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Uridine 5'-Monoselenoacetals As Substrates for Diastereoselective Homolytic C-C Bond Formation

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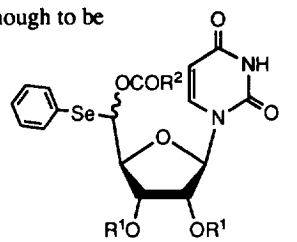
Key Words: monoselenoacetal; uridine; radical reaction; C-C bond formation; diastereoselectivity

Abstract: *Uridine 5'-monoselenoacetals prepared by the seleno-Pummerer reaction of 5'-deoxy-5'-phenylseleno-uridines were used as substrates for radical-mediated reactions with allyltributyltin. The reaction of the 2',3'-O-isopropylidene derivative gave cyclized products, 5-allyl-6,5'-cyclonucleosides, whereas those of the 2',3'-bis-O-(tert-butyldimethylsilyl derivatives underwent the C-C bond formation at the 5'-position to give (5'S)- and (5'R)-isomers. The stereochemical outcome of both types of reactions is discussed. The use of radical acceptors other than allyltributyltin was also examined.* Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Several methods are available for the preparation of monoselenoacetals (mixed O,Se-acetals)[1] which serve as useful precursors for generating α-alkoxylalkyl radicals by way of homolytic C-Se bond cleavage. The Pummerer reaction[2] of selenoxides (the seleno-Pummerer reaction) seemingly offers one general approach to the monoselenoacetals; however there have been only a few examples[3] of such a transformation, presumably because of the higher propensity of selenoxides to undergo spontaneous *syn*-elimination.

We have reported a method to introduce a phenylseleno group into various positions of the sugar moiety of uracil nucleosides[4a-c] and have verified that the resulting selenides, upon oxidation, can be used for the regio-defined preparation of unsaturated-sugar derivatives.[4c] During this study, it became apparent that selenoxides of the sugar moiety of nucleosides are, in most cases, stable enough to be isolated by usual workup, since their β-carbon is bound to an electronegative oxygen atom.[5] This fact enabled us to carry out the seleno-Pummerer reaction, which provided the corresponding acylated monoselenoacetals.[6]



1

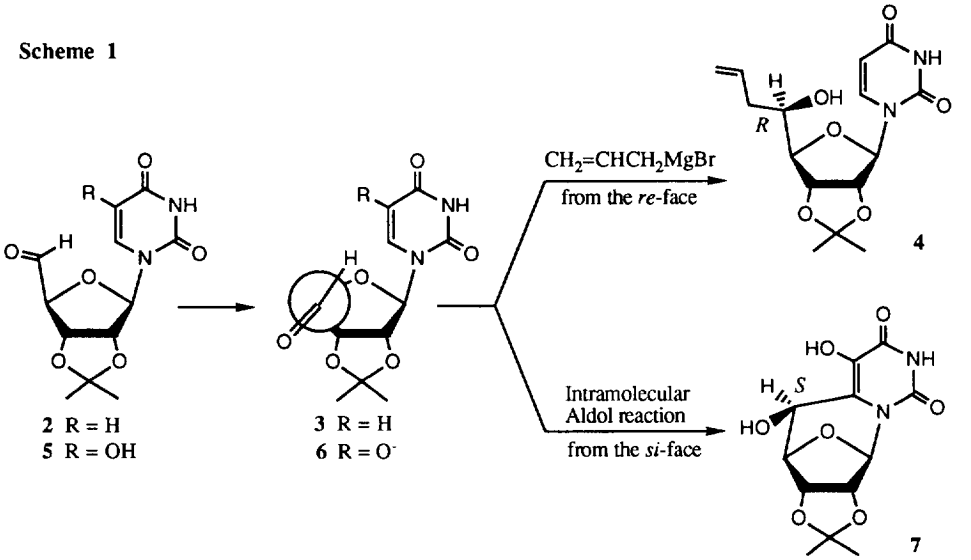
R^1 = protecting group
R^2 = Me or Ph

In the present study, uridine 5'-monoselenoacetals of general structure **1**, prepared from the 5'-phenylseleno derivatives by way of the seleno-Pummerer reaction, were subjected to homolytic cleavage of the C-Se bond with the aim of developing a new method for effecting stereoselective C-C bond formation at the 5'-position of nucleosides.[7]

HOMOLYTIC CLEAVAGE OF 5'-MONOSELENOACETALS DERIVED FROM 2',3'-*O*-ISOPROPYLIDENEURIDINE: INTRAMOLECULAR REACTIONS

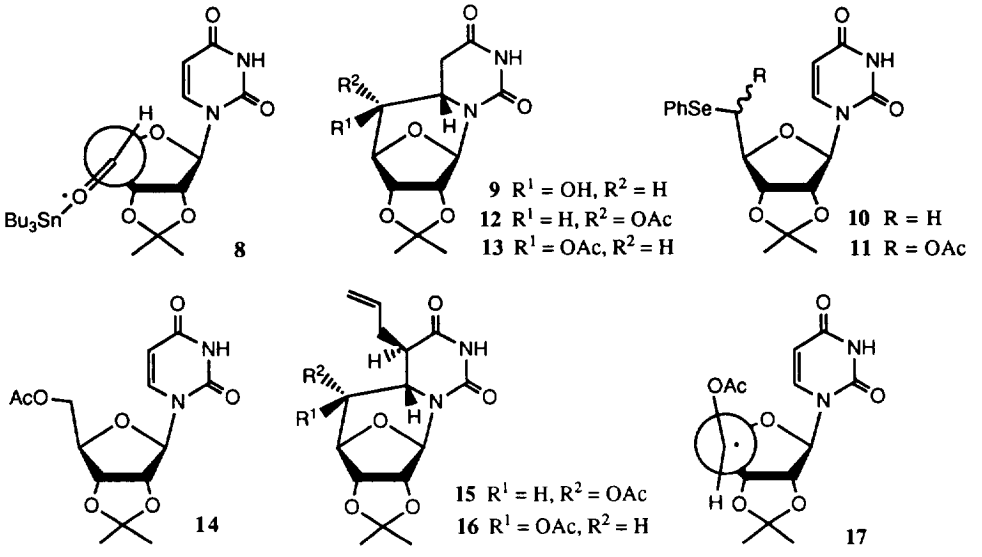
Reaction of allylmagnesium bromide with 2',3'-*O*-isopropylideneuridine 5'-aldehyde (**2**) has been used in an early step in the total synthesis of octosyl acid A.[8] The main 5'-*C*-allylated isomer (**4**, obtained in a ratio of 16:1) has (5'*R*)-configuration, suggesting that the nucleophile reacted from the *re*-face of the conformer **3** (Scheme 1). An intramolecular aldol reaction utilizing **5** has also been reported[9] to give **7** exclusively, the formation of which would be explicable based on the same rationale: the intramolecular reaction occurred solely from the *si*-face of **6**.

Scheme 1



In 1988, Ueda and his co-workers[10] showed that, in terms of the stereochemical course of the reaction, a tin radical-mediated intramolecular cyclization of **2** (Bu_3SnH/AIBN, in refluxing benzene) also falls into the above category: the putative intermediate which can be depicted as **8**, reacts across the 5,6-double bond at its *si*-face to furnish the (6*S*,5'*S*)-5,6-dihydro-6,5'-cyclouridine **9**[11] that has the same 5'-configuration as **7**.

In contrast to these precedents, we found that radical reaction of the acetylated monoselenoacetal **11**, prepared from **10** by way of the seleno-Pummerer reaction, follows a different stereochemical pathway with respect to the 5'-position. That is, when homolytic cleavage of the C5'-Se bond of **11** was carried out in refluxing benzene by adding a mixture of Bu_3SnH (2 equiv) and AIBN (0.5 equiv) *via* a syringe pump over 4 h, two isomeric products **12** and **13** [FAB-MS *m/z* 327 (M^++H)] were formed in 57% and 16% yields, respectively. The X-ray crystallographic analysis of the main product **12** (mp 182-184 °C, acetone-hexane) showed that it has the opposite (5'*R*)-configuration to **9**.[12] That the minor isomer **13** has (6*S*,5'*S*)-stereochemistry was determined based on ^1H NMR spectroscopy by inspecting the $J_{4',5'}$ (4.6 Hz) and $J_{5',6}$ (9.5 Hz) values (the respective values of **12** are $J_{4',5'}$= 2.2 and $J_{5',6}$= 3.5 Hz).[13] The diastereoselectivity (**12** *vs.* **13**) was improved to 7.5:1 by conducting the reaction of **11** at room temperature under photo-initiated conditions (Bu_3SnH/ $(Bu_3Sn)_2$/hv/benzene), although the combined yield of **12** plus **13** was only 49% due to



the formation of the reduction product **14** (35%). It should be mentioned that, when allyltributyltin was used in this reaction instead of Bu_3SnH, the yield of the cyclized products was improved significantly: compounds **15**[12] and **16** were isolated in 78% and 6.7% yields, respectively.[14]

The above-observed dominant formation of the (5'*R*)-isomer (**12** or **15**) from **11** suggests that a radical intermediate involved in these reactions can be depicted as **17**, which has an O4'-O5'-*gauche* conformation,[15] and the reaction with the 5,6-double bond took place from its *re*-face. The proposed conformational difference between **8** and **17** might be rationalized by taking the group electronegativity (χ)[16] into consideration: in the case where the 5'-oxygen carries an acyl group, which is fairly electronegative (χ value of acetyl group is 2.864), delocalization of its unshared electron to the 5'-carbon radical is highly unlikely, whereas this would be possible when the 5'-*O*-substituent is less electronegative such as the trialkylstannyl group (for example, χ value of triethylstannyl group is 1.795).

On the basis of the above assumption, one would readily anticipate that, if the intramolecular pathway can be eliminated, external radical acceptors could react with **17** preferentially from its *si*-face to furnish a new method for diastereoselective construction of C-C bonds at the 5'-position of uracil nucleosides. We next investigated this possibility.

