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Mechanism of 2-*O*→3-*O* silyl migration in cyclomaltohexaose (α-cyclodextrin)

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Abstract—To gain insight into the mechanism of the well-known 2-*O*→3-*O* silyl migration of 2-*O*-silylated cyclomaltooligosaccharides (cyclodextrins) under basic conditions, we have undertaken studies of the reaction of 2^A-*O*-TBDMSi-6^A-deoxy-6^A-*S*-phenyl-α-cyclodextrin with MeI and NaH. Under these conditions, the TBDMSi group on the C-2 oxygen was found to migrate onto the C-3 oxygen in the glucose residue in which the C-2 oxygen is located, and not onto the C-3 oxygen in the adjacent glucose residue.

Cyclomaltooligosaccharides (cyclodextrins) are cyclic oligosaccharides, typically consisting of six, seven, or eight α-1,4-linked D-(+)-glucopyranose units (α-, β-, and γ-cyclodextrins, respectively), forming cavities that are hydrophobic and optically active. Each glucopyranose unit possesses a primary hydroxyl group at the C-6 position and secondary hydroxyl groups at the C-2 and C-3 positions.[1] Because of the commercial availability of these cyclodextrins, they are widely utilized in the formation of inclusion complexes with various guest molecules, as transporters of hydrophobic molecules, or as building blocks for molecular mimics of enzymes.[2] In these cyclodextrins, the secondary hydroxyl faces, which are larger than the primary hydroxyl faces, serve as the preferential locus for the molecular inclusion of large molecules.[3] Accordingly, cyclodextrin derivatives that have modified secondary hydroxyl faces often possess significantly different properties than those that have their primary hydroxyl faces modified,[4] and consequently, functionalization of the secondary hydroxyl faces have been further investigated in order to enhance the utility of cyclodextrins. During these investigations, 2-*O*→3-*O* silyl migration of 2-*O*-silyl-cyclodextrins under basic conditions was observed,[5] which was subsequently employed as a method for the silyl protection of C-3 hydroxyl groups.[5a,d,6] Although the understanding of silyl migration is important towards the preparation of various 3-*O*-silyl-cyclodextrins, the mechanism of the migration has remained unclear. As shown in Figure 1, Stoddart et al.[5a] proposed intra-glucosidic 2-*O*→3-*O* silyl migration mechanism (Route A), whereas Konig et al.[5c] suggested possibility of inter-glucosidic 2-*O*→3-*O* silyl migration (Route B). In the cases where partially 2-*O*-silylated cyclodextrins are employed for the 2-*O*→3-*O* silyl migration, it is extremely important to predict to which C-3 oxygens

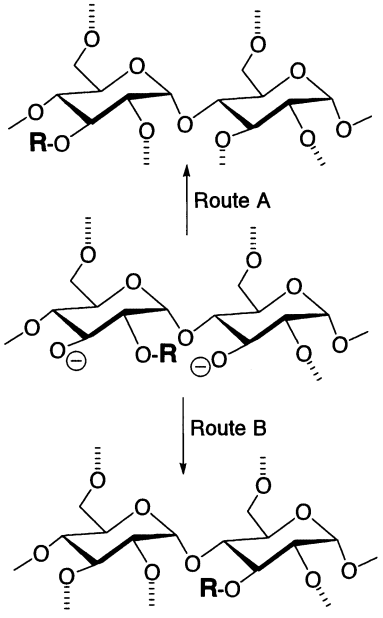

Figure 1. Proposed mechanisms for intra-glucosidic (route A) and inter-glucosidic (route B) 2-*O*→3-*O* silyl migration.

