New Permethyl-Substituted β-Cyclodextrin Polysiloxanes for Use as Chiral Stationary Phases in Open Tubular Column Chromatography

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Heptakis(2,3-di-*O*-methyl)-6-*O*-tosyl-β-cyclodextrin (**2**) was prepared from heptakis(2,3-di-*O*-methyl)-β-cyclodextrin (**1**) in a 31% yield. The tosyl group of **2** was substituted by *p*-(allyloxy)phenyl in a yield of 74% to produce 6-*O*-(*p*-(allyloxy)phenyl)heptakis(2,3-di-*O*-methyl)-β-cyclodextrin (**3**). This material was derivatized at the other 6-positions to produce persubstituted 6^A-*O*-(*p*-(allyloxy)phenyl)-β-cyclodextrins **4**, **5**, and **8**. Permethylated 6-*O*-tosyl-β-cyclodextrin **9**, which was used for the preparation of **10**-**12**, was obtained from **2** almost quantitatively. 6-*O*-(*tert*-Butyldimethylsilyl)-(heptakis(2,3-di-*O*-methyl)-β-cyclodextrin (**13**) was also obtained from **1** in a 33% yield. Permethylated 6^A-deoxy-6^A-methylene-β-cyclodextrin (**17**) was prepared from **13** by a 4-step process. Seven new permethyl-substituted β-cyclodextrins bound to polymethylsiloxane were prepared by a hydrosilylation reaction of the permethyl-substituted monoalkenyl-β-cyclodextrins with polyhydromethylsiloxane. The polymeric phases provide excellent enantiomeric separation of a variety of chiral solutes in open tubular column supercritical fluid chromatography (SFC) and gas chromatography (GC).

Introduction

Analytical separation of enantiomers has become very important in light of interest in the resolution of enantiomeric purity in drugs.[1,2] The use of chiral stationary phases (CSPs) in chromatography is the most convenient method for determining enantiomeric purity.[3] In recent years, the use of O-derivatized cyclodextrins as CSPs in capillary gas chromatography (GC) and supercritical fluid chromatography (SFC) has become a powerful tool in modern enantiomer analysis.[4,5] Most of the stationary phases derived from cyclodextrin are prepared by diluting the relevant cyclodextrin derivative in polysiloxane in order to obtain selective chiral separations at temperatures below the melting point of the pure cyclodextrin derivative. The state of the art in this field has been reviewed by Schurig and Nowotny.[4a] A few cyclodextrin stationary phases have been prepared by chemically bonding permethylated alkenyl-substituted β-cyclodextrin to a polysiloxane backbone by a hydrosilylation reaction.[5-7] In these cases, the permethylated alkenyl-substituted β-cyclodextrins were a mixture of cyclodextrins containing 1-7 alkenyl group(s) on the rim of the cyclodextrin instead of a pure monoalkenyl-substituted compound.

Our research objective is to reproducibly prepare quality cyclodextrin phases for capillary SFC and GC in an effort to find chiral phases with wide applicability and excellent properties and to elucidate the mechanism(s) of their enantioselectivity. We have reported the preparation of a novel chiral copolymeric stationary phase composed of cyclodextrin and oligodimethylsiloxane units for capillary SFC.[8] In this paper, we report the preparation of a series of β-cyclodextrins bound to polysiloxane by means of one spacer arm. First, the peralkyl-substituted monoalkenyl-substituted β-cyclodextrins were prepared (see Figure 1). The syntheses of these cyclodextrins are shown in Schemes I-III, and their attachment to a polysiloxane is shown in Scheme IV. The cyclodextrins have arms of various lengths and compositions which serve as models for studying the effect of the spacer arm on the enantiomeric separations of solute test molecules. Distinctly different substituents at the remaining 6-positions of cyclodextrin could help us understand the effect that different substituents on the cyclodextrin rims have on the mechanism of enantioselectivity. These new cyclodextrin-containing phases provide remarkable enantiomeric resolution of a variety of chiral organic solutes in both capillary SFC and GC. Details of these chromatographic results will be reported later. This paper reports the synthesis of these new stationary phases. Their utility in chromatography is shown by the separation of several racemic mixtures on four of the phases reported in this paper.

Results and Discussion

Cyclodextrin monofunctionalized at the 6-position has been prepared previously.[9] The pivotal step was the reaction of cyclodextrin with toluenesulfonyl (tosyl) chloride in pyridine to produce the monotosyl-substituted cyclodextrin. The tosyl group was then replaced by a variety of nucleophiles. Mono(6-*O*-tosyl)heptakis(2,3-di-*O*-methyl)-β-cyclodextrin (**2**, see Scheme I) was obtained in a 31% yield from heptakis(2,3-di-*O*-methyl)-β-cyclo-

(1) *Chem. Eng. News* **1990**, Mar. 19, 38.
(2) Stinson, S. C. *Chem. Eng. News* **1992**, Sept. 28, 46.
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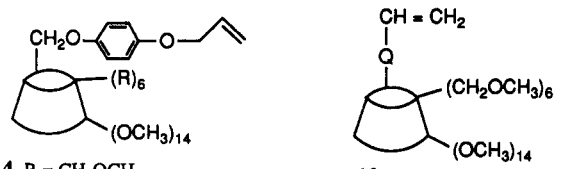
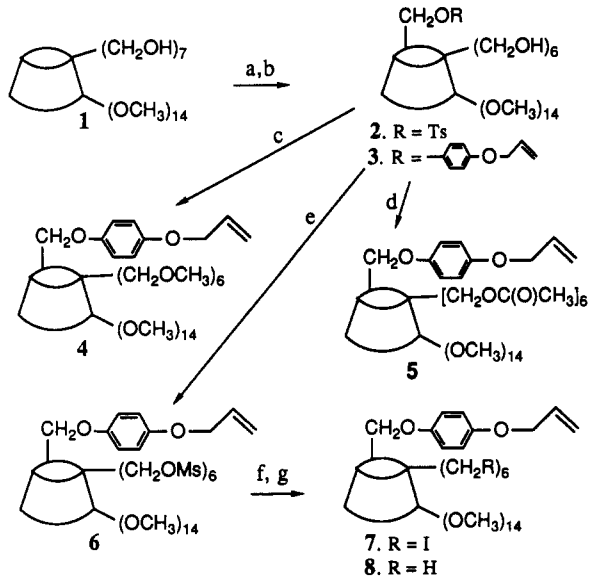


4. R = CH_2OCH_3
5. R = $CH_2OC(O)CH_3$
8. R = CH_3

10. Q = CH_2CH_2
11. Q = CH_2OCH_2
12. Q = $CH_2O(CH_2)_8CH_2$
17. Q = None

Figure 1. Structures of persubstituted monoalkenyl-β-cyclodextrins.

