New Types of Very Efficient Photolabile Protecting Groups Based upon the [2-(2-Nitrophenyl)propoxy]carbonyl (NPPOC) Moiety

by **Sigrid Bühler**[b]), **Irene Lagoja**[a]), **Heiner Giegrich**[a]), **Klaus-Peter Stengele**[b]) and **Wolfgang Pfleiderer**[a])*

[a]) Fachbereich Chemie, Universität Konstanz, Postfach 5560, D-78457 Konstanz
[b]) *Chemogenix*, Beuthener Str. 2, D-84478 Waldkraiburg

Based upon the photolabile [2-(2-nitrophenyl)propoxy]carbonyl group (NPPOC), a large number of modified 2-(2-nitrophenyl)propanol derivatives substituted at the phenyl ring (see **23**–**34** and **57**–**76**) as well as at the side-chain (see **85**–**92** and **95**–**98**) were synthesized to improve the photoreactivity of this new type of photolabile entity. The phenyl moiety was also exchanged by the naphthalenyl group (see **102**, **103**, **105**, **108**, **110**, **113**, and **114**), the thienyl substituent (see **115**, **117**, **118**, and **120**), and the benzothienyl substituent (see **121**). The 2-(2-nitroaryl- and heteroaryl)propanols were converted with diphosgene into the corresponding carbonochloridates, which reacted subsequently with thymidine to the thymidine 5′-(protected carbonates) **123**–**178** as the main reaction products. In several cases, the corresponding 3′-carbonates and 3′,5′-dicarbonates **179**–**212** were also isolated and characterized. Photolysis studies under standardized conditions (see *Table*) indicated that the rate of photocleavage varies in a broad range depending on the substituents. So far, the thymidine 5′-[2-(5-halo-2-nitrophenyl)propyl carbonates] **127**–**129**, 5′-[2-(nitro[1,1′-biphenyl]3-yl)propyl carbonates] **136**–**139**, 5′-{2-[2-nitro-5-(thianthren-1-yl)phenyl]propyl carbonate} (**140**), 5′-[2-(5-naphthalenyl-2-nitrophenyl)propyl carbonates] **141** and **142**, and 5′-[2-(2-nitro-5-thienylphenyl)propyl carbonates] **143** and **144** showed the best properties regarding fast and uniform deprotection. Since the nucleobases of **213**–**215** do not influence the photocleavage features, in general, the new type of photolabile building blocks allows in form of their 3′-phosphoramidites the photolithographic formation of high-quality biochips.

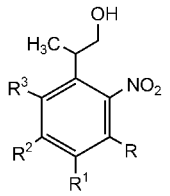
1. Introduction. – Photolabile protecting groups [1–3] are an interesting alternative to extend normal blocking-group strategies in synthetic organic chemistry into an orthogonal dimension. The most common representatives featuring the anticipated photochemical lability are derived from *o*-nitrobenzyl alcohol (=2-nitrobenzenemethanol) [1] and its derivatives. It was shown that the quantum yield of photodeprotection is strongly influenced by substituents at the phenyl moiety [5] and the $CH_2(\alpha)$ group [6], which on substitution by a Me group at $C(\alpha)$ revealed a fivefold increase in quantum yield of the photocleavage. The *o*-nitrobenzyl function has been used since its discovery in 1901 [7] to protect hydroxy, amino, mercapto, carboxy, and carbonyl functions [1–3][8] and is well established in nucleic acid [9–16], carbohydrate [17], and peptide [4][18–20] chemistry. More recently, photolabile protection of the 5′-OH of 2′-deoxyribonucleoside 3′-phosphoramidites [5][21–23] and of the 3′-OH of the isomeric 2′-deoxyribonucleoside 5′-phosphoramidites [24][25] has been employed in the solid-phase synthesis of DNA probe arrays [26][27]. For this purpose the [(*o*-nitroveratryl)oxy]carbonyl (=[(3,4-dimethoxy-2-nitrophenyl)methoxy]carbonyl; NVOC) and the [(α-methyl-*o*-nitropiperonyl)oxy]carbonyl (=[1-(1,3-benzodioxal-5-yl)ethoxy]carbonyl; MeNPOC) groups have been considered as excellent candidates in the biochip production of oligonucleotide arrays by the photolithographic technique

[5]. This method has already revolutionized microelectronics to a large extent and is now applied as another consequential technology in molecular biology to serve as analytic and diagnostic tool for DNA analyses [5][28][29] and as an alternative approach for DNA sequencing by hybridization (SBH) [30–32]. Besides the *o*-nitrobenzyl group and its modified derivatives, other types of photolabile functions have been found such as the benzoine (=1,2-diphenyl-2′-hydroxyethanone) residue [22][33][34], the pyrenylmethyl group [35], and the [(9,10-dihydro-9,10-dioxoanthracen-2-yl)methoxy]carbonyl group and the cinnamyl esters [36][37]. Their use, however, is limited to special applications, and the cleavage efficiences are only moderate.

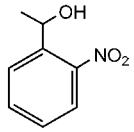
An improvement in the photolytic blocking-group strategy was achieved recently with the introduction of the [2-(2-nitrophenyl)ethoxy]carbonyl (NPEOC) [38][39] and the [2-(2-nitrophenyl)ethyl]sulfonyl (NPES) [39] group as new types of photolabile functions, especially prone for application in nucleoside and nucleotide chemistry. In contrast to the cleavage mechanism of the 2-nitrobenzyl group, which has been well studied [40][41], the photodecomposition of the NPEOC and NPES functions follows a new pathway established as a photoinduced β-elimination process [42]. Preliminary investigations have shown that the branching in α-position, preferentially by a Me group, increases also the quantum yield of photocleavage in this series by a factor of 10 [38]. It became obvious to modify in more detailed studies the 2-(2-nitrophenyl)propan-1-ol molecule at the phenyl moiety and by synthesis of structurally related 2-(2-nitroheteroaryl)propan-1-ols, to improve further the photolytic features. In this paper, the results of these broad structural variations will be reported and discussed comparatively.

2. Synthesis. – Our initial investigations on modified 2-(2-nitrophenyl)propan-1-ol derivatives [38] indicated that the most versatile approach to this group of compounds should start from 1-ethyl-2-nitro-substituted benzenes allowing many direct variations at the phenyl moiety. The 4-amino-substituted 1-ethyl-2-nitrobenzene **1** [43] was converted by known procedures applying the *Sandmeyer* reaction into the 4-chloro-, 4-bromo-, and 4-iodo-substituted 1-ethyl-2-nitrobenzenes **2**–**4**. In a similar manner, the 3-amino-substituted 1-ethyl-2-nitrobenzenamine **5** [44] was converted into the corresponding 3-chloro-, 3-bromo-, and 3-iodo-substituted 1-ethyl-2-nitrobenzenes **6**–**8**. Analogously, the 5-amino-substituted 1-ethyl-2-nitrobenzene **9** [45] yielded the 5-chloro-, 5-bromo-, and 5-iodo-substituted 1-ethyl-2-nitrobenzenes **10**–**12**. The introduction of the halogen atoms into 6-position afforded several steps to prepare first 1-ethyl-2,6-dinitrobenzene (**13**) [46], which was then reduced in MeCN with HCOOH in presence of Pd/C to give 6-amino-substituted 1-ethyl-2-nitrobenzene **14** [47] in 81% yield. The *Sandmeyer* reaction worked very well with **14** and led in high yields to the 6-bromo- and 6-iodo-substituted 1-ethyl-2-nitrobenzenes **15** and **16**. Since another interesting structural motif was seen in the 1-ethyl-dinitrobenzenes, the 2,3-, 2,4-, 2,5- and 2,6-dinitro derivatives were synthesized. The 1-ethyl-2,3-dinitrobenzene (**17**) [46] resulted from the 4-amino-substituted 1-ethyl-2,3-dinitrobenzene **18**, 1-ethyl-2,5-dinitrobenzene (**19**) [46] from the 4-amino-substituted 1-ethyl-2,5-dinitrobenzene **20**, and 1-ethyl-2,6-dinitrobenzene (**13**) from the 4-amino-substituted 1-ethyl-2,6-dinitrobenzene **21**, each by diazotation in conc. H_2SO_4 solution/AcOH and subsequent heating

	R	R^1	R^2	R^3
1	H	NH_2	H	H
2	H	Cl	H	H
3	H	Br	H	H
4	H	I	H	H
5	NH_2	H	H	H
6	Cl	H	H	H
7	Br	H	H	H
8	I	H	H	H
9	H	H	NH_2	H
10	H	H	Cl	H
11	H	H	Br	H
12	H	H	I	H
13	H	H	H	NO_2
14	H	H	H	NH_2
15	H	H	H	Br
16	H	H	H	I
17	NO_2	H	H	H
18	NO_2	NH_2	H	H
19	H	H	NO_2	H
20	H	NH_2	NO_2	H
21	H	NH_2	H	NO_2
22	H	NO_2	H	H



	R	R^1	R^2	R^3
23	H	Cl	H	H
24	H	Br	H	H
25	H	I	H	H
26	H	H	Cl	H
27	H	H	Br	H
28	H	H	I	H
30	H	H	H	Br
31	H	H	H	I
32	H	NO_2	H	H
33	H	H	H	NO_2
34	H	H	NO_2	H



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in EtOH. The 1-ethyl-2,4-dinitrobenzene (**22**) could not be obtained in pure form but only as a 1:1 mixture with 1-ethyl-2,6-dinitrobenzene (**13**).

The interconversion of the Et group into the corresponding 2-substituted propan-1-ol derivatives was achieved with paraformaldehyde under the catalysis of potassium *tert*-butoxide (^{t}BuOK) in aprotic dipolar solvents like DMSO, DMF, or hexamethylphosphoric triamide (HMPA) [48–50]. Such solvents are essential since, for the aldol-addition reaction, the activation of alkylbenzenes by only one NO_2 group is relatively weak and, therefore, needs more severe conditions [46]. The hydroxymethylation reactions to the 2-(2-nitrophenyl)propan-1-ols worked well with the 4-halogeno- and 5-halogeno-substituted 1-ethyl-2-nitrobenzenes **2**–**4** and **10**–**12**, respectively, to **23**–**28** in yields of 66–85%, however, the 3-halogeno derivatives **6**–**8** did not react under various modified reaction conditions. These findings are explained by the fact that the 2-NO_2 group is forced by the adjacent halogen-atoms to adapt a perpendicular conformation to the aromatic ring and thus can not activate the relevant H-atom of the Et group. The steric interference is also seen in the NMR spectra of **6**–**8** (MeCH_2 shifted up-field from δ 2.82–2.90 to 2.60). Analogously, 1-ethyl-2,3-dinitrobenzene (**18**) did not undergo the aldol-addition reaction. Problems were also encountered with the 6-iodo-substituted 1-ethyl-2-nitrobenzene **16**, which did not react with paraformaldehyde and ^{t}BuOK neither in DMSO nor in DMF. Other bases like DBU (1,8-

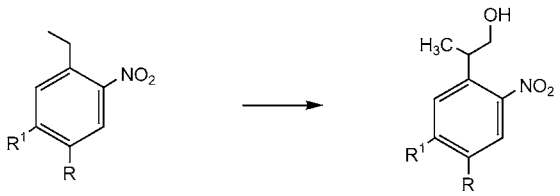
diazabicyclo[5.4.0]undec-7-ene) or NaH also showed no addition reaction, and the use of NaOMe in DMSO caused a drastic structural change in the molecule leading to 1-(2-nitrophenyl)ethanol (**29**) in 28% isolated yield. Analogous reactions with 6-bromo-substituted 1-ethyl-2-nitrobenzene **15** again were not successful. However, the treatment of **15** with paraformaldehyde in DMSO in presence of NaCN at room temperature led in very low yield of 6% to the anticipated 2-(2-bromo-6-nitrophenyl)propan-1-ol (**30**) besides the isolation of 77% of educt. The same reaction conditions were applied to **16**, which gave finally 5% of isolated 2-(6-iodo-2-nitrophenyl)-propan-1-ol (**31**). For the synthesis of the 2-(2,4-dinitrophenyl)propan-1-ol (**32**), a 1:1 mixture **13**/**22** was treated under the normal reaction conditions for 2 h at 80° leading to a mixture of 1-ethyl-2,6-dinitrobenzene (**13**), 34% of 2-(2,4-dinitrophenyl)propan-1-ol (**32**), and 5% of 2-(2,6-dinitrophenyl)propan-1-ol (**33**). If pure **13** was applied, the reaction was very slow, and even heating for 3 days was not satisfactory. Exchange of DMSO against DMF, however, made a big difference since 28% of **33** besides 70% of educt was isolated after 3 h heating to 90°. The same conditions were successful with **19**, which gave in DMF 25% of 2-(2,5-dinitrophenyl)propan-1-ol (**34**).

Since the photocleavage reactions are based on a n-π^* transition of low extinction, efforts were undertaken to extend the aromatic π-system by new conjugated substituents in 4- and 5-position. First, 4- and 5-amino-substituted 1-ethyl-2-nitrobenzenes **1** and **9** were phenylated under the conditions of the *Gomberg–Bachmann* reaction [51] to 4-ethyl-3-nitro- and 3-ethyl-4-nitro-1,1′-biphenyls **35** and **36**, respectively (*Scheme 1*). A more universal approach was the *Suzuki* coupling, which gave with 5-bromo-substituted 1-ethyl-2-nitrobenzene **11** and phenyl-, (4-methoxyphenyl)-, (3,4-dimethoxyphenyl)-, (4-phenoxyphenyl)-, (thianthren-1-yl)-, (1-naphthyl)-, (2-naphthyl)-, (2-thienyl)-, and (3-thienyl)boronic acid good yields of **36**–**44**. The 5-vinyl derivative **45** resulted from a *Stille* coupling [52] with tributyl(vinyl)stannane, bis(dibenzylideneacetone)palladium(0), and triphenylphosphine in 83% yield. Furthermore, 4-ethyl-3-nitrobenzoic acid (**46**) was esterified to the methyl and *tert*-butyl benzoates **47** and **48**. Furthermore, **46** was transformed into its acid chloride, which was subsequently treated with diphenylamine, diisopropylamine, and *N*-methylaniline to give the corresponding amides **50**–**52** and esterification of **46** with thiophenol gave **49**. Starting from 4- and 5-amino-substituted 1-ethyl-2-nitrobenzenes **1** and **9**, the *Sandmeyer* reaction with CuCN led to 4- and 5-cyano-substituted 1-ethyl-2-nitrobenzenes **53** and **54**. Hydrolysis of **54** to 3-ethyl-4-nitro-benzoic acid (**55**) and subsequent esterification with dicyclohexylcarbodiimide (DCC) in ^{t}BuOH under 4-pyrrolidinopyridine catalysis [53] afforded the *tert*-butyl ester **56** in good yield.

The hydroxymethylation reactions of **35**–**45**, **47**–**54**, and **56** proceeded well, except for **45** and **54**, applying paraformaldehyde in DMSO and in presence of ^{t}BuOK to give the corresponding 4- and 5-substituted 2-(2-nitrophenyl)propan-1-ols **57**–**76** (*Scheme 1*).

The next series of compounds are dealing with modifications in the side chain of 2-(2-nitrophenyl)ethanol. The synthetic approach started from 1-(2-nitrophenyl)propan-2-one (**77**) [54] and 2-(2-nitrophenyl)-1-phenylethanone (**78**) [55], which were alkylated in the exocyclic 1-position with MeI, EtI, or allyl bromide to form in good yields the corresponding ketones **79**–**84** (*Scheme 2*). $NaBH_4$ reduction of **77**–**84** led to the exocyclic 1-monosubstituted and 1,2-disubstituted 2-(2-nitrophenyl)ethanols

Scheme 1



	R	R^1
35	Ph	H
36	H	Ph
37	H	4-$MeOC_6H_4$
38	H	3,4-$(MeO)_2C_6H_3$
39	H	4-$PhOC_6H_4$
40	H	thianthren-1-yl
41	H	1-naphthyl
42	H	2-naphthyl
43	H	2-thienyl
44	H	3-thienyl
45	H	vinyl
46	COOH	H
47	COOMe	H
48	COO^{t}Bu	H
49	COSPh	H
50	$CONPh_2$	H
51	$CONⁱPr_2$	H
52	CO(Me)Ph	H
53	CN	H
54	H	CN
55	H	COOH
56	H	COO^{t}Bu

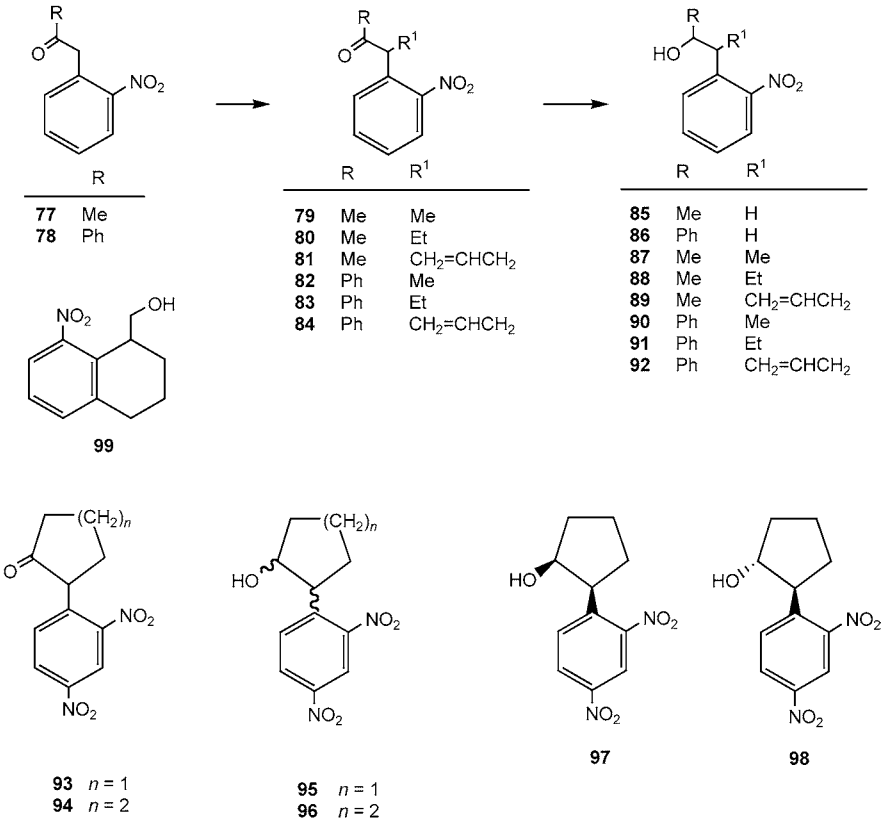
	R	R^1
57	Ph	H
58	H	Ph
59	H	4-$MeOC_6H_4$
60	H	3,4-$(MeO)_2C_6H_3$
61	H	4-$PhOC_6H_4$
62	H	thianthren-1-yl
63	H	1-naphthyl
64	H	2-naphthyl
65	H	2-thienyl
66	H	3-thienyl
67	H	vinyl
68	COOMe	H
69	COO^{t}Bu	H
70	COSPh	H
71	$CONPh_2$	H
72	$CONⁱPr_2$	H
73	CO(Me)Ph	H
74	CN	H
75	H	CN
76	H	COO^{t}Bu

85–**92**, which allowed studies regarding the influence of side-chain substituents on the photocleavage reaction.

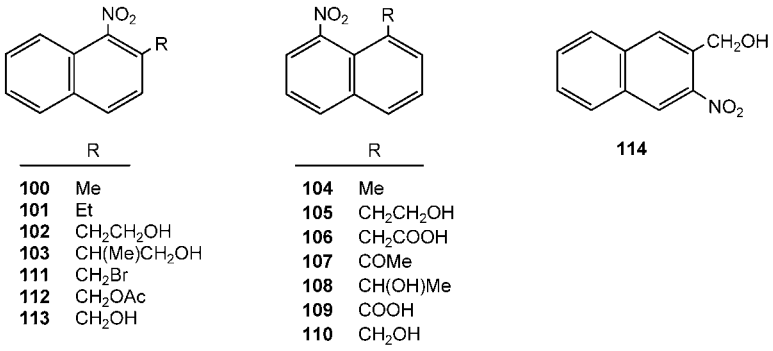
A formal exocyclic 1,2-disubstitution is also present in 4-(2-hydroxypentyl)- and 4-(2-hydroxyhexyl)-substituted 1,3-dinitrobenzenes **95** and **96**, which resulted from 2-(2,4-dinitrophenyl)cyclopentanone (**93**) [56] and 2-(2,4-dinitrophenyl)cyclohexanone (**94**) [56] by $NaBH_4$ reduction in form of diastereoisomer (*Scheme 2*) mixtures. In the case of **95**, separation into the *cis*- and *trans*-racemates **97** and **98** could be achieved by chromatography. Another formal exocyclic 1-substitution is also obvious in (1,2,3,4-tetrahydro-8-nitro-1-naphthyl)methanol (**99**), synthesized according to [57].

The substitution of the benzene ring by the naphthalene skeleton was the next challenge to synthesize new photolabile protecting groups. It was realized that the chemistry involved was much more difficult and, therefore, only a few *o*-nitronaphthyl alcohols were prepared. The synthesis of 2-(1-nitro-2-naphthyl)ethanol (**102**) and 2-(1-nitro-2-naphthyl)propan-1-ol (**103**) was achieved from 2-methyl- and 2-ethyl-1-nitronaphthalene (**100** and **101**, respectively) by the aldol-addition reaction with paraformaldehyde; however, the same reaction with 1-methyl-8-nitronaphthalene (**104**) to 2-(8-nitro-1-naphthyl)ethanol (**105**) was unsuccessful. Diborane reduction of (8-nitro-1-naphthyl)acetic acid (**106**) [58] on the other hand led to **105**. The isomeric 1-(8-nitro-1-naphthyl)ethanol (**108**) resulted from the reduction of 8-nitro-1-acetonaphthone (**107**) [59], and (8-nitro-1-naphthyl)methanol (**110**) [60] was synthesized from

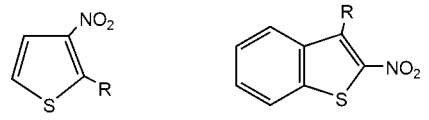
Scheme 2



8-nitro-naphthalene-1-carboxylic acid (**109**) by treatment with diborane. The (1-nitro-2-naphthyl)methanol (**113**) was prepared from 2-methyl-1-nitronapthalene (**100**) by monobromination to the 2-(bromomethyl) derivative **111**, followed by substitution with AcOK to give the 2-[(acetyloxy)methyl] compound **112** and subsequent hydrolysis. The (3-nitro-2-naphthyl)methanol (**114**) was obtained according to [61].



Finally, a few *o*-nitroheteroaryl alcohols based on the electronically similar thiophene ring were added as a potential photoactive alternative group. The (3-nitro-2-thienyl)methanol (**115**) was obtained in low yield according to [62]. The 2-ethyl-3-nitrothiophene (**116**) [63] was the starting material for the synthesis of 1-(3-nitro-2-thienyl)ethanol (**117**) [63], and the homologous 2-(3-nitro-2-thienyl)propan-1-ol (**118**) [63] resulted from the aldol addition of paraformaldehyde with ^{t}BuOK in DMSO. Similarly, 2-methyl-3-nitrothiophene (**119**) [64] reacted to 2-(3-nitro-2-thienyl)ethanol (**120**). In the benzothiophene series, only the 2-(2-nitrobenzo[*b*]-thien-3-yl)ethanol (**121**) was synthesized from 3-methyl-2-nitrobenzo[*b*]thiophene (**122**) [65] by reaction with paraformaldehyde since it turned out that **121** is photostable.



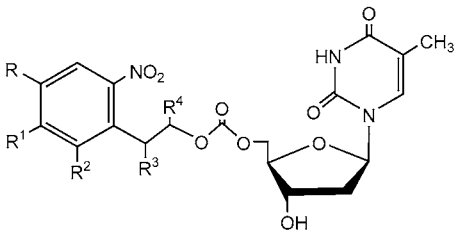
	R
115	CH_2OH
116	Et
117	CH(OH)Me
118	$CH(Me)CH_2OH$
119	Me
120	CH_2CH_2OH

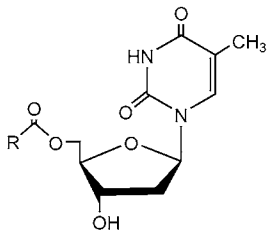
	R
121	CH_2CH_2OH
122	Me

3. Photoreactions. – To study the photoreactivity of the newly synthesized *o*-nitrophenyl-, *o*-nitronaphthyl, and *o*-nitroheteroaryl alcohols as versatile photolabile protecting groups in nucleoside and nucleotide chemistry, all the correspondingly esterified thymidine 5′-carbonates were synthesized by reacting the alcohol with phosgene or diphosgene to give the carbonochloridates, which were then further coupled to thymidine. The reactions took place preferentially at the 5′-OH group giving the thymidine 5′-monocarbonates **123**–**178** as the main reaction products.

As by-products also the 3′-monocarbonates, *e.g.*, **179**, and the 3′,5′-dicarbonates, *e.g.*, **180**, were formed in small amounts and could be isolated by column chromatography. In several cases, these by-products **179**–**203** were purified and characterized. To study the universal application of the NPPOC group in nucleic acid chemistry, N^4-benzoyl-2′-deoxycytidine, 2′-deoxy-N^4-isobutyrylcytidine, 2′-deoxy-N^6-(phenoxyacetyl)adenosine, and 2′-deoxy-N^2-(phenoxyacetyl)guanosine were coupled with 2-(2-nitrophenyl)propyl carbonochloridate to the corresponding 5′-carbonates **213**–**216**.

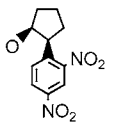
To compare the photolability of the various thymidine derivatives, we developed standardized conditions for the photolysis experiments. The thymidine 5′-(protected-carbonates) (100 μmol) were dissolved in MeOH/H_2O 1:1. An aliquot (25 μl) of the sample was analyzed by HPLC (*RP-18* column *Lichrosorb* (*Merck*), linear gradient MeCN/H_2O, monitoring at 260 nm). The solution (3 ml) was transferred to a 1-cm pathlength stoppered quartz cuvette and irradiated with a 200-W Hg arc lamp by using the 365-nm band, which was separated by filter systems according to the schematic apparatus shown in *Fig. 1*. The light is emitted from the light source (LQ) passing first



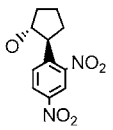


	R	R^1	R^2	R^3	R^4
123	H	H	H	Me	H
124	Cl	H	H	Me	H
125	Br	H	H	Me	H
126	I	H	H	Me	H
127	H	Cl	H	Me	H
128	H	Br	H	Me	H
129	H	I	H	Me	H
130	H	H	Br	Me	H
131	H	H	I	Me	H
132	NO_2	H	H	Me	H
133	H	H	NO_2	Me	H
134	H	NO_2	H	Me	H
135	Ph	H	H	Me	H
136	H	Ph	H	Me	H
137	H	4-$MeOC_6H_4$	H	Me	H
138	H	3,4-$(MeO)_2C_6H_3$	H	Me	H
139	H	4-$PhOC_6H_4$	H	Me	H
140	H	thianthren-1-yl	H	Me	H
141	H	1-naphthyl	H	Me	H
142	H	2-naphthyl	H	Me	H
143	H	2-thienyl	H	Me	H
144	H	3-thienyl	H	Me	H
145	H	vinyl	H	Me	H
146	COOMe	H	H	Me	H
147	COO^tBu	H	H	Me	H
148	COSPh	H	H	Me	H
149	$CONPh_2$	H	H	Me	H
150	$CONⁱPr_2$	H	H	Me	H
151	CON(Me)Ph	H	H	Me	H
152	CN	H	H	Me	H
153	H	CN	H	Me	H
154	H	COO^tBu	H	Me	H
155	H	H	H	H	Me
156	H	H	H	H	Ph
157	H	H	H	Me	Me
158	H	H	H	Et	Me
159	H	H	H	CH_2=$CHCH_2$	Me
160	H	H	H	Me	Ph
161	H	H	H	Et	Ph
162	H	H	H	CH_2=$CHCH_2$	Ph

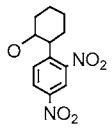
R



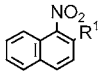
163



164

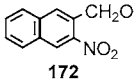


165

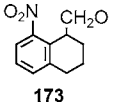


	R^1
166	CH_2CH_2O
167	$CH(Me)CH_2O$
168	CH_2O

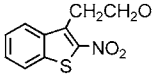
	R^1
169	CH_2CH_2O
170	MeCHO
171	CH_2O



172



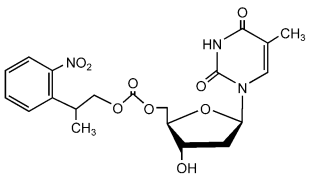
173



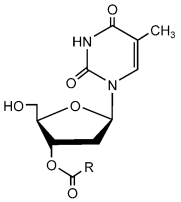
178

	R^1
174	CH_2O
175	MeCHO
176	$CH(Me)CH_2O$
177	CH_2CH_2O

an infrared filter (IF, H_2O) followed by the electronic shutter (S), going through a condensing lens (CL) and a broad band filter (BF; *UGI* from *Schott*) to avoid overheating of the UV filter (UV-F; *DAD-8-1* from *Schott*), before reaching the

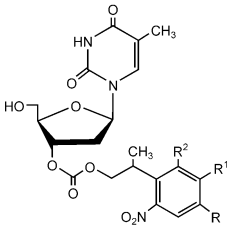


123

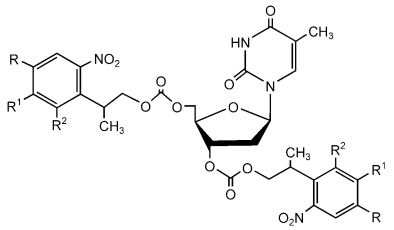


	R
206	$R^1 = CH_2CH_2O$
207	$R^1 = CH_2O$

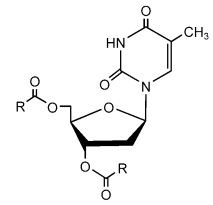
	R
210	$R^1 = CH(Me)CH_2O$
212	$R^1 = CH_2CH_2O$



	R	R^1	R^2
179	H	H	H
181	Br	H	H
183	H	Cl	H
185	H	Br	H
187	H	I	H
189	NO_2	H	H
191	H	H	NO_2
193	Ph	H	H
194	H	Ph	H
196	H	1-naphthyl	H
198	H	2-naphthyl	H
199	H	2-thienyl	H
201	H	3-thienyl	H
203	H	vinyl	H
204	COOMe	H	H
205	CN	H	H



	R	R^1	R^2
180	H	H	H
182	Br	H	H
184	H	Cl	H
186	H	Br	H
188	H	I	H
190	NO_2	H	H
192	H	H	NO_2
195	H	Ph	H
197	H	1-naphthyl	H
200	H	2-thienyl	H
202	H	3-thienyl	H

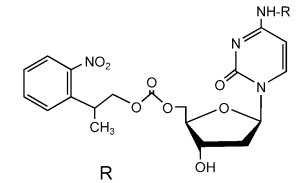


R

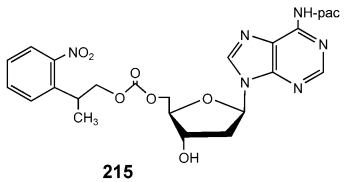
208

209

211

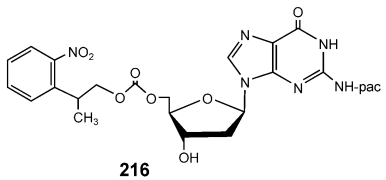


	R
213	PhCO
214	Me_2CHCO



215

pac = $PhOCH_2CO$



216

pac = $PhOCH_2CO$

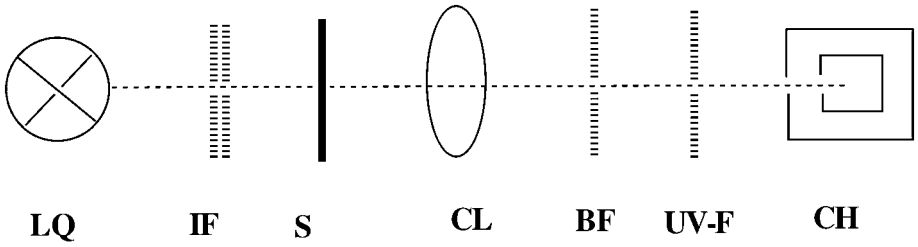


Fig. 1. *Schematic drawing of the photolysis apparatus*

cuvette in the cuvette holder (CH). Six cuvettes per experiment were used, each of which was irradiated in different time intervals and followed by HPLC-analysis for decreasing educt concentration and increasing thymidine formation.

Since there is no simple mathematical function describing the experimentally determined photolytic degradation of the thymidine 5′-(protected carbonates), the half-life was calculated from the slope of the section including the 50% concentration of the educt. A typical picture of this evaluation is seen in *Fig. 2* for **129**. The half-lifes of the photolabile protection groups determined under the described standard reaction conditions are listed in the *Table*.

The evaluation of the *Table* reveals several interesting effects of which a short half-life ($t_{1/2}$), a high thymidine concentration after cleavage ($c(\text{Thd})_{\text{end}}$), and an optimal disappearance of the educt ($c(\text{educt})_{\text{end}}$) are the ruling factors. In many cases, the photolysis of the educt was a very clean reaction leading to only thymidine without formation of other by-products. Analysis by HPLC (*Fig. 3*), however, indicates that also small amounts of the 2-nitroso derivatives such as **219** derived from the second possible degradation mode **129** → **217** → **218** → **219** (*Scheme 3*) were formed explaining the difference between the complete disappearance of the thymidine 5′-(protected carbonate) and the detection of thymidine concentrations $< 100\%$.

Starting the discussion with thymidine 5′-[2-(2-nitrophenyl)propyl carbonate] (**123**), it is noticed that the presence of a halogeno substituent at the 5-position of the phenyl group (see **127**–**129**), is associated with a fast cleavage rate and a high recovery of thymidine. These results can be attributed to a heavy-atom effect, which facilitates the intersystem-crossing mode. The best series of compounds so far are found among **135**–**145** where the π-system of the parent 2-(2-nitrophenyl) moiety is elongated in view of a biphenyl interaction. Thus, thymidine 5′-[2-(4-nitro[1,1′-biphenyl]-3-yl)propyl carbonate] (**136**) (NBPPOC-T) offers the highest quality with respect to the cleavage rate and purity of the photolysis products. Other functions like ester or cyano groups (see **146**–**154**) are also interesting since thymidine recovery is almost quantitative. Additional substitutions in the propyl side chain (see **155**–**165** and **173**) led to no improvement of the anticipated properties, and the exchange of the phenyl against the naphthyl or thienyl moiety as in **166**–**172** and **174**–**178**, respectively, can not be recommended at all.

