. phase evaporated to 40 ml and diluted with MeOH (5 ml) to give a second crop: 1.46 g (85%) of **17**. Yellowish crystal powder. M.p. 178–180°. TLC ($CHCl_3$/MeOH 9:1): R_f 0.44. UV (MeOH): 204 (4.30), 278 (4.22), 302 (4.20). ^{1}H-NMR ((D_6)DMSO): 8.24 (*d*, H–C(6)); 8.16 (*d*, *m*, 2 H *o* to NO_2 (npe)); 7.56 (*d*, 2 H *m* to NO_2 (npe)); 6.44 (*d*, H–C(5)); 5.73 (*d*, H–C(1′)); 5.52–5.02 (*m*, OH–C(2′), OH–C(3′), OH–C(5′)); 4.05–3.85 (*m*, H–C(2′), H–C(3′), H–C(4′)); 3.78–3.52 (*m*, 2 H–C(5′)); 3.47–3.48 (*t*, 2 H, OCH_2CH_2 (npe)); 3.15 (*t*, 2 H, OCH_2CH_2 (npe)). Anal. calc. for $C_{17}H_{19}N_3O_7S \cdot H_2O$ (427.4): C 47.77, H 4.95, N 9.83; found: C 47.89, H 5.00, N 9.71.

O^4*-Methyluridine* (**19**) [48]. a) *Triazolide Method*: At 0°, 1,2,4-1*H*-triazole (6.21 g, 90 mmol) in MeCN (20 ml) was treated with $POCl_3$ (1.87 ml, 20 mmol). Then within 30 min, Et_3N (12.5 ml, 90 mmol) was added dropwise, the mixture stirred for 60 min at 0°, and 2′,3′,5′-tri-*O*-acetyluridine (**18**) [49] in MeCN (60 ml) added and stirred for 16 h at r.t. The reaction was stopped by addition of Et_3N (13 ml) and H_2O (2 ml) and stirring for 15 min. After evaporation, the residue was dissolved in $CHCl_3$ (200 ml), the soln. washed with H_2O and $NaHCO_3$ soln. (2 × 30 ml), dried (Na_2SO_4), and evaporated, and the residue crystallized from H_2O/MeOH: *1-(2,3,5-tri-*O*-acetylribofuranosyl)-4-(1,2,4-1*H*-triazol-1-yl)pyrimidin-2(1*H*)-one*: 3.14 g (75%). Colorless crystals. M.p. 184–186°. UV (MeOH): 213 (4.23), 250 (4.13), 312 (3.83). Anal. calc. for $C_{17}H_{19}N_5O_8$ (421.4): C 48.46, H 4.55, N 16.62; found: C 48.34, H 4.51, N 16.59.

A soln. of 1-(2,3,5-tri-*O*-acetylribofuranosyl)-4-(1,2,4-1*H*-triazol-1-yl)pyrimidin-2(1*H*)-one (0.84 g, 2 mmol) in MeOH (20 ml) was stirred with 1M NaOMe (1 ml) for 4 h at r.t. then neutralized with 1N HCl, evaporated, and co-evaporated with MeOH. The residue was purified by CC (40 g of silica gel, 17 × 3 cm, $CHCl_3$/MeOH 20:1). The resulting foam was crystallized from AcOEt: 0.39 g (76%) of **19**. Colorless crystals. M.p. 140°.

b) *2,4,6-Triisopropylbenzenesulfonyl Chloride* (Tpbs-Cl) *Method*: A mixture of **18** (0.37 g, 1 mmol), Et_3N (0.7 ml, 5 mmol), Tpbs-Cl (0.61 g, 2 mmol), and DMAP (0.01 g, 0.05 mmol) in CH_2Cl_2 (10 ml) was stirred at r.t. for 4 h. MeOH (0.4 ml, 10 mmol), Et_3N (1.4 ml, 10 mmol), and after 30 min, DABCO (0.02 g, 0.2 mmol) were added. After stirring at r.t. for 2.5 h, the mixture was diluted with CH_2Cl_2 (30 ml), washed with H_2O (2 × 10 ml), dried ($MgSO_4$), and evaporated. The acetyl groups of the product were cleaved by treatment with NH_3/MeOH (4 ml) in dioxane (2 ml) for 16 h, evaporation, and co-evaporation with MeOH. Purification by CC (10 g of silica gel, 9 × 1.8 cm, $CHCl_3$/MeOH 20:1) gave 0.17 g (65%) of **19**. Amorphous powder. TLC ($CHCl_3$/MeOH 9:1): R_f 0.65. M.p. 139–140° ([48]: 141–142°). UV (MeOH): 205 (4.22), 218 (sh, 3.96), 276 (3.80). ^{1}H-NMR ((D$_6$)DMSO): 8.30 (*d*, H–C(6)); 6.03 (*d*, H–C(5)); 5.77 (*d*, H–C(1')); 5.45 (*d*, OH–C(3')); 5.15 (*t*, OH–C(5')); 5.02 (*d*, OH–C(2')); 3.92 (*m*, H–C(2'), H–C(3'), H–C(4')); 3.81 (*s*, MeO); 3.63 (*m*, 2 H–C(5')).

c) *2',3',5'-Tri-O-acetyl-O^4-[2-(4-nitrophenyl)ethyl]uridine* (**20**). As described for **12**, with **18** (1.11 g, 3 mmol), Ag_2CO_3 (1.24 g, 4.5 mmol), toluene (40 ml; 75 min reflux), and at 50°, 2 (4-nitrophenyl)ethyl iodide (1.46 g, 5.3 mmol; 50° for 40 h). CC (20 g of silica gel, 8 × 3 cm, toluene/AcOEt 2:1, 1:1, 1:2, and 1:3) gave 1.15 g (74%) of **20**. Colorless foam. TLC (toluene/AcOEt 1:1): R_f 0.37. UV (MeOH): 204 (4.47), 216 (sh, 4.25), 273 (4.20). ^{1}H-NMR ($CDCl_3$): 8.18 (*d*, 2 H *o* to NO_2 (npe)); 7.71 (*d*, H–C(6)); 7.42 (*d*, 2 H *m* to NO_2 (npe)); 6.13 (*d*, H–C(1')); 5.91 (*d*, H–C(5)); 5.34 (*m*, H–C(2'), H–C(3')); 4.66 (*t*, 2 H, OCH_2CH_2 (npe)); 4.40 (*m*, H–C(4'), 2 H–C(5')); 3.16 (*t*, 2 H, OCH_2CH_2 (npe)); 2.13, 2.11 (2*s*, 3 Ac). Anal. calc. for $C_{23}H_{25}N_3O_{11}$ (519.5): C 53.18, H 4.85, N 8.09; found: C 53.70, H 4.71, N 7.67.

O^4-[2-(4-Nitrophenyl)ethyl]uridine (**21**). a) *From* **20**: A soln. of **20** (1.15 g, 2.2 mmol) in dioxane (10 ml) was treated with sat. NH_3/MeOH (20 ml), stirred at r.t. for 16 h, then evaporated, and co-evaporated with MeOH. The residue was purified by CC (30 g of silica gel, 11 × 3 cm, $CHCl_3$/MeOH 20:1). The product was crystallized from AcOEt: 0.73 g (84%) of **21**. Amorphous powder.

b) *Triazolide Method*: A soln. of 1-(2,3,5-tri-*O*-acetylribofuranosyl)-4-(1,2,4-1*H*-triazol-1-yl)pyrimidin-2(1*H*)-one (1.26 g, 3 mmol), in toluene (30 ml) was refluxed with 2-(4-nitrophenyl)ethanol [50] (1.25 g, 7.5 mmol) and Et_3N (1.1 ml, 7.5 mmol) for 66 h, and finally evaporated. The residue was purified by CC (50 g of silica gel, 19 × 3 cm, toluene/$CHCl_3$/AcOEt 1:1:1). The pure product was treated with NH_3/MeOH as above. CC (20 g of silica gel, 16 × 2 cm, $CHCl_3$/MeOH 20:1) gave 0.27 g (23%) of **21**: Colorless powder.

c) *Tpbs-Cl Method*: As described for **19**, with **18** (0.37 g, 1 mmol), Et_3N (0.7 ml, 5 mmol), Tpbs-Cl (0.61 g, 2 mmol), DMAP (0.01 g, 0.05 mmol), CH_2Cl_2 (10 ml) 2-(4-nitrophenyl)ethanol (0.84 g, 5 mmol) instead of MeOH. Et_3N (1.4 ml, 10 mmol), and DABCO (0.02 g, 0.2 mmol; 21 h). The intermediate triacetate was purified by CC (40 g of silica gel, 16 × 3 cm, toluene/AcOEt 3:1 (200 ml); 2:1 (300 ml), and 1:1 (400 ml)): The acetyl groups were cleaved as described for **19**. CC (30 g of silica gel, 11 × 3 cm, $CHCl_3$/MeOH 20:1 (500 ml)) gave 0.29 g (68%) of **21**. Amorphous powder. TLC ($CHCl_3$/MeOH 19:1): R_f 0.78. M.p. 147–148°. UV (MeOH): 204 (4.43), 214 (sh, 4.28), 275 (4.22). ^{1}H-NMR ((D$_6$)DMSO): 8.29 (*d*, H–C(6)); 8.17 (*d*, 2 H *o* to NO_2 (npe)); 7.58 (*d*, 2 H *m* to NO_2 (npe)); 5.98 (*d*, H–C(5)); 5.76 (*d*, H–C(1')); 5.44 (*d*, OH–C(3')); 5.14 (*t*, OH–C(5')); 5.02 (*d*, OH–C(2')); 4.52 (*t*, 2 H, OCH_2CH_2 (npe)); 3.90 (*m*, H–C(2'), H–C(3'), H–C(4')); 3.70 (*m*, H–C(5')); 3.56 (*m*, 1 H–C(5')); 3.16 (*t*, 2 H, OCH_2CH_2 (npe)). Anal. calc. for $C_{17}H_{19}N_3O_8$ (393.4): C 51.91, H 4.87, N 10.68; found: C 51.42, H 4.90, N 10.69.

O^4-[2-(4-Cyanophenyl)ethyl]uridine (**22**). *Tpbs-Cl Method*: As described for **19**, with **18** (0.37 g, 1 mmol), Et_3N (0.7 ml, 5 mmol), Tpbs-Cl (0.61 g, 2 mmol), DMAP (0.01 g, 0.05 mmol), CH_2Cl_2 (10 ml), 2-(4-cyanophenyl)ethanol [33] (0.74 g, 5 mmol) instead of MeOH, Et_3N (1.4 ml, 10 mmol), and DABCO (0.02 g, 0.2 mmol; 3.5 h). After CC (20 g of silica gel, 15 × 2 cm), toluene/AcOEt 3:1 (200 ml), 2:1 (300 ml) and 1:1 (300 ml), the acetyl groups were cleaved as described for **19**. CC (10 g of silica gel, 11 × 3 cm, $CHCl_3$/MeOH 25:1 (300 ml)) gave 0.25 g (66%) of **22**. Amorphous powder which was crystallized from acetone to give colorless needles. TLC ($CHCl_3$/MeOH): R_f 0.61. M.p. 152–154°. UV (MeOH): 204 (4.46), 229 (4.32), 236 (sh, 4.24), 274 (3.88). ^{1}H-NMR ((D$_6$)DMSO): 8.29 (*d*, H–C(6)); 7.77 (*d*, 2 H *o* to CN (cpe)); 7.50 (*d*, 2 H *m* to CN (cpe)); 5.98 (*d*, H–C(5)); 5.76 (*d*, H–C(1')); 5.44 (*d*, OH–C(3')); 5.14 (*t*, OH–C(5')); 5.02 (*d*, OH–C(2')); 4.49 (*t*, 2 H, OCH_2CH_2 (npe)); 3.90 (*m*, H–C(2'), H–C(3'), H–C(4')); 3.71 (*m*, 1 H–C(5')); 3.56 (*m*, 1 H–C(5')); 3.10 (*t*, 2 H, OCH_2CH_2 (npe)). Anal. calc. for $C_{18}H_{19}N_3O_6$ (373.4): C 57.91, H 5.13, N 11.25; found: C 57.81, H 5.22, N 11.17.

'Ribothymidine' (= *5-Methyluridine* = *Ribosylthymine*; **23**) [50]. A suspension of thymine (12.6 g, 0.1 mol) in hexamethyldisilazane (HMDS) (100 ml) and NH_4SO_4 (100 mg) was refluxed for 20 h in an oil-bath of 140°, whereby a clear soln. was obtained after 3 h. Excess of HMDS was removed *in vacuo* and the remaining syrup was distilled at 0.01 Torr. The fraction distilling between 71 and 74°, *i.e.*, 24.8 g (90%) of 5-methyl-2,4-bis(trimethylsilyloxy)pyrimidine, was dissolved in 1,2-dichloroethane (70 ml) and added to a soln. of 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl ribofuranose (40.4 g, 0.08 mol) in dry 1,2-dichloroethane (200 ml) and cooled in an ice-bath. Dry $SnCl_4$ (15.66 g, 0.06 mol) in 1,2-dichloroethane (50 ml) was added dropwise with vigorous stirring (→clear pale yellow soln.). After stirring at r.t. for 20 h, a sat. $NaHCO_3$ soln. (100 ml) was added dropwise with vigorous stirring, the mixture filtered through *Celite*, and the org. layer dried (Na_2SO_4) and evaporated to give a colorless solid. Crystallization from EtOH/Et_2O gave 46 g (95%) of *2,3,5-tri-O-benzoylribosylthymine*. M.p. 167–168°. Debenzoylation was achieved by treatment of 10 g (9.4 mmol) with 0.018M NaOMe (200 ml) and by stirring and refluxing for 30 min. MeOH was evaporated and the residue treated with dry EtOH (2 × 20 ml) to remove methyl benzoate. The

yellowish solid was dissolved in H_2O (100 ml) and treated with activated *Lewatit* (H^+-resin) until the soln. became neutral. The resin was filtered off, the filtrate evaporated and co-evaporated with EtOH, and the residue crystallized from EtOH: 4.65 g (93%) of **23**. M.p. 183–184° ([50]: 183–185°).

*2′,3′,5′-Tri-*O*-acetylribosylthymine* (**24**). Ribosylthymine (**23**; 2.58 g, 1 mmol) was co-evaporated with anh. pyridine and then dissolved in pyridine (20 ml), and Ac_2O (3.1 ml, 3.3 mmol) was added dropwise and the clear soln. stirred at r.t. for 10 h. The solvent was evaporated and the residue dissolved in CH_2Cl_2 (50 ml), washed with $NaHCO_3$ (3 × 20 ml), dried (Na_2SO_4), and evaporated to a gum. CC (50 g of silica gel, $CHCl_3$) gave 3.62 g (94%) of **24**. Amorphous powder. TLC ($CHCl_3$/MeOH 19:1): R_f 0.38 UV (MeOH): 209 (4.00), 261 (3.96). ^1H-NMR ($CDCl_3$): 9.25 (*s*, NH); 7.20 (*s*, H–C(6)); 6.05 (br. *s*, H–C(1′)); 5.42 (*m*, H–C(2′), H–C(3′)); 4.38 (*m*, H–C(4′), 2 H–C(5′)); 2.26, 2.23, 2.18 (3*s*, 3 Ac); 1.88 (*s*, Me). Anal. calc. for $C_{16}H_{20}N_2O_9$ (402.4): C 47.76, H 5.51, N 6.96; found: C 47.55, H 5.56, N 6.71.

*2′,3′,5′-Tri-*O*-acetyl-*O*^{4}-(triisopropylbenzenesulfonyl)ribosylthymine* (**25**). A soln. of **24** (1.92 g, 5 mmol) in CH_2Cl_2 (40 ml) was treated with Et_3N (3.5 ml, 25 mmol), DMAP (0.03 g, 2.5 mmol), and Tpbs-Cl (3.05 g, 10 mmol). The mixture was stirred at r.t. for 4 h and diluted with $CHCl_3$. The org. phase was washed with H_2O (3 × 15 ml), dried (Na_2SO_4), and evaporated to a red syrup. CC (50 g of silica gel, 10–30% AcOEt/hexane) gave 2.5 g (76%) of **25** which was crystallized from $CHCl_3$. TLC ($CHCl_3$/MeOH 19:1): R_f 0.59. UV (MeOH): 204 (4.79), 234 (4.10), 287 (3.91). ^1H-NMR ($CDCl_3$): 7.62 (*s*, H–C(6)); 7.20 (*s*, 2 arom. H); 6.05 (*d*, H–C(1′)); 5.35 (*m*, H–C(2′), H–C(3′)); 4.38 (*m*, H–C(4′), 2 H–C(5′)); 4.28 (*m*, 3 Me_2CH); 2.20–2.10 (4*s*, 3 Ac, Me–C(5)); 1.35 (*m*, 3 Me_2CH). Anal. calc. for $C_{31}H_{42}N_2O_{11}S$ (650.7): C 57.21, H 6.50, N 4.30; found: C 57.38, H 6.53, N 4.23.

O^4*-2-[4-(Cyanophenyl)ethyl]ribosylthymine* (**26**). A soln. of **25** (0.65 g, 1 mmol) in CH_2Cl_2 (20 ml) was treated with Et_3N (0.151 g, 1.5 mmol), DABCO (0.01 g, 0.1 mmol), and 2-(4-cyanophenyl)ethanol (0.221 g, 1.5 mmol) and stirred at r.t. for 24 h. The mixture was diluted with $CHCl_3$ (20 ml), washed with H_2O (3 × 10 ml), dried (Na_2SO_4), evaporated, and co-evaporated with toluene. CC (20 g of silica gel, $CHCl_3$) gave 0.45 g (58%) of syrup *2′,3′,5′-tri-*O*-acetyl-*O*^{4}-2-[4-(cyanophenyl)ethyl]ribosylthymine*. A soln. of 0.77 g (1 mmol) of this syrup was taken up in dioxane, treated with sat. NH_3/MeOH, stirred at r.t. for 18 h, and evaporated. CC (20 g of silica gel, $CHCl_3$/MeOH 99:1) gave a colorless foam which was crystallized from acetone to give 0.36 g (73%) of **26**. TLC ($CHCl_3$/MeOH 9:1): R_f 0.43. UV (MeOH): 226 (4.31), 270 (3.80). ^1H-NMR ($CDCl_3$/(D_6)DMSO): 8.10 (*s*, H–C(6)); 7.63 (*d*, 2 H *o* to CN (cpe)); 7.40 (*d*, 2 H *m* to CN (cpe)); 5.85 (*d*, H–C(1′)); 5.29 (*d*, OH–C(2′)); 4.85 (*t*, OH–C(5′)); 4.60 (*t*, 2 H, OCH_2CH_2 (cpe)); 4.33 (*d*, H–C(2′)); 4.22 (*m*, H–C(3′)); 4.18 (*m*, H–C(4′)); 3.80 (*m*, 2 H–C(5′)); 3.14 (*t*, 2 H, OCH_2CH_2 (cpe)); 1.88 (*s*, Me–C(5)). Anal. calc. for $C_{19}H_{21}N_3O_6 \cdot H_2O$ (405.4): C 56.29, H 5.71, N 10.36; found: C 56.67, H 5.81, N 10.30.

O^4*-2-[4-(Nitrophenyl)ethyl]ribosylthymine* (**27**). As described for **26**, with **25** (5.0 g, 7.7 mmol), CH_2Cl_2 (50 ml), Et_3N (1.7 g, 17 mmol), DABCO (0.1 g), and 2-(4-nitrophenyl)ethanol (1.67 g, 10 mmol). The crude (no CC) syrupy triacetate was taken up in dioxane (20 ml) and treated with sat. NH_3/MeOH (20 ml), the mixture stirred at r.t. for 20 h and evaporated, and the syrup purified by CC (60 g of silica gel, $CHCl_3$/MeOH 49:1). The colorless foam was treated with Et_2O to give 2.2 g (70%) of **27**. M.p. 156–157°. TLC ($CHCl_3$/MeOH 19:1): R_f 0.12. UV (MeOH): 204 (4.44), 276 (4.12). ^1H-NMR ($CDCl_3$): 8.18–7.63 (*d*, 2 H *o* to NO_2 (npe)); 8.10 (*s*, H–C(6)); 7.46 (*d*, 2 H *m* to NO_2 (npe)); 5.88 (*d*, H–C(1′)); 5.28 (*d*, OH–C(2′)); 4.85 (*t*, OH–C(5′)); 4.65 (*t*, 2 H, OCH_2CH_2 (npe)); 4.30 (*d*, OH–C(5′)); 4.20 (*m*, H–C(2′), H–C(3′)); 4.10 (*m*, H–C(4′)); 3.90 (*m*, H–C(5′)); 3.78 (*m*, 1 H–C(5′)); 3.22 (*t*, 2 H, OCH_2CH_2 (npe)); 1.90 (*s*, Me–C(5)). Anal. calc. for $C_{18}H_{21}N_3O_8 \cdot H_2O$ (429.4): C 50.82, H 5.45, N 9.87; found: C 50.64, H 5.43, N 9.79.

N^2*-[2-(4-Nitrophenyl)ethoxycarbonyl]-*O*^{6}-[2-(4-nitrophenyl)ethyl]guanosine* (**28**). In dry dioxane (150 ml), 2′,3′-5′-tri-*O*-acetylguanosine [53] (10.1 g, 24.6 mmol), PPh_3 (9.8 g, 37.4 mmol), and 2-(4-nitrophenyl)ethanol [33] (5.85 g, 35 mmol) were stirred at 60°. Diethyl azodicarboxylate (5.88 ml, 37.5 mmol) was added (→clear soln.). After stirring at 60° for 1 h, the mixture was cooled to r.t. and evaporated. The residue was taken up in CH_2Cl_2 (30 ml), and on keeping it in a refrigerator, 2.6 g (41%) of diethyl hydrazine-1,2-dicarboxylate crystallized out. It was filtered off and washed with cold CH_2Cl_2. The filtrate was evaporated, the residue taken up in CH_2Cl_2/Et_2O 1:1, and the mixture submitted to CC (silica gel, 30 × 3.5 cm), Et_2O (500 ml), Et_2O/CH_2Cl_2 9:1, 4:1, and 1:1, CH_2Cl_2 (250 ml), CH_2Cl_2/MeOH 49:1, CH_2Cl_2/MeOH 19:1: *2′,3′,5′-tri-*O*-acetyl-*O*^{6}-[2-(4-nitrophenyl)ethyl]guanosine* as a syrup. After co-evaporation with pyridine (2 × 50 ml), the residue was taken up in pyridine (100 ml), cooled to 0°, and then a soln. of 2-(4-nitrophenyl)ethoxycarbonyl chloride [32] (8.04 g, 35 mmol) in CH_2Cl_2 (100 ml) was added dropwise within 10 min. After stirring at r.t. for 18 h, the solvent was evaporated. Co-evaporation with toluene (3 × 50 ml) and purification by CC (silica gel, 40 × 3.5 cm, CH_2Cl_2 (800 ml), $CHCl_3$) gave *2′,3′,5′-tri-*O*-acetyl-*N*^{2}-[2-(4-nitrophenyl)ethoxycarbonyl]-*O*^{6}-[2-(4-nitrophenyl)ethyl]guanosine* as a syrup. For deacetylation, the syrup was dissolved in MeOH (50 ml) and dioxane (50 ml), the soln. treated with 25% NH_3/H_2O, kept at 8° for 20 h, and evaporated, and the residue co-evaporated with toluene/MeOH 1:1. The resulting solid was crystallized from

MeOH/Et_2O 1:1 (100 ml): 7.4 g (48%) of **28**. Cream-colored amorphous powder. Evaporation of the mother liquor, CC (silica gel, 20 × 3.5 cm, CH_2Cl_2, $CHCl_3$), and crystallization gave another 0.5 g of **28**. Total yield 7.9 g (51%). The anal. probe was crystallized from MeOH/H_2O. TLC ($CHCl_3$/MeOH 9:1): R_f 0.50. M.p. 172–174°. UV (MeOH): 216 (4.62), 269 (4.53). ^{1}H-NMR ($CDCl_3$): 10.37 (*s*, NH); 8.42 (*s*, H–C(8)); 8.17 (*m*, 4 H *o* to NO_2 (npe, npeoc)); 7.64 (*d*, 2 H *m* to NO_2 (npe)); 7.61 (*d*, 2 H *m* to NO_2 (npeoc)); 7.27 (*s*, NH); 5.89 (*s*, H–C(1')); 5.49 (*d*, OH–C(2')); 5.20 (*d*, OH–C(3')); 4.98 (*t*, OH–C(5')); 4.77 (*t*, 2 H, OCH_2CH_2 (npeoc)); 4.60 (*m*, H–C(2')); 4.38 (*t*, 2 H, OCH_2CH_2 (npe)); 4.18 (*m*, H–C(3')); 3.92 (*m*, H–C(4')); 3.72–3.42 (*m*, 2 H–C(5')); 3.30 (*t*, 2 H, OCH_2CH_2 (npe)); 3.10 (*t*, 2 H, OCH_2CH_2 (npeoc)). Anal. calc. for $C_{27}H_{27}N_7O_{11} \cdot H_2O$ (643.5): C 50.38, H 4.54, N 15.23; found: C 50.40, H 4.38, N 15.25.

2-(4-Nitrophenyl)ethanesulfonyl Chloride (Npes-Cl) [38]. To a soln. of 2-(4-nitrophenyl)ethyl chloride [39] (20 g, 0.107 mol) in 50% MeOH/H_2O (480 ml) was added $Na_2S_2O_3 \cdot 5\ H_2O$ (54 g, 0.216 mol). The mixture was refluxed for 7–8 h, filtered hot, and evaporated until the thiosulfate salt began to crystallize. The mixture was chilled to 10°, diluted with ice (500 g) and AcOH (260 ml), and stirred vigorously while Cl_2 gas was passed through the soln. as rapidly as possible. The temp. was maintained below 10° by adding ice to the mixture. The reaction was over when the temp. remained constant (30 min). The precipitate was filtered, washed with excess of H_2O, and dried at 50°: 25.4 g (95%) of colorless crystals. M.p. 85°. TLC ($CHCl_3$): R_f 0.75. UV (MeOH): 214 (sh, 3.91), 267 (4.02). ^{1}H-NMR ($CDCl_3$): 8.23 (*d*, 2 H *o* to NO_2); 7.45 (*d*, 2 H *m* to NO_2); 3.96 (*m*, 2 H, SCH_2CH_2); 3.46 (*m*, 2 H, SCH_2CH_2).

N^6-*[2-(4-Nitrophenyl)ethoxycarbonyl]-2'*-O-*[2-(4-nitrophenyl)ethylsulfonyl]-3',5'*-O-*(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)adenosine* (**29**). In dry pyridine, **1** [51] [52] (3.52 g, 5 mmol) was co-evaporated (3 × 20 ml) and then dissolved in pyridine (15 ml). To this soln. Npes-Cl (2.5 g, 10 mmol) was added, the mixture stirred at r.t. for 2 h, and the reaction stopped with H_2O (50 ml). After extraction with $CHCl_3$ (3 × 50 ml), the combined org. layers were dried (Na_2SO_4), evaporated, and co-evaporated with toluene. CC (120 g of silica gel, 42 × 3.5 cm, CH_2Cl_2/$CHCl_3$ 1:1) gave 4.32 g (94%) of **29**. Amorphous powder. TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.88. UV (MeOH): 210 (sh, 4.62), 267 (4.60). ^{1}H-NMR ($CDCl_3$): 8.61 (*s*, H–C(8)); 8.57–8.10 (*m*, NH, H–C(2), 4 H *o* to NO_2 (npe)); 7.44 (*d*, 4 H *m* to NO_2 (npe)); 6.12 (*d*, H–C(1')); 5.52 (*d*, H–C(2')); 5.02–4.97 (*q*, H–C(3')); 4.51 (*t*, 2 H, OCH_2CH_2 (npeoc)); 4.23–3.97 (*m*, H–C(4'), 2 H–C(5')); 3.66 (*m*, 2 H, SCH_2CH_2 (npes)); 3.36 (*m*, 2 H, SCH_2CH_2 (npes)); 3.14 (*t*, 2 H, OCH_2CH_2 (npeoc)); 1.23–0.88 (*m*, 4 Me_2CH). Anal. calc. for $C_{39}H_{53}N_7O_{13}SSi_2$ (916.1): C 51.15, H 5.83, N 10.70; found: C 51.14, H 5.59, N 10.59.

N^4-*[2-(4-Nitrophenyl)ethoxycarbonyl]-2'*-O-*[2-(4-nitrophenyl)ethylsulfonyl]-3',5'*-O-*(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)cytidine* (**30**). As described for **29**, with **2** [52] (2.59 g, 3.8 mmol), pyridine (3 × 10 ml), pyridine (30 ml), and Npes-Cl (1.90 g, 7.6 mmol; 1 h). CC (80 g of silica gel, 20 × 3.5 cm, CH_2Cl_2/$CHCl_3$ 1:1) gave 2.4 g (71%) of **30**. Colorless foam. TLC ($CHCl_3$): 0.41. UV (MeOH): 213 (sh, 4.47), 263 (4.33). ^{1}H-NMR ($CDCl_3$): 8.17 (*dd*, H–C(6), 4 *o* to NO_2 (npe)); 7.65 (*s*, NH); 7.51 (*d*, 2 H *m* to NO_2 (npe)); 7.38 (*d*, 2 H *m* to NO_2 (npe)); 7.22 (*d*, H–C(5)); 5.77 (*s*, H–C(1')); 4.94 (*d*, H–C(2')); 4.43 (*t*, 2 H, OCH_2CH_2 (npeoc)); 4.01 (*m*, 6 H, H–C(3'), H–C(4'), 2 H–C(5'), SCH_2CH_2 (npes)); 3.34 (*t*, 2 H, SCH_2CH_2 (npes)); 3.10 (*t*, 2 H, OCH_2CH_2 (npeoc)); 1.05 (*m*, 4 Me_2CH). Anal. calc. for $C_{38}H_{53}N_5O_{14}SSi_2$ (892.1): C 51.16, H 5.99, N 7.85; found: C 51.15, H 6.33, N 7.84.