RADICAL-MEDIATED DIASTEREOSELECTIVE C-C BOND FORMATION AT THE 5'-POSITION OF URIDINE: INTERMOLECULAR REACTIONS

It has been known that closer disposition between the base moiety and the 5'-position results from 2',3'-*O*-isopropylidenation of ribonucleosides. Evidence for this conformational change has been demonstrated by an elegant study of H-5 exchange kinetics of a series of uracil derivatives in NaOMe/MeOD.[17] In this study, the rate for 2',3'-*O*-isopropylideneuridine is reported to be 67 times faster than that of uridine by virtue of the ready participation of its 5'-alkoxide across the 5,6-double bond. Based on the additional fact that the diminished rate

of uridine is almost comparable to that of 2'-deoxyuridine, we reasoned that 6,5'-cyclonucleoside formation could be suppressed if the radical generated from the thymidine derivative **19** is reacted in the presence of an external radical acceptor. We, therefore, first examined such a reaction of **19** which was obtained from **18** by oxidation followed by the seleno-Pummerer reaction.[18]

Scheme 2

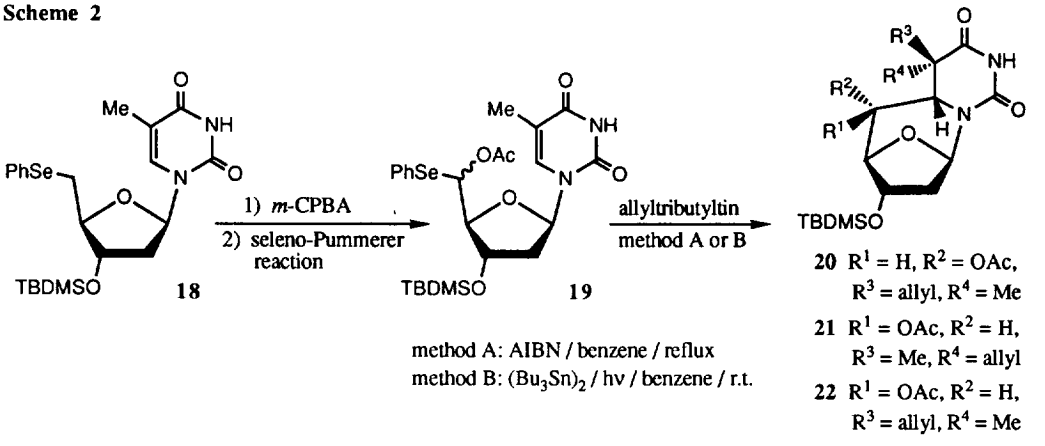


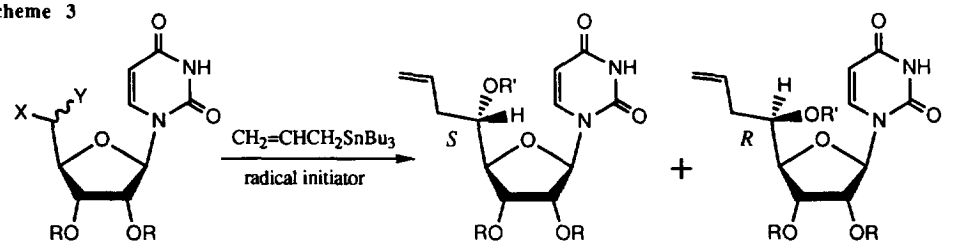
Table 1. Reactions between **19** and allyltributyltin

Reaction conditions	Isolated yield (%) of products			
	20	**21**	**22**	**23**
method A	55	16	8	9
method B	43	10	5	10

Contrary to our expectation, however, both the thermal (method A in Scheme 2) and photochemical (method B) reactions between **19** and allyltributyltin (5 equiv) proceeded largely through the intramolecular pathway which resulted in the formation of **20-22** (combined yield, 58-79%).[12,19] The 5'-*C*-allylated product **23** was obtained in only *ca.* 10% yield as a mixture of two diastereoisomers (Table 1). This led us to move to the uridine derivatives **24-26** having 2'- and 3'-*O*-protecting groups other than the isopropylidene group. The results are summarized in Table 2.

The use of the 2',3'-di-*O*-acetyl derivative **24** in the reaction with allyltributyltin (5 equiv) in refluxing benzene completely eliminated the intramolecular pathway, but the result was discouraging both in terms of the yield (**27** plus **28**) and diastereoselectivity (entry 1). The depicted C5'-stereochemistry of these products was confirmed by X-ray crystallographic analysis of **27**.[12,20] On the other hand, when the 2'- and 3'-hydroxyl functions were protected with the *tert*-butyldimethylsilyl (TBDMS) group as in **25**, improvement was seen not only in the yield (**29**[21] plus **30**) but also in the (5'*S*)-stereoselectivity (entries 2-4). Comparison of entry 2 with entry 4 shows the role of reaction temperature as an important determinant for the stereoselectivity. Entry 5 suggests that triethylborane would be inadequate for carrying out S_H2' type initiation. As can be seen in entries

Scheme 3



24 R = Ac, X = SePh, Y = OAc
25 R = TBDMS, X = SePh, Y = OAc
26 R = TBDMS, X = SePh, Y = OBz
33 R = TBDMS, X & Y: =O

27 R = R' = Ac
29 R = TBDMS, R' = Ac
31 R = TBDMS, R' = COPh
34 R = TBDMS, R' = H

28 R = R' = Ac
30 R = TBDMS, R' = Ac
32 R = TBDMS, R' = COPh
35 R = TBDMS, R' = H

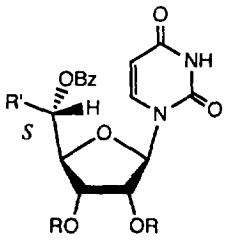
Table 2. Reactions of Uridine 5'-Monoselenoacetals (**24-26**) with Allyltributyltin

Entry	Compd.	Conditions	Yield (%)	Products (ratio)
1	**24**	AIBN/benzene/reflux, overnight	36	**27** and **28** (10:9.5)[a,b]
2	**25**	AIBN/benzene/reflux, overnight	84	**29** and **30** (3:1)
3	**25**	AIBN/benzene/reflux, overnight[c]	96	**29** and **30** (3.6:1)
4	**25**	$(Bu_3Sn)_2$/hv/benzene/r.t., 5 h	56	**29** and **30** (6:1)
5	**25**	Et_3B/O_2/THF/r.t., 3 days	0[d]	—
6	**26**	AIBN/benzene/reflux, overnight	70	**31** and **32** (6.6:1)[a,e]
7	**26**	$(Bu_3Sn)_2$/hv/benzene/r.t., 4 h	67	**31** and **32** (10.2:1)
8	**26**	$(Bu_3Sn)_2$/hv/benzene/r.t., 4 h[c]	70	**31** and **32** (9.9:1)
9	**26**	$(Bu_3Sn)_2$/hv/toluene/0 °C, 4 h	66	**31** and **32** (12.7:1)
10	**26**	$(Bu_3Sn)_2$/hv/benzene/r.t., 4 h[f]	69	**31** and **32** (4.8:1)

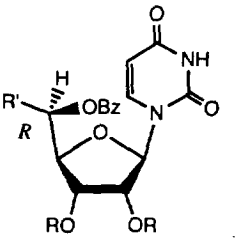
a) These products were obtained as an inseparable mixture. The ratio was determined by ^{1}H NMR spectroscopy.
b) Two unknown products were formed.
c) Allyltriphenyltin (5 equiv) was used.
d) The starting material (**25**) was recovered.
e) As a by-product, 5'-*O*-benzoyl-2',3'-bis-*O*-(*tert*-butyldimethylsilyl)uridine (14%) was also isolated.
f) Allyl chloride (5 equiv) was used.

6-9 (formation of **31**[21] and **32** from **26**), the introduction of a bulkier 5'-*O*-benzoyl group uniformly leads to a further improvement of the (5'*S*)-selectivity . The result in entry 10, when compared with that of entry 7, shows that an inexpensive allyl chloride[22] results in the loss of selectivity. An additional fact which may be noteworthy is that the ^{1}H NMR spectra of these products (**27-32**) showed that the H-6 resonance of the (5'*S*)-isomers uniformly appears at a lower field than that of the (5'*R*)-isomers [chemical shifts of H-6 δ ppm: **27**, 7.60; **28**, 7.20; **29**, 7.88; **30**, 7.21; **31**, 7.89; **32**, 7.19].

Although our initial prediction of (5'*S*)-selectivity came from the electronegative nature of the radical substituent (5'-*O*-acyl group) as mentioned earlier in the case of the 2',3'-*O*-isopropylidene derivative **11**, the results in Table 2 clearly indicate that bulkiness of the hydroxyl-protecting groups, both 3'- and 5'-positions,[23] plays an important role in the cases of **24-26**. Inspection of a molecular model suggested that, when the C5'-radical derived from **25** or **26** takes a O4'-O5'-*anti* conformation, there could be a considerable repulsive force at work between the 3'-*O*-TBDMS and 5'-*O*-acyl groups, especially in a 3'-*endo* sugar pucker conformation.[24]



R = TBDMS
36, **38**, **40**, **42**, and **44**



R = TBDMS
37, **39**, **41**, **43**, and **45**

Table 3. Photo-initiated Reactions of **26** with Various Types of Radical Acceptors[a)]

Entry	Radical acceptor	Reaction time (h)	R'	Product (% yield)	Ratio of 5'*S* / 5'*R*	Chemical shift of H-6 (δ ppm)
1	CH_2=C(Cl)CH_2Cl	4	$CH_2C(Cl)=CH_2$	**36** (56) **37** (9)	*ca.* 6 / 1	7.81 7.22
2	CH_2=C(Me)CH_2Cl	2	$CH_2C(Me)=CH_2$	**38** (55) **39** (9)	*ca.* 6 / 1	7.91 7.16
3	CH_2=CHCH(Me)Cl	4	$CH_2CH=CHMe$	**40** **41** (56)[b)]	6.6 / 1	7.88 and 7.92 7.19
4	BrCH=CH(Me)CN	4	CH=C(Me)CN	**42** (46)[c)] **43** (9)	*ca.* 5 / 1	7.90 and 7.85 7.30
5	CH_2=CHCN	3	CH_2CH_2CN[d)]	**44** (42) **45** (6)	7 / 1	7.80 7.15

a) All reactions, except entry 5, were carried out by using the respective acceptor (5 equiv) and $(Bu_3Sn)_2$ (1.5 equiv) in benzene at room temperature.
b) A combined yield (**40** and **41** were obtained as an inseparable mixture). Compound **40** consists of (*Z*)- and (*E*)-isomers.
c) A combined yield of (*Z*)- and (*E*)-isomers.
d) The reaction was carried out by using acrylonitrile (10 equiv), Bu_3SnH (1 equiv), and $(Bu_3Sn)_2$ (0.5 equiv) in benzene at room temperature. As a by-product, 5'-*O*-benzoyl-2',3'-bis-*O*-(*tert*-butyldimethylsilyl)uridine was also obtained (28%).