It is noteworthy to mention that the nucleobase has, as expected, no direct influence on the rate of the photolysis, which is very similar for the corresponding thymidine **123**, 2′-deoxycytidines **213** and **214**, 2′-deoxyadenosine **215**, and 2′-deoxyguanosine **216**

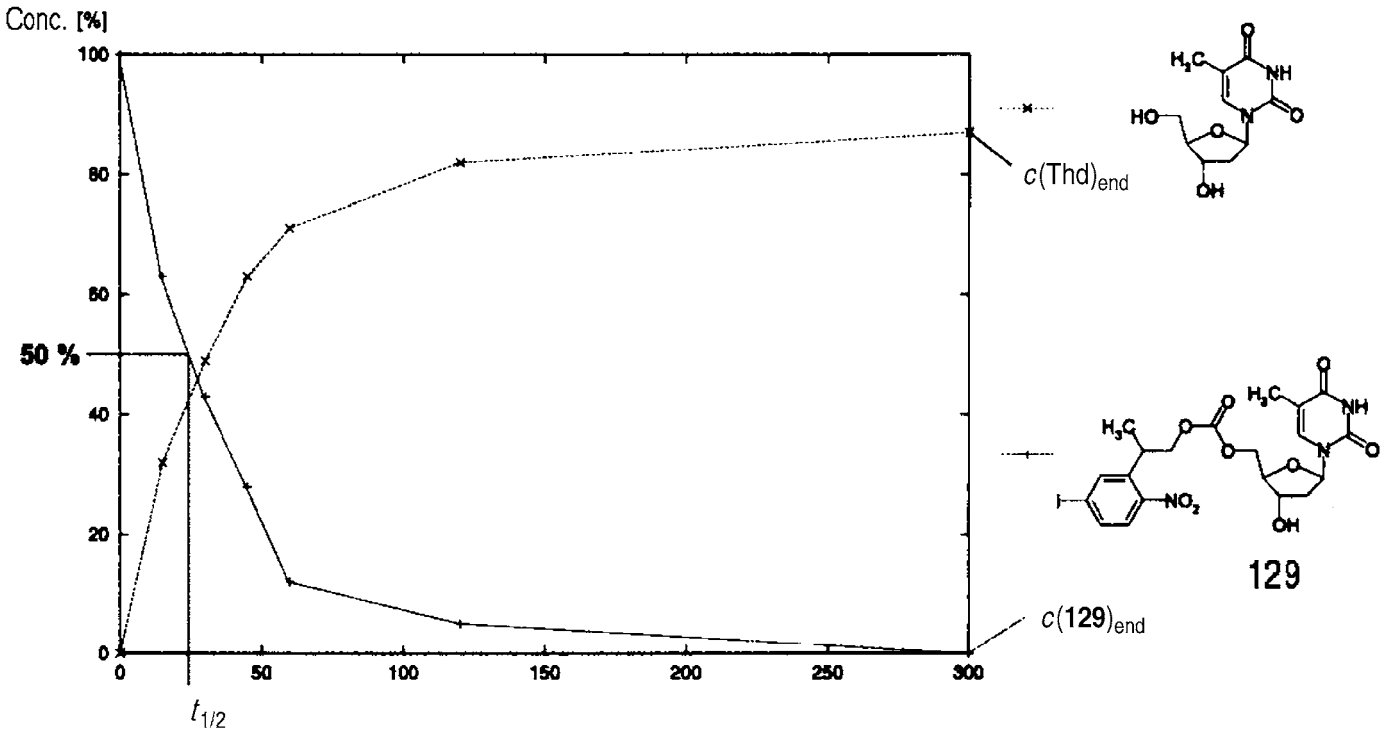


Fig. 2. *Time-dependent photolysis of* **129** *under standard cleavage conditions*

Table. *Photolysis of Thymidine 5′-Protected Carbonates*

	$t_{1/2}$ [s]	t_{end} [min]	$c(\text{Thd})_{end}$	$c(\text{educt})_{end}$		$t_{1/2}$ [s]	t_{end} [min]	$c(\text{Thd})_{end}$	$c(\text{educt})_{end}$
123	48	10	88	0	**152**	90	10	90	4
124	62	10	82	0	**153**	60	5	90	1
125	60	10	85	0	**154**	56	10	90	2
126	53	10	80	0	**155**	720	30	76	18
127	38	5	95	0	**156**	780	25	50	28
128	32	5	95	1	**157**	52	10	86	0
129	25	5	85	0	**158**	57	10	80	3
130	90	15	980	0	**159**	70	10	80	12
131	150	15	85	0	**160**	59	10	90	0
132	85	10	90	4	**161**	65	10	75	0
133	78	10	90	1	**162**	74	10	90	0
134	44	10	75	0	**163**	62	10	90	0
135	30	10	90	1	**164**	60	10	90	0
136	11	5	90	0	**165**	65	10	90	0
137	23	5	90	1	**166**	840	14	20	65
138	20	5	75	0	**167**	515	9	40	43
139	16	5	98	0	**168**	240	15	5	55
140	25	5	85	0	**169**	60	10	28	2
141	32	5	85	1	**170**	35	5	85	0
142	23	5	90	1	**171**	2	8	85	0
143	22	5	90	0	**172**	160	10	10	0
144	25	5	95	0	**173**	50	10	60	0
145	33	5	80	2	**174**	78	10	70	0
146	77	10	97	3	**175**	66	10	65	0
147	75	10	98	1	**176**	77	10	20	0
148	50	10	90	0	**177**	86	10	15	0
149	39	10	85	0	**178**	–	10	0	100
150	54	10	85	0	**213**	76	10	94	3
151	51	10	90	0	**214**	56	15	88	0
					215	52	15	77	0
					216	52	15	76	1

showing that these nucleic acid building blocks could be applied with the same efficencies as their phosphoramidites in photolithographic processes.

Experimental Part

General. Products were dried under high vacuum. Irradiation equipment: Hg-high-pressure lamp (200 W) and IR-filter (*Oriel*); electronic shutter (*Prontor*); broad-band filter *UG1* and interference filter *UV-DAD-8-1* (*Schott*). Melting point: *Büchi B545*. TLC: precoated silica gel thin-layer sheets *60* F_{254} (*Merck*). Column chromatography (CC): silica gel (*Baker*; 30–60 μm). Reversed-phase HPLC: *L-6000* pump and *AS-4000* autosampler (*Merck-Hitachi*); UV-detector *Uvikon 730 SLC* (*Kontron*); *RP-18* column, *LiChrosorb* 125 × 4 mm, 5 μm (*Merck*); gradient MeCN/H_2O, flow rate 1 ml/min. UV/VIS: *Perkin-Elmer Lambda 5*; δ_{max} in nm (log ε). ^{1}H-NMR: *Bruker AC-250*; δ in ppm rel. to $SiMe_4$ or $CDCl_3$ ((D_6)DMSO) as internal standard. ^{31}P-NMR: *Bruker DRX-600*; δ in ppm rel. to H_3PO_4.

1. *3-Ethyl-2-nitrobenzenamine* (**5**) [44]. $SnCl_2 \cdot 2\,H_2O$ (52 g, 0.23 mol) in sat. HCl/MeOH (65 ml) was added dropwise with stirring and cooling to a suspension of 1-ethyl-2,3-dinitrobenzene (**17**) (13.6 g, 69 mmol) in sat. HCl/MeOH (110 ml) whereby the temp. was kept below 8°. After stirring overnight at 8°, the mixture was

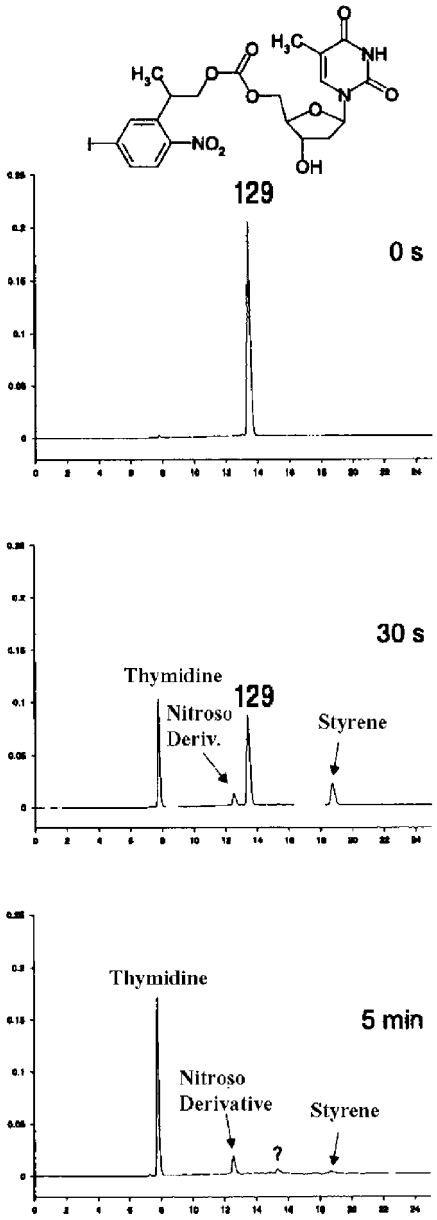
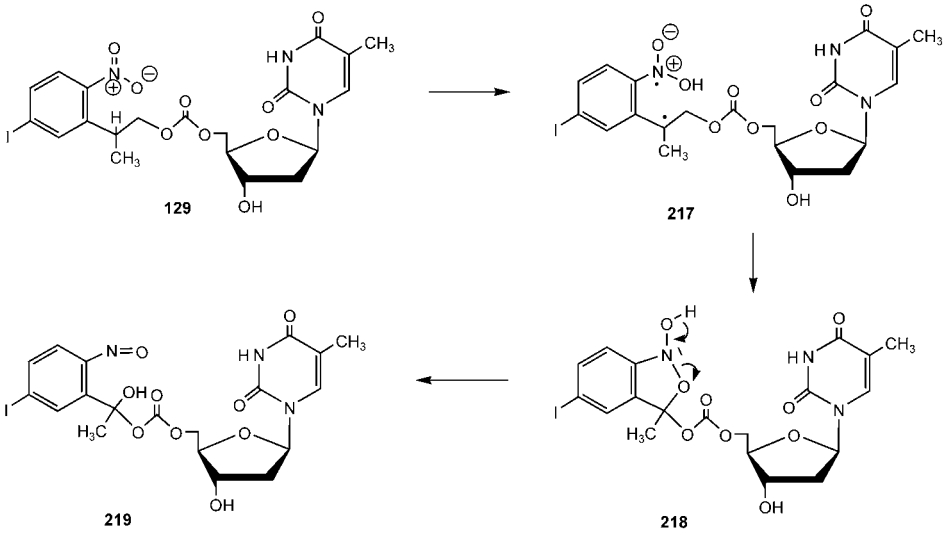


Fig. 3. *Time-dependent photocleavage of* **129** *followed by HPLC*

evaporated. H_2O (50 ml) was added, the mixture neutralized with 4N NaOH and extracted with Et_2O, the Et_2O phase dried (Na_2SO_4) and evaporated, and the residue distilled *in vacuo* at 89–102°/0.2 mbar ([44]: b.p. 120–130°/4 mbar). The crude product was purified by CC (SiO_2 (160 g), 6 × 16 cm; hexanes/AcOEt 15:1 → 1:2): 8.62 g (75%) of **5**. Orange solid. M.p. 31–32° ([44] 32–33°). TLC (hexanes/AcOEt 4:1): R_f 0.41. UV (MeOH): 203 (4.28), 235 (4.09), 255 (sh, 3.54), 277 (sh, 3.36), 402 (3.35). ^{1}H-NMR ((D$_6$)DMSO): 7.15 (*t*,

Scheme 3



H–C(5)); 6.76 (*d*, H–C(6)); 6.50 (*d*, H–C(4)); 6.05 (br., NH_2); 2.58 (*q*, MeCH_2); 1.15 (*t*, *Me*CH_2). ^{13}C-NMR (600 MHz, (D_6)DMSO): 142.77 (C(1)); 138.12 (C(3)); 135.68 (C(2)); 132.24 (C(5)); 116.75 (C(4)); 115.63 (C(6)); 25.37 (CH_2); 14.96 (Me).

2. *3-Chloro-1-ethyl-2-nitrobenzene* (**6**). Finely powdered **5** (2.7 g, 16 mmol) was added to conc. HCl soln. (20 ml) and H_2O (40 ml) at 60°, the soln. rapidly cooled to 0°, and the resulting suspension diazotized at 0–5° with $NaNO_2$ (1.24 g, 18 mmol) in H_2O (15 ml). After stirring for 5 min at 0°, the soln. was treated with urea and stirred for another 10 min. The mixture was then added under stirring to a 80°-warm suspension of CuCl (2.4 g, 24 mmol) in conc. HCl soln. (16 ml) and H_2O (8 ml). After 30 min, the mixture was cooled to r.t. and extracted with AcOEt. The org. phase was washed with 4N NaOH (50 ml), dried (Na_2SO_4), and evaporated. Purification by CC (SiO_2 (68 g), 4 × 16 cm; hexanes) gave 1.09 g (37%) of **6**. Yellow oil. TLC (hexanes/AcOEt 4 : 1): R_f 0.59. UV (MeOH): 202 (4.11), 208 (sh, 4.10), 238 (sh, 3.08), 342 (sh, 2.38). ^{1}H-NMR ($CDCl_3$): 7.34 (*m*, 2 arom. H); 7.24 (*m*, 1 arom. H); 2.60 (*q*, MeCH_2); 1.23 (*t*, *Me*CH_2). Anal. calc. for $C_8H_8ClNO_2$ (185.6): C 51.77, H 4.34, N 7.55; found: C 51.00, H 4.17, N 7.43.

3. *1-Bromo-3-ethyl-2-nitrobenzene* (**7**) [44]. Finely powdered **5** (2 g, 12 mmol) was added to 48% HBr soln. (15 ml) and H_2O (9 ml) at 60°, the soln. rapidly cooled to 0°, and the resulting suspension diazotized at 5–10° with $NaNO_2$ (0.91 g, 13 mmol) in H_2O (10 ml). After stirring for 10 min at 0°, the soln. was treated with urea, the mixture stirred for another 5 min and filtered, and the filtrate added at r.t. to a stirred suspension of $CuSO_4 \cdot 5$ H_2O (1.8 g, 7 mmol) and Cu powder (0.72 g, 11 mmol) in 48% HBr soln. (15 ml) and H_2O (9 ml). The mixture was heated to 80° for 30 min and, after cooling, extracted with AcOEt. The org. phase was washed with 4N NaOH (150 ml) and H_2O, dried (Na_2SO_4), and evaporated. CC (SiO_2 (61 g), 4 × 15 cm; hexanes) gave 1.59 g (58%) of **7**. Yellow oil. TLC (hexanes/AcOEt 4 : 1): R_f 0.61. UV (MeOH): 203 (4.35), 212 (sh, 4.25), 269 (3.66), 337 (sh, 2.81). ^{1}H-NMR ($CDCl_3$): 7.48 (*t*, H–C(5)); 7.27 (*m*, H–C(4), H–C(6)); 2.60 (*q*, MeCH_2); 1.23 (*t*, *Me*CH_2).

4. *1-Ethyl-3-iodo-2-nitrobenzene* (**8**). Finely powdered **5** (2 g, 12 mmol) was added to conc. H_2SO_4 soln. (4.5 ml) and H_2O (30 ml) at 50°. The resulting soln. was rapidly cooled to 0° and then diazotized at 0–5° with $NaNO_2$ (0.91 g, 13 mmol) in H_2O (10 ml). After stirring for 10 min at 0°, the soln. was treated with urea, stirred for another 5 min, and then added to a stirred KI soln. (3 g, 18 mmol) in H_2O (20 ml). The mixture was stirred for 1 h at r.t. and, after cooling, extracted with AcOEt. The org. phase was washed with 4N NaOH (60 ml) and H_2O, dried (Na_2SO_4), and evaporated. CC (SiO_2 (62 g), 4 × 15 cm; hexanes) gave 2.48 g (74%) of **8**. Red oil. TLC (hexanes/AcOEt 4 : 1): R_f 0.60. UV (MeOH): 203 (4.36), 228 (4.00), 336 (sh, 2.35). ^{1}H-NMR ($CDCl_3$): 7.70

(*d*, 1 arom. H); 7.28 (*d*, 1 arom. H); 7.11 (*t*, 1 arom. H); 2.60 (*q*, MeC*H*$_2$); 1.21 (*t*, *Me*CH$_2$). Anal. calc. for $C_8H_8INO_2$ (277.1): C 34.68, H 2.91, N 5.06; found: C 35.05, H 2.96, N 5.03.

5. *3-Ethyl-4-nitrobenzenamine* (**9**) [45]. Mechanical stirring is essential for this reaction! *N*-(3-Ethylphenyl)acetamide [45] (33 g, 0.2 mol) was added slowly to conc. H_2SO_4 (100 ml). The resulting soln. was cooled to $-15°$ and then fuming HNO_3 (9.5 g, 6.2 ml, 0.15 mol) added dropwise. The temp. was kept between $-20°$ and $-10°$ for 75 min. The soln. was poured on ice, neutralized with solid Na_2CO_3, and extracted with Et_2O (3 × 250 ml). The org. phase was washed with H_2O (600 ml), dried (Na_2SO_4), and evaporated. The crude dark yellow oil (39 g) was heated with conc. HCl soln. (125 ml) under reflux for 2.5 h. After cooling, the precipitate was filtered off, washed with H_2O, suspended in 1N NaOH (300 ml), and extracted with Et_2O (2 × 150 ml). The org. phase was dried (Na_2SO_4) and evaporated to give a brown solid (14.2 g). The combined filtrates and the NaOH phase were neutralized and again extracted with Et_2O. The org. phase yielded after drying (Na_2SO_4) and evaporation 16 g of a dark oil. The crude product was purified by CC (each fraction: SiO_2 (235 g), 7 × 14 cm; hexanes/AcOEt 20:1 → 2:1): 18.09 g (54%) of **9**. Yellow solid. M.p. 84–85° ([45]: 80–81°).TLC (hexanes/AcOEt 7:3): R_f 0.27. UV (MeOH): 203 (4.21), 231 (3.82), 245 (sh, 3.69), 372 (sh, 4.09). ^{1}H-NMR ($CDCl_3$): 7.96 (*m*, H–C(5)); 6.47 (*m*, H–C(2), H–C(4)); 4.23 (br., NH_2); 2.93 (*q*, MeC*H*$_2$); 1.24 (*t*, *Me*CH$_2$). ^{13}C-NMR ($CDCl_3$): 151.30 (C(1)); 143.25 (C(3)); 139.42 (C(4)); 128.35(C(5)); 115.35 (C(2)); 111.72 (C(6)); 27.48 (CH_2); 14.67 (Me).

6. *5-Chloro-1-ethyl-2-nitrobenzene* (**10**). Finely powdered **9** (10 g, 60 mmol) was added to conc. HCl soln. (90 ml) and H_2O (200 ml) at 60°. The resulting soln. was rapidly cooled to 0° and then diazotized at 0–3° with $NaNO_2$ (4.57 g, 66 mmol) in H_2O (20 ml). After stirring for 5 min at 0°, urea was added, the mixture stirred for another 10 min, and then the soln. added with stirring to a warmed (80°) suspension of CuCl (9.05 g) in conc. HCl soln. (60 ml) and H_2O (30 ml). After reaction for 2 h at 80°, the mixture was cooled and extracted with AcOEt. The org. phase was washed with 1N NaOH (100 ml) and H_2O (200 ml), dried (Na_2SO_4), and evaporated. CC (SiO_2 (120 g), 4 × 16 cm; hexanes) gave 7.2 g (64%) of **10**. Yellow oil. TLC (hexanes/AcOEt 4:1): R_f 0.77. UV (MeOH): 206 (4.09), 216 (sh, 3.91), 263 (3.79), 334 (sh, 2.84). ^{1}H-NMR ($CDCl_3$): 7.85 (*d*, H–C(3)); 7.34 (*d*, H–C(6)); 7.29 (*dd*, H–C(4)); 2.90 (*q*, MeC*H*$_2$); 1.27 (*t*, *Me*CH$_2$). Anal. calc. for $C_8H_8ClNO_2$ (185.6): C 51.77, H 4.34, N 7.55; found: C 51.65, H 4.34, N 7.63.

7. *5-Bromo-1-ethyl-2-nitrobenzene* (**11**). Finely powdered **9** (16.6 g, 0.1 mol) was added to 48% HBr soln. (95 ml) and H_2O (155 ml) at 60°. The resulting soln. was rapidly cooled to 0° and then diazotized at 0–3° with $NaNO_2$ (7.0 g, 0.1 mol) in H_2O (20 ml). After stirring for 5 min at 0°, the soln. was treated with urea (1 g), the mixture stirred for 10 min and filtered, and the filtrate added at r.t. to a stirred suspension of $CuSO_4 \cdot 5\ H_2O$ (15 g, 60 mmol) and Cu powder (6 g, 94 mmol) in HBr (63 ml) and H_2O (37 ml). The mixture was heated to 75° for 1 h and, after cooling, extracted with AcOEt. The org. phase was washed with 1N NaOH (150 ml) and H_2O (200 ml), dried (Na_2SO_4), and evaporated. 18.3 g (80%) of **11**. Yellow oil. B.p. 75–103°/0.005 bar. TLC (hexanes/AcOEt 4:1): R_f 0.76. UV (MeOH): 203 (4.19), 217 (sh, 3.98), 267 (3.91), 320 (sh, 3.21). ^{1}H-NMR ($CDCl_3$): 7.76 (*d*, H–C(3)); 7.50 (*d*, H–C(6)); 7.45 (*dd*, H–C(4)); 2.89 (*q*, MeC*H*$_2$); 1.27 (*t*, *Me*CH$_2$). Anal. calc. for $C_8H_8BrNO_2$ (230.1): C 41.77, H 3.50, N 6.09; found: C 41.71, H 3.59, N 6.08.

8. *1-Ethyl-5-iodo-2-nitrobenzene* (**12**). Finely powdered **9** (6.2 g, 37 mmol) was added to conc. H_2SO_4 soln. (11.2 ml) and H_2O (125 ml) at 60°. The resulting soln. was rapidly cooled to 0° and then diazotized at 0–3° with $NaNO_2$ (2.84 g, 41 mmol) in H_2O (15 ml). After stirring for 5 min at 0°, the soln. was treated with urea and the mixture stirred for 10 min and then added to a stirred soln. of KI (9.34 g) in H_2O (35 ml). The mixture was stirred for 2 h at r.t. and, after cooling, extracted with AcOEt. The org. phase was washed with 1N NaOH (100 ml) and H_2O (200 ml), dried (Na_2SO_4), and evaporated. Purification by CC (SiO_2 (120 g), 4 × 16 cm; hexanes) gave 8.7 g (84%) of **12**. Red oil. TLC (hexanes/AcOEt 4:1): R_f 0.78. UV (MeOH): 203 (4.22), 220 (sh, 3.88), 281 (3.87), 328 (sh, 3.22). ^{1}H-NMR ($CDCl_3$): 7.72 (*d*, H–C(6)); 7.66 (*dd*, H–C(4)); 7.58 (*d*, H–C(3)); 2.85 (*q*, MeC*H*$_2$); 1.25 (*t*, *Me*CH$_2$). Anal. calc. for $C_8H_8INO_2$ (277.1): C 34.68, H 2.91, N 5.06; found: C 34.84, H 2.92, N 4.90.

9. *2-Ethyl-1,3-dinitrobenzene* (**13**) [46]. $NaNO_2$ (1.38 g, 20 mmol) in H_2O (10 ml) was added dropwise to a suspension of 4-ethyl-3,5-dinitrobenzenamine (**21**; 3 g, 14 mmol) in AcOH (50 ml) and conc. H_2SO_4 soln. (8 ml) at 20–25°. The mixture was stirred for 1 h in an ice bath and then added to a suspension of Cu_2O (4 g, 28 mmol) in EtOH (35 ml). After stirring for 90 min at r.t., the mixture was filtered with suction, the filtrate evaporated, the residue treated with sat. $NaHCO_3$ soln. (100 ml) and then extracted with AcOEt (3 × 50 ml), the org. phase washed with sat. $NaHCO_3$ soln. (100 ml), dried (Na_2SO_4), and evaporated, and the crude product purified by CC (SiO_2 (80 g), 3.5 × 17 cm; hexanes/AcOEt 8:1): 2.08 g (76%) of **13**. Yellow solid. M.p. 56–58° ([46]: 57.5°). TLC (hexanes/AcOEt 7:3): R_f 0.63. UV (MeOH): 203 (4.16), 231 (sh, 3.95), 280 (sh, 3.20), 324 (sh, 3.14). ^{1}H-NMR ($CDCl_3$): 7.93 (*d*, H–C(4), H–C(6)); 7.50 (*t*, H–C(5)); 2.92 (*q*, MeC*H*$_2$); 1.32 (*t*, *Me*CH$_2$).

10. *2-Ethyl-3-nitrobenzenamine* (**14**) [47]. Formic acid (1.95 g, 42 mmol) in MeCN (5 ml) was added dropwise into a mixture of **13** (2.2 g, 11 mmol), Pd/C (0.11 g), and Et_3N (6 ml, 43 mmol) in MeCN (5 ml). The mixture was refluxed for 25 min and then cooled, the catalyst removed by filtration, the filtrate evaporated, and the crude product purified by CC (SiO_2 (42 g), 3.5 × 13 cm; hexanes/AcOEt 8:1 → 1:1): 1.21 g (81%) of **14**. Yellow solid. M.p. 84–86° ([47]: 85–85.5°). TLC (hexanes/AcOEt 7:3): R_f 0.40. UV (MeOH): 203 (4.22), 237 (4.13), 269 (sh, 3.49), 347 (3.12). ^{1}H-NMR ($CDCl_3$): 7.09 (*m*, 2 arom. H); 6.83 (*dd*, 1 arom. H); 3.91 (br., NH_2); 2.60 (*q*, MeCH_2); 1.27 (*t*, *Me*CH_2).

11. *1-Bromo-2-ethyl-3-nitrobenzene* (**15**) [66]. Finely powdered **14** (2.28 g, 14 mmol) was added to 48% HBr soln. (70 ml) and H_2O (42 ml), at 90° and the soln. was rapidly cooled to 0° and then diazotized at 5–10° with $NaNO_2$ (1.06 g, 15 mmol) in H_2O (20 ml). After stirring for 10 min at 0°, the soln. was treated with urea, the mixture stirred for another 5 min and filtered, and the filtrate added at r.t. to a stirred suspension of $CuSO_4 \cdot 5\ H_2O$ (2.04 g, 8 mmol) and Cu powder (0.84 g, 13 mmol) in 48% HBr soln. (40 ml) and H_2O (24 ml). The mixture was heated to 80° for 1 h and, after cooling, extracted with AcOEt. The org. phase was washed with 4N NaOH (100 ml), dried (Na_2SO_4), and evaporated, and the residue purified by CC (SiO_2 (61 g), 4 × 15 cm; hexanes/AcOEt): 2.73 g (87%) of **15**. Yellow solid. M.p. 32–36° ([68]: 33–34°). TLC (hexanes/AcOEt 7:3): R_f 0.84. UV (MeOH): 205 (sh, 4.06), 211 (4.08), 219 (sh, 4.05), 249 (sh, 3.44), 287 (sh, 3.03). ^{1}H-NMR ($CDCl_3$): 7.76 (*dd*, 1 arom. H); 7.67 (*dd*, 1 arom. H); 7.18 (*t*, H–C(5)); 2.89 (*q*, MeCH_2); 1.29 (*t*, *Me*CH_2).

12. *2-Ethyl-1-iodo-3-nitrobenzene* (**16**). Finely powdered **14** (1.8 g, 11 mmol) was added to conc. H_2SO_4 soln. (4.5 ml) and H_2O (30 ml) at 50°, the resulting soln. rapidly cooled to 0°, and the resulting suspension diazotized at 0–5° with $NaNO_2$ (2.83 g, 12 mmol) in H_2O (10 ml). After stirring for 10 min at 0°, the soln. was treated with urea. The mixture was stirred for another 5 min, then added to a stirred soln. of KI (2.73 g, 16.5 mmol) in H_2O (20 ml), stirred 1 h at r.t., and, after cooling, extracted with AcOEt. The org. phase was washed with 4N NaOH (100 ml), dried (Na_2SO_4), and evaporated. Purification by CC (SiO_2 (36 g), 3.5 × 11 cm; hexanes) gave 2.62 g (86%) of **16**. Yellow solid. M.p. 42–43°. TLC (hexanes/AcOEt 4:1): R_f 0.72. UV (MeOH): 204 (4.16), 229 (4.12), 256 (sh, 3.50), 300 (sh, 2.99). ^{1}H-NMR ($CDCl_3$): 78.02 (*dd*, 1 arom. H); 7.66 (*dd*, 1 arom. H); 7.01 (*t*, H–C(5)); 2.89 (*q*, MeCH_2); 1.26 (*t*, *Me*CH_2). Anal. calc. for $C_8H_8INO_2$ (277.1): C 34.68, H 2.91, N 5.06; found: C 34.77, H 2.93, N 4.84.

13. *1-Ethyl-2,3-dinitrobenzene* (**17**) [46]. 4-Ethyl-2,3-dinitrobenzenamine (**18**; 23 g, 0.11 mol) was added dropwise into a soln. of $NaNO_2$ (8.65 g, 0.125 mol) in conc. H_2SO_4 soln. (70 ml). The temp. was kept below 30°. After stirring for 40 min at r.t., EtOH (350 ml) was added to the cooled mixture. After 1 h of reflux, the mixture was cooled to r.t., poured into conc. H_2SO_4 soln. (400 ml) and H_2O (200 ml) and then steam-distilled. The distillate was extracted with Et_2O and the org. phase neutralized with sat. $NaHCO_3$ soln., dried (Na_2SO_4), and evaporated: 11.2 g (52%) of **17**. Recrystallization from EtOH/H_2O 4:1 gave yellow needles. M.p. 57–58° ([46]: 58.5°). TLC (hexanes/AcOEt 4:1): R_f 0.28. UV (MeOH): 205 (4.17), 213 (sh, 4.05), 255 (3.76), 287 (sh, 3.29), 333 (sh, 2.76). ^{1}H-NMR ($CDCl_3$): 8.02 (*dd*, 1 arom. H); 7.68 (*dd*, 1 arom. H); 7.59 (*t*, 1 arom. H); 2.68 (*q*, MeCH_2); 1.28 (*t*, *Me*CH_2).

14. *4-Ethyl-2,3-dinitrobenzenamine* (**18**) *and 4-Ethyl-2,5-dinitrobenzenamine* (**20**) [46]. *N*-(4-Ethyl-3-nitrophenyl)acetamide [46] (20.3 g, 0.1 mol) was added to a mixture of 65% HNO_3 soln. (80 ml) and conc. H_2SO_4 soln. (80 ml). After stirring for 3 days at r.t., the mixture was poured on ice. The precipitate was dissolved in CH_2Cl_2, H_2O (100 ml) was added, and the mixture was neutralized with solid Na_2CO_3. The org. layer was dried (Na_2SO_4) and evaporated. The crude product (20.6 g, 81%) was suspended in EtOH (200 ml) and heated with solid NaOH (2 g) under reflux. After 40 min, the mixture was cooled, silica gel (28 g) added, and the mixture evaporated. The resulting solid was put onto a silica-gel column and purified by CC (SiO_2 (140 g), 6 × 14 cm; hexanes/AcOEt 7:1 → 2:1): 1.75 g (8%) of **18** and 12.5 g (60%) of **20**.

Data of **18**: Red solid. M.p. 122–123° ([46]: 125°). TLC (hexanes/AcOEt 1:1): R_f 0.50. UV (MeOH): 202 (4.18), 227 (4.37), 265 (sh, 3.59), 411 (3.75). ^{1}H-NMR ($CDCl_3$): 7.26 (*d*, 1 arom. H); 6.90 (*d*, 1 arom. H); 6.03 (br., NH_2); 2.45 (*q*, MeCH_2); 1.18 (*t*, *Me*CH_2).

Data of **20**: Orange solid. M.p. 124–125° ([46]: 121.6°). TLC (hexanes/AcOEt 1:1): R_f 0.85. UV (MeOH): 226 (4.39), 243 (sh, 4.16), 266 (sh, 3.86), 422 (3.71). ^{1}H-NMR ($CDCl_3$): 8.11 (*s*, 1 arom. H); 7.27 (*s*, 1 arom. H); 6.07 (br., NH_2); 2.75 (*q*, MeCH_2); 1.24 (*t*, *Me*CH_2).

15. *2-Ethyl-1,4-dinitrobenzene* (**19**) [46]. A soln. of 4-ethyl-2,5-dinitrobenzenamine (**20**; 4 g, 19 mmol) in conc. H_2SO_4 soln. (50 ml) was diluted under cooling with H_2O (50 ml) and the resulting suspension diazotized at 0–10° with $NaNO_2$ (1.45 g, 18 mmol) in H_2O (15 ml). After stirring for 10 min at 0°, the soln. was added to boiling EtOH (100 ml). After 10 min of reflux, the mixture was cooled, poured on ice, and extracted with Et_2O (3 × 100 ml). The org. phase was washed with sat. $NaHCO_3$ soln. (200 ml), dried (Na_2SO_4), and evaporated. Purification by CC (SiO_2 (67 g), 4 × 12 cm; hexanes/AcOEt 8:1) gave 2.64 g (71%) of **19**. Orange solid: M.p.

57–60° ([46]: 57.4–59.9°). TLC (hexanes/AcOEt 4:1): R_f 0.60. UV (MeOH): 204 (4.26), 257 (4.02), 298 (sh, 3.37), 332 (sh, 3.06). ^{1}H-NMR ($CDCl_3$): 8.24 (*d*, H–C(3)); 8.16 (*dd*, H–C(5)); 7.95 (*d*, H–C(6)); 2.95 (*q*, MeCH_2); 1.34 (*t*, *Me*CH_2).

16. *4-Ethyl-3,5-dinitrobenzenamine* (**21**) [46][67]. Through a soln. of 2-ethyl-1,3,5-trinitrobenzene [68] (59 g, 0.24 mol) in dioxane (170 ml) and 2 drops of 20% ammonia, H_2S gas was passed. The exothermic reaction started on careful warming to 35° and addition of some more drops of ammonia. The temp. was kept at 35–40° by cooling, and when the exothermic reaction stopped, the mixture was cooled and filtered from sulfur, which was washed with little dioxane and Et_2O. The filtrate was neutralized by a few drops of conc. HCl soln. and then evaporated. The resulting oil was refluxed in the presence of conc. HCl soln. (750 ml) and KI (5 g) to transform possible hydroxylamine into the amino derivative. The mixture was filtered hot and the cooled filtrate neutralized with solid Na_2CO_3 and extracted with Et_2O (3 × 250 ml). The org. phase was dried (Na_2SO_4), and evaporated. Recrystallization from EtOH (700 ml) yielded 24.1 g (48%) of **21**. Yellow needles. M.p. 180–181° ([67]: 175°). TLC (hexanes/AcOEt 1:1): R_f 0.67. UV (MeOH): 202 (4.19), 243 (4.37), 369 (3.30). ^{1}H-NMR ($CDCl_3$): 7.24 (*s*, H–C(2), H–C(6)); 6.21 (br.), NH_2); 2.56 (*q*, MeCH_2); 1.22 (*t*, *Me*CH_2).

17. *1-Ethyl-2,4-dinitrobenzene* (**22**) [46]. As described in *Exper. 9*, with a 1:1 mixture of 4-ethyl-3,5-dinitrobenzenamine (**21**) and 2-ethyl-3,5-dinitrobenzenamine (1.9 g, 9 mmol) and $NaNO_2$ (0.69 g, 10 mmol). CC (SiO_2 (60 g), 4 × 14 cm; hexanes/AcOEt 9:1 → 4:1) gave 1.28 g (72%) of **13**/**22** 1:1. Yellow solid.

18. *2-(2-Nitrophenyl)propan-1-ol Derivatives: General Procedure.* 18.1. A mixture of the ethylbenzene derivative (5 mmol) and paraformaldehyde (5 mmol) in dry DMSO (10 ml) was treated with ^{t}BuOK (0.05–0.5 mmol) in ^{t}BuOH (3 ml). After stirring for 15 min at r.t. and 2 h at 80°, the mixture was neutralized, diluted with sat. NaCl soln. (25 ml), and extracted with AcOEt. The org. phase was dried (Na_2SO_4), filtered, and evaporated. The crude product was purified by CC (SiO_2 (45 g), 4 × 12 cm; toluene → toluene/AcOEt 8:1).

