chromatography (3:1 hexane–ethyl acetate) to afford veratryl acetate **12** (114 mg, 72%) as an oil.

**Preparation of *n*-Decyl Acetate (9) from *N*-*n*-Decyltrifluoroacetamide (8).** From trifluoroacetamide **8** (200 mg, 0.99 mmol) and $NaNO_2$ (683 mg, 10 equiv) in acetic acid (3 mL) and acetic anhydride (6 mL) at 0 °C in 18 h was obtained *n*-decyl acetate **9** (153 mg, 77%).

**Preparation of *n*-Decyl Acetate (9) from *N*-*n*-Decyltrichloroacetamide (10).** From trichloroacetamide **10** (200 mg, 0.66 mmol) and $NaNO_2$ (528 mg, 6 equiv) in acetic acid (5 mL) and acetic anhydride (10 mL) at 0 °C in 10 h was obtained *n*-decyl acetate **9** (93 mg, 70%).

**Preparation of Trifluoroacetamide 14 and Rearrangement to Monoacetate 15.** To a solution of aminotriol **13** (25 mg, 0.10 mmol) in dry pyridine (1 mL) containing (*N*,*N*-dimethylamino)pyridine (2 mg) was added trifluoroacetic anhydride (63 mg, 3 equiv) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 6 h. Pyridine was removed in vacuo, and the residue was dissolved in water (5 mL). After extracting with $CHCl_3$ (3 × 5 mL) to remove impurities, the aqueous phase was freeze-dried to afford the crude trifluoroacetamide. Flash chromatography (10:1 $CH_2Cl_2$–$CH_3OH$) afforded pure **14** (30 mg, 95%): mp 156–158 °C; $^1H$ NMR ($D_2O$) $\delta$ 3.81 (3 H, s, $OCH_3$), 3.80 (1 H, m, H-5), 3.65 (1 H, dd, $J$ = 13.8, 4.2 Hz, H-7), 3.46 (1 H, dd, $J$ = 13.6, 7.3 Hz, H-7′), 3.32 (1 H, dd, $J$ = 10.2, 9.8 Hz, H-4), 2.21–2.02 (2 H, m, H-$2_{eq}$, H-3), 1.89 (2 H, m, H-$2_{ax}$, H-$6_{eq}$), 1.74 (1 H, dd, $J$ = 13.4, 11.4 Hz, H-$6_{ax}$); IR (KBr) 3428, 1704–1734, 1262, 1139, 804 $cm^{-1}$; CIMS ($m/e$) 316 (5.6, M + 1).

To a solution of **14** (20 mg, 0.06 mmol) in acetic acid (250 $\mu$L) and acetic anhydride (500 $\mu$L) at 0 °C was added $NaNO_2$ (42 mg, 10 equiv). The reaction mixture was stirred for 17 h at 10 °C, poured over ice, and extracted with $CH_2Cl_2$ (3 × 10 mL) to remove impurities. The residual aqueous layer was freze-dried to afford crude monoacetate. Flash chromatography (10:1 $CH_2Cl_2$–$CH_3OH$) afforded pure **15** as a clear oil (10 mg, 65%): $^1H$ NMR ($CDCl_3$) $\delta$ 4.29 (2 H, br s, H-7, H-7′), 3.84 (3 H, s, $OCH_3$), 3.83 (1 H, m, H-5), 3.44 (1 H, dd, $J$ = 10.3, 9.9 Hz), 2.17 (3 H, s, $OCOCH_3$), 2.31–1.91 (5 H, br m, H-$6_{ax}$, H-$6_{eq}$, H-$2_{ax}$, H-$2_{eq}$, H-3); IR (KBr) 3400, 1740–1700 (broad), 1280, 1215, 1145, 1060 $cm^{-1}$; CIMS $m/e$ (relative intensity) 263 (M + 1, 21), 245 (M + 1 - $H_2O$, 13), 227 (M + 1 - $2H_2O$, 20%).

