JOC Article

Sulfur Extrusion with Tin Radical: Synthesis of 4′,5′-Didehydro-5′-deoxy-5′-(tributylstannyl)adenosine, an Intermediate for Potential Inhibitors against *S*-Adenosyl Homocysteine Hydrolase

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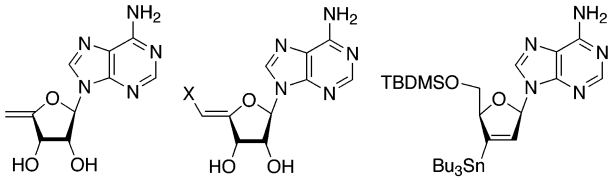
A new approach has been developed for the synthesis of potential inhibitors of *S*-adenosyl-L-homocysteine (AdoHcy) hydrolase. The key intermediate 9-[2,3-bis-*O*-(*tert*-butyldimethylsilyl)-5-(*Z*)-(tributylstannyl)-5-deoxy-*β*-D-*erythro*-pent-4-enofuranosyl]adenine (**12**) was prepared by sulfur extrusion reaction of 4′,5′-didehydro-5′-deoxy-5′-(phenylthio)adenosine (**11**) with tributyltin radical. It was found that this reaction proceeds stereoselectively, forming **12** irrespective of the geometry of **11**. Compound **12** readily underwent iodination, bromination, and chlorination with retention of configuration, whereas fluorination gave both (*Z*)- and (*E*)-isomers of vinyl fluoride. Because of the susceptibility of **12** to protodestannylation, the (*Z*)-vinyl iodide (**13**), prepared in quantitative yield from **12**, was used as a substrate for C−C bond formation. Various types of carbon substituents (phenyl, vinyl, trifluorovinyl, ethynyl, and cyano) were introduced to the 5′-position of the 5-deoxy-*β*-D-*erythro*-pent-4-enofuranosyl structure to open up a new route to potential inhibitors of AdoHcy hydrolase.

Introduction

S-Adenosyl-L-homocysteine (AdoHcy) hydrolase is one of the target enzymes for antiviral chemotherapy,[1] since deactivation of this enzyme leads to accumulation of AdoHcy (**A**) that inhibits methylation of viral mRNA as a potent feedback inhibitor. Scheme 1 shows that hydrolysis with AdoHcy hydrolase begins with oxidation of the 3′-hydroxyl group of **A** to the 3′-keto derivative **B** with the enzyme-bound NAD^+. Spontaneous elimination of Hcy (**D**) from **B** yields the 4′,5′-didehydro intermediate **C**, which in turn is hydrated to form the 3′-keto adenosine **E** which finally is reduced to adenosine (**F**) with the enzyme-bound NADH. The finding[2] that this enzyme converts 4′,5′-didehydro-5′-deoxyadenosine (**1**) to **A** and **F**, presumably through **C**, provides convincing support for this reaction sequence.

Synthetic endeavors have been devoted to the search for AdoHcy hydrolase inhibitors based on the above mechanism.[3−5] The designed inhibitors have the general structure **2** with X being the leaving group orientated in the *Z*-configuration so that, after oxidation of the 3′-hydroxyl group, a nucleophilic site of the enzyme can react through an addition−elimination pathway.



1 **2** **3**

We recently reported that the 3′-benzenesulfonyl derivative of 2′,3′-didehydro-2′,3′-dideoxyadenosine (d4A) undergoes ipso-substitution with tributyltin radical to give the stannylated product **3** and exemplified the usefulness of this vinylstannane for the preparation of a various types of 3′-substituted d4A analogues.[6] Such tin radical-mediated extrusion of sulfur atoms (sulfides and sulfones) bound to sp^2-carbon has been exploited on many occasions in synthetic chemistry[7,8] although the actual mechanism of these reactions is not clear.

In the present study, we planned to synthesize a vinylstannane **5** from **4** (Scheme 2) with the expectation that **5** would serve as a common precursor for a various types of potential AdoHcy hydrolase inhibitors.

Synthesis of (*Z*)-4′,5′-Didehydro-5′-deoxy-5′-(tributylstannyl)adenosine. Since **5** is not a simple vinyl-

* Corresponding author.

(1) De Clercq, E. *Biochem. Pharmacol.* **1987**, *36*, 2567.
(2) Palmer, J. L.; Abeles, R. H. *J. Biol. Chem.* **1979**, *254*, 1217.
(3) Jarvi, E. T.; McCarthy, J. R.; Mehdi, S.; Matthews, D. P.; Edwards, M. L.; Prakash, N. J.; Bowlin, T. L.; Sunkara, P. S.; Bey, P. *J. Med. Chem.* **1991**, *34*, 647.
(4) Wnuk, S. F.; Dalley, N. K.; Robins, M. J. *J. Org. Chem.* **1993**, *58*, 111.
(5) Robins, M. J.; Neschadimenko, V.; Ro, B.-O.; Yuan, C.-S.; Borchardt, R. T.; Wnuk, S. F. *J. Org. Chem.* **1998**, *63*, 1205.
(6) Onuma, S.; Kumamoto, H.; Kawato, M.; Tanaka, H. *Tetrahedron* **2002**, *58*, 2497.
(7) For the reaction of vinyl sulfides: (a) Schmidt, R. R.; Betz, R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 430. (b) Tanaka, H.; Hayakawa, H.; Obi, K.; Miyasaka, T. *Tetrahedron Lett.* **1985**, *26*, 6229. (c) Tanaka, H.; Hayakawa, H.; Obi, K.; Miyasaka, T. *Tetrahedron* **1986**, *42*, 4187. (d) Pallenberg, A. J.; White, J. D. *Tetrahedron Lett.* **1986**, *27*, 5591. (e) Hollingworth, G. J.; Perkins, G.; Sweeney, J. *J. Chem. Soc., Perkin Trans. 1* **1996**, 1913.

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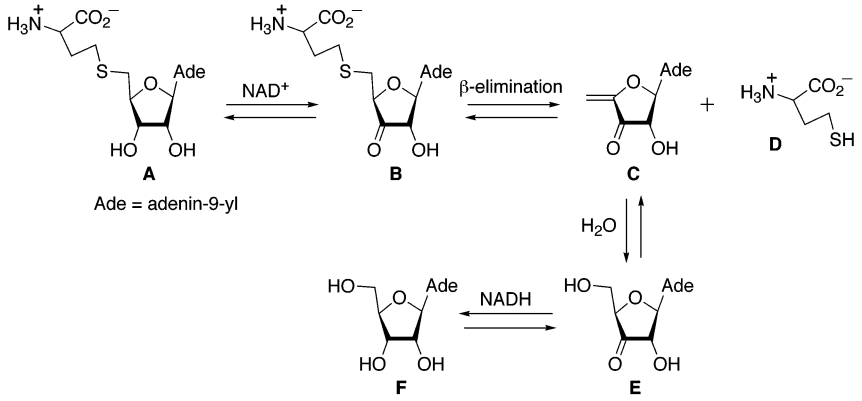
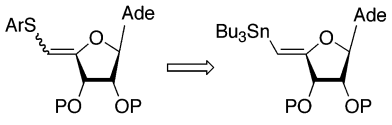
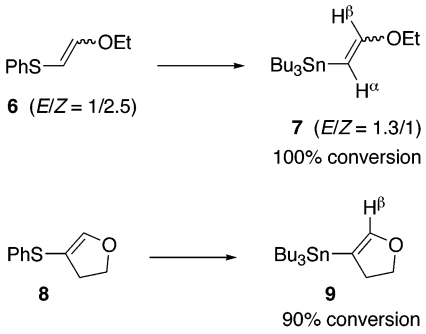
SCHEME 1