N^2-*[2-(4-Nitrophenyl)ethoxycarbonyl]*-O^6-*[2-(4-nitrophenyl)ethyl]-2'*-O-*[2-(4-nitrophenyl)ethylsulfonyl]-3',5'*-O-*(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)guanosine* (**31**). As described for **29**, with **3** [52] (2.6 g, 3 mmol), pyridine (3 × 10 ml), pyridine (20 ml), and Npes-Cl (1.49 g, 6 mmol; 3 h). CC (190 g of silica gel, 50 × 4.5 cm, $CHCl_3$ (1 l)) gave 2.6 g (82%) of **31**. Amorphous powder. Further purification by prep. TLC (silica gel, 20 × 20 × 0.2 cm, $CHCl_3$/MeOH 49:1; desorption with $CHCl_3$/MeOH 4:1) led to anal. pure material. TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.57. UV (MeOH): 214 (4.65), 269 (4.59). ^{1}H-NMR ($CDCl_3$): 7.93–7.86 (*m*, 6 H *o* to NO_2 (npe)); 7.27–7.02 (*d*, 6 H *m* to NO_2 (npe), NH, H–C(8)); 5.80 (*s*, H–C(1')); 5.16 (*d*, H–C(2')); 4.55–4.43 (*m*, 3 H, H–C(3'), OCH_2CH_2 (npe)); 4.12–3.98 (*m*, 3 H, H–C(4'), OCH_2CH_2 (npeoc)); 3.87–3.74 (*t*, 2 H, SCH_2CH_2 (npes)); 3.60–3.45 (*m*, 2 H–C(5')); 3.17–3.04 (*m*, 4 H, OCH_2CH_2 (npe, npeoc)); 2.82 (*m*, 2 H, SCH_2CH_2 (npes)); 1.07–0.74 (*m*, 4 Me_2CH). Anal. calc. for $C_{47}H_{60}N_8O_{16}SSi_2$ (1081.3): C 52.21, H 5.59, N 10.36; found: C 52.25, H 5.69, N 10.21.

2'-O-*[2-(4-Nitrophenyl)ethylsulfonyl]-3',5'*-O-*(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)uridine* (**32**). As described for **29**, with 3',5'-*O*-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)uridine (**4**) [40] [52] (0.25 g, 0.5 mmol) in dry pyridine (3 ml) and Npes-Cl (0.263 g, 1 mmol; 1 h). Workup with H_2O (20 ml) and $CHCl_3$ (3 × 20 ml) followed by prep. TLC (silica gel, 20 × 20 × 0.2 cm, $CHCl_3$/MeOH 49:1, desorption with $CHCl_3$/MeOH 4:1) gave 0.27 g (75%) of **32**. Colorless foam. TLC ($CHCl_3$/MeOH 49:1): R_f 0.39. UV (MeOH): 213 (sh, 4.17), 263 (4.30). ^{1}H-NMR ($CDCl_3$): 9.40 (*s*, NH); 8.16 (*d*, 2 H *o* to NO_2 (npes)); 7.78 (*d*, H–C(6)); 7.46 (*d*, 2 H *m* to NO_2 (npes)); 5.72 (*d*, H–C(5)); 5.66 (*s*, H–C(1')); 4.95 (*d*, H–C(2')); 4.31–4.22 (*m*, H–C(3'), H–C(4')); 4.05–3.94 (*m*, 2 H–C(5')); 3.80–3.29 (*m*, 4 H, SCH_2CH_2 (npes)); 1.27–0.89 (*m*, 4 Me_2CH). Anal. calc. for $C_{29}H_{45}N_3O_{11}SSi_2$ (699.9): C 49.76, H 6.48, N 6.00; found: C 50.00, H 6.40, N 6.31.

2′-O-[2-(4-Nitrophenyl)ethylsulfonyl]-3′,5′-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)pseudouridine (**33**). As described for **29**, with **5** (0.3 g, 0.62 mmol) in dry pyridine (6 ml) and Npes-Cl (0.23 g, 0.93 mmol, 2.5 h). Workup by evaporation, co-evaporation with toluene, extraction with $CHCl_3$ (40 ml) and H_2O (3 × 20 ml), and CC (20 g of silica gel, *d* 3.5 cm, $CHCl_3$ (200 ml)) gave 0.36 g (84%) of **33**. Colorless foam. TLC ($CHCl_3$/MeOH 49:1): R_f 0.38. UV (MeOH): 204 (4.33), 208 (4.29), 265 (4.26). ^{1}H-NMR ($CDCl_3$): 9.82 (br. *s*, H−N(3)); 9.57 (br. *d*, H−N(1)); 8.16 (*d*, 2 H *o* to NO_2 (npes)); 7.53 (*d*, H−C(6)); 7.47 (*d*, 2 H *m* to NO_2 (npes)); 4.98 (*d*, H−C(2′)); 4.82 (br. *d*, H−C(1′)); 4.31–3.58 (*m*, H−C(3′), H−C(4′), 2 H−C(5′), 2 H of SCH_2CH_2 (npes)); 3.37 (*t*, 2 H, SCH_2CH_2 (npes)); 1.08 (*m*, 4 Me_2CH). Anal. calc. for $C_{29}H_{45}N_3O_{11}SSi_2$ (699.9): C 49.77, H 6.48, N 6.00; found: C 49.87, H 6.42, N 5.89.

O^2,O^4-Bis[2-(4-nitrophenyl)ethyl]-2′-O-[2-(4-nitrophenyl)ethylsulfonyl]-3′,5′-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)pseudouridine (**34**). A soln. of **6** (1.02 g, 1.3 mmol) in pyridine (13 ml) was treated with Npes-Cl (0.487 g, 1.95 mmol) and stirred at r.t. for 3 h. After removal of the solvent, the residue was co-evaporated with toluene and taken up in AcOEt (70 ml), the soln. washed with sat. NaCl soln. (3 × 40 ml), dried (Na_2SO_4), and evaporated, and the residue purified by CC (50 g of silica gel, *d* 3.5 cm, toluene/AcOEt 9:1 (400 ml)): 1.11 g (86%) of **34**. Colorless foam. TLC (toluene/AcOEt 9:1): R_f 0.31. UV (MeOH): 203 (4.60), 214 (4.50), 268 (4.54). ^{1}H-NMR ($CDCl_3$): 8.50 (*s*, H−C(6)); 8.18 (*m*, 6 H *o* to NO_2 (npe)); 7.49–7.38 (*m*, 6 H *m* to NO_2 (npe)); 5.15 (*s*, H−C(2′)); 5.09 (*s*, H−C(1′)); 4.67 (*d*, 2 H, OCH_2CH_2 (npe)); 4.58 (*t*, 2 H, OCH_2CH_2 (npe)); 4.38–3.90 (*m*, H−C(3′), H−C(4′), 2 H−C(5′)); 3.63–3.17 (*m*, 8 H, 2 OCH_2CH_2 (npe), 2 SCH_2CH_2 (npes)); 1.10–0.88 (*m*, 4 Me_2CH). Anal. calc. for $C_{43}H_{59}N_5SSi_2$ (998.2): C 54.14, H 5.96, N 7.02; found: C 53.80, H 5.94, N 6.79.

5,6-Dihydro-2′-O-[2-(4-nitrophenyl)ethylsulfonyl]-3′,5′-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)uridine (**35**). A soln. of **7** (crude; from 3.17 g (12.8 mmol) of **14**; see above) in pyridine (150 ml) was treated with Npes-Cl (5.62 g, 22.5 mmol) at r.t. with stirring for 90 min. MeOH (10 ml) was added, after evaporation the residue taken up in CH_2Cl_2 (75 ml), the soln. washed with 0.1M phosphate buffer (pH 7.0), dried (Na_2SO_4), evaporated, and co-evaporated with toluene, and the residue purified by FC (250 g of silica gel, *d* 6 cm, hexane/AcOEt 7:3, 7:5, and 5:7): 2.97 g (33%) of **35**. Yellowish foam. Crystallization could be achieved with AcOEt/hexane 1:3 at −18°. TLC (hexane/AcOEt/Et_3N 7:7:1): R_f 0.65. M.p. 77–79°. UV (MeOH): 203 (4.18), 269 (4.02). Anal. calc. for $C_{29}H_{47}N_3O_{11}SSi_2$ (701.9): C 49.62, H 6.75, N 5.99; found: C 49.90, H 6.73, N 5.58.

S^4-[2-(4-Nitrophenyl)ethyl]-2′-O-[2-(4-nitrophenyl)ethylsulfonyl]-3′,5′-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)-4-thiouridine (**36**). As described for **35**, with **8** (1.5 g, 2.3 mmol), pyridine (20 ml), Npes-Cl (0.875 g, 3.5 mmol), and MeOH (2 ml). On evaporation after CC (60 g of silica gel, *d* 3 cm, hexane/AcOEt/Et_3N 7:3:1), the product began to crystallize, and to complete the crystallization, petroleum ether was added dropwise. After cooling to 4° for 20 h, the crystals were collected and dried: 1.39 g (70%) of **36**. Yellow powder. M.p. 135–137°. TLC (hexane/AcOEt/Et_3N 7:3:1): R_f 0.70. UV (MeOH): 274 (4.47), 290 (sh, 4.41), 301 (sh, 4.35), 313 (sh, 4.17). ^{1}H-NMR ($CDCl_3$): 8.20–8.15 (*m*, 4 H *o* to NO_2 (npe)); 7.50–7.40 (*m*, 4 H *m* to NO_2 (npe)); 5.68 (*s*, H−C(1′)); 4.95 (*d*, H−C(2′)); 4.25 (*m*, H−C(3′)); 4.15 (*m*, H−C(4′), 2 H−C(5′)); 3.70–3.40 (*m*, 4 H, OCH_2CH_2 (npe), SCH_2CH_2 (npes)); 3.55–3.15 (*m*, 4 H, OCH_2CH_2 (npe), SCH_2CH_2 (npes)); 1.27–0.89 (*m*, 4 Me_2CH). Anal. calc. for $C_{37}H_{52}N_4O_{12}S_2Si_2$ (865.2): C 51.37, H 6.06, N 6.48; found: C 51.36, H 6.05, N 6.42.

O^4-Methyl-2′-O-[2-(4-nitrophenyl)ethylsulfonyl]-3′,5′-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)uridine (**37**). As described for **35**, with **9** (0.89 g, 1.77 mmol), pyridine (15 ml), Npes-Cl (0.88 g, 3.54 mmol; 2.5 h), and MeOH (2 ml). Workup with $CHCl_3$ (60 ml) and H_2O (2 × 20 ml) instead of CH_2Cl_2/buffer. CC (40 g of silica gel, 15 × 3 cm, $CHCl_3$/petroleum ether 7:1 (300 ml)) and 6:1 (300 ml)) gave 0.98 g (78%) of **37**. Colorless foam. TLC (toluene/AcOEt 7:3): R_f 0.62. UV (MeOH): 203 (4.44), 216 (sh, 4.25), 2.60 (4.22). H-NMR ($CDCl_3$): 8.19 (*d*, 2 H *o* to NO_2 (npes)); 8.06 (*d*, H−C(6)); 7.54 (*d*, 2 H *m* to NO_2 (npes)); 5.59 (*d*, H−C(5)); 5.75 (*s*, H−C(1′)); 4.97 (*d*, H−C(2′)); 4.13 (*m*, 5 H, H−C(3′), H−C(4′), 1 H−C(5′), SCH_2CH_2 (npes)); 4.00 (*s*, MeO); 3.71 (*m*, 1 H−C(5′)); 3.38 (*t*, 2 H, SCH_2CH_2 (npes)); 1.06 (*m*, 4 Me_2CH). Anal. calc. for $C_{30}H_{47}N_3O_{11}SSi_2$ (714.0): C 50.47, H 6.64, N 5.89; found: C 50.58, H 6.71, N 5.74.

O^4-[2-(4-Nitrophenyl)ethyl]-2′-O-[2-(4-nitrophenyl)ethylsulfonyl]-3′,5′-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)uridine (**38**). As described for **35**, with **10** (1.27 g, 2 mmol), pyridine (20 ml), Npes-Cl (0.99 g, 4 mmol; 4.5 h), and MeOH (1 ml). Workup with $CHCl_3$ (80 ml) and H_2O (2 × 40 ml) instead of CH_2Cl_2/buffer. CC (60 g of silica gel, 21 × 3 cm, $CHCl_3$/petroleum ether 7:1 (600 ml) and 6:1 (250 ml)) gave 1.39 g (82%) of **38**. Colorless foam. TLC (toluene/AcOEt 7:3): R_f 0.78. UV (MeOH): 204 (4.55), 215 (sh, 4.41), 269 (4.43). ^{1}H-NMR ($CDCl_3$): 8.19 (*d*, 4 H *o* to NO_2 (npe, npes)); 8.06 (*d*, H−C(6)); 7.53 (*d*, 2 H *m* to NO_2 (npes)); 7.42 (*d*, 2 H *m* to NO_2 (npe)); 5.90 (*d*, H−C(5)); 5.73 (*s*, H−C(1′)); 4.96 (*d*, H−C(2′)); 4.67 (*m*, 2 H, OCH_2CH_2 (npe)); 3.99 (*m*, 6 H, H−C(3′), H−C(4′), 2 H−C(5′), SCH_2CH_2 (npes)); 3.38 (*t*, 2 H, SCH_2CH_2 (npes)); 3.19 (*t*, 2 H, OCH_2CH_2 (npe)); 1.05 (*m*, 4 Me_2CH). Anal. calc. for $C_{37}H_{52}N_4O_{12}SSi_2$ (849.1): C 52.34, H 6.17, N 6.60; found: C 52.09, H 6.28, N 6.41.

3′-O-(3-Hydroxy-1,1,3,3-tetraisopropyldisiloxan-1-yl)-N^6-[2-(4-nitrophenyl)ethoxycarbonyl]-2′-O-[2-(4-nitrophenyl)ethylsulfonyl]adenosine (**39**). To a soln. of **29** (4.32 g, 4.7 mmol) in dry dioxane (100 ml) was added 1N

HCl (50 ml). The mixture was stirred at r.t. for 1 h, then neutralized with Et_3N (11 ml), diluted with H_2O (100 ml), and extracted with $CHCl_3$ (3 × 50 ml) and the combined org. phase dried (Na_2SO_4) and evaporated several times with CH_2Cl_2: 4.03 g (88%) of **39**. Amorphous powder. Purification by prep. TLC (40 × 20 × 0.2 cm, $CHCl_3$/MeOH 9:1, desorption with $CHCl_3$/MeOH 4:1). TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.69. UV (MeOH): 210 (sh, 4.59), 266 (4.57). ^1H-NMR ($CDCl_3$): 8.69 (*s*, H–C(8)); 8.19–8.08 (*m*, 4 H *o* to NO_2 (npe)); 7.23 (*d*, 4 H *m* to NO_2 (npe)); 6.18 (*s*, H–C(1′)); 5.74–5.63 (*t*, *m*, H–C(2′), OH–C(5′)); 5.10 (*m*, H–C(3′)); 4.53 (*t*, 2 H, OCH_2CH_2 (npe)); 4.29 (*s*, H–C(4′)); 4.28–3.82 (*m*, 2 H–C(5′)); 3.40–3.06 (*m*, 7 H, OH–Si, OCH_2CH_2 (npe), SCH_2CH_2 (npes)); 1.65–0.89 (*m*, 4 Me_2CH). Anal. calc. for $C_{39}H_{55}N_7O_{14}SSi_2$ (934.1): C 50.14, H 5.93, N 10.49; found: C 49.95, H 5.77, N 10.31.

3′-O-(3-Hydroxy-1,1,3,3-tetraisopropyldisiloxan-1-yl)-N⁴-[2-(4-nitrophenyl)ethoxycarbonyl]-2′-O-[2-(4-nitrophenyl)ethylsulfonyl]cytidine (**40**). As described for **39**, with **30** (1.59 g, 1.78 mmol), dioxane (39 ml), 1N HCl (19 ml; 15 h), Et_3N (4.2 ml), and H_2O (50 ml). CC (120 g of silica gel, 45 × 4.5 cm, $CHCl_3$) gave 1.09 g (69%) of **40**. A small amount (0.1 g) was purified by prep. TLC (40 × 20 × 0.2 cm, twice CH_2Cl_2/AcOEt/hexane 1:1:1, desorption with $CHCl_3$/MeOH 4:1). TLC (CH_2Cl_2/AcOEt/hexane 1:1:1): R_f 0.38. UV (MeOH): 210 (sh, 4.46), 245 (sh, 4.32), 273 (4.42). ^1H-NMR ($CDCl_3$): 8.54 (*d*, H–C(6)); 8.15–8.06 (*m*, 4 H *o* to NO_2 (npe), NH); 7.45 (*dd*, 4 H *m* to NO_2 (npe)); 6.91 (*d*, H–C(5)); 5.75 (*s*, H–C(1′)); 5.35–5.28 (*d*, H–C(2′), OH–C(5′)); 4.58–4.41 (*m*, 3 H, H–C(3′), OCH_2CH_2 (npe)); 4.08–3.90 (*m*, 4 H, H–C(4′), OH–Si, SCH_2CH_2 (npes)); 3.67–3.62 (*m*, 2 H–C(5′)); 3.27 (*t*, 2 H, SCH_2CH_2 (npes)); 3.05 (*t*, 2 H, OCH_2CH_2 (npe)); 1.23–0.79 (*m*, 4 Me_2CH). Anal. calc. for $C_{38}H_{55}N_5O_{15}SSi_2$ (910.1): C 50.15, H 6.09, N 7.70; found: C 49.81, H 6.35, N 7.36.

3′-O-(3-Hydroxy-1,1,3,3-tetraisopropyldisiloxan-1-yl)-N²-[2-(4-nitrophenyl)ethoxycarbonyl]-O⁶-[2-(4-nitrophenyl)ethyl]-2′-[2-(4-nitrophenyl)ethylsulfonyl]guanosine (**41**). As described for **39**, with **23** (1.83 g, 1.8 mmol), dioxane (38 ml), 1N HCl (18 ml; 3 h), Et_3N (4 ml), and H_2O (50 ml): 1.73 g (91%) of **41**. Amorphous powder. A small amount (0.1 g) was purified by prep. TLC (silica gel, 40 × 20 × 0.2 cm, twice with $CHCl_3$/MeOH 100:1, desorption with $CHCl_3$/MeOH 4:1). TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.36. UV (MeOH): 214 (sh, 4.66), 269 (4.61). ^1H-NMR ($CDCl_3$): 9.04 (*s*, NH); 8.18–8.09 (*m*, 6 H *o* to NO_2 (npe)); 7.69 (*s*, H–C(8)); 7.50–7.24 (*m*, 6 H *m* to NO_2 (npe)); 6.02 (*s*, H–C(1′)); 5.72 (*s*, OH–C(5′)); 5.60 (*t*, H–C(2′)); 5.38 (*d*, H–C(3′)); 5.25 (*m*, OH–Si); 4.77–4.70 (*m*, 2 H, OCH_2CH_2 (npe)); 4.50–4.32 (*m*, 2 H, OCH_2CH_2 (npeoc)); 4.11–4.0 (*m*, 2 H, SCH_2CH_2 (npes)); 3.85 (*m*, H–C(4′)); 3.50–3.22 (*m*, 4 H, OCH_2CH_2 (npe, npeoc), 2 H–C(5′)); 3.08 (*t*, 2 H, SCH_2CH_2 (npes)); 1.08–0.85 (*m*, 4 Me_2CH). Anal. calc. for $C_{47}H_{62}N_8O_{16}SSi_2$ (1083.3): C 52.11, H 5.77, N 10.34; found: C 51.34, H 5.81, N 9.84.

3′-O-(3-Hydroxy-1,1,3,3-tetraisopropyldisiloxan-1-yl)-2′-O-[2-(4-nitrophenyl)ethylsulfonyl]uridine (**42**). As described for **39**, with **32** (1.78 g, 2.54 mmol), dioxane (50 ml), 1N HCl (30 ml; 45 min), Et_3N (4 ml), and H_2O (100 ml): 1.81 g (99%) of **44**. Amorphous powder. A small amount (0.1 g) was purified by prep. TLC (silica gel, 20 × 20 × 0.2 cm, twice $CHCl_3$/MeOH 19:1, desorption with $CHCl_3$/MeOH 4:1). TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.67. UV (MeOH): 262 (4.28). ^1H-NMR ($CDCl_3$): 9.23 (*s*, NH); 8.16 (*d*, 2 H *o* to NO_2 (npes)); 8.02 (*d*, H–C(6)); 7.43 (*d*, 2 H *m* to NO_2 (npes)); 5.79 (*d*, H–C(1′)); 5.70 (*d*, H–C(5)); 5.13 (*d*, H–C(2′)); 4.70 (*t*, H–C(3′)); 4.04–3.84 (*m*, OH–Si, H–C(4′), 2 H–C(5′)); 3.64–3.60 (*m*, 2 H, SCH_2CH_2 (npes)); 3.22 (*t*, 2 H, SCH_2CH_2 (npes)); 1.23–0.86 (*m*, 4 Me_2CH). Anal. calc. for $C_{29}H_{47}N_3O_{12}SSi_2$ (717.9): C 48.52, H 6.59, N 5.85; found: C 48.50, H 7.02, N 5.77.

3′-O-(3-Hydroxy-1,1,3,3-tetraisopropyldisiloxan-1-yl)-2′-O-[2-(4-nitrophenyl)ethylsulfonyl]pseudouridine (**43**). As described for **39**, with **33** (0.4 g, 0.57 mmol), dioxane (11 ml), 1N HCl (6.7 ml; 7 h), and Et_3N (0.9 ml; no H_2O). Workup with AcOEt (50 ml) and sat. NaCl soln. CC (25 g of silica gel, *d* 3.5 cm, AcOEt (150 ml), AcOEt/MeOH 9:1 (200 ml)) gave 0.22 g (54%) of **43** and 0.091 g (35%) of *2′-O-[2-(4-nitrophenyl)ethylsulfonyl]pseudouridine* (**57**) as colorless foams. **43**: TLC (CH_2Cl_2/MeOH 9:1): R_f 0.63. UV (MeOH): 204 (4.24), 209 (4.20), 265 (4.21). ^1H-NMR ((D_6)DMSO): 11.30 (*s*, H–N(3)); 11.09 (*d*, H–N(1)); 8.16 (*d*, 2 H *o* to NO_2 (npes)); 7.69 (*d*, H–C(6)); 7.58 (*d*, 2 H *m* to NO_2 (npes)); 5.14 (*t*, OH–C(5′)); 4.89 (*t*, H–C(2′)); 4.85 (br. *d*, H–C(1′)); 4.48 (*m*, H–C(3′)); 3.94–3.18 (*m*, 7 H, H–C(4′), 2 H–C(5′), SCH_2CH_2 (npes)); 0.92 (*m*, 4 Me_2CH). Anal. calc. for $C_{29}H_{47}N_3O_{12}SSi_2$ (717.9): C 48.52, H 6.60, N 5.85; found: C 48.59, H 6.95, N 5.55.

3′-O-(3-Hydroxy-1,1,3,3-tetraisopropyldisiloxan-1-yl)-O²,O⁴-bis[2-(4-nitrophenyl)ethyl]-2′-O-[2-(4-nitrophenyl)ethylsulfonyl]pseudouridine (**44**). As described for **39**, with **34** (0.41 g, 0.41 mmol), dioxane (8 ml), 1N HCl (4.8 ml; 7.5 h), and Et_3N (0.65 ml; no H_2O). Workup with AcOEt (50 ml) and sat. NaCl soln. (3 × 30 ml). CC (40 g of silica gel, *d* 3.5 cm, toluene/AcOEt 3:2 (300 ml)) gave 0.29 g (69%) of **44**. TLC (toluene/AcOEt 1:1). R_f 0.43. UV (MeOH): 202 (4.57), 214 (4.47), 268 (4.51). ^1H-NMR ($CDCl_3$): 8.52 (*d*, H–C(6)); 8.18 (*m*, 6 H *o* to NO_2 (npe)); 7.43 (*m*, 6 H *m* to NO_2 (npe)); 5.19 (*s*, H–C(2′)); 5.10 (*d*, H–C(1′)); 4.89 (br., OH–C(5′)); 4.70–4.52 (*m*, 5 H, H–C(3′), 2 OCH_2CH_2 (npe)); 4.02–3.68 (*m*, H–C(4′), 2 H–C(5′)); 3.57–3.18 (*m*, 8 H, 2 OCH_2CH_2 (npe), SCH_2CH_2 (npes));

1.04–0.83 (*m*, 4 Me_2CH). Anal. calc. for $C_{45}H_{61}N_5O_{16}SSi_2$ (1016.2): C 53.19, H 6.05, N 6.89; found: C 53.13, H 6.17, N 6.69.

5,6-Dihydro-3′-O-(3-hydroxy-1,1,3,3-tetraisopropyldisiloxan-1-yl)-2′-O-[2-(4-nitrophenyl)ethylsulfonyl]-uridine (**45**). A soln. of **35** (2.5 g, 3.56 mmol) in THF (75 ml) was stirred at r.t. for 5 h with AcOH (2 ml), H_2O (120 ml), and Et_3N/trihydrogen fluoride complex (1 ml). The mixture was evaporated to a small volume, the residue taken up in AcOEt (200 ml), and the soln. washed with 1M phosphate buffer (pH 7.0)/sat. $NaHCO_3$/sat. NaCl soln. 1:2:1, dried, and evaporated: 2.38 g (93%) of **45**. Yellow foam. The product was crystallized from $EtOH/H_2O$ 2:1: 1.41 g (55%) of colorless crystals. M.p. 132–134°. TLC (AcOEt): R_f 0.72. UV (MeOH): 203 (4.25), 212 (sh, 4.11), 268 (4.01). ^1H-NMR ($CDCl_3$): 8.15 (*m*, 2 H *o* to NO_2 (npes)); 7.55 (*m*, 2 H *m* to NO_2 (npes)); 6.05 (*s*, H−C(1′)); 5.20 (*m*, H−C(2′)); 4.55 (*m*, H−C(3′)); 3.95 (*m*, H−C(4′)); 3.75 (*m*, 2 H, SCH_2CH_2 (npes)); 3.45 (*m*, 2 H−C(5′)); 3.15 (*t*, 2 H, SCH_2CH_2 (npes)). Anal. calc. for $C_{29}H_{49}N_3O_{12}SSi_2$ (720.0): C 48.38, H 6.86, N 5.84; found: C 48.51, H 6.80, N 5.58.

3′-O-(3-Hydroxy-1,1,3,3-tetraisopropyldisiloxan-1-yl)-5′-O-(monomethoxytrityl)-N^6-[2-(4-nitrophenyl)-ethoxycarbonyl]-2′-O-[2-(4-nitrophenyl)ethylsulfonyl]adenosine (**46**). In dry pyridine (3 × 15 ml), **39** (4.03 g, 4.3 mmol) was co-evaporated and dissolved in pyridine (15 ml). To this soln., monomethoxytrityl chloride (MeOTr-Cl; 3.47 g, 11.2 mmol) was added and stirred at r.t. for 15 h. The mixture was quenched with MeOH (20 ml), evaporated, diluted with $CHCl_3$ (100 ml), and washed with H_2O (100 ml). The aq. phase was extracted back with $CHCl_3$ (50 ml), dried, evaporated, and co-evaporated with toluene (2 × 20 ml). CC (120 g of silica gel, 50 × 3.5 cm, $CHCl_3$) gave 4.86 g (94%) of **46**. Colorless foam. TLC (toluene/AcOEt/MeOH 5:4:0.1): R_f 0.66. UV (MeOH): 235 (4.36), 266 (4.58). ^1H-NMR ($CDCl_3$): 8.54 (*s*, H−C(8)); 8.19–8.09 (*m*, H−C(2), 4 H *o* to NO_2 (npe)); 7.94 (*s*, NH); 7.44–7.12 (*m*, 16 H, 4 H *m* to NO_2 (npe), MeO*Tr*); 6.80 (*d*, 2 H *o* to MeO); 6.37 (*d*, H−C(1′)); 5.97 (*t*, H−C(2′)); 4.99 (*m*, H−C(3′)); 4.52 (*t*, 2 H, OCH_2CH_2 (npeoc)); 4.34 (*m*, H−C(4′)); 3.78 (*s*, MeO); 3.57 (*m*, 2 H−C(5′)); 3.20 (*m*, 6 H, OCH_2CH_2 (npeoc), SCH_2CH_2 (npes)); 2.88 (*s*, OH−Si); 1.23–0.76 (*m*, 4 Me_2CH). Anal. calc. for $C_{59}H_{71}N_7O_{15}SSi_2$ (1206.5): C 58.73, H 5.93, N 8.12; found: C 58.72, H 5.68, N 8.42.