Keywords: cyclodextrin; silyl migration.
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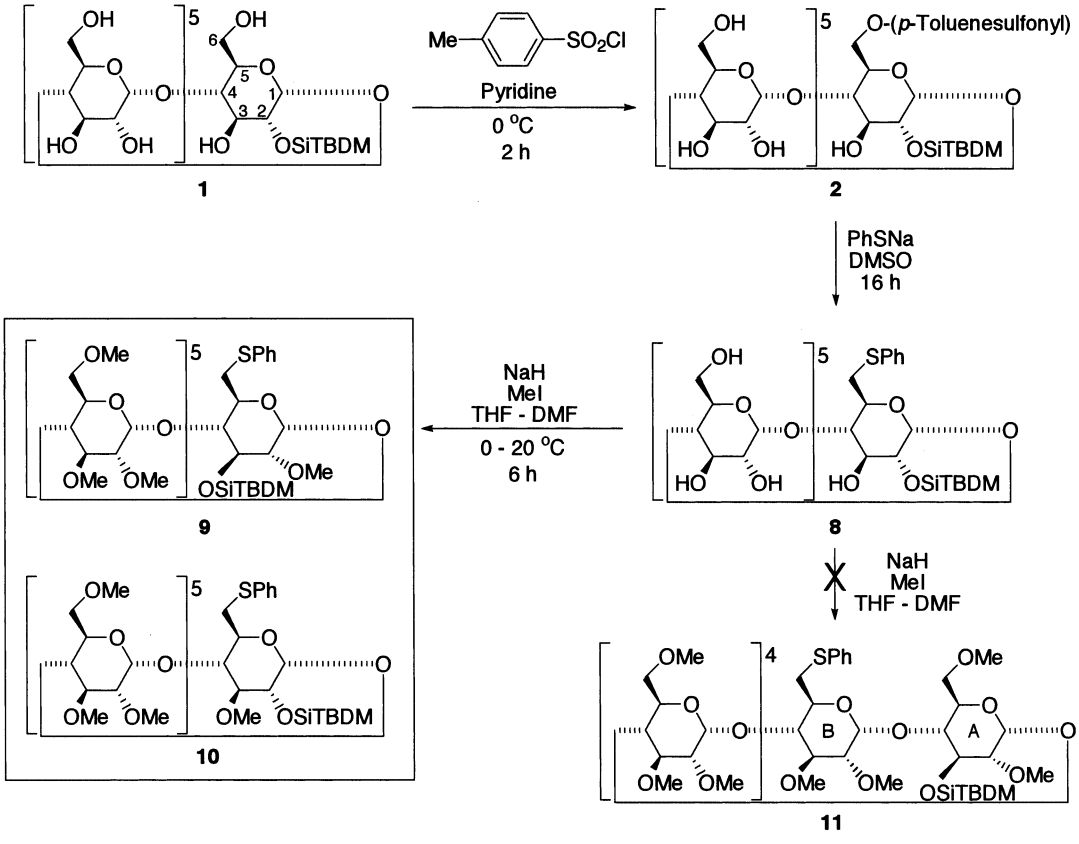
the silyl groups will migrate. Herein we report on our studies on mono-2-*O*-silyl-α-cyclodextrin, which provided valuable clues to describe the mechanisms of 2-*O*→3-*O* silyl migration.

Recently, as part of our studies on the regioselective chemical modification of the C-2 hydroxyl groups of cyclodextrins,[7] the regioselective mono-silylation of the C-2 hydroxyl group of α-cyclodextrin was successfully accomplished by using *tert*-butyldimethylsilyl (TBDMSi) imidazole in the presence of molecular sieves in *N*,*N*-dimethylformamide (DMF).[8] The regioselective silylation in affording 2-*O*-silylated cyclodextrins has proven to be valuable since the free C-6 hydroxyl groups can be subsequently modified without a deprotection step, since 6-*O*-silyl protecting groups are typically employed for 2-*O*-silylations.[5a,d,9] Consequently, this improved methodology allowed the introduction of a substituent as a 'marker' on the C-6 hydroxyl group of mono-2-*O*-TBDMSi-α-cyclodextrin (**1**)[8] for the mechanistic studies of the 2-*O*→3-*O* silyl migration of 2-*O*-silyl cyclodextrins.

Initially, as shown in Scheme 1, 2^{A}-*O*-TBDMSi-6^{A}-*O*-(*p*-toluenesulfonyl)-α-cyclodextrin (**2**) was prepared in a 5.4% yield by reaction of **1** (1.0 g, 0.921 mmol) with *p*-toluenesulfonyl chloride (0.263 g, 1.38 mmol) in pyridine at 0°C for 2 h; these conditions are typically employed for the sulfonylation of the C-6 hydroxyl groups of cyclodextrins.[10] As expected, this sulfonyl reaction resulted in the formation of six 6-*O*-sulfonyl regioisomers—the desired 2^{A}-*O*-TBDMSi-6^{A}-*O*-(*p*-toluenesulfonyl)-α-cyclodextrin (**2**), three regioisomers (**3**–**5**), and a mixture of two regioisomers (**6** and **7**) were readily separated by open reverse-phase column chromatography (15×150 mm, Fuji Silisia Chromatorex-ODS DM1020T gel, 10–50% aqueous MeOH), followed by preparative HPLC (20×250 mm, Cosmosil 5C18-MS column, 50–60% aqueous MeOH). The regiochemistries of the TBDMSi and *p*-toluenesulfonyl groups were determined by ^{1}H NMR spectroscopy (Fig. 2).

