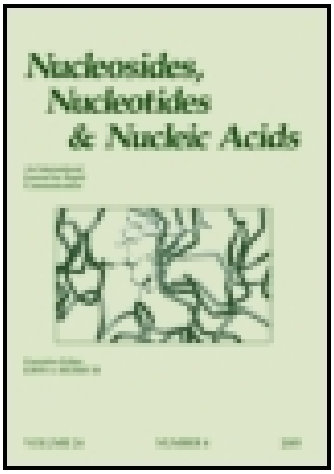

Nucleosides and Nucleotides
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lncn19

Radical-Mediated Cyclization of A 6-Chloro-9-(2-Deoxy--d erythro-pent-1-enofuranosyl)-8-(2,2-dibromovinyl) purine

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Published online: 20 Aug 2006.

To cite this article: Atsushi Kittaka, Naoki Yamada, Hiromichi Tanaka, Kazuo T. Nakamura & Tadashi Miyasaka (1996) Radical-Mediated Cyclization of A 6-Chloro-9-(2-Deoxy--d erythro-pent-1-enofuranosyl)-8-(2,2-dibromovinyl) purine, Nucleosides and Nucleotides, 15:9, 1447-1457, DOI: 10.1080/07328319608002446

To link to this article: http://dx.doi.org/10.1080/07328319608002446

NUCLEOSIDES & NUCLEOTIDES, 15(9), 1447-1457 (1996)

RADICAL-MEDIATED CYCLIZATION OF A 6-CHLORO-9-(2-DEOXY-D-*erythro*-PENT-1-ENOFURANOSYL)-8-(2,2-DIBROMOVINYL)PURINE

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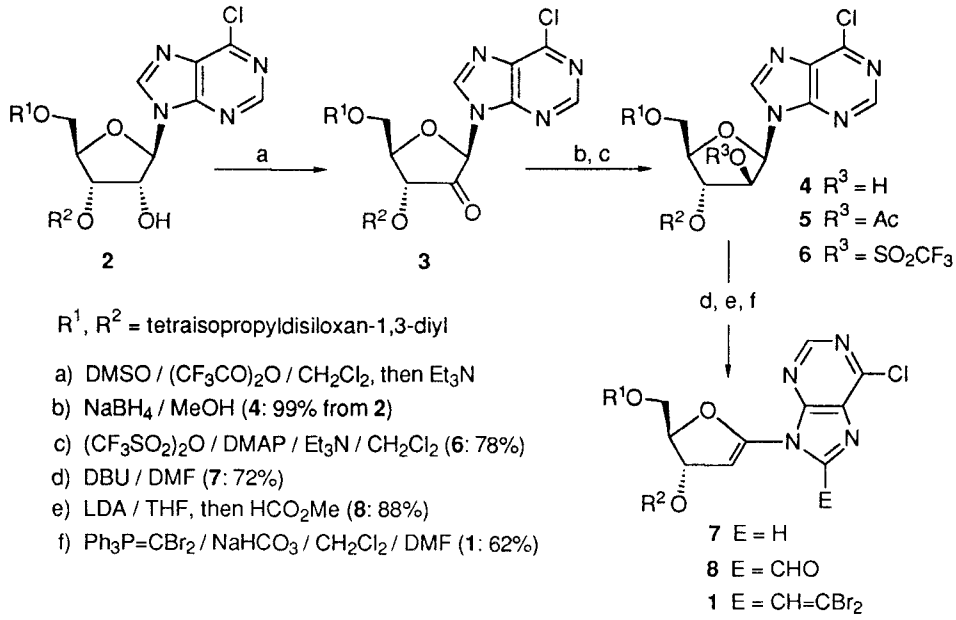
Abstract A vinyl radical generated from a 6-chloro-9-(2-deoxy-D-*erythro*-pent-1-enofuranosyl)-8-(2,2-dibromovinyl)purine effected cyclization either at the 1'- or at the 2'-position. The result is discussed in comparison with our previous study of the corresponding uracil derivative.

A class of nucleosides having a carbon-bridge between the base and sugar moieties are known as *C*-cyclonucleosides and serve as conformationally fixed models of naturally occurring nucleosides. Although there are a number of studies reported for the preparation of *C*-cyclonucleosides,[1] only one precedent had been available until recently for those fixed in *syn*-glycosidic conformation.[2] This may be due to the fact that transformation of common nucleosides to the *syn*-fixed derivatives inevitably involves C-C bond formation at the anomeric position, which is by no means so simple.[3]

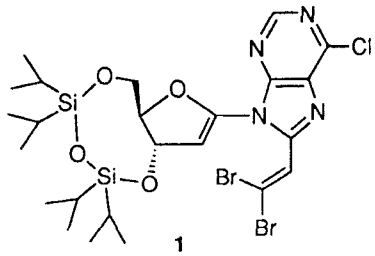
Our recent report,[4] which describes a vinyl radical-based cyclization of 6-substituted 1-(2-deoxy-D-*erythro*-pent-1-enofuranosyl)uracils leading to anomeric spiro derivatives, has disclosed a route to *syn*-fixed *C*-cyclouridines from uridine. The present article describes an attempt to extend this cyclization reaction to a purine nucleoside.