To a solution of monoacetate **15** (10 mg, 0.04 mmol) in anhydrous $CH_3OH$ (0.4 mL) was added 1% KOH in $CH_3OH$ (2 equiv). The solution was stirred at room temperature for 2 h and then concentrated in vacuo, and the residue was chromatographed (4:1 $CH_2Cl_2$–$CH_3OH$) to afford pure tetrol **16** (8 mg, 91%) as a colorless oil, identical in every respect with a previously prepared sample:[7] $[\alpha]_D$ +5.3° ($c$ = 1.5, $H_2O$); $^1H$ NMr ($D_2O$) $\delta$ 3.82 (3 H, s, $OCH_3$) 3.77 (2 H, br s, H-7, H-7′), 3.38 (1 H, dd, $J$ = 9.7, 9.6 Hz, H-4), 2.16 (1 H, ddd, $J$ = 13.5, 4.6, 2.9 Hz, H-$6_{eq}$), 1.98–1.87 (4 H, br m, H-$6_{ax}$, H-$2_{ax}$, H-$2_{eq}$, H-3); IR (film) 3350, 1735, 1240, 1060 $cm^{-1}$; CIMS $m/e$ 221 (5, M + 1).

**Preparation of 1-Adamantyl Acetate (18) from *N*-1-Adamantylacetamide (17).** To a solution of **17** (Aldrich; 500 mg, 2.6 mmol) in glacial acetic acid (9 mL) and acetic anhydride (17 mL) at 0 °C was added $NaNO_2$ (1.80 g, 26 mmol, 10 equiv). The resulting solution was stirred at 0 °C for 15 min, slowly warmed to room temperature, and stirred for 16 h. The reaction mixture was then poured into ice and extracted with ether (3 × 50 mL). The combined organic extracts were washed with water (50 mL), 5% $Na_2CO_3$ (2 × 50 mL), water (50 mL), and saturated NaCl (50 mL). After drying ($MgSO_4$) and filtration, the extracts were concentrated in vacuo to a white solid. Flash column chromatography (9:1 hexane–ethyl acetate) afforded pure 1-adamantyl acetate **18** (455 mg, 90%), which was identical in every respect with an authentic sample prepared by acetylation of 1-adamantanol.

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**Registry No.** **8**, 10574-25-1; **9**, 112-17-4; **10**, 123488-80-2; **11**, 122365-02-0; **12**, 53751-40-9; **13**, 123488-81-3; **14**, 123488-82-4; **15**, 123488-83-5; **16**, 123488-84-6; **17**, 880-52-4; **18**, 22635-62-7.

## [[2-(Methylthio)phenyl]thio]methyl (MTPM): A New Protecting Group of Hydroxyl Groups Capable of Conversion to a Methyl Group

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In the synthesis of natural products having complex structures such as macrolides, carbohydrates, and nucleosides, selective protection of a certain functionality is of great importance to realize stepwise construction of target molecules. In particular, the hydroxyl group has been masked with a wide variety of protecting groups during chemical conversions of other functional groups.[2-4] In this paper, we describe [[2-(methylthio)phenyl]thio]-methyl (MPTM) as a new type of protecting group of primary and secondary alcoholic functions, which can also serve as a precursor of the methyl group.

In a previous paper,[5] we reported that the 1,3-benzodithiol-2-yl (BDT) group could be converted to the methyl group via reductive C–S bond cleavage by Raney nickel. When this Raney nickel reduction was applied to the synthesis of 5′-*O*-methylthymidine (**2**) via 5′-*O*-(1,3-benzodithiol-2-yl)thymidine (**1**),[6] the yield (15–51%) of **2** varied depending on the freshness and the strong adsorptive property of the Ni surface.[7] In the hope of finding a more effective method for this conversion, reaction of **1** with 2.5 equiv of tributyltin hydride (TBTH)[8,9] was carried out in benzene in the presence of azobis(isobutyronitrile) (AIBN) under reflux for 1.5 h (Scheme I). However, this reaction did not give the desired product **2** but afforded instead quantitatively ring-opened product **3** on the basis of TLC analysis.[10] Isolation of this product by silica gel column chromatography caused considerable decomposition. Nevertheless, **3** was isolated in 36% yield and characterized.[11] The C–SAr bond of **3** was not reduced by TBTH upon prolonged heating. Since this result was rationalized in terms of the presence of the sterically hindered *o*-(tributylstannyl)thio group, the in situ S-methylation of **3** to form less hindered synthetic intermediate **4** was attempted. It was found that the methylation of **3** with 10 equiv of MeI was dependent upon the solvents employed. Benzene, dichloromethane, acetone, acetonitrile, and 2-propanol were ineffective. In contrast, it was found that treatment of **3** with MeI in dimethylformamide at room temperature for 2.5 h gave **4** in an optimized yield of 85%. In tetrahydrofuran (THF), the reaction proceeded rather slowly to give the desired *S*-methyl product **4** in ca. 60% yield after 2 days. Interestingly, the S-methylation was accelerated by addition

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(11) Gutierrez[10] also described that considerable decomposition of *S*-tributylstannane derivatives occurred during silica gel chromatography.

