# 17. Nucleotides

Part L[1])

## Aglycone Protection by the (2-Dansylethoxy)carbonyl ( = {2-{[5-(Dimethylamino)naphthalen-1-yl]sulfonyl}ethoxy}carbonyl; dnseoc) Group – A New Variation in Oligodeoxyribonucleotide Synthesis

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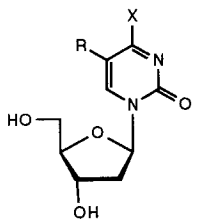
The (2-dansylethoxy)carbonyl ( = {2-{[5-(dimethylamino)naphthalen-1-yl]sulfonyl}ethoxy}carbonyl; dnseoc) group was employed for protection of the amino functions of the aglycone residues. The lactam function of 2′-deoxyguanosine was on the one hand unprotected and on the other hand alkylated at $O^6$ of the aglycone with the 2-(4-nitrophenyl)ethyl (npe) and 2-(phenylsulfonyl)ethyl (pse) group, respectively. The syntheses of monomeric building blocks, both phosphoramidites and nucleoside-functionalized supports, are described for the three common 2′-deoxynucleosides (2′-deoxycytidine, 2′-deoxyadenosine, 2′-deoxyguanosine). As kinetic studies with the tritylated nucleosides showed, the dnseoc group is more labile towards DBU cleavage than the corresponding 2-(4-nitrophenyl)ethyl-(npe) and [2-(4-nitrophenyl)ethoxy]carbonyl(npeoc)-protected analogues (see *Table 2*). These results were confirmed by the very fast deprotection rate of the dnseoc groups at some oligonucleotides.

**1. Introduction.** – The growing need of synthetic oligonucleotides for biological and biochemical research and the commercial interests in this type of chemistry require the development of more and more efficient and especially fast working oligodeoxyribonucleotide syntheses. The development of the 2-(4-nitrophenyl)ethyl (npe) and the [2-(4-nitrophenyl)ethoxy]carbonyl (npeoc) [2–4] protecting groups offered the opportunity to synthesize very pure oligonucleotides in a direct manner, since the blocking groups can be cleaved selectively by 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) or 1,5-diazabicyclo-[4.3.0]non-5-ene (DBN) in aprotic solvents, while the oligonucleotides are still bound to the solid phase. The cleavage of the npe/npeoc residues takes, however, normally 12 h [5], in a $\beta$-elimination process indicating that the cleavage step has to be accelerated. We introduced for this purpose the (2-dansylethoxy)carbonyl ( = {2-{[5-(dimethylamino)-naphthalen-1-yl]sulfonyl}ethoxy}carbonyl; dnseoc) group for protection of the aglycone functions, since this blocking group was already used for blocking the 5′-OH function in oligodeoxy- and oligoribonucleotide synthesis and found to be selectively and quantitatively removed with DBU in a very fast $\beta$-eliminating step [6] [7] (see **5** for dnseoc-Cl·HCl). During this short time period, the npe/npeoc groups are completely stable, which indicates the different stabilities between the dnseoc and npe/npeoc groups against DBU.

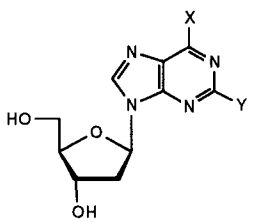
[1]) Part IL: [1].

In this paper, we wish to demonstrate the usefulness of the dnseoc group for base protection. We report the synthesis of the protected phosphoramidite building blocks and of the corresponding nucleoside-functionalized supports. The fast and effective cleavage of the dnseoc groups is established at the monomeric nucleoside as well as the oligodeoxyribonucleotide level.

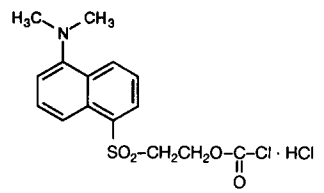
**2. Syntheses.** – It is common knowledge that the amino groups of the naturally occurring 2′-deoxyribonucleotides have to be protected in oligonucleotide synthesis, whereas the lactam function of thymidine (**1**) does not need any protection which is, however, recommended for 2′-deoxyguanosine (**4**) at $O^6$ to guarantee a minimum of side reactions [8–10].



**1** R = Me, X = OH
**2** R = H, X = $NH_2$



**3** X = $NH_2$, Y = H
**4** X = PH, Y = $NH_2$



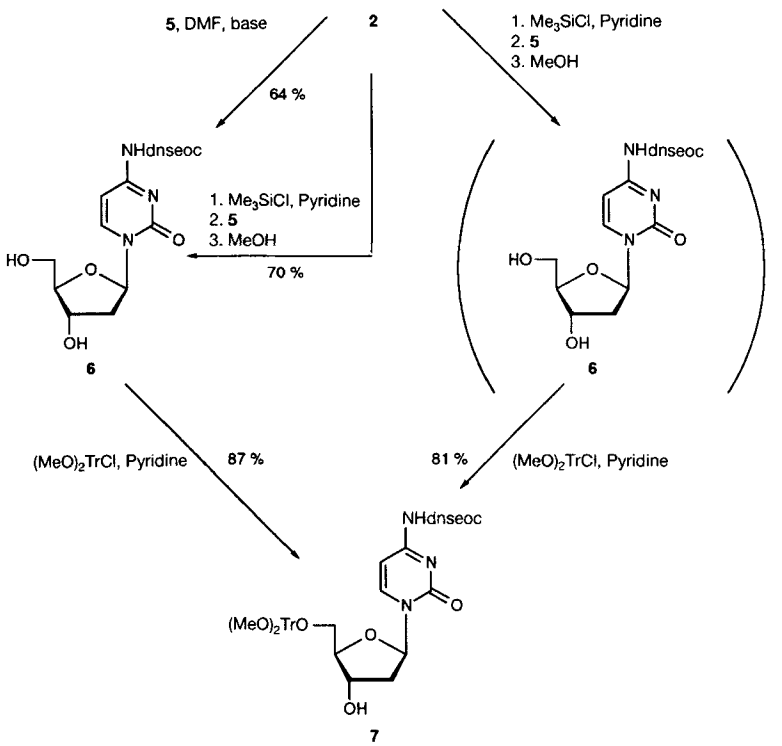
**5** dnseoc–Cl · HCl

The dnseoc group was introduced into the amino functions of 2′-deoxycytidine (**2**), 2′-deoxyadenosine (**3**), and 2′-deoxyguanosine (**4**) with 2-dansylethyl carbonochloridate hydrochloride (**5**) as the reactive reagent. $N^4$-[(2-Dansylethoxy)carbonyl]-2′-desoxycytidine (dnseoc$^4C_d$; **6**) can be prepared directly by adding a slight excess of **5** at 0° to a suspension of **2** in DMF in the presence of *N*-methyl-1*H*-imidazole (*Scheme 1*). Better yields, however are obtained by transient trimethylsilyl protection of the OH functions [11] of the sugar moiety, followed by subsequent reaction with **5** for 2 h and desilylation to dnseoc$^4C_d$ (**6**). Since **6** was obtained in form of a hygroscopic product, it is very important for the next step to co-evaporate several times with abs. pyridine to achieve a complete dimethoxytritylation of the 5′-OH function (→**7**). A more convenient way to synthesize [$(MeO)_2$Tr]dnseoc$^4C_d$ (**7**) from **2** is a one-pot reaction giving an overall yield of 81%.

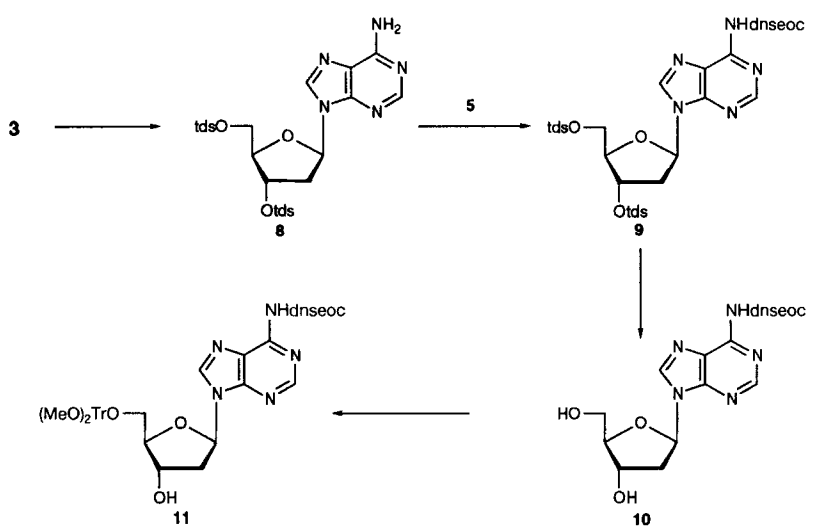
The conversion of **3** into $N^6$-[(dansylethoxy)carbonyl]-2′-deoxy-5′-*O*-(dimethoxytrityl)adenosine (**11**) was best achieved in a four-step synthesis (*Scheme 2*). At first, the OH functions of the sugar residue were protected quantitatively (→**8**, 98%) by consequent treatment with tdsCl (= dimethyl(1,1,2-trimethylpropyl)silyl chloride = dimethyl(thexyl)silyl chloride) and 1*H*-imidazole in DMF. $N^6$-Acylation of **8** with 2-dansylethyl carbonochloridate hydrochloride (**5**)/1-methyl-1*H*-imidazole in $CH_2Cl_2$ gave **9** in 93% yield, and subsequent desilylation resulted in 82% of dnseoc$^6A_d$ (**10**). Dimethoxytritylation of **10** with $(MeO)_2$TrCl in abs. pyridine gave under conventional conditions **11** in 94% yield.