A vinyl radical precursor **1** was designed, the 1',2'-double bond of which was set up as an acceptor of a predictable vinyl radical from the 8-substituent. To synthesize **1** from an intact purine ribonucleoside, two synthetic operations are necessary: 1) inversion of the 2'-configuration to effect *anti*-elimination between 1'- and 2'-positions, 2) introduction of a β,β-dibromovinyl group to the 8-position. These were accomplished as given in Scheme 1.



SCHEME 1

The 3'- and 5'-hydroxyl groups of 6-chloro-9-(β-D-ribofuranosyl)purine[5] were protected with tetraisopropyldisiloxan-1,3-diyl group to give **2**. Inversion of configuration at the 2'-position of **2** was accomplished by an oxidation-hydride reduction sequence, without isolating **3**, according to the published procedure.[6] This gave exclusively the arabinofuranosyl derivative **4** in high yield,[7] which was fully characterized after converting to its acetate **5**. β-Elimination of **6**, obtained by the sulfonylation of **4**, was carried out with DBU in DMF to yield the 1', 2'-unsaturated derivative **7**.



1

Introduction of a β,β-dibromovinyl group to **7** was initiated with *C*-formylation at the 8-position based on our previously reported regiospecific lithiation of purine nucleosides.[8] Thus, when **7** was lithiated with 1.5 equiv of LDA in THF at −78 °C and the resulting C8-lithiated species was reacted with methyl formate, **8** was obtained in high yield. The published procedure for the preparation of $Ph_3P{=}CBr_2$ necessitates the use of Ph_3P and

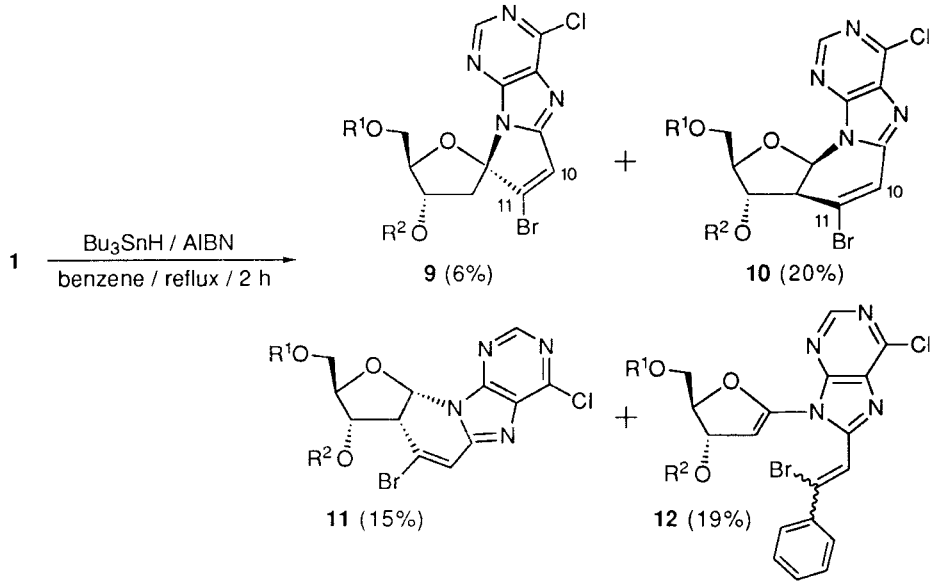
CBr_4, as well as Zn dust.[9] The Wittig reaction between **8** and this reagent gave **1** only in 31% yield. A higher yield of **1** was obtained when $NaHCO_3$ was added to the reagent.

Radical-mediated cyclization of **1** was carried out by adding a mixture of Bu_3SnH (4 equiv) and AIBN (0.5 equiv) to a refluxing benzene solution of **1** over 2 h by a syringe pump. Purification of the reaction mixture first by silica gel column chromatography and then by preparative TLC enabled the isolation of **9-12** (Scheme 2, yields are given in parentheses) along with the starting material **1** (20%). Although this reaction was repeated by varing solvent (toluene, cyclohexane),[10] reaction temperature (0-80 °C)[11] and amounts of Bu_3SnH (2-4 equiv), no significant change was seen either in terms of the total yield of the cyclized products or their distribution.