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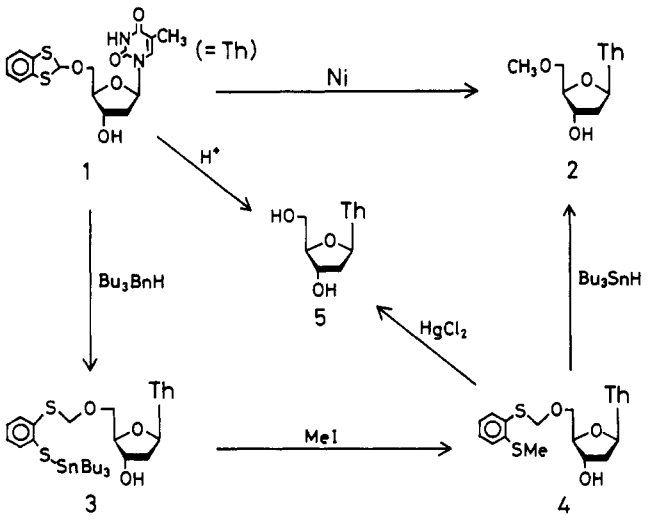
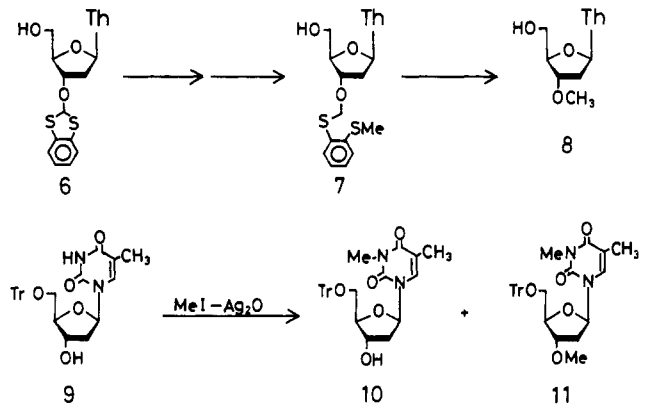
**Scheme I**




**Scheme II**




of CsF.[12] The effect of CsF-catalyzed methylation was evident when the methylation was repeated in benzene in the presence of 1 equiv of CsF. The reaction was completed within 3 h to give **4** in 63% yield. However, in this case, it was found that the CsF-catalyzed $N^3$-methylation also occurred competitively.

As expected, the reaction of **4** with 4 equiv of TBTH in the presence of 6 equiv of AIBN under reflux in toluene for 6 h resulted in the formation of **2** in 89% yield. In this reaction, stepwise addition of AIBN was essential. If smaller amounts of AIBN were used, the C–S bond cleavage was not complete. The excessive use of AIBN did not hamper the isolation of **2** since the decomposition products derived from this reagent were all volatile. In a similar manner, 3′-*O*-(1,3-benzodithiol-2-yl)thymidine (**6**)[6] was converted to 3′-*O*-[[[2-(methylthio)phenyl]thio]-methyl]thymidine (**7**) in 63% yield. Subsequently, 3′-*O*-methylthymidine (**8**) was obtained in 73% yield from **7** (Scheme II).

It should be noted that the conversion of **6** to **8** via **7** could be performed without protection of the imide group of the thymine residue. Our independent experiment on the methylation of 5′-*O*-tritylthymidine (**9**) with methyl iodide–$Ag_2O$[13,14] revealed that this reaction gave a mixture of $N^3$-methylthymidine and $N^3$,3′-*O*-dimethylthymidine derivatives (**10** and **11**) in 48% and 18% yields, respectively, without formation of the desired 3′-*O*-methylthymidine derivative. In this $Ag_2O$-mediated alkylation, the $N^3$-methylation occurred predominantly over the 3′-*O*-methylation. Therefore, the preprotection of the imide group should be required for the synthesis of **8** by this conventional approach. Since it is known that the BDT group can be introduced into the 3′-hydroxyl group of 5′-*O*-[(isobutyryloxy)carbonyl]thymidine[15] without protection of the imide moiety,[6] our approach provides an easy access to 3′-*O*-methylthymidine derivative such as **8**. Moreover, in our previous paper, we showed that the BDT group can be introduced selectively into the primary alcohol of thymidine in 83% yield.[6] Thus this method provides a convenient route to selectively methylate the primary alcohol in the presence of the secondary alcohol, as demonstrated by conversion of **1** to **2**.

