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Synthesis of [5′-^{13}C]Ribonucleosides and 2′-Deoxy[5′-^{13}C]ribonucleosides

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The present efficient synthesis of [5′-^{13}C]ribonucleosides and 2′-deoxy[5′-^{13}C]ribonucleosides is characterized by the synthesis of the D-[5-^{13}C]ribose derivative as an intermediate via the Wittig reaction of 4-*aldehydo*-D-erythrose dialkyl acetals with $Ph_3P^{13}CH_3I-BuLi$ to introduce the ^{13}C label at the 5-position of a pentose. This was followed by the highly diastereoselective osmium dihydroxylation for the preparation of 2,3-di-*O*-benzyl-D-[5-^{13}C]ribose dialkyl acetal and the cyclization from D-[5-^{13}C]ribose dialkyl acetal derivatives to the alkyl D-[5-^{13}C]ribofuranoside derivative by the use of $LiBF_4$. The obtained D-[5-^{13}C]ribose derivative was converted into [5′-^{13}C]-ribonucleosides and subsequently into the corresponding 2′-deoxynucleosides.

Introduction

The conformational diversity of the sugar−phosphate backbone and/or the sugar moieties in nucleic acids is considered to be important in the elucidation of nucleic acid−protein or −medicine recognition processes. An efficient synthetic method for 2′-deoxy[5′-^{2}H]ribonucleosides (5′*S*/5′*R* = ca. 2:1)[1] has been developed, with the expectation that this would enable us to assign unambiguously both the H5′ and H5″ signals of an oligodeoxyribonucleotide and to determine its sugar−phosphodiester backbone conformation spectroscopically by NMR. NOESY and DQF−COSY NMR analyses of the decamer d(G*C*A*T*T*A*A*T*G*C*) bearing these deuterium-labeled nucleotides were performed. The complete stereospecific assignments and the simplified spin systems enabled us to determine the 15 ^3J coupling constants between H4′ and H5′/H5″ and to assign unambiguously 135 NOESY cross-peaks originating from H4′/H5′/H5″ resonances.[2] In addition, the duplex d(C*G*C*G*A*-A*T*T*C*G*C*G*)$_2$ constructed from these labeled components proved their utility in 2D ^{1}H−^{31}P HSQC.[3]

From another point of view, the site-specific labeling of the 5′ position of nucleosides with ^{13}C could facilitate conformational studies of an oligonucleotide chain, in terms of heteronuclear multidimensional NMR spectroscopy.

The chemical syntheses of [5′-^{13}C]adenosine and D-[5-^{13}C]ribose have been reported by Matwiyoff et al.[4] and Serianni et al.,[5] respectively. Matwiyoff et al.[4] prepared [5′-^{13}C]adenosine by the coupling reaction of an adenine derivative with a D-[5-^{13}C]ribose derivative, which was synthesized by way of L-[1-^{13}C]ribonic acid obtained by the reaction of L-erythrose with K^{13}CN, followed by hydrolysis under acidic conditions. Serianni et al.,[5] on the other hand, synthesized D-[5-^{13}C]ribose from D-[6-^{13}C]-glucose, which was obtained by the reaction of 1,2-*O*-isopropylidene-α-D-*xylo*-pentdialdo-1,4-furanoside with K^{13}CN. These synthetic methods, however, inevitably involved multiple steps after the introduction of the ^{13}C label to attain the final product and were therefore judged impractical. Thus, more efficient processes were needed to prepare [5′-^{13}C]nucleosides. We have published a letter[6] and a short communication[7] regarding the efficient synthesis of 2′-deoxy[5′-^{13}C]ribonucleosides. The detailed results thus obtained are described herein.

Results and Discussion

I. Synthesis of 1-*O*-Acetyl-2,3,5,-tri-*O*-benzoyl-D-[5-^{13}C]ribofuranose from D-Ribose. The first step for the synthesis of [5′-^{13}C]nucleosides was the synthesis of 1-*O*-Ac-2,3,5-tri-*O*-benzoyl-D-[5-^{13}C]ribofuranose (**12**) from D-ribose (**1**) via D-[5-^{13}C]ribose dialkyl acetal derivatives (**7**).

Synthesizing the Substrate To Introduce the Carbon-13 Label at the 5 Position of D-Ribose (Scheme 1). The chemical conversion of D-ribose (**1**) into 4-*aldehydo*-2,3-di-*O*-benzyl-D-erythrose dibenzyl acetal (**5-Bn**) and the corresponding dimethyl acetal (**5-Me**),

(1) (a) Kawashima, E.; Toyama, K.; Ohshima, K.; Kainosho, M.; Kyogoku, Y.; Ishido, Y. *Chirality* **1997**, *9*(5/6), 435−442. (b) Kawashima, E., Toyama, K., Ohshima, K., Kainosho, M.; Kyogoku, Y.; Ishido, Y. *Tetrahedron Lett.* **1995**, *36*, 6699−6700.

(2) Kojima, C.; Kawashima, E.; Toyama, K.; Ohshima, K.; Ishido, Y.; Kainosho, M.; Kyogoku, Y. *J. Biomol. NMR* **1998**, *11*, 103−109.

(3) Ono, A.; Makita, T.; Tate, S.; Kawashima, E.; Ishido, Y.; Kainosho, M. *Magn. Reson. Chem.* **1996**, *34*, s40-s46.

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(7) Kawashima, E.; Sekine, T.; Umabe, K.; Naito, Y.; Kamaike, K.; Kojima, C.; Mizukoshi, T.; Suzuki, E.; Ishido, Y. *Nucleosides Nucleotides* **1999**, *18*, 1597−1598.

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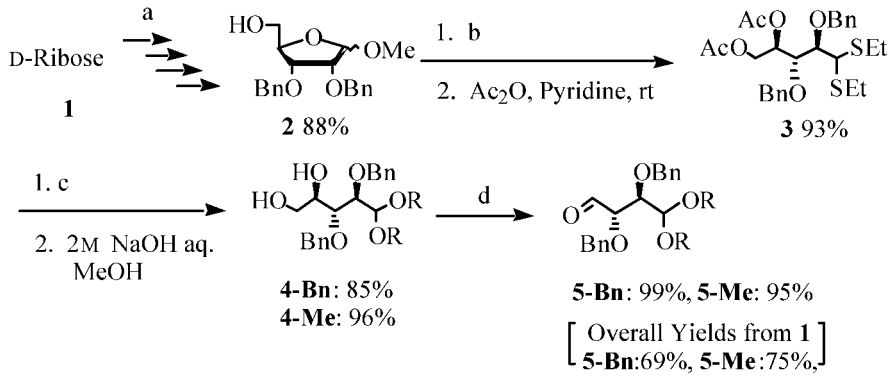
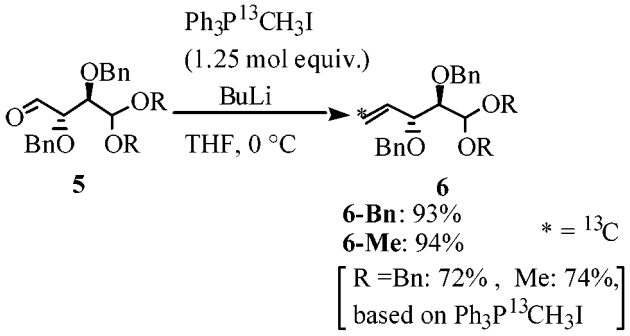
SCHEME 1. Synthesis of the Substrate for Introducing the ^{13}C Label at the 5 Position of D-Ribose[a]



[a] Reagent and conditions: (a) methyl ribosylation, 5-*O*-dimethoxytritylation, 2,3-di-*O*-benzylation, dedimethoxytritylation at the 5 position; (b) EtSH, concd HCl, 0 °C by the method of Stahley et al.;[8] (c) ROH (benzyl and methyl alcohol), HgO, $HgCl_2$, $CaSO_4$, 70 °C by the method of Serfontein et al.;[9] (d) **4-Bn**: $NaIO_4$, 5 mM H_2SO_4 in EtOH/H_2O (9/1), rt; **4-Me**: $NaIO_4$ in EtOH/H_2O (9/1), rt.

SCHEME 2. Introduction of the ^{13}C-Label at the C5 by the Wittig Reaction



which are the substrates to introduce the carbon-13 label at the 5 position of D-ribose by the Wittig reaction using a [^{13}C]methyltriphenylphosphonium iodide ($Ph_3P^{13}CH_3I$), was efficiently performed by the sequence reactions shown in Scheme 1. Compound **1** was successfully converted into **5-Bn** in 69% and **5-Me** in 75% overall yields in nine steps, respectively.

Introduction of the ^{13}C Label at the 5-Position of a D-Ribofuranose Derivative (Scheme 2). The introduction of the carbon-13 label proceeded by the Wittig reaction,[10] using a $Ph_3P^{13}CH_3I$−butyllithium (BuLi) system to give 2,3-di-*O*-dibenzyl-4,5-didehydro-4,5-dideoxy-D-[5-^{13}C]ribofuranose dibenzyl acetal (**6-Bn**) and dimethyl acetal (**6-Me**) in excellent yields of 93% and 94%, respectively (Scheme 2).

The ^{1}H NMR chart of **6-Bn** is shown in Figure 1, along with that of the corresponding nonlabeled sample, which demonstrates its reasonable structure by comparing that of the corresponding nonlabeled sample with respect to the H5 signal region. Only the C5 signal was recognized in the C-13 NMR chart of **6-Bn** in Figure 2. A comparison of these spectra shows the introduction of the ^{13}C label at the 5-position of **6-Bn** achieved in the present work.

Highly Diastereoselective Dihydroxylation Reaction with OsO_4 for the Preparation of the D-[5-^{13}C]-Ribose Derivative (Schemes 3 and 4). In the next step, we investigated the diastereoselective dihydroxylation of **6**. The asymmetric dihydroxylation (AD) reaction[11] of **6** with osmium tetraoxide (OsO_4), as well as the introduction of the carbon-13 label by the Wittig reaction, was also one of the important key steps in this synthetic route. By the use of nonlabeled 2,3-di-*O*-benzyl-4,5-didehydro-4,5-dideoxy-D-ribose dibenzyl acetal (**6′-Bn**), the reaction conditions were examined through two routes of stoichiometric[12a] (osmium tetraoxide 1.2 mol equiv in pyridine) and catalytic[12b] (osmium tetraoxide 0.05 mol equiv and 4-methylmorpholine *N*-oxide) procedures. Both of the reactions gave a mixture of 2,3-di-*O*-benzyl-D-ribose dibenzyl acetal (**7′-Bn**) (3,4-*anti*; 4*R*) and L-*lyxo* (3,4-*syn;* 4*S*) isomer, with the ratios of 92:8 and 93:7 in 97% yield, respectively (Table 1). The confirmation of structures and the proportions of these products were determined by comparison with **4-Bn** and by ^{1}H NMR spectroscopy after their conversion into the 4,5-di-*O*-benzoyl derivatives **8** (Scheme 3 and Table 1).

TABLE 1. OsO_4 Dihydroxylation Reaction of 6′-Bn (Nonlabeled)

procedure	reagents	**7′-Bn** (nonlabeled) yield (%)	4*R*/4*S*
stoichiometric	OsO_4 (1.2 mol equiv) pyridine	97	92:8
catalytic	OsO_4 (0.05 mol equiv) 4-methylmorpholine *N*-oxide	97	93:7

The efficiency under these conditions led us to use the catalytic procedure for the reaction of **6** to give a mixture of the 2,3-di-*O*-benzyl-D-[5-^{13}C]ribose dibenzyl acetal (**7-Bn**) and the L-*lyxo* isomer from **6-Bn** [quenching by sodium hydrogen sulfite ($NaHSO_3$)] and a mixture of the corresponding dimethyl acetal (**7-Me**) and the L-*lyxo* isomer from **6-Me** [quenching by an aqueous solution of saturated sodium disulfite ($Na_2S_2O_5$)[13]], in 99% (93:7) and

(8) (a) Kennea, G. W.; Robba, H. J.; Todd, A. R. *J. Chem. Soc.* **1949**, 1613−1620. (b) Wolfrom, M. I.; Newlin, M. R.; Stahly, E. E. *J. Am. Chem. Soc.* **1931**, *53*, 4379−4383.

(9) Jordaan, J. H.; Serfontein, W. J. *J. Org. Chem.* **1963**, 1395−1397.

