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Total synthesis of dapiramicin B

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Abstract—The first total synthesis of dapiramicin B, a nucleoside antibiotic, is described. The characteristic N-glycoside linkage in dapiramicin B was effectively constructed by way of the Pd-catalyzed coupling reaction of a heptopyranosylamine with a bromopyrrolopyrimidine derivative.

Dapiramicin B (**1**) is a nucleoside antibiotic produced by *Micromonospora* sp. SF-1917, and reported to show weak in vivo activity against the sheath blight of rice plants caused by *Rhizoctonia solani* in a green house test.[1] The structurally related antibiotic, dapiramicin A which is more potent than dapiramicin B, has been also isolated from the same microorganism. The structure of dapiramicin A was determined by careful spectral and degradation studies to be 2-[4′-(4″-*O*-methyl-β-D-glucopyranosyl)-6′-deoxy-α-D-glucopyranosyl]amino-5-cyano-4-methoxy-7*H*-pyrrolo[2,3-*d*]pyrimidine (Fig. 1).[2] By spectral comparison, it was shown that the structure of dapiramicin B (**1**) was closely related to dapiramicin A, and assigned to be a 6′-hydroxylated derivative of dapiramicin A possessing a β-N-glycoside linkage.[2] The structures of dapiramicins are unusual and quite unique among nucleoside antibiotics with respect to the N-glycoside structures; while conventional nucleoside antibiotics bear a sugar at the endocyclic nitrogen in the heterocycles, dapiramicins are glycosylated at the exocyclic nitrogen. In spite of their structural feature, no synthetic approach to dapiramicins has been reported. In this letter, we report the first total synthesis of dapiramicin B (**1**), which fully confirmed its unique structure.

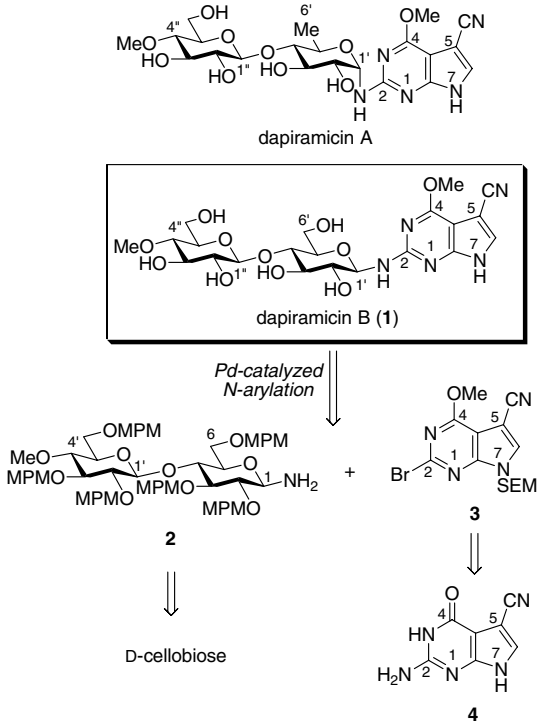

Figure 1. Structures of dapiramicins and retrosynthetic route to dapiramicin B (**1**). MPM = $-CH_2C_6H_4$(*p*-OMe), SEM = $-CH_2O-CH_2CH_2SiMe_3$.

Our retrosynthetic analysis (Fig. 1) suggested that the N-glycoside structure in **1** would be constructed by the Pd-catalyzed coupling reaction of protected glycosylamine **2** with bromo-heterocycle derivative **3**. This methodology, an important extension of the Buchwald–Hartwig N-arylation reaction,[3] proved to be effective for the construction of the N-glycoside bond between a