The mono-protected $N^2$-[(2-dansylethoxy)carbonyl]-2′-deoxyguanosine (**15**) was synthesized similarly to **10** (*Scheme 3*). Dimethyl(thexyl)silyl protection of the sugar OH

*Scheme 1*

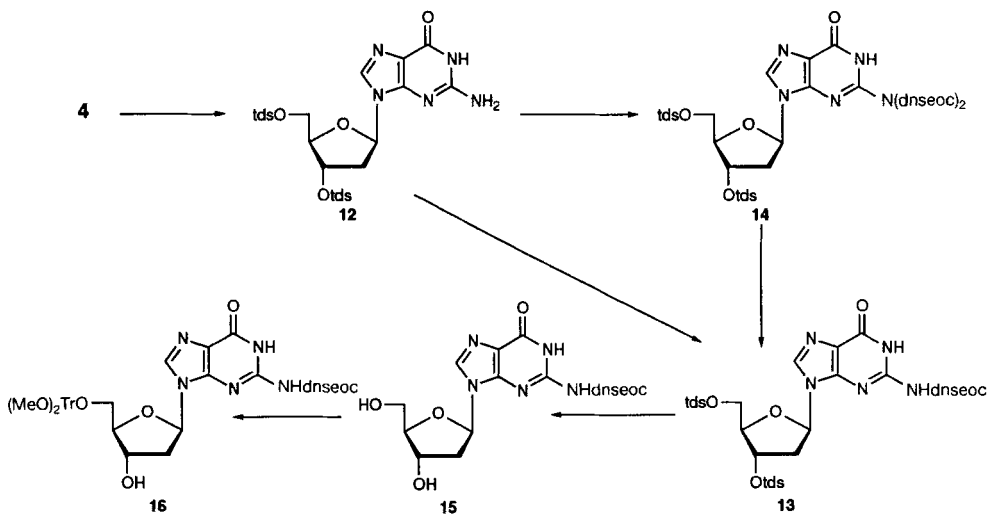



*Scheme 2*



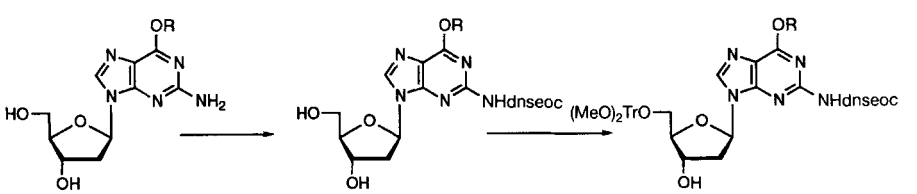
groups of **4** with tdsCl/1*H*-imidazole in DMF (→**12**, 93%) and subsequent acylation by (2-dansylethoxy)carbonyl chloride (**5**) led to a mixture of the corresponding $N^2$-mono- and $N^2$-bis[(dansylethoxy)carbonyl] derivative **13** and **14**, respectively, which can be isolated by silica-gel column chromatography. Treatment of **14** with pyridine/$H_2O$ 1:1 resulted in hydrolysis of one dnseoc group to give also **13** which was desilylated by $F^-$ ion in THF and in presence of AcOH to form selectively **15** (85%). Finally, dimethoxytritylation led in excellent yield to **16** (94%).

*Scheme 3*




To protect 2′-deoxyguanosine (**4**) at the amino as well as at the amide function, the $O^6$-[2-(4-nitrophenyl)ethyl] and $O^6$-[2-(phenylsulfonyl)ethyl] derivatives **17** [3] and **18** [12], respectively, were chosen as starting nucleosides. *O*-Alkylation was achieved by a *Mitsunobu* reaction by known procedures, and subsequent acylation at the amino groups afforded, after transient trimethylsilyl protection, **19** (79%) and **20** (84%), respectively, in very good yields. Dimethoxytritylation worked again very well due to the improved solubility of **19** and **20**, and a yield of over 98% could be recorded for **21** and **22**.

*Scheme 4*



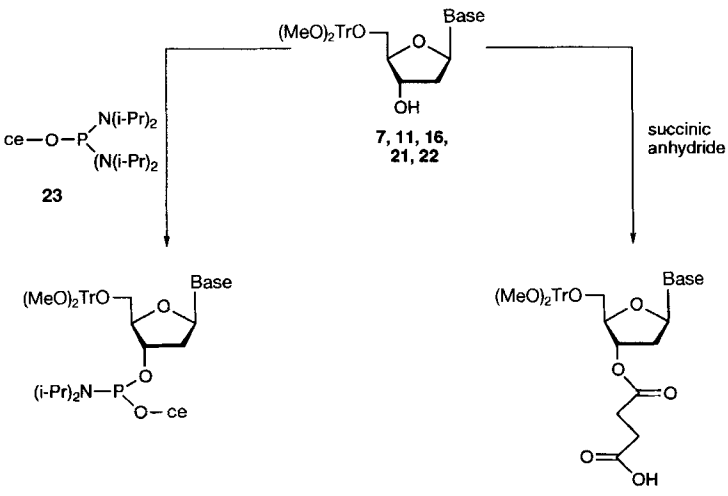

**17** R = npe
**18** R = pse

**19** R = npe
**20** R = pse

**21** R = npe
**22** R = pse

The described 5′-*O*-dimethoxytrityl derivatives **7**, **11**, **16**, **21**, and **22** play an important role as versatile intermediates in the preparation of the corresponding 3′-*O*-phosphoramidites and 3′-*O*-succinates, respectively. Their syntheses were achieved by common procedures using (2-cyanoethoxy)bis(diisopropylamino)phosphine (**23**) in the phosphitylation reactions [13] [14] (→**24**–**28**) and succinic anhydride for the acylation to **29**–**33** (*Scheme 5*).

*Scheme 5*




| | Base |
|---|---|
| **24** | dnseocCyt |
| **25** | dnseocAde |
| **26** | dnseocGua |
| **27** | $dnseoc^{npe}Gua$ |
| **28** | $dnseoc^{pse}Gua$ |

| | Base |
|---|---|
| **29** | dnseocCyt |
| **30** | dnseocAde |
| **31** | dnseocGua |
| **32** | $dnseoc^{npe}Gua$ |
| **33** | $dnseoc^{pse}Gua$ |

Compounds **29** and **30** were then reacted with 500-Å LCAMA-CPG ( = (long-chain-alkyl)methylamine controlled-pore glass; **34**) [15–17] using as coupling reagent 2-{{[(2-cyanoethoxy)carbonyl]methylidene}amino}-1,1,3,3-tetramethyluronium tetrafluoroborate (TOTU) and *N*-methylmorpholine in MeCN followed by a capping process with $Ac_2O$ and 4-(dimethylamino)pyridine in pyridine leading to loadings of 15 μmol/g (for **35**) and 18 μmol/g (for **36**), respectively.

[$(MeO)_2$TrO]dnseoc$^4C_d$-Suc-LCAMA-CPG **35**

[$(MeO)_2$TrO]dnseoc$^4A_d$-Suc-LCAMA-CPG **36**

The oligodeoxyribonucleotides **37**–**44** (see *Table 1*) were synthesized using the solid-phase phosphoramidite approach by *Caruthers* and coworkers [18–21]. Four chemical steps and intermediate washing steps were necessary for each elongation step. At first, the terminal dimethoxytrityl group was cleaved with 3% $CCl_3COOH$ in $CH_2Cl_2$. Thereby, the average coupling efficiency was monitored by absorption measurement of the released dimethoxytrityl solutions. During the coupling step (40 s), 0.1M nucleoside phos-

phoramidite (**24–28**) and 0.5M 1*H*-tetrazole in MeCN were mixed with the solid support by short flush pushes. After the condensation, the unreacted OH functions were subsequently blocked by acetylation ('capping', 15 s) with $Ac_2O$/2,6-dimethylpyridine/1-methyl-1*H*-imidazole in THF, and the phosphite-triester bridge was oxidized with 0.05M $I_2$ in THF/pyridine/$H_2O$ for 32 s. After the last synthesis cycle, the support was treated with 1M DBU in MeCN to remove all protecting groups. The isolated samples were cleaved from the support by treatment with concentrated $NH_3$ solution for 2 h, and then the solution was lyophilized in a *Speed-vac* concentrator. The completeness of the deprotection step and the quality of the synthesized oligonucleotides were checked by reversed-phase HPLC. The purity of the crude 19-mer **44** was also analyzed by polyacrylamide gel electrophoresis indicating one main product and no failure sequence. The starting nucleoside N ( = 3-methylisoxanthopterin) [22] was used as a fluorescent marker allowing direct detection by fluorescence determination.

Table 1. *Synthesized Oligodeoxyribonucleotides*

| Sequence | Phosphoramidites | Average coupling efficiency [%] |
|---|---|---|
| (5′-3′)[$(dC)_7$] **37** | **24** | 100 |
| (5′-3′)[d(A-A-A-A-A-C)] **38** | **25** | 99.8 |
| (5′-3′)[$(dA)^{10}$] **39** | **25** | 99.9 |
| (5′-3′)[d(G-G-G-G-C)] **40** | **28** | 100 |
| (5′-3′)[d(T-G-T-G-T-G-A)] **41** | **28** | 99.6 |
| (5′-3′)[d(T-G-T-G-T-G-A)] **42** | **26** | 100 |
| (5′-3′)[d(T-G-T-G-T-G-A)] **43** | **27** | 100 |
| (5′-3′)[d(G-T-G-T-G-G-A-A-A-A-T-C-T-C-T-A-G-C-N)] **44** | **24**, **25**, **28** | 99.8 |

**3. Kinetic Studies.** – For the examination of the deprotection rate of the tritylated nucleosides **7**, **11**, **16**, **21**, and **22**, we used a 20-fold excess of DBU in MeCN ($c$ = 0.5M). In fixed time intervals, the reactions were stopped with an excess of 0.5M AcOH and analyzed by reversed-phase HPLC. Under these conditions, the simple protected nucleosides **7**, **11**, and **16** obey a pseudo-first-order rate law, allowing half-life determination graphically. The pictures for the doubly protected guanine derivatives were more complex, and, therefore, we defined the half-life as the time of 50% deprotection of the corresponding nucleosides. The half-lives (*Table 2*) are only approximate values, but they show, in comparison to the npe/npeoc groups [11], a tremendous increase in cleaving rates making the dnseoc base protection an interesting alternative even to the commonly used acyl strategy.

Table 2. *Half-lives of the Tritylated Nucleoside Derivatives*

| Nucleoside | Half-life ($t_{1/2}$) | Nucleoside | Half-life ($t_{1/2}$) |
|---|---|---|---|
| $[(MeO)_2Tr]dnseoc^4C_d$ (**7**) | 27 s | $[(MeO)_2Tr]npeoc^2G_d$ | 148 min [23] |
| $[(MeO)_2Tr]npeoc^4C_d$ | 73 min [23] | $[(MeO)_2Tr]dnseoc^2pse^6G_d$ (**22**) | 9 min |
| $[(MeO)_2Tr]dnseoc^6A_d$ (**11**) | 123 s | $[(MeO)_2Tr]dnseoc^2npe^6G_d$ (**21**) | 31 min |
| $[(MeO)_2Tr]npeoc^6A_d$ | 90 min [23] | $npeoc^2npe^6G_d$ | 156 min [23] |
| $[(MeO)_2Tr]dnseoc^2G_d$ (**16**) | 30 min | | |

Kinetic studies were also performed with protected oligonucleotides by treatment with 1M DBU in the final cleavage step. Aliquots were taken in intervals of 20 min of the same preparation and then analyzed by HPLC. Whereas the protected precursor sequences of **37**–**39** were completely deprotected within 20 min, the guanosine-containing precursor sequences of the identical products **41**–**43** needed a longer base treatment, as expected from the values listed in *Table 2*. Comparing the deprotection rate of these latter precursor sequences, synthesized with the three differently blocked 2′-deoxyguanosine derivatives **26**–**28**, the monomeric building block **28** yielded the precursor which needed the shortest deprotection time of 40 min. This result was reconfirmed by the deprotection time of only 90 min for the precursor of 19-mer **44**. The reversed-phase HPLC of the crude oligonucleotide **44** (*Fig.*), isolated without any further purification, shows the efficiency of the automated solid-support synthesis and its actual, rapid deprotection procedure.