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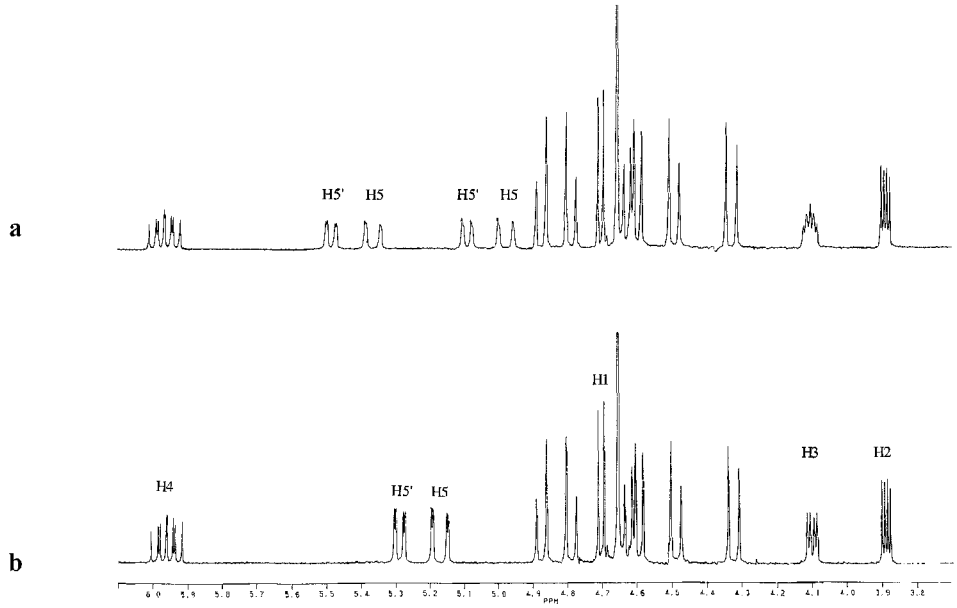

FIGURE 1. ^{1}H NMR spectra of 2,3-di-*O*-benzyl-4,5-didehydro-4,5-dideoxy-D-[5-^{13}C]ribose dibenzyl acetal (**6-Bn)** (panel a) and the corresponding nonlabeled D-ribose dibenzyl acetal **6′-Bn** (panel b). The spectra of a clearly show the *J* network through the H-5 and H-5′ protons and the 5-^{13}C.

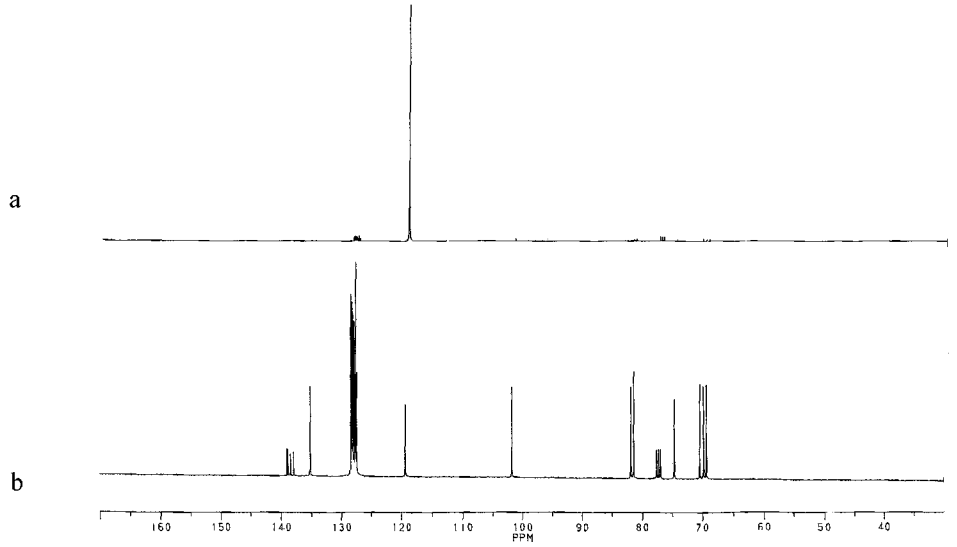

FIGURE 2. ^{13}C NMR spectra of 2,3-di-*O*-benzyl-4,5-didehydro-4,5-dideoxy-D-[5-^{13}C]ribose dibenzyl acetal (**6-Bn)** (panel a) and the corresponding nonlabeled D-ribose dibenzyl acetal **6′-Bn** (panel b).

96% (92:8) total yield, respectively. The mixtures were subjected to column chromatography again to give **7-Bn** and **7-Me** in 90% and 86% yield, respectively (Scheme 4).

In this manner, the (4*R*)-D-[5-^{13}C]ribose derivatives **7-Bn** and **7-Me** were successfully prepared as the main products, which had 3,4-*anti* relationships between the original and the newly formed stereogenic center. Although these results agree with the theories proposed by Stork[14] and Houk[15] regarding the AD reaction of allylic alcohol, these excellent results in the presence of only pyridine or 4-methylmorpholine *N*-oxide, without a bis-cinchona alkaloid ligand such as $(DHQD)_2PHAL$,[16] greatly exceeded their predictions. It was presumed that the 3,4-*anti* product (4*R*) was predominantly produced by the large steric hindrance arising at one side of the double bond from the "inside alkoxy effect".[17]

Synthesis of 1-*O*-Acetyl-2,3,5-tri-*O*-benzoyl-D-[5-^{13}C]ribose as the Glycosyl Donor (Scheme 5). Next, the chemical derivatization of (4*R*)-**7** to the glycosyl donor 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-D-[5-^{13}C]ribofuranose (**12**) was carried out. The benzyl acetal **7-Bn** was subjected

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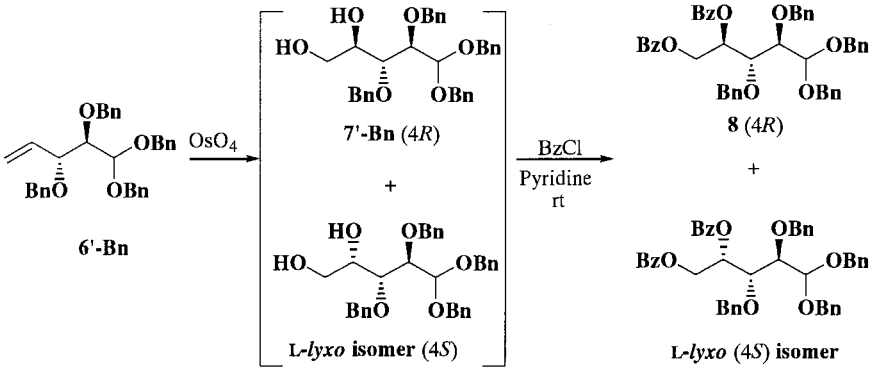
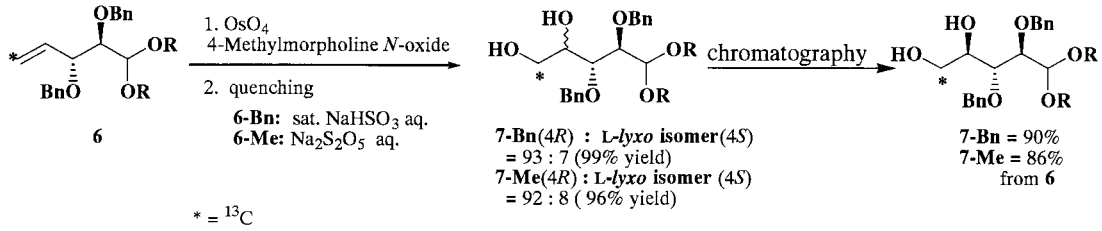
(17) (a) Houk, K. N.; Moses, S. R.; Wu, Y.-D.; Rondan, N. G.; Jäger, V.; Schohe, R.; Fronczek, F. R. *J. Am. Chem. Soc.* **1984**, *106*, 3880−3882. (b) Vedejs, E.; McClure, C. K. *J. Am. Chem. Soc.* **1986**, *108*, 1094−1096.

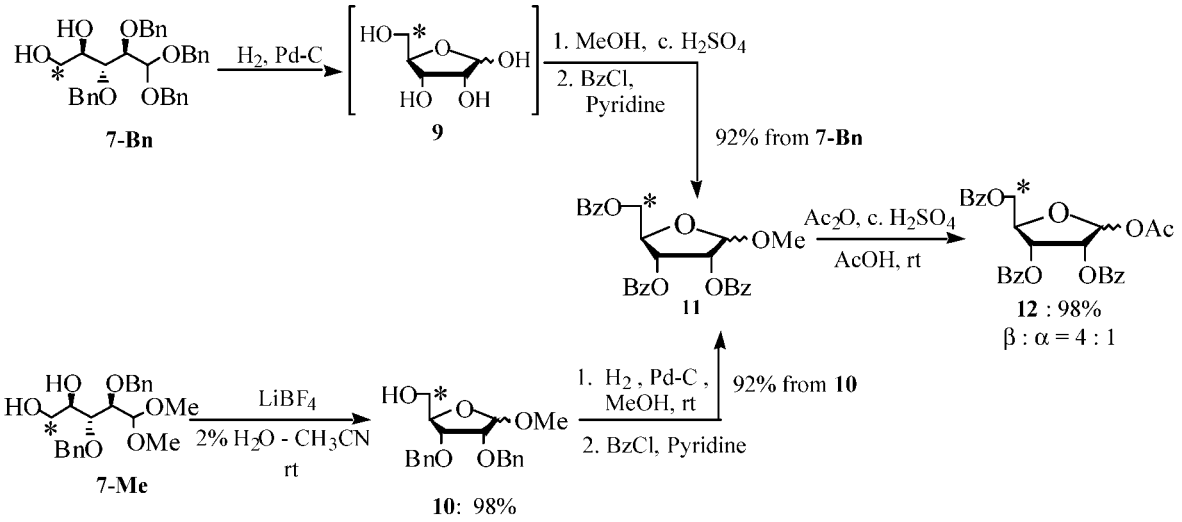
SCHEME 3. Highly Diastereoselective Dihydroxylation of Nonlabeled 6′-Bn with OsO_4 and Amine



SCHEME 4. Highly Diastereoselective Dihydroxylation with OsO_4 and Amine



SCHEME 5. Preparation of the D-[5-^{13}C]Ribofranose Derivative



to hydrogenation to give D-[5-^{13}C]ribose, methyl glycosylation to give methyl D-[5-^{13}C]ribofuranose, and benzoylation to give methyl 2,3,5-tri-*O*-benzoyl-D-[5-^{13}C]ribofuranoside (**11**), which was then subjected to acetolysis. Thus, the glycosylating agent **12** was obtained in an excellent yield of 98% as a 1:4 mixture of α- and *β*-anomers from **11**. On the other hand, **7-Me** was treated with lithium tetrafluoroborate ($LiBF_4$) according to the method of Harvey et al.,[18] with the expectation of yielding 2,3-di-*O*-benzyl-D-ribose. Contrary to our expectation, this reaction gave methyl 2,3-di-*O*-benzyl-D-[5-^{13}C]ribofuranoside (**10**) in 98% yield. This treatment is very useful for the conversion of a dialkyl acetal derivative into an alkyl D-ribofuranoside derivative. The resulting **10** was hydrogenated for debenzylation and then was converted into **12** via **11** by the usual method (Scheme 5).

II. Synthesis of 2′-Deoxy[5′-^{13}C]ribonucleoside Derivatives. Second, the resulting **12** was finally subjected to a coupling reaction with a persilylated nucleobase (persilylated N^6-benzoyladenine, N^2-acetyl-O^6-diphenylcarbamoylguanine, N^4-benzoylcytosine, thymine, and uracil) with Vorbrüggen's approach[19] to give the [5′-^{13}C]-ribonucleoside derivatives (**13**) (99 atom % ^{13}C) in good yields (80%, 79%, 96%, 98%, and 78%, respectively) (Table 2, Scheme 6). These [5′-^{13}C]ribonucleosides are interesting from the viewpoint of RNA science, of course, but were further converted into the corresponding 2′-deoxy derivatives for DNA analyses as well.

