Nucleosides

Part LXIII[1])

Acetals as New 2′-*O*-Protecting Functions for the Synthesis of Oligoribonucleotides: Synthesis of Uridine Building Blocks and Evaluation of Their Relative Acid Stability

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A broad variety of new acyclic vinyl ethers (see **6**–**41**) have been synthesized *via* the vinyl-interchange reaction of ethyl vinyl ether at room temperature using mercury(II) trifluoroacetate as a highly efficient catalyst. The appropriate vinyl ethers were reacted under acidic conditions with 3′,5′-*O*-silyl-protected uridine **42** to the corresponding 2′-*O*-(1-alkoxyethyl) derivatives **43**–**83** which gave, on desilylation of F^- ions, in high yields the uridine-2′-*O*-acetal derivatives **84**–**124**. The relative stabilities of the newly synthesized compounds under acidic and basic conditions were determined using TLC and HPLC techniques. Protected protecting groups offer the best properties for oligoribonucleotide syntheses. Interestingly, the very acid-stable acetals of the β-substituted ethyl-type **118**–**121** and **123** can be cleaved by a β-elimination process providing a series of base-labile acetals of potential synthetic value.

Introduction. – The chemical synthesis of oligonucleotides has been improved tremendously in recent years by the development of the phosphoramidite approach [2][3] which enables the very efficient automated builtup of oligodeoxyribonucleotides on different types of solid-support materials [4][5]. However, the machine-aided assembly of oligo*ribo*nucleotide chains [6], which become more and more important considering their function as antisense probes, ribozymes, and various types of templates [7–9] has only partially been successful due to principle difficulties encountered with the protection of the additional 2′-OH group in this series. Their chemical synthesis is, therefore, more complex since the additional 2′-OH function has to be protected in a special manner showing high stability as a so-called permanent blocking group during the manipulations to assemble the oligoribonucleotides, but must be cleavable under mild conditions in the final deprotection step to form the free oligomer without harming the internucleotidic phosphodiester linkage [10].

The most common 2′-*O*-blocking group is the **Tbds** ((*tert*-butyl)dimethylsilyl) residue [11–13] (see *Fig.*), a relatively stable silyl protecting group, which is readily removed by F^- ions, commonly after deprotection of the phosphate and base moieties, and cleavage from the support. But there remain still some problems like insufficient deprotection of longer sequences, instability in aqueous ammonia [14], and contamination of the crude oligomer with reagents and inorganic by-products.

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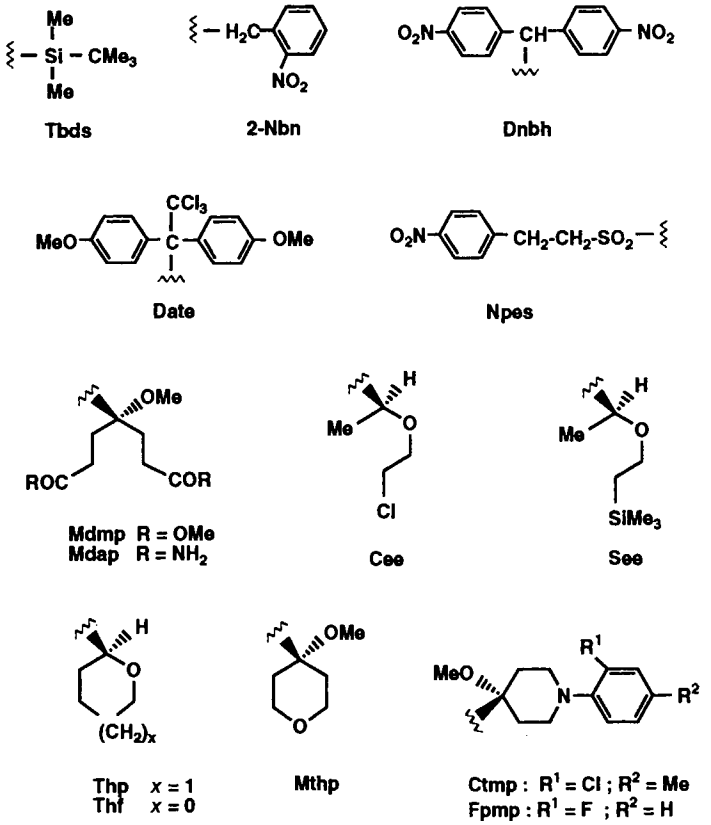


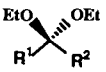
Figure. *2'-O-Protecting groups*

Other functions more or less orthogonal to the residual protecting groups in the molecules are cleaved by light (2-nitrobenzyl (**Nbn**)) [15], by oxidation (dianisyltrichloroethyl (**Date**)) [16], by reductive hydrolysis (4,4'-dinitrobenzhydryl (**Dnbh**)) [17], or by β-elimination (2-(4-nitrophenyl)ethylsulfonyl (**Npes**)) [18]. More convenient, however, is the use of an acetal function, recommended early by *Reese* and co-workers in applying the tetrahydro-2*H*-pyran-2-yl (**Thp**) [19], the tetrahydrofuran-2-yl (**Thf**), and the achiral 4-methoxy-2*H*-tetrahydropyran-2-yl (**Mthp**) [20] group, an approach more recently verified by the use of [(trimethylsilyl)ethoxy]ethyl (**See**) [21], 3-methoxy-1,5-bis-(methoxycarbonyl)pentan-3-yl (**Mdmp**) [22–24], and more simple groups such as 1-alkoxyethyl or 1-(2-chloroethoxy)ethyl (**Cee**) [25]. To combine a suitable acetal function with the common blocking group strategy, however, a more sophisticated tuning regarding the acid-labile 5'-*O*-dimethoxytrityl (Dmtr) and pixyl (Px) group, respectively, is crucial to achieve long-chain oligoribonucleotides of high homogenicity and purity. *Reese* and co-workers [26][27] offered the best solution of this problem so far, by introducing the 1-(2-chloro-4-tolyl)-4-methoxypiperidin-4-yl (**Ctmp**) [28][29] and the commercially available 1-(2-fluorophenyl)-4-methoxypiperidin-4-yl (**Fpmp**) [30][31] group.

The basic studies by *Kreevoy* and *Taft* [32] on the electronic influence of substituents R^1 and R^2 at the acetal C-atom (formally derived from the aldehyde or ketone) on the rates of hydrolysis of ketal and acetal structures indicate that the stability is mainly determined by the number of alkyl groups attached to the central C-atom (see *Table 1*). But there is also a significant electronic influence of additional substituents at the *O*-alkyl chains (formally derived from alcohols) due to σ-resonance along the C–C and C–O bonds which has already been evaluated regarding the stability of various acetal functions [26][28–31][33–35].

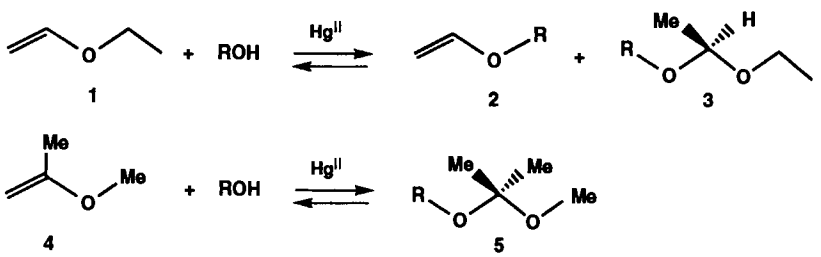
Table 1. *Relative Hydrolysis Rates of Diethyl Ketals and Acetals* [32]

R^1	R^2	Rel. hydrolysis rate
Me	Me	1
Me	$PhCH_2$	1/9
Me	$ClCH_2$	1/9000
H	Me	1/3000
H	$PhCH_2$	1/90000
H	$ClCH_2$	$1/7 \cdot 10^7$
H	H	$1/2 \cdot 10^7$



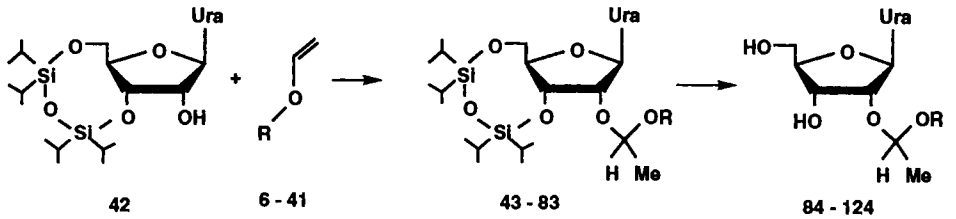
Based upon the findings of *Takaku* and co-workers [33–35], we focussed our attention on the influence of substituents on the hydrolytic stability of oligoribonucleotide acetals [36][37] through the *O*-side chain R (derived from alcohol ROH) of acetaldehyde acetals, since a broad variety of functionalities can easily be introduced into the precursor vinyl ethers **2** *via* the vinyl interchange reaction [37] which works with ethyl vinyl ether **1** under mercury(II)-salt catalysis even with base-labile alcohols ROH [39] (*Scheme 1*).

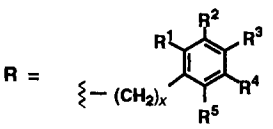
Scheme 1

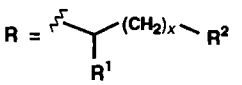


Results. – We found it very convenient to use mercury(II) trifluoroacetate instead of the acetate salt as catalyst in the preparation of the precursor vinyl ethers **2**, since, under these conditions, the always detected side reaction towards the unsymmetrical acetaldehyde *O*-alkyl *O*-ethyl acetal **3** was nearly suppressed, the reaction time was reduced to minutes, and the turnover rate was quantitative. Analogous transformations with 2-methoxypropene (**4**) under $Hg(OAc)_2$ or $Hg(OCOCF_3)_2$ catalysis led, however, quantitatively to the corresponding acetone alkyl methyl ketals **5** (*Scheme 1*). Using the procedure of type **1** → **2**, we prepared the precursor vinyl ethers **10**–**41** (see *Scheme 2*). Alternative-

Scheme 2







	x	R^1	R^2	R^3	R^4	R^5		
6	0	H	H	H	H	H	**43**	**84**
7	0	H	H	OMe	H	H	**44**	**85**
8	0	Cl	H	H	H	H	**45**	**86**
9	0	H	H	NO_2	H	H		
10	1	H	H	H	H	H	**46**	**87**
11	1	H	H	OMe	H	H	**47**	**88**
12	1	H	OMe	OMe	H	H	**48**	**89**
13	1	Cl	H	H	H	Cl	**49**	**90**
14	1	H	Cl	H	Cl	H	**50**	**91**
15	1	H	H	COOEt	H	H	**51**	**92**
16	1	H	H	NO_2	H	H	**52**	**93**
17	1	NO_2	H	H	H	H	**53**	**94**
18	1	NO_2	H	NO_2	H	H	**54**	**95**
19	1	H	H	OCOOnpe	H	H	**55**	**96**
	1	H	H	OH	H	H	**56**	**97**
20	1	Cl	H	OCOOnpe	H	H	**57**	**98**
	1	Cl	H	OH	H	H	**58**	**99**
21	1	H	Cl	OCOOnpe	H	H	**59**	**100**
	1	H	Cl	OH	H	H	**60**	**101**
22	1	H	F	OCOOnpe	H	H	**61**	**102**
	1	H	F	OH	H	H	**62**	**103**
23	1	Cl	H	OCOOnpe	Cl	H	**63**	**104**
	1	Cl	H	OH	Cl	H	**64**	**105**
24	1	Cl	H	$OCOCMe_3$	Cl	H	**65**	**106**
25	2	H	H	H	H	H	**66**	**107**
26	2	H	H	OMe	H	H	**67**	**108**
27	2	H	H	NO_2	H	H	**68**	**109**
28	2	NO_2	H	NO_2	H	H	**69**	**110**

	x	R^1	R^2		
29	0	H	COOnpe	**70**	**111**
30	0	H	$COOC_4H_9$	**71**	**112**
	0	H	$CONH_2$	**72**	**113**
31	1	Me	COOEt	**73**	**114**
32	1	H	COOEt	**74**	**115**
33	1	H	CONHMe	**75**	**116**
34	1	H	NMeCOMe	**76**	**117**
35	1	H	Cl	**77**	**118**
36	1	H	CN	**78**	**119**
37	1	H	NO_2	**79**	**120**
38	1	H	SO_2Me	**80**	**121**
39	1	H	SC_6H_5	**81**	**122**
40	1	H	$SO_2C_6H_5$	**82**	**123**
41	1	H	Phthalimido	**83**	**124**

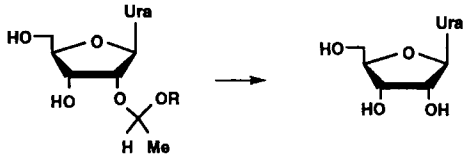
ly, the phenyl vinyl ethers **6**–**9** could be synthesized *via* nucleophilic displacement of one Br-atom in 1,2-dibromoethane by the phenolate; the following β-elimination led to the corresponding vinyl ethers in 50–60% yield. Isolation and purification of the high-boiling and solid derivatives **6**–**41** was easily achieved by means of chromatography due to large differences in mobilities of the vinyl ether, acetaldehyde acetal, and alcohol. Non-UV-absorbing derivatives were detected by the fast coloring reaction in an I_2 chamber.

The newly synthesized vinyl ethers **6**–**41** were then reacted with 3′,5′-*O*-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)uridine (**42**) to give the corresponding acetaldehyde uridin-2′-yl acetals **43**–**83** in very good yields of 70–95%; only the 4-nitrophenyl vinyl ether (**9**) did not react with alcohols under acidic conditions due to the strong mesomeric effect of the *p*-nitro group. The selective cleavage of the silyl residue of **43**–**83** to yield the uridine 2′-acetals **84**–**124** worked well with tetrabutylammonium fluoride (Bu_4NF) in dioxane, except for **78** and **79** which lost most of the acetal function by a β-elimination process initiated by the basic F^- ion under aprotic conditions. This side reaction could be suppressed by addition of AcOH as a buffer or the use of NH_4F in MeOH which required, however, higher temperatures and prolonged reaction times.

The comparative cleavage of the acetal functions of **84**–**124** under acidic conditions were performed by kinetic studies with 0.03M solutions of the uridine 2′-acetal in 80% AcOH (*Conditions A*) and/or 0.05N HCl/MeOH 1:1 (*Conditions B*) (*Table 2*). It is interesting to note that there are big differences in the acid stabilities, showing half-life values from 24 s to over 3000 s, which are due to the various functionalities in the R moiety of **84**–**124**. These facts demonstrate that the acetal protection is either too labile or too stable under the anticipated cleavage conditions recommended during the oligoribonucleotide approach. Nevertheless, we learned from these kinetic studies that the solution of the blocking-group problem has to be seen in the development of a suitable protecting group which is stable enough during the builtup and chain elongation of the oligoribonucleotide by the solid-support approach using the acid-labile 4,4′-dimethoxytrityl ($(MeO)_2Tr$) group for 5′-OH protection and which will be labilized during cleavage of the base and phosphate-blocking groups.

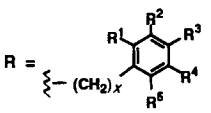
The benzyl acetals turned out to possess the needed properties since replacement of the benzyl group of 2′-*O*-[1-(benzyloxy)ethyl]uridine (**87**) by the 4-hydroxybenzyl group (see **97**) lowers the acid stability even from 66 to 24 s under the *Conditions B*. On the other hand, replacement of the OH group in **97** by the [2-(4-nitrophenyl)ethoxy]carbonyloxy group (see **96**) converts this function from an electron-donating into an electron-attracting substituent increasing the $t_{1/2}$ of the acid stability of **96** to 104 s. Since the acid stabilities of the pair **87**/**96** are, regarding the compatibility with the $(MeO)_2Tr$ group, to some extent too low, a fine-tuning of the 4-hydroxybenzyl group was achieved by preparing the corresponding *o*-chloro (**98**/**99**), *m*-chloro (**100**/**101**), *o*,*m*′-dichloro (**104**/**105**), and the *m*-fluoro pair **102**/**103**, respectively. The pair **102**/**103** offers the perfect stabilities with $t_{1/2}$ of 305 and 48 s for the standard phosphoramidite chemistry. The npeoc group can be cleaved very fast and quantitatively by DBU treatment in an aprotic solvent generating the acid labile 4-hydroxybenzyl acetal derivative **103**. There are also some advantages in applying **102** in form of its 5′-*O*-(4,4′-dimethoxytrityl)-3′-*O*-phosphoramidite in oligoribonucleotide synthesis over the 1-(2-fluorophenyl)-4-methoxypiperidin-4-yl (**Fpmp**) group of *Reese* [30][31] which is more difficult to synthesize and recruits its stability from pH variations, whereas our principle relies on orthogonal functionalities. Syntheses of oligoribonucleotides using the 2′-*O*-1-[3-fluoro-4-({[2-(nitrophenyl)ethoxy]carbonyl}oxy)benzyloxy]ethyl (**Fnbe**) group will be published soon in this journal.

In principle our new approach allows numerous modifications by substituent variations to construct the anticipated properties for special cases.

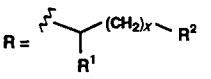


84 - 124

Table 2. *Half-lives of Acid Cleavages of Uridine 2'-Acetals in 0.05N HCl/MeOH 1:1 (Conditions A) and in 80% AcOH/H_2O (Conditions B)*

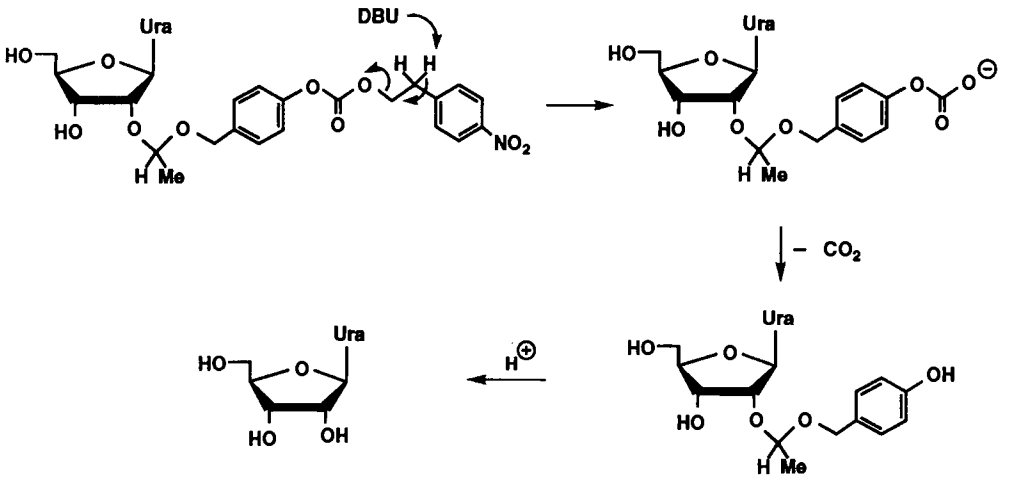


	x	R^1	R^2	R^3	R^4	R^5	*Conditions A* $t_{1/2}$ [s]	*Conditions B* $t_{1/2}$ [s]
84	0	H	H	H	H	H	>3000	
85	0	H	H	OMe	H	H	>3000	
86	0	Cl	H	H	H	H	>3000	
87	1	H	H	H	H	H	175	66
88	1	H	H	OMe	H	H	73	
89	1	OMe	H	OMe	H	H	82	
90	1	Cl	H	H	H	Cl	1130	
91	1	H	Cl	H	Cl	H	900	
92	1	H	H	COOEt	H	H	1190	
93	1	H	H	NO_2	H	H	1960	
94	1	NO_2	H	H	H	H	2240	
95	1	NO_2	H	NO_2	H	H	>3000	
96	1	H	H	OCOOnpe	H	H		104
97	1	H	H	OH	H	H		24
98	1	Cl	H	OCOOnpe	H	H		272
99	1	Cl	H	OH	H	H		69
100	1	H	Cl	OCOOnpe	H	H		288
101	1	H	Cl	OH	H	H		56
102	1	H	F	OCOOnpe	H	H		305
103	1	H	F	OH	H	H		48
104	1	Cl	H	OCOOnpe	Cl	H		1300
105	1	Cl	H	OH	Cl	H		250
106	1	Cl	H	OCO'Bu	Cl	H		1350
107	2	H	H	H	H	H	88	
108	2	H	H	OMe	H	H	115	
109	2	H	H	NO_2	H	H	215	
110	2	NO_2	H	NO_2	H	H	1200	



	x	R^1	R^2	*Conditions A* $t_{1/2}$ [s]	*Conditions B* $t_{1/2}$ [s]
111	0	H	COOnpe	>3000	
112	0	H	$COOC_4H_9$	>3000	
113	0	H	$CONH_2$	>3000	
114	1	Me	COOEt	70	32
115	1	H	COOEt	275	
116	1	H	CONHMe	170	
117	1	H	NMeCOMe	428	
118	1	H	Cl	620	380
119	1	H	CN	3370	
120	1	H	NO_2	4030	
121	1	H	SO_2Me	2980	1640
122	1	H	SC_6H_5	230	
123	1	H	$SO_2C_6H_5$	3120	1800
124	1	H	Phthalimido	840	

Scheme 3



Experimental Part

1. *General.* Org. solvents, 2-chloroethyl vinyl ether, ethyl vinyl ether, mercury(II) acetate, and mercury(II) trifluoroacetate were purchased from *Fluka* (Buchs, Switzerland). Products were dried under high vacuum or in a desiccator over $CaCl_2$. TLC: Precoated silica gel thin-layer sheets *F1500 LS 254* from *Schleicher & Schüll*; detection by UV or in a I_2 chamber. Flash column chromatography (FC): silica gel from *Baker* (30–60 mm), 0.3–0.5 bar. HPLC: *L-6200-Intelligent* pump, UV-integrator *L4000*, autosample *AS 4000*; software: *HPLC-Manager/Merck-Hitachi*; UV-detector *Uvikon 820* (Fa. *Kontron*), detection at 260 nm, column *RP-18* (*LiChrospher* 125 × 4 mm, 5 mm); elution: *A* = H_2O, *B* = H_2O/MeCN 1:1; 0% *B* (0–3 min), 0–80% *B* (3–20 min), 80% *B* (20–30 min), 80–0% *B* (30–35 min), 0% *B* (35–40 min). M.p.: *Gallenkamp* or *Büchi*, model *Dr. Tottoli*, melting-point apparatus; no corrections. UV/VIS: *Perkin-Elmer Lambda 5*; λ_{max} in nm (log ε). ^{1}H-NMR: *Bruker WM 250*; δ in ppm rel. to $SiMe_4$, *J* in Hz. ^{31}P-NMR: *AC 250*, *Jeol JM GX 400*; δ in ppm rel. to 85% phosphoric acid; $CDCl_3$ or (D_6)DMSO as internal standard.

