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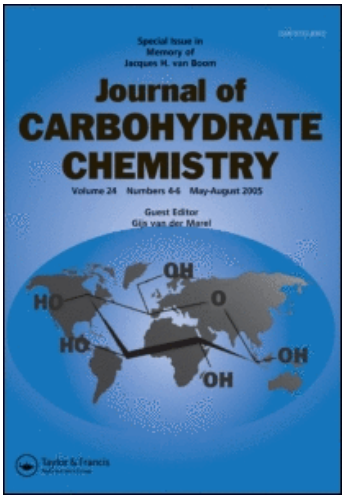

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Partial Protection of Carbohydrate Derivatives. Part 21. Lead(II) Nitrate Mediated Triisopropylsilyl Ether Formation; Preparation of 2'-Deoxy-3'-O-triisopropylsilylribonucleosides

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PARTIAL PROTECTION OF CARBOHYDRATE DERIVATIVES. PART 21[1]. LEAD(II) NITRATE MEDIATED TRIISOPROPYLSILYL ETHER FORMATION; PREPARATION OF 2'-Deoxy-3'-O-TRIISOPROPYLSILYLRIBONUCLEOSIDES

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ABSTRACT

Introduction of the triisopropylsilyl protecting group to the 3'-position of 5'-O-aroyl-2'-deoxyribonucleosides wa effectively performed by the use of triisopropylsilyl chlor ide in DMF in the presence of pyridine and lead(II) nitrate the latter was substituted in this reaction for silver nitr ate. Simple treatment of the resulting triisopropylsilyl ethers with sodium methoxide in THF gave 2'-deoxy-3'-O-tri-isopropylsilylribonucleosides in excellent yields.

INTRODUCTION

In a previous paper,[2] we reported a simple, efficient preparation of 5'-O-aroyl-2'-deoxyribonucleosides with

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an aroyl chloride in pyridine through the dilution - drop-by-drop - addition procedure, by which the products were obtained in 84 - 94% isolated yields, exceeding the yields obtained by more sophisticated reagent systems.[3,4] These products were converted into derivatives with a phosphorus function, in anticipation of establishing an alternate synthetic route to 2'-deoxyribonucleotide oligomers. Introduction of the triisopropylsilyl (TIPS) group onto the 3'-position of the 5'-aroates with TIPS chloride was also performed for potential use in oligomer synthesis, since the TIPS group is more stable than the tert-butyldimethylsilyl (TBDMS) group under basic conditions.[5] In addition, it was assumed that the TIPS group, being bulkier than the TBDMS group, would be more regioselective in partial protection of polyhydroxy compounds including glycosyl compounds. The reaction was investigated using imidazole, silver nitrate, or lead(II) nitrate in a comparative study; the latter addition was found to be of practical use and the results obtained are described herein.

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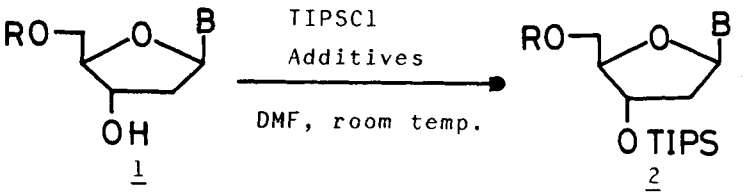
RESULTS AND DISCUSSION

Triisopropylsilylation reactions (Scheme 1) were performed under various conditions (Table 1). The reaction of 5'-O-benzoylthymidine (**1a**) with TIPS chloride (4 mol. equiv.) in the presence of imidazole (8 mol. equiv.) in N,N-dimethylformamide (DMF) took 72 h for completion (Entry 1). Imidazole has been used effectively as an additive for introducing TBDMS group at the 5' position of 2'-deoxyribonucleosides,[6] but not for a more hindered secondary alcohol such as