18.2. Analogously to *Exper. 18.1* by using DMF as the solvent and increasing the reaction time to 3 h at 90°.

19. *2-(4-Chloro-2-nitrophenyl)propan-1-ol* (**23**). According to *Exper. 18.1*, with 4-chloro-1-ethyl-2-nitrobenzene (**2**) [43] (3.56 g, 19 mmol), paraformaldehyde (575 mg, 19 mmol), DMSO (10 ml), ^{t}BuOK (360 mg, 3.2 mmol), and ^{t}BuOH (4 ml): 2.70 g (66%) of **23**. Yellow oil. TLC (hexanes/AcOEt 7:3): R_f 0.35. UV (MeOH): 214 (4.23), 248 (sh, 3.48), 293 (3.13). ^{1}H-NMR ($CDCl_3$): 7.73 (*d*, H–C(3)); 7.50 (*dd*, H–C(5)); 7.42 (*d*, H–C(6)); 3.72 (*m*, CH(Me)CH_2); 3.46 (*m*, C*H*(Me)CH_2); 1.82 (br., OH); 1.28 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_9H_{10}ClNO_3$ (215.6): C 50.13, H 4.67, N 6.50; found: C 50.24, H 4.68, N 6.28.

20. *2-(4-Bromo-2-nitrophenyl)propan-1-ol* (**24**). According to *Exper. 18.1*, with 4-bromo-1-ethyl-2-nitrobenzene (**3**) [43] (2.11 g, 9 mmol), paraformaldehyde (275 mg, 9 mmol), DMSO (10 ml), ^{t}BuOK (57 mg, 0.5 mmol), and ^{t}BuOH (4 ml): 1.62 g (69%) of **24**. Yellow oil. TLC (hexanes/AcOEt 7:3): R_f 0.38. UV (MeOH): 204 (sh, 4.16), 216 (4.25), 251 (sh, 3.51), 288 (sh, 3.13). ^{1}H-NMR ($CDCl_3$): 7.87 (*d*, H–C(3)); 7.66 (*dd*, H–C(5)); 7.36 (*d*, H–C(6)); 3.74 (*m*, CH(Me)CH_2); 3.45 (*m*, C*H*(Me)CH_2); 1.66 (br., OH); 1.29 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_9H_{10}BrNO_3$ (260.1): C 41.56, H 3.88, N 5.39; found: C 41.73, H 4.01, N 5.36.

21. *2-(4-Iodo-2-nitrophenyl)propan-1-ol* (**25**). According to *Exper. 18.1*, with 1-ethyl-4-iodo-2-nitrobenzene (**4**) [43] (2.77 g, 10 mmol), paraformaldehyde (0.3 g, 10 mmol), DMSO (10 ml), ^{t}BuOK (180 mg, 1.4 mmol), and ^{t}BuOH (4 ml): 2.53 g (82%) of **25**. Yellow oil. TLC (hexanes/AcOEt 7:3): R_f 0.35. UV (MeOH): 203 (4.23), 229 (4.28), 247 (sh, 3.84), 300 (sh, 3.12). ^{1}H-NMR ($CDCl_3$): 8.04 (*d*, H–C(3)); 7.85 (*dd*, H–C(5)); 7.23 (*d*, H–C(6)); 3.75 (*m*, CH(Me)CH_2); 3.45 (*m*, C*H*(Me)CH_2); 1.52 (br., OH); 1.29 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_9H_{10}INO_3$ (307.1): C 35.17, H 3.28, N 4.56; found: C 35.73, H 3.12, N 4.56.

22. *2-(5-Chloro-2-nitrophenyl)propan-1-ol* (**26**). According to *Exper. 18.1*, with **10** (895 mg, 4.8 mmol), paraformaldehyde (160 mg, 5.3 mmol), DMSO (10 ml), ^{t}BuOK (76 mg, 0.7 mmol), and ^{t}BuOH (4 ml): 0.87 g (84%) of **26**. Yellow oil. TLC (hexanes/AcOEt 7:3): R_f 0.27. UV (MeOH): 206 (4.17), 216 (4.06), 262 (3.76), 328 (sh, 2.95). ^{1}H-NMR ($CDCl_3$): 7.72 (*d*, H–C(3)); 7.45 (*d*, H–C(6)); 7.30 (*dd*, H–C(4)); 3.74 (*m*, CH(Me)CH_2); 3.54 (*sext.*, C*H*(Me)CH_2); 1.71 (br., OH); 1.30 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_9H_{10}ClNO_3$ (215.6): C 50.13, H 4.67, N 6.50; found: C 50.20, H 4.75, N 6.20.

23. *2-(5-Bromo-2-nitrophenyl)propan-1-ol* (**27**). According to *Exper. 18.1*, with **11** (1.39 g, 6 mmol), paraformaldehyde (210 mg, 7 mmol), DMSO (10 ml), ^{t}BuOK (0.1 g, 0.89 mmol), and ^{t}BuOH (4 ml): 1.32 g (85%) of **27**. Yellow oil. TLC (hexanes/AcOEt 7:3): R_f 0.57. UV (MeOH): 202 (4.16), 218 (sh, 3.95), 263 (3.76), 330 (sh, 2.96). ^{1}H-NMR ($CDCl_3$): 7.63 (*m*, H–C(3), H–C(6)); 7.47 (*dd*, H–C(4)); 3.74 (*m*, CH(Me)CH_2); 3.52 (*sext.*, C*H*(Me)CH_2); 1.68 (br., OH); 1.30 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_9H_{10}BrNO_3$ (260.1): C 41.56, H 3.88, N 5.39; found: C 41.74, H 3.95, N 5.27.

24. *2-(5-Iodo-2-nitrophenyl)propan-1-ol* (**28**). According to *Exper. 18.1*, with **12** (1.45 g, 5 mmol), paraformaldehyde (165 mg, 5.5 mmol), DMSO (10 ml), ^{t}BuOK (80 mg, 0.7 mmol), and ^{t}BuOH (4 ml): 1.36 g (85%) of **28**. Yellow oil. TLC (hexanes/AcOEt 4:1): R_f 0.29. UV (MeOH): 204 (4.29), 222 (sh, 3.93), 274

(3.80), 335 (sh, 3.18). ^{1}H-NMR ($CDCl_3$): 7.81 (*d*, H–C(6)); 7.69 (*dd*, H–C(4)); 7.46 (*d*, H–C(3)); 3.76 (*m*, CH(Me)CH_2); 3.48 (*sext.*, C*H*(Me)CH_2); 1.54 (br., OH); 1.29 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_9H_{10}INO_3$ (307.1): C 35.17, H 3.28, N 4.56; found: C 35.18, H 3.27, N 4.06.

25. *2-(2-Bromo-6-nitrophenyl)propan-1-ol* (**30**). A mixture of **15** (1.11 g, 4.8 mmol) and paraformaldehyde (435 mg, 14.5 mmol) in dry DMSO (10 ml) was treated with NaCN (235 mg, 4.8 mmol). After stirring for 2 h at r.t., the mixture was neutralized with HCl, diluted with sat. NaCl soln. (25 ml), and extracted with AcOEt. The org. phase was dried (Na_2SO_4), filtered, and evaporated. The crude product was purified by CC (SiO_2 (40 g), 3.5 × 11 cm; toluene → toluene/AcOEt 7:1): 0.85 g (77%) of **15**, 80 mg (6%) of **30**, and 20 mg (2%) of 2-(2-nitrophenyl)propan-1-ol.

Data of **30**: Yellow oil. TLC (hexanes/AcOEt 7:3): R_f 0.47. UV (MeOH): 202 (4.32), 209 (sh, 4.17), 239 (sh, 3.53), 282 (sh, 3.04). ^{1}H-NMR ($CDCl_3$): 7.75 (*dd*, 1 arom. H); 7.44 (*dd*, 1 arom. H); 7.19 (*t*, H–C(4)); 4.02 (*m,* CH(Me)CH_2); 3.87 (*m*, CH(Me)CH_2); 3.58 (*m,* C*H*(Me)CH_2); 1.65 (br., OH); 1.37 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_9H_{10}BrNO_3$ (260.1): C 41.56, H 3.88, N 5.39; found: C 41.46, H 3.99, N 5.18.

26. *2-(2-Iodo-6-nitrophenyl)propan-1-ol* (**31**). According to *Exper.* 25, with **16** (2.56 g, 9.2 mmol), paraformaldehyde (555 mg, 18.5 mmol), DMSO (30 ml), and NaCN (230 mg, 4.7 mmol): 2.18 g (86%) of **16** (yellow oil), 140 mg (5%) of **31**, and 60 mg (3%) of 2-(2-nitrophenyl)propan-1-ol.

Data of **31**: Yellow oil. TLC (hexanes/AcOEt 7:3): R_f 0.70. UV (MeOH): 203 (4.37), 230 (4.12), 287 (sh, 3.04), 336 (sh, 2.74). ^{1}H-NMR ($CDCl_3$): 8.07 (*d*, 1 arom. H), 7.45 (*d*, 1 arom. H); 7.01 (*t*, H–C(4)); 3.85 (*m*, CH(Me)CH_2); 3.54 (*m*, C*H*(Me)CH_2); 1.62 (br., OH); 1.33 (*d*, CH(*Me*)CH_2); Anal. calc. for $C_9H_{10}INO_3$ (307.1): C 35.17, H 3.28, N 4.56; found: C 35.45, H 3.29, N 4.48.

27. *2-(2,4-Dinitrophenyl)propan-1-ol* (**32**) *and 2-(2,6-Dinitrophenyl)propan-1-ol* (**33**). According to *Exper. 18.1*, with **22**/**13** 1:1 (1.27 g, 6.5 mmol), paraformaldehyde (215 mg, 7.1 mmol), DMSO (7 ml), ^{t}BuOK (100 mg, 0.89 mmol), and ^{t}BuOH (3 ml): 0.496 g (34%) of **32**, 72 mg (5%) of **33**, and 0.596 g (47%) of **13** as yellow oils.

Data of **32**: TLC (hexanes/AcOEt 7:3): R_f 0.18. UV (MeOH): 204 (4.15), 242 (4.07), 257 (sh, 4.04), 333 (sh, 2.83). ^{1}H-NMR ($CDCl_3$): 8.60 (*d*, H–C(3)); 8.39 (*dd*, H–C(5)); 7.74 (*d*, H–C(6)); 3.90–3.73 (*m*, CH(Me)CH_2); 3.61 (*sext.*, C*H*(Me)CH_2); 1.62 (br., OH); 1.36 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_9H_{10}N_2O_5$ (226.2): C 47.79, H 4.46, N 12.39; found: C 47.98, H 4.48, N 12.35.

28. *2-(2,6-Dinitrophenyl)propan-1-ol* (**33**). According to *Exper. 18.2*, with **13** (2.19 g, 11 mmol), paraformaldehyde (670 mg, 22 mmol), DMF (10 ml), ^{t}BuOK (200 mg, 1.8 mmol), and ^{t}BuOH: 1.52 g (72%) of 33. Yellow solid. M.p. 52–54°. TLC (hexanes/AcOEt 7:3): R_f 0.37. UV (MeOH): 205 (4.16), 226 (sh, 3.88), 267 (sh, 3.17), 324 (sh, 2.77). ^{1}H-NMR ($CDCl_3$): 7.73 (*d*, 2 H, H–C(3), H–C(5)); 7.51 (*t*, H–C(4)); 3.87 (*m*, CH(Me)CH_2); 3.40 (*sext.*, C*H*(Me)CH_2); 1.69 (*t*, OH); 1.33 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_9H_{10}N_2O_5$ (226.2): C 47.79, H 4.46, N 12.39; found: C 47.98, H 4.48, N 12.25.

29. *2-(2,5-Dinitrophenyl)propan-1-ol* (**34**). According to *Exper. 18.2*, with **19** (1.44 g, 7 mmol), paraformaldehyde (662 mg, 22 mmol), DMF (10 ml), ^{t}BuOK (200 mg, 1.8 mmol), and ^{t}BuOH (4 ml): 0.394 g (25%) of **34**. Yellow solid. M.p. 82–83°. TLC (hexanes/AcOEt 7:3): R_f 0.45. UV (MeOH): 205 (4.24), 256 (4.00), 289 (sh, 3.41), 334 (sh, 3.04). ^{1}H-NMR ($CDCl_3$): 8.38 (*d*, H–C(6)); 8.19 (*dd*, H–C(4)); 7.84 (*d*, H–C(3)); 3.90-3.72 (*m*, CH(Me)CH_2); 3.52 (*sext.*, C*H*(Me)CH_2); 1.55 (*t*, OH); 1.38 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_9H_{10}N_2O_5$ (226.2): C 47.79, H 4.46, N 12.39; found: C 48.01, H 4.42, N 12.33.

30. *4-Ethyl-3-nitro-1,1′-biphenyl* (**35**). Finely powdered 4-ethyl-3-nitrobenzenamine (**1**; 4.2 g, 25 mmol) was added to conc. HCl soln. (10 ml) and H_2O (50 ml) at 60°, the soln. rapidly cooled to 0°, and the resulting suspension diazotized at 0–4° with $NaNO_2$ (1.9 g, 27.5 mmol) in H_2O (10 ml). After stirring for 20 min at 0°, benzene (50 ml, 0.56 mol) was added, and the temp. was increased to 10°. After 10 min, AcOK (8.2 g, 83 mmol) in H_2O (10 ml) was dropped into the soln., and the mixture was stirred for 4 h at 10° and overnight at r.t. The aq. phase was extracted with toluene, the combined org. phase washed with 10% NaOH soln., dried (Na_2SO_4), and evaporated, and the residue purified by CC (SiO_2 (62 g), 3.5 × 17 cm; hexanes): 3.33 g (59%) of **35**. Yellow oil. TLC (hexanes/AcOEt 4:1): R_f 0.74. UV (MeOH): 204 (4.48), 247 (4.38), 309 (sh, 3.16). ^{1}H-NMR ($CDCl_3$): 8.09 (*d*, H–C(3)); 7.73 (*d*, H–C(5)); 7.57 (*m*, 2 arom. H); 7.43 (*m*, 4 arom. H); 2.94 (*q*, MeCH_2); 1.31 (*t*, *Me*CH_2).

31. *3-Ethyl-4-nitro-1,1′-biphenyl* (**36**). 31.1. Gomberg-Bachmann *Reaction.* According to *Exper. 30*, with finely powdered **9** (4.2 g, 25 mmol): 2.6 g (46%) of **36**. Yellow needles. M.p. 54–56°.

31.2. Suzuki *Reaction.* As described for **37**, with **11** (6 g, 26 mmol), toluene (40 ml), EtOH (10.5 ml), 2N $NaHCO_3$ (16 ml), phenylboronic acid (3.82 g, 31 mmol), and $[Pd(Ph_3P)_4]$ (400 mg, 0.35 mmol): 5.43 g (92%) of **36**. Yellow needles. M.p. 55°. TLC (hexanes/AcOEt 9:1): R_f 0.67. UV (MeOH): 205 (4.52), 225 (sh, 4.05), 391 (4.04). ^{1}H-NMR ($CDCl_3$): 7.99 (*d*, 1 arom. H); 7.61, 7.38 (*m*, 7 arom. H); 2.99 (*q*, MeCH_2); 1.33 (*t*, *Me*CH_2). Anal. calc. for $C_{14}H_{13}NO_2$ (227.3): C 73.99, H 5.75, N 6.16; found: C 73.84, H 5.68, N 5.81.

32. *3-Ethyl-4′-methoxy-4-nitro-1,1′-biphenyl* (**37**). A mixture of **11** (1.36 g, 5.9 mmol), toluene (15 ml), EtOH (4 ml), 2N $NaHCO_3$ (6 ml), (4-methoxyphenyl)boronic acid (1 g, 6.6 mmol), and $[Pd(Ph_3P)_4]$ (0.2 g, 0.17 mmol) was heated under reflux for 5 h. After cooling, the mixture was diluted with sat. aq. NaCl soln. (20 ml) and extracted with AcOEt (2 × 25 ml). The combined org. phase was dried and evaporated. Purification by CC (SiO_2 (42 g) 3 × 20 cm; hexanes/AcOEt 9:1 → 6:1) gave 1.41 g (93%) of **37**. Yellow solid. M.p. 94–95°. TLC (hexanes/AcOEt 9:1): R_f 0.42. UV (MeOH): 204 (4.52), 232 (4.13), 320 (4.07). ^{1}H-NMR ($CDCl_3$): 7.97 (*d*, 1 arom. H); 7.51 (*m*, 4 arom. H); 6.70 (*dd*, 2 arom. H); 3.85 (*s*, MeO); 2.99 (*q*, MeC*H*$_2$); 1.32 (*t*, *Me*CH_2). Anal. calc. for $C_{15}H_{15}NO_3$ (257.3): C 70.02, H 5.88, N 5.44; found: C 70.00, H 5.97, N 5.14.

33. *3-Ethyl-3′,4′-dimethoxy-4-nitro-1,1′-biphenyl* (**38**). According to *Exper. 32*, with **11** (1.5 g, 6.5 mmol), toluene (15 ml), EtOH (4 ml), 2N $NaHCO_3$ (6 ml), (3,4-dimethoxyphenyl)boronic acid (1.4 g, 7.8 mmol), and $[Pd(Ph_3P)_4]$ (200 mg, 0.17 mmol). Purification by CC (SiO_2 (42 g), 3 × 15 cm; hexane/AcOEt 20:1 → 5:1) gave 1.71 g (92%) of **38**. Yellow solid. M.p. 84–85°. TLC (hexane/AcOEt 3:1): R_f 0.40. UV (MeOH): 242 (4.03), 335 (4.03), 352 (3.92). ^{1}H-NMR ((D_6)DMSO): 7.98 (*d*, H–C(5)); 7.79 (*d*, H–C(2)); 7.72 (*dd*, H–C(6)); 7.32 (*m*, H–C(6′), H–C(2′)); 7.06 (*m*, H–C(5′)); 3.86 (*s*, MeO); 3.80 (*s*, MeO); 2.91 (*q*, MeC*H*$_2$); 1.25 (*t*, *Me*CH_2). Anal. calc. for $C_{16}H_{17}NO_4$ (287.31): C 66.89, H 5.96, N 5.96; found: C 66.87, H 5.96, N 4.92.

34. *3-Ethyl-4-nitro-4′-phenoxy-1,1′-biphenyl* (**39**). According to *Exper. 32*, with **11** (1.5 g, 6.5 mmol), toluene (15 ml), EtOH (4 ml), 2N $NaHCO_3$ (6 ml), (4-phenoxyphenyl)boronic acid (1.95 g, 9.1 mmol), and $[Pd(Ph_3P)_4]$ (200 mg, 0.17 mmol). Purification by CC (SiO_2 (42 g), 3 × 15 cm; hexane/AcOEt 20:1 → 5:1) gave 1.47 g (71%) of **39**. Light yellow solid. M.p. 61–62°. TLC (hexane/AcOEt 9:1): R_f 0.57. UV (MeOH): 235 (3.82), 306 (4.11), 352 (sh, 3.82). ^{1}H-NMR ((D_6)DMSO): 7.98 (*d*, 1 arom. H); 7.77 (*m*, 3 arom. H); 7.68 (*dd*, 1 arom. H); 7.41 (*m*, 2 arom. H); 7.17 (*m*, 1 arom. H); 2.89 (*q*, MeC*H*$_2$); 1.23 (*t*, *Me*CH_2). Anal. calc. for $C_{20}H_{17}NO_3$ (319.35): C 75.22, H 5.37, N 4.39; found: C 75.05, H 5.38, N 4.57.

35. *1-(3-Ethyl-4-nitrophenyl)thianthrene* (**40**). According to *Exper. 32*, with **11** (1.5 g, 6.5 mmol), toluene (15 ml), EtOH (4 ml), 2N $NaHCO_3$ (6 ml), (thianthren-1-yl)boronic acid (2.4 g, 9.1 mmol), and $[Pd(Ph_3P)_4]$ (200 mg, 0.17 mmol). Purification by CC (SiO_2 (42 g), 3 × 15 cm; hexane/AcOEt 20:1 → 5:1) gave 1.79 g (76%) of **40**. Light yellow solid. M.p. 143–145°. TLC (hexane/AcOEt 9:1): R_f 0.47. UV (MeOH): 252 (4.31), 278 (sh, 3.99), 336 (sh, 3.39); ^{1}H-NMR ((D_6)DMSO): 8.04 (*d*, 1 arom. H); 7.68 (*dd*, 1 arom. H); 7.59 (*m*, 2 arom. H); 7.52–7.24 (*m*, 6 arom. H); 2.90 (*q*, MeC*H*$_2$); 1.26 (*t*, *Me*CH_2). Anal. calc. for $C_{20}H_{15}NO_2S_2$ (365.47): C 65.73, H 4.14, N 3.83; found: C 65.86, H 4.08, N 3.84.

36. *1-(3-Ethyl-4-nitrophenyl)naphthalene* (**41**). According to *Exper. 32*, with **11** (1.36 g, 5.9 mmol), toluene (15 ml), EtOH (4 ml), 2N $NaHCO_3$ (6 ml), (1-naphthyl)boronic acid [69] (1.4 g, 8 mmol), and $[Pd(Ph_3P)_4]$ (200 mg, 0.17 mmol). Purification by CC (SiO_2 (37 g), 2.5 × 16 cm; hexanes/AcOEt 20:1 → 10:1) gave 1.59 g (97%) of **41**. Yellow oil. TLC (hexanes/AcOEt 9:1): R_f 0.68. UV (MeOH): 218 (4.79), 259 (sh, 3.96), 302 (sh, 3.89). ^{1}H-NMR ($CDCl_3$): 8.02 (*d*, 1 arom. H); 7.93 (*m*, 2 arom. H); 7.79 (*dd*, 1 arom. H); 7.57–7.39 (*m*, 6 arom. H); 3.00 (*q*, MeC*H*$_2$); 1.33 (*t*, *Me*CH_2). Anal. calc. for $C_{18}H_{15}NO_2$ (277.3): C 77.96, H 5.45, N 5.05; found: C 77.98, H 5.18, N 5.08.

37. *2-(3-Ethyl-4-nitrophenyl)naphthalene* (**42**). According to *Exper. 36*, with **11** (1.36 g, 5.9 mmol) and (2-naphthyl)boronic acid [76] (1.22 g, 7.1 mmol). Purification by CC (SiO_2 (37 g) 2.5 × 16 cm; hexanes/AcOEt 20:1 → 10:1) gave 1.52 g (93%) of **39**. Yellow solid. M.p. 110.5–111.5°. TLC (hexanes/AcOEt 9:1): R_f 0.55. UV (MeOH): 212 (4.61), 233 (4.59), 271 (sh, 4.15), 310 (4.14), 339 (sh, 3.96). ^{1}H-NMR ($CDCl_3$): 8.03 (*m*, 2 arom. H); 7.90 (*m*, 3 arom. H); 7.66 (*m*, 3 arom. H); 7.52 (*m*, 2 arom. H); 3.03 (*q*, MeC*H*$_2$); 1.36 (*t*, *Me*CH_2). Anal. calc. for $C_{18}H_{15}NO_2$ (277.3): C 77.96, H 5.45, N 5.05; found: C 77.79, H 5.25, N 4.76.

38. *2-(3-Ethyl-4-nitrophenyl)thiophene* (**43**). According to *Exper. 32*, with **11** (1.5 g, 6.5 mmol) and (2-thienyl)boronic acid (1 g, 7.8 mmol). Purification by CC (SiO_2 (34 g), 2.5 × 17 cm; hexanes/AcOEt 9:1 → 6:1) gave 0.89 g (59%) of **43**. Yellow oil. TLC (hexanes/AcOEt 9:1): R_f 0.67. UV (MeOH): 204 (4.34), 249 (3.90), 334 (4.08). ^{1}H-NMR ($CDCl_3$): 7.95 (*dd*, 1 arom. H); 7.52 (*m*, 2 arom. H); 7.40 (*m*, 2 arom. H); 7.11 (*m*, 1 arom. H); 2.97 (*q*, MeC*H*$_2$); 1.31 (*t*, *Me*CH_2). Anal. calc. for $C_{12}H_{11}NO_2S$ (233.3): C 61.78, H 4.75, N 6.00; found: C 61.55, H 4.60, N 6.90.

39. *3-(3-Ethyl-4-nitrophenyl)thiophene* (**44**). According to *Exper. 32*, with **11** (1.38 g, 6 mmol) and (3-thienyl)boronic acid (1 g, 7.8 mmol). Purification by CC (SiO_2 (33 g), 2.5 × 17 cm; hexanes/AcOEt 9:1 → 6:1) gave 1.35 g (96%) of **44**. Yellow oil. TLC (hexanes/AcOEt 9:1): R_f 0.65. UV (MeOH): 205 (4.46), 311 (4.02). ^{1}H-NMR ($CDCl_3$): 7.96 (*d*, 1 arom. H); 7.85–7.49 (*m*, 3 arom. H); 7.45–7.38 (*m*, 2 arom. H); 2.98 (*q*, MeC*H*$_2$); 1.31 (*t*, *Me*CH_2). Anal. calc. for $C_{12}H_{11}NO_2S$ (233.3): C 61.78, H 4.75, N 6.00; found: C 61.81, H 4.76, N 6.82.

40. *4-Ethenyl-2-ethyl-1-nitrobenzene* (**45**). Tributyl(ethenyl)stannane (1.9 g, 5 mmol), bis(dibenzylideneacetone)palladium(0) (0.2 g, 0.34 mmol), and Ph_3P (0.35 g, 1.33 mmol) were added under Ar to a soln. of **11** (1.36 g, 5.9 mmol) in abs. toluene (30 ml). The mixture was heated under reflux for 22 h. After cooling, the

mixture was evaporated, the residue dissolved in AcOEt (50 ml) and washed with 10% ammonia in H_2O (3×). After re-extraction of the aq. phase (2 × 30 ml AcOEt), the combined org. phase was dried and evaporated. Purification by CC (SiO_2 (33 g), 2.5 × 16 cm; hexanes → hexanes/AcOEt 8:1) gave 0.88 g (83%) of **45**. Yellow oil. TLC (hexanes/AcOEt 9:1): R_f 0.82. UV (MeOH): 205 (4.40), 227 (3.96), 289 (3.95). ^{1}H-NMR ($CDCl_3$): 7.87 (*d*, 1 arom. H); 7.33 (*m*, 2 arom. H); 6.71 (2*d*, CH_2=C*H*); 5.86 (*d*,1 H, CH_2=CH); 5.43 (*d*, 1 H, CH_2=CH); 2.92 (*q*, MeCH_2); 1.28 (*t*, *Me*CH_2). Anal. calc. for $C_{10}H_{11}NO_2$ (177.2): C 67.78, H 6.26, N 7.90; found: C 67.34, H 6.14, N 8.30.

41. *Methyl 4-Ethyl-3-nitrobenzoate* (**47**). A soln. of 4-ethyl-3-nitrobenzoic acid (**46**) [70] (5 g, 26 mmol) in dry MeOH (30 ml) and conc. H_2SO_4 soln. (1 ml) was heated to reflux for 3 h. After cooling down to r.t. CH_2Cl_2 (50 ml) was added to the mixture, which was then extracted with sat. $NaHCO_3$ soln. (50 ml). The aq. phase was re-extracted with CH_2Cl_2 (2 × 50 ml) and the combined org. phase dried (Na_2SO_4) and evaporated: 4.89 g (91%) of **47**. Light yellow oil. TLC (hexanes/AcOEt 9:1): R_f 0.59. UV (MeOH): 203 (4.05), 225 (4.35), 250 (sh, 3.78), 283 (sh, 3.17), 316 (sh, 2.70). ^{1}H-NMR ($CDCl_3$): 8.48 (*d*, H–C(2)); 8.15 (*dd*, H–C(6)); 7.44 (*d*, H–C(5)); 3.93 (*s*, COOMe); 2.93 (*q*, MeCH_2); 1.28 (*t*, *Me*CH_2).

42. tert-*Butyl 4-Ethyl-3-nitrobenzoate* (**48**). A soln. of **46** [70] (5.9 g, 30 mmol), dicyclohexylcarbodiimide (6.8 g, 33 mmol), ^{t}BuOH (2.4 g, 33 mmol), and 4-pyrrolidinopyridine (445 mg, 3 mmol) in dry CH_2Cl_2 (100 ml) was stirred for 3 h at r.t. and then filtered over diatomaceous earth. The filtrate was washed with H_2O, 5% AcOH, and H_2O (100 ml each), dried (Na_2SO_4), and evaporated. Purification by CC (SiO_2 (100 g), 5 × 16 cm; hexanes (300 ml), then hexanes/AcOEt 15:1 (800 ml) and 9:1 (300 ml)) gave 5.57 g (74%) of **48**. Light yellow oil. TLC (hexanes/AcOEt 9:1): R_f 0.55. UV (MeOH): 202 (4.12), 224 (4.39), 248 (sh, 3.83), 282 (sh, 3.24), 316 (sh, 2.89). ^{1}H-NMR ($CDCl_3$): 8.38 (*d*, H–C(2)); 8.07 (*dd*, H–C(6)); 7.39 (*d*, H–C(5)); 2.90 (*q*, MeCH_2); 1.56 (*s*, ^{t}Bu); 1.21 (*t*, *Me*CH_2).

43. S-*Phenyl 4-Ethyl-3-nitrobenzenecarbothioate* (**49**). According to *Exper. 42*, with **46** [70] (1.96 g, 10 mmol), dicyclohexylcarbodiimide (2.27 g, 11 mmol), thiophenol (2.2 g, 20 mmol), *N*,*N*-dimethylpyridin-4-amine (245 mg, 2 mmol), and CH_2Cl_2 (100 ml). CC (SiO_2 (43 g), 2.5 × 21 cm; hexanes → hexanes/AcOEt 10:1) gave 2.57 g (89%) **49**. Light yellow solid. M.p. 79–80°. TLC (hexane/AcOEt 9:1): R_f 0.45. UV (MeOH): 240 (4.14). ^{1}H-NMR ((D$_6$)DMSO): 8.37 (*d*, H–C(2)); 8.19 (*dd*, H–C(6)); 7.73 (*d*, H–C(5)); 7.52 (*s*, 5 arom. H); 2.88 (*q*, MeCH_2); 1.22 (*t*, *Me*CH_2).

44. *4-Ethyl-3-nitro*-N,N-*diphenyl-benzenecarboxamide* (**50**). A mixture of **46** [70] (1.95 g, 10 mmol) and thionyl chloride (10 ml) was refluxed for 4 h. After cooling, the reagent was evaporated and the remaining 4-ethyl-3-nitrobenzoyl chloride (2.2 g, 9.9 mmol, 99%) dissolved in dioxane (10 ml). To this soln. was added under cooling diphenylamine (6.8 g, 40 mmol) in dioxane (10 ml). After stirring for 30 min at r.t. and 2 h at reflux, the mixture was poured on ice, acidified with conc. HCl soln. and extracted with CH_2Cl_2. The combined org. phase was dried (Na_2SO_4) and evaporated and the crude product purified by CC (SiO_2 (150 g), 4.5 × 23 cm; hexane/AcOEt 4:1 → 1:1): 2.72 g (97%) of **50**. Light yellow solid. M.p. 139–140°. TLC (hexane/AcOEt 3:1): R_f 0.37. UV (MeOH): 234 (4.19), 268 (sh, 3.98), 345 (sh, 2.86). ^{1}H-NMR ((D$_6$)DMSO): 7.95 (*d*, H–C(2)); 7.64 (*dd*, H–C(6)); 7.41 (*d*, H–C(5)); 7.38–7.19 (*m*, Ph_2N); 2.81 (*q*, MeCH_2); 1.11 (*t*, *Me*CH_2).

45. *4-Ethyl*-N,N-*diisopropyl-3-nitrobenzenecarboxamide* (**51**). According to *Exper. 44*, with **46** [70] (1.95 g, 10 mmol), thionyl chloride (10 ml) (4 h), 4-ethyl-3-nitrobenzoyl chloride (2.12 g, 9.8 mmol, 98%) in dioxane (10 ml), and diisopropylamine (4.5 g, 6.3 ml, 45 mmol) in dioxane (10 ml) (20 min): 2.72 g (97%) of **51**. Light yellow solid. M.p. 55–60°. TLC (hexane/AcOEt 1:1): R_f 0.74. UV (MeOH): 229 (3.96), 286 (sh, 3.22). ^{1}H-NMR ((D$_6$)DMSO): 7.80 (*s*, 1 arom. H); 7.56 (*s*, 2 arom. H); 3.58 (*m*, 2 Me_2C*H*); 2.81 (*q*, MeCH_2); 1.23 (br., 2 Me_2CH, *Me*CH_2).

46. *4-Ethyl*-N-*methyl-3-nitro*-N-*phenylbenzenecarboxamide* (**52**). According to *Exper. 45* with **46** [70] (1.97 g, 10 mmol), thionyl chloride (10 ml), *N*-methylphenylamine (4.5 g, 4.5 ml, 42 mmol), and dioxane (2 × 10 ml). Purification by CC (SiO_2 (93 g), 3.5 × 21 cm; hexane/AcOEt 5:1 → 1:1) gave 2.48 g (87%) of **52**. Light yellow solid. M.p. 83–84°. TLC (hexane/AcOEt 1:1): R_f 0.74; UV (MeOH): 231 (4.06), 241 (sh, 4.04), 295 (sh, 3.38), 328 (sh, 2.89). ^{1}H-NMR ((D$_6$)DMSO): 7.79 (*d*, H–C(2)); 7.44 (*dd*, H–C(6)); 7.35–7.17 (*m*, H–C(5), PhN); 3.37 (*s*, MeN); 2.71 (*q*, MeCH_2); 1.09 (*t*, *Me*CH_2). Anal. calc. for $C_{16}H_{16}N_2O_3$ (284.32): C 67.59, H 5.67, N 9.85; found: C 67.61, H 5.88, N 9.74.

47. *3-Ethyl-4-nitrobenzonitrile* (**54**). Finely powdered **9** (9.4 g, 57 mmol) was added to conc. HCl soln. (30 ml) and H_2O (150 ml) at 60°, the resulting soln. rapidly cooled to 0°, and the resulting suspension diazotized at 0–5° with $NaNO_2$ (4.3 g, 62 mmol) in H_2O (20 ml). After stirring for 10 min at 0°, the mixture was added to a cooled (0°) soln. of CuCN (10.8 g, 0.1 mol) and NaCN (14.6 g, 0.3 mol) in H_2O (80 ml). The mixture was stirred at 0° for 1 h and then warmed to 50° for 45 min. After cooling, the filtered mixture was extracted with AcOEt. The org. phase was washed with 1M NaOH (90 ml) and H_2O (90 ml), dried (Na_2SO_4), and evaporated.

Purification by CC (SiO_2 (120 g), 6 × 14 cm; hexanes → hexanes/AcOEt 15:1) gave 3.41 g (34%) of **54**. Orange solid. M.p. 65–66°. TLC (hexanes/AcOEt 9:1): R_f 0.39. UV (MeOH): 202 (4.22), 216 (sh, 3.97), 225 (sh, 3.92), 249 (3.88), 282 (sh, 3.40), 322 (sh, 2.97). ^{1}H-NMR ($CDCl_3$): 7.90 (*d*, H–C(5)); 7.68 (*d*, H–C(2)); 7.63 (*dd*, H–C(6)); 2.90 (*q*, MeCH_2); 1.30 (*t*, *Me*CH_2). Anal. calc. for $C_9H_8N_2O_2$ (176.2): C 61.38, H 4.58, N 15.90; found: C 61.25, H 4.51, N 15.86.

48. *3-Ethyl-4-nitrobenzoic Acid* (**55**). A soln. of KOH (640 mg) in H_2O (5.7 ml) was added to a suspension of **54** (2 g, 11.4 mmol) in EtOH (20 ml). After 2.5 h reflux, the mixture was cooled to r.t. and evaporated. The residue was suspended in H_2O (20 ml) and acidified with conc. HCl soln. The precipitate was collected, dried at 80°, and purified by CC (silanized SiO_2 (40 g), 3 × 17 cm; hexanes/AcOEt, 9:1 → 1:1): 1 g (44%) of **55**. Yellow solid. M.p. 186–188°. TLC (AcOEt): R_f 0.24. UV (MeOH): 202 (4.21), 219 (sh, 3.91), 252 (3.85), 291 (sh, 3.44), 333 (sh, 2.96). ^{1}H-NMR ((D$_6$)DMSO): 13.59 (br., COOH); 8.03 (*s*, 1 arom. H); 7.95 (*m*, 2 arom. H); 2.32 (*q*, MeCH_2); 1.18 (*t*, *Me*CH_2).