SCHEME 2



SCHEME 3. Reactions of 6 and 8 with Bu_3SnH/AIBN[a]

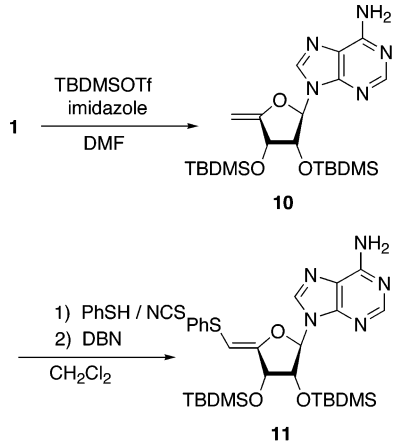


[a] Key: *i*-Pr_2NEt/benzene/80 °C/4 h.

stannane but it has an enol ether structure, we needed to see if the sulfur extrusion with tin radical also works with vinyl sulfides having a β-alkoxy substituent, and if the resulting products are stable enough for further manipulations. The initial study was, therefore, carried out by using simple β-alkoxy-substituted vinyl sulfides **6**[9] and **8** as model compounds (Scheme 3).

A 0.1 M solution of **6** in benzene containing Bu_3SnH (2.0 equiv), AIBN (0.2 equiv), and *i*-Pr_2NEt (3.0 equiv) was heated at 80 °C for 4 h. Despite the disappearance of **6**, no distinct product by TLC analysis (hexane) of the reaction mixture was observed. However, after removal of the solvent, ^{1}H NMR spectrum of the resulting mixture showed complete conversion to the desired vinylstannane **7** as evidenced by $J_{Sn,H}$: (*E*)-isomer, δ 4.63 (H^α, $J(^{119}Sn-^1H) = J(^{117}Sn-^1H) = 36.0$ Hz), 6.22 (H^β, $J(^{119}Sn-^1H) = J(^{117}Sn-^1H) = 33.6$ Hz); (*Z*)-isomer, δ 4.50 (H^α, $J(^{119}Sn-^1H) = J(^{117}Sn-^1H) = 47.6$ Hz), 6.78 (H^β, $J(^{119}Sn-^1H) = 98.0$ Hz, $J(^{117}Sn-^1H) = 95.6$ Hz).[10] The observed shift in the *E*/*Z* ratio from 1/2.5 of **6** to 1.3/1 of **7** suggests that partial inversion of the configuration occurred during this sulfur extrusion reaction. The instability to TLC of the stannylated product was also apparent for the reaction of 2,3-dihydro-4-phenylthiofuran (**8**), but again formation of **9** was confirmed by ^{1}H NMR spectrum of the reaction mixture: δ 6.08 (H^β, $J(^{119}Sn-^1H) = J(^{117}Sn-^1H) = 14.0$ Hz).

SCHEME 4



The preparation of a nucleosidic vinyl sulfide to be used as a substrate for the tin radical reaction was next carried out (Scheme 4). The starting material **1** was prepared from adenosine according to the published method.[11] Silylation of its 2′- and 3′-hydroxyl groups with TBDMSCl turned out to be unsatisfactory, resulting in a low yield of product with poor reproducibility. Use of TBDMSOTf gave **10** in 85% yield. Electrophilic addition of PhSCl was carried out by treating **11** with a mixture of PhSH (2.5

(8) For the reaction of vinyl sulfones: (a) Watanabe, Y.; Ueno, Y.; Araki, T.; Endo, T.; Okawara, M. *Tetrahedron Lett.* **1986**, *27*, 215. (b) Dubois, E.; Beau, J.-M. *Tetrahedron Lett.* **1990**, *31*, 5165. (c) McCarthy, J. R.; Matthews, D. P.; Stemerick, D. M.; Huber, E. W.; Bey, P.; Lippert, B. J.; Snyder, R. D.; Sunkara, P. S. *J. Am. Chem. Soc.* **1991**, *113*, 7439. (d) Wnuk, S. F.; Robins, M. J. *Can. J. Chem.* **1993**, *71*, 192. (e) McCarthy, J. R.; Huber, E. W.; Le, T.-B.; Laskovics, F. M.; Matthews, D. P. *Tetrahedron* **1996**, *52*, 45. (f) Kumamoto, H.; Onuma, S.; Tsuchiya, K.; Egusa, Y.; Tanaka, H.; Satoh, T. *Nucleosides Nucleotides Nucleic Acids* **2002**, *21*, 275.

(9) Vlattas, I.; Della Vecchia, L.; Lee A. O. *J. Am. Chem. Soc.* **1976**, *98*, 2008.

(10) For NMR data of vinylstannanes, see: Leusink, A. J.; Budding, H. A.; Drenth, W. *J. Organomet. Chem.* **1967**, *9*, 295.

(11) McCarthy, J. R., Jr.; Robins, R. K.; Robins, M. J. *J. Am. Chem. Soc.* **1968**, *90*, 4993.

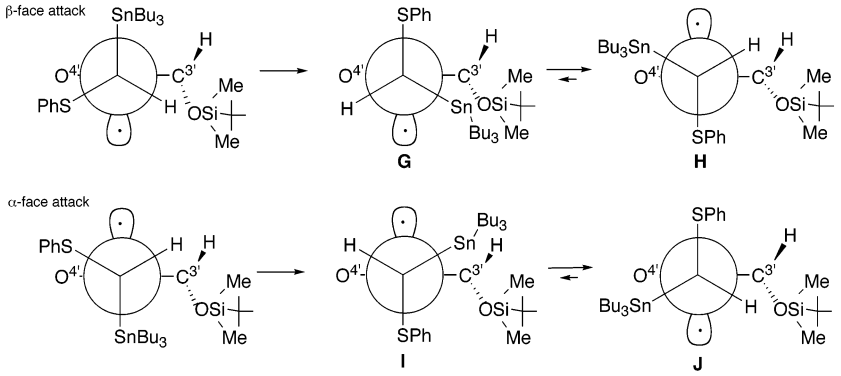


FIGURE 1. Possible stereochemical pathway for the selective formation of **12** from **11**.