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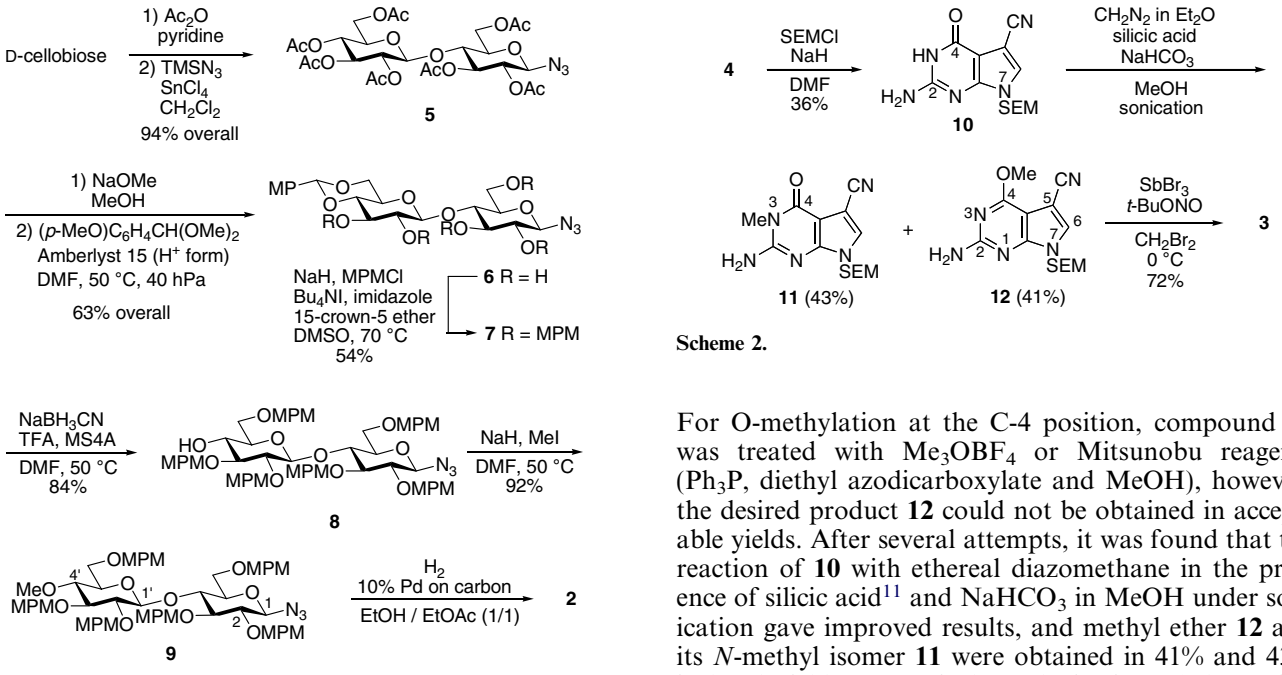


Scheme 1. MP = (*p*-MeO)C_6H_4–.

sugar and an exocyclic nitrogen of heterocycles[4] and was successfully utilized in our total synthesis of spicamycin, a nucleoside antibiotic possessing the similar N-glycoside bond between a sugar moiety and C-6 amino group of adenine.[5] The disaccharide–amine **2** was planned to be prepared from D-cellobiose, while the bromo-heterocycle **3** was envisioned as arising from the known 2-amino-5-cyanopyrrolo[2,3-*d*]pyrimidin-4-one (**4**).[6]

Synthesis of glycosylamine **2** commenced from commercially available D-cellobiose (Scheme 1). O-Acetylation of D-cellobiose, followed by introduction of an azide function to the anomeric carbon provided the known β-azide derivative **5**.[7] Removal of the *O*-acetyl groups and subsequent treatment with anisaldehyde dimethyl acetal gave 4′,6′-*O*-anisylidene compound **6**[8] in 63% yield. The remaining hydroxy groups in **6** was fully protected as *O*-MPM ethers to give **7** (54% yield). The anisilydene acetal in **7** was regioselectively cleaved by the action of $NaBH_3CN$ in the presence of trifluoroacetic acid (TFA)[9] to afford **8** in 84% yield, whose hydroxy group was converted into methyl ether to provide **9** in 92% yield. Hydrogenation of **9** in the presence of 10% Pd on carbon cleanly afford glycosylamine **2**,[10] whose anomeric configuration at C-1 was confirmed to be β by ^{1}H NMR analysis (H-1; $\delta = 4.06$, $J_{1,2} = 8.4$ Hz). Since amine **2** was found to be not so stable and was thus used without purification in the next coupling reaction.