49. tert-*Butyl 3-Ethyl-4-nitrobenzoate* (**56**). According to *Exper. 42*, with **55** (480 mg, 2.5 mmol), dicyclohexylcarbodiimide (560 mg, 2.7 mmol), ^{t}BuOH (370 mg, 5 mmol), 4-pyrrolidinopyridine (100 mg, 0.67 mmol), and CH_2Cl_2 (15 ml). Purification by CC (SiO_2 (20 g), 2 × 13 cm; hexanes → hexanes/AcOEt 15:1) gave 450 mg (72%) of **56**. Light yellow oil. TLC (AcOEt): R_f 0.31. UV (MeOH): 202 (4.29), 220 (sh, 3.96), 250 (3.90), 289 (sh, 3.41), 330 (sh, 2.97). ^{1}H-NMR ($CDCl_3$): 7.96 (*d*, H–C(2)); 7.89 (*dd*, H–C(6)); 7.82 (*d*, H–C(5)); 2.90 (*q*, MeCH_2); 1.59 (*s*, ^{t}Bu); 1.29 (*t*, *Me*CH_2). Anal. calc. for $C_9H_8NO_4$ (195.2): C 62.14, H 6.82, N 5.57; found: C 62.22, H 7.01, N 6.15.

50. *2-(3-Nitro[1,1′-biphenyl]-4-yl)propan-1-ol* (**57**). According to *Exper. 18.1*, with **35** (1.5 g, 6.6 mmol), paraformaldehyde (0.22 g, 7.3 mmol), DMSO (10 ml), ^{t}BuOK (160 mg, 1.3 mmol), and ^{t}BuOH (2 ml): 1.29 g (76%) of **57**. Yellow oil. TLC (hexanes/AcOEt 7:3): R_f 0.45. UV (MeOH): 205 (4.55), 248 (4.42), 304 (sh, 3.20). ^{1}H-NMR ($CDCl_3$): 7.95 (*d*, H–C(2)); 7.77 (*dd*, H–C(6)); 7.59–7.39 (*m*, 6 arom. H); 3.82 (*m*, CH(Me)CH_2); 3.54 (*m*, C*H*(Me)CH_2); 1.73 (br., OH); 1.35 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_{15}H_{15}NO_3$ (257.3): C 70.02, H 5.88, N 5.44; found: C 70.56, H 6.13, N 5.40.

51. *2-(4-Nitro[1,1′-biphenyl]-3-yl)propan-1-ol* (**58**). According to *Exper. 18.1*, with **36** (1.19 g, 5.2 mmol), paraformaldehyde (173 mg, 5.8 mmol), DMSO (10 ml), ^{t}BuOK (0.16 g, 1.3 mmol), and ^{t}BuOH (2 ml): 0.91 g (68%) of **58**. Yellow oil. TLC (hexanes/AcOEt 7:3): R_f 0.47. UV (MeOH): 204 (4.53), 231 (sh, 4.03), 281 (3.94), 336 (3.70). ^{1}H-NMR ($CDCl_3$): 7.85 (*d*, 1 arom. H); 7.65 (*d*, 1 arom. H); 7.59–7.38 (*m*, 6 arom. H); 3.83 (*m*, CH(Me)CH_2); 3.62 (*sext.*, C*H*(Me)CH_2); 1.73 (br., OH); 1.37 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_{15}H_{15}NO_3$ (257.3): C 70.02, H 5.88, N 5.44; found: C 69.67, H 5.73, N 5.30.

52. *2-(4′-Methoxy-4-nitro[1,1′-biphenyl]-3-yl)propan-1-ol* (**59**). According to *Exper. 18.1*, with **37** (1.03 g, 4 mmol), paraformaldehyde (135 mg, 4.4 mmol), DMSO (10 ml), ^{t}BuOK (0.12 g, 1 mmol), and ^{t}BuOH (2 ml) to give 0.65 g (57%) of **59**. Yellow solid. M.p. 103–105°. TLC (hexanes/AcOEt 7:3): R_f 0.45. UV (MeOH): 204 (4.56), 232 (4.13), 305 (4.01). ^{1}H-NMR ($CDCl_3$): 7.84 (*d*, 1 arom. H); 7.53 (*m*, 4 arom. H); 6.99 (*dd*, 2 arom. H); 3.83 (*m*, MeO, CH(Me)CH_2); 3.66 (*m*, C*H*(Me)CH_2); 1.60 (br., OH); 1.36 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_{16}H_{17}NO_4$ (287.3): C 66.89, H 5.96, N 4.88; found: C 66.78, H 5.83, N 4.77.

53. *2-(3′,4′-Dimethoxy-4-nitro[1,1′-biphenyl]-3-yl)propan-1-ol* (**60**). ^{t}BuOK (122 mg, 1 mmol) was added to a mixture of **38** (1.44 g, 5 mmol) and paraformaldehyde (180 mg, 6 mmol) in DMSO (5 ml). After stirring for 1.5 h at r.t., the mixture was neutralized, diluted with sat. NaCl soln. (15 ml), and extracted with AcOEt. The org. phase was dried (Na_2SO_4), filtered, and evaporated. The crude product was purified by CC (SiO_2 (38 g), 3 × 14 cm; hexane/AcOEt): 1.47 g (93%) of **60**. Yellow solid. M.p. 108–109°. TLC (hexanes/AcOEt 1:1): R_f 0.34. UV (MeOH): 244 (4.07), 316 (3.94), 352 (sh, 3.85). ^{1}H-NMR ((D$_6$)DMSO): 7.84 (*d*, H–C(5)); 7.76 (*dd*, H–C(2)); 7.68 (*d*, H–C(6)); 7.29 (*dd*, H–C(6′)); 7.27 (*s*, H–C(2′)); 7.06 (*d*, H–C(5′)); 4.78 (*t*, OH); 3.86 (*s*, MeO); 3.80 (*s*, MeO); 3.60 (*m*, CH(Me)CH_2); 3.32 (*m*, C*H*(Me)CH_2); 1.29 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_{17}H_{19}NO_5$ (317.34): C 64.34, H 6.03, N 4.41; found: C 64.19, H 5.87, N 4.35.

54. *2-(4-Nitro-4′-phenoxy[1,1′-biphenyl]-3-yl)propan-1-ol* (**61**). According to *Exper. 53*, with **39** (1.27 g, 4 mmol), paraformaldehyde (145 mg, 4.8 mmol) in DMSO (5 ml), and ^{t}BuOK (100 mg, 0.8 mmol): 1.24 g (89%) of **61**. Yellow oil. TLC (hexanes/AcOEt 3:1): R_f 0.33. UV (MeOH): 236 (4.11), 292 (4.05). ^{1}H-NMR ((D$_6$)DMSO): 7.86 (*d*, 1 arom. H); 7.77 (*m*, 3 arom. H); 7.67 (*dd*, 1 arom. H); 7.42 (*m*, 2 arom. H); 7.18 (*d*, 1 arom. H); 7.09 (*m*, 4 arom. H); 4.80 (*t*, OH); 3.59 (*m*, CH(Me)CH_2); 3.30 (*m*, C*H*(Me)CH_2); 1.28 (*d*, CH(*Me*)CH_2).

55. *2-[2-Nitro-5-(thianthren-1-yl)phenyl]propan-1-ol* (**62**). According to *Exper. 53*, with **40** (1.16 g, 3.2 mmol), paraformaldehyde (120 mg, 3.8 mmol) in DMSO (10 ml), and ^{t}BuOK (80 mg, 0.6 mmol): 720 mg (57%) of **62**. Light yellow solid. M.p. 147–148°. TLC (hexanes/AcOEt 1:1): R_f 0.67. UV (MeOH): 255 (4.36), 277 (sh, 4.00), 334 (sh, 3.41). ^{1}H-NMR ((D$_6$)DMSO): 7.91 (*d*, 1 arom. H); 7.66 (*dd*, 1 arom. H); 7.60 (*m*, 2 arom.

H); 7.49–7.28 (*m*, 7 arom. H); 4.83 (*t*, OH); 3.57 (*m*, CH(Me)CH_2); 3.30 (*m*, C*H*(Me)CH_2); 1.28 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_{21}H_{17}NO_3S_2$ (395.50): C 63.78, H 4.33, N 3.54; found: C 63.51, H 4.26, N 3.45.

56. *2-[5-(Naphthalen-1-yl)-2-nitrophenyl]propan-1-ol* (**63**). According to *Exper. 18.1*, with **41** (0.99 g, 3.6 mmol), paraformaldehyde (0.13 g, 4.3 mmol), DMSO (10 ml), *t*BuOK (0.12 g, 1 mmol), and *t*BuOH (2 ml): 0.104 g (69%) of **63**. Yellow oil. TLC (hexanes/AcOEt 7:3): R_f 0.63. UV (MeOH): 218 (4.77), 286 (3.91). ^{1}H-NMR ($CDCl_3$): 7.91 (*m*, 3 arom. H); 7.78 (*dd*, 1 arom. H); 7.60–7.39 (*m*, 6 arom. H); 3.80 (*m*, CH(Me)CH_2); 3.66 (*sext.*, C*H*(Me)CH_2); 1.62 (br., OH); 1.35 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_{19}H_{17}NO_3 \cdot 0.5$ AcOEt (351.4): C 71.77, H 6.02, N 3.99; found: C 71.85, H 5.87, N 3.61.

57. *2-[5-(Naphthalen-2-yl)-2-nitrophenyl]propan-1-ol* (**64**). According to *Exper. 18.1*, with **42** (740 mg, 2.7 mmol), paraformaldehyde (100 mg, 3.2 mmol), DMSO (10 ml), *t*BuOK (85 mg, 0.7 mmol), and *t*BuOH (2 ml): 0.572 g (69%) of **64**. Yellow oil. TLC (hexanes/AcOEt 7:3): R_f 0.63. UV (MeOH): 212 (4.61), 235 (4.57), 274 (sh, 4.14), 303 (sh, 4.09), 340 (sh, 3.85). ^{1}H-NMR ($CDCl_3$): 8.04 (*s*, 1 arom. H); 7.91 (*m*, 3 arom. H); 7.78 (*d*, 1 arom. H); 7.68 (*m*, 2 arom. H); 7.52 (*m*, 2 arom. H); 3.88 (*m*, CH(Me)CH_2); 3.67 (*sext.*, C*H*(Me)CH_2); 1.78 (br., OH); 1.41 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_{19}H_{17}NO_3$ (307.4): C 74.25, H 5.58, N 4.56; found: C 74.22, H 5.47, N 4.35.

58. *2-[2-Nitro-5-(2-thienyl)phenyl]propan-1-ol* (**65**). According to *Exper. 18.1*, with **43** (0.8 g, 3.4 mmol), paraformaldehyde (125 mg, 4.1 mmol), DMSO (5 ml), *t*BuOK (85 mg, 0.7 mmol), and *t*BuOH (1 ml): 0.747 g (82%) of **65**. Yellow oil. TLC (hexanes/AcOEt 7:3): R_f 0.51. UV (MeOH): 203 (4.32), 253 (3.91), 310 (4.02), 334 (sh, 3.98). ^{1}H-NMR ($CDCl_3$): 7.82 (*d*, 1 arom. H); 7.65 (*d*, 1 arom. H); 7.54 (*dd*, 1 arom. H); 7.40 (*m*, 2 arom. H); 7.12 (*m*, 1 arom. H); 3.83 (*m*, CH(Me)CH_2); 3.64 (*sext.*, C*H*(Me)CH_2); 1.61 (br., OH); 1.36 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_{13}H_{13}NO_3S \cdot 0.25\ H_2O$ (267.8): C 58.30, H 5.08, N 5.23; found: C 58.58, H 4.97, N 5.13.

59. *2-[2-Nitro-5-(3-thienyl)phenyl]propan-1-ol* (**66**). According to *Exper. 58*, with **44** (0.8 g, 3.4 mmol): 0.747 g (82%) of **66**. Yellow oil. TLC (hexanes/AcOEt 7:3): R_f 0.42. UV (MeOH): 205 (4.47), 242 (sh, 3.93), 297 (3.95). ^{1}H-NMR ($CDCl_3$): 7.82 (*d*, 1 arom. H); 7.65 (*d*, 1 arom. H), 7.53 (*m*, 2 arom. H); 7.40 (*m*, 2 arom. H); 3.82 (*m*, CH(Me)CH_2); 3.68 (*sext.*, C*H*(Me)CH_2); 1.68 (br., OH); 1.35 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_{13}H_{13}NO_3S \cdot 0.25\ H_2O$ (267.8): C 58.30, H 5.08, N 5.23; found: C 58.58, H 4.97, N 5.13.

60. *2-(5-Ethenyl-2-nitrophenyl)propan-1-ol* (**67**). According to *Exper. 18.2*, with **45** (0.7 g, 4 mmol), paraformaldehyde (120 mg, 4 mmol), DMF (10 ml), *t*BuOK (0.1 g, 0.8 mmol), and *t*BuOH (2 ml): 0.136 g (17%) of **67**. Yellow oil. TLC (hexanes/AcOEt 7:3): R_f 0.41. UV (MeOH): 206 (4.44), 231 (4.04), 282 (3.89), 332 (sh, 3.47). ^{1}H-NMR ($CDCl_3$): 7.75 (*d*, H–C(3)); 7.42 (*s*, H–C(6)): 7.37 (*dd*, H–C(4)); 6.72 (*2d*, CH_2=C*H*); 5.85 (*d*, 1 H, CH_2=CH); 5.44 (*d*, 1 H, CH_2=CH); 3.78 (*m,* CH(Me)CH_2); 3.57 (*sext.*, C*H*(Me)CH_2); 1.65 (br., OH); 1.32 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_{11}H_{13}NO_3$ (207.2): C 63.76, H 6.32, N 6.76; found: C 63.76, H 6.04, N 6.74.

61. *Methyl 4-(2-Hydroxy-1-methylethyl)-3-nitrobenzoate* (**68**). According to *Exper. 18.1*, with **47** (630 mg, 3 mmol), paraformaldehyde (135 mg, 4.5 mmol), DMSO (7 ml), *t*BuOK (40 mg, 0.33 mmol), and *t*BuOH (1 ml): 280 mg (39%) of **68**. Yellow oil. TLC (hexanes/AcOEt 7: 3): R_f 0.24. UV (MeOH): 202 (4.16), 226 (4.22), 278 (sh, 3.22), 322 (sh, 2.86). ^{1}H-NMR ($CDCl_3$): 8.36 (*d*, H–C(2)); 8.18 (*dd*, H–C(6)); 7.58 (*d*, H–C(5)); 3.93 (s, COOMe); 3.78 (*m*, CH(Me)CH_2); 3.54 (*sext.*, C*H*(Me)CH_2); 1.69 (*t*, OH); 1.32 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_{11}H_{13}NO_5$ (239.2): 55.23, H 5.48, N 5.85; found: C 55.22, H 5.48, N 5.72.

62. tert-*Butyl 4-(2-Hydroxy-1-methylethyl)-3-nitrobenzoate* (**69**). According to *Exper. 18.1*, with **48** (5.52 g, 22 mmol), paraformaldehyde (990 mg, 33 mmol), DMSO (10 ml), *t*BuOK (320 mg, 2.6 mmol), and *t*BuOH (3 ml): 5.5 g (89%) of **69**. Yellow oil. TLC (hexanes/AcOEt 7:3): R_f 0.44. UV (MeOH): 202 (4.14), 226 (4.33), 276 (sh, 3.21), 315 (sh, 2.85). ^{1}H-NMR ($CDCl_3$): 8.27 (*d*, H–C(2)); 7.58 (*dd*, H–C(6)); 7.53 (*d*, H–C(5)); 3.76 (*m*, CH(Me)CH_2); 3.50 (*sext.*, C*H*(Me)CH_2); 1.81 (*t*, OH); 1.57 (s, *t*Bu); 1.31 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_{14}H_{19}NO_5$ (281.3): C 59.78, H 6.81, N 4.98; found: C 59.53, H 6.75, N 4.77.

63. S-*Phenyl 4-(2-Hydroxy-1-methylethyl)-3-nitrobenzenecarbothioate* (**70**). According to *Exper. 53*, with **49** (860 mg, 3 mmol), paraformaldehyde (120 mg, 3.9 mmol), DMSO (10 ml), and *t*BuOK (75 mg, 0.6 mmol): 300 mg (35%) of **70**. Yellow oil. TLC (hexanes/AcOEt 2:1): R_f 0.51. UV (MeOH): 236 (4.13), 323 (sh, 2.68). ^{1}H-NMR ((D_6)DMSO): 8.25 (*dd*, H–C(2)); 8.14 (*d*, H–C(6)); 7.78 (*d*, H–C(5)); 7.52 (*m*, 2 arom. H PhS); 7.35 (*m*, 3 arom. H); 4.82 (*t*, OH); 3.51 (*m*, CH(Me)CH_2); 3.29 (*m*, C*H*(Me)CH_2); 1.22 (*d*, CH(*Me*)CH_2).

64. *4-(2-Hydroxy-1-methylethyl)-3-nitro-*N,N*-diphenylbenzenecarboxamide* (**71**). According to *Exper. 53*, with **50** (1.73 g, 5 mmol), paraformaldehyde (180 mg, 6 mmol), DMSO (10 ml), and *t*BuOK (125 mg, 1 mmol): 530 mg (28%) of **71**. Yellow solid. TLC (CH_2Cl_2/MeOH 24:1): R_f 0.56. ^{1}H-NMR ((D_6)DMSO): 7.81 (*d*, H–C(2)); 7.63 (*dd*, H–C(6)); 7.48 (*d*, H–C(5)); 7.38–7.20 (*m*, Ph_2N); 4.75 (*t*, OH); 3.41 (*m*, CH(Me)CH_2); 3.14 (*sext.*, C*H*(Me)CH_2); 1.13 (*d*, CH(*Me*)CH_2).

65. *4-(2-Hydroxy-1-methylethyl)*-N,N-*diisopropyl-3-nitrobenzenecarboxamide* (**72**). According to *Exper. 53*, with **51** (1.39 g, 5 mmol), paraformaldehyde (180 mg, 6 mmol), DMSO (10 ml), and ^{t}BuOK (125 mg, 1 mmol): 1.49 g (97%) of **72**. Yellow solid. M.p. 104–106°. TLC (hexane/AcOEt 1:1): R_f 0.24. UV (MeOH): 230 (3.96), 288 (sh, 3.15), 326 (sh, 2.80). ^{1}H-NMR ((D$_6$)DMSO): 7.69 (*d*, H–C(2)); 7.63 (*d*, H–C(6)); 7.54 (*dd*, H–C(5)); 4.80 (*t*, OH); 3.60 (br., CH(Me)C*H*$_2$); 3.52 (*t*, 2 Me$_2$C*H*); 3.22 (*sext.*, C*H*(Me)CH$_2$); 1.37–1.13 (br., CH(*Me*)CH$_2$, 2 *Me*$_2$CH). Anal. calc. for $C_{16}H_{24}N_2O_4$ (308.38): C 62.32, H 7.84, N 9.08; found: C 62.36, H 7.66, N 8.94.

66. *4-(2-Hydroxy-1-methylethyl)*-N-*methyl-3-nitro*-N-*phenylbenzenecarboxamide* (**73**). According to *Exper. 53*, with **52** (2.26 g, 5 mmol), paraformaldehyde (180 mg, 6 mmol), DMSO (10 ml), and ^{t}BuOK (125 mg, 1 mmol): 1.43 g (91%) of **73**. Brown oil. TLC (hexane/AcOEt 1:1): R_f 0.26. UV (MeOH): 231 (4.08), 242 (sh 4.04), 314 (sh 3.13). ^{1}H-NMR ((D$_6$)DMSO): 7.64 (*s*, H–C(2)); 7.44 (*s*, H–C(5), H–C(6)); 7.33–7.17 (*m*, PhN); 4.73 (*t*, OH); 3.41 (*m*, CH(Me)C*H*$_2$); 3.37 (*s*, MeN); 3.12 (*sext.*, C*H*(Me)CH$_2$); 1.12 (*d*, CH(*Me*)CH$_2$). Anal. calc. for $C_{17}H_{18}N_2O_4$ (314.35): C 64.96, H 5.77, N 8.91; found: C 64.97, H 5.39, N 8.63.

67. *4-(2-Hydroxy-1-methylethyl)-3-nitrobenzonitrile* (**74**). According to *Exper. 18.1*, with **53** [71] (325 mg, 2 mmol), paraformaldehyde (72 mg, 2.4 mmol), DMSO (5 ml), ^{t}BuOK (60 mg, 0.5 mmol), and ^{t}BuOH (0.5 ml): 190 mg (46%) of **74**. Light yellow solid. M.p. 78–79°. TLC (hexanes/AcOEt 7:3): R_f 0.32. UV (MeOH): 203 (4.20), 224 (4.35), 278 (sh, 3.10). ^{1}H-NMR (CDCl$_3$): 8.03 (*d*, H–C(2)); 7.78 (*dd*, H–C(6)); 7.51 (*d*, H–C(5)); 3.87–3.61 (*m*, CH(Me)C*H*$_2$); 3.57 (*sext.*, C*H*(Me)CH$_2$); 1.69 (br., OH); 1.32 (*d*, CH(*Me*)CH$_2$). Anal. calc. for $C_{10}H_{10}N_2O_3$ (206.2): C 58.25, H 4.89, N 13.59; found: C 58.18, H 4.95, N 13.22.

68. *3-(2-Hydroxy-1-methylethyl)-4-nitrobenzonitrile* (**75**). According to *Exper. 18.1*, with **54** (530 mg, 3 mmol), paraformaldehyde (110 mg, 3.6 mmol), DMSO (5 ml), ^{t}BuOK (90 mg, 0.75 mmol), and ^{t}BuOH (0.75 ml): 140 mg (26%) of **54** and 80 mg (13%) of **75**. Light yellow solid. M.p. 111–112°. TLC (hexanes/AcOEt 7:3): R_f 0.51. UV (MeOH): 203 (4.28), 219 (sh, 4.00), 241 (sh, 3.82), 289 (sh, 3.37), 316 (sh, 2.99). ^{1}H-NMR (CDCl$_3$): 7.83 (*d*, H–C(6)); 7.79 (*d*, H–C(2)); 7.64 (*d*, H–C(6)); 3.84, 3.73 (2*m*, CH(Me)C*H*$_2$); 3.48 (*sext.*, C*H*(Me)CH$_2$); 1.58 (br., OH), 1.33 (d, CH(*Me*)CH$_2$). Anal. calc. for $C_{10}H_{10}N_2O_3$ (206.2): C 58.25, H 4.89, N 13.59; found: C 58.18, H 4.77, N 13.56.

69. tert-*Butyl 3-(2-Hydroxy-1-methylethyl)-4-nitrobenzoate* (**76**). According to *Exper. 18.1*, with **56** (930 mg, 3.7 mmol), paraformaldehyde (170 mg, 5.7 mmol), DMSO (5 ml), ^{t}BuOK (115 mg, 0.9 mmol), and ^{t}BuOH (1 ml): 260 mg (25%) of **76**. Yellow oil. TLC (hexanes/AcOEt 7:3): R_f 0.52. UV (MeOH): 202 (4.35), 220 (sh, 4.05), 244 (sh, 3.90), 282 (sh, 3.51), 326 (sh, 2.06). ^{1}H-NMR (CDCl$_3$): 8.09 (*d*, H–C(2)); 7.91 (*dd*, H–C(6)); 7.71 (*d*, H–C(5)); 3.78 (*m*, CH(Me)C*H*$_2$); 3.48 (*sext.*, C*H*(Me)CH$_2$); OH not visible; 1.59 (*s*, ^{t}Bu); 1.32 (*d*, CH(*Me*)CH$_2$). Anal. calc. for $C_{14}H_{19}NO_5$ (281.3): C 59.78, H 6.81, N 4.98; found: C 59.77, H 6.76, N 4.90.

70. *3-(2-Nitrophenyl)butan-2-one* (**79**). Under Ar and with stirring, Na metal (0.35 g, 0.014 mol) was dissolved in ^{i}PrOH (15 ml) by heating to 80°. The soln. was cooled to r.t., (2-nitrophenyl)acetone (=1-(2-nitrophenyl)propan-2-one; **77**) [6][54] (2.5 g, 0.015 mol) was added, the violet soln. stirred for 10 min, and then MeI (4.0 g, 0.029 mol) was added dropwise (→ brown). After stirring for 30 min, the mixture was evaporated, the residue dissolved in AcOEt (200 ml) and washed several times with H_2O, and the org. layer dried (Na_2SO_4) and evaporated. Purification by CC (AcOEt/hexanes 1:4) gave 1.5 g (52%) of **79**. Syrup. TLC (AcOEt/hexanes 1:4): R_f 0.43. UV (MeOH): 206 (4.13), 257 (3.73), 333 (sh, 2.99). ^{1}H-NMR (CDCl$_3$): 7.92 (*d*, H–C(3)); 7.58 (*t*, H–C(5)); 7.47–7.36 (*m*, 2 arom. H); 4.36 (*q*, MeC*H*); 2.20 (*s*, MeCO); 1.47 (*d*, *Me*CH). Anal. calc. for $C_{10}H_{11}NO_3$ (193.2): C 62.17, H 5.74, N 7.25; found: C 62.42, H 5.59, N 7.62.

71. *3-(2-Nitrophenyl)pentan-2-one* (**80**). According to *Exper. 70*, with EtI (4.8 g, 0.032 mol): 1.42 g (43%) of **80**. Syrup. TLC (AcOEt/hexanes 1:4): R_f 0.59. UV (MeOH): 207 (4.13), 256 (3.67), 332 (sh, 2.83). ^{1}H-NMR (CDCl$_3$): 7.85 (*d*, H–C(3)); 7.57 (*t*, H–C(5)); 7.46–7.36 (*m*, 2 arom. H); 4.18 (*t*, MeCH$_2$C*H*); 2.18 (*s*, MeCO); 2.15–2.04 (*m*, 1 H, CH$_2$); 1.79–1.68 (*m*, 1 H, CH$_2$); 0.84 (*t*, *Me*CH$_2$CH). Anal. calc. for $C_{11}H_{13}NO_3$ (207.2): C 63.76, H 6.32, N 6.76; found: C 63.98, H 6.23, N 6.74.

72. *3-(2-Nitrophenyl)hex-5-en-2-one* (**81**). According to *Exper. 71*, with allyl bromide (5.0 g, 0.035 mol): 2.6 g (85%) of **81**. Syrup. TLC (AcOEt/hexanes 1:4): R_f 0.48. UV (MeOH): 209 (4.10), 256 (3.62), 295 (sh, 3.14), 330 (sh, 2.80). ^{1}H-NMR (CDCl$_3$): 8.09 (*d*, H–C(3)); 7.62 (*t*, H–C(5)); 7.46–7.36 (*m*, 2 arom. H); 5.61 (*m*, CH$_2$=C*H*); 4.96 (*m*, C*H*$_2$=CH); 4.39 (*t*, ArC*H*); 2.86–2.77 (*m*, 1 H, CH$_2$); 2.48 (*m*, 1 H, CH$_2$); 2.18 (*s*, MeCO). Anal. calc. for $C_{12}H_{13}NO_3$ (219.2): C 65.74, H 5.98, N 6.39; found: C 65.68, H 6.05, N 6.22.

73. *2-(2-Nitrophenyl)-1-phenylpropan-1-one* (**82**). To a soln. of 2-(2-nitrophenyl)-1-phenylethanone (**78**) [55] (2.5 g, 0.01 mol) in ^{i}PrOH (5 ml) was added under Ar and with stirring a soln. of Na (0.3 g, 0.013 mol) in ^{i}PrOH (5 ml). After stirring for 10 min, MeI (4.0 g, 0.029 mol) was added dropwise. The mixture was stirred for 30 min and then evaporated, the residue dissolved in AcOEt (200 ml), the soln. washed several times with H_2O, dried (Na_2SO_4), and evaporated, and the residue was purified by CC (AcOEt/hexanes 1:4): 2.56 g (97%) of **82**.

Orange syrup. TLC (AcOEt/hexanes 1:4): R_f 0.69. UV (MeOH): 206 (4.35), 245 (4.19), 276 (sh, 3.65), 332 (sh, 2.86). ^{1}H-NMR ($CDCl_3$): 7.92 (*d*, H–C(3)); 7.66-7.29 (*m,* 8 arom. H); 5.37 (*q*, CH); 1.58 (*d*, Me). Anal. calc. for $C_{15}H_{13}NO_3$ (255.3): C 70.58, H 5.13, N 5.49; found: C 70.65, H 5.16, N 5.51.

74. *2-(2-Nitrophenyl)-1-phenylbutan-1-one* (**83**). According to *Exper. 73*, with EtI (4.5 g, 0.03 mol): 1.73 g (64%) of **83**. Orange syrup. TLC (AcOEt/hexanes 1:4): R_f 0.69. UV (MeOH): 205 (4.36), 245 (4.15), 273 (sh, 3.66), 333 (sh, 2.92). ^{1}H-NMR ($CDCl_3$): 8.00–7.34 (*m,* 9 arom. H); 5.25 (*t*, CH); 2.24 (*m*, 1 H, CH_2); 1.89 (*m*, 1 H, CH_2); 0.05 (*t*, Me). Anal. calc. for $C_{16}H_{17}NO_3$ (271.3): C 71.36, H 5.61, N 5.20; found: C 71.32, H 5.56, N 5.13.

75. *2-(2-Nitrophenyl)-1-phenylpent-4-en-1-one* (**84**). According to *Exper. 73*, with allyl bromide (4.0 g, 0.028 mol): 2.42 g (83%) of **84**. Orange syrup. TLC (AcOEt/hexanes 1:4): R_f 0.54. UV (MeOH): 206 (4.36), 246 (4.18), 277 (sh, 3.66), 331 (sh, 2.98). ^{1}H-NMR ($CDCl_3$): 7.96–7.31 (*m,* 9 arom. H); 5.67 (*m*, CH_2=C*H*); 5.46 (*t*, ArC*H*); 5.01 (*m*, CH_2=CH); 2.89 (*m*, 1 H, CH_2); 2.55 (*m*, 1 H, CH_2). Anal. calc. for $C_{17}H_{15}NO_3$ (281.3): C 72.58, H 4.98, N 5.37; found: C 72.59, H 5.40, N 4.73.

76. *1-(2-Nitrophenyl)propan-2-ol* (**85**). A soln. of **77** (1.79 g, 0.01 mol) in MeOH (12 ml) was treated with $NaBH_4$ (0.57 g, 0.015 mol) under stirring for 30 min. After addition of ice (50 g), a yellow precipitate separated. Purification by recrystallization from EtOH gave 1.18 g (65%) of **85**. Yellow crystals: M.p. 45–46°. TLC ($CHCl_3$/MeOH 9:1): R_f 0.66. UV (MeOH): 206 (4.06), 258 (3.64), 332 (sh, 2.77). ^{1}H-NMR ($CDCl_3$): 7.91 (*d*, H–C(3)); 7.58 (*t*, H–C(5)); 7.43–7.23 (*m*, 2 arom. H); 4.11 (*dd*, Me*CH*); 3.15 (*m*, 1 H, CH_2); 2.96 *(m*, 1 H, CH_2); 1.62 (br., OH); 1.30 (*d*, *Me*CH). Anal. calc. for $C_9H_{11}NO_3$ (181.2): C 59.66, H 6.12, N 7.73; found: C 59.71, H 5.99, N 7.62.

77. *2-(2-Nitrophenyl)-1-phenylethanol* (**86**). According to *Exper. 76*, with **78** (2.41 g, 0.01 mol): 2.3 g (94%) of **86**. Yellowish crystals. M.p. 70–72°. TLC ($CHCl_3$/MeOH 9:1): R_f 0.63. UV (MeOH): 208 (4.26), 257 (3.65), 333 (sh, 2.77). ^{1}H-NMR ($CDCl_3$): 7.94 (*d*, H–C(3)); 7.50 (*t*, H–C(5)); 7.43–7.31 (*m*, 7 arom. H); 5.03 (*dd*, CH); 3.40 (*m*, 1 H, CH_2); 3.22 (*m*, 1 H, CH_2); 1.98 (br., OH). Anal. calc. for $C_{14}H_{13}NO_3$ (243.3): C 69.12, H 5.39, N 5.76; found: C 69.09, H 5.28, N 5.74.

78. *3-(2-Nitrophenyl)butan-2-ol* (**87**). According to *Exper. 76*, with **79** (1.93 g, 0.01 mol). After addition of ice, the resulting oil was extracted with AcOEt. The org. phase was dried (Na_2SO_4) and evaporated, and the residue was purified by CC ($CHCl_3$/MeOH 9:1): 1.74 g (89%) of **87**. Orange syrup. TLC ($CHCl_3$/MeOH 9:1): R_f 0.64. UV (MeOH): 206 (4.09), 255 (3.60), 332 (sh, 2.93). ^{1}H-NMR ($CDCl_3$): 7.72 (*m*, H *o* to NO_2); 7.58–7.33 (*m*, 3 H, arom. H); 4.01–3.86 (*m*, C*H*OH); 3.28 (*q*, ArC*H*); 1.31 (*d*, *Me*CHOH); 1.26 (*d*, *Me*CHAr). Anal. calc. for $C_{10}H_{13}NO_3$ (195.2): C 61.53, H 6.71, N 7.17; found: C 61.65, H 6.35, N 7.69.

79. *3-(2-Nitrophenyl)pentan-2-ol* (**88**). According to *Exper. 78*, with **80** (2.07 g, 0.01 mol): 1.78 g (85%) of **88**. Orange syrup. TLC (AcOEt/hexanes 1:4): R_f 0.64. UV (MeOH): 206 (4.15), 258 (3.60), 332 (sh, 2.82). ^{1}H-NMR ($CDCl_3$): 7.65 (*d*, H *o* to NO_2); 7.55–7.30 (*m*, 3 arom. H); 3.96 (*m*, C*H*OH); 3.18–3.01 (*q*, ArC*H*); 1.85–1.64 (*m*, EtCH_2); 1.19 (*d*, *Me*CHOH); 0.74 (*d*, *Me*CH_2). Anal. calc. for $C_{10}H_{13}NO_3$ (209.2): C 63.14, H 7.23, N 6.68; found: C 63.44, H 7.07, N 6.86.

80. *3-(2-Nitrophenyl)hex-5-en-2-ol* (**89**). According to *Exper. 78*, with **81** (2.19 g, 0.01 mol): 1.94 g (88%) of **89**. Orange syrup. TLC (AcOEt/hexanes 1:4): R_f 0.20. UV (MeOH): 206 (4.08), 255 (3.53), 333 (sh, 2.78). ^{1}H-NMR ($CDCl_3$): 7.68–7.29 (*m,* 4 arom. H); 5.65–5.51 (*m*, CH_2=C*H*); 4.93 (m, 2 CH_2=CH); 4.03 (*m*, C*H*OH); 3.27 (*m*, ArC*H*); 2.60–2.44 (*m*, CH_2); 1.15 (*d*, *Me*CHOH). Anal. calc. for $C_{12}H_{15}NO_3$ (221.2): C 65.14, H 6.83, N 6.33; found: C 65.40, H 6.71, N 6.23.