Scheme I. Preparation of Persubstituted Mono((allyloxy)phenyl)-β-cyclodextrins 4, 5, and 8[a]

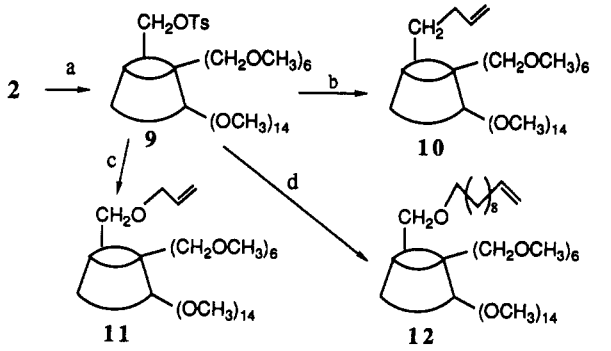


[a] Key: (a) TsCl, pyridine; (b) sodium *p*-(allyloxy)phenoxide, DMF; (c) NaH, CH_3I, DMF; (d) $(CH_3CO)_2O$, pyridine; (e) MsCl, pyridine; (f) NaI, DMF; (g) $NaBH_4$, DMF.

dextrin (1) in a manner similar to that reported for the di(6-*O*-tosyl) analog.[8] The reaction of **2** with sodium *p*-(allyloxy)phenoxide in DMF gave 6-*O*-(*p*-(allyloxy)-phenyl)heptakis(2,3-di-*O*-methyl)-β-cyclodextrin (**3**) in a yield of 74%. 6-O-(*p*-(Allyloxy)phenyl)-β-cyclodextrin could not be prepared from the 6-*O*-tosyl-β-cyclodextrin mentioned above[9] under the same reaction conditions, probably, because of the formation of 3,6-anhydro-β-cyclodextrin.[10] Intermediate **3** was converted into other β-cyclodextrin derivatives with different substituents at the other 6-O positions (**4**, **5**, and **8**) (see Scheme I). Methylation of **3** with sodium hydride and iodomethane in DMF gave permethylated 6-*O*-(*p*-(allyloxy)phenyl)-β-cyclodextrin (**4**). Acetylation of **3** with acetic anhydride in pyridine gave hexaacetate ester **5**. Treatment of **3** with methanesulfonyl (mesyl) chloride in pyridine produced hexamesylate ester **6** in a good yield. The mesyl groups of **6** were replaced by the iodine anion in DMF to produce hexaiodo-β-cyclodextrin derivative **7**, which was transformed into 6^A-*O*-(*p*-(allyloxy)phenyl)heptakis(2,3-di-*O*-methyl)-6^B,6^C,6^D,6^E,6^F,6^G-hexadeoxy-β-cyclodextrin (**8**) by reduction with sodium borohydride in DMF. Reduction of **7** with samarium iodide in HMPA was not possible. These syntheses have allowed the preparation of monosubstituted β-cyclodextrins with *O*-methyl, *O*-acetyl, *O*-

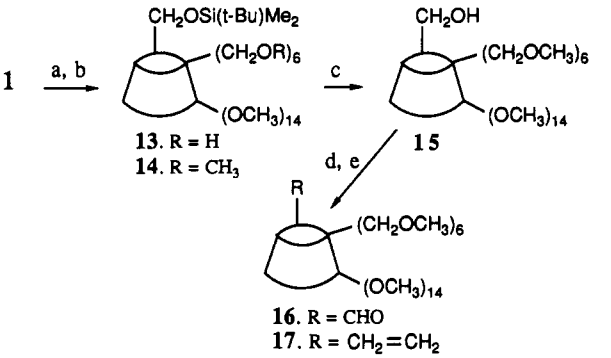
(10) Ashton, P. R.; Ellwood, P.; Staton, I.; Stoddart, J. F. *J. Org. Chem.* **1991**, *56*, 7275.

Scheme II. Preparation of Permethylated Monoalkenyl-β-cyclodextrins 10–12[a]



[a] Key: (a) F_3CSO_3Me, 2,6-di-*tert*-butyl-4-methylpyridine, CH_2Cl_2; (b) allyl-MgBr, Li_2CuCl_4, benzene/ether; (c) sodium allyloxide, DMF; (d) sodium ω-undecenyloxide, DMF.

Scheme III. Preparation of Permethylated 6-Deoxy-6-methylene-β-cyclodextrin 17[a]



[a] Key: (a) *tert*-butyldimethylsilyl chloride, imidazole, DMF; (b) NaH, CH_3I, DMF; (c) NH_4F, CH_3OH; (d) periodinane, CH_2Cl_2; (e) Ph_3PCH_3I, PhLi, THF.

mesyl, or deoxy units in the other 6-positions. These materials will help determine the effect of substituents at the 6-position on the ability of the corresponding phases to separate enantiomers.

Monotosylate ester **2** was methylated under mild conditions using methyl trifluoromethanesulfonate and 2,6-*tert*-butyl-4-methylpyridine in dichloromethane to give permethylated monotosyl-β-cyclodextrin **9** in an excellent yield (Scheme II). A coupling reaction of **9** with freshly prepared allylmagnesium bromide in the presence of dilithium tetrachlorocuprate produced permethylated monoallyl-β-cyclodextrin (with a non-oxy spacer) (**10**). Nucleophilic substitution of the tosylate group of **9** with sodium allyloxide or sodium ω-undecylenyloxide in DMF gave permethylated monoalkenyl-β-cyclodextrins **11** and **12**. Alkene-substituted cyclodextrins **10**–**12** will allow us to study cyclodextrin phases that have a short nonaromatic ring-containing tether to the polysiloxane (from **10** and **11**) and one that has a long chain aliphatic tether (from **12**).

Compound **1** was treated with *tert*-butyldimethylsilyl chloride and imidazole in DMF to produce 6-*O*-(*tert*-butyldimethylsilyl)heptakis(2,3-di-*O*-methyl)-β-cyclodextrin (**13**), which was in turn methylated to give permethylated 6-*O*-(*tert*-butyldimethylsilyl)-β-cyclodextrin **14** (Scheme III). Cyclodextrin derivative **14** was deprotected using NH_4F[11] to form monohydroxy cyclodextrin **15**.

(11) Zhang, W.-J.; Robins, M. J. *Tetrahedron Lett.* **1992**, *33*, 1177.

Aldehydo derivative 16 was prepared by oxidizing 15 with periodinane.[12] Unsubstituted 6-aldehydo-α-cyclodextrin was prepared by oxidation of 6-amino-6-deoxy-α-cyclodextrin with ninhydrin or by photolysis of 6-azido-6-deoxy-α-cyclodextrin.[9b] Permethylated 6-deoxy-6-methylene-β-cyclodextrin 17 was obtained by the reaction of aldehyde 16 with methyltriphenylphosphonium iodide and phenyllithium in THF in a yield of 64%. Cyclodextrin derivative 17 leads to a polysiloxane-containing permethylated cyclodextrin without an oxygen atom in the tether.

Persubstituted β-cyclodextrin-bound polymethylsiloxanes 19–25, shown in Scheme IV, were synthesized by the hydrosilylation of 4, 5, 8, 10, 11, 12, and 17 with polyhydromethylsiloxane 18 in a manner similar to that previously reported.[13] The mole ratio of cyclodextrin to Si–H in the hydrosilylation reaction was 0.8. An excess of 1-octene was reacted in a second step so that all Si–H units were reacted. Assuming that all alkene-substituted cyclodextrin reacted with 18, the resulting polymer would have a ratio of 50 dimethylsiloxanes to 4 methylcyclodextrin-substituted siloxanes to 1 methyloctylsiloxane.

Polyhydromethylsiloxane 18 was prepared by copolymerizing 10 parts of the cyclic tetramer of dimethylsiloxane and 1 part of the cyclic tetramer of hydromethylsiloxane in a manner similar to that reported.[14] The molecular weight of copolymer 18 was 15 000 as determined by the amount of hexamethyldisiloxane, the endcapping agent, used in the reaction. By these reactions, the relative amounts of substituent cyclodextrin and the octyl group as well as the molecular weights of the resulting polymers were determined.

The newly synthesized cyclodextrin-bound polysiloxanes (19–25) were applied as stationary phases in GC and SFC and were found to be highly efficient. In GC, for example, efficiency values of over 2500 effective theoretical plates per meter were regularly obtained for most chiral solutes. These efficiency values are much higher than those recently reported by Schurig and co-workers[15] who synthesized similar cyclodextrin stationary phases and measured efficiencies for over 100 chiral solutes. The efficiency values reported by those authors ranged between 300 and 2100 effective theoretical plates per meter. For more than 70% of the solutes, the efficiency values were below 1500 effective plates per meter.