The ^{1}H NMR spectrum of **1** (5% D_2O in DMSO-d_6; 60°C; ref., DMSO, δ 2.49 ppm) exhibited a signal corresponding to one H-2 proton of the silylated glucose residue at δ 3.50 ppm, which was downfield from those of the five remaining H-2 protons (δ 3.26–3.33 ppm).[8a] In contrast, the ^{1}H NMR spectrum (similar conditions as above) of mono-6-*O*-(*p*-toluenesulfonyl)-α-cyclodextrin[10] showed a signal for the H-2 proton of the sulfonylated glucose residue at δ 3.20 ppm, which was upfield from those of the five remaining H-2 protons (δ 3.25-3.31 ppm).[11] The ^{1}H NMR properties of **1** and mono-6-*O*-(*p*-toluenesulfonyl)-α-cyclodextrin suggested that when one C-2 hydroxyl group and one C-6 hydroxyl group on the same glucose residue of α-cyclodextrin are simultaneously silylated and *p*-toluenesulfonylated, respectively, the ^{1}H NMR signal of the H-2 proton of the sulfonylated glucose residue should be affected by a combination of the downfield-shift effect by the silyl group and the upfield-shift effect by the sulfonyl group, and should be present at around δ



Scheme 1.

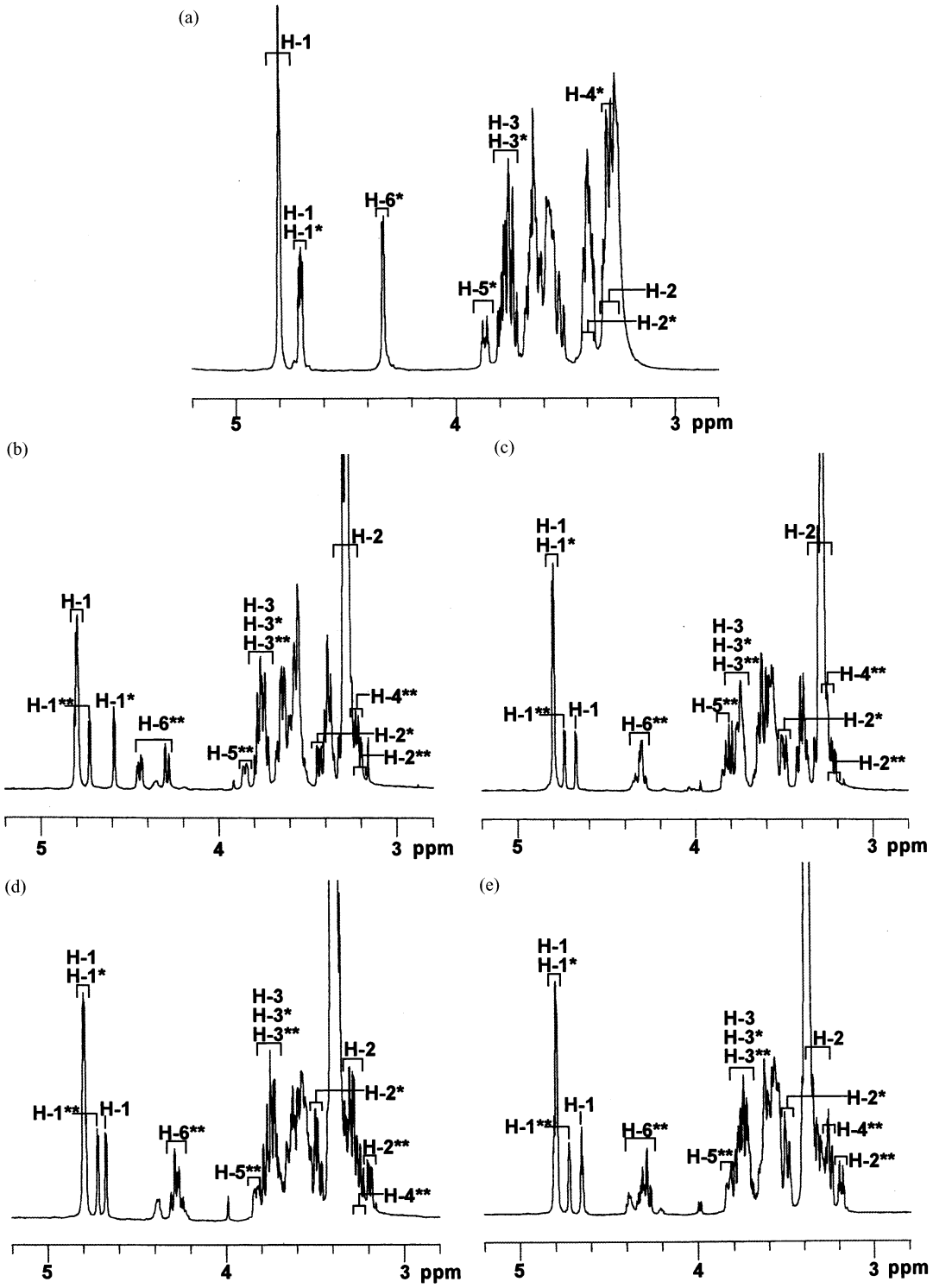


Figure 2. Partial ^{1}H NMR spectra of **2**–**7** (5%D_2O in DMSO-d_6; ref., DMSO, δ 2.49 ppm). The assigned signals are numbered according to the usual convention shown in Scheme 1, and the symbols * and ** refer to the 2-*O*-silylated glucose residue and the 6-*O*-sulfonylated glucose residue, respectively. In case of **2**, the symbol * refers to the 2-*O*-silylated and 6-*O*-sulfonylated glucose residue. [a] ^{1}H NMR of **2** at 80°C;[12] [b] ^{1}H NMR of **3** at 60°C; [c] ^{1}H NMR of **4** at 60°C; [d] ^{1}H NMR of **5** at 60°C; [e] ^{1}H NMR of a mixture of **6** and **7** at 60°C.

3.40 ppm. The five remaining H-2 protons should be at around δ 3.25–3.33 ppm. On the other hand, if the 2-*O*-silyl group and the 6-*O*-sulfonyl group are located on different glucose residues, the H-2 proton of the silylated glucose residue should be expected at around δ 3.50 ppm as the result of only the downfield-shift effect by the silyl group, whereas the H-2 proton of the sulfonylated glucose residue should be expected at around δ 3.20 ppm as the result of only the upfield-shift effect by the sulfonyl group.