SCHEME 5

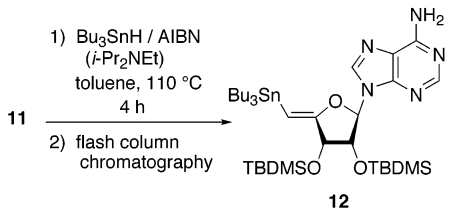


TABLE 1. Reaction of 11 with Tributyltin Radical

entry	*i*-Pr$_2$NEt (equiv)	purification	product (isolated yield, %)
1		silica gel	**12** (47), **10** (45)
2		Florisil	**12** (84), **10** (9)
3	3.0	Florisil	**12** (94)

equiv) and NCS (2.5 equiv) in CH_2Cl_2 at 0 °C. Subsequent elimination proceeded simply by adding DBN (2.0 equiv.) and then refluxing the reaction mixture. The product (*Z*)-4′,5′-didehydro-5′-deoxy-5′-(phenylthio)adenosine (**11**)[12] was isolated upon short column chromatography followed by crystallization in 68% yield (contaminated with succinimide, the yield was calculated by ^{1}H NMR spectroscopy).

Reaction of **11** with tributyltin radical was investigated (Scheme 5). The procedure employed is very simple, simply refluxing a mixture of **11** (0.1 M in toluene), Bu_3-SnH (3.0 equiv), and AIBN (0.5 equiv) for 4 h either in the presence or absence of *i*-Pr$_2$NEt (3.0 equiv). The stannylated product **12** was sufficiently stable[13] to permit its isolation by flash column chromatography (Table 1). As shown in entry 1, even by flash chromatography, silica gel caused a significant extent of protodestannylation leading to **10**. Use of Florisil as an absorbent greatly improved the isolated yield of **12** (entry 2), but a small amount of **10** was still isolated. The best result was obtained by conducting the reaction in the presence of *i*-Pr$_2$NEt (entry 3). The vinylstannane structure of **12** was readily elucidated from a characteristic splitting of H-5′ (δ 4.81) due to tin isotopes ($J(^{119}\mathrm{Sn}-^1\mathrm{H}) = J(^{117}\mathrm{Sn}-^1\mathrm{H}) = 37.6$ Hz). Its (*Z*)-stereochemistry was determined based on NOE experiment: H-5′/H-3′ (6.1%).

The observed sole formation of the stannylated (*Z*)-isomer (**12**) from **11** would be explicable based on the conformational preference of the intermediate C4′-radical as depicted in Figure 1. In the case of β-face attack of tributyltin radical, two conformers **G** and **H** are possible upon departure of thiyl radical. Since **G** is considered to be less favored because of the sterically constrained accommodation of the 3′-*O*-TBDMS group, surrounded by two bulky substituents $SnBu_3$ and SPh, elimination of the thiyl radical would take place from **H**. The same applies to conformers **I** and **J** which result from α-face attack of tributyltin radical. Overall, irrespective of the face-selectivity of tin radical attack, only the (*Z*)-isomer (**12**) is formed in this sulfur extrusion reaction. In support of the above proposed mechanism is the fact that a mixture of **11** and its (*E*)-isomer ($E/Z = 1.0/1.4$),[14] when subjected to the tin radical reaction, gave **12** as the sole product in 86% yield.

Synthesis of Potential Inhibitors against *S*-Adenosyl Homocysteine Hydrolase. Stannyl groups bound to sp^2-carbon atom can be manipulated in various ways.[15] Simple vinylstannanes are known to undergo halogenation with retention of configuration.[16] Halogenation was first examined by using (*Z*)-4′,5′-didehydro-5′-deoxy-5′-(tributylstannyl)adenosine (**12**). Iodination carried out with iodine in THF gave the (*Z*)-vinyl iodide **13**[17] in quantitative yield within 1 h at room temperature. Under similar conditions, NBS also works effectively to give **14** in 97% yield. The depicted *Z*-configuration of these compounds was confirmed based on NOE experiment: **13**, H-5′/H-3′ (7.5%); **14**, H-5′/H-3′ (8.7%). Chlorination of **12** with NCS, on the other hand, proceeded rather sluggishly, and required heating at 60 °C for 12 h. The product **15** (76% yield) was desilylated with TBAF (tetrabutylammonium fluoride) in THF to give the free nucleoside **16**, which gave an identical ^{1}H NMR spectrum

(12) The *Z*-configuration of **11** was determined on the basis of NOE experiments: H-5′/3′-O-SiMe (4.1%), H-5′/H-3′ (5.8%).

(13) For complete conversion of the isolated **12** to **10**, it took 57 h in 3 M AcOH in THF at room temperature.

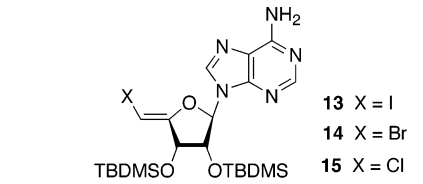
(14) This mixture was obtained by HPLC purification (hexane/EtOAc = 2/3, t_R 17.4−18.2 min) of the filtrate resulting from crystallization of **11**.

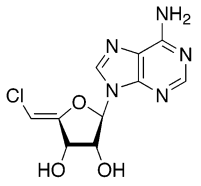
(15) Pereyre, M.; Quintard, J.-P.; Rahm, A. *Tin in Organic Synthesis*; Butterworth: London, 1987.

(16) (a) Collins, P. W.; Jung, C. J.; Gasiecki, A.; Pappo, R. *Tetrahedron Lett.* **1978**, 3187. (b) Chen, S.-M. L.; Schaub, R. E.; Grudzinskas, C. V. *J. Org. Chem.* **1978**, *43*, 3450.

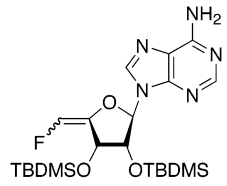
(17) Electrophilic addtion-elimination of AgF/iodine to N^6,N^6-dibenzoyl-4′,5′-didehydro-5′-deoxy-2′,3′-*O*-isopropylideneadenosine has been reported to yield the corresponding (*E*)-5′-iodo derivative: Jenkins, I. D.; Verheyden, J. P. H.; Moffatt, J. G. *J. Am. Chem. Soc.* **1976**, *98*, 3346.

(measured in DMSO-d_6) to the reported (*Z*)-isomer.[4]





16



a mixture of two geometrical isomers

17

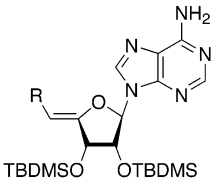
Fluorination with XeF_2 according to the reported method[18] gave an intractable mixture of products. Fluorination was more successful using 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (Selectfluor)[19] as an electrophilic fluorinating agent (in CH_3CN at room temperature for 15 min). However, there was obtained an inseparable mixture of the vinyl fluoride **17** [two geometrical isomers, ^{19}F NMR ($CDCl_3$) δ (relative to $CFCl_3$): −66.7 (d, J = 78.8 Hz) and −61.8 (d, J = 75.2 Hz), combined yield of 43% and diastereomeric ratio of ca. 3:1 calculated by ^1H NMR] and the destannylated byproduct **10** (53% by ^1H NMR). From the reported chemical shift of H-5′,[4,20] we assume that the (*E*)-isomer is dominant over the (*Z*)-isomer in this mixture.