The structure of the anomeric spiro nucleoside **9**, which derived from a 5-*exo-trig* cyclization of a vinyl radical, was suggested by the absence of H-1' in the ^1H NMR spectrum, and its β-anomeric stereochemistry was unambiguously determined by X-ray crystallographic analysis. The ORTEP stereoview of **9** is shown in Fig. 1. That both **10** and **11** are 6-*endo-trig* cyclized products was deduced from the fact that their ^1H NMR spectra showed the presence of H-1' resonance (**10**, δ 6.52 ppm; **11**, δ 6.45 ppm) as a doublet ($J_{1',2'}$= 6.6 Hz). The depicted stereochemistry of **10** and **11** came from the observed NOE enhancements: **10**, 5.8% (H-1' and -4'), 16.6% (H-1' and -2'); **11**, 13.5% (H-1' and -2'), 14.6 % (H-2' and -3'). Compound **12**, which apparently resulted from the reaction of a vinyl radical with the solvent, was obtained as a mixture of two geometrical isomers (*ca.* 3:1, olefinic configurations not known).

Our previous study[4a] on radical-based cyclization of 1-(2-deoxy-D-*erythro*-pent-1-enofuranosyl)-6-(2,2-dibromovinyl)uracil showed that, irrespective of the reaction temperature, a bromovinyl radical favours reaction at the anomeric position (5-*exo-trig* cyclization) which yields anomeric spiro nucleosides. Since vinyl radicals are known to be nucleophilic,[11a] it was assumed that comparatively lower electron density of the anomeric position to that of 2'-position in the 1-enofuranosyl system would be responsible for the regio-chemical outcome. However, the present reaction of the purine counterpart **1** apparently proceeded with prepondrance of the 6-*endo-trig* pathway leading to **10** and **11**. This suggests the intervention of an additional factor which governs the regioselectivity. One possible explanation of the present result would be as follows. The vinyl group of **1** is bound to a 5-membered imidazole ring and thus the distance between vinyl radical and the anomeric carbon would be slightly longer than that of uracil case.

In conclusion, a carbon-bridged (anomeric spiro) purine nucleoside fixed in the *syn*-glycosidic conformation[12] has been prepared for the first time as a result of the vinyl radical cyclization with 1-enofuranosyl structure. Through the present study, it became apparent that regiochemistry of the cyclization (whether at the 1'- or 2'-position) is highly



SCHEME 2 R^1, R^2 = tetraisopropyldisiloxan-1,3-diyl

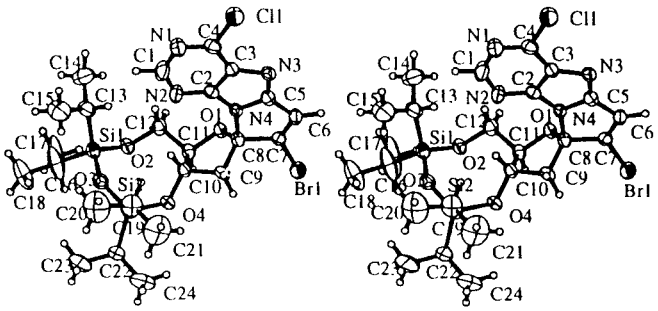


FIG. 1. ORTEP Stereoview of **9**.

dependent on the actual distance between vinyl radical and olefinic carbons. We recently found that a radical 1,5-translocation strategy of dibromovinyl-substituted nucleosides can also be used for the synthesis of anomeric spiro derivatives. Details of this alternative will be reported separately.[13]

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 a JEOL SX-102A (in FAB mode, *m*-nitrobenzyl alcohol as a matrix) spectrometer. 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. Ultraviolet spectra (UV) were recorded on a JASCO Ubest-55 spectrophotometer. 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).