The ^{1}H NMR spectra of **2**–**7**, as shown in Figure 2, include partial spectral assignments of **2**–**7** using ^{1}H–^{1}H COSY and HOHAHA experiments. As shown in Figure 2(a),[12] the ^{1}H NMR spectrum of **2**[13] exhibited an appreciable downfield-shift of one H-2 proton (δ 3.38 ppm). HOHAHA experiments showed a correlation between this proton and the H-6 protons that are located at the sulfonylated C-6 position, indicating that the structure of **2** is 2^A-*O*-TBDMSi-6^A-*O*-(*p*-toluenesulfonyl)-α-cyclodextrin (the glucose residues are designated using letters A through F, clockwise, as viewed from the primary hydroxyl face). Furthermore, the ^{1}H NMR characteristics of the H-2 proton of **2** were in agreement to the expected ^{1}H NMR chemical shift of the H-2 proton that was described in the above section. The ^{1}H NMR spectra of **3**–**7**, as shown in Figure 2(b) and (e), respectively, showed characteristic signals for the H-2 proton at around δ 3.20 ppm and for the H-2 protons at around δ 3.50 ppm. The results of the HOHAHA experiments indicated that the former protons corresponded to the 6-*O*-sulfonylated glucose residues, and therefore, the latter protons can be assigned as the H-2 protons of the 2-*O*-silylated glucose residues, as expected from the ^{1}H NMR chemical shifts of the H-2 proton as described in the above section. The results of these studies indicated that **3**–**7** do not possess TBDMSi and sulfonyl groups in the same glucose residue of the cyclodextrin molecules. Detailed regiochemistries of **4**–**7** were not obtained using NMR spectroscopic studies. However, the assignment of **3** as 2^A-*O*-TBDMSi-6^F-*O*-(*p*-toluenesulfonyl)-α-cyclodextrin was accomplished using 2D ROESY NMR technique, which indicated a cross-peak between the H-4 proton of the 6-*O*-sulfonylated glucose residue and the H-1 proton of the 2-*O*-silylated glucose residue.