2. *Hydrolysis Rates of the Uridine 2'-Acetals*: *General Procedure.* The rough hydrolysis rates were first determined by qualitative TLC tests. These preliminary data were used to set an appropriate time frame for the quantitative experiments. The carefully dried nucleoside **84**–**124** (*ca.* 45 mmol, 20–30 mg) was dissolved in the corresponding volume (1.5 ml) of the acidic medium (20°, magnetic stirring). The temp. of the clear 0.03N soln., controlled with an adjustable water-bath (± 0.5°), was put to 20°. After the appropriate reaction times, 20-µl aliquots (10–15 per experiment) were quenched with cold buffer solns. 0.15N KH_2PO_4/Na_2HPO_4 (pH 7.5; 1 ml) for HCl/MeOH (*Conditions A*) and 0.2N Na_2CO_3 for 80% AcOH/H_2O (*Conditions B*). These probes (20 ml) were injected into the HPLC system and the relative ratio of the hydrolysis products (uridine + cleaved alcohol) and educts detected at 260 nm. Quantitation of the results was achieved using EXCEL software (*Microsoft*). In all cases, pseudo-first-order kinetics were observed ($t_{1/2}$: ± 10%).

3. *Phenyl Vinyl Ethers* **6**–**9**. 3.1. *General Procedure* [40]. A mixture of the phenol derivative (0.3 mol) and 1,2-dibromoethane (0.4 mol) was heated in H_2O (230 ml) to reflux. Then NaOH (15.84 g) in H_2O (100 ml) was added in several portions within 2–3 h and the resulting mixture refluxed for additional 12–16 h. After cooling and addition of AcOEt (300 ml), the org. layer was extracted with 1.0N NaOH (2 × 200 ml) and sat. NaCl soln. (2 × 200 ml). After drying with Na_2SO_4, filtering, and evaporation, the resulting residue was distilled or crystallized from MeOH/H_2O. Yields of 2-bromoethyl aryl ether, 56–79%.

Dehydrohalogenation was achieved by dissolving the appropriate 2-bromoethyl aryl ether (50 mmol) in toluene (150 ml), addition of tetrabutylammonium hydrogensulfate (50 mmol), and then adding dropwise NaOH (50%, 50 ml) to the emulsion. After stirring overnight, the org. layer was extracted with H_2O (4 × 100 ml), dried (Na_2SO_4), and evaporated. The residue was distilled (**6**–**8**) or sublimated under high vacuum (**9**).

3.2. *Phenyl Vinyl Ether* (**6**). Distillation; b.p. 156°. Yield 70%. TLC (CCl_4): R_f 0.63. ^{1}H-NMR ($CDCl_3$): 7.23 (*m*, 5 arom. H); 6.51 (*dd*, CH_2=C*H*); 4.66 (*dd*, 1 H, CH_2=CH, *trans* to H); 4.31 (*dd*, 1 H, CH_2=CH, *cis* to H).

3.3. *4-Methoxyphenyl Vinyl Ether* (**7**). Distillation; b.p. 102°/15 Torr. Yield 71%. TLC (CCl_4/Et_2O 10:1): R_f 0.74. ^{1}H-NMR ($CDCl_3$): 6.98 (*d*, 2 H_m); 6.88 (*d*, 2 H_o); 6.61 (*dd*, CH_2=C*H*); 4.68 (*dd*, 1 H, CH_2=CH, *trans* to H); 4.38 (*dd*, 1 H, CH_2=CH, *cis* to H).

3.4. *2-Chlorophenyl Vinyl Ether* (**8**). Distillation; b.p. 71°/12 Torr. Yield 70%. TLC (CCl_4): R_f 0.68. ^{1}H-NMR ($CDCl_3$): 7.42–7.00 (*m*, 4 arom. H); 6.59 (*dd*, CH_2=C*H*); 4.74 (*dd*, 1 H, CH_2=CH, *trans* to H); 4.48 (*dd*, 1 H, CH_2=CH, *cis* to H).

3.5. *4-Nitrophenyl Vinyl Ether* (**9**) [41]. Crystallization. Yield 76%. M.p. 61°. TLC (CCl_4/Et_2O): R_f 0.64. ^{1}H-NMR ($CDCl_3$): 8.20 (*d*, 2 H_m); 7.05 (*d*, 2 H_o); 6.66 (*dd*, CH_2=C*H*); 4.97 (*dd*, 1 H, CH_2=CH, *trans* to H); 4.67 (*dd*, 1 H, CH_2=CH, *cis* to H).

4. *Vinyl Ethers* **10**–**41**. 4.1 *General Procedure*. The required alcohol (0.5 mol) was dissolved in 2–5 equiv. of ethyl vinyl ether. *Procedure a*: Starting with crystalline alcohols, anh. toluene (100–200 ml) was added followed by mercury(II) acetate (1.59 g, 5.00 mmol) in 3–4 portions. Then the soln. was stirred for 12–48 h at r.t. (TLC control). *Procedure b*: The soln. was cooled with ice, then mercury(II) trifluoracetate (0.215 g, 0.5 mmol) was added and the mixture stirred without further cooling at r.t. for 20–60 min (TLC control). The mixture was diluted with AcOEt (300 ml) and subsequently washed with sat. $NaHCO_3$ (2 × 200 ml) and NaCl soln. (2 × 100 ml) and the org. layer dried (Na_2SO_4), and evaporated. Low-boiling vinyl ethers were distilled *via* a 'Spaltrohrkolonne'. High-boiling and solid vinyl ethers were purified by FC with toluene as eluent.

4.2. *Benzyl Vinyl Ether* (**10**). Distillation; b.p. 47°/15 Torr. Yield 19%. Colourless oil. TLC (toluene/AcOEt 10:1): R_f 0.78 (I_2). ^{1}H-NMR ($CDCl_3$): 7.38–7.30 (*m*, 5 arom. H); 6.61 (*dd*, ^3J = 14.3, 6.8, CH_2=C*H*); 4.77 (*s*, CH_2O); 4.32 (*dd*, ^2J = 1.70, 1 H, CH_2=CH, *trans* to H); 4.06 (*dd*, 1 H, CH_2=CH, *cis* to H).

4.3. *4-Methoxybenzyl Vinyl Ether* (**11**). Distillation; b.p. 84°/0.3 Torr. Yield 48%. Colourless oil. TLC (toluene): R_f 0.89. UV (MeOH): 225 (4.08), 273 (3.22), 279 (sh, 3.16). ^{1}H-NMR ($CDCl_3$): 7.29 (*d*, 2 H_o); 6.91 (*d*, 2 H_m); 6.54 (*dd*, *J* = 14.3, 6.9, CH_2=C*H*); 4.68 (*s*, CH_2O); 4.29 (*dd*, ^2J = 2.08, CH_2=CH, *trans* to H); 4.06 (*dd*, 1 H, CH_2=CH, *cis* to H); 3.80 (*s*, MeO).

4.4. *3,4-Dimethoxybenzyl Vinyl Ether* (**12**). Distillation; b.p. 86°/0.45 Torr. Yield 48%. Colourless oil. TLC (toluene): R_f 0.79. ^{1}H-NMR ($CDCl_3$): 6.90–6.50 (*m*, 3 arom. H); 6.53 (*dd*, ^3J = 14.33, 6.80, CH_2=C*H*); 4.67 (*s*, CH_2O); 4.29 (*dd*, ^2J = 2.12, 1 H, CH_2=CH, *trans* to H); 4.06 (*dd*, 1 H, CH_2=CH, *cis* to H); 3.88 (*s*, 1 MeO); 3.86 (*s*, 1 MeO).

4.5. *2,6-Dichlorobenzyl Vinyl Ether* (**13**). Distillation; b.p. 56°/0.001 Torr. Yield 68%. Colourless oil. TLC (toluene/AcOEt 10:1): R_f 0.88. ^{1}H-NMR ($CDCl_3$): 7.25 (*d*, H–C(3), H–C(5)); 7.16 (*m*, H–C(4)); 6.52 (*dd*, ^3J = 14.21, 6.77, CH_2=C*H*); 4.92 (*s*, CH_2O); 4.30 (*dd*, ^2J = 2.29, 1 H, CH_2=CH, *trans* to H); 4.05 (*dd*, 1 H, CH_2=CH, *cis* to H).

4.6. *3,5-Dichlorobenzyl Vinyl Ether* (**14**). Yield 78%. Colourless oil. TLC (toluene/AcOEt 10:1): R_f 0.83. ^{1}H-NMR ($CDCl_3$): 7.38–7.15 (*m*, H–C(2), H–C(4), H–C(5)); 6.54 (*dd*, ^3J = 14.34; 6.88, CH_2=C*H*); 4.78 (*s*, CH_2O); 4.30 (*dd*, 1 H, ^2J = 2.37, CH_2=CH, *trans* to H); 4.14 (*dd*, 1 H, CH_2=CH, *cis* to H).

4.7. *Ethyl 4-[(Vinyloxy)methyl]benzoate* (**15**). Yield 75%. Colourless oil. TLC (toluene/AcOEt 4:1): R_f 0.88 (I_2). UV (MeOH): 267 (2.95), 234 (4.18). ^{1}H-NMR ($CDCl_3$): 8.05 (*d*, 2 H_o); 7.41 (*d*, 2 H_m); 6.55 (*dd*, CH_2=C*H*); 4.81 (*s*, ArCH_2O); 4.35 (*q*, MeCH_2O); 4.31 (*dd*, 1 H, CH_2=CH, *trans* to H); 4.10 (*dd*, CH_2=CH, *cis* to H); 1.4 (*t*, $MeCH_2O$).

4.8. *4-Nitrobenzyl Vinyl Ether* (**16**). Crystallization. Yield 47%. M.p. 42°. Colourless needles. TLC (toluene): R_f 0.65. UV (MeOH): 203 (4.15), 213 (sh, 3.93), 266 (4.00). ^{1}H-NMR ($CDCl_3$): 8.22 (*d*, 2 H_m); 7.52 (*d*, 2 H_o); 6.58 (*dd*, ^3J = 14.3, 6.83, CH_2=C*H*); 4.87 (*s*, CH_2O); 4.31 (*dd*, ^2J = 2.48, 1 H, CH_2=CH, *trans* to H); 4.16 (*dd*, 1 H, CH_2=CH, *cis* to H). Anal. calc. for $C_9H_9NO_3$ (179.2): C 60.33, H 5.06, N 7.82; found: C 60.54, H 5.07, N 8.00.

4.9. *2-Nitrobenzyl Vinyl Ether* (**17**). Distillation; b.p. 96–98°/0.0015 Torr. Yield 45%. Yellow oil (light-sensitive). TLC (toluene): R_f 0.68. UV (MeOH): 203 (4.20), 258 (3.76). ^{1}H-NMR ($CDCl_3$): 8.11 (*d*, H–C(3)); 7.77 (*d*, H–C(6)); 7.68 (*t*, H–C(5)); 7.47 (*t*, H–C(4)); 6.55 (*dd*, ^3J = 14.29, 6.78, CH_2=C*H*); 4.87 (*s*, CH_2O); 4.36 (*dd*, ^2J = 2.40, 1 H, CH_2=CH, *trans* to H); 4.14 (*dd*, 1 H, CH_2=CH, *cis* to H). Anal. calc. for $C_9H_9NO_3$ (179.2): C 60.33, H 5.06, N 7.82; found: C 60.44, H 5.36, N 7.77.

4.10. *2,4-Dinitrobenzyl Vinyl Ether* (**18**). Crystallization. Yield 30%. M.p. 48°. Colourless needles (toluene). TLC (toluene): R_f 0.58. UV (MeOH): 202 (4.13), 240 (4.20), 293 (sh, 2.77). ^{1}H-NMR ($CDCl_3$): 8.98 (*d*, H–C(3)); 8.50 (*d*, H–C(5)); 8.06 (*d*, H–C(6)); 6.58 (*dd*, ^3J = 14.3, 6.83, CH_2=C*H*); 5.26 (*s*, CH_2O); 4.38 (*dd*, ^2J = 2.74, 1 H, CH_2=CH, *trans* to H); 4.22 (*dd*, 1 H, CH_2=CH, *cis* to H). Anal. calc. for $C_9H_8N_2O_5$ (224.17): C 48.22, H 3.60, N 12.50; found: C 48.49, H 3.75, N 12.37.

4.11. *2-(4-Nitrophenyl)ethyl 4-[(Vinyloxy)methyl]phenyl Carbonate* (**19**). As described in *4.12*, starting from 4-hydroxybenzyl alcohol. Crystallization. Yield 89%. M.p. 64°. Colourless needles. TLC (toluene/AcOEt 3:1): R_f 0.88. UV (MeOH): 268 (4.01). ^{1}H-NMR ($CDCl_3$): 8.18 (*d*, 2 H *o* to NO_2); 7.47–7.31 (*m*, 2 H *m* to NO_2, 2 H *m*

to OCO); 7.12 (*m*, 2 H *o* to OCO); 6.52 (*dd*, ^3J = 14.3, 6.8, CH_2=C*H*); 4.73 (*s*, CH_2O); 4.48 (*t*, CH_2CH_2O); 4.29 (*dd*, ^2J = 2.5, 1 H, CH_2=CH, *trans* to H); 4.08 (*dd*, 1 H, CH_2=CH, *cis* to H); 3.15 (*t*, CH_2CH_2O). Anal. calc. for $C_{18}H_{17}NO_6$ (343.3): C 62.97, H 4.99, N 4.08; found: C 62.96, H 5.00, N 4.04.

4.12. *3-Chloro-4-[(vinyloxy)methyl]phenyl 2-(4-Nitrophenyl)ethyl Carbonate* (**20**). A soln. of 3-chlorophenol (25.7 g, 0.2 mol) in 20% KOH soln. (60 ml) was heated to 60°. Then a formaldehyde soln. (100 ml; prepared from 30 ml of a 37% soln. by dilution; 0.37 mol) was added dropwise within 3 h under stirring. TLC: two products, the faster moving being the desired one. After heating to 60° for another 3 h, the mixture was cooled, diluted with ice-water (500 ml) and AcOEt (300 ml), and neutralized with conc. HCl soln. to pH 5–6. The org. phase was separated and washed with phosphate buffer pH 6.0 (2 × 300 ml) and sat. NaCl soln. (300 ml). The aq. phases were extracted again with AcOEt (2 × 150 ml). The washing procedure was repeated and then the combined AcOEt extract dried (Na_2SO_4) and evaporated to a syrup. Purification was achieved by FC (200 g of silica gel, toluene; toluene/AcOEt 200:0, 450:50, 400:100, 350:150, 300:200 ml; 100-ml fractions). The combined product fraction was concentrated to *ca.* 100 ml and cooled overnight to form (scratching) colourless crystals of *2-chloro-4-hydroxybenzyl alcohol* (28%). M.p. 127°. UV (MeOH): 206 (4.53), 222 (3.84), 279 (3.28), 285 (sh, 3.23). ^{1}H-NMR ((D$_6$)DMSO): 9.72 (*s*, O*H*–C_6H_3); 7.29 (*s*, H–C(3)); 6.75 (*m*, H–C(5), H–C(6)); 5.13 (*t*, CH_2OH); 4.45 (*d*, CH_2). Anal. calc. for $C_7H_7ClO_2$ (158.6): C 53.02, H 4.45; found: C 53.31, H 4.56.

To a soln. of 2-chloro-4-hydroxybenzyl alcohol (4.76 g, 30 mmol) in abs. pyridine (70 ml), 4-methoxytrityl chloride (11 g, 35.6 mmol) was added and stirred at r.t. for 6 h (TLC control). The reaction was stopped by addition of MeOH (20 ml) and stirring for 30 min. After concentration to 30 ml, AcOEt (300 ml) was added, the mixture washed with sat. NaCl soln. (3 × 300 ml), the org. phase dried (Na_2SO_4) and evaporated, and the residue twice co-evaporated with toluene to a syrup. The crude product was purified by FC (230 g of silica gel, toluene; toluene/AcOEt 500:0, 475:25, 450:50 ml). Evaporation and two co-evaporations with MeOH (30 ml) gave a solid foam (93%) of *3-chloro-4-{[(4-methoxytrityl)oxy]methyl}phenol*.

The 3-chloro-4-{[(methoxytrityl)oxy]methyl}phenol (12.9 g, 30 mmol) was co-evaporated with abs. toluene and dissolved in abs. MeCN (50 ml). Then 2-(4-nitrophenyl)ethoxycarbonyl-1-methyl-1*H*-imidazolium chloride and 4-(dimethylamino)pyridine (DMAP, 0.7 g) were added and stirred at r.t. for 30 min (→ clear soln.). The soln. was evaporated to a small volume, diluted with AcOEt (300 ml), washed with sat. $NaHCO_3$ (200 ml) and NaCl soln. (200 ml), dried (Na_2SO_4), and evaporated to a syrup.

The crude 3-chloro-4-{[(4-methoxytrityl)oxy]methyl}phenyl 2-(4-nitrophenyl)ethyl carbonate was then detritylated by stirring at r.t. for 3 h in $CHCl_3$/MeOH 4:1 (50 ml) and *p*-toluenesulfonic acid (1 g). The soln. was diluted with AcOEt (200 ml) and then treated with cold $NaHCO_3$ (200 ml) and NaCl soln. (200 ml). The org. layer was dried (Na_2SO_4) and evaporated to an oil. Purification by FC (250 g of silica gel, toluene, toluene/AcOEt 300:0, 450:50, 400:100, 350:150, 300:200 ml) gave a solid foam (76%) of *3-chloro-4-(hydroxymethyl)phenyl 2-(4-nitrophenyl)ethyl carbonate*. ^{1}H-NMR ((D$_6$)DMSO): 8.18 (*d*, 2 H *o* to NO_2); 7.49 (*d*, H–C(6)); 7.40 (*m*, 2 H *m* to NO_2); 7.17 (*d*, H–C(3)); 7.05 (*d*, H–C(5)); 4.74 (*s*, CH_2OH); 4.48 (*t*, CH_2CH_2O); 3.14 (*t*, CH_2CH_2O); 1.88 (br. *s*, OH).