6-Chloro-9-[3,5-*O*-(tetraisopropyldisiloxan-1,3-diyl)-β-D-ribofuranosyl]purine (2) To a solution of 6-chloro-9-(β-D-ribofuranosyl)purine (1.0 g, 3.47 mmol) and imidazole (473 mg, 6.96 mmol) in DMF (14 mL), 1,3-dichlorotetraisopropyldisiloxane (1.1 g, 3.49 mmol) was added, and the mixture was stirred at room temperature for 1 h. The reaction mixture was partitioned between EtOAc and H_2O. Silica gel column chromatography (EtOAc/hexane = 1/9-2/8) of the organic layer gave **2** (1.54 g, 84%) as a solid, which was crystallized from hexane (mp 107.5-108 °C). UV (MeOH) λ_{max} 264 nm (ε 9100), λ_{min} 226 nm (ε 2000); ^{1}H NMR ($CDCl_3$) δ 1.00-1.12 (28H, m, SiPr-*i*), 3.13 (1H, br, 2'-OH), 4.02-4.16 (3H, m, H-4' and H-5'), 4.58 (1H, d, $J_{2',3'}$= 5.5 Hz, H-2'), 5.02 (1H, dd, $J_{3',4'}$= 8.1 Hz, H-3'), 6.06 (1H, s, H-1'), 8.29 and 8.70 (2H, each as s, H-8 and H-2); FAB-MS *m/z* 531 and 529 (M^++H), 487 and 485 (M^+–Pr-*i*). Anal. Calcd for $C_{22}H_{37}ClN_4O_5Si_2$: C, 49.93; H, 7.05; N, 10.59. Found: C, 49.94; H, 7.02; N, 10.47.

6-Chloro-9-[3,5-*O*-(tetraisopropyldisiloxan-1,3-diyl)-β-D-arabinofuranosyl]purine (4) A CH_2Cl_2 (35 mL) solution of DMSO (1.0 mL, 14.0 mmol) was treated with $(CF_3CO)_2O$ (2.9 mL, 20.9 mmol) at –65 °C and stirred for 0.5 h. To this, **2** (3.70 g, 7.0 mmol) in CH_2Cl_2 (30 mL) was added dropwise at –78 °C. After being stirred for 1 h, the mixture was treated with Et_3N (9.2 mL, 66.3 mmol) and stirring was continued further for 1 h. The reaction mixture was partitioned between CH_2Cl_2 and H_2O. The organic layer was dried (Na_2SO_4) and evaporated to leave a syrup containing **3**, which was dissolved in MeOH (190 mL) and then treated with $NaBH_4$ (343 mg, 9.1 mmol) for 20 min at room temperature. Silica gel column chromatography (hexane/EtOAc = 8/2) of the

reaction mixture gave **4** (3.65 g, 99%) as a pale yellow foam. UV (MeOH) λ_{max} 264 nm, λ_{min} 228 nm; ^{1}H NMR ($CDCl_3$) δ 1.04-1.13 (28H, m, SiPr-*i*), 2.86 (1H, d, $J_{2',OH}$= 5.9 Hz, 2'-OH), 3.89 (1H, dt, $J_{3',4'}$= 7.7, $J_{4',5'}$= 2.9 Hz, H-4'), 4.05 and 4.11 (2H, each as dd, J_{gem}= 13.2 Hz, H-5'), 4.55 (1H, t, $J_{2',3'}$= $J_{3',4'}$= 7.7 Hz, H-3'), 4.71 (1H, dt, $J_{1',2'}$= $J_{2',OH}$= 5.9, $J_{2',3'}$= 7.7 Hz, H-2'), 6.34 (1H, d, H-1'), 8.48 and 8.69 (2H, each as s, H-8 and H-2); FAB-MS *m/z* 531 and 529 (M^++H). HRMS (*m/z*) calcd for $C_{22}H_{37}ClN_4O_5Si_2$ 529.2070 [MH^+], found 529.2050.

6-Chloro-9-[2-*O*-acetyl-3,5-*O*-(tetraisopropyldisiloxan-1,3-diyl)-β-D-arabinofuranosyl]purine (5) To a solution of **4** (184 mg, 0.35 mmol) and DMAP (21 mg, 0.17 mmol) in CH_2Cl_2 (4 mL), Et_3N (121 μL, 0.87 mmol) and Ac_2O (66 μL, 0.70 mmol) were added and the whole mixture was stirred for 3 h. The reaction mixture was partitioned between EtOAc and H_2O. Silica gel column chromatography (hexane/EtOAc = 95/5-93/7) of the organic layer gave **5** (168 mg, 85%) as a solid, which was crystallized from EtOAc (mp 142-143 °C). UV (MeOH) λ_{max} 264 nm (ε 8900), λ_{min} 224 nm (ε 1900); ^{1}H NMR ($CDCl_3$) δ 1.00-1.18 (28H, m, SiPr-*i*), 3.95 (1H, dt, $J_{3',4'}$= 8.43, $J_{4',5'}$= 3.3 Hz, H-4'), 4.07 (1H, dd, J_{gem}= 13.0 Hz, H-5'), 4.22 (1H, dd, H-5'), 4.89 (1H, t, $J_{2',3'}$= 8.4 Hz, H-3'), 5.60 (1H, dd, $J_{1',2'}$= 6.6 Hz, H-2'), 6.52 (1H, d, H-1'), 8.71 and 8.36 (2H, each as s, H-8 and H-2); FAB-MS *m/z* 573 and 571 (M^++H), 529 and 527 (M^+–Pr-*i*). Anal. Calcd for $C_{24}H_{39}ClN_4O_6Si_2$: C, 50.46; H, 6.88; N, 9.81. Found: C, 50.24; H, 7.05; N, 9.58.