3′-O-(3-Hydroxy-1,1,3,3-tetraisopropyldisiloxan-1-yl)-5′-O-(monomethoxytrityl)-N^4-[2-(4-nitrophenyl)-ethoxycarbonyl]-2′-O-[2-(4-nitrophenylethylsulfonyl]cytidine (**47**). As described for **46**, with pyridine (3 × 10 ml), **38** (0.621 g, 0.683 mmol), pyridine (10 ml), MeOTr-Cl (0.422 g, 1.37 mmol; 15 h), and MeOH (10 ml). Workup with $CHCl_3$ (30 ml), H_2O (30 ml), and $CHCl_3$ (30 ml). CC (120 g of silica gel, 40 × 3.5 cm, $CHCl_3/CH_2Cl_2$ 1:1) gave 0.5 g (62%) of **47**. Colorless foam. For elemental analysis, 0.1 g of product was purified by prep. TLC (20 × 20 × 0.2 cm, CH_2Cl_2/hexane/AcOEt 1:1:1, desorption with $CHCl_3$/MeOH 4:1). TLC (toluene/AcOEt/MeOH 5:4:0.1): R_f 0.43. UV (MeOH): 236 (4.43), 247 (sh, 4.38), 274 (4.43). ^1H-NMR ($CDCl_3$): 8.43 (*d*, H−C(6)); 8.10 (*dd*, 4 H *o* to NO_2 (npe), NH); 7.45–7.11 (*m*, 16 H, 4 H *m* to NO_2 (npe), MeO*Tr*); 6.77 (*d*, 2 H *o* to McO); 6.58 (*d*, H−C(5)); 5.93 (*s*, H−C(1′)); 5.09 (*m*, H−C(2′)); 4.61–4.57 (*m*, H−C(3′)); 4.34 (*t*, 2 H, OCH_2CH_2 (npe)); 4.16 (*m*, H−C(4′)); 3.95–3.80 (*m*, 3 H, OH−Si, SCH_2CH_2 (npes)); 3.74 (*s*, MeO); 3.49 (*m*, 2 H−C(5′)); 3.25 (*t*, 2 H, SCH_2CH_2 (npes)); 3.02 (*t*, 2 H, OCH_2CH_2 (npe)); 1.16–0.89 (*m*, 4 Me_2CH). Anal. calc. for $C_{58}H_{71}N_5O_{16}SSi_2 \cdot H_2O$ (1200.5): C 58.03, H 6.13, N 5.83; found: C 57.72, H 5.99, N 5.86.

3′-O-(3-Hydroxy-1,1,3,3-tetraisopropyldisiloxan-1-yl)-5′-O-(monomethoxytrityl)-N^2-[2-(4-nitrophenyl)-ethoxycarbonyl]-O^6-[2-(4-nitrophenyl)ethyl]-2′-O-[2-(4-nitrophenyl)ethylsulfonyl]guanosine (**48**). As described for **46**, with pyridine (3 × 10 ml), **41** (1.49 g, 1.4 mmol), pyridine (20 ml), MeOTr-Cl (0.89 g, 2.88 ml; 15 h), and EtOH (5 ml). Workup with $CHCl_3$ (50 ml), H_2O (30 ml), and $CHCl_3$ (30 ml). CC (120 g of silica gel, 40 × 3.5 cm, $CHCl_3/CH_2Cl_2$ 1:1) gave 1.71 g (91%) of **48**. Colorless foam. For elemental analysis, 0.2 g of product were purified by prep. TLC (40 × 20 × 0.2 cm, $CHCl_3$/MeOH 100:1, desorption with $CHCl_3$/MeOH 4:1). TLC ($CHCl_2$/hexane/AcOEt 1:1:1): R_f 0.71. UV (MeOH): 218 (sh, 4.70), 236 (4.37), 269 (4.60). ^1H-NMR ($CDCl_3$): 8.14–8.04 (*m*, NH, H−C(8), 6 H *o* to NO_2 (npe)); 7.98 (*s*, H−C(8)); 7.51–7.11 (*m*, 18 H, 6 H *m* to NO_2 (npe), MeO*Tr*); 6.75 (*m*, 2 H *o* to MeO); 6.21 (*s*, H−C(1′)); 6.03 (*t*, H−C(2′)); 4.91 (*m*, H−C(3′)); 4.74 (*t*, 2 H, OCH_2CH_2 (npe)); 4.31–4.27 (*m*, 3 H, OH−Si, OCH_2CH_2 (npeoc)); 3.74 (*s*, MeO); 3.49–3.25 (*m*, 5 H, H−C(4′), 2 H−C(5′), SCH_2CH_2 (npes)); 3.15–2.98 (*m*, 6 H, OCH_2CH_2 (npe, npeoc), SCH_2CH_2 (npes)); 1.23–0.83 (*m*, 4 Me_2CH). Anal. calc. for $C_{67}H_{78}N_8O_{18}SSi_2 \cdot H_2O$ (1389.6): C 57.91, H 5.80, N 8.06; found: C 57.61, H 5.85, N 8.15.

3′-O-(3-Hydroxy-1,1,3,3-tetraisopropyldisiloxan-1-yl)-5′-O-(monomethoxytrityl)-2′-O-[2-(4-nitrophenyl)-ethylsulfonyl]uridine (**49**). As described for **46**, with pyridine (3 × 20 ml), **42** (1.70 g, 2.56 mmol), pyridine (40 ml), MeOTr-Cl (1.46 g, 4.73 mmol; 15 h), and MeOH (10 ml). Workup with $CHCl_3$ (70 ml), H_2O (30 ml), and $CHCl_3$ (30 ml). CC (80 g of silica gel, 42 × 3.5 cm, $CHCl_3$) gave 1.76 g (75%) of **49**. Colorless foam. For elemental analysis, 0.1 g of product was purified by prep. TLC (40 × 20 × 0.2 cm, $CHCl_3$/MeOH 49:1, desorption with $CHCl_3$/MeOH 4:1). TLC (toluene/AcOEt/MeOH 5:4:0.1): R_f 0.76. UV (MeOH): 232 (4.33), 262 (4.32). ^1H-NMR ($CDCl_3$): 9.49 (*s*, NH); 8.09 (*d*, 2 H *o* to NO_2 (npes)); 7.89 (*d*, H−C(6)); 7.46–7.12 (*m*, 14 H, 2 H *m* to NO_2 (npes), MeO*Tr*); 6.79 (*d*, 2 H *o* to MeO); 5.94 (*d*, H−C(1′)); 5.24 (*t*, H−C(2′)); 5.07 (*d*, H−C(5)); 4.71 (*t*, H−C(3′)); 4.11 (*m*, H−C(4′));

3.73 (*s*, MeO); 3.68–3.39 (*m*, 4 H, 2 H–C(5′), SCH_2CH_2 (npes)); 3.23 (*t*, 2 H, SCH_2CH_2 (npes)); 3.11 (*s*, OH–Si); 1.21–0.69 (*m*, 4 Me_2CH). Anal. calc. for $C_{49}H_{63}N_3O_{13}SSi_2 \cdot H_2O$ (1008.3): C 58.37, H 6.49, N 4.17; found: C 58.59, H 6.55, N 4.35.

3′-O-(3-Hydroxy-1,1,3,3-tetraisopropyldisiloxan-1-yl)-5′-O-(monomethoxytrityl)-O^2,O^4-bis[2-(4-nitrophenyl)ethyl]-2′-O-[2-(4-nitrophenyl)ethylsulfonyl]pseudouridine (**50**). As described for **46**, with pyridine (3 × 20 ml), **44** (0.186 g, 0.18 mmol), pyridine (2 ml), MeOTr-Cl (0.085 g, 0.28 mmol; 18 h; no MeOH). Workup with AcOEt (40 ml) and sat. NaCl soln. (3 × 20 ml). CC (30 g of silica gel, *d* 3.5 cm, toluene/AcOEt 9:1 (50 ml) and 4:1 (100 ml)) gave 0.2 g (85%) of **50**. Colorless foam. TLC (toluene/AcOEt 4:1): R_f 0.56. UV (MeOH): 203 (4.88), 216 (sh, 4.63), 234 (sh, 4.34), 268 (4.50). ^{1}H-NMR ($CDCl_3$): 8.44 (*d*, H–C(6)); 8.15 (*m*, 6 H *o* to NO_2 (npe)); 7.49–7.18 (*m*, 18 H, 6 H *m* to NO_2 (npe), MeO*Tr*); 6.80 (*d*, 2 H *o* to MeO); 5.32 (*m*, H–C(1′), H–C(2′)); 4.68–4.40 (*m*, 5 H, H–C(3′), 2 OCH_2CH_2 (npe)); 4.21 (*m*, H–C(4′)); 3.77 (*s*, MeO); 3.52–2.84 (*m*, 10 H, 2 H–C(5′), 2 OCH_2CH_2 (npe), SCH_2CH_2 (npes)); 0.99 (*m*, 4 Me_2CH). Anal. calc. for $C_{65}H_{77}N_5O_{17}SSi_2$ (1288.6): C 60.59, H 6.02, N 5.43; found: C 60.37, H 6.22, N 5.62.

5′-O-(Monomethoxytrityl)-N^6-[2-(4-nitrophenyl)ethoxycarbonyl]-2′-O-[2-(4-nitrophenyl)ethylsulfonyl]-adenosine (**51**). In dry THF (15 ml), **46** (4.86 g, 4 mmol) and $Bu_4NF \cdot 3\,H_2O$ (1.52 g, 4.8 mmol) were dissolved and stirred at 0° for 1 min and then diluted with H_2O (100 ml). The product was extracted with $CHCl_3$ (3 × 50 ml), the combined org. phase dried (Na_2SO_4) and evaporated, and the residue purified by CC (120 g of silica gel, 35 × 3.5 cm, $CHCl_3$): 3.7 g (98%) of **51**. Amorphous powder. A sample (0.2 g) was further purified by prep. TLC (silica gel, 40 × 20 × 0.2 cm, CH_2Cl_2/hexane/AcOEt 1:1:1, desorption with $CHCl_3$/MeOH 4:1 and recrystallized from $CHCl_3$/hexane). TLC (toluene/AcOEt/MeOH 5:4:0.1): R_f 0.36. UV (MeOH): 235 (4.33), 267 (4.55). ^{1}H-NMR ($CDCl_3$): 8.55 (*s*, H–C(8)); 8.29 (*s*, NH); 8.19–8.09 (*m*, H–C(2), 4 H *o* to NO_2 (npe)); 7.05–6.88 (*m*, 16 H, 4 H *m* to NO_2 (npe), MeO*Tr*); 6.80 (*d*, 2 H *o* to MeO); 6.25 (*d*, H–C(1′)); 5.84 (*t*, H–C(2′)); 4.83 (*m*, H–C(3′)); 4.51 (*t*, 2 H, OCH_2CH_2 (npeoc)); 4.28 (*m*, H–C(4′)); 3.77 (*s*, MeO); 3.54–3.34 (*m*, 6 H, OCH_2CH_2 (npeoc), SCH_2CH_2 (npes)). Anal. calc. for $C_{47}H_{43}N_7O_{13}S$ (946.0): C 59.68, H 4.58, N 10.37; found: C 60.14, H 4.66, N 10.17.

5′-O-(Monomethoxytrityl)-N^4-[2-(4-nitrophenyl)ethoxycarbonyl]-2′-O-[2-(4-nitrophenyl)ethylsulfonyl]-cytidine (**52**). As described for **51**, with THF (4 ml), **47** (0.386 g, 0.32 mmol), $Bu_4NF \cdot 3\,H_2O$ (1.248 g, 0.39 mmol), and H_2O (20 ml). Workup with $CHCl_3$ (3 × 20 ml). CC (30 g of silica gel, 20 × 3.5 cm, $CHCl_3$) gave 0.17 g (58%) of **52**. Amorphous powder. Further purification (0.1 g) was achieved by CC (silica gel, 10 × 1 cm, $CHCl_3$). TLC ($CHCl_3$/MeOH 49:1): R_f 0.27. UV (MeOH): 236 (4.38), 246 (sh, 4.35), 274 (4.42). ^{1}H-NMR ($CHCl_3$): 8.45 (*d*, H–C(6)); 8.14 (*dd*, 4 H *o* to NO_2 (npeoc)); 8.01 (*d*, NH); 7.49–7.26 (*m*, 16 H, 4 H *m* to NO_2 (npe), MeO*Tr*); 6.94 (*d*, H–C(5)); 6.84 (*d*, 2 H *o* to MeO); 5.86 (*s*, H–C(1′)); 5.04 (*d*, H–C(2′)); 4.55 (*m*, H–C(3′)); 4.42 (*t*, 2 H, OCH_2CH_2 (npeoc)); 4.15 (*m*, H–C(4′)); 3.95–3.52 (*s*, *m*, 7 H, MeO, 2 H–C(5′), SCH_2CH_2 (npes)); 3.31 (*t*, 2 H, OCH_2CH_2 (npeoc)); 3.08 (*t*, 3 H, SCH_2CH_2 (npes), OH–C(3′)). Anal. calc. for $C_{46}H_{43}N_5O_{14}S$ (921.9): C 59.93, H 4.70, N 7.60; found: C 59.58, H 5.20, N 7.20.

5′-O-(Monomethoxytrityl)-N^2-[2-(4-nitrophenyl)ethoxycarbonyl]-O^6-[2-(4-nitrophenyl)ethyl]-2′-O-[2-(4-nitrophenyl)ethylsulfonyl]guanosine (**53**). As described for **51**, with THF (14 ml), **48** (1.5 g, 1.15 mmol), $Bu_4NF \cdot H_2O$ (0.43 g, 1.3 mmol; 2 min), and H_2O (50 ml). CC (120 g of silica gel, 40 × 3.5 cm, $CHCl_3$/CH_2Cl_2) gave 0.83 g (67%) of **53**. Amorphous powder. A sample (0.1 g) was further purified by prep. TLC (silica gel, CH_2CH_2/hexane/AcOEt 1:1:1, desorption with $CHCl_3$/MeOH 4:1). TLC (CH_2Cl_2/hexane/AcOEt 1:1:1): R_f 0.47. UV (MeOH): 237 (sh, 4.38), 269 (4.61). ^{1}H-NMR ($CDCl_3$): 8.15–8.03 (*m*, 6 H *o* to NO_2 (npe)); 7.93 (*s*, H–C(8)); 7.48–7.18 (*m*, 19 H, NH, 6 H *m* to NO_2 (npe), MeO*Tr*); 6.73 (*d*, 2 H *o* to MeO); 6.28 (*d*, H–C(1′)); 5.93 (*m*, H–C(2′)); 5.21 (*m*, H–C(3′)); 4.70 (*t*, 2 H, OCH_2CH_2 (npe)); 4.31 (*t*, 2 H, OCH_2CH_2 (npeoc)); 4.19 (*m*, H–C(4′)); 3.73 (*s*, MeO); 3.47–3.41 (*m*, 4 H, 2 H–C(5′), SCH_2CH_2 (npes)); 3.36–3.16 (*m*, 5 H, OH–C(3′), OCH_2CH_2 (npe, npeoc)); 2.98 (*t*, 2 H, SCH_2CH_2 (npes)). Anal. calc. for $C_{55}H_{50}N_8O_{16}S$ (1111.1): C 59.45, H 4.54, N 10.09; found: C 59.42, H 4.74, N 9.83.

5′-O-(Monomethoxytrityl)-2′-O-[2-(4-nitrophenyl)ethylsulfonyl]uridine (**54**) *and 2,2′-Anhydro-5′-O-(monomethoxytrityl)uridine* (**150**). As described for **51**, with THF (25 ml), **49** (1.54 g, 1.56 mmol), $Bu_4NF \cdot 3\,H_2O$ (0.59 g, 1.89 mmol; 2 min), and H_2O (50 ml). Workup with $CHCl_3$ (2 × 70 ml). CC (silica gel, 30 × 3.5 cm, $CHCl_3$, $CHCl_3$/MeOH 49:1, and MeOH) gave 0.501 g (46%) of **54** and crude **150**. A small amount of **54** (0.1 g) was further purified by prep. TLC (silica gel, 20 × 20 × 0.2 cm, $CHCl_3$/MeOH 19:1, desorption with $CHCl_3$/MeOH 4:1): pure **54**. Crude **150** (MeOH eluate) was also purified by prep. TLC (silica gel, 40 × 20 × 0.2 cm, $CHCl_3$/MeOH 9:1, desorption with $CHCl_3$/MeOH 4:1): 0.349 g (45%) of **150**. Colorless foam.

54: TLC (toluene/AcOEt/MeOH 5:4:0.1): R_f 0.14. UV (MeOH): 231 (4.27), 263 (4.28). ^{1}H-NMR ($CDCl_3$): 9.36 (*s*, NH); 8.12 (*d*, 2 H *o* to NO_2 (npes)); 7.91 (*d*, H–C(6)); 7.42–7.27 (*m*, 14 H, 2 H *m* to NO_2 (npes), MeO*Tr*); 6.83 (*d*, 2 H *o* to MeO); 5.90 (*d*, H–C(1′)); 5.34 (*d*, H–C(5)); 5.13 (*m*, H–C(2)); 4.61 (*t*, H–C(3′)); 4.08 (*m*, H–C(4′)); 3.77 (*s*, MeO); 3.73–3.51 (*m*, 4 H, 2 H–C(5′), SCH_2CH_2 (npes)); 3.28 (*t*, 2 H, SCH_2CH_2 (npes)); 2.75 (*s*, OH–C(3′)). Anal. calc. for $C_{37}H_{35}N_3O_{11}S$ (729.8): C 60.89, H 4.83, N 5.75; found: C 60.56, H 5.04, N 5.82.

150: TLC ($CHCl_3$/MeOH 9:1): R_f 0.26. UV (MeOH): 229 (sh, 4.23), 262 (sh, 3.78). ^{1}H-NMR ($CDCl_3$): 7.95 (*d*, H–C(6)); 7.38–7.19 (*m*, 10 H, MeO*Tr*); 7.12 (*d*, 2 H *m* to MeO); 6.83 (*d*, 2 H *o* to MeO); 6.31 (*d*, H–C(5)); 5.97 (*d*, OH–C(3′)); 5.86 (*d*, H–C(1′)); 5.19 (*m*, H–C(2′)); 4.29–4.21 (*m*, H–C(3′), H–C(4′)); 3.34 (*s*, MeO); 2.95–2.75 (*m*, 2 H–C(5′)). Anal. calc. for $C_{29}H_{27}N_2O_6 \cdot 1.5\,H_2O$ (527.8): C 66.15, H 5.74, N 5.32; found: C 66.48, H 5.56, N 5.26.

5′-O-(Monomethoxytrityl)-S⁴-[2-(4-nitrophenyl)ethyl]-2′-O-[2-(4-nitrophenyl)ethylsulfonyl]-4-thiouridine (**55**). A soln. of **56** (0.625 g, 1 mmol) in dry THF/nitromethane 2:1 (30 ml) was treated with 2,6-di(*tert*-butyl)-4-methylpyridine (0.411 g, 2 mmol) and 4-methoxytrityl tetrafluoroborate (0.5 g, 1.25 mmol). The appearing dark red color turned yellow within 15 min. After stirring at r.t. for 1 h, the solvent was removed and the crude product purified by FC (15 g of silica gel, *d* 3 cm, hexane/AcOEt/Et_3N 7:7:1): 0.673 g (75%) of **55**. Yellow foam; stored at −18°.

S⁴-[2-(4-Nitrophenyl)ethyl]-2′-O-[2-(4-nitrophenyl)ethylsulfonyl]-4-thiouridine (**56**). A soln. of **36** (3.2 g, 3.7 mmol) in dry THF (75 ml) was treated successively with AcOH (2 ml), H_2O (120 µl), and Et_3N/trihydrogen fluoride complex (1 ml) with stirring at r.t. for 7 h. The soln. was concentrated and partitioned between 0.1M phosphate buffer (pH 7.0)/sat. $NaHCO_3$/sat. NaCl soln. (100 ml) and AcOEt (200 ml). The org. layer was washed with NaCl soln., dried (Na_2SO_4), and concentrated to *ca.* 30 ml. Crystallization was induced by adding petroleum ether. After 20 h standing at 4°, the crystals were filtered off and dried: 1.9 g (82%) of **56**. TLC (AcOEt/MeOH 100:1): R_f 0.30. M.p. 87–89°. ^{1}H-NMR ($CDCl_3$): 8.05 (*m*, 4 H *o* to NO_2); 7.40–7.30 (*m*, 4 H *m* to NO_2); 5.70 (*d*, H–C(1′)); 4.95 (*m*, H–C(2′)); 4.25 (*m*, H–C(3′)); 3.35 (*t*, 4 H, OCH_2CH_2 (npe), SCH_2CH_2 (npes)); 3.00 (*m*, 4 H, OCH_2CH_2 (npe), SCH_2CH_2 (npes)). Anal. calc. for $C_{25}H_{28}N_4O_{11}S_2$ (624.7): C 48.07, H 4.52, N 8.97; found: C 47.51, H 4.56, N 8.73.

2′-O-[2-(4-Nitrophenyl)ethylsulfonyl]pseudouridine (**57**). A soln. of **33** (0.553 g, 0.79 mmol) in dioxane (15 ml) was treated with 1M HCl (10.8 ml) and stirred at r.t. for 2.5 h. The mixture was neutralized with Et_3N (1.3 ml), diluted with AcOEt (40 ml), and washed with sat. NaCl soln. (3 × 20 ml), the org. phase dried (Na_2SO_4) and evaporated, and the residue purified by CC (40 g of silica gel, *d* 3.5 cm, AcOEt/MeOH 19:1 (300 ml)): 0.33 g (91%) of **57**. Colorless foam. TLC (CH_2Cl_2/MeOH 9:1): R_f 0.24. UV (MeOH): 204 (4.27), 210 (4.21), 265 (4.24). ^{1}H-NMR ((D_6)DMSO): 11.25 (*s*, H–N(3)); 11.01 (*d*, H–N(1)); 8.16 (*d*, 2 H *o* to NO_2); 7.67 (*d*, H–C(6)); 7.58 (*d*, 2 H *m* to NO_2); 5.58 (*d*, OH–C(3′)); 4.98 (*t*, OH–C(5′)); 4.89 (*t*, H–C(2′)); 4.79 (*d*, H–C(1′)); 4.17 (*q*, H–C(3′)); 3.84 (*t*, 2 H, SCH_2CH_2 (npes)); 3.72–3.18 (*m*, 5 H, H–C(4′), 2 H–C(5′), SCH_2CH_2 (npes)). Anal. calc. for $C_{17}H_{19}N_3O_{10}S$ (457.7): C 44.64, H 4.19, N 9.19; found: C 44.14, H 4.65, N 8.87.

O²,O⁴-Bis[2-(4-nitrophenyl)ethyl]-2′-O-[2-(4-nitrophenyl)ethylsulfonyl]pseudouridine (**58**). A soln. of **34** (1.06 g, 1 mmol) in THF (20 ml) was treated with AcOH (0.8 ml) and $Bu_4NF \cdot 3\,H_2O$ (1.26 g, 4 mmol) and stirred at r.t. for 2 h. The mixture was diluted with CH_2Cl_2 (80 ml) and washed with H_2O (3 × 20 ml), the org. phase dried and evaporated, and the crude product purified by CC (40 g of silica gel, *d* 3.5 cm, CH_2Cl_2 (200 ml), CH_2Cl_2/MeOH 97:3 (200 ml) and 19:1 (100 ml)): 0.695 g (92%) of **58** which still contained traces of Bu_4NF. A sample (0.07 g) was purified by prep. TLC (silica gel, 20 × 20 × 0.2 cm, CH_2Cl_2/MeOH 19:1, desorption with CH_2Cl_2/MeOH 4:1). On standing in CH_2Cl_2, part of **58** crystallized out. TLC (AcOEt/MeOH 19:1): R_f 0.42. M.p. 93°. UV (MeOH): 203 (4.60), 214 (4.49), 268 (4.54). ^{1}H-NMR ($CDCl_3$): 8.28 (*s*, H–C(6)); 8.12 (*m*, 6 H *o* to NO_2); 7.45–7.33 (*m*, 6 H *m* to NO_2); 4.98 (*m*, H–C(1′), H–C(2′)); 4.72–4.48 (*m*, 4 H, 2 OCH_2CH_2 (npe)); 4.28 (*t*, H–C(3′)); 3.98–3.68 (*m*, H–C(4′), 2 H–C(5′)); 3.63–3.08 (*m*, 8 H, OCH_2CH_2 (npe), SCH_2CH_2 (npes)); 2.75 (*m*, OH–C(3′)). Anal. calc. for $C_{33}H_{33}N_5O_{14}S$ (755.7): C 52.45, H 4.40, N 9.27; found: C 52.03, H 4.53, N 9.05.

5′-O-(Monomethoxytrityl)-N⁶-[2-(4-nitrophenyl)ethoxycarbonyl]adenosine (**59**) [34]. A soln. of **51** (0.132 g, 0.14 mmol) in 0.1M DBU (7 ml) in MeCN was stirred at r.t. for 1.5 h and then neutralized by 1M AcOH/MeCN. The mixture was diluted with CH_2Cl_2 (25 ml) and washed with H_2O (25 ml) and the org. phase evaporated and co-evaporated with toluene. FC (silica gel, 5 × 2 cm, CH_2Cl_2 (50 ml), CH_2Cl_2/MeOH 99:1 (100 ml) and 97:3 (100 ml)) gave 0.095 g (93%) of **59**, identical with an authentic sample [34].

5′-O-(Monomethoxytrityl)-N⁴-[2-(4-nitrophenyl)ethoxycarbonyl]cytidine (**61**) [34]. As described for **59**, with **52** (0.369 g, 0.4 mmol), 0.1M DBU (20 ml; 2 h), and 1M AcOH/MeCN (2 ml). Workup with CH_2Cl_2 (50 ml) and H_2O (40 ml). FC (silica gel, 8 × 2 cm, CH_2Cl_2 (30 ml), CH_2Cl_2/MeOH 99:1 (100 ml), 49:1 (100 ml), and 97:3 (100 ml)) gave 0.227 g (80%) of **61**, identical with authentic material [34].

5′-O-(Dimethoxytrityl)-N⁴-[2-(4-nitrophenyl)ethoxycarbonyl]cytidine (**62**). In dry pyridine (2 × 50 ml), 4.36 g (6.1 mmol) of *N*⁴-[2-(4-nitrophenyl)ethoxycarbonyl]cytidine [32] was co-evaporated and dissolved in dry pyridine (70 ml), and then dimethoxytrityl chloride (($(MeO)_2$Tr-Cl; 3.73 g, 11 mmol) was added. The mixture was stirred at r.t. for 2.5 h, then quenched with MeOH (15 ml), and stirred at r.t. for another 30 min. The soln. was concentrated to *ca.* ½ of the volume, diluted with $CHCl_3$ (100 ml), and washed with H_2O (100 ml). After back extracting the H_2O phase with $CHCl_3$ (2 × 40 ml), the org. phase was dried (Na_2SO_4), evaporated, and co-evaporated with toluene (2 × 50 ml). CC (100 g of silica gel, 22 × 4 cm, $CHCl_3$ (900 ml), $CHCl_3$/MeOH 50:1 (900 ml) and 100:3 (100 ml)) gave 6.56 g (89%) of **62**. Colorless foam. TLC ($CHCl_3$/MeOH 19:1): R_f 0.49. UV (MeOH): 236 (4.54), 275 (4.23), 280 (sh, 4.23), 297 (sh, 4.09). ^{1}H-NMR ($CDCl_3$): 8.16 (*d*, H–C(6), 2 H *o* to NO_2 (npeoc)); 7.40–7.21 (*m*, 11 H, 2 H *m* to NO_2 (npeoc), $(MeO)_2$*Tr*); 7.19 (*d*, H–C(5)); 6.80 (*dd*, 4 H *o* to MeO); 5.83 (*s*, H–C(1')); 5.81 (br. *s*, OH–C(3')); 4.41 (*m*, 5 H, H–C(2'), H–C(3'), H–C(4'), OCH_2CH_2 (npeoc)); 3.76 (*s*, 2 MeO)); 3.39 (*m*, 2 H–C(5'), OH–C(2')); 3.09 (*t*, 2 H, OCH_2CH_2 (npeoc)). Anal. calc. for $C_{39}H_{38}N_4O_{11}$ (738.8): C 63.41, H 5.18, N 7.58; found: C 63.12, H 5.07, N 7.59.

5'-O-(Monomethoxytrityl)-N^2-[2-(4-nitrophenyl)ethoxycarbonyl]-O^6-[2-(4-nitrophenyl)ethyl]guanosine (**63**) [34]. At r.t., **53** (0.333 g, 0.3 mmol) was treated with 0.1M DBU (15 ml) in MeCN and stirred for 100 min. The soln. was neutralized with 1M AcOH/MeCN, diluted with CH_2Cl_2 (50 ml), and washed with H_2O (25 ml). The org. phase was dried (Na_2SO_4), evaporated, and co-evaporated with toluene (30 ml). FC (silica gel, 8 × 2 cm, CH_2Cl_2 (50 ml), CH_2Cl_2/MeOH 97:3 (100 ml)) gave 0.219 g (81%) of **63**, identical with an authentic sample [34].

5'-O-(Dimethoxytrityl)-N^2-[2-(4-nitrophenyl)ethoxycarbonyl]-O^6-[2-(4-nitrophenyl)ethyl]guanosine (**64**). As described for **62**, with pyridine (3 × 20 ml), **28** (5 g, 8 mmol), pyridine (40 ml), $(MeO)_2$Tr-Cl (3.25 g, 9.6 mmol; 16 h), and MeOH (5 ml; 0 min). Evaporation to *ca.* ⅓ of the volume, CC (40 × 3.5 cm), $CHCl_3$ (900 ml), $CHCl_3$/MeOH 19:1 (700 ml), and co-evaporation with toluene (2 × 50 ml) gave an amorphous solid which was dissolved in $CHCl_3$ (70 ml) and added dropwise to vigorously stirred Et_2O (70 ml). On standing in a refrigerator for 20 h, the crystalline product was filtered and dried at 40° *in vacuo*: 6.23 g (84%) of **64**. TLC (AcOEt): R_f 0.63. M.p. 127° (softening) and 146° (dec.). UV (MeOH): 236 (sh, 4.48), 270 (4.55). ^{1}H-NMR ((D_6)DMSO): 10.33 (*s*, NH); 8.30 (*s*, H–C(8)); 8.15 (*d*, 4 H *o* to NO_2 (npe)); 7.61 (2*d*, 4 H *m* to NO_2 (npe)); 7.29–7.13 (*m*, 9 H, $(MeO)_2$*Tr*); 6.74 (*d*, 4 H *o* to MeO); 5.91 (*d*, H–C(1')); 5.60 (*d*, OH–C(3')); 5.12 (*d*, OH–C(2')); 4.72 (*t*, 2 H, OCH_2CH_2 (npe)); 4.34 (*m*, 2 H, OCH_2CH_2 (npeoc)); 4.01 (*m*, H–C(4')); 3.68 + 3.66 (2*s*, 2 MeO); 3.38–3.15 (*m*, 4 H, OCH_2CH_2 (npe), 2 H–C(5')); 3.08 (*t*, 2 H, OCH_2CH_2 (npeoc)). Anal. calc. for $C_{48}H_{45}N_7O_{13}$ (927.9): C 62.13, H 4.89, N 10.57; found: C 62.05, H 4.95, N 10.34.