If such a steric factor actually governs the conformational preference of the radical intermediate, a similar (5'*S*)-selectivity can be seen in the reaction of the uridine 5'-aldehyde **33** with allyltributyltin. This turned out to be the case. When **33** was reacted with allyltributyltin under the thermal conditions, **34** and **35** were obtained in a ratio of 3.6 : 1.[25)]

Finally, to investigate the scope of the radical-mediated C-C bond formation of uridine 5'-monoseleno-acetals, several different types of radical acceptors were examined for reaction with **26** in benzene at room temperature under photo-irradiation, the results of which are listed in Table 3. In these instances, the depicted 5'-stereochemistry of the products (**36**-**45**) is tentative: it was assumed simply on the basis of ^{1}H NMR criterion by comparing H-6 chemical shifts between (5'*S*)- and (5'*R*)-isomers, which is mentioned above for **27**-**32**.

Entries 1-3 are additional examples of S_H2' type C-C bond formation. As we have already seen in Table 2 (entry 10), these allyl chlorides gave a comparatively lower diastereoselectivity than allyltributyltin did (*cf.* entry 7 in Table 2). Entry 4 shows that the present reaction is also applicable to direct substitution for activated vinyl

halides. The use of monoselenoacetal radical chemistry is further illustrated in entry 5 by the addition reaction to an electron-deficient olefin. These results clearly show that a variety of carbon-functionalities can be stereoselectively introduced to the 5'-position of uridine by the use of commercially available reagents as radical acceptors.

CONCLUSION

Radical-mediated reactions, both intra- and intermolecular, of uridine 5'-monoselenoacetals were studied. The observed diastereofacial selectivity of the intramolecular cyclization of the 2',3'-*O*-isopropylidene derivative (**11**) can be explained by taking the electronegativity of the 5'-*O*-acyl group into consideration. In contrast to this, in the cases of intermolecular reactions of 2',3'-bis-*O*-(*tert*-butyldimethylsilyl) derivatives (**25** and **26**), steric hindrance between the 5'-*O*-acyl and the 3'-*O*-silyl groups seems to be responsible for the selectivity. By using **26**, it became possible to introduce a variety of carbon-functionalities with opposite 5'-stereochemistry to the reported ionic reactions of uridine 5'-aldehyde.

EXPERIMENTAL

Melting points were determined with a Yanagimoto micro melting point apparatus and are uncorrected. ^{1}H NMR spectra were measured at 23 °C (internal standard, Me_4Si) with either a JEOL JNM-GX 400 or a JEOL JNM-LA 500 spectrometer. Mass spectra (MS) were taken on either a JEOL SX-102A spectrometer in FAB mode (*m*-nitrobenzyl alcohol as a matrix) or a JEOL JMS-D 300 in EI mode. In the cases of selenium-containing compounds, ion peaks corresponding ^{80}Se are shown. High resolution mass spectrometry (HRMS) was performed in the FAB mode (*m*-nitrobenzyl alcohol as a matrix) with a JEOL HX-110 spectrometer. HRMS data of compounds containing chlorine atom are calculated based on ^{35}Cl. Column chromatography was carried out on silica gel (Silica Gel 60, Merck). Thin layer chromatography (TLC) was performed on silica gel (precoated silica gel plate F_{254}, Merck).

5'-Deoxy-2',3'-*O*-isopropylidene-5'-phenylselenouridine (10) To a dioxane (20 mL) solution of phenylselenide anion, prepared from $(PhSe)_2$ (3.42 g, 10.96 mmol) and $LiAlH_4$ (311 mg, 8.19 mmol),[4c] 2',3'-*O*-isopropylidene-5'-*O*-(*p*-toluenesulfonyl)uridine (3.0 g, 6.84 mmol) in dioxane (20 mL) was added and the mixture was stirred overnight at room temperature. The reaction mixture was quenched with AcOH, evaporated to dryness, and chromatographed on a silica gel column (2-5% EtOH in $CHCl_3$). This gave **10** (2.66 g, 92%) as a foam. ^{1}H NMR ($CDCl_3$) δ 1.33 and 1.53 (6H, each as s, isopropylidene-Me), 3.21 and 3.26 (2H, each as dd, J_{gem}= 11.9, $J_{4',5'}$= 3.7 and 4.0 Hz, H-5'), 4.25-4.35 (1H, m, H-4'), 4.78 (1H, dd, $J_{3',4'}$= 3.9, $J_{2',3'}$= 6.4 Hz, H-3'), 4.97 (1H, dd, $J_{1',2'}$= 2.4 Hz, H-2'), 5.60 (1H, d, H-1'), 5.67 (1H, dd, $J_{5,NH}$= 1.9, $J_{5,6}$= 7.8 Hz, H-5), 7.16-7.36 (4H, m, H-6 and Ph), 7.51-7.55 (2H, m, Ph), 8.92 (1H, br, NH); MS *m/z* 424 (M^+). Anal. Calcd for $C_{18}H_{20}N_2O_5Se$: C, 51.07; H, 4.76; N, 6.62. Found: C, 50.92; H, 4.74; N, 6.52.

5'-*O*-Acetyl-2',3'-*O*-isopropylidene-5'-phenylselenouridine (11) A mixture of **10** (635 mg, 1.5 mmol) and *m*-CPBA (310.6 mg, 1.2 mmol) in CH_2Cl_2 (20 mL) was stirred at room temperature for 0.5 h. The mixture was neutralized with Et_3N and then partitioned between aqueous $NaHCO_3$ and $CHCl_3$. Silica gel short column chromatography (7% EtOH in CH_2Cl_2) of the organic layer gave the corresponding selenoxide (496 mg, 75%) as a foam. A CH_2Cl_2 (5 mL) solution of the selenoxide (254 mg, 0.58 mmol) was treated with Ac_2O (274 μL, 2.9 mmol) at room temperature overnight. The reaction mixture was partitioned between aqueous $NaHCO_3$ and $CHCl_3$. Silica gel column chromatography (hexane/EtOAc = 2/1-1/1) of the organic layer

gave **11** (a mixture of two diastereomers, *ca.* 2:1, 248 mg, 89%) as a foam. FAB-MS *m/z* 483 (M^++H), 423 (M^+–OAc). Anal. Calcd for $C_{20}H_{22}N_2O_7Se$: C, 49.90; H, 4.61; N, 5.82. Found: C, 49.72; H, 4.74; N, 5.65. ^{1}H NMR ($CDCl_3$) data of the major isomer: δ 1.37 and 1.52 (6H, each as s, isopropylidene-Me), 2.03 (3H, s, Ac), 4.35 (1H, dd, $J_{2',3'}$= 3.3, $J_{3',4'}$= 8.6 Hz, H-3'), 4.96-5.02 (2H, m, H-2' and H-4'), 5.68 (1H, d, $J_{4',5'}$= 2.6 Hz, H-1'), 5.71 (1H, d, $J_{5,6}$= 8.1 Hz, H-5), 6.41 (1H, d, $J_{1',2'}$= 8.4 Hz, H-5'), 7.23-7.38 and 7.64-7.69 (6H, each as m, Ph and H-6), 8.59 (1H, br, NH). Selected ^{1}H NMR ($CDCl_3$) data of the minor isomer: δ 1.34 and 1.55 (6H, each as s, isopropylidene-Me), 2.07 (3H, s, Ac), 4.41 (1H, $J_{2',3'}$= 3.7, $J_{3',4'}$= 5.5 Hz, H-3'), 4.86 (1H, dd, $J_{4',5'}$= 6.6 Hz, H-4'), 5.59 (1H, d, $J_{1',2'}$= 1.5 Hz, H-1'), 6.41 (1H, d, H-5').

Homolysis of 5'-monoselenoacetals in refluxing benzene in the presence of Bu_3SnR and AIBN. Formation of (6*S*,5'*R*)-5'-*O*-acetyl-5,6-dihydro-2',3'-*O*-isopropylidene-6,5'-cyclouridine (12) and its 5'-epimer (13) from 11 as a typical example. To a refluxing solution of **11** (95.4 mg, 0.2 mmol) in benzene (4 mL), a mixture of Bu_3SnH (108 μL, 0.4 mmol) and AIBN (16.4 mg, 0.1 mmol) in benzene (4 mL) was added dropwise over 4 h using a syringe pump. The whole reaction mixture was applied to a silica gel short column. The column was washed with hexane/EtOAc = 20/1 and then a crude mixture containing **12** and **13** was eluted with EtOAc. Purification of this mixture by preparative TLC (hexane/EtOAc = 1/1) gave **12** (solid, 37 mg, 57%) and **13** (solid, 10.4 mg, 16%).

Physical data of **12**: mp 182-184 °C (acetone-hexane); ^{1}H NMR ($CDCl_3$) δ 1.33 and 1.49 (6H, each as s, isopropylidene-Me), 2.17 (3H, s, Ac), 2.53 and 2.74 (2H, each as dd, J_{gem}= 16.9, $J_{5,6}$= 5.1 and 11.0 Hz, H-5), 3.68-3.74 (1H, m, H-6), 4.52 (1H, d, $J_{4',5'}$= 2.2 Hz, H-4'), 4.69 and 4.70 (2H, each as d, *J*= 5.5 Hz, H-2' and H-3'), 4.75 (1H, dd, $J_{4',5'}$= 2.2, $J_{5',6}$= 3.5 Hz, H-5'), 6.12 (1H, s, H-1'), 8.19 (1H, br, NH); FAB-MS *m/z* 327 (M^++H). Anal. Calcd for $C_{14}H_{18}N_2O_7 \cdot 1/3H_2O$: C, 50.60; H, 5.66; N, 8.43. Found: C, 50.88; H, 5.74; N, 8.44.

Physical data of **13**: ^{1}H NMR ($CDCl_3$) δ 1.34 and 1.50 (6H, each as s, isopropylidene-Me), 2.13 (3H, s, Ac), 2.56 and 2.81 (2H, each as dd, J_{gem}= 16.9 Hz, $J_{5,6}$= 12.1 and 4.4 Hz, H-5), 3.39 (1H, m, H-6), 4.47 (1H, d, $J_{4',5'}$= 4.6 Hz, H-4'), 4.62 and 4.82 (2H, each as d, *J*= 5.9 Hz, H-2' and H-3'), 4.85 (1H, dd, $J_{4',5'}$= 4.6 Hz, $J_{5',6}$= 9.5 Hz, H-5'), 6.06 (1H, s, H-1'), 7.98 (1H, br, NH); FAB-MS *m/z* 327 (M^++H). Anal. Calcd for $C_{14}H_{18}N_2O_7 \cdot 1/4H_2O$: C, 50.83; H, 5.64; N, 8.47. Found: C, 50.93; H, 5.59; N, 8.25.