Introduction of carbon substituents was next investigated. Although ample precedents of the Stille reaction[21] are available, vinylstannanes having an alkoxy group at the β-position have scarcely been used as substrates.[22] When the Stille coupling between **12** and PhI/($Pd(PPh_3)_4$/DMF) was carried out at room temperature, no reaction occurred irrespective of the presence or absence of CuI. At an elevated temperature of 80 °C, in the presence of CuI, protodestannylation to yield **10** was the sole observable event. These results led us to use the vinyl iodide **13** for C−C bond-forming reactions.

Although **13** remained unchanged upon reacting with $SnPh_4$ in the presence of $Pd(PPh_3)_4$ and CuI (in DMF, 80 °C, for 24 h), replacement of the catalyst with $(PPh_3)_2PdCl_2$ gave the desired product **18** in 12% yield.

Due to the poor solubility of $SnPh_4$, the reaction was reexamined by employing Bu_3SnPh. This gave a higher yield of **18** as shown in entry 1 of Table 2. In Table 2 are also included the results of other C−C bond-forming reactions. The reaction with $Bu_3SnCH{=}CH_2$ under similar conditions gave the conjugated diene **19** in good yield (entry 2). Use of $Bu_3SnCF{=}CF_2$[23] considerably shortened the reaction time to give **20** (entry 3), as can be expected from the highly electron-withdrawing nature of the trifluorovinyl group.[24] In entry 4 is exemplified a coupling reaction with a terminal alkyne by the formation of **21**.[25]

TABLE 2. Carbon−Carbon Bond-Forming Reactions Using 13[a]

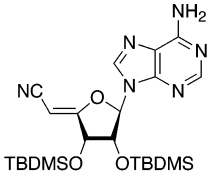


18 R = Ph
19 R = CH=CH$_2$
20 R = CF=CF$_2$
21 R = C≡CSiMe$_3$

entry	reagent (equiv)	*T* (°C)	reaction time	product (isolated yield, %)
1	Bu_3SnPh (3.0)	60	15 h	**18** (48)
2	$Bu_3SnCH{=}CH_2$ (4.0)	60	24 h	**19** (76)
3	$Bu_3SnCF{=}CF_2$ (5.0)	60	40 min	**20** (71)
4	$Me_3SiC{\equiv}CH$ (3.0)[b]	70	45 min	**21** (67)

[a] All reactions were carried out in DMF in the presence of CuI (0.2 equiv) and $(PPh_3)_2PdCl_2$ (0.2 equiv). [b] Triethylamine (3.0 equiv) was added to the reaction mixture.

TABLE 3. Transformation of 13 to the Vinylnitrile 22[a]



22

entry	$(PPh_3)_2PdCl_2$ (equiv)	CuI (equiv)	yield (%) of **22**
1	0.2		2
2	0.2	0.2	9
3	0.5	0.5	69
4	0.2	1.0	80
5	-	1.0	64

[a] All reactions were carried out in DMF by using Bu_3SnCN (4.0 equiv) at 120 °C for 24 h.

Finally, introduction of a cyano group was carried out. Nair et al. reported the first example of a Pd-catalyzed coupling between Bu_3SnCN and an aryl iodide, 2-iodoadenosine.[26] Compound **13** remained unchanged (recovery 90%) when reacted with Bu_3SnCN (3.0 equiv.) under Nair's conditions, $Pd(PPh_3)_4$/DMF/120 °C/20 h. By changing the catalyst to $(PPh_3)_2PdCl_2$, however, a small amount of the vinylnitrile **22** was formed as shown in entry 1 in Table 3. It was observed that addition of CuI to the reaction medium increased the yield of **22** (entries 2−4), although not exactly proportional. Quite unexpectedly,

(18) Tius, M. A.; Kawakami, J. K. *Synthetic Commun.* **1992**, *22*, 1461.

(19) Matthews, D. P.; Miller, S. C.; Jarvi, E. T.; Sabol, J. S.; McCarthy, J. R. *Tetrahedron Lett.* **1993**, *34*, 3057.

(20) The ^1H NMR spectrum of this mixture measured in $CDCl_3$ showed two H-5′ resonances corresponding to **17**: 6.85 (d, J = 78.8 Hz) for major isomer; 6.39 (d, J = 75.2 Hz) for minor isomer.

(21) For a review, see: Mitchell, T. N. *Synthesis* **1992**, 803.

(22) To the best of our knowledge, there has been only one report available for the Stille reaction of β-alkoxyvinylstannanes, see: Piers, E.; Lu, Y.-F. *J. Org. Chem.* **1988**, *53*, 926.

(23) For the preparation of this reagent, see: Burdon, J.; Coe, P. L.; Haslock, I. B.; Powell, R. L. *Chem. Commun.* **1996**, 49.

(24) Electron-withdrawing groups on the phenyl ring of Bu_3SnCH_2-Ph accelerate the coupling reaction with PhCOCl; see: Stille, J. K. *Angew. Chem., Int. Engl.* **1986**, *25*, 508.

(25) (a) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467. (b) Heck, R. F. *Acc. Chem. Res.* **1979**, *12*, 146.

(26) Nair, V.; Buenger, G. S. *J. Am. Chem. Soc.* **1989**, *111*, 8502.

a significant yield was seen even in the absence of the catalyst (entry 5).[27]

One might speculate that CuCN formed in this reaction could be the actual reactive species for this transformation, since there is a precedent that CuCN effects such reaction of a vinyl iodide.[28] This, however, still remains questionable, because no reaction was observed when **13** was treated with CuCN (3.0 equiv) in DMF at 120 °C for 24 h.

Conclusion

To develop a new approach to potential inhibitors to *S*-adenosyl-L-homocysteine (AdoHcy) hydrolase, sulfur extrusion reaction of 4′,5′-didehydro-5′-deoxy-5′-(phenylthio)adenosine was examined with tributyltin radical. As a result, exclusive formation of 9-[2,3-bis-*O*-(*tert*-butyldimethylsilyl)-5-(*Z*)-(tributylstannyl)-5-deoxy-*β*-D-*erythro*-pent-4-enofuranosyl]adenine (**12**) was observed, irrespective of the geometry of the substrate. Although **12** was stable enough to be isolated by flash column chromatography, its further manipulation was possible only for halogenation. Carbon−carbon bond-forming reactions at the 5′-position of the 5-deoxy-*β*-D-*erythro*-pent-4-enofuranosyl structure were, therefore, carried out by using the vinyl iodide (**13**) which was readily prepared from **12** in quantitative yield. Various types of carbon-substituents (phenyl, vinyl, trifluorovinyl, and ethynyl) were introduced based on palladium-catalyzed cross-coupling reaction. It was found that, in the case of introducing a cyano group, the presence of the Pd-catalyst was not necessarily required, although the actual reactive species involved in this reaction still remains to be identified.