81. *2-(2-Nitrophenyl)-1-phenylpropan-1-ol* (**90**). According to *Exper. 78*, with **82** (2.55 g, 0.01 mol): 2.05 g (80%) of **90**. Orange syrup. TLC ($CHCl_3$/MeOH 9:1): R_f 0.66. UV (MeOH): 207 (4.31), 248 (3.59), 333 (sh, 2.94). ^{1}H-NMR ($CDCl_3$): 7.73 (*m*, H *o* to NO_2); 7.68–7.30 (*m,* 8 arom. H); 4.68 (*m*, C*H*OH); 3.75 (*m*, MeC*H*); 1.15 (*d*, *Me*CH). Anal. calc. for $C_{15}H_{15}NO_3$ (257.3): C 70.02, H 5.88, N 5.44; found: C 70.00, H 5.97, N 5.25.

82. *2-(2-Nitrophenyl)-1-phenylbutan-1-ol* (**91**). According to *Exper. 78*, with **83** (2.69 g, 0.01 mol): 2.33 g (86%) of **91**. Orange syrup. TLC (AcOEt/hexanes 1:4): R_f 0.32. UV (MeOH): 206 (4.32), 251 (3.62), 281 (sh, 3.41), 333 (sh, 3.05). ^{1}H-NMR ($CDCl_3$): 7.68–7.28 (*m,* 9 arom. H); 4.85 (*m*, C*H*OH); 3.60–3.40 (*m*, ArC*H*); 1.60–1.19 (*m*, OH, CH_2); 0.65 (*t*, *Me*CH_2). Anal. calc. for $C_{16}H_{17}NO_3$ (271.3): C 70.83, H 6.32, N 5.16; found: C 70.68, H 6.31, N 4.96.

83. *2-(2-Nitrophenyl)-1-phenylpent-4-en-1-ol* (**92**). According to *Exper. 78*, with **84** (2.81 g, 0.01 mol): 2.52 g (89%) of **92**. Orange syrup. TLC (AcOEt/hexanes 1:4): R_f 0.29. UV (MeOH): 207 (4.35), 251 (3.71), 288 (sh, 3.44), 333 (sh, 2.96). ^{1}H-NMR ($CDCl_3$): 7.68–7.25 (*m,* 9 arom. H); 5.54 (*m*, CH_2=C*H*); 4.91–4.77 (*m*, C*H*OH, CH_2=CH); 3.79 (*m*, ArC*H*); 2.41 (*m*, CH_2). Anal. calc. for $C_{16}H_{17}NO_3$ (283.3): C 72.07, H 6.05, N 4.94; found: C 72.22, H 5.75, N 4.93.

84. *Cyclopentanol* **95**: *(1*RS,*2*RS*)-2-(2,4-Dinitrophenyl)cyclopentanol* (**97**) *and (1*RS,*2*SR*)-2-(2,4-Dinitrophenyl)cyclopentanol* (**98**). $NaBH_4$ (1.33 g, 35 mmol) was added slowly to a suspension of 2-(2,4-dinitrophenyl)cyclopentanone (**93**) [56] (2 g, 8 mmol) in MeOH (50 ml), so that the temp. was kept below 25°. After stirring for 3 h at r.t., the mixture was acidified with conc. HCl soln. (pH 2) and evaporated. The residue (20 ml) was dissolved in H_2O (50 ml) and extracted with CH_2Cl_2 (2 × 40 ml). The combined org. layer was dried (Na_2SO_4) and evaporated, and the crude product purified by CC (SiO_2 (62 g), 4 × 16 cm; hexanes/AcOEt, 6:1 → 2:1): 370 mg (18%) of **97** and 800 mg (39%) of **98** as yellow oils.

Data of **97**: TLC (hexanes/AcOEt 7:3): R_f 0.46. UV (MeOH): 206 (4.12), 253 (4.05), 323 (sh, 2.95). ^{1}H-NMR ((D$_6$)DMSO): 8.63 (*d*, H–C(3′)); 8.41 (*dd*, H–C(5′)); 7.89 (*d*, H–C(6′)); 4.67 (br., OH); 4.19 (*s*, H–C(1)); 3.25 (*m*, H–C(2)); 2.05 (*m*, 1 H–C(3)); 1.94 (*m*, 1 H–C(5)); 1.91 (*m*, 1 H–C(4)); 1.89 (*m*, 1 H–C(3)); 1.65 (*m*, 1 H–C(5)); 1.64 (*m*, 1 H–C(4)). ^{13}C-NMR ((D$_6$)DMSO): 150.27, 145.55, 142.31 (C(2′), C(4′), C(1′)); 132.81 (C(6′)); 125.51 (C(5′)); 118.56 (C(3′)); 73.30 (C(1)); 45.92 (C(2)); 35.14 (C(5)); 29.12 (C(3)); 21.97 (C(4)).

Data of **98**: TLC (hexanes/AcOEt 7:3): R_f 0.31. UV (MeOH): 207 (4.11), 262 (4.02), 322 (sh, 3.03). ^{1}H-NMR ((D$_6$)DMSO): 8.62 (*d*, H–C(3′)); 8.42 (*dd*, H–C(5′)); 7.91 (*d*, H–C(6′)); 4.92 (*d*, OH), 4.12 (*m*, H–C(1)); 3.26 (*m*, H–C(2)); 2.14 (*m*, 1 H–C(3)); 1.98 (*m*, 1 H–C(5)); 1.77 (*m*, CH_2(4)); 1.64 (*m*, 1 H–C(3)); 1.55 (*m*, 1 H–C(5)). ^{13}C-NMR ((D$_6$)DMSO): 150.51, 145.53, 145.08 (C(2′), C(4′), C(1′)); 130.21 (C(6′)); 126.71 (C(5′)); 118.89 (C(3′)); 78.56 (C(1)); 48.51 (C(2)); 34.14 (C(5)); 31.90 (C(3)); 21.53 (C(4)). Anal. calc. for $C_{11}H_{12}N_2O_5$ (257.2): C 52.38, H 4.80, N 11.11; found: C 52.39, H 4.87, N 11.13.

85. *2-(2,4-Dinitrophenyl)cyclohexanol* (**96**). According to *Exper. 84*, with 2-(2,4-dinitrophenyl)cyclohexanone (**94**) [56] (2 g, 7.6 mmol), $NaBH_4$ (1.25 g, 33 mmol), and MeOH (50 ml). Purification by CC (SiO_2 (54 g), 3.5 × 14 cm; hexanes/AcOEt, 8:1 → 3:1) gave 1.13 g (56%) of **96**. Yellow oil. TLC (hexanes/AcOEt 7:3): R_f 0.45. UV (MeOH): 203 (4.13), 248 (4.04), 314 (sh, 3.05). ^{1}H-NMR ((D$_6$)DMSO): 8.59 (*d*, H–C(3′)); 8.43 (*dd*, H–C(5′)); 7.95 (*d*, H–C(6′)); 4.66 (*d*, OH); 3.58 (*m*, CH (chx)); 2.58 (*m*, CH (chx)); 1.98–1.13 (*m*, 8 CH (chx)). Anal. calc. for $C_{12}H_{14}N_2O_5 \cdot 0.24\ C_4H_8O_2$ (AcOEt) (288.3): C 54.16, H 5.59, N 9.72; found: C 53.94, H 5.88, N 9.62.

86. *(1,2,3,4-Tetrahydro-8-nitro-naphthalen-1-yl)methanol* (**99**) [57]. According to *Exper. 18.1*, with a 1.5:1 mixture of 1,2,3,4-tetrahydro-5-nitro- and 1,2,3,4-tetrahydro-6-nitronaphthalene [72], paraformaldehyde (450 mg, 15 mmol), DMSO (10 ml), ^{t}BuOK (370 mg, 3 mmol), and ^{t}BuOH (3 ml): 960 mg (31%) of **99**. Red oil. TLC (hexanes/AcOEt 7:3): R_f 0.52. UV (MeOH): 207 (4.15), 263 (3.56), 294 (sh, 3.30), 332 (sh, 2.94). ^{1}H-NMR ((D$_6$)DMSO): 7.57 (*d*, H–C(7)); 7.38 (*d*, H–C(5)); 7.30 (*d*, H–C(6)); 4.85 (br., CH_2O*H*); 3.50 (*m*, H–C(1)); 3.35, 3.29 (2*m*, C*H*$_2$OH); 2.84 (*m*, H–C(4)); 2.76 (*m*, H–C(4)); 2.03 (*m*, H–C(2)); 1.77 (*m*, H–C(3)): 1.64 (*m*, H–C(2), H–C(3)). ^{13}C-NMR ((D$_6$)DMSO): 151.06 (C(8)); 140.08 (C(4a)); 133.40 (C(5)); 130.78 (C(8a)); 126.50 (C(6)); 121.60 (C(7)); 68.85 (*C*H$_2$OH); 34.83 (C(1)); 28.95 (C(4)); 22.85 (C(2)); 17.08 (C(3)).

87. *2-Methyl-1-nitronaphthalene* (**100**) [73]. A soln. of 2-methylnaphthalene (14.2 g, 0.1 mol) in AcOH (50 ml) was cooled to 10°. Then, under stirring, fuming HNO_3 (8 ml) was added dropwise. After 2 h, the soln. was diluted with H_2O (150 ml) and then extracted with CH_2Cl_2 (150 ml). The org. phase was washed with $NaHCO_3$ soln. (foaming), dried (Na_2SO_4), and evaporated. The residue was recrystallized from MeOH (20 ml): 13.0 g (68%) of **100**. Yellow needles. M.p. 79–80° ([73]: 80–81°). TLC (Et_2O): R_f 0.63. UV (MeOH): 220 (4.76), 265 (4.02), 317 (sh, 3.53), 344 (sh, 3.31). ^{1}H-NMR ($CDCl_3$): 7.86 (*m*, H–C(4), H–C(5)); 7.70 (*d*, H–C(8)); 7.61-7.50 (*m*, H–C(6), H–C(7)); 7.37 (*d*, H–C(3)); 2.47 (*s*, Me).

88. *2-Ethyl-1-nitronaphthalene* (**101**) [74]. According to *Exper. 87*, with 2-ethylnaphthalene (5 g) and fuming HNO_3 (3 ml). CC (SiO_2; AcOEt/hexanes 1:8) gave 5.66 g (88%) of **101**. Yellow syrup. TLC (AcOEt/hexanes 1:4): R_f 0.51. UV (MeOH): 221 (4.74), 265 (4.04), 316 (sh, 3.50), 345 (sh, 3.28). ^{1}H-NMR ($CDCl_3$): 7.79 (*m*, H–C(4), H–C(5)); 7.70 (*d*, H–C(8)); 7.48 (*m*, H–C(6), H–C(7)); 7.38 (*d*, H–C(3)); 2.75 (*q*, MeC*H*$_2$); 1.30 (*t*, *Me*CH$_2$).

89. *2-(1-Nitronaphthalen-2-yl)ethanol* (**102**). A soln. of **100** (5.5 g, 30.4 mmol) and paraformadehyde (8.87 g, 30.4 mmol) in DMSO (150 ml) was treated with ^{t}BuOK (1.3 g) in ^{t}BuOH (15 ml) for 15 min at r.t. and then for 2 h at 80°. After cooling, the mixture was neutralized with HCl, diluted with H_2O (200 ml), and extracted with AcOEt (3 × 150 ml). The org. phase was dried (Na_2SO_4) and evaporated, and the resulting syrup was purified by CC (SiO_2; AcOEt/hexanes 1:4). The residue of the main fraction was recrystallized from EtOH: 5.4 g (85%) of **102**. Yellow crystals. M.p. 117–118°. TLC (AcOEt/hexanes 1:4): R_f 0.11. UV (MeOH): 221 (4.81), 266 (4.04), 287 (sh, 3.84), 314 (sh, 3.48), 3.44 (sh, 3.31). ^{1}H-NMR ($CDCl_3$): 7.88 (*m*, H–C(4), H–C(5)); 7.61 (*d*, H–C(8)); 7.56 (*m*, H–C(5), H–C(7)); 7.46 (*d*, H–C(3)); 3.79 (*t*, C*H*$_2$OH); 3.03 (*t*, CH_2); 1.64 (*t*, OH). Anal. calc. for $C_{12}H_{11}NO_3$ (217.2): C 66.35, H 5.10, N 6.45; found: C 66.43, H 5.20, N 6.47.

90. *2-(1-Nitronaphthalen-2-yl)propan-1-ol* (**103**). According to *Exper. 89*, with **101** (2.0 g, 10 mmol), paraformaldehyde (4,0 g, 0.13 mol), ^{t}BuOK (0.45 g, 0.33 mmol), and DMSO (15 ml) at 80° for 48 h. 1.4 g (61%) of **103**. Brownish syrup. TLC (Et_2O): R_f 0.42. UV (MeOH): 223 (4.79), 266 (4.00), 284 (sh, 3.80), 315 (sh, 3.45), 359 (sh, 3.21). ^{1}H-NMR ($CDCl_3$): 7.96 (*d,* H–C(5)); 7.88 (*d*, H–C(8)); 7.70–7.54 (*m*, 3 arom. H); 3.85 (*t*, CH_2OH); 3.18 (*m*, MeC*H*); 1.64 (*s*, OH); 1.39 (*d*, *Me*CH).

91. *1-Methyl-8-nitronaphthalene* (**104**). According to [74]. M.p. 63–65°. ^{1}H-NMR ($CDCl_3$): 7.98 (*d*, H–C(5)); 7.77 (*d*, H–C(4)); 7.62 (*d*, H–C(7)); 7.46 (*m*, H–C(2), H–C(3), H–C(6)); 2.53 (*s*, Me).

92. *2-(8-Nitronaphthalen-1-yl)ethanol* (**105**). Protecting gas was used until to the addition of $BF_3 \cdot Et_2O$. To a suspension of $NaBH_4$ (363 mg, 9.6 mmol) in diglyme (5 ml) was added under cooling (8-nitronaphthalen-1-yl)acetic acid (**106**) [58] (734 mg, 3.2 mmol). After stirring for 10 min in the ice-bath, $BF_3 \cdot Et_2O$ (2.4 ml, 19 mmol) in diglyme (5 ml) was dropped slowly to the mixture. After stirring for 90 min at r.t., the mixture was cooled to 0° again, $BF_3 \cdot Et_2O$ (1.2 ml, 9.6 mmol) in diglyme (5 ml) was added, and the mixture was stirred for 1 h at r.t. The mixture was poured on ice and extracted with AcOEt (3 × 50 ml), the combined org. phase washed with ice water (5 ×) to remove the diglyme, dried (Na_2SO_4), and evaporated, and the crude product purified by CC (SiO_2 (22 g), 2.5 × 15 cm; toluene/AcOEt 9:1): 552 mg (79%) of **105**. Yellow solid. M.p. 53–54°. TLC (hexanes/AcOEt 1:1): R_f 0.62. UV (MeOH): 209 (sh, 4.50), 220 (4.72), 246 (sh, 3.69), 343 (sh, 3.17). ^{1}H-NMR ($CDCl_3$): 8.01 (*dd*, 1 arom. H); 7.83 (*dd*, 1 arom. H); 7.65–7.43 (*m*, 4 arom. H); 3.86 (*t*, CH_2CH_2OH); 3.07 (*t*, CH_2CH_2OH); 1.51 (*s*, CH_2CH_2O*H*). Anal. calc. for $C_{12}H_{11}NO_3$ (217.2): C 66.35, H 5.10, N 6.45; found: C 66.33, H 5.14, N 6.42.

93. *1-(8-Nitronaphthalen-1-yl)ethanol* (**108**). $NaBH_4$ (450 mg, 13 mmol) was added slowly to a suspension of 1-(8-nitronaphthalen-1-yl)ethanone (**107**) [59] (500 mg, 2.3 mmol) in MeOH (40 ml). After stirring overnight at r.t., $NaBH_4$ (450 mg, 13 mmol) was added. After stirring for 3 days at r.t., the mixture was acidified with 2N HCl and evaporated. The residue (20 ml) was dissolved in H_2O (25 ml) and extracted with Et_2O (2 × 25 ml), the combined org. phase dried (Na_2SO_4) and evaporated, and the crude product purified by CC (SiO_2 (22 g), 2 × 14 cm; hexanes → hexanes/AcOEt 3:7): 245 mg (49%) of **108**. Brown solid. M.p. 70–73°. TLC (hexanes/AcOEt 4:1): R_f 0.37. UV (MeOH): 209 (sh, 4.50), 221 (4.71), 238 (sh, 3.81), 282 (sh, 3.54), 335 (sh, 3.26). ^{1}H-NMR ($CDCl_3$): 8.03 (*dd*, 1 arom. H); 7.97 (*dd*, 1 arom. H); 7.86 (*dd*, 1 arom. H); 7.77 (*dd*, 1 arom. H); 7.63 (*t*, 1 arom. H); 7.46 (*t*, 1 arom. H); 5.21 (*q*, CH); 2.05 (br., OH); 1.55 (*d*, Me). Anal. calc. for $C_{12}H_{11}NO_3$ (217.2): C 66.35, H 5.10, N 6.45; found: C 66.85, H 5.23, N 6.18.

94. *(8-Nitronaphthalene-1-yl)methanol* (**110**) [60] *and (5-Nitronaphthalen-1-yl)methanol*. Under Ar and under cooling, 8-nitronaphthalene-1-carboxylic acid (**109**)/5-nitronaphthalene-1-carboxylic acid 5:1 [75] (7.1 g, 33 mmol) was added to a suspension of $NaBH_4$ (1.9 g, 50 mmol) in diglyme (55 ml). $BF_3 \cdot Et_2O$ (10 ml, 80 mmol) in diglyme (15 ml) was dropped slowly during 3 h to the mixture. After stirring for 2 h at r.t., the mixture was poured on ice and extracted with AcOEt (3 × 100 ml). The combined org. phase was washed with ice water (5 × 70 ml) to remove the diglyme and sat. $NaHCO_3$ soln. (2 × 50 ml), dried (Na_2SO_4), and evaporated, and the crude product was purified by CC (SiO_2 (60 g), 4 × 14 cm; toluene/AcOEt 9:1): 3.57 g (53%) of **110** and 920 mg (14%) of (5-nitronaphthalen-1-yl)methanol as yellow solids.

Data of **110**: M.p. 63–65° ([60]: 72–73°). TLC (CH_2Cl_2/MeOH 10:1): R_f 0.73. UV (MeOH): 218 (4.63), 240 (sh, 3.87), 288 (3.47). ^{1}H-NMR ((D_6)DMSO): 8.28 (*d*, 1 arom. H); 8.04 (*t*, 2 arom. H); 7.82 (*d*, 1 arom. H); 7.64 (*q*, 2 arom. H); 5.29 (*t*, CH_2O*H*); 4.75 (*d*, CH_2OH).

Data of (5-Nitronaphthalen-1-yl)methanol: M.p. 119–120°. TLC (CH_2Cl_2/MeOH 10:1): R_f 0.63. UV (MeOH): 209 (sh, 4.51), 216 (4.59), 244 (sh 3.85), 332 (3.50). ^{1}H-NMR ((D_6)DMSO): 8.48 (*d*, 1 arom. H); 8.24 (*d*, 1 arom. H); 8.18 (*dd*, 1 arom. H); 7.73 (*m*, 3 arom. H); 5.50 (*t*, CH_2O*H*); 5.01 (*d*, CH_2OH). Anal. calc. for $C_{11}H_9NO_3$ (203.2): C 65.02, H 4.46, N 6.89; found: C 64.85, H 4.40, N 6.77.

95. *(1-Nitronaphthalen-2-yl)methanol* (**113**). A soln. of 2-methyl-1-nitronaphthalene (**100**; 5.53 g, 0.03 mol) in CCl_4 (40 ml) was treated with *N*-bromosuccinimide (5.25 g, 0.03 mol) by heating to 80° and then with dibenzoyl peroxide (10 mg). The reaction was complete after 5 h reflux. The mixture was cooled to filter off the precipitate of succinimide. The filtrate was evaporated, yielding crude 2-(bromomethyl)-1-nitronaphthalene (**111**), which was used without further purification in the next step. A mixture of **111** and AcOK (6.3 g) in AcOH (100 ml) refluxed for 2 h. After stirring at r.t. overnight followed by evaporation, the crude syrupy acetate **112** was dissolved in EtOH (50 ml), 1N NaOH (200 ml) was added, and the mixture was stirred overnight at r.t. Then the soln. was extracted with CH_2Cl_2 (3 × 50 ml), the org. phase dried (Na_2SO_4) and evaporated, and the residue purified by CC (SiO_2; AcOEt/hexanes 1:4): 0.83 g (14%) of **113**, which crystallized on treatment with EtOH. Yellowish crystals. M.p. 170–171°.

96. *(3-Nitronaphthalen-2-yl)methanol* (**114**). According to [61].

97. *(3-Nitro-2-thienyl)methanol* (**115**) [62]. To cold Ac_2O (50 ml) was added dropwise fuming HNO_3 (25 ml). This soln. was then added slowly (40 min) to (2-thienyl)methyl acetate in Ac_2O (120 ml, $-10°$). The mixture was stirred for 3.5 h at $-20°$ to 0°, then 1 h at r.t., and afterwards poured onto ice. After extraction with Et_2O (2×200 ml), the org. phase was washed with H_2O (2×250 ml), treated with $NaHCO_3$, again washed with H_2O, dried ($CaCl_2$), and evaporated to give a mixture of (3-nitro-2-thienyl)methyl and (5-nitro-2-thienyl)methyl acetate (53.1 g, 70%). The mixture was refluxed in 10% H_2SO_4 soln. (950 ml) for 75 min, treated hot with charcoal, filtered, and after cooling extracted with Et_2O (4×200 ml). The org. phase was washed with sat. $NaHCO_3$ soln., dried ($CaCl_2$), and evaporated and the dark syrup (38 g) purified by CC (SiO_2; toluene → toluene/AcOEt 10:1): 26.7 g (65%) of (5-nitro-2-thienyl)methanol and 3.7 g (9%) of **115**. **115**: M.p. 65–66° ([62]: 71–72°), after recrystallization from Et_2O/hexanes 1:1. TLC (toluene/AcOEt 3:1): R_f 0.50. UV (MeOH): 212 (4.18), 222 (sh, 4.05), 267 (3.98), 299 (sh, 3.64). ^{1}H-NMR ($CDCl_3$): 7.58 (*d*, H–C(4)); 7.18 (*d*, H–C(5)); 5.16 (*s*, C*H*$_2$OH); 2.81 (br., CH$_2$O*H*).

98. *2-(3-Nitro-2-thienyl)propan-1-ol* (**118**) [63]. According to *Exper. 18.1*, with 2-ethyl-3-nitrothiophene (**116**) [63] (2 g, 13 mmol), paraformaldehyde (382 mg, 13 mmol), DMSO (15 ml), *t*BuOK (150 mg, 1.3 mmol), and *t*BuOH (4 ml): 1.94 g (80%) of **118**. Yellow oil. TLC (hexanes/AcOEt 7:3): R_f 0.32. UV (MeOH): 216 (4.06), 272 (3.83), 295 (sh, 3.61). ^{1}H-NMR ($CDCl_3$): 7.55 (*d*, 1 arom. H); 7.13 (*d*, 1 arom. H); 4.21 (*sext.*, C*H*(Me)CH$_2$); 3.79 (*d*, CH(Me)C*H*$_2$); 1.78 (br., OH); 1.39 (*d*, CH(*Me*)CH$_2$).

99. *2-(3-Nitro-2-thienyl)ethanol* (**120**) *and 2-(3-Nitro-2-thienyl)-propane-1,3-diol.* According to *Exper. 18.1* with 2-methyl-3-nitrothiophene (**119**) [64] (4 g, 28 mmol), paraformaldehyde (840 mg, 28 mmol), DMSO (30 ml), *t*BuOK (160 mg, 1.4 mmol), and *t*BuOH (4 ml) for 15 min at 70°: 1.08 g (27%) of **119**, 1.72 g (35%) of **120**, and 1.48 g (26%) of the propanediol.

Data of **120**: Red-yellow oil. TLC (hexanes/AcOEt 1:1): R_f 0.86. UV (MeOH): 216 (4.09), 272 (3.87), 301 (sh, 3.56). ^{1}H-NMR ($CDCl_3$): 7.57 (*d*, 1 arom. H); 7.10 (*d*, 1 arom. H); 3.96 (*t*, CH$_2$C*H*$_2$O); 3.46 (*t*, C*H*$_2$CH$_2$O); 1.78 (br., OH). Anal. calc. for $C_6H_7NO_3S$ (173.2): C 41.61, H 4.07, N 8.09; found: C 41.61, H 4.27, N 8.10.

2-(3-Nitro-2-thienyl)propane-1,3-diol: Colorless solid. M.p. 66–68°. TLC (hexanes/AcOEt 1:1): R_f 0.32. UV (MeOH): 217 (4.07), 274 (3.83), 298 (sh, 3.60). ^{1}H-NMR ($CDCl_3$): 7.60 (*d*, 1 arom. H); 7.18 (*d*, 1 arom. H); 4.34 (*m*, C*H*(CH$_2$OH)$_2$); 4.11 (*m*, CH(C*H*$_2$OH)$_2$); 3.99 (*m*, CH(C*H*$_2$OH)$_2$); 2.20 (br., 2 OH). Anal. calc. for $C_7H_9NO_4S$ (203.2): C 41.37, H 4.46, N 6.86; found: C 41.42, H 4.58, N 6.80.

100. *2-(2-Nitrobenzo[*b*]thien-3-yl)ethanol* (**121**). According to *Exper. 18.1*, with 3-methyl-2-nitrobenzo[*b*]-thiophene (**122**) [65] (1 g, 5 mmol), paraformaldehyde (155 mg, 5 mmol), DMSO (20 ml), *t*BuOK (58 mg, 0.5 mmol), and *t*BuOH (3 ml) for 1 h at 80°: 655 mg (58%) of **121**. Yellow-brown solid. M.p. 106–107°. TLC (hexanes/AcOEt 4:1): R_f 0.13. UV (MeOH): 212 (4.14), 237 (sh, 4.02), 330 (4.13). ^{1}H-NMR ($CDCl_3$): 7.98 (*dd*, 1 arom. H); 7.80 (*dd*, 1 arom. H); 7.61–7.46 (*m*, 2 arom. H); 4.01 (*t*, CH$_2$C*H*$_2$O); 3.62 (*t*, C*H*$_2$CH$_2$O); 1.66 (br., OH). Anal. calc. for $C_{10}H_9NO_3S$ (223.3): C 53.80, H 4.06, N 6.27; found: C 54.04, H 4.09, N 6.37.

101. *5′-Protected Thymidine Derivatives: General Procedure.* To a cold soln. (0°) of diphosgene (6 mmol) in dry THF (8 ml) was added the appropriate alcohol (5 mmol) and Et_3N (5 mmol) in dry THF (8 ml). After stirring for 1 h at 0°, the mixture was filtered and the filtrate evaporated to give the corresponding alkyl carbonochloridate in approximately quantitative yield.

Thymidine (1 mmol) was co-evaporated with dry pyridine (3×3 ml) and then dissolved in dry pyridine (3 ml). The soln. was cooled to $-40°$, then a soln. of the alkyl carbonochloridate (1.35 mmol) in dry CH_2Cl_2 (3 ml) was added dropwise, and after stirring for 5 h at -50 to $-20°$, the mixture was diluted with H_2O (10 ml) and extracted with CH_2Cl_2 (3×10 ml). The org. phase was dried (Na_2SO_4) and evaporated, and the residue co-evaporated with toluene (3×10 ml) and purified by CC (SiO_2 (20 g), 2×14 cm; CH_2Cl_2, then CH_2Cl_2/MeOH 100:1, 100:2, 100:3, 100:3.5 and 100:4 (100 ml each)). The products eluted in the order thymidine 3′,5′-dicarbonate, 3′-carbonate, and 5′-carbonate. The fractions were evaporated and the resulting solid foams dried at 35° *in vacuo*.

102. *Thymidine 5′-[2-(2-Nitrophenyl)propyl Carbonate]* (**123**), *3′-[2-(2-Nitrophenyl)propyl Carbonate]* (**179**), *and 3′,5′-Bis[2-(2-nitrophenyl)propyl Carbonate]* (**180**). According to *Exper. 101*, with thymidine (0.242 g, 1 mmol): 0.359 g (80%) of **123**, 9 mg (2%) of **179**, and 92 mg (14%) of **180** as yellow solid foams.

Data of **123**: TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.31. UV (MeOH): 206 (4.37), 263 (4.05), 332 (sh, 2.75). ^{1}H-NMR ($CDCl_3$): 8.66, 8.64 (2*s*, 1 H, NH, diastereoisomers); 7.77 (*m*, 1 arom. H); 7.59 (*m*, 1 arom. H); 7.43 (*m*, 2 arom. H); 7.33, 7.30 (2*s*, 1 H, H–C(6)); 6.31 (*m*, H–C(1′)); 4.49–4.09 (*m*, H–C(3′), H–C(4′), CH$_2$(5′)), CH(Me)C*H*$_2$,); 3.80 (*m*, C*H*(Me)CH$_2$); 2.61 (2*d*, OH–C(3′)); 2.39 (*m*, 1 H–C(2′)); 2.18 (*m*, 1 H–C(2′)); 1.75 (2*s*, Me–C(5)); 1.38 (2*d*, CH(*Me*)CH$_2$). Anal. calc. for $C_{20}H_{23}N_3O_9$ (449.4): C 53.45, H 5.16, N 9.35; found: C 53.14, H 5.21, N 9.16.

Data of **179**: TLC (toluene/AcOEt/MeOH 5 : 4 : 1): R_f 0.38. UV (MeOH): 206 (4.26), 262 (4.03), 329 (sh, 2.75). ^{1}H-NMR ($CDCl_3$): 8.18 (br., NH); 7.81 (*m*, 1 arom. H); 7.61 (*m*, 1 arom. H), 7.44 (*m*, 2 arom. H, H–C(6)); 6.15 (*m*, H–C(1′)); 5.25 (*m*, H–C(3′)); 4.33 (*m*, CH(Me)CH_2,); 4.14 (*m*, H–C(4′)); 3.90 (*m*, CH_2(5′)); 3.78 (*m*, C*H*(Me)CH_2); 2.44 (*m*, CH_2(2′), OH–C(5′)); 1.93 (*s*, Me–C(5)); 1.38 (*m*, CH(*Me*)CH_2). Anal. calc. for $C_{20}H_{23}N_3O_9$ (449.4): C 53.45, H 5.16, N 9.35; found: C 53.43, H 5.24, N9.01.

Data of **180**: TLC (toluene/AcOEt/MeOH 5 : 4 : 1): R_f 0.68. UV (MeOH): 205 (4.50), 259 (4.22), 333 (sh, 3.29); ^{1}H-NMR ($CDCl_3$): 8.32 (*s*, NH); 7.80 (*m*, 2 arom. H); 7.61 (*m*, 2 arom. H); 7.45 (*m*, 4 arom. H); 7.30 (*m*, H–C(6)); 6.36 (*m*, H–C(1′)); 5.13 (*m*, H–C(3′)), 4.48–4.17 (*m*, H–C(4′), 2 CH(Me)CH_2, CH_2(5′)); 3.80 (*m*, 2 C*H*(Me)CH_2); 2.49 (*m*, 1 H–C(2′)); 2.22 (*m*, 1 H–C(2′)), 1.87, 1.77 (2*s*, Me–C(5)); 1.40 (*d*, 2 CH(*Me*)CH_2). Anal. calc. for $C_{30}H_{32}N_4O_{13}$ (656.6): C 54.88, H 4.91, N 8.53; found: C 54.91, H 5.01, N 8.28.

103. *Thymidine 5′-[2-(4-Chloro-2-nitrophenyl)propyl carbonate]* (**124**). According to *Exper. 101*, with **23**: 0.344 g (71%) of **124**. Colorless foam. TLC (toluene/AcOEt/MeOH 5 : 4 : 1): R_f 0.41. UV (MeOH): 206 (sh, 4.37), 212 (4.43), 263 (4.05), 332 (sh, 2.75). ^{1}H-NMR ($CDCl_3$): 8.75 (br., NH); 7.77 (*d*, arom. H–C(3″)); 7.54 (*dd*, H–C(5″)); 7.39 (*d*, H–C(6″)); 7.27 (*dd*, H–C(6)); 6.29 (*m*, H–C(1′)); 4.46–4.07 (*m*, CH(Me)CH_2, H–C(3′), H–C(4′), CH_2(5′)); 3.74 (*m*, C*H*(Me)CH_2); 2.49 (*m*, OH–C(3′)); 2.37 (*m*, 1 H–C(2′)), 2.18 (*m*, 1 H–C(2′)); 1.82 (*d*, Me–C(5)); 1.34 (*dd*, CH(*Me*)CH_2). Anal. calc. for $C_{20}H_{22}ClN_3O_9$ (483.9): C 49.65, H 4.58, N 8.68; found: C 49.54, H 4.67, N 8.61.

104. *Thymidine 5′-[2-(4-Bromo-2-nitrophenyl)propyl Carbonate]* (**125**), *3′-[2-(4-Bromo-2-nitrophenyl)-propyl Carbonate]* (**181**), *and 3′,5′-Bis[2-(4-bromo-2-nitrophenyl)propyl Carbonate]* (**182**). According to *Exper. 101* with **24**: 0.396 g (75%) of **125**, 11 mg (2%) of **181**, and 98 mg (12%) of **182** as colorless foams.

Data of **125**: TLC (toluene/AcOEt/MeOH 5 : 4 : 1): R_f 0.51. UV (MeOH): 204 (sh, 4.39), 212 (4.42), 263 (4.07), 333 (sh, 2.75). ^{1}H-NMR ($CDCl_3$): 8.67 (br., NH); 7.89 (*d*, H–(3″)); 7.68 (*dd*, H–C(5″)); 7.30 (*m*, H–C(6″), H–C(6)); 6.30 (*m*, H–C(1′)); 4.43–4.07 (*m*, CH(Me)CH_2, H–C(3′), H–C(4′), CH_2(5′); 3.73 (*sext.*, C*H*(Me)CH_2); 2.59 (br., OH–C(3′)); 2.37 (*m*, 1 H–C(2′)); 2.15 (*m*, 1 H–C(2′)); 1.82 (2*s*, Me–C(5)); 1.34 (*dd*, CH(*Me*)CH_2). Anal. calc. for $C_{20}H_{22}BrN_3O_9$ (528.3): C 45.47, H 4.20, N 7.95; found: C 45.45, H 4.23, N 7.89.

Data of **181**: TLC (toluene/AcOEt/MeOH 5 : 4 : 1): R_f 0.59. UV (MeOH): 203 (4.41), 212 (4.42), 261 (4.09), 334 (sh, 2.90); ^{1}H-NMR ($CDCl_3$): 8.40 (br., NH); 7.93 (*d*, H–(3″)); 7.71 (*dd*, H–C(5″)); 7.39 (*d*, H–C(6″)); 7.34 (*s*, H–C(6)); 6.12 (*m*, H–C(1′)); 5.22 (*d*, H–C(3′)); 4.35, 4.20 (2*m*, CH(Me)CH_2); 4.12 (*m*, H–C(4′)); 3.90 (*m*, CH_2(5′)); 3.78 (*sext.*, C*H*(Me)CH_2); 2.54–2.34 (*m*, OH–C(5′), CH_2(2′)); 1.90 (*s*, Me–C(5)); 1.35 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_{20}H_{22}BrN_3O_9$ (528.3): C 45.47, H 4.20, N 7.95; found: C 45.38, H 4.37, N 7.47.

Data of **182**: TLC (toluene/AcOEt/MeOH 5 : 4 : 1): R_f 0.83. UV (MeOH): 202 (4.52), 214 (4.56), 256 (4.16), 334 (sh, 3.06). ^{1}H-NMR ($CDCl_3$): 8.62 (br., NH), 7.90 (2*d*, 2 H–C(3″)); 7.80 (*m*, 2 H–C(5″)); 7.30 (*m*, 2 H(6″), H–C(6)); 6.32 (*m*, H–C(1′)); 5.10 (*t*, H–C(3′)); 4.43–4.14 (*m*, 2 CH(Me)CH_2, H–C(4′), CH_2(5′)); 3.73 (*sext.*, 2 C*H*(Me)CH_2); 2.41 (*m*, 1 H–C(2′)); 2.23 (*m*, 1 H–C(2′)); 1.83 (2*s*, Me–C(5)); 1.34 (*d*, 2 CH(*Me*)CH_2). Anal. calc. for $C_{30}H_{30}Br_2N_4O_{13}$ (814.4): C 44.24, H 3.71, N 6.88; found: C 44.37, H 3.88, N 7.21.