Kaneda et al. have reported the successful methylation of mono-6-*O*-(*p*-toluenesulfonyl)-cyclodextrins under basic conditions using MeI and NaH in DMF without the cleavage of the *p*-toluenesulfonyl group.[14] In this present study, **2** was treated with MeI and NaH in a mixture of THF and DMF (5:1) at 0–20°C, resulting in the cleavage of the *p*-toluenesulfonyl group as the 'marker', which can be attributed to the high proportion of THF in the reaction solvent.[15] Since the *p*-toluenesulfonyl group cannot function as the 'marker' under basic conditions, **2** was consequently derivatized as 2^A-*O*-TBDMSi-6^A-deoxy-6^A-*S*-phenyl-α-cyclodextrin (**8**)[16] in a 91% yield by treatment with NaSPh (2.0 equiv.) in DMSO under argon gas (Scheme 1). The structure of **8** was determined by ^{1}H NMR, which exhibited a significant downfield-shift of one H-2 proton (δ 3.55 ppm) against the remaining H-2 protons (δ 3.26–3.40 ppm), indicating that the TBDMSi group did not migrate to the C-3 position. Additionally, treatment of compound **8** with NaH without MeI in a mixture of THF and DMF (10:1) afforded only **8**, indicating that the 2-*O*-TBDMSi group is unable to migrate in the basic condition without MeI and supporting that the TBDMSi group of **2** did not migrate to other hydroxyl groups in the reaction with NaSPh that is more basic-less than NaH. Subsequently, the silyl migration of **8** was investigated using MeI and NaH in the mixture of THF and DMF (10:1)[15] at 0–20°C, as shown in Scheme 1. A ratio of the resulting crude products, methylated 3^A-*O*-TBDMSi-6^A-deoxy-6^A-*S*-phenyl-α-cyclodextrin (**9**)[17] and methylated 2^A-*O*-TBDMSi-6^A-deoxy-6^A-*S*-phenyl-α-cyclodextrin (**10**)[18] was determined by HPLC and ^{1}H NMR as 4.5:1 and 4.3:1, respectively, and then these products were isolated using preparative HPLC (20×250 mm, Cosmosil 5C18-MS column, 80% aqueous EtOH), in 56 and 7.8% yields, respectively. The structures of **9** and **10** were confirmed by ^{1}H and ^{13}C NMR spectroscopy. As shown in Figure 3(a), the ^{1}H NMR spectrum of **9**, which were assigned using ^{1}H–^{1}H COSY, HOHAHA ^{13}C–^{1}H COSY, and DEPT experiments, showed a significant downfield-shift of the H-3 proton (δ 4.13 ppm) of the 6-phenylthiolated glucose residue relative to the H-3 protons (δ 3.52–3.63 ppm) of other glucose residues. Furthermore, the H-2 proton (δ 3.12 ppm) of the 6-phenylthiolated glucose residue showed a slight upfield-shift against the remaining H-2 protons (δ 3.13–3.20 ppm), indicating that the TBDMSi group was not located on the C-2 oxygen of the 6-phenylthiolated glucose residue. If the silyl group was located on the C-2 oxygen, the ^{1}H NMR spectrum should show a downfield shift of the H-2 proton of the 2-*O*-silylated glucose residue against the remaining H-2 proton. These ^{1}H NMR characteristics of the H-2 and H-3 protons of the 6-phenylthiolated glucose residue of **9** indicated that the TBDMSi group on the C-2 oxygen of the 6-phenylthiolated glucose residue of **8** migrated onto the C-3 oxygen of the same glucose residue. As shown in Figure 3(c), the ^{1}H NMR spectrum of **10**, which was assigned using ^{1}H-^{1}H COSY, HOHAHA ^{13}C–^{1}H COSY, and DEPT experiments, exhibited i) appreciable downfield-shift of the H-2 proton (δ 3.57 ppm) of the 6-phenylthiolated glucose residue relative to the remaining H-2 protons (δ 3.12–3.20 ppm) and ii) an insignificant shift of the H-3 proton (approximately 3.50 ppm) of the 6-phenylthiolated glucose residue relative to the remaining H-3 protons (δ 3.50–3.65 ppm). These results indicated that the TBDMSi group was located on the C-2 oxygen of the 6-phenylthiolated glucose residues of **10**. The ^{13}C NMR spectra of **9** and **10**, as shown in Figure 3(b) and (d), respectively, which was assigned using ^{13}C–^{1}H COSY and DEPT experiments, showed significant upfield-shifts of one C-3 carbon of **9** and one C-2 carbon of **10** relative to the other carbons of **9** and **10**, thus supporting that the TBDMSi group was located on the C-3 oxygen of **9** or on the C-2 oxygen of **10**. These results undoubtedly demonstrated that the TBDMSi group on the C-2 oxygen of **8** rearranged onto the C-3 oxygen via intra-glucosidic silyl migration (Fig. 1, Route A), and not via inter-glucosidic silyl migration (Fig. 1, Route B), which affords 3^A-*O*-TBDMSi-6^B-deoxy-6^B-*S*-phenyl-α-cyclodextrin (**11**) (Scheme 1). In the case of the present methylation of **8** under the basic condition, HPLC, NMR, and TLC techniques showed that only **9** and **10** were afforded as the methylated products, without other methylated *O*-TBDMSi-6-*S*-phenyl-α-cyclodextrins, thus indicating that the silyl migration mechanism for **8** must occur through intra-glucosidic silyl migration.