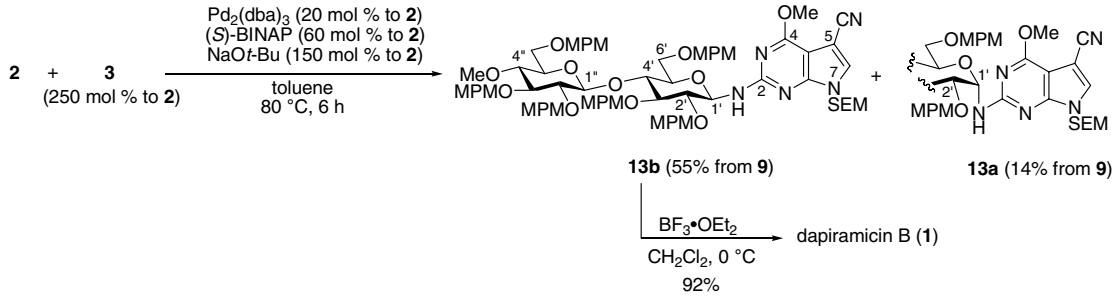
The requisite counter part of the coupling reaction, bromo-heterocycle **3** was synthesized as shown in Scheme 2. Treatment of the known 5-cyanopyrrolopyrimidine **4**,[6] prepared in 70% yield by condensation of 2-chloro-2-formylacetonitrile with 2,4-diamino-6-hydroxypyrimidine, with 2-(trimethylsilyl)ethoxymethyl chloride (SEMCl) in the presence of NaH gave **10** in 36% yield.

Scheme 2.

For O-methylation at the C-4 position, compound **10** was treated with Me_3OBF_4 or Mitsunobu reagents (Ph_3P, diethyl azodicarboxylate and MeOH), however, the desired product **12** could not be obtained in acceptable yields. After several attempts, it was found that the reaction of **10** with ethereal diazomethane in the presence of silicic acid[11] and $NaHCO_3$ in MeOH under sonication gave improved results, and methyl ether **12** and its *N*-methyl isomer **11** were obtained in 41% and 43% isolated yields, respectively. Substitution of the amino function in **12** into a bromo substituent was successfully achieved by treatment of **12** with $SbBr_3$ and *t*-BuONO in CH_2Br_2[12] to afford **3**[10] in 72% yield.

Having completed the preparation of both glycosylamine **2** and heterocycle **3**, we next investigated the key reaction, construction of the N-glycoside (Scheme 3). Reaction of **2** with **3** (200 mol % to **2**) under the similar reaction conditions employed in the synthesis of spicamycin [$Pd_2(dba)_3$ (10 mol % to **2**), (*S*)-BINAP (20 mol % to **2**) and NaO-*t*-Bu (150 mol % to **2**) in toluene][3f,4,5b] at 100 °C for 1 h in a sealed tube successfully provided coupling products **13b**[10] and **13a**[10] in moderate yields (**13b** in 30% and **13a** in 12% yields from **9**, respectively). After some attempts, **13b** and **13a** were obtained in 55% and 14% isolated yields, respectively, when the reaction was carried out in the presence of the increased amount of **3** (250 mol % to **2**), $Pd_2(dba)_3$ (20 mol % to **2**) and (*S*)-BINAP (60 mol % to **2**) in toluene at 80 °C for 6 h.[13] The observed signals of anomeric protons of the N-glycoside moiety in **13b** ($\delta = 5.31$, $J_{1',2'} = 9.0$, $J_{1',NH} = 9.0$ Hz) and **13a** ($\delta = 5.77$, $J_{1',2'} = 4.8$, $J_{1',NH} = 6.0$ Hz) in the ^{1}H NMR spectra clearly assigned their anomeric configurations. The correlation between H-1′ (anomeric proton) and C-2 on the heterocycle observed in HMBC experiments of **13b** also supported its N-glycoside structure. Whereas an anomerically pure β-glycosylamine **2** was employed as the starting material, the coupling products **13a** and **13b** were obtained as an anomeric mixture. These results suggested that the anomerization of **2**, **13a** and/or **13b** had occurred during the reaction.[14] Similar thermal anomerization of glycoslyamines[15a] and N-glycosides possessing a protected adenine[5b] and other substituents,[15] which are proposed to involve imine or iminium intermediates,[15c] have been reported from several groups.