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SCHEME 6. Chemical Conversion of a D-[5-^{13}C]Ribose Derivative into the Corresponding 2′-Deoxy[5′-^{13}C]nucleoside Derivatives

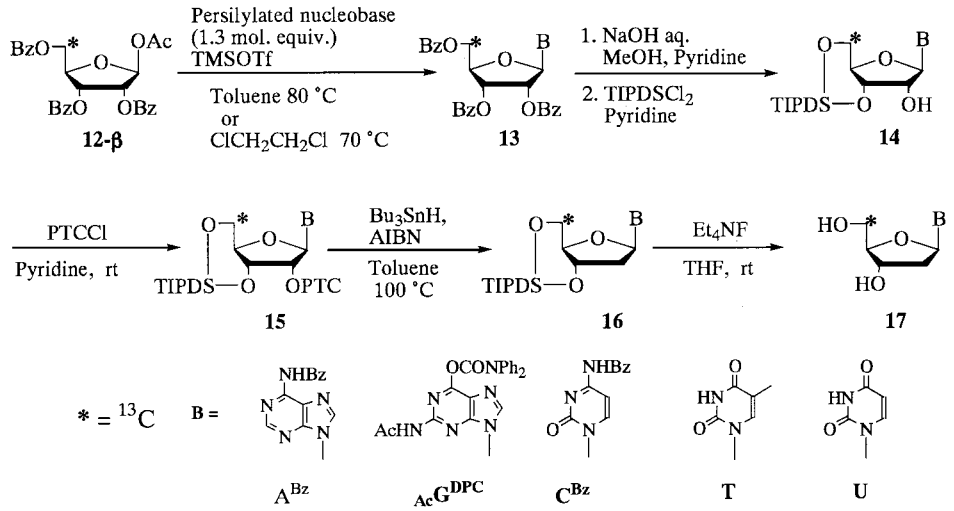

TABLE 2. Coupling of 12 with Persilylated Nucleobase[a]

B	**13** yield (%)
A^{Bz}	80
$_{Ac}G^{DPC}$	79
C^{Bz}	96
T	98
U	78

[a] Abbreviation: A^{Bz} = N^6-Benzoyladenin-9-yl, $_{Ac}G^{DPC}$ = N^2-Acetyl-O^6-diphenylcarbamoylguanin-9-yl, C^{Bz} = N^2-Benzoylcytosin-1-yl, T = Thymin-1-yl, U = Uracil-1-yl.

TABLE 3. Yields (%) of Compounds 14, 15, 16, and 17 on Conversion into 2′-Deoxy[5′-^{13}C]ribonucleosides[a]

B	**14**	**15**	**16**	**17**
A^{Bz}	74	84	92	98
$_{Ac}G^{DPC}$	45	86	97	90
C^{Bz}	78	86	76	96
T	72	92	98	98

[a] Abbreviation: A^{Bz} = N^6-benzoyladenin-9-yl, $_{Ac}G^{DPC}$ = N^2-Acetyl-O^6-diphenylcarbamoylguanin-9-yl, C^{Bz} = N^2-Benzoylcytosin-1-yl, T = Thymin-1-yl.

Compounds **13** were successfully transformed into the corresponding 2′-deoxy[5′-^{13}C]ribonucleoside derivatives **17** in the established manner, i.e., debenzoylation, protection of both the 3′- and 5′-hydroxyl groups with a 1,1,3,3-tetraisopropyldisiloxane-1,3-diyl (TIPDS) group,[20] introduction of a phenoxythiocarbonyl group at the 2′ position,[21] the reduction with tributyltin hydride,[21] followed by the deprotection of TIPDS with tetraethylammonium fluoride (Scheme 6); the yields of the reactions for each 2′-deoxyribonucleoside (**17**) are summarized in Table 3.

The proton and carbon-13 NMR spectra of 3′,5′-*O*-TIPDS-[5′-^{13}C]thymidine are demonstrated in Figure 3a and b, respectively. The spectra of the other nucleosides **17** were obtained in the same way.

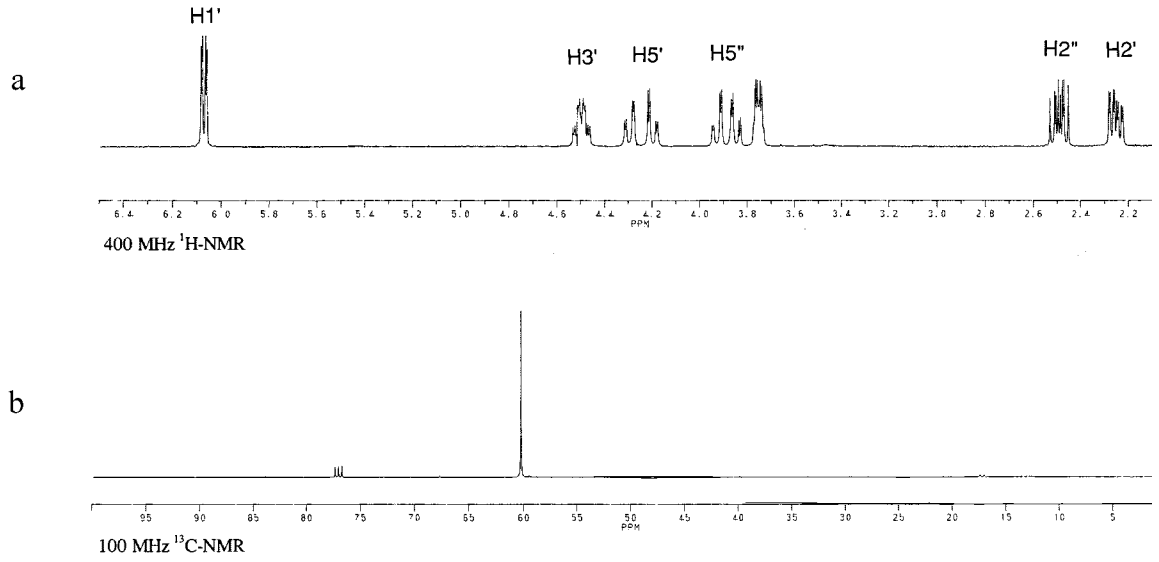

FIGURE 3. ^{1}H NMR (panel a) and carbon-13 NMR (panel b) spectra of 3′,5′-*O*-TIPDS-[5′-^{13}C]thymidine (**16T**). These spectra clearly show the introduction of the ^{13}C label at the 5′-position of **16T** achieved in the present work.

Conclusion

The present synthesis of D-[5-^{13}C]ribofuranose derivatives is characterized by the introduction of the carbon-13 label at the 5 position of D-ribose, through the Wittig reaction using $PhP^{13}CH_3I$, the subsequent highly diastereoselective dihydroxylation using osmium tetraoxide, and the cyclization from D-[5-^{13}C]ribose dimethyl acetal derivatives to the methyl D-[5-^{13}C]ribofuranoside derivative by the use of $LiBF_4$. The efficiency of the present approach from **1** to **12** is characterized by a 58% overall yield of **12** from $Ph_3P^{13}CH_3I$, i.e., after the introduction of the ^{13}C label by the Witting reaction, in contrast with the 4% overall yield of **12** from [^{13}C]KCN reported by Matwiyoff et al.[4] and the 25% overall yield of **9** from [^{13}C]-KCN reported by Serianni et al.[5] after introduction of the ^{13}C label.

Experimental Section

General Procedures. Melting points were uncorrected. ^{1}H and ^{13}C NMR spectra were recorded at 400 and 300 MHz and at 100 and 75 MHz, respectively. Chemical shifts were recorded in the δ scale relative to an internal reference of $CDCl_3$ (7.26 ppm for ^{1}H NMR and 77.0 ppm for ^{13}C NMR spectra), unless otherwise noted. Dimethyl sulfoxide-d_6 (DMSO-d_6) (2.50 ppm for ^{1}H spectra) was occasionally used as an internal reference. The signal peaks of the ^{13}C NMR spectra were assigned by the DEPT experiment. Mass spectra (MS), high-resolution mass spectra (HRMS), and elemental analyses were recorded at The Tokyo University of Pharmacy and Life Science Chemical Instrumentation Center. TLC was performed on aluminum plates precoated with Merck silica gel 60 F_{254}, and spots were detected with a UV lamp (253.7 nm). Column chromatography was performed on silica gel (Wakogel C-300, purchased from Wako Pure Chemicals Co., Ltd.) and Kieselgel 60 (Merck Co., Ltd.). Solvents were reagent grade and in many cases were dried before use.

4-*Aldehydo*-2,3-di-*O*-benzyl-D-erythrose Dibenzyl Acetal (5-Bn). Compound **5-Bn** was prepared by oxidation using a solution of $NaIO_4$ (450 mg, 2.1 mmol) in 5.0 mM aqueous H_2SO_4 (4.0 mL) at rt from **4-Bn** (1.06 g, 2.0 mmol) in 99% (980 mg) yield. ^{1}H NMR ($CDCl_3$): δ 9.56 (1H, d, $J_{3,4}$ = 0.8 Hz, H4), 7.2−7.4 (20H, m, Ph-H), 4.98 (1H, d, $J_{1,2}$ = 6.6 Hz, H1), 4.5−4.8 (8H, m, Bn-CH × 8), 4.14 (1H, dd, $J_{2,3}$ = 2.1 Hz, $J_{3,4}$ = 0.8 Hz, H3), 3.98 (1H, dd, $J_{1,2}$ = 6.6 Hz, $J_{2,3}$ = 2.1 Hz, H2). ^{13}C NMR ($CDCl_3$): δ 201.29, 137.79, 137.72, 137.35, 137.16, 128.38, 128.32, 127.91, 127.87, 127.71, 127.67, 127.63, 101.17, 83.07, 81.72, 73.21, 73.06, 70.40, 69.60. Anal. Calcd for $C_{33}H_{36}O_6$·0.3 H_2O: C, 76.57; H, 6.94. Found: C, 73.84; H, 6.80.

4-*Aldehydo*-2,3-di-*O*-benzyl-D-erythrose Dimethyl Acetal (5-Me). Compound **5-Me** was prepared by oxidation using 9.3 mL of an aqueous solution of $NaIO_4$ (1.05 g, 4.9 mmol) at rt from **4-Me** (1.75 g, 4.7 mmol) in 95% (1.52 g) yield. ^{1}H NMR ($CDCl_3$): δ 9.55 (1H, d, $J_{3,4}$ = 0.8 Hz, H4), 4.76 (1H, d, Bn-H), 4.69 (1H, d, J = 12.1 Hz, Bn-H), 4.67 (1H, d, J = 11.8 Hz, Bn-CH), 4.62 (1H, d, J = 11.6 Hz, Bn-H), 4.58 (1H, d, $J_{1,2}$ = 6.8 Hz, H1), 4.06 (1H, d, $J_{3,2}$ = 2.1 Hz, H3), 3.81(1H, dd, $J_{2,3}$ = 2.1 Hz, $J_{2,1}$ = 6.8 Hz, H2), 3.40 & 3.41 (6H, s, OCH_3). ^{13}C NMR ($CDCl_3$): δ 201.29, 137.79, 137.72, 137.35, 127.16, 128.38, 128.32, 127.91, 127.87, 127.71, 127.67, 127.63, 101.17, 83.07, 81.72, 73.21, 73.06, 70.40, 69.60. Anal. Calcd for $C_{20}H_{24}O_5$·0.7 H_2O: C, 67.62; H, 7.15. Found: C, 67.67; H, 6.86.