Both in GC and SFC, the cyclodextrin-bound stationary phases described in this paper demonstrated excellent selectivities for a wide variety of chiral solutes of various chemical classes. Figure 2 illustrates the GC separation of mandelic acid methyl ester enantiomers on phase 19 (see Scheme IV). Base-line resolution was easily achieved. The chromatograms presented in Figure 3 illustrate the GC (A) and the SFC (B) separations of (±)-*trans*-1,2-cyclohexanediol enantiomers on phase 21. SFC separation of (±)-2,4-pentanediol enantiomers on phase 23 is demonstrated in Figure 4. In spite of the high susceptibility of the diols toward adsorption, sharp peaks were obtained, which is indicative of the inertness of the prepared columns. Base-line resolution was obtained in both GC and SFC.

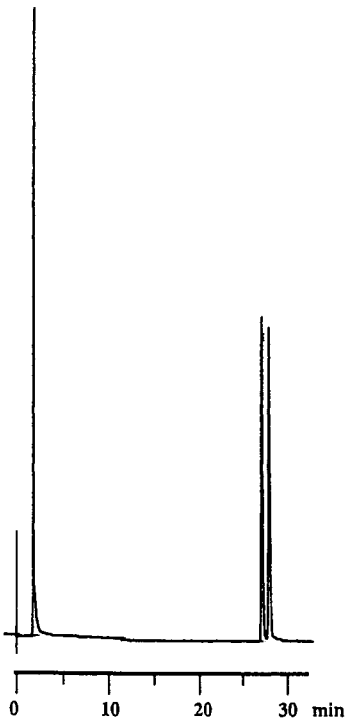
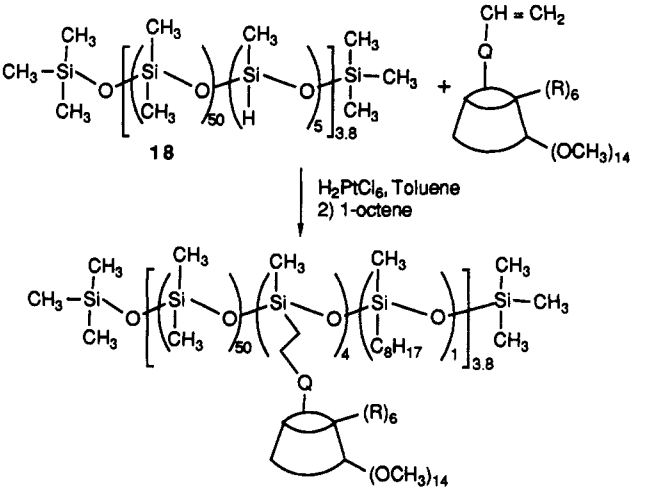


Figure 2. GC separation of mandelic acid methyl ester enantiomers on β-cyclodextrin-bound polysiloxane stationary phase 19 (see Scheme IV). Conditions: 30 m × 250 μm i.d. fused silica column, 0.25-μm film thickness; 120 °C; helium carrier gas; FID.

Scheme IV. Preparation of Persubstituted β-Cyclodextrin-Bound Polymethylsiloxanes



Polymer	Q	R
19	CH_2O–C$_6$H$_4$–OCH_2	CH_2OCH_3
20	CH_2O–C$_6$H$_4$–OCH_2	$CH_2OC(O)CH_3$
21	CH_2O–C$_6$H$_4$–OCH_2	CH_3
22	CH_2CH_2	CH_2OCH_3
23	CH_2OCH_2	CH_2OCH_3
24	$CH_2O(CH_2)_8CH_2$	CH_2OCH_3
25	None	CH_2OCH_3

GC and SFC separations of (±)-α-(trifluoromethyl)benzyl alcohol on phases 21 and 24 are illustrated in Figure 5.

All of the chromatograms presented above are indicative of high separation efficiencies and excellent chiral selectivities of the newly synthesized stationary phases.

(12) (a) Dess, D. B.; Martin, J. C. *J. Org. Chem.* **1983**, *48*, 4156. (b) Samano, V.; Robins, M. J. *Org. Chem.* **1990**, *55*, 5186.
(13) Bradshaw, J. S.; Aggarwal, S. K.; Tarbet, B. J.; Markides, K. E.; Lee, M. L. *J. Chromatogr.* **1987**, *405*, 169.
(14) Bayona, J. M.; Tarbet, B. J.; Chang, H.-C. K.; Schregenberger, C. M.; Nishioka, M.; Markides, K. E.; Bradshaw, J. S.; Lee, M. L. *Int. J. Environ. Anal. Chem.* **1987**, *28*, 263.
(15) Schmalzing, D.; Jung, M.; Mayer, S.; Rickert, J.; Schurig, V. *J. High Resolut. Chromatogr.* **1992**, *15*, 723.

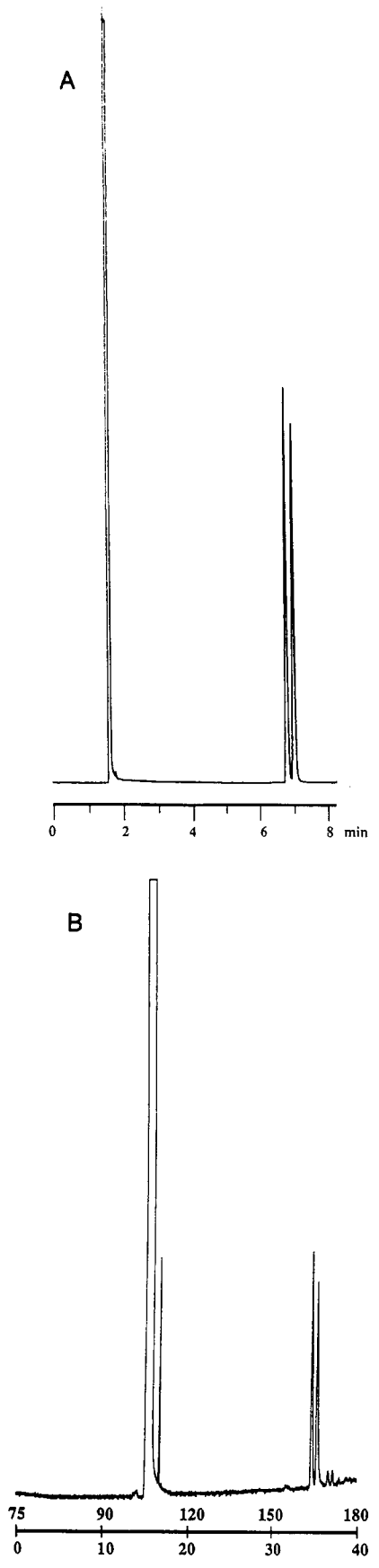


Figure 3. Separation of (±)-*trans*-1,2-cyclohexanediol enantiomers on β-cyclodextrin-bound polysiloxane phase **21** by (A) GC and (B) SFC. Conditions: (A) 30 m × 250 μm i.d. column, 0.25-μm film thickness; 140 °C; helium carrier gas; FID; (B) 15 m × 50 μm i.d. column, 0.20-μm film thickness; 60 °C; pressure program from 75 atm, 5 min hold, at a rate of 3 atm min^{-1}, to 180 atm.