Finally, treatment of **13b** with excess BF_3OEt_2[16] in CH_2Cl_2 at 0 °C for 30 min removed the *O*-MPM as well



Scheme 3.

as *N*-SEM protecting groups to furnish dapiramicin B (**1**) in 92% yield after purification with the reversed-phase and gel filtration chromatographies. The physical properties as well as spectral data (^{1}H NMR and IR) of synthetic specimen {mp 241–244 °C; $[\alpha]_D^{20}$ −36.3 (*c* 0.12, 50% aqueous AcOH)} showed good accordance with those reported for natural dapiramicin B {mp 241–243 °C; $[\alpha]_D^{20}$ −37.6 (*c* 1.0, 50% aqueous AcOH)}.[2a]

In summary, the first total synthesis of dapiramicin B (**1**) has been accomplished. This synthesis fully confirmed the proposed structure of the natural product and revealed that the Pd-catalyzed N-arylation methodology is highly effective for construction of N-glycoside structures in which an exocyclic nitrogen of the heterocycle is connected to the sugar. Further study for the stereoselective synthesis of dapiramicin A based on the same methodology is underway.

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10. *Data of compound* **2**: $[\alpha]_D^{23}$ +24.8 (*c* 1.00, $CHCl_3$); ν_{max} (neat) 3400 and 3330 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.31–7.18 (m, 12H), 6.88–6.72 (m, 12H), 5.01 (d, 1H, $J = 10.8$ Hz), 4.79 and 4.77 (2d, each 1H, $J = 10.5$ Hz), 4.73 (d, 1H, $J = 10.8$ Hz), 4.69 (d, 2H, $J = 10.5$ Hz), 4.65 and 4.63 (2d, each 1H, $J = 10.8$ Hz), 4.55 (d, 1H, $J = 12.0$ Hz), 4.43 (s, 2H), 4.32 (d, 1H, $J = 12.0$ Hz), 4.31 (d, 1H, $J = 8.5$ Hz), 4.06 (d, 1H, $J = 8.4$ Hz), 3.95 (dd, 1H, $J = 9.0$ and 9.0 Hz), 3.80–3.77 (m, 1H), 3.80 (s, 6H), 3.78, 3.78, 3.77 and 3.73 (4s, each 3H), 3.71 (dd, 1H, $J = 11.4$ and 0.9 Hz), 3.59 (dd, 1H, $J = 10.8$ and 1.5 Hz), 3.57 (dd, 1H, $J = 9.0$ and 9.0 Hz), 3.54 (dd, 1H, $J = 11.4$ and 5.1 Hz), 3.48 (s, 3H), 3.34 (ddd, 1H, $J = 9.0$, 3.0 and 1.5 Hz), 3.30–3.16 (m, 4H) and 3.12 (dd, 1H, $J = 9.0$ and 8.4 Hz); ^{13}C NMR ($CDCl_3$, 300 MHz): δ 159.09, 159.06, 159.00, 158.84, 158.74, 131.47, 130.88, 130.70, 130.65, 130.62, 129.80, 129.78, 129.75, 129.63, 129.40, 129.33, 128.92, 113.74, 113.67, 113.60, 113.56, 113.33, 102.27, 86.18, 84.51, 83.58, 82.30, 82.21, 79.88, 76.58, 75.80, 75.13, 75.04, 74.66, 74.52, 74.40, 72.94, 72.85, 68.74, 67.81, 60.51, 55.21, 55.19, 55.17, 55.11 and 55.06; MS (FAB) *m*/*z* 1076 $(M+H)^+$. *Data of compound* **3**: mp 113–116 °C; ν_{max} (neat) 2235 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.67 (s, 1H), 5.57 (s, 2H), 4.17 (s, 3H), 3.54 (t, 2H, $J = 8.1$ Hz), 0.91 (t, 2H, $J = 8.1$ Hz) and −0.05 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 162.92, 152.29, 145.35, 133.44, 113.68, 103.58, 85.98, 73.74, 67.44, 55.25, 17.60 and −1.53; MS (EI) *m*/*z* 384 (M+2, 13%), 382 (M^+, 13), 341 (29), 339 (30), 326 (73), 324 (72), 311 (23), 309 (27), 268 (62), 266 (62), 245 (23), 103 (26), 73 (100); HRMS (EI) *m*/*z* 384.0441, calcd for $C_{14}H_{19}{}^{81}BrN_4O_2Si$ (M^+); 384.0440. *Data of compound* **13a**: $[\alpha]_D^{23}$ +56.6 (*c* 0.80, $CHCl_3$); ν_{max} (neat) 3440, 3370 and 2210 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.42 (s, 1H), 7.33–7.08 (m, 12H), 6.86–6.66 (m, 12H), 5.80 (d, 1H, exchangeable with D_2O, $J = 6.0$ Hz), 5.77 (dd, 1H, $J = 6.0$ and 4.8 Hz), 5.48 and 5.38 (2d, each 1H, $J = 10.7$ Hz), 4.98 (d, 1H, $J = 11.4$ Hz), 4.72 (d, 1H, $J = 10.5$ Hz), 4.70 (d, 1H, $J = 10.8$ Hz), 4.66 (d, 1H, $J = 10.5$ Hz), 4.65 (d, 1H, $J = 11.4$ Hz), 4.60 (d, 1H, $J = 11.3$ Hz), 4.59 (d, 1H, $J = 10.8$ Hz), 4.54 (d, 1H, $J = 11.7$ Hz), 4.43 (s, 2H), 4.43 (d, 1H, $J = 11.3$ Hz), 4.29 (d, 1H, $J = 6.9$ Hz), 4.29 (d, 1H, $J = 11.7$ Hz), 4.05 (s,

