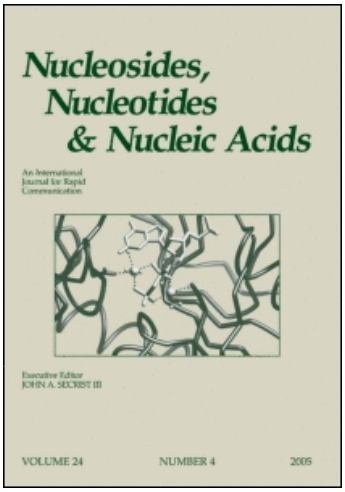


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# Reaction of the 2'-Silyl and 2'-Stannyl Derivatives of 6-(Bromomethyl)Dimethylsilyl-1',2'-Unsaturated Uridine Under Radical Conditions

Junko Ogamino[a]; Hideaki Mizunuma[a]; Hiroki Kumamoto[a]; Kazuhiro Haraguchi[a]; Hiromichi Tanaka[a]
[a] School of Pharmaceutical Sciences, Showa University, Shinagawa-ku, Tokyo, Japan

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# REACTION OF THE 2′-SILYL AND 2′-STANNYL DERIVATIVES OF 6-(BROMOMETHYL)DIMETHYLSILYL-1′,2′-UNSATURATED URIDINE UNDER RADICAL CONDITIONS

**Junko Ogamino, Hideaki Mizunuma, Hiroki Kumamoto, Kazuhiro Haraguchi, and Hiromichi Tanaka** □ *School of Pharmaceutical Sciences, Showa University, Shinagawa-ku, Tokyo, Japan*

□ *The mode of cyclization (5-exo versus 6-endo) of 2-sila-5-hexen-1-yl radicals generated from 2′-tributylstannyl- and 2′-trimethylsilyl-6-(bromomethyl)dimethylsilyl-1′,2′-unsaturated uridines (***8** *and* **9***) was investigated. Although the actual structure of the reaction products differ from each other, reflecting the ease of elimination of the 2′-substituent, it was found that both substrates prefer the 5-exo-cyclization pathway.*

**Keywords** 1′,2′-Unsaturated nucleoside; Radical cyclization; Silyl tether; 2-Sila-5-hexenyl radical



## INTRODUCTION

In contrast to the well appreciated 5-*exo*-ring closure of 5-hexenyl radicals,[1–3] simple 2-sila- and 3-sila-counterparts have been reported to undergo preferential 6-*endo*-cyclization[4] due to the longer C-Si bond.[5] Recently, we have studied the radical reaction of 6-(bromomethyl)dimethylsilyl-1′,2′-unsaturated uridine (**1**) and its 2′-substituted derivatives (**2-5**) with the aim of determining the mode of cyclization of 2-sila-hexenyl radicals derived from these substrates.[6] As a result, it was found that the 2′-unsubstituted 6-silicon-tethered substrate (**1**) undergoes exclusive

In honor and celebration of the life and career of Dr. John A. Montgomery.