N^2-Isobutyryl-5'-O-(monomethoxytrityl)-O^6-[2-(4-nitrophenyl)ethyl]guanosine (**65**). As described for **62**, with pyridine (3 × 15 ml), *N*^{2}-isobutyryl-*O*^{6}-[2-(4-nitrophenyl)ethyl]guanosine [32] (5 g, 10 mmol), pyridine (80 ml), MeOTr-Cl (3.7 g, 12 mmol; 24 h) and MeOH (5 ml; 0 min). Concentration to a smaller volume and CC (silica gel, 40 × 3.5 cm, $CHCl_3$, $CHCl_3$/MeOH 49:1) gave, after drying at 40° *in vacuo*, 7.65 g (98%) of **65**. Amorphous powder. TLC ($CHCl_3$/MeOH 99:1): R_f 0.60. UV (MeOH): 236 (sh, 4.26), 270 (4.43), 281 (4.32). ^{1}H-NMR ((D_6)DMSO): 10.40 (*s*, NH); 8.33 (*s*, H–C(8)); 8.17 (*d*, 4 H *o* to NO_2 (npe)); 7.66 (2*d*, 4 H *m* to NO_2 (npe)); 7.29–7.13 (*m*, 12 H, MeO*Tr*); 6.78 (*d*, 2 H *o* to MeO); 5.94 (*d*, H–C(1')); 5.60 (*d*, OH–C(3')); 5.12 (*d*, OH–C(2')); 4.80 (*t*, 2 H, OCH_2CH_2 (npe)); 3.71 (*s*, MeO); 3.30 (*t*, 2 H, OCH_2CH_2 (npe)); 2.82 (*m*, Me_2C*H*); 1.05 (*dd*, *Me*$_2$CH). Anal. calc. for $C_{42}H_{42}N_6O_9$ (774.8): C 65.10, H 5.46, N 10.84; found: C 65.45, N 5.66, N 10.92.

5'-O-(Monomethoxytrityl)-S^4-[2-(4-nitrophenyl)ethyl]-4-thiouridine (**67**). As described for **62**, with pyridine (3 × 40 ml), **17** (2.5 g, 6.1 mmol), pyridine (75 ml), MeOTr-Cl (2.27 g, 7.33 mmol; ice-cooling, then r.t. for 20 h), and MeOH (5 ml; 0 min). After complete evaporation, workup with $CHCl_3$ (100 ml), sat. $NaHCO_3$/NaCl soln. (100 ml) instead of H_2O, $CHCl_3$ (30 ml), and toluene (3 × 20 ml). FC (100 g of silica gel, *d* 5 cm, AcOEt) gave 3.96 g (95%) of **67**. Amorphous foam which crystallized from $EtOH/H_2O$ 5:1. TLC (toluene/AcOEt 7:3): R_f 0.15. M.p. 99–103°. UV (MeOH): 227 (sh, 4.31), 276 (4.26), 301 (sh, 4.24), 316 (sh, 4.08). ^{1}H-NMR ($CDCl_3$): 8.18 (*m*, 2 H *o* to NO_2 (npe)); 7.65 (*m*, 2 H *m* to NO_2 (npe)); 6.77 (*d*, 2 H *o* to MeO); 5.85 (*d*, H–C(1')); 4.40 (*m*, H–C(2')); 4.35 (*m*, H–C(3')); 3.79 (*s*, MeO); 3.40 (*m*, H–C(4'), 2 H–C(5')); 3.45 (*t*, 2 H, SCH_2CH_2 (npe)); 3.15 (*t*, 2 H, SCH_2CH_2 (npe)). Anal. calc. for $C_{37}H_{35}N_3O_8SSi_2$ (681.8): C 65.18, H 5.17, N 6.16; found: C 64.09, H 5.37, N 5.88.

5'-O-(Dimethoxytrityl)-O^4-methyluridine (**68**). A soln. of **19** (0.15 g, 0.58 mmol) in dry pyridine (5 ml) was stirred with $(MeO)_2$Tr-Cl (0.26 g, 0.75 mmol) at r.t. for 20 h. The reaction was stopped with MeOH (5 ml). After evaporation the residue was taken up in $CHCl_3$ (100 ml) and washed with sat. $NaHCO_3$/NaCl soln. (100 ml). After back extracting the H_2O phase with $CHCl_3$ (30 ml), the org. phase was dried (Na_2SO_4), evaporated, and co-evaporated with toluene (3 × 20 ml). CC (15 g of silica gel, 14 × 1.8 cm, $CHCl_3$, $CHCl_3$/MeOH 99:1) gave 0.3 g (93%) of **68**. Colorless foam. TLC ($CHCl_3$/MeOH 19:1): R_f 0.54. UV (MeOH): 204 (4.79), 231 (4.33), 274 (3.94), 281 (sh, 3.91). ^{1}H-NMR ($CDCl_3$): 8.07 (*d*, H–C(6)); 7.28 (*m*, 9 H, $(MeO)_2$*Tr*); 6.81 (*d*, 4 H *o* to MeO); 5.85 (*d*, H–C(1')); 5.71 (*d*, H–C(5)); 5.49 (*d*, OH–C(3')); 4.37 (*m*, H–C(2'), H–C(3'), H–C(4')); 3.97 (*s*, MeO); 3.79 (*s*, MeO); 3.42 (*m*, 2 H–C(5'), OH–C(2')). Anal. calc. for $C_{31}H_{32}N_2O_8 \cdot H_2O$ (578.6): C 64.35, H 5.92, N 4.84; found: C 63.34, H 6.07, N 4.37.

5'-O-(Dimethoxytrityl)-O^4-[2-(4-nitrophenyl)ethyl]uridine (**69**). As described for **68**, with **21** (3.5 g, 8.9 mmol), pyridine (70 ml), $(MeO)_2$Tr-Cl (3.93 g, 11.6 mmol), and MeOH (5 ml). CC (150 g of silica gel, 20 × 5 cm, AcOEt) gave 4.89 g (79%) of **69**. Colorless foam. TLC ($CHCl_3$/MeOH 19:1): 0.73. UV (MeOH): 204 (4.83), 232

(4.35), 274 (4.24), 280 (sh, 4.22). ^{1}H-NMR ($CDCl_3$): 8.17 (*d*, 2 H *o* to NO_2 (npe)); 8.03 (*d*, H–C(6)); 7.41 (*d*, 2 H *m* to NO_2 (npe)); 7.28 (*m*, 9 H, $(MeO)_2$*Tr*); 6.81 (*d*, 4 H *o* to MeO); 5.80 (*d*, H–C(1′)); 5.71 (*d*, H–C(5)); 5.40 (*d*, OH–C(3′)); 4.66 (*t*, 2 H, OCH_2CH_2 (npe)); 4.35 (*m*, H–C(2′), H–C(3′), H–C(4′)); 3.78 (*s*, 2 MeO); 3.38 (*m*, 2 H–C(5′), OH–C(2′)); 3.18 (*t*, 2 H, OCH_2CH_2 (npe)). Anal. calc. for $C_{38}H_{37}N_3O_{10}$ (695.7): C 65.60, H 5.36, N 6.04; found: C 65.58, H 5.95, N 6.70.

O^4-*[2-(4-Cyanophenyl)ethyl]-5′-O-(dimethoxytrityl)uridine* (**70**). As described for **68**, with **22** (1.16 g, 3.1 mmol), pyridine (25 ml), $(MeO)_2$Tr-Cl (1.36 g, 4 mmol), and MeOH (5 ml). CC (70 g of silica gel, 20 × 3.5 cm, $CHCl_3$, $CHCl_3$/MeOH 99:1) gave 1.65 g (79%) of **70**. Colorless foam. TLC ($CHCl_3$/MeOH): R_f 0.85. UV (MeOH): 205 (4.82), 231 (4.59), 236 (sh, 4.56), 274 (4.00). ^{1}H-NMR ($CDCl_3$): 8.13 (*d*, H–C(6)); 7.59 (*d*, 2 H *o* to CN (cpe)); 7.29 (*m*, 11 H, 2 H *m* to CN (cpe), $(MeO)_2$*Tr*); 6.81 (*d*, 4 H *o* to MeO); 5.84 (*d*, H–C(1′)); 5.64 (*d*, H–C(5)); 5.57 (*d*, OH–C(3′)); 4.61 (*t*, 2 H, OCH_2CH_2 (cpe)); 4.36 (*m*, H–C(2′), H–C(3′), H–C(4′)); 3.78 (*s*, 2 MeO); 3.41 (*m*, 2 H–C(5′), OH–C(2′)); 3.11 (*t*, 2 H, OCH_2CH_2 (cpe)). Anal. calc. for $C_{39}H_{37}N_3O_8$ (675.7): C 69.32, H 5.52, N 6.22; found: C 69.25, H 6.16, N 5.72.

5′-O-(Dimethoxytrityl)pseudouridine (**72**). After co-evaporation with pyridine, as described for **68**, with pseudouridine (0.49 g, 2 mmol) pyridine (3.5 ml), $(MeO)_2$Tr-Cl (0.81 g, 2.4 mmol; 14 h; no MeOH). Workup by diluting with AcOEt (50 ml), washing with sat. $NaHCO_3$/NaCl soln. (3 × 20 ml), and back extracting with AcOEt (2 × 20 ml). CC (30 g of silica gel, *d* 2.5 cm, $CHCl_3$/MeOH 99:1 (300 ml), 24:1 (300 ml), and 9:1 (100 ml)) gave 0.8 g (73%) of **72**. Colorless foam. TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.33. UV (MeOH): 204 (4.79), 234 (4.33), 264 (3.98). ^{1}H-NMR ((D_6)DMSO): 11.14 (*s*, H–N(3)); 10.90 (br. *d*, H–N(1)); 7.47–7.17 (*m*, 10 H, H–C(6), $(MeO)_2$*Tr*); 6.87 (*d*, 4 H *o* to MeO); 5.10–4.88 (2*d*, OH–C(2′), OH–C(3′)); 4.52 (*d*, H–C(1′)); 3.94–3.77 (*m*, H–C(2′), H–C(3′), H–C(4′)); 3.72 (*s*, 2 MeO); 3.10 (*m*, 2 H–C(5′)). Anal. calc. for $C_{30}H_{30}N_2O_8 \cdot H_2O$ (564.6): C 63.82, H 5.71, N 4.96; found: C 63.66, H 5.68, N 4.74.

5′-O-(Monomethoxytrityl)-O^2,*O*^{4}-*bis[2-(4-nitrophenyl)ethyl]pseudouridine* (**73**). A soln. of **13** (1.35 g, 2.48 mmol) in dry pyridine was twice co-evaporated and then dissolved in pyridine (10 ml). MeOTr-Cl (1.15 g, 3.73 mmol) was added and the mixture stirred at r.t. for 16 h, then evaporated, and co-evaporated with toluene (3 × 10 ml). The residue was dissolved in $CHCl_3$ (80 ml) and the soln. washed with H_2O (3 × 20 ml), dried (Na_2SO_4), and evaporated. CC (80 g of silica gel, *d* 2.5 cm, $CHCl_3$ (200 ml), $CHCl_3$/MeOH 100:1 (200 ml), and 24:1 (150 ml)) gave 1.88 g (93%) of **73**. Colorless foam. TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.68. UV (MeOH): 204 (4.88), 232 (4.39), 269 (4.44). ^{1}H-NMR ($CDCl_3$): 8.34 (*s*, H–C(6)); 8.17 (*d*, 4 H *o* to NO_2 (npe)); 7.50–7.20 (*m*, 16 H, 4 H *m* to NO_2 (npe), MeO*Tr*); 6.81 (*d*, 2 H *o* to MeO); 4.90 (*d*, H–C(1′)); 4.59 (*m*, 4 H, OCH_2CH_2 (npe)); 4.14–3.95 (*m*, H–C(2′), H–C(3′), H–C(4′)); 3.78 (*s*, MeO); 3.39 (*d*, 2 H, OCH_2CH_2 (npe)); 3.20 (*m*, 2 H, OCH_2CH_2 (npe)); 0.56 (*d*, OH–C(2′)); 0.48 (*m*, OH–C(3′)). Anal. calc. for $C_{45}H_{42}N_4O_{11} \cdot H_2O$ (832.9): C 64.90, H 5.32, N 6.72; found: C 64.89, H 5.01, N 6.63.

5′-O-(Dimethoxytrityl)-O^2,*O*^{4}-*bis[2-(4-nitrophenyl)ethyl]pseudouridine* (**74**). A soln. of **13** (2 g, 3.68 mmol) in dry pyridine was co-evaporated, then dissolved in pyridine (15 ml), and stirred with $(MeO)_2$Tr-Cl (1.87 g, 5.53 mmol) at r.t. for 23 h. The mixture was diluted with $CHCl_3$ (100 ml) and washed with H_2O (3 × 30 ml) and the org. phase dried (Na_2SO_4) and evaporated. CC (50 g of silica gel, *d* 3.5 cm, $CHCl_3$ (500 ml)) gave 2.7 g (87%) of **74**. TLC ($CHCl_3$): R_f 0.18. UV (MeOH): 204 (4.87), 233 (sh, 4.44), 269 (4.44). ^{1}H-NMR ($CDCl_3$): 8.35 (*s*, H–C(6)); 8.15 (*d*, 4 H *o* to NO_2 (npe)); 7.46–7.25 (*m*, 13 H, 4 H *m* to NO_2 to (npe), $(MeO)_2$*Tr*); 6.82 (*d*, 4 H *o* toMeO); 4.87 (*d*, H–C(1′)); 4.60 (*m*, 4 H, OCH_2CH_2 (npe)); 4.07–3.98 (*m*, H–C(2′), H–C(3′), H–C(4′)); 3.77 (*s*, 2 MeO); 3.39 (*m*, 2 H–C(5′)); 3.18 (*m*, 4 H, OCH_2CH_2 (npe)); 2.63 (*m*, OH–C(2′), OH–C(3′)). Anal. calc. for $C_{46}H_{44}N_4O_{12} \cdot 1.5\ H_2O$ (871.9): C 63.37, H 5.43, N 6.43; found: C 63.30, H 5.20, N 6.24.

O^4-*2-[4-(Cyanophenyl)ethyl]-5′-O-(monomethoxytrityl)ribosylthymine* (**76**). In dry pyridine (3 × 15 ml), **26** (0.77 g, 2 mmol) was co-evaporated, then taken up in pyridine (20 ml), and stirred with MeOTr-Cl (0.8 g, 2.6 mmol) at r.t. for 24 h. H_2O (20 ml) was added, the soln. extracted with $CHCl_3$ (3 × 20 ml), and the org. phase dried (Na_2SO_4), evaporated, and co-evaporated with toluene. CC (35 g of silica gel, *d* 3.5 cm, $CHCl_3$, $CHCl_3$/MeOH 99:1) gave, after drying at 40° *in vacuo*, 0.89 g (85%) of **76**. Colorless foam. TLC ($CHCl_3$/MeOH 19:1): R_f 0.54. UV (MeOH): 202 (4.84), 228 (4.46), 279 (3.82). ^{1}H-NMR ($CDCl_3$): 7.89 (*s*, H–C(6)); 7.59 (*d*, 2 H *o* to CN (cpe)); 7.25 (*m*, 14 H, 2 H *m* to CN (cpe), MeO*Tr*); 6.81 (*d*, 2 H *o* to MeO); 5.83 (*d*, H–C(1′)); 5.68 (*s*, OH–C(2′)); 4.64 (*t*, 2 H, OCH_2CH_2 (cpe)); 4.40 (*m*, H–C(2′), H–C(3′), H–C(4′)); 3.79 (*s*, MeO); 3.50 (*m*, OH–C(3′), 1 H–C(5′)); 3.32 (*m*, 1 H–C(5′)); 3.14 (*t*, 2 H, OCH_2CH_2 (cpe)); 1.88 (*s*, Me–C(5)). Anal. calc. for $C_{39}H_{37}N_3O_7 \cdot 2\ H_2O$ (695.7): C 67.32, H 5.36, N 6.03; found: C 67.33, H 5.44, N 6.08.

5′-O-(Monomethoxytrityl)-O^4-*2-[4-(nitrophenyl)ethyl]ribosylthymine* (**77**). In dry pyridine (3 × 15 ml), **27** (4 g, 10 mmol) was co-evaporated, then taken up in pyridine (15 ml), and stirred with MeOTr-Cl (3.7 g, 12 mmol) at r.t. for 24 h. The reaction was quenched with MeOH (5 ml), the mixture evaporated, H_2O (20 ml) added, the soln. extracted with AcOEt (3 × 15 ml), and the org. phase dried (Na_2SO_4), evaporated, and co-evaporated with toluene.

CC (70 g of silica gel, *d* 3.5 cm, $CHCl_3$) gave 4.1 g (62%) of **77**. Colorless foam. TLC ($CHCl_3$/MeOH 19:1): R_f 0.31. UV (MeOH): 203 (4.92), 231 (4.32), 275 (4.23). ^{1}H-NMR ($CDCl_3$): 8.18 (*d*, 2 H *o* to NO_2 (npe)); 7.90 (*s*, H–C(6)); 7.41 (*m*, 2 H *m* to NO_2 (npe)); 7.35 (*m*, 12 H, MeO*Tr*); 6.80 (*d*, 2 H *o* to MeO); 5.85 (*d*, H–C(1')); 5.16 (*s*, OH–C(2')); 4.68 (*t*, 2 H, OCH_2CH_2 (npe)); 4.50 (*m*, H–C(2'), H–C(3')); 4.33 (*m*, H–C(4')); 3.79 (*s*, MeO); 3.50 (*m*, OH–C(3'), 1 H–C(5')); 3.30 (*m*, 1 H–C(5')); 3.20 (*t*, 2 H, OCH_2CH_2 (npe)); 1.88 (*s*, Me–C(5)). Anal. calc. for $C_{38}H_{37}N_3O_9$ (679.7): C 67.14, H 5.48, N 6.18; found: C 66.27, H 5.54, N 6.07.

*2',3'-Bis-*O*-[(*tert*-butyl)dimethylsilyl]-5'-*O*-(monomethoxytrityl)-*N^4*-[2-(4-nitrophenyl)ethoxycarbonyl]cytidine* (**78**), *2'-*O*-[(*tert*-Butyl)dimethylsilyl]-5'-*O*-(monomethoxytrityl)-*N^4*-[2-(4-nitrophenyl)ethoxycarbonyl]cytidine* (**79**), *and 3'-*O*-[(*tert*-Butyl)dimethylsilyl]-5'-*O*-(monomethoxytrityl)-*N^4*-[2-(4-nitrophenyl)ethoxycarbonyl]cytidine* (**80**). A mixture of **61** [34] (2.77 g, 4 mmol) and 1*H*-imidazole (0.65 g, 9.6 mmol) in pyridine (2 × 20 ml) was co-evaporated, then dissolved in pyridine (20 ml), and stirred for 19 h with (*t*-Bu)Me_2SiCl (0.724 g, 4.8 mmol). After quenching with MeOH (10 ml), the mixture was evaporated and the residue taken up in $CHCl_3$ (50 ml) and washed with H_2O (2 × 20 ml). After back extracting of the aq. phase with $CHCl_3$ (30 ml), the org. phase was dried (Na_2SO_4), evaporated and co-evaporated with toluene (2 × 20 ml). CC (80 g of silica gel, 25 × 3 cm, toluene/AcOEt 5:2 and 3:7) gave 0.37 g (10%) of **78**, 1.41 g (43%) of **79**, and 1.06 g (32%) of **80** as colorless foams.

78: TLC (toluene/AcOEt 3:7): R_f 0.68. UV (MeOH): 234 (4.40), 272 (4.23), 280 (sh, 4.22). ^{1}H-NMR ($CDCl_3$): 8.64 (*d*, H–C(6)); 8.17 (*d*, 2 H *o* to NO_2 (npeoc)); 7.52 (br. *s* NH); 7.38–7.17 (*m*, 14 H, 2 *H m* to NO_2 (npeoc), MeO*Tr*); 6.83 (*d*, 2 H *o* to MeO); 6.73 (*d*, H–C(5)); 5.74 (*s*, H–C(1')); 4.40 (*t*, 2 H, OCH_2CH_2 (npeoc)); 4.21 (*m*, H–C(2')); 4.13 (*m*, H–C(3')); 3.79 (*s*, 1 H–C(5'), MeO); 3.35 (*m*, H–C(5')); 3.08 (*t*, 2 H, OCH_2CH_2 (npeoc)); 0.88 (*s*, *t*-Bu); 0.70 (*s*, *t*-Bu); 0.25 (*s*, SiMe); 0.11 (*s*, SiMe); –0.06 (*s*, SiMe); –0.16 (*s*, SiMe). Anal. calc. for $C_{50}H_{64}N_4O_{10}Si_2$ (937.3): C 64.08, H 6.88, N 5.98; found: C 63.96, H 6.98, N 5.82.

79: TLC (toluene/AcOEt 3:7): R_f 0.56. UV (MeOH): 236 (4.42), 275 (4.18), 280 (sh, 4.18), 298 (sh, 4.01). ^{1}H-NMR ($CDCl_3$): 8.41 (*d*, H–C(6)); 8.17 (*d*, 2 H *o* to NO_2 (npeoc)); 7.41–7.14 (*m*, 14 H, 2 H *m* to NO_2 (npeoc), MeO*Tr*); 6.83 (*d*, H–C(5), 2 H *o* to MeO); 5.87 (*s*, H–C(1')); 4.41 (*t*, 2 H, OCH_2CH_2 (npeoc)); 4.29 (*m*, H–C(2'), H–C(3')); 4.07 (*m*, H–C(4')); 3.79 (*s*, MeO); 3.53 (*m*, 2 H–C(5')); 3.09 (*t*, 2 H, OCH_2CH_2 (npeoc)); 2.31 (*s*, OH–C(3')); 0.91 (*s*, *t*-Bu); 0.29 (*s*, SiMe); 0.17 (*s*, SiMe). Anal. calc. for $C_{44}H_{50}N_4O_{10}Si$ (823.0): C 64.22, H 6.12, N 6.81; found: C 63.62, H 6.07, N 6.75.

80: TLC (toluene/AcOEt 3:7): R_f 0.16. UV (MeOH): 236 (4.40), 275 (4.17), 280 (sh, 4.17). ^{1}H-NMR ($CDCl_3$): 8.32 (*d*, H–C(6)); 8.17 (*d*, 2 H *o* to NO_2 (npeoc)); 7.48 (br. *s*, NH); 7.38–7.17 (*m*, 14 H, 2 H *m* to NO_2 (npeoc), MeO*Tr*); 6.83 (*d*, 2 H *o* to MeO); 5.99 (*s*, H–C(1')); 4.40 (*t*, 2 H, OCH_2CH_2 (npeoc)); 4.32 (*t*, H–C(2')); 4.13 (*m*, H–C(3'), H–C(4')); 3.79 (*s*, MeO); 3.65 (*m*, 1 H–C(5')); 3.26 (*m*, 1 H–C(5')); 3.08 (*t*, 3 H, OCH_2CH_2 (npeoc), OH–C(2')); 0.80 (*s*, *t*-Bu); 0.01 (*s*, SiMe); –0.11 (*s*, SiMe). Anal. calc. for $C_{44}H_{50}N_4O_{10}Si$ (823.0): C 64.22, H 6.12, N 6.81; found: C 63.54, H 6.28, N 6.67.

*2',3'-Bis-*O*-[(*tert*-butyl)dimethylsilyl]-5'-*O*-(dimethoxytrityl)-*N^4*-[2-(4-nitrophenyl)ethoxycarbonyl]cytidine* (**81**), *2'-*O*-[(*tert*-Butyl)dimethylsilyl]-5'-*O*-(dimethoxytrityl)-*N^4*-[2-(4-nitrophenyl)ethoxycarbonyl]cytidine* (**82**), *and 3'-*O*-[(*tert*-Butyl)dimethylsilyl]-5-*O*-(dimethoxytrityl)-*N^4*-[2-(4-nitrophenyl)ethoxycarbonyl]cytidine* (**83**). As described for **78**–**80**, with pyridine (2 × 20 ml), **62** (2.8 g, 3.79 mmol), 1*H*-imidazole (0.72 g, 10.6 mmol), pyridine (20 ml), (*t*-Bu)Me_2SiCl (0.89 g, 5.31 mmol; 20 h, and MeOH (10 ml). Workup with CH_2Cl_2 (50 ml), phosphate buffer (pH 7.0; 3 × 50 ml), instead of H_2O, CH_2Cl_2 (30 ml), and toluene (3 × 40 ml). CC (110 g of silica gel, 50 × 4.5 cm, toluene/AcOEt 100:35, 5:2 (280 ml, **81**), 2:1 (280 ml, **81** and **82**), 2:1 (750 ml, pure **83**), and 3:7)) gave 0.13 g (4%) of **81**, 1.56 g (48%) of **82**, and 0.99 g (31%) of **83** as colorless foams.

81: TLC (toluene/AcOEt 3:7): R_f 0.82. UV (MeOH): 235 (4.51), 273 (4.22), 280 (sh, 4.21), 298 (sh, 4.01). ^{1}H-NMR ($CDCl_3$): 8.68 (*d*, H–C(6)); 8.17 (*d*, 2 H *o* to NO_2 (npeoc)); 7.45 (br. *s*, NH); 7.38–7.27 (*m*, 11 H, 2 H *m* to NO_2 (npeoc)); $(MeO)_2$*Tr*); 6.83 (*d*, 4 H *o* to MeO); 6.74 (*d*, H–C(5)); 5.87 (*s*, H–C(1')); 4.39 (*t*, 2 H, OCH_2CH_2 (npeoc)); 4.15 (*m*, H–C(2'), H–C(3'), H–C(4')); 3.79 (*s*, 2 MeO, 1 H–C(5')); 3.31 (*m*, 1 H–C(5')); 3.08 (*t*, 2 H, OCH_2CH_2 (npeoc)); 0.89 (*s*, *t*-Bu); 0.69 (*s*, *t*-Bu); 0.26 (*s*, SiMe); 0.11 (*s*, SiMe); –0.06 (*s*, SiMe); –0.16 (*s*, SiMe). Anal. calc. for $C_{51}H_{66}N_4O_{11}Si_2$ (967.3): C 63.33, H 6.88, N 5.79; found: C 63.06, H 7.19, N 5.63.

82: TLC (toluene/AcOEt 3:7): R_f 0.68. UV (MeOH): 236 (4.53), 275 (4.22), 280 (sh, 4.21), 298 (sh, 4.01). ^{1}H-NMR ($CDCl_3$): 8.46 (*d*, H–C(6)); 8.17 (*d*, 2 H to NO_2 (npeoc)); 7.50 (br. *s*, NH); 7.39–7.21 (*m*, 11 H, 2 H *m* to NO_2 (npeoc), $(MeO)_2$*Tr*); 6.84 (*d*, 4 H *o* to MeO, H–C(5)); 5.87 (*s*, H–C(1')); 4.40 (*t*, 2 H, OCH_2CH_2 (npeoc)); 4.27 (*m*, H–C(2'), H–C(3')); 4.09 (*m*, H–C(4')); 3.79 (*s*, 2 MeO); 3.55 (*m*, 2 H–C(5')); 3.08 (*t*, 2 H, OCH_2CH_2 (npeoc)); 3.55 (*s*, OH–C(3')); 0.91 (*s*, *t*-Bu); 0.29 (*s*, SiMe); 0.17 (*s*, SiMe). Anal. calc. for $C_{45}H_{52}N_4O_{11}Si$ (841.0): C 63.34, H 6.15, N 6.57; found: C 63.62, H 6.30, N 6.57.

83: TLC (toluene/AcOEt 3:7): R_f 0.35. UV (MeOH): 236 (4.52), 275 (4.22), 280 (sh, 4.21), 298 (sh, 4.08). ^{1}H-NMR ($CDCl_3$): 8.38 (*d*, H–C(6)); 8.16 (*d*, 2 H *o* to NO_2 (npeoc)); 7.41 (br. *s*, NH); 7.38–7.17 (*m*, 11 H, 2 H *m* to NO_2 (npeoc), $(MeO)_2$*Tr*); 6.83 (*d*, 4 H *o* to MeO, H–C(5)); 5.83 (*s*, H–C(1')); 4.40 (*t*, 2 H, OCH_2CH_2 (npeoc));

4.31 (*m*, H–C(3′)); 4.12 (*m*, H–C(2′), H–C(4′)); 3.78 (*s*, 2 MeO); 3.69 (*m*, 1 H–C(5′)); 3.30 (*m*, 1 H–C(5′)); 3.07 (*t*, 3 H, OCH_2CH_2 (npeoc), OH–C(2′)); 0.79 (*s*, *t*-Bu); 0.00 (*s*, SiMe); –0.11 (*s*, SiMe). Anal. calc. for $C_{45}H_{52}N_4O_{11}Si$ (841.0): C 63.34, H 6.15, N 6.57; found: C 62.84, H 6.20 N 6.25.