3H), 4.02 (dd, 1H, $J = 9.4$ and 7.8 Hz), 3.85 (dd, 1H, $J = 10.8$ and 2.4 Hz), 3.79–3.67 (m, 4H), 3.79 and 3.78 (2s, each 3H), 3.75 (s, 6H), 3.74 and 3.72 (2s, each 3H), 3.60–3.45 (m, 2H), 3.54 (t, 2H, $J = 8.3$ Hz), 3.48 (s, 3H), 3.33–3.14 (m, 4H), 0.88 (t, 2H, $J = 8.3$ Hz) and −0.06 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 163.59, 159.23, 159.18, 159.08, 158.97, 158.90, 158.85, 153.81, 131.41, 130.90, 130.71, 130.68, 130.61, 129.87, 129.84, 129.70, 129.57, 129.50, 129.43, 129.32, 128.98, 115.17, 113.71, 113.68, 113.58, 113.55, 113.52, 113.40, 102.66, 98.24, 85.47, 84.51, 82.24, 79.75, 79.68, 77.77, 77.20, 76.26, 75.17, 74.96, 74.52, 74.43, 73.33, 72.91, 72.80, 72.49, 70.47, 68.75, 67.54, 66.92, 60.53, 55.24, 55.20, 55.18, 55.15, 55.12, 55.07, 54.09, 17.74 and −1.41; MS (FAB) m/z 1379 $(M+H)^+$. Anal. Calcd for $C_{75}H_{91}N_5O_{18}Si$: C, 65.34; H, 6.65; N, 5.08. Found: C, 65.47; H, 6.64; N, 4.89. *Data of compound* **13b**: $[\alpha]_D^{25}$ +11.9 (c 0.80, $CHCl_3$); ν_{max} (neat) 3350 and 2230 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, 45 °C): δ 7.38 (s, 1H), 7.32–7.11 (m, 12H), 6.85–6.76 (m, 12H), 5.44 and 5.37 (2d, each 1H, $J = 10.5$ Hz), 5.31 (dd, 1H, $J = 9.0$ and 9.0 Hz), 5.19 (d, 1H, exchangeable with D_2O, $J = 9.0$ Hz), 5.05 (d, 1H, $J = 10.8$ Hz), 4.76 (d, 1H, $J = 11.1$ Hz), 4.74 (d, 1H, $J = 11.0$ Hz), 4.70 (d, 1H, $J = 10.8$ Hz), 4.69 (d, 1H, $J = 10.8$ Hz), 4.68 (d, 1H, $J = 10.8$ Hz), 4.65 (d, 1H, $J = 11.0$ Hz), 4.63 (d, 1H, $J = 11.1$ Hz), 4.52 (d, 1H, $J = 11.9$ Hz), 4.48 and 4.43 (2d, each 1H, $J = 11.4$ Hz), 4.37 (d, 1H, $J = 7.2$ Hz), 4.28 (d, 1H, $J = 11.9$ Hz), 4.04 (s, 3H), 4.04 (dd, 1H, $J = 9.0$ and 9.0 Hz), 3.83 (dd, 1H, $J = 11.3$ and 3.3 Hz), 3.80–3.72 (m, 1H), 3.80 (s, 6H), 3.79, 3.77, 3.76 and 3.75 (4s, each 3H), 3.70 (dd, 1H, $J = 9.0$ and 9.0 Hz), 3.60(dd, 1H, $J = 11.3$ and 1.5 Hz), 3.58–3.47 (m, 2H), 3.53 (t, 2H, $J = 8.0$ Hz), 3.48 (s, 3H), 3.44 (ddd, 1H, $J = 9.0$, 3.3 and 1.5 Hz), 3.35 (dd, 1H, $J = 9.0$ and 9.0 Hz), 3.31–3.22 (m, 3H), 0.88 (t, 2H, $J = 8.0$ Hz) and −0.05 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz, 45 °C): δ 163.63, 159.36, 159.24, 