Next, the stability of the MPTM group of **4** was examined. This protecting group was found to be stable under both acidic and basic conditions such as (a) 80% acetic acid to 100 °C for 3 h, (b) 5% trifluoroacetic acid in $CH_2Cl_2$ at room temperature for 3 h, (c) concentrated ammonia at room temperature for 2 days, and (d) 2 M NaOH–pyridine (1:1, v/v) at room temperature for 4 h.

Since the MPTM group has two sulfur atoms that can coordinate more effectively with divalent metal cations, the MPTM group can be readily removed from **4** and **7** under mild conditions. Treatments of **4** and **7** with 5 equiv of mercury(II) chloride in acetonitrile–water (4:1, v/v)[16] at room temperature for 30 min gave thymidine in 95% and 85% isolated yields, respectively. It was also found that the BDT group could be slowly removed from **1** under similar conditions. Only a trace amount of thymidine was detected after 30 min and complete removal of the BDT group required 19 h.

In conclusion, the MPTM group will be useful not only for the protection of primary and secondary hydroxyl groups but also as a latent *O*-methyl group.

## Experimental Section

$^1$H NMR spectra were recorded at 60 MHz on a Hitachi 24B spectrometer using TMS as an internal standard. UV spectra were obtained on a Hitachi 220A spectrophotomer. Column chromatography was performed with silica gel C-200 purchased from Wako Co. Ltd. and a minipump for a goldfish bowl was conveniently used to attain sufficient pressure for rapid chromatographic separation.[17] TLC was performed on precoated TLC plates of silica gel 60 F-254 (Merck). Benzene and toluene were distilled and stored over molecular sieves 3A. $Bu_3SnH$ was purchased from Kanto Kagaku Co. Ltd., and the other reagents from Tokyo Kasei Co. Ltd. Elemental analyses were performed by the Microanalytical Laboratory, Tokyo Institute of Technology, at Nagatsuta.

**5′-*O*-[[[2-[(Tributylstannyl)thio]phenyl]thio]methyl]-thymidine (3).** A mixture of **1** (394 mg, 1 mmol), TBTH (533 μL, 2 mmol), and AIBN (32 mg, 0.2 mmol) in toluene (10 mL) was stirred at 110–115 °C under an argon atmosphere. Heating was continued for 1.5 h, when TLC showed 95% conversion of **1** to **3**. Then TBTH (533 μL, 2 mmol) was added and the mixture was continuously heated at 115 °C for an additional 1 h. After the solvent was removed under reduced pressure, the residue was chromatographed on a column of silica gel (14 g) with $CH_2Cl_2$–MeOH to give **3** (249 mg, 36%) as a foam: $^1$H NMR ($CDCl_3$) δ 0.63–1.70 (27 H, m, $C_4H_9$), 1.83 (3 H, s, $CH_3$), 2.22 (2 H, m, 2′-H), 3.31 (1 H, br, OH), 3.85 (2 H, m, 5′-H), 4.08 (1 H, m, 4′-H), 4.32 (1 H, m, 3′-H), 4.95 (1 H, d, $J$ = 11.8 Hz, OCHaS), 5.22 (1 H, d,

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$J$ = 11.8 Hz, OCHbS), 6.30 (1 H, t, $J$ = 7 Hz, 1'-H), 6.72–7.63 (5 H, m, Ar H and 6-H), 9.63 (1 H, br, NH). Anal. Calcd for $C_{29}H_{46}N_2O_5S_2Sn$: C, 50.81; H, 6.76; N, 4.09. Found: C, 50.54; H, 6.70; N, 4.33.