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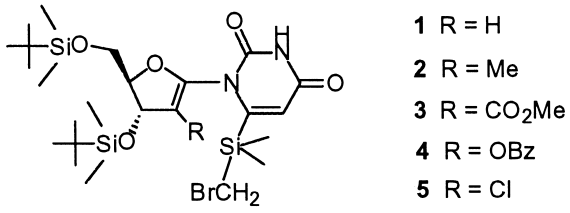
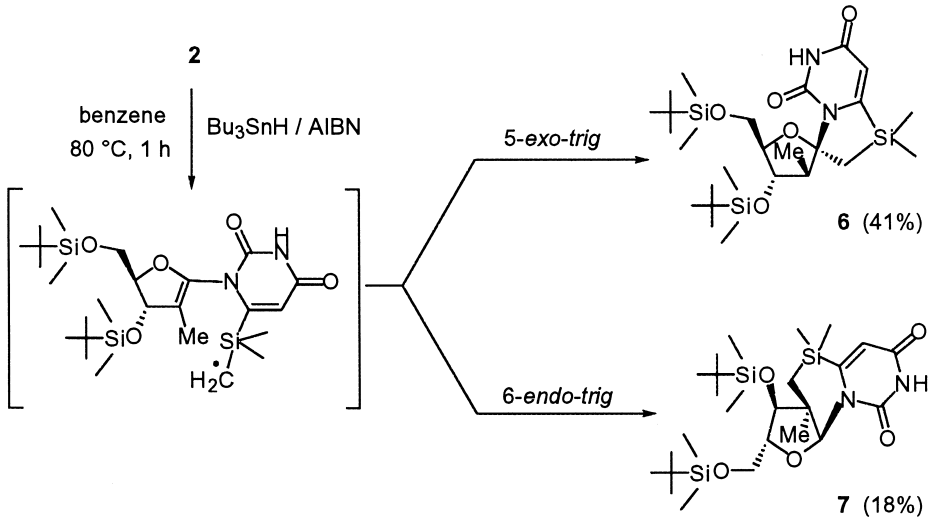
Address correspondence to Hiromichi Tanaka, School of Pharmaceutical Sciences, Showa University, 1-5-8 Hatanodai, Shinagawa-ku, Tokyo 142-8555, Japan. E-mail: hirotnk@pharm.showa-u.ac.jp

6-*endo*-cyclization, whereas the reaction of the 2′-substituted derivatives (**2**-**5**) uniformly proceeded in preferential or exclusive 5-*exo*-mode.

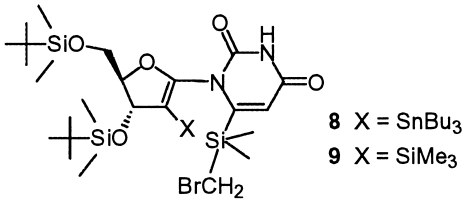



The exclusive 5-*exo*-cyclization of **3**-**5** is explicable in terms of the polar effect[7] of the 2′-substituent, whereas the preferential formation of 5-*exo* product **6** from **2** (Scheme 1) would be attributable to either steric hindrance of the 2′-methyl group or stabilization of the intermediary tertiary 2′-carbon-radical.




**SCHEME 1**

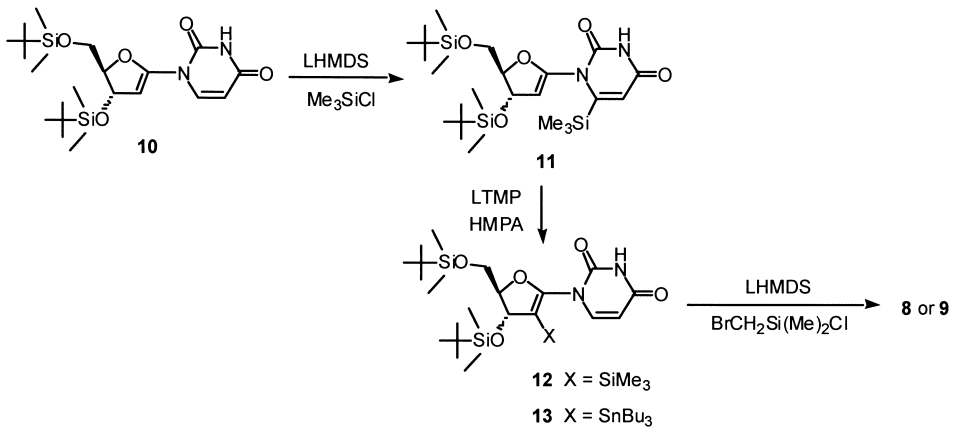
In this paper, we report further examples of radical reaction of 6-(bromomethyl)dimethylsilyl-1′,2′-unsaturated uridine analogues: 2′-tributylstannyl (**8**) and 2′-trimethylsilyl (**9**) derivatives.