Experimental Section

Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded at 500 MHz. Chemical shifts are reported relative to Me_4Si. ^{19}F NMR spectra were measured at 400 MHz with $CFCl_3$ as an internal standard. Mass spectra (MS) were taken in FAB mode with *m*-nitrobenzyl alcohol as a matrix. Column chromatography was carried out on silica gel (silica gel 60, Merck) unless otherwise noted. Thin-layer chromatography (TLC) was performed on silica gel (precoated silica gel plate F_{254}, Merck). HPLC was carried out on a Shimadzu LC-6AD with a Shim-pack PREP-SIL (H)· KIT column (2 × 25 cm).

Reaction of 6 with Tributyltin Radical: Formation of Tributyl(2-ethoxyvinyl)tin (7). A mixture of **6** (297 mg, 1.65 mmol), Bu_3SnH (890 μL, 3.3 mmol), AIBN (54 mg, 0.33 mmol), and *i*-Pr_2NEt (862 μL, 4.95 mmol) in benzene (16.5 mL) was heated at 80 °C for 4 h under positive pressure of dry Ar. Evaporation of the reaction mixture was followed by drying under reduced pressure. The resulting oily residue was analyzed by ^{1}H NMR spectroscopy to confirm quantitative conversion to **7**. For ***7E***: ^{1}H NMR ($CDCl_3$) δ 0.89−0.95 (9H, m, SnBu), 1.15−1.24 (9H, m, SnBu and CH_2CH_3), 1.28−1.35 (6H, m, SnBu), 1.49−1.66 (6H, m, SnBu), 3.79 (2H, q, J = 6.8 Hz, CH_2CH_3), 4.63 (1H, d, J = 15.6 Hz, $J_{Sn,H}$ = 36.0 Hz, SnC*H*=CH), 6.22 (1H, d, J = 15.6 Hz, $J_{Sn,H}$ = 33.6 Hz, SnCH=C*H*). For ***7Z***: ^{1}H NMR ($CDCl_3$) δ 0.89−0.95 (9H, m, SnBu), 1.15−1.24 (9H, m, SnBu and CH_2CH_3), 1.28−1.35 (6H, m, SnBu), 1.49−1.66 (6H, m, SnBu), 3.76 (2H, q, J = 6.8 Hz, CH_2-CH_3), 4.50 (1H, J = 7.2 Hz, $J_{Sn,H}$ = 47.6 Hz, SnC*H*=CH), 6.78 (1H, d, J = 7.2 Hz, $J_{Sn,H}$ = 98.0, 95.6 Hz, SnCH=C*H*).

2,3-Dihydro-4-phenylthiofuran (8). To a THF (15 mL) solution of 2,3-dihydrofuran (500 μL, 6.6 mmol) was added dropwise freshly prepared PhSCl[29] (950 μL) at −70 °C under positive pressure of dry Ar. After being stirred for 15 min, the mixture was further treated with KOBu-*t* (1.11 g, 9.9 mmol), and allowed to warm to room temperature over 1 h. The resulting mixture was partitioned between hexane and saturated aqueous $NaHCO_3$. The organic layer was dried (Na_2SO_4), evaporated, and purified by column chromatography (hexane/EtOAc = 50/1). This gave **8** (830 mg, 71%) as an oil: ^{1}H NMR ($CDCl_3$) δ 2.70 (2H, dt, J = 9.6, 2.0 Hz, H-3), 4.53 (2H, t, J = 9.6 Hz, H-2), 6.70 (1H, t, J = 2.0 Hz, H-5), 7.14−7.18 (1H, m, Ph), 7.27−7.29 (4H, m, Ph); FAB-MS *m*/*z* 178 (M^+ + H).

2,3-Dihydro-4-(tributylstannyl)furan (9). This compound was prepared from **8** by the procedure used for the preparation of **7** from **6**: ^{1}H NMR ($CDCl_3$) δ 0.87−0.97 (9H, m, SnBu), 1.05−1.16 (6H, m, SnBu), 1.26−1.36 (6H, m, SnBu), 1.47−1.62 (6H, m, SnBu), 2.59−2.68 (2H, m, H-3), 4.20 (2H, t, J = 9.2 Hz, H-2), 6.08 (1H, t, J = 2.0 Hz, $J_{Sn,H}$ = 14.0 Hz, H-5).

9-[2,3-Bis-*O*-(*tert*-butyldimethylsilyl)-5-deoxy-*β*-D-*erythro*-pent-4-enofuranosyl]adenine (10). To a mixture of **1** (4.84 g, 19.2 mmol) and imidazole (6.61 g, 97.1 mmol) in DMF (150 mL) was added TBDMSOTf (16.0 mL, 68 mmol) at 0 °C. The reaction mixture was stirred at rt for 48 h and then was partitioned between EtOAc and saturated aqueous $NaHCO_3$. Column chromatography (hexane/EtOAc = 1/1) of the organic layer gave **10** (7.9 g, 85%) as a foam. For physical data of **10**, see the supporting information of ref 30.

9-[2,3-Bis-*O*-(*tert*-butyldimethylsilyl)-5-deoxy-5-(*Z*)-(phenylthio)-*β*-D-*erythro*-pent-4-enofuranosyl]adenine (11). To a CH_2Cl_2 (15 mL) solution of NCS (349 mg, 2.61 mmol) was added PhSH (270 μL, 2.31 mmol) at 0 °C. After the mixture was stirred for 0.5 h, **10** (500 mg, 1.05 mmol) was added and stirring was continued further 0.5 h at 0 °C. After addition of DBN (260 μL, 2.1 mmol), the mixture was refluxed for 15 h. The reaction mixture was partitioned between CH_2Cl_2 and saturated aqueous $NaHCO_3$. Column chromatography (hexane/EtOAc = 1/1) of the organic layer gave a crude mixture of products, which was crystallized from ether−hexane to give **11** (441 mg). This material was contaminated with succinimide (ca. 5%) and the actual yield of **11** was 68% based on ^{1}H NMR spectroscopy. An analytical sample of **11** was obtained by HPLC (hexane/EtOAc = 1/2, t_R = 17.6 min) purification: mp 210−213 °C; UV (MeOH) λ_{max} 258 nm (ϵ 26 700), λ_{min} 232 nm (ϵ 12 600); ^{1}H NMR ($CDCl_3$) δ −0.29, −0.04, 0.16 and 0.17 (12H, each as s, SiMe), 0.78 and 0.96 (18H, each as s, Bu-*t*), 4.79 (1H, d, J = 4.0 Hz, H-3'), 5.20 (1H, dd, J = 6.0, 4.0 Hz, H-2'), 5.44 (1H, s, H-5'), 5.63 (2H, br, NH_2), 6.19 (1H, d, J = 6.0 Hz, H-1'), 7.14−7.18 (1H, m, Ph), 7.24−7.28 (2H, m, Ph), 7.34−7.36 (2H, m, Ph), 7.87 and 8.35 (2H, each as s, H-2 and H-8); FAB-MS *m*/*z* 586 (M^+ + H). Anal. Calcd for $C_{28}H_{43}N_5O_3Si_2$: C, 57.40; H, 7.40; N, 11.95. Found: C, 57.38; H, 7.48; N, 12.11.