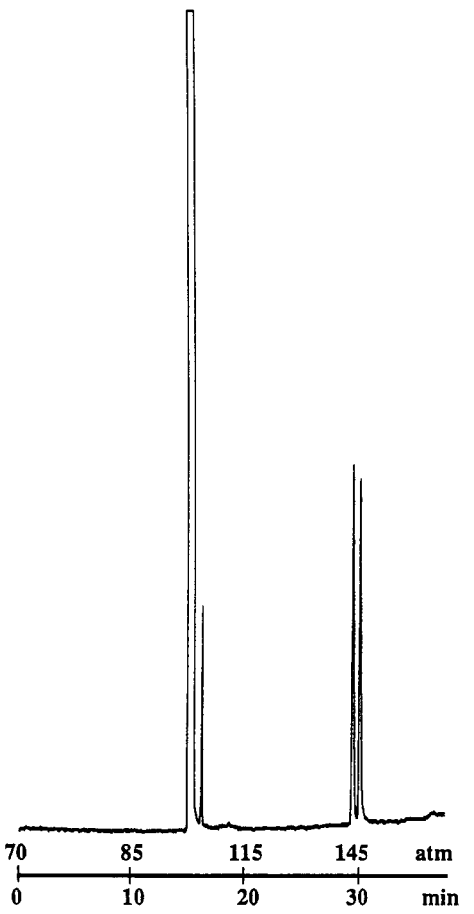


Figure 4. SFC separation of (±)-2,4-pentanediol enantiomers on β-cyclodextrin-bound polysiloxane phase **23**. Conditions: 15 m × 50 μm i.d. column, 0.20-μm film thickness; 60 °C; pressure program from 75 atm, 5 min hold, at a rate of 3 atm min^{-1}, to 180 atm.

Experimental Section

Proton and carbon NMR spectra were recorded in CD_3Cl_3 at 200 MHz. Heptakis(2,3-di-*O*-methyl)-β-cyclodextrin **1**[8] and periodinane[12a] were prepared as reported.

Heptakis(2,3-di-*O*-methyl)-6-*O*-(*p*-toluenesulfonyl)-β-cyclodextrin (2) (Scheme I). A solution of tosyl chloride (1.56 g, 8.2 mmol) in 30 mL of dry pyridine was added dropwise to a solution of 14.9 g (11.2 mmol) of **1** in 120 mL of dry pyridine cooled to 5 °C or below. After being stirred overnight at rt, the mixture was evaporated under reduced pressure at 40 °C to dryness. The residue was dissolved in $CHCl_3$, and the solution was washed with water, cold 3% HCl, aqueous $NaHCO_3$, and water and then dried ($MgSO_4$). The solid produced from evaporating the solvents was subjected to column chromatography on silica gel ($CHCl_3$:CH_3OH/15:1, then 8:1) to give 5.07 g (31%) of **2**: mp 156.5–158 °C; $[\alpha]^{25}_D$ +132.2° (*c* 3.28, $CHCl_3$); ^1H NMR δ 7.81 (d, *J* = 6.8 Hz, 2 H), 7.40 (d, *J* = 6.8 Hz, 2 H), 5.24–4.98 (m, 7 H), 4.45 (d, *J* = 7.3 Hz, 2 H), 4.28 (s, 6H, OH), 4.09–3.30 (m, 75 H), 3.27–2.96 (m, 7 H), 2.46 (s, 3 H); ^{13}C NMR δ 145.5, 133.4, 130.3, 128.6, 99.2, 98.9, 98.7, 98.5, 82.6, 82.5, 82.4, 82.3, 82.1, 80.5, 72.7, 72.6, 62.0, 61.8, 61.5, 59.2, 59.0, 58.8, 22.1. Anal. Calcd for $C_{63}H_{104}O_{37}S$: C, 50.94; H, 7.06. Found: C, 51.07; H, 7.18.

6-*O*-(*p*-(Allyloxy)phenyl)heptakis(2,3-di-*O*-methyl)-β-cyclodextrin (3) (Scheme I). A mixture of *p*-(allyloxy)phenol (3.1 g, 20.5 mmol) and NaH (0.49 g, 20.5 mmol) in 100 mL of anhydrous THF was refluxed for 30 min and then concentrated. A solution of the residue and **2** (5.1 g, 3.4 mmol) in 100 mL of dry DMF was stirred for 24 h at rt and then concentrated. The residue was partitioned between $CHCl_3$ and water. The organic layer was separated, dried, and concentrated. The crude product was subjected to column chromatography on silica gel ($CHCl_3$:CH_3-

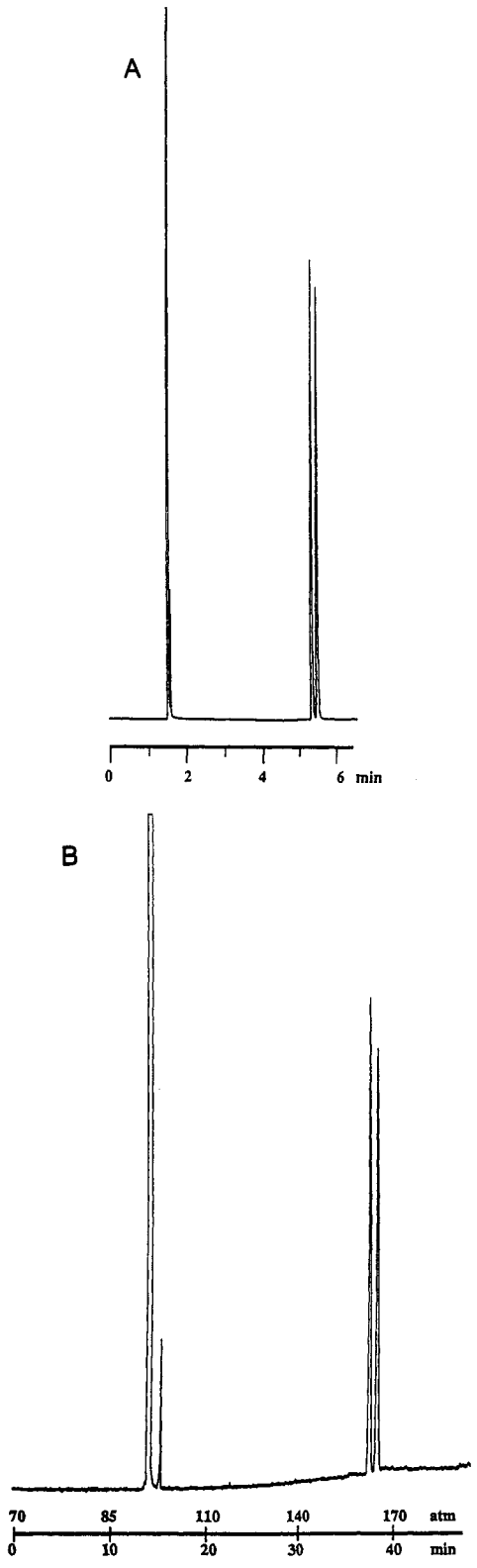


Figure 5. Separation of (±)-α-(trifluoromethyl)benzyl alcohol enantiomers by (A) GC and (B) SFC. Conditions: (A) phase 24, 30 m × 250 μm i.d. fused silica column, 0.25-μm film thickness; 140 °C; helium carrier gas, FID; (B) phase 21, 15 m × 50 μm i.d. fused silica column, 0.20-μm film thickness; 60 °C; pressure program from 75 atm, 5 min hold, at a rate of 3 atm min^{-1}, to 200 atm.