1 2

Scheme 1

at the 3'-position. On the other hand, preparation of bis-(tert-butyldimethylsilyl)ribonucleosides has been successfully performed using equimolar amounts of silver nitrate[7] and TBDMS chloride. The reactions of **1a** (Entry 2), N^4,5'-dibenzoyl-2'-deoxycytidine (**1b**)(Entry 4), and N^6,5'-dibenzoyl-2'-deoxyadenosine (**1e**)(Entry 8) were carried out in DMF by the use of TIPS chloride (1.5 - 1.8 mol. equiv.), pyridine (4 mol. equiv.), and silver nitrate (1.5 mol. equiv.), over 4.5, 5.5, and 2 h, respectively, with excellent results being obtained. However, the reactions were expensive to perform due to the use of silver nitrate. Lead(II) nitrate[8] was chosen to replace silver nitrate in the reaction based on the small solubility product constant of the resulting lead(II) chloride (Ksp = 1.7×10^{-5}), although the affinity of lead(II) ion toward chloride ion is smaller than that of silver ion. The reactions of **1a** (Entry 3), **1b** (Entry 5), N^4,5'-ditoluoyl-2'-deoxycytidine (**1c**)(Entry 6), and N^2-isobutyryl-5'-O-benzoyl-2'-deoxyguanosine (**1d**)(Entry 7) were performed by the use of lead(II) nitrate (1.0 - 1.5 mol. equiv.) under the conditions shown in the table and were over after 21, 28, 24, and 24 h, respectively. The reaction of **1a** in pyridine (Entry 9) suggests some potential participation of DMF in activation of TIPS chloride as will be discus-

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TABLE 1

Comparative Time Study for Completion of 3'-O-Triisopropylsilylation of 2'-Deoxyribonucleosides (1) with TIPS Chloride in the Presence of Additives as Monitored by TLC[a]

Entry	Compound 1			TIPS chloride (mol. equiv.)	Additive (mol. equiv.)	Time (h) required for completion of reaction
		B	R			
1	**1a**	T	Bz	4.0	imidazole (8.0)	72
2	**1a**	T	Bz	1.8	$AgNO_3$ (1.5) - pyridine (4.0)	4.5
3	**1a**	T	Bz	2.5	$Pb(NO_3)_2$ (1.25) - pyridine (5.0)	21
4	**1b**	C^{Bz}	Bz	1.8	$AgNO_3$ (1.5) - pyridine (4.0)	5.5
5	**1b**	C^{Bz}	Bz	3.0	$Pb(NO_3)_2$ (1.5) - pyridine (6.0)	28
6	**1c**	C^{Tol}[b]	Tol	2.0	$Pb(NO_3)_2$ (1.0) - pyridine (4.0)	24
7	**1d**	G^{iBu}[c]	Bz	2.0	$Pb(NO_3)_2$ (1.0) - pyridine (4.0)	24
8	**1e**	A^{Bz}	Bz	1.5	$AgNO_3$ (1.5) - pyridine (4.0)	2
9[d]	**1a**	T	Bz	2.5	$Pb(NO_3)_2$	48

[a] All of the reactions were performed by the use of **1** (0.4 mmol) in DMF (1 mL) at room temperature, and were monitored by TLC (9:1 chloroform - methanol). [b] Tol stands for o-toluoyl group. [c] iBu stands for isobutyryl group. [d] Pyridine was used as the solvent in place of DMF.

sed later. These results suggest the utility of lead(II) nitrate for the triisopropylsilylation reaction. By comparison, the reaction of TIPS chloride - ethyldiisopropylamine[9] with **1a** gave 5'-O-benzoyl-3'-O-triisopropylsilylthymidine (**2a**) in only 35% in spite of using excess reagents (5.5 mol. equiv. to **1a**). The triisopropylsilylation did not occur in pyridine. Moreover, when the reaction was performed under similar conditions to that in Entry 2 (Table 1), but substituting the amine for pyridine no product was observed even by monitoring with TLC. Furthermore, attempting the reactions in acetonitrile or in tetrahydrofuran in place of DMF gave only poor yields of the product judging from TLC.

Considering the potential utility of lead(II) nitrate in the triisopropylsilylation reaction, we examined the effect of molar equivalent ratios of TIPS chloride and the nitrate on reaction time under the conditions shown in Table 2; 2.0 mol. equiv. of pyridine to TIPS chloride were used in each reaction. All the reactions were monitored by TLC, and the proportions of lead(II) nitrate to TIPS chloride were plotted against the time for their completion with respect to each of the reactions using 1.5, 2.0, and 2.5 mol. equiv. of TIPS chloride. The results are summarized in Table 2 and illustrated in Fig. 1. It was concluded that the reaction time was the longest with 0.5 mol. equiv., an amount equal to the chloride ion liberated by the reaction, and that the amount of lead(II) nitrate exceeding 0.5 mol. equiv. is necessary to complete the triisopropylsilylation reaction. The effect of the molar ratio of pyridine