To a soln. of 3-chloro-4-(hydroxymethyl)phenyl 2-(4-nitrophenyl)ethyl carbonate (7.45 g, 20 mmol) in ethyl vinyl ether (120 ml), mercury(II) trifluoroacetate (0.68 g) was added and stirred at r.t. for 6 h. The mixture was diluted with AcOEt (300 ml) and mixed with sat. $NaHCO_3$ soln. (200 ml), the org. phase washed again with $NaHCO_3$ (100 ml) and NaCl soln. (100 ml), dried (Na_2SO_4), and evaporated, and the residue purified by FC (150 g of silica gel, toluene). Evaporation and co-evaporation with MeOH gave a syrup: 6.78 g (82%) of **20**. ^{1}H-NMR ($CDCl_3$): 8.18 (*m*, 2 H *o* to NO_2); 7.50 (*d*, H–C(6)); 7.42 (*d*, 2 H *m* to NO_2); 7.20 (*d*, H–C(3)); 7.05 (*dd*, H–C(5)); 6.53 (*dd*, ^3J = 14.3, 6.8, CH_2=C*H*); 4.78 (*s*, CH_2); 4.48 (*t*, CH_2CH_2O); 4.30 (*dd*, ^2J = 2.3, 1 H, CH_2=CH, *trans* to H); 4.12 (*dd*, 1 H, CH_2=CH, *cis* to H); 3.18 (*t*, CH_2CH_2O).

4.13. *2-Chloro-4-[(vinyloxy)methyl]phenyl 2-(4-Nitrophenyl)ethyl Carbonate* (**21**). As described in *4.12*, starting from 2-chlorophenol to give first 3-chloro-4-hydroxybenzyl alcohol in 23% yield. M.p. 125°. UV (MeOH): 206 (4.12), 219 (3.85), 280 (3.40), 285 (sh, 3.37). ^{1}H-NMR ((D$_6$)DMSO): 10.05 (br. *s*, OH–C_6H_3); 7.28 (*s*, H–C(2)); 7.08 (*d*, H–C(6)); 6.90 (*d*, H–C(5)); 5.12 (br. *s*, CH_2OH); 4.35 (*s*, CH_2).

Monomethoxytritylation led to 2-chloro-4-{[(4-methoxytrityl)oxy]methyl}phenol in 89% yield. Reaction with (2-(4-nitrophenyl)ethoxycarbonyl-1-methyl-1*H*-imidazolium chloride gave 2-chloro-4-{[(4-methoxytrityl)-oxy]methyl}phenyl 2-(4-nitrophenyl)ethyl carbonate which was converted by detritylation to 2-chloro-4-(hydroxymethyl)phenyl 2-(4-nitrophenyl)ethyl carbonate in 74% yield. ^{1}H-NMR ($CDCl_3$): 8.29 (*d*, 2 H *o* to NO_2); 7.50 (*m*, 3 H *m* to NO_2, H–C(2)); 7.35 (*d*, H–C(6)); 7.31 (*d*, H–C(5)); 4.72 (*s*, CH_2); 4.58 (*t*, CH_2CH_2O); 3.25 (*t*, CH_2CH_2O); 2.35 (br. *s*, CH_2OH).

Reaction with ethyl vinyl ether gave **21** in 75% yield. Colourless oil. TLC (toluene/AcOEt 10:1): R_f 0.70. ^{1}H-NMR ((D$_6$)DMSO): 8.17 (*d*, 2 H *o* to NO_2); 7.46–7.73 (*m*, 2 H *m* to NO_2, H–C(2)); 7.29–7.20

(*dd*, H–C(6)); 7.13 (*d*, H–C(5)); 6.53 (*dd*, ^3J = 14.3, 6.8, CH_2=C*H*); 4.71 (*s*, CH_2O); 4.51 (*t*, CH_2CH_2O); 4.27 (*dd*, ^2J = 2.36, 1 H, CH_2=CH, *trans* to H); 4.10 (*dd*, 1 H, CH_2=CH, *cis* to H); 3.15 (*t*, CH_2CH_2O).

4.14. *2-Fluoro-4-[(vinyloxy)methyl]phenyl 2-(4-Nitrophenyl)ethyl Carbonate* (**22**). As described in *4.12* starting with 2-fluorophenol to give first 3-fluoro-4-hydroxybenzyl alcohol. 10.3 g (36%). M.p. 101°. UV (MeOH): 202 (3.75), 222 (3.91), 273 (3.25), 277 (sh, 3.20). ^{1}H-NMR ((D$_6$)DMSO): 9.80 (*s*, O*H*–C_6H_3); 7.05 (*s*, H–C(2)); 6.95–6.80 (*m*, H–C(6), H–C(5)); 5.12 (*t*, CH_2OH); 4.35 (*d*, CH_2). Anal. calc. for $C_7H_7FO_2$ (142.1): C 59.15, H 4.96; found: C 59.36, H 4.96.

Selective monomethoxytritylation led to 2-fluoro-4-{[(4-methoxytrityl)oxy]methyl}phenol as a syrup in 95% yield. The crude product was converted into 2-fluoro-4-{[(4-methoxytrityl)oxy]methyl}phenyl 2-(4-nitrophenyl)ethyl carbonate and then directly detritylated to give 2-fluoro-4-(hydroxymethyl)phenyl 2-(4-nitrophenyl)ethyl carbonate as an amorphous solid in 76% yield. ^{1}H-NMR ($CDCl_3$): 8.17 (*d*, 2 H *o* to NO_2); 7.40 (*m*, 2 H *m* to NO_2); 7.23–7.10 (*m*, H–C(3), H–C(5), H–C(6)); 4.66 (*s*, CH_2); 4.49 (*t*, CH_2CH_2O); 3.15 (*t*, CH_2CH_2O); 1.83 (br. *s*, CH_2OH).

The final product **22** resulted from reaction with ethyl vinyl ether as an oil in 87% yield. TLC (toluene/AcOEt 10:1): R_f 0.72. ^{1}H-NMR ((D$_6$)DMSO): 8.18 (*d*, 2 H *o* to NO_2); 7.40 (*m*, 2 H *m* to NO_2); 7.21–7.06 (*m*, H–C(2), H–C(5), H–C(6)); 6.52 (*dd*, ^3J = 14.35, 6.7, CH_2=C*H*); 4.72 (*s*, CH_2O); 4.50 (*t*, CH_2CH_2O); 4.26 (*dd*, 1 H, CH_2=CH, *trans* to H); 4.09 (*dd*, 1 H, CH_2=CH, *cis* to H); 3.15 (*t*, CH_2CH_2O).

4.15. *2,5-Dichloro-4-[(vinyloxy)methyl]phenyl 2-(4-Nitrophenyl)ethyl Carbonate* (**23**). As described in *4.12* starting from 2,5-dichlorophenol to give first 2,5-chloro-4-hydroxybenzyl alcohol in 33% yield. M.p. 144°. UV (MeOH): 206 (4.53); 223 (sh, 3.95), 283 (3.53), 290 (sh, 3.49). ^{1}H-NMR ((D$_6$)DMSO): 10.52 (*s*, O*H*–C_6H_3); 7.40 (*s*, H–C(6)); 6.95 (*s*, H–C(3)); 5.31 (*t*, CH_2OH); 4.44 (*d*, CH_2).

Selective monomethoxytritylation led to 2,5-dichloro-4-{[(4-methoxytrityl)oxy]methyl}phenol in 88% yield. ^{1}H-NMR ((D$_6$)DMSO): 10.68 (br. *s*, O*H*–C_6H_2); 7.48–7.10 (*m*, 13 H, arom. H, 2 H *m* to MeO, H–C(6)); 6.90 (*m*, H–C(3), 2 H *o* to MeO); 4.03 (*s*, CH_2); 3.73 (*s*, MeO).

Conversion into 2,5-dichloro-4-(hydroxymethyl)phenyl 2-(4-nitrophenyl)ethyl carbonate *via* 2,5-dichloro-4-{[(4-methoxytrityl)oxy]methyl}phenyl 2-(4-nitrophenyl)ethyl carbonate proceeded in 62% yield. ^{1}H-NMR ((D$_6$)DMSO): 8.18 (*d*, 2 H *o* to NO_2); 7.65–7.52 (*m*, 2 H *m* to NO_2, H–C(3), H–C(6)); 5.63 (*t*, CH_2OH); 4.52 (*m*, CH_2CH_2O); 3.15 (*t*, CH_2CH_2O).

Compound **23** resulted from reaction with ethyl vinyl ether in 84% yield. Colourless crystals. M.p. 48°. TLC (toluene/AcOEt 10:1): R_f 0.78. UV (MeOH): 208 (4.42), 218 (sh, 4.24), 265 (4.05). ^{1}H-NMR ($CDCl_3$): 8.18 (*d*, 2 H *o* to NO_2); 7.57 (*s*, H–C(6)); 7.41 (*d*, 2 H *m* to NO_2); 7.21 (*s*, H–C(3)); 6.55 (*dd*, ^3J = 14.2, 6.9, CH_2=C*H*); 4.78 (*s*, CH_2O); 4.53 (*t*, CH_2CH_2O); 4.33 (*dd*, ^2J = 2.5, 1 H, CH_2=CH, *trans* to H); 4.13 (*dd*, 1 H, CH_2=CH, *cis* to H); 3.17 (*t*, CH_2CH_2O). Anal. calc. for $C_{18}H_{15}Cl_2NO_6$ (412.2): C 52.45, H 3.67, N 3.40; found: C 52.07, H 3.73, N 3.83.

4.16. *2,5-Dichloro-4-[(vinyloxy)methyl]phenyl 2,2-Dimethylpropanoate* (**24**). As described in *4.15* starting from 2,5-dichloro-4-{[(4-methoxytrityl)oxy]methyl}phenol (12 g, 24.2 mmol) by reaction with pivalic acid anhydride (13.8 g, 74 mmol) in MeCN (150 ml) and DMAP (0.8 g) by stirring for 30 min at r.t. The mixture was evaporated to 50 ml, diluted with AcOEt (200 ml), and washed with sat. $NaHCO_3$ (200 ml) and NaCl soln. (200 ml). The org. phase was dried (Na_2SO_4) and evaporated to yield crude 2,5-dichloro-4-{[(4-methoxytrityl)oxy]methyl}phenyl 2,2-dimethylpropanoate which was detritylated to 2,5-dichloro-4-(hydroxymethyl)phenyl 2,2-dimethylpropanoate in an overall yield of 90%. ^{1}H-NMR ($CDCl_3$): 7.58 (*s*, H–C(3)); 7.12 (*s*, H–C(5)); 4.70 (*s*, CH_2); 1.38 (*s*, Me_3C).

Compound **24** resulted from reaction with ethyl vinyl ether in 56% yield. Colourless oil. TLC (toluene/AcOEt 20:1): R_f 0.81 (I_2). ^{1}H-NMR ($CDCl_3$): 7.53 (*s*, H–C(6)); 7.15 (*s*, H–C(3)); 6.53 (*dd*, ^3J = 14.3, 6.86, CH_2=C*H*); 4.78 (*s*, CH_2O); 4.36, 4.28 (*dd*, ^2J = 2.5, 1 H, CH_2=CH, *trans* to H); 4.13 (*dd*, 1 H, CH_2=CH, *cis* to H); 1.38 (*s*, Me_3C).

4.17. *2-Phenylethyl Vinyl Ether* (**25**). Distillation; b.p. 26°/0.003 Torr. Yield 70%. TLC (CCl_4): R_f 0.54 (I_2). ^{1}H-NMR ($CDCl_3$): 7.32–7.17 (*m*, 5 arom. H); 6.43 (*dd*, CH_2=C*H*); 4.14 (*dd*, 1 H, CH_2=CH, *trans* to H); 3.96 (*dd*, 1 H, CH_2=CH, *cis* to H); 3.85 (*t*, CH_2CH_2O); 2.93 (*t*, CH_2CH_2O). Anal. calc. for $C_{10}H_{12}O$ (148.2): C 77.03, H 7.83; found: C 77.92, H 7.88.

4.18. *2-(4-Methoxyphenyl)ethyl Vinyl Ether* (**26**). Distillation; b.p. 54°/0.003 Torr. Yield 56%. TLC (CCl_4/Et_2O): R_f 0.75 (I_2). ^{1}H-NMR ($CDCl_3$): 7.15 (*d*, 2 H_o); 6.84 (*d*, 2 H_m); 6.47 (*dd*, CH_2=C*H*); 4.18 (*dd*, 1 H, CH_2=CH, *trans* to H); 4.00 (*dd*, 1 H, CH_2=CH, *cis* to H); 3.85 (*t*, CH_2CH_2O); 2.91 (*t*, CH_2CH_2O). Anal. calc. for $C_{11}H_{14}O_2$ (178.2): C 74.12, H 7.91; found: C 73.50, H 7.80.

4.19. *2-(4-Nitrophenyl)ethyl Vinyl Ether* (**27**) [41]. Crystallization. Yield 56%. M.p. 49°. TLC (CCl_4/Et_2O 10:1): R_f 0.75. ^{1}H-NMR ($CDCl_3$): 8.14 (*d*, 2 H_m); 7.39 (*d*, 2 H_o); 6.41 (*dd*, CH_2=C*H*); 4.16 (*dd*, 1 H, CH_2=CH,

trans to H); 4.00 (*dd*, 1 H, CH_2=CH, *cis* to H); 3.90 (*t*, CH_2CH_2O); 3.05 (*t*, CH_2CH_2O). Anal. calc. for $C_{10}H_{11}NO_3$ (193.2): C 62.16, H 5.73, N 7.24; found: C 62.01, H 5.61, N 7.43.

4.20. *2-(2,4-Dinitrophenyl)ethyl Vinyl Ether* (**28**). Yield 89%. Yellowish oil. TLC (toluene/AcOEt 10:1): R_f 0.88. ^{1}H-NMR ($CDCl_3$): 8.77 (*d*, H–C(3)); 8.37 (*dd*, H–C(5)); 7.64 (*d*, H–C(6)); 6.40 (*dd*, ^3J = 14.35, 7.00, CH_2=CH); 4.20 (*dd*, ^2J = 2.31, 1 H, CH_2=CH, *trans* to H); 4.05 (*dd*, 3 H, CH_2=CH (*cis* to H), CH_2CH_2O); 3.38 (*t*, CH_2CH_2O).

4.21. *2-(4-Nitrophenyl)ethyl (Vinyloxy)acetate* (**29**). From 2-(4-nitrophenyl)ethyl hydroxyacetate in 6% yield. Colourless oil. TLC (toluene): R_f 0.74. ^{1}H-NMR ($CDCl_3$): 8.17 (*dd*, 2 H_m); 7.38 (*dd*, 2 H_o); 6.45 (*dd*, *J* = 14.2, 7.0, CH_2=CH); 4.43 (*t*, CH_2CH_2O); 4.29 (*s*, OCH_2CO); 4.17, 4.11 (*dd*, ^2J = 2.9, 1 H, CH_2=CH, *trans* to H); 4.11–4.07 (*m*, 1 H, CH_2=CH, *cis* to H); 3.07 (*t*, CH_2CH_2O).

4.22. *Butyl (Vinyloxy)acetate* (**30**). From butyl hydroxyacetate in 15% yield. Colourless oil. TLC (toluene): R_f 0.93 (I_2). ^{1}H-NMR ($CDCl_3$): 6.48 (*dd*, ^3J = 14.3, 6.84, CH_2=CH); 4.28 (*s*, OCH_2CO); 4.24–4.08 (*m*, CH_2CH_2O, CH_2=CH); 1.62 (*q*, CH_2CH_2O); 1.37 (*q*, $MeCH_2$); 0.81 (*t*, $MeCH_2$).

4.23. *Ethyl 3-(Vinyloxy)butanoate* (**31**). From *rac*-ethyl 3-hydroxybutanoate, the racemic mixture was obtained by distillation; b.p. 62°/24 Torr. Yield 36%. Colourless oil. TLC (toluene/AcOEt 1:2): R_f 0.56 (I_2). ^{1}H-NMR ($CDCl_3$): 6.25 (*dd*, ^3J = 14.2, 6.6, CH_2=CH); 4.40–4.23 (*m*, ^2J = 1.69, 2 H, CH_2=CH (*trans* to H), H–C(3)); 4.11 (*q*, $MeCH_2O$); 4.00 (*dd*, 1 H, CH_2=CH, *cis* to H); 2.64, 2.38 (*dd*, 2 H–C(2)); 1.25 (*m*, Me(4), $MeCH_2O$). Anal. calc. for $C_8H_{14}O_2$ (142.2): C 60.73, H 8.92; found: C 60.43, H 8.94.

4.24. *Ethyl 3-(Vinyloxy)propanoate* (**32**). From ethyl 3-hydroxypropanoate [42] Distillation; b.p. 71°/16 Torr. Yield 64%. n_D^{20} = 1.4132. TLC (toluene): R_f 0.29. ^{1}H-NMR ($CDCl_3$): 6.45 (*dd*, CH_2=CH); 4.24 (*d*, 1 H, CH_2=CH, *trans* to H); 4.17 (*q*, 2 H–C(3)); 4.03 (*dd*, 1 H, CH_2=CH, *cis* to H); 3.97 (*q*, $MeCH_2O$); 2.67 (*t*, 2 H–C(2)); 1.27 (*t*, $MeCH_2O$).

4.25. *N-Methyl-3-(vinyloxy)propanamide* (**33**). Compound **32** (1.5 g, 10 mmol) was treated with 47% $MeNH_2$/EtOH (30 ml) in THF (30 ml) for 24 h at r.t. The mixture was evaporated and the residue purified by FC (20 g of silica gel, toluene/AcOEt 1:0, 9:1, 7:3, 6:4, 1:1, 100 ml each). Evaporation and co-evaporation with MeOH and CH_2Cl_2 gave a solid foam: 0.88 g (66%). TLC (toluene/AcOEt 1:4): R_f 0.30 (I_2). ^{1}H-NMR ($CDCl_3$): 6.44 (*dd*, CH_2=CH); 6.01 (*s*, NH); 4.23 (*dd*, 1 H, CH_2=CH, *trans* to H); 4.05 (*dd*, 1 H, CH_2=CH, *cis* to H); 3.97 (*t*, 2 H–C(3)); 2.86 (*d*, Me); 2.55 (*t*, 2 H–C(2)). Anal. calc. for $C_6H_{11}NO_2$ (126.1): C 55.80, H 8.59, N 10.85; found: C 55.88, H 8.62, N 11.00.

4.26. *N-Methyl-N-[2-(vinyloxy)ethyl]acetamide* (**34**). From *N*-(2-hydroxyethyl)-*N*-methylacetamide. Distillation; b.p. 68°/0.04 Torr. Yield 58%. TLC ($CHCl_3$/MeOH 10:1): R_f 0.73 (I_2). Colourless oil. ^{1}H-NMR ($CDCl_3$): 6.45 (*dd*, CH_2=CH); 4.22 (*dd*, 1 H, CH_2=CH, *trans* to H); 4.03 (*dd*, 1 H, CH_2=CH, *cis* to H); 3.85 (*m*, CH_2O); 3.63 (*m*, CH_2N); 3.09, 2.96 (2*s*, MeN); 2.14, 2.09 (2*s*, MeCO). Anal. calc. for $C_7H_{13}NO_2$ (143.18): C 58.72, H 9.15, N 9.78; found: C 58.41, H 9.15, N 10.00.

4.27. *2-Chloroethyl Vinyl Ether* (**35**). From *Fluka* (No. 23075), Buchs, Switzerland.

4.28. *3-(Vinyloxy)propanenitrile* (**36**) [43]. Distillation; b.p. 28°/0.028 Torr. Yield 20%. n_D^{20} = 1.430 [43]: 1.4335). Colourless oil. TLC (pentane/AcOEt 10:1): R_f 0.21 (I_2). ^{1}H-NMR ($CDCl_3$): 6.45 (*dd*, ^3J = 14.35, 6.89, CH_2=CH); 4.23 (*dd*, ^2J = 2.56, 1 H, CH_2=CH, *trans* to H); 4.12 (*dd*, 1 H, CH_2=CH, *cis* to H); 3.91 (*t*, 2 H–C(3)); 2.72 (*dd*, 2 H–C(2)).

4.29. *2-Nitroethyl Vinyl Ether* (**37**). Distillation; b.p. 35°/0.035 Torr. Yield 18%. n_D^{20} = 1.4448. Yellow oil. TLC (hexane/AcOEt 10:1): R_f 0.34 (I_2). ^{1}H-NMR ($CDCl_3$): 6.55 (*dd*, ^3J = 14.3, 6.7, CH_2=CH); 4.64 (*t*, $OCH_2CH_2NO_2$); 4.28–4.21 (*m*, 3 H, CH_2=CH (*trans* to H), $OCH_2CH_2NO_2$); 4.12 (*dd*, 1 H, CH_2=CH, *cis* to H). Anal. calc. for $C_4H_7NO_3$ (117.1): C 41.03, H 6.03, N 11.96; found: C 40.95, H 6.03, N 12.00.