OH 15:1) to give **3** (3.68 g, 74%): mp 156–158 °C; $[\alpha]^{25}_D$ +142.1° (*c*, 1.83, $CHCl_3$); ^1H NMR δ 6.92–6.75 (m, 4 H), 6.05 (m, 1 H), 5.37 (m, 2 H), 5.04 (m, 7 H), 4.46 (d, *J* = 5.2 Hz, 2 H), 4.32 (s, 6H, OH), 4.07–3.02 (m, 84 H); ^{13}C NMR δ 153.4, 153.3, 134.1, 117.8, 116.4, 116.0, 99.6, 99.2, 99.0, 98.3, 82.4, 82.0, 81.6, 81.5, 81.4, 81.0, 80.7, 80.5, 80.4, 80.3, 79.0, 72.7, 72.6, 72.4, 72.3, 72.1, 71.1, 71.0, 69.8, 69.6, 62.0, 61.8, 61.7, 61.5, 61.3, 61.2, 61.1, 59.4. Anal. Calcd for $C_{65}H_{106}O_{36}$: C, 53.34; H, 7.30. Found: C, 53.23; H, 7.43.

6^A-*O*-(*p*-(Allyloxy)phenyl)heptakis(2,3-di-*O*-methyl)-6^B,6^C,6^D,6^E,6^F,6^G-hexa-*O*-methyl-β-cyclodextrin (4) (Scheme I). A solution of **3** (3.1 g, 2.1 mmol) in 50 mL of DMF was treated with NaH (3.0 g, 126 mmol) at rt for 2 h. The mixture was cooled to 0 °C and 21.4 g (151 mmol) of CH_3I was added. The mixture was stirred at 0 °C for 2 h and at rt for 24 h and CH_3OH was added to decompose the excess NaH. The reaction mixture was evaporated to dryness and the residue was partitioned between $CHCl_3$ and water. The organic phase was separated, washed successively with water, aqueous $Na_2S_2O_3$, and water, and then dried and concentrated. Column chromatography on silica gel ($CHCl_3$:CH_3OH 80:1) of the crude product gave **4** (1.76 g, 54%): mp 220–222 °C; $[\alpha]^{25}_D$ +150.1° (*c* 2.50, $CHCl_3$); ^1H NMR δ 6.87–6.71 (m, 4 H), 5.99 (m, 1 H), 5.28 (m, 2 H), 5.15–4.98 (m, 7 H), 4.42 (d, *J* = 5.19 Hz, 2 H), 4.28–3.00 (m, 102 H); ^{13}C NMR δ 153.6, 153.4, 133.9, 117.8, 115.9, 99.8, 99.4, 99.3, 82.5, 82.4, 82.2, 81.2, 80.9, 80.8, 80.7, 71.9, 71.7, 71.4, 70.9, 69.8, 62.0, 61.9, 59.4, 59.3, 59.1, 59.0, 58.9, 58.7. Anal. Calcd for $C_{71}H_{118}O_{36}$: C, 55.06; H, 7.75. Found: C, 55.03; H, 7.68.

6^A-*O*-(*p*-(Allyloxy)phenyl)heptakis(2,3-di-*O*-methyl)-6^B,6^C,6^D,6^E,6^F,6^G-hexa-*O*-acetyl-β-cyclodextrin (5) (Scheme I). A solution of **3** (0.24 g, 0.16 mmol) in 10 mL of acetic anhydride and 10 mL of pyridine was stirred at 100 °C for 4 h and then concentrated. Column chromatography ($CHCl_3$:CH_3OH 80:1) of the residue produced amorphous **5** (0.26 g, 93%): mp 102–104 °C; $[\alpha]^{25}_D$ +130.6° (*c*, 0.96, $CHCl_3$); ^1H NMR δ 6.93–6.75 (m, 4 H), 6.04 (m, 1 H), 5.34 (m, 2 H), 5.18–4.98 (m, 7 H), 4.63–4.38 (m, 8 H), 4.38–4.03 (m, 6 H), 4.03–3.76 (m, 6 H), 3.76–3.30 (m, 59 H), 3.30–3.04 (m, 7 H), 2.20–1.98 (m, 18 H); ^{13}C NMR δ 171.0, 170.9, 153.5, 153.2, 134.1, 117.8, 116.3, 116.1, 100.2, 99.6, 98.7, 82.6, 82.4, 82.2, 82.0, 81.8, 81.7, 81.6, 81.3, 80.9, 71.3, 70.2, 70.1, 69.8, 69.6, 67.5, 64.0, 63.8, 62.2, 62.0, 61.9, 61.8, 59.6, 59.5, 59.2, 58.8, 21.3. Anal. Calcd for $C_{77}H_{118}O_{42}$: C, 53.90; H, 6.93. Found: C, 53.78; H, 7.06.

6^A-*O*-(*p*-(Allyloxy)phenyl)heptakis(2,3-di-*O*-methyl)-6^B,6^C,6^D,6^E,6^F,6^G-hexa-*O*-(methanesulfonyl)-β-cyclodextrin (6) (Scheme I). A solution of **3** (2.0 g, 1.36 mmol) in 20 mL of dry pyridine was cooled to −10 °C, treated with CH_3SO_2Cl (1.9 g, 16.3 mmol), and kept overnight at 5 °C. The mixture was poured into 100 mL of ice water, and the precipitate was filtered, washed with cold water, and dissolved in $CHCl_3$. The solution was washed with water, dried, and concentrated. The residue was subjected to column chromatography (C_6H_6:C_2H_5OH 40:1, then 30:1) to produce **6** (1.95 g, 74%): mp 134–135 °C; $[\alpha]^{25}_D$ +112.8° (*c* 0.88, $CHCl_3$); ^1H NMR δ 6.92–6.77 (m, 4 H), 6.02 (m, 1 H), 5.31 (m, 2 H), 5.16–5.00 (m, 7 H), 4.73–3.38 (m, 79 H), 3.31–3.12 (m, 7 H), 3.08 (s, 18 H); ^{13}C NMR δ 153.5, 153.3, 134.1, 117.9, 116.2, 115.9, 99.5, 99.3, 98.3, 82.2, 82.1, 81.9, 81.8, 81.6, 81.0, 80.7, 80.2, 79.5, 70.9, 70.1, 69.8, 69.6, 67.8, 62.1, 61.9, 61.8, 61.6, 59.8, 59.7, 59.3, 59.2, 59.0, 37.7, 37.6, 37.3. Anal. Calcd for $C_{71}H_{118}O_{48}S_6$: C, 44.14; H, 6.16. Found: C, 44.26; H, 6.30.

6^A-*O*-(*p*-(Allyloxy)phenyl)heptakis(2,3-di-*O*-methyl)-6^B,6^C,6^D,6^E,6^F,6^G-hexadeoxy-6^B,6^C,6^D,6^E,6^F,6^G-hexaiodo-β-cyclodextrin (7) (Scheme I). A solution of **6** (1.86 g, 0.96 mmol) in 50 mL of DMF was stirred with NaI (2.34 g, 15.6 mmol) at 100 °C for 3 h. The mixture was concentrated. The residue was partitioned between $CHCl_3$ and water. The organic layer was separated, washed with water, dried, and concentrated. Column chromatography (silica gel) (C_6H_6:C_2H_5OH 30:1) of the product gave **7** (1.68 g, 82%): mp 128–130 °C; $[\alpha]^{25}_D$ +89.2° (*c*, 1.14, $CHCl_3$); ^1H NMR δ 6.92–6.78 (m, 4 H), 6.03 (m, 1 H), 5.46–5.00 (m, 9 H), 4.48 (m, 2 H), 4.27–3.04 (m, 84 H); ^{13}C NMR δ 153.6, 153.2, 134.1, 134.1, 117.9, 116.3, 116.1, 99.7, 98.7, 98.5, 84.9, 84.7, 84.3, 84.0, 82.3, 82.1, 82.0, 81.9, 81.8, 71.4, 70.9, 70.7, 70.4, 69.9, 62.1, 61.9, 59.5, 59.4, 59.3, 59.2, 59.1, 10.2. Anal. Calcd for $C_{65}H_{100}O_{30}I_6$: C, 36.78; H, 4.75. Found: C, 36.89; H, 4.62.