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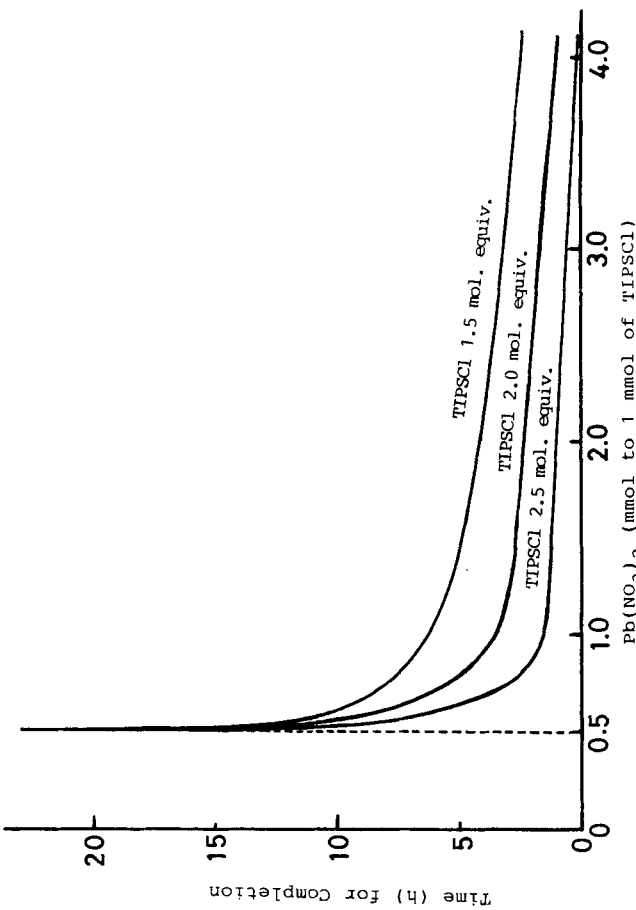

Fig. 1. Outline of the Effect of the Amount of $Pb(NO_3)_2$ on 3'-O-Triisopropylsilylation

TABLE 2

Time (h) for Completion of 3'-Triisopropylsilylation of 1a [a]

TIPS chloride (mol. equiv.)	$Pb(NO_3)_2$ (mmol to 1 mmol of TIPSCl) 0.5	0.65	1.0	2.0	4.0
1.5	>24	9.0	6.25	4.0	2.5
2.0	22.75	7.0	3.5	2.3	1.0
2.5	21	4.8	1.5	1.0	0.2

[a] All of the reactions were performed by the use of 1a (0.4 mmol) in DMF (1 mL) at room temperature in the presence of pyridine (2.0 mmol to 1 mmol of TIPSCl).

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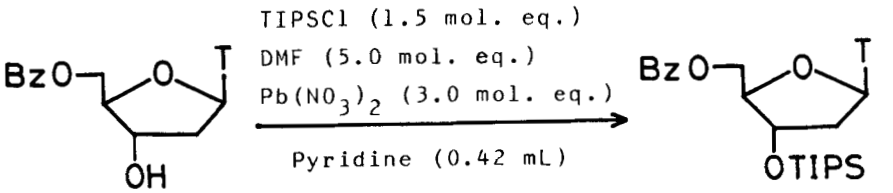
TABLE 3

The Effect of the Molar Proportion of Pyridine toward TIPS Chloride on the Time (h) Required for Completion of Triisopropylsilylation[a]

Pyridine (mmol/1 mmol of TIPSCl)	$Pb(NO_3)_2$ (mmol/1 mmol of TIPSCl) 1.0	2.0	4.0
0.67	10.5 (h)	5.5 (h)	3.25 (h)
1.0	6.0	3.0	2.0
2.0	6.25	4.0	2.5

[a] All of the experiments were performed by the use of **1a** (0.4 mmol) and TIPSCl (1.5 mol. equiv.) in DMF (1 mL) at room temperature.