## RESULTS AND DISCUSSION

As reported earlier, trimethylsilyl and tributylstannyl groups undergo an intramolecular anionic migration from the 6-position of 1-(2-deoxy-D-*erythro*-pent-1-enofuranosyl)uracil to the 2′-position.[8] Introduction of the silyl group to the 6-position of **10** was carried out with LHMDS (lithium hexamethyldisilazide) and $Me_3SiCl$ through the recently reported temporary $O^4$-silylation[9] to give **11** in 92% yield (Scheme 2). Compound **11** was then subjected to anionic migration by using LTMP (lithium 2,2,6,6-tetramethylpiperidide) in the presence of HMPA (hexamethylphosphoric triamide) in THF (below −70°C, for 1 h). The 2′-trimethylsilylated product (**12**) was isolated in 81% yield. Preparation of the corresponding 2′-stannylated derivative (**13**) has already been reported.[8] Attempted introduction of the silyl tether, which works as a radical precursor, to the 6-position of **12** by LDA (lithium diisopropylamide)-lithiation resulted in a complex mixture of products, presumably due to $\alpha$-elimination of $BrCH_2Si(Me)_2Cl$. On the other hand, the use of LHMDS (in THF, below −70°C) gave the desired product in good yield: **8**, 79%; **9**, 85%.

Radical reaction of the 2′-tributylstannyl derivative (**8**) was carried out in refluxing benzene by adding a mixture of AIBN (0.2 equiv) and $Bu_3SnH$ (2.0 equiv) via a motor-driven syringe over 1.5 h at 80°C (final concentration of the substrate: ca. 0.01 M). HPLC purification of the reaction mixture enabled isolation of two products. FAB-MS spectra [$m/z$ 525 ($M^+$+H)] of these products indicated that both lack the 2′-tributylstannyl group and are an isomeric pair. Although their $^1$H NMR spectra are very similar, one feature of the major isomer (isolated yield: 71%) is a characteristic low field shift of H-3′ ($\delta$ 5.53) compared with that of the minor isomer ($\delta$ 4.80, isolated yield: 13%) or those of the compounds prepared in this study:

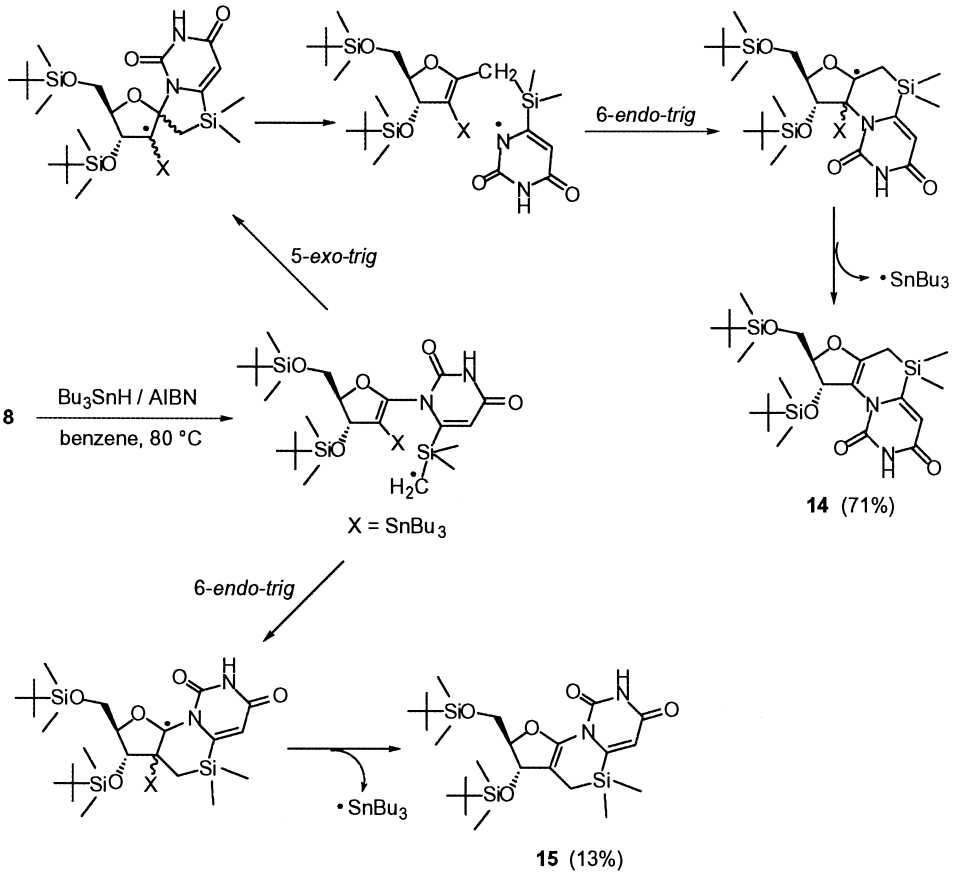



**SCHEME 2**

**8**, $\delta$ 4.94; **9**, $\delta$ 4.96; **11**, $\delta$ 4.98; **12**, $\delta$ 5.00; **13**, $\delta$ 4.94. An additional difference is that only the minor isomer showed a correlation between $C^6$-Si<u>C</u>$H_2$ and H-3′ in its HMBC (heteronuclear multiple bond connectivity) spectrum.

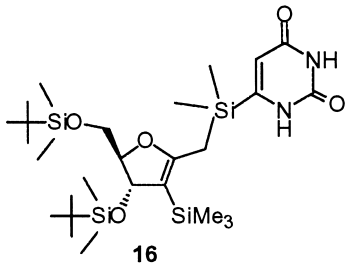
The above mentioned NMR spectroscopic data combined with conceivable reaction pathways shown in Scheme 3 led us to depict structure **14** for the major product and **15** for the minor one. The radical reaction of **8** was also examined at lower temperatures ($Et_3B$, room temperature and 0°C), but no significant difference was seen in the product distribution, except that the reduced product was formed in these experiments.

When the 2′-trimethylsilyl derivative (**9**) was reacted with $Bu_3SnH$/AIBN in refluxing benzene, **16** (29%) and **17** (38%) were formed in addition to a small amount of the 6-*endo*-cyclized product **15** (5%). It is apparent that both **16** and **17**[10] were formed as a consequence of 5-*exo-trig* cyclization. As shown in Scheme 3, in the case of the 2′-tributylstannyl derivative (**8**), the incipient uracil-1-yl radical resulting from 5-*exo*-cyclization reacted further at

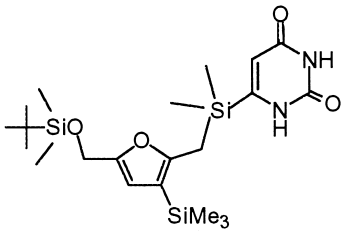



**SCHEME 3**

the 2′-position to give the final product **14**. Lack of such a reaction pathway in the reaction of **9** may be explained by the fact that silyl radical formation is a much slower process than that of tin radicals.[11]




**16**




**17**

In conclusion, the present study clearly showed that both 2′-tributylstannyl- and 2′-trimethylsilyl-6-(bromomethyl)dimethylsilyl-1′,2′-unsaturated uridines (**8** and **9**) undergo preferential 5-*exo-trig* ring closure under radical reaction conditions. Although there may be several factors involved in the observed preference of 5-*exo*-cyclization, one major factor working here, at least in the case of the 2′-trimethylsilylated substrate **9**, would be stabilization of the intermediary $\alpha$-silyl-2′-carbon-radical by vicinal (d-p)$\pi$ overlap.[12] Another possibility is steric hindrance of these seemingly bulky substituents to the 2′-carbon atom. However, this is rather questionable, since C-Sn (2.14 Å) and C-Si (1.87 Å) bonds are significantly longer than C-C bond (alkane, 1.54 Å).