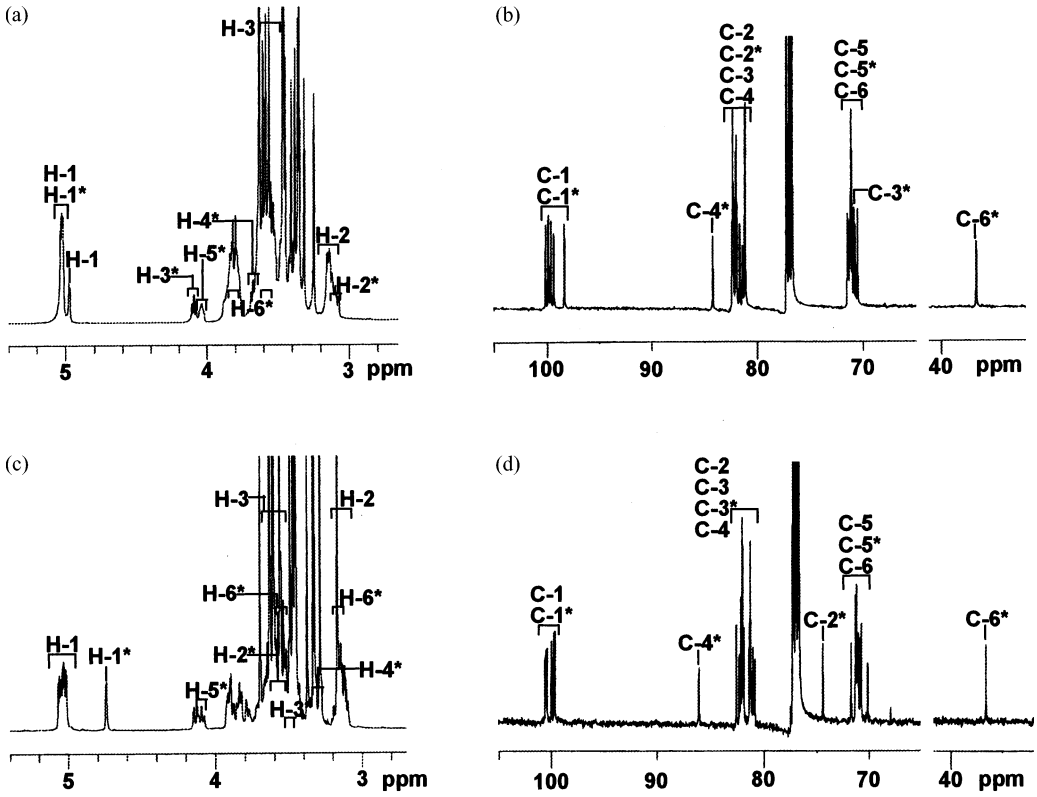


Figure 3. Partial ^{1}H and ^{13}C NMR spectra of **9** and **10** ($CDCl_3$; 20°C; ref., TMS, δ 0.00 ppm). The assigned signals are numbered according to the usual convention shown in Scheme 1, and the symbol * refers to the silylated glucose residue. (a) ^{1}H NMR of **9**; (b) ^{13}C NMR of **9**; (c) ^{1}H NMR of **10**; (d) ^{13}C NMR of **10**.