105. *Thymidine 5′-[2-(4-Iodo-2-nitrophenyl)propyl Carbonate]* (**126**). According to *Exper. 101* with **25**: 0.414 g (72%) of **126**. Colorless solid foam. TLC (toluene/AcOEt/ MeOH 5 : 4 : 1): R_f 0.54. UV (MeOH): 203 (4.43), 228 (4.30), 261 (4.09), 332 (sh, 2.87). ^{1}H-NMR ($CDCl_3$): 8.45 (br., NH); 8.05 (*d*, H–C(3″)); 7.87 (*dd*, H–C(5″)); 7.26 (*dd*, H–C(6)); 7.18 (*d*, H–C(6″)); 6.29 (*m*, H–C(1′)); 4.45–4.06 (*m*, CH(Me)CH_2, H–C(3′), H–C(4′), CH_2(5′)); 3.71 (*sext.*, C*H*(Me)CH_2); 2.37 (*m*, OH–C(3′), 1 H–C(2′)), 2.16 (*m*, 1 H–C(2′)); 1.82 (*dd*, Me–C(5)); 1.33 (*dd*, CH(*Me*)CH_2). Anal. calc. for $C_{20}H_{22}IN_3O_9$ (575.3): C 41.76, H 3.85, N 7.30; found: C 41.49, H 3.98, N 7.40.

106. *Thymidine 5′-[2-(5-Chloro-2-nitrophenyl)propyl Carbonate]* (**127**), *3′-[2-(5-Chloro-2-nitrophenyl)-propyl Carbonate]* (**183**), *and 3′,5′-Bis[2-(5-chloro-2-nitrophenyl)propyl Carbonate]* (**184**). According to *Exper. 101*, with **26**: 0.334 g (69%) of **127**, 19 mg (4%) of **183**, and 43 mg (6%) of **184**. Colorless solid foams.

Data of **127**: TLC (toluene/AcOEt/MeOH 5 : 4 : 1): R_f 0.40. UV (MeOH): 207 (4.32), 263 (4.15), 335 (sh, 2.92). ^{1}H-NMR ($CDCl_3$): 8.75 (br., NH); 7.74 (*d*, 1 arom. H); 7.41 (*d*, 1 arom. H); 7.34 (*dd*, 1 arom. H); 7.29 (*s*, H–C(6)); 6.31 (*m*, H–C(1′)); 4.47–4.08 (*m*, CH(Me)CH_2, H–C(3′), H–C(4′), CH_2(5′)); 3.82 (*m*, C*H*(Me)CH_2); 2.66 (*d*, OH–C(3′)); 2.37 (*m*, 1 H–C(2′)); 2.17 (*m*, 1 H–C(2′)); 1.80 (2*s*, Me–C(5)); 1.34 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_{20}H_{22}ClN_3O_9$ (483.9): C 49.65, H 4.58, N 8.68; found: C 49.31, H 4.57, N 8.54.

Data of **183**: TLC (toluene/AcOEt/MeOH 5 : 4 : 1): R_f 0.55. UV (MeOH): 207 (4.37), 263 (4.17), 331 (sh, 2.96). ^{1}H-NMR ($CDCl_3$): 8.31 (br., NH); 7.78 (*dd*, 1 arom. H); 7.40 (*m*, 2 arom. H, H–C(6)); 6.12 (*m*, H–C(1′)); 5.23 (*m*, H–C(3′)); 4.38 (*m*, H–C(4′)); 4.24–4.11 (*m*, CH(Me)CH_2); 3.84 (*m*, CH_2(5′), C*H*(Me)CH_2); 2.59–2.36 (*m*, OH–C(5′), CH_2(2′)); 1.90 (*s*, Me–C(5)); 1.36 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_{20}H_{22}ClN_3O_9$ (483.9): C 49.65, H 4.58, N 8.68; found: C 49.58, H 4.70, N 8.02.

Data of **184**: TLC (toluene/AcOEt/MeOH 5 : 4 : 1): R_f 0.79. UV (MeOH): 207 (4.64), 262 (4.32), 327 (sh, 3.34). ^{1}H-NMR ($CDCl_3$): 8.03 (br., NH); 7.76 (*m*, 2 arom. H); 7.37 (*m*, 4 arom. H); 7.26 (*m*, H–C(6)); 6.32 (*m*, H–C(1′)); 5.11 (*m*, H–C(3′)); 4.46–4.12 (*m*, 2 CH(Me)CH_2, H–C(4′), CH_2(5′)); 3.82 (*m*, 2 C*H*(Me)CH_2); 2.46 (*m*, 1 H–C(2′)), 2.22 (*m*, 1 H–C(2′)); 1.80 (2*s*, Me–C(5)); 1.36 (*d*, 2 CH(*Me*)CH_2). Anal. calc. for $C_{30}H_{30}Cl_2N_4O_{13}$ (725.5): C 49.67, H 4.17, N 7.72; found: C 49.55, H 4.32, N 7.42.

107. *Thymidine 5′-[2-(5-Bromo-2-nitrophenyl)propyl Carbonate]* (**128**), *3′-[2-(5-Bromo-2-nitrophenyl)-propyl Carbonate]* (**185**), *and 3′,5′-Bis[2-(5-bromo-2-nitrophenyl)propyl Carbonate]* (**186**). According to *Exper. 101* with **27**: 0.39 g (74%) of **128**, 16 mg (2%) of **185**, and 98 mg (12%) of **186**. Colorless foams.

Data of **128**: TLC (toluene/AcOEt/MeOH 5 : 4 : 1): R_f 0.42. UV (MeOH): 205 (4.41), 265 (4.18), 337 (sh, 2.95). ^{1}H-NMR ($CDCl_3$): 8.71 (br., NH); 7.65 (*d*, 1 arom. H); 7.57 (*d*, 1 arom. H); 7.51 (*dd*, 1 arom. H); 7.29 (*s*, H–C(6)); 6.31 (*m*, H–C(1′)); 4.28–4.11 (*m*, CH(Me)CH_2, H–C(3′), H–C(4′), CH_2(5′)); 3.80 (*m*, C*H*(Me)CH_2); 2.64 (br., OH–C(3′)); 2.37 (*m*, 1 H–C(2′)); 2.05 (*m*, 1 H–C(2′)); 1.80 (2*s*, Me–C(5)); 1.35 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_{20}H_{22}BrN_3O_9$ (528.3): C 45.47, H 4.20, N 7.95; found: C 45.09, H 4.14, N 7.54.

Data of **185**: TLC (toluene/AcOEt/MeOH 5 : 4 : 1): R_f 0.54. UV (MeOH): 202 (4.36), 264 (4.18), 333 (sh, 3.02). ^{1}H-NMR ($CDCl_3$): 7.98 (br., NH); 7.69 (*dd*, 1 arom. H); 7.58 (*d*, 1 arom. H); 7.52 (*dd*, 1 arom. H); 7.38 (*dd*, H–C(6)); 6.12 (*m*, H–C(1′)); 5.23 (*m*, H–C(3′)); 4.38 (*m*, H–C(4′)); 4.24–4.10 (*m*, CH(Me)CH_2); 3.91–3.74 (*m*, CH_2(5′), C*H*(Me)CH_2); 2.56–2.34 (*m*, CH_2(2′)); OH–C(5′) not visible; 1.91 (*s*, Me–C(5)); 1.36 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_{20}H_{22}BrN_3O_9$ (528.3): C 45.47, H 4.20, N 7.95; found: C 45.15, H 4.21, N 7.57.

Data of **186**: TLC (toluene/AcOEt/MeOH 5 : 4 : 1): R_f 0.78. UV (MeOH): 202 (4.61), 216 (sh, 4.42), 263 (4.34), 333 (sh, 3.33). ^{1}H-NMR ($CDCl_3$): 8.12 (br., NH); 7.67 (*m*, 2 arom. H); 7.53 (*m*, 4 arom. H); 7.26 (*m*, H–C(6)); 6.33 (*m*, H–C(1′)); 5.11 (*m*, H–C(3′)); 4.46–4.11 (*m*, 2 CH(Me)CH_2, H–C(4′), CH_2(5′)); 3.79 (*m*, 2 C*H*(Me)CH_2); 2.46 (*m*, 1 H–C(2′)); 2.22 (*m*, 1 H–C(2′)); 1.80 (2*s*, Me–C(5)); 1.35 (*d*, 2 CH(*Me*)CH_2); Anal. calc. for $C_{30}H_{30}Br_2N_4O_{13}$ (814.4): C 44.24, H 3.71, N 6.88; found: C 44.28, H 3.72, N 6.80.

108. *Thymidine 5′-[2-(5-Iodo-2-nitrophenyl)propyl Carbonate]* (**129**), *3′-[2-(5-Iodo-2-nitrophenyl)propyl Carbonate]* (**187**), *and 3′,5′-Bis[2-(5-iodo-2-nitrophenyl)propyl Carbonate]* (**188**). According to *Exper. 101*, with **28**: 0.42 g (73%) of **129**, 17 mg (3%) of **187**, and 0.1 g (11%) of **188**. Colorless foams.

Data of **129**: TLC (toluene/AcOEt/MeOH 5 : 4 : 1): R_f 0.46. UV (MeOH): 204 (4.41), 267 (4.16), 335 (sh, 3.19). ^{1}H-NMR ($CDCl_3$): 8.51 (br., NH); 7.74 (*m*, 2 arom. H); 7.47 (*d*, 1 arom. H); 7.29 (2*s*, H–C(6)); 6.31 (*m*, H–C(1′)); 4.46–4.10 (*m*, CH(Me)CH_2, H–C(3′), CH_2(5′), H–C(4′)); 3.75 (*m*, C*H*(Me)CH_2); 2.49 (br., OH–C(3′)); 2.37 (*m*, 1 H–C(2′)); 2.18 (*m*, 1 H–C(2′)); 1.80 (2*s*, Me–C(5)); 1.35 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_{20}H_{22}IN_3O_9$ (575.3): C 41.76, H 3.85, N 7.30; found: C 41.46, H 3.88, N 7.18.

Data of **187**: TLC (toluene/AcOEt/MeOH 5 : 4 : 1): R_f 0.53. UV (MeOH): 202 (4.49), 267 (4.17), 333 (sh, 3.19). ^{1}H-NMR ($CDCl_3$): 7.78 (br., NH); 7.73 (*m*, 2 arom. H); 7.51 (*dd*, 1 arom. H); 7.39 (*dd*, H–C(6)); 6.12 (*m*, H–C(1′)); 5.23 (*m*, H–C(3′)); 4.36 (*m*, CH(Me)CH_2); 4.20 (*m*, 1 H, CH(Me)CH_2); 4.13 (*m*, H–C(4′)); 3.87 (*m*, CH_2(5′)); 3.74 (*sext.*, C*H*(Me)CH_2); 2.69 (br., OH–C(5′)); 2.56–2.39 (*m*, CH_2(2′)); 1.91 (*s*, Me–C(5)); 1.35 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_{20}H_{22}IN_3O_9$ (575.3): C 41.76, H 3.85, N 7.30; found: C 42.22, H 3.85, N 7.20.

Data of **188**: TLC (toluene/AcOEt/MeOH 5 : 4 : 1): R_f 0.84. UV (MeOH): 202 (4.69), 267 (4.30), 333 (sh, 3.45). ^{1}H-NMR ($CDCl_3$): 8.26 (br., NH); 7.74 (*m*, 4 arom. H); 7.49 (*m*, 2 arom. H); 7.27 (*m*, H–C(6)); 6.34 (*m*, H–C(1′)); 5.12 (*m*, H–C(3′)); 4.45–4.10 (*m*, 2 CH(Me)CH_2, H–C(4′), CH_2(5′)); 3.75 (*m*, 2 C*H*(Me)CH_2); 2.45 (*m*, 1 H–C(2′)); 2.24 (*m*, 1 H–C(2′)); 1.80 (2*s*, Me–C(5)); 1.35 (*d*, 2 CH(*Me*)CH_2). Anal. calc. for $C_{30}H_{30}I_2N_4O_{13}$ (908.4): C 39.67, H 3.33, N 6.17; found: C 39.61, H 3.39, N 5.99.

109. *Thymidine 5′-[2-(2-Bromo-6-nitrophenyl)propyl Carbonate]* (**130**). According to *Exper. 101*, with **30**: 0.248 g (47%) of **130**. Colorless foam. TLC (toluene/AcOEt/MeOH 5 : 4 : 1): R_f 0.27. UV (MeOH): 203 (4.38), 208 (sh, 4.35), 263 (4.03), 342 (sh, 2.90). ^{1}H-NMR ($CDCl_3$): 8.28 (br., NH); 7.76 (*dd*, 1 arom. H); 7.47 (*dd*, 1 arom. H); 7.32 (*s*, H–C(6)); 7.22 (*m*, H–C(4)); 6.30 (*t*, H–C(1′)); 4.56–4.28 (*m*, CH(Me)CH_2, H–C(3′), CH_2(5′)); 4.09 (*m*, H–C(4′)); 3.75 (*m*, C*H*(Me)CH_2); 2.35 (*m*, 1 H–C(2′)); 2.25 (br., OH–C(3′)); 2.14 (*m*, 1 H–C(2′)); 1.80 (2*s*, Me–C(5)); 1.35 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_{20}H_{22}BrN_3O_9$ (528.3): C 45.47, H 4.20, N 7.95; found: C 45.21, H 4.21, N 7.48.

110. *Thymidine 5′-[2-(2-Iodo-6-nitrophenyl)propyl Carbonate]* (**131**) According to *Exper. 101* with **31**: 0.362 g (55%) of **131**. Colorless foam. TLC (toluene/AcOEt/MeOH 5 : 4 : 1): R_f 0.41. UV (MeOH): 203 (4.47), 227 (sh, 4.17), 263 (4.06), 336 (sh, 2.80). ^{1}H-NMR ($CDCl_3$): 8.09 (*dd*, br. *s*, 1 arom. H, NH); 7.49 (*dd*, 1 arom. H); 7.32 (*m*, H–C(6)); 7.06 (*m*, H–C(4)); 6.30 (*t*, H–C(1′)); 4.54–4.28 (*m*, CH(Me)CH_2, H–C(3′), CH_2(5′)); 4.10 (*m*, H–C(4′)); 3.72 (*m*, C*H*(Me)CH_2); 2.34 (*m*, 1 H–C(2′)); 2.15 (*m*, 1 H–C(2′)); 2.06 (br., OH–C(3′)); 1.80 (2*s*, Me–C(5)); 1.39 (*m*, CH(*Me*)CH_2). Anal. calc. for $C_{20}H_{22}IN_3O_9 \cdot 0.5\ H_2O$ (584.3): C 41.11, H 3.97, N 7.19; found: C 41.45, H 3.94, N 6.73.

111. *Thymidine 5′-[2-(2,4-Dinitrophenyl)propyl Carbonate]* (**132**), *3′-[2-(2,4-Dinitrophenyl)propyl Carbonate]* (**189**), *and 3′,5′-Bis[2-(2,4-dinitrophenyl)propyl Carbonate]* (**190**). According to *Exper. 101*, with **32**: 0.366 g (74%) of **132**, 15 mg (3%) of **189**, and 52 mg (7%) of **190**. Colorless foams.

Data of **132**: TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.43. UV (MeOH): 204 (4.39), 259 (4.29), 334 (sh, 2.81). ^{1}H-NMR ($CDCl_3$): 8.61 (*m*, NH, H–C(3″)); 8.41 (*dd*, H–C(5″)); 7.69 (*d*, H–C(6″)); 7.25 (2*s*, H–C(6)); 6.26 (*m*, H–C(1′)); 4.49–4.05 (*m*, CH(Me)CH_2, H–C(3′), H–C(4′), CH_2(5′)); 3.86 (*sext.,* C*H*(Me)CH_2); 2.53 (*m,* OH–C(3′)); 2.38 (*m*, 1 H–C(2′)); 2.16 (*m*, 1 H–C(2′)); 1.84 (2*s*, Me–C(5)); 1.41 (*m*, CH(*Me*)CH_2). Anal. calc. for $C_{20}H_{22}N_4O_{11}$ (494.4): C 48.59, H 4.49, N 11.33; found: C 48.12, H 4.49, N 11.28.

Data of **189**: TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.48. UV (MeOH): 206 (4.34), 259 (4.28), 327 (sh, 2.73). ^{1}H-NMR ($CDCl_3$): 8.69 (br., NH); 8.65 (*s*, H–C(3″)); 8.44 (*d*, H–C(5″)); 7.72 (*t*, H–C(6″)); 7.41 (2*s*, H–C(6)); 6.13 (*t*, H–C(1′)); 5.22 (*m*, H–C(3′)); 4.42 (*m*, 1 H, CH(Me)CH_2); 4.26 (*t*, 1 H, CH(Me)CH_2); 4.12 (*m*, H–C(4′)); 3.86 (*m*, CH_2(5′), C*H*(Me)CH_2); 2.63 (*m,* OH–C(5′)); 2.52–2.32 (*m*, CH_2(2′)); 1.89 (*s*, Me–C5)); 1.41 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_{20}H_{22}N_4O_{11}$ (494.4): C 48.59, H 4.49, N 11.33; found: C 48.35, H 4.67, N 10.88.

Data of **190**: TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.73. UV (MeOH): 204 (4.61), 254 (4.48), 324 (sh, 3.15). ^{1}H-NMR ($CDCl_3$): 8.62 (*m*, 2 H–C(3″)); 8.54 (br., NH); 8.43 (*m*, 2 H–C(5″)); 7.71 (*m*, 2 H–C(6″)); 7.15 (*s*, H–C(6)); 6.26 (*m*, H–C(1′)); 5.06 (*m*, H–C(3′)); 4.50–4.16 (*m*, 2 CH(Me)CH_2, H–C(4′), CH_2(5′)); 3.89 (*m*, 2 C*H*(Me)CH_2); 2.42 (*m*, 1 H–C(2′)); 2.22 (*m*, 1 H–C(2′)); 1.84 (2*s*, Me–C(5)); 1.42 (*d*, 2 CH(*Me*)CH_2). Anal. calc. for $C_{30}H_{30}N_6O_{17}$ (746.6): C 48.26, H 4.05, N 11.26; found: C 48.58, H 4.21, N 11.04.

112. *Thymidine 5′-[2-(2,6-Dinitrophenyl)propyl Carbonate]* (**133**), *3′-[2-(2,6-Dinitrophenyl)propyl Carbonate]* (**191**), *and 3′,5′-Bis[2-(2,6-dinitrophenyl)propyl Carbonate]* (**192**). According to *Exper. 101*, with **33**: 0.386 g (78%) of **133**, 20 mg (4%) of **191**, and 30 mg (4%) of **192**. Colorless foams.

Data of **133**: TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.44. UV (MeOH): 205 (4.40), 261 (4.03), 333 (sh, 2.81). ^{1}H-NMR ((D$_6$)DMSO): 11.31 (br., NH); 8.13 (*d*, H–(3″), H–C(5″)); 7.77 (*t*, H–C(4″)); 7.39 (2*s,* H–C(6)); 6.16 (*m*, H–C(1′)); 5.42 (*d*, OH–C(3′)); 4.42–4.18 (*m*, CH(Me)CH_2, H–C(3′), CH_2(5′)); 3.89 (*m*, H–C(4′)); 3.47 (*m*, C*H*(Me)CH_2); 2.09 (*m*, CH_2(2′)); 1.71 (2*s*, Me–C(5)); 1.28 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_{20}H_{22}N_4O_{11} \cdot 1.5\ H_2O$ (521.4): C 46.07, H 4.83, N 10.74; found: C 46.14, H 4.46, N 10.74.

Data of **191**: TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.49. UV (MeOH): 207 (4.29), 261 (4.04), 324 (sh, 2.74). ^{1}H-NMR ($CDCl_3$): 8.23 (br., NH); 7.79 (*d*, H–C(3″), H–C(5″)); 7.58 (*t*, H–C(4″)); 7.40 (2*s*, H–C(6)); 6.13 (*t*, H–C(1′)); 5.24 (*m*, H–C(3′)); 4.45 (*m*, CH(Me)CH_2); 4.14 (*m*, H–C(4′)); 3.91 (*m*, CH_2(5′)); 3.62 (*sext.*, C*H*(Me)CH_2); 2.51–2.33 (*m*, OH–C(5′), CH_2(2′)); 1.90 (*s*, Me–C(5)); 1.39 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_{20}H_{22}N_4O_{11}$ (494.4): C 48.59, H 4.49, N 11.33; found: C 48.55, H 4.66, N 10.93.

Data of **192**: TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.72. UV (MeOH): 207 (4.56), 231 (sh, 4.27), 254 (sh, 4.17), 325 (sh, 3.05). ^{1}H-NMR ($CDCl_3$): 8.52 (br., NH); 7.78 (*t*, 2 H–C(3″), 2 H–C(5″)); 7.57 (*m*, 2 H–C(4″)); 7.29 (2*s,* H–C(6)); 6.32 (*m*, H–C(1′)); 5.13 (*m*, H–C(3′)); 4.64–4.21 (*m*, 2 CH(Me)CH_2, H–C(4′), CH_2(5′)); 3.75–3.57 (*m*, 2 C*H*(Me)CH_2); 2.46 (*m*, 1 H–C(2′)); 2.25 (*m*, 1 H–C(2′)); 1.80 (2*s*, Me–C(5)); 1.35 (*d*, 2 CH(*Me*)CH_2). Anal. calc. for $C_{30}H_{30}N_6O_{17}$ (746.6): C 48.26, H 4.05, N 11.26; found: C 48.35, H 4.15, N 11.10.

113. *Thymidine 5′-[2-(2,5-Dinitrophenyl)propyl Carbonate]* (**134**). According to *Exper. 101*, with **34**: 0.342 g (68%) of **134**. Colorless foam. TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.34. UV (MeOH): 205 (4.47), 258 (4.26), 334 (sh, 3.02). ^{1}H-NMR ($CDCl_3$): 9.11 (br., NH); 8.33 (*d*, H–C(6″)); 7.23 (*m*, H–C(4″)); 7.87 (*dd*, H–C(3″)); 7.27 (*s*, H–C(6)); 6.28 (*m*, H–C(1′)); 4.51–4.17 (*m*, CH(Me)CH_2, H–C(3′), CH_2(5′)); 4.10 (*m*, H–C(4′)); 3.74 (*m*, C*H*(Me)CH_2); 3.03 (*m*, OH–C(3′)); 2.38 (*m*, 1 H–C(2′)); 2.17 (*m*, 1 H–C(2′)); 1.79 (*d*, Me–C(5)); 1.43 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_{20}H_{22}N_4O_{11} \cdot 0.5\ H_2O$ (503.4): C 47.71, H 4.60, N 11.13; found: C 48.08, H 4.67, N 11.01.

114. *Thymidine 5′-[2-(3-Nitro[1,1′-biphenyl]-4-yl)propyl Carbonate]* (**135**) *and 3′-[2-(3-[1,1′-biphenyl]-4-yl)propyl Carbonate* (**193**). According to *Exper. 101*, with **57**: 0.236 g (45%) of **135** and 32 mg (6%) of **193**. Light yellow foams.

Data of **135**: TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.43. UV (MeOH): 205 (4.63), 250 (4.48), 313 (sh, 3.22). ^{1}H-NMR ($CDCl_3$): 8.43 (br., NH); 7.96 (*d*, arom. H–C(2″)); 7.78 (*dd*, arom. H–C(6″)); 7.59–7.36 (*m*, 6 arom. H); 7.29 (*m*, H–C(6)); 6.29 (*m*, H–C(1′)); 4.48–4.18 (*m*, CH(Me)CH_2, H–C(3′), CH_2(5′)); 4.09 (*m*, H–C(4′)); 3.79 (*m*, C*H*(Me)CH_2); 2.34 (*m*, 1 H–C(2′)); 2.12 (*m*, 1 H–C(2′)); 1.94 (br., OH–C(3′)); 1.87, 1.77 (2*s*, Me–C(5)); 1.38 (*m*, CH(*Me*)CH_2). Anal. calc. for $C_{26}H_{27}N_3O_9$ (525.5): C 59.42, H 5.18, N 8.00; found: C 59.11, H 5.22, N 7.87.

Data of **193**: TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.51. ^{1}H-NMR ($CDCl_3$): 7.99 (*d*, arom. H–C(2″)); 7.96 (br., NH); 7.80 (*d*, arom. H–C(6″)); 7.59–7.37 (*m*, 6 arom. H, H–C(6)); 6.12 (*t*, H–C(1′)); 5.23 (*m*,

H–C(3′)); 4.43–4.24 (*m*, CH(Me)CH_2); 4.14 (*m*, H–C(4′)); 3.82 (*m*, CH_2(5′), C*H*(Me)CH_2); 2.43 (*m*, CH_2(2′)); OH–C(5′) not visible; 1.90 (*s*, Me–C(5)); 1.40 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_{26}H_{27}N_3O_9$ (525.5): C 59.42, H 5.18, N 8.00; found: C 59.08, H 5.57, N 6.97.

115. *Thymidine 5′-[2-(4-Nitro[1,1′-biphenyl]-3-yl)propyl Carbonate]* (**136**), *3′-[2-(Nitro[1,1′-biphenyl]-3-yl)propyl Carbonate]* (**194**), *and 3′,5′-Bis[2-(4-Nitro[1,1′-biphenyl]-3-yl)propyl Carbonate]* (**195**). According to *Exper. 101*, with **58**: 0.352 g (66%) of **136**, 5 mg (1%) of **194**, and 33 mg (4%) of **195**. Light yellow foams.

Data of **136**: TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.43. UV (MeOH): 203 (4.69), 263 (4.25), 295 (sh, 3.95), 335 (3.80). ^{1}H-NMR ($CDCl_3$): 8.91 (br., NH); 7.86 (*d*, 1 arom. H); 7.61–7.38 (*m*, 7 arom. H); 7.28 (*s*, H–C(6)); 6.30 (*t*, H–C(1′)); 4.52–4.21 (*m*, CH(Me)CH_2, H–C(3′), CH_2(5′)); 4.09 (*m*, H–C(4′)); 3.89 (*m*, C*H*(Me)CH_2); 3.65 (br., OH–C(3′)); 2.32 (*m*, 1 H–C(2′)); 2.10 (*m*, 1 H–C(2′)); 1.76 (*d*, Me–C(5)); 1.41 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_{26}H_{27}N_3O_9 \cdot 0.5\ H_2O$ (534.5): C 58.42, H 5.28, N 7.86; found: C 58.82, H 5.26, N 7.58.

Data of **194**: TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.50. UV (MeOH): 203 (4.64), 263 (4.22), 293 (sh, 3.92), 341 (3.78). ^{1}H-NMR ($CDCl_3$): 8.61 (br., NH); 7.88 (*d*, 1 arom. H); 7.62–7.37 (*m*, 7 arom. H, H–C(6)); 6.08 (*m*, H–C(1′)); 5.25 (*m*, H–C(3′)); 4.36 (*m*, CH(Me)CH_2); 4.08 (*m*, H–C(4′)); 3.87 (*m*, CH_2(5′), C*H*(Me)CH_2); 2.54–2.15 (*m*, CH_2(2′), OH–C(5′)); 1.89 (*s*, Me–C(5)); 1.42 (*d*, CH(*Me*)CH_2).

Data of **195**: TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.78. UV (MeOH): 205 (4.87), 270 (4.40), 294 (sh, 4.26), 325 (sh, 4.00). ^{1}H-NMR ($CDCl_3$): 8.22 (br., NH); 7.88 (*m*, 2 arom. H)); 7.62–7.40 (*m*, 14 arom. H, H–C(6)); 6.30 (*m*, H–C(1′)); 5.06 (*m*, H–C(3′)); 4.49–4.16 (*m*, 2 CH(Me)CH_2, H–C(4′), CH_2(5′)); 3.87 (*m*, C*H*(Me)CH_2); 2.37 (*m*, 1 H–C(2′)); 2.12 (*m*, 1 H–C(2′)); 1.78, 1.72 (2*s*, Me–C(5)); 1.42 (*d*, 2 CH(*Me*)CH_2). Anal. calc. for $C_{42}H_{40}N_4O_{13} \cdot H_2O$ (826.8): C 61.01, H 5.12, N 6.78; found: C 61.24, H 4.87, N 6.81.

116. *Thymidine 5′-[2-(4′-Methoxy-4-nitro[1,1′-biphenyl]-3-yl)propyl Carbonate]* (**137**). According to *Exper. 101*, with **59**: 0.456 g (82%) of **137**. Yellow foam. TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.38. UV (MeOH): 203 (4.65), 258 (4.21), 315 (4.00). ^{1}H-NMR ($CDCl_3$): 8.71 (br., NH); 7.85 (*d*, 1 arom. H); 7.52 (*m*, 4 arom. H); 7.28 (*m*, H–C(6)); 6.98 (*dd*, 2 arom. H); 6.29 (*t*, H–C(1′)); 4.50–4.20 (*m*, CH(Me)CH_2, H–C(3′), CH_2(5′)); 4.08 (*m*, H–C(4′)); 3.86 (*m*, C*H*(Me)CH_2); 3.85 (*s*, MeO); 2.30 (*m*, 1 H–C(2′)); 2.10 (*m*, 1 H–C(2′)); OH–C(3′) not visible; 1.80, 1.72 (2*s*, Me–C(5)); 1.41 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_{27}H_{29}N_3O_{10}$ (555.5): C 57.44, H 5.36, N 7.44; found: C 57.62, H 5.29, N 7.37.

117. *Thymidine 5′-[2-(3,4-Dimethoxy-4-nitro[1,1′-biphenyl]-3-yl)propyl Carbonate]* (**138**). According to *Exper. 101*, with **60**: 0.890 g (76%) of **138**. Yellow foam. TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.32. UV (MeOH): 234 (4.11), 260 (4.25), 336 (3.93). ^{1}H-NMR ((D$_6$)DMSO): 7.90 (*m*, NH, 1 arom. H); 7.74 (*dd*, 1 arom. H); 7.37 (*s*, 1 arom. H); 7.30 (*m*, 2 arom. H); 7.30 (*m*, 1 arom. H, H–C(6)); 6.14 (*m*, H–C(1′)); 5.41 (br., OH–C(3′)); 4.42 (*m*, CH(Me)CH_2); 4.23 (*m*, CH_2(5′)); 4.16 (*m*, H–C(3′)); 3.86 (*m*, 4 H–C(4′), MeO); 3.80 (*s*, MeO); 3.63 (*m*, C*H*(Me)CH_2); 2.06 (*m*, CH_2(2′)); 1.67 (*s*, Me–C(5)); 1.35 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_{28}H_{31}N_3O_{11} \cdot H_2O$ (603.58). C 55.71, H 5.51, N 6.96; found: C 55.60, H 5.09, N 6.83.

118. *Thymidine 5′-[2-(4-Nitro-4′-phenoxy[1,1′-biphenyl]-3-yl)propyl Carbonate]* (**139**). According to *Exper. 101*, with **61**: 0.640 g (54%) of **139**. Yellow foam. TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.28. UV (MeOH): 240 (4.24), 265 (4.24), 295 (sh, 4.06). ^{1}H-NMR ((D$_6$)DMSO): 11.30 (*s*, NH); 7.92 (*m*, 2 arom. H); 7.76 (*m*, 3 arom. H); 7.21–7.06 (*m*, 4 arom. H, H–C(6)); 6.14 (*m*, H–C(1′)); 5.41 (*d*, OH–C(3′)); 4.41 (*m*, CH(Me)CH_2), 4.22 (*m*, CH_2(5′)); 4.16 (*m*, H–C(3′)); 3.86 (*m*, H–C(4′)); 3.61 (*m*, C*H*(Me)CH_2); 2.06 (*m*, CH_2(2′)); 1.66 (*s*, Me–C(5)); 1.34 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_{32}H_{31}N_3O_{10} \cdot 0.5\ H_2O$ (626.62). C 61.33, H 5.15, N 6.71; found: C 61.35, H 4.90, N 6.68.

119. *Thymidine 5′-(2-[2-nitro-5-(thianthren-1-yl)phenyl]propyl Carbonate]* (**140**). According to *Exper. 101*, with **62**: 0.430 g (65%) of **140**. Light yellow foam. TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.37. UV (MeOH): 230 (sh, 4.21), 245 (sh, 4.41), 258 (4.53), 309 (sh, 3.67). ^{1}H-NMR ((D$_6$)DMSO): 11.30 (*s*, NH); 7.97 (*d*, 1 arom. H); 7.77 (*s*, 1 arom. H); 7.68 (*dd*, 1 arom. H); 7.60 (*dd*, 1 arom. H); 7.48–7.24 (*m*, 5 arom. H, H–C(6)); 6.15 (*m*, H–C(1′)); 5.42 (br., OH–C(3′)); 4.38 (*m*, CH(Me)CH_2); 4.25 (*m*, CH_2(5′)); 4.16 (*m*, H–C(3′)); 3.87 (*m*, H–C(4′), 3.60 (*m*, C*H*(Me)CH_2); 2.09 (*m*, CH_2(2′)); 1.69, 1.67 (2*s*, Me–C(5)); 1.34 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_{32}H_{29}N_3O_9S_2 \cdot H_2O$ (681.74): C 56.37, H 4.58, N 6.16; found: C 56.23, H 4.31, N 6.04.

120. *Thymidine 5′-[2-[5-(Naphthalen-1-yl)-2-nitrophenyl]propyl Carbonate]* (**141**), *3′-[2-[5-(Naphthalen-1-yl)-2-nitrophenyl]propyl Carbonate]* (**196**), *and 3′,5′-Bis[2-[5-(Naphthalen-1-yl)-2-nitrophenyl]propyl Carbonate]* (**197**). According to *Exper. 101*, with **63**: 0.409 g (70%) of **141**, 18 mg (3%) of **196**, and 53 mg (6%) of **197**. Light yellow foams.

Data of **141**: TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.39. UV (MeOH): 218 (4.83), 263 (4.23), 302 (sh, 3.85). ^{1}H-NMR ($CDCl_3$): 9.00 (br., NH); 7.91 (*m*, 3 arom. H); 7.74 (*m*, 1 arom. H); 7.56–7.42 (*m*, 5 arom. H); 7.37 (*d*, 1 arom. H); 7.28 (*d*, H–C(6)); 6.30 (*t*, H–C(1′)); 4.49–4.21 (*m*, CH(Me)CH_2, H–C(3′), CH_2(5′)); 4.08

(*m*, H–C(4′)); 3.91 (*m*, C*H*(Me)CH_2); 2.87 (br., OH–C(3′)); 2.29 (*m*, 1 H–C(2′)); 2.08 (*m*, 1 H–C(2′)); 1.81, 1.74 (2*s*, Me–C(5)); 1.40 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_{30}H_{29}N_3O_9 \cdot 0.5\ H_2O$ (584.6): C 61.63, H 5.17, N 7.19; found: C 61.62, H 5.05, N 7.13.

Data of **196**: TLC (toluene/AcOEt/MeOH 5 : 4 : 1): R_f 0.51. UV (MeOH): 218 (4.80), 262 (4.20), 300 (sh, 3.82); ^{1}H-NMR ($CDCl_3$): 8.17 (*d*, NH); 7.94 (*m*, 3 arom. H); 7.77 (*d*, 1 arom. H); 7.58–7.34 (*m*, 6 arom. H, H–C(6)); 6.08 (*m*, H–C(1′)); 5.23 (*m*, H–C(3′)); 4.41 (*m*, CH(Me)CH_2); 4.30 (*m*, CH(Me)CH_2); 4.14, 4.08 (*m*, H–C(4′)); 3.88 (*m*, CH_2(5′), C*H*(Me)CH_2); 2.51 (*m*, OH–C(5′), 1 H–C(2′)); 2.35 (*m*, 1 H–C(2′)); 1.90 (*s*, Me–C(5)); 1.40 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_{30}H_{29}N_3O_9 \cdot 2\ H_2O$ (611.6): C 58.92, H 5.44, N 6.87; found: C 59.34, H 4.97, N 6.24.