4.30. *2-(Methylsulfonyl)ethyl Vinyl Ether* (**38**). Yield 31%. Colourless crystals (toluene/hexane 1:1). M.p. 29°. TLC (toluene): R_f 0.87 (I_2). ^{1}H-NMR ($(D)_6$DMSO): 6.52 (*dd*, ^3J = 14.25, 6.8, CH_2=CH); 4.28 (*dd*, ^2J = 2.10, 1 H, CH_2=CH, *trans* to H); 4.09–3.99 (*m*, 3 H, CH_2=CH (*cis* to H), $OCH_2CH_2SO_2$); 3.48 (*t*, $OCH_2CH_2SO_2$); 2.96 (*s*, $MeSO_2$). Anal. calc. for $C_5H_{10}O_3S$ (150.2): C 39.99, H 6.71; found: C 40.05, H 6.69.

4.31. *2-(Phenylthio)ethyl Vinyl Ether* (**39**). Distillation; b.p. 78–79°/0.0025 mbar. Yield 48%. TLC (toluene/AcOEt 1:1): R_f 0.87. UV (MeOH): 204 (sh, 4.21), 253 (3.88). ^{1}H-NMR ($CDCl_3$): 7.42–7.18 (*m*, 5 arom. H); 6.43 (*dd*, ^3J = 14.3, 6.8, CH_2=CH); 4.15 (*dd*, ^2J = 2.2, 1 H, CH_2=CH, *trans* to H); 3.99 (*dd*, 1 H, CH_2=CH, *cis* to H); 3.84 (*t*, OCH_2CH_2S); 3.16 (*t*, OCH_2CH_2S). Anal. calc. for $C_{10}H_{12}OS$ (180.3): C 66.63, H 6.70; found: C 66.81, H 6.77.

4.32. *2-(Phenylsulfonyl)ethyl Vinyl Ether* (**40**). Compound **39** (9.9 g, 55 mmol) was dissolved in EtOH (60 ml) and H_2O (10 ml), then $NaWO_4 \cdot 2\,H_2O$ (0.2 g) and 30% H_2O_2 soln. (11.5 ml) were added. The mixture was heated to 60° for 3 h with stirring. The excess of H_2O_2 was destroyed with Na_2SO_3 soln. and the mixture extracted with AcOEt (4 × 100 ml). The org. phase was dried (Na_2SO_4) and evaporated and the residue purified by FC (60 g of

silica gel, toluene). Evaporation and co-evaporation with MeOH and CH_2Cl_2 gave 5.6 g (48%). Colourless oil. TLC (toluene/AcOEt 3:1): R_f 0.70 (I_2). ^{1}H-NMR ($CDCl_3$): 7.95–7.83 (*m*, H–C(2), H–C(6)); 7.68–7.48 (*m*, H–C(3), H–C(4), H–C(5)); 6.24 (*dd*, ^3J = 14.30, 6.88, 1 H, CH_2=C*H*); 4.12–3.93 (*m*, 4 H, CH_2=CH $OCH_2CH_2SO_2$); 3.48 (*t*, $OCH_2CH_2SO_2$).

4.33. *2-Phthalimidoethyl Vinyl Ether* (**41**). Yield 72%. Colourless crystals. M.p. 114°. TLC (toluene/AcOEt 10:1): R_f 0.78. UV (MeOH): 205 (sh, 4.42), 217 (4.61), 238 (sh, 4.19), 230 (sh, 4.00), 292 (3.29). ^{1}H-NMR ($CDCl_3$): 7.84–7.80 (*m*, 2 H *o* to CO); 7.72–7.67 (*m*, 2 H *m* to CO); 6.39 (*dd*, ^3J = 14.4, 6.9, CH_2=C*H*); 4.14 (*dd*, ^2J = 1.7, 1 H, CH_2=CH, *trans* to H); 3.99–3.85 (*m*, 5 H, CH_2=CH (*cis* to H), CH_2CH_2) Anal. calc. for $C_{12}H_{11}NO_3$ (217.2): C 66.35, H 5.10, N 6.45; found: C 66.32, H 5.14, N 6.42.

5. *Acetalization to* **43**–**83**. 5.1. *General Procedure.* The 3′,5′-*O*-(1,1,3,3-tetraisopropyldisiloxan-1,3-diyl)-uridine (**42**; 3.5 g, 7.2 mmol) was co-evaporated with anh. toluene (2 × 50 ml). The colourless foam was dissolved in anh. toluene (100 ml) and treated with the corresponding vinyl ether (1.1–1.5 equiv.) in anh. toluene (50 ml). Then anh. camphersulfonic acid or TsOH (50–100 mg) was added and the mixture stirred for 4–6 h at 20° (TLC control). After dilution with AcOEt (300 ml), the reaction was quenched by washing with 0.25N $NaHCO_3$ (2 × 300 ml) and sat. NaCl soln. (300 ml). The org. phase was dried (Na_2SO_4) and evaporated. The crude product was purified by FC (silica gel, toluene/AcOEt). The resulting oil was co-evaporated with MeOH (2 × 20 ml) and CH_2Cl_2 (2 × 20 ml) and the resulting solid foam dried in a desiccator under high vacuum.

5.2. *2′-O-(1-Phenoxyethyl)-3′,5′-O-(1,1,3,3-tetraisopropyldisiloxan-1,3-diyl)uridine* (**43**). According to *5.1*. Yield 74%. Colourless foam. TLC (toluene/AcOEt 1:1): R_f 0.59. UV (MeOH): 262 (4.02), 205 (4.02). ^{1}H-NMR ($CDCl_3$): 8.28 (*s*, H–N(3)); 7.79 (*s*, H–C(6)); 7.21–6.94 (*m*, Ph); 5.75–5.59 (*m*, H–C(5), H–C(1′)); 4.34–3.91 (*m*, H–C(2′), H–C(3′), H–C(4′), 2 H–C(5′), $MeCH(O)_2$); 1.53 (*d*, *Me*$CH(O)_2$); 1.08–0.82 (*m*, 4 Me_2CH). Anal. calc. for $C_{29}H_{46}N_2O_8Si_2$ (606.9): C 57.39, H 7.64, N 4.61; found: C 57.75, H 8.02, N 4.45.

5.3. *2′-O-[1-(4-Methoxyphenoxy)ethyl]-3′,5′-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)uridine* (**44**). According to *5.1*. Yield 89%. Colourless foam. TLC (toluene/AcOEt 1:1): R_f 0.55. UV (MeOH): 263 (4.02), 208 (4.15). ^{1}H-NMR ($CDCl_3$): 9.21 (*s*, H–N(3)); 7.73 (*d*, H–C(6)); 7.13–6.71 (*m*, 2 H_o, 2 H_m); 5.78–5.55 (*m*, H–C(1′), H–C(5), $MeCH(O)_2$); 4.34–3.90 (*m*, H–C(2′), H–C(3′), H–C(4′), 2 H–C(5′)); 3.73 (*s*, MeO); 1.46 (2*d*, *Me*$CH(O)_2$); 1.07–0.86 (*m*, 4 Me_2CH). Anal. calc. for $C_{30}H_{48}N_2O_9Si_2$ (636.9): C 57.57, H 7.59, N 4.39; found: C 57.79, H 7.76, N 4.21.

5.4. *2′-O-[1-(2-Chlorophenoxy)ethyl]-3′,5′-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)uridine* (**45**). According to *5.1*. Yield 74%. Colourless foam. TLC (toluene/AcOEt 1:1: R_f 0.59. UV (MeOH): 262 (4.02), 208 (4.20). ^{1}H-NMR ($CDCl_3$): 8.28 (*s*, H–N(3)); 7.79 (*s*, H–C(6)); 7.21–6.94 (*m*, 2 H_o, 2 H_m); 5.75–5.59 (*m*, H–C(1′), H–C(5)); 5.34–3.91 (*m*, $MeCH(O)_2$, H–C(2′), H–C(3′), H–C(4′), 2 H–C(5′)); 1.53 (*d*, *Me*$CH(O)_2$); 1.08–0.82 (*m*, 4 Me_2CH). Anal. calc. for $C_{29}H_{46}N_2O_8Si_2$ (606.9): C 57.39, H 7.64, N 4.61; found: C 57.75, H 8.02, N 4.45.

5.5. *2′-O-[1-(Benzyloxy)ethyl]-3′,5′-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)uridine* (**46**). According to *5.1*. Yield 89%. Colourless foam. TLC (toluene/AcOEt 1:1): R_f 0.60, 0.66. UV (MeOH): 203 (4.56), 230 (sh, 3.98), 262 (4.01). ^{1}H-NMR ($CDCl_3$): 8.84 (br. *s*, H–N(3)); 7.93 (*d*, H–C(6)); 7.42–7.22 (*m*, Ph); 5.83, 5.72 (2*s*, H–C(1′)); 5.68 (*d*, H–C(5)); 5.14 (*q*, $MeCH(O)_2$); 4.96–4.58 (*m*, $PhCH_2$); 4.32–3.93 (*m*, H–C(2′), H–C(3′), H–C(4′), 2 H–C(5′)); 1.48 (2*d*, *Me*$CH(O)_2$); 1.16–0.84 (*m*, 4 Me_2CH). Anal. calc. for $C_{30}H_{48}N_2O_8Si_2$ (620.89): C 58.03, H 7.79, N 4.51; found: C 58.50, H 7.93, N 4.30.

5.6. *2′-O-[1-(4-Methoxybenzyloxy)ethyl]-3′,5′-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)uridine* (**47**). According to *5.1*. Yield 78%. Colourless foam. TLC (toluene/AcOEt 1:1): R_f 0.50, 0.54. UV (MeOH): 202 (4.38), 225 (sh, 4.18), 264 (4.06). ^{1}H-NMR ($CDCl_3$): 9.00 (br. *s*, H–N(3)); 7.95 (2*d*, H–C(6)); 7.40–7.20 (*m*, 2 H_o); 6.85 (2*d*, 2 H_m); 5.83, 5.71 (2*s*, H–C(1′)); 5.68 (*d*, H–C(5)); 5.09 (2*q*, $MeCH(O)_2$); 4.91–4.44 (*m*, $ArCH_2$); 4.32–3.91 (*m*, H–C(2′), H–C(3′), H–C(4′), 2 H–C(5′)); 1.47 (*d*, *Me*$CH(O)_2$); 1.18–0.88 (*m*, 4 Me_2CH). Anal. calc. for $C_{31}H_{50}N_2O_9Si_2$ (650.9): C 57.20, H 7.74, N 4.30; found: C 57.01, H 7.79, N 4.17.

5.7. *2′-O-[1-(3,4-Dimethoxybenzyloxy)ethyl]-3′,5′-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)uridine* (**48**). According to *5.1*. Yield 72%. Colourless foam. TLC (toluene/AcOEt 1:1): R_f 0.36, 0.33. UV (MeOH): 203 (4.56), 230 (sh, 3.96), 265 (4.03). ^{1}H-NMR ($CDCl_3$): 9.42–8.81 (br. *s*, H–N(3)); 7.92 (*d*, H–C(6)); 6.97–6.74 (*m*, 3 arom. H); 5.76 (*m*, H–C(1′)); 5.67 (*d*, H–C(5)); 5.09 (2*q*, $MeCH(O)_2$); 4.92–4.41 (*m*, $ArCH_2$); 4.30–4.08 (*m*, H–C(2′), H–C(3′), H–C(4′)); 4.01–3.78 (*m*, 2 H–C(5′), 2 MeO); 1.44 (2*d*, *Me*$CH(O)_2$); 1.15–0.86 (*m*, 4 Me_2CH). Anal. calc. for $C_{32}H_{52}N_2O_{10}Si_2$ (680.9): C 56.44, H 7.70, N 4.11; found: C 56.49, H 7.77, N 3.91.

5.8. *2′-O-[1-(2,6-Dichlorobenzyloxy)ethyl]-3′,5′-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)uridine* (**49**). According to *5.1*. Yield 89%. Colourless foam. TLC (toluene/AcOEt 1:1): R_f 0.59. UV (MeOH): 203 (4.56), 230 (sh, 3.98), 262 (4.04), 278 (3.94). ^{1}H-NMR ($CDCl_3$): 9.75, 9.45 (br. *s*, H–N(3)); 7.90 (*d*, H–C(6)); 7.33–7.11 (*m*, 3 arom. H); 5.80 (*m*, H–C(1′)); 5.69 (*m*, H–C(5)); 5.20–4.74 (*m*, $MeCH(O)_2$, $ArCH_2$); 4.36–3.93 (*m*, H–C(2′), H–C(3′), H–C(4′), 2 H–C(5′)); 1.47 (*d*, *Me*$CH(O)_2$); 1.16–0.84 (*m*, 4 Me_2CH). Anal. calc. for $C_{30}H_{46}Cl_2N_2O_8Si_2$ (689.8): C 52.24, H 6.72, N 4.06; found: C 52.16, H 6.91, N 4.27.

5.9. *2'-O-[1-(3,5-Dichlorobenzyloxy)ethyl]-3',5'-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)uridine* (**50**). According to *5.1*. Yield 93%. Colourless foam. TLC (toluene/AcOEt 1:1): R_f 0.57. ^{1}H-NMR ((D)$_6$DMSO): 11.41 (*s*, H–N(3)); 7.67 (*d*, H–C(6)); 7.50–7.21 (*m*, 3 arom. H); 5.63 (*s*, H–C(1')); 5.51 (*d*, H–C(5)); 5.07 (*q*, MeC*H*(O)$_2$); 4.79, 4.58 (*d*, ArCH_2); 4.45, 4.33 (*d*, H–C(2')); 4.27–4.16 (*m*, H–C(3'), H–C(4')); 4.09–3.91 (*m*, 2 H–C(5')); 1.40, 1.34 (*d*, *Me*CH(O)$_2$); 1.06–0.96 (*m*, 4 Me$_2$CH).

5.10. *2'-O-{1-[4-(Ethoxycarbonyl)benzyloxy]ethyl}-3',5'-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)uridine* (**51**). According to *5.1*. Yield 79%. Colourless foam. TLC (toluene/AcOEt 1:1): R_f 0.44, 0.51. UV (MeOH): 258 (4.02), 237 (4.36). ^{1}H-NMR ((D)$_6$DMSO): 11.46 (*s*, H–N(3)); 7.94 (*d*, 2 H$_m$); 7.68 (*d*, H–C(6)); 7.44 (*d*, 2 H$_o$); 5.66 (*d*, H–C(1')); 5.51 (*d*, H–C(5)); 5.10 (*m*, MeC*H*(O)$_2$); 4.7–3.9 (*m*, ArCH_2, MeCH_2O, H–C(2'), H–C(3'), H–C(4'), 2 H–C(5')); 1.41 (*m*, *Me*CH(O)$_2$); 1.31 (*t*, *Me*CH$_2$O); 1.10–0.9 (*m*, 4 Me$_2$CH). Anal. calc. for $C_{33}H_{52}N_2O_{10}Si_2$ (692.9): C 57.29, H 7.43, N 4.05; found: C 57.01, H 7.60, N 4.08.

5.11. *2'-O-[1-(4-Nitrobenzyloxy)ethyl]-3',5'-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)uridine* (**52**). According to *5.1*. Yield 92%. Colourless needles (470 mg in 11 ml of MeOH/H_2O 10:1). M.p. 111°. TLC (toluene/AcOEt 1:2): R_f 0.65, 0.72. UV (MeOH): 211 (4.29), 265 (4.26). ^{1}H-NMR ($CDCl_3$): diastereoisomer 1 (R_f 0.72): 10.17 (br. *s*, H–N(3)); 8.15 (*d*, 2 H$_m$); 7.88 (*d*, H–C(6)); 7.51 (*d*, 2 H$_o$); 5.76 (*s*, H–C(1')); 5.65 (*d*, H–C(5)); 5.12 (*q*, MeC*H*(O)$_2$); 4.91–4.72 (*d*, ArCH_2); 4.26–3.91 (*m*, H–C(2'), H–C(3'), H–C(4'), 2 H–C(5')); 1.42 (*d*, *Me*CH(O)$_2$); 1.12–0.82 (*m*, 4 Me$_2$CH); diastereoisomer 2 (R_f 0.65): 9.30 (br. *s*, H–N(3)); 8.16 (*d*, 2 H$_m$); 7.94 (*d*, H–C(6)); 7.46 (*d*, 2 H$_o$); 5.69 (*s*, H–C(1')); 5.67 (*dd*, H–C(5)); 5.21 (*q*, MeC*H*(O)$_2$); 4.98, 4.68 (*d*, ArCH_2); 4.30–3.88 (*m*, H–C(2'), H–C(3'), H–C(4'), 2 H–C(5')); 1.50 (*d*, *Me*CH(O)$_2$); 1.15–0.80 (*m*, 4 Me$_2$CH). Anal. calc. for $C_{30}H_{47}N_3O_{10}Si_2$ (665.9): C 54.11, H 7.11, N 6.31; found: C 53.71, H 7.04, N 5.99.

5.12. *2'-O-[1-(2-Nitrobenzyloxy)ethyl]-3',5'-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)uridine* (**53**). According to *5.1*. Yield 88%. Colourless foam (light sensitive!). TLC (toluene/AcOEt 1:2): R_f 0.68 and 0.74. UV (MeOH): 206 (4.19), 260 (4.16). ^{1}H-NMR ($CDCl_3$): 8.48, 8.29 (2br. *s*, H–N(3)); 8.11 (*d*, H–C(3)(Ar)); 7.90 (*d*, H–C(6)); 7.84 (*t*, H–C(6), H–C(6)(Ar)); 7.60 (*m*, H–C(5)(Ar)); 7.39 (*m*, H–C(4)(Ar)); 5.76, 5.68 (2*s*, H–C(1')); 5.64 (*m*, H–C(5)); 5.32–4.97 (*m*, MeC*H*(O)$_2$, ArCH_2); 4.26–3.88 (*m*, H–C(2'), H–C(3'), H–C(4'), 2 H–C(5')); 1.51 (*d*, *Me*CH(O)$_2$); 1.14–0.84 (*m*, 4 Me$_2$CH). Anal. calc. for $C_{30}H_{47}N_3O_{10}Si_2$ (665.9): C 54.11, H 7.11, N 6.31; found: C 54.00, H 7.08, N 6.18.

5.13. *2'-O-[1-(2,4-Dinitrobenzyloxy)ethyl]-3',5'-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)uridine* (**54**). According to *5.1*. TLC (toluene/AcOEt 1:2): R_f 0.62, 0.65. Not isolated.

5.14. *2'-O-(1-{4-[2-(4-Nitrophenyl)ethoxycarbonyloxy]benzyloxy}ethyl)-3',5'-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)uridine* (**55**). According to *5.1*. Yield 88%. Colourless foam. TLC (toluene/AcOEt 1:3): R_f 0.82, 0.84. UV (MeOH): 204 (4.49), 214 (sh, 4.19), 264 (4.30). ^{1}H-NMR ($CDCl_3$): 8.42 (br. *s*, H–N3)); 8.18 (*d*, 2 H *o* to NO$_2$); 7.92 (*d*, H–C(6)); 7.46–7.28 (*m*, 2 H *m* to NO$_2$, 2 H *o* to OCO); 7.06 (*d*, 2 H *m* to OCO); 5.80, 5.70 (2 *s*, H–C(1')); 5.65 (*dd*, H–C(5)); 5.13 (*m*, MeC*H*(O)$_2$); 4.93–4.52 (*m*, ArCH_2); 4.49 (*t*, CH$_2$CH_2O); 4.30–3.91 (*m*, H–C(2'), H–C(3'), H–C(4'), 2 H–C(5')); 3.15 (*t*, CH_2CH$_2$O); 1.45/1.48 (*d*, *Me*CH(O)$_2$); 1.15–0.90 (*m*, 4 Me$_2$CH). Anal. calc. for $C_{39}H_{55}N_3O_{13}Si_2$ (830.05): C 56.43, H 6.68, N 5.06; found: C 56.32, H 6.71, N 5.04.

5.15. *2'-O-(1-{2-Chloro-4-[2-(4-nitrophenyl)ethoxycarbonyloxy]benzyloxy}ethyl)-3',5'-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)uridine* (**57**). According to *5.1*. Yield 78%. Colourless foam. TLC (toluene/AcOEt 1:1): R_f 0.65, 0.69. UV (MeOH): 202 (4.56), 212 (sh, 4.44), 265 (4.29). ^{1}H-NMR ($CDCl_3$): 8.42 (br. *s*, H–N(3)); 8.18 (*d*, 2 H *o* to NO$_2$); 7.88 (*d*, H–C(6)); 7.53 (*m*, H–C(3)(Ar)); 7.40 (*d*, 2 H *m* to NO$_2$); 7.17 (*m*, H–C(5)(Ar)); 7.00 (*m*, H–C(6)(Ar)); 5.78, 5.68 (2*s*, H–C(1')); 5.64 (*dd*, H–C(5)); 5.23 (*m*, MeC*H*(O)$_2$); 4.93–4.59 (*m*, ArCH_2); 4.48 (*t*, CH$_2$CH_2O); 4.30–3.91 (*m*, H–C(2'), H–C(3'), H–C(4'), 2 H–C(5')); 3.14 (*t*, CH_2CH$_2$O); 1.49 (*d*, *Me*CH(O)$_2$); 1.18–0.88 (*m*, 4 Me$_2$CH). Anal. calc. for $C_{39}H_{54}ClN_3O_{13}Si_2$ (864.5): C 54.19, H 6.30, N 4.86; found: C 54.13, H 6.44, N 4.82.