6^A-*O*-(*p*-(Allyloxy)phenyl)heptakis(2,3-di-*O*-methyl)-6^B,6^C,6^D,6^E,6^F,6^G-hexadeoxy-β-cyclodextrin (8) (Scheme I). A solution of **7** (280 mg, 0.13 mmol) in 10 mL of DMF was stirred with $NaBH_4$ at 70 °C for 2 h and evaporated to dryness under reduced pressure. The solution of the residue in 150 mL of $CHCl_3$ was washed twice with water, dried, and concentrated. Column chromatography (silica gel) (C_6H_{14}:$CH_3CO_2C_2H_5$:C_2H_5OH 40:10:

1) of the crude product gave **8** (0.11 g, 61%): mp 104–106 °C; $[\alpha]^{25}_D$ +135.1° (*c* 0.87, $CHCl_3$); ^1H NMR δ 6.89–6.78 (m, 4 H), 6.03 (m, 1 H), 5.32 (m, 2 H), 5.11 (d, *J* = 3.1 Hz, 1 H), 5.08–4.89 (m, 6 H), 4.46 (m, 2 H), 4.38–3.34 (m, 59 H), 3.34–2.95 (m, 13 H), 1.60–1.13 (m, 18 H); ^{13}C NMR δ 153.4, 134.0, 117.9, 116.0, 115.9, 99.6, 99.3, 99.0, 87.6, 87.5, 87.2, 87.1, 87.0, 83.0, 82.9, 82.8, 82.5, 82.4, 82.1, 81.0, 77.7, 70.9, 69.8, 69.6, 68.1, 67.6, 67.5, 62.1, 61.9, 61.8, 61.7, 59.1, 59.0, 58.9, 18.8, 18.6. Anal. Calcd for $C_{65}H_{106}O_{30}$: C, 57.09; H, 7.81. Found: C, 56.99; H, 7.80.

Heptakis(2,3-di-*O*-methyl)-6^B,6^C,6^D,6^E,6^F,6^G-hexa-*O*-methyl-6^A-*O*-(toluenesulfonyl)-β-cyclodextrin (9) (Scheme II). A mixture of **2** (0.22 g, 0.15 mmol), methyl triflate (0.15 mL, 1.33 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (0.37 g, 1.80 mmol) in 6 mL of CH_2Cl_2 was heated in a sealed tube for 2.5 h at 80 °C and cooled. CH_3OH (2 mL) was added, and the mixture was kept for 30 min at rt and concentrated. A solution of the residue in $CHCl_3$ was washed successively with water, cold 3% HCl, aqueous $NaHCO_3$, and water and then dried and concentrated. The product was subjected to column chromatography on silica gel ($CHCl_3$:CH_3OH 100:1) to produce **9** (0.43 g, 93%): mp 98–100 °C; $[\alpha]^{25}_D$ +131.9° (*c*, 2.22, $CHCl_3$); ^1H NMR δ 7.75 (d, *J* = 6.8 Hz, 2 H), 7.35 (d, *J* = 6.8 Hz, 2 H), 5.21–4.92 (m, 7 H), 4.45 (d, *J* = 7.3 Hz, 2 H), 4.17–3.26 (m, 93 H), 3.26–2.95 (m, 7 H), 2.43 (s, 3 H); ^{13}C NMR δ 145.2, 133.8, 130.3, 128.4, 99.7, 99.6, 99.4, 99.1, 98.8, 82.7, 82.6, 82.4, 82.1, 81.0, 80.8, 80.1, 79.9, 71.7, 71.6, 71.4, 71.1, 69.9, 62.1, 62.0, 61.9, 61.7, 59.6, 59.4, 59.3, 59.0, 58.8, 58.7, 58.5, 22.1. Anal. Calcd for $C_{69}H_{116}O_{37}S$: C, 52.80; H, 7.45. Found: C, 53.06; H, 7.72.

6^A-Allyl-6^A-deoxyheptakis(2,3-di-*O*-methyl)-6^B,6^C,6^D,6^E,6^F,6^G-hexa-*O*-methyl-β-cyclodextrin (10) (Scheme II). A solution of 0.47 g (0.30 mmol) of **9** in 10 mL of dry benzene was slowly added to 10 mL of a stirred 1.0 M ethereal solution of allylmagnesium bromide (freshly prepared) at 0 °C under an argon atmosphere. Li_2CuCl_4 (3 mL in THF) was added and the reaction mixture was stirred for 30 min at 0 °C and for 22 h at rt. Saturated aqueous NH_4Cl solution (20 mL) was added at 0 °C to decompose the excess Grignard reagent. The mixture was diluted with $CHCl_3$, and organic layer was separated and washed with water and then dried and concentrated. The residue was purified by column chromatography on silica gel (CH_3OH:$CHCl_3$ 80:1) to give **10** (0.24 g, 55%): mp 75–77 °C; $[\alpha]^{25}_D$ +140.7° (*c* 1.10, $CHCl_3$); ^1H NMR δ 5.83 (m, 1 H), 5.23–4.90 (m, 9 H), 4.06–3.29 (m, 93 H), 3.18 (dd, J_1 = 6.7 Hz, J_2 = 3.2 Hz, 7 H), 2.05 (m, 2 H), 1.60 (m, 2 H); ^{13}C NMR δ 139.0, 115.0, 99.8, 99.4, 99.3, 99.2, 98.6, 83.7, 83.2, 82.4, 82.3, 82.1, 81.2, 80.8, 80.6, 79.9, 71.9, 71.8, 71.7, 71.6, 71.5, 71.4, 71.2, 70.8, 62.2, 62.1, 62.0, 61.9, 61.7, 61.5, 59.7, 59.5, 59.4, 59.2, 59.1, 59.0, 58.9, 58.7, 58.6, 31.7, 30.0. Anal. Calcd for $C_{65}H_{114}O_{34}$: C, 54.53; H, 8.04. Found: C, 54.38; H, 7.79.

6^A-*O*-Allylheptakis(2,3-di-*O*-methyl)-6^B,6^C,6^D,6^E,6^F,6^G-hexa-*O*-methyl-β-cyclodextrin (11) (Scheme II). A solution of allyl alcohol (0.29 g, 5.0 mmol) in 20 mL of DMF was treated with NaH (96 mg, 4 mmol) for 4 h at rt. Monotosylate ester **9** (0.31 g, 0.2 mmol) was added at 0 °C and the mixture was stirred for 24 h at rt. CH_3I was added to decompose the excess allyloxide at 0 °C and the mixture was concentrated. A solution of the residue in $CHCl_3$ was washed twice with water, dried, and concentrated. Column chromatography (silica gel) ($CHCl_3$:CH_3OH 40:1) of the product gave **11** (0.20 g, 69%): mp 86–88 °C; $[\alpha]^{25}_D$ +138.6° (*c* 0.90, $CHCl_3$); ^1H NMR δ 5.83 (m, 1 H), 5.12 (m, 2 H), 5.05 (d, *J* = 3.1 Hz, 7 H), 3.96 (d, *J* = 4.1 Hz, 2 H), 3.84–3.23 (m, 95 H), 3.10 (dd, J_1 = 6.8 Hz, J_2 = 3.1 Hz, 7 H); ^{13}C NMR δ 135.6, 117.0, 99.7, 82.5, 82.2, 80.9, 80.8, 72.5, 71.8, 71.5, 71.3, 69.4, 61.8, 59.3, 58.9, 58.8. Anal. Calcd for $C_{65}H_{114}O_{35}$: C, 53.64; H, 7.89. Found: C, 53.55; H, 7.91.