In conclusion, we have demonstrated that the silyl migration mechanism of 2^{A}-*O*-TBDMSi-6^{A}-deoxy-6^{A}-*S*-phenyl-α-cyclodextrin occurs via intra-glucosidic silyl migration. This insight can be useful for the preparation of partial-3-*O*-TBDMSi-α-cyclodextrins from partial-2-*O*-TBDMSi-α-cyclodextrins by means of silyl migration, because the regiochemistry between the TBDMSi groups in the partial-3-*O*-TBDMSi-α-cyclodextrins can be expected to remain unchanged from that of partial-2-*O*-TBDMSi-α-cyclodextrins. Stoddart et al.[5a] reported that the efficiencies of the silyl migration reactions of per(2,6-di-*O*-TBDMSi)-α-, β-, and γ-cyclodextrins with MeI and NaH were different, suggesting that there may be a possibility that the type of cyclodextrin influences the migration route, such as intra- and/or inter-glucosidic migrations. Investigation on the silyl migration mechanism of 2-*O*-TBDMSi-β- and 2-*O*-TBDMSi-γ-cyclodextrins is currently in progress.

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11. ^{1}H NMR chemical shifts (5%D_2O in DMSO-d_6; 60°C; ref., DMSO, δ 2.49 ppm) of mono-6-*O*-(*p*-toluenesulfonyl)-α-cyclodextrin: δ 2.39 (3H, s, CH_3), 3.20 (1H, dd, $J=3.1$ and 9.8 Hz, H-2 proton of sulfonylated glucose residue), 3.25 (1H, t, $J=9.2$ Hz, H-4 proton of sulfonylated glucose residue), 3.25–3.31 (5H, m, H-2 protons of unsulfonylated glucose residues), 3.34–3.41 (5H, m, H-4 protons of unsulfonylated glucose residues), 3.47–3.76 (m), 3.82 (1H, H-5 proton of sulfonylated glucose residue), 4.26–4.32 (2H, m, H-6 protons of sulfonylated glucose residue), 4.66 (1H, d, $J=3.1$ Hz, H-1 proton of unsulfonylated glucose residue), 4.72 (1H, d, $J=3.7$ Hz, H-1 proton of sulfonylated glucose residue), 4.77–4.81 (4H, m, H-1 proton of no-sulfonylated glucose residue), 7.42 (2H, d, $J=7.9$ Hz, ArH), and 7.72 (2H, d, $J=7.9$ Hz, ArH).
12. The ^{1}H NMR chemical shifts of **2** measured at 60°C (5%D_2O in DMSO-d_6) were not significantly different from those measured at 80°C. However, since the signals observed in the spectrum at 60°C were slightly broader, the spectrum at 80°C is presented herein.
13. Data for **2**. Colorless powder. Mp. 142°C (dec.). IR (KBr) ν 3389 and 2928 cm^{-1}. ^{1}H NMR (5% D_2O in DMSO-d_6; 80°C; ref., DMSO, δ 2.49 ppm) omitted in Fig. 2(a): δ 0.08 (3H, s, SiCH_3), 0.10 (3H, s, SiCH_3), 0.87 (9H, s, SiC(CH_3)$_3$), 7.41 (2H, d, $J=8.6$ Hz, Ar*H*), and 7.72 (2H, d, $J=8.6$ Hz, Ar*H*). ^{13}C NMR (5% D_2O in DMSO-d_6; 80°; ref., DMSO, δ 39.50 ppm): δ −3.44 (Si*C*H$_3$), 17.52 (Si*C*(CH$_3$)$_3$), 20.93 (Ph*C*H$_3$), 25.65 (SiC(*C*H$_3$)$_3$), 59.91–60.09 (C-6), 69.18 (C-5*), 69.44 (C-6*), 71.54–73.11 (C-2, C-3, C-5, C-2*, C-3*), 81.61–82.04 (C-4, C-4*), 101.39–101.98 (C-1, C-1*), 127.38 (Ar*C*), 129.80 (Ar*C*), 132.75 (Ar*C*), and 144.71 (Ar*C*). The symbol * refers to the silylated glucose residue. MALDI-TOF-MS m/z 1263.3 for [M+Na]$^+$. Anal. Found: C, 47.05; H, 6.88%, Calcd for $C_{49}H_{80}O_{32}SSi$: C, 47.41; H, 6.50%.