159.21, 159.05, 159.03, 158.90, 153.96, 131.52, 131.10, 130.91, 130.50, 130.33, 130.06, 129.87, 129.75, 129.60, 129.33, 129.26, 128.94, 115.01, 113.83, 113.77, 113.75, 113.68, 113.52, 102.34, 98.18, 85.69, 84.63, 84.05, 82.42, 80.20, 79.64, 76.58, 76.28, 75.30, 75.09, 74.75, 74.44, 74.20, 73.34, 73.02, 69.05, 67.80, 66.98, 60.45, 55.25, 55.20, 55.15, 55.07, 53.76, 17.82 and −1.41; MS (FAB) m/z 1379 $(M+H)^+$. *Data of compound* **1**: mp 241–244 °C; $[\alpha]_D^{24}$ −36.3 (c 0.12, 50% aqueous AcOH), {lit.[2a] mp 241–243 °C; $[\alpha]_D^{20}$ −37.6 (c 1.00, 50% aqueous AcOH)}; ν_{max} (KBr) 3400 and 2235 cm^{-1}; ^{1}H NMR (DMSO-d_6/D_2O = 10/1, 300 MHz): δ 7.81 (s, 1H), 5.04 (d, 1H, $J = 8.3$ Hz), 4.27 (d, 1H, $J = 7.8$ Hz), 3.97 (s, 3H), 3.70–3.55 (m, 1H), 3.50–3.20 (m, 9H), 3.40 (s, 3H), 3.01 (dd, 1H, $J = 8.4$ and 7.8 Hz), and 2.92 (dd, 1H, $J = 9.3$ and 8.4 Hz); ^{13}C NMR (DMSO-d_6, 75 MHz, 50 °C): δ 162.4, 158.8, 154.7, 131.3, 115.9, 102.7, 96.53, 82.43, 82.05, 80.16, 79.30, 76.06 (2C), 75.80, 75.38, 73.43, 71.90, 60.52, 60.40, 59.36, 53.08; HRMS (FAB) m/z 528.1938, calcd for $C_{21}H_{29}N_5O_{11}$ $(M+H)^+$ 528.1942. The IR and ^{1}H NMR data were fully identical with those reported for natural dapiramicin B (^{13}C NMR data of natural dapiramicin B have not been reported).[2a]

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13. When (*R*)-BINAP was employed as a ligand, the similar reaction conditions (100 °C, 6 h) afforded **13b** and **13a** in 46% and 9% isolated yields from **9**, respectively. Use of other ligands such as 2-(dicyclohexylphosphino)biphenyl,[3b] 2-(dicyclohexylphosphino)-2′,4′,6′-triisopropylbiphenyl,[3c] or 2-(di-*t*-butylphosphino)binaphthyl,[3d] which have been reported to be effective for the Pd-catalyzed N-arylation of simple amines,[3] significantly decreased the yields of **13b** and **13a**.
14. When the toluene solutions of anomerically pure **13a** and **13b** (2 mM) were separately heated at 100 °C in sealed tubes, both N-glycosides **13a** and **13b** showed thermal anomerization and reached equilibrium at α:β = 1:1.8 after ca. 120 h.
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