2,3-Di-*O*-benzyl-4,5-didehydro-4,5-dideoxy-D-[5-^{13}C]ribose Dibenzyl Acetal (6-Bn). BuLi (1.6 M) in hexane (1.35 mL) was added to methyl-^{13}C-triphenylphosphonium iodide (1.0 g, 2.5 mmol) in THF (10 mL) under an argon atmosphere at 0 °C, and the mixture was stirred for 20 min. A solution of **5-Bn** (980 mg, 2.0 mmol) in THF (10 mL) was added dropwise to the resulting solution, and the whole was stirred for 3 h at 0 °C. The reaction was quenched by addition of 1.0 M aqueous ammonium chloride (30 mL), which was extracted with Et_2O (50 mL × 3). The Et_2O layer was washed with brine (50 mL), dried ($MgSO_4$), and concentrated to dryness. The residue was subjected to silica gel column chromatography, with hexane−AcOEt as eluent, to give **6-Bn** (908 mg, 93%). ^{1}H NMR ($CDCl_3$): δ 7.2−7.4 (20H, m, Ph-H), 5.96 (1H, ddd, $J_{3,4}$ = 8.0 Hz, $J_{4,5}$ = 17.4 Hz, $J_{4,5'}$ = 10.4 Hz, H4), 5.29 (1H, ddd, $J_{4,5'}$ = 10.4 Hz, $J_{5,5'}$ = 1.9 Hz, $J_{5',C5}$ = 158.4 Hz, H5′), 5.17 (1H, ddd, $J_{4,5}$ = 17.4 Hz, $J_{5,5'}$ = 1.9 Hz, $J_{5,C5}$ = 155.2 Hz, H5), 4.87 (1H, d, J = 11.5 Hz, Bn-CH), 4.78 (1H, d, J = 11.5 Hz, Bn-CH), 4.70 (1H, d, $J_{1,2}$ = 6.4 Hz, H1), 4.58−4.68 (4H, m, Bn-CH x 4), 4.49 (1H, d, J = 11.7 Hz, Bn-CH), 4.32 (1H, d, J = 12.0 Hz, Bn-CH), 4.10 (1H, dd, $J_{2,3}$ = 3.3 Hz, $J_{3,4}$ = 8.0 Hz, $J_{3,C5}$ = 4.3 Hz, H3), 3.98 (1H, dd, $J_{1,2}$ = 6.4 Hz, $J_{2,3}$ = 3.3 Hz, H2). ^{13}C NMR ($CDCl_3$): δ 138.80, 138.68, 138.21, 137.72, 134.99 (d, $J_{4,5}$ = 68.8 Hz), 128.36, 128.32, 128.26, 128.08, 127.93, 127.83, 127.66, 127.54, 127.38, 127.34, 119.30, 101.61, 81.69, 81.24, 74.41, 70.16, 69.51, 69.03. Anal. Calcd for $C_{32}{}^{13}CH_{36}O_6$· 0.1H_2O: C, 79.85; H, 6.95. Found: C, 79.75; H, 7.03.

2,3-Di-*O*-benzyl-4,5-didehydro-4,5-dideoxy-D-[5-^{13}C]ribose Dimethyl Acetal (6-Me). Compound **5-Me** (654 mg, 1.9 mmol) was treated in a manner similar to that for **5-Bn** to give **6-Me** in 94% (612 mg) yield. ^{1}H NMR ($CDCl_3$): δ 7.39−7.25 (10H, m, Ph-H), 5,97 (1H, ddd, $J_{3,4}$ = 7.8 Hz, $J_{4,5}$ = 10.1 Hz, $J_{4,5'}$ = 17.6 Hz, H4), 5.34 (1H, ddd, $J_{4,5}$ = 10.5 Hz, $J_{5,5'}$ = 2.0 Hz, $J_{5,5C}$ = 158.1 Hz, H5), 5.30 (1H, ddd, $J_{4,5'}$ = 18.2 Hz, $J_{5,5'}$ = 2.1 Hz, $J_{5',5C}$ = 154.9 Hz, H5′), 4.82 (1H, d, J = 11.6 Hz, Bn-CH), 4.76 (1H, d, J = 11.6 Hz, Bn-CH), 4.63 (1H, d, J = 12 Hz, Bn-CH), 4.38 (1H, d, J = 11.9 Hz, Bn-CH), 4.31 (1H, d, $J_{1,2}$ = 6.1 Hz, H1), 4.03 (1H, dd, $J_{2,3}$ = 8.2 Hz, $J_{3,4}$ = 8.2 Hz, H3), 3.71 (1H, dd, $J_{1,2}$ = 6.1 Hz, $J_{2,3}$ = 3.6 Hz, H2), 3.40 (3H, s, OCH_3), 3.35 (3H, s, OCH_3). ^{13}C NMR ($CDCl_3$): δ 138.74, 138.57, 134.98 (d, $J_{4,5}$ = 47.8 Hz), 127.92, 127.22, 118.90, 104.73, 81.15, 80.94, 74.18, 73.90, 70.09, 55.15, 54.64. HRMS $(M + H)^+$: calcd for $C_{20}{}^{13}CH_{26}O_4$ 343.1824, found 343.1810.

Nonlabeled 4,5-Di-*O*-benzoyl-2,3-di-*O*-dibenzyl-D-ribose Dibenzyl Acetal (8). Stoichiometric Method. To **6′-Bn** (nonlabeled) (247 mg, 0.5 mmol) under an argon atmosphere (1.0 mL) in a mixture of pyridine (1.0 mL)−THF (4.0 mL) was added 1.0 M OsO_4 in *t*-BuOH (0.6 mL) at rt and the mixture stirred for 1.5 h. The solution of $NaHSO_3$ (230 mg, 2.35 mmol) in H_2O (3.8 mL)−pyridine (2.5 mL) was added and the resulting mixture stirred for 2 h. To the reaction mixture was added saturated aqueous $NaHCO_3$ (30 mL) followed by extraction with $CHCl_3$ (50 mL × 3). The extract was washed with brine (50 mL) and dried ($MgSO_4$) (**7′-Bn**). After the organic layer was evaporated to dryness, the residue was coevaporated with pyridine twice under an argon atmosphere. The residue was dissolved in CH_2Cl_2 (5.0 mL), benzoyl chloride (0.13 mL, 1.1 mmol) and 4-(dimethylamino)pyridine (DMAP) (274 mg, 2.25 mmol) were added, and the mixture was stirred for 1 h at rt. The reaction was quenched with MeOH (1.0 mL), 5% citric acid in H_2O (30 mL) was added, and the mixture was extracted with Et_2O (40 mL × 3). The extract was washed with saturated $NaHCO_3$ solution in H_2O (40 mL) and brine (40 mL) and then dried ($MgSO_4$). After filtration, the solution was evaporated, and the residue was subjected to silica gel column chromatography employing hexane−AcOEt to give **8** (nonlabeled) (357 mg, 97%), 4*R*/4*S* = 92:8. ^{1}H NMR ($CDCl_3$): δ 7.2−8.0 (30H, m, Ph-H), 5.88 (1H, m, H4), 5.02 (0.08H, d, $J_{1,2}$ = 5.5 Hz, H1(4*S*)), 4.92 (0.92H, d, $J_{1,2}$ = 6.0 Hz, H1(4*R*)), 4.4−4.9 (10H, m, H5, H5', Bn-CH x 8), 4.18 (0.92H, $J_{2,3}$ = 3.4 Hz, $J_{3,4}$ = 5.3 Hz, H3(4*R*)), 4.2 (0.08H, $J_{2,3}$ = 4.1 Hz, $J_{3,4}$ = 4.8 Hz, H3 (4*S*)), 3.93 (1H, dd, $J_{1,2}$ = 6.0 Hz, $J_{2,3}$ = 3.4 Hz, H2).

Catalytic Method. To solution of **6′-Bn** (nonlabeled) (247 mg, 0.5 mmol) in H_2O−acetone (1:8) (9 mL) were added

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(22) 50% (w/w) in $CHCl_3$ was produced from Kobayashi Kagaku.

4-methylmorpholine *N*-oxide 2-hydroxide (488 mg, 3.6 mmol) and 1.0 M OsO_4 in *t*-BuOH (86 μL, 0.005 mol equiv) at rt. After being stirred for 24 h, the mixture was quenched with saturated aqueous $NaHSO_3$ (5.0 mL) and stirred for 30 min. Water (40 mL) was added to the reaction mixture, which was then partitioned between $CHCl_3$ (50 mL × 3) and H_2O. The $CHCl_3$ layer was washed with brine (50 mL) and dried ($MgSO_4$) (**7′-Bn**). After the organic layer was evaporated to dryness, the residue was treated similarly to the stoichiometric method to give benzoyl derivative **8** (nonlabeled) (356 mg, 97%) 4*R*/4*S* = 93:7: ^{1}H NMR ($CDCl_3$): δ 7.2−8.0 (30H, m, Ph-H), 5.88 (1H, m, H4), 5.02 (0.07H, d, $J_{1,2}$ = 5.5 Hz, H1(4*S*)), 4.92 (0.93H, d, $J_{1,2}$ = 6.0 Hz, H1(4*R*)), 4.4−4.9 (10H, m, H5, H5′, Bn-CH × 8), 4.18 (0.93H, $J_{2,3}$ = 3.4 Hz, $J_{3,4}$ = 5.3 Hz, H3(4*R*)), 4.16 (0.07H, $J_{2,3}$ = 4.1 Hz, $J_{3,4}$ = 4.8 Hz, H3(4*S*)), 3.93 (1H, dd, $J_{1,2}$ = 6.0 Hz, $J_{2,3}$ = 3.4 Hz, H2).

2,3-Di-*O*-benzyl-D-[5-^{13}C]ribose Dibenzyl Acetal (7-Bn). Compound **6-Bn** (852 mg, 1.7 mmol) in H_2O−acetone (1:8) (27 mL) was treated similarly to the catalytic method. After the $CHCl_3$ layer was evaporated to dryness, the residue was subjected to silica gel column chromatography employing hexane−AcOEt to give a mixture of D-ribose derivative **7-Bn** and the corresponding L-*lyxo* isomer (899 mg, 99% 93:7). The mixture was subjected to silica gel column chromatography employing hexane−AcOEt again to give D-ribose derivative **7-Bn** (817 mg, 90%). ^{1}H NMR ($CDCl_3$): δ 7.2−7.4 (20H, m, Ph-H), 4.90 (1H, d, $J_{1,2}$ = 5.7 Hz, H1), 4.81 (1H, d, J = 11.5 Hz, Bn-CH), 4.76 (1H, d, J = 11.5 Hz, Bn-CH), 4.72 (1H, d, J = 11.6 Hz, Bn-CH), 4.70 (1H, d, J = 11.7 Hz, Bn-CH), 4.65 (1H, d, J = 11.7 Hz, Bn-CH), 4.58 (1H, d, J = 11.5 Hz, Bn-CH), 4.57 (1H, d, J = 11.6 Hz, Bn-CH), 4.48 (1H, d, J = 11.5 Hz, Bn-CH), 3.4−4.0 (5H, m, H2, H3, H4, H5, H5′), 3.12 (1H, t, J = 4.4 Hz, 4-OH), 2.08 (1H, m, 5-OH). ^{13}C NMR ($CDCl_3$): δ 137.96, 137.77, 137.16, 128.52, 128.47, 128.42, 128.07, 128.00, 127.90, 127.82, 101.72, 80.71, 79.30, 74.38, 72.92, 71.24 (d, $J_{4,5}$ = 40.1 Hz), 70.55, 70.22, 63.94. Anal. Calcd for $C_{32}{}^{13}CH_{36}O_6$: C, 74.97; H, 6.86. Found: C, 74.67; H, 6.95.

2,3-Di-*O*-benzyl-D-[5-^{13}C]ribose Dimethyl Acetal (7-Me). A solution of **6-Me** (64.5 mg, 0.19 mmol) in H_2O−acetone (1:9) (2 mL) was treated similarly to the catalytic method. The reaction was quenched with a sodium disulfite ($Na_2S_2O_5$)(57 mg, 0.29 mmol) and stirred for 1 h. Water (20 mL) was added to the reaction mixture, which was then partitioned between Et_2O (50 mL × 3). The Et_2O layer was washed with brine (50 mL) and dried ($MgSO_4$). After filtration, the solution was evaporated and the residue was subjected to silica gel column chromatography, using hexane−AcOEt as eluent, to give **7-Me** and the corresponding L-*lyxo* isomer (69 mg, 96%, 92:8). The mixture was subjected to silica gel column chromatography employing hexane−AcOEt again to give D-ribose derivative **7-Me** (62 mg, 86%). ^{1}H NMR ($CDCl_3$): δ 7.38−7.28 (10H, m, Ph-H), 4.80 (1H, d, J = 11.6 Hz, Bn-H), 4.74 (1H, d, J = 11.6 Hz, Bn-H), 4.67 (1H, d, J = 11.4 Hz, Bn-CH), 4.54 (1H, d, J = 11.4 Hz, Bn-CH), 4.50 (1H, d, $J_{1,2}$ =5.7 Hz, H1), 3.92−3.50 (1H, m, H2, H3, H4, H5, H5′), 3.47 (6H, s, OCH_3), 3.19 (1H, J = 2.8 Hz, 4-OH), 2.19 (1H, b, 5-OH). ^{13}C NMR ($CDCl_3$): δ 138.00, 128.24, 127.86, 124.85, 108.75, 105.20, 79.86, 79.46, 74.09, 72.96, 71.31(d, $J_{4,5}$ = 40.1 Hz), 70.92, 63.86, 63.72. Anal. calcd for $C_{20}{}^{13}CH_{28}O_6\cdot 0.2H_2O$: C, 66.45; H, 7.51. Found: C, 66.52; H, 7.49.