1a (0.2 mmol) 2a

Scheme 2

to TIPS chloride (1.5 mol. equivalents to **1a**) for completion of the reaction in DMF was examined similarly by TLC monitoring under the conditions shown in Table 3. As seen from Table 3, reaction was the fastest using an equivalent amount of pyridine to TIPS chloride. In contrast, the reaction of **1a** (0.2 mmol) with TIPS chloride (1.5 mol. equiv.) in pyridine (0.42 mL, 26 mol. equiv.) in the presence of DMF (5.0 mol. equiv.) and lead(II) nitrate (3.0 mol. equiv.) (Scheme 2) was performed, but left **1a** unchanged even after 10 h. This reaction was slow (16 h for completion) but still faster than that in pyridine as has been shown in Entry 9 of Table 1. Treatment of **2a** in DMF in the presence of lead(II) chloride (1 mol. equiv.), pyridine (1 mol. equiv.), and TIPS chloride (1 mol. equiv.) for 24 h at room temperature, followed by quenching with methanol, was carried out in order to determine if chloride ion produced in the triisopropylsilylation harms the resulting TIPS ether. Quantitative recovery of **2a** showed that chloride ion had no effect on the stability of this product.

As described, the reaction proceeds effectively using pyridine, lead(II) nitrate (more than 1 mol. equiv. to TIPS chloride), and is accelerated by the addition of DMF to the reaction system. The results suggest that triisopropylsilyl-

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pyridinium nitrate and/or a Vilsmeier reagent type nitrate are involved in the reaction as the triisopropylsilylating entity, and resulting chloride ion is effectively scavenged by the lead(II) ion.

On the basis of the results obtained above, preparations of 3'-O-triisopropylsilyl-2'-deoxyribonucleosides (**3**) from **1** were performed; the results and the conditions used are summarized in Table 4. Compounds **2** obtained as described, after 5'-O-dearoylation with sodium methoxide in THF, gave **3** in excellent yields. The 5'-O-dearoylation procedure with sodium methoxide in THF is easy to carry out and N-aroyl groups on the nucleic acid base moieties completely survive as we have already established.[10] The 3'-triisopropylsilyl ether derivatives can, on the other hand, be used as the 3'-terminus portion of a 2'-deoxyribonucleotide oligomer chain in DNA-type oligomer synthesis.

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EXPERIMENTAL

General methods. Melting points were determined with a Yanagimoto Micro-Melting-Point apparatus, and are uncorrected. ^{1}H NMR spectra were recorded on a Varian T-60 apparatus and JEOL JNM FX-200 using tetramethylsilane as the internal standard. TLC was conducted on Merck Silica Gel 60 F_{254} coated plates using 9:1 chloroform - methanol. Column chromatography was performed with Merck Kieselgel 60 (70 - 230 mesh, ASTM) with chloroform - methanol solvent systems. Triisopropylsilyl chloride and sodium methoxide were purchased from Aldrich Co. Ltd. and Merck Co. Elemental analyses were carried out on a Perkin Elmer 240-002

TABLE 4

Preparation of 2'-Deoxy-3'-O-triisopropylsilylribonucleosides (3) from 5'-O-Acyl-2'-deoxyribonucleosides (1) via 2

Entry	1			Time (h) required for completion of TIPS-ation [a]	5'-O-Deacylation			Overall yield (%) of 3	
		B	R		Solvent (mL)	Reaction time (min)	NaOMe (mol. equiv.)		
1	**1a**	T	Bz	1.5	THF (3) and MeOH (1.5)	30	4.0	**3a**	97
2	**1b**	C^{Bz}	Bz	2.0	THF (6)	30	5.0	**3b**	93
3	**1c**	C^{Tol}	Tol	2.0	THF (6)	40	5.0	**3c**	94
4	**1d**	G^{iBu}	Bz	3.5	THF (6)	20	4.0	**3d**	97
5	**1e**	A^{Bz}	Bz	3.5	THF (6)	3	4.0	**3e**	98

[a] All of the reactions were performed by the use of a solution of **1** (0.5 mmol) in DMF (1 mL) in the presence of TIPSCl (2.0 mol. equiv.), $Pb(NO_3)_2$ (4.0 mol. equiv.), and pyridine (2.0 mol. equiv.), at room temperature.

apparatus in the Department of Chemistry, Tokyo Institute of Technology.