5.16. *2'-O-[1-(2-Chloro-4-hydroxybenzyloxy)ethyl]-3',5'-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)uridine* (**58**). A soln. of **57** (0.346 g, 0.4 mmol) in 0.1N DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) in MeCN (10 ml) was stirred at r.t. for 4 h. The mixture was diluted with AcOEt (100 ml), the soln. washed with sat. $NaHCO_3$ (2 × 50 ml) and NaCl soln. (50 ml), dried (Na_2SO_4) and evaporated, and the oil purified by FC (silica gel (10 g), toluene/AcOEt 50:0, 90:10, 70:30, 50:50 ml). Evaporation and co-evaporation with MeOH and CH_2Cl_2 gave a solid foam (0.239 g, 89%). TLC (toluene/AcOEt 1:1): R_f 0.23 and 0.25. UV (MeOH): 204 (4.55), 225 (sh, 3.92), 265 (4.04). ^{1}H-NMR ($CDCl_3$): 8.86 (br. *s*, H–N(3)); 7.84 (*d*, H–C(6)); 7.31 (*dd*, H–C(6)(Ar)); 6.81 (*dd*, H–C(3)(Ar)); 6.68 (*d*, H–C(5)(Ar)); 6.6 (br. *s*, O*H*–C$_6$H$_3$); 5.78, 5.70 (2*s*, H–C(1')); 5.64 (*dd*, H–C(5)); 5.17 (*q*, MeC*H*(O)$_2$); 4.88–3.97 (*m*, ArCH_2, H–C(2'), H–C(3'), H–C(4'), 2 H–C(5')); 1.46 (*d*, *Me*CH(O)$_2$); 1.15–0.82 (*m*, 4 Me$_2$CH). Anal. calc. for $C_{30}H_{47}ClN_2O_9Si_2$ (671.3): C 53.67, H 7.06, N 4.17; found: C 53.48, H 7.06, N 4.34.

5.17. *2'-O-(1-{3-Chloro-4-[2-(4-nitrophenyl)ethoxycarbonyloxy]benzyloxy}ethyl)-3',5'-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)uridine* (**59**). According to *5.1*. Yield 86%. Colourless foam. TLC (toluene/AcOEt 1:1):

R_f 0.56, 0.58. UV (MeOH): 202 (4.48), 212 (sh, 4.39), 264 (4.28). ^{1}H-NMR ($CDCl_3$): 8.85 (br. *s*, H–N(3)); 8.18 (*d*, 2 H *o* to NO_2); 7.90 (*d*, H–C(6)); 7.50–7.08 (*m*, 2 H *m* to NO_2, H–C(2)(Ar), H–C(5)(Ar), H–C(6)(Ar)); 5.78, 5.69 (2*s*, H–C(1')); 5.67 (*dd*, H–C(5)); 5.16 (*m*, MeC*H*$(O)_2$); 4.90–4.53 (*m*, ArCH_2); 4.51 (*t*, CH_2CH_2O); 4.29–3.91 (*m*, H–C(2'), H–C(3'), H–C(4'), 2 H–C(5')); 3.14 (*t*, CH_2CH_2O); 1.45, 1.48 (2*d*, *Me*CH$(O)_2$); 1.12–0.88 (*m*, 4 Me_2CH); Anal. calc. for $C_{39}H_{54}ClN_3O_{13}Si_2$ (864.5): C 54.19, H 6.30, N 4.86; found: C 54.14, H 6.39, N 4.88.

5.18. *2'-O-[1-(3-Chloro-4-hydroxybenzyloxy)ethyl]-3',5'-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)uridine* (**60**). Analogous to *5.16*. Yield 96%. Colourless foam. TLC (toluene/AcOEt 1:1): R_f 0.22, 0.24. UV (MeOH): 204 (4.55), 221 (sh, 3.98), 265 (4.05). ^{1}H-NMR ($CDCl_3$): 8.63 (br. *s*, H–N(3)); 7.90 (*d*, H–C(6)); 7.34 (*dd*, H–C(2)(Ar)); 7.13 (*dd*, H–C(6)(Ar)); 6.94 (*d*, H–C(5)(Ar)); 5.80, 5.70 (2*s*, H–C(1')); 5.68 (*d*, H–C(5)); 5.58 (br. *s*, O*H*–C_6H_3); 5.08 (*m*, MeC*H*$(O)_2$); 4.83–4.44 (*q*, ArCH_2); 4.30–3.87 (*m*, H–C(2'), H–C(3'), H–C(4'), 2 H–C(5')); 1.44, 1.46 (*d*, *Me*CH$(O)_2$); 1.15–0.82 (*m*, 4 Me_2CH). Anal. calc. for $C_{30}H_{47}ClN_2O_9Si_2$ (671.3): C 53.67, H 7.06, N 4.17; found: C 53.56, H 7.05, N 4.13.

5.19. *2'-O-(1-{3-Fluoro-4-[2-(4-nitrophenyl)ethoxycarbonyloxy]benzyloxy}ethyl)-3',5'-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)uridine* (**61**). According to *5.1*. Yield 77%. Colourless foam. TLC (toluene/AcOEt 1:1): R_f 0.60, 0.65. UV (MeOH): 205 (4.37), 265 (4.33). ^{1}H-NMR ($CDCl_3$): 8.83 (br. *s*, H–N(3)); 8.19 (*m*, 2 H *o* to NO_2); 7.93, 7.84 (2*d*, H–C(6)); 7.48–7.29 (*m*, 2 H *m* to NO_2); 7.18–6.87 (*m*, H–C(2)(Ar), H–C(5)(Ar), H–C(6)(Ar)); 5.78, 5.68 (2*s*, H–C(1')); 5.68–5.59 (*m*, H–C(5)); 5.14 (*m*, MeC*H*$(O)_2$); 4.78–4.46 (*m*, ArCH_2, CH_2CH_2O); 4.29–3.41 (*m*, H–C(2'), H–C(3'), H–C(4'), 2 H–C(5')); 3.14 (*t*, CH_2CH_2O); 1.49 (*t*, *Me*CH$(O)_2$). Anal. calc. for $C_{39}H_{54}FN_3O_{13}Si_2$ (848.0): C 55.24, H 6.42, N 4.96; found: C 55.06, H 6.48, N 5.07.

5.20. *2'-O-[1-(3-Fluoro-4-hydroxybenzyloxy)ethyl]-3',5'-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)uridine* (**62**). Analogous to *5.16*. Yield 96%. Colourless foam. TLC (toluene/AcOEt 1:1): R_f 0.21, 0.23. UV (MeOH): 208 (4.15), 217 (sh, 4.11), 262 (4.05). ^{1}H-NMR ($CDCl_3$): 8.43 (br. *s*, H–N(3)); 7.92 (2*d*, H–C(6)); 7.18–6.82 (*m*, H–C(2)(Ar), H–C(5)(Ar), H–C(6)(Ar)); 5.80, 5.90 (2*s*, H–C(1')); 5.66 (*d*, H–C(5')); 5.16 (br. *s*, O*H*–C_6H_3); 5.08 (*m*, MeC*H*$(O)_2$); 4.82–4.44 (*m*, ArOH_2); 4.28–3.94 (*m*, H–C(2'), H–C(3'), H–C(4'), 2 H–C(5')); 1.42, 1.44 (2*d*, *Me*CH$(O)_2$); 1.13–0.82 (*m*, 4 Me_2CH). Anal. calc. for $C_{30}H_{47}FN_2O_9Si_2$ (654.9): C 55.02, H 7.23, N 4.28; found: C 55.21, H 7.21, N 4.38.

5.21. *2'-O-(1-{2,5-Dichloro-4-[2-(4-nitrophenyl)ethoxycarbonyloxy]benzyloxy}ethyl)-3',5'-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)uridine* (**63**). According to *5.1*. Yield 76%. Colourless foam. TLC (toluene/AcOEt 1:1): R_f 0.66, 0.69. UV (MeOH): 203 (4.66), 212 (sh, 4.34), 426 (4.13), 264 (4.26). ^{1}H-NMR ($CDCl_3$): 9.03, 8.78 (br. *s*, H–N(3)); 8.19 (*d*, 2 H *o* to NO_2); 7.88 (*d*, H–C(6)); 7.62 (*m*, H–C(3)(Ar)); 7.40 (*d*, 2 H *m* to NO_2); 7.18 (*m*, H–C(6)(Ar)); 5.77, 5.68 (2*s*, H–C(1')); 5.66 (*dd*, H–C(5)); 5.30, 5.22 (2*q*, MeC*H*$(O)_2$); 4.88–4.57 (*m*, ArCH_2); 4.52 (*t*, CH_2CH_2O); 4.30–3.91 (*m*, H–C(2'), H–C(3'), H–C(4'), 2 H–C(5')); 3.15 (*t*, CH_2CH_2O); 1.50, 1.52 (2*d*, *Me*CH$(O)_2$); 1.12–0.89 (*m*, 4 Me_2CH). Anal. calc. for $C_{39}H_{53}Cl_2N_3O_{13}Si_2$ (898.9): C 52.11, H 5.94, N 4.67; found: C 52.06, H 5.50, N 4.57.

5.22. *2'-O-[1-(2,5-Dichloro-4-hydroxybenzyloxy)ethyl]-3',5'-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)-uridine* (**64**). Analogous to *5.15*. Yield 78%. Colourless foam. TLC (toluene/AcOEt 1:2): R_f 0.47, 0.49. UV (MeOH): 204 (4.69), 224 (sh, 4.06), 262 (4.04); 288 (sh, 3.63). ^{1}H-NMR ($CDCl_3$): 8.77 (br. *s*, H–N(3)); 7.90 (*d*, H–C(6)); 7.48 (*d*, H–C(6)(Ar)); 7.00 (*s*, H–C(3)(Ar)); 5.79 (br. *s*, O*H*–C_6H_2); 5.78, 5.69 (2*s*, H–C(1')); 5.65 (*dd*, H–C(5)); 5.21 (*q*, MeC*H*$(O)_2$); 4.78 (*d*, H–C(2')); 4.58 (*d*, H–C(3')); 4.29–3.91 (*m*, ArCH_2, H–C(4'), 2 H–C(5')); 1.48, 1.51 (*d*, *Me*CH$(O)_2$); 1.18–0.86 (*m*, 4 Me_2CH). Anal. calc. for $C_{30}H_{46}Cl_2N_2O_9Si_2$ (705.8): C 51.05, H 6.57, N 3.97; found: C 51.00, H 6.61, N 4.02.

5.23. *2'-O-(1-{2,5-Dichloro-4-[(2,2-dimethylpropanoyl)oxy]benzyloxy}ethyl)-3',5'-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)uridine* (**65**). According to *5.1*. Yield 88%. Colourless foam. TLC (toluene/AcOEt 1:1): R_f 0.72, 0.79. UV (MeOH): 203 (4.63), 221 (sh, 4.20), 262 (4.04). ^{1}H-NMR ($CDCl_3$): 9.02, 8.78 (2br. *s*, H–N(3)); 7.90 (2*d*, H–C(6)); 7.60 (*d*, H–C(3)(Ar)); 7.11 (*d*, H–C(6)(Ar)); 5.77, 5.69 (2*s*, H–C(1')); 5.67 (*m*, H–C(5)); 5.25 (*q*, MeC*H*$(O)_2$); 4.86, 4.79, 4.68, 4.60 (4*d*, ArCH_2); 4.29–3.89 (*m*, H–C(2'), H–C(3'), H–C(4'), 2 H–C(5')); 1.55 (*d*, *Me*CH$(O)_2$); 1.39 (*s*, Me_3C); 1.14–0.90 (*m*, 4 Me_2CH). Anal. calc. for $C_{35}H_{54}Cl_2N_2O_{10}Si_2$ (789.9): C 53.22, H 6.89, N 3.55; found: C 53.87, H 7.09, N 3.61.

5.24. *2'-O-[1-(2-Phenylethoxy)ethyl]-3',5'-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)uridine* (**66**). According to *5.1*. Yield 97%. Colourless foam. TLC (toluene/AcOEt 1:1): R_f 0.54, 0.64. UV (MeOH): 263 (3.99), 206 (4.23). ^{1}H-NMR ($CDCl_3$): 8.72, 8.59 (2*s*, H–N(3)); 7.95, 7.88 (2*d*, H–C(6)); 7.28–7.19 (*m*, Ph); 5.78, 5.68 (2*s*, H–C(1')); 5.67 (*m*, H–C(5)); 5.06, 4.97 (2*m*, MeC*H*$(O)_2$); 4.28–3.59 (*m*, H–C(2'), H–C(3'), H–C(4'), CH_2CH_2O, 2 H–C(5)); 2.97–2.86 (*m*, CH_2CH_2O); 1.45, 1.38 (2*d*, *Me*CH$(O)_2$); 1.00–0.90 (*m*, 4 Me_2CH). Anal. calc. for $C_{31}H_{50}N_2O_8Si_2$ (634.9): C 58.64, H 7.93, N 4.41; found: C 59.05, H 8.00, N 4.05.

5.25. *2'-O-{1-[2-(4-Methoxyphenyl)ethoxy]ethyl}-3',5'-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)uridine* (**67**). According to *5.1*. Yield 93%. Colourless foam. TLC (toluene/AcOEt 1:1): R_f 0.54, 0.70. UV (MeOH): 264 (4.02), 220 (sh, 4.16), 208 (4.19). ^{1}H-NMR ($CDCl_3$): 9.63, 9.42 (2*s*, H–N(3)); 7.88 (*d*, H–C(6)); 7.17–6.75 (*m*, 4 arom. H); 5.74, 5.65 (2*s*, H–C(1')); 5.66–5.63 (*m*, H–C(5)); 5.04, 4.98 (*q*, MeC*H*(O)$_2$); 4.24–3.55 (*m*, H–C(2'), H–C(3'), H–C(4'), CH_2CH_2O, 2 H–C(5')); 3.75, 3.74 (2*s*, MeO); 2.84–2.76 (*m*, CH_2CH_2O); 1.42, 1.34 (2*d*, *Me*CH(O)$_2$); 1.06–0.87 (*m*, 4 Me$_2$CH). Anal. calc. for $C_{32}H_{52}N_2O_9Si_2$ (665.0): C 57.80, H 7.88, N 4.21; found: C 58.08, H 8.13, N 3.95.

5.26. *2'-O-{1-[2-(4-Nitrophenyl)ethoxy]ethyl}-3',5'-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)uridine* (**68**). According to *5.1*. Yield 82%. M.p. 145°. TLC (toluene/AcOEt 1:1): R_f 0.47, 0.55. UV (MeOH): 265 (4.28), 210 (sh, 4.20). ^{1}H-NMR ($CDCl_3$): 9.24 (*m*, H–N(3)); 8.10 (*d*, 2 H$_m$); 7.91 (*m*, H–C(6)); 7.40 (*d*, 2 H$_o$); 5.68 (*m*, H–C(1'), H–C(5)); 5.02–4.91 (*m*, MeC*H*(O)$_2$); 4.26–3.60 (*m*, H–C(2'), H–C(3'), H–C(4'), CH_2CH_2O, 2 H–C(5')); 3.03, 2.92 (2*m*, CH_2CH_2O); 1.39, 1.33 (2*d*, *Me*CH(O)$_2$); 1.07–0.90 (*m*, 4 Me$_2$CH). Anal. calc. for $C_{31}H_{49}N_3O_{10}Si_2$ (679.9): C 54.76, H 7.26, N 6.18; found: C 54.60, H 7.26, N 6.09.

5.27. *2'-O-{1-[2-(2,4-Dinitrophenyl)ethoxy]ethyl}-3',5'-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)uridine* (**69**). According to *5.1*. Yield 86%. Colourless foam. TLC (toluene/AcOEt 1:1): R_f 0.46, 0.48. UV (MeOH): 206 (4.29), 256 (4.32). ^{1}H-NMR ($CDCl_3$): 9.02 (br. *s*, H–N(3)); 8.73 (*d*, H–C(3)(Ar)); 8.38 (*d*, H–C(6)(Ar)); 7.92 (*m*, H–C(5)(Ar)); 7.74 (*d*, H–C(6)); 5.66 (*s*, H–C(1')); 5.67 (*d*, H–C(5)); 4.97 (*m*, MeC*H*(O)$_2$); 4.29–3.70 (*m*, CH_2CH_2O, H–C(2'), H–C(3'), H–C(4'), 2 H–C(5')); 3.42–3.21 (*m*, CH_2CH_2O); 1.34 (*d*, *Me*CH(O)$_2$); 1.14–0.84 (*m*, 4 Me$_2$CH). Anal. calc. for $C_{31}H_{48}N_4O_{12}Si_2$ (703.9): C 51.36, H 6.67, N 7.73; found: C 51.11, H 6.78, N 7.64.

5.28. *2'-O-(1-{2-[(4-Nitrophenyl)ethoxy]-2-oxoethoxy}ethyl)-3',5'-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)uridine* (**70**). According to *5.1*. Yield 69%. Colourless foam. TLC (toluene/AcOEt 5:4:1): R_f 0.54, 0.58. UV (MeOH): 202 (4.33), 209 (4.25), 264 (4.27). ^{1}H-NMR ($CDCl_3$): 9.34 (br. *s*, H–N(3)); 8.14 (*d*, 2 H$_m$); 7.85 (*d*, H–C(6)); 7.39 (2*d*, 2 H$_o$); 5.70, 5.62 (2*s*, H–C(1')); 5.64 (*d*, H–C(5)); 5.15 (*q*, MeC*H*(O)$_2$); 4.45–3.87 (*m*, H–C(2'), H–C(3'), H–C(4'), CH_2CH_2O, $ArCH_2$, 2 H–C(5')); 3.04 (*t*, CH_2CH_2O); 1.42 (*d*, *Me*CH(O)$_2$); 1.13–0.88 (*m*, 4 Me$_2$CH). Anal. calc. for $C_{33}H_{51}N_3O_{12}Si_2$ (738.0): C 53.71, H 6.97, N 5.69; found: C 53.76, H 7.00, N 5.70.

5.29. *2'-O-[1-(2-Butoxy-2-oxoethoxy)ethyl]-3',5'-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)uridine* (**71**). According to *5.1*. Yield 89%. Colourless foam. TLC (toluene/AcOEt 1:2): R_f 0.86, 0.88. UV (MeOH): 205 (3.95), 260 (4.01). ^{1}H-NMR ($CDCl_3$): 10.32, 10.15 (br. *s*, H–N(3)); 7.81 (*d*, H–C(6)); 5.70, 5.63 (2*s*, H–C(1')); 5.61 (*d*, H–C(5)); 5.14 (*m*, MeC*H*(O)$_2$); 4.32–3.86 (*m*, $MeCH_2CH_2CH_2$, H–C(2'), H–C(3'), H–C(4'), 2 H–C(5'), OCH_2COO); 1.64–1.20 (*m*, $MeCH_2CH_2CH_2$, *Me*CH(O)$_2$); 1.10–0.78 (*m*, 4 Me$_2$CH). Anal. calc. for $C_{29}H_{52}N_2O_{10}Si_2$ (644.9): C 54.01, H 8.13, N 4.34; found: C 54.09, H 8.09, N 4.70.

5.30. *2'-O-[1-(2-Amino-2-oxoethoxy)ethyl]-3',5'-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)uridine* (**72**). Not isolated.

5.31. *2'-O-[1-(3-Ethoxy-1-methyl-3-oxopropoxy)ethyl]-3',5'-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)-uridine* (**73**). According to *5.1*. Yield 75%. Colourless foam. TLC (toluene/AcOEt 1:1): R_f 0.36, 0.39. ^{1}H-NMR ($CDCl_3$): 8.53 (br. *s*, NH); 7.89 (*m*, H–C(6)); 5.72, 5.64 (2*s*, H–C(1')); 5.60 (*d*, H–C(5)); 5.09 (*m*, MeC*H*(O)$_2$); 4.57–3.83 (*m*, H–C(2'), H–C(3'), H–C(4'), 2 H–C(5'), $MeCH_2O$, OC*H*(Me)CH_2COO); 2.72–2.35 (*m*, OCH(Me)CH_2COO); 1.45–1.18 (*m*, *Me*OH(O)$_2$, *Me*CH_2O, OCH(*Me*)CH_2COO); 1.11–0.85 (*m*, 4 Me$_2$CH).