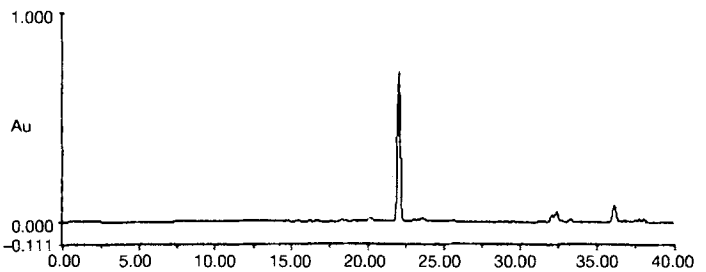



Figure. *HPLC Profile of crude (5′-3′)[d(G-T-G-T-G-G-A-A-A-A-T-C-T-C-T-A-G-C-N)]* (**44**)

## Experimental Part

*General.* Products were dried under high vacuum. TLC: Precoated silica gel thin-layer sheets *F1500 LS 254* from *Schleicher & Schuell*. Flash chromatography (FC): silica gel (*Baker*, 30–60 μm); 0.2–0.3 bar. M.p.: *Gallenkamp* melting-point apparatus; no corrections. UV/VIS: *Perkin-Elmer Lambda 15*; $\lambda_{max}$ in nm (log ε). $^1$H-NMR: *Bruker AC 250*; in ppm rel. to $SiMe_4$ or $CDCl_3$ ($(D_6)$DMSO) as internal standard. $^{31}$P-NMR: *Joel 400 MHz*; in ppm rel. to $H_3PO_4$.

1. $N^4$-*[(2-Dansylethoxy)carbonyl]-2′-deoxycytidine* (**6**). 1.1. A suspension of 2′-deoxycytidine (**2**; 264 mg, 1 mmol) in DMF (5 ml) was cooled in an ice bath to 0°, and then 1-methyl-1*H*-imidazole (280 mg, 3.4 mmol) and finally **5** (450 mg, 1.2 mmol) were added. The mixture was stirred for 3 h after warmup to r.t. After evaporation, the residue was dissolved in MeOH (3 ml), $SiO_2$ (0.8 g) was added, and the mixture co-evaporated. The residue was purified by FC (silica gel, 12 × 2 cm, $CH_2Cl_2$/MeOH 100:3 (0.5 l), 100:4 (1.0 l), 100:6 (0.4 l), 100:10 (0.3 l)): 340 mg (64%) of **6**. Hygroscopic solid.

1.2. In dry pyridine (10 ml), **2** (1.58 g, 6 mmol) was co-evaporated and then taken up in dry pyridine (20 ml). The soln. was stirred with $Me_3SiCl$ (3.8 ml, 30 mmol) for 30 min at r.t., and then **5** (2.5 g, 6.6 mmol) was added. The mixture was stirred for further 3 h, the precipitate filtered off, and then the reaction stopped with MeOH (20 ml). After stirring for 2 h, silica gel (3 g) was added and the mixture evaporated. Purification by FC (silica gel, 10 × 5 cm, $CH_2Cl_2$/MeOH 100:3 (0.5 l), 100:4 (1.0 l), 100:6 (0.4 l), 100:10 (0.3 l)) gave 2.26 g (70%) of **6**. Hygroscopic solid. $^1$H-NMR ($(D_6)$DMSO): 10.44 (br. *s*, NH); 8.51 (*d*, H–C(2)(Dns)); 8.25–8.20 (*m*, H–C(6), H–C(4)(Dns), H–C(8)(Dns)); 7.69–7.63 (*m*, H–C(3)(Dns), H–C(7)(Dns)); 7.25 (*d*, H–C(6)(Dns)); 6.72 (*d*, H–C(5)); 6.08 (*t*, H–C(1′)); 5.27 (*d*, OH–C(3′)); 5.06 (*t*, OH–C(5′)); 4.41–4.37 (*t*, $CH_2OCO$); 4.24–4.20 (*m*, H–C(3′)); 3.92–3.85 (*m*, H–C(4′), $SO_2CH_2$); 3.64–3.53 (*m*, 2 H–C(5′)); 2.79 (*s*, $Me_2N$); 2.30–1.99 (*m*, 2 H–C(2′)). Caused by the hygroscopic character of **6**, no UV spectrum was measured and no correct elemental analysis was obtained.

2. $N^4$-*[(2-Dansylethoxy)carbonyl]-2′-deoxy-5′-*O-*(dimethoxytrityl)cytidine* (**7**). 2.1. In dry pyridine (10 ml), **2** (1 g, 3.79 mmol) was co-evaporated and then taken up in dry pyridine (15 ml). $Me_3SiCl$ (2.7 ml, 21.4 mmol) was added, the mixture stirred for 2 h, **5** (1.58 g, 4.2 mmol) added, and the mixture stirred for 2.5 h. After filtration, the reaction was stopped with $H_2O$ (30 ml, 30 min), the soln. evaporated, and the residue co-evaporated with dry pyridine (2 × 10 ml) and then taken up in dry pyridine (20 ml). After addition of dimethoxytrityl chloride (1.92 g, 5.67 mmol), the soln. was stirred for 2 h, and an additional amount of the reagent (640 mg, 1.89 mmol) was added. After 30 min, the mixture was diluted with $CH_2Cl_2$ (30 ml) and washed with phosphate buffer (20 × 20 ml), the aq. phase extracted with $CH_2Cl_2$ (2 × 10 ml), the combined org. layer dried ($Na_2SO_4$), evaporated, and co-evaporated with toluene (2 × 20 ml), and the residue purified by FC (silica gel, 22 × 3.5 cm, toluene/AcOEt/MeOH 100:100:0 (1.0 l), 100:100:4 (0.6 l)): 2.55 g (81%) of **7**. Yellow foam.

2.2. In dry pyridine (2 × 10 ml), **6** (860 mg, 1.6 mmol) was co-evaporated and then taken up in dry pyridine. Dimethoxytrityl chloride (700 mg, 2.08 mmol) was added. The soln. was stirred for 1.5 h at r.t., diluted with $CH_2Cl_2$ (20 ml), and washed with sat. $NaHCO_3$ soln. (2 × 20 ml), the aq. phase extracted with $CH_2Cl_2$ (20 ml), and the combined org. layer dried ($Na_2SO_4$) and evaporated. The residue was purified by FC (silica gel, 10 × 2.5 cm, toluene/AcOEt/MeOH 100:100:0 (1.0 l), 100:100:4 (0.6 l)): 1.16 g (87%) of **7**. Yellow foam. UV (MeOH): 204 (5.01), 235 (4.60), 292 (sh, 3.96), 340 (3.58). $^1$H-NMR ($CDCl_3$): 8.61 (*d*, H–C(2)(Dns)); 8.32–8.18 (*m*, H–C(6), H–C(4)(Dns), H–C(8)(Dns)); 7.63–7.54 (*m*, H–C(3)(Dns), H–C(7)(Dns)); 7.40–7.16 (*m*, H–C(6)(Dns), 9 H of $(MeO)_2Tr$); 6.86–6.77 (*m*, 4 H *o* to MeO, H–C(5)); 6.22 (*t*, H–C(1′)); 4.51–4.46 (*m*, $CH_2OCO$, H–C(3′)); 4.16–4.08 (*m*, H–C(4′)); 3.78 (*s*, 2 MeO); 3.74–3.69 (*m*, $SO_2CH_2$); 3.49–3.38 (*m*, 2 H–C(5′)); 2.87 (*s*, $Me_2N$); 2.75–2.62 (*m*, H–C(2′)); 2.32–2.19 (*m*, H–C(2′)). Anal. calc. for $C_{45}H_{46}N_4O_{10}S$ (834.95): C 64.73, H 5.55, N 6.71; found: C 64.84, H 5.75, N 6.69.

3. *2′-Deoxy-3′,5′-bis-*O-*[dimethyl(1,1,2-trimethylpropyl)silyl]adenosine* (**8**). A soln. of 2′-deoxyadenosin (**3**; 3.95 g, 15 mmol), 1*H*-imidazole (6.11 g, 90 mmol) and dimethyl(1,1,2-trimethylpropyl)silyl chloride ( = dimethyl-(thexyl)silyl chloride; 8.82 ml, 45 mmol) in abs. DMF (30 ml) was stirred overnight. After dilution with $CH_2Cl_2$ (50 ml), the soln. was washed with $H_2O$ (20 ml), the combined org. layer dried ($Na_2SO_4$) and evaporated, and the residue purified by FC (silica gel, 22 × 3.5 cm, toluene/AcOEt/MeOH 10:0:0 (0.5 l), 9:1 (0.4 l), 4:1 (0.3 l), 5:4:1 (0.3 l)): 7.9 g (98%) of **8**. Colourless solid. M.p. 108–111°. UV (MeOH): 207 (4.33), 258 (4.20). $^1$H-NMR ($(D_6)$DMSO): 8.27, 8.12 (2*s*, H–C(2), H–C(8)); 7.28 (br. *s*, NH); 6.30 (*t*, H–C(1′)); 4.59 (*m*, H–C(3′)); 3.81–3.62 (*m*, H–C(4′), 2 H–C(5′)); 2.93–2.79 (*m*, 1 H–C(2′)); 2.30–2.18 (*m*, 1 H–C(2′)); 1.62–1.48 (*m*, 2 $Me_2CH$); 0.88–0.77 (*m*, 4 $Me_2C$); 0.13–0.03 (*m*, 2 $Me_2Si$). Anal. calc. for $C_{26}H_{49}N_5O_3Si_2$ (535.88): C 58.28, H 9.22, N 13.07; found: C 58.06, H 9.13, N 12.87.