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15. During our studies on the silyl migration, it was shown that the higher the proportion of DMF in the mixture of THF and DMF as the reaction solvent, the lower the efficiency of the silyl migration. Consequently, to attain efficient migration, the proportion of DMF had to be as low as possible, and thus the mixture of THF and DMF was reluctantly used due to the insolubility of **8** for THF.
16. Data for **8**. Colorless powder. Mp. 240°C (dec.). IR (KBr) ν 3398 and 2929 cm^{-1}. ^{1}H NMR (5% D_2O in DMSO-d_6; 50°C; ref., DMSO, δ 2.49 ppm): δ 0.09 (3H, s, SiCH_3), 0.12 (3H, s, SiCH_3), 0.88 (9H, s, SiC(CH_3)$_3$), 3.13 (1H, dd, $J=7.9$, and 13.5 Hz, CH_2SPh), 3.26–3.84 (m), 4.77–4.81 (5H, m, H-1 protons of glucose residues), 4.84 (1H, d, $J=3.7$ Hz), 7.12 (1H, t, $J=7.3$ Hz, Ar*H*), 7.20 (2H, t, $J=7.3$ Hz, ArH), and 7.30 (2H, d, $J=7.3$ Hz, Ar*H*). MALDI-TOF-MS m/z 1201.1 for [M+Na]$^+$. Anal. Found: C, 48.52; H, 6.84%, Calcd for $C_{48}H_{78}O_{29}SSi$: C, 48.89; H, 6.67%.
17. Data for **9**. Colorless powder. Mp. 103–106°C. IR (KBr) ν 3449 and 2929 cm^{-1}. ^{1}H NMR ($CDCl_3$; 20°C; ref., TMS, δ 0.00 ppm) omitted in Figure 3(a): δ 0.15 (3H, s, SiCH_3), 0.21 (3H, s, SiCH_3), 0.94 (9H, s, SiC(CH_3)$_3$), 7.16 (1H, t, $J=7.3$ Hz, Ar*H*), 7.27 (2H, t, $J=7.3$ Hz, ArH), and 7.40 (2H, d, $J=7.3$ Hz, Ar*H*). ^{13}C NMR ($CDCl_3$; 20°C; ref., TMS, δ 0.00 ppm) omitted in Figure 3(b): δ −3.68 (Si*C*H$_3$), −3.08 (Si*C*H$_3$), 18.27 (Si*C*(CH$_3$)$_3$), 26.17 (SiC(*C*H$_3$)$_3$), 125.79 (Ar*C*), 128.79 (Ar*C*), 129.08 (Ar*C*), and 137.11 (Ar*C*). MALDI-TOF-MS m/z 1425.4 for [M+Na]$^+$. Anal. Found: C, 54.51; H, 8.13%, Calcd for $C_{64}H_{110}O_{29}SSi$: C, 54.76; H, 7.90%.
18. Data for **10**. Colorless powder. Mp. 108–112°C. IR (KBr) ν 3449 and 2930 cm^{-1}. ^{1}H NMR ($CDCl_3$; 20°C; ref., TMS, δ 0.00 ppm) omitted in Figure 3(c): δ 0.15 (6H, s, SiCH_3), 0.97 (9H, s, SiC(CH_3)$_3$), 7.19 (1H, t, $J=7.3$ Hz, Ar*H*), 7.28 (2H, t, $J=7.3$ Hz, ArH), and 7.35 (2H, d, $J=7.3$ Hz, Ar*H*). ^{13}C NMR ($CDCl_3$; 20°C; ref., TMS, δ 0.00 ppm) omitted in Figure 3(d): δ −4.65 (Si*C*H$_3$), 18.32 (Si*C*(CH$_3$)$_3$), 25.90 (SiC(*C*H$_3$)$_3$), 125.84 (Ar*C*), 128.82 (Ar*C*), 128.82 (Ar*C*), and 137.66 (Ar*C*). MALDI-TOF-MS m/z 1425.3 for [M+Na]$^+$. Anal. Found: C, 54.48; H, 8.17%, Calcd for $C_{64}H_{110}O_{29}SSi$: C, 54.76; H, 7.90%.