Heptakis(2,3-di-*O*-methyl)-6^B,6^C,6^D,6^E,6^F,6^G-hexa-*O*-methyl-6^A-*O*-(ω-undecylenyl)-β-cyclodextrin (12) (Scheme II). Cyclodextrin derivative **12** was prepared as **11** above from 0.82 g (4.8 mmol) of ω-undecenyl alcohol, 0.12 g (4.8 mmol) of NaH, and 0.37 g (0.24 mmol) of **9** to give 0.19 g (50%) of **12**: mp 77–79 °C; $[\alpha]^{25}_D$ +135.7° (*c* 1.30, $CHCl_3$); ^1H NMR δ 5.74 (m, 1 H), 5.08 (d, *J* = 3.1 Hz, 7 H), 4.91 (m, 2 H), 3.90–3.25 (m 97 H), 3.13 (dd, J_1 = 6.8 Hz, J_2 = 3.1 Hz, 7 H), 1.98 (m, 2 H), 1.52 (m, 2 H), 1.22 (m, 12 H); ^{13}C NMR δ 139.5, 114.6, 99.4, 99.2, 82.6, 82.4, 82.2, 81.1, 80.9, 80.8, 80.6, 71.9, 71.7, 71.4, 61.9, 59.4, 59.0, 58.9, 34.2, 30.2, 30.1, 30.0, 29.9, 29.5, 29.3, 26.7. Anal. Calcd for $C_{73}H_{130}O_{35}$: C, 55.92; H, 8.36. Found: C, 56.17; H, 8.43.

6-*O*-(*tert*-Butyldimethylsilyl)heptakis(2,3-di-*O*-methyl)-β-cyclodextrin (13) (Scheme III). To a stirred mixture of dried **1** (8.9 g, 6.7 mmol) and imidazole (0.82 g, 12.1 mmol) in 100 mL of dry DMF, was added, dropwise during 30 min at rt, a solution of *tert*-butyldimethylsilyl chloride (1.5 g, 10.5, mmol) in 30 mL of dry DMF. The mixture was stirred for 3 h at rt and concentrated. A solution of the residue in $CHCl_3$ was washed successively with water, cold 3% HCl, aqueous $NaHCO_3$, and water and then dried and concentrated. Column chromatography on silica gel ($CHCl_3$:CH_3OH 15:1) of the product gave **13** (3.22 g, 33%): mp 149–150 °C; $[\alpha]^{25}_D$ +138.1° (*c* 1.24, $CHCl_3$); ^1H NMR δ 5.29–4.94 (m, 7 H), 4.60 (br s, 6H, OH), 4.20–3.28 (m, 77 H), 3.28–3.00 (m, 7 H), 0.86 (s, 9 H), 0.03 (s, 6 H); ^{13}C NMR δ 99.3, 98.8, 98.7, 82.8, 82.7, 82.5, 82.4, 82.3, 82.2, 82.1, 82.0, 81.9, 81.8, 81.4, 81.1, 81.0, 78.4, 73.1, 72.8, 72.7, 72.4, 72.3, 62.5, 62.3, 62.2, 62.0, 61.9, 61.8, 61.6, 61.4, 61.3, 59.6, 59.0, 58.8, 58.3, 26.4, 18.8, -4.6, -4.7. Anal. Calcd for $C_{62}H_{112}O_{35}Si$: C, 51.51; H, 7.81. Found: C, 51.39; H, 7.64.

6^A-*O*-(*tert*-Butyldimethylsilyl)heptakis(2,3-di-*O*-methyl)-6^B,6^C,6^D,6^E,6^F,6^G-hexa-*O*-methyl-β-cyclodextrin (14) (Scheme III). A solution of **13** (0.66 g, 0.46 mmol) in 20 mL of DMF was treated with NaH (0.79 g, 32.9 mmol), followed by addition of CH_3I (5.60 g, 39.5 mmol). The mixture was stirred for 24 h at rt. CH_3OH was added at 0 °C to decompose the excess NaH, and the mixture was concentrated. The residue was partitioned between $CHCl_3$ and water. The organic layer was separated, washed with aqueous $Na_2S_2O_3$ and water, and then dried and concentrated. The crude product was purified by column chromatography ($CHCl_3$:CH_3OH 80:1) to give **14** (0.48 g, 69%): mp 103–104 °C; $[\alpha]^{25}_D$ +130.6° (*c* 1.09, $CHCl_3$); ^1H NMR δ 5.14–4.97 (m, 7 H), 4.05–3.24 (m, 95 H), 3.10 (dd, J_1 = 6.75 Hz, J_2 = 3.12 Hz, 7 H), 0.81 (s, 9 H), -0.02 (s, 6 H); ^{13}C NMR δ 99.6, 99.4, 99.2, 99.0, 98.6, 82.5, 82.3, 82.2, 82.1, 81.1, 81.0, 80.7, 80.6, 80.3, 80.1, 79.7, 72.6, 71.8, 71.3, 61.9, 61.8, 59.4, 59.1, 58.9, 58.8, 26.4, 18.8, -4.6, -4.7. Anal. Calcd for $C_{68}H_{124}O_{35}Si$: C, 53.39; H, 8.17. Found: C, 53.24; H, 7.92.

Heptakis(2,3-di-*O*-methyl)-6^B,6^C,6^D,6^E,6^F,6^G-hexa-*O*-methyl-β-cyclodextrin (15) (Scheme III). A solution of **14** (0.36 g, 0.24 mmol) in 70 mL of CH_3OH was refluxed with NH_4F (104 mg, 2.82 mmol) for 24 h and then concentrated. The solution of the residue in ethyl acetate was filtered through Celite, and the filtrate was concentrated. Column chromatography ($CHCl_3$:CH_3OH 80:1) of the crude product gave **15** (0.24 g, 73%): mp 99–101 °C; $[\alpha]^{25}_D$ +142.3° (*c* 1.07, $CHCl_3$); ^1H NMR δ 5.25–4.97 (m, 7 H), 4.05–3.29 (m, 95 H), 3.15 (dd, J_1 = 6.8 Hz, J_2 = 3.1 Hz, 7 H), 2.65 (s, 1H, OH); ^{13}C NMR δ 99.4, 99.3, 82.8, 82.6, 82.5, 82.4, 82.3, 82.2, 82.1, 81.9, 81.6, 81.0, 80.5, 80.3, 79.0, 72.0, 71.9, 71.8, 71.6, 71.5, 71.3, 62.0, 61.9, 61.8, 61.7, 61.5, 59.5, 59.4, 59.1, 58.9, 58.8, 58.7, 58.6. Anal. Calcd for $C_{62}H_{110}O_{35}$: C, 52.61; H, 7.83. Found: C, 52.79; H, 8.00.