Homolysis of 5'-monoselenoacetals at room temperature under photo-initiated conditions in the presence of Bu_3SnR and $(Bu_3Sn)_2$. Formation of (5*R*,6*S*,5'*R*)-5'-*O*-acetyl-5-allyl-5,6-dihydro-2',3'-*O*-isopropylidene-6,5'-cyclouridine (15) and its 5'-epimer (16) as a typical example. In a 100 mL photochemical reactor fitted with a water-jacketed immersion well, containing a 400-W high-pressure mercury lamp surrounded by a Pyrex filter, a mixture of **11** (71.7 mg, 0.15 mmol), allyltributyltin (93 μL, 0.3 mmol), and $(Bu_3Sn)_2$ (39 μL, 0.075 mmol) in benzene (10 mL) was placed. The irradiation was continued for 3 h at room temperature. The whole reaction mixture was applied to a silica gel short column. The column was washed with hexane/EtOAc = 20/1 and then a crude mixture containing **15** and **16** was eluted with EtOAc. Purification of this mixture by preparative TLC (hexane/EtOAc = 1/1) gave **15** (solid, 42.9 mg, 78%) and **16** (syrup, 3.7 mg, 7.0%).

Physical data of **15**: 121-123 °C (acetone-ether); ^{1}H NMR ($CDCl_3$) δ 1.34 and 1.49 (6H, each as s, isopropylidene-Me), 2.11-2.23 (1H, m, H-5), 2.17 (3H, s, Ac), 2.69-2.82 (2H, m, $CH_2CH=CH_2$), 3.43 (1H, dd, *J*= 3.3 and 9.5 Hz, H-6), 4.53 (1H, d, *J*= 2.2 Hz, H-4'), 4.61 (1H, d, $J_{2',3'}$= 5.5 Hz, H-3'), 4.63 (1H, d, H-2'), 4.74 (1H, dd, $J_{4',5'}$= 2.2, $J_{5',6}$= 3.3 Hz, H-5'), 5.15-5.20 (2H, m, $CH_2CH=CH_2$), 5.65-5.76 (1H, m,

$CH_2CH{=}CH_2$), 6.15 (1H, s, H-1'), 7.90 (1H, br, NH); MS *m/z* 367 (M^++H). Anal. Calcd for $C_{17}H_{22}N_2O_7$: C, 55.73; H, 6.05; N, 7.65. Found: C, 55.60; H, 6.09; N, 7.48.

Physical data of **16**: ^{1}H NMR ($CDCl_3$) δ 1.34 and 1.50 (6H, each as s, isopropylidene-Me), 2.12 (3H, s, Ac), 2.28-2.44 (1H, m, H-5), 2.17 (3H, s, Ac), 2.60-2.71 (2H, m, $CH_2CH{=}CH_2$), 3.52 (1H, dd, *J*= 3.3 and 9.7 Hz, H-6), 4.49 (1H, d, $J_{4',5'}$= 5.1 Hz, H-4'), 4.58 and 4.83 (2H, each as d, $J_{2',3'}$= 5.7 Hz, H-2' and H-3'), 5.09-5.16 (2H, m, $CH_2CH{=}CH_2$), 5.23 (1H, dd, $J_{4',5'}$= 5.1, $J_{5',6}$= 9.7 Hz, H-5'), 5.64-5.82 (1H, m, $CH_2CH{=}CH_2$), 6.01 (1H, s, H-1'), 7.67 (1H, br, NH); MS *m/z* 367 (MH^+). HRMS (*m/z*) calcd for $C_{17}H_{23}N_2O_7$ 367.1506 [M^++H], found 367.1494.

3'-*O*-(*tert*-Butyldimethylsilyl)-5'-deoxy-5'-phenylselenothymidine (18) This compound was obtained as a syrup in 85% yield from 3'-*O*-(*tert*-butyldimethylsilyl)-5'-*O*-(*p*-toluenesulfonyl)thymidine by the procedure described for the preparation of **10**. ^{1}H NMR ($CDCl_3$) δ 0.03 and 0.05 (6H, each as s, SiMe), 0.87 (9H, s, SiBu-*t*), 1.83 (3H, d, $J_{6,Me}$= 1.1 Hz, 5-Me), 2.10-2.17 and 2.25-2.31 (2H, each as m, H-2'), 3.16 and 3.24 (2H, each as dd, *J*= 4.8 and 5.1, J_{gem}= 13.2 Hz, H-5'), 4.09-4.13 (1H, m, H-4'), 4.27-4.31 (1H, m, H-3'), 6.23 (1H, t, $J_{1',2'}$= 7.0 Hz, H-1'), 7.26-7.28 and 7.51-7.53 (5H, each as m, SePh), 7.33 (1H, d, H-6); FAB-MS *m/z* 497 (M^++H). Anal. Calcd for $C_{22}H_{32}N_2O_4SeSi$: C, 53.32; H, 6.51; N, 5.65. Found: C, 53.42; H, 6.62; N, 5.70.

5'-*O*-Acetyl-2'-*O*-(*tert*-butyldimethylsilyl)-5'-phenylselenothymidine (19) This compound (foam, a mixture of two diastereomers *ca.* 10:7) was obtained in 69% yield from **18** by the procedure described for the preparation of **11**. ^{1}H NMR ($CDCl_3$) δ 0.04, 0.06, 0.09, and 0.10 (6H, each as s, SiMe), 0.87 and 0.89 (9H, each as s, SiBu-*t*), 1.89 and 1.93 (3H, each as d, *J*= 1.5 and 1.1 Hz, 5-Me), 2.04 and 2.06 (3H, each as s, Ac), 1.97-2.35 (2H, m, H-2'), 4.15 and 4.24 (1H, each as dd, *J*= 2.6 and 3.9 Hz, *J*= 2.2 and 5.5 Hz, H-4'), 4.36-4.39 and 4.43-4.45 (1H, each as m, H-3'), 6.30 and 6.37 (1H, each as dd, *J*= 8.4 and 5.9 Hz, H-1'), 6.36 and 6.39 (1H, each as d, *J*= 4.0 and 5.5 Hz, H-5'), 7.29-7.69 (6H, m, SePh and H-6), 8.44 and 8.47 (1H, each as br, NH); FAB-MS *m/z* 555 (M^++H). Anal. Calcd for $C_{24}H_{34}N_2O_6SeSi{\cdot}1/2H_2O$: C, 51.19; H, 6.27; N, 4.98. Found: C, 51.36; H, 6.33; N, 4.76.

(5*R*,6*S*,5'*R*)-5'-*O*-Acetyl-5-allyl-3'-*O*-(*tert*-butyldimethylsilyl)-5,6-dihydro-6,5'-cyclothymidine (20), the (5*S*,6*S*,5'*S*)-isomer (21), the (5*R*,6*S*,5'*S*)-isomer (22), and 5'-*O*-acetyl-5'-*C*-allyl-3'-*O*-(*tert*-butyldimethylsilyl)thymidine (23) These compounds were obtained from **19** either by thermal or by photochemical reactions (both procedures are described above for the reactions of **11**). The following reagents and **19** (219.1 mg, 0.4 mmol in benzene 6 mL) were used in the thermal reaction: allyltributyltin (0.62 mL, 2.0 mmol) and AIBN (32.8 mg, 0.2 mmol) in benzene (2 mL). The reaction mixture was refluxed overnight. Silica gel column chromatography (hexane/EtOAc = 10/1-2/1) followed by preparative TLC (hexane/EtOAc = 2/1) of the mixture gave **20** (solid, 96.6 mg, 55%), **21** (syrup, 28.8 mg, 16%), **22** (syrup, 14.5 mg, 8%), and **23** (syrup, 16.5 mg, 9%).

Physical data of **20**: mp 140-143 °C (ether-hexane); ^{1}H NMR ($CDCl_3$) δ 0.10 and 0.11 (6H, each as s, SiMe), 0.88 (9H, s, SiBu-*t*), 1.08 (3H, s, 5-Me), 2.05 (3H, s, Ac), 2.17-2.22 (1H, m, H-2'), 2.32-2.40 (3H, m, $CH_2CH{=}CH_2$ and H-2'), 3.33 (1H, d, *J*= 2.2 Hz, H-6), 4.34-4.37 (2H, m, H-3' and H-4'), 4.49 (1H, dd, $J_{6,5'}$= 2.2, $J_{4',5'}$= 2.6 Hz, H-5'), 5.17 (1H, dd, *J*= 1.0 and 17.1 Hz, $CH_2CH{=}CH_2$), 5.28 (1H, dd, *J*= 1.0 and 10.3 Hz, $CH_2CH{=}CH_2$), 5.68-5.76 (1H, m, $CH_2CH{=}CH_2$), 6.47 (1H, d, $J_{1',2'}$= 7.0 Hz, H-1'), 7.44 (1H, br, NH); FAB-MS *m/z* 439 (M^++H). Anal. Calcd for $C_{21}H_{34}N_2O_6Si{\cdot}1/4H_2O$: C, 56.92; H, 7.93; N, 6.32. Found: C, 56.95; H, 7.89; N, 6.34.

Physical data of **21**: ^{1}H NMR ($CDCl_3$) δ 0.05 and 0.06 (6H, each as s, SiMe), 0.87 (9H, s, SiBu-*t*), 1.14 (3H, s, 5-Me), 2.10 (3H, s, Ac), 2.17-2.19 (1H, m, H-2'), 2.25-2.34 (2H, m, H-2' and $CH_2CH=CH_2$), 2.49-2.50 (1H, m, $CH_2CH=CH_2$), 3.46 (1H, d, $J_{6,5'}$= 8.8 Hz, H-6), 4.33 (1H, d, $J_{4',5'}$= 5.5 Hz, H-4'), 4.57 (1H, dd, $J_{2',3'}$= 3.3 and 7.3 Hz, H-3'), 5.07-5.11 (2H, m, $CH_2CH=CH_2$), 5.26 (1H, dd, $J_{4',5'}$= 5.5 Hz, H-5'), 5.66-5.67 (1H, m, $CH_2CH=CH_2$), 6.27 (1H, d, $J_{1',2'}$= 5.9 Hz, H-1'), 7.91 (1H, br, NH); FAB-MS *m/z* 439 (M^++H). Anal. Calcd for $C_{21}H_{34}N_2O_6Si$: C, 57.51; H, 7.81; N, 6.39. Found: C, 57.23; H, 8.06; N, 6.26.