4. $N^6$-*[(2-Dansylethoxy)carbonyl]-2′-deoxy-3′,5′-bis-*O-*[dimethyl(1,1,2-trimethylpropyl)silyl]adenosine* (**9**). A suspension of **5** (635 mg, 1.68 mmol) and some molecular sieves in abs. $CH_2Cl_2$ was cooled to 0°. After addition of 1-methyl-1*H*-imidazole (286 mg, 3.36 mmol) and **8** (600 mg, 1.12 mmol), the mixture was stored in the refrigerator overnight. After filtration and evaporation, the residue was purified by FC (silica gel, 19 × 2.5 cm, toluene/AcOEt 9:1 (0.3 l), 4:1 (0.3 l), 1:1 (0.3 l)): 880 mg (93%) of **9**. Yellow foam. UV (MeOH): 210 (4.87), 259 (4.46), 344 (3.64). $^1$H-NMR ($(D_6)$DMSO): 10.25 (br. *s*, NH); 8.54, 8.50 (2*s*, H–C(8), H–C(2)); 8.42, 8.39 (2*d*, H–C(2)(Dns)); 8.15–8.21 (*t*, H–C(4)(Dns), H–C(8)(Dns)); 7.64–7.55 (*m*, H–C(3)(Dns), H–C(7)(Dns)); 7.21 (*d*, H–C(6)(Dns)); 6.39 (*t*, H–C(1′)); 4.62–4.57 (*m*, H–C(3′)); 4.43 (*t*, $CH_2OCO$); 3.89–3.64 (*m*, $SO_2CH_2$, H–C(4′), 2 H–C(5′)); 3.03–2.88 (*m*, 1 H–C(2′)); 2.77 (*s*, $Me_2N$); 2.40–2.20 (*m*, 1 H–C(2′)); 1.68–1.51 (*m*, 2 $Me_2CH$); 0.90–0.77 (*m*, 4 $Me_2C$); 0.15–0.18 (*m*, 2 $Me_2Si$). Anal. calc. for $C_{41}H_{64}N_6O_7SSi_2 \cdot \frac{1}{2}\ H_2O$ (841.24): C 57.92, H 7.71, N 9.88; found: C 57.95, H 7.56, N 9.72.

5. $N^6$-*[(2-Dansylethoxy)carbonyl]-2′-deoxyadenosine* (**10**). To a soln. of $(Bu_4N)F \cdot 2\ H_2O$ (1.4 g, 3 mmol) and AcOH (1.71 ml, 30 mmol) in THF (20 ml), **9** (1.68 g, 2 mmol) was added. After stirring for 2 days at r.t., the soln. was diluted with $CH_2Cl_2$ (20 ml) and washed with 0.1M AcOH (4 × 15 ml), the org. layer dried ($Na_2SO_4$) and evaporated, and the residue purified by FC (silica gel, 18 × 3.5 cm, toluene/AcOEt/MeOH 1:4:0 (0.5 l), 5:4:1 (0.5 l), 0:10:1 (0.5 l)). The product was dissolved in $CH_2Cl_2$ (20 ml) and the soln. washed with 0.1M AcOH, dried ($Na_2SO_4$), and evaporated: 860 mg (82%) of **10**. Yellow foam. UV (MeOH): 211 (4.89), 260 (4.53), 345 (3.65). $^1$H-NMR ($(D_6)$DMSO): 10.28 (br. *s*, NH); 8.62, 8.55 (2*s*, H–C(2), H–C(8)); 8.47, 8.43 (2*d*, H–C(2)(Dns)); 8.25–8.17 (*t*, H–C(4)(Dns), H–C(8)(Dns)); 7.67–7.58 (*m*, H–C(3)(Dns), H–C(7)(Dns)); 7.28, 7.22 (*d*, H–C(6)(Dns)); 6.45 (*t*, H–C(1′)); 5.38, 5.36 (2*d*, OH–C(3′)); 5.06 (*t*, OH–C(5′)); 4.46–4.37 (*m*, H–C(3′), $CH_2OCO$); 3.93–3.87 (*m*, H–C(4′), $SO_2CH_2$); 3.72–3.54 (*m*, 2 H–C(5′)); 2.78–2.64 (*m*, 1 H–C(2′), $Me_2N$); 2.41–2.30 (*m*, 1 H–C(2′)). Anal. calc. for $C_{25}H_{28}N_6O_7S \cdot 1.75\ H_2O$ (588.6): C 51.06, H 5.39, N 14.29; found: C 51.52, H 5.23, N 13.67.

6. $N^6$-*[(2-Dansylethoxy)carbonyl]-2′-deoxy-5′-*O*-(dimethoxytrityl)adenosine* (**11**). In dry pyridine (2 × 10 ml), **10** (2.35 g, 4.22 mmol) was co-evaporated and then taken up in dry pyridine (20 ml). $(MeO)_2TrCl$ (1.86 g, 5.49 mmol) was added and the mixture stirred at r.t. for 2 h. The soln. was diluted with $CH_2Cl_2$ (20 ml) and washed with sat. $NaHCO_3$ soln. (2 × 20 ml), the aq. phase extracted with $CH_2Cl_2$ (2 × 20 ml), the combined org. layer dried ($Na_2SO_4$), evaporated, and co-evaporated with toluene (2 × 20 ml), and the residue purified by FC (silica gel, 7 × 2 cm, toluene/AcOEt/MeOH 1:1:0 (1.0 l), 15:15:1 (0.4 l), 10:10:1 (0.8 l)): 3.4 g (94%) of **11**. Yellow foam. UV (MeOH): 204 (5.10), 236 (4.57), 263 (4.52), 346 (3.67). $^1$H-NMR ((D$_6$)DMSO): 10.27 (br. *s*, NH); 8.50–8.38 (*m*, H–C(2), H–C(8), H–C(2)(Dns)); 8.21–8.16 (*t*, H–C(4)(Dns), H–C(8)(Dns)); 7.64–7.54 (*m*, H–C(3)(Dns), H–C(7)(Dns)); 7.33–7.16 (*m*, H–C(6)(Dns), 9 H of $(MeO)_2Tr$); 6.78 (*t*, 4 H *o* to MeO); 6.49–6.40 (*t*, H–C(1′)); 5.41 (*d*, OH–C(3′)); 4.49–4.31 (*m*, H–C(3′), $CH_2OCO$); 4.04–3.99 (*m*, H–C(4′)); 3.87 (*t*, $SO_2CH_2$); 3.70, 3.69 (2*d*, 2 MeO); 3.19–3.16 (*m*, 2 H–C(5′)); 2.98–2.84 (*m*, 1 H–C(2′)); 2.74 (*s*, $Me_2N$); 2.42–2.28 (*m*, 1 H–C(2′)). Anal. calc. for $C_{46}H_{46}N_6O_9S$ (858.98): C 64.32, H 5.40, N 9.78; found: C 64.37, H 5.60, N 9.29.

7. *2′-Deoxy-3′,5′-bis-*O*-[dimethyl(1,1,2-trimethylpropyl)silyl]guanosine* (**12**). As described in *Exper. 3*, with 2′-deoxyguanosine (**4**; 3.9 g, 12.9 mmol), abs. DMF (40 ml), 1*H*-imidazole (5.25 g, 77 mmol), and dimethyl(thexyl)-silyl chloride (7.1 ml, 39 mmol) (overnight, r.t.). After dilution with $CH_2Cl_2$ (150 ml), the soln. was extracted with $H_2O$ (50 ml), the aq. phase extracted with $CH_2Cl_2$ (2 × 50 ml), and the combined org. layer dried ($Na_2SO_4$) and evaporated. The residue was boiled in $Et_2O$ for a short time and collected: 6.58 g (93%) of **12**. Colourless solid. M.p. > 340°. UV (MeOH): 203 (4.33), 254 (4.25), 272 (sh, 4.09). $^1$H-NMR ((D$_6$)DMSO): 10.62 (br. *s*, NH); 7.87 (*s*, H–C(8)); 6.47 (br. *s*, $NH_2$); 6.10–6.05 (*t*, H–C(1′)); 4.47–4.45 (*m*, H–C(3′)); 3.79–3.76 (*m*, H–C(4′)); 3.69–3.54 (*m*, 2 H–C(5′)); 2.71–2.58 (*m*, 1 H–C(2′)); 2.28–2.15 (*m*, 1 H–C(2′)); 1.61–1.54 (*m*, 4 $Me_2N$); 0.12–0.06 (*m*, 2 $Me_2Si$). Anal. calc. for $C_{26}H_{49}N_5O_4Si_2$ (551.88): C 56.59, H 8.94, N 12.69; found: C 56.53, H 8.62, N 12.50.

8. $N^2$-*[(2-Dansylethoxy)carbonyl]-2′-deoxy-3′,5′-bis-*O*-[dimethyl(1,1,2-trimethylpropyl)silyl]guanosine* (**13**) *and* $N^2$,$N^2$-*Bis[(2-dansylethoxy)carbonyl]-2′-deoxy-3′,5′-bis-*O*-[dimethyl(1,1,2-trimethylpropyl)silyl]guanosine* (**14**). In dry pyridine (10 ml), **12** (2.5 g, 4.5 mmol) was co-evaporated and then taken up in dry pyridine/$CH_2Cl_2$ 1:1 (40 ml). Trimethylsilyl chloride (1.17 ml, 9 mmol) was added and the mixture stirred for 30 min. The resulting suspension was cooled to 0°, **5** (3.05 g, 8.1 mmol) added, and the mixture stirred overnight at r.t. After dilution with $CH_2Cl_2$ (20 ml), the soln. was washed with phosphate buffer (pH 7, 3 × 20 ml), the aq. phase extracted with $CH_2Cl_2$, the combined org. layer dried ($Na_2SO_4$), evaporated, and co-evaporated with toluene (20 ml), and the residue purified by FC (silica gel, 24 × 3.5 cm, toluene/AcOEt/MeOH 4:1:0 (0.4 l), 1:1 (500 ml), 5:4:1 (900 ml), 0:10:1 (400 ml)): 1.2 g (31%) of **13**, 700 mg (13%) of **14**, 600 mg (24%) of **12**, and 1.9 g of **13**/**14** as yellow foams. The mixture **13**/**14** (1.9 g) and the pure foam of **14** were combined, dissolved in $H_2O$/pyridine 1:1 (50 ml) and stirred at r.t. for 2 days. After extraction with $CH_2Cl_2$ (3 × 30 ml), the combined org. phase was dried ($Na_2SO_4$), evaporated, and co-evaporated with toluene (20 ml). The residue was purified by FC (silica gel, 17 × 3 cm, toluene/AcOEt 4:1 (0.3 l), 1:1 (0.7 l)): 1.46 g (38%) of **13**. Yellow foam. Overall yield of **13**: 2.66 g (69%).