6-Chloro-9-[3,5-*O*-(tetraisopropyldisiloxan-1,3-diyl)-2-*O*-trifluoromethanesulfonyl-β-D-arabinofuranosyl]purine (6) To an ice-cooled CH_2Cl_2 (95 mL) solution containing **4** (3.38 g, 6.4 mmol), DMAP (2.34 g, 19.1 mmol), and Et_3N (4.5 mL, 31.9 mmol) was added $(CF_3SO_2)_2O$ (3.2 mL, 19.1 mmol) dropwise and the mixture was stirred for 0.5 h. The reaction mixture was partitioned between CH_2Cl_2 and H_2O. Silica gel column chromatography (hexane/EtOAc = 8/2) of the organic layer gave **6** (3.30 g, 78%) as a pale yellow syrup. ^{1}H NMR ($CDCl_3$) δ 0.99-1.12 (28H, m, SiPr-*i*), 3.98 (1H, ddd, $J_{3',4'}$= 7.7, $J_{4',5'}$= 4.8 and 2.9 Hz, H-4'), 4.10 (1H, dd, $J_{4',5'}$= 2.9, J_{gem}= 12.8 Hz, H-5'), 4.20 (1H, dd, $J_{4',5'}$= 4.8 Hz, H-5'), 5.27 (1H, dd, $J_{2',3'}$= 7.2 Hz, H-3'), 5.52 (1H, dd, $J_{1',2'}$= 6.2 Hz, H-2'), 6.49 (1H, d, H-1'), 8.31 and 8.75 (2H, each as s, H-8 and H-2); FAB-MS *m/z* 663 and 661 (M^++H), 619 and 617 (M^+–Pr-*i*).

6-Chloro-9-[2-deoxy-3,5-*O*-(tetraisopropyldisiloxan-1,3-diyl)-D-*erythro*-pent-1-enofuranosyl]purine (7) A mixture of **6** (2.56 g, 3.9 mmol) and DBU (1.2 mL, 7.7 mmol) in DMF (45 mL) was stirred for 3 h at room temperature. The reaction mixture was partitioned between EtOAc and H_2O. Silica gel column chromatography (hexane/Et_2O = 93/7) of the organic layer gave **7** (1.42 g, 72%) as a foam. UV (MeOH) λ_{max} 239 and 248 nm, λ_{min} 243 nm; ^{1}H NMR ($CDCl_3$) δ 0.99-1.13 (28H, m,

SiPr-*i*), 3.81 (1H, t, J_{gem}= $J_{4',5'}$= 11.2 Hz, H-5'), 4.30 (1H, dd, $J_{4',5'}$= 4.8 Hz, H-5'), 4.70 (1H, ddd, $J_{3',4'}$= 4.4 Hz, H-4'), 5.55 (1H, dd, $J_{2',3'}$= 2.9 Hz, H-3'), 5.95 (1H, d, H-2'), 8.40 and 8.85 (2H, each as s, H-8 and H-2); FAB-MS *m/z* 512 and 510 (M^++H), 469 and 467 (M^+–Pr-*i*). HRMS (*m/z*) calcd for $C_{22}H_{35}ClN_4O_4Si_2$ 511.1964 [MH^+], found 511.1948.

6-Chloro-9-[2-deoxy-3,5-*O*-(tetraisopropyldisiloxan-1,3-diyl)-D-*erythro*-pent-1-enofuranosyl]-8-formylpurine (8) To a THF (38 mL) solution of LDA (5.73 mmol), **7** (1.96 g, 3.8 mmol) in THF (38 mL) was added dropwise under positive pressure of dry Ar, while maintaining the temperature below –70 °C. After being stirred for 0.5 h at below –70 °C, the mixture was treated with methyl formate (2.6 mL, 42 mmol) and the stirring was continued for another 0.5 h. The reaction mixture was quenched by adding AcOH, and partitioned between EtOAc and saturated aqueous $NaHCO_3$. Silica gel short column chromatography (hexane/EtOAc = 9/1) of the organic layer gave **8** (1.82 g, 88%) as a yellow syrup. ^{1}H NMR ($CDCl_3$) δ 1.07-1.11 (28H, m, SiPr-*i*), 3.97 (1H, t, J_{gem}= $J_{4',5'}$= 11.2 Hz, H-5'), 4.19 (1H, dd, $J_{4',5'}$= 4.7 Hz, H-5'), 4.73 (1H,dt, $J_{3',4'}$= 4.7 Hz, H-4'), 5.52 (1H, d, $J_{2',3'}$= 2.9 Hz, H-2'), 5.57 (1H, dd, H-3'), 8.94 (1H, s, H-2), 10.12 (1H, s, CHO); FAB-MS *m/z* 541 and 539 (M^++H).