Physical data of **22**: ^{1}H NMR ($CDCl_3$) δ 0.06 and 0.07 (6H, each as s, SiMe), 0.88 (9H, s, SiBu-*t*), 1.27 (3H, s, 5-Me), 2.12 (3H, s, Ac), 2.16-2.20 (1H, m, H-2'), 2.32 (1H, dd, J_{gem}= 14.7, $J_{2',3'}$= 7.3 Hz, H-2'), 1.94 and 2.85 (2H, each as m, $CH_2CH=CH_2$), 3.64 (1H, d, $J_{6,5'}$= 9.5 Hz, H-6), 4.30 (1H, d, $J_{4',5'}$= 5.1 Hz, H-4'), 4.54 (1H, dd, $J_{2',3'}$= 3.1 and 7.1 Hz, H-3'), 5.14-5.19 (3H, m, H-5' and $CH_2CH=CH_2$), 5.71-5.77 (1H, m, $CH_2CH=CH_2$), 6.32 (1H, d, $J_{1',2'}$= 5.9 Hz, H-1'), 7.91 (1H, br, NH); FAB-MS *m/z* 439 (M^++H). Anal. Calcd for $C_{21}H_{34}N_2O_6Si$: C, 57.51; H, 7.81; N, 6.39. Found: C, 57.58; H, 7.99; N, 6.09.

Physical data of **23** (a mixture of two diastereomers, *ca.* 10:4.3): FAB-MS m/z 439 (M^++H). Anal. Calcd for $C_{21}H_{34}N_2O_6Si$: C, 57.51; H, 7.81; N, 6.39. Found: C, 57.59; H, 8.06; N, 6.18. ^{1}H NMR data ($CDCl_3$) of the major isomer: δ 0.06 (6H, s, SiMe), 0.88 (9H, s, SiBu-t), 1.96 (3H, d, *J*= 1.2 Hz, 5-Me), 1.93-1.99 and 2.25-2.30 (2H, each as m, H-2'), 2.10 (3H, s, Ac), 2.46-2.49 (2H, m, $CH_2CH=CH_2$), 3.96 (1H, t, $J_{3',4'}$= $J_{4',5'}$= 3.2 Hz, H-4'), 4.18-4.21 (1H, m, H-5'), 5.09-5.19 (3H, m, H-3' and $CH_2CH=CH_2$), 5.72-5.81 (1H, m, $CH_2CH=CH_2$), 6.31 (1H, dd, $J_{1',2'}$= 3.1 and 6.9 Hz, H-1'), 7.51 (1H, d, H-6), 8.30 (1H, br, NH). ^{1}H NMR ($CDCl_3$) data of the minor isomer: δ 0.06 and 0.07 (6H, each as s, SiMe), 0.90 (9H, s, SiBu-*t*), 1.92 (3H, d, *J*= 1.2 Hz, 5-Me), 1.93-2.01 and 2.20-2.30 (2H, each as m, H-2'), 2.08 (3H, s, Ac), 2.37-2.40 and 2.46-2.50 (2H, each as m, $CH_2CH=CH_2$), 3.96 (1H, dd, *J*= 2.3 and 5.6 Hz, H-4'), 4.38-4.40 (1H, m, H-5'), 5.03-5.07 (1H, m, H-3'), 5.12-5.16 (2H, m, $CH_2CH=CH_2$), 5.72-5.81 (1H, m, $CH_2CH=CH_2$), 6.23 (1H, dd, $J_{1',2'}$= 5.5 and 8.5 Hz, H-1'), 7.07 (1H, d, H-6), 8.11 (1H, br, NH).

2',3',5'-Tri-*O*-acetyl-5'-phenylselenouridine (24) This compound (foam, a mixture of two diastereomers, *ca.* 10:9.2) was obtained from **10**: removal of the 2',3'-*O*-isopropylidene group (50% aqueous CF_3CO_2H) followed by acetylation (Ac_2O/pyridine) gave 2',3'-di-*O*-acetyl-5'-deoxy-5'-phenylselenouridine (foam, 91%), which was subjected to seleno-Pummerer reaction (73%) according to the procedure described for the preparation of **11**. MS *m/z* 526 (M^+), 369 (M^+–SePh). Anal. Calcd for $C_{21}H_{22}N_2O_9Se$: C, 49.90; H, 4.61; N, 5.82. Found: C, 49.72; H, 4.74; N, 5.65. ^{1}H NMR ($CDCl_3$) data of the major diastereomer: δ 2.08, 2.12, and 2.13 (9H, each as s, Ac), 4.52 (1H, dd, $J_{1',2'}$= 4.4, $J_{2',3'}$= 2.9 Hz, H-2'), 5.31-5.48 (2H, m, H-3' and H-4'), 5.79 (1H, dd, $J_{5,NH}$= 1.5, $J_{5,6}$= 8.1 Hz, H-5), 6.15 (1H, d, $J_{4',5'}$= 5.5 Hz, H-5'), 6.44 (1H, d, H-1'), 7.27-7.70 (6H, m, H-6 and Ph), 8.40 (1H, br, NH). Selected ^{1}H NMR ($CDCl_3$) data of the minor diastereomer: δ 2.07, 2.09, and 2.11 (9H, each as s, Ac), 4.41 (1H, dd, $J_{1',2'}$= 3.3, $J_{2',3'}$= 2.9 Hz, H-2'), 5.80 (1H, dd, H-5), 6.11 (1H, d, $J_{4',5'}$= 6.6 Hz, H-5'), 6.41 (1H, d, H-1').

5'-*O*-Acetyl-2',3'-bis-*O*-(*tert*-butyldimethylsilyl)-5'-phenylselenouridine (25) For the preparation and physical data of this compound, see reference 6.

5'-*O*-Benzoyl-2',3'-bis-*O*-(*tert*-butyldimethylsilyl)-5'-phenylselenouridine (26) This compound (foam, a mixture of two diastereomers, *ca.* 10:8.1) was obtained in 93% yield from 2',3'-bis-*O*-(*tert*-butyldimethylsilyl)-5'-deoxy-5'-phenylselenouridine[6] by the procedure described for the preparation of **11**. FAB-MS *m/z* 675 (M^+–Bu-*t*), 575 (M^+–SePh). Anal. Calcd for $C_{34}H_{48}N_2O_7SeSi_2 \cdot 1/2H_2O$: C, 55.12; H,

6.67; N, 3.78. Found: C, 55.49; H, 6.95; N, 3.40. Selected ^{1}H NMR ($CDCl_3$) data of the major diastereomer: δ −0.09, −0.05, 0.01, and 0.05 (12H, each as s, SiMe), 0.83 and 0.89 (18H, each as s, SiBu-*t*), 5.72 (1H, dd, $J_{5,NH}$= 1.8, $J_{5,6}$= 8.1 Hz, H-5), 5.92 (1H, d, J= 4.8 Hz, H-5'), 6.69 (1H, d, $J_{1',2'}$= 4.0 Hz, H-1'), 7.27-8.01 (11H, m, H-6 and Ph), 8.87 (1H, br, NH). Selected ^{1}H NMR ($CDCl_3$) data of the minor diastereomer: δ -0.05, 0.04, 0.09, and 0.11 (12H, each as s, SiMe), 0.85 and 0.90 (18H, each as s, SiBu-*t*), 5.41 (1H, dd, $J_{5,NH}$= 2.2, $J_{5,6}$= 8.1 Hz, H-5), 5.97 (1H, d, J= 7.0 Hz, H-5'), 6.67 (1H, d, $J_{1',2'}$= 4.8 Hz, H-1'), 8.71 (1H, br, NH).

(5'*S*)-2',3',5'-Tri-*O*-acetyl-5'-*C*-allyluridine (27) and its 5'-epimer (28) These compounds were obtained as an inseperable mixture. The following physical data of **27** were obtained by conversion of **29** (desilylation with Bu_4NF/THF followed by acetylation): mp 172-174 °C (acetone-hexane); ^{1}H NMR ($CDCl_3$) δ 2.09, 2.13, and 2.16 (9H, each as s, Ac), 2.42-2.50 (2H, m, C*H*$_2$CH=CH$_2$), 4.26 (1H, t, J= 3.1 Hz, H-4'), 5.11-5.21 (4H, m, CH$_2$CH=C*H*$_2$, H-3', and H-5'), 5.27 (1H, t, $J_{1',2'}$= $J_{2',3'}$= 6.2 Hz, H-2'), 5.68-5.75 (1H, m, CH$_2$CH=C*H*$_2$), 5.84 (1H, dd, $J_{5,NH}$= 2.2, $J_{5,6}$= 8.1 Hz, H-5), 6.20 (1H, d, H-1'), 7.60 (1H, d, H-6), 9.52 (1H, br, NH); FAB-MS *m/z* 411 (M$^+$+H). Anal. Calcd for $C_{18}H_{22}N_2O_9$: C, 52.68; H, 5.40; N, 6.83. Found: C, 52.65; H, 5.47; N, 6.69.

Selected ^{1}H NMR ($CDCl_3$) data of **28**: δ 4.18 (1H, t, $J_{3',4'}$= $J_{4',5'}$= 4.0 Hz, H-4'), 5.50 (1H, dd, $J_{1',2'}$= 6.2, $J_{2',3'}$= 4.0 Hz, H-2'), 5.78 (1H, d, $J_{5,6}$= 8.1 Hz, H-5), 5.98 (1H, d, H-1'), 7.18 (1H, d, H-6).

(5'*S*)-5'-*O*-Acetyl-5'-*C*-allyl-2',3'-bis-*O*-(*tert*-butyldimethylsilyl)uridine (29) and its 5'-epimer (30) Compounds **29** (syrup) and **30** (foam) were isolated from the reaction mixture by silica gel column chromatography (hexane/EtOAc = 10/1-2/1) followed by preparative TLC (hexane/EtOAc = 3/1).