**13**: UV (MeOH): 205 (4.80), 254 (4.53), 344 (3.65). $^1$H-NMR ((D$_6$)DMSO): 11.11, 11.02 (2 br. *s*, 2 NH); 8.49 (*d*, H–C(2)(Dns)); 8.23–8.16 (*m*, H–C(8), H–C(8)(Dns), H–C(4)(Dns)); 7.70–7.62 (*m*, H–C(3)(Dns), H–C(7)(Dns)); 7.23 (*d*, H–C(6)(Dns)); 6.13 (*t*, H–C(1′)); 4.48–4.44 (*m*, H–C(3′), $CH_2OCO$); 3.94 (*t*, $SO_2CH_2$); 3.83–3.80 (*m*, H–C(4′)); 3.73–3.58 (*m*, 2 H–C(5′)); 2.74–2.70 (*m*, H–C(2′), $Me_2N$); 2.32–2.25 (*m*, H–C(2′)); 1.63–1.51 (*m*, 2 $Me_2CH$); 0.89–0.80 (*m*, 4 $Me_2CH$); 0.14–0.06 (*m*, 2 $Me_2Si$). Anal. calc. for $C_{41}H_{64}N_6O_8SSi_2$ (857.24): C 57.45, H 7.53, N 9.80; found: C 57.57, H 7.44, N 9.54.

**14**: UV (MeOH): 212 (5.05), 252 (4.67), 343 (4.98). $^1$H-NMR ((D$_6$)DMSO): 8.54 (*d*, 2 H–C(2)(Dns)); 8.32 (*s*, H–C(8)); 8.08–8.04 (*m*, 2 H–C(4)(Dns), 2 H–C(8)(Dns)); 7.67–7.53 (*m*, 2 H–C(3)(Dns), 2 H–C(7)(Dns)); 7.21 (*d*, 2 H–C(6)(Dns)); 6,25 (*t*, H–C(1′)); 4.48–4.30 (*m*, H–C(3′), 2 $CH_2OCO$); 3.84–3.50 (*m*, 2 $SO_2CH_2$, H–C(4′), 2 H–C(5′)); 2.84–2.68 (*m*, H–C(2′), 2 $Me_2N$); 2.32–2.23 (*m*, H–C(2′)); 1.63–1.53 (*m*, 2 $Me_2CH$); 0.89–0.80 (*m*, 4 $Me_2CH$); 0.14–0.06 (*m*, 2 $Me_2Si$). Anal. calc. for $C_{56}H_{79}N_7O_{12}S_2Si_2$ (1162.59): C 57.86, H 6.84, N 8.43; found: C 57.91, H 6.99, N 8.26.

9. $N^2$-*[(2-Dansylethoxy)carbonyl]-2′-deoxyguanosine* (**15**). As described in *Exper. 5*, with **13** (730 mg, 0.85 mmol), THF (20 ml), AcOH (2.95 ml, 51.7 mmol), and $(Bu_4N)F \cdot 3\,H_2O$ (1.63 g, 5.17 mmol) (4 days, r.t.). Workup with $CH_2Cl_2$ (20 ml), 0.1M AcOH (2 × 10 ml), $CH_2Cl_2$ (2 × 20 ml), and $MgSO_4$. Purification by FC (silica gel, 8 × 3 cm, $CH_2Cl_2$/MeOH 100:4 (0.3 l), 100:5 (0.4 l), 100:6 (0.3 l)) gave 440 mg (85%) of **15**. Yellow foam. UV (MeOH): 207 (4.77), 254 (4.51), 345 (3.60). $^1$H-NMR ((D$_6$)DMSO): 11.18, 11.01 (2 br. *s*, 2 NH); 8.49 (*d*, H–C(2)(Dns)); 8.23–8.20 (*m*, H–C(4)(Dns), H–C(8)(Dns), H–C(8)); 7.71–7.62 (*m*, H–C(3)(Dns), H–C(7)(Dns)); 7.23 (*d*, H–C(6)(Dns)); 6.15 (*t*, H–C(1′)); 5.32 (*d*, OH–C(3′)); 4.93 (*t*, OH–C(5′)); 4.47–4.38 (*m*, $CH_2OCO$, H–C(3′)); 3.96–3.82 (*m*, $SO_2CH_2$, H–C(4′)); 3.57–3.47 (*m*, 2 H–C(5′)); 2.74 (*s*, $Me_2N$); 2.65–2.50 (*m*, H–C(1′)); 2.26–2.22 (*m*, H–C(1′)). Anal. calc. for $C_{25}H_{27}N_6O_8S$ (571.59): C 52.53, H 4.76, N 14.70; found: C 52.05, H 5.12, N 14.41.

10. $N^2$-*[(2-Dansylethoxy)carbonyl]-2′-deoxy-5′*-O-*(dimethoxytrityl)guanosine* (**16**). As described in *Exper. 6*, with **15** (240 mg, 0.42 mmol), abs. pyridine (2 × 10 ml), and $(MeO)_2TrCl$ (180 mg, 0.52 mmol) (4 h, r.t.). Workup with $CH_2Cl_2$ (20 ml), sat. $NaHCO_3$ soln. (3 × 10 ml), $CH_2Cl_2$ (3 × 10 ml), and $MgSO_4$. FC (silica gel, 8 × 2 cm, toluene/AcOEt/MeOH 1:1 (0.2 l), 5:4:1 (0.1 l)) gave 345 mg (94%) of **16**. Yellow foam. UV (MeOH): 204 (5.04), 236 (4.56), 254 (sh, 4.54), 344 (3.59). $^1$H-NMR ($(D_6)$DMSO): 11.17, 11.00 (2 br. *s*, 2 NH); 8.49 (*d*, H–C(2)(Dns)); 8.22 (*d*, H–C(4)(Dns), H–C(8)(Dns)); 8.07 (*s*, H–C(8)); 7.70–7.61 (*dd*, H–C(3)(Dns), H–C(7)(Dns)); 7.33–7.17 (*m*, 9 H of $(MeO)_2Tr$, H–C(6)(Dns)); 6.82–6.75 (*m*, 4 H *o* to MeO); 6.20 (*t*, H–C(1′)); 5.33 (*d*, OH–C(3′)); 4.47–4.40 (*m*, $CH_2OCO$, H–C(3′)); 3.96–3.94 (*m*, $SO_2CH_2$, H–C(4′)); 3.69 (*s*, 2 MeO); 3.24–3.08 (*m*, 2 H–C(5′)); 2.73–2.60 (*m*, $Me_2N$, 1 H–C(2′)); 2.37–2.24 (*m*, 1 H–C(2′)). Anal. calc. for $C_{46}H_{46}N_6O_{10}S$ (874.98): C 63.14, H 5.30, N 9.60; found: C 62.60, H 5.37, N 9.31.

11. $N^2$-*[(2-Dansylethoxy)carbonyl]-2′-deoxy-*$O^6$-*[2-(4-nitrophenyl)ethyl]guanosine* (**19**). As described in *Exper. 11*, with **17** (4.0 g, 9.6 mmol), dry pyridine (20 ml, 50 ml), $Me_3SiCl$ (6.24 ml, 48 mmol; 30 min, r.t.), and **5** (5.76 g, 11.5 mmol; overnight, r.t.). Purification by FC (15 × 5 cm, toluene/AcOEt/MeOH 10:10:0 (1.0 l), 10:10:1 (1.0 l), 10:10:2 (1.0 l)) gave 5.81 g (84%) of **19**. Yellow foam. UV (MeOH): 213 (4.81), 257 (4.43), 344 (3.60). $^1$H-NMR ($(D_6)$DMSO): 10.0 (br. *s*, NH); 8.46–8.39 (*m*, H–C(8), H–C(2)(Dns)); 8.24–8.13 (*m*, H–C(4)(Dns), H–C(8)(Dns), 2 H *o* to $NO_2$); 7.65–7.57 (*m*, H–C(3)(Dns), H–C(7)(Dns), 2 H *m* to $NO_2$); 7.19 (*d*, H–C(6)(Dns)); 6.27 (*t*, H–C(1′)); 5.31 (*d*, OH–C(3′)); 4.87 (*t*, OH–C(5′)); 4.69 (*t*, $CH_2OCO$); 4.42–4.38 (*m*, $CH_2CH_2O$ of npe, H–C(3′)); 3.90–3.81 (*m*, H–C(4′), $SO_2CH_2$); 3.58–3.49 (*m*, 2 H–C(5′)); 3.27 (*t*, $CH_2CH_2O$ of npe); 2.72–2.62 (*m*, $Me_2N$, 1 H–C(2′)); 2.20–2.10 (*m*, 1 H–C(2′)). Anal. calc. for $C_{33}H_{35}N_7O_{10}S \cdot {}^1/_7$ toluene (734.87): C 55.57, H 4.95, N 13.34; found: C 55.63, H 5.14, N 13.06.

12. $N^2$-*[(2-Dansylethoxy)carbonyl]-2′-deoxy-*$O^6$-*[2-(phenylsulfonyl)ethyl]guanosine* (**20**). In dry pyridine (10 ml), **18** (1.21 g, 2.78 mmol) was co-evaporated and then taken up in dry pyridine (40 ml). $Me_3SiCl$ (2.1 ml, 16.1 mmol; 30 min, r.t.) and finally **5** (1.57 g, 3.12 mmol) were added (overnight, r.t.). The reaction was stopped with MeOH (10 ml, 2 h, r.t.), the mixture diluted with $CH_2Cl_2$, the soln. washed with sat. $NaHCO_3$ soln. (2 × 20 ml), the aq. phase extracted with $CH_2Cl_2$ (2 × 10 ml), the combined org. layer dried ($MgSO_4$) and evaporated, the residue purified by FC (silica gel, 9 × 3.5 cm, $CH_2Cl_2$/MeOH 100:3 (1.0 l)): 1.62 g (79%) of **20**. Yellow foam. UV (MeOH): 215 (4.82), 254 (4.41), 346 (3.58). $^1$H-NMR ($(D_6)$DMSO): 10.06 (br. *s*, NH); 8.44 (*d*, H–C(2)(Dns)); 8.37 (*s*, H–C(8)); 8.23–8.19 (*m*, H–C(4)(Dns), H–C(8)(Dns)); 7.85 (*d*, 2 H *o* to $SO_2$); 7.66–7.53 (*m*, H–C(3)(Dns), H–C(7)(Dns), 2 H *m* to $SO_2$, 1 H *p* to $SO_2$); 7.19 (*d*, H–C(6)(Dns)); 6.25 (*t*, H–C(1′)); 5.31 (*d*, OH–C(3′)); 4.89 (*t*, OH–C(5′)); 4.65 (*t*, $CH_2OCO$); 4.43–4.38 (*m*, $CH_2CH_2O$ of pse, H–C(3′)); 4.10 (*t*, $SO_2CH_2$); 3.92–3.83 (*m*, $CH_2CH_2O$ of pse, H–C(4′)); 3.59–3.48 (*m*, 2 H–C(5′)); 2.73–2.63 (*m*, $Me_2N$, H–C(2′)); 2.28–2.22 (*m*, H–C(2′)). Anal. calc. for $C_{33}H_{37}N_6O_{10}S_2 \cdot H_2O$ (759.84): C 52.16, H 5.17, N 11.06; found: C 52.48, H 4.93, N 10.92.