*2′,3′-Bis-*O*-[(*tert*-butyl)dimethylsilyl]-5′-*O*-(monomethoxytrityl)-*N^2*-[2-(4-nitrophenyl)ethoxycarbonyl]-*O^6*-[2-(4-nitrophenyl)ethyl]guanosine* (**84**), *2′-*O*-[(*tert*-Butyl)dimethylsilyl]-5′-*O*-(monomethoxytrityl)-*N^2*-[2-(4-nitrophenyl)ethoxycarbonyl]-*O^6*-[2-(4-nitrophenyl)ethyl]guanosine* (**85**), *and 3′-*O*-[(*tert*-Butyl)dimethylsilyl]-5′-*O*-(monomethoxytrityl)-*N^2*-[2-(4-nitrophenyl)ethoxycarbonyl]-*O^6*-[2-(4-nitrophenyl)ethyl]guanosine* (**86**). In dry pyridine (3 × 5 ml), **63** (1.38 g, 1.5 mmol) was co-evaporated and the residue dissolved in dry pyridine (3 ml). Then (*t*-Bu)Me_2SiCl (0.331 g, 2.2 mmol) and 1*H*-imidazole (0.292 g, 4.3 mmol) were added and stirred at r.t. for 4 h. The mixture was diluted with $CHCl_3$ (70 ml) and washed with H_2O (70 ml). After back extracting of the aq. phase with $CHCl_3$ (2 × 50 ml), the org. phase dried (Na_2SO_4), evaporated, and co-evaporated with toluene (3 × 15 ml). CC (silica gel, 26 × 4.5 cm, toluene/AcOEt 7:1 (1.0 l), 6:1 (1.3 l, **84**), 5:1 (0.9 l; **85**, **85**/**86**, **86**), 4:1, 3:1, and 2:1 (each 200 ml; **86**), AcOEt (200 ml, **86**)), followed by prep. TLC (silica gel, 40 × 20 × 0.2 cm, toluene/AcOEt 1:1, desorption with $CHCl_3$/MeOH 4:1) of the mixed fractions, yielded 0.118 g (7%) of **84**, 0.394 g (26%) of **85**, and 0.786 g (52%) of **86** as colorless foams.

84: TLC (toluene/AcOEt 1:1): R_f 0.81. UV (MeOH): 216 (sh, 4.74), 235 (4.37), 254 (4.44), 269 (4.54), 278 (sh, 4.47). ^{1}H-NMR ($CDCl_3$): 8.14 (2*d*, 4 H *o* to NO_2 (npe)); 8.01 (*s*, H–C(8)); 7.54–7.06 (*m*, 17 H, 4 H *m* to NO_2 (npe), NH, MeO*Tr*); 6.81 (*d*, 2 H *o* to MeO); 5.89 (*d*, H–C(1′)); 4.84 (*t*, 2 H, OCH_2CH_2 (npe)); 4.82 (*d*, H–C(2′)); 4.37 (*t*, 2 H, OCH_2CH_2 (npeoc)); 4.22 (*d*, H–C(3′)); 4.14 (*t*, H–C(4′)); 3.77 (*s*, MeO); 3.50, 3.25 (2*m*, 2 H–C(5′)); 3.30 (*t*, 2 H, OCH_2CH_2 (npe)); 3.03 (*t*, 2 H, OCH_2CH_2 (npeoc)); 0.85 (*s*, *t*-Bu); 0.76 (*s*, *t*-Bu); 0.03 (*s*, SiMe); –0.06 (*s*, SiMe); –0.07 (*s*, SiMe); –0.35 (*s*, SiMe). Anal. calc. for $C_{59}H_{71}N_7O_{12}Si_2$ (1126.4): C 62.91, H 6.35, N 8.70; found: C 62.78, H 6.51, N 8.76.

85: TLC (toluene/AcOEt 1:1): R_f 0.67. UV (MeOH): 216 (sh, 4.78), 234 (4.41), 269 (4.56), 277 (sh, 4.50). ^{1}H-NMR ($CDCl_3$): 8.16 (*d*, 4 H *o* to NO_2 (npe)); 7.98 (*s*, H–C(8)); 7.54–7.07 (*m*, 17 H, 4 H *m* to NO_2 (npe), NH, MeO*Tr*); 6.79 (*d*, 2 H *o* to MeO); 5.91 (*d*, H–C(1′)); 5.02 (*t*, H–C(2′)); 4.84 (*t*, 2 H, OCH_2CH_2 (npe)); 4.41 (*m*, H–C(3′)); 4.36 (*t*, 2 H, OCH_2CH_2 (npeoc)); 4.22 (*d*, H–C(4′)); 3.77 (*s*, MeO); 3.50, 3.36 (2*m*, 2 H–C(5′)); 3.33 (*t*, 2 H, OCH_2CH_2 (npe)); 3.02 (*t*, 2 H, OCH_2CH_2 (npeoc)); 2.69 (*d*, OH–C(3′)); 0.83 (*s*, *t*-Bu); –0.02 (*s*, SiMe); –0.20 (*s*, SiMe). Anal. calc. for $C_{53}H_{57}N_7O_{12}Si$ (1012.2): C 62.89, H 5.68, N 9.69; found: C 63.23, H 5.71, N 9.44.

86: TLC (toluene/AcOEt 1:1) R_f 0.52. UV (MeOH): 216 (sh, 4.77), 235 (sh, 4.39), 269 (4.55), 277 (sh, 4.50). ^{1}H-NMR ($CDCl_3$): 8.16 (*d*, 4 H *o* to NO_2 (npe)); 8.04 (*s*, H–C(8)); 7.51–7.16 (*m*, 17 H, 4 H *m* to NO_2 (npe), NH, MeO*Tr*); 6.75 (*d*, 2 H *o* to MeO); 5.91 (*d*, H–C(1′)); 4.79 (*t*, 2 H, OCH_2CH_2 (npe)); 4.71 (*q*, H–C(2′)); 4.56 (*t*, H–C(3′)); 4.44 (*t*, 2 H, OCH_2CH_2 (npeoc)); 4.23 (*d*, OH–C(2′)); 4.19 (*d*, H–C(4′)); 3.75 (*s*, MeO); 3.30 (*m*, 4 H, 2 H–C(5′), OCH_2CH_2 (npe)); 3.10 (*t*, 2 H, OCH_2CH_2 (npeoc)); 0.88 (*s*, *t*-Bu); 0.10 (*s*, SiMe); 0.03 (*s*, SiMe). Anal. calc. for $C_{53}H_{57}N_7O_{12}Si$ (1012.2): C 62.89, H 5.68, N 9.69; found: C 63.12, H 5.89, N 9.47.

*2′,3′-Bis-*O*-[(*tert*-butyl)dimethylsilyl]-5′-*O*-(dimethoxytrityl)-*N^2*-[2-(4-nitrophenyl)ethoxycarbonyl]-*O^6*-[2-(4-nitrophenyl)ethyl]guanosine* (**87**), *2′-*O*-[(*tert*-Butyl)dimethylsilyl]-5′-*O*-(dimethoxytrityl)-*N^2*-[2-(4-nitrophenyl)ethoxycarbonyl]-*O^6*-[2-(4-nitrophenyl)ethyl]guanosine* (**88**), *and 3′-*O*-[(*tert*-butyl)dimethylsilyl]-5′-*O*-(dimethoxytrityl)-*N^2*-[2-(4-nitrophenyl)ethoxycarbonyl]-*O^6*-[2-(4-nitrophenyl)ethyl]guanosine* (**89**). As described for **84**–**86**, with pyridine (3 × 8 ml), **64** (5.57 g, 6 mmol), pyridine (12 ml), (*t*-Bu)Me_2SiCl (1.32 g, 8.8 mmol), and 1*H*-imidazole (1.17 g, 17.2 mmol; 3.5 h). Workup with $CHCl_3$ (150 ml), H_2O (150 ml), $CHCl_3$ (2 × 150 ml), and toluene (3 × 40 ml). CC (silica gel, 80 × 3 cm, toluene/AcOEt 10:1 (6.6 l), 5:1 (3 l), and 1:1 (1 l)), followed by CC (silica gel, 80 × 3 cm, toluene/AcOEt 15:1, 12:1, 10:1, 9:1, 8:1, 7:1, and 6:1, AcOEt) of the mixed fractions, gave 1.19 g (17%) of **87**, 1.69 g (27%) of **88**, and 3.23 g (52%) of **89** as colorless foams.

87: TLC (toluene/AcOEt 1:1): R_f 0.86. UV (MeOH): 214 (sh, 4.79), 237 (sh, 4.49), 269 (4.57). ^{1}H-NMR ($CDCl_3$): 8.14 (*d*, 4 H *o* to NO_2 (npe)); 8.02 (*s*, H–C(8)); 7.54–7.10 (*m*, 14 H, 4 H *m* to NO_2 (npe), NH, $(MeO)_2$*Tr*); 6.80 (*d*, 4 H *o* to MeO); 5.90 (*d*, H–C(1′)); 4.84 (*t*, 3 H, OCH_2CH_2 (npe), H–C(2′)); 4.38 (*m*, 2 H, OCH_2CH_2 (npeoc)); 4.22 (*d*, H–C(3′)); 4.13 (*m*, H–C(4′)); 3.77 (*s*, 2 MeO); 3.51, 3.29 (2*m*, 2 H–C(5′)); 3.33 (*t*, 2 H, OCH_2CH_2 (npe)); 3.04 (*t*, 2 H, OCH_2CH_2 (npeoc)); 0.85 (*s*, *t*-Bu); 0.77 (*s*, *t*-Bu); 0.04 (*s*, SiMe); –0.05 (*s*, SiMe); –0.06 (*s*, SiMe); –0.33 (*s*, SiMe). Anal. calc. for $C_{60}H_{73}N_7O_{13}Si_2$ (1156.5): C 62.32, H 6.36, N 8.48; found: C 61.86, H 6.58, N 8.35.

88: TLC (toluene/AcOEt 1:1): R_f 0.71. UV (MeOH): 213 (sh, 4.79), 237 (sh, 4.48), 269 (4.57). ^{1}H-NMR ($CDCl_3$): 8.15 (*d*, 4 H *o* to NO_2 (npe)); 7.99 (*s*, H–C(8)); 7.54–7.11 (*m*, 14 H, 4 H *m* to NO_2 (npe), NH, $(MeO)_2$*Tr*); 6.78 (*d*, 4 H *o* to MeO); 5.92 (*d*, H–C(1′)); 5.03 (*t*, H–C(2′)); 4.84 (*t*, 2 H, OCH_2CH_2 (npe)); 4.41 (*m*, H–C(3′)); 4.37 (*t*, 2 H, OCH_2CH_2 (npeoc)); 4.22 (*d*, H–C(4′)); 3.76 (*s*, 2 MeO); 3.50, 3.36 (2*m*, 2 H–C(5′)); 3.33 (*t*, 2 H, OCH_2CH_2 (npe)); 3.02 (*t*, 2 H, OCH_2CH_2 (npeoc)); 2.71 (*d*, OH–C(3′)); 0.84 (*s*, *t*-Bu); 0.00 (*s*, SiMe); –0.20 (*s*, SiMe). Anal. calc. for $C_{54}H_{59}N_7O_{13}Si$ (1042.2): C 62.23, H 5.71, N 9.41; found: C 61.73, H 5.85, N 9.19.

89: TLC (toluene/AcOEt 1:1): R_f 0.50. UV (MeOH): 213 (sh, 4.79), 236 (sh, 4.48), 269 (4.54). ^{1}H-NMR ($CDCl_3$): 8.15 (*d*, 4 H *o* to NO_2 (npe)); 8.05 (*s*, H–C(8)); 7.50–7.15 (*m*, 14 H, 4 H *m* to NO_2 (npe), NH, $(MeO)_2$*Tr*); 6.74 (*d*, 4 H *o* to MeO); 5.93 (*d*, H–C(1′)); 4.78 (*t*, 2 H, OCH_2CH_2 (npe)); 4.71 (*q*, H–C(2′)); 4.56 (*q*, H–C(3′)); 4.44 (*t*, 2 H, OCH_2CH_2 (npeoc)); 4.29 (*d*, OH–C(2′)); 4.19 (*d*, H–C(4′)); 3.75 (*s*, 2 MeO); 3.30 (2 *m*, 2 H–C(5′)); 3.29 (*t*, 2 H, OCH_2CH_2 (npe)); 3.09 (*t*, 2 H, OCH_2CH_2 (npeoc)); 0.89 (*s*, *t*-Bu); 0.11 (*s*, SiMe); −0.04 (*s*, SiMe). Anal. calc. for $C_{54}H_{59}N_7O_{13}Si$ (1042.2): C 62.23, H 5.71, N 9.41; found: C 61.78, H 5.74, N 9.21.

*2′,3′-Bis-*O*-[(*tert*-butyl)dimethylsilyl]-*N^2*-isobutyryl-5′-*O*-(monomethoxytrityl)-*O^6*-[2-(4-nitrophenyl)ethyl]guanosine* (**90**), *2′-*O*-[(*tert*-Butyl)dimethylsilyl]-*N^2*-isobutyryl-5′-*O*-(monomethoxytrityl)-*O^6*-[2-(4-nitrophenyl)ethyl]guanosine* (**91**), *and 3′-*O*-[(*tert*-Butyl)dimethylsilyl]-*N^2*-isobutyryl-5′-*O*-(monomethoxytrityl)-*O^6*-[2-(4-nitrophenyl)ethyl]guanosine* (**92**). As described for **78–80**, with pyridine (3 × 15 ml), **65** (2.32 g, 3 mmol), 1*H*-imidazole (0.464 g, 6.8 mmol), pyridine (20 ml), $(t\text{-Bu})Me_2SiCl$ (0.512 g, 3.4 mmol; 20 h), and MeOH (5 ml). Workup with $CHCl_3$ (150 ml), phosphate buffer (pH 7.0; 3 × 100 ml) instead of H_2O, $CHCl_3$ (30 ml), and toluene (2 × 50 ml). CC (silica gel, 20 × 6 cm, toluene/AcOEt 4:1 and 3:1) gave 0.40 g (13%) of **90**, 0.72 g (27%) of **91**, and 1.41 g (53%) of **92** as colorless foams.

90: TLC (toluene/AcOEt 7:3): R_f 0.67. UV (MeOH): 237 (sh, 4.31), 269 (4.45), 280 (sh, 4.33). ^{1}H-NMR ($CDCl_3$): 8.14 (*d*, 2 H *o* to NO_2 (npe)); 7.99 (*s*, H–C(8)); 7.50–7.15 (*m*, 15 H, 2 H *m* to NO_2 (npe), NH, MeO*Tr*); 6.81 (*d*, 2 H *o* to MeO); 5.88 (*d*, H–C(1′)); 4.90 (*t*, H–C(2′)); 4.83 (*t*, OCH_2CH_2 (npe)); 4.18 (*m*, H–C(3′)); 4.09 (*m*, H–C(4′)); 3.76 (*s*, MeO); 3.54 (*m*, H–C(5′)); 3.31 (*t*, 2 H, OCH_2CH_2 (npe)); 3.15 (*m*, 1 H–C(5′)); 2.19 (*m*, Me_2CH); 0.97, 0.88 (*dd*, Me_2CH); 0.83 (*s*, *t*-Bu); 0.73 (*s*, *t*-Bu); 0.00 (*s*, SiMe); −0.07 (*s*, SiMe); −0.13 (*s*, SiMe); −0.40 (*s*, SiMe). Anal. calc. for $C_{54}H_{70}N_6O_9Si_2$ (1003.4): C 64.64, H 7.03, N 8.37; found: C 64.48, H 6.84, N 8.09.

91: TLC (toluene/AcOEt 7:3): R_f 0.38. UV (MeOH): 235 (sh, 4.31), 268 (4.45), 281 (sh, 4.33). ^{1}H-NMR ($CDCl_3$): 8.14 (*d*, 2 H *o* to NO_2 (npe)); 7.94 (*s*, H–C(8)); 7.50–7.15 (*m*, 15 H, 2 H *m* to NO_2 (npe), NH, MeO*Tr*); 6.78 (*d*, 2 H *o* to MeO); 5.84 (*d*, H–C(1′)); 5.16 (*t*, H–C(2′)); 4.85 (*t*, 2 H, OCH_2CH_2 (npe)); 4.32 (*m*, H–C(3′)); 4.22 (*m*, H–C(4′)); 3.75 (*s*, MeO); 3.52 (*m*, 1 H–C(5′)); 3.32 (*t*, 2 H, OCH_2CH_2 (npe)); 3.18 (*m*, 1 H–C(5′)); 1.90 (*m*, Me_2CH); 0.94 (*d*, 3 H, Me_2CH); 0.82 (*m*, 12 H, *t*-Bu, Me_2CH); −0.03 (*s*, SiMe); −0.27 (*s*, SiMe). Anal. calc. for $C_{48}H_{56}N_6O_9Si_2$ (889.1): C 64.84, H 6.34, N 9.45; found: C 65.00, H 6.48, N 9.64.

92: TLC (toluene/AcOEt 7:3): R_f 0.22. UV (MeOH): 236 (sh, 4.31), 269 (4.45), 281 (sh, 4.33). ^{1}H-NMR ($CDCl_3$): 8.13 (*d*, 2 H *o* to NO_2 (npe)); 8.02 (*s*, H–C(8)); 7.50–7.15 (*m*, 15 H, 2 H *m* to NO_2 (npe), NH, MeO*Tr*); 6.75 (*d*, 2 H *o* to MeO); 5.87 (*d*, H–C(1′)); 4.82 (*t*, 2 H, OCH_2CH_2 (npe)); 4.69 (*q*, H–C(3′)); 4.54 (*m*, H–C(2′)); 4.15 (*m*, H–C(4′)); 3.88 (*d*, OH–C(2′)); 3.74 (*s*, MeO); 3.41–3.18 (*m*, 4 H, 2 H–C(5′), OCH_2CH_2 (npe)); 2.58 (*m*, Me_2CH); 1.13 (*dd*, Me_2CH); 0.86 (*s*, *t*-Bu); −0.07 (*s*, 3 H, SiMe); −0.01 (*s*, SiMe). Anal. calc. for $C_{48}H_{56}N_6O_9Si_2$ (889.1): C 64.84, H 6.34, N 9.45; found: C 65.04, H 6.35, N 9.42.

*2′,3′-Bis-*O*-[(*tert*-butyl)dimethylsilyl]-5′-*O*-(dimethoxytrityl)-*O^4*-[2-(4-nitrophenyl)ethyl]uridine* (**93**), *2′-*O*-[(*tert*-Butyl)dimethylsilyl]-5′-*O*-(dimethoxytrityl)-*O^4*-[2-(4-nitrophenyl)ethyl]uridine* (**94**), *and 3′-*O*-[(*tert*-Butyl)dimethylsilyl]-5′-*O*-(dimethoxytrityl)-*O^4*-[2-(4-nitrophenyl)ethyl]uridine* (**95**). As described for **84–86**, with pyridine (2 × 20 ml), **69** (2.6 g, 3.74 mmol), pyridine (15 ml), $(t\text{-Bu})Me_2SiCl$ (0.73 g, 4.86 mmol), and 1*H*-imidazole (0.88 g, 12.85 mmol; 7 h). After quenching with MeOH (10 ml) and evaporation, workup with $CHCl_3$ (50 ml), H_2O (3 × 10 ml), $CHCl_3$ (30 ml), and toluene (2 × 40 ml). CC (100 g of silica gel, 20 × 4 cm, toluene/AcOEt 9:1 (800 ml), 4:1 (300 ml), 7:3 (500 ml), and 3:2 (500 ml)) gave 0.15 g (4%) of **93**, 1.45 g (48%) of **94**, and 1.07 g (35%) of **95** as colorless foams.

93: TLC (toluene/AcOEt 7:3): R_f 0.76. UV (MeOH): 204 (4.90), 232 (sh, 4.41), 274 (4.29), 281 (sh, 4.26). ^{1}H-NMR ($CDCl_3$): 8.59 (*d*, H–C(6)); 8.17 (*d*, 2 H *o* to NO_2 (npe)); 7.33 (*m*, 11 H, 2 H *o* to NO_2 (npe), $(MeO)_2$*Tr*); 6.83 (*d*, 4 H *o* to MeO); 5.76 (*s*, H–C(1′)); 5.39 (*d*, H–C(5)); 4.63 (*m*, 2 H, OCH_2CH_2 (npe)); 4.17 (*m*, H–C(2′), H–C(3′), H–C(4′)); 3.82 (*m*, 2 MeO, 1 H–C(5′)); 3.31 (*m*, 1 H–C(5′)); 3.16 (*t*, 2 H, OCH_2CH_2 (npe)); 0.90 (*s*, *t*-Bu); 0.71 (*s*, *t*-Bu); 0.29 (*s*, SiMe); 0.14 (*s*, SiMe); −0.03 (*s*, SiMe); −0.13 (*s*, SiMe). Anal. calc. for $C_{50}H_{65}N_3O_{10}Si_2$ (924.3): C 64.98, H 7.09, N 4.55; found: C 64.63, H 7.08, N 5.09.

94: TLC (toluene/AcOEt 7:3): R_f 0.55. UV (MeOH): 204 (4.88), 232 (sh, 4.40), 2.74 (sh, 4.28). ^{1}H-NMR ($CDCl_3$): 8.33 (*d*, H–C(6)); 8.16 (*d*, 2 H *o* to NO_2 (npe)); 7.33 (*m*, 11 H, 2 H *o* to NO_2 (npe), $(MeO)_2$*Tr*); 6.83 (*d*, 4 H *o* to MeO); 5.85 (*s*, H–C(1′)); 5.44 (*d*, H–C(5)); 4.63 (*m*, 2 H, OCH_2CH_2 (npe)); 4.35 (*m*, H–C(3′)); 4.28 (*m*, H–C(2′)); 4.07 (*m*, H–C(4′)); 3.79 (*s*, 2 MeO); 3.53 (*m*, 2 H–C(5′)); 3.15 (*t*, 2 H, OCH_2CH_2 (npe)); 2.36 (*d*, OH–C(3′)); 0.93 (*m*, *t*-Bu); 0.32 (*s*, SiMe); 0.19 (*s*, SiMe). Anal. calc. for $C_{44}H_{51}N_3O_{10}Si$ (810.0): C 65.25, H 6.35, N 5.19; found: C 64.80, H 6.11, N 5.09.

95: TLC (toluene/AcOEt 7:3): R_f 0.23. UV (MeOH): 204 (4.89), 232 (sh, 4.41), 274 (4.28), 280 (sh, 4.26). ^{1}H-NMR ($CDCl_3$): 8.23 (*d*, H–C(6)); 8.17 (*d*, 2 H *o* to NO_2 (npe)); 7.31 (*m*, 11 H, 2 H *o* to NO_2 (npe), $(MeO)_2$*Tr*); 6.83 (*d*, 4 H *o* to MeO); 6.02 (*d*, H–C(1′)); 5.52 (*d*, H–C(5)); 4.64 (*m*, 2 H, OCH_2CH_2 (npe)); 4.37 (*m*, H–C(3′));

4.10 (*m*, H–C(2′), H–C(4′)); 3.79 (*m*, 2 MeO); 3.68 (*m*, 1 H–C(5′)); 3.28 (*m*, 1 H–C(5′)); 3.15 (*t*, 2 H, OCH_2CH_2 (npe)); 2.99 (*d*, OH–C(2′)); 0.81 (*m*, *t*-Bu); 0.02 (*s*, SiMe), –0.09 (*s*, SiMe). Anal. calc. for $C_{44}H_{51}N_3O_{10}Si$ (810.0): C 65.25, H 6.35, N 5.19; found: C 64.72, H 6.13, N 5.21.

*3′-O-[(*tert*-Butyl)dimethylsilyl]-5′-O-(dimethoxytrityl)-N^6-[2-(4-nitrophenyl)ethoxycarbonyl]-2′-O-[2-(4-nitrophenyl)ethylsulfonyl]adenosine* (**96**). In dry pyridine (2 × 10 ml), 3′-*O*-[(*tert*-butyl)dimethylsilyl]-5′-*O*-(dimethoxytrityl)-N^6-[2-(4-nitrophenyl)ethoxycarbonyl]adenosine [42] (0.44 g, 0.52 mmol) was co-evaporated, then dissolved in pyridine (5 ml), and Npes-Cl (0.26 g, 1.04 mmol) was added and stirred at r.t. for 2 h. The reaction was stopped with MeOH (5 ml). Evaporation, co-evaporation with toluene (2 × 20 ml), and CC (silica gel, 33 × 2 cm, $CH_2Cl_2/CHCl_3$ 1:1), followed by co-evaporation with CH_2Cl_2, gave 0.493 g (90%) of **96**. Colorless foam. TLC (toluene/AcOEt 1:1): R_f 0.48. UV (MeOH): 236 (4.47), 266 (4.57), 274 (sh, 4.52). ^{1}H-NMR ($CDCl_3$): 8.56 (*d*, H–C(8)); 8.18–8.09 (*m*, H–C(2), 4 H *o* to NO_2 (npe)); 7.90 (*s*, NH); 7.44–7.14 (*m*, 13 H, 4 H *m* to NO_2 (npe), $(MeO)_2$*Tr*); 6.78 (*d*, 4 H *o* to MeO); 6.26 (*s*, H–C(1′)); 5.86 (*t*, H–C(2′)); 4.70 (*t*, H–C(3′)); 4.52 (*t*, 2 H, OCH_2CH_2 (npeoc)); 4.19 (*q*, H–C(4′)); 3.75 (*s*, 2 MeO); 3.54–3.33 (*m*, 4 H, 2 H–C(5′), SCH_2CH_2 (npes)); 3.14–3.04 (*t*, *m*, 4 H, OCH_2CH_2 (npeoc), SCH_2CH_2 (npes)); 0.85 (*s*, *t*-Bu); 0.11 (*s*, SiMe); –0.01 (*s*, SiMe). Anal. calc. for $C_{54}H_{59}N_7O_{14}SSi \cdot H_2O$ (1108.3): C 58.52, H 5.54, N 8.84; found: C 58.66, H 5.50, N 9.02.

*N^6-Benzoyl-3′-O-[(*tert*-butyl)dimethylsilyl]-5′-O-(monomethoxytrityl)-2′-O-[2-(4-nitrophenyl)ethylsulfonyl]adenosine* (**97**). As described for **96**, with pyridine (2 × 15 ml), N^6-benzoyl-3′-*O*-[(*tert*-butyl)dimethylsilyl]-5′-*O*-(monomethoxytrityl)adenosine [54] (1.14 g, 1.5 mmol), pyridine (25 ml), Npes-Cl (0.75 g, 3 mmol; 2 h), and MeOH (5 ml). Evaporation to 1/2 of its volume, workup with H_2O (50 ml) and $CHCl_3$ (100 ml), drying (Na_2SO_4), co-evaporation with toluene (2 × 20 ml), and CC (silica gel, 19.5 × 3.5 cm, $CHCl_3$) gave, after drying 1.32 g (91%) of **97**. TLC (toluene/AcOEt 1:1): R_f 0.66. UV (MeOH): 230 (sh, 4.49), 275 (4.48), 230 (sh, 4.49). ^{1}H-NMR ($CDCl_3$): 8.93 (*s*, NH); 8.66 (*s*, H–C(2)); 8.25 (*s*, H–C(8)); 8.17 (*d*, 2 H *o* to NO_2 (npes)); 8.02 (*dd*, 2 H *o* to C=O); 7.7–7.5 (*m*, 3 H, *Ph*CO); 7.45–7.20 (*m*, 14 H, 2 H *m* to NO_2 (npes), MeO*Tr*); 6.83 (*d*, 2 H *o* to MeO); 6.32 (*s*, H–C(1′)); 5.94 (*m*, H–C(2′)); 4.75 (*t*, H–C(3′)); 4.24 (*q*, H–C(4′)); 3.80 (*s*, MeO); 3.64–3.54 (*m*, 1 H–C(5′)); 3.42–3.28 (*m*, 3 H, 1 H–C(5′), SCH_2CH_2 (npes)); 3.26 (*m*, 2 H, SCH_2CH_2 (npes)); 0.90 (*s*, *t*-Bu); 0.15 (*s*, SiMe); –0.03 (*s*, SiMe). Anal. calc. for $C_{51}H_{54}N_6O_{10}SSi \cdot H_2O$ (989.2): C 61.92, H 5.70, N 8.49; found: C 62.27, H 5.54, N 8.54.

*3′-O-[(*tert*-Butyl)dimethylsilyl]-5′-O-(monomethoxytrityl)-N^4-[2-(4-nitrophenyl)ethoxycarbonyl]-2′-O-[2-(4-nitrophenyl)ethylsulfonyl]cytidine* (**98**). As described for **96**, with pyridine (2 × 10 ml), **80** (0.66 g, 0.8 mmol), pyridine (5 ml), and Npes-Cl (0.40 g, 1.6 mmol; 2 h; no MeOH). After dilution with H_2O (50 ml), extraction with $CHCl_3$ (3 × 50 ml), drying (Na_2SO_4), co-evaporation with toluene (2 × 20 ml), and CC (silica gel, 30 × 2 cm, CH_2Cl_2, $CH_2Cl_2/CHCl_3$ 1:1) gave, after co-evaporated with CH_2Cl_2 0.34 g (40%) of **98**. Colorless foam. A sample (0.1 g) was purified by prep. TLC (silica gel, toluene/AcOEt 1:1, desorption with $CHCl_3$/MeOH 4:1). TLC (toluene/AcOEt 1:1): R_f 0.66. UV (MeOH): 236 (4.46), 248 (sh, 4.39), 274 (4.44), 281 (sh, 4.41). ^{1}H-NMR ($CDCl_3$): 8.51 (*d*, H–C(6)); 8.16 (*dd*, 4 H *o* to NO_2 (npe)); 7.51–7.19 (*m*, 17 H, NH, 4 H *m* to NO_2 (npe), MeO*Tr*); 6.84 (*d*, 2 H *o* to MeO); 6.75 (*d*, H–C(5)); 5.96 (*s*, H–C(1′)); 4.92 (*d*, H–C(2′)); 4.41 (*t*, 2 H, OCH_2CH_2 (npeoc)); 4.32 (*m*, H–C(3′)); 4.16 (*m*, H–C(4′)); 3.82 (*m*, 3 H, 1 H–C(5′), SCH_2CH_2 (npes)); 3.80 (*s*, MeO); 3.32 (*m*, 3 H, 1 H–C(5′), SCH_2CH_2 (npes)); 3.08 (*t*, 2 H, OCH_2CH_2 (npeoc)); 0.73 (*s*, *t*-Bu); 0.03 (*s*, SiMe); –0.21 (*s*, SiMe). Anal. calc. for $C_{52}H_{57}N_5O_{14}SSi$ (1036.2): C 60.28, H 5.54, N 6.76; found: C 60.07, H 5.43, N 6.68.