## EXPERIMENTAL

Melting points are uncorrected. $^1$H NMR and $^{13}$C NMR were measured on a JEOL JNM-LA 500 (500 MHz). Chemical shifts are reported relative to $Me_4Si$. Mass spectra (MS) were taken in FAB mode with *m*-nitrobenzyl alcohol as a matrix on a JEOL JMS-700. Ultraviolet spectra (UV) were recorded on a JASCO V-530 spectrophotometer. Column chromatography was carried out on silica gel (Micro Bead Silica Gel PSQ 100B, Fuji Silysia Chemical Ltd.). Thin-layer chromatography (TLC) was performed on silica gel (precoated silica gel plate $F_{254}$, Merck). Where necessary, analytical samples were purified by high-performance liquid chromatography (HPLC). HPLC was carried out on a Shimadzu LC-6AD with a Shim-pack PREP-SIL (H)·KIT column (2 × 25 cm). THF was distilled from benzophenone ketyl.

**6-Trimethylsilyl-1-[3,5-*bis*-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-D-*erythro*-pent-1-enofuranosyl]uracil (11).** To a mixture of **10** (1.0 g, 2.20 mmol) and $Me_3SiCl$ (0.56 mL, 8.80 mmol) in THF (30 mL) was added LHMDS (1.58 M in THF, 8.36 mL, 13.2 mmol) at below −70°C under positive pressure of dry Ar. After stirring for 20 min, the reaction mixture was diluted

with saturated aqueous $NH_4Cl$. Extraction with EtOAc followed by column chromatography (hexane/EtOAc = 5/1) gave **11** (1.03 g, 92%) as a foam: UV (MeOH) $\lambda_{max}$ 266 nm ($\varepsilon$ 9900), $\lambda_{min}$ 235 nm ($\varepsilon$ 2700); $^1$H NMR ($CDCl_3$) $\delta$ 0.08, 0.10, 0.11, and 0.12 (12H, each as s, OSiMe), 0.36 (9H, s, $C^6$-$SiMe_3$), 0.87 and 0.92 (18H, each as s, SiBu-*t*), 3.62 (1H, dd, $J$ = 10.4 and 8.0 Hz, H-5′), 3.82 (1H, dd, $J$ = 10.4 and 6.4 Hz, H-5′), 4.39–4.43 (1H, m, H-4′), 4.98 (1H, t, $J$ = 2.8 Hz, H-3′), 5.14 (1H, d, $J$ = 2.8 Hz, H-2′), 5.89 (1H, d, $J$ = 2.4 Hz, H-5), 8.13 (1H, br, NH); FAB-MS *m/z* 527 ($M^+$+H). Anal. calcd for $C_{24}H_{46}N_2O_5Si_3$: C, 54.71; H, 8.80; N, 5.32. Found: C, 54.90; H, 9.09; N, 5.32.

**1-[3,5-*bis*-*O*-(*tert*-Butyldimethylsilyl)-2-trimethylsilyl-2-deoxy-D-*erythro*-pent-1-enofuranosyl]uracil (12).** To a mixture of LTMP (16.55 mmol) and HMPA (7.2 mL, 41.4 mmol) in THF (15 mL) was added a THF (30 mL) solution of **11** (2.18 g, 4.14 mmol) at below −70°C under positive pressure of dry Ar. After stirring for 1 h, the reaction mixture was diluted with saturated aqueous $NH_4Cl$. Extraction with EtOAc followed by column chromatography (hexane/EtOAc = 9/1) gave **12** (1.77 g, 81%) as a solid: mp 149–151°C; UV (MeOH) $\lambda_{max}$ 257 nm ($\varepsilon$ 9700), $\lambda_{min}$ 236 nm ($\varepsilon$ 6300); $^1$H NMR ($CDCl_3$) $\delta$ 0.09, 0.13, and 0.14 (12H, each as s, OSiMe), 0.10 (9H s, $C^{2'}$-$SiMe_3$) 0.90 and 0.91 (18H, each as s, SiBu-*t*), 3.60 (1H, dd, $J$ = 10.4 and 7.2 Hz, H-5′), 3.77 (1H, dd, $J$ = 10.4 and 5.2 Hz, H-5′), 4.38 (1H, ddd, $J$ = 7.2, 5.2, and 2.0 Hz, H-4′), 5.00 (1H, d, $J$ = 2.0 Hz, H-3′), 5.75 (1H, d, $J$ = 8.0 Hz, H-5), 7.21 (1H, d, $J$ = 8.0 Hz, H-6), 8.06 (1H, br, NH); FAB-MS *m/z* 527 ($M^+$+H). Anal. calcd for $C_{24}H_{46}N_2O_5Si_3$: C, 54.71; H, 8.80; N, 5.32. Found: C, 54.93; H, 9.07; N, 5.31.