Methyl 2,3-Di-*O*-benzyl-D-[5-^{13}C]ribofuranoside (10). To **7-Me** (1.18 g, 3.13 mmol) in 2% H_2O−CH_3CN (30 mL) was added $LiBF_4$ (382 mg, 4.07 mmol) at rt. After being stirred for 20 h, the reaction mixture was quenched with the saturated $NaHCO_3$ solution in H_2O (20 mL) and then partitioned between $CHCl_3$ (50 mL × 3). The $CHCl_3$ layer was washed with brine (50 mL) and dried ($MgSO_4$). After filtration, the solution was evaporated, and the residue was subjected to silica gel column chromatography, using hexane−AcOEt as eluent, to give **10** (1.06 g, 98%). (β-Anomer). ^{1}H NMR ($CDCl_3$): δ 7.3−7.4 (10H, m, Ph-H), 4.89 (1H, s, H1), 4.67 (1H, d, J = 12.0 Hz, Bn-CH), 4.63 (1H, d, J = 12.0 Hz, Bn-CH), 4.58 (1H, d, J = 11.7 Hz, Bn-CH), 4.50 (1H, d, J = 11.7 Hz, Bn-CH), 4.28 (1H, m, H4), 4.13 (1H, dd, $J_{2,3}$ = 4.5 Hz, $J_{3,4}$ = 7.0 Hz, $J_{3,5C}$ = 4.5 Hz, H3), 3.87 (1H, d, $J_{2,3}$ = 4.7 Hz, H2), 3.80 (1H, m, $J_{5',5-OH}$ = 3.0 Hz, $J_{4,5'}$ = 3.0 Hz, $J_{5',5}$ = 12.0 Hz, $J_{5',5C}$ = 143.8 Hz, H5′), 3.59 (1H, m, $J_{5,5OH}$ = 3.6 Hz, $J_{4,5}$ = 3.6 Hz, $J_{5',5}$ =12.1 Hz, $J_{5,5C}$ = 142.5 Hz, H5), 3.37 (3H, s, OCH_3), 1.95 (1H, b, 5-OH). ^{13}C NMR ($CDCl_3$): δ 137.69, 130.26, 128.71, 127.71, 106.98, 82.19 ($J_{5,4}$ = 29.6 Hz), 80.32, 77.32, 72.52, 72.34, 62.68, 61.72, 55.43. Anal. Calcd for $C_{19}{}^{13}CH_{24}O_5$: C, 69.83; H, 7.00. Found: C, 69.75; H, 6.97.

Methyl 2,3,5-Tri-*O*-benzoyl-D-[5-^{13}C]ribofuranoside (11). Method A: From 7-Bn. To **7-Bn** (899 mg, 1.7 mmol) in MeOH (17 mL) was added 10% Pd−C (170 mg) at rt and the mixture stirred under hydrogen gas for 36 h. After the filtrate was evaporated, the residue was solved in dry MeOH (10 mL), concd H_2SO_4 (0.05 mL) was added at 0 °C, and the mixture was stirred for 24 h. The reaction solution was neutralized with Dowex 1-X2 (OH^-), the filtrate was evaporated, and the residue was coevaporated with dry pyridine (5 mL) three times. Benzoyl chloride (0.69 mL, 6.0 mmol) in pyridine (20 mL) was added under an argon atmosphere. After being stirred for 32 h, the reaction was quenched with MeOH (1.0 mL), 5% citric acid in H_2O (40 mL) was added, and the mixture was extracted with Et_2O (40 mL × 3). The extract was washed with a saturated aqueous $NaHCO_3$ (40 mL) and brine (40 mL) and then dried ($MgSO_4$). After filtration, the solution was evaporated, and the residue was subjected to silica gel column chromatography employing hexane−AcOEt to give **11** (748 mg, 92%).

(α-Anomer). ^{1}H NMR ($CDCl_3$): δ 7.28−8.10 (15H, m, Ph-H), 5.72 (1H, ddd, $J_{2,3}$ = 7.1 Hz, $J_{3,4}$ = 3.5 Hz, $J_{3,C5}$ = 3.8 Hz, H3), 5.39 (1H, d, $J_{1,2}$ = 4.4 Hz, H1), 5.33 (1H, dd, $J_{1,2}$ = 4.4 Hz, $J_{2,3}$ = 7.1 Hz, H2), 4.74 (1H, ddd, $J_{4,5'}$ = 3.4 Hz, $J_{5,5'}$ = 12.0 Hz, $J_{5',C5}$ = 149.7 Hz, H5′), 4.65 (1H, m, H4), 4.61 (1H, ddd, $J_{4,5}$ = 4.0 Hz, $J_{5,5'}$ = 12.0 Hz, $J_{5,C5}$ = 148.5 Hz, H5), 3.49 (3H, s, 1-OCH_3). ^{13}C NMR ($CDCl_3$): δ 166.15, 165.93, 165.46, 133.34, 133.22, 129.90, 129.80, 129.68, 129.58, 129.47, 129.15, 128.49, 128.43, 128.28, 101.90, 79.39(d, $J_{4,5}$ = 43.9 Hz), 71.76, 70.76, 64.03, 55.72. Anal. Calcd for $C_{26}{}^{13}CH_{24}O_8$: C, 67.92; H, 5.07. Found: C, 67.89; H, 5.11. (β-Anomer). ^{1}H NMR ($CDCl_3$): δ 7.3−8.1 (15H, m, Ph-H), 5.87 (1H, ddd, $J_{2,3}$ = 4.9 Hz, $J_{3,4}$ = 7.0 Hz, $J_{3,C5}$ = 4.5 Hz, H3), 5.68 (1H, d, $J_{2,3}$ = 4.9 Hz, H2), 5.16 (1H, s, H1), 4.3−5.0 (3H, m, H4, H5, H5′), 3.42 (3H, s, 1-OCH_3). ^{13}C NMR ($CDCl_3$): δ 166.14, 165.31, 165.19, 133.40, 133.30, 133.05, 129.72, 129.67, 129.18, 128.90, 128.41, 128.29, 128.20, 106.34, 78.94 (d, $J_{4,5}$ = 43.7 Hz), 75.39, 72.38, 64.71, 55.29. Anal. Calcd for $C_{26}{}^{13}CH_{24}O_8$: C, 67.92; H, 5.07. Found: C, 67.89; H, 5.11.

Method B: From 10. To **10** (1.34 g, 3.87 mmol) in dry MeOH (40 mL) was added 10% Pd−C (160 mg) at rt and the mixture stirred under hydrogen gas for 44 h. After the filtrate was evaporated, the residue was coevaporated with dry pyridine (5 mL) three times, and to it was added benzoyl chloride (1.53 mL, 12.8 mmol) in pyridine (20 mL) under an argon atmosphere. After being stirred for 25 h, the reaction was quenched with MeOH (1.0 mL), and the reaction mixture was extracted with Et_2O (50 mL × 3). The extract was washed with saturated aqueous $NaHCO_3$ (40 mL) and brine (40 mL) and then dried ($MgSO_4$). After filtration, the solution was evaporated, and the residue was subjected to silica gel column chromatography employing hexane−AcOEt to give **11** (1.8 g, 92%).

1-*O*-Acetyl-2,3,5-tri-*O*-benzoyl-D-[5-^{13}C]ribose (12). To the solution of **11** (747 mg, 1.6 mmol) and acetic anhydride (1.0 mL) in acetic acid (4.3 mL) was added concd H_2SO_4 (0.23 mL) at 0 °C and the mixture stirred for 3 h. Ice−H_2O (30 mL) was added to the reaction mixture, which was extracted with Et_2O (50 mL × 3) and washed with H_2O (50 mL), a saturated aqueous $NaHCO_3$ (50 mL × 2), and brine (50 mL), and then the Et_2O layer was dried ($MgSO_4$). After filtration, the extract was evaporated, and the residue was subjected to silica gel column chromatography, using hexane−AcOEt as eluent, to

give **12** (775 mg, 98%). The resulting solid was crystallized from $CHCl_3$−hexane to give the β-anomer of **12**. Moreover, the filtrate was concentrated to dryness and again was crystallized from hexane for anomerization to give the crystal β-anomer of **12**. mp: 130−131 °C. (β-Anomer). ^{1}H NMR ($CDCl_3$): δ 7.3−8.1 (15H, m, Ph-H), 6.43 (1H, s, H1), 5.91 (1H, ddd, $J_{2,3} = 4.9$ Hz, $J_{3,4} = 7.1$ Hz, $J_{3,C5} = 4.5$ Hz, H3), 5.79 (1H, d, $J_{2,3} = 4.9$ Hz, H2), 4.79 (1H, m, H4), 4.77 (1H, ddd, $J_{4,5'} = 3.8$ Hz, $J_{5,5'} = 12.1$ Hz, $J_{5',C5} = 149.7$ Hz, H5′), 4.51 (1H, ddd, $J_{4,5} = 4.6$ Hz, $J_{5,5'} = 12.1$ Hz, $J_{5,C5} = 148.2$ Hz, H5), 2.01(3H, s, $COCH_3$). ^{13}C NMR ($CDCl_3$): δ 169.07, 165.98, 165.36, 165.02, 133.67, 135.56, 133.26, 129.84, 129.76, 129.58, 128.82, 128.66, 128.54, 128.41, 98.40, 79.66 (d, $J_{4,5} = 43.7$ Hz), 74.99, 71.37, 63.72, 20.89. Anal. Calcd for $C_{27}{}^{13}CH_{24}O_9$: C, 66.53; H, 4.79. Found: C, 66.36; H, 4.81.

Procedure for Coupling Reaction of Compound 12 with a Persilylated Nucleobase. The coupling reaction of compound **12** with a persilylated nucleobase (persilylated N^6-benzoyladenine, N^2-acetyl-O^6-diphenylcarbamoylguanine, N^4-benzoylcytosine, thymine, and uracil) was performed according to the method of Vorbrügen[19] by use of trimethylsilyl trifluoromethanesulfonate (TMSOTf) as Lewis acid to give **13A^{Bz}**, **13$_{Ac}$G^{DPC}**, **13C^{Bz}**, **13U**, and **13T**.

***N*,^{6}*O*$^{2'}$,*O*$^{3'}$,*O*$^{5'}$-Tetrabenzoyl[5′-^{13}C]adenosine (13A^{Bz}).** Compound **13A^{Bz}** (544 mg, 80%) was prepared from persilylated N^6-benzoyladenine (1.30 mmol) and the β-anomer of **12** (505 mg, 1.0 mmol). ^{1}H NMR ($CDCl_3$): δ 8.93 (1H, bs, 6-NH), 8.71 (1H, s, H8), 8.17 (1H, s, H2), 7.3−8.1 (20H, m, Ph-H), 6.50 (1H, d, $J_{1',2'} = 5.3$ Hz, H1′), 6.43 (1H, dd, $J_{1',2''} = J_{2',3'} = 5.3$ Hz, H2′), 6.27 (1H, m, H3′), 4.93 (1H, ddd, $J_{4',5''} = 3.2$ Hz, $J_{5',5''} = 12.3$ Hz, $J_{5'',C5'} = 145.0$ Hz, H5″), 4.85 (1H, m, H4′), 4.71(1H, ddd, $J_{4',5'} = 4.3$ Hz, $J_{5',5''} = 12.3$ Hz, $J_{5',C5'} = 149.2$ Hz, H5′). ^{13}C NMR ($CDCl_3$): δ 166.12, 165.32, 165.13, 164.41, 153.05, 151.69, 149.71, 141.57, 133.83, 133.76, 133.48, 132.81, 129.83, 129.74, 129.29, 128.88, 128.70, 128.62, 128.57, 128.53, 128.34, 127.82, 123.53, 87.01, 80.95 (d, $J_{4',5'} = 43.0$ Hz), 73.91, 71.50, 63.53. HRMS (M + H)$^+$: calcd for $C_{37}{}^{13}CH_{29}N_5O_8$ 685.2128, found 68.2101. Anal. Calcd for $C_{37}{}^{13}CH_{29}N_5O_8{\cdot}0.5H_2O$: C, 65.79; H, 4.32; N, 10.10. Found: C, 65.84; H, 4.25; N, 10.15.