Data of **197**: TLC (toluene/AcOEt/MeOH 5 : 4 : 1): R_f 0.85. UV (MeOH): 218 (5.07), 257 (sh, 4.16), 304 (sh, 3.90). ^{1}H-NMR ($CDCl_3$): 8.25 (*d*, NH); 7.92 (*m*, 6 arom. H); 7.74 (*m*, 2 arom. H); 7.57–7.36 (*m*, 12 arom. H); 7.23 (*m*, H–C(6)); 6.30 (*m*, H–C(1′)); 5.08 (*m*, H–C(3′)); 4.45–4.15 (*m*, CH(Me)CH_2, H–C(4′), CH_2(5′)); 3.91 (*m*, 2 C*H*(Me)CH_2); 2.38–2.05 (*m*, CH_2(2′)); 1.82, 1.74 (2*s*, Me–C(5)); 1.40 (*d*, 2 CH(*Me*)CH_2).

121. *Thymidine 5′-{2-[5-(Naphthalen-2-yl)-2-nitrophenyl]propyl Carbonate}* (**142**) *and 3′-{2-[5-(Naphthalen-2-yl)-2-nitrophenyl]propyl Carbonate}* (**198**). According to *Exper. 101*, with **64**: 0.415 g (71%) of **142** and 12 mg (2%) of **198**. Light yellow foams.

Data of **142**: TLC (toluene/AcOEt/MeOH 5 : 4 : 1): R_f 0.47. UV (MeOH): 212 (4.69), 235 (4.59), 251 (sh, 4.45), 268 (sh, 4.35), 306 (sh, 4.08), 336 (sh, 3.89). ^{1}H-NMR ($CDCl_3$): 8.63 (br., NH); 8.01 (*s*, 1 arom. H); 7.90 (*m*, 4 arom. H); 7.74 (*m*, 3 arom. H); 7.53 (*m*, 2 arom. H); 7.25 (*d*, H–C(6)); 6.26 (*t*, H–C(1′)); 4.56–4.24 (*m*, CH(Me)CH_2, H–C(3′), CH_2(5′)); 4.06 (*m*, H–C(4′)); 3.93 (*m*, C*H*(Me)CH_2); 2.57 (br., OH–C(3′)); 2.28 (*m*, 1 H–C(2′)); 2.09 (*m*, 1 H–C(2′)); 1.80, 1.73 (2*s*, Me–C(5)); 1.45 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_{30}H_{29}N_3O_9 \cdot 0.5\ H_2O$ (584.6): C 61.63, H 5.17, N 7.19; found: C 61.85, H 5.30, N 7.00.

Data of **198**: TLC (toluene/AcOEt/MeOH 5 : 4 : 1): R_f 0.56. UV (MeOH): 212 (4.64), 235 (4.54), 252 (4.40), 305 (sh, 4.03), 340 (sh, 3.84). ^{1}H-NMR ($CDCl_3$): 8.71 (br., NH); 8.03 (*s*, 1 arom. H); 7.91 (*m*, 4 arom. H); 7.70 (*m*, 3 arom. H); 7.53 (*m*, 2 arom. H); 7.34 (*d*, H–C(6)); 6.07 (*m*, H–C(1′)); 5.22 (*m*, H–C(3′)); 4.50–4.31 (*m*, CH(Me)CH_2); 4.08 (*m*, H–C(4′)); 3.90 (*m*, CH_2(5′), C*H*(Me)CH_2); 2.77 (br., OH–C(5′)); 2.48 (*m*, 1 H–C(2′)); 2.33 (*m*, 1 H–C(2′)); 1.87 (*s*, Me–C(5)); 1.46 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_{30}H_{29}N_3O_9 \cdot 2\ H_2O$ (611.6): C 58.92, H 5.44, N 6.87; found: C 59.18, H 4.92, N 6.47.

122. *Thymidine 5′-{2-[2-Nitro-5-(2-thienyl)phenyl]propyl Carbonate}* (**143**), *3′{2-[2-Nitro-5-(2-thienyl)phenyl]propyl Carbonate}* (**199**), *and 3′,5′-Bis{2-[2-Nitro-5-(2-thienyl)phenyl]propyl Carbonate}* (**200**). According to *Exper. 101*, with **65**: 0.420 g (79%) of **143**, 10 mg (2%) of **199**, and 70 mg (13%) of **200**. Light yellow foams.

Data of **143**: TLC (toluene/AcOEt/MeOH 5 : 4 : 1): R_f 0.40. UV (MeOH): 215 (4.36), 262 (4.19), 314 (3.99). ^{1}H-NMR ($CDCl_3$): 8.57 (br., NH); 7.83 (*d*, 1 arom. H); 7.78 (*m*, 2 arom. H); 7.40 (*m*, 2 arom. H); 7.28 (*s*, H–C(6)); 7.12 (*m*, 1 arom. H); 6.29 (*t*, H–C(1′)); 4.53–4.19 (*m*, CH(Me)CH_2, H–C(3′), CH_2(5′)); 4.09 (*m*, H–C(4′)); 3.90 (*m*, C*H*(Me)CH_2); 2.52 (br., OH–C(3′)); 2.33 (*m*, 1 H–C(2′)); 2.12 (*m*, 1 H–C(2′)); 1.79, 1.74 (2*s*, Me–C(5)); 1.41 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_{24}H_{25}N_3O_9S$ (531.5). C 54.23, H 4.74, N 7.91; found: C 54.04, H 4.71, N 7.80.

Data of **199**: TLC (toluene/AcOEt/MeOH 5 : 4 : 1): R_f 0.51. UV (MeOH): 203 (4.51), 262 (4.42), 313 (4.00). ^{1}H-NMR ($CDCl_3$): 8.79 (br., NH); 7.86 (*dd*, 1 arom. H); 7.63 (*d*, 1 arom. H); 7.56 (*dd*, 1 arom. H); 7.40 (*m*, 2 arom. H, H–C(6)); 7.12 (*m*, 1 arom. H); 6.10 (*m*, H–C(1′)); 5.21 (*m*, H–C(3′)); 4.46–4.26 (*m*, CH(Me)CH_2); 4.08 (*m*, H–C(4′)); 3.88 (*m*, CH_2(5′), C*H*(Me)CH_2); 2.81 (br., OH–C(5′)); 2.53–2.31 (*m*, CH_2(2′)); 1.88 (*s*, Me–C(5)); 1.41 (*d*, CH(*Me*)CH_2).

Data of **200**: TLC (toluene/AcOEt/MeOH 5 : 4 : 1): R_f 0.81. UV (MeOH): 203 (4.69), 257 (4.37), 313 (4.32). ^{1}H-NMR ($CDCl_3$): 7.96 (*d*, NH); 7.84 (*m*, 2 arom. H); 7.58 (*m*, 4 arom. H); 7.39 (*m*, 4 arom. H); 7.24 (*s*, H–C(6)); 7.12 (*m*, 2 arom. H); 6.29 (*m*, H–C(1′)); 5.08 (*m*, H–C(3′)); 4.50–4.24 (*m*, 2 CH(Me)CH_2, CH_2(5′)); 4.16 (*m*, H–C(4′)); 3.89 (*m*, C*H*(Me)CH_2); 2.38 (*m*, 1 H–C(2′)); 2.14 (*m*, 1 H–C(2′)); 1.77, 1.74 (2*s*, Me–C(5)); 1.41 (*d*, 2 CH(*Me*)CH_2).

123. *Thymidine 5′-{2-[2-Nitro-5-(3-thienyl)phenyl]propyl Carbonate}* (**144**), *3′-{2-[2-Nitro-5-(3-thienyl)-phenyl]propyl Carbonate}* (**201**), *and 3′,5′-Bis{2-[2-Nitro-5-(3-thienyl)phenyl]propyl Carbonate}* (**202**). According to *Exper. 101*, with **66**: 0.395 g (73%) of **144**, 11 mg (2%) of **201**, and 90 mg (11%) of **202** as light yellow foams.

Data of **144**: TLC (toluene/AcOEt/MeOH 5 : 4 : 1): R_f 0.40. UV (MeOH): 205 (4.52), 267 (4.20), 301 (sh, 3.94). ^{1}H-NMR ($CDCl_3$): 8.54 (br., NH); 7.84 (*d*, 1 arom. H); 7.57 (*m*, 3 arom. H); 7.44 (*m*, 1 arom. H); 7.36 (*m*, 1 arom. H); 7.27 (*s*, H–C(6)); 6.29 (*m*, H–C(1′)); 4.52–4.20 (*m*, CH(Me)CH_2, H–C(3′), CH_2(5′)); 4.08 (*m*, H–C(4′)); 3.40 (*sext.*, C*H*(Me)CH_2); 2.50 (br., OH–C(3′)); 2.22 (*m*, 1 H–C(2′)); 2.11 (*m*, 1 H–C(2′)); 1.80,

1.72 (2*s*, Me–C(5)); 1.41 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_{24}H_{25}N_3O_9S \cdot 0.5\ H_2O$ (540.6): C 53.33, H 4.85, N 7.77; found: C 53.72, H 4.77, N 7.53.

Data of **201**: TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.50. UV (MeOH): 204 (4.63), 267 (4.18), 302 (sh, 4.06). ^{1}H-NMR ($CDCl_3$): 8.51 (br., NH); 7.88 (*dd*, 1 arom. H); 7.63 (*d*, 1 arom. H); 7.56 (*dd*, 1 arom. H); 7.45 (*m*, 1 arom. H); 7.37 (*m*, 1 arom. H, H–C(6)); 6.08 (*m*, H–C(1′)); 5.21 (*m*, H–C(3′)); 4.46–4.27 (*m*, CH(Me)CH_2); 4.08 (*m*, H–C(4′)); 3.86 (*m*, CH_2(5′), CH(Me)CH_2); 2.70 (br., OH–C(5′)); 2.49 (*m*, 1 H–C(2′)); 2.35 (*m*, 1 H–C(2′)); 1.89 (2*s*, Me–C(5)); 1.41 (*d*, CH(*Me*)CH_2).

Data of **202**: TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.77. UV (MeOH): 204 (4.81), 268 (4.35), 299 (sh, 4.23). ^{1}H-NMR ($CDCl_3$): 8.06 (br., NH); 7.85 (*m*, 2 arom. H); 7.58 (*m*, 6 arom. H); 7.40 (*m*, 4 arom. H); 7.24 (*s*, H–C(6)); 6.28 (*m*, H–C(1′)); 5.05 (*m*, H–C(3′)); 4.49–4.21 (*m*, 2 CH(Me)CH_2, CH_2(5′)); 4.16 (*m*, H–C(4′)); 3.89 (*m*, 2 C*H*(Me)CH_2); 2.38 (*m*, 1 H–C(2′)); 2.10 (*m*, 1 H–C(2′)); 1.77, 1.72 (2*s*, Me–C(5)); 1.41 (*d*, 2 CH(*Me*)CH_2). Anal. calc. for $C_{38}H_{36}N_4O_{13}S_2$ (820.9): C 55.60, H 4.42, N 6.83; found: C 55.55, H 4.65, N 6.87.

124. *Thymidine 5′-[2-(5-Ethenyl-2-nitrophenyl)propyl Carbonate]* (**145**) *and 3′-[2-(5-Ethenyl-2-nitrophenyl)propyl Carbonate]* (**203**). According to *Exper. 101*, with **67**: 0.271 g (51%) of **145** and 9 mg (2%) of **203** as colorless foams.

Data of **145**: TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.36. UV (MeOH): 205 (4.55), 268 (4.18), 297 (sh, 3.86), 337 (sh, 3.40). ^{1}H-NMR ($CDCl_3$): 8.65 (br., NH); 7.76 (*d*, H–C(3″)); 7.40 (*m*, H–C(4″), H–C(6″)); 7.28 (*m*, H–C(6)); 6.70 (2*d*, 1 olef. H); 6.30 (*t*, H–C(1′)); 5.85 (*d*, 1 olef. H); 5.45 (*d*, 1 olef. H); 4.48–4.07 (*m*, CH(Me)CH_2, H–C(3′), H–C(4′), CH_2(5′)); 3.85 (*m*, C*H*(Me)CH_2); 2.61 (br., OH–C(3′)); 2.35 (*m*, 1 H–C(2′)); 2.14 (*m*, 1 H–C(2′)); 1.83, 1.72 (2*s*, Me–C(5)); 1.36 (*m*, CH(*Me*)CH_2). Anal. calc. for $C_{22}H_{25}N_3O_9$ (475.5): C 55.58, H 5.30, N 8.84; found: C 55.21, H 5.27, N 8.72.

Data of **203**: TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.44. UV (MeOH): 204 (4.59), 268 (4.26), 293 (sh, 3.95), 332 (sh, 3.52). ^{1}H-NMR ($CDCl_3$): 7.93 (br., NH); 7.80 (*m*, H–C(3″)); 7.38 (*m*, H–C(4″), H–C(6″), H–C(6)); 6.73 (*m*, 1 olef. H); 6.09 (*m*, H–C(1′)); 5.87 (*d*, 1 olef. H); 5.47 (*d*, 1 olef. H); 5.22 (*m*, H–C(3′)); 4.37 (*m*, 1 H, CH(Me)CH_2); 4.26 (*m*, 1 H, CH(Me)CH_2); 4.11 (*m*, H–C(4′)); 3.84 (*m*, CH_2(5′), C*H*(Me)CH_2)); OH–C(5′) not visible; 2.52–2.37 (*m*, CH_2(2′)); 1.91 (*s*, Me–C(5)); 1.38 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_{22}H_{25}N_3O_9$ (475.5): C 55.58, H 5.30, N 8.84; found: C 55.37, H 5.36, N 8.30.

125. *Thymidine 5′-[2-[4-(Methoxycarbonyl)-2-nitrophenyl]propyl Carbonate]* (**146**) *and 3′-[2-[4-(Methoxycarbonyl)-2-nitrophenyl]propyl Carbonate]* (**204**). According to *Exper. 101*, with **68**: 0.540 g (67%) of **146** and 30 mg (4%) of **204** as colorless foams.

Data of **146**: TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.37. UV (MeOH): 209 (sh, 3.71), 221 (3.78), 261 (3.43), 302 (sh, 2.33). ^{1}H-NMR ($CDCl_3$): 8.83 (br., NH); 8.38 (*d*, H–C(3″)); 8.19 (*dd*, H–C(5″)); 7.54 (*d*, H–C(6″)); 7.26 (*m,* H–C(6)); 6.28 (*m*, H–C(1′)); 4.47–4.09 (*m*, CH(Me)CH_2, H–C(3′), CH_2(5′), H–C(4′)); 3.94 (s, COOMe); 3.80 (*sext.*, C*H*(Me)CH_2); 2.81 (br., OH–C(3′)); 2.35 (*m*, 1 H–C(2′)); 2.13 (*m*, 1 H–C(2′)); 1.85, 1.76 (2*s*, Me–C(5)); 1.37 (*m*, CH(*Me*)CH_2). Anal. calc. for $C_{22}H_{25}N_3O_{11} \cdot 0.25\ H_2O$ (512.0): C 51.61, H 4.98, N 8.21; found: C 51.51, H 5.05, N 8.18.

Data of **204**: TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.40. UV (MeOH): 202 (4.43), 222 (4.44), 258 (4.13), 292 (sh, 3.38). ^{1}H-NMR ($CDCl_3$): 8.42 (*d*, H–C(3″)); 8.22 (*dd*, H–C(5″)); 7.98 (br., NH); 7.57 (*dd*, H–C(6″)); 7.38 (2*s*, H–C(6)); 6.09 (*m*, H–C(1′)); 5.22 (*m*, H–C(3′)); 4.37, 4.24 (2*m*, CH(Me)CH_2); 4.11 (*m*, H–C(4′)); 3.94 (*s*, COOMe); 3.90 (*m*, CH_2(5′)); 3.78 (*sext.*, C*H*(Me)CH_2); 2.52–2.33 (*m*, CH_2(2′)); OH–C(5′) not visible; 1.91 (*s*, Me–C(5)); 1.39 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_{22}H_{25}N_3O_{11}$ (507.5): C 52.07, H 4.97, N 8.28; found: C 52.11, H 4.91, N 8.07.

126. *Thymidine 5′-[2-[4-(*tert*-Butoxycarbonyl)-2-nitrophenyl]propyl Carbonate]* (**147**). According to *Exper. 101*, with **69**. 0.420 g (56%) of **147**. Colorless foam. TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.39. UV (MeOH): 208 (4.37), 222 (4.45), 260 (4.10), 299 (sh, 3.14). ^{1}H-NMR ($CDCl_3$): 8.89 (br., NH); 8.29 (*d*, H–C(3″)); 8.14 (*dd*, H–C(5″)); 7.51 (*d*, H–C(6″)); 7.27 (2*s,* H–C(6)); 6.29 (*m*, H–C(1′)); 4.45–4.08 (*m*, CH(Me)CH_2, H–C(3′), CH_2(5′), H–C(4′)); 3.78 (*sext.*, C*H*(Me)CH_2); 2.87 (br., OH–C(3′)); 2.34 (*m*, 1 H–C(2′)); 2.16 (*m*, 1 H–C(2′)); 1.85, 1.79 (2*s*, Me–C(5)); 1.58 (s, ^{t}Bu); 1.36 (*m*, CH(*Me*)CH_2). Anal. calc. for $C_{25}H_{31}N_3O_{11} \cdot 0.25\ H_2O$ (554.1): C 54.20, H 5.73, N 7.58; found: C 54.28, H 6.00, N 7.40.

127. *Thymidine 5′-[2-[4-[(Phenylthio)carbonyl]-2-nitrophenyl]propyl Carbonate]* (**148**). According to *Exper. 101*, with **70**: 0.250 g (70%) of **148**. Colorless foam. TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.39. UV (MeOH): 231 (4.33), 258 (sh, 4.10), 304 (2.91). ^{1}H-NMR ((D_6)DMSO): 11.16 (br., NH); 8.25 (*s*, 1 arom. H); 8.12 (*d*, 1 arom. H); 7.84 (*d*, 1 arom. H); 7.48 (*m*, 2 arom. H (PhS)); 7.37–7.27 (*m*, 3 arom. H (PhS), H–C(6)); 6.12 (*t*, H–C(1′)); 5.33 (br., OH–C(3′)); 4.38–4.12 (*m*, CH(Me)CH_2), CH_2(5′), H–C(3′)); 3.85 (*m*, H–C(4′), 3.56 (*m*, C*H*(Me)CH_2); 2.08 (*m*, CH_2(2′)); 1.71, 1.69 (2*d*, Me–C(5)); 1.30 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_{27}H_{27}N_3O_{10}S \cdot 0.5\ H_2O$ (594.59): C 54.54, H 4.75, N 7.07; found: C 54.46, H 4.84, N 7.10.

128. *Thymidine 5′-[2-[4-[(Diphenylamino)carbonyl]-2-nitrophenyl]propyl Carbonate]* (**149**). According to *Exper. 101*, with **71**: 0.320 g (45%) of **149**. Colorless solid. TLC (CH_2Cl_2/MeOH 24:1): R_f 0.30. UV (MeOH): 230 (4.26), 260 (4.21), 305 (3.59), 329 (3.19). ^{1}H-NMR ((D_6)DMSO): 11.24 (*s*, NH); 7.84 (*d*, H–C(3″)); 7.68 (*dd*, H–C(5″)); 7.56 (*dd*, H–C(6″)); 7.41–7.24 (*m*, Ph_2N, H–C(6)); 6.15 (*t*, H–C(1′)); 5.39 (br., OH–C(3′)); 4.23 (*m*, CH(Me)CH_2, CH_2(5′), H–C(3′)); 3.89 (*m*, H–C(4′), 3.45 (*m*, C*H*(Me)CH_2); 2.14 (*m*, CH_2(2′)); 1.73 (2*s*, Me–C(5)); 1.21 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_{33}H_{32}N_4O_{10}\cdot 1.5\ H_2O$ (671.66): C 59.01, H 5.25, N 8.34; found: C 58.95, H 4.80, N 7.83.

129. *Thymidine 5′-[2-[4-[(Diisopropylamino)carbonyl]-2-nitrophenyl]propyl Carbonate]* (**150**). According to *Exper. 101*, with **72**: 0.180 g (45%) of **150**. Light yellow foam. TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.21. UV (MeOH): 226 (4.07), 260 (4.07), 302 (3.09). ^{1}H-NMR ((D_6)DMSO): 11.32 (*s*, NH); 7.74 (*m*, 2 arom. H); 7.59 (*d*, 1 arom. H); 7.40 (*s*, H–C(6)); 6.16 (*t*, H–C(1′)); 5.43 (br., OH–C(3′)); 4.29 (*m*, CH(Me)CH_2), 4.20 (*m*, CH_2(5′), H–C(3′); 3.87 (*m*, H–C(4′)); 3.61–3.45 (*m*, 2 Me_2C*H*, C*H*(Me)CH_2); 2.09 (*m*, CH_2(2′)); 1.71 (2*s*, Me–C(5)); 1.39–1.12 (br., CH(*Me*)CH_2, *Me*$_2$CH). Anal. calc. for $C_{27}H_{36}N_4O_{10}$ (576.60): C 56.24, H 6.29, N 9.72; found: C 56.18, H 6.07, N 9.35.

130. *Thymidine 5′-[2-[4-[[Methyl(phenyl)amino]carbonyl]-2-nitrophenyl]propyl Carbonate]* (**151**). According to *Exper. 101*, with **73**: 0.240 g (32%) of **151**. Light yellow foam. TLC (CH_2Cl_2/MeOH 24:1): R_f 0.18. UV (MeOH): 227 (4.17), 258 (4.19), 302 (3.29). ^{1}H-NMR ((D_6)DMSO): 11.22 (*s*, NH); 7.67 (*s*, 1 arom. H); 7.47 (*m*, 2 arom. H); 7.35 (*s*, H–C(6″)); 7.22 (*m*, PhN); 6.14 (*t*, H–C(1′)); 5.38 (*d*, OH–C(3′)); 4.20 (*m*, CH(Me)CH_2, CH_2(5′), H–C(3′)); 3.85 (*m*, H–C(4′)); 3.39 (*m*, C*H*(Me)CH_2); 3.29 (*s*, MeN); 2.09 (*m*, CH_2(2′)); 1.71 (2*s*, Me–C(5)); 1.19 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_{28}H_{30}N_4O_{10}\cdot 0.5\ H_2O$ (591.57): C 56.84, H 5.28, N 9.47; found: C 56.98, H 5.22, N 9.26.

131. *Thymidine 5′-[2-(4-Cyano-2-nitrophenyl)propyl Carbonate]* (**152**) *and 3′-[2-(4-Cyano-2-nitrophenyl)-propyl Carbonate]* (**205**). According to *Exper. 101*, with **74**: 0.310 g (71%) of **152** and 20 mg (5%) of **205** as colorless foams.

Data of **152**: TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.43. UV (MeOH): 202 (4.41), 221 (4.45), 262 (4.04), 298 (sh, 3.06). ^{1}H-NMR ($CDCl_3$): 8.96 (br., NH); 8.06 (*d*, H–C(3″)); 7.85 (*dd*, H–C(5″)); 7.62 (*m*, H–C(6″)); 7.25 (*m,* H–C(6)); 6.28 (*m*, H–C(1′)); 4.46–4.18 (*m*, CH(Me)CH_2, H–C(3′), CH_2(5′)); 4.11 (*m*, H–C(4′)); 3.81 (*m*, C*H*(Me)CH_2); 2.86 (br., OH–C(3′)); 2.38 (*m*, 1 H–C(2′)); 2.16 (*m*, 1 H–C(2′)); 1.86, 1.80 (2*s*, Me–C(5)); 1.38 (2*d*, CH(*Me*)CH_2). Anal. calc. for $C_{21}H_{22}N_4O_9\cdot 0.5\ H_2O$ (483.4): C 52.17, H 4.80, N 11.58; found: C 52.51, H 4.88, N 11.45.

Data of **205**: TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.49. UV (MeOH): 203 (4.34), 217 (4.48), 260 (4.10), 296 (sh, 3.35). ^{1}H-NMR ($CDCl_3$): 8.60 (br., NH); 8.09 (*d*, H–C(3″)); 7.87 (*dd*, H–C(5″)); 7.65 (*d*, H–C(6″)); 7.41 (*m*, H–C(6)); 6.14 (*t*, H–C(1′)); 5.22 (*m*, H–C(3′)); 4.39, 4.26 (2*m*, CH(Me)CH_2); 4.12 (*m*, H–C(4′)); 3.95–3.77 (*m*, CH_2(5′), CH(Me)CH_2); 2.54 (br., OH–C(5′)); 2.52–2.33 (*m*, CH_2(2′)); 1.90 (*s*, Me–C(5)); 1.39 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_{21}H_{18}N_4O_9$ (474.4): C 52.17, H 4.80, N 11.58; found: C 52.51, H 4.88, N 11.45.

132. *Thymidine 5′-[2-(5-Cyano-2-nitrophenyl)propyl Carbonate]* (**153**). According to *Exper. 101*, with **75**: 0.260 g (66%) of **153**. Light yellow foam. TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.44. UV (MeOH): 202 (4.43), 259 (4.11), 298 (sh, 3.28). ^{1}H-NMR ($CDCl_3$): 8.87 (br., NH); 7.82 (*d*, H–C(3″)); 7.77 (*d*, H–C(6″)); 7.70 (*dd*, H–C(4″)); 7.27 (*s*, H–C(6)); 6.28 (*t*, H–C(1′)); 4.47–4.16 (*m*, CH(Me)CH_2, H–C(3′), CH_2(5′)); 4.11 (*m*, H–C(4′)); 3.73 (*m*, C*H*(Me)CH_2); 2.83 (br., OH–C(3′)); 2.38 (*m*, 1 H–C(2′)); 2.17 (*m*, 1 H–C(2′)); 1.83, 1.78 (2*s*, Me–C(5)); 1.38 (2*d*, CH(*Me*)CH_2). Anal. calc. for for $C_{21}H_{22}N_4O_9\cdot 0.5\ H_2O$ (483.4): C 52.17, H 4.80, N 11.58; found: C 52.37, H 4.42, N 11.75.

133. *Thymidine 5′-[2-[5-(*tert*-Butoxycarbonyl)-2-nitrophenyl]propyl Carbonate]* (**154**). According to *Exper. 101*, with **76**: 0.270 g (55%) of **154**. Light yellow foam. TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.46. UV (MeOH): 202 (4.44), 260 (4.14), 297 (sh, 3.36). ^{1}H-NMR ($CDCl_3$): 8.72 (br., NH); 8.07 (*d*, H–C(6″)); 7.92 (*dd*, H–C(4″)); 7.72 (*dd*, H–C(3″)); 7.29 (*m,* H–C(6)); 6.31 (*m*, H–C(1′)); 4.53–4.12 (*m*, CH(Me)CH_2, H–C(3′), CH_2(5′)); 4.09 (*m*, H–C(4′)); 3.71 (*m*, C*H*(Me)CH_2); OH–C(3′) not visible; 2.39 (*m*, 1 H–C(2′)); 2.13 (*m*, 1 H–C(2′)); 1.81, 1.76 (2*s*, Me–C(5)); 1.58 (*s*, *t*Bu); 1.38 (*m*, CH(*Me*)CH_2). Anal. calc. for $C_{25}H_{31}N_3O_{11}\cdot 0.5\ H_2O$ (558.6): C 53.76, H 5.77, N 7.52; found: C 53.95, H 5.61, N 7.50.

134. *Thymidine 5′-[1-Methyl-2-(2-nitrophenyl)ethyl Carbonate]* (**155**). According to *Exper. 101*, with **85**: 0.332 g (74%) of **155**. Orange oil. TLC ($CHCl_3$/MeOH 9:1): R_f 0.23. UV (MeOH): 205 (4.31), 263 (4.10). ^{1}H-NMR ((D_6)DMSO): 11.32 (br., NH); 7.80 (*m*, H–C(3″)); 7.57 (*m*, H–C(4″)); 7.43 (*m*, 3 arom. H, H–C(6)); 6.15 (*m*, H–C(1′)); 5.41 (*m*, OH–C(3)); 5.12–4.89 (m, C*H*(Me)CH_2); 4.13 (*m*, H–C(3′), CH(Me)CH_2)); 3.70 (*m*, H–C(4′)); 3.32–3.15 (m, CH_2(5′)); 2.09 (*m*, CH_2(2′)); 1.73 (*m*, Me–C(5)); 1.25 (*m*, CH(*Me*)CH_2). Anal. calc. for $C_{20}H_{23}N_3O_9\cdot 0.5\ H_2O$ (458.4): C 52.40, H 5.28, N 9.17; found: C 52.47, H 5.19, N 9.21.

135. *Thymidine 5′-[2-(2-Nitrophenyl)-1-phenylethyl Carbonate]* (**156**). According to *Exper. 101*, with **86**: 0.379 g (86%) of **156**. Orange oil. TLC ($CHCl_3$/MeOH 9:1): R_f 0.24. UV (MeOH): 206 (4.43), 263 (4.06). ^{1}H-NMR ((D_6)DMSO): 11.32 (br., NH); 7.92 (*m*, H *o* to NO_2)); 7.57 (*m*, H *m* to NO_2); 7.40 (*m*, 2 arom. H); 7.30 (*m*, 5 arom. H, H–C(6)); 6.15 (*m*, H–C(1′)); 5.84 (*m*, C*H*(Me)CH_2); 5.45 (*m*, OH–C(3)); 4.13 (*m*, H–C(3′), CH(Me)CH_2)); 3.82 (*m*, H–C(4′)); 3.32–3.15 (*m*, CH_2(5′)); 2.16–1.99 (*m*, CH_2(2′)); 1.73 (*m*, Me–C(5)). Anal. calc. for $C_{25}H_{25}N_3O_9 \cdot 0.5\ H_2O$ (520.5): C 57.69, H 5.04, N 8.07; found: C 57.93, H 5.10, N 7.90.

136. *Thymidine 5′-[1-Methyl-2-(2-nitrophenyl)propyl Carbonate]* (**157**). According to *Exper. 101*, with **87**: 0.296 g (67%) of **157**. Yellow syrup. TLC ($CHCl_3$/MeOH 9:1): R_f 0.24. UV (MeOH): 207 (4.29), 262 (4.06). ^{1}H-NMR ((D_6)DMSO): 11.32 (br., NH); 7.81–7.35 (*m*, 5 arom. H); 6.15 (*m*, H–C(1′)); 5.40 (*m*, OH–C(3)); 4.93 (*m*, MeC*H*O); 4.23–4.04 (*m*, H–C(3′), CH_2(5′)); 3.82 (*m*, H–C(4′)); 3.31 (*m*, MeC*H*); 2.10–1.97 (*m*, CH_2(2′)); 1.73 (*m*, Me–C(5)); 1.21 (*m*, 2 Me). Anal. calc. for $C_{21}H_{25}N_3O_9$ (463.4): C 54.43, H 5.18, N 9.07; found: C 54.56, H 5.45, N 9.10.

137. *Thymidine 5′-[1-Methyl-2-(2-nitrophenyl)butyl Carbonate]* (**158**). According to *Exper. 101*, with **88**: 0.267 g (56%) of **158**. Yellow foam. TLC ($CHCl_3$MeOH 9:1): R_f 0.47. UV (MeOH): 205 (4.42), 262 (4.11). ^{1}H-NMR ((D_6)DMSO): 11.32 (br., NH); 7.78–7.30 (*m*, 4 arom. H, H–C(6)); 6.17 (*m*, H–C(1′)); 5.41 (*m*, OH–C(3)); 4.94 (*m*, C*H*(Me)O); 4.13 (*m*, H–C(3′), CH_2(5′)); 3.84 (*m*, H–C(4′)); 3.12 (*m*, MeCH_2*CH*); 2.06 (*m*, CH_2(2′)); 1.73 (*m*, MeCH_2, Me–C(5)); 1.14 (*m*, *Me*CHO); 0.69 (*t*, *Me*CH_2CH). Anal. calc. for $C_{22}H_{27}N_3O_9$ (477.5): C 55.34, H 5.70, N 8.80; found: C 55.35, H 5.82, N 8.57.

138. *Thymidine 5′-[1-Methyl-2-(2-nitrophenyl)pent-4-enyl Carbonate]* (**159**). According to *Exper. 101*, with **89**: 0.416 g (85%) of **159**. Yellow foam. TLC ($CHCl_3$/MeOH 9:1): R_f 0.45. UV (MeOH): 206 (4.34), 262 (4.07). ^{1}H-NMR ((D_6)DMSO): 11.32 (*s*, NH); 7.79–7.38 (*m*, 4 arom. H, H–C(6)); 6.16 (*m*, H–C(1′)); 5.53 (*m*, CH_2=C*H*); 5.40 (*m*, OH–C(3)); 5.01–4.88 (m, MeC*H*O, CH_2=CH); 4.12 (*m*, H–C(3′), CH_2(5′)); 3.86 (*m*, H–C(4′)); 3.31 (*m*, ArC*H*); 2.05 (*m*, CH_2(2′)); 1.73 (*m*, Me–C(5)); 1.07 (*m*, MeCHO). Anal. calc. for $C_{23}H_{27}N_3O_9$ (489.5): C 56.44, H 5.56, N 8.58; found: C 56.54, H 5.71, N 8.35.

139. *Thymidine 5′-[2-(2-Nitrophenyl)-1-phenylpropyl Carbonate]* (**160**). According to *Exper. 101*, with **90**: 0.147 g (28%) of **160**. Yellow foam. TLC ($CHCl_3$(MeOH 9:1): R_f 0.24. UV (MeOH): 205 (4.47), 262 (4.07). ^{1}H-NMR ((D_6)DMSO): 11.30 (br., NH); 7.84–7.25 (*m*, 10 arom. H); 6.10 (*m*, H–C(1′)); 5.77 (*m*, OH–C(3)); 5.36 (*m*, PhC*H*); 4.10–3.97 (*m*, MeC*H*, CH_2(5′)); 3.74 (*m*, H–C(3′), H–C(4′)); 1.97 (*m*, CH_2(2′)); 1.77 (*s*, Me–C(5)); 1.68 (*m*, MeCH). Anal. calc. for $C_{26}H_{27}N_3O_9$ (525.5): C 59.42, H 5.18, N 8.00; found: C 59.62, H 5.24, N 8.00.

140. *Thymidine 5′-[2-(2-Nitrophenyl)-1-phenylbutyl Carbonate]* (**161**). According to *Exper. 101*, with **91**: 0.13 g (23%) of **161**. Yellow foam. TLC ($CHCl_3$MeOH 9:1): R_f 0.51. UV (MeOH): 205 (4.47), 263 (4.05). ^{1}H-NMR ((D_6)DMSO): 11.30 (br., NH); 7.81–7.23 (*m*, 10 arom. H, H–C(6)); 6.14 (*m*, H–C(1′)); 5.78 (*m*, OH–C(3); 5.36 (*m*, PhC*H*O)); 4.10–3.79 (*m*, ArC*H*, CH_2(5′)); 3.58 (*m*, H–C(3′)); 3.35 (*m*, H–C(4′)); 1.97 (*m*, CH_2(2′)); 1.73 (*m*, 1 H, MeCH_2); 1.65 (*s*, Me–C(5)); 1.38 (*m*, 1 H, MeCH_2)); 0.58 (*m*, *Me*CH_2). Anal. calc. for $C_{27}H_{29}N_3O_9 \cdot 1.5\ H_2O$ (566.5): C 57.24, H 5.69, N 7.42; found: C 57.26, H 5.28, N 7.39.