Physical data of **29**: ^{1}H NMR ($CDCl_3$) δ 0.01, 0.05, 0.08, and 0.13 (12H, each as s, SiMe), 0.88 and 0.89 (18H, each as s, SiBu-*t*), 2.09 (3H, s, Ac), 2.50-2.54 (2H, m, C*H*$_2$CH=CH$_2$), 3.83 (1H, dd, $J_{3',4'}$= 5.7, $J_{4',5'}$= 4.0 Hz, H-4'), 4.06 (1H, dd, $J_{1',2'}$= 3.3, $J_{2',3'}$= 2.2 Hz, H-2'), 4.16 (1H, dd, H-3'), 4.99-5.03 (1H, m, H-5'), 5.13-5.19 (2H, m, CH$_2$CH=C*H*$_2$), 5.74 (1H, dd, $J_{5,NH}$= 2.2, $J_{5,6}$= 8.4 Hz, H-5), 5.71-5.78 (1H, m, CH$_2$C*H*=CH$_2$), 5.79 (1H, d, H-1'), 7.88 (1H, d, H-6), 8.67 (1H, br, NH); FAB-MS *m/z* 555 (M$^+$+H). Anal. Calcd for $C_{26}H_{46}N_2O_7Si_2$: C, 56.28; H, 8.36; N, 5.05. Found: C, 56.49; H, 8.55; N, 4.70.

Physical data of **30**: ^{1}H NMR ($CDCl_3$) δ −0.01, 0.04, 0.08, and 0.09 (12H, each as s, SiMe), 0.85 and 0.92 (18H, each as s, SiBu-*t*), 2.10 (3H, s, Ac), 2.28-2.52 (2H, m, C*H*$_2$CH=CH$_2$), 3.97 (1H, dd, $J_{3',4'}$= 2.2, $J_{4',5'}$= 7.0 Hz, H-4'), 4.02 (1H, dd, $J_{2',3'}$= 4.4 Hz, H-3'), 4.42 (1H, dd, $J_{1',2'}$= 6.6 Hz, H-2'), 5.09-5.16 (3H, m, H-5' and CH$_2$CH=C*H*$_2$), 5.65 (1H, d, H-1'), 5.73 (1H, dd, $J_{5,NH}$= 2.2, $J_{5,6}$= 8.1 Hz, H-5), 5.69-5.99 (1H, m, CH$_2$C*H*=CH$_2$), 7.21 (1H, d, H-6), 8.84 (1H, br, NH); FAB-MS *m/z* 555 (M$^+$+H). Anal. Calcd for $C_{26}H_{46}N_2O_7Si_2$: C, 56.28; H, 8.36; N, 5.05. Found: C, 56.68; H, 8.68; N, 4.78.

(5'*S*)-5'-*C*-allyl-5'-*O*-benzoyl-2',3'-bis-*O*-(*tert*-butyldimethylsilyl)uridine (31) and its 5'-epimer (32) These compounds were obtained as an inseparable mixture (foam). FAB-MS *m/z* 617 (M$^+$+H), 559 (M$^+$−Bu-*t*). Anal. Calcd for $C_{31}H_{48}N_2O_7Si_2$: C, 60.36; H, 7.84; N, 4.54. Found: C, 60.49; H, 8.15; N, 4.38.

^{1}H NMR ($CDCl_3$) data of **31**: δ −0.04, −0.02, −0.01, and 0.04 (12H, each as s, SiMe), 0.83 and 0.90 (18H, each as s, SiBu-*t*), 2.61-2.70 (2H, m, C*H*$_2$CH=CH$_2$), 3.94-3.99 (2H, m, H-2' and H-3'), 4.26 (1H, dd, $J_{3',4'}$= 5.1, $J_{4',5'}$= 2.2 Hz, H-4'), 5.13 and 5.37 (2H, each as dd, J_{gem}= 1.5, J= 10.1 and 17.0 Hz, CH$_2$CH=C*H*$_2$), 5.37 (1H, ddd, J= 2.2 and 7.1 Hz, H-5'), 5.69 (1H, d, $J_{5,6}$= 8.4 Hz, H-5), 5.80-5.86 (1H,

m, $CH_2CH{=}CH_2$), 5.87 (1H, d, $J_{1',2'}$= 3.7 Hz, H-1'), 7.31-7.50, 7.60-7.64, and 7.95-7.97 (5H, each as m, COPh), 7.89 (1H, d, H-6), 9.40 (1H, br, NH).

Selected ^{1}H NMR ($CDCl_3$) data of **32**: δ 0.85 and 0.90 (18H, each as s, SiBu-*t*), 2.46-2.54 (2H, m, $CH_2CH{=}CH_2$), 4.36 (1H, dd, *J*= 4.0 and 5.9 Hz, H-4'), 5.45-5.50 (1H, m, H-5'), 5.66 (1H, d, $J_{1',2'}$= 5.5 Hz, H-1'), 7.19 (1H, d, $J_{5,6}$= 8.1 Hz, H-6).

Preparation of 2',3'-bis-*O*-(*tert*-butyldimethylsilyl)uridine 5'-aldehyde (33) and its reaction with allyltributyltin under thermal conditions. A mixture of CrO_3 (400 mg, 4.0 mmol), DMF (1 mL), pyridine (0.65 mL, 8.6 mmol) in CH_2Cl_2 (4 mL) was stirred at room temeprature for 20 min and then treated with Ac_2O (0.38 mL, 4.0 mmol). To this, a solution of 2',3'-bis-*O*-(*tert*-butyldimethylsilyl)uridine (236.4 mg, 0.5 mmol) in CH_2Cl_2 (3 mL)-DMF (0.5 mL) was added dropwise. After being stirred for 15 min at room temperature, the reaction mixture containing **33** was quenched with EtOH (0.5 mL), poured into EtOAc, and filtered through a silica gel (20 g) short column wet with EtOAc. The filtrate was evaporated to dryness and dissolved in benzene (7 mL) containing allyltributyltin (0.78 mL, 2.5 mmol). While refluxing this solution, AIBN (82.1 mg, 0.5 mmol) in benzene (2 mL) was added dropwise over 1 h using a syringe pump. The whole reaction mixture was refluxed overnight and then purified by silica gel column chromatography (hexane/EtOAc = 2/1) to give a-mixture of **34** and **35** (*ca.* 3.6:1, syrup, 98.5 mg, 38%). FAB-MS *m/z* 513 (M^++H). Anal. Calcd for $C_{24}H_{44}N_2O_6Si_2$: C, 56.21; H, 8.65; N, 5.46. Found: C, 56.46; H, 8.82; N, 5.41.

^{1}H NMR ($CDCl_3$) data of **34**: δ 0.04, 0.05, 0.06, and 0.07 (12H, each as s, SiMe), 0.87 and 0.89 (18H, each as s, SiBu-*t*), 2.30-2.40 (2H, m, $CH_2CH{=}CH_2$), 3.71-3.72 (1H, m, H-5'), 3.96 (1H, dd, $J_{3',4'}$= 3.6, $J_{4',5'}$= 2.1 Hz, H-4'), 4.13 (1H, dd, $J_{2',3'}$= 4.4 Hz, H-3'), 4.48 (1H, dd, $J_{1',2'}$= 5.1 Hz, H-2'), 5.15-5.19 (2H, m, $CH_2CH{=}CH_2$), 5.53 (1H, d, H-1'), 5.73 (1H, dd, $J_{5,NH}$= 2.2, $J_{5,6}$= 8.1 Hz, H-5), 5.77-5.87 (1H, m, $CH_2CH{=}CH_2$), 7.76 (1H, d, H-6), 9.48 (1H, br, NH).

Selected ^{1}H NMR ($CDCl_3$) data of **35**: δ –0.03, –0.01, 0.10, and 0.11 (12H, each as s, SiMe), 0.85 and 0.91 (18H, each as s, SiBu-*t*), 2.15-2.26 (1H, m, $CH_2CH{=}CH_2$), 3.85-3.91 (1H, m, H-5'), 3.94 (1H, m, H-4'), 4.17-4.19 (1H, m, H-3'), 4.64 (1H, dd, $J_{1',2'}$= 7.0, $J_{2',3'}$= 4.4 Hz, H-2'), 7.56 (1H, d, $J_{5,6}$= 8.1 Hz, H-6), 8.73 (1H, br, NH).

(5'*S*)-5'-*O*-Benzoyl-2',3'-bis-*O*-(*tert*-butyldimethylsilyl)-5'-*C*-(2-choloroallyl)uridine (36) and its 5'-epimer (37) The following reagents and **26** (145.5 mg, 0.20 mmol) were used for the preparation of these compounds: $CH_2{=}C(Cl)CH_2Cl$ (92.2 μL, 1.0 mmol), $(Bu_3Sn)_2$ (163 μL, 0.3 mmol), and benzene (15 mL). Silica gel column chromatography (hexane/EtOAc = 20/1 and then EtOAc) followed by preparative TLC (hexane/EtOAc = 3/1) of the reaction mixture gave **36** (syrup, 73.3 mg, 56%) and **37** (syrup, 12.3 mg, 9%).

Physical data of **36**: ^{1}H NMR ($CDCl_3$) δ –0.08, –0.07, and 0.03 (12H, each as s, SiMe), 0.81 and 0.91 (18H, each as s, SiBu-*t*), 2.86 and 2.96 (2H, each as dd, J_{gem}= 14.3, *J*= 6.6 and 7.7 Hz, $CH_2C(Cl){=}CH_2$), 3.94 (1H, t, *J*= 4.4 Hz, H-3'), 3.99 (1H, t, *J*= 4.4 Hz, H-2'), 4.26 (1H, dd, $J_{3',4'}$= 4.4, $J_{4',5'}$= 2.2 Hz, H-4'), 5.29 and 5.32 (2H, each as d, J_{gem}= 1.5 Hz, $CH_2C(Cl){=}CH_2$), 5.67 (1H, d, $J_{5,6}$= 8.1 Hz, H-5), 5.69-5.73 (1H, m, H-5'), 5.90 (1H, d, $J_{1',2'}$= 4.4 Hz, H-1'), 7.47-7.51, 7.60-7.65, and 7.96-7.99 (5H, each as m, COPh), 7.81 (1H, d, H-6), 9.42 (1H, br, NH); FAB-MS *m/z* 635 and 651 (M^++H), 595 and 593 (M^+–Bu-*t*). Anal. Calcd for $C_{31}H_{47}ClN_2O_7Si_2 \cdot 1/2EtOAc$: C, 57.00; H, 7.39; N, 4.02. Found: C, 57.23; H, 7.69; N, 3.82.