***N*^{2}-Acetyl-2′,3′,5′-tri-*O*-benzoyl-6-*O*-diphenylcarbamoyl-[5-^{13}C]guanosine (13$_{Ac}$G^{DPC}). 13$_{Ac}$G^{DPC}** (658 mg, 79%) was prepared from persilylated N^2-acetyl-6-O-diphenylcarbamoylguanine[20] (1.3 mmol) and the β-anomer of **12** (505 mg, 1.0 mmol). ^{1}H NMR ($CDCl_3$): δ 8.08 (1H, bs, 2-NH), 8.06 (1H, s, H8), 7.20−8.03 (25H, m, Ph-H), 6.2−6.4 (3H, m, H1′, H2′, H3′), 4.91 (1H, ddd, $J_{4',5''} = 3.4$ Hz, $J_{5',5''} = 12.3$ Hz, $J_{5'',C5'} = 149.7$ Hz, H5″), 4.85 (1H, m, H4′), 4.71 (1H, ddd, $J_{4',5'} = 5.1$ Hz, $J_{5',5''} = 12.3$ Hz, $J_{5',C5'} = 149.8$ Hz, H5′), 2.46 (3H, s, $COCH_3$). ^{13}C NMR ($CDCl_3$): δ 169.88, 166.16, 165.20, 165.08, 156.39, 154.30, 152.27, 150.15, 142.35, 141.68, 133.82, 133.66, 133.40, 139.79, 129.60, 129.17, 128.69, 128.54, 128.51, 128.32, 127.07 (br), 121.30, 87.46, 80.56 (d, $J_{4',5'} = 43.4$ Hz), 74.18, 71.45, 63.62, 25.09. HRMS (M + H)$^+$: calcd for $C_{45}{}^{13}CH_{36}N_6O_{10}$ 834.2605, found 834.2570. Anal. Calcd for $C_{45}{}^{13}CH_{36}N_6O_{10}{\cdot}0.4H_2O$: C, 65.70; H, 4.41; N, 9.99. Found: C, 65.55; H, 4.37; N, 10.03.

Tetra-*N*^{4},*O*$^{2'}$,*O*$^{3'}$,*O*$^{5'}$-benzoyl[5′-^{13}C]cytidine (13C^{Bz}). Compound **13C^{Bz}** (315 mg, 96%) (mp 211−212 °C) was prepared from persilylated N^4-benzoylcytosine (0.65 mmol) and the β-anomer of **12** (252 mg, 0.5 mmol). ^{1}H NMR ($CDCl_3$): δ 8.72 (1H, bs, 4-NH), 7.3−8.2 (22H, m, H5, H6, Ph-H), 6.50 (1H, d, $J_{1',2'} = 4.6$ Hz, H1′), 5.93 (1H, ddd, $J_{2',3'} = 5.6$ Hz, $J_{3',4'} = 3.4$ Hz, $J_{3',C5'} = 5.5$ Hz, H3′), 5.86 (1H, dd, $J_{1',2'} = 4.6$ Hz, $J_{2',3'} = 5.6$ Hz, H2′), 4.86 (1H, ddd, $J_{4',5''} = 2.8$ Hz, $J_{5',5''} = 12.5$ Hz, $J_{5'',C5'} = 150.3$ Hz, H5″), 4.85 (1H, m, H4′), 4.71 (1H, ddd, $J_{4',5'} = 4.0$ Hz, $J_{5',5''} = 12.5$ Hz, $J_{5',C5'} = 148.9$ Hz, H5′). ^{13}C NMR-($CDCl_3$): δ 166.03, 165.15, 165.07, 162.59, 154.50, 144.26, 133.51, 133.23, 133.06, 129.85, 129.72, 129.58, 129.17, 128.85, 128.63, 128.55, 128.35, 127.61, 97.43, 89.44, 80.65 (d, $J_{4',5'} = 43.2$ Hz), 74.72, 70.94, 63.57. HRMS (M + H)$^+$: calcd for $C_{36}{}^{13}CH_{29}N_3O_9$ 661.2016, found 661.1977. Anal. Calcd for $C_{36}{}^{13}CH_{29}N_3O_9$: C, 67.26; H, 4.42; N, 6.36. Found: C, 67.04; H, 4.39; N, 6.61.

2′,3′,5′-Tri-*O*-benzoyl[5′-^{13}C]ribosylthymine (13T). Compound **13T** (280 mg, 98%) was prepared from 2,4-bis(trimethylsilyloxy)-5-methylpyrimidine in $CHCl_3$ (50% w/w) (0.3 mL) and the β-anomer of **12** (252 mg, 0.5 mmol). ^{1}H NMR ($CDCl_3$): δ 7.3−8.2 (16H, m, H3, Ph-H), 7.16 (1H, d, $J_{5Me,6} = 1.2$ Hz, H6), 6.43 (1H, d, $J_{1',2'} = 6.4$ Hz, H1′), 5.91(1H, m, H3′), 5.75 (1H, dd, $J_{1',2'} = 6.4$ Hz, $J_{2',3'} = 6.2$ Hz, H2′), 4.89 (1H, m, H5″), 4.70 (1H, m, H4′), 4.65 (1H, ddd, $J_{4',5'} = 3.4$ Hz, $J_{5',5''} = 12.3$ Hz, $J_{5',C5'} = 148.3$ Hz, H5′), 1.60 (3H, d, $J_{5Me,6} = 1.2$ Hz, 5-CH_3). ^{13}C NMR ($CDCl_3$): δ 165.98, 165.40, 164.32, 163.07, 150.17, 134.78, 133.79, 133.73, 129.92, 129.83, 129.63, 129.20, 128.87, 128.56, 128.54, 128.34, 112.19, 86.87, 80.61 (d, $J_{4',5'} = 42.8$ Hz), 73.34, 71.42, 63.91, 12.08. HRMS (M + H)$^+$: calcd for $C_{30}{}^{13}CH_{26}N_2O_9$ 572.1750, found 572.1744. Anal. Calcd for $C_{30}{}^{13}CH_{26}N_2O_9{\cdot}0.2\ H_2O$: C, 64.74; H,4.63; N,4.87. Found: C, 64.60; H, 4.57; N, 5.19.

2′,3′,5′-Tri-*O*-benzoyl[5-^{13}C]uridine (13U). Compound **13U** (87 mg, 78%) was prepared from persilylated uracil (0.26 mmol) and the β-anomer of **12** (101 mg, 0.2 mmol). ^{1}H NMR ($CDCl_3$): δ 7.3−8.2 (17H, m, H3, H6, Ph-H), 6.31 (1H, d, $J_{1',2'} = 5.6$ Hz, H1′), 5.88 (1H, m, H3′), 5.75 (1H, dd, $J_{1',2'} = 5.6$ Hz, $J_{2',3'} = 5.8$ Hz, H2′), 5.61 (1H, d, $J_{5,6} = 8.1$ Hz, $J_{3,5} = 2.3$ Hz, H5), 4.84 (1H, ddd, $J_{4',5''} = 3.0$ Hz, $J_{5',5''} = 12.4$ Hz, $J_{5',C5'} = 150.5$ Hz, H5″), 4.72 (1H, m, H4′), 4.67 (1H, ddd, $J_{4',5'} = 3.9$ Hz, $J_{5',5''} = 12.4$ Hz, $J_{5',C5'} = 149.0$ Hz, H5′). ^{13}C NMR ($CDCl_3$): δ 166.02, 165.31, 165.26, 162.78, 150.08, 139.58, 133.78, 133.72, 133.62, 129.88, 129.80, 129.61, 129.19, 128.73, 128.51, 128.32, 103.39, 88.08, 80.48 (d, $J_{4',5'} = 43.1$ Hz), 73.71, 71.11, 63.71. Anal. Calcd for $C_{29}{}^{13}CH_{24}N_2O_9{\cdot}0.2H_2O$: C, 64.21; H, 4.38; N, 4.99. Found: C, 64.17; H, 4.37; N, 5.32.

Synthesis of 14A^{Bz}, 14$_{Ac}$G^{DPC}, 14C^{Bz}, and 14T. Compounds **14A^{Bz}**, **14$_{Ac}$G^{DPC}**, **14C^{Bz}**, and **14T** were prepared from **13A^{Bz}**, **13$_{Ac}$G^{DPC}**, **13C^{Bz}**, and **13T** according to the method of Markiewicw[20] after debenzoylation.

***N*^{6}-Bz-3′,5′-*O*-TIPDS-[5′-^{13}C]adenosine (14A^{Bz})** was obtained from **13A^{Bz}** (342 mg, 0.5 mmol) in 74% yield (228 mg). ^{1}H NMR ($CDCl_3$): δ 9.00 (1H, bs, 6NH), 8.75 (1H, s, H8), 8.14 (1H, s, H2), 7.4−8.1 (5H, m, Ph-H), 6.04 (1H, d, $J_{1',2'} = 1.2$ Hz, H1′), 5.13 (1H, m, H3′), 4.64 (1H, m, H2′), 4.14 (1H, ddd, $J_{4',5''} = 4.8$ Hz, $J_{5',5''} = 12.5$ Hz, $J_{5',C5'} = 146.2$ Hz, H5″), 3.72 (1H, m, H4′), 3.67 (1H, ddd, $J_{4',5'} = 3.2$ Hz, $J_{5',5''} = 12.5$ Hz, $J_{5',C5'} = 142.2$ Hz, H5′), 3.21 (1H, bs, 2′-OH), 0.9−1.3 (28H, m, ^{i}Pr x 4). ^{13}C NMR ($CDCl_3$): δ 164.72, 152.74, 51.06, 149.75, 142.04, 133.73, 132.80, 128.87, 127.95, 123.72, 89.88, 82.28 (d, $J_{4',5'} = 43.8$ Hz), 75.12, 70.79, 61.65, 17.48, 17.40, 17.33, 17.15, 17.03, 16.96, 13.33, 13.09, 12.81, 12.66. HRMS (M + H)$^+$: calcd for $C_{28}{}^{13}CH_{43}N_5O_6Si_2$ 615.2684, found 615.2860.

***N*^{2}-Acetyl-6-*O*-diphenylcarbamoyl-3′,5′-*O*-TIPDS-[5′-^{13}C]guanosine (14$_{Ac}$G^{DPC})** was obtained from **13$_{Ac}$G^{DPC}** (416 mg, 0.5 mmol) in 45% yield (171 mg). ^{1}H NMR ($CDCl_3$): δ 8.12 (1H, s, H8), 7.96 (1H, bs, 2-NH), 7.2−7.5 (10H, m, Ph-H), 5.98 (1H, d, $J_{1',2'} = 1.2$ Hz, H1′), 4.68 (1H, m, H3′), 4.46 (1H, m, H2′), 4.14 (1H, ddd, $J_{4',5''} = 4.1$ Hz, $J_{5',5''} = 12.9$ Hz, $J_{5'',C5'} = 146.6$ Hz, H5″), 3.85 (1H, m, H4′), 3.71 (1H, ddd, $J_{4',5'} = 3.0$ Hz, $J_{5',5''} = 12.8$ Hz, $J_{5',C5'} = 141.6$ Hz, H5′), 3.17 (1H, bs, 2′-OH), 2.54 (3H, s, $COCH_3$), 0.9−1.2 (28H, m, ^{i}Pr × 4). ^{13}C NMR ($CDCl_3$): δ 170.50, 156.22, 154.02, 152.11, 150.29, 141.92, 141.70, 129.17, 126.89 (br), 121.32, 89.32, 82.22 (d, $J_{4',5'} = 43.5$ Hz), 74.86, 70.34, 61.33, 25.14, 17.42, 17.34, 17.28, 17.19, 17.10, 17.01, 16.95, 16.91, 13.31, 13., 12.85, 12.58. HRMS (M + H)$^+$: calcd for $C_{36}{}^{13}CH_{51}N_6O_8Si_2$ 764.3341, found 764.3366.