5.32. *2'-O-[1-(3-Ethoxy-3-oxopropoxy)ethyl]-3',5'-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)uridine* (**74**). According to *5.1*. Yield 95%. Colourless foam. TLC (toluene/AcOEt 1:1): R_f 0.57. UV (MeOH): 263 (3.99), 208 (3.96). ^{1}H-NMR ($CDCl_3$): 8.86 (*s*, H–N(3)); 7.91 (*d*, H–C(6)); 5.75 (*d*, H–C(5)); 5.62 (*d*, H–C(1')); 5.05 (*q*, MeC*H*(O)$_2$); 4.3–3.6 (*m*, $MeCH_2O$, CH_2CH_2O, H–C(2'), H–C(3'), H–C(4'), 2 H–C(5')); 2.61 (*m*, CH_2CH_2O); 1.39, 1.41 (2*d*, *Me*CH(O)$_2$), 1.25 (*t*, *Me*CH_2O); 1.15–0.9 (*m*, 4 Me$_2$CH). Anal. calc. for $C_{28}H_{50}N_2O_{10}Si_2$ (630.9): C 53.31, H 7.99, N 4.44; found: C 53.27, H 8.06, N 4.44.

5.33. *2'-O-{1-[3-(Methylamino)-3-oxopropoxy]ethyl}-3',5'-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)uridine* (**75**). Treatment of **73** (1 g, 1.6 mmol) with abs. $MeNH_2$/EtOH soln. (25 ml) for 24 h at r.t., evaporation and purification by FC (silica gel (40 g), toluene/AcOEt 9:1, 3:1, 7:3, 6:4, 1:1, and toluene/AcOEt/MeOH 50:50:5) yielded, after evaporation and co-evaporation with CH_2Cl_2, a colourless solid foam (0.53 g, 54%). TLC (toluene/AcOEt/MeOH 5:5:2): R_f 0.48. UV (MeOH): 263 (3.97), 204 (4.11). ^{1}H-NMR ($CDCl_3$): 9.05 (*s*, H–N(3)); 7.94 (*d*, H–C(6)); 6.35 (*d*, NH); 5.71 (*d*, H–C(5)); 5.68 (*d*, H–C(1')); 5.06 (*q*, MeC*H*(O)$_2$); 4.3–3.7 (*m*, CH_2CH_2O, H–C(2'), H–C(3'), H–C(4'), 2 H–C(5')); 2.79 (*d*, MeN); 2.48 (*m*, CH_2CH_2O); 1.40, 1.43 (2*d*, *Me*CH(O)$_2$); 1.15–0.9 (*m*, 4 Me$_2$CH). Anal. calc. for $C_{27}H_{49}N_3O_9Si_2$ (615.9): C 52.66, H 8.02, N 6.82; found: C 53.83, H 8.12, N 7.37.

5.34. *2'-O-{1-{2-[Acetyl(methyl)amino]ethoxy}ethyl}-3',5'-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)uridine* (**76**). According to *5.1*. Yield 83%. Colourless foam. TLC (toluene/AcOEt 1:4): R_f 0.12, 0.14. UV (MeOH): 263 (3.98), 205 (4.06). ^{1}H-NMR ($CDCl_3$): 8.74 (*s*, H–N(3)); 5.73 (*d*, H–C(1')); 5.66 (*d*, H–C(5)); 5.03 (*q*, MeC*H*(O)$_2$); 4.21–3.54 (*m*, NCH_2CH_2O, H–C(2'), H–C(3'), H–C(4'), 2 H–C(5')); 3.00 (*d*, MeN); 2.10 (*d*, MeCO); 1.43, 1.38 (2*d*, *Me*CH(O)$_2$); 1.10–0.9 (*m*, 4 Me_2CH). Anal. calc. for $C_{28}H_{51}N_3O_9Si_2$ (629.9): C 53.40, H 8.16, N 6.67; found: C 53.41, H 8.24, N 6.76.

5.35. *2'-O-[1-(2-Chloroethoxy)ethyl]-3',5'-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)uridine* (**77**). According to *5.1*. Yield 77%. Colourless foam [34].

5.36. *2'-O-[1-(2-Cyanoethoxy)ethyl]-3',5'-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)uridine* (**78**). According to *5.1*. Yield 89%. Colourless foam. TLC (toluene/AcOEt 1:2): R_f 0.86, 0.88. UV (MeOH): 206 (3.82), 262 (3.98). ^{1}H-NMR ($CDCl_3$): 9.36, 9.22 (2br. *s*, H–N(3)); 7.94 (*d*, H–C(6)); 5.72 (*m*, H–C(5), H–C(1')); 5.13 (*m*, MeC*H*(O)$_2$); 4.31–3.86 (*m*, CH_2CH_2O, H–C(2'), H–C(3'), H–C(4'), 2 H–C(5')); 2.73–2.69 (*m*, CH_2CH_2O); 1.45 (*d*, *Me*CH(O)$_2$); 1.33–0.94 (*m*, 4 Me_2CH). Anal. calc. for $C_{26}H_{45}N_3O_8Si_2$ (583.8): C 53.49, H 7.77, N 7.20; found: C 5.23.20, H 7.77, N 7.07.

5.37. *2'-O-[1-(2-Nitroethoxy)ethyl]-3',5'-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)uridine* (**79**). According to *5.1*. Yield 84%. Colourless foam. TLC (toluene/AcOEt 1:2): R_f 0.80, 0.82. UV (MeOH): 204 (4.06), 262 (3.98). ^{1}H-NMR ($CDCl_3$): 9.61, 9.33 (2br. *s*, H–N(3)); 7.91 (*d*, H–C(6)); 5.73 (*s*, H–C(1')); 5.70 (*dd*, H–C(5)); 5.10 (*m*, MeC*H*(O)$_2$); 4.71–3.92 (*m*, CH_2CH_2O, H–C(2'), H–C(3'), H–C(4'), 2 H–C(5')); 1.42 (*d*, *Me*CH(O)$_2$); 1.18–0.94 (*m*, 4 Me_2CH). Anal. calc. for $C_{25}H_{45}N_3O_{10}Si_2$ (603.8): C 49.73, H 7.51, N 6.96; found: C 49.54, H 7.52, N 6.76.

5.38. *2'-O-{1-[2-(Methylsulfonyl)ethoxy]ethyl}-3',5'-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)uridine* (**80**). According to *5.1*. Yield 88%. Colourless foam. TLC (toluene/AcOEt 1:1): R_f 0.32, 0.34 (below educt). ^{1}H-NMR ($CDCl_3$): 8.86 (br. *s*, H–N(3)); 7.91 (*d*, H–C(6)); 5.65 (*m*, H–C(5), H–C(1')); 5.06 (*m*, MeC*H*(O)$_2$); 4.30–3.86 (*m*, CH_2CH_2O, H–C(2'), H–C(3'), H–C(4'), 2 H–C(5')); 3.40–3.18 (*m*, CH_2CH_2O); 2.98 (*s*, $MeSO_2$); 1.44 (*d*, *Me*CH(O)$_2$); 1.12–0.89 (*m*, 4 Me_2CH).

5.39. *2'-O-{1-[2-(Phenylthio)ethoxy]ethyl}-3',5'-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)uridine* (**81**). According to *5.1*. Yield 78%. Colourless foam. TLC (toluene/AcOEt 1:1): R_f 0.50, 0.52. ^{1}H-NMR ($CDCl_3$): 8.21 (br. *s*, NH); 7.88 (*d*, H–C(6)); 7.38–7.09 (*m*, 5 arom. H); 5.69, 5.60 (2*s*, H–C(1')); 5.64 (*d*, H–C(5)); 5.06 (*m*, MeC*H*(O)$_2$); 4.28–3.68 (*m*, SCH_2CH_2O, H–C(2'), H–C(3'), H–C(4'), 2 H–C(5')); 3.28–3.07 (*m*, SCH_2CH_2O); 1.41, 1.35 (2*d*, *Me*CH(O)$_2$); 1.12–0.88 (*m*, 4 Me_2CH).

5.40. *2'-O-{1-[2-(Phenylsulfonyl)ethoxy]ethyl}-3',5'-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)uridine* (**82**). According to *5.1*. Yield 86%. Colourless foam. TLC (toluene/AcOEt 1:1): R_f 0.32, 0.34. ^{1}H-NMR ($CDCl_3$): 9.85 (br. *s*, H–N(3)); 7.98–7.80 (*m*, 2 H_m, H–C(6)); 7.68–7.42 (*m*, 3 arom. H); 5.66 (*d*, H–C(5)); 5.64, 5.58 (2*s*, H–C(1')); 4.87 (*m*, MeC*H*(O)$_2$); 4.30–3.67 (*m*, CH_2CH_2O, H–C(2'), H–C(3'), H–C(4')); 3.55–3.29 (*m*, 2 H–C(5'), CH_2SO_2); 1.20 (*m*, *Me*CH(O)$_2$); 1.12–0.88 (*m*, 4 Me_2CH).

5.41. *2'-O-[1-(2-Phthalimidoethoxy)ethyl]-3',5'-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)uridine* (**83**). According to *5.1*. Yield 85%. Colourless foam. TLC (toluene/AcOEt 1:1): R_f 0.39, 0.41. UV (MeOH): 218 (4.60), 230 (sh, 4.19), 240 (4.12), 263 (4.04). ^{1}H-NMR ($CDCl_3$): 8.89, 8.78 (2br. *s*, H–N(3)); 7.98–7.88 (*d*, H–C(6)); 7.42–7.22 (*m*, 5 arom. H); 5.83, 5.72 (2*s*, H–C(1')); 5.68 (*d*, H–C(5)); 5.14 (*q*, MeC*H*(O)$_2$); 4.96–4.58 (*m*, CH_2CH_2O); 4.32–3.93 (*m*, H–C(2'), H–C(3'), H–C(4'), 2 H–C(5')); 1.47 (*d*, *Me*CH(O)$_2$); 1.16–0.84 (*m*, 4 Me_2CH). Anal. calc. for $C_{33}H_{49}N_3O_{10}Si_2$ (703.9): C 56.31, H 7.02, N 5.97; found: C 55.95, H 6.98, N 6.01.

6. *Desilylation of* **43**–**83** *to* **84**–**124**. 6.1. *General Procedure*. For the deprotection of 2'-*O*-(1-alkoxyethyl)-protected-3',5'-*O*-(1,1,3,3-tetraisopropyldisiloxan-1,3-diyl)uridine, 0.16N $Bu_3NF \cdot 3\,H_2O$ in abs. dioxane (50 mg/ml) was used (conditions *a*). To deprotect base-sensitive acetal groups, the $Bu_4NF \cdot 3\,H_2O$ dioxane soln. was buffered by addition of AcOH (0.05 ml/ml soln.) (conditions *b*). The 2'-*O*-(1-alkoxyethyl)-protected 3',5'-*O*-(1,1,3,3-tetraisopropyl-disiloxan-1,3-diyl)uridine (5 mmol) was dissolved in $Bu_4NF \cdot 3\,H_2O$/dioxane soln. (80 ml, 12 mmol) and stirred at r.t. for several hours (*a*) or overnight (*b*). After TLC control, the soln. was evaporated at 40° and the resulting liquid residue purified by FC (toluene/AcOEt/MeOH). The product was co-evaporated with MeOH (2 × 20 ml) and CH_2Cl_2 (2 × 20 ml) and the resulting solid foam dried in a desiccator under high vacuum. Crystallization was achieved as described below.

6.2. *2'-O-[1-(Phenoxy)ethyl]uridine* (**84**). According to *6.1* (*a*). Yield 75%. M.p. 171°. TLC (CH_2Cl_2/MeOH 10:1): R_f 0.32. UV (MeOH): 261 (3.98), 218 (4.02). ^{1}H-NMR ((D$_6$)DMSO): 11.32, 10.84 (2br. *s*, H–N(3)); 7.74 (*d*, H–C(6)); 7.23–6.83 (*m*, 5 arom. H); 5.92 (*d*, H–C(5)); 5.74–5.37 (*m*, H–C(1'), MeC*H*(O)$_2$); 5.24–5.09 (*m*, OH–C(3'), OH–C(5')); 4.41–4.25 (*m*, H–C(2')); 4.05 (*m*, H–C(3')); 3.87 (*m*, H–C(4')); 3.54 (*m*, 2 H–C(5')); 1.43 (*d*, *Me*CH(O)$_2$). Anal. calc. for $C_{17}H_{20}N_2O_7$ (364.4): C 56.04, H 5.53, N 7.68; found: C 55.63, H 5.51, N 7.69.

6.3. *2′-O-[1-(4-Methoxyphenoxy)ethyl]uridine* (**85**). According to *6.1* (*a*). Yield 74%. M.p. 176°. TLC (CH_2Cl_2/MeOH 10:1): R_f 0.41. UV (MeOH): 261 (3.97), 220 (4.14), 206 (4.02). ^{1}H-NMR ((D$_6$)DMSO): 11.34, 10.93 (2*s*, H–N(3)); 7.79, 7.69 (*d*, H–C(6)); 6.86–6.65 (*m*, 4 arom. H); 5.93, 5.88 (2*d*, H–C(5)); 5.61–5.41 (*d*, H–C(1′)); 5.48, 5.32 (2*q*, MeC*H*(O)$_2$); 5.23–5.09 (*m*, OH–C(3′), OH–C(5′)); 4.41–4.22 (*m*, H–C(2′)); 4.07 (*m*, H–C(3′)); 3.86 (*m*, H–C(4′)); 3.66 (*s*, MeO); 3.54 (*m*, 2 H–C(5′)); 1.43, 1.34, (2*d*, *Me*CH(O)$_2$). Anal. calc. for $C_{18}H_{22}N_2O_8 \cdot 0.5\ H_2O$ (403.39): C 53.59, H 5.74, N 6.94; found: C 53.67, H 5.61, N 6.97.

6.4. *2′-O-[1-(2-Chlorophenoxy)ethyl]uridine* (**86**). According to *6.1* (*a*). Yield 71%. M.p. 175°. TLC (CH_2Cl_2/MeOH 10:1): R_f 0.33. UV (MeOH): 261 (4.00), 218 (4.07). ^{1}H-NMR ((D$_6$)DMSO): 11.38, 11.32 (2*s*, H–N(3)); 7.75 (2*d*, H–C(6)); 7.57–6.88 (*m*, 4 arom. H); 5.79, 5.74 (2*d*, H–C(1′)); 5.68, 5.60 (2*d*, H–C(5)); 5.25–5.03 (*m*, OH–C(3′), OH–C(5′)); 4.83 (*q*, MeC*H*(O)$_2$); 4.42 (*m*, H–C(2′)); 4.04 (*m*, H–C(3′)); 3.88 (*m*, H–C(4′)); 3.56 (*m*, 2 H–C(5′)); 1.42 (*d*, *Me*CH(O)$_2$). Anal. calc. for $C_{17}H_{19}N_2O_8 \cdot H_2O$ (416.8): C 48.98, H 5.07, N 6.72; found: C 49.03, H 4.88, N 6.78.

6.5. *2′-O-[1-(Benzyloxy)ethyl]uridine* (**87**). According to *6.1* (*a*). Yield 74%. Colourless foam. TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.67, 0.70. UV (MeOH): 206 (4.57), 227 (sh, 3.98), 261 (4.01). ^{1}H-NMR ((D$_6$)DMSO): 11.36 (br. *s*, H–N(3)); 7.93 (*dd*, H–C(6)); 7.33–7.23 (*m*, 5 arom. H); 5.93 (*m*, H–C(1′)); 5.62 (*m*, H–C(5)); 5.26–5.11 (*m*, OH–C(3′), OH–C(5′)); 4.90 (*m*, MeC*H*(O)$_2$); 4.62–4.28 (*m*, PhCH_2); 4.25 (*m*, H–C(2′)); 4.09 (*m*, H–C(3′)); 3.89 (*m*, H–C(4′)); 3.70–3.50 (*m*, 2 H–C(5′)); 1.44–1.18 (*m*, *Me*CH(O)$_2$). Anal. calc. for $C_{18}H_{22}N_2O_7 \cdot 0.5\ H_2O$ (387.39): C 55.81, H 5.98, N 7.23; found: C 56.04, H 5.95, N 7.33.

6.6. *2′-O-[1-(4-Methoxybenzyloxy)ethyl]uridine* (**88**). According to *6.1* (*a*). Yield 62%. Colourless foam. TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.38, 0.40. UV (MeOH): 203 (4.35), 225 (sh, 4.22), 262 (4.05). ^{1}H-NMR ((D$_6$)DMSO): 11.36 (*s*, H–N(3)); 7.92 (*d*, H–C(6)); 7.15 (*d*, 2 H$_o$); 6.83 (*d*, 2 H$_m$); 5.93 (*m*, H–C(1′)); 5.64 (*m*, H–C(5)); 5.26–5.11 (*m*, OH–C(3′), OH–C(5′)); 4.86 (*q*, MeC*H*(O)$_2$); 4.63–4.18 (*m*, ArCH_2, H–C(2′)); 4.16 3.98 (*m*, H–C(3′)); 3.89 (*m*, H–C(4′)); 3.72 (*s*, MeO); 3.79–3.27 (*m*, 2 H–C(5′)); 1.25 (*d*, *Me*CH(O)$_2$). Anal. calc. for $C_{19}H_{24}N_2O_8$ (408.4): C 55.87, H 5.92, N 6.86; found: C 55.57, H 6.11, N 6.77.

6.7. *2′-O-[1-(3,4-Dimethoxybenzyloxy)ethyl]uridine* (**89**). According to *6.1* (*a*). Yield 87%. Colourless foam. TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.44, 0.46. UV (MeOH): 204 (4.56), 227 (sh, 3.98), 265 (4.03). ^{1}H-NMR ((D$_6$)DMSO): 11.37 (*s*, H–N(3)); 7.93 (*d*, H–C(6)); 6.80 (*m*, 3 arom. H); 5.93 (*m*, H–C(1′)); 5.64 (*m*, H–C(5)); 5.19 (*m*, OH–C(3′), OH–C(5′)); 4.89 (*m*, MeCH(O)$_2$); 4.58–4.18 (*m*, H–C(2′), ArCH_2); 4.08 (*m*, H–C(3′)); 3.90 (*m*, H–C(4′)); 3.79–3.52 (*m*, 2 H–C(5′), 2 MeO); 1.28 (*m*, *Me*CH(O)$_2$). Anal. calc. for $C_{20}H_{26}N_2O_9$ (438.4): C 54.79, H 5.98, N 6.39; found: C 54.28, H 5.98, N 6.16.

6.8. *2′-O-[1-(2,6-Dichlorobenzyloxy)ethyl]uridine* (**90**). According to *6.1* (*a*). Yield 75%. Colourless foam. TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.67, 0.70. UV (MeOH): 203 (4.57), 227 (sh, 3.97), 261 (4.03), 282 (sh, 3.93). ^{1}H-NMR ((D$_6$)DMSO): 11.36 (br. *s*, H–N(3)); 7.99, 7.80 (2*d*, H–C(6)); 7.50–7.31 (*m*, 3 arom. H); 5.94 (*m*, H–C(1′)); 5.65 (*m*, H–C(5)); 5.20 (*m*, OH–C(3′), OH–C(5′)); 4.96 (*m*, MeC*H*(O)$_2$); 4.89–4.52 (*m*, ArCH_2); 4.30 (*m*, H–C(2′)); 4.10 (*m*, H–C(3′)); 3.90 (*m*, H–C(4′)); 3.71–3.50 (*m*, 2 H–C(5′)); 1.30 (*m*, *Me*CH(O)$_2$). Anal. calc. for $C_{18}H_{22}N_2O_7 \cdot 0.5\ H_2O$ (387.4): C 55.81, H 5.98, N 7.23; found: C 56.04, H 5.95, N 7.33.

6.9. *2′-O-[1-(3,5-Dichlorobenzyloxy)ethyl]uridine* (**91**). According to *6.1* (*a*). Yield 79%. Colourless foam. TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.65, 0.68. ^{1}H-NMR ((D$_6$)DMSO): 11.30 (*s*, H–N(3)); 7.95 (*d*, H–C(6)); 7.39 (*s*, H–C(4)(Ar)); 7.27 (*s*, H–C(2)(Ar), H–C(6)(Ar)); 5.98 (*m*, H–C(1′)); 5.57 (*m*, H–C(5)); 5.30–5.05 (*m*, OH–C(3′), OH–C(5′)); 4.93 (*m*, MeC*H*(O)$_2$); 4.68–4.38 (*m*, ArCH_2); 4.23 (*m*, H–C(2′)); 4.08 (*m*, H–C(3′)); 3.85 (*m*, H–C(4′)); 3.72–3.52 (*m*, 2 H–C(5′)); 1.30 (*m*, *Me*CH(O)$_2$).