*3′-O-[(*tert*-Butyl)dimethylsilyl]-5′-O-(dimethoxytrityl)-N^4-[2-(4-nitrophenyl)ethoxycarbonyl]-2′-O-[2-(4-nitrophenyl)ethylsulfonyl]cytidine* (**99**). As described for **96**, with pyridine (2 × 20 ml), **83** (1.38 g, 1.62 mmol), pyridine (30 ml), Npes-Cl (0.81 g, 3.24 mmol; 2 h), and MeOH (20 ml). CC (silica gel, 30 × 3.5 cm), CH_2Cl_2 (360 ml), $CH_2Cl_2/CHCl_3$ 5:1 (360 ml) and 5:4 (300 ml), followed by CC (silica gel, 15 × 3.5 cm, $CH_2Cl_2/CHCl_3$ 5:3 (480 ml) and 1:1, $CHCl_3$ (650 ml)), gave 1.36 g (79%) of **99**. Colorless foam. TLC (toluene/AcOEt 3:7): R_f 0.72. UV (MeOH): 235 (4.56), 274 (4.46), 281 (4.43). ^{1}H-NMR ($CDCl_3$): 8.56 (*d*, H–C(6)); 8.17 (*dd*, 4 H *o* to NO_2 (npe)); 7.51–7.19 (*m*, 14 H, NH, 4 H *m* to NO_2 (npe), $(MeO)_2$*Tr*); 6.84 (*d*, 4 H *o* to MeO); 6.74 (*d*, H–C(5)); 5.96 (*s*, H–C(1′)); 4.91 (*d*, H–C(2′)); 4.41 (*t*, 2 H, OCH_2CH_2 (npeoc)); 4.33 (*m*, H–C(3′)); 4.15 (*m*, H–C(4′)); 3.88 (*m*, 3 H, 1 H–C(5′), SCH_2CH_2 (npes)); 3.80 (*s*, 2 MeO); 3.35 (*m*, 3 H, 1 H–C(5′), SCH_2CH_2 (npes)); 3.09 (*t*, 2 H, OCH_2CH_2 (npeoc)); 0.73 (*s*, *t*-Bu); 0.03 (*s*, SiMe); –0.21 (*s*, SiMe). Anal. calc. for $C_{53}H_{59}N_5O_{15}SSi \cdot H_2O$ (1084.2): C 58.71, H 5.67, N 6.46; found: C 58.85, H 5.59, N 6.40.

*3′-O-[(*tert*-Butyl)dimethylsilyl]-5′-O-(dimethoxytrityl)-N^2-[2-(4-nitrophenyl)ethoxycarbonyl]-O^6-[2-(4-nitrophenyl)ethyl]-2′-O-[2-(4-nitrophenyl)ethylsulfonyl]guanosine* (**100**). As described for **96**, with pyridine (3 × 5 ml), **86** (1.25 g, 1.2 mmol), pyridine (12 ml), and Npes-Cl (0.6 g, 2.4 mmol; 1 h; no MeOH). After co-evaporation with toluene (2 × 15 ml) and CH_2Cl_2 (15 ml), the orange residue was taken up in CH_2Cl_2 (15 ml) and purified by CC (silica gel, 30 × 3.5 cm, toluene/AcOEt 8:1 (270 ml), 7:1 (240 ml), 5:1 (480 ml), and 4:1 (1 l)) gave 1.33 g (88%) of **100**. TLC (toluene/AcOEt 1:1): R_f 0.62. UV (MeOH): 212 (sh, 4.86), 237 (4.51), 269 (4.63). ^{1}H-NMR ($CDCl_3$): 8.12

(*m*, 6 H *o* to NO_2 (npe)); 8.02 (*s*, H–C(8)); 7.51–7.13 (*m*, 16 H, 6 H *m* to NO_2 (npe), NH, $(MeO)_2$*Tr*); 6.76 (*d*, 4 H *o* to MeO); 6.14 (*s*, H–C(1′)); 5.90 (*t*, H–C(2′)); 4.75 (*t*, 2 H, OCH_2CH_2 (npe)); 4.70 (*m*, H–C(3′)); 4.33 (*m*, 2 H, OCH_2CH_2 (npeoc)); 4.12 (*m*, H–C(4′)); 3.75 (*s*, 2 MeO); 3.51, 3.13 (2*m*, 2 H–C(5′)); 3.29 (2*t*, 4 H, OCH_2CH_2 (npe), SCH_2CH_2 (npes)); 3.02 (*t*, 4 H, OCH_2CH_2 (npeoc), SCH_2CH_2 (npes)); 0.85 (*s*, *t*-Bu); 0.10 (*s*, SiMe); –0.01 (*s*, SiMe). Anal. calc. for $C_{62}H_{66}N_9O_{17}SSi$ (1255.4): C 59.32, H 5.30, N 8.93; found: C 58.88, H 5.27, N 8.55.

*3′-*O*-[(*tert*-Butyl)dimethylsilyl]-*N*²-isobutyryl-5′-*O*-(monomethoxytrityl)-*O*⁶-[2-(4-nitrophenyl)ethyl]-2′-*O*-[2-(4-nitrophenyl)ethylsulfonyl]guanosine* (**101**). As described for **96**, with pyridine (2 × 10 ml), **92** (1.5 g, 1.69 mmol), pyridine (15 ml), Npes-Cl (0.85 g, 3.38 mmol; 1 h; no MeOH). After dilution with $CHCl_3$ (100 ml), washing with H_2O (100 ml), back extraction with $CHCl_3$ (2 × 100 ml), drying (Na_2SO_4), and co-evaporation with toluene (30 ml) and CH_2Cl_2 (20 ml), drying *in vacuo* gave **101** (2.32 g) as yellowish foam, pure enough for further reaction. A sample (0.404 mg) was purified by prep. TLC (silica gel, 2 × 40 × 20 × 0.2 cm (toluene/AcOEt 1:1), desorption with $CHCl_3MeOH$ 4:1): 0.273 g (85%) of **101**. Amorphous powder. TLC (toluene/AcOEt 1:1): R_f 0.64. UV (MeOH): 235 (sh, 4.35), 269 (4.57), 282 (sh, 4.43). ^{1}H-NMR ($CDCl_3$): 8.14 (2*d*, 4 H *o* to NO_2 (npe)); 8.01 (*s*, H–C(8)); 7.51–7.15 (*m*, 17 H, 4 H *m* to NO_2 (npe), NH, MeO*Tr*); 6.77 (*d*, 2 H *o* to MeO); 6.13 (*d*, H–C(1′)); 5.98 (*t*, H–C(2′)); 4.77 (*t*, 2 H, OCH_2CH_2 (npe)); 4.66 (*t*, H–C(3′)); 4.13 (*m*, H–C(4′)); 3.74 (*s*, MeO); 3.53 – 2.99 (*m*, 8 H, 2 H–C(5′), OCH_2CH_2 (npe), SCH_2CH_2 (npes)); 2.12 (*m*, Me_2CH); 1.00 (*d*, 3 H, Me_2CH); 0.90 (*d*, 3 H, Me_2CH); 0.82 (*s*, *t*-Bu); 0.06 (*s*, SiMe); –0.06 (*s*, SiMe). Anal. calc. for $C_{56}H_{63}N_7O_{13}SSi \cdot H_2O$ (1120.3): C 60.04, H 5.85, N 8.75; found: C 59.65, H 5.84, N 8.51.

*3′-*O*-[(*tert*-Butyl)dimethylsilyl]-5′-*O*-(dimethoxytrityl)-*O*⁴-[2-(4-nitrophenyl)ethyl]-2′-*O*-[2-(4-nitrophenyl)ethylsulfonyl]uridine* (**102**). As described for **96**, with pyridine (2 × 5 ml), **95** (0.344 g, 0.42 mmol), pyridine (7 ml), Npes-Cl (0.21 g, 0.84 mmol; 3 h; no MeOH). Evaporation to ½ of its volume, workup with $CHCl_3$ (50 ml) and H_2O (2 × 10 ml), drying (Na_2SO_4), co-evaporation with toluene (2 × 10 ml), and CC (silica gel, 14 × 2 cm, toluene/AcOEt 9:1 (300 ml) and 4:1 (200 ml)) gave 0.294 g (68%) of **102**. Colorless foam after drying *in vacuo*. TLC (toluene/AcOEt 7:3): R_f 0.58. UV (MeOH): 204 (4.94), 232 (sh, 4.45), 273 (4.46), 280 (sh, 4.42). ^{1}H-NMR ($CDCl_3$): 8.45 (*d*, H–C(6)); 8.18 (*d*, 4 H *o* to NO_2 (npe)); 7.51 (*d*, 2 H *m* to NO_2 (npe)); 7.40 (*d*, 2 H *m* to NO_2 (npes)); 7.25 (*m*, 9 H, $(MeO)_2$*Tr*); 6.85 (*d*, 4 H *o* to MeO); 5.90 (*s*, H–C(1′)); 5.41 (*d*, H–C(5)); 4.93 (*t*, H–C(2′)); 4.64 (*t*, 2 H, OCH_2CH_2 (npe)); 4.37 (*m*, H–C(3′)); 4.30 (*m*, 3 H, H–C(4′), SCH_2CH_2 (npes)); 3.75 (*s*, 1 H–C(5′), 2 MeO); 3.35 (*m*, 3 H, 1 H–C(5′), SCH_2CH_2 (npes)); 3.17 (*t*, 2 H, OCH_2CH_2 (npe)); 0.75 (*s*, *t*-Bu); 0.05 (*s*, SiMe); –0.20 (*s*, SiMe). Anal. calc. for $C_{52}H_{58}N_4O_{14}SSi$ (1023.2): C 61.04, H 5.71, N 5.48; found: C 60.64, H 5.59, N 5.46.

*5′-*O*-(Dimethoxytrityl)-*N*⁶-[2-(4-nitrophenyl)ethoxycarbonyl]-2′-*O*-[2-(4-nitrophenyl)ethylsulfonyl]adenosine* (**103**). Compound **96** (1.22 g, 1.12 mmol) was dissolved in dry THF (5.2 ml), then treated with $Bu_4NF \cdot 3 H_2O$ (1.05 g, 3.33 mmol). After stirring at –6 to –10° for 25 min, the mixture was diluted with $CHCl_3$ (20 ml) and purified by CC (silica gel, 25 × 5 cm, $CHCl_3$ (335 ml), $CHCl_3$/MeOH 50:1 (280 ml)): 0.86 g (79%) of **103** and 8% of **60**. *Data of* **103**: identical with those of an authentic sample prepared by direct sulfonylation.

*5′-*O*-(Monomethoxytrityl)-*N*⁴-[2-(4-nitrophenyl)ethoxycarbonyl]-2′-*O*-[2-(4-nitrophenyl)ethylsulfonyl]cytidine* (**104**). In a cold (–30°) soln. of dry THF (0.4 ml), **98** (0.116 g, 0.11 mmol) was dissolved and treated with $Bu_4NF \cdot 3 H_2O$ (0.116 g, 0.37 mmol). After stirring at –30° for 1.5 h, the mixture was diluted with $CHCl_3$ and purified by prep. TLC (40 × 20 × 0.2 cm, toluene/AcOEt 1:1, desorption with $CHCl_3$/MeOH 4:1). Co-evaporation with CH_2Cl_2 gave 0.075 g (72%) of **104**. TLC (toluene/AcOEt 3:7): R_f 0.73. UV (MeOH): 236 (4.44), 274 (4.10), 281 (sh, 4.41). ^{1}H-NMR ($CDCl_3$): 8.43 (*d*, H–C(6)); 8.14 (*dd*, 4 H *o* to NO_2 (npe)); 7.49–7.18 (*m*, 16 H, 4 H *m* to NO_2 (npe), MeO*Tr*); 6.93 (*d*, H–C(5)); 6.84 (*d*, 2 H *o* to MeO); 5.89 (*s*, H–C(1′)); 5.07 (*d*, H–C(2′)); 4.58 (*m*, H–C(3′)); 4.41 (*t*, 2 H, OCH_2CH_2 (npeoc)); 4.15 (*m*, H–C(4′)); 3.78 (*s*, MeO); 3.68 (*m*, 4 H, 2 H–C(5′), SCH_2CH_2 (npes)); 3.31 (*t*, 2 H, SCH_2CH_2 (npes)); 3.08 (*t*, 3 H, OH–C(3′), OCH_2CH_2 (npeoc)). Anal. calc. for $C_{46}H_{43}N_5O_{14}S$ (922.0): C 59.93, H 4.70, N 7.60; found: C 59.58, H 5.20, N 7.20.

*5′-*O*-(Dimethoxytrityl)-*N*⁴-[2-(4-nitrophenyl)ethoxycarbonyl]-2′-*O*-[2-(4-nitrophenyl)ethylsulfonyl]cytidine* (**105**). In a cold (–12°) soln. of dry THF (4 ml), **99** (1.26 g, 1.18 mmol) was dissolved and treated with $Bu_4NF \cdot 3 H_2O$ (1.23 g, 3.89 mmol) for 20 min. The mixture was diluted with $CHCl_3$ (10 ml) and purified by CC (silica gel, 10 × 2.5 cm, $CHCl_3$ (200 ml), $CHCl_3$/MeOH 100:0.5 (200 ml) and 100:1 (200 ml)): 0.096 (8%) of starting material and 0.645 g (57%) of **105**. Further elution with $CHCl_3$/MeOH 50:1→20:1 yielded 0.038 g (4%) of **62** and 0.097 g (11%) of *5′-*O*-(dimethoxytrityl)-*N*⁴-[2-(4-nitrophenyl)ethoxycarbonyl]arabinocytidine*. *Data of* **105**: identical with those of an authentic sample prepared by direct sulfonylation.

*N*⁶*-Benzoyl-5′-*O*-(monomethoxytrityl)-2′-*O*-[2-(4-nitrophenyl)ethylsulfonyl]adenosine* (**106**). In a cold soln. (–18°) of dry THF (5.2 ml), **97** (1.22 g, 1.12 mmol) was dissolved and treated with $Bu_4NF \cdot 3 H_2O$ (1.32 g, 1.54 mmol) with stirring for 100 min. The mixture was diluted with $CHCl_3$ (20 ml) and purified by CC (silica gel, 24.5 × 3.5 cm, $CHCl_3$ and $CHCl_3$/MeOH 97:3): **106**. The substance was taken up in CH_2Cl_2, the soln. washed with phosphate buffer (pH 7.0; 2 × 25 ml) and H_2O (20 ml), dried (Na_2SO_4), and evaporated, the residue which contained still some Bu_4NF again dissolved in CH_2Cl_2 (14 ml), and this soln. added dropwise with vigorous stirring into pentane (17 ml) and Et_2O (50 ml). The precipitate was filtered and dried *in vacuo* at 40°: 0.635 g (67%) of **106**. TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.69. UV (MeOH): 276 (4.44), 231 (sh, 4.44). ^{1}H-NMR ($CDCl_3$): 8.91 (*s*, NH); 8.66 (*s*, H–C(2)); 8.16 (*s*, H–C(8); *d*, 2 H *o* to NO_2 (npes)); 8.02 (*d*, 2 H *o* to C=O); 7.7–7.5 (*m*, PhCO); 7.47–7.15 (*m*, 14 H, 2 H *m* to NO_2 (npes), MeO*Tr*); 6.83 (*d*, 2 H *o* to MeO); 6.30 (*s*, 1 H–C(1′)); 5.92 (*t*, H–C(2′)); 4.90 (*q*, H–C(3′)); 4.30 (*q*, H–C(4′)); 3.80 (*s*, MeO); 3.64–3.54 (*m*, 4 H, 2 H–C(5′), SCH_2CH_2 (npes)); 3.35–3.10 (*m*, 2 H, SCH_2CH_2 (npes)); 2.64 (*d*, OH–C(2′)). Anal. calc. for $C_{45}H_{39}N_6O_{10}S \cdot 0.5\ H_2O$ (864.9): C 62.49, H 4.66, N 9.71; found: C 62.69, H 4.78, N 9.73.

5′-O-(Monomethoxytrityl)-N^6-[2-(4-nitrophenyl)ethoxycarbonyl]-2′,3-bis-O-[2-(4-nitrophenyl)ethylsulfonyl]adenosine (**107**), *5′-O-(Monomethoxytrityl)-N^6-[2-(4-nitrophenyl)ethoxycarbonyl]-2′-O-[2-(4-nitrophenyl)ethylsulfonyl]adenosine* (**51**), *and 5′-O-(Monomethoxytrityl)-N^6-[2-(4-nitrophenyl)ethoxycarbonyl]-3′-O-[2-(4-nitrophenyl)ethylsulfonyl]adenosine* (**108**). In dry pyridine (2 × 5 ml), **59** (0.1 g, 0.136 mmol) was co-evaporated and then dissolved in pyridine (3 ml). Npes-Cl (0.06 g, 0.238 mmol) was added and the mixture stirred at r.t. for 62 h. Another 20 mg (0.08 mmol) of Npes-Cl was added and stirring continued for 5 h. The mixture was diluted with $CHCl_3$ (10 ml) and washed with H_2O (10 ml), the org. phase dried (Na_2SO_4), evaporated, and co-evaporated with toluene (2 × 10 ml), and the residue purified by prep. TLC (40 × 20 × 0.2 cm, toluene/AcOEt/MeOH 5:4:0.2, desorption with $CHCl_3$/MeOH 4:1). The products were reprecipitated from $CHCl_3$ into hexane: 19 mg (12%) of **107**, 0.046 g (35%) of **51**, and 0.038 g (29%) of **108**. Amorphous powders.

107: TLC (toluene/AcOEt/MeOH 5:4:0.2): R_f 0.65. UV (MeOH): 238 (4.42), 266 (4.68), 274 (sh, 4.63). ^{1}H-NMR ($CDCl_3$): 8.52 (*s*, H–C(8)); 8.18–8.05 (*m*, 8 H, H–C(2), NH, 6 H *o* to NO_2 (npe)); 7.42–7.15 (*m*, 18 H, 6 H *m* to NO_2 (npe), MeO*Tr*); 6.71 (*d*, 2 H *o* to MeO); 6.19 (*s*, H–C(1′)); 6.14 (*m*, H–C(2′)); 5.75 (*t*, H–C(3′)); 4.53 (*t*, 2 H, OCH_2CH_2 (npeoc)); 4.43 (*q*, H–C(4′)); 3.73 (*s*, MeO); 3.66–3.10 (*m*, 12 H, 2 H–C(5′), OCH_2CH_2 (npeoc), 2 SCH_2CH_2 (npes)). Anal. calc. for $C_{55}H_{50}N_8O_{17}S_2$ (1159.2): C 56.99, H 4.35, N 9.67; found: C 56.52, H 4.52, N 9.42.

108: TLC (toluene/AcOEt/MeOH 5:4:0.2): R_f 0.35. UV (MeOH): 235 (4.37), 267 (4.59), 275 (sh, 4.53). ^{1}H-NMR ($CDCl_3$): 8.70 (*s*, H–C(8)); 8.15 (*m*, 6 H, H–C(2), NH, 4 H *o* to NO_2 (npe)); 7.41 (*dd*, 4 H *m* to NO_2 (npe)); 7.20–7.01 (*m*, 12 H, MeO*Tr*); 6.74 (*d*, 2 H *o* to MeO); 5.93 (*m*, H–C(1′)); 5.68 (br. *s*, OH–C(2′)); 5.23 (*m*, H–C(2′)); 5.15 (*m*, H–C(3′)); 4.54 (*t*, 3 H, H–C(4′), OCH_2CH_2 (npeoc)); 3.75 (*s*, MeO); 3.63–3.11 (*m*, 8 H, 2 H–C(5′), OCH_2CH_2 (npeoc), SCH_2CH_2 (npes)). Anal. calc. for $C_{47}H_{43}N_7O_{13}S$ (946.0): C 59.68, H 4.58, N 10.37; found: C 58.90, H 4.63, N 10.10.

5′-O-(Dimethoxytrityl)-N^6-[2-(4-nitrophenyl)ethoxycarbonyl]-2′,3′-bis-O-[2-(4-nitrophenyl)ethylsulfonyl]adenosine (**109**), *5′-O-(Dimethoxytrityl)-N^6-[2-(4-nitrophenyl)ethoxycarbonyl]-2′-O-[2-(4-nitrophenyl)ethylsulfonyl]adenosine* (**103**), *and 5′-O-(Dimethoxytrityl)-N^6-[2-(4-nitrophenyl)ethoxycarbonyl]-3′-O-[2-(4-nitrophenyl)ethylsulfonyl]adenosine* (**110**). In cold $CHCl_3$ (2 ml, −6°), **60** [42] (0.382 g, 0.5 mmol) was dissolved, Et_3N (0.2 ml, 1.5 mmol) was added and then dropwise Npes-Cl (0.187 g, 0.75 mmol) in CH_2Cl_2 (2 ml). After stirring at −6° for 15 min and at r.t. for 3 h, the mixture was diluted with $CHCl_3$ (100 ml), washed with H_2O (2 × 50 ml), dried (Na_2SO_4), and evaporated. CC (silica gel, 15 × 2.5 cm, toluene/AcOEt 3:2, 1:1, and 2:3) gave 0.045 g (7.5%) of **109**, 0.2 g (41%) of **103**, and 0.183 g (38%) of **110**, as colorless foams.

109: TLC (toluene/AcOEt 1:10): R_f 0.91. UV (MeOH): 238 (4.51), 267 (4.67), 274 (sh, 4.63). ^{1}H-NMR ($CDCl_3$): 8.55 (*s*, H–C(8)); 8.19–8.06 (*m*, 7 H, H–C(2), 6 H *o* to NO_2 (npe)); 7.96 (*s*, NH); 7.46–7.15 (*m*, 15 H, 6 H *m* to NO_2 (npe), $(MeO)_2$*Tr*); 6.72 (*d*, 4 H *o* to MeO); 6.19 (*m*, H–C(1′), H–C(2′)); 5.72 (*t*, H–C(3′)); 4.53 (*t*, 2 H, OCH_2CH_2 (npeoc)); 4.43 (*q*, H–C(4′)); 3.73 (*s*, 2 MeO); 3.66–3.32 (*m*, 12 H, 2 H–C(5′), OCH_2CH_2 (npeoc), 2 SCH_2CH_2 (npes)). Anal. calc. for $C_{56}H_{52}N_8O_{18}S_2$ (1189.2): C 56.56, H 4.41, N 9.42; found: C 56.08, H 4.24, N 8.68.

103: TLC (toluene/AcOEt 1:10): R_f 0.58 UV (MeOH): 236 (4.42), 267 (4.58), 274 (sh, 4.54). ^{1}H-NMR ($CDCl_3$): 8.56 (*s*, H–C(8)); 8.15–8.10 (*m*, 5 H, H–C(2), 4 H *o* to NO_2 (npe)); 8.04 (*s*, NH); 7.44–7.19 (*m*, 13 H, 4 H *m* to NO_2 (npe), $(MeO)_2$*Tr*); 6.78 (*d*, 4 H *o* to MeO); 6.25 (*d*, H–C(1′)); 5.84 (*t*, H–C(2′)); 4.80 (*m*, H–C(3′)); 4.52 (*t*, 2 H, OCH_2CH_2 (npeoc)); 4.25 (*m*, H–C(4′)); 3.76 (*s*, 2 MeO); 3.51 (*m*, 4 H, 2 H–C(5′), SCH_2CH_2 (npes)); 3.21 (*m*, 4 H, OCH_2CH_2 (npeoc), SCH_2CH_2 (npes)); 1.55 (*m*, OH–C(3′)). Anal. calc. for $C_{48}H_{45}N_7O_{14}S \cdot H_2O$ (994.0): C 58.00, H 4.77, N 9.86; found: C 57.66, H 4.74, N 9.63.

110: Data identical with those of authentic material [42].

5′-O-(Dimethoxytrityl)-N^4-[2-(4-nitrophenyl)ethoxycarbonyl]-2′,3′-bis-O-[2-(4-nitrophenyl)ethylsulfonyl]cytidine (**111**), *5′-O-(Dimethoxytrityl)-N^4-[2-(4-nitrophenyl)ethoxycarbonyl]-2′-O-[2-(4-nitrophenyl)ethylsulfonyl]cytidine* (**112**), *and 5′-O-(Dimethoxytrityl)-N^4-[2-(4-nitrophenyl)ethoxycarbonyl]-3′-O-[2-(4-nitrophenyl)ethylsulfonyl]cytidine* (**113**). As described for **109**/**103**/**110**, with CH_2Cl_2 (4 ml), **62** (0.37 g, 0.5 mmol), Et_3N (0.16 ml, 1.1 mmol), Npes-Cl (0.137 g, 0.55 mmol), and CH_2Cl_2 (1 ml, 60 min at −6°). Workup with CH_2Cl_2 (20 ml) and

H_2O (2 × 20 ml). CC (silica gel, 13 × 2 cm, toluene/AcOEt 5:2 and 2:1, AcOEt) gave 0.061 g (11%) of **111**, 0.136 g (29%) of **112**, and 0.11 g (23%) of **113** as colorless foams.

111: TLC (toluene/AcOEt 1:3): R_f 0.57. UV (MeOH): 237 (4.61), 247 (sh, 4.56), 264 (sh, 4.59), 271 (4.60). ^{1}H-NMR ($CDCl_3$): 8.37 (*d*, H–C(6)); 8.18 (*m*, 6 H *o* to NO_2 (npe)); 7.53–7.23 (*m*, 16 H, NH, 6 H *m* to NO_2 (npe), MeO*Tr*); 6.86 (*d*, 4 H *o* to MeO); 6.77 (*d*, H–C(5)); 5.90 (*d*, H–C(1′)); 5.54 (*dd*, H–C(2′)); 5.52 (*m*, H–C(3′)); 4.44 (*t*, 2 H, OCH_2CH_2 (npeoc)); 4.34 (*m*, H–C(4′)); 3.73 (*s*, 2 MeO); 3.51 (*m*, 10 H, 2 H–C(5′), 2 × SCH_2CH_2 (npes)); 3.11 (*t*, 2 H, OCH_2CH_2 (npeoc)). Anal. calc. for $C_{55}H_{52}N_6O_{19}S_2$ (1165.2): C 56.70, H 4.50, N 7.21; found: C 56.30, H 4.37, N 7.29.

112: TLC (toluene/AcOEt 3:7): R_f 0.53. UV (MeOH): 236 (4.56), 274 (4.46), 281 (sh, 4.43). ^{1}H-NMR ($CDCl_3$): 8.25 (*d*, H–C(6)); 8.16 (*m*, H–C(2), 4 H *o* to NO_2 (npe)); 7.67 (br. *s*, NH); 7.51–7.25 (*m*, 13 H, 4 H *m* to NO_2 (npe), MeO*Tr*); 6.91 (*d*, H–C(5)); 6.84 (*d*, 4 H *o* to MeO); 5.89 (*s*, H–C(1′)); 5.04 (*d*, H–C(2′)); 4.56 (*m*, H–C(3′)); 4.42 (*t*, 2 H, OCH_2CH_2 (npeoc)); 4.14 (*m*, H–C(4′)); 3.99–3.52 (*s*, *m*, 10 H, 2 MeO, 2 H–C(5′), SCH_2CH_2 (npes)); 3.33 (*t*, 2 H, SCH_2CH_2 (npes)); 3.10 (*t*, 2 H, OCH_2CH_2 (npeoc)); 8.21 (br. *s*, OH–C(3′)). Anal. calc. for $C_{47}H_{45}N_5O_{15}S$ (952.0): C 59.30, H 4.76, N 7.36; found: C 59.02, H 5.06, N 7.17.

113: TLC (toluene/AcOEt 1:3): R_f 0.12. UV (MeOH): 236 (4.57), 272 (4.43), 280 (sh, 4.40). ^{1}H-NMR ($CDCl_3$): 8.21 (*d*, H–C(6)); 8.14 (*dd*, 4 H *o* to NO_2 (npe)); 7.96 (br. *s*, NH); 7.42–7.22 (*m*, 13 H, 4 H *m* to NO_2 (npe), MeO*Tr*); 7.08 (*d*, H–C(5)); 6.84 (*d*, 4 H *o* to MeO); 5.88 (*s*, *d*, H–C(1′), OH–C(2′)); 5.19 (*d*, H–C(3′)); 3.79 (*s*, 2 MeO); 3.45 (*m*, 2 H, OCH_2CH_2 (npeoc)); 3.34 (*m*, 6 H, 2 H–C(5′), SCH_2CH_2 (npes)); 2.97 (*m*, 2 H, OCH_2CH_2 (npeoc)). Anal. calc. for $C_{47}H_{45}N_5O_{15}S$ (952.0): C 59.30, H 4.76, N 7.36; found: C 59.46, H 5.20, N 7.03.

N^4*-Benzoyl-5′-*O*-(monomethoxytrityl)-2′,3′-bis-*O*-[2-(4-nitrophenyl)ethylsulfonyl]cytidine* (**114**), N^4*-Benzoyl-5′-*O*-(monomethoxytrityl)-2′-*O*-[2-(4-nitrophenyl)ethylsulfonyl]cytidine* (**115**), *and* N^4*-Benzoyl-5′-*O*-(monomethoxytrityl)-3′-*O*-[2-(4-nitrophenyl)ethylsulfonyl]cytidine* (**116**). To a soln. of *N*^{4}-benzoyl-5′-*O*-(monomethoxytrityl)cytidine [55] (1.24 g, 2 mmol) and Et_3N (0.84 ml, 6 mmol) in CH_2Cl_2 (16 ml), cooled in an ice-bath, a soln. of Npes-Cl (0.749 g, 3 mmol) in CH_2Cl_2 (3 ml) was added slowly and dropwise. After 45 min stirring, H_2O (20 ml) was added, the product extracted with $CHCl_3$ (2 × 20 ml), the org. phase dried (Na_2SO_4) and evaporated, and the residue purified by CC (80 g of silica gel, 30 × 3 cm, toluene/AcOEt 3:2, AcOEt): 0.164 g (8%) of **114**, 0.392 g (24%) of **115**, and 0.33 g (20%) of **116** as colorless foams.