**6-(Bromomethyl)dimethylsilyl-1-[3,5-*bis*-*O*-(*tert*-butyldimethylsilyl)-2-tributylstannyl-2-deoxy-D-*erythro*-pent-1-enofuranosyl]uracil (8).** To a mixture of **13**[5] (1.35 g, 1.82 mmol) and $BrCH_2Si(Me)_2Cl$ (0.99 mL, 7.26 mmol) was added LHMDS (1.54 M in THF, 7.26 mL, 11.2 mmol) at below −70°C under positive pressure of dry Ar. After stirring for 30 min, the reaction mixture was diluted with saturated aqueous $NH_4Cl$. Extraction with EtOAc followed by column chromatography (hexane/EtOAc = 15/1) gave **8** (1.28 g, 79%) as a oil: UV (MeOH) $\lambda_{max}$ 269 nm ($\varepsilon$ 9600), $\lambda_{min}$ 244 nm ($\varepsilon$ 5200), $\lambda_{shoulder}$ 270 nm ($\varepsilon$ 9500); $^1$H NMR ($CDCl_3$) $\delta$ 0.07, 0.08, 0.13, and 0.18 (12H, each as s, OSiMe), 0.49 and 0.50 (6H, each as s, $C^6$-$SiMe_2$), 0.91 (18H, s, SiBu-*t*), 0.86–0.94 and 1.24–1.53 (27H, each as m, SnBu), 2.75 (2H, s, $C^6$-$SiCH_2$), 3.53 (1H, dd, $J$ = 10.1 and 8.4 Hz, H-5′), 3.74 (1H, dd, $J$ = 10.1 and 6.2 Hz, H-5′), 4.38 (1H, ddd, $J$ = 8.4, 6.2, and 1.2 Hz, H-4′), 4.94 (1H, d, $J$ = 1.2 Hz, H-3′), 5.94 (1H, s, H-5) 7.97 (1H, br, NH); FAB-MS *m/z* 895 ($M^+$+H). Anal. calcd for $C_{36}H_{71}BrN_2O_5Si_3Sn$: C, 48.32; H 8.00; N, 3.13. Found: C, 48.62; H, 8.20; N, 3.10.

**6-(Bromomethyl)dimethylsilyl-1-[3,5-*bis*-*O*-(*tert*-butyldimethylsilyl)-2-trimethylsilyl-2-deoxy-D-*erythro*-pent-1-enofuranosyl]uracil (9).** This compound was prepared from **12** in 85% yield as a foam by the procedure used for the preparation of **8**. Eluent used for its column chromatography is hexane/EtOAc = 10/1: UV (MeOH) $\lambda_{max}$ 268 nm ($\varepsilon$ 9800), $\lambda_{min}$ 241 nm ($\varepsilon$ 4000); $^1$H NMR ($CDCl_3$) $\delta$ 0.08, 0.14, and 0.19 (9H, each as s, $C^{2'}$-$SiMe_3$), 0.09 (12H, s, OSiMe), 0.50 and 0.52 (6H, each as s, $C^6$-$SiMe_2$), 0.91 (18H, s, SiBu-*t*), 2.76 (1H, s, $C^6$-$SiCH_2$), 3.52 (1H, dd, $J$ = 10.0 and 9.2 Hz, H-5′), 3.74 (1H, dd, $J$ = 10.0 and 6.0 Hz, H-5′), 4.40 (1H, ddd, $J$ = 9.2, 6.0, and 1.2 Hz, H-4′), 4.96 (1H, d, $J$ = 1.2 Hz, H-3′), 5.95 (1H, s, H-5), 8.27 (1H, br, NH); FAB-MS *m/z* 677 and 679 ($M^+$+H). Anal. calcd for $C_{27}H_{53}BrN_2O_5Si_4$: C, 47.83; H, 7.88; N, 4.13. Found: C, 48.00; H, 8.24; N, 4.10.