9-[2,3-Bis-*O*-(*tert*-butyldimethylsilyl)-5-(*Z*)-(tributylstannyl)-5-deoxy-*β*-D-*erythro*-pent-4-enofuranosyl]adenine (12). A mixture of **11** (1.0 g, 1.7 mmol), Bu_3SnH (1.38 mL, 5.12 mmol), AIBN (140 mg, 0.85 mmol), and *i*-Pr_2NEt (890 μL, 5.12 mmol) in toluene (17 mL) was refluxed for 4 h under positive pressure of dry Ar. The reaction mixture was evaporated, and the residue was purified by flash Florisil column chromatography (hexane/EtOAc = 4/1). This gave **12** (1.23 g, 94%) as an oil: UV (MeOH) λ_{max} 259 nm (ϵ 17 200) λ_{min} 240

(27) The NOE correlations (measured in $CDCl_3$) between H-5′ and H-3′ of **18**−**20** and **22** are as follows: **18** 8.6%; **19** 6.6%; **20** 7.2%; **22** 5.9%. The *Z*-stereochemistry of **21** was confirmed after converting to the corresponding free nucleoside (H-5′/H-3′, 1.8% in DMSO-d_6).

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nm (ϵ 11 000); ^{1}H NMR ($CDCl_3$) δ −0.31, −0.07, 0.13 and 0.15 (12H, each as s, SiMe), 0.75 and 0.93 (18H, each as s, Bu-*t*), 0.78−0.82 (15H, m, SnBu), 1.14−1.26 (6H, m, SnBu), 1.34−1.44 (6H, m, SnBu), 4.49 (1H, d, J = 4.4 Hz, H-3'), 4.81 (1H, $J(^{119}Sn-^1H) = J(^{117}Sn-^1H)$ = 37.6 Hz, H-5'), 5.03 (1H, dd, J = 6.0, 4.4 Hz, H-2'), 5.64 (2H, br, NH_2), 6.09 (1H, d, J = 6.0 Hz, H-1'), 7.86 and 8.35 (2H, each as s, H-2 and H-8); FAB-MS *m*/*z* 769 (M^+ + H). Anal. Calcd for $C_{34}H_{66}N_5O_3Si_2Sn$: C, 53.19; H, 8.66; N, 9.12. Found: C, 53.27; H, 8.36; N, 9.09.

9-[2,3-Bis-*O*-(*tert*-butyldimethylsilyl)-5-deoxy-5-(*Z*)-iodo-*β*-D-*erythro*-pent-4-enofuranosyl]adenine (13). A mixture of **12** (722 mg, 0.94 mmol) and iodine (359 mg, 1.41 mmol as I_2) in THF (10 mL) was stirred for 1 h at rt. The reaction mixture was partitioned between $CHCl_3$ and saturated aqueous $Na_2S_2O_3$. Column chromatography (hexane/EtOAc = 1/1) of the organic layer gave **13** (565 mg, 100%) as a solid: mp 251−254 °C; UV (MeOH) λ_{max} 259 nm (ϵ 17 500), λ_{min} 238 nm (ϵ 9500); ^{1}H NMR ($CDCl_3$) δ −0.31, −0.07, 0.14 and 0.15 (12H, each as s, SiMe), 0.75 and 0.94 (18H, each as s, Bu-*t*), 4.74 (1H, d, J = 4.0 Hz, H-3'), 5.15 (1H, dd, J = 6.4, 4.0 Hz, H-2'), 5.23 (1H, s, H-5'), 5.61 (2H, br, NH_2), 6.21 (1H, d, J = 6.4 Hz, H-1'), 7.90 and 8.36 (2H, each as s, H-2 and H-8); FAB-MS *m*/*z* 604 (M^+ + H). Anal. Calcd for $C_{22}H_{38}IN_5O_3Si_2$: C, 43.77; H, 6.35; N, 11.60. Found: C, 44.05; H, 6.34; N, 11.59.

9-[5-(*Z*)-Bromo-2,3-bis-*O*-(*tert*-butyldimethylsilyl)-5-deoxy-*β*-D-*erythro*-pent-4-enofuranosyl]adenine (14). A mixture of **12** (785 mg, 1.02 mmol) and NBS (273 mg, 1.54 mmol) in THF (10 mL) was stirred for 1 h at rt. The reaction mixture was partitioned between $CHCl_3$ and saturated aqueous $NaHCO_3$. Column chromatography (hexane/EtOAc = 1/1) of the organic layer gave **14** (533 mg, 94%) as a solid: mp 249−251 °C; UV (MeOH) λ_{max} 259 nm (ϵ 17 600), λ_{min} 231 nm (ϵ 8000); ^{1}H NMR ($CDCl_3$) δ −0.31, −0.07, 0.45 and 0.16 (12H, each as s, SiMe), 0.75 and 0.95 (18H, each as s, Bu-*t*), 4.69 (1H, d, J = 4.4 Hz, H-3'), 5.16 (1H, dd, J = 6.8, 4.4 Hz, H-2'), 5.39 (1H, s, H-5'), 5.87 (2H, br, NH_2), 6.21 (1H, d, J = 6.8 Hz, H-1'), 7.92 and 8.34 (2H, each as s, H-2 and H-8); FAB-MS *m*/*z* 556 and 558 (M^+ + H). Anal. Calcd for $C_{22}H_{38}BrN_5O_3Si_2$: C, 47.47; H, 6.88; N, 12.58. Found: C, 47.76; H, 6.95; N, 12.44.

9-[2,3-Bis-*O*-(*tert*-butyldimethylsilyl)-5-(*Z*)-chloro-5-deoxy-*β*-D-*erythro*-pent-4-enofuranosyl]adenine (15). A mixture of **12** (148 mg, 0.19 mmol) and NCS (40 mg, 0.29 mmol) in THF (5 mL) was heated at 60 °C for 12 h. The reaction mixture was partitioned between $CHCl_3$ and saturated aqueous $NaHCO_3$. Column chromatography (hexane/EtOAc = 1/1) of the organic layer gave **15** (74 mg, 76%) as a solid: mp 243−245 °C; UV (MeOH) λ_{max} 259 nm (ϵ 16 200), λ_{min} 232 nm (ϵ 5400); ^{1}H NMR ($CDCl_3$) δ −0.32, −0.07, 0.14 and 0.15 (12H, each as s, SiMe), 0.75 and 0.95 (18H, each as s, Bu-*t*), 4.68 (1H, d, J = 4.0 Hz, H-3'), 5.20 (1H, dd, J = 6.8, 4.0 Hz, H-2'), 5.40 (1H, s, H-5'), 5.68 (2H, br, NH_2), 6.20 (1H, d, J = 6.8 Hz, H-1'), 7.90 and 8.36 (2H, each as s, H-2 and H-8); FAB-MS *m*/*z* 513 (M^+ + H). Anal. Calcd for $C_{22}H_{38}ClN_5O_3Si_2$: C, 51.59; H, 7.48; N, 13.67. Found: C, 51.83; H, 7.71; N, 13.65.