6-Chloro-9-[2-deoxy-3,5-*O*-(tetraisopropyldisiloxan-1,3-diyl)-D-*erythro*-pent-1-enofuranosyl]-8-(2,2-dibromovinyl)purine (1) To a mixture of Zn-powder (41.2 mg, 0.6 matom) and PPh_3 (165.2 mg, 0.6 mmol) in CH_2Cl_2 (0.7 mL), CBr_4 (209 mg, 0.6 mmol) in CH_2Cl_2 (0.6 mL) was added at 0 °C under positive pressure of dry Ar. The resulting suspension was stirred for 28 h at room temperature while shading a light. After treatment of this suspension with $NaHCO_3$ (52 mg, 0.6 mmol), a DMF (2.6 mL) solution of **8** (115 mg, 0.2 mmol) was added. The whole was stirred for 1.5 h and then poured into EtOAc. The resulting suspension was washed successively with saturated aqueous $NaHCO_3$ and with brine. The organic layer was chromatographed on a silica gel column (hexane/Et_2O = 96/4) to gave **1** (90 mg, 62%) as a solid, which was crystallized from hexane (mp 122-123 °C). UV (MeOH) λ_{max} 236 (ε 16700) and 302 nm (ε 18400), λ_{min} 266 nm (ε 9100); ^{1}H NMR ($CDCl_3$) δ 1.06-1.11 (28H, m, SiPr-*i*), 3.86 (1H, t, J_{gem}= $J_{4',5'}$= 11.0 Hz, H-5'), 4.26 (1H, dd, $J_{4',5'}$= 4.8 Hz, H-5'), 4.70 (1H, dt, $J_{3',4'}$= $J_{4',5'}$= 4.8 Hz, H-4'), 5.55 (1H, dd, $J_{2',3'}$= 2.6 Hz, H-3'), 5.64 (1H, d, H-2'), 7.75 (1H, s, H-10), 8.80 (1H, s, H-2); FAB-MS *m/z* 699, 697, 695, and 693 (M^++H). Anal. Calcd for $C_{24}H_{35}BrClN_4O_4Si_2$: C, 41.48; H, 5.08; N, 8.07. Found: C, 41.60; H, 4.98; N, 7.93.

Radical-Mediated Cyclization of 1: Formation of 9, 10, 11, and 12. To a refluxing solution of **1** (103 mg, 0.15 mmol) in benzene (14.8 mL), a mixture of Bu_3SnH (159 μL, 0.59 mmol) and AIBN (12 mg, 0.07 mmol) in benzene (5 mL) was

added dropwise over 2 h using a syringe pump. The whole reaction mixture was applied to a silica gel column. Elution with 1-5% Et_2O in hexane followed by 20% EtOAc in hexane gave five fractions. Compounds **9** (solid, 5 mg, 6%) and **10** (syrup, 18 mg, 20%) were isolated by preparative TLC (hexane/EtOAc = 9/1) from the fraction eluted with 5% Et_2O in hexane. Compounds **11** (syrup, 14 mg, 15%) and **12** (syrup, 19 mg, 19%) were isolated by preparative TLC (hexane/EtOAc = 7/1) from the fraction eluted with 20% EtOAc in hexane.

Physical data of **9** are as follows: mp 160-162 °C (ether-hexane); UV (MeOH) λ_{max} 297 (ε 18800) and 307 nm (ε 18300), $\lambda_{shoulder}$ 320 nm (ε 9000), λ_{min} 250 nm (ε 3900); ^1H NMR ($CDCl_3$) δ 1.05-1.07 (28H, m, SiPr-*i*), 2.51 (1H, dd, J_{gem}= 13.2, $J_{2',3'}$= 7.0 Hz, H-2'), 2.91 (1H, dd, $J_{2',3'}$= 10.3 Hz, H-2'), 4.03 (1H, dd, J_{gem}= 11.4, $J_{4',5'}$= 3.3 Hz, H-5'), 4.15 (1H, ddd, $J_{3',4'}$= 7.3 Hz, H-4'), 4.24 (1H, dd, $J_{4',5'}$= 7.3 Hz, H-5'), 5.80 (1H, dt, H-3'), 6.96 (1H, s, H-10), 8.56 (1H, s, H-2); FAB-MS *m/z* 619, 617, and 615 (M^++H), 575, 573, and 571 (M^+–Pr-*i*). Anal. Calcd for $C_{24}H_{36}BrClN_4O_4Si_2$: C, 46.79; H, 5.88; N, 9.09. Found: C, 46.47; H, 5.79; N, 8.82.