6.10. *2′-O-{1-[4-(Ethoxycarbonyl)benzyloxy]ethyl}uridine* (**92**). According to *6.1* (*a*). Yield 61%. TLC (toluene/AcOEt/MeOH 5:5:2): R_f 0.47. UV (MeOH): 258 (4.01), 237 (4.27). ^{1}H-NMR ((D$_6$)DMSO): 11.38 (*s*, H–N(3)); 7.95 (*m*, 2 H$_m$, H–C(6)); 7.42 (*m*, 2 H$_o$); 5.95 (*m*, H–C(1′)); 5.60 (*d*, H–C(5)); 5.23 (*m*, OH–C(3′), OH–C(5′)); 4.96 (*q*, MeC*H*(O)$_2$); 4.55 (*m*, ArCH_2, H–C(2′)); 4.15 (*m*, H–C(3′)); 4.10–3.65 (*m*, H–C(4′), 2 H–C(5′), MeCH_2O); 1.41 (*m*, *Me*CH(O)$_2$, *Me*CH$_2$O). Anal. calc. for $C_{21}H_{25}N_2O_9$ (450.4): C 55.99, H 5.82, N 6.21; found: C 55.88, H 5.81, N 6.17.

6.11. *2′-O-[1-(4-Nitrobenzyloxy)ethyl]uridine* (**93**). According to *6.1* (*b*). Yield 58%. Colourless needles (toluene/Et$_2$O 1:1). M.p. 69°. TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.32, 0.34. UV (MeOH): 205 (4.26), 263 (4.26). ^{1}H-NMR ((D$_6$)DMSO): 11.28 (br. *s*, H–N(3)); 8.15 (*d*, 2 H$_m$); 7.86 (*d*, H–C(6)); 7.49 (*d*, 2 H$_o$); 5.88 (*dd*, H–C(1′)); 5.54 (*dd*, H–C(5)); 5.31–5.15 (*m*, OH–C(3′), OH–C(5′)); 4.96 (*m*, MeC*H*(O)$_2$); 4.79–4.52 (*m*, ArCH_2); 4.25 (*m*, H–C(2′)); 4.08 (*m*, H–C(3′)); 3.87 (*m*, H–C(4′)); 3.63 (*m*, H–C(5′)); 1.32 (*d*, *Me*CH(O)$_2$). Anal. calc. for $C_{18}H_{21}N_3O_9$ (423.4): C 51.06, H 5.00, N 9.93; found: C 50.84, H 5.05, N 9.92.

6.12. *2′-O-[1-(2-Nitrobenzyloxy)ethyl]uridine* (**94**). According to *6.1* (*b*). Yield 40%. Colourless foam (light-sensitive). TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.30, 0.32. UV (MeOH): 204 (4.26), 263 (4.16). ^{1}H-NMR

((D$_6$)DMSO): 11.28 (br. *s*, H–N(3)); 8.06 (*d*, H–C(3)(Ar)); 7.84 (*m*, H–C(6)); 7.70 (*m*, H–C(6)(Ar), H–C(5)(Ar)); 7.55 (*m*, H–C(4)(Ar)); 5.90 (*dd*, H–C(1′)); 5.50 (*dd*, H–C(5)); 5.31–5.08 (*m*, OH–C(3′), OH–C(5′)); 5.02–4.70 (*m*, MeC*H*(O)$_2$, ArCH_2); 4.28 (*m*, H–C(2′)); 4.08 (*m*, H–C(3′)); 3.85 (*m*, H–C(4′)); 3.59 (*m*, H–C(5′)); 1.31 (*d*, *Me*CH(O)$_2$). Anal. calc. for $C_{18}H_{21}N_3O_9$ (423.4): C 51.06, H 5.00, N 9.93; found: C 50.69, H 5.01, N 9.89.

6.13. *2′-O-[1-(2,4-Dinitrobenzyloxy)ethyl]uridine* (**95**). According to *6.1* (*b*). Yield 52% (2 steps). Colourless foam (light-sensitive). TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.30, 0.32. UV (MeOH): 206 (4.17), 254 (4.29). ^{1}H-NMR ((D$_6$)DMSO): 11.38, 11.19 (2br. *s*, H–N(3)); 8.78 (*d*, H–C(3)(Ar)); 8.52 (*m*, H–C(4)(Ar)); 7.98 (*m*, H–C(5)(Ar)); 7.83 (*d*, H–C(6)); 5.88 (*dd*, H–C(1′)); 5.49 (*dd*, H–C(5)); 5.32–4.93 (*m*, OH–C(3′), OH–C(5′), MeC*H*(O)$_2$, ArCH_2); 4.28 (*m*, H–C(2′)); 4.09 (*m*, H–C(3′)); 3.85 (*m*, H–C(4′)); 3.59 (*m*, 2 H–C(5′)); 1.35 (*d*, *Me*CH(O)$_2$). Anal. calc. for $C_{18}H_2N_4O_{11}$ (468.4): C 46.16, H 4.30, N 11.96; found: C 46.10, H 4.58, N 11.20.

6.14. *2′-O-{1-{4-[2-(4-Nitrophenyl)ethoxycarbonyloxy]benzyloxy}ethyl}uridine* (**96**). According to *6.1* (*b*). Yield 76%. Colourless foam. TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.38, 0.40. UV (MeOH): 204 (4.42), 209 (sh, 4.22), 264 (4.29). ^{1}H-NMR ((D$_6$)DMSO): 11.36 (br. *s*, H–N(3)); 8.19 (*d*, 2 H *o* to NO$_2$); 7.95 (*d*, H–C(6)); 7.59 (*d*, 2 H *m* to NO$_2$); 7.26 (*d*, 2 H *o* to OCO): 7.11 (*d*, 2 H *m* to OCO); 5.92 (*m*, H–C(1′)); 5.62 (*dd*, H–C(5)); 5.28–5.12 (*m*, OH–C(3′), OH–C(5′)); 4.92 (*m*, MeC*H*(O)$_2$); 4.69–4.35 (*m*, ArCH_2, CH$_2$CH_2O); 4.24 (*m*, H–C(2′)); 4.09 (*m*, H–C(3′)); 3.88 (*m*, H–C(4′)); 3.60 (*m*, 2 H–C(5′)); 3.15 (*t*, CH_2CH$_2$O); 1.30 (*m*, *Me*CH(O)$_2$). Anal. calc. for $C_{27}H_{29}N_3O_{12}$ (587.5): C 55.20, H 4.97, N 7.15; found: C 54.91, H 5.02, N 7.13.

6.15. *2′-O-[1-(4-Hydroxybenzyloxy)ethyl]uridine* (**97**). Compound **96** (0.12 g, 0.2 mmol) was stirred in conc. ammonia (10 ml) at r.t. for 15 h. The mixture was evaporated and co-evaporated with dioxane and the resulting syrup purified by FC (silica gel (10 g), toluene/AcOEt 5:0, 10:1, 1:1, and toluene/AcOEt/MeOH 1:1:2). Evaporation and co-evaporation with MeOH and CH_2Cl_2 gave a colourless solid foam (0.077 g, 93%). TLC (toluene/AcOEt 5:4:1): R_f 0.15. UV (MeOH): 207 (4.30), 263 (4.04). ^{1}H-NMR ((D$_6$)DMSO): 11.30 (br. *s*, H–N(1)); 9.38 (br. *s*, O*H*–C$_6$H$_4$); 7.88 (*dd*, H–C(6)); 7.05 (*d*, 2H$_o$); 6.66 (*d*, 2H$_m$); 5.93 (*dd*, H–C(1′)); 5.62 (*d*, H–C(5)); 5.24–5.11 (*m*, OH–C(3′), OH–C(5′)); 4.81, 4.83 (2*q*, MeC*H*(O)$_2$); 4.53–3.45 (*m*, H–C(2′), H–C(3′), H–C(4′), 2 H–C(5′), ArCH_2); 1.22 (*m*, *Me*CH(O)$_2$). Anal. calc. for $C_{18}H_{22}N_2O_8 \cdot 1\,H_2O$ (412.4): C 52.42, H 5.87, N 6.79; found: C 52.42, H 5.74, N 6.69.

6.16. *2′-O-{1-{2-Chloro-4-[2-(4-nitrophenyl)ethoxycarbonyloxy]benzyloxy}ethyl}uridine* (**98**). According to *6.1* (*b*). Yield 82%. Colourless foam. TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.61, 0.63. UV (MeOH): 202 (4.55), 212 (sh, 4.45), 264 (4.28). ^{1}H-NMR ((D$_6$)DMSO): 11.32 (br. *s*, H–N(3)); 8.18 (*d*, 2H *o* to NO$_2$); 7.95 (*d*, H–C(6)); 7.59 (*d*, 2 H *m* to NO$_2$); 7.42 (*m*, H–C(3)(Ar)); 7.29 (*m*, H–C(5)(Ar), H–C(6)(Ar)); 5.91 (*m*, H–C(1′)); 5.61 (*dd*, H–C(5)); 5.30–5.13 (*m*, OH–C(3′), OH–C(5′)); 4.93 (*m*, MeC*H*(O)$_2$); 4.68–4.38 (*m*, ArCH_2, CH$_2$CH_2O); 4.26 (*m*, H–C(2′)); 4.08 (*m*, H–C(3′)); 3.90 (*m*, H–C(4′)); 3.60 (*m*, 2 H–C(5′)); 3.15 (*t*, CH_2CH$_2$O); 1.30 (*m*, *Me*CH(O)$_2$). Anal. calc. for $C_{27}H_{28}ClN_3O_{12}$ (621.9): C 52.14, H 4.54, N 6.76; found: C 51.91, H 4.70, N 6.76.

6.17. *2′-O-[1-(2-Chloro-4-hydroxybenzyloxy)ethyl]uridine* (**99**). According to *6.1* (*a*). Yield 92%. Colourless foam. TLC (toluene/AcOEt/MeOH 30:30:12): R_f 0.45, 0.47. UV (MeOH): 204 (4.52), 224 (sh, 3.97), 261 (4.03). ^{1}H-NMR ((D$_6$)DMSO): 11.36 (br. *s*, H–N(3)); 10.13 (br. *s*, O*H*–C$_6$H$_3$); 7.95 (*dd*, H–C(6)); 7.20 (*dd*, H–C(6)(Ar)); 6.99 (*m*, H–C(3)(Ar)); 6.87 (*dd*, H–C(5)(Ar)); 5.91 (*t*, H–C(1′)); 5.63 (*d*, H–C(5)); 5.20 (*m*, OH–C(3′), OH–C(5′)); 4.86 (*q*, MeC*H*(O)$_2$); 4.51–4.21 (*m*, H–C(2′), ArCH_2); 4.06 (*m*, H–C(3′)); 3.88 (*m*, H–C(4′)); 3.68 (*m*, 2 H–C(5′)); 1.28–1.22 (*m*, *Me*CH(O)$_2$). Anal. calc. for $C_{18}H_{21}ClN_2O_8 \cdot 1H_2O$ (428.8): C 48.38, H 5.03, N 6.26; found: C 48.20, H 4.90, N 6.21.

6.18. *2′-O-{1-{3-Chloro-4-[2-(4-nitrophenyl)ethoxycarbonyloxy]benzyloxy}ethyl}uridine* (**100**). According to *6.1* (*b*). Yield 97%. Colourless foam. TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.35, 0.38. UV (MeOH): 204 (4.55), 212 (sh, 4.46), 265 (4.27). ^{1}H-NMR ((D$_6$)DMSO): 11.32 (br. *s*, H–N(3)); 8.20 (*d*, 2 H *o* to NO$_2$); 7.90 (*d*, H–C(6)); 7.60 (*d*, 2H *m* to NO$_2$); 7.46 (*m*, H–C(5)(Ar)); 7.37 (*d*, H–C(2)(Ar)); 7.18 (*dd*, H–C(6)(Ar)); 5.93 (*m*, H–C(1′)); 5.59 (*dd*, H–C(5)); 5.30–5.21 (*m*, OH–C(3′), OH–C(5′)); 4.99 (*m*, MeC*H*(O)$_2$); 4.70–4.38 (*m*, ArCH_2, CH$_2$CH_2O); 4.28 (*m*, H–C(2′)); 4.09 (*m*, H–C(3′)); 3.90 (*m*, H–C(4′)); 3.62 (*m*, 2 H–C(5′)); 3.18 (*t*, C*H*CH$_2$O); 1.38, 1.31 (2*d*, *Me*CH(O)$_2$). Anal. calc. for $C_{27}H_{28}ClN_3O_{12}$ (621.9): C 52.14, H 4.54, N 6.76; found: C 52.14, H 4.56, N 6.53.

6.19. *2′-O-[1-(3-Chloro-4-hydroxybenzyloxy)ethyl]uridine* (**101**). According to *6.1* (*a*). Yield 82%. Colourless foam. TLC (toluene/AcOEt/MeOH 30:30:12): R_f 0.42, 0.45. UV (MeOH): 204 (4.52), 224 (3.97), 261 (4.03). ^{1}H-NMR ((D$_6$)DMSO): 11.35 (br. *s*, H–N(3)); 9.87 (br. *s*, O*H*–C$_6$H$_3$); 7.93 (*dd*, H–C(6)); 7.16 (*dd*, H–C(2)(Ar)); 6.78 (*d*, H–C(6)(Ar)); 6.68 (*dd*, H–C(5)(Ar)); 5.91 (*dd*, H–C(1′)); 5.61 (*d*, H–C(5)); 5.23–5.15 (*m*, OH–C(3′), OH–C(5′)); 4.90 (*q*, MeC*H*(O)$_2$); 4.58–4.18 (*m*, H–C(2′), ArCH_2); 4.06 (*m*, H–C(3′)); 3.88

(*m*, H–C(4')); 3.61 (*m*, 2 H–C(5')); 1.26 (*m*, *Me*CH(O)$_2$). Anal. calc. for $C_{18}H_{21}ClN_2O_8 \cdot 1H_2O$ (446.8): C 48.38, H 5.08, N 6.26; found: C 47.90, H 4.91, N 6.36.

6.20. *2'-O-{1-{3-Fluoro-4-[2-(4-nitrophenyl)ethoxycarbonyloxy]benzyloxy}ethyl)uridine* (**102**). According to *6.1* (*b*). Yield 89%. Colourless foam. TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.45, 0.47. UV (MeOH): 205 (4.38), 212 (sh, 4.28), 264 (4.31). ^{1}H-NMR ((D$_6$)DMSO): 11.28 (br. *s*, H–N(3)); 8.18 (*m*, 2H *o* to NO$_2$); 7.88 (*m*, H–C(6)); 7.63–7.09 (*m*, 2H *m* to NO$_2$, H–C(2)(Ar), H–C(6)(Ar), H–C(5)(Ar)); 5.91 (*m*, H–C(1')); 5.53 (*m*, H–C(5)); 5.29–5.09 (*m*, OH–C(3'), OH–C(5')); 4.95 (*m*, MeC*H*(O)$_2$); 4.70–4.36 (*m*, ArCH_2, CH$_2$CH_2O); 4.26 (*t*, H–C(2')); 4.06 (*m*, H–C(3')); 3.87 (*m*, H–C(4')); 3.78–3.48 (*m*, 2 H–C(5')); 3.12 (*t*, CH_2CH$_2$O); 1.42 (*d*, *Me*CH(O)$_2$). Anal. calc. for $C_{27}H_{28}FN_3O_{12}Si_2 \cdot 0.5\,H_2O$ (614.5): C 53.56, H 4.66, N 6.94; found: C 52.86, H 4.83, N 6.91.

6.21. *2'-O-[1-(3-Fluoro-4-hydroxybenzyloxy)ethyl]uridine* (**103**). According to *6.1* (*a*). Yield 89%. Colourless foam. TLC (toluene/AcOEt/MeOH 30:30:12): R_f 0.43, 0.47. UV (MeOH): 211 (4.13), 219 (sh, 4.09), 263 (4.05). ^{1}H-NMR ((D$_6$)DMSO): 11.38 (br. *s*, H–N(3)); 9.79 (br. *s*, OH–C$_6$H$_3$); 7.95 (*dd*, H–C(6)); 7.00 (*d*, H–C(2)(Ar)); 6.85 (*m*, H–C(5)(Ar), H–C(6)(Ar)); 5.91 (*dd*, H–C(1')); 5.62 (*d*, H–C(5)); 5.28–5.12 (*m*, OH–C(3'), OH–C(5')); 4.86 (*q*, MeC*H*(O)$_2$); 4.51–4.18 (*m*, H–C(2'), ArCH_2); 4.06 (*m*, H–C(3')); 3.88 (*m*, H–C(4')); 3.61 (*m*, 2 H–C(5')); 1.25 (*m*, *Me*CH(O)$_2$). Anal. calc. for $C_{18}H_{21}FN_2O_8 \cdot 0.5\,H_2O$ (421.4): C 51.31, H 5.26, N 6.65; found: C 51.41, H 5.34, N 6.49.

6.22. *2'-O-{1-{2,5-Dichloro-4-[2-(4-nitrophenyl)ethoxycarbonyloxy]benzyloxy}ethyl)uridine* (**104**). According to *6.1* (*b*). Yield 69%. Colourless foam. TLC (toluene/AcOEt/MeOH 1:1): R_f 0.66, 0.69. UV (MeOH): 203 (4.66), 266 (sh, 4.13), 264 (4.26). ^{1}H-NMR ((D$_6$)DMSO): 11.30 (br. *s*, H–N(3)); 8.18 (*d*, 2H *o* to NO$_2$); 7.87 (*d*, H–C(6)); 7.57 (*m*, 2 H *m* to NO$_2$, H–C(3)(Ar), H–C(6)(Ar)); 5.91 (*m*, H–C(1')); 5.61 (*dd*, H–C(5)); 5.28–5.09 (*m*, OH–C(3'), OH–C(5')); 5.01 (*m*, MeC*H*(O)$_2$); 4.69–4.38 (*m*, ArCH_2, CH$_2$CH_2O); 4.29 (*m*, H–C(2')); 4.08 (*m*, H–C(3')); 3.90 (*m*, H–C(4')); 3.61 (*m*, 2 H–C(5')); 3.17 (*t*, CH_2CH$_2$O); 1.35 (*d*, *Me*CH(O)$_2$). Anal. calc. for $C_{27}H_{27}Cl_2N_3O_{12}$ (656.4): C 49.40, H 4.15, N 6.40; found: C 48.99, H 4.31, N 6.29.

6.23. *2'-O-[1-(2,5-Dichloro-4-hydroxybenzyloxy)ethyl]uridine* (**105**). According to *6.1* (*b*). Yield 92%. Colourless foam. TLC (toluene/AcOEt/MeOH 5:5:2): R_f 0.43, 0.44. UV (MeOH): 206 (4.59), 224 (sh, 3.97), 261 (4.03), 290 (sh, 3.43). ^{1}H-NMR ((D$_6$)DMSO): 11.30 (br. *s*, H–N(1)); 10.64 (br. *s*, O*H*–C$_6$H$_2$); 7.89 (*dd*, H–C(6)); 7.30 (*s*, H–C(6)(Ar)); 6.94 (*s*, H–C(3)(Ar)); 5.91 (*dd*, H–C(1')); 5.57 (*d*, H–C(5)); 5.29–5.08 (*m*, OH–C(3'), OH–C(5')); 4.93 (*q*, MeC*H*(O)$_2$); 4.60–4.23 (*m*, H–C(2'), ArCH_2); 4.09 (*m*, H–C(3')); 3.88 (*m*, H–C(4')); 3.68 (*m*, 2 H–C(5')); 1.32–1.26 (*m*, *Me*CH(O)$_2$). Anal. calc. for $C_{18}H_{20}Cl_2N_2O_8 \cdot 0.5\,H_2O$ (463.3): C 45.78, H 4.48, N 5.98; found: C 45.48, H 4.56, N 6.18.

6.24. *2'-O-{1-{2,5-Dichloro-4-[(2,2-dimethylpropanoyl)oxy]benzyloxy}ethyl)uridine* (**106**). According to *6.1* (*a*). Yield 85%. Colourless foam. TLC (toluene/AcOEt/MeOH 1:1): R_f 0.72, 0.79. UV (MeOH): 203 (4.56), 221 (sh, 4.18), 262 (4.02). ^{1}H-NMR (CDCl$_3$): 8.52 (br. *s*, H–N(3)); 7.53, 7.33 (2*d*, H–C(6), H–C(3)(Ar)); 7.11 (*s*, H–C(6)(Ar)); 5.62 (*m*, H–C(1'), H–C(5)); 5.07 (*m*, MeC*H*(O)$_2$); 4.77–4.50 (*m*, ArCH_2, H–C(2')); 4.34, 4.23 (2*m*, H–C(3')); 4.11 (*m*, H–C(4')); 3.90, 3.77 (2*m*, 2 H–C(5')); 3.20, 2.98, 2.76, 2.60 (4br. *s*, OH–C(3'), OH–C(5')); 1.46 (*d*, *Me*CH(O)$_2$); 1.38 (*s*, Me$_3$C). Anal. calc. for $C_{23}H_{28}Cl_2N_2O_9$ (547.4): C 50.47, H 5.16, N 5.12; found: C 50.31, H 5.42, N 5.11.