141. *Thymidine 5′-[2-(2-Nitrophenyl)-1-phenylpent-4-enyl Carbonate]* (**162**). According to *Exper. 101*, with **92**: 0.302 g (53%) of **162**. Yellow foam. TLC ($CHCl_3$/MeOH 9:1): R_f 0.51. UV (MeOH): 207 (4.50), 263 (4.09). ^{1}H-NMR ((D_6)DMSO): 11.30 (br., NH); 7.82–7.20 (*m*, 10 arom. H, H–C(6)); 6.12 (*m*, H–C(1′)); 5.82 (*m*, OH–C(3)); 5.48 (*m*, CH_2=C*H*); 5.41 (*m*, PhC*H*O); 4.81 (*m*, CH_2=CH); 4.87–4.12 (*m*, ArC*H*, CH_2(5′)); 3.80 (*m*, H–C(3′), H–C(4′)); 2.48 (*m*, 1 H, CH_2=CHCH_2); 2.15 (*m*, 1 H, CH_2=CHCH_2)); 2.01 (*m*, CH_2(2′)); 1.70 (*m*, Me–C(5)). Anal. calc. for $C_{28}H_{29}N_3O_9 \cdot H_2O$ (569.5): C 59.05, H 4.49, N 7.38; found: C 58.42, H 5.15, N 7.15.

142. *Thymidine 5′-[(1*RS,*2*RS*)-2-(2,4-Dinitrophenyl)cyclopentyl Carbonate]* (**163**). According to *Exper. 101*, with **97**: 0.260 g (59%) of **163**. Light yellow foam. TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.47. UV (MeOH): 204 (4.36), 262 (4.30), 297 (sh, 3.47). ^{1}H-NMR ($CDCl_3$): 9.26 (br., NH), 8.65 (*m*, H–C(3″)); 8.34 (*m*, H–C(5″)); 7.75 (*m*, H–C(6″)); 7.20 (*s*, H–C(6)); 6.17 (*t*, H–C(1′)); 5.40 (*m*, H–C(1) (cp)); 4.26–3.88 (*m*, CH_2(5′), H–C(3′), H–C(4′)), 3.70 (*m*, H–C(2) (cp)); OH–C(3′) not visible; 2.40–1.75 (*m*, CH_2(2′), 6 CH (cp)); 1.88 (*s*, Me–C(5)). Anal. calc. for $C_{22}H_{24}N_4O_{11}$ (520.5): C 50.77, H 4.65, N 10.77; found: C 50.52, H 4.93, N 10.40.

143. *Thymidine 5′-[1*RS,*2*SR*)-2-(2,4-Dinitrophenyl)cyclopentyl Carbonate]* (**164**). According to *Exper. 101*, with **98**: 0.440 g (74%) of **164**. Light yellow foam. TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.31 and 0.29. UV (MeOH): 205 (4.33), 262 (4.31), 299 (sh, 3.41). ^{1}H-NMR ($CDCl_3$): 9.19 (2 br., NH); 8.58 (*m*, 1 H–C(3″)); 8.38 (*m*, H–C(5″)); 7.59 (*m*, H–C(6″)); 7.37, 7.30 (2*s*, H–C(6)); 6.29 (*m*, H–C(1′)); 5.08 (*m*, H–C(1) (cp)); 4.43–4.21 (*m*, CH_2(5′), H–C(3′)); 4.08 (*m*, H–C(4′)); 3.71 (*m*, H–C(2) (cp)): 2.58 (br., OH–C(3′)); 2.42–1.63 (*m*, CH_2(2′), 6 CH (cp)); 1.90, 1.82 (2*s*, Me–C(5)). Anal. calc. for $C_{22}H_{24}N_4O_{11}$ (520.5): C 50.77, H 4.65, N 10.77; found: C 50.46, H 5.05, N 10.51.

144. *Thymidine 5′-[2-(2,4-Dinitrophenyl)cyclohexyl Carbonate]* (**165**). According to *Exper. 101*, with **96**: 0.280 g (35%) of **165**. Light yellow foam. TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.44. UV (MeOH): 203 (4.26), 261 (4.26), 297 (sh, 3.34). ^{1}H-NMR ($CDCl_3$): 9.17 (br., NH); 8.55 (*m*, H–C(3″)); 8.37 (*m*, H–C(5″)); 7.72 (*m*, H–C(6″)); 7.27, 7.20 (2*d*, H–C(6)); 6.30, 6.18 (2*t*, H–C(1′)); 4.83 (*m*, CH (chx)); 4.32–4.00 (*m*, CH_2(5′), H–C(3′), H–C(4′)); 3.42 (*m*, CH (chx)); 2.32–1.46 (*m*, OH–C(3′), CH_2(2′), 8 CH (chx)); 1.90, 1.82 (2*s*, Me–C(5)). Anal. calc. for $C_{23}H_{26}N_4O_{11}\cdot H_2O$ (556.8): C 50.00, H 5.11, N 10.14; found: C 49.97, H 4.99, N 9.66.

145. *Thymidine 5′-[2-(1-Nitronaphthalen-2-yl)ethyl Carbonate]* (**166**). According to *Exper. 101*, with **102**: 0.165 g (34%) of **168**. Light yellow foam. TLC ($CHCl_3$/MeOH 9:1): R_f 0.32. UV (MeOH): 215 (4.67), 222 (4.69), 265 (4.13), 319 (sh, 3.11), 343 (sh, 2.95). ^{1}H-NMR ((D$_6$)DMSO): 11.30 (br., NH); 8.15–8.04 (*m*, 2 arom. H); 7.70–7.59 (*m*, 4 arom. H); 7.39 (*m*, H–C(6)); 6.18 (m, H–C(1′)); 5.44 (*m*, OH–C(3′)); 4.42 (*m*, CH_2 CH_2O)); 4.45–4.19 (*m*, H–C(3′), CH_2(5′)); 3.90 (*m*, H–C(4′)); 3.22 (*m*, CH_2CH_2O)); 2.12 (*m*, CH_2(2′)); 1.63 (br., Me–C(5)). Anal. calc. for $C_{23}H_{23}N_3O_9$ (485.5): C 56.91, H 4.78, N 8.66; found: C 56.78, H 5.01, N 8.63.

146. *Thymidine 5′-[2-(1-Nitronaphthalen-2-yl)propyl Carbonate]* (**167**). According to *Exper. 101*, with **103**: 0.185 g (37%) of **167**. Light yellow foam. TLC ($CHCl_3$/MeOH 9:1): R_f 0.20. UV (MeOH): 222 (4.68), 265 (4.10). ^{1}H-NMR ((D$_6$)DMSO): 11.28 (br. NH); 8.20–8.05 (*m*, 2 arom. H); 7.80–7.53 (*m*, 4 arom. H); 7.35 (*m*, H–C(6)); 6.14 (*m*, H–C(1′)); 5.41 (*m*, OH–C(3′)); 4.38 (*m*, CH_2O)); 4.19 (*m*, H–C(3′), CH_2(5′)); 3.86 (*m*, H–C(4′)); 3.22 (*m*, MeC*H*)); 2.09–1.99 (*m*, CH_2(2′)); 1.60 (br., Me–C(5)); 1.30 (*m*, MeCH). Anal. calc. for $C_{24}H_{25}N_3O_9$ (499.5): C 57.71, H 5.05, N 8.41; found: C 57.50, H 4.96, N 8.21.

147. *Thymidine 5′-[(1-Nitronaphthalen-2-yl)methyl Carbonate]* (**168**). According to *Exper. 101*, with **113**: 0.193 g (41%) of **168**. Light yellow foam. TLC ($CHCl_3$/MeOH 9:1): R_f 0.33. UV (MeOH): 215 (4.80), 255 (4.17), 334 (3.52). ^{1}H-NMR ((D$_6$)DMSO): 11.28 (br., NH); 8.35–7.69 (*m*, 6 arom. H); 7.42 (*m*, H–C(6)); 6.18 (m, H–C(1′)); 5.45 (*m*, OH–C(3′)); 5.40 (*m*, CH_2O)); 4.33–4.25 (*m*, H–C(3′), CH_2(5′)); 3.94 (*m*, H–C(4′)); 2.13 (*m*, CH_2(2′)); 1.62 (br., Me–C(5)). Anal. calc. for $C_{22}H_{21}N_3O_9\cdot 0.5\ H_2O$ (471.4): C 55.00, H 4.62, N 8.75; found: C 55.20, H 4.64, N 8.76.

148. *Thymidine 5′-[2-(8-Nitronaphthalen-1-yl)ethyl Carbonate]* (**169**) *and 3′-[2-(8-Nitronaphthalen-1-yl)ethyl Carbonate]* (**206**). According to *Exper. 101*, with **105**: 0.173 g (43%) of **169** and 12 mg (3%) of **206** as yellow foams.

Data of **169**: TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.50. UV (MeOH): 209 (sh, 4.64), 220 (4.83), 263 (4.12), 345 (sh, 3.18). ^{1}H-NMR ($CDCl_3$): 8.10 (br., NH); 8.03 (*dd*, 1 arom. H); 7.85 (*m*, 1 arom. H); 7.67 (*dd*, 1 arom. H); 7.57–7.46 (*m*, 3 arom. H); 7.32 (*d*, H–C(6)); 6.31 (*t*, H–C(1′)); 4.50–4.28 (*m*, $CH_2C H_2O$, CH_2(5′), H–C(3′)); 4.09 (*q*, H–C(4′)); 3.19 (*t*, CH_2CH_2O); 2.34 (*m*, 1 H–C(2′)); 2.16 (*m*, 1 H–C(2′), OH–C(3′)); 1.78 (*m*, Me–C(5)). Anal. calc. for $C_{23}H_{23}N_3O_9\cdot 0.5\ H_2O$ (494.5): C 55.87, H 4.89, N 8.50; found: C 55.74, H 4.76, N 8.33.

Data of **206**: TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.58. UV (MeOH): 209 (sh, 4.67), 220 (4.82), 261 (4.12), 338 (sh, 3.37). ^{1}H-NMR ($CDCl_3$): 8.25 (br., NH); 8.03 (*dd*, 1 arom. H); 7.86 (*dd*, 1 arom. H); 7.61–7.46 (*m*, 3 arom. H); 7.40 (*d*, H–C(6)); 6.13 (*q*, H–C(1′)); 5.20 (*m*, H–C(3′)); 4.40 (*t*, $CH_2C H_2O$); 4.09 (*q*, H–C(4′)); 3.94–3.81 (*m*, CH_2(5′)); 3.19 (*t*, CH_2CH_2O); 2.54–2.33 (*m*, CH_2(2′)); 1.89 (*d*, Me–(5)); 1.64 (br., OH–C(3′)). Anal. calc. for $C_{23}H_{23}N_3O_9$ (485.45): C 56.91, H 4.78, N 8.66; found: C 56.62, H 4.96, N 8.09.

149. *Thymidine 5′-[1-(8-Nitronaphthalen-1-yl)ethyl Carbonate]* (**170**). Methyltrifluoromethanesulfonate (633 mg, 3.86 mmol) was added to a cooled (0°) soln. of 1,1′-carbonylbis[1*H*-imidazole] (313 mg, 1.93 mmol) in dry nitromethane (9 ml). After stirring for 20 min at 0° and 30 min at r.t., this mixture was added to **108** (420 mg, 1.93 mmol) and stirred for another 2 h. This soln. of the triflate derivative of **108** was dropped to a soln. of thymidine (467 mg, 1.93 mmol, 3 × co-evaporated with 10 ml pyridine) in dry pyridine (9 ml) and stirred for 1 h at r.t. The mixture was diluted with H_2O (25 ml) and extracted with CH_2Cl_2 (3 × 20 ml), the org. extract dried (Na_2SO_4) and evaporated, and the residue co-evaporated with toluene (3 × 10 ml) and purified by CC (SiO_2 (18 g) 2.5 × 13 cm; CH_2Cl_2, then CH_2Cl_2/MeOH 100:1, 100:2, 100:3, 100:3.5, and 100:4 (100 ml each); SiO_2 (19 g), 2.5 × 14 cm; AcOEt/hexanes, 6:1 → 8:1): 167 mg (18%) of **170**. Yellow foam. TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.42. UV (MeOH): 208 (sh, 4.62), 220 (4.83), 263 (4.15), 318 (sh, 3.35), 342 (sh, 3.31). ^{1}H-NMR ($CDCl_3$): 8.20 (br., NH); 8.05 (*dd*, 1 arom. H); 7.90 (*m*, 1 arom. H); 7.84 (*m*, 2 arom. H); 7.60 (*m*, 1 arom. H); 7.50 (*t*, 1 arom. H); 7.29 (*m*, H–C(6)); 6.25 (*q*, H–C(1′)); 5.94 (*m*, MeC*H*O); 4.43–4.15 (*m*, CH_2(5′), H–C(3′)); 4.02 (*m*, H–C(4′)); 2.32 (*m*, OH–C(3′), 1 H–C(2′)); 2.10 (*m*, 1 H–C(2′)); 1.74 (*m*, Me–C(5), *Me*CHO). Anal. calc. for $C_{23}H_{23}N_3O_9\cdot 0.5\ C_4H_6O_2$ (AcOEt) (561.5): C 56.32, H 5.01, N 8.04; found: C 56.44, H 4.95, N 8.19.

150. *Thymidine 5′-[(8-Nitronaphthalen-1-yl)methyl Carbonate]* (**171**), *3′-[(8-Nitronaphthalen-1-yl)methyl Carbonate]* (**207**), *and 3′,5′-Bis[(8-Nitronaphthalen-1-yl)methyl Carbonate]* (**208**). According to *Exper. 101*, with **110**: 1.61 g (70%) of **171**, 68 mg (3%) of **207**, and 209 mg (6%) of **208** as colorless foams.

Data of **171**: TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.40. UV (MeOH): 208 (sh, 4.57), 217 (4.70), 261 (4.03), 299 (sh, 3.41), 330 (sh, 3.40). ^{1}H-NMR ((D$_6$)DMSO): 11.23 (br., NH); 8.36 (*d*, 1 arom. H); 8.21 (*d*, 1 arom. H); 8.11 (*d*, 1 arom. H); 7.87 (*d*, 1 arom. H); 7.71 (*m*, 2 arom. H); 7.36 (*s*, H–C(6)); 6.16 (*t*, H–C(1′)); 5.42 (*m*, OH–C(3′)); 5.39 (*s*, CH$_2$OC); 4.26 (*d*, CH$_2$(5′)); 4.21 (*m*, H–C(3′)); 3.89 (*m*, H–C(4′)); 2.14–2.07 (*m*, CH$_2$(2′)); 1.47 (*s*, Me–C(5)). Anal. calc. for $C_{22}H_{21}N_3O_9 \cdot 0.5\ H_2O$ (480.4): C 55.00, H 4.61, N 8.75; found: C 54.89, H 4.74, N 8.54.

Data of **207**: TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.48. UV (MeOH): 207 (sh, 4.62), 217 (4.76), 258 (4.17), 306 (sh, 3.52), 333 (sh, 3.43). ^{1}H-NMR ((D$_6$)DMSO): 11.33 (br., NH); 8.37 (*d*, 1 arom. H); 8.22 (*d*, 1 arom. H); 8.13 (*d*, 1 arom. H); 7.88 (*d*, 1 arom. H); 7.22 (*m*, 2 arom. H, H–C(6)); 6.15 (*t*, H–C(1′)); 5.39 (*s*, CH$_2$OC); 5.22 (*t*, OH–C(3′)); 5.14 (*m*, H–C(3′)); 4.01 (*m*, H–C(4′)); 3.62 (br., CH$_2$(5′)); 2.28 (*m*, CH$_2$(2′)); 1.76 (*s*, Me–C(5)). Anal. calc. for $C_{22}H_{21}N_3O_9 \cdot 0.5\ H_2O$ (480.4): C 55.00, H 4.61, N 8.75; found: C 55.31, H 4.40, N 8.60.

Data of **208**: TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.64. UV (MeOH): 207 (sh, 4.86), 217 (5.02), 252 (sh, 4.30), 312 (sh, 3.76), 333 (sh, 3.73). ^{1}H-NMR ((D$_6$)DMSO): 11.34 (br., NH); 8.35 (2*d*, 2 arom. H); 8.21 (2*d*, 2 arom. H); 8.11 (*t*, 2 arom. H); 7.87 (*d*, 2 arom. H); 7.71 (*m*, 4 arom. H); 7.40 (*s*, H–C(6)); 6.15 (*t*, H–C(1′)); 5.39 (*s*, 2 CH$_2$OC); 5.13 (*m*, H–C(3′)); 4.31 (*m*, CH$_2$(5′)); 4.20 (*m*, H–C(4′)); 2.40–2.21 (*m*, CH$_2$(2′)); 1.51 (*s*, Me–C(5)). Anal. calc. for $C_{34}H_{28}N_4O_{13}$ (470.6): C 58.29, H 4.03, N 8.00; found: C 57.95, H 4.09, N 7.90.

151. *Thymidine 5′-[(3-Nitronaphthalen-2-yl)methyl Carbonate]* (**172**). According to *Exper. 101*, with **114**: 0.212 g (45%) of **172**. Light yellow foam. TLC (CHCl$_3$/MeOH 9:1): R_f 0.22. UV (MeOH): 214 (4.68), 255 (4.20). ^{1}H-NMR ((D$_6$)DMSO): 11.30 (br., NH); 9.00–7.50 (*m*, 6 arom. H); 7.42 (*m*, H–C(6)); 6.21 (*m*, H–C(1′)); 5.45 (*m*, OH–C(3′)); 5.61 (*m*, OCH$_2$); 4.52–4.40 (*m*, H–C(3′), CH$_2$(5′)); 4.10 (*m*, H–C(4′)); 2.15 (*m*, CH$_2$(2′)); 1.62 (br., Me–C(5)). Anal. calc. for $C_{22}H_{21}N_3O_9$ (471.4): C 56.05, H 4.49, N 8.91; found: C 56.40, H 4.71, N 8.78.

152. *Thymidine 5′-[(1,2,3,4-Tetrahydro-8-nitronaphthalen-1-yl)methyl Carbonate]* (**173**) *and 3′,5′-Bis[(1,2,3,4-tetrahydro-8-nitronaphthalen-1-yl)methyl Carbonate]* (**209**). According to *Exper. 101*, with **99**: 0.520 g (79%) of **173** and 30 mg (3%) of **209** as colorless foams.

Data of **173**: TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.44. UV (MeOH): 208 (4.37), 264 (4.11), 294 (sh, 3.40). ^{1}H-NMR ((D$_6$)DMSO): 11.31 (*s*, NH); 7.67 (*m*, H–C(7″)); 7.45 (*m*, H–C(5″)); 7.42 (*m*, H–C(6)); 7.38 (*m*, H–C(6″)); 6.18 (*m*, H–C(1′)); 5.43 (*d*, OH–C(3′)); 4.26 (*m*, 1 H–C(5′)); 4.23 (*m*, 1 H–C(5′), H–C(3′)); 4.18 (*m*, 1 H, C*H*$_2$OC(O)); 4.08 (*m*, 1 H, C*H*$_2$OC(O)); 3.91 (*m*, H–C(4′)); 3.75 (*m*, H–C(1″)); 2.90 (*m*, 1 H–C(4″)); 2.81 (*m*, 1 H–C(4″)); 2.16 (*m*, 1 H–C(2′)); 2.08 (*m*, 1 H–C(2′)); 1.92 (*m*, 1 H–C(2″)); 1.83 (*m*, 1 H–C(3″)); 1.76, 1.73 (2*s*, Me–C(5)); 1.73 (*m*, 1 H–C(2″)); 1.92 (*m*, 1 H–C(3″)). Anal. calc. for $C_{22}H_{25}N_3O_9$ (475.4): C 55.58, H 5.30, N 8.84; found: C 55.33, H 5.33, N 8.71.

Data of **209**: TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.64. UV (MeOH): 207 (4.56), 263 (4.23), 296 (sh, 3.62). ^{1}H-NMR (CDCl$_3$): 8.33 (br., NH); 7.61 (2*d*, 2 arom. H); 7.42–7.22 (*m*, 4 arom. H, H–C(6)); 6.42 (*m*, H–C(1′)); 5.23 (*m*, H–C(3′)); 4.46–4.17 (*m*, 2 C*H*$_2$OC(O), CH$_2$(5′)); 4.12–3.97 (*m*, H–C(4′), 2 CH); 2.88 (*m*, 4 CH); 2.65 (br., OH–C(3′)); 2.42 (*m*, CH$_2$(2′)); 2.07 (*m*, 8 CH); 1.94, 1.62 (2*s*, Me–C(5)). Anal. calc. for $C_{34}H_{36}N_4O_{13}$ (708.7): C 57.62, H 5.12, N 7.91; found: C 57.48, H 5.26, N 7.74.

153. *Thymidine 5′-[(3-Nitro-2-thienyl)methyl Carbonate]* (**174**). According to *Exper. 101*, with **115** [62]: 0.224 g (63%) of **174**. Colorless solid. TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.45. UV (MeOH): 212 (sh, 4.30), 265 (4.21), 298 (sh, 3.57), 330 (sh, 2.23). ^{1}H-NMR ((D$_6$)DMSO): 11.29 (br., NH); 7.68 (2*d*, 2 arom. H); 7.44 (*d*, H–C(6)); 6.19 (*t*, H–C(1′)); 5.70 (*s*, CH$_2$OC); 5.44 (*d*, OH–C(3′)); 4.36 (*m*, CH$_2$(5′)); 4.26 (*m*, H–C(3′)); 3.94 (*m*, H–C(4′)); 2.15 (*m*, CH$_2$(2′)); 1.74 (*s*, Me–C(5)).

154. *Thymidine 5′-[1-(3-Nitro-2-thienyl)ethyl Carbonate]* (**175**). According to *Exper. 101*, with 1-(3-nitro-2-thienyl)ethanol (**117**) [63]: 0.288 g (79%) of **175**. Colorless foam. TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.43. UV (MeOH): 212 (4.30), 266 (4.21), 295 (sh, 3.60), 334 (sh, 2.87). ^{1}H-NMR (CDCl$_3$): 9.40 (br., NH); 7.55 (*d*, 1 arom. H); 7.35 (*s*, H–C(6)); 7.22 (*d*, 1 arom. H); 6.65 (*m*, MeC*H*OC); 6.31 (*m*, H–C(1′)); 4.51–4.33 (*m*, CH$_2$(5′), H–C(3′)); 4.14 (*m*, H–C(4′)); 2.67 (br., OH–C(3′)); 2.39 (*m*, 1 H–C(2′)); 2.18 (*m*, 1 H–C(2′)); 1.86 (*s*, Me–C(5)); 1.71 (*dd*, MeCHOC). Anal. calc. for $C_{17}H_{19}N_3O_9S$ (441.4): C 46.26, H 4.34, N 9.52; found: C 46.45, H 4.31, N 9.25.

155. *Thymidine 5′-[2-(3-Nitro-2-thienyl)propyl Carbonate]* (**176**), *3′-[2-(3-Nitro-2-thienyl)propyl Carbonate]* (**210**), *and 3′,5′-Bis[2-(3-nitro-2-thienyl)propyl Carbonate]* (**211**). According to *Exper. 101*, with **118**: 0.534 g (53%) of **176**, 31 mg (3%) of **210**, and 18 mg (1%) of **211** as colorless foams.

Data of **176**: TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.32. UV (MeOH): 212 (4.34), 267 (4.21), 296 (sh, 3.64), 334 (sh, 3.05). ^{1}H-NMR (CDCl$_3$): 9.09 (br., NH); 7.55 (*d*, 1 arom. H); 7.31 (*s*, H–C(6)); 7.17 (*d*, 1 arom. H); 6.31 (*m*, H–C(1′)); 4.51–4.22 (*m*, 6 H, CH(Me)C*H*$_2$, C*H*(Me)CH$_2$, CH$_2$(5′), H–C(3′)); 4.09 (*m*,

H–C(4′)); 3.06 (br., OH–C(3′)); 2.39 (*m*, 1 H–C(2′)); 2.15 (*m*, 1 H–C(2′)); 1.82 (2*s*, Me–C(5)), 1.43 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_{18}H_{21}N_3O_9S$ (455.4): C 47.47, H 4.65, N 9.23; found: C 47.16, H 4.45, N 9.11.

Data of **210**: TLC (toluene/AcOEt/MeOH 5 : 4 : 1): R_f 0.45. UV (MeOH): 212 (4.31), 267 (4.22), 296 (sh, 3.66), 333 (sh, 3.09). ^{1}H-NMR ($CDCl_3$): 9.09 (br., NH); 7.57 (*d*, 1 arom. H); 7.45 (*s*, H–C(6)); 7.18 (*dd*, 1 arom. H); 6.14 (*m*, H–C(1′)); 5.24 (*m*, H–C(3′)); 4.39 (*m*, CH(Me)CH_2), 4.01 (*m*, C*H*(Me)CH_2, H–C(4′)); 3.89 (*m*, CH_2(5′)); 2.95 (br., OH–C(5′)); 2.54–2.35 (*m*, CH_2(2′)); 1.88 (*s*, Me–C(5)); 1.44 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_{18}H_{21}N_3O_9S$ (455.4): C 47.47, H 4.65, N 9.23, found: C 47.33, H 4.82, N 8.72.

Data of **211**: TLC (toluene/AcOEt/MeOH 5 : 4 : 1): R_f 0.64. UV (MeOH): 213 (4.54), 268 (sh, 4.37), 295 (sh, 3.93), 338 (sh, 3.28). ^{1}H-NMR ($CDCl_3$): 8.46 (br., NH); 7.57 (*m*, 2 arom. H); 7.29 (*s*, H–C(6)); 7.20 (*m*, 2 arom. H); 6.33 (*m*, H–C(1′)); 5.13 (*m*, H–C(3′)); 4.49–4.16 (*m*, 2 CH(Me)CH_2, 2 C*H*(Me)CH_2, CH_2(5′), H–C(4′)); 2.46 (*m*, 1 H–C(2′)); 2.18 (*m*, 1 H–C(2′)); 1.84 (*s*, Me–C(5)); 1.44 (*m*, 2 CH(*Me*)CH_2). Anal. calc. for $C_{26}H_{28}N_4O_{13}S_2$ (668.7): C 46.70, H 4.22, N 8.38; found: C 46.89, H 4.65, N 8.15.

156. *Thymidine 5′-[2-(3-Nitro-2-thienyl)ethyl Carbonate]* (**177**), *and 3′-[2-(3-Nitro-2-thienyl)ethyl Carbonate]* (**212**). According to *Exper. 101*, with **120**: 1.2 g (79%) of **177**, and 63 mg (4%) of **212** as colorless foams.

Data of **177**: TLC (toluene/AcOEt/MeOH 5 : 4 : 1): R_f 0.28. UV (MeOH): 211 (4.37), 267 (4.25), 299 (sh, 3.60), 330 (sh, 3.11). ^{1}H-NMR ((D$_6$)DMSO): 11.31 (br., NH); 7.60 (*d*, 1 arom. H); 7.55 (*d*, 1 arom. H); 7.42 (*s*, H–C(6)); 6.17 (*t*, H–C(1′)); 5.75 (br., OH–C(3′)); 4.38 (*t*, CH_2CH_2O); 4.23 (*m*, CH_2(5′), H–C(3′)); 3.88 (*m*, H–C(4′)); 3.53 (*t*, CH_2CH_2O); 2.21–2.04 (*m*, CH_2(2′)); 1.73 (2*s*, Me–C(5)). Anal. calc. for $C_{17}H_{19}N_3O_9S$ (441.4): C 46.26, H 4.34, N 9.52; found: C 46.05, H 4.47, N 9.48.

Data of **212**: TLC (toluene/AcOEt/MeOH 5 : 4 : 1): R_f 0.37. UV (MeOH): 211 (4.32), 267 (4.24), 294 (sh, 3.68), 331 (sh, 3.09). ^{1}H-NMR ((D$_6$)DMSO): 11.35 (br., NH); 7.70 (*s*, H–C(6)); 7.62 (*d*, 1 arom. H); 7.56 (*d*, 1 arom. H); 6.13 (*t*, H–C(1′)); 5.22 (*m*, H–C(3′)); 5.12 (br., OH–C(5′)); 4.44 (*t*, CH_2CH_2O); 4.00 (*m*, H–C(4′)); 3.56 (*m*, CH_2(5′), CH_2CH_2O); 2.26 (*m*, CH_2(2′)); 1.77 (*d*, Me–C(5)). Anal. calc. for $C_{17}H_{19}N_3O_9S$ (441.4): C 46.26, H 4.34, N 9.52; found: C 46.43, H 4.35, N 9.59.

157. *Thymidine 5′-[2-(2-Nitrobenzo[*b*]thien-3-yl)ethyl Carbonate]* (**178**). According to *Exper. 101*, with **121**: 0.323 g (66%) of **178**. Light yellow solid. TLC (toluene/AcOEt/MeOH 5 : 4 : 1): R_f 0.32. UV (MeOH): 211 (4.71), 257 (4.14), 331 (4.08). ^{1}H-NMR ((D$_6$)DMSO): 11.31 (br., NH); 8.11 (*m*, 2 arom. H); 7.67 (*t*, 1 arom. H); 7.56 (*t*, 1 arom. H); 7.37 (*s*, H–C(6)); 6.19 (*t*, H–C(1′)); 5.41 (*d*, OH–C(3′)); 4.44 (*m*, CH_2(5′)), 4.22 (*t*, CH_2CH_2O); 4.16 (*m*, H–C(3′)); 3.85 (*m*, H–C(4′)); 3.69 (*t*, CH_2CH_2O); 2.07 (*m*, CH_2(2′)); 1.70 (2*s*, Me–C(5)). Anal. calc. for $C_{21}H_{21}N_3O_9S$ (509.5): C 49.51, H 4.55, N 8.26; found: C 49.74, H 4.25, N 8.25.

158. N^4*-Benzoyl-2′-deoxycytidine 5′-[2-(2-Nitrophenyl)propyl Carbonate]* (**213**). According to *Exper. 101*, with 2-(2-nitrophenyl)propan-1-ol and *N*^{4}-benzoyl-2′-deoxycytidine: 0.28 g (52%) of **213**. Colorless solid foam. TLC (toluene/AcOEt/MeOH 5 : 4 : 1): R_f 0.41. UV (MeOH): 203 (4.58), 258 (4.44), 302 (4.07). ^{1}H-NMR ($CDCl_3$): 8.79 (br., NH); 8.05 (2*s*, H–C(6)); 7.90 (*m*, 2 arom. H); 7.74 (*m*, 1 arom. H); 7.63–7.33 (*m*, 6 arom. H, H–C(5)); 7.12 (*m*, 1 arom. H); 6.29 (*m*, 1 H–C(1′)); 4.41–4.14 (*m*, H–C(3′), H–C(4′), CH_2 (5′)), CH(Me)CH_2)); 3.77 (*sept.*, C*H*(Me)CH_2); 3.25 (br., OH–C(3′)); 2.68 (*m*, 1 H–C(2′)); 2.14 (*m*, 1 H–C(2′)); 1.35 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_{26}H_{26}N_4O_9$ (538.5): C 57.99, H 4.87, N 10.40; found: C 57.75, H 5.29, N 10.31.

159. *2′-Deoxy-*N^4*-isobutyrylcytidine 5′-[2-(2-Nitrophenyl)propyl Carbonate]* (**214**). According to *Exper. 101*, with 2-(2-nitrophenyl)propan-1-ol and 2′-deoxy-*N*^{4}-isobutyrylcytidine [76]: 0.307 g (61%) of **213**. Colorless solid foam. TLC (toluene/AcOEt/MeOH 5 : 4 : 1): R_f 0.30. UV (MeOH): 208 (4.40), 248 (4.25), 297 (3.93), 330 (sh, 2.91). ^{1}H-NMR ($CDCl_3$): 8.45 (br., NH); 8.02 (*m*, H–C(6)); 7.78 (*m*, 1 H *o* to NO_2); 7.60 (*m*, 1 arom. H); 7.44 (*m*, 1 arom. H, H–C(5)); 6.33 (*m*, H–C(1′)); 4.46–4.17 (*m*, H–C(3′), H–C(4′), CH_2(5′)), CH(Me)CH_2)); 3.78 (*m*, C*H*(Me)CH_2, OH–C(3′)); 2.74 (*m*, 1 H–C(2′)); 2.64 (*m*, Me_2CHCO); 2.10 (*m*, 1 H–C(2′)); 1.38 (*d*, CH(*Me*)CH_2); 1.25 (d, $(Me)_2$CHCO). Anal. calc. for $C_{23}H_{28}N_4O_9$ (504.5): C 54.76, H 5.59, N 11.11; found: C 54.52, H 5.59, N 11.10.

160. *2′-Deoxy-*N^6*-(phenoxyacetyl)adenosine 5′-[2-(2-Nitrophenyl)propyl Carbonate]* (**215**). According to *Exper. 101*, with 2-(2-nitrophenyl)propanol and 2′-deoxy-*N*^{6}-(phenoxyacetyl)adenosine [76]: 0.45 g (76%) of **215**. Colorless solid foam. TLC (CH_2Cl_2/MeOH 9:1): R_f 0.56. UV (MeOH): 208 (4.56), 259 (sh, 4.20), 270 (4.28), 307 (sh, 3.05). ^{1}H-NMR ($CDCl_3$): 9.45 (2*s*, NH); 8.78 (br., H–C(2)); 8.20 (2*s*, H–C(8)); 7.78 (*m*, 1 H *o* to NO_2); 7.59 (*m*, 1 arom. H); 7.49 (*d*, 1 arom. H); 7.37 (*m*, 3 arom. H); 7.06 (*m*, 3 arom. H); 6.53 (*m*, H–C(1′)); 4.88 (*s*, OCH_2COO); 4.72 (*m*, H–C(3′)); 4.45–4.16 (*m*, H–C(4′, CH_2(5′), CH(Me)CH_2)); 3.81 (*m*, C*H*(Me)CH_2); 2.88 (*m*, 1 H–C(2′)); 2.59 (*m*, OH–C(3′), 1 H–C(2′)); 1.38 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_{28}H_{28}N_6O_9$ (592.6): C 56.75, H 4.76, N 14.18; found: C 56.48, H 4.81, N 14.26.

161. *2′-Deoxy-*N^2*-(phenoxyacetyl)guanosine 5′-[2-(2-Nitrophenyl)propyl Carbonate]* (**216**). According to *Exper. 101*, with 2-(2-nitrophenyl)propan-1-ol and 2′-deoxy-*N*^{2}-(phenoxyacetyl)guanosine [74]: 0.505 g (83%)

of **216**. Colorless solid. TLC (CH_2Cl_2/MeOH 9:1): R_f 0.46. UV (MeOH): 205 (4.57), 255 (sh, 4.27), 259 (4.28), 266 (sh, 4.21), 271 (4.17), 280 (sh, 4.15), 330 (sh, 2.85). ^{1}H-NMR ($C(D_6)$DMSO): 11.78 (br., 2 NH); 8.14 (2*s*, H–C(8)); 7.82 (*m*, 1 H *o* to NO_2); 7.67 (*m*, 2 arom. H); 7.47 (*d*, 1 arom. H); 7.31 (*m*, 2 arom. H); 6.99 (*m*, 3 arom. H); 6.23 (*m*, H–C(1′)); 5.51 (*d*, OH–C(3′)); 4.86 (*s*, OCH_2COO); 4.38 (*m*, H–C(3′)); 4.19 (*m*, CH_2(5′), CH(Me)CH_2)); 3.99 (*m*, H–C(4′)); 3.46 (*m*, C*H*(Me)CH_2); 2.65 (*m*, 1 H–C(2′)); 2.32 (*m*, 1 H–C(2′)); 1.26 (*d*, CH(*Me*)CH_2). Anal. calc. for $C_{28}H_{28}N_6O_{10}$ (608.6): C 55.26, H 4.64, N 13.81; found: C 55.41, H 4.97, N 13.42.

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