13. $N^2$-*[(2-Dansylethoxy)carbonyl]-2′-deoxy-5′*-O-*(dimethoxytrityl)*-$O^6$-*[2-(4-nitrophenyl)ethyl]guanosine* (**21**). As described in *Exper. 6*, with **19** (5.8 g, 7.2 mmol), dry pyridine (10 ml, 40 ml), and $(MeO)_2TrCl$ (3.16 g, 9.36 mmol; 2.5 h, r.t.). Workup with $CH_2Cl_2$ (50 ml), sat. $NaHCO_3$ soln. (3 × 20 ml), $CH_2Cl_2$ (3 × 20 ml), and $Na_2SO_4$. Purification by FC (20 × 5 cm, toluene/AcOEt/MeOH 4:1:0 (0.5 l), 5:4:1 (0.4 l)) gave 7.36 g (92%) of **21**. Yellow foam. UV (MeOH): 204 (5.02), 237 (4.55), 257 (sh, 4.54), 343 (3.57). $^1$H-NMR ($(D_6)$DMSO): 10.0 (br. *s*, NH); 8.42 (*d*, H–C(2)(Dns)); 8.29–8.15 (*m*, H–C(8), H–C(4)(Dns), H–C(8)(Dns), 2 H *o* to $NO_2$); 7.66–7.56 (*m*, H–C(3)(Dns), H–C(7)(Dns), 2 H *m* to $NO_2$); 7.25–7.12 (*m*, H–C(6)(Dns), 9 H of $(MeO)_2Tr$); 6.75–6.67 (*m*, 4 H *o* to MeO); 6.31 (*t*, H–C(1′)); 5.29 (*d*, OH–C(3′)); 4.69 (*t*, $CH_2OCO$); 4.50–4.36 (*m*, $CH_2CH_2O$ of npe, H–C(3′)); 3.95–3.87 (*m*, H–C(4′), $SO_2CH_2$); 3.68, 3.66 (2*s*, 2 MeO); 3.30–3.10 (*m*, 2 H–C(5′), $CH_2CH_2O$ of npe); 2.82–2.70 (*m*, $Me_2N$, 1 H–C(2′)); 2.32–2.27 (*m*, 1 H–C(2′)). Anal. calc. for $C_{54}H_{53}N_7O_{12}S$ (1024.13): C 63.33, H 5.21, N 9.57; found: C 63.31, H 5.44, N 9.61.

14. $N^2$-*[(2-Dansylethoxy)carbonyl]-2′-deoxy-5′*-O-*(dimethoxytrityl)*-$O^6$-*[2-(phenylsulfonyl)ethyl]guanosine* (**22**). As described in *Exper. 6*, with **20** (1.6 g, 2.16 mmol), dry pyridine (10 ml, 20 ml), and $(MeO)_2TrCl$ (1.06 g, 3.14 mmol; 2.5 h, r.t.). Workup with $CH_2Cl_2$ (30 ml), sat. $NaHCO_3$ soln. (3 × 20 ml), $CH_2Cl_2$ (3 × 20 ml), and $Na_2SO_4$. Purification by FC (15 × 2.5 cm, toluene/AcOEt/MeOH 10:10:0 (0.5 l), 5:4:1 (0.2 l)) and co-evaporation of the product with $CH_2Cl_2$ gave 2.14 g (95%) of **22**. Yellow foam. UV (MeOH): 203 (5.01), 234 (4.52), 254 (4.48), 344 (3.56). $^1$H-NMR ($(D_6)$DMSO): 9.98 (*s*, NH); 8.42 (*d*, H–C(2)(Dns)); 8.25–8.18 (*m*, H–C(8), H–C(4)(Dns), H–C(8)(Dns)); 7.86 (*d*, 2 H *o* to $SO_2$); 7.62–7.45 (*m*, H–C(3)(Dns), H–C(7)(Dns), 2 H *m* to $SO_2$, 1 H *p* to $SO_2$); 7.29–7.12 (*m*, 9 H of $(MeO)_2Tr$, H–C(6)(Dns)); 6.76–6.67 (*m*, 4 H *o* to MeO); 6.37 (*t*, H–C(1′)); 5.29 (*d*, OH–C(3′)); 4.65 (*t*, $CH_2OCO$); 4.47–4.38 (*m*, H–C(3′), $CH_2CH_2O$ of pse); 4.08 (*t*, $SO_2CH_2$); 3.94–3.85 (*m*, $CH_2CH_2O$ of pse, H–C(4′)); 3.68, 3.67 (2*s*, 2 MeO); 3.28–3.07 (*m*, 2 H–C(5′)); 2.85–2.69 (*m*, 1 H–C(2′)); 2.32–2.23 (*m*, 1 H–C(2′)). Anal. calc. for $C_{54}H_{55}N_6O_{12}S_2 \cdot H_2O$ (1062.21): C 61.06, H 5.41, N 7.91; found: C 61.31, H 5.22, N 7.73.

15. $N^4$-*[(2-Dansylethoxy)carbonyl]-2′-deoxy-5′-*O*-(dimethoxytrityl)cytidine 3′-(2-Cyanoethyl Diisopropylphosphoramidite)* (**24**). A mixture of **7** (330 mg, 0.39 mmol), (2-cyanoethoxy)bis(diisopropylamino)phosphine (**23**; 176 mg, 0.585 mmol), and 1*H*-tetrazole (14 mg, 0.2 mmol) was stirred in abs. MeCN (1.5 ml) under $N_2$ for 1 h. After dilution with $CH_2Cl_2$ (20 ml), the soln. was washed with phosphate buffer (pH 7, 2 × 10 ml), the aq. phase extracted with $CH_2Cl_2$ (2 × 10 ml), the combined org. layer dried ($MgSO_4$) and evaporated and the crude foam purified by FC (10 × 2 cm, petroleum ether/acetone 4:1 (0.2 l), 3:1 (0.2 l), 2:1 (0.15 l), 1:1 (0.15 l)). The product fractions were co-evaporated with $CH_2Cl_2$: 315 mg (78%) of **24**. Yellow foam. UV (MeOH): 204 (5.01), 236 (4.62), 292 (sh, 3.98), 343 (3.59). $^1$H-NMR ((D$_6$)DMSO): 10.43 (br. *s*, NH); 8.48 (*d*, H–C(2)(Dns)); 8.22–8.06 (*m*, H–C(4)(Dns), H–C(8)(Dns), H–C(6)); 7.65–7.58 (*m*, H–C(3)(Dns), H–C(7)(Dns)); 7.36–7.18 (*m*, H–C(6)(Dns), 9 H of (MeO)$_2$*Tr*); 6.89–6.85 (*m*, 4 H *o* to MeO); 6.59 (*d*, H–C(5)); 6.16–6.08 (*m*, H–C(1′)); 4.56–4.48 (*m*, H–C(3′)); 4.37 (*t*, $CH_2OCO$); 4.12–4.07 (*m*, H–C(4′)); 3.88 (*t*, $SO_2CH_2$); 3.76 (*s*, 2 MeO); 3.68–3.27 (*m*, 2 H–C(5′), 2 $Me_2CH$, $OCH_2CH_2CN$); 2.76 (*s*, $Me_2N$); 2.64 (*t*, $OCH_2CH_2CN$); 2.52–2.10 (*m*, 2 H–C(2′)); 1.13–0.96 (*m*, 2 $Me_2CH$). $^{31}$P-NMR ((D$_6$)DMSO): 148.57, 148.26. Anal. calc. for $C_{54}H_{64}N_5O_{11}PS$ (1036.18): C 62.60, H 6.23, N 8.11; found: C 63.36, H 6.37, N 7.87.

16. $N^6$-*[(2-Dansylethoxy)carbonyl]-2′-deoxy-5′-*O*-(dimethoxytrityl)adenosine 3′-(2-Cyanoethyl Diisopropylphosphoramidite)* (**25**). As described in *Exper. 15*, with **11** (258 mg, 0.3 mmol), 1*H*-tetrazole (11 mg, 0.15 mmol), and **23** (135 mg, 0.45 mmol) in abs. MeCN (3 ml). FC (8 × 2 cm, petroleum ether/acetone 3:1 (0.4 l), 2:1 (0.3 l), 1:1 (0.1 l) gave 250 mg (79%) of **25**. Yellow foam. UV (MeOH): 204 (5.06), 237 (4.55), 265 (4.49), 343 (3.65). $^1$H-NMR ((D$_6$)DMSO): 10.25 (br. *s*, NH); 8.53–8.40 (*m*, H–C(2), H–C(8), H–C(2)(Dns)); 8.21–8.15 (*m*, H–C(4)(Dns), H–C(8)(Dns)); 7.63–7.52 (*m*, H–C(3)(Dns), H–C(7)(Dns)); 7.30–7.16 (*m*, H–C(6)(Dns), 9 H of (MeO)$_2$*Tr*); 6.81–6.74 (*m*, 4 H *o* to MeO); 6.47–6.43 (*m*, H–C(1′)); 4.82–4.77 (*m*, H–C(3′)); 4.43–4.38 (*t*, $CH_2OCO$); 4.16–4.10 (*m*, H–C(4′)); 3.89–3.84 (*t*, $SO_2CH_2$); 3.80–3.03 (*m*, 2 MeO, $OCH_2CH_2CN$, 2 $Me_2CH$, 2 H–C(5′), 1 H–C(2′)); 2.74 (*s*, $Me_2N$); 2.68–2.64 (*t*, $OCH_2CH_2CN$); 2.52–2.48 (*m*, 1 H–C(2′)); 1.17–0.98 (*m*, 2 $Me_2CH$). $^{31}$P-NMR ((D$_6$)DMSO): 148.56, 148.00. Anal. calc. for $C_{55}H_{63}N_8O_{10}PS$ (1059.20): C 62.37, H 6.00, N 10.58; found: C 61.91, H 6.24, N 10.04.