6.25. *2'-O-[1-(2-Phenylethoxy)ethyl]uridine* (**107**). According to *6.1* (*a*). Yield 84%. M.p. 171°. TLC (CH$_2$Cl$_2$/MeOH 9:1): R_f 0.38, 0.42. UV (MeOH): 261 (3.95), 206 (4.18). ^{1}H-NMR ((D$_6$)DMSO): 11.37 (*s*, H–N(3)); 7.92 (*d*, H–C(6)); 7.24–7.15 (*m*, Ph); 5.88 (*m*, H–C(1')); 5.67 (*m*, H–C(5)); 5.13 (*m*, OH–C(3'), OH–C(5')); 4.87–4.78 (*m*, MeC*H*(O)$_2$); 4.16 (*m*, H–C(2')); 4.03 (*m*, H–C(3')); 3.86 (*m*, H–C(4')); 3.69–3.46 (*m*, CH$_2$CH_2O, 2 H–C(5')); 2.73–2.68 (*m*, CH_2CH$_2$O); 1.22, 1.17 (2*d*, *Me*CH(O)$_2$). Anal. calc. for $C_{19}H_{24}N_2O_7$ (392.4): C 58.15, H 6.16, N 7.13; found: C 57.76, H 6.22, N 6.97.

6.26. *2'-O-{1-[2-(4-Methoxyphenyl)ethoxy]ethyl}uridine* (**108**). According to *6.1* (*a*). Yield 74%. Colourless foam. TLC (CH$_2$Cl$_2$/MeOH 9:1): R_f 0.57, 0.65. UV (MeOH): 263 (3.97), 219 (4.06), 201 (4.18). ^{1}H-NMR ((D$_6$)DMSO): 11.36 (*s*, H–N(3)); 7.94, 7.83 (2*d*, H–C(6)); 7.06 (*d*, 2 H$_o$); 6.80 (*d*, 2 H$_m$); 5.87 (*m*, H–C(1')); 5.67 (*m*, H–C(5)); 5.19–5.05 (*m*, OH–C(3'), OH–C(5')); 4.79 (*q*, MeC*H*(O)$_2$); 4.14 (*m*, H–C(2')); 4.02 (*m*, H–C(3')); 3.86 (*m*, H–C(4')); 3.69 (*s*, MeO); 3.64–3.46 (*m*, CH$_2$CH_2O, 2 H–C(5')); 2.63 (*m*, CH_2CH$_2$O); 1.19 (*d*, *Me*CH(O)$_2$). Anal. calc. for $C_{20}H_{26}N_2O_8$ (422.4): C 56.86, H 6.20, N 6.63; found: C 56.86, H 6.51, N 6.30.

6.27. *2'-O-{1-[2-(4-Nitrophenyl)ethoxy]ethyl}uridine* (**109**). According to *6.1* (*b*). Yield 88%. M.p. 162°. TLC (CH$_2$Cl$_2$/MeOH 9:1): R_f 0.42, 0.46. UV (MeOH): 265 (4.23), 214 (sh, 4.10), 203 (4.22). ^{1}H-NMR ((D$_6$)DMSO): 11.36 (*s*, H–N(3)); 8.12 (*d*, 2 H$_m$); 7.90 (*m*, H–C(6)); 7.47 (*d*, 2H$_o$); 5.87 (*m*, H–C(1')); 5.64 (*m*, H–C(5)); 5.18 (*m*, OH–C(3'), OH–C(5')); 4.81 (*m*, MeC*H*(O)$_2$); 4.16–3.50 (*m*, H–C(2'), H–C(3'), H–C(4'), CH$_2$CH$_2$O, 2 H–C(5')); 2.90 (*m*, CH_2CH$_2$O); 1.22, 1.13 (*m*, *Me*CH(O)$_2$). Anal. calc. for $C_{19}H_{23}N_3O_9$ (437.4): C 52.17, H 5.30, N 9.60; found: C 51.71, H 5.47, N 9.20.

6.28. *2'-O-{1-[2-(2,4-Dinitrophenyl)ethoxy]ethyl}uridine* (**110**). According to *6.1* (*b*). Yield 76%. Colourless foam. TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.32, 0.34. UV (MeOH): 205 (4.26), 256 (4.32). ^{1}H-NMR ($CDCl_3$): 8.74 (*m*, H–C(3)(Ar)); 8.68 (br. *s*, H–N(3)); 8.38 (*d*, H–C(5)(Ar)); 7.65 (*d*, H–C(6), H–C(6)(Ar)); 5.70 (*m*, H–C(1'), H–C(5)); 4.84 (*m*, MeC*H*(O)$_2$); 4.39–3.63 (*m*, H–C(2'), H–C(3'), H–C(4'), 2 H–C(5'), CH_2CH_2O); 3.28 (*t*, CH_2CH_2O); 2.72, 2.58 (2*m*, OH–C(3'), OH–C(5')); 1.26 (*d*, *Me*CH(O)$_2$). Anal. calc. for $C_{19}H_{22}N_4O_{11}$ (482.4): C 47.31, H 4.60, N 11.61; found: C 47.04, H 4.63, N 11.41.

6.29. *2'-O-{2-{1-[(4-Nitrophenyl)ethoxy]-2-oxoethoxy}ethyl}uridine* (**111**). According to *6.1* (*b*). Yield 54%. Colourless foam. TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.21, 0.23. UV (MeOH): 202 (4.33), 209 (4.25), 264 (4.27). ^{1}H-NMR ((D$_6$)DMSO): 11.36 (br. *s*, H–N(3)); 8.19 (*d*, 2 H$_m$); 7.89 (*d*, H–C(6)); 7.54 (*d*, 2 H$_o$); 5.85 (*d*, H–C(1')); 5.66 (*d*, H–C(5)); 5.28–5.10 (*m*, OH–C(3'), OH–C(5')); 4.86 (*m*, MeC*H*(O)$_2$); 4.38–3.82 (*m*, H–C(2'), H–C(3'), H–C(4'), CH_2CH_2O, ArCH_2); 3.60 (*m*, 2 H–C(5')); 3.06 (*t*, CH_2CH_2O); 1.25, 1.18 (2*d*, *Me*CH(O)$_2$). Anal. calc. for $C_{21}H_{25}N_3O_{11} \cdot 0.5H_2O$ (504.5): C 50.00, H 5.20, N 8.33; found: C 50.00, H 5.24, N 8.23.

6.30. *2'-O-[1-(2-Butoxy-2-oxoethoxy)ethyl]uridine* (**112**). According to *6.1* (*b*). Yield 96% (two steps). Colourless foam. TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.27, 0.30. UV (MeOH): 206 (3.94), 260 (3.99). ^{1}H-NMR ((D$_6$)DMSO): 11.35 (br. *s*, H–N(3)); 7.90 (*d*, H–C(6)); 5.85 (*m*, H–C(1')); 5.62 (*m*, H–C(5)); 5.24–5.10 (*m*, OH–C(3'), OH–C(5')); 4.89 (*m*, MeC*H*(O)$_2$); 4.26–3.80 (*m*, H–C(2'), H–C(3'), H–C(4'), $MeCH_2CH_2CH_2$, ArCH_2); 3.74–3.49 (*m*, H–C(5')); 1.53 (*m*, $MeCH_2CH_2CH_2$); 1.25 (*m*, $MeCH_2CH_2CH_2$, *Me*CH(O)$_2$); 1.21 (*t*, $MeCH_2CH_2CH_2$). Anal. calc. for $C_{17}H_{26}N_2O_9$ (402.4): C 50.74, H 6.51, N 6.96; found: C 50.57, H 6.58, N 6.96.

6.31. *2'-O-[1-(2-Amino-2-oxoethoxy)ethyl]uridine* (**113**). Analogously to *6.15* with **72** (0.2 mmol). Yield 61%. Colourless foam. TLC (AcOEt/MeOH 10:1): R_f 0.13, 0.15. UV (MeOH): 207 (3.90), 260 (4.00). ^{1}H-NMR ((D$_6$)DMSO): 11.32 (br. *s*, H–N(3)); 7.93 (*t*, H–C(6)); 7.24, 7.08 (2br. *s*, NH$_2$); 5.82 (*dd*, H–C(1')); 5.62 (*d*, H–C(5)); 5.22–5.09 (*m*, OH–C(3'), OH–C(5')); 4.88 (*q*, MeC*H*(O)$_2$); 4.23 (*m*, H–C(2')); 4.07 (*m*, H–C(3')); 3.94–3.49 (*m*, H–C(4'), 2 H–C(5'), ArCH_2); 1.23, 1.26 (2*d*, *Me*CH(O)$_2$). Anal. calc. for $C_{13}H_{19}N_3O_8$ (345.3): C 45.22, H 5.55, N 12.16; found: C 44.54, H 5.61, N 12.07.

6.32. *2'-O-[1-(3-Ethoxy-1-methyl-3-oxopropoxy)ethyl]uridine* (**114**). According to *6.1* (*a*). Yield 88%. Colourless foam. TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.76, 0.79. UV (MeOH): 206 (4.03), 260 (3.99). ^{1}H-NMR ($CDCl_3$): 9.28 (br. *s*, H–N(3)); 7.88–7.58 (*m*, H–C(6)); 5.87–5.61 (*m*, H–C(1'), H–C(5)); 5.09–4.79 (*m*, MeC*H*(O)$_2$); 4.52–3.70 (*m*, H–C(2'), H–C(3'), H–C(4'), 2 H–C(5'), MeCH_2O, OC*H*(Me)CH_2COO); 3.37–2.88 (br. *s*, OH–C(3'), OH–C(5')); 2.62–2.30 (*m*, OCH(Me)CH_2COO); 1.41–1.15 (*m*, *Me*CH(O)$_2$, *Me*CH$_2$O, OCH(Me)CH_2COO). Anal. calc. for $C_{19}H_{24}N_2O_7 \cdot 0.5\,H_2O$ (404.4): C 50.74, H 6.51, N 6.96; found: C 50.42, H 6.68, N 6.75.

6.33. *2'-O-[1-(3-Ethoxy-3-oxopropoxy)ethyl]uridine* (**115**). According to *6.1* (*a*). Yield 91%. TLC (toluene/AcOEt/MeOH 5:5:2): R_f 0.38, 0.53. UV (MeOH): 261 (3.96), 207 (3.96). ^{1}H-NMR ((D$_6$)DMSO): 11.35 (*s*, H–N(3)); 7.94 (*d*, H–C(6)); 5.88 (*m*, H–C(1')); 5.66 (*d*, H–C(5)); 5.20 (*m*, OH–C(3'), OH–C(5')); 4.82 (*q*, MeC*H*(O)$_2$); 4.16–3.45 (*m*, CH_2CH_2O, MeCH_2O, H–C(2'), H–C(3'), H–C(4'), 2 H–C(5')); 2.48 (*m*, CH_2CH_2O); 1.21 (*m*, *Me*CH(O)$_2$, *Me*CH$_2$O). Anal. calc. for $C_{16}H_{25}N_2O_9$ (388.34): C 49.49, H 6.23, N 7.21; found: C 49.68, H 6.39, N 7.56.

6.34. *2'-O-{1-[3-(Methylamino)-3-oxopropoxy]ethyl}uridine* (**116**). According to *6.1* (*a*). Yield 89%. TLC (toluene/AcOEt/MeOH 5:5:2): R_f 0.42, 0.55. UV (MeOH): 260 (3.99), 207 (4.01). ^{1}H-NMR ((D$_6$)DMSO): 11.33 (*s*, H–N(3)); 7.91 (*d*, H–C(6)); 7.73 (*s*, CONHMe); 5.85 (*m*, H–C(1')); 5.45 (*d*, H–C(5)); 5.17 (*s*, OH–C(3')); 5.10 (*s*, OH–C(5')); 4.77 (*q*, MeC*H*(O)$_2$); 4.21–3.23 (*m*, CH_2CH_2O, H–C(2'), H–C(3'), H–C(4'), 2 H–C(5')); 2.53 (*d*, MeN); 2.19 (*m*, CH_2CH_2O); 1.17 (2*d*, *Me*CH(O)$_2$). Anal. calc. for $C_{15}H_{24}N_3O_8 \cdot 1H_2O$ (373.34): C 47.12, H 6.32, N 10.99; found: C 46.72, H 6.31, N 10.66.

6.35. *2'-O-{1-{2-[Acetyl(methyl)amino]ethoxy}ethyl}uridine* (**117**). According to *6.1* (*a*). Yield 79%. TLC (toluene/AcOEt/MeOH 5:5:2): R_f 0.54. UV (MeOH): 260 (3.99), 207 (4.01). ^{1}H-NMR ((D$_6$)DMSO): 11.37 (*s*, H–N(3)); 7.93 (*m*, H–C(6)); 5.84 (*m*, H–C(1')); 5.68 (*d*, H–C(5)); 5.19 (*m*, OH–C(3'), OH–C(5')); 4.89 (*q*, MeC*H*(O)$_2$); 4.17 (*m*, H–C(2')); 4.15 (*m*, H–C(3')); 3.87 (*s*, H–C(4')); 3.57 (*m*, H–C(5')); 3.38 (*m*, NCH_2CH_2O); 2.92, 2.75 (2*s*, MeN); 1.95 (*d*, MeCO); 1.21 (*m*, *Me*CH(O)$_2$). Anal. calc. for $C_{16}H_{26}N_3O_8 \cdot 1H_2O$ (406.4): C 47.76, H 6.51, N 10.44; found: C 47.86, H 6.42, N 10.28.

6.36. *2'-O-[1-(2-Chloroethoxy)ethyl]uridine* (**118**). According to *6.1* (*a*). Yield 88%. Colourless foam. Physical data in [34].

6.37. *2'-O-[1-(2-Cyanoethoxy)ethyl]uridine* (**119**). According to *6.1* (*b*). Yield 90%. Colourless foam. TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.43, 0.45. UV (MeOH): 206 (3.82), 260 (4.00). ^{1}H-NMR ((D$_6$)DMSO): 11.35 (br. *s*, H–N(3)); 7.95 (*d*, H–C(6)); 5.84 (*m*, H–C(1')); 5.63 (*m*, H–C(5)); 5.25–5.13 (*m*, OH–C(3'), OH–C(5'));

4.89 (*m*, MeC*H*(O)$_2$); 4.21–4.00 (*m*, H–C(2'), H–C(3')); 3.85 (*m*, H–C(4')); 3.80–3.45 (*m*, CH_2CH_2O, 2 H–C(5')); 2.80–2.62 (*m*, CH_2CH_2O); 1.21 (*d*, *Me*CH(O)$_2$). Anal. calc. for $C_{14}H_{19}N_3O_7 \cdot 0.5\ H_2O$ (350.3): C 48.00, H 5.75, N 11.99; found: C 48.33, H 5.70, N 11.92.

6.38. *2'-O-[1-(2-Nitroethoxy)ethyl]uridine* (**120**). According to *6.1* (*b*). Yield 81%. Colourless foam. TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.38, 0.41. UV (MeOH): 204 (4.06), 260 (3.99). ^{1}H-NMR ((D$_6$)DMSO): 11.35 (br. *s*, H–N(3)); 7.95 (*d*, H–C(6)); 5.84 (*m*, H–C(1')); 5.65 (*m*, H–C(5)); 5.28–5.11 (*m*, OH–C(3'), OH–C(5')); 4.90 (*m*, MeC*H*(O)$_2$); 4.70 (*m*, CH_2CH_2O); 4.21–3.78 (*m*, H–C(2'), H–C(3'), H–C(4'), CH_2CH_2O); 3.60 (*m*, 2 H–C(5')); 1.20, 1.24 (2*d*, *Me*CH(O)$_2$). Anal. calc. for $C_{13}H_{19}N_3O_9$ (361.3): C 43.22, H 5.30, N 11.63; found: C 43.00, H 5.37, N 11.50.

6.39. *2'-O-{1-[2-(Methylsulfonyl)ethoxy]ethyl}uridine* (**121**). According to *6.1* (*b*). Yield 90% (two steps). Colourless foam. TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.28, 0.32. UV (MeOH): 207 (3.94), 261 (3.99). ^{1}H-NMR ((D$_6$)DMSO): 11.35 (br. *s*, H–N(3)); 7.95 (*d*, H–C(6)); 5.85 (*m*, H–C(1')); 5.67 (*m*, H–C(5)); 5.32–5.13 (*m*, OH–C(3'), OH–C(5')); 4.90 (*m*, MeC*H*(O)$_2$); 4.28–3.48 (*m*, H–C(2'), H–C(3'), H–C(4'), CH_2CH_2O, 2 H–C(5')); 3.32 (*m*, CH_2CH_2O); 2.93 (*s*, $MeSO_2$); 1.26 (*d*, *Me*CH(O)$_2$). Anal. calc. for $C_{14}H_{22}N_2O_9S \cdot 0.5\ H_2O$ (403.4): C 41.68, H 5.75, N 6.94; found: C 41.68, H 5.77, N 6.77.

6.40. *2'-O-{1-[2-(Phenylthio)ethoxy]ethyl}uridine* (**122**). According to *6.1* (*a*). Yield 90%. Colourless foam. TLC (toluene/AcOEt/MeOH 1:1): R_f 0.58, 0.61. UV (MeOH): 204 (4.26), 254 (4.21). ^{1}H-NMR ($CDCl_3$): 8.75 (br. *s*, H–N(3)); 7.60 (*d*, H–C(6)); 7.35–7.14 (*m*, 5 arom. H); 5.75–5.64 (*m*, H–C(1'), H–C(5)); 4.86 (*m*, MeC*H*(O)$_2$); 4.48 (*t*, H–C(2')); 4.28 (*m*, H–C(3')); 4.08 (*m*, H–C(4')); 3.98–3.55 (*m*, SCH_2CH_2O, 2 H–C(5')); 3.12–2.64 (*m*, SCH_2CH_2O, OH–C(3'), OH–C(5')); 1.30 (*d*, *Me*CH(O)$_2$). Anal. calc. for $C_{19}H_{24}N_2O_7S$ (424.5): C 53.76, H 5.70, N 6.60; found: C 53.26, H 5.70, N 6.47.

6.41. *2'-O-{1-[2-(Phenylsulfonyl)ethoxy]ethyl}uridine* (**123**). According to *6.1* (*b*). Yield 85% (two steps). Colourless foam. TLC (toluene/AcOEt/MeOH 5:4:1): R_f 0.58, 0.61. UV (MeOH): 210 (4.12), 258 (sh, 4.00), 262 (4.01), 268 (sh, 3.95). ^{1}H-NMR ((D$_6$)DMSO): 11.35 (br. *s*, H–N(3)); 7.88 (*m*, 2 H$_m$, H–C(6)); 7.79–7.58 (*m*, 3 arom. H); 5.80, 5.65 (2*m*, H–C(1'), H–C(5)); 5.23–5.08 (*m*, OH–C(3'), OH–C(5')); 4.70 (*m*, MeC*H*(O)$_2$); 4.12–3.48 (*m*, H–C(2'), H–C(3'), H–C(4'), CH_2CH_2O, 2 H–C(5'), CH_2CH_2O); 0.98 (*d*, *Me*CH(O)$_2$). Anal. calc. for $C_{19}H_{24}N_2O_9S$ (456.5): C 50.00, H 5.30, N 6.14; found: C 49.86, H 5.27, N 6.15.

6.42. *2'-O-[1-(2-Phthalimidoethoxy)ethyl]uridine* (**124**). According to *6.1* (*a*). Yield 76%. Colourless foam. TLC (toluene/AcOEt/MeOH 1:1): R_f 0.34, 0.36. UV (MeOH): 218 (4.61), 230 (sh, 4.21), 240 (4.12), 263 (4.05). ^{1}H-NMR ((D$_6$)DMSO): 11.31 (br. *s*, NH); 7.96–7.78 (*m*, H–C(6), 4 arom. H); 5.83 (*m*, H–C(1')); 5.62 (*m*, H–C(5)); 5.20–5.06 (*m*, OH–C(3'), OH–C(5')); 4.83 (*m*, MeC*H*(O)$_2$); 4.18–3.46 (*m*, H–C(2'), H–C(3'), H–C(4'), 2 H–C(5'), CH_2CH_2O); 1.15 (*m*, *Me*CH(O)$_2$). Anal. calc. for $C_{21}H_{23}N_3O_9 \cdot 1H_2O$ (479.4): C 52.61, H 4.84, N 8.76; found: C 52.49, H 5.09, N 8.51.

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