114: TLC (toluene/AcOEt 1:1): R_f 0.78. UV (MeOH): 236 (4.45), 263 (4.62), 300 (sh, 4.19), 314 (sh, 3.97). ^{1}H-NMR ($CDCl_3$): 8.68 (br. *s*, NH); 8.41 (*d*, H–C(6)); 8.18 (*dd*, 4 H *o* to NO_2 (npes)); 7.87 (*d*, 2 H *o* to C=O); 7.67–7.16 (*m*, 20 H, 4 H *m* to NO_2 (npes), MeO*Tr*, bz, H–C(5)); 6.88 (*d*, 2 H *o* to MeO); 5.95 (*s*, H–C(1′)); 5.64 (*dd*, H–C(2′)); 5.31 (*d*, H–C(3′)); 4.37 (*m*, H–C(4′)); 3.99 (*m*, 1 H–C(5′)); 3.82 (*s*, MeO); 3.69 (*m*, 4 H, 2 SCH_2CH_2 (npes)); 3.51 (*m*, 1 H–C(5′)); 3.33 (*m*, 4 H, 2 SCH_2CH_2 (npes)). Anal. calc. for $C_{52}H_{47}N_5O_{15}S_2$ (1046.1): C 59.71, H 4.53, N 6.69; found: C 60.48, H 4.75, N 6.31.

115: TLC (toluene/AcOEt 1:1): R_f 0.40. UV (MeOH): 234 (4.42), 262 (sh, 4.48), 300 (sh, 4.13), 312 (sh, 4.01). ^{1}H-NMR ($CDCl_3$): 8.83 (br. *s*, NH); 8.55 (*d*, H–C(6)); 8.08 (*d*, 2 H *o* to NO_2 (npes)); 7.93 (*d*, 2 H *o* to C=O); 7.88–7.04 (*m*, 18 H, 2 H *m* to NO_2 (npes), MeO*Tr*, bz, H–C(5)); 6.87 (*d*, 2 H *o* to MeO); 5.95 (*s*, H–C(1′)); 5.18 (*d*, H–C(2′)); 4.69 (*dd*, H–C(3′)); 4.19 (*m*, H–C(4′)); 3.97 (*m*, 1 H–C(5′)); 3.80 (*s*, MeO); 3.69 (*m*, 3 H, 1 H–C(5′), SCH_2CH_2 (npes)); 3.32 (*m*, 2 H, SCH_2CH_2 (npes)). Anal. calc. for $C_{44}H_{40}N_4O_{11}S$ (832.9): C 63.25, H 4.84, N 6.73; found: C 62.93, H 5.04, N 6.42.

116: TLC (toluene/AcOEt 1:1): R_f 0.13. UV (MeOH): 234 (4.42), 262 (4.52), 300 (sh, 4.10), 314 (sh, 3.69). ^{1}H-NMR ($CDCl_3$): 8.82 (br. *s*, NH); 8.17 (*dd*, H–C(6), 2 H *o* to NO_2 (npes)); 7.88 (*d*, 2 H *o* to C=O); 7.65–7.13 (*m*, 18 H, 2 H *m* to NO_2 (npes), MeO*Tr*, bz, H–C(5)); 6.86 (*d*, 2 H *o* to MeO); 5.92 (*s*, H–C(1′)); 5.80 (br. *s*, OH–C(2′)); 5.24 (*m*, H–C(3′)); 4.68 (*t*, H–C(2′)); 4.59 (*m*, H–C(4′)); 3.77 (*s*, MeO); 3.70 (*m*, 1 H–C(5′)); 3.43 (*m*, 5 H, 1 H–C(5′), SCH_2CH_2 (npes)). Anal. calc. for $C_{44}H_{40}N_4O_{11}S$ (832.9): C 63.45, H 4.84, N 6.73; found: C 63.45, H 4.96, N 6.44.

N^4*-Benzoyl-5′-*O*-(dimethoxytrityl)-2′,3′-bis-*O*-[2-(4-nitrophenyl)ethylsulfonyl]cytidine* (**117**), N^4*-Benzoyl-5′-*O*-(dimethoxytrityl)-2′-*O*-[2-(4-nitrophenyl)ethylsulfonyl]cytidine* (**118**), *and* N^4*-Benzoyl-5′-*O*-(dimethoxytrityl)-3′-*O*-[2-(4-nitrophenyl)ethylsulfonyl]cytidine* (**119**). As described for **114**–**116**, with *N*^{4}-benzoyl-5′-*O*-(dimethoxytrityl)cytidine [56] (1.95 g, 3 mmol), Et_3N (1.44 ml, 10.2 mmol), CH_2Cl_2 (24 ml), Npes-Cl (1.3 g, 5.1 mmol), and CH_2Cl_2 (15 ml; 1 h). Workup with H_2O (20 ml) and CH_2Cl_2 (2 × 30 ml). CC (70 g silica gel, 26 × 3 cm, toluene/AcOEt 7:3) gave 0.29 g (9%) of **117**, 0.698 g (27%) of **118**, and 0.682 g (26%) of **119** as colorless foams.

117: TLC (toluene/AcOEt 3:7): R_f 0.78. UV (MeOH): 236 (4.56), 263 (4.64), 298 (sh, 4.21), 313 (sh, 3.98). ^{1}H-NMR ($CDCl_3$): 8.63 (br. *s*, NH); 8.43 (*d*, H–C(6)); 8.18 (*dd*, 4 H *o* to NO_2 (npes)); 7.87 (*d*, 2 H *o* to C=O); 7.64–7.15 (*m*, 16 H, 4 H *m* to NO_2 (npes), $(MeO)_2$*Tr*, bz); 6.88 (*d*, H–C(5), 4 H *o* to MeO); 5.96 (*s*, H–C(1′)); 5.57 (*m*, H–C(2′)); 5.28 (*m*, H–C(3′)); 4.37 (*m*, H–C(4′)); 4.01 (*m*, 1 H–C(5′)); 3.82 (*s*, 2 MeO); 3.74 (*m*, 4 H, 2

SCH_2CH_2 (npes)); 3.51 (*m*, 1 H–C(5′)); 3.35 (*m*, 4 H, 2 SCH_2CH_2 (npes)). Anal. calc. for $C_{53}H_{49}N_5O_{16}S_2$ (1076.1): C 59.16, H 4.59, N 6.51; found: C 58.75, H 4.71, N 6.22.

118: TLC (toluene/AcOEt 3:7): R_f 0.62. UV (MeOH): 236 (4.51), 298 (sh, 4.15), 314 (sh, 3.92), 262 (4.48). ^{1}H-NMR ($CDCl_3$): 8.81 (br. *s*, NH); 8.54 (*d*, H–C(6)); 8.11 (*d*, 2 H *o* to NO_2 (npes)); 7.86 (*d*, 2 H *o* to C=O); 7.61–7.01 (*m*, 14 H, 2 H *m* to NO_2 (npes), $(MeO)_2$*Tr*, bz); 6.86 (*d*, 4 H *o* to MeO); 6.71 (*d*, H–C(5)); 5.95 (*s*, H–C(1′)); 5.17 (*d*, H–C(2′)); 4.67 (*m*, H–C(3′)); 4.21 (*m*, H–C(4′)); 3.90 (*m*, 1 H–C(5′)); 3.80 (*s*, 2 MeO); 3.68 (*m*, 3 H, 1 H–C(5′), SCH_2CH_2 (npes)); 3.21 (*t*, 2 H, SCH_2CH_2 (npes)). Anal. calc. for $C_{45}H_{42}N_4O_{12}S$ (862.9): C 62.64, H 4.91, N 6.49; found: C 62.87, H 5.21, N 6.08.

119: TLC (toluene/AcOEt 3:7): R_f 0.42. UV (MeOH): 236 (4.52), 262 (4.53), 302 (sh, 4.09), 312 (sh, 3.92). ^{1}H-NMR ($CDCl_3$): 8.74 (br. *s*, NH); 8.18 (*dd*, H–C(6), 2 H *o* to NO_2 (npes)); 7.88 (*d*, 2 H *o* to C=O); 7.66–7.16 (*m*, 15 H, 2 H *m* to NO_2 (npes), $(MeO)_2$*Tr*, bz, H–C(5)); 5.89 (*d*, H–C(1′)); 5.68 (br. *s*, OH–C(2′)); 5.17 (*m*, H–C(3′)); 4.68 (*t*, H–C(2′)); 4.60 (*m*, H–C(4′)); 3.77 (*s*, MeO); 3.76 (*s*, MeO); 3.72 (*m*, 3 H, 1 H–C(5′), SCH_2CH_2 (npes)); 3.42 (*m*, 3 H, 1 H–C(5′), SCH_2CH_2 (npes)). Anal. calc. for $C_{45}H_{42}N_4O_{12}S$ (862.9): C 62.64, H 4.91,N 6.49; found: C 62.89, H 5.04, N 6.14.

5′-O-(Dimethoxytrityl)-2′,3′-bis-O-[2-(4-nitrophenyl)ethylsulfonyl]uridine (**120**), *5′-O-(Dimethoxytrityl)-2′-O-[2-(4-nitrophenyl)ethylsulfonyl]uridine* (**121**), *and 5′-O-(dimethoxytrityl)-3′-O-[2-(4-nitrophenyl)ethylsulfonyl]uridine* (**122**). *a*) To an ice-cold soln. of 5′-*O*-(dimethoxytrityl)uridine (**66**) [55] (2.19 g, 4 mmol) in dry pyridine (35 ml) was added Npes-Cl (1.5 g, 6 mmol). After stirring at r.t. for 2 h, the mixture was diluted with $CHCl_3$ (100 ml) and washed with H_2O (2 × 20 ml). The org. layer was dried ($MgSO_4$), evaporated, and co-evaporated with toluene (2 × 20 ml) and the crude product purified by CC (120 g silica gel, 23 × 4 cm, with toluene/AcOEt 4:1 (500 ml), 3:1 (400 ml), 2:1 (600 ml), and 1:1 (600 ml)): 0.47 g (12%) of **120**, 1.10 g (36%) of **121**, and 0.62 g (20%) of **122** as colorless foams.

b) A soln. of uridine (0.49 g, 2 mmol), dibutyltin oxide (0.56 g, 2.25 mmol), Npes-Cl (0.84 g, 3.35 mmol), and tetrahexylammonium chloride (0.78 g, 2 mmol) in MeCN (50 ml) was stirred at r.t. for 26 h. The solvent was evaporated and the residue purified by CC (50 g silica gel, 8 × 35 cm, AcOEt (400 ml), AcOEt/MeOH 100:1 (300 ml)): 0.7 g of a yellow foam. The crude product was dissolved in dry pyridine (10 ml) and treated with $(MeO)_2$Tr-Cl (0.73 g, 2.1 mmol), and after stirring at r.t. for 8 h, the soln. was diluted with $CHCl_3$ (40 ml), washed with H_2O (3 × 10 ml), dried ($MgSO_4$), evaporated, and co-evaporated with toluene (2 × 10 ml). The residue was purified by CC (40 g of silica gel, 16 × 3 cm, toluene/AcOEt 3:1 (400 ml), 2:1 (300 m), and 1:1 (300 ml)): 0.34 g (22%) of **121** and 0.35 g (23%) of **122** as colorless foams.

c) A soln. of **66** [55] (0.82 g, 1.5 mmol), dibutyltin oxide (0.42 g, 1.7 mmol), Npes-Cl (0.63 g, 2.5 mmol), and tetrahexylammonium chloride (0.59 g, 1.5 mmol), in MeCN (30 ml) was stirred at r.t. for 22 h. The solvent was evaporated and the residue purified by CC (50 g silica gel, 20 × 3 cm, toluene/AcOEt 4:1 (400 ml), 3:1 (300 ml), 2:1 (300 ml), and 1:1 (400 ml)): 0.08 g (6%) of **120**, 0.35 g (31%) of **121**, and 0.44 g (39%) of **122** as colorless foams.

120: TLC (toluene/AcOEt 3:7): R_f 0.70. UV (MeOH): 204 (4.86), 236 (4.41), 263 (4.42). ^{1}H-NMR ($CDCl_3$): 8.64 (*s*, NH); 8.17 (*m*, 4 H *o* to NO_2 (npes)); 7.76 (*d*, H–C(6)); 7.32 (*m*, 13 H, 4 H *m* to NO_2 (npes), $(MeO)_2$*Tr*); 6.85 (*d*, 4 H *o* to MeO); 5.92 (*d*, H–C(1′)); 5.48 (*m*, H–C(2′)); 5.35 (*m*, H–C(5), H–C(3′)); 4.29 (*d*, H–C(4′)); 3.79 (*s*, 2 MeO); 3.48 (*m*, 10 H, 2 H–C(5′), 2 SCH_2CH_2 (npes)). Anal. calc. for $C_{46}H_{44}N_4O_{16}S_2$ (973.0): C 56.78, H 4.56, N 5.76; found: C 56.75, H 5.00, N 5.04.

121: TLC (toluene/AcOEt 3:7): R_f 0.45. UV (MeOH): 205 (4.86), 235 (4.43), 264 (4.30), 281 (sh, 4.09). ^{1}H-NMR ($CDCl_3$): 9.57 (*s*, NH); 8.13 (*m*, 2 H *o* to NO_2 (npes)); 7.93 (*d*, H–C(6)); 7.30 (*m*, 11 H, 2 H *m* to NO_2 (npes), $(MeO)_2$*Tr*); 6.84 (*d*, 4 H *o* to MeO); 5.93 (*d*, H–C(1′)); 5.35 (*d*, H–C(5)); 5.16 (*m*, H–C(2′)); 4.64 (*m*, H–C(3′)); 4.12 (*m*, H–C(4′)); 3.78 (*s*, 2 MeO); 3.64 (*m*, 4 H, 2 H–C(5′), SCH_2CH_2 (npes)); 3.29 (*t*, 2 H, SCH_2CH_2 (npes)); 3.03 (*d*, OH–C(3′)). Anal. calc. for $C_{38}H_{37}N_3O_{12}S \cdot H_2O$ (777.8): C 58.68, H 5.05, N 5.40; found: C 59.80, H 5.00, N 4.71.

122: TLC (toluene/AcOEt 3:7): R_f 0.26. UV (MeOH): 204 (4.92), 235 (4.45), 265 (4.45), 280 (sh, 4.19). ^{1}H-NMR ($CDCl_3$): 11.31 (*s*, NH); 8.05 (*m*, 2 H *o* to NO_2 (npes)); 7.77 (*d*, H–C(6)); 7.29 (*m*, 11 H, 2 H *m* to NO_2 (npes), $(MeO)_2$*Tr*); 6.83 (*d*, 4 H *o* to MeO); 5.77 (*d*, H–C(1′)); 5.58 (*d*, OH–C(2′)); 5.28 (*m*, H–C(5), H–C(3′)); 4.76 (*m*, H–C(2′)); 4.25 (*m*, H–C(4′)); 3.71 (*m*, 9 H, 2 MeO, SCH_2CH_2 (npes), 1 H–C(5′)); 3.42 (*m*, 1 H–C(5′)); 3.28 (*m*, 2 H, SCH_2CH_2 (npes)). Anal. calc. for $C_{38}H_{37}N_3O_{12}S \cdot H_2O$ (777.8): C 58.68, H 5.05, N 5.40; found: C 58.94, H 4.90, N 5.10.

5′-O-(Dimethoxytrityl)-O^4-methyl-2′,3′-bis-O-[2-(4-nitrophenyl)ethylsulfonyl]uridine (**123**), *5′-O-(Dimethoxytrityl)-O^4-methyl-2′-O-[2-(4-nitrophenyl)ethylsulfonyl]uridine* (**124**), *and 5′-O-(Dimethoxytrityl)-O^4-methyl-3′-O-[2-(4-nitrophenyl)ethylsulfonyl]uridine* (**125**). To an ice-cold soln. (−15°) of **68** (0.42 g, 0.75 mmol) and Et_3N (0.25 ml, 1.8 mmol) in CH_2Cl_2 (5 ml), Npes-Cl (0.22 g, 0.9 mmol) in CH_2Cl_2 (2 ml) was added dropwise.

After stirring for 10 min, H_2O (25 ml) was added, the aq. phase extracted with CH_2Cl_2 (2 × 20 ml), the combined org. phase dried ($MgSO_4$) and evaporated, and the residue purified by CC (40 g of silica gel, 15 × 3 cm, toluene/AcOEt 4:1, 7:3, 3:2, and 1:1 (each 300 ml)): 0.067 g (9%) of **123**, 0.172 g (30%) of **124**, and 0.14 g (24%) of **125**.

123: TLC (toluene/AcOEt 1:1): R_f 0.67. UV (MeOH): 203 (4.81), 233 (4.39), 268 (4.44), 280 (sh, 4.35). ^{1}H-NMR ($CDCl_3$): 8.19 (*m*, H–C(6), 4 H *o* to NO_2 (npes)); 7.30 (*m*, 13 H, 4 H *m* to NO_2 (npes), $(MeO)_2$*Tr*); 6.85 (*d*, 4 H *o* to MeO); 5.85 (*d*, H–C(1′)); 5.56 (*m*, H–C(2′)); 5.47 (*m*, H–C(5)); 5.24 (*m*, H–C(3′)); 4.33 (*d*, H–C(4′)); 4.06 (*m*, 1 H–C(5′)); 3.96 (*s*, MeO–C(4)); 3.79 (*s*, 2 MeO); 3.51 (*m*, 9 H, 1 H–C(5′), 2 SCH_2CH_2 (npes)). Anal. calc. for $C_{47}H_{46}N_4O_{16}S_2 \cdot H_2O$ (1005.0): C 56.17, H 4.18, N 5.57; found: C 56.52, H 4.73, N 5.14.

124: TLC (toluene/AcOEt 1:1): R_f 0.41. UV (MeOH): 204 (4.85), 232 (4.35), 270 (4.24), 280 (sh, 4.16). ^{1}H-NMR ($CDCl_3$): 8.30 (*d*, H–C(6)); 8.17 (*d*, 2 H *o* to NO_2 (npes)); 7.52 (*d*, 2 H *m* to NO_2 (npes)); 7.23 (*m*, 9 H $(MeO)_2$*Tr*); 6.83 (*d*, 4 H *o* to MeO); 5.86 (*d*, H–C(1′)); 5.59 (*d*, H–C(5)); 5.08 (*m*, H–C(2′)); 4.62 (*m*, H–C(3′)); 4.14 (*m*, H–C(4′)); 4.03 (*m*, 1 H–C(5′)); 3.95 (*s*, MeO–C(4)); 3.78 (*s*, 2 MeO); 3.62 (*m*, 1 H–C(5′), SCH_2CH_2 (npes)): 3.36 (*t*, 2 H, SCH_2CH_2 (npes)); 2.96 (*d*, OH–C(3′)). Anal. calc. for $C_{39}H_{39}N_3O_{12}S \cdot H_2O$ (791.8): C 59.16, H 5.22, N 5.31; found: C 58.83, H 5.22, N 4.94.

125: TLC (toluene/AcOEt 1:1): R_f 0.17. UV (MeOH): 204 (4.85), 232 (4.34), 272 (4.24), 280 (sh, 4.18). ^{1}H-NMR ($CDCl_3$): 8.18 (*d*, 2 H *o* to NO_2 (npes)); 7.94 (*d*, H–C(6)); 7.41 (*d*, 2 H *m* to NO_2 (npes)); 7.27 (*m*, 9 H, $(MeO)_2$*Tr*); 6.83 (*d*, 4 H *o* to MeO); 5.83 (*m*, H–C(1′), H–C(5)); 5.44 (*d*, OH–C(2′)); 5.03 (*m*, H–C(3′)); 4.55 (*m*, H–C(2′), H–C(4′)); 3.98 (*s*, MeO–C(4)); 3.78 (*m*, 2 MeO); 3.46 (*m*, 6 H, 2 H–C(5′), SCH_2CH_2 (npes)). Anal. calc. for $C_{39}C_{39}N_3O_{12}S \cdot H_2O$ (791.8): C 59.16, H 5.22, N 5.31; found: C 60.03, H 4.96, N 5.10.

5′-O-(Dimethoxytrityl)-O^4-[2-(4-nitrophenyl)ethyl]-2′,3′-bis-O-[2-(4-nitrophenyl)ethylsulfonyl]uridine (**126**), *5′-O-(Dimethoxytrityl)-O^4-[2-(4-nitrophenyl)ethyl]-2′-O-[2-(nitrophenyl)ethylsulfonyl]uridine* (**127**), *and 5′-O-(Dimethoxytrityl)-O^4-[2-(4-nitrophenyl)ethyl]-3′-O-[2-(4-nitrophenyl)ethylsulfonyl]uridine* (**128**). *a*) To a soln. of **69** (0.696 g, 1 mmol) and Et_3N (0.49 ml, 3.5 mmol) in CH_2Cl_2 (6 ml) was added dropwise under stirring Npes-Cl (0.437 g, 1.75 mmol) in CH_2Cl_2 (3 ml). After 25 min at −10°, H_2O (15 ml) was added, the aq. phase extracted with CH_2Cl_2 (2 × 20 ml), the combined org. phase dried ($MgSO_4$) and evaporated, and the residue purified by CC (40 g of silica gel, 15 × 3 cm, toluene/AcOEt 7:3 (300 ml) and 3:2 (400 ml)): 0.305 g (27%) of **126**, 0.273 g (30%) of **127**, and 0.241 g (27%) of **128** as colorless foams.

b) A mixture of O^4-[2-(4-nitrophenyl)ethyl]uridine (**21**) [32] (0.197 g, 0.5 mmol), dibutyltin oxide (0.139 g, 0.56 mmol), Npes-Cl (0.212 g, 0.85 mmol), and tetrahexylammonium chloride (0.195 g, 0.5 mmol) in MeCN (15 ml) was stirred at r.t. for 20 h. The solvent was evaporated and the residue purified by CC (20 g of silica gel, 20 × 1.5 cm, AcOEt (300 ml)): yellow foam (0.258 g). The crude product in dry pyridine (5 ml) was treated with $(MeO)_2$Tr-Cl (0.18 g, 0.55 mmol), and after stirring at r.t. for 4 h, MeOH (1 ml) was added. The mixture was diluted with $CHCl_3$ (30 ml), washed with H_2O (2 × 10 ml), dried ($MgSO_4$), evaporated, and co-evaporated with toluene (2 × 10 ml). The residue was purified by CC (20 g of silica gel, 15 × 2 cm, toluene/AcOEt 7:3 and 3:2 (each 200 ml)) 0.076 g (20%) **127** of 0.15 g (39%) of **128** as colorless foams.

c) A soln. of **69** (0.174 g, 0.25 mmol), dibutyltin oxide (0.07 g, 0.28 mmol), 2-(4-nitrophenyl)ethylsulfonyl chloride (0.106 g, 0.43 mmol), and tetrahexylammonium chloride (0.098 g, 0.25 mmol) in MeCN (8 ml) was stirred at r.t. for 24 h. The solvent was evaporated and the residue purified by CC (15 g of silica gel, 11 × 2 cm, toluene/AcOEt 7:3 and 3:2 (each 200 ml)): 0.045 g (20%) of **127**, 0.096 g (42%) of **128** as colorless foams.

126: TLC (toluene/AcOEt 1:1): R_f 0.76. UV (MeOH): 204 (4.96), 235 (4.45), 270 (4.56). ^{1}H-NMR ($CDCl_3$): 8.19 (*m*, H–C(6), 6 H *o* to NO_2 (npe)); 7.30 (*m*, 15 H, 6 H *o* to NO_2 (npe), $(MeO)_2$*Tr*); 6.84 (*d*, 4 H *o* to MeO); 5.81 (*d*, H–C(1′)); 5.55 (*m*, H–C(2′)); 5.43 (*m*, H–C(5)); 5.23 (*m*, H–C(3′)); 4.65 (*t*, 2 H, OCH_2CH_2 (npe)); 4.32 (*m*, H–C(4′)); 4.04 (*m*, 1 H–C(5′)); 3.80 (*s*, 2 MeO); 3.43 (*m*, 11 H, H–C(5′), OCH_2CH_2 (npe), 2 SCH_2CH_2 (npes)). Anal. calc. for $C_{54}H_{51}N_5O_{18}S_2$ (1122.2): C 57.80, H 4.58, N 6.24; found: C 57.32, H 4.62, N 5.87.

127: TLC (toluene/AcOEt 1:1): R_f 0.57. UV (MeOH): 204 (4.87), 233 (4.38), 271 (4.42), 280 (sh, 4.36). ^{1}H-NMR ($CDCl_3$): 8.31 (*d*, H–C(6)); 8.18 (*d*, 4 H o to NO_2 (npe)); 7.25 (*m*, 13 H, 4 H *o* to NO_2 (npe), $(MeO)_2$*Tr*); 6.83 (*d*, 4 H *o* to MeO); 5.84 (*s*, H–C(1′)); 5.54 (*d*, H–C(5)); 5.06 (*m*, H–C(2′)); 4.62 (*m*, 3 H, H–C(3′), OCH_2CH_2 (npe)); 4.13 (*m*, H–C(4′)); 4.00 (*m*, H–C(5′)); 3.79 (*s*, 2 MeO); 3.64 (*m*, 3 H, 1 H–C(5′), SCH_2CH_2 (npes)); 3.36 (*t*, 2 H, SCH_2CH_2 (npes)); 3.17 (*t*, 2 H, OCH_2CH_2 (npe)); 2.72 (*d*, OH–C(3′)). Anal. calc. for $C_{46}H_{44}N_4O_{14}S$ (908.9): C 60.79, H 4.88, N 6.16; found: C 60.06, H 5.01, N 5.76.

128: TLC (toluene/AcOEt 1:1): R_f 0.24. UV (MeOH): 204 (4.90), 234 (4.42), 272 (4.45), 281 (sh, 4.39). ^{1}H-NMR ($CDCl_3$): 8.17 (2*d*, 4 H *o* to NO_2 (npe)); 7.97 (*d*, H–C(6)); 7.41 (*d*, 4 H *m* to NO_2 (npe)); 7.27 (*m*, 9 H, $(MeO)_2$*Tr*); 6.81 (*d*, 4 H *o* to MeO); 5.79 (*m*, H–C(1′), H–C(5)); 5.30 (*d*, OH–C(2′)); 5.09 (*m*, H–C(3′)); 4.66 (*t*, 2 H, OCH_2CH_2 (npe)); 4.55 (*m*, H–C(2′), H–C(4′)); 3.78 (*m*, 2 MeO); 3.48 (*m*, 6 H, 2 H–C(5′), SCH_2CH_2 (npes));

3.18 (*t*, 2 H, OCH_2CH_2 (npe)). Anal. calc. for $C_{46}H_{44}N_4O_{14}S$ (908.9): C 60.79, H 4.88, N 6.16; found: C 60.54, H 5.01, N 6.10.

5′-O-(Dimethoxytrityl)-O⁴-[2-(4-cyanophenyl)ethyl]-2′,3′-bis-O-[2-(4-nitrophenyl)ethylsulfonyl]uridine (**129**), *5′-O-(Dimethoxytrityl)-O⁴-[2-(4-cyanophenyl)ethyl]-2′-O-[2-(4-nitrophenyl)ethylsulfonyl]uridine* (**130**), *and 5′-O-(Dimethoxytrityl)-O⁴-[2-(4-cyanophenyl)ethyl]-3′-O-[2-(4-nitrophenyl)ethylsulfonyl]uridine* (**131**). As described for **114**–**116**, with **70** (1.35 g, 2 mmol), Et_3N (0.74 ml, 5.2 mmol), CH_2Cl_2 (10 ml; −15°), Npes-Cl (0.65 g, 2.6 mmol), and CH_2Cl_2 (5 ml; 30 min at −15°). Workup with H_2O (10 ml), CH_2Cl_2 (2 × 25 ml), and $MgSO_4$. CC (50 g of silica gel, 15 × 3 cm, toluene/AcOEt 4:1 and 7:3 (each 300 ml)) yielded 0.20 g (9%) of **129**, 0.52 g (29%) of **130**, and 0.52 g (29%) of **131** as colorless foams.

129: TLC (toluene/AcOEt 1:1): R_f 0.86. UV (MeOH): 203 (4.92), 231 (4.55), 270 (4.37). ^{1}H-NMR ($CDCl_3$): 8.19 (*m*, H−C(6), 4 H *o* to NO_2 (npes)); 7.62 (*d*, 2 H *o* to CN (cpe)); 7.50 (*d*, 2 H *m* to CN (cpe)); 7.26 (*m*, 13 H, 4 H *o* to NO_2 (npes), $(MeO)_2$*Tr*); 6.84 (*d*, 4 H *o* to MeO); 5.81 (*d*, H−C(1′)); 5.55 (*m*, H−C(2′)); 5.43 (*m*, H−C(5)); 5.23 (*m*, H−C(3′)); 4.61 (*t*, 2 H, OCH_2CH_2 (cpe)); 4.32 (*d*, H−C(4′)); 4.04 (*m*, 1 H−C(5′)); 3.79 (*s*, 2 MeO); 3.45 (*m*, 9 H, 1 H−C(5′), 2 SCH_2CH_2 (npes)); 3.12 (*t*, 2 H, OCH_2CH_2 (cpe)). Anal. calc. for $C_{55}H_{51}N_5O_{16}S_2 \cdot H_2O$ (1120.2): C 58.97, H 4.77, N 6.25; found: C 59.36, H 4.77, N 5.71.