17. $N^2$-*[(2-Dansylethoxy)carbonyl]-2′-deoxy-5′-*O*-(dimethoxytrityl)guanosine 3′-(2-Cyanoethyl Diisopropylphosphoramidite)* (**26**). As described in *Exper. 15*, with **16** (437 mg, 0.5 mmol), 1*H*-tetrazole (18 mg, 0.25 mmol), and **23** (225 mg, 0.75 mmol) in abs. MeCN (5 ml). Repeated FC (8 × 2 cm, AcOEt 0.16 l) gave 420 mg (79%) of **25**. Yellow foam. UV (MeOH): 204 (5.03), 237 (4.54), 255 (sh, 4.53), 346 (3.59). $^1$H-NMR ((D$_6$)DMSO): 11.10, 11.01 (2 br. *s*, 2 NH); 8.49 (*d*, H–C(2)(Dns)); 8.24–8.08 (*m*, H–C(4)(Dns), H–C(8)(Dns), H–C(8)); 7.69–7.61 (*m*, H–C(3)(Dns), H–C(7)(Dns)); 7.34–7.16 (*m*, 9 H of (MeO)$_2$*Tr*, H–C(6)(Dns)); 6.83–6.76 (*m*, 4 H *o* to MeO); 6.23–6.16 (*m*, H–C(1′)); 4.62–4.47 (*m*, $CH_2OCO$, H–C(3′)); 4.08–3.93 (*m*, $SO_2CH_2$, H–C(4′)); 3.70–3.50 (*m*, 2 MeO, $OCH_2CH_2CN$, 2 $Me_2CH$); 3.24–3.20 (*m*, 2 H–C(5′)); 2.86–2.35 (*m*, $Me_2N$, 2 H–C(2′), $OCH_2CH_2CN$); 1.20–0.99 (*m*, 2 $Me_2CH$). $^{31}$P-NMR ((D$_6$)DMSO): 148.66, 147.98. Anal. calc. for $C_{55}H_{63}N_8O_{11}PS$ (1075.22): C 61.38, H 5.91, N 10.42; found: C 60.43, H 6.04, N 9.97.

18. $N^2$-*[(2-Dansylethoxy)carbonyl]-2′-deoxy-5′-*O*-(dimethoxytrityl)-*$O^6$*-[2-(4-nitrophenyl)ethyl]-2′-deoxyguanosine 3′-(2-Cyanoethyl Diisopropylphosphoramidite)* (**27**). As described in *Exper. 15*, with **22** (1.11 g, 1.0 mmol), 1*H*-tetrazole (35 mg, 0.5 mmol), and **23** (450 mg, 1.5 mmol) in abs. MeCN (5 ml). FC (20 × 2.5 cm, toluene/AcOEt 4:1 (0.1 l), 2:1 (0.1 l), 1:1 (200 ml)) gave 920 mg (75%) of **27**. Yellow foam. UV (MeOH): 204 (5.09), 237 (4.55), 257 (sh, 4.54), 345 (3.59). $^1$H-NMR ((D$_6$)DMSO): 9.97 (*d*, NH); 8.42 (*d*, H–C(2)(Dns)); 8.30 (*d*, H–C(8)); 8.24–8.14 (*m*, H–C(4)(Dns), H–C(8)(Dns), 2 H *o* to $NO_2$); 7.65–7.55 (*m*, H–C(3)(Dns), H–C(7)(Dns), 2 H *m* to $NO_2$); 7.26–7.11 (*m*, H–C(6)(Dns), 9 H of (MeO)$_2$*Tr*); 6.75–6.66 (*m*, 4 H *o* to MeO); 6.36–6.31 (*t*, H–C(1′)); 4.71–4.66 (*m*, $CH_2OCO$, H–C(3′)); 4.37 (*t*, $CH_2CH_2O$ of npe); 4.08–4.02 (*m*, H–C(4′)); 3.86 (*t*, $SO_2CH_2$); 3.74–3.12 (*m*, 2 MeO, 1 H–C(5′), $CH_2CH_2O$ of npe, $OCH_2CH_2CN$, 2 $Me_2CH$); 3.05–2.98 (*m*, 1 H–C(5′)); 2.77–2.47 (*m*, $OCH_2CH_2CN$, $Me_2N$, 2 H–C(2′)); 1.20–0.97 (*m*, 2 $Me_2CH$). $^{31}$P-NMR ((D$_6$)DMSO): 148.70, 148.05. Anal. calc. for $C_{63}H_{70}N_9O_{13}PS$ (1224.35): C 61.80, H 5.76, N 10.29; found: C 61.95, H 5.87, N 9.96.

19. $N^2$-*[(2-Dansylethoxy)carbonyl]-2′-deoxy-5′-*O*-(dimethoxytrityl)-*$O^6$*-[2-(phenylsulfonyl)ethyl]guanosine 3′-(2-Cyanoethyl Diisopropylphosphoramidite)* (**28**). As described in *Exper. 15*, with **22** (626 mg, 0.6 mmol), 1*H*-tetrazole (21 mg, 0.3 mmol), and **23** (270 mg, 0.9 mmol) in abs. MeCN (5 ml). FC (9.5 × 2.5 cm, petroleum ether/acetone 3:1 (0.3 l), 1.5:1 (0.32 l)) gave 580 mg (78%) of **28**. Yellow foam. UV (MeOH): 203 (5.04), 236 (4.54), 254 (4.47), 345 (3.59). $^1$H-NMR ((D$_6$)DMSO): 9.93 (br. *s*, NH); 8.49 (*d*, H–C(2)(Dns)); 8.27–8.19 (*m*, H–C(8), H–C(4)(Dns), H–C(8)(Dns)); 7.89–7.82 (*m*, 2 H *o* to $SO_2$); 7.62–7.43 (*m*, H–C(3)(Dns), H–C(7)(Dns), 2 H *m* to $SO_2$, 1 H *p* to $SO_2$); 7.29–7.08 (*m*, H–C(6)(Dns), 9 H of (MeO)$_2$*Tr*); 6.80–6.64 (*m*, 4 H *o* to MeO); 6.32–6.24 (*m*, H–C(1′)); 4.80–4.62 (*m*, H–C(3′), $CH_2OCO$); 4.47 (*t*, $CH_2CH_2O$ of pse); 4.08–3.98 (*m*, H–C(4′), $SO_2CH_2$);

3.88 (*t*, $CH_2CH_2O$ of npe); 3.76–3.48 (*m*, 2 MeO, 2 $Me_2CH$, $OCH_2CH_2CN$); 3.43–3.19 (*m*, 1 H–C(5′)); 3.08–2.96 (*m*, 1 H–C(5′)); 2.76–2.47 (*m*, $Me_2N$, 2 H–C(2′), $OCH_2CH_2CN$); 1.27–1.05 (*m*, 2 $Me_2CH$). $^{31}$P-NMR ((D$_6$)DMSO): 148.76, 148.09. Anal. calc. for $C_{63}H_{71}N_8O_{13}PS_2$ (1243.32): C 60.86, H 5.76, N 9.01; found: C 60.52, H 5.88, N 8.98.

20. *3′-O-(3-Carboxypropanoyl)-N$^4$-[(2-dansylethoxy)carbonyl]-2′-deoxy-5′-O-(dimethoxytrityl)cytidine* (**29**). In $CH_2Cl_2$ (5 ml), **7** (418 mg, 0.5 mmol), succinic anhydride (100 mg, 1 mmol), and 4-(dimethylamino)pyridine (74 mg, 0.6 mmol) were stirred at r.t. for 2 h. Then, the mixture was diluted with $CH_2Cl_2$ (20 ml) and washed with 10% citric acid (2 × 20 ml) and NaCl soln. (2 × 20 ml). The aq. phase was extracted with $CH_2Cl_2$ (2 × 10 ml) and the combined org. layer dried ($Na_2SO_4$) and evaporated: 460 mg (100%) of **29**. Yellow foam. UV (MeOH): 204 (4.98), 236 (4.58), 293 (sh, 3.94), 344 (3.56). $^1$H-NMR ((D$_6$)DMSO): 8.46 (*d*, H–C(2)(Dns)); 8.24–8.14 (*m*, H–C(4)(Dns), H–C(8)(Dns)); 7.88 (*d*, H–C(6)); 7.67–7.49 (*m*, H–C(3)(Dns), H–C(7)(Dns)); 7.38–7.18 (*m*, H–C(6)(Dns), 9 H of $(MeO)_2Tr$); 6.89–6.85 (*m*, 4 H *o* to MeO); 6.60 (*d*, H–C(5)); 6.10 (*t*, H–C(1′)); 5.24–5.18 (*m*, H–C(3′)); 4.43–4.37 (*t*, $CH_2OCO$); 4.21–4.15 (*m*, H–C(4′)); 3.94–3.86 (*t*, $SO_2CH_2$); 3.72 (*s*, 2 MeO); 3.35–3.25 (*m*, 2 H–C(5′)); 2.78 (*s*, $Me_2N$); 2.52–2.18 (*m*, $CH_2CH_2$, 2 H–C(2′)). Anal. calc. for $C_{46}H_{50}N_4O_{13}S \cdot {}^3/_2\ H_2O$ (962.04): C 53.45, H 4.68, N 10.85; found: C 53.44, H 4.70, N 10.89.