9-[2,3-Bis-*O*-(*tert*-butyldimethylsilyl)-5-deoxy-5-fluoro-*β*-D-*erythro*-pent-4-enofuranosyl]adenine (17). A mixture of **12** (139 mg, 0.18 mmol) and Selectfluor (96 mg, 0.27 mmol) in CH_3CN (5 mL) was stirred at room temperature for 15 min under positive pressure of dry Ar. The reaction mixture was partitioned between $CHCl_3$ and saturated aqueous $NaHCO_3$. Column chromatography (hexane/EtOAc = 1/1) of the organic layer gave a mixture of **17*Z***, **17*E***, and **10** (84 mg, **17*Z***/**17*E***/**10** = 1/3/5). Yields of the products were calculated by ^{1}H NMR spectroscopy by integrating H-5′: **17**, 43%; **10**, 53%: ^{19}F NMR ($CDCl_3$) δ −66.7 (d, J = 78.8 Hz), −61.8 (d, J = 75.2 Hz). Partial ^{1}H NMR data for **17*E***: ^{1}H NMR ($CDCl_3$) δ −0.37, −0.15, and 0.04 (12H, each as s, SiMe), 0.59 and 0.80 (18H, each as s, Bu-*t*), 4.93 (1H, q, J = 4.4, 2.0 Hz, H-3′), 5.23 (1H, dd, J = 8.0, 4.4 Hz, H-2′), 6.10 (1H, d, J = 8.0 Hz, H-1′), 6.85 (1H, d, J = 78.8 Hz, H-5′), 7.87 and 8.37 (2H, each as s, H-2 and H-8). Partial ^{1}H NMR data for **17*Z***: ^{1}H NMR ($CDCl_3$) δ 5.23 (1H, m, H-2′), 5.15 (1H, d, J = 7.2 Hz, H-1′), 6.39 (1H, d, J = 75.2 Hz, H-5′), 7.89 and 8.36 (2H, each as s, H-2 and H-8); FAB-MS for **17** *m*/*z* 497 (M^+ + H).

9-[2,3-Bis-*O*-(*tert*-butyldimethylsilyl)-5-deoxy-5-(*Z*)-phenyl-*β*-D-*erythro*-pent-4-enofuranosyl]adenine (18). A mixture of **13** (200 mg, 0.33 mmol), $PhSnBu_3$ (323 μL, 0.99 mmol), $(PPh_3)_2PdCl_2$ (49 mg, 0.07 mmol), and CuI (13 mg, 0.07 mmol) in DMF (1.5 mL) was heated at 60 °C for 15 h under positive pressure of dry Ar. The reaction mixture was partitioned between EtOAc and saturated aqueous $NaHCO_3$. Column chromatography (hexane /EtOAc = 1/1) of the organic layer gave **18** (88 mg, 48%) as a solid: mp 222−224 °C; UV (MeOH) λ_{max} 263 nm (ϵ 38 700), λ_{min} 229 nm (ϵ 9900); ^{1}H NMR ($CDCl_3$) δ −0.30, −0.06, 0.17 and 0.20 (12H, each as s, SiMe), 0.76 and 0.96 (18H, each as s, Bu-*t*), 4.68 (1H, d, J = 4.4 Hz, H-3'), 5.10 (1H, dd, J = 6.8, 4.4 Hz, H-2'), 5.55 (1H, s, H-5'), 5.62 (2H, br, NH_2), 6.34 (1H, d, J = 6.8 Hz, H-1'), 7.11−7.15 (1H, m, Ph), 7.22−7.26 (2H, m, Ph), 7.45−7.47 (2H, m, Ph), 7.95 and 8.36 (2H, each as s, H-2 and H-8); FAB-MS *m*/*z* 554 (M^+ + H). Anal. Calcd for $C_{28}H_{43}N_5O_3Si_2$: C, 60.72; H, 7.83; N, 12.65. Found: C, 60.52; H, 8.06; N, 12.54.

9-[2,3-Bis-*O*-(*tert*-butyldimethylsilyl)-5-deoxy-5-(*Z*)-vinyl-*β*-D-*erythro*-pent-4-enofuranosyl]adenine (19). A mixture of **13** (400 mg, 0.66 mmol), tributylvinyltin (775 μL, 2.65 mmol), $(PPh_3)_2PdCl_2$ (98 mg, 0.13 mmol), and CuI (26 mg, 0.13 mmol) in DMF (3 mL) was heated at 60 °C for 24 h under positive pressure of dry Ar. The reaction mixture was partitioned between EtOAc and saturated aqueous $NaHCO_3$. Column chromatography (hexane/EtOAc = 1/1) of the organic layer gave **19** (252 mg, 76%) as a solid: mp 211−215 °C; UV (MeOH) λ_{max} 248 nm (ϵ 35 500), λ_{min} 222 nm (ϵ 11 500), 260 nm (shoulder); ^{1}H NMR ($CDCl_3$) δ −0.31, −0.08, 0.13 and 0.15 (12H, each as s, SiMe), 0.75 and 0.92 (18H, each as s, Bu-*t*), 4.56 (1H, d, J = 4.0 Hz, H-3'), 4.96 (1H, dd, J = 10.8, 2.0 Hz, CH=CH_2), 5.05 (1H, dd, J = 6.4, 4.0 Hz, H-2'), 5.13 (1H, dd, J = 17.2, 2.0 Hz, CH=CH_2), 5.32 (1H, d, J = 10.8 Hz, H-5'), 5.74 (2H, br, NH_2), 6.19 (1H, d, J = 6.4 Hz, H-1'), 6.50 (1H, dt, J = 17.2, 10.8 Hz, CH=CH_2), 7.92 and 8.37 (2H, each as s, H-2 and H-8); FAB-MS *m*/*z* 504 (M^+ + H). Anal. Calcd for $C_{24}H_{41}N_5O_3Si_2$: C, 57.22; H, 8.20; N, 13.90. Found: C, 57.30; H, 8.44; N, 13.78.