General Procedure for the Preparation of 2'-Deoxy-3'-O-triisopropylsilylribonucleosides (3) from 5'-O-Aroyl-2'-deoxyribonucleosides (1) by Way of 2 (See Table 4). 5'-O-Aroyl-2'-deoxyribonucleosides[2] (0.5 mmol; 1a = 173 mg, 1b = 218 mg, 1c = 232 mg, 1d = 221 mg, and 1e = 230 mg) and lead(II) nitrate (662 mg, 2.0 mmol, 4.0 mol. equiv.) were dissolved in DMF by heating, and possible residual moisture removed by co-evaporation with DMF with a high vacuum rotary pump (3 times). The air in the flask was then replaced with nitrogen. The residue was dissolved in DMF (1 mL) and pyridine (0.081 mL, 1.0 mmol, 2.0 mol. equiv.) with stirring, and the resulting solution was stirred with TIPS chloride (0.214 mL, 1.0 mmol, 2.0 mol. equiv.) at room temperature until the spot of 1 disappeared (1.5 - 3.5 h). After quenching the mixture with a small volume of methanol, 2:1 acetone - chloroform was added, resulting in the precipitation of a white powder, which was removed by filtration using a filter-cell. The filtrate was concentrated and the residue distributed between chloroform and aqueous sodium bicarbonate solution; the aqueous layer was further extracted with chloroform (4 - 5 times). The organic extracts were combined and dried over anhydrous sodium sulfate, and after filtering off the desiccant, concentrated. The residue was dissolved in benzene, and the moisture was azeotropically removed by distillation (3 times). The residue thus obtained was dissolved in THF or THF-MeOH (4 - 6 mL), pulverized sodium methoxide (108 mg, 4.0 mol. equiv.) was then added to the solution, and the dearoylation was monitored

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by TLC until the spot of **2** disappeared. The resulting mixture was quenched by the addition of Dowex 50W (H^+ form) with stirring, and the ion-exchange resin was filtered off. The filtrate was evaporated to dryness, and the residue chromatographed on a column of the silica gel to give the 2'-deoxy-3'-O-triisopropylsilylribonucleosides (**3**) in the yields as shown in Table 4.

Compound **2a** had ^{1}H NMR ($CDCl_3$): δ 9.42 (1H, bs, NHCO), 8.03 (2H, d, J 8.3 Hz, o-protons of Bz group), 7.62 (1H, t, J 7.3 Hz, p-proton of Bz group), 7.48 (1H, s, H-6), 7.47 (2H, t, m-protons of Bz group), 6.36 (1H, dd, $J_{1',2'}$ 5.6 Hz and $J_{1',2''}$ 7.5 Hz, H-1'), 4.65 (1H, dd, $J_{5',5''}$ 12.0 Hz and $J_{4',5'}$ 3.4 Hz, H-5'), ca. 4.62 (1H, H-3'), 4.50 (1H, dd, $J_{4',5''}$ 3.4 Hz, H-5"), 4.29 (1H, dt, $J_{3',4'}$ ca. 3Hz, H-4'), 2.44 (1H, ddd, $J_{2',2''}$ 14.0 Hz and $J_{2',3'}$ ca. 3 Hz, H-2'), 2.13 (1H, ddd, $J_{2'',3'}$ 6.2 Hz, H-2"), 1.66 (3H, s, CH_3-5), and 1.08 (21H, m, iPr x 3).

Compound **3a** had mp 91.0 - 93.0°C (from ethanol - water), ^{1}H NMR ($CDCl_3$ - CD_3OD): δ 7.65 (1H, s, H-6), 6.23 (1H, t, $J_{1',2'}$ 7 Hz, H-1'), 4.55 (1H, m, H-3'), 3.95 (1H, m, H-4'), 3.76 (2H, m, H-5' and 5"), 2.22 (2H, m, H-2' and 2"), 1.88 (3H, s, CH_3-5), and 1.1 (21H, m, iPr x 3).

Anal. Calcd for $C_{19}H_{34}O_5N_2Si$: C, 57.26; H, 8.60; N, 7.03. Found: C, 56.98; H, 8.36; N, 7.20.

Compound **3b** was a glass and had ^{1}H NMR ($CDCl_3$ - CD_3OD): δ 8.37 (1H, d, $J_{5,6}$ 7.2 Hz, H-6), 8.0 - 7.7 (2H, m, o-protons of Bz group), 7.6 - 7.3 (4H, m, H-5 and m- and p-protons of Bz group), 6.18 (1H, t, $J_{1',2'} = J_{1',2''}$ 6.3 Hz, H-

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1'), 4.52 (1H, m, H-3'), 4.01 (1H, m, H-4'), 3.79 (2H, m, H-5' and 5"), 2.39 (1H, m, H-2'), 1.85 (1H, m, H-2"), and 1.05 (21H, m, iPr x 3).