Physical data of **10** are as follows: UV (MeOH) λ_{max} 304 nm (ε 29500), $\lambda_{shoulder}$ 298 (ε 26500) and 320 nm (ε 19300), λ_{min} 254 nm (ε 4500); ^1H NMR ($CDCl_3$) δ 0.87-1.40 (28H, m, SiPr-*i*), 3.59 (1H, dd, J_{gem}= 11.0, $J_{4',5'}$= 9.0 Hz, H-5'), 3.66 (1H, ddd, $J_{1',2'}$= 6.6, $J_{2',3'}$= 3.3 Hz, H-2'), 4.03 (1H, dd, $J_{4',5'}$= 4.0 Hz, H-5'), 4.12 (1H, dt, $J_{3',4'}$= 4.1 Hz, H-4'), 4.89 (1H, dd, H-3'), 6.52 (1H, d, H-1'), 7.19 (1H, d, *J*= 1.8 Hz, H-10), 8.76 (1H, s, H-2); FAB-MS *m/z* 619, 617, and 615 (M^++H). Anal. Calcd for $C_{24}H_{36}BrClN_4O_4Si_2$: C, 46.79; H, 5.88; N, 9.09. Found: C, 47.17; H, 5.93; N, 8.88.

Physical data of **11** are as follows: UV (MeOH) λ_{max} 306 and 320 nm, $\lambda_{shoulder}$ 296 nm, λ_{min} 316 nm; ^1H NMR ($CDCl_3$) δ 0.99-1.07 (28H, m, SiPr-*i*), 3.77 (1H, dd, $J_{1',2'}$= 6.6, $J_{2',3'}$= 7.7 Hz, H-2'), 3.78 (1H, dd, J_{gem}= 11.6, $J_{4',5'}$= 9.5 Hz, H-5'), 4.03 (1H, dt, $J_{4',5'}$= 9.5, $J_{3',4'}$= $J_{4',5'}$= 4.0 Hz, H-4'), 4.25 (1H, dd, H-5'), 4.85 (1H, dd, H-3'), 6.45 (1H, d, H-1'), 7.25 (1H, s, H-10), 8.76 (1H, s, H-2); FAB-MS *m/z* 619, 617, and 615 (M^++H). HRMS (*m/z*) calcd for $C_{24}H_{36}BrClN_4O_4Si_2$ 617.1205 and 615.1225 [MH^+], found 617.1193 and 615.1164.

Physical data of **12** (a mixture of two isomers, *ca.* 3:1) are as follows: UV (MeOH) λ_{max} 261 and 311 nm, λ_{min} 277 nm; FAB-MS *m/z* 695, 693, and 691 (M^++H), 651, 649, and 647 (M^+–Pr-*i*). HRMS (*m/z*) calcd for $C_{30}H_{40}BrClN_4O_4Si_2$ 693.1518 and 691.1538 [MH^+], found 693.1508 and 691.1511. ^1H NMR ($CDCl_3$) data of the major isomer: δ 1.08-1.12 (28H, m, SiPr-*i*), 3.85 (1H, t, J_{gem}= $J_{4',5'}$= 11.3 Hz, H-5'), 4.26 (1H, dd, $J_{4',5'}$= 4.7 Hz, H-5'), 4.66 (1H, dt, $J_{3',4'}$= 4.7 Hz, H-4'), 5.36 (1H, d, $J_{2',3'}$= 2.6 Hz, H-2'), 5.48 (1H, dd, H-3'), 7.29 (1H, s, H-10), 8.72 (1H, s, H-2), 7.29-7.33 (5H, m, Ph). ^1H NMR ($CDCl_3$) data of the minor isomer: δ 1.05-1.10 (28H, m, SiPr-*i*), 3.86 (1H, t,

TABLE 1. Atomic Coordinates and B*iso*/B*eq* of Non-hydrogen Atoms Used for Crystallographic Analysis of **9**.