***N*^{4}-Benzoyl-3′,5′-*O*-TIPDS-[5′-^{13}C]cytidine (14C^{Bz})** was obtained from **13C^{Bz}** (330 mg, 0.5 mmol) in 78% yield (231 mg). ^{1}H NMR ($CDCl_3$): δ 8.70 (1H, bs, 4NH), 8.23 (1H, d, $J_{5,6} = 7.5$ Hz, H6), 7.5−8.0 (6H, m, H5, Ph-H), 5.85 (1H, s, H1′), 4.68 (1H, m, H3′), 4.29 (1H, dd, $J_{5',5''} = 13.4$ Hz, $J_{5'',C5'} = 148.2$ Hz, H5″), 4.26 (1H, d, $J_{2',3'} = 4.7$ Hz, H2′), 3.83−4.23 (2H, m, H4′, H5′), 2.97 (1H, bs, 2′-OH), 0.9−1.2 (28H, m, ^{i}Pr × 4). ^{13}C NMR ($CDCl_3$): δ 166.75, 162.56, 154.72, 144.46, 133.07, 128.92, 127.60, 96.35, 91.64, 81.94 (d, $J_{4',5'} = 43.1$ Hz), 75.09, 68.45, 59.94, 17.39, 17.34, 17.23, 16.91, 16.83, 18.75, 13.32, 12.87,

12.40. HRMS (M + H)$^+$: calcd for $C_{27}{}^{13}CH_{43}N_3O_7Si_2$ 591.2751, found 591.2727.

3′,5′-*O*-TIPDS-[5′-^{13}C]ribosylthymine (14T) was obtained from **13T** (278 mg, 0.5 mmol) in 72% yield (175 mg). ^{1}H NMR ($CDCl_3$): δ 7.94 (1H, bs, H3), 7.35 (1H, d, $J_{5Me,6}$ = 0.9 Hz, H6), 5.70 (1H, d, $J_{1',2'}$ = 0.9 Hz, H1′), 4.43 (1H, m, H3′), 4.19 (1H, m, H2′), 4.17 (1H, dd, $J_{4',5''}$ = 2.8 Hz, $J_{5',5''}$ = 13.0 Hz, $J_{5'',C5'}$ = 147.7 Hz, H5″), 4.06 (1H, m, H4′), 4.01 (1H, dd, $J_{4',5'}$ = 3.0 Hz, $J_{5',5''}$ = 13.0 Hz, $J_{5',C5'}$ = 140.0 Hz, H5′), 3.00 (1H, bs, 2′OH), 1.91 (3H, d, $J_{5Me,6}$ = 0.9 Hz, 5-CH_3), 0.9−1.2 (28H, m, ^{i}Pr × 4). ^{13}C NMR ($CDCl_3$): δ 164.13, 150.30, 135.54, 110.53, 91.13, 81.79 (d, $J_{4',5'}$ = 43.0 Hz), 74.95, 60.16, 17.38, 18.31, 17.20, 17.02, 16.93, 16.78, 13.38, 12.90, 12.68, 12.55, 12.42. HRMS (M + H)$^+$: calcd for $C_{21}{}^{13}CH_{40}N_2O_7Si_2$ 502.2486, found 502.2509.

Synthesis of 15A^{Bz}, 15$_{Ac}$G^{DPC}, 15C^{Bz}, and 15T. Compounds 15A^{Bz}, **15$_{Ac}$G^{DPC}**, **15C^{Bz}**, and **15T** were prepared from **14A^{Bz}**, **14$_{Ac}$G^{DPC}**, **14C^{Bz}**, and **14T** according to the method of Robins.[21]

***N*^{6}-Benzoyl-2′-*O*-phenoxythiocarbonyl-3′,5′-*O*-TIPDS-[5′-^{13}C]adenosine (15A^{Bz})** was obtained from **14A^{Bz}** (220 mg, 0.36 mmol) in 68% yield (184 mg). ^{1}H NMR ($CDCl_3$): δ 8.97 (1H, bs, 6-NH), 8.77 (1H, s, H8), 8.18 (1H, s, H2), 7.1−8.1 (10H, m, Ph-H), 6.40 (1H, dd, $J_{1',2'}$ = 0.9 Hz, $J_{2',3'}$ = 5.3 Hz, H2′), 6.23 (1H, d, $J_{1',2'}$ = 0.9 Hz, H1′), 5.37 (1H, m, H3′), 4.19 (1H, ddd, $J_{4',5''}$ = 2.7 Hz, $J_{5',5''}$ = 12.9 Hz, $J_{5',C5'}$ = 147.4 Hz, H5″), 4.16 (1H, m, H4′), 4.08 (1H, ddd, $J_{4',5'}$ = 2.5 Hz, $J_{5',5''}$ = 12.9 Hz, $J_{5',C5'}$ = 140.3 Hz, H5′), 0.9−1.3 (28H, m, ^{i}Pr × 4). ^{13}C NMR ($CDCl_3$): δ 193.88, 164.66, 153.28, 152.72, 151.00, 149.73, 141.97, 133.55, 132.70, 129.54, 128.75, 126.71, 123.57, 121.62, 87.41, 83.80, 82.14 (d, $J_{4',5'}$ = 43.4 Hz), 69.28, 60.24, 17.35, 17.29, 17.23, 17.07, 16.99, 16.89, 13.20, 12.91, 12.77, 12.75. HRMS (M + H)$^+$: calcd for $C_{35}{}^{13}CH_{47}N_5O_7SSi_2$ 751.2847, found 751.2784.

***N*^{2}-Acetyl-6-*O*-diphenylcarbamoyl-2′-*O*-phenoxythiocarbonyl-3′,5′-*O*-TIPDS-[5′-^{13}C]guanosine (15$_{Ac}$G^{DPC})** was obtained from **14$_{Ac}$G^{DPC}** (502 mg, 0.66 mmol) in 68% yield (403 mg). ^{1}H NMR ($CDCl_3$): δ 8.18 (1H, s, H8), 7.90 (1H, bs, 2-NH), 7.2−7.5 (15H, m, Ph-H), 6.24 (1H, dd, $J_{1',2'}$ = 1.2 Hz, $J_{2',3'}$ = 5.2 Hz, H2′), 6.20 (1H, d, $J_{1',2'}$ = 1.2 Hz, H1′), 4.87 (1H, m, H3′), 4.22 (1H, ddd, $J_{4',5''}$ = 2.5 Hz, $J_{5',5''}$ = 12.9 Hz, $J_{5'',C5'}$ = 147.9 Hz, H5″), 4.17 (1H, m, H4′), 4.08 (1H, ddd, $J_{4',5'}$ = 2.5 Hz, $J_{5',5''}$ = 12.9 Hz, $J_{5',C5'}$ = 140.0 Hz, H5′), 2.58 (3H, s, $COCH_3$), 0.9−1.2 (28H, m, ^{i}Pr × 4). ^{13}C NMR ($CDCl_3$): δ 193.74, 170.96, 156.35, 153.82, 153.31, 152.33, 150.16, 141.64, 141.55, 129.59, 129.14, 128.90, 128.40, 128.33, 126.90, 126.76 (br), 121.57, 121.11, 86.90, 83.38, 82.40 (d, $J_{4',5'}$ = 43.1 Hz), 69.04, 60.21, 25.20, 17.37, 17.29, 17.22, 17.01, 16.89, 13.32, 12.90, 12.76. HRMS (M + H)$^+$: calcd for $C_{43}{}^{13}CH_{54}N_6O_9SSi_2$ 900.3323, found 900.3271.

***N*^{4}-Benzoyl-2′-*O*-phenoxythiocarbonyl-3′,5′-*O*-TIPDS-[5′-^{13}C]cytidine (15C^{Bz})** was obtained from **14C^{Bz}** (267 mg, 0.45 mmol) in 86% yield (284 mg). ^{1}H NMR ($CDCl_3$): δ 8.66 (1H, bs, 4-NH), 8.27 (1 H, d, $J_{5,6}$ = 7.5 Hz, H6), 7.1−8.0 (11 H, m, H5, Ph-H), 6.09 (2H, m, H1′, H2′), 3.8−4.6 (4 H, m, H3′, H4′, H5′, H5″), 0.9−1.2 (28 H, m, ^{i}Pr × 4). ^{13}C NMR ($CDCl_3$): δ 193.42, 167.10, 162.72, 153.42, 144.02, 133.11, 129.40, 128.93, 127.57, 126.48, 121.75, 96.61, 89.13, 83.52, 82.32 (d, $J_{4',5'}$ = 42.7 Hz), 67.90, 59.34, 17.37, 17.33, 17.21, 17.19, 16.89, 16.84, 13.26, 12.93, 12.81, 12.73. HRMS (M + H)$^+$: calcd for $C_{34}{}^{13}CH_{47}N_3O_8SSi_2$ 727.2734, found 727.2681.

2′-*O*-Phenoxythiocarbonyl-3′,5′-*O*-TIPDS-[5′-^{13}C]ribosylthymine (15T) was obtained from **14T** (300 mg, 0.6 mmol) in 87% yield (333 mg). ^{1}H NMR ($CDCl_3$): δ 8.41(1H, bs, H3), 7.35 (6H, m, H6, Ph-H), 6.10 (1H, d, $J_{2',3'}$ = 5.1 Hz, H2′), 5.92 (1H, s, H1′), 4.60 (1H, m, H3′), 3.8−4.5 (3H, m, H4′, H5′, H5″), 1.93 (3H, s, 5-CH_3), 0.9−1.2 (28H, m, ^{i}Pr x 4). ^{13}C NMR ($CDCl_3$): δ 193.76, 163.80, 153.41, 149.72, 135.15, 129.49, 126.60, 121.74, 111.02, 88.55, 83.80, 82.00 (d, $J_{4',5'}$ = 43.3 Hz), 68.37, 59.50, 17.37, 17.32, 17.22, 16.99, 16.897, 13.36, 12.88, 12.79, 12.69, 12.55. HRMS (M + H)$^+$: calcd for $C_{28}{}^{13}CH_{44}N_2O_8SSi_2$ 638.2469, found 638.2435.

Synthesis of 16A^{Bz}, 16$_{Ac}$G^{DPC}, 16C^{Bz}, and 16T. Reductive deoxygenation of **15A^{Bz}**, **15$_{Ac}$G^{DPC}**, **15C^{Bz}**, and **15T** was performed according to the method of Robins et al.[21]

***N*^{6}-Benzoyl-2′-deoxy-3′,5′-*O*-TIPDS-[5′-^{13}C]adenosine (16A^{Bz})** was obtained from **15A^{Bz}** (150 mg, 0.2 mmol) in 85% yield (101 mg). ^{1}H NMR ($CDCl_3$): δ 9.02(1H, bs, 6-NH), 8.78 (1H, s, H8), 8.22 (1H, s, H2), 7.5−8.1 (5H, m, Ph-H), 6.36 (1H, dd, $J_{1',2'}$ = 2.5 Hz, $J_{1',2''}$ = 7.5 Hz, H1′), 4.99 (1H, m, H3′), 4.06 (2H, m, H5′, H5″), 3.92 (1H, m, H4′), 2.79 (1H, ddd, $J_{1',2'}$ = 2.5 Hz, $J_{2',2''}$ = 13.4 Hz, $J_{2',3'}$ = 7.4 Hz, H2′), 2.69 (1H, ddd, $J_{1',2''}$ = 7.5 Hz, $J_{2',2''}$ = 13.4 Hz, $J_{2'',3'}$ = 9.0 Hz, H2″), 0.9−1.3 (28H, m, ^{i}Pr x 4). ^{13}C NMR ($CDCl_3$): δ 164.60, 152.51, 150.87, 149.51, 141.49, 133.678, 132.68, 127.78, 127.82, 123.60, 85.26 (d, $J_{4',5'}$ = 43.6 Hz), 83.39, 69.88, 61.74, 39.94, 17.45, 17.35, 17.29, 16.99, 16.93, 16.85, 13.32, 13.06, 12.,82, 12.49. HRMS (M + H)$^+$: calcd for $C_{28}{}^{13}CH_{43}N_5O_5Si_2$ 599.2915, found 599.2856.