Anal. Calcd for $C_{25}H_{37}O_5N_3Si$: C, 61.57; H, 7.65; N, 8.62. Found: C, 61.29; H, 7.84; N, 8.63.

Compound **3c** was a glassy mass but had mp 76.0 - 79.0 °C; ^{1}H NMR ($CDCl_3$ - CD_3OD): δ 8.37 (1H, d, $J_{5,6}$ 7 Hz, H-6), 7.6 - 7.0 (5H, m, aromatic protons of o-toluoyl group), 6.15 (1H, t, $J_{1',2'} = J_{1',2"}$ 6.4 Hz, H-1'), 4.51 (1H, m, H-3'), 4.01 (1H, m, H-4'), 3.77 (2H, m, H-5' and 5"), ca. 2.4 (5H, m, H-2', 2", and CH_3 protons of o-toluoyl group), and 1.05 (21H, m, iPr x 3).

Anal. Calcd for $C_{26}H_{39}O_5N_3Si$: C, 62.24; H, 7.83; N, 8.38. Found: C, 62.00; H, 7.60; N, 8.12.

Compound **3d** had mp 114.5 - 116.5°C (from ethanol - water); ^{1}H NMR ($CDCl_3$ - CD_3OD): δ 7.89 (1H, s, H-8), 6.19 (1H, dd, $J_{1',2'}$ 5.8 Hz and $J_{1',2"}$ 7.6 Hz, H-1'), 4.63 (1H, m, H-3'), 4.04 (1H, m, H-4'), 3.80 (2H, m, H-5' and 5"), 2.6 (3H, m, H-2', 2", and =CH of isobutyl group), 1.21 (6H, d, J 7.2 Hz, CH_3 of isobutyl group x 2), and 1.05 (21H, m, iPr x 2).

Anal. Calcd for $C_{23}H_{39}O_5N_5Si$: C, 55.96; H, 7.96; N, 14.19. Found: C, 55.66; H, 8.26; N, 13.96.

Compound **2e** had ^{1}H NMR ($CDCl_3$ - D_2O): δ 8.75 and 8.15 (2H, s x 2, H-2 and 8), 8.02 (2H, d, J 7.1 Hz, o-protons of Bz group), 7.96 (2H, d, J 8.3 Hz, o-protons of Bz group), 7.6 - 7.3 (6H, m, m- and p-protons of Bz group x 2), 6.47 (1H, dd, $J_{1',2'}$ 5.7 Hz and $J_{1',2"}$ 6.7 Hz, H-1'), 4.93 (1H, m, H-3'), 4.69 (1H, dd, $J_{5',5"}$ 12.2 Hz and $J_{4',5'}$ 4.5 Hz,

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H-5'), 4.50 (1H, dd, $J_{4',5''}$ 5 Hz, H-5"), 4.39 (1H, m, H-4'), 3.08 (1H, ddd, $J_{2',2''}$ 13.4 Hz and $J_{2',3'}$ 5.5 Hz, H-2'), 2.59 (1H, ddd, $J_{2'',3'}$ 3.5 Hz, H-2"), and 1.1 (21H, m, iPr x 3). ^{1}H NMR ($CDCl_3$): δ 9.19 (1H, s, NHBz).

Compound **3e** had mp 75 - 77°C (from ethyl acetate - hexane); ^{1}H NMR (CD_3OD): δ 8.48 and 8.43 (2H, s x 2, H-2 and H-8), 8.0 - 7.8 (2H, m, o-protons of Bz group), 7.6 - 7.3 (3H, m, m- and p-protons of N-Bz group), 6.43 (1H, t, $J_{1',2'} = J_{1',2''}$ 6.7 Hz, H-1'), ca. 4.75 (1H, m, H-3'), 4.05 (1H, m, H-4'), 3.74 (2H, m, H-5' and 5"), 2.7 (2H, m, H-2' and 2"), and 1.1 (21H, m, iPr x 3).

Anal. Calcd for $C_{26}H_{37}O_4N_5Si$: C, 61.03; H, 7.29; N, 13.69. Found: C, 60.79; H, 7.27; N, 13.70.

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