9-[2,3-Bis-*O*-(*tert*-butyldimethylsilyl)-5-deoxy-5-(*Z*)-(trifluorovinyl)-*β*-D-*erythro*-pent-4-enofuranosyl]adenine (20). A mixture of **13** (400 mg, 0.66 mmol), tributy(trifluorolvinyl)-tin (1.23 g, 3.31 mmol), $(PPh_3)_2PdCl_2$ (98 mg, 0.13 mmol), and CuI (26 mg, 0.13 mmol) in DMF (3 mL) was heated at 60 °C for 40 min under positive pressure of dry Ar. The reaction mixture was partitioned between EtOAc and saturated aqueous $NaHCO_3$. Florisil column chromatography (hexane/EtOAc = 2/1) of the organic layer gave **20** (263 mg, 71%) as a solid: mp 152−154 °C; UV (MeOH) λ_{max} 249 nm (ϵ 23 400), λ_{min} 225 nm (ϵ 17 000); ^{1}H NMR ($CDCl_3$) δ −0.21, −0.04, 0.15 and 0.16 (12H, each as s, SiMe), 0.79 and 0.96 (18H, each as s, Bu-*t*), 4.80 (1H, d, J = 4.4 Hz, H-3'), 5.03 (1H, dd, $J_{H,F}$ = 22.8, 3.6 Hz, H-5'), 5.10 (dd, J = 5.2, 4.4 Hz, H-2'), 5.60 (2H, br, NH_2), 6.17 (1H, d, J = 5.2 Hz, H-1'), 7.87 and 8.35 (2H, each as s, H-2 and H-8); ^{13}C NMR ($CDCl_3$) δ −5.2, −4.7, −4.5 and −4.4 (SiMe), 17.9 and 18.0 (*C*Me_3), 25.6 and 25.8 (C*Me*$_3$), 73.0 (C-3'), 73.6 (C-2'), 87.4 (dd, $J_{C,F}$ = 20.7, 5.2 Hz, C-5'), 90.6 (C-1'), 120.5 (C-5), 125.6 (ddd, $J_{C,F}$ = 231.7, 50.7, 20.7 Hz, C-6'), 140.0 (C-8), 149.8 (C-4), 152.3 (ddd, $J_{C,F}$ = 290.7, 281.4, and 47.6 Hz, C-7'), 153.2 (C-2), 155.6 (C-6), 156.5 (dd, $J_{C,F}$ = 9.3, 4.1 Hz, C-4'); ^{19}F NMR ($CDCl_3$) δ −175.5 (ddd, $J_{F,F}$= 110.9, 30.2 Hz, $J_{H,F}$= 22.8 Hz), −117.3 (ddd, $J_{F,F}$ = 110.9, 69.2 Hz, $J_{H,F}$ = 3.6 Hz), −103.7 (dd, $J_{F,F}$ = 69.2 and 30.2 Hz). FAB-MS *m*/*z* 558 (M^+ + H). Anal. Calcd for $C_{24}H_{38}F_3N_5O_3Si_2$: C, 51.68; H, 6.87; N, 12.56. Found: C, 51.88; H, 6.95; N,12.63.

9-[2,3-Bis-*O*-(*tert*-butyldimethylsilyl)-5-deoxy-5-(*Z*)-(trimethysilylethynyl)-*β*-D-*erythro*-pent-4-enofuranosyl]adenine (21). A mixture of **13** (700 mg, 1.16 mmol), trimethylsilylacetylene (491 μL, 3.48 mmol), $(PPh_3)_2PdCl_2$ (161 mg, 0.23 mmol), CuI (44 mg, 0.23 mmol), and *i*-Pr_2NEt (606 μL, 3.48

mmol) in DMF (10 mL) was heated at 70 °C for 45 min under positive pressure of dry Ar. The reaction mixture was partitioned between EtOAc and saturated aqueous $NaHCO_3$. Column chromatography (hexane/EtOAc = 1/1) of the organic layer gave **21** (446 mg, 67%) as a solid: mp 150−154 °C; UV (MeOH) λ_{max} 254 nm (ϵ 35 900), λ_{min} 224 nm (ϵ 12 500); ^{1}H NMR ($CDCl_3$) δ −0.21, −0.03, 0.14 and 0.15 (12H, each as s, SiMe), 0.14 (9H, s, TMS), 0.79 and 0.65 (18H, each as s, Bu-*t*), 4.82 (1H, s, H-5'), 4.83 (1H, d, J = 4.4 Hz, H-3'), 4.96 (1H, dd, J = 5.2, 4.4 Hz, H-2'), 5.63 (2H, br, NH_2), 6.23 (1H, d, J = 5.2 Hz, H-1'), 7.91 and 8.36 (2H, each as s, H-2 and H-8); FAB-MS *m*/*z* 574 ($M^+ + H$). Anal. Calcd for $C_{27}H_{47}N_5O_3Si_3$: C, 56.50; H, 8.25; N, 12.20. Found: C, 56.73; H, 8.50; N, 12.14.

9-[2,3-Bis-*O*-(*tert*-butyldimethylsilyl)-5-(*Z*)-cyano-5-deoxy-*β*-D-*erythro*-pent-4-enofuranosyl]adenine (22). A mixture of **13** (200 mg, 0.33 mmol), tributyltin cyanide (420 mg, 1.33 mmol), $(PPh_3)_2PdCl_2$ (55 mg, 0.07 mmol), and CuI (63 mg, 0.33 mmol) in DMF (1.5 mL) was heated at 120 °C for 24 h under positive pressure of dry Ar. The reaction mixture was partitioned between EtOAc and saturated aqueous $NaHCO_3$. Column chromatography (hexane/EtOAc = 1/3) of the organic layer gave **22** (132 mg, 80%) as a solid, which was crystallized from Et_2O−hexane: mp 249−251 °C; UV (MeOH) λ_{max} 257 nm (ϵ 15 700) and 233 nm (ϵ 18 500), λ_{min} 248 nm (ϵ 15 600) and 223 nm (ϵ 17 000); ^{1}H NMR ($CDCl_3$) δ −0.09, 0.03, 0.17, and 0.18 (12H, each as s, SiMe), 0.84 and 0.96 (18H, each as s, Bu-*t*), 4.59 (1H, d, J = 1.2 Hz, H-5'), 5.15 (1H, dd, J = 4.8, 3.2 Hz, H-2'), 5.39 (1H, dd, J = 4.8, 1.2 Hz, H-3'), 5.95 (2H, br, NH_2), 6.16 (1H, d, J = 3.2 Hz, H-1'), 7.88 and 8.31 (2H, each as s, H-2 and H-8); ^{13}C NMR ($CDCl_3$) δ −5.0, −4.7, −4.6 and −4.5 (SiMe), 17.9 and 18.1 (*C*Me_3), 25.6 and 25.7 (C*Me*$_3$), 70.5 (C-5'), 72.5 (C-3'), 73.0 (C-2'), 92.3 (C-1'), 114.9 (CN), 120.5 (C-5), 140.3 (C-8), 149.3 (C-4), 153.3 (C-2), 155.9 (C-6), 173.7 (C-4'); FAB-MS *m*/*z* 503 ($M^+ + H$). Anal. Calcd for $C_{23}H_{38}N_6O_3Si_2$: C, 54.95; H, 7.62; N, 16.72. Found: C, 54.93; H, 7.76; N, 16.66.

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