***N*^{2}-Acetyl-2′-deoxy-6-*O*-diphenylcarbamoyl-3′,5′-*O*-TIPDS-[5′-^{13}C]guanosine (16$_{Ac}$G^{DPC}).** Compound **15$_{Ac}$G^{DPC}** (343 mg, 0.38 mmol) was treated similarly to **16A^{Bz}** to give **16$_{Ac}$G^{DPC}** (255 mg, 90%). ^{1}H NMR ($CDCl_3$): δ 8.16 (1H, s, H8), 7.90 (1H, bs, 2-NH), 7.2−7.5 (10H, m, Ph-H), 6.28 (1H, dd, $J_{1',2'}$ = 3.3 Hz, $J_{1',2''}$ = 6.64 Hz, H1′), 4.72 (1H, m, H3′), 4.04 (2H, m, H5′, H5″), 3.88 (1H, m, H4′), 2.65 (2H, m, H2′, H2″), 2.55 (3H, s, $COCH_3$), 0.9−1.2 (28H, m, ^{i}Pr × 4). ^{13}C NMR ($CDCl_3$): δ 170.72, 156.12, 154.00, 152.02, 150.33, 141.84, 141.72, 129.14, 126.94 (br), 121.22, 85.20 (d, $J_{4',5'}$ = 43.1 Hz), 83.07, 69.53, 61.51, 39.89, 25.07, 17.45, 17.35, 17.29, 17.14, 16.99, 16.94, 16.85, 13.37, 13.05, 12.91, 12.49. HRMS (M + H)$^+$: calcd for $C_{36}{}^{13}CH_{50}N_6O_7Si_2$ 748.3391, found 748.3441.

***N*^{4}-Benzoyl-2′-deoxy-3′,5′-*O*-TIPDS-[5′-^{13}C]cytidine (16C^{Bz}).** Compound **15C^{Bz}** (200 mg, 0.28 mmol) was treated similarly to **16A^{Bz}** to give **16C^{Bz}** (120 mg, 76%). ^{1}H NMR ($CDCl_3$): δ 8.65 (1H, bs, 4-NH), 8.31 (1H, d, $J_{5,6}$ = 7.4 Hz, H6), 7.4−8.0 (6H, m, H5, Ph-H), 6.10 (2H, d, $J_{1',2''}$ = 6.3 Hz, H1′), 3.7−4.5 (4H, m, H3′, H4′, H5′, H5″), 2.61 (1H, ddd, $J_{1',2''}$ = 6.3 Hz, $J_{2',2''}$ = 13.22 Hz, $J_{2'',3'}$ = 10.9 Hz, H2″), 2.38 (1H, dd, $J_{2',2''}$ = 13.2 Hz, $J_{2',3'}$ = 7.4 Hz, H2′), 0.9−1.2 (28H, m, ^{i}Pr x 4). ^{13}C NMR ($CDCl_3$): δ 166.64, 162.30, 154.66, 144.34, 133.00, 128.88, 128.53, 96.04, 85.60, 85.20 (d, $J_{4',5'}$ = 43.1 Hz), 66.33, 59.69, 39.61, 17.41, 17.36, 17.24, 16.93, 16.87, 16.75, 13.32, 12.95, 12.88, 12.33. HRMS (M + H)$^+$: calcd for $C_{27}{}^{13}CH_{43}N_3O_6Si_2$ 575.2802, found 575.2781.

3′,5′-*O* -TIPDS-[5′-^{13}C]thymidine (16T). Compound **15T** (165 mg, 0.27 mmol) was treated similarly to **16A^{Bz}** to give **16T** (124 mg, 98%). ^{1}H NMR ($CDCl_3$): δ 8.30 (1H, bs, H3), 7.41 (1H, d, $J_{5Me,6}$ = 1.2 Hz, H6), 6.07 (1H, dd, $J_{1',2'}$ = 2.3 Hz, $J_{1',2''}$ = 7.4 Hz, H1′), 4.50 (1H, m, H3′), 4.11 (1H, ddd, $J_{4',5''}$ = 2.5 Hz, $J_{5',5''}$ = 13.1 Hz, $J_{5'',C5'}$ = 147.2 Hz, H5″), 4.02 (1H, ddd, $J_{4',5'}$ = 3.0 Hz, $J_{5',5''}$ = 13.1 Hz, $J_{5',C5'}$ = 139.5 Hz, H5′), 3.75 (1H, m, H4′), 2.49 (1H, ddd, $J_{1',2''}$ = 7.4 Hz, $J_{2',2''}$ = 13.5 Hz, $J_{2'',3'}$ = 9.7 Hz, H2″), 2.38 (1H, ddd, $J_{1',2'}$ = 2.3 Hz, $J_{2',2''}$ = 13.5 Hz, $J_{2',3'}$ = 7.5 Hz, H2′), 1.93 (3H, d, $J_{5Me,6}$ = 1.2 Hz, 5-CH_3), 0.9−1.2 (28H, m, ^{i}Pr x 4). ^{13}C NMR ($CDCl_3$): δ 164.03, 150.24, 135.13, 110.52, 84.89 (d, $J_{4',5'}$ = 43.3 Hz), 83.73, 67.52, 60.14, 39.76, 17.42, 14.37, 17.29, 17.25, 17.06, 16.96, 16.81, 13.44, 12.97, 12.73, 12.60, 12.42. HRMS (M + H)$^+$: calcd for $C_{21}{}^{13}CH_{40}N_2O_6Si_2$ 486.2537, found 486.2498.

***N*^{6}-Benzoyl-2′-deoxy[5′-^{13}C]adenosine (17A^{Bz}).** To **16A^{Bz}** (101 mg, 0.17 mmol) in THF (20 mL) was added tetraethylammonium fluoride (Et_4NF)·2H_2O (703 mg, 3.8 mmol) at rt and the mixture stirred for 4 h. MeOH (20 mL) and silica gel (10 g) were added to the reaction mixture, and then solvent was slowly evaporated to dryness. The slurry was subjected to flash column chromatography employing a CH_2Cl_2−MeOH system to give **17A^{Bz}** (59.2 mg, 98%). ^{1}H NMR (MeOH-d_4): δ 8.70 (1H, s, H8), 8.65 (1H, s, H2), 7.5−8.1 (5H, m, Ph-H), 6.57 (1H, dd, $J_{1',2'}$ = 6.1 Hz, $J_{1',2''}$ = 6.2 Hz, H1′), 4.61 (1H, m, H3′), 4.07 (1H, m, H4′), 3.84 (1H, ddd, $J_{4',5''}$ = 3.3 Hz, $J_{5',5''}$ = 12.01 Hz, $J_{5'',C5'}$ = 142.2 Hz, H5′), 3.75 (1H, ddd, $J_{4',5'}$ = 3.8 Hz, $J_{5',5''}$ = 12.0 Hz, $J_{5',C5'}$ = 140.9 Hz, H5′), 2.86 (1H, ddd, $J_{1',2'}$ = 6.1 Hz, $J_{2',2''}$ = 13.5 Hz, $J_{2',3'}$ = 7.2 Hz, H2′), 2.69 (1H, ddd, $J_{1',2''}$ = 6.2 Hz, $J_{2',2''}$ = 13.5 Hz, $J_{2'',3'}$ = 3.4 Hz, H2″). ^{13}C NMR (MeOH-d_4): δ 168.06, 152.89, 151.16, 144.51, 134.93, 133.88, 129.73,

129.41, 125.44, 89.69 (d, $J_{4',5'} = 41.5$ Hz), 86.69, 72.66, 63.30, 41.47. HRMS (M + H)$^+$: calcd for $C_{16}{}^{13}CH_{17}N_5O_4$ 357.1392, found 357.1403.

***N*^{2}-Acetyl-2′-deoxy-6-*O*-diphenylcarbamoyl[5′-^{13}C]guanosine ($\mathbf{17_{Ac}G^{DPC}}$).** Compound $\mathbf{16_{Ac}G^{DPC}}$ (222 mg, 0.30 mmol) was treated similarly to $\mathbf{17A^{Bz}}$ to give $\mathbf{17_{Ac}G^{DPC}}$ (134.3 mg, 89%) as a foam. ^{1}H NMR (MeOH-d$_4$): δ 8.58 (1H, s, H8), 7.2−7.5 (10H, m, Ph-H), 6.51 (1H, dd, $J_{1',2'} = 6.4$ Hz, $J_{1',2''} = 6.5$ Hz, H1′), 4.64 (1H, m, H3′), 3.5−4.0 (3H, m, H4′, H5′, H5′), 2.82 (1H, ddd, $J_{1',2'} = 6.4$ Hz, $J_{2',2''} = 13.62$ Hz, $J_{2',3'} = 6.4$ Hz, H2′), 2.47 (1H, ddd, $J_{1',2''} = 6.5$ Hz, $J_{2',2''} = 13.6$ Hz, $J_{2'',3'} = 4.2$ Hz, H2″), 2.29 (3H, s, $COCH_3$). ^{13}C NMR (MeOH-d$_4$): δ 173.71, 158.43, 157.21, 155.15, 153.78, 146.98, 144.80, 131.73, 129.97-(br), 123.68, 90.75 (d, $J_{4',5'} = 40.1$ Hz), 87.68, 73.66, 64.54, 42.82, 26.10. HRMS (M + H)$^+$: calcd for $C_{24}{}^{13}CH_{24}N_6O_6$ 506.1869, found 506.1853.

***N*^{4}-Benzoyl-2′-deoxy[5′-^{13}C]cytidine ($\mathbf{17C^{Bz}}$).** Compound $\mathbf{16C^{Bz}}$ (57 mg, 0.1 mmol) was treated similarly to $\mathbf{17A^{Bz}}$ to give $\mathbf{17C^{Bz}}$ (31.8 mg, 96%) as a foam. ^{1}H NMR (MeOH-d_4): δ 8.54 (1H, d, $J_{5,6} = 7.5$ Hz, H6), 7.5−8.0 (6H, m, H5, Ph-H), 6.24 (2H, dd, $J_{1',2'} = 6.3$ Hz, $J_{1',2''} = 6.2$ Hz, H1′), 4.39 (1H, m, H3′), 4.01 (1H, m, H4′), 3.84 (1H, ddd, $J_{4',5''} = 3.2$ Hz, $J_{5',5''} = 12.1$ Hz, $J_{5'',C5'} = 142.9$ Hz, H5″), 3.75 (1H, ddd, $J_{4',5'} = 3.8$ Hz, $J_{5',5''} = 12.1$ Hz, $J_{5',C5'} = 140.1$ Hz, H5′), 2.52 (1H, ddd, $J_{1',2''} = 6.2$ Hz, $J_{2',2''} = 13.7$ Hz, $J_{2'',3'} = 4.3$ Hz, H2″), 2.20 (1H, ddd, $J_{1',2'} = 6.3$ Hz, $J_{2',2''} = 13.7$ Hz, $J_{2',3'} = 6.3$ Hz, H2′). ^{13}C NMR (MeOH-d_4): δ 169.09, 164.77, 157.86, 146.45, 134.74, 134.08, 129.83, 129.15, 98.27, 89.52 (d, $J_{4',5'} = 41.7$ Hz), 88.76, 71.64, 62.45, 42.54. HRMS (M + H)$^+$: calcd for $C_{15}{}^{13}CH_{17}N_3O_5$ 333.1280, found 333.1250.

[5′-^{13}C]Thymidine (17T). Compound **16T** (47 mg, 0.1 mmol) was treated similarly to $\mathbf{17A^{Bz}}$ to give **17T** (22.8 mg, 92%). ^{1}H NMR (MeOH-d_4): δ 7.81 (1H, d, $J_{5Me,6} = 1.2$ Hz, H6), 6.27 (1H, d, $J_{1',2'} = J_{1',2''} = 6.7$ Hz, H1′), 4.39 (1H, m, H3′), 3.91 (1H, m, H4′), 3.79 (1H, ddd, $J_{4',5''} = 3.2$ Hz, $J_{5',5''} = 12.1$ Hz, $J_{5'',C5'} = 142.3$ Hz, H5″), 3.65 (1H, ddd, $J_{4',5'} = 3.7$ Hz, $J_{5',5''} = 12.1$ Hz, $J_{5',C5'} = 140.3$ Hz, H5′), 2.22 (2H, m, H2′, H2″). ^{13}C NMR (MeOH-d_4): δ 166.37, 152.34, 137.15, 111.50, 88.76 (d, $J_{4',5'} = 41.6$ Hz), 86.23, 72.17, 62.81, 41.15, 12.43; HRMS (M + H)$^+$: calcd for $C_93CH_{14}N_2O_5$ 244.1015, found 244.0992.

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Supporting Information Available: Copies of the ^{1}H NMR, ^{13}C NMR, and mass spectra or analytical data of compounds **2**, **3**, **4-Bn**, and **4-Me**. This material is available free of charge via the Internet at http://pubs.acs.org.

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