**5'-*O*-[[[2-(Methylthio)phenyl]thio]methyl]thymidine (4).** A mixture of **1** (197 mg, 0.5 mmol) and TBTH (336 μL, 1.25 mmol) in dry benzene (5 mL) was refluxed under an argon atmosphere, and a solution of AIBN (123 mg, 0.75 mmol) in dry benzene (1 mL) was added dropwise for 1 h. After being refluxed for an additional 1 h, the mixture was cooled to room temperature and evaporated under reduced pressure. The residue was dissolved in dry DMF (5 mL) and MeI (311 μL, 5 mmol) was added. The solution was stirred for 2.5 h and then partitioned with $CH_2Cl_2$–$H_2O$ in a separating funnel. The organic phase was washed seven times with $H_2O$. Each washing was back-extracted with more $CH_2Cl_2$ in another separating funnel. This extensive extractive workup led to complete removal of DMF. The $CH_2Cl_2$ extracts were combined, dried over $Na_2SO_4$, filtered, and evaporated under reduced pressure. The residue was chromatographed on a column of silica gel (8 g) with $CH_2Cl_2$–MeOH to give **4** (175 mg, 85%): mp 108–111 °C (acetone); $^1$H NMR ($CDCl_3$) δ 1.77 (3 H, s, $CH_3$), 2.11 (2 H, m, 2'-H), 2.42 (3 H, s, $SCH_3$), 3.83 (2 H, m, 5'-H), 4.07 (1 H, m, 4'-H), 4.27 (1 H, m, 3'-H), 5.00 (3 H, s, $SCH_2O$), 6.25 (1 H, t, $J$ = 6 Hz, 1'-H), 6.83–7.67 (5 H, m, Ar H and 6-H). Anal. Calcd for $C_{18}H_{22}N_2O_5S_2 \cdot {}^1/_4H_2O$: C, 52.10; H, 5.47; N, 6.75. Found: C, 52.07; H, 5.42; N, 6.76.

When the methylation at the second step was carried out in benzene in the presence of 1 equiv of CsF at room temperature for 3 h, **4** was obtained in 63% yield.

**3'-*O*-[[[2-(Methylthio)phenyl]thio]methyl]thymidine (7).** This compound was synthesized as a foam from **6** on a 0.5-mmol scale according to the procedure described above. The yield was 168 mg (82%). **7**: $^1$H NMR ($CDCl_3$) δ 1.87 (3 H, s, $CH_3$), 2.41 (4 H, m, $SCH_3$ and 2'-H), 3.77 (2 H, m, 5'-H), 3.99 (1 H, m, 4'-H), 4.57 (1 H, m, 3'-H), 4.96 (2 H, s, $SCH_2O$), 6.05 (1 H, m, 1'-H), 6.90–7.67 (5 H, m, Ar H and 6-H). Anal. Calcd for $C_{18}H_{22}N_2O_5S_2 \cdot {}^2/_3H_2O$: C, 51.17; H, 5.57; N, 6.63. Found: C, 51.12; H, 5.62; N, 6.54.

**5'-*O*-Methylthymidine (2).**[18] To a solution of **4** (82 mg, 0.2 mmol) and TBTH (215 μL, 0.8 mmol) in refluxing toluene (2 mL) was added portionwise a solution of AIBN (16.4 μg, 0.1 mmol) in toluene (0.5 mL) six times during 2.5 h. The mixture was then evaporated and chromatographed on preparative TLC plates developed with $CH_2Cl_2$–MeOH (9:1, v/v) to give **2** (1310 OD unit at 267 nm, 68%) as a glassy material: UV (MeOH) $\lambda_{max}$ 266 nm, $\lambda_{min}$ 236 nm; $^1$H NMR ($CDCl_3$–$CD_3OD$, 5:1, v/v) δ 1.90 (3 H, s, 5-$CH_3$), 2.25 (2 H, m, 2'-H), 3.42 (3 H, s, $OCH_3$), 3.60 (2 H, m, 5'-H), 4.04 (1 H, m, 4'-H), 4.39 (1 H, m, 3'-H), 6.29 (1 H, t, $J$ = 6.9 Hz, 1'-H), 7.62 (1 H, s, 6-H).

**3'-*O*-Methylthymidine (8).**[7] This compound was synthesized from **7** (82 mg, 0.2 mmol) as a glassy material by the procedure described above. The yield was 1410 OD unit (73%) at 266 nm. **8**: UV (MeOH) $\lambda_{max}$ 266 nm, $\lambda_{min}$ 234.5 nm; $^1$H NMR ($CDCl_3$) δ 1.89 (3 H, s, 5-$CH_3$), 2.31 (2 H, m, 2'-H), 3.33 (3 H, s, $OCH_3$), 3.47 (2 H, m, 5'-H), 3.83 (1 H, m, 4'-H), 4.03 (1 H, m, 3'-H), 6.04 (1 H, t, $J$ = 7.0 Hz, 1'-H), 7.37 (1 H, s, 6-H).