Physical data of **37**: ^{1}H NMR ($CDCl_3$) δ 0.02, 0.04, and 0.06 (12H, each as s, SiMe), 0.86 and 0.89 (18H, each as s, SiBu-*t*), 2.78 and 2.90 (2H, each as dd, J_{gem}= 15.0, *J*= 8.8 and 3.7 Hz, $CH_2C(Cl){=}CH_2$),

4.12-4.17 (2H, m, H-2' and H-3'), 4.45 (1H, dd, J= 4.0 and 6.0 Hz, H-4'), 5.26 (2H, s, $CH_2C(Cl)=CH_2$), 5.51 (1H, d, $J_{5,6}$= 8.1 Hz, H-5), 5.66-5.71 (1H, m, H-5'), 5.75 (1H, d, $J_{1',2'}$= 5.9 Hz, H-1'), 7.22 (1H, d, H-6), 7.45-7.49, 7.59-7.63, and 8.03-8.05 (5H, each as m, COPh), 8.59 (1H, br, NH); FAB-MS *m/z* 635 and 651 (M^++H), 595 and 593 (M^+–Bu-*t*). HRMS (*m/z*) calcd for $C_{31}H_{48}ClN_2O_7Si_2$ 651.2689 [MH^+], found 651.2682.

(5'*S*)-5'-*O*-Benzoyl-2',3'-bis-*O*-(*tert*-butyldimethylsilyl)-5'-*C*-(2-methylallyl)uridine (38) and its 5'-epimer (39) The following reagents and **26** (98.3 mg, 0.13 mmol) were used for the preparation of these compounds: $CH_2=C(Me)CH_2Cl$ (64 μL, 0.65 mmol), $(Bu_3Sn)_2$ (106 μL, 0.20 mmol), and benzene (15 mL). Silica gel column chromatography (hexane/EtOAc = 20/1 and then EtOAc) followed by preparative TLC (hexane/EtOAc = 4/1) of the reaction mixture gave **38** (syrup, 45.3 mg, 55%) and **39** (syrup, 7.7 mg, 9%).

Physical data of **38**: ^{1}H NMR ($CDCl_3$) δ –0.05, –0.03, 0.01, and 0.04 (12H, each as s, SiMe), 0.83 and 0.91 (18H, each as s, SiBu-*t*), 1.83 (3H, s, $CH_2C(Me)=CH_2$), 2.53 and 2.64 (2H, each as dd, J_{gem}= 13.7, J= 6.6 and 7.7 Hz, $CH_2C(Me)=CH_2$), 3.92-3.96 (2H, m, H-2' and H-3'), 4.24 (1H, dd, $J_{3',4'}$= 5.0, $J_{4',5'}$= 1.8 Hz, H-4'), 4.86 (2H, s, $CH_2C(Me)=CH_2$), 5.49-5.53 (1H, m, H-5'), 5.65 (1H, d, $J_{5,6}$= 8.1 Hz, H-5), 5.88 (1H, d, $J_{1',2'}$= 3.7 Hz, H-1'), 7.46-7.53, 7.59-7.64, and 7.95-7.97 (5H, each as m, COPh), 7.91 (1H, d, H-6); FAB-MS *m/z* 631 (M^++H), 573 (M^+–Bu-*t*). Anal. Calcd for $C_{32}H_{50}N_2O_7Si_2 \cdot 1/4H_2O$: C, 60.49; H, 8.01; N, 4.41. Found: C, 60.23; H, 8.08; N, 4.25.

Physical data of **39**: ^{1}H NMR ($CDCl_3$) δ –0.02, –0.05, 0.06, and 0.08 (12H, each as s, SiMe), 0.86 and 0.90 (18H, each as s, SiBu-*t*), 1.82 (3H, s, $CH_2C(Me)=CH_2$), 2.44 and 2.53 (2H, each as dd, J_{gem}= 14.1, J= 8.8 and 4.0 Hz, $CH_2C(Me)=CH_2$), 4.15 (1H, dd, $J_{3',4'}$= 5.3, $J_{4',5'}$= 3.1 Hz, H-4'), 4.19 (1H, dd, $J_{2',3'}$= 4.4, $J_{3',4'}$= 5.3 Hz, H-3'), 4.35 (1H, dd, $J_{1',2'}$= 5.9 Hz, H-2'), 4.79-4.81 (2H, m, $CH_2C(Me)=CH_2$), 5.37 (1H, d, $J_{5,6}$= 8.1 Hz, H-5), 5.58-5.65 (1H, m, H-5'), 5.74 (1H, d, H-1'), 7.16 (1H, d, H-6), 7.45-7.51, 7.59-7.63, and 8.01-8.03 (5H, each as m, COPh), 8.32 (1H, br, NH); FAB-MS *m/z* 631 (M^++H), 573 (M^+–Bu-*t*). HRMS (*m/z*) calcd for $C_{32}H_{51}N_2O_7Si_2$ 631.3235 [MH^+], found 631.3225.

(5'*S*)-5'-*O*-Benzoyl-2',3'-bis-*O*-(*tert*-butyldimethylsilyl)-5'-*C*-(3-methylallyl)uridine (40) and its 5'-epimer (41) The following reagents and **26** (103.6 mg, 0.14 mmol) were used for the preparation of these compounds: $CH_2=CHCH(Cl)Me$ (70 μL, 0.7 mmol), $(Bu_3Sn)_2$ (100 μL, 0.21 mmol), and benzene (15 mL). Silica gel column chromatography (hexane/EtOAc = 20/1-1/1) followed by preparative TLC (hexane/EtOAc = 4/1) of the reaction mixture gave a mixture of **40** and **41** (syrup, 62.6 mg, 56%). ^{1}H NMR spectrum of this mixture showed the presence of two geometrical isomers of **40**, while **41** consisted of a single isomer. FAB-MS *m/z* 631 (M^++H), 573 (M^+–Bu-*t*). Anal. Calcd for $C_{32}H_{50}N_2O_7Si_2$: C, 59.11; H, 7.52; N, 6.67. Found: C, 59.00; H, 7.69; N, 6.50.

^{1}H NMR ($CDCl_3$) data of the major geometrical isomer of **40**: δ –0.06, –0.04, and 0.04 (12H, each as s, SiMe), 0.83 and 0.90 (18H, each as s, SiBu-*t*), 1.63 (3H, d, J= 5.5 Hz, $CH_2CH=CHMe$), 2.51-2.58 (2H, m, $CH_2CH=CHMe$), 3.95-3.99 (2H, m, H-2' and H-3'), 4.25-4.26 (1H, m, H-4'), 5.28-5.32 (1H, m, H-5'), 5.38-5.47 and 5.58-5.65 (2H, each as m, $CH_2CH=CHMe$), 5.68 (1H, d, $J_{5,6}$= 8.1 Hz, H-5), 5.88 (1H, d, $J_{1',2'}$= 3.3 Hz, H-1'), 7.46-7.50, 7.60-7.64, and 7.95-7.97 (5H, m, COPh), 7.88 (1H, d, H-6), 9.16 (1H, br, NH).

(5'*S*)-5'-*O*-Benzoyl-2',3'-bis-*O*-(*tert*-butyldimethylsilyl)-5'-*C*-[(2-cyano-2-methyl)-vinyl]uridine (42) and its 5'-epimer (43) The following reagents and **26** (198.3 mg, 0.13 mmol) were

used for the preparation of these compounds: BrCH=C(CN)Me (63 μL, 0.65 mmol), $(Bu_3Sn)_2$ (106 μL, 0.20 mmol), and benzene (20 mL). Silica gel column chromatography (hexane/EtOAc = 20/1 and then EtOAc) followed by preparative TLC (hexane/EtOAc = 4/1) of the reaction mixture gave the major geometrical isomer of **42** (foam, 30 mg, 36%), the minor isomer of **42** (syrup, 8.1 mg, 10%), and **43** (syrup, 7.4 mg, 9%).

Physical data of the major geometrical isomer of **42**: ^{1}H NMR ($CDCl_3$) δ 0.04, 0.05, and 0.07 (12H, each as s, SiMe), 0.88 and 0.90 (18H, each as s, SiBu-*t*), 2.06 (3H, d, *J*= 1.5 Hz, CH=C(CN)*Me*), 4.11 (1H, dd, $J_{2',3'}$= 4.0, $J_{3',4'}$= 5.2 Hz, H-3'), 4.17 (1H, t, $J_{1',2'}$= $J_{2',3'}$= 4.0 Hz, H-2'), 4.28 (1H, dd, $J_{4',5'}$= 3.3 Hz, H-4'), 5.76 (1H, dd, $J_{5,NH}$= 2.2, $J_{5,6}$= 8.1 Hz, H-5), 5.82 (1H, d, H-1'), 5.96 (1H, dd, $J_{5',6'}$= 8.3 Hz, H-5'), 6.30 (1H, dq, *J*= 1.5 and 8.3 Hz, CH_2CH=C(CN)Me), 7.44-7.51, 7.57-7.65, and 7.98-7.99 (5H, each as m, COPh), 7.90 (1H, d, H-6); FAB-MS *m/z* 642 (M^++H), 584 (M^+-Bu-*t*). Anal. Calcd for $C_{32}H_{47}N_3O_7Si_2$·1/5EtOAc: C, 59.73; H, 7.43; N, 6.37. Found: C, 59.80; H, 7.59; N, 6.10.

Physical data of the minor geometrical isomer of **42**: ^{1}H NMR ($CDCl_3$) δ 0.05, 0.06, and 0.12 (12H, each as s, SiMe), 0.89 and 0.90 (18H, each as s, SiBu-*t*), 2.13 (3H, d, *J*= 1.5 Hz, CH=C(CN)*Me*), 4.04 (1H, dd, *J*= 4.4 and 6.6 Hz, H-3'), 4.17-4.19 (2H, m, H-2' and H-4'), 5.70 (1H, d, $J_{5,6}$= 8.1 Hz, H-5), 5.72 (1H, d, $J_{1',2'}$= 2.6 Hz, H-1'), 5.86 (1H, dd, *J*= 2.6 and 9.3 Hz, H-5'), 6.47 (1H, dd, *J*= 1.5 and 9.3 Hz, C*H*=C(CN)Me), 7.48-7.52, 7.63-7.68, and 7.93-7.95 (5H, each as m, COPh), 7.85 (1H, d, H-6), 8.49 (1H, br, NH); FAB-MS *m/z* 642 (M^++H), 584 (M^+-Bu-*t*). Anal. Calcd for $C_{32}H_{47}N_3O_7Si_2$: C, 59.27; H, 7.42; N, 6.48. Found: C, 59.64; H, 7.80; N, 6.08.