Atom	X	Y	Z	*Beq* (Å^2)
Cl (1)	-0.2412(2)	-0.9064(2)	-0.6122(2)	6.91(9)
Si (1)	-0.1771(2)	-0.3052(2)	-0.5439(2)	4.55(7)
Si (2)	-0.3776(2)	-0.3225(2)	-0.4990(2)	5.17(8)
Br (1)	-0.58967(8)	-0.5017	-0.92798(8)	5.65(3)
O (1)	-0.3714(4)	-0.4786(4)	-0.7975(4)	4.1(2)
O (2)	-0.2211(4)	-0.3086(4)	-0.6573(4)	4.5(2)
O (3)	-0.2624(4)	-0.3119(4)	-0.4883(4)	4.9(2)
O (4)	-0.4257(4)	-0.3527(4)	-0.6072(4)	4.6(2)
N (1)	-0.1835(6)	-0.7508(7)	-0.5405(6)	6.5(3)
N (2)	-0.2512(6)	-0.6062(6)	-0.5947(6)	5.5(2)
N (3)	-0.3892(6)	-0.7729(6)	-0.7462(5)	4.4(2)
N (4)	-0.3856(5)	-0.6216(5)	-0.7300(5)	3.8(2)
C (1)	-0.1896(8)	-0.6621(9)	-0.5396(7)	6.7(3)
C (2)	-0.3125(6)	-0.6523(7)	-0.6592(6)	4.2(2)
C (3)	-0.3150(7)	-0.7444(7)	-0.6714(6)	4.2(3)
C (4)	-0.2452(7)	-0.7913(7)	-0.6074(7)	5.0(3)
C (5)	-0.4267(7)	-0.6964(7)	-0.7764(7)	4.3(3)
C (6)	-0.5043(7)	-0.6658(7)	-0.8538(6)	4.7(3)
C (7)	-0.5065(7)	-0.5799(6)	-0.8494(7)	4.0(3)
C (8)	-0.4348(7)	-0.5361(6)	-0.7670(6)	4.2(3)
C (9)	-0.4763(6)	-0.4883(6)	-0.6944(6)	4.2(2)
C (10)	-0.3938(6)	-0.4268(6)	-0.6494(6)	4.0(2)
C (11)	-0.3517(7)	-0.4012(7)	-0.7353(6)	4.1(3)
C (12)	-0.2452(6)	-0.3867(7)	-0.7150(6)	4.8(3)
C (13)	-0.0969(8)	-0.4021(8)	-0.5061(8)	6.3(3)
C (14)	-0.0173(8)	-0.4111(9)	-0.5614(9)	8.9(4)
C (15)	-0.0614(10)	-0.4121(9)	-0.4033(8)	9.4(4)
C (16)	-0.121(1)	-0.1950(9)	-0.5203(8)	10.4(5)
C (17)	-0.095(1)	-0.150(1)	-0.5881(10)	16.5(7)
C (18)	-0.090(1)	-0.1672(9)	-0.4220(8)	11.2(5)
C (19)	-0.3937(10)	-0.4143(9)	-0.4156(9)	7.8(4)
C (20)	-0.339(1)	-0.399(1)	-0.3183(10)	14.5(7)
C (21)	-0.496(1)	-0.436(1)	-0.415(1)	13.3(6)
C (22)	-0.4306(8)	-0.2111(9)	-0.4890(9)	8.6(4)
C (23)	-0.383(1)	-0.160(1)	-0.409(2)	26(1)
C (24)	-0.536(1)	-0.2072(9)	-0.5112(9)	9.9(5)

J_{gem}= $J_{4',5'}$= 11.5 Hz, H-5'), 4.21 (1H, dd, $J_{4',5'}$= 4.4 Hz, H-5'), 4.68 (1H, m, H-4'), 5.55 (1H, dd, $J_{2',3'}$= 2.6, $J_{3',4'}$= 4.7 Hz, H-3'), 5.62 (1H, d, H-2'), 7.46 (1H, s, H-10), 8.80 (1H, s, H-2), 7.41-7.72 (5H, m, Ph).

Data used for X-ray analysis of 9. Crystal data: space group $P2_1$ (monoclinic), Z = 4, a = 14.263(2), b = 14.960(1), c = 14.620(2) Å, V = 3045.2(6) Å^3, Dc = 1.344 g/cm^3, R= 0.044, β = 102.51(1)°

Acknowledgement This work has been supported by a British Council Collaborative Research Project (to H. T.). The authors are grateful to Dr. Kentaro Yamaguchi (Chemical Analysis Center, Chiba University) for performing HRMS.

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Received April 4, 1996
Accepted May 22, 1996