**Methylation of 5'-*O*-Tritylthymidine (9).** To a mixture of **9** (benzene adduct, 562 mg, 1 mmol) and silver oxide (3 mmol) was added MeI (10 mL). The resulting mixture was refluxed for 1 h 15 min and then filtered through Celite to remove silver salts. The salts were washed with $CH_2Cl_2$. The filtrate and washing were combined and evaporated under reduced pressure, and the residue was chromatographed on a column of silica gel (15 g) using $CH_2Cl_2$–MeOH as eluent to give **10** (243 mg, 48%) and **11** (92 mg, 18%) as foamy materials. **10**: $^1$H NMR ($CDCl_3$) δ 1.50 (3 H, s, 5-$CH_3$), 2.38 (2 H, m, 2'-H), 3.26 (3 H, s, $N^3$-$CH_3$), 3.41 (2 H, m, 5'-H), 4.07 (1 H, m, 4'-H), 4.54 (1 H, m, 3'-H), 6.38 (1 H, t, $J$ = 6.5 Hz, 1'-H), 7.23 (15 H, m, Ar H), 7.55 (1 H, s, 6-H). Anal. Calcd for $C_{30}H_{30}O_5N_2$: C, 72.27; H, 6.07; N, 5.62. Found: C, 71.91; H, 6.16; N, 5.31. **11**: 1.53 (3 H, s, 5-$CH_3$), 2.20 (2 H, m, 2'-H), 3.25 and 3.29 (6 H, s, $N^3$-$CH_3$ and 3'-$OCH_3$), 3.30 (2 H, m, 5'-H), 4.04 (2 H, m, 3',4'-H), 6.28 (1 H, t, $J$ = 6.8 Hz, 1'-H), 7.24 (15 H, m, Ar H), 7.53 (1 H, s, 6-H). Anal. Calcd for $C_{31}H_{32}O_5N_2$: C, 72.64; H, 6.29; N, 5.46. Found: C, 72.35; H, 6.27; N, 4.74.

Acetylation of **10** (33 mg, 0.066 mmol) with acetic anhydride (0.1 mL) in dry pyridine (0.5 mL) for 2 h gave the 3'-*O*-acetyl derivative (32 mg, 89%) as a foam: $^1$H NMR ($CDCl_3$) δ 1.47 (3 H, s, 5-$CH_3$), 2.04 (3 H, s, 3'-OAc), 2.41 (2 H, m, 2'-H), 3.32 (3 H, s, $N^3$-$CH_3$), 3.42 (2 H, m, 5'-H), 4.07 (1 H, m, 4'-H), 5.37 (1 H, m, 3'-H), 6.38 (1 H, s, t, $J$ = 7.0 Hz, 1'-H), 7.24 (15 H, m, Ar H), 7.48 (1 H, s, 6-H). Anal. Calcd for $C_{32}H_{32}O_6N_2 \cdot {}^2/_3H_2O$: C, 69.55; H, 6.08; N, 5.07. Found: C, 69.52; H, 5.96; N, 4.89.

**Removal of the MPTM Group from 4 or 7.** Compound **4** or **7** (20.5 mg, 0.05 mmol) was dissolved in acetonitrile (1.8 mL). Water (0.2 mL) and mercury chloride(II) (68 mg, 0.25 mmol) were successively added to the solution. The mixture was vigorously stirred at room temperature for 30 min. The resulting precipitate was removed by filtration and washed with acetonitrile–water (4:1, v/v, 10 mL). The filtrate and washing were combined and evaporated, and the residue was chromatographed on Toyo Roshi no. 51 paper with 2-propanol–concentrated ammonia–water (7:1:2, v/v/v) to give **5** (443 $A_{266\,nm}$, 92% from **4** and 410 $A_{266\,nm}$, 85% from **7**).

**Removal of the BDT Group from 1.** Compound **1** (19.7 mg, 0.05 mmol) was dissolved in acetonitrile (1.6 mL). Water (0.4 mL) and mercury chloride(II) (67.9 mg, 0.25 mmol) were successively added to the solution. The mixture was vigorously stirred at room temperature for 19 h. The workup and chromatographic separation as described in the above experiment gave **5** (470 $A_{266\,nm}$, 98%).

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**Registry No.** **1**, 84752-63-6; **2**, 14504-60-0; **3**, 122902-44-7; **4**, 122902-45-8; **5**, 50-89-5; **6**, 84752-64-7; **7**, 122902-46-9; **8**, 108895-42-7; **9**, 7791-71-1; **10**, 122902-47-0; **10** (3'-*O*-acetyl deriv), 122902-49-2; **11**, 122902-48-1.

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