Physical data of **43** (obtained as a single isomer): ^{1}H NMR ($CDCl_3$) δ 0.02, 0.07, and 0.08 (12H, each as s, SiMe), 0.87 and 0.91 (18H, each as s, SiBu-*t*), 2.04 (3H, d, *J*= 1.5 Hz, CH=C(CN)*Me*), 4.21-4.25 (2H, m, H-3' and H-4'), 4.33 (1H, dd, $J_{1',2'}$= 6.6, $J_{2',3'}$= 4.4 Hz, H-2'), 5.48 (1H, d, $J_{5,6}$= 8.1 Hz, H-5), 5.89 (1H, d, H-1'), 5.95 (1H, dd, *J*= 5.9 and 8.0 Hz, H-5'), 6.21 (1H, dd, *J*= 1.5 and 8.0 Hz, C*H*=C(CN)Me), 7.30 (1H, d, H-6), 7.47-7.52, 7.61-7.66, and 8.05-8.07 (5H, each as m, COPh), 8.47 (1H, br, NH); FAB-MS *m/z* 642 (M^++H), 584 (M^+-Bu-*t*). HRMS (*m/z*) calcd for $C_{32}H_{48}N_3O_7Si_2$ 642.3031 [MH^+], found 642.3008.

(5'*S*)-5'-*O*-Benzoyl-2',3'-bis-*O*-(*tert*-butyldimethylsilyl)-5'-*C*-(2-cyanoethyl)uridine (44) and its 5'-epimer (45) The following reagents and **26** (82.9 mg, 0.11 mmol) were used for the preparation of these compounds: acrylonitrile (72.4 μL, 1.1 mmol), $(Bu_3Sn)_2$ (28 μL, 0.055 mmol), Bu_3SnH (30 μL, 0.11 mmol), and benzene (15 mL). Silica gel column chromatography (hexane/EtOAc = 20/1-1/1) followed by preparative TLC (hexane/EtOAc = 4/1) of the reaction mixture gave **44** (solid, 29 mg, 42%), **45** (syrup, 4.1 mg, 6%), and 5'-*O*-benzoyl-2',3'-bis-*O*-(*tert*-butyldimethylsilyl)uridine (syrup, 17.7 mg, 28%).

Physical data of **44**: mp 109-110 °C (ether); ^{1}H NMR ($CDCl_3$) δ –0.03, –0.01, and 0.04 (12H, each as s, SiMe), 0.84 and 0.90 (18H, each as s, SiBu-*t*), 2.24-2.37 (2H, m, CH_2CH_2CN), 2.52-2.60 (2H, m, CH_2CH_2CN), 3.94 (1H, m, H-3'), 4.22 (1H, m, H-2'), 4.22 (1H, dd, *J*= 2.0 and 5.7 Hz, H-4'), 5.47 (1H, m, H-5'), 5.60 (1H, d, $J_{5,6}$= 8.1 Hz, H-5), 5.81 (1H, d, $J_{1',2'}$= 3.3 Hz, H-1'), 7.49-7.53, 7.63-7.66, and 7.99-8.02 (5H, each as m, COPh), 7.80 (1H, d, H-6), 9.17 (1H, br, NH); FAB-MS *m/z* 630 (M^++H), 572 (M^+–Bu-*t*). Anal. Calcd for $C_{31}H_{47}N_3O_7Si_2$: C, 60.92; H, 7.99; N, 4.44. Found: C, 61.05; H, 8.22; N, 4.25.

Physical data of **45**: ^{1}H NMR ($CDCl_3$) δ –0.01 and 0.05 (12H, each as s, SiMe), 0.85 and 0.87 (18H, each as s, SiBu-*t*), 2.06-2.14 and 2.26-2.33 (2H, each as m, CH_2CH_2CN), 2.45-2.54 (2H, m, CH_2CH_2CN), 4.00-4.03 (1H, m, H-3'), 4.11 (1H, m, H-2'), 4.74 (1H, dd, *J*= 4.0 and 6.8 Hz, H-4'), 5.49-5.58 (2H, m, H-5' and H-5), 5.82 (1H, d, $J_{1',2'}$= 3.7 Hz, H-1'), 7.15 (1H, d, $J_{5,6}$= 8.1 Hz, H-6), 7.46-7.51, 7.60-7.65,

and 8.00-8.07 (5H, each as m, COPh), 8.70 (1H, br, NH); FAB-MS *m/z* 630 (M^++H), 572 (M^+–Bu-*t*). Anal. Calcd for $C_{31}H_{47}N_3O_7Si_2$: C, 59.11; H, 7.52; N, 6.67. Found: C, 59.03; H, 7.83; N, 6.62.

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REFERENCES AND NOTES

1) Krief, A.; Hobe, M.; Badaoui, E.; Bousbaa, J.; Dumont, W.; Nazih, A. *Synlett* **1993**, 707-709 and references cited therein.
2) For a review: De Lucchi, O.; Miotti, U.; Modena, G. Org. React. (N. Y.) **1991**, *40*, 157-405.
3) a) Fukuyama, T.; Robins, B. D.; Sachleben, R. A. *Tetrahedron Lett.* **1981**, *22*, 4155-4158. b) Marshall, J. A.; Royce, R. D., Jr. *J. Org. Chem.* **1982**, *47*, 693-698. c) Schreiber, S. L.; Santini, C. *J. Am. Chem. Soc.* **1984**, *106*, 4038-4039.
4) a) Haraguchi, K.; Tanaka, H.; Hayakawa, H.; Miyasaka, T. *Chem. Lett.* **1988**, 931-934. b) Haraguchi, K.; Tanaka, H.; Miyasaka, T. *Synthesis* **1989**, 434-436. c) Haraguchi, K.; Tanaka, H.; Maeda, H.; Itoh, Y.; Saito, S.; Miyasaka, T. *J. Org. Chem.* **1991**, *56*, 5401-5408.
5) Kondo, N.; Fueno, H.; Fujimoto, H.; Makino, M.; Nakaoka, H.; Aoki, I.; Uemura, S. *J. Org. Chem.* **1994**, *59*, 5254-5263.
6) Haraguchi, K.; Saito, S.; Tanaka, H.; Miyasaka, T. *Nucleosides Nucleotides* **1992**, *11*, 483-493.
7) Part of this study has been published as a communication: Haraguchi, K.; Tanaka, H.; Saito, S.; Yamaguchi, K.; Miyasaka, T. *Tetrahedron Lett.* **1994**, *35*, 9721-9724.
8) Hanessian, S.; Kloss, J.; Sugawara, T. *J. Am. Chem. Soc.* **1986**, *108*, 2758-2759.
9) Rabi, J. A.; Fox, J. J. *J. Org. Chem.* **1972**, *37*, 3898-3901.
10) Sugawara, T.; Otter, B. A.; Ueda, T. *Tetrahedron Lett.* **1988**, *29*, 75-78.
11) For ease of comparison with ordinary nucleosides, the trivial 6,5'-cyclo designation with conventional nucleoside ring numbering is used in this article.
12) The atomic coordinates for **12**, **15**, **20**, and **27** are available on request from the Cambridge Crystallographic Data Centre, University of Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK.
13) Another evidence of the depicted stereochemistry of **13** came from an NOE enhancement observed between H-6 and H-2' (5.9%).
14) The depicted stereochemistry of **16** was assumed by comparing its coupling constants with those of **15**: **15**, $J_{4',5'}$= 2.2, $J_{5',6}$= 3.3, $J_{5,6}$= 3.3 Hz; **16**, $J_{4',5'}$= 5.1, $J_{5',6}$= 9.7, $J_{5,6}$= 3.3 Hz.
15) For a review concerning the gauche effect: Wolfe, S. *Acc. Chem. Res.* **1972**, *5*, 102-111.
16) Inamoto, N.; Masuda, S. *Chem. Lett.* **1982**, 1003-1006.
17) Santi, D. V.; Brewer, C. F. *J. Am. Chem. Soc.* **1968**, *90*, 6236-6238.
18) The present strategy has recently been applied to the synthesis of 5'-*C*-deuterium-labelled 2'-deoxyribonucleosides: Kawashima, E.; Toyama, K.; Ohshima, K.; Kainosho, M.; Kyogoku, Y.; Ishido, Y. *Tetrahedron Lett.* **1995**, *36*, 6699-6700.
19) The depicted stereochemistry of **21** and **22** was assumed by comparing their coupling constants as well as NOE enhancements with those of **20**. Compound **20**: $J_{4',5'}$= 2.6, $J_{5',6}$= 2.2 Hz; NOE enhancements,

3.3% (H-6 *vs.* $CH_2CH{=}CH_2$), 12.3% (H-6 *vs.* H-3'). Compound **21**: $J_{4',5'}$= 5.5, $J_{5',6}$= 8.8 Hz; NOE, 3.5% (H-6 *vs.* 5-Me), 9.1% (H-5' *vs.* $CH_2CH{=}CH_2$), 9.1% (H-6 *vs.* H-3'). Compound **22**: $J_{4',5'}$= 5.1, $J_{5',6}$= 9.5 Hz; NOE, 6.6% (H-6 *vs.* $CH_2CH{=}CH_2$), 3.0% (H-5' *vs.* 5-Me), 11.2% (H-6 *vs.* H-3').

20) Compound **27** (mp 172-174 °C, acetone-hexane) used for X-ray crystallographic analysis was obtained from **29** by desilylation followed by acetylation.

21) The stereochemistry of **29** and **31** was confirmed by conversion to **27**.

22) Huval, C. C.; Singleton, D. A. *Tetrahedron Lett.* **1993**, *34*, 3041-3042.

23) It is also conceivable that a buttressing effect of the 2'-*O*-protecting group to the 3'-position is working as an additional factor to increase the steric encumberment.

24) The 3'-*endo* sugar pucker of **27** was evident from its X-ray analysis.

25) Compound **33** was prepared by oxidation of 2',3'-bis-*O*-(*tert*-butyldimethylsilyl)uridine according to the published procedure: Camarasa, M-J.; De las Heras, F. G.; Pérez-Pérez, M. J. *Nucleosides Nucleotides* **1990**, *9*, 533-546.

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