6^A-Formylheptakis(2,3-di-*O*-methyl)-6^B,6^C,6^D,6^E,6^F,6^G-hexa-*O*-methyl-β-cyclodextrin (16) (Scheme III). A solution of **15** (0.56 g, 0.4 mmol) in 5 mL of CH_2Cl_2 was stirred with periodinane (0.50 g, 1.2 mmol) for 2 h at 0 °C and then for 20 h at rt. The mixture was diluted with 20 mL of ethyl ether, poured into 20 mL of ice-cold saturated $NaHCO_3$ containing $Na_2S_2O_3$ (2.5 g, 10 mmol), and shaken for 5 min. The organic phase was separated and washed with saturated $NaHCO_3$, water, and brine and then dried and concentrated. Column chromatography on silica gel ($CHCl_3$:CH_3OH 80:1) of the product gave **16** (0.27 g, 48%): mp 88–90 °C; $[\alpha]^{25}_D$ +134.0° (*c* 1.05, $CHCl_3$); ^1H NMR δ 9.69 (d, *J* = 2.1 Hz, 1 H), 5.25–5.02 (m, 7 H), 4.25 (m, 1 H), 3.95–3.02 (m, 99 H); ^{13}C NMR δ 198.2, 99.5, 99.4, 99.2, 99.1, 82.6, 82.5, 82.4, 82.2, 81.9, 81.3, 81.2, 81.1, 81.0, 80.7, 80.3, 80.0, 71.9, 71.8, 71.6, 71.5, 71.4, 71.2, 62.1, 62.0, 61.8, 61.3, 59.4, 59.0, 58.9, 58.8. Anal. Calcd for $C_{62}H_{108}O_{35}$: C, 52.68; H, 7.70. Found: C, 52.71; H, 7.57.

6^A-Deoxyheptakis(2,3-di-*O*-methyl)-6^B,6^C,6^D,6^E,6^F,6^G-hexa-*O*-methyl-6^A-methylene-β-cyclodextrin (17) (Scheme III). A 100-mL three-necked round-bottomed flask equipped with a pressure-equalizing dropping funnel, thermometer, magnetic stirring bar, and serum caps was charged with 121 mg (0.3 mmol) of $(C_6H_5)_3PCH_3I$ and 10 mL of THF and then was flushed with argon. The flask was cooled in an ice bath and the suspension was stirred under a positive pressure of argon. About 30 μL of 2 M (0.06 mmol) C_6H_5Li in 30:70 ether–cyclohexane was added dropwise until the suspension developed a permanent yellow

color. C_6H_5Li (0.12 mL of 2 M, 0.24 mmol) was added dropwise over 10 min. The ice bath was removed and the orange suspension containing excess phosphonium salt was stirred at rt for 30 min. The reaction mixture was stirred and cooled to 0 to 5 °C and a solution of **16** (0.28 g, 0.2 mmol) in 10 mL of THF was added dropwise over 10 min. The dropping funnel was rinsed with a small amount of THF. The mixture was stirred at rt for 2 h. The light orange mixture was hydrolyzed by adding 2 mL of CH_3OH and most of the solvent was removed under reduced pressure to give a slurry. The slurry was diluted with 50 mL of ethyl acetate and the suspension was filtered through 5 g of Celite and 5 g of Florisil. The Celite and Florisil were washed with 100 mL of ethyl acetate. Rotary evaporation of the filtrate provided 0.32 g of crude product, which was subjected to column chromatography ($CHCl_3$:CH_3OH 80:1) to give **17** (0.18 g, 64%): mp 95–97 °C; $[\alpha]^{25}_D$ +140.4° (*c*, 0.54, $CHCl_3$); ^1H NMR δ 6.08 (m, 1 H), 5.49–5.00 (m, 9 H), 4.21 (m, 1 H), 4.03–3.02 (m, 99 H); ^{13}C NMR δ 136.8, 118.6, 99.6, 99.5, 99.4, 99.2, 99.0, 98.7, 83.5, 83.0, 82.6, 82.5, 82.4, 82.3, 82.2, 82.0, 81.9, 81.7, 81.6, 81.5, 81.4, 81.3, 81.2, 80.9, 80.6, 80.0, 72.1, 71.8, 71.6, 71.5, 71.4, 71.2, 71.1, 71.0, 62.3, 62.1, 62.0, 61.7, 61.6, 59.7, 59.4, 59.3, 59.0, 58.8, 58.6. Anal. Calcd for $C_{63}H_{110}O_{34}$: C, 53.61; H, 7.85. Found: C, 53.51; H, 7.97.

Preparation of Copolymer 18. A mixture of 2.97 g (10 mmol) of 1,1,3,3,5,5,7,7-octamethylcyclotetrasiloxane (D_4), 0.24 g (1 mmol) of 1,3,5,7-tetramethylcyclotetrasiloxane (D'_4), and 45 μL (0.035 mg, 2×10^{-4} mmol) of hexamethyldisiloxane was stirred with 4 mg of triflic acid in a 50-mL Teflon centrifuge tube for 50 h at rt. This reaction was similar to that reported.[14] The mixture was neutralized with 30 mg of hexamethyldisilazane while being stirred for 5 min. The resulting polymer (MW about 15 000) was dissolved in 10 mL of CH_2Cl_2, the polymer was precipitated by adding 30 mL of CH_3OH, the mixture was centrifuged, and the solvent was decanted. The polymer was again dissolved in CH_2Cl_2 and precipitated by CH_3OH for a total of four more times. The polymer was then dried for 10 h under reduced pressure.

General Procedure for the Preparation of β-Cyclodextrin-Containing Methylpolysiloxanes 19-25 (Scheme IV). A typical synthetic procedure is given for polymer **19**. Alkene **4** (0.12 g, 0.08 mmol), hydromethylpolysiloxane **18** (0.08 g, 0.1 mmol of Si–H),[14] and 3 g of toluene were placed in a 50-mL Teflon centrifuge tube. Parafilm was placed around the cap to keep out moisture. The mixture was heated in an oil bath at 85–90 °C for 1 h. Then 40 μL of 1% H_2PtCl_6 (in THF–ethanol) was added. The mixture was stirred at 85–90 °C for 72 h. After 1 g of 1-octene was added, the reaction mixture was stirred overnight at 85–90 °C. The solvent was evaporated. The residue was dissolved in 10 mL of CH_2Cl_2, followed by 10 mL of CH_3OH and 10 mL of water. The mixture was centrifuged and the water–CH_3OH layer was removed. This process was repeated three more times. The CH_2Cl_2 was evaporated and the residue was dried under vacuum for 10 h at 60 °C to give 0.17 g (82%) of **19**. The proton NMR spectrum of **19** was consistant with the structure shown in Scheme IV. The other polymers were prepared in a like manner.

Preparation of Capillary Columns. GC and SFC columns, 250 and 50 μm i.d., respectively, were prepared using cyanodeactivated[16] fused silica capillaries. The static coating technique[17] was employed for column preparation. CH_2Cl_2/*n*-C_5H_{12} mixtures were used as solvents. The coating bath temperature was set at 40 °C. After coating, the columns were purged with nitrogen for 40 min and then cross-linked using azo-*tert*-butane[18] as a free radical initiator. The columns were thermally treated by temperature programming from 40 to 220 °C, at a rate of 4 °C min^{-1}, holding at the final temperature for 30 min. The columns were then rinsed with the coating solvent (1 mL for a GC column, and 0.5 mL for an SFC column) and purged with nitrogen for 40 min. Finally, the columns were conditioned under helium purge by programming the temperature from 40 to 230 °C at a rate of 1 °C min^{-1} with a holding time of 2 h at the final temperature.

Gas Chromatography. GC experiments were performed on an HP Model 5890 gas chromatograph (Hewlett Packard, Avondale, PA) equipped with a flame ionization detector. Helium was used as the carrier gas. Split injection (200:1) was used. An HP Model 3392A recording integrator (Hewlett Packard) was used to record the solute retention times and peak areas.

Supercritical Fluid Chromatography. SFC experiments were conducted using a Lee Scientific Model 501 SFC system (Dionex, Sunnyvale, CA) equipped with a flame ionization detector. SFC grade CO_2 was used as the mobile phase. A helium actuated automatic Valco injector (Valco, Houston, TX) was used for sample introduction. Homemade integral type restrictors were used. Pressure programming was employed for SFC separations of the chiral solutes.

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