**Radical Reaction of 8: Formation of 14 and 15.** To a refluxing solution of **8** (105 mg, 0.117 mmol) in benzene (6 mL) was added a mixture of AIBN (4 mg, 0.023 mmol) and $Bu_3SnH$ (71 $\mu$L, 0.235 mmol) in benzene (6 mL) over 1 h via a motor-driven syringe under positive pressure of dry Ar. After further refluxing for 0.5 h, the reaction mixture was evaporated. HPLC purification (hexane/EtOAc = 2/1) of the resulting residue gave **14** ($t_R$ = 13.2 min, 43.5 mg, 71%, as an oil) and **15** ($t_R$ = 12.7 min, 7.9 mg, 13%, as an oil).

Physical data of **14** are as follows: UV (MeOH) $\lambda_{max}$ 235 nm ($\varepsilon$ 12,900) and 312 nm ($\varepsilon$ 3700), $\lambda_{min}$ 276 nm ($\varepsilon$ 2800); $^1$H NMR ($CDCl_3$) $\delta$ −0.03, 0.06, and 0.10 (12H, each as s, OSiMe), 0.33 and 0.45 (6H, each as s, $C^6$-$SiMe_2$), 0.79 and 0.92 (18H, each as s, SiBu-*t*), 1.72 (1H, d, $J$ = 15.8 Hz, $C^6$-$SiCH_2$), 1.81 (1H, dd, $J$ = 15.8 and 1.2 Hz, $C^6$-$SiCH_2$), 3.62 (1H, dd, $J$ = 10.6 and 7.0 Hz, H-5′), 3.77 (1H, dd, $J$ = 10.6 and 6.6 Hz, H-5′), 4.34 (1H, ddd, $J$ = 7.0, 6.6, and 1.2 Hz, H-4′), 5.53 (1H, t, $J$ = 1.2 Hz, H-3′), 5.86 (1H, d, $J$ = 2.0 Hz, H-5), 8.06 (1H, br, NH); $^{13}$C NMR ($CDCl_3$) $\delta$ −5.5, −5.4, −5.2, −5.0, −4.6, and −3.7 (SiMe), 11.0 ($SiCH_2$), 17.8 and 18.5 (quaternary carbon of SiBu-*t*), 25.8 and 26.0 (SiBu-*t*), 62.4 (C5′), 74.8 (C3′), 89.1 (C4′), 109.1 (C5), 115.3 (C2′), 148.9 (C1′), 149.1 (C2), 158.0 (C6), 162.1 (C4); FAB-MS *m/z* 525 ($M^+$+H). Anal. calcd for $C_{24}H_{44}N_2O_5Si_3$: C, 54.92; H, 8.45; N, 5.34. Found: C, 54.55; H, 8.50; N, 5.11.

Physical data of **15** are as follows: UV (MeOH) $\lambda_{max}$ 239 nm ($\varepsilon$ 10,600), $\lambda_{min}$ 224 nm ($\varepsilon$ 10,100); $^1$H NMR ($CDCl_3$) $\delta$ 0.09 and 0.12 (12H, each as s, OSiMe), 0.35 and 0.36 (6H, each as s, $C^6$-$SiMe_2$), 0.90 (18H, s, SiBu-*t*), 1.44 (1H, dd, $J$ = 16.3 and 0.6 Hz, $C^6$-$SiCH_2$), 1.51 (1H, d, $J$ = 16.3 Hz, $C^6$-$SiCH_2$), 3.61 (1H, dd, $J$ = 10.5 and 7.6 Hz, H-5′), 3.87 (1H, dd, $J$ = 10.5 and 4.8 Hz, H-5′), 4.40 (1H, ddd, $J$ = 7.6, 4.8, and 2.4 Hz, H-4′), 4.80 (1H, d, $J$ = 2.4 Hz, H-3′), 5.86 (1H, s, H-5), 7.88 (1H br, NH); $^{13}$C NMR ($CDCl_3$) $\delta$ −5.5, −5.4, −4.4, −4.2, −3.6, and −3.1 (SiMe), 5.3 ($SiCH_2$), 18.0 and 18.6 (quaternary carbon of SiBu-*t*), 25.8 and 26.0 (SiBu-*t*), 62.1 and 78.3 (C3′),