21. *3′-O-(3-Carboxypropanoyl)-N$^6$-[(2-dansylethoxy)carbonyl]-2′-deoxy-5′-O-(dimethoxytrityl)adenosine* (**30**). As described in *Exper. 20*, with **11** (250 mg, 0.3 mmol). Workup yielded 280 mg (97%) of **30**. Yellow foam. UV (MeOH): 204 (5.09), 237 (4.57), 261 (sh, 4.52), 346 (3.66). $^1$H-NMR ((D$_6$)DMSO): 12.23 (br. *s*, COOH); 10.30 (br. *s*, NH); 8.54–8.40 (*m*, H–C(2), H–C(8), H–C(2)(Dns)); 8.24–8.17 (*m*, H–C(4)(Dns), H–C(8)(Dns)); 7.65–7.55 (*m*, H–C(3)(Dns), H–C(7)(Dns)); 7.28–7.11 (*m*, 9 H of $(MeO)_2Tr$, H–C(6)(Dns)); 6.84–6.78 (*m*, 4 H *o* to MeO); 6.49–6.44 (*m*, H–C(1′)); 5.46–5.43 (*m*, H–C(3′)); 4.46–4.41 (*t*, $CH_2OCO$); 4.23–4.20 (*m*, H–C(4′)); 3.92–3.87 (*m*, $SO_2CH_2$); 3.71 (*s*, 2 MeO); 3.34–3.22 (*m*, 2 H–C(5′)); 2.75 (*s*, $Me_2N$); 2.59–2.42 (*m*, 2 H–C(2′), $CH_2CH_2$). Anal. calc. for $C_{50}H_{50}N_6O_{12}S$ (959.05): C 62.62, H 5.26, N 8.76; found: C 63.01, H 5.45, N 8.20.

22. *3′-O-(3-Carboxypropanoyl)-N$^2$-[(2-dansylethoxy)carbonyl]-2′-deoxy-5′-O-(dimethoxytrityl)guanosine* (**31**). As described in *Exper. 20*, with **16** (220 mg, 0.25 mmol). Workup yielded 240 mg (99%) of **31**. Yellow foam. UV (MeOH): 203 (5.01), 236 (4.52), 254 (sh, 4.52), 346 (3.56). $^1$H-NMR ((D$_6$)DMSO): 8.51 (*d*, H–C(2)(Dns)); 8.19 (*d*, H–C(4)(Dns), H–C(8)(DNS)); 7.86 (*s*, H–C(8)); 7.54–7.47 (*m*, H–C(3)(Dns), H–C(7)(Dns)); 7.30–7.08 (*m*, 9 H of $(MeO)_2Tr$); 6.78 – 6.69 (*m*, 4 H *o* to MeO, H–C(6)(Dns)); 5.99 (*t*, H–C(1′)); 5.39–5.36 (*m*, H–C(3′)); 4.47–4.45 (*m*, $CH_2OCO$); 4.19–4.17 (*m*, H–C(4′)); 3.73–3.61 (*m*, $SOCH_2$, 2 MeO, 1 H–C(5′)); 3.30–3.24 (*m*, 1 H–C(5′)); 2.81–2.52 (*m*, $Me_2N$, 2 H–C(2′), $CH_2CH_2$). Anal. calc. for $C_{50}H_{50}N_6O_{13}S \cdot H_2O$ (993.07): C 60.47, H 5.27, N 8.46; found: C 60.48, H 5.23, N 8.57.

23. *3′-O-(3-Carboxypropanoyl)-N$^2$-[(2-dansylethoxy)carbonyl]-2′-deoxy-5′-O-(dimethoxytrityl)-O$^6$-[2-(4-nitrophenyl)ethyl]guanosine* (**32**). As described in *Exper. 20*, with **22** (190 mg, 0.17 mmol; 3 h, r.t.). Workup yielded 200 mg (97%) of **33**. Yellow foam. UV (MeOH): 204 (5.01), 237 (4.54), 257 (sh, 4.52), 343 (3.56). $^1$H-NMR ((D$_6$)DMSO): 12.26 (br. *s*, COOH); 10.00 (br. *s*, NH); 8.42 (*d*, H–C(2)(Dns)); 8.31 (*d*, H–C(8)); 8.22–8.17 (*m*, H–C(4)(Dns), H–C(8)(Dns), 2 H *o* to $NO_2$); 7.67–7.55 (*m*, H–C(3)(Dns), H–C(7)(Dns), 2 H *m* to $NO_2$); 7.23–7.10 (*m*, H–C(6)(Dns), 9 H of $(MeO)_2Tr$); 6.73–6.63 (*m*, 4 H *o* to MeO); 6.33 (*t*, H–C(1′)); 5.35–5.33 (*m*, H–C(3′)); 4.69 (*t*, $CH_2OCO$); 4.37 (*t*, $CH_2CH_2O$ of npe); 4.16–4.14 (*m*, H–C(4′)); 3.86 (*t*, $SO_2CH_2$); 3.68–3.66 (2*s*, 2 MeO); 3.39–3.11 (*m*, 2 H–C(5′), $CH_2CH_2O$ of npe); 2.77–2.70 (*m*, $Me_2N$, 1 H–C(2′)); 2.49–2.40 (*m*, 1 H–C(2′), $CH_2CH_2$). Anal. calc. for $C_{58}H_{57}N_7O_{15}S \cdot H_2O$ (1142.22): C 60.98, H 5.20, N 8.58; found: C 61.22, H 5.16, N 8.86.

24. *3′-O-(3-Carboxypropanoyl)-N$^2$-[(2-dansylethoxy)carbonyl]-2′-deoxy-5′-O-(dimethoxytrityl)-O$^6$-[2-(phenylsulfonyl)ethyl]guanosine* (**33**). As described in *Exper. 20*, with **22** (240 mg, 0.23 mmol). Workup yielded 240 mg (91%) of **33**. Yellow foam. UV (MeOH): 203 (5.01), 236 (4.53), 254 (sh, 4.52), 346 (3.56). $^1$H-NMR ($CDCl_3$): 8.62 (*d*, H–C(2)(Dns)); 8.34 (*d*, 2 H *o* to $SO_2$); 7.97–7.94 (*m*, H–C(8), H–C(4)(Dns), H–C(8)(Dns)); 7.65–7.49 (*m*, 2 H *m* to $SO_2$, 1 H *p* to $SO_2$, H–C(3)(Dns), H–C(7)(Dns)); 7.40–7.16 (*m*, H–C(6)(Dns), 9 H of $(MeO)_2Tr$); 6.83–6.78 (*d*, 4 H *o* to MeO); 6.38–6.32 (*m*, H–C(1′)); 5.48–5.46 (*m*, H–C(3′)); 4.82 (*t*, $CH_2OCO$); 4.58 (*t*, $CH_2CH_2O$ of pse); 4.31–4.26 (*m*, H–C(4′)); 3.78–3.72 (*m*, 2 MeO, 2 H–C(5′), $SO_2CH_2$); 3.40 (*t*, $CH_2CH_2O$ of pse); 2.85 (*s*, $Me_2N$); 2.73–2.58 (*m*, $CH_2CH_2$, 2 H–C(2′)). Anal. calc. for $C_{58}H_{58}N_6O_{15}S_2$ (1143.26): C 60.93, H 5.11, N 7.35; found: C 61.42, H 5.68, N 6.81.

25. *Solid-Support Material* **35** *and* **36** *from 500-Å LCAMA-CPG* (**34**) *and* **29** *and* **30**, *Respectively*. A mixture of **34** (200 mg), **29** (9 mg, 10 μmol) or **30** (19 mg, 20 μmol), TOTU (5 mg (15 mmol) or 10 mg (30 mmol), resp.), abs. MeCN (3 ml), and *N*-methylmorpholine (4 μl (40 μmol) or 8 μl (80 μmol), resp.) was gently shaked for 1 or 1.5 h, resp. The CPG material was collected in a glass funnel and washed with MeOH, DMF, pyridine, MeOH, acetone,

and $Et_2O$. Capping procedure: The nucleoside-functionalized CPG was treated with a mixture of 4-(dimethylamino)pyridine (50 mg, 0.41 mmol), abs. pyridine (10 ml), and $Ac_2O$ (1 ml, 10.6 mmol) for 45 min at r.t. by gentle shaking. Then **35** or **36** was collected, washed with MeOH, DMF, MeOH, acetone, and $Et_2O$, and dried in an exsiccator. Determination of loading: A defined amount of **35** or **36** (5–10 mg) was treated in a 10-ml calibrated flask (10 ml) with 0.2M TsOH in MeCN (10 ml). After 1 min, the absorbance at 498 nm was measured against 0.2M TsOH in MeCN. The loading $L$ [μmol/g] can be calculated by the formula $L = A \cdot 10 \cdot 14.4/m$ ($A$ = absorbance at 498 nm; $m$ = weight of CPG material **35** or **36** in mg) and gave for **35** $L = 15$ and **36** $L = 18$ μmol/g.

26. *Assembly of Oligodeoxynucleotides.* Syntheses were carried out using an *Applied Biosystems 392 DNA/RNA* synthesizer. Nucleoside-functionalized CPG material **35** or **36** (0.2–0.6 μmol) was packed into a small *ABI* column, and cycles of nucleotide addition were carried out by programmed series of reagent and solvent washes based on recommended procedures with the following main steps: *1*) 5′-*O*-$(MeO)_2$Tr-Deprotection in 135 s; the eluate from this step was collected and the absorbance at 498 nm measured to determine the condensation yields. *2*) Coupling: 0.1M phosphoramidite and 0.5M 1*H*-tetrazole in dry MeCN, delivered in alternating reagent pushes with a subsequent wait time of 60 s. *3*) Capping: $Ac_2O$/2,6-dimethylpyridine/THF 1:1:8 and 1-methyl-1*H*-imidazole/THF 16:84, delivered in one 10-s push with a subsequent wait time of 5 s. *4*) Oxidation: 0.05M $I_2$ in THF/$H_2O$/pyridine 7:2:1, delivered in one 10-s push with a subsequent wait time of 15 s.

Then a cleavage programme was carried out: *1*) Cleavage of the base-protecting groups: 1M DBU in MeCN delivered in several pushes and following wait steps (total wait time: 20 min). This cycle was repeated as much as necessary. *2*) Cleavage from the support: conc. $NH_3$ soln. delivered in one push with a consecutive wait time of $4 \times 900$ s (total wait time 1 h). The reaction soln. containing only the oligonucleotide and $NH_3$ was collected and, after determination of the isolated amount of oligonucleotide by measurement of the absorbance at 260 nm, lyophilized in a *Speed-vac* concentrator under high vacuum.

27. *Kinetic Studies of the Partially Protected Nucleosides* **7**, **11**, **16**, **21**, *and* **22**. To a soln. of the tritylated nucleosides **7**, **11**, **16**, **21**, or **22** (10 μmol) in MeCN (0.5 ml) or MeCN/DMF 4:1 (for the 2′-deoxyguanosine derivatives), respectively, 1M DBU (0.5 ml) was added. In determinated time intervals (30 s, 60 s, 5 min *etc.*), 25 μl of the reaction soln. were taken out and added to 0.5M AcOH (0.25 ml). After shaking for a few min, the sample was analysed by reversed-phase HPLC.

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