130: TLC (toluene/AcOEt 1:1): R_f 0.51. UV (MeOH): 203 (4.93), 231 (4.60), 271 (4.27). ^{1}H-NMR ($CDCl_3$): 8.31 (*d*, H−C(6)); 8.15 (*d*, 2 H *o* to NO_2 (npes)); 7.60 (*d*, 2 H *o* to CN (cpe)); 7.50 (*d*, 2 H *m* to NO_2 (npes)); 7.21 (*m*, 11 H, 2 H *m* to CN (cpe), $(MeO)_2$*Tr*); 6.82 (*d*, 4 H *o* to MeO); 5.84 (*s*, H−C(1′)); 5.54 (*d*, H−C(5)); 5.08 (*m*, H−C(2′)); 4.61 (*m*, 3 H, H−C(3′), OCH_2CH_2 (cpe)); 4.13 (*m*, H−C(4′)); 3.98 (*m*, 1 H−C(5′)); 3.78 (*s*, 2 MeO); 3.67 (*m*, 3 H, 1 H−C(5′), SCH_2CH_2 (npes)); 3.34 (*t*, 2 H, SCH_2CH_2 (npes)); 3.06 (*m*, 3 H, OH−C(3′), OCH_2CH_2 (cpe)). Anal. calc. for $C_{47}H_{44}N_4O_{12}S \cdot H_2O$ (906.9): C 62.24, H 5.11, N 6.17; found: C 62.78, H 5.25, N 5.78.

131: TLC (toluene/AcOEt 1:1): R_f 0.28. UV (MeOH): 204 (4.89), 232 (4.59), 273 (4.27). ^{1}H-NMR ($CDCl_3$): 8.16 (*d*, 2 H *o* to NO_2 (npes)); 7.97 (*d*, H−C(6)); 7.60 (*d*, 2 H *o* to CN (cpe)); 7.30 (*m*, 13 H, 2 H *m* to NO_2 (npes), 2 H *m* to CN (cpe), $(MeO)_2$*Tr*); 6.81 (*d*, 4 H *o* to MeO); 5.79 (*m*, H−C(1′), H−C(5)); 5.35 (*d*, OH−C(2′)); 5.09 (*m*, H−C(3′)); 4.62 (*t*, 2 H, OCH_2CH_2 (cpe)); 4.53 (*m*, H−C(2′), H−C(4′)); 3.78 (*m*, 2 MeO); 3.46 (*m*, 6 H, 2 H−C(5′), SCH_2CH_2 (npes)); 3.18 (*t*, 2 H, OCH_2CH_2 (cpe)). Anal. calc. for $C_{47}H_{44}N_4O_{12}S \cdot H_2O$ (906.9): C 62.24, H 5.11, N 6.17; found: C 61.99, H 5.06, N 5.78.

5′-O-(Monomethoxytrityl)-2′,3′-bis-O-[2-(4-nitrophenyl)ethylsulfonyl]pseudouridine (**132**), *5′-O-(Monomethoxytrityl)-2′-O-[2-(4-nitrophenyl)ethylsulfonyl]pseudouridine* (**133**), *and 5′-O-(Monomethoxytrityl)-3′-O-[2-(4-nitrophenyl)ethylsulfonyl]pseudouridine* (**134**). In dry pyridine (2 × 10 ml), 5′-*O*-(monomethoxytrityl)pseudouridine (**71**) [57] (1.03 g, 2 mmol) was co-evaporated and then dissolved in dry pyridine (10 ml) and cooled to −20°. After adding Npes-Cl (0.75 g, 3 mmol), the soln. was stirred for 1 h at −20° and further for 1 h at −50°. The mixture was diluted with $CHCl_3$ (100 ml), washed with H_2O (3 × 40 ml), dried (Na_2SO_4), evaporated, and co-evaporated with toluene. CC (60 g of silica gel, *d* 3.5 cm, $CHCl_3$) gave 0.44 g (23%) of **132**, 0.42 g (29%) of **133**, and 0.42 g (29%) of **134** as colorless foams.

132: TLC ($CHCl_3$/MeOH 24:1): R_f 0.62. UV (MeOH): 204 (4.86), 232 (sh, 4.29), 265 (4.44). ^{1}H-NMR ((D$_6$)DMSO): 11.33 (*s*, H−N(3)); 11.15 (*d*, H−N(1)); 8.11 (*m*, H−C(6), 4 H *o* to NO_2 (npes)); 7.67–7.19 (*m*, 17 H, H−C(6), 4 H *m* to NO_2 (npes), MeO*Tr*); 6.85 (*d*, 2 H *o* to MeO); 5.52 (*t*, H−C(2′)); 5.43 (*m*, H−C(5)); 5.33 (*t*, H−C(3′)); 4.85 (*m*, H−C(1′)); 4.15 (*m*, H−C(4′)); 3.75 (*s*, MeO); 3.60–3.01 (*m*, 10 H, 2 H−C(5′), 2 SCH_2CH_2 (npes)). Anal. calc. for $C_{45}H_{42}N_4O_{15}S_2$ (943.0): C 57.32, H 4.49, N 5.94; found: C 57.18, H 4.85, N 5.74.

133: TLC ($CHCl_3$/MeOH 24:1): R_f 0.42. UV (MeOH): 205 (4.77), 231 (4.22), 265 (4.24). ^{1}H-NMR ((D$_6$)DMSO): 11.26 (*s*, H−N(3)); 11.07 (*d*, H−N(1)); 8.19 (*d*, 2 H *o* to NO_2 (npes)); 7.59 (*d*, H−C(6)); 7.48–7.19 (*m*, 14 H, 2 H *m* to NO_2 (npes), MeO*Tr*); 6.89 (*d*, 2 H *o* to MeO); 5.63 (*d*, OH−C(3′)); 5.03 (*m*, H−C(2′)); 4.81 (*m*, H−C(1′)); 4.22 (*q*, H−C(3′)); 3.74 (*s*, MeO); 3.93–3.07 (*m*, 7 H, H−C(4′), 2 H−C(5′), SCH_2CH_2 (npes)). Anal. calc. for $C_{37}H_{35}N_3O_{11}S$ (729.8): C 60.90, H 4.83, N 5.76; found: C 61.38, H 5.43, N 5.18.

134: TLC ($CHCl_3$/MeOH 24:1): R_f 0.34. UV (MeOH): 205 (4.77), 231 (4.23), 265 (4.24). ^{1}H-NMR ((D$_6$)DMSO): 11.20 (*s*, H−N(3)); 11.07 (*d*, H−N(1)); 8.13 (*d*, 2 H *o* to NO_2 (npes)); 7.52 (*d*, H−C(6)); 7.44–7.17 (*m*, 14 H, 2 H *m* to NO_2 (npes), MeO*Tr*); 6.85 (*d*, 2 H *o* to MeO); 5.76 (*d*, OH−C(2′)); 5.00 (*m*, H−C(3′)); 4.49 (*m*, H−C(1′), H−C(2′)); 4.11 (*q*, H−C(4′)); 3.72 (*s*, MeO); 3.73–3.12 (*m*, 6 H, 2 H−C(5′), SCH_2CH_2 (npes)). Anal. calc. for $C_{37}H_{35}N_3O_{11}S$ (729.8): C 60.90, H 4.83, N 5.76; found: C 61.05, H 5.39, N 5.31.

5′-O-(Dimethoxytrityl)-2′,3′-bis-O-[2-(4-nitrophenyl)ethylsulfonyl]pseudouridine (**135**), *5′-O-(Dimethoxytrityl)-2′-O-[2-(4-nitrophenyl)ethylsulfonyl]pseudouridine* (**136**), *and 5′-O-(Dimethoxytrityl)-3′-O-[2-(4-nitrophenyl)ethylsulfonyl]pseudouridine* (**137**). As described for **132**–**134**, with pyridine (2 × 10 ml), **72** (1.107 g, 2.02 mmol), pyridine (18 ml), Npes-Cl (0.75 g, 3 mmol; at −20° for 2 h), and $CHCl_3$ (50 ml). CC (60 g of silica gel, *d* 3.5 cm, toluene/AcOEt 4:1 (300 ml), 3:1 (560 ml), 5:2 (280 ml), 2:1 (150 ml), and 1:1 (200 ml)) gave 0.25 g (13%) of **135**, 0.384 g (25%) of **136**, and 0.476 g (31%) of **137** as colorless foams.

135: TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.74. UV (MeOH): 204 (4.71), 238 (4.23), 264 (4.45). ^{1}H-NMR ($CDCl_3$): 9.54 (br. *s*, H–N(3)); 8.68 (br. *s*, H–N(1)); 8.11 (*m*, 4 H *o* to NO_2 (npes)); 7.42–7.14 (*m*, 14 H, H–C(6), 4 H *m* to NO_2 (npes), $(MeO)_2$*Tr*); 6.78 (*d*, 4 H *o* to MeO); 5.45–5.30 (*m*, H–C(2′), H–C(3′)); 4.76 (br. *s*, H–C(1′)); 4.14 (*m*, H–C(4′)); 3.72 (*s*, 2 MeO); 3.72–3.17 (*m*, 10 H, 2 H–C(5′), 2 SCH_2CH_2 (npes)). Anal. calc. for $C_{46}H_{44}N_4O_{16}S_2$ (973.0): C 56.78, H 4.56, N 5.76; found: C 56.82, H 4.85, N 5.28.

136: TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.65. UV (MeOH): 204 (4.81), 235 (4.34), 265 (4.32). ^{1}H-NMR ((D_6)DMSO): 11.26 (*s*, H–N(3)); 11.07 (*d*, H–N(1)); 8.17 (*d*, 2 H *o* to NO_2 (npes)); 7.66–7.17 (*m*, 12 H, H–C(6), 2 *m* to NO_2 (npes), $(MeO)_2$*Tr*); 6.89 (*d*, 4 H *o* to MeO); 5.63 (*d*, OH–C(3′)); 5.03 (*m*, H–C(2′)); 4.86 (*d*, H–C(1′)); 4.23 (*q*, H–C(3′)); 3.92–3.17 (*m*, 13 H, H–C(4′), 2 MeO, 2 H–C(5′), SCH_2CH_2 (npes)). Anal. calc. for $C_{38}H_{37}N_3O_{12}S \cdot 0.5\ H_2O$ (768.8): C 59.37, H 4.98, N 5.46; found: C 59.18, H 5.25, N 5.03.

137: TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.52. UV (MeOH): 204 (4.84), 235 (4.31), 265 (4.29). ^{1}H-NMR ((D_6)DMSO): 11.19 (*s*, H–N(3)); 11.03 (br. *s*, H–N(1)); 8.13 (*d*, 2 H *o* to NO_2 (npes)); 7.54–7.18 (*m*, 12 H, H–C(6), 2 H *m* to NO_2 (npes), $(MeO)_2$*Tr*); 6.84 (*d*, 4 H *o* to MeO); 5.75 (*d*, OH–C(2′)); 4.99 (*t*, H–C(3′)); 4.49 (*m*, H–C(1′), H–C(2′)); 4.23 (*q*, H–C(4′)); 3.71 (*s*, 2 MeO); 3.71–3.07 (*m*, 6 H, 2 H–C(5′), SCH_2CH_2 (npes)). Anal. calc. for $C_{38}H_{37}N_3O_{12}S$ (759.8): C 60.07, H 4.91, N 5.53; found: C 60.71, H 5.23, N 5.11.

5′-O-(Monomethoxytrityl)-O^2,O^4-bis[2-(4-nitrophenyl)ethyl]-2′,3′-bis-O-[2-(4-nitrophenyl)ethylsulfonyl]pseudouridine (**138**), *5′-O-(Monomethoxytrityl)-O^2,O^4-bis[2-(4-nitrophenyl)ethyl]-2′-O-[2-(4-nitrophenyl)ethylsulfonyl]pseudouridine* (**139**), *and 5′-O-(Monomethoxytrityl)-O^2,O^4-bis[2-(4-nitrophenyl)ethyl]-3′-O-[2-(4-nitrophenyl)ethylsulfonyl]pseudouridine* (**140**). *a*) In dry pyridine (1 ml), **73** (0.1 g, 0.12 mmol) was co-evaporated and then dissolved in dry pyridine (1 ml) and cooled to –2°. After addition of Npes-Cl (0.046 g, 0.18 mmol), the soln. was stirred at –2° for 1 h and at r.t. for 2 h, diluted with $CHCl_3$ (20 ml), washed with H_2O (3 × 10 ml), dried (Na_2SO_4), evaporated, and co-evaporated with toluene. CC (15 g of silica gel, *d* 1 cm, $CHCl_3$/AcOEt 9:1 (50 ml), 4:1 (100 ml), and 7:3 (100 ml)) gave 0.053 g (35%) of **138**, 0.029 g (23%) of **139**, and 0.037 g (30%) of **140** as colorless foams.

b) To a soln. of **73** (0.1 g, 0.12 mmol) and Et_3N (60 µl, 0.43 mmol) in dry CH_2Cl_2 (1 ml) at –13°, Npes-Cl (0.053 g, 0.21 mmol) in CH_2Cl_2 (0.5 ml), was added and stirred at –13° for 2.5 h. Then the temp. was allowed to rise to –1° for 1 h. Workup and purification as described in *a*) gave 0.037 g (30%) of **138**, 0.015 g (12%) of **139**, and 0.068 g (54%) of **140** as colorless foams.

c) To a soln. of **73** (0.1 g, 0.12 mmol) and *Hünig*'s base (70 µl, 0.43 mmol) in dry CH_2Cl_2 (1 ml) at –13°, Npes-Cl (0.053 g, 0.21 mmol) in CH_2Cl_2 (0.5 ml) was added and stirred at –13° for 2.5 h. Then the temp. was allowed to rise –1° within 1 h. Workup and purification as described in *a*) gave 0.037 g (30%) of **138**, 0.015 g (12%) of **139**, and 0.068 g (54%) of **140** as colorless foams.

138: TLC ($CHCl_3$/AcOEt 7:3): R_f 0.78. UV (MeOH): 202 (4.96), 232 (4.42), 269 (4.63). ^{1}H-NMR ($CDCl_3$): 8.41 (*s*, H–C(6)); 8.15 (*m*, 8 H *o* to NO_2 (npe)); 7.46–7.18 (*m*, 20 H, 8 H *m* to NO_2 (npe), MeO*Tr*); 6.76 (*d*, 2 H *o* to MeO); 5.22 (*t*, H–C(2′)); 5.14 (*t*, H–C(3′)); 5.08 (*d*, H–C(1′)); 4.58 (*m*, 4 H, OCH_2CH_2 (npe)); 4.20 (*q*, H–C(4′)); 3.75 (*s*, MeO); 3.59 (*dd*, 1 H–C(5′)); 3.50–3.08 (*m*, 13 H, 1 H–C(5′), 2 OCH_2CH_2 (npe), 2 SCH_2CH_2 (npes)). Anal. calc. for $C_{61}H_{56}N_6O_{19}S_2$ (1241.3): C 59.03, H 4.55, N 6.77; found: C 58.91, H 4.61, N 6.43.

139: TLC ($CHCl_3$/AcOEt 7:3): R_f 0.58. UV (MeOH): 203 (5.02), 233 (sh, 4.49), 268 (4.53). ^{1}H-NMR ($CDCl_3$): 8.33 (*s*, H–C(6)); 8.17–8.12 (*m*, 6 H *o* to NO_2); 7.45–7.24 (*m*, 18 H, 6 H *m* to NO_2, MeO*Tr*); 6.83 (*d*, 2 H *o* to MeO); 5.09 (*m*, H–C(2′), H–C(1′)); 4.60 (*m*, 4 H, 2 OCH_2CH_2 (npe)); 4.22 (*m*, H–C(3′)); 4.03 (*m*, H–C(4′)); 3.78 (*s*, MeO); 3.57–3.11 (*m*, 10 H, 2 H–C(5′), 2 OCH_2CH_2 (npe), SCH_2CH_2 (npes)); 2.43 (*d*, OH–C(3′)). Anal. calc. for $C_{53}H_{49}N_5O_{15}S \cdot 0.5\ H_2O$ (1037.1): C 61.38, H 4.86, N 6.75; found: C 61.17, H 4.94, N 6.72.

140: TLC ($CHCl_3$/AcOEt 7:3): R_f 0.38. UV (MeOH): 202 (4.98), 232 (sh, 4.48), 268 (4.56). ^{1}H-NMR ($CDCl_3$): 8.39 (*s*, H–C(6)); 8.16 (*m*, 6 H *o* to NO_2 (npe)); 7.50–7.18 (*m*, 18 H, 6 H *m* to NO_2 (npe), MeO*Tr*); 6.78 (*d*, 2 H *o* to MeO); 4.96 (*t*, H–C(3′)); 4.83 (*d*, H–C(1′)); 4.68–4.52 (*m*, 4 H, 2 OCH_2CH_2 (npe)); 4.21 (*m*, H–C(2′), H–C(4′)); 3.73 (*s*, MeO); 3.50 (*dd*, 1 H–C(5′)); 3.42–3.10 (*m*, 9 H, 1 H–C(5′), OCH_2CH_2 (npe), SCH_2CH_2 (npes)); 2.36 (*m*, OH–C(2′)). Anal. calc. for $C_{53}H_{49}N_5O_{15}S \cdot 0.5\ H_2O$ (1037.1): C 61.38, H 4.86, N 6.75; found: C 61.14, H 5.13, N 6.89.

5′-O-(Dimethoxytrityl)-O^2,O^4-bis[2-(4-nitrophenyl)ethyl]-2′,3′-bis-O-[2-(4-nitrophenyl)ethylsulfonyl]pseudouridine (**141**), *5′-O-(Dimethoxytrityl)-O^2,O^4-bis[2-(4-nitrophenyl)ethyl]-2′-O-[2-(4-nitrophenyl)ethylsulfonyl]pseudouridine* (**142**), *and 5′-O-(Dimethoxytrityl)-O^2,O^4-bis[2-(4-nitrophenyl)ethyl]-3′-O-[2-(4-nitrophenyl)ethylsulfonyl]pseudouridine* (**143**). To a soln. of **74** (1 g, 1.18 mmol) in dry pyridine (10 ml) cooled to –3°, Npes-Cl (0.44 g, 1.78 mmol) was added and stirred at –3° for 1 h and at r.t. for 1 h. The mixture was diluted with $CHCl_3$ (50 ml), washed with H_2O (3 × 40 ml), dried (Na_2SO_4), evaporated, and co-evaporated with toluene. CC

(50 g of silica gel, *d* 3.5 cm, $CHCl_3$ (100 ml), $CHCl_3$/AcOEt 19:1 (300 ml) and 9:1 (50 ml)) gave 0.45 g (30%) of **141**, 0.349 g (29%) of **142**, and 0.374 g (30%) of **143** as colorless foams.

141: TLC ($CHCl_3$/AcOEt 9:1): R_f 0.74. UV (MeOH): 203 (5.02), 233 (4.55), 268 (4.67). ^{1}H-NMR ($CDCl_3$): 8.40 (*s*, H−C(6)); 8.15 (*m*, 8 H *o* to NO_2 (npe)); 7.47–7.15 (*m*, 17 H, 8 H *m* to NO_2 (npe), $(MeO)_2$*Tr*); 6.76 (*d*, 4 H *o* to MeO); 5.25 (*t*, H−C(2′)); 5.14 (*m*, H−C(3′)); 5.08 (*d*, H−C(1′)); 4.60 (*m*, 4 H, 2 OCH_2CH_2 (npe)); 4.21 (*q*, H−C(4′)); 3.75 (*s*, 2 MeO); 3.59 (*dd*, 1 H−C(5′)); 3.46–3.11 (*m*, 13 H, 1 H−C(5′), 2 OCH_2CH_2 (npe), 2 SCH_2CH_2 (npes)). Anal. calc. for $C_{62}H_{58}N_6O_{20}S_2$ (1271.3): C 58.58, H 4.60, N 6.61; found: C 58.64, H 4.55, N 6.14.

142: TLC ($CHCl_3$/AcOEt 9:1): R_f 0.54. UV (MeOH): 204 (4.92), 234 (sh, 4.46), 269 (4.54). ^{1}H-NMR ($CDCl_3$): 8.35 (*s*, H−C(6)); 8.15 (*m*, 6 H *o* to NO_2 (npe)); 7.43–7.18 (*m*, 15 H, 6 H *m* to NO_2 (npe), $(MeO)_2$*Tr*); 6.80 (*d*, 4 H *o* to MeO); 5.11 (*m*, H−C(1′), H−C(2′)); 4.62 (*m*, 4 H, 2 OCH_2CH_2 (npe)); 4.18 (*m*, H−C(3′)); 4.02 (*m*, H−C(4′)); 3.75 (*s*, 2 MeO); 3.53–3.15 (*m*, 10 H, 2 H−C(5′), 2 OCH_2CH_2 (npe), SCH_2CH_2 (npes)); 2.44 (br. *s*, OH−C(3′)). Anal. calc. for $C_{54}H_{50}N_5O_{16}S \cdot 0.5\ H_2O$ (1066.1): C 60.84, H 4.82, N 6.57; found: C 60.57, H 5.06, N 6.35.

143: TLC ($CHCl_3$/AcOEt 9:1): R_f 0.42. UV (MeOH): 204 (4.94), 233 (sh, 4.49), 268 (4.57). ^{1}H-NMR ($CDCl_3$): 8.41 (*s*, H−C(6)); 8.15 (*m*, 6 H *o* to NO_2 (npe)); 7.42 (*m*, 6 H *m* to NO_2 (npe)); 7.30–7.15 (*m*, 9 H, $(MeO)_2$*Tr*); 6.78 (*d*, 4 H *o* to MeO); 4.98 (*m*, H−C(3′)); 4.86 (*d*, H−C(1′)); 4.70–4.56 (*m*, 4 H, 2 OCH_2CH_2 (npe)); 4.20 (*m*, H−C(2′), H−C(4′)); 3.74 (*s*, 2 MeO); 3.54–3.12 (*m*, 10 H, 2 H−C(5′), 2 OCH_2CH_2 (npe), SCH_2CH_2 (npes)); 2.38 (*m*, OH−C(2′)). Anal. calc. for $C_{54}H_{50}N_5O_{16}S$ (1057.1): C 61.36, H 4.77, N 6.62; found: C 60.89, H 4.94, N 6.26.

5′-O-(Monomethoxytrityl)-2′,3′-bis-O-[2-(4-nitrophenyl)ethylsulfonyl]ribosylthymine (**144**), *and 5′-O-(Monomethoxytrityl)-2′-O-[2-(4-nitrophenyl)ethylsulfonyl]ribosylthymine* (**145**). To a soln. of 5′-*O*-(monomethoxytrityl)ribosylthymine (**75**; 1.06 g, 2 mmol) in dry pyridine (8 ml) at 4°, Npes-Cl (0.76 g, 3 mmol) was added and stirred at 4° for 1 h. The mixture was diluted with $CHCl_3$ (30 ml), washed with H_2O (3 × 15 ml), dried (Na_2SO_4), evaporated, and co-evaporated with toluene. CC (50 g of silica gel, $CHCl_3$/MeOH 9:1) gave 0.37 g (21%) of **144** and 0.64 g (43%) of **145**.

144: TLC ($CHCl_3$/MeOH 19:1): R_f 0.71. M.p. 104°. UV (MeOH): 202 (4.35), 231 (4.92), 266 (4.45). ^{1}H-NMR ($CDCl_3$): 9.28 (*s*, NH); 8.17 (*m*, 4 H *o* to NO_2 (npes)); 7.50 (*s*, H−C(6)); 7.30 (*m*, 16 H, 4 H *m* to NO_2 (npes), MeO*Tr*); 6.72 (*d*, 2 H *o* to MeO); 6.00 (*d*, H−C(1′)); 5.50 (*m*, H−C(2′), H−C(3′)); 4.42 (*m*, H−C(4′)); 3.72 (*s*, MeO); 3.60 (*m*, 4 H, 2 SCH_2CH_2 (npes)); 3.45 (*m*, 2 H−C(5′)); 3.28 (*m*, 4 H, 2 SCH_2CH_2 (npes)); 1.42 (*s*, Me−C(5)). Anal. calc. for $C_{46}H_{44}N_4O_{15}S_2 \cdot H_2O$ (851.5): C 56.66, H 4.54, N 5.74; found: C 56.45, H 4.56, N 5.14.

145: TLC ($CHCl_3$/MeOH 19:1): R_f 0.60. M.p. 86–87°. UV (MeOH): 203 (4.84), 265 (4.82). ^{1}H-NMR ($CDCl_3$): 9.42 (*s*, NH); 8.15 (*s*, 2 H *o* to NO_2 (npes)); 7.63 (*s*, H−C(6)); 7.30 (*m*, 14 H, 2 H *m* to NO_2 (npes), MeO*Tr*); 6.74 (*d*, 2 H *o* to MeO); 6.05 (*d*, H−C(1′)); 5.28 (*t*, H−C(2′)); 4.70 (*m*, H−C(3′)); 4.19 (*m*, H−C(4′)); 3.78 (*s*, MeO); 3.60 (*m*, 4 H, 2 H−C(5′), SCH_2CH_2 (npes)); 3.30 (*t*, 2 H, SCH_2CH_2 (npes)); 3.05 (*m*, OH−C(3′)); 1.38 (*s*, Me−C(5)). Anal. calc. for $C_{38}H_{37}N_3O_{11}S$ (812.7): C 61.36, H 5.01, N 5.64; found: C 61.23, H 4.93, N 5.26.

O^4-[2-(4-Cyanophenyl)ethyl]-5′-O-(monomethoxytrityl)-2′,3′-bis-O-[2-(4-nitrophenyl)ethylsulfonyl]ribosylthymine (**146**), *O^4-[2-(4-Cyanophenyl)ethyl]-5′-O-(monomethoxytrityl)-2′-O-[2-(4-nitrophenyl)ethylsulfonyl]ribosylthymine* (**147**), *and O^4-[2-(4-Cyanophenyl)ethyl]-5′-O-(monomethoxytrityl)-3′-O-[2-(4-nitrophenyl)ethylsulfonyl]ribosylthymine* (**148**). As described for **144**/**145**, with **76** (0.65 g, 1 mmol), pyridine (10 ml; 2°) and Npes-Cl (0.35 g, 1.4 mmol; 2.5 h at 2°). Workup with $CHCl_3$ (100 ml) and H_2O (3 × 110 ml). CC (70 g of silica gel, toluene/AcOEt 3:2) gave 0.18 g (19%) of **146**, 0.28 g (34%) of **147**, and 0.22 g (26%) of **148** as colorless foams.

146: TLC (toluene/AcOEt 1:1): R_f 0.64. UV (MeOH): 202 (5.03), 226 (4.65), 272 (4.30). ^{1}H-NMR ($CDCl_3$): 8.18 (*m*, 4 H *o* to NO_2 (npes)); 7.92 (*s*, H−C(6)); 7.60 (*d*, 2 H *o* to CN (cpe)); 7.55–7.15 (*m*, 18 H, 4 H *m* to NO_2 (npes), 2 H *m* to CN (cpe), MeO*Tr*); 6.72 (*d*, 2 H *o* to MeO); 5.81 (*d*, H−C(1′)); 5.55 (*m*, H−C(2′)); 5.28 (*m*, H−C(3′)); 4.62 (*t*, 2 H, OCH_2CH_2 (cpe)); 4.32 (*d*, H−C(4′)); 3.80 (*m*, MeO); 3.75–3.00 (2*m*, 12 H, 2 H−C(5′), OCH_2CH_2 (cpe), 2 SCH_2CH_2 (npes)); 1.46 (*s*, Me−C(5)). Anal. calc. for $C_{54}H_{51}N_5O_{15}S_2$ (1074.1): C 60.37, H 4.78, N 6.52; found: C 59.95, H 5.03, N 5.96.

147: TLC (toluene/AcOEt 1:1): R_f 0.52. UV (MeOH): 202 (4.84), 226 (4.55), 272 (4.93). ^{1}H-NMR ($CDCl_3$): 8.22 (*d*, 2 H *o* to NO_2 (npes)); 7.82 (*s*, H−C(6)); 7.62 (*d*, 2 H *o* to CN (cpe)); 7.50–7.15 (*m*, 16 H, 2 H *m* to NO_2 (npes), 2 H *m* to CN (cpe), MeO*Tr*); 6.86 (*m*, 2 H *o* to MeO); 5.86 (*d*, H−C(1′)); 5.15 (*t*, H−C(2′)); 4.70 (*m*, *t*, 4 H, H−C(3′), H−C(4), OCH_2CH_2 (cpe)); 3.80 (*s*, MeO); 3.70–3.10 (*m*, 8 H, 2 H−C(5′), SCH_2CH_2 (npes), OCH_2CH_2 (cpe)); 3.05 (*m*, OH−C(3′)); 1.60 (*s*, Me−C(5)). Anal. calc. for $C_{47}H_{44}N_4O_{11}S$ (872.9): C 64.66, H 5.08, N 6.47; found: C 64.77, H 5.35, N 5.87.

148: TLC (toluene/AcOEt 1:1): R_f 0.27. UV (MeOH): 202 (4.99), 228 (4.62), 272 (4.28). ^{1}H-NMR ($CDCl_3$): 8.18 (*d*, 2 H *o* to NO_2 (npes)); 7.80 (*s*, H−C(6)); 7.60 (*d*, 2 H *o* to CN (cpe)); 7.42–7.08 (*m*, 16 H, 2 H *m* to NO_2 (npes), 2 H *m* to CN (cpe), MeO*Tr*); 6.84 (*m*, 2 H *o* to MeO); 5.95 (*d*, H−C(1′)); 5.56 (*m*, OH−C(2′)); 4.68–4.46 (*m*, 5 H, H−C(2′), H−C(3′), H−C(4′), OCH_2CH_2 (cpe)); 3.76 (*s*, MeO); 3.65–3.00 (*m*, 8 H, 2 H−C(5′), OCH_2CH_2 (cpe)); SCH_2CH_2 (npes)); 3.05 (*m*, OH−C(3′)); 1.62 (*s*, Me−C(5)). Anal. calc. for $C_{47}H_{44}N_4O_{11}S \cdot H_2O$ (897.7): C 63.35, H 5.30, N 6.28; found: C 64.30, H 5.39, N 6.00.

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