87.5 (C4′), 95.6 (C2′), 110.0 (C5), 146.1 (C1′), 147.5 (C2), 157.4 (C6), 161.6 (C4); FAB-MS *m/z* 525 ($M^+$+H). Anal. calcd for $C_{24}H_{44}N_2O_5Si_3$: C, 54.92; H, 8.45; N, 5.34. Found: C, 54.89; H, 8.49; N, 5.25.

**Radical Reaction of 9: Formation of 15-17.** To a refluxing solution of **9** (100 mg, 0.15 mmol) in benzene (4 mL) was added a mixture of $Bu_3SnH$ (85 $\mu$L, 0.30 mmol) and AIBN (5 mg, 0.03 mmol) in benzene (6 mL) over 1 h via a motor-driven syringe under positive pressure of dry Ar. After further refluxing for 3.5 h, the reaction mixture was evaporated. Short column chromatography (hexane/EtOAc = 10/1 and then EtOAc) of the resulting residue followed by HPLC purification (hexane/EtOAc = 1/1) gave **15** ($t_R$ = 8.6 min, 3.7 mg, 5% as an oil), **16** ($t_R$ = 10.2 min, 25.2 mg, 29%, as a foam), and **17** ($t_R$ = 11.5 min, 27.4 mg, 38%, as a foam).

Physical data of **16** are as follows: UV (MeOH) $\lambda_{max}$ 269 nm ($\varepsilon$ 9000), $\lambda_{min}$ 246 nm ($\varepsilon$ 5300); $^1$H NMR ($CDCl_3$) $\delta$ 0.06, 0.07, 0.10, and 0.11 (12H, each as s, OSiMe), 0.14 (9H, s, $C^{2'}$-$SiMe_3$), 0.32 and 0.33 (6H, each as s, $C^6$-$SiMe_2$), 0.87 and 0.89 (18H, each as s, SiBu-*t*), 1.90 (1H, dd, $J$ = 14.8 and 1.2 Hz, C6-$SiCH_2$), 1.97 (1H, d, $J$ = 14.8 Hz, C6-$SiCH_2$), 3.56 (1H, dd, $J$ = 10.5 and 6.4 Hz, H-5′), 3.71 (1H, dd, $J$ = 10.5 and 5.0 Hz, H-5′), 4.35 (1H, ddd, $J$ = 6.4, 5.0, and 1.6 Hz, H-4′), 4.89 (1H, s, H-3′), 5.75 (1H, s, H-5), 8.08 and 9.20 (2H, each as br, NH); FAB-MS *m/z* 599 ($M^+$+H). Anal. calcd for $C_{27}H_{54}N_2O_5Si_4$: C, 54.13; H, 9.09; N, 4.68. Found: C, 54.17; H, 9.30; N, 4.72.

Physical data of **17** are as follows: $^1$H NMR ($CDCl_3$) $\delta$ 0.10 (6H, s, OSiMe), 0.18 (9H, s, $C^{2'}$-$SiMe_3$), 0.36 (6H, s, $C^6$-$SiMe_2$), 0.90 (9H, s, SiBu-t), 2.35 (2H, s, $C^6$-$SiCH_2$), 4.75 (2H, s, H-5′), 5.77 and 6.07 (2H, each as s, H-3′ and H-5), 8.52 and 8.99 (2H, each as br, NH); FAB-MS *m/z* 505 ($M^+$+H).



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